GEOCHEMISTRY OF BALTIC SEA SURFACE SEDIMENTS

SCIENTIFIC EDITOR

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MINISTRY OF THE ENVIRONMENT

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Chapter 1

INTRODUCTION

The Baltic Sea is relatively small and shallow of limited water exchange due to the narrow and shallow Danish Straits. The surface area of the Baltic Sea is roughly a quarter of its catchment area. It belongs to nine highly industrialized states: Denmark, Germany, Poland, Lithuania, Latvia, Estonia, Russia, Finland, and Sweden. This area is inhabited by 85 million people. Owing to the conditions, each interference with the sea environment: fishery, shipping, industrial and municipal waste water discharge, as well as any activity related to sea bottom exploitation and management has a considerable effect on the delicate ecological balance of the sea.

The interest in the Baltic Sea floor grows with each passing year. Crude oil and natural gas is extracted from deposits under the sea bottom and increasing volumes of sand and gravel are dredged from the sea bottom surface. There are pipelines, electric power and telecommunication cables on the sea bottom, and wind farms are erected. Ports, sewage collectors, piers for strollers, fishing havens, and even underground storage tanks for liquid hydrocarbons are constructed along the coast. The storage of carbon dioxide under the sea bottom deposits is also planned.

Different kinds of pollution reach the sea, including those from the rivers, air, harbours, coastal towns and ships. These contaminants generally affect the condition of the Baltic waters, and finally they accumulate in the bottom sediments. The sea bottom stores many hazardous wastes ranging from conventional and chemical ammunition that sunk after World War II to the spoil taken during the dredging of harbours or water lanes.

Global climate changes alter the hydrological conditions of the Baltic Sea. Climate warming increases the temperature of the seawater surface in summer and reduces the area of the ice cover in winter. The seawater temperature determines the volume of the primary production to a large extent. In recent decades, a radical change in the frequency and intensity of the ocean water inflows into the Baltic Sea has been observed. These inflows played and are still playing a key role in the formation of its ecological status. The reduction in frequency of the aerated saline water from the North Sea leads to oxygen deficit and to the occurrence of hydrogen sulphide in near-bottom waters in many deep-water basins. As a result of the interaction between these changes, the balance between the numerous elements in the natural environment may be easily disturbed by both natural and man-made factors.

All these are key elements in managing and using the Baltic Sea areas and its bottom natural resources. Therefore, extensive, sound and detailed knowledge concerning the geological structure, nature of the bottom deposit cover and the processes taking part in the sea bottom sediments are required. Until the 1980s, research into the Baltic Sea waters was undertaken and the changes monitored. The marine deposits, especially their geochemistry, were investigated to a much less extent. From that time the issues concerning geochemistry of the sea bottom deposits have become a subject of numerous studies and publications; however, there is no work summarizing our knowledge in this field.

This gap is to be filled by the present monograph, which comprises a set of the latest data collected from different sources and supported by the experience of researchers from the Polish Geological Institute, the Institute of Oceanography and the Faculty of Chemistry at the University of Gdańsk, and the Medical University of Gdańsk. The information on the chemical composition of the Baltic Sea sediments is sourced from data achieved within the scope of the international project "The Baltic Sea Sediment Baseline Study" conducted in 1993–1996 under the auspices of the Helsinki Commission (HELCOM – Baltic Marine Environment Protection) and International Council for the Exploration of the Sea (ICES).

In June, 1993, a research cruise involving the R/V Aranda took place, during which sediment cores were taken from the stations of all the main sedimentary basins of the Baltic Sea (Fig. 1.1). The core acquisition at each station was preceded by a detailed examination involving the use of echo-sounding equipment with operating frequencies of 100 and 12–15 kHz, which enabled the recognition of the sea bottom relief and the thickness of silt-clay deposits. For details, the sediment surface was inspected with a video camera system. The Gemini corer designed by L. Niemistö allows to extract two parallel cores 800 mm in diameter and up to 50 cm long (Fig. 1.2). At each station, several cores were extracted and each core was cut into 1cm thick slices, and stored in a deep freeze.

The analyses of the chemical composition were carried out by accredited laboratories to assure a suitable level of accuracy and the repeatability of the results. The total metal content (complete dissolution) was determined by the laboratories of the German Federal Office of Maritime Navigation and Hydrography (Bundesamt für Seeschiffahrt und Hydrographie – BSH) and the Finnish Institute of Marine Research – FIRM. Determinations of the total organic carbon (TOC), phosphorus and nitrogen were made by the Department of Physical Geography and Quaternary Geology of Stockholm University, BSH and FIRM. The contents of polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) were determined by the Department of Zoology of Stockholm University.

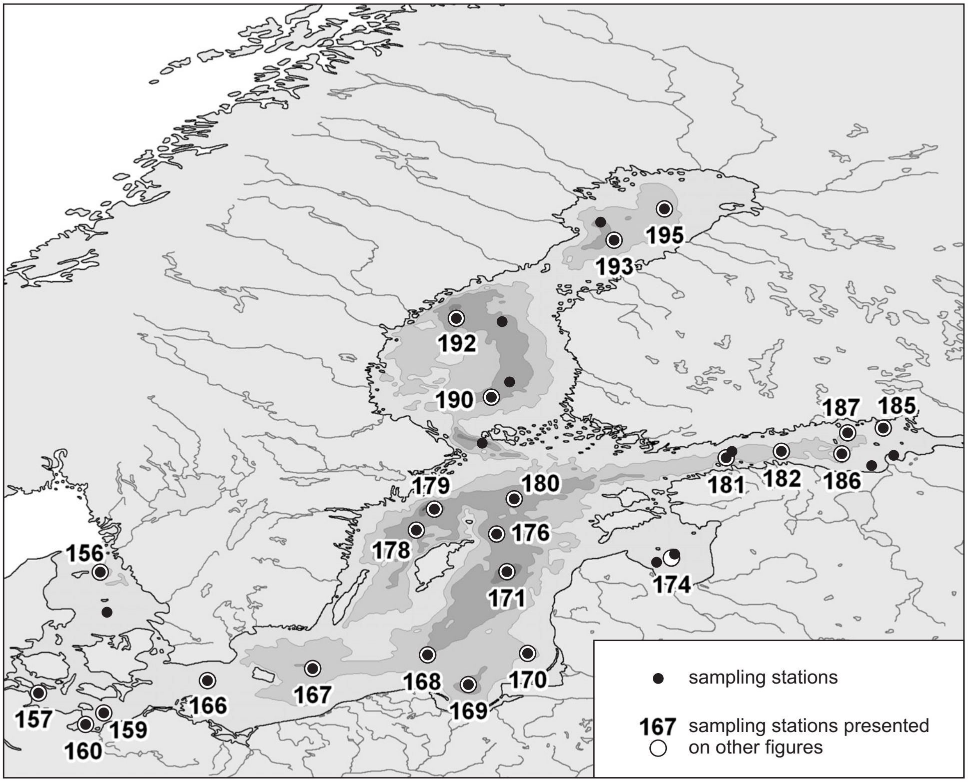


Fig. 1.1. Location of research stations of the project "The Baltic Sea Sediment Baseline Study"

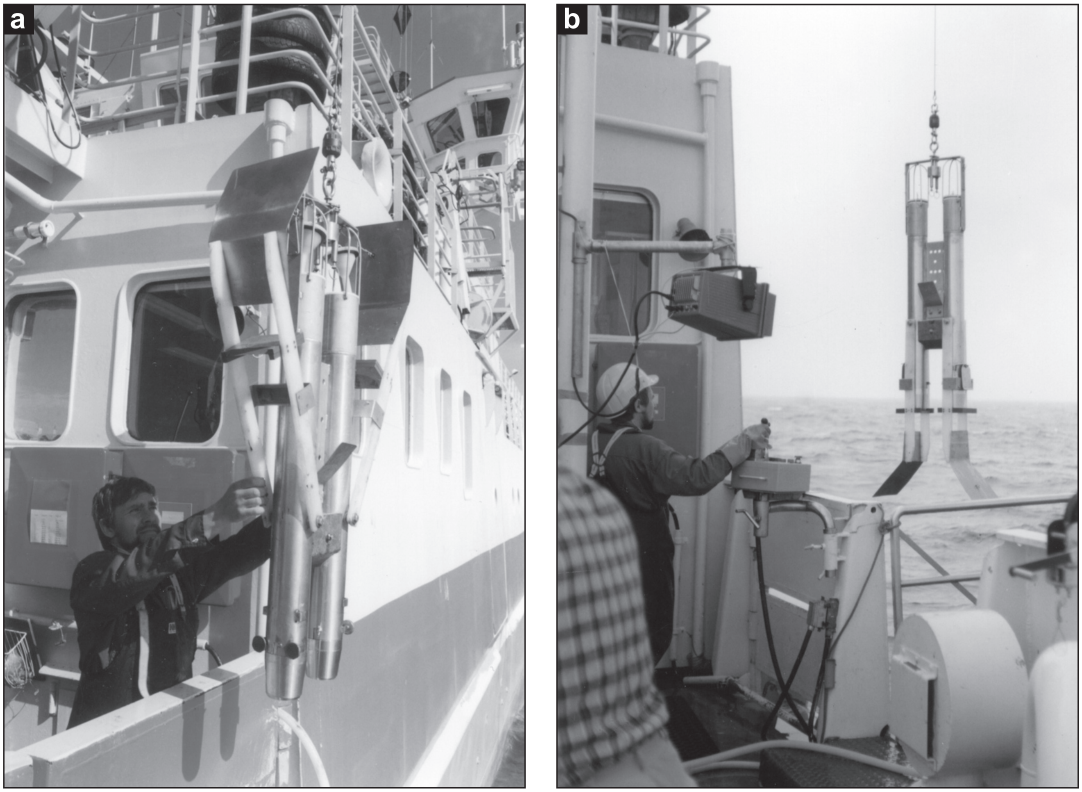


Fig. 1.2. Sample acquisition on the R/V Aranda; the GEMINI corer ready to extract sediment cores (a) and after extracting the cores (b)

The Polish Geological Institute (PGI) participated in both the working group and the research, developing the project and working out the results of the sample analyses. The PGI laboratories also analysed the mineralogical composition and the grain size of the sediments. The results of the project were published by the individual participants, including: Carman (1998), Leivuori (1998), Vallius and Leivuori (1999), Jonsson (2000), Leivuori *et al*. (2000), and Perttilä ed. (2003).

The results achived during the "Baltic Sea Sediment Baseline Study" presents the state of seabed sediments in 1993. Up until now, it has been the most complete and coherent set of information on the chemical composition of the Baltic Sea sediments, forming a basis and reference for further research.

In the present monograph, the results of the project were used to describe the variability in the contents of the individual chemical elements and other substances in the seabed sediments of the surface layer (0–1 cm) and in the vertical section in the whole Baltic Sea to create a perfect background for more detailed discussions concerning the geochemistry of the seabed sediments in the southern part of the Baltic Sea.

A wide range of issues connected with the chemistry of the bottom sediments in the Polish part of the Baltic Sea was made possible by a multi-year research projects carried out by domestic scientific institutions and universities. The studies were financed by, i.a., the Ministry of the Environment, the National Fund for Environmental Protection and Water Management (NFOŚiGW), the Ministry of Science and Higher Education (MNiSzW), and by European Union funds and NATO grants within the framework of international projects.

A basic cartographic image of the chemical contents in the surface sediments was possible due to two projects financed by NFOŚiGW: "Geochemical Atlas of the Southern Baltic" (1994) and "Recognition and Visualisation of the Geological Structure of the Gulf of Gdańsk for Natural Resources Management" (2007), implemented by the Marine Geology Branch of the Polish Geological Institute (PIG-PIB). A large amount of detailed information on the dependence of the chemical substances occurring in sediments and on geochemical processes was gathered while drafting international and domestic grants. The most important projects concerning all Polish sea areas included the grant for the Scientific Research Committee (KBN) "The Assessment of Global Changes in Ecological Conditions of the Southern Baltic Sea Induced by Metallic Contamination against the Background of Other World Water Regions", implemented at Gdańsk Medical University as part of the LOICZ international programme. Particular data concerning the geochemistry of sediments of the Vistula and Szczecin lagoons were provided by two NATO grants: "Heavy Metal Pollution in the Vistula Lagoon, Poland" and "Heavy Metal Pollution in the Sediments of the Szczecin Lagoon" prepared by Gdańsk Medical University. In addition, the University of Gdańsk, Institute of Oceanography, implemented many research projects financed by the Ministry of Science and Higher Education, the results of which have been included in the present monograph. The most significant include the following: "Atmospheric Inflow of Nitrogen, Phosphorus and Iron Compounds in the Light of Eutrophication of the Gdańsk Basin", "Carcinogenic and Neurotoxic Compounds in Aerosols in Inhaled Air Near and Far from Pollutant Emitters" and "Phosphorus Forms in the Sediments of the Gulf of Gdańsk". Detailed studies, focused on implementing geochemical monitoring of sediments, were also made by the Polish Geological Institute. They included the Polish-Dutch project "Geological and Geochemical Monitoring of the Bottom of the Gulf of Gdańsk" (1994) and the Polish-British-Dutch-Lithuanian project within the framework of the INCO-Copernicus programme entitled "The Assessment and Monitoring of the Sea Environment of the Gdańsk Basin" (1998).

The monograph focuses mainly on the seabed area and its sediments in the Polish part of the Baltic Sea. However, all the issues discussed here are presented against the background of the whole Baltic Sea.

The problems concerning the geochemistry of marine sediments were preceded by information on the natural environment and economical use of the sea and its catchment area. The geological structure, soils and river sediments of the catchment area were also analysed. In addition, basic data on the hydrological conditions shaping the sedimentary environment of the Baltic Sea and data on the geological structure and sediments of the seabed were considered. The inflow paths into the Baltic Sea were discussed concerning chemical substances, including their amounts and types. The issues contained in these chapters will provide the reader with sufficient information to recognise the complexity of the reasons behind the spatial diversification of individual constituents in the seabed sediments and the processes occurring there. The following chapters contain detailed data on the contents and distribution of different substances in the present-day surface sediments, including the main constituents, total organic carbon (TOC), nutrients, trace elements, and stable organic pollutants, up to radionuclides. The last chapters deal with issues concerning interstitial waters and gases in the seabed deposits, and the transformation of the suspended matter in the marine environment.

The authors' intention was to present the results of geochemical research on the Baltic Sea deposits conducted in recent decades. Many issues concerning the sediment chemical composition and geochemical processes, crucial for the ecological condition of the marine environment, have already been recognised. However, quite a number of questions still require answers and new ones continue to arise as the progress in research and knowledge is being made. The authors hope that this publication will be useful for the next generations of scholars and enthusiasts of Earth sciences, motivating them to project further studies and facilitating the interpretation of the results.

The Editor and the Authors of this monograph express their gratitude to Dr. Mirja Leivuori and Dr. Matti Perttilä for making available the results of analyses, and in doing so considerably facilitating the work on this publication and enriching its content.

We thank Madame Gabriella Lindholm, the Chairwoman of the Helsinki Commission, and Madame Anne Brusendorff, Executive Secretary of the Helsinki Commission, for providing data from the Baltic Sea Environmental Proceedings from the years 1989–2010.

Chapter 2

THE BALTIC SEA CATCHMENT AREA

2.1. The Baltic Sea: Location, Division and Catchment Area

The Baltic Sea is a brackish semi-enclosed intracontinental sea surrounded by land on all sides. It is bounded by Scandinavia in the north-west and by the lowlands of Central and Eastern Europe in the south and east. It is connected with the North Sea through the narrow and shallow Danish Straits. The surface area of the Baltic Sea, including these straits, i.e., the Belt Sea, the Sound and the Kattegat, is about 418 500 km^2.

According to the division used by the Helsinki Commission (HELCOM), the following regions are distinguished within the limits of the Baltic Sea, considering the hydrographic conditions and shoreline: the Bothnian Bay, the Bothnian Sea, the Archipelago Sea, the Gulf of Finland, the Gulf of Riga, the Baltic Proper (central Baltic Sea), the Belt Sea, the Sound and the Kattegat (Fig. 2.1).

The varied configuration of the Baltic Sea bed determines its division into several basins and depths that are separated by elevations and thresholds. In the southern part (Baltic Proper) we can distinguish: the Arkona Basin (max. depth 53 m), the Bornholm Basin (105 m) and the Gdańsk Basin (107 m). The Bornholm Basin and the Gdańsk Basin is connected by the Słupsk Furrow (95 m). In the northern part of the Baltic Proper are the Eastern Gotland Basin (243 m), the Western Gotland Basin (in its northern part is the deepest area of the Baltic Sea known as the Landsort Deep) (459 m), and the North-Central Basin (200 m).

The Maritime Areas of the Republic of Poland cover 30 600 km^2, which is equivalent to 10% of the land surface area of Poland. They include the internal sea waters (western part of the Gulf of Gdańsk with the Puck Bay and the Puck Lagoon (Inner Puck Bay), the Vistula Lagoon and the Szczecin Lagoon), a 12-mile wide belt of territorial waters and the Exclusive Economic Zone which stretches from the seaward edge of state's territorial waters out to the borders dividing the Baltic Sea between Poland and its neighbouring states: Germany, Denmark, Sweden and Russia (Fig. 2.2).

In the southern part of the Baltic Proper, between the coast and slopes of deep water basins, the seabed gently slopes down to depths of app. 30–40 m. In this area there are bottom rises called banks: Odra, Eagle (Adler Grund), Rönne, Słupsk and Stilo. Besides, to the north of the Słupsk Furrow are the Southern Middle Bank and Northern Middle Bank (Södra Midsjöbanken and Norra Midsjöbanken). Further to the north, around Gotland Isle, are the following banks: Hoburgs, Klints and Sandö.

The catchment area of the Baltic Sea covers app. 1 748 300 km^2, a little over four times larger than the surface area of the sea itself. Both the sea and its catchment area lie along a north-south line. The longitudinal length of the Baltic Sea between the latitudes of 53°95'N in the Pomerania Bay and 65°46'N in the northern coasts of the Bothnian Bay, is about 1300 km, and the length of its catchment area is 2300 km: from the Carpathians in the south to the northernmost part of the Scandinavian Mountains behind the Arctic Circle in the north (Fig. 2.3). The east-west line between the borders of the catchment area

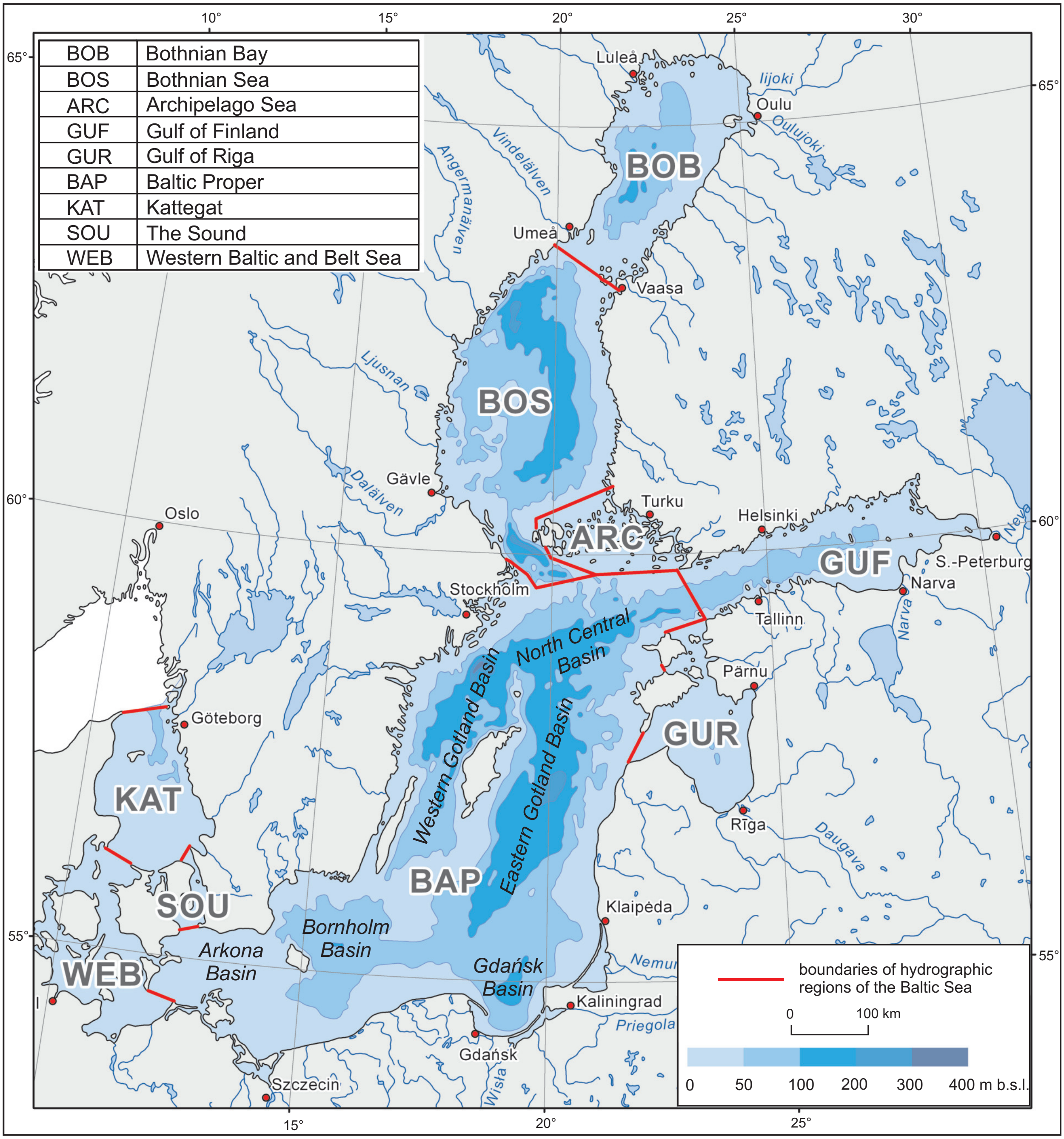


Fig. 2.1. Division of the Baltic Sea into hydrographic regions and main sedimentary basins

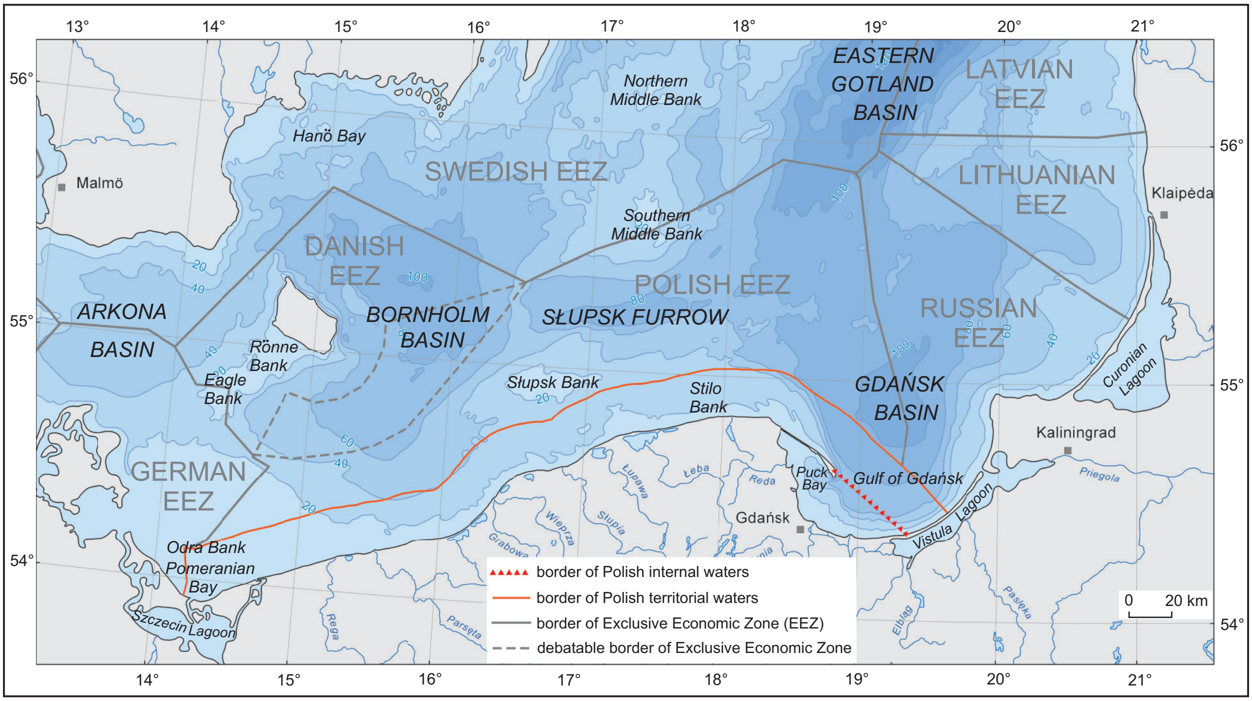


Fig. 2.2. Maritime territories of the Republic of Poland

is shorter. The Baltic Sea stretches between 10° and 30°E longitude. However, generally its width is considerably smaller and, for example, in the southern part, between Jutland and the Lithuanian coast, it is app. 750 km, while in the central part, between Stockholm and Sankt Petersburg, it is app. 650 km. In the narrowest parts, in the Åland Islands region, the sea belt is up to 180 km wide, but in the Kverken Archipelago region, between the towns of Vaasa and Umeå, it is only app. 100 km. The catchment area is slightly larger and stretches between 8° and 38°E.

In the north-west, the western borders of the catchment area of the Baltic Sea border the Scandinavian Mountains, while the Sudetes and the western part of the Carpathians form its southern borders. In the west, east and north-east, the area of the catchment area is limited mainly by culminations of moraine hills of Pleistocene glaciations. The geologic structure means that the larger part of the catchment area is lowland of up to 200 m a.s.l. The territories of elevations from 0 up to 50 m account for 17.4% of the catchment area, from 50 to 100 m – 19.1%, and from 100 to 200 m – 35.1%. Uplands are located mainly in southern Poland (Małopolska Upland and Lublin Upland), in north-western Finland (Maanselkä) and in northern Sweden (Norrland). Smaller upland territories are located in eastern Pomerania, northern Belarus, western Russia (Valdai Upland) and in southern Sweden (Småland). Surface areas at elevations from 200 to 300 m account for 13.3% of the catchment area, while from 300 to 500 m – account for 8.5% of the surface area. Mountainous areas from 500 to 1000 m account for 5.9%, and areas from 1000 to 2655 m account for 0.7%. The highest peaks located within the borders of the Baltic Sea catchment area are: Kebnekaise (2117 m) in the Scandinavian Mountains, Śnieżka (1605 m) in the Sudetes and Gerlach (2655 m) in the Tatra Mountains.

The Baltic Sea catchment area is characterised by a large number of lakes of postglacial origin. The largest lakes of Europe can be found in this area: Ladoga and Onega. Finland has the largest area of lakes, with numerous marshes and bogs. The longest rivers emptying into the Baltic Sea are the Vistula, Odra, Nemunas, Daugava, and Neva. They drain the southern and south-eastern lowlands and their drainage basins cover 780 000 km^2, that is about 50% of the total surface area of the Baltic

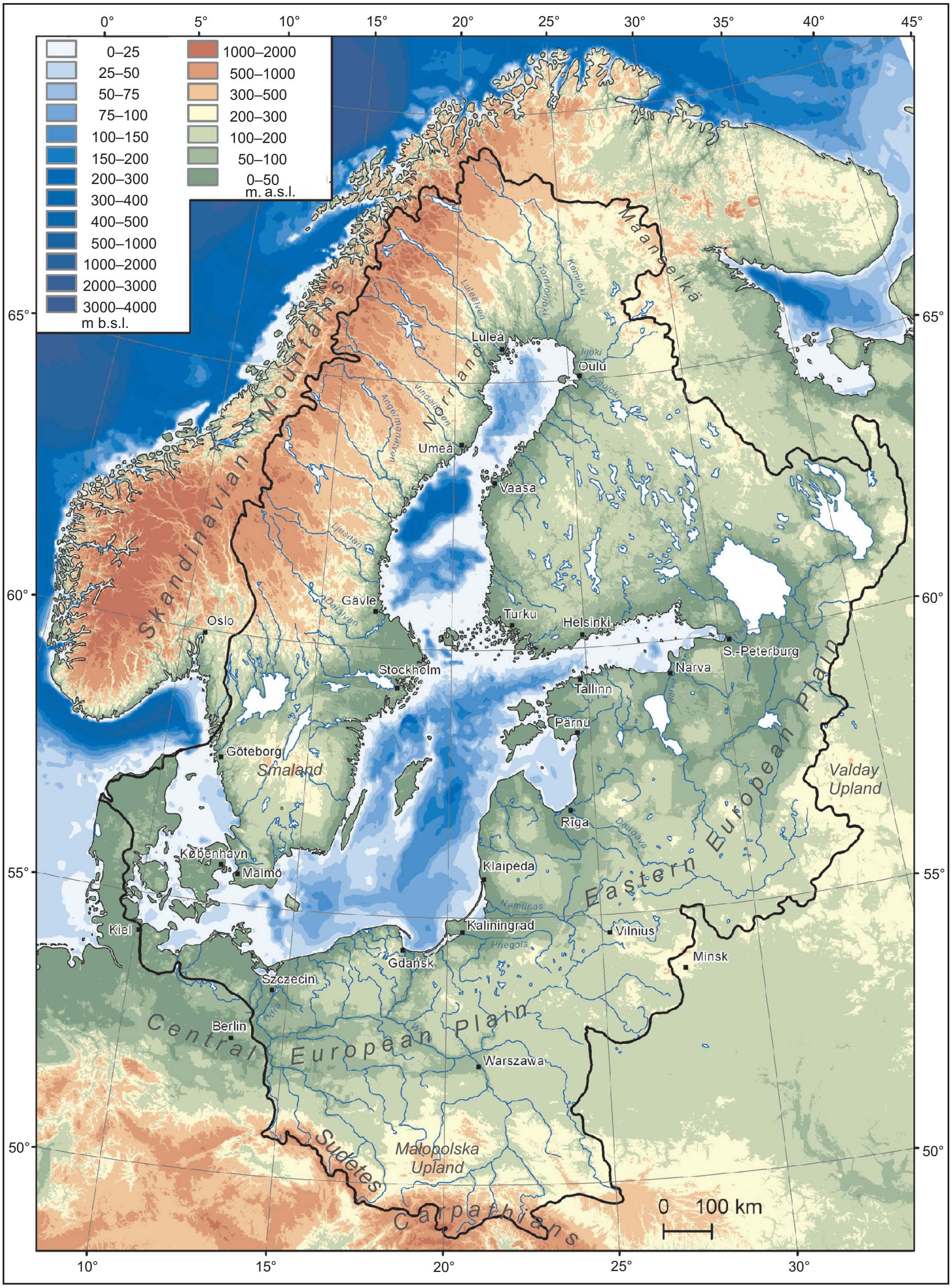


Fig. 2.3. Orography and hydrography of the Baltic Sea catchment area (boundaries of the catchment area marked with a black line)

Sea catchment area. These rivers pass 168 km^3 of water, which is 39% of the total water drainage to the Baltic Sea. In the southern and eastern part of the catchment area, rivers have mainly the character of lowland rivers with wide and mostly marshy valleys. In the north and north-west, rivers are shorter and have substantially higher gradients while their valleys are usually not much wider than their beds. As opposed to the rivers that run off to the Baltic Sea from the south and the east, where the cover of Pleistocene sediments is thick and we can find Holocene deposits in the river valleys, rivers in the northern part of the catchment area flow down the territories with a thin cover of loose sediments mostly on outcrops of older, solid beds.

As can be seen from the information presented here, the most important orographic features of the Baltic Sea catchment area are a definite dominance of lowlands and flatlands covered with Quaternary deposits, and the existence of upland and mountainous territories on the periphery of the catchment area.

2.2. An Outline of the Geologic Structure of the Baltic Sea Catchment Area

The catchment area of the Baltic Sea is located within the limits of three geologic-structural units. The largest portion covers the East European Platform, the smaller, south-western one extends in the Paleozoic West European Platform, while the southern segment of the catchment area belongs to the Carpathian area of the Alpine orogeny (Fig. 2.4).

The northern segment of the catchment area is featured by outcropping crystalline bedrock of the Precambrian craton that forms a vast Baltic Shield built of magmatic and metamorphic Precambrian rocks. The oldest, Archaean rocks of the shield, dated at 3.0–2.5 bln years, extend from the region of the Ladoga and Onega lakes to the northern coasts of the Bothnian Bay. These are various gneisses and migmatites, diorites, granodiorites and granites (Lundqvist, Bygghammar, 1994). In the central part of the shield (north and central Sweden and the prevailing area of Finland) is the so-called “Svecokarelian” province, where Proterozoic rocks occur. Granitoides (1.9–1.6 bln years) are dominant in this area. In Laponia we can find basalts (2.5–2.0 bln years) and some upper quartzites, phyllites, mica schists, and dolomites. The remaining part of the province typically features metamorphic sedimentary and volcanic rocks (1.88–1.87 bln years). The south-western section of the Baltic Shield, consisting of three lower order units, is of more complex geological structure. In the Transscandinavian Granite-Porphyry Belt that stretches out from the Öland Isle towards the NNW, apart from granites and porphyries, we can find gabbro, diorites and local Jotnian red sandstones that are crossed by basalt volcanites. The western coasts of Sweden, situated along the Kattegat, as well as the southern part of Norway, belong to the Southwest Scandinavian Province dominated by gneisses (1.8–0.9 bln years), and subordinate metamorphic sedimentary volcanic rocks. In the Hanö Bay is the Blekinge Region, for which quartzites and acid volcanic rocks, gneisses and granites are characteristic. The rocks are dated at 1.8–1.7 bln, with some granites 1.4–1.35 bln years old, and are crossed with dolerite dykes dated at 0.9 bln years (Lundqvist, Bygghammar, 1994).

The crystalline bedrock gradually drops, generally from NE to SW, from the line of Ladoga and Onega lakes through the southern coasts of Sweden to the Danish Straits. The bedrock surface changes in the NW–SE direction, forming the Peribaltic Depression and the Podlasie-Brest Depression separated by the Masurian-Belorussian Elevation. These geologic units are composed of crystalline basement rocks and a platform cover that imitates the morphology of the base with its Ediacaran–early Paleozoic and Devonian–Carboniferous complexes. The older complexes are unconformably overlain by Permian–Mesozoic, Paleogene–Neogene and Quaternary deposits. The sedimentation of these deposits is related to the development of younger structural units and will be described later in this chapter.

The Peribaltic Depression spreads from Pomerania in the south-west to Riga in the north-east. The crystalline basement dips to the south-west within the limits of this unit to about 6–8 km in the peripherial zone of the craton. The oldest rocks that fill the Peribaltic Depression are local Ediacaran conglomerates and arkosic sandstones

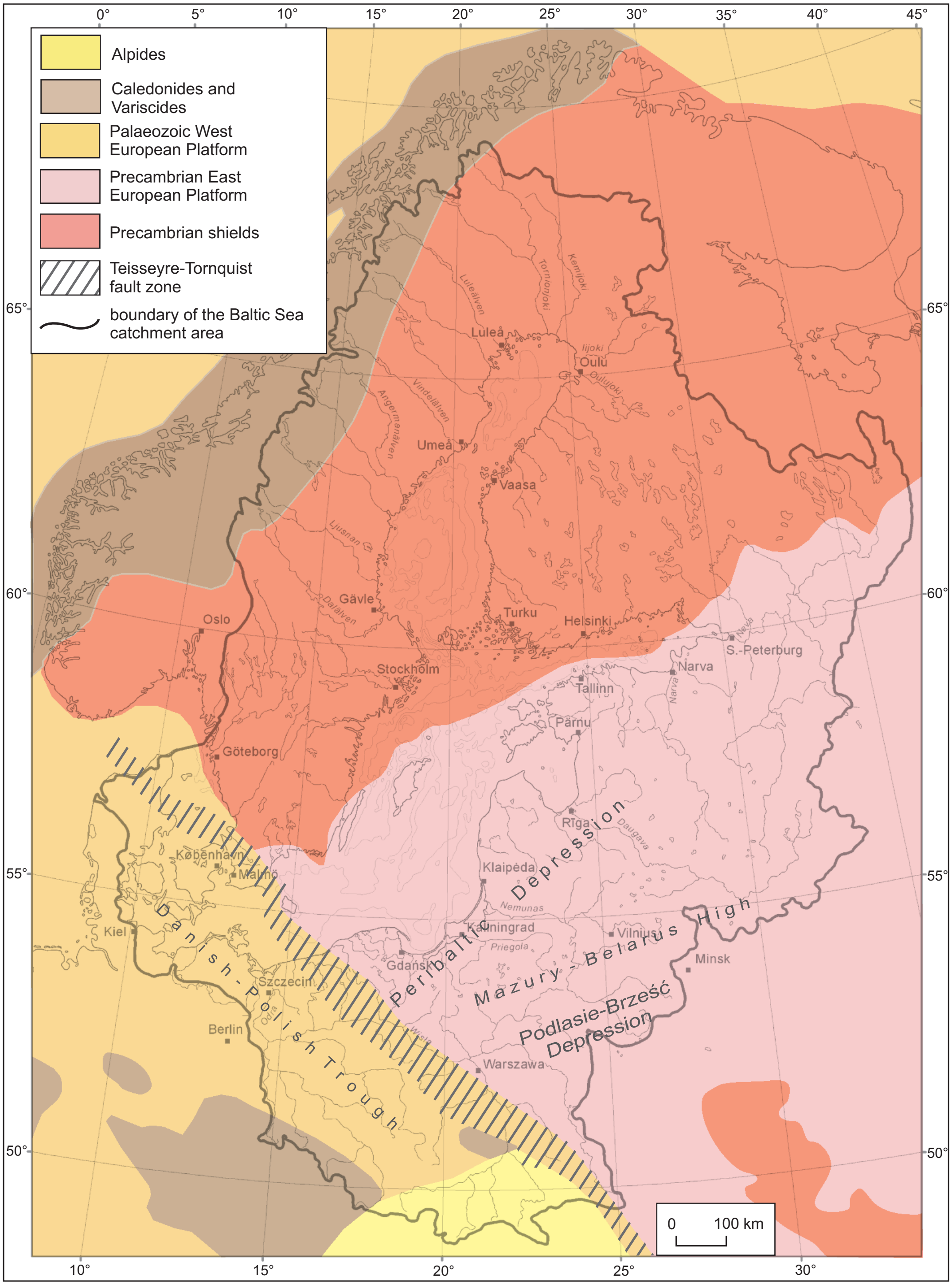


Fig. 2.4. Structural-tectonic outline of the Baltic Sea catchment area

representing large alluvial fans (Jaworowski, 1979). The Cambrian is represented by sandstones and mudstones with admixtures of carbonate rocks in the upper part of the section. The Ordovician is composed of carbonate rocks with shale interbeds, with a transition from calcareous to clayey facies as moving from the east to the west. The Silurian attains the largest thickness of up to 2000 m. In the north and the east it is represented by carbonate facies, whereas in the south – clayey facies predominate. The Devonian rocks occur only in the eastern part of the depression, mainly as terrigenous sandstones. The Carboniferous appears only locally in southern Latvia and northern Lithuania and is represented by mudstones with dolomites and marlstones passing up into fine-grained sandstones with clay interbeds (Winterhalter *et al*., 1981; Blazhchishin *et al*., 1982).

The Masurian-Belorussian Elevation stretches WSW–ENE and is located to the south of the Peribaltic Depression. The crystalline basement of the unit is situated at depths from 1500 m b.s.l. in the south up to about 100 m b.s.l. in the north, in Belarus. That unit is devoid of early Paleozoic sediments over a considerable area, Precambrian rocks are directly overlain by the Triassic and Jurassic formations (Stupnicka, 1989; Mizerski, 2004). The Ediacaran–early Paleozoic complex is present only in the periphery of the elevation.

The Podlasie-Brest Depression is situated to the south of the Masurian-Belorussian Elevation. The axis of this geologic unit runs almost latitudinally. The crystalline basement dips from a few hundred metres b.s.l. in the east down to about 4000 m in the vicinity of the Vistula River. The oldest section of the platform cover consists mainly of the complex of Ediacaran clastic and volcanic rocks. The Cambrian is represented by a monotonous series of shelf sandstones and mudstones of up to 700 m in thickness. The Ordovician and Silurian are characterised by various carbonate, marlestone and clayey lithofacies related to the development of a marine basin. The thickness of the Ordovician deposits is approximately several tens of metres, while the Silurian deposits are more than 1200 m thick. The older rock formations are overlain by the Devonian–Carboniferous complex, intersected with diabase veins.

In the south-east, the East European Precambrian Platform borders on the West European Paleozoic Platform along the Teisseyre-Tornquist (TTZ) fault zone. In the area of TTZ, the crystalline bedrock, cut by many faults, rapidly drops from 5–6 to 10–12 km. The platform basement is composed of folded lower Paleozoic deposits of large thicknesses. They are covered by the Devonian–Carboniferous complex with a system of blocks, grabens and horsts. The structural evolution and age of these tectonic deformations has long been discussed in the literature (vide Mizerski, 2009). Generally, in the northern part of this area as well as along the edge of the Precambrian Platform is a zone of Caledonides, but the south-western part of the area belongs to the Variscan structures.

Paleozoic structures are visible on the surface within the Paleozoic core of the Świętokrzyskie (Holy Cross) Mountains and in the Sudetes located in the north-western periphery of the catchment area. In the rest of the West European Paleozoic Platform and in the East European Precambrian Platform, the Paleozoic formations are covered with the Permian–Mesozoic complex. The main structural unit of this complex is the Danish-Polish Basin (Danish-Polish Trough) where marine and continental clastic and carbonate deposits were accumulated during Permian and Mesozoic through Paleocene times. The thickness of the rock series in Poland is locally up to 10 000 m. The Baltic Sea catchment area includes the following geographic units: Jutland, Mecklenburg and western Poland. Deep embayments being at different phases of the basin development form part of the territories of northern and eastern Poland, Lithuania and Latvia, located in the East European Precambrian Platform.

Early Permian was a period of development of volcanic covers, amongst which continental clastic rocks are represented by the Rotliegend facies. The Zechstein consists of four cyclothems whose complete sedimentary successions are as follows: clays, limestones and dolomites, gypsum and anhydrites, and finally potassium and magnesium rock-salts. The most complete section is observed in the central part of the basin, in western Poland. The thickness of the deposits exceeds 1600 m in this area. The peripheral zones of the basin are dominated by clastic facies or bryozoan-algae reefs.

The Triassic deposits lie on Permian sediments and are represented mainly by Buntsandstein clastic deposits accumulated in shallow flood waters, Muschelkalk marine formations as well as Keuper alluvial and limnic sediments. The thickness of the Triassic in the Paleozoic platform exceeds 2500 m.

The Jurassic sedimentation was of a cyclic character involving ingressions and regressions of marine waters. The Jurassic section in the Paleozoic platform in its bottom part consists of mainly continental fluvial, deltaic and lacustrine deposits, with a few silty or brackish series. In the upper part of the section, the deposits pass into marine clastics with an increasing amount of marls and mudstones. Carbonate sedimentation prevailed in the Late Jurassic.

The Lower Cretaceous is represented by clastic facies of mixed origin: both marine and continental. The Upper Cretaceous section is composed of marine carbonates represented by limestones, marlstones, chalk, opokas and gaizes. The thickness of the Upper Cretaceous deposits locally attains 2000 m.

The remnant marine basin survived into the lower Paleocene when the Laramide movements induced the inversion of the Danish-Polish Trough, the restructuring of Permian–Mesozoic deposits and the formation of smaller units along the NW–SE axis. The main area of sedimentation was the Marginal Trough located along the edge of the East European Platform, where the Paleocene sea reached with a vast bay into the Masurian and Sambian area. The Marginal Trough was an area of carbonate-clastic sedimentation with sandy facies prevailing in the north-east.

In the late Paleogene, sedimentation of sands and silts prevailed in the epicontinental basin of the platform areas in shallow, coastal and lagoonal-deltaic waters. The Neogene is represented by Miocene, mostly marine, sandy and silty sediments in Denmark, and by continental and brackish deposits with brown coal in the western part of Poland and in Germany. The Pliocene is composed of variegated clays deposited in an intracontinental sedimentary basin that covered the area of central and western Poland.

The smallest surface area of the Baltic Sea catchment area is occupied by the Alpine orogen including the Carpathians and Carpathian Foredeep. There are mainly Paleogene and Neogene formations forming part of the strongly thrust and overthrust nappes of the Carpathian flysch.

The whole Baltic Sea catchment area is covered by Quaternary sediments. The Pleistocene is represented mainly by glacial tills and sands, silts and clays of variable thicknesses. In the area of the Baltic Shield, Scandinavian Mountains, Sudetes, Carpathians and uplands of southern Poland, the thickness of the Pleistocene cover scarcely exceeds a few metres. Locally, the bedrock outcrops uncovered by any Quaternary sediments. The thickness of the Pleistocene series rapidly increases from the eastern and southern coast of the Baltic Sea to the south and southeast. The maximum thickness, up to 200–300 m, is observed in northern Germany, Poland and Lithuania.

The Holocene deposits are represented mainly by sands, silts and peats, but their thickness is only occasionally greater than a few metres (Starkel, 1977; Mojski, 1993). The Holocene occurs mainly in deltas and valleys of rivers, on coastal lowlands and peatland.

2.3. Soils in the Baltic Sea Catchment Area

Soil is a crucial component of the natural environment situated between the lithosphere and atmosphere. The most important functions of soil are biomass production, humus accumulation as well as storage and circulation of chemical elements and water. Large part of the soil cover is used for agriculture. From the chemical point of view, soil can be defined as multi-component, open biogeochemical systems where continuous processes of the exchanging matter and energy with the surrounding atmosphere, hydrosphere and biosphere occur (Aswathanarayana, 1999). The main factors that affect its chemical composition are natural conditions and processes, such as the chemical composition of parent rocks and climate.

Over much of the Baltic Sea catchment area, soil degradation can be found, that results from both natural and man-induced processes. The natural factors include processes of rock and soil erosion, while the human-induced ones include agriculture and forestry, urbanization, building industry, transport, mining and processing of mineral deposits, as well as atmosphere depositions. Degradation resistance of soils depends on their composition and physical and chemical properties, such as acidity, sorption and oxido-reduction capabilities. Heavier soils and those rich in humus are more resistant than light soils, which are poor in both mineral and organic components (Dobrzański, Zawadzki, eds., 1993).

2.3.1. Genetic Soil Types

The main factors that shape the soils in the Baltic Sea catchment area are a complex geologic structure and relief, climate and plant cover. Due to the diversity of bedrocks on which the soils originated, and the diversity of climatic conditions, the soil system is of a mosaic character (Bednarek, Prusinkiewicz, 1997; Jones *et al*., 2005).

In the northern and central parts of the catchment area, there are common acidic igneous rocks of the Fennoscandian Shield which, in the Quaternary, were the source of material for glacial and glaciofluvial deposits, both within its borders and to the south. In the Scandinavian countries, on a base of till and glaciofluvial deposits developed mainly Podzols. In northern Sweden and Finland, large areas are covered by Histosols. In the north of the Gulf of Finland and southern Sweden, there is a considerable proportion of Cambisols. In southern Sweden, there are also Regosols (Jones *et al*., 2005).

The soil-forming material in the southern and south-eastern part of the catchment area (in Germany, Belarus, Lithuania, Latvia and Estonia) are Pleistocene glaciation deposits represented by tills, sands, gravels as well as stagnant water and aaeolian deposits, characterised by variable bedding, grain-size and mineral composition. An additional factor differentiating the soil cover in this area is the age of parent rocks resulting in the older material (in central and southern Poland) being more weathered and more deeply delimed than the deposits of the youngest glaciation in the north of the region. The area of Lithuania, Latvia and Estonia is covered mainly by Gleysols and Albeluvisols accompanied by Arenosols and Podzols. Albeluvisols prevail in the area of Belarus (Jones *et al*., 2005). The northern part of Poland and Germany is covered by Luvisols, Cambisols and Podzols. In central Poland, they occur together with Phaezems and Rendzinas. Fluvisols and Umbrisols are of a much smaller significance.

Anthrosols prevail in cities and towns located on the Baltic Sea coast.

2.3.2. Grain Size and Geochemistry

To assess the geochemical characteristics and grain-size of soils, the results of the FOREGS – Geochemical Atlas of Europe project were used (Salminen ed., 2005; de Vos, Tarvainen, eds., 2006). For the purpose of this study, soil samples were collected according to a unified procedure for the area of the whole Europe (Salminen *et al*., 1998). In 1999–2000, mineral soil samples were taken from a depth of 0–25 cm with an average density of 1 sample/4700 km^2 (Salminen ed., 2005). Their location within the Baltic Sea catchment area is shown in Figures 2.5–2.14. Statistical parameters of chemical components of these soils, their acidity and grain size are presented in Table 2.1.

The **grain size,** characterizing the small variability in time, belongs to the group of significant characteristic features of soils (Usowicz *et al*., 2004). The topsoils of the Baltic Sea catchment are characterised by a coarse grain-size. The soils of the significant part of Finland, Poland and Germany are rich in sand fractions (>0.10 mm). The mean grain size (median) of these soils is 0.18 mm (Salminen *et al*., 2005; de Vos, Tarvainen, eds., 2006). Their chemical composition is dominated by quartz, which is expressed by the content of SiO_2 (average 76%) and by an insignificant content of clay fraction (<0.002 mm) – average 1.54%. The soils of Sweden, Lithuania, Latvia and some part of Estonia, as well as of mountainous regions of Poland, contain 1.83–4.54% of the clay fraction. The soils of eastern Latvia are distinguished by the clay fraction content of up to 9%. The amount of silt-clay fraction (<0.06 mm) in these soils ranges from 1.28 to 89.36%. Soils containing large amounts of the silt-clay fraction (up to 76.60%) occur in the Carpathians and Sudetes.

Acidity (Fig. 2.5). In the northern part of the Baltic Sea catchment area, under cold climate conditions of tundra areas covered with Quaternary deposits and devoid of carbonate rocks, with the participation of scant vegetation (mainly mosses and lichens), there are thin soils having a low content of humus and acidic values (pH <5). Biological activity of bacteria in these soils is considerably restricted and the inhibition of advantageous transformations of nitrogen compounds occur

Table 2.1

Statistical parameters of chemical elements and pH of topsoils in the Baltic Sea catchment area (data from the FOREGS Project)

Element/ compound	Analytical method	Unit	Detection limit	n	Range	Arithmetic mean	Geometric mean	Median
Ag	ICP-MS	mg/kg	0.01	209	0.08–0.78	0.34	0.31	0.33
As	ICP-MS	mg/kg	0.2	209	0.3–15.2	3.1	2.4	2.3
Al_2O_3	XRF	%	0.05	211	1.02–15.80	8.77	7.70	9.70
Ba	ICP-AES	mg/kg	1	211	12–136	45	40	40
CaO	XRF	%	0.01	211	0.03–15.44	1.20	0.80	1.00
Cd	ICP-MS	mg/kg	0.01	209	0.02–0.96	0.11	0.09	0.08
Ce	ICP-MS	mg/kg	0.15	210	5.47–83.00	31.67	27.59	28.20
Cr	XRF	mg/kg	3	211	<3–213	40	33	33
Cs	ICP-MS	mg/kg	0.5	209	<0.5–12.3	2.2	1.7	1.7
Cu	ICP-MS	mg/kg	0.01	209	0.87–28.00	6.09	4.82	4.36
Dy	ICP-MS	mg/kg	0.1	210	0.4–7.2	2.3	2.0	2.1
Er	ICP-MS	mg/kg	0.1	210	0.3–4.0	1.4	1.3	1.3
Eu	ICP-MS	mg/kg	0.05	210	0.05–1.63	0.53	0.46	0.52
Fe_2O_3	XRF	%	0.01	211	0.16–7.40	2.47	1.95	2.17
Ga	ICP-MS	mg/kg	0.2	210	1.5–20.9	10.6	9.1	11.2
Gd	ICP-MS	mg/kg	0.1	210	0.4–9.3	2.5	2.2	2.4
Hf	ICP-MS	mg/kg	0.2	210	1.0–16.0	6.0	5.5	5.7
Hg	CV-AAS	mg/kg	0.0001	211	0.006–0.096	0.026	0.022	0.022
Ho	ICP-MS	mg/kg	0.02	210	0.09–1.34	0.47	0.41	0.43
In	ICP-MS	mg/kg	0.01	209	<0.01–0.08	0.04	0.03	0.03
K_2O	XRF	%	0.010	211	0.34–4.10	2.11	1.94	2.15
La	ICP-MS	mg/kg	0.1	210	2.7–37.1	15.4	13.5	13.7
Lu	ICP-MS	mg/kg	0.02	210	0.04–0.58	0.23	0.20	0.22
MgO	XRF	%	0.01	211	<0.01–3.54	0.61	0.40	0.44
MnO	XRF	%	0.001	211	0.006–0.326	0.048	0.040	0.041
Mo	ICP-MS	mg/kg	0.1	209	<0.1–4.9	0.6	0.5	0.5
Na_2O	XRF	%	0.010	211	0.08–3.76	1.60	1.20	1.46
Nb	ICP-MS	mg/kg	0.1	210	1.6–16.8	7.3	6.5	6.7
Nd	ICP-MS	mg/kg	0.15	210	2.27–37.90	13.37	11.65	12.10
Ni	ICP-MS	mg/kg	2	210	2–175	12	9	8
P_2O_5	XRF	%	0.001	211	0.020–1.022	0.122	0.010	0.102
Pb	ICP-MS	mg/kg	3	210	5–42	17	16	16
pH	potentiometric	pH units		208	3.90–7.22	5.32	5.25	5.02
Pr	ICP-MS	mg/kg	0.1	210	0.7–9.7	3.6	3.1	3.2
Rb	XRF	mg/kg	2	211	15–192	72	66	69

Table 2.1 continued

Element/ compound	Analytical method	Unit	Detection limit	n	Range	Arithmetic mean	Geometric mean	Median
Sb	ICP-MS	mg/kg	0.02	209	0.04–2.32	0.30	0.25	0.26
Sc	ICP-MS	mg/kg	0.5	210	0.7–16.8	5.9	4.8	5.2
SiO_2	XRF	%	0.1	211	50.96–96.02	77.05	76.44	75.79
Sm	ICP-MS	mg/kg	0.1	210	0.4–8.4	2.6	2.2	2.3
Sn	XRF	mg/kg	2	211	<2–11	3	2	2
Sr	XRF	mg/kg	2	211	8–346	122	97	103
Ta	ICP-MS	mg/kg	0.05	210	0.10–1.30	0.54	0.48	0.49
Tb	ICP-MS	mg/kg	0.02	210	0.05–1.28	0.40	0.34	0.36
Te	ICP-MS	mg/kg	0.02	209	<0.02–0.12	0.02	0.02	0.02
Th	ICP-MS	mg/kg	0.1	210	1.2–13.9	5.1	4.5	4.5
TiO_2	XRF	%	0.001	211	0.091–1.145	0.429	0.377	0.390
Tl	ICP-MS	mg/kg	0.01	209	0.13–1.53	0.59	0.59	0.53
Tm	ICP-MS	mg/kg	0.02	210	0.05–0.57	0.22	0.19	0.20
TOC	coulometric	%	0.01	212	0.15–7.93	1.49	1.23	1.22
U	ICP-MS	mg/kg	0.1	210	0.4–5.9	1.5	1.4	1.4
V	ICP-MS	mg/kg	0.5	210	2.7–140.0	39.1	30.3	31.6
Y	XRF	mg/kg	3	211	<3–50	14	12	13
Yb	ICP-MS	mg/kg	0.05	210	0.34–4.19	1.51	1.34	1.44
Zn	XRF	mg/kg	3	211	<3–230	32	23	24
Zr	XRF	mg/kg	3	211	46–640	246	226	238
Grain size <0.002 mm		%		209	0–11.50	2.03	1.14	1.54
Grain size <0.06 mm		%		209	1.28–89.36	29.37	23.46	26.55

(Dobrzański, Zawadzki, eds., 1993). The original soil acidity is an effect of natural soil-forming processes. The process of soil acidity lowering in other areas of the catchment area is the result of using mineral fertilisers, and dissemination of gaseous air pollutants, such as sulphur dioxide and nitrogen oxides, which reach the soils and water in the form of acid rain and the so-called dry fallout. In the soils showing strongly acidic reaction, we can observe a shortage in basic ions (calcium, magnesium and potassium) and the release of components (aluminium, iron, manganese) harmful to plants, as well as the increase in mobility and plant availability of heavy metals.

Only about 10% of the soils (mainly in Lithuania, Latvia and Estonia) are characterised by neutral pH. A similar distribution of soil pH values in this part of Europe was found during an earlier survey (Reimann et al., 2003).

The **geochemical variation** of the chemical elements in the soils reflects mainly the natural conditions (type of parent rocks, climate, weathering and soil forming processes), which have been disturbed by human economic activities, regionally or locally.

Soils of this region are characterised by especially low contents of most chemical elements. This depletion is related to long-lasting leaching of some components by acidic periglacial waters and their runoff into surface and underground waters. Leaching processes were much more intense thanks to earlier mechanical changes (grinding and crumbling) of parent rocks during recent glaciations.

Aluminium is the major component of most soil minerals. It is able to form numerous mineral and organic complexes and its solubility is the highest in the pH 4–4.5. In the analysed soils, the Al_2O_3 content is between 1.02 and 15.80%. The distribution map of this component (Fig. 2.6) shows its variable concentrations. The lowest Al_2O_3 contents are observed in the sandy soils of Poland and Germany (an average of 3.5%). Higher concentrations were found in the soils of Lithuania, Latvia and Estonia (4–12%), and the soils richest in this component are found in Finland (8–15%). Worth noting is a distinct negative correlation between the Al_2O_3 content and soil acidity.

Silicon is one of the most abundant chemical components of soils (50.96–96.02% SiO_2; median: 75.79%). The richest in this element are the podsols in Poland (Fig. 2.7) with the average content of 89% SiO_2. Silicon is contained mainly in the sand and silt fractions of soils, being a constituent of quartz and aluminosilicates.

Iron is characterised by its high mobility and large changeability in soil profiles (Dobrzański, Zawadzki, eds., 1993). Its sources are hydrated oxides and aluminosilicates. Soils of the Baltic Sea catchment area contain 0.44% Fe_2O_3 on average, and its distribution pattern is very diversified (Fig. 2.8) The most abundant in Fe_2O_3 (5–7%) are the soils of the northern part of the catchment area, while the poorest are the soils in Poland (on average 1%).

Phosphorus. Both apatite group minerals and fertilisation with phosphorus fertilisers are significant sources of phosphorus. The median value of P_2O_5 is 0.102%, ranging from 0.020 to 1.022%. The poorest soils in phosphorus (<0.100%) occur in central Finland, western Sweden and central-eastern Poland (Fig.2.9).

Potassium and sodium. The median values of K_2O and Na_2O for the whole are on average2.15% and 1.46%, respectively. The lowest contents of these elements are observed in the soils of Poland (1.25% and 0.49%, respectively), which is related to a very low content of the silt fraction that accumulates these elements. The highest amount (>3%) of K_2O and Na_2O was found in the soils of Sweden and Finland, which are rich in clay minerals, micas and feldspars.

Calcium and magnesium. The CaO content is very diverse. In the northern periphery of Sweden and Finland, it exceeds 2%. Intermediate values are characteristic for the middle part of the basin, but in the area of Poland, the CaO value is below 0.60%. The MgO content is low (median 0.44%) in relation to its content for the whole of Europe – 0.77% (Salminen ed., 2005). In the area of Poland and Germany, the contents of these components are even lower than the above mentioned.

Total organic carbon. The content of total organic carbon (TOC) is a measure of the amount of humus in soils and it rarely exceeds 2% in the study area (Fig. 2.10). Humus, which collects carbon in soils, contains nutrients and water – the components that determine soil fertility. Organic substance of soil is very prone to changes in environmental factors such as climate, vegetation and soil management. In the region of the Gulf of Finland, in southern Sweden and in the German part of the catchment area, the TOC content sometimes reaches 4–6%, however in the soils of Poland it is only 0.86%.

Trace elements. The processes of accumulation of trace elements in soils, especially metals, are combined with both their natural cycles and human activity. The highest pollution with metals occurs in the areas under the influence of non-ferrous metallurgy. Metal compounds accumulated in the soils penetrate plants and then penetrate into animal bodies.

Among the trace elements, heavy metals, typically cadmium, copper, mercury, lead, chromium, nickel and zinc, are usually used as indicators of anthropopression.

The median value of **cadmium** in the soils of the Baltic Sea catchment area is 0.08 mg/kg. A slightly elevated amount (>0.26 mg/kg) is characteristic for a regional geological-anthropological anomaly and occurs in southern Poland (Fig. 2.11). The average content of this element in the arable soils of Poland varies from 0.22 to 0.51 mg/kg (Terelak *et al*., 1997).

The contents of **chromium** in the soils that undergo no anthropogenic effects is dependent on its amount in the parent rocks. The distribution pattern of chromium is similar to the aluminium, cobalt and nickel patterns. Within the confines of the Baltic Sea catchment area, the total chromium concentration is 33 mg/kg. The chromium content in the soils of individual countries is: 34.6 mg/kg in

Lithuania (Kadūnas *et al*., 1999) and 60 mg/kg in Finland (Koljonen ed., 1992). In Poland, the variability in the geochemical background of chromium in soils is dependent on the parent rock lithology. The median chromium values are 3 mg/kg for the soils of the Polish Lowland and 10 mg/kg for the soils of the southern geochemical province of the country (the Carpathians and the Sudetes).

The **copper** content varies between 0.87 and 28 mg/kg; median is 4.36 mg/kg. About 75% of the analysed soils contain <7.5 mg/kg of copper (Fig. 2.12). The low content of this element is related to the acidic conditions of soils in which cationic forms of copper are mobile and outwash. A similar copper content in the agricultural soils of Poland, 6.5 mg/kg on average, was shown by Czarnowska and Gworek (1987), and Terelak *et al*. (1997). In the soils of Lithuania, the average copper content is 7.5 mg/kg (Kadūnas *et al*., 1999), compared to that for tills of Finland – 20 mg/kg (Koljonen ed., 1992). In Finland and Sweden, elevated concentrations of copper (like of iron, nickel and zinc) were found in areas of sulphide deposits of these metals. In Poland, an increased copper content, between 7–24 mg/kg, is characteristic for the geochemical province of southern Poland (Pasieczna, 2003). The anomaly (>25 mg/kg of copper), associated with mining and metallurgy of copper ores, is observed in the area of North Sudetic Depression and within the Legnica-Głogów Copper District.

Mercury is toxic to plants and animals even when it occurs in very low concentrations. Plants take it up from both the soil and the air, and transport it easily in tissues, resulting in poisoning. Mercury is an element dispersed throughout the lithosphere and its content rarely exceeds hundreds of mg/kg (Steinnes, 1995; Alloway, Ayres, 1999). Its higher concentrations (up to 0.40 mg/kg) occur in some organic and clay deposits. Atmospheric mercury gathers mainly in the topsoil thanks to its fixation with humus, sulphur and clay minerals. Hence, organic soils are the richest in this element – 0.41 mg/kg in Canada (Kabata-Pendias, Pendias, 1999), while the average content in the soils of the world is estimated by different authors within a considerably lower range (0.05–0.06 mg/kg – Freedman, 1989; Reimann *et al*., 1998; 0.02–0.15 mg/kg – Mihaljevič, 1999). In the analysed soils, the mercury content is low (median 0.022 mg/kg). Only about 10% of the samples show the contents of above 0.06 mg/kg (Fig. 2.13).

The **lead** content in non-contaminated soils is mainly related to its concentration in the parent rocks and varies within quite wide limits. The amount and form of lead in soils depends on soil reaction and the contents of components with a suitable soil absorption capacity. In acidic soils, the fixation of this element in organic compounds prevails; some of these compounds are soluble and migrate (Kabata-Pendias, Pendias, 1999).

In the study area, the mean lead content is 16 mg/kg, and is similar to the lead amounts determined in other parts of Europe. The geometric mean for the lead content in the sandy topsoils of the Frisian Islands (Germany) is 7.9 mg/kg (Severson *et al*., 1992). In the soils of Scotland, the mean value is 13 mg/kg Pb for mineral soils and 30 mg/kg for organic soils (Reaves, Berrow, 1984). The geochemical background of lead in the soils of Saxony is estimated at 53 mg/kg (Rank *et al*., 1999).

Zinc is one of the most intensely used non-ferrous metals. It is easily available to plants and takes part in many biochemical processes. However, both its shortage and excess lead to tissue damage. Within the Baltic Sea catchment area, the zinc content varies from <3 up to 230 mg/kg. In 90% of the tested soil samples, its concentration does not exceed 70 mg/kg. More than 100 mg/kg of zinc is contained exclusively in the topsoil of southern Poland and of small areas in Finland (Fig. 2.14).

Zinc content is related to its concentration in the parent rocks and the genetic group of soil. In Poland, light soils (sandy) contain on average 33 mg/kg of zinc, medium (loamy and silty) soils – 52 mg/kg, and heavy (loamy) soils – 80 mg/kg (Kabata-Pendias, Pendias, 1999). In Germany, the average zinc content is 83 mg/kg, in Austria – 65 mg/kg, and in Scotland – 58 mg/kg (Kiekens, 1995). In the soils of Lithuania, it varies from 1 up to 185 mg/kg Zn (Kadūnas *et al*., 1999), and in Norway it is 40 mg/kg Zn (Reimann *et al*., 1998).

*

The topsoil of the Baltic Sea catchment area is characterised by coarse grains, acidic reaction and a low content of most elements. Such a poor chemical composition of soils is related to long-lasting washing of the parent rocks by periglacial waters and carrying the elements into the surface and groundwater. The soils of this part of Europe are very rich in silica only, and are extremely impoverished in magnesium and iron.

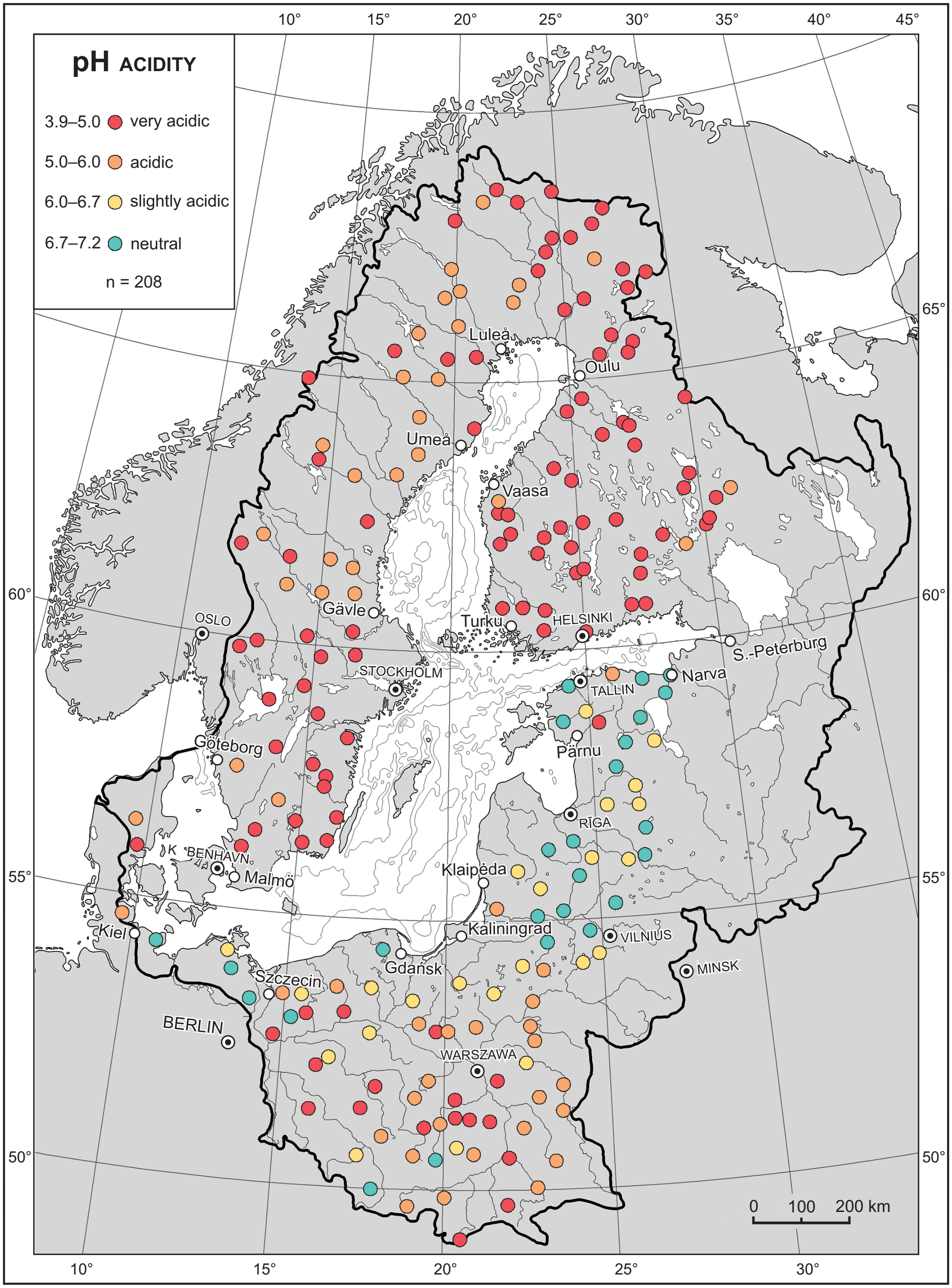


Fig. 2.5. Topsoil acidity (pH)

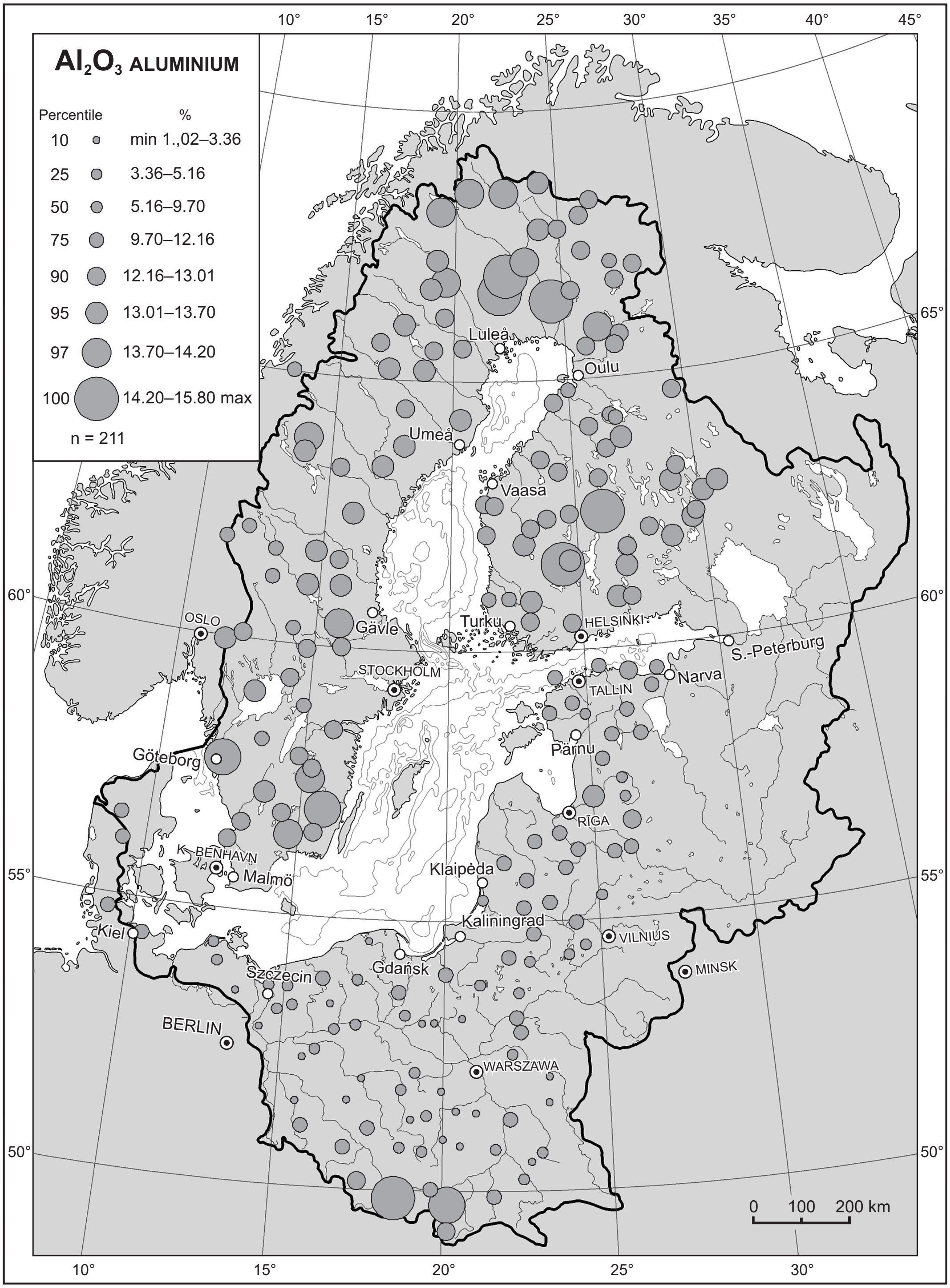


Fig. 2.6. Al_2O_3 content in topsoil

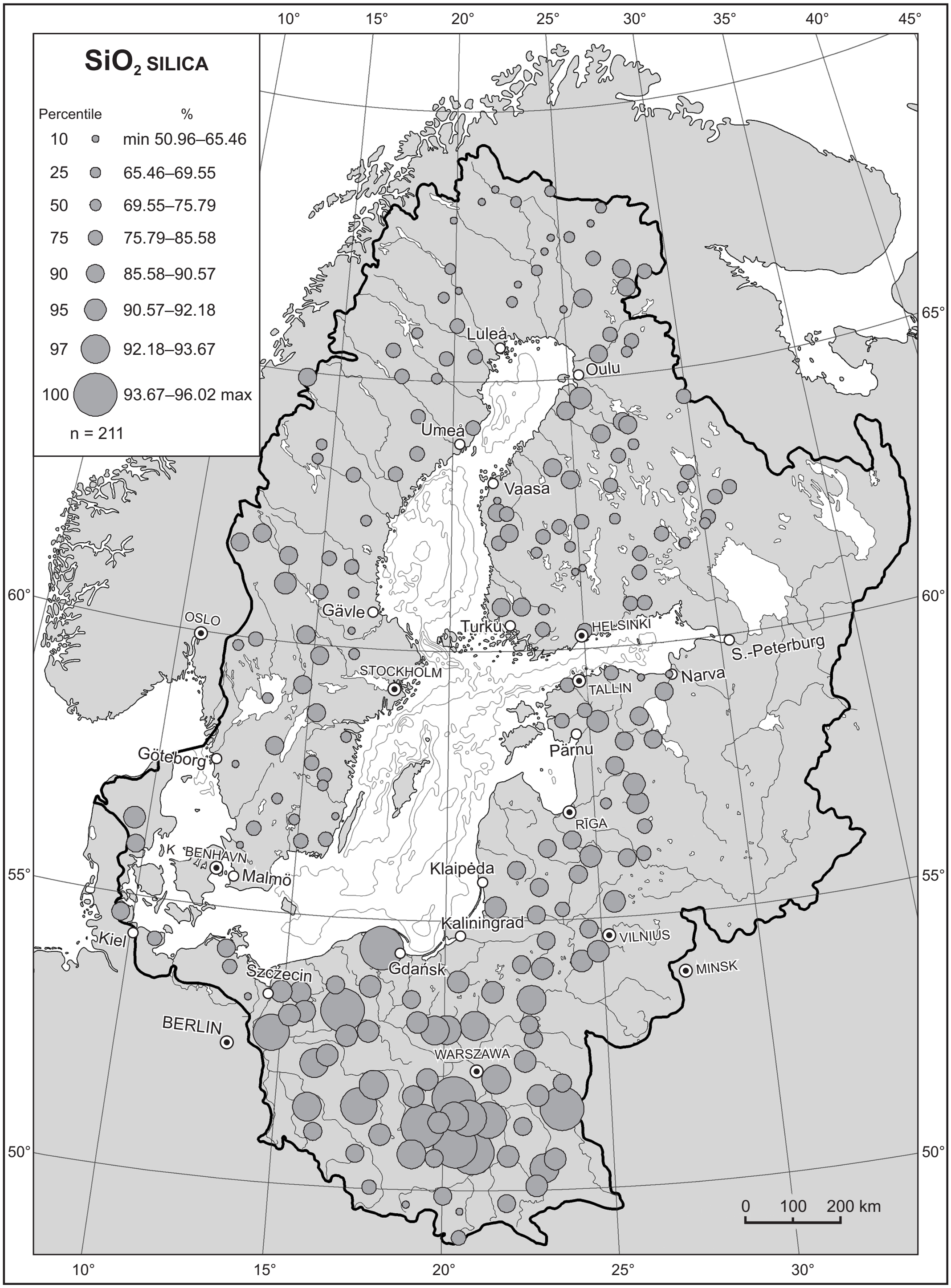


Fig. 2.7. SiO_2 content in topsoil

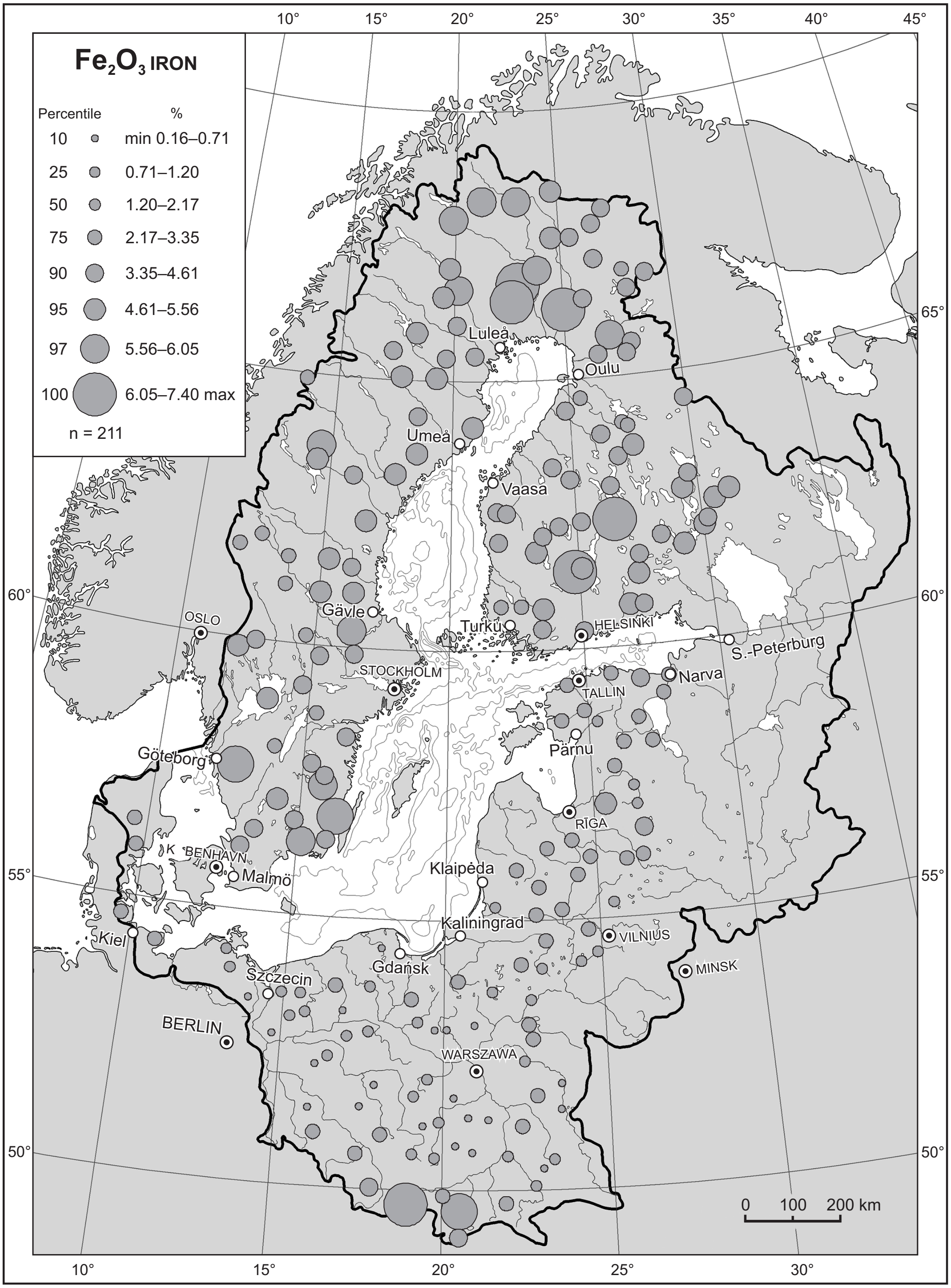


Fig. 2.8. Fe_2O_3 content in topsoil

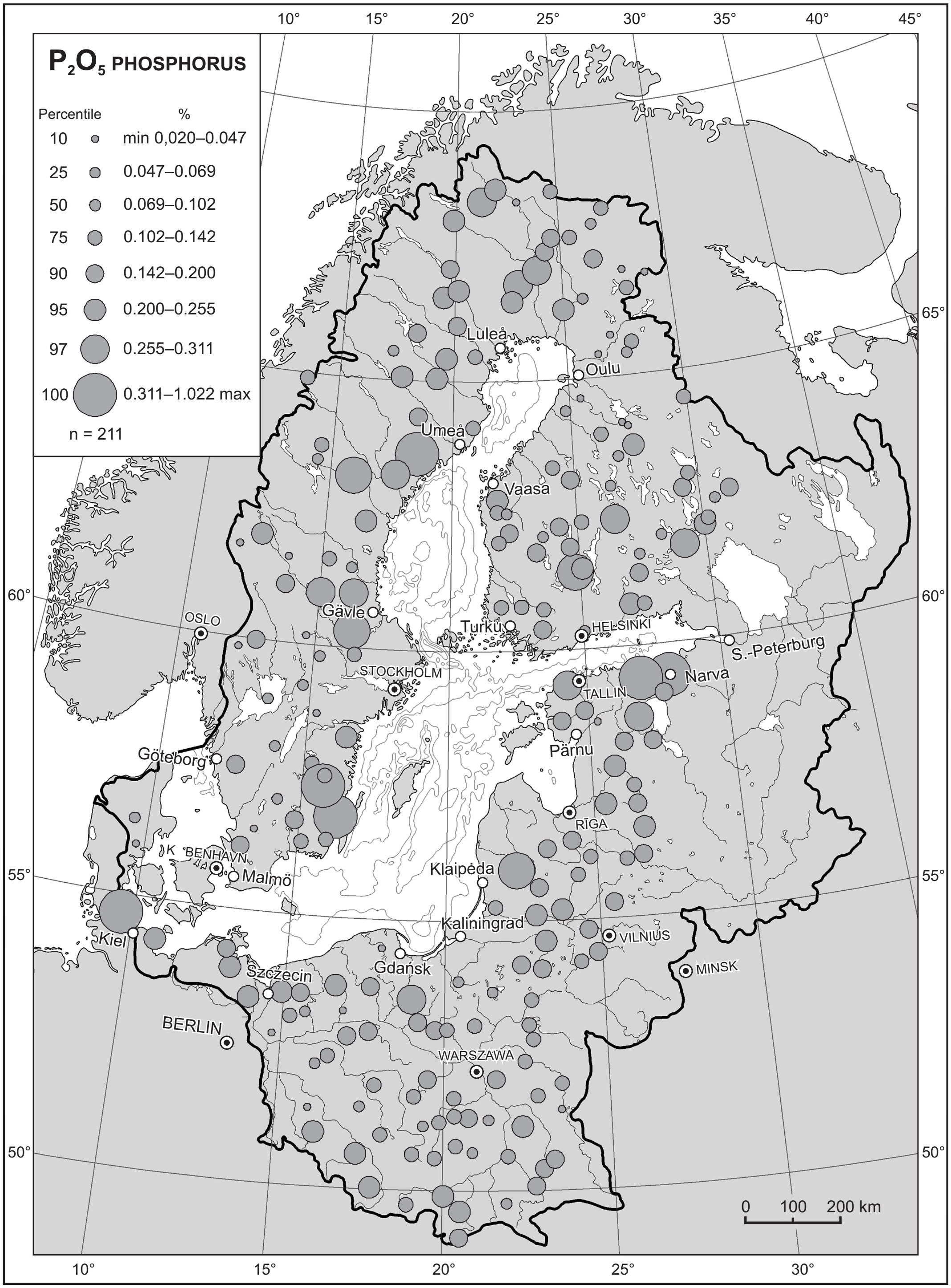


Fig. 2.9. P_2O_5 content in topsoil

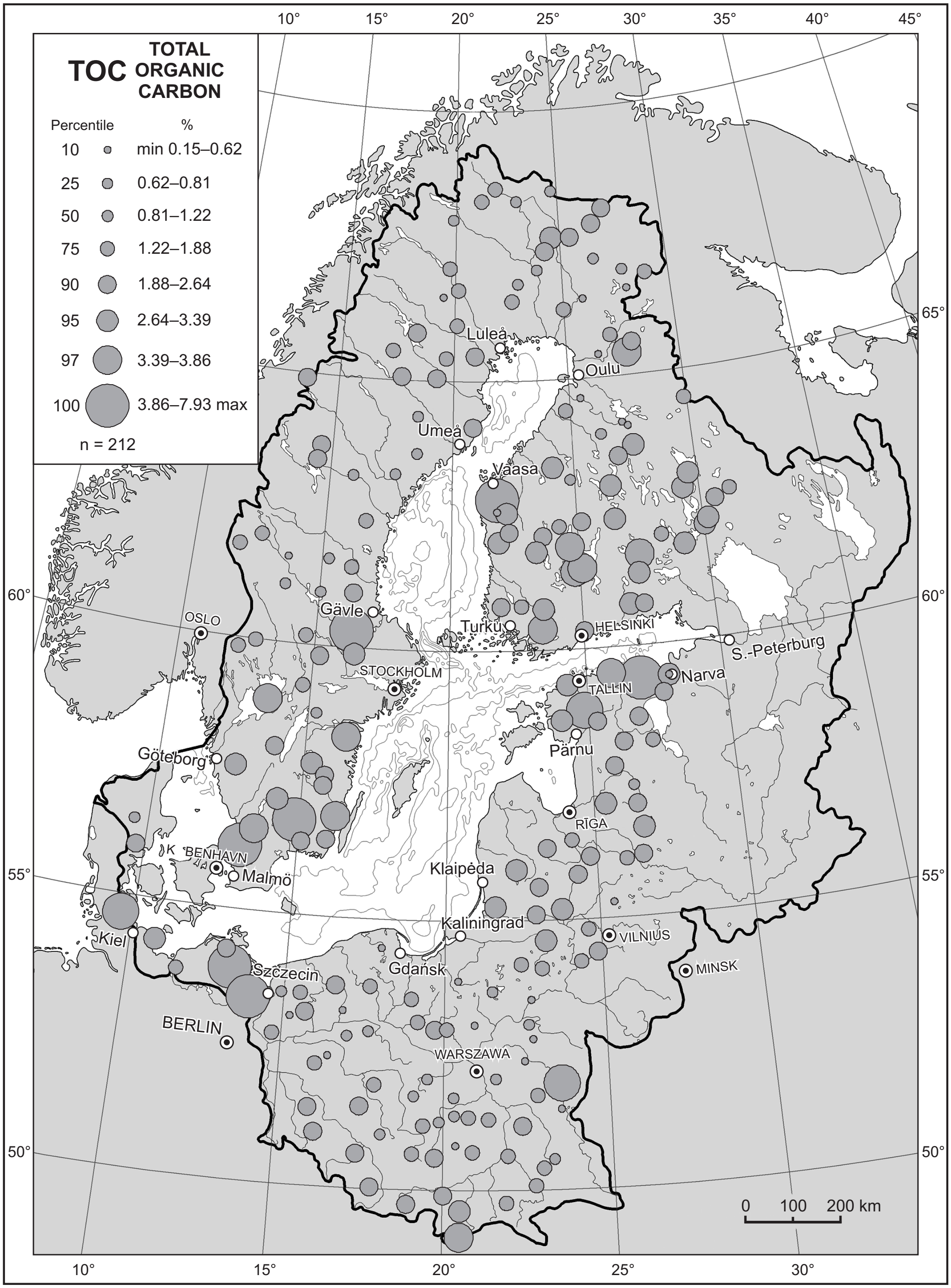


Fig. 2.10. TOC content in topsoil

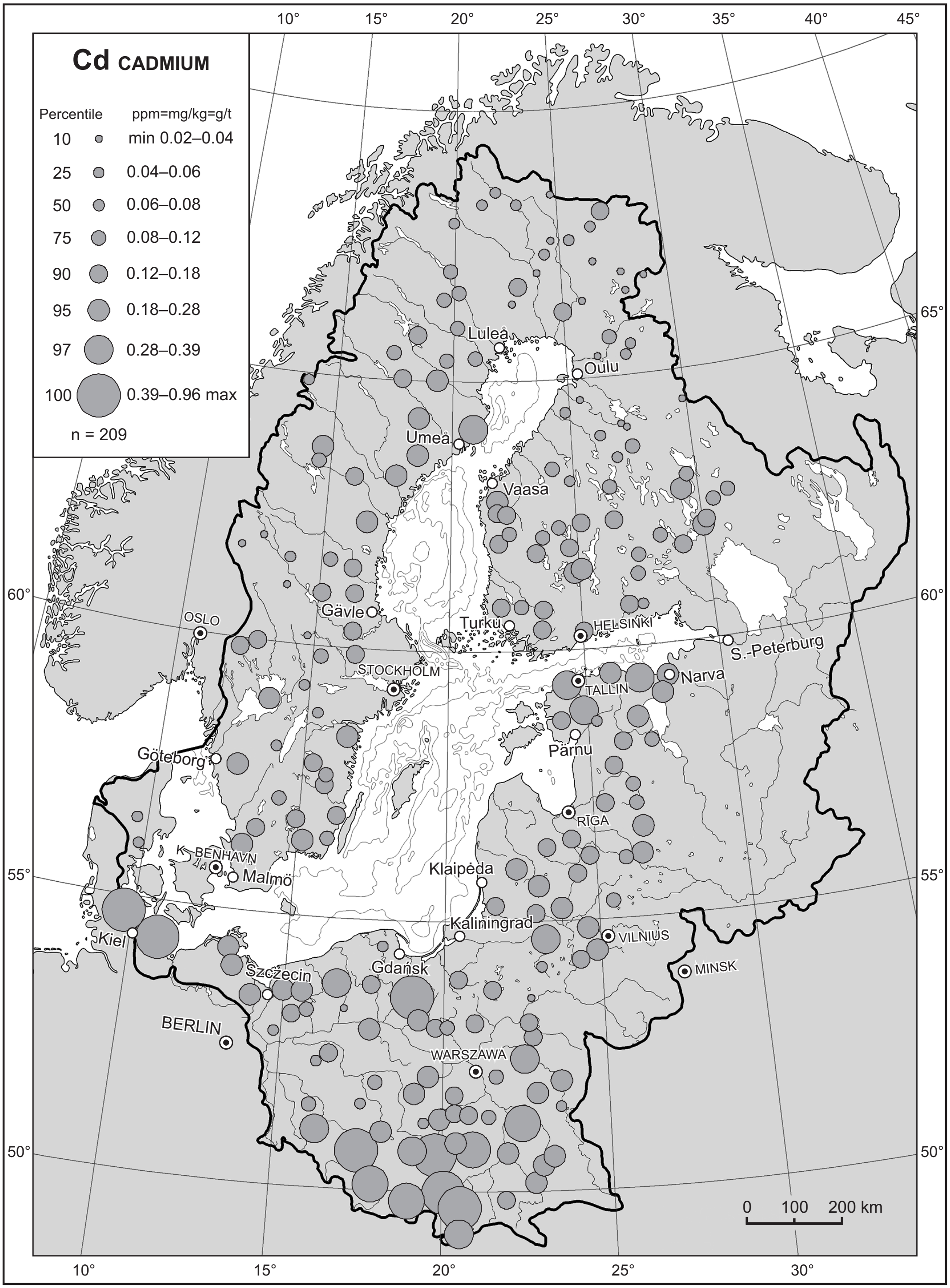


Fig. 2.11. Cd content in topsoil

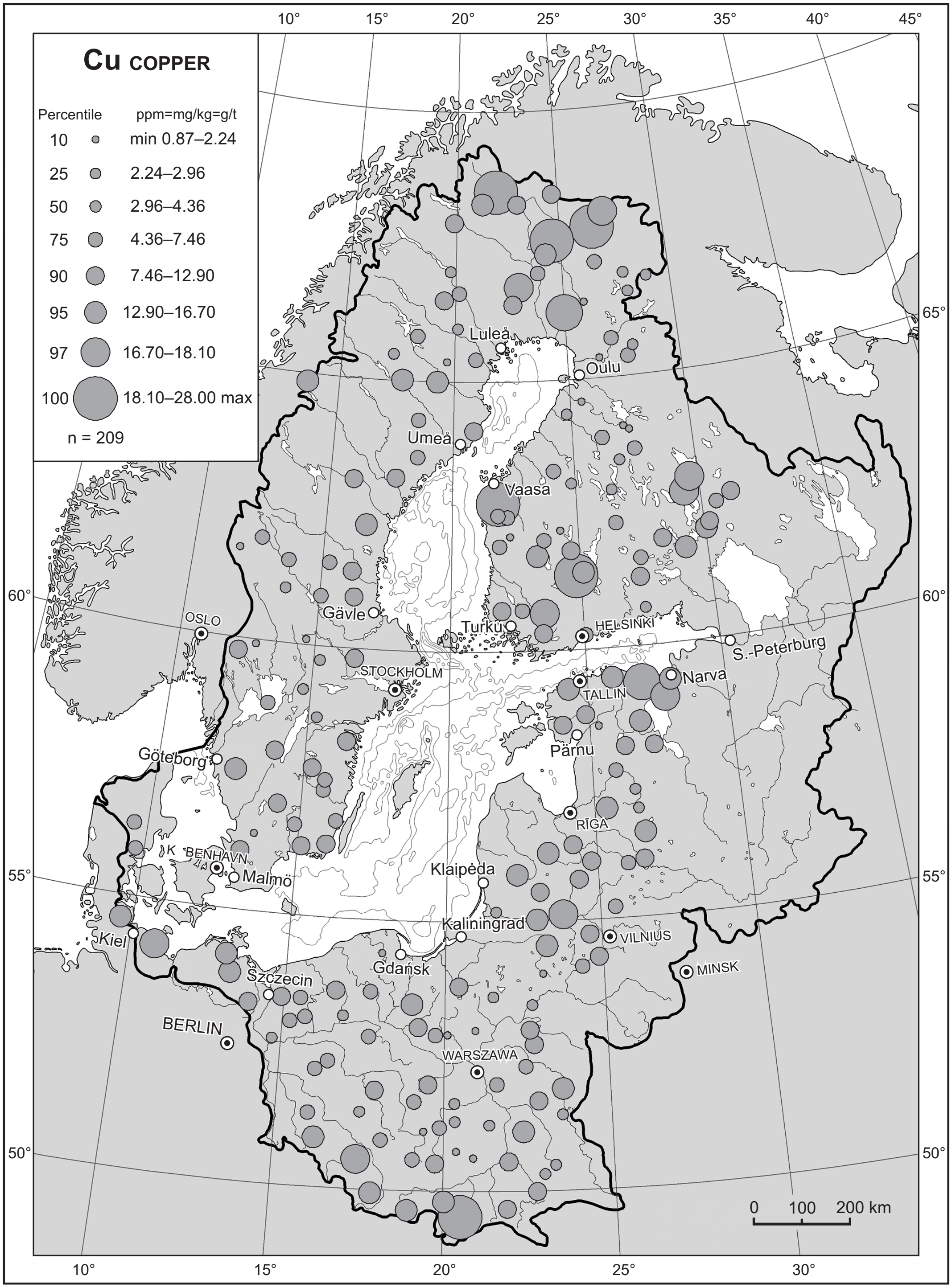


Fig. 2.12. Cu content in topsoil

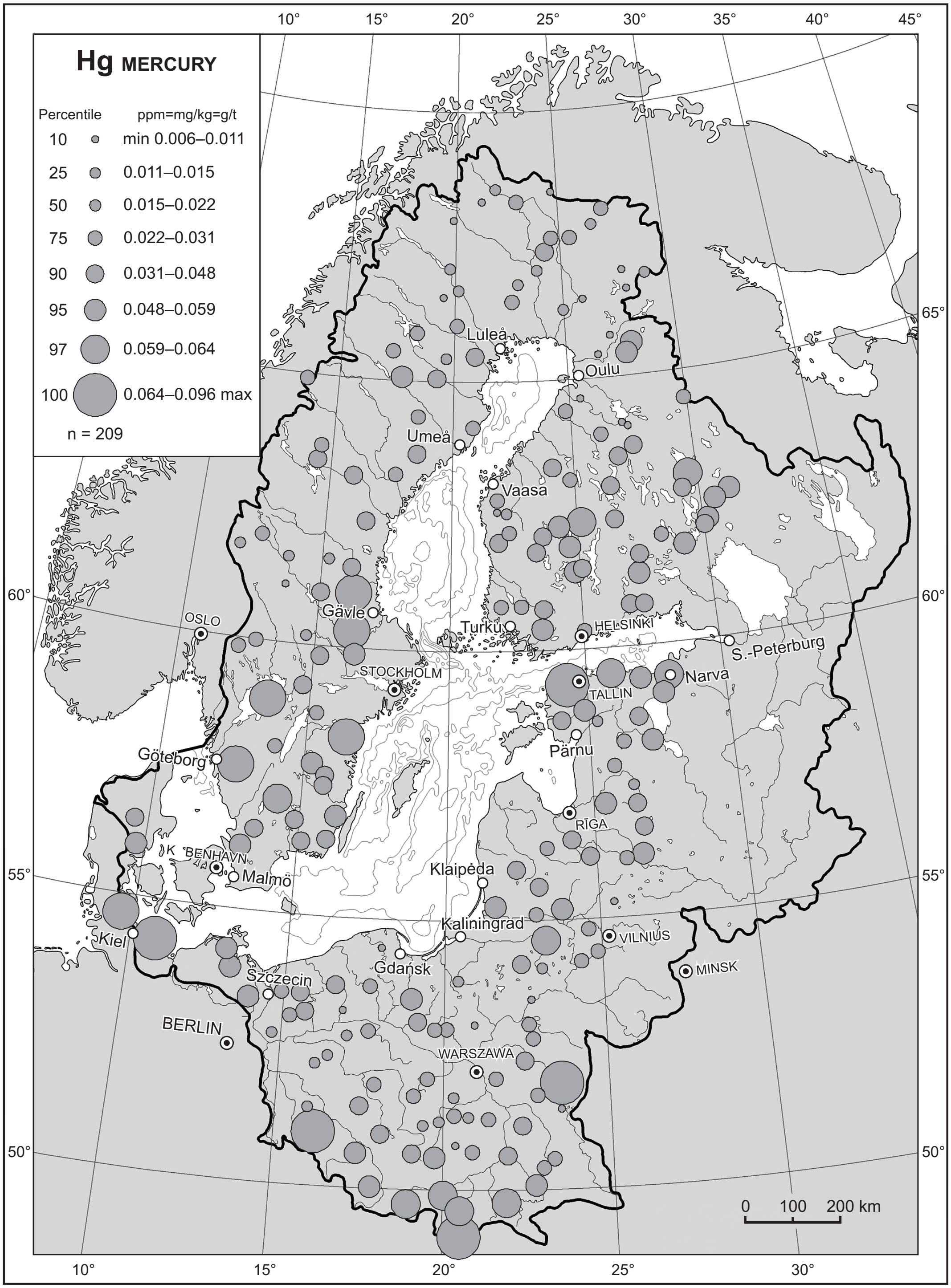


Fig. 2.13. Hg content in topsoil

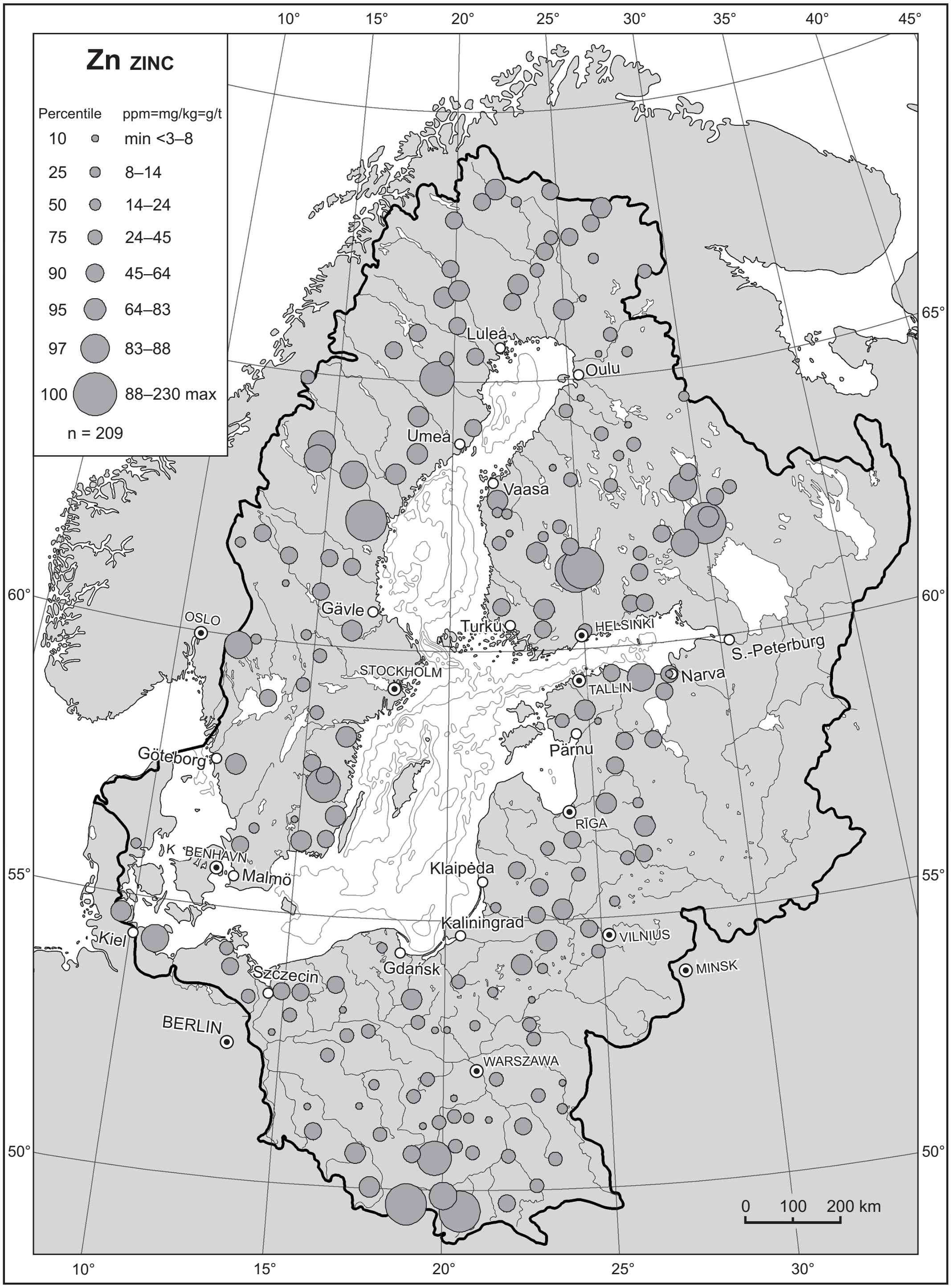


Fig. 2.14. Zn content in topsoil

2.4. Geochemical Characteristics of River Sediments in the Baltic Sea Catchment Area

The pollution of recent water sediments is one of the major environmental problems because they retain harmful metalloids, metals, and organic compounds that may have a negative effect on the biological resources and often indirectly on human health. Heavy metals and other hazardous substances occurring in sediments can accumulate in the marine food chain up to the level that is toxic for marine organisms, especially predators. In addition, part of the harmful components contained in sediments may be released into the water as the result of chemical and biochemical processes running in the sediments, as well as through the mechanical movements of contaminated sediments deposited earlier due to natural processes or during transport or dredging (Bordas, Bourg, 2001; Sjöblom *et al*., 2004).

Chemical composition of the unconsolidated surface sediment layer, especially the concentration of trace elements and organic impurities, undergoes permanent transformations due to breakdown of organic matter, mineral precipitation and component exchange between water and sediments (sorption-desorption, dissolution-precipitation) associated with changes in physicochemical conditions (temperature, pH, Eh, salinity) (Vink, 2009). In anaerobic conditions, the concentration of metals such as: copper, mercury and cadmium, and, to a lesser extent, zinc and lead, decreases as the result of the formation of insoluble sulphides, while metals such iron, chromium, arsenic, manganese and cobalt are released from the sediments. Depending on the temperature, some compounds are able to pass into a gas phase (Li *et al*., 2009). Microbiological processes, such as methylation, can also release e.g. mercury. In sediments, potentially toxic elements combine mostly with hydrated iron hydroxides, clay minerals, sulphides and phosphates, whereas organic pollutants – with organic matter and black carbon (soot).

Contaminated sediments commonly contain elevated levels of metals having an economic use worldwide in the present and past times, and released into the environment during processing in mineral and industrial production. The metals and metalloids polluting sediments and creating the greatest threat to the biosphere include silver, arsenic, beryllium, zinc, chromium, copper, mercury, nickel, lead, antimony, selenium and thallium (Sparks, 2005). The increase in the concentrations of potentially toxic elements and persistent organic pollutants in contemporary sediments results not only from wastewater discharge into the surface waters but also from the deposition for example, lead, arsenic, cadmium, mercury and chloroorganic compounds from the atmosphere as well as from surface run-off from both urban (heavy metals, PAH) and agricultural areas (arsenic, mercury, chloroorganic pesticides (Ramamoorthy, Ramamoorthy, 1997; Howsam, Jones, 1998; Birch *et al*., 2001; Lindeström, 2001; Reiss *et al*., 2004; Rocher *et al*., 2004; Jiao *et al*., 2009; Teršič *et al*., 2009).

Chemical composition of the recent sediments in the Baltic Sea is dependent on the erosion and weathering of rocks that occur in the source area, the properties of material originating from atmospheric deposition, and material brought by rivers. The chemistry of the material transported and supplied by river waters into the Baltic Sea is well represented by the chemical composition of the sediments deposited in river mouths near the sea. Concentration of trace elements in sediments of many of these rivers is determined by sewage discharge from towns and industrial plants operating within their catchment areas. The average water inflow from all the rivers flowing into the Baltic Sea is 15 190 m^3/s, half of which originates from the following seven largest rivers: Neva (71 km, 2488 m^3/s), Vistula (1074 km, 1081 m^3/s), Daugava (1020 km, 637 m^3/s), Nemunas (937 km, 664 m^3/s), Kemijoki (600 km, 553 m^3/s), Odra (854 km, 574 m^3/s) and Göta älv (902 km with Klarälven, 572 m^3/s).

2.4.1. Metals and Metalloids in the River Sediments of the Baltic Sea Catchment Area

Amongst the group of trace elements (As, Cd, Hg, and Tl, which are most important because of their high mobility and potential hazard to the environment), arsenic (As) in river sediments of the Baltic Sea catchment area occurs generally in small contents of below 5 mg/kg (Salminen ed., 2005; de Vos, Tarvainen, eds., 2006). Very low As concentrations, below 2 mg/kg, are characteristic of sediments of the rivers flowing into the eastern part of the catchment area in the Bothnian Bay and Gulf of Riga. Higher As contents are found in river sediments of the south-western coasts of Finland (Salminen ed., 2005). The arsenic content of above 8–10 mg/kg occurs in river sediments of northern Sweden in the area of Norrbotten, and in the rivers flowing down from the mineralised area of Skellefteå into the Bothnian Bay (de Vos, Tarvainen, eds., 2006). Human economic activity contributes to the increase in As concentrations in sediments of some rivers. Thus, the elevated arsenic contents in sediments of central Sweden rivers are related to mining; e.g. the Vormbäcken River, a tributary of the Vindelälven flowing into the Bothnian Bay, receives arsenic from the wastes deposited near Kristineberg, whereas the Dalälven River receives it from the landfills at Falun (Ingri *et al*., 1993; Widerlund *et al*., 2004).

Cadmium occurs in sediments of rivers flowing into the Baltic Sea in very low concentrations, below 0.29 mg/kg (Salminen ed., 2005). Its lowest concentrations, below 0.18 mg/kg, are observed in river sediments of Finland, Estonia, Lithuania and Poland (de Vos, Tarvainen, eds., 2006). Slightly higher contents, above 0.4 mg/kg, are recorded in alluvial deposits of areas adjacent to the Gulf of Riga, in the eastern and northern parts of Germany and in Denmark. The cadmium contamination of river sediments of geogenic character is observed in the southern coasts of Finland, e.g. in the Teuvanjoki and Maalahdenjoki rivers. In this area, cadmium is leached from the acidic soils developed on marine silt-clay sediments that contain iron sulphides (Åström, 2001; Roos, Åström, 2006; Fältmarsch *et al*., 2008). As a result of anthropogenic activity, very high Cd contents in river sediments occur in Antskog region (Finland), associated with the historic smelting of copper (Åström, Nylund, 2000). In Sweden, sediments of the Skellefte and Vormbäcken rivers are contaminated with cadmium as a result of releasing this element from weathered mining wastes deposited in landfills near Kirstineberg and Stekenjokk (Holmström, Öhlander, 1999; Holmström *et al*., 2001; Carlsson *et al*., 2002). Cadmium pollution is also in the Dalälven River, the drainage basin of which is the mining area of Falun and Garpenberg (Baresel *et al*., 2006). The increase in cadmium concentrations in sediments of the rivers that flow into the Baltic Sea is caused by not only mining and processing of nonferrous metal ores but also by other industrial activities and economic activities of cities and towns. Thus, the cadmium contents sometimes exceeding 2 mg/kg are observed in sediments of some rivers in Latvia, which flow into the Gulf of Riga: Venta, Lielupe, Daugava (Klavins *et al*., 1992; Kļaviņš *et al*., 2000; Seisuma, Kulikova, 2007; Yurkovskis, Poikāne, 2008). Similar cadmium concentrations are also present in the sediments of the Neva (Vallius, Leivuori, 1999). **Mercury** occur in sediments of most rivers in the Baltic Sea catchment area in very low concentrations, generally below 0.030 mg/kg. Low Hg concentrations also take place in sediments of the rivers in Finland, Estonia, Latvia, Lithuania, and northern Poland (Salminen ed., 2005; de Vos, Tarvainen, eds., 2006). Higher contents of this element, above 0.068 mg/kg, are characteristic of sediments in the rivers of central Sweden (Hälsingland), and even higher in southern Sweden (Smålandia and Östergötlandia) and Denmark. Considerably higher mercury concentrations are observed in sediments of the rivers receiving industrial and municipal wastewaters, e.g. Daugava River (up to 0.193 mg/kg Hg), and in sediments of the Neva estuary (up to 0.4 mg/kg) (Ussenkov, 1997; Vallius, Leivuori, 1999; Kulikova, Seisuma, 2005; Seisuma, Kulikova, 2007). The source of Hg in alluvial deposits also involves the leaching of this element from mining wastes, e.g. sediments of the Dalälven River are polluted with mercury that originates from wastes stored near the Kristineberg mine (Carlsson *et al*., 2002).

Thallium occurs in sediments of the rivers of Poland and Germany in very low contents, not exceeding 0.2 mg/kg. Slightly higher concentrations (mostly up to 0.5 mg/kg) are present in sediments of the rivers of Lithuania, Estonia, Latvia and Finland, and the highest ones were recorded in the bottom deposits of the rivers of Sweden (Vallius, Leivuori, 1999; Salminen ed., 2005; de Vos, Tarvainen, eds., 2006).

Of trace elements (Cr, Cu, Ni, Pb, V, and Zn), important for the environment quality, but of less hazardous for it, **chromium** is present in low contents of below 13 mg/kg in sediments of most rivers of Denmark, southern Sweden, northern Germany, Poland, Latvia and Estonia, which are overlain by Quaternary deposits (de Vos, Tarvainen, eds., 2006). Low Cr concentrations are also observed in alluvial sediments of much of the Swedish territory and southern Finland. Elevated concentrations of this element (above 33 mg/kg) are present in river deposits of northern (the area of greenstones) and southern Finland (Salminen ed., 2005; de Vos, Tarvainen, eds., 2006). The sediments of rivers, which are recharged with municipal and/or industrial wastewaters are characterised by elevated Cr contents, e.g. alluvial deposits of the Neva contain above 100 mg/kg of this element, and estuarine sediments of the Daugava River contain an average of 57 mg/kg (Ussenkov, 1997; Vallius, Leivuori, 1999; Yurkovskis, Poikāne, 2008).

Copper in river sediments of Poland, Lithuania, Latvia, Estonia and central and northern Finland occurs in relatively small concentrations of below 11 mg/kg. Slightly higher Cu contents are observed in river sediments of northern Germany, Denmark and southern Sweden. Naturally elevated Cu contents, above 24 mg/kg, occur in river sediments of southern Finland (Salminen ed., 2005). The occurrence of elevated Cu concentrations in the Vörå River located in western Finland and in the rivers of southern Finland related to the leaching of this element from very acidic soils developed on marine sulphide-rich deposits (Åström, 2001; Roos, Åström, 2006; Nordmyr *et al.*, 2008). The increase in copper concentration in sediments of some rivers flowing into the Baltic Sea is largely due to economic activities of cities and towns, mining activity and copper metallurgy. High contents of this element, sometimes more than 100 mg/kg, were determined in sediments of the Daugava River (upon which a large portion of the city of Riga is located) as well as the Neva River (Ussenkov, 1997; Vallius, Leivuori, 1999; Kulikova, Seisuma, 2005; Seisuma, Kulikova, 2007). High copper concentrations are also present in river sediments of the Antskog region (Finland), where copper smelting was developed in the past (Åström, Nylund, 2000; Åström, 2001), and in sediments of the Dalälven River (copper mining at Falun and Garpenberg). High Cu contents in sediments of the Skellefte and Vormbäcken rivers are due to the release and migration of this element from weathered wastes at the former mining sites of Cu–Zn-bearing pyrites near Kristineberg and Stekenjokk (Holström, Öhlander, 1999; Holmström *et al.*, 2001; Carlsson *et al.*, 2002).

Nickel, in river sediments of the southern part of the Baltic Sea catchment area covered with Quaternary deposits, including the coasts of Poland, Germany, Latvia, Estonia and central Finland, occurs in low concentrations, below 13 mg/kg. Equally low Ni concentrations are observed in river sediments of southern Sweden (Salminen ed., 2005; de Vos, Tarvainen, eds., 2006). Elevated Ni contents were determined in river sediments of central Sweden. Still higher Ni concentrations, above 24 mg/kg, are observed in river sediments of southern Finland, which is caused by a geological factor, namely the release of Ni from the acid soils of this region (Åström, 2001; Roos, Åström, 2006). An anthropogenic factor, the discharge of industrial wastewaters, increases the contents of nickel in sediments of the Daugava River; the median value in the river estuary sediments is 57 mg/kg (Yurkovskis, Poikāne, 2008). The Ni pollution observed in water sediments of the Vindelälven drainage basin originates from weathering processes, i.e. mining wastes stored near Stekenjokk (Holström, Öhlander, 1999).

Lead occurs in river sediments of southern Sweden, most of Finland, Lithuania, Latvia, Estonia, and major part of Poland in very low concentrations, below 9 mg/kg. It is due to Quaternary deposits occurring in these areas. Elevated Pb concentrations are observed in river sediments of southern Finland and central and southern Sweden. Still higher Pb contents, above 19 mg/kg, were determined in alluvial deposits of central Svealand, near Åmmebergle, Örebro, Falun and Alcesta (de Vos, Tarvainen, eds., 2006). Due to mining activity, an increase in Pb concentrations in sediments was observed in the Dalalven and Skellefte rivers (Holström, Öhlander, 1999; Holmström *et al.*, 2001; Carlsson *et al.*, 2002; Baresel *et al.*, 2006). Elevated lead contents of, up to several tens of mg/kg, were found in alluvial sediments of the Daugava and Neva rivers (Kļaviņš *et al.* 1992; Ussenkov, 1997; Kļaviņš *et al.*, 2000; Kulikova, Seisuma, 2005). **Vanadium** is present in low concentrations, below 23 mg/kg, in river sediments of the southern part of the Baltic Sea catchment area and in Latvia and Estonia. High geogenic V contents, more than 89 mg/kg, occur in river deposits of the Norrbotten, Ounasselka and Kivalo, close to the northern part of the Bothnian Bay, in southern Finland, and Hälsingland, Sweden. (Salminen ed., 2005; de Vos, Tarvainen, eds., 2006).

The **zinc** concentrations in river sediments of the southern part of the Baltic Sea catchment, including the territories of Poland, Lithuania, Latvia, Estonia, NE Germany, northern Finland and Sweden, are low, below 45 mg/kg. Higher values, above 109 mg/kg, are characteristic of sediments from the rivers in southern Finland and northern (Skellefte mineralised belt) and southern Sweden (de Vos, Tarvainen, eds., 2006). Elevated contents of zinc in river sediments of southern Finland are due to the leaching of this element from the very acid soils occurring in this region (Åström, 2001; Roos, Åström, 2006; Nordmyr *et al*., 2008). High Zn amounts flow into the Dalälven River, where mining activities in the catchment area pollute the Skellefteälven and Vindelälven rivers by leaching from mining wastes stored at Kristineberg and Stekenjokk (Ingri *et al*., 1993; Holström, Öhlander, 1999; Holmström *et al*., 2001; Widerlund *et al*., 2004; Baresel, Destouni, 2009). The human activities also produce high Zn contents (median >300 mg/kg), which can be observed in the sediments of the Daugava estuary and the Neva River – up to 398 mg/kg (Ussenkov, 1997; Yurkovskis, Poikāne, 2008).

Of the other trace elements (Ag, Sb, Sn, Co, Ba, Sr, Mn), which are less important for the quality of the environment due to their low contents or the lack of any harmful effect on living organisms, low level of **barium** (>52 mg/kg) is found in river sediments in Poland, around the Gulf of Riga and along the southern coasts of central Finland. Higher Ba contents, up to 128 mg/kg, are observed in alluvial deposits of Germany, Denmark, Lithuania and Latvia. Barium concentrations exceeding 128 mg/kg are characteristic of river sediments from the southern periphery of Finland and Sweden (Salminen ed., 2005).

The **cobalt** contents are very low, below 2 mg/kg, in the southern part of the Baltic Sea catchment area covered by Quaternary deposits. Slightly higher concentrations, up to 6 mg/kg, are observed in river sediments in Lithuania, Latvia, central Finland and northern Sweden. Increased Co contents of above 10 mg/kg occur in river sediments in the southern Sweden and southern Finland (de Vos, Tarvainen, eds., 2006). Also in this case, the occurrence of elevated Co concentrations in the rivers of southern Finland is caused by the leaching of these elements from strongly acid soils covering the area (Nordmyr *et al*., 2008). Cobalt contents in sediments of the Latvian rivers of Venta, Lielupe, Daugava, and Gauja occasionally exceed 5 mg/kg (Klavins *et al.*, 1992; Kļaviņš *et al*., 2000).

River sediments in central Sweden and in the territories of Denmark, Germany, Poland, Lithuania, Latvia, and Estonia, covered with Quaternary glaciofluvial deposits, show low **strontium** contents. Higher concentrations, exceeding 200 mg/kg, are chracterized of river sediments in most of Finland as well as in northern and southern Sweden (de Vos, Tarvainen, eds., 2006).

Iron and manganese hydrated hydroxides and iron sulphides play a key role in retaining trace elements in sediments. **Iron** occurs in low concentrations, below 1.52%, in river sediments of northern Germany, Poland, Latvia and Estonia. In relatively low concentrations, it is also present in fluvial sediments of central Finland. High concentrations, above 2.48%, are observed in river sediments of northern Sweden, southern Finland and areas of iron ore occurrence (de Vos, Tarvainen, eds., 2006). Sediments of the rivers flowing into the Baltic Sea from the areas of Germany and Poland, from the regions adjacent to the Gulf of Riga, Gulf of Finland, southern part of the Gulf of Finland and eastern part of the Bothnian Bay, show low **manganese** contents**,** below 327 mg/kg. Manganese concentrations of above 600 mg/kg are observed in river sediments of western Lithuania and Latvia, and even higher (above 800 mg/kg) occur in river sediments of central Sweden (de Vos, Tarvainen, eds., 2006).

2.4.2. Metals and Metalloids in River Sediments of the Polish Baltic Sea Coast

The geochemical research of river sediments in the Baltic Sea catchment area has been carried out since 1990 under the State Environmental Monitoring (SEM). Its aim is to observe changes in the contents of potentially hazardous elements (As, Ba, Zn, Cr, Cd, Co, Cu, Ni, Pb, Hg, Ag) and persistent organic pollutants (PAHs, PCBs and chloroorganic pesticides) in the recent sediments of surface waters in Poland. The project also includes the lower courses of rivers near their mouths, including the Odra, Rega, Parsęta, Dzierżęcinka, Grabowa, Wieprza, Słupia, Łupawa, Łeba, Reda, Radunia, Vistula, Elbląg, and Pasłęka (Tab. 2.2, Figs. 2.15, 2.16).

Amongst the group of elements that are most important for the environment quality in river sediments of Poland, the concentrations of arsenic, cadmium and mercury are monitored. Sediments deposited at the mouths of the rivers along the Polish coast of the Baltic Sea are characterised by the **arsenic** contents of mostly below 5 mg/kg. The maximum content of 23 mg/kg was recorded in the Odra sediments in 1995 (in the past, the Odra received

Table 2.2

Monitored rivers of the Polish Baltic Sea coast

River	River length [km]	Catchment area [km²]	Mean flow at the mouth [m³/s]	Important towns situated on the rivers
Odra	854.3 (in Poland 741.9)	118 861 (in Poland 106 050)	535	Ostrava (Czech Rep.), Racibórz, Kędzierzyn-Koźle, Opole, Brzeg, Wrocław, Brzeg Dolny, Głogów, Nowa Sól, Krosno Odrzańskie, Eisenhüttenstadt (Germany), Frankfurt (Germany), Kostrzyn / Küstriner Vorland, Schwedt (Germany), Gryfino, Szczecin and Police
Rega	172.5	2724.9	21.8	Gryfice, Trzebiatów, Mrzeżyno
Parsęta	132	3 151	29.5	Białogard, Karlino, Kołobrzeg
Dzierżęcinka	26	130		Koszalin
Grabowa	71	534		
Wieprza	112	2 170	22.3	Sławno, Darłowo
Słupia	138.6	1 623	17.3	Słupsk, Ustka
Łupawa	98.7	924.5	21.2	Smołdzino, Czarna Dąbrówka, Łupawa
Łeba	117	1801	18.5	Lębork, Łeba
Reda	51	485	21.2	Wejherowo, Reda
Radunia	103.2	837		Żukowo, Pruszcz Gdański, Gdańsk
Vistula	1047	194 424	1054	Czechowice-Dziedzice, Oświęcim, Kraków, Tarnobrzeg, Sandomierz, Puławy, Warszawa, Płock, Włocławek, Toruń, Bydgoszcz, Świecie, Grudziądz, Tczew, Gdańsk
Elbląg	59.9 (with Dzierzgoń)		21.2	Elbląg
Pasłęka	169	2295	21.2	Braniewo

Prepared according to the data of the Hydrological Atlas of Poland (1986), encyclopaedia and geographic maps.

huge loads of this metalloid from mining and ore processing of silver-copper ores in the Legnica–Głogów Copper District). **Cadmium** concentrations in sediments of most rivers flowing into the sea from the area of Poland are lower than the value of the geochemical background for this element (<0.5 mg/kg). Elevated Cd contents in sediments of the Pomeranian region were observed predominantly in the early 1990s, for example, in the Łeba (mean content 0.7 mg/kg in 1990–2009) and Odra sediments. Slightly elevated Cd contents, but not exceeding 1 mg/kg, were also detected sporadically in sediments of other rivers, such as the Parsęta (flowing through Kołobrzeg, a town with a population of 45,000) and the Dzierżęcinka (flowing through Koszalin, a town with a population of 108,000 and factories of the electro-mechanical, wood processing and food processing industries). **Mercury** concentrations are mostly below 0.050 mg/kg, and the average values in individual rivers range from 0.024–0.359 mg/kg. Significantly elevated mercury contents were observed in sediments of the Dzierżęcinka and Rega rivers (flowing through Mrzeżyno – a holiday resort and a military training ground). In 1994–1997, very high mercury contents of about 10–20 mg/kg were found in the Rega River sediments.

Amongst the second group of trace elements important for environment quality in fluvial deposits of the

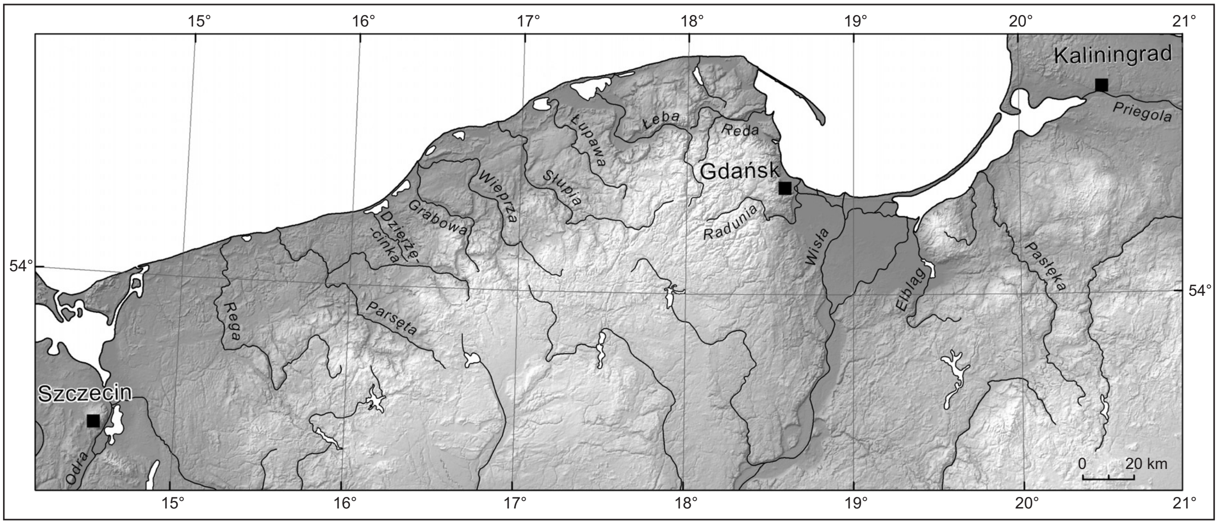


Fig. 2.15. Monitored rivers of the Polish Baltic Sea coast

Pomeranian region, copper, nickel, lead, vanadium and zinc contents were determined. **Chromium** concentrations were above 60 mg/kg. Significantly elevated concentrations of this element were recorded in sediments of the Pasłęka River (average 25 mg/kg) flowing through the town of Braniewo (population: 18,000, electro-mechanical, leather and food industries). Sediments of the Dzierżęcinka River (average 22 mg/kg) are also characterised by an elevated Cr content, while in the other rivers of the Pomeranian region the average concentration of this element does not exceed 10 mg/kg, which is typical of stream sediments in the areas covered with Quaternary postglacial deposits. **Copper** concentrations range from <1 to 68 mg/kg in the monitored river sediments. High contents were recorded in sediments of the Dzierżęcinka and Elbląg rivers (average values >25 mg/kg). In sediments of the other rivers, the average values do not exceed 10 mg/kg. **Nickel** concentrations were recorded in the range from <1 to 25 mg/kg. Similarly to most elements presented, elevated nickel concentrations are characteristic of sediments of the Dzierżęcinka River. The other rivers show average Ni concentrations ranging from 1 to 5 mg/kg. **Lead** concentrations in river sediments of the Pomeranian region amount up to 95 mg/kg. Elevated concentrations are recorded in sediments of the Dzierzęcinka (average 37 mg/kg) and Elbląg rivers (average 38 mg/kg). Sediments of the other rivers showed considerably lower average lead contents from below 10 to 20 mg/kg. **Vanadium** concentrations in river sediments are up to almost 22 mg/kg. **Zinc** concentrations in river sediments are up to 200 mg/kg. Distinctly elevated zinc concentrations are characteristic of the Dzierżęcinka River deposits (average 172 mg/kg). In sediments of the other rivers, its average concentrations do not exceed 70 mg/kg.

For the group of trace elements, including Ag, Sb, Sn, Co, Ba, Sr, Mn, an elevated content of **silver** was recorded only in sediments of the Dzierżęcinka River (average 1.5 mg/kg), which receives wastewaters from Koszalin. Noticeably increased **barium** content also occurs in these sediments, as compared to the other rivers monitored. Elevated concentrations of this element are also characteristic of the Odra, Rega and Parsęta river sediment. As regards the Odra sediments (374 mg/kg Ba in 1995), the source of this element may be pollutant loads derived from wastewater discharges from mining of coal and copper ores (Bojakowska et al., 1998). **Cobalt** concentrations in river sediments of the Pomeranian region are below 10 mg/kg with the average ranging from 1 to 2 mg/kg**. Strontium** contents vary from 3 to 88 mg/kg. Generally, the strontium concentration in most of the monitored rivers does not exceed 20 mg/kg. Slightly higher average Sr concentrations are characteristic of sediments of the Dzierżęcinka and Elbląg rivers.

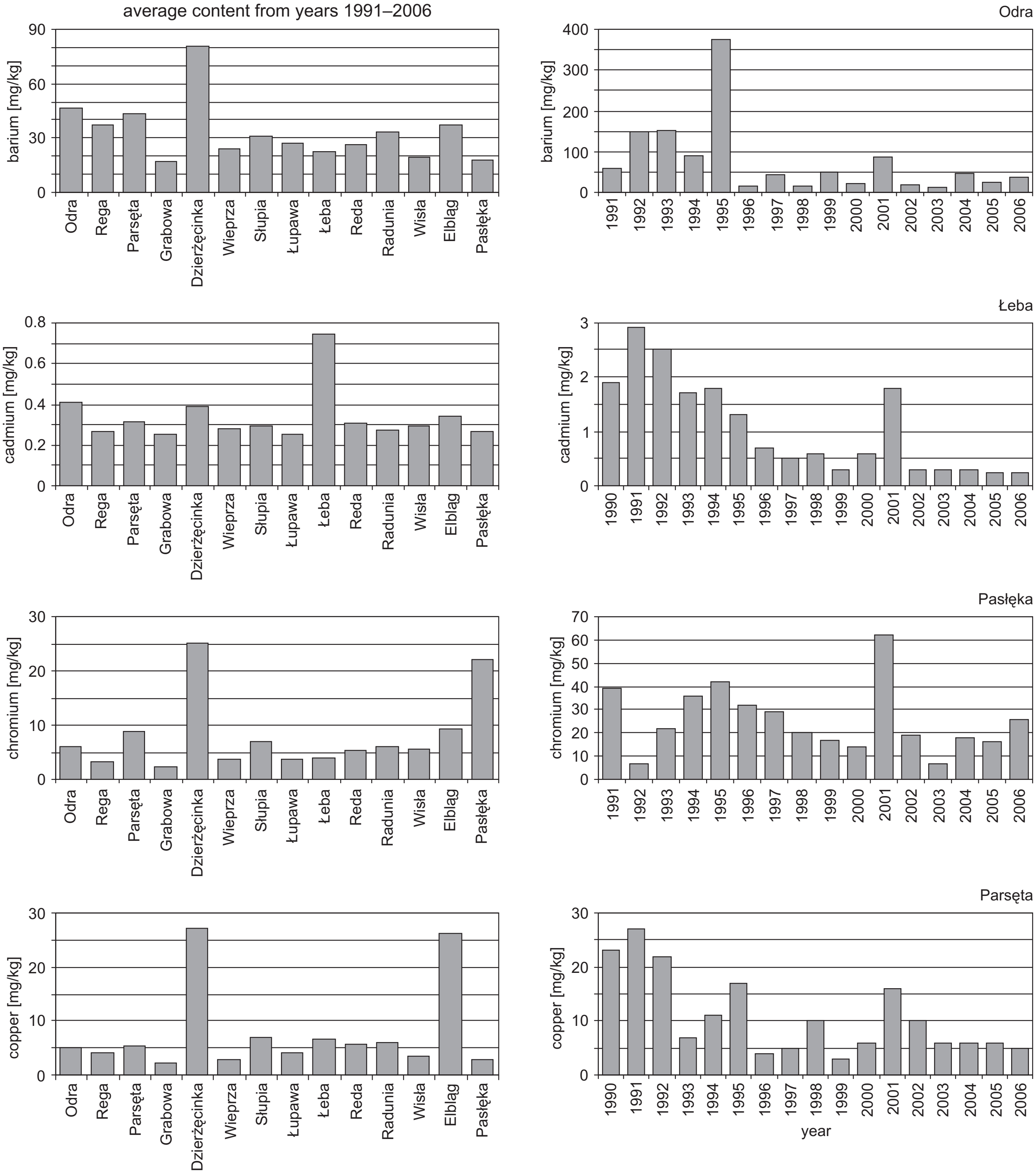
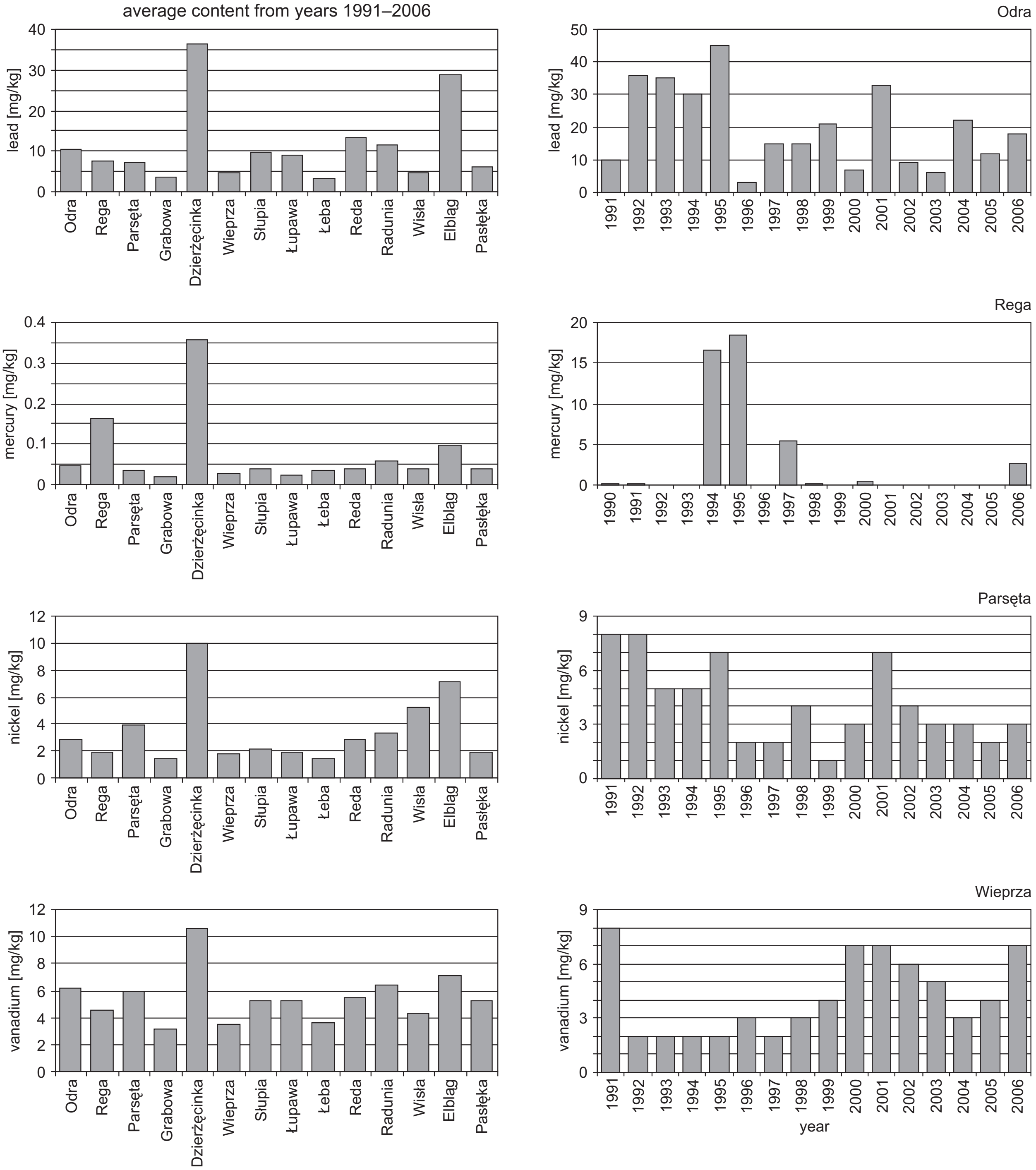


Fig. 2.16. Variability of trace elements in river sediments of the Polish



Baltic Sea coast (acc. to data of State Environmental Monitoring, 1991–2006)

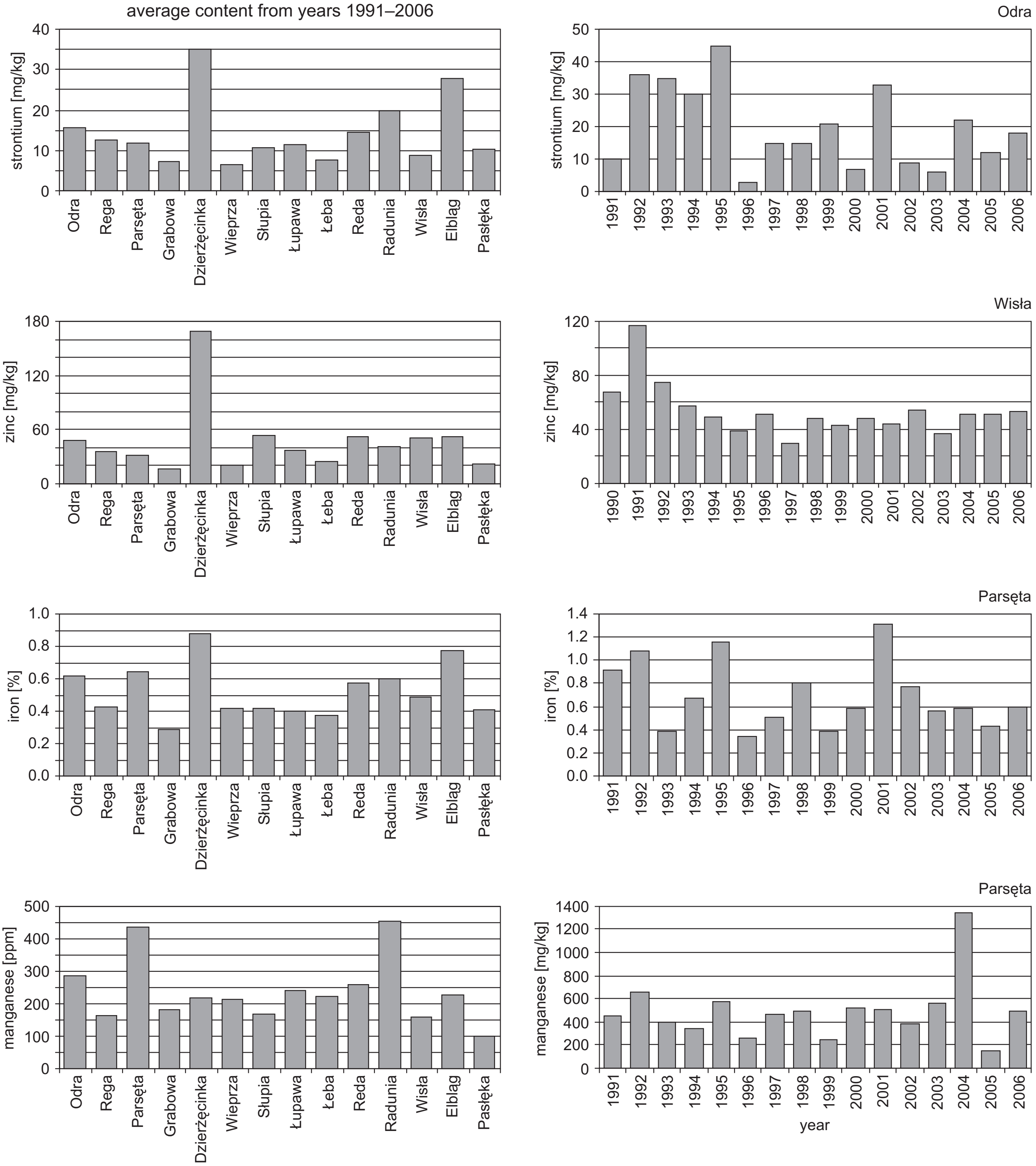


Fig. 2.16. continued

Iron compounds play an important role in retaining trace elements in the environment, and their concentrations vary within a wide range from 0.12 to 4.90% in river sediments of the Pomeranian region, with the average contents in individual rivers varying between 0.28% (Grabowa River) and 0.88% (Dzierżęcinka River). **Manganese** concentrations range up to 3200 mg/kg. Its average contents in river sediments vary from 100 mg/kg (Pasłęka River) to 453 mg/kg (Radunia River). Such variations are due to the redox conditions and organic matter content.

The sediments of most rivers flowing into the Baltic Sea from the Polish area are characterised by very low contents of trace elements, predominantly not more than their geometric mean calculated for water sediments of Poland, assumed as the geochemical background (Pasieczna, Lis, 1995). The mean contents higher than the geochemical background value are typical of river sediments from the Dzierżęcinka (barium, chromium, copper, mercury, nickel, lead and zinc), Elbląg (copper, mercury and lead), Rega (mercury), Łeba (cadmium) and Pasłęka (copper). Elevated levels of cadmium in the Łeba sediments, and of mercury in the Rega deposits were observed during the last decade of the 20th century. Today, they are considerably lower and the sediments of the rivers show low contents of these elements, similar to the values of their geochemical background. High concentrations of some elements are still observed only in sediments of the Dzierżęcinka, Elbląg and Pasłęka rivers. However, none of these rivers escapes directly into the Baltic Sea: the Elbląg and Pasłęka rivers flow into the Vistula Lagoon, and the Dzierżęcinka – into Lake Jamno.

2.4.3. Persistent Organic Pollution in River Sediments of the Polish Baltic Sea Coast

Contents of the following persistent organic substances were determined in sediments of the Polish rivers monitored: polychlorinated biphenyls (PCBs), chloroorganic pesticides and polyaromatic hydrocarbons (PAHs). Concentrations of chroloorganic compounds, exceeding the limits of determination, are recorded sporadically in river sediments of the Pomeranian region.

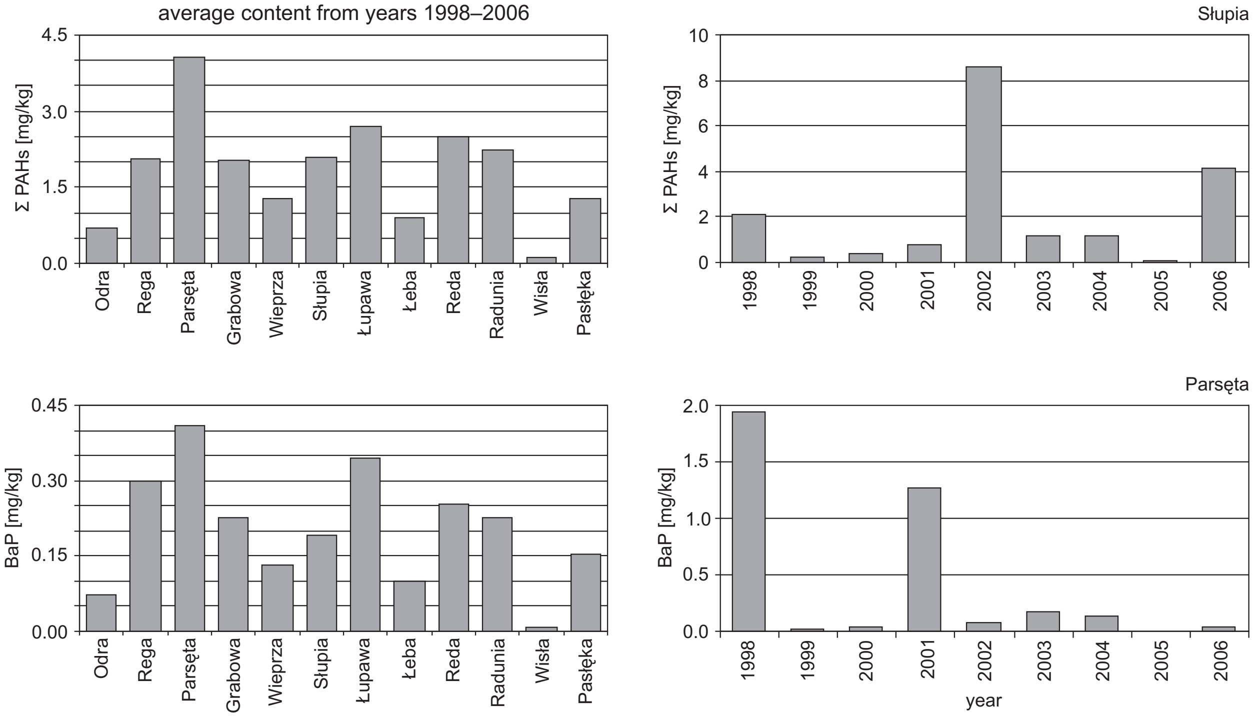


Fig. 2.17. Variability of PAHs in river sediments of the Polish Baltic Sea coast

Contents of **polychlorinated biphenyls** (congeners: PCB28, PCB52, PCB101, PCB118, PCB153, PCB138, PCB180) are generally below the determination limit (0.1 µg/kg for the individual congeners determined). PCBs concentration of 3.1 µg/kg was determined only in in the Słupia deposits. Slightly higher concentrations of polychlorinated biphenyls, exceeding the determination limit, are observed in river sediments of the Rega, Reda and Odra. PCB 153 and 138 were the most frequently detected congeners.

Amongst **chloroorganic pesticides** contents exceeding the determination limits (HCH isomers <0.5 µg/kg, heptachlor epoxide u, aldrin, dieldrin, p,p'-DDE., p,p'-DDD – <0.1 µg/kg, endrin and endosulfan II – 0.3 µg/kg, endosulfan I, p,p'-DDT – 0.5 µg/kg) were observed only for p,p'-DDE and p,p'-DDD in sediments of the Pasłęka, Reda and Radunia rivers. Endosulfan I (0.8 µg/kg), endosulfan II (2.4 µg/kg) and p,p'-DDT (0.8 µg/kg) were recorded in river sediments of the Łupawa.

Concentrations of polycyclic aromatic hydrocarbons (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene, indeno(1.2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene) were detected in sediments of the monitored rivers in the range of 0.020–19.04 mg/kg (mean 2.034 mg/kg, and the geometric mean was 0.694 mg/kg). The highest PAH contents were determined in sediments of the Parsęta River (Fig. 2.17). 4- and 5-ring hydrocarbons originating from burning of fossil fuels predominate in the PAHs spectra.

The lowest values were observed in sediments of the Vistula and Odra rivers (sandy sediments of both the rivers are characterised by a very low content of organic matter). The PAH contents, including benzo(a)pyrene, in river sediments demonstrate a high variability, which is usually an effect of high diversity in the organic matter content.

2.5. Land Development of the Baltic Sea Catchment Area

The Baltic Sea links the territories of nine highly industrialised countries. The region is populated by about 85 million people (Lundberg, 2005). The factors that influence the quality status of the entire Baltic Sea result from land development and the hydrological conditions occurring across its diverse geographic and climatic regions. In recent years, the land development of coastal areas has been increasingly affected by the globalisation of the world economy, enforcing an increase in the importance of sea ports and container freight handling, and, consequently, the necessity of improving the solutions concerning the protection of the natural environment. Those substances that generate unfavourable changes in the environment of the Baltic Sea are not only nitrogen and phosphorus compounds but also persistent organic pollutants (POPs), including chloroorganic pesticides and dioxins, the detrimental significance of which is still increasing.

The following countries have direct contact with the Baltic Sea: Denmark, Sweden, Finland, Estonia, Latvia, Lithuania, Russia, Poland and Germany, and which cover about 93% of the entire catchment area. The remaining 7% of the catchment area belongs to Norway, the Czech Republic, Slovakia, Ukraine, and Belarus (HELCOM, 2004). With the present-day economic development of these countries, huge amounts of industrial and agricultural wastes are produced and large amounts of atmospheric pollutants are emitted. Human impact on the sea waters is distributed unequally. The most exposed are the coastal zones, mainly in the vicinity of municipal and industrial sewage collectors, harbour basins and river estuaries (Gospodarka Morska, 2009).

Within the boundaries of the Baltic Sea catchment area, there are almost 600 local sewage treatment plants situated in towns with more than 10,000 residents, and more than 2,000 wastewater treatment facilities in smaller localities. 200 large industrial plants, 1085 smaller factories and more than 200 large fish farms are located in this territory. Most of industrial pollutants come from 95 paper mill plants, 25 mines and metal ore enrichment plants, 23 chemical works, 22 non-ferrous metallurgy plants, as well as from leather and textile factories and petrochemical plants (HELCOM, 2004).

The regions with the highest population density and the highest percentage of arable lands are found in the southern parts of the Baltic Sea catchment area, including Denmark, Germany, Poland and Russia (Figs. 2.18, 2.19). They are the reason behind the increased amount of pollution (nutrients mainly) transported through the rivers into the coastal zone of the southern part of the Baltic Sea.

The countries located around the Baltic Sea are characterised by a diverse land development structure as regards the amount of forest and agriculture areas (Fig. 2.20), which results in the variable use of pesticides and mineral fertilisers. The type of dominant industry, as well as the level of water and wastewater management is also variable.

Almost 50% of the residents in the Baltic Sea catchment area live in Poland, and the percentage of arable land in this area amounts to 40%, which means the largest loads of nitrogen and phosphorus running into the sea among the Baltic countries. However, when calculated per 1 resident, the loads become some of the lowest (Niemirycz *et al*., 1996). In order to fulfil the requirements of the EU Directive 91/271/EWG of 1991 on sewage treatment, the government of the Republic of Poland, in December 2003, approved the implementation of "The National programme for municipal wastewater treatment" (Gromiec, 2004). The programme contains a list of agglomerations with a population equivalent (PE) of not less than 2,000 and a list of necessary undertakings as regards the building, development and modernisation of municipal effluent treatment plants, as well as the construction and modernisation of collective sewerage systems, which these agglomerations need to implement by the end of 2015. Along the Polish coastline, 65 new modern wastewater treatment plants financed by the EkoFundusz (EcoFund) organisation have been erected. The analyses of how the undertaken investments affect the reduction of the pollutants running from Poland into the sea are in progress.

