Report

A Review of Arsenic in Ambient Air in the UK

Prepared on behalf of :

Department of the Environment, Transport and the Regions
Scottish Executive
The National Assembly for Wales

February 2000

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Executive Summary

This report reviews the occurrence of arsenic (*As*) as an atmospheric pollutant in the UK. Specifically, it considers the sources of emissions of arsenic in the UK and reviews the available data on ambient arsenic concentrations in the UK atmosphere. Consideration is given to the measurement methods for the determination of arsenic concentrations in suspended particulate matter; the most appropriate capturing medium for particulate capture; and the subsequent analytical methods employed for the determination of arsenic concentrations. The occurrence of vapour phase arsenic is also discussed, alongside recent developments in analytical procedures for the measurement thereof.

The review highlights that ambient concentrations of particulate-bound arsenic have been declining over the last two decades. This downward trend reflects the decrease in emissions of arsenic in the UK, notably as a consequence of changes in the power generation sector where switches have been made from traditional coal-burning facilities to those that now burn natural gas as a cheaper alternative. In addition, advances in clean technology and a greater regulation of industrial processes, both through Integrated Pollution Control (IPC) and Local Authority Air Pollution Control (LAAPC), have facilitated this decline.

Currently, annual mean concentrations of arsenic in the UK rural environment are typically in the range of 1 - 4 ng m^{-3}, whilst annual mean urban concentrations are higher, in the range of 5 - 7 ng m^{-3}. Typically, the highest concentrations of arsenic in the UK are found at sites located in the immediate vicinity of industrial processes such as smelters, incinerators and cement works. For example, the highest reported concentrations of arsenic in the UK have been found in the vicinity of a smelter in Walsall, West Midlands. For the monitoring period covering 1975 - 1990, the highest annual mean concentration of arsenic reported at the site was 223 ng m^{-3}, whilst for other urban sites, during the same period, annual mean values were found to vary from 1 - 18 ng m^{-3}. The highest reported concentration (quarterly mean) of arsenic found at the Walsall site was 573 ng m^{-3}.

Current gaps in the knowledge of arsenic occurrence have been identified in the current work. Notably, there is a lack of information surrounding monitored levels of arsenic in Scotland and Wales – concentrations reported here concern mostly the Midlands area in England. Moreover, there is a lack of information surrounding the identification of different arsenic species in air - to date, only total arsenic concentrations have been reported - and the reporting of vapour-phase concentrations (as arsenic trioxide (AsO_3). In the case of the latter it is envisaged that this is only a problem in respect of occupational exposure or in the vicinity of industrial processes where methylated forms (monomethylarsonic

acid (MMA) and dimethylarsinic acid (DMA)) of arsenic may occur. For population exposure, it has been shown that it is the ultrafine fraction of particulates ($PM_{2.5}$) for which arsenic compounds are mostly bound.

The review highlights that there is currently a paucity in monitoring of arsenic in the UK. Specifically, the inclusion of various industrial sectors that may be emitting relatively high levels of arsenic at a local scale. A recent programme of monitoring has begun at 30 sites within the vicinity of various industrial processes to determine ambient concentrations of lead and heavy metals (of which arsenic is included) in the UK. The programme, funded by the Department of the Environment, Transport and the Regions and carried out by consultants, Stanger Science and Environment, has been initiated in response to the recent Review of the UK National Air Quality Strategy (NAQS), and in anticipation of the future EC Daughter Directive which will aim to set limit values for a number of pollutants, including heavy metals. The programme is scheduled to run for a period of 12 months. It is anticipated that a full set of results will be made available in December 2000.

1. Introduction

This report has been prepared to assess the current knowledge of arsenic as an atmospheric pollutant in the UK. The atmospheric chemistry and sources of arsenic emissions are considered, alongside current guidelines on acceptable limits for the protection of human health. Measurement techniques and the results of previous monitoring programmes for arsenic carried out in the UK are also discussed.

A technical annex is included in this review which gives a detailed overview of the properties of arsenic and its various compounds and the various issues relating to its presence in air. These issues are dealt with only broadly in the following section.

2. Physical and Chemical Nature of Arsenic

2.1. Properties of Arsenic

Elemental arsenic (*As*) is a silver-grey crystalline metallic solid that exhibits low thermal conductivity. Although arsenic is often referred to as a metal, it is classified chemically as a non-metal or metalloid belonging to Group 15 (VA) of the periodic table. The principle valances of arsenic are +3, +5 and -3. The main physical properties of arsenic are presented in Table 2.1 below.

Table 2.1: Physical Properties of Arsenic

Property	**Value**
Atomic weight	74.92
Melting point	816 °C
Boiling point	615 °C
Specific gravity (26°C)	5,778 kg/m^3
Specific heat	24.6 J/(mol.K)
Latent heat of fusion	27,740 cal/g
Latent heat of sublimation	31,974 cal/mol
Linear coefficient of thermal expansion (20°C)	5.6 µm/m°C
Electrical resistivity (0°C)	26 µΩ/cm
Crystal system	hexagonal (rhombohedral)
Lattice constants (26°C, mm)	a = 0.376 e = 1.0548

‘Metallic’ arsenic remains stable in dry air, but its surface will oxidise when exposed to humid air, creating a superficial bronze tarnish that turns black upon prolonged exposure. It typically exists in two forms; the ‘alpha’ crystalline metallic form which is steel grey in appearance and brittle in nature, and the ‘beta’ form; a dark grey amorphous solid.

2.2. Occurrence of Arsenic

Arsenic is found widely in nature, most often combined with oxygen, chlorine and sulphur. It is found in trace quantities in all living things, the atmosphere, water and geological formations. It is usually found in ores containing gold, silver, cobalt, nickel and antimony. There are over 150 known arsenic-bearing minerals, the most common of which are summarised in Table 2.2 below.

Table 2.2 : Important Arsenic-Bearing Minerals

Mineral	**Arsenic Content, %**
Arsenopyrite	46
Lollingite	73
Orpiment	61
Realger	70
Native Arsenic	90 - 100

Compounds of arsenic can be typically divided into two categories : inorganic and organic forms. Inorganic arsenic occurs naturally in many kinds of rocks as highlighted in Table 2.2 - the most commonly found inorganic form is with sulphide ores, such as arsenopyrite.

Organic compounds of arsenic occur due to its affinity as an element to combine easily with carbon to form a wide variety of organic compounds with one or more *As*-C bonds. Organic species of arsenic in air are considered to be negligible, although the most commonly occurring organic forms are monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA).

The main inorganic and organic compounds of arsenic are dealt with in more detail in Annex 2.

3. The Atmospheric Chemistry of Arsenic

Arsenic is released to air from natural sources (e.g., volcanoes and forest fires) and from anthropogenic emissions from various industrial sources (e.g. coal combustion, smelter and mining activities) and pesticide application. Annual global emissions from natural sources have been estimated to be approximately 8,000 tonnes per year (Becher and Wahrendorf, 1992; WHO, 1987) whilst emissions from anthropogenic sources have been estimated to be approximately three times higher, in the region of 23,600 tonnes per year (WHO, 1987). It is estimated that a total of 575 tonnes of arsenic are emitted to the atmosphere in Europe (1990) most of which occur as a result of the combustion of fossil fuels from stationary sources.

In the United Kingdom, estimated total annual arsenic emissions in 1996 were 51 tonnes (NAEI, 1997), although these have been decreasing steadily to levels of around 8 tonnes per annum in 1998 (Pollution Inventory, 1998) as a result of an increase in the use of natural gas for power generation in favour of coal burning.

The use of organic arsenic compounds in pesticides and herbicides used to be an important source of arsenic emissions to the atmosphere. However, as arsenic-based pesticides, specifically insecticides, have been gradually replaced by alternatives, emissions have significantly decreased in certain parts of the world (WHO (in preparation); Becher and Wahrendorf, 1992).

3.1. Particulate Arsenic

Arsenic in air primarily exists in the form of various compounds adsorbed onto the surface of fine particles (mostly in particles less than 2 µm in diameter) and is usually a mix of arsenite and arsenate (see Annex 2).

These particles can be transported by wind and air currents until they are brought back to earth by wet or dry deposition. The residence time of particulates depends not only on the size of the particles and the prevailing meteorological conditions, but also the operational conditions of the industrial process. For example, levels of arsenic in air vary according to the distance from the source; the height of the stack; the exit velocity of the flue gas and the prevailing wind speed to name just a few parameters. Areas in close proximity to non-ferrous metal smelters have reported high concentrations of arsenic in air (Lee et al., 1994).

In general, larger urban conurbations have higher arsenic-in-air concentrations than smaller ones. Historically, this has been due to the contribution of emissions from domestic coal burning although recent shifts in the number of households burning coal in the UK mean that this is no longer necessarily the case.

Due to the accumulative nature of arsenic, the long-term effects rather than the short-term effects are those that are of most concern in the UK and other countries. Deposition studies facilitate the understanding of accumulation and likely occurrence of damaging effects of metals and metalloid species in the environment. The effective dry deposition rate of the average arsenic-containing aerosol is about 0.2 cm s^{-1} in the vicinity of emission sources. During transport in the atmosphere, the deposition rate decreases due to preferential removal of larger particles. A representative deposition rate of 0.1 cm s^{-1} is found for arsenic in outdoor air (Slooff et al, 1990). For the Netherlands, the removal through dry deposition takes place at an average rate of 0.5% per hour and through wet deposition at 1.2-1.5% per hour. From this, a mean lifetime of atmospheric arsenic aerosol of about 2.5 days can be calculated, allowing for arsenic aerosol to be transported over distances of 1000 km or more (Slooff et al.,1990).

