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## HYDRODYNAMIC CHARACTERISTICS AND NITRATE PROPAGATION IN SPARTA AQUIFER

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**Abstract**—During the 1994–1997 water years, a hydrogeological study was carried out on the alluvial aquifer of Sparta in the Peloponnese, where the concentration of nitrate ions in groundwater, as  $\text{NO}_3^-$ , is well over the highest recommended WHO limits of  $50 \text{ mg l}^{-1}$ . Under specific hydrological and chemical conditions with high amounts of dissolved oxygen, the migration of nitrate ions in the aquifer, seems to be unaffected by any hydrological process, chemical substance or reaction. Examination of the relationship between nitrate concentration and aquifer properties shows that maximum nitrate concentration values follow the main axes of groundwater movement, while zones of increased recharge coincide with zones of diluted nitrate concentration.

Profiles of the evolution of chemical parameters vs depth, show that the main process causing nitrate increase in groundwater, is the oxidation of ammonia originating from the rapid leaching of inorganic fertilizers applied to cultivated areas. © 2000 Elsevier Science Ltd. All rights reserved

**Key words**—aquifers, saturated and non-saturated zones, nitrate migration

### INTRODUCTION

Many previous studies on groundwater quality have shown that nitrate is derived from various point and non-point sources, such as feed lots, septic tanks, and oxidation of organically bound soil nitrogen (N). In shallow groundwater, however, increase of nitrate concentration is due to the extensive application of agricultural fertilizers. According to Hallberg (1989), the application of nitrogen-based fertilizers on irrigated crops is the most extensive human source of  $\text{NO}_3^-$  in groundwater systems. The amount of nitrate leached from agricultural lands is strongly influenced by factors inherent in nature such as soil type and climatic conditions (Mikkelsen, 1992).

In groundwater and pore water that is strongly oxidizing,  $\text{NO}_3^-$  is the stable form of dissolved nitrogen. It moves with the groundwater and experiences no chemical transformation and little, or no, retardation (Freeze and Cherry, 1979). Very shallow groundwater in highly permeable sediment or fractured rock, commonly contains considerable amounts of dissolved oxygen. It is in these hydrogeological environments that  $\text{NO}_3^-$  migrates large

distances from its input areas (Shimajima and Sharma, 1995).

The aim of this research was to investigate the mode of nitrate ion transport through the non-saturated and saturated zone in relation to the hydrodynamic characteristics of the aquifer.

### MATERIALS AND METHODS

In order to understand the mode of nitrate movement, investigation in the Sparta region involved determination of the hydrogeological characteristics of the aquifer and its hydraulic properties. The properties of the unsaturated zone were also defined in the same way. Investigation was made during 1994–1997, while all measurements presented in this paper are considered representative and were taken in 1996–1997.

A series of 125 wells was used for piezometric measurements and groundwater sample collection. Thirteen short-duration pumping tests (“slug tests”) were conducted in order to determine the hydraulic conductivity of the aquifer using the Bouwer and Rice (1976) method. Elements for construction of the spatial distribution map of clay content (%) at different depths of the unsaturated zone were drawn up from Memmos (1969). This study was realized using the American Standards (SCS) on the soil series level. For this research, 537 soils measurements were taken using post-hole Dutch auger equipment, and 79 samples were taken from control holes with a density of one sample per 150 ha. To determine the organic matter content (%), 17 soil samples were taken from the region using a Gouge auger of 30 mm diameter. These samples were dried for 24 h in an oven at  $105^\circ\text{C}$  and were then

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analyzed to determine their organic matter content using the dichromate potassium ( $K_2Cr_2O_7$ ) method. To ascertain the saturated hydraulic conductivity of the unsaturated zone, the Nasberg and Terletska (1978) method was used.

In the unsaturated zone, chemical analyses of the pore water were carried out on 10 samples taken from different areas and at the depths of 0.5, 1.0 and 1.5 m, using a "suction lysimeter" sampler. Chemical analyses in groundwater samples in neighbouring wells were also made at depths of 2, 3 and 7–8 m below the water-table in order to complete the profiles of  $Cl^-$ ,  $NH_3$ ,  $NO_2^-$  and  $NO_3^-$ . Complete chemical analyses were performed on 20 groundwater samples taken at a depth of 1.5 m below the water-table. The first sample of 0.5 l volume was acidified for cation analysis. Two series of samples were taken for each year at highest and lowest water levels. Analysis of the unstable parameters such as dissolved oxygen (DO), temperature, electrical conductivity (EC), and pH was performed in the field immediately after collection, as was laboratory analysis of the following parameters:  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $HCO_3^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NO_2^-$  and  $SiO_2$ . Overall precision of the analysis is within  $\pm 5\%$ . Processing of the data was carried out using a software package developed

in the Laboratory of Hydrogeology, University of Patras (Lambrakis, 1991).