Significant is the part of the Pomeranian region known as Żuławy (Vistula Delta), the settlement of which dates back between 2500 and 1700 years B.C. Because of the fact that these areas have developed from deltaic deposits, their soils are extremely fertile. Owing to its specificity and considerable proportion of depression areas, the Żuławy region (Vistula Delta) has been included in the EU programme of "Żuławy integrated flood protection to the year 2030" (Czarnecka, 2001; Biuletyn, 2009).

In Sweden, arable lands of the Scania region (app. 2.5% of the whole area of this country) fulfil the needs of the citizens. Intense agricultural production and improper drainage water discharge contributed to polluting the sea waters in this region with nitrogen compounds in the early 1990s. At present, the outflow per unit of nitrogen by Swedish rivers is one of the lowest in the Baltic Sea catchment area. Basic agricultural production in Sweden includes: stock-breeding, poultry keeping and swine farming.

The traditional branch of the Finnish economy is the wood and paper industry. Its development is based on huge forest resources. The main industrial centres are concentrated in the southern part of the country and along the coastline. Paper production has become a source of the presence of dioxins and toxic chloro-organic substances, persistent and undergoing bioaccumulation and biomagnification in both bottom sediments and live organisms. The central part of the Baltic Sea is a region featuring the highest accumulation of dioxins (HELCOM, 2010).

Danish cereal cultivation is one of the most productive in the world. However, dairy farming and swine breeding are crucial for the economy of this country. Denmark takes the first place in the world with its 15% share in the international meat market. Unit loads with both nitrogen and phosphorous compounds in the drainage basins of the Danish rivers are the highest among the Baltic states.

The Neva estuary belongs to the most contaminated river mouths. Its drainage basin includes the entire catchment area of Lake Ladoga and its tributaries: the Svir, Volkhov and Vuokosi. This is the reason why the Neva, despite its short length (71 km), attains the highest average river flow rate within the whole Baltic Sea catchment area (2,488 m^3/s). In this area, the local wood and paper industry may be a source of hazardous dioxins; however, there are no literature reports concerning this issue.

The Daugava estuary also belongs to the polluted regions of the Baltic Sea. The Daugava River inflows to the Gulf of Riga at the territory of Latvia, while its drainage basin also includes some parts of Belarus and Russia. The Lithuanian territory includes the polluted Nemunas River, flowing into the Curonian Lagoon through its eight-branched delta. This river is linked with the Vistula drainage basin by the Augustów Canal. The economies of Lithuania, Latvia and Estonia increasingly deserve to be referred to as "Tigers of the Eastern Europe". It may be assumed that these states will improve their water and

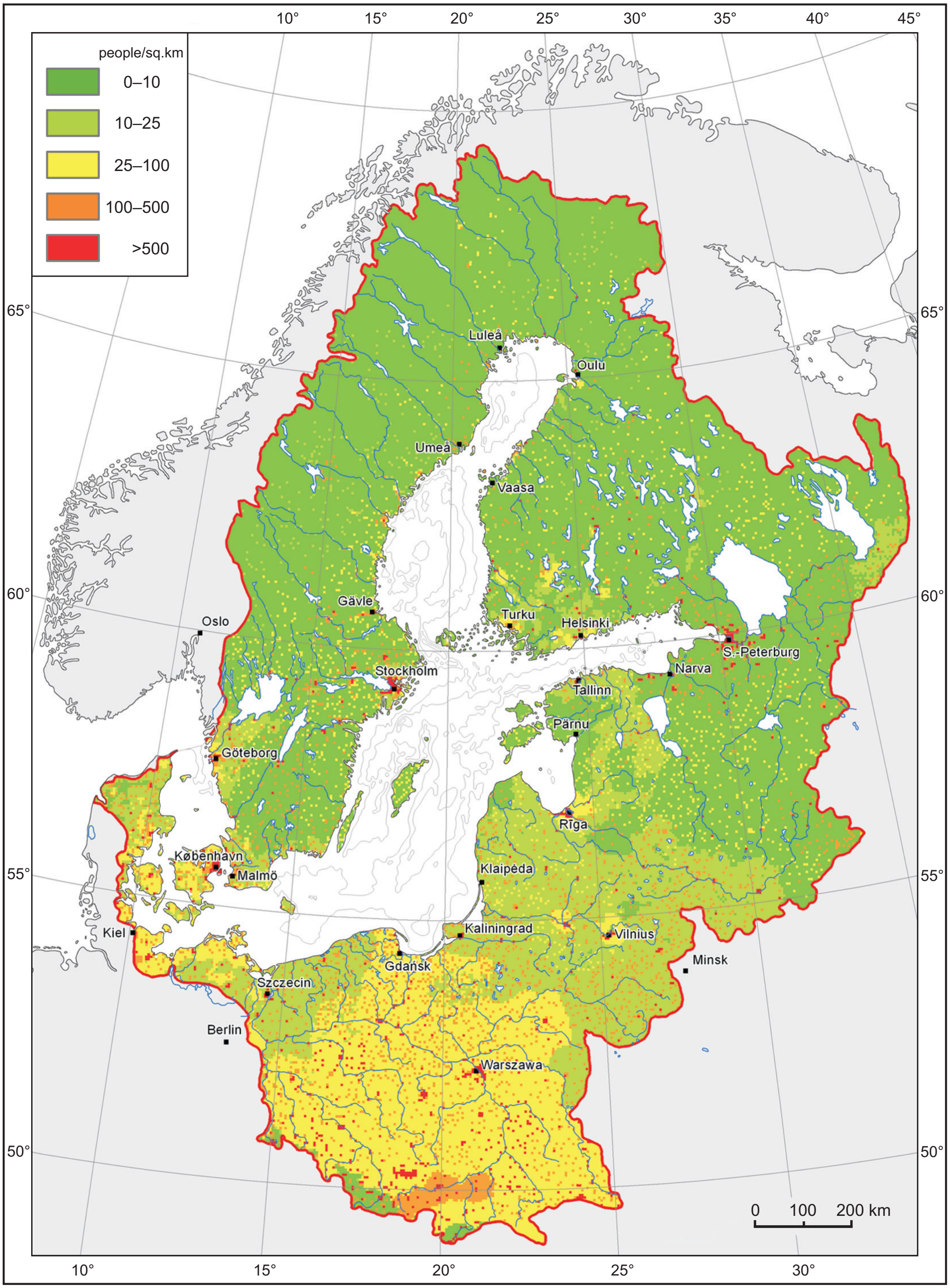


Fig. 2.18. Population density in the Baltic Sea catchment area (data from 1989 to 1993) (www.grida.no, free access unrestricted)

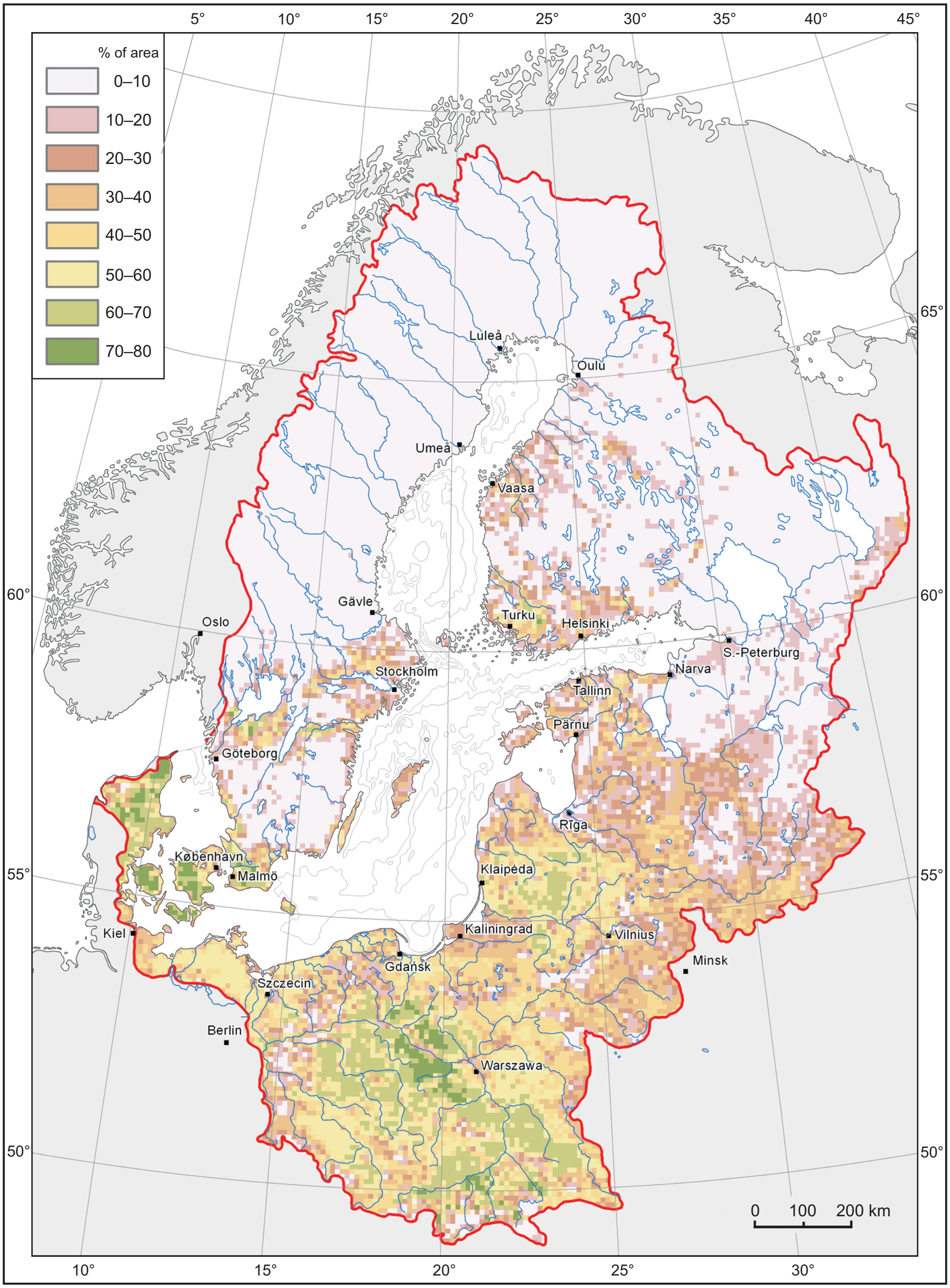


Fig. 2.19. Arable land percentage in the Baltic Sea catchment area (data from 1987 to 1993) (www.grida.no, free access unrestricted)

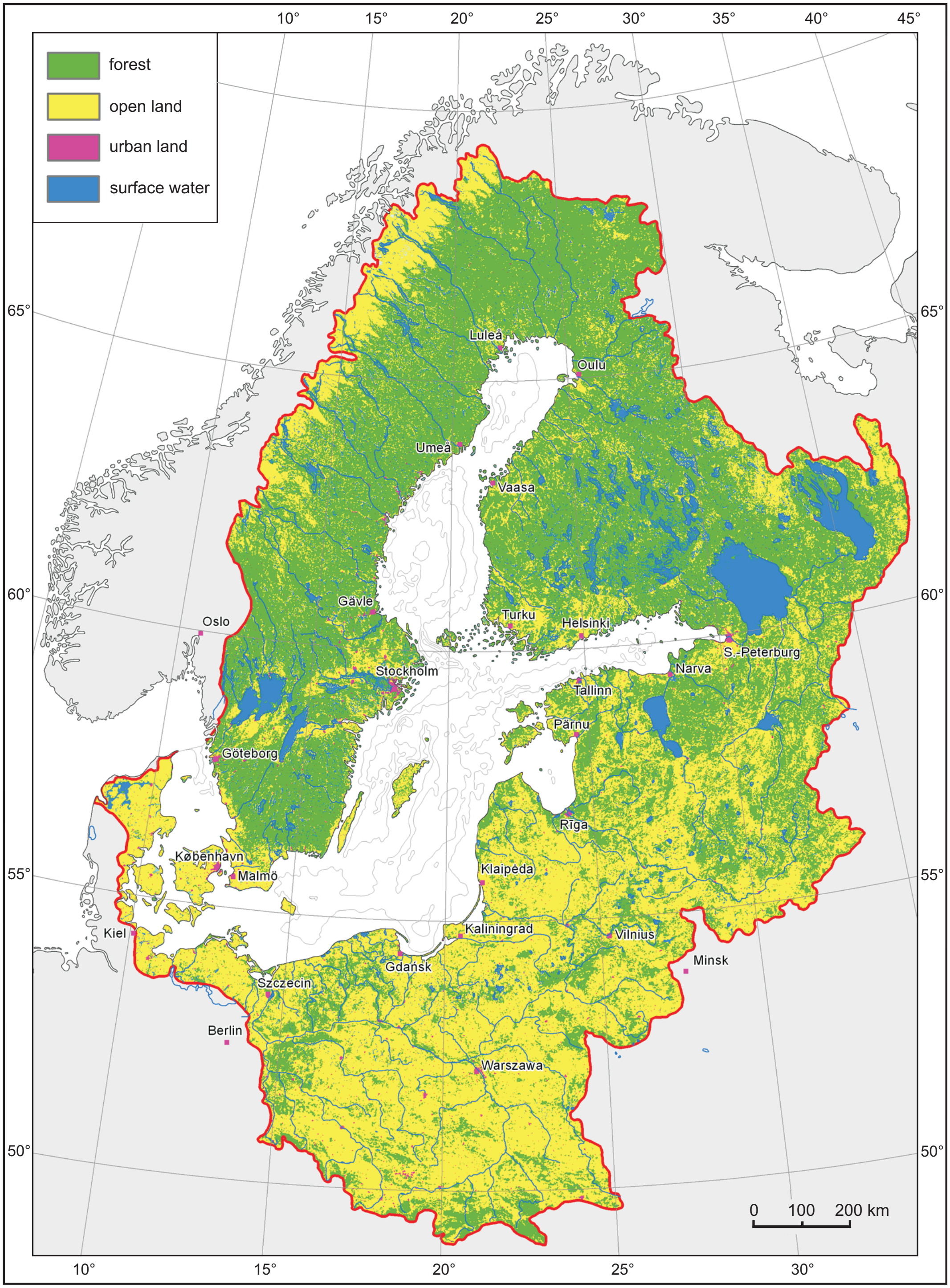


Fig. 2.20. Land use in the Baltic Sea catchment area (data from 1997 to 2000) (www.grida.no, free access unrestricted)

wastewater management systems in the nearest future, which will reduce the runoff of pollutants into the sea.

The development of the Baltic Sea coast depends on the progress of globalisation in the world markets. Fast growth in the production of SE Asia countries has changed the logistics and intensified the development of seaborne trade. The forecasts for freight handling turnover for the Baltic harbours suggest an increase from 540 million to 635 million tons in 2010 and up to 735 million tons in 2015. The large-scale development of containerisation for freight handling in the sea harbours and better quality of services, including their effectiveness, imposes on the same harbours the necessity of implementing changes both in the economic activities and in environmental protection (Grzybowski, 2009). Only four ferry terminals are situated on the Polish coast: Gdańsk, Gdynia, Szczecin and Świnoujście, which are of primary significance for the Polish national economy (Ustawa ..., 2002; Staniszewska, Bistram, 2006).

Fishery on the Baltic Sea is an activity that includes all the countries of this region, because the relatively low economic yield of fishing grounds is compensated by their close reach. Owing to the low salinity of the Baltic Sea surface waters (5–8‰), the resources and the diversity of fish are several times lower than in the neighbouring North Sea. The largest amount of fish (cod, herring, sprat, flatfish) per year is caught in Sweden (233 thousand tons), Denmark (211 thousand tons), Poland (153 thousand tons) and Finland (113 thousand tons). In the other five Baltic countries, the amount of caught fish is app. 230 thousand tons per year. Today, the level of fishing in Poland is four times lower than that in the 1970s. The difficulties for Polish fishing result from the naturally low biological yield of this sea area on the one hand, and regulatory conditions imposed by the European Union on the other. A constant reduction of the fishing fleet can be observed: 212 in 2007, 197 in 2008, and 161 in 2009. (Gospodarka Morska, 2009).

The condition of the water in the Baltic Sea is also dependent on marine engineering structures. Oil platforms, offshore wind power plants and transport pipelines have to satisfy technical standards concerning environmental protection.

Atmospheric deposition is an additional source of pollutant transport from the land to the sea. The reduction of atmospheric pollutants can be achieved by the installation of industrial filters and by improving the processing parameters of waste combustion plants. The restrictions on dust and gas emissions are particularly important as regards hazardous substances from the group of organic halogen compounds belonging to the persistent organic compounds. These substances are introduced into the natural environment as pesticides, anti-pyrenes, polychlorinated biphenyls and dioxins. They are easily adsorbed onto fine dusts (diameter <2.5 µm) and are transported by air over long distances. The most important regulations concerning environmental protection against persistent organic pollutants (POPs) are the UNECE Convention on the Long-Range Transboundary Air Pollution, 1979, including the Protocol on POPs, 1998, and the Stockholm Convention, 2001 (Niemirycz, 2008).

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Chapter 3

CLIMATE, HYDROLOGY AND HYDRODYNAMICS OF THE BALTIC SEA

This climatic-hydrological description of the Baltic Sea has been mainly based on data from the following studies: Majewski, Lauer, ed. (1994), Miętus, ed. (1996), Feistel, Nausch, ed. (2008) and von Storch, Omstedt, ed. (2008). In addition to those, materials from some meteorological stations located around the sea were utilized to characterise the climate of the region (Fig. 3.1).

A separate source that becomes commonly used in both climatologic and oceanographic research is data (frequently in the grid form) from processing the original results using mathematical models. Such data, being recently the basis for numerous studies, has a particularly high value in the study of spatial climate variation.

Extremely valuable knowledge about the Baltic Sea also provides a series of publications from the Baltic Sea Environment Proceedings issued under the auspices of the HELCOM (2007, 2009).

3.1. Major Elements of the Climate

Solar Radiation. The main source of heat shaping thermal conditions at the surface waters of the Baltic Sea is solar radiation. The results of measurements at the actinometry stations located in Kołobrzeg, Gdynia, St. Petersburg, Helsinki and Stockholm, fluctuate around 3500 MJ/m^{2}year for the total incoming radiation, showing differences of several percent between these stations (the highest in Kołobrzeg, the lowest in St. Petersburg). An important indicator of insolation, is the element expressed in the number of hours “with the sun”. This indicator varies from 1592 in Lund to 1881 in Visby.

During the year, insolation can be clearly perceived in December and January (<40 hours at all stations, and <20 hours in Tallinn), and there are high amounts of insolation from May to August (>200 hours per month), with a distinct dominance in Maarianhamina (Åland Islands), Tallinn and Visby, where it exceeds 300 hours in June.

Cloud cover in the Baltic Sea region, expressed as a percentage of sky covered by clouds, is rather high. The annual mean values are between 65% (Arkona, Maarianhamina, Visby) and 71% (Kołobrzeg). The most cloudy is the autumn–winter period lasting from November to February (with a cloud cover >70%), particularly in November–December with ≥80% for most stations. The cloud cover was distinctly lower between May and August, for most stations it was below 60%, or it slightly exceeding this value.

The element frequently associated with the cloud cover is the number of sunny or cloudy days. Cloudy days are recognised as when the daily state of the sky’s cloud cover equals or exceeds 80%, whereas sunny days when

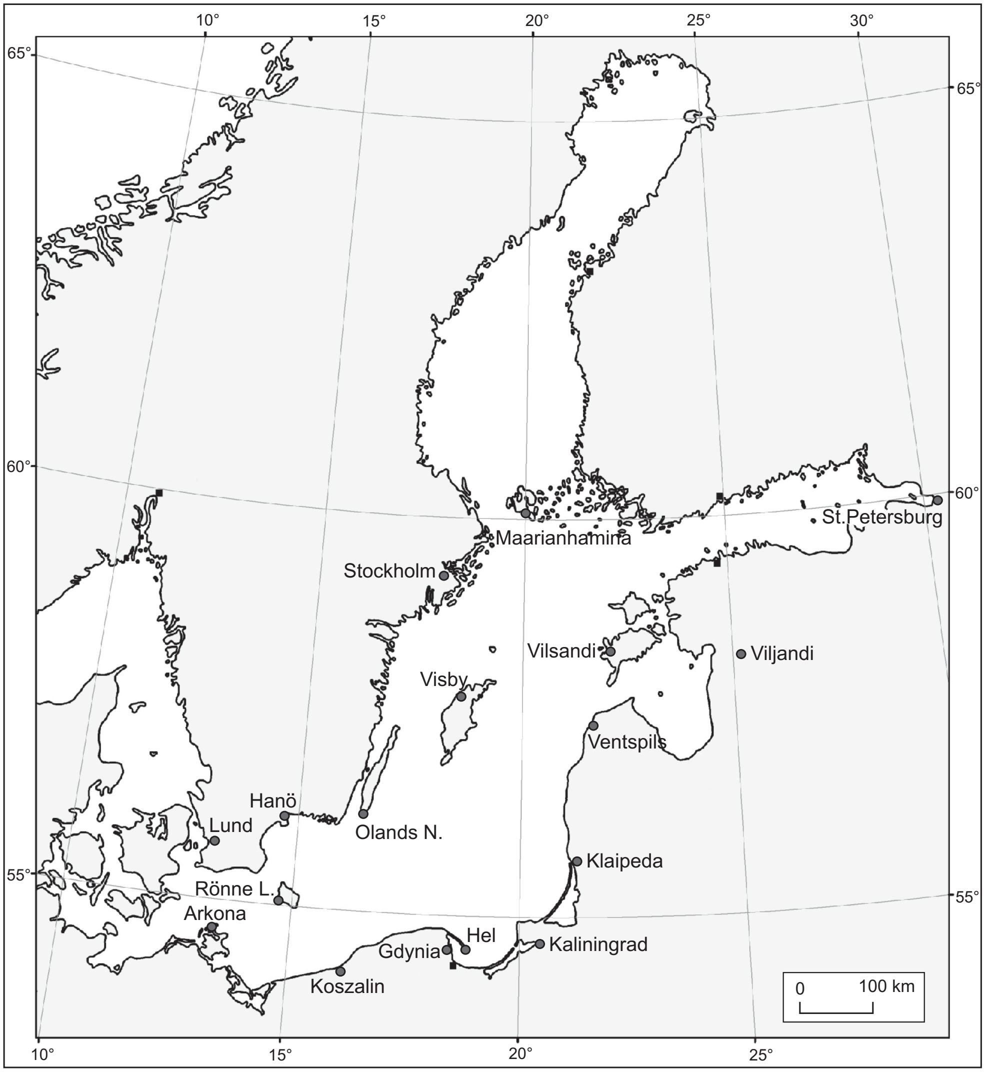

Fig. 3.1. Meteorological stations on the Baltic Sea coast

it equals or is lower than 20%. The distribution of sunny days during the year is geographically more diverse. The town of Hel is a leading example, where over 5 sunny days may be recorded from March to September, and more than 7 days in May, June and August. A clear minimum of sunny days is observed in the autumn–winter period. The highest number of cloudy days occurs in Kołobrzeg, the lowest in Arkona, while the highest number of sunny days occurs in Hel and the lowest in Tallinn. The annual distribution of cloudy days is similar to the mean state of the sky. More than half of the cloudy days at some stations equates to more than 20 days, falling in November and December.

Fog is a frequent event that occurs at the Baltic Sea. During the year, it occurs on more than 60 days on the coast of Sweden (Visby and Hanö), near Rügen in Arkona, and on the coast of Latvia (Ventspils), slightly more rarely in the other places, but extraordinary privileged are Rönne in Bornholm and Hel (less than 30 days a year). The most frequent fogs occur in December, March and

April, with more than 5 days per month. In the period from May to September, there are only a few foggy days (on average 2–3 days).

Average annual and monthly values of **atmospheric pressure** show no significant spatial and seasonal differences. The difference between annual mean values in Arkona (1015.1 hPa) most in the south and Maarianhamina most in the north (1011.9 hPa) is only 3.2 hPa. Elevated values of the average monthly pressure (>1015 hPa) are usually observed in May, January, February and October. A typical winter pattern of isobars indicates the dominance and intensification of polar-marine air masses from the Atlantic flowing onto the Baltic Sea catchment area. Next, in summer, we can observe a clear weakening of the polar-marine air mass inflow, with half the differences in pressure and with an almost latitudinal pattern of isobars.

Wind. Wind directions – annual and monthly means, indicate a dominance of air mass inflow from the southwest (section 180–270°). Relatively rare are dominant winds from the north sector NW–NE (315–45°), which occur mainly in the warm half year.

Average annual wind velocities over the Baltic Sea range from 3.2 m/s in Kaliningrad and 3.4 m/s in Kołobrzeg up to 7.8 m/s in Hanö; at the other stations the wind velocity is 4–5 m/s. Higher mean monthly values of wind velocities are observed in the autumn–winter period. Hanö and Arkona are definitely different within the group of 16 analysed stations; in Hanö, every month is characterised by wind velocities exceeding 6 m/s, whereas in Arkona only in June is it lower (5.7 m/s).

Wind velocities in the open space above the water surface of the Baltic Sea, owing to the lack of natural obstacles, are slightly higher than those recorded at the stations located onshore. Smaller disturbances in wind direction make the vectors of prevailing directions (from SW) less diverse. The mean annual wind velocity for the Baltic Sea area is within the range of 6–8 m/s. Values lower than 6 m/s occur in the coastal zone. Values higher than 7 m/s are observed over the Baltic Proper, and the highest ones, more than 8 m/s, in the Pomerania Bay.

Winds, particularly strong (storm), over the Baltic Sea are related to the movement of low pressure centres, which are not rare in the late autumn and early winter. Their routes to the Baltic Sea are prevailingly from the North Sea or the Norwegian Sea. A boundary value classifying the wind as a storm is 8°B, which corresponds to 17 m/s. Sometimes, slightly weaker winds, even 15 m/s, are classified as a storm. Most of them are active from October to January. Storms are observed mostly from the Danish Straits through the southern part of the Baltic Proper up to the Gulf of Finland (2–8% of the observed cases). In October and November, another centre (territorially smaller but active) is evident; 3–5% of cases over the Bothnian Sea, spreading over the Bothnian Bay in December. In January, a considerable number of storms (5–10% of cases) occur over the Baltic Proper.

The frequency of storm appearances over the Baltic Sea in individual years is diverse, e.g. in the southern Baltic Sea, in the 1970–2003 period, the number ranged from 5 to 37, with a mean annual value of 19. A similar frequency of these events is observed over the northeast region of the Baltic Proper, on the Saaremaa Island coast, where 2 to 36 cases occurred per year between 1948–2003, with an average of 20 (Fig. 3.2). Storms cannot be clearly categorised. The effects of their impact on the environment and the economy are in fact different: devastating for coastal zone and marine transport, but also improving the qualities of marine waters by intensive mixing related to waves.

Air temperature. The mean annual air temperature at the boundaries of the southern Baltic Sea ranges from 5.3°C in Maarianhamina to 7.9°C in Arkona and Kołobrzeg. More distinct are the differences in monthly values. The earliest negative average monthly temperatures appear on the east coast (Kaliningrad, Ventspils and Tallinn) and on the Åland Isles (Maarianhamina). In winter (January and February), negative temperatures are observed at all stations excluding Arkona, and in Tallinn and Maarianhamina also in March. Higher temperatures, above 15°C, occur in summer: from June to August.

The spatial variability of the Baltic Sea air temperature in February shows its decrease from positive values for the Danish Straits to –4°C in the northern part of the Baltic Proper and lower than –10°C in the northern part of the Bothnian Bay. The pattern of isotherms in the eastern and north-eastern part of the Baltic Sea indicates the influence of East European continental air masses.

Air temperature over the Baltic Sea in summer (August) is less variable than in winter. The isotherm pattern is nearly latitudinal. In the south, the values of 17°C

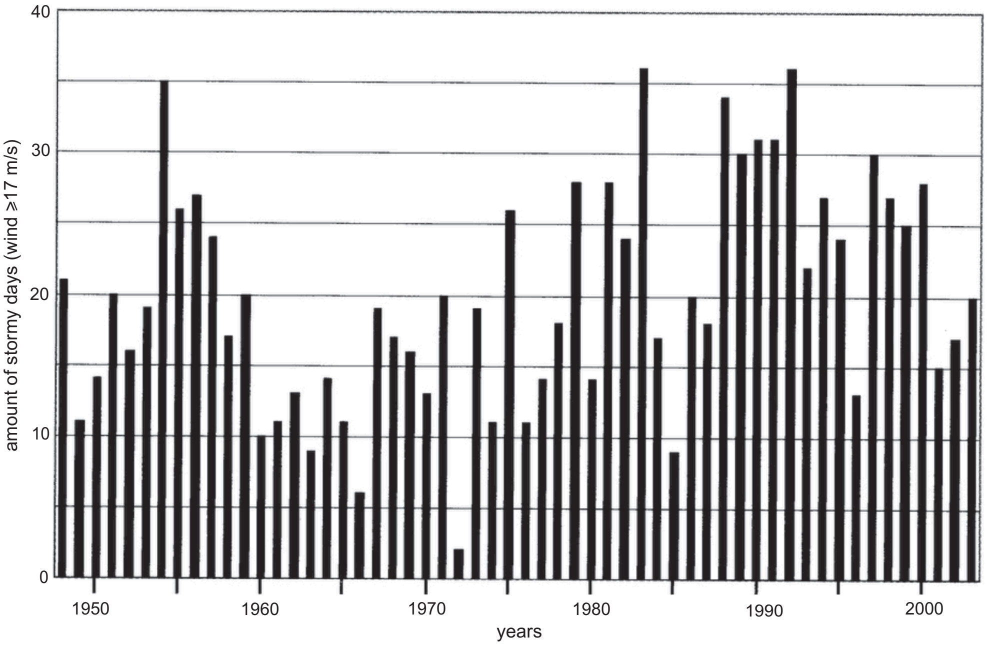

Fig. 3.2. Number of storm days in the north-eastern region of the Baltic Proper

correspond to the Polish coastline of the Baltic Sea, the 15°C isotherm runs near the Åland Islands, and the 13°C isotherm borders on the shore of the Bothnian Bay to the north.

The lowest air temperatures observed in the analysed stations (in 1961–1990) ranged from –32.9°C in Maarianhamina to –17.0°C in Arkona. July and August were the only months with no negative temperatures at any station. In June, negative temperatures were still observed in Ventspils, Maarianhamina and Visby; while in September, they did not fall below zero except in Arkona and Hanö.

The highest recorded temperatures exceeded 30°C everywhere, in Kołobrzeg and in Hanö it was 34.6°C, and it was 30.7°C in Maarianhamina. Relatively high values of maximum temperature, above 10°C, were observed in the winter months as well.

Precipitation (defined as a fall of water >0.1 mm per day) is a very frequent event in the Baltic Sea area. The data analysis of 30 years of observations (1961–1990) indicates that the number of days with precipitation in the periphery of the Baltic Sea ranged from 158 to 182 and was slightly lower than the number of days in half a year. Precipitation occurs most frequently in Kołobrzeg, Kaliningrad and Tallinn (≥180 days). November, December and January are the precipitation-richest months (rain/snow for about 20 days in each of those months), while the rarest rainfall is recorded between April and September (no more than 15 days).

Baltic Sea climatic water balance. The idea of water balance includes the atmospheric exchange of water within the relations of precipitation–evaporation. Assessing of both these elements involves difficulties while establishing them for specific areas, in particular for sea areas. In 1979–2002, the precipitation onto the surface area of the Baltic Sea was on average app. 600 mm, evaporation from its free surface area was 460 mm, and the difference (between precipitation and evaporation) was positive and amounted to 140 mm. Over the 23-year period, the amount of precipitation did not change, while evaporation increased. As a result, the balance difference is tending to decrease, which makes the precipitation net profit lower. During an annual cycle, a distinct rhythm between the two analysed parameters can be observed – lower precipitation in the second half of winter and spring, and higher – in summer and autumn. The annual pattern of climatic water loss is typical of the Baltic Sea – heat accumulated in water is used in late summer, especially in autumn and early winter. Consequently, the surplus of fresh water from precipitation occurs from January to July (in December the amount is trace), and from August to November it does not increase in the Baltic Sea (Omstedt *et al*., 1997; Tutgersson *et al*., 2002).

River water inflow into the Baltic Sea. River water plays a crucial role as a component of the fresh water balance, consisting in forming and modifying the salinity of the Baltic Sea water. Hundreds of rivers carry fresh water into the Baltic Sea, the annual volume of which exceeds 500 km^3 and which is almost 9-time higher than the volume of fresh water falling directly onto the surface of the sea (the result of difference in the climatic P–E balance). The distribution of mean yearly values of the river water inflow in 1901–1990 varied from 350 to 650 km^3 and resembles the normal distribution. Considering the total volume of the river water flowing into the Baltic Sea, about 20% is the inflow to the Baltic Proper (most water comes from the Vistula, Odra and Nemunas rivers). Annual values of the inflow to this sea region varied between 75 and 150 km^3 for 1951–1990, manifesting no significant trend; however, relatively high fluctuations of the inflow water volumes were observed (Cyberski, Wróblewski, 2000). The highest volumes of water are introduced into this region of the Baltic Sea after the spring melts (March to May), and the lowest occurring in late summer and earliest autumn.

3.2. Hydrology and Hydrodynamics of the Baltic Sea

Salinity is the most conservative component of the sea water. In oceans, it is weakly variable both on the horizontal surface and in vertical profiles, and the differences do not exceed a few psu (practical salinity unit). Differences in salinity occur in those seas with a limited communication with the oceans, such as the Baltic Sea. The surface layer of the Baltic waters has the following salinity spatial pattern: high values of 18–28 psu in the Kattegat, 10–20 psu in the Danish Straits, 6–10 psu in the Baltic Proper, and lower values of about 4 psu in the eastern part of the Gulf of Finland and in the Bothnian Bay (Cyberska, 1994). The salinity of the surface layer of the Baltic Sea results from the relationship between the components of the water balance (positive climatic balance and abundant fresh water inflow into the sea). However, the effect of balance and generally lower salinity increase the water level in the Baltic Sea, which makes the inflow of marine waters from the North Sea difficult. The anemometric conditions (prevailing winds from the west sector) form the pattern of surface sea currents, also affecting the pattern of isohalines. In the eastern part of the sea, the isohalines are bent to the north, and to the south in its western part.

Characteristic of the Baltic Sea is a double-layered distribution of salinity in the vertical profile, which is distinguished by an upper isohaline layer, less salty and of the same salinity, and a lower layer of more salty water. These layers are separated by a halocline, within which there are significant changes in salinity. Such a profile is not identical for the entire Baltic Sea, but spatially variable. In the Kattegat, the halocline occurs at a depth of less than 20 m, in the Arkona Basin at 30–40 m, in the Bornholm Basin about 20 m deeper (55–65 m), and still deeper (70–90 m) in the Eastern Gotland Basin and Landsort Deep (Kôuts, Omstedt, 1993). In the Bothnian Bay, the salinity is not so clearly laid out. The depth where the halocline forms and the vertical salinity profile are not stable, they fluctuate as a result of the thermohalinic sea water circulation induced by local anemometric factors, a variable system of sea currents and a diverse inflow of fresh water, including a saline water inflow from the North Sea.

On average, on the longitudinal section of the Baltic Sea from the Kattegat to the eastern side of the Gulf of Finland, as well as from the Åland Sea to the northern coasts of the Bothnian Bay, the salinity steadily decreases. As the distance from the Danish Straits increases, the isohaline concentration reduces, manifesting the progress of loss of distinction in the vertical salinity gradient owing to the small inflow of more brackish waters. In the deep layer, the sea water salinity tends to be 30–100% higher than in the top layer. At the same time,

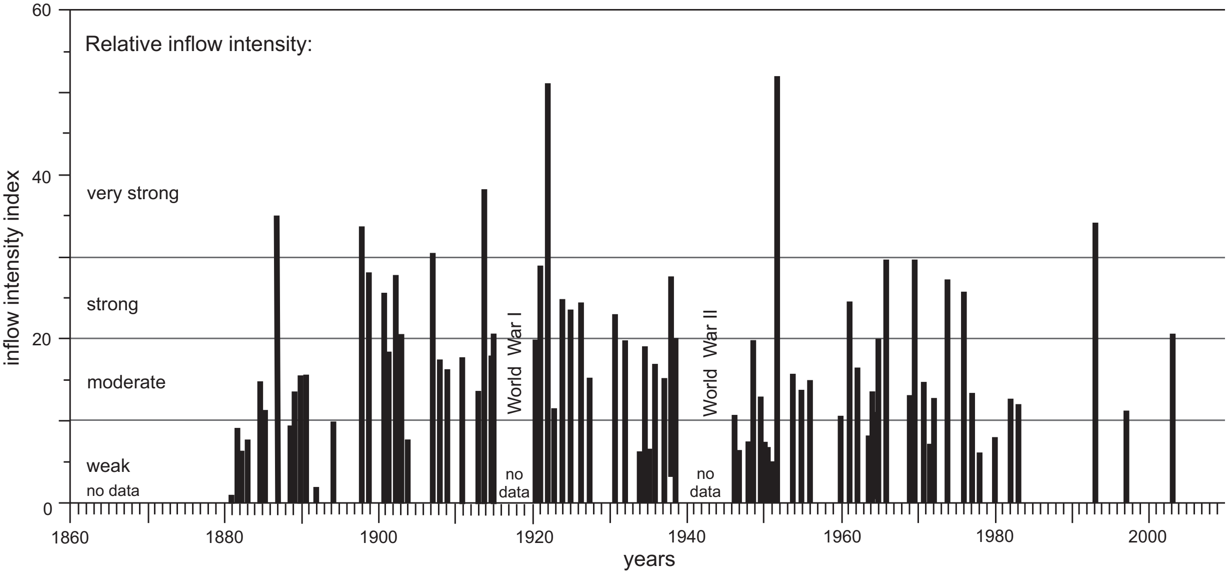

Fig. 3.3. Inflow of saline water into the Baltic Sea (acc. to Matthäus, 2006)

characteristic clusters of more salty waters are formed at the sea-bottom depressions. High salinity results in higher water density; it isolates depressions and makes the water circulation difficult, which affects the environmental conditions.

The water salinity and oxygenation values in deep parts of the Baltic Sea depend on the abundance and frequency of saline water inflows from the North Sea. The intensity of the inflows is assessed based on both the water salinity in the Belt Sea and the inflow duration (which is connected with the inflow volume). The inflow intensity index may range between 0 and 100. The series of inflows in 1880–2005, excluding the period of the two world wars, was analysed by Matthäus (2006). The largest inflow after World War II occurred in 1951 with the index exceeding 50. Large inflows are occasional events. High abundant inflows (index >30) took place only 7 times within the research period. More frequent were inflows classified as moderate or low, although a clear decrease in intensity has been recently noticed within this group (Fig. 3.3). Characteristic is their seasonal nature; except in May, June and July, they occurred in all the months, while the largest inflows took place only in autumn and winter, the maximum in December.

The inflows of more salty and usually more oxygenated waters reaching the Baltic depths exert a significant effect on their oxygen conditions. These relationships are exemplified by a large number of research results in the Bornholm Basin for the 1960–2005 period (Nausch *et al.*, 2006), including information by Matthäus about inflows (2006). Due to the longer breaks between the inflows, the oxygen content in the water layers below the 70 m depth reduces distinctly to values near zero (or even slightly lower – the so-called negative oxygen = hydrogen sulphide). Aerated inflow waters, that reach the Baltic Sea, quickly and significantly increase the oxygen content, which is shown in the events of 1993 and 2003 when they eliminated hydrogen sulphide in the deep water layers for some time.

Considering the incidental nature of more abundant ocean inflows and the impediments in the flow of deep water over the bottom thresholds separating the individual sea basins, they rarely reach the depths located in the far east and north of the Baltic Proper or the Bothnian Sea. It results in seasonal or even long-lasting underaeration (≤2.1 ml/l) of the bottom waters in the following basins: Bornholm, Gdańsk, Eastern and Western Gotland, North-Central, and the depths of the Gulf of Finland. In the relatively shallow regions in the south-western part of the Baltic Sea, including the Arkona Basin, strong short-period fluctuations in salinity are observed in the sea-bottom layer, not always induced by the water intrusions classified as ocean inflows, but by disturbances in the processes of water exchange in the Danish Straits.

Water temperature. Cyclical and seasonal variability of water temperature in the top layers of the Baltic Sea is their most characteristic feature. In winter (e.g. in February), water temperature of the Bothnian Bay, Bothnian Sea and gulfs of Finland and Riga drops down to 0°C in their top water layers, sometimes even to the freezing point of brackish water (app. –0.5°C). In the Baltic Proper, owing to its considerable source of heat accumulated in high volumes of water, the process of cooling is slower, which explains why the water temperature drops slower and maintains the positive temperature from 1 to 2°C in winter, and even up to 4°C in mild winters. In summer (e.g. August), the sea water temperature of the top layer exceeds 12–13°C in the Bothnian Bay, 16°C in the Baltic Proper and 17–18°C in its south-eastern coastal zone (Cyberska, 1994). Water temperature, in particular of the top layer, undergoes large variations induced mainly by variable weather conditions, such as fluctuations of the sun energy, advection of air masses of different physical features, cloudiness and precipitation, anemometric conditions as well as physicochemical and natural properties of the top layer of the Baltic Sea water.

The range of annual changes in water temperature includes not only the top layer but also reaches the very deep layers of the sea, causing its specific thermal stratification. Three seasonal thermal layout of water masses are characteristic of the Baltic Sea waters: summer, unified and reversed (Łomniewski, 1975). Summer stratification – with the warmest water in the top layer, app. 20–30 m deep, and a lower located layer of (summer) thermocline, below which cold water from the previous winter is situated. Unified thermal layout of water masses (homothermal, isothermal) appears in autumn and spring, almost equalling the temperature over the entire water column (4–6°C), with a gentle increase towards the seabed. Reversed stratification occurs in winter, when the top layer of the sea water shows the lowest temperature, higher than 1°C in most of the Baltic Sea area, and increasing towards the sea bottom by as much as 4–6°C. Relatively high temperatures at greater depths are an effect of the accumulation of waters originated from the so-called warm inflows.

Thermohaline water structure. Two physical parameters: temperature and salinity, shape the thermohaline structure of the sea water. In the Baltic Sea, four water layers are distinguished (Fig. 3.4), two of which are autochthonous and form, at the top, summer water (A) and winter water (B), separated by the summer thermocline. Allochthonous brackish waters (layers C and D), genetically associated with the inflow of waters from the North Sea, are situated below these layers. Waters of gently elevated temperature occur under the halocline (H1), but their salinity is higher than that of the autochthonous winter waters (in zone B). Under these layers, there is an old water from earlier inflows (D), separated from the underlying water mass (C) by the secondary halocline

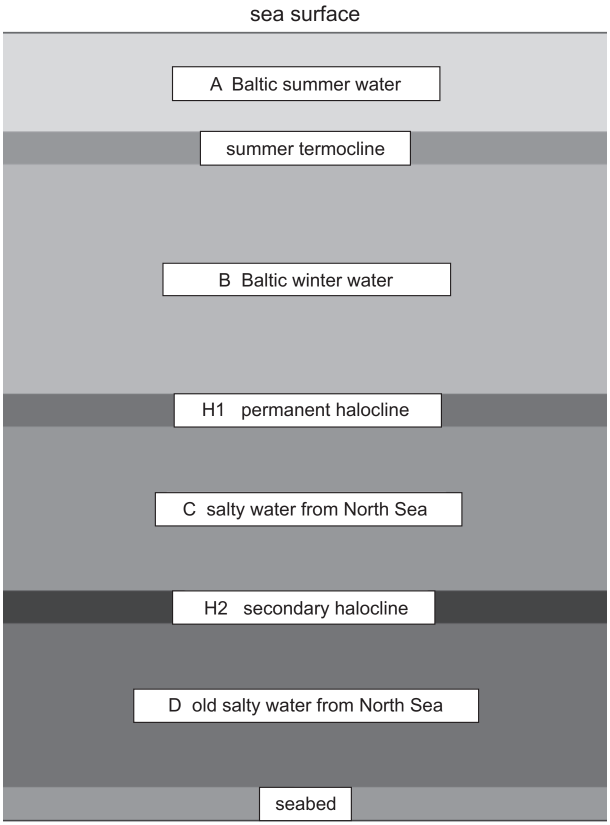

Fig. 3.4. Simplified diagram of the thermohaline structure of the Baltic Sea

(H2) that occurs sometimes and not in all regions of the Baltic Sea.

Water transparency. The transparency of the top sea water layer depends on thermal conditions and human activity. Information from numerous measurements made using the Secci disc, collected over many decades, enables the assessment of the changes in the transparency of the Baltic Sea water. Additional studies on the chlorophyll content in the two-metre deep top layer of the sea water show some spatial differences in transparency. This parameter has values between 5 and 10 Secci metres, whereas better conditions are observed in the Kattegat than in the Gulf of Finland. Furthermore, higher transparency is seen in the Kattegat and Arkona Basin, but it is worse in the gulfs of Finland and Bothnia. The chlorophyll content (in μgL^{-1}) in summer is the lowest in the Kattegat and Arkona Basin (less than 2 μgL^{-1}), with a clear tendency to increase in the 1975–2005 period in the Gulf of Finland.

Density of sea water (σt) expressed in Baume degrees, is physically dependent on temperature, salinity and hydrostatic pressure. In the ocean, where differences in salinity are insignificant, water temperature and hydrostatic pressure determine its value. Considering the significant differences in salinity and relatively low depths, salinity determines water density in the Baltic Sea, while the effect of hydrostatic pressure is of secondary importance and can be negligible. A distinct influence of water temperature on water density is observed above the constant halocline, in the upper isohaline layer (of balanced salinity). Below the halocline, the salinity is a decisive parameter for water density and the effect of temperature is not observable.

In the vertical water profile, seasonal variations in density are related to cyclical temperature changes, resulting in reduced density in the warmer season of the year and increased in the cooler season within the range of 1–3 units σt. A noticeable abrupt change in water density is observed within the pycnocline, the location of which corresponds to the halocline. The differences in the water density between the top water layer of the sea and its bottom layer range from 2 to 10 units σt; they are definitely higher in the southwest Baltic Sea.

In the longitudinal profiles of the Baltic Sea, water density distribution represents three periods: the end of winter and the beginning of spring, summer, and autumn, during which the interaction between water temperature and water density is noticeable. The considerable high water density gradient occurs in regions of high salinity gradients (Bornholm Basin and Słupsk Furrow), and in the Eastern Gotland Basin, where it is distinctly lower. With the general trend of isopycnes lowering, while moving from the Bornholm Basin to the Gulf of Finland, which is similar to the case with salinity (lowering of isohalines), a partial tempering of this phenomenon is observed which is a result of the influence of the water temperature in summer in the upper sea water layer.

Ice condition in the Baltic Sea occurs each winter; however, with variable intensity. Ice cover is a phenomenon observed with the following parameters: a maximal surface of the sea area covered with ice, ice thickness, ice mass and its structure, the period and time of the ice event occurrence, dates for the beginning and the end of the phenomena, and the dynamics of the thickening and vanishing of the ice. Commonly accepted are historic materials that document icing events in the Baltic Sea, dating back to 1720. The Baltic Sea area covered by ice oscillates between 0 km^2 (complete lack of ice cover) and 420,000 km^2 (totally frozen surface of the sea). Therefore, it was considered that ice MIB index, defined by large annual variation, can be used in climatology as a measure of severity of winters in the Baltic Sea (Figure 3.5).

The duration of the ice cover on the Baltic Sea is geographically very diverse. In the Bothnian Bay, the ice remains the longest: from 130 to almost 200 days, in the Bothnian Sea: from 50 to 140 days, in the Gulf of Finland: from 40 to 140 days, in the Gulf of Riga: from 70 to 110 days, and in the Baltic Proper from 0 to 40 days (Dziadziuszko, 1994).

Currents in the Baltic Sea occurs as two types of horizontal movement of the sea water: barotropic and baroclinic. Barotropic currents are usually generated by the wind, water level slope and the inflow of river water into the sea. They are observed in the entire Baltic Sea and their development follows general rules of circulation typical for estuarine areas. The reasons why baroclinic currents take place are gradients in density and hydrostatic pressure. This kind of water mass transportation occurs in those parts of the Baltic Sea with a distinct density stratification of the sea water, i.e. from the Kattegat to the Danish Straights, Belt Sea

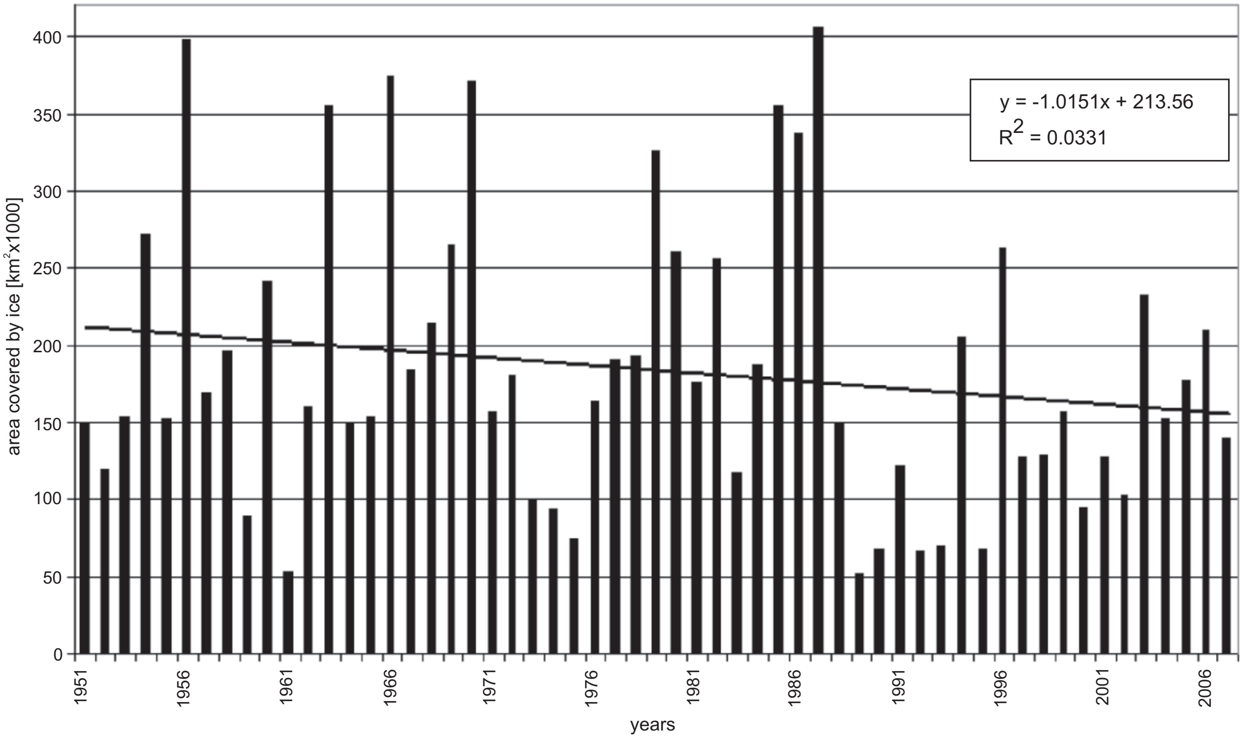

Fig. 3.5. The maximum area of the Baltic Sea ice cover in 1951–2007

and Baltic Proper. The velocities of these sea currents are variable and range from 10^{-1} to 10^{2} cm/s, lower values dominate in the Baltic Proper region, and higher ones occur in the Danish Straits (Jacobsen, 1980; Jankowski, 1988).

Baroclinic currents play a crucial role in supporting the water salinity of deep-water layers of the Baltic Sea. Under average hydrological conditions, the highly saline water inflows as a compensation current from the North Sea through the Skagerrak, Kattegat and Danish Straits into the Arkona Basin, undergoing considerable alterations and lowering its salinity. Then, it flows into the Bornholm Basin and intrudes (owing to similar water densities) into its water masses at the level of similar water densities. The water salinity of this current is not the only criterion that determines the depth of its main stream, since water density is also dependent on temperature. In the situation of the so-called warm inflows (lower density waters), the barocline current may flow over some distance from the sea bottom and, at the same time, saline water masses resting in the deep layers of the sea are not dislodged. High salinity currents, additionally of low water temperature (due to higher water aeration), play a highly advantageous role by refreshing (venting) the deep sea water.

Since the barotropic surface currents of the Baltic Sea are generated mainly by winds, their general pattern is similar to the dominant wind directions. The velocities of the observed currents are usually not high, mainly app. 20 cm/s, occasionally a few tens of cm/s. Those velocities exceeding 100 cm/s may occur in coastal zones as rip currents, i.e. narrow streams perpendicular to the coastline that transport water into the open sea. During heavy storms, the velocities of these currents can even exceed 200 cm/s.

Upwelling – the phenomenon of elevating the water masses from the depths to the surface, known from many areas on the globe and observed in the Baltic Sea, plays an extremely important role in carrying nutrients, oxygen and transformation of water thermal systems, particularly in the coastal zone. In summer, there have been numerous instant cases of water temperature dropping (to 10°C) on the beaches, disturbing the leisure of beach users and inducing deep fogs in the vicinity. The origin of coastal upwelling is related to the Coriolis force caused by the rotary movement of the Earth, the coast location and the direction of the coastal current. Upwelling is induced by the lack of water mass in the coastal zone flowing out into the open sea. This gap is compensated by the inflow of water from the depths, whose temperature is naturally much lower. The velocities of the rising abyssal water to the surface range up to several tens of metres a day and depend on meteorological and bathymetric conditions.

Seiches and internal waves. The deflection of the sea level (on the interface between the air phase and water phase) caused by changes in either the atmospheric pressure or the wind pressure (in general: the disturbances of the water area balance) sometimes leads to swaying, long-lasting oscillations of the water surface. The seiche sways in the Baltic Sea have oscillations ranging up several hours and the amplitude of up to tens of centimetres, in extreme cases they exceed 2 m. Seiche movements occur quite often in the Baltic Sea and their effects may be severe, e.g. floods in St. Petersburg, and river backflows.

An event of similar character and origin, but taking place inside the water mass, within the same medium and with different density, is the internal wave motion (inner seiche). In the Baltic Sea, the phenomenon is observed on the surfaces separating waters of different densities, which corresponds to the depths similar to that of maximum density occurrence. The first measurements of internal wave movement carried out in the Gulf of Gdańsk (Kowalik, 1963) revealed that these waves may achieve high amplitudes (app. 14 m). However, the amplitudes do not often reach such high values. The suppression of both the surface seiche and the internal wave, as well as achieving a balance, depends on gravity force and the resistance of the medium in which the wave movement takes place, with the simultaneous ceasing of the reasons that earlier triggered the water oscillations.

Wind waves and storm surges. Sea surface waves show seasonal variations correlated with the wind velocity. Very small (0–0.75 m) and small waves (0.75–1.75 m) occur most frequently in the southern part of the Baltic Proper. Medium waves (1.75–3.25 m) appear from April to July with a 5% probability, and slightly higher in the other months. Despite their occurrence in all months, the proportion of high waves (3.25–4.75 m) does not exceed 1% from April to August. Finally, very high waves (>4.75 m) occur only from September to March, showing a small relative frequency of 0.1 to 0.7%.

Storm winds induce a strong waving of the sea surface and coastal storm water surges reaching as much as 2 m above the mean sea level.

Sea level changes. The Baltic Sea water level in the section from the northern part of the Bothnian Bay to Mecklenburg Bay shows a vertical deflection of over 20 cm (higher in the Bothnian Bay). It is upheld by a salinity gradient, a positive water balance (mainly a fresh water factor) and anemometric conditions. Apart from short-time changes deforming the water surface and caused by the wind waving, long-time sea-level changes can be observed. Annual cycles of sea-level changes in the Baltic Sea are represented by seasonally variable volumes of river water flowing into the sea, wind directions dominating in a given season, and changes related to seasonal differences of sea water temperature.

Long-term secular trends are shaped by global climatic changes, which are also observable in the Baltic Sea. The role of positive vertical movements of the Earth crust is also significant. The bottom of the northern part of the Baltic Proper, Bothnian Sea and Bothnian Bay is uplifting faster than the rise of the water level in the oceans. In the southern part of the Baltic Proper, depending on the length of the observational series, the calculated average value of the trend of sea-level rise is about 1–3 mm/year.

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Chapter 4

GEOLOGICAL SETTING AND BOTTOM SEDIMENTS IN THE BALTIC SEA

4.1. The Quaternary Basement

The Baltic Sea is an intracontinental sea, which means that it covers an area of geological structures similar to the land surrounding the basin. The north part of the Baltic Sea lies within the Baltic Shield, while the southern part is situated on the East European Platform. A small, south-western part of the Baltic Sea lies on the Paleozoic West European Platform separated from the East European Platform by the Teisseyre-Tornquist Fault Zone (Fig. 2.4).

In the Baltic Shield area of the Baltic Sea, crystalline Precambrian rocks outcrop in the coastal zone and on the sea-bottom elevations. In the depressions within the Bothnian Bay and the Bothnian Sea, the top of the crystalline massif is covered with younger sedimentary rocks. The Archean, represented by metamorphic and volcanic rocks (gneisses, enderbites and migmatites), occurs at the bottom of the Baltic Sea only in the far northern, coastal part of the Bothnian Bay, directly under a thin cover of Quaternary deposits, or on the sea bottom (Lundqvist, Bygghammar, 1994).

Proterozoic igneous rocks extend much further. The northern part of the Baltic Sea is dominated by granitoids, occasionally by dolerites and metamorphic sedimentary and volcanic rocks in the Svecokarelian province. In the Kattegat, Proterozoic rocks belong to the South-West Scandinavian Province, including mainly gneisses as well as metamorphic, sedimentary and volcanic rocks. Proterozoic intrusions of rapakivi granites occur at the bottom of the Baltic Sea, in the region of the Åland Islands and in the north-eastern part of the Gulf of Finland.

Proterozoic igneous rocks, directly underlying the Quaternary, are located on the coastlines of the Bothnian Bay, Bothnian Sea, along the northern shores of the Gulf of Finland, in the Archipelago Sea, along the coasts of Sweden, and along the east shores of the Kattegat. On the elevations, the rocks outcrop at the sea bottom. Particularly numerous outcrops occur in the Archipelago Sea basin, Åland Isles, along the shores of Sweden between Stockholm and Öland, and along the eastern coasts of the Kattegat.

Red Jotnian sandstones, also included into the Proterozoic Svecokarelian province, occur upon Proterozoic igneous magmatic rocks in the Bothnian Bay and Bothnian Sea, and behind the coastal zone (Lundqvist, Bygghammar, 1994). Lower Paleozoic sedimentary deposits overlie the Jotnian sandstones in the northern part of the Bothnian Bay and in the western part of the Bothnian Sea, Cambrian sandstones in the Bothnian Bay, and Cambrian sandstones and Ordovician limestones in the Bothnian Sea (Fig. 4.1).

The top of the Precambrian drops towards the south and southeast, forming the crystalline basement of the East European Platform. In the southern coasts of the Bal-

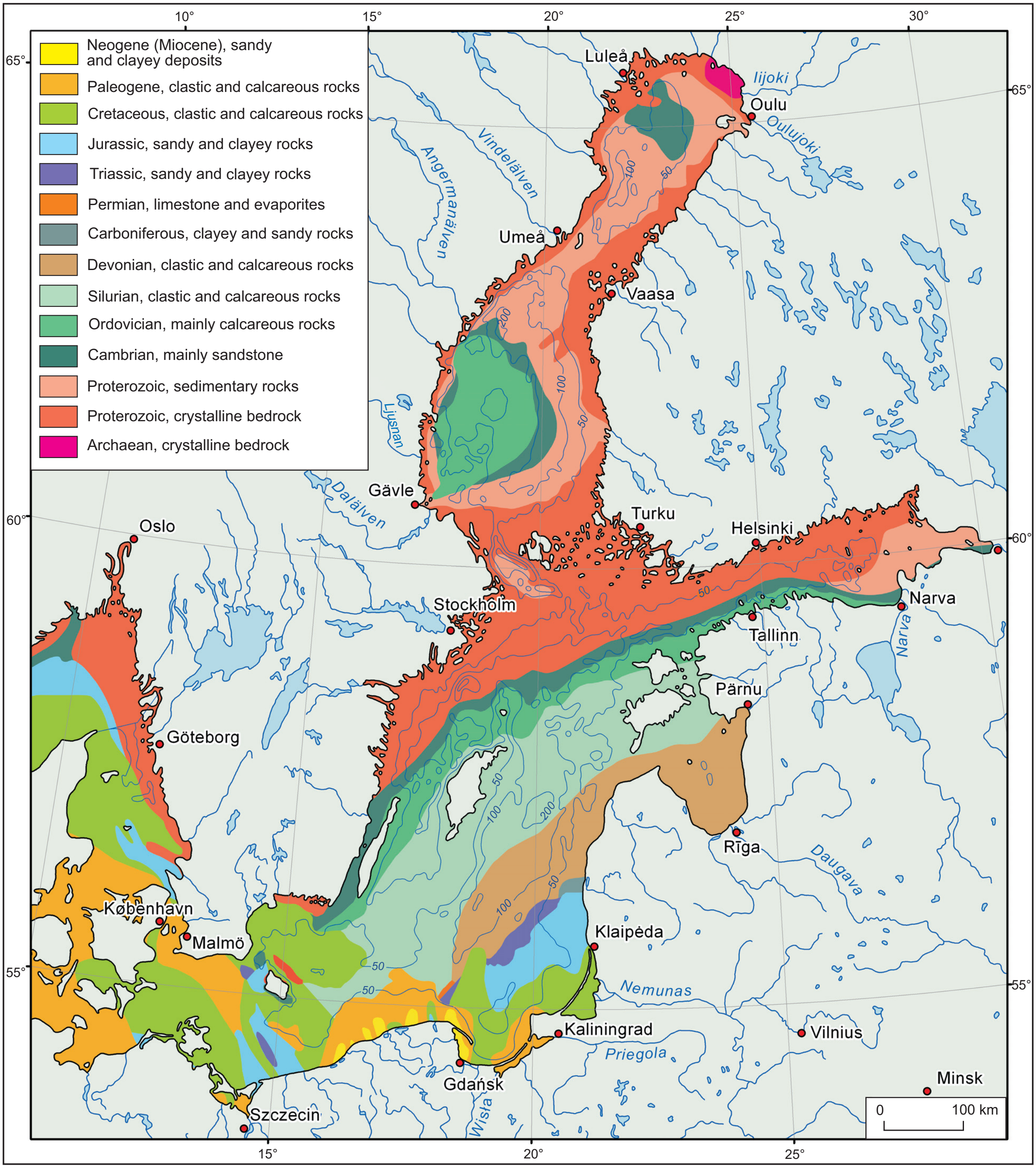

Fig. 4.1. Geological map of the Baltic Sea without Quaternary sediments (based on Norling, 1994; Sigmond, 2002, simplified)

tic Sea, near Koszalin in the northeast of the Teisseyre-Tornquist Fault Zone, the top of Precambrian rocks lies at a depth of 8,000 m and rises gently to the northeast up to 5,000 m near Darłowo and up to 3,800 m in the vicinity of Ustka (Ryka, 1995; Pokorski, Modliński, eds., 2007). Further towards the east, between Ustka and the eastern part of the Gulf of Gdańsk, the depth to the crystalline basement changes slightly. The Precambrian formations have been drilled to a depth of 3,419 m in Smołdzino, to 3,303 m in Łeba, to 3,231 m in Żarnowiec, to 3,483 m in Jastarnia on the Hel Peninsula, and to 3,485 m near the Vistula River mouth (Ryka, 1995). In the western part of the Gulf of Gdańsk, the crystalline basement gently declines, reaching a depth of app. 3,750 m in the region between Gdynia and Gdańsk (Pokorski, Modliński, eds., 2007). From the south-eastern part of the Gulf of Gdańsk towards the north-east, the top of the Precambrian basement rises gradually. Near the shorelines of the Sambian Peninsula, it occurs at a depth of app. 2,800–3,000 m. Along the eastern coasts of the Baltic Sea, the crystalline basement rises towards the north. On the Lithuanian coast, near Klaipeda, it is located at a depth of about 2,200 m (Suveizdis, 2003; Pokorski, Modliński, eds., 2007). In the northern part of the Latvian coast, near Ventspils, the crystalline basement occurs at a depth of about 1,200 m, and in the southern part of the Gulf of Riga at app. 1,000 m (Pokorski, Modliński, eds., 2007). On Saaremaa Island, the Precambrian basement is situated at a depth of about 800 m and on the north shore of Estonia, near Tallinn at app. 200–400 m (Golub, Sidorow, 1971).

In the East European Platform, the thickness of the sedimentary cover increases towards the southeast and south, whereas the top of the crystalline basement drops. At the sea bottom, under the Quaternary, the sedimentary formations occur from the Cambrian in the north-west to the Neogene in the south and southeast. In the northern part of the Baltic Proper, Paleozoic sediments directly underlie the Quaternary cover. In the eastern and southern parts, they are covered with Mesozoic and Cenozoic sediments.

In the area of Paleozoic West European Platform (west of the Teisseyre-Tornquist Fault Zone), the top of Precambrian rocks is situated at about 10–12 km depth. Higher up are lower Paleozoic (Cambrian, Ordovician and Silurian) corrugated deposits, which are covered with upper Paleozoic and Mesozoic, locally Paleogene, sediments. These sediments form two platform complexes of the Carboniferous–Devonian and the Permian–Mesozoic, split into two smaller units at the turn of the Cretaceous and Paleogene. A few local anticlines with Jurassic and even Triassic deposits in their cores, and a few NW–SE-oriented synclines, divided into smaller fault blocks, occur in this area. In the Baltic Sea, west of the Teysseyre-Tornquist Fault Zone, Mesozoic and Paleogene deposits occur at the bottom under the Quaternary cover.

Cambrian sandstones appear in the bottom of the Baltic Sea along a scarp (erosional step) known as the Cambrian glint along the coasts of Estonia, and then towards the southwest and south, along the coast of Sweden to Scania. In the central and southern part of the Baltic Proper, gas and crude oil deposits are associated with the Cambrian sediments.

The Ordovician red and grey limestones form the Baltic Sea floor along the scarp of the so-called Ordovician glint, stretching from the southern side in parallel to the Cambrian outcrops. The Ordovician sediments also show gas- and oil-bearing features.

The Silurian sedimentary formations appear under the Quaternary deposits over large areas of the Baltic Proper. The erosional range of these deposits runs from Hiiumaa Island and turns southwest and north towards Gotland Island, forming the Silurian scarp (called the Silurian glint), including the western coasts of Gotland. The Silurian glint is composed of reef limestones. Towards the south, the Silurian sediments pass into clayey facies deposited in deeper sea environments.

The Devonian sedimentary formations occur only in the south-eastern part of the Baltic Proper, forming a belt spreading from the southern coasts of Estonia through the Gulf of Riga towards the west from the Latvian and Lithuanian coast. The Lower Devonian is represented mainly by terrigenous sandstones deposited in a continental environment, the Middle Devonian is composed of sandstones overlain by dolomites. The Upper Devonian is represented by gypsum and anhydrite.

Carboniferous fine-grained sandstones with thin clay interbeds conformably overlying the Devonian, occur in a very limited area. Under the Quaternary, they appear only near the coasts of Latvia and run as a narrow belt towards the east.

The Permian sedimentary formations are represented only by Zechstein carbonate-evaporate facies. They are widely distributed in the southern part of the Baltic Proper, but in very small areas located to the east of the Lithuanian coast as well as along the Polish coast to the north of the Rozewie Cape, they directly underlie the Quaternary.

The Triassic of the southern part of the Baltic Sea can be found directly under the Quaternary deposits in a belt extending from the southern coasts of Latvia to the northern part of the Gdańsk Basin, and locally to the north of the Rozewie Cape and near Żarnowiec. In the East European Platform, continental deposits prevail represented by red sandstones and claystones, as well as limestones deposited in fluvial, lacustrine and lagoonal environments. In the West European Platform, Triassic sediments are also mainly of continental origin; however, locally there are also brackish formations (Winterhalter *et al*., 1981). In the central and southern parts of the Kołobrzeg Fault Block, there is only the Upper Triassic immediately beneath the Quaternary cover, represented by red clay deposits (Kramarska ed., 1999).

The Jurassic of Baltic Sea in the East European Platform occurs only in its south-eastern part. It consists of thin marine clastic sediments (sandstones, mudstones) of the Middle and Upper Jurassic. Directly under the Quaternary, these sediments appear as a narrow belt running from the southern coast of Latvia towards the southeast to the north-eastern part of the Gdańsk Basin. In the West European Paleozoic Platform, a complete Jurassic section is observed, characteristic of this part of the Danish-Polish Trough. The Lower Jurassic is composed mainly of inland clastic sediments: alluvial, bottomset and lacustrine deposits, with a few interbeds of marine or brackish clay deposits. Middle Jurassic marine sediments consist alternately of clays and sands. The Upper Jurassic sediments are clastic at the base, with the increasing proportion of marl and clay deposits towards the top of the section. The Jurassic occurs under the Quaternary at the wings of the Kołobrzeg anticline and in the axis of the Kamień anticline (Kramarska ed., 1999).

The Cretaceous occurs in large areas of the southern part of the East European Precambrian Platform, from the Lithuanian coasts to Scania. These are Upper Cretaceous marine deposits, mainly fine-clastic with a large proportion of carbonate-siliceous sediments (opokas and gaizes). They underlie Quaternary deposits in the area extending from the south of the Curonian Lagoon to the central and southern part of the Gulf of Gdańsk and in the north-western part of the Gdańsk Basin. Within the limits of the Paleozoic Platform, the Cretaceous underlies Cenozoic deposits over a considerably large area. During almost the whole Early Cretaceous, the marine basin was confined to the trough, widening slightly with time and including external zones of the Precambrian Platform; the Lower Cretaceous is represented by clastic facies of mixed origin: marine and terrigenous. The sedimentation changed alternately from shallow marine to open shelf and brackish. Within the Danish-Polish Depression, the Upper Cretaceous is largely represented by carbonates, with sand layers in the lower part and siliceous rocks in its upper part. The Cretaceous deposits occur immediately under the Quaternary in the eastern part of the Kołobrzeg Fault Block, in large areas of the Gryfice Fault Block and over the whole blocks of Wolin and Arkona through Rugen and Zealand. Besides, the Cretaceous sediments are outcropped in the Kattegat (Winterhalter *et al*., 1981; Kramarska ed., 1999).

Within the Precambrian platform, the Paleogene occurs directly under the Quaternary deposits in a belt extending from Sambia westwards along the Polish coast. The Paleocene marine deposits have been preserved at the bottom of this part of the Baltic Sea only in the southern part of the Bornholm Basin, within the Darłowo Block. They are composed of carbonate-clay facies and calcareous sands with glauconite. Within the limits of the Paleozoic Platform, the Paleocene is locally found in the southern part of the Bornholm Basin, northern part of the Arkona Basin, in the SW part of Scania, as well as in the area of the Belt Sea (Danish Straits), including the southern part of the Kattegat.

Eocene marine sediments of the Baltic Sea bottom generally occur in the Precambrian East European Platform. They are widespread from Kołobrzeg on the western coast of Poland through the Słupsk Bank and Słupsk Furrow to the western slope of the Gdańsk Basin (at Kuźnica on the Hel Peninsula) in the east. In the north, they reach the Southern Middle Bank. The deposits are represented by sandy mudstones containing phosphorite concretions, with clay deposits at some places, quartz-glauconite with numerous pyrite agglomerates, sparsely with fine phosphorites and quartz gravels. The Eocene deposits also occur in the eastern slopes of the Gdańsk Basin and in Sambia (Kaliningrad region). They are deltaic sediments containing considerable amounts of amber. In the West European Paleozoic Platform, the Eocene sediments appear directly under the Quaternary in the Mecklenburg Bay and locally in the Danish Straits.

Oligocene sediments in the Precambrian East European Platform occur possibly locally in the coastal zone of the southern Baltic Sea. Near the Chłapowo cliff, there are muddy-sandy sediments with brown coal dust deposited in the brackish environment. West of the Teisseyre-Tornquist Fault Zone, the Oligocene clay and sand sediments occur locally on the coasts of the Mecklenburg Bay and Jutland Peninsula.

The Neogene is represented only by Miocene deposits in the Precambrian East European Platform. Sandy silts with interbeds of brown silts occur in the Puck Bay, and locally in the coastal zone from the Hel Peninsula to Koszalin.

4.2. An Outline of the History of the Baltic Sea

The Baltic Sea is a very young sea that has existed in its presents shape for only a few thousand years. The process began in the Neogene with the formation of a depression in the Earth's crust, which was then filled by water to form the present Baltic Sea. In the Miocene, the ocean level dropped to a level that enabled the area of the present Baltic Sea to become land. Its southern part was flooded by a shallow sea at the end of Paleogene. Climate cooling at the end of the Miocene and in the Pliocene created favourable conditions to develop the processes of rock weathering and strong erosion. Weathered loose debris was removed by rivers flowing down from elevated areas of Scandinavia through the region of the present Baltic Sea and the carving primary contours of the Baltic depression.

About 950 thousand years ago, the climate became cold enough that glaciers formed in Scandinavia. They subsequently gradually spread into the area of the present Baltic Sea and the lowlands of central and eastern Europe. During the last few hundred thousand years, the process of cyclic glaciations alternated with short breaks of climate warming when the continental glaciers melted. Each time when the continental glacier developed, much of the water volume was icebound, resulting in lowered water levels in the oceans. Under the pressure of the ice mass, the Earth's crust subsided. During the interglacial periods, the continental glaciers melted resulting in the rise of the ocean level and allowing the Earth's crust to uplift. Continental glaciers in Scandinavia developed several times, and each time they extended to the south and east through the area of the present Baltic Sea. The advance of the continental glacier resulted in the destruction of bedrock and in deepening of the Baltic Sea basin. During the periods of climate warming, when the continental glacier melted, the Baltic basin was filled with sea water. In many locations along the coasts of the Baltic Sea, the sediments of former seas have been preserved, including Holsteinian (410–390 thousand years ago) and Eemian (126–115 thousand years ago).

The last continental glacier covered the area of the Baltic Sea about 22 thousand years ago, destroying at the same time a large part of the deposits left by earlier glaciers and seas that existed during the interglacial periods. The beginning of the present-day Baltic Sea is associated with the recession of the last Scandinavian continental glacier. The retreat of this glacier from the European lowlands began about 20–19 thousand years ago. In the southern region of the present-day Baltic Sea, the glacier melted about 15–13 thousand years ago (Uścinowicz, 1999). Waters of the melting glacier gathered in front of it, creating increasingly large ice-dammed lakes as the glacier retreated. About 14.5–14.0 thousand years ago, local marginal lakes located at that time in the Bornholm and Gdańsk basins, merged. They formed a water basin known as the Baltic Ice Lake, which stretched from the coasts of Lithuania in the east to Denmark in the west. This lake was limited in the north by the edge of the continental glacier. The basin existed for about 2,500 years, increasing its area as the glacier melted (Fig. 4.2a). The oscillations of the glacier front in central Sweden, opening and closing the

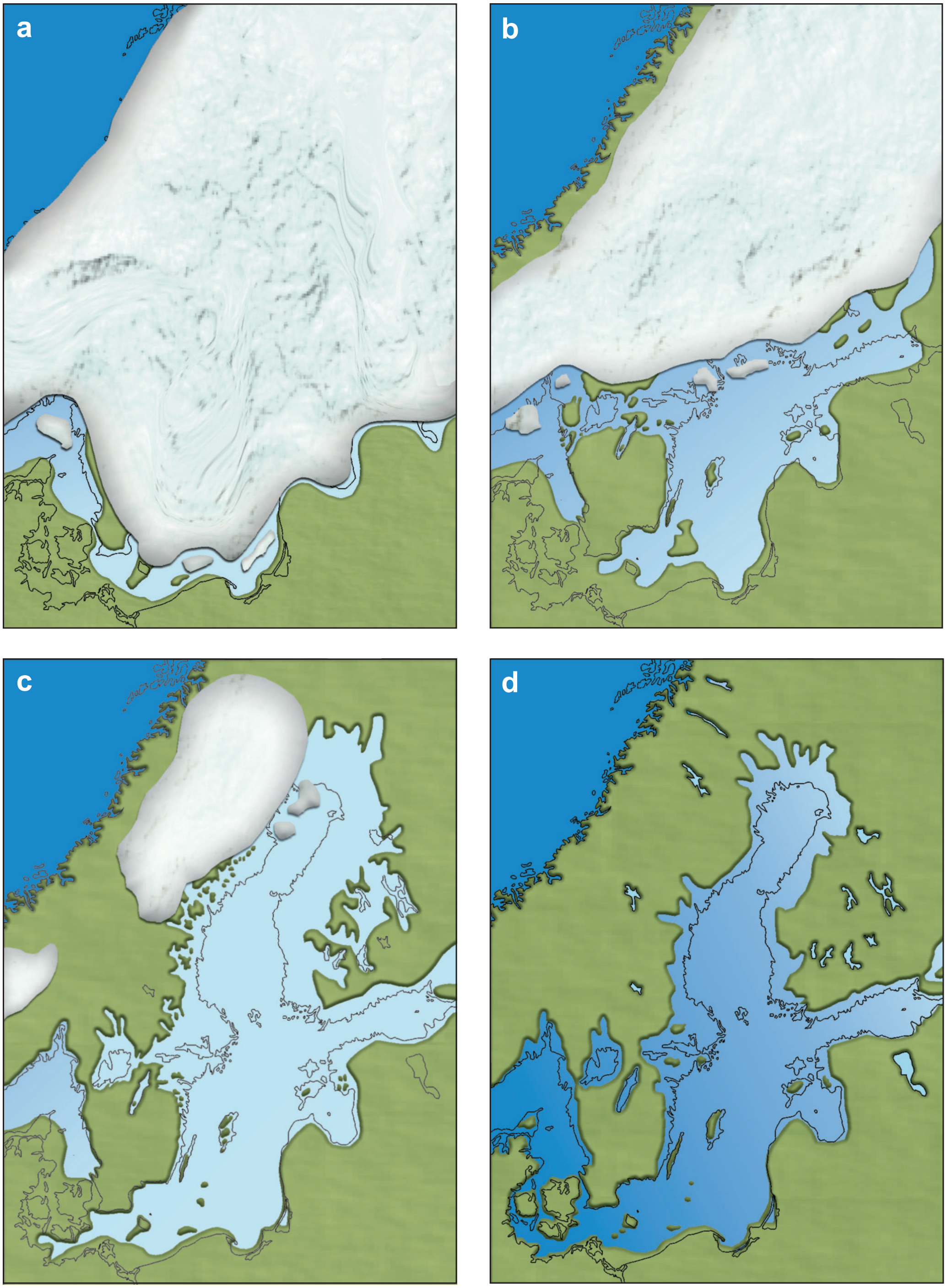

Fig. 4.2. Development of the Baltic Sea: a – Baltic Ice Lake (14,500–14,000 years ago), b – Yoldia Sea (11,500 years ago), c – Ancylus Lake (10,400 years ago), d – Littorina Sea (8,000 years ago)

connection with the ocean, resulted in rapid water-level changes in the Baltic Ice Lake.

The water level in the Baltic Ice Lake was 20 to 50 m lower than it is at present in the Baltic Sea. The ocean level at that time was app. 110 m lower than at present (e.g. Fairbanks, 1989; Blanchon, Shaw, 1995). The Earth's crust within the area of the southern Baltic Sea was 90 m lower than at present (Uścinowicz, 2003); however, when it was released from the ice, it uplifted in a short time.

Approximately 11.7 thousand years ago the glacier was in the process of melting, uncovering the lowlands of central Sweden. This enabled establishing the communication between the Baltic Ice Lake and the ocean. The water level in the ocean was at that time app. 25–27 m lower than the Baltic Ice Lake water level, resulting in the lake water to flow down into the ocean. The free water level of the Baltic Ice Lake dropped by app. 25 m over a period of some decades (Björck, 1995). The area of the basin shrank and its southern coasts shifted to the north. At the Pleistocene/Holocene boundary, successive ocean-level rise resulted in the flow of saline ocean water into the Baltic Sea. A brackish basin was formed, called the Yoldia Sea (Fig. 4.2b).

The uplift rate of Scandinavia, released from the glacier, was at that time higher than the rise of the ocean's water level, thus the Yoldia Sea was isolated from the ocean about 10.7 thousand years ago. The sea, deprived of an inflow of saline ocean water, was transformed within a short period into a freshwater basin known as the Ancylus Lake. The permanent inflow of river and melt waters from the ice-sheet, with limited outflow to the ocean, resulted, in a rising water level by 4–5 cm a year in the southern part of the basin. The lake at its maximum size reached beyond the present-day areas of the gulfs of Bothnia, Finland and Riga (Fig. 4.2c). However, the rapid glacio-isostatic rise of Scandinavia resulted in relative lowering of the water level of the Ancylus Lake in its northern areas.

In the south of the Baltic Sea, the transgression continued during this period. The southern edge of the lake moved into the land. About 9,500 years ago, the ocean level rose so that saline ocean water started to flow through the Danish Straits, and the Ancylus Lake was transformed into a brackish water sea called the Littorina Sea. This was a sea of higher salinity and warmer than the present Baltic Sea. In that period, the post-glacial rebound of the southern coasts ceased (Uścinowicz, 2003), so that the rising sea level was at a rate similar to that of the rising water level in the ocean. This induced a rapid transgression of the sea onto those areas that had been land until then (Fig. 4.2d).

From about 7,000 years ago, the rise in the ocean level started to decrease. In the northern parts of the Baltic Sea, the rate of glacio-isostatic land uplift was faster than the rise of the ocean level, the regression of the sea continued and the coastline moved towards the sea. In the southern part of the Baltic Sea, the transgression rate started to decrease; however, the sea still inundated the land.

Approximately 5,500 years ago, a small rise in the Earth's crust in the Danish Straits region made free water exchange with the North Sea more difficult, resulting in the Baltic Sea being transformed into a sea of lower salinity, known as the Post-Littorina Sea. The Baltic Sea coastline was still changing in a similar way as it had earlier: the sea was regressing from the northern areas and transgressing onto the land in the southern parts.

The last 200 years in the history of the Baltic Sea shows a clear impact of the continuously developing economic activity. The growth in industrial and agricultural production induced the inflow of different types of pollutions into the Baltic Sea, which resulted in changes in the chemical composition of the water and sea bottom sediments. The development of hydro-technical structures, such as harbour breakwaters and coastal protection facilities, altered the natural processes that affect the coast.

4.3. Quaternary Cover of the Baltic Sea Bottom

The Quaternary cover of the whole sea bottom area of the Baltic Sea is composed of Pleistocene glacial and glaciofluvial deposits and Holocene marine sediments. However, its distribution, deposition style and thickness differ between the southern and northern parts. In the southern part of the Baltic Sea, in those areas where the basement is composed of sedimentary rocks, the sea bottom relief is relatively gentle, and the Pleistocene and Holocene sedimentary cover is homogeneous over large areas. In those areas where the basement is composed of igneous and metamorphic rocks (northern part of the Baltic Sea), the sea bottom morphology is constrained by an uneven crystalline bedrock with narrow and relatively deep depressions featuring steep slopes, and the sedimentary cover is of mosaic character. Its character and thickness varies within small distances. The basement rocks outcrop at the surface on seabed elevations.

The thickness of the Quaternary sediments varies widely; it is lowest in the areas of the present deep-water basins, where Pleistocene glacial exaration processes occurred. Small thicknesses (<10 m) of the sedimentary cover is observed in those areas where erosional processes prevailed also during the Holocene. In the southern part of the Baltic Sea, such areas include the bottom and the southern slopes of the Słupsk Furrow and the southern peripheries of the Gotland Basin. Greater thicknesses of the Quaternary are represented mainly by Pleistocene formations, which occur only locally in deeply incised valleys of the Quaternary basement (subglacial channels) and in glaciofluvial landforms (eskers in the Bornholm Basin, Bothnian Sea and Bothnian Bay). The greatest thickness of the Pleistocene succession (up to 200–300 m) is observed in the subglacial channels along the southern shores of the Baltic Sea. In the northern part of the Baltic Proper, in the Landsort Deep, which is a typical fault trough deepened by glacial exaration and where app. 150 m of Quaternary sediments has accumulated (Winterhalter *et al*., 1981).

Pleistocene glacial sediments of large areas of the Baltic Sea bottom, both in deep-water basins and in shallow peripheries, are represented by a single till layer of the most recent glaciation. Locally, in the south and north, different glaciofluvial landforms and sediments, such as deltas and eskers, occur in the bottom of the Baltic Sea. In deep-water basins, they are hidden under a younger sedimentary cover whereas in shallow-water areas they are partly eroded and transformed by the marine environment. In the southern part of the Baltic Sea, the glacial and glaciofluvial deposits were destroyed during the early and middle Holocene transgression. In the north of the Baltic Sea, erosion of these sediments took place as the sea bottom rose, exposing them to the effect of wave activity.

Glacial and glaciofluvial sediments of the older glaciations have been preserved mainly in deep subglacial troughs or in depressions of the crystalline basement, like in the Landsort Deep. Much more complex is the Pleistocene structure on basin slopes, especially in the shallow-water, southern part of the Baltic Sea. Apart from a few till horizons, we can observe here glaciofluvial and glaciolacustrine sediments as well as interglacial deposits.

The postglacial (Late Pleistocene and Holocene) sediment cover and its stratigraphic units are the same for the whole area of the Baltic Sea: from the Arkona Basin in the southwest to the Bothnian Bay in the north. The lower parts of the stratigraphic sequence, i.e. Late Glacial and early Holocene sediments, are diachronous whereas the upper part, i.e. middle and late Holocene sediments, are synchronous.

The postglacial silt-clay sediments in the bottom of the sedimentary basins are represented by three main lithostratigraphic units (Fig. 4.3): Baltic brown clays of limnoglacial origin (Baltic Ice Lake), Baltic grey clays of limnoglacial origin (Yoldia Sea and Ancylus Sea), and Baltic olive-grey muds of marine origin (Littorina and post-Littorina). These units correspond with glacial clays and silts, transitional clays and postglacial muds, distinguished by Winterhalter *at al*. (1981) and Winterhalter (1992). The units were identified based on their physical properties by Harff *et al*. (2001), and correspond to A1, A2–A6, and B1–B6, respectively.

The Baltic brown clays consist of three lower order units: varve clay-silt sediments that pass into micro-laminated (crypto-laminated) clays and then into homogeneous clays, as going up through the bottom sediment section. The term of clay has been used here in a wider

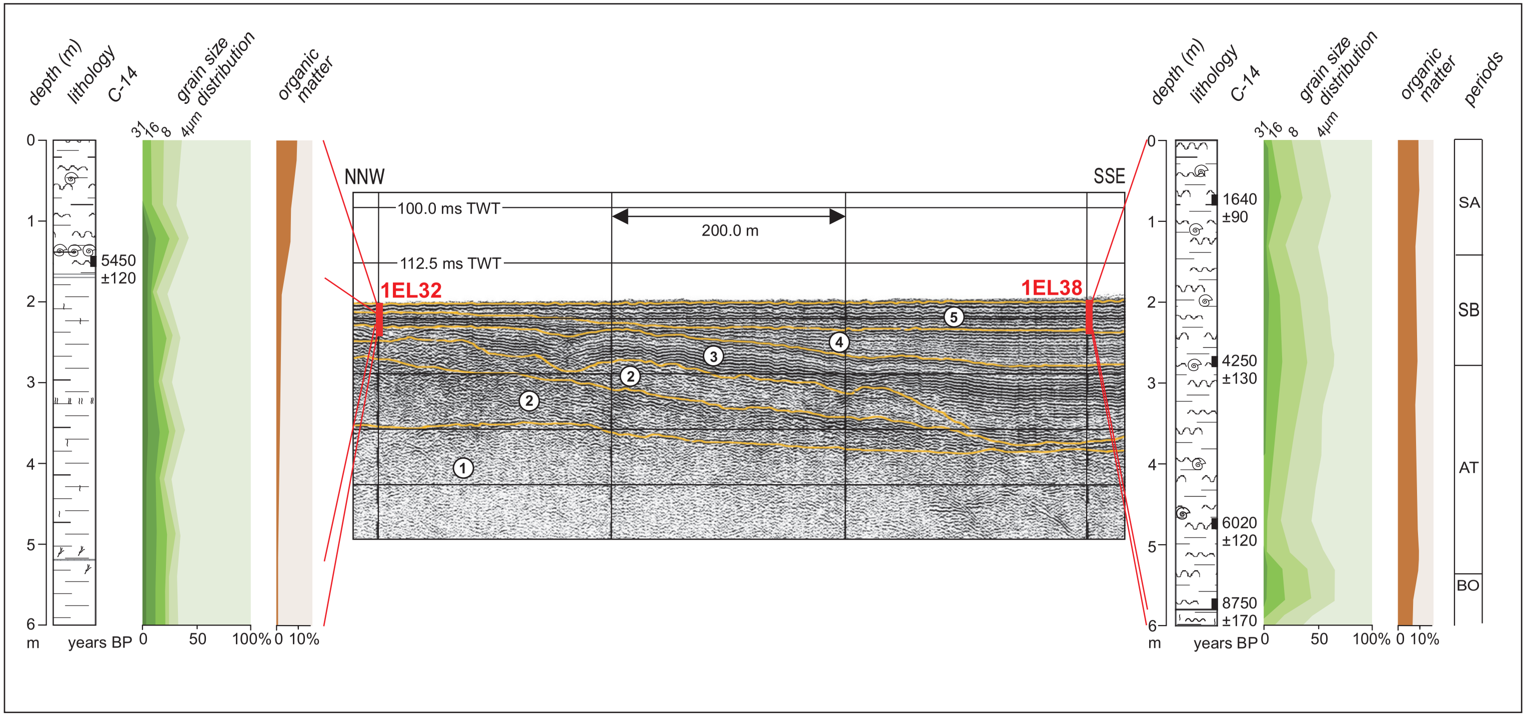

Fig. 4.3. Seismo-acoustic profile from the Gdańsk Basin with marked lithostratigraphic units and lithological logs of cores (after Zachowicz *et al.*, 2008)

1 – Cretaceous basement, 2 – tills, 3 – Baltic brown clays, 4 – Baltic grey clays, 5 – Baltic olive-grey muds; periods: SA – Sub-Atlantic, SB – Sub-Boreal, AT – Atlantic, BO – Boreal

meaning. Although clays are present here, i.e deposits of the dominant fraction <0.004 mm, there are also clays with admixture of the silt or even sand fractions. There are also silts with admixture of the clay and/or sand fractions. Both sand interbeddings and single gravel grains occur in these sediments, especially in the lower unit. The total thickness of varve, micro-laminated and homogeneous sediments, laying concordantly on a relief surface of tills, is the highest in the southern parts of the Baltic Sea and is about 10 m in the central areas of the deep-water basins. Small amounts of organic substances (commonly below 1.5%) and a considerable amount of carbonates (up to 20%) are characteristic for these sediments. In the roof sections of the deposits, the homogeneous clays can be noncalcareous. Occasionally in the brown calcerous clays of the Baltic Sea, black laminae or spot agglomerations of iron sulphides occur and their colour grades from brown into light brownish and brown-grey at the top. In the southern Baltic Sea, the deposition of the Baltic brown clays started in the Bølling. Their lithographic features indicate that the deposition took place near the melting continental glacier, initially very close to its front, where varve sediments would settled. As deglaciation progressed, farer of the glacier front micro-laminated and homogeneous clays were deposited. These sediments were formed at the stage of the Baltic Ice Lake (Zachowicz *et al*., 2008).

The Baltic grey clays conformably overlie the brown clays. For that reason, the basal surface of the layer is poorly marked. According to their names, these sediments have the character of dominating clay fractions. However, there are also sediments that contain both the clay and silt fractions, sometimes the sand fraction in different proportions. The distinguishing features are as follows: lack or very small content of calcium carbonate, small content (up to 2%) of organic matter and the existence of black micro-beddings and irregular agglomerations of iron sulphides. The colour of the sediments varies from grey-brown in the lower parts of the layer to grey and light grey, often with a bluish tint at the top. Apart from the change in colour, there is also a slight upward increase in organic matter contents. The timing of the deposition of the Baltic grey clays has been determined based on palinological analyses as early Holocene: pre-Boreal and early Boreal. Diatom spectra indicate that these sediments were deposited generally in a freshwater (limnoglacial) environment, and only in the early pre-Boreal period was there a short, slight increase in water salinity spatially limited to the north-western and central parts of the Baltic Proper (Gotland Basin). The lower member of the Baltic grey clays is generally diachronic in the whole Baltic Sea, similarly to the brown clays observed lower in the vertical section (Winterhalter *et al*., 1981; Winterhalter, 1992); however, they are definitely synchronic over a particular area of the southern Baltic Sea. Gray clays of a total thickness up to 5–8 m were deposited during the stages of the Yoldia Sea and Ancylus Lake.

The Baltic olive-grey muds unconformably overlie the Baltic grey clays. The term “mud” is used here in a wide meaning and includes several granulometric types that are identified based on the proportions of participating silt and clay fractions, e.g. silt, clayey silt, silty clay, and clay. The Baltic olive-grey muds consists of two lithological units of lower order: laminated grey muds with an olive shade as well as dark grey, locally black, silt and clay sediments, also with a characteristic olive tint*. The sediments of the latter unit are generally homogeneous with traces of bioturbation; however, they are occasionally laminated as well. Both the layers are enriched in organic matter, the content of which may be up to 10–15%, and they generally lack calcium carbonates. According to palynological and radiocarbon dating, the laminated grey muds with an olive tint (lower/bottom layer) originated in the late Boreal and early Atlantic periods. They were deposited in a brackish water environment, which is confirmed by the increase in the content of brackish (mesohalobic) diatoms. The beginning of sedimentation of the upper/top layer of olive-grey muds has been determined for the end of early Atlantic period. Euhalobic and mesohalobic diatoms dominate in this layer, thus indicating marine conditions during deposition. The thickness of the olive-grey muds is up to 4–5 m, locally exceeding 6 m. The boundary between the grey clays and the upper olive-grey muds is often erosional. On the peripheries of the sedimentary basins, seabed elevations inside these basins and thresholds separat-

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* In later chapters of this study concerning geochemical issues related to these deposits, the term “silty clay” will be used.

ing individual basins, the origin of marine stage, increase in salinity and formation of haline stratification were distinguished by erosion, locally emphasized by a thin sand layer.

The lithological components of the olive-grey muds originated in marine stages of the Baltic Sea development, i.e. in the Mastogloia Sea (a transition stage from the freshwater to marine basin), the Littorina Sea and Post-Littorina Sea.

Sand facies coeval with the Baltic brown clays and genetically related to them, occur probably only in the bottom of the southern part of the Baltic Sea. In the northern part, in those areas that underwent a glacio-isostatic uplift, they presently occur on land. The case for shallow-water sediments of the same age as the Baltic grey clays is similar. In sandy facies they occur in places such as the southern slopes of the Bornholm Basin. Starting from the Latvian coasts and heading towards the north, the shallow-water sediments are presently observed on land in Estonia, Finland and Sweden, and are predominantly represented by gravel and cobble facies.

Apart from sand facies associated with the Baltic brown and grey clays, relics of terrestrial (boggy, limnic and deltaic) deposits: peats, gyttjas, silts and sands, have been preserved on the sea bottom in the shallow-water zone of the southern part of the Baltic Proper and in the Belts Sea, i.e. in those areas included the middle Holocene transgression.

Sand and gravel facies coeval with the Baltic olive-grey muds, i.e. marine deposits, were deposited in the middle and late Holocene (Littorina and Post-Littorina seas) and occur on the slopes of depositional basins and in nearshore areas. Over much of the shallow-water zone, the thickness of marine sands and gravels is usually less than 2 m, however in most areas it is less than 1 m. Only locally does the thickness of marine sands exceed 3 m. Thicker layers are present on the eastern coasts of the Baltic Sea, and are related to the sandy barriers (spits) which developed during the Atlantic (Littorina) transgression.

4.4. Surface Sediments and Sedimentation Processes

The catchment area of the Baltic Sea is covered predominantly by Pleistocene glacial and glaciofluvial deposits. These sediments are transported by rivers or directly enter the sea by coastal and partially seabed erosion. In coastal zones, the sediment material is selected and transported as a result of the effect of wind waving and sea currents. Differentiation and distribution of the individual types of surface sediments at the sea bottom result of the activity of hydrodynamic processes, wind waving and sea bottom currents, which are present especially during storms. Hydrodynamic processes controlled the distribution of different types of sediments is related *i.a.* to the sea depth, development of the shoreline and sea-bottom relief. The shoreline development and seabed relief are of special significance for the western and northern parts of the Baltic Sea basin, where numerous islands limit free water circulation and reduce the wave base in such a way that fine-grained sediments accumulate even in shallow basins.

Erosion, redeposition and deposition processes that transform glacial and glaciofluvial deposits into marine sediments started at the beginning of the Atlantic period. In the southern parts of the Baltic Sea, the sea transgressed onto the land destroying Pleistocene deposits in the coastal zone. However, for 5 thousand years, since the rate of sea-level rise in the southern part of the Baltic Sea significantly decreased, the sedimentation conditions have remained relatively stable. In the northern part, owing to both the permanent uplift of the land and the sea regression, there is a process of erosion of the Pleistocene and Holocene sediments deposited during earlier stages of the development of the Baltic Sea and those that were previously located on the sea bottom beyond the reach of the erosional activities of sea waves.

Various hydrodynamic processes, the frequency of their occurrence, water mass movement intensity and direction, as well as the seabed relief gave rise to areas (zones) featuring dominant, specific litho-dynamic processes. Pratje (1948) and Kolp (1966) indicated the zonal occurrence of sediments on the bottom surface of the Baltic Proper in the southern part.

Above the pycnocline, there are sand-gravel and sand sediments. Hydrodynamic processes make the stable deposition of silt-clay sediments impossible. The contents of fractions finer than 0.063 mm are generally present in quantities lower than 1%, and often lower than 0.5%. The finer-grained deposits of silts and clays are usually present below the pycnocline.

Surface silt-clay sediments (i.e. the Baltic olive-grey muds), containing fractions finer than 0.063 mm, are present in amounts of more than 75%, occupying wide seabed areas in all the Baltic Sea sedimentary basins (Fig. 4.4). In the Baltic Proper, there are the following basins: Arkona, Bornholm, Gdańsk, Eastern and Western Gotland, and North Central. The deposits also cover large and deepest parts of the Bothnian Sea and Bothnian Bay, as well as the Gulf of Finland and Gulf of Riga. Smaller silt-clay areas are present in the south-western Baltic Sea, in the Mecklenburg and Kiel bays and in the Kattegat. A special area is that of the Archipelago Sea, where there are numerous small basins of different depths, in which the accumulation of silt-clay sediments often occur above the pycnocline. The present accumulation rate of the silt-clay sediments is diverse and varies from 0.5 to 2 mm/year (Winterhalter *et al.*, 1981; Pempkowiak, 1992; Walkusz *et al.*, 1992; Cato, Kjellin, 1994; Szczepańska, Uścinowicz, 1994; Hille *et al.*, 2006; Mattila *et al.*, 2006). It is higher in the central deep-water parts of the basins than in their peripheries, and there are regional differences. Depending on oxygen conditions, there are diverse inner sedimentary structures of the deposits. In the sediments covering the sea bottom in areas where near-bottom water masses contain oxygen, bioturbation structures are present as the result of activity of benthic organisms, mainly *Macoma baltica* and *Mesidotea entomon* (Appendix 3, Fig. 5). In deeper areas of the sea bottom located outside the range of the effect of pycnocline, laminated deposits are being deposited under anaerobic conditions, which

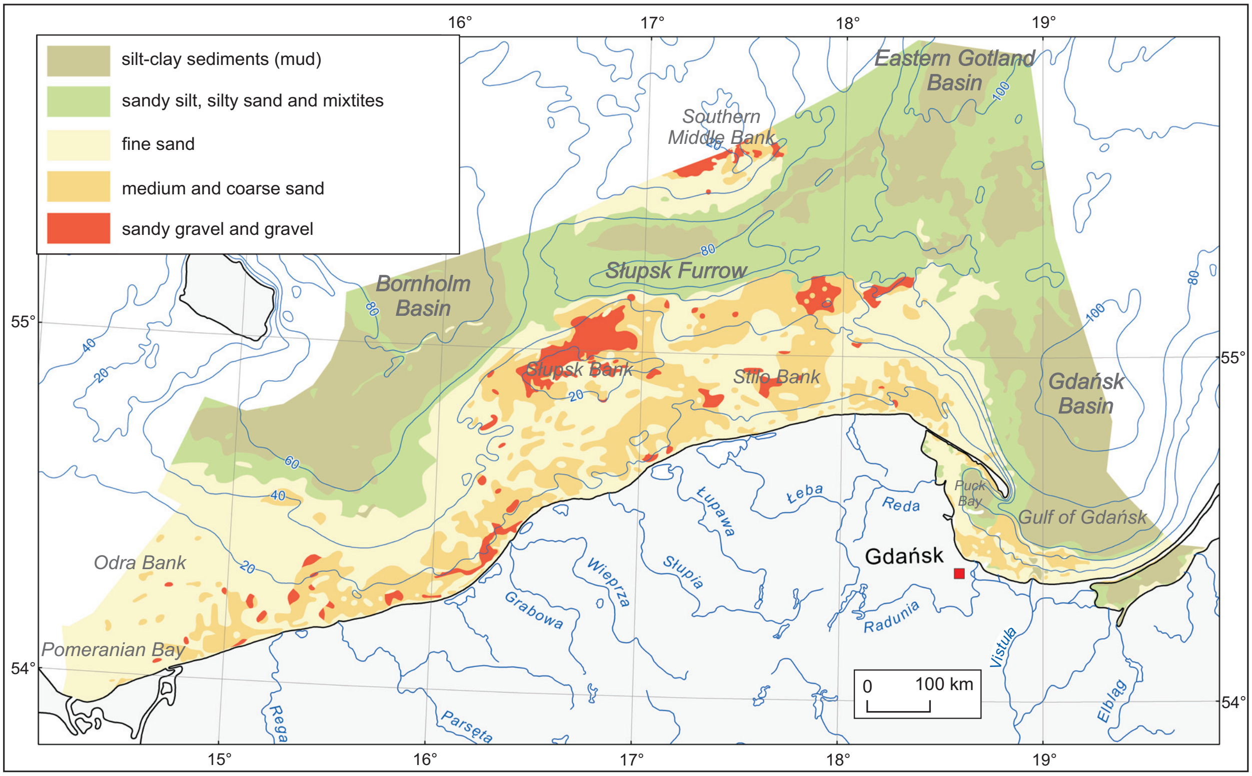

Fig. 4.4. Surface sediments in the Polish part of the Baltic Sea (based on Mojski ed., 1989–1995, simplified)

reflects the annual sedimentary rhythmicity (Appendix 3, Fig. 5). These sediments occur over the largest areas in the Western and Eastern Gotland basins, as well as in the Gulf of Finland, Gdańsk Basin and Bornholm Basin. The seabed area of laminated sediments expands every year. A particularly rapid expansion was noticed from the end of the 1940s, together with worsening aerobic conditions in the sea bottom waters (Jonsson, 1992; Kotilainen *et al*., 2007).

In the transition zone between the silt-clay (mud) sediments, sands and gravels, in the peripheries of the sedimentary basins, there are sand-silt deposits or mixtites, i.e. sediments composed of sand, gravel and silt grains, often associated with iron-manganese concretions. These formations prevail in the bottom areas of the Baltic Proper, where the pycnocline approaches the sea bottom. They are distinguished by diverse grain size, including the following fractions in variable proportions: gravel (64.0–2.0 mm), sand (2.0–0.062 mm), silt (0.062–0.004 mm) and clay (<0.004 mm). The sediments are poorly sorted. The thickness of the sand-silt sediments and mixtites is often less than 0.2 m, locally lower than 0.1 m. They are underlain by Pleistocene glacial deposits or clay sediments from early development stages of the Baltic Sea (Baltic brown clays and Baltic grey clays). Lithological features and the sonar image of the sea bottom from the area of sand-silt sediments and mixtites indicate the occurrence of bottom currents of considerable velocities. Significant are also the inner waves that are formed within the limits of the pycnocline. Sand-silt deposits and mixtites that overlie glacial clays occupy considerably larger areas of the sea bottom in the Archipelago Sea and in the Bothnian Sea as well as in the Bothnian Bay, where older deposits can be observed on the sea bottom.

Above the pycnocline, sandy and gravelly sediments prevail. Sand and sand-gravel sediments cover large areas of the sea bottom in the southern and south-eastern parts of the Baltic Proper – to the north of the coasts of Germany and Poland, and to the east of the coasts of Lithuania and Latvia. They also occupy considerable areas of the sea bottom in the coastal parts of the Belts Sea. In these sectors of the Baltic Sea, the sands and gravels of the sea bottom formed as the result of long-lasting and multiple redeposition of glacial and glaciofluvial sediments. The original features of these sediments vanished and transformed into features typical of epicontinental sea sediments. In the northern part of the Baltic Sea, i.e. in the Gulf of Finland, the Bothnian Sea and in the Bothnian Bay, sandy and sand-gravel deposits are less common. These are predominantly glaciofluvial sediments, e.g. sands and gravels of glaciofluvial deltas or eskers, currently washed out and transformed into marine sediments.

Deeper, below the storm wave base (>25–30 m), fine-grained sands dominate. They are characterised by good and very good sorting and almost symmetric and positive skewness of grain size distributions. A small thickness of the fine-grained sands, less than 2 m, indicates that they are transported probably only during extremely strong storms, and deposition of the sediments takes place periodically. According to Kolp (1966), small ripple marks, up to 1 cm high, may occur on the sea bottom in this zone. However, it seems that more typical and more common in the area of sedimentation of fine-grained sands are biogenic structures of benthic organisms, which can be seen on the sea bottom. Among the typical are crawling and browsing traces of *Mesidotea entomon* crustaceans, and dwelling structures of Oligochaetae and *Macoma baltica* clams.

In the southern and eastern part of the Baltic Proper, at the depths of app. 10 m to 25–30 m, medium- and coarse-grained sands, as well as gravelly sands and sandy gravels occur most often (Fig. 4.4). Those sediments are moderately sorted. Locally occurring boulders and pebbles form the residue of washed-out Pleistocene deposits. In the regions of boulders occurrence, gravel and gravelly-sand deposits are found together with very thin sand layers, often less than 20 cm in thickness, and of moderate to very poor sorting. Ripple marks are common on the sediment surface in this zone (10–30 m). Ripples with distances between crests (wave length) from 0.1 m to 0.4 m and a height from about 0.02 m to 0.05 m occur in fine- and medium-grained sands. In coarse-grained and gravelly sands, the ripple wave length ranges from 0.5 m to 1.5 m, the ripple height is from 0.08 m to 0.3 m, and the crest line extends over several tens of metres. On the sand surface, in the area of sea depths between 10 and around 30 metres, in addition to ripple marks there are also large-scale bedforms, such as megaripples and sand waves of a few hundred metres long crests. Their wave length is from a few to several tens of metres and the height is from 0.5 m to 2 m.

On the surfaces of gravel and gravelly-sand sediments, there are also large sand patches and bedforms similar to sand ribbons known from the North Sea and the Danish Straits, but less regular. The size of the sand patches is variable, from a few up to several hundred metres. Their shapes are often irregular, sometimes oval or elongated. These bedforms similar to sand ribbons are up to 500 m long and app. 40–50 m wide, and show variable spacing. The deposits in this zone are found within the effect of mean storm waves on the sea bottom. During strong storms, fine-grained sands migrate over the surfaces of gravelly-sand deposits as sandy waves or patches and ribbons of sands, and after multiple repositions, they leave the zone of storm wave activity.

In the coastal zone, down to a depth of app. 10 m, fine- and medium-grained sands dominate. Coarser-grained sediments occur locally on erosional sections of the coastal zone, especially at the foot of cliffs. Deposits in the coastal zone undergo frequent repositioning by waves of the surf zone. During strong storms, not only is the seashore damaged. The Pleistocene deposits, occurring at the base of marine sediments within the underwater shore slope, can also be washed out. Fine-grained sands of the coastal zone are characterized by negative skewness of grain size distribution, and good or very good sorting. Typical bedforms of the coastal zone are bars separated by trouhghs, canals and cones of rip currents.

In the northern part of the Baltic Sea, in the Bothnian Sea and Bothnian Bay, there are no wide sandy covers typical of the southern and eastern parts of the Baltic Proper. In the coastal areas, there are small sand covers, but thin and pathy-shape gravelly-cobble lag deposits or outcrops of glacial sediments are dominant.

The mineral composition of the recent surface sediments in the Baltic Sea is strictly associated with the material of the Pleistocene glacial and glaciofluvial sediments. The Pleistocene deposits reveal regional differences in mineral composition due to the lithology of the older basement.

The petrographic and mineral composition of the Baltic Sea sediments varies depending on the grain size. Amongst boulders, pebbles and gravels, fragments of crystalline and sedimentary rocks dominate; and as the fragments decrease in size, there are less sedimentary rocks (first carbonates, then sandstones) and the proportion of crystalline rocks increases. Among crystalline rocks, the most common are granites, diorites and gneisses. The proportion of resistant components in the source sediments, such as crystalline rocks, increases clearly in marine sediments. As the grain size reduces, there is an increase in quartz grains dominating in the sand fractions. Feldspars, fragments of crystalline and sedimentary rocks as well as heavy minerals occur as admixtures. In fine-grained sands, the content of quartz exceeds 90%. The processes of grain selection during transport cause that area heavy minerals (mainly garnets, amphiboles, epidotes, tourmalines, zircon and others) in fine-grained sands of the shallow water constitute locally additives of up to several percent.

The mineral composition of fine-grained (silt-clay) sediments also reflects the geology of the areas from where these components are transported into the sea. The material carried down by the rivers into the sea and that originating from erosion of Pleistocene deposits on the coasts and seabed is primary of terrigenous origin and includes quartz, feldspars, illite, chlorite, and, in smaller amounts, kaolinite and carbonates. Terrigenous and biogenic-originated calcium carbonate is rapidly mechanically destroyed and dissolved. Considerable carbonate additives occur only in outcrops of Silurian and Ordovician carbonate rocks in the northern part of the Baltic Proper. Silica of biogenic origin (diatom opal) is also found in fine-grained sediments, but it is not a considerable addition. In the Baltic Sea, other authigenic minerals, included into the sediment composition, also occur. Their formation and preservation depend on the physico-chemical conditions in the bottom and interstitial waters. Minerals such as pyrite (including hydrotroillite), kutnohorite and vivianite form under anaerobic conditions, while goethite originates under aerobic conditions.

Silt-clay sediments are mainly composed of minerals of terrigenous origin: quartz, feldspars, illite and chlorites. These minerals occur in variable proportions in all the Baltic Sea basins (e.g. Blazhchishin, 1982; Gingele, Leipe, 1997; Uścinowicz *et al*., 2003).

The content of quartz in the surface silt-clay sediments of the Baltic Sea is commonly less than 40% and depends on the contents of the silt and clay fractions.

The smallest amount of quartz is found in the clays from the deepest parts of the sedimentary basins, far away from source areas (e.g. silty clays of the Eastern Gotland Basin).

Feldspars, represented mainly by plagioclases and potassium feldspars, account for 5% in the Landsort Deep to 25% in the Kattegat in the surface silt-clay sediments of the Baltic Sea. However, the content of feldspars does not exceed 15%. A weak correlation occurs between the contents of quartz and feldspars, i.e. the fewer feldspars the higher the quartz content (Fig. 4.5).

Illite dominates among clay minerals. It occurs only occasionally and locally in lower amounts than other clay minerals.

Chlorite is usually found in smaller amounts than illite. However, locally in the gulfs of Riga and Finland, the content of chlorite is higher than of illite, whereas in the Eastern Gotland Basin, it takes the second place to kaolinite.

Kaolinite occurs regionally. This mineral has been identified in sediments of the southern part of the Gulf of Finland, Gulf of Riga, Western and Eastern Gotland Basins, as well as in the north-eastern part of the Gdańsk Basin (Uścinowicz *et al*., 2003). The occurrence of kaolinite in these regions is probably associated with Palaeozoic rocks located in Estonia, Latvia and northern Lithuania, containing this mineral. The Kiel Bay and the Kattegat in the western Baltic Sea is the second area where kaolinite occurs in the silty surface sediments.

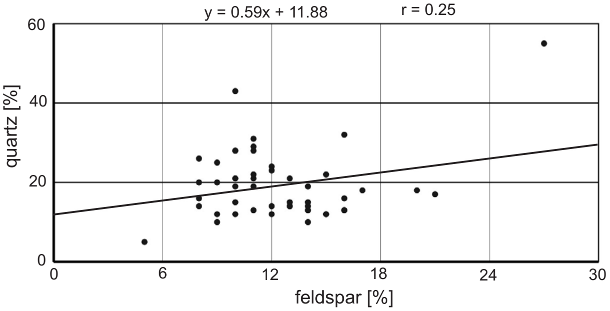

Fig. 4.5. Relationship between the contents of quartz and feldspar in the surface layer silt-clay sediments of the Baltic Sea (Baltic olive-grey muds)

Illite-montmorillonite was determined only in the northern (Bothnian Bay, Bothnian Sea and Archipelago Sea) and southern part of the Baltic Sea (SW part of the Gdańsk Basin, Bornholm and Arkona basins).

Other terrigenous minerals, such as calcite, manganese calcite, dolomite, kaolinite, montmorillonite, vermiculite, beidellite, mixed-layered minerals (illite-montmorillonite, illite-chlorite) occur locally and often only in trace amounts (Stoch *et al*., 1980; Blazhchishin, 1982; Śliwiński, Uścinowicz, 1983). There are only small differences observed in the contents of terrigenous minerals that form fine-grained sediments. Carbonates (calcite and dolomite) have been found in all the Baltic Sea regions. However, they occur mostly in very small amounts, not exceeding 1%. More significant are carbonates only in the regions where carbonate formations occur in the bedrock.

Silt-clay sediments covering the bottom of the sedimentary basins contain the following authigenic minerals: kutnohorite, rodochrosite, witherite, vivianite, pyrite, marcasite, goethite, barite, and locally gypsum. These minerals are found in smaller amounts than the terrigenous ones; however, the variability of their occurrence on a regional scale and in the vertical section is considerably higher than of terrigenous minerals. It results from the variable hydrochemical conditions, both at present and in the past, in different areas of the Baltic Sea, as well as from the complex early diagenetic processes (Alvi, Winterhalter, 2001). The variability of hydrochemical conditions, particularly redox conditions and oxygen concentrations in bottom waters, is a good illustration of the diversity of iron forms inside and between the basins.

Considering the mineral composition of fine-grained sediments, the Bothnian Bay is specific amongst the regions of the Baltic Sea, where amphiboles and witherites occur in addition to typical terrigenous and authigenic minerals found in silt-clay deposits (Uścinowicz *et al*., 2003).

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Chapter 5

INFLOW OF CHEMICAL SUBSTANCES INTO THE BALTIC SEA

5.1. Deposition of Chemical Substances from the Atmosphere

The interaction between the land, sea and atmosphere is a complex process of exchanging substances. On the one hand, the exchange determines air quality, while on the other hand, it affects the chemical contents of the surface water layer, where chemical and biochemical processes are the next stage of matter transformation deciding about the trend of its flow in the sea.

There are many ways for substances to be transported into the sea. One of them is transport *via* the atmosphere, which transfers the substances in gaseous, liquid and solid phases from the source areas to the sea areas.

In the air layers adjacent to surfaces of seas and oceans, the greatest mass is made by nuclei of sea salts. When sea surf and water droplets are swept away by the wind, or gaseous bubbles burst, water drops and inorganic compounds (chlorides, sulphates, carbonates), organic substances (such as: sterols, fatty acids, glycerides, phosphatides, hydrocarbons), as well as plankton organisms (bacteria, viruses and algae) are thrown out of the sea surface into the air. In the marine atmosphere, the concentration of particles varies on average from 100 to 300 per 1 cm^3 (Garbalewski, 1999) however, apart from the nuclei of salts there are other components of non-marine origin. These include mineral particles derived from erosion of rocks and volcanic eruptions, as well as particles emitted to the atmosphere as a result of burning fuels and biomass. Terrigenous aerosols formed over the land areas make the largest contribution in the total mass of aerosols. Their global mass is estimated at $16.4 \cdot 10^{12}$ g (Erickson *et al.*, 1997). In the North Hemisphere, the most important sources of such aerosols include the Sahara and Sahel region in North Africa, as well as the Gobi and Taklamakan deserts in Asia. Terrigenous aerosols of small (0.01 and 0.05 μm in diameter) and large (more than 10 μm in diameter) sizes can be transported very high in the troposphere, above the continents, eventually falling onto the land or water. Atmospheric transport of terrigenous aerosols embraces huge spaces of the terrestrial globe. Clouds of solid particles from Asian deserts reach the west coasts of the United States of America, while those from the Sahara reach the Gulf of Mexico or even central and northern Europe (Falkowska, Lewandowska, 2009). Anthropogenic particles, often called urban aerosols, constitute the finest submicron fraction which forms aggregates with the natural components of air as a result of adhesion, condensation, coalescence or sorption over the land and on coastal zones.

Aerosols and gases found in the atmosphere, are deposited due to direct sedimentation or are transported to the basement by diffusion (Fig. 5.1). Dry atmospheric deposition is defined as removing solid, liquid and gaseous substances absorbed into the sedimenting particles of aerosols and adsorbed on their surfaces. Dry deposition also includes gases that are directly adsorbed on the sea water surface. During deposition of gaseous molecules, solubility and chemical reactions with water as well as turbulent mixing of the surface sea layer play a significant role. Therefore, the vertical transport of chemical

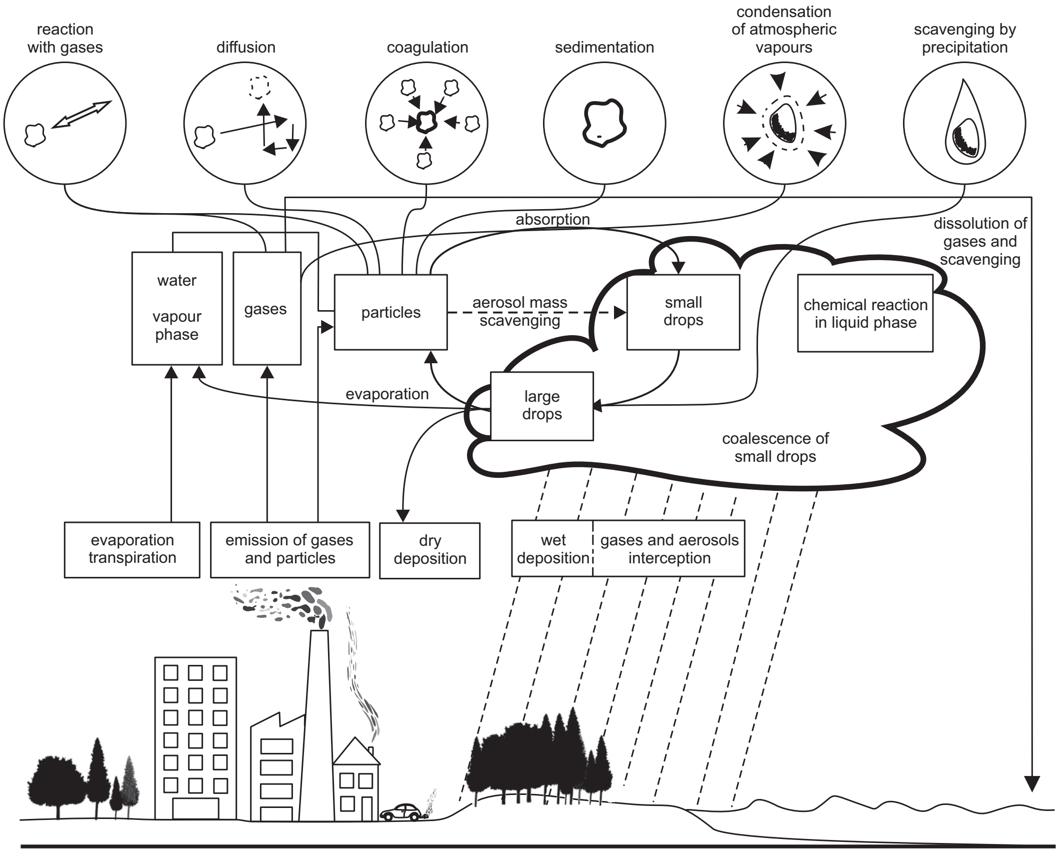

Fig. 5.1. Wet and dry deposition processes responsible for atmosphere cleansing of gaseous and particulate chemical compounds (Falkowska, Korzeniewski, 1998, modified by authors)

substances in dry deposition may undergo one or more of the following processes: gravitational sedimentation (effective only for relatively coarse aerosol particles), turbulent diffusion, molecular diffusion, inert settling, and Brownian motion.

The load of atmospheric aerosol deposition is determined by the particle size, mass and meteorological condition. The increase in wind velocity enhances both the flux of coarse aerosol particles and their proportion in the dry deposition, despite the lower quantitative fraction. The settling velocity of the particles below 1 μm in diameter is lower than that of coarse aerosols and is a result of the gravitational deposition and Brownian motion. The finest particles of diameters about 0.05 μm are generally influenced by Brownian motion, and form the most effective mechanism of their transport. Brownian motion together with thermophoresis often results in the capture of submicron particles by falling aerosols. The atmospheric lifetime of such particles may even be several days, before they are removed from the air by dry fallout, fog or rain. Consequently, the increase in their size and mass may enhance the inflow rate (Garbalewski, 1977).

Wet fallout is a natural process, during which chemical substances in the form of gaseous components of air and aerosols are removed from the atmosphere by hydrometeors such as fog or cloud droplets, rain and snow. Washing-out is an effective process of cleaning the atmosphere. It has been estimated that in temperate latitudes, rains remove 70–80% of the aerosol masses from the atmosphere. Wet fallout consists of two stages. It begins with water condensation on solid particles, goes through coalescence and formation of large drops in clouds, and ends as fallout in a liquid or solid phase. A centre where chemical transformations take place is formed in clouds. These transformations would not be possible in a gaseous phase or they would proceed very slowly (Fig. 5.2). This can be exemplified by the results of studies indicating that, on a global scale, more than 70% of sulphur dioxide occurs inside cloud droplets as SO_4^{2-} (Langner, Rodhe, 1991). The chemical constituents of water phase in clouds originate from soluble compounds in aerosol particles, which formed condensation nuclei for cloud droplets. In this way, they are removed from the atmosphere inside the rain drops, where many other trace gaseous substances may also be dissolved. Chemical substances contained in cloud droplets may form various products in the aqueous phase due to various chemical reactions. The clouds trap even isolated fine particles in their vicinity.

The deposition of various substances from the atmosphere is extremely abundant and is the result of interactions that occur while the particles form; however it is also a function of time and location. Marine aerosols, reflecting in their chemical composition both inorganic and organic substances dissolved and suspended in the sea water, return directly to the surface of the sea. Terrigenous and anthropogenous particles coming from close and distant source areas are also introduced. The struggles of air masses over the shoreline, dominated by the marine and terrestrial aerosols mostly enriched with contaminants, produce an abundant mixture of variable ions washed out from the atmosphere by wet fallout. The studies undertaken in 2005–2006 in the coastal zone of the Gulf of Gdańsk may be a good example. The greatest participation in rains is from sea-

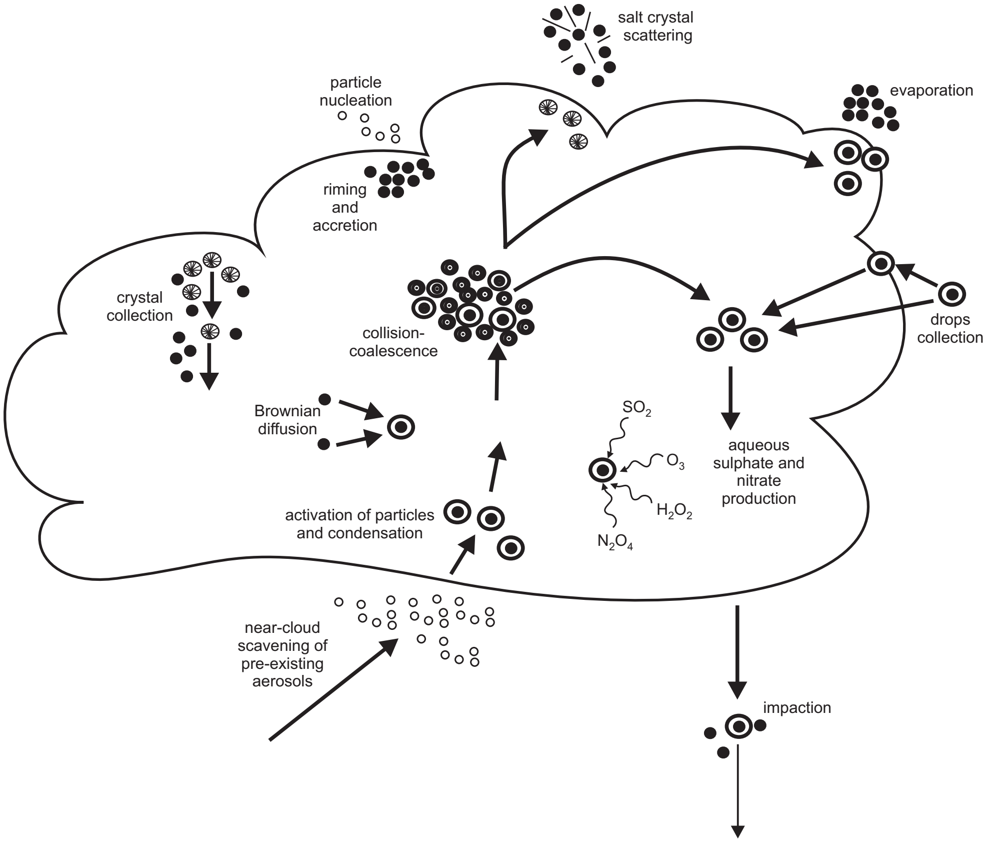

Fig. 5.2. Processes occurring inside the clouds and in their immediate vicinity, which can affect chemical and physical properties of gases and aerosols (Falkowska, Lewandowska, 2009, modified by authors)

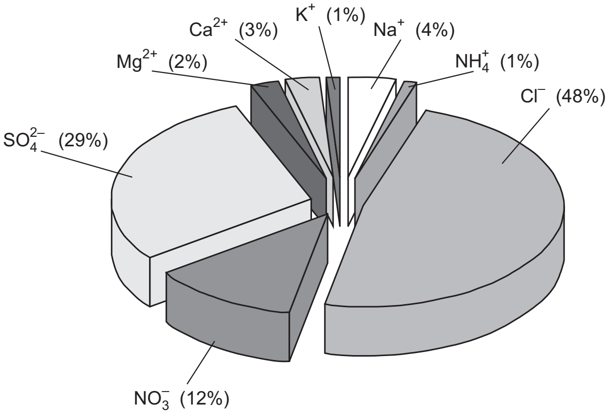

Fig. 5.3. Contribution of particulate ions to the total mass of inorganic salts in the precipitation in the industrialized coastal zone of the Gulf of Gdańsk in the years 2005–2006 (Falkowska, Lewandowska, 2009)

origin chloride ions, sulphate ions originated from the sea and from pollutants derived from the land, as well as nitrates mainly of anthropogenous origin. The other cations can originate from sea water or the land (Fig. 5.3). Ions are eliminated from the atmosphere as mist, rain or snow droplets.

Chemical elements and compounds introduced into the sea from the atmosphere play a significant role, depending on their properties and involvement in biological processes. If they belong to the group of nutrient compounds (gases: SO_2, NH_3, N_2, NO, NO_2, CO_2, VOC*; aerosols: salts of nitrogen and phosphorus – NO_3^-, NH_4^+, PO_4^{3-}; trace elements: Fe, Ca, Mn, Ni, Cu, Zn, Br, Co, F), they have an effect on sea fertility and may increase sea productivity and be conducive to frequent algal blooms. A consequence of biomass growth is always an increase in the flux of settling detritus and worsening aerobic conditions in the benthic waters and sediments. The lack of oxygen results in slowing down the kinetics of the transformations of organic matter and in upsetting the biogeochemical cycles of carbon, nitrogen, phosphorus, iron or other trace metals.

Trace elements and gases unnecessary or probably unnecessary for life in the sea (Be, Cr, Ge, Se, Ag, Cd, Hg, Po, Pb, Sn, Al and others) are also introduced into the marine water from the atmosphere. Their presence in the sea water worsens the living conditions of marine organisms or even makes them toxic, which results in dying algal cells and increases mortality rates of organisms on higher trophic levels. The above is a consequence of bioaccumulation and biomagnification, i.e. the processes in which toxic metals, particularly their organic forms or stable organic contaminants, including dioxins and DDT**, are embodied into an organic tissue and transit into the trophic chain up to the last link, i.e. marine birds and mammals.

5.1.1. Nitrogen Compounds

Nitrogen compounds belong to the group of biogenic substances (nutrients). They occur in the form of salts necessary for algal organisms. Their shortage limits primary production in the sea, whereas their excess stimulates productivity and leads to the eutrophication of the water region.

The atmosphere directly over the sea surface is a natural and the most abundant sink, rich in molecular nitrogen, where N_2 solubility and the balance in gas exchange depend on temperature and salinity. The sea air also contains other inorganic nitrogen compounds (N_2O, NO, NO_2, HNO_2, HNO_3, NO_3^-, NH_3, NH_4^+) and many organic compounds in gaseous or aerosol forms. Nitrogen compounds may occur in a few phases, for example, nitrates in the air may form vapours of nitric acid, ions dissolved in rain or cloud droplets, or they may be nitrate salts in aerosols. Photochemical processes lead to chemical reactions with a participation of nitrogen compounds, forming activated, ionized molecules of high reactivity. Apart from nitrogen inorganic and organic compounds naturally formed in the atmosphere, there are also ones of anthropogenic origin. As regards nitrogen oxides and ammonia, the compounds from industrial, agricultural and farming activities dominate in the atmosphere. In global emission, the proportion of natural emission sources is smaller. The atmospheric transport of gaseous molecules is able to transport them over very large distances before they are embedded into rain drops or undergo conversion into suspended parti-

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* VOC – abbr. Volatile Organic Compounds

** DDT – Dichlorodiphenyltrichloroethane cles, forming clouds as condensation nuclei. Aerosols in the atmosphere have short live-times and are removed within a few days. The atmospheric precipitation rate increases with the growth in the particle size and mass. Fine aerosols, less than 1 μm in grain diameter, appear as a result of chemical and photochemical reactions when nitrogen oxides are transformed into nitric salts, and ammonia into ammonium nitrate, ammonium chloride, ammonium sulphate, or ammonium bisulphate. Particles of diameter larger than 1 μm are formed in the marine atmosphere when the air masses from the land mix with the air saturated with marine aerosols. At that time, reaction between vapours of nitric acid and marine salt takes place:

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl$$

Vapours of nitric acid may be rapidly removed through the reaction with marine aerosols into the surface waters as dry fallout of particles or they fall as rain droplets. Ammonia also undergoes rapid atmospheric deposition. The resident time of ammonia aerosols amounts to a few days and after that time they are deposited or, under favourite meteorological conditions, they are transported over considerable distances. A main mechanism of removing ammonium from the air to the sea water is a reaction with sulphuric and nitric acids:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$$

Studies conducted in the atmosphere above the urbanised and industrialised coastal zones of the Gulf of Gdańsk demonstrated the dominant role of sulphate ions reacting with ammonia molecules. Ammonium nitrate and ammonium chloride were of secondary significance in the form of wet fallout (Fig. 5.4). Thus, the man activity, both industrial and agricultural, is a main source of ions of inorganic salts introduced with precipitation into the surface waters of the South Baltic coastal zone.

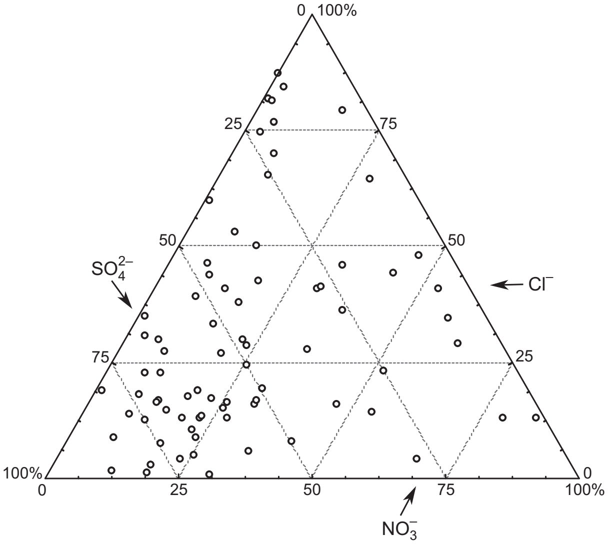

Fig. 5.4. Sulfates, nitrates and chlorides in the precipitation collected in the coastal zone of the Gulf of Gdańsk in the years 2005–2006 (Falkowska, Lewandowska, 2009)

The estimated inflow of nitrogen compounds from the atmosphere into the Baltic Sea has been decreasing since the 1980s, because their emission into the atmosphere is still being reduced. The HELCOM studies (2005) confirm this trend. Comparing the first years of the 21st century to the 1980s, a drop in emission by 40% is observed. It contributed to a proportional decrease in the total nitrogen flux into the sea (Fig. 5.5).

The study of the Polish coastal zone in 2005–2007 showed that a mean annual inflow of total nitrogen in a form of precipitation was $3.42 \cdot 10^4$ μmol/m^2, and then,

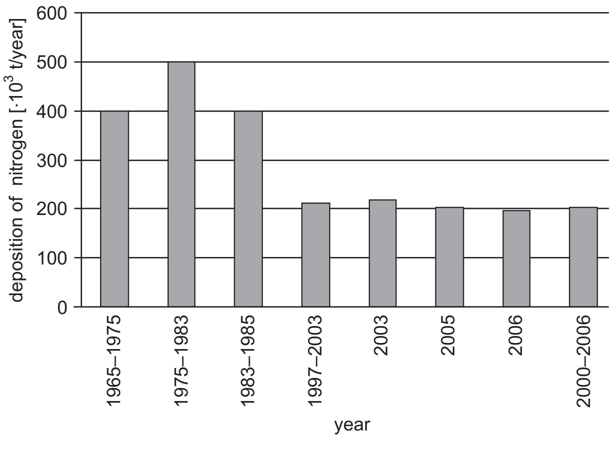

Fig. 5.5. Estimated net input of nitrogen to the Baltic from the atmosphere in the years 1965–2006 (Rodhe *et al.*, 1980; Ferm, 1984; Baltic Marine, 1987; Eliassen *et al.*, 1988; Schneider, 1988; HELCOM, 1989; Bartnicki *et al.*, 2008)

over the next three years, the annual inflow grew from $2.88 \cdot 10^4$ to $4.31 \cdot 10^4$ μmol/m^2. These significant fluctuations in the amount of nitrogen compound inflow in the individual years might have been a result of different meteorological conditions (wind velocities and direction during precipitation) (Sikorowicz, 2008). In 2005, the precipitation was mainly associated with winds from the directions: NW–W–SW and with some participation of east winds, whereas in the next year, a considerable proportion of the winds from the south was observed, in addition to the winds blowing from the west. In 2007, winds from the southern sector (SW–S–SE) were dominant during the precipitation. The variable pattern of winds and their low mean velocities (2–3 m/s) indicated local sources of nitrogen compounds removed from the atmosphere into the coastal zone.

In the total atmospheric nitrogen inflow to the Baltic Sea, two forms of nitrogen dominate: oxidised and reduced, with a higher proportion of the oxidised variety (Fig. 5.6). An opposite tendency was observed in the coastal zone of the South Baltic. The three-year study period on the chemical contents of air precipitation and meteorological conditions showed that the amount of nitrate in the analysed precipitation was decreasing, whereas the amount of ammonia and organic nitrogen was growing. The increase in the proportion of these forms was strongly associated with human agricultural activity. Therefore, the air that flows into the South Baltic from the land increases the deposition of ammonia with reference to nitrates. The prevalence of the reduced forms of nitrogen over the oxidised ones also occurs in the Danish Straits (Bartnicki *et al*., 2008). The results from the EMEP background station in Poland show the same tendency in relation to air precipitation. The deposition of NH_4^+ is higher by 21% than that of nitrogen oxidised forms (Kryza *et al*., 2009).

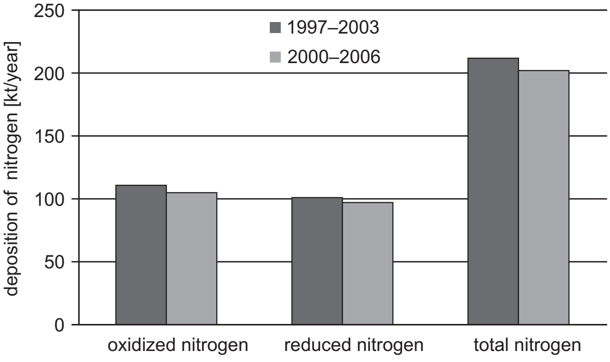

Fig. 5.6. Oxidised, reduced and total nitrogen deposition variability (Bartnicki *et al*., 2008)

5.1.2. Phosphorus Compounds

The issue of phosphorus in aerosols and its deposition is a poorly recognised problem, mainly owing to the small fraction of this element as an atmospheric component in the biogeochemical cycle. Phosphorus compounds in the atmosphere, which often occur together with aluminosilicates, take the form of terrigenous particles coming from the weathering of rocks and soils. It is assumed that 0.05% of the total phosphorus mass is in the top 50-cm layer of soil (Stevenson, Cole, 1999). Phosphorus is present in many minerals, reacts both with metals and non-metals, such as: iron, calcium, sodium, potassium, manganese, copper, lead, or chlorine. Weathered crustal particles are transported by aeolian processes over different distances, depending on meteorological conditions. However, erosion is not a very effective source of this element in the atmosphere. Strong winds from the Sahara are able to transport a large mass of particles, but with a low fraction of phosphorus compounds. Its deposition rate does not exceed 0.1 kg/ha (Stoorvogel *et al*., 1997). The lack of gaseous forms does not limit the transformation of phosphorus compounds in the atmosphere.

Smil (2000) estimated that the annual mean deposition into the oceans amounted to $3.0–3.5 \cdot 10^6$ tons of phosphorus, 90% of which were the particles of erosion origin. The results of a study conducted over ten years show that 90% of phosphorus is transported by rivers to the oceans, while 10% is delivered by the atmosphere. However, unlike the river route, this source is able to affect large sea spaces (Markaki *et al*., 2003). Phosphorus contained in crustal particles is characterised by insignificant solubility. Graham and Duce (1979, 1982) proved that the solubility of phosphorus from air aerosols collected over the North Atlantic was app. 36%. Similar results were achieved on the coasts of Israel (Herut *et al*., 1999). Despite the sparingly soluble compounds, phosphorus introduced with dusts to the eastern part of the Mediterranean Sea shows new primary production of up to 38% (Markaki *et al*., 2003).

Atmospheric deposition of phosphorus into the Baltic Sea seems to be insignificant, owing to the lack of the effective natural sources of its emission; nevertheless, it may be extremely important for the growth of blue-green algae in the marine areas limited with phosphorus. Trzosińska (1990) claims that 1–5% of total phosphorus load introduced into the Baltic Sea, comes from the air, but it does not exceed 0.8% to the Gulf of Gdańsk. The assessment of the amounts of phosphorus inflow in the 1970s indicates app. 1.4 kilotons of the annual flux of total phosphorus into the Baltic Sea (Rodhe *et al*., 1980), and 6 kilotons in 1983–1985 (HELCOM, 1989). The yearly flux of phosphorus in the form of wet fallout over the coastal zone of the southern Baltic Sea in 2005–2007 ranged from 58.8 to 91.7 μmol/m^2. The bio-accessible form of phosphate ions in the total phosphorus inflow was from 21 to 97% (Sikorowicz, 2008).

5.1.3. Biogenic Metals: Iron

Iron is an indispensable element for the biochemical and physiological functioning of plankton organisms in the sea. Phytoplankton uses iron to maintain numerous processes, such as: photosynthesis, chlorophyll production, nitrates reduction, binding of air molecular nitrogen, and other oxidizing reactions. Owing to its low concentrations (0.05–2.00 nmol/dm^3), iron is an element that limits the primary production and regulates the structure of the marine ecosystem (Martin *et al*., 1989). So, apart from river inflow, the atmosphere is becoming an important means of transport for nutrient compounds and micro-compounds, including iron compounds introduced into the surface waters in trace amounts. The results of many studies indicate that the air deposition can stimulate primary production and consequently control the transition of sedimenting matter from the top euphotic layer into the marine abysses and down to the bottom deposits (Duce, Tindale, 1991; Jickells *et al*., 2005).

In a boundary marine layer adjacent to the sea surface water, iron occurs in aerosols that are a mixture of land particles originating from weathered rocks and soils and photochemical processes, as well as from marine salt and acidic sulphate aerosols. Therefore, they contain sparingly soluble oxides and hydroxides, minerals, salts and dissolved forms. Mineral iron occurring in aerosols is not dissolved and bio-accessible for autotrophic organisms, but transported over long distances from several kilometres to several hundred thousands, the aerosols undergo numerous processes. The acidic nature of the aerosols and photochemical redox processes transform iron into chemically soluble forms of Fe(II) and Fe(III). Wet fallout is considered the main source of iron for marine waters and is estimated at app. 80% of the whole atmospheric deposition (Duce, Tindale, 1991). Martin *et al.* (1989) estimated that atmospheric deposition ranges from 84 to 93% of the total external inflow of iron into the surface sea water. The richest in iron are aerosol particles and those originated from man-made processes. Iron concentrations in aerosols coming from arable lands vary from 0.05 to 15 μg/m^3, and from the industrial lands: from 0.02 to 30 μg/m^3 (Zhuang *et al*., 1995). In the marine areas of the North Pacific, total iron concentrations range from 0.01 to 0.15 μg/m^3, where the bio-accessible form of Fe(II) accounts for 11 to 100%.

Since the amount of iron inflow from the atmosphere into the sea depends on the geographical situation of the water basin, meteorological conditions and time, it must be of irregular character. Therefore, some marine organisms have developed the ability to store the iron, with the diatoms of *Thalassiosira pseudonana* and *T. weissflogii* being outstanding. They can collect a surplus of 20–40 times the cell iron above that required for their maximum growth. Such ability is also important for those organisms blooming episodically. Cyanobacteria (*Trichodesmium*) are able to extract iron from the mineral aerosols supplied from the air and introduce a new iron and molecular nitrogen into the ecosystem cycle (Wells, 2003). The remaining afloat colonies of *Trichodesmium* assimilate iron directly from the particles sedimenting gravitationally onto the sea water surface.

The coastal zone of the Southern Baltic as well as its open waters is supplied with iron coming from rainfall and its concentration ranges widely from 0.1 up to almost 100 μmol/dm^3. Most of the precipitation is characterised by a low content of iron, below 1 μmol/dm^3, and high values occur occasionally and usually in summer. This variability is determined mainly by the amount of precipitation, its pH and the length of time without precipitation preceding the rainfall or snowfall; also important is the direction of the inflowing air. Onto the South Baltic, western air masses flow the most frequently, carrying iron that originates from terrigenous sources. This can be proved by high (above 90%) participations of Fe(II) in the total

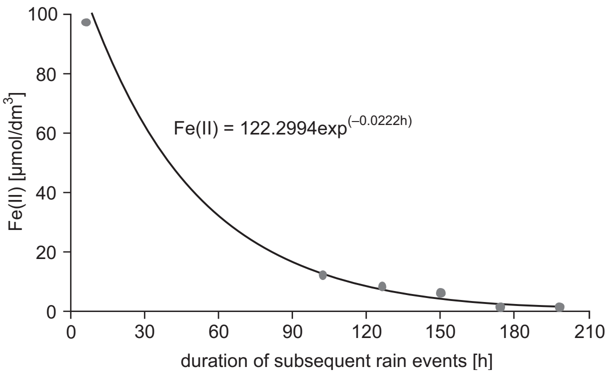

Fig. 5.7. Fe(II) removal from the atmosphere as a function of rain duration ($r = –0.91$, $p = 0.0106$) (Falkowska *et al.*, 2008)

iron found in wet fallout (Falkowska *et al.*, 2008; Sikorowicz, 2008). The effectiveness of eluting iron from the atmosphere is an exponential function of the precipitation amount and its time of duration (Fig. 5.7).

The inflow of atmospheric iron into the World Ocean is 450 Tg/year, of which the inflow to the Atlantic accounts for 47% (Jickells *et al.*, 2005). Expressed per square metre of the ocean surface area, the annual inflow of total iron, Fe (II) and Fe(III) is 450, 60 and 42 μmols, respectively (Kieber *et al.*, 2001). In the South Baltic, the fluxes of total iron coming with wet fallout were by one order of magnitude lower than over the Atlantic and reached 40.8 μmol/m^2 in 2006 and 72 μmol/m^2 in 2007 (Sikorowicz, 2008). This depletion in iron supply into the Baltic Sea results from a scarce contribution of alkaline dusts coming from the Sahara and dominating over the ocean. However, when the South Baltic region receives mineral aerosols from both distant land (agricultural, desert) and neighbouring (trenches and excavations) areas, precipitation introduces the load of iron that is comparable or even three times higher than the inflow to the Atlantic. In 2005, the coastal zone of the Gulf of Gdańsk received 1438 μmols of total iron per square metre of the sea surface area in wet fallouts with pH >5.6 (Sikorowicz, 2008).

5.1.4. Toxic Metals

In the latter decades of the last century, the role of atmospheric deposition was perceived in the balance of metal concentrations in the marine environment (Buat-Menard, 1986), especially in landlocked seas (Rodhe *et al.*, 1980). It is particularly essential for the Baltic Sea, which is almost totally surrounded by numerous man-made atmospheric emission sources. The association of the atmospheric deposition of metals with the urban and industrial development is unquestionable. The concentrations of metals deposited on the surface of glaciers at the end of the 20th century with reference to the period preceding the industrial epoch were many times higher, e.g.: zinc – 2.3 times, copper – 2.7 times, cadmium – 10 times, lead – 250 times (Condelone *et al.*, 1995). Both the transport and deposition of particles in different regions of the Earth depend on the dynamics of the atmosphere. Circulation systems of air masses on local, regional and global scales are decisive for the intensity of the sources emitting aerosol particles with metals into the atmosphere. The Baltic Sea is a good example of a deposition area, where air masses from different sides either flow through or struggle with each other. Over the Central Baltic, for 60° of the northern latitude, the prevailing winds are from the SW (26%) and S (9%) (Schneider *et al.*, 2000). It means that the south-western sector is the most important route for air masses to reach the Baltic Sea. The emissions into the atmosphere from Western Europe, i.e. from the countries far from the Baltic Sea, account for 25% of the total deposition of metals into the Baltic Sea (Krüger, 1996).

Some attempts have been made to assess the scale of the atmospheric flow of trace metals into the Baltic Sea. The first estimates made by Rohde and co-workers (1980) indicated a significant influence of the atmosphere on the metal flow to the Baltic Sea. The annual deposition of lead, zinc, copper and cadmium was estimated at 2400, 6000, 1400 and 80 t, respectively (Tab. 5.1). Over the following years, the Baltic Marine Environment Protection Commission (also known as HELCOM or Helsinki Commission) initiated a monitoring programme to monitor atmospheric pollution (EGAP), dealing with the deposition of metals. Published in the 1980s and based on new measurements and tools, the results of the metal flow into the Baltic Sea provided a variety of information, indicating significant procedural differences. In the 1990s, new models of metal deposition in the Baltic Sea were developed, which assessed the inflow in different ways, basing on different assumptions (Petersen, Krüger, 1993; HELCOM, 1997). The international BASYS programme was carried out on the Baltic Sea in 1997–1998

Table 5.1

Atmospheric metal input estimates in the years 1965–2006, based on metal concentration measurements in aerosols and precipitation or emission data and models

Years	Cd	Cu	Zn	Pb	Hg	References
	[t/year]					
1965–1975	80	1400	6000	2400	30*	Rodhe *et al*., 1980
1975–1983	80	600	8000	3000	–	Ferm, 1984
Eighties	60	500	5200	2300	–	Baltic Marine, 1987
Eighties	57	1210	4740	1030	–	Schneider, 1988
Eighties	20	–	–	1150	–	Eliassen *et al*., 1988
1983–1985	59	510	5200	2305	–	HELCOM, 1989
1984–1985	77	–	–	1400	–	Petresen, Krüger, 1993
1986	35	–	–	1560	–	HELCOM, 1989
1985–1987	60	–	–	1000	–	Duce *et al*., 1989
1986–1989	77	–	–	1600	–	Schneider, 1993
1986–1990	–	–	–	1285	–	HELCOM, 1991
1990	13.0	–	–	698	4.4	Bartnicki *et al*., 2008
1991	11.1	–	–	546	4.1	
1992	11.4	–	–	527	4.2	
1993	11.9	–	–	463	4.2	
1994	11.3	–	–	409	3.9	
1995	9.6	–	–	338	3.8	
1996	10.6	–	–	333	4.0	
1997	8.3	–	–	277	3.4	
1998	8.4	–	–	320	3.8	
1997–1998	33	–	–	550	–	Schneider *et al*., 2000
1999	8.9	–	–	313	3.6	Bartnicki *et al*., 2008
2000	9.9	–	–	341	3.8	
2001	8.4	–	–	257	3.6	
2002	7.8	–	–	252	3.1	
2003	8.4	–	–	283	3.4	
2004	7.4	–	–	238	3.0	
2005	7.7	–	–	238	3.0	
2006	7.1	–	–	234	3.4	

* Estimation based on wet deposition only

and combined environmental investigations with theoretical work on models. In this way, the annual lead inflow per square metre was estimated at 6.37 μmols, and cadmium at 0.71 μmol. The annual inflow of lead and cadmium over the entire Baltic Sea was 550 and 33 tons, respectively (Schneider *et al.,* 2000). The report by Bartnicki *et al.* (2008) determined the total deposition of cadmium in the Baltic Sea in 2006 at 7.1 t, which indicated almost a four times lower flux than that reported in the study by Schneider *et al*. (2000) and a half lower inflow than the fluxes determined in 1990 (13 t). In 2006, the total lead deposition in the Baltic Sea was assessed at 234 t, which proved the almost a three times lower inflow of PB into the sea compared to that in 1990 (698 t).

A decrease in the air-borne inflow of metals into the Baltic Sea is associated with the reduction in their emission into the air. The use of lead-free petrol has the highest contribution to the reduction of air emissions in the Scandinavian countries: from 7840 to 1089 t/year. The largest changes in lead transfer to the air were noticed in Sweden: from 361 t during 1990 to 14 t in 2006. In Poland, at the same time, the annual emission of lead decreased by almost three times: from 1327 to 524 t/a. The lowest changes were recorded in Estonia and Lithuania (Bartnicki *et al*., 2008).