For the Netherlands, during the period 1978-1982, dry deposition has been estimated at 70-220 $\mu g\ m^{-2}\ yr^{-1}$ and wet deposition i.e., the wash-out of from the atmosphere in rainwater, has been estimated at 0.75-1.5 $\mu g\ l^{-1}\ yr^{-1}$ - equivalent to about 400-680 $\mu g\ m^{-2}\ yr^{-1}$ (Slooff et al.,1990). Elsewhere in Europe, deposition values have been determined for a number of discreet areas. For example, in Germany, the dry deposition rates for arsenic vary from about 0.5 $\mu g\ m^{-2}\ day^{-1}$ in remote areas; below 3 $\mu g\ m^{-2}\ day^{-1}$ in rural areas; 3-9 $\mu g\ m^{-2}\ day^{-1}$ in urban areas, and >15 $m^{-2}\ day^{-1}$ in the vicinity of emission sources (Kuhling and Peters, 1994).

For the UK, there is a distinct lack of available information on the dry and wet deposition of arsenic, both at the local level and at the regional scale.

3.2. Vapour-phase Arsenic

Lahmann et al (1986) highlight in their consideration of heavy metal pollution across Europe, that there exists the possibility that a number of metals may occur in the gaseous state as a result of high temperature volatilization. For example, metallic mercury, as well as organic and inorganic mercury compounds, are known to occur in the vapour phase, as well as being bound to particulates.

In general, Lahmann et al report that vapour phase concentrations of metals and their compounds are unlikely to be a problem in the atmosphere and pose little in the way of danger to health. In particular, the issue of lead alkyl compounds, which have previously made a significant contribution to air pollution owing to their volatility, are no longer regarded as a problem since their use in fuel additives in large quantities is now restricted. However, it is possible that methylated species of arsenic (e.g. monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA)) may occur as a consequence of chemical transformations in the atmosphere around certain industrial processes.

For arsenic, arsine (AsH_3) and arsenic trioxide (As_2O_3) are known to occur in the vapour phase. Whether these compounds occur at such high concentrations to warrant extra attention is uncertain. In any case, it is likely that problems will only exist in the vicinity of industrial processes in which these compounds are used. To date, there has been no reporting of vapour phase concentrations of arsenic in the UK, or anywhere else in Europe.

4. UK Sources of Arsenic

The following section outlines the primary sources of particulate-bound arsenic emissions in the UK, and reports on latest emissions estimates from the UK National Atmospheric Emissions (UK NAEI) and the Environment Agency's Pollution Inventory.

4.1. Combustion Sources

By far the most significant emission sources for arsenic in the UK (ca. 87%) are found in the 'combustion source' category. This occurs primarily as a result of the concentration of arsenic in coal which are known to vary from trace to 1-2%.

Emissions of arsenic from stationary combustion sources are only relevant for processes where fuel burning results in a considerable ash residue. For example, in coal-fired units, the fineness of grinding is the controlling parameter - the level of 'fly ash' carried by the stack emissions and, consequently the quantities of particulate-bound metals, is dependent upon this parameter. In order that the residual products are dealt with accordingly, it is necessary for the units to use dust separators. The quantities of heavy metals released into the atmosphere is therefore also dependent upon the efficiency of these dust separators. In contrast, where fuel oils are burnt, the level of particulates in the emissions is dependent mainly on the efficiency of combustion.

Commercial and residential thermal generators have similar characteristics to larger power generation units although, in general, lack the dust separators employed by the larger units. Thus, where a large number of commercial or residential thermal generators are present, the cumulative emissions of particulates can be significant.

In all combustion processes, arsenic is generally present in the flue gas as compounds (e.g. oxides, chlorides, etc.) condensed onto the surface of particles. In addition, it has been estimated that arsenic is emitted to a small extent in the vapour phase - calculated as 0.5% (wt) from the arsenic content of coal (USEPA, 1998).

Results for the latest estimates of emissions of arsenic in the UK obtained from the National Atmospheric Emissions Inventory (NAEI, 1997) indicate that, of the top ten companies emitting arsenic to the atmosphere, eight of the top ten positions are held by companies belonging to the power generation sector

(Table 4.1). The remaining two positions are held by companies belonging to the mineral and metal production industrial sectors.

Table 4.1: Top Ten Emitters of Arsenic in the UK, 1997 (Pollution Inventory, 1999)

Company Name, Postcode	**Industry**	**Emissions of Arsenic (tonnes)**
Rugby Group plc., DN18 6JL	Mineral Industries	1.0000
PowerGen (UK) plc., ME3 9LY	Fuel and power generation	0.8166
Britannia Zinc Ltd., BS11 8HT	Metal production	0.7359
PowerGen (UK) plc., WF11 8SQ	Fuel and power generation	0.5430
PowerGen (UK) plc., WA5 2UT	Fuel and power generation	0.5140
PowerGen (UK) plc., DN22 0EU	Fuel and power generation	0.4970
National Power plc., DN14 0UZ	Fuel and power generation	0.4690
National Power Drax Ltd., YO8 8PJ	Fuel and power generation	0.4090
Eastern Merchant Generation Ltd., DN22 9BL	Fuel and power generation	0.3940
Eastern Merchant Generation Ltd., NG23 6SE	Fuel and power generation	0.2400

4.2. Production Processes

Commercial arsenic is primarily produced as a by-product in the smelting of non-ferrous metal ores containing gold, silver, lead, nickel and cobalt. The amount of arsenic found in lead and copper ores may range from a trace to 2 - 3 %.

The primary uses of arsenic containing compounds in the UK today are as wood preservatives and in the manufacture of chemical compounds (with arsenic trioxide (AsO_3) being the sole base material). In recent years, the use of refined arsenic trioxide, used as a decoloriser and finishing agent in the manufacturing of bottle glass and other types of glassware, has been replaced by arsenic acid. In addition, there is also a limited demand for high-purity arsenic (99.9% and greater) for use in the semiconductor and electronics industry where it is used together with gallium or indium for producing light emitting diodes (LED), infrared detectors, and lasers.

The following sections consider some of the more relevant processes in more detail :

4.2.1. Non-ferrous Metal Industry

Smelting processes are carried out at high temperatures and large quantities of dust and metal oxides fumes can be generated as a result. It is known that a large number of trace elements present in ores, and in concentrates, are volatilized by the high temperatures used in processes such as roasting, syntering, smelting and converting operations (Lahmann et al, 1986).

Small amounts (around 0.5%) of arsenic are added to lead-antimony grid alloys, used in lead acid batteries, to increase endurance and corrosion resistance. Additions of the same order (0.02% to 0.5%) to copper alloys raise the re-crystallisation temperature and improve high temperature stability and corrosion resistance of the alloys. Other uses of metallic arsenic include the addition (up to 2%) to lead in shot to improve the sphericity of lead ammunition.

Arsenic trioxide is easily volatilized during the smelting of copper and lead concentrates, and is known to become concentrated in the flue dust. Crude flue dust may contain up to 30% arsenic trioxide. This crude flue dust is subsequently upgraded by mixing with a small quantity of pyrite or galena and roasting the subsequent mixture. During the roasting process the gases and vapours are allowed to pass through a cooling flue which consists of a series of brick chambers or rooms called ‘kitchens’. The arsenic vapour which condenses in these chambers is of varying purity (from 90 to 95%). Higher purity products can be obtained by resubliming the crude trioxide, an operation typically carried out in a reverberatory furnace.

4.2.2. Iron & Steel Industry

Iron ores contain a number of arsenic compounds that can be released as particle-bound pollutants during different production processes from the iron and steel industry. The exact profile of emitted metal compounds is dependent upon the composition of the ores used and the individual production steps in the iron and steel industry make varying contributions to arsenic levels in the atmosphere. Most emissions of arsenic from the iron and steel industry result from blast furnace charging where coarse dust (with particle sizes > 10 µm) is found. Other relevant emissions occur in connection with melting processes of arsenic-polluted scrap in electric arc furnaces.

4.2.3. Sinter Plants

Another relevant source of emissions of arsenic in the UK is the sintering process, an ore pre-treatment step in primary metals production where fine particles of metal ores are agglomerated to briquettes, sinter or pellets. The whole sintering process consists of several steps (e.g. mixing, crushing, sieving and sintering) where emissions of metal-containing dusts can occur. Hutton & Symon (1986) estimate that sinter production in the UK produced atmospheric emissions of 7.5 tonnes arsenic per year in 1986.

4.2.4. Non-ferrous Metal Mining

Hutton and Symon (1986) highlight that a large number of disused mines in the UK could represent a potentially significant source of contamination of arsenic at the local level through wind dispersal of material from unstable spoil heaps at these sites. However, despite the widespread occurrence of such heaps, it is currently not possible to estimate the quantities of elements released into the atmosphere due to uncertainties in emissions and the reliance on local meteorological conditions.

4.2.5. Waste Treatment and Disposal

Emissions of arsenic from waste incinerators are wholly dependent upon the composition of the waste, the combustion conditions and the clean technology applied to the stack. Incineration is a complex combustion process involving several key steps: pyrolitic decomposition; surface and gas combustion; conductive, convective and radiative heat transference, and gas flow through beds of materials whose quality, size and shape are continuously changing. Due to the complex nature of the waste incineration process, it is difficult for operators to define optimum conditions for operation and thus environmental problems can result as a consequence of emissions. It has been shown that urban incinerators can be an important source of airborne heavy metals such as arsenic (Law & Gordon, 1979). In addition, waste sites have been shown to be sources of methylated gaseous compounds (Feldmann et al., 1994).

4.2.6. Timber Industry

The manufacture of copper chromium arsenic (CCA) wood preservatives can lead to significant emissions of arsenic to the UK atmosphere. For example, the disposal of treated timber after use results in an estimated environmental discharge of approximately 9 tonnes arsenic per year as a result of burning (Hutton and Symon, 1986). Currently, a large quantity of CCA-treated timber is still in service making it likely to remain a potentially significant emission source in the future. This fact has been emphasised in a recent report[1] by WS Atkins in which the relevant risks associated with the use arsenic-based wood preservatives, covering the manufacture of CCA and the production, use and disposal of CCA-impregnated wood is discussed. In its appraisal of the report, the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE)[2], broadly accept the risk assessment methodology which highlights that, in general, the risks most associated with the use of CCA-impregnated wood are those resulting from the leaching of CCA into water and soil. For emissions to air, the report indicates that it is the disposal of CCA-impregnated wood that is likely to represent the largest risk. In particular, uncontrolled burning of CCA-treated wood in homes or on open ground.