## HYDROGEOLOGY

### General hydrogeological description

The post-orogenic rocks, Plio–Pleistocene sediment including terrestrial and lacustrine facies of western Lakonia (Fig. 1), occupy a broad graben between Mounts Parnon and Taygetos. These sediments have been uplifted and dissected on the eastern margin of the graben, but appear to be still accumulating on the western margin (Piper *et al.*, 1982). The shallow aquifer of Sparta is developed into the coarse phases of these sediments. The bedrock of these formations is composed of crystalline limestones of the zone of Plattenkalk, low metamorphism rocks, phyllites and quartzites, and limestones of the zone of Tripolis (Jacobshagen *et al.*,

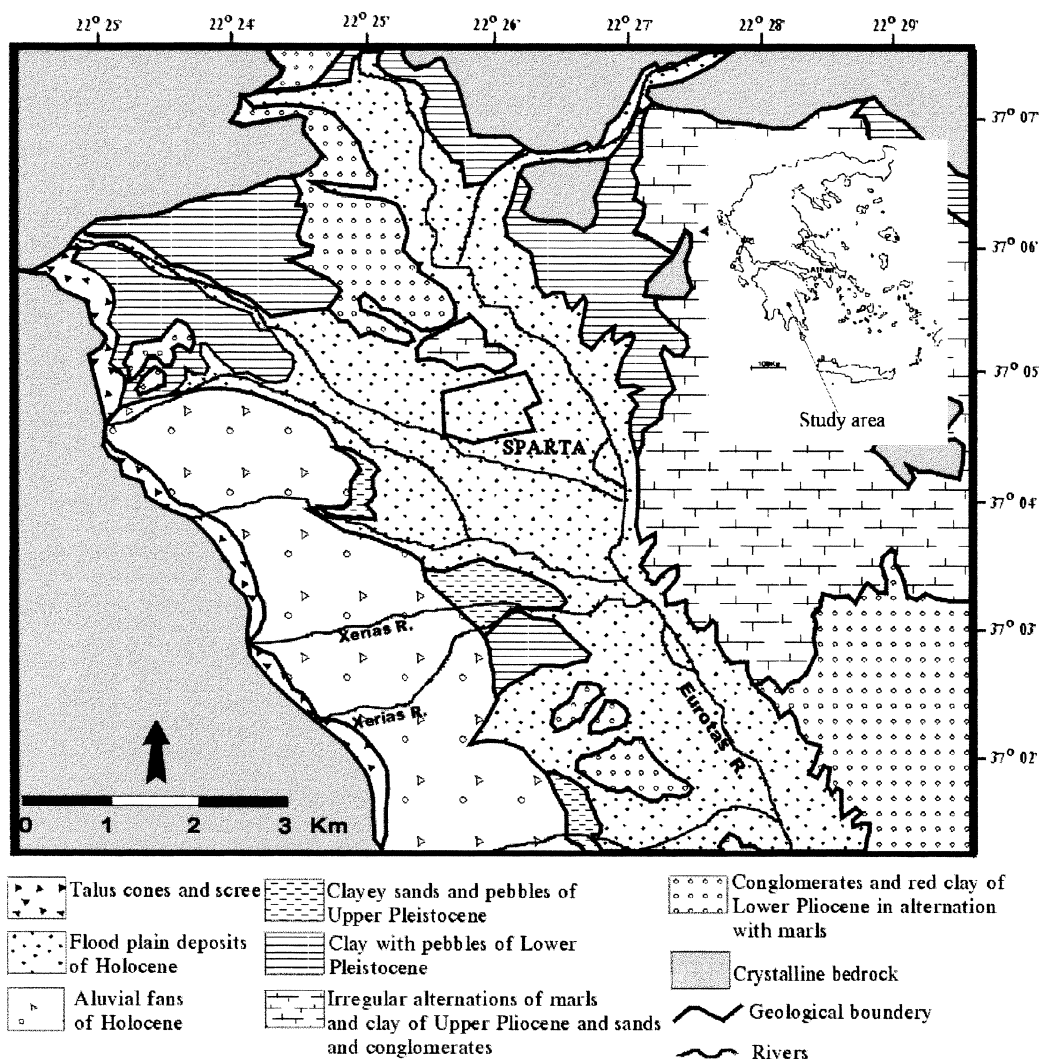


Fig. 1. Geological map of study area.

1978). In the (basement) carbonate rocks, a second important karstic aquifer has developed which laterally recharges the studied aquifer.

#### *Lithology of the shallow aquifer of Sparta*

The Pliocene terrestrial deposits in the Eurotas valley consist of red conglomerates and poorly-sorted sands deposited on the crystalline bedrock (Panagos *et al.*, 1976). The well-rounded clastics of this facies suggest a braided river deposit (Piper *et al.*, 1982). This formation is overlain by yellowish terrestrial facies which consist of silty muds and interbedded sands and conglomerates, and there may be periodic formation and filling of shallow lakes on the Eurotas flood plain (Piper *et al.*, 1982). The lower Pleistocene deposits consist of grey silts in alternate beds with conglomerates, while those of the upper Pleistocene consist of silty-sands with interbeds of conglomerates alternating with beds of sands. Holocene sediments contain more locally derived clasts, consisting of silty sands with gravels and pebbles. Into the coarse beds of these rocks the shallow unconfined aquifer of Sparta has developed and is becoming semi-confined in its centre due to the formation of lenticular interbeds.

