Arsenic in the environment

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ARSENIC IN THE ENVIRONMENT

by

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ABSTRACT

Arsenic, long synonymous in people's mind with poison exhibits a varied, fascinating and dynamic biogeochemistry. Chemically and biologically reactive, its chemical form, or speciation, changes with slight variations in chemical or biological conditions. Depending upon the extent to which any arsenic containing system is dominated by physical/chemical or biological process, the forms of arsenic may change between the various inorganic and methylated species, and may alter rapidly with varying conditions.

Early research revolved around the formulation of pigments, and later in the development of effective medicines. Later still, thanks due to its long history as a poison, arsenic was included in numerous agricultural practices, mainly as a herbicide or pesticide. It has also seen service in the rather more specialised field of chemical warfare, and still poses threats as a result of improper disposal.

Much of the recent research has focused on the identification of previously unknown organoarsenic species found in estuarine and marine waters. This work is building up an understanding of the biological pathways involved in the biochemical cycling of arsenic. Little work has been carried out with respect to the cycling of arsenic in freshwaters in comparison to that in marine and estuarine waters. Similarly, there has been less work performed on the speciation of arsenic in freshwater sediment interstitial waters, than there has on marine sediments, or intertidal sediments.

The characterisation of arsenic in dynamic porewater poses a set of unusual and difficult problems, not the least being the procurement of representative, discrete samples. A number of potential sampling methods are reviewed, and variations on the thin film gel sampling technique are thought to provide perhaps the best option, although this will depend upon the type of intertidal sediment being investigated, and the information sought.

It may be impossible to propose a general model of arsenic cycling either at a local scale or at a global level. This is of course due to the great diversity in ecosystems, each having different controls over arsenic speciation, and containing different biological communities. Once a given system has been described, the patterns of arsenic speciation (both spatially and temporally) are explainable, and potential impacts can be identified,
but they cannot be transferred to another system. The continuing accumulation of information regarding arsenic speciation in different systems is helping in the unravelling of the larger global arsenic cycle. Such an understanding can only be a benefit in the development of safe and efficient remediation schemes for contaminated soil and aquatic systems.

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Chapter 1

INTRODUCTION

Arsenic has achieved great notoriety because of both the toxic and therapeutic properties of a number of its compounds. The combined affect of these on human attitude has resulted in widespread concern about the natural and anthropogenic levels of arsenic in the environment. Arsenical compounds were used in medicine 2000-3000 years ago in the Orient (Ferguson and Gavis, 1972) and therapeutic applications have continued throughout the ages. Concurrent with this, arsenic gained a reputation as a dangerous poison, used both on the small scale and more widely as a chemical warfare agent. It has also found use in a wide variety of other applications including, but not limited to, insecticides, herbicides, pigments and in the glass industry.

The primary stimuli for research connected with arsenic have therefore generally been associated with one or more of the following:

i) the long history of arsenic as a homicidal poison;
ii) the industrial use of arsenicals and the resultant environmental exposure to them;
iii) the clinical application of arsenicals in protozoal and neoplastic diseases; and
iv) the use of arsenicals in chemical warfare.

Arsenic in water supplies has caused poisonings, usually of a chronic rather than an acute nature. Chronic arsenic poisonings have been recorded as occurring with arsenic levels of about 0.2 mg/l (ppm). The toxicity of arsenic increases significantly when arsenic is reduced from a +5 to a +3 oxidation state, but is more toxic still in the -III oxidation state, although these compounds are not particularly thermodynamically stable. Unlike mercury the methylated arsenic forms are less toxic than inorganic forms. The physical properties of elemental arsenic and of various arsenic compounds are presented as Appendix A.

Standards for arsenic levels in drinking water supplies have been established by a number of governmental, national and international agencies as may be seen in Table 1.1, but it is very important to note that these levels refer to TOTAL arsenic, not to

specific arsenic species, some of which are much more toxic than others (Hering, 1996). The major arsenic species found in environmental and clinical samples include arsenite [As(III)], arsenate [As(V)], monomethylarsonic(V) acid (MMAA), dimethylarsinic(V) acid (DMAA), arsenobetaine (AsBe), and arsenocholine (AsC). The toxicity of these compounds decreases in the approximate order As(III), As(V), MMAA, DMAA, AsBe, AsC. Other important compounds also found in environmental samples and which act as intermediates, or which result from some of the biological reactions undergone by arsenic, include arsenious acid, arsenic acid, arsine, monomethylarsine (MMA), dimethylarsine (DMA), trimethylarsine (TMA), trimethylarsine oxide (TMAO), monomethylarsonous(III) acid [MMAA(III)] and dimethylarsonous(III) acid [DMAA(III)]. There is quite a degree of confusion over the naming of some arsenic compounds, particularly MMAA and DMAA (both oxidation states), and so the nomenclature of Hasegawa et al (1994) has been adopted throughout. A comparison of the various names is given in Appendix B.

Table 1.1. Arsenic limits for drinking water supplies.

WHO (1984)	EEC (1980)	US-EPA (1992)	CANADA (1992)
50 ppb[1]	50 ppb[1]	50 ppb[1]	25 ppb[1]
10 ppb[2]	10 ppb[3]	2.0 ppb[2]	← Proposed

ppb parts per billion. From [1]Gliek, 1993; [2]Pearce, 1993; [3]EEC, 1995; [1,2,3]Hering, 1996.

It is also very important to note that the majority of analytical methods employed until recently to determine the monomethylarsenic and dimethylarsenic species, did just that, being unable to distinguish between MMAA(III) and MMAA(V), and between DMAA(III) and DMAA(V). Older references must therefor be read with care, as 'DMAA' is most likely to refer to dimethylarsenic, rather than to DMAA *per se* (the same is applicable to MMAA).

It is thus neccessary to make clear that in this work, unless specified, DMAA may apply to either DMAA(V) or to total dimethylarsenic, with the same caveat applying to MMAA. To be absolutely certain, the reader is advised to check the original references. However, the errors arising from this assumption are likely to be small, as the proportions of MMAA(III) and DMAA(III) present in the environment are very small compared to MMAA(V) and DMAA(V) [Hasegawa et al, 1994]. Any other non-

complex monomethylarsenic and dimethylarsenic species are unlikely to be separated successfully using present speciation and detection technologies.

Work in the United States over the past thirty years on arsenic levels in surface fresh waters found that the United States Public Health Service Standards (maximum permissible limit of 0.05 mg/l, or 50 ppb) were exceeded by arsenic more frequently than for any other element potentially hazardous to human health. It is probable that arsenic concentrations in natural waters often approach or exceed levels thought to be safe for drinking water, although of course, not all waters are use for drinking, particularly seawater. As a result of such observations, and due to the occasional poisonings resulting from arsenic ingestion (via various pathways), many governments have drawn up legislation regarding the amount of arsenic in soils, water and foodstuffs. Generally, such legislation sets a target concentration or range of concentrations, excedance of which may pose an unacceptable risk to human or animal health. It is important to note, however, that although regulatory-driven risk estimates for arsenic are thought to be conservative and are necessary to meet statutory requirements and regulatory deadlines, they may not reflect actual health risks of arsenic. Arsenic is known to bioaccumulate in shrimps and some edible shellfish, but in a form that is not highly toxic. It does not, however, like mercury, biomagnify (Blanck et al, 1986; Millward et al, 1996). A brief review of the legislation covering arsenic in the UK and EEC is presented as Appendix C.

There are several questions which arise from these observations of arsenic levels:

i) what proportion of the current environmental levels of arsenic result from natural sources and how much is anthropogenic?

ii) what is the relationship of total concentrations to toxicity and what are the relative amounts of highly toxic reduced forms and less toxic oxidised and methylated forms in given water systems?

iii) what are the precise mechanisms and relative rates by which arsenic is removed from solution and incorporated into sediments, or vice-versa?

iv) to what extent do inorganic and methylarsenicals occur, what is the relationship between them, and what are the pathways taken by such compounds to man?

Arsenic undergoes reactions of oxidation-reduction, precipitation-dissolution, adsorption-desorption, and chemical, organic and biochemical methylation. All of these reactions control the mobilisation, bioaccumulation and hence concentration within the environment. Arsenic concentration in soils and water, or its availability to living organisms is generally governed by the arsenic species present rather than the total amount of arsenic present.

The precise mechanisms and pathways involved in the cycling of arsenic in the environment are not fully understood, either on a global macro-scale, or on a much more local micro-scale. The speciation of arsenic has been extensively studied in soils, sea and surface freshwaters and to a lesser extent in groundwaters, freshwater sediments, marine sediments and estuarine waters or intertidal sediments.

In this work, the occurrence of arsenic in the environment is examined in some detail in Chapter Two. Here, the general relative concentration of arsenic (and to a lesser extent arsenic speciation) in rocks, soils, natural waters, air masses and precipitation, and living things are reported, before a brief mention of anthropogenic arsenic inputs to the environment is made. Chapter Three reports the current and historical uses of arsenic in a wide variety of industries, before mentioning arsenic production. This is then followed by an introduction to the global cycling of arsenic.

Chapters Four and Five introduce the mechanisms behind arsenic mobility, and the processes responsible for the transport of arsenic between the major natural global arsenic reservoirs. Chapter Four deals with the redox reactions of arsenic. An introduction to the concepts of pH, Eh and pH/Eh diagrams is made, before comments on the potential for arsenic to be used as a redox indicator, and redox rates are made. Adsorption/desorption processes affecting arsenic are also described, before sections relating to arsenic mobility within more specific localised environments. Chapter Five describes arsenic's biochemistry and toxicology. Descriptions are given about the various biomethylation processes undergone by arsenic, together with some exocellular or abiotic methylation processes and demethylation. The reasoning behind observed seasonality in dissolved arsenic concentrations in various natural waters is also discussed, before an introduction is made to some of the more complex organoarsenicals now being detected in natural systems.

Chapters Six, Seven, Eight and Nine deal with the various steps involved in the sampling, preservation and laboratory analysis of arsenic species. Chapter Six introduces

the various methods employed in procuring representative samples for environmental analysis. This chapter concentrates on porewater sampling, specifically for arsenic speciation, although some consideration is also given to soil, rock and other water sampling strategies. Also introduced in this chapter are some ideas that might be used in the sampling of porewaters from intertidal sediments. Chapter Seven then goes on to review the various methods that have been employed in preserving the chemical integrity of the sample over the time from sampling to laboratory analysis. The preparations involved in ensuring adequate separation of the individual arsenic species present in the sample to ensure speciation data is accurately obtained is reviewed in Chapter Eight, together with a brief mention of the preparation necessary to determine the total arsenic concentration in a sample. Chapter Nine is devoted to some of the analytical techniques used in arsenic detection. Some of these methods (such as colorimetry or molecular absorption spectophotometry and stripping voltammetry) determine arsenic species directly, while all the others require one of the careful preparations described in Chapter Eight.

Chapter Ten attempts to draw conclusions concerning the local cycling of arsenic within specific environments, and advances some methods for alleviation of localised arsenic pollution. It also includes recommendations on the sampling of porewaters, together with suitable preservation and determination methods from the as yet unresearched area of arsenic speciation within intertidal sediments.

CHAPTER 2

OCCURRENCE OF ARSENIC

2.1. Introduction

Arsenic is the twentieth most abundant element in the earth's crust (Sandberg and Allen, 1975; Cullen and Reimer, 1989; Bhumbla and Keefer, 1994; Pontius et al, 1994) although Wood (1984) states that it is the twenty sixth most abundant and Peters et al (1996) quote a ranking of fifty second. In the universe, arsenic is ranked eighteenth, fourteenth in seawater, and twelfth in the human body (Sandberg and Allen, 1975). The occurrence of arsenic in nature is generally associated with sedimentary rocks of marine origin, weathered volcanic rocks, fossil fuels, geothermal areas, volcanic eruptions, mineral deposits, mining wastes, agricultural use or irrigation practices and other anthropogenic inputs. It is generally agreed that most anthropogenic input is from smelting operations and fossil fuel combustion. These inputs are responsible for the emission of arsenic to the atmosphere, from where it is redistributed on the earth's surface by rainfall and dry fallout and also by dissolution in water, with aquatic and soil/sediment concentrations being controlled by a variety of input and removal mechanisms.

Recent estimates have put the ratio of natural to anthropogenic atmospheric inputs at about 60:40 (Cullen and Reimer, 1989), although Peters et al (1996) state that anthropogenic inputs generally exceed natural inputs. It is the arsenic present in certain solid phases, particularly iron oxides, organic matter and sulphides that are the primary sources of arsenic in aqueous systems. Elevated occurrences of arsenic in aqueous systems may therefore be expected where these solid phases are unstable.

It is apparent that arsenic is a ubiquitous trace element found in the aquatic environment, in soils and sediments, the atmosphere, and in organisms. Because both natural and anthropogenic inputs vary geographically, environmental substrates show wide ranges of arsenic concentrations. It is thus quite difficult to establish typical arsenic values, making comparisons difficult. Total arsenic concentrations are quite easy to measure and approximate concentrations in the natural arsenic reservoirs can be made, as shown in Table 2.1.

However, there has been, for a considerable number of years a growing realisation that the environmental behaviour of arsenic is dependent on the physical and chemical properties, toxicity, mobility and biotransformation of individual arsenic compounds or species (Cullen and Reimer, 1989). Most work carried out in the pursuance of arsenic species determination has been performed in conjunction with studies of the aquatic - particularly the marine - environment.

Table 2.1. Calculated ratios of arsenic concentrations in natural reservoirs with respect to soils

Reservoir	Approximate ratio with respect to soil
Rocks	25,000
Oceans	4
Soil	1
Biota (all living things)	0.0005
Atmosphere	0.000001

From Bhumbla and Keefer, 1994.

The arsenic biogeochemical cycle can only be understood properly in terms of the dynamic balance of biological, chemical, physical and geological processes on individual arsenic species. Major processes responsible for the observed concentrations of arsenic in groundwater include: mineral precipitation/dissolution, adsorption/desorption, chemical transformations, ion exchange and biological activity. In addition, factors such as pH, Eh, solution composition, competing and complexing ions, aquifer mineralogy, reaction kinetics and the hydraulics of the groundwater system can all affect the arsenic concentration (Welch et al, 1988).

2.2 Rocks

Arsenic occurs in the earth's crust at an average level of about 1.8ppm (Bowie and Thornton, 1985; Fergusson, 1990) or in the range of 2-5ppm (Morita and Edmonds, 1992; Manahan, 1993), although Bowen (1979) suggests a lower value of 1.5ppm. Natural arsenic occurring in aqueous systems generally has its origins in igneous, metamorphic and sedimentary rocks. An obvious difference in arsenic concentrations in igneous rocks of different origins does not occur, although arsenic is enriched in some minerals more than in others. Arsenic may substitute for silicon (As^{5+} for Si^{4+}), ferric iron (As^{3+} for Fe^{3+}), titanium (As^{3+} for Ti^{4+}) and aluminium (As^{3+}, As^{5+} for Al^{3+}) in crystal lattices of silicate minerals (Onishi and Sandell, 1955; Esson et al, 1965)

presumably in the melt phase, although it has been assumed that the concentration of As^{5+} in magmas is low, especially when the Fe^{2+}/Fe^{3+} ratio is high (Onishi and Sandell, 1955). However, the arsenic present in silicate glasses tend to indicate that As(V) is by far the predominant arsenic form in glass melts, and it is thus thought that both valence states are about equally important in magmas, even where the Fe^{2+}/Fe^{3+} ratio is high. Consequently, arsenic concentrations tend to be relatively high in volcanic glasses, aluminosilicate minerals and igneous rocks containing iron oxides. Arsenic concentrations in metamorphic rocks are more wide ranging due to the variable contents of the arsenic in the source rocks. Sedimentary rocks (especially shales and clays) generally contain the highest arsenic concentrations, as may be seen from Table 2.2.

Table 2.2. Ranges and mean concentrations of arsenic in igneous and sedimentary rocks (ppm).

Reference	Basaltic igneous	Granitic igneous	Shales and clays	Limestones	Sandstones
Range[1]	0.2-10	0.2-13.8	-	0.1-8.1	0.6-9.7
Mean[1]	2.0	2.0	10.0	1.7	2.0
Mean[2]	1.5	1.75	15.0	2.5	1.0
Mean[3]	1.5	1.5	13.0	1.0	1.0
Mean[4]	1.8		13.0	-	1.0

From [1]Cannon et al, 1978; [2]Bowie and Thornton, 1985; [3]Fergusson, 1990 and [4]Lemmo et al, 1983.

The ranges of arsenic concentrations given above are in fact averages, and the ranges and means of arsenic concentrations in a range of igneous and sedimentary rocks are given in Tables 2.3 and 2.4 respectively. The arsenic concentrations of metamorphic rocks are obviously closely linked to the parent material, together with the process of metamorphism applied to the parent material in order to transform them.

Table 2.3. Ranges and mean concentrations of arsenic in igneous rocks (ppm).

	Ultrabasic	Basic	Intermediate	Granitic	Acidic
Range	0.3-6.6	0.066-33.0	0.5-5.8	0.0-8.5	0.2-12.2
Mean	5.0	1.5	2.1	1.5	2.7

From Onishi, 1978.

Coals have long been known to have reasonably high contents of arsenic. The ranges and means of the arsenic contents of coals and coal ashes from around the world are summarised in Table 2.5 where it may be seen that ranges of arsenic concentrations range widely. Bertine and Goldberg (1971) suggested an average arsenic concentration

in coal of 5ppm, which given the ranges seen may appear somewhat low when looking at the whole, although the concentrating effect of combustion gives lignite ashes a range of 1,000-10,000ppm. Peters et al (1996) make the point that although arsenic concentrations are generally moderately low in coals, and average <0.2mg/kg in petroleum fuels, that the sheer volume of these fuels burnt each year results in a significant amount of arsenic being introduced into the environment by this route.

It has been found recently that chemical data on vitrinite concentrates can yield information on the source of the elements in coal and on the partitioning of the elements during peatification and diagenesis of coals (Lyons et al, 1989). Vitrinite is one of the major macerals of the coal lithotypes vitrain and clarain, both of which are macroscopic constituents of coal. The range of concentrations of arsenic in vitrinites is also given in Table 2.5.

Table 2.4. Ranges and mean concentrations of arsenic in sedimentary rocks (ppm).

	Shales and slates	Sandstones	Carbonate rocks	Phosphate rocks
Range	0.3-59.0*	0.6-17.0	0.1-23.5	0.4-188
Mean	13.0*	1.0	1.0	21.0

From Onishi, 1978, and Bowen, 1979.
*Copper shales are reported to have a range of 100-900ppm, and some samples of marine shales and claystones have values of 100 and 490ppm.

Table 2.5. Ranges and mean concentrations of arsenic in coals and coal ashes (ppm).

	Coals*	Bitum-inous	Brown	Lignite[1]	Coal ash	Vitrinite[2]
Range	0-1,500[3]	<1-17	1-3	1.0-55	<80-700	0.61-12.4
Mean	-	3.0	-	-	-	-

From Onishi, 1978; [1]Bowen, 1979, [2]Lyons et al, 1989; [3]Peters et al, 1996. *Unspecified rank.

In coals from the Eastern United States, when arsenic concentrations in vitrinites are compared relative to the whole coal arsenic concentration, the arsenic is regarded as having an inorganic association (most of the arsenic is found in minerals or the whole coal). In Australian and English coals, however, arsenic is found to have a more organic association, although this might be due to finely disseminated pyrite within the vitrinite (Lyons et al, 1989).

2.2.1 *Rock-arsenic speciation*

It is important to note that little or no work has been performed with regards to identifying the oxidation state of arsenic in rocks, due to there being no reliable method for the separate determination of As(III) and As(V) in silicate rocks (Onishi, 1979), so works tend to either assume that As(V) is the dominant form, or simply report total arsenic concentrations, although Fergusson (1990) suggests that As(V) is present as the dominant arsenic species in around 60% of the minerals containing arsenic. Esson et al, (1965), presumed that arsenic is present in both the trivalent and pentavalent states in magmas, with As(III) dominating in rock forming minerals, through substitution, while As(V) tends to be concentrated in the residual solution. Both As(III) and As(V) are detected in fumeroles and geothermal waters (White, 1968; Ellis 1979; Stauffer and Thompson, 1984; Yokoyama et al, 1993).

2.3 Soils

Arsenic is usually present in soils contained in unweathered sulphide minerals, as an inorganic compound, or bound to an organic fraction in the soil. The arsenic content of a soil will be primarily determined by the soil's parent materials and by any subsequent anthropogenic or natural inputs (see Table 2.6) such as applied herbicides or volcanic eruption fallout (Huang, 1994). The concentration of various arsenic species in the soil, however, will be controlled by the prevailing environmental conditions, such as pH and Eh (see Chapter 4), together with the amount of rainfall, but generally decreases with increasing depth. A global average soil arsenic concentration has been estimated at around 1.5ppm (Bowie and Thornton, 1985), although Onishi (1979) and Fergusson (1990) suggest a higher figure in the range 5-10ppm, a range falling in the lower part of the 'normal' range of arsenic in soils in England and Wales suggested by Webb et al (1978) given in Table 2.7. A range of 0.1-40ppm for soils in general is given by Walsh and Keeney (1975), Bowen (1979), Morita and Edmonds (1992) and Huang (1994). Surface soils in gardens in the historical Cornish mining areas, however, have total natural arsenic concentrations in the higher range of 144-892ppm (mean of 322ppm), with exceptional values in soils near old mining spoil heaps reaching values of up to 2,500ppm (Thornton, 1983; Bowie and Thornton, 1985), while those overlying sulphide deposits reaching as high as 8,500ppm (Peters et al, 1996). A similar wide range is quoted by Huang (1994) with respect to the range of 0.01-626ppm for all types of soils

in China, although the mean was only 11.2ppm. Fergusson (1990) gives a range of arsenic concentrations in a wide variety of soils from around the world and these generally fall in the range of 0.02-97μg/g, with a global average of 11.3μg/g.

The lowest arsenic levels are usually associated with sandy soils, especially those derived from granites. Very high soil arsenic levels have been recorded in contaminated soils (see Table 2.8), particularly those associated with metal processing plants, the use of arsenical pesticides and from the mining of arsenic containing ores. The high levels of total soil arsenic have been observed more often where crops have been treated with an arsenical insecticide compared with a defoliant. This is due to the relative amounts applied. For example, research has shown that some orchards have received over 1000kg of arsenic per hectare as insecticides, compared with around 10kg/ha when used as a defoliant (Walsh and Keeney, 1975).

Table 2.6. Arsenic concentrations in soils derived from normal and geochemically anomalous parent materials.

Normal range in soil (ppm)	Metal rich soils (ppm)	Sources	Possible effects
<5-40	up to 2500	Mineralisation	Toxicity in plants and livestock; excess in food crops
	up to 250	Metamorphosed rocks - Dartmoor	

From Thornton, 1983; Bowie and Thornton, 1985.

Table 2.7. Soil arsenic levels (ppm) over England and Wales.

Clarke Value*	Low	Normal	High	Very High
1.8	<8.0	8.0-29.0	>29.0	>70

*Average concentration in the earth's crust. After Webb et al, 1978

Table 2.8. Levels of arsenic in contaminated surface soils.

Country	Source of contamination	Range (μg/g)	Mean (μg/g)
Canada	Metal processing	33-2000	-
England	Mining area	90-900	-
	Mining area	23-1080	228
Hungary	Chemical works	10-2000	-
Japan	Metal processing	38-2470	-
	Pesticides	38-400	-
USA	Around a smelter (1.5-2km)	89-110	80 (*sic*)
	Pesticides	31-625	-
	Pesticides	1-2553	-
	Sludged land	1.13-6.21	3.08

From Walsh and Keeney, 1975; Fergusson, 1990.

These high values, are however, not generally transported into the aerial parts of plants (Xu and Thornton, 1985; Peters et al, 1996). It is interesting to note that the arsenic concentrations of some vegetables grown in the Cornish soils are statistically related to the soil arsenic content, and this is discussed further in Section 2.6.6.

Table 2.9. Concentration of arsenic in garden soils in Cornwall.

	Total	Water soluble	Acid Extractable
Range	144-892	0.31-2.78	0.45-16.95
Geometric Mean	322	0.89	4.97

From Xu and Thornton, 1985.

Xu and Thornton (1985), investigated the relative proportions of water soluble and dilute acid-fluoride soluble arsenic relative to total soil arsenic concentration. Their results are based on the analysis of 32 garden soil samples, and are presented as Table 2.9. They found that both water soluble and extractable arsenic expressed as a percentage of the total amount of arsenic present decreased with increasing soil iron concentrations, and concluded that this was due to the formation of relatively low solubility iron arsenates coupled with the probable adsorption of arsenic onto hydrous iron oxides. The reasons behind these relationships are discussed more fully in Chapter 4.

2.3.1 *Soil-arsenic speciation*

Arsenic in soils occurs mainly as inorganic species, but may also be found bound to organic materials. Inorganic arsenic may also be converted to organoarsenic compounds by soil micro-organisms, or may be inadvertently or deliberately added as a herbicide or pesticide. The relative proportions of As(III) to As(V) will be controlled by the redox potential of all the reducing and oxidising reactions occurring in the soil. Under reducing conditions, As(III) dominates (Deuel and Swoboda, 1972), although elemental arsenic and arsine may also be present (Walsh and Keeney, 1975). These relationships are generally complex, and so the redox value for the soil is not generally proportional to the As(III):As(V) ratio (Huang, 1994). This is discussed further in Chapter 4.

In many instances, fertilisers, both organic and inorganic are applied to soils in order to improve fertility. These are often found to contain variable quantities of arsenic

(see Tables 2.10, 2.11 and 2.12) and may significantly increase the arsenic concentration in soils. However, the EEC Directive 86/278/EEC on protection of the soil, when sewage sludge is used in agriculture states that sewage sludge should be used only under conditions which ensure that the soil, and the surface and groundwater are protected in accordance with EEC Directives 75/440/EEC and 80/68/EEC which are outlined in Appendix C. Additionally, the addition of phosphate containing fertilisers has been shown to enhance arsenic mobility in the soils to which they are added (Davenport and Peryea, 1991; Peters et al, 1996). This is described in more detail in Section 2.7.3.4.

Table 2.10. Range of Arsenic contamination (ppm).

Sewage sludge	1.1-230	Thornton (1983); Bhumbla and Keefer (1994)
Fly ash	2.0-6300	Bhumbla and Keefer (1994)
Soils	0.1-40[1]	Bowen (1979); Thornton (1983); Bowie and Thornton, (1985)

[1]'Normal' range in soil.

Since the concentrations of arsenic in these soil additives are known, and the quantity of each additive used is also known, then the total amount of arsenic added to the soil can be estimated. From the results of rough calculations, arsenic tends to build up in soils, mainly because inputs exceed the outputs such as drainage and cropping, although atmospheric inputs from dust and rain are thought to be more important than additions from fertilisers, but not as important as localised high use of arsenical pesticides and herbicides (Fergusson, 1990).

Table 2.11. Range of As concentration (μg/g) in fertilisers, limestone and soils.

Nitrogen	Phosphate	Sewage sludge	Manure	Limestone
2-120	>1-1200	2-30	<1-25	0.1-24

From Fergusson, 1990.

Table 2.12. Range of As concentration (mg/kg) in Japanese fertilisers.

Ammonium sulphate	Calcium perphosphate	Potassium sulphate	Compound fertiliser	Mixed fertiliser
0-450	8-600	0-400	0-850	0-800

From Kanamori and Sugawara, 1965b.

Plants grown on soils subject to fly-ash additions have also shown significant accumulation of arsenic.

2.4 Natural waters

Naturally occurring arsenic is present in a broad range of natural waters at a wide range of concentrations as is seen in Table 2.13.

Table 2.13. Range of arsenic concentrations (μg/l) in natural waters.

Range of concentrations	Aquatic medium
0.2-230.0	freshwaters (Bowen, 1979)
0-198,000[1]	natural freshwaters (Woolson, 1975)
0.16-54.5	lakes (Onishi, 1978)
0.2-25.0	rivers (Onishi, 1978)
0.001-13.9	rain over Japan (Kanamori and Sugawara, 1965a; Onishi, 1979)
0.2-1.0	rainwater over N. Pacific (Kanamori and Sugawara, 1965a)
<0.002-0.59	rain and snow (Andreae, 1980)
0.6-0.75	snow and ice (Kanamori and Sugawara, 1965)
0.08-22.0	groundwater (Onishi, 1978)
0.15-6.0	seawater (Kanamori, 1965; Onishi, 1978; Morita and Edmonds, 1992)
0.5-3.7	seawater (Bowen, 1979)

[1]a highly saline natural lake (Searles Lake, California) in the US.

2.4.1 *Groundwater and geothermal waters*

In non-thermal groundwater, unaffected by mans activities, elevated levels of arsenic are most commonly associated with black shales and with volcanically derived sediments, and their source rocks - notably those of intermediate to acidic composition. However, although the arsenic may ultimately be a result of weathering of volcanic rocks, the elevated arsenic concentrations in sedimentary areas may be a result of reactions occurring within volcanically derived sediments. Additionally, it is important to emphasise the possibility of pollution resulting from a wide range of human activities, some of which are mentioned in Section 2.7.

High levels of arsenic have been found in some drinking waters (see Table 2.14). Contamination of these waters may arise from obtaining waters that pass through layers of arsenic rich pyrites, leaching of mine wastes, or drilling wells through previously contaminated soils. Generally, however, drinking waters are relatively arsenic free. An interesting and unexplained observation of groundwater arsenic concentrations was made by Frost et al (1993). They report up to 19 fold variations of arsenic concentrations in drinking water from wells in Washington (USA), and cite three other studies also from the United States where seasonal variations were observed and unaccounted for.

Table 2.14. Arsenic content of some drinking waters

Source	Concentration (µg/l)
Argentina	trace-300
Argentina, Cordoba Province	300-1,000[1]
Canada	300-7,500
United States	trace-100[2]
Wenatchee, Washington (US)	5-6[3]
Minnesota (US)	11,800-21,000[4]
Taiwan	250-850[5]
West Bengal, India	3.7mg/l[a]

[1]Contains waste products from mining; [2]10% exceeded 10µg/l; [3]watershed treated with lead arsenate; [4]well dug through contaminated soil; [5]naturally contaminated artesian well water.
From Woolson (1975), and [a]Bagla and Kaiser (1996).

In general, geothermal water has higher arsenic concentrations than non-thermal water that does not drain from mineralised areas, as seen in Table 2.15. The geochemical controls and sources of arsenic in geothermal systems are not well understood, with great debate as to whether the arsenic in geothermal systems is primarily of magmatic origin or of rock leaching origin. Links are thought to exist between arsenic and chloride (Stauffer and Thompson, 1984; Sonderegger and Ohguchi, 1988) and arsenic and sulphide minerals such as orpiment and realgar, indeed, chloride is the principle correlate of arsenic in all of the explored high temperature igneous systems (Stauffer and Thompson, 1984).

Table 2.15. Arsenic concentrations in geothermal waters and brines.

Location	Range (mg/l)	Source of Reference
Imperial Valley, California:	0.025-12.0	White, (1968)
Steamboat Springs, Nevada:	2.1-3.3	Ellis (1979); Stauffer and Thompson (1984)
Lassem Park, California:	2.2-24.3	Stauffer and Thompson (1984)
El Tatio, Chile:	47.0	Stauffer and Thompson (1984)
Broadlands, New Zealand:	3.2; 5.7	Ellis (1979); Stauffer and Thompson (1984)
Kyushu, Japan & Wairakei, New Zealand	0.5-4.8	Ellis (1979); Yokoyama et al (1993)
Kizildare, Turkey	38.0	Ellis (1979)

Yokoyama et al (1993) in studies in Japan and New Zealand, found that, in general, As(III) dominates in geothermal waters directly discharged from deep underground reservoirs, but that As(V) predominates in carbonate type geothermal springs. The thermodynamic properties of As(III) and As(V) have recently been estimated; however, critically evaluated data for arsenic minerals and aqueous complexes are not available. Thus the evaluation of saturation of geothermal water with

respect to arsenic minerals in geothermal systems is not presently possible (Welch et al, 1988).

Groundwaters are isolated from the atmosphere, resulting in a generally depressed redox condition. As a result, arsenic that is present in these waters will exist primarily in the trivalent state, unlike surface waters where As(V) predominates (Peters et al, 1996).

2.4.2 *Seawater*

The concentrations of the various commonly occurring arsenic species in the surface waters of the world's oceans are given in Table 2.16.

Table 2.16. Arsenic concentrations in the surface waters of the oceans (µg/l).

As species	East Indian Ocean	Antarctic Ocean	North Indian Ocean (Ave)	China Sea	Indonesian Archipelago
As(V)	0.452	1.045	0.47	0.34	0.418
As(III)	0.232	0.003	0.196	0.172	0.175
MMAA	0.032	0.007	0.033	0.016	0.033
DMAA	0.05	0.023	0.176	0.085	0.089

From Santosa et al, 1994.

It is some twenty years since Andreae (1978) found that within the upper layers of seawater, the distribution of arsenic is fairly even between As(III), As(V), MMAA and DMAA, whilst below the photic zone, nearly all the arsenic is present as As(V). The 'upper layers' are taken as meaning the photic zone, which is defined as the waters above the point at which light intensity is reduced to 1% of its surface value (Andreae, 1978). [Note: this is not a physical boundary, as the density transition or thermocline is].

2.4.2.1 *Photic zone*

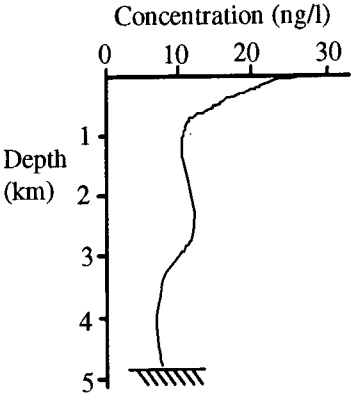
i) Organoarsenicals

MMAA and DMAA are found to be almost exclusively confined to the photic zone, both showing similar profiles of decreasing concentrations with increasing depth, although MMAA concentrations are generally much less than those of DMAA (Andreae, 1978; Santosa et al, 1994). A generalised vertical profile of DMAA in the deep ocean is given in Figure 2.1. Generally, the percentage of organoarsenic compounds as a percentage of total dissolved arsenic is in the order of 11 to 30%

(Millward et al, 1996), although levels of around 62% have been reported from Chesapeake Bay (Millward et al, 1996) and up to 87% has been found in the Gulf of Finland (Blanck et al, 1989).