4.3. Emission Inventory Estimates

The UK National Atmospheric Emissions Inventory (NAEI) currently reports emissions of arsenic on an annual basis. The reported figures cited in Table 4.2 and Figure 4.1 are quoted from the latest (1997) report. Results show that emissions have declined by 78% since 1970.

In the UK, the main source of arsenic emissions has been the combustion of fossil fuel (notably coal), other sources being small in comparison. In part, the reduction in UK emissions of arsenic over the past two decades has resulted as a consequence of a decline in coal use, in favour of natural gas use as a cheaper alternative.

In addition to the NAEI emissions estimates of arsenic, the Environment Agency have recently disseminated information regarding a wide variety of industrial processes in England and Wales through the Pollution Inventory[3]. In Scotland, this duty falls to the Scottish Environment Protection Agency for which currently no similar database of emitters is available. Thus, without detailed scrutiny of the Public Registers, there is a lack of available information reported in the current context.

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[1] Assessment of the risks to health and to the environment of arsenic in wood preservatives and of the effects of further restrictions on its marketing and use. WS Atkins International Ltd. (Vol. B).

[2] http://europa.eu.int/comm/dg24/health/sc/sct/out18_en.html

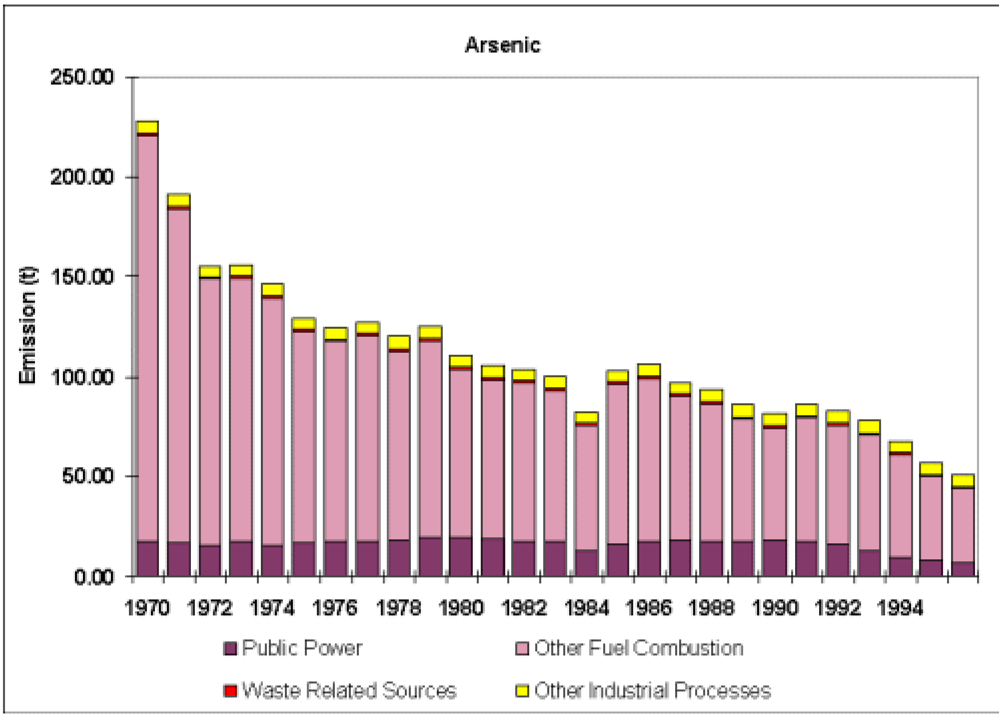
[3] http://193.122.103.90/wiyby/html/q_isr_a.htm

The Pollution Inventory has been developed to provide information on annual mass releases of specified substances to air, water land or produced as waste which arise from any large industrial sites (i.e. those authorised by the Environment Agency under Integrated Pollution Control (IPC)). The reporting requirements for the Pollution Inventory encompass emissions from the whole of the IPC authorisation. That is, it includes, along with the specific release points (point sources, e.g. chimneys), non-point sources and fugitive emissions (e.g. leaks or spillages).

All authorisations for large industrial sites (i.e. those under IPC) have a condition requiring the annual reporting of releases of a "core" list of substances and groups of substances These are substances considered to be important in relation to environmental protection. By ensuring that all sites report, the Environment Agency can be more confident that they are getting a complete picture of what is being released nationally from large industrial sites.

The latest (1998) Pollution Inventory estimates of arsenic emissions for large industrial sites in England and Wales are summarised in Annex 1.

Figure 4.1 : Annual UK Emission of Arsenic (1970 - 1996) (NAEI)



Results of the NAEI confirm Pollution Inventory estimates on arsenic emissions in the UK which indicate that the largest emission sources of arsenic in the UK are associated with combustion processes related to the power generation sector.

PowerGen, National Power, and Eastern Merchant Generation power generating plants dominate the top ten rankings. In addition to these power generators, other large emission sources of arsenic in England and Wales include the Rugby Group plc. plant on Humberside, and the Britannia Zinc Ltd. plant in Avonmouth, Bristol. In 1998, arsenic emissions from these plants were estimated at 1.000 tonnes and 0.7359 tonnes, respectively.

Table 4.2 : UK Emissions of Arsenic by UNECE Category (tonnes) (NAEI, 1997).

	1970	**1975**	**1980**	**1985**	**1990**	**1993**	**1994**	**1995**	**1996**
By UNECE Category									
Comb in Energy Prod & Trans	26	23	23	18	19	14	11	9	7
Comb in Comm/Inst/Res/Agri									
Domestic	88	51	39	38	19	20	17	12	12
Other	19	9.1	8.4	7.9	5.6	3.9	3.4	2.4	2.7
Combustion in Industry									
Treated Wood	9	9	9	9	9	9	9	9	9
Iron & Steel	4.1	1.6	1.0	0.4	0.3	0.3	0.2	0.5	0.7
Other Combustion in Industry	73	30	24	23	23	24	21	18	13
Non-Ferrous Metals	2.9	2.5	3.1	3.2	3.2	3.4	3.3	3.0	3.2
Cement Manufacture	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.1
Glass Production	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Production Processes									
Processes in Industry	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Iron & Steel	2.4	1.9	1.2	1.6	1.8	1.7	1.7	1.7	1.8
Extraction and Distribution of Fossil Fuels	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Road Transport	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Other Transport & Machinery	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Waste Treatment & Disposal	1.1	1.1	1.1	1.1	0.9	0.8	0.6	0.5	0.3
Total	**228**	**129**	**110**	**103**	**82**	**78**	**68**	**57**	**51**

5. Air Quality Guidelines

At present, there are no UK or EU guidelines set for arsenic in ambient air. Specifically in the UK, limits have been set for large industrial processes under Integrated Pollution Control (IPC) as part of the authorisation permitted by the Environment Agency for the operation of such facilities in England and Wales. In Scotland, corresponding duties are undertaken by the Scottish Environmental Protection Agency (SEPA). However, these limits are set on the basis of best practice and process control, rather than being set for the protection of human health.

The lack of ambient air quality guidelines in Europe for arsenic is, in part, due to the fact that the likely levels of arsenic in air are, in general, low. This fact highlights that exposure via air is less significant that other routes, e.g. the consumption of foodstuffs and drinking water.

Currently, the unit risk value cited in the update of the WHO Air Quality Guidelines (WHO, in preparation) is 1.5×10^{-3} per $\mu g\ m^{-3}$ of pollutant, based upon observations of lung cancer in the population at ambient concentrations of $1 - 30\ \mu g\ m^{-3} \times 10^{-3}$.

The unit risk value has been given an International Agency for Research on Cancer (IARC) classification of ‘1’ - that is, arsenic is a proven carcinogen[4].

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[4] Chemicals or groups of chemicals for which there is sufficient evidence from epidemiological studies to support a causal association between the exposure and cancer.

6. Measurement Techniques

This section gives a general overview of methods employed for the measurement of arsenic concentrations in air in the UK. It outlines analytical methods employed for the analysis of total suspended particulates. In addition, consideration is given to the determination of vapour-phase arsenic.

6.1. Sampling

Conventional measurement methods for arsenic typically involve a two-stage process whereby samples are collected and then analysed at a later date.

A variety of sampling and analytical techniques have been used to measure trace metal concentrations in air which include impingers, electrostatic precipitators and filters. Common features to these sampling and analysis techniques employed in the UK over the last 15 - 20 years are:

- total atmospheric particulate samples are collected and analysed with no distinction between particle sizes;
- the duration of sampling varies but typically spans one week (in the UK). The temporal resolution thus tends to be less than for many other pollutants measured in the UK with the consequence that ‘peak’ short-term concentrations may pass unrecorded.

Over recent years, filters have been favoured over other measurement methods due to their high efficiency of collection of small particles. Specifically, sampling of arsenic in the UK has been undertaken using the ‘M-Type’ sampler. This sampler has been designed to measure airborne particulate matter in a size range that is representative of respirable material and consists of two distinct parts: a control box and a sample hood and stand. The flow rate is controlled to 0.3 m^3/h and material collected over a one-week period onto Millipore Aerosol Field Monitor filters (mixed cellulose esters, size 37 mm diameter, 0.8 micron retention).

6.2. Filter Media

Typically, a number of different filter media have been considered for the determination of trace metal concentrations in air. These include glass fibre filters (borosilicate glass), quartz fibre filters, membrane filters and teflon filters.

An important consideration in selecting the most appropriate filter medium for the collection of trace elements in particulate matter is the background metal concentration of the filter material (the blank value). For example, Harrison (1986) determined that the blank value of arsenic in glass fibre filters was 80 ng *As* cm^{-2}. Teflon filters are generally considered to be the best filter collecting medium for the determination of trace metal concentrations due to the very low blank levels. Table 6.1 shows typical properties of the filter types including blank values.

Table 6.1 : Properties of different filters types used for the collection of particulate matter in air.