Since 2001, lead deposition has not changed much. It shows how significant were the effect of using leaded petrol on the amount of lead in the air. Lower Pb emissions to the air caused lower deposition of this metal into the Baltic Sea, as well as the reduction in Pb concentration in the sea and in the fish bodies (Bignert, Nyberg, 2006; HELCOM, 2007).

The emission of cadmium undergoes permanent reduction. The atmospheric inflow of lead and cadmium exceeds the river inflow. Air deposition is the main source, accounting for 60% of the total inflow of these metals into the Baltic Sea (Schneider *et al*., 2000). Considering the atmospheric deposition of metals into the Baltic Sea, natural sources account for 0.5 to 20%, whereas the inflow of natural origin metals from rivers may become higher, from 9 to 60%.

The first estimation of the mercury atmospheric inflow into the Baltic Sea was presented by Rodhe *et al*. (1980), indicating an annual inflow from 5 to 50 t. In 1990, the mercury inflow to the Baltic Sea was estimated at 4.4 t, and then in 2006 at 3.4 t. Such a considerable reduction in atmospheric inflow resulted from improved analytical methods on the one hand, and from systematic lower emissions of mercury into the atmosphere by the Baltic countries on the other hand. The most restrictive reduction of mercury was recorded in Germany: from 19.2 t in 1990 to 2.8 t in 2006. Poland lowered the annual emission of mercury from 33.3 to 21.3 t in the years 1990–2006. Lithuania, Latvia, Estonia and Sweden keep their Hg emissions into the air below 1 t/year (Bartnicki *et al*. 2008).

The analysis of the amount of atmospheric mercury deposition in the 21st century over the Baltic Proper shows small variations despite the fact that emissions are clearly decreasing nearly everywhere in Europe. The lack of a directly proportional relation between the emission and imission of this metal should be associated with another source, which is the reemission of mercury from both the land and the sea. Mercury is a volatile metal; it evaporates at room temperature. As the analyses carried out in 2007–2009 showed, the long-lasting emission of Pb and Hg to the atmosphere and, in consequence, their deposition in the sea made the metals accumulate in water. Therefore, in a warm season, the sea becomes a source of these elements as well. This is indicated by the increase in metal concentrations in large aerosols in the marine air masses that flow in to the coastal zone of the South Baltic (Murawiec *et al*., 2009).

Seasonal variations in the air inflow of metals into the Baltic Sea reveal maximal values in the heating season, when higher concentrations of mercury, cadmium and lead are emitted. The highest seasonal changes concern lead deposition in the region of the Baltic Proper and the Bothnian Bay. In the warm months, despite intense rains, the deposition of lead and cadmium is lower than in the winter. As the reports of HELCOM (2007) suggest, no such relation concerning mercury deposition has been noticed so far.

*

The report of the Helsinki Commission (Bartnicki *et al*., 2008) states that the countries of the Baltic Sea basin emit from the atmosphere into the Baltic Sea from a few to several percent of metals from their territories. In total, all HELCOM countries supplied 40% of cadmium, 21% of mercury, and 16% of lead in 2006. Those European countries, forming part of the atmospheric monitoring system (EMEP), emitted 10% of cadmium, 8% of mercury and 7% of lead into the Baltic Sea. The highest contribution to the amount of deposition was remote emission sources, natural emission and re-emission, including 50% of the deposition of cadmium, up to 71% of mercury and 76% of lead. Long distance transport of toxic metals deposited into the sea areas shows the large spatial scale of this issue and makes the pollution of the Baltic Sea more important than air circulation of a local nature. Amongst the Baltic countries, Poland has the highest contribution in the emission of mercury, cadmium and lead into the atmosphere. In 2006, the deposition of cadmium, mercury and lead emitted from Poland was almost 1.9 t, 0.34 t and 19 t, respectively.

5.1.5. Persistent Organic Pollutants

Persistent organic pollutants (POPs) are introduced into the Baltic Sea from anthropogenic sources. These substances belong to the group of the most hazardous chloroorganic compounds, such as pesticides, polychloroorganic biphenyls (PCBs), dibenzo-p-dioxins and dibenzofurans. They disturb the normal functioning of organisms and make the environment toxic. Their chemical stability means that the atmosphere can be one of the transportation paths for these substances over large distances from their sources of emission (Niemirycz, 2006). PCBs enter the atmosphere by evaporation from waste landfills, leakages, combustion, and disposal of processing wastewaters. In the atmosphere, the vapours of polychlorinated biphenyls adsorb into aerosols and enter soils and water as dry fallout (Andrijewski *et al*., 2003). The highest PCBs concentrations are found in the vicinities of their sources, especially in places of processing or discharging municipal wastewaters into the rivers, lakes or coastal sea waters. Dissolved in water, the fraction joins the natural circulation through bioconcentration, bioaccumulation and biomagnification in all organisms living in the water, which introduce it into the bottom sediments.

Although the production and use of PCBs are banned in Poland (Bogutyn, 2002), these substances are permanently present in the air, soil and surface water; however, their concentrations have been decreasing since the 1990s (EMEP/MSC-E wge, 2004; Kopańska *et al.*, 2005; Niemirycz, 2006). The data collection of the EMEP on the emission and deposition of POPs in Europe indicates a clear tendency in the reduction of emissions and depositions of hexachlorobenzene (HCB), polychlorinated hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), which was also observed in the last decade of the 20th century (EMEP/MSC-E wge, 2004). The deposition of dioxins and furans onto the water surface of the Baltic Sea showed a permanent downward trend after 1992 (Fig. 5.8). Studies made by expert groups (Bartnicki *et al*., 2008) prove that in 2006, remote sources of emission and the re-emission most significantly contributed to the amount of dioxins and furans, including toxic metals. At the same time, they indicate the long-range transboundary flow of POPs into the sea, accounting for 50%. The HELCOM countries participate in 40% of the whole deposition of PCDD/Fs, including Poland with its highest level of 12%. Russia, Denmark and Sweden introduce 7% each. The contribution of dioxins and furans to the deposition into the Baltic Sea was calculated at 10%.

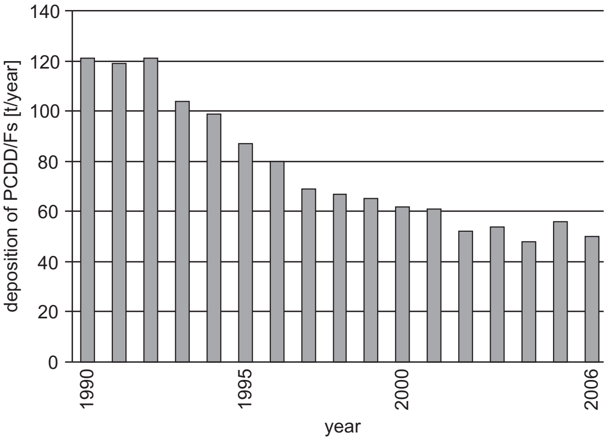

Fig. 5.8. Total atmospheric input of dioxins and furans (PCDD/Fs) to the Baltic Sea (based on HELCOM data; Bartnicki *et al*., 2008)

5.2. River Discharge of Chemical Substances

Matter migration by inland waters is a result of the interactions between hydrological phenomena and the physical, chemical and biological processes that occur in the environment of a catchment area, more or less changed by human activities. Thus, mineral and organic substances load going into the sea is controlled by a group of natural and anthropogenic factors.

Almost all of Polish territory (99.7%) is situated in the Baltic Sea catchment area, so the interpretation of river discharge into the sea is also an assessment of the events on a country-wide scale (Chapter 2.5). The knowledge of how individual factors or groups participate in forming chemical run-off from the catchment area shows a direction and a range of possible interventions to limit their negative effects on the water environment. This is the basis for working out an effective policy to protect against polluting water resources and the environment.

The assessments of the total contaminant run-off into the Baltic Sea, which is worked out by all Contracting Parties of the Helsinki Convention (Denmark, Estonia, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden) every 5 years according to the recommendations of the Helsinki Commission, included only a few selected contaminating substances and ignored pollutants from atmospheric deposition (the last assessment was made in 2004), taking into consideration only the run-offs of inland waters, primarily river waters. For those chemical compounds that are water insoluble and easily absorbed by airborne dusts, such as metals, pesticides and dioxins, it may be a source of significant inaccuracies in the assessment of total load that is transported from the land. According to the latest research, the atmospheric deposition of persistent organic pollutants (POPs) is estimated at more than 40% of the river run-off (Hites, 2006). Atmospheric POPs fallout on the surface of the Baltic Sea is being investigated by researchers of the Norwegian Meteorological Institute in Oslo (Vestreng *et al*., 2005). A three-dimensional model, known as Meteorological Synthesizing Centre East – Persistent Organic Pollutants (MSCE-POPs), is used to make maps of the pollutants being examined. The model is based on data from the EMEP research stations (European Monitoring and Evaluation Programme; Cooperative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe). The model includes the following processes: transport, diffusion, dry and wet deposition, stability of basic substance, and exchange between atmosphere and the surface of soils, waters and plants.

5.2.1. Assessment of Pollution Load Entering the Sea *via* Rivers

The run-off of contaminants carried by rivers to the Baltic Sea originates from different sources:, industry, municipal sewage treatment plants, rural areas, and fish farms, up to the run-off from areas of plant cultivation, forests and atmospheric deposition. The direct point sources of pollution loads are often maintained at the same level, regardless of the seasons of the year. However, the loads from diffuse sources (arable lands, forests) vary according to hydrometeorological changes in the river drainage basins, achieving the highest values during the spring and autumn rains. **Area specific load** is a parameter that enables us to compare the amounts of pollutants from different river drainage basins and describing the contamination of drainage basins irrespective of their sizes, is a unit load calculated by dividing the total river load by the drainage basin surface. Total loads and area specific loads may decrease due to the changes in the increased retention of waters, nitrogen denitrification or due to the increased inflow of groundwater to the river. Those processes are of higher significance in rivers with large drainage basins.

Apart from river run-off, direct run-off is also an important source of water pollution. It includes discharges of municipal and industrial sewage from direct point sources as well as effluents from fish farms located in the coastal zone. The volumes of the direct run-off discharged by the Baltic countries in 2000 are shown in Figure 5.9. The effective and prompt implementation of the National Programme for Municipal Wastewater Treatment (Gromiec, 2004) and the erection of 65 wastewater treatment plants in the coastal areas enable the maintenance of the lowest direct outflow from the Polish coast.

Seven rivers, each with an average capacity of more than 500 m^3/s, flow into the Baltic Sea (Tab. 5.2). This amount has a dominant effect on the total inflow from river waters. In the balance of pollutants introduced by rivers, other rivers with a flow rate of more than 5 m^3/s are also taken into consideration. Smaller rivers incidentally show such high concentrations of pollution. Locally, they may be a serious ecological problem and therefore they were also included in the inflow balance.

The Contracting Parties, according to the Art. 6 of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1992 (the updated version of the Helsinki Convention, 1974), committed themselves to

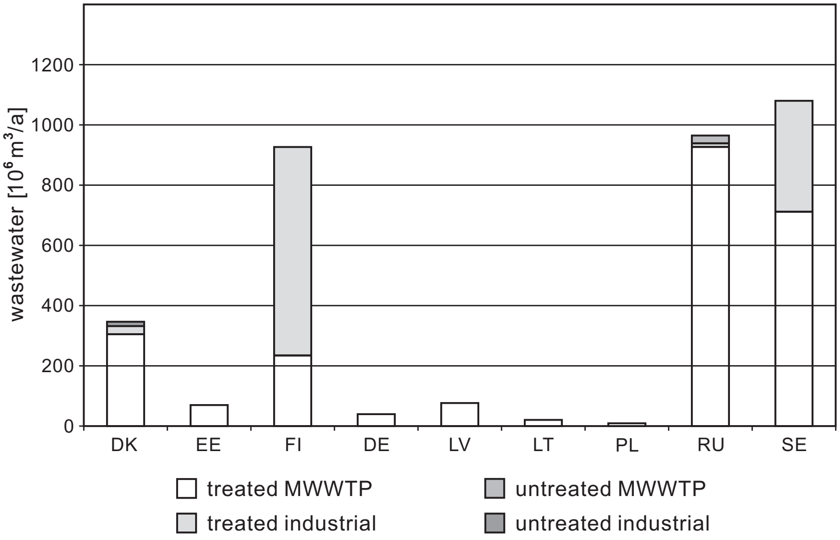

Fig. 5.9. Distribution of wastewater loads from inland direct point sources (mainly municipal effluents) discharged directly into the Baltic Sea (HELCOM, 2004)

DK – Denmark, EE – Estonia, FI – Finland, DE – Germany, LV – Latvia, LT – Lithuania, PL – Poland, RU – Russia, SE – Sweden; MWWTP – municipal wastewater treatment plant

Table 5.2

Hydrological characteristics of the seven Baltic rivers of the largest water resources (HELCOM, 2004)

Rivers	Neva	Vistula	Nemunas	Daugava	Odra	Göta	Kemijoki	Total
Mean long-term run-off								
in m^3/s	2,488	1,081	664	637	574	572	553	6,569
period	1859–1988	1951–1990	1811–1995	1881–1914; 1924–2000	1951–990	1961–1990	1961–1990	–
River length								
in km	71	1,047	937	1,020	854	902	600	–
River drainage basin within the borders of Contracting Parties in km^2								
Finland	56,200						49,470	105,670
Russia	215,600		3,170	27,000			1,660	244,130
Estonia				2,360				
Latvia			90	23,700				23,840
Lithuania			46,700	1,860				48,560
Poland		168,700	2,510		106,060			277,270
Germany					5,590			5,590
Denmark								
Sweden						42,780		42,780
Areas of river drainage basins within the borders of Non-Contracting Parties in km^2								
Belarus		12,600	45,450	33,300				83,850
Ukraine		11,170						11,170
Czech Republic					7,190			7,190
Slovakia		1,950						1,950
Norway						7,450		7,450
Total area of river drainage basins in km^2								
Total	271,800	194,420	97,920	88,220	118,840	50,230	51,130	859,450

undertake suitable actions in order to monitor and decrease the amount of pollution discharged to the Baltic Sea from the land sources. Those actions are coordinated by the Helsinki Commission as an executive body of the Convention. To implement the tasks of the Convention, some reliable data regarding the pollution discharge to the Baltic Sea from its whole catchment area were necessary. By the 1980s, a decision was made on the development of a common assessment for pollution run-off.

Periodical assessments of pollutant discharges into the Baltic Sea (Pollution Load Compilation – PLC) aimed to:

- define the amount of direct discharges of the most hazardous contaminants,
- establish a ranking of the substances and direct point sources of highest to lowest effect on the marine water quality,
- assess the activities undertaken to reduce pollutant loads,

– supply information to assess the condition of the open sea and its coastal zones.

The most important part of the assessment was to define properly the amount of the river run-off, which plays a significant role in that respect, and, in the case of water dissoluble substances (nitrogen and phosphorus compounds) – a dominant role in transporting pollutants from the land to the sea.

The assessments (PLC-1, PLC-2, PLC-3, PLC-4) included data from 1986, 1990, 1995 and 2000 (Niemirycz, Walkowiak, 1996; HELCOM, 1998, 2004). The first Baltic Sea Pollution Load Compilation (PLC-1) was only an approximate set of data submitted to Helsinki Commission by Contracting Parties, without any suitable verification of the data. In the following studies, the data became more reliable and enabled us to compare the amounts of pollutant run-off. The PLC-3 and PLC-4 assessments were based on the earlier issue of "Guidelines for Third/Fourth Pollution Load Compilation", which helped individual countries to make their reports (HELCOM, 1998, 2004). The state laboratories which made the necessary analyses of contaminant concentrations were submitted for international intercalibration. The method of calculating the loads of the run-off for all Baltic countries has been developed in Poland (Niemirycz, 2008).

The following contaminating substances were selected to make the assessments:

– organic substances expressed by the following general indexes: biological oxygen demand within 7 days (BOD_7), chemical oxygen demand – oxidation with dichromate (COD_{Cr}), total organic carbon (TOC)*, adsorbable organic halogens (AOX)*;

– biogenic substances (nutrients): total phosphorus, soluble phosphates, total nitrogen, ammonium nitrogen, nitrate and nitrite nitrogen;

– metals: mercury, cadmium, zinc, copper, lead.

The amounts of water resources for the area are best described by a run-off module defined as the mean volume of the drained water. They can be assessed in absolute units as a volume of run-off per time unit (river flow) or in relative units with reference to one square kilometre of the catchment area surface (Michalczyk, 2009).

In 2000, the total river water run-off in the Baltic Sea catchment area achieved the value of 532,900 million m^3. In the Baltic catchment area included into the monitoring (1.32 million km^2; 97% of the total area of the Baltic Sea catchment area), the area specific load was 11 $l/s \cdot km^2$. The largest volumes of river waters (app. 60%) are observed in Sweden and Finland (Fig. 5.10).

The organic matter load going into the sea (measured as BOD_7) is shown in Figures 5.11 and 5.12. The area specific load of BOD_7 from Poland is less than the outflow from load from Lithuania and similar to loads from Denmark, Germany, Finland, Russia and Sweden. In 2000 the total BOD_7 load going into the Baltic Sea amounted to 1,040,000 tons (610 kg/km^2).

Biogenic compounds in rivers, like other contaminants dissolved in water, generally come from diffuse pollution sources, mostly from farming agriculture. The temporally invariable loads, discharged with wastewaters from direct point sources to the rivers overlaps the contaminants eluted from the drainage basin area in a way depending on many factors, primarily on meteorological conditions. This is the reason why discharge of most of pollution by rivers changes synchronously according to the water outflow.

The total load of **nitrogen** entered the Baltic Sea *via* rivers was 706,000 t (420 kg N/km^2) in 2000. The characteristics of nitrogen discharged by the Contracting Parties of Helsinki Convention and by the regions of the Baltic Sea indicated by HELCOM are presented in Figures 5.13 and 5.14. The highest nitrogen load (75%) enters into the Baltic Proper region from the Vistula, Odra, and Nemunas rivers. Simultaneously, this region is also contaminated by one of the lowest area specific load. The highest area specific load is observed in the Sound region. High area specific load, characteristic of Denmark, Germany, and southern Sweden, are mostly a result of intense farming (especially discharging wastewaters from large animal farms) and the outflow of excessive natural and artificial fertilisers from arable fields. The southern Baltic and the Archipelago Sea are contaminated at 80% by a soluble form of inorganic nitrogen in contrast to the Bothnian Bay, where nitrogen combined with organic substances forms a larger part of the load.

In 2000 the total load of riverine **phosphorus** going into the Baltic Sea amounted to 31,800 t (19 kg P/km^2).

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* The parameters reported to the assessment optionally.

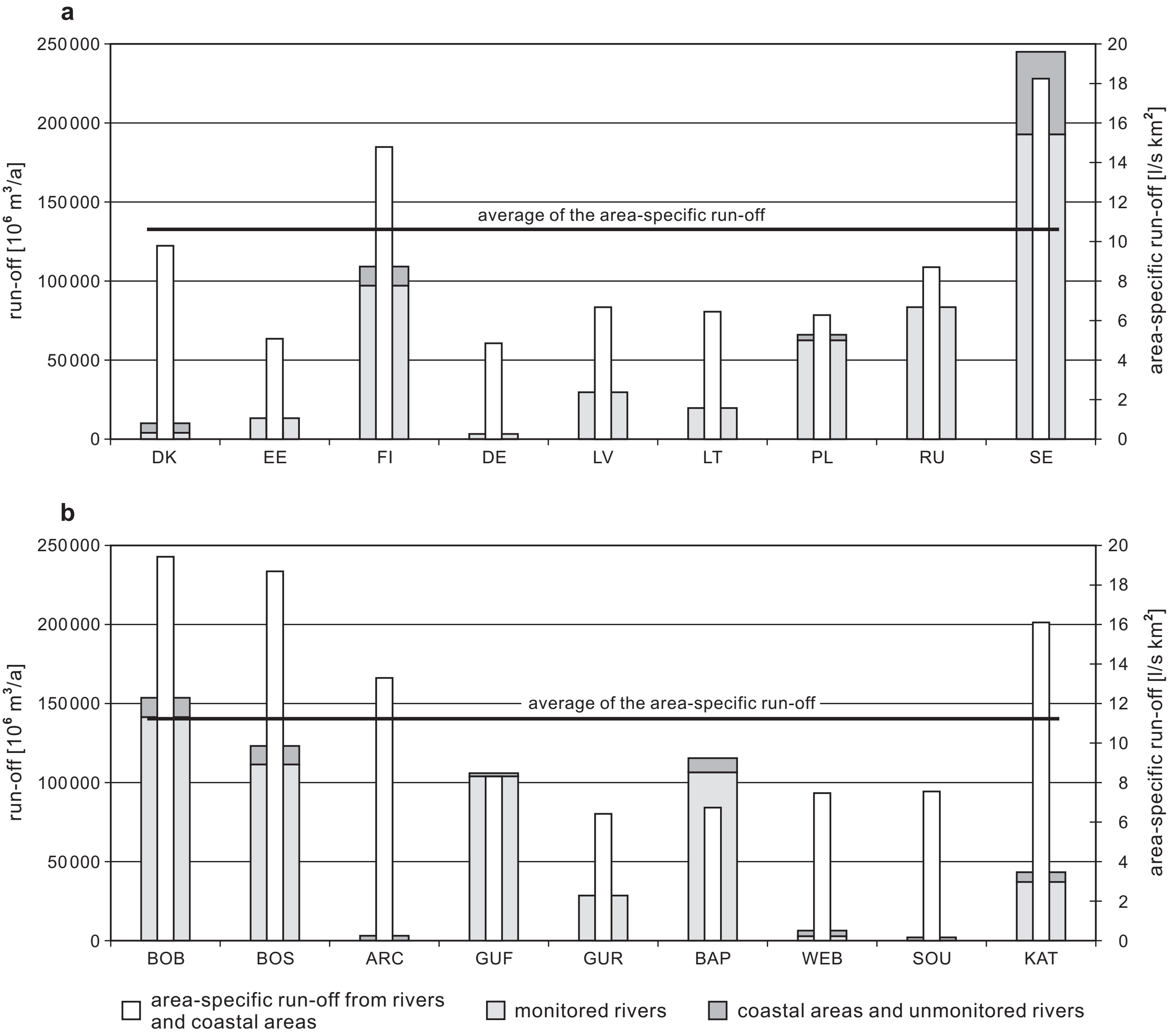

Fig. 5.10. Riverine run-off into the Baltic Sea in 2000 (HELCOM, 2004): a – by Contracting Parties, b – by sub-regions; names of sub-regions – see Fig. 2.1

The loads discharged by the countries located around the Baltic Sea into the different regions of the sea are given in Figures 5.15 and 5.16.

The Baltic Proper shows the largest (about 50% of the total load introduced) phosphorus load from the rivers of Vistula (7,490 t), Odra (3740 t) and Nemunas (1840 t), which makes, if consider the above characteristics of nitrogen, the highest inflow of biogenic substances into this zone of the Baltic Sea. The area specific load of phosphorus are as follows: the highest values occur in the Archipelago Sea (90 kg/km^2), Western Baltic (35 kg/km^2) and the Sound (30 kg/km^2), whereas the lowest values are reported from the Baltic Proper (29 kg/km^2). Such a distribution results from many factors: population, industrial and farming wastewater inflow, as well as types of soils and their permeability.

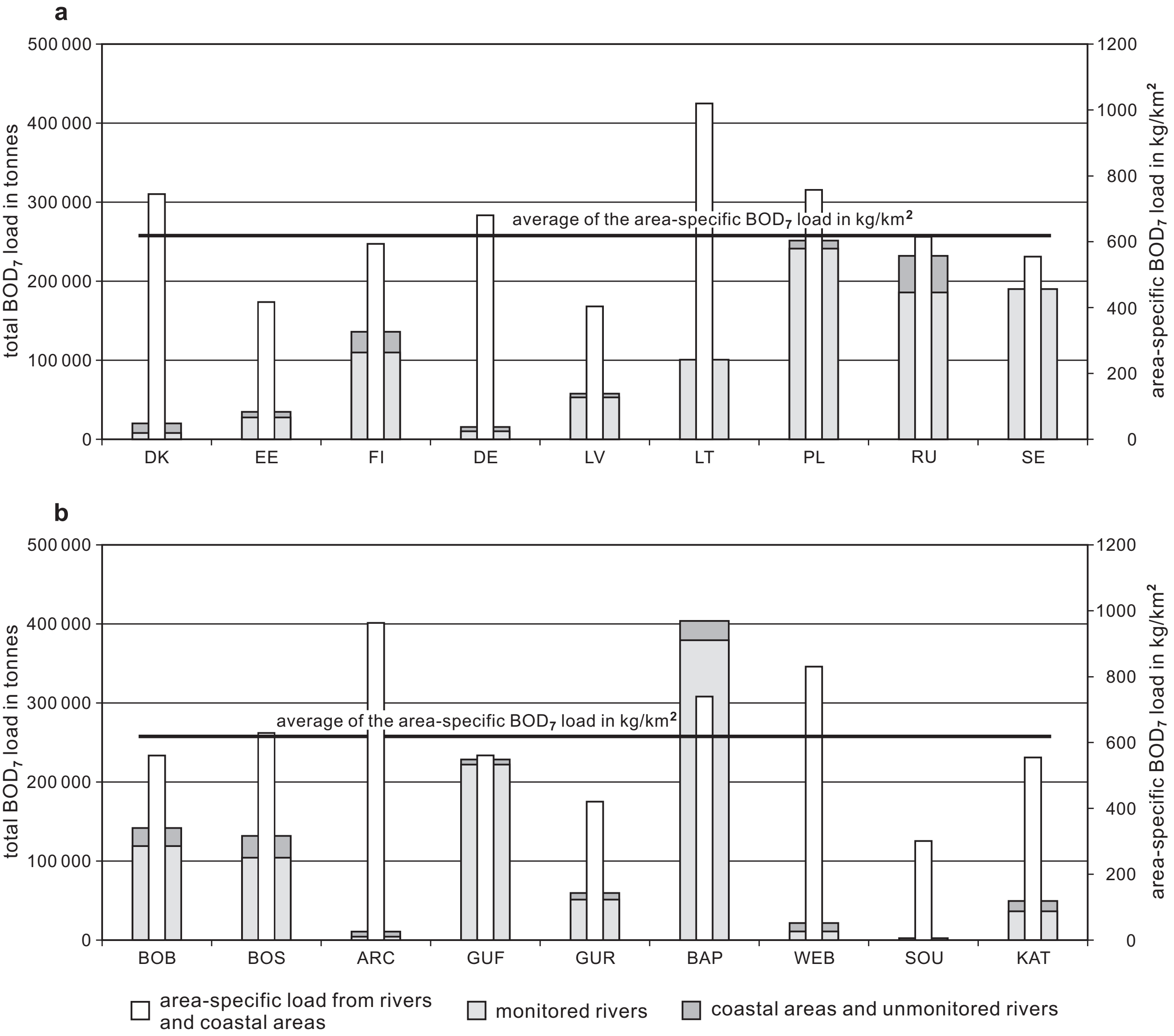

Fig. 5.11. Riverine run-off of organic substance (BOD_7) into the Baltic Sea in 2000 (HELCOM, 2004): a – by Contracting Parties, b – by sub-regions

The assessment of the metals load going into the Baltic Sea is approximate owing to the problems associated with taking representative water samples for analysis and the lack of data from many countries (Fig. 5.17).

While analysing load of metals into the Baltic Sea in 1995–2000, a decreasing tendency was observed. Lead was the only exception; the increase in the lead load (app. 40%) could be explained by a considerable increase in the number of cars in the countries, located in catchment area (Chapter 2.5).

Although the assessments of pollution load made by HELCOM are a meaningful source of information, they are not devoid of methodological errors. Considerable difficulties arise while taking into account the processes of self-purification of the rivers that do not introduce contaminants directly to the sea, but through lagoons, lakes

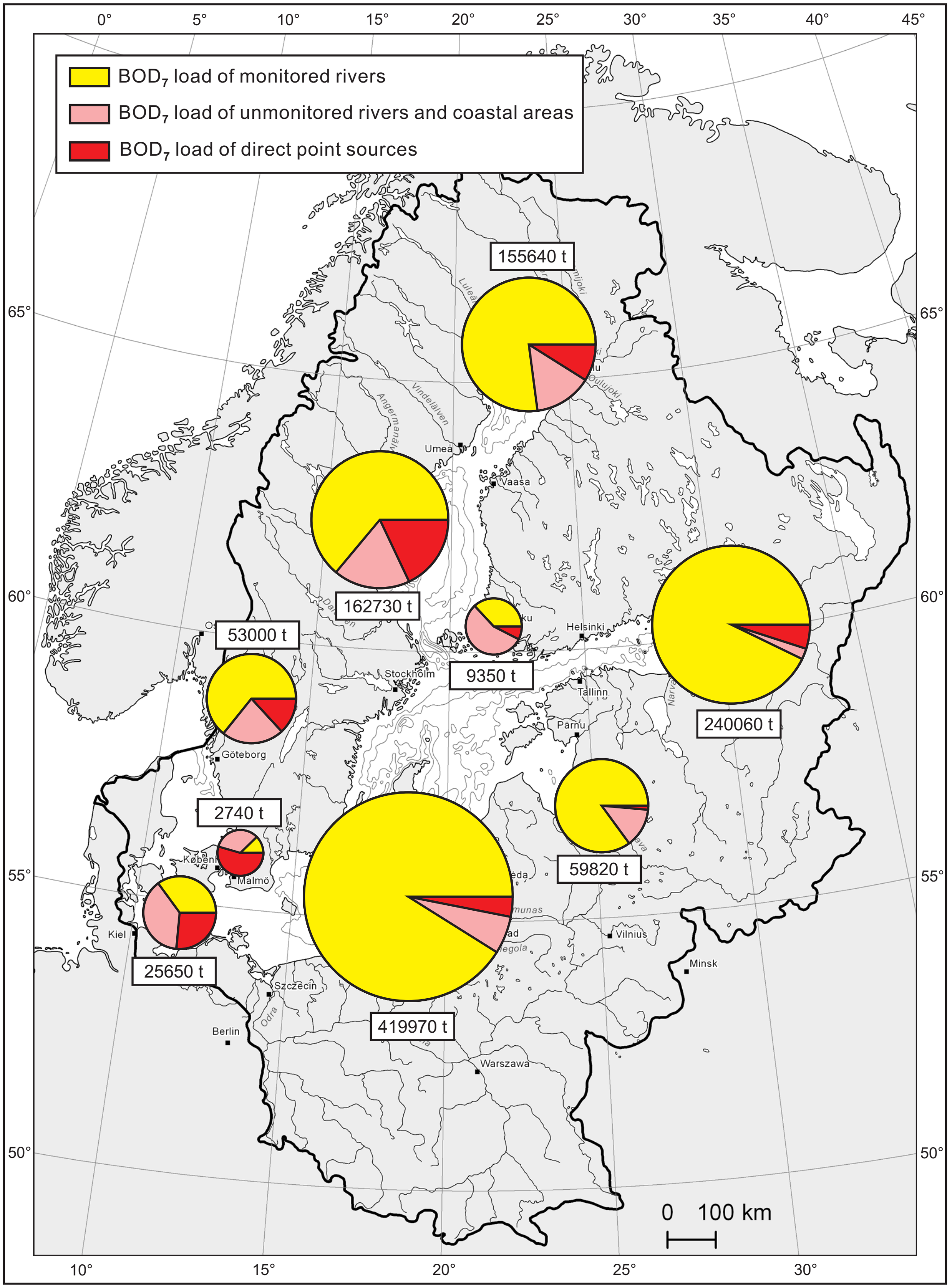

Fig. 5.12. BOD$_7$ load into the Baltic Sea in 2000 by sub-regions (HELCOM, 2004)

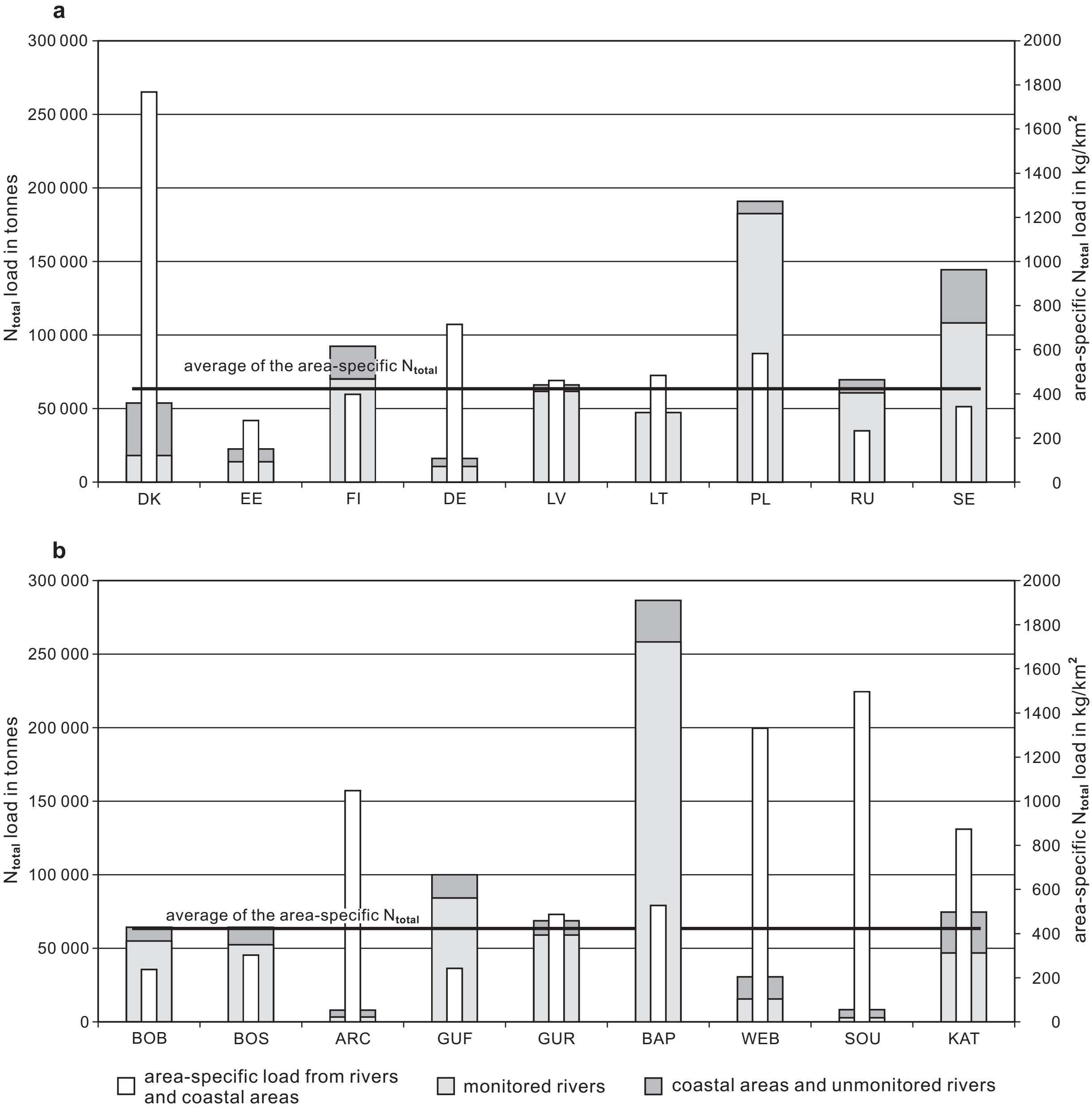

Fig. 5.13. Riverine total nitrogen (N_{total}) load into the Baltic Sea in 2000 (HELCOM, 2004):
a – by Contracting Parties, b – by sub-regions

or bays. The differences in geographic configuration and geological structure of the river mouth bottoms are also significant. Therefore, the assessments undergo methodical modifications to be able to record the pollutant run-off level in the most reliable way. A significant modification introduced recently is assessing pollutant loads as a unit measure, e.g. per km^2 of the surface catchment area, which helps to compare the pollution level in different regions. The introduction of such pollution parameters as organic halogen pesticides or dioxins (representing per-

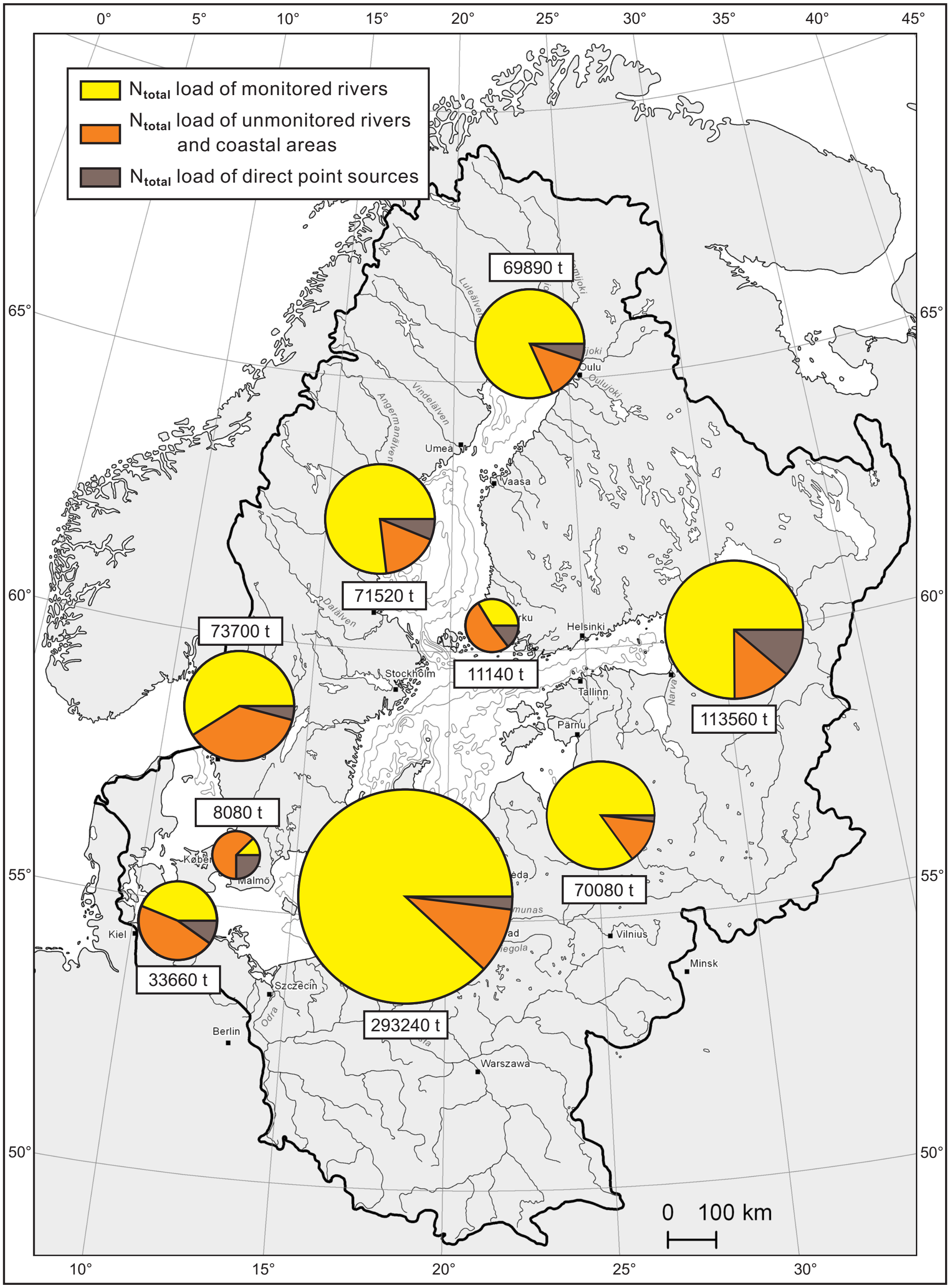

Fig. 5.14. Total nitrogen (N_{total}) load into the Baltic Sea in 2000 (HELCOM, 2004)

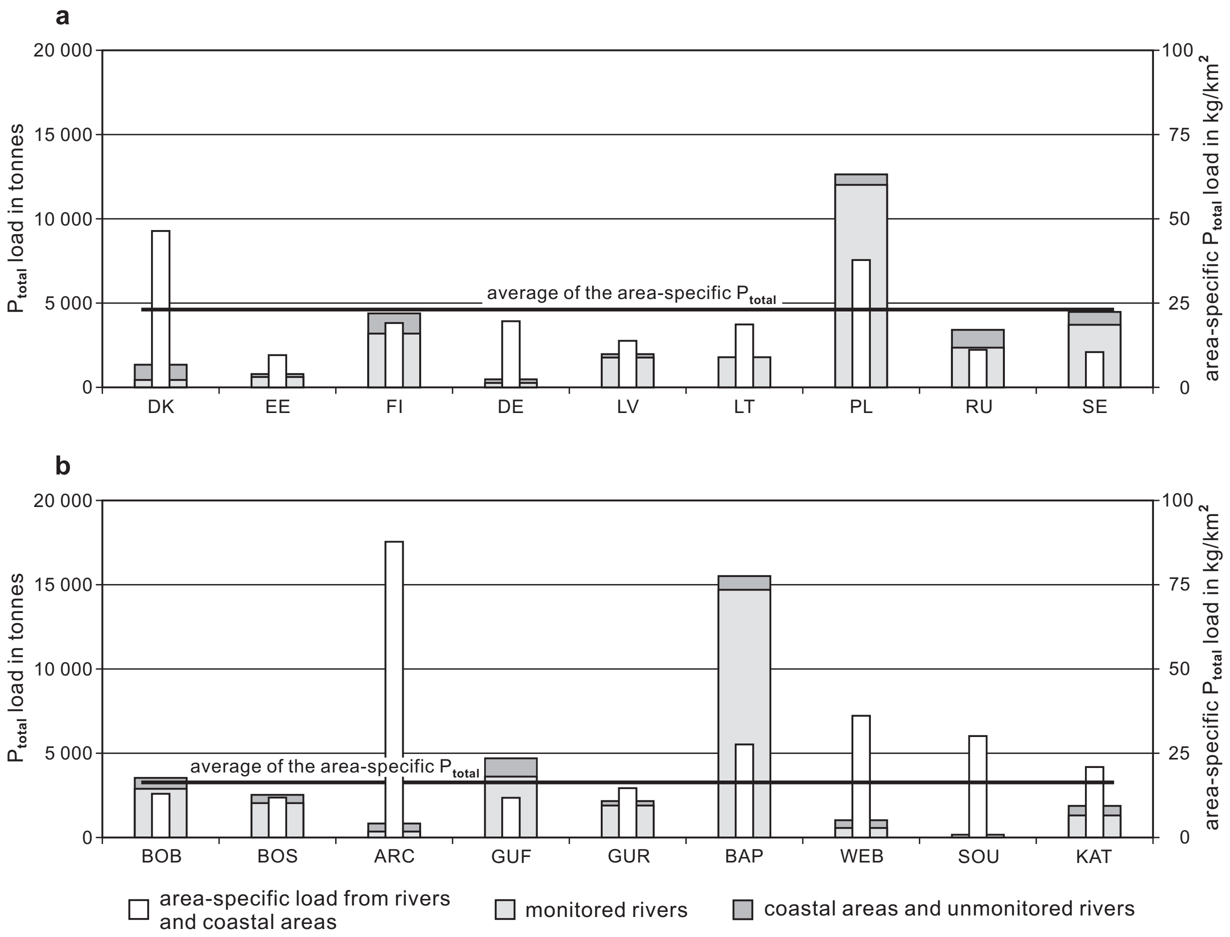

Fig. 5.15. Riverine total phosphorus (P_{total}) load into the Baltic Sea in 2000 (HELCOM, 2004): a – by Contracting Parties, b – by sub-regions

sistent organic substances) would be an important step in the completion of the assessment of the pollutants from the land. The information from the assessment of run-off is basic for undertaking strategic decisions to improve the condition of the environment in the Baltic Sea.

5.2.2. Methods Defining the Origin of the Pollution Load *via* Rivers in Selected Contracting Parties of Helsinki Convention

If the concentration of a given pollutant and the flow of the river, corresponding to the time of measurement, is correct, the volume of the run-off L_r, or, more precisely, the load per second can be accurately determined. Assuming a linear variability of those loads for the duration between two measurements, we can calculate the mean annual loads (L_r) according to the equation:

$$L_r = \frac{m}{n}\sum_{i=1}^{n} C_i\, Q_i \qquad [5.1]$$

where:

L_r – annual load calculated from the mean value of loads per second (t/year or kg/year)
n – set size,
C_i – momentary concentration of the constituent achieved in the i-th measurement (g/m³),
Q_i – momentary (per second) flow that corresponds to the concentration C_i (m³/s),
m – unit conversion factor.

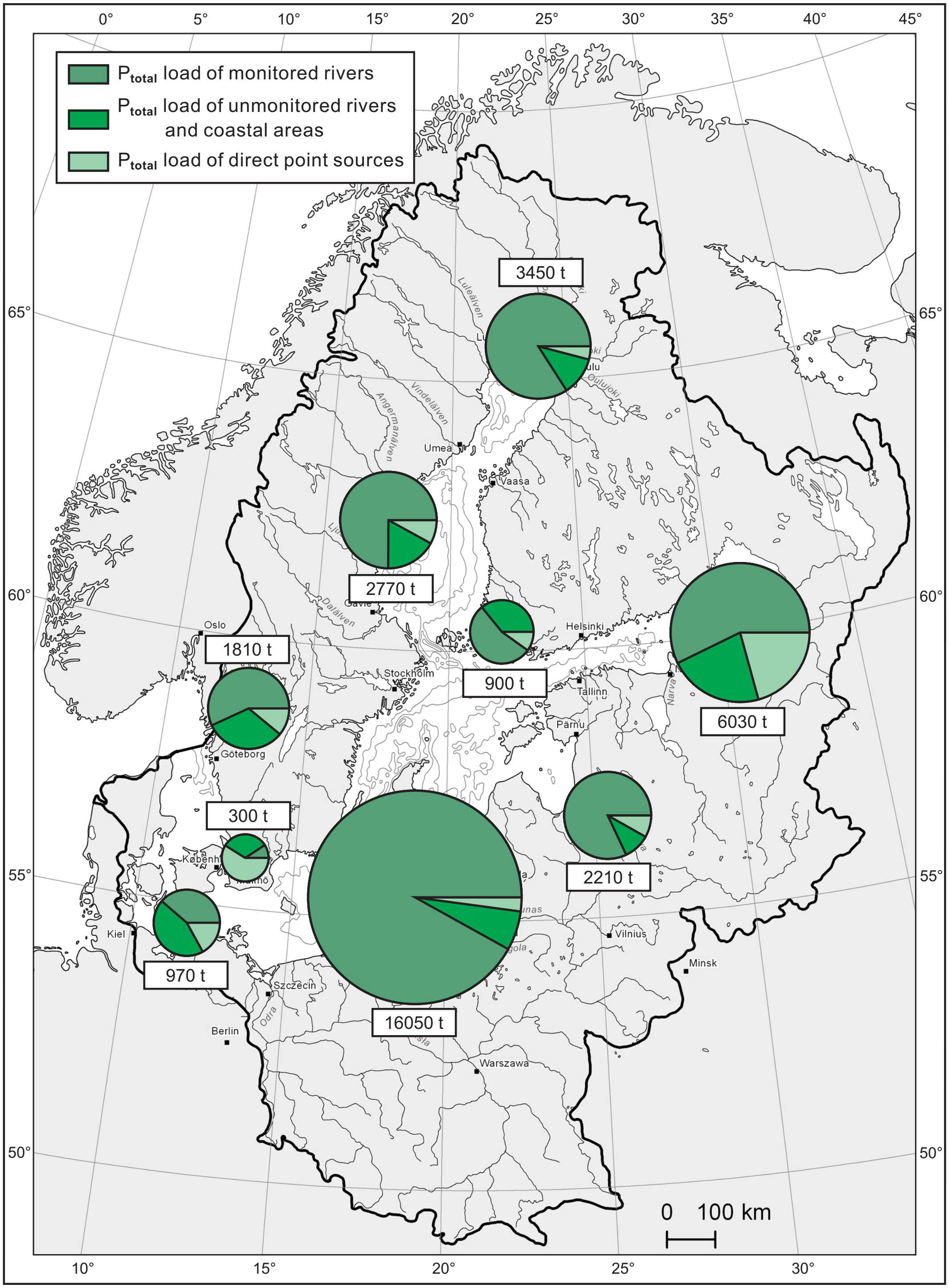

Fig. 5.16. Total phosphorus (P_{total}) load into the Baltic Sea in 2000 (HELCOM, 2004)

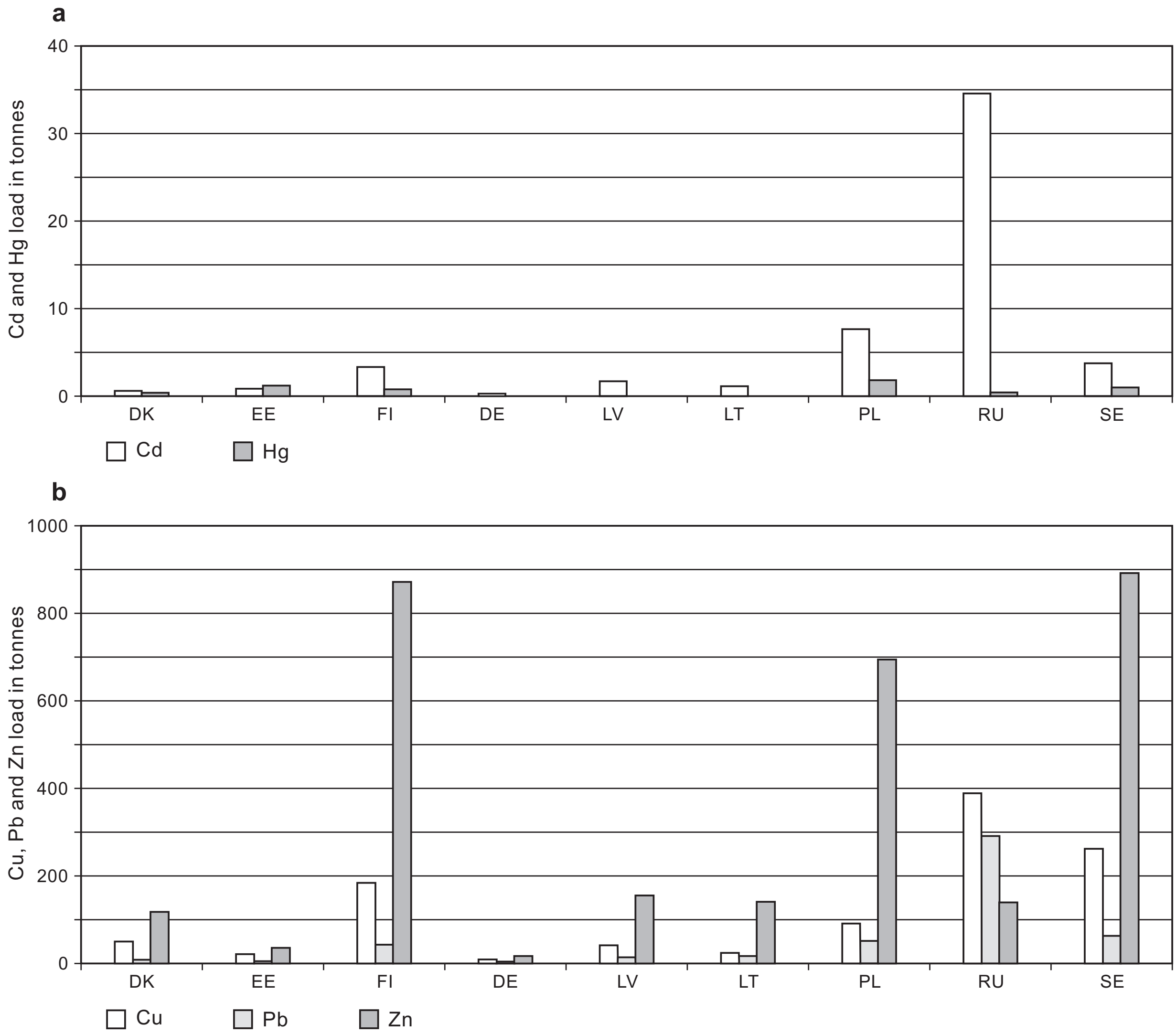

Fig. 5.17. Riverine heavy metal load into the Baltic Sea from Contracting Parties in 2000 (HELCOM, 2004); Pb loads for Poland – data from 2010

The above method of calculating loads, proposed by Poland when the Helsinki Commission was preparing the assessment of the pollution load run-off (Pollution Load Compilation), was also accepted by other Contracting Parties (Niemirycz *et al*., 1996).

A much more complex problem than calculating the load per second or total load is to establish where a given polluting substance originates from, which has an effect on the amount of the run-off, i.e. to what extent the run-off is shaped by natural conditions and how much of it is a function of human activity, or whether contaminations from point sources (sewage sewers) have a larger contribution than the pollutants from diffused sources.

In small river drainage basins (up to 5,000 m^2), the best method is to identify all contaminant sources and to measure the discharged load. For large drainage basins, such as the Vistula (more than 194,000 m^2), such measurements are impossible for many reasons (measurement precision, considering the processes of retention and self-purification). The division of pollutions sources into direct point and diffuse sources induces the necessity of using indirect methods that are based on the water balance in the river drainage basin. Lack of rainfall reduces the outflow of groundwater and practically cuts the supply of soil waters. In such a case, pollution of river waters mostly comes from point sources. The amount of diffuse run-off depends on many factors. Apart from permanent factors, such as soil properties, land configuration and water conditions in the drainage basin, a significant role is also played by variable factors such as: contamination of the area with pollutants and the volume of water taking part in washing out the substances, i.e. meteorological and associated hydrological conditions (Wrzesiński, 2007; Zalewski, Niemirycz, 2011).

According to European (mainly Scandinavian) publications, the assessment of pollutant loads from diffused sources related to agriculture is performed most often by calculating the total load in the river mouth cross-sections reduced by the sum of loads from direct point sources, and possibly also by the natural background. The result gives the load of pollutants originating mostly from farming, which is usually reduced by an assumed amount of self-purification.

In **Denmark**, the total load of nitrogen and phosphorus (A) is determined in the river mouth cross-sections based on the concentrations of biogenic compounds in water taken with a frequency of 12–36 samples per year, and on everyday measurement of the water flow volume. For each basin, the load is estimated from direct point sources (B), e.g. from the municipal sewage treatment plants of more than 30 PE (population equivalent), industrial wastewaters, freshwater fish farming, overflows from rainwater reservoirs and other rainwater sewage systems. The background load (D) is calculated on the basis of the amount of biogenic substance run-off from 10 small, non-agricultural drainage basins, separately for drainage basins of sandy and clay soils. Annual weighted averages are calculated for the concentrations of total nitrogen and the values of annual water run-off. For instance, in 1995, mean values of weighted concentrations and background loads for nine drainage basins were, respectively: 1.4 mg N/l and 0.0055 mg P/l as well as 290 kg N/km^{2}year and 7.3 kg P/m^{2}year.

The river run-off for nitrogen and phosphorus of diffuse sources (farming and dispersed rural land development) is estimated according to the equation:

$$F = A - B - D \qquad [5.2]$$

In **Finland**, two methods are used for calculation of the riverine source nitrogen and phosphorus loads (Behrendt, 1995; Salo *et al*., 1997). In the first method, the run-off of biogenic substances is defined similarly to the one used in Denmark; but the other method calculates the run-off based on many-year studies in small rural drainage basins. The results are used to determine unit loads of nitrogen and phosphorus of agricultural origin.

In **Germany**, emission and imission methods are used to assess the contribution of the nutrients from direct point and diffuse sources to the total river run-off (Draft report, 1994; Behrendt 1995; Salo *et al*., 1997). In the first method, the inventory of direct point sources is used to assess the amount of the nitrogen and phosphorus emissions from these sources. In the diffuse source assessment of the nutrient emission into the surface waters, the following aspects are taken into account: precipitation in the drainage basin under study, mineral and animal fertilisation, transport and storage of the fertilisers and silages, pastures and sewer-unconnected dispersed buildings. To achieve this, the following data are considered: land use, land configuration of the catchment area (Geographic Information System – GIS), livestock population and the use of fertilisers. The method requires the data difficult to obtain or define, such as: size of erosion, transport emission to waters, storage of fertilisers, as well as sewer-unconnected buildings within the studied drainage area.

The imission method enables us to divide the total run-off of nitrogen and phosphorus within a cross-section closing the studied river drainage basin into the imission from diffuse sources (farming and background) and direct point sources (industrial and municipal). The method is based on the following assumptions:

- nitrogen and phosphorus loads from direct point sources vary to a small extent in terms of both quality and quantity; their amounts do not practically depend on meteorological conditions; the discharge locations are possible to identify;
- nitrogen and phosphorus loads from diffuse sources varies in time; the variations are often of several orders of magnitude and are strictly associated with meteorological conditions (precipitation); the diffuse sources are often difficult to identify or to determine.

The method requires continuous measurement of flows and determination of analysed component concentrations with high frequency, as well as data concerning the amount of load discharges from the point sources.

In **Poland**, to define the riverine nitrogen and phosphorus loads, the following methods, developed at Marine Branch of Institute of Meteorology and Water Management, recently modified by Zalewski, Niemirycz (2011), were used:

- hydrographical method (Niemirycz *et al*., 1993; Dojlido *et al*., 1994) based on the assumption that a shortage in precipitation limits the groundwater run-off and practically stops the supply of soil water; then the contamination of river waters comes mainly from the direct point sources. In periods of extensive rainfall, the dominant role is played by diffused sources of contaminants with their characteristic large variations in run-off. The method assumes a shortage in diffused sources of pollution at the ten lowest flow rates of river water per year. Based on this assumption and the monitored data, the mean load discharged from direct point sources is determined;
- imission method in which the origin of the pollution loads is interpreted as a relation between the loads and the water run-off (Rybiński, Niemirycz, 1986);
- method that uses hydrological data to define such a case in which water quality is measured by determining only one component of the load being a sum of direct point and diffused sources of pollution (Rybiński *et al*., 1996).

Among the above-presented methods of identification of the loads of pollutants discharged by rivers, the most reliable are undoubtedly those based on the emission balance of the contaminants. However, it is the most important to obtain precise data as regards discharging pollutants from point and diffusse sources. In the Danish and Finnish methods, the loads of biogenic substances from the rural areas were determined based on the total load in the river mouth cross-section. Its value was calculated based on the determined concentrations and a permanent measurement of the river flow. The frequency of taking samples in the monitoring programmes for the Scandinavian rivers seems to be too low, which, for small rivers in particular, may lead to underestimating the annual diffuse contaminant load calculated as a difference between the total and direct point load. The German emission method requires many assumptions and data, often difficult to achieve or to assess, to determine the load of biogenic substances from the rural areas. It is thus a troublesome and laborious method.

Among the imission methods, the simplest and easiest is that based on the lowest flows; in Poland, it provides the results that are mostly comparable to those received by the laborious German emission method.

5.2.3. Pollution Load Going into the Baltic Sea *via* Rivers of Poland

River run-off from the area of Poland accounts for 11.2% of the Baltic Sea water supply. It occurs through the Odra River and the Szczecin Lagoon (30.0%), Pomerania rivers (7.8%), the Vistula (57.5%), the Vistula Lagoon (2.0%) as well through the drainage basins of the Pregolya and Nemunas rivers (2.7%). The last-mentioned value is an outflow outside the area of Poland (Russia, Lithuania). The Polish coast is 524 km long, including the 71 km of the Hel Peninsula (Rocznik statystyczny, 2005). Seven large rivers discharge water directly to the Baltic Sea on the Polish coast. Two of them, the Vistula and Reda rivers, flow into the Gulf of Gdańsk, and five (Rega, Parsęta, Grabowa, Wieprza and Słupia rivers) flow directly into the Baltic Proper. The Odra and Ina rivers flow into the Szczecin Lagoon, the Łupawa River into Lake Gardno, the Łeba River into Lake Łebsko, and the Pasłęka River into the Vistula Lagoon (Stachý, 1986). The lagoons and coastal lakes very often show a decrease in the amount of pollution loads due to natural self-purification processes. The pollution load calculated for mouth sections of the monitored rivers (selected as the last point of the river cross-section with no sea water penetration) are higher than the actual load going into the Baltic Sea. However, there are no experimental data to define that difference. It is estimated that the decrease in pollutant concentration owing to self-purification in the river mouth section may be up to 30%.

Pollution from land run-off (river run-off and run-off from direct point contamination sources) and pollution transported by the air is discharged down to the sea (Doskey, Andren, 1981; Niemirycz *at al*., 1983–1985, 1996, 1999). The assessment of factors constraining the levels

Table 5.3

Hydrological characteristics of the rivers of Poland in the Baltic Sea catchment area (Niemirycz *et al.*, 2004)

Rivers	Drainage basin [km^2]	Long-term mean	Run-off [km^3/year]							
			1994	1995	1996	1997	1998	1999	2000	2001
Vistula	194,424	34.3	32.3	32.9	35.6	37.2	43.5	44.8	42.4	41.2
Odra	118,861	18.2	19.4	17.0	20.1	23.6	21.4	19.0	15.9	19.1
Polish coastal rivers	17,359	4.5	4.9	4.7	4.1	4.3	5.9	5.7	4.5	4.5
Total	330,644	57.0	56.6	54.6	59.8	65.7	70.9	69.5	63.0	64.8

of the outflow of metals and biogenic substances was a subject of earlier studies (Grimvall, 1990, Rybiński, 1993) and, as far as organic halogens are concerned, recent papers (Niemirycz, 2008; HELCOM, 2010).

In the hydrological system of Poland, almost 90% of the river run-off to the Baltic Sea is carried by the Vistula and Odra rivers, with the Vistula run-off being permanently almost twice that of the Odra run-off (Table 5.3). The Vistula water run-off in the period of 1974–2006 is an example of the amounts and considerable changes in the run-off (Fig. 5.18). After the dry years of 1982–1993, a systematic increase in run-off was observed, reaching its maximum in 1998–2001. Until 2003, the run-off dropped by app. 55% to achieve its long-term average level again in 2006.

The analysis of data presented in Table 5.3 shows a small variability in run-off over time for Polish coastal rivers, which has also been confirmed by numerous hydrological studies (Stachý, 1980; Drwal, 1982; Bogdanowicz, Fac-Beneda, 2009). Considering the annual run-off balance, extreme flood events that occur seasonally in the drainage basins are poorly marked. The year 1997 saw one of the largest floods within the Odra drainage basin, where the annual run-off increased by 15% in comparison to the previous year.

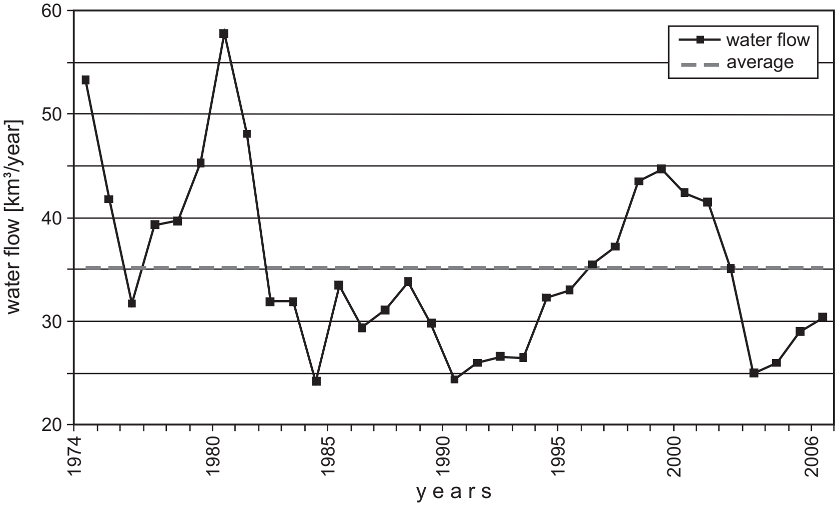

Fig. 5.18. Long-term variability of the Vistula run-off entered into the Baltic Sea in 1975–2006 (Niemirycz *et al.*, 2004; Rocznik hydrologiczny, 2006)

Outflow of organic substances

In the last decades, a permanent increase of organic substances load inputs into the sea – from dissolvents, detergent constituents, cosmetic and pharmaceutical agents, textile and construction additives, up to pesticides, polychlorinated biphenyls (PCBs) and dibenzo-p-dioxins as well as dibenzofurans (dioxins) – has been observed as a result of human activities. These substances remain in the environment for a long time, resisting to physical, chemical and biological processes of degradation. They constitute a group of substances characterised by high solubility in fats and, therefore, they easily accumulate in the tissues of living organisms, disturbing their natural functioning even at very small concentrations. Owing to their toxic effect on the organism, their dissemination in the environment is of particular interest to the world scientific institutions.

The concentrations of organic substances can be estimated by using the concentrations of the individual organic compounds or substitute indexes such as biochemical or chemical oxygen demand ($BOD_{5/7}$ and COD), total organic carbon (TOC) as well as adsorbable or extractable organic halogens (AOX/EOX) (Dojlido, 1995; Dojlido, Niemirycz, 2002; Niemirycz, 2009; Niemirycz, Sapota, 2010).

In 2000, the sum of BOD_5 and COD loads discharged by rivers to the Baltic Sea was 221,068 t O_2/year and 1,822,255 t O_2/year, respectively (Table 5.4). The contribution of rivers to the total load was as follows: for BOD_5 – 65.7% for the Vistula, 29.4% for the Odra, and 4.9% for the Polish coastal rivers , whereas the COD values were as follows: 58.2% for the Vistula, 34.7% for the Odra, and 7.1% for the Polish coastal rivers. The Odra River is usually more contaminated with organic substances than the Vistula River because its outflow is almost twice greater.

The changes in run-off by the Vistula for both parameters in 1975–2006 show a clear relation between the water outflow and the organic matter run-off (Fig. 5.19).

Outflow of persistent organic pollutants

According to the international classifications, including those of the European Union, man-made organic compounds occurring in different chemical forms are recognised as hazardous substances. They are characterised by: high resistance to degradation, by toxicity, and by high capability to accumulate biological substances and to be transported over long distances. The most abundant group of hazardous organic substances is represented by organic halogen compounds, usually referred to as persistent organic pollutants (Czarnomski, 2003).

The EU Water Framework Directive divides hazardous substances into two groups (Mehlhorn, 2002):

– Priority hazardous substances – substances especially harmful to the water environment that should

Table 5.4

Input of organic substances by the rivers of Poland into the Baltic Sea in 1994–2000 (Niemirycz *et al.*, 2004)

Year	Vistula		Odra		Polish coastal rivers	
	BOD_5	COD	BOD_5	COD	BOD_5	COD
	[t O_2/year]					
1994	124 867	863 004	86 348	900 997	15 488	142 595
1995	140 702	783 151	74 904	579 044	15 057	130 287
1996	144 271	831 158	74 616	648 993	14 055	114 429
1997	151 880	1 066 048	118 229	833 491	14 353	115 255
1998	156 573	1 186 546	97 142	844 510	17 781	185 979
1999	146 314	1 125 965	68 825	747 731	12 746	130 146
2000	145 212	1 060 603	65 057	632 673	10 799	128 979

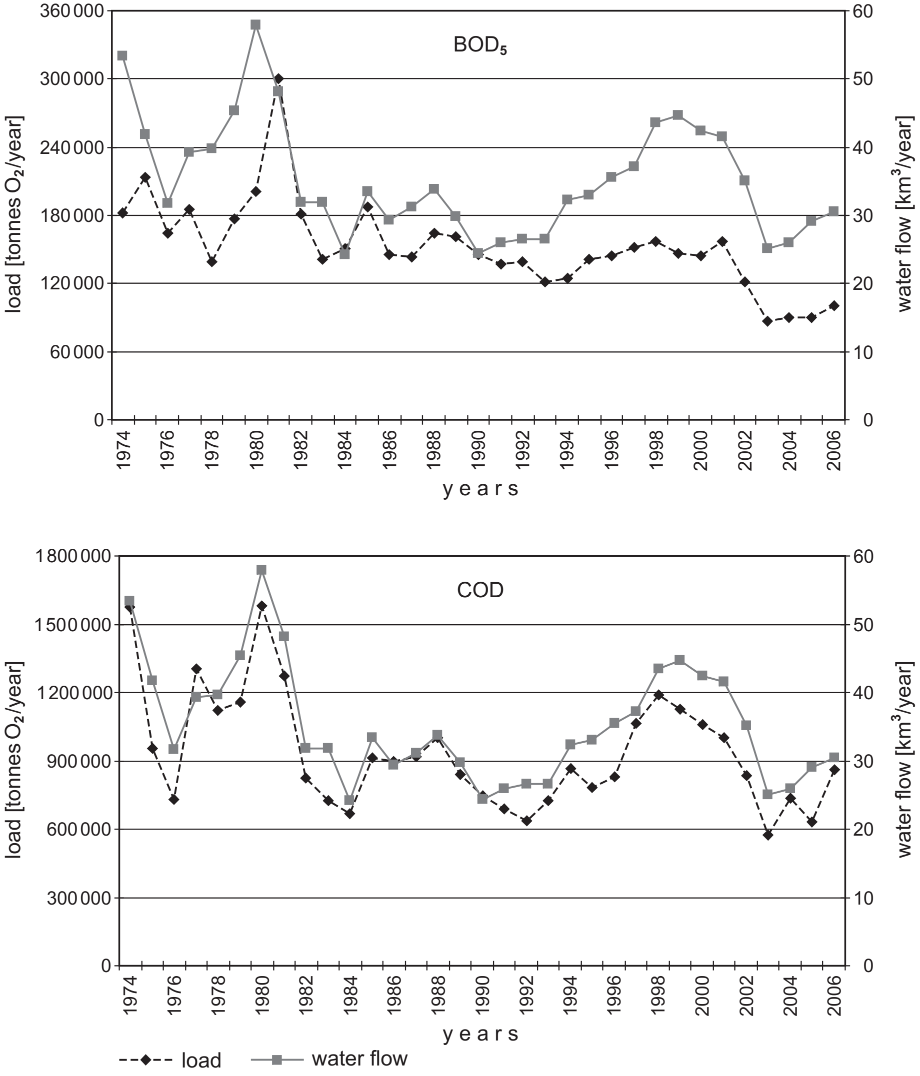

Fig. 5.19. Long-term changeability of the BOD$_5$ and COD inputs from the Vistula in 1975–2006 (Zalewski, Niemirycz, 2011)

be totally eliminated through actions aimed at stopping their discharge, emission and waste;

- Hazardous substances – substances especially hazardous to the water environment whose discharge should be limited.

The most important legal regulations concerning the environmental protection against the pollution with hazardous substances are:

- Water Framework Directive 2000/60/EC of 2000, together with Decision No. 2455/2001/EC of 2001, including Directive No. 76/464/ EEC and related directives of 1976. (Andrijewski *et al*. 2003);
- Stockholm Convention (Żurek, 2002);
- EEA, UN Convention on Long-range Transboundary Air Pollution of 1979, with Protocol on Persistent Organic Pollutants of 1998 (Jagusiewicz *et al*., 2004);
- Conventions on the protection of the marine waters: 2nd Helsinki Convention of 1992 (Baltic Sea), International Marine Organisation Convention (IMO),

Oslo and Paris Conventions (OSPAR) (North-East Atlantic), Barcelona Convention (Mediterranean Sea) (HELCOM, 1990, 1997, 1998).

The Frame Water Directive 2000/2001 established a list of hazardous substances. This list is verified every 4 years because of changes in the assessment of harmful impacts of especially environmentally toxic substances (Gromiec, 2001).

Considering the Stockholm Convention, organic hazardous substances were divided into the following groups:

– Substances that should be eliminated from production and use: aldrine, chlordan, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, and polychlorinated biphenyls;
– Substances, the use of which should be limited to strictly defined purposes: DDT;
– Substances, the production of which is unintentional, so they are waste products during manufacturing processes or while using other substances: HCB, PCBs, PCDDs, and PCDFs.

In 2001, Poland and another 113 countries signed the Stockholm Convention ratified in 2008 (Dz.U. on 31 July, 2008). Polish acts and regulations on harmful substances are included in the "National Implementation Plan for the Stockholm Convention" (Krajowy program wdrażania Konwencji Sztokholmskiej, Sadowski, 2004).

Rivers play a dominant role in transporting specific organic contaminations from the land into the Baltic Sea. In the open sea, pollutants enter the seawater from atmospheric deposition and from the ships and industrial installations (offshore drilling platforms, pipelines) (Olańczuk-Neyman, Mazurkiewicz, 1998).

The water repellent properties of organic halogen compounds make their adsorption on suspended particles easier, resulting in the substances that fall to the sea bottom and accumulate in the sea bottom sediments. The concentration of a compound contained in a water sample depends on various physical processes, such as mixing, sedimentation and sorption. For that reason, the assessment of the run-off of organic halogen compounds into the sea is difficult in terms of a straightforward qualitative and mathematical determination.

The basic assumption made to estimate the river run-off as regards organic halogen compounds was the dominant effect of hydrological aspects on the time and spatial size of the run-off. The obtained run-off values were verified with literature data (Vestreng *et al*., 2005; Jędrasik, 2006).

Table 5.5

Balance of the total transport of hazardous substances into the Baltic Sea (Niemirycz, 2008)

Transport	∑ DDT	γ HCH	PCBs	PCDD/F
	[kg/year]			
River run-off from Poland	530	380	260	0.05
River run-off from the Baltic Sea catchment area	4,820	3,390	2,360	0.43
Atmospheric deposition*	1,930	3,400	715	0.13
Total transport	6,750	6,790	3,075	0.58

* Pekar *et al*., 1999; Baker, Hites 2000; Bartnicki *et al*., 2000

The results of the studies by Niemirycz (2008), completed with literature data, made it possible to estimate a balance of the total transport of hazardous substances into the Baltic Sea, including atmospheric deposition (Table 5.5). The estimation neglected the run-off from Polish coastal rivers because the few percent load of the substances carried into the Baltic Sea was assumed to be within the limit of error. The information that the river run-off from Poland's territory accounts for 11.2% of the river water run-off for the entire Baltic Sea catchment area was also taken into consideration (HELCOM, 2002).

Outflow of biogenic substances

The discharge of biogenic substances, which increased several times in the second half of the last century, resulted in the process of marine water euthrophication. The effects of this phenomenon, including dissolved oxygen deficits, species changes in biocenoses and other negative phenomena are observed (Trzosińska, Łysiak-Pastuszak, 1996).

The level of the biogenic substance load going into sea is primarily dependent on hydrometeorological conditions shaping the amount of the river water flow that affects the amount of pollutants washed out of the drainage basin, i.e. diffuse source contaminants (Niemirycz *et al.,* 1993; Bogacka *et al.*, 1996; Bogdanowicz, 2004).

Actions to restrict the emission of biogenic substances from direct point sources were undertaken at the end of the 1980s. Changes in fertiliser doses used in farming and in hydrological conditions in river drainage basins, as well as improvement in water and wastewater management, affected the outflow of **nitrogen** and **phosphorus** in the rivers of Poland (Jagusiewicz ed., 2006).

The use of fertilisers in Poland dropped in 2004 by 40% in comparison to 1990 (Fig. 5.20). Compared to the other European countries, the amounts of fertilisers currently used are relatively low in Poland.

The improvement in water and wastewater management in towns and cities resulted in an almost 45% reduction in the volume of the discharged municipal wastewater in 2004 in comparison to 1990. At the same time, the treatment quality of municipal wastewaters is still improving (increased elimination of nutrients, utilisation of hazardous substances).

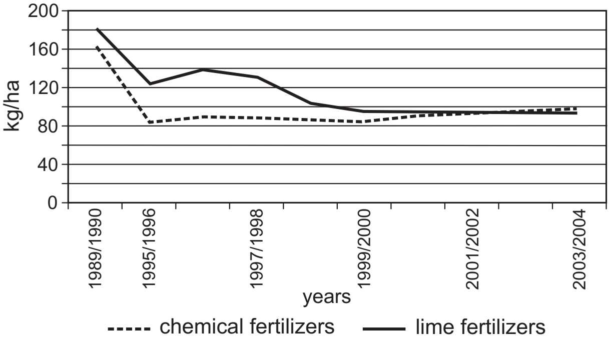

Fig. 5.20. Consumption of chemical and lime fertilizers in Poland in 1990–2004 (by active substance) (Rocznik statystyczny, 2005)

Table 5.6

Input of the nitrogen and phosphorus compounds by the rivers of Poland into the Baltic Sea in 1994–2000 (Niemirycz *et al.*, 2001, 2004)

River	Year	N-NH_4	N-NO_2	N-NO_3	$N_{org.}$	N_{min}	N_{total}	P-PO_4	P_{total}
Vistula	1994	10670	481	79599	39389	90749	130776	3486	5982
	1995	7639	563	65618	38972	73821	112793	4428	7321
	1996	12486	649	60613	88669	73748	162417	4022	5572
	1997	6535	751	53650	58275	61027	119790	5461	7636
	1998	8597	752	90798	48216	100147	148363	6671	8988
	1999	15967	750	76792	50024	91513	141537	5256	9688
	2000	15498	707	73955	45852	74662	120514	3660	7672
Odra	1994	2523	424	64546	32051	67493	99115	1644	5216
	1995	3810	301	46082	26780	50193	76973	1489	4922
	1996	8586	399	48726	25979	57614	83593	2082	6296
	1997	5930	520	40710	27808	47160	74969	2307	7113
	1998	2273	359	63194	28596	65827	94423	1355	5569
	1999	1521	361	56723	23293	58602	81895	1113	4188
	2000	1207	301	36893	18395	38413	56808	1169	3916
Polish coastal rivers	1994	1140	135	9002	6271	10277	16444	424	950
	1995	987	122	7337	6041	8457	14498	421	985
	1996	1126	110	5474	4780	6772	11544	332	869
	1997	1066	118	6414	4489	7598	12088	408	861
	1998	1152	145	11520	6378	12817	19195	476	1005
	1999	1025	114	8838	4978	9969	14947	422	1023
	2000	619	107	7758	4006	8510	12516	393	803

In 2000, a considerable decrease the riverine total nitrogen load (189,838 t), as compared to 1995 (204,264 t) and 1998 (261,981 t), was observed (Table 5.6). In 2006, the load of total nitrogen was 151,684 tons (Szczepański, 2007). The highest reduction in the total nitrogen load, its mineral and organic forms, occurred in the Odra, which was the most contaminated river with these substances (Zalewski, Niemirycz, 2011).

In recent years, the riverine total phosphorus load has also decreased. In 2000, it was 12,391 t, a reduction of 7% as compared to 1995 (13,228 t) and of 20% as compared to 1998 (15,562 t) (Table 5.6). In 2006, the total phosphorus load decreased to 10,164 t (Szczepański, 2007). Total phosphorus in the Odra River accounts for app. 35% of the total phosphorus that runs off in all rivers of Poland. This is a high contribution, while considering the flow rate, which is twice smaller in the Odra than in the Vistula.

The changes of Vistula River total nitrogen and total phosphorus load in 1975–2006 are given ion Fig. 5.21.

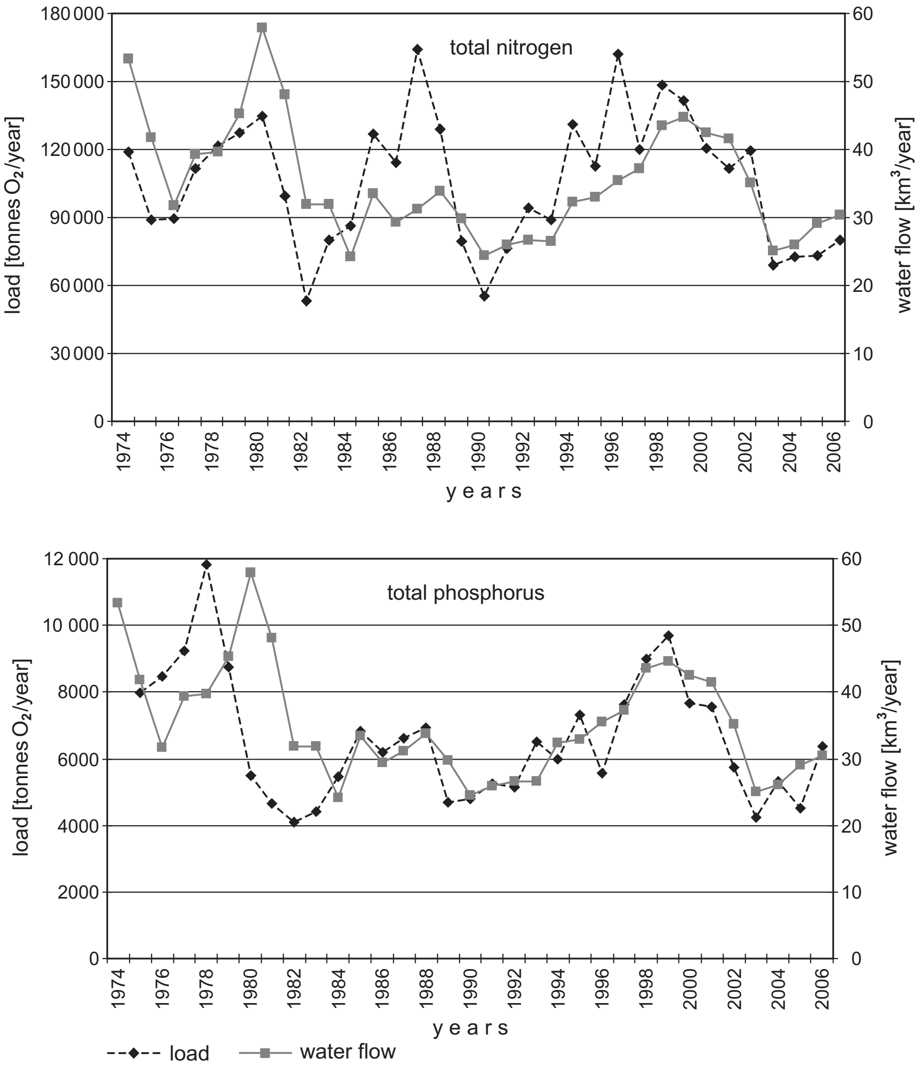

Fig. 5.21. Long-term changeability of the total nitrogen (N_{total}) and total phosphorus (P_{total}) inputs from the Vistula in 1975–2006 (Zalewski, Niemirycz, 2011)

Outflow of heavy metals

The outflow of heavy metals by river waters results from natural processes that occur in the areas drained by a river, as well as from human activity. Natural processes dominate in relation to the metals most common in nature, such as calcium, magnesium and potassium. The annual load of these metals going to the Baltic Sea via Polish rivers is 150 thousand t of potassium, 510 thousand t of magnesium, and 3500 thousand t of calcium. Heavy metals (of specific weight exceeding 4.5 g/cm^3) have been classified to substances especially harmful to living organisms. The list of heavy metals and their compounds published in the HELCOM document includes the following elements: mercury (Hg), cadmium (Cd), copper (Cu), zinc (Zn), and lead (Pb). According to the Declaration of Ministers in Ronneby issued in 1988, the run-off of these metals was to be reduced by 50% by 1995. Although the terms recommended in the declaration have not been fulfilled completely, there is a continuous tendency to reduce the metal outflow to the Baltic Sea. The concentrations of the above-mentioned elements are measured at the cross-sections near the river mouths of the Vistula, Odra and other rivers of the coastal zone of Poland under the State Environmental Monitoring program. In 2000, the riverine cadmium and mercury load was stabilised at 2.3 and 2.1 t, respectively. For zinc, copper and lead, it was 682, 112 and 24 t, respectively. The loads are lower than those discharged by some Scandinavian states by more than 10% (Fig. 5.17).

5.3. Inflow of Radionuclides to the Baltic Sea

5.3.1. Natural and Artificial Radionuclides in the Environment

The radionuclides occurring in the Earth can be classified into two groups depending on their origin: natural radioactive elements and artificial radioactive isotopes.

The group of natural radioelements includes:

- Radionuclides produced in the process of primary matter formation (the most important of these are potassium ^{40}K and rubidium ^{87}Rb);
- Radionuclides of uranium (^{238}U and ^{235}U) and thorium (^{232}Th) with their products of decay (mainly uranium ^{234}U, thorium ^{230}Th and ^{228}Th, radium ^{226}Ra, radon ^{222}Rn, lead ^{210}Pb, and polonium ^{210}Po), that form the natural radioactive series;
- Radionuclides that are formed continuously under the activity of cosmic radiation (mainly tritium ^{3}H and carbon ^{14}C).

Artificial radioisotopes have been produced by man in many fields, mainly in science, engineering, nuclear medicine and the armaments industry. They can be divided into:

- Radionuclides of technetium (^{99}Tc) and promethium (^{147}Pm);
- Radionuclides produced in the neutron-induced activation process (mainly sodium ^{22}Na, manganese ^{54}Mn, iron ^{55}Fe, cobalt ^{60}Co, nickel ^{63}Ni, copper ^{64}Cu, zinc ^{65}Zn, silver ^{110m}Ag, and antimony ^{124}Sb and ^{125}Sb);
- Radionuclides produced due to fission of nuclei of uranium ^{235}U and plutonium ^{239}Pu (the most important of these are strontium ^{90}Sr, iodine ^{131}I and ^{132}I, tellurium ^{132}Te, caesium ^{137}Cs and cerium ^{144}Ce);
- Radionuclides of transuranic elements (mainly neptunium ^{237}Np, plutonium ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Pu, as well as americium ^{241}Am and ^{243}Am).

Considering the half-lives, types of decay and radiotoxicity of radioactive elements to living matter, the most important radionuclides that occur in environmental samples are, amongst natural radioactive elements, mainly those from the uranium-radium radioactive series: ^{210}Po, ^{210}Pb, ^{222}Rn, ^{226}Ra, ^{234}U, ^{235}U, and ^{238}U, whereas amongst the artificial alpha- and beta-radio emitters: ^{90}Sr, ^{137}Cs, ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu. In nature, they occur in trace amounts, but they are usually found in all components of the environment (Skwarzec, 2002; Bem, 2005).

Amongst the radionuclides, alpha-particle emitters play the most important role as they are highly radiotoxic to animal organisms (Skwarzec, 1995). From the point of view of radiological protection, the key radionuclides are the natural radioactive elements: polonium (^{210}Po), radium (^{226}Ra) and uranium (^{234}U, ^{235}U, and ^{238}U), as well as artificial isotopes of plutonium (^{238}Pu, $^{239+240}$Pu, and ^{241}Pu) (Skwarzec, 2002).

Strontium ^{90}Sr and caesium ^{137}Cs are β^- particle emitters distinguished by relatively long half-lives of 28.5 and 30 years, respectively (Browne, Firestone, 1986). The amount of ^{90}Sr emitted to the atmosphere, mainly after the nuclear explosions in 1958–1962, was estimated at 780 PBq (151.1 kg), including 318 PBq (61.6 kg) that was deposited on land and 462 PBq (89.5 kg) on the surface of the seas and oceans. The total emission of ^{137}Cs from all sources into the natural environment at that time was assessed at more than 1100 PBq (340 kg). The Chernobyl nuclear power plant accident caused the emission of 57 PBq radioisotopes of caesium, including 38 PBq (11.8 kg) in the form of ^{137}Cs and 19 PBq (0.4 kg) as ^{134}Cs (IAEA, 1986).

Polonium ^{210}Po belongs to the natural uranium-radium series, the fate of which depends on radium ^{226}Ra and lead ^{210}Pb. The main source of ^{210}Po in the environment is radon ^{222}Rn released from the Earth's surface and produced from ^{226}Ra (Skwarzec, 2002). 112 million km^2 of active land surface area releases daily 130 PBq of radon, producing annually about 26 PBq of lead ^{210}Pb (Jaworowski, Kownacka, 1976; Skwarzec, 1995). Taking the mean activity ratio ^{210}Po/^{210}Pb in the air (app 0.15) as a basis, it was estimated at about 4 PBq of ^{210}Po (Skwarzec, 2002). Except for the ^{210}Po that is produced as the result of radioactive disintegration of ^{210}Pb in the air, additional amounts are emitted from the land as the result of forest fires (Moore *et al*., 1976) and volcanic eruptions (app 1.8 PBq) (Lambert *et al*., 1979). 0.52 PBq of ^{210}Pb is annually released from the oceans (Skwarzec, 2002). Apart from natural ^{210}Po, the atmospheric air also contains some amounts of man-made polonium that comes from the decay of ^{210}Pb formed mainly during nuclear bomb testing, and, to a lower degree, that emitted by the nuclear industry. In 1962, the activity of ^{210}Pb from these sources was estimated at almost 33 PBq. Furthermore, it was manifested that the most of lead ^{210}Pb is of artificial origin (Skwarzec, 1995, 2002). Polonium falls from the atmosphere onto the land and oceans together with rain, snow and atmospheric dusts. Deposition of ^{210}Po with dry atmospheric fallout is geographically diverse: it is the highest in the 30–60° N zone and ranges from 10 to 500 Bq/m^2 per year (Hardy *et al*., 1973; Skwarzec, 2002). Natural values of polonium in the environment can be elevated due to human activity, especially farming, manufacturing and use of phosphatic fertilisers, combustion of hard and brown coal, and mine water removal (Bem, 2005; Daish *et al*., 2005).

Radium has four natural isotopes: ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra. The most abundant and the most radiotoxic are ^{226}Ra and ^{228}Ra. The former belongs to the uranium-radon series and emits α and γ-radiation, with a half-life of 1620 years. The latter belongs to the thorium radioactive decay chain, is the emitter of β^- particles and its half-life is 5.75 years (Browne, Firestone, 1986). Radium is an element that rarely occurs in nature, it appears in the Earth's crust at $7\cdot10^{-12}$% wt. (which corresponds to the activity of 25 Bq/kg) (Ciba *et al*., 1996). Like uranium, radium is a constituent of the minerals that form the rocks of aquifers. Radium isotopes may enter water by the dissolving of rock material or owing to the recoil effect during alpha decay of the parent thorium ^{230}Th and ^{232}Th. In natural waters, radium occurs in surplus relative to thorium. This is related to its higher solubility comparing to thorium that is practically insoluble in a water environment and is adsorbed on the surface of the solid phase. After the decay of ^{230}Th and ^{232}Th adsorbed mainly on the surfaces of grains of clay and carbonate minerals, the newly produced ^{226}Ra and ^{228}Ra atoms desorb themselves into the water solution.

Radium has properties similar to barium and calcium, which are more easily sorbed from underground water by clay minerals and organic substances. However, the presence of sulphates in water limits aqueous migration of radium due to the formation of sparingly soluble $BaSO_4$ (Williams, Kirchmann, 1990; Chałupnik, Lebecka, 1995). Mining uranium ores and other useful minerals, their processing and using as well as the application of phosphate fertilisers with elevated amounts of radium induces an increase in its content in soil, groundwater and surface waters. The sources of radium in the atmosphere are: resuspension of soil and salt dust from the oceans, volcanic eruptions, forest fires and human activity, including: dusts from uranium ore mines, carbon combustion, production and using phosphate fertilisers, and the cement industry (Bem, 2005). The concentration of ^{226}Ra in the near-ground layer of the atmosphere in the northern latitudes and temperate climates is 0.5 μBq/m^3 (UNSCEAR, 1993). In marine waters, the distribution of radium concentrations varies with water depth, salinity and latitude. For example, in the top water layer of the Pacific, the ^{226}Ra concentration is on average 1.2 Bq/m^3, but in the bottom water layer it is 4.5–7.0 Bq/m^3 (Okubo, 1990). In the surface waters of the southern Baltic, the distribution of ^{226}Ra is uniform; in 2005 its concentration was 3.09 ±0.30 Bq/m^3 (Suplińska, Adamczyk, 2002).

Uranium is a natural radioactive element, very common in the Earth's crust. In nature, it often occurs as a dissipated element whose concentration in the topsoil layer is from below 1 up to 20 mg/kg (average 2 mg/kg). Most of uranium in the soil is found on grain surfaces and may undergo a leaching process. High uranium concentrations, 50–300 mg/kg, are observed, for example, in phosphate rocks used to produce artificial fertilisers (apatites). In some minerals, its content exceeds 50%, for example, in uraninite, pitchblende and becquerelite (Skwarzec, 1995). Natural uranium consists of three alpha radioisotopes of the following isotope constitution: ^{238}U (99.2745%), ^{235}U (0.7200%), and ^{234}U (0.0055%). In the natural environment, the ^{234}U and ^{238}U isotopes, although belonging to the same uranium-radium series, are not in the radioactive balance. Radioactive transformation energy that is associated with α particles from ^{238}U atomic nuclei, produces both the "recoil" of newly formed isotopes (mainly ^{234}Th) from the locations in their crystal lattices by the substrate atoms of ^{238}U, as well as the oxidation of U(IV) to U(VI) during the radioactive decay of ^{238}U through ^{234}Th and ^{234}Pa to ^{234}U. Therefore, the ^{234}U atoms are more weakly bonded within the mineral structure than the ^{238}U atoms, so they more easily diffuse to the surfaces of mineral grains and into inter-granular cracks. They are also more easily leached by water from the surface layers of minerals (Kigashi, 1971; Fleischer, Raabe, 1978). As a result, the waters contain more ^{234}U than ^{238}U, while the opposite relation is observed in the rocks. Deflections from the equilibrium state between the ^{234}U and ^{238}U isotopes are usually distinct in groundwater and brines, and surface waters of land areas, where the activity ratio ^{234}U/^{238}U takes the values between 1 and 8. In the rocks, it is significantly lower, ranging from 0.2 to 1 (Skwarzec, 2002; Skwarzec *et al.*, 2004).

Uranium in soils, rocks and sediments is leached by water and transported by rivers to the seas and oceans and this process is a significant source of this element in the marine environment (Skwarzec, 1995). Considerable amounts of uranium also fall directly from the atmosphere onto the surfaces of the seas and oceans as terrigenous particles formed in the processes of rock erosion and soil resuspension (Skwarzec, 2002). In the marine environment, uranium occurs in two oxidation states as U(IV) and U(VI). The chemical compounds, in which the reduced form of this element is found, are insoluble and, under reducing conditions, autogenic suspension that contains uranium(IV) is precipitated at the bottom of the basin. Uranium occurs mainly in marine and river water in the oxidised form as carbonate complexes $[UO_2(CO_3)_2]^{2-}$ and $[UO_2(CO_3)_3]^{4-}$, which do not sorb on the suspension and do not form any slightly soluble compounds with other constituents of the marine water (Langmuir, 1978).

Plutonium occurs in the form of four isotopes, three of which are α particle emitters: ^{238}Pu, ^{239}Pu and ^{240}Pu. The last one, ^{241}Pu, is the emitter of β^- particles and decays to highly radiotoxic ^{241}Am, which is an emitter of alpha particles. Plutonium is one of the most important elements as regards radiological protection because it is artificial. Its isotopes have long half-lives and remain in living organisms for a long time (Coughtrey *et al.*, 1984; Browne, Firestone, 1986). At present, more than 80% of plutonium contained in the natural environment comes from nuclear bomb tests. As a result of 423 nuclear detonations into the atmosphere, 14.8 PBq (4550 kg) isotopes of $^{239+240}$Pu was released, approximately 315 TBq (0.5 kg) of ^{238}Pu and 222 PBq (about 53 kg) of ^{241}Pu, including 12.0 PBq (app. 3700 kg) which was dissipated in the biocenosis (Hardy *et al.*, 1973; Skwarzec, 1995). One of the main sources of plutonium, especially in the marine environment, is used-fuel processing plants. Low active leaks from these plants contain plutonium, a part of which is emitted into the environment. About 0.6 PBq (185 kg) of $^{239+240}$Pu from the nuclear fuel processing works in Sellafield (United Kingdom) was released into the Irish Sea by the end of 1989. The leaks from the used nuclear fuel in Cap de la Hague (France) introduced about 2.6 TBq of plutonium, including 1.7 TBq (0.53 kg) in the form of ^{239}Pu and ^{240}Pu isotopes, to the English Channel in 1962–1982 (Hermann *et al.*, 1995; Leonard *et al.*, 1999). The accident in the

Chernobyl nuclear power plant caused the emission of app. 61.5 TBq (18 kg) of $^{239+240}$Pu, 30 TBq (48 g) of ^{238}Pu and 5 PBq (1.31 kg) of ^{241}Pu (Skwarzec, 1995). There are four ways for plutonium to enter the Baltic Sea: from the atmosphere (dry and wet fallouts), with periodical inflows of marine waters from the North Sea, with river waters, and owing to the release during the fire in the Chernobyl nuclear power plant (Aarkrog, 1988).

Solubility of plutonium compounds in marine water is low because their hydrolysis produces barely soluble plutonium dioxide in the form of $PuO_2 \cdot H_2O$. The occurrence of organic matter in marine water (mainly as humic and fulvic acids) plays a double role: complexing and reducing. The reduction of Pu(VI) to Pu(V) with humic acids proceeds rapidly, but the reduction of Pu(V) to Pu(IV) is much slower (Choppin, Allard, 1985). In the marine environment, only a few percent of plutonium remains in solution, while the rest is deposited in the sediments where its concentration depends on the grain size of the sea bottom sediment, decreasing with the grain size increase from 0.037 to 2 mm (Coughtrey *et al*., 1984; Gasco et al., 2002).

5.3.2. Run-off of Radionuclides from the Baltic Sea Catchment Area

The Baltic Sea is one of the most polluted water regions in the world. The catchment area involves numerous factories and industrial centres, large arable lands and seven active nuclear power plants with 20 active nuclear reactors (Sosnovy Bor in Russia, Loviisa and Olkiluoto in Finland and Forsmark, Bärseback, Oskorshamn and Ringhals in Sweden). It is a rich source of industrial, municipal and farming contaminants (nutrients), as well as radionuclides (Skwarzec, 1995). In addition, the Baltic Sea is marked by a considerable inflow of freshwater, which exceeds evaporation. There is also a strong human impact in this area. Mean residence time for waters in the Baltic Sea is estimated at 20 to 30 years (Szefer, 2002). This enables radionuclides to accumulate longer than in other seas around the Atlantic.

The Baltic Sea catchment area covers an area of app. 1.75 million km^2, including almost 250 rivers with a yearly water volume totalling 446 km^3 (Szefer, 2002). Both natural and artificial radionuclides are carried by rivers into the sea. Considerable amounts of nuclides, especially of anthropogenic origin (^{90}Sr, ^{137}Cs, and $^{239+240}$Pu) are introduced into the Baltic waters together with annual inflows of saline and well-aerated waters from the North Sea, with their higher concentrations of radionuclides (Kershaw *et al*., 1995; Leonard *et a*l., 1999).

Only 4% of the dissolved radionuclides from the used nuclear fuel processing plant in Sellafield and 8% from the works in Cap de la Hague enter the Kattegat Strait. Merely 1% of the isotopes from Sellafield reach the Baltic Proper (HELCOM 1995). Moreover, about 30% of plutonium in this region comes from the used fuel processing plant in Sellafield, whereas the rest 70% originates from global wastes (Holm, 1995). It is estimated that every year slightly more than 5 GBq of $^{239+240}$Pu enters the Baltic Sea through the Danish Straits (Skwarzec, 1995). The total amount of plutonium from global fallout deposited in the Baltic Sea is estimated at 16.5 TBq, over 90% of which is located in the sea bottom sediments, app. 0.2 TBq is contained in water, and merely a few GBq is found in marine organisms (Salo *et al*., 1986; Holm, 1995). Rivers that flow into the Baltic Sea carry app. 1.3–1.5 GBq of $^{239+240}$Pu every year. The inflows from the North Sea increase the contents of plutonium, particularly in the Danish Straits and Bornholm Basin. The direct plutonium fallout from the atmosphere into the surface of the Baltic Sea is less significant and currently amounts to about 1 GBq of $^{239+240}$Pu per year (Skwarzec, 2002). About 1.5 TBq of $^{239+240}$Pu entered the Baltic Sea as a result of the Chernobyl accident (Holm, 1995).

The residence time of plutonium in drainage basins of the rivers that flow into the Baltic Sea is estimated at 10^3–$2 \cdot 10^4$ years. One of the more important processes regulating the contents of plutonium in the river water is its sorption on particles of suspended matter and colloids, and their transport to the bottom (Alberts, Walhgreen, 1981). Mean concentrations of ^{90}Sr and ^{137}Cs in the river waters of the Baltic Sea catchment area before 1986 ranged between 3 and 5 Bq/m^3. The $^{239+240}$Pu concentrations were 3–4 mBq/m^3. Immediately before the Chernobyl explosion, the radiostrontium and plutonium concentrations were slightly elevated, whereas the ^{137}Cs concentration rapidly increased, especially in the waters of the rivers that flow into the Gulf of Finland and Bothnian Sea (HELCOM, 1995). Since the early 1990s, a systematic reduction in the ^{137}Cs concentrations in the

Baltic rivers has been observed, and it is beginning to achieve values typical for the time before the Chernobyl accident. Assuming the current average concentrations of the nuclides (3.5 Bq/m^3 for ^{137}Cs, 4 Bq/m^3 for ^{90}Sr and 3 mBq/m^3 for $^{239+240}$Pu), we are able to assess their annual flow from the Baltic Sea drainage basin as: 1.5 TBq for ^{137}Cs, 1.8 TBq for ^{90}Sr and 1.3 GBq for $^{239+240}$Pu, respectively (Salo *et al.*, 1984; Skwarzec, 1995, 2009; Saxen, Ilus, 2000; Szefer, 2002).

The concentrations of natural radioelements in the rivers of the Baltic catchment area range from 0.2 to 1.4 mg/m^3 for uranium (which corresponds to the activity of 2.5–17.0 Bq/m^3 of ^{234}U and ^{238}U isotopes), 1–3 Bq/m^3 for polonium ^{210}Po, and 0.5–2.0 Bq/m^3 for radium ^{226}Ra (Andersson *et al.*, 1998; Szefer, 2002; Skwarzec, 2009). Assuming the current average concentrations of the radionuclides at: 1,5 Bq/m^3 for ^{210}Po, 1 Bq/m^3 for ^{226}Ra and 5 Bq/m^3 for each of the ^{234}U and ^{238}U isotopes, we may conclude that their annual run-off from the Baltic Sea catchment area is: 0.7 TBq for ^{210}Po, 0.5 TBq for ^{226}Ra, and 4.5 TBq for $^{234+238}$U. The results confirm the significant role of river water run-off as a source of radionuclides in the Baltic Sea.

At present, the Baltic Sea receives annually from its catchment area about 3.3 TBq of artificial β^- emitters: ^{90}Sr and ^{137}Cs, 5.7 TBq of natural polonium, radonium and uranium radionuclides, and 1.3 GBq of anthropogenic $^{239+240}$Pu isotopes. If, in the future, there will be no emission of radioactive contaminants from new sources into the natural environment, the contribution of the anthropogenic component in the global run-off of radioactive substances by rivers to the Baltic Sea will decrease, and the natural component will remain at a similar level. Thus, we can expect that during the next 300 years, the activity of artificial ^{90}Sr and ^{137}Cs radionuclides will disappear in the ecosystem of the Baltic Sea, but the $^{239+240}$Pu plutonium isotopes, having long half-lives, will remain (Skwarzec, 2009).

5.3.3. Radionuclides Run-off from the Drainage Basins of the Vistula, Odra and Pomeranian Rivers

Almost 60 thousand km^3 of water is discharged annually from Poland into the Baltic Sea. About 50% of this volume is the run-off from the Vistula drainage basin, 34% from the Odra drainage basin, and almost 10% from the Pomeranian rivers (Makinia *et al.*, 1996). This area is characterised by high industrial and farming activities, contributing to the annual run-off from the Vistula and Odra rivers by app. 2.1 million m^3 of industrial waste waters with about 1.8 million tons of salts from mining waters discharged in Upper Silesia (Chałupnik, Lebecka, 1995). These salts contain significant amounts of natural radioactive elements belonging to the uranium-radium series (^{238}U, ^{234}U, ^{226}Ra, ^{210}Pb, and ^{210}Po) (Flues *et al.*, 2002; Bem, 2005). Moreover, phosphatic fertilisers and phosphogypsums, used in farming as post-production wastes, contain considerable amounts of polonium and uranium (Boryło *et al.*, 2009). In Poland, farming areas account for over 50% of the countryside area (16.6 million ha), and about 3.1 $\cdot$ 10^5 tons of phosphatic fertilisers is used (Skwarzec *et al.*, 2010).

The contents of **^{90}Sr** and **^{137}Cs** in the natural environment of Europe and Poland after the Chernobyl accident systematically decrease. This is a result of the radioactive decay of the two nuclides, their penetration into the soil profile, and their flow with pore and river waters into the Baltic Sea (Saxen, Ilus, 2000; Smith *et al.*, 2000; Pietrzak-Flis *et al.*, 2001). The inflow of river waters has an essential effect on the distribution of ^{90}Sr and ^{137}Cs in the coastal zones and river estuaries of the southern Baltic Sea. In the 1990s, the concentration of the two radionuclides in the river waters was 10–20 times lower compared to the concentrations in the Baltic water. In 1994, the mean activity of ^{137}Cs in the surface waters of the drainage basins of the Vistula, Odra and the Pomeranian rivers was 6.8, 9.6 and 4.4 Bq/m^3, respectively. However, the mean ^{90}Sr concentration in the Vistula mouth achieved 5.4 Bq/m^3. The studies of 2005–2007 indicated a decrease in the concentrations of ^{90}Sr and ^{137}Cs radionuclides in the waters of the Vistula and Odra drainage basins (Table 5.7). The inflow of radionuclides from land in 1994–2005 reduced the activity of ^{90}Sr and ^{137}Cs in the coastal zone, especially in the river mouths, proportionally to the decrease in the water salinity (IMGW, 1991–2004).

The ^{90}Sr and ^{137}Cs radionuclides found in the topoil layer undergo partial outwashing and flow from the drainage basins into the southern Baltic Sea. The amount of run-off depends mainly on the radiostrontium and

Table 5.7

Mean concentration of ^{90}Sr and ^{137}Cs in waters of the Vistula and Odra drainage basins and their run-off to the southern Baltic in 2005 and 2007 years (Pietrzak-Flis *et al.*, 2007)

Drainage basin	^{90}Sr		^{137}Cs		^{90}Sr	^{137}Cs
	[Bq/m^3]					
	2005	2007	2005	2007	Run-off in 2007 [GBq]	
Vistula	4.3	3.0	2.2	1.8	100	60
Odra	4.4	3.7	3.4	3.0	65	55

radiocaesium concentrations, and on the soil composition. Their largest contents in soil were observed in the Odra drainage basin (Katowice, Opole, Wrocław, and Wałbrzych provinces; Radiological Atlas of Poland, 1992; Strzelecki *et al*., 1993). Based on the mean annual water flows of the Vistula and Odra rivers, the current flow of ^{90}Sr and ^{137}Cs from the two drainage basins was calculated in 2007 (Table 5.7). In general, about 280 GBq of both the radioisotopes flowed from the Vistula and Odra drainage basins in 2007.

The research on the flow of the **polonium, uranium** and **plutonium radionuclides** from the drainage basins of the Vistula River, Odra River and the Pomeranian rivers was carried out in 2002–2004. The sampling locations are shown in Figure 5.22.

The Vistula drainage basin. Mean annual concentrations of ^{210}Po, ^{238}U and $^{239+240}$Pu in the waters of the Vistula and its tributaries are presented in Table 5.8. The highest concentrations of the radionuclides in the Vistula waters are at Dęblin (polonium, plutonium) and Malbork (uranium), whereas the lowest are at Sandomierz (plutonium), Kraków (uranium, plutonium) and Grudziądz (plutonium). Amongst the Vistula tributaries, the highest concentrations of the radionuclides occur in the Bzura (polonium), Bug (uranium) and Drwęca (plutonium). The lowest values were measured in the Drwęca (polonium), Brda (uranium), Bug (plutonium) and Narew (plutonium).

Based on the water flow rates in the Vistula River and its tributaries, the annual flow of polonium, uranium and plutonium was assessed for the Vistula drainage basin (Table 5.9). The annual flow of ^{210}Po in both branches of the Vistula (Leniwka and Nogat) is 71.6 GBq at Kiezmark and 2.1 GBq at Malbork. Amongst the tributaries of the Vistula, the Bug and Narew shows the largest run-off of ^{210}Po (34.53 GBq). In turn, the highest flow of ^{238}U in the Vistula waters was observed at Kiezmark (222.8 GBq), whereas the lowest – at Kraków (7.0 GBq). The maximum yearly uranium flow was observed in the Bug and Narew (81.2 GBq), the lowest – in the Brda (3.1 GBq). It means that the uranium run-off from the Vistula drainage basin is almost 6 times higher in comparison to the polonium flow. This may indicate a considerable effect of the anthropogenic component due to human activity (phosphatic fertilisers in farming, coal combustion, mining water discharge) on the level of the uranium run-off from the Vistula drainage basin. The largest $^{239+240}$Pu flow in the Vistula waters was measured at Kiezmark (86.0 MBq), the lowest – at Malbork (2.90 MBq). Amongst the tributaries of the Vistula, the highest plutonium run-off was observed in the upland San River (42.7 MBq), whereas the lowest – in the Nida River (2.30 MBq). The total annual $^{239+240}$Pu flow from the Vistula drainage basin to the Baltic Sea amounts to 89 MBq. As time goes on, especially after the Chernobyl nuclear explosion, its flow in the Vistula waters has continued to drop. Similar estimations made in 1989 showed a mean $^{239+240}$Pu flow in the Vistula waters to the Gulf of Gdańsk at 192 MBq (Skwarzec, Bojanowski, 1992). It suggests that the plutonium run-off from the Vistula drainage basin reduced almost twice over about 15 years.

Based on the surface areas of the drainage basins of the Vistula tributaries, the annual flows of the polonium, uranium and plutonium radionuclides per km^2 were calculated (Figs. 5.23–5.25). Mean yearly run-offs of polonium and uranium from the Vistula drainage basin were the highest in the upland tributary of the Dunajec (1720 kBq/km^2 for ^{210}Po and 2330 kBq/km^2 for ^{238}U), whereas the lowest were observed in the lowland tributary of the Narew (150 kBq/km^2 for ^{210}Po and 430 kBq/km^2 for ^{238}U). The most important sources of polonium in the upland tributaries of the Vistula drainage basin are erosion of rock material, leaching as well as wet and dry atmospheric fallout (Skwarzec, 2002). The situation is similar for the anthropogenic $^{239+240}$Pu, whose largest surface flows are in the upland tributar-

Fig. 5.22. River sampling sites for chemical analyses (Skwarzec, 2009)

ies: the San (2553 kBq/km^2) and the Dunajec (1994 kBq/km^2), while the lowest in the lowland tributary of the Narew (220 kBq/km^2) (Skwarzec, Jahnz, 2007; Skwarzec, 2009).

The Odra drainage basin. The yearly mean concentrations of ^{210}Po, ^{238}U, and $^{239+240}$Pu in the samples taken from the Odra and its tributaries are given in Table 5.10. The highest ^{210}Po, ^{238}U and $^{239+240}$Pu concentrations in the Odra River are observed at Słubice (polonium), Głogów (uranium) and Chałupki (plutonium), the lowest – at Głogów (polonium), Chałupki (uranium) and Widuchowa (plutonium). Amongst the Oder tributaries, the maximum ^{210}Po, ^{238}U, and $^{239+240}$P concentrations were observed in the Nysa Łużycka, Bystrzyca, Mała Panew and Barycz rivers.

The annual flow of polonium, uranium and plutonium was estimated in the Odra drainage basin based on the water flows in this river (Table 5.11). The highest yearly ^{210}Po run-off in the Odra waters was noted at Gozdowice, whereas lowest – at Chałupki. Among the Odra tributaries, the Warta River is marked by the highest polonium run-off. The maximum ^{238}U flow in the Odra waters was measured at Widuchowa, the lowest – at Chałupki. In turn, the largest $^{239+240}$Pu run-off in the main stream of the Odra was recorded at Gozdowice, the smallest – at Chałupki. The maximum plutonium flow was characteristic for the Warta, and the minimum – for the Barycz.

Based on the surface area of the drainage basins of the Odra tributaries, the flow of radionuclides per

Table 5.8

Mean annual concentrations of ^{210}Po, ^{238}U and $^{239+240}$Pu in waters of the Vistula and its tributaries (Skwarzec, 2009)

Sample location	^{210}Po	^{238}U	$^{239+240}$Pu [mBq/m^3]
	[Bq/m^3]		
Vistula			
Cracow	2.00 ±0.03	5.25 ±0.22	2.23 ±0.41
Sandomierz	1.94 ±0.03	5.38 ±0.17	3.54 ±0.52
Dęblin	3.21 ±0.04	5.36 ±0.14	4.95 ±0.75
Warsaw	2.81 ±0.04	6.70 ±0.25	3.62 ±0.55
Toruń	2.21 ±0.05	6.37 ±0.23	3.40 ±0.76
Grudziądz	2.35 ±0.04	7.44 ±0.26	2.22 ±0.40
Malbork	3.17 ±0.05	11.49 ±0.21	4.32 ±0.54
Kiezmark	2.33 ±0.04	8.43 ±0.20	3.08 ±0.54
Tributaries of the Vistula			
Nida	2.85 ±0.03	7.57 ±0.24	4.87 ±2.78
Dunajec	2.24 ±0.05	4.62 ±0.14	3.31 ±0.85
San	2.49 ±0.04	6.37 ±0.18	8.83 ±2.98
Wieprz	4.91 ±0.05	6.71 ±0.19	6.27 ±1.17
Pilica	4.32 ±0.03	6.30 ±0.17	8.44 ±1.74
Narew	3.44 ±0.04	8.28 ±0.31	6.92 ±1.04
Bug	3.65 ±0.03	10.31 ±0.19	5.90 ±1.26
Bug and Narew	4.23 ±0.04	9.43 ±0.18	3.16 ±0.67
Drwęca	2.15 ±0.04	6.97 ±0.17	10.33 ±1.69
Brda	2.33 ±0.04	3.83 ±0.10	7.99 ±2.47
Bzura	6.03 ±0.03	9.83 ±0.37	5.81 ±1.46

Table 5.9

Annual flow of ^{210}Po, ^{238}U and $^{239+240}$ Pu in the Vistula basin (Skwarzec, 2009)

Sample location	^{210}Po	^{238}U	$^{239+240}$ Pu [MBq]
	[GBq]		
Vistula			
Cracow	3.60	7.0	4.20
Sandomierz	16.45	45.3	34.5
Dęblin	52.51	65.4	83.3
Warsaw	41.95	96.8	44.1
Toruń	58.30	142.8	70.7
Grudziądz	61.92	182.6	61.3
Malbork	2.14	7.8	2.90
Kiezmark	71.57	222.8	86.0
Tributaries of the Vistula			
Nida	1.43	3.4	2.30
Dunajec	11.7	15.9	13.6
San	10.69	26.7	42.7
Wieprz	5.89	6.5	7.24
Pilica	5.48	8.5	12.7
Narew	11.32	32.1	25.3
Bug	13.71	50.7	19.7
Bug and Narew	34.53	81.2	25.2
Drwęca	1.97	5.9	9.51
Brda	1.84	3.1	6.47
Bzura	3.26	6.2	2.99

1 km^2 was calculated for polonium, uranium, and plutonium (Figs. 5.23–5.25). The highest yearly surface flows of ^{210}Po are noted in the upland tributaries: the Nysa Łużycka (245 kBq/km^2) and the Nysa Kłodzka (229 kBq/km^2). The lowest flows are observed in the Barycz (8 kBq/km^2). A particularly high surface flow of ^{238}U was observed in the Bystrzyca (5244 kBq/km^2), and the lowest – in the Mała Panew (126 kBq/km^2). Very high uranium run-off from the Bystrzyca drainage basin, several times larger than in the other tributaries, is a result of weathering and erosional processes of the Sudetic rocks, which contain elevated natural concen-

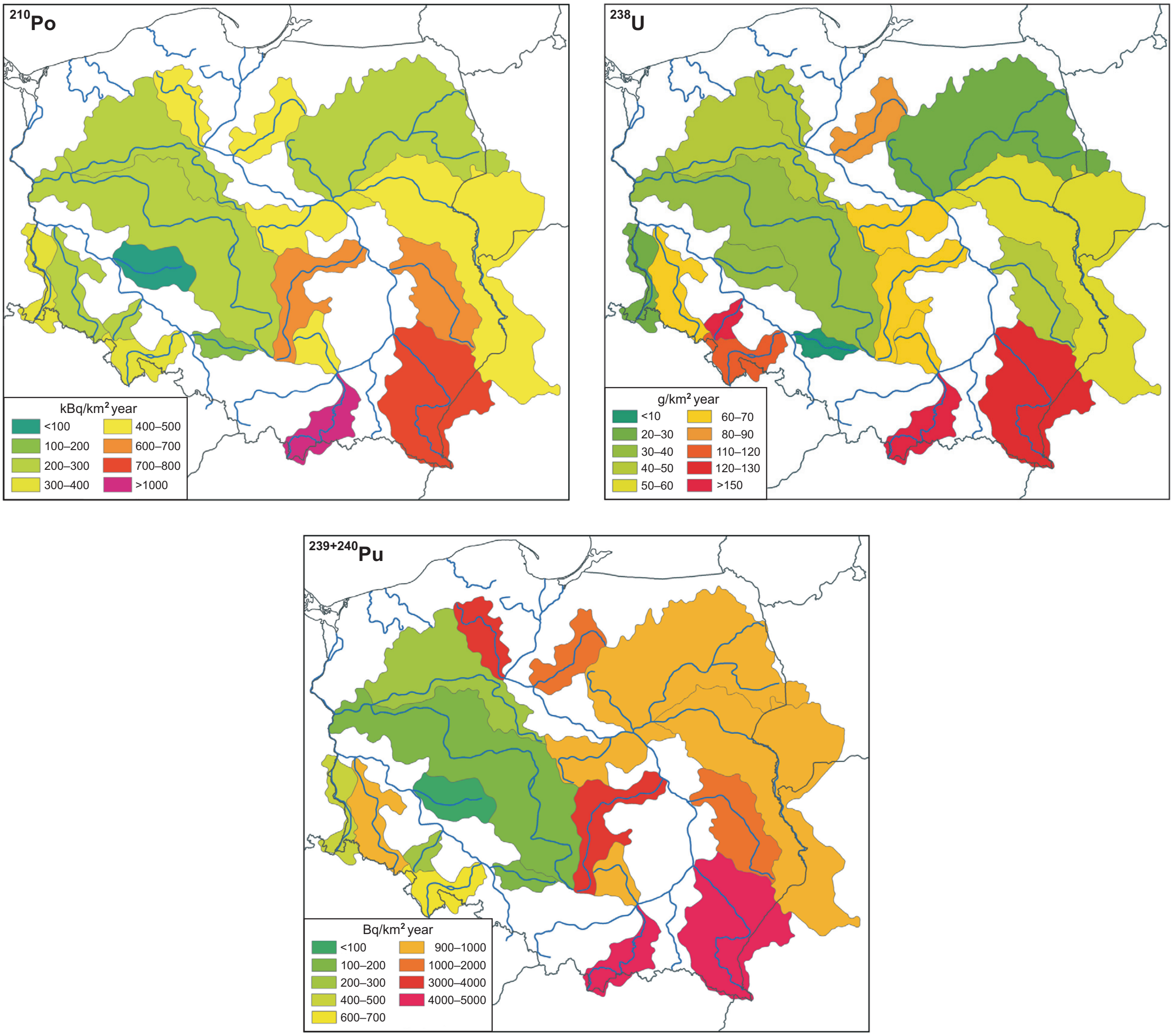

Fig. 5.23. Annual surface run-off of ^{210}Po, ^{238}U, $^{239+240}$Pu from the Vistula and Odra drainage basins (Skwarzec, 2009)

trations of uranium and radium (Bem, 2005). The maximum annual surface flow of $^{239+240}$Pu occurs in the Bóbr (1230 Bq/km^2), whereas the minimum values are found in the Barycz (67 Bq/km^2).

The Pomeranian rivers. The mean contents of polonium, uranium, and plutonium in the waters of the three most important Pomeranian rivers along the Polish coast are given in Table 5.12. The annual run-offs on these radionuclides from the Pomeranian rivers were as follows: for ^{210}Po 0.72–3.48 GBq, for ^{238}U 1.64–3.84 GBq, and for $^{239+240}$Pu 0.64–7.20 MBq (Skwarzec, 2009).

Radium ^{226}Ra in the rivers of Poland. The Polish rivers contain small amounts of ^{226}Ra, varying from 0.50 to 56.9 Bq/m^3. However, for most rivers the values do not exceed 2 Bq/m^3 (Wardaszko *et al.*, 2001). The highest values were observed in the Upper Vistula River, which

Table 5.10

Mean annual concentrations of ^{210}Po, ^{238}U and $^{239+240}$Pu in the Odra drainage basin (Skwarzec, 2009)

Sample location	^{210}Po	^{238}U	$^{239+240}$Pu [mBq/m^3]
	[Bq/m^3]		
Odra			
Chałupki	2.00 ±0.05	3.91 ±0.12	4.59 ±0.89
Głogów	1.46 ±0.06	11.11 ±0.32	2.85 ±0.65
Słubice	2.39 ±0.05	10.05 ±0.31	3.41 ±0.86
Gozdowice	1.89 ±0.05	7.55 ±0.23	3.54 ±0.69
Widuchowa	1.65 ±0.05	8.45 ±0.27	1.99 ±0.47
Tributaries of the Odra			
Mała Panew	1.99 ±0.05	1.94 ±0.06	2.18 ±0.45
Nysa Kłodzka	2.96 ±0.06	10.73 ±0.24	4.32 ±0.66
Bystrzyca	3.39 ±0.06	68.24 ±1.42	2.78 ±0.47
Barycz	1.02 ±0.06	6.85 ±0.21	1.62 ±0.46
Bóbr	1.88 ±0.06	5.23 ±0.16	7.27 ±1.39
Nysa Łużycka	3.64 ±0.07	3.35 ±0.07	3.99 ±0.55
Warta	1.85 ±0.05	6.02 ±0.29	2.73 ±0.86
Noteć	1.48 ±0.06	6.06 ±0.22	3.48 ±0.72

Table 5.11

Annual flow of ^{210}Po, ^{238}U and $^{239+240}$Pu in the Odra drainage basin (Skwarzec, 2009)

Sample location	^{210}Po	^{238}U	$^{239+240}$ Pu [MBq]
	[GBq]		
Odra			
Chałupki	1.20	4.99	15.41
Głogów	3.75	51.88	17.32
Słubice	8.91	78.14	26.64
Gozdowice	14.76	100.08	45.86
Widuchowa	13.11	107.00	23.01
Tributaries of the Odra			
Mała Panew	0.15	0.27	0.48
Nysa Kłodzka	1.05	6.65	3.16
Bystrzyca	0.22	9.27	0.46
Barycz	0.04	2.05	0.37
Bóbr	0.85	5.25	7.23
Nysa Łużycka	1.05	1.47	1.95
Warta	6.25	26.99	12.10
Noteć	2.22	11.06	5.92

is associated with discharging mining waters from Upper Silesian hard coal mines through settling ponds and minor watercourses (Chałupnik *et al*., 2001). The Upper Silesian Coal Basin is marked by one of the largest radiohydrogeological anomalies in the world, as far as the radium concentration and the intensity of the radioactive water outflow are concerned. In saline waters that flow out of the rock mass of the Upper Silesian mines, the concentrations are considerably higher than in the river waters and maximally reach 420 kBq/m^3, including 390 kBq/m^3 of ^{226}Ra, and 30 kBq/m^3 of ^{228}Ra and ^{224}Ra (Lebecka *et al*., 1986; Chałupnik, Lebecka, 1995; Pociask-

Table 5.12

Mean concentration of ^{210}Po, ^{238}U and $^{239+240}$Pu in the Pomeranian rivers (Skwarzec, 2009)

River	^{210}Po	^{238}U	$^{239+240}$Pu [mBq/m^3]
	[Bq/m^3]		
Rega	3.82 ±0.24	8.97 ±0.52	3.38 ± 0.98
Parsęta	5.50 ±0.33	6.19 ±0.30	11.58 ±0.49
Słupia	4.84 ±0.21	5.10 ±0.29	3.90 ±1.08

Karteczka *et al*., 2001). Higher concentrations of ^{226}Ra, exceeding 3 Bq/m^3, were observed in the rivers of farming area (e.g. in the Warta); they were due to washing out of radium from applied phosphatic fertilisers. Taking into account the mean ^{226}Ra content in the waters of Polish rivers (1 Bq/m^3) and the mean yearly flow of the river waters from the basins of the Vistula, Oder and Pomeranian rivers, the annual run-off of this radionuclide to the Baltic Sea has been estimated at 60 GBq.

*

The drainage basins of the Vistula, Oder and Pomeranian rivers are the main sources of polonium, radium and plutonium in the southern Baltic Sea (Table 5.13), 97% of the radionuclides from the Vistula basin flow into the Gulf of Gdańsk, and 3% of them – into the Vistula Lagoon. Wet and dry atmospheric fallout (both containing terrigenous material), particles of weathered rocks (^{210}Po, ^{238}U) and radioactive particles from nuclear explosions in the atmosphere (global radioactive atmospheric fallout) and from the Chernobyl nuclear power plant (^{90}Sr, ^{137}Cs, $^{239+240}$Pu) are the main sources of radionuclides in the land and water environment of Poland. Another source of polonium and uranium in the natural environment is intense coal combustion (app. 100 million tons) (Niewiadomski *et al*., 1988; Nowina-Konopka, 1993). The content of heavy elements and radionuclides (e.g. ^{238}U, ^{226}Ra, ^{210}Po, ^{210}Pb) in hard coal is below 0.1% of its mass and its considerable part is emitted to the atmosphere as gases and flue dusts during the process of combustion. The rest passes out with the ash (Nakaoka *et al*., 1984; Flues *et al.,* 2002; Bem, 2005). Atmospheric dusts that form during coal combustion contain about 1700 Bq/kg of ^{210}Po and 200 Bq/kg of ^{238}U (Baxter, 1996).

Table 5.13

Annual flow of ^{210}Po, ^{234}U, ^{238}U, ^{238}Pu and $^{239+240}$Pu from the drainage basins of the Vistula, the Odra and the Pomeranian rivers into the Baltic Sea (Skwarzec, 2009)

Radionukclide	Drainage basin of the Vistula	Drainage basin of the Odra	Pomeranian rivers	Total
^{210}Po [GBq]	73.70	14.76	6.00	94.46
^{234}U [GBq]	276.80	126.29	8.24	411.33
^{238}U [GBq]	230.60	100.80	7.36	338.76
U total [t]	18.80	8.19	0.60	27.59
^{238}Pu [MBq]	10.13	9.51	2.60	22.24
$^{239+240}$Pu [MBq]	82.50	45.86	9.28	137.64

The flow of uranium and radium through drainage basins is intensified by human activities, mainly farming (the use of phosphatic fertilisers) and heavy industry (metallurgy and mining) by discharging mining and post-metallurgical waters into the rivers. Phosphatic rocks used to manufacture phosphatic fertilisers are considerably enriched with polonium, uranium and radium radionuclides (Bolivar *et al*., 1995; Chałupnik *et al*., 2001; Bem, 2005). During the manufacturing of phosphatic fertilisers, about 10% of ^{226}Ra, 20% of uranium and 85% of ^{210}Po are transferred to the phosphogypsum wastes (Carvalho *et al*., 2007). Near the factories of the phosphatic fertilisers in Gdańsk (Vistula River estuary) and Police (Odra River mouth), the uranium and polonium concentrations are much higher compared to the non-contaminated areas (Boryło *et al*., 2009; Skwarzec *et al*., 2010). As a consequence, the uranium concentration in the water from the Vistula River mouth is considerably higher than the extrapolated value obtained from the relation of its concentration as a function of the Baltic Sea water salinity. It demonstrates the contribution of anthropogenic components in the river waters that flow to the southern Baltic Sea (Skwarzec, 1995).

Different values of the plutonium run-off from the drainage basins of the Vistula, Odra, and Pomeranian rivers may also result from its various contents in the topsoil layer and in the river deposits. The lowest $^{239+240}$Pu concentration in river sediment samples taken in 2007 was measured in Warsaw (Vistula River) – 4.8 mBq/kg, whereas the highest – at Chałupki (Odra River) – 151 mBq/kg. The mean plutonium concentration in the river sediments of the Odra drainage basin is almost twice as high as in the Vistula drainage basin. In addition, 30% of plutonium found in the river bottom sediments at Pułtusk (Narew River) and Chałupki (Odra River) is of Chernobyl origin (Pietrzak-Flis *et al*., 2007).

Appendix 1

Glossary

(for Chapters 5.3. and 10)

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Activity – number of radioactive decays occurring within a time unit. The unit of activity in the SI System is becquerel (1 Bq is one decay per second).

BCF – bioconcentration factor defined as the ratio of nuclide concentration in a biological tissue (Bq/kg w.w) to its concentration in water (Bq/dm^3).

DC (distribution coefficient) – enrichment factor defined as the ratio of a nuclide concentration in the suspended matter (Bq/kg w.w.) to the concentration of its all forms dissolved in water (Bq/dm^3).

d.w. – dry weight.

Effective dose – total of doses from the outer and inner exposure in all organs and tissues with suitable weight coefficients of ionising radiation and tissues. In the SI system, a unit of the effective dose is sievert (Sv).

Radiation equilibrium – stationary state in which the number of the produced nuclide nuclei is equal to the number of nuclide nuclei undergoing the decay per time unit.

Radiation protection – the whole of issues concerning the protection of people and the environment against the detrimental effects of ionising radiation.

Radioactivity – the ability to emit ionising radiation (α, β, γ).

Radioactive decay – spontaneous transformation of the nuclei of one radionuclide into the nuclei of another one with simultaneous emission of corpuscular particles (α or β) and electromagnetic radiation γ that sometimes accompanies them.

Radioelement – chemical element that has at least one of its isotopes radioactive.

T – half-life (half-life of radioisotope) – period of time after which a number of nuclei for a given nuclide undergoing radioactive decay will be reduced by half.

TF – transfer factor defined as the ratio of nuclide concentration within the consumer body (Bq/kg w.w.) to its concentration in food (Bq/dm^3).

w.w. – wet weight.

5.4. Natural Migration of Liquid and Gaseous Subsurface Hydrocarbons into Bottom Sediments and Waters

The Polish Exclusive Economic Zone of the Baltic Sea involves liquid and gaseous hydrocarbons that currently migrate into the sediments and sea bottom waters from the hydrocarbon deposits occurring in the basement, and from the gas- and oil-bearing rocks. They have been recognised as geogenic substances whose origin, chemical composition and physical properties result from natural geological processes, contrary to commonly known anthropogenous pollution. Besides hydrocarbons, there are also mineralised brines containing various heavy metals, thermal waters and hydrogen sulphide.

The regional geological deep survey conducted so far by the Polish Geological Institute-National Research Institute in the far northern part of Poland as well as the prospecting works carried out offshore by Petrobaltic S.A. suggest the occurrence of lithological complexes in the basement of the Polish Exclusive Economic Zone of the Baltic Sea, which may be the source of harmful geogenic substances. These complexes include:

- Black shales containing radioelements and heavy metals (Cambrian, Ordovician);
- Reservoir rocks for hydrocarbons containing, apart from the discovered and undiscovered crude oil and/or natural gas deposits, carbon dioxide, hydrogen sulphide and methane (Middle Cambrian, Carboniferous, Rotliegend, Zechstein);
- Volcanics, the source of thermal water enrichment with sulphides, heavy metals (also with mercury) as well as extremely high concentrations of gases: hydrogen, nitrogen, and both carbon oxide and dioxide (Rotliegend);
- Evaporites, the source of concentrated salt leaches (Zechstein);
- Reservoir rocks of highly mineralised and thermal waters (Cambrian, Devonian, Carboniferous, Rotliegend, Zechstein, Buntsandstein, Lower and Upper Jurassic, Lower Cretaceous).

The main migration pathways of geogenic substances, including hydrocarbons, onto the sea bed are major fault zones and the areas of sediment pinchouts that contain these substances.

Polish and international achievements concerning the geochemical survey of the southern Baltic sediments and petroleum exploration are very modest. The western part of the Polish Exclusive Economic Zone of the Baltic Sea was included into the German SASO programme (near the Wolin Block). The programme did not deal with geochemical contamination of the German part of the sea (or any other), but contained elements that might be useful for its estimation (Schlüter *et al*., 1997). In the utmost western part of the Baltic Sea, in the Eckenfoerde Bay (a small branch of the Kiel Bay), a study of the pockmark type structures occurring on the surface of the sea bottom sediments was carried out. It was proved that they were formed as a result of the undersea outflows of artesian freshwaters. These waters originate from the Cenozoic groundwater reservoir (Khandriche, Werner, 1995). The studies were included into the international Sub-GATE programme that also involved selected regions of Skagerrak and the Irish Sea. The problem of faults as migration pathways of geogenic substances to the Baltic Sea waters is discussed in the studies by Jurgens *et al*. (2000), and Kvenvolden and Cooper (2003).

No special study on the contamination of the Baltic Sea environment with harmful substances from the subsurface (pre-Cenozoic) geological structures was conducted at that time. Although the occurrence of natural substances of geologic provenance, harmful to the environment, was obvious, it has never been taken into account in the environmental assessments of the southern part of the Baltic Sea.

In 1999–2001, Petrobaltic S.A. carried out a local geochemical study of the Łeba Block within its exploration work. The results directly proved the active role of faults in transporting substances both harmful to the natural environment and originating from subsurface geological structures in the Polish Exclusive Economic Zone of the Baltic Sea (Jaworowski *et al*., 2001; Strzetelski *et al*., 2004).

The implementation of the issue “Geochemical studies of sediments from the southern Baltic Sea based on analyses of geogenic contaminations and petroleum exploration" made in 2005–2008 became a breakthrough (Anolik, Karczewska, eds., 2008; Jaworowski, Wagner, eds., 2008). The studies proved the occurrence of ascending migration of gaseous and liquid hydrocarbons along the major fault zones, including non-hydrocarbon fluids and gases concerning toxic hydrogen sulphide and aqueous solutions containing heavy metals. The occurrence of anomalies in the form of liquid and gaseous hydrocarbons accompanying the fault zones was recognised in the sea bottom sediments and waters, where any relationships of those substances with the human activity were excluded. Thus, these anomalies were of natural origin, what proves undoubtedly the existence of geogenic substances that are harmful to the environment (Jaworowski *et al*., 2010).

Petroleum exploration also provided some material to assess possible migration pathways through the zones of pinchouts of sediment complexes (Anolik, Karczewska, eds., 2008). Since no sophisticated studies of this type were carried out in other parts of the Baltic Sea, the Polish Exclusive Economic Zone may become a testing ground to assess the occurrence of this phenomenon and its scale. Undoubtedly, conclusions drawn in this area may be typical of the whole sea.

5.4.1. Migration of Subsurface Hydrocarbons Through Major Fault Zones

The main migration routes of liquid and gaseous hydrocarbons originating from subsurface geological structures are discontinuous tectonic deformations, i.e. major fault zones and related systems of fissures. The main faults located in the Polish Exclusive Economic Zone that could serve as the migration pathways for geogenic substances are shown in a structural-tectonic map of the southern Baltic Sea (Fig. 5.24).

In the area of the East European Craton, the main, deeply rooted fault zones of Darłowo, Ustka, Łeba, Smołdzino, Kuźnica and Sambia were active in the early Paleozoic, partly as syn-sedimentary faults, and also in the late Paleozoic (Carboniferous–Permian) (Fig. 5.25). At that time, the following fault blocks were formed in the cratonic part of the sea: Darłowo, Ustka, Słupsk, Smołdzino, Łeba, Żarnowiec, Rozewie, Courland, and Gdańsk. The fault zones were renewed as part of the inversion processes of the Middle Polish Trough at the turn of the Cretaceous and Paleogene, and they all reach either the sub-Cenozoic surface or even the recent bottom sediments. These faults resulted from multiple renewals and activations of large discontinuity zones in the crystalline basement. This view is confirmed by observations of the terrestrial part of the Peri-Baltic Syneclise, where large contact zones of different age crystalline complexes manifested their activities in later geologic epochs.

As regards the East European Craton, repeatedly renewed faults are very important potential migration pathways for geogenic substances. Environmentally harmful hydrocarbons may reach the Baltic Sea bottom sediments and waters through the faults. Within the craton are the faults that penetrate the very thick and continuous cover of the Silurian claystones and mudstones, and, in the southern part, also the Zechstein evaporites, huge complexes of strata that seal older formations and make the migration of solutions along the borders of the Lower Paleozoic sedimentary complexes impossible.

In the western part of the Polish Exclusive Economic Zone of the Baltic Sea, i.e. within the borders of the Paleozoic platform, there are three large fault zones: Koszalin, Trzebiatów and Kamień Pomorski. Similarly to the Scandinavian section of the Teisseyre-Tornquist Zone (TTZ), they may be considered as old Precambrian fissures. According to other opinions, they should be associated with the Caledonian folding-overthrust orogeny or accretionary mosaic of fault blocks – terranes formed between the Ordovician and middle Middle Silurian or in the Silurian, or at the end of the Silurian and at the beginning of the Devonian. No matter which opinion will prove to be the most likely (Znosko, 1962, 1998; Dadlez, 2000), it can be assumed that the final layout of the blocks was established at the end of the Carboniferous and early Permian. At the end of the Mesozoic, during the Cretaceous tectonic inversion, three fault zones were rejuvenated. In the craton and in the Paleozoic platform (the blocks of Wolin, Gryfice and Kołobrzeg), the fault zones are migration pathways for hydrocarbons.

The interpretation of the geogenic activity generally depends on the intensity of the flux of geogenic substances, but the type of sea bottom sediments, water movements, seismic activity, etc. should also be taken

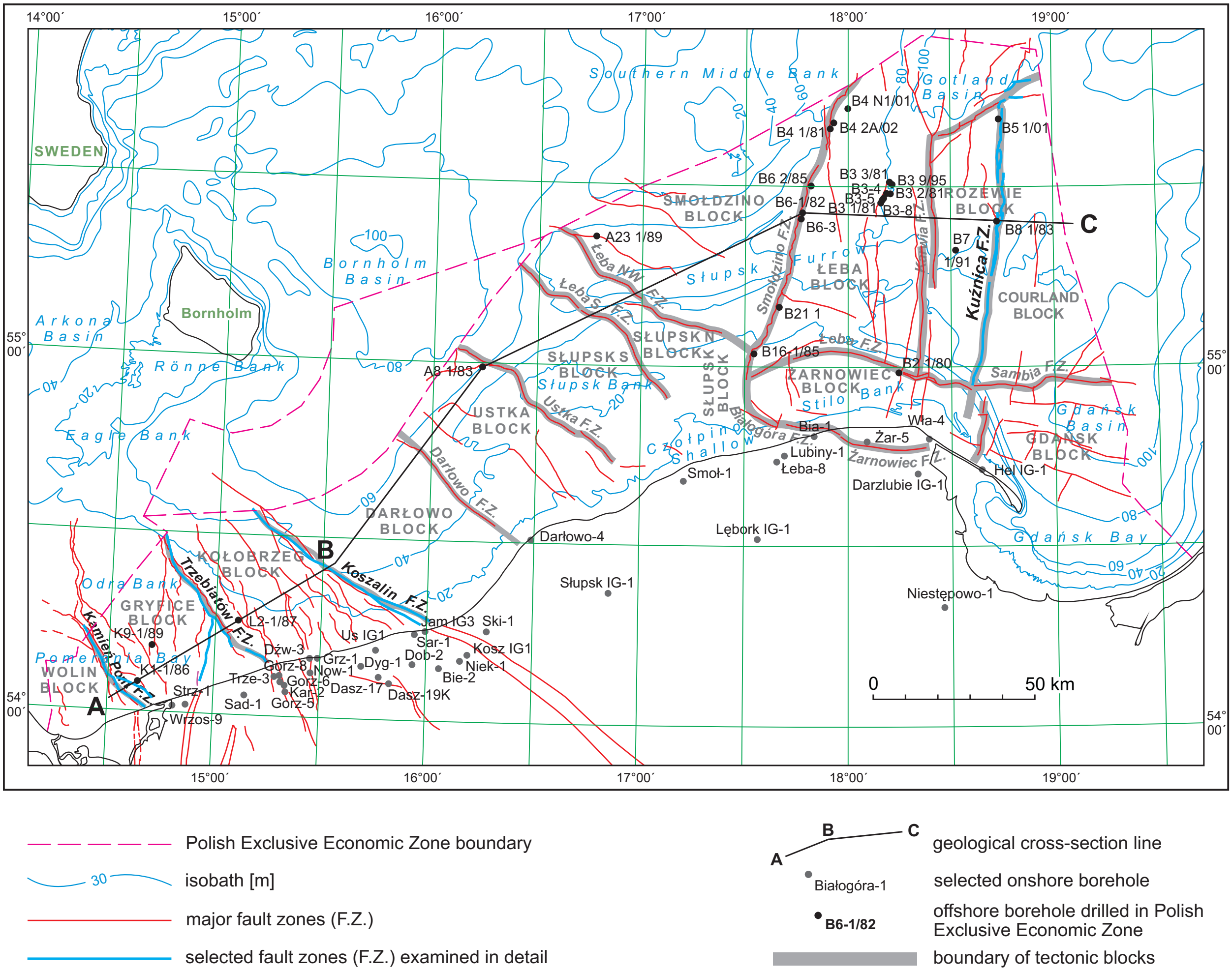

Fig. 5.24. Structural-tectonic sketch map of the Polish Exclusive Economic Zone of the Baltic Sea (after Jaworowski *et al.*, 2010)

into consideration. The variability of these conditions, especially seismic activity, has a significant effect on the variability of the analytically determined concentrations of geogenic substances. Clay and muddy (silty) sediments have high sorption susceptibility for hydrocarbons, which may achieve considerable concentrations. In sand and gravel sediments, the contents of hydrocarbons are insignificant. Gaseous and liquid hydrocarbons in the sea bottom water layers are particularly effective at washing out during intense wave motions, which is demonstrated by the considerable reduction of their concentrations in samples taken under storm conditions.

The tectonic movements of the Earth's crust, even in very distant areas, have also a large or even a decisive effect on the intensity of the flux of geogenic substances. During the seismic restrain, the content of hydrocarbons in samples distinctly decreases to be rapidly elevated during the tectonic movements.

Detailed studies performed to check unambiguously the possibility of vertical migration of geogenic substances were made for four major fault zones. In the

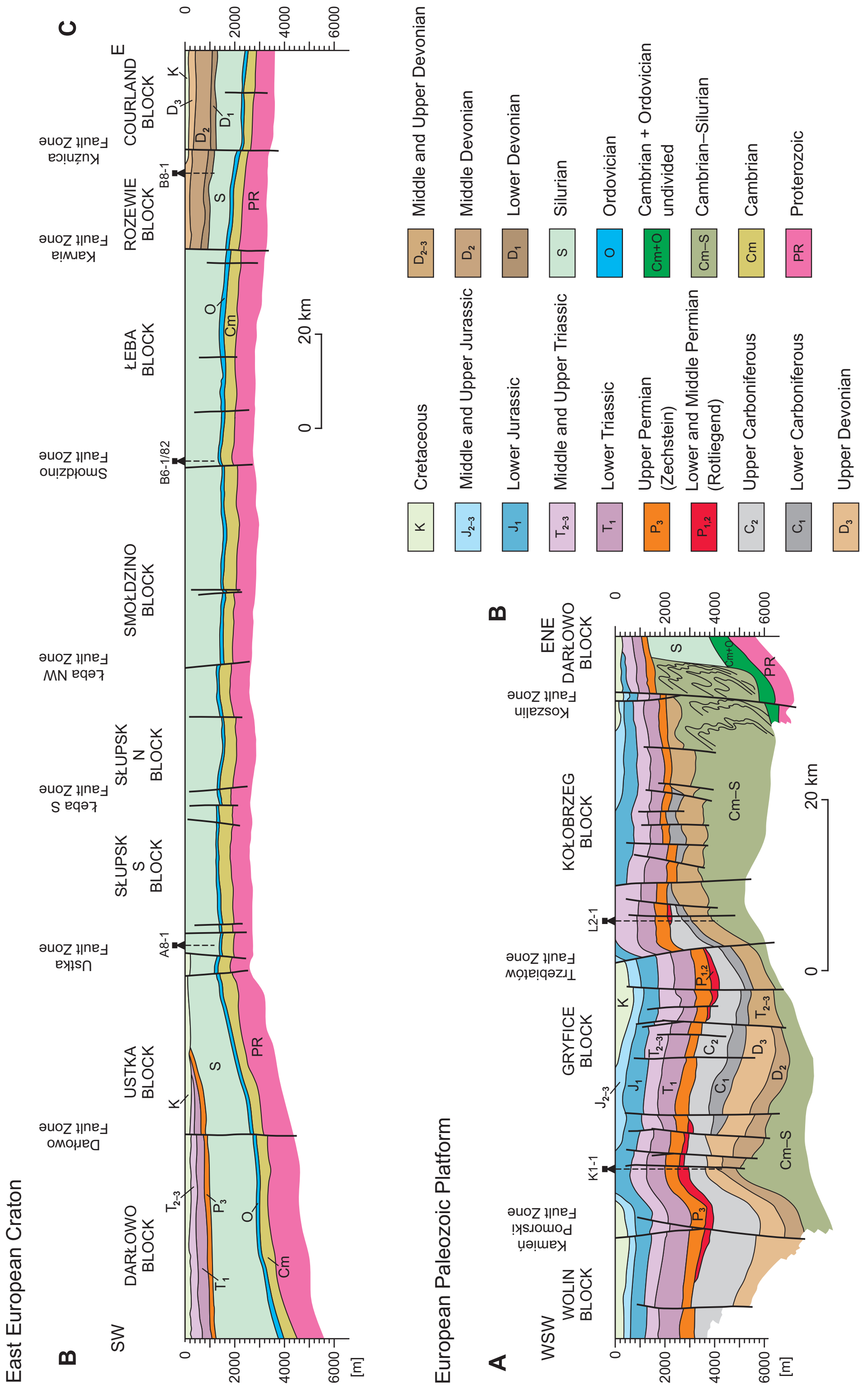

Fig. 5.25. Regional geological cross-section A–B; B–C (after Jaworowski *et al.*, 2010)

craton, it was the Kuźnica Fault Zone, and in the Paleozoic platform – the fault zones of Koszalin, Trzebiatów and Kamień Pomorski (Jaworowski, Wagner, eds., 2008; Jaworowski *et al*., 2010). Each fault zone was investigated with three geochemical profiles located in the western wing, in the axis of the fault and in the eastern wing.

The Kuźnica Fault Zone, situated on the East European Craton, in the eastern part of the Polish Exclusive Economic Zone of the Baltic Sea, is more than a 100-km long tectonic fracture deeply rooted in the top part of the lithosphere in the N–S axis. It separates two fault blocks: the Courland Block in the east and the Rozewie Block in the west. Together with the Karwia and Smołdzino faults, located further to the west and characterised by similar directions and origins, the Kuźnica Fault Zone played a very important role in the tectonic evolution of this area (Dadlez, 1990; Dadlez, Pokorski, 1995; Pokorski, Modliński, eds., 2007).

The fault zone probably originated in the early Proterozoic, or in the Cambrian, affecting facies differentiation in the early Paleozoic, particularly in the Middle Cambrian, determining distribution of source rocks for crude oil and natural gas deposits in the Cambrian formations. The most important role was played by this zone at the end of the Carboniferous, actively influencing the formation of the present erosive ranges of the older and younger Paleozoic. The zone was also active in the Mesozoic and the Cenozoic up to the present time. Generally, the hanging wall is located to the east of the fault. In the southern part, the Kuźnica Fault Zone is crossed by the Sambia fault in the latitudinal direction.

The Kuźnica Fault Zone was selected for the study of geogenic events owing to its activity along a short section of the B8 oil deposit (Jaworowski *et al*., 2001). In the uplifted western wing, near the fault, there are two crude oil deposits in the Cambrian formations: deposit B8 and B5, situated to the north of the first one. Thus, the investigation of almost the entire fault zone created the best opportunities to catch its geogenic activities (Fig. 5.26).

The sea near the fault is 80–90 m deep and lowers to 105 m only in the northern part, on the slope of the Gotland Basin. In the southern part of the Sambia fault, the sea bottom rises up to 55 m. Under normal weather conditions, the considerable depths of the sea protects against washing carbonate concentrations due to wave motion.

The sea bottom sediments are usually composed of Holocene clays and clayey muds with a subordinate fraction of fine-grained sands. The character of the sea bottom sediments was favourable for the sorption of hydrocarbons in the sediments.

Many times higher contents of liquid hydrocarbons in the sea bottom waters were found along the axis of the fault zone compared to the fault wings (Table 5.14). At the same time, the mean contents of liquid hydrocarbons in the sediment along the fault axis (C) and in the hanging wall (E) are similar, with a minimal advantage for profile E. The concentrations of methane in the bottom sea water are the highest in profile E, while in the sediments – in profile W. Methane is always associated with heavy hydrocarbons. These data make it possible to define the axial zone of the Kuźnica Fault as very active in the processes of the migration and outflow of liquid and gaseous hydrocarbons, definitely more active than in either wall.

In this tectonic zone geogenic phenomena were the most intensive in its northern and central part. Strong and very strong anomalies in liquid hydrocarbons contents in the bottom marine waters, occurring as oil spills, ranging from 50 to 195 mg/l and up to 0.8 wt.% in the bottom sediments and hazardous for natural environment, are associated with crude oil deposits B5 and B8 in the Middle Cambrian. The outflows are entering the sea bottom surface along the tectonic zone, despite the large thickness (from 1,000 to 1,700 m) of the Silurian claystones being very good sealing rocks.

The lack of anomalies in the contents of hydrocarbons in the southern part of the Kuźnica Fault may result from seismic restrain while taking samples, and, which is more probable, with the occurrence of Zechstein rock salts as sealing layers. Only gaseous anomalies were observed here. Being more mobile, gases can more easily migrate through rock salt.

The isotopic content of gases shows that, in most samples, methane is one of the main product of the thermogenous processes of transformation of fossil organic substance (Anolik, Karczewska, eds., 2008).