#### *The piezometric map of the aquifer*

Piezometric map (Fig. 2) provide a good description of the aquifer. From this map, it can be seen that the tributaries with a low angle direction towards the piezometric curves have no influence in

the piezometry. This is due to the fact that flow of these tributaries is not permanent and takes place only a few days after precipitation. The shallow aquifer of Sparta is relatively homogeneous and lacks strong variations in the hydraulic gradient, which varies between 0.01 and 0.03. The fairly high values of the gradient are due to a relatively important flow through the aquifer as indicated by transmissivity map (Fig. 3b). Groundwater drainage is observed to occur in easterly and northerly directions, while the aquifer is recharged mainly from the mountainous regions through the crystalline carbonate rocks. On its west bank, the River Eurotas drains the entire aquifer, while recharging the aquifer on its east bank.

#### *Spatial distribution of the hydraulic conductivity of the aquifer*

To evaluate the hydraulic conductivity, and then the transmissivity, a series of 13 slug tests was made according to the Bouwer and Rice method, concerning the whole thickness of the aquifer. The choice of testing wells was based on the geological knowledge of the area taking into account the heterogeneity of lithology. The thickness of the saturated zone varies between 10 and 60 m, increasing gradually from the north and east to the south and west. Permeability values vary between  $1 \times 10^{-4}$  and  $6.3 \times 10^{-4} \text{ m s}^{-1}$ . Transmissivity values vary between  $3 \times 10^{-3}$  and  $14 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ , while the storage of the aquifer varies between  $1.1 \times 10^{-2}$  and

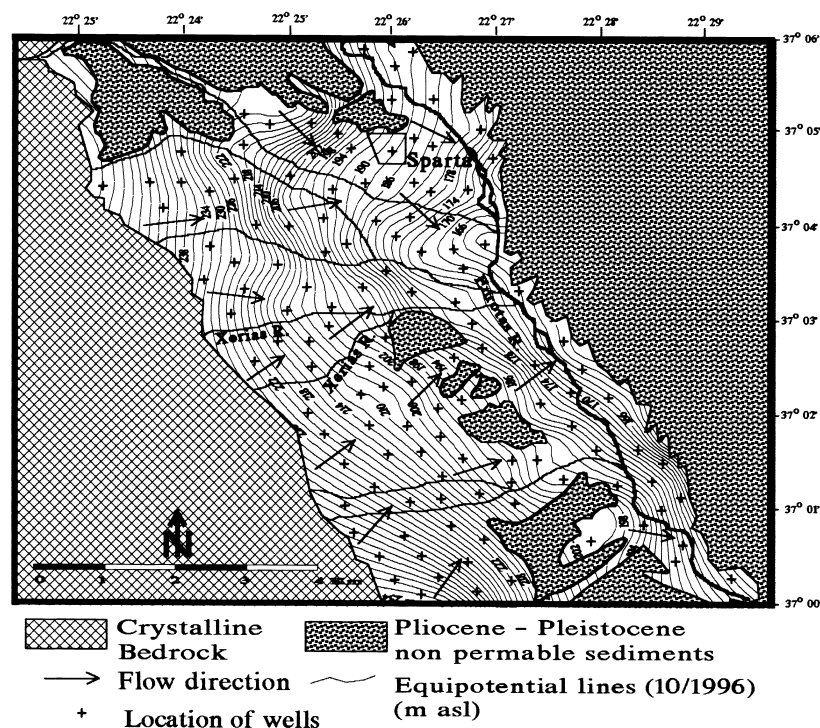


Fig. 2. Piezometric map of the shallow aquifer of the Holocene sediments of Sparta.

$1.3 \times 10^{-3}$ . Based on these results, the spatial distribution maps of hydraulic conductivity and transmissivity (Fig. 3a and 3b) suggests that there is a zone of high values around the stream of Xerias. It is also obvious from these maps that a trend of increased values of hydraulic conductivity and transmissivity can be observed towards the margins of the west of the graben, while in the centre there is a decreasing trend.

#### DETERMINATION OF THE CHARACTERISTIC PROPERTIES OF THE UNSATURATED ZONE

In the present study, the main properties of the unsaturated zone were determined as the following: the clay content of sediments at a 1-m depth, after Memmos (1969), the organic matter content of sediments at the same depth, and the saturated hydraulic conductivity at the same depth.