The concentrations of MMAA and DMAA, drop off markedly just before the base of the photic zone, suggesting that they are produced by the phytoplankton or by heterotrophes associated with primary producers within this zone. Further evidence is given by the highly significant correlations of methylarsenical concentrations with chlorophyll concentration and ^{14}C-uptake (Andreae, 1978), together with total nitrogen and phosphate (Santosa et al, 1994), although Millward et al (1996) point to an inverse relationship between dissolved arsenic concentrations and chlorophyll-a concentrations as providing circumstantial evidence for arsenic uptake by phytoplankton. A high degree of correlation also exists between the concentration of DMAA and the ratio of As(V) to inorganic phosphate. Arsenic has for some time been known to be a competitive inhibitor of phosphate uptake in algae, and this correlation is related to the detoxification mechanism, by which algae methylate or reduce arsenic in order to avoid poisoning (Andreae, 1978). More recent work (Howard and Comber, 1989, 1992) suggests that the concentration of dissolved arsenic in coastal waters is underestimated by up to 25%, due to the types of analytical procedures utilised by previous researchers. UV irradiation of surface water samples resulted in the breakdown of non-hydride forming arsenicals to DMAA and TMAO. It is thought that the majority of the 'hidden' arsenicals originates from algal arsenosugars.

Figure 2.1. Vertical profile of DMAA in the eastern South Pacific.

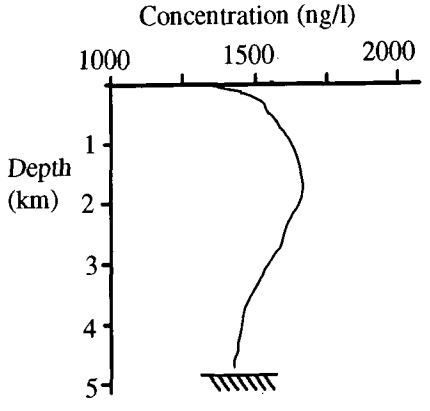


From Santosa et al (1994).

ii) Inorganic arsenicals

A generalised vertical profile of total inorganic arsenic in the deep ocean is given in Figure 2.2. As(III) is less uniformly distributed than the organoarsenicals, and Andreae (1978) found two differing depth concentration profiles for this species. In one, the concentrations show little change throughout the euphotic zone and decrease beneath it, whilst in the other, the As(III) concentrations show a marked increase towards the bottom of the photic zone, with some increase below it, before concentrations decrease. The producers of As(III) in the surface ocean waters have not been identified (Andreae, 1978), although the reduction of As(V) to As(III) by various organisms has been identified, e.g. by marine bacteria (Johnson, 1972), and a variety of phytoplankton (Sanders and Windom, 1980; Sanders and Riedel, 1993). As(III) is slowly oxidised to As(V) in seawater even under sterile conditions. The oxidation of As(III) to As(V) is, however, known to take place rapidly (10mg/l to zero in under 10 minutes) in aerated distilled water subjected to UV radiation, although the rate is almost two orders of magnitude slower if the water is deaerated (Brockbank et al, 1988). The photolyses of MMAA and DMAA are both complete in about 100 minutes under aerated conditions, with 85% of AsBe being oxidised ultimately to As(V) after 300 minutes (Brockbank et al, 1988). In seawater, the rates of oxidation are slower; the half-life of As(III) being in the order of 5 minutes, rather than 2 as for distilled water.

Figure 2.2. Vertical profile of As(III) + As(V) in the eastern South Pacific.



From Santosa et al (1994).

As(V) levels in surface waters are much lower than in deeper waters. This suggests a biological removal of As(V) from the surface waters, downward transport in

biogenic particles and release below the euphotic zone by heterotrophic processes, similar to phosphate (Woolson, 1975; Andreae, 1978; Santosa et al, 1994). The close correlation between total arsenic and phosphate concentrations supports this point. Some workers have erroneously stated that all inorganic arsenic present in seawater is As(III), including Luh et al (1973).

2.4.2.2 *Deeper waters*

i) Organoarsenicals

Below the euphotic zone, organoarsenical concentrations drop to below detection limits, with DMAA being found only in a few samples below 200m (Andreae, 1978). Santosa et al (1994) also found a significant decrease in DMAA concentrations with depth, with concentrations at 4.5km being less than a third of that present in near surface waters, as can be seen in Figure 2.1.

ii) Inorganic arsenicals

As(III) concentrations generally decrease with depth, although higher values are thought to be a result of water mass mixing, with surface waters rich in organic matter and oxygen coming into contact with nutrient rich oxygen depleted deep waters. This could support an elevated activity of heterotrophic organisms that reduce As(V) to As(III) [Andreae, 1978].

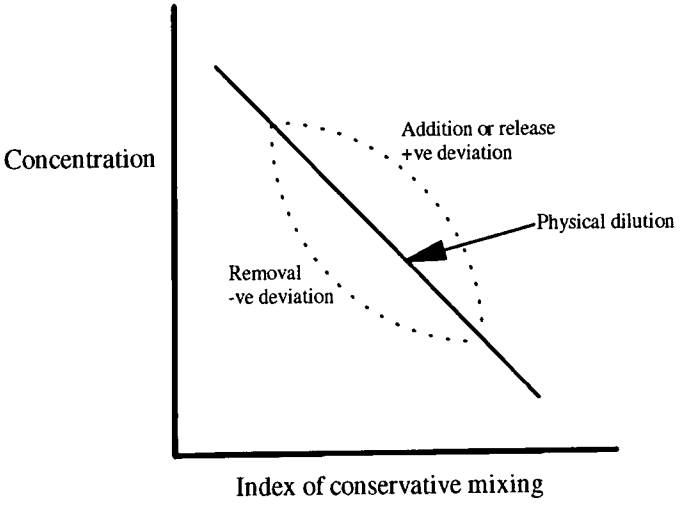
Total dissolved arsenic concentrations generally increase with depth. This increase is most pronounced at intermediate depths (100-400m), suggesting regeneration of inorganic arsenic from organic matter (Andreae, 1978). Santosa et al (1994) found that total inorganic arsenic concentrations increased down to around 2000m depth, beyond which there was a gradual decrease to the seabed. This was found to be concurrent with an increase in dissolved oxygen and these conditions are suitable for the coprecipitation of arsenic with hydrated heavy-metal oxides (Santosa et al, 1994). As(V) accounts for almost all of the dissolved arsenic at these depths.

2.4.3 *Estuarine waters and sediments*

Estuaries tend to act as sinks for heavy metals coming from rivers and the atmosphere, and arsenic is no exception to this. Because of their sheltered environment, there is time for chemical and physical processes to occur to sediments before they are swept out to sea. An important process for the concentration of arsenic, and other trace elements, in estuaries is the mixing of the fresh and saline waters and sediments. Stable particle suspensions in freshwaters become unstable in saline waters due to double layer compression, leading to flocculation and subsequent elemental concentration in suspended particles and sediments.

Arsenic concentrations generally decrease in river sediments as they mix with saline waters. This behaviour, if there is no loss of arsenic from the system is termed 'conservative', portrayed by the solid negative deviation line in Figure 2.3. If, however, mobilisation of the arsenic from the sediments into solution occurs, then 'non-conservative' behaviour may occur, particularly if arsenic is added to (+ve deviation) or

Figure 2.3. Behaviour of metals on mixing of fresh and saline waters and sediments.



From Bourg, 1981a; Fergusson, 1990.

lost from (-ve deviation) the system as a result. A number of different factors operate to give these results:

a) Dilution of the fluvial sediments can occur with less contaminated marine sediments.

b) Mobilisation may be achieved through the mass action effect of increasing cation concentration in the saline water.

c) Decay of organic material in the estuary produces organic ligands that give additional metal binding sites, resulting in metal extraction from sediments into the overlying water.

d) Alteration of the solid species (such as clays and organic particles) on mixing, and changes in grain size distribution will change the number of potential binding sites.

e) Tailing off of the metal concentration with increasing distance from source as deposition occurs.

It is not possible to predict which of the above factors is likely to dominate in any particular estuary, as the concentrations of arsenic vary from place to place and from sediment to sediment, depending upon the local inputs, but the fraction of arsenic which leaves an estuary will depend on the flux between dissolved and suspended matter. Arsenic concentrations in estuarine sediments varies considerably, as may be seen in Table 2.17.

However, most of these processes are surface dependent through surface charge, nucleation process or uptake by plants and organisms (Bourg, 1981a). Additionally, all of these processes are pH dependent, as will be discussed in later chapters.

Table 2.17. Arsenic concentrations in some estuarine sediments.

Location	Sediment concentration
Nigeria	4.7-7.6μg/g
Restronguet Estuary (UK)	900μg/g
San Francisco Bay (USA)	8-12μg/g
Yxpila Bay (Finland)	39-470mg/kg[1]
Rönnskär (E Sweden)	16000mg/kg[1]

From Fergusson, 1990: [1]Karlman, 1981.

It is interesting to note, however, that a linear relationship between arsenic and salinity has been made in estuarine waters (Maeda, 1994). As salinity increases, so too does dissolved arsenic, suggesting that arsenic does not behave conservatively in estuaries receiving little anthropogenic input (Maeda, 1994). This is also seen in some European estuaries, such as the Tamar, where arsenic undergoes biologically mediated

removal and mid-estuary addition, and the Scheldt estuary, where arsenic undergoes addition as a result of variations in river flow (Millward, 1995).

2.4.4 *River and lake waters and sediments*

As with marine waters, arsenic in rivers and lakes is divided between suspended particles and sediments, and the operationally defined 'dissolved' phases. Factors influencing the partitioning of arsenic between these two compartments include:

a) arsenic speciation, controlled by pH, redox conditions (discussed in Chapter 4), and other species present;
b) uptake and excretion by animals and plants (discussed in Chapter 5);
c) seasonally variable redox conditions causing formation or dissolution of insoluble compounds.

A major contributor of arsenic to both rivers and lakes is the proximity of mining and mineralised areas, with the oxidation of sulphides leading to the generation of acidic waters (acid mine drainage) which will contribute to the increased solubility of arsenic and other metal species.

A general comparison of the arsenic contents of various freshwaters is given in Table 2.18, while an approximate breakdown of the various arsenic species present in freshwater is given in Table 2.19.

Table 2.18. Arsenic concentrations (μg/l) in freshwaters.

Freshwater	Rivers, non-polluted	Rivers, polluted	Rivers, mining areas	Lakes
<1-5	<1-10	10-1000	100-5000	1-70

From Fergusson, 1990.

Table 2.19. Concentration of some arsenic species in freshwaters in the US (μg/l).

Location	As(III)	As(V)	MMAA	DMAA	Total As
Withlacoochee River	<0.02	0.16	0.06	0.20	0.42
Remote pond (Withlacoochee Forest)	<0.02	0.32	0.12	0.62	1.06
Residential Lake A, Tampa	0.76		0.07	0.16, +0.14 TMAO	1.13
Residential Lake B, Tampa	2.74	0.41	0.11	0.32	3.58
Residential Lake C	0.89	0.49	0.22	0.15	1.75

From Braman, 1975.

The level of arsenic in river and lake sediments varies greatly depending upon location, and direct comparison of concentrations is not easy. A useful summary, however, that introduces the diversity of influencing factors has been suggested by Förstner and co-workers (Fergusson, 1990), who state that the concentration of the trace element of interest in the sediment of interest is a function of the influence of the lithogenous units (L), hydrological effects (H), geological features (G), man made (cultural) influences (C), the influence of vegetation (V), mineralised zone effects (M), and the error or other factors not taken into consideration (e).

At any location, one or more of these factors may be dominant, and the level of arsenic in the sediment will also depend upon the intensity of these contributing factors. With arsenic, the influences of hydrology and vegetation are minor in comparison with the other contributory factors, and a few examples are to be found in Table 2.20.

Table 2.20. Arsenic concentrations in some freshwater top sediments.

Location	Concentration (μg/g)	Comments	Dominant Factor(s)
Canadian lakes	2.7-13.2	Near natural	L, G
Adriondack lakes (USA)	5.3-6.5	Near natural	L, G
River Niger	3.9-4.3	Near natural	L, G
Niagra river system	2.7-14	Polluted	L, G, C
Lake Michigan	8.0-30.5	Industrial	L, G, C
Japanese rivers	79-760	Arsenic mining area	M, C
Nova Scotia streams	>3000	Gold mining area	M, C
Big Cedar lake (USA)	150-659	$NaAsO_2$ herbicide	C
UK streams	<50-5000	Mining areas	M, C
Green Bay (USA)	10.9-42.5	Pulp/paper industry	C

From Fergusson, 1990.

If the arsenic source is a point source, then concentration should decrease with increasing distance from the source, due to dilution with less contaminated sediments, although this is not always the case (Bright et al, 1994). Non-point or diffuse sources will obviously have a lesser local effect, but may cause pollution over a much wider area. Changes may also occur with time, either as more or less arsenic is added to the sediment due to changing land use or industry, or as controlling environmental factors vary (such as tides, rainfall, temperature, etc.).

In deep lakes, a similar stratification with regard to arsenic speciation as observed in the marine environment is seen, with precipitation, oxidation and reduction, and adsorption, reduction and methylation all occur within a single lake (Woolson 1975;

Seyler and Martin, 1989; Bright et al, 1994). However, this stratification is often seasonal, with the development of both thermal and dissolved oxygen stratification. This layering controls the concentrations of dissolved arsenic species, with redox processes being dependent upon the dissolved oxygen concentrations (see Chapter 4) and the temperature controlling the activity of microorganisms (see Chapter 5).

2.5 Air masses and precipitation

The atmosphere is an important vector of global metal transport between regions, from land to sea and from sea to land. Direct atmospheric deposition tends, however, to make only a small contribution to the total metal contents of the lithosphere, because of the relatively large reservoir in soils and rocks (see Table 2.1).

The atmospheric input of trace metals (including arsenic) has now been regarded as being of considerable importance to the marine system, however, riverine inputs have, for many years, been thought to be the dominant input route for many metals to the oceans. Recent studies show, however, that arsenic terrestrial fluxes may be equalled or even exceeded by atmospheric inputs (Spokes and Jickells, 1995). The impact of arsenic inputs on ocean biogeochemistry is, however, strongly dependent upon the physical and chemical form in which arsenic enters the marine system. In terms of the physical form, inputs of particulate material are unlikely to have a significant impact on biological activity, since the material has a short (<100 days) residence time in the surface ocean. Soluble inputs in contrast, have much longer residence times and can be much more easily taken up by the biota, have a more profound effect on ocean biogeochemistry (Spokes and Jickells, 1995).

It should be noted that arsenic can occur at quite high concentrations in airborne particulates (0.5-85mg/kg over London and Milan) compared to total air contents (0.007-1.9ng/m^3 from clean areas; 1.5-53.0ng/m^3 over Europe and 5.5-850ng/m^3 over volcanoes) [Bowen, 1979]. The oxidation state and chemical speciation of arsenic also play an important role in governing the availability and toxicity to the biota, with reduced forms being more toxic than the oxidised forms, and methylarsenicals generally being less toxic than the inorganic forms. This is discussed in Section 2.5.1.

Of the northern hemisphere marine area, around 71% (the Pacific and Indian oceans) has an atmospheric arsenic concentration in the order of 0.07ng/m^3 (Walsh et al, 1979b). The Atlantic area (the remaining 29% of the northern hemisphere marine area)

To enable the prediction of concentrations of trace elements in precipitation originating from air masses or vice versa, Cawse (1974) determined the normalising empirical 'washout factor', where:

$$\left[\frac{(\mu gAs/l\ rain)}{(\mu gAs/m^3\ air)}\right] = 335$$

The results of Andreae (1980) correlate very well with values of arsenic in precipitation predicted by this formula. The concentration in rain derived from unpolluted oceanic air masses is in the order of 0.019µg/l, and from terrestrial air masses about 0.2µg/l-0.4µg/l (Andreae, 1980).

Higher than average arsenic concentrations in precipitation are often associated with urban areas (7.0µg/l from Seattle, for example [Fergusson, 1990]) and other localised anthropogenic sources, such as metal smelters (Carpenter et al, 1978), although volcanic inputs are thought to be important in the long-term (Ferguson and Gavis, 1972), with concentrations falling in the range 63-812µg/l (Fergusson, 1990). Combustion of coals is estimated to release an average of 2.5g of arsenic into the atmosphere for every ton of coal consumed (Ferguson and Gavis, 1972) although using the information of Bertine and Goldberg (1971), this figure may be closer to 0.25g, with oil combustion releasing around 0.001g/tonne.

It is also interesting to note that arsenic has been identified as showing seasonal variations with regard to aerosol behaviour, with increases in concentration during the winter months. These increases were related to the increased domestic use of coal as a heating source. The general decline in both overall atmospheric arsenic concentrations and in these seasonal fluctuations over Britain over the period 1957 to 1974 has been related to the introduction of the 1956 Clean Air Act (Bowen, 1979).

2.5.1 *Atmospheric-arsenic speciation*

Andreae (1980) found no trace of the organoarsenicals MMA, MMAA, DMAA or TMAO (detection limits: 0.1ppt for DMAA and 2.0ppt for the other species) in any of the rainwater samples taken for his study. It was therefore concluded that due to the high stability of DMAA, organoarsenicals must not be a major component of atmospheric arsenic concentrations. This is in broad agreement with the general finding

that, although arsenic biomethylation does occur in the oceans, volatile arsine and methylarsines have not yet been detected in marine (or fresh) waters, although incubation of sediments with culture media has resulted in their formation (Walsh et al, 1979b; Reimer, 1989). DMAA and other more common organoarsenicals released by phytoplankton are not volatile and are highly soluble [MMAA is completely soluble; DMAA has a solubility of 660g/l at 25°C (Pontius et al, 1994)]. As(V) is the dominant form of arsenic in the open ocean (Andreae, 1979), and it is to be expected that most arsenic injected into the atmosphere from the ocean would be in the inorganic pentavalent form. Most industrial emissions (particularly those from smelters) are in the form of arsenic trioxide (As_2O_3) with arsenic in the trivalent form (Andreae, 1980). This suggests that, as most arsenic detected in airborne particulates is in the pentavalent form, then if coal and smelting are the dominant anthropogenic sources, then oxidation of the As(III) to As(V) must be fairly rapid.

The major fraction (>90%) of atmospheric arsenic is particulate (Walsh et al, 1979a), so solid phase reactions would be expected to dominate, with both oxidation of As(III) [by ozone, molecular oxygen at pH's of between 0-6 and by H_2O_2 activities of 10^{-40} or greater] and the reduction of As(V) [most likely by dissolved SO_2 or bisulphite (hydrogensulphite) ion, even at very low concentrations] being possible (Andreae, 1980). The oxidation state of arsenic in the atmosphere is therefore controlled by a balance of reducing and oxidising species within an air parcel, and by competing reaction and diffusion kinetics. It may thus be possible to use the oxidation state of arsenic in precipitation or in atmospheric particulate material as an indication of the prevailing redox condition in the atmospheric environment (Andreae, 1980). As(V) is the major arsenic species present in coal fly ash, whilst As(III) species (particularly As_2O_3) are thought to predominate in smelter dusts (Andreae, 1980; Bhumbla and Keefer, 1994; EPRI, 1995). This is discussed further in Section 2.7.1.

As(V) and DMAA have been detected in rainwater, and inorganic As(V) is the only arsenic species to be detected in airborne particulates over temperate near-shore waters. Recent work, however, has shown that almost 10% of air particulate arsenic may comprise methylarsenicals (Maher and Butler, 1988). They also showed this to be subject to seasonal variations, with concentrations being high in the summer and low in the winter, in accordance with the observed temperature changes.

Methylarsines formed from the microbial degradation of alkylarsenicals are very unstable in air at concentrations above 0.05ppm to 0.10ppm (Sandberg and Allen, 1975) and are rapidly oxidised to less reduced arsenic species such as DMAA and TMAO, probably on the surfaces of airborne particles. It is therefore clear that methylated arsenical compounds are present in the atmosphere in association with particulate matter, but little is known about the vapour-phase distribution of these compounds. Although methylarsenicals such as DMAA are quite stable, they may be demethylated by UV irradiation. This may only be significant at altitude, as MMAA and DMAA, have been found to be unaffected by exposure to sunlight at ground level (Cullen and Reimer, 1989), although Brockbank et al (1988) have found this not to be the case (see Section 2.4.2.1).

2.6 Living things

The first systematic study of the biological formation of arsines [$(CH_3)_{3-n}AsH_n$ (where n = 0-3)] was provided by Gosio in 1893, who reported that a number of fungi gave off a strong garlic like odour when they were grown in the presence of sodium arsenite. Later workers erroneously concluded that the gas was diethylarsine, but Challenger et al (1933) proved that the gas was in fact TMA, and investigated the ability of a number of arsenic derivatives to act as precursors in arsine synthesis. Subsequent studies have shown that the ability to produce TMA is widespread amongst yeasts and fungi. However, bacterial transformations of arsenic were only relatively recently identified by McBride and Wolfe in 1971. The theoretical biological pathways involved in organoarsenical formation are described in Chapter 5.

The presence of MMA, DMA and TMA has not been reported in terrestrial or marine waters (Andreae, 1977, 1978), although incubation of sediments with culture media has been shown to produce the volatile arsenic compounds arsine [AsH_3], MMA, TMA and the methylarsenic(V) compounds $(CH_3)_nAs(O)(OH)_{3-n}$ (n = 1, 2, 3) [Reimer, 1989]. Arsenic's speciation varied, with time being controlled by the biochemical activity of the dominant microbe(s) (Reimer, 1989). The proportion of methylarsenic(V) compounds in coastal sediment interstitial waters gave no relationship to the organic content of the sediment, nor to the singular presence of high arsenic concentrations - evidence points to in situ microbial methylation and demethylation (Reimer, 1989), a view partly contradicted by Bowell et al (1994).

It is now known that a wide range of anaerobic and aerobic bacteria are capable of methylating arsenic (Cullen and Reimer, 1989; Fergusson, 1990). The major difference between fungi and bacteria appears to be the greater variety of arsines produced by bacteria (Cullen and Reimer, 1989).

DMAA has been suggested (Ridley et al, 1977) as being the dominant methylated species in both freshwaters and seawater. Walton et al (1986), Anderson and Bruland (1991) and Millward et al (1993) showed that DMAA is the dominant methylated arsenic species released from sediments in freshwaters, while MMAA is the dominant form released from saltwater sediments, although in estuaries, DMAA tends to dominate (Walton et al, 1986; Millward et al, 1993; Kitts et al, 1994). In some cases, however, MMAA concentrations are close to or exceed those of DMAA. Dimethylarsenic species are generally regarded as being the dominant organoarsenicals in ocean seawater (see Table 2.16). Arsenic containing ribofuranosides are ubiquitous in algae, and arsenobetaine is the predominant form in marine animals. These forms, however, probably do not make up the bulk of the arsenic budget in natural waters, since the products excreted by algae and aquatic animal culture appear to be limited to the inorganic and methylated forms (Cullen and Reimer, 1989).

It is not clear if these excreted compounds have any physiological significance or whether they merely represent stages in a sequence of detoxification and elimination (Edmonds et al, 1993). Marine biomethylation of arsenic has been associated with phytoplankton because of their need to take up phosphate from the water column. Difficulties arise during this process because As(V) is chemically similar to phosphate and the phosphate/arsenate concentrations may be close to equimolar in the coastal boundary zone (Millward et al, 1993). Previous work, reported in Millward et al (1993), has indicated that phytoplankton discrimination between As(V) and phosphate at equimolar concentrations is relatively poor, being only a factor of between two and ten. In biologically productive waters, phytoplankton may take up As(V), leading to poisoning by uncoupling of the oxidative phosphorylation mechanism (Lindsay and Sanders, 1990). Phytoplankton cells metabolise As(V) to methylated species and more complex molecules such as arsenosugars possibly as a detoxification pathway (Cullen and Reimer, 1989). The consequence of these biological processes is that dissolved methylated arsenic species have been detected in estuarine and coastal waters, and that whilst MMAA and DMAA may be the most common, other more complex

organoarsenicals have been identified (Howard and Comber, 1989, 1992; Hasegawa et al, 1994; Hamasaki et al, 1995; Millward et al, 1996).

Micro-organisms have also been shown (Ehrlich, 1963, 1964) to increase the rate of arsenic release from minerals including orpiment (As_2S_3), enargite (Cu_3AsS_4) and arsenopyrite (FeAsS). Autotrophic bacteria probably catalyse the oxidation of sulphide to sulphate and ferrous iron to ferric iron. Oxidation of As(III) to As(V) which also occurs, could then be purely a chemical reaction (Ferguson and Gavis, 1972).

Recently, trivalent organoarsenic compounds have been found and measured in natural waters (Hasegawa et al, 1994). These compounds, while not present at such concentrations as their pentavalent counterparts (about 20 to 60 times less for DMAA, and less than 2.5 times for MMAA) are important as they help in understanding the biosynthesis of some of the other organoarsenicals. MMAA(III) and DMAA(III) are thought to be produced through the reduction of MMAA and DMAA by hydrogen sulphide and may exist for some considerable time even under aerobic conditions. It is thought that the trivalent methylarsenicals are probable intermediates in the biosynthesis of organoarsenicals where the methylation of As(V) proceeds through alternating reductive and oxidative methyl transfer (McBride and Wolfe, 1971). In addition, Hasegawa et al (1994), state that MMAA(III) and DMAA(III) are more toxic than inorganic As(III).

It appears that biological reactions play a secondary role in the appearance of As(III) in groundwater (Korte and Fernando, 1991). These reactions are important in lowering the redox potential, and their effect on the distribution of arsenic species in groundwater has not been studied, but apparently is minor (Korte and Fernando, 1991).

2.6.1 *Accumulation*

Concentrations of methylated forms of arsenic in natural waters (fresh and saline water) have been generally reported in connection with developing analytical methodologies. It is well known that marine crustacea, shellfish and algae accumulate arsenic at the order of mg/kg, although terestrial organisms do so only at the order of μg/kg (Morita and Edmonds, 1992; Edmonds et al, 1993; Hamasaki, 1995). The forms of arsenic in sea organisms are mostly the methylated forms (trimethylated forms in animals, particularly arsenobetaine, and dimethylated forms in plants), with only a small part being inorganic (the exception being a species of brown algae: *Hizikia fusiforme*

[Phillips, 1994]). Although heavy metals such as Hg, Cd and Cu are apt to combine with proteins, arsenic does not exist in a form combined to proteins, and more than 80% is water soluble (Hamasaki et al, 1995). Little is known as to the change in concentration with an increase in size or age of any organism, although it is known that there is little in the way of concentration up through the food-chain (Ferguson and Gavis, 1972). The structures of most of the arsenic compound mentioned above, are given in Appendix B.

2.6.2 *Marine organisms*

The concentration of organic arsenic in marine organisms (fishes, invertebrates) ranges from 4.2mg/kg to 50mg/kg (in some cases as much as 100mg/kg to 300mg/kg) (Morita and Edmonds, 1992; Hamasaki et al, 1995), although Onishi (1979) gives a range in the order of <0.0036mg/kg to 50mg/kg. The mean arsenic levels in fish caught in UK coastal waters range from 0.4mg/kg to 43mg/kg, with fish that live on or close to the seabed, such as plaice, dabs, flounder and skate having consistently higher levels than most other fish. Fish origin is also a significant factor, as was shown by the range of arsenic concentrations in plaice caught in different localities (MAFF, 1982). The levels of arsenic in UK coastal shellfish show much variation with concentrations varying from 0.9mg/kg to 80mg/kg (MAFF, 1982). Arsenic may be present in shrimp at concentrations of up to 200.0mg/kg. A comparison of the arsenic concentrations found in the soft and hard parts of marine organisms may be made by comparing Tables 2.22 and 2.23. These natural levels of arsenic are far and away greater than any terrestrial

Table 2.22. Arsenic contents of soft parts of marine animals (mg/kg).

Annelida	Coelenterata	Crustacea	Echinodermata	Mollusca	Pisces
6.0	20.0	30.0	5.0	0.005-20.0	0.2-10

From Bowen, 1979.

Table 2.23. Arsenic contents of hard parts of marine biota (mg/kg).

Porifera (SiO_2)	Echinoderms ($CaCO_3$)	Molluscs($CaCO_3$)
3.5	8.0	0.23

From Bowen, 1979.

organisms, and stimulated research into the identification of the arsenic compounds present. Early work showed the non-toxic and metabolically inert nature of the so called 'shrimp arsenic' compared to arsenic trioxide. Later work (Edmonds and Francesconi,

1977) described the methylated cationic nature of the arsenic compounds present, but stopped short of characterising the compound or compounds present. Edmonds et al (1977) isolated and characterised the arsenic compound arsenobetaine (tetramethylarsonioacetate) from the tail muscle of the western rock lobster *Panulirus longipes cygnus* George, where it was found to be the dominant arsenical.

Arsenobetaine is a predominant organoarsenic compound in a wide variety of marine animals including sponges, coelenterates, echinoderms, bivalve, gastropod and cephalopod molluscs, crustaceans, and in both teleost fishes and sharks. Although arsenobetaine is the major arsenical compound to be found in virtually all marine organisms, so far investigated, other arsenicals have been found (Cullen and Reimer, 1989; Edmonds et al, 1993; Hamasaki et al, 1995). There remains some doubt as to whether arsenobetaine is the result of external microbially mediated transformations or of processes occurring inside the animal body (Edmonds et al, 1992).

Arsenocholine, TMAO and tetramethylarsonium ion are also found in marine animals and the two former species are thought to be derived from arsenobetaine, with any biogenic or metabolic connection between arsenobetaine and tetramethylarsonium ion remaining unresolved (Edmonds et al, 1993). TMAO has also been found to occur naturally in some marine organisms, where it is thought to have arisen from the methylation of As(V) by bacteria in the digestive tract (Edmonds et al, 1993). TMA has been detected in some deep sea crustacea, possibly as a result of reduction of TMAO. Arsenosugars (arsenoribosides) are predominant in marine algae (see below), and glycerylphosphorylarsenocholine has been detected in the digestive gland of the Western rock lobster.

2.6.3 *Freshwater organisms*

Little work appears to have been carried out with regard to determining the arsenic concentrations of freshwater organisms, but Onishi (1979) gives the results of a few studies which suggest that freshwater fish contain arsenic in the range 0.02-10.7ppm, and Morita and Edmonds (1992) suggest a range in the order of 0.05-0.2mg/kg. MAFF (1982) gives mean arsenic concentrations in the order of <0.02mg/kg to 1.4mg/kg for trout, both wild and farmed. Accumulations of arsenic is much lower in freshwater organisms than in their marine counterparts (in the order of 10-100 times lower), although freshwater snails (for example) may accumulate from <1-68 times the

which belong to the Sargasso species contain significant amounts of inorganic As(V). Lipid soluble arsenic also identified in brown algae was identified as an acylated derivative of an arsenic-ribofuranoside (Morita and Shibata, 1989).

A few further studies have tried unsuccessfully to determine the nature of other arsenic compounds present in marine algae. These resulted in the production of an abundance of arsenic compounds, mostly at only trace concentrations, but apart from MMAA and DMAA, none were identified (Edmonds et al, 1993).

Due to arsenic's similarity to phosphorus, it may replace it, especially in phosphorus deficient waters, accumulating in algae in a non-methylated form, bound strongly to protein or polysaccharides in the algal cell (Maeda et al, 1990).

2.6.5 *Freshwater plants*

Freshwater plants do not accumulate arsenic to the same degree as do their saltwater counterparts (Woolson, 1975). A general set of ranges of arsenic concentrations for various freshwater plants is given in Table 2.25. It is likely that the same chemical and biological controls which apply to arsenic uptake in marine plants will apply in the uptake of arsenic by freshwater plants, although little work appears to have been carried out to this end. However, Woolson (1975) reports that algae accumulate DMAA to a much higher degree than As(V).

Table 2.25. Ranges of arsenic concentrations in some freshwater plants.

Species	Concentration (µg/g)
Algae	2-550
Submerged weeds	20-971
Emerged weeds	8-12
Lakeweeds	11-1450
Duckweeds	1-3

From Woolson, 1975.

The arsenic levels in aquatic plants vary seasonally, with maximum concentrations recorded in spring or early summer, followed by reductions of up to 90% or more in only three months. This rapid drop in arsenic concentrations may be due to the dilution effect from the large increase in plant biomass during this period (Clayton and Tanner, 1994).

2.6.6 *Terrestrial organisms*

Little or no work has been carried out on this subject except to either determine the effects of acute and chronic effects of arsenic poisoning or to assess the concentrations in foodstuffs. Indeed, it has been found that meat products are the main food, other than fish, where consistent positive arsenic levels are detected (MAFF, 1982). Most values reported in Table 2.26 are at or near the then (1982) level of detection, but pig and chicken livers and products derived from these tissues show consistently elevated levels. These residues are almost certainly due to the use of organoarsenical feed additives. These additives can be used for growth promotion purposes, e.g. in chickens and pigs, or maybe used as medicinal feed additives for the control of scour in pigs. Normally, a specified period of withdrawal of the additive should be observed before slaughter which, if obeyed, leads to lower arsenic tissue levels. The figures in Table 2.26, which refer to the emergency slaughter of pigs give some indication of the expected arsenic levels that might be expected if a period of withdrawal from the medicament were not observed (MAFF, 1982).

Table 2.26. Arsenic concentrations (mg/kg) in meat and meat products.

Food		Range	Mean
Cooked Meats		<0.05-<0.25	-
Canned Meat Products		<0.05-<0.25	-
Meat pastes and spreads		<0.25	<0.25
Fresh:			
Liver	pigs	<0.1-9.0	<0.4
	pigs (emergency slaughter)	<0.1-2.0	<0.7
	ox	<0.01-0.5	<0.1
	chicken	<0.05-3.2	<0.9
	lamb	<0.01-0.5	<0.1
Muscle	pigs	<0.05-0.1	<0.1
	ox	<0.01	<0.01
	chicken	<0.05-0.05	<0.05
	lamb	<0.05-0.1	<0.05
Hearts	pig, ox, lamb	<0.05-<0.1	-
Kidney	pig	<0.02-1.4	<0.14
	ox	<0.05-0.5	<0.11
	lamb	<0.05-0.37	<0.14

From MAFF 1982.

Levels of arsenic in animal foodstuffs are restricted to 2mg/kg overall, as shown in Table 2.27, with the exceptions indicated. Levels above this are only allowed in

materials prescribed for veterinary or medicinal purposes (The Feeding Stuffs Regulations, 1995).

Cattle grazed on pasture containing 10-11mg/kg arsenic close to a metal refining plant have had analysis performed on a range of internal organs on slaughter. The results are given in Table 2.28. It is interesting to note that the muscle in animals grazed on uncontaminated pastures contained only 0.25mg/kg in kidney samples (MAFF, 1982).