In the eastern part of the East European Craton, detailed investigations were carried out only in the Kuźnica Fault Zone. There is no doubt that other fault

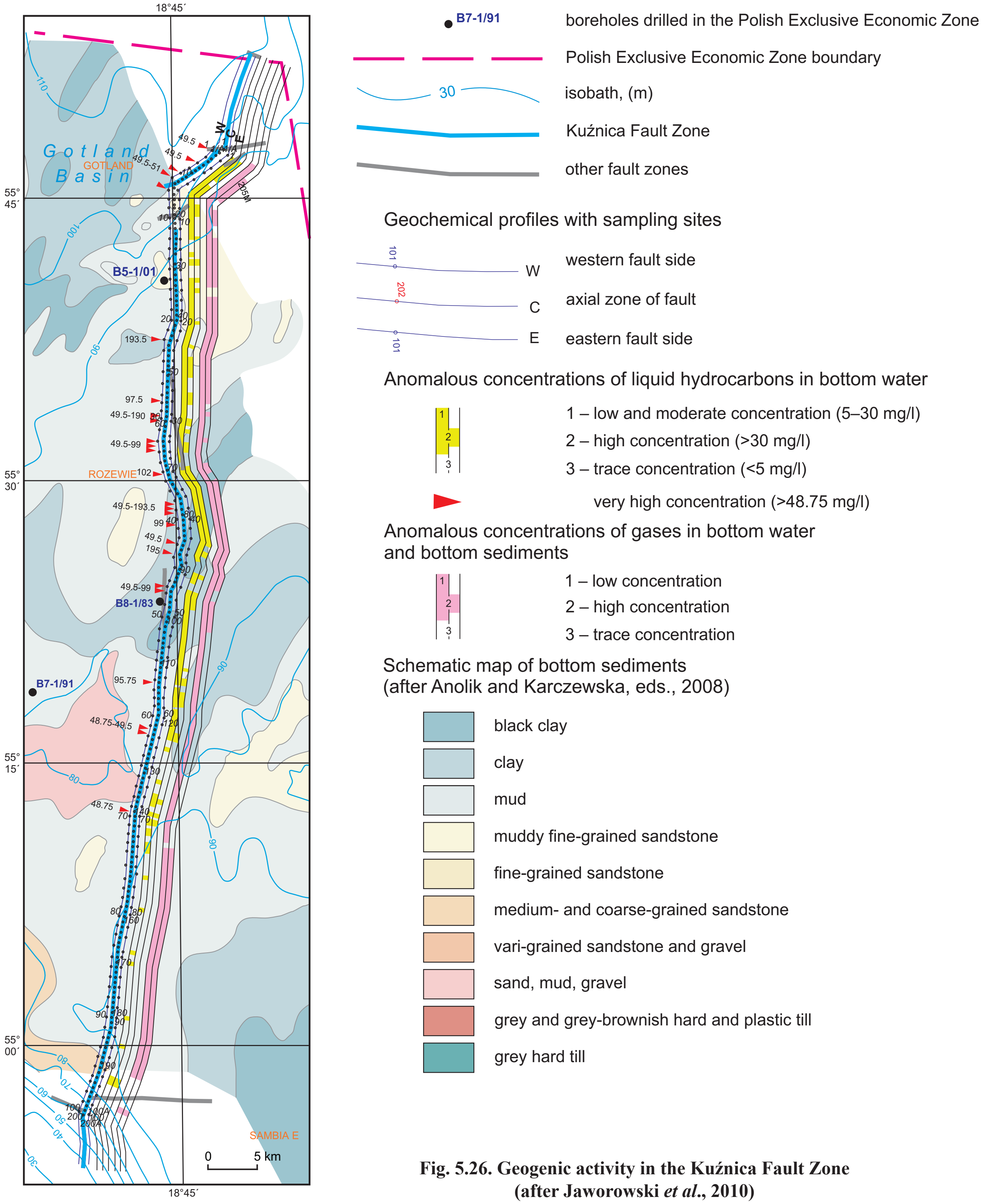

Fig. 5.26. Geogenic activity in the Kuźnica Fault Zone (after Jaworowski *et al.*, 2010)

Table 5.14

Geochemical characteristic of geogenic activity in the Kuźnica Fault Zone (Jaworowski *et al.*, 2010)

Geochemical parameter	Geochemical profiles		
	W (Łeba Block)	C (fault axis)	E (Courland Block)
Liquid hydrocarbons in bottom water (mg/l)	0.74 to 51.00 (101) **2.25** (6.43)	1.12 to 195.00 (202) **6.75** (23.06)	1.12 to 27.00 (101) **3.00** (4.39)
Liquid hydrocarbons in sediments (wt.%)	0.0055 to 0.5277 (98) **0.0518** (0.0966)	0.0093 to 0.8308 (190) **0.0543** (0.1128)	0.0106 to 0.5493 (96) **0.1012** (0.1650)
Methane concentration in water ($\times 10^{-4}$ vol.%)	5.6 to 96 500 (100) **30.80** (2 455.25)	4.50 to 328 100.00 (200) **31.10** (4 827.61)	6.7 to 627 500.00 (101) **42.25** (8 974.38)
Methane concentration in sediments ($\times 10^{-4}$ vol.%)	17.45 to 141.31 (29) **57.90** (64.12)	3.64 to 149.03 (86) **38.61** (56.02)	8.96 to 145.17 (93) **30.64** (36.78)

Range of geochemical parameters is given as numerator, median value in denominator – **bold**; in parentheses: number of analyses (numerator), arithmetic mean (denominator).

zones on the fault blocks of Kuźnica and Łeba, not investigated in detail so far, will also be shown to transmit subsurface hydrocarbons, especially the Smołdzino Fault Zone with its several gas and oil deposits (B16, B21, B6, B4).

The Koszalin Fault Zone, oriented NW–SE, constitutes the northern part of a wide fracture referred to as the Teisseyre-Tornquist Zone (TTZ) and is deeply rooted down to the Moho surface. The TTZ runs across Poland, from the Lublin Upland to Pomerania, being part of a great global lineament spreading out from Dobrogea to Oslo. That zone, in its northern section, from the Baltic Sea and Scania to Oslo, is called the Sorgenfrei-Tornquist Zone (STZ). The TTZ and STZ form, to a large extent, the western border of the East European Craton (EEC).

The Koszalin Fault Zone is situated in the western periphery of the East European Craton, forming the border between the Darłowo and Kołobrzeg fault blocks and bordering on the Paleozoic platform, although it is not a border for these two huge platforms, each of which dates back to different ages. The Koszalin fault is associated with the western periphery of the folded early Paleozoic (Caledonian deformations). The Caledonides are overthrust on the craton, on the autochthonous lower Paleozoic of the Precambrian platform. The scale of this thrust is very diverse and may reach even several tens of kilometres (Fig. 5.25).

The Koszalin Fault Zone is represented offshore by a reverse fault with a western footwall and hanging wall of up to 200–300 m. In the south section, this fault is accompanied by one or two normal faults with the east hanging wall.

The Koszalin Fault Zone played a great role in the geological evolution of this region with its effect on the palaeographic development of the geologic systems. This zone was rejuvenated at the end of the late Paleozoic, forming an outstanding tectonic element that diversifies the subsidence in the western part (strong subsidence) and in the eastern part (weak subsidence) in Permian and Mesozoic times.

The sea depth in the SE part of the Koszalin Fault is shallow, approximately 10 m, and increases gradually up to about 50 m in the NW part. Generally, the fault is located in a shallow part of the sea that is susceptible to storm activities.

The sea bottom sediments consist of sand and gravel only. These are extremely unfavourable conditions for liquid hydrocarbons to become preserved in the sedi-

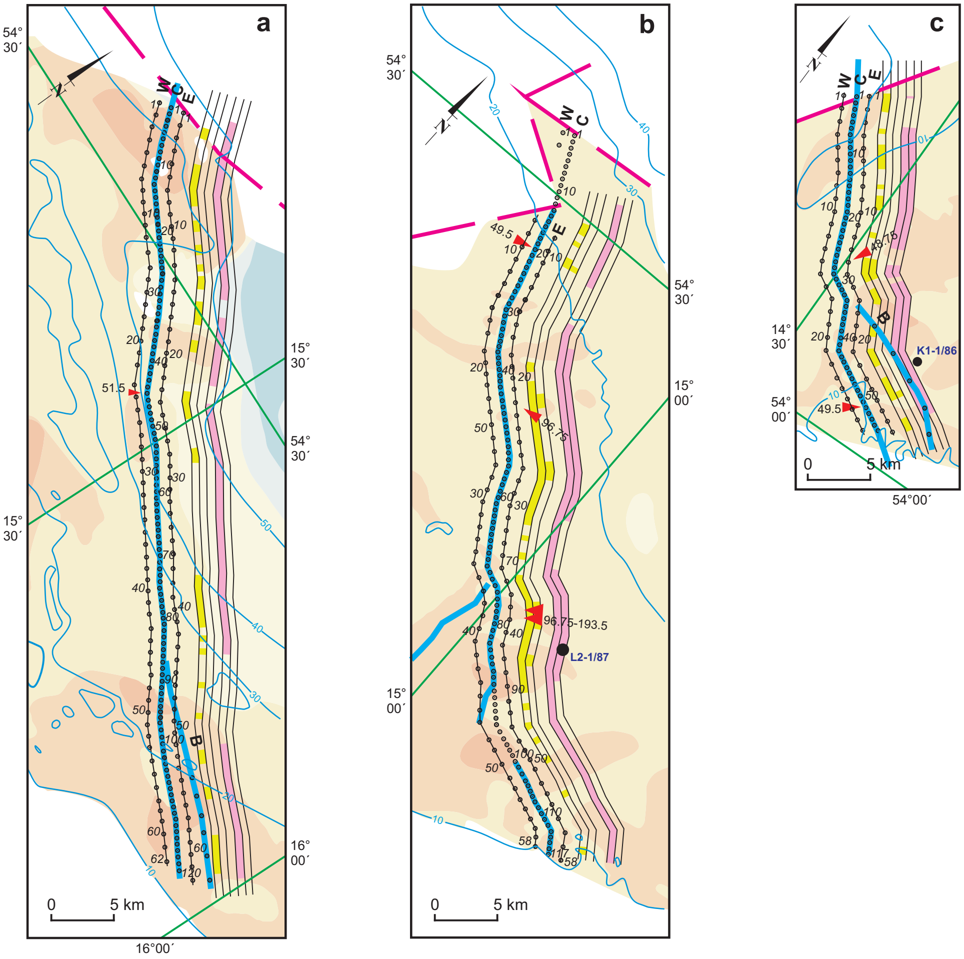

Fig. 5.27. Geogenic activity in the Koszalin (a), Trzebiatów (b) and Kamień Pomorski (c) fault zones (after Jaworowski *et al*., 2010). For explanations see Fig. 5.26

ments, because these types of sediments show no sorbing ability.

The Koszalin Fault Zone was investigated with three parallel geochemical profiles, running 500 m apart, with an additional profile (B) in the southern part of the fault (Fig. 5.27a).

Geochemical anomalies of the Koszalin Fault Zone are marked by low contents of liquid and gaseous hydrocarbons in the sea bottom water, whereas they do not occur in the central part of the fault zone (Table 5.15). The comparison between medians and arithmetic means indicates slightly higher contents of hydrocarbons in the axis of the fault zone for liquid hydrocarbons and methane concentrations. Generally, their values are comparable. The results suggest that the Koszalin Fault Zone is a very weak source of geogenic hazards.

The Trzebiatów Fault Zone belongs to the most important tectonic elements of the Paleozoic platform, separating the Kołobrzeg Block from the Gryfice Block. This zone is a set of several faults trending nearly NW-SE. The primary fault is deeply rooted in the crystalline basement.

The Trzebiatów Fault Zone can be considered the old Precambrian tectonic structure. The final layout of the

Table 5.15

Geochemical characteristic of geogenic activity in the Koszalin Fault Zone (Jaworowski *et al.*, 2010)

Geochemical parameter	Geochemical profiles			
	W (Kołobrzeg Block)	C (fault axis)	E (Darłowo Block)	B (Darłowo Block)
Liquid hydrocarbons in bottom water [mg/l]	1.50 to 21.00 (62) **3.75** (4.20)	1.50 to 51.00 (120) **2.25** (4.88)	1.50 to 25.50 (62) **2.25** (4.79)	2.25 to 4.50 (6) **1.5** (2.50)
Methane concentration in water [$\times 10^{-4}$ vol.%]	3.84 to 8.86 (62) **5.28** (5.75)	4.20 to 11.58 (131) **5.54** (6.19)	0.00 to 11.13 (62) **5.31** (5.90)	7.52 to 8.48 (6) **8.15** (8.11)
Methane concentration in sediments [$\times 10^{-4}$ vol.%]	–	14.57 to 5 674.81 (4) **144.12** (1 550.03)	341 to 592.73 (2) **467.22** (467.22)	–

Range of geochemical parameters is given as numerator, median value in denominator – **bold**; in parentheses: number of analyses (numerator), arithmetic mean (denominator).

Kołobrzeg and Gryfice fault blocks was fixed between the Carboniferous and early Permian periods, when the main restructuring of the Devonian–Carboniferous complex took place. The whole area was strongly faulted and a complicated mosaic of blocks of different sizes was formed. The next fundamental structural rebuilding took place in the latest Cretaceous–earliest Paleogene times, when the Trzebiatów Zone was rejuvenated. These tectonic processes, including the inversion, finally formed the present structural pattern of this area. During rejuvenation, the eastern or north-eastern parts of this zone were uplifted and the Triassic and Jurassic formations came out on the sub-Cenozoic surface resulting in the formation of the Kołobrzeg Swell. In the western part, the Trzebiatów tectonic basin was formed and filled with Cretaceous deposits.

In northern part of the Trzebiatów Fault Zone, the fault throws are up to 1,000 m, whereas in the southern part, they decline to 200–300 m; however, in Dadlez's opinion (1990), the fault passes into a steep flexure. The sea depth in this region is shallow, from 10 m to 30 m. The fault is located in a shallow part of the sea, susceptible to the impacts of storms. The bottom sea sediments are composed of sand and gravel only. These are extremely unfavourable conditions for liquid hydrocarbon accumulations in sediments due to lack of sorption ability.

The Trzebiatów Fault Zone was investigated with three parallel geochemical profiles, running 500 m apart (Fig. 5.27b).

The highest concentrations of liquid hydrocarbons in the sea bottom water were determined in profile E, i.e. theoretically located in the eastern wall of the fault (Table 5.16). The methane content in water was slightly higher in profile C.

Higher geochemical activity in profile E is explained by the incorrect location of some part of profile C beyond the axis zone and by conducting a larger part of profile E exactly in the axis of the fault. This mistake could have resulted from the incorrect assessment of the Trzebiatów fault plane, which caused the inexact calculation of intersectional cross-cut of the fault axial zone with the sea bottom surface. On the other hand, it should be considered that the samples in profile C were taken when the North European seismic activity was decreasing, unlike profile E, where the activity was very high, which could affect the results of the analyses to a considerable extent.

The Trzebiatów Fault Zone is very active in the processes of migration and seepage of liquid and gaseous hydrocarbons. In terms of liquid hydrocarbon seepage into bottom waters, the most active is the central part of profile E that probably goes through

Table 5.16

Geochemical characteristic of geogenic activity in theTrzebiatów Fault Zone (Jaworowski *et al.*, 2010)

Geochemical parameter	Geochemical profiles		
	W (Gryfice Block)	C (fault axis)	E (Kołobrzeg Block)
Liquid hydrocarbons in bottom water [mg/l]	2.25 to 51.00 (45) **4.50** (5.93)	1.50 to 49.5 (117) **3.75** (5.63)	2.25 to 193.5 (30) **6.00 (**19.33)
Methane concentration in water [$\times10^{-4}$ vol.%]	0.00 to 10.51 (64) **7.30** (7.01)	4.70 to 60.10 (117) **8.10** (8.94)	4.52 to 20.00 (61) **7.30** (7.71)
Methane concentration in sediments [$\times10^{-4}$ vol.%]	7.07 to 7.69 (2) **7.38** (7.38)	0.00 to 10.51 (117) **7.76** (8.24)	–

Range of geochemical parameters is given as numerator, median value in denominator – **bold**; in parentheses: number of analyses (numerator), arithmetic mean (denominator).

the axial fault zone. The contents of liquid hydrocarbons, attaining the maximum values of 96–193 mg/l, make a considerable pollution of natural environment. Profiles W and C are marked by weaker anomalies, although individual analyses show quite high values of 30–50 mg/l. The content of methane in waters is high in the southern part of the fault zone, attaining 10.5–60.1 $\times10^{-4}$ vol. %.

Vertical migration of gaseous and in particular liquid hydrocarbons occurs despite sealing horizons of the Zechstein rock salt. Considering the isotope composition of the gaseous hydrocarbons, methane was formed mainly in thermogenous processes of metamorphosis of fossil organic substance, as most samples proved (Anolik, Karczewska, eds., 2008).

The Kamień Pomorski Fault Zone separates the Gryfice Block from the Wolin Block. It is a set of several faults trending approximately NW–SE. In the German part of the Baltic Sea, it passes into the Adler Fault Zone and for that reason its other name is the Kamień Pomorski–Adler Fault. The main fault is deeply rooted into the crystalline basement. The tectonic origin and evolution of this zone is the same as the Trzebiatów Zone, i.e. it was tectonically rebuilt during two stages: at the turn of Carboniferous and Permian, and latest Cretaceous and earliest Paleogene. The fault zone was rejuvenated during the inversion, which finally fixed its present structural location. The main fault of this zone is a reverse fault. The size of the fault throw also varies, reaching up to 500 m. In the eastern side of the fault, Jurassic deposits subcrop at the sub-Cenozoic surface, forming the Kamień Pomorski anticline with the Lower Jurassic strata in its core. Upper Cretaceous deposits occur in the western part of the fault with a few anticlines in the southern part and with Jurassic deposits overlying the salt structures. The fault is detected by drilling and seismic surveys down to the base of the Zechstein.

The sea depth in the vicinity of the Kamień Pomorski Fault is not large, from 8 to 14 m. The fault is located in a very shallow part of the sea, on the Oder Bank, which is subject to storms effects.

The bottom sea sediments are composed of sand and gravel only. These are extremely unfavourable conditions for liquid hydrocarbon accumulations in sediments due to lack of sorbtion ability.

The Kamień Pomorski Fault Zone was surveyed with three parallel geochemical profiles, running 500 m apart, with an additional profile (B) (Fig. 5.27c).

The highest concentrations of liquid hydrocarbons in the sea bottom waters were observed in profile E, on the eastern side of the fault. The content of methane in

Table 5.17

Geochemical characteristic of geogenic activity in the Kamień Pomorski Fault Zone (Jaworowski *et al.*, 2010)

Geochemical parameter	Geochemical profiles			
	W (Wolin Block)	C (fault axis)	E (Gryfice Block)	B (Gryfice Block)
Liquid hydrocarbons in bottom water [mg/l]	9.00 to 24.75 (28) **9.00** (6.75)	1.50 to 49.5 (56) **3.00** (5.00)	1.50 to 75.00 (28) **3.00** (7.63)	3.00 to 6.00 (5) **4.50** (4.50)
Methane concentration in water [$\times 10^{-4}$ vol.%]	7.50 to 12.10 (27) **10.05** (9.88)	6.30 to 16.70 (57) **9.55** (9.66)	7.70 to 10.4 (27) **8.40** (9.33)	8.30 to 9.40 (5) **8.90** (8.96)
Methane concentration in sediments [$\times 10^{-4}$ vol.%]	4.71 to 9.14 (27) **7.71** (7.29)	0.00 to 10.40 (55) **8.51** (7.00)	3.74 to 10.34 (27) **7.67** (7.59)	0.00 to 8.58 (5) **5.25** (8.48)

Range of geochemical parameters is given as numerator, median value in denominator – **bold**; in parentheses: number of analyses (numerator), arithmetic mean (denominator).

waters and sediments is comparable in all profiles (Table 5.17).

Similarly to the Trzebiatów Fault Zone, any comparison between arithmetic means and medians for the individual profiles in order to indicate the highest activity of the fault axial zone is pointless for the Kamień Pomorski Fault Zone. This is because the samples were taken not exactly from the axial zone, owing to the variable inclination of the fault zone. However, it enables us to compare the intensity of the geogenic events in the individual fault zones.

The Kamień Pomoski Fault Zone is marked by high concentrations of gaseous hydrocarbons (methane and butylene) and heavy hydrocarbons in the sea bottom waters, definitely contaminating the natural environment. The butylene fractions, being part of the hydrocarbon phase of this zone, are by one order of magnitude higher than other gaseous hydrocarbons, including methane, forming huge concentrations, which suggests their crude oil origin. The contents of liquid hydrocarbons are low, with isolated large seepage spots where concentration values range from 48.75 to 75 mg/l. The isotope content indicates that, for a definite majority of the tested samples, methane was formed mainly as a result of thermogenous processes of alteration of fossil organic matter (Anolik, Karczewska, eds., 2008).

5.4.2. Migration of Subsurface Hydrocarbons through the Pinchout Zones of Sedimentary Complexes

Apart from disjunctive tectonic deformations, important migration routes for harmful geogenic substances, including hydrocarbons, may be regional pinchout zones of sedimentary complexes. The zones of erosional pinchouts associated with post-Cretaceous erosion may play a special role in transporting geogenic liquids and gases (Kramarska *et al*., 1999). As regards the cratonic part of the Baltic Sea basement (Gdańsk, Courland, Rozewie, Łeba, Żarnowiec, Smołdzino, Słupsk, Ustka and Darłowo blocks), these types of zones involve pinchouts resulted from erosional truncation of gentle, broad elevations of the Paleozoic–Mesozoic sedimentary cover with Cenozoic deposits. There are also pinchouts associated with the original (sedimentary) extents of the occurrences of Paleozoic and Mesozoic sedimentary complexes in this area. The events of middle Paleozoic and post-Cretaceous erosion, essential for the trends of the pinchout zones, decreased the areas of these occurrences. With the reference to the Paleozoic platform in the Baltic Sea basement (Kołobrzeg, Gryfice and Wolin blocks), the regional pinchout zones resulted from erosional truncation of relatively narrow fold structures

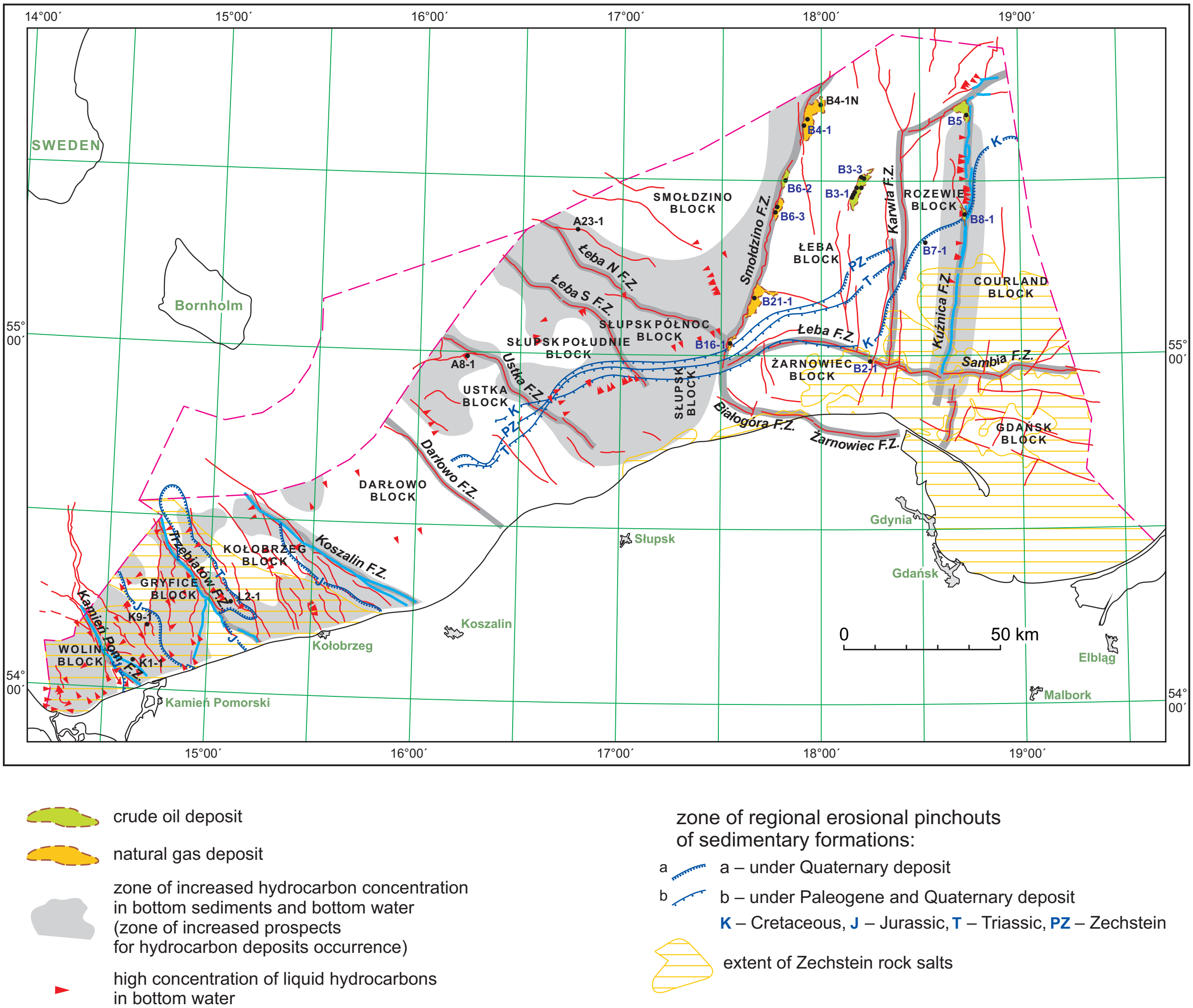

Fig. 5.28. Areas at the greatest risk from geogenic pollution (after Jaworowski *et al*., 2010, modified). For other explanations see Fig. 5.24

of the Mesozoic cover. During the construction of the geological map of the Baltic Sea bottom, “fans” of gases penetrating into the bottom sediments were discovered in the seismo-acoustic profiles (Uścinowicz, Zachowicz, 1992). They were situated crosswise to the fault zones and parallel to the regional pinchouts of the basement deposits. Also during the survey conducted for the needs of the crude oil prospecting, a series of gaseous anomalies was detected. The anomalies were not associated with fault zones and were located parallel to the regional pinchouts of the basement deposits (Fig. 5.28).

In the East European Craton, both hydrocarbon deposits and their parent formations occur under a thick cover of Silurian claystones, whereas in the southern part of the area they are overlain by sealing horizons of Zechstein evaporites, including rock salt. It may be assumed that under these conditions hydrocarbons migrate through vertical fault zones cutting the lower Paleozoic sedimentary cover and reaching not only the Mesozoic cover but also the recent sediments. Part of the migrating hydrocarbons may be subsequently transported through the Mesozoic reservoir horizons towards regional uplifts to reach the pinchout zones of these sediments, penetrating through the recent sediments to the waters of the Baltic Sea.

The results of recent studies confirm this model, making it more precise and modifying it (Jaworowski *et al*., 2010). The role of vertical migration through the fault zones is dominant. Nevertheless, the lateral migration also led to significant anomalies along regional and sub-Cenozoic outcrops of Zechstein, Triassic and Cretaceous deposits.

Lower and upper Paleozoic sediments occur within the Paleozoic platform in the Polish part of the Baltic Sea, i.e. in the Kołobrzeg, Gryfice and Wolin blocks, under the Permian–Mesozoic structural complex. Devonian and Carboniferous deposits, forming several blocks of strata dipping towards the NE, are observed here (Dadlez, Pokorski, 1995). The sediments are sealed by the salt-bearing Zechstein (Wagner, 1990) as well as by thick Mesozoic formations, and they cannot play any significant role in lateral migration.

The Mesozoic deposits are the only good migration paths for hydrocarbons penetrating the fault zones, originating from still undiscovered accumulations in the upper Paleozoic. The regional pinchout zones occur on sides of anticline structures. In the Kołobrzeg and Gryfice blocks, erosional limits of Triassic, Jurassic and Cretaceous strata subcrop onto the Quaternary surface.

The elevated concentrations of hydrocarbons correlate very well with the fault and petroleum deposit zones (Fig. 5.28). In the southern part of the Rozewie Block, there is a regional zone of pinchouts, defined by the extent of Cretaceous deposits overlying the Devonian. It subcrops onto the sub-Quaternary surface. In the southern part of the Łeba Block, we can observe regional pinchout zones defined by the boundariess between the Cretaceous and Triassic deposits, Triassic and Zechstein deposits, as well as Zechstein and Silurian deposits. The western part of the pinchout zone underlies Paleogene deposits, and the southern one subcrops at the sub-Quaternary surface (Jaworowski *et al*., 2010). It may be assumed that the pinchout zones will be active in the processes of subsurface migrations of hydrocarbons, analogically to the migrations in these zones found in the neighbouring Słupsk blocks. Worth noting are also the anomalies of high concentrations of hydrocarbons observed in the clay bottom sediments of the Słupsk Furrow, i.e. on the outskirts of the mentioned regional zones of the erosional pinchouts in the Permian–Mesozoic deposits.

No hydrocarbon deposits have been discovered so far in the area of the Paleozoic platform of the Baltic Sea basin, which does not mean that they do not occur there, similarly to the West Pomerania, where several small deposits have been discovered in the Carboniferous and Zechstein. The high activity of the Trzebiatów and Kamień Pomorski fault zones for the migration of subsurface hydrocarbons may suggest the occurrence of hydrocarbon accumulations in the Baltic Sea. The activity of the Koszalin Fault Zone is relatively weak.

In the Trzebiatów Fault Zone, there is a sub-Quaternary regional pinchout zone determined by the erosional limit of Triassic and Jurassic deposits.

A distinct zone of pinchouts determined by the erosional limits of Jurassic and Cretaceous deposits runs NW–SE approximately along the axial part of the Gryfice Block. A small section of the pinchout zone on the border of the Cretaceous and Jurassic areas is located in the utmost south-eastern part of the Gryfice Block. The pinchout zones subcrop onto the sub-Quaternary surface. Chaotically scattered occurrences of high concentrations of liquid hydrocarbons in the sea bottom waters suggest a dense network of faults that reach the sub-Quaternary surface and numerous pinchout zones (Jaworowski *et al*., 2010).

The results of the studies confirmed fully the earlier suggestions that liquid and gaseous hydrocarbons of subsurface origin leach into the waters of the Baltic Sea, and the scale of this event exceeded any expectations (Jaworowski *et al*., 2010).

5.5. Groundwater Discharge in the Baltic Sea Basin

The phenomena of groundwater discharge that occur in the Baltic Sea basin are mostly analysed in the coastal zone. Scarcely analysed is the run-off of groundwater to the sea directly through bottom sediments and of the substances that the water contains. However, in the last thirty years, several domestic and international projects dealing with these problems have been implemented. Additionally, different methods of the assessment of the phenomenon have been tested.

The bottom of the Baltic Sea is a final element in draining the aquifer system of fresh waters flowing down the land towards the sea. Mineralised and thermal waters from deep aquifer structures also infiltrate through the bottom deposits. Depending on the intensity of these processes, the submarine groundwater discharge (SGD) shows different symptoms. One of them includes alterations in salinity and temperature in the vertical section (inversions) and also changes in chloride concentrations in the pore waters of the bottom deposits. The occurrence of the pockmark-type structures or concentrations of freshwater diatom species may also indicate places of the underground freshwater outflow. The alterations in the chemical composition of the bottom sediments and their pore waters are an important but still poorly recognised effect of groundwater discharge. Neither do we have detailed information about the dynamics of groundwater infiltration through the bottom sediments, including the distribution and intensity of these processes. The exception is the Puck Bay, where a trial was undertaken to recognise the symptoms of freshwater outflows from the sea bottom and the width of the SGD (Piekarek-Jankowska, 1994).

The study methods concerning the assessment of the events related to SGD are taken from a wide range of offshore geological surveys, and from classic hydrogeological methods. Seismo-acoustic research is one of the basic methods to evaluate the geological structure and topography of the sea bottom, especially the methods of sonar profiling of the side-scan sonar type. It is necessary to survey directly the sea bottom deposits. It involves taking samples of the sediments and the water, and measuring the hydrological structure of the sea water, especially profiling of salinity changes and temperature. In shallow marine areas, it is possible to carry out field investigations to measure directly the underground outflow by using infiltrometers. Laboratory tests complement the field surveys and enable us to make complex analyses of the sea bottom deposits, to test chlorides in the pore waters and to analyse concentrations of stable isotopes of oxygen and hydrogen in the bottom waters and pore waters of the bottom sediments.

A complex analysis of hydrogeological conditions requires the identification of a coastal aquifer system onshore and, if possible, offshore. It is also recommended to recognise a hydrodynamic field of the Baltic Sea coastal groundwater. A mathematical model of the water flow and mass transport enables the final verification of the assumed water circulation system and the estimation of the groundwater volume, drained through the sea bottom sediments in the multi-layered aquifer system.

One of the first attempts to assess the occurrence of groundwater under the Baltic Sea bottom adjacent to the Polish coast was presented by Dowgiałło, Kozerski (1975) and Pietrucień (1983). Kozerski and Sadurski (1983) attempted to classify hydrologically the coastal zone of the southern Baltic Sea. A complex assessment of the direct groundwater discharge into the sea basin exemplified by the Puck Bay was presented by Piekarek-Jankowska (1994) who indentified forms and types of SGD, the contribution of the individual aquifer formations and the intensity of the processes. She also indicated the existing symptoms of the groundwater discharge in the sea bottom of the Puck Bay. Similar documentary work was carried out by Kryza (2005) and its team. The work estimated the conditions of the direct groundwater outflow into the Baltic Sea, including the analysis of the possibilities of groundwater management and protection. However, the studies did not go beyond the coastal zone and the phenomenon of the drainage was analysed immediately near the shoreline. Worth noting is also the research results undertaken for the international SEAREG and ASTRA programmes.

An important issue concerning the hydrogeology of the Baltic Sea coast is the occurrence of mineralised (brines) and curative waters. These issues have been available in literature for many years (e.g. Agopsowicz, Pazdro, 1964; Kolago, 1964; Dowgiałło, 1965, 1988; Bojarski, 1966, 1978, 1996; Kwaterkiewicz, Sadurski, 1986; Płochniewski, 1986). However, all the above-mentioned studies focused on mineral waters occurring on land. There is still little information about mineral waters occurring in the aquifer formations under the bottom of the Baltic Sea.

The hydrogeological conditions under the sea bottom in the eastern part of the Baltic Sea are much better explored. In the region of the Gulf of Finland and Gulf of Riga, the groundwater discharge towards the Baltic Sea was observed in deep hydrogeological structures (Silin-Biekczurin, 1958; Verte, 1965). A similar situation occurs in the region of the Sambia Peninsula and the Curonian Lagoon within the boundaries of the Baltic artesian basin (Verte, 1965; Zecker, 1968; Dzilna, 1970). The occurrence of widespread aquifer structures under the bottom of the southern Baltic Sea was also confirmed by Zuzevicius (2010). He made an attempt to reconstruct the hydrogeological conditions under the Baltic Sea artesian basin in the late Pleistocene.

This short presentation of the studies and publications does not exhaust the whole list of hydrogeological works considering the groundwater discharge into the Baltic Sea. Worth mentioning are documentary and mapping studies as well as numerous geotechnical surveys presenting the results of analyses in the field of engineering geology, carried out in the coastal zone and in the shallow waters of river estuaries and sea ports. The results of offshore geological surveys constitute a huge source of information. A suitable analysis of these studies may be useful to solve the issues of the SGD.

5.5.1. Factors Shaping the Submarine Groundwater Discharge

The intensity of groundwater discharge in the bottom deposits of sea basins depends on several factors. The most essential is the geological structure, especially the occurrence of aquifer outcrops, major fault zones, faults and regions susceptible to seismic activity. The sea bottom relief and type, and permeability of the sea bottom sediments are also significant. The symptoms of the SGD may also be significantly modified by the movement of the sea waters, particularly in the near-bottom zone.

The second group of factors affecting the SGD is the hydrogeological conditions onshore and under the sea bottom. Obviously, the amount of hydrogeological reconnaissance is much higher onshore along the coastline. Therefore, it is necessary to recognise the whole hydrostructural system in this area, including the groundwater circulation system that is crucial for the formation of groundwater flows directed towards the sea. The intensity of the SGD is significantly affected by hydrostatic pressures in shallow groundwater reservoirs and by formation pressures of deep aquifers of mineralised and thermal waters. In the regions of intense groundwater extraction, the flow of waters towards the bottom deposits may be reduced or even inverted, which may contribute to the declining of SGD.

A comprehensive analysis of the above-mentioned factors and thorough characteristics of the SGD, including its influence on the chemical condition of the bottom sediments in the southern Baltic Sea, exceeds the scope of this publication. The present stage of recognition permit a general description of the most important factors that constitute SGD, the preliminary identification of the SGD, and the preliminary assessment of the effect of SGD on the chemical condition of the sea bottom sediments.

Geological structure and seabed relief. Fault zones, small thickness of the Cenozoic sediments, subcrops of the Paleozoic and Cretaceous under the Quaternary, and the type of bottom sediments are the factors favourable for the effect of SGD.

In the western part of the coast and the Baltic Sea basin, Upper Cretaceous, Jurassic and Upper Triassic deposits occur under the Quaternary formations. The position of Permian and Triassic deposits directly under the Pleistocene favours the infiltration of mineralised waters into the bottom sediments in this part of the Baltic Sea. Fault zones, characterised by various densities of the fault network, are also crucial for the identification of migration paths of ascending groundwater. Generally, they are oriented perpendicularly to the seashore and occasionally they cut the whole Paleozoic and Mesozoic sedimentary succession. The opposite situation occurs in the eastern part of the southern Baltic Sea. Off the coast, Cretaceous, Neogene and Paleogene deposits occur directly under the Quaternary in vast areas. They are overlain by Lower Triassic and Zechstein deposits. In the Eastern Gotland Basin and to the north of the Słupsk Furrow, Silurian and Devonian, and locally Zechstein and Lower Triassic formations subcrop directly under the Quaternary. Fault zones also occur in the eastern part of the Baltic Sea, although they are considerably less numerous than in the western part of the sea.

The bathymetry of the southern Baltic Sea largely follows the Quaternary surface relief. Near Jarosławiec and Darłówko, numerous depressions occur, reaching 1300–150 m b.s.l. In the vicinity of the erosional incisions (subglacial channels) at Smołdzino and Dębki they reach 240 m b.s.l. These incisions generally continue into the adjacent onshore areas. Subglacial channels are often filled with sandy and sandy-gravelly formations. They are peculiar collectors that transmit groundwater flows to the final basement of the drainage in the bottom sediments of the southern Baltic Sea.

Hydrogeological conditions. The coastal zone of the southern Baltic Sea is distinguished by a multilevel hydrostructural system that includes Cenozoic, locally also Cretaceous and Jurassics aquifers. In the vertical section of the lowland coastal zone, the multiaquifer formation reaches 250 m, and in the vicinity of Gdańsk, it increases to almost 400 m. It mostly contain usable fresh waters, with total dissolved solids (TDS) <1 g/dm^3. Apart from fresh waters, there are also mineralised waters that locally fill the whole of the water-bearing deposits.

The Jurassic multiaquifer formation occurs in the western part of the coast, although it does not show a continuous character. Fresh waters have been found, among others, in Gostyń, Sulikowo, Łukęcin, Rybice, Pobierowo, Trzęsacz, Mrzeżyno, Bagicz and Podczel. They are mostly HCO_3–Ca–Mg type waters, typical of an active exchange zone. The top of the aquifer is at the depth of several metres. Its artesian and subartesian water table stabilizes at 1–18 m a.s.l. It explicitly shows the water flow direction to the Baltic Sea.

In the other regions of the western coast, the Jurassic waters are highly mineralised and used for curative purposes, e.g. in Dziwnówek, Kamień Pomorski and Kołobrzeg. These are Cl–Na or Cl–Ca type, bromide-iodide-boron-ferruginous brines. Their TDS reaches 65 g/dm^3, and the content of chloride ion is even up to 40 g/dm^3. These waters are drained from the bottom sediments of the southern Baltic Sea.

The Cretaceous multiaquifer formation has a diverse character. In the western and central coast, between Uznam Island and the Puck Bay, usable waters occur only locally in the Niechorze, Sarbinowo, Dworek, Jarosławiec, Darłówek, Ustka and Słupsk regions. In the areas in between, there are brines or waters with elevated salinity and TDS content from 0.8 to 10 g/dm^3 (Agopsowicz, Pazdro, 1964). These are Cl–HCO_3–Na type waters, and, at lower chloride concentrations, HCO_3–Cl–Ca–Na–Mg type waters. In Świnoujście, highly mineralised Cretaceous waters are used for curative purposes.

In the eastern coast, near Gdańsk, the Cretaceous waters form an extensive aquifer developed in the Santonian and Coniacian sands. The thickness of the aquifer is up to 100–150 m. Its top is at 160–180 m below sea level (b.s.l.). This is the so-called Gdańsk sub-basin with the Major Groundwater Basin No.111. This reservoir is also widespread under the bottom of the Gulf of Gdańsk and reaches the Hel Peninsula. In the southern part of this reservoir, fissure waters have been found in Maastrichtian carbonates. The Cretaceous aquifer contains low-mineralised groundwater of HCO3–Na type, and, more rarely, of HCO_3–Ca type. High concentrations of the fluoride ion are also a specific feature of these waters, reaching even 5 mg/dm^3 in some places. West of the Vistula River mouth, the Cretaceous waters lose their usable character, and their TDS reaches 10 g/dm^3. Hydrodynamically, it ought to be recognised that the Upper Cretaceous aquifer in the Gdańsk region and under the sea bottom of the Gulf of Gdańsk conducts artesian waters. The vector of hydrostatic pressures is directed upward and the final drainage basis for these waters is situated in the sea bottom sediments of the Gulf of Gdańsk and Puck Bay. In 1960–1995, owing to extraction of the Cretaceous waters for consumption and economic purposes, the hydrostatic pressures were considerably reduced and finally the bottom of the Gulf of Gdańsk stopped playing a role of the drainage base level. However, in 2000, the extraction of the Upper Cretaceous groundwater drastically decreased and their natural hydrodynamic character recovered.

The Paleogene and Neogene multiaquifer formations occur almost on the entire Polish coast of the Baltic Sea, excluding depressions (troughs) in the Quaternary basement, e.g. in the western coast up to Bagicz, near Gąski–Tymień, in the vicinity of Jarosławiec, Smołdzino and Łeba, and in the Hel and Vistula spits.

The waters of these formations are mostly represented by two formations: Oligocene and Miocene. The Oligocene deposits occur at the depth from 50 to 120 m and are mainly characterised by artesian hydrodynamic conditions. The final drainage basis of these waters is in the nearshore sea bottom zone, from a few hundred metres to app. 1–2 km seaward. Locally, the Oligocene waters are marked by elevated contents of chlorides, e.g. a few hundred mg of Cl/dm^3 near Łopienica, Wicko Morskie, Rowy, Łeba, and even to 5,000 mg Cl/dm^3 in the Mielno region.

The Miocene multiaquifer formation occurs locally and consists of two or even three aquifers lying at the depth of 10–100 m. Its water table is mainly of sub-artesian character and it is slightly above the sea level in the coastal zone: from 2 to 0 m a.s.l. The Miocene groundwater also locally shows elevated salinity values (Darłówek, Rowy, Dąbki and Jastrzębia Góra). It usually does not exceed 600 mg Cl/dm^3; however, it reaches 6,800 mg Cl/dm^3 in Mielno.

The Quaternary multiaquifer formation is the most widespread in the Baltic Sea coastal zone. The ground waters occur within inter-till, valley, deltaic, ice-marginal valley, outwash and sandbar deposits and subglacjal channels. In many cases, these are extremely water-abundant aquifers and many of them achieved the status of major groundwater basins (MGWB Nos.: 102, 107, 108, 109, 110 and 112). The aquifers are mainly at depths of 2 to100 m. They conduct freshwaters containing below 600 mg/dm^3 of total dissolved solids. Only locally, the waters may be saline, owing to salt-water intrusion induced by excessive exploitation. In Żuławy Wiślane (Vistula Delta), the salinity is much higher and reaches 3,000 mg Cl/dm^3. Young fossil waters of marine origin occur in that area. The coastal zone is the main drainage basis for all Quaternary aquifers. Only an insignificant part of waters from deeply seated aquifers and from cliff regions flows down into the sea, infiltrating into the sea bottom deposits within a zone of a few hundred metres from the coastline.

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Several deep aquifers containing highly mineralised and thermal waters were discovered in the Paleozoic and the Mesozoic formations of the coastal zone of the southern Baltic Sea. They are located under a thick cover of sedimentary rocks of younger geological formations, occasionally exceeding 1000 m in thickness. It may be supposed that they also spread under the bottom of the Baltic Sea. Owing to high formation pressures and concentrations of many components, they undoubtedly affect the chemical condition of the bottom deposits. In Międzyzdroje, Cl–Na type water containing 17.4% of TDS was extracted from a depth of 1209–1240 m (Lower Cretaceous). In Międzywodzie, Wolin Island, Cl–Na, J type brines containing 9.4% of TDS were found in the Upper Triassic formations (Keuper) at a depth of 953 m. In Kamień Pomorski, Cl–Na, J type water containing 3.5% of TDS was found in the Lower Jurassic at a depth of 335–414 m. In Ustka, Cl–Na, J, S type waters containing 3.3% of TDS, and a temperature of 21°C, were found in the Permian deposits at a depth of 680 m. In the eastern part of the Baltic Sea, near the Gulf of Gdańsk (Sopot, Jastarnia, Krynica Morska, Jantar), a widespread reservoir was found in the Lower Triassic (Bundsandstein) at a depth of 400–1000 m. It contains Na–Cl type, J mineralised water containing 1.5–5% of TDS and a temperature of 22°C. High formation pressure induces artesian conditions, which finally results in stabilising the free water table at the elevation from several to 40 m above ground level.

The infiltration intensity of the mineralised water through poorly permeable rocks (aquitard) depends largely on the mineralisation of the infiltrating water. It is the more intense the higher the difference in mineralisation of waters from the adjacent reservoirs or aquifers is.

5.5.2. Groundwater Discharge Zones in Bottom Deposits of the Southern Baltic Sea

The Baltic Sea bottom and its shoreline constitute the main base levels of groundwater drainage from all aquifers and multiaquifer formations. The main groundwater recharge areas of this circulation system are located in the lakelands on morainic uplands located south of the Baltic coast. The groundwater flows are directed towards the sea.

Assessment of the direct water outflow to the sea was the subject of several research projects and documentary works. The first evaluation based on analytical calculations was made by Drwal (1967) and concerned only a small part of the Baltic coast. Pietrucień (1983) estimated the groundwater run-off along the whole Baltic coastline. He claims that 0.78 km^3/year flows down directly to the Baltic Sea, which makes app. 89,280 m^3/h. However, this estimation does not include deeper Paleogene, Cretaceous and Jurassic aquifers. The next documentary project, including all the coastal zone of the southern Baltic Sea, was made by Kryza and the team (2005). The volume of the direct groundwater run-off to the Baltic catchment area was estimated at 16,568 m^3/h, including:

from the Quaternary:	11,411 m^3/h over a section of 462.25 km
from the Neogene and Paleogene:	2,941 m^3/h over a section of 149.75 km
from the Cretaceous:	1,019 m^3/h over a section of 107.50 km
from the Jurassic–Cretaceous:	1,197 m^3/h over a section of 135.00 km.

The waters of considerably elevated TDS contents partly flow down into the sea from the Jurassic and Cretaceous deposits. The highest intensity of groundwater discharge takes place in the Gdańsk region, where 1 km of the seashore supplies from 24 to 45 m^3/h of water to the sea. Silmilarly high is the run-off from Wolin Island, app. 32 m^3/h.

These two assessments of the groundwater run-off show considerable differences. Owing to the use of two different calculation methods (field measurements, hydrogeological surveys and modelling analyses of groundwater flow), the results achieved by Kryza should be recognised as more reliable. In turn, the research group that implemented the international project “Groundwater inflow from coastal aquifers to the Baltic Sea” estimated the direct flow of groundwater from the Polish and German coasts to the Baltic Sea as 45 m^3/s (16,2000 m^3/h), including app. 40% from the Polish coast (Peltonen, ed., 2002). In the eastern part of the coast, between Ustka and the Vistula River mouth, the direct run-off of freshwater to the Baltic Sea from Cenozoic and Upper Cretaceous deposits was defined as app. 2,800 m^3/h (Lidzbarski, 2005). However, this outflow is reduced by the groundwater withdrawal by municipal and industrial intakes (app. 3,000 m^3/h), which limits the rate of groundwater flow towards the sea. Similar investigations by Piekarek-Jankowska (1994) estimated the rate of the submarine groundwater discharge to the Puck Bay from the Quaternary, Neogene, Paleogene and Upper Cretaceous aquifers as app. 3,500 m^3/h. Slightly higher values of the groundwater run-off to the Gulf of Gdańsk and Puck Bay are presented by Kozerski (ed. 2007) – app. 6,700 m^3/h, including app. 1,100 m^3/h from Upper Cretaceous deposits.

The above-presented data show that the groundwater run-off to the Baltic Sea in the Gdańsk region has been analysed the most frequently. However, the individual assessments differ considerably, despite the use of similar estimating methods (hydrogeological and modelling analyses of groundwater flow). Therefore, the state of recognition of the direct groundwater run-off is not satisfactory. It can be assumed that, in the region of the Gulf of Gdańsk, the water run-off into the Baltic Sea from the whole aquifer system under natural conditions reaches 8,000 m^3/h.

The shortage of information does not presently allow us to assess the volume of the mineralised and thermal waters that run into the Baltic Sea and occur in the deep Cretaceous and Paleozoic reservoirs.

The range of zones of the submarine groundwater discharge at the sea bottom depends mainly on the drainage type, isolation of aquifer layers that continue under the Baltic Sea bottom, hydrostatic pressure and groundwater flow rates. Shallow waters of Quaternary deposits meet sea waters mainly through direct contact on the shoreline or on the sea bottom a short distance from the coast. The width of the SGD zone for these waters does not exceed 20 m, although in some cases it may reach several hundred metres, e.g. in the Gdańsk region, between the mouths of the Dead Vistula and Śmiała rivers. A slightly wider zone of the SGD is observed in the deeper Pleistocene, Neogene and Paleogene aquifers. For these aquifers, waters flowing under the Baltic Sea are isolated by a slightly permeable rock complex. Drainage into the sea bottom sediments takes place by ascension in a belt of app. 1–2 km from the seashore. Locally, it may be larger and reach even 10 km (Piekarek-Jankowska, 1994). The drainage of the Upper Cretaceous waters occurs the farthest from the seashore. In the region of the Gulf of Gdańsk, it reaches several tens of kilometres, up to Hel. The submarine part of this reservoir is recharged with water mainly from the Kashubian Lake District (Sadurski, 1989). According to Breive (1973), the Upper Cretaceous aquifer under the Gulf of Gdańsk is also recharged by waters from the Prussian Lowland.

However, owing to the intense groundwater exploitation, it was considerably limited. The regional cone of depression have recovered within the last ten years and now water pressures in the Cretaceous aquifers have returned to their natural level. It means that the SGD in the sea bottom of the Gulf of Gdańsk and Puck Bay has probably recovered.

Intense groundwater drainage also occurs in the regions of deep sub-Quaternary structures that cut the bedrock and continue in the sea bottom under the Holocene deposits. The Żarnowiec tunnel valley and the group of tunnel valleys near the Łebsko and Gardno lakes may be an example.

The range of ascent of mineralised waters in the sea bottom is still unknown. However, it is supposed to reach a few tens of kilometres from the seashore and follow the limit of Jurassic and Paleozoic deposits. It may be confirmed by elevated concentrations of some metals in the sea-bottom sediments, in the outcrops of "reservoir" deposits and along major fault zones.

An indirect method for assessing the groundwater effect on the chemical constitution of sea bottom deposit is normalised maps of the distribution of some metals (Fig. 29). The results of geochemical mapping compared with the geological structure of the southern Baltic Sea allow the preliminary identification of the groundwater discharge zones.

The map of normalised barium contents reveals elevated Ba/Al values in the area of the Słupsk Bank, Słupsk Furrow and Eastern Gotland Basin. They can be correlated with the pinchout zone of Permian–Mesozoic deposits and the faults of Smołdzino, Karwia and Kuźnica. In the Pomerania Bay, the elevated Ba/Al contents seem to correlate with the fault zones. Both the highest barium contents and the normalised barium contents related to the aluminium contents are associated with the areas of iron-manganese concretions.

A zone of relatively high strontium concentrations occurs in the region of the Słupsk Bank and north of the Stilo Bank. It corresponds to the zone of the regional pinchout of Permian–Mesozoic deposits. Elevated strontium contents also occur near the coast in the region of the Kopań, Wicko, Łebsko and Żarnowieckie lakes. They are related to deep erosional channels within the Quaternary cover. Onshore, thermal waters and brines enriched with strontium were found in Permian and Triassic deposits near erosional incisions. So, the sea bottom deposits are supposed to have been enriched with strontium due to the ascent of mineralised and thermal waters. In the Pomerania Bay, in the Gryfice and Kołobrzeg blocks, large areas with relative enrichment of sandy sediments in strontium can also be observed. A dense network of faults is observed in this area and there are evident zones of erosional pinchouts of Triassic and the Jurassic deposits under the Quaternary (Kramarska ed., 1999).

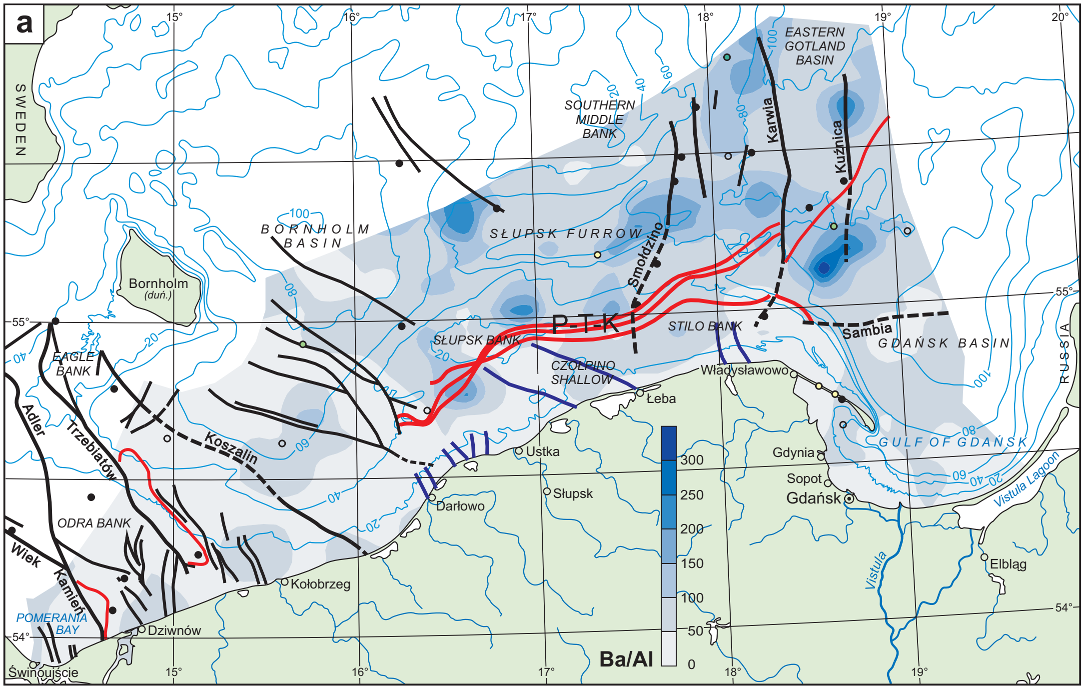
The distribution of normalised vanadium contents reveals similar correlations with the geological structure to barium and strontium. Although, the elevated vanadium concentrations suggest the routes of hydrocarbon flows, however, in some cases they may also be correlated with brine leaks or possibly with thermal outflows.

It concerns particularly the region of the Słupsk and Stilo banks, as well as some areas of the Baltic Sea located near the coast, where the Permian, Triassic and Cretaceous water-bearing deposits pinchout.

The analysis of the geological structure and hydrogeological conditions as well as the results of geochemical mapping of bottom deposits makes it possible to identify the submarine groundwater discharge zones. Freshwater of all the onshore Cenozoic aquifers and aquifer formations, Cretaceous and Jurassic mineralised waters and Permian and Triassic brines and thermal waters are drained through the bottom sediments of the southern Baltic Sea

The extent of the discharge zone of shallow Quaternary and Neogene groundwater does not exceed several hundred metres. As regards the deep Paleogene, Cretaceous and Jurassic aquifers, the discharge zone is considerably wider and reaches a few tens of kilometres. The Puck Bay and Gulf of Gdańsk are amongst the most important groundwater discharge zones, where freshwaters of the Cenozoic and Upper Cretaceous formations infiltrate.

The direct groundwater run-off into the Gulf of Gdańsk is estimated at app. 8,000 m^3/h. The highest contribution in the drainage belongs to the waters from Quaternary deposits. At the present stage of recognition, it is difficult to assess the run-off for the waters on the entire southern coast of the Baltic Sea.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BAY
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Trzebiatów
Koszalin
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Smołdzino
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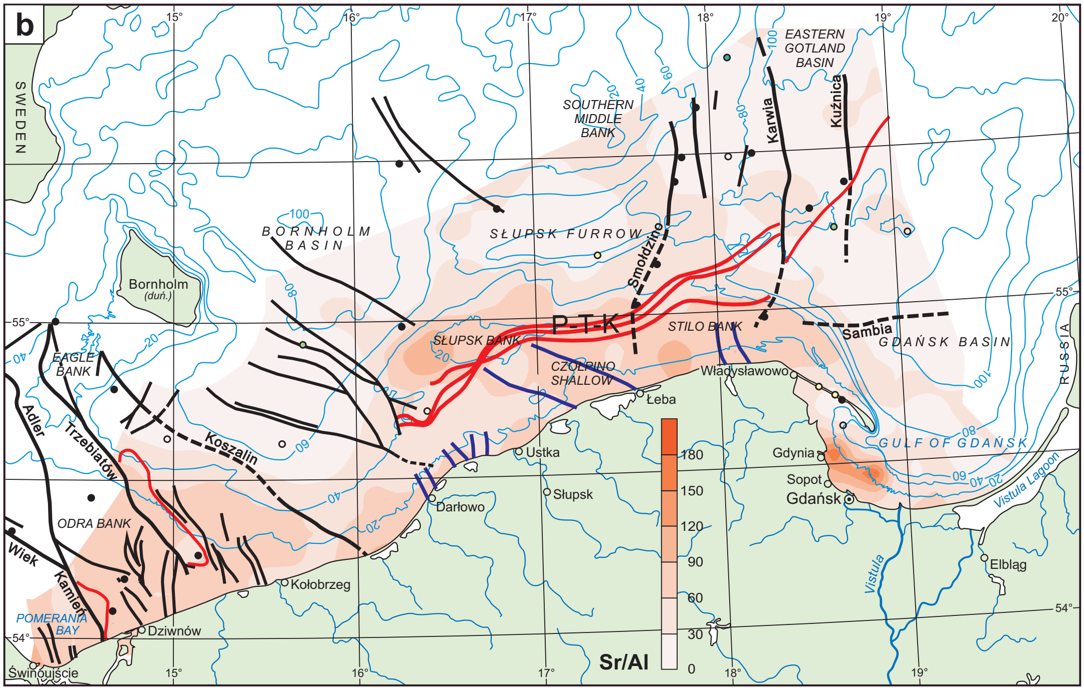
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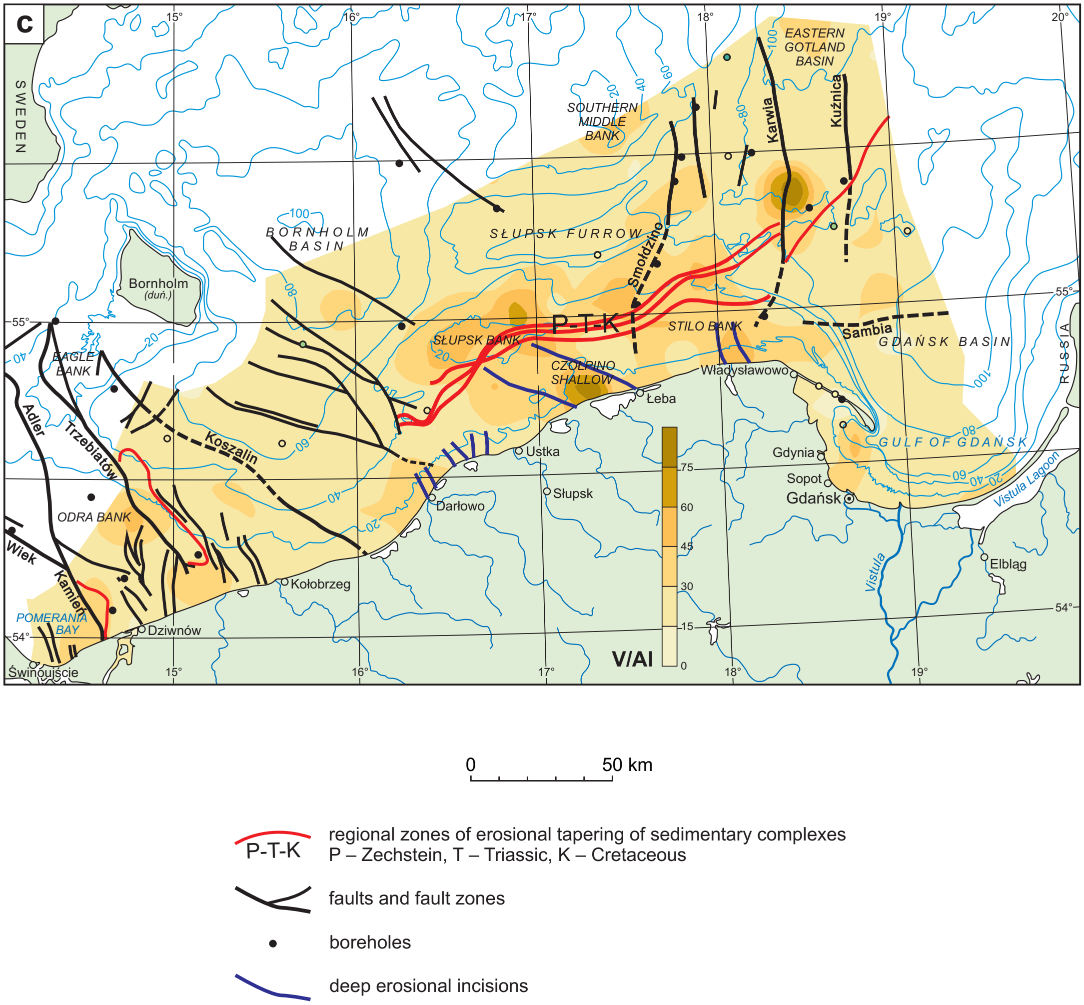


Fig. 5.29. Maps of normalised contents of some metals in the bottom sediments of the Baltic Sea (Uścinowicz *et al.*, 2004): a – Ba/Al, b – Sr/Al, c – V/Al

The most important symptoms of groundwater discharge include: changes in seawater salinity and temperature in the vertical section (inversions), changes in chloride concentrations in pore waters of bottom sediments, the occurrence of pockmark type structures and changes in chemical constitution of bottom deposits and their pore waters.

A clear effect of groundwater ascent on chemical composition of the bottom sediments is noticeable. The areas of relatively elevated contents of barium, strontium and vanadium distinctly correlate with fault zones, pinchout zones and deep incisions into the sub-Quaternary cover. The coincidence of elevated concentrations of Ba/Al, Sr/Al and V/Al with structural geological and morphological elements of the sub-Quaternary basement may suggest discharge zones of groundwater from the Cenozoic and Cretaceous deposits, and the outflows of brines and thermal waters from the Permian and Mesozoic formations.

5.6. Chemical Weapons and Wrecks at the Bottom of the Baltic Sea

The end of the 1980s and beginning of the 1990s was marked by the increased activity of state governments, who signed the Helsinki Convention (1992), in scope of seeking optimal solutions with the problems connected with chemical munitions being dumped into the bottom of the Baltic Sea (Kasperek, 2001), and how to deal with the wrecks.

The problems with the sea environmental hazard which was created by the shipwrecks was revealed to be so considerable that in 1997, the Finnish Ministry of Environment requested HELCOM to implement a uniform classification of shipwrecks in all Baltic countries, due to their serious hazards for the marine environment (Szulc, 2001). The Finnish classification is mainly based on the potential risk of contamination by leaking oil stored in the shipwrecks. The maximum volume of tanks with oil on the given wreck may be the measure of the potential pollution as a result of oil leakage from the wreck (Gajewski *et al.*, 1999). The main purpose of the Finnish classification is to define a category of wrecks, considering the stage of their recognition and the hazard they may constitute for the marine environment, and to define the actions needed in order to eliminate this hazard (Szulc, 2001).

An example of the threat posed by shipwrecks on the environment of the Baltic Sea may be the sinking of the “Stuttgart” vessel. Although that catastrophe took place more than 60 years ago, it illustrates how long some products of crude oil processing (mazout, in this case) stay in the marine environment at the bottom of the sea and just what kind of ecological effects are created as a result of oil leakage. The “Stuttgart” was a German auxiliary vessel for transporting patients during World War II. It was built in 1923 in the AG Vulkan shipyard in Szczecin. In 1939–1943, it served as a hospital ship in Norway. It was a medium-sized vessel, 160 m long, 19.8 m wide and 10.5 m high, with a six-cylinder steam engine of a double compression ratio, mazout-fired (Fig. 5.30). In October 1943, a fire broke out on the vessel while docking at the Gdynia harbour. It was probably sabotage or a bomb explosion during an American bombing raid on Gdynia. In order to avoid more victims and the fire risk of the harbour, the ship on fire was hastily towed away far into the gulf where it sank near the entry to the port of Gdynia at the depth of 25 m, including the wounded on its deck. Very few persons who were on the ship deck survived (www.balticwrecks.com.pl). At the turn of the 1950s and 1960s, the vessels of the Polish Ship Rescue Service (currently the Polish Maritime Search and Rescue Service) carried out their actions in that place to get the wreck out onto the surface, as it was an obstacle for sailing. These actions were stopped in 1962, after issuing a ban for using pyrotechnic methods.

The divers from the Central Maritime Museum in Gdańsk undertook several attempts to localise the ship wreck. Reaching the position given in the state government lists of ship wrecks, they found only some pieces of steel sheets. After numerous attempts, they realized that the most effective method appeared to be to locate spills of petroleum substances on the sea surface, which were most likely the aftermath of the earlier pyrotechnic actions. The search was repeated in 1992 and then the divers found a large contamination with mazout. Working alongside a British crew of divers as well as using a magnetometer, the wreckage was finally found. The divers reported that it was lying in the bottom sticking out roughly 2 m high. The divers who examined the sea bottom disturbed mazout spilled at the bottom, and large spots of oil substances on the water surface were observed. After getting onto the ship deck, it turned out that the suits of the divers who were at the sea bottom were covered with a layer of mazout (www.zoo.im.gda.pl).

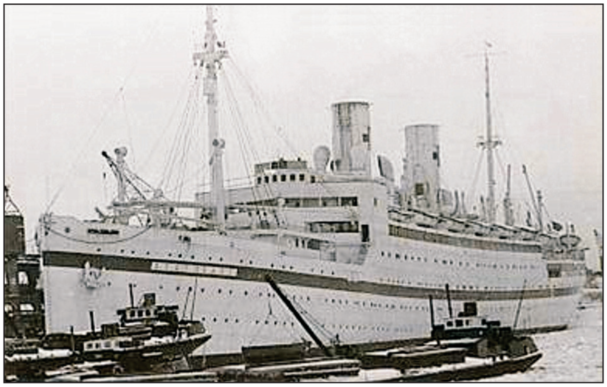


Fig. 5.30. The “Stuttgart” hospital ship (www.wlb-stuttgart.de)

The wreck of the “Stuttgart” ship was localised at the following coordinates: 54°33’33,2” N and 18°36’59,6” E, at a depth of about 20 m, with its longitudinal axis towards north-east. The distance between the extreme points sticking out of the sea bottom is app. 140 m and its width does not exceed 20 m. Above the bottom of the sea, there are metal sheets and rods located generally along the contour of the ship wreck. Some objects are sticking out above the bottom for app. 3 m (Gajewski *et. al*., 1999).

In 1997, the Maritime Institute in Gdańsk conducted its own investigation of the German shipwreck that was located at the bottom of the Gulf of Gdańsk. The studies showed a contamination of the sea bottom with mazout up to twenty hectares around the wreck. In some places, a layer of dense liquid fuel that spilled in the bottom reached up to 40 cm. There were many skeletons and dead fish found in this zone (Szulc, 2001), suggesting that despite the passage of time the wreck still poses a threat for living organisms.

In order to assess the effects of oil in the tanks of the sunken shipwrecks on the marine environment, it is necessary to monitor the waters and sediments in these areas by means of chemical methods. It is particularly significant to check the contamination of the sea bottom sediments with substances leaking from the ship wrecks. Such contaminations are most stable and accumulate in the sediments. Since its sinking, the “Stuttgart” shipwreck has been a source of permanent pollution of the sea bottom sediments and the water with petroleum products, and is hazardous for biological life.

At the beginning of the 1990s, the chemical weapon (CW), which dumped into the Baltic Sea, became of particular interest for the Helsinki Commission. A direct reason why this issue was undertaken was a case of finding a chemical bomb filled with yperite in Bornholm on 18th February, 1992. By the decision of the 14th Conference of the Helsinki Commission in 1993, a Working Group on Dumped Chemical Munitions was established (HELCOM CHEMU, 1994). In 1995, after the working group was dissolved, the tasks concerning the dumped chemical munitions were taken over by the Environment Committees (EC) and the Combatting Committee with Spills (CC). Denmark was entrusted with leadership. At that time, the Baltic region countries prepared a few state reports (Paka, 2007).

Huge amounts of conventional ammunition, gaseous missiles and blister agents in metal containers were dumped in different regions of the Baltic Sea from 1945 to 1948 (Korzeniewski, 1994). Shortly before the end of World War II the German occupation authorities in Denmark ordered discharges of weapons and equipment into to the sea. This operation was also ordered by the Allies after the end of World War II, which was reinforced with the Decision of the Conference in Potsdam of 2nd August, 1945.

Chemical weapon in the Baltic Sea was dumped in three main regions: the Little Belt (54°48’22”N, 10°13’22”E, 54°50’N, 54°47E, 10°08’E, 10°15’E), the Bornholm Deep – east of Bornholm (the region where the dumping took place had a radius of 3 NM, the centre of this region has coordinates 55°21’N and 15°37’E; the depth of the sea in this area is from 70 to 105 m) and the south-eastern part of the Gotland Deep (56°16’N, 18°39’E, 56°16’N, 18°51’E, 56°20’N, 18°55’E, 56°20’N, 19°31’E, 56°07’N, 19°15’E, 55°66’N, 19°15’E, 55°56’N, 18°39’E; the basin depth from 70 to 120 m) (Fig. 5.33). In most cases, the warfare agents (WA) filled artillery shells, mines, smoke grenades, aircraft and high-explosive bombs; they were also dumped in different metal containers (cans, barrels). Chemical weapons were also thrown into the sea in bulks or in wood boxes, whereas some of them were stored in areas of the sunken ships (HELCOM, 1996). Many circumstances indicate that some amount of chemical weapon was thrown out into the sea, also during the transport to the planned region of sinking. Moreover, the chemical ammunition dumped in wood boxes drifted for some time before it sunk and fell onto the sea bottom. Nobody knows how many tons were thrown out in this way (Andrulewicz, 1996; Schultz-Ohlberg *et al*., 2002). The information about the regions of catching and finding the chemical ammunition provides additional knowledge about possible places of its dumping (Fig. 5.31). Likely reports state that chemical weapons were thrown out in small distances from Dziwnów, Kołobrzeg, Darłowo and Hel, as well as near the Gdańsk Deep. It particularly refers to that kind of load that could have been dangerous to the crews that were transporting it to the appointed regions of discharge into the sea.

The dumping of toxic war remains in shallow sea areas of high environmental dynamics as well as in the regions of intense fishing (eastern Bornholm Basin) made

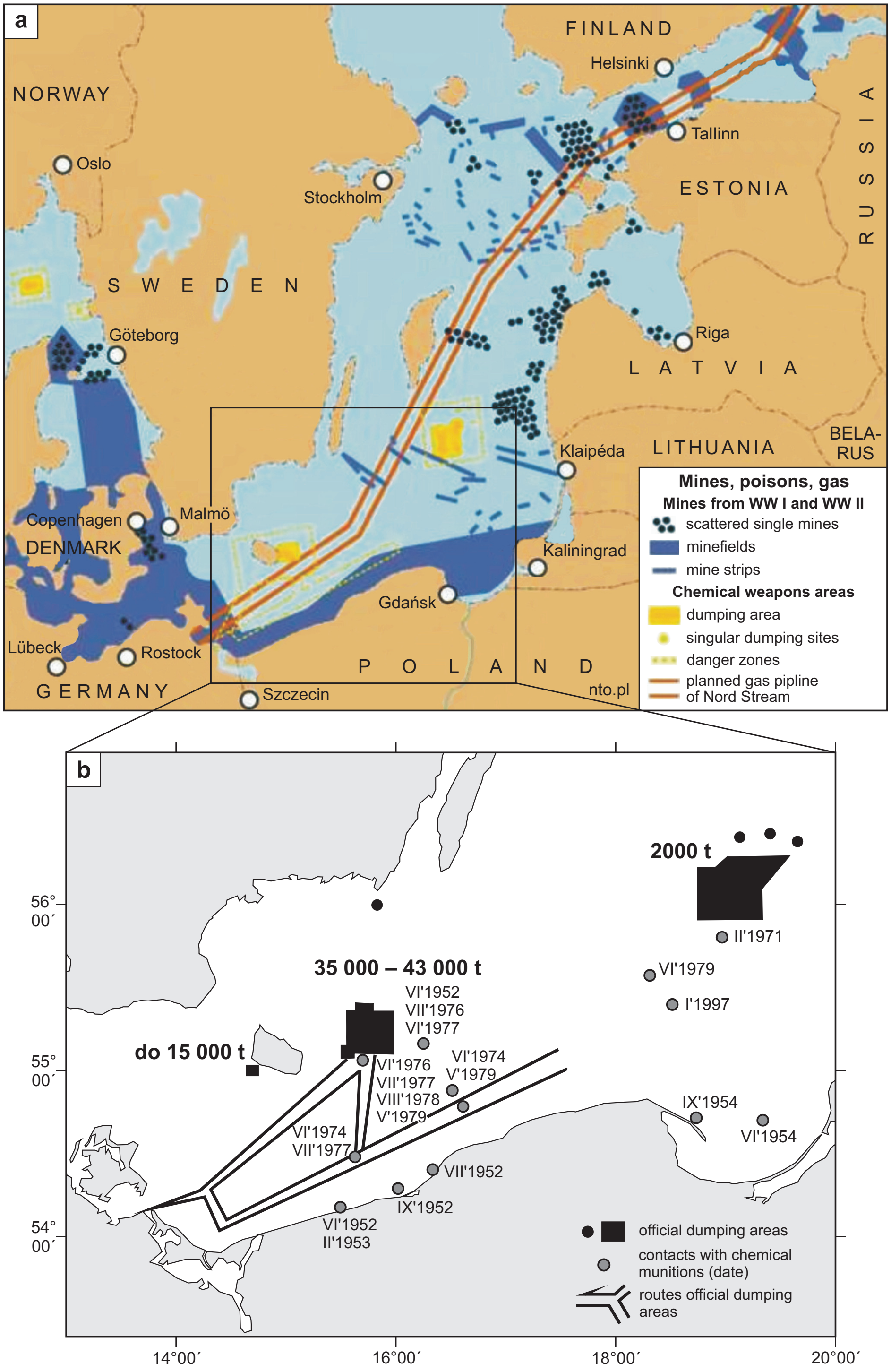


Fig. 5.31. a – Location of the dumped conventional and chemical ammunition; b – contacts with warfare agents (WA) in the Baltic Sea (HELCOM CHEMU, 1994; Kasperek, 1999; www.nto.pl)

hazard not only to the marine environment, but also to the densely populated coastal zone. In the after-war period, the incidents of catching chemical ammunition and throwing containers with toxic agents onto the seashore were noticed in Poland, Sweden, Germany, Denmark, Lithuania, and Latvia (HELCOM CHEMU, 1994). In the Polish coastal zone, the cases of burning with unknown substances occurred in the western and central coast near Ustka, on the Hel Peninsula and near Jurata (HELCOM, 1993).

The frequency of contacts with chemical weapons is not occasional; however the information about these cases is not complete. The most reliable are the data described by the Danish. Danish fishermen are paid compensations for damages resulted from the contamination of their fishing, which is a consequence of conducting a thorough register of the recovered unknown objects. Therefore, the number of the incidents of contact with toxic chemical agents (CW), reported by Denmark, was incomparably higher than that in all other countries. In the eastern coasts of Bornholm, from 1985 to1992, 342 "catches" of CW of total mass of 17 tons were recovered (HELCOM CHEMU, 1994). The highest number (103) of incidents was reported in 1991. Later, in 1995–2005, 98 pieces of CW were recovered, the total mass of which exceeded 3.5 tons. A greatest number of chemical weapon (23 pieces) weighing over 1 ton was reported in 2003 (HELCOM CHEMU, 2006). Until 1993, Germany, Poland, Sweden, Lithuania, and Latvia reported totally no more than 50 incidents of contact with chemical weapon. Yperite is the most frequently found chemical toxicant which people have contact with (Fig. 5.32).

First incidents of people's contact with chemical weapon in the Polish Exclusive Economic Zone were recorded in the 1950s (Table 5.18). The most dramatic event took place on the beach in Darłówek in July 1955, where the sea waves threw over the breakwater a metal barrel filled up with condensed yperite. The children playing on the beach started to roll it, not noticing that a brown-black liquid was leaking from the barrel. The first symptoms of contaminating with sulphur yperite appeared just after half an hour. A hundred and two children were burnt and four children had serious eye injuries. After that accident, the access to the beach was closed and the contaminated area was neutralised (3 tons of chlorinated lime was scattered every day for seven days). The beach was opened after 3 months (Korzeniewski, 1994).

Fishermen are especially exposed to risk of contact with warfare agents. As a result of catching WA, a crew can be burnt and fishing nets with accessories and boat can be contaminated. The first accident of this type took place in 1963, and the last one was observed in January, 1997. In the latter case, 30 NM to the north of the Władysławowo, the crew of the ship WŁA 206 caught a brown lump of almost 5 kg of weight, resembling a clod of loam. Unconscious of the hazard, the fishermen were injured with heavy burns (Kasperek, 1999).

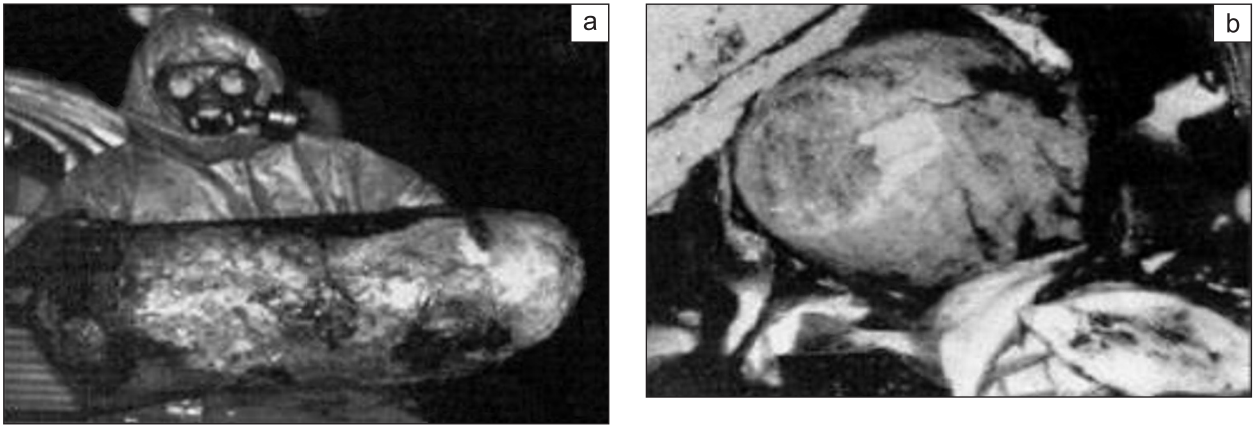


Fig. 5.32. A bomb filled with yperite (a) and an yperite lump among fishes (b) (http://levis.sggw.waw.pl)

Table 5.18

Chemical ammunition found in the Polish Exclusive Economic Zone (Kasperek, 1999)

Year	Number of events at sea/on the beach	Place of event	Number of the contaminated people, equipment	Remarks
1952	1/2	E Bornholm, Kołobrzeg beach, Dziwnów beach		including the years 1952–1954 5 bombs were found – unknown content
1953	–/1	Dziwnów beach		
1954	1/1	Gulf of Gdańsk, Jurata beach		
1955	–/1	Darłówek beach	102 children	barrel filled with liquid chemical agent
1963	1/–	J-7	3 fishermen from the ship UST 2	fishing net contaminated with yperite
1967, July	1/–	H-9, E Bornholm	crew of the ship KOŁ 158	contaminated fishing net
1969, July	1/–	HJ-8, E Bornholm	part of crew, ship UST 3	contaminated fishing net
1971	1/–			
1974	2/–			
1976	2/–		6 fishermen from Darłowo	
1977	4/–	central Baltic Sea	12 fishermen, ship KOŁ 158	about 20 kg body
1979	3/–		3 fishermen from Kołobrzeg; 5 fishermen from Ustka, cutter WŁA 152	the shipowner of the cutter WŁA 152 was PPiUR SZKUNER
1980	1/–		cutter from Władysławowo	
1994	1/–	H-9, E Bornholm	Łeb 5	a bomb was raised to the surface, turned over in Nexo (skipper was punished)
1997 9 January	1/–	app. 30 NM to the N of Władysławowo	8 fishermen, ship WŁA 206	4–5 kg body

Also marine organisms, if they have a direct contact with WA, are heavily wounded or contaminated (Fig. 5.32). In the Puck Bay, at the turn of the 1970s, many dead fish and seaweeds were thrown out onto the seashore by the waves. Some researchers associate that fact with the chemical weapon dumped in the sea.

About 40 to 60 thousand tons of chemical ammunition, including 12–13 thousand tons of WA is supposed to be deposited at the bottom of the Baltic Sea (Table 5.19). The following toxic agents are among WA dumped after World War II: tabun, sarin, soman, sulphur yperite, nitrogen yperite, viscid yperite, lewisite, phosgene, diphosgene, triphosgene, chlorine, chloroacetophenone, hydrogen cyanide, cyanogen chloride, adamsite, Clark I and Clark II (HELCOM CHEMU, 1994; Korzeniewski, 1994; Kasperek, 2004; Andrulewicz, 2007). Those substances occur in solid, liquid and gaseous phases. They belong to physiologically active compounds with heteroatoms in their molecules. Considering their chemical structure, the following compounds can be distinguished: haloorganic, sulfoorgan-

Table 5.19

Chemical ammunition and warfare agents dumped into the Baltic Sea (area included into the Helsinki Convention) and near Mäseskär (west of Sweden) in the southern Skagerrak (HELCOM CHEMU, 1994)

Location	Ammunition [t]	Warfare agents [t]	Types of warfare agents
Bornholm Basin (E of Bornholm)	app. 32,000	app. 11,000	sulphur mustard gas, Clark I, Clark II, adamsite, chloroacetophenone, probably: phosgene, nitrogen mustard, tabun
Basin located E of Bornholm	8,000 (not verified)		no information
Basin located SE of Bornholm	app.15,000 (not verified)		no information
Gotland Basin (SW of Liepaja)	app. 2,000	app. 1,000	sulphur mustard gas, adamsite chloroacetophenone
Little Belt	app. 5,000	750 (assumed value of 15% of the ammunition mass)	tabun, phosgene
Mäseskär west of Sweden (not included into the Helsinki Convention)	app. 20,000 (not verified)		sulphur mustard gas (other types not verified)

ic, arsenoorganic or nitroorganic (Korzeniewski, 1998). WA can also be divided by applying tactic classification according to their destructive activities: burning (yperite, lewisite), paralysing and irritating (adamsite, sarin, tabun, cyanodiphenylarsine and chloroacetophenone), choking (chloropicrin, phosgene and diphosgene) and blood agents (hydrogen cyanide, cyanogen chloride).

Although the areas of the ammunition discharge differ in the amount of the dumped chemical weapons (Table 5.19), they show a considerable similarity as far as the type of warfare agents is concerned. Excluding dumping near the Little Belt (where tabun was mainly sunk), yperite was the dominant WA. Both in the Bornholm Basin (Fig. 5.33) and in the Gotland Basin, it is installed prevailingly in aircraft bombs (of diameter 200–500 mm, length 1–1.8 m and wall thickness to 3 mm), in artillery shells, and high-explosive bombs. Yperite accounts for 60% of all WA in both areas of the discharge. Chemical weapon containing arsenic is a second group of chemical compounds (app. 30%) dumped in the Baltic Sea. Arsenic occurs in similar amounts in aircraft bombs and in metal containers.

A hazard of warfare agents for both the marine environment and humans depends on the type and concentration of the toxic compound. The behaviour of WA in the marine environment depends on physico-chemical properties of these substances (Table 5.20) and on the environmental factors, such as temperature, salinity, pH and water mixing (Korzeniewski, 1998; Garnaga *et al.*, 2006;

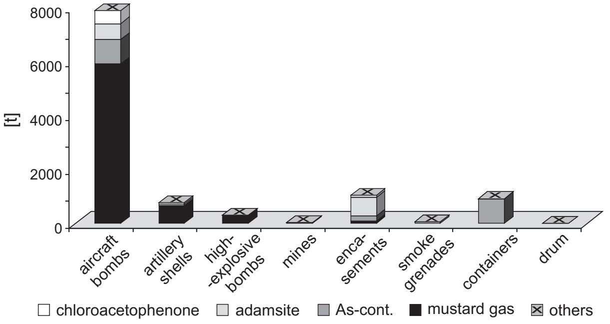


Fig. 5.33. Amounts and types of chemical weapons accumulated in the Bornholm Basin (based on HELCOM CHEMU, 1994)

Hart, Stock, 2008). A crucial process of the chemical weapons degradation in the water environment is their dissolution. The reactions, in which chemical compounds of the WA participate, depend on their hydrolysis and oxidation. Under normal conditions, this process leads to forming new compounds, distinguished by features from the substrates. In most cases, WA loses its combat properties of toxic agents, as it undergoes decay into non-toxic or less toxic compounds, and in many cases, mineralisation produces the compounds that are elements of biogeochemical cycles (Korzeniewski, 1998). It is more difficult to reconstruct degradation stages of WA in sea water, where processes can be carried out under different pressure, depending on the depth: on the surface of the sand bottom or under a layer of mud in anoxic conditions. An additional hazard is a possibility of forming new compounds that have been unidentified until now, the toxicity of which remains unknown and which can be formed due to many different toxic substances discharged at the same time (Witkiewicz, 2008).

Taking into account the properties, amounts and type of the dumped chemical ammunition, the most hazardous to the environment are sulphur or nitrogen yperite and chemical weapons containing arsenic (lewisite, Clark I and Clark II, and adamsite). In case of yperite, especially the hardened one, the hazard is due to its long stay in the environment, unchanged or weakly changed, as well as from the toxicity of the agent in all its aggregation states.

Table 5.20

Physico-chemical characteristics of the selected chemical weapons (Kasperek, 1999; Andrulewicz, 2007; Hart, Stock 2008; Missiaen *et al.*, 2010)

Chemical substance, chemical formula	Name of chemical weapon (symbol)	Melting point [°C]	Boiling point [°C]	Density [g/cm^3] in 20 °C	Solubility [g/dm^3]	Hydrolysis rate in water	Toxicity of hydrolizate
2-chloroacetophenone C_8H_7ClO	(CN)	54–56	244	1.32	1	very slow	no
Diphenylchlorarsine $(C_6H_5)_2AsCl$	Clark I (DA)	44	333	1.39	2	very slow	yes (As compounds)
Diphenylcyanoarsine $(C_6H_5)_2AsCN$	Clark II (DC)	31.5	346	1.33	2	very slow	yes (As compounds)
Diphenylaminechlorarsine $HN (C_6H_4)_2AsCl$	Adamsite (DM)	195	410	1.65	0.002	very slow	yes (As compounds)
N-ethylo-2,2'-dichlorodiethylamine $C_6H_{13}Cl_2N$	nitrogen mustard (HN_1)	–4	239	1.24	0.16	very slow	yes (little)
Bis (dichloroethyl)-sulphide $(ClCH_2CH_2)_2S$	sulphur yperite, mustard gas (HD),	13–14	216	1.27	0.8	slow	Yes (some compounds)
2-chlorovinyl dichlorarsine $ClCH\ CHAsCl_2$	lewisite (L)	–18	190	1.89	0.5	slow	yes (As compounds)
Carbonyl chloride $COCl_2$	phosgene (CG)	–128	7.6	1.37	9	fast	no
Ethyl N, N dimethyl-phosphoramidocyanidate $C_2H_5OP(O)(CN)N(CH_3)$	tabun (GA)	–50	220–246	1.07	120	fast	no

Due to very weak solubility, additionally obstructed by a cover produced while contacting with sea water, slowing down further hydrolysis, the substance is still raised to the surface as lumps that are dangerous for life and health (Fig. 5.32). The main problem related to WA containing arsenic consists in the fact that the products of hydrolysis also contain arsenic (Table 5.20). Inorganic arsenic compounds do not decay and, staying in the environment for a long time, they may affect it in a toxic way.

In the marine environment, research is conducted to localise and verify the WA, and to estimate its threat to the ecosystem. This information is still not satisfactory. The research primarily includes sediments and some toxic compounds that constitute these sediments, as well as the products of their decay (HELCOM CHEMU, 1994; Witkiewicz, 1996; Korzeniewski, 1998; Garnaga, Stankevičius, 2005; Paka, 2007; Missiaen *et al*., 2010). The studies on the effects of WA on living organisms are also carried out (Garnaga *et al*., 2006). Interesting is the effect of WA on, e.g. the quality of fish within the fisheries located above the places of WA discharges (hot spot), the human health and economic costs of their influence on the environment (Sanderson *et al*., 2008).

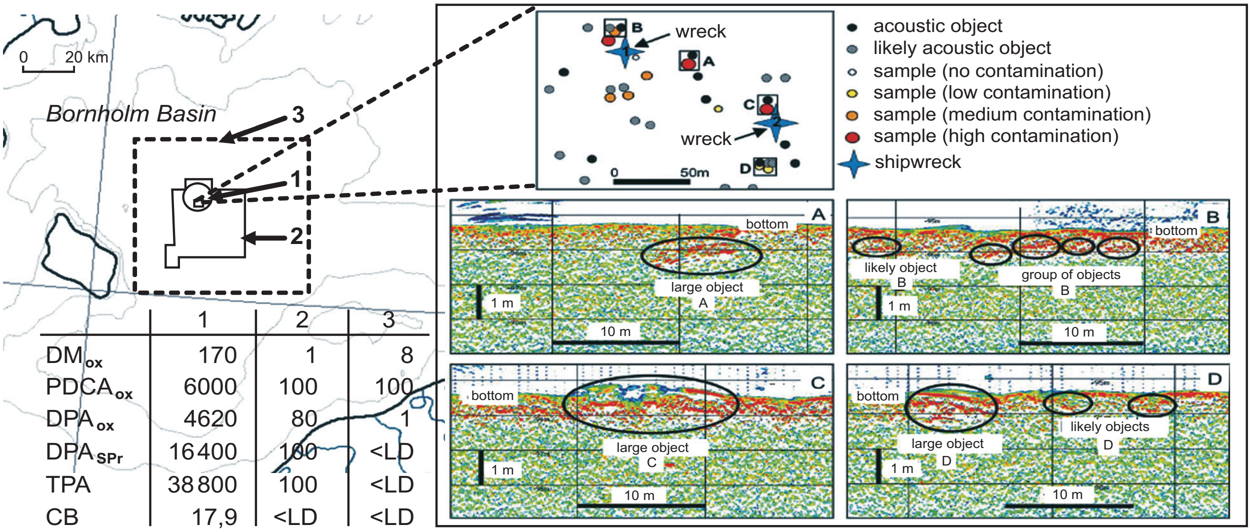
One of the first results of the studies describing the WA content in the Baltic Sea coastal zone is presented by Korzeniewski (1998). He detected the presence of yperite in samples of water and sand taken from the eastern beach in Darłowo (1955) and on fishing nets from the fishing net store of the PPiUR Barka Company in Kołobrzeg (1967). A bomb with yperite, raised to the surface in 1997, was also analysed. During the studies, two chemical compounds not described earlier in literature were detected (Witkiewicz, 2008).

Comprehensive research on sediments and bottom sea waters were conducted in 2007 and 2008 in the area of the Bornholm Basin. They concerned the contents of WA toxic agents such as: adamsite (DM), Clark I (DC) and Clark II (DA), sulphur yperite (H), chlorobenzene (CB), as well as arsine oils: trichloroarsine (TCA), triphenylarsine (TPA) and diphenyldichlorarsine (DPCA), and revealed that these contaminants spread far outside the region of CW discharges (hot spots) (Missiaen *et al*., 2010). Excluding TPA and CB, the toxic agents of CW did not stay undisturbed, but occurred as the products of degradation of WA and/or as their derivatives. All the above-listed toxic agents of WA were determined in the analysed samples. It was surprising that the products of degradation were observed only in one sample, considering the amount of yperite dumped in this area. It was partly because of the fact that yperite forms polymerised lumps that are weakly soluble in water (Fig. 5.32). The highest concentrations of WA were determined in a small distance from wrecks and large objects located just under the surface of bottom sediments (Fig. 5.34). Outside the area of the main CW discharge, the concentrations of the individual compounds dropped a few hundred up to several thousand times or were undetectable. Only in case of degradation products of diphenyldichloroarsine (PDCA) and adamsite (DM), the contamination of sediment samples with these compounds was observed even 30 km from the main discharging area (area 3).

Moreover, the relation between the concentration of WA in sediments and the location of the found objects is not direct. It may suggest that a large amount of dumped ammunition “leaks” and through years the contaminants enriched the marine sediments in this region.

The analysis of arsenic contents in water and sediment samples may be used to define the condition of dumped ammunition, amount of WA leakage into the marine environment and its distribution (Garnaga, Stankevičius, 2005; Paka, 2007). The WA containing arsenic accounts for almost 1/3 of the dumped chemical ammunition (HELCOM CHEMU, 1994). High concentrations of arsenic (up to 277 mg/kg) with reference to the background are observed in the sediments of the Bornholm Basin in the regions where chemical ammunition was dumped, but also along the routes of its transport (Fig. 5.35). The fact indicating that arsenic contained in these areas is anthropogenous and not natural, like in the Bothnian Bay, is its high variability of concentrations within the range of more than 250 mg/kg (Garnaga, Stankevičius, 2005).

In order to verify the location of chemical weapons, geophysical methods can be applied (Fig. 5.34). The research with the use of side sonar, magnetometer and multi-beam sounder, carried out east of Bornholm, revealed objects buried under a layer of sediments. The increase in their occurrence when getting closer to the centre of discharge location shows with a high probability that this is WA dumped after World War II. The objects observed on echograms are located just under the sea-bottom surface (app. 10 cm). The results of the research also suggest that it is possible to unveil them, especially in shallower



	1	2	3
DM_{ox}	170	1	8
$PDCA_{ox}$	6000	100	100
DPA_{ox}	4620	80	1
DPA_{SPr}	16400	100	<LD
TPA	38800	100	<LD
CB	17,9	<LD	<LD

Fig. 5.34. Research area divided into a region of primary discharge (1), extended discharge (2) and no discharge area (3). Location of samples and identified objects situated near wrecks 1 and 2 (area 1). Echograms with detected objects shown as rectangles A–D. Maximal concentrations (mg/kg of wet mass of the sediment) of chemical weapons (TPA and CB) and products of their degradation (Clark as DPA and DPA, diphenyldichlorarsine as DPCA, adamsite as DM) with reference to the distance from the main area of chemical weapon dumping (Missiaen *et al.*, 2010)

and more dynamic areas of the Baltic Sea (Missiaen *et al.*, 2010).

The chemical weapon dumped in the Baltic Sea is nowadays one of the greatest chemical hazards for this natural surface water reservoir. At times of increasing interference of man in the Baltic Sea area (fishery, navigation, underwater tourism, pipeline and cable installations, etc.), there is a problem concerning the safety of operations at sea and the ecological and economic effects in case the dumped ammunition is disturbed (HELCOM CHEMU, 1994; Andrulewicz, 2007; Kasperek, 2007; Paka, 2007; Sanderson *et al.*, 2008).

The process of WA releasing in the marine environment starts from the moment of its dumping, partly as a result of mechanical damage of its containers (bombs, shells, etc.) and partly because of corrosion. At the same time, toxic agents become degraded as a result of hydrolysis and the oxidising of the released compounds. Consequently, the concentrations of toxic substances in places of their discharges are reduced (Kasperek, 2007).

The information received while recovering dumped hazardous objects (i.a., two shipwrecks loaded with missiles filled with tabun were pulled out in 1956–1957 in a position 7 NM southeast of Pøls Huk, near the entry to the Little Belt) revealed that:

– The thick-walled (more than 10 mm) artillery ammunition, lying on sand and gravel, is corroded only to the depth of a few mm, fuses are oxidised totally, part of the ammunition shows inner overpressure

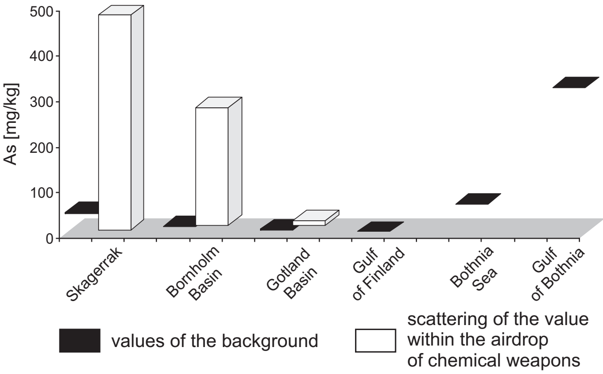


Fig. 5.35. Arsenic content in the Baltic Sea sediments (Garnaga, Stankevičius, 2005)

because the gases liberated during the decay of WA, which increases the hazard of explosion;

- The shells in containers covered with mud are in good condition and often are suitable for using;
- Thin-walled bombs (1.5–3.0 mm) that lie on the hard sea bottom are corroded and contain no WA (Korzeniewski, 1998).

Considering the fact that the thickness of containers (for bombs, missiles, etc.) used to accommodate 80% of all types of ammunition was small, and that the CW was dumped 60 years ago, we may assume that its large part has been totally corroded. It concerns especially well-aerated bottom waters of marine areas and shallowly buried objects, periodically uncovered by dynamic marine processes. In this situation, disturbing the corroded elements of the ammunition may probably accelerate the release of toxic agents into the marine environment, which increases their concentrations in the ecosystem. Then, living organisms that have a direct contact with these toxic substances will suffer the most (Kasperek, 2007; Paka, 2007).

Owing to the intensifying economic activities undertaken by people in the Baltic Sea region, a further closer co-operation between the Baltic region countries is necessary to:

- Achieve a complete identification and stocktaking of the current chemical weapon hazards,
- Establish the way of carrying out the research to assess the scale and types of hazards from chemical weapons dumped in the Baltic Sea,
- Define the range and methods of information exchange by institutions,
- Develop a method of conducting the operations with the dumped ammunition.

The answer to the above-formulated issues is, among others, a European project of MERCW (2006) whose first results were presented by Paka (2007) and Missiaen *et al.* (2010).

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Chapter 6

MAIN CONSTITUENTS OF THE BALTIC SEA SEDIMENTS

Pleistocene sediments covering the catchment area and the bottom of the Baltic Sea were deposited as a result of the activities of continental glaciers that invaded the area of the Baltic Sea several times and eroded crystalline and sedimentary rocks of the basement. Sedimentary material transported into the Baltic Sea from the catchment area and the coastal zone originates mainly from washing out of Pleistocene glacial and glaciofluvial deposits. Chemical composition of the bottom sediments of the Baltic Sea, apart from the dominant terrigenous components, also includes autogenic constituents, both chemogenous and biogenic, but most often in small amounts.

Silicon is the main constituent of the Baltic Sea sediments. It occurs as quartz, silicates, aluminosilicates and amorphous silica. The mean SiO_2 content in the recent sediments of the Baltic Sea ranges from about 51% in silt-clay sediments to 89% in sands (Blazhchishin, 1982).

The silicon content in the sediments strongly depends on their grain size (Fig. 6.1). In sands from the seabed surface of the southern Baltic Proper, the amount of SiO_2 varies mostly from 80 to 95%. Especially high silica contents are found in the well-sorted fine-grained sands, even above 95%. In sands, silica occurs mainly as quartz.

In silt-clay sediments, the amount of SiO_2 ranges mostly from 50 to 70%. In the finest-grained sediments (clays and silty clays of the deepest parts of the Bornholm and Gdańsk basins), silica accounts for 40 to 60% of the total sediment composition. Quartz occurs here in smaller amounts, silicates are dominant.

The results of the project "The Baltic Sea Sediment Baseline Study" reveal that, in the northern Baltic Proper and in the Gulf of Finland, the SiO_2 content in silt-clay sediments varies between 31.7% in the North-Central Basin and 70.2% in the north-eastern Gulf of Finland. The silica contents in silt-clay deposits, despite the shortage in the sand fractions, depend on the proportion between the silty fraction (0.063–0.004 mm) and the clay fraction (<0.004 mm).

Apart from terrigenous silica, the sediments of the Baltic Sea also contain biogenic amorphous silica: an average of 1% in sandy deposits, and about 2.2% in silt-clay sediments. These are exoskeletons of diatoms, the fraction of which may reach as much as 3.5% in silty sediments (Blazhchishin, 1982).

Aluminium. Since the occurrence of aluminium oxide is strictly connected with clay minerals, their highest contents occur in clayey sediments. The lowest amount of Al_2O_3 is contained in well sorted fine-grained sands, with a dominance of quartz. The Al_2O_3 content in modern sediments of the Baltic Sea ranges from 0.3% in sands to app. 18% in clays (Blazhchishin, 1982). The Al_2O_3 content in the surface sediments of the southern Baltic Proper varies within a similar range (Fig. 6.2).

The results of the project "The Baltic Sea Sediment Baseline Study" suggest that the Al_2O_3 content in silt-clay sediments of the main Baltic basins (30 stations located from the Kattegat to the Bothnian Bay) varies from 6.6 to 16.9%. The lowest value was recorded in the sediments of the Western Gotland Basin, where the proportion between the silt and clay fractions was about 1:1. This

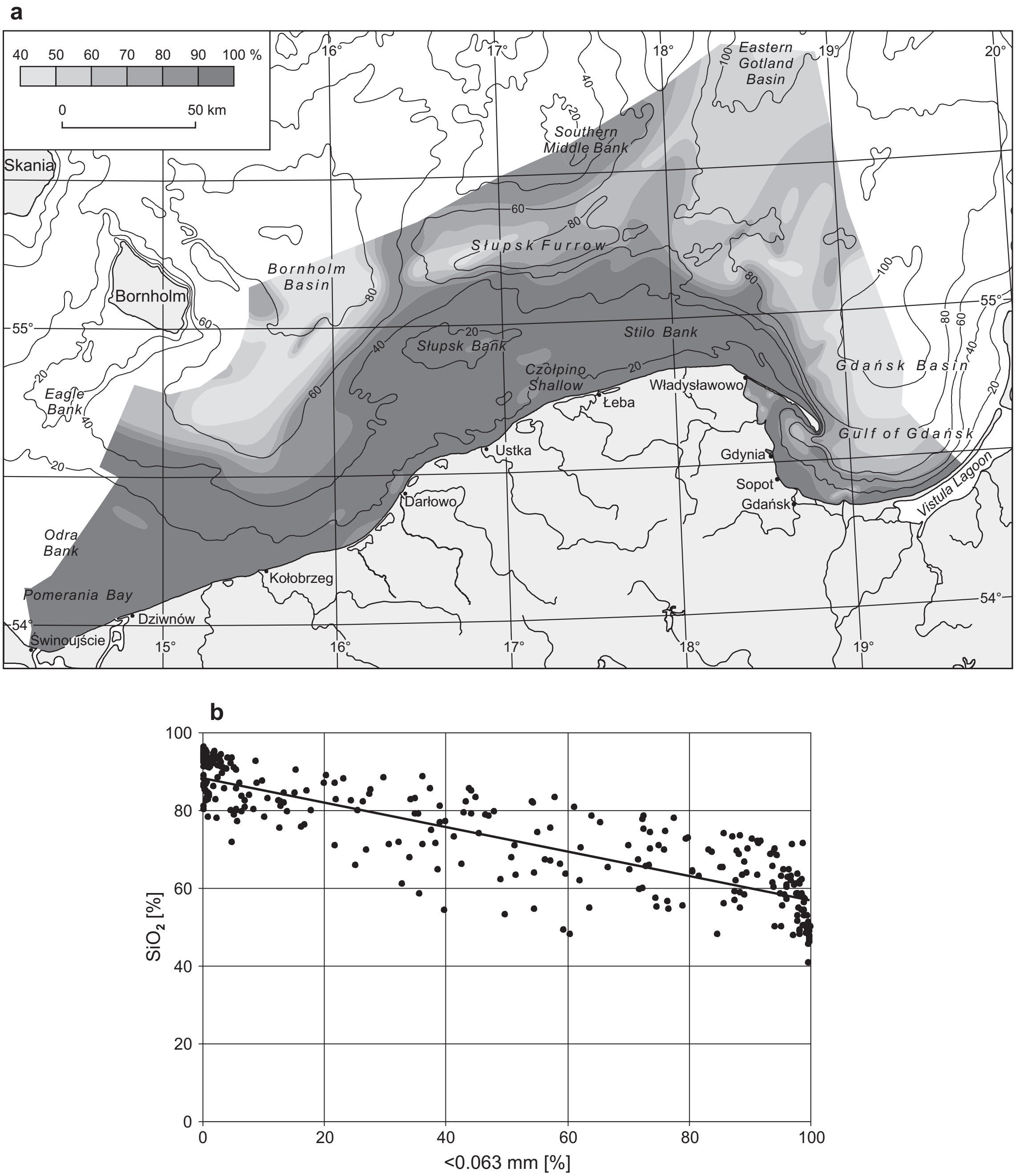

Fig. 6.1. a – SiO_2 contents in sediments of the southern Baltic Proper; b – relation between the SiO_2 concentration and the <0.063 mm fraction content in sediments of the southern Baltic Proper (based on the Geological Map of the Baltic Sea Bottom 1:200,000, 1989–1995)

is an atypical situation, because in the Farö and North-Central basins, situated slightly to the north, the Al_2O_3 concentration in the sediments containing about 75% of the silt fraction varies from 7.1 to 8.7%. The highest Al_2O_3 contents (16.4%) was noticed in the sediments of the Bothnian Bay, where the clay fraction (<0.004 mm) accounts for as much as 60%, whereas the sand fractions are in trace amounts.

Titanium. In the surface sediments of the Baltic Sea, titanium occurs in as a variety of minerals of terrigenous origin. The main titanium minerals found in the Baltic Sea sediments are rutile, ilmenite and leucoxene. Titanium occurs occasionally as endomorphs in biotite. TiO_2 concentration in the surface sediments of the Baltic Sea varies from <0.1 to 1.2% (Blazhchishin, 1982) and does not show any distinct correlation with the grain size. Both minimum and maximum titanium contents are observed in sands (Fig. 6.3). Elevated TiO_2 contents (more than app. 0.2–0.3%) are associated with the concentrations of heavy minerals, including rutile, ilmenite and leucoxene, occurring in well sorted fine-grained sands of a shallow-water zone. Lower titanium contents (<0.2–0.3%) occur in coarse- and medium-grained sands, where the contents of fraction 0.25–0.063 mm is low, as well as in fine-grained sands deposited at depths greater than 25–30 m.

In the silt-clay sediments of the southern Baltic Proper, the TiO_2 content is between 0.5 and 0.9%. Similar values are presented by Blazhchishin (1982). According to the results achieved under the project “The Baltic Sea Sediment Baseline Study”, the TiO_2 content in the silt-clay sediments of the main sedimentary basins of the Baltic Sea ranges from 0.13% in the Western Gotland Basin to 0.72% in the Bothnian Sea, whereas the grain-size distribution in sediment samples from both these regions is similar. So far, there have been no studies explaining the reasons of both elevated concentrations and a considerable differentiation in the TiO_2 contents in silt-clay sediments. Blazhchishin (1982) claims that the elevated TiO_2 contents may be associated with the formation of autogenic iron phosphates.

Iron is introduced into the Baltic Sea together with the sediments originated from coastal erosion and river runoff. The eroded Pleistocene sediments contain iron in different mineral forms. Mineral grains of the sand

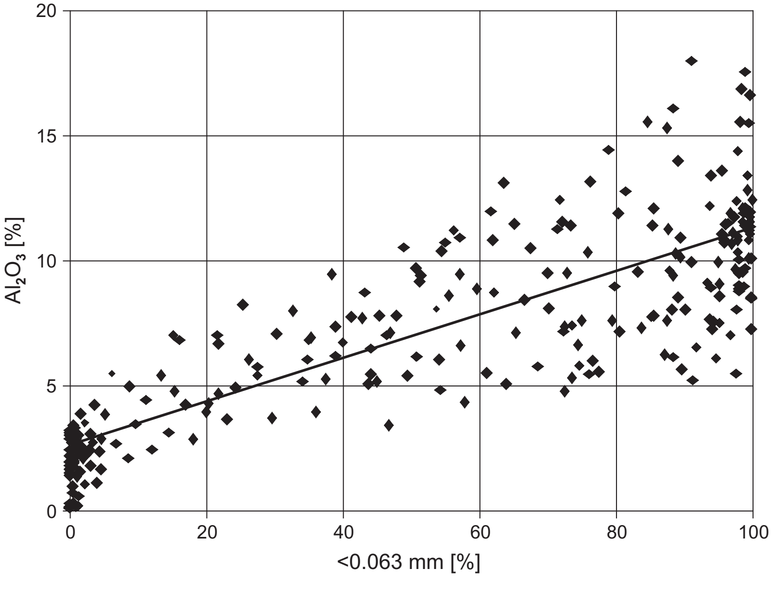

Fig. 6.2. Interrelation between the Al_2O_3 concentration and the <0.063 mm fraction content in sediments of the southern Baltic Proper (based on the Geological Map of the Baltic Sea Bottom 1:200,000, 1989–1995)

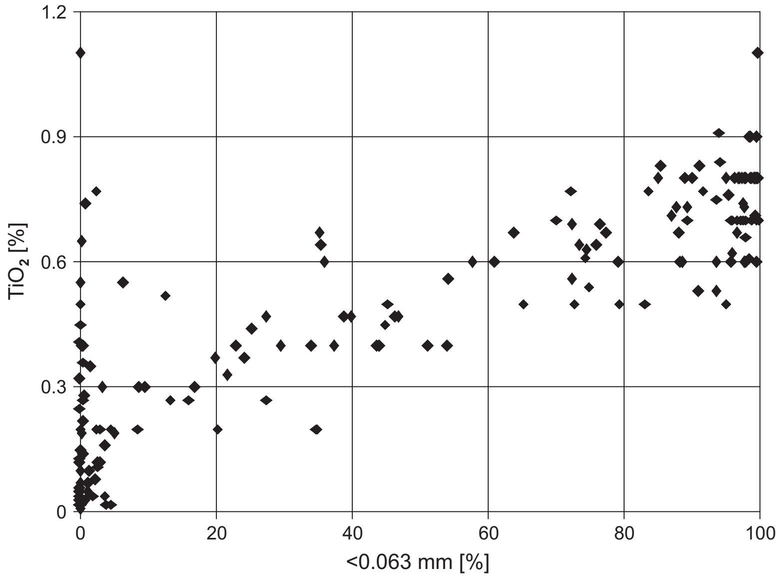

Fig. 6.3. Interrelation between the TiO_2 concentration and the <0.063 mm fraction content in sediments of the southern Baltic Proper (based on the Geological Map of the Baltic Sea Bottom 1:200,000, 1989–1995)

fractions, which contain iron, are usually represented by magnetite, haematite, biotite and glauconite. In the clay and colloid fractions, iron mostly occurs as hydroxides. Most of iron is transported into the Baltic Sea by rivers, especially by the Vistula and Odra rivers, as complex organic compounds leached from podzols.

In the Baltic Sea sediments, iron occurs in a dissipated form and as iron-manganese concretions. Dissipated forms mainly consist of terrigenous constituents with small admixtures of autogenic minerals. Autogenic iron minerals, such as pyrite (including hydrotroilite), marcasite and vivianite, form under anaerobic conditions in the bottom sea waters, in the Eastern Gotland Basin (Alvi, Winterhalter, 2001) and in some other sedimentary basins.

The iron contents in recent surficial deposits depend on the grain size. The highest iron contents (Fe_2O_3) occur in silt-clay sediments: from 1.9 and 3.5% in the Eastern Gotland Basin and Farö Basin (stations: 171 and 176; Fig. 1.1) to 9.8 and 12.1% in the southern Bothnian Sea (stations: 190 and 191). The atypically low iron concentration in the silt-clay sediments of the Eastern Gotland Basin is hard to explain.

In the southern Baltic Proper, the Fe_2O_3 content varies from 0.04% in sands up to 7.44% in silt-clay sediments (Fig. 6.4). In sands, the Fe_2O_3 content is between 0.04% and 1.9%. The sand-silt sediments that occur in the peripheries of the sedimentary basins contain from about 0.5 to about 3.2% of Fe_2O_3. The highest Fe_2O_3 contents (6.00–7.44%) are concentrated in silt-clay deposits in the central parts of the basins. Silt-clay sediments occurring in the Słupsk Furrow, Gulf of Gdańsk and between the basins of Gdańsk and Bornholm contain from 2 to 4% of Fe_2O_3. In the Gulf of Gdańsk, outside the areas of silt-clay sediments, elevated Fe_2O_3 amounts are concentrated in sands deposited in front of the Vistula River mouth, clearly showing a role of this river as a supplier of iron compounds into the Baltic Sea (Fig. 6.5).

Manganese, similar to iron, is derived from soils and eroded Pleistocene deposits and discharged into the Baltic Sea by rivers and as a result of coastal erosion. As opposed to iron, the river waters flowing down into the northern Baltic Sea are relatively more abundant in manganese than the rivers of the southern parts (Blazhchishin, 1982). In sandy deposits, the occurrence of manganese is

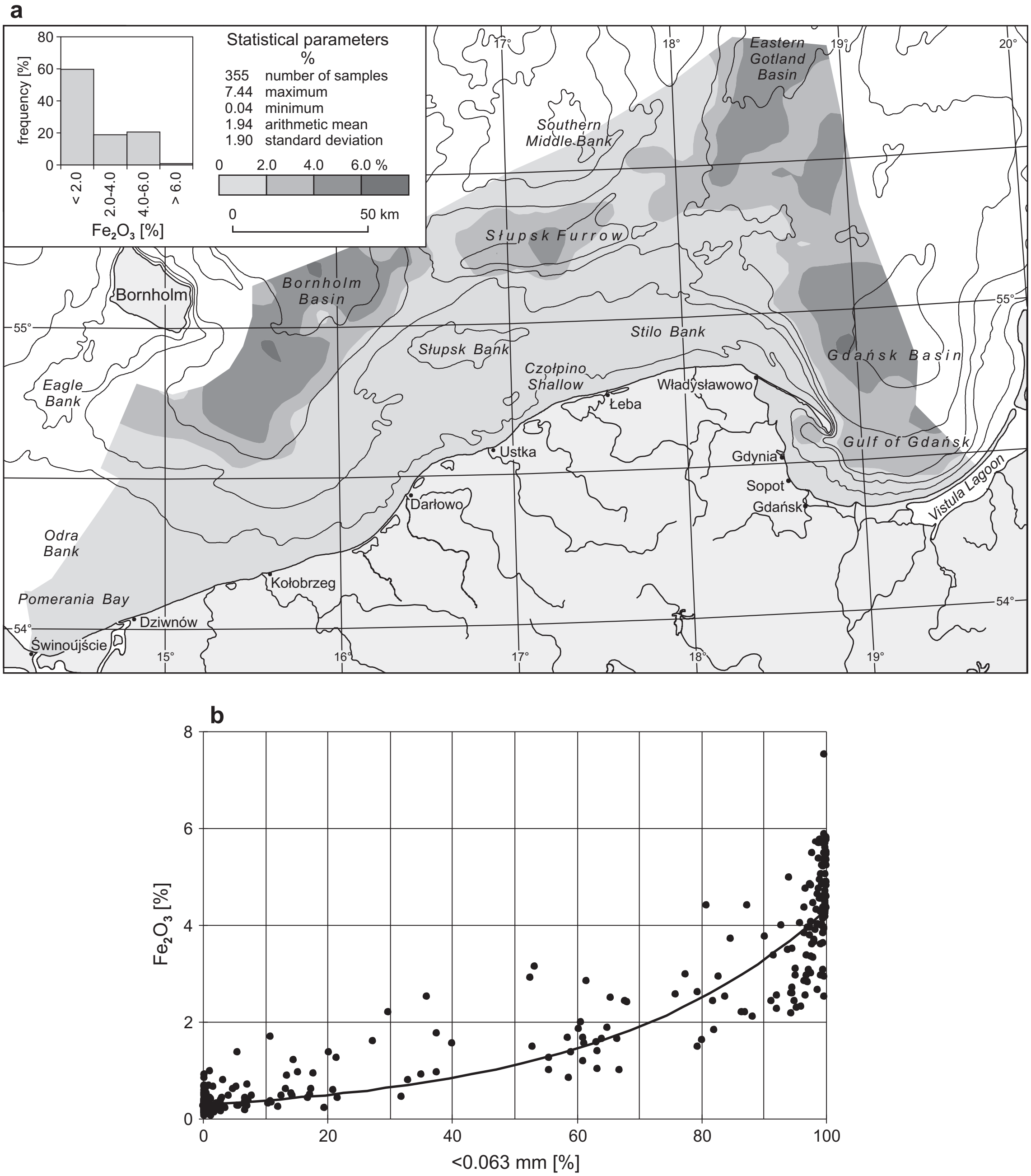

Fig. 6.4. a – Fe_2O_3 content in the surface layer sediments (0–2 cm) of the southern Baltic Proper; b – relation between the Fe_2O_3 concentration and the <0.063 mm fraction content in the sediments of the southern Baltic Sea (Szczepańska, Uścinowicz, 1994)

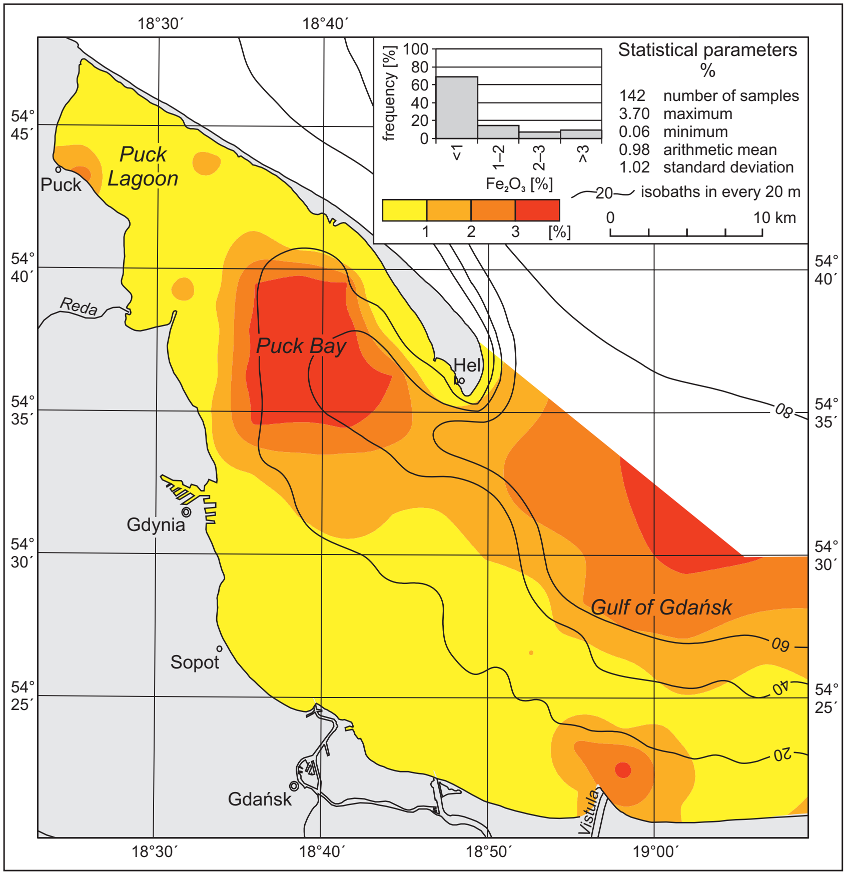

Fig. 6.5. Fe_2O_3 content in the surface layer sediments (0–2 cm) of the western Gulf of Gdańsk

associated with ilmenite. In fine-grained sediments, it is related to clay minerals and autogenic minerals formed in anaerobic conditions.

According to the results achieved in the project "The Baltic Sea Sediment Baseline Study", the MnO contents in fine-grained deposits of the main sedimentary basins of the Baltic Sea range between 0.29% in silt-clay sediments of the eastern Gdańsk Basin (station 170) and 16.0–16.6% in the North-Central Basin (station 180) and the southern Bothnian Bay (station 193). The above-mentioned results suggest a slight correlation between the manganese content and the grain size.

In the southern Baltic Proper, the MnO contents are from below 0.001 to 0.989% (Fig. 6.6). In individual grain-size types of surface sediments, the manganese content varies within a wide range. The MnO content in sands ranges between <0.001% and 0.95%, in sand-silt sediments – between 0.1 and 0.41 %, and in silt-clay sediments – between 0.1 and 0.52%.

It is due to the fact that the elevated amounts of manganese occur not only in a scattered form in the fine-grained sediments of anaerobic water zones, but also as coatings on mineral grains in places where Mn–Fe concretions occur.

The contribution of the Vistula River in supplying manganese into the Gulf of Gdańsk is more clearly reflecte in the sediments than in the case of iron. The MnO content in sands and silty sands in front of the Vistula mouth is twice as high as in the silt-clay sediments of the deep-water zone (Fig. 6.7).

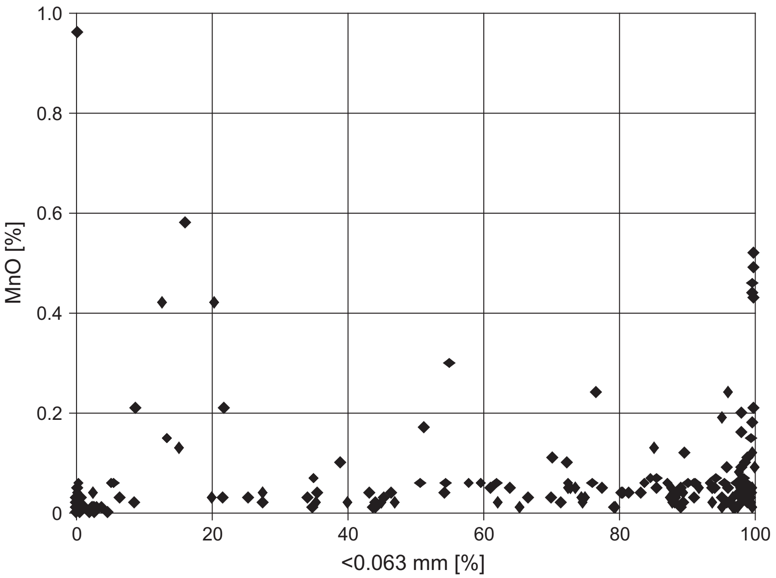

Fig. 6.6. Interrelation between the MnO concentration and the <0.063 mm fraction content in the sediments of the southern Baltic Proper (based on the Geological Map of the Baltic Sea Bottom 1:200,000, 1989–1995)

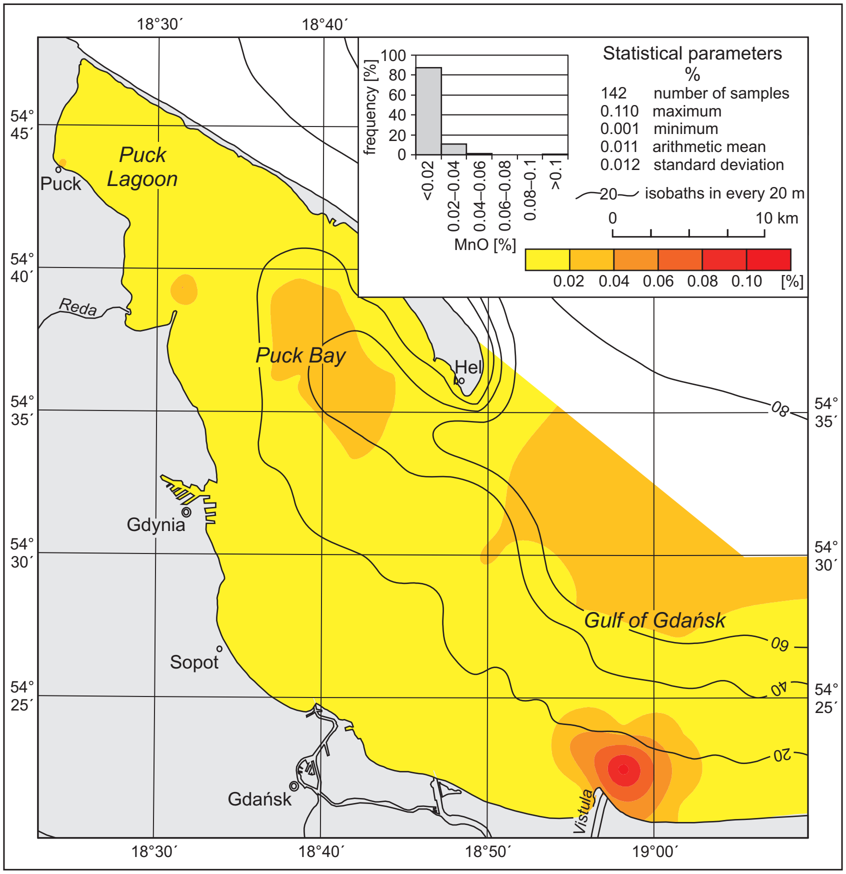

Fig. 6.7. MnO content in the surface layer sediments (0–2 cm) of the western Gulf of Gdańsk

Calcium. Calcium carbonate in the Baltic sediments is of both terrigenous and biogenic origin. Terrigenous carbonates occur as calcite and dolomite. Biogenic calcites occur in a form of shell detritus. Both terrigenous and biogenic carbonate detritus are quickly destroyed. Calcite and dolomite grains together with shell detritus show low resistance to mechanical destruction. In addition, since the shells of Baltic calms are small and thin their disintegration is more effective. Calcium carbonate also undergoes the process of chemical dissolution in the Baltic Sea because its waters are unsaturated with $CaCO_3$.

Calcium carbonate occurs in sandy and silty-clay sediments, mostly below 1%. Slightly elevated $CaCO_3$ contents are found only in the northern Baltic Proper, in the regions where Silurian and Ordovician limestones outcrop on the coast and at the sea bottom. In the Sarema, Hiuma and Gotland regions, the calcium carbonate content in top layer sediments may be up to 5%.

The lack or a very low content (<1%) of calcium carbonate in sandy sediments of the southern Baltic Proper is a good criterion enabling us to distinguish modern marine sands from Pleistocene glaciofluvial sands.

Another issue is the contemporary formation of autogenic carbonate minerals in the Baltic Sea. Under anaerobic conditions that occur in the Baltic depths, Ca-containing complex minerals, such as kutnahorite and gypsum, are formed (Alvi, Winterhalter, 2001).

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Chapter 7

ORGANIC CARBON AND NUTRIENTS IN THE BALTIC SEA SEDIMENTS

7.1. Factors Affecting Organic Carbon and Nutrient Contents in Sediments

The content of organic carbon and nutrients in marine sediments are determined by a complex interplay of biotic and abiotic factors. Benthic organisms limit the accumulation of organic matter in the bottom, thus shaping vertical and horizontal distribution of carbon and nutrient elements in sediments. The intensity of erosion in the catchment area affects the sedimentation rate and oxygen conditions in an aquatic ecosystem, and as a consequence it has an influence on the sorption capacity of the sediments as well as on the physical and biological activity of benthic organisms. Changes in pH of the water column induce changes in the processes of metal (Ca, Fe, Al) phosphates precipitation as well as in sorption capacity of suspended matter and surface sediment. Water dynamics results in the stratification of sediments and, as a consequence, affects diagenetic processes and the horizontal distribution of sediments.

In the relatively shallow Baltic Sea, bathymetry and the seasonally variable wave action show the essential effect on the dynamics of the near-bottom water and sediments (Jönsson *et al*., 2005). The differences in frequencies and intensities of sea water mixing above the sea bottom are reflected not only in grain size of the sediments, but also in their water content (W), loss on ignition (LOI) and the contents of carbon and nutrients. These elements are closely connected with each other (Table 7.1, Fig. 7.1). Fine-grained, highly hydrated sediments are marked by high loss on ignition and a high content of carbon and nutrients. The relations that connect these elements may indicate regional variability. The reasons for this type of variability are related with, for example, a different hy-

Table 7.1

The indexes of function as: W = a·ln(LOI) + b describing relations between water content (W) and the loss on ignition (LOI) in the sediments of different regions of the Baltic Sea (Carman, Cederwall, 2001)

Region	Coefficients		Coefficient of determination R^2
	a	b	
Bothnian Bay	24.6	20.6	0.88
Bothnian Sea	27.8	12.9	0.94
Bałtic Proper	24.4	15.2	0.91
Gulf of Finland	27.7	7.8	0.93
Gulf of Riga	23.5	20.3	0.96
Gulf of Gdańsk*	21.5	24.2	0.98
Bałtic Sea	23.7	17.9	0.90

* Graca, 2009

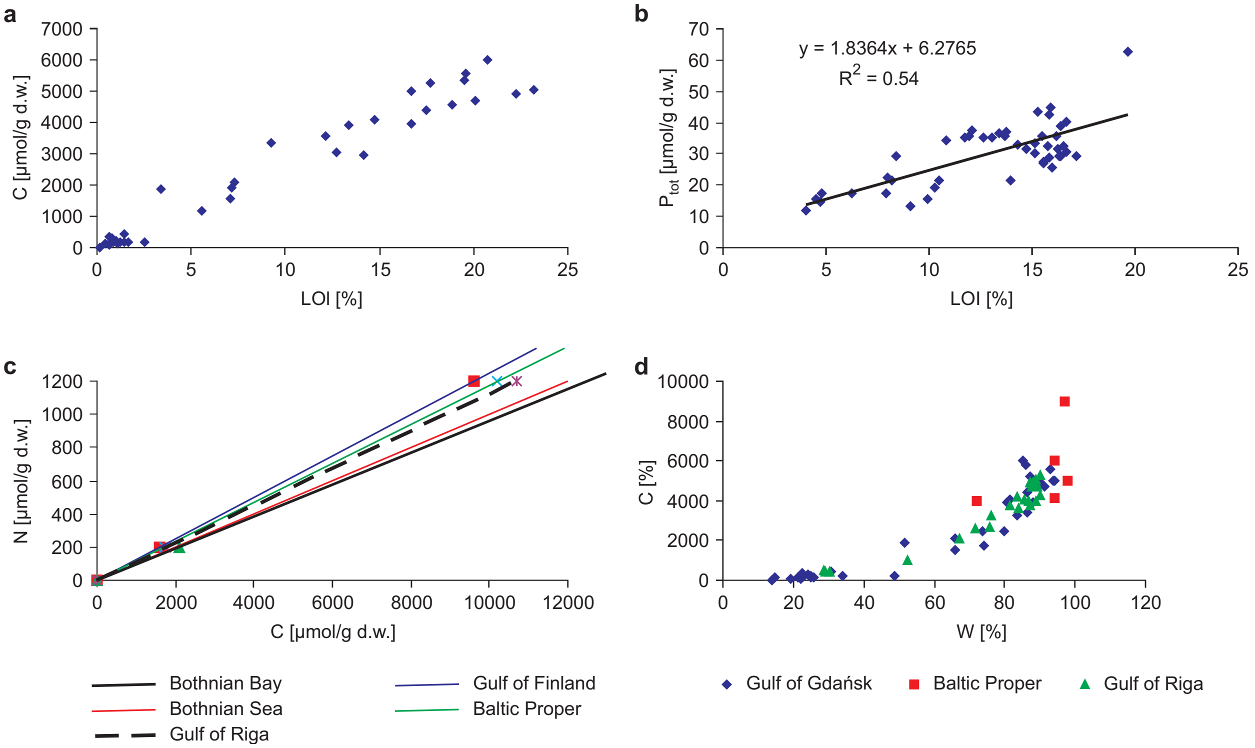


Fig. 7.1. Relations between (a) carbon and loss on ignition in the surface sediment layer in the Gulf of Gdańsk, (b) total phosphorus and loss on ignition in the surface sediment layer in the Gulf of Gdańsk (Graca, Bolałek, 1998), (c) nitrogen and carbon ($0.95 \leq r \leq 0.99$) (Carman, Cederwall, 2001), and (d) carbon and water contents in different regions of the Baltic Sea (after Carman *et al.*, 1996; Carman, Rahm, 1997; Conley *et al.*, 1997; Edlund, Carman, 2001)

drological system of sea basins or with the geochemical composition of the sediment material that eroded from the catchment area.

In the Baltic Sea, three sea bottom functional zones have been distinguished (Håkanson *et al.*, 2003). In the erosion bottom zone (zone E), the permanent physical activity of water induces sediment resuspension and prevents deposition of grains up to their certain critical size. Sediment water content in this zone does not exceed 50% and the loss on ignition (LOI) – 4%. The opposite is represented by the accumulation bottom zone (zone A), where the conditions are favourable for the undisturbed deposition of fine-grained sediments. The sediments of the accumulation zone are characterised by high water content (W> 75%) and loss on ignition (LOI> 10%). The transportation bottom (zone T) is a transitional area between the erosion and accumulation bottom types. Periods of intense resuspension and transport of the fine-grained sediments alternate with low water dynamics and with the deposition of the sediments. Indication of this type of the sea bottom can sometimes raise difficulties. As a result the division into the accumulation and non-accumulation sea bottom is used as an alternative (Jönsson *et al.*, 2005). In the zone of the transportation sea bottom, the water content and the ignition losses are 50–75% and 4–10%, respectively. In most Baltic Sea regions, the erosion zone is marked by the smallest surface area of the sea bottom (Table 7.2).

The fine-grained sediments, typical of the accumulation zone, are deposited under calm hydrodynamic conditions from a relatively homogeneous suspension. As

Table 7.2

The percentage contribution of the areas in relation to individual sea bottom zones in different regions of the Baltic Sea (Carman, Cederwall, 2001)

Region	Area [10^3 km^2]	Bottom zones		
		A	T	E
Bothnian Bay	36	33	43	24
Bothnian Sea (with the Åland Sea)	70	30	46	24
Gulf of Finland	30	41	39	19
Gulf of Riga	19.2	28	39	33
Gulf of Gdańsk (without the Puck Bay and Vistula Lagoon)*	4.6	40	31	29
Baltic Proper	206	38	38	24

* Graca, 2009

a consequence, the chemical composition of these sediments usually are characterized by regular vertical profiles. More than 80% of sedimentary material can get into the regions of accumulation sea bottom as a result of resuspension and subsequent transport from shallow-water regions (Jonsson *et al.*, 1990). In the transportation bottom zone, the sedimentation processes undergo stronger fluctuations and, consequently, the content of carbon as well as other chemical components shows less regular variations within the profile and wide ranges in their values. The erosion bottom zone is characterised by low concentrations of C, N and P and their irregular variations within the sediment profile.

The boundary between the accumulation and non-accumulation zone of the sea bottom is often referred to as the sea depth. In the Baltic Sea, this boundary is determined by an isobath of 75 m (Carman, Wulff, 1989). In the Gulf of Gdańsk (excluding the Puck Bay), the contribution of fine-grained sediments increases with the increase in the water depth. As a result, the loss on ignition and water content of the sediments are also strongly associated with the sea depth (Fig. 7.2). Approximate limits between erosion, transportation and accumulation zones in this area are determined by isobaths of 40 m and 80 m.

The conventionality of such a division should be emphasized in this place. The geochemical condition of the sea bottom sediments results from many factors and the sea depth is not always a basic criterion.

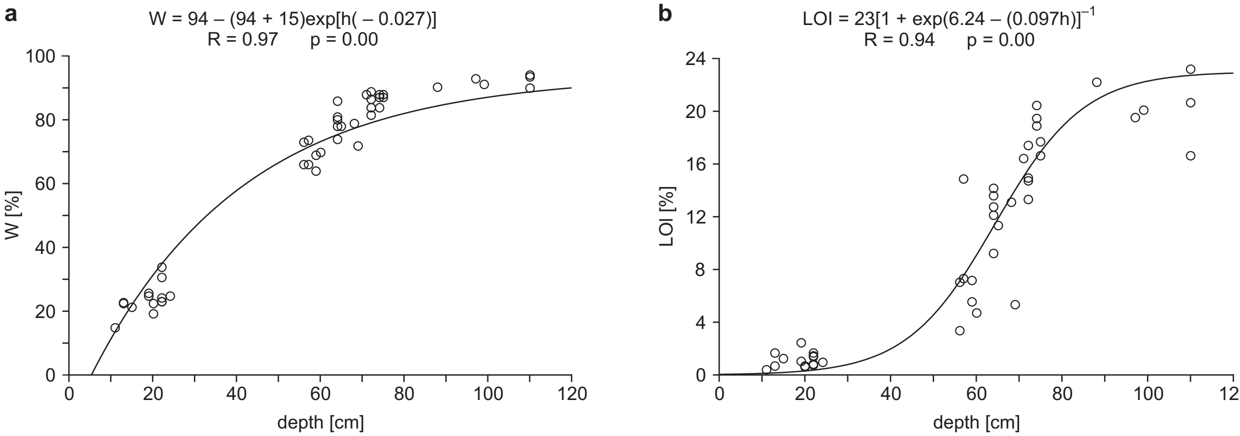


Fig. 7.2. Correlation between the sea depth and (a) water content (W), (b) loss on ignition (LOI) in the surface sediment layer (0–1 cm) in the Gulf of Gdańsk (Graca, 2009)

7.2. Organic Carbon

The intense economic activity in the Baltic Sea catchment area in the past 100–150 years induced increased eutrophication, the effect of which is an excessive influx of organic matter to the sea-bottom sediments. The enrichment of sea-bottom sediments with organic carbon intensifies the biogeochemical processes, having an effect on the thickness of the bottom sediment, oxygen conditions, and as a consequence, inducing alterations in biocoenoses. Organic carbon present in the sediments, as a parameter controlling the mineralisation processes and matter exchange between the sediments and water, is a significant element in the global carbon circulation. Sediments are a main location for their long-term storage. The carbon accumulation in sea-bottom sediments is a key long-term mechanism that leads to reduce the level of atmospheric CO_2.

The identification of the role of carbon in the marine and global cycle as well as the reference to the regulation of local climate is one of important issues in contemporary oceanographic research. The estimation of regional and seasonal contents of organic carbon in sea-bottom sediments allows the assessment of the changes in the marine sedimentary environment (Emeis *et al*., 2003; Leipe *et al*., 2008).

7.2.1. Carbon Cycle in a Marine Environment

There are three main reservoirs of carbon in its global cycle: the atmosphere, oceans and seas, and the terrestrial biosphere. The ocean is a huge water reservoir that contains 50 times more CO_2 than the atmosphere and 20 times more than the terrestrial biosphere. 50% of the emitted carbon dioxide stays in the atmosphere, while the remaining 50% is absorbed by the terrestrial vegetation and the oceans (Schulz, Zobbel, 2000). The oceans play a special role in the catchment of carbon dioxide from the atmosphere, where the transport of CO_2 into the deep waters of the oceans is carried out under the effect of both physical (physical pump) and biological (biological pump) processes.

Dissolved inorganic carbon (DIC), present in water mainly as HCO_3^- and CO_3^{2-} ions, is assimilated by autotrophs in the process of photosynthesis and it can also be assimilated by rare chemosynthesising microorganisms (Pilson, 1998). Organic carbon occurring in the form of suspensions (POC – particulate organic carbon) is transported into the deep sea waters and finally to the sea-bottom sediments. In the form of suspension inorganic carbon (PIC – particulate inorganic carbon) also occurs in the seas and oceans, mainly as calcium and magnesium carbonates. A significant role in the carbon cycle is also played by dissolved organic carbon (DOC) that is excreted by autotrophic organisms: it is produced as part of the processes of autolysis and released from dead cells, and in the processes of hydrolysis as the result of the activity of bacterial extracellular enzymes. In the total sum of organic carbon occurring in the seas and oceans, DOC constitutes about 80% (Pempkowiak, 1997). In the process of organic matter microbiological degradation, besides DOC, dissolved inorganic carbon returns into the circulation.

The production of organic matter in the surface layer of sea water is a main factor in the enrichment of the sea sediments with organic carbon (Pedersen, Calvert, 1990). Apart from autochthonous carbon, a significant source of organic carbon is terrigenous influx with the contribution of river transport, which is a dominant factor for the Baltic Sea. In the sediments of the Baltic Sea, the fraction of organic carbon of terrigenous origin is significantly higher than in the sediments of the open seas and oceans, and reaches 10–30% of the total organic carbon (TOC) contained in marine sediments (Miltner, Emeis, 2000, 2001). The amount and quality of terrestrial material in sediments depends mainly on the type of the drainage basin basement, the mode of land use (farming, industrial) and the degree of plant cover.

Sedimentation rate is another parameter that affects the TOC contents in sediments. Increasing sedimentation rate leads to accumulation of carbon in sediments. In the open oceans, the carbon flux through the water column drops exponentially with increasing depth as the result of organic matter degradation under oxygen conditions (Suess, 1980). The fraction of refractive carbon in the settling matter grows at the expense of its labile form (Bertrand, Lallier-Verges, 1993). Only a small part (1.5%) of TOC produced in the surface oceanic layer reaches the oceanic bottom, whereas a considerably higher part (up to 17%) is accumulated in the shelf zone and the continental slopes (Schlitzer, 2002). In the sea bottom, organic carbon undergoes diagenetic transformations, e.g. it is oxidised to CO_2. Finally, from 0.5 to 3% of TOC remains in the sediments of continental shelves and slopes, whereas only 0.014% of TOC from primary production remains in the oceans.

The degradation and the deposition rate of organic carbon in the marine environment depends on, for example, the degradability of organic matter and oxygen availability. Organic matter consists of heterogeneous mixture of particles and molecules of different physical properties and chemical features. The mixture of such matter is characterised by various products of degradation and their turnover (Müller, 2002). Decomposition under oxygen conditions is regarded as more effective, especially in case of refractive matter, than under anoxic conditions (Arnosti *et al*., 2005), and deep anoxic sedimentary basins are areas of intense deposition of organic carbon. In anoxic conditions, decomposition of organic matter essentially depends on the reduction of sulphates, the effectiveness of which can be compared with aerobic degradation.

The distribution of TOC in bottom sediments significantly depends on the occurrence of benthic organisms (Witte *et al*., 2003). Macro- and meiofauna are responsible for transporting organic carbon into the sea-bottom deposits. They oxygenate sediments in the processes of bioturbation and bioirrigation and simultaneously accelerate organic matter degradation. Microorganisms consume fresh organic matter that is dereved from the euphotic zone, as well as organic matter processed by benthic organisms and co-participating in further degradation of organic carbon (Arnosti *et al*., 2005). A small fraction of organic matter is buried in the sediments and thus close the way for its later participation in the carbon cycle (Yakushev *et al*., 2007). These organisms are also an important component of organic carbon in the sea-bottom sediments.

Organic carbon content in sea-bottom deposits is, therefore, a resultant of carbon supply to a sedimentary basin from different sources and the processes that reduce the contents of this element in the water depths and in the sea-bottom sediments. TOC in the surface sediment layer reflects primarily the distribution and the amount of pelagic primary production; however it also depends on, for example, the amount, quality and distance from the terrigenous sources, the seabed topography, depth of the water reservoir, type of sediment and horizontal transport between sedimentary basins (Baldock *et al*., 2004).

7.2.2. Distribution of Organic Carbon in Recent Surface Sediments of the Baltic Sea

Total organic carbon (TOC) content in the surface sediments of the Baltic Sea varies over a wide range, from values close to zero up to more than 16% (i.e. Pęcherzewski, 1976; Szczepańska, Uścinowicz, 1994; Carman, Rahm, 1996; Emelyanov, 2001, 2002; Miltner, Emeis, 2001; Perttilä *et al*., 2003; Virtasalo *et al*., 2005; Leipe *et al*., 2008). The lowest contents of TOC were determined in sandy sediments, mainly in shallow coastal regions. The highest values are recorded in deep sedimentary basins with silty sediments. Regional and seasonal differences in the contents of organic carbon occur both in shallow-water and deep-water deposits of the Baltic Sea.

Amongst deep sedimentary basins, the lowest organic carbon contents (3–4%) are found in sediments of the Kattegat, Bothnian Sea and Bothnian Bay. The sediments richest in TOC (even over 4-times more than in the Kattegat) occur in the north-eastern part of the Gotland Basin. Moderate (6–8%) and high (8–10%) contents of TOC are present in the sediments of the Bornholm Basin and Gdańsk Basin (Fig. 7.3).

The Kattegat region, the westernmost and smallest subregion of the Baltic Sea, is marked by high (125 mg C/m^2 year) primary production (Wania *et al*., 2001). Nonetheless, organic matter enriches to a small degree the bottom sediments in this area. This is an effect of the occurrence of persistent, periodically strong currents transporting organic matter into other areas of the Baltic Sea together with bottom waters from the North Sea. Also, the poorly shaped seabed does not create favourable conditions for preventing organic carbon in the sea-bottom sediments. Low concentration of organic carbon in sediments of the Bothnian Sea and Bothnian Bay mainly results from small productivity of the waters in this area (2 to 5 times lower primary production than in the Kattegat) and a low salinity that is favourable for mixing waters and, as a consequence, intense mineralisation of organic matter in the water column.

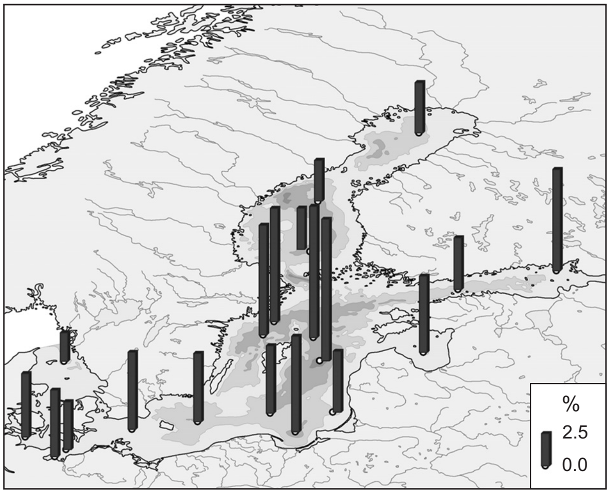


Fig. 7.3. TOC content in the surface sediment layer (0–1 cm) of the Baltic Sea (Carman *et al.*, 1996; Miltner, Emeis, 2001; Perttilä *et al.*, 2003)

The maximum contents of organic carbon (locally more than 15%) that occur in the northern and eastern part of the Eastern Gotland Basin are the result of the highest Baltic production (mainly of blue-green algae and diatoms) and the largest inflow of the matter from all neighbouring basins of the Baltic region. Moreover, thermal-salinity stratification and irregular inflows of oxygen-rich waters from the North Sea slow the mineralisation rate of organic matter reaching the sea bottom here. This autochthonous source of TOC is responsible for 90% of organic carbon in the sediments of this region. A significant cause of the small contribution of terrigenic organic carbon in the sediments of the Gotland Basin is the decrease in the load of matter transported by rivers over long distances. Abrasion of the basin slopes is more important than river transport as a source of TOC in this area (Miltner, Emeis, 2001).

Amongst the three deep basins located in the southern Baltic Sea, the highest values of total organic carbon are characteristic of the sediments of the Gdańsk Basin (Fig. 7.3). In addition to the highest primary production that is close to the highest for the Baltic Sea, carbon of terrigenous origin (up to 30% TOC in the Gdańsk Basin) significantly contributes to the TOC content in the sediments of this area (Miltner, Emeis, 2001). A high contribution of terrigenous TOC was also observed in the sediments of the Arkona Basin. In both cases, it is the effect of the inflow of Vistula and Odra river waters.

The Baltic deeps are not only the areas of high TOC contents in the sea-bottom sediments. Lagoons and half-open bays are particular regions where preliminary sedimentation of suspended solids rich in organic matter occurs. These solids are transported by rivers; organic matter is additionally produced in the reservoirs, e.g. lagoons, as the effect of intense supply of biogenic salts. The distribution of TOC in sediments of these areas depends on the sea-bottom topography and related current circulation. The occurrence of local sedimentary basins in the region of organic matter transport results in higher accumulation of organic carbon in these “traps” when a source of organic matter is closer and more productive.

The Puck Lagoon, like the Vistula, Szczecin and Curonian lagoons, is one of those areas where the TOC content in sediments is often higher than in the neighbouring deep sedimentary basins (Table 7.3, Fig. 7.3). The high-

Table 7.3

Minimal and maximal content of total organic carbon (TOC) in the top layer of sediments for the selected reservoirs of the Baltic Sea

Region	TOC [%]	Layer of sediments [cm]	References
Gulf of Riga	0.53–6.32	0–1	Carman *et al.*, 1996
Curonian Lagoon	0.40–6.64	0–5	Emelyanov ed., 2002
Vistula Lagoon	0.50–10.20	0–10	Uścinowicz, Zachowicz, 1996; Emelyanov ed., 2002; Chechko, Blazhchishin, 2002
Puck Lagoon	0.23–8.18	0–2	Uścinowicz, 2008
Puck Bay	0.10–7.98	0–2	Uścinowicz, 2008
Szczecin Lagoon	0.41–13.1	0–1	Miltner i Emeis, 2001; Emeis *et al.*, 2002

est content of TOC (13.2%), deposited here as the effect of transport by the Odra River, and produced in huge amounts in the process of photosynthesis owing to high concentrations of biogenic substances, was measured in sediments of the Szczecin Lagoon. More than 10% of TOC is present in silty sediments of the north-western part of the Vistula Lagoon (Chechko, Blazhchishin, 2002).

The bays of limited access to the open waters of the Baltic Sea also belong to the areas of high TOC contents in sediments. The sediments of the coastal zone of the Gulf of Finland contain from 10 to 12% of organic carbon. Organic carbon carried out by the Neva River waters and originated from the primary production of this basin is deposited in sediments in a considerable amount due to the small depth of the gulf. The topography of this area with numerous local cave-ins separated with small rises (skerries) is favourable for accumulation. The lowest values of TOC concentrations are characteristic of the sediments of the shallow Gulf of Riga. However, also for this case the content of organic carbon locally increases to 7%.