Filter Type	**Blank value ng *As* cm^{-2} filter area**	**Properties**
Glass Fibre	40.0 - 60.0	Borosilicate glass, blank values can be variable, low flow resistance.
Quartz Fibre	0.5 - 5.0	Quartz glass, lower blank values for many elements compared to glass fibre filters, similar flow resistance to glass fibre filters. Total digestion is easier than glass fibre filters. Relatively expensive.
Membrane	0.1 - 4.0	Cellulose acetate or cellulose nitrate, low blank values, high flow resistance (increased under high humidity conditions). Prone to electrostatic charge.
Teflon	ca. 0.3	Very low blank values. High flow resistance. Relatively expensive.

For quality assurance, field filter blanks should be included in any monitoring programme. These filters should be handled in the same way as ‘normal’ filters but without sucking ambient air through them. In addition, laboratory filter blanks should be analysed.

6.3. Sample Preparation and analysis

In dust analysis, the analytical step is generally preceeded by an appropriate preparation of the sample in order to dissolve the collected particulate matter. This dissolution can be achieved by either wet or dry procedures.

After dissolution, analysis is carried out using a number of different techniques which vary in their procedures and detection limits. They include; atomic absorption spectrometry (AAS); inductively coupled plasma spectrometry (ICP); or, X-ray fluorescence spectrometry (XRF).

Further details of the sample preparation and the analytical techniques are given below:

6.3.1. Sample Preparation

In wet digestion procedures, the sample is treated with a mixture of different acids, e.g., HCL, HNO_3, $HClO_4$ or HF, at normal or elevated pressure. The choice of acid and digestion conditions depends upon the filter material used to collect the sample and the element to be determined. In many cases, digestion with hot nitric acid (with the addition of perchloric acid if the sample has been collected on a membrane filter) has proved satisfactory.

Recent cross-comparisons between sample dissolution methods (ultrasonic agitation, hot-plate digestion and micro-wave assisted digestion procedures) indicate that variable results can be obtained. For example, Butler & Howe (1999) report that ultrasonic agitation digestion methods were satisfactory for most of the elements with the exception of chromium and nickel which showed up to 30% lower recovery values than micro-wave assisted digestion. For laboratories carrying out digestions utilising hot-plates, Butler & Howe report the largest amount of variation. Errors with this method were attributed to the fact that the analyst is required to heat the samples to a ‘fuming’ end-point which was open to interpretation. Insufficient or excessive ‘fuming’ were likely to introduce errors through acid-matrix mismatches.

Small filters (width up to 50 mm diameter) can be digested whole. For filters that are larger than 50 mm, it is recommended that these filters be partitioned into smaller pieces in order to reduce the amount of digestion solution involved and to improve the homogeneity of the collection efficiency over the surface of the complete filter area. If partitioning of filters is used, it is necessary to ensure that sub-samples are representative of the entire filter.

In dry pre-analysis treatment, the sample is dry-ashed, preferably at low temperature (within the range 100 - 150 ^{o}C). An advantage of this type of sample preparation is that no reagents are required and hence, blank values can be kept low. However, care is required in order to minimise losses of volatile elements from the sample.

6.3.2. Commonly Used Analytical Methods

The following section describes briefly the most commonly used analytical methods for the determination of trace metal concentrations. It does not attempt to produce a detailed review of the techniques which has been carried out previously by a number of workers (e.g. see Harrison & Perry, 1977).

Atomic Absorption Spectrometry (AAS)

AAS is probably the most frequently used analytical method for the determination of particle-bound heavy metals concentrations in air. In this technique, the analyte is aspirated into an ionising flame that causes a chemical reduction of metal ions to ground state atoms, the light absorption of which is measured. The atomic absorptions are discrete lines of narrow band-width at wavelengths which are characteristic of the given element. The wavelength range of AAS is limited by light absorption by the flame that is used for the analysis. For arsenic, an argon-hydrogen-entrained air flame is used with a typical atomic absorption spectrophotometer such as a Perkin-Elmer. Typically, the detection limits for arsenic quoted for the Perkin-Elmer spectrophotometer are 0.05 μg ml^{-1} (double-beam instrument).

Inductively Coupled Plasma / Mass Spectrometry (ICP-MS)

This technique includes the following general procedures; the analyte solution is first transferred into a pneumatic nebulizer to produce an aerosol. A stream of argon carries this aerosol into the inductively coupled plasma formed by ionising and exciting the inert argon gas. De-solvation, atomisation and ionisation of the analyte occurs in the plasma with the resultant ions separated in a vacuum on the basis of their mass-to-charge ratio by the mass spectrometer. The ions transmitted through the mass spectrometer are quantified by a pulse counting detector. Calibration with reference solutions, based on the linear relationship between concentration and measured pulse rate, allows a quantitative analysis of the sample analyte.

Analysis of X-Ray Fluorescence (XRF)

This technique relies on the principal that a metal target bombarded with X-rays results in absorption and resultant secondary emission of X-rays (fluorescence) characteristic to the irradiated metal. Using appropriate instrumentation, the intensity of the secondary emissions may, by comparison with a suitable standard, be used to give a quantitative measure of the metal. X-ray fluorescence of particulate matter has the advantage over other analytical techniques in that it is rapid, samples need no pre-treatment (i.e. digestion) and it is non-destructive. Typical detection limits for X-ray fluorescence analysis of particulate material collected on filter papers have been reported by Harrison (1986). For arsenic, a value of 100 ng cm^{-2} for arsenic has been cited, based upon energy dispersive analysis using radioisotopes utilising a 10 minute count.

Neutron-Activation Analysis (NAA)

NAA is a non-destructive technique used in a number of studies to determine the elemental composition of particulate matter (e.g. Dams et al., 1970). The sample is irradiated with a flux of neutrons which induces the formation of isotopes emitting a characteristic radiation. Specific detectors characterise the individual elements. Although NAA is a relatively sensitive analytical technique, some elements have been shown to be difficult to analyse (e.g. Pb and Cr), and should therefore be determined using other methods.

6.4. Vapour-Phase Arsenic

A recent update to the Health and Safety Executive's (HSE's) guideline document *Methods for the Determination of Hazardous Substances* series MDHS 41 ' Arsenic and inorganic compounds of arsenic in air', includes the determination of vapour phase arsenic (as arsenic trioxide) in the workplace where exposure of individuals to arsenic may occur during the manufacture and use of arsenic compounds.

The procedure relies on the collection of arsenic compounds (particulate and vapour (only arsenic trioxide; arsine is not trapped)) by drawing air through a two-stage sampling unit containing two filters. The first, a cellulose ester membrane filter captures particulate arsenic and inorganic arsenic compounds whilst the second, a sodium carbonate impregnated back-up paper pad, captures arsenic trioxide vapour. This vapour is collected by the reaction with sodium carbonate on the impregnated back-up filter pad through the following stoichiometric relationship:

$$As_2O_3 + Na_2CO_3 \rightarrow 2NaAsO_2 + CO_2$$

Analysis of the cellulose ester membrane and sodium carbonate back-up pads is carried out using atomic absorption spectrometry (AAS), This requires the initial digestion of the filters with an acid mixture containing nitric acid, sulphuric acid and hydrogen peroxide. Further details of the AAS method are given above.

6.5. Proposed Sampling Method

The EC Working Group for metals has recommended that the reference method for the determination of ambient metals in air be based upon the Low Volume Sampler (LVS) as described in EN 12341 (CEN, 1998). A low metal background filter material (quartz), and total digestion and analysis with AAS-technology is recommended by the Working Group. Other methods can be used, if their equivalence has been demonstrated.

CEN/TC 264/WG 14 is currently formulating the full Reference Method for the determination of Pb, Cd, As and Ni in ambient air, which will take note of the EC group recommendation. A laboratory and field validation programme is currently being formulated and will contain the following elements:

(a) Sampling of particulates using the LVS (described in EN 12341) for 24-hour sampling periods
(b) Collection of particulates on quartz fibre and membrane filters (not Teflon)
(c) Total digestion with and without HF (digestion procedure to be investigated using Certified Reference Material filters).
(d) Mandatory measurement with AAS, with optional measurements using ICP-MS.

To date, there has been a paucity in monitoring data for arsenic and other trace elements in ambient air within the UK. The adoption of the common procedures and the recommendations of the CEN Working Group will greatly increase the level of confidence in the results obtained from future monitoring programmes.

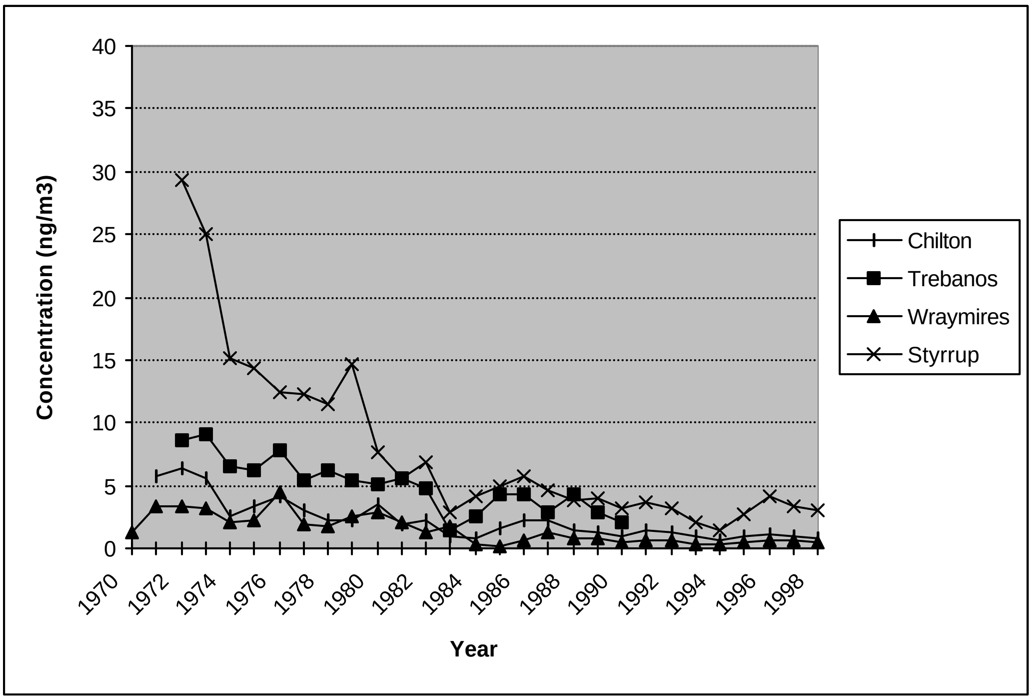
7. Monitoring in the UK

The following section reviews airborne concentrations of arsenic in the UK. It details the results of monitoring programmes that have been carried out under both the auspices of the national monitoring network and also individual ad-hoc studies carried out by private institutions and universities published in scientific journals and/or reviews.