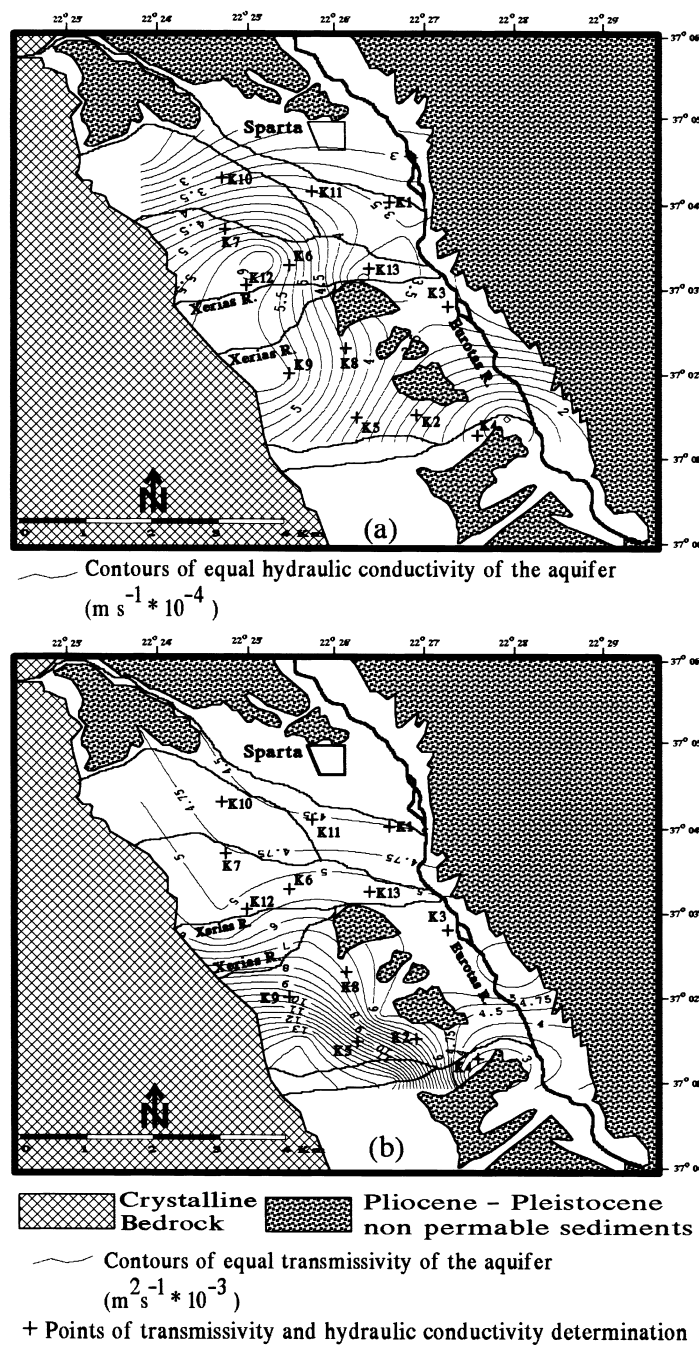


Fig. 3. Contours of equal hydraulic (a) conductivity ( $\text{m s}^{-1} \times 10^{-4}$ ) and (b) transmissivity ( $\text{m}^2 \text{s}^{-1} \times 10^{-3}$ ) of the aquifer.

Based on the results of the region's soil study (Memmos, 1969), a clay content distribution map was constructed for the depth of 1 m below surface (Fig. 4a). Clay content at this depth varies between 20 and 40%. From this map it is obvious that the highest values are observed around the Plio–Pleistocene sediments, while lower values are observed on the western margin of the graben. Along with Fig. 3, this confirms the section of the aquifer where conditions are most favourable for permeability.

Organic matter levels were shown to vary between 0.3 and 1.4% C, and the distribution map (Fig. 4b) shows a pattern similar to that of Fig. 4a. Organic matter content increases around the Plio–Pleistocene sediments.

Saturated hydraulic conductivity of the unsaturated zone varies between  $8 \times 10^{-5}$  and  $2 \times 10^{-7} \text{ m s}^{-1}$ . The highest values are observed in the north and west of the region, while the lowest values are observed in the centre (Fig. 5).