Elevated TOC contents may also occur in river mouths (Fig. 7.4). Changes in TOC concentrations in the region affected by the river water inflow depend mainly on the amount and quality of the loading organic matter load, intensity of dynamic processes in the estuary area, as well as on the topography of the reservoir receiving the

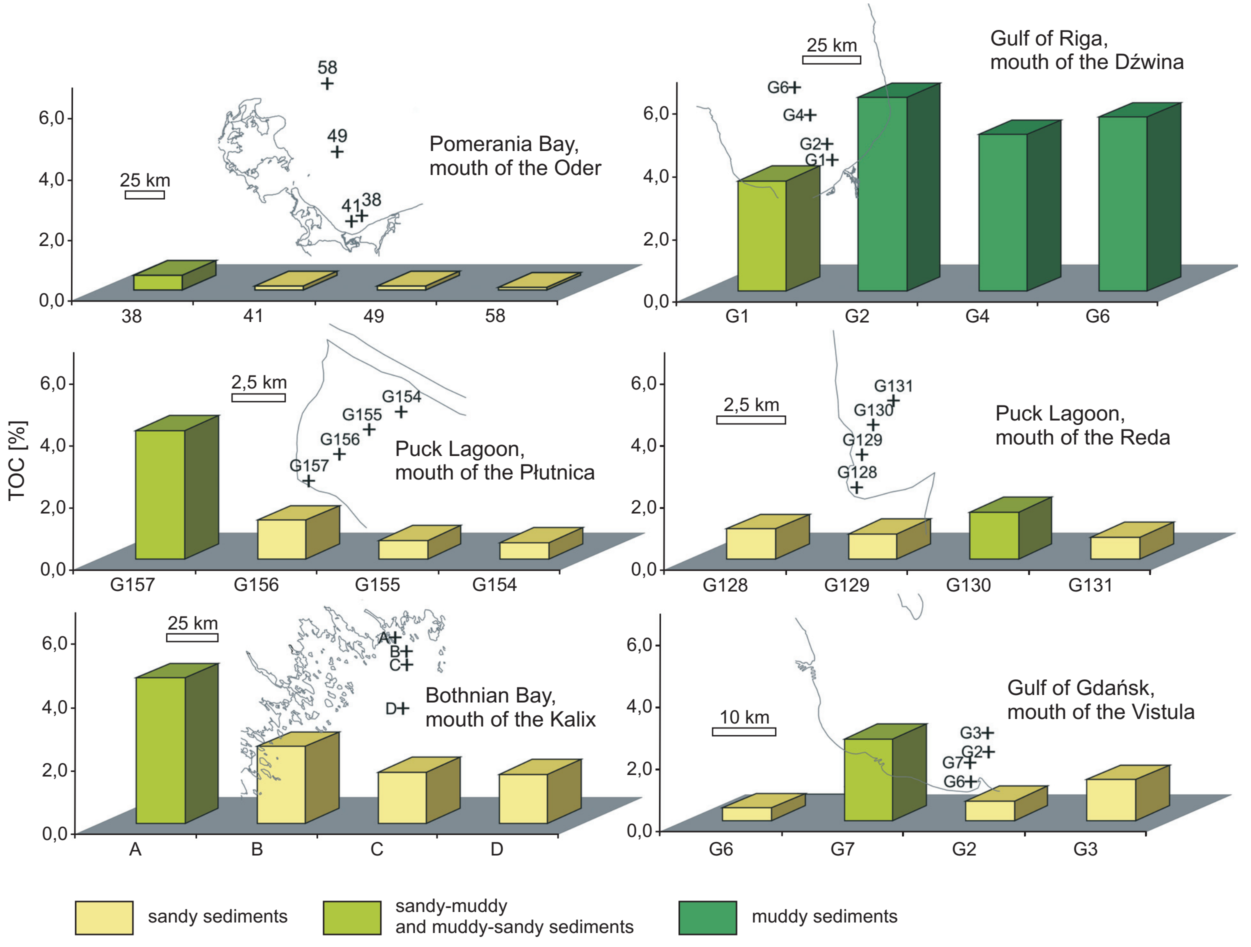


Fig. 7.4. TOC content in sediments near the river mouths (based on Carman *et al.*, 1996; Burska *et al.*, 1999; Uścinowicz, 2008; Vonk *et al.*, 2008)

riverine waters. The TOC value may decrease, keep on a constant level or increase depending on the distance from the terrigenous source of organic carbon.

The lowest concentrations of organic carbon occur in sandy sediments of both the coastal zone and open waters of the Baltic Sea. Due to the inflow from the land and high primary production in the coastal zone, this area is marked by high contents of organic matter in the water column and by its considerable flux to the sediments. Thus, the low concentration of organic carbon in coastal sands is not an effect of low activity in delivering carbon to the sediments but the result of rapid matter turnover (Huettel *et al*., 1998). Organic matter goes through many cycles of sedimentation and resuspension when transported through shallow coastal areas and is intercepted by water currents and wave movements. In the coastal zone, the process of washing out (leaching) rapidly removes dissolved substances (interstitial waters) from the sediments and considerably affects organic matter decomposition.

Organic carbon contents of in sandy sediments is usually lower by an order of magnitude than those observed in silty sediments (Szczepańska, Uścinowicz, 1994; Maksymowska, 1996; Emeylanov, 2001, 2002; Burska *et al*., 2003; Uścinowicz, 2008). According to Emeylanov (2001), the TOC content ranged from 0.02% to 0.98% in the 10-cm layer of sandy sediments in the Gdańsk Basin, and the highest values were observed in the Sambia Peninsula region. There is a clear difference between sandy sediments east and west of the Vistula River mouth. In the east, the TOC content reaches 0.18%, whereas on the other side of the Vistula estuary, the total organic carbon concentration is more than 3 times higher. A slightly lower range of TOC values (0.04–0.66%) is typical of the surface sediment layer (0–2.5 cm) in the Pomeranian Bay (Burska *et al*., 1999). The highest TOC content in sediments occurs in the Odra River mouth. Sandy deposits in the regions situated far from the coastline show lower TOC contents than the sediments in the coastal zone. The TOC content in surface bottom sediments of a submarine threshold located between the Gdańsk and Gotland basins does not exceed 0.5% (Szczepańska, Uścinowicz, 1994; Emeylanov, 2001).

TOC contents in the surface sediment layer of the Polish Economic Zone are well known. The research on TOC in the deposits of this region was carried out in the 1970s by Pęcherzewski (1976). A wide database of TOC measurements in the deposits of the Gdańsk Basin, including data from the 1970s, was presented by Emelyanov (ed., 2002). However, the most detailed results are those from the Geochemical Atlas of the Southern Baltic (Szczepańska, Uścinowicz, 1994) and the recent data of 2005–2006 from the Gulf of Gdańsk and Puck Bay (Uścinowicz, 2008).

Surface layer sediments of the southern Baltic Sea contain from 0.01 to 8.77% of organic carbon (Figs. 7.5, 7.6, Table 7.4). The content distinctly depends on the contents of fine-sized fractions in the tested sediments. The concentrations of organic carbon grow with the increase in the contribution of the grain size fraction finer than 0.063 mm.

The lowest TOC concentrations, like elsewhere in the Baltic Sea, are observed in sandy deposits, whereas the highest ones – in silty sediments (Fig. 7.7). The increase in the TOC contents follows the increase in the basin depth, which is a result of a higher contribution of the fractions finer than 0.063 mm. However, there are many regional and local deviations from the above correlations, due to distributing natural and artificial sources of supply with individual components and from different environmental conditions, such as sea current circulation systems, seabed topography or a variable oxygen concentration in the sea-bottom waters.

About 75% of the TOC content measurements in sandy sediments shows values lower than 0.4% (Table 7.4). The lowest TOC contents (<0.1%) occur in sandy sediments in the southern and south-western coasts of the Baltic

Table 7.4

Statistical analysis of the total organic carbon content (TOC) in the top layer (0–2 cm) sediments of the southern Baltic Sea (after Szczepańska and Uścinowicz, 1994; Uścinowicz, 2008)

Sediments	n	min	$k_{25\%}$	x ±SD	max	$k_{75\%}$
Sands	269	>0.01	0.05	0.29 ±0.41	3.75	0.41
Silty sands and sandy muds	60	0.18	0.73	1.46 ±0.95	4.28	2.04
Muds and clays	157	0.12	3.06	4.42 ±1.77	8.77	5.57

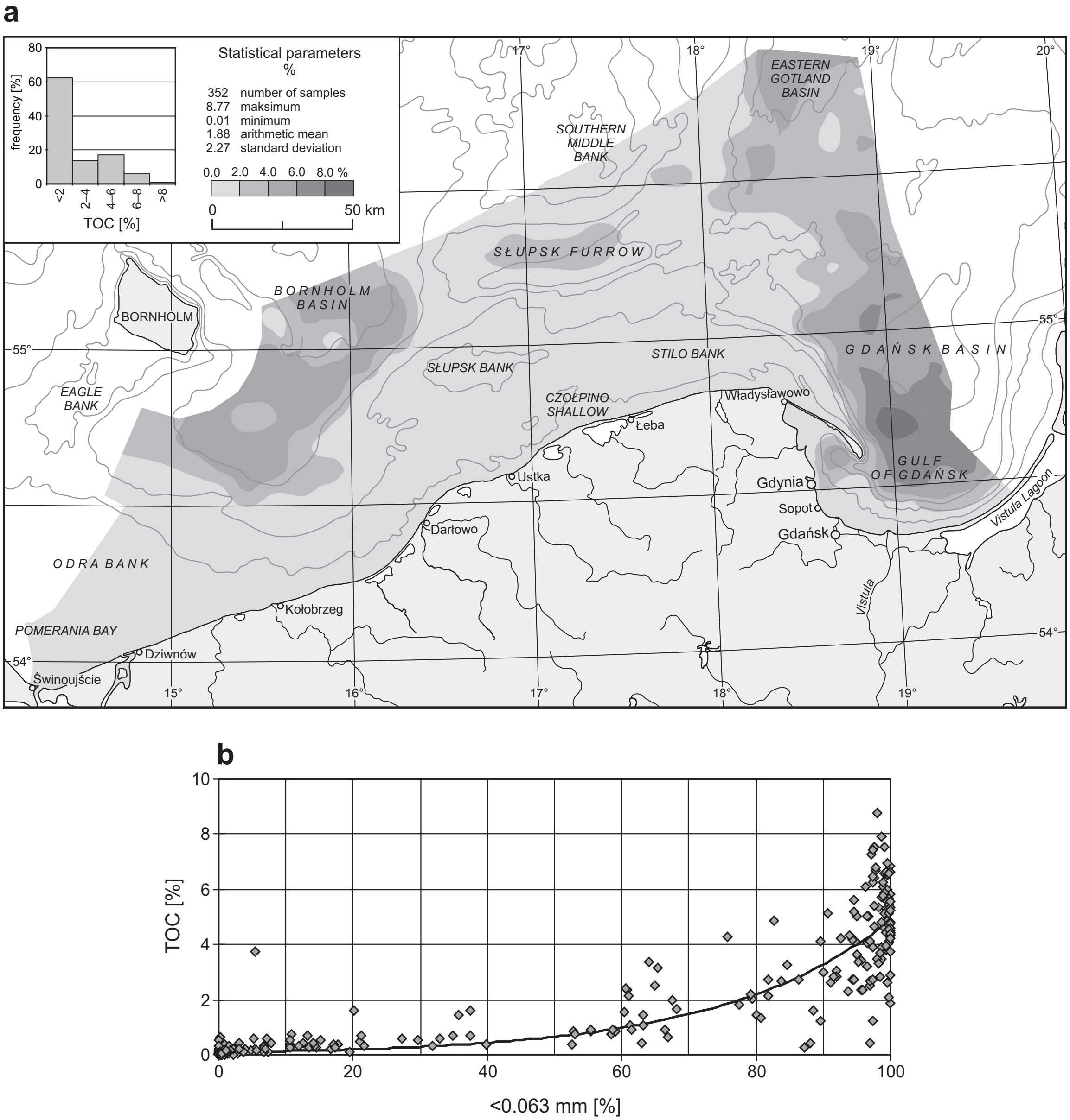


Fig. 7.5. TOC content in the surface sediment layer (0–2 cm) of the southern Baltic Sea (a) and with reference to the contribution of the fraction <0.063 mm (b) (Szczepańska, Uścinowicz, 1994)

Sea (Emeylanov, ed., 2002), coinciding with the areas of strong and frequent processes of resuspension induced by wind wave movements (Danielsson *et al*., 2007). Higher TOC contents are observed in the sediments in the forefield of river mouths (Fig. 7.4), and in the areas of intense economic activity, such as harbours and shipyards. The highest value of the total organic carbon in sandy sediments (3.75%) was noticed in the entrance to the Gdynia harbour, which is probably associated with the contamination of the sediments with petroleum derivatives.

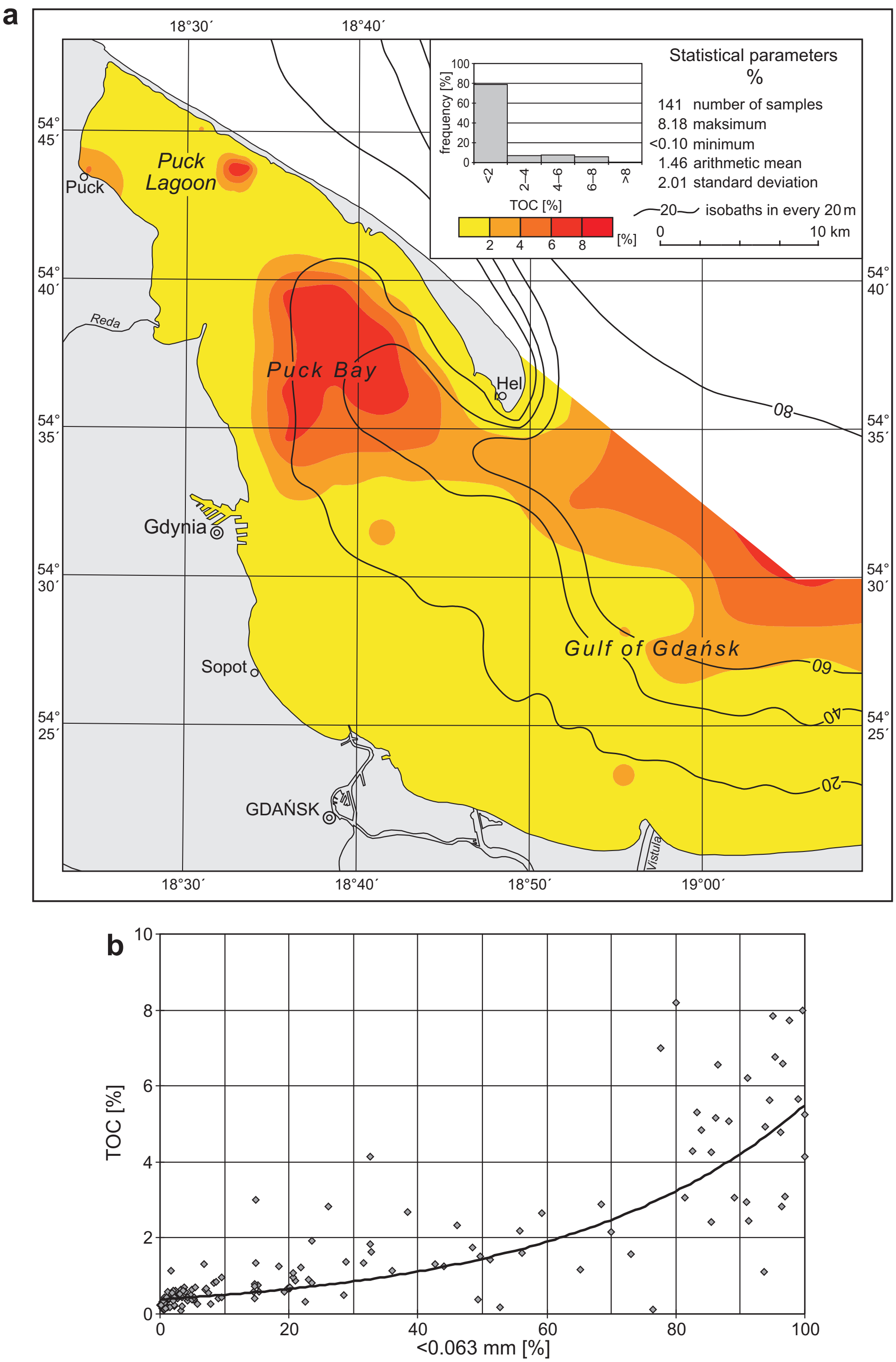


Fig. 7.6. TOC content in the surface sediment layer (0–2 cm) of the Gulf of Gdańsk (a) and with reference to the contribution of the fraction <0.063 mm (b) (Uścinowicz, 2008)

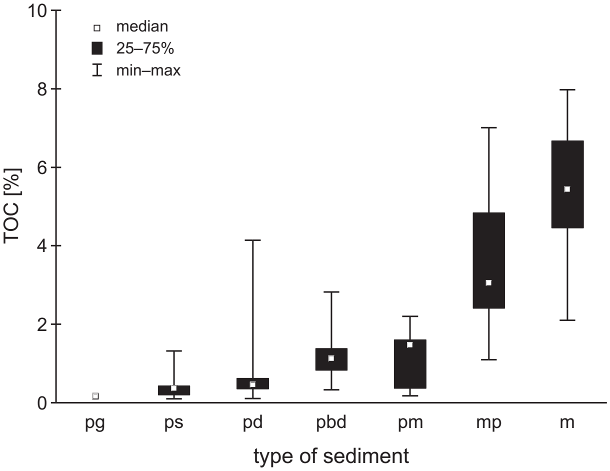


Fig. 7.7. Variability in the TOC content as a function of the sediment type (Uścinowicz, 2008)

pg – coarse-grained sands, ps – medium-grained sands, pd – fine-grained sands, pbd – very fine-grained sands, pm – silty sands, mp – sandy silts, m – silts

Silty sands and sandy silts show 5-times higher TOC contents (Table 7.4). The maximum content of total organic carbon in those sediments occurred in the Bornholm Basin. High TOC concentration (4.14%) in the sediments in the forefield of the Płutnica River mouth (Puck Lagoon) is associated with small dynamics of this region, which is favourable for the deposition of organic material flowing down the river.

In the silty sediments of the southern Baltic Sea, the total organic carbon content was higher than 3% in 75 percent cases. The highest TOC concentrations, exceeding 8%, account for less than 1% of all observed results and occurred in the sediments of the Puck Lagoon (Jama Kuźnicka) and in the central part of the Gulf of Gdańsk (Figs. 7.5, 7.6). Similarly to other types of sediments, the TOC content in silts differs regionally. The highest content is characteristic of silts in the Puck Lagoon and Gulf of Gdańsk. The lowest contents are observed in the Słupsk Furrow (Fig. 7.8). Such large accumulation in the Puck Lagoon is adequately illustrated by the content of organic carbon in artificial pits formed during excavation work in the coastal zone of the Puck Bay in 1980–1990. In comparison with a natural bottom depression in this region, the dredging pits are small but quite deep (Jankowska, Łęczyński, 1993). They are places where fine-dispersive sediments and organic matter accumulate. Due to the direct inflow of organic matter from the land and high primary production induced by the run-off of biogenic salts, the content of organic carbon in sediments of these regions increased even up to 17% (Fig. 7.9). The TOC content in particular pits depends on, for example, their depths, season of the year and the distance from the base of the Hel Peninsula. In the dredging pits near Kuźnica, the accumulation rate of organic carbon was estimated at 63 g/m^2 per year and it was three times higher than the accumulation rate in the natural Jama Kuźnicka depression (Graca *et al*., 2004).

Changes in organic carbon concentrations in deeper layers of the sediments depend on the sediment type and result from the processes of mineralisation and accumulation of organic matter delivered to the sediment. The accumulation of sediments may take place under oxygen or anoxic conditions. The occurrence of hydrogen sulphide in the sediments results from the imbalance between the amount of the supplied carbon and the availability of oxygen required for mineralisation. Under anoxic conditions, iron sulphides are formed, imparting the black colour to the sediments (Fig. 7.10). In a core of silty sediments, oxygen periods of lower contents of organic carbon are clearly distinguished from the deposits rich in TOC (black sediment) and accumulated in the past 100–150 years under anoxic conditions. Thus, the vertical

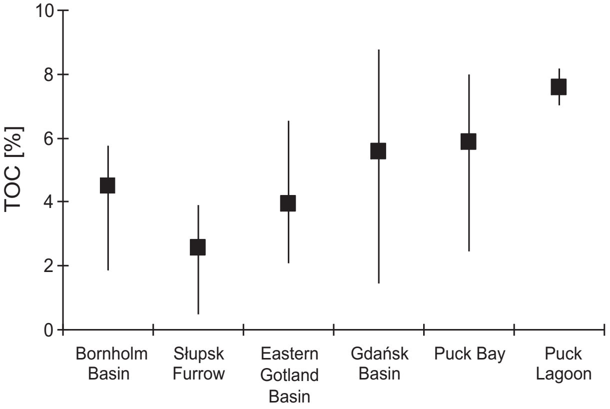


Fig. 7.8. Regional changes of the TOC content in silty sediments in the southern part of the Baltic Sea (minimum, average, maximum)

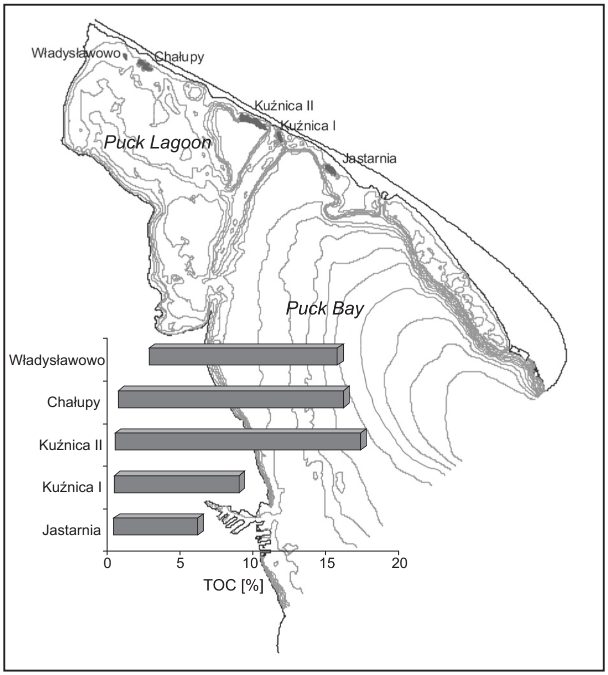


Fig. 7.9. Location of post-dredging pits in the Puck Lagoon (Bradtke, Urbański, 2008) and the TOC content in surface sediment layer (0–2 cm) from the pits (in 2007 and 2008)

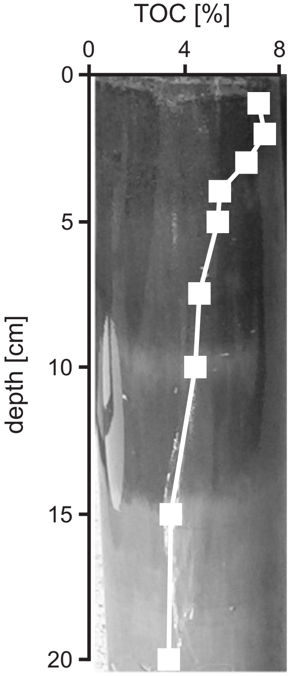


Fig. 7.10. TOC content in the sediments of the Gulf of Gdańsk (western slope of the Gdańsk Basin at the prolongation of the Słupsk Furrow axis, depth 90 m, April, 2005)

TOC profiles in silty sediments provide information about the history of organic carbon in the Baltic Sea.

Vertical TOC profiles are characterised, among others, by the following authors: Carman *et al*. (1996), Carman and Rahm (1996), Maksymowska (1996), Burska *et al.* (1999, 2003), Graca *et al*. (2004). A constant value of TOC in the tested sediment corresponds to the constant value of the accumulation rate. Such a vertical profile of the organic carbon contents in the tested sediments is observed in the Arkona Basin (Fig. 7.11). High TOC contents in the surface sediment layer and their drop with the depth suggest increased carbon accumulation in the basin. The difference between the TOC content in the surface (recently deposited) and lower (10–15 cm) layer of the sediments may reach 8% (Eastern Gotland Basin) or about 4% (Gdańsk Basin). It shows that the organic carbon accumulation is clearly higher in the sediments of the Eastern Gotland Basin. High TOC values of up to 15% and irregular variations indicate high dynamics of the processes of supplying and mineralising organic matter in the northern part of the Eastern Gotland Basin.

Vertical profiles of TOC contents vary depending on the sediment type. A distinct enrichment of sediments in organic carbon is observed offshore from the coastline (Fig. 7.12). Elevated TOC contents in a few-cm top layer of the sediment is an effect of eutrophication of the Gdańsk Basin. This process affects the TOC contents in this region to a different degree. The TOC/Al profiles suggest the preferential enrichment in TOC of sediments of the Polish costal zone as compared to the Lithuanian coastal zone. Considering the TOC value in sediments unaffected by anthropogenic influence (geochemical background for the Gdańsk Basin has been established in the 18–20 cm sediment layer) and normalising the concentrations of organic carbon with reference to aluminium, Szczepańska and Uścinowicz (1994) estimated the contamination level of surface layer sediments with organic carbon. The calculated enrichment factor (EF) for the southern Baltic Sea is from 0.4 to 6.4. The poorest

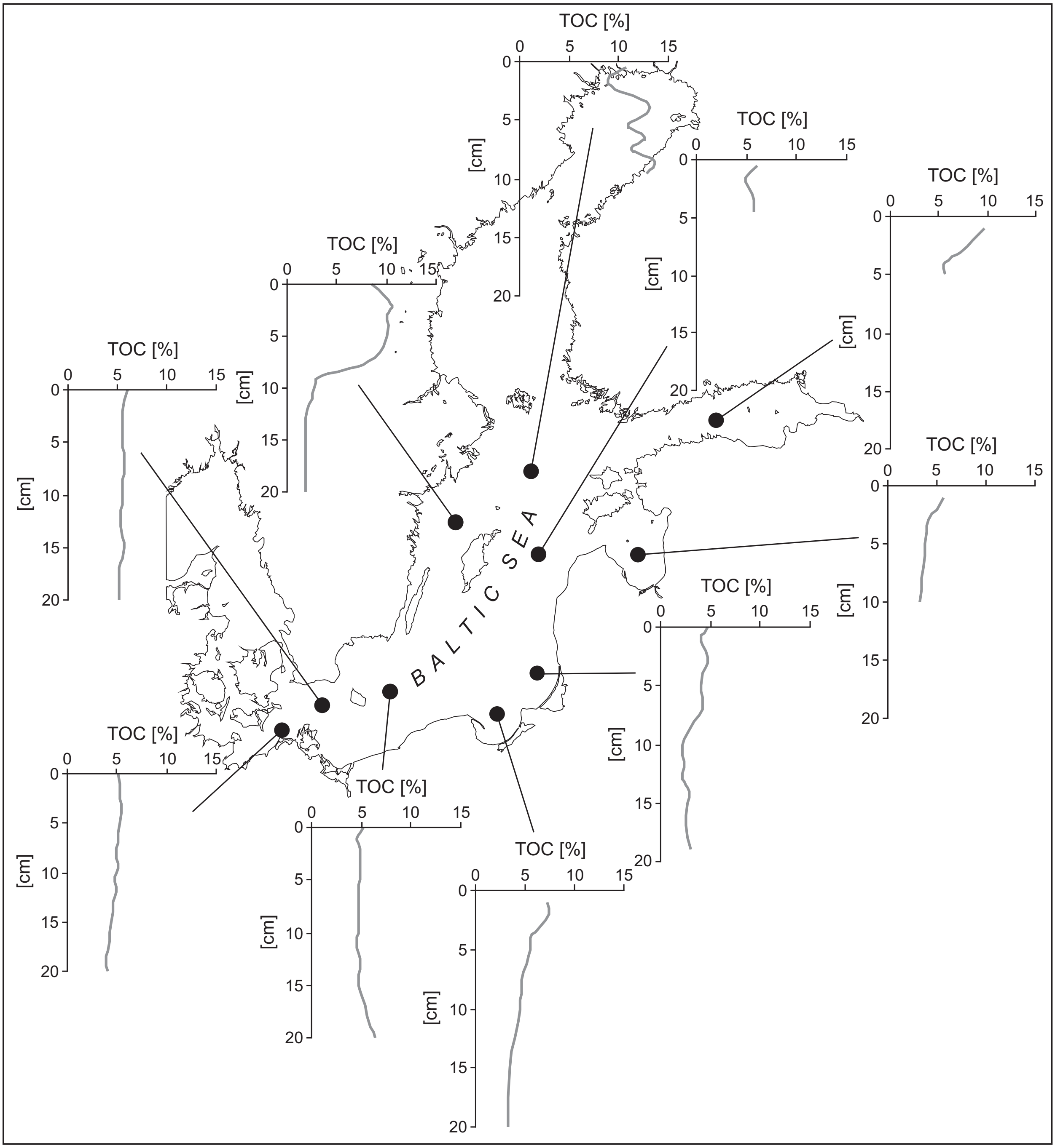


Fig. 7.11. Changes in the TOC content with sediment depth (Carman *et al*., 1996; Aigars, Carman, 2001; Burska *et al*., 2003)

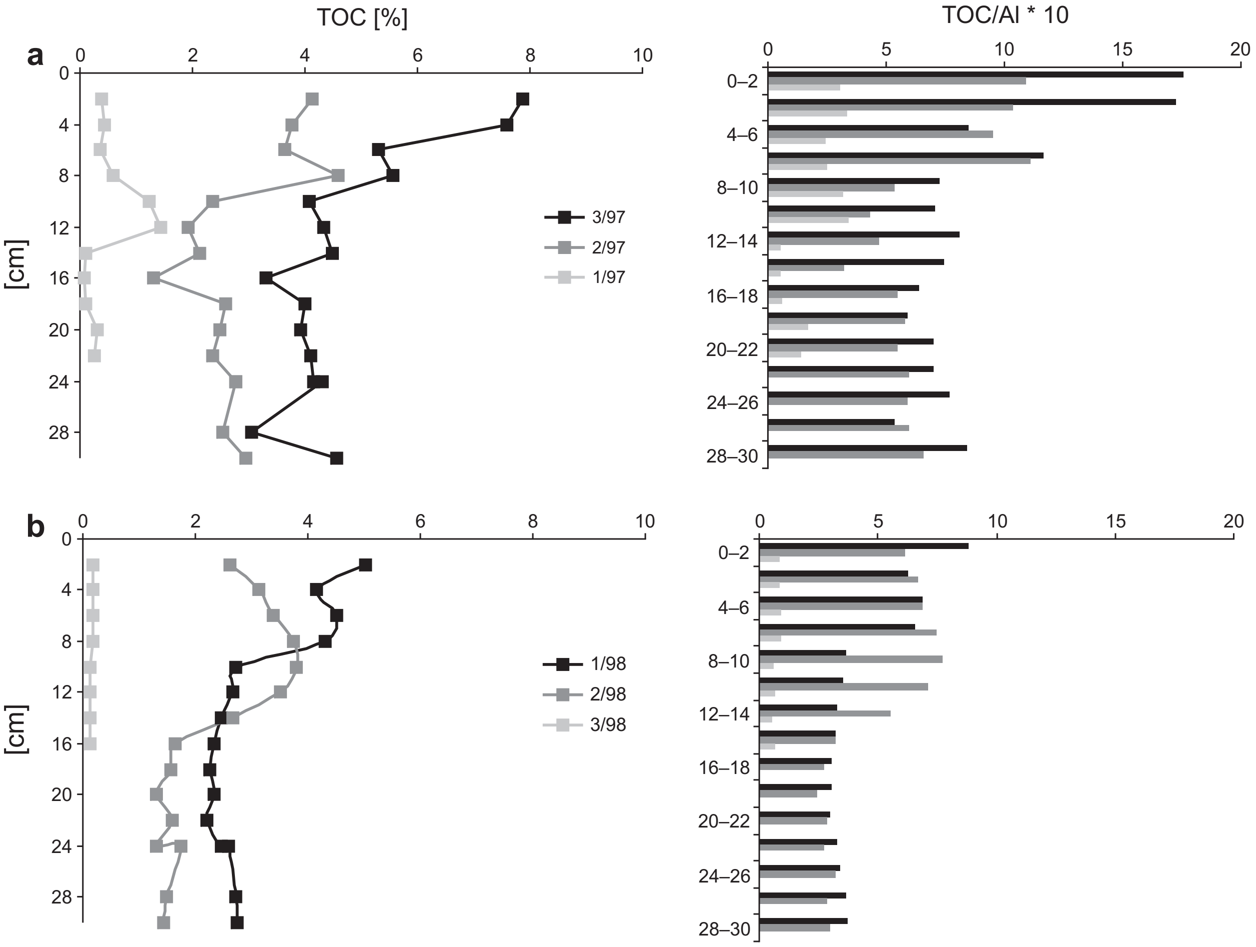


Fig. 7.12. Changes in the TOC content with sediment depth and with reference to TOC/A1 as a function of the distance from the shore: a – Vistula River mouth, Gdańsk Basin, b – Lithuanian coast, Klaipeda, Gdańsk Basin (for location and source of data see Appendix 3)

in organic carbon are the silty sediments of the Bornholm Basin (mean factor EF = 1.2), and the richest are the sediments in the Puck Bay (mean factor EF = 4).

The organic carbon content in surface sediment layer also undergoes seasonal variations (Burska *et al.*, 1999, 2003; Aigars, Carman, 2001). These changes are constrained by the seasonally variable supply of organic matter to the sediment. From 10 to 80% of the matter produced in the euphotic layer may reach the coastal and estuarine sediments, depending on the depth of the water column (Suess, 1980; Walsh, 1991). Clearly higher TOC values in the surface layer sediments of the Baltic Sea region are observed in the period from April to November. The processes of organic matter degradation and hydrodynamic washing prevail in sediments in late autumn and winter. In that period, the TOC parameter in sediments has the lowest value in the year.

The highest supply of organic carbon into the Baltic sediments takes place after the spring phytoplankton bloom (Smetacek, 1980; Heiskanen, Tallberg, 1999). High productivity in this period is typical of temperate and boreal zones, and spring sedimentation is a main source of energy for benthic fauna in the aphotic water layer (Elmgren, 1984). Depending on the types of

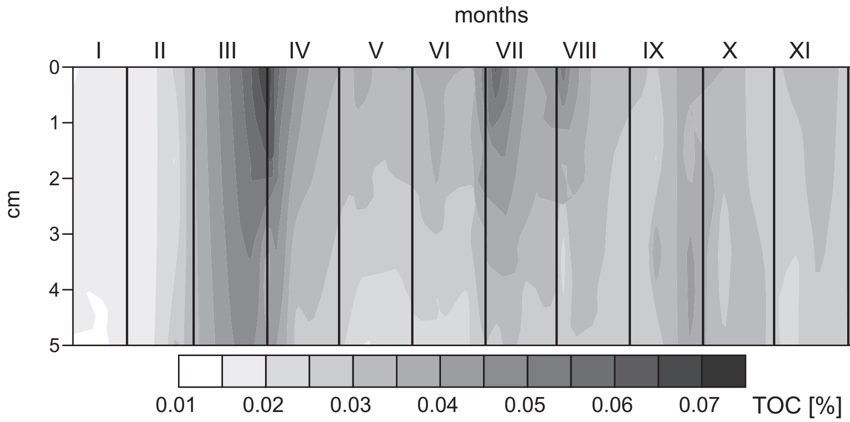


Fig. 7.13. TOC content in the surface layer of shallow-water sediments (below isobath 2 m) in the Gulf of Gdańsk (2007)

sediments, the changes in organic carbon contents in the year may exceed 100%. The TOC content in the surface sediment layer of the Gulf of Finland increased by 50% during nearly twenty days after phytoplankton blooming. The elevated contents of total organic carbon in sediments from 5.1% in April to 9.1% at the beginning of May were observed in nearshore shallow-marine regions (Tamelander, Heiskanen, 2004). Seasonal TOC variations decrease when the distance from the shore and the sea depth increase. The TOC contents in surface layer sediments of deeper areas of the Gulf of Finland increased by 20% only (TOC increase from 10% to 12%). Similar changes were observed in the surface sediment layer of the Gulf of Riga (Aigars, Carman, 2001). In April, the TOC content increased from 4 to 4.5% and stayed at the same level until autumn, when sediments received another larger portion of the matter. In sediments of the Gulf of Riga, the autumn increase in TOC values was not as high as in April. The TOC content measured in autumn was related to both the delivery of organic matter after the autumn blooming of phytoplankton and the accumulation of organic matter when the vegetation period started. The autumn increase of TOC was also observed in the sediments of the Puck Bay (Graca *et al.*, 2004), Pomeranian Bay (Burska *et al.*, 1999) and Kiel Bay (Suess, 1980).

The range of TOC variations in the sediments, caused by the seasonal supply of organic matter, depends on the sediment type. Organic carbon is transported in a suspended and dissolved form in the water column into the sediments. The migration of organic carbon into deeper sediment layers depend on both hydrodynamic processes and such events as sea-bottom currents, waving, upwellings or downwellings, and activities of benthic organisms. Macrofauna may be responsible for as much as 50% of organic carbon transported into the bottom sediments (Rusch *et al.*, 2000). In porous sandy sediments, seasonal changes are observed in the deepest layers. The finer sediments, the shallower seasonal changes are (Aigars, Carman, 2001). In silty sediments of the Bothnian Bay, the spring and autumn TOC increase reached the depth of 3 cm, which corresponds to the depth to the chemocline. Aigars and Carman (2001) observed changes at depths of up to 5 cm in the sediments of the Gulf of Riga. The most clear seasonal changes are observed in coastal sandy sediments characterised by a rapid response to the supply of organic carbon from the water depths. However, TOC content in those sediments is very low, clear seasonal differences (7-fold) are observed (Fig. 7.13). The TOC increase in the surface sediment layer is associated with organic matter supply after intense primary production and may be up to 5–8 cm deep. The concentration of carbon is also 1.4 to 5.3 times higher than its concentration in deeper sediment layers (Rusch *et al.*, 2000).

7.3. Phosphorus

7.3.1. Phosphorus Cycle in Marine Sediments

Phosphorus in the bottom sediments is conventionally referred to as labile (mobile, reactive) and refractory. Refractory forms include phosphorus bounds to calcium, aluminium, clay minerals, and organic forms of this element resistant to degradation. Refractory phosphorus undergoes deposition in sediments and thereby is removed from the cycle in the water column. Its concentrations in the sediment profile vary over a small range. Labile phosphorus forms include phosphorus contained in fresh organic matter, phosphates in interstitial water of sediments and phosphorus bounds to Fe^{3+} and phosphates weakly adsorbed to different elements of sediments. These forms easily return into the near-bottom water mainly due to mineralisation of organic matter and dissolution of the redox dependent phosphorus forms (P bounds to Fe^{3+}).

Labile phosphorus concentrations usually decrease with sediment depth, which is a result of its return to the near-bottom water or transformations into refractory forms. Since the refractory forms of phosphorus usually maintain approximately constant concentration, the labile forms shape the vertical distribution of phosphorus in sediments.

Organically bound phosphorus may constitute from 0 to 90% of the sediment phosphorus (Frink, 1967; Sommers *et al*., 1970). The largest amounts of organic phosphorus are characteristic for sediments in the continental shelf (Morse, Cook, 1978). The most common organic phosphorus forms in sediments are orthophosphate esters and diesters. Phospholipids account for a small part of the organic phosphorus pool (Ingall *et al*., 1990). They supply the refractory phosphorus pool together with organic phosphorus forms adsorbed by sediments (Martynova, 1984).

The labile organic phosphorus forms are mainly composed of monosaccharides, fatty acids and proteins (Danovaro *et al*., 1993). These compounds undergo decomposition, the final products of which are phosphates.

The main source of phosphates in the interstitial waters is the degradation of organic matter and dissolution of phosphorus bounds to iron (Fe^{3+}). Phosphates produced in this way may diffuse according to the concentration's gradient into the near-bottom waters or into other areas of the bottom sediments. They may precipitate in an oxygenated layer of sediment as iron, manganese, magnesium and aluminium phosphates, they may also be adsorbed by different components of the sediment, or may be built into the biomass (Balzer, 1986; Gächter *et al*., 1988; Sundby *et al*., 1992; Andrieux-Loyer, Aminot, 2001).

Phosphates in the sediment as in the water, are adsorbed on organic matter, humuses, on iron, aluminium and manganese hydroxides, on clay minerals and on calcium carbonate (Martynova, 1984; Böstrom *et al*., 1988; Carman, Wulff, 1989; Szefer, 1998).

Important process of phosphorus burial in marine sediments is forming of authigenic minerals. The most common phosphorus minerals in the marine environment are apatites. Part of the apatite phosphorus is of allochtonous origin and is mainly supplied with river suspension (Berner *et al*., 1993).

7.3.2. Phosphorus Distribution in Bottom Sediment and in Interstitial Waters

Bottom sediments are important field of phosphorus cycle in water reservoirs. Sediment phosphorus distribution and content is determined by complex interplay of numerous factors such as water depth and its dynamic, sediment grain size and oxic condition, etc. Strong anthropopression and specific natural conditions are the main reasons of the Baltic Sea eutrophication. It is manifested by the enrichment of the surface layer of fine-grained sediment of this reservoir in phosphorus (Szczepańska, Uścinowicz, 1994).

The load of phosphorus in the surface sediment of the Baltic Sea is estimated at $1{,}295 \cdot 10^3$ t (Table 7.5). Its amount per km^2 of the bottom is associated with, among others, the phosphorus sorption capacity of sediments. The capacity is restricted under reductive conditions (Carman, Wulff, 1989). In the Baltic Proper, a considerable part of the sediments is reductive (Jonsson *et al*., 1990). As a result, the sediments in this region store less phosphorus than the sediments in the Bothnian Sea and in the gulfs, where better oxygen conditions occur.

Table 7.5

The phosphorus load in surface layer (0–5 cm) of fine-grained sediments in different regions of the Baltic Sea (acc. to Carman, Cederwall, 2001)

Region	Phosphorus load	
	[t/km^2]	[10^3 t]
Bothnian Bay	11.4	205
Bothnian Sea	15.6	281
Baltic Proper	7.6	564
Gulf of Finland	13.9	171
Gulf of Riga	13.8	74
Baltic Sea	–	**1295**

Benthic phosphorus in the Baltic Sea is an issue of numerous studies. Usually, they have a limited territorial range, are made with the use of different analytical methods and different types of sediment samplers, and they do not take into account seasonal variations (Table 7.6). One of few, territorially wider studies (Carman, 2003) is based on the analyses of sediment cores taken in summer 1993. The results of this research suggest that the phosphorus content in fine-grained sediments of the Baltic Sea increases approximately from the west to the east, and the highest concentrations are observed in the estuary of the Neva River in the Gulf of Finland (Fig. 7.14).

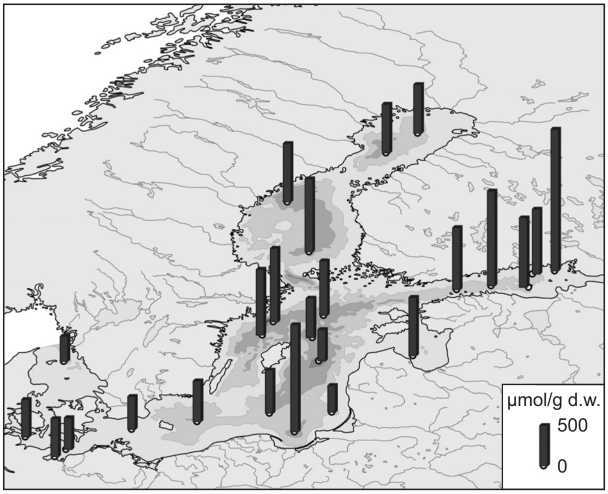


Fig. 7.14. Phosphorus contents in silty sediments of the Baltic Sea (0–1 cm surface layer, concentration range 48–523 μmol/g d.w.) (Carman, 2003)

The phosphorus content in the surface layer of the Baltic Sea sediments is strictly related to their lithology. Phosphorus concentrations in the region of permanent accumulation of fine-grained sediments are higher than that observed in the region of their transport and erosion (Fig. 7.15). Phosphorus contents increase when the contribution of fine-grained sediments is greater, which is the case with the Polish Economic Zone, including the Gulf of Gdańsk (Figs. 7.16, 7.17). It is related to the increase in both the distance from the land and the sea depth (Graca, Bolałek, 1998; Łukawska-Matuszewska, Bolałek, 2008). Typically, the phosphorus concentrations in sediments of the Baltic Sea do not exceed 200 μmol/g d.w. (Table 7.6). Higher values are associated with the occurrence of iron-manganese nodules. They occur, for example, in the Gulf of Riga, western part of the Gulf of Finland, in the Bothnian Bay and in the Bothnian Sea (Winterhalter *et al.*, 1981; Szefer, 2002; Zhamoida *et al.*, 2007). Extremely high phosphorus concentrations were incidentally noted in the Gdańsk Deep (Table 7.6), shortly after an unusually long period of water stagnation in this region (Graca *et al.*, 2006). An increase in phosphorus concentrations in sediments is also recorded when aerobic conditions in the region of the Gotland Deep improve (Winterhalter *et al.*, 1981).

The phosphorus content in the Baltic Sea usually decreases with the sediment depth, which is a result of decrease in concentration of labile phosphorus forms in the anaerobic layers of the sediment (Fig. 7.18). The exceptions are the Bothnian Bay and Bothnian Sea. Most regions of the Bothnian Bay show better oxygen conditions and deeper oxygen penetration into the sediments than in other parts of the Baltic Sea. In addition, manganese concretions rich in iron and manganese occur in the fine-grained sediment accumulation zone of these regions (Szefer, 2002). This results in high concentrations of mobile forms of phosphorus, also in the deeper layers of sediment.

Table 7.6

Phosphorus contents in the surface sediment layer of different regions of the Baltic Sea

Region	Phosphorus content [µmol/g d.w.]	Layer [cm]	Remarks	References
Baltic Sea	48–523	0–1	Fine-dispersive sediments	Carman, 2003
Bornholm Basin	48 ±11	0–1	mean ±S.D., silt	Szczepańska, Uścinowicz, 1994
Słupsk Furrow	39 ±12	0–1	mean ±S.D., silt	Szczepańska, Uścinowicz, 1994
Gotland Basin	55 ±19	0–1	mean ±S.D., silt	Szczepańska, Uścinowicz, 1994
Gdańsk Basin	52 ±22	0–1	mean ±S.D., silt	Szczepańska, Uścinowicz, 1994
Baltic Proper	46 ±14	0–1	bottom zone A	Carman, Cederwall, 2001
	35 ±12.2		bottom zone T	
	22 ±8.7		bottom zone E	
North-western Baltic Proper	13.4–38.6	0–2	bottom zone E/T	Carman, Jonsson, 1991
	24.2–66.1		bottom zone A	
Baltic Proper (central part)	30–175*	0–1	180–241 m	Edlund, Carman, 2001
Aarhus Bay	38–60*	0–1	bottom zone A	Jensen *et al*., 1995
Kiel Bay	12–28* 12–16 30–36	0–1	sandy silt, silty sand silt	Balzer, 1986
Gdańsk Deep	153.2–957.2	0–5	bottom zone A	Łukawska-Matuszewska, Bolałek, 2008
Gulf of Gdańsk	3.1–22.6	0–5	2–24 m	Łukawska-Matuszewska, Bolałek, 2008
	4.9–379		54–74 m	
	103.2–192.6	0–5	bottom zone A	Graca, Bolałek, 1998
Puck Bay	31.9–93.5	0–5	3–43 m	Graca, Bolałek, 1998
	35 ±18	0–1	silts	Szczepańska, Uścinowicz, 1994
Gulf of Riga	65–89	0–1	bottom zone A	Aigars, 2001
	63.4	0–1	bottom zone A	Carman *et al*., 1996
	29.3		bottom zone T/E	
	64 ±12.7	0–1	bottom zone A	Carman, Cederwall, 2001
	40 ±12.8		bottom zone T	
	14 ±4.3		bottom zone E	
Gulf of Finland	80 ±28	0–1	bottom zone A	Carman, Cedereall, 2001
	46 ±10		bottom zone T	
	26 ±5		bottom zone E	
	32–68*	0–1		Vaalgamaa, Conley, 2006
	103	0–1	mean	Lehtoranta, 2003
	35.5–141.9 (93.5)	0–1	range (mean), bottom zone A, western part of the bay	Lehtoranta *et al*., 1997
Bothnian Sea	55	0–1	h <60m (mean)	Niemistö *et al*., 1978
	52		h >60m (mean)	Niemistö *et al*., 1978
	42		(mean)	Leivouri, 2000
	49 ±8	0–1	bottom zone A	Carman, Cederwall, 2001
	38 ±6.2		bottom zone T	
	26 ±7.9		bottom zone E	
Bothnian Bay	48	0–1	(mean)	Leivouri, 2000
	48 ±6.5	0–1	bottom zone A	Carman, Cederwall, 2001
	38 ±7.4		bottom zone T	
	58 ±33		bottom zone E	
Baltic Sea	**3–957**			

S.D. – standard deviation; bottom zones: A – accumulation, T – transportation, E – erosion
* interpreted from a graph

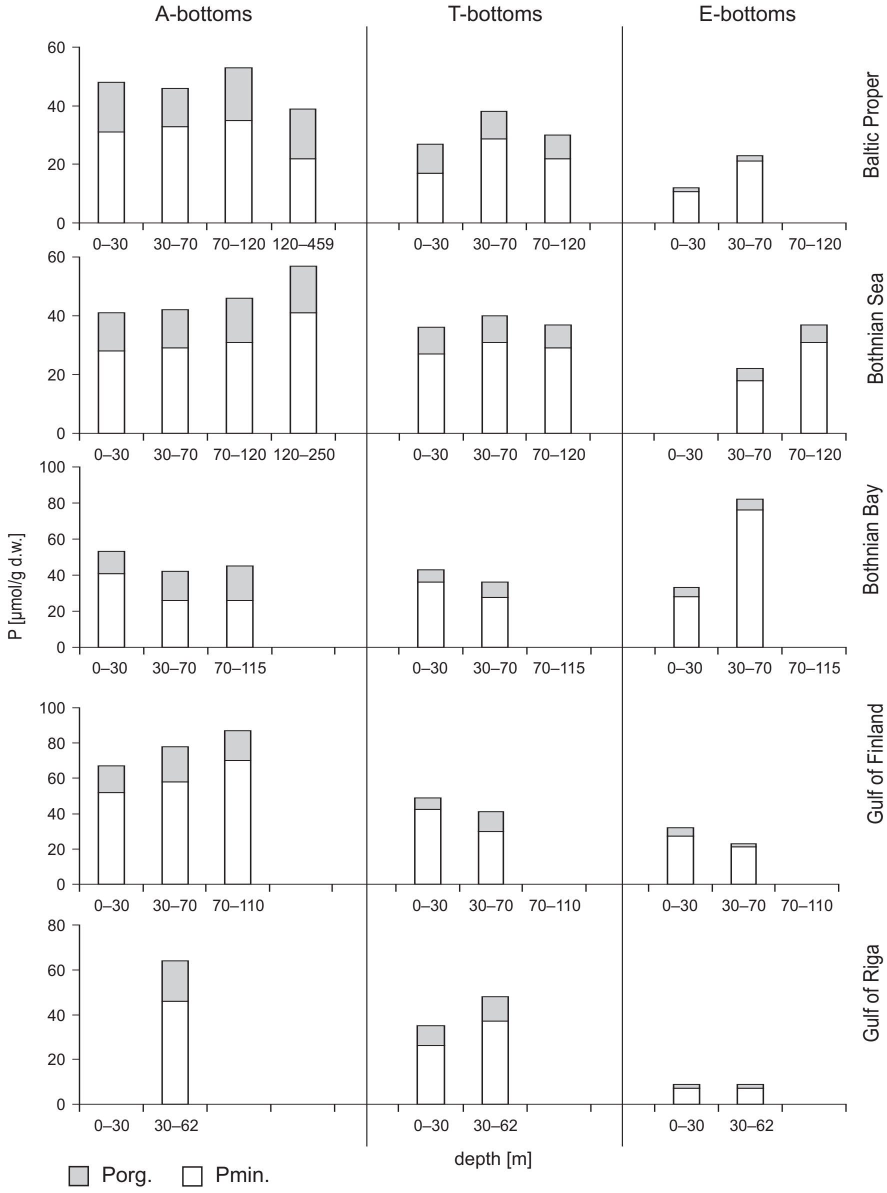


Fig. 7.15. Changes in the mean content of inorganic (Pmin) and organic (Porg) phosphorus in the surface sediment layer of the accumulation (A), transportation (T) and erosion (E) bottom zone relative to the water depths in different regions of the Baltic Sea (based on Carman and Cederwall, 2001)

The lack of a generally accepted method of analysing phosphorus forms in sediments makes it difficult to compare their regional variabilities. In most cases, inorganic phosphorus bounds constitutes more than 50% of the total phosphorus (Fig. 7.15). The ratio of organic to inorganic phosphorus higher then 1 was noted only in sediment of deep anoxic regions. It is due to potentially weaker degradation processes of

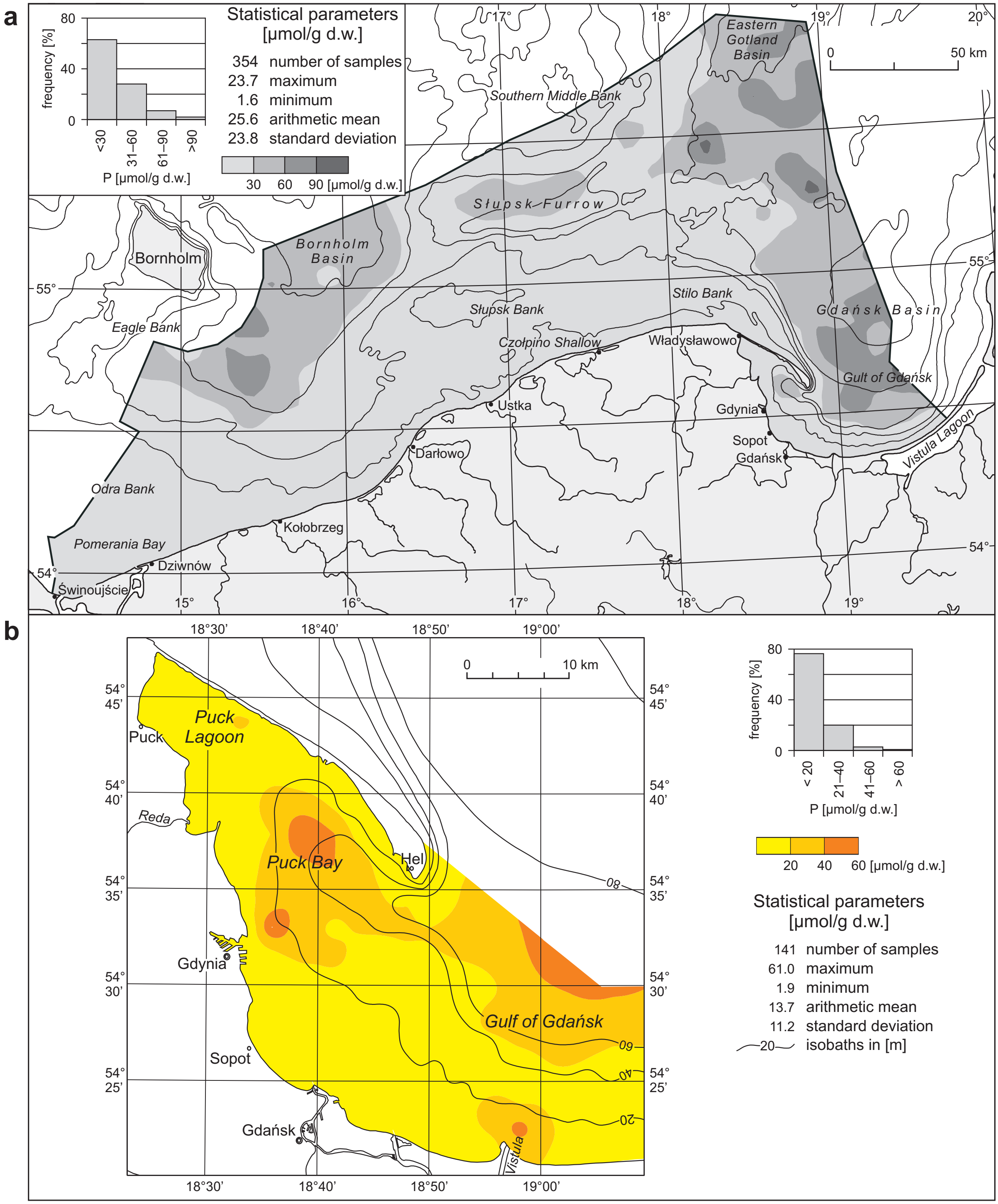


Fig. 7.16. Phosphorus contents in the surface sediment layer (0–2 cm) in: (a) Polish Economic Zone of the Baltic Sea (Szczepańska, Uścinowicz, 1994), (b) western part of the Gulf of Gdańsk (Uścinowicz *et al.*, 2008)

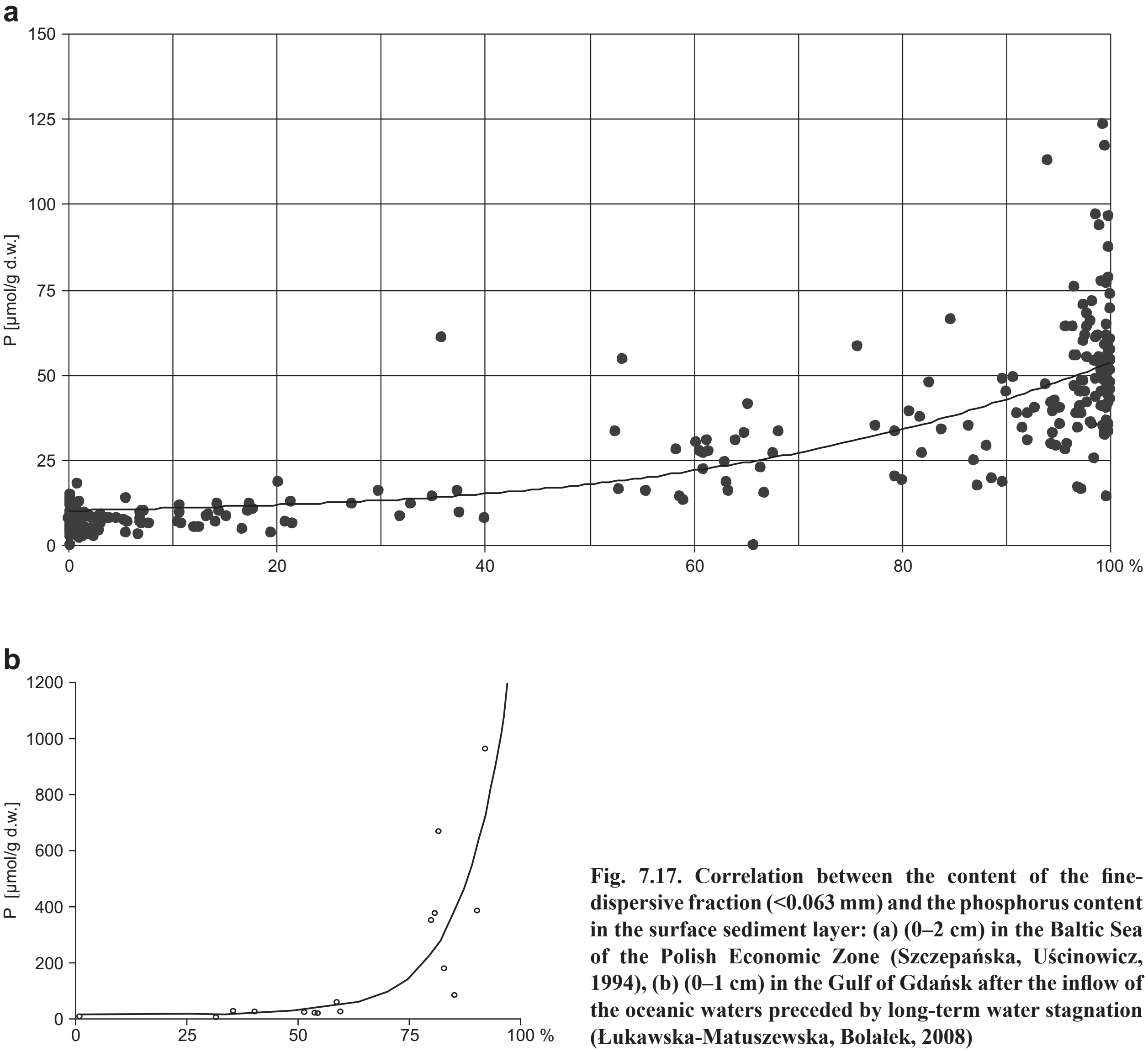


Fig. 7.17. Correlation between the content of the fine-dispersive fraction (<0.063 mm) and the phosphorus content in the surface sediment layer: (a) (0–2 cm) in the Baltic Sea of the Polish Economic Zone (Szczepańska, Uścinowicz, 1994), (b) (0–1 cm) in the Gulf of Gdańsk after the inflow of the oceanic waters preceded by long-term water stagnation (Łukawska-Matuszewska, Bolałek, 2008)

organic matter in anoxic conditions (Edlund, Carman, 2001).

The content of apatite phosphorus in the Baltic Proper ranges from 7.4 to 16.5 µmol/g and slightly changes with the sediment depth. In turn, the concentrations of labile bounds of phosphorus distinctly decrease with the sediment depth, and their content changes from 0.8 to 30.4 µmol/g. The highest values were observed in oxygenated sediment layers (Carman, Rahm, 1997).

In the north-eastern part of the Baltic Sea (Gulf of Finland, Archipelago Sea), phosphorus bounds to aluminium account for 2–24%, to calcium 4–60%, and to the refractory organic phosphorus to 4–38% of the total phosphorus. Reactive forms of phosphorus account for 19–74% of the total phosphorus, of which the proportion loosely adsorbed phosphorus usually does not exceed 3%, the phosphorus bound with iron accounts for 4–53%, and labile organic forms of phosphorus account

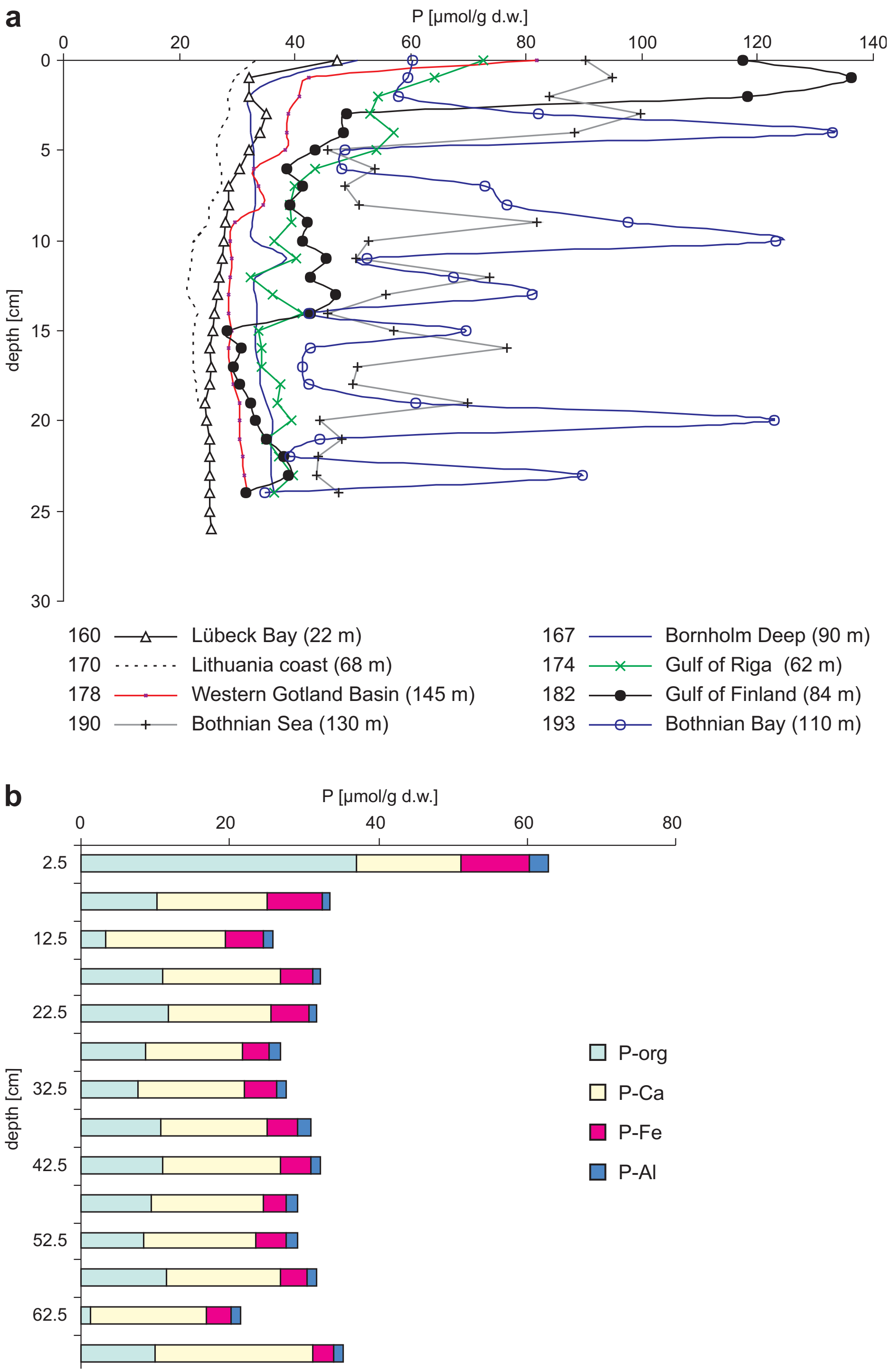


Fig. 7.18. Changes in contents of: (a) phosphorus in the vertical profile of sediments in different parts of the Baltic Sea (Carman, 2003), (b) forms of phosphorus in the Gdańsk Deep (Graca, 1998)

for 8–43% of the reactive phosphorus. In the shallow estuaries of this Baltic Sea region, high concentrations are characterised phosphorus bounds to oxyhydroxides of iron and aluminium. In regions of large supply and transport of fine-grained sediments, such as inner estuaries and the shallow coastal zone of the Gulf of Finland, the sediments are rich in phosphorus bonds to calcium. This form also occurs in the western, open part of the Gulf of Finland and in the northern regions of the Baltic Proper, where sediments are poor in phosphorus labile forms. In the eastern part of the gulf, high contents of organic carbon correspond with high contents of phosphorus in organic compounds (Lukkari, 2008).

In the shallow, semi-enclosed Gulf of Riga, inorganic phosphorus concentration exceeds the concentrations of organic forms of this element (Fig. 7.15). As regards inorganic forms, labile bonds constitute more than 50% of the total phosphorus (Carman *et al*., 1996). In the accumulation bottom of this gulf, labile bonds prevail in the surface, oxygenated sediment layer (0–1cm), whereas in a deeper layer, where reductive conditions dominate, labile phosphorus accounts for 16–18% of the total phosphorus (Aigars, 2001).

In the coastal sands of the Gulf of Gdańsk, apatite and organically bound phosphorus prevails. Those forms account for almost 80% of the total phosphorus (Fig. 7.19). In the Vistula River mouth, the contribution of phosphorus bounds with iron increases. In the central part of the gulf more than 70% is represented by inorganic phosphorus forms, in which the phosphorus bonds to clay minerals and aluminium oxides dominates. In the Gdańsk Deep region, the fraction of organic bonds increases to 50% of the phosphorus. Among inorganic compounds, refractory forms prevail in the Gdańsk Deep.

Some parts of the Baltic Sea showed seasonal variations of phosphorus concentrations in sediments. In the outer Puck Bay, the increase in the contents of this constituent occurs in the groving season (Graca, 1998; Graca, Bolałek, 2000) (Fig. 7.20). This is the period when the sediments are supplied with organic matter produced by phytoplankton in the water column. The studies by Łukawska-Matuszewska and Bolałek (2008) suggest an increase in the total phosphorus contents in the surface sediments of the Gulf of Gdańsk in spring compared to summer. In the Gulf of Riga, an increase in the contents of labile phosphorus forms in the surface sediment layer is observed in summer (Aigars, 2001). A significant role was attributed to microorganisms. They show abilities to cumulate phosphorus in the form of polyphosphates during a period of good aerobic conditions and high concentrations of phosphates (Gächter *et al*., 1988).

Phosphate concentration in interstitial waters may be several hundred times higher than in near-bottom waters. High concentrations are characteristic of reductive sediment layers, where phosphorus bounds to iron dissolve (Fig. 7.21). For example, the value of about 250 μmol/dm^3 was observed in anaerobic sediment layers in the central part of the Gulf of Finland (Conley *et al*., 1997) and in

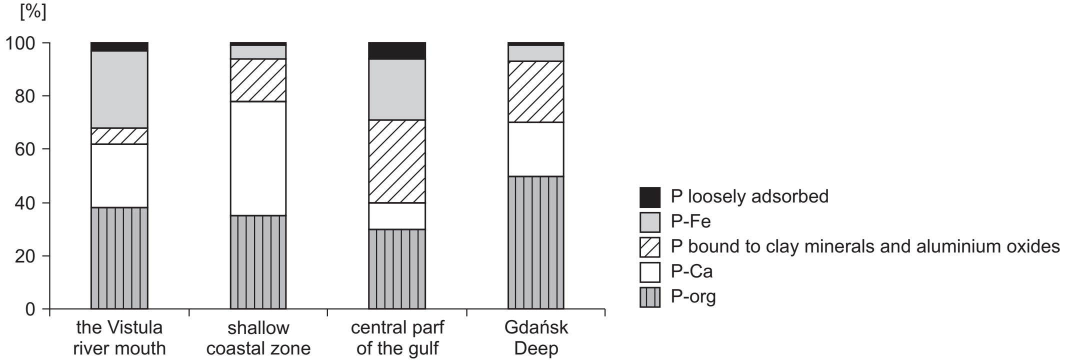


Fig. 7.19. Contribution of phosphorus forms in the surface sediment layer (0–1 cm) of different parts of the Gulf of Gdańsk (based on Łukawska-Matuszewska, Bolałek, 2008)

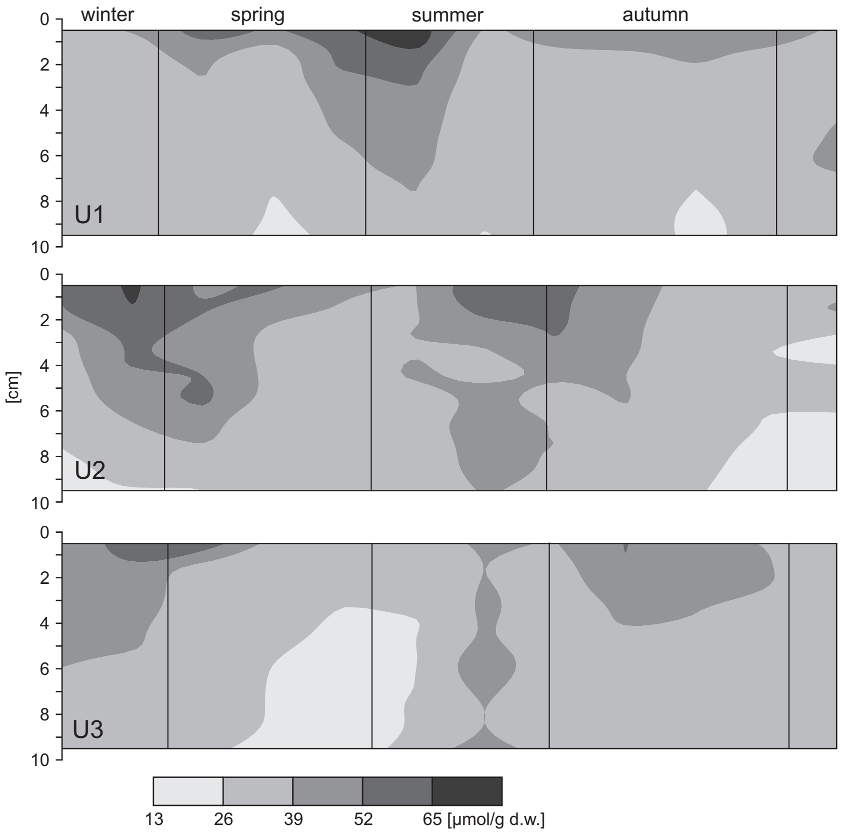


Fig. 7.20. Seasonal changes in total phosphorus concentrations in the surface sediment layer (0–10 cm) of the Gulf of Gdańsk (Graca, 1998)

U1, U2 and U3 – stations located in a transportation bottom zone

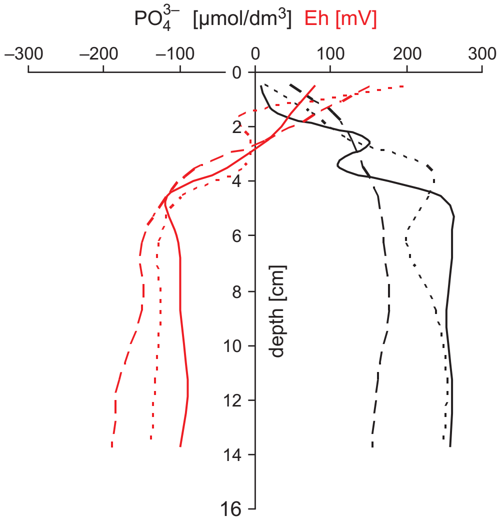


Fig. 7.21. Vertical profiles of interstitial phosphate (black lines) and sediment redox potential (red lines) in the Gdańsk Deep

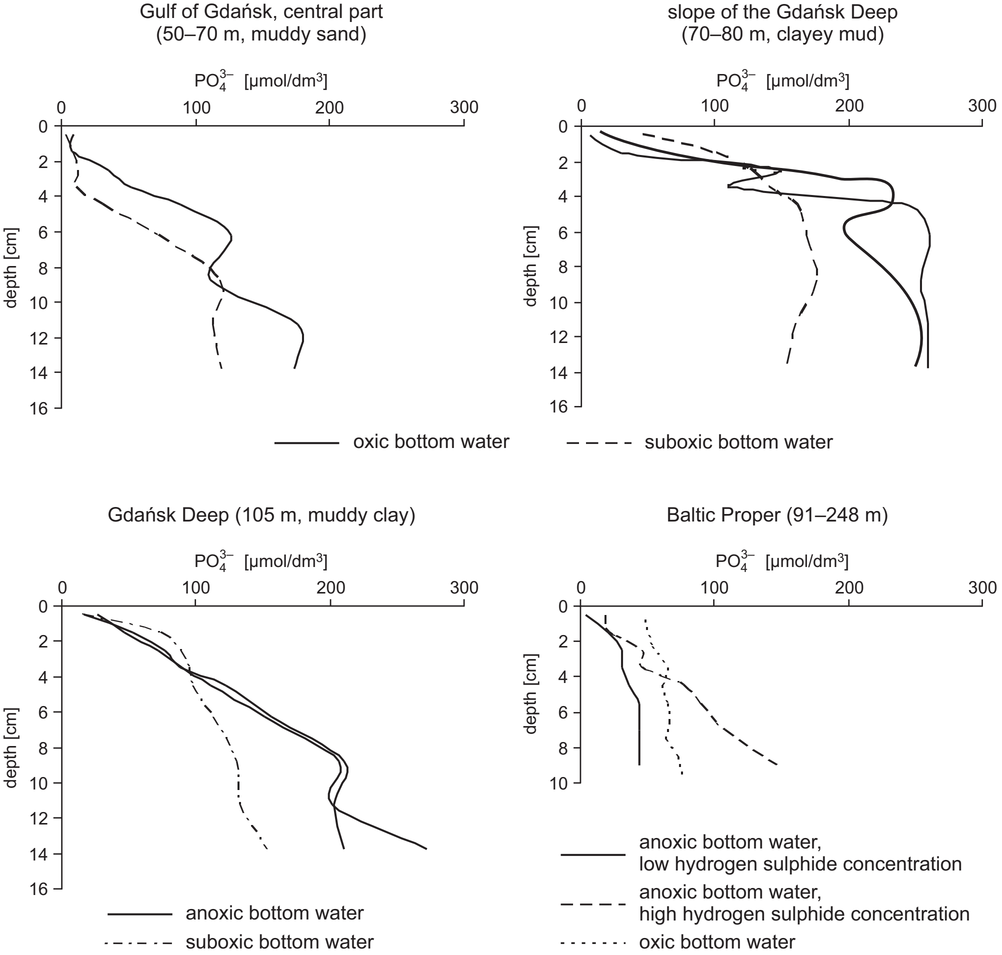
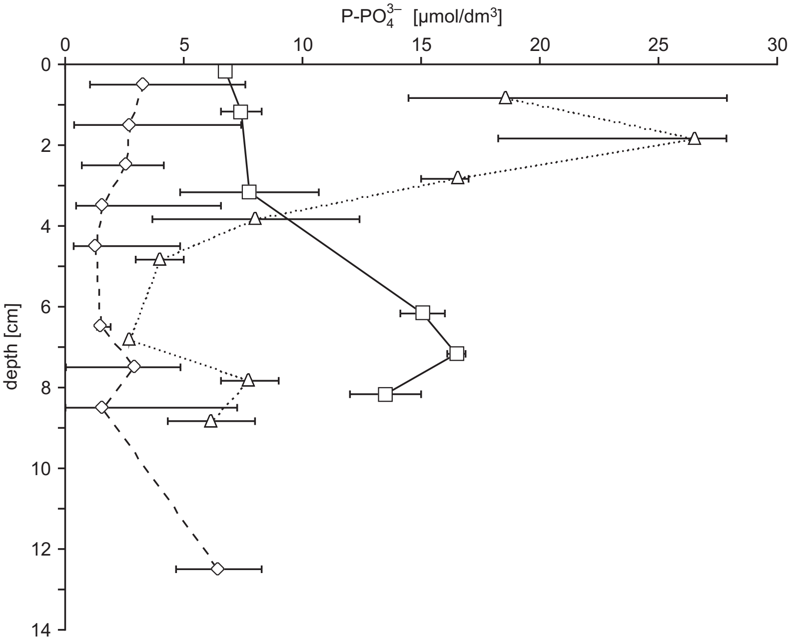


Fig. 7.22. Interstitial phosphate in regions of the Baltic Sea characterized by different water depth and oxygen condition in near-bottom water (based on: Carman, Rahm, 1996; Graca *et al.*, 2006).

Suboxia means oxygen concentrations higher than 0 cm^3/dm^3 and smaller than 2 cm^3/dm^3, anoxia means no oxygen, and aerated waters correspond to oxygen concentrations of more than 2 cm^3/dm^3

the central (Matthiesen *et al.*, 1998) and southern Baltic Proper (Carman, Rahm, 1997). In the western part of the Baltic Proper, interstitial phosphate concentrations reaching 700 µmol/dm^3 have been recorded (Matthiesen *at al.*, 1998). In the regions of limited water dynamics and oxygen deficits, interstitial phosphate concentration increases exponentially (Fig. 7.22). The long-term oxygen deficiency and the occurrence of hydrogen sulphide may bring a periodical decrease in the concentrations of phosphates as a result of their removal to the near-bottom water. Then the vertical profiles undergo flattening and are linearly shaped in the first section of the sediment. Small and aligned phosphate concentrations are characteristic for oxygenated surface sediments. Concentraton increases at deeper layer where reductive condition limits phosphate adsorption. In zones where waters mix intensely and benthic organisms occur in large amounts, the vertical profiles of phosphate concentration are usually irregular and characterised by low values, as can be observed in the coastal zone of

Fig. 7.23. Phosphate concentrations in interstitial waters in three selected regions of the Gulf of Gdańsk at the depth <30 m (Graca, 2009). A non-outlier range and a median values are shown



the Gulf of Gdańsk (Fig. 7.23). In this region, after the periods of intense water mixing (the cold half-year), a decrease in phosphate concentrations is observed in interstitial waters. The near-bottom water temperature increase and the supply of organic matter during the warm half-year induces, in turn, an increase in interstitial phosphate concentrations in this area of the Gulf of Gdańsk (Graca *et al.*, 2006).

7.4. Nitrogen

7.4.1. Sediment Nitrogen Cycle

The main source of nitrogen in bottom sediments is organic matter. Organically bound nitrogen is usually a predominant form of this element in sediment. Inorganic forms of nitrogen occur as exchangeable and fixed nitrogen. Exchangeable nitrogen (EN) includes ammonia adsorbed on the surface of clay minerals and/or organic matter. It is easily displaced by other cations. Fixed nitrogen (FN) is ammonia absorbed into the crystalline structure of clay minerals that hardly undergoes any ion exchange. In interstitial waters, the inorganic forms of nitrogen include NH_4^+, NO_3^- and NO_2^-, whereas the organic forms of this element are such compounds as proteins, amino acids and amines (Martynowa, 1984).

Nitrogen cycling, in both aquatic and terrestrial environments, occurs with the direct and indirect participation of numerous microorganisms while oxic conditions play an important role in nitrogen transformations.

Ammonia is produced during enzymatic decomposition of organic matter in sediments. It proceeds in aerobic and anaerobic conditions. A significant microbiological process that includes the production of this compound is ammonification (deamination). Ammonia produced in sediments may be oxidised, adsorbed on different particles of sediments, removed to the solution of interstitial waters and transported according to the concentration gradient (Fig. 7.24). The accumulation of ammonia is carried out in the anaerobic layers of the sediments.

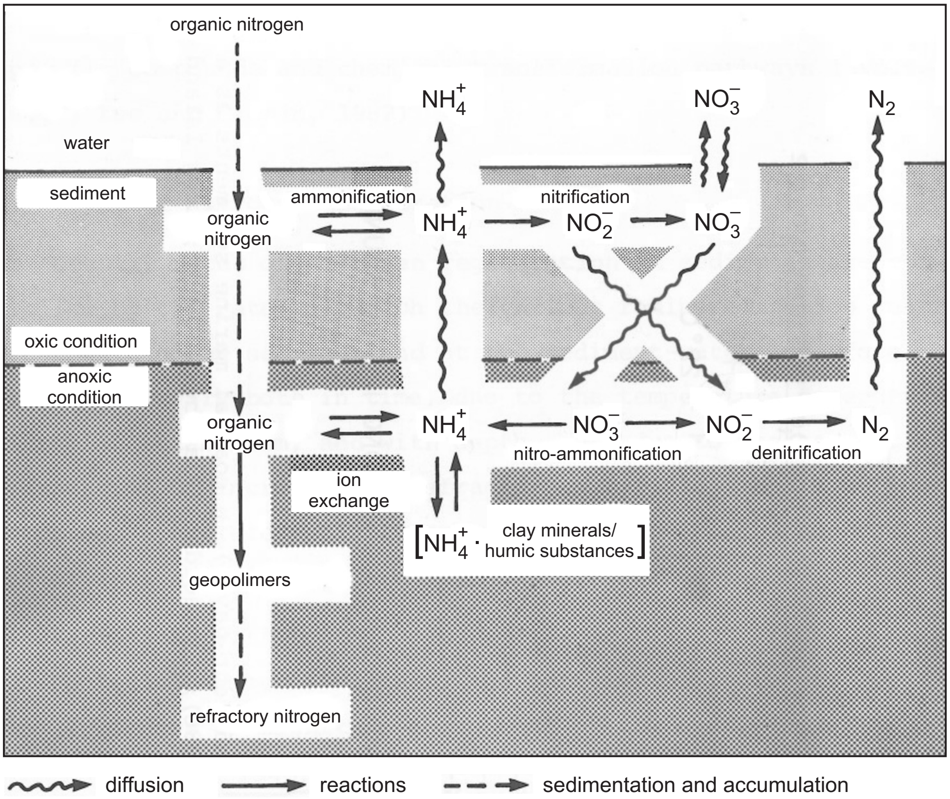


Fig. 7.24. Nitrogen cycling in a sediment-water interface of the marine environment (val Klump, Martens, 1983)

Very high concentrations of ammonia in interstitial waters are favourable for the precipitation of autogenic minerals that contain ammonia (Martens *et al*., 1978).

In anoxic sediment layers, ammonia is removed from the solution of interstitial waters by a process of reversible ion exchange. Sediments rich in organic matter may include more than 2/3 of ammonia in an adsorbed form (Morse, Morin, 2005). Ammonia in a solution and exchangeable ammonia are usually linearly correlated. The ammonia sorption capacity of the sediment is controlled, among others, by temperature, salinity, contents of organic matter and clay minerals, grain size, and redox potential.

During diagenesis, a part of labile organic nitrogen compounds, such as amino acids, is included into humic substances by condensation and polymerisation processes . It increases the resistance of organic nitrogen to microbiological decomposition. Geopolymers, formed in this way, constitute a refractory form of nitrogen.

Oxidation of ammonia to nitrates (aerobic nitrification) is made by bacteria of the Nitrobacteriaceae family, classified as chemolithotrophs . They are fully aerobic; however, they are already active in very low oxygen concentrations of about 0.05–0.07 cm^3 O_2/dm^3 (Carlucci, McNally, 1969). Light inhibits nitrification; in consequence, this process is limited in water column and is more intense in aerobic layers of sediments.

The reduction of nitrates in the marine environment is conducted by assimilatory reduction, denitrification and dissimilatory reduction (nitroammonification, ammonia fermentation). Assimilatory nitrate reduction results in producing organic matter. Bacterial denitrification, the final product of which is nitrogen, usually takes place under anaerobic conditions because oxygen blocks denitrification enzymes (see chapter 13.2 for a detailed description of this process). Dissimilatory nitrate reduction, the product of which is ammonia, is mainly carried out by fermentation bacteria. Microorganisms conducting denitrification and nitroammonification compete for nitrates (Sørensen, 1978). While denitrificators find optimal conditions in sediments just below the oxic sediment layer, the bacteria that reduce nitrates to ammonia are active in deeper sediment layers.

Moreover, in anaerobic sediment layers, ammonia and nitrates undergo enzymatic transformation into molecular nitrogen by the process of anammox.

7.4.2. Nitrogen Distribution in the Sediments of the Baltic Sea

In the Baltic sediments, nitrogen occurs mainly in an organic form and its regional variability is similar to the variability of carbon (Carman, 2003). The nitrogen content in the Baltic sediments varies from a few to more than 1150 μmol/g d.w. (Table 7.7, Fig. 7.25). Small values are characteristic of shallow-water coastal regions (Fig. 7.26), where high hydrodynamic activity usually occurs. It limits the deposition of fine-grained sediments and consequently of organic matter (Fig. 4.4). The in-

Table 7.7

Nitrogen content in sediments from different regions of the Baltic Sea

Region	Nitrogen content [μmol/g d.w.]	References
Puck Bay	<36 (sand + silt) 64 (silt + fine-grained sand) 329 (silt) 164 (clay)	Bolałek, 1993
Gulf of Gdańsk	121–486 (silt and clayey silt) 0–93 (sand)	Kępińska, Wypych, 1990
Gulf of Gdańsk	0–964	Burska *et al*., 2003
Gulf of Riga	20–521 449 (accumulation bottom) 135 (transportation bottom)	Carman *et al*., 1996
Gulf of Riga	228 ±163 (316)*	Danielsson *et al*., 1998
Gulf of Finland	271–729	Conley *et al*., 1997
Southern Baltic Sea	7–186 (14)** (sand) 79–221 (136) (sand +clay and clay + sand) 136–679 (336) (clay) 121–329 (143) (loam)	Pęcherzewski, 1972
Baltic Proper	171–700 (0–5 cm)	Carman, Rahm, 1997
Baltic Proper	<143 (erosion bottom) 71–214 (transportation bottom) >357 (accumulation bottom)	Håkanson, 1991
Baltic Proper	400–900 (0–1 cm)	Edlund, Carman, 2001
Baltic Sea	107–1157 (0–1 cm, fine-grained sediments)	Carman, 2003
Baltic Sea	**0–1,157**	

* average ± standard deviation (median); ** range (median)

crease in nitrogen content in sediment occurs in the sea-bottom areas where transport processes prevail over erosional processes, and the highest values are characteristic of the regions where accumulation processes dominate. In these regions, a significant part of nitrogen is supplied to the bottom by advection of the particles and its transport over the sea bottom. For instance, in deep-water regions of the Gotland Sea, the nitrogen accumulation rate is 2 to 7 times higher than its flux from the water column (Struck *et al*., 2004).

As regards the Baltic Sea regions covered with fine-grained sediments, the Gotland Basin sediments are especially rich in nitrogen (Gotland Deep, vicinities of the Landsort Deep and the northern Gotland Basin), whereas relatively low nitrogen contents occur in the Bothnian Bay, Bothnian Sea and Skagerrak (Fig. 7.25).

Inorganic forms of nitrogen in bottom sediments usually account for no more than 10% of the total nitrogen.

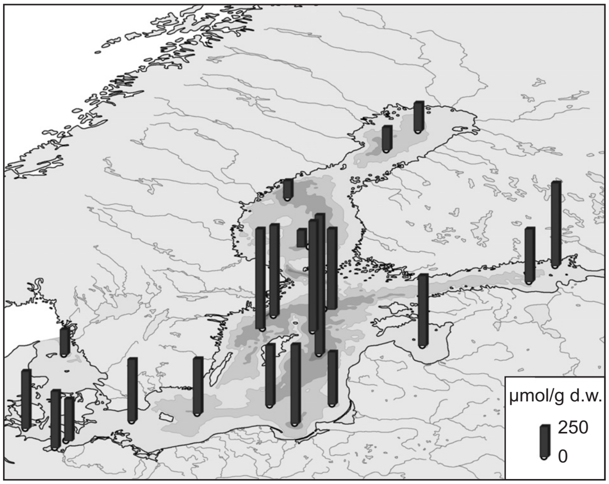


Fig. 7.25. Nitrogen content in silty sediments of the Baltic Sea (layer 0–1 cm, concentration range 107–1157 µmol/g d.w.) (Carman, 2003)

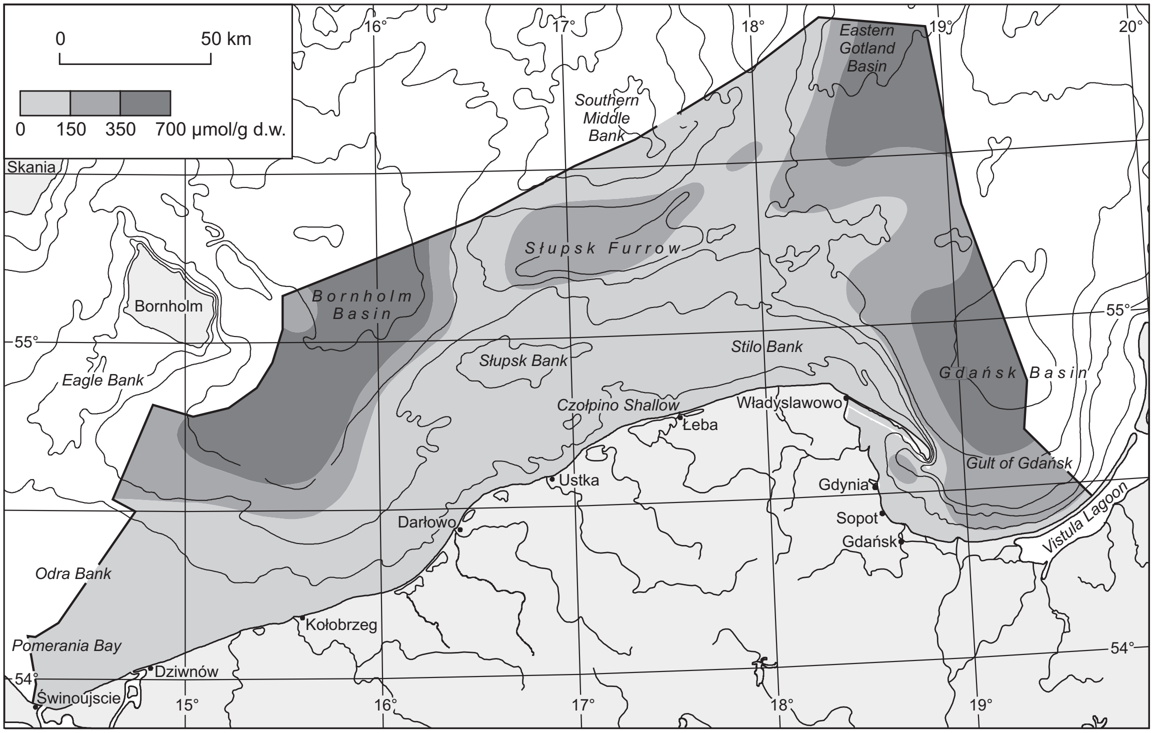


Fig. 7.26. Nitrogen content in the surface sediment layer of the southern Baltic Sea (after Pęcherzewski, 1972, revised)

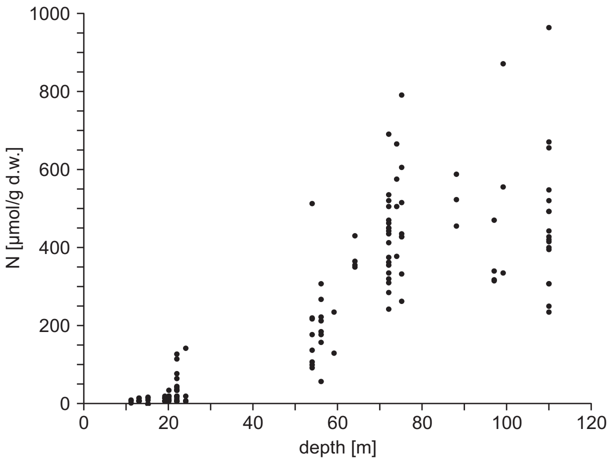


Fig. 7.27. Changes in nitrogen contents in sediments of the Gulf of Gdańsk depending on the sea depth (Burska *et al*., 2003)

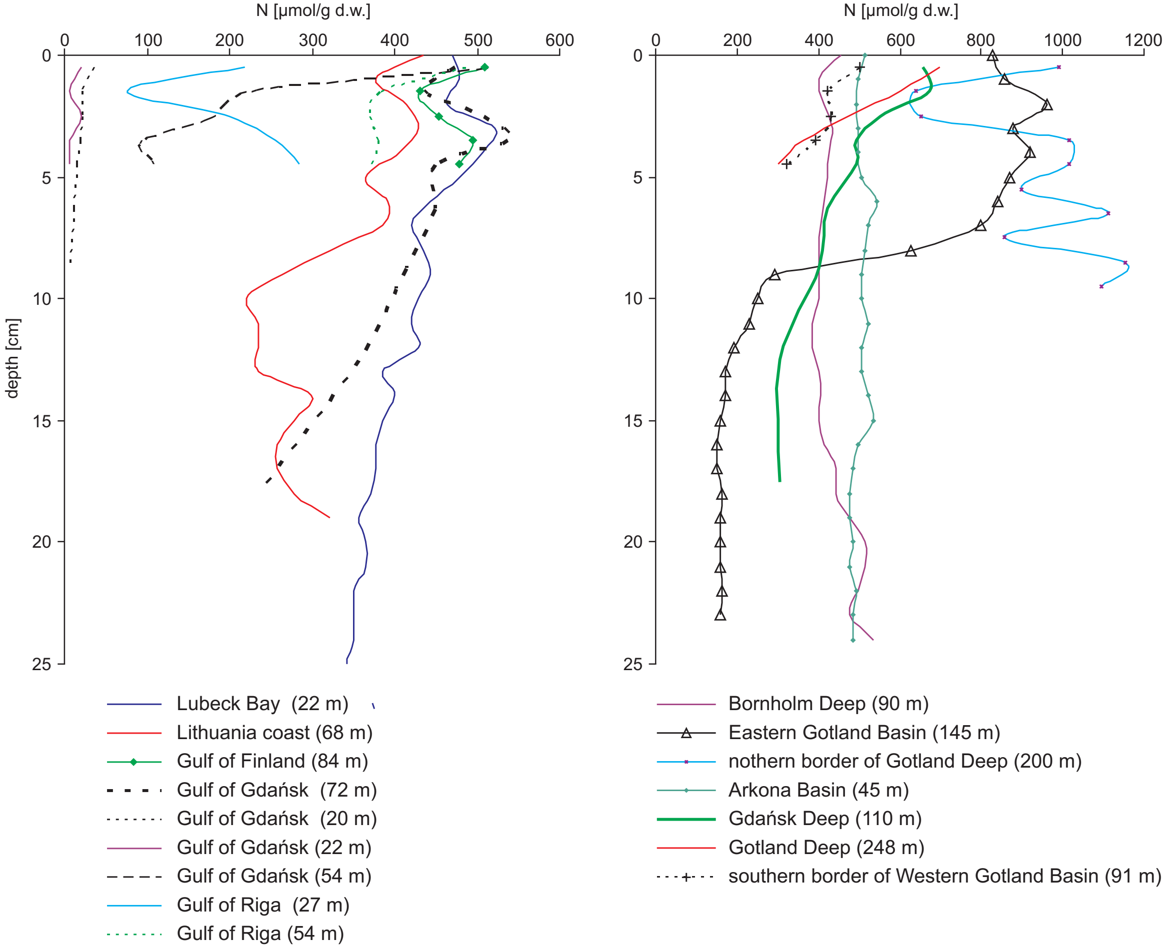
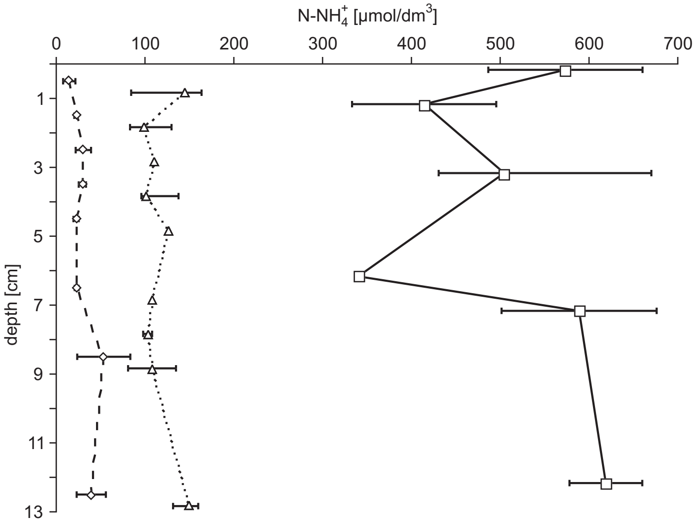
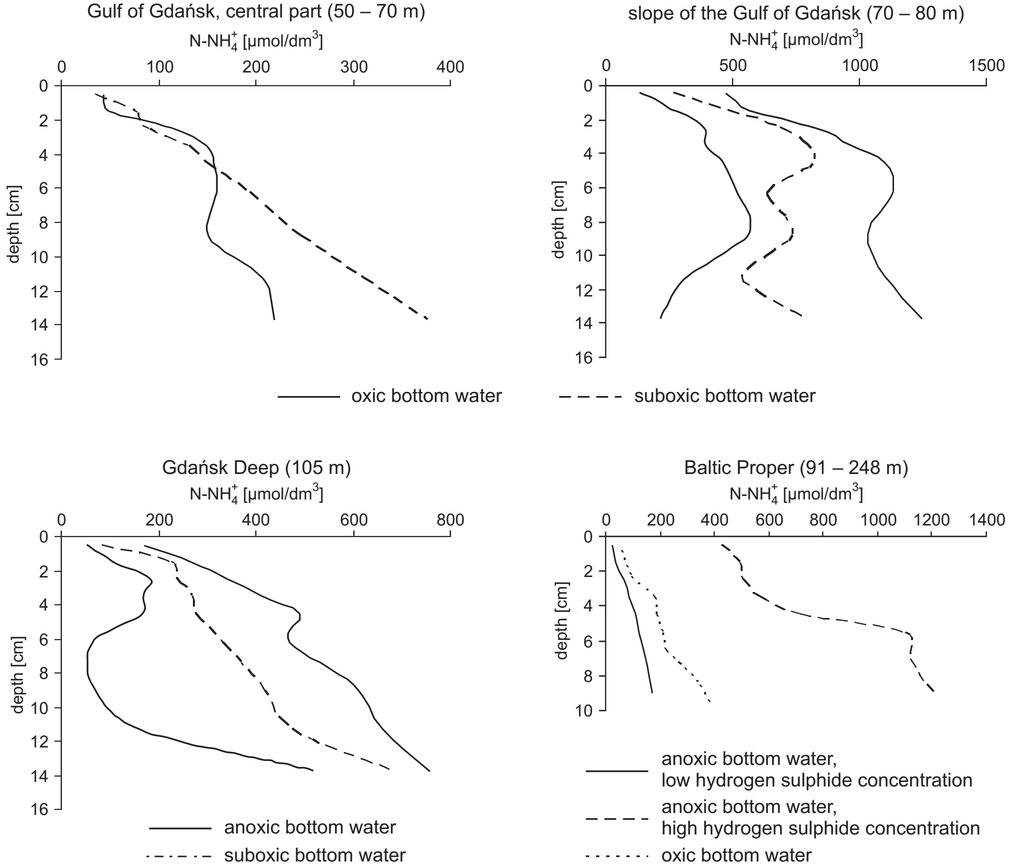


Fig. 7.28. Nitrogen in the sediment profiles from different regions of the Baltic Sea (Carman *et al*., 1996; Carman, Rahm, 1997; Burska *et al*., 2003)

Fig. 7.29. Ammonia concentrations in interstitial waters for three selected regions from the coastal zone of the Gulf of Gdańsk (h < 30 m) (Graca, 2009). In this figure, a non-outlier value range and medians are presented




Gulf of Gdańsk, central part (50 – 70 m)

slope of the Gulf of Gdańsk (70 – 80 m)

Gdańsk Deep (105 m)

Baltic Proper (91 – 248 m)

Fig. 7.30. Ammonia concentrations in interstitial waters from different regions of the Baltic Sea (based on Carman, Rahm, 1997; Graca *et al.*, 2006)

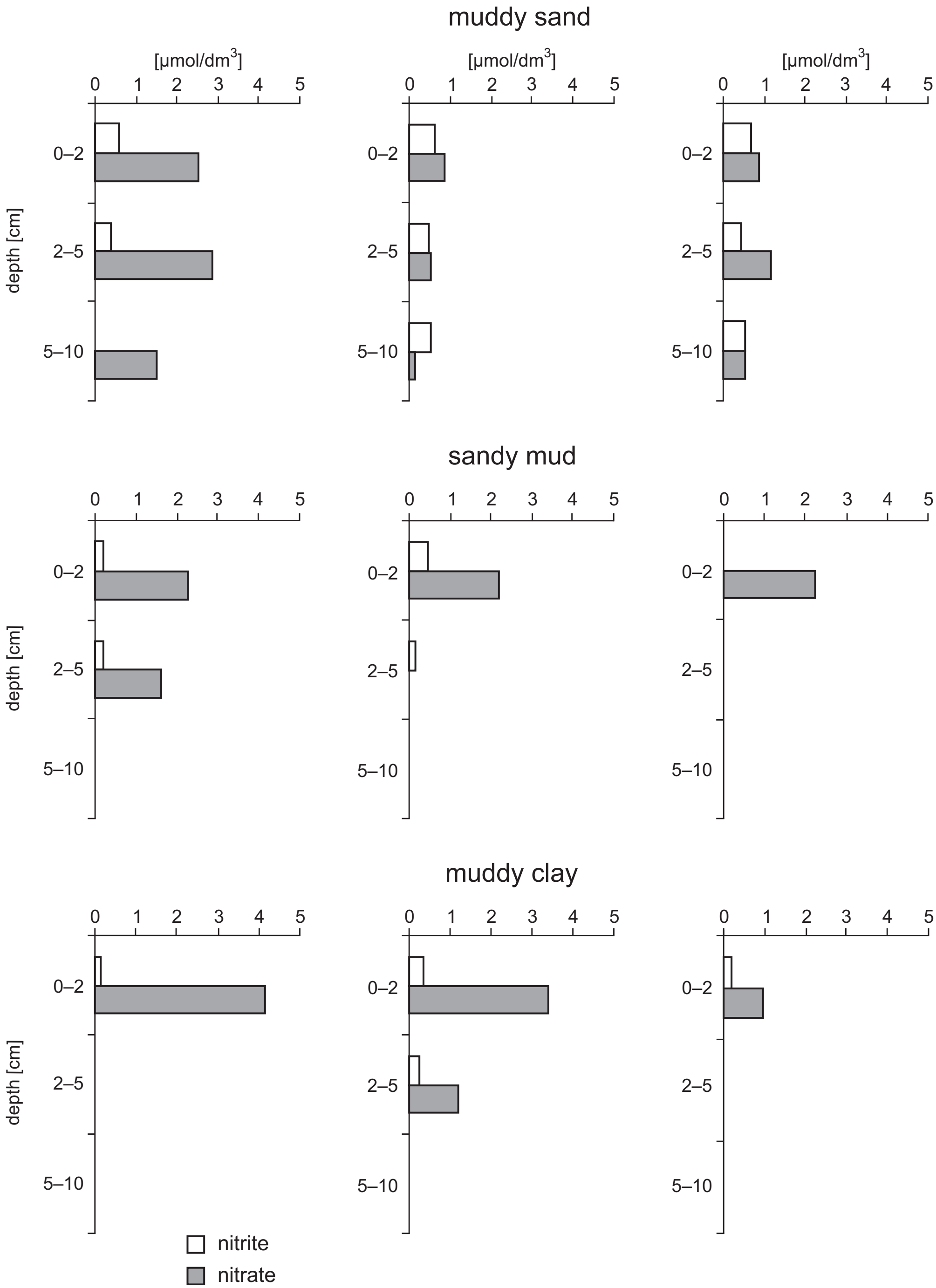


Fig. 7.31. Vertical changes in concentrations of nitrates and nitrites in interstitial waters of different grain-sized sediments (Graca, 2009)

For instance, inorganic nitrogen in the central parts of the Baltic Sea, accounts for 6 ±3% of the total nitrogen, while only 8 ±5% of nitrogen is represented by exchangeable forms. The rest is represented by fixed nitrogen (Carman, Rahm, 1997).

The increase of inorganic nitrogen is possible in the erosion or transportation bottom. Such situation occurs in the Gulf of Riga, where inorganic nitrogen locally accounts for 50–70% of the total nitrogen content (Carman *et al.*, 1996).

In the Gulf of Gdańsk, high amounts of nitrogen in sediments (>400 µmol/g d.w.) are observed below the isobath of 70 m (Fig. 7.27). In the region of coastal sands, the contents rarely exceed 50 µmol/g d.w.

The nitrogen content decreases with the sediment depth (Fig. 7.28) and fluctuations in its flux from the water column as well as increased hydrodynamic activity or benthic organisms may be a cause of variability in the contents of this component in the vertical sediment profile.

Seasonal variations of the nitrogen content in the surface layer of the Baltic Sea sediments are associated with the production cycle. The increase of N content in the sediment is observed after the spring and autumn blooming of phytoplankton, when a load of fresh organic matter is supplied from the water column to the sediments (Aigars, Carman, 2001).

Ammonia is a dominant form of nitrogen in the interstitial waters of the Baltic Sea. Its concentrations range widely from 0 to 2,000 µmol/dm^3. In the Baltic Proper, the highest ammonia concentrations (app. 1,400 µmol/dm^3) were observed in the areas of oxygen deficits and high concentrations of hydrogen sulphide. Low concentrations usually occur in sands. For example, in the coastal zone (h <30 m) of the Gulf of Gdańsk 75% of the results do not exceed 138 µmol/dm^3 (Fig. 7.29). A higher local ammonia concentration in this part of the bay is observed in the areas of strong anthropopression (Vistula River mouth, city surroundings). In the central part of the bay (transportation bottom), the ammonia concentrations range from 1.5 to 2,147 µmol/dm^3, but half of the values show a considerably narrower range from 148 to 699 µmol/dm^3. In areas deeper than 80 m, including the Gdańsk Deep, the ammonia concentrations are within the range of 54–826 µmol/dm^3. Half of the values are between 204 and 451µmol/dm^3.

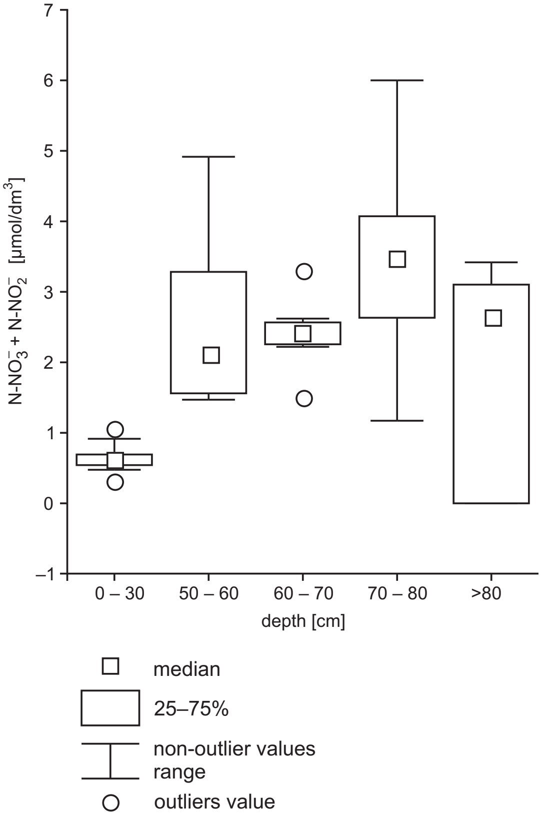


Fig. 7.32. Concentrations of the sum of nitrates and nitrites in interstitial waters of the surface sediment layer (0–1 cm) in the region of the Gulf of Gdańsk with different depths of the sea water (Graca, 2009)

In areas of high water dynamics and numerous benthic organisms, changes in ammonia concentrations in the vertical profile of sediments are typically irregular. In the deep-water regions where hydrodynamic activity as well as the abundance and biomass of benthic organisms usually decrease, an almost exponential or linear increase in ammonia concentrations with the sediment depth was observed (Fig. 7.30).

Nitrates and nitrites occur in interstitial waters, mainly in the surface sediment layer, like e.g. in the Gulf of Gdańsk (Fig. 7.31). The maximum depth of their occurrence decreases in the bay with the increase in the sediment dispersion. Nitrite concentrations are usually lower than nitrate concentrations, being considerably affected by complex interactions of such factors as sediment type, oxygen conditions, contents of organic matter, and benthic organisms. For instance, low concentrations in the Gulf of Gdańsk are characteristic of sandy coastal areas; they increase below the isobath of 50 m, and diminish in the Gdańsk Deep region during long-term anoxia in the near-bottom waters (Fig. 7.32).

It should be emphasized that the resolution used to analyse interstitial waters significantly effects the concentration values of ammonia, nitrates and nitrites, as well as the profile of a given substance. For example, the concentration for the interstitial waters from a 1-cm thick sediment layer represents a mean content of the analysed component in this layer. Especially high approximation is observed with the values achieved in the surface sediment layer, where potentially intense nitrification and coupled nitrification/denitrification occur.

7.5. Biogenic Silica

An increase in diatom production due to eutrophication leads to higher sedimentation rates and a larger amount of biogenic silica deposited in the bottom sediments (Conley *et al*., 2008; Papush *et al*., 2009). Since silicon is not as effectively regenerated from sedimenting cells as phosphorus or nitrogen, silica concentrations decrease in the water column and the return of this compound to the amount of silicon available for phytoplankton is delayed (Burska *et al.*, 1997). Additionally, the increase in deposition rate of organic matter induces as much as a 4-time lower mineralisation rate of biogenic silica in the sediments (Conley, Johnstone, 1995).

Faster depletion of silicate rather than nitrate or phosphate leads to the replacement of diatoms, dominant in early spring blooming, by other plankton organisms, for which silicon is not an element essential for life. An increased biomass (90%) of dinoflagellates (mainly *Peridinella catenata*) in spring was observed by Wrzołek in the 1990s (1996) in the Gdańsk Deep waters.

The occurrence of silicon in the Baltic Sea waters is balanced by a regular supply from river waters. However, it is not an element for which the concentration may be increased to a considerable degree by human activity, as it happens with phosphorus or nitrogen. Its concentration may be lowered by river regulation and hydrotechnic structures. Average annual concentrations of biogenic silica (BSi) and dissolved silicate (DSi), observed in the waters of the Odra, Vistula and Daugava, suggest that silicon loads decrease significantly with the degree of river regulation (Humborg *et al*., 2002, 2006).

7.5.1. Silicon Cycle in the Marine Environment

Silicon in natural waters originates from constituents of the lithosphere dissolved by water and CO_2. Silicates and aluminosilicates occurring in the process of weathering undergo partial or total hydrolysis. Therefore, silicon occurs in sea water as dissolved sodium, potassium and magnesium silicates, and a molecular solution (H_2SiO_4) or colloid solutions of $SiO_2{\cdot}H_2O$ (Pilson, 1998). These compounds are a material used for building silica exoskeletons. Marine organisms, such as diatoms, radiolaria, siliceous sponges or silicoflagellates, build their cell walls with dissolved silicate producing biogenic silica – hydrated silicon dioxide (Ragueneau *et al*., 2000). The produced hydrogel ($SiO_2{\cdot}nH_2O$), the hydration of which may reach 12–14%, is much (10–20 times) better soluble than quartz, owing to its structure (Pilson, 1998). Therefore, silica skeletons and frustules are soluble in water column and sediments, releasing silicon available for phytoplankton. Biogenic silica solubility grows with an increase in temperature, pH and pressure. Mineralisation of biogenic silica depends on the diatom species, adequate surface structures of diatom skeletons and the size of organisms. Also the contribution of zooplankton and benthic organisms are among significant factors intensifying the return of biogenic silica into circulation (Natori *et al*., 2006). The process of dissolving biogenic silica in the sediment is much slower than in the column water, particularly when the silica forms part of organic matter, or metals such as Al, Be, Fe, Ba are adsorbed on its surface. That causes the effective diminishing of the surface that undergoes dissolution, silica shows weaker reactivity, and consequently the dissolution is reduced.

Dissolution of biogenic silica in sea-bottom sediments induces the increase in concentration of dissolved silicate (DSi) in interstitial waters. A difference in the DSi between the reaction media stimulates the amount and direction of the flux of this compound. Raising silicate to the surface layers of the sea waters is supported by water mixing, sea currents or upwellings.

The content of biogenic silica in sediments depends on the productivity of the reservoir, its depth and on the residence time in the water column. It is also associated with the mineralisation rate, which depends partly on temperature, pH, pressure, and the contents and activity of organisms in a trophic chain.

7.5.2. Variability of Biogenic Silica Content in Recent Surface Sediments of the Baltic Sea

Biogenic silica content (BSi) (calculated as SiO_2 %) in surface sediments of the Baltic Sea changes widely from below 0.1% up to 15–20% (Emelyanov, 1988; Emelyanov ed., 2002; Burska *et al*., 2005, Conley *et al*., 2008; Pastuszak *et al*., 2008). The information about the contents of amorphous silica in sediments described by Emelyanov (1988; ed., 2002) concerns the largest area of the Baltic Sea. Except the Bothnian Bay, Bothnian Sea and Kattegat, it includes all subregions of the Baltic Sea, the Gdańsk Basin in particular.

Mean BSi values in sediments of the main basins of the Baltic Sea are within the range of 1.95 to 5.16% (Conley *et al*., 2008; Pastuszak *et al*., 2008) and are slightly higher than the values presented earlier by Emelyanov (ed., 2002). The highest mean content of biogenic silica was observed in the sediments of the Szczecin Lagoon, whereas the lowest – in the Gulf of Riga (Fig. 7.33). Still more distinct differences between the regions concern extreme values of BSi concentrations in sediments. In the sediments of the Szczecin and Curonian lagoons, the silica contents reach 6–8% (Emelyanov ed., 2002; Pastuszak *et al*., 2008), 8–10% in the Gulf of Gdańsk (Emelyanov ed., 2002; Burska, unpubl. data), and up to 15–20% in the Gotland Basin (Conley *et al*., 2008).

The highest BSi contents are found in silty sediments (Emelyanov, 2001, ed., 2002). Diatom sediments are classified as aleuritic-silty and silty deposits, which results from the small sizes of diatoms and losses in SiO_2 after dissolution in both the water column and the sediments (Gudelis, Emelyanow, 1982). The lowest BSi contents concern sandy sediments, which is related to intense mineralisation of silicon material during settling.

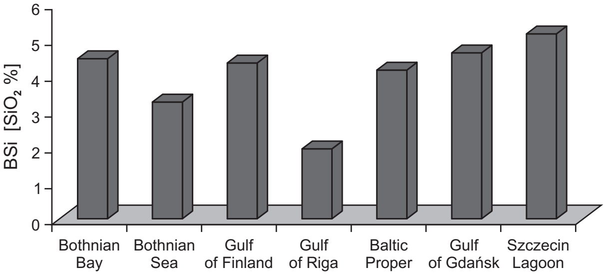


Fig. 7.33. Mean content of biogenic silica in the surface sediment layer (0–2 cm) of the Baltic Sea (based on Burska *et al*., 2005; Conley *et al*., 2008; Pastuszak *et al*., 2008)

The biogenic silica content in the sediments of the Gdańsk Basin varies from 0.1 to 9.63% (Kępińska, Wypych, 1990; Emelyanov, ed., 2002; Burska, unpubl. data). The highest BSi values (>5%) occur in silty sediments of the central part of the Gulf of Gdańsk (Fig. 7.34), where the main part of both autochthonous and allochtonous organic matter is deposited (Emelyanov, ed., 2002). The mean content of biogenic silica in the surface layer of silty sediments (0–2 cm) is 4.87% in this area, which is one of the highest averages in the Baltic Sea (Fig. 7.33). The remaining sediments located below the 40–50 m isobath shows a lower (3–5%) BSi content. The lowest values of biogenic silica (<0.5%) occur in the coastal zone (down to the 20–30 m isobath) covered with sandy sediments.

Changes in biogenic silica in the vertical profile of sediments depend mainly on the flux of silicon matter reaching the sea bottom, on the mineralisation rate of settling and already deposited matter, and on the hydrodynamic processes that control both the settling of the matter in the sea bottom and the exchange of the dissolved silicon at the sediment-water interface.

In deep sedimentary basins of the Baltic Sea, the changes in the biogenic silica content in down the sedi-

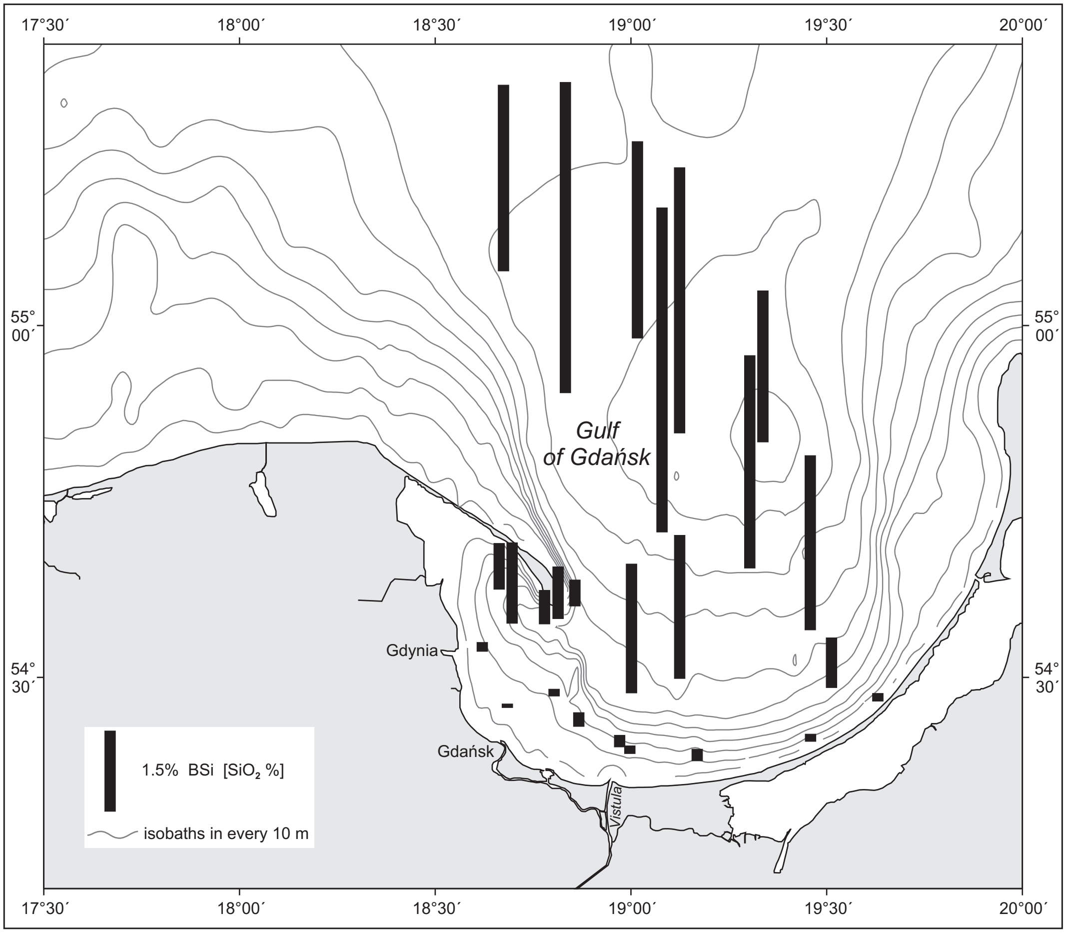


Fig. 7.34. Contents of biogenic silica (BSi) (SiO_2 %) in the surface sediment layer (0–2 cm) of the Gdańsk Basin (in 2000–2005) (Burska, unpubl. data)

ment column suggest increased deposition of diatom matter in the sediments over the last 100–150 years (Conley *et al*., 2008). The highest accumulation of biogenic silica occurs in the Baltic Proper. The enrichment factor of 3.22 for this basin is twice higher than for the other accumulation basins, while it is almost three times higher for the Bothnian Bay. That situation is reflected in the vertical profiles of the biogenic silica content. The BSi content in the Baltic Proper sediments drops more rapidly than in other parts of the Baltic Sea, achieving equalised values at the depth of 15–20 cm. The difference in BSi in the surface sediment layer and in the stabilisation layer in the sediments of the Arkona, Gdańsk and Eastern Gotland basins is approximately 1%, 5%, and 17%, respectively (Conley *et al*., 2008).

Similarly to the whole Baltic Sea, the content of biogenic silica in silty sediments of the Gulf of Gdańsk decreases in the sediment profile. Its content usually stabilises at a depth of 15–20 cm, or even at 25 cm (Fig. 7.35). Depending on the sediment type and its location, the changes in the contents of biogenic silica in sediments may show different features. Vertical BSi profiles can have an equalised course in the whole 20-cm thick layer (E35), they can be characterised by a distinct, almost linear, drop (G2, P110) or growth down the sediment profile

(E52a, St2), by a stepwise lowering below the surface layer of the invariably high BSi content (P116, E36a), or by the occurrence of irregular maxima at different levels (P104).

The almost equalised course of the biogenic silica content in the top 10-cm layer of the sediments in the central part of the Gulf of Gdańsk (Fig. 7.36) shows the relatively time-constant intensity of the primary produc-

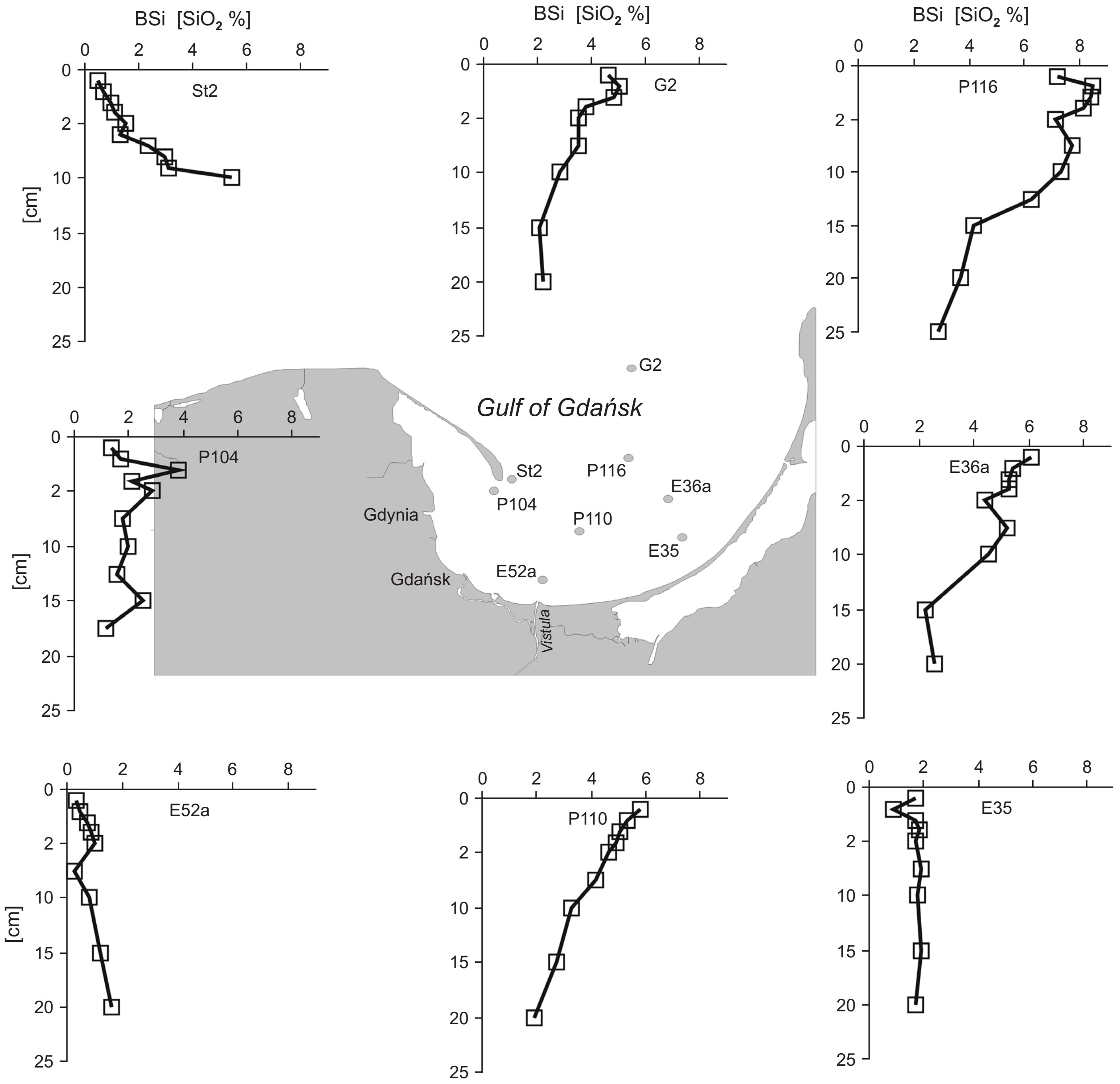


Fig. 7.35. Changes in biogenic silica content (BSi) (SiO_2 %) in the vertical profile of sediments in the Gulf of Gdańsk (in 2000–2005) (Burska, unpubl. data)

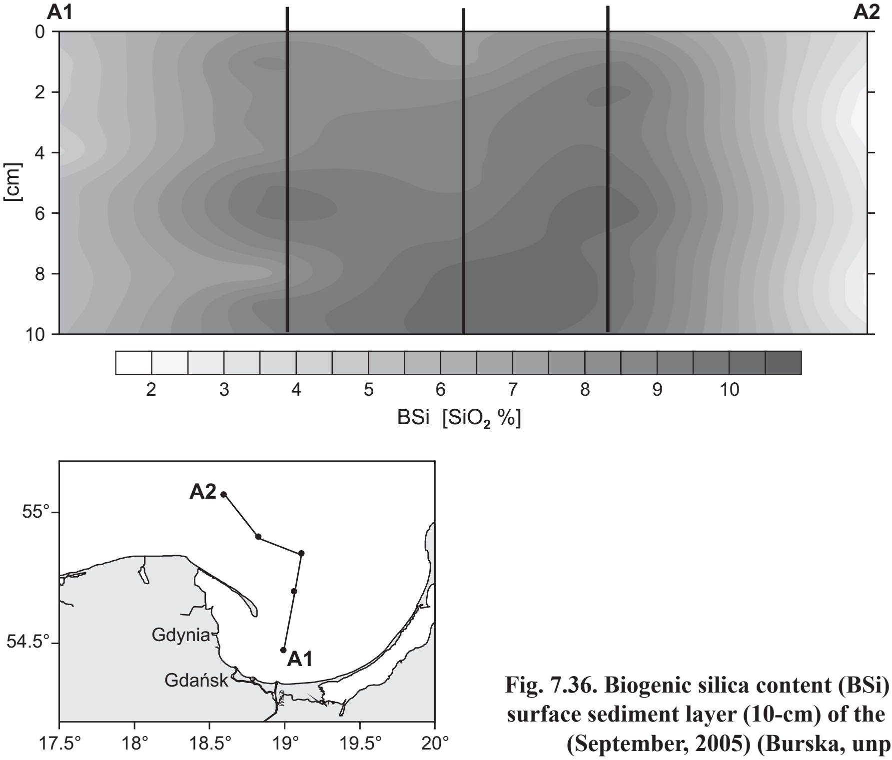


Fig. 7.36. Biogenic silica content (BSi) (SiO$_2$ %) in the surface sediment layer (10-cm) of the Gulf of Gdańsk (September, 2005) (Burska, unpubl. data)

tion, the amount of terrigenous matter and the small variability in hydrodynamic conditions favourable for depositing diatom matter in this area. Despite high biogenic silica values (up to 10.5%) in the vertical profile, slightly higher values were observed in the surface sediment layer (0–1 cm).

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Chapter 8

TRACE ELEMENTS IN THE BALTIC SEA SEDIMENTS

The natural cycle of elements in nature is marked by a balance between the amount of elements released by weathering processes and their amount bound in the soils and sediments. Under natural conditions, not disturbed by human activities, the contents and amounts of trace chemical elements, including heavy metals accumulating in the sediments, is mainly the effect of a lithological structure and climatic conditions in the catchment area of the sedimentary basin. Both climatic conditions and the type of rocks define the form of weathering processes and chemical element release. In the previous centuries, industrial activities disturbed the natural cycling of the elements. They are now supplied not only from natural sources, but also as an effect of anthropogenous processes, which means that the sediments formed during the last few hundred years may contain excessive amounts of heavy metals. The problem of contamination with heavy metals as well as other toxic substances is important because these substances, by entering the trophic chain, pose a threat to animals and humans.

Metals, occurring in sediments in different chemical forms (known as speciates) bound with the crystal lattice of minerals, are adsorbed by clay minerals and organic matter, and by iron and manganese hydroxides. Considering the above, there is a strong relation between the contents of metals and the grain size of the sediment as well as the content of organic matter (Tables 8.1, 8.2). It is possible that, owing to environmental conditions and sedimentary processes in the past, the metal contents in sediments formed at that time are higher than in the contemporaneous sediments polluted by man. For example, sediments of the early development stages of the Baltic Sea, i.e. the Baltic Late Pleistocene and Early Holocene deposits (Baltic Ice Lake, Yoldia Sea and Ancylus Lake), poor in organic matter, contain some metals in higher amounts than the sediments of the Middle and Late Holocene characterised by similar grain size and enriched in organic matter (Table 8.1).

Sediments from the earlier development stages and eroded in specific conditions may be a source of metals for sediments deposited in the present. This process is particularly significant in the northern part of the Baltic Sea (Bothnian Sea and Bothnian Bay including Gulf of Finland), where, owing to the glacio-isostatic uplifting of the Earth's crust, deposits of the early development stages of the Baltic Sea are now exposed to erosion. The acid sulphide soils of Finland, developed on Holocene marine muds, are a good example. From these agriculturally cultivated soils, considerable amounts of metals are washed out and flow down to the Baltic Sea by rivers. It has been shown that the runoff of metals, i.e. Cd, Co, Ni, and Zn, from this source is higher than the downflow of metals from the whole Finnish industry (Fältmarsch *et al.*, 2008).

Also the southern Baltic Sea, e.g. in the areas of thresholds separating the Bornholm Basin from Słupsk Furrow, the Gdańsk Basin from Gotland Basin, and the slopes of the Słupsk Furrow, is featured by outcrops of deposits of the early development stages of the Baltic Sea that are undergoing contemporaneous erosion.

Each chemical form of the metals shows different behaviour in the biogeochemical cycle and features a di-

Table 8.1

Mean contents of metals in the Baltic Sea sediments in relation to age and grain-size category (grain-size categories acc. to the Shepard classification, 1954; sediments were completely digested, metals were determined using Atomic Absorption Spectrometry AAS; based on data by Uścinowicz, Zachowicz 1992, 1994)

Region of the Baltic Sea	Age of sediment and development phases of the Baltic Sea	Grain-size category and organic matter contents (number of analyses)	Contents of metals [mg/kg]					
			Co	Cr	Cu	Ni	Pb	Zn
Gdańsk Basin	Late Pleistocene (Baltic Ice Lake)	clay, 1.1% (14)	**36.3**	**89.3**	32.7	**60.6**	58.4	**112.2**
		silty clay, 0.8% (6)	**30.6**	**77.0**	29.2	55.4	64.5	99.4
	early Holocene (Yoldia Sea and Ancylus Lake)	clay, 1.1% (10)	**36.4**	**94.2**	38.6	**63.0**	56.0	**151.6**
		silty clay, 1.2% (16)	**31.7**	**80.8**	34.5	57.6	61.4	109.9
	middle and late Holocene (Littorina Sea and Post-Littorina Sea)	clay 11.1% (2)	29.1	77.5	39.4	57.4	–	106.0
		silty clay, 12.8% (17)	27.9	75.8	39.8	58.0	66.9	110.9
Bornholm Basin	Late Pleistocene (Baltic Ice Lake)	clay 2.5% (17)	**35.1**	94.2	35.0	**66.5**	–	**185.6**
		silty clay, 2.4% (6)	**41.0**	73.2	34.4	**75.5**	–	**193.0**
	early Holocene (Yoldia Sea and Ancylus Lake)	clay, 2.7% (10)	**34.0**	86.8	42.0	**62.5**	–	**176.2**
		silty clay, 3.3% (3)	**31.7**	86.8	44.2	**58.7**	–	**161.0**
	middle and late Holocene (Littorina Sea and Post-Littorina Sea)	clay, 10.9% (7)	26	–	–	44.0	50.0	91.0
		silty clay, 9.9% (10)	18.0	–	–	40.0	48.0	119.9

* Highest concentrations are marked in bold.

verse range of the bioaccumulation ratio in marine organisms. Depending on the purpose of the research, different types of analytical methods can be used. In order to determine the content of chemical components in the bottom sediments, a sample needs to be prepared for analysis, and this depends on what chemical components are to be determined and what type of analytical technique is to be applied. Trace metals in sediments are determined by using the methods of Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), Inductively Coupled

Table 8.2

Contents of metals in grain-size fractions of the surface layer (0–10 cm) in the Słupsk Furrow (separated by centrifuging after removing organic matter using perhydrol, complete dissolving, metals determined by Atomic Absorption Spectroscopy AAS)

No. and description of sample	Fraction [mm]	Fe	Mn	Co	Cr	Cu	Ni	Pb	Zn
		[%]		[mg/kg]					
5 Ł φ 55°17’10” λ 17°06’44” Depth 81.5 m Md = 0.008 mm Organic matter = 5.1%	<0.001	7.77	0.63	43.8	111.0	144.0	81.4	188.7	302.4
	0.001–0.004	3.62	0.36	30.1	109.7	41.0	63.7	71.6	169.8
	0.004–0.016	2.35	0.23	18.9	42.2	21.0	31.3	53.4	98.9
	0.016–0.063	1.12	0.19	9.7	14.7	14.0	11.5	37.4	29.3
19 Ł φ 5°16’35” λ 17°10’43” Depth 74.5 m Md = 0.005 mm Organic matter = 6.5%	<0.001	7.19	0.43	38.5	104.7	116.0	69.7	154.0	237.8
	0.001–0.004	3.20	0.30	27.9	61.2	55.0	45.1	57.2	231.8
	0.004–0.016	2.22	0.22	20.4	63.0	26.0	36.9	40.2	63.9
	0.016–0.063	0.96	0.17	10.5	21.4	16.0	13.2	30.9	21.9
20 Ł φ 55°18’32” λ 17°10’09” Depth 75.5 m Md = 0.005 mm Organic matter = 5.3%	<0.001	7.27	0.43	38.5	98.4	125.0	69.7	165.0	271.6
	0.001–0.004	4.45	0.36	29.1	84.6	123.0	55.6	111.2	244.5
	0.004–0.016	2.43	0.22	21.2	34.6	32.0	27.1	53.3	76.5
	0.016–0.063	0.95	0.15	13.9	10.7	19.0	12.3	40.0	23.0

Plasma – Mass Spectrometry (ICP-MS) and Atomic Absorption Spectrometry (AAS). For analytical techniques, samples are prepared in a similar way: when dried – mainly in a freeze dryer – the sample is decomposed in a mixture of oxidising acids, and then it is introduced to the measurement system of the analytical equipment in the dissolved form.

In order to determine the total content of the compound, the sample is to be mineralised with a mixture of oxidising acids with addition of hydrofluoric acid. Since biogeochemical processes at the water-sediment interface involve only those forms of metals that are weakly bound with the structure of sediment, techniques of partial dissolving are frequently used in order to release the most mobile forms of metals. For this purpose, aqua regia, nitric acid or perchloric acid may be used in different concentrations (see Appendix No. 4).

The International Council for the Exploration of the Sea – ICES allows for both methods, suggesting, however, that extracting mixtures – excluding HF – should be used in national research programmes concerning local areas only. In international monitoring programmes, complete dissolving is suggested by using HF in combinations with one of the oxidising acids or their mixture, e.g. aqua regia (Perttilä, Brügmann, 1992). Such a method was applied in the first international research project concerning chemical contamination of the Baltic Sea sediments (Perttilä, ed., 2003).

8.1. Trace Elements in Surface Layer of Sediments

For several hundred years, as the process of civilisation development continuous, the natural cycling of chemical elements has been overlapping with the processes related to human economic activities. In industrialised areas, different types of pollution are discharged into the environment. Sewage disposal and emission of contaminants into the atmosphere, including heavy metals, result in final bottom sediment deposition of contaminants together with wet precipitation and the surface water runoff into the sea. Therefore, the surface layer sediments, as compared to those deposited in the preindustrial times, show higher levels of heavy metal concentrations in many regions of the sea.

The contents of trace elements in silt-clay sediments of the Baltic Sea from its main sedimentary basins (Baltic deeps), both in the surface layer (0–1 cm) and in deeper layers, are presented on the basis of results of the project implemented at the beginning of the 1990s under the auspices of ICES and the Helsinki Commission (HELCOM) (Perttilä ed., 2003). In 1993, the sea bottom sediments were taken from the stations located in the main sedimentary basins of the Baltic Sea and then analysed (Fig. 1.1). The samples were collected using a Niemistö (Gemax) twin gravity corer down to the depths of 30–40 cm below the sea bottom. The following total contents were determined in the material: Al, Li, As, Cd, Cr, Cu, Hg, Ni, Pb, Ti, V, Zn, Fe and Mn.

The Baltic Sea

The contents of trace elements in silt-clay sediments of the surface layer (0–1 cm) from the Baltic Sea are presented in Figs. 8.1. Arsenic, cadmium, chromium, copper, mercury, lead, zinc and other elements are marked by a diversity of concentrations in the surface sediment layer in individual regions of the Baltic Sea.

Arsenic rivets our attention owing to extreme spatial variations in its contents from 3.89 to 215.98 mg/kg. In the Kattegat, Belts Sea, Baltic Proper and Gulfs of Riga and Finland, the arsenic concentrations in the surface layer of silt-clay sediments are low and do not exceed 34 mg/kg. Higher levels of arsenic, from 46.22 to 84.78 mg/kg, occur in the Bothnian Sea (stations 190 and 192 – Fig. 8.1), and the highest contents (215.98 and 167.01 mg/kg) are observed in silt-clay sediments of the Bothnian Bay (stations 193 and 195). Undoubtedly, such high pollution with arsenic is associated with the activity of heavy industry in Sweden (Rönnskärsverket Works in Skellefteå). Despite the fact that Sweden has considerably restricted the discharge of pollutants into the Bothnian Bay over many years, the results of earlier activities are still observable in the sea-bottom sediments (Borg, Jonsson, 1996; Albrecht *et al*., 2003).

Cadmium ranges its highest amounts from 2.05 to 4.38 mg/kg and occurs in the northern part of the Baltic Proper (Eastern and Western Gotland, and North-Central basins; stations 171, 176, 178, 179, and 180). Cadmium can be released into the environment through wastewater from facilities operated by the metallurgic, electronic, plastic and dye industries. Improper management with phosphatic fertilisers and pesticides may be a source of over-concentration of cadmium. However, the occurrence of the highest cadmium concentrations in the deepest parts of the Baltic Sea may suggest that this chemical element accumulates most effectively in the areas of anaerobic conditions in bottom sea waters. Although it is difficult to indicate a direct source of cadmium in this part of the Baltic Sea, the influence of Stockholm and its suburbs cannot be excluded. The Gdańsk Basin also shows anaerobic conditions in the sea bottom waters, but in spite of many potential sources of pollution (mouth of the Vistula River, Gdańsk and Kaliningrad with their suburbs), the cadmium content is smaller (1.28 mg/kg – station 169). Other studies and analyses made in laboratories of the Polish Geological Institute, British Geological Survey and the Geological Survey of the Netherlands also reveal that the cadmium concentration in the surface layer of the silt-clay sediments of the Gdańsk Basin (including the Gulf of Gdańsk) generally do not exceed 1.5 mg/kg and locally reach 2.5 mg/kg.

The lowest cadmium content was observed in the Kattegat (0.15 mg/kg) and the Bothnian Sea (0.35–0.36 mg/kg). In the other parts of the Baltic Sea, the content of this element ranges from 0.39 to 1.98 mg/kg. Locally, elevated concentrations, e.g. in the Lübeck Bay (1.27 mg/kg, station 160), Gulf of Finland (1.98 mg/kg, station 187) or Bothnian Bay (1.98 mg/kg, station 193), may suggest local anthropogenous effects.

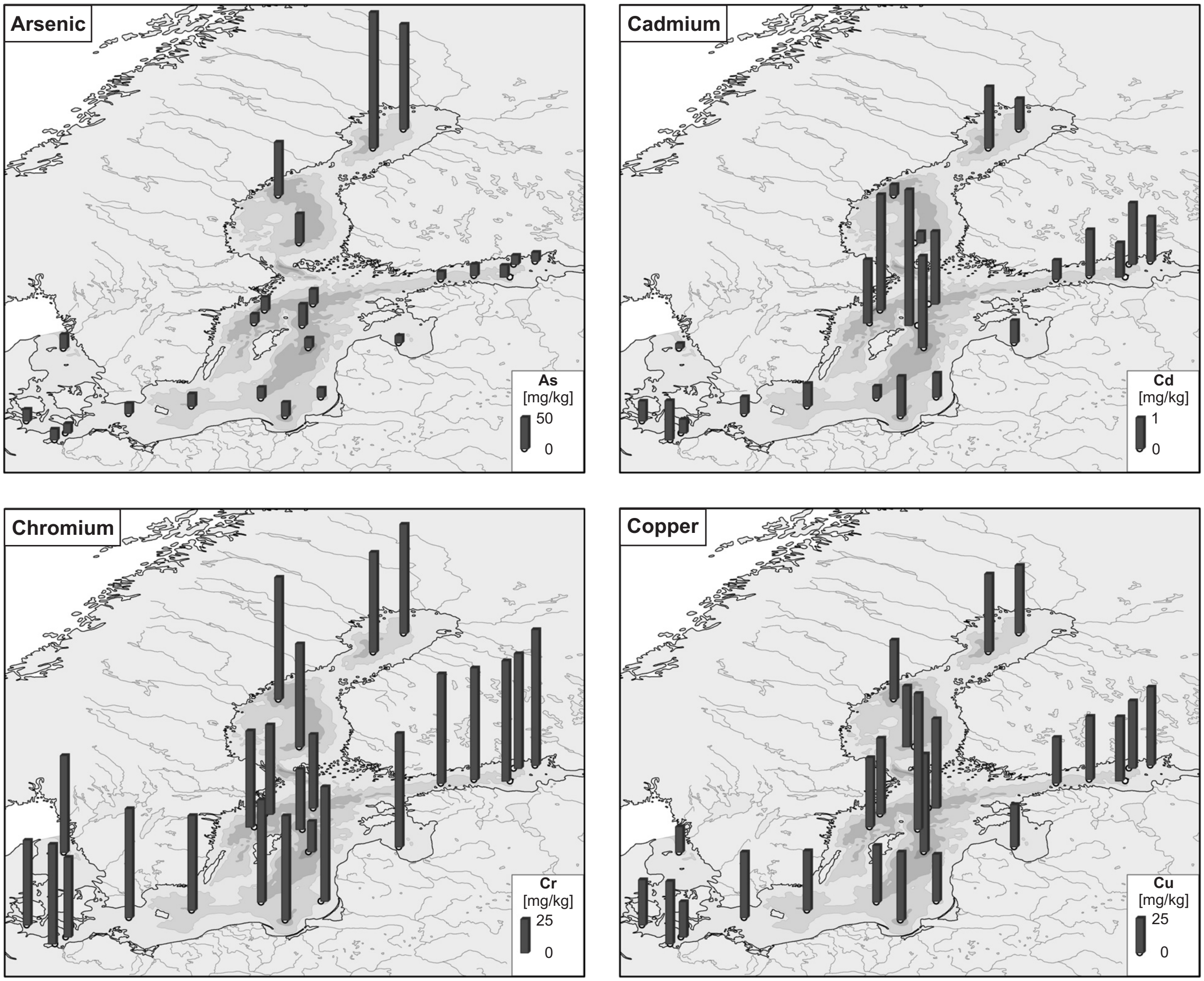


Fig. 8.1. Contents of trace elements (As, Cd, Cr, Cu, Hg, Pb, and Zn) in the surface layer (0–1 cm) of silt-clay sediments in the Baltic Sea; as of 1993 (acc. to Perttilä, ed., 2003)

Chromium occurs in all sedimentary basins in similar amounts in the surface layer silt-clay sediments of the Baltic Sea. The most frequent anthropogenous source of chromium is wastewater discharged from tanneries and metallurgic factories. The lowest chromium contents were found in the Eastern Gotland Basin (22.8–71.6 mg/kg, stations 171 and 178), whereas the highest one – in the eastern part of the Gulf of Finland (101 mg/kg, station 185). In other parts of the Gulf of Finland, chromium occurs in slightly higher amounts than in the rest of the Baltic Sea.

Copper is present in the concentrations ranging from 18.5 mg/kg in the Kattegat (station 156) to 98.4 mg/kg in the Eastern Gotland Basin (station 176) in the surface layer of silt-clay sediments. Higher copper concentrations than in the rest of the Baltic Sea were also observed in other parts of the Eastern Gotland Basin and in the Western Gotland Basin.

The highest amounts **of mercury** (0.36 mg/kg) were noticed in silt-clay sediments of the Bothnian Bay (station 193) and in the northeast part of the Gulf of Finland (0.25–0.22 mg/kg, stations 185 and 187). Effluents

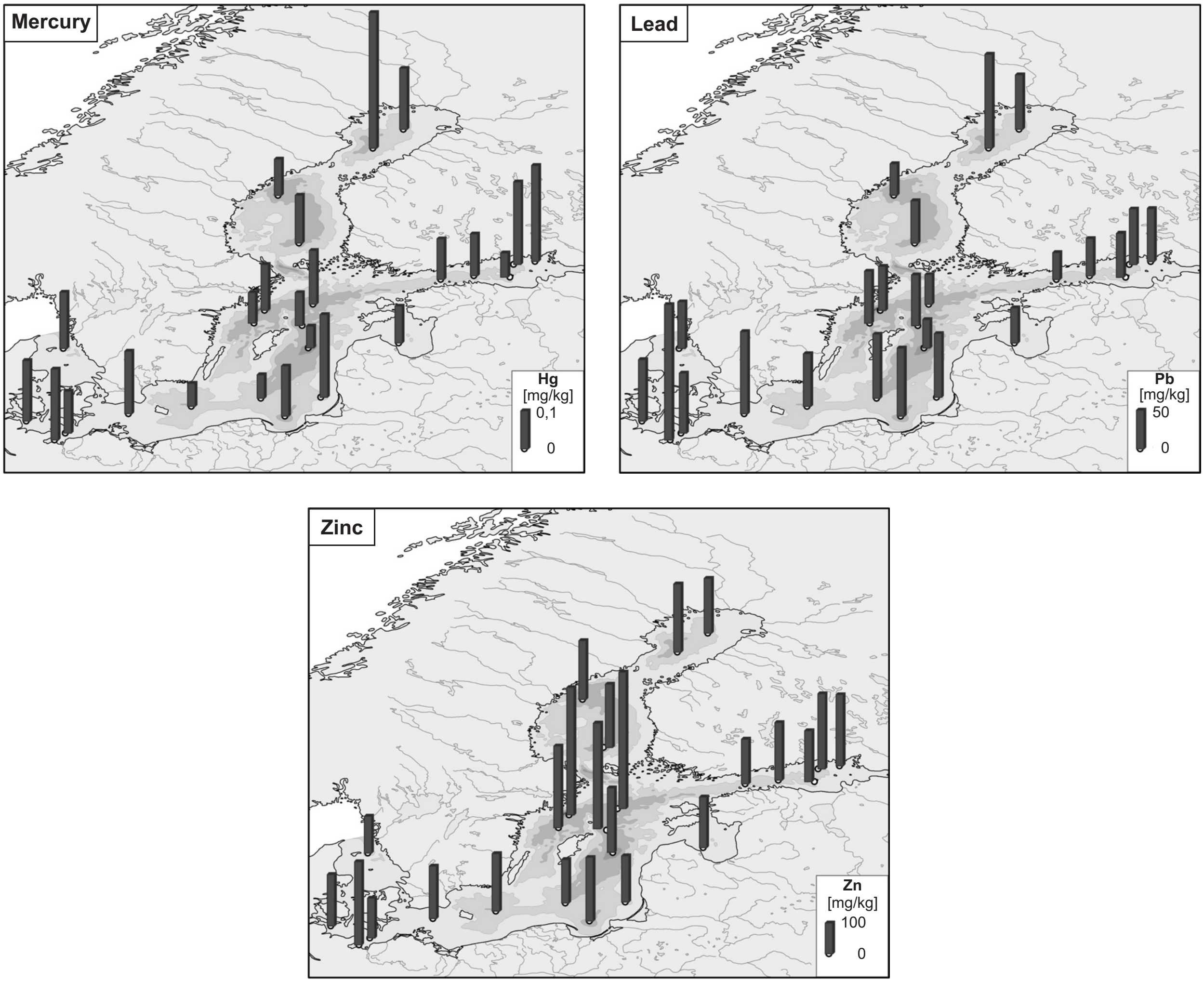


Fig. 8.1. Continued

from paper mills, municipal sewage, and waste waters discharged from the factories producing synthetic fibres and chlorine may be anthropogenous sources of mercury in the sediments (Bojakowska, Sokołowska, 1998).

The elevated level of mercury concentrations in the Gulf of Finland is undoubtedly the effect of the paper industry in Finland, while the origin of increased concentrations of this component in the Bothnian Bay is not yet clear. Lower amounts of mercury were found in the sediments from the north-east part of the Gdańsk Basin, not far from Klaipeda (0.22 mg/kg, station 170), and in the sediments of the Arkona Basin (0.17 mg/kg, station 166) and Lübeck Bay (0.19 mg/kg, station 160). Muddy sediments of the rest of the Baltic Sea showed mercury concentrations below 0.15 mg/kg.