7.1. Rural Network Data

Four long-term rural background sites have been monitoring particulate arsenic levels since 1972; Chilton (Oxfordshire), Styrrup (Nottinghamshire), Windermere (Wraymires, Cumbria) and Trebanos (West Glamorgan). The annual mean concentrations for 1970 to 1998 are shown in Figure 7.1.

Figure 7.1 Annual mean concentrations of arsenic at rural monitoring locations in the UK (1970 - 1998).



Results show a decline in the ambient levels of arsenic in rural areas throughout the UK. This decline is more prominent at the Styrrup site where ambient concentrations have declined from around 30 ng m^{-3} in 1972 to around 3 ng m^{-3} in 1998. The higher concentrations of arsenic reported at this site, compared to concentrations recorded during the same period (1972 - 1981) for other sites, are likely to be the result of emissions from coal-fired power stations. These occur at a much higher frequency in The Midlands than in other parts of the UK.

Recent analysis of the data obtained from these sites has been presented (Cawes et al, 1994) with the long-term trends having been analysed over the last two decades (covering 1972-1981 and 1982-1991). Results are summarised in Table 7.1.

Table 7.1 : Rural concentrations of arsenic in particulate matter in the UK (1972 - 1991) from Cawes et al, 1994.

Site	**Concentration (ng m^{-3})**			
	Mean	**Trend**	**Mean**	**Trend**
	1972 - 1981	**%/year**	**1982 - 1991**	**%/year**
Harwell, Oxfordshire	4	-10.0	1.7	-7.8
Styrrup, Nottinghamshire	15	-14.3	4.4	-5.2
Trebanos, Glamorgan	7	-6.0	3.5	-
Wraymires, Cumbria	3	no sig. trend	0.8	-7.3

The highest arsenic concentration over the period 1972-1981 (15 ng m^{-3}) was found at the site in Nottinghamshire, whilst the second highest concentration (7 ng m^{-3}), over the same period, was found at the site in West Glamorgan. In contrast, sites in Oxfordshire and Cumbria showed the lowest concentrations of arsenic, 3-4 ng m^{-3}, during the same period.

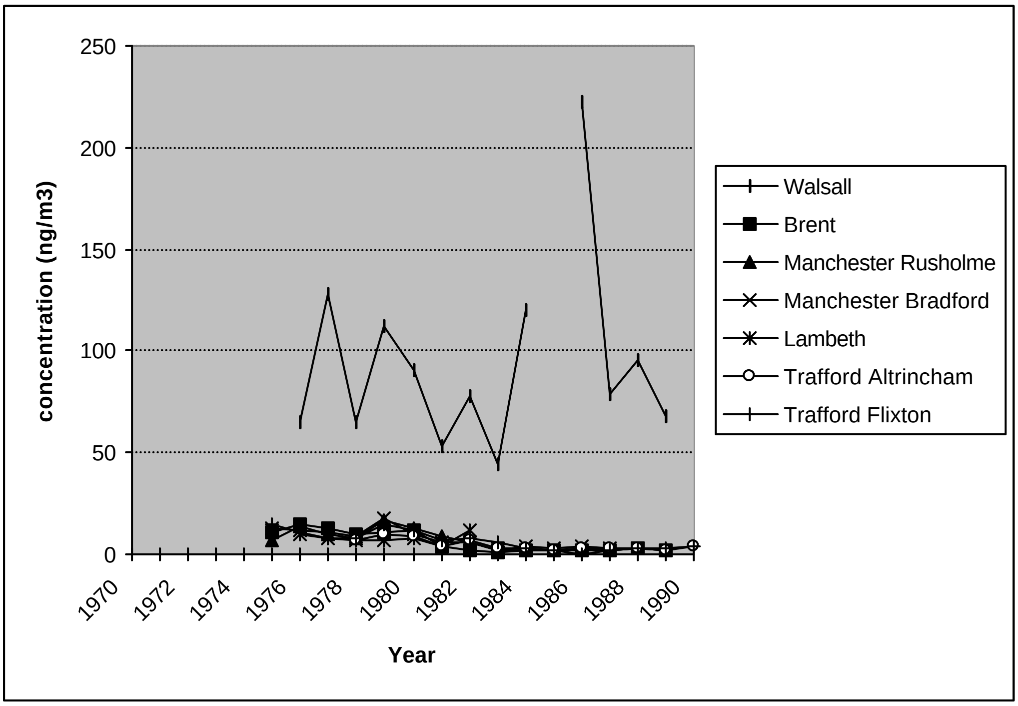
Results presented by Cawes et al (1994) showed lower concentrations of arsenic were observed at all sites covering the period 1982-1991. A similar picture in the ranking of sites with respect to the concentrations was found: sites in Nottinghamshire and West Glamorgan showed the highest concentrations of arsenic with sites in Oxfordshire and Cumbria showing the lower concentrations.

Results from the rural network highlight that ambient concentrations of arsenic in the UK have been steadily declining over the last two decades. This rate of decline has been generally higher in the first decade of monitoring (1972-1981) compared to results of the monitoring carried out for the period 1982-1991. This can be attributed to improvements to abatement technology and the availability of natural gas as a cheaper alternative to traditional coal-burning in the power generation sector.

7.2. Urban Network Data

In addition to the four rural monitoring stations, arsenic in particulate matter has been monitored at a number of urban and residential sites throughout the UK from the mid 1970's to the late 1980's. Results for this network have been recently published by Lee et al (1994) and previously reviewed by QUARG (1993), and are shown in Figure 7.2 and are summarised in Table 7.2.

Figure 7.2 Annual mean concentrations of arsenic at urban monitoring locations in the UK (1975 - 1990).



Results of the annual mean urban concentrations show the highest annual mean concentration of arsenic (223 ng m^{-3}) occurred at an industrial site in Walsall in 1986. This site is in the vicinity of a smelter and has continually recorded the highest concentration of arsenic at any site in the UK since monitoring commenced in the mid 1970s. Annual mean concentrations recorded at other urban monitoring locations show similar values of around 10-15 ng m^{-3} in the mid 1970s to values around 5 ng m^{-3} in the early 1990s when monitoring ceased.

Analysis of data by Lee et al (1994) has reflect the trends observed in the annual mean data. The highest mean concentrations for the period covering mid 1970s to the late 1980s was recorded at Walsall (93 ng m^{-3}), whilst the second highest mean concentration over the period of monitoring was recorded at the urban site in Swansea (19.0 ng m^{-3}). Results reported by Lee at al (1994) indicate that concentrations of arsenic in residential areas are typically in the region of 5 - 7 ng m^{-3}, approximately 3-4 times higher than those observed at rural monitoring locations.

The seasonal variability of arsenic has been examined by Lee et al (1994) over all urban sites (except Walsall where a single dominant source was known to influence concentrations). This was carried out through determining the ratio of the quarterly mean to the annual mean concentration. In general, higher concentrations of arsenic were found in the first quarter of the year when compared to any other period - a ratio to mean just above 1.4, whilst concentrations of arsenic were very similar in the second and fourth quarters of the year showing a ratio to mean of approximately 0.9. The lowest arsenic concentrations were observed during the third quarter of the year where a quarter mean ratio to annual mean value of approximately 0.7 was reported. Lee et al (1994) offer no explanation for the seasonal variability in this element although it can be hypothesised that the seasonal variability may be explained in terms of its predominant source, coal and fuel-oil combustion. The higher concentrations in the first quarter, when demand for heating and electricity is greater, support this hypothesis. The seasonal variability in concentrations highlights the fact that anomalous results in monitoring programmes will be obtained with respect to the determination of annual mean concentrations where the observation period are based on a short duration, e.g. 3 months in the winter.

Table 7.2 : Urban Concentrations of Arsenic in the UK (1972 - 1989) from Lee et al. (1994).

Location	**Site Classification**	**Period**	**Mean (ng m^{-3})**	**Min (ng m^{-3})**	**Max (ng m^{-3})**
Trafford - Altrincham	Residential	1978 - 89	4.7	0.4	17.6
London- Brent	Residential	1975 - 89	6.1	0.2	24.3
Trafford - Flixton	Residential	1975 - 89	7.1	0.4	30.6
London - Lambeth	Residential	1976 - 82	7.2	0.8	15.3
Manchester City North	Industrial / Residential	1975 - 88	7.6	0.2	43.0
Manchester City South	Residential	1975 - 89	6.5	0.2	41.0
Swansea	Urban	1972 - 81	19.0		
Walsall	Industrial	1976 - 89	93.9	10.6	572.3

Long-term trend analysis carried out by Lee et al (1994) on arsenic concentrations in the UK indicate a decline in concentration across all urban sites (excluding Walsall) over the last two decades. For example, the mean arsenic concentration for 1975-1978 was 10.3 ng m^{-3} which fell by 74% to a concentration of 2.7 ng m^{-3} for the period 1986-1989. Lee et al (1994) highlight the decline in domestic emissions of coal covered by the Clean Air Act (1956), as the possible leading factor in the decrease of ambient levels of arsenic in recent years.