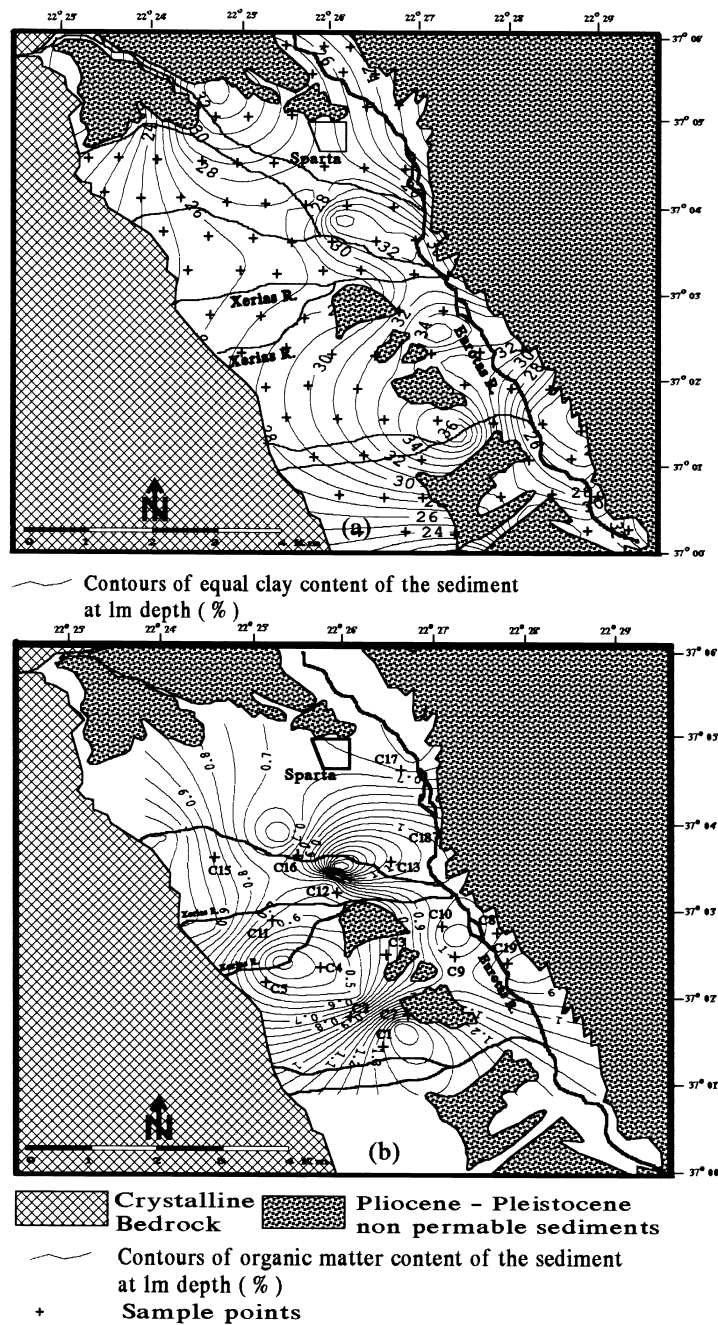


Fig. 4. Contours of equal (a) clay content (%) and (b) organic matter content (%) of the sediments at 1 m depth.

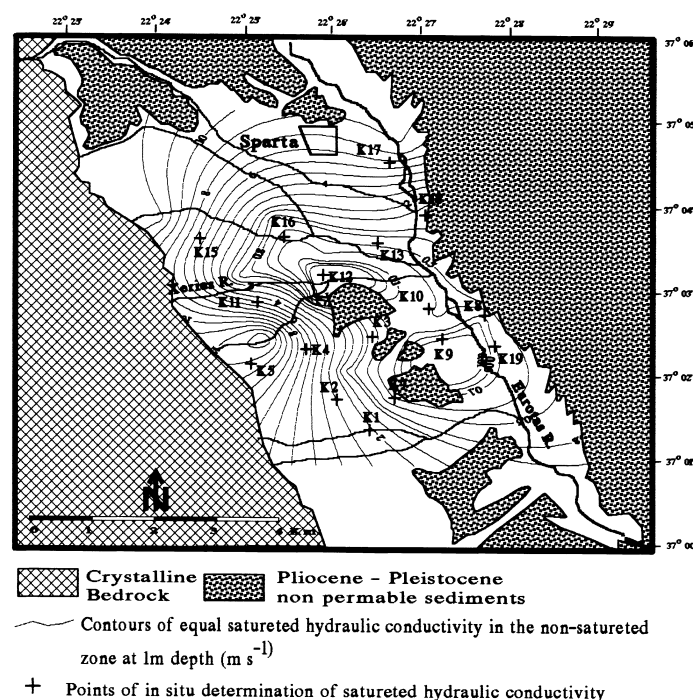


Fig. 5. Contours of equal saturated hydraulic conductivity in the non-saturated zone ( $\text{m s}^{-1}$ ) at 1 m depth.

The above-mentioned hydrogeological observations of the unsaturated zone contribute to a clear picture of the hydrological conditions of the shallow aquifer of Sparta. The aquifer is unconfined in the west and north of the region, but becomes semi-confined in the south and centre due to an increase in clay content, probably in the shape of lentils related to the Eurotas flood plain (Piper *et al.*, 1982). It is recharged by surface waters from the north and by lateral infiltration through carbonate rocks in the west of the region, while buried springs due to limestone karstification should not be excluded. Also in the west, there is an axis of increased permeability running parallel to the Xerias stream, and here values of hydraulic conductivity and saturated hydraulic conductivity are increased. An extended faulted zone along the Xer-

ias tributary seems to amplify the recharge of the aquifer.