Lead concentrations in the surface layer of silt-clay sediments of the Baltic Sea range from 34.9 to 175.0 mg/kg. Besides natural sources, this element enters into the environment as the effect of battery production, lead glass processing, pigment production and as a result of leaded petrol combustion by road transport. The lowest levels of lead concentrations are observed in the western part of the Gulf of Finland (34.9 mg/kg, station 181), in the northern part of the Baltic Proper (36.8–67.3 mg/kg, stations 171, 176, 178, 179, 180) and in the Bothnian Sea (40.8–54.4 mg/kg, stations 190 and 192). The lead concentration reaches its maximum in the Lübeck Bay region (175 mg/kg, station 160), Arkona Basin (106 mg/kg, station 166), Bothnian Bay (121 mg/kg, station 193) and Gdańsk Basin (82.4–87.9 mg/kg, stations 168–170). Such distribution of elevated levels of lead concentrations in the surface sediments of industrial areas, especially those where industry developed the earliest, i.e. in the south-western Baltic Sea (Lübeck and Szczecin) and the south-eastern Baltic Sea (Gdańsk, Königsberg, Klaipėda), suggests direct relations with the sources of pollution. Besides industry, a considerable source of lead at the end of the 20th century was petrol which contained tetraethyl lead (TEL). The anthropogenous effect on the lead content in the sediments, related to metallurgic industry, is also observed in the Bothnian Bay (station 193).

Zinc can enter into sea waters and then to sediments by the surface run-off from soils, as a result of, for example, wearing of car tyres, from pesticides and phosphatic fertilisers, and from fuel combustion, especially coal. Metallurgic and chemical industries, especially paint production, are anthropogenous sources of this element. The highest zinc concentrations occur in the northern part of the Baltic Proper. The zinc content in this region ranges between 210.0 mg/kg in the Eastern Gotland Basin (station 171) and 443.2 mg/kg in the North-Central Basin (station 180). Locally, elevated zinc levels are observed in the Lübeck region (271 mg/kg, station 160), Gulf of Gdańsk (207 mg/kg, station 169) and eastern part of the Gulf of Finland (231.0–243.4 mg/kg, stations 185 and 187). The elevated zinc content in the Western and Eastern Gotland basins seems to suggest that zinc is effectively transported over considerable distances from its sources of pollution into areas of the greatest deeps. However, the maximum local concentrations of this metal in the vicinity of the early industrialised regions (Lübeck, Gdańsk) may suggest other sources of zinc in the sediments, such as the emission of this element from Stockholm or Petersburg, including their suburbs.

The Southern Baltic Sea

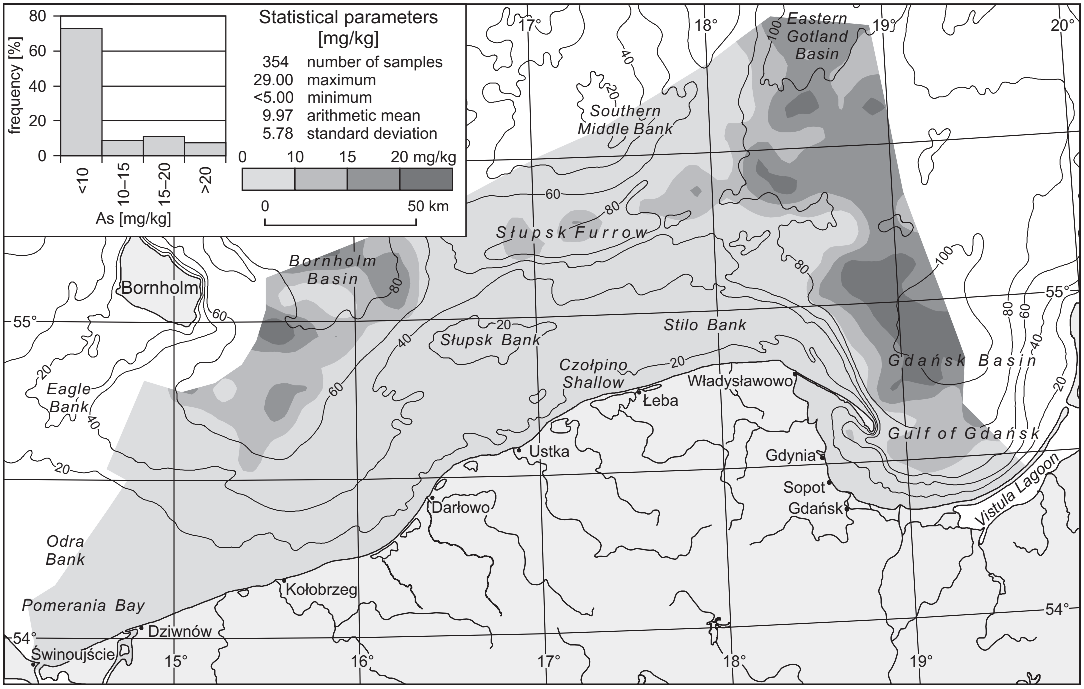
The content of trace elements in deposits of the southern part of the Baltic Proper, which is hereafter referred to as the southern Baltic, has been based on the results of research performed in 1991–1994 by the Marine Geology Branch of the Polish Geological Institute–National Research Institute within the framework of implementing the Geochemical Atlas of the Southern Baltic Sea (Szczepańska, Uścinowicz, 1994). The survey included the Polish Exclusive Economic Zone of the Baltic Sea covering an area of 30 532 km^2. In 1991–1993, samples of surface sediments were taken at 368 survey stations. The research stations were arranged within a regular net, one station per about 100 km^2, and were located in the range of the sediment grain size type that dominated in a given net square.

Silt-clay and silt-sand sediment samples were taken by using a Niemistö core catcher. Cores from the 0–6 cm segment were cut into 1-cm pieces; 2-cm pieces were acquired from the deeper core sections (6–20 cm), whereas for the depths below 20 cm, 5-cm layers were taken. The specimens were placed in plastic boxes and stored at a temperature of –20°C. Sands and silty sands were taken with a Van Veen grab sampler that enabled the researchers to gather the material from a surface area of about 0.2 m^2. These samples were taken from the 0–5 cm deep layer.

The scope of chemical analyses involved the determination of the following contents: C_{org}, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, S, Sr, V, and Zn. After drying at room temperature and powdering, the sediment samples were dissolved. The contents of trace elements were determined by the method of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Atomic Absorption Spectrometry (AAS). In the selected sediment cores, the variability in the contents of the tested components in a vertical section and the sedimentation rate were defined by the ^{210}Pb method. The description of the individual components includes the sediment grain size. There were the following lithologies: sands (>0.063 mm fraction content is more than 75%), silty-sandy sediments (<0.063 mm fraction between 25 and 75%) and silt-clay sediments (<0.063 mm fraction more than 75%).

Arsenic occurs at the level between <5 and 29 mg/kg (Fig. 8.2) in sediments of the southern Baltic Sea. The arsenic content in sands is predominantly below 8 mg/kg, in silty-sandy sediments it is generally between 5 and 15 mg/kg. In the surface layer of silt-clay

Arsenic



Cadmium

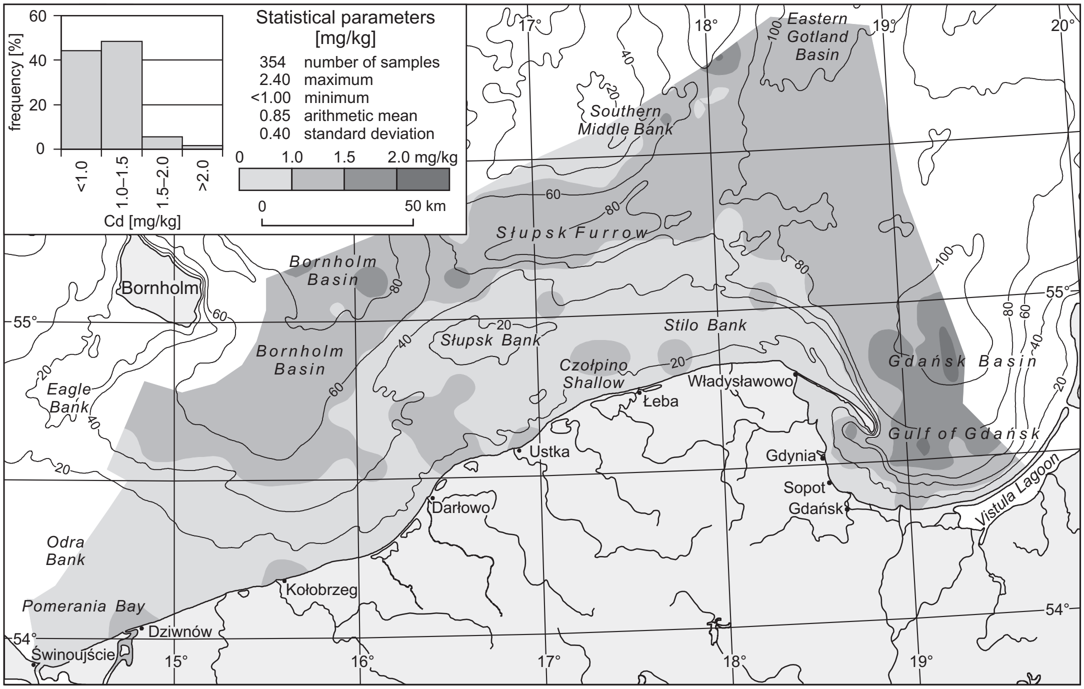


Fig. 8.2. Arsenic and cadmium contents in surface layer of sediments of the southern Baltic Sea, as of 1991–1993 (Szczepańska, Uścinowicz, 1994)

sediments, the amount of this element ranges mostly between 15 and 29 mg/kg. The maximum value of 29 mg/kg was observed in the Bornholm Basin, and values above 20 mg/kg locally in the Eastern Gotland and Gdańsk basins, near the border with the Polish Economic Zone. The lowest concentrations of this metal occur in the surface layer of silt-clay sediments from the Słupsk Furrow and Puck Bay. There is a region of elevated levels of arsenic in the Bornholm Basin, situated at dumping sites of chemical weapons, which seems to be the cause of the local contamination.

In sands, covering the southern Baltic Sea bottom, **cadmium** occurs mostly at the detectability limit of the applied analytical method, i.e. <1 mg/kg. Characteristic, slightly elevated cadmium concentrations (up to 1.5 mg/kg) occur in sediments near the Dziwnów, Kołobrzeg and Ustka harbours and near the Vistula mouth, indicating undoubtedly the sources of the element inflow to the southern Baltic Sea. Similar cadmium concentrations (1.0 to 1.5 mg/kg) are determined in sand-silt and most of silt-clay sediments. The highest concentrations of this element (2.0–2.5 mg/kg) were observed locally in the Gdańsk Basin (Fig. 8.2). Cadmium shows very weak correlations with the grain size of the tested sediments.

In the southern Baltic Sea, **chromium** concentrations vary from <1.0 to 77 mg/kg, with the average of 23.5 mg/kg (Fig. 8.3). The chromium contents show exponential dependence on the grain size of the sediments with a high correlation coefficient. In sand sediments, the chromium content sometimes exceeds 10 mg/kg, only in 5% of the specimens was the content of this metal higher, reaching 18 mg/kg. Silty sands and sandy silts have only a slightly wider range of chromium contents, with a maximum of 33 mg/kg and, most frequently, ranging from 10 to 30 mg/kg. Silt-clay sediments contain from 40 to 70 mg/kg Cr, with moderate values observed in the Bornholm, Eastern Gotland and Gdańsk basins, from 52 to 53 mg/kg. Elevated levels of the chromium concentrations (50–70 mg/kg) were observed in the surface sediment layer from the Gdańsk and Bornholm basins. In the Bornholm Basin, the sediments of significant Cr concentrations cover an area larger than in the Gdańsk Basin. The lowest chromium contents were observed in silt-clay sediments of the Słupsk Furrow, where the value does not exceed 50 mg/kg.

The amount of **copper** in the surface layer of bottom sediments of the southern Baltic Sea is from below 1 mg/kg in sands to 56 mg/kg in silt-clay sediments (Fig. 8.4). The largest areas of the sea bottom are covered with sands containing below 10 mg/kg of copper, only in sands from the peripheries of deep-water basins, copper can occur in the maximum amounts of up to 22 mg/kg. Silty sands and sandy silts mostly contain below 20 mg Cu/kg, attaining the maximum of 28 mg/kg.

The highest copper concentrations were observed in silt-clay sediments – from 40 to 50 mg/kg. Similarly to chromium, the copper contents reveal a high correlation with the grain size of the sediments, and the regression curve is exponential.

The largest areas covered with silt-clay deposits containing the elevated copper contents (from 50 to 56 mg/kg) occur in the Gdańsk Basin. In the Eastern Gotland and Bornholm basins, similar amounts of copper appear only locally, whereas in the Słupsk Furrow, the contents were below 42 mg/kg.

Mercury concentrations in the sediments of the southern Baltic Sea generally range from <0.02 to 0.1 mg/kg. Values exceeding 0.1 mg/kg occur only in small areas of the Bornholm, Gdańsk and Eastern Gotland basins (Fig. 8.5). Sands show mercury contents lower than the detectability limit of the applied analytical method, i.e. <0.02 mg/kg. The content of this metal in silty sands and sandy silts generally is below 0.05 mg/kg. In the surface layer of silt-clay sediments, the mercury concentration varies from 0.05 to 0.10 mg/kg. Higher concentrations (app. 0.2 mg/kg) occur locally in the western part of the Bornholm and Gdańsk basins and at the south-western boundaries of the Eastern Gotland Basin. The mercury contents in sediments show a weak correlation with the grain size, similarly to cadmium. The maximum content of 0.5 mg/kg was locally found on the threshold separating the Gdańsk Basin from the Eastern Gotland Basin, at the dumping sites of World War II ammunition.

The **lead** concentrations in the surface layers of the bottom deposits from the southern Baltic Sea range from <5 mg/kg in sands to 106 mg/kg in silt-clay sands (Fig. 8.6). There is a high correlation between the lead concentrations and the sediment grain size. Sandy deposits contain from <5 to 21 mg/kg of lead. Slightly higher contents were observed only in small sand areas

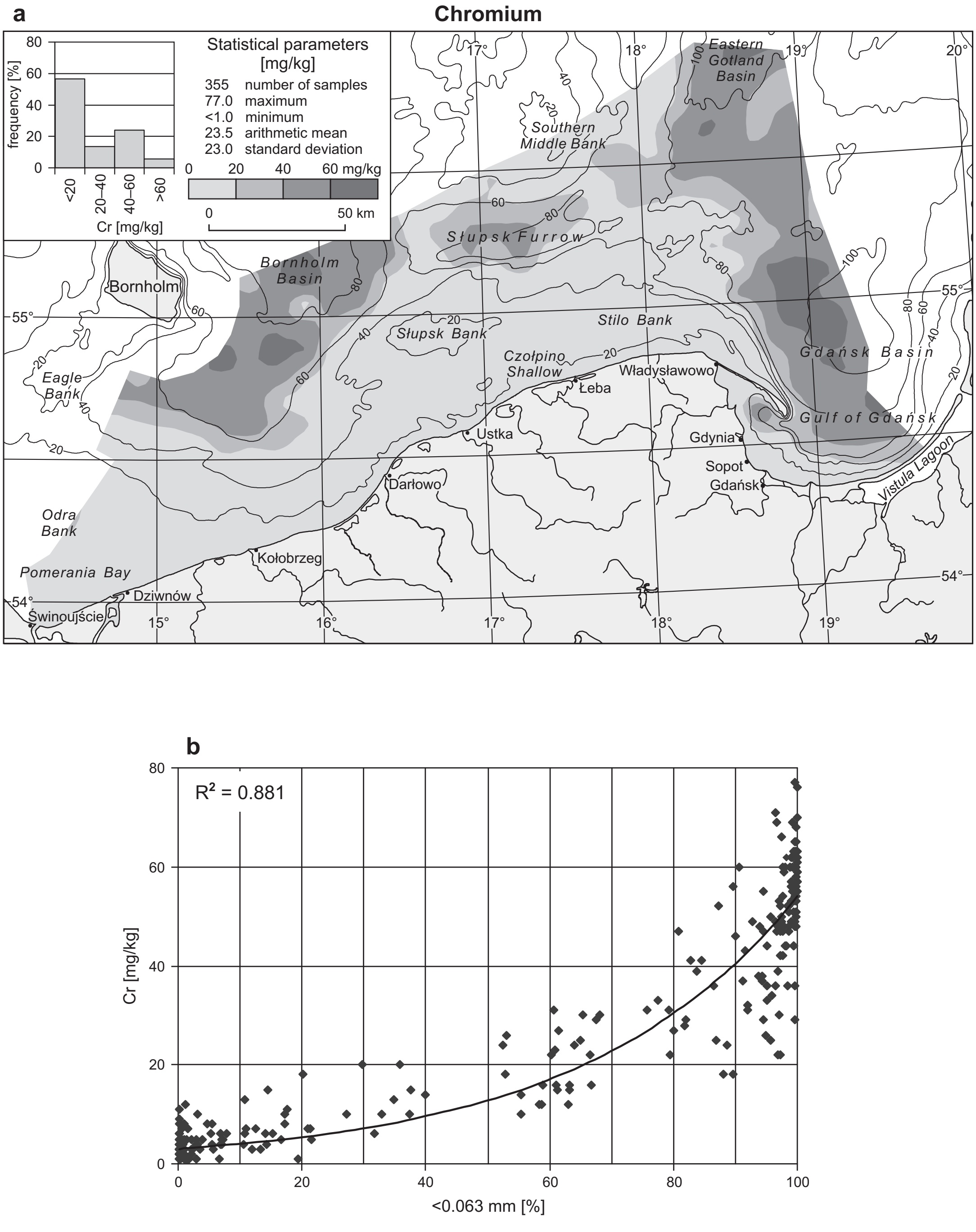


Fig. 8.3. Chromium contents in surface layer of sediments of the southern Baltic Sea (a) and in relation to the proportion of the <0.063 mm fraction (b); as of 1991–1993 (Szczepańska, Uścinowicz, 1994)

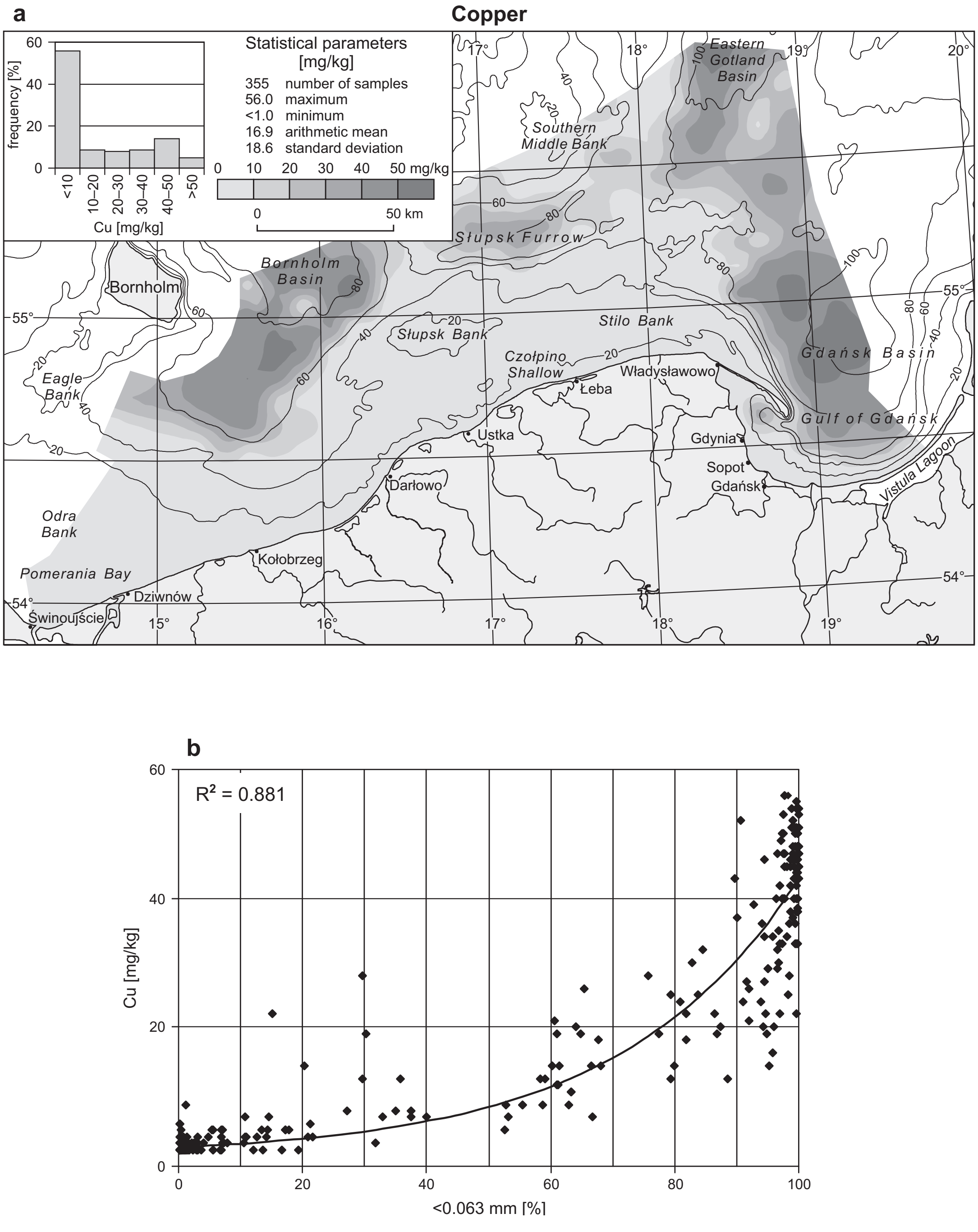


Fig. 8.4. Copper content in surface layer of sediments of the southern Baltic Sea (a) and in relation to the proportion of the <0.063 mm fraction (b); as of 1991–1993 (Szczepańska, Uścinowicz, 1994)

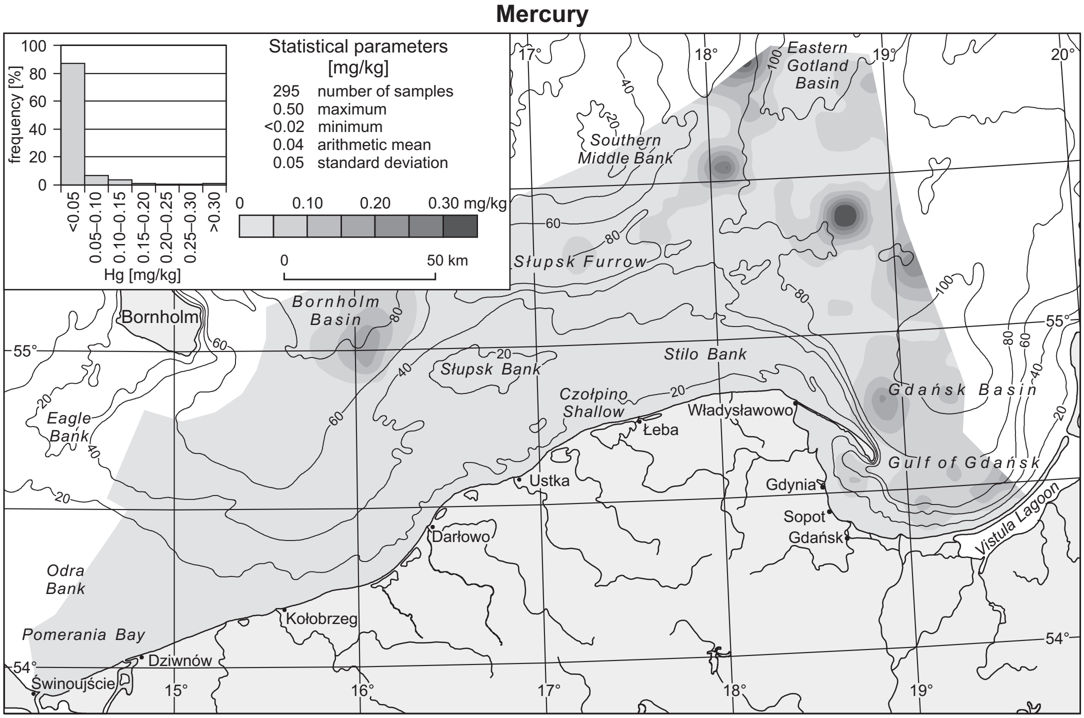


Fig. 8.5. Mercury content in surface layer of sediments of the southern Baltic Sea, as of 1991–1993 (Szczepańska, Uścinowicz, 1994)

near Gdynia, the Słupsk Bank and the Odra Bank. Silty sands and sandy silts contain from 5 to 57 mg/kg of this metal. About 70% of the samples from these sediments contain from 10 to 30 mg Pb/kg of lead.

Silt-clay sediments are marked by a wide range of lead concentration from 8 to 106 mg/kg. Small concentrations, up to 30 mg/kg, were found in the north-western part of the Gdańsk Basin and in the north-eastern part of the Słupsk Furrow. In the other areas of the Baltic Sea, silt-clay sediments contain above 30 mg/kg of lead. In the central parts of all sedimentary basins the values exceed 60 mg/kg. A particularly high level of Pb content was found in the Bornholm Basin (max. 106 mg/kg) and Gdańsk Basin (max. 92 mg/kg).

The **zinc** concentration in sands is from <5 to 50 mg/kg. The values exceeding 20 mg/kg were recorded only in the southern part of the Pomerania Bay and in the western part of the Gulf of Gdańsk. Similar values were also observed in sands at the boundaries of the Bornholm and Gdańsk basins and the Słupsk Furrow. Silty sands and sandy silts contain from 11 to 108 mg/kg Zn with not clearly marked dominant values.

In silt-clay sediments, relatively small amounts of zinc (40–120 mg/kg) occur in the peripheries of deep-water sedimentary basins and locally in sea-floor elevations of the Bornholm Basin. In the Słupsk Furrow, these sediments mostly contain from 100 to 157 mg/kg Zn. Higher zinc concentrations, up to 182 mg/kg, occur in the Eastern Gotland Basin. The highest zinc content was found in the Bornholm and Gdańsk basins, where large parts of the sea bottom are covered with silt-clay sediments containing, respectively, from 160 to 238 mg/kg, and from 160 to 259 mg/kg Zn (Fig. 8.7).

Some other metals that occur in trace amounts in the deposits of the southern Baltic Sea: barium, cobalt, nickel, strontium and vanadium show similar regularities in concentrations in silt-clay deposits of the Bornholm Basin, Słupsk Furrow, Gdańsk Basin (including the Gulf of Gdańsk and Puck Bay), and in the southern part of the Eastern Gotland Basin. Their concentrations,

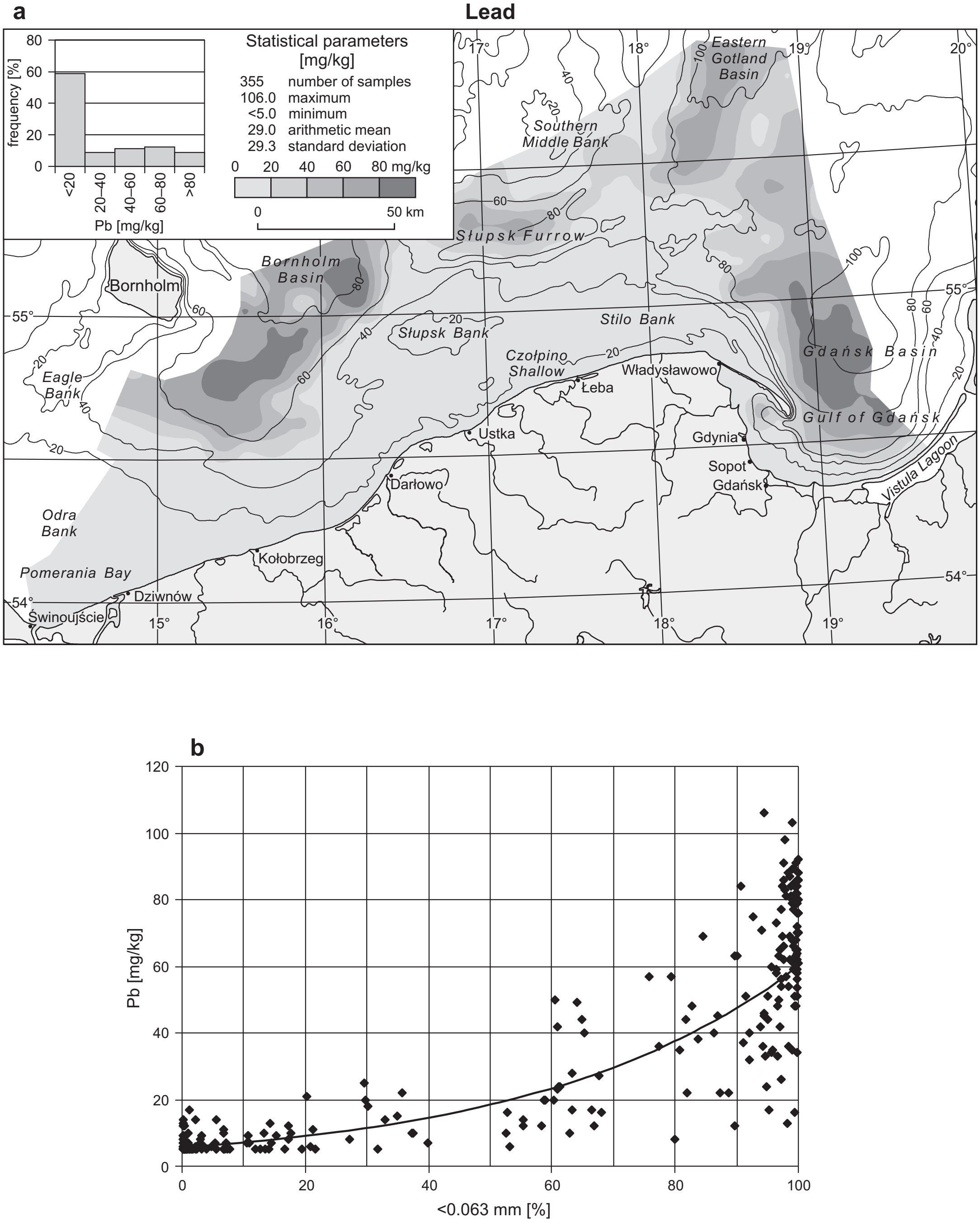


Fig. 8.6. Lead content in surface layer of sediments of the southern Baltic Sea (a) and in relation to the proportion of the <0.063 mm fraction (b); as of 1991–1993 (Szczepańska, Uścinowicz, 1994)

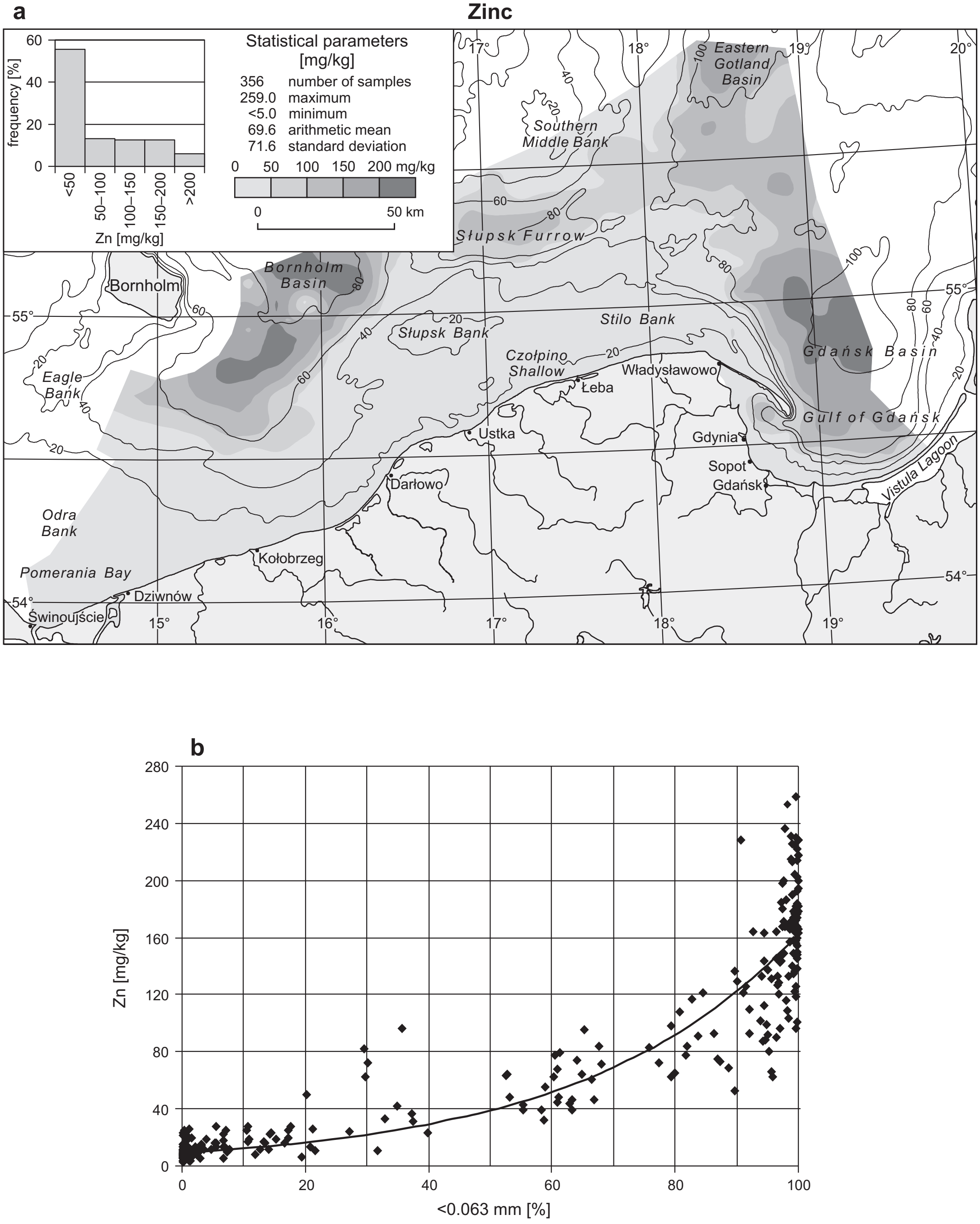


Fig. 8.7. Zinc content in surface layer of sediments of the southern Baltic Sea (a) and in relation to the proportion of the <0.063 mm fraction (b); as of 1991–1993 (Szczepańska, Uścinowicz, 1994)

like other metals, in sand sediments of shallow-water areas are low.

In 94% of the surface sand layer, the **barium** concentrations range from 2 to 50 mg/kg. The contents between 50 and 100 mg Ba/kg dominate in silty sands and sandy silts; however there are locally higher concentrations of up to 510 mg/kg Ba. The surface layer of silt-clay deposits mostly contains from 100 to 200 mg/kg of barium (67% of samples). The maximum of 460 mg/kg was observed in the Gdańsk Basin. Locally, in the Eastern Gotland Basin, the Ba contents are from 250 to 314 mg/kg. The maximum barium content was recorded in silty sands of the transition area between the Gdańsk and Gotland basins. Lower values, from 50 to 150 mg/kg Ba, were recorded in silt-clay sediments of the Słupsk Furrow, Gulf of Gdańsk and Puck Bay.

Sand sediments are characterised by a small **cobalt** content, generally not exceeding 5 mg/kg. The cobalt content in silty sands and sandy silts is also small; in 79% of the cases it does not exceed 10 mg/kg Co with a maximum level of 18 mg/kg. A distinct increase in the Co value occurs in the surface layer of silt-clay sediments, and is usually from 10 to 24 mg/kg. The highest cobalt content, app. 20–24 mg/kg, occurs in large areas of the Bornholm Basin. Individual small areas of surface sediments showing a similar Co concentration occur in the Słupsk Furrow and Gotland Basin. Silt-clay surface layers in the Gulf of Gdańsk and Puck Bay are marked by relatively low cobalt concentrations, below 10 mg/kg.

The **nickel** concentrations in the sediments of the southern Baltic Sea range from 1 mg/kg in sands to 50 mg/kg in silt-clay sediments. The largest sea-bottom areas are covered with sands containing from 1 to 5 mg/kg Ni. Only 2% of sand samples showed a nickel content exceeding 10 mg/kg. The maximum Ni content in sands was 14 mg/kg. Slightly greater variations in the nickel concentration is observed in silty sands and sandy silts: from 3 to 38 mg mg/kg. The content range of 10 to 20 mg/kg Ni is characteristic of 57% of the analysed samples of silty sands and sandy silts. The nickel concentration in the silt-clay deposits is mostly from 30 to 40 mg/kg (47% of all samples). These sediments, containing more Ni ranging from 40 to 50 mg/kg in their surface layer, include the largest areas at the boundary of the Bornholm Basin. The lowest nickel levels were found in silt-clay sediments of the Słupsk Furrow and Puck Bay.

The **strontium** concentrations in the sands of the southern Baltic Sea mostly range from 2 to 10 mg/kg Sr. Locally, in the coastal zone of the Świnoujście and Dziwnów regions and near the lakes of Bukowo and Łebsko, they range from 10 to 20 mg/kg. Elevated levels were observed in sands near Lake Jamno and in the western part of the Gulf of Gdańsk (up to 30 mg/kg Sr), particularly in the roadstead of the Gdynia harbour (up to 50 mg/kg). Silty sands and sandy silts are marked by a wide range of Sr concentrations from 8 to 74 mg/kg, with a clear domination between 20 and 30 mg/kg Sr (45% of samples). Increased strontium contents in silty sands and sandy silts are observed in sea-floor elevations, in the Bornholm Basin and in the eastern part of the Eastern Gotland Basin.

In the surface layer of silt-clay sediments, the strontium concentration varies from 13 to 90 mg/kg. Layers containing below 40 mg/kg Sr were observed in the southern peripheries of the Bornholm and Gdańsk basins, in the northern part of the Słupsk Furrow, as well as in the south-western border of the Eastern Gotland Basin. The most frequently observed concentrations of 40–70 mg/kg Sr were recorded in large sea-bottom areas of the Bornholm, Eastern Gotland and Gdańsk basins. In the Słupsk Furrow, the strontium content generally does not exceed 50 mg/kg. Elevated values of this metal (70–80 mg/kg) were observed in three isolated regions of the Bornholm Basin, in the Puck Bay, in four regions of the Gdańsk Basin and two regions of the Eastern Gotland Basin. The highest strontium concentrations (80–90 mg/kg) were noticed in the western part of the Gdańsk Basin and in the southern part of the Eastern Gotland Basin.

The **vanadium** concentrations in sands of the southern Baltic Sea vary mostly within the range from 1 to 10 mg/kg, reaching the maximum value of 21 mg/kg in only a few locations, far from the coast. In silty sands and sandy silts, the values range from 20 to 40 mg/kg (54% of samples). Higher values, up to 80 mg/kg, were found in 28% of the samples. Silt-clay deposits contain 9 to 140 mg/kg V. Low levels of vanadium (<60 mg/kg) were observed in the southern parts of the Bornholm and Gdańsk basins, especially in the Gulf of Gdańsk and Słupsk Furrow. The highest amounts of vanadium (80 to 108 mg/kg) accumulated in the surface layer of silt-clay sediments in the Bornholm Basin, below the isobath of 70 m. The maximum concentration of this metal, 140 mg/kg, was found in the western part of the Gdańsk Basin. However, it occurs locally, only in a small area of the sea bottom. In the other parts of the Gdańsk Basin, the vanadium content does not exceed 80 mg/kg.

The Gulf of Gdańsk

The contents of trace elements in the surface sediments of the western part of the Gulf of Gdańsk (Fig. 8.8) are characterised based on materials collected in 2005–2006 within the frame of the project "The Recognition and Visualisation of the Geological Structure of the Gulf of Gdańsk for the Needs of Natural Resources Management" (Uścinowicz *et al*., 2008).

In the western part of the Gulf of Gdańsk, sediment samples were taken with a box-corer type sampler over a grid measuring 3×3 km. Owing to the specificity of the area and its natural values, survey stations in the Puck Lagoon were scattered across a 1.5×1.5 km grid. The samples from the sea bottom of the Puck Lagoon were taken by a Kajak-type gravity core sampler, operated by a scuba diver. The analyses of metal contents in the surface layer (0–2 cm) of the sea bottom sediments were made by the ICP-OES method, after decomposing the bottom samples using aqua regia. The mercury content was determined by the method of "cold vapour" atomic absorption spectrometry (CVAAS).

Arsenic occurs in the surface sediment layer of the western part of the Gulf of Gdańsk and its concentration is 5 to 13 mg/kg. In sand sediments, the As concentrations are below 5 mg/kg, i.e. below the determination limit for the analytical method applied. In the surface layer of sandy silts and silty sands, the mean arsenic content is 3.05 mg/kg, maximally of 11 mg/kg. In silt-clay sediments, the mean content of this element is around 10.17 mg/kg, with the maximum of 12 mg/kg.

Cadmium occurs in the surface sediment layer of the western part of the Gulf of Gdańsk in the concentrations range from below 1.0 to 2 mg/kg. In most areas of the sea bottom, the cadmium concentration does not exceed 1 mg/kg. A slightly higher Cd content was recorded in sand and silty sands on the outskirts of the Vistula mouth and in the silt-clay sediments of the Puck Bay and Gulf of Gdańsk. The highest levels of this element (2 mg/kg) occur in the north-eastern part of the Puck Bay (app. 15 km NE of Gdynia) and in the Jama Kuźnicka (Kuźnicka Pit) in the Puck Lagoon.

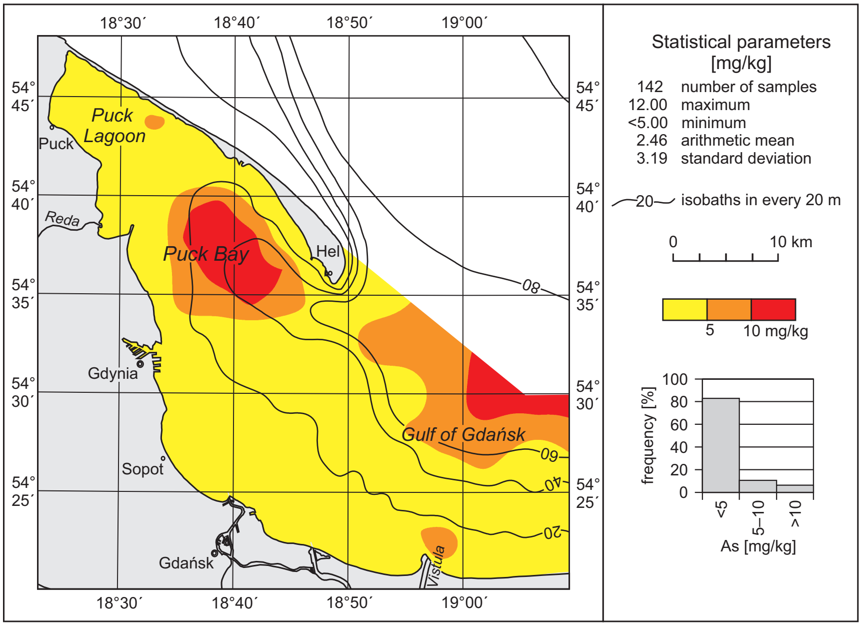
Chromium occurs in the sea bottom sediments of the Gulf of Gdańsk and Puck Bay in quite a wide range, from below 1.0 to 63 mg/kg. Silty sands and sandy silts show a wide range of the chromium contents from 3 to 56 mg/kg, with the mean value of 15.95 mg/kg. The highest mean chromium content (40.33 mg/kg) is observed in silt-clay sediments. Its maximum concentrations (like for cadmium) were noticed in mud samples from the Puck Bay. Silt-clay sediments of the southern part of the Gulf of Gdańsk and Jama Kuźnicka (Puck Lagoon) contain from 20 to 40 mg/kg of chromium. Similar concentrations Cr occur in silty sands near the Vistula mouth. Sands cover most of the Gulf of Gdańsk (included into the survey). In sand sediments, the chromium concentrations are from 1.0 to 10 mg/kg, with the mean content of 4.23 mg/kg.

The surface sediment layer of the Gulf of Gdańsk contains from below 1.0 to 43 mg/kg of **copper**, with the mean content of 8.49 mg/kg. Over most of the bottom area, the copper concentration does not exceed 10 mg/kg. Elevated copper contents were observed in silt-clay sediments in the southern part of the Gulf of Gdańsk, Puck Bay, in Jama Kuźnicka (the Puck Lagoon), and in silty sands on the outskirts of the Vistula mouth. The maximum concentration of Cu (43 mg/kg) was observed in the Puck Bay, similarly to Cd and Cr.

Mercury occurs in the sediments of the Puck Bay and Gulf of Gdańsk at the concentration levels varying from below 0.02 to 0.35 mg/kg. In sandy sediments, the content of this element is very small (<0.05 mg/kg), only locally it can reach the value of 0.1 mg/kg. The highest mercury concentrations are observed in silt-clay deposits of the eastern part of the Puck Bay and on the outskirts of the Vistula mouth. The mean value of mercury in silt-clay sediments is 0.19 mg/kg.

Lead is an element occurring in the sediments of the Gulf of Gdańsk and Puck Bay with the concentrations ranging from below 5 to 56 mg/kg. Sandy sediments contain up to 13 mg/kg of lead. In most areas of the sea bottom covered with sand sediments, this element does not exceed 5 mg/kg. Silty sands and sandy silts are marked by a wide range of lead contents up to 52 mg/kg. In silt-clay sediments, the concentrations

Arsenic



Cadmium

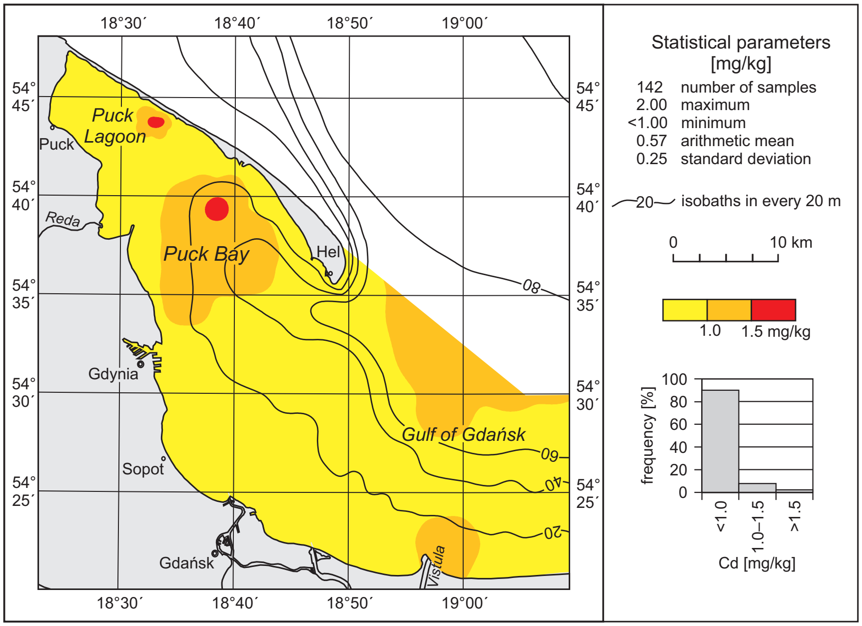
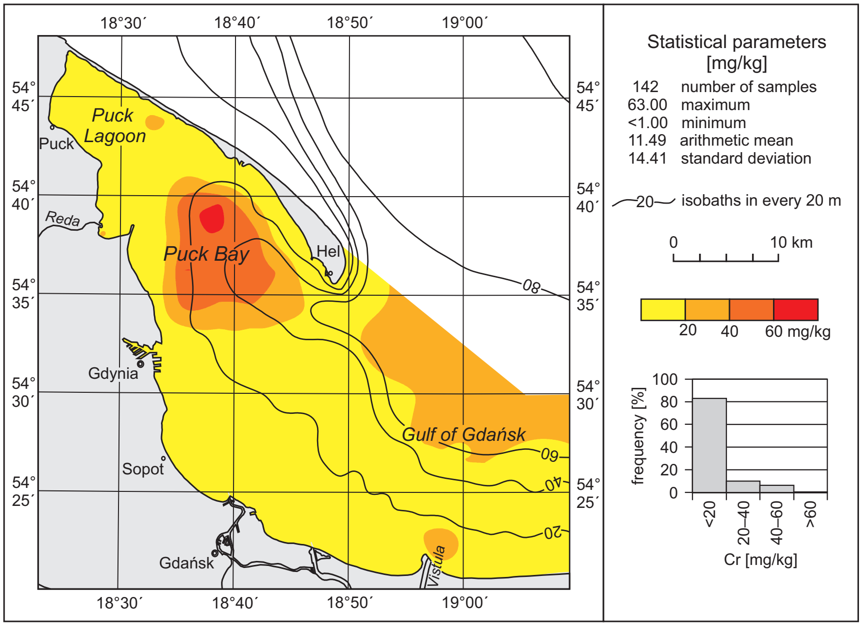


Fig. 8.8. Contents of trace elements (As, Cd, Cr, Cu, Hg, Pb, and Zn) in surface layer of sediments of the western part of the Gulf of Gdańsk, as of 2005–2006 (Uścinowicz *et al.*, 2008)

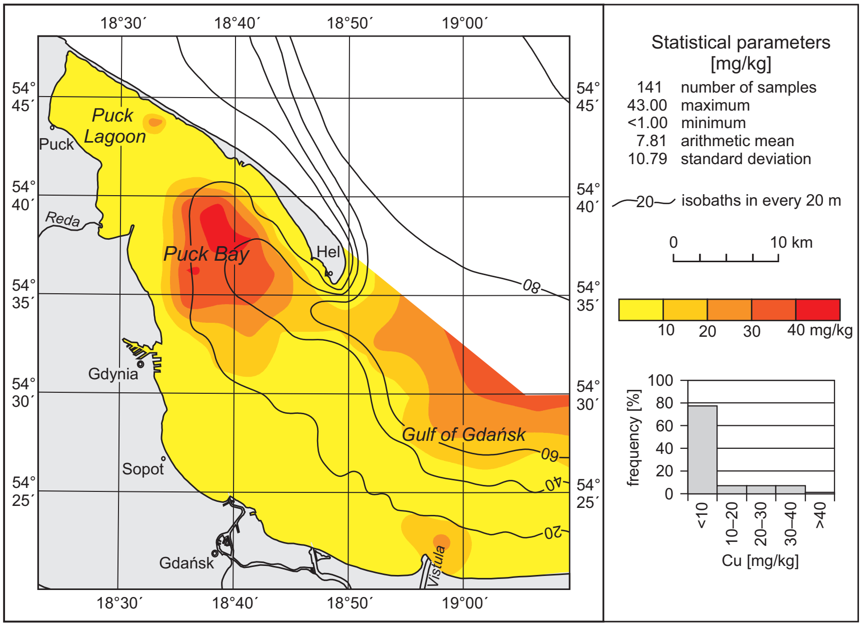
Chromium



Statistical parameters [mg/kg]

142	number of samples
63.00	maximum
<1.00	minimum
11.49	arithmetic mean
14.41	standard deviation

Copper

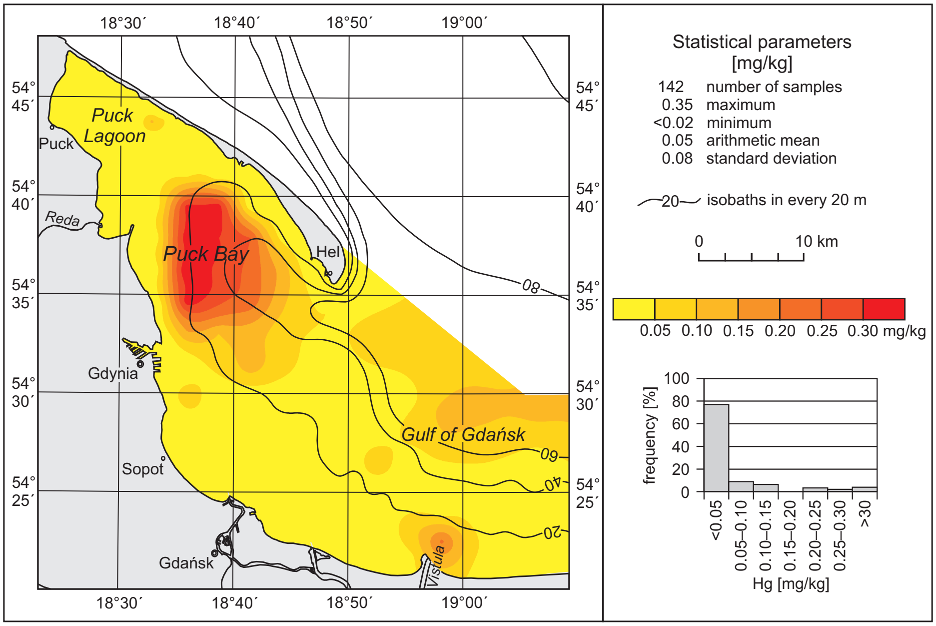


Statistical parameters [mg/kg]

141	number of samples
43.00	maximum
<1.00	minimum
7.81	arithmetic mean
10.79	standard deviation

Fig. 8.8. Continued

Mercury



Lead

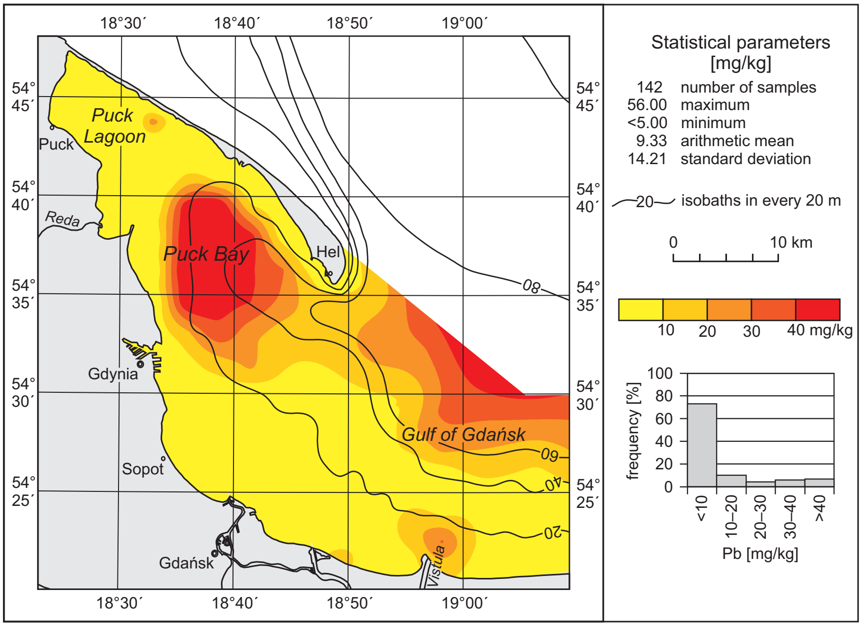


Fig. 8.8. Continued

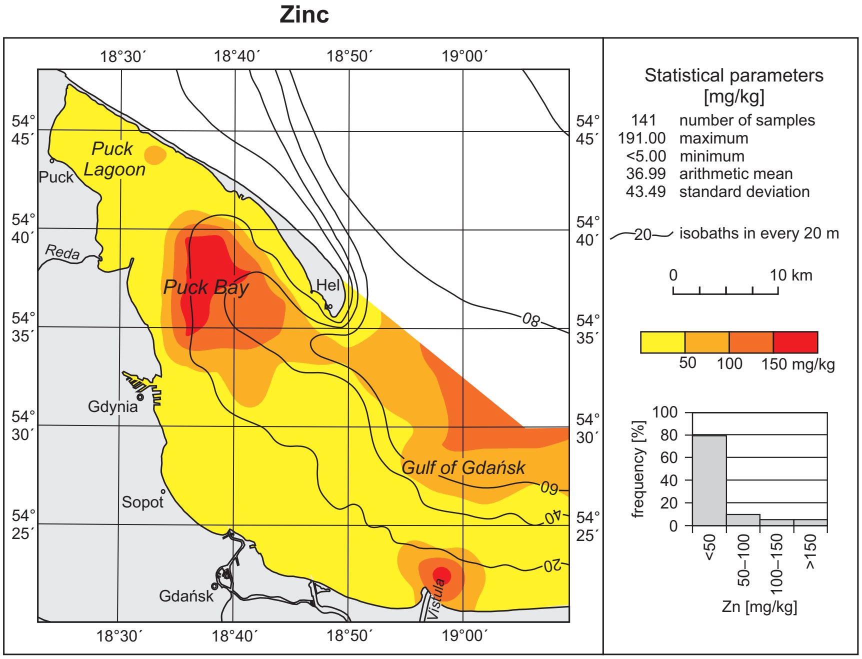


Fig. 8.8. Continued

of this element vary from 11 to 56 mg/kg. The highest levels of lead (40–56 mg/kg) were found in the central part of the Puck Bay.

The **zinc** concentrations in the sediments of the Gulf of Gdańsk and Puck Bay range from 3 to 191 mg/kg (mean 40 mg/kg). Sand sediments of the two bays show a low content of this element from 3 to 67 mg/kg (mean 13.34 mg/kg). The highest levels of zinc content are associated with silt-clay sediments, and the average concentration is 119.89 mg/kg. Especially large zinc contents were observed in the Puck Bay and on the outskirts of the Vistula mouth. Other metals also show elevated concentration levels in sediments bordering directly on the area of the Vistula River mouth; however, such different concentrations are most noticeable for zinc.

Some other trace elements: bar, cobalt, nickel, strontium and vanadium, show similar spatial distribution in the sediments of the Gulf of Gdańsk and their contents are elevated in silt-clay sediments of the Puck Bay, on the outskirts of the Vistula mouth and in the Jama Kuźnicka of the Puck Lagoon.

The **barium** concentration in the surface sediment layer of the Gulf of Gdańsk and Puck Bay ranges from 7 to 93 mg/kg (mean 29.99 mg/kg), whereas in the surface layer of sands – mostly from 7 to 45 mg/kg (mean 16.93 mg/kg). The highest content of 60–93 mg/kg (mean 72.50 mg/kg) was observed in silt-clay sediments.

The maximum **cobalt** concentration is 8 mg/kg (Vistula River mouth). The largest mean content of this element was recorded in silt-clay sediments (5.61 mg/kg). Sands are characterised by small cobalt content, not exceeding 3 mg/kg and mostly below 1 mg/kg.

The **nickel** concentration in the sediments of the Gulf of Gdańsk and Puck Bay, reaches the maximum level of 33 mg/kg (mean 7.19 mg/kg). Sands of the coastal zone contain up to 11 mg Ni/kg. Wide areas of the sea bottom are covered with silt-clay sediments containing from 17 to 33 mg/kg of nickel.

Sediments of the Gulf of Gdańsk and Puck Bay contain 6 to 119 mg/kg (mean 24.73 mg/kg) of **strontium**. The smallest concentrations of this element occur in sands, from 6 to 77 mg/kg. Silty sands and sandy silts show a wide range of strontium contents from 12 to 119 mg/kg. The highest mean strontium content of 50.72 mg/kg is observed in silt-clay sediments, but in similar sediments near the Vistula River mouth, it exceeds 100 mg/kg.

The **vanadium** concentration in sediments of the Gulf of Gdańsk ranges from 1 to 47 mg/kg (mean 11.39 mg/kg). The largest amounts of this metal occur in silt-clay sediments, from 25 to 47 mg/kg (mean 34 mg/kg). The lowest vanadium concentrations are characteristic of sands: from 1 to 16 mg/kg (mean 4.57 mg/kg).

Owing to human activities, the increased inflow of metals affects the contents of metals in the surface sediment layer. However, analysing the spatial distribution of metal contents across the whole Baltic Sea, we should take into account the variable sedimentary conditions that occur in its southern part, or in the Gulf of Gdańsk.

Apart from the anthropogenous factors, even if we consider only silt-clay sediments where most metals accumulate, the sediments may be deposited at the same time in different regions of the sea, under different redox conditions and, moreover, they may contain silt and clay fractions in different proportions and a variable content of organic matter.

8.2. Trace Elements in Vertical Sections of Sediments

The Baltic Sea

In many regions of the Baltic Sea, the surface layer sediments, compared to the sediments deposited in pre-industrial times, contain higher concentrations of trace elements. In order to determine the contamination ratio of sediments, we have to recognise the natural chemical composition of sediments from the period before the industrial development, in other words we should determine the so-called geochemical background. The results of the sediment core analyses published by different authors suggest a distinct elevation of metal contents in the surface layer of sea bottom sediments (to 10–15 cm) as compared to the layers deposited at greater depths (e.g. Szefer, Skwarzec, 1988; Brügman, Lange, 1990; Hallberg, 1991; Szefer *et al*., 1993, 1995, 1998; Paetzel *et al*., 1994; Szczepańska, Uścinowicz, 1994; Leivuori, Niemistö, 1995; Borg, Jonsson, 1996; Neumann *et al*., 1996; Leivuori, 1998; Vallius, 1999a, b; Vallius, Leivuori, 1999; Sternbeck *el al*., 2000).

The enrichment of sediments with heavy metals and other chemical components may result from either their natural geochemical properties or an anthropogenous effect. The estimation of the contamination ratio is possible by comparing the content of a given element with its concentration in the reference layer, i.e. with the geochemical background. To indicate the location of the geochemical background layer, not contaminated with anthropogenous effects, many natural factors should be considered: sedimentation rate, the amount of sediment mixing owing to bioturbation and the effect of bottom sea currents, and the rate and extent of pore water diffusion. Natural depositional processes can be disturbed by human activities: fishing, sailing, telecommunication facilities, pipelines, etc.

It is not easy to interpret the metal accumulation history in sediments. It is a multi-sided problem, but it seems that one of the main factors that affects metal concentrations in sediments are changes in the redox potential dependent on the influx of aerated waters after a stagnation period. These alterations recorded in the bottom waters of the Baltic Sea are natural events occurring in the present and in the past. A restricted water exchange in the Baltic Sea and its considerable thermohaline stratification generate more or less long-lasting periods of oxygen deficits in some deep-water basins of the Baltic Sea. Anaerobic conditions are observed periodically (from a few to about fifteen weeks), also in the shallow-water part of the Belt Sea below a depth of 20 m. In anaerobic bottom waters, the concentrations of elements, such as Fe(II), Mn(II), Cr, As, and Co of sedimentary origin, are increased, whereas the concentration levels of Cu, Cd and, to a lesser extent, Pb and Zn – are decreased. The inflow of aerated and saline water from the North Sea results in oxidising Fe(II) and Mn(II) to hydroxides of Fe(III) and Mn(IV), and in settling precipitated complex compounds on the sea bottom, together with other trace metals (Moenke-Blankenburg *et al*., 1989).

All these natural conditions of changes in the contents of metals should be taken into account while defining the geochemical background, which may differ depending on the region of the Baltic Sea. Silt-clay sediments can be deposited in different parts of the Baltic Sea under different redox conditions, and can also contain variable proportions of silt and clay fractions with diverse contents of organic matter. Besides, the mineral composition of soils and rocks in the Baltic Sea catchment area is variable, which can affect natural metal contents in the sea-bottom sediments.

The maximum concentrations of individual trace elements and some other pollutants, e.g.: PAH and PCB, in different regions of the Baltic Sea, occur at different depths below the sea bottom. This is caused by different factors. The first one is the different history of individual regions of the Baltic Sea – different substances flowed into different parts of the sea at different times, which resulted from the non-uniform economic development in the Baltic Sea catchment area. The other factor is a variable sediment deposition rate. The surface layer predominantly shows slightly lower concentrations of trace elements compared to the maximum values; however, they are still higher than the concentrations typical of the geochemical background. One of the reasons why the contents of trace elements were lower in the surface layer is the reduction in the inflow of contaminants to the Baltic Sea over the last few decades.

The variability in concentrations of arsenic, cadmium, chromium, copper, mercury, lead and zinc is presented in Figure 8.9.

Variable **arsenic** contents in core sections from the main sedimentary basins of the Baltic Sea prove the general regularities known from literature. A clear increase in this element in all regions of the sea is observed beneath the depth of approximately 15 cm below the sea bottom. Excluding the station 167 (Bornholm Basin), the arsenic content at the depth of 20–25 cm under the sea bottom is stable and the concentrations can be considered natural, i.e. they originate in the pre-industrial epoch and are typical of the geochemical background. Arsenic concentrations typical of the geochemical background in the Baltic Sea sediments are within the range of 5 to 20 mg/kg. The lowest values of the geochemical background of arsenic (<10 mg/kg) occurs in the Gulf of Riga, in the West Gotland Basin and in the Gulf of Finland. An abnormal variability of arsenic concentrations in the vertical section of a core acquired from the Bornholm Basin (station 167) may originate from chemical ammunition that sank in this basin.

The maximum arsenic concentrations in different regions of the Baltic Sea occur at different depths under the sea bottom. The highest concentrations, reaching up to 383 mg/kg in the 4–5 cm sediment layer below the sea bottom, were observed in the Bothnian Bay (station 193). Slightly lower values (14 mg/kg in the 3–4 cm layer) were found in the northern part of the Bothnian Sea (station 192). In the East Gotland Basin, the maximum arsenic contents occur at the greatest depths under the sea bottom (station 171, 33–44 mg/kg at the depth of 8 to 14 cm). The maxima that occur closest to the bottom surface layer are observed in the southern part of the Bothnian Sea (55 mg/kg at the depth of 3–4 cm) and in the North Central Basin (station 182, 30 mg/kg at the depth of 1–2 cm).

The variations of **cadmium** content in the core sections from the main sedimentary basins of the Baltic Sea also stay in accordance with literature data. Elevated cadmium concentrations occur in all regions, from the depth of app. 15 cm under the sea bottom downwards. The content of this metal clearly increases from the depth of 15 cm below the sea bottom in the Gulf of Finland (station 182) and from app. 10 cm in the Gdańsk Basin (station 170). The lowest cadmium contents (<0.5 mg/kg) occur at the depth of 17–25 cm in the western and southern Baltic Sea in the Lubeck Bay (station 160), Bornholm Basin (station 167), Gdańsk Basin (station 170), Western Gotland Basin (station 178), Gulf of Finland (station 82), Bothnian Sea (station 190) and Bothnian Bay (station 193). Slightly higher cadmium contents, but still below 1 mg/kg, are characteristic of the geochemical background in the gulfs of Riga and Finland and in the Bothnian Sea (stations 174, 182, 193). The cadmium concentrations at the depth of 18–25 cm under the sea bottom, typical of silt-clay sediments in the Baltic Sea, are lower than 1 mg/kg and are probably natural values that correspond to the geochemical background.

The highest cadmium concentrations (up to 12.2 mg/kg) occur in the West Gotland Basin at the depth of 7–8 cm under the sea bottom, and in the East Gotland Basin at the depth of 8–14 cm (station 171, 9.54–9.56 mg/kg).

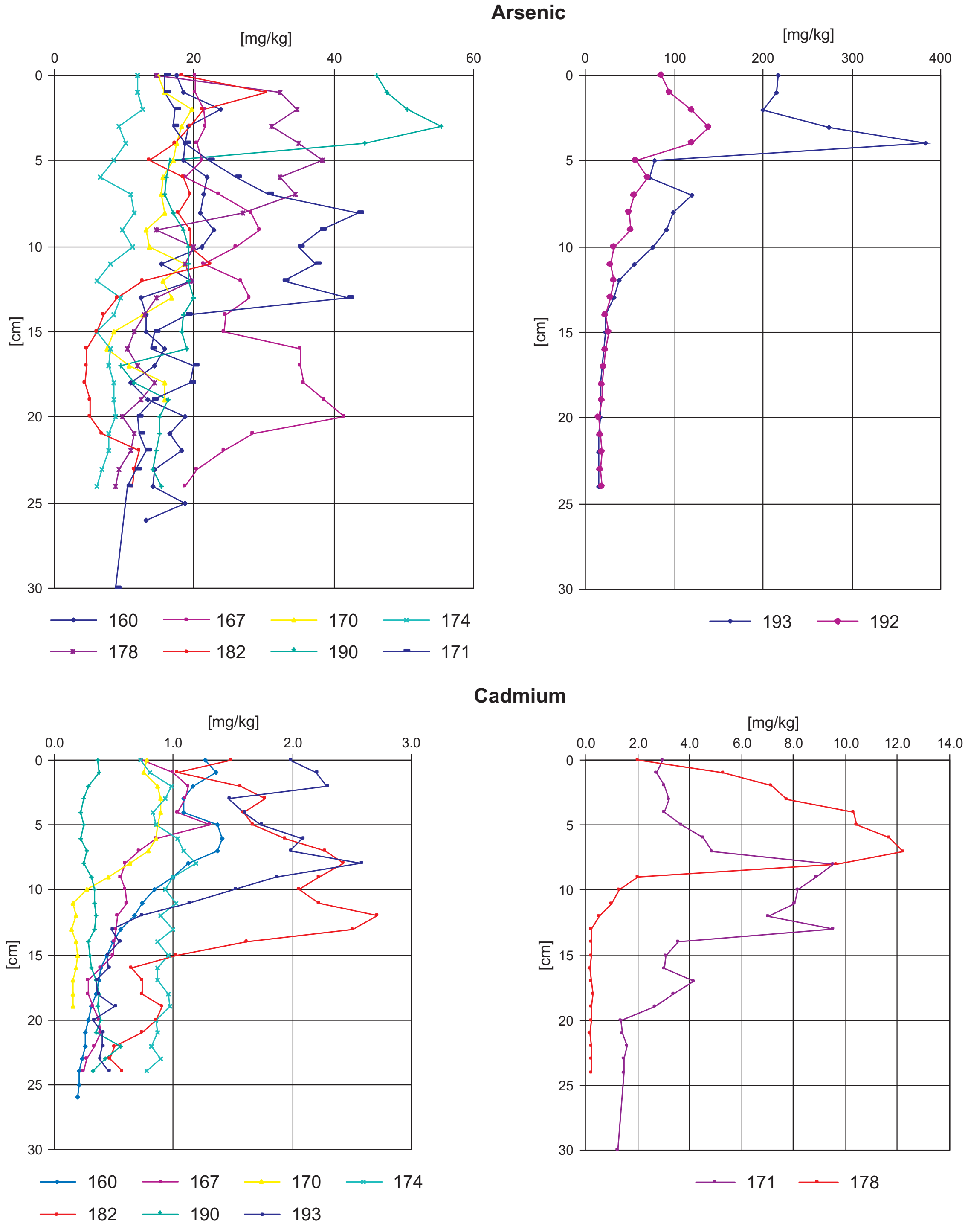


Fig. 8.9. Variability of trace elements in the vertical section of silt-clay sediments in different regions of the Baltic Sea (acc. to Perttilä, ed., 2003); for location of survey stations see Fig. 1.1

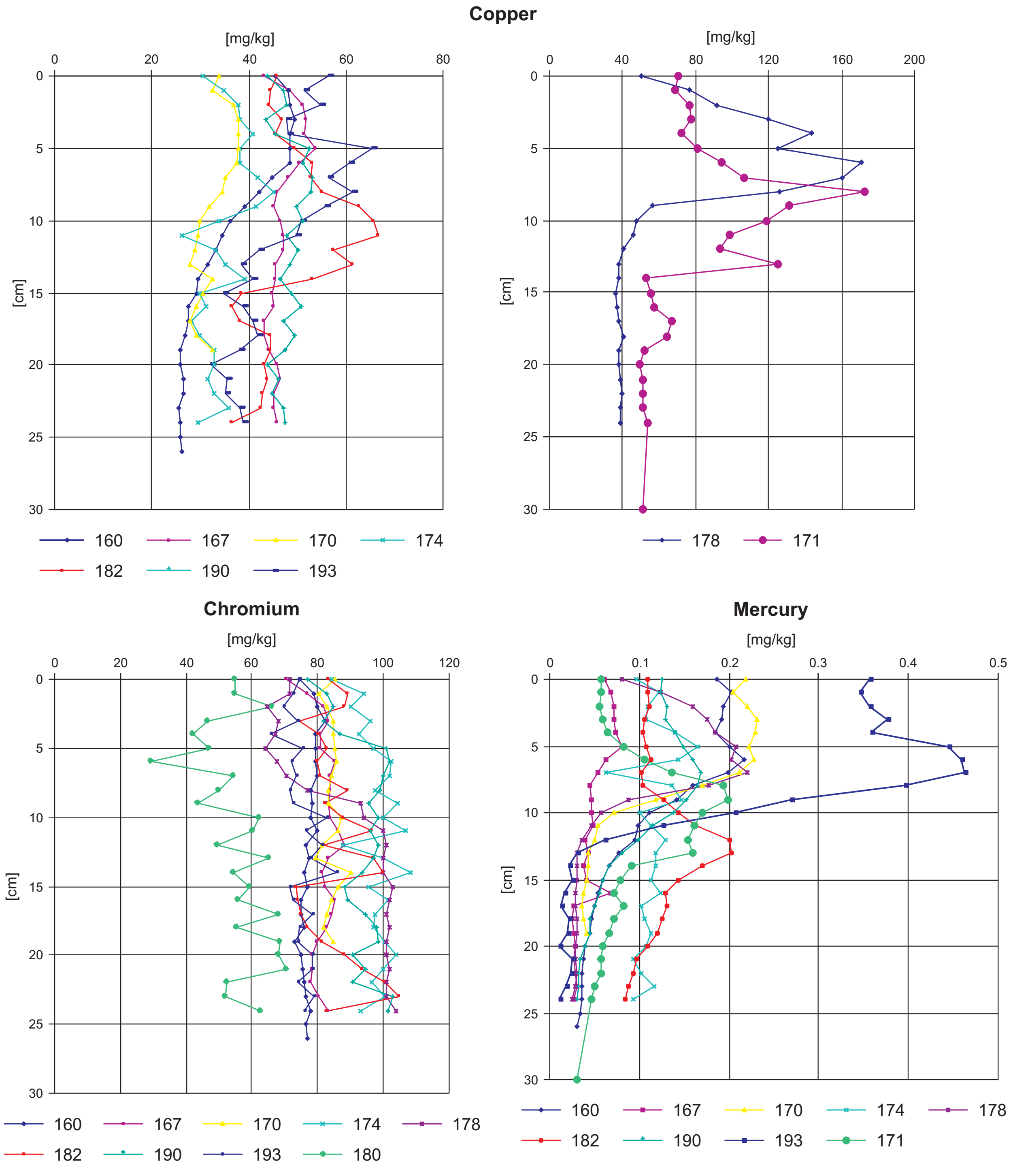
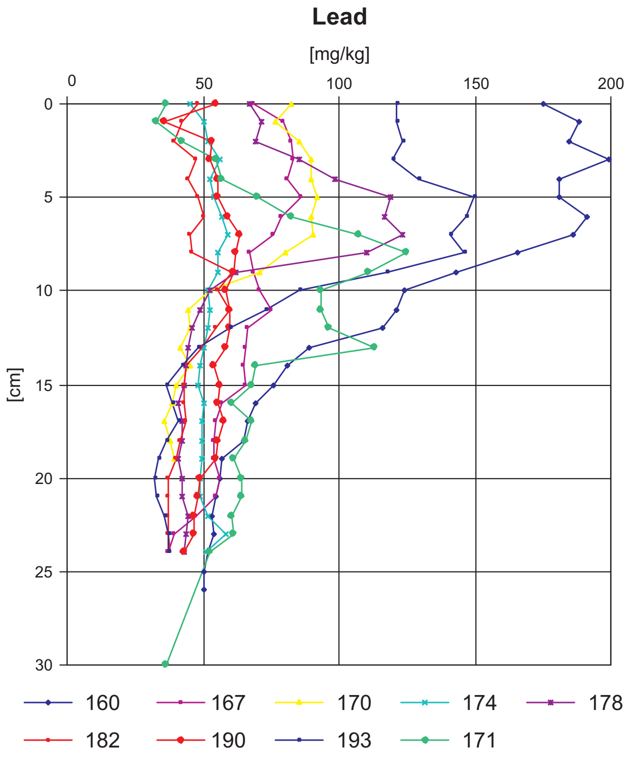


Fig. 8.9. Continued



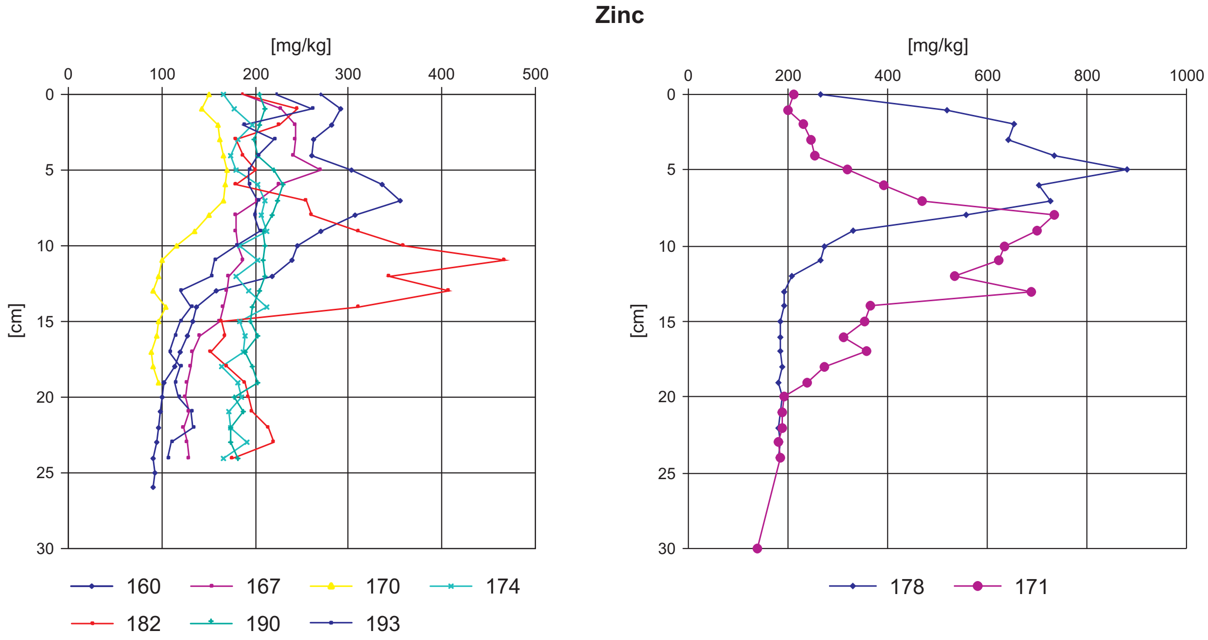


Fig. 8.9. Continued

Changes in the **chromium** concentration in the tested cores are irregular and poorly diversified. Lower core segments (20–25 cm) contain from 52 to 104 mg/kg of chromium. Higher values, 93–104 mg/kg, occur in the gulfs of Riga and Finland (stations 174 and 182), in the West Gotland Basin (station 178) and in the southern part of the Bothnian Sea (station 190). Lower chromium concentrations, 52–85 mg/kg, in the lower parts of the cores were found in the North Central Basin (station 180), Mecklenburg Bay (station 160), Bornholm Basin (station 167), Gdańsk Basin (station 170) and Bothnian Bay (station 193). The chromium content in the surface layer of bottom sediments, contrary to other metals, does not increase, and is usually lower than the values typical of the geochemical background.

The **copper** content shows variability in the core sections, typical of most metals. The lowest values occur in the bottom parts of the cores and range from 26 mg/kg in the Mecklenburg Bay (station 160) to 54 mg/kg in the East Gotland Basin (station 171). The copper concentrations increase from the level of 10–15 cm upwards and attain the highest values 12 to 5 cm under the sea bottom, and then the values gradually decrease towards the sea bottom.

It can be assumed that natural concentrations of copper (geochemical background), typical of silt-clay sediments, range from 25 to 50 mg/kg. However, analysing the effect of anthropogenous contaminants on the copper contents in the Baltic Sea sediments, we should take into account regional variations in the geochemical background values. For instance, in the Mecklenburg Bay (station 160), the geochemical background for copper is 26–27 mg/kg, the maximum value (50 mg/kg) occurs 3–4 cm below the sea bottom, but on the sea bottom (layer 0–1 cm), the copper content is 46 mg/kg, proving the contamination of the surface sediment layer. In the Gdańsk Basin (station 170), the Cu concentration at the depth of 19–20 cm under the sea bottom (geochemical background) is 33 mg/kg, the maximum values at the depth of 3–7 cm are 38 mg/kg, decreasing at the sea bottom (0–1 cm) to 34 mg/kg. In the Western and Eastern Gotland basins, the geochemical background values at the depth of 20–25 cm range from 38 to 54 mg/kg and are higher than the concentrations in the upper, contaminated parts of the sediment cores from the Gdańsk Basin, Gulf of Riga (station 174) and Mecklenburg Bay.

The curves showing changes in the **mercury** contents in the vertical section of sea-bottom sediments is similar to those of other metals (except for chromium). The lowest values of Hg concentrations occur in the bottom parts of the sediment cores, but from the depth of 10–15 cm, the contents of this element start to increase distinctly. The maxima in the mercury contents occur mostly at the depth of 5–7 cm and the values range from 0.08 mg/kg in the Bornholm Basin (station 167) to 0.46 mg/kg in the Bothnian Bay (station 182). A small decrease in the concentration is observed in the surface layer.

In the lower segments of the sediment cores (20–25 cm), the mercury concentrations do not exceed 0.05 mg/kg. The exception is sediment cores taken in the gulfs of Riga (station 174) and Finland (station 182), where the mercury contents at this level are from 0.08 to 0.11 mg/kg. It can be assumed that the geochemical background values for Hg are generally lower than 0.05 mg/kg and reach a maximum of 0.1 mg/kg.

The variability in **lead** contents in silt-clay sediments of the Baltic Sea at the depth of 20–25 cm under the sea bottom is small and ranges from 32–37 mg/kg in the Bothnian Bay (station 193), to 37–56 mg/kg in the Mecklenburg Bay (station 160) and Bornholm Basin (station 167), reaching 53–64 mg/kg in the Eastern Gotland Basin (station 171). Since the increase in lead contents first started in the Mecklenburg Bay, and is recorded at app. 20 cm depth, it can be assumed that natural lead contents do not exceed 60 mg/kg in silt-clay sediments of the Baltic Sea. In the gulfs of Riga and Finland, as well as in the southern part of the Bothnian Sea, there are slight changes in Pb concentrations in the vertical sediment sections. In the other parts of the Baltic Sea, there is a variable increase in lead contents towards the surface of the sea-bottom sediments. The maximum lead like in case of mercury strongly differ between the individual sedimentary basins: in the Bothnian Bay – 150 mg/kg (station 193), in the Mecklenburg near Lübeck Bay – 200 mg/kg (station 160).

Apart from mercury, the changes in **zinc** contents in the sediment cores best reflect both regional differences in the history of Baltic Sea pollution by metals and in the natural contents of this metal in sediments. In the sediment layer from the depth of 20–25 cm below the sea bottom, the zinc content in the Mecklenburg Bay (station 160), Bornholm and Gdańsk basins (stations 167 and

170), as well as in the Bothnian Bay (station 193) ranges between 91 and 134 mg/kg. In the Gulf of Riga (station 174), Eastern (station 171) and Western Gotland basins (station 178), Gulf of Finland (station 182) and in the southern part of the Bothnian Sea (station 190), the Zn contents are from 166 to 200 mg/kg.

The most polluted with zinc are sediments in the Western (880 mg/kg in horizon of 5–6 cm) and Eastern Gotland basins (688–734 mg/kg in horizon of 8–14 cm), the Gulf of Finland (467 mg/kg in horizon 11–12 cm), and the Mecklenburg Bay near Lübeck (356 mg/kg in horizon 7–8 cm). Similarly to copper and mercury, the zinc content in the contaminated surface layer sediments in some regions of the Baltic Sea is lower than the values of geochemical background in other regions. For instance, the concentrations of zinc in the surface layer of the bottom sediments in the Gdańsk Basin and the Gulf of Riga are at the level of geochemical background in the Eastern and Western Gotland basins.

More detailed research on the natural contents of metals in silt-clay bottom sediments in the southern part of the Baltic Proper revealed their possible considerable differentiation inside particular sedimentary basins. The survey made in 1991–1994 by the Polish Geological Institute included the Polish Exclusive Economic Zone (30,532 km^2). Samples of sea bottom sediments were taken from 368 survey stations. The contents of metals were determined for 63 core samples of silt-clay sediments from the 18–20 cm depth layer under the sea bottom (Table 8.3).

The mean contents of metals in the 18–20 cm layer of silt-clay sediments from the southern Baltic Sea are convergent with the values of geochemical background from the other regions of the sea discussed earlier. Standard deviations, however, show that the distribution of the natural contents of metals in the tested sediments can be slightly greater. It may result from local variability in chemical composition of the sediments transported into a given sedimentary basin, variations in hydrodynamic conditions inducing differences in sediment grain sizes, as well as from hydrochemical conditions (i.e. diverse redox conditions).

The Gdańsk Basin

Geochemical surveys, especially on metal contents, were carried out in the Gdańsk Basin in 1993–1994 within the framework of the Dutch-Polish Research Project (Appendix No. 2) and in 1997–1998 under the Polish-Lithuanian-Dutch-British Project (Appendix 3). Both

Table 8.3

Mean contents (numerator) and standard deviation of metals (denominator) in silt-clay sediments of the southern Baltic Sea; layer 18–20 cm (digested in HNO$_3$ 1:1, determined by ICP method; after Szczepańska and Uścinowicz, 1994, supplemented)

Region (number of analyses)	As	Cd	Cr	Cu	Hg	Pb	Zn
	[mg/kg]						
Bornholm Basin (26)	$\frac{21.9}{10.7}$	$\frac{< 1.0}{–}$	$\frac{57.1}{9.4}$	$\frac{39.2}{4.6}$	$\frac{0.02}{0.01}$	$\frac{43.6}{11.4}$	$\frac{110.0}{22.6}$
Słupsk Furrow (5)	$\frac{8.8}{3.8}$	$\frac{< 1.0}{–}$	$\frac{39.6}{5.4}$	$\frac{29.2}{4.2}$	$\frac{0.03}{0.01}$	$\frac{36.4}{6.2}$	$\frac{79.6}{12.7}$
Gotland Basin (10)	$\frac{14.4}{6.8}$	$\frac{< 1.0}{–}$	$\frac{52.7}{11.8}$	$\frac{34.5}{9.7}$	$\frac{0.04}{0.06}$	$\frac{36.1}{14.1}$	$\frac{98.2}{28.2}$
Gdańsk Basin (22)	$\frac{16.5}{7.0}$	$\frac{< 1.0}{–}$	$\frac{60.5}{14.4}$	$\frac{37.1}{11.1}$	$\frac{0.04}{0.02}$	$\frac{54.2}{23.8}$	$\frac{122.0}{43.1}$

these projects dealt with the variability of metal contents in sediments with reference to the differentiation in sedimentary environments and the ditribution of deposits in the basin.

In the Gdańsk Basin, silt-clay sediments occur in three sedimentary environments connected with a stable density stratification of water: above the pycnocline, at the pycnocline/sea bottom contact, and below the pycnocline. In the Gdańsk Basin, the pycnocline occurs at a depth between 55 and 80 m. Above the pycnocline, at depths from about 25 to app. 55 m, silt-clay sediments occur in the Puck Bay. The bottom waters within the pycnocline and above it are generally well aerated, and the sea bottom can be affected by storm or inner waves. Silt-clay sediments deposited in these zones contain admixtures of sand-size particles (up to 20%); moreover, bioturbation structures and erosional surfaces occur here. Below the pycnocline, anaerobic conditions dominate in the bottom sea waters, often with hydrogen sulphide. Silt-clay sediments occurring below the pycnocline contain less than 1% of sand-size particles and show horizontal lamination down to the depth of 6–14 cm under the sea bottom (Uścinowicz, 1997; Uścinowicz *et al*., 1998).

The vertical distribution of the concentrations of metals in silt-clay sediments in the Gdańsk Basin are presented below. The metals were deposited in two different sedimentary environments (Fig. 8.10). The sediment cores 2/97 and 2/98, taken from the depths of 55 and 65 m, represent pycnocline/sea bottom contact sediments. The cores 3/97 and 1/98 were taken from the depths of 101.5 and 82 m (for core location – see Appendix 3).

The **arsenic** concentration variations in the vertical section of the core are strongly diversified, depending on both the sedimentary environment and the region of the sedimentary basin. The contents below 15 mg/kg As occur in sediments from the pycnocline/sea bottom contact zone (cores 2/97 and 2/98). Sediments deposited below the pycnocline contain up to 24 mg/kg of arsenic at the depth of 4–8 cm under the sea bottom; however, at depths below 20 cm, the concentration does not exceed 20 mg/kg (cores 3/97, 1/98). Arsenic is extremely sensitive to changes in redox potential and that is the reason of its considerable variations in contents in the vertical section, including the elevated values in the bottom parts of the cores. However, the effect of anthropogenous pollutants is very distinct. In the north-eastern part of the basin, regardless of the sedimentary environment, the increase in arsenic content is clearly observed, starting from the 16–18 cm depth. In the southern part of the Gdańsk Basin (cores 2/97 and 3/97) an increase in the As content towards the sea bottom is less clear; however, the maximum contents of this element in both the basin regions occur at the depths from 2 to 8 cm below the sea bottom. Irrespective of the sedimentary region and its environment, a decline in arsenic concentration is observed in the surface sediment layer (0–2 cm), which should be explained by the decrease in the inflow of this element to the Baltic Sea. The As content in the surface layer does not exceed 20 mg/kg, i.e. the value corresponds to the geochemical background.

The vertical distribution of **cadmium** in the bottom sediments clearly shows the history of polluting the environment with this chemical element. The bottom parts of the sediment cores contain less than 0.6 mg/kg of cadmium, which can be accepted as a value typical of natural cadmium concentrations in the bottom sediments of the Gdańsk Basin (Table 8.4) and other Baltic Sea regions. A distinct increase in the Cd content occurs from the depth of 12–14 cm under the sea bottom, reaching 1.6 mg/kg (4–6 cm) in the NE part of the basin, and 1.9 mg/kg (2–4 cm) in its southern part. Despite lower Cd concentrations in the surface sediment layer, the values remarkably exceed those typical of the geochemical background.

The changes in the **chromium** contents in the cores from the Gdańsk Basin, as in other regions of the Baltic Sea, are irregular and invariable. The Cr content in the lower parts of the cores is between 50 and 93 mg/kg and is similar to that from other regions of the Baltic Sea.

The **copper** content variability in the lower sections of cores (20–30 cm under the sea bottom) is inconsiderable and amounts to app. 20 mg/kg in the areas where the pycnocline contacts the sea bottom (cores 2/97 and 2/98) and 32–37 mg/kg in the areas located below the pycnocline (cores 3/97 and 1/98). It can be assumed that the natural copper contents in silt-clay sediments of the Gdańsk Basin do not exceed 45 mg/kg. The increase in copper concentrations associated with contaminations is slightly higher in the southern part of the basin than in

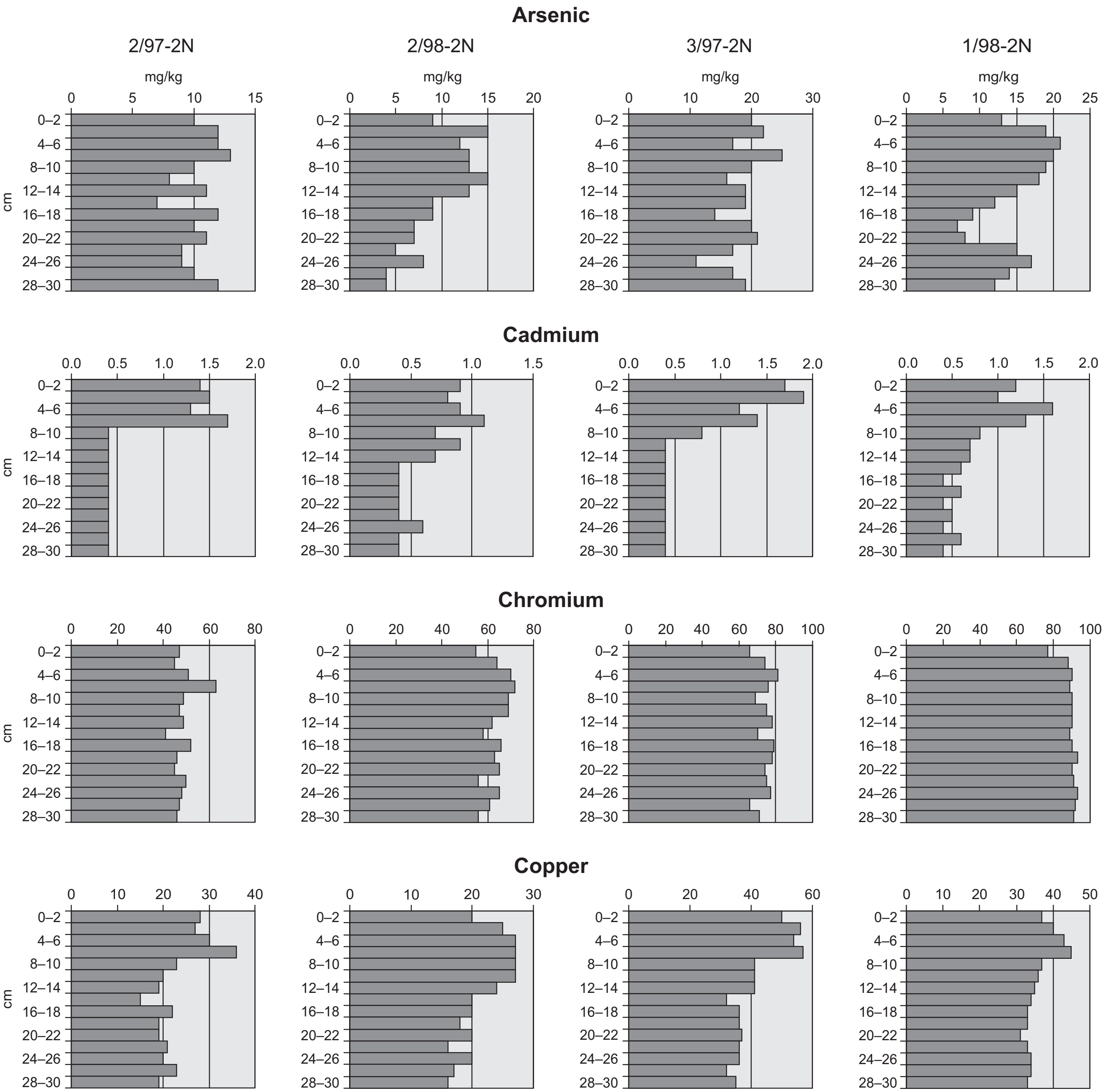


Fig. 8.10. Variability of trace elements (As, Cd, Cr, Cu, Hg, Pb and Zn) in the vertical section of silt-clay sediments of the Gdańsk Basin (acc. to the Project MASS; for location of survey stations see Appendix 3, Fig. 1)

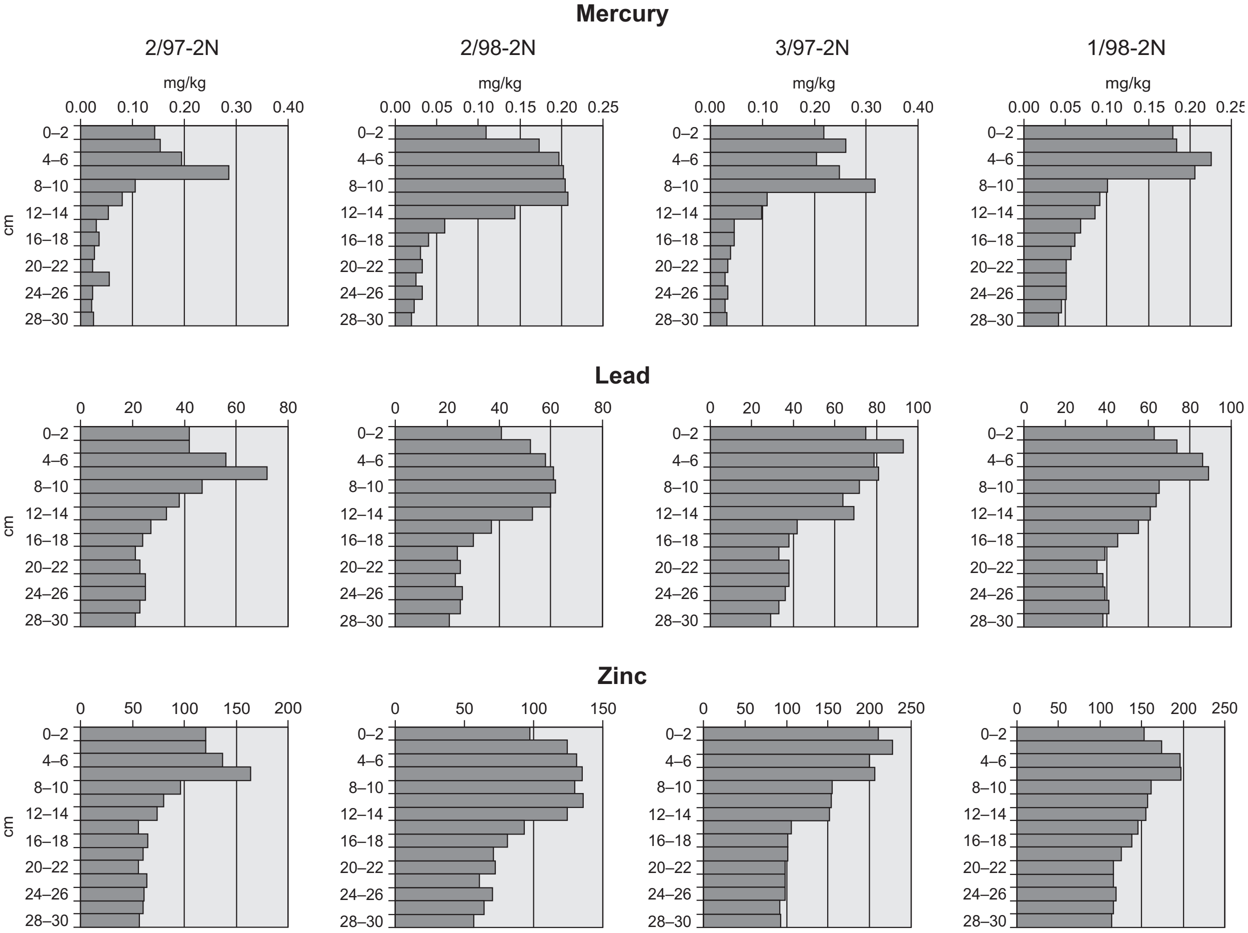


Fig. 8.10. Continued

its north-eastern part, but it is generally small. The maximum copper contents occur at the depths from 10–12 cm to 2–4 cm and reach 57 mg/kg. Similarly to other metals, a slight decrease in the Cu concentrations is observed in the surface sediment layer (0–2 cm).

The variability of **mercury** concentrations in cores is very clear. Although the Hg content does not exceed 0.05 mg/kg at depths greater than 20 cm below the sea bottom, the contents increase considerably from the depth of 12–14 cm, being four to six times greater than its natural concentrations. The maximum mercury concentrations occur at the depth of 10–12 cm in the north-eastern part of the Gdańsk Basin (max. 0.23 mg/kg) and at 4–6 cm in its southern part (max. 0.32 mg/kg).

Natural **lead** contents of in silt-clay sediments of the Gdańsk Basin do not exceed 26 mg/kg in the areas of the pycnocline/sea bottom contact, and 41 mg/kg below the pycnocline. The geochemical background values can be slightly higher and locally reach 73 mg/kg (Tables 8.3, 8.4). The increase in Pb concentrations caused by anthropogenous contaminations is up to 89 mg/kg in the NE part of the basin, and up to 93 mg/kg in the southern part.

The **zinc** content in sediment layers not contaminated by anthropogenous impact does not exceed 120 mg/kg, and can locally reach 150 mg/kg (Tables 8.3, 8.4). The contamination-related increase in the zinc concentrations in the upper parts of cores is well marked, but not sig-

Table 8.4

Contents of trace elements in silt-clay sediments of the Gulf of Gdańsk (acc. to Laban *et al.*, 1994; Uścinowicz *et al.*, 1998; Ebbing *et al.*, 2002)

Region	As	Ba	Cd	Co	Cr	Cu	Ni	Pb	Sr	V	Zn
	[mg/kg]										
Puck Bay (above the pycnocline, stations 14/94, 15/94, 16/94)	79.6 8–11	328–346 340–365	0.96–2.05 0.31–0.42	8–9 13–14	99–133 95–107	33–51 24–31	31–39 41–48	58–80 28–47	108–217 88–103	73–76 100–117	140–216 89–125
Gulf of Gdańsk (within the pycnocline, stations 20/94, 21/94, 22/94)	11–16 7–17	340–359 362–392	1.34–1.93 0.13–0.24	9–10 9–12	75–86 75–88	26–38 19–29	24–33 26–34	48–72 35–43	105–177 97–98	52–68 73–93	118–167 70–96
Gulf of Gdańsk (below the pycnocline, stations 23/94, 24/94, 25/94)	17–22 13–19	343–394 394–455	2.11–2.16 0.21–0.28	10–13 12–17	86–95 83–102	56–59 31–44	40–44 32–44	102–106 66–83	93–101 100–104	77–96 84–121	209–228 100–151

Numerator: layer 0–2 cm, nominator: layer 22–24 cm; total content determined by XRF method, excluding Cd; location of samples – Appendix 2

nificant, as it is for copper. The maximum zinc contents reach 228 mg/kg.

The results of analyses of the sediments from the Gulf of Gdańsk (Table 8.4; Appendix 2) show similar relationships of the distribution of trace element in the vertical sections of bottom sediments, and the variabilities in their concentrations induced by the environmental conditions, mainly by variable redox conditions, to the above presented. The geochemical background values of the individual trace elements measured in the sediments of the Gdańsk Basin (including the Gulf of Gdańsk) are similar to those from many other regions of the Baltic Sea. The sediments from the depth of 2 to 14 cm under the sea bottom are more of less significantly enriched with the individual trace elements. These enrichments are similar to those from other regions of the Baltic Sea, and sometimes even many times smaller than in the most contaminated regions. In the surface sediment layer, a decrease in the contents of all trace elements is observed, which is probably related to a smaller discharge of pollutants into the Baltic Sea. Apart from a group of elements whose concentrations are remarkably elevated in the surface sediment layer (Cd, Cu, Hg, Pb, Zn), there are also the elements (Ba, Co, Cr, Ni, V) whose concentrations in the surface sediment layer are most frequently lower than at greater depths (Table 8.4).

Appendix 2

Geological and Geochemical Seabed Monitoring of the Gulf of Gdańsk

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A joint Geological Survey of the Netherlands (TNO-GSN) and Polish Geological Institute-National Research Institute (PGI-NRI) research programme named "Geological and geochemical seabed monitoring of the Gulf of Gdańsk" was carried out in order to gain an insight into the historical build-up of seabed sedimentation and contamination. The programme carried out during the years 1993–1994 was planned with the aim of identifying and describing presumed anthropogenic polluted sediments "hot spots", and also to establish a suitable data base for modelling purposes. The special attention was paid on sedimentary environment influenced content of contaminants in the seabed sediments. An important object of the programme was scientific and technological transfer between participating organizations.

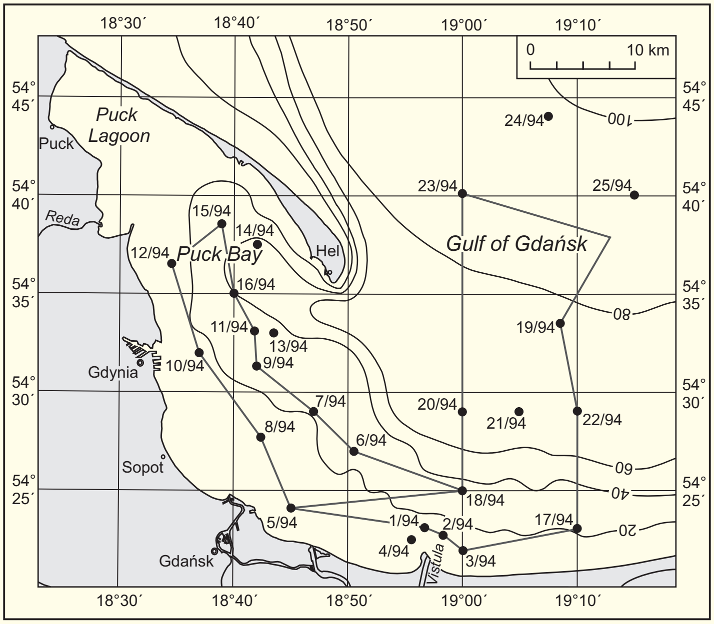

Fig. 1. Sampling location and side scan-sonar, and seismoacoustic profiles

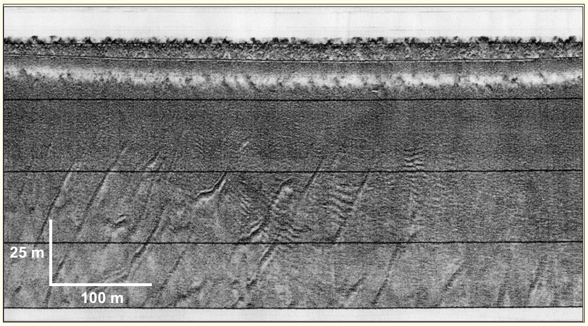

Fig. 2. An example of a side-scan sonar record over a sand wave field in a sandy depositional area (water depth ca. 15 m); two generations of sand waves are visible; larger – with crest lengths of ca. 30–60 m, spacing between crests ca. 20–30 m and crest orientation W–E, smaller – with crest lengths of ca. 25–50 m, spacing between crests ca. 2.5–3.0 m and crest orientation N–S

According to the existing seabed sediment maps with available geochemical data, a total of 25 locations were chosen to include sites with varying sedimentological composition and also potential "hot spots" for detailed studies. A seismic and sonar survey was carried out over sampling locations (Figs. 1, 2).

At each location a sample of very high quality was taken with the box-corer. The average recovery of the cores was 0.30 m, the maximum being 0.44 m and the minimum being 0.15 m. The box-corer was used at all 25 locations and on both muddy and sandy bottoms (Fig. 3). Special tubes enabled subsamples to be taken for various purposes notably description of the seabed, organic and inorganic analysis and X-ray photography.

In the laboratory of TNO-GSN, both major and trace elements (Cr, Cu, Ni, Pb, Zn and others), were analysed on pressed powder tablets by XRF using an ARL 8410. For calibration purposes, pressed powder tablets of international rock standards were used. The total extractable Cd was determined using a Sintrex AAZ 2 AAS.

An important feature in the Baltic Sea is a thermohaline stratification of the water column. A pycnocline is present in the water column of the Gulf of Gdańsk at a depth of about 55–70 m. Above the pycnocline sandy sediment prevails. Dynamic processes, occurring in the water layer above the pycnocline, make permanent deposition of silty and clayey fractions in such areas impossible. Only in the Puck Bay protected by Hel Peninsula and in front of the Vistula River mouth sandy mud and mud occurs above the pycnocline. At depths under the influence of storm waves and where currents are active, sandy sediments are often redeposited. Most

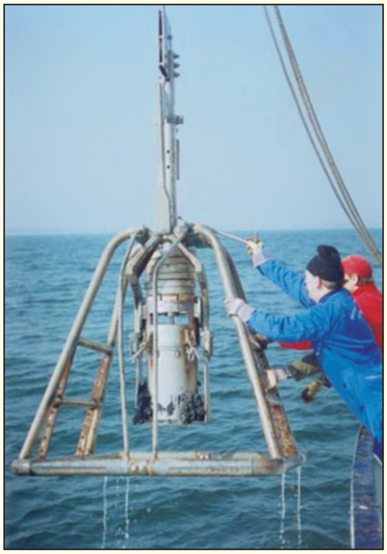

Fig. 3. Method of seabed sediment sampling with a box-corer. On the left an example of a box-corer with a sediment sample inside. On the right a view of the top of a seabed sample with wave ripplemarks

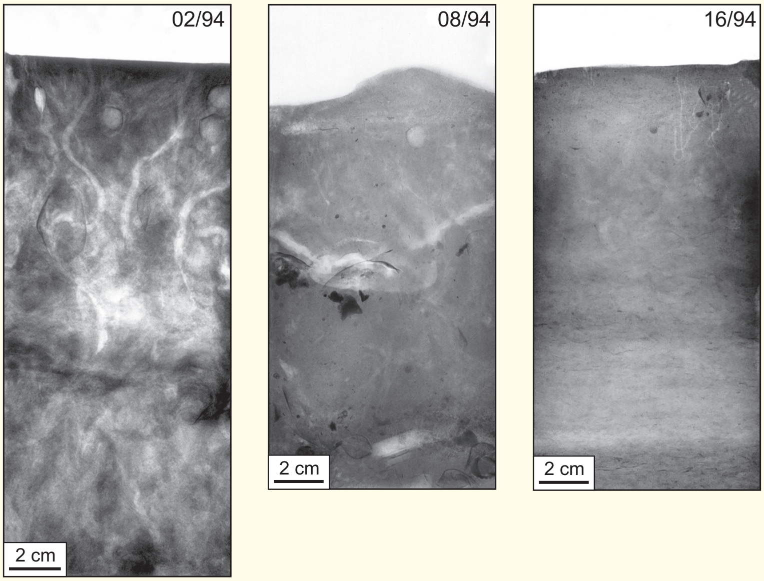

Fig. 4. X-ray photos of sedimentary structures from shallow water sedimentary environments in the Gulf of Gdańsk

02/94 – strongly bioturbated sandy-muddy sediments in the front of Vistula River mouth; 08/94 – by wave action and bioturbation reworked sands; 16/94 – bioturbation structures and erosional surfaces in muds from the Puck Bay

cores taken above the pycnocline display erosion surfaces and bioturbations (Fig. 4).

The variability of the oxygen content is apparently related to the stratification in the water column. In the zone where the pycnocline makes contact with the sea bottom, dominantly muddy-sandy and muddy occur while below the pycnocline only muddy deposits are present. Above and within the pycnocline, the oxygen saturation varies from 100% at the sea surface to 70% in the deeper layers, but below the pycnocline the saturation is less than 20%, and anaerobic conditions periodically occur at or near the seabed. Within the pycnocline in muddy sediments erosion horizons occur, while below the pycnocline no bioturbation (due to a lack of oxygen) is evident and laminated sediments do occur (Fig. 5).

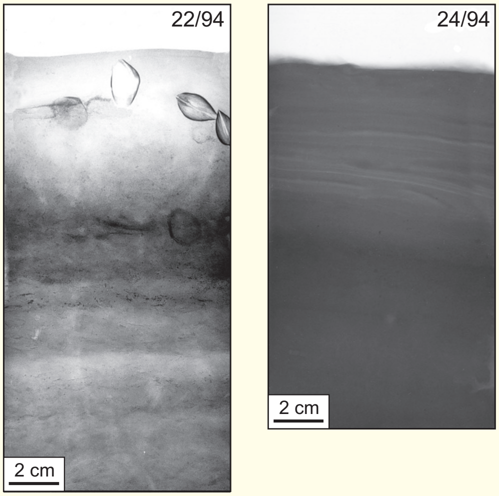

Fig. 5. X-ray photos of sedimentary structures from deep water sedimentary environments in the Gulf of Gdańsk

22/94 – silty-clayey sediments deposited within the pycnocline, in upper part bioturbated by *Macoma* sp., in lower part with erosional surfaces; 24/94 – silty-clayey sediments deposited below the pycnocline, in upper part laminated, in lower part homogenous

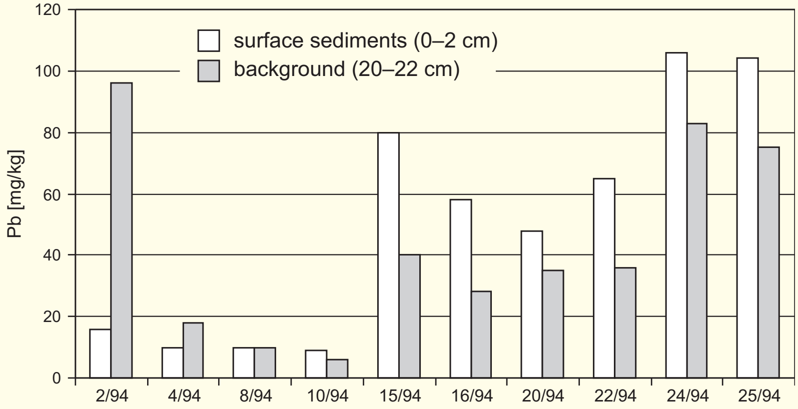

Fig. 6. Content of Pb in surface sediments and background in different sedimentary environment of the Gulf of Gdańsk

(2/94, 4/94 – muddy sands deposited in front of the Vistula River mouth; 8/94, 10/04 – sandy depositional area in shallow water area; 15/94, 16/94 – muds deposited above the pycnocline in the Puck Bay; 20/94, 22/94 – muds deposited within the pycnocline; 24/94, 25/94 – muds deposited below the pycnocline

Background values were established for the muddy sediments in the Puck Bay and in the Gulf of Gdańsk. To find the background value for sandy sediments is more complicated. In the nearshore zone sands are under constant reworking due to wave activity. As a result the selection of true geochemical background samples representing coastal sands is difficult. For muddy sediments in the semi-enclosed Puck Bay and Gulf of Gdańsk all elements, except Cr and Ni are enriched in the seabed surface layer. This points to a strong anthropogenic influence, for Cu, Pb, Zn in both Puck Bay and the Gulf of Gdańsk, while Cd is extremely enriched in the Puck Bay. The background values of Pb (Fig. 6) and other metals are similar in sediments from the Puck Bay and sediments from the Gulf of Gdańsk deposited in an oxygenated environment (within the pycnocline). Background values in the samples from an anoxic environment have values that are almost twice as high. This could only be partly explained by differences in grain size distribution. The most important factor for those differences is a difference in redox conditions. A special situation occurs in front of the Vistula River mouth, where background values seem much higher than the content of heavy metals in the surface layer (Fig. 6). This contradiction is caused by the high sedimentation rate in that area. High content of metals in lower parts of the cores taken in front of the Vistula River mouth reflect, most probably, high contamination of the Vistula waters during the years 1950–1980. As a result of the study also possible buried “hot spots” were found, especially near the mouth of the Vistula River, and in the muddy part of the Puck Bay (Laban, *et al*., 1994).

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Appendix 3

Mass Project – Marine Environmental Assessment and Monitoring of the Gulf of Gdańsk Seabed

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In an attempt to develop an enhanced and standardised approach to marine environmental assessment and monitoring, applicable to both western and eastern Europe, a cooperative project was conducted in the Polish and Lithuanian sectors of the Gdańsk Basin to examine site selection, sampling and laboratory procedures. The MASS project, involving Lithuania, Poland, the Netherlands and the UK, was carried out within the INCO-COPERNICUS programme in the years 1997–1998.

In the Polish sector of the Gdańsk Basin sediment cores were taken at three stations sited on the basis of a seismic and sonar profile ca. 50 km long (Fig. 1). At the first (nearshore) location, two sandy sediment cores were taken using an Oscor sampler. At the second and third stations, moving progressively seawards, three cores of muddy sediments were taken using a Niemistö corer. In the Lithuanian sector a 70 km long seismic survey track was

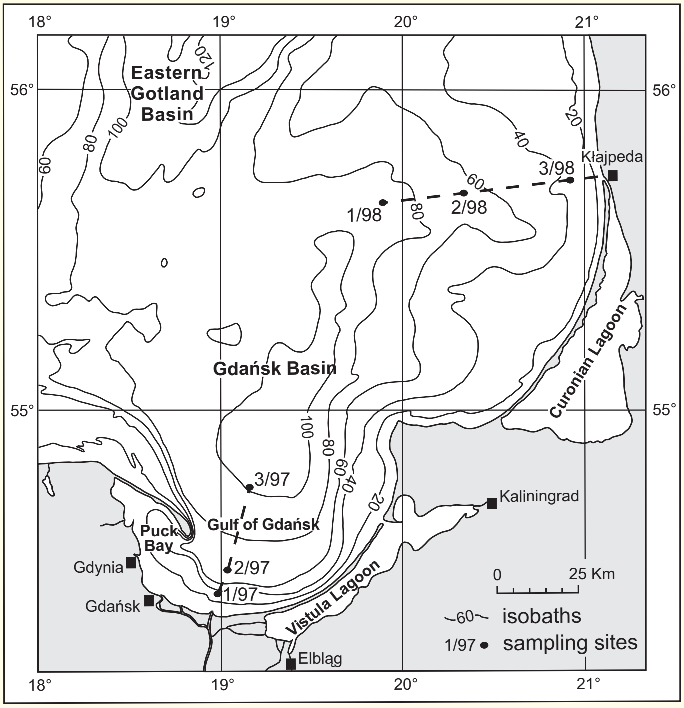

Fig. 1. Sampling sites

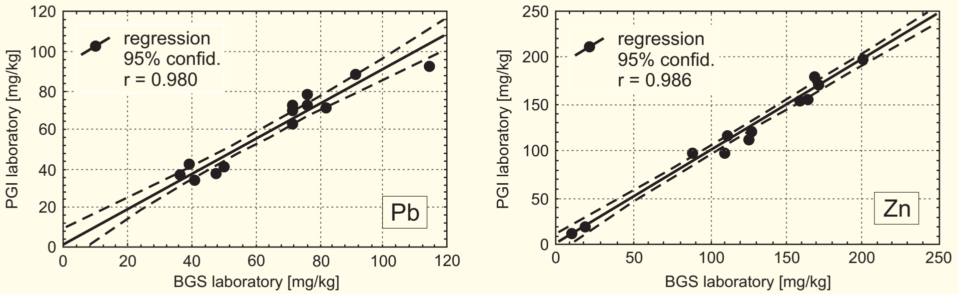

Fig. 2. Correlation of BGS and PGI laboratories data

used to determine the location of the 3 sampling sites. At each of the 2 deeper locations, 5 cores of muddy sediments were taken by Niemistö sampler. At the third, nearshore location, 5 cores of sandy sediments were taken by box corer. The distance between cores at each station was ca. 100–200 m. The cores were cut into 2 cm slices and frozen at –20°C on the board ship.

Each sample was divided into two sub-samples and analyzed in the Central Chemical Laboratory of the Polish Geological Institute (PGI) with a smaller subset being analysed at the British Geological Survey (BGS) for inter-laboratory comparison. Determination of Al, As, Cd, Cr, Cu, Fe, Li, Ni, Pb, Zn, P and total organic carbon (TOC) was carried out by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) after total digestion with HF, HNO_3 and $HClO_4$. The mercury content was determined using cold vapour atomic absorption spectrometry (AAS). The total organic carbon (TOC) content was determined by a coulometric method.

Metal data from both laboratories were statistically compared. Very high correlation coefficients, with only small standard deviations from regressions lines, were obtained (Fig. 2). Inter-laboratory comparisons were also made on the uppermost samples (0–2 cm) from 5 cores at one site, used to assess within site variation (Fig. 3).

The results of both methods of comparison allowed to estimate of analytical errors and the degree of intra-site variation to be made. The following maximum analytical errors were estimated: As ~4 mg/kg, Cd ~0.5 mg/kg,

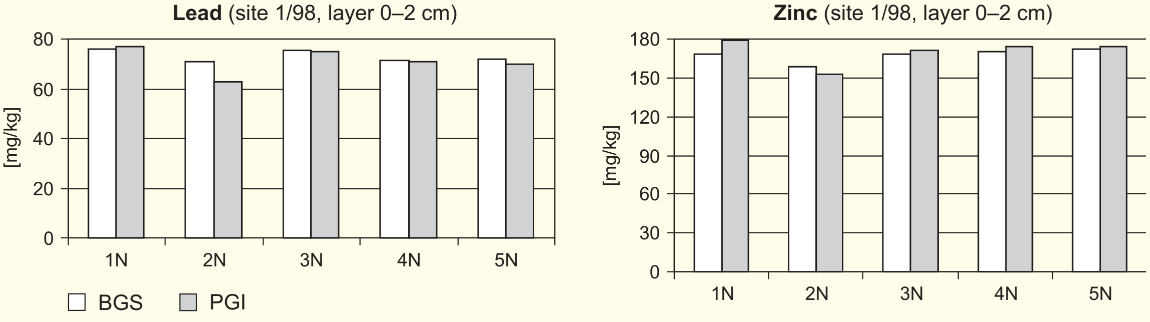

Fig. 3. Intra-site variability in the uppermost layer (0–2 cm) according to BGS and PGI data (1N–5N are Niemistö core identifiers)

Table 1

Maximum intra-site variability

Sample		Al	Fe	P	As	Cd	Cr	Cu	Hg	Li	Ni	Pb	Zn	TOC [%]
		[%]			[mg/kg]									
2 cores per site	1/97 0–2	0.13	0.04	0.001	<det. lim.	<det. lim.	1	0	0.012	0	0.0	0	11	0.01
	1/97 8–10	0.38	0.27	0.007	3	<det. lim.	10	8	0.082	4	6.0	11	36	0.68
	1/97 16–18	0.31	0.34	0.002	<det. lim.	<det. lim.	7	4	0.012	4	4.0	3	15	0.14
	2/97 0–2	0.11	0.12	0.020	2	0.1	2	0	0.022	2	2.0	4	0	0.71
	2/97 8–10	0.11	0.17	0.007	2	<det. lim.	5	4	0.012	3	3.0	8	18	0.33
	2/97 18–20	0.26	0.31	0.002	2	<det. lim.	4	1	0.001	3	1.0	4	1	0.17
	2/97 28–30	0.08	0.17	0.001	2	<det. lim.	2	1	0.005	2	0.0	1	2	0.25
	3/97 0–2	0.01	0.31	0.011	0	0.0	2	3	0.018	0	1.0	1	4	0.78
	3/97 8–10	0.69	0.48	0.002	1	<det. lim.	7	1	0.221	9	4.0	13	8	0.19
	3/97 18–20	0.46	0.00	0.001	2	<det. lim.	2	1	0.028	1	1.0	24	19	0.14
	3/97 28–30	0.12	0.22	0.002	1	<det. lim.	3	1	0.019	3	0.0	5	1	0.45
5 cores per site	1/98 0–2	0.50	0.69	0.024	7	0.6	5	5	0.039	5	5.0	14	26	0.60
	1/98 28–30	0.25	1.30	0.009	10	<det. lim.	2	2	0.004	3	6.0	4	8	0.40
	2/98 0–2	0.20	0.34	0.011	2	0.4	5	3	0.010	2	4.0	5	10	0.51
	2/98 28–30	0.98	0.31	0.007	<det. lim.	<det. lim.	16	6	0.012	12	7.0	4	22	0.48
	3/98 0–2	0.12	0.10	0.007	<det. lim.	<det. lim.	3	1	0.003	0	1.0	2	5	1.10

Estimated maximum analytical errors: As ~4 mg/kg, Cd ~0.5 mg/kg, Cr ~5 mg/kg, Cu ~4 mg/kg, Hg ~0.06 mg/kg, Ni ~8 mg/kg, Pb ~8 mg/kg, Za~10 mg/kg; 7 intra-site variations bigger than estimated analytical error; <det. lim. – below the detection limit

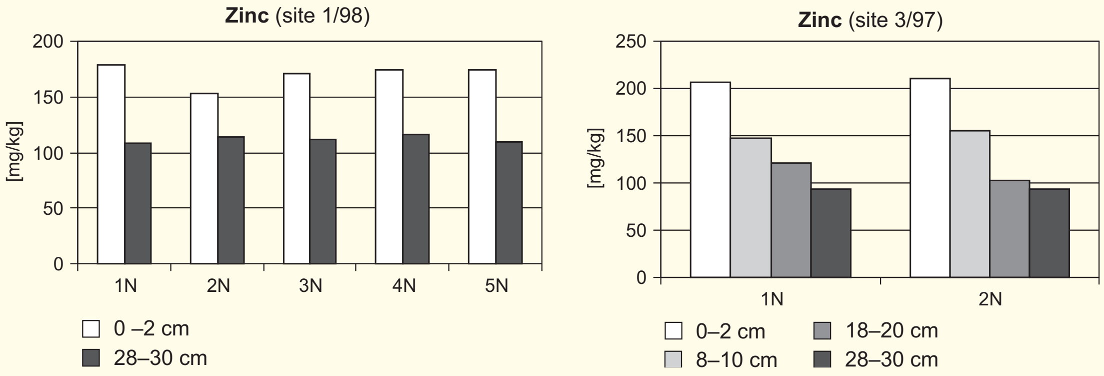

Fig. 4. Intra-site variability of Zn content in down core profiles

Cr ~5 mg/kg, Cu ~4 mg/kg, Hg ~0.06 mg/kg, Ni ~8 mg/kg, Pb ~8 mg/kg, Zn ~10 mg/kg.

Intra-site variability was also checked by comparing of metal contents at different depths in parallel cores taken from the same sites (Fig. 4). It is evident that intra-site variability is, in general, smaller in the lower parts of cores than in the topmost parts. The variations in the uppermost samples (0–2 cm) could represent real intra-site differences or could be due to coring technique effects on the topmost soft sediments. Intra-site variations were greater than estimated analytical errors in only a few cases, and these may show genuine differences between cores (Tab. 1).

Studies of down core profiles show that metal concentrations in muddy sediments start to increase, presumably due to contamination, at depths of between 10 and 16 cm, but the pattern of variation differs in detail for each core and sedimentary environment (Fig. 8.10 shows examples). In all cores of muddy sediments, the topmost 2 cm shows a reduction from maximum metal levels. This probably represents a genuine reduction of metal loads. The northern part of the Gdańsk Basin (Lithuanian sector) seems to be slightly less contaminated by metals than the southern part (Polish sector). This could be because the Vistula River in the Polish sector discharges directly into the Gulf of Gdańsk, whereas the Nemunas, in the Lithuanian sector, discharges into the northern part of the Gdańsk Basin via the Curonian Lagoon, which may act as a sink for contaminants.

8.3. Normalised Values of Trace Elements in Surface Sediments

Trace elements, such as: arsenic, cadmium, chromium, copper, mercury, lead, and zinc are considered particularly hazardous to the marine environment due to the role they play in biochemical processes. The knowledge about regions where the content of toxic elements is higher than the geochemical background enables us to plan and undertake suitable protective and preventative actions. Owing to normalisation of the trace element contents, it is possible to identify those areas of the surveyed sea bottom where increased amounts of chemical constituents of anthropogenous origin are accumulated regardless of the grain-size type of sedimentary material. Isoline maps of normalised values for trace elements can be useful to identify the sources of contaminant inflow into the marine ecosystems.

A map of the zinc content normalised with reference to iron **(Zn/Fe)** is a good illustration for the southern Baltic Sea (Fig. 8.11). The areas of a relatively higher zinc content are situated around the Pomeranian Bay and in front of the Vistula River mouth. That location can suggest that the pollutions supplied by the Oder and the Vistula are the main cause of zinc enrichment in sediments. In the Bornholm Basin, near the northern border of the Polish economic zone, there is a small but most contaminated area. It seems that one of the main reasons of the local contamination may be ammunition dumped nearby after World War II.

Owing to numerous stations for bottom sediment sampling in the Gulf of Gdańsk, the isoline maps of normalised values of trace element indicate more precisely the areas threatened with contaminants, including the sources of pollutions (Fig. 8.12).

As/Fe. The horizontal distribution pattern of normalised arsenic values shows that the main sources of the metal inflow to the Gulf of Gdańsk and Puck Bay are located in the western part of the Puck Bay, along the Hel Peninsula and between Władysławowo and Hel. The significance of the fishing harbours in Kuźnica and Jastarnia is particularly apparent.

Cd/Fe. Cadmium, when in excess, is one of the most hazardous elements to ecosystems. Elevated Cd/Fe values are located, similarly to As/Fe, mainly in the north-western part of the Puck Bay, in the area between Władysławowo and Hel.

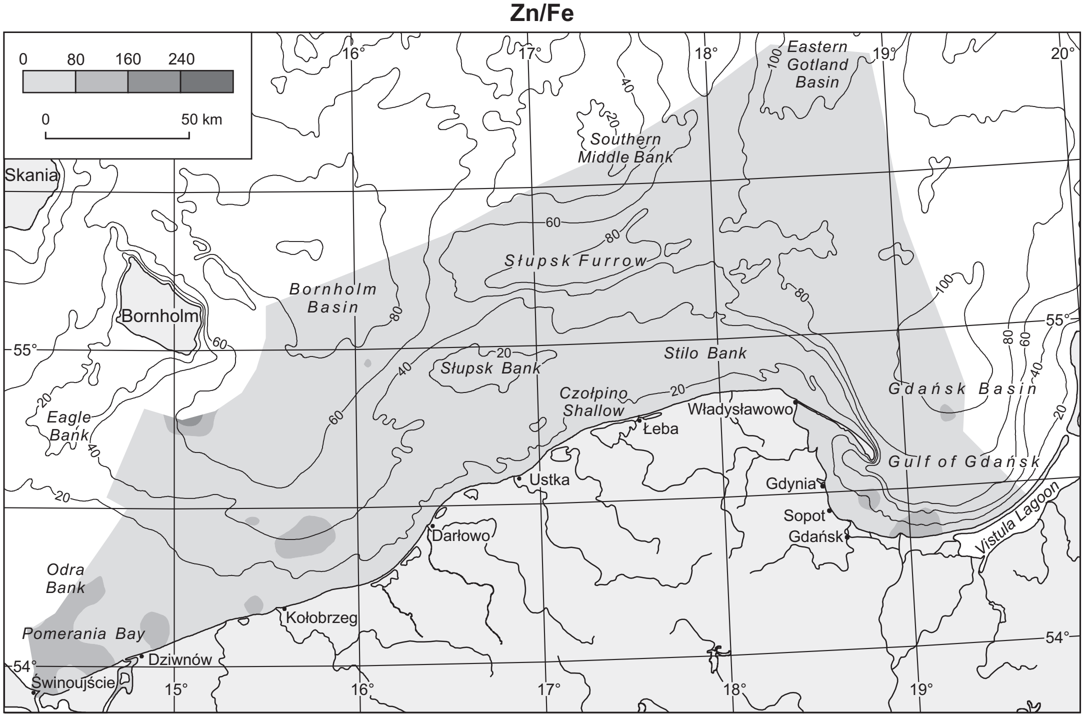

Fig. 8.11. Contents of zinc normalised with reference to iron (Zn/Fe) in surface sediments of the southern Baltic Sea (based on data for the Geochemical atlas of the southern Baltic Sea, Szczepańska, Uścinowicz, 1994)

Cr/Fe. Chromium enters into the Puck Bay mainly from the Reda River drainage basin. Moreover, slightly elevated Cr/Fe values were recorded southwest of Kuźnica along the Hel Peninsula, and in the Puck Bay – between Oksywie and Hel.

Cu/Fe. Copper flows into the Gulf of Gdańsk and Puck Bay from a few sources. The highest Cu/Fe values are recorded along the Hel Peninsula, in the vicinity of Chałupy and Jastarnia. Elevated values are also observed near Sobieszewo, west of the mouth of the Vistula-Śmiała River. Threatened with contamination by copper are also the areas of the sea bottom in the Puck Bay from the Gdynia harbour towards Jastarnia (on the Hel Peninsula), as well as silt-clay sediments in the central part of the Gulf of Gdańsk.

Hg/Fe. Mercury, like cadmium, is one of the most toxic chemical constituents. Elevated Hg/Fe values concentrate predominantly in the Puck Lagoon, near Chałupy, and in the Bay of Puck to the north and north-east of the Gdynia harbour – between Oksywie and Jastarnia, and in the vicinity of the Orłowo Headland. Slightly elevated Hg/Fe values also occur near the the Vistula River mouth, and locally in small areas of the sea bottom in the southern part of the Gulf of Gdańsk.

Pb/Fe. The highest Pb/Fe values are observed app. 6 km to the north-east of the Gdynia harbour. High Pg/Fe values also concentrate in the area of Jastarnia on the Hel Peninsula and near the mouth of the Vistula-Śmiała. Probable sources of contamination are the harbours at Gdynia and Jastarnia. Of interest is the case of the Vistula-Śmiała River mouth. In 1840–1895, it was the main mouth of the Vistula. At that time a huge river mouth fan was formed. The elevated values of the index Pb/Fe in the mouth fan sediments of the Vistula-Śmiała River may suggest their contamination with lead. The

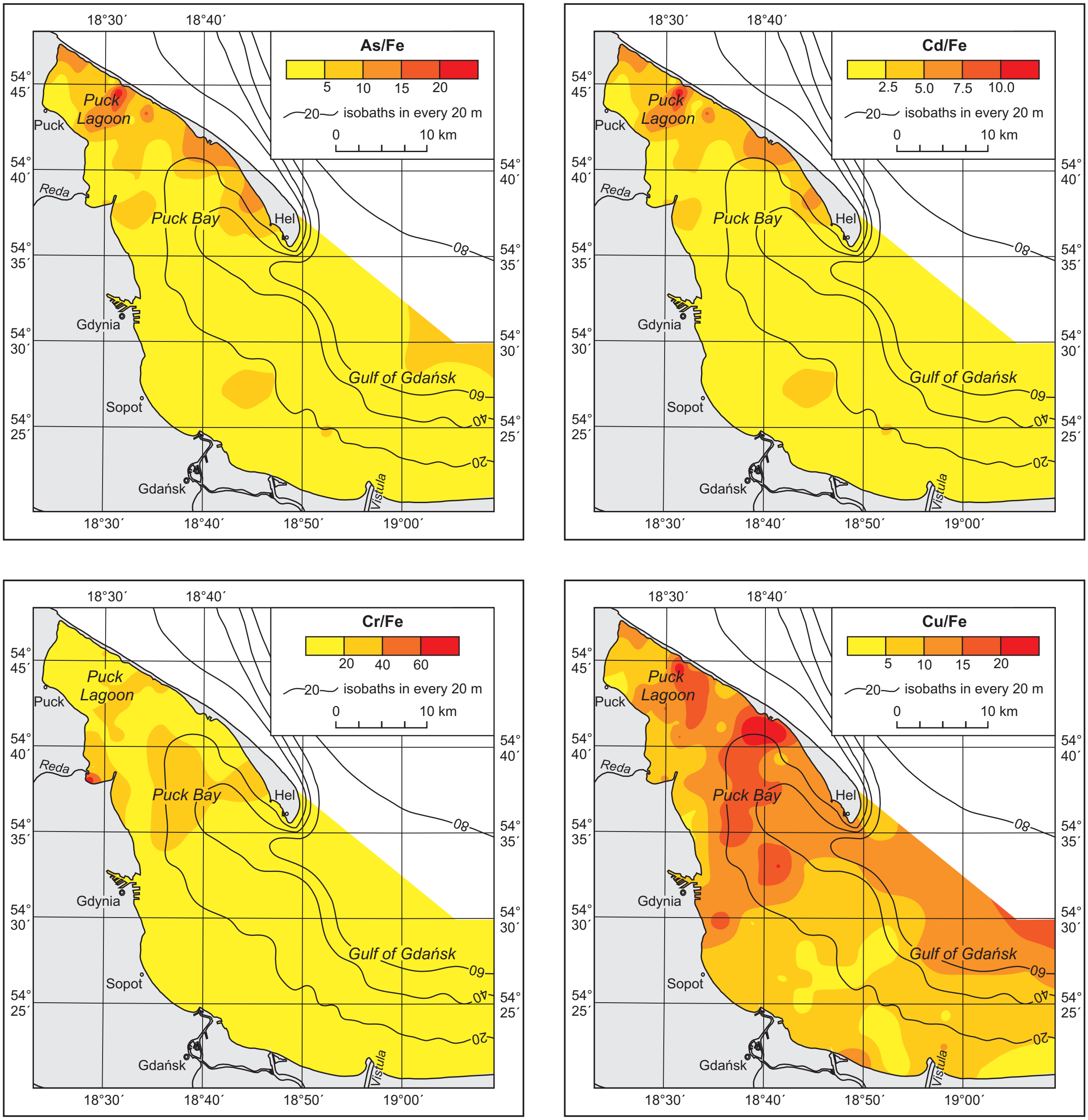

Fig. 8.12. Contents of trace elements normalised with reference to iron in surface sediments of the Gulf of Gdańsk (Uścinowicz *et al.*, 2008)

currently washed out sediments of this river mouth fan may be a secondary source of lead in the ecosystem of the Gulf of Gdańsk.

Zn/Fe. Elevated Zn/Fe indices observed near Kuźnica and Jastarnia on the Hel Peninsula indicate the fishing harbours as zinc sources. However, greater

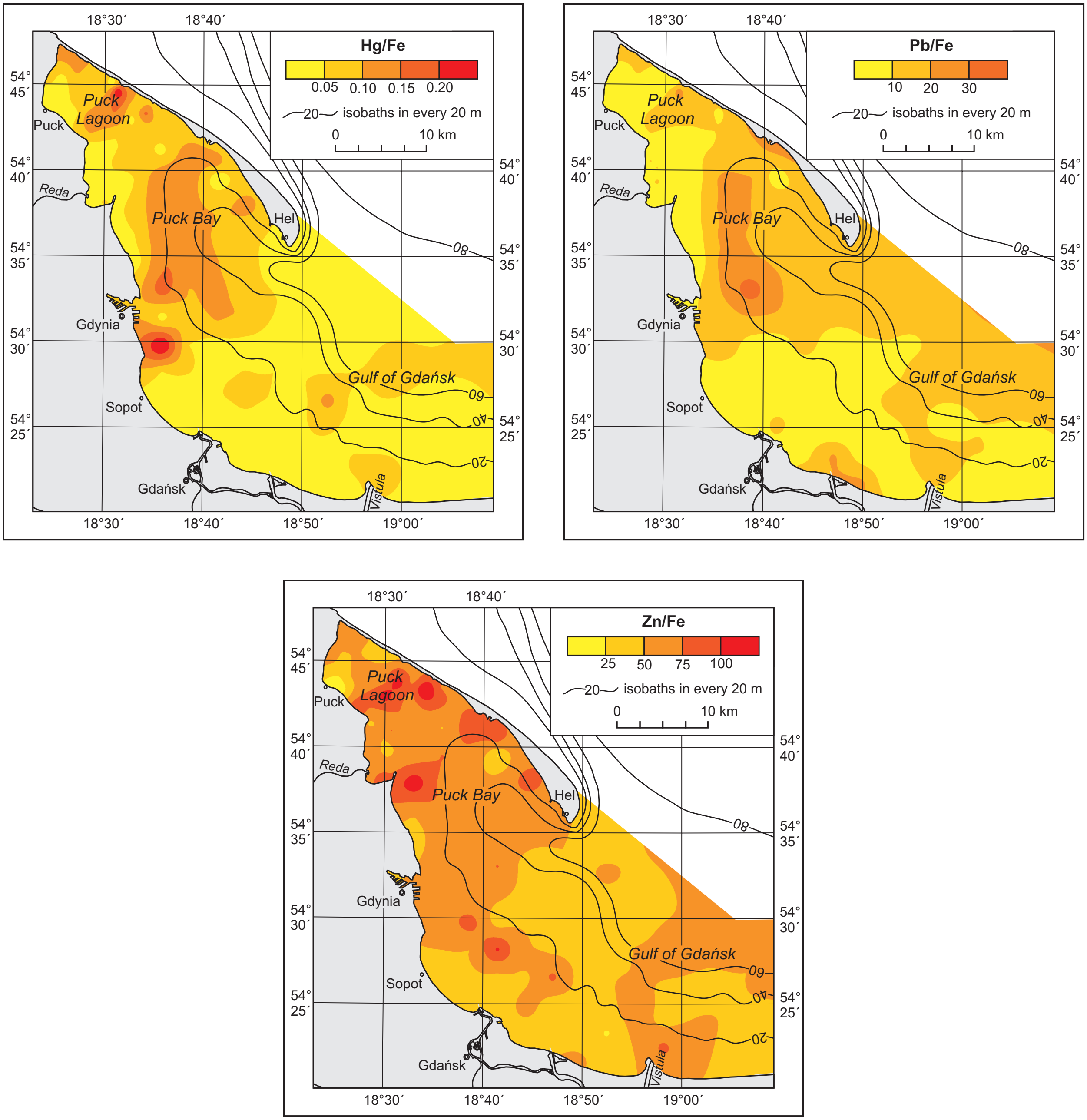

Fig. 8.12. Continued

zinc contents, reported from the area located to the east of Mechelinki and the Rewski Tip, probably originate from the municipal sewage of Gdynia discharged by the trunk sewer into the bay. Elevated Zn/Fe values were also recorded in the Vistula River mouth in the Gulf of Gdańsk.

Appendix 4

Normalisation of Geochemical Data

Szymon Uścinowicz[1], *Piotr Szefer*[2], *Krzysztof Sokołowski*[1]

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The contents of trace elements (metals) in sediments of both natural origin and anthropogenic impurities depend primarily on the sediment grain size (Fig. 1). Fine-grained sediments such as silts and clays contain considerably more metals than sands as they are bound mainly by clay minerals and organic matter, and by iron and manganese hydroxides. An elevated content of the sand fraction (>0.063 mm) effects the decrease in absolute content of metals in the whole sample.

If you wish to compare metal concentrations in sediments of different grain size in order to localise polluted areas where metals occur with concentrations higher than normal for the given area, it is important to apply a normalised procedure, i.e. one that enables you to eliminate the effect of deposit particle size on the chemical component content. The simplest way is to separate the sand fractions (>0.063 mm) from the sample before its chemical analysis. This method, however simple to perform, is effective only for sandy-silty sediments. For sands, the content of fractions finer than 0.063 mm is usually very low, so it is difficult to achieve a suitable amount of the material. For silty-clayey sediments, the content of sand fractions is so low that it does not affect the results of the analyses. The separation of the finest fractions from, for example, 0.016 mm or 0.004 mm by using depositional methods, as is sometimes applied, is labour-consuming. Therefore, there are procedures of normalisation used which refer to the total content of a given element in the sample but which are not divided into separated fractions to the component of the reference, the total content of which in the tested sediment is not related to the effect of man-made pollution. The normalisation makes it possible to compare specimens of different grain size and to determine any man-made effect on the contents of chemical components.

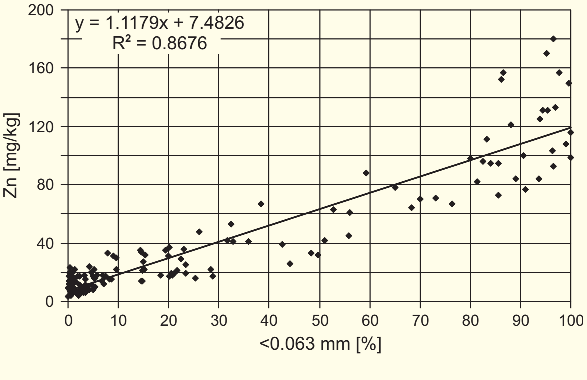

Fig. 1. The relationship between zinc concentration and the content of fraction <0.063 mm (from the western part of the Gulf of Gdańsk)

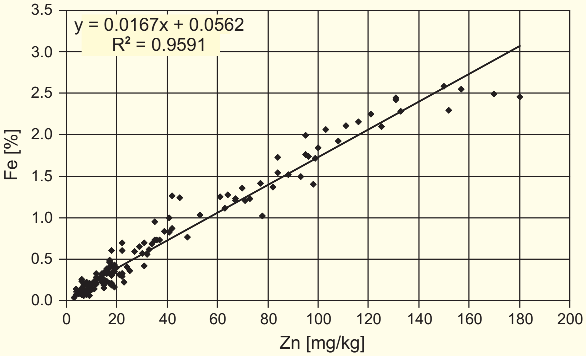

Fig. 2. The relationship between zinc concentration and iron content (from the western part of the Gulf of Gdańsk)

Elements such as aluminium, iron, lithium, scandium, and caesium are used as normalisation agents. Their content is properly correlated with the sediment grain size and the presence of clay minerals and alumosilicates. The basis for this type of standardisation is the issue that the presence of a standardisation component is a result of natural processes, and on the fact that in natural sediments a linear relation exists between the content of the determined element and the content of the normalisation agent (Fig. 2).

In sediments, metals occur in different chemical forms, in more or less mobile forms, and at the same time they enter more or less easily into biogeochemical reactions. Depending on the purpose of the research, different types of analytical methods can be used. It is possible to determine the total content of metals in the tested sediment, or one of their forms. However, individual metals behave differently, depending on the extraction techniques applied to the sediment material (Fig. 3).

With the use of partial dissolving, aluminium undergoes the extraction process to a substantially lower degree than iron. With extraction using nitric acid, scandium and lithium undergo more intense leaching than aluminium. Aluminium is liberating to the 67% level, scandium to 76%, lithium to 80.5% and iron up to 92%. Considering this, the efficiency of the normalisation procedure by partial dissolving will also differ while applying different normalisation elements.

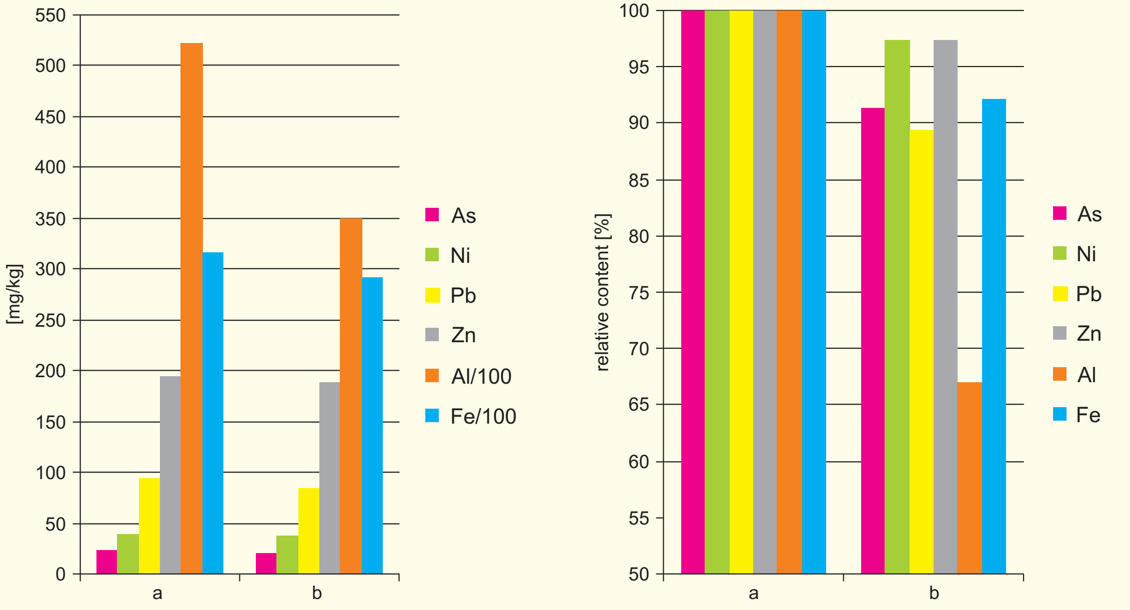

Fig. 3. The comparison of metal determination in a sample of mud from the Gulf of Gdańsk with reference to the applied extraction method: a – complete dissolution (mixture of HF, HNO_3, $HCLO_4$), b – partial dissolution (HNO_3 1:1)

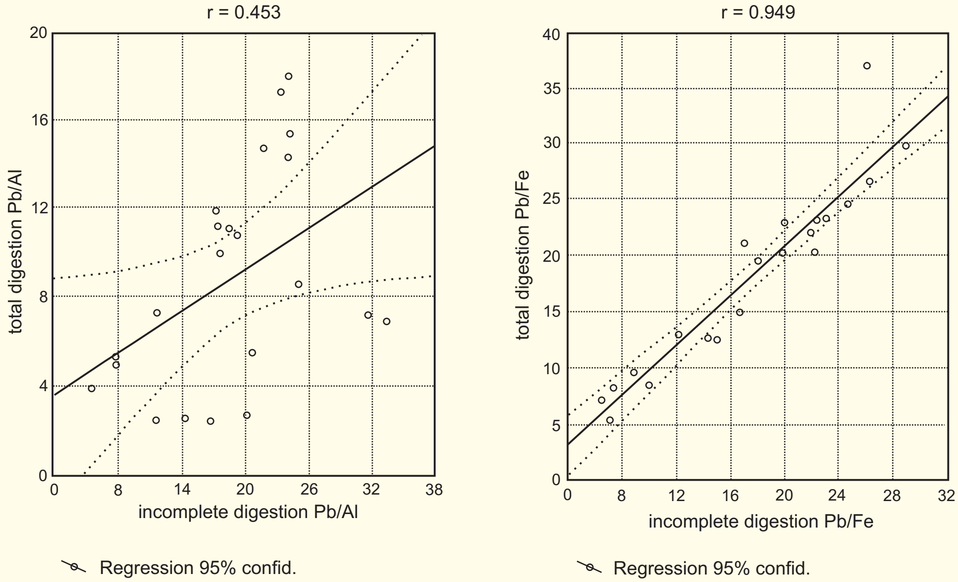

Fig. 4. The comparison of lead concentrations normalised with reference to Al and Fe for samples of bottom sediments from the Gulf of Gdańsk for complete and partial dissolution sediments

The results for the normalised contents of metals with reference to iron, scandium and lithium correlate well regardless of the method of sediment dissolution. The normalisation with reference to aluminium does not give a satisfactory value of correlation coefficient (Table 1, Fig. 4).

Comparing different normalisation methods of analytical results of trace element contents in bottom sediments from the Gulf of Gdańsk, it can be clearly seen that iron is the best normaliser. These results can be extended with high probability for the whole area of the Baltic Sea. The results of comparing different normalisation methods seem to confirm the earlier stated opinions (Böstrom *et al.*, 1978, Loring, 1978, 1979, Loring, Rantala, 1992) that aluminium is not an effective normaliser in those areas where the sediments were formed as a consequence of repeatedly processed products of weathering igneous rocks during the coast and bottom sea erosion of glacial debris.

Table 1

The correlation coefficients for the contents of As, Ni, Pb, Zn with reference to the concentrations of Al, Sc, Li, Fe in samples of bottom sediments from the Gulf of Gdańsk (completely dissolved in the mixture of acids HF, HNO_3, $HClO_4$ and partially dissolved in HNO_3 1:1)

As/Al = 0.11	As/Sc = 0.94	As/Li = 0.85	As/Fe = 0.96
Ni/Al = –0.12	Ni/Sc = 0.32	Ni/Li = 0.29	Ni/Fe = 0.90
Pb/Al = 0.45	Pb/Sc = 0.89	Pb/Li = 0.69	Pb/Fe = 0.95
Zn/Al = 0.66	Zn/Sc = 0.87	Zn/Li = 0.86	Zn/Fe = 0.99

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8.4. Sediment Contamination Factors

The enrichment of the surface sediment layer with heavy metals and other chemical components may be caused by natural features of the sedimentary environment or by human activity. In order to estimate the enrichment ratio of the surface layer of bottom sediments with metals and metalloids, two indices are used: anthropogenic factor (AF) and enrichment factor (EF).