Table 2.27. Arsenic prescribed limits in feeding stuffs.

Feeding Stuffs	Maximum arsenic content (mg/kg)*
Straight feeding stuffs	2.0
except:	
-meal made from grass, dried lucerne or dried clover	4.0
-dried sugar beet pulp or dried molassed sugar beet	4.0
-phosphates and feeding stuffs obtained from the processing of fish or other marine animals	10.0
Complete feeding stuffs	2.0
except:	
-complete feeding stuffs for fish	4.0
Complimentary feeding stuffs	4.0
except:	
-mineral feeding stuffs	12.0
Arsenic as a substance in phosphate ingredients	20.0

*referred to a moisture content of 12%. From The Feeding Stuffs Regulations, 1995.

Table 2.28 Arsenic concentrations (mg/kg) in internal cattle organs.

Organ	Number analysed	Range	Mean
Liver	4	1.8-6.0	4.1
Kidney	4	1.2-4.0	2.2
Muscle	7	0.25-0.5	0.32

From MAFF, 1982.

The tissues of humans have also been analysed for arsenic content, mainly in an effort to estimate arsenic's potential as a health hazard, and to monitor health effects in relation to population intakes. The few reliable analyses available have led to disagreements by an order of magnitude or more. The hair and nails have been identified as arsenic accumulating tissues in humans, although of course, as may be seen in Tables 2.29 and 2.30, arsenic is by no means restricted to those tissues. The hair is the most frequently studied tissue for estimation of arsenic, due to its accumulative nature. The range of hair arsenic concentrations given in Table 2.29 is for persons not exposed to large arsenic doses, but workers in copper smelting plants have been reported as having

hair arsenic concentrations of up to 36.57μg/g. Unless a person has been exposed to varying amounts of arsenic, there does not appear to be any significant variation in arsenic concentration along the length of individual hair fibres. The arsenic in blood serum has been related to dietary intake with a fish diet giving rise to a significantly elevated arsenic level. (Fergusson, 1990).

Both urine and hair have been used as bioindicators for estimating exposure to arsenic both at work and at home, and the transfer from the workplace home has been reported as being indicated by elevated arsenic levels in the children of copper smelter workers (about five times higher than for unexposed children). Parental smoking also has an effect on children's urinary arsenic levels, with levels four times higher in children whose parents both smoked compared with those whose parents were non-smokers (Fergusson, 1990).

Table 2.29. Ranges of arsenic contents of human tissues, and fluids (mg/kg, wet weight) and of 'Reference Man' in mg/70kg fresh weight.

Tissue	Bowen (1979)	Fergusson (1990)
Kidney	0.007-1.5	0.00043-0.037
Liver	0.023-1.6	0.002-1.02
Muscle	0.009-0.65	0.031-0.058
Bone	0.08-1.6[1]	0.08-1.6[1]
Hair	0.06-3.7[1]	0.02-2.0[1]
Nail	0.2-3.0	0.2-3.0
Brain	-	0.024-0.037
Heart	-	0.00097-0.037
Lungs	-	0.0056-0.36
Urine	-	0-353.7
Placenta	-	0.27-1.08[1]
Milk	-	0.0016-0.0060
Reference Man	18.0	18.0

[1]Dry weight

Table 2.30. Arsenic concentration in human blood and blood constituents in mg/l.

Whole blood	Red cells	Plasma	Serum
0.0017-0.09	0.0027	0.0024	0.03?

?, inconsistent or unconfirmed data. From Bowen, 1979.

2.6.7 *Terrestrial plants*

Ecotypes of various plant species can accumulate arsenic to extreme levels (Douglas Fir needles have been reported as containing up to 10,000ppm ash weight), and these have been related to the total arsenic present in the soil (Porter and Peterson, 1975; Xu and Thornton, 1985). Djingova and Kuleff (1994) stress the point that, given the same environmental conditions, the concentration of any metal will be a function of the stage of development of the plant (namely its age), which determines among other things the degree of exposure, the direction and the level of transportation and localisation.

Morita and Edmonds (1992) suggest a general range of 0.05-0.2mg/kg for the arsenic content of terrestrial plants, although with so many different species, this figure must be regarded with that in mind. Fergusson (1990) suggests a slightly wider range of 0.02-7.0μg/g for land plants generally, and 0.01-1.5μg/g for edible plants. The arsenical component of several groups of terrestrial plants, and non-vascular terrestrial plants is presented in Tables 2.31 and 2.32.

Arsenic containing pesticides, have for a long time, been used in pest control in orchard areas and this has led, in many instances to elevated arsenic levels in the soils. The actual concentrations in the fruits are low, with apples and pears only showing a range of 0.05mg/kg to 0.3mg/kg (MAFF, 1982), although concentrations would be higher immediately after spraying, and before washing (Walsh and Keeney, 1975). Soft fruits such as raspberries and blackcurrants contain slightly higher levels in the range 0.01mg/kg to 0.18mg/kg after washing (MAFF, 1982). Vegetables contain arsenic in the range <0.01mg/kg to 0.06mg/kg.

Table 2.31. Arsenic contents of terrestrial non-vascular plants (mg/kg).

	Lichens	Fungi	Bryophytes
Range	20-6,000	30-350	500-6,000

From Bowen, 1979.

Table 2.32. Arsenic contents of terrestrial vascular plants (mg/kg).

Horsetails	Ferns	Woody gymnosperms	Woody angiosperms	Herbaceous vegetables	Kale
0.2	1.3	0.2-1.2	2.0	0.01-1.5	0.12

From Bowen, 1979.

Crops grown near metal refining plants, or in/on soils with raised arsenic concentrations show only slightly raised arsenic concentrations. This is partly due to the fact that arsenic from a metal refining plant would be deposited from the air, and is easily washed off. It has also been shown that arsenic is not readily translocated from roots to edible portions, even in vegetables such as potatoes and carrots (Sandberg and Allen, 1975; Walsh and Keeney, 1975; MAFF, 1982; Xu and Thornton, 1985; Fergusson, 1990), although there is often a correlation between increasing soil arsenic concentrations and increasing plant arsenic concentrations (Walsh and Keeney, 1975; Fergusson, 1990). There are however, some plants which seem to accumulate arsenic to quite high levels. For example, *Calluna vulgaris* (L), accumulated up to 4,130ppm (mean, 1,260ppm dry weight basis) when grown in contaminated soils, but only 0.33ppm (mean, 0.30ppm), from 'uncontaminated' sites. Similarly, *Agrostis tenuis* Sibth. contained 3,470ppm (mean 1,480ppm) from arsenic contaminated sites, but only 0.28ppm (mean 0.23ppm) from clean sites (Porter and Peterson, 1975). Comparing the highest arsenic values with the background values, a 20,000-fold range of arsenic contents is established.

Xu and Thornton (1985) investigated the arsenic contents of six salad and vegetable crops grown in gardens with elevated arsenic concentrations (see Table 2.9), and found the arsenic concentrations in the vegetables to be quite variable (see Table 2.33). The relationship between the arsenic contents of lettuce, onion, beetroot and pea and both total and extractable (water and weak acid fluoride) arsenic in the soil was found to be statistically significant, showing increasing arsenic contents in the edible tissues with increasing soil arsenic concentrations. The lack of a correlation between carrot and bean arsenic content and soil arsenic concentrations was not found to be significant, although this might be ascribed to analysis of insufficient samples (Xu and Thornton, 1985). In general, a pH increase (becoming more alkaline) or an decrease in Eh (becoming more reducing) result in a lowering of arsenic availability to plants (Fergusson, 1990).

The levels of arsenic found in the Cornish plants may be compared with some other plant arsenic concentrations given in Table 2.34. Plants growing on unpolluted or non-mineralised soils generally have very low arsenic concentrations (<1μg/g) [Fergusson, 1990]. Extreme arsenic soil concentrations result in phytotoxic response by most plants (see Section 5.9.7). Although a degree of arsenic bioaccumulation has been

recorded in pine cones, and this has been exploited as an aid in mineral exploration (Ashton and Riese, 1989). In relative terms, arsenic uptake in edible plants may be generalised (as long as the same sections of plants are compared), with beans, peas, spinach, clover, rice and peaches showing a low reactive arsenic uptake; radish, turnip, corn and cherries a medium uptake; and cabbage, tomato, oats, wheat, apples and pears a high uptake.

Table 2.33. Arsenic content in Cornish garden vegetables(ppm)

Vegetable	Range	Geometric Mean
Lettuce	0.15-3.88	0.85
Onion	0.10-0.49	0.20
Beetroot	0.02-0.93	0.17
Carrot	0.10-0.93	0.21
Pea	0.01-0.93	0.04
Bean	0.02-0.09	0.04

From Xu and Thornton, 1985.

Table 2.34. Arsenic levels in plant tissues.

Plant and tissue	Concentration (μg/g)
Clover, tops	0.28-0.33
Grass, tops	0.02-0.16
Barley, grain	0.003-0.018
Oat, grain	0.01
Rice (brown) grain	0.11-0.2
Wheat, grain	0.07, 0.05, 0.01
Cabbage, leaves	0.02-0.05
Carrot, leaves	0.04-0.08
Lettuce, leaves	0.02-0.25
Potato, tuber	0.03-0.2

From Fergusson, 1990.

Huang (1994) gives a number of regression equations relating the arsenic concentration in the soil and/or aqueous phase (in the case of paddy rice) to that found in the plants growing in that medium. In general, arsenic contents were found to increase in rice, wheat, rye grass, sweet potato and blueberry, with increasing soil concentration, although in rice, the correlation was greater in the leaves, stems and roots than the ears. In general, the distribution of arsenic in any plant is in decreasing order from the root to stem and leaf to edible parts. Porter and Peterson (1975) found that plant (*Agrostis tenuis* Sibth.) leaves of different ages exhibited a ten-fold increase in arsenic concentration, from 100ppm in the youngest leaves to 1,340 in the oldest. This contrasts

with the Douglas Fir, which showed that recent growth contained more arsenic than the older growth, and that stems contained more than the needles they bear. The process of arsenic accumulation with leaf age may represent a detoxification process (Porter and Peterson, 1975).

The effects of MMAA and DMAA as herbicides have been investigated, and the arsenic residues shown to adversely affect the growth and productivity of soybean. Other crops are not affected in the same way, with the yields of cotton corn, oats, vetch, sorghum-sudan hybrid, and crimson clover unaffected by previous arsenic treatments. However, the seeds of cotton, and soybeans accumulated more arsenic than did corn, forage from sorghum, or the winter crops (Huang, 1994).

2.7 Anthropogenic inputs

The extraction, processing and utilisation of natural resources release arsenic into the air, soil and water. This activity results in environmental input that exceeds all natural sources (Peters et al, 1996). The unintentional or deliberate release of arsenic into the environment from human activities cover a wide range of activities. These include smelting or roasting of any sulphide containing mineral, combustion of fossil fuels, application of arsenic containing pesticides and herbicides, rapid weathering or leaching of exposed wastes from mining and ore processing activity, from the manufacture of arsenicals, from industrial or other waste disposal, from chemical warfare agent disposal and due to the greatly accelerated erosion of land. Of these, only the erosion of uncontaminated land always results in low concentrations in the aquatic environment.

2.7.1 *Mining, smelting and power generation*

The geochemical controls are generally poorly known for mineralised areas where mining has taken place, mainly as a result of few secondary arsenic bearing minerals being identified. Arsenopyrite (FeAsS) is a likely source for some dissolved arsenic in these areas, although such minerals as orpiment and realgar, together with arsenic-rich iron oxides are also important. Scorodite ($FeAsO_4.2H_2O$), a secondary mineral resulting from weathering, may limit arsenic concentrations in some areas (Dove and Rimstidt, 1985). Ferric oxyhydroxide contains high arsenic concentrations in stream sediments of mineralised areas indicating that iron oxyhydroxides may limit the aqueous

arsenic concentrations where it is forming (Bowell, 1994; Bowell et al, 1994). The processes controlling the role of iron oxyhydroxides are discussed more fully in Chapter 4 (Section 4.8.4.1).

In Cornwall, arsenic levels in some agricultural soils near former mining areas are as high as 2,500ppm. These high levels are due to rainfall leaching arsenic from old spoil heaps and natural mineralised deposits, together with aerial fallout of arsenic from the former copper, tin and arsenic smelting works. This historical pollution generally dates from between 1860 and 1900, when Cornwall was the world's major producer of arsenic, importing additional arsenical ores for smelting at the industry's height (Xu and Thornton, 1985).

Combustion of coals is estimated to release an average of 2.5g of arsenic into the atmosphere for every ton of coal (depending upon the arsenic content of the coal) consumed (Ferguson and Gavis, 1972), although using the information of Bertine and Goldberg (1971), this figure may be closer to 0.25g, with oil combustion releasing around 0.001g/tonne. Obviously, in the days of the industrial revolution, and before the introduction of air quality legislation, the relative proportion of arsenic released into the atmosphere from coal combustion was considerably higher than today.

Both inorganic arsenic species are released from coal on combustion, and total arsenic concentrations are higher in fuel ash than in bottom ash or flu gas desulphurisation sludge (Bhumbla and Keefer, 1994). As(V) is thought to be the dominant arsenic species in coal combustion by-products, whilst As(III) species (particularly As_2O_3) are thought to predominate in smelter dusts (Andreae, 1980; Bhumbla and Keefer, 1994; EPRI, 1995). Arsenic in fly ash is derived from the decomposition of pyritic material in coal during combustion, when it is volatised and subsequently condenses on the surface of fly ash particles, where it is significantly enriched compared to the interior of fly ash particles. In addition, the amount of this surface accumulation of arsenic depends on the aggregate particle surface area available for condensation, which has been shown to be inversely proportional to the particle diameter. Thus, small particles of fly ash can accumulate more arsenic than larger sized particles (Bhumbla and Keefer, 1994). The arsenic species predominating on fly ash particles is As(V), due to there being a predominance of Al, Fe and Mn, to which As(V) is adsorbed more strongly than As(III). This has important potential health implications

(as described in Section 5.9) although the mechanisms of arsenic adsorption-desorption are complex (see Chapter 4).

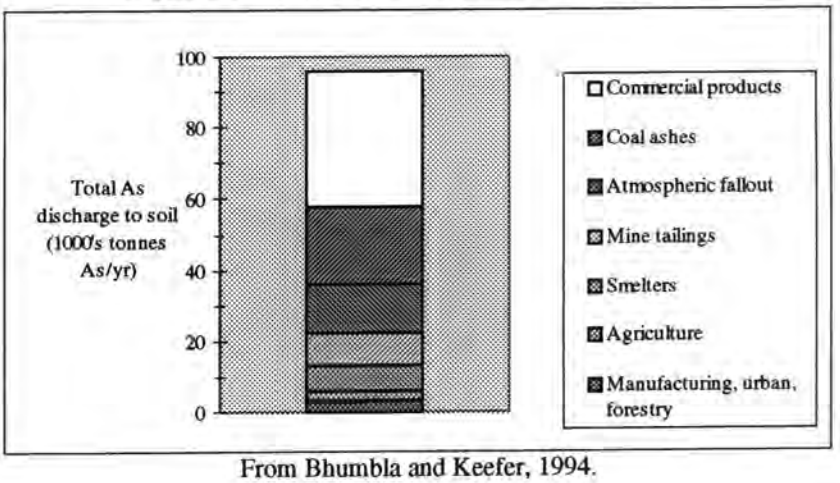
Arsenic is a natural contaminant in lead, zinc, gold and copper ores and can be released during both mining and smelting operations. The resulting stack emissions of dust and flue gasses from these smelters often contaminate soils with arsenic downwind from the operation (see Table 2.8). The arsenic associated with these emissions is generally accepted to be mainly As(III) as As_2O_3, and the potential health implications are described in Chapter 5. The Tacoma copper smelter (Washington State, USA) is a good example of this. During the period 1970 to 1980, the smelter had arsenic emission factors varying from 1.8 to 16.8kg As/t of copper produced. The degree of soil contamination around the smelter, which is now closed was a function of prevailing wind direction and distance from the smoke stack. On islands downwind of the smelter, the soils contained 90-340mg/kg arsenic, whereas on the upwind side, the corresponding values were 1-90mg/kg arsenic (Crecelius, 1975; Carpenter et al, 1978; O'Neill, 1990). Additionally, arsenic (mainly as dissolved [As(III)] species) in liquid effluents was discharged directly into Puget Sound, and also as a component of crystalline slag also dumped into Puget Sound (Carpenter et al, 1978).

2.7.2 *Soil additions*

The use of the various arsenic containing pesticides, herbicides and insecticides is briefly described in Section 3.2.5. The use, and in some cases the overuse of many of these arsenicals has resulted in many soils having high arsenic concentrations (see Table 2.8); this is especially true for many fruit orchards and cotton plantations, where soil arsenic concentrations have been reported as reaching as high as, and in some cases, exceeding 2500ppm (Walsh and Keeney, 1975), although the extent of crop damage due to arsenic phytotoxicity depends upon the pH, amount of phosphorus, iron and aluminium present, the amount of organic material present and the plant species (Sandberg and Allen, 1975, Hiltbold, 1975; Davenport and Peryea, 1991; Bhumbla and Keefer, 1994). The effects of arsenical additions to soils is more fully described below in Section 2.7.3.4.

Estimates of the amount of arsenic added to soils by various human activities vary, but a useful set of estimations are set out in Figure 2.4 and are based on figures produced in 1988.

Figure 2.4. World-wide additions of arsenic to soils.



From Bhumbla and Keefer, 1994.

As will be discussed in Section 3.4, the mass of material moved to the oceans globally is estimated to have increased from 9.3×10^{15} g/yr to 24×10^{15} g/yr (Ferguson and Gavis, 1972), as a result of accelerated erosion caused by intensive land use. Therefore, the quantity of arsenic released is at least in proportion, with an approximate increase from about 45×10^{9} g/yr to about 117×10^{9} g/yr, although Bertine and Goldberg (1971) suggest a figure of 72×10^{9} g/yr as a figure representing the weathering mobilisation of arsenic by river flow. The sum of cultural contributions that can be estimated, average 110×10^{9} g/yr for this century, approximately three times the lowest value contribution from weathering. The influence of this increase on the concentration of a well mixed ocean would, however, be negligible for many thousands of years (Ferguson and Gavis, 1972). These estimates from models of the global cycling of arsenic are often in error as they neglect to consider processes that remove arsenic in its passage from estuary to the open ocean (Maher and Butler, 1988). For example, physical processes such as flocculation of particulates and adsorption of dissolved arsenic onto freshly precipitated hydrous iron oxides, transfer the element into the estuarine sediments. Biological filters such as fringing marshes can also remove arsenic from the water column, its free dispersal in the open ocean can be further restricted by incorporation into coastal and near shore sediments.

2.7.3 *Pollution and disposal*

There have, of course been incidents where relatively large amounts of arsenic have been disposed of with no regard for the environment into which they were introduced. Indeed, arsenic has been found in at least 781 of the 1,300 National Priorities List sites identified by the United States Environmental Protection Agency (US Agency for Toxic Substances and Disease Registry (US-ATSDR), 1993).This problem may be viewed from a number of perspectives. In the one instance, disposal would not be thought of as affecting anything because no effects were seen for many years - the 'out of sight out of mind' philosophy. In the second instance, there is the philosophy that the benefits of production outweigh the costs on the environment caused by waste disposal. A third example would be the deliberate introduction of waste into the environment to avoid proper and safe disposal due to the high costs now involved in such a process. Lastly, there is the inadvertent blanket or non-point source pollution caused by soil treatment by farmers, either to increase crop growth by the addition of fertilisers containing arsenic, or by the application of arsenical herbicides and pesticides. Examples of each are usually quite easy to find, both in the literature and in newspapers, although by then the damage has been done.

2.7.3.1 *Out-of-sight-out-of-mind*

An example of the 'out-of-sight-out-of-mind' methodology of dealing with arsenic containing substances was the sea dumping of unused or obsolete chemical weapons. Arsenic containing chemical weapons are described more fully in Section 3.2.8 and their chemical form in Appendix B. From World War I until the 1970's, the dumping of chemical weapons at sea was the accepted method for their disposal. Little documentation of this practice can be found before the mid 1940's, but since then, ocean dumping has occurred in many areas, including the Baltic Sea, around Japan, the coastal waters of the United States (Mitretek, 1996), off Scotland (Nuttall, 1996; Hanley, 1996) and in the Irish Sea (Handley and Bodden, 1996; Hanley, 1996). An estimate of the amounts of arsenic containing chemical weapons dumped is difficult, but a few figures are available for selected areas, see Table 2.35. The dumping of such materials at sea is now banned through the International Sea Dumping Conventions (Nuttall, 1996), although due to their chemical nature, some chemical weapons retain their potency.

Table 2.35. Sea dumping of chemical weapons.

Location	Date	Chemical Agent Type	Chemical Agent Quantity (tons)
Bornholm basins, Baltic	1946-1947	Clark I, Clark II, Adamsite and other non As agents	5,300-6,500
12 miles off Chichagoff	1947	Lewisite	Unspecified
Site 'Baker'	1946	Lewisite	1,222
'300 miles off Florida'	1948	Lewisite	3,154
37°; 50'N, 70°; 50'W	1957	Lewisite	41
38°; 30'N, 72°; 06'W	1960	Lewisite	2
38°; 30'N, 71°; 10'W	1962	Lewisite	1
37°; 40'N, 125°; 0'W	1958	Lewisite	1,542
'Off South Carolina'	1958	Lewisite	1,281
Beaufort's Dyke off Scotland	1920-1976	Unspecified	Unspecified $>1\times10^6$ tonnes of munitions
Irish Sea	Unknown	Unspecified	Unspecified

From Mitretek, 1996.

Mustard gas (not containing arsenic per se), for example, forms a thick outer crust when dumped in seawater. The internal core of mustard is unaffected, and can cause injuries if the crust is broken (Mitretek, 1996). Lewisite might have been mixed with mustard in the past, so it might persist in the core of dumped mustard. Adamsite is also reported to form an oxide crust when dumped in seawater. Generally, however, the arsenic containing chemical weapons do hydrolyse in water, although they or the hydrolysis products may be insoluble. The ultimate end products of the hydrolysis are inorganic arsenic and organoarsenicals, although the exact reaction rates are unknown (Mitretek, 1996). Whilst this suggests there is little risk from arsenic, studies carried out around the Beaufort Dyke site have shown arsenic levels in fish to be 10 times above 'normal limits', although apparently more testing is due to be carried out in the near future (Hanley, 1996).

2.7.3.2 *Political reasoning*

An example of economics dictating arsenic containing waste disposal, is to be found in the Czech Republic. Under the post-war communist regime, the mining companies and large chemical companies enjoyed an exclusive position in the social economy. They did not have to deal with legal or financial problems and their interests were a governmental priority. This policy, aimed to maximise industrial output, led the former Czechoslovakia to being the second largest exporter of lignite in the world. However, at the same time, this policy ignored any financial, social or environmental

costs. Consequently, many environmental problems exist, but the companies responsible do not have the capital necessary to effect solutions since the removal of their financial guarantees as a result of the collapse of the communist regime in 1989. An example is to be found in northern Bohemia. Just outside the city of Ústí nad Labem lies the village of Chabarovice, close to which lies a former uncontrolled chemical waste disposal site, parts of which contains very high levels of arsenic (up to 3,200mg/kg). Because the tip is open to the elements, precipitation is not precluded from entering the waste and percolating through it, or reacting with the chemicals on its passage through it. Similarly, there is little to prevent a strong breeze carrying contaminated dust from the site to Chabarovice or other nearby villages. The water percolating through the tip emerges as the appropriately named Green and Yellow Springs. The Green Spring has the highest arsenic concentration with levels up to 14mg/l (Thomas et al, 1994). Although monitoring is taking place, the cost of the clean up of this site would be prohibitive, even though the near-surface aquifers beneath the tip are a local water resource (Šilar and Thomas, 1994).

Another example is the recent admission of responsibility by the Japanese Government for the safe disposal of a huge number (in excess of 700,000) chemical weapons left in China by its Imperial Army (Whymant, 1997). These chemical weapons, which include Lewisite, were used by the Japanese during the Sino-Japanese war of 1937-1945 and those remaining were abandoned during the Japanese retreat. These weapons have been deteriorating since their abandonment, and are apparently in an extremely poor condition, with some leaking. The extraordinary delay in the disposal of these weapons revolves around several factors. These include the political isolation of China for more than three decades after the 1949 revolution, the destruction of key Japanese war documents, and Japan's reluctance to confront its war record, including its involvement in chemical and biological warfare.

Under the 1993 Chemical Warfare Convention (which came into force in April 1997), signatories are obliged to remove chemical weapons left in other countries. However, in this case, due to the excessive hazards involved in shipping these weapons back to Japan, their disposal will take place in China. However, the biggest problem is in what technology to use in their disposal, Japan having had no involvement in such weaponry for over 50 years. The delays in prompt disposal of such stockpiles would be both politically and environmentally unacceptable (Whymant, 1997).

2.7.3.3 Industrial incidents

The remaining disposal 'philosophy', although seemingly minor in comparison with the two already described is widespread, and has caused great problems in some land development programs. It does not command the same attention, be it academic or from the media, mainly due to the relatively small amounts involved, although accidental spillages on roads or in other public areas, of course, do get the publicity. An example of the latter is the UK company National Power, who were threatened with prosecution over illegal arsenic discharges from the Drax power station into the River Aire (Ryan, 1993). A major accidental release of arsenic containing waste water occurred in 1992, when millions of gallons of contaminated mine water escaped from the former Wheal Jane mine, polluting the Carnon River and Restronguet Creek in Cornwall. The NRA were unable to bring a prosecution against the mine's former owners due to their limited powers and the complex mining history of the area (NRA, 1994). Since then, there has been increased public interest in the possibility of further pollution incidents, following the privatisation of British Coal and the subsequent closure of many deep mines. This is discussed more fully in Appendix C.

2.7.3.4 Non-point source

The non-point source pollution caused by insecticide, pesticide and herbicide spraying is another important source of anthropogenic arsenic pollution. It has been ascribed to causing widespread livestock poisoning, together with wiping out colonies of bees, in addition to the target organisms and plants (Carson, 1962). A wide range of arsenic containing chemicals have been used for these purposes, indeed, before the introduction of DDT in 1947, acid lead arsenate was the primary material used for insect control in deciduous fruit orchards (Davenport and Peryea, 1991). Other common pesticides included lead arsenate, sodium arsenate and calcium arsenate as described in Section 3.2.5. These chemicals have been used world-wide and overuse in some areas (up to 80kg/ha) has led to soil concentrations as high as 550ppm (Bear, 1964; Sandberg and Allen, 1975; Davenport and Peryea, 1991; Elfving et al, 1994). Arsenic trioxide, as an extreme example has at times been applied at rates of up to 2,520kg/ha as a soil sterilant and the persistence of inorganic arsenical applications has been emphasised, when phytotoxic effects of 2,690kg/ha sodium arsenite addition were observed 14 years after treatment (Sandberg and Allen, 1975).

Organoarsenical herbicides and pesticides are, however, generally applied at rates much lower than their inorganic counterparts, and as well as being less phytotoxic, also leave a lower proportion of toxic soil residuals (Sandberg and Allen, 1975), possibly due to either volatilisation, or through oxidative leaching.

It must be emphasised, however, that phytotoxicity due to arsenical residues in soils is not necessarily related to total soil arsenic (see Sections 2.6.7, 4.10, 5.9.7). Soils with high reactive levels of aluminium have been reported as being less phytotoxic than those with low levels of reactive aluminium (Sandberg and Allen, 1975).

Although increased concentrations of arsenic have been found in earthworms and voles, with concurrent increases in the tissues of predators fed exclusively on them, no clear relationship was found between exposure times and health effects in a study of orchard workers who had used lead arsenate for up to 21 years (Elfving et al, 1994).

The release of arsenic from soils contaminated with arsenic through applied herbicides and pesticides may occur through leaching or wind and water erosion (including biological volatilisation). As discussed in Chapter 4 leaching is not considered particularly important, although addition of phosphate containing fertilisers causes an increase in arsenic mobility, causing some downward movement (Davenport and Peryea, 1991; Peters et al, 1996). However, erosion of soils has been conservatively estimated at 2.78tons per acre per year when corn, wheat and clover are grown in rotation, If the average arsenic content of the soil is assumed to be 10ppm, then approximately 60g As/ha/year is lost from the soil to be deposited elsewhere (Sandberg and Allen, 1975).

There is no evidence to suggest that man is likely to change the world-wide distribution of arsenic appreciably, but arsenic is highly concentrated in many local environments due to man's activities (Ferguson and Gavis, 1972). The industries which use arsenic either as a major or a minor part of the manufacturing process will cause a release, be it large or small, into the environment, and obviously, some industries will produce more arsenic containing wastes and by-products than others. This generation of wastes thus requires their safe disposal, so as to prevent release into the environment, unless it can be shown that such a release will not impact upon the environment so causing any deleterious effects.

CHAPTER 3

USES, PRODUCTION AND GLOBAL MASS BALANCE

3.1 Introduction

Arsenic, a naturally occurring, ubiquitous element, is currently used primarily in the production of pesticides and wood preservatives. In the past, arsenic compounds have been used in a huge variety of industries including medicine, although arsenic will always be a synonym for poison in most people's minds.

3.2 Uses of arsenic

3.2.1 *Alloys*

Early uses of arsenic have included alloying with copper and lead, to produce metal alloys with properties similar to those of copper-tin bronze. These alloys are particularly suitable for sophisticated metallurgical production of tools and ornaments and have found use world-wide. Arsenic has also found use in the production of speculum metals (alloys of copper and tin) which give the silvery surface on mirrors and animal statuettes by the Egyptians (Dewey, 1920; Azcue and Nriagu, 1994). Trace amounts of arsenic are added to lead-antimony grid alloys used in acid batteries, and the addition of up to 3% hardens the lead and minimises the softening of lead base bearing alloys in internal combustion engines (Azcue and Nriagu, 1994). Automotive body solders usually contain 0.5% of arsenic.

3.2.2 *Medicines*

Both realgar and orpiment have been used in medicine and references are made to both in the writings of Pliny for the curing of an extremely wide range of malaises from asthma and coughs to haemorrhoids and leprosy, although Indian medical texts (the *Ras-Jala nidhi*) also warn of the dangers of these compounds. Many obscure and seemingly implausible medicinal mixtures were concocted during the middle ages by various alchemists who gave these recipes names to match, such as *Zenexton Paracelsi* and *arsenicum fixum* (Azcue and Nriagu, 1994).

Until the nineteenth century, arsenic trioxide (As_2O_3) or white arsenic was the favoured poison for persons engaged in such practices, until inevitably possession was declared illegal. Despite this, a number of more plausible therapeutic arsenic containing medicines began to make their appearance. Fowler's solution (a 1% potassium arsenate solution) was discovered in 1786 and remained the most widely used medicine for a wide range of illnesses for the next 150 years. Donovans's solution (arsenic iodide) and de Valagan's solution (arsenic trichloride) were also recommended for the treatment of rheumatism, arthritis, asthma, malaria, trypanosome infections, tuberculosis and diabetes. Pearson's solution (a sodium dimethylarsenate solution) was used as a general tonic. Finally, Salvarsan (arsphenamine, see Appendix B for structure), discovered in 1909 by Paul Ehrlich and co-workers was used as the main treatment of syphilis, together with Neoarsphenamine (see Appendix B for structure) until the discovery of antibiotics in the 1940's (Rochow, 1966; Peoples, 1975; Azcue and Nriagu, 1994). Phenylarsenic ($C_6H_5AsO(OH)_2$) and other substituted phenyl- and diphenyl-diarseno compounds have also been used as chemotherapy treatments for some trypanosomal infections (Ferguson and Gavis, 1972). A number of arsenical drugs used in medicine during the 1930's are shown in Table 3.1, together with their therapeutic dose levels. It is interesting to note that it would require the ingestion of 10kg of food containing 5ppm of DMAA to obtain a therapeutic dose (Peoples, 1975).

Arsenic, arsenic trioxide, lead arsenate, and potassium arsenate are used in various veterinary medicines. Disodium hydrogen arsenate was used in this function, but is no more.

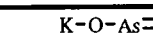
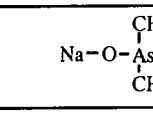
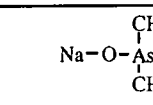
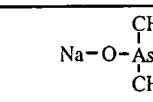
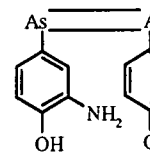
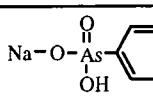
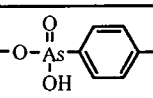
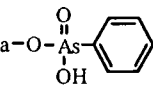
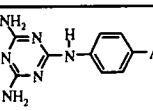
3.2.3 *Pigments and Poisonings*

The natural sulphides, orpiment and realgar have had a long history of use as pigments for both ornamental and cosmetic purposes, with orpiment (As_2O_3) giving a bright yellow and realgar (AsS) a red colour. Indeed, the name arsenic comes from the ancient words for orpiment, *arsenikon* in Greek and *az-zernikh* in Arabic (Rochow, 1966).

In the nineteenth century, arsenic was an important ingredient in many organic and inorganic colouring agents, such as King's yellow (As_2S_3), mineral blue, or copper potassium arsenate, Scheele's green, and Paris or emerald green. In many others, such as some of the aniline (phenylamine) dyes, arsenic was an impurity. The last pigment

($Cu(AsO_2)_2Cu(C_2H_3O_2)_2$) was given a variety of names such as Paris, emerald, French, Parrot, Vienna, Schweinfurt, Mitis and Imperial green in an effort to conceal the poisoning nature of the active ingredient (Azcue and Nriagu, 1994).

Table 3.1. Arsenical drugs used in treating human diseases.

Drug	Dose (g)	Use	Formula
Fowler's solution	0.005	Leukaemia, tonic	
Pearson's solution	0.005	Tonic	
Arrhenal	0.05	Tonic	
Sodium DMAA	0.05	Tonic	
Arsphenamine	0.3-0.6	Syphilis	
Atoxyl	0.02-0.2	Trypanosomiasis	
Tryparsamide	2.0	Trypanosomiasis	
Carbasone	0.75	Amebiasis	
Melarsprol	0.18	Trypanosomiasis	

From Peoples, 1975.