7.3. North-Sea Programme

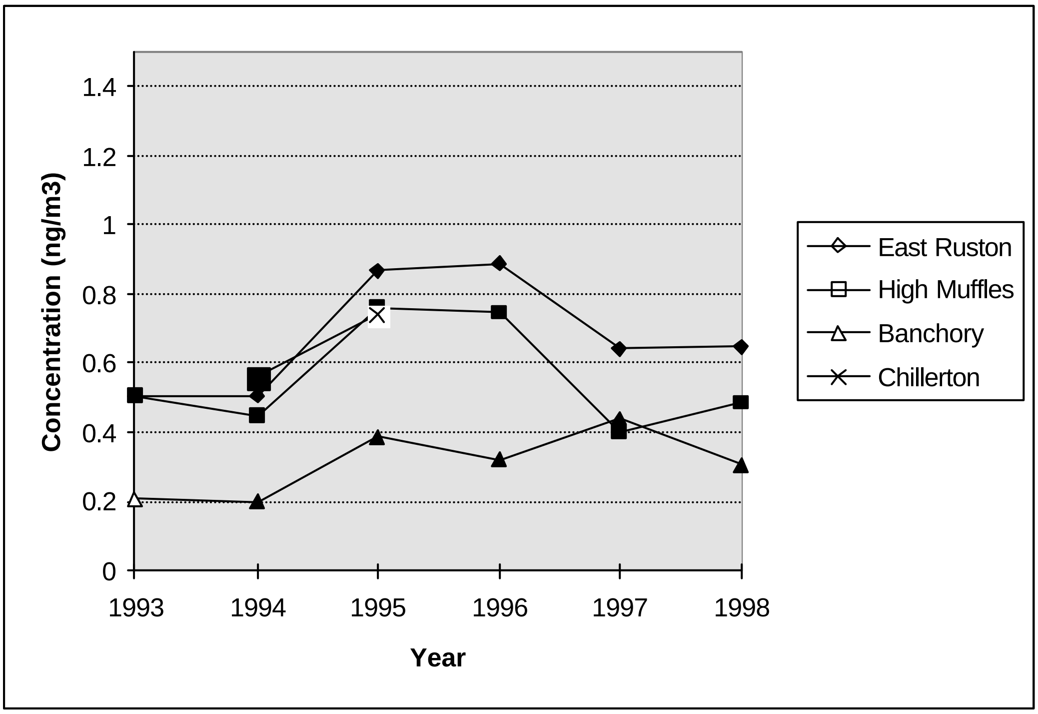
In addition to the rural and urban monitoring stations within the UK, monitoring for arsenic has been carried out at a small number of stations in relation to the North Sea Project of the Natural Environment Research Council.

The Humber Estuary receives significant inputs of arsenic as a result of the relatively dense industrial units located along the River Trent (Millward et al., 1997). Increased arsenic concentrations (of DMA (dimethylarsenic)) in estuarine waters have been shown to occur as far afield as the Wash in Norfolk as a result of atmospheric enrichment from industrial processes located on the Humber estuary (Millward et al., 1997).

In addition to the number of estuarine sites reported by Millward et al. (1997), three land sites have been included in the study at East Ruston (Norfolk), High Muffles (Yorkshire) and Banchory (Kincardinshire). Results for the monitoring period covering 1993 - 1998 are shown in Figure 7.3.

Results show similar concentrations to those observed at rural monitoring locations elsewhere. That is, annual average concentrations of arsenic of around 0.5 to 1.0 ng m^{-3}.

Figure 7.3 Annual mean concentrations of arsenic at land sites included in the North-Sea monitoring programme (1993 - 1998).



8. Conclusions

Particulate-phased arsenic concentrations have been monitored in the UK at a number of sites covering rural (Cawes, 1994) and urban locations (Lee et al., 1994) for the past two decades. Results show that concentrations around individual industrial installations can be high (572 ng m^{-3} - 3 month mean at Walsall (as cited in Lee et al., 1994)). In general, urban concentrations of particulate-phased arsenic fall within the range 5 - 7 ng m^{-3} with rural locations falling within the range 0.8 - 4.5 ng m^{-3}.

Currently, no air quality standard exists in the UK for arsenic in air. Arsenic is a known carcinogen and the World Health Organisation (WHO, 1987) acknowledges that there is no acceptable limit to be set. However, health risk assessments have been made which report a unit risk value of 1.5×10^{-3} for each $\mu g\ m^{-3}$ of arsenic to which an individual is exposed (WHO, 1987).

Emissions estimates for arsenic obtained from both ad-hoc studies and the UK National Air Emissions Inventory (NAEI) indicate that combustion of fossil fuels such as lignite (brown coal), hard coal and heating oil account for the largest proportion of total UK emissions of arsenic. Other relevant emission sources of arsenic to air in the UK include ferrous and non-ferrous production processes. In each case, the emissions of arsenic to air are largely dependent upon the arsenic content of the metals ore and/or fossil fuel and the propensity of the process to produce particulate emissions. Emissions from the chemical, glass and cement industries are generally much smaller than those from other industrial sectors of the UK.

Trend analysis of ambient concentrations of arsenic in the UK indicate that concentrations have been steadily decreasing over the 20 or so years that monitoring has taken place. Such a trend is likely to reflect the advances in clean technology and pollutant abatement schemes (e.g. flue gas desulphurisation (FGD) and electrostatic precipitators (ESP)) integrated as a condition of the authorisation for many of the processes from which arsenic is known to be emitted. In addition, the switch from traditional coal-burning to natural gas as a cheap alternative in the power generation sector are likely to have made the largest significant decrease in emissions of arsenic to air in recent years.

The present review highlights a number of gaps in the current knowledge of arsenic occurrence in the UK. In particular, any detailed monitoring in Scotalnd and Wales. Notably, there has been little work carried out on identifying different species of arsenic in the atmosphere - to date, all ambient monitoring of arsenic carried out has reported total arsenic concentrations in the particulate phase. The review highlights that more consideration is required to determine vapour-phase concentrations (as arsenic trioxide (AsO_3)) of arsenic, but acknowledges that this is likely to be a problem with regards to occupational exposure only.

In addition, the review highlights that a cohesive approach to the monitoring of arsenic is required within the UK in which monitoring methods are standardised with respect to the particulate fraction to be collected. Traditionally, the monitoring of arsenic has been made on the total suspended particulates in air. Recently, an increased understanding of the occurrence of particulates in air highlight the importance of the fine (PM_{10}) and ultra-fine ($PM_{2.5}$) fraction (APEG, 1999).

The first Daughter Directive published in 1997 by the European Commission reached the common position in June 1998 for a number of pollutants with the proposals to set limit values for sulphur dioxide, nitrogen dioxide, particulate and lead. The Commission intends that future Daughter Directives will set limit values for a number of other pollutants for which arsenic (among other heavy metals) has been included. Currently, the Department of the Environment, Transport and the Regions is funding consultants, Stanger Science and Environment to undertake 12 months monitoring of lead and heavy metal concentrations in response to these Commission's proposals. In light of the recent review of the National Air Quality Strategy (HMSO, 1999) the main focus of attention in the 12 month monitoring period is in the vicinity of industrial processes. Results are likely to be made available in December 2000.

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10. Annex 1: Pollution Inventory Estimates

Table Annex 1. 1998 Estimates of Arsenic Emissions to Air from Industrial Units in England and Wales (Pollution Inventory).

Company Name, Postcode	Industry	Process	Emissions of Arsenic (tonnes)
Rugby Group plc., DN18 6JL	Mineral Industries	Cement / lime manufacture	1.0000
PowerGen (UK) plc., ME3 9LY	Fuel and power generation	Combustion processes	0.8166
Britannia Zinc Ltd., BS11 8HT	Metal production and processing	Non-ferrous metals	0.7359
PowerGen (UK) plc., WF11 8SQ	Fuel and power generation	Combustion processes	0.5430
PowerGen (UK) plc., WA5 2UT	Fuel and power generation	Combustion processes	0.5140
PowerGen (UK) plc., DN22 0EU	Fuel and power generation	Combustion processes	0.4970
National Power plc., DN14 0UZ	Fuel and power generation	Combustion processes	0.4690
National Power Drax Ltd., YO8 8PJ	Fuel and power generation	Combustion processes	0.4090
Eastern Merchant Generation Ltd., DN22 9BL	Fuel and power generation	Combustion processes	0.3940
Eastern Merchant Generation Ltd., NG23 6SE	Fuel and power generation	Combustion processes	0.2400
IMI Refiners Ltd., WS2 9SJ	Metal production and processing	Non-ferrous metals	0.2100
National Power plc., OXC11 7HA	Fuel and power generation	Combustion processes	0.2000
National Power plc., CF62 4ZW	Fuel and power generation	Combustion processes	0.1940
National Power plc., RM18 8UJ	Fuel and power generation	Combustion processes	0.1690
Tyseley Waste Disposal Ltd., B11 2BA	Waste disposal and recycling	Incineration	0.1600
British Steel Engineering, S60 1DW	Metal production and processing	Iron and steel	0.1500
Eastern Merchant Generation Ltd., TF8 7BL	Fuel and power generation	Combustion processes	0.1290
Coventry and Solihull Waste Disposal Co. Ltd., CV3 4AN	Waste disposal and recycling	Incineration	0.1060
Castle Cement, PE9 3SX	Mineral Industries	Cement / lime manufacture	0.1031
Lafarge Redland Aggregates Ltd., S80 3LJ	Mineral Industries	Cement / lime manufacture	0.0975
Eastern Merchant Generation Ltd., WS15 1PF	Fuel and power generation	Combustion processes	0.0900