The AF enables us to estimate an increase in metal concentrations in surface layer sediments with reference to deeper sediments known as the geochemical background. The AF is calculated by using the following formula:

$$\mathrm{AF} = M_s/M_d \qquad [8.1]$$

where: M_s and M_d mean average content of a given element in the surface layer and in a deeper layer of the core. The value of AF >1 means that the contemporaneously deposited surface layer is enriched with a given element with reference to a layer located deeper and corresponding to the "pre-industrial era".

Since the contents of elements in sediments depend strictly on their grain size, the enrichment factor (EF) is also used to assess the pollution. The factor eliminates a potential effect of differences in the grain size of the sediment surface layer and the sediments of geochemical background. The EF is calculated according to the formula:

$$\mathrm{EF} = \frac{M_{s(P)}}{M_{d(P)}} : \frac{M_{s(T)}}{M_{d(T)}} \qquad [8.2]$$

where:

$M_{s(P)}$ – concentration of chemical constituent in the sediment surface layer,

$M_{s(T)}$ – concentration of chemical constituent in the sediment layer of geochemical background,

$M_{d(P)}$ – concentration of a normalising agent in the sediment surface layer,

$M_{d(T)}$ – concentration of a normalising agent in the sediment layer of geochemical background.

The normalising agent may be a selected grain size fraction representing the content of the fine-grained particles (e.g. <0.02 mm) or metal – mostly Al or Fe, whose content in sediment does not depend on anthropogeonous sources, and is strictly associated with the grain size of the sediment and their natural chemical composition (see Appendix 4). The EF values, when close to 1, suggest that the analysed element is of natural (terrigenous) origin, whereas the factor values exceeding 1 show its enrichment as possibly anthropogenous in origin.

Tables 8.5 and 8.6 present variability in the values of the AF and EF factors for the surface layer of silt-clay sediments from the southern Baltic Sea. The concentrations of the analysed element at the depth of 18–20 cm under the sea bottom were assumed as the "geochemical background" values. In the central parts of the Bornholm and Gdańsk basins, where the sedimentation rate is 1 to 2 mm/year, a 20-cm thick layer of silt-clay sediments is deposited during a period of app. 100–200 years. Macroscopic observations and X-ray radiographs of the sediment cores revealed that contemporaneous biturbation processes generally do not reach layers deeper than 5–10 cm. So, the sediments that occur at 18–20 cm below sea bottom were generally deposited before intensive industrial development in the Baltic Sea catchment area and should not contain anthropogenous contaminations. Iron was used as a normalising factor.

For the southern Baltic Sea, the EF and AF values are similar. However, the procedure of normalisation makes the EF values slightly higher, emphasising the effect of anthropogenous activities on enriching the surface layer of the sea-bottom sediments with some trace elements. The values of AF and EF show that the surface layer is enriched with almost all trace elements.

The AF and EF values of **arsenic** vary within a very wide range: AF from 0.32 to 4.5, and EF from 0.28 to 2.96. The mean values of these factors for silt-clay sediments in the southern Baltic Sea are 1.06 and 1.14, respectively. There are only a few small areas where the surface sediment layers are distinctly enriched with arsenic. EF values of more than 2 were observed only at two stations in the Bornholm Basin, two stations in the Słupsk Furrow, three stations in the southern part of the Gotland Basin, and two stations in the Gdańsk Basin. Considerably larger are the sea-bottom areas where the AF and EF values do not exceed 1, which means

Table 8.5

Statistical parameters of the AF factor in the surface layer of silt-clay sediments in the southern Baltic Sea (based on Geochemical atlas of southern Baltic Sea, Szczepańska, Uścinowicz, 1994)

Area	Statistical parameter	As	Cd	Cr	Cu	Hg	Pb	Zn
Gdańsk Basin	n	21	21	22	22	10	22	22
	min.	0.64	0.90	0.47	0.68	0.63	0.72	0.85
	max.	1.71	2.40	1.88	2.47	3.50	3.00	2.98
	arithm. mean	1.00	1.40	0.96	1.23	1.63	1.40	1.52
	SD	0.30	0.47	0.29	0.41	0.84	0.57	0.47
Słupsk Furrow	n	5	5	5	5	2	5	5
	min.	0.50	1.00	0.78	0.81	1.25	1.11	0.98
	max.	4.50	1.00	1.24	1.40	4.00	2.64	2.07
	arithm. mean	1.63	1.00	0.98	1.09	2.63	1.71	1.48
	SD	1.63	0.00	0.20	0.24	1.94	0.68	0.45
Bornholm Basin	n	23	26	26	26	12	26	26
	min.	0.32	0.92	0.81	1.00	0.33	1.06	1.19
	max.	2.43	2.00	2.14	1.64	4.00	3.21	2.76
	arithm. mean	0.85	1.07	1.02	1.19	1.46	1.94	1.72
	SD	0.53	0.27	0.25	0.14	1.01	0.53	0.34
Eastern Gotland Basin	n	9	10	10	10	7	10	10
	min.	0.70	0.90	0.88	0.98	0.25	1.00	1.24
	max.	2.44	1.00	1.22	1.58	4.00	2.55	1.90
	arithm. mean	1.30	0.99	1.04	1.19	1.79	1.80	1.53
	SD	0.53	0.03	0.10	0.18	1.18	0.46	0.23
Southern Baltic Sea	n	61	65	65	65	33	65	65
	min.	0.32	0.49	0.47	0.68	0.25	0.68	0.85
	max.	4.50	2.40	2.14	2.47	4.00	3.21	2.98
	arithm. mean	1.06	1.16	1.00	1.19	1.63	1.69	1.59
	SD	0.66	0.37	0.24	0.27	1.02	0.59	0.39

that there is more arsenic in the sediments that are not anthropogenously contaminated than in those deposited contemporaneously. This can be explained by worse aerobic conditions of the sea-bottom waters observed in the last one hundred years. The oxygen-free sea-bottom waters show elevated concentrations of e.g. iron, manganese, arsenic and chromium that can migrate from the sediments to the water.

Chromium, similarly to arsenic, is rarely and to a small degree enriched in the surface layer of silt-clay sediments in the southern Baltic Sea. This metal occurs very often in larger amounts in the 18–20-cm depth layer,

Table 8.6

Statistical parameters of the enrichment factor (EF) in the surface layer of silt-clay sediments in the southern Baltic Sea; normalisation with reference to iron (based on Geochemical atlas of southern Baltic Sea, Szczepańska, Uścinowicz, 1994)

Area	Statistical parameter	As	Cd	Cr	Cu	Hg	Pb	Zn
Gdańsk Basin	n	21	21	22	22	9	22	22
	min.	0.71	0.67	0.60	0.69	0.72	0.73	0.79
	max.	1.85	3.57	1.78	2.30	6.45	3.11	2.98
	arithm. mean	1.18	1.64	1.10	1.41	2.11	1.65	1.77
	SD	0.30	0.64	0.24	0.34	1.75	0.68	0.49
Słupsk Furrow	n	5	5	5	5	2	5	5
	min.	0.56	0.66	0.74	0.92	2.08	1.50	1.36
	max.	2.96	1.66	1.33	1.55	2.63	1.85	1.63
	arithm. mean	1.45	1.10	1.03	1.14	2.35	1.69	1.49
	SD	0.91	0.40	0.21	0.24	0.39	0.14	0.11
Bornholm Basin	n	23	26	26	26	12	26	26
	min.	0.28	0.38	0.42	0.44	0.32	0.65	0.57
	max.	2.11	2.15	1.55	1.70	5.06	3.73	2.60
	arithm. mean	0.86	1.15	1.07	1.28	1.60	2.10	1.84
	SD	0.48	0.34	0.21	0.24	1.35	0.73	0.44
Eastern Gotland Basin	n	9	10	10	10	7	10	10
	min.	0.78	0.75	0.88	0.89	0.25	1.12	1.25
	max.	1.93	1.35	1.23	1.64	3.49	2.26	1.98
	arithm. mean	1.26	1.02	1.06	1.21	1.78	1.81	1.56
	SD	0.36	0.19	0.11	0.21	0.99	0.38	0.26
Southern Baltic Sea	n	60	64	65	65	32	65	65
	min.	0.28	0.38	0.42	0.44	0.25	0.65	0.57
	max.	2.96	3.57	1.78	2.30	6.45	3.73	2.98
	arithm. mean	1.14	1.32	1.09	1.31	1.84	1.85	1.75
	SD	0.55	0.56	0.22	0.30	1.31	0.67	0.44

which is referred to as the geochemical background. The mean AF and EF values calculated for the individual basins oscillate around 1. Only in one location in the southwestern part of the Bornholm Basin and in the southwestern part of the Gdańsk Basin (the Puck Bay) do these factors exceed 1.5.

Copper enriches surface sediment layers only to a slightly higher degree. The mean AF and EF values of copper in the southern part of Baltic Sea are 1.19 and 1.31, respectively. However, unlike chromium, values exceeding 1.5 occur in all the basins and over larger areas. The maximum EF values (2.3) were observed in the Puck Bay (SW part of the Gdańsk Basin).

In the surface layers of silt-clay sediments in the southern Baltic Sea, **cadmium** generally occurs in amounts close to the geochemical background value. The mean AF and EF values of cadmium are close to 1 in each basin. Higher mean values are recorded in the Gdańsk Basin where AF is 1.4 and EF is 1.64. The maximum AF values of 2.4 and EF values of 3.57 were observed in the Puck Bay. Values exceeding 2 occur in a few locations of the Gulf of Gdańsk and at one of the survey stations in the central part of the Bornholm Basin.

Mercury is an element which often occurs in the surface sediment layer in considerably higher amounts than in layers anthropologically uncontaminated. The mean AF and EF values of mercury in the silt-clay sediments of the southern Baltic Sea are 1.63 and 1.84, respectively. Considerable contamination with mercury occur in the southern part of the Bornholm Basin (EF 2.2–5.1) and in the southern part of the Gulf of Gdańsk (EF 1.49–6.45). AF and EF values exceeding 2 are also observed locally in the Słupsk Furrow and in the southern part of the Eastern Gotland Basin.

The amounts of **lead** in the surface sediment layer, like of mercury, are often much higher than those observed in the layers uncontaminated by human activities. The mean AF and EF values exceed 1.5 in all the basins. The largest areas, where these indices are higher than 2, occur in the Bornholm Basin; however, locally the contamination with lead was twice higher than its natural contents in the Gdańsk and Eastern Gotland basins.

Apart from mercury and lead, **zinc** is another element whose content in the surface sediment layer exceeds considerably the natural values observed in the sediments from the pre-industrial epoch. The mean AF and EF values of zinc in the silt-clay sediments of the southern Baltic Sea are 1.59 and 1.75, respectively. Insofar as the lead contamination was typical of the surface layer sediments in the southern Bornholm Basin, the sediments contaminated with zinc include not only these of the Bornholm Basin, but also those of the Gdańsk Basin. The maximum AF and EF values of zinc were found in the Puck Bay (SW part of the Gdańsk Basin). As opposed to lead and mercury, the Słupsk Furrow and the southern part of Eastern Gotland Basin are polluted with zinc to a less degree.

*

To sum up, it should be stated that the surface layer of silt-clay sediments in the southern Baltic Sea, especially in the Bornholm and Gdańsk basins, are clearly enriched with zinc, lead and mercury. The Gdańsk Basin, in addition to the above-mentioned metals, is also contaminated with cadmium and, to a small degree, with copper. However, despite the occasional high metal enrichment factors of the surface layer of sea-bottom sediments, the absolute contents of the metals do not exceed the standards assumed for sediments and soils considered as contaminated. Moreover, the sediments deposited 30–50 years ago contain more metals than the sediments deposited contemporaneously, which distinctly shows the decreasing inflow of contaminants into the Baltic Sea.

8.5. Distribution Pattern of Elements in Sediments Based on the Results of the Chemometric Analysis

The characteristics of the geochemical history of metals require the interpretation of the observed trends and functional relations based on thousands of measurement data obtained from the sediment material. For such a rich database, it is necessary to apply multi-variation computer techniques in order to limit a large number of variables to only a few, usually to three factors that are not correlated with each other (orthogonal). Those statistical methods are important and usable tools used to assess the layout and correlations among toxic metals in the marine ecosystems.

In order to confirm measurement data processed by using the multi-variation technique, the enrichment factor (EF) was calculated. As a terrigenic normaliser, ytterbium (Yb) was applied (apart from Al), because it is not included into the contents of pollutions, unlike, for example, lanthanum (La) which is a catalyst used in cracking and reforming of petroleum, as well as in desulphurisation. In order to estimate if the geochemical composition of the sedimentary material is modified during its riverine transport, the obtained results of the element contents in the tested samples were normalised in relation to the reference material, i.e. clay shales (McLennan, 1989).

The data on the contents of elements in the sedimentary material were chemometrically processed by using the following techniques: Factor Analysis (FA), Principal Component Analysis (PCA), or Endmember Analysis (EMA) to reduce the large number of variables (chemical elements) to two or three orthogonal factors or components not correlated with each other. If the sets of points are separated on a three dimensional scatter plot (e.g. F1/F2) corresponding to the sediment samples (when the Ev eigenvalues for several factors F are higher than 1), we deal with a significant variability between the samples, which depends on many factors. The separation of the object samples is constrained by the chemometric distribution of the "loadings", i.e. the analysed elements known as descriptors.

Chemometric techniques made it possible to assess the distribution pattern and to identify potential sources of origin of the elements in the study area.

8.5.1. Horizontal Distribution Pattern of Elements in Surface Sediments

Southern Baltic Sea

The distribution of points corresponding to the numbers of samples on a plot in a system of the Cartesian coordinates F1/F2/F3 is presented in Figure 8.13. Samples taken at stations located far from the coasts, known as "open sea" samples (no. 25–29), are grouped in the upper left part of the plot (Fig. 8.13a) as opposed to the group of points located on the other side corresponding to the samples taken from the Vistula River mouth (no. 6, 7, 16, and 17). The other points are arranged between the "open sea" and "river mouth" sets, which suggests a transitional character of this sea water reservoir that is less exposed to the effect of the alluvial material, i.e. of Vistula origin (Szefer *et al.*, 1995).

Figure 8.13b images a factorial distribution profile of loadings, i.e. the elements in the system of three-dimensional scatter plot. The layout of these points corresponds to the location observed for the samples (objects). In the factorial plot, elements such as K, Mg, Ca, Na, and Sr form a cluster that is distinctly separated from the second group composed of Zn, Cd, Ag, Cu, Cr, Pb, chlorophyll-a, and Fe. The location of the latter (characterised by lower F3 values) enables us to identify the samples taken from the region of the Vistula River mouth (characterised also by lower values F3). The set of points (of higher F3 values) located in the upper part of the plot represents typically "open sea" samples (also characterised by higher F3 values).

In order to recognise labile, easily bioavailable forms of elements in the bottom sediments, analyses were carried out to determine the contents of elements in the extracts of labile sedimentary fraction in 1 M HCl. The obtained chemometrical data are given in Figure 8.14. We can observe a considerable similarity between the factorial distribution of the samples and elements given in Figures 8.13 and 8.14. The co-occurrence of points corresponding to the elements such as Zn, Cd, Pb, Cu, Ag, and P accompanied by Mn and Fe (Fig. 8.14b) allows the conclusion that the Fe–Mn matrix is responsible for bonding labile, easily extractable forms of Zn, Cd, Pb, Cu, Ag, and P in the estuary area. These elements probably adsorb on the surface of particles of amorphous Fe and Mn oxides / hydroxides in the area of hydrological front where the Vistula waters are mixed with brackish bay waters (Szefer *et al.*, 1995). Since heavy metals occur in marine water as negatively charged soluble complex compounds (Li, 1981a, b), they tend to bind with positively charged particles of amorphous Fe/Mn hydroxy-oxides, which is reflected in a correlation of Fe and Mn with the above-mentioned heavy metals.

In the inner part of the Gulf of Gdańsk Rb, Co, Li, Ni, and Cs show the statistically significant correlation with Al, which allows us to conclude that they are mainly adsorbed on the surface of aluminosilicate particles (Szefer *et al.*, 1995). Since alkaline and rare earth elements occur in marine water as positively charged simple ions (Li, 1981a, b), they willingly bond with negatively charged particles of aluminosilicates, which can explain their factorial co-existence with Al and K (Fig. 8.14b).

Amongst macro-elements, K, Na, Mg, Ca, and Sr occur in the highest concentrations in open-marine sedi-

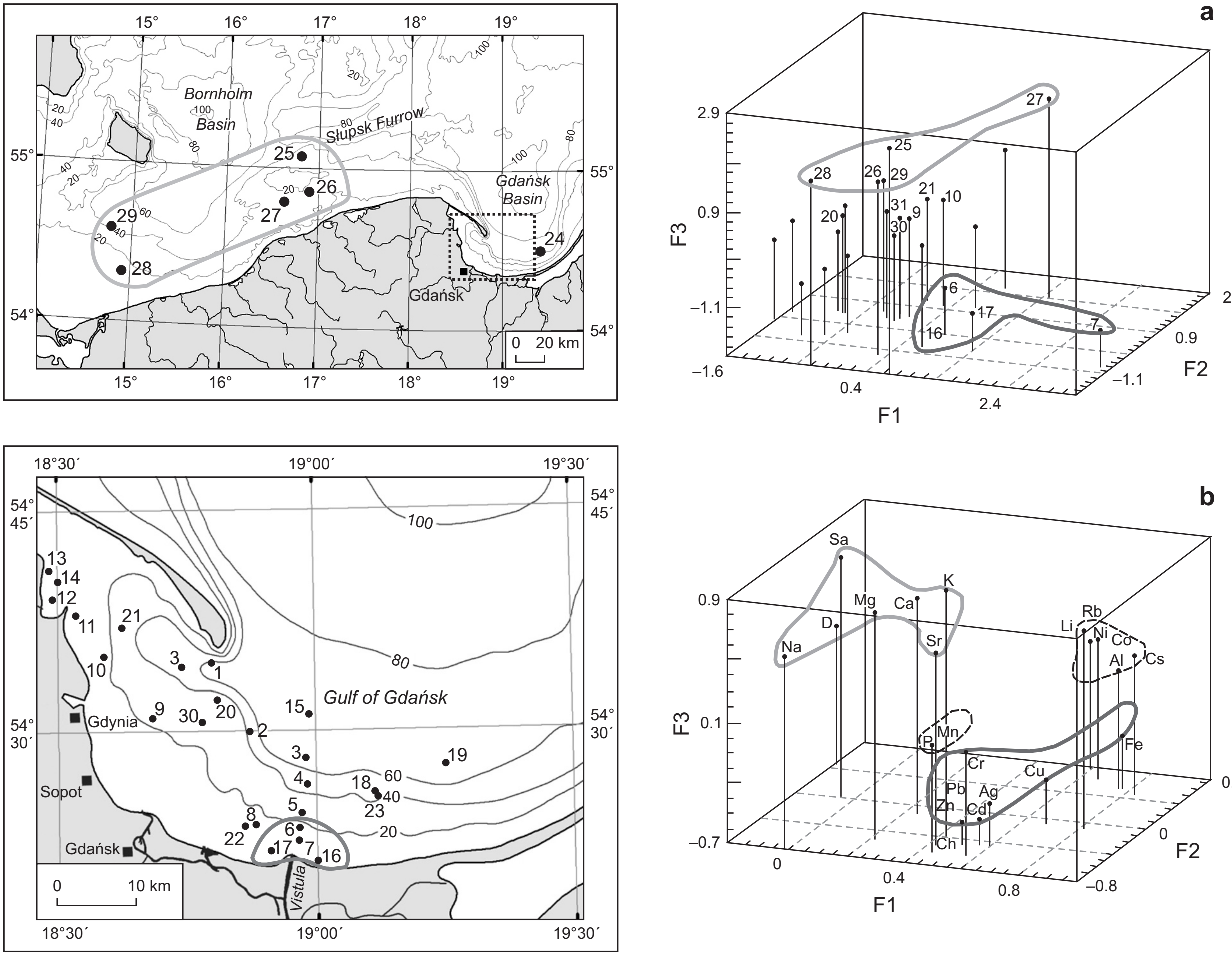


Fig. 8.13. Location of survey stations in the southern Baltic Sea from where sediment samples were taken, and a 3D diagram of the object sample layout (a) and loads represented by individual variables (b) obtained for samples of the <0.080 mm grain-size fraction, digested in a mixture of concentrated HNO_3 and $HClO_4$ (Szefer *et al.*, 1995)

Samples were numbered in accordance with the numeration of the survey stations of sampling. Sa – salinity, D – water depth, Ch – chlorophyll-a. Samples marked as 6, 7, 16, and 17 come from the Vistula estuary, samples numbered 25–29 are taken from open-marine Baltic waters

ments, suggesting their origin from more saline waters than the bay waters of the southern Baltic Sea.

The Vistula Lagoon

Figure 8.15 shows a distribution pattern of points corresponding to the individual samples in the F3–F1 coordination system. The sets of samples taken in the western (1–11), eastern (21–25), and central (12–20) parts of the lagoon can be specified. The samples representing the western part, including the object that corresponds to the Szkarpawa River (26), are characterised by the highest factorial values of F1 and F3, which means that this area is clearly affected by anthropogenous material of fluvial origin. On the other hand, these samples show the highest contents of Zn, Pb, and Cd (the highest F3 values) as well as Ni, Co, Bi, Cu, Cs, Rb, Ag (the highest F1 values). The objects in the eastern part of the Vistula Lagoon are

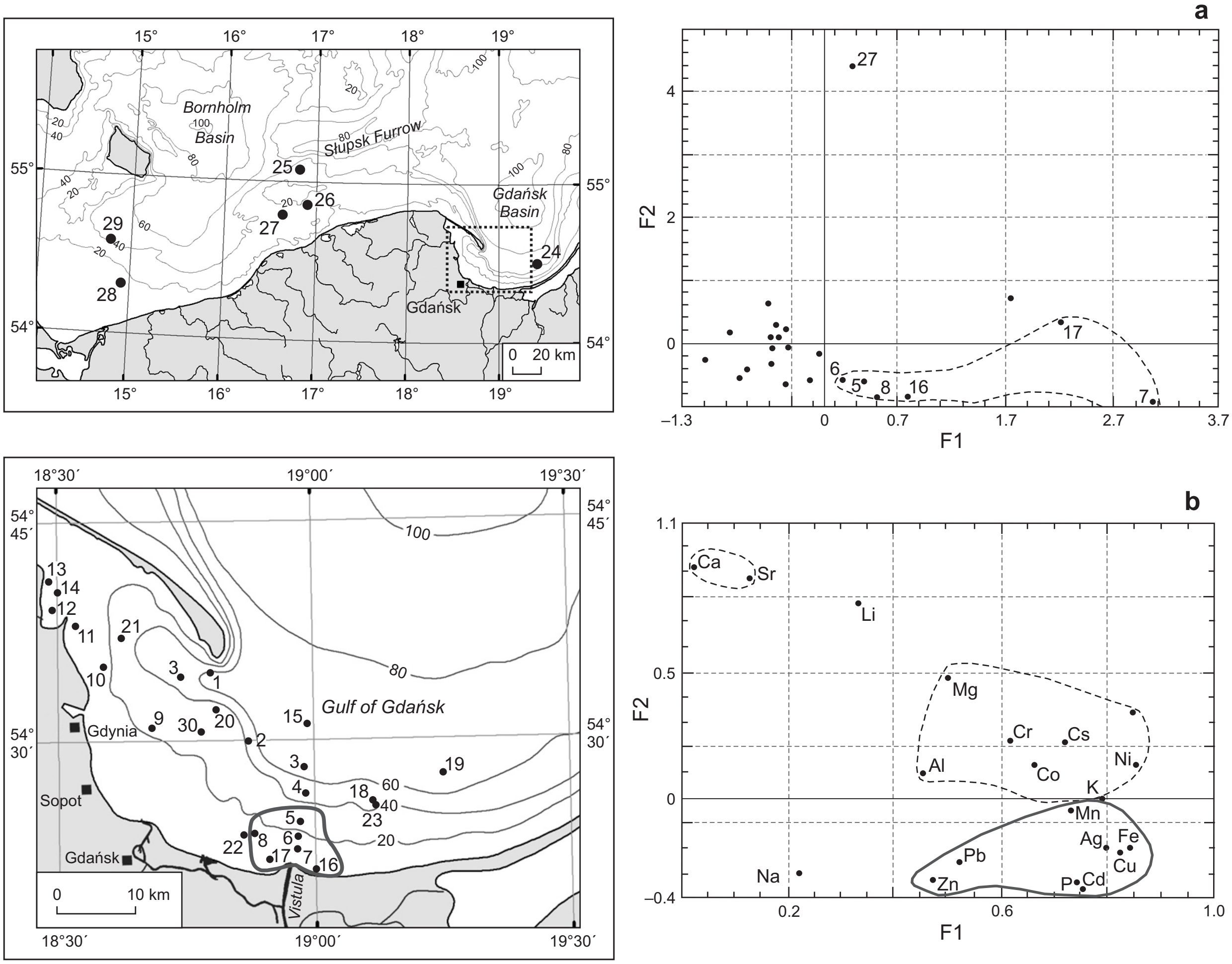


Fig. 8.14. Diagram of factorial layout of sample objects (a) and loads represented by individual variables (b) in the Cartesian coordinate system F1 and F2 for extracts (in 1 M HCl) of labile fraction from bottom sediment (grain-size fraction <0.080 mm) (Szefer *et al*., 1995)

grouped near the F1 zero line and correspond to the values of F3 ≤0. In turn, the samples that represent the central part of the lagoon are located in the left quarter of the plot (lowest F1 and F3 values). The elements responsible for such regional diversification are Ba and Yb (lowest F1 values) as well as Sr and As (lowest F3 values).

The distribution pattern of the objects probably depends on the geographical features of the study areas in the Vistula Lagoon, reflecting a higher sedimentation rate of the clay fraction in the sedimentary material at the front of the lagoon.

Samples taken from the Szkarpawa River and the western part of the Vistula Lagoon are marked by higher Zn, Pb, and Cd contents. It means that this area is significantly affected by the discharge of anthropogenous material of fluvial origin. The samples taken in the central part of the lagoon show co-occurrence of Yb with other elements. Ytterbium is a typical terrigenous element, which allows the conclusion that the accompanying elements in the region are also of natural origin.

The analysed elements are arranged in a series according to their decreasing EF values: Ag (10), Sb (7.5), As

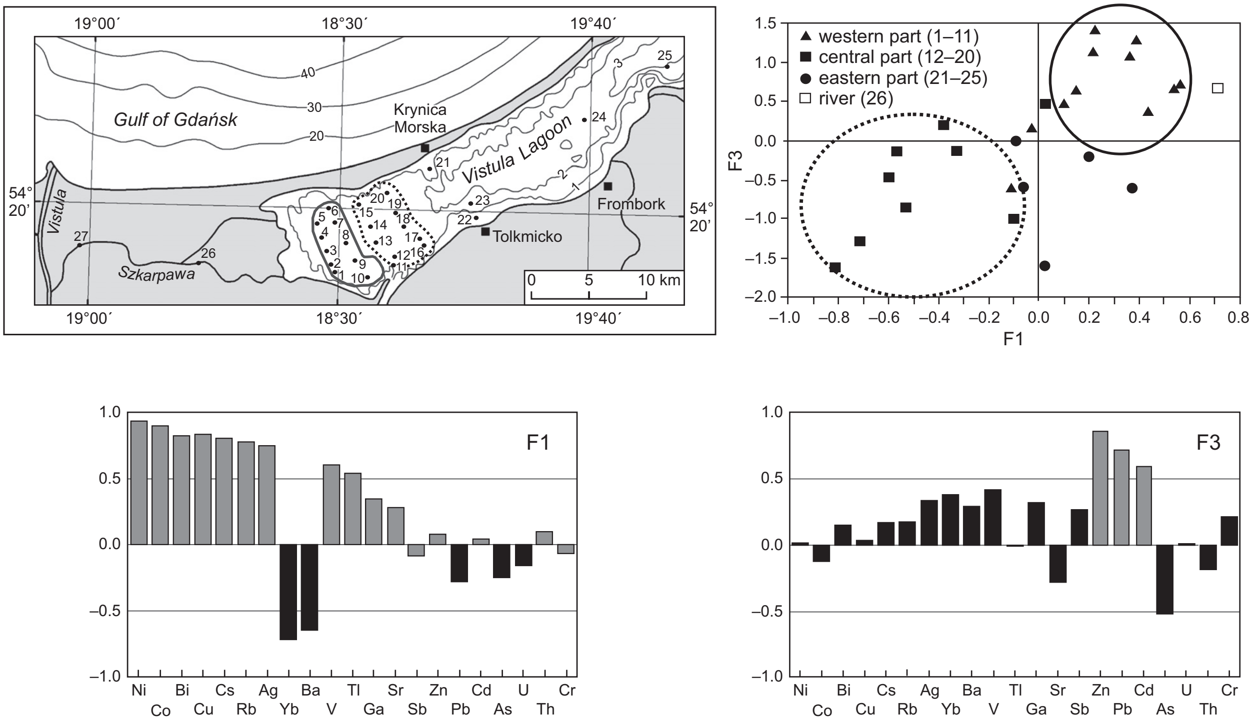


Fig. 8.15. Location of survey stations in the Vistula Lagoon (territory of Poland) from where sediment samples (fraction <0.063 mm) were taken, and the Cartesian coordinate system F1 and F3 for the objects of samples (numbers 1–26) grouped in three clusters with reference to the western, central and eastern parts of the lagoon (including a sample taken from the Szkarpawa River) and loads representing 21 chemical elements (Szefer *et al.*, 1999)

(5.8), Cd (5.2), Pb (3.7), Zn (2.3). It means that the elements with EF >1 undergo a significant accumulation in sediments with reference to their natural geochemical composition (Szefer *et al*., 1999).

The contents of rare earth elements (REE) normalised with reference to the chemical composition of shales suggest that the deposited sedimentary material was not significantly modified during its migration as a suspended solid with riverine runoff. We observed only inconsiderable depletion of the analysed deposits in HREE elements, i.e. those marked by higher atomic mass with reference to LREE (of lower atomic masses). It means that some of the HREE elements undergo a leaching process from the suspension during riverine transportation, but only to a small degree. The redox processes do not play any significant role in the functioning of REE either, which was demonstrated based on the lack of clear anomalies in the distribution of the elements sensible to changes in redox potential, i.e. Ce and Eu (Szefer *et al*., 1999).

Szczecin Lagoon

Taking into account the distribution pattern of the object scores and loading values, three main areas corresponding to their geographic locations can be distinguished (Glasby *et al*., 2004). A factorial plot (Fig. 8.16) shows the groups of points corresponding to the different location of samples. The set of objects representing the western part of the lagoon (2–5, 7–9, 19) is located in the right part of the diagram (marked by high F1 values). The group of points also described by high loadings corresponds to Pb, Cd, Cu, Zn, Co, Ni, V, Mn, Sb, and Al. It means that sediments in this area of the lagoon are significantly affected by the riverine load transporting particles of specific suspended solids that are rich in these chemical elements.

Whereas the group of points that correspond to the samples of sediments taken in the eastern part of the lagoon (6, 11, 12, 15–17, 21) is situated in the left part of the plot and is described by lower F1 values. The elements that control such a regional location of the objects are Yb, Th, U, and Sr.

The points that correspond to the north-western part of the lagoon (10, 20) are located in the central part of the plot between the extreme sets of points. The location of the two samples overlaps with the location of Mo. The sample distribution pattern reveals a high coincidence with the chemometric distribution published by Osadczuk and Wawrzyniak-Wydrowska (1998), illustrating the distribution of the individual geochemical facies.

The factorial isolation of the western part of the lagoon with high concentrations of Pb, Cd, Cu, Zn, Co, Ni, V, Mn, and Sb suggests deposition of the riverine originated suspension composed mainly of particles of specific geochemical contents (so-called fluffy material), marked by a high ability to accumulate heavy metals. Based on the results of the multi-variance analysis, Pempkowiak *et al*. (2005) described the effect of different environmental factors on the properties of this type of sediment in the regions of the Odra River mouth, Pomerania Bay and Arkona Basin.

In turn, the distribution pattern of the object scores for the eastern part of the Szczecin Lagoon, assigned to the elevated levels of Yb accompanied by Th, U, and Sr, shows unequivocally the terrigenous origin of the sedimentary material. Mo, probably mainly of biogenic origin, is an identifier for the north-western part of the tested area.

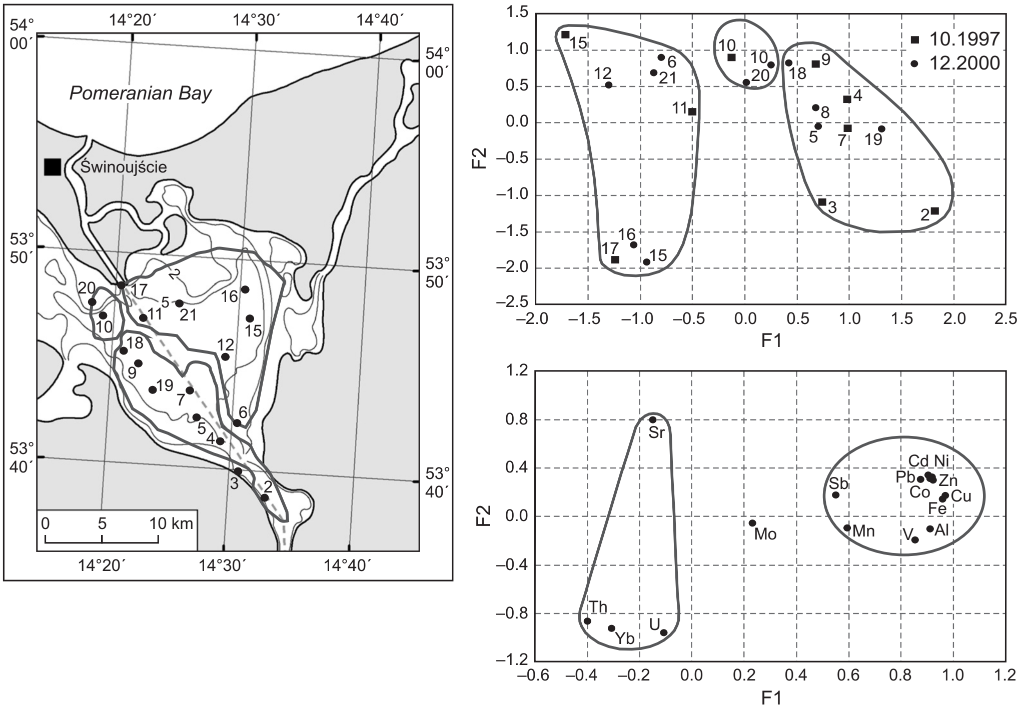


Fig. 8.16. Location of survey stations in the Szczecin Lagoon from where bottom sediment samples (fraction <0.063 mm) were taken, and the Cartesian coordinate system F1 and F2 for the objects of 21 samples grouped in clusters with reference to the western, eastern and north-western parts of the lagoon and loads represented by 16 chemical elements (Glasby *et al.*, 2004)

It has been stated that the EF values decrease according to the following series: S (45), Cd (31), Zn (18), Pb (15), Sb (11), P (5,3), Mn (3,1), Cu (1,9), Cr (1,6), Ba (1,4), U (1,3), Th (1,3), Mo (1,3), Si (1,3). It points out that S, Cd, Zn, Pb, Sb, P, and Mn show the highest level of accumulation in sediments.

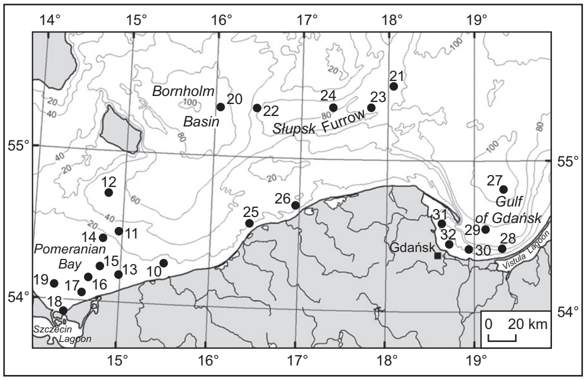
Based on normalised measurement data obtained for REE, it has been shown that suspended solids transported with the waters of the Odra River, like in the case of the Vistula River material, do not undergo any significant transformation of its geochemical composition (Glasby *et al*., 2004).

The Southern Baltic Sea including the Vistula Lagoon and the Szczecin Lagoon

The element contents in sediments of the southern Baltic Sea, including the Vistula and Szczecin lagoons, have been chemometrically processed by using two multivariate techniques, i.e. the Factor Analysis (FA) and Endmember Analysis (EMA) (Szefer, 2002; Gełdon, 2004).

Figure 8.17 gives the factorial distribution pattern as a three-dimensional scatter plot of F1-F2 for the objects and elements of individual regions of the southern Baltic Sea, i.e. the Pomerania Bay, Gulf of Gdańsk, Słupsk Furrow and Bornholm Basin, including the Vistula and Szczecin lagoons.

Points corresponding to sediment samples in the Szczecin Lagoon form a separate cluster (high F1 values) closely adjoining the group of points assigned to the Pomerania Bay. However, the samples taken in the Vistula Lagoon (low F1 values) are located close to the points of the Gulf of Gdańsk (Fig. 8.17a). The diagram suggests large differentiation in the geochemical sediment material taken in the Vistula and Szczecin lagoons. The similarity in the factorial distribution pattern of samples taken from the Szczecin Lagoon and, Pomerania Bay, as well as from the Vistula Lagoon and Gulf of Gdańsk can be explained by the fact that both the lagoons and the corresponding bays are parts of the estuaries of the Odra and Vistula rivers. The chemical elements critical for distinctness between samples taken from the Szczecin and Vistula lagoons (Fig. 8.17b)



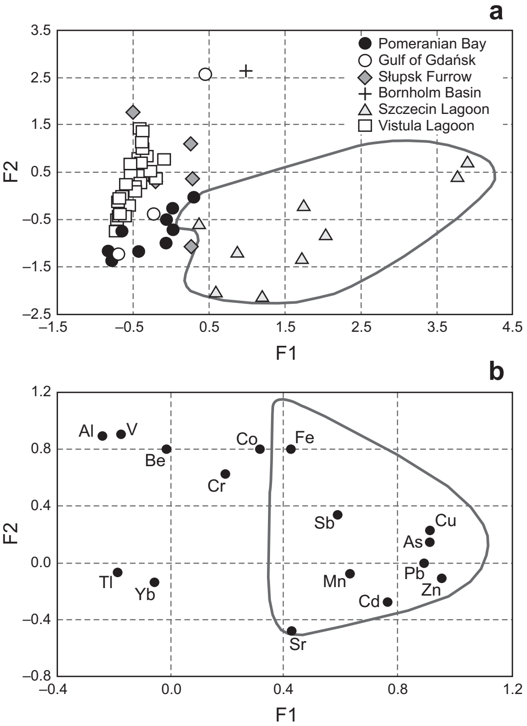


Fig. 8.17. Location of survey stations in the southern Baltic Sea, including the Vistula and Szczecin lagoons, from where bottom sediment samples were taken, and diagrams of object sample layout (a) and loads represented by individual variables (b) in the Cartesian coordinate system F1 and F2 for samples of sea bottom sediments (<0.063 mm fraction) from individual regions of the southern Baltic Sea (Szefer, 2002; Gełdon, 2004)

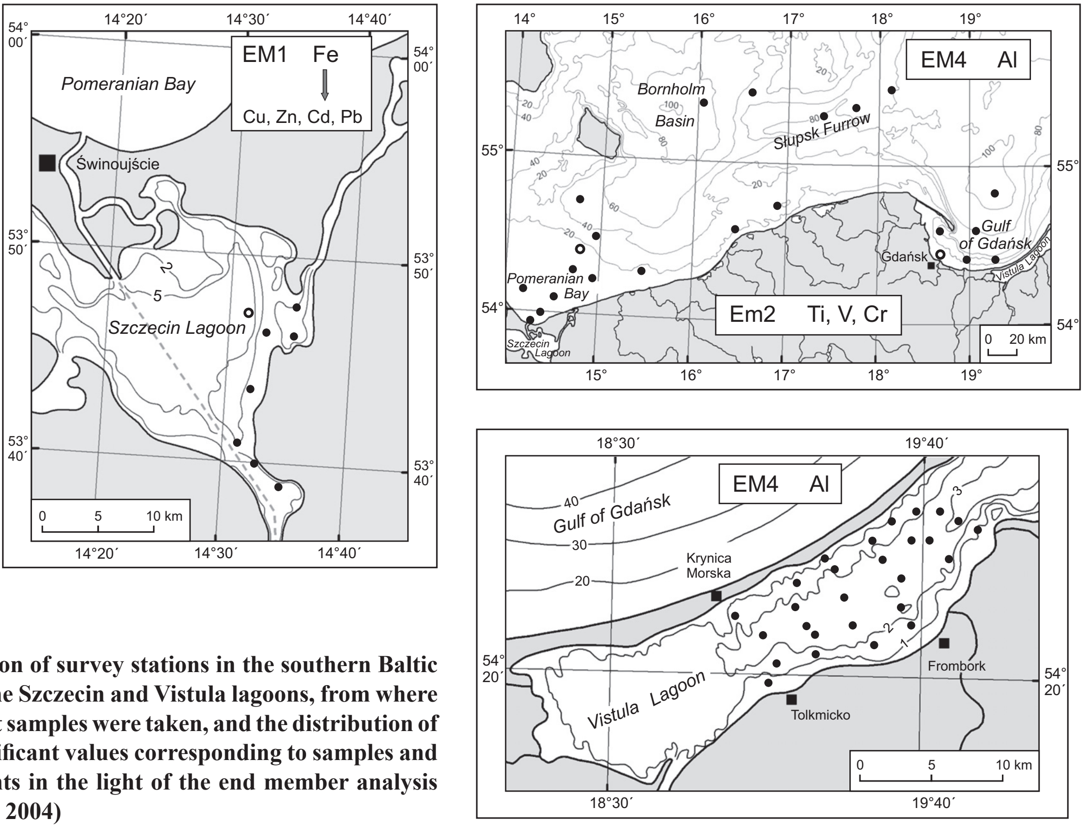


Fig. 8.18. Location of survey stations in the southern Baltic Sea, including the Szczecin and Vistula lagoons, from where bottom sediment samples were taken, and the distribution of statistically significant values corresponding to samples and chemical elements in the light of the end member analysis (EMA) (Gełdon, 2004)

are, respectively: Zn, Cu, As, Pb, Cd, Sb, Mn, Fe, and Sr (high F1 values) and Al, V, Tl, Be, and Yb (low F1 values). Considering the fact that Yb and Al are terrigenous elements, whereas Cd and Pb belong to the elements potentially anthropogenous, the Szczecin Lagoon, unlike the Vistula Lagoon, is the most contaminated reservoir of the southern Baltic Sea (Szefer, 2002).

The above results of the factorial analysis (FA) were confirmed by another chemometric technique (EMA) through analysis of sedimentary samples taken during a different survey period from the southern Baltic Sea. Figure 8.18 shows a distribution pattern of statistically significant members EM1 (for Cu, Zn, Cd, and Pb in sediments of the Szczecin Lagoon) and EM4 (for Al in sediments of the open sea waters of the southern Baltic Sea and Vistula Lagoon). It means that, in the light of the FA and EMA techniques, the Szczecin Lagoon sediments, showing a fluffy material structure, (Löffler *et al*., 2000; Emeis *et al*., 2002; Christiansen *et al*., 2002; Glasby *et al*., 2004; Gełdon, 2004) are enriched with Cu, Zn, Cd, and Pb, whereas the sediments deposited in the Vistula Lagoon and open sea waters of the southern Baltic Sea are dominated by elements of terrigenous origin.

Figure 8.19 suggests that the distribution pattern of rare earth elements (REE) does not significantly differ from the contents of REE in the reference material, i.e. clay shales from the North American Shale Composite (NASC). It means that the sedimentary material transported by the Vistula River does not undergo any geochemical transformations. The Ce/Eu concentration ratio allows us to suppose that the redox processes do not play any considerable role in fractionation of rare earth elements during their alluvial transportation (Glasby *et al*., 2004).

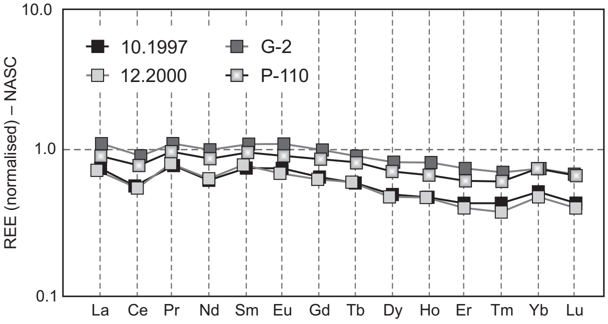


Fig. 8.19. Mean concentrations of rare earth elements in sediment samples taken at survey stations G-2 and P-110 (Gdańsk Basin) and in the Szczecin Lagoon, normalised in relation to their contents in the reference material, i.e. North American Shale Composition (NASC) (after Glasby *et al.*, 2004). The concentration values in the reference material were taken from the study by McLennan (1989)

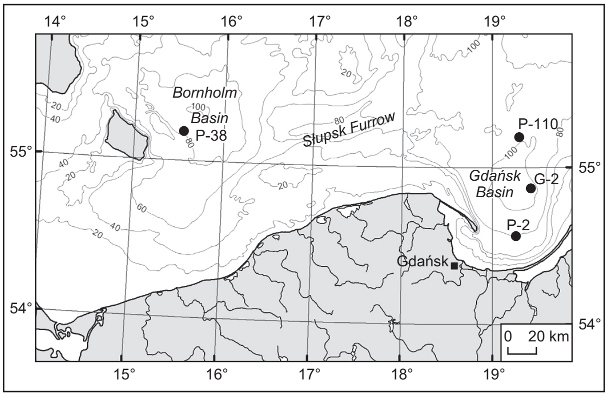
8.5.2. Vertical Distribution Pattern of Elements in Bottom Sediments

The vertical distribution pattern of the analysed elements in sediment cores is marked by a significant variability (Szefer *et al.*, 1998). For example, the distribution of Ag, Cd, Zn, Pb, Cu, and Sb shows an increase in their concentrations towards the surface layers in the coastal area of the Gulf of Gdańsk. The core taken in the Gdańsk Deep also shows higher contents of Cd, Zn, Pb, Cu, and Sb from the deep layers to the surface (Glasby *et al.*, 2004).

Figure 8.20 presents the location of survey stations and the list of objects numbered according to the depths of samples in four cores (from the surface sediment layer towards deeper core segments).

On the basis of the principal component analysis (PCA) made for sea bottom sediment cores taken from the Gulf of Gdańsk and open waters of the southern Baltic Sea, it was possible to differentiate elements assuming that the organic carbon (C_{org}) is representative for the organic matter, whereas aluminium (Al) is a typical element of terrigenous origin (Szefer, 1998). To illustrate the correlations between the location of the core segments and the analysed elements, corresponding plots were prepared in the PC2/PC1 and PC3/PC1 systems (Fig. 8.21).

Since elements, such as Fe, Ti, K, Th, Co, and Ni (elevated PC1 values) are situated near Al, it means that they are of terrigenous origin, whereas N, Cu, Pb, Zn, Cd, and partially P (lower PC1 values) accompanied by C_{org} (Fig. 8.21a) can be classified as biogenic (Szefer, 1998). Both groups refer to the surface (exposed to the effects of anthropogenous factors) and bottom (formed in pre-civilisation epoch) segments of the analysed four sediment cores (Fig. 8.21b). The obtained clusters enable us to identify elements penetrating into contemporarily



Sample number	Sample depth in core [cm]	Sample number	Sample depth in core [cm]
	P-2		**P-110**
2	0.7 – 2.0	1	0.0 – 1.6
4	3.0 – 4.0	3	2.6 – 3.9
6	5.0 – 6.0	5	5.5 – 7.4
7	6.0 – 7.0	6	7.4 – 9.2
8	7.0 – 8.0	7	9.2 – 11.4
10	10.0 – 12.0	8	11.4 – 14.1
11	12.0 – 15.0	9	14.1 – 17.8
12	15.0 – 20.0	10	17.8 – 21.5
13	20.0 – 25.0	11	21.5 – 25.8
14	25.0 – 30.0	12	25.8 – 31.3
		13	31.3 – 34.8
	G-2		**P-38**
1	0.0 – 1.0	1	0.0 – 0.7
2	1.0 – 2.0	2	0.7 – 1.8
4	3.0 – 4.0	5	5.0 – 6.2
5	4.0 – 5.0	6	6.2 – 8.1
6	5.0 – 6.0	7	8.1 – 9.7
10	9.0 – 10.0	8	9.7 – 12.1
11	10.0 – 12.0		
12	12.0 – 15.0		
13	15.0 – 20.0		
14	20.0 – 25.3		

Fig. 8.20. Location of survey stations in the southern Baltic Sea from where bottom sediment core samples were taken, and a list of object numbers corresponding to the depths of samples from cores (Szefer, 1998)

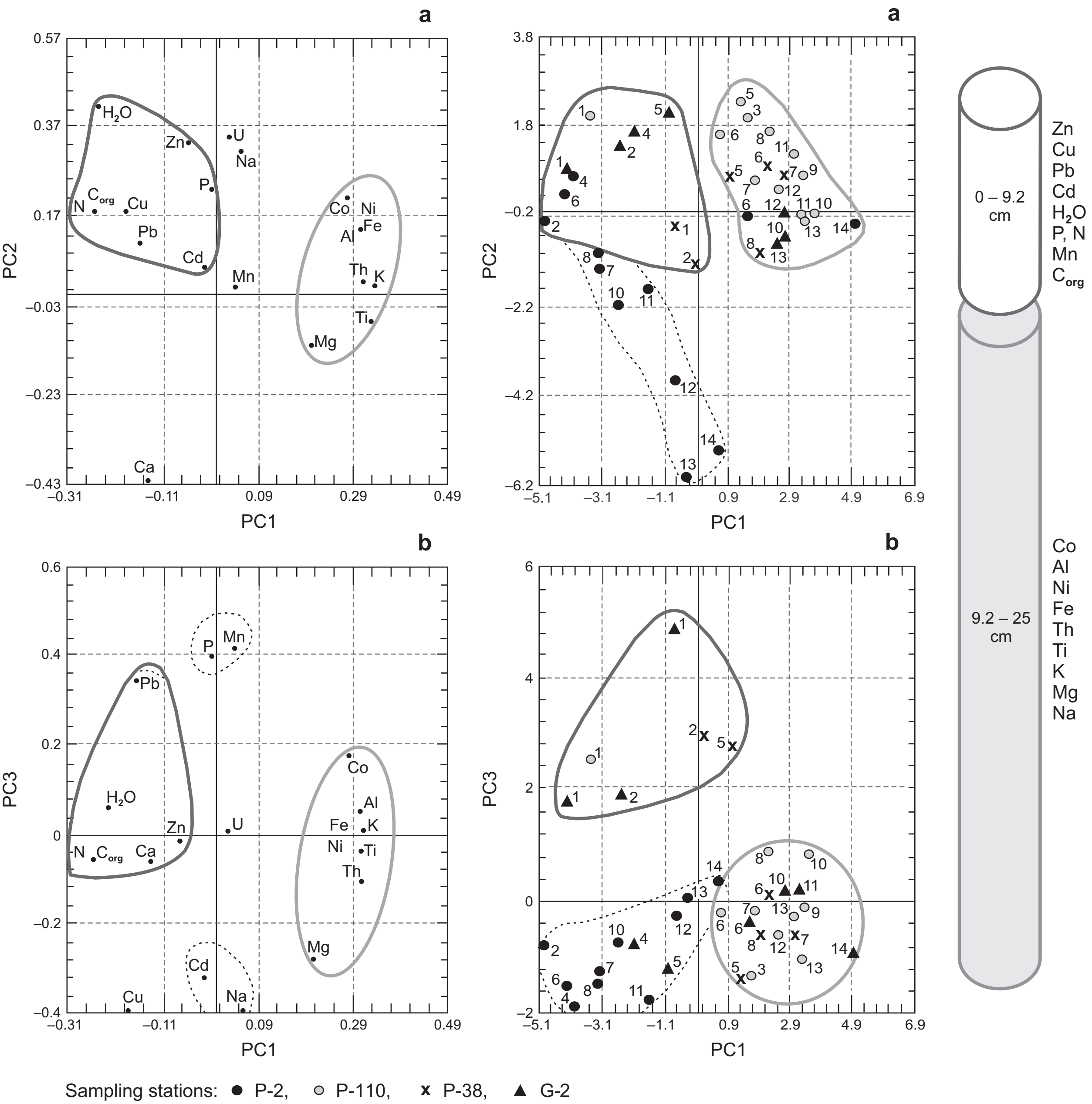


Fig. 8.21. Layout of the sample objects and loads corresponding to sequential segments of bottom sediment cores from the southern Baltic Sea (Szefer, 1998)

The objects of samples from survey stations P-2, P-110, P-38 and G-2 were numbered according to the numeration given in Fig. 8.20

deposited surface sediment layers mainly as a result of human economic activities. Strictly speaking, the surface sediment segments (marked with lower object numbers), contemporarily deposited in the civilisation epoch, are closely correlated with biogenic elements, probably of anthropogenous origin

The AF values of Cu, Pb, Zn, and Cd, exceeding 1, confirm the assumption that heavy metals penetrated into the system of the Gulf of Gdańsk as a result of human economic activities (Szefer, Skwarzec, 1988).

The deeper sediment segments, deposited in the pre-civilisation epoch, represent the natural contents of the Earth's crust (geochemical background); hence they are exclusively represented by the elements of natural terrigenous origin. The atypical distribution of points (Fig. 8.21b) corresponding to the sequential segments of the core P-2 taken from the central part of the Gulf of Gdańsk, reflects the occurrence of sedimentary material abundant in calcium carbonate (from 22.5 to 37.2 mg Ca/g in surface and bottom layers, respectively; Szefer, Skwarzec, 1988).

A similar profile of the vertical distribution pattern of elements in sediment cores of the Gulf of Gdańsk was observed in the samples taken in 1991 (Szefer *et al*., 1998). It was found that the Ag, Cd, Zn, Pb, Cu, and Sb concentrations generally increased towards the surface sediment layer in the coastal areas of the gulf. In one core, the highest levels of the tested metals were observed at the depth of 10–15 cm under the sea bottom. Anomalies of significant variability in the concentrations observed in the surface (0–5 cm) and slightly deeper layers (5–10 cm) of the sediment core can be associated with the reduced inflow of heavy metals to the Gulf of Gdańsk after 1980 owing to the economic crisis, i.e. a considerable reduction in industrial activity. The emission of chemical pollutants decreased at that time, which was reflected in lower metal concentrations in the 0–5 cm sediment surface layer that developed in the 1980s (Szefer, 2002).

The lack of distinct stratification of the concentrations in the core taken on the outskirts of the Vistula River mouth results from both a very high sedimentation rate and an intense process of mixing of sediment layers in a shallow-water area. The sedimentary material accumulated during several tens of years, i.e. in a period of intense economic activity in the catchment area (Szefer *et al*., 1996, 1998; Szefer, 2002), was exposed to the process of intense turbulence which mixed the layers of the core down to a depth of 20 cm. This process was associated with very dynamic conditions leading to a higher sedimentation rate of up to 7.7 mm/year (Szefer, 2002). Disturbances in the vertical stratification of sedimentary material induced by turbulences make it impossible to trace long-term changes in the metal inflow in the Vistula mouth.

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Chapter 9

PERSISTENT ORGANIC POLLUTANTS IN THE BALTIC SEA SEDIMENTS

Persistent organic pollutants (POPs) are organic compounds resistant to environmental chemical, biological and photolytic degradation. They are widespread in all elements of the environment. In addition to their persistence in the environment, some of these compounds are characterised by high vapour pressure and therefore can be transported in the atmosphere for long distances (Ramamoorthy, Ramamoorthy, 1997). Most of these compounds are poorly soluble in water and well soluble in fats, which results in easy penetration through phospholipid membranes and bioaccumulation in fatty tissues. These compounds may be bioaccumulated in human and animal tissues and undergo biomagnification in the trophic chain (Strandberg *et al*., 2000; Henny *et al*., 2003; Nfon *et al*., 2008). The exposure of people to POPs may cause death or health problems following the endocrine, reproductive and immune systems disorders. They may also cause neurobehavioral disorders and cancers.

The persistent contamination, most of all, includes: chloroorganic pesticides (aldrine, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, and toxaphene), polychlorinated biphenyls (PCBs) and dioxins (PCDDs, PCDFs). In the past, most of these organic compounds have been widely used in agriculture as pesticides, in electrical engineering as dielectric liquids and as preservatives for wood and fabrics, plasticizers agents for plastics, paints and lacquers as well as anti-ignitable additives for plastics (polyurethane foams). Although their production and trade were banned, the problem has not been eliminated. These compounds still remain in the environment (pesticide wastes, oils in transformers and condensers). Some of them, e.g. dioxins, are still unintentionally produced in some processing installations as undesirable by-products. Persistent organic pollutants (POPs) include also other toxic organic micro-pollutants, such as carcinogenic polycyclic aromatic hydrocarbons, some flame brominated retardants and organometallic compounds, such as TBT (tributyltin).

Because of the low solubility of POPs in water, these compounds are most often adsorbed on fine-grained material transported in the atmosphere or in the waters. Consequently, they are accumulated in sediment together with suspended solids (Abbt-Braun, Frimmel 1996; Lohmann *at al*., 2005). In surface waters, most POPs remain in sediment; however, some of them may enter the food chain. Generally, the concentration of organic pollutants in sediments is several hundred orders of magnitude higher than in the water above. The concentrations of organic micro-pollutants vary over a wide range. The content of POPs in sediments is generally determined to a large degree by organic matter concentration. Lower concentrations occur in sandy deposits, whereas organic silty clay contain many more (Sapota, 2006).

The Baltic Sea is one of the marine areas whose sediments are the most contaminated with persistent organic pollutants. High contents in fish, among others dioxins introduced the implementation of recommendations to limit human consumption of fish from the Baltic Sea. POPs are introduced to the Baltic Sea mainly by the atmosphere, entering river and point emission sources located along the coastline areas. POPs occur in waste waters discharged from some of the industrial plants (e.g. paper mills, industrial organic chemistry works, coking plants, metal smelters) and from municipal sewage.

According to HELCOM Thematic Reports No. 83, 98, 99 (2001a, b, 2002), there are numerous pollution sources in the Baltic Sea catchment area of which the POPs can be directly or indirectly introduced to the sea. In Sweden, important sources of POPs are sewage discharged from Göteborg and Stockholm, five paper mills that transport their waste waters to the bays of Hanö and Sundsvall, as well as a metal smelter in Skelleftehamn. In Finland, the sources of POPs are the municipal sewage of Helsinki, paper mills in Kotka (waste waters are discharged to the Gulf of Finland) and Kemi (waste waters are discharged to the Bothnian Bay), and a metal smelter in Harjavalta. In Germany, pollutants are brought by industrial and municipal waste waters from Beck, Wismar and Rostock to the Belts Sea, and from Greifswald, Neubrandenburg, Stralsund and Stavenhagen to the Arkona Basin. From Russia, industrial and municipal waste waters are discharged from St. Petersburg (aluminium smelter, paper mills) to the Gulf of Finland. In the Gulf of Gdańsk, a petroleum refinery and industrial and municipal waste waters of the Gdańsk–Sopot–Gdynia agglomeration area are the sources of contaminants. In Latvia, POPs are brought with the industrial and municipal effluents of Riga, and from paper-mills in Sloka (effluents are discharged through the Lielupe River). In Lithuania, the source of POPs is the Mažeikiai petroleum refinery, a marine terminal and the paper industry in Klaipėda. In Estonia, POPs are emitted into the environment mostly by paper and pulp plants in Kehra.

9.1. Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs), whose chemical compounds are very persistent, non-flammable, lipophilic and poorly soluble in water, had broad industrial applications from the 1930s to the early 1970s. They were used as dielectric liquids for capacitors and high voltage transformers, as working liquids in hydraulic actuators and heat exchangers, additives for paints and lacquers, plasticisers for plastics, filling materials in pesticides, as well as substances for coating surfaces, flame retardants used for wood impregnation and production of copying materials (Ramamoorthy, Ramamoorthy, 1997). After discovering their carcinogenic, toxic, teratogenic and immunosuppressive properties, as well as their bioaccumulative abilities, the production and use of PCBs were stopped in 1977, but they are still found in the existing equipment and products that remain in use.

Polychlorinated biphenyls are also released to the environment during coal combustion in power plants, hospital waste incineration, hard coal and wood combustion in the housing and municipal sector. Their occurrence in the natural environment also results from lubricant leakages from machines and vehicles, leakages from damaged heat exchangers and transformers, migrations from waste disposal damps, and the emission from certain processes. Due to their high vapour pressure, PCBs easily escape from surface waters, clarifier sludge, soils and waste disposal damps, and therefore their atmospheric deposition of both dry and wet precipitation plays an important role in the circulation of these contaminants in the environment (Offenberg, Baker, 1997; Eisenberg *et al*., 1998; Hsu *et al*., 2003; Totten *et al*., 2003). Polychlorinated biphenyls are detected in recent sediments in the contents of even up to several hundred mg/kg (Kannan *et al*., 1997). Alike other POPs, polychlorinated biphenyls usually concentrate in fine-grained sediments enriched with organic matter and their concentrations in sediments vary widely.

9.1.1. Polychlorinated Biphenyls in Surface Layer of Sediments

The Baltic Sea sediments show a very high variability in the PCB contents. Sediment samples collected near Stockholm showed the contents of 100 ng/g (Meili *et al*., 2000), in the Landsort Deep: 3–10 ng/g (Witt *et al*., 1997), in the Gotland Deep: 14.3 ng/g (Biselli *et al*., 2005). The PCB contents in surface sediments of the coastal zone of the Bothnian Bay range from 0.9 to 3.5 ng/g in the northern part of the gulf and from

4.1 to 6.5 ng/g in its southern part (van Bavel *et al*., 1996). Later studies revealed the concentration of PCBs in this area at 9–9.3 ng/g (Strandberg *et al*., 2000). In the Bothnian Bay, near Iggesund (where a paper mill is located), surface sediments contain above 4 ng/g of the total of 14 congeners (Olsson *et al*., 2004). The PCB content in sediment samples taken in 2001–2002 in the Gulf of Finland ranged from 2.5 to 4.1 ng/g, it indicates a reduction in the content (Pikkarainen, 2007). In the earlier tested deposits, higher concentrations of PCBs were determined (Jonsson, 2000). In the Gulf of Finland, very high level of PCBs in sediments was recorded near the estuary of the Kymijoki River. The load of PCBs in the contaminated sediments of the Kymijoki River was estimated at 2020 kg (Isosaari *et al*., 2002). In the western Baltic Sea, the highest concentration of PCBs (13 congeners) was observed in the estuary of the Warnow River (214 ng/g) and in the Wismar Bay (Dannenberg, Lerz, 1996). Very high levels were also noticed near the Peene River mouth (122 ng/g) (Müller, Schilling, 1998). Within the Arkona Basin, the content of the sum of 23 PCB congeners varied from <0.13 do 16.2 ng/g (Dannenberger *et al*., 1997). Research of Biselli *et al*. (2005) on the surface deposits in the Arkona Basin showed the contents of 5 ng/g of PCB (10 congeners). Similar contents (5.7 ng/g PCB, 33 congeners) in sediment samples taken in this basin were determined by Ricking and co-workers (2005).

Samples of surface sediments (0–2 cm) collected in the Baltic Sea in 1993 under the ICES/HELCOM Sediment Baseline Study project (Perttilä ed., 2003) showed the contents of PCBs (routine tests of 7 congeners: 52, 101, 118, 105, 153, 138, 180) varying from 4.1 to 54.7 ng/g (Jonsson, Kankaanpää, 2003), with a mean content of 16.5 ng/g. The study showed the highest PCB contents in the Baltic Proper sediments, especially in the East Gotland and Gdańsk basins, as well as in the bays of Kiel and Lübeck (Fig. 9.1). The results of this project indicate that the content of PCBs increases from the north towards the south. The tested sediments of the northern Baltic Sea contained an average of 213 ng/g C, expressed in terms of organic carbon, whereas the sediments in the southern part of the sea contained 382 ng/g C (Jonsson, 2000). This variability suggests a significant influence of atmospheric deposition of pollutants on the content of PCBs in the Baltic Sea sediments.

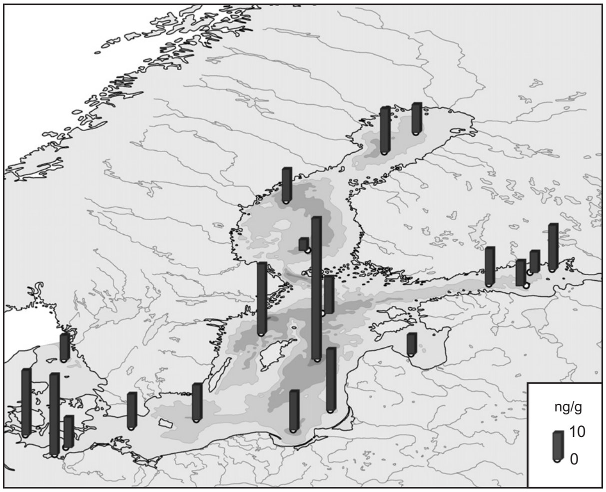

Fig. 9.1. Occurrence of PCBs in the surface sediments (0–2 cm) of the Baltic Sea; min. 4.1 ng/g, max. 54.7 ng/g d.w. (after Jonsson, Kankaanpää, 2003, revised)

The average content of PCBs (for 7 congeners) in the surface sediments of the Baltic Sea was estimated at 302 ng/g C, and in the Stockholm Archipelago deposits – at 183 ng/g C (Jonsson *et al*., 2000). The annual PCB deposition in the Baltic Sea sediments was calculated at 923 kg (7 congeners), and the amount of PCBs contained in the sediments of the Baltic Sea was about 30 t (Jonsson, 2000).

9.1.2. Polychlorinated Biphenyls in the Vertical Section of Sediments

Studies of sediments from the north-western Baltic Proper showed a variability in PCB contents in the vertical profile. The sediments dated to have been deposited in 1882–1938 showed low but significant PCB concentrations (7 congeners) ranging from 0.18 to 0.31 ng/g. In the sediments dated to have been deposited in 1954–1970, the range of PCB contents clearly increased and was between 0.5 to1.5 ng/g. The highest contents were noticed in the sediments from 1978: 10.9 ng/g. In 1985, the PCB content decreased and was 2.63 ng/g (Keller, Rappe, 1995). A decrease in the PCB content was observed in modern laminated silty deposits (Olsson *et al*., 2000). The sediments from 1970 showed the maximum content of PCBs: 60 ng/g

(Jonsson *et al*., 2000). Later research on the Baltic Sea sediments showed lower concentrations of PCB (7 congeners), which fluctuated within the range of 0.2–78 ng/g (Pikkarainen, 2007). The highest drop in the PCB content was observed in the sediments of the Gulf of Finland. Based on studies of PCBs in surface sediments of the Stockholm Archipelago, it was concluded that their contents expressed in terms of organic carbon were dependent on neither the depth nor the sediment type (Jönsson, Carman, 2000).

The research carried out under the ICES/HELCOM Baltic Sea Sediment Baseline Study project (Perttilä ed., 2003) revealed changes in the PCB contents in a vertical profile. The highest PCB content (92.84 ng/g) was observed in the North-Central Basin (station 180) in a sediment layer at a depth of the 5–7 cm below the bottom surface, whereas in surface layer of 0–2 cm, the content was 14.08 ng/g (Fig. 9.2).The PCBs content changes in the vertical profile in different ways, depending on the sedimentary basin of the Baltic Sea and its part. Similar maximum PCB contents occurred under the sea bottom in the Bornholm Basin (station 169), western part of the Western Gotland Basin (station 178), and in the Gulf of Finland (station 187). A continuous increase in the contents of PCBs (at least until 1993) was observed in the Gdańsk Basin (stations 169 and 170) and in the Eastern Gotland Basin (station 171).

Surface sediment samples taken in the southern part of the Baltic Sea in 1996–1999 contain from 1 to 149 ng/g (mean below 40 ng/g) of PCBs (7 congeners). After the flood in 1997, the increase in the PCB concentration was observed, but in the next years, it decreased again. The study of sediments from the Gdańsk Basin revealed that they contained 27 ng/g PCB (the sum of 6 congeners) – much higher than the deposits sampled near the Gdynia harbour (14 ng/g) and Vistula River mouth (7 ng/kg) (Kowalewska, Konat, 2001). Although both the Gdynia harbour and Vistula River mouth are the sources of PCB for the Gulf of Gdańsk, their elevated concentrations in the Gdańsk Basin sediments confirm that the fine-grained fractions and organic matter dominate in pollutant accumulation. Sandy sediments occur both on the outskirts of the Vistula estuary and near the Gdynia harbour.

The studies of sediments, carried out by Pazdro (2004) in the Gulf of Gdańsk, showed that the content of the indi-

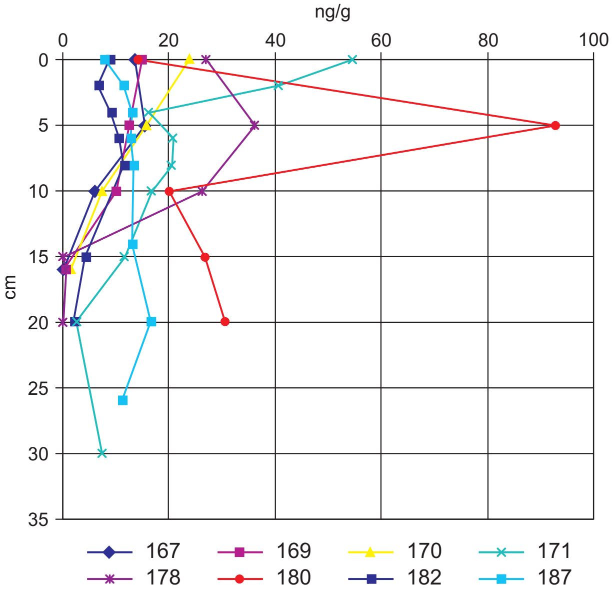

Fig. 9.2. PCB contents in vertical section of the Baltic Sea sediments (after Jonsson, Kankaanpää, 2003); for location of the station see Fig. 1.1

Table 9.1

Contents of polychlorinated biphenyls (PCB) and organic carbon (TOC) in the Gdańsk Basin sediments (based on the MASS Project data); for location of survey stations see Appendix 3 Fig. 1

Sample No.	PCB [ng/g]		Sediment type and the content of fraction >0.05 mm	TOC [%]
	lab. PGI	lab. BGS		
1/97	0.3	0.6	fine-grained sand (98%)	0.39
2/97	9.7	8.6	slightly sandy silt (17%)	3.41
3/97	17.1	16.1	silt (1.5%)	7.1
1/98	8.3	6.6	silt (1.1%)	5.02
2/98	4.2	4.0	slightly sandy silt (16.9%)	2.61
3/98	0.1	0.1	fine-grained sand (95.4%)	0.17

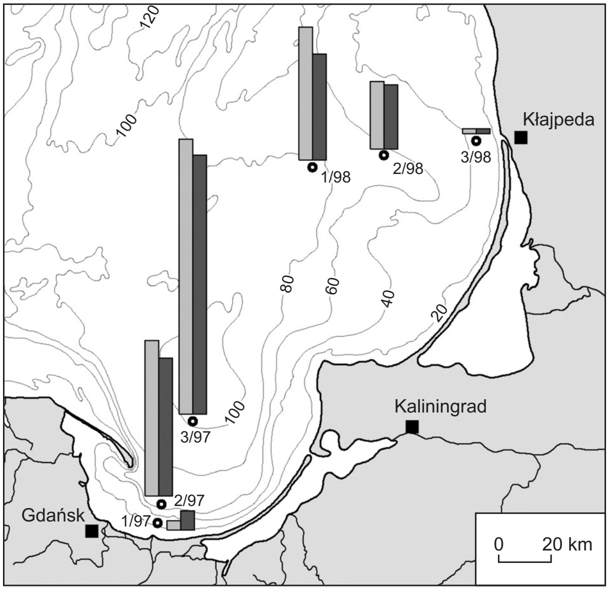

Fig. 9.3. PCB contents (7 congeners) in the surface sediments (0–2 cm) of the Gdańsk Basin sediments; min. 0.1 ng/g, max. 17.1 ng/g (based on MASS Project data)

Left bar – the analyses made by the Central Chemical Laboratory of the Polish Geological Institute; right bar – made by the laboratory of the British Geological Survey

vidual congeners of PCBs varied from 0.3 to 12.21 ng/g. Higher contents were usually observed near the fairway from Świnoujście to Szczecin in the Szczecin Lagoon. The highest concentrations were found in sediments of the Gdańsk Basin. The study by Sapota (2006) showed a lower content of PCBs in the Gdańsk Basin and the ΣPCBs content of 5 ng/g. In the western Baltic Sea sediments the values are 1.9–2.5 ng/g.

In 1997–1998, the contents of 7 congeners of PCB were determined in the surface sediments of the Gdańsk Basin under the joint Polish-Lithuanian-Dutch-British project Marine Environmental Assessment and Monitoring of Gdańsk Gulf Basin (MASS) (Uścinowicz *et al.* 1999). The analyses made for the same samples in the laboratories of the Polish Geological Institute and the British Geological Survey (BGS) revealed high coincidence of the achieved results. The highest concentrations of PCBs were observed in the southern, deepest part of the Gdańsk Basin, in silt-clay sediments enriched with organic matter (Fig. 9.3, Table 9.1). The PCB contents in the sediments of the Lithuanian part of the Gdańsk Basin is about twice lower that in the Polish part, including both silty and sandy deposits.

Lower contents of PCBs in the sediments from the northern part of the Gdańsk Basin (samples 1/98, 2/98, 3/98) can be only partly explained by the lower content of organic carbon because these differences are lower than for PCBs. It is particularly distinctly marked in the sand samples taken from the coastal zone. Higher PCB contents in the sands from the vicinity of the Vistula estuary (specimen 1/97) compared to those from the vicinity of the Klaipėda harbour (specimen 3/98) indicate a significant role of the Vistula River in supplying polychlorinated biphenyls to the Gdańsk Basin.

9.2. Chloroorganic Pesticides

Chloroorganic pesticides, used for decades to remove and destroy weeds, control parasites and reduce crop losses during their storage, also caused many adverse effects in the environment (Ramamoorthy, Ramamoorthy, 1997. Because of their harmful effects on animals and their small susceptibility to degradation in the environment, many of these agents were withdrawn from production and use in many countries, although they are still produced and used in developing countries. Unfortunately, due to physical properties of those compounds (high vapour pressure), some of these pesticides from arable land and plantations in tropical countries, especially in soils containing low amounts of organic matter and under strong solar radiation. They relatively easily enter the atmosphere and can be transported by air masses over long distances towards the poles. Some of them go with precipitation into the soils of temperate zones (Ramamoorthy, Ramamoorthy, 1997; Grynkiewicz *et al.*, 2003). Due to their poor water solubility, these compounds are adsorbed on the particles of the suspended solids and together with them they are deposited in the bottom sediments.

Of the group of chloroorganic pesticides, the most serious problem is related to DDT residues and its metabolites (p,p'-DDE, p,p'-DDD), stereoisomers of hexachlorocyclohexane (α-HCH, β-HCH, γ-HCH, δ-HCH) and heptachlor, aldrin and dieldrin. In recent aquatic sediments, the contents of the individual chloroorganic pesticides range from the values below the limit of detection up to several hundred thousand ng/g under extreme conditions. Generally, the content of these compounds does not exceed 1000 ng/g even in very contaminated sediments. Chloroorganic pesticides cause long-term genotoxic (mutagenic, teratogenic and carcinogenic), neurotoxic (central and peripheral) immunotoxic, embryotoxic effects in animals and humans, and they influence the body's hormonal balance of the organisms and enzymatic processes.

There is very little information about DDT in the sediments of the Baltic Sea. The content of DDT in the sediments of the southern Baltic Sea is 0.4–1.9 ng/g, in the Gotland Basin: 0.7–1.9 ng/g, in the north of the Baltic Proper and in the Gulf of Finland: 1.2–3.2 and 2.6–5.0 ng/g (Pikkarainen, 2007), respectively. The highest concentrations were found in the eastern part of the Gulf of Finland. However, they are lower than the ones presented earlier.

The earlier research showed higher DDT concentrations in sediments:

- In the Gotland Basin: p,p-DDD – 8.41 ng/g, p,p-DDE – 9.6 ng/g (Biselli *et al*., 2005);
- In the Bothnian Bay 1.9–18 ng/g, the Bothnian Sea 0.5–3.4 ng/g (Strandberg *et al*., 2000);
- Inn the western Baltic Sea up to 85 ng/g DDT (the Warnow estuary), β-HCH up to 2.8 ng/g (Dannenberg, Lerz, 1996);
- In the German coast, near the Peene River mouth, the average value was 70 ng DDT/g (Müller, Schilling, 1998);
- In the Arkona Basin 9.6 ng/g of DDT (Ricking *et al*., 2005); in the tested sediments, metabolites dominate: p,p'-DDD – 2.44 ng/g and p,p'-DDE – 1.92 ng/g (Biselli *at al*., 2005).

The lindane contents in the Baltic Sea sediments vary from 0.003 to 0.24 ng/g, in the western Baltic Sea the values are up to 1.5 ng/g (Dannenberg, Lerz, 1996; Pikkarainen, 2007

The surface sediments of the southern Baltic Sea, analysed in 1996–2005, show the highest values of pesticides in the Gdańsk Basin, where the contaminants transported by the Vistula River accumulated. The contents of ΣHCH were 1.73 ng/g, and ΣDDTs – 4.39 ng/g. In the Bornholm Basin, where contaminants transported by the Odra River accumulated, the content of ΣHCH was 2.13 ng/g, ΣDDTs – 0.98 ng/g. Sediments accumulated in shallow waters were characterised by slightly higher concentrations (Sapota, 2006). Similar ranges for chloroorganic pesticides were presented by Pazdro (2004): in the Gulf of Gdańsk, the DDTs content was 1.5–6 ng/g, and the lindane content ranged from 0.5 to 4 ng/g.

9.3. Dioxins

Dioxin is the common name for a group of organic chemical compounds that are derivatives of oxantren (dibenzo-p-dioxin). They are composed of two benzene rings combined with each other by two oxygen atoms and one to eight chlorine atoms bonded to benzene rings. Similar compounds are dibenzophurans, sometimes classified as dioxins. Dioxins are characterised by extremely weak water solubility and a very low vapour pressure, and they typically show very ~~a~~ strong adsorption on the surface~~s~~ of particles. Polychlorinated dibenzo-p-dioxins and dibenzophurans (PCDD/Fs) are a common pollution in the natural environment. They occur in soils, bottom sediments, inland waters and in the suspended particles in the air. They occur in relatively high concentrations in chemical wastes, pesticides, fly ash from waste combustion, including the combustion of municipal wastes. Under natural conditions, they are formed in trace amounts as products of volcanic activities and natural fires of forest, peat bogs or steppe.

Inadvertent formation of dioxins and their introduction into natural environment has been associated with technological activity of people for at least a hundred years. Their main sources are: the production of herbicides and pentachlorophenols, bleaching processes in paper industry, combustion of municipal and industrial wastes and wood impregnation. Polyvinyl chloride, commonly used as plastic to make all types of packaging, construction details and insulations, is a basic source of chlorine in combusted wastes. The precursors of dioxins in municipal wastes are also other organic compounds in the presence of sodium chloride (table salt) and catalysts, such as copper (Addink, Olie, 1995). The source of dioxins in the environment involves processes of hard coal combustion. However, they cause the emission of dioxins at much lower level than the combustion of municipal wastes, due to the massive burning of coal. It is considered that the coal-based energy is the meaningful source of dioxins in the environment. At present, it is believed that the main source of dioxin emission to the atmosphere is forest fires, the amount of which exceeds many times the emission from industrial sources.

The specific composition of congeners is reflected by the source of pollution: 2,3,7,8-TCDD, 2,3,7,8-TCDF and OCDF are indicators of paper pulp bleaching and the production of vinyl chloride, the congener 1,2,3,4,6,7,8-HpCDF is an indicator of the production of chlorophenols, OCDD is the main congener in atmospheric dusts and processing contamination of pentachlorophenols and is produced photochemically and thermally. The composition (spectrum) of dioxins from copper and iron smelters is similar to the spectrum of dioxins from municipal wastes incineration. Emission from the plants producing chlorine and sodium are characterised by considerable proportion of higher chlorinated compounds (Keller, Rappe, 1995; Sundqvist *et al*., 2009).

Dioxins are accumulated due to their lipophilic properties. Their detrimental activity in general consists in disturbing the internal functions of steroid hormones secretions. They may act teratogenically and mutagenically and are suspected to be carcinogenic to humans. Dioxins induce pathological changes in the central and peripheral nervous systems, cause the immune system damage, disturbances in functioning thyroid gland and diabetes. High concentrations of dioxins cause allergic reaction, especially dermal. Their half-life in human organisms is estimated at 7.8–132 years. They are supposed to be rapidly oxidised by cytochrome 450 and quickly removed outside the organism.

Studies of the sediments in the Baltic Sea revealed small, but significant contents in PCDD/Fs in the range of 91–234 pg/g in the deposits dated to have been deposited in 1882–1962. In sediments from 1970–1985, the range of PCDD/Fs contents clearly increased and was between 520 and 1800 pg/g. At the same time, the spectrum of those compounds changed (Keller, Rappe, 1995). The highest contents of dioxins occur in sediments of the northern coast of the Gulf of Finland (Verta *et al*., 2007). Sediments from the Gulf of Finland are highly contaminated with PCDD/Fs; the highest contents were found along the coasts of Finland, where locally their total concentration reaches even up to 101,000 pg/g (Isosaari *et al*., 2002). Two point sources were identified: the production of vinyl chloride plants in Sköldvik and the production of chlorophenols in two plants located upon the Kymijoki River. At present, both plants are closed, but the contaminated sediments of the Kymijoki River are still a source of dioxins for the Gulf of Finland. The Kymijoki, the fourth longest river of Finland, was strongly contaminated by waste waters discharged from paper mills and chemical works. The average content of PCDD/Fs in sediments of this river in the most polluted site, near the source of emission, was 42,000 pg/g. In coastal sediments of the Gulf of Finland, it was on average 15 pg/g. The transportation of pollutants by the river has been found to be the main source of PCDD/Fs in the deposits of the Gulf of Finland (Salo *et al*., 2008). It is estimated that this contaminated zone spreads for 75 km off the shore and the load of PCDD/Fs accumulated in the polluted sediments amounts to 1,770 kg (Isosaari *et al*., 2002).

Other sources of contamination with dioxins are industrial works located in Iggesund (Sweden) and Pietarsaari (Finland), chemical works producing chlorine and soda near Oulu and Pori, and iron mills. No significant source of dioxins was found in St. Petersburg. In the Arkona Basin sediments, the content of PCDFs varied from 2.5 to 820 pg/g. The content of PCDDs was between 12.7 and 2,991 pg/g (Dannenberger *et al*., 1997). Later research in this basin showed the concentration of 4,840 pg/g ΣPCDD/F (Ricking *et al*., 2005). The content of PCDDs in the western Baltic Sea sediments (Belts Sea and Arkona Basin) ranged from 2100 to 66,200 pg/g C, and the highest concentrations were found in the estuary of the Warnow River (Witt *et al*., 1997).

Appendix 5

Dioxins in Sediments from the Polish Coastal Zone of the Baltic Sea

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The analyses of dioxins (polychlorinated dibenzo-p-dioxines and dibenzofuranes, PCDD/Fs) in the surface bottom sediments in Poland started in 2002 within the scope of the international project GF/POL/01/IOŚ/004, which was basis for the development of the National Implementation Plan for the Stockholm Convention (Sadowski, 2004). The research included bottom sediments of estuary areas of the Vistula and Odra rivers, Gulf of Gdańsk and Włocławek Reservoir.

Owing to the noxious effect on organisms, dioxin concentrations are expressed with the toxic equivalent quantity (TEQ). A numeric value of TEQ is calculated by multiplying the concentration of an individual congener of PCDD/Fs (m) by the respective partial toxicity equivalent factor (TEF), acc. to the formula: $TEQ = \Sigma (m \times TEF)$. Many scientists assume the value of 5 pg I-TEQ /g d.w. as characteristic for the "ecologically clean" territories. The concentrations of dioxins in the river deposits of estuary zones of the Vistula and Odra rivers, calculated by using the toxic equivalent quantity (TEQ), ranged from 0.7 to 5.4 pg WHO-PCDD/F-TEQ/g d.w.

Based on studied concentrations a characteristic profile of congeners was determined (Fig. 1), informing

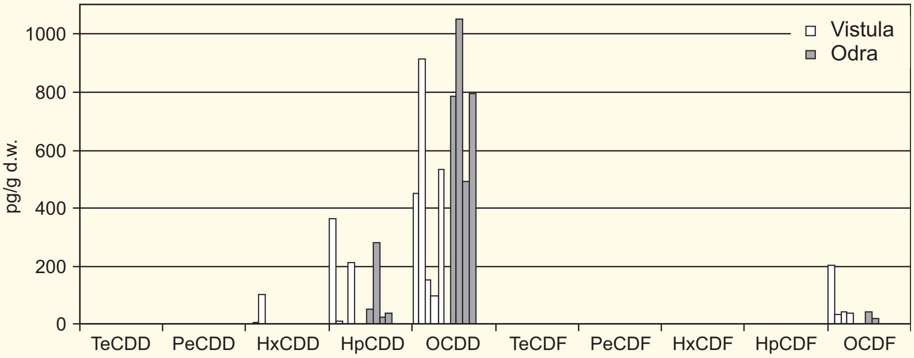

Fig. 1. The PCDD/Fs congener profile in bottom sediments of estuary areas of the Vistula and Odra rivers (Niemirycz, 2008)

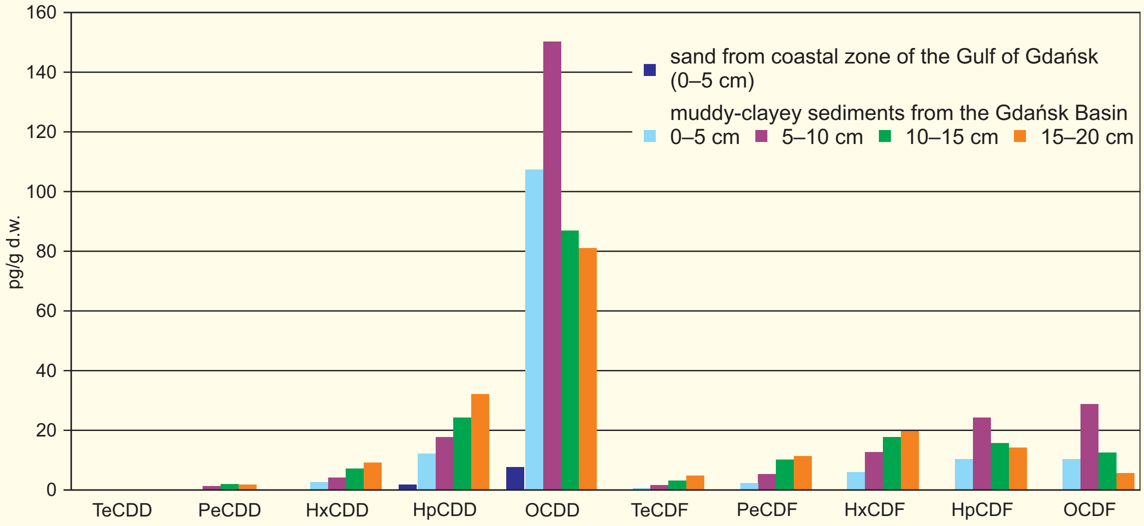

Fig. 2. The PCDD/Fs congener profile in bottom sediments of the Gulf of Gdańsk (Niemirycz, Jankowska, 2011)

about the amount of dioxins and the sources of their origin (Grochowalski, 2001; Dudzińska, 2003). The profile shows elevated contents of octa- and hepta-chlorodibenzodioxins (OCDD and HpCDD) in the sediments, but the fraction of the most toxic congeners: hexa-, penta- and tetra-chlorodibenzo-p-dioxins (HxCCD, PeCCD and TeCCD) is lower. This fact reveals rather an insignificant inflow of dioxins from man-made sources such as manufacturing paper or chloroorganic pesticides. The occurrence of PCDFs in bottom sediments points to the effect of air pollutants: mainly of different type combustion gases, including exhaust gases of vehicle engines (Rappe 1994; Verta *et al*., 2007).

In 2008 and 2009, analyses were made of dioxin concentrations in the sea-bottom sediments of the coastal zone of the Gulf of Gdańsk and in the central part of the Gdańsk Deep. The highest concentrations of dioxins were found in the surface layer (0–5 cm) of silt-clay bottom sediments of the Gdańsk Deep. The lowest contents were measured in coastal sands of the Gulf of Gdańsk. Bottom deposits of the Polish coastal zone may be recognised as slightly polluted with dioxins as their concentrations do not exceed 5–10 pg I-TEQ /g d.w. The PCDD/Fs congener profile in bottom deposits of the coastal zone in the Southern Baltic Sea was also defined (Fig. 2).

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9.4. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that are widely distributed in the natural environment. Their occurrence was also detected in all environmental compartments, as well as in various products, e.g. tar, asphalt, creosote oil (Harvey, 1998; Howsam, Jones, 1998; Maliszewska-Kordybach, 2000; Naraoka *et al*., 2002; Bojakowska, Sokołowska, 2003). Under natural conditions, polycyclic aromatic hydrocarbons are formed as a result of high-temperature pyrolysis of organic material during natural fires of plant communities (Koziński, Saade, 1998). These compounds can be synthesised by plants, might be products of metabolic transformations of microorganisms decomposing plant and animal residues. PAHs are formed during diagenesis and catagenesis of organic matter, especially during the generation of crude oil and transformation of organic matter into coal; besides, polyarenes are also formed during volcano eruptions (Capaccioni *et al*., 1995; Harvey, 1998; Howsam, Jones, 1998; Neilson, Hynning, 1998).

The PAH content in sandy, uncontaminated aquatic sediments, is very low, about 0.1 μg/g, while the deposits rich in organic matter, e.g. lake sediments, are often characterised by PAH contents near 1 μg/g. PAH content may be extremely high in sediments of rivers receiving waste water from, e.g. coking plants. The concentration of PAH in aquatic sediments and in soils depends on their properties, the most important of which is undoubtedly the content of organic matter.

The contents of PAHs in soils vary in a wide range from 0.005 μg/g on land far away from industrial centres and non-agricultural areas to a few thousand μg/g in the sediments near petroleum refineries or coking plants. The average PAH contents in arable soils of Poland, about 0.3 μg/g, are similar to that in soils of other European countries (Maliszewska-Kordybach, 2000).

Some PAH compounds are characterised by toxic, carcinogenic and mutagenic properties; e.g. anthracene, anphthalene, phenanthrene and pyrene are allergenic compounds that cause dermatological lesions, and benzo(a) pyrene is carcinogenic. The strongest carcinogenic and mutagenic effect on animals is from hydrocarbons, which contain a benzo(a)anthracene ring in their chemical structure. These are, among others: benzo(a)pyrene, benzo(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(k) fluoranthene, indeno(1,2,3–c,d)pyrene, dibenzo(ah) anthracene, benzo(ghi)perylene, dibenzo(a,h)acridine, dibezno(a,j)acridine and dibenzo(a,e)pyrene.

At present, PAHs are released into the natural environment during processing of hard coal in coking plants, coal combustion in households, fuel combustion by transport, oil processing in refineries, liquid fuel combustion in motor-car and aircraft engines, excavating, transporting and storing liquid fuels, as well as during the combustion of municipal wastes and metallurgical processes (Bradley *et al*., 1994; McGroddy, Farrington, 1995; Ollivon *et al*., 1995; Howsam, Jones, 1998; Grynkiewicz *et al*., 2003). Extremely hazardous are processing waste waters discharged by petrochemical and coking plants. It is considered that the main source of PAHs in recent sediments of surface waters is the deposition of particulates from the combustion of fossil fuels and biomass.

9.4.1. Polycyclic Aromatic Hydrocarbons in Surface Layer of Sediments

In the Gotland Basin, the PAH content is 1.22 μg/g (Biselli *et al*., 2005). In the surface layer sediments of the Arkona Basin, the PAH content varies between 0.011 μg/g in sandy sediments and 1.9 μg/g in muddy sediments (Witt, Trost, 1999). Ricking *et al*., (2005) determined the PAH content (33 compounds) in surface sediments of the Arkona Basin at 4.591 μg/g, and Biselli *et al.* (2005) – at 0.920 μg PAH/g.

Studies conducted in 1993 for the ICES/HELCOM Baltic Sea Sediment Baseline Study project (Perttilä ed., 2003) showed that the PAH contents changed from 0.45 to 3.52 μg/g in surface silt-clay sediments of the main sedimentary basins of the Baltic Sea, and the average content was 1.57 μg/g (Fig. 9.4). The concentration of benzo(a) pyrene (BaP) in the silty-clay surface layer of the Baltic Sea sediments ranges between 0.014 and 0.239 μg/g, and the average content is 0.094 μg/g (Fig. 9.5). Considerably higher PAH contents were observed in the sediments

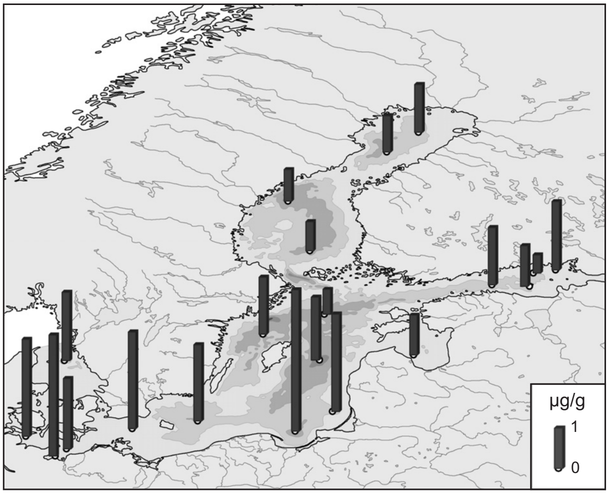

Fig. 9.4. Occurrence of PAHs (the sum of 18 components) in the surface sediments (0–2 cm) of the Baltic Sea; min. 0.45 µg/g, max. 3.52 µg/g d.w. (after Jonsson, Kankaanpää, 2003, revised)

of the southern Baltic Sea compared with the northern area. Very high PAH contents were noticed in the Gdańsk Basin and in the Lübeck Bay.

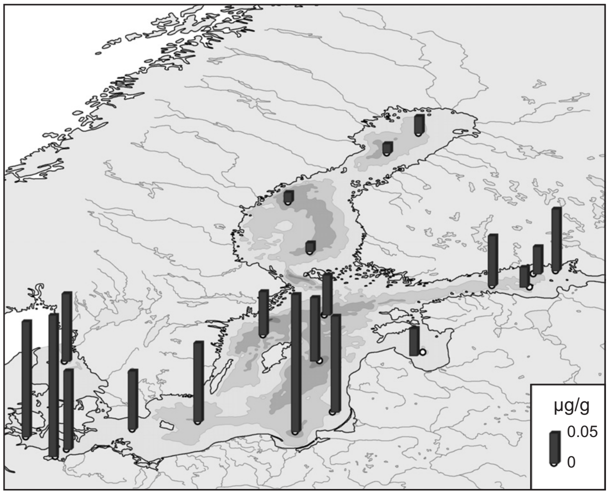

Fig. 9.5. Occurrence of BaP in the surface sediments (0–2 cm) of the Baltic Sea (after Jonsson, Kankaanpää, 2003, revised)

9.4.2. Polycyclic Aromatic Hydrocarbons in Vertical Section of Sediments

The study of sediments taken from the Mecklenburg Bight near Lübeck, where wastes were stored, showed that the PAH contents (16 compounds) in a layer from a depth of 14–16 cm was significantly elevated to 5.44 µg/g C, whereas in the reference layer (geochemical background), their concentrations were 0.017 µg C/g (Wölz *et al.*, 2009). The PAH contents (35 compounds) in older sediments of the Baltic Sea, deposited 200–250 years ago, are below 0.100 µg/g (Ricking, Schulz, 2002).

The 1993 research under the ICES/HELCOM Baltic Sea Sediment Baseline Study project (Perttilä ed., 2003) showed that the surface sediments were characterised by PAH contents lower than the older deposits located beneath. The highest PAH content, 7.85 µg/g, was observed in the North-Central Basin (station 180) in the 5–7 cm layer below the bottom surface, whereas in the surface layer (0–2 cm), their content was 0.54 µg/g (Fig. 9.6). In the underlying sediment layers located deeper than 15 cm, the PAH content is often below 1 µg/g. A similar variability in the profile is shown by BaP (Fig. 9.7).

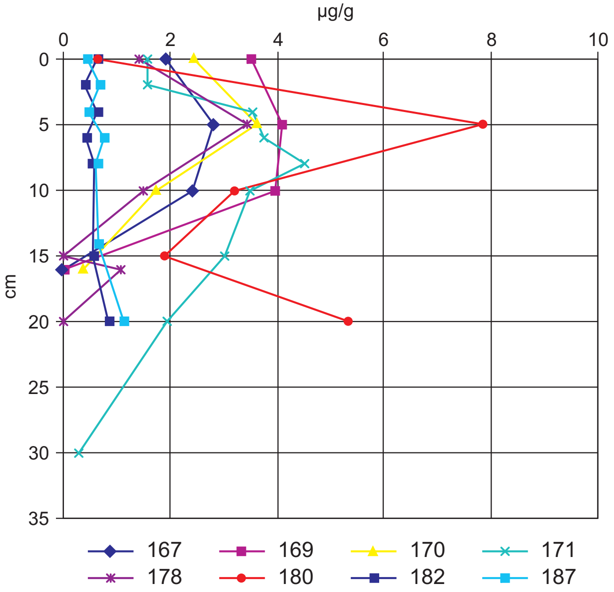

Fig. 9.6. PAH contents in vertical section of the Baltic Sea sediments (after Jonsson, Kankaanpää, 2003)

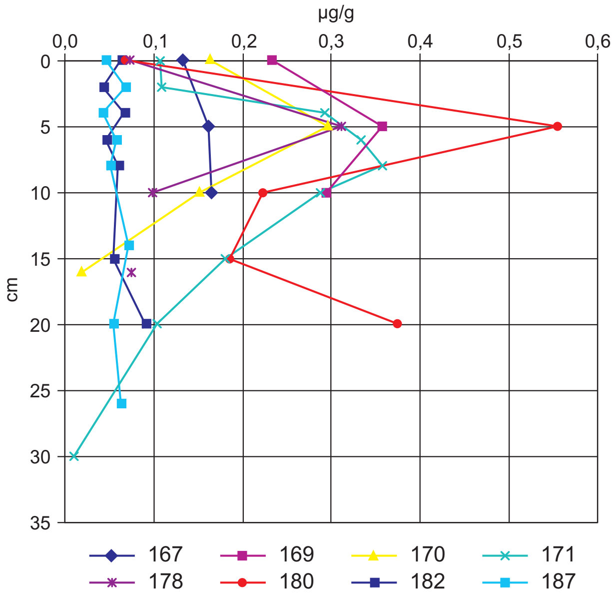

Fig. 9.7. BaP contents in vertical section of the Baltic Sea sediments; (acc. to Jonsson, Kankaanpää, 2003); for station location see Fig. 1.1

Table 9.2

Content of polycyclic aromatic hydrocarbons (PAH) and organic carbon (TOC) in the Gdańsk Basin sediments (based on the MASS Project data); for location of survey stations see Appendix 3 Fig. 1

Sample No.	WWA [µg/g]		Sediment type and the content of fraction >0.05 mm	TOC [%]
	lab. PGI	lab. BGS		
1/97	0.3	0.5	fine-grained sand (98%)	0.39
2/97	1.4	1.3	slightly sandy silt (17%)	3.41
3/97	3.3	5.9	silt (1.5%)	7.1
1/98	9.0	7.6	silt (1.1%)	5.02
2/98	2.3	1.8	slightly sandy silt (16.9%)	2.61
3/98	0.2	0.1	fine-grained sand (95.4%)	0.17

9.4.3. Polycyclic Aromatic Hydrocarbons in the Sediments of the Southern Baltic Sea

The analysis of sediment samples taken from the southern Baltic Sea in 1994–1996 showed that the contents of 12 unsubstituted PAHs ranged from 0.010 to 7.0 µg/g (on average 1.830 µg/g), including BaP whose content is 0.003–0.418 µg/g (on average 0.098 µg/g) (Kowalewska, Konat, 1997). In the Gulf of Gdańsk, the contents of individual PAHs vary from 0.016 to 0.400 µg/g, whereas of total PAHs – from 0.235 to 2.205 µg/g (Pazdro, 2004). The highest concentration was reported in the areas of intense sediment accumulation in the deeper part of Gdańsk Basin.

The highest contents of PAHs were found in silty-clay sediments of the north-eastern part of the Gdańsk Basin near the Lithuanian waters, as evidenced by the study of marine bottom sediments as part of the Marine Environmental Assessment and Monitoring Gdańsk Gulf Basin (MASS) project (Uścinowicz *et al.*, 1999). A higher content of PAHs also occurs in sandy silts from the Lithuanian part of the Gdańsk Basin, as compared to sim-

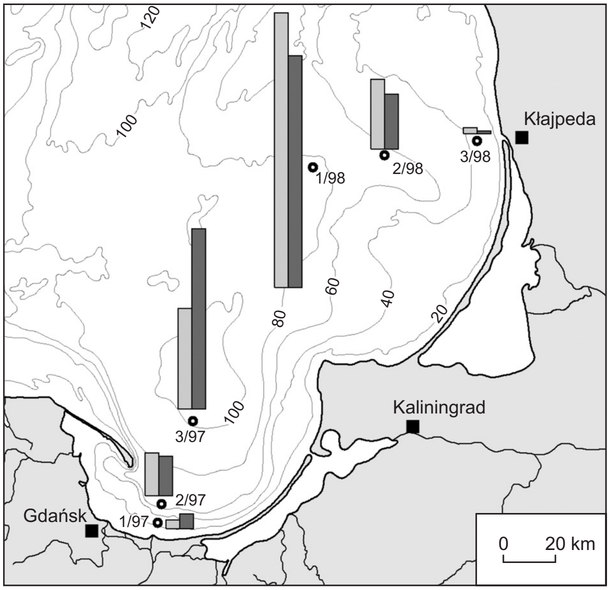

Fig. 9.8. The content of the sum of 15 PAHs in the Gdańsk Basin sediments; min. 0.1 µg/g, max. 9.0 µg/g (based on MASS Project data)

Left bar – the analyses made by the Central Chemical Laboratory of the Polish Geological Institute; right bar – made by the laboratory of the British Geological Survey ilar sediments in the Polish part of the basin (Table 9.2; Fig. 9.8). It is worth noting that the PAH contents in the northern part of the Gdańsk Basin, both in silty clay and sandy silts, are higher than in the southern part despite lower contents of organic carbon. A slightly higher PAH concentration than in sandy sediments near Klaipėda are observed only in sandy sediments in front of the Vistula River mouth.

In 2005–2006, the Polish Geological Institute performed detailed geochemical maps of the south-western part of the Gulf of Gdańsk (Uścinowicz *et al*., 2008). Determinations of the concentrations of seven PAHs were carried out for 59 samples of the surface layer sediments (0-2 cm layer). The total contents of 7 PAHs ranged from 0.005 to 2.24 μg/g (Fig. 9.9). In most of the Gulf of Gdańsk and Puck Bay, the sum of 7 PAHs in the surface sediment layer (0–2 cm) is lower than 0.5 μg/g, which indicates that these areas are not contaminated with polycyclic aromatic hydrocarbons.

On the outskirts of the Vistula River mouth and in the silty sediments of the southern part of the Gulf of Gdańsk, the sum of PAHs is between 0.5 and 1.0 μg/g. Elevated PAH contents (1.0–2.0 μg/g) occur in the Puck Bay and near Kuźnica. The maximum content (2.24 μg/g) was found in the area located 2–3 km to the NE from the entrance to the port of Gdynia. The maximum concentra-

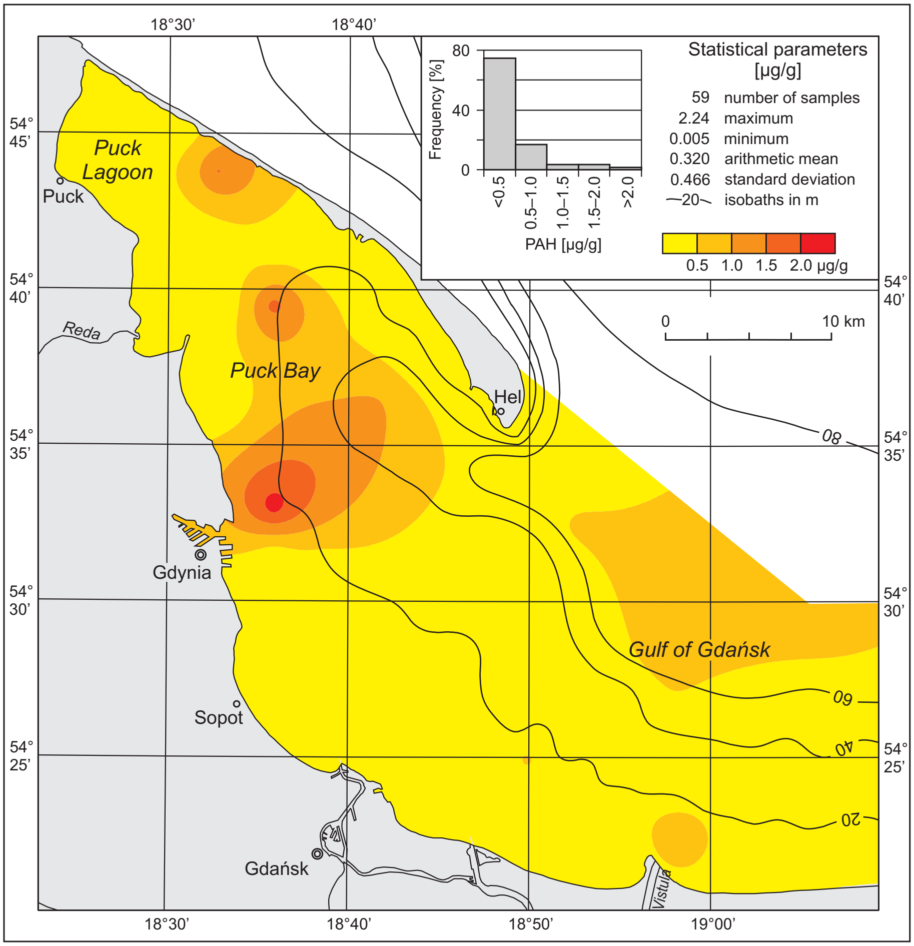

Fig. 9.9. The content of the sum of 7 PAHs in the surface sediments (0–2 cm) of the Gulf of Gdańsk (after Uścinowicz *et al*., 2008)

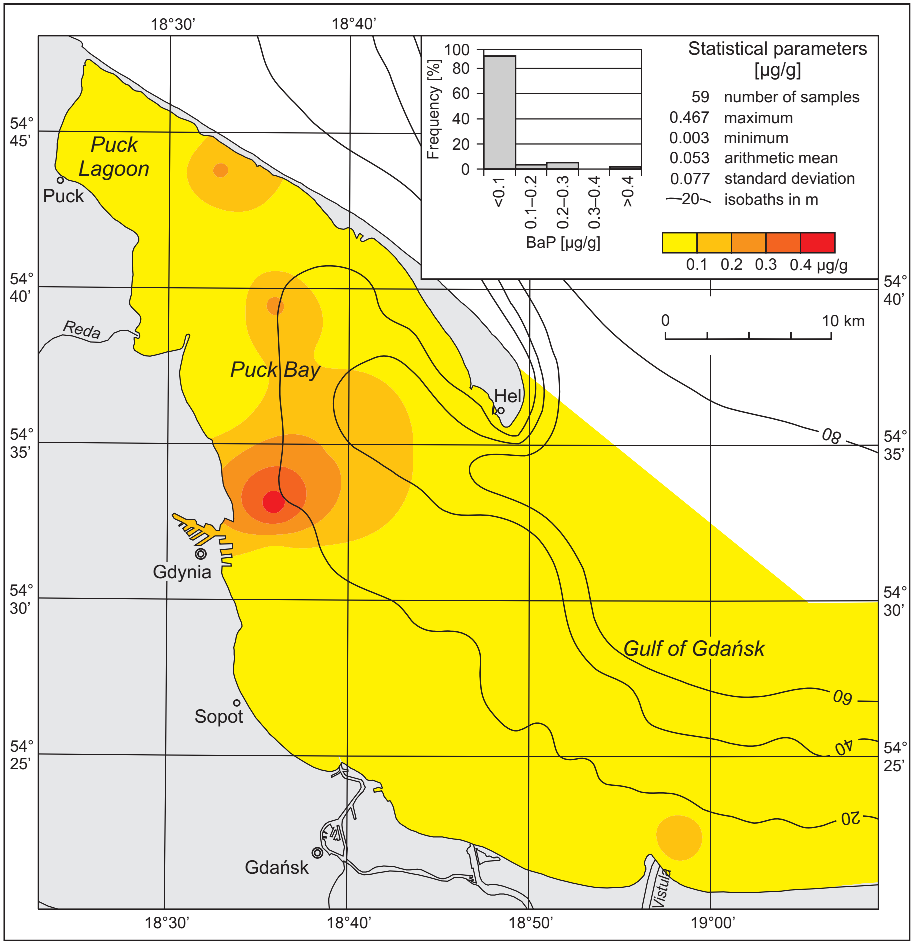

Fig. 9.10. Contents of benzo(a)pyrene in the surface sediments (0–2 cm) of the Gulf of Gdańsk (after Uścinowicz *et al.*, 2008)

tions of PAHs near the port (a commercial port and a naval harbour) and near the fishing port at Kuźnica in the Hel Peninsula clearly indicate the source of their origin. The benzo(a)pyrene content in the sediments of the Gulf of Gdańsk and Puck Bay is up to 0.467 μg/g. The content of this component in silty sediments is from 0.066 to 0.205 μg/g. The highest concentrations of benzo(a)pyrene occur near the port of Gdynia (0.467 μg/g) – Fig. 9.10.

The average content of benzo(a)anthracene is 0.508 μg/g. The highest level of this component was recorded near the port of Gdynia (0.527 μg/g). The content of benzo(b)fluoranthene of the Gulf of Gdańsk and Puck Bay varies from below the determination limit (<0.003 μg/g) to 0.384 μg/g. Particularly high levels of benzo(b) fluoranthene is observed in the sediments of the Puck Bay near Kuźnica – 0.357 μg/g and in the central part of the Bay – 0.345 μg/g. Very high concentrations of benzo(b) fluoranthene were observed near the port of Gdynia (0.384 μg/g), elevated contents also occur at the mouth of the Vistula River (0.215 μg/g) and in the silts in the central part of the Gulf of Gdańsk (0.262 μg/g).

Over most of the sea bottom of the Gulf of Gdańsk, the sediments contain below 0.050 μg/g of benzo(k) fluoranthene. The highest concentrations of this hydrocarbon occur in the central part of the Puck Bay (0.182

μg/g) and near the Gdynia harbour (0.223 μg/g). The concentration of benzo(ghi)perylene varies from below the determination limit (<0.005 μg/g) to 0.290 μg/g (mean 0.0593 μg/g). The highest concentrations of this hydrocarbon were recorded in the central part of the Puck Bay (0.290 μg/g) and near the port of Gdynia (0.273 μg/g).

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Chapter 10

RADIONUCLIDES IN SEDIMENTS AND BENTHIC ORGANISMS

10.1. Radionuclides in the Sea Bottom Sediments

Strontium ^{90}Sr and caesium ^{137}Cs

In the 1950s and 1960s, global radioactive fallout was the main source of strontium ^{90}Sr and caesium ^{137}Cs in the Baltic Sea, but in the early 1970s, additional activities of artificial nuclides were introduced by the Danish Straits as an effect of well aerated but more radioactively contaminated water inflows from the North Sea (Aarkrog *et al*., 1986; Herrmann *et al*., 1995). Unlike radiostrontium, the analyses of radiocaesium concentrations in of the Baltic Sea sediments have been carried out on a quite regular base for over 30 years. The deposition of ^{90}Sr and ^{137}Cs in the Baltic sediments was dependent on their contents in water and suspended solids, as well as on the sedimentation rate in the individual basins (IMGW, 1991–2004).

At the beginning of the 1980s, the contents of ^{90}Sr and ^{137}Cs in the Baltic Sea waters were, respectively: 12.9–25.7 and 7.8–42.8 Bq/m^3 (HELCOM, 1995). The radioactive concentration decreased towards the east of the Danish Straits. A slight increase in the radioactive concentration of the Baltic waters in 1977 was recorded after the explosion of a Chinese atomic bomb on 26th September, 1976. Before 1986, the concentration of ^{137}Cs in the surface layer (0–5 cm) of the sea bottom sediments did not exceed 100 Bq/kg d.w. (Ilus *et al*., 1995). After the Chernobyl nuclear accident, the concentration of ^{137}Cs in the Baltic Sea waters significantly increased and a new isotope ^{134}Cs with a 2.6-year half life appeared. In the first months after the accident, the surface contamination of the Baltic Sea increased locally to more than 200 Bq/m^3; this is over ten times greater than before April 1986. After the Chernobyl accident, the radioactivity of ^{137}Cs in the surface layers of the individual basins ranged from120 to 130 Bq/m^3 in the Bothnian Sea, from 90 to 100 Bq/m^3 in the Baltic Proper, from 40 to 80 Bq/m^3 in the Danish Straits, and from 90 to 110 Bq/m^3 in the southern Baltic Sea (HELCOM, 1995; IAEA, 1986; IMGW, 1991–2004). Radioactive particles containing ^{137}Cs were deposited in bottom sediments, especially in their silty structures. Large contents of ^{137}Cs, exceeding 1000 Bq/kg d.w., were observed in the surface layers of the sediments in the Baltic Proper and the Bothnian Sea, and its highest concentrations were recorded in the surface layers in the Gulf of Finland, taken in 1987 (3400 Bq/kg d.w.; Ilus *et al*., 1995). In this basin, the largest deposit of ^{137}Cs, 43,000 Bq/m^2, was observed in 1990 (HELCOM, 1995). As the time passed by, ^{137}Cs, deposited in sediments, was bound with organic matter and dissolved due to diagenetic processes, with increased activity in the pore (interstitial) and bottom waters. The recent years have been particularly characterized by a clear transport of Chernobyl radiocaesium from the sediments into the water (IMGW, 1991–2004). The horizontal distribution pattern of the Chernobyl ^{137}Cs concentrations in the deep-water zone of the southern Baltic Sea tends to decrease from the Gdańsk Basin towards the Bornholm Basin (HELCOM, 1995).

As opposed to caesium ^{137}Cs, the concentration of strontium ^{90}Sr in the Baltic Sea scarcely changed after the nuclear accident in Chernobyl: it slightly increased in 1986 and gradually reduced over the next few years. In sediments, ^{90}Sr is sorbed and bound with the carbonate fraction. Few measurements of ^{90}Sr in the Baltic Sea bottom sediments indicate that its concentration in the southern surface layer (0–5 cm) amounts to 24 Bq/kg d.w., whereas in the 5–10 cm layer it is considerably less and reaches the value of 2.6 Bq/kg d.w. (Ilus *et al.*, 1987; IMGW, 1991–2004).

The main contamination sources in the Baltic Sea waters with ^{90}Sr and ^{137}Cs radionuclides are precipitation, riverine run-off and inflow from the North Sea. A potential risk is nuclear power plants located in Sweden, Finland and Russia. The inflow of radioactive pollutants from the atmosphere generally depends on both radionuclide concentrations in the air layer over the surface sea waters and the intensity with which the concentrations are removed from the atmosphere into the sea. The mean annual concentration of ^{137}Cs in the air layer adjacent to the surface sea water layer of the coastal zone in the southern Baltic Sea rapidly increased after 1986 and during the next few years were slowly decreasing, reaching 2.8 μBq/m^3 in 1993. The mean yearly inflow of ^{137}Cs from the atmosphere into the sea in the coastal zone of the southern Baltic Sea reached 4.2 Bq/m^2/year in 1993, whereas the annual inflow of ^{90}Sr in that period was three times lower and did not exceed 1.4 Bq/m^2/year (IMGW, 1991–2004). Next, the mean concentrations of ^{90}Sr and ^{137}Cs in the southern Baltic Sea waters usually ranged between 11 and 31 Bq/m^3 before 1986 (Table 10.1). After the Chernobyl accident, the concentrations of ^{137}Cs in the Baltic Sea water increased to 120 Bq/m^3, then decreased to 58 Bq/m^3, and again increased to about 100 Bq/m^3, maintaining this level with small variations until the present (IMGW, 1991–2004; Bojanowski *et al.*, 1995a; Styro *et al.*, 2001; Szefer, 2002).

In the individual reservoirs of the southern Baltic Sea, the contents of ^{137}Cs in the surface layer sediments before the Chernobyl accident were as follows: 27 Bq/kg d.w. in the Słupsk Furrow, 73 Bq/kg d.w. in the Bornholm Basin and 129 Bq/kg d.w. in the Gulf of Gdańsk (Jaworowski *et al.*, 1986). After 1986, radiocaesium emitted to the atmosphere precipitated rapidly on the surface of the southern Baltic Sea, where it settled before being deposited in the sea bottom sediments. The concentrations of ^{137}Cs in superficial sediments rapidly increased and achieved 129 Bq/kg d.w. in the Bornholm Basin and more than 300 Bq/kg d.w. in the Gulf of Gdańsk and the Gdańsk Basin (Skwarzec, Bojanowski, 1992). The deposition of ^{137}Cs in 1988 was the highest in the Gdańsk Basin (2338 Bq/m^2), lower in the Bornholm Basin (1146 Bq/m^2), and the lowest on the Gotland Basin (292 Bq/m^2). In the analysed cores of the bottom sediments in the basins of Gdańsk, Bornholm and Gotland, the concentration of ^{137}Cs lowered with depth and vanished in the layers below 30 cm. The surveys show that the Chernobyl nuclear accident was the most important source of radiocaesium in the southern Baltic Sea (IMGW, 1991–2004; Skwarzec, Bojanowski 1992, Bojanowski *et al.*, 1995a, b).

Table 10.1

The ^{90}Sr and ^{137}Cs concentrations in the southern Baltic Sea water (IMGW, 1994–2004; Skwarzec, 2002)

Year	^{90}Sr	^{137}Cs
	[Bq/m^3]	
1960	13	11
1970	25	31
1980	22	21
1985	22	21
1986	30	120
1987	19	58
1990	18	96
1992	17	96
1994	15	87

Polonium ^{210}Po

The average concentration of ^{210}Po in the waters of the southern Baltic Sea is 0.59 Bq/m^3, including app. 80% of its dissolved forms. The concentration of ^{210}Po in the Baltic suspension is 74 Bq/kg d.w., and the distribution coefficient (DC) of this radionuclide for the suspended solids is $2 \cdot 10^5$. Polonium is sorbed on the suspended particles and the intensity of this process depends on the contents of organic matter contained in the suspended solids (Skwarzec, Bojanowski, 1988; Bojanowski *et al*., 1995b; Skwarzec, 1995, 1997). In those reservoirs of the Baltic Sea where the process of sedimentation of suspended solids proceeds relatively fast (Gotland, Bornholm and Gdańsk basins), the polonium concentration is reduced with depth of the sediment beds. In the Baltic Sea bottom sediments, the concentration of ^{210}Po in the surface layer (0–1 cm) is 224 Bq/kg (Gdańsk Basin) and 209 Bq/kg (Arkona Basin), whereas in the layers deeper than 10 cm, it decreases to below 100 Bq/kg (Skwarzec, 1995). This drop is justified, since (under conditions of the radiation equilibrium) the activity of ^{210}Po, being in activity equilibrium with ^{210}Pb, depends on the content of ^{238}U, or rather on the activity of ^{226}Ra, which is the longest-living preceding nuclide in the natural uranium–radium decay series. In the sediments separated from outer effects, an equilibrium activity of ^{210}Pb is established after about 200 years (Robins, 1978). Sediments formed later from the sedimentary environment generally contain an excess of ^{210}Pb with reference to ^{226}Ra occurring in the analyzed sediment. This excess comes from ^{222}Rn contained in the atmosphere and water. The measurement of the excess activity relation of ^{210}Pb in the adjacent sediment horizons enables us to calculate the rate with which the sediments settled and this is calculated as a difference between the activity of any segment reduced by the equilibrium activity. At the same time, the activity of ^{210}Pb at any depth of the core with reference to its activity in its surface layer is the measurement of the age. Figure 10.1 presents a scheme of the ^{210}Pb concentration in the Baltic Sea sediment (Skwarzec, 2008).

In the radiolead ^{210}Pb method, the age of the core segment is calculated acc. to the following formula:

$$t = \frac{1}{\lambda}\ln\frac{A_0}{A_1} = 32.12\ \ln\frac{A_0}{A_1} \qquad [10.1]$$

where:

A_0 – excess equilibrium activity of ^{210}Pb in the upper segment of the sediment,

A_1 – excess equilibrium activity of ^{210}Pb in the lower part of the sediment,

λ – decay constant ^{210}Pb ($\lambda = \frac{\ln 2}{T} = \frac{0.693}{22.26\ \text{years}}$).

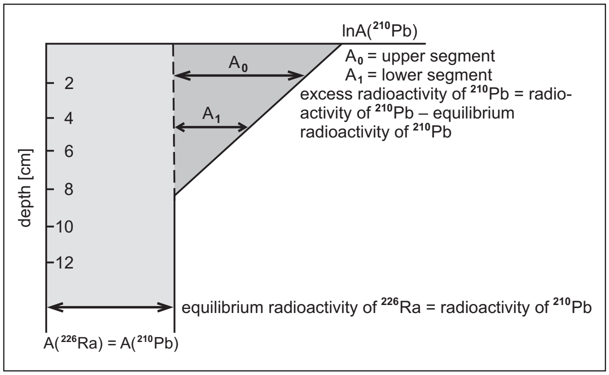

Fig. 10.1. Changes in the ^{210}Pb concentration with depth of the sea bottom core (Skwarzec, 2008)

Using a mathematical model suggested by Carpenter *et.al.* (1985) to describe water reservoirs with steady sedimentation and insignificant mixing of the sediment surface layers, it is possible to calculate the sedimentation rate R:

$$R = \frac{\text{increase in sediment thickness [mm]}}{\text{sediment age [years]}} \qquad [10.2]$$

Thanks to this method the sedimentation rates could be calculated for most marine basins, particularly for places where the sediment deposition rate is relatively high (from 1 to 3 mm per year) (Skwarzec, 2002). For the southern Baltic Sea the sedimentation rate *R* is from 0.9 in the Bornholm Basin to 2.2 in the Gulf of Gdańsk and the Arkona Basin (Pempkowiak, 1991; Skwarzec, 1995, 2008; Suplińska, Pietrzak-Flis, 2008).

Uranium ^{238}U and ^{234}U

The uranium concentration in the Baltic Sea waters correlates with salinity, and its value increases from 0.15 μg/kg in the southern part of the Bothnian Bay to app. 1.0 μg/kg in the Danish Straits (Lofvendahl, 1987). Under the redox conditions of the Baltic waters (Gotland and Bornholm basins), soluble forms of U(VI) may be reduced to insoluble forms of U(IV), and then complexed by organic matter (Prange, Kremling, 1985). In turn, in aerated waters of low salinity, uranium may be adsorbed on particles of iron hydroxide Fe(OOH), and then removed from the water depths in the sedimentation process (Porcelli *et al*., 1997; Andersson *et al*., 1998). The studies on uranium deposition in the bottom sediments of the Baltic Sea were carried out mainly in basins located in its southern part (Skwarzec *et al*., 2002; Skwarzec, 2009).

Uranium concentration in the southern Baltic Sea surface water ranges between 0.68 and 0.85 μg/dm^3, the mean value of the activity ratio $^{234}U/^{238}U$ is 1.17 and its amount decreases with the increase in water salinity (Skwarzec, 1995). Uranium contained in the water depths as terrigenous or autogenous suspension is settled and deposited on the surface of the bottom sediments. The studies on the uranium measurement in the bottom sediments of the Baltic Sea revealed its variable content (Figs. 10.2 and 10.3). The highest values of uranium concentrations were determined in the sediments of the Słupsk Furrow, whereas the lowest were found in the sediments of the Bornholm Basin. Irrespective of geographical diversity, the whole area of the southern Baltic Sea shows a decrease in the uranium concentration with sediment depth, which suggests its diffusion from bottom sediments to the bottom water through pore waters (interstitial waters) and is a result of diagenetic transformations in the sedimentary material (Boryło, 2000). For most regions of the southern Baltic Sea bottom sediments, a relative equilibrium between the isotopes of uranium is observed, which is reflected by the activity ratio $^{234}U/^{238}U$ ranging between 0.9 and 1.1. Only in the sediments from the peripheries of the Słupsk Bank does the activity ratio $^{234}U/^{238}U$ decrease with sediment layer depth, reaching 0.48 (Skwarzec *et al*., 2002). Significant is the role of the pore water (interstitial water) in uranium migration through the sea bottom sediments, which increases the uranium concentration by penetrating sediment layers, elevating the activity ratio $^{234}U/^{238}U$ from 1.0 to 1.17, i.e. to the value characteristic of the Baltic water (Skwarzec *et al*., 2004). The survey made for the reductive regions (the presence of hydrogen sulphide) in the Gdańsk Basin

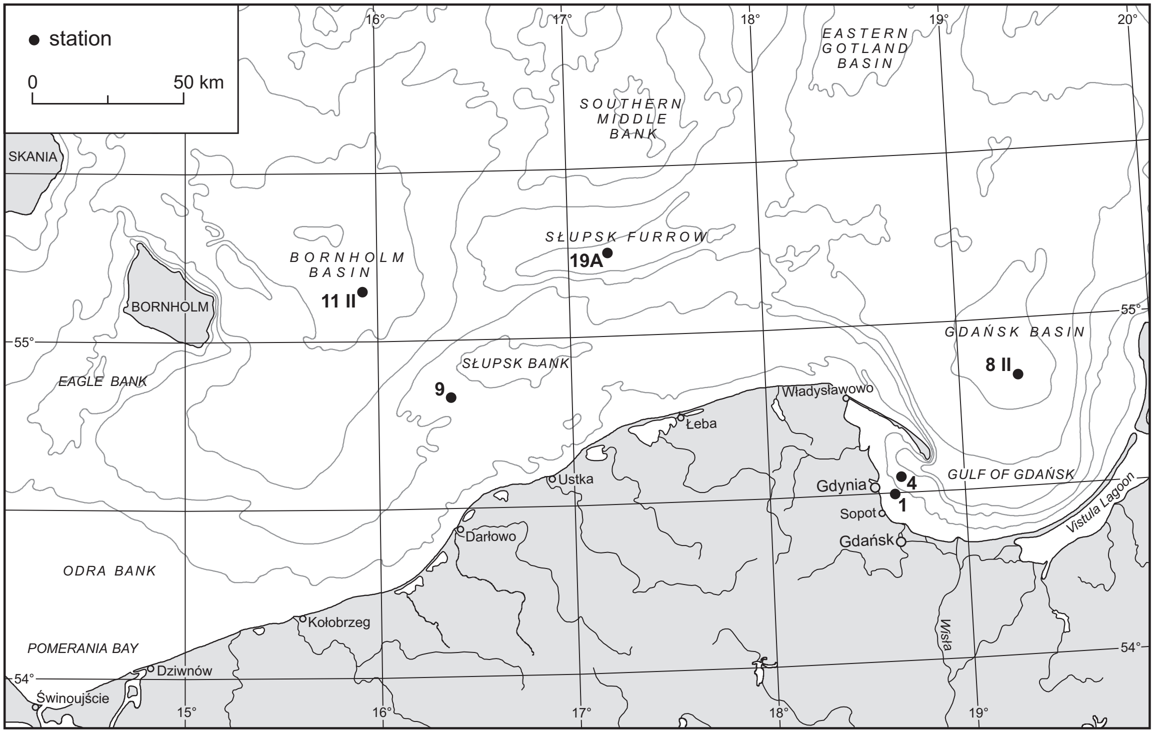

Fig. 10.2. Location of sampling sites of sea bottom sediments

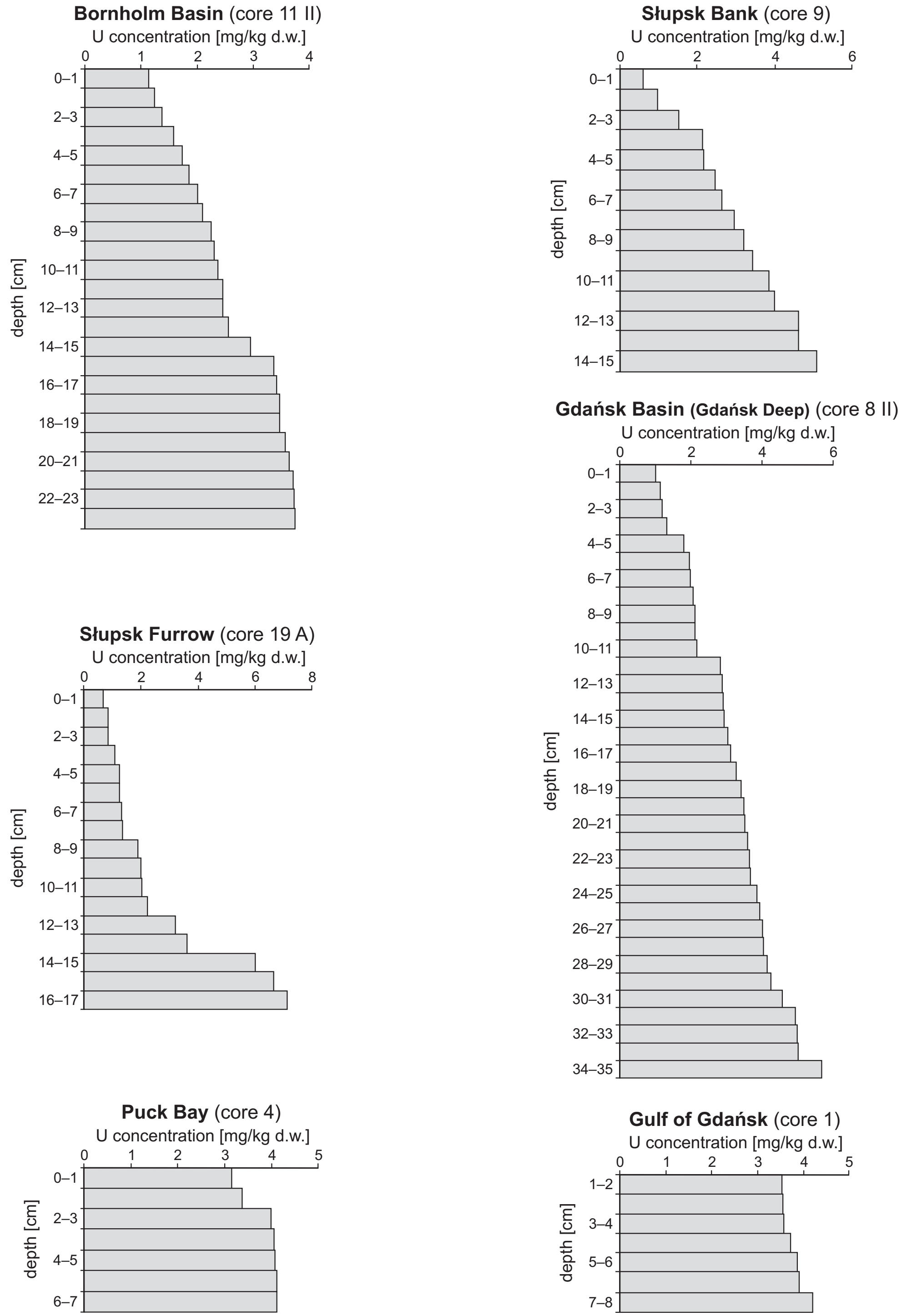

Fig. 10.3. The uranium concentration in bottom sediments of the southern Baltic Sea (Boryło, 2000; Skwarzec *et al.*, 2002)

and the Bornholm Basin did not confirm the possibility of intense precipitation of U(IV) from the bottom water into the bottom sediments in these areas (Skwarzec *et al.*, 2002, 2004).

Plutonium ^{238}Pu, $^{239+240}$Pu and ^{241}Pu

The concentration of $^{239+240}$Pu in the surface waters of the Baltic Sea is relatively low and usually does not exceed 10 mBq/m^3 (Holm, 1995; Skwarzec, 1995). Plutonium in the sea water shows strong affinity with the suspended matter, especially with the organic one (Ostlund, 1991). During the process of sedimentation, two stages are possible; the first includes adsorption of Pu(V) in the dissolved organic matter and colloid forms of iron (α-FeOOH), and the other is associated with its desorption after the reduction to Pu(IV) and complexing with humic substances. Relatively small amounts of plutonium were observed in the atmospheric precipitation over the Baltic Sea after the Chernobyl accident, hence its contribution in plutonium contained in the surface layer sediments is low (Ilus *et al.*, 1995; Holm, 1995). The fraction of the Chernobyl plutonium in the Baltic Sea bottom sediments became apparent mainly after the contents of isotopes ^{238}Pu and ^{241}Pu increased (Holm, 1995). The total amount of plutonium from the global fallout in the period 1958–1962 and deposited in the Baltic Sea is estimated to be 16.5 TBq, including over 90% deposited in bottom sediments (Salo *et al.*, 1986; Holm, 1995). Baltic sediments usually contain a few Bq/kg d.w. $^{239+240}$Pu, and the amount of plutonium deposited in them depends on the chemical composition of sediments and the amount of the plutonium emission into the natural environment (Holby, Evans, 1996).

The mean concentration of $^{239+240}$Pu in the waters of the southern Baltic Sea is 4.8 mBq/m^3, including 70% of soluble forms. In suspension, the plutonium concentration reaches 1.5 Bq/kg d.w. and the distribution coefficient (DC) amounts to $4 \cdot 10^5$ (Skwarzec, 1995). In turn, ^{241}Pu in the waters of the Bay of Gdańsk and the Gdańsk Basin is from 0.11 to 0.23 Bq/m^3 (Table 10.2). Most of plutonium supplied to the Baltic Sea is quickly deposited in the sea bottom. The sedimentation rate differs in the individual basins and depends on their depths, redox potentials at the bottom zones and on the water suspension contents (Coughtrey *et al.*, 1984). The sandy sediments in the bays of Gdańsk and Puck, and the Słupsk Furrow contain considerably less plutonium compared to the silty sediments in the Gdańsk Basin where hydrogen sulphide occurs and the silty sediments are enriched with organic matter that complexes plutonium. Owing to the above, the concentration of $^{239+240}$Pu in the surface layer of the bottom silty sediments was the highest and reached 6.5 Bq/kg d.w. In the deeper layers of the sediments, the plutonium concentration decreases and becomes rare below 20 cm (Skwarzec, 1995).

Table 10.2

The ^{241}Pu concentration in marine water and bottom sediments of the southern Baltic Sea in May 1987 (Strumińska, Skwarzec, 2006; Skwarzec, 2009)

Sample	^{241}Pu [Bq/m^3]	Activity ratio ^{241}Pu/$^{239+240}$Pu
Marine water:		
Gulf of Gdańsk	0.23 ±0.03	140
Gdańsk Basin	0.11 ±0.02	53
Sediments:		
Gulf of Gdańsk	0.90 ±0.14	7.5
Southern Gulf of Gdańsk	0.16 ±0.02	16
Gdańsk Basin	14.2 ±2.5	39
Inner Puck Bay	2.93 ±0.27	7.2
Outer Puck Bay	1.52 ±0.12	6.6

In turn, in the Gulf of Gdańsk, higher plutonium concentrations occur in the 3–9 cm layer, while lower ones are observed in the 0–3 cm layer (Suplińska, 1995). A very low concentration of $^{239+240}$Pu (below 0.02 Bq/kg d.w.) was noticed in the sediment near the Vistula River mouth. This is caused by the low content of the sediment fine fractions (<63 μm) and by a diffusing effect of macroclastic material on the content of plutonium in the silt fraction from the Vistula River mouth (Skwarzec, 1995).

In the southern Baltic Sea, Chernobyl plutonium was observed in the sediment surface layer (0–3 cm) in the Vistula River mouth and in the Gulf of Gdańsk, which was related to its downflow in the Vistula waters. In the Gulf of Gdańsk and the Gdańsk and Bornholm basins, the maximal concentrations of $^{239+240}$Pu (from 6 to 11 Bq/kg d.w.) from the general radioactive fallout were recorded in the 8–15 cm depth (Pawlukowska, 2009). Plutonium contained in the Baltic Sea waters is removed quite rapidly and the rate of this process depends on the depths of the basins, currents of water masses and on the physicochemical parameters of the water (Skwarzec, 1995; Suplińska, Pietrzak-Flis, 2008). The survey revealed a large diversification of plutonium deposition in the southern part of the Baltic Sea: from the lowest values in the Słupsk Furrow (11 Bq/m^2), the Puck Bay (18 Bq/m^2) and the Gotland and Bornholm basins (30 and 48 Bq/m^2), through higher ones in the Gdańsk Basin (98 Bq/m^2) and the Bothnian Bay (99 Bq/m^2), to the highest concentrations in the Gulf of Finland (245 Bq/m^2) and the Kattegat region (247 Bq/m^2) (Skwarzec, Bojanowski, 1992; Dahlgaard, 1994). A relatively high deposition of $^{239+240}$Pu in the Gdańsk Basin and the Gulf of Finland is caused by the downflow of plutonium in the waters of the Vistula and Neva rivers from their drainage basins, while in the Danish Straits (Kattegat), plutonium comes from the North Sea, from the sources in Sellafield and Cap de la Haque where spent nuclear fuel is processed (Skwarzec, 1995; Leonard *et al*., 1999).

Analysing the percentage contribution of the individual plutonium fractions in the tested cores of the bottom sediments in the southern Baltic Sea, it was found that the highest amounts of $^{239+240}$Pu were associated with a carbonate fraction in the Vistula River estuary (34%), Gulf of Gdańsk (42%) and Bornholm Basin (35%). In the Gdańsk Basin, plutonium is contained mainly in a fraction digested by mineral acids (40%). Considerable amounts of $^{239+240}$Pu are also found in a fraction complexed with organic matter (29%). The lowest contribution of plutonium is associated with a mobile fraction soluble in water, in an oxide fraction that is potentially bioavailabe, from which $^{239+240}$Pu can be liberated under specific conditions and in practically immobile reminder that is built mainly of silicate structures. The carbonate fraction is regarded as mobile; it attains maximal amounts of plutonium in the deepest horizons of sediment cores (5–8 cm) from the Vistula River mouth. However, in the Gulf of Gdańsk, it is the highest in the sediment surface layer (0–8 cm), which is favourable for liberating plutonium into pore and bottom waters, its remobiling and reintroduction into the water environment. Releasing plutonium from the surface layer sea bottom sediments has a direct effect on its biogeochemical cycle in the environment of the southern Baltic Sea. A similar situation occurs in the Bornholm Basin, where the contribution of plutonium in the carbonate fraction decreases with the depth of the sediment core, and the highest plutonium concentrations in this fraction are observed at 2 cm. In turn, in the Gdańsk Basin, 40% of $^{239+240}$Pu occurs in the almost immobile fraction digested in mineral acids, which is not as hazardous for the marine ecosystem as plutonium in the carbonate fraction of the sediment (Pawlukowska, 2009).

Based on the contents of plutonium in the individual components of biocoenosis in both the Gulf of Gdańsk and the Gdańsk Basin, and considering its sources of origin, an inventory of $^{239+240}$Pu in these reservoirs has been achieved (Figs. 10.4 and 10.5) (Skwarzec *et al*., 2003a; Strumińska, Skwarzec, 2009). The main source of plutonium in the Gulf of Gdańsk is the Vistula River, which enriched this reservoir with 192 MBq a year in the late 1990s and now with app. 90 MBq of $^{239+240}$Pu. For the Gdańsk Basin, the Vistula and Nemunas catchment areas supply about 312 MBq of plutonium per year. Rainfall and snowfall supply the area of the Gulf of Gdańsk and Gdańsk Basin with 12 and 44 MBq $^{239+240}$Pu per year, respectively, and the direct deposition of dry fallout from the atmosphere supplies yearly22 and 82 MBq of plutonium, respectively. The total amount of $^{239+240}$Pu deposited in the Gulf of Gdańsk is 1.18 TBq, and 3.76 TBq in the Gdańsk Basin. Bottom sediments are the largest reservoir of plutonium, accumulating almost 99.8% of its total amount in both parts of this water area, and the rest 0.2% occurs in water with the suspended matter. The organisms in the Gulf of Gdańsk and the Gdańsk Basin contain, respectively, 3.81 and 7.45 MBq $^{239+240}$Pu (which accounts for app. 0.0003%), the most (82%) of which is stored in zoobenthos. The bottom sediments of the Gulf of Gdańsk and Gdańsk Basin store, 6.4 and 22% of the total amount of plutonium deposited in the Baltic Sea sediments, respectively, whereas the area of the two reservoirs accounts for 1.2 and 4.4% of the Baltic Sea area, respectively. So, the results of the research indicate the enrichment of the bottom sediments of these reservoirs with $^{239+240}$Pu. Plutonium contained in the sea bottom sediments is

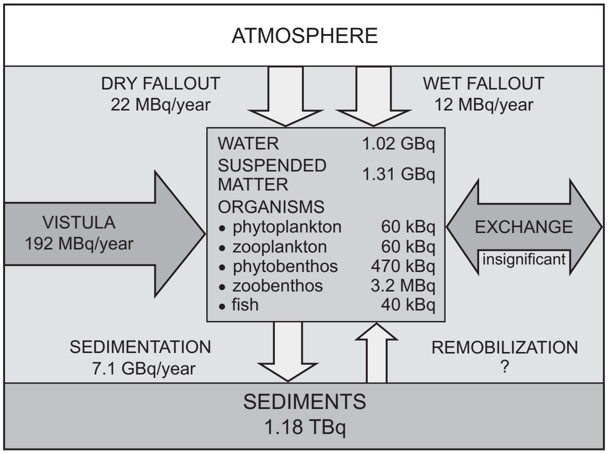

Fig. 10.4. The outline of inventory for $^{239+240}$Pu in the Gulf of Gdańsk (Skwarzec *et al*., 2003a; Skwarzec, 2009)

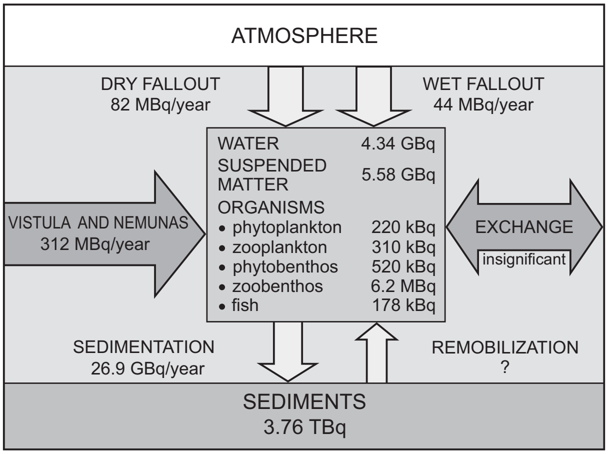

Fig. 10.5. The outline of inventory for $^{239+240}$Pu in the Gdańsk Basin (Skwarzec *et al*., 2003a; Skwarzec, 2009)

slowly remobilized by benthonic organisms and in this way it starts to circulate in the ecosystem of the southern Baltic Sea. Moreover, the research also showed that the estuaries of the Vistula, Odra and Nemunas rivers are strongly contaminated with plutonium (Holm, 1995; Skwarzec *et al*., 2003a; Skwarzec, 2009).

10.2. Radionuclides in Benthic Organisms

Strontium ^{90}Sr and Caesium ^{137}Cs

The measurements of ^{90}Sr and ^{137}Cs contents in organisms living in the Baltic Sea have been carried out for over 30 years and are used for the assessment of radioactive contamination of the Baltic Sea, for seeking bioindicators which cumulate large amounts of radionuclides, as well as for controlling their migrations and releasing from the bottom sediments to the bottom waters (Szefer, 2002). Among seed plants, it was *Fucus vesiculosus* (brown alga) that was used as a bioindicator of contamination with radiostrontium and radiocaesium from the coastal zones of Poland, Sweden, Finland and Denmark, both before 1986 (Bojanowski, Pempkowiak, 1977; Aarkrog *et al*., 1986) and after the Chernobyl nuclear accident (Carlson, 1990; Dahlgaard, 1994). Plankton organisms were also a subject of some research (Ilus *et al*., 1987; Bojanowski *et al*., 1995b). The most numerous group of Baltic animals included in the study on the accumulation of ^{90}Sr and ^{137}Cs were, in particular, representatives of zoobenthos, molluscs and crustaceans. Some of them, e.g. mussel *Mytilus trossulus,* Bivalve mollusc *Macoma baltica* or benthic isopod crustacean *Saduria entomon*, cumulate both radionuclides and may serve as bioindicators of radiologic contamination of the sea bottom sediments with radiocaesium and radiostrontium (Holm *et al*., 1986; Skwarzec, Bojanowski, 1992; Bojanowski *et al*., 1995a; HELCOM, 1995). After the Chernobyl accident, the highest concentrations of ^{137}Cs were found in the soft tissue of clams taken from the Bothnian Bay in 1986–1987 and from the coastal regions of Forsmark (Sweden) in 1989, while of ^{90}Sr – in the shells of molluscs (HELCOM, 1995). In turn, in the crustacean *Saduria entomon,* the highest concentrations of ^{90}Sr and^{137}Cs were observed in individuals taken from the Gulf of Finland in 1986–1987 (Kanisch *et al*., 1995), and the results were more than 15-times higher than in those caught in the Bay of Pomerania (Bojanowski *et al*., 1995a). Baltic fish, both pelagic and demersal, have been subject to research. The contents of ^{90}Sr and ^{137}Cs were determined in soft tissues (fillet) and bones (Ilus *et al*., 1987; Holm, 1994; Kanisch *et al*., 1995). The highest concentrations of ^{137}Cs, exceeding 200 Bq/kg w.w., were found in fish fillets taken from the Bothnian Bay and the Gulf of Finland, caught in 1986 and 1987. The concentrations of ^{90}Sr were below 0.1 Bq/kg w.w. and compared to the years before 1986, they did not change significantly (HELCOM, 1995; Kanisch *et al*., 1995). Fish caught in the southern Baltic Sea (Bornholm Basin, Bay of Pomerania and Gulf of Gdańsk) were marked by almost ten-times lower concentrations of ^{137}Cs (Grzybowska, 1989; Bojanowski *et al*., 1995a). Radionuclides ^{90}Sr and ^{137}Cs dissolved in the Baltic waters and deposited in the bottom sediments accumulate in different ratios, both in benthonic and open water organisms. In Baltic organisms, the concentration of ^{137}Cs grows in the series of plankton < water plants < crustaceans and clams, and the values of the bioconcentration factor (BCF) for these organisms range from 20 to 70 (Table 10.3).

Of Baltic organisms, crustaceans are characterized by a higher accumulation of ^{90}Sr than ^{137}Cs. An opposite relation is observed in fish, however, ^{90}Sr accumulates more intensely in fish bones than in their muscles. Analyses of ^{137}Cs contents in some Baltic fish (herring, flounder, and cod), made in 1985–1995, showed an increase in the concentrations of ^{137}Cs after the Chernobyl accident from about 2 Bq/kg w.w. in 1985 to almost 20 Bq/kg w.w. in 1988 and in the next years it still maintained a high level. This means that ^{137}Cs is desorbed from the bottom sediments and accumulated in Baltic fish, and the value of BCF factor in the soft tissues of those fish is 165 (Table 10.3). The muscles of the Baltic herring and cod showed ^{90}Sr concentrations at 0.01–0.08 Bq/kg w.w. and it did not increase significantly after the explosion in the Chernobyl nuclear plant. As a consequence, there are relatively low values of the BCF factor of radiostrontium in fish fillets, amounting to 10 (IMGW, 1991–2004; Skwarzec, 2002, 2009).

Table 10.3

The bioconcentration factor (BCF) of strontium ^{90}Sr and caesium ^{137}Cs in Baltic Sea organisms (IMGW, 1991–2004; Skwarzec, 2002)

Organism	Bioconcentration factor (BCF)	
	^{90}Sr	^{137}Cs
Plankton	–	20
Water plants	70	50
Crustaceans and Clams	300	70
Fish:		
flesh	10	165
bones	50	–

Polonium ^{210}Po

Polonium is highly accumulated in organisms of the southern Baltic Sea and the mean values of the bioconcentration factor (BCF) are within the limits of $1.5 \cdot 10^3 - 3.2 \cdot 10^4$ (Table 10.4).

In plankton, the BCF factor values increase in the series of phytoplankton < macrozooplankton < mesozooplankton, whereas in the representatives of Baltic zoob-

Table 10.4

The values of ^{210}Po concentration and bioconcentration factor (BCF) in organisms of the southern Baltic Sea (Skwarzec, 1995, 2002)

Organism	^{210}Po [Bq/kg d.w.]	BCF·10^3
Phytoplankton	41	4.2
Phytobenthos	9	1.8
Zooplankton	126	32
Zoobenthos:		
Polychaeta	65	17
Priapulida	53	7.5
Crustacea	60	25
Clams (Bivalvia):	29	23
flesh	143	37
shell	8.5	12
Fish:	27	11
digestive tract	420	70
muscles	4.5	1.5

enthos, they increase in the series of priapulid worms < polychaetes < crustaceans < clams (soft tissue) (Skwarzec, 1988, 1995; Skwarzec, Bojanowski, 1988; Skwarzec, Falkowski, 1988; Holm, 1994; Dahlgaard, 1996; Skwarzec *et al*., 2003b).

Polonium is distributed uniformly in the tested representatives of crustaceans and clams (Table 10.5 and 10.6).

The highest concentrations of ^{210}Po were found in hepatopancreas of the benthic isopod crustacean *Saduria entomon* and in the soft-shell clam *Mya arenaria*, which includes more than 30% of the polonium accumulated in organisms. In Baltic crustaceans and clams, the concentration of ^{210}Po increases in the series of hepatopancreas > gills > muscles. In fish from the southern Baltic Sea, higher polonium concentrations occur in visceras (intestine, liver, pyloric caeca, spleen), and lower in the muscles. The contribution of the visceral organs in accumulating polonium in fish depends not only on the species but also on the type and quantity of ingesta (chyme). In cod and herring visceral organs accumulated from 65 to 80% of the total ^{210}Po. The results indicate that polonium may be one of the natural indicators of food biomass in Baltic fish (Skwarzec, 1995). Moreover, ^{210}Po and ^{210}Pb (the precursor of ^{210}Po) in Baltic organisms are not in a radioactive equilibrium state; the activity ratio of ^{210}Po/^{210}Pb reaches 70, lower values were found in the hard tissues of fish, and higher values – in the inner organs of fish and mussels (*Mytilus trossulus*) (Skwarzec, 1988, 1995, 1997; Skwarzec, Falkowski, 1988).