Several poisoning cases have been reported from the historical use of arsenical pigments in artificial flowers, toys, wallpaper, wrapping paper and furthermore, they have found uses in pyrothechnics, calico-painting, and vermicides and febrifuge in medicine (Dewey, 1920). Scheele's Green ($CuHAsO_4$ [or $CuHAsO_3$ from Fergusson, 1990]) was also used as a pigment, and both it and Paris Green were even used as colouring agents in confectionery and fancy desserts before the symptoms of arsenic poisoning could be accurately diagnosed. This was initially achieved by the use of the Marsh test developed in 1836, although it only allowed the presence of arsenic to be demonstrated, and was not quantitative (Rachow, 1966). Not long after this, a committee of the Medical Society of London issued a quite long and comprehensive list

of arsenic containing goods, and also concluded that some of these arsenic applications were unnecessary and should be prohibited on health grounds - the first suggestion ever made that toxic hazards in the environment should be controlled by prescribing maximum possible levels (Azcue and Nriagu, 1994).

Amongst the most famous of historical persons supposedly poisoned with arsenic is Napoleon. Napoleon died in 1821, only four years after he was exiled to Saint. Helena and it has been suggested that the dampness of the house in which he lived encouraged the growth of fungi on the wallpaper, which was coloured using green arsenic containing pigments. The fungal growth resulted in the release of arsine, which is highly poisonous (the mechanism is described more fully in Chapter 5), and is thought to have been at least contributory to his death. Recent analysis of surviving fragments of wallpaper from Napoleon's house gave an average arsenic concentration of 0.12g As/m^2. Wallpaper samples from Lord Armstrong's house 'Cragside' in Northumberland have been found to have arsenic concentrations of up to 6g As/m^2 (though this only resulted in relatively mild sickness in wallpaper conservators), although levels from a late 19th century US study gave levels in the range 0.015-0.6g As/m^2 from wallpaper known to have caused poisonings (Jones, 1982). A more recent suggestion as to the death of Napoleon comes from France, where a recent literary find included a supposed confession by Count Charles de Montholon (the head of the household in Napoleon's house on Saint Helena), who apparently put arsenic in Napoleon's wine over the years 1817-1821 (The Times, 1994). Other notables include the death of Mrs. Clare Booth Luce, the US Ambassador to Italy in 1947 (thought to have been caused by 17th century green paint containing lead arsenate [Stuttaford, 1994]), Leopold I of Austria in 1670 (thought to have been poisoned by wax candles impregnated with arsenic trioxide, which sublimes on heating -see Appendix A) [Azcue and Nriagu, 1994], together with James Maybrick one of the most likely Jack-the-Ripper suspects who was poisoned by his wife (Sunday Times, 1993), and Tchaikovski who committed suicide (Stuttaford, 1993).

Chronic poisoning has also come via some more obscure pathways. In 1900, the beer drinkers of Lancashire fell sick by the thousand due to what was eventually diagnosed as chronic arsenic poisoning, 80 dying as a result. The arsenic source was finally traced to the sulphuric acid used in refining the sugar used in the brewing process (Rochow, 1966; Peters et al, 1996), the arsenic being originally associated with the sulphides used in the sulphuric acid manufacturing process. In 1955, 12,131 Japanese

infants were poisoned by dried milk made with arsenic contaminated sodium phosphate as a stabiliser. This incident resulted in 130 fatalities. Another 400 people were poisoned in Japan in 1956 due to soy sauce that was contaminated with arsenic (Peters et al, 1996).

3.2.4 *Glass manufacture*

In the glass industry, arsenic trioxide is used as a fluxing agent to aid in clearing iron impurities from the glass melt ensuring the glass is clear. Arsenic trioxide was commonly used until it was discovered to be carcinogenetic; arsenic acid is now typically used. In addition, arsenic is used in the manufacture of plate glass and enamels and also of low melting glasses for semiconductor and infrared applications (Dewey, 1920; US National Toxicological Program (US-NTP), 1994; Azcue and Nriagu, 1994; Peters et al, 1996).

3.2.5 *Agriculture*

Before the introduction of DDT in 1947, lead arsenate ($PbHAsO_4$) was the primary chemical used in agricultural pest control (Davenport and Peryea, 1991). It was originally part of agricultural herbicide and insecticide formulations, especially in orchards, although this has almost completely ceased, leaving many orchards with high soil arsenic concentrations (as discussed briefly in Section 2.7.3.4). In the State of Washington (United States), the estimated peak use of lead arsenate insecticides occurred in 1943, when the average annual rate of application was 56.0kg of elemental arsenic per hectare (Sandberg and Allen, 1975). Arsenic trioxide was used as a soil sterilant to control vegetation at application rates of 504-2,520kg/ha (Sandberg and Allen, 1975).Calcium arsenate [$Ca_3(AsO_4)_2$] was, and might still be in some circumstances, used as an insecticide on cotton (to control the boll weevil and cotton leaf worm) and against certain soil insects, as a herbicide for treating turf and lawns to control weeds, and as a pesticide on fruits and vegetables (Lemmo et al, 1983; US-NTP, 1994). Calcium arsenite [$Ca_3(AsO_3)_2$] was used as an insecticide, pesticide, and molluscicide (Lemmo et al, 1983). Sodium arsenate (Na_3AsO_4) is used in ant and termite killers and in animal dips, as an insecticide, and as a herbicide and soil steriliser on the Malayan rubber plantations and US and European railways (Ferguson and Gavis, 1972; Luh et al, 1973; US-NTP, 1994). Sodium arsenite (Na_3AsO_3) is also used in low

percentages in herbicides for weed control (potato vine desiccant), for destroying trees and stumps, and was added to lakes at up to 10mg/l (10g/m^3) to control aquatic weeds (Ferguson and Gavis, 1972; Luh et al, 1973; Clayton and Tanner, 1994). Arsenic pentoxide (As_2O_5) is used as a pre-harvest defoliant of cotton (Lemmo et al, 1983).

Paris Green ($Cu(AsO_2)_2Cu(C_2H_3O_2)_2$) has found use in a great variety of things: as a pesticide in the orchards of Canada, the US, Australia and Algiers, together with the French vineyards and East Indies and Malay rubber plantations, and for sheep dip (Dewey, 1920). Arsenic containing pesticides have also been widely used in the treatment of animal hides, resulting in high concentrations in tannery wastes (Davis et al, 1994; Peters et al, 1996).

Some of the more common organoarsenicals have also found uses in agricultural pest control measures, taking over from the inorganic arsenicals. Monosodium methylarsonate (MSMA) is used as a post-emergence herbicide, in cotton weed control and other general weed control, whilst disodium methylarsonate (DSMA) is used as a non-selective weed control herbicide and as a cotton defoliant (Hiltbold, 1975; Lemmo et al, 1983). DMAA and sodium dimethylarsinate are non-selective, foliar contact-type herbicides, generally restricted to non-crop areas, with the added advantages of relative inactivity in soil and lack of residual phytotoxicity (Hiltbold, 1975). In perspective, organoarsenical herbicides are applied at considerably lower single and annual rates than the inorganic forms, and have a lesser impact on both crop phytotoxicity and the amount of soil residues (Sandberg and Allen, 1975).

On a more positive side, arsanilic acid and related compounds are used as growth promoting factors and used as food additives in swine and poultry feeds (Luh et al, 1973; Azcue and Nriagu, 1994) and also as an antidote for selenium poisoning in animals (Luh et al, 1973). The compound arsanilic acid was discovered in 1907 by Erlich and Bertheim, and this, together with 3-nitro-4-hydroxyphenylarsonic acid (discovered in 1945 by Morehouse and Mayfield) have been used both as medicines and growth promoters in chickens and pigs. Since then, other organoarsenicals including arsenobenzene, 4-nitrophenylarsonic acid and p-ureidobenzenearsonic acid (for chemical formulae, Appendix B) have been shown to have both therapeutic and growth-promotant properties as feed additives for both poultry and swine (Calvert, 1975), together with carbosone (Peters et al, 1996).

The theories behind how these arsenicals act as growth promoters have been open to debate for years, with a number of viable explanations. These include the inhibition of organisms which cause a thickening of the gut wall, thus resulting in more efficient food absorption; another theory suggests that these compounds act as antibiotics, inhibiting harmful bacteria. Another suggests that arsenicals may exert a sparing effect on protein. Thus, while there are a number of theories, no one mechanism is enough to explain the action of an arsenical, and probably a combination of factors produce the observed responses (Calvert, 1975).

3.2.6 *Wood Preservatives*

The wood preservative industry is the major market for arsenic in the United States, accounting for 70% of domestic demand, although this industry is losing ground in the arsenic consumption stakes to the electronics industry. Lead arsenate [$Pb_3(AsO_4)_2$], sodium arsenite, calcium arsenate, together with arsenic pentoxide, were all used in wood preservative formulations, but arsenic trioxide is the preferred arsenic compound today due to its use in formulating chromated copper arsenate (CCA) [$CrCu_2(AsO_4)_2$]. While wood designed to be placed on land generally receives 6.4kg/m^3, wood designed for marine use receives 24.0kg/m^3, or in some cases as much as 40.0kg/m^3 (Weis and Weis, 1992). Arsenic is also used in the production of other wood preservatives such as acid copper arsenate ($CuHAsO_4$) and ammoniacal copper arsenate ($CuNH_4AsO_4$) [Warner and Solomon, 1990; US-NTP, 1994; Azcue and Nriagu, 1994].

Paris Green has been used as a preservative in the hold of ships to prevent the decay of the wooden hulls (Dewey, 1920), with arsenic also being an ingredient in a number of antifouling paints.

3.2.7 *Electronics*

Gallium arsenide is used as a compound semiconductor, requiring very high purity (99.999%) arsenic metal and has long competed with silicon components in the electronics industry. Gallium arsenide is faster, but silicon is much cheaper. Arsine is used as a background gas in the manufacture of some semiconductor parts (Lemmo et al, 1983). Arsenic is also used in the manufacture of solar cells, infrared emitters, laser windows, microwave devices, and in LED's for digital watches (Azcue and Nriagu, 1994; Peters et al, 1996).

3.1.8 *Warfare*

During the First World War, due to a shortage of antimony, arsenic was used in the manufacture of chilled shot, and also found use in lead shot manufacture, where additions of 0.5-2% helped make the lead form the spherical drops in shot towers.

Lewisite [(2-chloroethenyl)arsonous dichloride ($ClCH=CHAsCl_2$)] was invented for use as a chemical warfare agent (Ferguson and Gavis, 1972; Mitretek, 1996), but was never used because of the armistice. It was, like mustard gas, a vesicant (blistering agent), but was considered obsolete following World War II due to the discovery of cheap and effective antidote "British anti-lewisite" or BAL (a dithiol, 2,3-dimercapto-1-propanol), although it was used by the Japanese in the Sino-Japanese war of 1937-1945 (Whymant, 1997) and it may have been used more recently by the Iraqis (Mitretek, 1996). Other arsinous chemical warfare agents include the so called Clark I and Clark II compounds (diphenylarsinous chloride and diphenylarsinous cyanide, respectively) and adamsite (10-chloro-5, 10-dihydrophenarsazine), also vesicant agents (Mitretek, 1996). Although now not likely to be used in warfare, huge quantities of these compounds have been dumped in the oceans (see Section 2.7.3.1), on land (see Section 2.7.3.2), and are occasionally recovered accidentally, often causing injury (Handley and Bodden, 1996; Nuttall, 1996; Mitretek, 1996).

3.2.9 *Embalming*

From 1880 to about 1910, arsenic was widely used as an ingredient in embalming fluid, although prior and subsequently to this arsenic was also used in taxidermy. During the American Civil War, the only alternative was to use ice, and so this fluid was considered a major advancement and was soon adopted throughout the country. Research has shown that thousands of bodies buried during the Civil War era, and for two decades thereafter, were embalmed with this arsenic-based solution. The solution was invented and popularised by Dr. Thomas Holmes of Washington, DC, known as the 'father of modern embalming', and up to 1.4kg of arsenic could be used to embalm a single body.

In 1910, the use of arsenic in embalming fluid was banned by the federal government - not because of its danger to ground water, or even to undertakers, but because its use was interfering with the investigation of suspected arsenic poisonings. It

was replaced with formaldehyde, which had been discovered several years before but was not yet widely used (Unknown, 1990).

3.2.10 *Mineral prospecting*

Arsenic is a good geochemical indicator of bedrock gold mineralisation, and the presence of anomalous arsenic concentrations in soils may indicate the presence of near surface mineralisation. The use of arsenic for this purpose, depends on the close association between arsenopyrite and gold in the mineralised lodes, and for this technique to be of use relies on the local soils having low natural arsenic levels and the greater solubility of arsenic compared with the other elements associated with the mineralisation, leading to a wider dispersion in the soils (Bowell, 1994; Bowell et al, 1994; Azcue et al, 1994b; Azcue and Nriagu, 1995).

3.3 Arsenic production

Prior to the First World War, world annual production of arsenic trioxide (white arsenic) rose gradually to about 10,000 tonnes. Owing to the increased demand for insecticides, production of this compound more then doubled in the following 15 years. Production has increased since then (as seen in Table 3.2 , with a sudden increase to 62,000 tonnes in 1960, an increase of 32% on the previous year's production. This increase was attributed to a general increase in world-wide production of other metals with which arsenic is associated (Azcue and Nriagu, 1994).

Ferguson and Gavis (1972), gave estimates of world arsenic (metal) production as averages of 10-year periods. This information covered most of the 20th century up to 1970, and is given in Table 3.3. Arsenic production had grown to about 50,000 tonnes by 1972, with US production making up 15% of this, and US consumption about 50% of the total (Ferguson and Gavis, 1972). By 1975 world production and consumption of arsenic and arsenic compounds was in the order of 60,000tons/yr (Morita and Edmonds, 1992), and this has since continued to increase, as may be seen in Table 3.4 if the United States is taken as an example. These figures may be compared with world mine production figures, given in Table 3.5. It is evident that, while overall global production has reached an almost static level at around 47,000 to 48,000 tonnes/yr, and prices of arsenic metal are generally decreasing, prices of the trioxide are gradually increasing,

mainly due to the fact that arsenic trioxide is the source for 97% of all arsenic products, the remainder being made up by the metal (US-NTP, 1994; Azcue and Nriagu, 1994).

Table 3.2. Average world production of arsenic trioxide(metric tonnes).

Years	Total	Years	Total
1927-1930	48,691	1961-1965	54,621
1931-1935	53,700	1966-1970	60,318
1936-1940	60,940	1970-1975	54,673
1941-1945	57,200	1976-1980	34,474
1946-1950	46,400	1981-1985	45,211
1951-1955	49,200	1986-1990	51,628
1956-1960	48,800		

From Azcue and Nriagu, 1994.

Table 3.3. World production of arsenic (metal) in tonnes/yr.

Years	Total
1911-1920	12,600
1921-1930	21,700
1931-1940	39,400
1941-1950	44,000
1951-1960	34,400
1961-1970	42,700*

*Excluding US production. From Ferguson and Gavis, 1972.

Most of the arsenic produced today is obtained as a by-product of the smelting of copper, gold, lead and cobalt ores, with gold ores containing up to 11% arsenic, compared to 2-3% associated with lead and copper ores. In the United States, the sole domestic producer of arsenic ceased operation in 1985. Since then all of the arsenic consumed domestically has been imported (import sources (1990-93): China, 30%; Chile, 22%; Mexico, 15%; and other, 33%), nearly all as arsenic trioxide.

Table 3.4. Arsenic production and consumption (tonnes) in the United States.

Salient Statistics--United States:	1990	1991	1992	1993	1994[1]
Imports for consumption:					
Metal	796	1,008	740	767	1,400
Trioxide[2]	26,256	27,142	30,671	27,530	23,900
Compounds[3]	21	374	40	-	10
Exports, metal	149	233	94	364	100
Consumption, apparent, arsenic content	20,500	21,600	23,900	21,300	19,400

[1]Estimated. [2]Arsenic trioxide (As_2O_3) contains 75.7% arsenic by weight.
[3]Almost entirely arsenic acid. From US Bureau of Mines, 1995.

More than 90% of the arsenic used in the United States was consumed in compound form, mainly by one producer of agricultural chemicals and three producers of wood preservative chemicals. Metallic arsenic was used only for the production of non-ferrous alloys and semiconductor materials (such as gallium arsenide), although this latter use is the fastest growing, with demand having increased sevenfold in the US and fivefold in Japan since 1984 (Narbrough, 1992). The estimated end-use distribution of arsenic in the United States in 1994 was 74% in wood preservatives, 12% in agricultural chemicals (principally herbicides), 4% in glass, 8% in non-ferrous alloys and semiconductors, and 2% in other uses. The total value of arsenic metal and compounds consumed was estimated, in 1995, to be about $20 million (US Bureau of Mines, 1995).

Table 3.5. World Mine Production and Reserves (tonnes/yr.).

	Mine production	Mine production	Reserves
	1993	1994[1]	
United States[2]	-	-	
Belgium	2,000	2,000	
Chile	6,200	6,000	World reserves are believed to be about 20 times annual world production.
China	13,000	13,000	
Ghana[3]	9,000	9,000	
Kazakhstan	2,000	2,000	
Mexico	4,168	4,000	
Namibia	2,472	2,000	
Philippines	2,000	2,000	
Russia	2,000	2,000	
Other countries	4,900	5,000	
World total (may be rounded)	48,000	47,000	

[1]Estimated. [2]Reserves for the United States were 50,000 metric tons. [3]By-product of gold processing only. It is unclear how much of this material is of commercial grade. From US Bureau of Mines, 1995.

However, consumption of some arsenic compounds, especially those used in wood preservation is steadily dropping due to heightened international pressure for non-toxic alternatives. Lead acid batteries , which use arsenic metal, are also ceding ground to arsenic-free alternatives. On the shorter term, slumps in house building will always result in a drop in demand for treated wood. Indeed, in July 1995, New Jersey became the first US state to restrict the use of the wood preservative CCA in marine environments. State officials believed that CCA could leach from wood and then bioaccumulate in clams, oysters, and mussels. Under New Jersey's new regulations, the use of CCA-treated wood will be prohibited in the construction of new or rebuilt marine

structures at marinas of five or more boats on the Navesink, Shrewsbury, and Manasquan Rivers and St. Georges' Thorofare (US Bureau of Mines, 1995).

Past work has shown that although arsenic will leach from CCA treated timber structures, the general hydrodynamic regime around such structures generally keeps concentrations low (Evans, 1987; Weis et al, 1993). The sediments closest to bulkhead structures have very low (often <1%) percentages of clay and silt sized particles (although of course this is dependent upon the local water flow regime), but very high concentrations of all three metals associated with the fine particles. Sediments further away from such bulkheads have higher concentrations of silts and clays with lower concentrations of the metals. Consequently, there is a decrease in metal concentrations with increasing distance from the bulkhead. The greatest metal concentrations are associated with new timbers, indicating leaching is most rapid from new wood (Weis and Weis, 1992). It is not known, however, whether organisms living immediately adjacent to CCA treated timber, which are subject to low overall metal levels but very high concentrations in the scarce fine grained particles, are at a higher or lower risk than those living at a greater distance, subject to greater overall metals due to the greater percentage of fine grained particles (Weis et al, 1993). Earlier work has, however, been carried out on the effects on organisms growing directly on such treated timber (Weis and Weis, 1992). This showed that timber treatment resulted in decreased species richness, diversity and biomass, and high accumulation of the metals involved.

3.3.1 *Arsenic Substitutes*

Substitutes for arsenic exist in most major end uses, although arsenic may be the preferred material because of its lower cost. An environmental alternative to CCA for protecting wood against rot is ammoniacal copper quaternary (ACQ). Reportedly, ACQ is just as effective as CCA, but may cost 10% to 20% more. The wood preservatives pentachlorophenol and creosote may be substituted for chromated copper arsenate where odour and paintability are not problems and where permitted by local regulations. Non-wood alternatives such as concrete, steel, and vinyl and plastic lumbers may be substituted for arsenical pressure-treated wood. New York State, New York City, and Connecticut reportedly have used a South American hardwood called Ipe (EYE-pay) to rebuild some structures along shorelines. The hardwood, which needs no chemical

treatment, lasts up to 50 years (US Bureau of Mines, 1995).

3.3.2 *Resources*

World resources of copper and lead contain about 11 million tonnes of arsenic. Substantial resources of arsenic occur in copper ores in northern Peru and the Philippines and in copper-gold ores in Chile. In addition, world gold resources, particularly in Canada, contain substantial resources of arsenic (US Bureau of Mines, 1995).

3.4 Global arsenic mass balance

For every trace element, including arsenic, the total amount present is divided among the various compartments (spheres) making up the physical world. Each sphere contains a pool of arsenic, which is calculated from the product of the mass of material in the pool, and the concentration of arsenic within that material. Large errors (up to 20%) may occur in both of these values.

The movement of arsenic between the various spheres is called the arsenic flux, and in most natural systems, this is at a steady state. Anthropogenic inputs (and some sudden large natural input, such as a volcano) upset this equilibrium. If, however, a steady state is assumed, then the fluxes may be estimated, although large errors will inevitably arise. Because of the uncertainties involved, residence times so calculated are not precise, but an idea may be gained from the data presented in Table 3.6. The figure for atmospheric residence, given by Peters et al (1996) is in close agreement with that suggested by Müller (1981), who developed an equation linking an element's boiling and melting points to calculate an approximation for vapour pressure, which is generally extremely low for heavy metals (including arsenic). By application of this calculated 'volatility point', the residence time of an element associated with particulate matter may be predicted (Müller, 1981).

Early attempts to obtain an atmospheric mass balance for arsenic (Lantzy and MacKenzie, 1979), used previously available data (Kanamori and Sugawara, 1965; Onishi, 1969, for example) to estimate the rates of arsenic removal from the atmosphere. The results gave flux values of 970×10^8 g/yr to the land surface, and 1970×10^8 g/yr to the oceans. This flux is almost exclusively by wet fallout (deposition of aerosol particles and gases in rain, fog, hail and snow), with a

comparatively negligible amount (around 1%) by dry (deposition of aerosol particles to water, soil buildings or plants) fallout (actually 0.86% and 0.82% for fallout to the oceans and to the land respectively). To account for this large amount of atmospheric arsenic, it was thought that the arsenic had its origins in biological mediated volatilisation from the oceans (Lantzy and MacKenzie, 1979).

Table 3.6. Residence times for arsenic globally.

Author	Atmosphere	Hydrosphere		Lithosphere[b]	Biosphere
	(days)	Oceans (10^3 yr)[a]	Lakes	Soil (yr)	Humans (days)
Bowen (1979)	Short lived	280	≈30yrs.	1000-3000	200-400
Fergusson (1990)	Short lived	550[c]-930[d]	415 days	2000	8-18[e], 360[f]
Peters et al (1996)	9	9.4	-	99,800,000	25[g]; 17 yr[h]

[a]In surface ocean waters, residence times can be quite short due to volatilisation; [b]If buried in marine sediments, then lithification may eventually occur, lengthening residence time; [c]estimated from a steady state riverine input only; [d]estimated from output via sediments; [e]estimated via diet; [f]estimated from urinary output; [g]marine biota; [h]terrestrial biota.

The idea of biological mediated volatilisation was based around the concepts of interference and enrichment factors applied to trace metals. The interference factor is defined as:

$$\text{Interference factor} = \frac{\text{Total anthropogenic emissions}}{\text{Total natural emissions}} \times 100$$

and the enrichment factor as:

$$\text{Enrichment factor} = \frac{As/Al_{(atmos)}}{As/Al_{(soil)}}$$

although for marine areas Na or Cl is used in place of Al.

Elements with high interference factors (IF's) are termed 'atmophile' elements (e.g. arsenic, selenium and mercury), and more of the element is transported annually to the oceans through the atmosphere than by streams (for example from coal combustion, smelting and methylation). The reverse is true for elements with low IF values (e.g. iron and manganese), the 'lithophile' elements. It is assumed that for atmophile elements, the natural continental and volcanic dusts are the most important natural emission sources, and that other sources cause a lowering of IF values. An enrichment factor (EF) of ≤10 suggests that the element is not significantly enriched in atmospheric particles relative to a crustal or oceanic source, whilst an EF of ≈100-

100,000 suggests just the opposite. Kanamori and Sugawara (1965a) report an arsenic marine EF in the order of 16,000, while a value for Britain is estimated to lie in the range 50-500 (Bowen, 1979). Data given by Fergusson (1990) shows arsenic EF values of 24 for dry deposited urban aerosols, 100 for urban suspended particles and 800 for urban rainwater.

An element may have a large EF value for the following reasons:

i) sources other than seawater or rocks exposed at the surface;

ii) there is a low temperature process selectively releasing the metal to the atmosphere, such as: aerosol generation at the ocean surface, physical or biologically mediated volatilisation from the earth's surface or release of metal rich particulates from vegetation;

iii) there is a high temperature process selectively releasing the metal to the atmosphere, such as: vulcanism, burning of vegetation, industrial activities or fossil fuel combustion.

There is a significant correlation between interference and enrichment factors for a wide range of trace metals, including arsenic (Lantzy and MacKenzie, 1979). Hence, as arsenic was calculated to have an IF of 2,786%, it was also expected to have a high EF, such as the value of 16,000 reported by Kanamori and Sugawara (1965a). Indeed, in terms of volatility, arsenic ranks among one of the most volatile trace metals, be it in an oxide, elemental or sulphide state (Bertine and Goldberg, 1971). The IF value of Lantzy and MacKenzie (1979) was calculated with a few assumptions, including the following:

a) that anthropogenic inputs are not reduced for near-production fallout due to atmophile element emissions generally being associated with very fine grained (micrometer to sub-micrometer, 0.74μm mean diameter- Kanamori and Sugawara, 1965a) emissions;

b) that 90% of the arsenic in oil and coal is released on combustion;

c) that volcanic gas flux is insignificant as a source globally compared to volcanic particulate (dust) flux, or continental dust flux except in the close proximity of a volcano.

Lantzy and MacKenzie (1979), used a mathematical model to calculate present day enrichment factors in both hemispheres based on both natural and anthropogenic influxes, effluxes and transfers between hemispheres. They found the

calculated enrichment factors to be in good agreement with observed values for lithophile elements at mid and high latitudes, and at mid latitudes for atmophile elements. However, calculated values for atmophile elements are much lower than observed in high latitudes, and based on this observation it was suggested that there is a significant ocean to atmosphere flux. The high arsenic IF value of 2,786% shows that the anthropogenic flux is considerably greater than the natural flux, although EF's for arsenic in atmospheric particles do not provide a unique measure of whether or not the metal enrichment is derived from a natural or anthropogenic source. It is important to note that a calculated EF for arsenic will vary greatly, not only from area to area, but also with time. For example, if an area uses a lot of coal for domestic heating, then the EF value for that area will probably be higher during the winter months, when more fuel is consumed.

Lantzy and MacKenzie (1979), suggest the global balance of arsenic given in Table 3.7.

Table 3.7. Global balance of arsenic (after Lantzy and MacKenzie, 1979).

Route	Flux 10^8g/yr	Remarks
Land to:		
1) Atmosphere	25.0	Calculated from the total continental dust flux of 5×10^{14}g/yr and mean As soil conc. of 5ppm.
2) Atmosphere (emissions)	21.0 600.0 158.0 0.3	Cement manufacture. Sulphide ore roasting. Lignite-coal combustion. Oil-gas combustion.
3) Atmosphere (vapour)	209.6	Calculated from an estimate of As vapour released to the atmosphere annually (1.2×10^{-8}g/cm^2) and the surface area of land (less ice) (1.33×10^{18}cm^2). Plus estimate of As vapour released from pesticide use (50×10^8g/yr).
Atmosphere to:		
1) Land (dust)	8.0	Calculated assuming that continental dust fallout is distributed to land and ocean in proportion to their areas.
2) Land (rain)	970.0	Calculated from total global rainfall (4.2×10^{20}g/yr), conc. of As in oceanic (0.6ppb) and continental (1.6ppb) rain, the proportion of each (90% and 10%), and that 1/3 falls out on the land.
3) Ocean (dust)	17.0	Calculated assuming that continental dust fallout is distributed to land and ocean in proportion to their areas.
4) Ocean (rain)	1,970.0	Calculated from total global rainfall (4.2×10^{20}g/yr), mean conc. of As in rain (0.7ppb), and that 2/3 falls out on the ocean.
Ocean to:		
Atmosphere	1,951.1	Difference between the total flux to the atmosphere and the fluxes from the atmosphere.

Another estimate of the removal of atmospheric arsenic by rain and dry deposition over the oceans is 27.6×10^8 g/yr (Walsh, 1977). If it is taken that 1.0×10^8

g/yr are lost to the atmosphere from the oceans, then the maximum net arsenic flux from the atmosphere to the oceans is 26.5×10^8 g/yr

In the southern hemisphere, 79% of the total global rainfall of 4.2×10^{20} g/yr, falls over the oceans, resulting in a deposition of 63×10^8 g/yr of arsenic, assuming an arsenic rain concentration of 0.019μg/l (an average of south Californian and Hawaiian rain concentrations, [Andreae, 1980]). There is no comparable information available for continental precipitation of arsenic, but a concentration of 0.46μg/l has been predicted (Andreae, 1980), based on the arsenic concentrations of atmospheric particulates given by Walsh et al (1979a), and by using the empirical formula of Cawse (1974). This value is much lower than some reported values, but most continental air masses contain a moderately large proportion of anthropogenically generated arsenic. As a consequence, it is thought that earlier work (such as that of Lantzy and MacKenzie, 1979) tended to overestimate the contribution of marine rain as the dominant sink of atmospheric arsenic. Andreae (1980), estimated that the global atmospheric arsenic deposition is in the order of 300×10^8 g/yr, a figure in close agreement with that of Walsh et al (1979b). This removal can be balanced completely by known sources of atmospheric arsenic, about 75% of which are anthropogenic. Biological volatilisation is therefore not considered a major source of atmospheric arsenic (Walsh et al, 1979b; Andreae, 1980). This is a reversal of Lantzy and MacKenzie's, (1979) work for the reasons given above, and also that only relatively small amounts of methylarsenicals have been found in the atmosphere. Recently, however, with the development of more sophisticated and sensitive analytical techniques, (Maher and Butler, 1988) have shown that almost 10% of atmospheric particulate arsenic may comprise methylarsenicals. Walsh et al (1979b), suggest the contents of Table 3.8 for a global balance of arsenic.

As can be seen, by far the greatest source for atmospheric arsenic are the continental areas. However, it has been suggested more recently (Cullen and Reimer, 1989), that much of the data used in the works mentioned, uses arsenic concentrations and emission factors that are out of date with regard to existing environmental control strategies and analytical techniques. They suggest a ratio of natural to anthropogenic atmospheric inputs of 60:40, while from the data given above, Lantzy and Mackenzie (1979), suggest a ratio of 74:26, that of Walsh et al

(1979b) gives 76:24 whilst the sparse data presented by Bowen (1979) gives a ratio of 34:66.

Table 3.8. Global balance of arsenic (after Walsh et al, 1979b).

Route	Flux 10^8g/yr	Remarks
Land to:		
1) Atmosphere	2.4	Crustal weathering products.
	70.0	Volcanoes.
	1.6	Forest wild fires.
2) Atmosphere (emissions)	5.5	Coal.
	0.0007	Light fuels.
	0.041	Residual fuels.
	6.0	Wood fuel.
	5.6	Agricultural burning.
	4.3	Waste incineration.
	42.0	Iron/steel production.
	130.0	Copper production.
	22.0	Lead/zinc production.
	0.13	Mining mineral ore.
	2.0	Arsenic/chemicals.
	19.0	Arsenic/agriculture.
	0.23	Cotton/ginning.
3) Atmosphere (vapour)	0.007	Direct volatilisation, not including pesticide vapours.
	2.6	Submicrometer particle or vapour emissions by plants and biogenic As emissions from soil.
Atmosphere to:		
1) Land	276.0	Removal by both wet and dry fallout
2) Ocean	27.6	Removal by both wet and dry fallout
Ocean to:		
Atmosphere	0.28	Bubble bursting.
	1.1	Gas exchange.

More recently, Lindsay and Sanders give an estimate of 30:70 (natural to anthropogenic) distribution of the 155,000 tonnes of arsenic released annually. Whilst the former three are in close agreement, it must also be realised that a large proportion of the natural sources of arsenic for all of these models comes from single sources. Lantzy and Mackenzie (1979), suggest an ocean to atmospheric flux of $1{,}970\times10^8$g/yr and a volcanic gas flux of 3.1×10^8g/yr, whilst Walsh et al (1979) use figures of 1.38×10^8g/yr and 70×10^8g/yr respectively. The total anthropogenic atmospheric inputs are also very different, with Lantzy and Mackenzie (1979) suggesting a figure of 780×10^8g/yr, Walsh et al (1979) using a figure of only 236×10^8g/yr whilst Bowen (1979) uses a figure of 485×10^8g/yr, thus leaving to the reader to decide the more likely!

Bowen (1979) also makes use of previously available data to calculate the figures given in Table 3.9. While the figures are in broad agreement with those of both Lantzy and Mackenzie (1979) and Walsh et al (1979), it must be pointed out that all three models use data that are at best notably uncertain. Estimates of weathering range widely, with the mass of material moved to the oceans globally estimated to have increased from 9.3×10^{15} g/yr to 24×10^{15} g/yr (Ferguson and Gavis, 1972), as a result of accelerated erosion caused by intensive land use. Therefore, the quantity of arsenic released is at least in proportion, with an approximate increase from about 45×10^{9} g/yr to about 117×10^{9} g/yr, although Bertine and Goldberg (1971) suggest a figure of 72×10^{9}g/yr as a figure representing the weathering mobilisation of arsenic by river flow, and Johnson and Pilson (1975) estimate an input of 3×10^{11} g/yr from both rain and rivers. The sum of cultural contributions that can be estimated, averaging 110×10^{9} g/yr for this century, is approximately three times the lowest value contribution from weathering. These estimates from models of the global cycling of arsenic are often in error as they neglect to consider processes that remove arsenic in its passage from estuary to the open ocean (Maher and Butler, 1988). For example, physical processes such as flocculation of particulates and adsorption of dissolved arsenic onto freshly precipitated hydrous iron oxides, transfer the element into the estuarine sediments, possibly removing it from the cycle for some considerable time. Biological filters such as fringing marshes can also remove arsenic from the water column, its free dispersal in the open ocean can be further restricted by incorporation into coastal and near shore sediments.

Table 3.9. Annual transfer of arsenic in 10^{8}g/yr.

Weathering	60	Assuming 4×10^{12}kg crustal rock weathers annually with As content of 1.5ppm.
River output	185	Assuming 3.7×10^{16}kg river water reaches the sea each year with As content of 0.5µg/l.
Mining	470	
Combustion	15	Assuming combustion rates of coal and petroleum products at 2.62×10^{12}kg and 3.7×10^{12}kg with As contents of 5ppm and 0.26ppm respectively, and a 10% transfer of ash to atmosphere.