#### HYDROCHEMISTRY OF THE SHALLOW AQUIFER OF SPARTA

Chemical analysis of the groundwater samples produced the statistical values as shown in Table 1. These results show that in 65% of the samples, nitrate concentration surpassed that of  $50 \text{ mg l}^{-1}$  as  $\text{NO}_3^-$ , which is the highest nitrate concentration permitted in drinking water by the World Health Organization (Safe Drinking Water Comm., 1980 and the EEC standards). In the majority of samples, concentration of sulphate ions varies in high levels. Table 1 shows that the quality of drinking water taken from the aquifer is problematic.

Table 1. Statistical parameters of the groundwater chemical analysis (40 samples)

Parameter	Mean	Minimum	Maximum	Range	Standard Deviation
$\text{Na}^+$ ( $\text{mg l}^{-1}$ )	12.274	3.7	19.9	16.2	5.196
$\text{K}^+$ ( $\text{mg l}^{-1}$ )	1.915	1.29	4.8	3.51	0.977
$\text{Ca}^{2+}$ ( $\text{mg l}^{-1}$ )	113.140	67.6	164	96.4	27.013
$\text{Mg}^{2+}$ ( $\text{mg l}^{-1}$ )	31.222	15.5	52.4	36.9	10.212
$\text{Cl}^-$ ( $\text{mg l}^{-1}$ )	19.565	10.8	27.2	16.4	4.736
$\text{HCO}_3^-$ ( $\text{mg l}^{-1}$ )	275.300	192	341	149	38.936
$\text{SO}_4^{2-}$ ( $\text{mg l}^{-1}$ )	98.700	32	192	160	48.758
$\text{SiO}_2$ ( $\text{mg l}^{-1}$ )	9.770	3.8	14.6	10.8	2.480
$\text{NO}_3^-$ ( $\text{mg l}^{-1}$ )	62.616	4.42	177.12	172.7	49.059
Diss. $\text{O}_2$ ( $\text{mg l}^{-1}$ )	4.991	3.08	7.26	4.18	0.935
pH	7.229	6.96	7.52	0.56	0.153
E.C ( $\mu\text{Scm}^{-1}$ )	723.700	473	997	524	164.510

Based on the chemical analyses, the chloride concentration map (Fig. 6a) is constructed. It shows the general distribution of dissolved salts and hence the hydrochemical patterns of the aquifer. Maximum chloride concentration is observed along the principle axis of aquifer discharge, parallel to the Eurotas river. From the same Figure, the general direction of groundwater movement (flow lines perpendicular to the contours of equal chloride concentration), and

groundwater recharge with waters with low  $\text{Cl}^-$  content from the north and west are obvious.

In Fig. 6b, the iso-ratio contours of the  $\text{rHCO}_3^-/\text{rCl}^-$  show clearly the hydraulic relationship between the shallow aquifer and the carbonate aquifer. Increased values of the  $\text{rHCO}_3^-$  to  $\text{rCl}^-$  ratio, mainly around the stream of Xerias, suggest increased  $\text{HCO}_3^-$  concentrations which result from dissolution of the carbonate rocks. For example, in an open system, a mole of calcite or dolomite gives

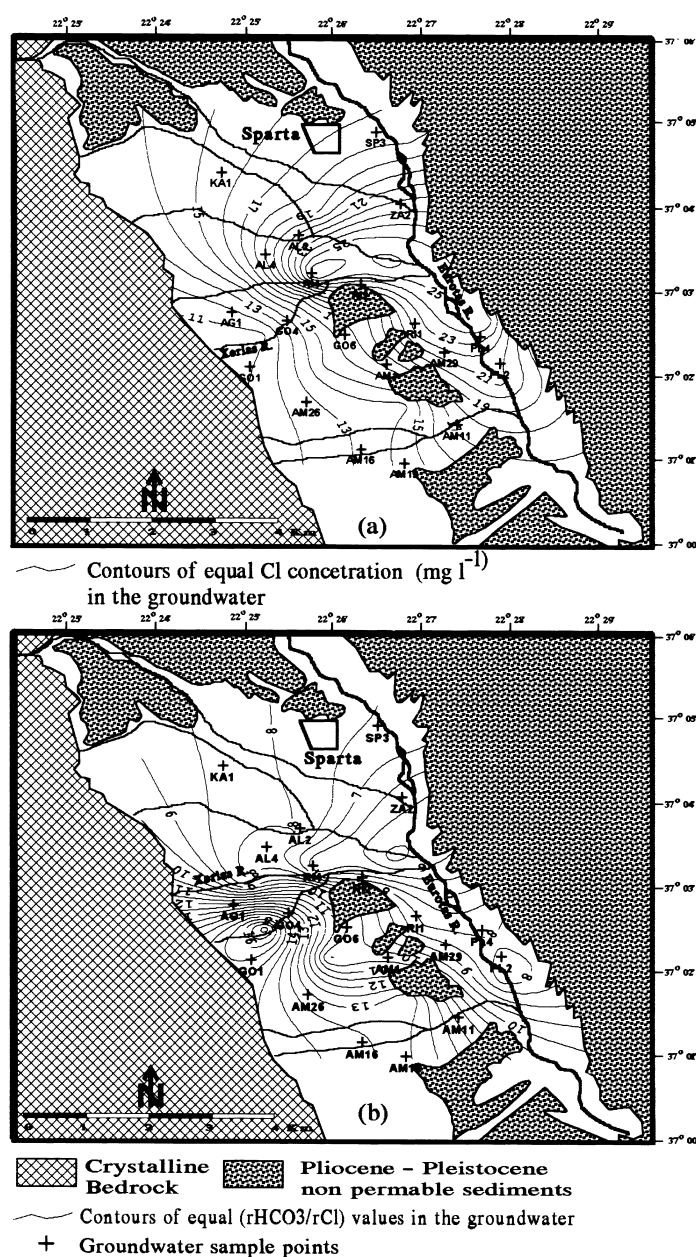
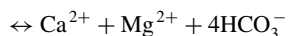
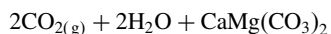
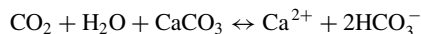