Baltic fish are the main source of polonium (more than 30%) for Poland's inhabitants and their consumption supplies annually an effective radiation dose of 43 μSv (Skwarzec, 2002). Also marine birds that live on the southern Baltic Sea coast accumulate polonium that enters their bodies as a result of eating marine organisms, mainly small fish and molluscs (Skwarzec, Fabisiak, 2007). In the biocoenose of the southern Baltic Sea, the content of ^{210}Po in organisms living in the marine environment increases in the series of marine birds < fish < zooplankton < phytoplankton < phytobenthos < crustacean < clams.

Figure 10.6 presents a cycling diagram for ^{210}Po in the southern Baltic Sea ecosystem. The main source of polonium is atmospheric fallout of ^{210}Pb and ^{210}Po, but to a smaller degree. The behaviour of these nuclides in the Baltic environment is different. Lead is sorbed in mineral suspended solids, but polonium is bound with biogenic suspension and dissolved organic substances (DOS) and is strongly cumulated in Baltic organisms. In the sea bottom sediments, the concentration of polonium depends to a considerable degree on the contents of detritus formed mostly from the settled dead cells of phytoplankton and excrements of both zooplankton and fish. In this way,

Table 10.5

The ^{210}Po and ^{210}Pb concentrations and the ^{210}Po/^{210}Pb activity ratio in the tissues and organs of the crustacean *Saduria entomon* from the Gdańsk Basin (Skwarzec, 1995, 2002)

Organ, tissue	^{210}Po concentration	^{210}Pb concentration	Activity ratio ^{210}Po/^{210}Pb
	[Bq/kg d.w.]		
Hepatopancreas	544	51	10.6
Alimentary system	354	55	6.4
Muscles	52	14	3.6
Gonads	12	4	3.2
Head	8.5	2	4.4
Chitin plate	0.64	2.6	0.2
Haemolymph	11	70	0.2
Whole organism	29.5	6.2	4.8

Table 10.6

The ^{210}Po and ^{210}Pb concentrations and the ^{210}Po/^{210}Pb activity ratio in the tissues and organs of the mussel *Mytilus trossulus* from the Gulf of Gdańsk (Stepnowski, Skwarzec, 2000a, b; Skwarzec, 2002)

Organ, tissue	^{210}Po concentration	^{210}Pb concentration	Activity ratio ^{210}Po/^{210}Pb
	[Bq/kg d.w.]		
Hepatopancreas	1026	15	68.4
Branchiae	232	11	21.0
Muscles	57	1.4	41.8
Byssus	30	5	6.0
Shell	1	0.64	1.4
Whole organism	24	1.1	22.2

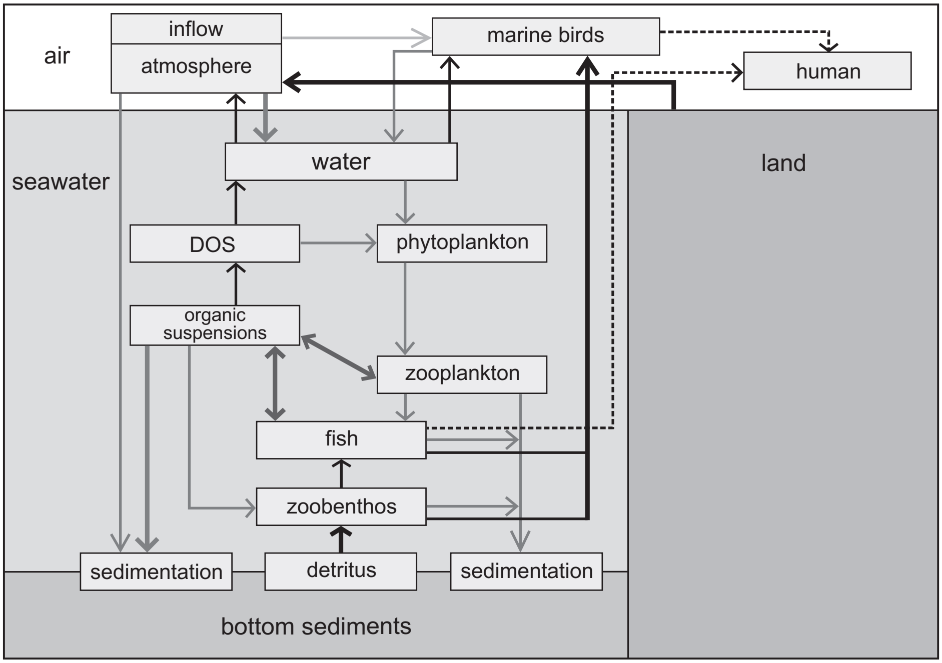

Fig. 10.6. Migration of polonium in the southern Baltic Sea ecosystem (Skwarzec, 1995, 2002)

they contribute to fast removing of polonium from the marine waters. Through eating the detritus and filtering sea bottom and pore waters, zoobenthos contribute to concentrating polonium. In turn, fish that feed with crustaceans and clams accumulate ^{210}Po which earlier settled on the sea bottom. Therefore, the migration of polonium in the southern Baltic Sea ecosystem is to some extent consistent with the matter cycle in the individual links of the food chain (Skwarzec, 1995, 2009).

Uranium ^{238}U and ^{234}U

Uranium, opposite to polonium, is poorly accumulated in Baltic organisms and the bioconcentration factors (BCF) range from 0.4 to 82 (Table 10.7).

Phytoplankton contains twice more uranium than zooplankton. In the tested organisms of the sea bottom fauna, the uranium concentration is higher in soft tissues of clams than in crustaceans. A bivalve mollusc (*Macoma baltica*) from the Puck Bay contains almost twice more uranium than the same organism living in the Gulf of Gdańsk. Uranium is distributed unevenly in several organs and tissues of the Baltic fish. Its concentration increases in the series

Table 10.7

The values of ^{238}U concentration and bioconcentration factor (BCF), and the ^{234}U/^{238}U activity ratio in organisms of the southern Baltic Sea (Skwarzec, 1995, 2002)

Organism	^{238}U [Bq/kg d.w.].	BCF	Activity ratio ^{234}U/^{238}U
Phytoplankton	5.5	45	1.15
Phytobenthos	3.5	48	1.14
Zooplankton	1.3	30	1.15
Zoobenthos:			
Crustacea	1.5	51	1.15
Clams (Bivalvia):	0.9	55	1.15
flesh	4.5	82	
shell	0.3	30	
Fish:	0.05	1.3	1.12
digestive system	0.64	7.6	
muscles	0.0112	0.4	

of muscles > fish bones > viscera (Skwarzec, 1995, 1997). Higher concentrations of uranium in viscera of cod or herring show the essence of their food composed mainly of clams and smaller fish, which is a source of this element in fish. The BCF factor values for uranium in fish are generally by two orders of magnitude lower than in the other Baltic organisms and oscillate around 1. In Baltic organisms, the activity ratio values of ^{234}U/^{238}U range between 1.12 and 1.15 and are close to the value characteristic of marine water (1.17), which indicates that they take uranium from water and participate in its deposition in the bottom sediments to a small degree (Fig. 10.7). Besides, marine birds, who feed on clams, (auk, common murre, diver) accumulate uranium and the calculated values of the transfer factor (TF) exceed 2 (Fabisiak, 2007).

Based on the determined average uranium concentrations in the individual representatives of the southern Baltic Sea biocoenosis (Skwarzec, 1995, 2009; Szefer, 2002; Fabisiak, 2007), it was found that the uranium content in organisms living in the marine environment increases in the following series of fish < marine birds < zooplankton < phytoplankton < phytobenthos < crustaceans < clams (bivalves).

The diagram presented in Figure 10.8 shows the interactions and migration of uranium in the southern Baltic Sea ecosystem. The geochemical process of the uranium circulation in this region originates from weathering rocks and soil erosion. Terrigenous material is transferred to the Baltic Sea by the atmosphere and riverine waters of this drainage basin. Riverine waters, mainly those of the Vistula and Odra rivers, are additionally enriched with anthropogenous uranium originated from the economic activity. In sea water depths, uranium settles and then undergoes diagenetic processes that lead to its diffusion by pore (interstitial) waters to the sea bottom waters. In geochemical migration of uranium in the Baltic Sea, organisms that take uranium from water play a smaller part, participating in its deposition to the sea bottom sediments to an insignificant degree (Skwarzec, 1995, 2009).

Plutonium ^{238}Pu, $^{239+240}$Pu and ^{241}Pu

Plutonium, like polonium, is highly accumulated in Baltic organisms and the BCF factor values range between 25 and 27·10^3 (Table 10.8). In Baltic animals, the $^{239+240}$Pu concentration is very variable and ranges from

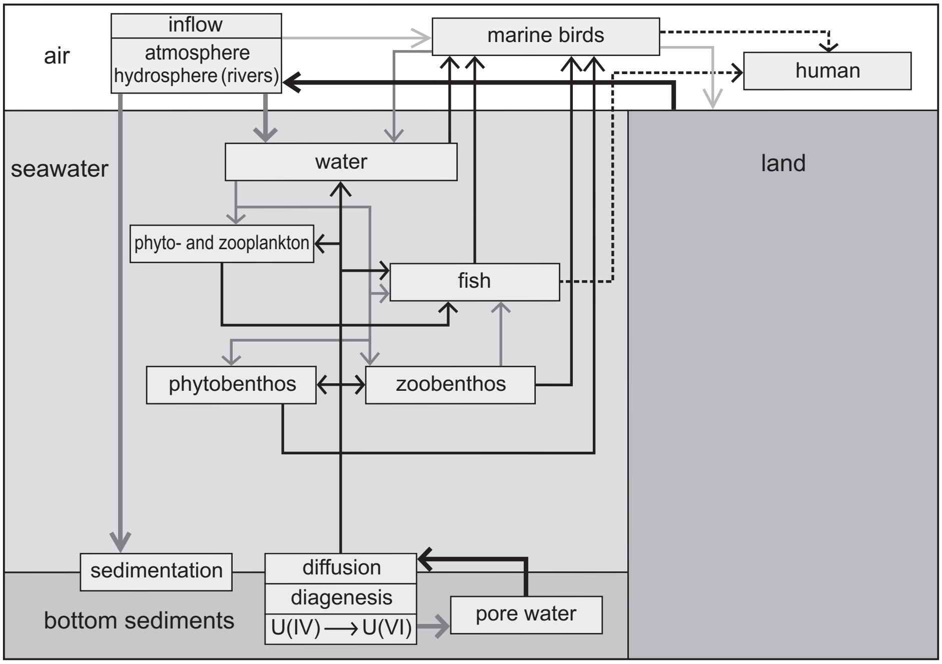

Fig. 10.7. Circulation of uranium in the southern Baltic Sea ecosystem (Skwarzec, 1995, 2002)

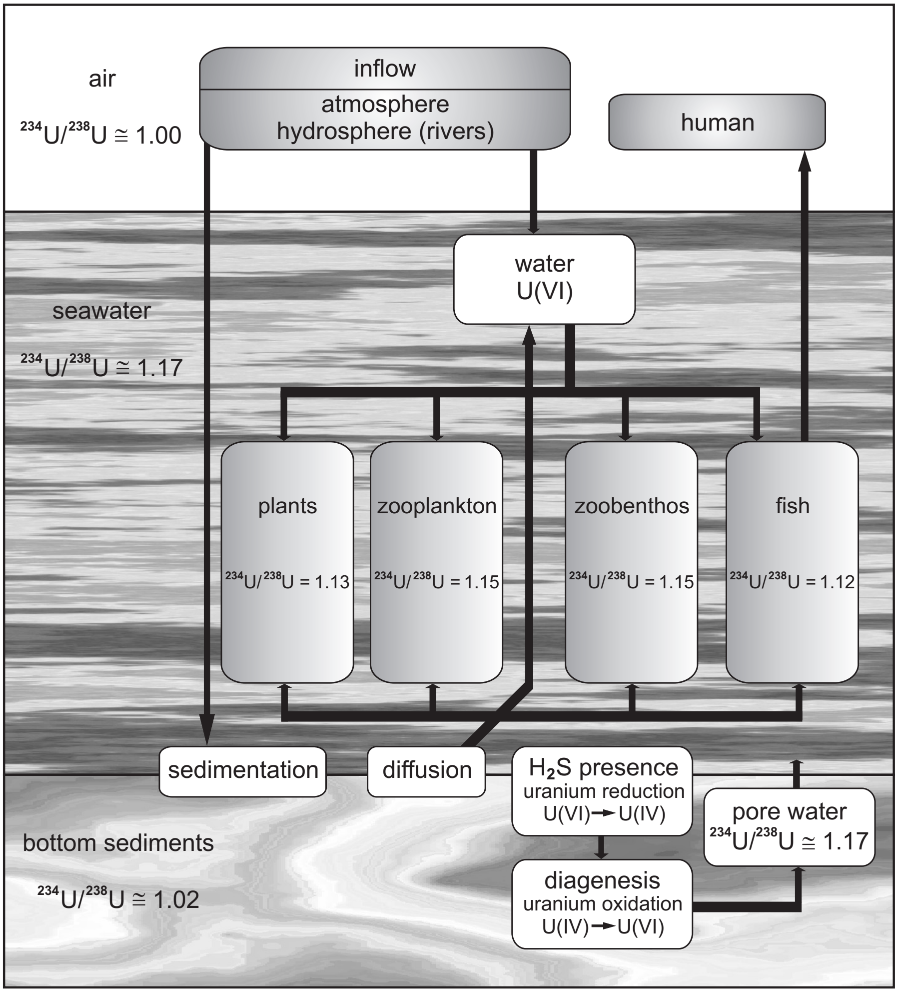

Fig. 10.8. The influence and migration of uranium in the southern Baltic Sea ecosystem (Skwarzec, 1995, 2002)

0.014 Bq/kg d.w. in fish to 0.957 Bq/kg d.w. in the priapulid warm *Halicriptus spinulosus*. For the tested organisms of benthonic and demersal fauna, higher concentrations of plutonium were observed in the representatives of Priapulida and Polychaeta, whereas lower contents of plutonium were recorded in Crustacea and in soft tissues of Bivalvia. Among sedentary plants from the Bay of Puck, the highest $^{239+240}$Pu concentration was observed in the brown alga *Pylaiella litoralis* taken in 1987. In Baltic fish, the distribution of $^{239+240}$Pu is non-uniform. In cod and herring, it decreases in the series of viscera > head > skeleton > muscles. The viscera have half of the total plutonium contained in these fish, and its considerable part is located in digestive systems. Especially high $^{239+240}$Pu concentrations were found in the intestines of cod and in the gills of herring (Skwarzec, Strumińska, 2001; Strumińska, Skwarzec, 2006).

Based on the activity ratio of ^{238}Pu/$^{239+240}$Pu, the proportion of the Chernobyl plutonium was determined in its total contents in selected components of the southern Baltic Sea ecosystem. This contribution was insignificant in zoobenthos and in the sea bottom sediments in the period of 1987–1991 and was apparent generally in clams (app. 10%), but it was essentially higher in the

Table 10.8

The values of $^{239+240}$Pu concentration and bioconcentration factor (BCF) in organisms of the southern Baltic Sea (Skwarzec, 1995, 2002)

Organism	$^{239+240}$Pu [Bq/kg d.w.]	BCF·10^3
Phytoplankton	0.006	0.6
Phytobenthos	0.118	3.5
Zooplankton	0.004	0.025
Zoobenthos:		
Polychaeta	0.169	5.5
Priapulida	0.957	27.0
Crustacea	0.046	2.7
Clams (Bivalvia):		
soft tissue	0.073	3.2
Fish:	0.014	0.9
digestive tract	0.100	2.9
muscles	0.0039	0.25

Table 10.9

The ^{241}Pu concentration in phyto- and zoobenthos of the Puck Bay in 1986–1987 (Strumińska, Skwarzec, 2006)

Organism	^{241}Pu concentration [Bq/kg d.w.]	Activity ratio ^{241}Pu/$^{239+240}$Pu
Phytobenthos:		
Cladophora rupestris	0.30 ±0.05	5.4
Ulva lactuca	0.28 ±0.08	28
Elodea canadensis	0.22 ±0.09	9.2
Potamogeton pectinalis	0.39 ±0.06	35
Pylaiella litoralis	1.01 ±0.12	9.4
Zostera marina	0.24 ±0.06	18
Zoobenthos:		
Antinöella sarsi	7.71 ±0.85	59
Balanus improvisus	0.20 ±0.02	29
Cardium glaucum	1.66 ±0.02	64
Gammarus sp.	1.80 ±0.21	30
Halicryptus spinulosus	9.20 ±1.20	11
Mytilus trossulus	0.28 ±0.03	1.7
Saduria entomon	0.13 ±0.06	5

fauna representatives taken in 1998: from 20% for the round goby *Neogobius melanostomus* to 70% for herring (Skwarzec, Strumińska, 2001; Strumińska, Skwarzec, 2004).

Besides alpha emitters of ^{238}Pu, ^{239}Pu and ^{240}Pu, the natural environment also contains ^{241}Pu, which belongs to β^- emitters. After the Chernobyl nuclear accident on 26th April, 1986, its activity in the air increased by 3500 times, reaching 3643 Bq/kg d.w. in dry atmospheric fallout (Strumińska, Skwarzec, 2006). Meanwhile, the ^{241}Pu concentration in the waters of the Bay of Gdańsk was 0.23 Bq/m^3, and the activity ratio of ^{241}Pu/$^{239+240}$Pu was 140 at that time. The ^{241}Pu isotope, like the $^{239+240}$Pu radionuclides, is also highly accumulated in Baltic organisms (Table 10.9).

Amongst the representatives of zoobenthos, higher ^{241}Pu concentrations were observed in the priapulid worm *Halicryptus spinulosus* and the polychaeta *Antinöella sarsi*, whereas lower values were recorded in crustaceans: the isopod *Saduria entomon* and the acorn barnacle *Balanus improvisus*. It means that higher ^{241}Pu concentrations occur in the representatives of Priapulida and Polychaeta, while lower – in Crustacea. For seaweeds from the Puck Bay, the highest ^{241}Pu concentrations were observed in the macrophyte *Elodea canadensis* and the seagrass *Zostera marina,* as well as in the brown alga *Pylaiella litoralis*. Owing to the morphologic structure and a large surface area of the thalli *Pylaiella litorali,* both radionuclides and heavy metals are more susceptible to sorb in it (Szefer, 2002). The activity ratios of ^{241}Pu/$^{239+240}$Pu in phytobenthos were between 5.4 for the Chlorophyta *Cladophora rupestris* and 35 for the representative of the spermatophyte *Potamogeton pectinalis*. For the representatives of the benthonic fauna, the values varied from 1.7 in the mussel *Mytilus trossulus* to 64 in the mollusc *Cardium glaucum*. It means that zoobenthonic organisms contain more ^{241}Pu than spermatophytae. They accumulate plutonium from bottom sediments and interstitial waters, contrary to phytobenthos which ab-

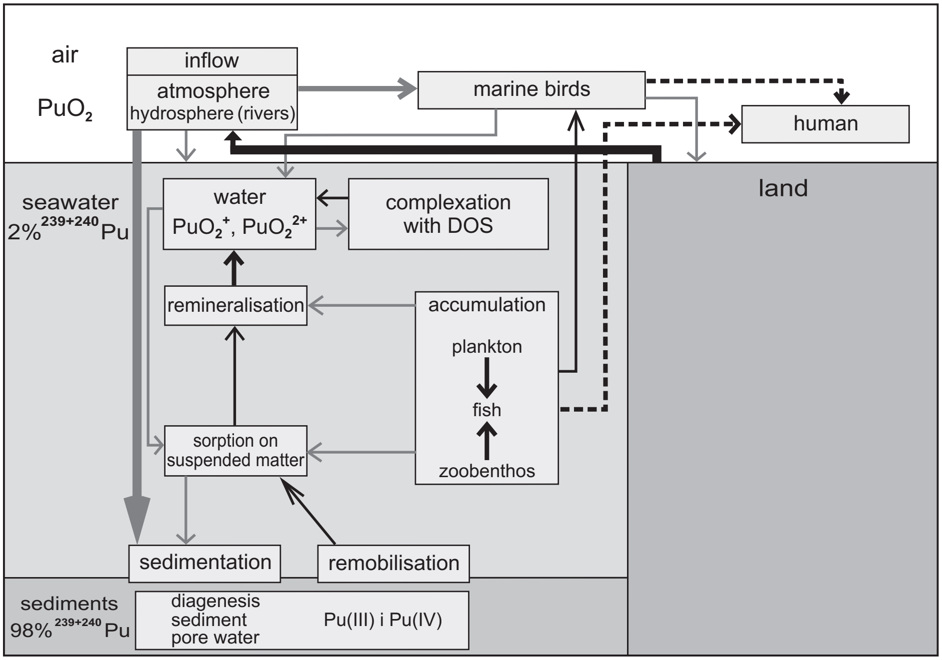

Fig. 10.9. The influence and migration of plutonium in the southern Baltic Sea ecosystem (Skwarzec, 1995, 2002)

sorb plutonium contained in marine waters (Strumińska, Skwarzec, 2006).

Also marine birds accumulate plutonium, however higher $^{239+240}$Pu concentrations are observed in the birds preferring mixed animal food (molluscs, crustaceans and fish) with some plant food (long-tailed duck and common eider), and in organisms preferring generally plant food (tufted duck) (Fabisiak, 2007; Skwarzec, 2009).

Based on the determined mean concentrations of plutonium for the individual representatives of the southern Baltic Sea biocoenosis (Skwarzec, 1995, 1997; Skwarzec, Strumińska, 2001; Strumińska, Skwarzec, 2004), it can be stated that its contents in organisms residing in the marine environment increase in the series of marine birds < fish < zooplankton < phytoplankton < zoobenthos < phytobenthos.

Figure 10.9 presents the diagram of interactions and migrations of plutonium in the southern Baltic Sea ecosystem. The most important constituents for the plutonium circulation are the processes of riverine runoff and atmospheric fallout, and sedimentation in water. Plutonium deposited in the sea bottom sediments undergoes the processes of diagenesis and remobilisation (releasing to water) whose rates depend on the chemical forms in which it occurs.

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Chapter 11

CHEMICAL COMPOSITION OF INTERSTITIAL WATERS

Studies of the Baltic interstitial waters from sea-bottom sediments began in the first half of the 20th century (Grippenberg, 1934; Kullenberg, 1952; Mikkelsen, 1956). An elution method was applied to analyse the contents. However, these data have only a historical value (Bolałek, 1988) due to defects in achieving the material for testing interstitial waters in this way. The chemical composition of interstitial water reflects the reactions that occur between sedimentary particles and the solution. Chemical analysis of these waters helps to increase knowledge about the early stages of diagenesis and enables us to:

- Detect diagenetic reactions in bottom sediments,
- Estimate exchange fluxes on the sediment-water interface,
- Close the biogeochemical cycles of macro- and micro-components in the sea water.

The basic chemical composition of interstitial waters is generally very complex and does not coincide with the near-bottom water composition. Basic components of interstitial waters, including marine waters are chloride (Cl^-), sulphate (SO_4^{2-}) and bicarbonate (HCO_3^-) anions, and sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+) and, occasionally, strontium (Sr^{2+}) cations.

The distinctness of the chemical composition of interstitial waters with reference to the near-bottom waters depends on many factors (Bolałek, 1992), e.g. location in relation to the land (distance to the coastline, watercourses), geological conditions (variability of minerals, grain size of sediments), sedimentary conditions, hydrogeological conditions (groundwater inflow), physicochemical conditions (redox potential, sorption processes, hydrostatic pressure in the marine water over the tested sediment), biological conditions (bioturbation and bioirrigation, organic matter inflow in a form of detritus) and anthropopression. The main role should be assigned to the factors that determine the intensity and direction of the processes taking place when the chemical composition is formed in the waters. These factors include water mixing, degradation of organic matter and its basic mineralising component and adsorption of elements on the solid particles of the sediment. These processes help to establish a physico-chemical balance between the chemical composition of interstitial waters and the ambient sediments. The concentration ratio of the basic salinity factors to the chloride concentration in marine water is approximately constant, but differs for the individual constituents of the salinity and is regionally variable (Table 11.1). The highest differences between the interstitial waters and the near-bottom water occur in relation to these constituents that are sensitive to both the changes in a redox potential (sulphates, alkalinity) and inflow of fresh waters (calcium and chloride ions). The main factors determining the chemical composition of the Baltic Sea interstitial waters are as follows (Jørgensen *et al*., 1990; Bolałek, 1992; Carman, Rahm, 1997; Schlüter *et al*., 2004):

– Oxidation of organic matter and the reduction of some chemical compounds (e.g. nitrates, sulphates);

– Groundwater inflow expressed by changes in chloride ion concentrations;

Table 11.1

Weight ratio of the concentrations of ionic macro-components and chlorides in the Baltic Sea and ocean waters

Region	Estimator	$HCO_3^-:Cl^-$	$SO_4^{2-}:Cl^-$	$Na^+:Cl^-$	$Mg^{2+}:Cl^-$	$Ca^{2+}:Cl^-$	$K^+:Cl^-$	References
Baltic Proper – interstitial waters	min.	0.014	0.060	0.391	0.032	0.020	0.018	Carman, Rahm, 1997
	max.	0.062	0.160	0.525	0.068	0.027	0.026	
	mean	0.029	0.110	0.461	0.048	0.023	0.022	
	SD	0.015	0.022	0.034	0.009	0.002	0.002	
Gotland Deep – interstitial waters	min.	0.036	0.000	0.444	0.051	0.024	0.010	Shishkina *et al.*, 1980
	max.	0.203	0.102	0.548	0.067	0.101	0.029	
	mean	0.102	0.018	0.508	0.058	0.054	0.018	
	SD	0.050	0.033	0.035	0.006	0.028	0.007	
Puck Bay – interstitial waters	min.	0.016	0.000	0.503	0.011	0.019	0.012	Bolałek, 1992
	max.	0.357	0.438	0.650	0.099	0.298	0.036	
	mean	0.197	0.109	0.556	0.063	0.048	0.025	
	SD	0.064	0.074	0.028	0.012	0.053	0.005	
Puck Bay – near-bottom waters	min.	0.023	0.145	0.537	0.068	0.027	0.018	Bolałek, 1992
	max.	0.036	0.172	0.560	0.069	0.035	0.021	
	mean	0.030	0.159	0.552	0.069	0.030	0.020	
	SD	0.004	0.008	0.008	0.001	0.003	0.001	
Gulf of Gdańsk – water column		0.043	0.144	0.551	0.067	0.033	0.021	Młodzińska, 1975
Southern Baltic Sea – water column		0.020	0.141	0.534	0.067	0.026	0.021	Trzosińska, 1977
Ocean		0.007	0.140	0.536	0.067	0.0210	0.021	Culkin, 1965

SD – standard deviation.

– Hydrostatic pressure of the marine water over the sea bottom;

– Reactions of ion exchange;

– Reverse weathering reaction.

Figures 11.1 and 11.2 present the changes in the concentrations of macro-components in interstitial waters of the Baltic Proper and Puck Bay, respectively.

Chloride ion does not form any insoluble compounds with other macro-components of marine and interstitial waters. It does not participate in the processes of absorption and its concentration in the marine environment is not dependent on chemical and biogeochemical composition of marine sediments. Owing to high solubility of chlorine compounds, 97% to 99% of their total contents refer to interstitial waters (Shishkina, 1972). The concentration of chloride ion in interstitial waters is generally associated with its concentration in near-bottom waters. The change in chloride concentrations in interstitial waters results from the processes of diffusion, migration induced by the compaction, and submarine discharge of groundwater of different chemical composition. This process of desalination is clearly observed in the bays where water from proglacial river valleys flows under the sea bottom. The variability of many parameters in the interstitial waters of the Puck Bay (southern Baltic Sea) (Fig. 11.2) and different chloride concentration in the interstitial waters of the Eckernförde Bay (western Bal-

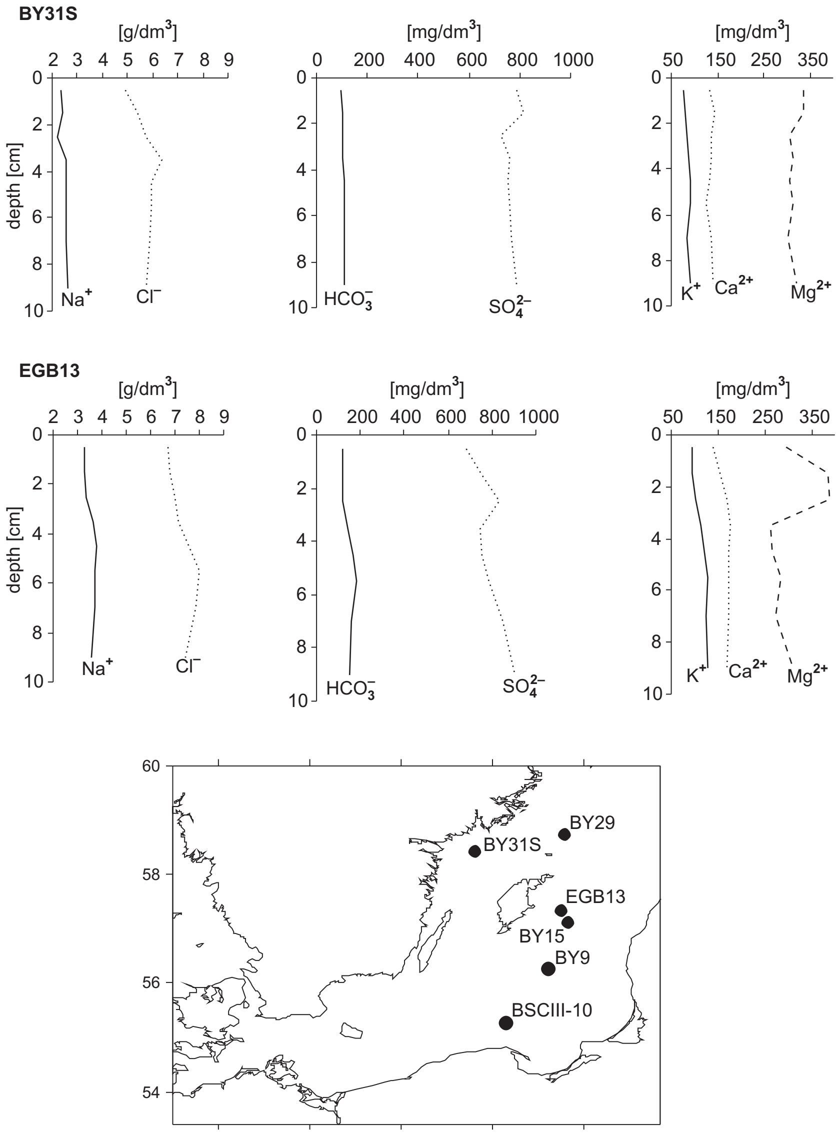

Fig. 11.1. Vertical changes in concentrations of ionic macro-components in interstitial waters of the Baltic Proper (data by Carman and Rahm, 1997)

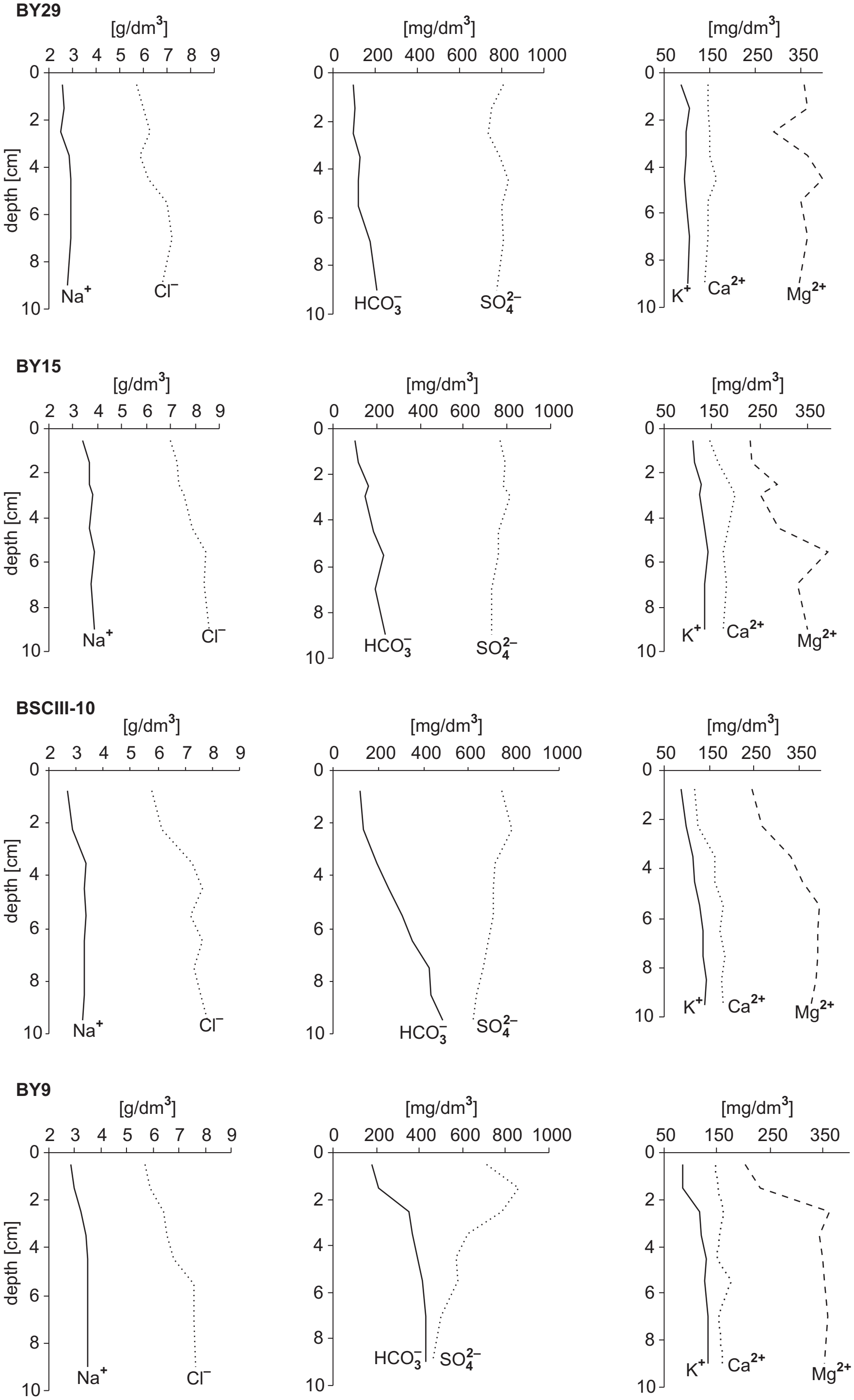

Fig. 11.1. continued

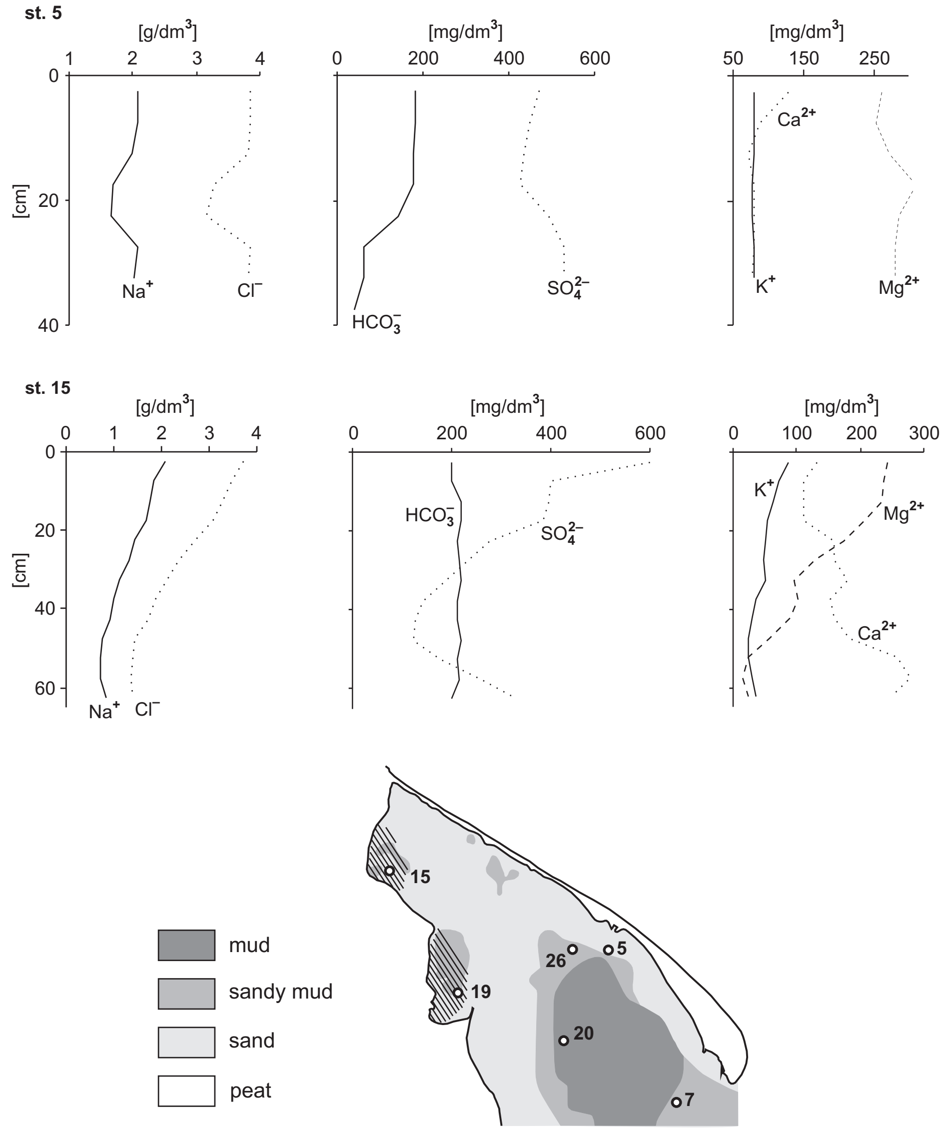

Fig. 11.2. Vertical changes in the concentrations of ionic macro-components in interstitial waters of the Puck Bay (Bolałek, 1992)

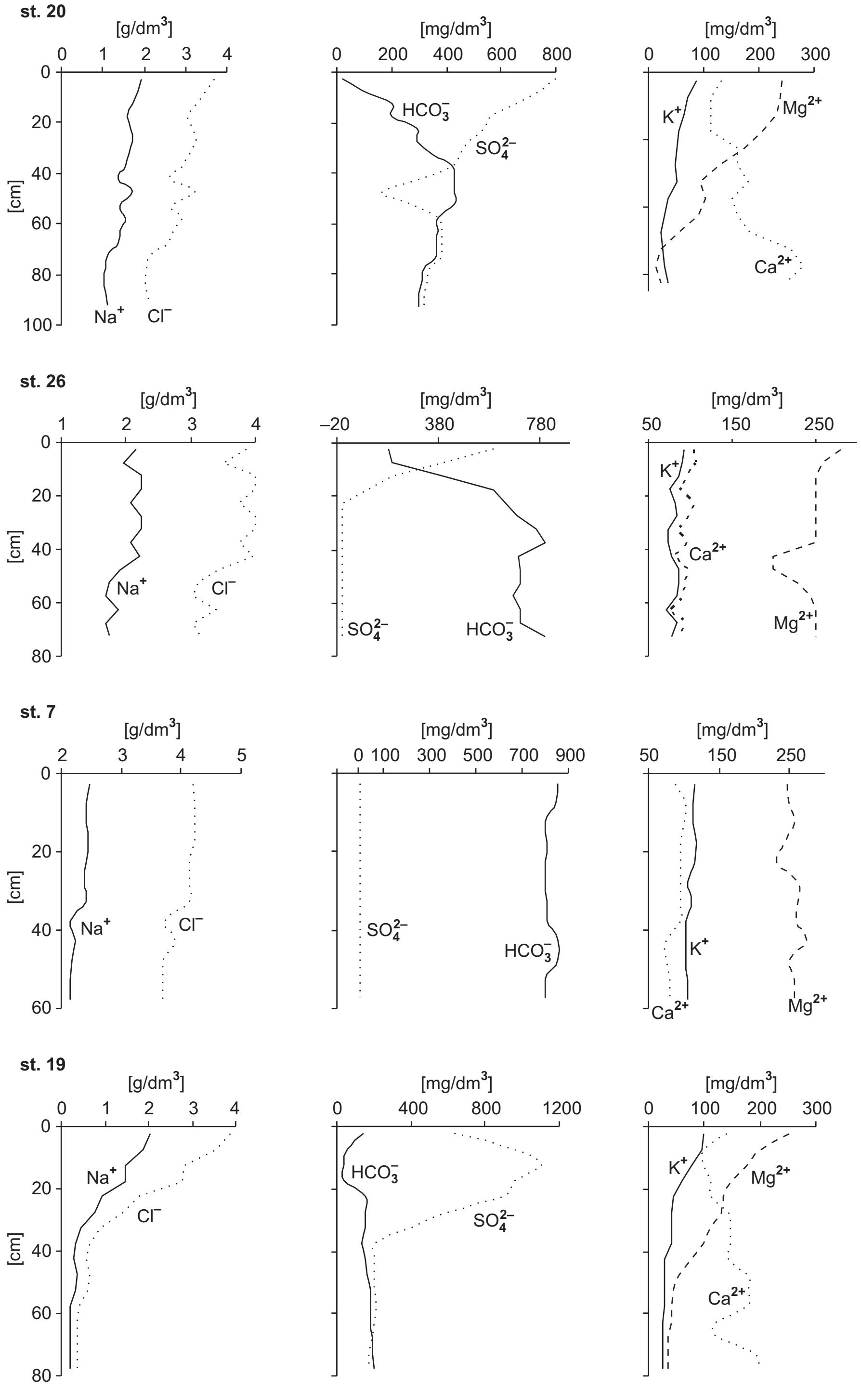

Fig. 11.2. continued

tic Sea) are good examples. The concentration of chlorides drops even below 10% of the concentration of this component in the near-bottom waters (Schlüter *et al.*, 2004). Also, the sediments of the Puck Bay, where the groundwater inflow was observed, showed the lowest concentration of chlorides (0.37 g/dm^3; Table 11.2) at 8.7% of the highest value of this component concentration (4.24 g/dm^3). Falkowska and Piekarek-Jankowska (1999) claimed groundwater discharge to the bottom of the Gdańsk Deep.

In most cases, the concentrations of **sulphates** in interstitial waters reveal the variability associated with a sediment type. They are lower than it results from their ratio to the concentration of chlorides in marine waters. The higher the content of organic matter in sediments, the potentially lower the concentrations of sulphates in interstitial waters are. This is related to microbiological reduction of sulphates to hydrogen sulphite (desulphatisation). The drop in sulphate concentrations in the interstitial waters, as a result of bacterial reduction, is often observed in marine sediments and generally can be described by the following reaction:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$

where:

CH_2O – source of organic carbon.

The bicarbonate ion formed during this reaction increases the alkalinity of interstitial water. Low and zero concentrations of sulphates correspond to the concentrations of bicarbonates (Fig. 11.3).

The elevated concentrations of sulphates in the surface sediment layer that are usually well oxygenated result from oxidation of hydrogen sulphide diffusing from deeper parts of the sediment: $H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$. In such cases, the weight ratio of the parameter to the concentration of chloride ion is essentially lower (Table 11.1) than that in the sea-bottom waters. This often occurs in anoxic silty sediments. The drop in sulphate concentrations in the interstitial water is associated with an increase in methane concentrations (Fig. 11.4). This is a result of methanogenesis:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 53CH_4 + \\ + 16NH_3 + H_3PO_4$$

Table 11.2

Concentration* of ionic macro-components in the Baltic Sea interstitial waters

Region	Estimator	Cl^-	HCO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	Ca^{2+}	K^+	Sr^{2+}	References
Baltic Proper	N	49	49	49	49	49	49	49	49	Carman, Rahm, 1997
	min.	4.93	96	464	2.24	202	120	104	1.32	
	max.	8.60	488	904	3.90	401	200	192	2.36	
	mean	6.87	202	741	3.17	325	158	149	1.95	
	SD	0.88	116	86	0.47	51	19	27	0.29	
Gotland Deep	N	10	10	10	10	10	10	10		Shishkina *et al.*, 1980
	min.	5.25	226	0	2.48	274	172	63		
	max.	7.18	1415	346	3.84	476	639	203		
	mean	6.52	675	61	3.31	375	343	120		
	SD									
Puck Bay	N	183	181	161	171	175	177	173		Bolałek, 1992
	min.	0.37	45	0	0.20	14	52	9		
	max.	4.24	1065	1109	2.49	387	281	127		
	mean	3.12	328	280	1.73	202	112	79		
	SD	0.88	274	240	0.55	82	51	30		

* Cl^- and Na^+ concentration in g/dm^3, other concentrations in mg/dm^3;
N – number of samples;
SD – standard deviation.

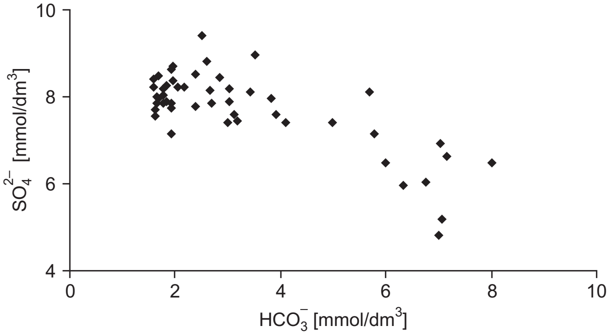

Fig. 11.3. Relationship between the concentration of sulphates and bicarbonates in interstitial waters of the Baltic Proper (data by Carman and Rahm, 1997)

An increase in **carbonate alkalinity** (carbonate basicity) with the depth of the sediment is observed in almost all sediments (Jørgensen *et al.*, 1990; Bolałek, 1992; Carman, Rahm, 1997). A high linear correlation between the alkalinity and sulphate concentrations suggests that the bacterial reduction of sulphates is a main source of alkalinity (basicity). Assuming that the alkalinity mostly originates from the contents of bicarbonates, their ratio to chlorides in interstitial waters varies between values close to those observed in the near-bottom water of the Baltic Sea (Table 11.1) and several times higher values, of about 0.35.

The horizontal and vertical distributions of **sodium** concentrations in of the Baltic Sea interstitial waters show a similar character to those observed in chlorides. For instance, the coefficient of the linear correlation Na–Cl (0.99) in the waters of the Puck Bay shows a high mutual dependence of these two elements and proves the same origin (Bolałek, 1992). The weight ratio of sodium to chlorides in the open Baltic Sea interstitial waters, lower than that in the Puck Bay (Table 11.1) is a result of engaging sodium in the reactions of ionic exchange (Shishkina *et al*., 1980). After the diffusion of chloride ions with sodium ions from the bottom water to the interstitial waters, mineralisation of organic matter and precipitation of $CaCO_3$ induced by the reduction of sulphates, the balance in the system between interstitial water and exchangeable complex is disturbed. The process leads to a cation exchange. The concentration of calcium in the interstitial waters increases while that of magnesium, sodium and potassium decreases (Fig. 11.5).

Numerous investigations showed a decrease in the concentration of **magnesium** under reducing conditions in interstitial waters when the depth of sediments increased (Shishkina *et al.*, 1980; Sayles, 1981; Carman, Rahm, 1997). Finally, the magnesium concentrations in interstitial waters are lower than the concentrations of chloride ions indicate, and the ratio of these components is also lower than that in the sea-bottom waters (Table 11.1). Carman and Rahm (1997) claim that such variability in magnesium concentrations is induced by the mechanism of removing iron(III) oxides from some of clay minerals. Furthermore, it may be associated with the precipitation from the solution or with recrystallisation of biogenic “low-

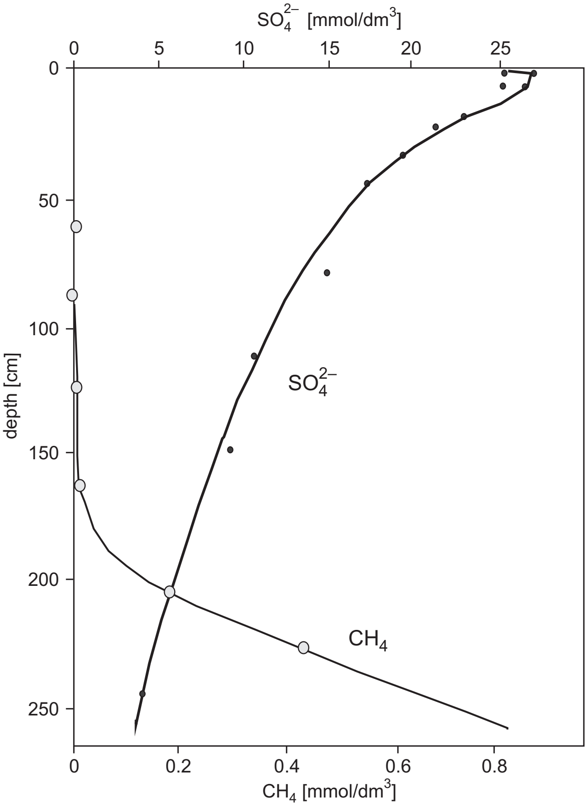

Fig. 11.4. Changes in the concentrations of sulphates and methane in interstitial waters of the Great Belt (Jørgensen *et al.*, 1990)

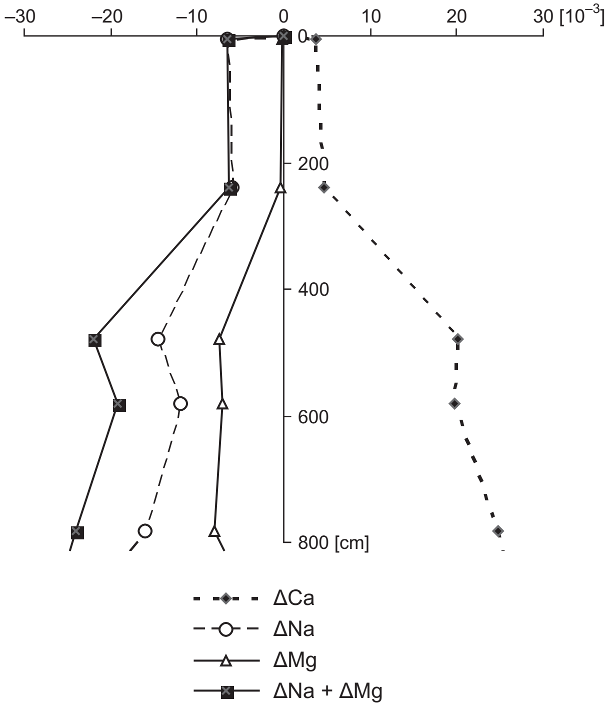

Fig. 11.5. Vertical changes in the calcium, magnesium and sodium concentrations in interstitial waters of the Baltic Sea (data by Shishkina *et al.*, 1980)

magnesium detrital carbonates", which leads to forming dolomite.

The **calcium** concentration in the open-sea interstitial waters (Shishkina *et al.*, 1980; Carman, Rahm, 1997) changes inconsiderably in comparison to the Puck Bay, where the inflow of fresh groundwater is the main factor affecting the interstitial water contents (Bolałek, 1992). In both cases, an increase in the concentration of this element deep into the sediment has been observed. As regards the open sea, the changes may result from the cation exchange, but in the Puck Bay, they can be caused by the inflow of waters containing considerable amounts of calcium. In the surface layer of interstitial waters of the open sea (0–10 cm), the weight ratio of calcium to chlorides varies within a small range between 0.020 and 0.027, whereas in the layer down to 1,000 cm, it varies from 0.024 to 0.101 (Shishkina *at al.*, 1980). A considerably higher range of changes in this weight ratio has been observed in the Puck Bay, where calcium is supplied with inflowing groundwater and therefore no significant correlation occurs between the concentrations of calcium and chlorides in the interstitial waters (Bolałek, 1992).

In the Baltic Sea, Shishkina *et al*. (1980) discovered interstitial waters that had a low **potassium** concentration and a low (<0.020) K^+:Cl^- ratio with reference to the near-bottom water. This is associated with engaging the potassium ions, similarly to the sodium ions, into the processes of cationic exchange. The potassium concentration in the Baltic Sea interstitial waters ranges from almost 10 to slightly more than 200 mg/dm^3. In some regions of the Baltic Sea, an increase in potassium concentrations was observed with reference to the contents of chlorides, which may be caused by the decay of omnipresent feldspars.

$$\underset{\text{feldspar}}{2KAlSi_3O_8} + 8H_2O + 5Mg^{2+} \rightarrow$$
$$\rightarrow \underset{\text{chlorite}}{Mg_5Al_2Si_3O_{10}(OH)_8} + 8H^+ + 2K^+ + 3SiO_2$$

Most macro-components contained in the Baltic Sea interstitial waters participate in ion exchange reactions and in the reactions of reverse weathering. One instance showing the participation of potassium and sodium in the formation of a new mineral is the reaction presented above. This participation is caused by a decrease in concentrations of sulphate ions to a degree larger than

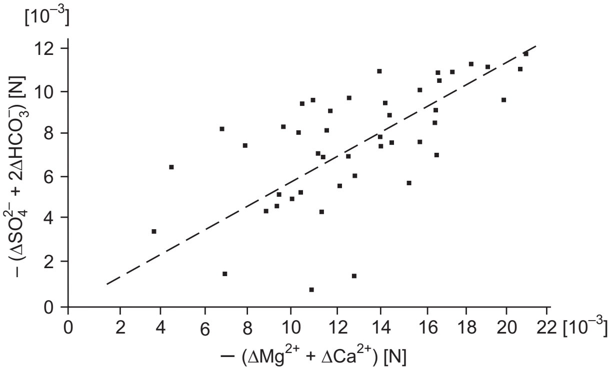

Fig. 11.6. Relationship between the total sum of the concentrations of bicarbonates and sulphates, and the concentrations of calcium and magnesium in interstitial waters (Bolałek, 1992)

the equivalent increase in bicarbonate ions. Figure 11.6 shows the relation between the concentration of the two anions and the sum of magnesium and calcium. The expression ΔX denotes a difference between the actual concentration of a given ion in the interstitial water (X_{iw}) and the concentration calculated from the ratio of a given ion to a chlorine equivalent in the near-bottom water (k):

$$\Delta X = (X_{iw} - k \cdot Cl_{iw})$$

where:

Cl_{iw} – concenration of chlorine ion in interstitial waters.

Data concerning the exchange of sodium and magnesium with ions of calcium (Fig. 11.5) were calculated in the same way. A decrement in the sum of sodium and magnesium concentrations in interstitial water is nearly equal to the increase in the concentration of the dissolved calcium.

The obtained relation between the concentration of calcium, magnesium, sulphate and bicarbonate ions is associated mainly with dissolution of calcite of biogenic origin and with recrystalization and dolomitisation (Sayles, Manheim, 1975):

$$2(Ca_x, Sr_{1-x})CO_3 + Mg^{2+} \rightarrow$$
$$\rightarrow CaMg(CO_3)_2 + (2x-1)Ca^{2+} + 2(1-x)Sr^{2+}$$

Dissolution of calcite of organic origin, which contains trace amounts of Sr^{2+}, increases the concentration of Ca^{2+} and Sr^{2+}. Then, a considerable part of Mg^{2+} and some Ca^{2+} precipitate as a form of dolomite, a surplus of Ca^{2+} and Sr^{2+} is formed in water and the concentration of Mg^{2+} decreases. A drop in the magnesium concentration and the lack of HCO_3^- ions to balance the SO_4^{2-} ions can also be explained by the following reaction of dolomitisation:

$$CaCO_3 + Mg^{2+} + HCO_3^- \rightarrow CaMg(CO_3)_2 + CO_2 + H_2O$$

The bicarbonate ion formed during the oxidation of the organic matter with sulphates is bound to form dolomite in the process of calcite recrystalization mentioned above. Hence we can observe unbalanced amounts of bicarbonate and sulphate ions and an unbalanced increase in the calcium concentrations with reference to the drop in the magnesium concentration.

The chemical composition of the Baltic Sea interstitial waters differs from the composition of the water column. These differences are expressed not only by the quantity of concentrations, but also by the weight ratios of the individual ions to chlorides and mutual relationships between cations and anions. The main factors that affect the concentrations of sulphates and bicarbonates are: the processes of the sulphates bacterial reduction and the reactions of reverse weathering and ion exchange. The two last factors cause changes in the concentrations of the main cations in the interstitial water. The concentration of chlorides, the most conservative constituent of these waters, undergoes variations as a result of groundwater inflow, which occurs in the zones of the proglacial river valley mouth.

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Chapter 12

GASES IN THE BALTIC SEA SEDIMENTS

The bottom sediments of seas and oceans play an important role in the biogeochemical circulation of some gases, greenhouse in particular. The processes that occur in the sediments are a source of both inorganic (nitrogen, carbon dioxide, hydrogen sulphide, nitrous oxide, argon, helium) and organic gases (hydrocarbons with one to four atoms of carbons in a molecule). The quantitative and qualitative contribution of gases in the sediments results from the conditions of the environment.

Carbon dioxide in marine sediments originates mainly from the processes of organic matter decomposition. Its presence in a gaseous form is controlled by the pH of the environment. In the range of pH 7.0–8.5, which is typical of marine waters, only 0–10% of the total carbon may occur as carbon dioxide (Korzeniewski, 1995). In the Baltic Proper, the pH for interstitial waters in the surface (0–10 cm) sediment layer oscillates between 6.98 and 8.26 (Carman and Rahm, 1997). Therefore, gaseous carbon dioxide practically does not occur in these sediments. The ionic form of carbon, HCO_3^-, predominates.

The HS^- ions are essential for **hydrogen sulphide** (Bolałek, Falkowska, 1999). The main source of hydrogen sulphide in sediments is the microbial sulphate reduction. This is one of the stages of organic matter degradation. It occurs when other, more energetically advantageous electron acceptors, such as oxygen, oxides of iron and manganese, have been exhausted (Froelich *et al.*, 1979).

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} \rightarrow$$
$$\rightarrow 106CO_2 + 16NH_3 + 53S^{2-} + H_3PO_4 + 106H_2O$$

Hydrogen sulphide originates also from the reduction of sulphides, which occurs in the process of anaerobic oxidation of methane (AOM) (Barnes, Goldberg, 1996).

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

This process usually takes places in deep layers of sediments.

The presence of hydrogen sulphide in deep-water regions of the Baltic Sea is constrained predominantly by the frequency and range of oceanic waters flowing through the Danish Straits. While moving along the sea bottom, denser and better aerated oceanic waters improve the oxygen conditions in the sediments (Fonselius, Valderrama, 2003). Longer periods of stagnation result in the appearance of hydrogen sulphide in the sediments and in near-bottom waters (Fig. 12.1).

The HS^- concentrations in interstitial (pore) waters of the Baltic Proper range between 0 and 0.474 mmol/dm^3 (Fig. 12.2), with a mean value of 0.172 ±0.146 mmol/dm^3 (Carman and Rahm, 1997). The concentrations increase with sediment depth as the contents of sulphates and the value of Eh decrease. The highest concentrations of hydrogen sulphide are observed in the Gotland Basin, where particularly long stagnation periods are recorded in the Gotland Deep (Eastern Gotland Basin). Such conditions result in almost constant presence of hydrogen sulphide not only in sediments but also in the near-bottom waters (Emeis *et al.*, 2000). The highest hydrogen sulphide concentrations, app. 1–10 mmol/dm^3, were observed in the 10–20 cm layer of the sediment (Piker *et al.*, 1998).

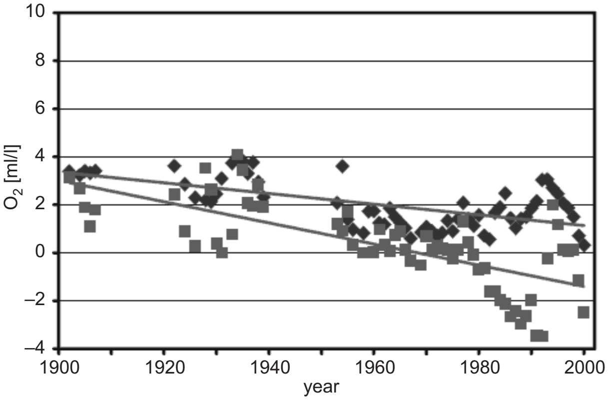

Fig.12.1. Mean annual concentrations of oxygen and hydrogen sulphide (expressed as negative oxygen) in the waters of the Eastern Gotland Basin in 1902–2000 (squares correspond to the depth of 100 m, and diamonds to the values near the sea bottom). According to: Fonselius, Valderrama, 2003

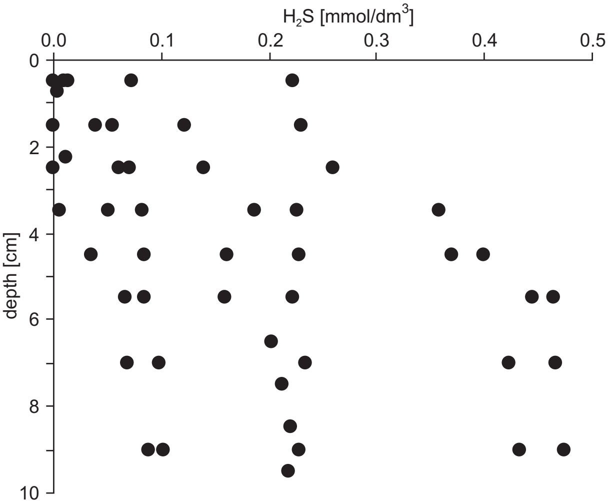

Fig. 12.2. Hydrogen sulphide concentrations in interstitial waters of the Baltic Proper (data by Carman, Rahm, 1997)

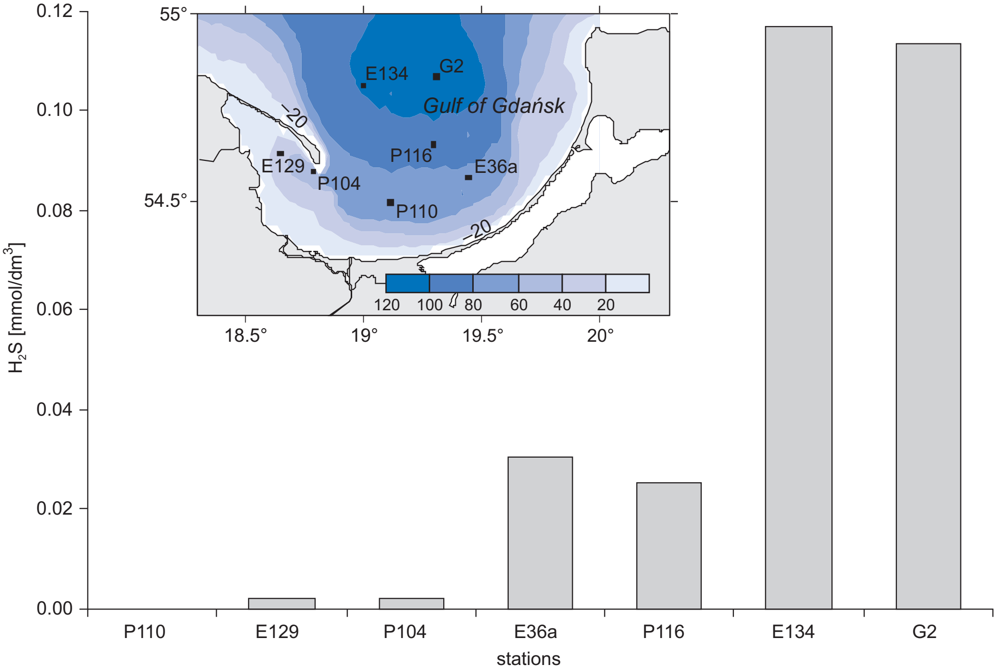

Fig. 12.3. Hydrogen sulphide concentrations in sediment cores from the Gdańsk Deep (Gdańsk Basin) and from a station located 20 km to the north of the Vistula River mouth (September, 2000). Source: Institute of Oceanography of Gdańsk University

These values exceed the maximal concentrations in the Baltic Proper published by Carman and Rahm (1997).

In the Gulf of Gdańsk, hydrogen sulphide occurs in the surface sediment layer (0–1 cm) usually in the regions located below the depth of permanent halocline (Fig. 12.3). The highest concentrations are recorded in the Gdańsk Deep (Gdańsk Basin). In the central, shallower part of the gulf, hydrogen sulphide (0.060 mmol/dm^3 on avearge) is observed usually below the depth of 5 cm (Fig. 12.4). Like in other regions of the Baltic Sea, the concentrations of hydrogen sulphide in the sediments of the gulf increase with the sediment depth (Mudryk *et al*., 2000; Łukawska-Matuszewska *et al*., 2009).

Both the concentration value and the sediment layer where hydrogen sulphide occurs, undergo variations. As mentioned earlier, the ocean water inflows reduce hydrogen sulphide in the surface layers of the near-bottom sediments. On the other hand, the inflow waters may "push through" old oxygen-free waters into shallower regions, contributing to increasing the concentrations of hydrogen sulphide in the sediments in these regions (Graca, 2009).

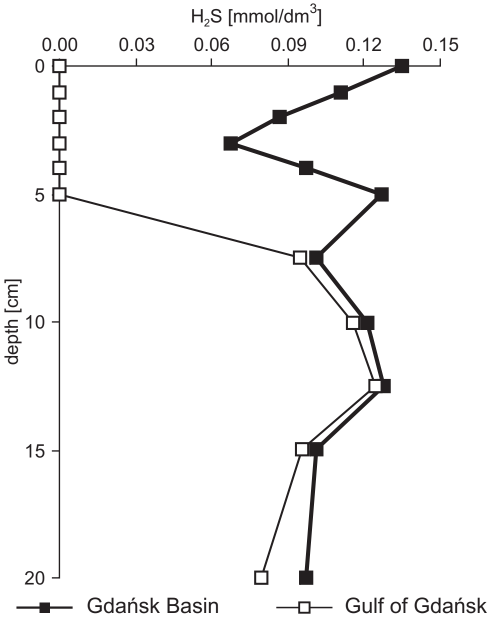

Fig. 12.4. Hydrogen sulphide concentrations in the surface sediment layer (0–1 cm) at some stations of the Gdańsk Basin (September, 2000). Source: Institute. of Oceanography of Gdańsk University

Table 12.1

Areal range and duration of anoxia in the near-bottom waters of the Gdańsk Deep in 1992–2002 (Graca *et al*., 2006)

Area of anoxia [10^3 km^2]	Anoxia duration [months]
66.0	1
3.40	9
0.91	17.5
0.06	3.5
Total	31.0

Based on data by: Baltic Environmental Database (http://data.ecology.su.se//Models.bed/htm), Monitoring of Inspection for Environmental Protection, (2003) and Łysiak-Pastuszak and Drgas (2000).

Table 12.1 shows an areal range and duration of anaerobic conditions in the sea bottom of the Gdańsk Deep in 1992–2002. These conditions correspond to the presence of hydrogen sulphide in the sediment-water interface. The table indicates that these conditions occurred for less than 3 years during this decade and covered an area of slightly more than 2% of the total Baltic Sea surface.

It is worth noting that hydrogen sulphide also occurs in the sediments of the shallow-water coastal zone of the Gulf of Gdańsk, usually in summer (Bolałek *et al*., 1993). This is a result of the complex effect of factors such as: increase in the water temperature, growth in the organic matter supply, decrease in the oxygen content in water, and intensification of the organic matter decomposition processes in sediments.

In the marine environment, **methane** may occur both in water (secondarily as a result of bottom emission) and in the bottom sediments. Depending on the physicochemical conditions in the sediments, it occurs in the following forms: dissolved in the interstitial waters, as gaseous bubbles (liberated after supersaturation of interstitial methane-containing waters), as deposits of free gas located mainly under weakly or impermeable sediment layers, below a methane-containing layer of anaerobic oxidation, or as clathrate methane compounds (other names: methane hydrates, methane ice).

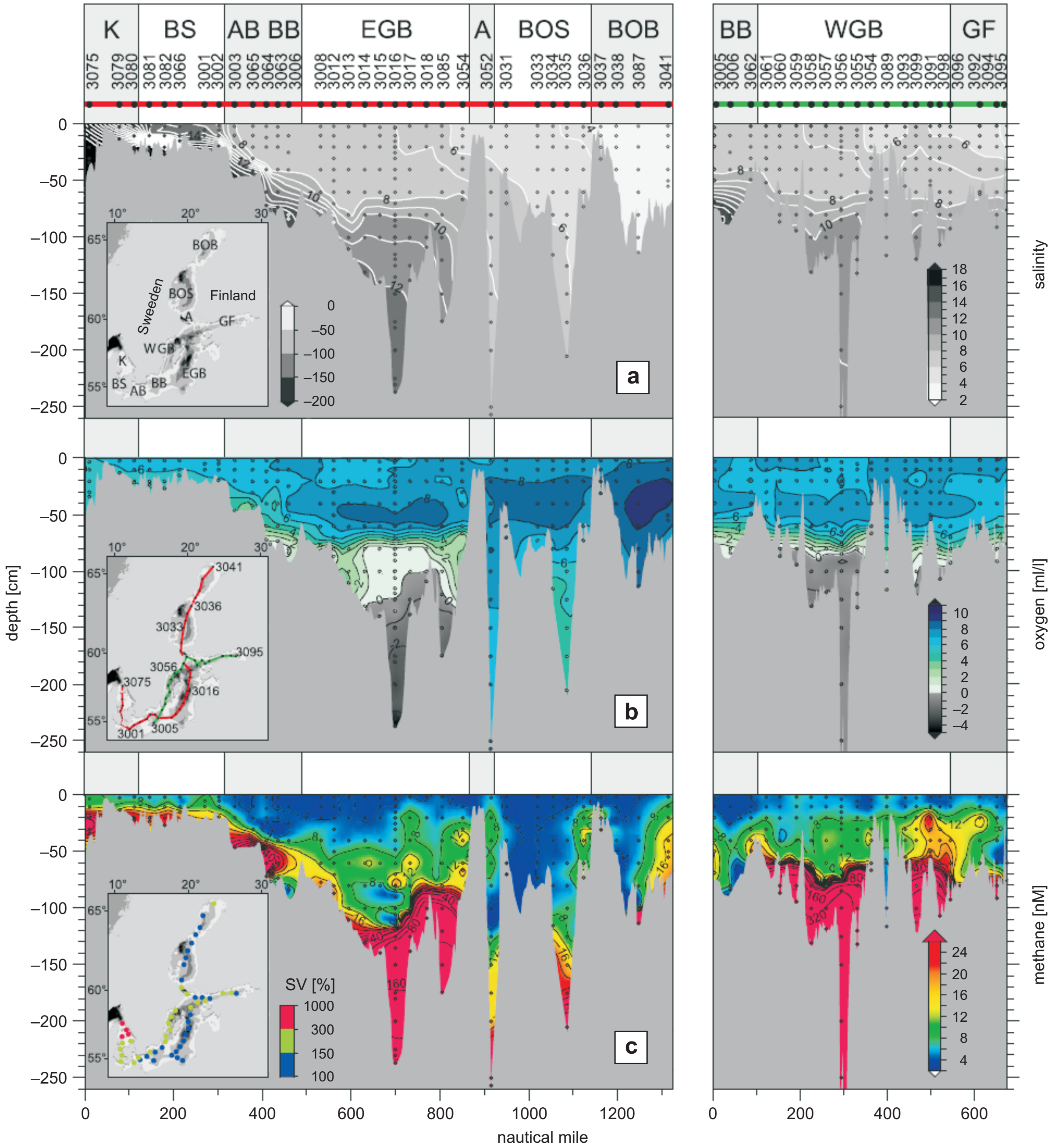

Fig. 12.5. Water column of (a) salinity, (b) oxygen, and (c) methane along two sections across the Baltic Sea. Hydrogen sulphide was expressed as a negative oxygen concentration. Figure a shows the bathymetry and the location of the main basins (K, Kattegat; BS, Belt Sea; AB, Arkona Basin; BB, Bornholm Basin; WGB, Western Gotland Basin; EGB, Eastern Gotland Basin; A, Åland Sea; BOS, Bothnian Sea; BOB, Bothnian Bay; GF, Gulf of Finland). Part b shows the trends of profiles and the names of selected stations. Part c shows saturation (SV – saturation value) with methane in the surface sea waters (Schmale *et al*., 2010)

High primary production in coastal zones leads to deposition of large amounts of organic matter in sediments. This is favourable for microbiological production of methane in the anaerobic sediment layers (Froelich *et al*., 1979) and for releasing this component to the sea water and then to the atmosphere.

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow$$
$$\rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$$

The emission of methane constitutes 3% of the total emission of this constituent from natural sources (Houweling *et al*., 1999). It is estimated that app. 90% of the methane flux from the sediments is absorbed by the process of microbial anaerobic oxidation of this component (AOM) (Treude, 2003). Methanotrophes oxidise methane also in aerobic conditions (Hanson and Hanson, 1996).

A series of studies confirms the production of methane in the Baltic Sea bottom (Table 12.2). Although no comprehensive studies on methane in the sediments of this reservoir can be found, there are some studies concerning this problem for open sea waters (Schmale *et al*., 2010). They seem to be a good indicator of the production of this gas in the bottom sediments. High methane concentrations in the water column are observed in the central, deep basins of the Eastern Gotland Basin (Fig. 12.5). The highest values of concentrations are also characteristic of the suboxia or anoxia regions.

Methane concentrations in the sediments of the Gotland Deep (Eastern Gotland Basin) increase almost linearly from the surface layer to app. 50 cm deep in the sediments, and then the increase is exponential. The most intensive production of this gas probably occurs in sediments below a depth of 80–90 cm (Piker *et al*., 1998). The transport of methane released from the sediment in the water column in the East Gotland Basin is limited by the water stratification and by the methane oxidation in the redoxycline. This results in a relatively low saturation of the surface waters with methane (120–260%). The lowest methane concentrations in the water column are observed in the Bothnian Sea and Bothnian Bay. The saturation of surface waters with methane reaches 106–116% in these regions. The sources of methane emission into the atmosphere are surface waters in the shallow-water western part of the Baltic Sea, where saturation with methane reaches 746%.

In the Polish zone of the Baltic Sea, deposits of this gas containing 70–90% vol. of methane have been discovered in Middle Cambrian quartz sandstones (Domżalski *et al*., 2004).

Table 12.2

Methane concentration in sediments from some regions of the Baltic Sea

Region	Methane concentration [mmol/dm^3]	References
Eastern Gotland Basin	0.008–5.00	Piker *et al*., 1998
Danish Straits	0–8*	Jørgensen *et al*., 1990
Eckernförde Bay	0.034–6.421	Martens *et al*., 1999
Eckernförde Bay	4.5**	Schlüter, Sauter, 2004
Kiel Bay	0–4	Schmaljohann 1996
Arkona Basin	0.004–7.660	Thiesen *et al*., 2006

* value read from the Figure
** maximum value

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Chapter 13

THE TRANSFORMATION OF SUSPENDED MATTER IN THE MARINE ENVIRONMENT AND THE PROCESSES OF COMPONENT EXCHANGE AT THE SEA WATER–SEDIMENT INTERFACE

13.1. Carbon and Biogenic Substances in Suspended Matter

13.1.1. Suspended Matter in the Marine Environment

Suspended matter (SPM – suspended particulate matter) is the main component of the sea water, in addition to solutes. The suspension is composed of POM (particulate organic matter), living organisms and detritus, and of PIM (particulate inorganic matter). The particles feature diverse shapes and sizes as well as different physical and chemical properties. Carbon, nitrogen, phosphorus and sulphur are the basic constituents of organic matter. Chemical composition of inorganic suspensions includes siliceous minerals (e.g. K, Mg and Fe aluminosilicate), carbonate minerals, metal oxides and metal sulphides. Apart from lithogenic silicon, the suspended matter contains biogenic-originated silicon, the material used for building skeletons and the frustules of phytoplankton organisms, mainly diatoms.

The suspension significantly affects the functioning of water ecosystems. The particles of suspended matter are responsible for transport, accumulation and transformation of many chemical compounds, such as biogenic substances, metals, radionuclides and persistent organic pollutants (POPs) inputted into the Baltic Sea (e.g.: Szefer, 2002; Turner, Millward, 2002). Suspended particles also affect the optical properties of water, and change the transmission of light into the sea depths, absorbing and scatterring it.”

In the sea, suspended particulate matter is formed as a result of biological production, coastal and bottom abrasion as well as in the processes of precipitation from dissolved matter. Primary production, the key autochthonous source of organic matter in the Baltic Sea, is associated with the availability of phosphorus and nitrogen as well as with climatic factors such as temperature, light or water transparency. The quantity and quality of this matter show seasonal variability that depends, among others, on the taxonomic composition of phytoplankton. In the estuary zone, the process of flocculation is an important source of suspended organic matter. Consequently, 3–11% of the dissolved organic carbon is precipitated, forming suspended particulates (Sholkowitz, 1976).

The external sources of suspended particles are rivers, the atmosphere and groundwater. Rivers are the most important allochthonous source of suspended matter. The quantity and quality of the matter transported by rivers depend on the type of drainage basin, flow rate, type of matter cycling in the river, presence of conurbations and industrial areas, as well as on hydrotechnical structures such as dams or weirs (Humborg *et al*., 2006). The main organic constituent of the river waters is soil humus and other products of plant disintegration. These are usually compounds highly resistant to biochemical oxidation.

The time that a particle remains in suspension in water depends on its size and type, the depth of the reservoir, trophic chain structure and hydrodynamic processes. The sedimentation of suspended particles from the surface layer into the deeper waters or sediments is a key factor decreasing their concentration in the water column.

Organic matter, while settling, undergoes many processes: aggregation, de-aggregation, microbiological degradation, consumption by zooplankton and mineralization that affects both the circulation of the dissolved matter in the sea and the process of settling particles in the sea-bottom sediments. All these factors change the quantities and qualities of the particles suspended in the water column.

The amount and quality of the particles in the water are also affected by the intensity of hydrodynamic processes, such as currents or wave refraction (Danielsson *et al*., 2007). Depending on the morphometry of the coastal zone and the sediment type, waves may induce the process of both deposition and resuspension, contributing to the redistribution of the settled material. Hydrodynamic processes may also be favourable for particulate coagulation through the increase in the number of collisions between them. Waves and currents also intensify the recycling of biogenic substances from sediments to water, which elevates biological productivity in shallow waters.

The concentration of suspended particles varies in time, as regards region and location in the water column, which results from many superimposing factors, such as: the intensity of primary production, the presence of heterotrophs, the distance from a river mouth, the geological structure of the coastline and seabed, wave height and drift current speeds.

13.1.2. Distribution Pattern of Suspended Matter in the Baltic Sea

The concentration of suspended particles in the Baltic waters varies widely from 0.3 mg/dm^3 up to almost 500 mg/dm^3 (Table 13.1). The concentration of SPM in open surface waters of the Baltic Sea achieves a mean value 3–3.3 mg/dm^3 (Pustelnikov, 1977; Emelyanov, 2002). The concentration of suspended matter increases to several or even up to hundreds of mg/dm^3 in the coastal zone, lagoons and estuaries, particularly in the river estuaries (Eisma *et al*., 1991; Krężel, Cyberski, 1993; Emelyanov, 2002; Schiewer, 2008). Elevated concentrations of suspended particles are also observed in the bottom waters (Sokołowski *et al*., 2001, Burska *et al*., 2005b).

Table 13.1

SPM concentration in the Baltic Sea

Area	SPM [mg/dm^3]	References	Remarks
Western Baltic Sea	0.51–5.98	Ferrari *et al*., 2003	Heringsdorf, German coast
	2–500	Eisma *et al*., 1991	Ems, German coast
Szczecin Lagoon	9–60	Schiewer, 2008	
Pomeranian Bay	0.5–12	Christiansen *et al*., 1997; Leipe *et al*., 2000; Pempkowiak *et al*., 2002	
Southern Baltic Sea	0.27–1.78	Pempkowiak *et al*., 2000	
Gdańsk Basin	1.3–12.9	Burska *et al.*, 2005	Gdańsk Deep
	1.1–16.6	Maksymowska, 1998	Inner part of the Gulf of Gdańsk
	0.36–5.47	Bradtke *et al*., 2005	Coastal zone in the Hel upwelling
	0.5–35	Krężel, Cyberski, 1993	Inner part of the Gulf of Gdańsk and the Puck Bay
Vistula Lagoon	3.1–138.1	Emelyanov, 2002	
Curonian Lagoon	1.4–21.3	Emelyanov, 2002	
Gotland Basin	0.67–4.86	Håkanson, Eckhéll, 2005	Sweden coast
Gulf of Riga	1–10	Regstad *et al*., 1999, Poikäne *et al*., 2005; Yurkovskis, 2005	

The mean concentration of suspended particulate matter in the Gdańsk Basin amounts to 4.4 mg/dm^3 and is higher than that for the Baltic Sea surface waters (Emelyanov, 2002). The highest SPM values in this reservoir occur in the Vistula River mouth (Fig. 13.1). The load of suspended matter supplied by rivers changes throughout the year and reaches the maximum values (70 thousand tons of SPM per month) at the end of March and at the beginning of April, and the lowest values (<30 thousand tons per month) in late summer. SPM concentrations of up to 36 mg/dm^3 were observed in the Vistula River mouth in the periods of higher run-off of snowmelt waters (Maksymowska, 1998). The average content of suspended mineral particles in the total suspended matter in this region is close to 25%; however, it can reach even 90% of the transported matter (Bradtke, 2004).

The location of the Vistula hydrological front results from a flow rate of the river and from the speed and direction of the wind. In most cases, the Vistula fresh waters in the Gulf of Gdańsk are transported to the east and northeast. The decrease in concentrations of suspended matter in this direction was claimed by Bradke (2004) in her research concerning the particle size distribution (PSD) in the Gulf of Gdańsk. The accordance in the concentration of riverine-originated suspensions with the course of the river's hydrological front can be clearly seen on its western side in particular (Fig. 13.2). Moreover, this research showed that, apart from a clear reduction in large diameter particles, small particles can also be reduced in the same area. It suggests that strong flocculation processes remove small particles near the Vistula River mouth. The increase in the concentration of chlorides at the fresh water/marine water interface is favourable for the above process, elevating the strength of the particle attraction.

In the coastal zone of the Gulf of Gdańsk, the local increase in the concentration of suspended particles is also caused by the abrasion process (e.g. Redłowo Cliff), intense economic activity (industry, sea harbours, wastewater treatment plants) and by the exploitation of different deposits (amber excavation near the Taran cape, Emelyanov, 2002). High and very high concentrations of suspended particles (125 mg/dm^3), mainly organic ones, occur periodically in a breaker zone. This results from high primary production caused by a permanent anthro-

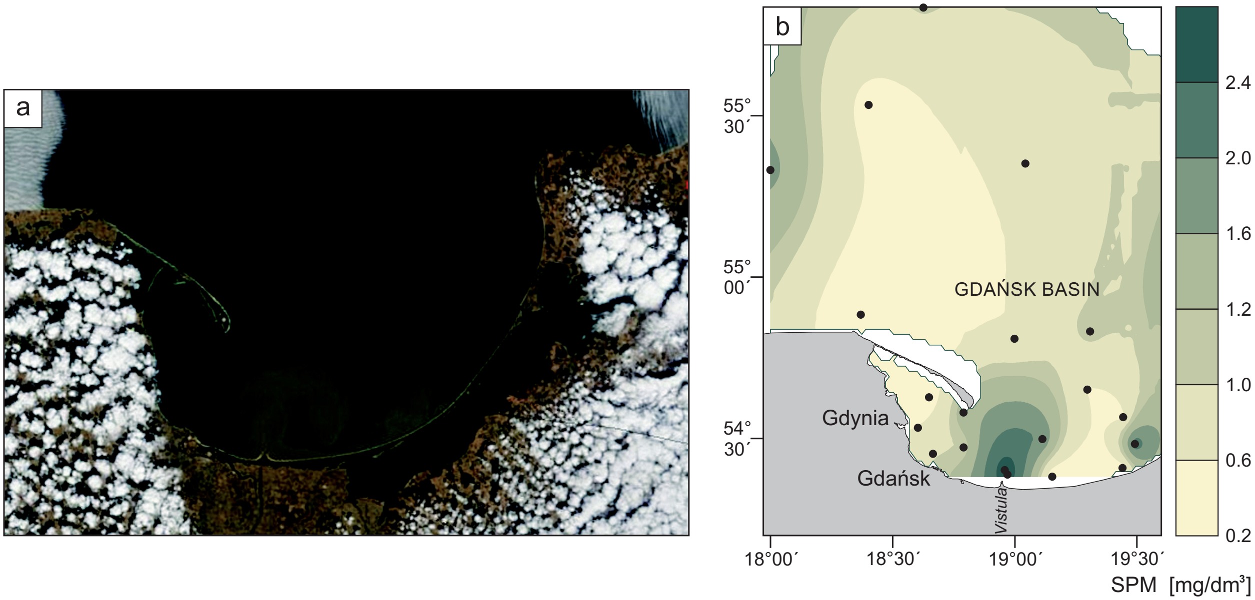

Fig. 13.1. Outflow of the Vistula River waters with high concentration of suspended matter (11.04.2006) seen in the RGB MODIS/Aqua image (source: MODIS Rapid Response System, http://rapidfire.sci.gsfc.nasa.gov) – a; SPM concentration in the surface waters of the Gdańsk Basin (August/September, 2000) – b

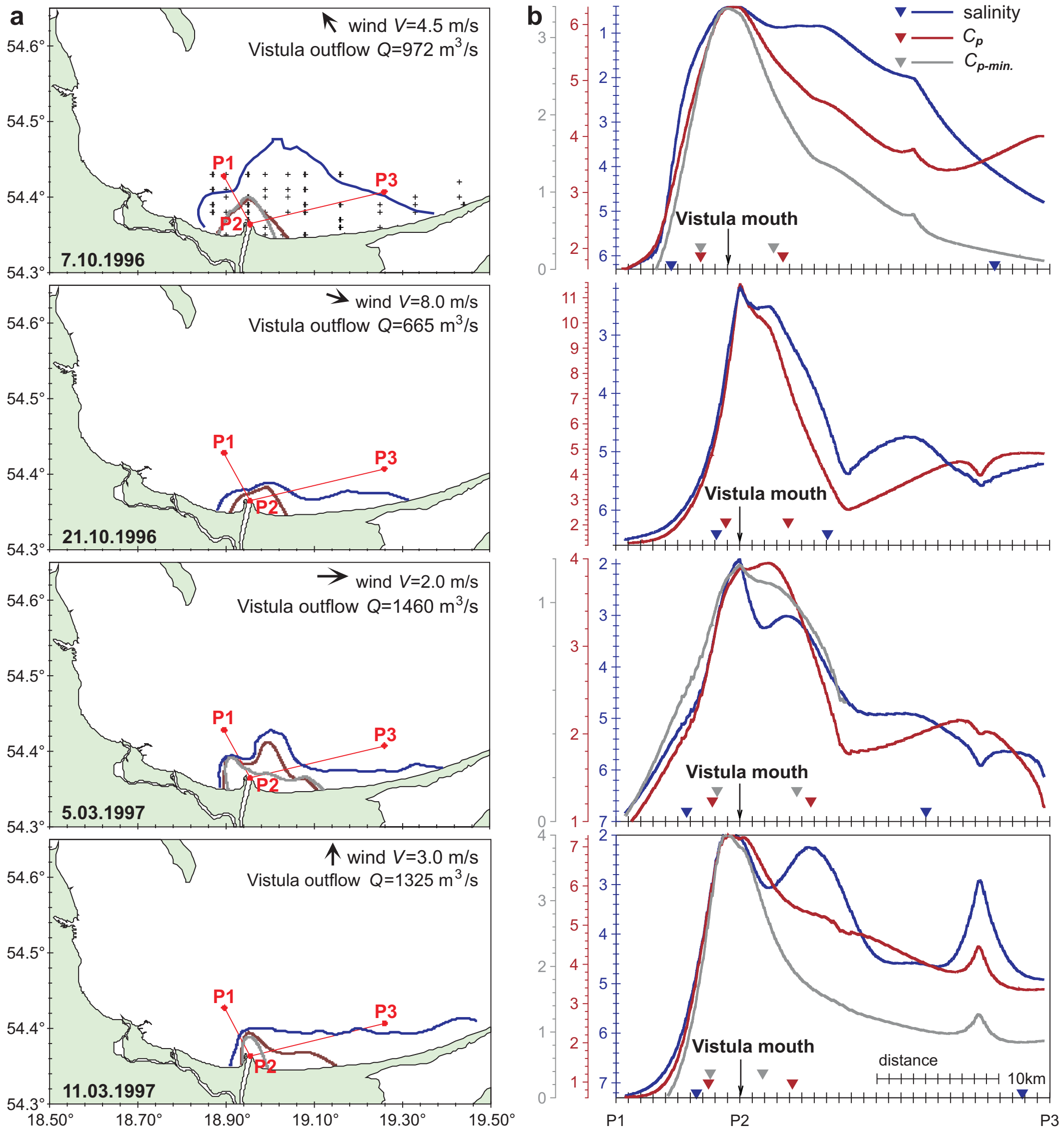

Fig. 13.2. Distribution of the total (C_p) and mineral ($C_{p\text{-}min}$) suspended matter in surface waters in the Vistula River mouth in different wind situations, at the background of the Vistula River hydrological front range – a, sections through the fields of the tested features along the profiles P1-P2-P3 – b, triangles show intersections of profiles with lines determining the range (Bradtke, 2004)

pogenous inflow of nutrients and by advantageous meteorological conditions (wind blowing towards land) that affect the accumulation of suspended particulate matter within this zone (Kotwicki *et al*., 2002).

In the Gulf of Gdańsk, it is the organic matter that is 85% responsible for the differentiation in the suspended solid concentration in the marine water column. During the vegetation period, the contribution of organic suspended matter in the total suspended matter may even reach 100%. Consequently, the concentration of suspended particulate matter in the Gulf of Gdańsk varies depending on the season. The lowest SPM concentration (average 3 mg/dm^3) in the water column was observed in late autumn, whereas the highest one was (7 mg/dm^3) in spring (Krężel, Cyberski, 1993).

The dominant contribution of primary production in forming suspension is reflected in the vertical distribution pattern of SPM concentration (Fig. 13.3, Burska *et al.*, 2005a, b). The SPM concentration decreases rapidly below the productive layer, the range of which depends in principle on lighting conditions. The vertical concentration profile may be modified by the occurrence of layers of density changes. In these layers, the settling particles are decelerated, which is observed as an increase in SPM concentrations. Even a very weak thermocline may induce cumulative suspension above and inside the layer of thermal changes (Bradtke *et al.*, 1997; Burska *et al.*, 2005b; Pryputniewicz, 2007).

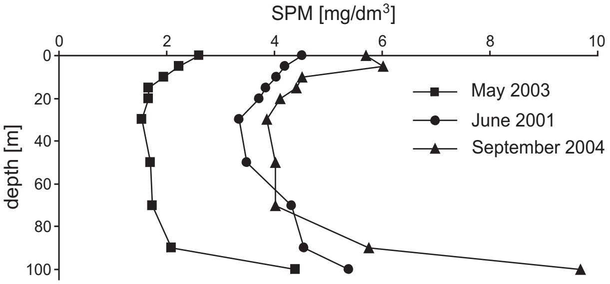

Fig. 13.3. Mean many day concentration of SPM in the deep-water part of the Gulf of Gdańsk

Increased SPM concentrations are also recorded in the marine water layer directly over the seabed surface (Fig. 13.4). This may result from the process of resuspension, suspension transport towards the sedimentary basin or from transport between the basins. In the transition region between the Skagerrak and Kattegat, the SPM concentration increases to 20–22 mg/dm^3 in the bottom water layer (Lund-Hansen, Christiansen, 2008). Similar SPM concentrations (24 mg/dm^3) are observed in the Pomeranian Bay (Leipe *et al.*, 2000), whereas the concentrations in the Gulf of Gdańsk waters reach the value of 30 mg/dm^3 (Sokołowski *et al.*, 2001).

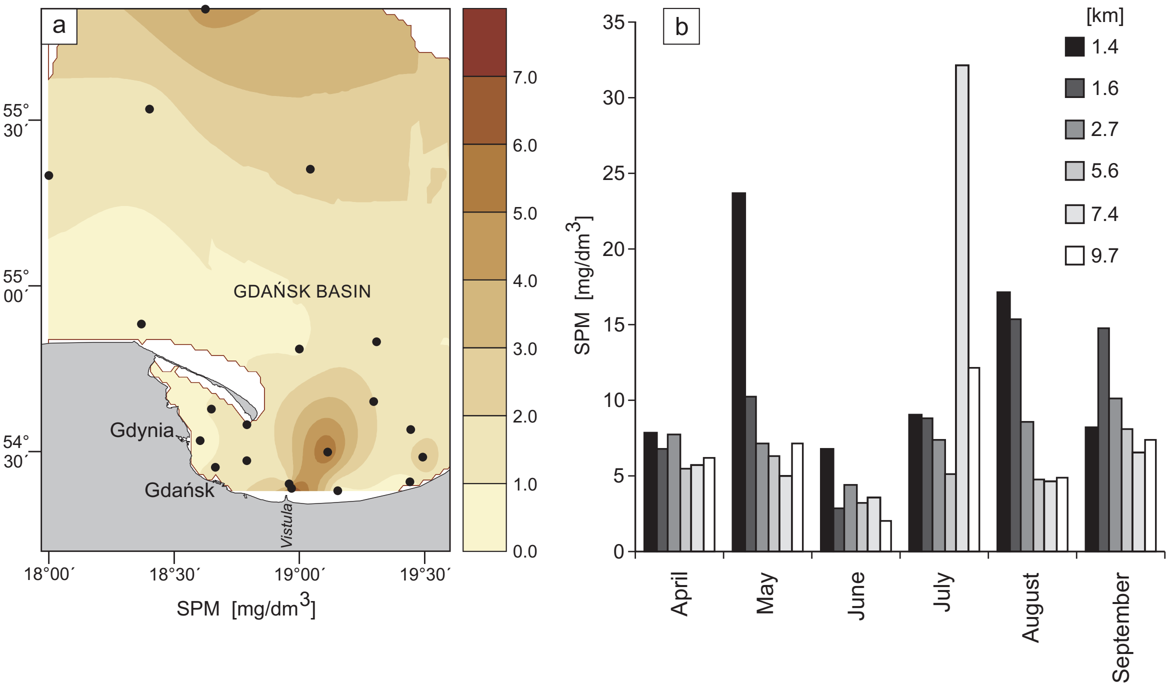

Fig. 13.4. SPM concentration in bottom waters: a – Gdańsk Basin (August/September, 2000); b – the Vistula River mouth during the vegetation period; based on: Sokołowski *et al.*, 2001

The amount of suspended particulates in the sea bottom waters, as in the surface marine waters, changes seasonally, which is associated with cyclical supplies of river waters and seasonal fluctuations of the primary production. In the bottom waters in front of the Vistula River mouth, there are two distinct periods of high SPM values: May and August/September (Fig. 13.4). In most periods, the concentration of suspended matter decreases in proportion to that in the Vistula River mouth.

Due to the dominant role of organic particulate matter in the total suspended matter, the concentration of basic chemical elements (C, N, P), which form the organic matter, depends on the suspension concentration (Ferrari *et al*., 2003; Burska *et al*., 2005b, Pryputniewicz, 2007; Graca, 2009). When the SPM concentration increases, so do the concentrations of: POC (particulate organic carbon), PON (particulate organic nitrogen), TPP (total particulate phosphorus) and BSi (biogenic silica) (Burska *et al*., 2003; Humborg *et al*., 2006). The power of this relationship is dependent on both the suspension type (terrigenous, diatomaceous and organic) and its degradation ratio. In the Baltic Sea, as Emelyanov (2002) claims, terrigenous matter contains about 10% of organic carbon and 5% of biogenic silica. In diatomaceous matter, the fraction of biogenic silica increases to 74%, while the amount of organic carbon increases up to about 16%. The organic matter is composed of app. 28.9% of organic carbon and a small (less than 2%) amount of biogenic silica.

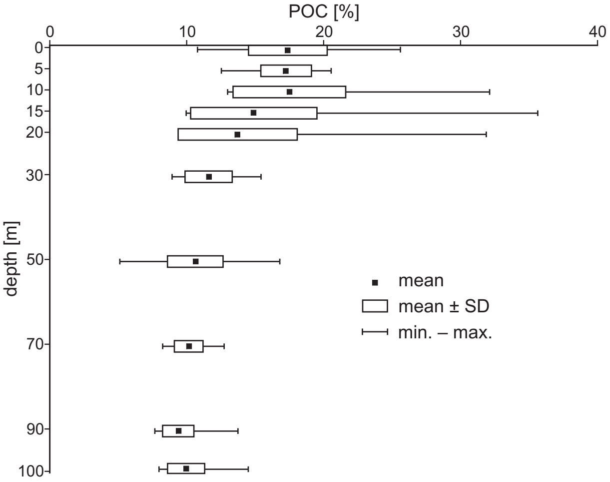

Fig. 13.5. Percentage contribution of suspended organic carbon (POC) in the suspended particulate matter (SPM) in the Gdańsk Deep waters (30.05–06.06.2001); based on: Burska *et al*., 2005b

In the open-marine surface waters of the Baltic Sea, the concentration of organic carbon usually does not exceed 1.5 mg/dm^3 during the vegetation period (Pęcherzewski, 1976; Pempkowiak *et al*., 2000; Nausch *et al*., 2009). The concentrations of organic carbon are higher in the suspension observed in the coastal zone, especially in estuaries, as well as in areas of upwellings. Extremely high POC concentrations (6.2–35.5 mg/dm^3) occur in the Neva River estuary; these values are even twice higher than the POC concentrations in the Pomeranian Bay and Darß-Zingst Bodden (15.4 and 13.9 mg/dm^3) and about 10 times higher than in the Vistula River mouth (Maksymowska, 1998; Schiewier, 2008).

In the vegetation period, the highest concentrations of particulated organic carbon are related to phytoplankton spring bloom, while another noticeable increase in POC occurs in autumn. Such a situation can be observed in the coastal zone of the Gulf of Finland, where the POC concentration may increase in the first week by up to 2.2 mg/dm^3 (Tamelander, Heiskanen, 2004). However, in those zones of permanent inflow of nutrients, the primary production can remain high throughout the whole vegetation period. In the Kattegat waters, the POC concentrations exceeding 4 mg/dm^3 occur from April (7 mg/dm^3) to September (5.5 mg/dm^3), with the lowest POC values being observed in June (Olesen, Lundsgaard, 1994).

Areas of upwellings are also the zones of high POC concentrations. Enriching marine surface waters with biogenic salt, the upwellings intensify primary production and elevate POC concentrations. It is observed in the Eastern Gotland Basin, on the coastline of Gotland. Locally, the concentration of organic carbon increased to 12.8 mg/dm^3 (Nausch *et al*., 2009).

In the Gdańsk Basin, the concentration of particulated organic carbon ranges from 0.1 to 3.03 mg/dm^3, which is one magnitude higher than the concentrations of particulated organic nitrogen (Pęcherzewski, 1976; Maksymowska, 1998; Pempkowiak, 2000; Burska *et al*., 2005a, b). The TPP concentration in the Gulf of Gdańsk waters varies between 0.18 and 96.1 µg/dm^3, with a mean value of 21.79 µg/dm^3 (Graca, 2009).

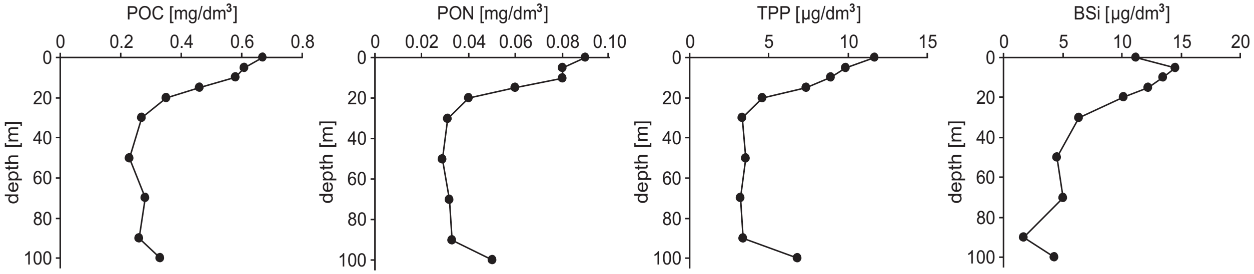

Fig. 13.6. Concentration of particulate organic carbon (POC) and particulate organic nitrogen (PON), total particulate phosphorus (TPP) and biogenic silica (BSi) in the deep-water part of the Gulf of Gdańsk (31.05–06.2001)

Similarly to the whole Baltic Sea, the concentrations of POC, PON, and TPP reach their highest values between April and early October. The lowest POC concentrations (<0.2 mg/dm^3) occur from November to March (see Maksymowska, 1998). A rapid increase in the organic carbon concentration (more than 1–1.6 mg/dm^3) is observed in April and May, and after that period the values drop to increase once again between August and October. The percentage content of POC in the suspended particulate matter over the year varies from 3% to 42% and changes regionally (it increases with increasing distance from the shoreline), seasonally (it increases when primary production grows) and with the sea depth (it increases with decreasing water depth). In summer, the contribution of organic carbon to the total suspended solids was 35.1% in the euphotic layer of the Gdańsk Deep (Fig. 13.5). The mean POC fraction in SPM (14.6%) in this layer was twice higher than in the indirect layer and about two and a half times higher than in the bottom water.

In the deep-water zone of the Gulf Gdańsk, the highest concentrations of POC, PON, TPP and BSi occur in the 10-metre surface layer. Below the layer, a stepwise drop is observed in the contents of these chemical elements (Fig. 13.6).

Information about the content of biogenic silica in suspended matter of the Baltic Sea is poor. Emelyanov (2002) claims that the mean value of biogenic silica in the Baltic phytoplankton is 0.32%. In the particulated suspension, it is 1.55%, varying from 1% to 28.1%. Relatively low contents of biogenic silica in the suspended particulate matter result from the high proportion of blue-green algae blooms. In the coastal zone, a higher increase in the content of biogenic silica in the marine water suspension

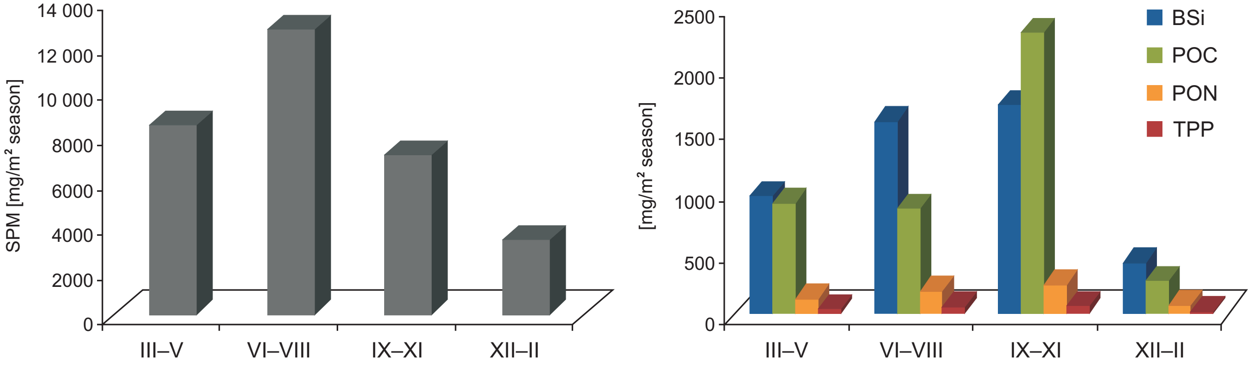

Fig. 13.7. Seasonal changes in the settling matter flux: SPM, BSi, POC, PON and TPP in the Gotland Basin; based on: Struck *et al*., 2004

can be observed. For the Gdańsk Basin, the mean value of BSi contents in the SPM is 4–6%.

At the end of May and at the beginning of June 2001, the BSi concentrations ranged between 0.009 and 0.131 mg/dm^3 in the Gdańsk Deep waters (Burska *et al*., 2003). At that time, the mean content of biogenic silica in SPM was maximally 0.5%, which suggests a small proportion of diatomaceous matter in this period. The highest concentrations of biogenic silica were observed at the depth of 5 m due to optimal lighting conditions for diatom (Fig.13. 6). In summer, the suspended matter may be stopped by density slopes while settling. Fine and more delicate silicate detritus remains on the pycnocline, which puts a question mark on whether it reaches the seabed.

The variations in biogenic silica concentrations in the mouths of the Odra, Vistula and Daugava rivers during the year were described by Humborg *et al*. (2006). The authors showed the effect of hydrotechnical structures of these rivers on the reduction in the concentrations of dissolved silicates (DSi), which caused a decrease in the BSi concentrations in the main streams of these rivers. Of the rivers mentioned above, the Odra has the fewest dams and the highest observable concentrations of biogenic silica, with an annual mean of 0.116 mg/dm^3. The highest BSi concentrations (from app. 0.580 to 2.900 mg/dm^3) occurred in the Odra from March to September. Over twice lower mean concentrations of biogenic silica were observed in the Vistula which is one of the least regulated rivers (Włocławek Dam). Similarly to the Odra, the elevated concentrations of biogenic silica in the Vistula River waters (from 0.435 to 2.175 mg/dm^3) are observed in the vegetation period. The highest number of dams occurs on the Daugava, where the BSi concentrations are the lowest (annual mean concentration is 0.017 mg/dm^3). Contrary to the Odra and Vistula rivers, no periods of increased BSi concentrations were recorded on this river. Considering the multiyear annual mean SPM concentrations in the mouths of the Odra, Vistula and Daugava: 22, 17 and 4 mg/dm^3, respectively, the BSi proportion in the total suspended solids varied from 3.5% in the Vistula to 6% in the Odra.

The concentrations of biogenic silica in the SPM between February and March, 2001, in the Vistula mouth and in the river outflow, ranged from 0.039 mg/dm^3 to 0.273 mg/dm^3, which corresponded to the values of biogenic silica described for this period by Humborg *et al.* (2006). The BSi concentration decreased from the Vistula River mouth towards northeast, depending on the atmospheric situation (Burska, unpublished data).

The flux of suspended matter to the Baltic Sea bottom ranges between 0.9 and 81g/m^2·d, resulting from regional and seasonal variabilities (Heiskanen *et al*., 1998; Heiskanen and Tallberg, 1999; Struck *et al*., 2004). The fluxes of POC, PON, TPP and BSi also show high variability (Table 13.2). The highest sedimentation of all the matter components was observed in the coastal waters of the Gulf of Finland (Regstad *et al*., 1999). Similar fluxes of organic matter to the sea bottom occurred in the Gdańsk Basin (Burska *et al*., 2005b; Graca, 2009). Distinct differences in sedimentation, which was approximately 6 times lower in the Gulf of Gdańsk than in the Gulf of Finland, referred to phosphorus. The lowest fluxes of all the com-

Table 13.2

Sedimentation rate of C, BSi, N and P in individual regions of the Baltic Sea

Region	C	BSi	N	P
	[mg/m^2·d]			
Gulf of Finland	110–2600[3, 4, 5, 10]		10–310[3, 4, 5]	1.0–30.01[3, 4, 5]
Baltic Proper (Gotland Basin)	1.3–98.9[9]	0.12–60.72[9]	0.12–10.68[9]	0.12–0.84[9]
Gulf of Riga	100–1270[6]		47–250[7]	0.71–6.7[7]
Gulf of Gdańsk	96–190[11]	0.97–83.89[8]	4.8–384[11]	0.1–5.2[12]
SW Kattegat	220–700[1]		35.31[1]	2.4[2]

[1]Olesen, Lundsgaard, 1994; [2]Christiansen *et al*., 1997; [3]Heiskanen *et al*., 1998; [4]Leivuori, Vallius, 1998; [5]Heiskanen, Tallberg, 1999; [6]Lundsgaard *et al*., 1999; [7]Regstad *et al*., 1999; [8]Burska *et al*., 2003; [9]Struck *et al*., 2004; [10]Tamelander, Heiskanen, 2004; [11]Burska *et al*., 2005b; [12]Graca, 2009.

ponents of suspended matter were observed in the waters of the Gotland Deep. It was related to the high depth of this sedimentary basin and clearly lower diatomaceous blooms in the open waters of the Baltic Sea with reference to the blue-green alga blooms (Emelyanov, 2002; Struck *et al*., 2004). Consequently, the maximum flux of organic matter occurs in the summer–autumn period (Fig. 13.7), with a simultaneous high content of organic carbon (34–38%) in the suspended matter flux, indicating authothonous source of the matter.

Sedimentation of organic matter (POC, PON, and TPP) and BSi in the Baltic Sea shows a seasonal variability (Olesen, Lundsgaard, 1994; Regstad *et al*., 1999; Heiskanen, Tallberg, 1999). The highest flux in suspended matter during the year generally occurs in spring and is associated with the organic matter supply from the spring water blooming. The proportion of organic carbon in the suspended particulate matter (25–34%) is one of the highest at that time (Leivuori, Vallius 1998; Struck *et al*., 2004). In the density-stratified waters of the Kattegat, the highest flux of organic carbon (up to 700 $mg/m^2{\cdot}d$) was recorded at the end of March and at the beginning of April (Olesen, Lundsgaard, 1994). Clearly lower values of this flux are observed in June and August (app. 500–550 $mg/m^2{\cdot}d$). In spring, when the primary production is higher than the processes of consumption, sedimentation is the most important process in discharging matter from the productive marine water layer (Heiskanen, Tallberg, 1999). In this period, the sediments receive phytoplankton, spores and tissue aggregates that are biologically degraded to the smallest degree. In the stratified period, the excretion products of heterotrophs prevail in the settling matter, the maximum abundance of which is at that time. It leads to the intense degradation of the detritus and the regeneration of biogenic substances. The studies conducted in the Gulf of Riga on the effect of the trophic chain structure and aggregation processes on the organic matter flux confirm the pattern described above. Organic matter supplied in spring may, on average, exceed three times the summer flux and twice the autumn flux (Lundsgard *at al*., 1999).

13.2. Benthic Nutrient Fluxes

13.2.1. Factors Affecting Phosphorus and Nitrogen Benthic Fluxes in the Marine Environment

Only part of nitrogen and phosphorus flux from the water column is buried in sediment. Some of their load is returned to the water mainly as inorganic compounds. Nitrogen and phosphorus fluxes at the sediment–water interface can be turned to the near-bottom water or to the sediment. Over a longer timescale, the N and P flux from the water column is balanced by their accumulation in the sediments and removal from them. The benthic fluxs determine the load (g, µmol) of a given form of nitrogen and phosphorus released or absorbed per unit of sediment surface (m^2, km^2) in a unit of time (h, day, year).

High supply of nitrogen and phosphorus to the bottom of a given reservoir, causes high accumulation and the potentially stronger release of N and P from the sediment.

Nutrient exchange across the sediment–water interface is controlled by complex interplay of numerous abiotic and biotic factors. Basic abiotic factors include turbulent and molecular diffusion. Water circulation is a driving force behind the turbulent diffusion. The driving force in the turbulent and molecular diffusion is water dynamics and concentration gradient respectively. Nutrient exchange is enhanced with an increase of water dynamics.

It is also modified by benthic organisms. They intensify the exchange and stimulate the processes responsible for self-purification of water systems: the coupled nitrification/denitrification and the retention of phosphorus in sediment. The benthic exchange rate also undergoes seasonal variations. The fluxes values are significantly affected by the method of their estimation. The simplest method is based on the Fick's first law, allowing assessing the diffusion exchange. Other methods include different kinds of laboratory experiments consisting in the incubation of sediments, or the so-called "benthic chambers" carried out directly in the natural environment. Benthic fluxes can also be estimated by computer modelling. The advantages and disadvantages of different methods of estimating the fluxes have been discussed, for example, in the study by Zabel *et al*. (2000).

Phosphorus sorption capacity of sediment strongly influences the exchange of this element at the sediment––water interface. It depends on the content of the sediment sorption complex and on such factors as temperature, Eh, pH, oxygen conditions, equilibrium concentration of phosphates, sediment grain size and the content of sulphates. Thanks to the processes of sorption, even with the intense production of phosphates in the sediment, their concentrations in interstitial waters and their gradient at the water–sediment interface can be low.

The compounds with iron play a crucial role in the phosphorus exchange at the water–sediment interface. These compounds are dissolved when the redox potential decreases below its critical value. The value of 200 mV is the most often cited literature data (e.g.: Böstrom *et al*., 1988). Phosphates and iron(II) ions released in this way, diffuse according to the concentration gradient towards the sediment surface up to the regions where the conditions for oxidation of Fe^{2+} ions are favourable. There, the iron-bound phosphorus precipitate again. The phosphates can be readsorbed on oxic sediment layer and can recirculate with iron several times through the redox boundary layer, before they finally will be removed from the sediment. However, poorer oxygen conditions in near--bottom water are related to a flux of Fe^{2+} and PO_4^{3-} to the water. Simultaneously, if hydrogen sulphide is produced in the environment, iron(II) ions are partly immobilised in sediments as slightly soluble sulphides (Fig. 13.8). It results in the decreasing of Fe^{2+}: $(HPO_4^{2-} + H_2PO_4^-)$ concentration ratio in interstitial and near-bottom waters to a value below 2 (molar ratio). This results in weaker abilities of sediments to retain phosphorus even when oxygen conditions are improved (e.g.: Lehtoranta, Heiskanen, 2003).

Nitrogen is removed from the sediment as NH_4^+, NO_3^-, NO_2^- and N_2. A form in which it returns from sediments to the water is determined by the relations of such processes as: ammonification, coupled nitrification/denitrification and nitroammonification. Frequent oxygen deficits in near-bottom water and the reducing conditions in sediments are favourable for the production of ammonia and its subsequent release into the near-bottom water. The ammonia released from the sediments is mainly a product of microbiological degradation of organic matter. The increase in temperature intensifies the ammonia flux from the sediment, as it favours the microorganisms development.

Oxic near-bottom water and high organic matter content in sediment stimulates the coupled nitrification/denitrification. Then a part of nitrogen returns to the cycle in water as nitrates(V) or as the molecular nitrogen. Molecular nitrogen is, among others, a product of denitrification. The denitrification rate in the bottom sediments of water reservoirs depends on several factors. The necessary condition is the availability of nitrates(V) as a substrate. As the result, the denitrification rates depends on the nitrate transport into the anoxic zone of sediment. Finally, denitrification usually occurs just under the sediment surface, where oxic conditions change into reducing, and increases in the sediment colonized by benthic organisms.

In the marine environment, the main source of nitrates(V) used in the process of denitrification is nitrification in sediment. In highly eutrophicated reservoirs, increases importance of near-bottom water as a source

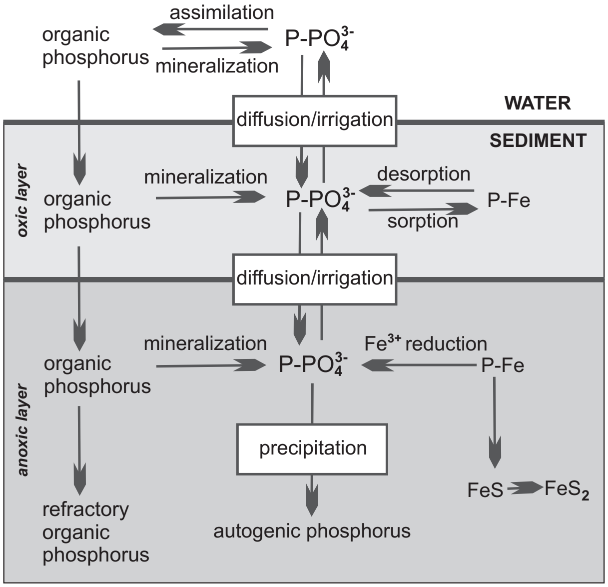

Fig. 13.8. Simplified phosphorus cycle in water and sediment (modified after Slomp *et al*., 1996; Haese, 2000)

of nitrates for denitrification in sediment (Middelburg *et al*., 1996). A higher supply of nitrogen into the sediments from the water column intensifies the denitrification rate. Since most denitrificators belong to heterotrophic bacteria, this process requires organic matter, the quality of which affects its intensity. Denitrification is supported by the mean contents of organic carbon in sediment (which does not limit mineralisation and nitrification) and simultaneously low rates of sulphate reduction or lack of this process.

The oxygen deficit intensifies denitrification; however, the long lasting anoxia and the presence of hydrogen sulphide may limit this process owing to nitrate deficit (limited nitrification) and the competition of microorganisms that reduce nitrates(V) to ammonia.

Denitrification is seasonally variable. The seasonal cycle of denitrification in the coastal zone is characterised by spring, and sometimes autumn maxima and summer minima. The spring maximum is associated with a supply of fresh organic matter into the bottom sediments. The decrease in the rate of this process in summer results from the higher water temperature and from the intense mineralisation of the organic matter at the sediment–water interface which limits the penetration of oxygen into the sediment and, consequently, the nitrification itself.

13.2.2. Spatial and Seasonal Variations of Benthic Phosphorus Flux

In the 1990s, the Baltic sediments returned approximately $18 \cdot 10^3$ t/a of phosphorus (Savchuk, 2005). Most of this load ($14 \cdot 10^3$ t/a) is released in the Gotland Deep. Since the early 1970s, the near-bottom waters of this area have been permanently anoxic and contained hydrogen sulphide (Emeis *et al*., 2000).

Phosphorus returns from the sediments to the water mainly as phosphate. The fluxes of phosphates in the Baltic Sea reveal high variability (Table 13.3) due to changeable spatial and seasonal environmental conditions. The increase in benthic phosphate flux usually occurs in the warm half of the year (Klump, Martens, 1981; Forja *et al*., 1994; Jensen *et al*., 1995). It corresponds to the complex effect of temperature increase, worse oxygen condition and organic matter accumulation in sediment. For instance, in the Gulf of Gdańsk, phosphates are removed from sediment most intensely in late summer, while the process is at its weakest in early spring (Graca, 2009).

The spatial variability of phosphate fluxes in this region is correlated with the water depth (Fig. 13.9). The weakest fluxes of phosphates were observed in the shallow-water zone covered with sandy sediments poor in phosphorus. The fluxes generally increase when the water depths increase, which is in accordance with the decrease in their variability. The highest values of fluxes were observed in the regions below the 70 m isobath, including the Gdańsk Deep and its slope. During periods of long lasting anoxia in this region, the reserves of phosphorus accumulated in the sediments are removed to the water column. It is worth noting that, of all the Baltic deeps, only in the Gotland Deep, phosphorus are removed from the sediments to an extent, which is significant for the entire Baltic Sea.

Rough estimations indicate that from $1.87 \cdot 10^3$ to $2.32 \cdot 10^3$ tons of phosphorus per year are released from the deposits of the Gdańsk Deep to the water column. These loads cover about 9–11% of phytoplankton demand for phosphorus (Graca, 2009).

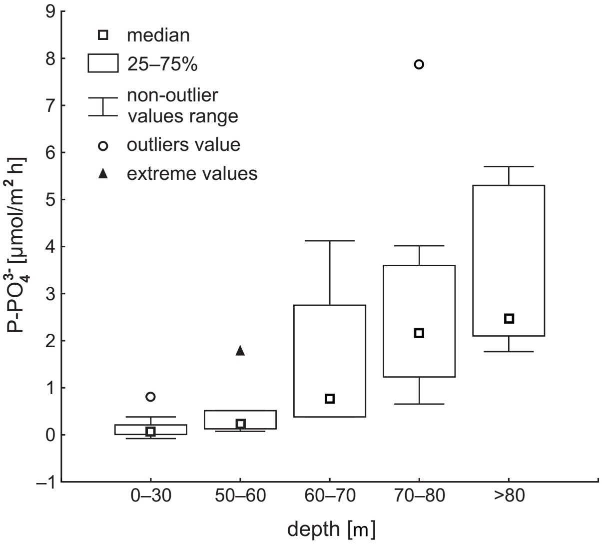

Fig. 13.9. Benthic phosphate fluxes in regions of the Gulf of Gdańsk characterized by different water depths (Graca, 2009)

Table 13.3

Phosphate benthic fluxes ($F_{PO_4^{3-}}$) in individual regions of the Baltic Sea (negative values denote flux from water into the sediment)

Region	Estimation method	$F_{PO_4^{3-}}$ (μmol/m^{2}h)	References
Puck Bay	benthic chambers	1.2–11.5 (mean 6.5)	Bolałek, 1992
	Fick's first law	0.04–3.17 (mean 0.90)	Bolałek, 1992
	laboratory experiments	0.42–2.87 (mean 1.52)	Bolałek, 1992
	benthic chambers	8.75–32.5	Bolałek *et al.*, 1991
Pomeranian Bay	laboratory experiments	0.75–23.58 (mean 8.33)	Frankowski and Bolałek, 1999
Gulf of Finland	sediment incubations	1.59–28.5	Conley *et al.*, 1997
	sediment incubations	(–1.3)–28.2	Pitkänen *et al.*, 2001
	Fick's first law	(–0.3)–22.8	Heiskanen *et al.*, 1999
	model	2.5	Kiirikki *et al.*, 2006
Baltic Proper	sediment incubations	2–40 (anoxia)	Koop *et al.*, 1990
Laholm Bay	sediment incubations	0–(–5) (0–10 anoxia)	Enoksson, 1987
Kiel Bay	benthic chambers	2.28 (annual mean)	Balzer, 1984
Gulf of Gdańsk	Fick's first law	(–0.1)–7.9	Graca, 2009
Gulf of Gdańsk (areas of 59–72 m water depth)	sediment incubations	(–0.5)–11.3	Graca, 2009
Baltic Sea	**(–1.3)–40**		

13.2.3. Spatial and Seasonal Variations of Benthic Nitrogen Flux

In the Baltic Sea, nitrogen is released from the sediment to the near-bottom water mainly as ammonia. The fluxes of ammonia in this sea vary across a wide range. The highest values were observed in areas of strong anthropopressure, e.g.: Gulf of Gdańsk, Gulf of Finland and Laholm Bay (Table 13.4). Apart from regional variability, the ammonia release from the bottom sediments shows seasonal variability. For instance, in the Gulf of Gdańsk, the increase in releasing ammonia is observed at the end of the vegetation season. At that time, the higher water temperature favours the growth of microorganisms, decomposition of organic matter in sediment, and worsening of oxic conditions. Additionally, the fluxes increase in proportion to the depth of the sea water (Fig. 13.10). The highest fluxes are recorded in the regions located below the halocline (70 m) including the Gdańsk Deep together with its slope.

Rough estimations revealed that from $16.61 \cdot 10^3$ to $20.71 \cdot 10^3$ t N/a are released from the sediment to the near-bottom water in the Gulf of Gdańsk as ammonia nitrogen. This load covers maximally 13% of the phytoplankton demand for nitrogen. In the Gulf of Finland, the value is 20% (Heiskanen *et al.*, 1999).

A sum of the nitrate and nitrite benthic fluxes vary in the Baltic Sea from (–21) to 12.5 μmol/m^{2}h (Nedwell

Table 13.4

Ammonia benthic fluxes ($F_{NH_4^+}$) in individual regions of the Baltic Sea (negative values denote flux from water into sediment)

Region	Estimation method	$F_{NH_4^+}$ (μmol/m^{2}h)	References
Puck Bay	Fick's first law/ benthic chambers	0.2–59.7	Bolałek, Graca, 1996
Gulf of Gdańsk (western part)	Fick's first law	22.1 (annual mean), 53.6 (maximum)	Maksymowska-Brossard, Piekarek-Jankowska, 2001
Pomeranian Bay	laboratory experiments	4.2–91.7	Frankowski, Bolałek, 1999
Gulf of Finland	sediment incubations	9.37–34.7	Conley *et al.*, 1997
	sediment incubations	(–23.8)–110.1	Pitkänen *et al.*, 2001
	Fick's first law	(–2.4)–74.4	Heiskanen *et al.*, 1999
Kiel Bay	benthic chambers	5.0–27.8 (18.3 annual mean)	Balzer, 1984
Baltic Proper	sediment incubations	1–35	Koop *et al.*, 1990
	based on budget components	18	Wulff, Stigebrandt, 1989
Laholm Bay	sediment incubations	50 (200 anoxia)	Enoksson, 1987
Bothnian Bay	sediment incubations	0.2–39.8	Nedwell *et al.*, 1983
Gulf of Gdańsk	Fick's first law	0–148.3	Graca, 2009
Gulf of Gdańsk (areas of 59–73 m water depths)	sediment incubations	1.9–88.1	Graca, 2009
Baltic Sea	**(–2.4)–200**		

et al., 1983; Conley *et al.*, 1997; Pitkänen *et al.*, 2001; Graca *et al.*, 2004). These values prove that the consumption prevails over the release of these components by sediments. It can be observed, for example, in the Gulf of Gdańsk (Fig. 13.11), where the fluxes of nitrates and nitrites correspond to the consumption by sediments of about 127 t N/a (Graca, 2009).

13.2.4. Spatial and Seasonal Variations in Denitrification Rate

In the Baltic Sea, 80–90% of denitrification occurs in the sediments and 10–20% of denitrification takes place in the oxygen-poor deep waters (O_2 <0.2 cm^3/dm^3; Rönner, 1983; Rönner, Sörensson, 1985). The process of denitrification removes from the water of the Baltic Sea the nitrogen load, which is equal to its atmospheric supply (app. 30% of the total external supply; Falkowska, 1985; Rheinheimer, 1987; Stockenberg, 1998).

An increase in the denitrification rate usually occurs in areas of strong anthropopressure with a high external load of nitrogen (Seitzinger, 1988). Therefore, the bays and estuaries are characterised by potentially strong denitrification, where this process may affect primary production (Nixon, 1981). It can be seen in the Baltic Sea (Table. 13.5), where a high denitrification rate was noticed, e.g. in the Gulf of Finland and in the Gulf of Gdańsk. In 1997–2003, the latter received a nitrogen load from the

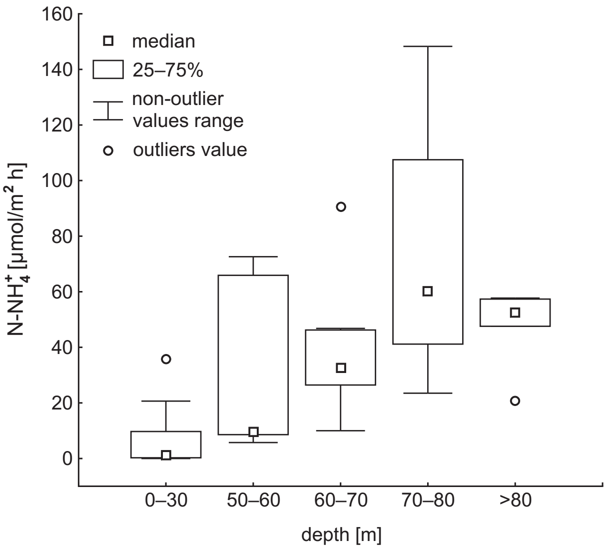

Fig. 13.10. Benthic ammonia fluxes in regions of the Gulf of Gdańsk characterized by different water depths (Graca, 2009)

waters of the Vistula River, corresponding to 16% of the total external supply of this component to the Baltic Sea (Graca, 2009).

In the Gulf of Gdańsk, the rate of denitrification ranges from 3.4 to 230 µmol N/m^{2}h. It is lower in the regions of coastal sands than in deeper areas where sediments are finer, contain more organic matter and show higher concentrations of nitrates(V) in the interstitial and near-bottom waters.

The process of nitrification in bottom sediments is the main source of nitrates used in the process of denitrification in the Gulf of Gdańsk. Rough estimations showed that from $16.85 \cdot 10^3$ to $20.41 \cdot 10^3$ t N/a is removed from the water owing to denitrification in this region (Graca, 2009). It accounts for 13–15% of the total external nitrogen load to this water reservoir.

The denitrification rate in the coastal zone of the Gulf of Gdańsk increases in spring, when the fresh organic matter load from the water column reaches the bottom sediments. The decrease in the rate of denitrification was observed in summer. This is related to a frequent (at that time) decrease in the depth of oxygen penetration into the sediment, limiting coupled denitrification/nitrification as a consequence (Graca, 2004).

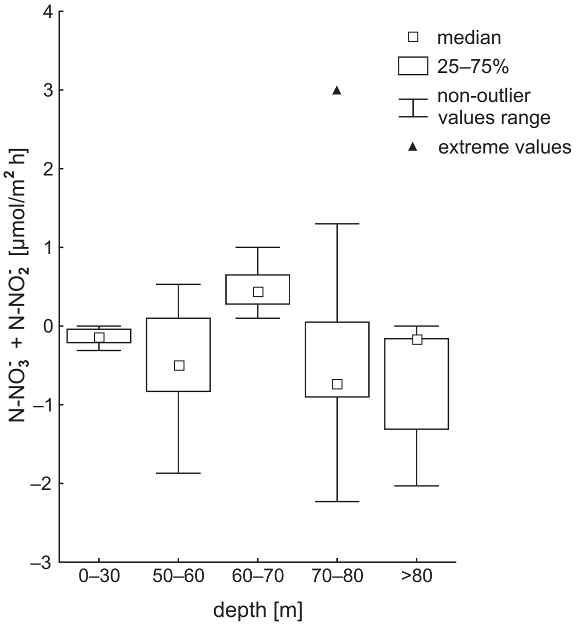

Fig. 13.11. Benthic fluxes of nitrate and nitrite in regions of the Gulf of Gdańsk characterized by different water depths (Graca, 2009)

13.2.5. Benthic-pelagic Interactions

Removing some of the N and P loads from the biological cycle in the water column due to their accumulation and denitrification in bottom sediment mitigates the process of euthrophication. Moreover, the return of N and P from the sediment to the water occurs with some delay. In a shallow-water zone, N and P released from the sediments into the water may be included into the biological cycle during the same vegetation season in which they were delivered into the sediment. In deeper water regions, their return to the euphotic zone is slower. The rate of this return is significantly affected by, among others, the intensity of water mixing, and the inflow of ocean waters (for the Baltic Sea) or upwellings. In the Baltic deeps positive, linear correlation between salinity and phosphate, and nitrate concentrations in surface water are noticed during winter. These relationships were first recorded in the Bornholm Deep in the early 1970s (Francke and Nehring, 1971). In the Gdańsk Deep, such correlations were observed by Trzosińska (1990). They

Table 13.5

Denitrification rate in individual regions of the Baltic Sea

Region	Survey period	Denitrification (μmol N/m^{2}h)	References
Laholm Bay	late summer	19–24	Enoksson, 1987[1]
Aarhus Bay	annual	4–21 (max 42)	Jensen *et al*., 1988[2]
Lendrup Vig.	spring	13–213	Andersen *et al*., 1984[2]
Norsminde Fiord	annual	83–416 (mean 205)	Jørgensen, Sørensen, 1988[2]
Baltic Proper	annual	16	Wulff, Stigebrandt, 1989[3]
	annual	74	Shaffer, Rönner, 1984[3]
	annual	14	Rönner, 1985[2]
		0.4–12.5	Tuominen *et al*., 1998[4]
Laholm Bay		10	Sahlsten, Sörensson, 1986[2]
Central Gulf of Finland		6.3–27.1	Tuominen *et al*., 1998[4]
Gulf of Finland	summer	6.6–11.5	Conley *et al*., 1997[1]
		20.2	Kiirikki *et al*., 2006[4]
	annual	0.3–116 (mean 18)	Heiskanen *et al*., 1999[4]
	annual	0.4–50	Gran, Pitkänen, 1999
Bothnian Bay	8 months	0–39.2	Stockenberg, Johnstone, 1997[2]
River mouths in the Archipelago Sea (southern part of the Bothnian Bay and the Gulf of Finland)	annual	3.7–37.9	Silvennoinen *et al*., 2007[4]
River mouths in the Bothnian Bay (northern part)	annual	9.6–13.3	Silvennoinen *et al*., 2007[4]
Puck Bay	annual	0–42.2 (mean 11)	Graca, 2004[2]
Gulf of Gdańsk		53	Witek *et al*., 2003[3]
	spring, summer	3–230 (58 ±75) 11–48 (36)	Graca, 2009[1, 3] (range, mean ±S.D., lower quartile– upper quartile, median)
Baltic Sea	**0–416**		

[1] estimations of denitrification based on the ammonia flux,

[2] estimations of denitrification based on the acetylene inhibition technique,

[3] estimations of denitrification based on the biogenic salt budget,

[4] estimations by isotope pairing technique.

Table 13.6

Nitrogen accumulation and denitryfication, and accumulation of phosphorus in the sediments of individual regions of the Baltic Sea

Process	Bothnian Bay[1]	Bothnian Sea[1]	Central Baltic[1]	Gulf of Finland[1]	Gulf of Riga[1]	Danish Straits[1]	Gulf of Gdańsk[2]	Baltic Sea[1]
	µmol/m^{2}a							
Nitrogen accumulation and denitrification	29	112	259	198	313	135	328	201
Phosphorus accumulation	3.4	8.3	–2.8	6.5	3.2	5.4	8.8	1.6

[1] Savchuk, 2005, [2] Graca, 2009.

indicate occurence of mechanism, due to which N and P released from the sediment in deep regions, could influence euphotic layer. The effect of nutrients, accumulated under the halocline in the deep-water regions, on the resources of these salts in the euphotic zone of the Baltic Sea was discussed by Nausch *et al*. (2008). Therefore, marine sediment acts as source or sink for nitrogen and phosphorus in sea-water and their significance as a secondary source of these components to the water increases in the eutrophic environment. Particularly important may become the nitrogen and phosphorus loads released from the sediments of the marine reservoirs with the restricted water exchange, such as the Baltic Sea. Moreover, a long-time effect of sediments on the N and P loads in the water column should be considered, taking into account both the shallow- and deep-water zones.

The estuaries play an important role in regulating bioavailable loads of nitrogen and phosphorus in the marine environment. They act rather like filters, which partially retain nutrients on their way to the open marine waters (Nixon *et al*., 1996; Conley, 2000). This retention occurs, among others, as a result of the above-mentioned accumulation and denitrification of nitrogen and accumulation of phosphorus in sediments (Table 13.6). For instance, in the Vistula estuary phosphorus accumulation in sediment corresponds to 10–15% of its external loading to this region. In turn, the accumulation and denitrification in sediments induce the retention of the nitrogen load corresponding to 13–19% of its outer supply (Graca, 2009).

The ratio in which nitrogen and phosphorus are delivered from the external sources into the marine environment exceeds 16 (Conley, 2000). Hence, the accessibility of P is a good restriction on biological production. In spite of this, nitrogen is often the nutrient that limits primary production in seas (Oviatt *et al*., 1995; Nixon *et al*., 1996). For a change, in the freshwater environment, the production is limited mainly by the accessibility of phosphorus (e.g. Hecky, Kilham, 1988). The differences between these environments are associated with, among others, the processes that nitrogen and phosphorus undergo in the bottom sediment. The concentrations of sulphates are higher in the marine waters than in fresh waters. As a result, in marine environment decomposition of organic matter in sediment undergoes to a larger extent by reduction of sulphates. Hydrogen sulphide formed in this process decreases the phosphorus retention in sediments, which is favourable for its release into the water (Chapter 7.3). It is recognised as one of the reasons for which nitrogen limits the production of phytoplankton in the marine environment. This approach is, however, a large simplification, as under natural conditions the dynamics of transformations of nitrogen and phosphorus is more complex.

An important role in forming the ratio of nitrogen to phosphorus in water column is assigned to differences in the rate of these elements removing from the water column due to denitrification and accumulation in sediment. For instance, in the Gulf of Gdańsk, these processes remove the load of about 21.26 t N/a and 1.16 t P/a from the water. These values correspond to app. 56% and 35% of the nitrogen and phosphorus supply from the water to the sediment (Graca, 2009).

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Chapter 14

THE EFFECT OF POLLUTION ON THE BALTIC SEA ORGANISMS

Since chemical elements are everywhere, non-degradable and durable in their terrestrial and water ecosystems, they generate hazards for living environmental resources. Vital elements necessary for organism to function properly include: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Sn, and Sb; whereas the elements that are physiologically unnecessary include: Pd, Ag, Cd, Pt, Hg, and Pb (Luoma, Rainbow, 2008).

The toxicity of trace elements depends, for example, on their type, concentration and the chemical form of their functioning in their natural environment. Toxicity varies in the following series: (Luoma, Rainbow, 2008):

$$Hg > Ag > Cu > Cd > Zn > Ni > Pb > Cr > Sn$$

Based on the above, physiologically necessary trace elements (e.g. Cu, Zn) may show, in specific conditions, higher toxicity than the elements physiologically unnecessary (e.g. Pb).

Their contents in marine organisms depend, among other factors, on their concentrations in the environment that they live in, i.e. the seabed sediments, suspended matter, or marine waters.

For benthic organisms, i.e. the representatives of fauna living in the surface layer of the sea bed, these are fine particles (<63 µm) in the sediment material, serving as their food. Considering the above, in order to estimate the bioavailability ratio of a given element with reference to the tissues of the benthic fauna representatives, its content in a labile fraction of the fine-grained sediment material, i.e. in the water extracts of diluted hydrochloric acid, should be also determined (Bryan *et al*., 1985; Luoma, Rainbow, 2008).

Worth noting is the extraction of labile forms of elements with 1 M HCl or 0.1 M NaOH (grain size <100 µm or <63 µm). The aim of this procedure is to achieve standardisation and to select the fine clay fraction that will contain the most bioavailable chemical forms of metals. In order to leach "mobile" speciates of elements, a diluted solution of HCl or NaOH is used (Luoma, Bryan, 1981; Bryan, Langston, 1992; Szefer *et al*., 1995; Luoma, Rainbow, 2008).

Hydrochloric acid liberates to the extract those labile forms of elements that are adsorbed on the surfaces of particles of Fe and Mn hydroxyoxides and aluminosilicate minerals, or those associated with organic matter.

The above-described procedure was used, among others, in the analyses of sea-bottom sediments in the southern Baltic Sea, determining the contents of mobile speciates of chemical elements (Szefer et al., 1995; Szefer, Szefer, 1990).

The sequential extraction of the individual forms of elements according to Tessier and others (1979) (grain size <63 µm) aims to separate (by using suitably selected extractants) chemical forms of elements occurring in the five fractions of the tested sediments:

- Exchangeable (the solution of $MgCl_2$),
- Extractable, with reference to the elements associated with carbonates (NaOAc),
- Reduced, with reference to the elements associated with hydroxyoxides of Fe and Mn ($NH_2OH \times HCl$),

- Oxidised, with reference to the elements bound with organic matter or/and sulphides (HNO_3, H_2O_2, NH_4OAc),
- Residual with reference to the elements bound up in a crystal lattice of minerals ($HClO_4$ and HF in the volume ratio of 1:5).

The results of the sequential analysis of bottom sediment samples taken in the Gulf of Gdańsk were published in Belzunce-Segarra *et al*. (2007).

Concentration Factor (CF). The main source of chemical elements in the marine zoobenthos are their forms of sediment or suspension origin. The so-called deposit feeders (e.g. *Mya arenaria*,) receive the elements mainly from the particulates of surface layer sediments, whereas the filter feeders (e.g. *Mytilus edulis*) assimilate metals from the bottom suspended particulates. In turn, molluscs that are facultative deposit feeders (e.g. *Macoma baltica*), feed on the particles of both sediment and suspension origin. The so-called labile fraction is the most easily bioavailable group of micro- and macroelements occurring in the surface layer of bottom sediments. In order to determine mutual qualitative proportions, in which a chemical element occurs in the zoobenthos, as well as a labile fraction of the sedimentary or suspended material, it is necessary to calculate concentration factors (CF) with reference to its wet mass (w.m.) (Szefer, 1991; Szefer, Szefer, 1991):

$$CF = \frac{C_x}{C_s}$$

where:

C_x – mean element content in the wet mass of the organism [µg/g w.m.],

C_s – mean value of a chemical element in its environment (labile sediment fraction), [µg/g].

The value of CF ≈1 indicates the equilibrium between the content of an element in its environment and in the tested organism, and CF>1 shows its accumulation in the biological material, which may result from influence of both biotic and abiotic factors. The CF values estimated for the benthos of the southern Baltic Sea have been presented in a monograph (Szefer, 2002). Considering for example *Saduria entomon* from the southern Baltic Sea, the CF factors achieved the highest values for Cu and Ag, and the lowest for Ni. Whereas the soft tissue of the mollusc *Macoma baltica* is marked by the highest affinity for Cu and Zn, and the lowest for Ni, Fe, and Co (Góral *et al*., 2009; Hendożko *et al*., 2010).

The results of factorial analysis suggest a significant effect of the grain size of bottom sediment as a substrate on the bioavailability ratio of the tested metal elements. The individuals of *S. entomon* living in silty sediments were generally characterised by a higher bioaccumulation ratio compared to those living in the sandy seabed. The elements that differentiated the pattern of silty and sandy samples in respect to grain size were the following: Zn, Fe, Cu, and Pb, as well as Mn and Cr (Góral *et al*., 2009).

The results of the factorial analysis also proved that the labile (1 M HCl) fraction of the bottom deposits is a significant source of Cd, Zn, Fe, and Cu (to some degree) in the Gulf of Gdańsk, and Ni, Co and Mn in the open waters of the southern Baltic Sea. However, we cannot exclude another source of metals, although less significant, which is near-bottom suspended matter, because *M. baltica* is a facultative deposit feeder (Hendożko *et al*., 2010).

Biomagnification Factor (BMF). The food eaten by marine organisms may become an important source of trace elements in their tissues. This situation occurs when metal contaminants are assimilated from the food, and then accumulated for a longer period in the tissues of predators. For this reason, the information on the contents of the individual elements in the particular levels of the trophic pyramid helps to assess their magnification and transition ratios along the sequential links of the food chain. A quantitative measure of this metal accumulation process is the BMF factor expressed by the following formula (Szefer, 1991):

$$BMF = \frac{C_c}{C_p}$$

where: C_c and C_p denominate, respectively, the content of an element (µg/g) in an organism at a higher trophic level, i.e. a predator, and at a lower trophic level, i.e. a prey. The value of BMF ~1 indicates there is no biomagnification of a given element in the predator with reference to its prey, whereas a BMF >1 shows its biomagnification in relation to lower trophic levels.

Based on the trophic relation: great black cormorant–fish, it has been shown that Hg accumulates in the ecosystem of the Vistula Lagoon in the whole mass of this bird species with reference to its food, i.e. different species of fish (Misztal-Szkudlińska *et al*., 2011).

It is worth emphasising that easily bio-available forms of Hg in the labile sediment fraction may be accumulated, for example, in the soft parts of the marine zoobenthos that are eaten by predators at higher levels of the trophic pyramid, e.g. by the benthos-eating fish (flounder, cod). It leads to the bioaccumulation of Hg in their tissues, reaching maximum levels in the human body that tops the pyramid.

For that reason, the accumulation of toxic elements along the particular links of the marine trophic chain may result in serious hazards for human health, considering the fact that marine food resources may be contaminated by the metallic pollutants deposited in the sea-bottom sediments. Particles of the sediment material are a basic food source for many zoobenthos organisms, either directly eaten by man as seafood (molluscs, crustaceans) or being food for organisms representing higher trophic levels (e.g. edible fish). In this way, a consumer may be exposed directly to sediment-origin toxic metals occurring in seafood, or indirectly, i.e. by eating the representatives of higher links in the food chain, e.g. benthos-eating fish often containing multiplied levels of a given element (Hg) as compared to those observed in lower organisms (i.e. in their preys – molluscs, crustaceans) (Kwoczek *et al*., 2006). Therefore, knowing the contents of a given element in the labile sediment fraction helps to estimate the ratio of its bioavailability in the tissues of the benthos, which is particularly significant for the ecotoxicological assessment of edible marine resources.

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Chapter 15

A FEW FINAL REMARKS

The progress in technology made by humanity has enabled the development of natural sciences, including marine geochemistry. To a certain degree, it is an exceptional domain as it combines many fields of sciences: geology, chemistry, biology, mineralogy and oceanography. The geochemistry of marine sediments sets the task to understand not only the chemical contents of the bottom sediments, but the primary aspiration to understand the mutual relations between the different components of the marine environment: waters, sediments, organisms that live at the sea bottom, as well as climate and its effect on the processes occurring in the bottom sediments. At present, although our knowledge on this area is very extensive, there are still many gaps. We are often unable to understand the changes of the surrounding environment, the evolution of which is permanently disturbed by us on both a local and global scale. However, in order to evaluate the aspects that we already know, it is worth reviewing and making available the relevant information. An attempt of this kind was undertaken in the present monograph with respect to the Baltic Sea.

The catchment area of this geologically young sea has a population of 85 million citizens. This water reservoir is susceptible to degradation, which is associated partly with water stratification and their limited exchange with the ocean, as well as with the small area of the Baltic Sea in relation to its catchment area. The Baltic Sea is under strong anthropopressure, which in recent decades has contributed to the eutrophication and pollution of this water reservoir with different toxic substances. Accumulation of many chemical substances has been observed in the bottom sediments; however, in specific conditions, the contaminants may be remobilized from sediments to the water depths. Owing to changes in oxygen conditions and the redox potential, the Baltic Sea bottom area increases its oxygen deficiency, which may release toxic components into the environment and include them into the food chain. Therefore, it is important to conduct studies in order to determine the amounts of toxic substance loads that may be released from the sediments into the waters. Significant is also the assessment of their effect on the biocenosis.

Biogenic substances, trace metals, radionuclides and stable organic pollutants are the most important groups of substances that flow into the Baltic Sea. The development of more advanced measurement techniques enables us to determine the concentrations of different chemical substances at the level of ng/kg or pg/kg. It offers a large area for geochemical surveys. These techniques are used, for example, to analyse the contents of dioxins or residuals of pharmaceuticals. This is an extremely wide range of chemical substances hard to decompose in the environment, undergoing bioaccumulation and biomagnification. The research on the pharmaceutical residuals in the Baltic Sea is already underway. Since these agents are commonly used and they impart potentially strong effect on water organisms, these studies seem to be the next priority.

As far as the entire whole Baltic Sea is concerned, the chemical composition of sediments and interstitial waters, as well as their regional differentiation depend on climate, hydrological regime, sources and the amounts and types of substances supplied from the outside. The biotic and abiotic factors affecting the sediment content also include a primary production level, sea depth, water density stratification and water hydrodynamics. In some regions of the Baltic Sea, the chemical content of interstitial waters is modified by the groundwater drainage and geogenic substances, e.g. hydrocarbons. An important part in the circulation of the substances at the water-sediments interface is also played by organisms that live in sediments.

At present, the geochemical monitoring of bottom sediments becomes particularly significant. It is recommended, among others, by the Water Framework Directive (WFD). The main aims of the WFD include: to protect and improve the conditions of the water ecosystems, and, if it is impossible, to maintain their present-day state, to propagate sustainable water management based on the long-term protection of the available water resources, and finally, to undertake tasks to improve the ecological status of the water environment. According to WFD, these aims should restrict the emission of substances that are especially hazardous for the marine environment. While planning activities aiming at improving the quality of the marine waters, in addition to outer sources, we should also consider sediments as a potential, secondary source of contamination. However, the restrictions applied on land may be unsatisfactory for improving the quality of waters, mainly owing to the release of contaminants from the sea-bottom sediments accumulated in previous years.

The ecological status of the marine environment is significantly controlled by climatic and hydrological changes. The decrease in the intensity of water inflows from the North Sea in the recent decades has resulted in anoxia of the sea-bottom waters. With the increasing water temperature, the rates of geochemical processes that determine the water quality change. Eutrophication and elongation of the vegetation season increase primary production, which, in turn, increases the mineralisation rate and deepens oxygen deficiency in the sea-bottom waters. It also results in the production of hydrogen sulphide and in the remobilisation of biogenic substances (mainly phosphorus) and some metals from the bottom sediments. More intense precipitation induces an increase in the erosion intensity and in the runoff of pollutants to the sea. The quality of the bottom sediments is also modified by climatic changes, extreme weather events and associated processes, such as marine currents or seabed erosion. During the resuspension of sediments, pollutants are released from the sediments to the sea bottom waters. The distribution of marine organisms is also partly controlled by temperature. An increase in the water temperature may change the pattern (migration of species to the north) of species distribution, or even lead to the extinction of some of them in extreme conditions, which, in turn, affects the circulation of substances in the marine environment.

The bottom of the Baltic Sea has also been interfered with by man in numerous and direct ways. Many telecommunication cables and pipelines run through the sea bottom. Apart from that, natural raw materials are extracted and the commercial trawling is carried out. In the coastal zone, the sea bottom is regularly disturbed in many places while strengthening the shoreline and deepening the water tracks. The bottom of the Baltic Sea is also an area where different materials are discharged, first and foremost, all the spoil extracted by ships dredging harbours. It is also the place where chemical weapons were sunk after World War II. Besides, there are plans to use geological structures under the Baltic Sea bottom to store CO_2 (geo-sequestration). In the age of global warming, it seems especially significant to understand the character of CO_2 migration and its behaviour in geological layers where the gas will be potentially injected, especially the mechanisms of its physical and chemical trapping. All these human activities have or may have an effect on the sediment stability in the future and may be a serious threat for ecological safety in this region. An important question arises: are we able to assess correctly the effect of this type of interference in the environment of the Baltic Sea?

All the problems and questions outlined above are valid for the next generations, for decades or hundreds of years. It seems that the tasks undertaken so far, including the recommendations by the Helsinki Commission, International Council for the Exploration of the Sea (ICES) or the European Union (e.g. Water Framework Directive), have decreased the inflow of pollutants to the Baltic Sea since the 1980s. This process is not only observed by chemical monitoring of marine waters, but it is also recorded in the sea-bottom sediments. The sediments deposited in the 1990s and in this century contain much less toxic substances, including heavy metals or persistent organic pollutants (PAH, PCB), than the sediments deposited from the 19th century until the 1980s, as shown in this study.

The research on the changes in the environment, the record of which is found in older sediments, casts a new light on the processes that occur in the Baltic Sea in the present. Especially important is the information about natural periods when oxygen deficiency occurred in the sea-bottom waters. During the past 8,000 years, such stages appeared several times, which was quite natural. At that time, the natural plankton bloomed, anaerobic conditions, including hydrogen sulphide production, were observed in the bottom water and laminated sediments appeared, which is usually ascribed only to human activities. Obviously, those sediments do not contain such high concentrations of metals as contemporaneous deposits do, nor do they contain other anthropogenous contaminants. However, they still provide essential information about natural climate oscillations and the changes in the ecological conditions of the Baltic Sea.

Remaining open is the question about the future of the Baltic Sea in the longer perspective. Two answers are possible.

As much as the global warming is really a result of human activity and produces durable climatic changes, the contaminated contemporaneous sediments of the Baltic Sea will be covered by the next sediments with lower contents of anthropogenous substances, becoming a guiding bed reflecting the thoughtlessness and incomplete knowledge of 20th-century people concerning the rules of nature. However, if the man’s effect on natural cyclic climatic changes turns to be insignificant, we ought to expect a considerable climate cooling in the next few centuries. The next glaciation period will occur and a continental glacier, originated in Scandinavia, will spread southwards through the area of the Baltic Sea, as has happened several times during the last few hundred thousand years, destroying all traces of the reckless activity of the mankind.

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