Note: there is no mention of atmospheric cycling, nor what proportion is transferred to the oceans. From Bowen, 1979.

There is no evidence to suggest that man is likely to change the world-wide distribution of arsenic appreciably, but arsenic is highly concentrated in many local environments due to man's activities (Ferguson and Gavis, 1972). It is also worthy to note that stricter pollution controls are reducing the anthropogenic input to the global

cycling of arsenic. This may also partly be due to the increased demand for high purity arsenic by industry, resulting in more efficient recycling. Additionally, there is evidence that atmospheric concentrations vary significantly, both spatially and temporally, suggesting that the concept of a constant background arsenic concentration in air, rain and dry deposition is not valid (Cullen and Reimer, 1989).

CHAPTER 4

REDOX REACTIONS AND SOLUBILITY

4.1 Introduction

The solubility and speciation of arsenic in the environment is governed mainly by redox potential and pH (Masscheleyn et al, 1991; Mok and Wai, 1994) although biological controls of arsenic speciation are more important under certain circumstances, and these will be discussed in the next chapter. However, before any discussion of the reduction-oxidation (redox) reactions involving arsenic, and how these reactions control the occurrence of the various arsenic species in the natural environments, it is useful to define exactly what controls these reactions in the first place.

The reduction and oxidation of arsenicals occurs through one of two processes:

i) chemical reactions on inorganic, and to a lesser extent organic arsenicals;

ii) biological reactions, affecting both inorganic and organic arsenicals.

Purely chemical reactions are controlled predominantly by the prevailing pH and Eh conditions of the environment in question, while biological reactions are controlled by a much wider range of conditions.

The measurement of Eh and pH has become a routine procedure in most investigations into metal cycling, and their use as characterising variables in reactions involving dissolved species allows the construction of the useful Eh-pH stability diagrams, discussed in Sections 4.4.1 and 4.4.2.

The oxidation state of each atom in a covalent compound is the charge remaining on the atom when each shared pair of electrons is assigned completely to the more electronegative of the two atoms sharing them. For example, the oxidation state of arsenic in H_3AsO_4, H_3AsO_3, and AsH_3 is +V, +III, and -III respectively. The sum of all atoms in the molecules is equal to zero, and for monoatomic ions is equal to the charge on the ion. Oxidation reactions involve the loss of electrons; reduction the gain of electrons. The oxidation state of an element is increased after oxidation, and lowered after reduction.

4.2 pH

pH is defined as:

$$pH = -\log[H^+]$$

where $[H^+]$ is the activity or 'effective concentration' of hydrogen ions in solution.

This definition, although exact, is flawed as it involves only the activity of a single ion, something that cannot be measured directly. As a result, measured pH is defined in terms of an operational procedure.

pH is generally measured using a glass electrode dipping into the test solution, together with a reference electrode. The reference electrode is usually a mercury-mercurous chloride (calomel) electrode in a saturated KCl solution, and exhibits a constant potential. The glass electrode (the second electrode), comprising a bulb of special glass containing an acid solution, and an inner electrode of fixed voltage (usually Ag-AgCl) to conduct electrons reversibly into and out of the solution, has a potential that will vary with the hydrogen ion activity. The glass electrode is a high resistance electrode and the 'pH-meter' a high impedance electrometer. Temperature affects readings, but most modern pH-meters have internal compensators which correct for temperature variations. In addition, it is important to ensure that the electrodes are thoroughly rinsed in distilled water to remove adsorbed ions between successive readings. The insertion of electrodes into the solutions to be measured, be they samples, or in situ, causes a modification of the system (especially those not in contact with the atmosphere), be it an introduction of gases, adsorbed species or the escape of volatile (Garrels and Christ, 1965).

The difficulties encountered in sampling homogenous solutions, although considerable, are minor compared with the problems related to measuring and interpreting the results of pH determinations on mineral suspensions or porewaters. The pH of stirred solutions, for example, may be different to that of the solution after settling, indicating a reaction between the suspended particles and hydrogen ions (Garrels and Christ, 1965). It is therefore of great importance to ensure that the electrodes are in contact with what the experimenter is wanting to measure.

4.3 Eh

The oxidation potential, Eh, is defined as the potential of a half cell, referred to the standard hydrogen half cell (the potential of which is taken as zero at all temperatures). For a chemical half cell reaction of the general expression:

$$bB + cC = dD + eE + n$$

where B, C, D and E are the reactants involved, *b*, *c*, *d* and *e* are the stochiometric (whole number) amounts of each present and *n* represents the number of electrons involved, Eh may be written as:

$$Eh = E^\circ + \frac{RT}{nF} \ln \frac{a_D^d a_E^e}{a_B^b a_C^c} \quad \text{or} \quad Eh = E + \frac{2.303RT}{nF} \log_{10} \frac{a_D^d a_E^e}{a_B^b a_C^c}$$

This equation is known as the Nernst Equation, where E° (the standard electrode potential) is the voltage of the reaction when all substances involved are at unit activity (for example: the reaction, $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$, has an E° of +0.77volts), F is the Faraday constant (96486.7 Coulombs/mol), R is the gas constant (8.314×10^{-3}kJ/mol), T the absolute temperature (in °Kelvin) and *a* represents the activities of each reactant (a range of values of E° for arsenic are set out in Appendix A). High values of Eh are thus measures of the ability of the system to accept or transfer electrons (i.e. oxidising systems), while low Eh values are indicative of reducing conditions. Valid results calculated using this equation do, however, depend upon certain assumptions:

1) That all species involved in the oxidation-reduction reaction system are in internal equilibrium. This is generally a satisfactory assumption, although exceptions include sulphate or bisulphate ions and dissolved oxygen.
2) That the platinum or gold electrodes function as truly as inert electrodes. Under certain conditions, these metals will react with another substance, and their surfaces become coated (poisoned). Whilst this does not affect the equation, the results gained are not a true representation of redox values.
3) That the important multivalent species in solution must be electroactive, that is, they must undergo voltage-generating reactions with the metallic electrode (Cherry et al, 1979).

For the data to have an exact meaning in the thermodynamic sense, the redox species in the solution must be in equilibrium, although even if the results are only vaguely reproducible, the results may be regarded as useful.

An alternative way of expressing redox equilibria in aqueous systems, and which more clearly illustrates the electron activity over many orders of magnitude, is the concept of pE (Manahan, 1991). This term is analogous to pH and numerically, it is simply the following:

$$pE = \frac{E}{\frac{2.303RT}{F}} \quad \text{(at 25 C)}$$

where all the symbols are as previously defined. pE is defined in a way very similar to that of pH, namely:

$$pE = -\log[e^-]$$

where $[e^-]$ is the activity or 'effective concentration' of electrons in solution.

Eh and pE may be inter-converted using the expression:

$$pE = \left(\frac{F}{2.303RT}\right)Eh\,.$$

The oxidation potential is measured with an electrode pair consisting of an inert electrode and a calomel reference electrode. The inert electrode is usually bright platinum, although gold is sometimes used. As with pH measurements, the calomel electrode is used to supply a known potential and to make electrical contact with the system to be measured. The inert electrode acts as an electron donor or acceptor to the ions in the measured solution, depending on whether the potential of the half cell containing the dissolved species is greater or less than that of the calomel reference electrode, and works best if it has a large surface area.

Precautions against spurious readings are generally the same as with the taking of pH measurements, except that the measuring circuit has a relatively low resistance. Most difficulties are associated with the 'poisoning' of the inert electrode, and it has been shown that even duplicate readings vary by at least 5mV, although a difference of

10-20mV is more usual (Garrels and Christ, 1965). Norrström (1994) also shows that if electrodes are introduced into reduced environments, it might take from 10-15 hours for an equilibrium to be reached. This is probably due to the introduction of a small amount of oxygen with the electrode as it is introduced into the soil (Norrström, 1994).

As with pH, there are definable limits to the natural range of measurable Eh values. Because reactions at 25°C and one atmosphere pressure occur in the presence of H_2O, the upper and lower limits of Eh are restricted by the stability of H_2O under extreme conditions of oxidation or reduction respectively (Lumsden and Evans, 1995).

An alternative approach to the measurement of redox status in natural waters involves the measurement of the concentration of two or more dissolved species containing different oxidation states. The concentration may be converted to an Eh value using the Nernst equation. Suitable redox pairs include SO_4^{2-} and HS^- or S^{2-}, HCO_3^- or CO_2 and CH_4, NO_3^- and NH_4^+, Fe^{3+} and Fe^{2+}, or Mn(IV) and Mn(II). For a system to be at equilibrium, computed redox levels from each of these analytical pairs have the same value (Patrick and Delaune, 1972; Cherry et al, 1979; Barcelona et al, 1989; Davis et al, 1994). The problems with this conceptually sound and attractive method, however, include:

i) that many of those redox reactions involving nitrogen, sulphur and carbon are biologically mediated and are often irreversible;

ii) that in the Eh/pH domain of natural waters, the concentration of one species of a redox pair is often close to, or below the analytical level of detection (e.g. Fe^{3+}, S^{2-}, or HS^-) [Cherry et al, 1979];

and iii) that it is assumed that the concentrations of the dissolved constituents represent the free ionic concentrations, which does not include ion pairs and complexes in the water (Cherry et al, 1979).

Bourg and Richard-Raymond (1994), however, have used this method using the manganese redox couples, $Mn^{2+}/MnO_{2(S)}$ and $Mn^{2+}/MnOOH_{(S)}$. The presence of a reduced zone in a shallow alluvial aquifer was detected, not by the measured Eh values, but rather by a peak in dissolved (reduced) manganese. The origin of such a localised zone was put down to either localised areas of slower water flow, favouring the development of slow redox reactions (slow pore velocity), or the presence of areas capable of providing an extra carbon supply , thus also enhancing biological activity; both hypotheses were found to be valid [Bourg and Richard-Raymond (1994)].

4.4 Eh and pH in natural systems

Eh

There is little range in the Eh values of systems in equilibrium with the atmosphere, and these seldom exceed +400mV in oxygenated waters, although values in surface soils are known to reach as high as +800mV (Crecelius et al, 1986). Groundwaters tend to have lower values, mainly grouped between +700 and -100mV (Barcelona et al, 1989). Indeed the readings indicate that dissolved oxygen does not exert the potential expected if it is functioning at equilibrium; rather it acts as a very weak oxidising agent [with hydrogen peroxide as an intermediate (Barcelona et al, 1989)]. Consequently, the admission of air into systems that originally had low Eh (reducing/low dissolved oxygen conditions; bacterial production of hydrogen sulphide from sulphate occurs only below 100mV) values is followed by rapid reaction in order to try and bring the system into equilibrium with the atmosphere. Also, there seems to be some tendency for direct reaction of dissolved oxygen with the platinum electrode, so the potential observed in systems containing dissolved air is to a certain extent independent of the oxidation state of the dissolved components. It has been shown (Garrels and Christ, 1965) that systems exposed to air show potentials according to the approximate relation:

$$Eh = 0.70 - 0.059pH$$

This is in contrast to the expected (computed) equilibrium value of:

$$Eh = 1.23 - 0.059pH$$

Where 1.23V is the standard electrode potential (E°) of water with an oxygen partial pressure of 1 atmosphere.

It is therefore clear that measurement of Eh (and pE) values is difficult in systems out of equilibrium with air, because the introduction of electrodes into these systems is fraught with problems relating to contamination, both by air and other ionic species (Norrström, 1994). There is some debate as to what Eh values actually measure, especially if it is a slurried soil sample that is under study (the relative proportions of

soluble ion pairs will be measured, but will this value relate to the bulk sediment composition or to the porewater?). However, if care is taken in limiting uncertainties, then meaningful results can be gained. Indeed, Barcelona et al (1989), used platinum electrode measurements, supplemented with measured redox couple data to build up some detail on the spatial and temporal variations in redox conditions in a terrestrial aquifer. They concluded that there are three redox domains in the subsurface environment: those with measurable dissolved oxygen (i.e., aerobic zone), those with no dissolved oxygen and ferrous iron concentrations in excess of 10^{-4}M (reduced or anaerobic zone), and an intermediate or transitional zone characterised by strong concentration gradients in principal oxidised or reduced species. This is in good agreement with the earlier work of Patrick ad Delaune (1972). Norrström (1994), however, found regions as small as 10cm in diameter had redox potentials covering several hundred mV, making the identification of any seasonal variations difficult.

pH

pH values in surface waters vary from as low as 1.7 in some volcanically formed lakes containing free sulphuric acid, to 12.0 or more for some closed alkaline lakes rich in sodium carbonate. Acid mine drainage from sulphide bearing deposits or wastes may have pH values as low as 0.8. The pH range for open freshwater lakes is generally in the range 6.0 to 9.0 (Crecelius et al, 1986).

If care is taken in measuring both pH and Eh, then these results can be used in determining the dissolved species that should be the most thermodynamically stable given the conditions prevailing in the system under study. This is generally done using stability diagrams constructed using theoretically derived values for Eh or pE for a specified pH value, which are called, appropriately enough, pH-Eh or pH-pE diagrams, depending which value is used in their construction.

4.4.1 pH-Eh or pH-pE diagrams

Arsenic pH-Eh (or pH-pE) diagrams such as those included in Appendix D, show the regions of stability and the boundary lines for various inorganic arsenic species in water. Each line on these diagrams (separating the domains of two species) represents points of equal activity of the two species. From each line towards the centre of a

domain, the proportion of the species indicated increases, whilst the total activity of dissolved arsenic remains constant. Because of the numerous species that may be formed, such diagrams can become extremely complicated. Arsenic may exist in several oxidation states, hydroxyl complexes and different forms of the solid oxide and hydroxide exist in different regions described by the diagram. Most waters contain carbonate, and may also contain sulphates and sulphides, each forming compounds with arsenic that will similarly predominate in different parts of the diagram.

There are, as with any theoretical device, drawbacks with this potentially very useful tool. To obtain a numerical value of E° , the standard free energy (F°_r) is obtained and substituted into the equation:

$$E = \frac{\Delta F_r}{nF}$$

where $\Delta F^\circ_r = -RT \ln K$, and K is the equilibrium constant of the reaction involving the species of interest.

The complete thermodynamic system has not been critically evaluated for arsenic, although some workers have done work that permits the evaluation of the state of saturation with respect to some arsenic minerals. Hess and Blancher (1976) constructed a stability diagram of several selected metal arsenates using their own data together with that of previous workers, and pH-Eh diagrams have been produced for the arsenic system by a number of workers over the years, including Ferguson and Gavis (1972), Wagemann, (1978); Cherry et al (1979), Lemmo et al (1983), Crecelius et al (1986), Cullen and Reimer, 1989; Fergusson (1990), Xu et al, 1991; Bowell (1994) and Bowell et al (1994). The diagrams produced by these researchers are included in Appendix D.

The standard free energy of formation data are generally very variable in their accuracy, and this is reflected in the variations observed in the position of phase boundaries on these diagrams, a number of which are to be found in Appendix D (a range of standard free energy of formation data is to be found in Appendix A). Most of the uncertainty stems from the difficulty in defining the precise nature of the substance, many solids have several polymorphs, and very few minerals exist in nature in anything close to resembling a pure form. Additionally, diagrams are generally constructed using calculations assuming 25°C and 1 atmosphere total pressure, conditions that will

obviously vary daily in many natural environments, even though these variations will generally be small. Another problem arises if an unconsidered species has the ability to interact with species in the system under observation. The result of this might allow two mineral phases shown not to be in equilibrium according to calculations, to coexist in equilibrium in reality. Although the aquatic arsenic system is slightly simplified because arsenic forms only a few aqueous complexes, it does form a number of solids with different metals, and thermodynamic data for the various organoarsenicals is scarce (Crecelius et al, 1986). The concentration of As(III) is controlled by the solubility of the arsenic sulphide minerals under some circumstances, although evidence has been put forward to suggest that Fe(II) would limit sulphide activity and hence arsenic-sulphide would not reach saturation (Kanamori, 1965).

Butler and Smith (1985), in an investigation into arsenic stability within two isolated pools of seawater underlying river water, found that inorganic As(III) and As(V) coexisted, and so were described as existing in a system at 'transition pE', which is defined as the redox potential at thermodynamic equilibrium, for which the ratio of oxidised and reduced species of an element is at unity. In their case, this 'transition pE' for arsenic fell in the range of >12 to <-3 dictated by the presence of measurable amounts of dissolved oxygen and sulphide. At the pH of 7.3 prevalent in the system under study, the transition pE for arsenic was -0.1, although the use of measured arsenic species concentrations to determine the redox potential specifically was not appropriate in this study due to the inherent instability of the kinetically controlled, not thermodynamically controlled system.

4.4.2 Drawbacks of Eh-pH diagrams

Eh/pH diagrams are very useful tools in attempting to predict the dominant arsenic species under any specific conditions, but they do not take into account a number of important factors, including the effects of solid surfaces, organic arsenicals and biological reactions. The limits of usefulness of Eh/pH diagrams are demonstrated by apparently anomalous results from several field studies:

a) although As(V) is the more thermodynamically stable inorganic arsenic species in aerobic systems, such as surface waters, As(III) is found in seawater and oxic freshwaters (Johnson and Pilson, 1972; Butler and

Smith, 1985; Seyler and Martin, 1989; Anderson and Bruland, 1991; Santosa et al, 1994);

b) Haswell et al (1985), reported that up to 80% of arsenic present in aerobic soil may be As(III), and As(V) has also been found in anoxic environments (Peterson and Carpenter, 1986).

Therefore, if Eh/pH diagrams are to be believed as they stand, significant quantities of arsenic are expected only where oxidised sulphur and reduced iron exist simultaneously. Siami et al (1987) found that these conditions do persist in parts of lake Michigan at certain times of the year, and As(III) is stable in some stratified lake waters (Seyler and Martin, 1989; Crecelius et al, 1994) and in lake sediments, and by analogy is found and remains stable in some groundwaters (Korte and Fernando, 1991). The effects of:

a) micro-organisms,

b) solid surfaces -and how these vary with i) temperature,
ii) pH,
and iii) Eh,

have not yet been described in any great detail, although both Ahmann et al (1994) and Dowdle et al (1996) show that the reduction of As(V) to As(III) in sediments may be controlled by certain strains of bacteria which exhibit respiratory growth, utilising As(V) as an electron acceptor. Dowdle et al (1996), went on to show that this phenomenon takes place in both freshwater and marine sediments, suggesting it is not a localised occurrence. Indeed, it is interesting to note that the microbes present used As(V) preferentially as an electron donor over both phosphate and sulphate, although nitrate was preferred to As(V). This is particularly interesting as the chemical similarity of phosphate to arsenic results in their competition for sorptive sites in sediments (Kuwabara et al, 1990; Peters et al, 1996).

4.5 Interactions with solids (oxidation/reduction processes)

The kinetics of oxidation of arsenite ($H_nAsO_3^{3-n}$) to arsenate ($H_nAsO_4^{3-n}$) with oxygen are very slow at neutral pH, but comparatively rapid in strongly acidic (Cherry et al, 1979) or alkaline conditions (Ferguson and Gavis, 1972). The reaction rarely proceeds to completion in the surface aquatic environment (Ferguson and Gavis, 1972) and as a result of this slow rate of reaction, the predicted proportions of

arsenic species (based on thermodynamic calculations) do not always match. The redox reaction of the As(III)/As(V) system, may be described by the following equation:

$$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_4AsO_3 + H_2O \qquad E° = +0.56V$$

If the Nernst equation is applied for the redox potential at pH7, a value of +0.147V is calculated for the same concentration of both forms. For a 99% oxidation of As(III), however, +0.206V is required, indicating an easy oxidation, even by dissolved oxygen. The kinetics of a homogenous oxidation by dissolved oxygen are, however, very slow, and may lead to a conversion rate of only a few percent per week (Jekel, 1994).

Manganese(IV) and iron(III) oxides present on the surfaces of organic and mineral compounds present in sediments may be primarily responsible for catalysing the reaction through an electron transfer mechanism:

$$MnO_2 + HAsO_2 + 2H^+ \rightarrow Mn^{2+} + H_3AsO_4 \qquad E° = +0.67v$$

$$2Fe^{3+} + HAsO_2 + 2H_2O \rightarrow 2Fe^{2+} + H_3AsO_4 + 2H^+ \qquad E° = +0.21v.$$

where E° = standard electrode potential: +ve oxidising, -ve reducing, (Oscarson, 1981c, 1983), although microorganisms are also thought to be important (Ferguson and Gavis, 1972).

Addition of As(III) as $NaAsO_2$ to untreated or MnO_2 coated sediments results in oxidation of the arsenic to As(V), or adsorption onto the oxide surfaces (Oscarson et al, 1981b, c, 1983). The oxidation of As(III) by MnO_2 proceeds in the following manner:

$$HAsO_2 + MnO_2 \rightarrow (MnO_2)\bullet HAsO_2$$

$$(MnO_2)\bullet HAsO_2 + H_2O \rightarrow H_3AsO_4 + MnO$$

$$H_3AsO_4 \rightarrow H_2AsO_4^- + H^+$$

$$H_2AsO_4^- \rightarrow HAsO_4^{2-} + H^+$$

$$(MnO_2)\bullet HAsO_2 + 2H^+ \rightarrow H_3AsO_4 + Mn^{2+}$$

and is dependent upon the nature of the manganese present, there being three main manganese dioxides, birnessite, cryptomelane and pyrolusite. Each of these has a different specific surface and point of zero charge (see Section 4.8.1), leading to different reaction rates (Oscarson et al, 1983).

Manganese is a very effective oxidising agent, but while iron is much slower (Oscarson, 1981b), iron is more important over longer periods of time. Iron and phosphate concentrations were found to be significant factors in the establishment of arsenic levels (Clement and Faust, 1981), with arsenic release being dependent upon reduction of Fe^{3+} to Fe^{2+} However, adsorption-desorption equilibria as well as the amount of 'available' arsenic greatly influence the soluble arsenic concentration found in the aqueous phase.

4.6 Arsenic as a redox indicator

It has been suggested (Cherry et al, 1979; Tallman and Shaikh, 1980) that arsenic species may be used as an indicator of redox conditions in groundwater, provided that accurate concentrations of the arsenic species present can be made and that there are no competing redox reactions taking place. The usefulness of using arsenic for this purpose is doubtful (Butler and Smith, 1985; Welch et al, 1988; Holm and Curtiss, 1989), possibly due to the fact that As(III) is not completely oxidised to As(V) unless microorganisms catalyse the reaction (Ferguson and Gavis, 1972); and Cherry et al (1979) admit that at the concentrations of H_2S, $H_2PO_2^-$, H_2, Fe^{3+}, Fe^{2+} and O_2 that occur in natural water, oxidation (or reduction) of As(III) [or As(V)] could require many months or years, making it unsuitable for anything other than groundwater. A lack of chemical equilibrium may also be a common feature in groundwater (Lindberg and Runnells, 1984), suggesting that either the system is not yet in equilibrium, or that some biological species must be present to reduce As(V) [Peters et al, 1996], or perhaps to oxidise the As(III). Although the potential for methylation of arsenic exists in these waters, the much lower levels of biological activity at these depths make this process doubtful. This is supported by the fact that the methylated forms commonly found in surface waters, have yet to be detected in groundwaters (Peters et al, 1996), although there are a number of recent reports of both micro-and macrobiota inhabiting karstified aquifers (Waters and Banks, 1997), together with aquifer dwelling bacteria capable of oxidising both iron carbonate to

ferric oxide and sulphide to elemental sulphur (West and Chilton, 1997; Tyrrel and Howsam, 1997). Clearly, however, microbial life requires the presence of carbon, electron donors and acceptors, a water supply and porosity (particularly secondary porosity) [West and Chilton, 1997], all of which are not prevalent in every aquifer.

4.7 Arsenic redox rates

The rate of change in the oxidation state of arsenic is not generally regarded as being rapid (especially in aqueous systems), so the thermodynamically predicted proportions of arsenic species rarely correspond to the concentrations measured *in situ* (Reimer et al, 1988; O'Neill, 1990; Bowell et al, 1994).

Little is known about the rate of oxidation of As(III) to As(V) in natural waters (Johnson and Pilson, 1975; Aggett and Kriegmann, 1988), but it is comparatively rapid in strongly acidic (Ferguson and Gavis, 1972; Cherry et al, 1979) or alkaline conditions (Ferguson and Gavis, 1972) and slow at neutral pH (Lemmo et al, 1983). No quantitative information is available on aerobic surface waters (Ferguson and Gavis, 1972). In surface ocean waters, the As(V)/total inorganic arsenic ratio is approximately 0.8 (Ferguson and Gavis, 1972). In lakes the residence time is shorter than in the oceans, and without the actions of micro-organisms, the oxidation of As(III) is thought unlikely to proceed far (Ferguson and Gavis, 1972). The confusion and numerous theories regarding sample preservation highlights the lack of agreement on this subject and obviously, the rate of As(V) reduction and As(III) oxidation cannot be based on a few simple measurements (a discussion of sample preservation techniques is presented in Chapter 7).

Larsen et al (1993) found that As(III) was oxidised to As(V) in urine samples, but not in samples made up with water, indicating that the urine matrix plays a role in the conversion of As(III). The As(III) was also oxidised if the standard mixtures were made up with the HPLC basic mobile phase (pH 10.3), indicating that with increasing pH, the potential necessary to oxidise As(III), decreases. They reported no evidence of any conversion of either MMAA or DMAA.

Johnson and Pilson (1975) give data that show As(III) oxidation in seawater is a function of pH, salinity and temperature, as well as initial As(III) concentration. From their data, they were able to derive a regression equation for As(III) oxidation taking these controlling factors into account. They also report the oxidising effect of sunlight

on As(III), both in natural seawater and deionised water samples, although obviously this effect will in nature be limited by the depth of sunlight penetration. Brockbank et al (1988) found that As(III) oxidation was very rapid in aerated distilled water exposed to UV radiation, with the rate being slowed by two orders of magnitude under deaerated conditions. In seawater samples, the rate of photochemical oxidation was slower still, with the half-life of As(III) increasing from 2 minutes to 5 minutes. The effect of sunlight is expected to be more important in As(III) oxidation in freshwaters (Brockbank et al, 1988).

A temperature increase of 10°C generally results in an increase in As(III) oxidation by a factor of two. At a given temperature, the initial rate of oxidation is affected approximately equally by a change in initial As(III) concentration, salinity or (inversely) by pH (Johnson and Pilson, 1975). Oxygen was present in each experiment in excess compared with As(III) and had little affect on oxidation rate. Changes in As(III) oxidation with salinity might be explained by differences in the concentrations of one or more catalysts (such as transition metals present in trace amounts), which act with dissolved oxygen to oxidise As(III) [Johnson and Pilson, 1975].

Cherry et al (1979) found that pH controlled the rate of oxidation of As(III) by Fe^{3+} and the reduction of As(V) by H_2S. In both cases, a reduction of pH brings around an increase in either the oxidation or reduction rate.

Oscarson et al (1983) found that the rate of As(III) oxidation by manganese oxides is dependent upon mineral specific surface areas and crystallinity, point of zero charge (ZPC) [see Section 4.8.1 for definition] and temperature, with reaction rate increasing with elevated temperature, and generally increasing with decreasing ZPC and increasing specific surface area. The reaction also involves at least two reaction rates, one within the first 30 minutes and another thereafter. The initial reaction rate is much greater, but the exact rates were not evaluated due to experimental limitations (Oscarson et al, 1983). Bowell et al (1994) working with tropical soils, found that As(III) production is not influenced by total arsenic concentration, but rather by soil processes, and had little to do with microbial activity.

McGeehan and Naylor (1994) showed that As(V) reduction can take place in a matter of days in an anaerobic soil, in broad agreement with previous reports for lacustrine sediments (Aggett and O'Brien, 1985), groundwater (Cherry et al, 1979) and is more rapid than reported for ocean sediments (Andreae, 1979). The results of this

study show that As(V) is desorbed prior to reduction, indicating the importance of ferric iron concentrations in sediments (McGeehan and Naylor, 1994).

4.8 Removal from solution/solid phase and transport

Arsenic generally forms negatively charged anions. Consequently, it will coprecipitate and adsorb onto clay particles and also coprecipitate with metal-ion complexes. Arsenic will also form insoluble precipitates with some other elements. Arsenic removal from a solution phase to a solid phase may therefore occur by one of these three major processes:

i) adsorption onto hydroxides, clays and other surfaces,

ii) coprecipitation with metal ion precipitates,

iii) precipitation.

Similarly, release from a solid phase will occur by the reversal of one of the above processes, although this is often thought of as a slower process (Davis et al, 1989; Korte and Fernando, 1991; Peters et al, 1996; Kuhlmeier, 1997), and consequently may exert a control on arsenic adsorbed to suspended particles (Carpenter et al, 1978).

Factors limiting the ability to define geochemical reactions responsible for arsenic concentrations in groundwater include:

a) thermodynamic data for the aqueous complexes and minerals of arsenic have not been critically evaluated;

b) although arsenic exists in more than one oxidation state in most groundwater systems, only limited analytical data are presently available that include speciation [generally, As(III) is regarded as being more soluble and hence more mobile than As(V)];

c) adsorption of trace constituents can be affected by a variety of factors including competition with other anionic solutes for the same adsorption sites, and composition of solid phases present in an aquifer (minerals, organics and amorphous oxides). Additionally, adsorption reactions may be irreversible.

4.8.1 *Inorganic arsenic adsorption*

Adsorption is best described as the aggregation of matters on an interface, and a number of adsorption reactions may occur:

a) electrostatic interactions, such as: i) coulombic attraction,
ii) ion exchange,
iii) specific adsorption, which includes specific 'chemical' adsorption;

b) adsorption due to induced polarisation;

c) covalent bonding;

and d) Van der Waals forces (Lo et al, 1992).

Adsorption is the most likely process for arsenic removal from solution as coprecipitated and precipitated compounds are generally formed only slowly (Lemmo et al, 1983; Peters et al, 1996). Adsorption of inorganic arsenic onto clays is dependent on pH, texture, iron and aluminium content, organic carbon content and time of reaction (Bowell et al, 1994), although bauxite (aluminium hydroxide) and silicates are usually only moderately enriched in arsenic (Onishi and Sandell, 1955). Tourtelot (1964) found that, in general, arsenic in non marine shales and clays had been adsorbed by the clay minerals, whilst in marine shales and clays, the arsenic is generally present in pyrite and organic matter.

Arsenic is adsorbed onto hydrous iron oxides, and although arsenic was thought to be absent from manganese oxides (Shnyukov, 1963), [due to manganese oxides generally having a negative charge and being much more soluble than iron oxides], the phenomenon of induced polarisation often allows the adsorption of arsenic species (Oscarson et al, 1981b, c, 1983; Mok and Wai, 1994), as does the common coexistence of iron and manganese in ferromanganese nodules, where it is thought that iron rather than the manganese is the cause for their efficient scavenging of arsenic from solution (Carpenter et al, 1978).

Holm et al (1979) showed that in the presence of phosphate, phosphate was adsorbed onto anaerobic river sediments to a greater extent than As(V), MMAA, As(III) and DMAA in that order. This phenomenon was also shown to occur in aerobic alluvial soils, but in this case, the order was As(V) $\approx$ MMAA > DMAA > PO_4, probably due to the presence of $Fe(OH)_3$ rather than the more soluble $Fe(OH)_2$ which would be

present in the anaerobic soils (Holm et al, 1979). This phenomenon has also been reported by Davenport and Peryea (1991), who found that addition of either monoammonium phosphate or monocalcium phosphate fertilisers caused an increase in soil arsenic mobility. The rate of arsenic release was correlated to phosphate addition in the case where the soil was amended with monoammonium phosphate, but not with monocalcium phosphate.

Adsorption of Na_2HAsO_4 [As(V)] by micaceous colloids was studied by Huang (1975). Muscovite and biotite adsorbed 423µg/g and 408µg/g respectively after 24 hours. Muscovite and biotite also adsorbed more arsenic as particle sizes decreased from 2-5µm (it is generally accepted that particles <5µm are colloidal) to <0.08µm. The capacity of a sediment to retain and concentrate arsenic is controlled primarily by grain size (Horowitz, 1992, 1996), because smaller grains have a greater surface area and hence a higher adsorptive capacity per unit weight. Azcue et al (1994a), however, found that the highest sediment arsenic concentrations in their study of lake sediments were associated with the 45-53µm fraction, with decreasing concentrations in the smaller size fractions. This is important, as arsenic bound to such 'large' particles tends to be less mobilised by erosional processes (Azcue et al, 1994a).

Arsenous [As(III)] acid species will adsorb or coprecipitate with iron and manganese oxides (Oscarson, 1981a, b, c, 1883) and will also adsorb onto activated aluminium oxide and bauxite, and illite (Abdelghani et al, 1981). However, fewer investigations have been carried out with regards to As(III) adsorption onto clays, carbonates or other hydroxides as compared with As(V).

Several studies of arsenic adsorption have been carried out but their conclusions are often contradictory, mainly because of the differing experimental conditions under which they were performed.

The combined effect of pH and the adsorbents zero point of charge (ZPC) explain many of the observed differences reported by various authors. The effect of variation in pH is the observed dissociations of acids in solution. The ZPC is that pH at which the positive and negative charges on a colloid are balanced. At a pH above the ZPC, minerals have an excess negative charge density and hence have a cation exchange capacity; below the ZPC, an excess positive charge density and an anion exchange capacity (Xu et al, 1991; Appello and Postma, 1994), so that generally, oxide surfaces will change from being positively charged at low pH to being negatively charged at high

pH (Bowell, 1994). Soils typically have a negative charge due to the negative charges on layer silicates and organic matter. The ZPC's of some common environmental materials are shown in Table 4.1.

The adsorption of As(V) by goethite, haematite and lepidocrocite is greater than for either As(III), MMAA or DMAA over the pH range 3-9, but only slightly greater at both extremely acidic (pH<3) and alkaline (pH>9) conditions (Bowell, 1994). This is, however, to be expected if one examines the dissociation constants for these compounds (see Appendix A).

Table 4.1. Zero point charges for some environmental materials.

Material	pH at ZPC
α-Al_2O_3 (corundum)	9.1
α-$Al(OH)_3$ (gibbsite)	5.0
α-Fe_2O_3 (haematite)	8.5; 6.5-8.6[1]; 7.1[2]
γ-Fe_2O_3 (maghemite)	6.7
α-FeOOH (goethite)	7.3 (7.6-8.1[1])
γ-FeOOH (lepidocrocite)	7.8-8.0[1]
$Fe(OH)_3$ amorphous	8.5
α-MnO_2 (cryptomelane)	2.8
β-MnO_2 (pyrolusite)	6.4
δ- MnO_2 (birnessite)	2.3
SiO_2 (quartz)	2.9
SiO_2 unspecified	2.0
Feldspar unspecified	8.5[2]
Kaolinite	4.6
Montmorillonite	2.5
Calcite	8-9.5

From Fergusson, 1990; Oscarson et al, 1983;
Appello and Postma, 1994; [1]Bowell, 1994; [2]Prasad, 1994.