Fig. 6. Contours of (a) equal  $\text{Cl}^-$  concentration ( $\text{mg l}^{-1}$ ) and (b) of equal  $\text{rHCO}_3^-/\text{rCl}^-$  values in the groundwater.

2 or 4 moles of bicarbonate during their dissolution in groundwater, as the following reaction equations indicate (Appelo and Postma, 1993):



Combination of the two maps confirms that the aquifer is recharged from the north and west, the

western recharge being eventually related to the underlying karstic limestone.

The iso-concentrations of the nitrate and sulphate ion maps (Fig. 7a and 7b) show similar patterns. The regions of high concentration of both ions coincide and their spatial distributions have the same characteristics. This is a major indication that these ions originated from the same source. From mineral investigations (Panagos *et al.*, 1979), the lack of gypsum and anhydrite in the region is recognized. Pyrite, the oxidation of which gives considerable amounts of sulphates in groundwater (Lowson, 1982), is also not a common mineral in the local

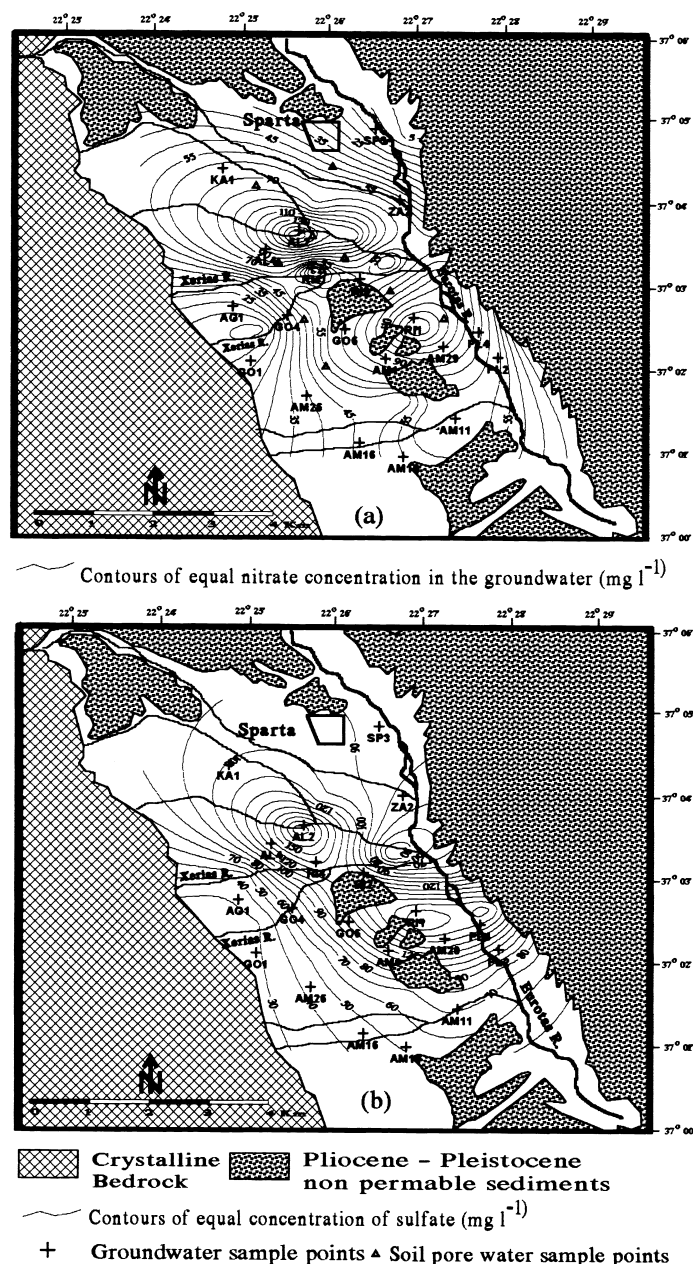
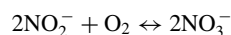


Fig. 7. Contours of equal (a) nitrate and (b) sulphate concentration ( $\text{mg l}^{-1}$ ) in the groundwater.



sediments. Throughout the Sparta region there is intensive application of agricultural fertilizers. The most common fertilizers are  $[(\text{NH}_4\text{NO}_3)(\text{CaCO}_3)]$  and  $[(\text{NH}_4)_2\text{SO}_4]$ , the dissolution of which gives high concentrations of nitrate and sulphate ions in groundwater. Increased values of nitrate and sulphate ions are observed in the middle of the aquifer, while the contribution of the Xerias stream to the recharge of the aquifer has the effect of decreasing these ions due to dilution of the chemical component.