Company Name, Postcode	**Industry**	**Process**	**Emissions of Arsenic (tonnes)**
Eastern Merchant Generation Ltd., DE15 9TZ	Fuel and power generation	Combustion processes	0.0860
Blyth Power Station, NE22 7BW	Fuel and power generation	Combustion processes	0.0806
Blue Circle Industries plc., NG13 9JT	Mineral Industries	Cement / lime manufacture	0.0700
Castle Cement, BB7 4QF	Mineral Industries	Cement / lime manufacture	0.0570
Esso Petroleum Co. Ltd., SO45 1TX	Fuel and power generation	Combustion processes	0.0500
Fibrogen Ltd., DN15 8S	Fuel and power generation	Combustion processes	0.0498
British Steel plc., DN16 1BP	Fuel and power generation	Galvanization processes	0.0420
Blue Circle Industries, DA11 9AN	Mineral Industries	Cement / lime manufacture	0.0399
Blue Circle Industries, ST10 3EQ	Mineral Industries	Cement / lime manufacture	0.0382
Brookside Metal Co. Ltd., WV13 2QE	Metal production and processing	Non-ferrous metals	0.0360
Fine Organics, TS2 1UB	Waste Disposal and recycling	Incineration	0.0280
British Steel plc., SA13 2NG	Fuel and power generation	Carbonisation and associated processes	0.0270
Lindsey Oil Refinery Ltd., DN40 3LW	Fuel and power generation	Petroleum processes	0.0260
National Power plc., DE6 6DF	Fuel and power generation	Combustion processes	0.0248
British Steel plc., NP9 0XN	Fuel and power generation	Carbonisation and associated processes	0.0247
British Steel plc., TS10 5QW	Metal production and processing	Iron and Steel	0.0230
Sheffield Forgemasters Rolls Ltd., CW1 6DB	Metal production and processing	Iron and Steel	0.0220
Rubgy Cement, CV23 8RA	Mineral Industries	Cement / lime manufacture	0.0200
Lafarge Redland Aggregates Ltd., DL17 9EY	Mineral Industries	Cement / lime manufacture	0.0191
BP Oil (UK) Ltd., SS17 9LL	Fuel and power generation	Combustion processes	0.0160
Owens Corning Fibreglas (GB) Ltd., LL13 9JU	Mineral Industries	Other mineral fibres	0.0130

Company Name, Postcode	**Industry**	**Process**	**Emissions of Arsenic (tonnes)**
Londonwaste Ltd., N18 3AG	Waste disposal and recycling	Incineration	0.0126
Blue Circle Industries, PL9 7JA	Mineral Industries	Cement / lime manufacture	0.0116
Elf Oil UK Ltd., SA73 3JD	Fuel and power generation	Petroleum processes	0.0109
Britannia Recycling Ltd. , WF3 3BS	Metal production and processing	Non-ferrous metals	0.0106
Shell (UK) Ltd. , L65 4HB	Fuel and power generation	Petroleum processes	0.0100
Avesta Sheffield Ltd., S9 1TR	Metal production and processing	Iron and Steel	0.0100
Yorkshire Environmental Solutions Ltd., NG2 3JH	Waste disposal and recycling	Incineration	0.0096
Britannia Refined Metals, DA11 9BG	Metal production and processing	Non-ferrous metals	0.0090
British Steel plc., TS10 5QW	Fuel and power generation	Carbonisation and associated processes	0.0090
HJ Enthoven and Sons, DE4 2LP	Metal production and processing	Non-ferrous metals	0.0088
Thames Water Utilities, IG11	Waste disposal and recycling	Incineration	0.0086
Blue Circle Industries plc., IP6 0JX	Mineral Industries	Cement / lime manufacture	0.0079
Castle Cement Ltd., CH7 4HB	Mineral Industries	Cement / lime manufacture	0.0079
Thames Water Utilities, SE2 (A	Waste disposal and recycling	Incineration	0.0076
Johnson Mathey plc., EN3 7PW	Chemical Industry	Inorganic chemical processes	0.0071
British Steel plc., SA13 2NG	Fuel and power generation	Carbonisation and associated processes	0.0070
William Blythe Ltd., BB5 4PD	Chemical Industry	Inorganic chemical processes	0.0066
Blue Circle Industries, S33 6RP	Mineral Industries	Cement / lime manufacture	0.0063
Rugby Cement, CV21 2UZ	Mineral Industries	Cement / lime manufacture	0.0055
Contract Heat and Power Ltd., NE6 2AB	Fuel and power generation	Combustion processes	0.0049
British Steel, TS10 5QW	Fuel and power generation	Carbonisation and associated	0.0043

Company Name, Postcode	**Industry**	**Process**	**Emissions of Arsenic (tonnes)**
		processes	
Blue Circle Industries, BA13 4LX	Mineral Industries	Cement / lime manufacture	0.0042
North West Water Ltd., WA8 0WB	Waste disposal and recycling	Incineration	0.0041
Texaco Ltd., SA71 5SJ	Fuel and power generation	Petroleum processes	0.0038
Medical Energy (Worcs.) Ltd., B98 1UB	Waste disposal and recycling	Incineration	0.0036
Rugby Group plc., ME2 1AW	Mineral Industries	Cement / lime manufacture	0.0036
ASW Sheerness Steel Ltd., ME12 1TH	Metal production and processing	Iron and Steel	0.0034
Shell UK Ltd., SS17 9LD	Fuel and power generation	Combustion processes	0.0032
PowerGen (UK) Ltd., NG11 0EE	Fuel and power generation	Combustion processes	0.0027
Yorkshire Water Services Ltd., S9 1HF	Waste disposal and recycling	Incineration	0.0027
National Power plc., SO45 1TW	Fuel and power generation	Combustion processes	0.0026
Severn Trent Water Ltd., B46 1NX	Waste disposal and recycling	Incineration	0.0025
Midland Lead Manufacturers Ltd., DE11 8ED	Metal production and processing	Non-ferrous metals	0.0024
Slough Heat and Power Ltd., SL1 4QQ	Fuel and power generation	Combustion processes	0.0021
Blue Circle Industries plc., CF62 3ZR	Mineral Industries	Cement / lime manufacture	0.0020
Battery Rolled Metals Ltd., B29 6AB	Metal production and processing	Non-ferrous metals	0.0017
New Holland UK Ltd., SS14 3AD	Fuel and power generation	Combustion processes	0.0016
Robinson Group Ltd., NE21 5NJ	Metal production and processing	Non-ferrous metals	0.0016
Northwick Park Hospital NHS Trust, HA1 3UJ	Waste disposal and recycling	Incineration	0.0014
Blue Circle Industries, DL13 2AA	Mineral Industries	Cement / lime manufacture	0.0014
Rugby Group plc., OX9 4AY	Mineral Industries	Cement / lime manufacture	0.0013
SARP Facilities Management Ltd., S21 2DR	Waste disposal and recycling	Incineration	0.0012
Rugby Group plc., CB2 5RG	Mineral Industries	Cement / lime manufacture	0.0011

Company Name, Postcode	**Industry**	**Process**	**Emissions of Arsenic (tonnes)**
Owens-Corning Building Products (UK) Ltd., CH5 2DB	Mineral Industries	Other mineral fibres	0.0011
S Grundon (Services) Ltd., SL3 0EG	Waste disposal and recycling	Incineration	0.0011
Heckett Multiserv (Sheffield) Ltd., S65 3SR	Metal production and processing	Iron and Steel	0.0010
Contract Heat and Power Ltd.	Fuel and power generation	Combustion processes	0.0090
Epitaxial Products International Ltd., CF3 0EG	Chemical Industry	Inorganic chemical processes	0.0050
Rentokil Ltd., L33 7U	Chemical Industry	Inorganic chemical processes	0.0030
Mounstar Metal Corporation Ltd., NE16 6EA	Metal production and processing	Non-ferrous metals	0.0020
City Works, NE6 1AH	Waste disposal and recycling	Production of fuel from waste	0.0013
		Total Annual Emissions	**8.2737**

11. Annex 2 : Arsenic Compounds

This Annex provides further details with respect to some of the more commonly occurring compounds of arsenic, both inorganic and organic forms, and their main uses.

Table A1 summarises the main uses of the more commonly found arsenic compounds.

Table A1 : Common Arsenic Compounds and Their Uses

Compound	**Chemical Formula**	**Uses**
Arsenic acid	H_3AsO_4	Manufacture of arsenates, glass making, wood treating process, defoliant, desiccant for cotton, soil sterilant.
Arsenic disulphide	As_2S_2	Leather industry, depilatory agent, paint pigment, shot manufacture, fireworks, pest control, taxidermy.
Arsenic pentafluoride	AsF_5	Doping agent in electroconductive polymers
Arsenic pentasulphide	As_2S_5	Paint pigments, light filters, other arsenic compounds
Arsenic pentoxide	As_2O_5	Arsenates, insecticides, dyeing and printing, weed killer, coloured glass, metal adhesives
Arsenic thioarsenate	$As(AsS_4)$	Scavenger for certain oxidation catalysts and thermal protectant for metal bonded adhesives and coating resins
Arsenic tribromide	$AsBr_3$	Analytical chemistry and medicine.
Arsenic trichloride	$AsCl_3$	Intermediate for organic arsenicals, ceramics
Arsenic trifluoride	AsF_3	fluorinating reagent, catalyst, ion implantation source and dopant
Arsenic trioxide	As_2O_3	Pigments, ceramic enamels, aniline colours, decolourising agent in glass, insecticide, rodenticide, herbicide, sheep and cattle dip, hide preservative, preparation of other arsenic compounds.
Arsenic trisulphide	As_2S_3	Pigment, reducing agent, pyrotechnics, glass used for infrared lenses, semiconductors, hide tanning
Arsenic hydride	AsH_3	Organic synthesis, chemical warfare, doping agent for solid state electronic compounds.
Monomethylarsonic acid (MMA)	$(CH_3)AsO(OH)_2$	Pesticide industry

Compound	**Chemical Formula**	**Uses**
Dimethylarsinic acid (DMA)	$(CH_3)_2AsO(OH)$	Pesticide industry

A more detailed consideration of inorganic and organic arsenic compounds is given below.

Inorganic Arsenic Compounds

Arsenic Hydrides

Arsine (AsH_3) is used as a dopant in the semiconductor industry, and is used to produce gallium arsenide (GaAs) which is used in the field of opto-electronic and microwave devices.

Arsine is a colourless, very poisonous gas that exhibits an unpleasant garlic-like odour. It is the only known hydrogen compound of arsenic and is formed when any inorganic arsenic metal is brought into contact with zinc or sulphuric acid. It can be accidentally formed by the reaction of arsenic impurities in commercial acids stored in metal tanks. Arsine is not particularly stable and begins to decompose into its constituent elements below 572°F. In the presence of moisture, light can affect the decomposition.