It is thought that under most environmental conditions (soil adsorbents, pH6-8), As(III) adsorption will increase with pH to a maximum at a pH of 7 to 9 (Frost and Griffin, 1977; Korte and Fernando, 1991; Xu et al, 1991), although this will vary depending upon the ZPC of the adsorbent (Bowell, 1994). As(V) adsorption, however, is high at lower pH (around pH 5) and decreases markedly with both increasing and decreasing pH (Frost and Griffin, 1977; Xu et al, 1991). Laboratory work on adsorption of arsenic on ferric oxyhydroxide indicates that at high pH values, the lower adsorption values are probably due to the formation of negative surface charges on the ferric oxyhydroxide, resulting in electrostatic repulsion between the sorbent and arsenic anion. Ferric oxyhydroxide is nearly always found in oxidised sedimentary environments, and

this lowered adsorptive capacity at elevated pH is consistent with a tendency for slightly alkaline, non-thermal groundwater to have elevated arsenic concentrations (Welch et al, 1988).

The contradictory results reported are probably due to the inherent difficulty encountered in accurately measuring the pH of the ZPC (Korte and Fernando, 1991). Both specific adsorption (adsorption under the combined influence of ionic and non-ionic bonding may occur even when the surface is uncharged) and electrostatic effects may be important depending on the pH and the nature of the adsorbent.

At low arsenic concentrations, As(III) adsorption increases with time, with 50% to 90% complete in the initial few minutes and completion occurring within a few days. However, whilst adsorption equilibrium is quickly reached, desorption is slow (Davis et al, 1989; Korte and Fernando, 1991; Kuhlmeier, 1997). Indeed, under certain circumstances, adsorption is irreversible, indicating only a change in Eh and associated alteration of the oxide structure will result in the release of the arsenic (Hingston et al, 1974).

4.8.2 *Organoarsenic adsorption*

As mentioned in Section 3.2.5, DMAA is generally inactive as a phytotoxin in soil, and this may be attributed to adsorption by soil colloids (Hiltbold, 1975). Indeed, the adsorption of phosphate and a number of arsenicals by a wide range of soils appears to increase in the order: phosphate < sodium dimethylarsenate (Na-DMAA) < disodium methylarsenate (DSMA) ≈ As(V), with adsorption in every case being positively correlated with soil clay content (Hiltbold, 1975). The fact that dimethylarsinates are less strongly sorbed is presumably due to their higher dissociation constant and larger size (O'Neill, 1990). Sub-soils have also been reported as being much more adsorptive of MSMA than surface soils, presumably due to the higher concentrations of clay and iron oxides found there. Abdelghani et al (1981) found that MSMA exhibited the highest affinity for ferric oxide, with organics, activated carbon and octodecyclamine also having a high adsorptive capacity. Clays and fine sand had much lower affinities for MSMA.

When several clay minerals of the same particle size were compared with respect to their DSMA adsorptive powers, kaolinite was found to be considerably more effective than vermiculite over a wide range of solution concentrations. The greater

adsorptive capacity of kaolinite and limonite relative to the 2:1 type clays vermiculite and montmorillonite (see Table 4.2) has been attributed to methylarsenate's affinity for mineral surfaces with exposed hydroxyl groups.

The amount of methylarsenate adsorbed also increases with the arsenic concentration of the equilibrium solution, with a clay soil being reported as adsorbing as much as 2270µg As/g in equilibrium with a DSMA solution containing 75ppm arsenic, while another clay adsorbed a DSMA equivalent of 81µg As/g in equilibrium with a 3ppm arsenic solution (Hiltbold, 1975). It is important to note, however, that the potential for arsenic phytotoxicity comes not from the amount of adsorbed arsenic, but from the concentration in the equilibrium soil solution (this is discussed more fully in Section 5.9.7).

Table 4.2. Adsorption of DSMA from 25ml of 5ppm As solutions by 1g samples of reference materials.

Material	Equilibrium solution ppm As	DMSA adsorbed	
		µg As per g	% total applied
Limonite	0	125.0	100
Montmorillonite	4.39	15.3	12
Kaolinite	1.20	95.1	76
Vermiculite	3.71	32.3	26

From Hiltbold, 1975.

4.8.3 *Adsorption isotherms*

There are two equations used to describe adsorption of metals to substrates.

a) Langmuir isotherms, are based upon three assumptions:

i) that there is a constant energy of adsorption which is independent of surface coverage (homogenous effect);

ii) that adsorption occurs at specific sites with no interaction between adsorbate molecules;

iii) that the maximum adsorption possible is a complete monomolecular layer.

Essentially, then, the Langmuir isotherm describes the situation where the surface of the solid consists of an array of adsorption sites of equal energy with each site being capable of adsorbing one species, as might be expected on the surface of a pure crystalline solid with few defects (Carpenter et al, 1978; O'Neill, 1990). Fitting to Langmuir isotherms demonstrates that the reactions are reversible.

b) Freundlich isotherms which assume that there is a decrease in energy of adsorption with increasing surface coverage due to surface heterogeneity.

The Freudlich isotherm, then describes surface heterogeneity with groups of different homogenous adsorptive sites of differing energy each following Langmuir-type interactions. This may be envisaged in a soil consisting of a range of minerals each with its own individual surface properties and with possible associated surface coatings of various hydrated oxides of Fe, Mn and Al (O'Neill, 1990).

Several workers have reported differing results when trying to apply isotherms to their data:

1) Holm et al (1979) reported that As(V), MMAA and DMAA adsorption on river sediments followed a Langmuir isotherm although As(III) appeared to be linearly dependent on concentration and did not follow an isotherm;
2) Carpenter et al (1978) found that over a stable arsenic [as As(V)] concentration range of less than a factor of 10, the system (natural sediments from Puget Sound) investigated could be described by the Langmuir isotherm. However, if the stable arsenic concentrations were varied over several orders of magnitude, the adsorption data better fitted a Freundlich isotherm. This suggests that the adsorption energy is changing with surface coverage; that is, As(V) adsorbs onto the energetically more favourable sites first, leaving the less favourable sites for additional uptake.
3) Livesey and Huang (1981) used Langmuir-type isotherms to describe the adsorption of As(V) on soils, finding that an increasing proportion of arsenic was adsorbed with increasing equilibrium arsenic concentrations until a critical equilibrium was reached (which varied according to soil type), when the trend reverted. At the lower arsenic concentrations, the inverse relationship was thought to be due to other soil anions competing fro sorption sites;
4) Puttemans and Massart (1982) showed that As(III) adsorption could be described by the Langmuir isotherms;
5) Moore et al (1988) used Langmuir-type isotherms to describe the adsorption of As(V) on aluminium hydroxide;

6) Elkhatib et al (1984a) fitted their data from a series of soils to a modified version of the Freudlich isotherm. The differences in the rates of sorption by the various soils were explained by differences in pH, Fe_2O_3 content and organic carbon content. The amount of As(III) desorption was very low, but could be related to pH and the percentage of Fe_2O_3.

4.8.4 *Sorption (coprecipitation and adsorption)*

Arsenic has been found to be effectively removed from acidic solutions by adsorption onto soil minerals and other solid phases, indicating that arsenic oxyanions were naturally retained in the presence of clay minerals, and iron, aluminium and manganese oxides (Frost and Griffin, 1977; Holm et al, 1979; Oscarson et al, 1981a, b, c, 1983).

Arsenic has been shown to coprecipitate or adsorb with or onto the following phases:

a) hydrous iron oxides and iron oxyhydroxides (Jacobs et al, 1970; Pierce and Moore, 1982; Siami et al, 1987; Davis et al, 1989; Seyler and Martin, 1989; Belzile and Tessier, 1990; Mok and Wai, 1994; Azcue et al, 1994a, 1994b; McGeehan and Naylor, 1994; Webster et al, 1994; Bright et al, 1994; Azcue and Nriagu, 1995),

b) aluminium (Jacobs et al, 1970; Oscarson et al, 1981a, b, 1983; Mok and Wai, 1994),

c) manganese (Oscarson et al, 1981a, b, c, 1983; Mok and Wai, 1994; Azcue et al, 1994b; Bright et al, 1994; Azcue and Nriagu, 1995),

d) clay (Frost and Griffin, 1977; Holm et al, 1979; Oscarson et al, 1981a),

e) sulphide (Mok and Wai, 1994),

and f) organic matter (Wegemann, 1978; Xu et al, 1991).

Other anions, when present, can compete with arsenic for adsorption sites. This is especially true in the case of phosphate ($H_2PO_4^-$) when the sites are on aluminium or iron oxide surfaces. Other ions are less successful in displacing arsenic, with the order of effectiveness decreasing for As(V) in the order of $H_2PO_4^- > H_2AsO_4^- > SO_4^{2-} > CO_3^{2-}$, and for As(III) in the order of $H_2PO_4^- > H_3AsO_3 > F^- > SO_4^{2-} > CO_3^{2-}$. Phosphate

substantially suppresses arsenic adsorption, but this varies from soil to soil (Carpenter et al, 1978; Livesey and Huang, 1981).

Carbonates are important factors to be taken into account with respect to sorption processes. Carbonates may 'armour' sediment oxide surfaces creating a diffusion barrier which may greatly reduce both the oxide dissolution and sorption capacity of hydrous oxides. Additionally, carbonates may act as an important sink for many trace elements, particularly when these are at concentrations high enough to saturate other sediment sinks (Oscarson et al, 1981a).

Wegemann (1978) suggested that even under somewhat reducing conditions, barium arsenate may exert some control over total dissolved arsenic, due to its low solubility, whereas Essington (1988) reports that barium arsenate is considerably less stable than previously believed, especially in the presence of carbon dioxide, sodium and chloride; and the accuracy of the equilibrium constant has also been questioned (Crecelius et al, 1986), again suggesting there is little or no agreement in the literature on this subject.

Adsorption of arsenic depends upon its oxidation state, with oxides generally adsorbing As(V) more strongly then As(III) [Holm et al, 1979; Gulens et al, 1979; Seyler and Martin, 1989; Belzile and Tessier, 1990; Bhumbla and Keefer, 1994.], although Oscarson (1981b) states that As(III) is more strongly adsorbed by Fe(III) than As(V). As(III) adsorption is maximised at a pH of 7-9 (Bhumbla and Keefer, 1994). Belzile and Tessier (1990) showed through calculation that As(V) rather than As(III) is associated with iron oxyhydroxides due to the ease by which both manganese and iron oxyhydroxides oxidise As(III) to As(V) [Peterson and Carpenter, 1983)], both reactions being thermodynamically favourable:

$$MnO_{2(s)} + H_3AsO_3 \leftrightarrow Mn^{2+} + HAsO_4^{2-} + H_2O$$

$$(\Delta G^\circ_r = -86.9kJ/mol)$$

$$2Fe(OH)_{3(s)} + H_3AsO_3 + 2H^+ \leftrightarrow 2Fe^{2+} + HAsO_4^{2-} + 5H_2O$$

$$(\Delta G^\circ_r = -32.6kJ/mol)$$

As(III) species will also coprecipitate with iron oxides, although not as strongly as with As(V). As(III) has a strong affinity for sulphur and readily adsorbs onto or

coprecipitates with sulphides. Elkhatib et al (1984a, b) could not distinguish between adsorption and precipitation and so called the process sorption. They found that sorption increases as As(III) concentration increases, and that Eh and the amount of iron oxides were the primary soil properties controlling the rate of As(III) adsorption. As both increase, the rate of As(III) sorption also increases.

4.8.4.1 *Iron*

Faust et al (1987 a, b, c) studied sorption of different arsenic species on various sediment types. They found that organic sediments sorbed all arsenic species more than sandy sediments, and that part of the effect could be explained by coprecipitation with iron. Elkhatib et al (1984a, b) also showed that iron oxides were important at high initial arsenic concentrations, whilst clay content became more important at lower arsenic concentrations. It is thought that arsenic forms covalent bonds with iron atoms through displacement of OH or OH_2 ligands (Elkhatib et al, 1984a). The results indicate that sorption can occur both through electrostatic reaction and specific adsorption, with the latter process dominating when iron oxide is present in the sorbent. Indeed, coprecipitation of arsenic with hydrous iron oxides, ultimately leads to the formation of the mineral scorodite ($FeAsO_4 \bullet H_2O$), according to the following reaction:

$$Fe(OH)_3 + H_3AsO_4 \leftrightarrow FeAsO_4 \bullet H_2O + 2H_2O$$

Coprecipitation can occur by adsorption or inclusion of impurities in a precipitate. In this context, coprecipitation means that As(V), or As(III), is associated with the surface of ferric oxide particles via adsorption, even though these surfaces will become the 'internal surfaces' of coagulated colloids. This is a fairly rapid process at a constant pH, as has been shown by adding As(V) to solutions in which the ferric oxides have already precipitated. A change in pH (either an increase or decrease) causes a slowing in reaching equilibrium (Davis et al, 1989).

The arsenic sorbed onto iron compounds may be released into solution if the iron is reduced upon burial of sediments. Iron(III) is almost insoluble, while the reduced Fe(II) is highly soluble. Subsequently, the released arsenic and iron may diffuse upwards or downwards in the sediment porewaters. Upward diffusion into more oxic conditions may result in reformation of authigenic iron oxyhydroxides with which the arsenic may

associate, either through adsorption or coprecipitation or, under anoxic conditions may result in the release of the arsenic and iron into the overlying waters. Downward diffusion results in the formation (assuming their presence) of iron sulphides, arsenic sulphides or iron-arsenic sulphides (Ferguson and Gavis, 1972; Siami et al, 1987; Moore et al, 1988; Cullen and Reimer, 1989; Belzile and Tessier, 1990; Masscheleyn et al, 1991; Mok and Wai, 1994; Bright et al, 1994; Azcue and Nriagu, 1995), although the precise solid phase formed has not yet been identified (Belzile and Tessier, 1990).

Additionally, iron(III) oxides have been shown to undergo diurnal redox reactions in response to small (0.3-0.5 pH units) pH fluctuations caused by the action of photosynthetic algae (Davis et al, 1989; Olem, 1989; Kuwabara et al, 1990). Such redox reactions have important implications in the potential mobility of arsenic in acid mine drainage systems, and fluctuations of up to 30-40% have been observed in dissolved As(V) concentrations. These fluctuations could only be accounted for by adsorption/desorption processes (Davis et al, 1989). Overall, these observations suggest that arsenic chemistry is closely related to that of iron in sedimentary environments, and this cycle is shown diagramatically in Figure 4.1.

It has been shown that the action of burrowing organisms will increase the flux of dissolved material between a sediment and the overlying water, by causing particle and fluid transport within a deposit (Aller, 1978), and this might have important implications for arsenic cycling in areas heavily populated by such creatures. Biogenic particle diffusion is not considered to be as important as the movement of fluids through burrows, although the subduction of fresh organic matter that would otherwise have decomposed at or near the sediment surface results in the redistribution of reactive particles. In the case of decomposition products subject to precipitation, adsorption or coprecipitation reactions, this might result in a change in the release of these products into the overlying water. If the organisms form numerous permanent or semi-permanent tubes, then the sediment becomes a body permeated with cylinders filled with water with the same chemistry as the overlying water, resulting in a redistribution of porewater diffusion geometry. Additionally, if there is a high rate of decomposition within burrows, then the resulting reducing conditions may also be important. Here, Fe may be mobilised by both reduction in outer burrow walls and oxidation of Fe-sulphides along the inner burrow surfaces, leading to the development of acid mine-like conditions in dwelling

tubes (Aller, 1978). The action of such organisms may also introduce a seasonal aspect to arsenic removal and release into both sediment porewaters and overlying waters.

It has also been suggested that As(III) is more strongly adsorbed by Fe(III) than As(V). This is attributed to the structural and charge differences between the two arsenic complexes; H_3AsO_3 [As(III)] co-ordination geometry is pyramidal (at pH<~9.2, it is predominantly a neutral complex), while H_3AsO_4 [As(V)] co-ordination geometry is tetrahedral (at pH>~2.2, it is largely dissociated and negatively charged) [Oscarson et al, 1981b].

Arsenic is chemically similar to phosphorus and may substitute isomorphously into phosphate minerals (Wagemann, 1978). However, in some Florida phosphate pebbles, arsenic is proportional to iron and inversely proportional to phosphate, thus showing that arsenic's affinity for iron is predominant over its substitution for phosphorus (Stowe, 1969). Gulbrandsen (1966) has shown positive correlation between high arsenic contents in phosphorites and organic content.

Phosphate has, however, been shown to displace arsenic held by humic acids (Mok and Wai, 1994), and may also play a part in arsenic release from aerobic sediments (Clement and Faust, 1981; Davenport and Peryea, 1991).

4.8.4.2 *Manganese*

Arsenic species may be immobilised by, adsorbed onto, and coprecipitated with hydrous manganese oxides (Oscarson et al, 1981a, b, c, 1983; Azcue et al, 1994b), although they adsorb little As(V) [Oscarson et al, 1981b]. These oxides have ZPC's in the order of 2-6.5 (see Table 4.1) and so carry a net negative surface charge at the pH of most river sediments (pH5-8), though the charge density varies depending upon the phase present (Oscarson et al, 1983). Although the exact phase distribution of the manganese oxides in sediments is not possible, manganese does apparently exist in a labile state in the sediments, as a coating on other soil/sediment components and as discreet particles, as backed up by the relative ease by which a weak extractant may remove it (see Section 8.4.4) [Oscarson et al, 1981a].

The net negative surface charge suggests that hydrous manganese oxides would not adsorb arsenic anions (Mok and Wai, 1994). However, the surface charge of these oxides can be changed by the adsorption of other divalent ions, leading to a decrease in the negative surface charge and finally a positive charge, giving them the ability to

remove As(III) and As(V) from the water. As(V) may also be incorporated into sediments by coprecipitation with hydrous manganese oxides in the following manner:

$$3MnOOH + 2HAsO_4^{2-} + 7H^+ + 3e^- \leftrightarrow Mn_3(AsO_4)_2 + 6H_2O$$

while As(III) will not, leading to the idea that arsenic will be more mobile in sediments with low concentrations of iron and manganese oxides (Mok and Wai, 1994). Conversely, Oscarson et al (1983) suggest that, at neutral pH, As(III) is neutrally charged, whilst As(V) is negatively charged (see Eh/pH diagrams in Appendix D). This leads to the suggestion that As(III) is preferentially scavenged and oxidised to As(V), some of which is then released but most of which is retained due to there being no electrostatic repulsion to overcome as is the case when As(V) is adsorbed from solution.

The vertical distribution of arsenic in sediment profiles has been positively correlated (coefficient of 0.99) with that of manganese. The high arsenic concentrations in the surface sediments result from post depositional remobilisation processes in sediment-reducing zones. This is followed by upward migration of the released arsenic through the interstitial waters and then by oxidation-adsorption-precipitation reactions with hydrous manganese oxides, as well as with hydrous iron oxides, in the near surface oxidising layers (Mok and Wai, 1994). Azcue et al (1994b) go on to suggest that any release of arsenic due to manganese dissolution may be masked by readsorption by iron oxyhydroxide phases.

4.8.4.3 *Aluminium and clay*

In addition to iron and manganese, aluminium compounds are also sinks for arsenic. Consequently, aluminium also affects the mobility of arsenic in the environment. Both As(III) and As(V) are adsorbed by aluminium hydroxides and aluminium rich clay minerals (especially kaolinite). At low pH (less than pH 4), the dominant aluminium species is $Al(H_2O)_6^{3-}$. As the pH increases, hydroxyaluminium species begin to form. These comprise simple monomeric ions such as $Al(H_2O)_{6-n}(OH)_n^{+3-n}$ polynuclear species of various sizes and degree of basicity, or a complex mixture of both. The ZPC of amorphous $Al(OH)_3$ is 8.5 (see Table 4.1), and such hydroxides are extremely efficient adsorbers of arsenic. At low pH, the surface of the aluminium hydroxide complex is positive, and adsorption of arsenic species is mainly by coulombic attraction, while at

higher pH, the surface charge is negative, and specific adsorption must compete with coulombic repulsion (Mok and Wai, 1994). The fact that there is any adsorption when the pH is above the ZPC is attributable to specific binding, rather than chemical adsorption onto the hydroxide surface.

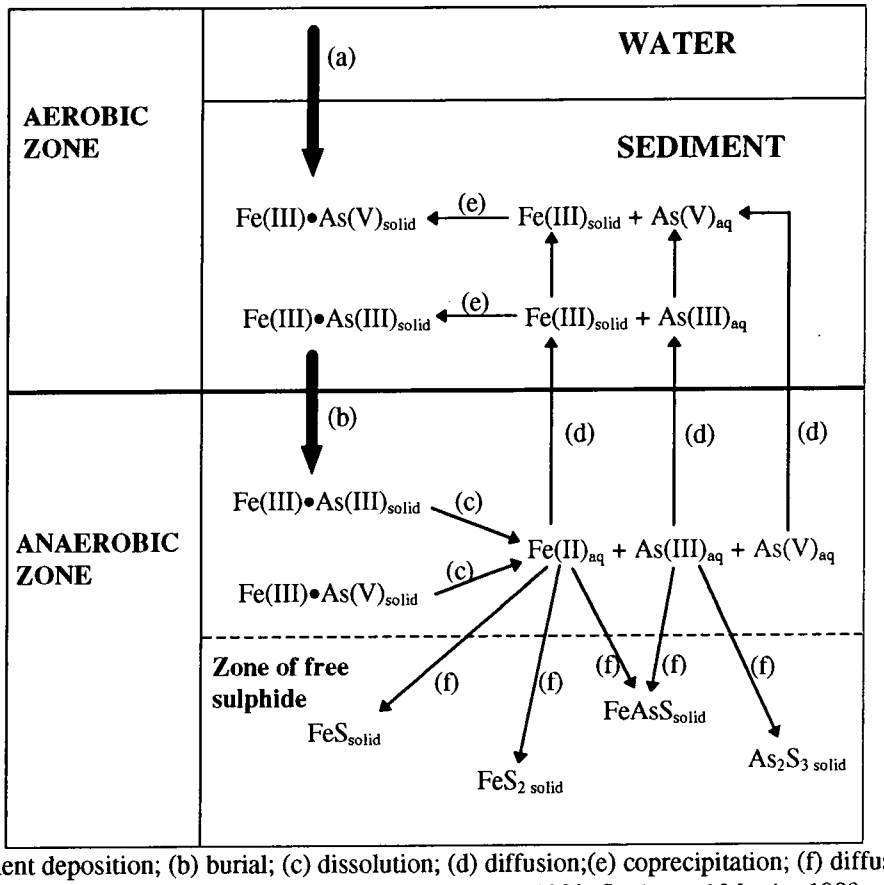
The very reactive $Al(OH)_3$ adsorbed onto the clay portion of sediments thus accounts for the high adsorption capacity of arsenic, because of the exposed octahedral cations on the broken clay particle, and the clay interlayer hydroxyaluminium polymers (Frost and Griffin, 1977; Schulthess and Huang, 1990). Other crystalline clay minerals present in the colloidal fractions of sediments include smectite, vermiculite, mica, quartz and feldspar. The clay minerals, particularly kaolinite, smectite and vermiculite, because of their large surface area and high cation exchange capacity, may be important in controlling many processes occurring at the sediment-water interface. Carpenter et al (1978) found that As(V) was most strongly adsorbed by illite, montmorillonite was intermediate, and kaolinite had the smallest capacity. This is in contradiction to the adsorptive capacities of these minerals for organoarsenic compounds (see Section 4.8.2). Kaolinite was found to be considerably more effective than vermiculite over a wide range of solution arsenic concentrations. The greater adsorptive capacity of kaolinite and limonite relative to the 2:1 type clays vermiculite and montmorillonite (see Table 4.2) has been attributed to methylarsenic(V)'s affinity for mineral surfaces with exposed hydroxyl groups (Hiltbold, 1975).

4.8.4.4 *Sulphide*

Sulphide minerals play an important role in controlling arsenic solubility. In arsenic containing sediments, where surface layers are oxidised, whilst those below are reduced, the concentration and partitioning of arsenic will be controlled by the redox interface. In the presence of sulphide in the reduced sediments, arsenic changes from a predominantly oxyhydroxide phase (generally iron) to a sulphide phase across the boundary interface (Siami et al, 1987; Moore et al, 1988; Cullen and Reimer, 1989; Seyler and Martin, 1989; Mok and Wai, 1994). This is shown diagramatically in Figure 4.1. In such a reduced zone, at low redox potential, iron minerals are partially reduced to ferrous [Fe(II)] iron, and manganese is partly reduced to the manganous [Mn(II)] state. When this reduction occurs, the adsorbed and coprecipitated arsenic is released into the porewaters (Ferguson and Gavis, 1972; Moore et al, 1988; Cullen and Reimer,

1989; Seyler and Martin, 1989; Belzile and Tessier, 1990; Masscheleyn et al, 1991; Mok and Wai, 1994). Sulphides in the anaerobic reduced environment will scavenge the arsenic with the formation of the iron, manganese and arsenic sulphides. The formation of the sulphides also accompanies the reduction of As(V) to As(III), leading to As(III) being the dominant dissolved arsenic species in the porewaters (Peterson and Carpenter 1986; Seyler and Martin, 1989), although porewater concentrations will not always coincide with solid phase arsenic concentrations (Peterson and Carpenter 1986; Bright et al, 1994). Due to the similarity of arsenic and phosphorus, it might be assumed that in phosphorus rich sediments, arsenic might be in competition with phosphorus for the sulphides. This is, however, not the case as phosphorus does not combine with sulphide as arsenic does (Siami et al, 1987).

Figure 4.1. The role of sulphides in the cycling of arsenic in sediments.



(a) Sediment deposition; (b) burial; (c) dissolution; (d) diffusion;(e) coprecipitation; (f) diffusion and reaction with sulphide. From Cullen and Reimer, 1989; Seyler and Martin, 1989.

Bowell et al (1994) found that in aerobic soils, the ratio of arsenic in solution to total soil arsenic concentration increases with depth to the water table, suggesting that leaching is more active at the water table than elsewhere in the soil profile. An

interesting suggestion put forward is that in this region, the breakdown of organic matter may result in the release of methylating agents, which, together with microorganisms could form soluble organoarsenic compounds (Bowell et al, 1994). However, other compounds resulting from the breakdown of vegetable matter actively scavenge arsenic and this is described in Section 4.8.4.5.

The significance of such transformations and the confinement of the arsenic to reducing layers is that in areas where redox fluctuations are possible (such as in intertidal sediments and some river and reservoir sediments), or where removal of the sediments from a reducing environment to one of a more oxidising nature may occur, then the sulphides would undergo oxidation, so releasing the bound arsenic back into solution. The formation of authigenic arsenic sulphides may thus act as a potential source of secondary pollution, unless there is a localised reservoir of iron oxyhydroxides to scavenge the released arsenic back out of solution.

It has been reported, however, that sulphide and oxygen may coexist in seawater due to the kinetic restraint on sulphide oxidation (Crecelius et al, 1986). Similarly, iron oxides and sulphides have been shown to coexist, due to there being a wide range of oxyhydroxide particles, some of which are more reactive and hence reduced much more quickly than others (Davison, 1993).

4.8.4.5 *Organic matter*

Organic matter in sediments, particularly humic substances (degradation resistant by-products of vegetation degradation) occur naturally in aquatic systems. Because of their acid-base, sorptive and complexing properties, they have a strong effect on the properties of water (Manahan, 1991), and thus play a part in the mobility of arsenic in aquatic systems (Bourg, 1981b; Mok and Wai, 1994). The uptake of arsenic by humic acids (insoluble humic substances) is controlled by adsorbate concentrations, pH, and ash content of the substrate. The adsorption of arsenic by humic acids is high in the pH range 5 to 7, particularly when they have high ash and calcium contents. Under acidic conditions, humic acids may retain more arsenic than clays and some metal hydrous oxides. The main retention sites on humic acids are amine groups (Mok and Wai, 1994).

Fulvic acids are soluble humic substances, and are known to be involved in iron solubilisation and transport (Manahan, 1991). Consequently, the presence of fulvic acids is likely to increase the leaching and mobility of arsenic (Xu et al, 1991), due to their

being adsorbed onto hydrous oxides in sediments by coulombic attraction (which leads to the formation of predominantly negative charged surfaces, through deprotonisation of functional groups) [Mok and Wai, 1994]. The effects of fulvic acid on inorganic arsenic adsorption is most marked in the pH range 4-8, with no effect above pH9 or below pH3. In addition, fulvic acids can react directly with arsenic (although this would be via a metal-organic acid complex analogous to that for phosphorus, as arsenic does not form cations), resulting in decrease in adsorption of the corresponding arsenic complex (Wagemann, 1978.; Xu et al, 1991; Bowell, 1994).

Organic sediments have both a greater affinity and a greater capacity for arsenic sorption than do sandy sediments (Faust et al, 1987a, b), although Jacobs et al (1970) state that organic matter contributes little to arsenic sorption. Sorption of arsenic species from aqueous systems onto organic sediments occurred in the order: As(III) > MMAA >As(V) > DMAA, with sandy sediments sorbing little if any arsenic at all.

4.9 Arsenic solubility

In soils, arsenic forms solids with Fe, Al, Ca, Mg, and Ni, but there are no arsenic solids, other than As_2S_3, with solubilities <0.05mg/l (Buhmbler and Keefer, 1994). Iron arsenate is extremely insoluble, maintaining an As(V) concentration of only about 10^{-11}M in solution, compared to about 10^{-5}M for the calcium or magnesium arsenates. Since calcium arsenate is more soluble than either iron or aluminium arsenate, the role of calcium arsenate in soil arsenic fixation is less pronounced than that of either aluminium or iron (Bhumbla and Keefer, 1994), although the thermodynamic calculations of Sadiq et al (1983) suggest the opposite. However, the addition of lime to a soil with phytotoxic levels of arsenic did not improve its ability to support plant life, although barley has been reported as having a slightly increased yield when either lime or gypsum were added to an arsenic polluted soil (Bhumbla and Keefer, 1994). It is possible that the formation of calcium arsenate simply reduces the amount of arsenic available to plants.

At the oxic/anoxic boundary of the lakes in Canada studied by Belzile and Tessier (1990), dissolved arsenic concentrations were not found to be in equilibrium with Ca, Fe, or Al arsenates or As oxides. Indeed, solubility calculations on the overlying waters showed that saturation indexes were all very low for all of these

compounds, indicating them to be subsaturated and hence too soluble. The *Saturation Index* (SI) is defined as:

$$SI = \log (IAP/K)$$

(which is the log of the *Saturation State*) where K is the solubility product (i.e. activity at equilibrium), and IAP is the ion activity product which is the analogue product of activities derived from the water analysis. For SI = 0, there is equilibrium between the mineral and the solution; SI < 0 reflects subsaturation, and SI > 0 supersaturation. Normally, equilibrium is not found and the saturation state merely indicates the direction the process may go; for subsaturation dissolution is expected, and supersaturation suggests precipitation (Appelo and Postma, 1994).

Retardation of arsenic mobility in soils is related to the amount of phosphate present from fertilisers (Davenport and Peryea, 1991) or deposited wastes, but is not related to any variations in the concentrations of Cl^-, NO_3^- or SO_4^{2-} (Livesey and Huang, 1981).

4.10 Arsenic mobility in the environment

Desorption and remobilisation of arsenic from sediments is controlled by pH, Eh and arsenic concentrations in the interstitial waters, together with changes in the total iron, extractable iron, extractable manganese, mineral oxides and the calcium carbonate equivalent in the sediments (Masscheleyn, 1991; Mok and Wai, 1994), although in aerobic soils, phosphate also exerts an important influence (Davenport and Peryea, 1991). Other soil components contributing to the sorption and retention of arsenic are generally the oxides of Al, Fe, and Mn, soil mineralogy (especially clays) and organic matter (Bhumbla and Keefer, 1994). Ultimately, however, more obviously physical processes may be the cause for the distribution of arsenic. The movement of water or sediments from previously reducing conditions into an oxidising environment, or the introduction of air into a reduced environment (via a borehole, for example), may cause the oxidation of diagenetic or authogenic sulphides and subsequent release of arsenic and other trace elements. Similarly, arsenic adsorbed on oxide surfaces may be released if the local environment becomes reducing.

Soluble arsenic concentrations are usually controlled by redox conditions, pH, biological activity and adsorption processes, and not by solubility equilibria (Bhumbla and Keefer, 1994). In both soil and water systems, arsenic species are subject to both

chemical and biological oxidation and reduction (Walsh and Keeney, 1975). As can be seen from the Eh-pH diagrams given in Appendix D, at high Eh values, As(V) exists as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}, while at low Eh, the corresponding As(III) species are present (H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$), together with AsS^{2-} (Ferguson and Gavis, 1972).

The reduced inorganic trivalent arsenic species [As(III)], is more soluble and mobile than inorganic As(V) [Deuel and Swoboda, 1972], although in many cases, As(V) is preferentially adsorbed onto clays, especially montmorillonite, kaolinite (Frost and Griffin, 1977) and illite (Carpenter et al, 1978). Organoarsenicals are also found almost universally, although elevated arsenic concentrations may inhibit the activity of microorganisms capable of arsenic methylation.

With the exception of agricultural practices, occurrences of arsenic in north American groundwater have typically been associated with aerobic environments. Studies in the eastern US have also attributed high arsenic levels to the mobility of the oxidised species (Korte and Fernando, 1991).

4.10.1 *Atmospheric arsenic redox interactions*

The major fraction (>90%) of atmospheric arsenic is particulate (Walsh et al, 1979a), so solid phase reactions would be expected to dominate, with both oxidation of As(III) [by ozone, molecular oxygen at pH's of between 0-6 and by H_2O_2 activities of 10^{-40} or greater] and the reduction of As(V) [most likely by dissolved SO_2 or bisulphite (hydrogen sulphite) ion, even at very low concentrations] being possible. The oxidation state of arsenic in the atmosphere is therefore controlled by a balance of reducing and oxidising species within an air parcel, and by competing reaction and diffusion kinetics. It may thus be possible to use the oxidation state of arsenic in precipitation or in atmospheric particulate material as an indication of the prevailing redox condition in the atmospheric environment (Andreae, 1980). As(V) is the major arsenic species present in coal fly ash, whilst As(III) species (particularly As_2O_3) are thought to predominate in smelter dusts (Andreae, 1980; Bhumbla and Keefer, 1994; EPRI, 1995). This is discussed further in Sections 2.5.1 and 2.7.1.