Figure 8a and 8b show the evolution of clay content (%) with depth in the unsaturated zone, the evolution of organic matter content (%) with depth in the same zone, and concentrations of  $\text{Cl}^-$ ,  $\text{NH}_3$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . The profiles in Fig. 8a were constructed from samples taken in the area of continuous fertilizer usage, while the profiles in Fig. 8b, were constructed from samples taken in an area where fertilizers had not been added during the preceding cultivation period. Profiles of ammonia concentration vs depth show a decrease in Fig. 8a, but an increase in Fig. 8b, (note the differences in scale). In the unsaturated zone the decrease in ammonia concentrations can be related to its oxidation (nitrification process) as shown in the following Redox reaction equations:



During nitrification bacteria oxidize ammonia from organic matter to nitrite and nitrate, the concentration of which is very transient.

According to Watkins *et al.*, 1972, a proportion of the ammonia present in the upper soil layers is lost via volatilization due to higher soil tempera-

tures. In deeper layers this oxidation process continues even in times of no fertilizer addition.

In the saturated zone, the concentration of nitrate vs depth remains constant. A slight decrease in concentration with respect to the unsaturated zone can be attributed to dilution effects. In such an environment, denitrification processes, which are well documented in Obermann (1982), Mariotti (1986), Trudell *et al.* (1986), and Postma *et al.* (1991), do not take place. This is in agreement with the results of chemical analysis, which shows that the concentration of oxygen remains almost constant with depth. The profiles of  $\text{NO}_3^-$  and  $\text{Cl}^-$  (which is considered an inactive ion) concentrations are similar, and this can be explained by a similar spreading process of these two chemical substances, which suggests that nitrate reduction does not take place. Nitrate transport through the unsaturated and saturated zones follows groundwater transport.

## CONCLUSIONS

In the shallow aquifer of Sparta, the main source of groundwater contamination by nitrate is inorganic fertilizers and nitrates ions. Nitrate ions result from oxidation of the ammonia contained in these fertilizers. This chemical process takes place gradually and continues even in years that fertilizers are not applied, working on the previous year's residue. The strong oxidation conditions, which do not permit that the denitrification process take place in the aquifer, are due mainly to the provision via carbonate formations, of relatively high amounts of oxygenated water and to the lack of reduced conditions.

The properties of the non-saturated zone (with a thin layer of organic matter) do not affect the migration of nitrate ions which follows groundwater displacement. The hydrogeological conditions in relation to the distribution of nitrate ions is very im-

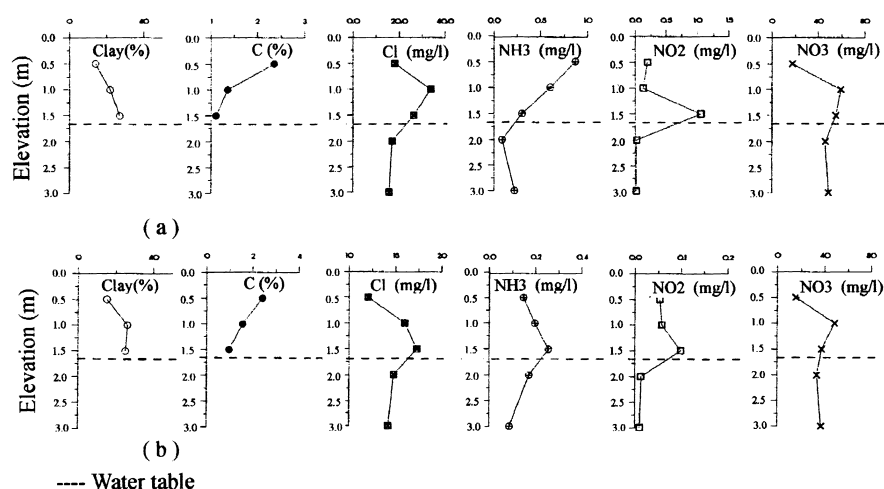


Fig. 8. Distribution of clay content, organic matter content and concentrations of  $\text{Cl}^-$ ,  $\text{NH}_3$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . (a) Continuous fertilizer usage, (b) non-continuous fertilizer usage.

portant. In the case of the Sparta aquifer, where nitrate ions behave as non-reactive chemical components, the axis of their maximum accumulation follows the main discharge axis of the aquifer. Zones of increased recharge of the aquifer coincide with zones of diluted nitrate ion concentration.

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