In general, other than arsine, other arsenic hydrides have little commercial use. Diarsine (As_2H), is formed as a by-product from the preparation of arsine (AsH_3) by treatment of a magnesium aluminium arsenide alloy with dilute sulphuric acid. Diarsine can also occur by passing arsine at low pressure through an ozoniser-type discharge tube.

Arsenic Halides

Table A2 below lists some known arsenic halides.

All of the arsenic halides are covalent compounds which hydrolyse in water and can be formed by direct combination of the elements. Arsenic trichloride is the most common and commercially significant of all arsenic halides. With a low boiling point, it is easily separated from tin chloride and the chlorides of other metals. It can also be formed by spontaneous combustion of the elements. Arsenic trichloride has been used as a starting material for the production of numerous organoarsenic compounds and for the preparation of chlorine derivatives of the arsines. In addition, it is used as a dopant in the semiconductor industry and in the production of high-purity arsenic metal. Other arsenic halides include arsenic trifluoride, arsenic pentafluoride, arsenic pentachloride, arsenic tribromide, arsenic triiodide, and arsenic diiodide.

Arsenic Oxides and Acids

Arsenic trioxide (As_2O_3) is the most commercially important arsenic compound. It can occur in two different crystalline forms and one amorphous variety. The octahedral (or cubic) modification, arsenolite, is the most common form and is stable at room temperature. It changes into a monoclonic modification, (consisting of sheets of AsO_3 pyramids sharing oxygen) at temperatures above 221°C. This modification is formed when condensation occurs at temperatures above 430°F. Condensation above 250°C will generally form the amorphous, glassy phase which devitrifies into the octahedral modification at room temperature. This octahedral variety is a white solid that sublimes above 135 °C and melts at 275°C under its own vapour pressure.

Arsenic trioxide slightly dissolves in water to form a weakly acidic solution. It is soluble in acids and bases (amphoteric). It can be made by burning arsenic in air, or by the hydrolysis of an arsenic trihalide. Commercially, it is prepared by roasting arsenopyrite. It is often used as primary analytical standard in oxidimetry since it is readily attainable in a high state of purity and is quantitatively oxidised by many reagents commonly used in volumetric analysis. (e.g. dichromate, nitric acid, hypochlorite, and iron(III)).

Arsenic pentoxide (As_2O_5) is a ‘white glassy mass’ made up of equal numbers of octahedral and tetrahedral sharing corner oxygens to give cross linked strands. It is an oxidising agent capable of liberating chlorine from hydrogen chloride. The compound deliquesces in air to form arsenic acid. It dissolves water slowly, is thermally unstable, and begins to decompose near the melting point, around 300°C. The vapour is made up of arsenic trioxide and oxygen. The pentoxide can be made by reacting arsenic trioxide with oxygen under pressure, or by dehydration of crystalline arsenic acid at temperatures above 200°C.

Table A2 : Physical Properties of Arsenic Halides

Arsenic halide	**Colour and Physical State at 25 °C**	**Mp[5], (°C)**	**Bp[6], (°C)**
Arsenic trifluoride (AsF_3)	colourless liquid	-6.0	62.8
Arsenic pentafluoride (AsF_5)	colourless gas	-79.8	2.8
Arsenic trichloride ($AsCl_3$)	colourless liquid	-16.2	130.2
Arsenic tribromide ($AsBr_3$)	yellow solid	31.2	221
Arsenic triiodide (AsI_3)	red solid	ca. 400	ca. 400

Arsenic acid is known in the solid state as the hemihydrate $H_3AsO_4.0.5H_20$ and occurs as rhombic, deliquescent crystals. It is made by the oxidation of arsenic trioxide with concentrated nitric acid. Arsenic acid will lose water upon heating to 120°C and forms pyroarsenic acid. At elevated temperatures, more water is lost and meta-arsenic acid forms. In an acidic solution, arsenic acid and its salts are strong oxidising agents. Arsenic acid is used as a defoliant and as a starting material for important inorganic and organic arsenic compounds. Various salts (arsenates) are derived from arsenic acid, and are described in detail below.

Arsenates

Arsenates are oxidising agents and are reduced with concentrated hydrochloric acid or sulphur dioxide. Of the many salts of arsenic acid, the salts of potassium, sodium, calcium and lead are important commercially. Arsenates of calcium or lead are often used as insecticides. When a solution of ortho-arsenate is treated with silver nitrate in neutral solution, a chocolate brown precipitate of silver ortho-arsenate form. Silver ortho-arsenate can be used as a test to distinguish arsenates from phosphates. With hydrofluoric acid, ortho-arsenate solutions yield hexafluoroarsenates (e.g. potassium hexafluoroarsenate).

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[5] Mp = Melting point

[6] Bp = Boiling point

Arsenic Sulphides

Table A3 below presents the common physical properties of the common arsenic sulphides. These are described in more detail below.

Table A3 : Physical Properties of common arsenic sulphides

Arsenic Sulphides	**Molecular Formula**	**Colour and Physical State at 25° C**
Arsenous sulphide	As_2S_3	yellow solid
Arsenic sulphide	AsS_4	gold or orange solid
Arsenic pentasulphide	As_4S_{10}	yellow solid
Tetraarsenic trisulphide	As_4S_3	orange yellow
Tetraarsenic pentasulphide	As_4S_5	(not known)

Arsenic disulphide (‘red glass’) exists in the ruby-red crystals or as an amorphous reddish mass. It occurs naturally as the mineral realger. At 5267°C it changes into a black allotrophic modification and at 307°C the compound melts. Its purity and fineness rather than its chemical composition determine its commercial value. Industrially manufactured red arsenic glass varies in composition. Today, red glasses typically contain around 61 to 64% arsenic and 39 to 36% sulphur. Commercially, the compound is produced by heating a mixture of iron pyrites and arsenopyrites or by heating arsenic trioxide with sulphur. It can also be made by prolonged treatment of arsenous sulphide with boiling aqueous sodium bicarbonate, or by heating a sodium bicarbonate-arsenous sulphide mixture in a sealed tube. Water does not affect it, however it will oxidise in nitric acid and inflame in chlorine. ‘Red glass’ is primarily used as depilatory in the manufacture of fine leather, and also used in pyrotechnics.

Arsenic (III) sulphide is known as orpiment and occurs as a yellow mineral. It is made by precipitation of trivalent arsenic compounds with hydrogen sulphide. The colloidal solution of the arsenic trisulphide can be flocculated with hydrochloric acid, in which it is insoluble. It readily dissolves in basic reagents. Orpiment contains unchanged arsenic trioxide and is poisonous. It was used in the past for cosmetic purposes, but currently it is used in the semiconductor industry, in the production of infrared-permeable windows, and as a pigment.

Arsenic (V) sulphide (also referred to as arsenic pentasulphide) is made by fusing stoichiometric quantities of arsenic and sulphur powder or by precipitation from highly acidic arsenate (V) solution with H_2S. Arsenic (V) sulphide will decompose into arsenic (III) sulphide and sulphur. The compound is stable in air up to temperatures of 95°C, but begins to dissociate into arsenous sulphide and sulphur at higher temperatures. It can be hydrolysed by boiling with water resulting in arsenous acid and sulphur.

Organic Arsenic Compounds

Arsenic combines easily with carbon to form a wide variety of organic compounds with one or more As-C bonds. There are many known organoarsenic compounds. Table A4 below presents a number of examples.

Organic arsenic compounds, once used in agricultural pesticides, have now largely been replaced by metal-free compounds. Organic arsenic compounds can be grouped together into aliphatic organoarsenic compounds and aromatic organoarsenic compounds. Both of these groups are described in detail below.

Aliphatic Organoarsenic Compounds

The use of aliphatic organoarsenic compounds is largely restricted in the UK as a result of increased awareness of their detrimental effects on the environment. However, they are still used as herbicides and fungicides in Eastern Asia. The main aliphatic organoarsenic compounds are described below;

- monomethylarsonic acid (MMA), particularly the iron ammonium salt, Neoasozin, are used as a fungicide in rice growing. The sodium, ammonium, and diethanolammonium salts are used as herbicides in cotton growing.
- dimethylarsinic acid (DMA), also called Ansar 160, is used as a total herbicide and desiccant. Generally, it is produced by reaction of methyl halide with a salt of arsenous acid.

Aromatic Organoarsenic Compounds

The primary use of arsonic acids was in their supplementary processing to arsenobenzenes and "arsenic oxides" by reduction with SO_2, phosphorus trichloride, sodium dithionite, phosphorous acid, or tin (II) chloride. Reduction with zinc dust and hydrochloric acid yields the arsines, which are re-oxidised in air (e.g. phenylarsine is rapidly oxidised in air to form the arseno compound C_6H_5As).

The aromatic arsonic acids are dibasic. Aqueous solutions of the monosodium salts are neutral to mildly acidic, whereas those of the disodium salts are slightly alkaline (pH of 8-9). Magnesium and calcium salts are typically soluble in cold water, but upon heating, they precipitate to practically insoluble deposits. Because magnesium and calcium salts are soluble in cold water, they can be used to separate arsonic salts from cold solutions. Arsonic acids generally crystallise well, and their stability depends upon the substituents on the benzene ring. Some form azo dyes that contain both arsonic acid and sulphonic acid groups, and are used in the analysis of metals.

Aromatic Arsenobenzenes

Aromatic arseno compounds have amino or hydroxyl groups and are soluble in acids and alkalis. Aromatic arseno compounds will become soluble in water with the addition of a formaldehyde sulphoxylate or formaldehyde hydrogen sulphite into the amino group.

Organic Oxoarsenic Compounds

Organic oxoarsenic compounds are the anhydrides of the arsonous acids. They are extremely poisonous amphoteric substances barely soluble in water. When dissolved in acids and alkalis, they form salts and can be precipitated from those solutions by carbon dioxide or ammonium chloride.

The reduction of organoarsenic compounds can be controlled by using an appropriate reducing agent so that reaction terminates at the preferred intermediate stage. However, this does not occur with oxidation. In the most commonly used method for the production of organic oxoarsenic compounds from arsonic acids, the acid is directly reduced to the anhydride of the arsonous acid with SO_2.