Recent work, has shown that almost 10% of air particulate arsenic may comprise methylarsenicals (Maher and Butler, 1988), who went on to show this is also subject to

seasonal variations, with concentrations being high in the summer and low in the winter, in accordance with the observed temperature changes.

Methylarsines formed from the microbial degradation of alkylarsenicals are very unstable in air at concentrations above 0.05ppm to 0.10ppm (Sandberg and Allen, 1975) and are rapidly oxidised to less reduced arsenic species such as DMAA and TMAO, probably on the surfaces of airborne particles. It is therefore clear that methylated arsenical compounds are present in the atmosphere in association with particulate matter, but little is known about the vapour-phase distribution of these compounds. Although methylarsenicals such as DMAA are quite stable, they may be demethylated by UV irradiation. This may only be significant at altitude, as MMAA and DMAA, have been found to be unaffected by exposure to sunlight at ground level (Cullen and Reimer, 1989). However, Brockbank et al (1988) determined that the photolysis of MMAA in aerated distilled water resulted in 100% conversion to As(V) after about 100 minutes, about the same amount of time was required for DMAA photolysis, but MMAA was formed as a precursor to As(V), the ultimate end product. In seawater, the photolysis rates are much slower. The reaction of DMAA resulted in only 20% conversion to MMAA after 300 minutes, with no other products detectable. Irradiation of MMAA over the same period confirmed no demethylation over this time period, perhaps backing the idea that this process will be more effectual at high altitude.

4.10.2 *Sand columns, muds and sediments*

In the pH range from 2 to 11, the release of As(V) and As(III) from sediments to the overlying waters has been found to follow a pattern of substantial release with decreasing pH. The release of arsenic also rises sharply at high pH. At the lower pH values, metal ions (such as iron and manganese) are solubilised from the sediment with the concurrent release of arsenic. At high pH levels, the increased hydroxide concentration causes displacement of the arsenic species from their binding sites in a ligand exchange-type mechanism (Clement and Faust, 1981).

The hydrous oxides of Al, Fe and Mn can all affect the surface reactions of arsenic (Hingston et al, 1974):

$$M\text{-}OH + H_2O \rightleftharpoons M\text{-}OH_2^+ + OH^-$$

$$M\text{-}OH_2^+ + H_2AsO_4^- \rightleftharpoons M\text{-}OH_2^{+\cdots}H_2AsO_4^-$$

or

$$M\text{-}OH_2^+ + H_2AsO_4^- \rightleftharpoons M\text{-}AsO_4 + H_2O$$

Hydrated iron oxides are more efficient adsorbents than their manganese counterparts due to their loose and highly hydrated form, allowing other hydrated ions to diffuse freely throughout the structure without being restricted to external adsorption sites, as is the case with more crystalline solids. This is very important in the case where acid mine drainage waters (which may themselves contain high arsenic concentrations) may precipitate out hydrated iron compounds, which will be incorporated into future sediments. However, the environmental conditions of the sediments have a greater influence upon the arsenic speciation and mobility than does the total concentration of arsenic in the sediment (Bhumbla and Keefer, 1994), with sediment particle size being of great importance (Oscarson et al, 1981a). This is especially true when it is realised that aluminium, iron and manganese hydroxides may form coatings on crystalline minerals (thus increasing their surface area) or complex with humic substances (Oscarson et al, 1981a). Perhaps of greater importance still is the rate of diffusion of dissolved species within the sediments as compared with the overlying sediments. Davison (1982), estimated that eddy diffusion, dominant in the waters overlying sediments, is about 10^3 times faster than molecular diffusion, leading to complex concentration gradient shapes, especially if the redox boundary is situated at or close to the sediment/water interface.

Gulens et al (1979), studied the effects of pH and redox reactions on the mobility of arsenic through sand columns. They found that the mobility of As(III) is significantly different to As(V), and that this difference was perhaps due to the greater solubility of an Fe^{3+}-As^{3+} complex compared to an Fe^{3+}-As^{5+} complex, but they were unable to determine whether pH or redox environment exerted most control over arsenic mobility.

Davenport and Peryea (1991) report that addition of phosphate rich fertilisers significantly enhance arsenic mobility in soils previously treated with arsenate pesticides. The amount of leachable arsenic after phosphate addition was dependent upon rate of phosphate application; higher rates leading to greater leaching (for monoammonium but not for monocalcium phosphate fertilisers) and soil texture, with finer soils being less

efficiently leached. The mechanism of arsenic release is thought to be due to competitive anion exchange (Davenport and Peryea, 1991).

Leaching studies using soil columns treated with DSMA (112kg/ha equivalent) have shown that about 52% of the applied arsenic was leached from a loamy soil, while none was leached from a clayey loam. Subsequent analysis of the clayey loam revealed the vast proportion of arsenic in the top 2.5cm, and all within the top 15cm. Another study showed that variation in soil pH in the range 5.5 to 6.5 did not affect the leaching of MMAA in a loamy sand, although given the dissociation constants of MMAA (See Appendix A), which mean the univalent form dominates, this is not surprising. For 20% of the undissociated acid or the divalent ion to be present, the soil pH would have to be 4.2 or 7.6, respectively. The pH found in agricultural soils (generally in the range 5.0 to 7.0) is not likely to influence the chemical form of MMAA. Soil pH influences the activity of aluminium in clay and hydrous oxides of the soil colloid system, but apparently the adsorptive capacity of the soil is determined more by the amount of these colloids than by pH effects on their activity (Hiltbold, 1975; Sandberg and Allen, 1975). The rate of application of methylarsenic herbicides does not appear to affect the rate of downward movement of arsenic into the soil profile, although it does affect the amount of arsenic found at different levels in the soil profile (Hiltbold, 1975; Sandberg and Allen, 1975). Indeed, Sandberg and Allen (1975) conclude that the possibility of groundwater contamination by leaching of applied arsenicals is very insignificant. All of the conditions which favour leaching (high rates of arsenic applied, light soils, and heavy leaching pressures) were tested but leaching below 90cm depth of soil was not observed; for most tests, this depth was considerably less. It is also important to note that as well as leaching, arsenic may be lost through biological processes (see Chapter 5).

Experiments have been carried out on stream muds and sediments contaminated with arsenic to determine the release of arsenic into the overlying water (Clement and Faust, 1981). Arsenic contents of the muds were determined and natural stream water was used. The experimental systems were carried out at various temperatures in the range 4 to 25°C under aerobic conditions, and with dissolved oxygen levels of 10% to 100%, and at 20°C and 10°C under anaerobic conditions. The distribution coefficient was then determined for: $\frac{\text{As water}}{\text{As mud}}$.

In all cases, the lower the temperature: the lower the distribution, i.e. $As_{water} \rightleftharpoons As_{mud}$; at any set temperature there was little change with any alteration of dissolved oxygen concentrations [above 10% of saturation (around 1mg/l)]; under anaerobic conditions, the levels of arsenic [mainly As(III)] were 7 times the concentrations reached in aerobic conditions; the anaerobic As/aerobic As ratio decreased with the decrease in temperature; in the aerobic experiments, 70% of the arsenic was present as As(V), and 20% as organic-arsenic (not arsines); little effect of pH was observed in the range pH6.0-8.5.

4.10.3 *Mine spoil*

Arsenic in mining spoil is generally associated with sulphur compounds, mainly arsenopyrite (FeAsS). When these materials are brought to the surface, from a predominantly reducing environment into a generally oxidising environment, the presence of oxygen, water and sulphur oxidising bacteria result in the oxidation of the pyrite. This oxidation results in the release of H^+ (acidity), Fe^{2+}, Fe^{3+} and SO_4^{2-}, together with any associated trace metals. The arsenopyrite oxidation process may be represented by the equation:

$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4FeSO_4 + 4H_3AsO_4.$$

Under highly acidic conditions, arsenic in this form is highly mobile. Thus, when the groundwater is recharged (in the spring for example), the As(V):As(III) ratio may increase due to the water containing freshly oxidised pyritic arsenic from this pyrite oxidation.

The arsenic released from sulphur-containing minerals can be absorbed by plants, released to surface and subsurface waters, mobilised and leached from the surface soils, or accumulated in the subsurface soils. If the mine wastes are particularly acidic, then the reaction products of the pyrite oxidation may precipitate as secondary minerals, with which arsenic may coprecipitate, or the arsenic may by adsorbed onto the surfaces of newly formed amorphous iron oxides (Bhumbla and Keefer, 1994; Mok and Wai, 1994).

As acid mine drainage flows away from source, its pH will gradually increase. In the upper streams, the acid water (pH2-6.5) keeps other metals in solution, rather than

precipitating or adsorbing onto solid surfaces, except for arsenic, which is almost completely scavenged from these waters. The particulate matter (iron hydroxides) become more positively charged as pH decreases, which lowers its ability to scavenge positively charged metal ions. On the other hand, arsenic exists mainly in anionic form ($H_2AsO_4^-$) and is therefore scavenged very efficiently by the associated particulate matter and sediments, leading to low arsenic concentrations within a relatively short distance of the source. If, however, these sediments are subject to transport processes, then they themselves may become a source of particulate contamination further downstream (Mok and Wai, 1994). Additionally, diurnal fluctuations in acid mine drainage have been measured, resulting from algal photosynthesis. Such fluctuations, although slight, have resulted in iron reduction and mobilisation. If arsenic is associated with the iron, then the arsenic would be released back into solution, and be transported until readsorption took place, and the cycle restarted (Davis et al, 1989; Olem, 1989; Kuwabara et al, 1990).

It is safe to assume that arsenic may be associated with most pyrite containing materials, including mine overburden materials, acid shales and coal cleaning wastes, and that leachate generation may be a potential hazard with each (Carlson, 1990). Another potential source of arsenic is from abandoned mines, both metaliferous, and certain non-metaliferous (coal, for example), where mine drainage pumps have been switched off, allowing natural groundwater recovery to flood the mine, potentially bringing large amounts of metals (including arsenic) to the surface or to intermediate aquifers (Coalfield Communities Campaign, 1995). The Wheal Jane incident in west Cornwall in 1991 was one of the most dramatic examples of this.

As(V) is reported as the predominant water-soluble arsenic species in oxidised mine spoils; however, dimethylarsenic compounds and TMA may also be present (Bhumbla and Keefer, 1994).

Arsenic retention and release from sediments depends on the chemical properties of the sediments, particularly the amount of iron and aluminium oxides and hydroxides they contain (Ferguson and Gavis, 1972; Robertson, 1989; Bhumbla and Keefer, 1994). However, the mechanism of arsenic retention, whether by adsorption or coprecipitation, is not known due to the difficulty in determination. The distribution coefficient (K_D)

defined below:

$$K_D = \frac{\text{concentration in solid phase}}{\text{concentration in liquid phase}}$$

is often used to evaluate the effect of sediment properties on the partitioning of arsenic between sediments and leachate or porewater. More of the total sediment arsenic would be retained by a sediment with a high K_D value than one with a low K_D value. In arsenic contaminated sediments, K_D values may fall anywhere in the range from 12 to 1250 (although generally, the value is less than 350), whilst in sediments derived from mining wastes, the K_D values are much higher, in the range 384 to 2032. These values show the strong retentional properties of mining waste derived sediments (Bhumbla and Keefer, 1994).

In sediments containing manganese, As(III) has been reported as being abiotically oxidised to As(V) under anoxic conditions (Oscarson et al, 1981b, 1983).

Release of arsenic into the environment can be enhanced from lake or river sediments by subjecting them to oxidation (Moore et al, 1988).

Adsorption may also be related to the presence of iron oxyhydroxide in natural waters (Matisoff et al, 1982).

The solubility of arsenic in freshwater seems to be controlled by Ba, Cr, Cu and Fe compounds (Wagemann, 1978), but its release from arsenic contaminated streams is pH-dependent and related to total iron, free iron, aluminium oxides, and immobile iron and aluminium compounds in the sediments (Bhumbla and Keefer, 1994).

4.10.4 *Stratified lakes*

Within seasonally stratified lakes, such as Lake Windermere (UK), Jack of Clubs Lake (British Columbia), Lake Pavin (France) and Lake Ohakuri (New Zealand), or in certain estuarine locations such as Saanich Inlet (Vancouver), the zero electrical potential (Eh = pE = 0) is seen to move in accordance with the prevailing seasonal conditions. In the summer months, when the lake is stratified (with well mixed waters overlying the more stagnant bottom waters), the zero electrical potential lies at its shallowest within the sediments, or even in the water a distance above the sediment surface. Upon the onset of overturn (the mixing of the whole water column, due to the onset of more turbulent winter conditions), the zero electrical potential moves deeper

down the water column or deeper into the sediment with the level at any one time being dependent upon the balance between the rates of oxygen passage through the water/sediment, and the oxygen demand of the water/sediment, although water turbulence is also a factor. The movement may only be in the order of 10-20mm, however. In deep lake and marine sediments (where the zero electrical potential is less likely to move due to there being generally less turbulence), the influence of such shifts in the potential-defined zero oxygen level on exchanges between sediment and water is slight as long as the changeover from oxidising to reducing conditions occurs below the sediment-water interface. It is well known that the depth of changeover within sediments corresponds, within a few millimetres, to an observable colour discontinuity, together with chemical evidences of oxidation and reduction. In the lower layers, iron and manganese are present in the reduced ferrous (Fe^{2+}) and manganous (Mn^{2+}) forms, giving a greyish colour. In the upper oxidised layers, iron and manganese are present predominantly as precipitated hydrated oxides and hydroxides.

The oxidised upper layer therefore forms an efficient trap for manganese and iron, together with other metals. This oxidised layer is thus capable of preventing transport (by adsorption, complexing and coprecipitation, for example) of materials such as arsenic, out of the sediment into the water, whilst also scavenging some materials from the water (Mortimer, 1971).

If however, oxygen supply to a sediment is reduced or even completely halted, then the zero oxygen level will move up out of the sediment into the overlying water. This is accompanied by a concurrent (or after a slight delay) release into the overlying water, of reduced metal and other species. It is worthy to note that manganese is reduced and mobilised in sediments at higher potentials than iron, resulting in it being mobilised first, and should oxidising conditions return then iron will be immobilised before manganese (Davison, 1982). This is important in the cycling of arsenic as it means that arsenic released from manganese will be intercepted by iron, before it escapes into the overlying water. Only when the iron is reduced is the arsenic released into the overlying water, where it will remain as As(III), be reduced to As(V) or scavenged onto the surface of particulate matter.

In additional to the release of materials from the sediment to the overlying water, reduction also removes a barrier to free diffusion across the sediment-water interface, speeding sediment leaching. Davison (1982), estimated that free diffusion occurs at a

rate of about 10^{-3}-10^{-2}cm^2/s, while molecular diffusion occurs at a much lower rate in the order of 10^{-6}-10^{-5}cm^2/s.

When the whole water column is well mixed, the oxygen supplied by the atmosphere and as a by-product of photosynthesis is continually delivered to the sediment surface by turbulent water movements, and the concentration is maintained close to saturation at all depths in the water (Mortimer, 1971). The depth to which oxygen can penetrate into the sediment (assuming molecular diffusion) will be controlled by the rate of supply to a unit area of sediment surface, and by the oxygen demand per unit volume of sediment, be it biological or chemical.

It is then obvious that the position of the zero oxygen concentration line is controlled by these factors, and this is the critical factor regulating chemical exchange between sediments and water. However, it is also important to realise that the zero oxygen concentration line and the line of zero electrical potential, whilst very close do not necessarily coincide exactly, but are generally accepted to do so.

4.10.4.1 *Seasonality*

Crecelius et al (1994), in their study of lakes receiving fly-ash pond effluents, found that seasonal variations of manganese and arsenic in the surface waters indicate that during the summer, when dissolved oxygen is at low concentrations, manganese and arsenic are released into the water column and tend to be higher in the more anoxic bottom waters. During the winter, when the water column is better oxygenated, manganese and arsenic are removed from the water column, presumably by adsorption and precipitation onto suspended matter or sediments. The predominant arsenic species was found to be As(V), although As(III) dominated in some bottom waters which contained high concentrations of Fe(II) and low dissolved oxygen, findings in general agreement with those of Aggett and Kriegman (1988).

Azcue et al (1994a), however, found that the concentrations of dissolved arsenic were not different between the surface and bottom waters of Jack of Clubs Lake (British Columbia) during the period of stratification, suggesting that the sediments are acting as a 'sink', rather than a 'source'.

4.10.4.2 *Porewaters*

Lake porewater arsenic concentrations are considerably higher than the concentrations found in the overlying water column (Crecelius et al, 1994). Arsenic sources in porewaters are most probably iron and manganese oxides that dissolve under reducing conditions. During oxic periods, iron and manganese undergo oxidation, forming particulate oxides that remove arsenic from both the porewaters and the water column, thus acting as an arsenic 'sink'. These particulates are trapped within the sediment, or fall into the sediment. When anoxic conditions prevail, these oxides are reduced, releasing the arsenic back into the porewaters and overlying water, so acting as an arsenic 'source'. It is thus clear that sediment porewater is the medium of arsenic transport within sediments, and plays a key role in the linkage between sediments and the overlying water (Azcue et al, 1994b).

4.10.5 *Sediment-water interface*

Within every soil and sediment, the zone of transformation from oxic to anoxic conditions varies in its precise location both spatially and temporally. In terrestrial soils, this boundary is closely related to the water table, either above, or below, depending on the prevailing local conditions. In aquatic and marine sediments, the position of the oxic-anoxic boundary is controlled by a wide range of mechanisms including: sediment permeability and chemistry, depth, chemistry and oxygen concentration of the overlying water, rate of deposition of sediment, biologically derived material and oxygen, turbulence of the overlying water and the action of any burrowing organisms in the sediment. Generally, in relatively low energy environments, the oxic-anoxic boundary is close to the sediment water interface, sometimes above, sometimes below, although some lakes are seasonally anoxic, with almost the entire water body being anoxic during the late summer due to intensive bacterial or algal activity depleting the water of oxygen. Conversely, in high energy environments, the boundary is likely to be found deeper in the sediment.

As already described, the oxic-anoxic boundary is a very important chemically active zone, controlling the release and uptake of both inorganic and organic ions, and so exerting a control on the concentration gradients of biologically available metals (availability is here taken to mean 'dissolved', and not bound by cation-exchanging clays, bound to hydrated oxides, or chelated by insoluble organic compounds).

Exchanges across this interface are regulated by a variety of mechanisms including: mineral-water equilibria, sorption processes (notably ion exchange), redox interactions dependent upon oxygen supply and the activities of organisms (Mortimer, 1971). Additionally, groundwater flow through the sediments may exert some control on reactions in this zone. Exchange rates are dependent on local diffusion rates and local environmental control of inorganic and organic reactions.

Sediments are highly variable in nature, and may vary widely even on a small scale, containing variable proportions of organic material, which is commonly correlated in magnitude with the intensity of biological production or of organic pollution of the overlying water (Mortimer, 1971; Siami et al, 1987). This organic material is continually being broken down by bottom living organisms, bacteria and possibly also by free enzymes, whilst fresh organic material is perpetually being added at the sediment surface. This breakdown of organic material demands a constant supply of oxygen, resulting in sediments acting as a sink for that gas. The oxygen may only be supplied through the sediment surface, and at a rate governed by:

i) a biological oxygen demand arising from respiration and metabolic activities carried out by any organisms in the sediment;

ii) a chemical oxygen demand arising from the accumulation of reduced forms of inorganic elements such as Fe^{2+} released into the sediment from decomposing biological structures

iii) diffusion, which regulates transport and which is molecular within the sediment, but is increased near the top by the action of turbulence in the overlying water (Siami et al, 1987).

Estimates of the diffusive flux of arsenic (J) can be calculated using Fick's First Law (Peterson and Carpenter, 1986; Millward et al, 1997):

$$J = \phi D_s \frac{d[As]}{dz}$$

where ϕ is the sediment porosity, D_s is the diffusion coefficient of arsenic in porewater and d[As]/dz is the dissolved arsenic gradient, with d[As] being the difference between the maximum porewater dissolved arsenic concentration and the dissolved arsenic in the water above the sediment over the depth dz. Positive values of J indicate fluxes from the

sediment into the overlying water. As with any model, however, there are a number of limiting assumptions:

i) the dissolved arsenic gradients in the porewater are assumed to be linear;

ii) interactions with the solid phase are negligible;

iii) viscosity and charge coupling effects are minimal;

iv) in the absence of the self diffusion coefficients for As(III), MMAA, DMAA and any other arsenic species, it is assumed that they have the same value as As(V);

v) the concentrations of arsenic determined in the water column are representative of those at the sediment-water interface.

The self diffusion coefficient (D) for As(V) at 25°C and at infinite dilution is $9.05\times10^{-6}cm^2/s$, with a temperature dependency between 0°C and 25°C given by $D_{25}/D_0 = 2.19$ (Li and Gregory, 1974; Millward et al, 1997). Assuming linear behaviour, D can be estimated for different sediment temperatures and the diffusion coefficient in porewaters is dependent upon the sediment porosity and for muddy sediments $D_s = \phi^2 D$ (Millward et al, 1997). This is similar to the relationship between the true diffusion of ions in deep sea sediments and that of ions in seawater proposed by Li and Gregory (1974): $D_{sed} = D_w\alpha/\theta^2$; where D_{sed} is the diffusion coefficient in sediment interstitial waters; D_w is the coefficient in seawater; α is the ratio of viscosity of the bulk solution to the average viscosity of the interstitial solution, and tortuosity, θ, is the average ratio of the actual tortuous diffusional path of ions around the sediment particles over the straight distance of that path interval. α is a function of both the porosity of the sediment and the salt concentration of the interstitial solution. The factor α/θ^2 can be determined easily by measuring the diffusion coefficient of Cl^- or SO_4^{2-} in the sediment using the technique of Li and Gregory (1974).

A problem associated with trying to measure the ion diffusion coefficient is that the ion may be adsorbed onto solid surfaces, or exchange with other adsorbed ions. In this case, what is measured is the apparent ion diffusion coefficient D'_{sed} which can be related to D_{sed} by the equation:

$$D'_{sed} = \frac{D_{sed}}{1+K_D} = \frac{D_w}{\theta^2(1+K_D)}$$

where K_D is the distribution coefficient as described in Section 4.10.3. The apparent ion diffusion coefficient is applicable only when diffusion is accompanied by the adsorption of the diffusing substance on the sediment. Consequently, D'_{sed} should not be confused with D_{sed} and uncritically applied to any other general diffusion problem (Li and Gregory, 1974).

Additionally, the equation based upon Fick's First Law is based on molecular diffusion and yields underestimates for arsenic porewater fluxes. No account is taken of wave action, which could increase the sediment-water exchange by a factor of 100, nor increases in sediment porosity caused by the action of burrowing organisms (Millward et al, 1997), although the effects are described in Section 5.1 (Aller 1978).

CHAPTER 5

BIOCHEMISTRY AND ECOTOXICOLOGY

5.1 Introduction

Organisms may accumulate (Lindsay and Sanders, 1990), transport (Kuwabara, 1990) or transform (Cullen and Reimer, 1989) arsenic within the environment. The biotransformation of toxic substances, such as arsenic, in the environment is of vital importance from the standpoint of public health, since it is the molecular form of these species which controls their persistence, bioaccumulation and toxicity. Acute toxicity is not considered a particularly important factor in terms of arsenic distribution due to the acutely toxic levels being well above most environmental concentrations (Ferguson and Gavis, 1972) and although chronic arsenic poisoning in humans is widely documented, acute poisoning is rare (and this is discussed more fully in Section 5.9). Most studies involving arsenic biochemistry have focused on marine water and to a lesser degree marine sediment biogeochemical transformations.

The first systematic study of the biological formation of arsines [$(CH_3)_{3-n}AsH_n$ (where n = 0 ,1, 2, 3)] is generally regarded as having been provided by Gosio in 1893, who reported that a number of fungi gave off a strong garlic like odour when they were grown in the presence of sodium arsenite. Peters et al (1996), state that this important first step in the research into the biochemical cycle of arsenic was made by Gmelin in 1815. Later workers erroneously concluded that the gas described by Gosio was diethylarsine and it was Challenger et al, 1933) who proved that the gas was in fact TMA, and who later investigated the ability of a number of arsenic derivatives to act as precursors in arsine synthesis. Subsequent studies have shown that the ability to produce TMA and other organoarsenical compounds is widespread amongst yeasts and fungi. However, bacterial transformations of arsenic were only relatively recently identified by McBride and Wolfe in 1971. A list of examples of bacteria and fungi reported to methylate arsenic and some other metals is tabulated in Table 5.1.

Organic transformations, such as methylation are not thermodynamically favourable in water and almost exclusively occur in the presence of organisms (Ferguson and Gavis, 1972), although chemical methylation (exocellular methylation) is also believed to occur (Fergusson, 1990; Hamasaki et al, 1995) and such biological transformations may be stimulated by the addition of nutrients. A selection of some of the more common organoarsenicals and their formulae may be seen in Appendix B, which also introduces the considerable inconsistency in synonyms under which some of these compound have been known in the literature. Indeed, much of the confusion both in the formal naming of these compounds, stems from the inconsistency of the concept of formal oxidation numbers, which should be used with some caution, as it is sometimes confused with valence (Zignaro and Irgolic, 1974; Wood, 1975).

Table 5.1. Some bacteria and fungi involved in arsenic methylation.

Micro-organism	Other metals methylated
Bacteria	
Aeromonas sp.	Se, Pb
Alcaligenes sp.	Pb
Escherichia coli	Hg, Pb
Flavobacterium sp.	Se, Pb
Methanobacterium sp.	Hg
Methanobacterium MoH	Hg
Staphylococus aureus	Cd
Fungi (moulds)	
Aspergillus niger	Se, Te, Hg
Aspergillus glaucus	-
Aspergillus versicolor	-
Candidia humicola	Se, Te
Gliocladium roseum	As(organo)
Penicillium chrysogenium	Se, Te
Penicillium notatum	Se, Te
Scopulariopsis brevicaulis	Se, Te, Hg

From Fergusson, 1990.

The presence of MMA, DMA, and TMA has not been reported in terrestrial or marine waters (Andreae, 1977, 1978), although incubation of sediments with culture media has been shown to produce the volatile arsines arsine [AsH_3], MMA [CH_3AsH_2], TMA [$(CH_3)_3As$] and the methylarsenic(V) compounds $(CH_3)_nAs(O)(OH)_{3-n}$ (n = 1, 2, 3) [Braman, 1975; Reimer, 1989]. It is thought that the volatile arsines are often lost during sampling, unless special provision is made.

Arsenic's speciation varies, with time being controlled by the biochemical activity of the dominant microbe(s) [Reimer, 1989]. The proportion of pentavalent methylarsenic compounds in coastal sediment interstitial waters gives no relationship to the organic content of the sediment, nor to the singular presence of high arsenic concentrations - evidence instead points to in situ microbial methylation and demethylation (Reimer, 1989; Millward et al, 1993), a view partly contradicted by other researchers who state that the breakdown of organic matter releases may release methylating agents, which, along with microorganisms, could form organoarsenical compounds (Bowell et al, 1994; Francesconi and Edmonds, 1994). Bowell et al (1994) go on to suggest that there is a threshold level, below which microbial reduction of arsenic does not occur. The loss of arsenic from soils treated with disodium methanearsonic acid (DSMA), however, has been shown to be related to the amount of moisture and organic matter present. Soils treated with DMAA have also been shown to lose arsenic, but extensive (60%) losses occurred under anaerobic conditions, whilst only around 35% was lost under aerobic conditions (Bhumbla and Keefer, 1994).

It is now known that a wide range of anaerobic and aerobic bacteria are capable of methylating arsenic, the only major difference between fungi and bacteria appears to be the greater variety of arsines produced by bacteria (Cullen and Reimer, 1989).

DMAA has been reported (Ridley et al, 1977) as being the dominant methylated species in both freshwaters and seawater. More recently, however, it has been shown that DMAA is the dominant methylated arsenic species in freshwaters, while MMAA is the dominant form in seawater (Walton et al, 1986; Anderson and Bruland, 1991; Millward et al, 1993; Bright et al, 1994, 1996), although in estuaries, DMAA tends to dominate (Millward et al, 1993; Kitts et al, 1994). In some cases, however, MMAA concentrations are close to or exceed those of DMAA. Arsenic containing ribofuranosides are ubiquitous in algae, and AsBe is the predominant form in marine animals. These forms, however, probably do not make up the bulk of the arsenic budget in natural waters, since the products excreted by algae and aquatic animal culture appear to be limited to the inorganic and simple methylated forms (Cullen and Reimer, 1989). A simple explanation of the observation that MMAA is present in lower concentrations than DMAA is that it is an intermediate in DMAA

production (see Section 5.3) [Baker et al, 1981]. This explanation in itself does not explain the higher MMAA concentrations found in freshwaters.

In tropical soils, where the porewaters have high As(III) contents, MMAA and DMAA are either absent or present in low concentrations. Where, however, As(III) concentrations are relatively low, and total arsenic concentrations are sufficiently high, methylation of arsenic by soil microorganisms occurs, producing MMAA and DMAA, suggesting a threshold level exists, below which microbial reduction of arsenic does not occur (Bowell et al, 1994). This is partly contradicted by Bright et al (1996), who found that in lake sediments there was a significant correlation between total methylarsenic concentrations and the solid phase arsenic concentration. Also, total methylarsenic was correlated with As(III) concentrations in porewaters.

In the surface photic zone of the oceans, the reduced and methylated arsenic species of arsenic account for 5-20% of the total dissolved arsenic, with DMAA at a fairly constant 5-10%. As(III) is variable and MMAA is only present in trace amounts (Andreae, 1978, 1979; Maher and Butler, 1988). The proportion of methylated arsenic species in estuarine waters is highly variable (Kitts et al, 1994), and may be anywhere between 10% and 87% of the total arsenic present (Blank et al, 1989). Arsenic may also undergo chemical transformations and remobilisation due to redox and methylation reactions within sediments (Kitts et al, 1994). In estuarine porewaters methylated arsenical species account for around 1-4% of the total dissolved arsenic (Ebdon et al, 1987), although Anderson and Bruland (1991) report total methylarsenicals accounting for between 1 and 59% of total dissolved arsenic in a variety of lake waters.

It is important to keep in mind that in bottom areas inhabited by long-lived sedentary fauna, measurable horizontal as well as vertical gradients in sedimentary chemistry may develop (Aller, 1978). These will have an impact not only on the distribution of inorganic arsenic species through redox reactions, but also on organoarsenicals due to the presence of microorganisms feeding on the decaying material present in such burrows.

Organoarsenicals were first detected in estuarine porewaters in any real concentration (0.04-0.7μg/l) by Ebdon et al (1987), but they were unable to prove whether these organoarsenicals were formed in situ or not. An additional source of methylated arsenic species could be from infusions of sediment porewaters (Reimer,

1989), where it has been shown that in marine sediments MMAA is the dominant arsenic species averaged over the year, while DMAA is the dominant form in freshwater sediments. The relative importance and the seasonal interplay between each of these sources is, however, either not known or only poorly understood.

Seawater inorganic As(V) concentration is in the order of 0.97-4.04μg/l (Onishi, 1978), with inorganic As(III) concentrations being around 10% of this value (Hunt and Howard, 1994), although the data found in Table 2.16, from the open oceans (Santosa et al, 1994), give As(III) concentrations varying from 0.29% to 51.3% averaging at 37% of As(V) values. This suggests, perhaps that the 10% value is not universally applicable to seawater, the term used by Hunt and Howard (1994). These values are considerably higher than thermodynamically predicted. The predicted As(III)/As(V) ratio under oxic seawater conditions is $10^{-26.5}$ (Maher and Butler, 1988). With the complete, or near complete removal of oxygen from isolated bodies of water, there is a corresponding shift to more reducing conditions. In these circumstances, thermodynamic calculations predict a change in speciation to a distribution favouring As(III) [Maher and Butler, 1988]. Reimer (1989) estimated that methylarsenic(V) species accounted for less than 1% of the arsenic species present in the porewaters of British Columbian coastal sediments. Marine flora and fauna contain a number of compounds in which arsenic has replaced nitrogen or phosphorus, examples of which include AsBe, AsC and algal arsenosugars (Howard and Comber, 1992; Philips, 1994) [see Appendix B], although the role of some arsenicals, such as the tetramethylarsonium ion, in the arsenic cycle is not yet clear (Hanaoka et al, 1994).

Walton et al (1986) noted that total arsenic concentrations in estuarine macroalgae did not equal the total $NaBH_4$ reducible species, and suggest that this shortfall is due to the presence of non $NaBH_4$ reducible species such as AsBe, AsC, arsenolipids, arsenosugars and their metabolites or precursors, but did not go on to prove this. Bright et al (1996) found a range of mono- di- and trimethylated arsenic(III)thiols, of the form $(CH_3)_nAs^{III}(SR)_{3-n}$ (n = 1, 2, 3), the existence of which had been predicted but not previously demonstrated in the environment.

5.2 Methylation

The activity of microbial methylation reactions is poorly understood, particularly in contaminated soils (partly through the inability to precisely analyse the different arsenic species present in the solution), and this has greatly restricted a comprehensive study of arsenic speciation (Bowell et al, 1994). Arsenic is known to undergo methylation to various gaseous derivatives of arsine in reactions carried out by certain fungi, bacteria and yeasts. The biological function of this process is, however, unknown, but may be due to microbes using As(V) as an electron acceptor in the absence of O_2 and NO_3^- in heterotrophic metabolism (Ferguson and Gavis, 1972), by iron-reducing, manganese-reducing and sulphate-reducing bacteria in aerobic conditions (Bright et al, 1996) and as a detoxification process (Sandberg and Allen, 1975; Maher and Butler, 1988).

Arsenic methylation was first studied by the Italian, Gosio in 1893 who determined that some fungi released volatile arsenical compounds from arsenic containing pigments in wallpaper, and later by Challenger, Higginbottom and co-researchers (1933, 1935), who demonstrated that the bread mould *Scopuloriopsis brevicaulis* was capable of synthesising TMA from inorganic arsenic salts.

Cox (1975) reports on work which isolated three fungi in sewage that were capable of producing TMA from either organic or inorganic arsenic. Cox (1975) also reported the formation of TMA from methylated arsenic substrates at neutral or acidic pH by the three species of fungi: *Candidia humicola* (able to methylate DMAA, MMAA, As(III) and As(V), but only under acidic conditions), *Gliocladium roseum*, and a *Penicillium* (both of which produced TMA from only MMAA and DMA, but under both alkali and neutral conditions).

It has also been shown (McBride and Wolfe, 1971) that in solution, *methanobacterium* strain MoH is capable of reducing and methylating arsenic to DMA, under anaerobic conditions, although this was previously only thought to occur in aerobic metabolism (Ferguson and Gavis, 1972). Ridley (1977) suggests that the bio-synthesis of methylarsenicals must occur in a reducing environment. Brinkman et al (1977) has shown that a mixed fungal bacterial population cultured from a fresh pond sediment was capable of releasing TMA under both aerobic and anaerobic conditions, using DMAA as the arsenic source. The loss of applied DMAA from soils may occur by two processes. Under aerobic conditions, about 41% of the DMAA was oxidised to CO_2

and As(V), while 35% was lost from the soil as a volatile organoarsenical compound over a 24 week period. Under anaerobic conditions, degradation to CO_2 was nil, yet 61% of the applied DMAA was volatilised, possibly as DMA (Hiltbold, 1975).

Some microorganisms can fully methylate arsenic over a wide range of Eh and pH conditions, whilst others are far more specific (Baker et al, 1981; Bowell, 1994; Bowell et al, 1994). Even in culture experiments involving a single bacterial strain that has been treated with As(V), several gaseous products, $(CH_3)_nAsH_{3-n}$ (n = 1,2,3), are found (Cullen and Reimer, 1989). In a limited number of cases, arsine itself is produced. MMAA, DMAA and TMAO are likely intermediates in these biomethylation reactions, a view substantiated by the formation of similar methylarsines when cultures are inoculated with MMAA, DMAA and TMAO.

It has been suggested (Bowell et al, 1994), that in tropical soil pore waters where As(V) is the dominant arsenic species, there is a threshold level of total arsenic concentration required, above which methylation of arsenic by soil micro-organisms takes place. Where As(III) concentrations are greater than those of As(V), no organoarsenical species were observed.

Phosphate has been reported as inhibiting formation of TMA from As(III), As(V) and MMAA. However, additions of as much as eight times as much phosphate as caused inhibition of TMA formation from As(V) had no effect upon TMA formation from DMAA (Cox, 1975). In marine environments, the uptake of inorganic arsenic (but not DMAA) by algae generally occurs when dissolved phosphate becomes depleted (Sanders and Windom, 1980), or arsenic concentration increases (Sanders et al, 1994). An enrichment in phosphorus significantly decreases uptake of arsenic by phytoplankton (Sanders and Windom, 1980), although there is evidence that arsenic removal also occurs in phosphate rich waters (Anderson and Bruland, 1991). Kuwabara et al (1990) found that sorption of phosphate onto algal cell surfaces can be 1-2 orders of magnitude greater than for arsenic. They also discovered that heat-killed cells of a species isolated from an area of elevated dissolved As(V) accumulated less arsenic than did cells of the same species but from an area not subject to high As(V) concentrations than when both cell types were exposed to high As(V) and low phosphate concentrations. Baker et al (1981) report that nitrate (or nitrite from nitrate reduction) may inhibit the methylation of arsenic, but provide no further information on the subject.

DMAA is the main arsenic metabolite in most mammals and it has been generally considered as the endpoint of the *in-vivo* methylation of inorganic arsenic, acting as a detoxification process. However, studies on the fate of DMAA administered to man, mouse and hamster, have shown that about 5% of the ingested DMAA was further methylated and excreted in the urine as TMAO within 48 hours (Vahter, 1994). There are major differences in the metabolism of inorganic arsenic, while AsBe and AsC metabolism seems quite similar. Inorganic As(III) is methylated in the liver of most mammals. As(V) is first reduced in the blood to As(III). DMAA is the main metabolite of most mammals, but MMAA is produced and excreted by humans to a greater extent than other mammals (Thompson, 1993; Vahter, 1994).

5.3 Formation of methylarsenicals

There are three major co-enzymes (non-protein molecules which associate with enzymes in catalysing biochemical reactions) known to be involved in methyl transfer in biological systems (Wood, 1974; Ridley et al, 1977; Cullen and Reimer, 1989; Fergusson, 1990):

i) S-adenosylmethionine (SAM), transferring methyl groups as CH_3^+ (carbonium) from nucleophilic attack by the arsenic on the C-S bond in SAM.

ii) N^5-methyltetrahydrofolate derivatives, transfer methyl groups as CH_3^+

iii) Vitamin B_{12} (methylcorroid) derivatives, transferring methyl groups as CH_3^-, from nucleophilic attack by the arsenic, or as $CH_3\bullet$ (free radical) from free radical attack on the C-Co bond (pH dependent).

SAM is a nucleotide (an organic compound consisting of a nitrogenous base linked to a sugar) and an amino acid molecule.

N^5-methyltetrahydrofolate derivatives are apparently not methyl donors to arsenic compounds (McBride and Wolfe, 1971; Wood, 1974), and will not be considered here.

Neither SAM nor N^5-methyltetrahydrofolate derivatives are capable of transferring carbonium methyl groups to As(III) or As(V), because for both of these coenzymes, the methyl group is transferred as CH_3^+. SAM, but not N^5-methyltetrahydrofolate derivatives have been shown to undergo nucleophilic attack

(McBride and Wolfe, 1971), enabling a methyl free radical transfer. McBride and Wolfe (1971) showed that, along with Me-B_{12}, CO_2 also acts as a precursor for alkylarsine synthesis with methylation by the product of CO_2 reduction (CH_4) following the same scheme as that of Me-B_{12}.

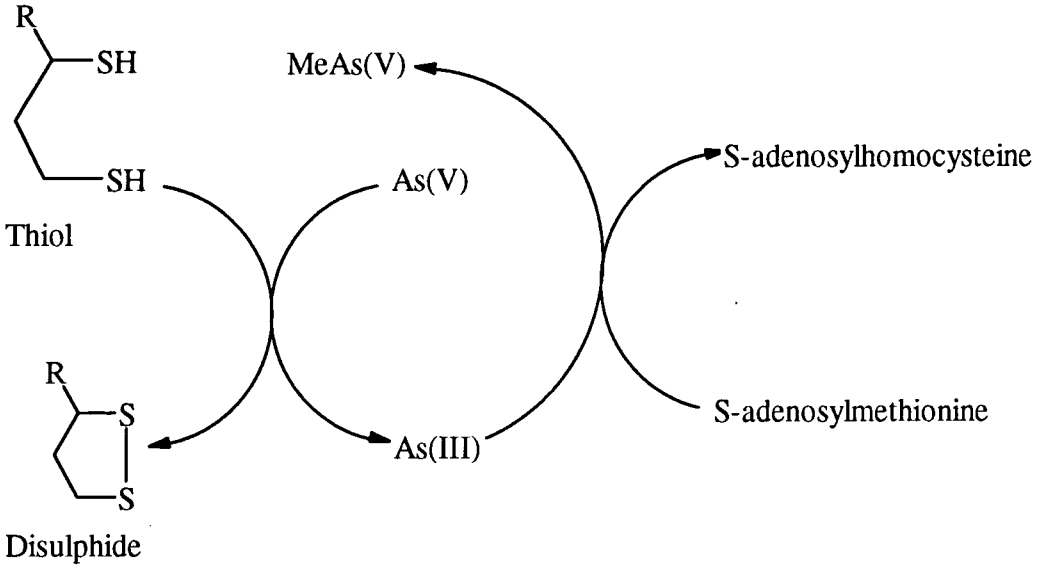
5.3.1 *Methyl transfer from SAM*

SAM has been implicated in the methylation of arsenic, initially mainly in fungi (Cullen and Reimer, 1989), but more recently in mammals as well (Thompson, 1993) via an enzymatic pathway. In this case, the methyl transfer must occur by nucleophilic attack (the attacking element is oxidised) by some reduced arsenic salt [As(III)], on the C-S bond of SAM (Ridley et al, 1977; Cullen and Reimer, 1989; Fergusson, 1990; Thompson, 1993; Vahter, 1994), with the transfer of carbonium ions (CH_3^+) via a monomethyltransferase to form a monomethlarsenic(V) or (III) compound and the reduced S-adenosylhomocysteine, as seen in a simplified form in Figure 5.1 (Cullen et al, 1984; Cullen and Reimer, 1989). The initial reductant (electron donor) of As(V) to As(III) could be any one of a range of thiols or dithiols, including cysteine, glutathione, lipoic acid, mercaptoethanol, and dithiothreitol, at neutral pH (Cullen et al, 1984; Cullen and Reimer, 1989; Thompson, 1993; Bright et al, 1996). In addition, several thiols, including glutathione, cysteine, 3-mercaptopropionate and methanethiol, have been identified in the porewater of marine sediments (Bright et al, 1996). Lipoic acid and glutathione, in particular are attractive options as they also reduce DMAA(V) species to organo As(III) species. The methylarsenic(III) products would likely be sulphides if a high concentration of thiols was present in biological systems. If the concentration of thiols was low, the products would be methylarsenic(III) oxo species (i.e. an oxygen containing compound), such as methylarsonous-acid anhydride and tetramethylarsinous-acid anhydride, the structures of which are given in Appendix B.

However, the resultant methylarsenic(III)-thiol complexes are unstable and rapidly degrade to DMAA and disulphides, and have only recently been observed in the porewaters of lake sediments (Bright et al, 1996). Stable methylarsenic(III)-thiol complexes (e.g. DMA-haemoglobin complexes) also exist, but the role of protein binding in arsenic biotransformation is not clear (Cullen and Reimer, 1989, Vahter, 1994).

Once the MMAA is produced, it is reduced to MMAA(III) by a thiol such as glutathione, and another methyl group is added, via a dimethyltransferase. It is suggested that a different methyltransferase is used in each methylation step. The dithiols (either cofactors or methyltransferases) are required for both mono- and dimethylation and where dithiols are involved, oxidative methylation reduces the stability of the arsenic-sulphur complex and permits dissociation of the arsenic species. This lower affinity of the pentavalent organoarsenic species for dithiols is part of the reason why methylation of arsenic can be a detoxification mechanism, when the As(III) intermediates are not permitted to accumulate (Thompson, 1993).

Figure 5.1. S-adenosylmethionine methyl transfer (from Cullen and Reimer, 1989).



This scheme would suggest that the biosynthesis of methylarsenic compounds occurs in a reducing environment. However, McBride and Wolfe (1971) found that methylcobalamin was capable of functioning as a methyl donor in the non-enzymatic biosynthesis of DMA from As(V) or As(III) in cell extracts of the bacterium *methanobacillus* MoH. It has been suggested that the Co-C bond of methylcobalamin is susceptible to nucleophilic attack by the thioloate ions to give thioethers as products (Ridley et al, 1977). If this is true, then it is reasonable to assume that reduced As(III) also functions as a nucleophile (Ridley et al, 1977).

Edmond and Francesconi (1987), suggest a slightly different pathway in the algal production of AsBe. During the methylation phase of the reaction, the adenosyl part of the methylating agent is transferred to the arsenic atom, rather than the methyl group. A

series of further reactions involving arsenosugar compounds as yet unobserved eventually result in the production of dimethylarsinoylethanol (on the decomposition of the macroalgae). The route from dimethylarsinoylethanol to AsBe which may proceed via AsC or dimethylarsinoylacetic acid is presently unknown (Edmonds and Francesconi, 1987). The pathways involved also explain why arsenosugars are found only in primary producers (Philips, 1995).

It is clear that, in theory, the methylation of arsenic is a moderately simple process. However, it is important to note that even though enough information exists to present a cohesive hypothesis, many of the intermediates involved in the various steps have not been identified in practice (Thompson, 1993).

5.3.2 *Vitamin B_{12} dependent methyl transfer*

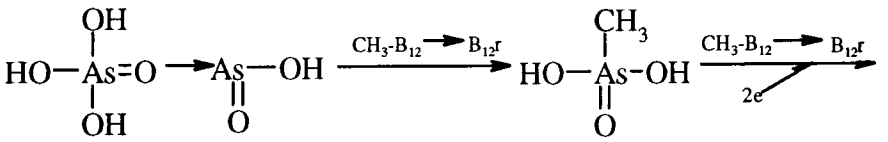
Methylcobalamin (a Vitamin B_{12} derivative, where the CN^- group is replaced by CH_3^-) has been implicated, but not yet established in the methylation of a number of metals as well as arsenic, and a number of other metalloids (Wood, 1974; Reisinger et al, 1981; Cullen and Reimer, 1989) and there are two theoretical mechanisms which may be involved (Ridley et al, 1977), depending on the pH of the environment. For example, the redox potential of the As(V)/As(III) couple is +0.559V under acidic conditions, and -0.67V under basic conditions [although the same redox couples are given values of +0.68V and -0.67V by Fergusson (1990)]. The reduction potential of a couple is an indication of the relative thermodynamic tendency of the species involved to accept or donate electrons. Therefore, one might expect elements with a high reduction potential to be good oxidising agents and to react by an electrophilic (attack by a positive ion) mechanism. Elements with a low reduction potential are, on a relative scale, better reducing agents and it would be logical for them to react by a nucleophilic (attack by a negative ion) mechanism. Indeed, it is thought that under acidic conditions, arsenic (acting as an electrophile) will be involved in a reaction involving heterolytic cleavage (the two resulting fragments are oppositely charged) of the Co-C bond of methylcobalamin with the transfer of a carbanion (CH_3^-) methyl group to the more oxidised state of the element [As(V)]. Under basic conditions, the reaction involves homolytic cleavage (the two fragments are uncharged free radicals) of the Co-C bond, with methyl free radical transfer to the reduced [As(III)] member of the redox couple. Fergusson (1990),

however, suggests that where the reduction potential of the metal being methylated has E_o >+0.8V, then CH_3^- transfer occurs, but if E_o <+0.6V, then the transfer is oxidative addition of a free radical with homolytic cleavage of the Co-C bond. Additionally, there may be circumstances, where, under slightly acidic conditions, both oxidation states [(As(III) and As(V)] are necessary for methylation to occur (Ridley et al, 1977). Cullen and Reimer (1989) report that a methylcobaloxime (a model for methylcobalamin), reacts with As_2O_3 in the presence of a reducing agent such as dithiothreitol to give low yields of CH_3AsH_2 and $(CH_3)_2AsH$. They speculate that compounds with As-Co bonds could be intermediates. Reactions between prepared dimethylarsino compounds containing cobalt and methyl iodide resulted in methylation at both metal centres (Cullen and Reimer, 1989). Methyl(pyridine) cobaloxime (a potential source for CH_3^-) also reacts to give TMA. Thus, both nucleophilic and electrophilic attack on the Co-C bond can result in the methylation of arsenic. However, methylcobaloximes do not react with arsenohalides such as $AsCl_3$, AsI_3 or CH_3AsCl_2 to afford methylarsenicals (Cullen and Reimer, 1989).

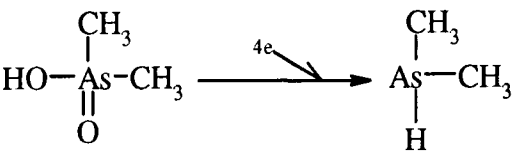
McBride and Wolfe's (1971) mechanism for vitamin B_{12} dependent methyl transfer to arsenic is shown schematically below in Figure 5.2.

Laboratory observations have shown that there is no doubt that methylcobalamin (Me-B_{12}) can act as a methyl source for methylarsenical production in cell extracts of Methanobacterium strain MoH, although the true methyl precursor has been shown to be 2,2' dithiodiethanesulphonic acid [$HSCH_2CH_2SO_3^{2-}$ or coenzyme-M (HS-CoM)] as may be seen below in Figure 5.3, from Cullen and Reimer (1989).

Figure 5.2. Vitamin B_{12} dependent methyl transfer.



Arsenate Arsenite Monomethylarsonic acid



Dimethylarsinic acid Dimethylarsine

From McBride and Wolfe, 1971.

where CH_3-B_{12} is methylcob(III)alamin, and B_{12r} is cob(II)alamin.

Figure 5.3. Vitamin B_{12} methyl transfer showing the role of coenzyme-M.

$$(SCH_2CH_2SO_3^-)_2 \xrightarrow{H_2} HSCH_2CH_2SO_3^- \xrightarrow{CH_3\text{-}X}$$

$$\underset{\text{MeS-CoM}}{CH_3SCH_2CH_2SO_3^-} \xrightarrow{H_2} \underset{\text{HS-CoM}}{HSCH_2CH_2SO_3^-} + CH_4$$

From Cullen and Reimer, 1989.

The possibilities seem to be as follows:

a) MeS-CoM is produced from Me-B_{12} and this becomes involved with the methylation of arsenic;

b) Me-B_{12} reacts with the arsenical in a chemical or biological process that is not part of the normal cell response;

c) Me-B_{12} provides the methyl group to the component in the cell extract (e.g. methionine), which is the ultimate methyl donor to arsenic, again in a reaction that is not a normal part of the whole cell chemistry.

Unfortunately, the data available do not allow a distinction to be made (Cullen and Reimer, 1989). In the absence of Me-B_{12}, the cell extracts produce an arsine [presumably $(CH_3)_2AsH$], from dimethylarsinate. However, no arsine is produced from methylarsonate (McBride and Wolfe, 1971).

It appears therefore that methyl transfer reactions to metalloids such as arsenic occur by either free radical attack on the Co-C bond of methylcobalamin, or nucleophilic attack on SAM, as well as methylcobalamin. In either case, the reaction is likely to occur under anaerobic conditions and will generate volatile products such as DMA (Ridley et al, 1977). Reimer (1989), however, showed that microorganisms in both natural marine sediments and sediments contaminated with mine tailings were capable of methylating arsenic under both aerobic and anaerobic conditions. In mammals, methylation of inorganic arsenic is thought to occur via carbonium ion transfer from SAM in the liver (Vahter, 1994).

5.4 Exocellular or abiotic methylation

Methylation by non-enzymatic $MeCoB_{12}$ may be treated as abiotic, except that the reagent is produced biologically and may be re-methylated biologically. The two main abiotic methylation processes are transmethylation and photochemical methylation.

Chemical methylation may occur in natural conditions with exocellular methylating agents such as methylcobalamin, methyl iodide and dimethylsulphate, in a similar way to tin and mercury (Cullen and Reimer, 1989), although little has been reported. Hamasaki (1995) illustrated the role of methyl iodide in arsenic methylation, emphasising the recycled use of methyl iodide in the environment. Chemical transmethylation may occur among methylmetal derivatives and other inorganic trace elements. For example, methylarsenic acid can act as a methyl donor to produce trimethyltin (Hamasaki 1995).

In photochemical methylation, the CH_3 group is produced photochemically when compounds such as acetate, methanol, ethanol or aliphatic α-amino acids are exposed to intense ultraviolet radiation (Fergusson, 1990). These volatile products (arsines) are slowly oxidised by molecular oxygen to give stable water soluble species such as DMAA, which will theoretically form the most abundant methylated arsenic compound in both freshwater and seawater (Ridley et al, 1977).

A passive metabolism of MMAA has also been suggested as occurring in soils, with oxidation being proportionally related to the soil organic matter content, or the total CO_2 evolution. As most micro-organisms generally use energy sources other than MMAA, the evidence supports this suggestion(Hiltbold, 1975).

More recently, the discovery of dimethylarsinothiols in lake sediments (Bright et al, 1996) suggests that DMAA may result from exocellular methylation under reducing conditions and in the presence of sulphides and/or thiolic compounds. Conversely, DMAA may be produced during the upward diffusion of porewaters containing dimethylarsinothiols into more oxidising environments (Bright et al, 1996).

5.5 Demethylation

It has been suggested that biological demethylation is the dominant process responsible for the regeneration of inorganic arsenic from methylated arsenicals in seawater (Andreae, 1979; Sanders, 1979; Millward et al, 1996). Holm et al (1979) found that demethylation of both MMAA and DMAA to As(V) in incubated river sediments was microbially mediated. The decomposition of the methylated acids involves sequential demethylation with the intermediate formation of As(III) being only visible in deaerated solutions. The rate of degradation of DMAA and MMAA is not as markedly affected by the concentration of dissolved oxygen as that of As(III), presumably because the rate-determining step involves demethylation with no change in oxidation state of the arsenic. The demethylation possibly involves hydroxyl radicals produced by hydrated electrons formed in the UV irradiated water (Brockbank et al, 1988).

The photolysis of MMAA in aerated distilled water resulted in 100% conversion to As(V) after about 100 minutes, about the same amount of time was required for DMAA photolysis, but MMAA was formed as a precursor to As(V), the ultimate end product. In seawater, the photolysis rates are much slower. The reaction of DMAA resulted in only 20% conversion to MMAA after 300 minutes, with no other products detectable. Irradiation of MMAA over the same period confirmed no demethylation over this time period. In freshwater, however, the effect of light is likely to be significant, especially on the methylated species (Brockbank et al, 1988), although it seems little work has been performed to this end.

The degradation of AsBe has been thoroughly investigated by Hanaoka and co-workers (Hanoaka et al, 1994). The degradation activity is higher in microorganisms occurring in sediments and suspended particulate matter, in which AsBe is degraded to inorganic As(V), via TMAO, DMAA and MMAA. In contrast to MMAA, DMAA and TMAO, AsBe degradation occurs to a greater degree under aerobic conditions. AsC, which is regarded as a precursor to AsBe, has been proven to be converted to AsBe by microorganisms occurring in sediments. Degradation of AsC results in the formation of TMAO and DMAA. This latter bioconversion has also been confirmed in mammals and fish (Hanaoka et al, 1994). DMAA may also be derived from algal arsenosugars (arsenoribosides) and not from AsBe (Howard and Comber, 1989, 1992).

Degradation of a tetramethylasonium salt was investigated by Hanaoka et al (1994). These researchers found that this compound degraded only in the presence of microorganisms. Under anaerobic conditions and with samples sediment, the degradation products were DMAA and TMAO; with suspended particulate material the sole product was DMAA. Under aerobic conditions with suspended particulate material the products were TMAO and As(V). This behaviour is similar to the demethylation of TMAO, DMAA and MMAA, with degradation occurring more under anaerobic conditions. The mechanistic meaning of this degradation is unknown, but it may point to degradation mainly being carried out by microorganisms in anaerobic zones such as bottom sediments, rather than in the aerobic water column (Philips, 1994).

Methylarsines are very unstable in air at concentrations above 0.05-0.1ppm, and are rapidly (within a few hours or days) oxidised to less reduced arsenic species (Sandberg and Allen, 1975). The reductive pathway put forward by McBride and Wolfe (1971) could be reversed (Sandberg and Allen, 1975), and the conclusions of Braman and Foreback (1973) also support this oxidative pathway.

5.6 Biologically mediated redox reactions

The extent and impact of biological reactions is debatable (Korte and Fernando, 1991). Both organic and inorganic arsenicals may be oxidised or reduced by micro-organisms e.g. bacteria. The oxidation of As(III) to As(V) is known to be catalysed by a number of bacteria, marine phytoplankton (Andreae, 1977; 1979) and methanogenic bacteria (Welch et al, 1988), and may significantly affect the relative concentrations of both As(V) and As(III), since the reaction is slow in natural waters in the absence of micro-organisms at neutral pH (Ferguson and Gavis, 1972). Turner and Legge (1954) showed that at least 15 strains of bacteria could oxidise As(III) from cattle dip solution to As(V). Turner and Legge (1954) also found that cytochrome a enhanced As(III) oxidation, suggesting the bacteria were obtaining energy from the oxidation. However, Haswell et al (1985) have stated that the microbial oxidation of As(III) is unimportant.

The reduction of As(V) to As(III) reportedly occurs best at a pH of between 6.0 and 6.7, the E_o of the reaction being between 77mv and 177mv (Walsh and Keeney, 1975). The process may be performed by *Flavobacterium* and four other bacterial species (Lemmo et al, 1983), and has also been reported as having been

carried out by methanogenic bacteria (Braman and Foreback, 1973), which also methylate the arsenic once reduction has occurred. Laboratory studies using cultures of a wide range of marine phytoplankton demonstrate that phytoplankton can mediate arsenic speciation (Maher and Butler, 1988; Sanders and Riedel, 1993), although Millward et al (1996) suggest that neither MMAA nor DMAA are excreted by phytoplankton during their growth stage. Sanders and Riedel (1993) found that DMAA appeared during phytoplankton blooms. As(V) concentrations were seen to decrease, accompanied by an increase in As(III) concentrations. The decrease in As(V) concentrations was coincident with minimum phosphate concentrations. As As(III) increased, DMAA started to appear, but it is not clear whether MMAA production is a result of DMAA degradation or of biological production (Blanck et al, 1989; Sanders and Riedel, 1993).

Sanders and Windom (1980), found that arsenic speciation within phytoplankton cells changes when cells are grown in arsenic enriched artificial media (in the laboratory), with increasing amounts of organic arsenic being formed. A portion of the arsenic is incorporated into the cell, but the majority is apparently metabolised and rapidly released. For example, the inorganic/organic arsenic ratio in *Skeletenema costatum* changes significantly from approximately 45/55 to 30/70 when grown in As(V) enriched media. *Valonia macrophysa* (a macro-alga) showed similar behaviour, with a ratio shift from 75/25 to 58/42. In seawater media, the changes are even more dramatic, with As(V) reduction (and subsequent increase in As(III) and DMAA concentration) occurring only during the log phase of phytoplankton cell growth. Cultures enriched in As(III) showed an increase in As(V), but it was not clear whether this was mainly chemical or biologically mediated oxidation. It seems likely that arsenic is taken up as As(V) since the most logical pathway is via the phosphate active transport system. Addition of DMAA caused no significant speciation changes. In outdoor experimental enclosures, the arsenic speciation changes were similar to those observed in the laboratory, but proceeded at a slower rate (Sanders and Windom, 1980).

The effect of biological activity depends upon factors such as temperature, phytoplankton populations and pre-existing arsenic speciation. As(V) and to a lesser degree As(III) are bioactive, but MMAA and DMAA are intractable to all but a few bacteria and fungi. Many of the reactions of arsenic influenced by marine biota arise because of the chemical similarities between As(V), and the nutrient phosphate. To

avoid the toxic effects of inorganic arsenic, phytoplankton either discriminate against it, or detoxify it by forming methylarsenic compounds, which are rapidly excreted (Sanders and Windom, 1980; Maher and Butler, 1988). It is thought that the As(V) is metabolically reduced to As(III) and then further methylated (Sandberg and Allen, 1975). Organoarsenicals may be reduced to more volatile forms due to microbial degradation (McBride and Wolfe, 1971; Wood, 1974). Ten species of *Scopulariopsis* and fourteen strains of *Aspergillus*, both commonly found in soil, actively produce arsine from organic arsenicals (Sandberg and Allen, 1975). Methylarsines formed from the microbial degradation of alkylarsenicals are very unstable in air at concentrations above 0.05ppm to 0.10ppm and are rapidly oxidised to less reduced arsenic species (Sandberg and Allen, 1975).

5.7 Seasonality

Estuaries and mid-latitude waters show a seasonality in the appearance of methylated species, such that they are detected when the water temperature exceeds 12°C (referred to in Millward et al, 1993; Riedel, 1993; Millward et al, 1996) although Sanders and Riedel (1993) and Riedel (1993) report the occurrence of methylated arsenic in conjunction with mid-winter phytoplankton blooms. This temperature dependence could mean that higher-latitude waters are characterised by much lower levels of organoarsenical species.

Salinities greater than 24‰ are also desirable for high organoarsenical production (Ebdon et al, 1987), although Millward et al (1996, 1997) found no statistical link between dissolved arsenic species and salinity in the southern North Sea and Sanders et al (1994) report work that shows that most methylarsenicals were produced in the salinity range 10-25‰.

The appearance of methylated species in estuaries has been linked with the presence of dense dinoflagelate blooms and the resulting phosphate depletion (Riedel, 1993) and other algal blooms (Kitts et al, 1994), and has been variously ascribed to their exudates or to the results of the bacterial decay of their tissues (Anderson and Bruland, 1991). There are, however, other sources of methylated species. Macroalgae can contain significant concentrations of DMAA, while MMAA concentrations are negligible (Walton et al, 1986; Millward et al, 1993). DMAA may also be derived from algal arsenosugars (arsenoribosides) and not from AsBe

(Howard and Comber, 1989, 1992). Blanck et al (1986) report work carried out in a littoral zone model ecosystem. Macroalgae were found to show seasonal variations in their tissue total arsenic concentrations. Increases in arsenic concentration were found to be in direct proportion to increasing temperatures.

5.8 Complex organoarsenicals

Howard and Comber (1989), suggest that a gross underestimate of arsenic concentration (of up to 25%, although Bright et al (1996) found a shortfall ranging from 18-420%) is inherent with currently used analytical techniques due to the fact that the main methods used all employ sodium borohydride ($NaBH_4$) reduction to form volatile arsines, yet arsenic compounds such as AsBe, AsC, arsenosugars and arsenolipids do not form volatile arsines when treated in this manner. It has been suggested that AsBe is formed from arsenosugars by decomposition, reduction and methylation, but neither AsBe, nor arsenosugars have yet been found in the water column (Edmonds et al, 1992). Both acid and base hydrolysis result in the degradation of the arsenosugar 2-hydroxy-3-sulphopropyl-5-deoxy-5-(dimethylarseno)furanoside to DMAA, and similar end products may well result from microbial activity in the water column and underlying sediments (Howard and Comber, 1993). There is little evidence to demonstrate the conversion of algal arsenosugars to AsBe by higher organisms. More complex organoarsenicals may exist in the water column, but as yet remain undetected.

To detect AsBe, it may first be reduced to TMAO by hot aqueous sodium hydroxide, which can then be reduced to TMA by $NaBH_4$. AsC, however, cannot be detected using the same technique. Irradiation of these complex organoarsenicals (1000W lamp) results in the release of significant amounts of DMAA, with smaller amounts of MMAA and small but significant amounts of inorganic arsenic (Howard and Comber, 1989, 1992). If less severe irradiation is used (generated by a 200W short arc lamp) demethylation of either MMAA or DMAA can be avoided (Howard and Comber, 1989, 1992). Bright et al (1996) used a 450W medium pressure lamp to irradiate samples for up to 12 hours, or exposed them to microwave radiation.

Howard and Comber (1989, 1992) found an increase in total arsenic, MMAA and DMAA concentrations following irradiation of estuarine and coastal water samples. There was no evidence of either methylation or demethylation, so where did

this extra inorganic arsenic, MMAA and DMAA, come from? The inorganic arsenic may result from photochemically induced demethylation, but this would result in a concurrent reduction in the concentrations of the methylated species, which is not seen, or it may be bound to colloidal material or incorporated in organoarsenicals in non-methylated forms (which do not form volatile arsines on treatment with $NaBH_4$) which are present in high concentrations in the summer months. Alternatively, the 'extra' arsenic may be derived from dimethylarsenoribosides rather than AsBe, as AsBe forms trimethylarsine under the experimental conditions used (Howard and Comber, 1989, 1992; Philips, 1994; Bright et al, 1996). The complete identification of these 'hidden' or refractory arsenicals has yet to be completed, and the digestion systems used so far to reduce them to $NaBH_4$ reducible fractions, may cause some confusion with different compounds being degraded to the same end-point. de Bettencourt et al (1994) make this point , finding that assigning structures to analytical results proved extremely difficult. They concluded that many refractory arsenicals could be the result of halogenation of rather common arsenical compounds, leading to halo-arsenobetaines or halo-arsenocholines, or eventually both. The possibility that both fluorinated and chlorinated arsenic species could be present in the same sample is also a possibility (de Bettencourt et al, 1994).

5.9 Ecotoxicology

The observed health effects of arsenic exposure are not entirely understood, primarily because of the complex arsenic chemistries involved in both the intoxication and detoxification processes. Conversions between the various oxidation states and organometalloid species alter the binding affinities of arsenic for different proteins, thus altering the relative toxicities of the various arsenic species (Thompson, 1993).

Compounds of arsenic are notorious as poisons to an extremely broad spectrum of organisms, but at the same time, there are indications that arsenic is an essential element in some biochemical reactions, and in some circumstances arsenic compounds are used in both human medicine and veterinary applications.

The essentiality of any element X may be described in any one of three ways:

1) The organism can neither grow, nor complete its life cycle without X.

2) X cannot be wholly replaced by any other element.

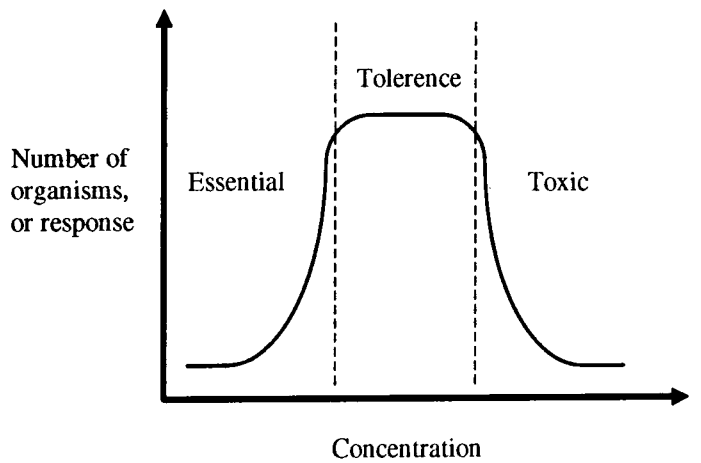
3) X has a direct influence on the organism, and is involved in its metabolism.

In practice, X can never be entirely removed, thus 'without X' may be taken to mean 'X supplied at a sufficiently low concentration'. There is also the possibility that two closely related elements may be mutually exchangeable in their essentiality (Bowen, 1979; Pais, 1994). The essentiality of an element may also be described by a response versus concentration curve, of the type shown in Figure 5.4.

The deficiency of an element is usually observed as resulting in abnormal or stunted growth due to an insufficiency of an essential element in the nutrient intake. Serious deficiency can lead to growth or reproductive failure, or in more extreme cases, death. These abnormalities are accompanied by specific biochemical changes that can be remedied or prevented when the deficiency is checked.

Toxicity can result from too high a concentration of an element in the nutrient uptake, and also gives rise to abnormal growth, disease or death. All elements may be toxic if present in high concentrations, even essential ones. It is also well known that toxicity depends not only upon the chemical nature of the species containing the element concerned, but also upon the oxidation state that the element is in. Living organisms can rarely take up chemical elements in elemental form, but mostly as compounds. Some criteria for the toxicity of a form are the solubility in water or weakly acidic media, or the formation of chelates that can be taken up into the digestive system.

Figure 5.4. Dose response relationship between organisms and element concentration.



Arsenic toxicity is mainly dependent upon its chemical form, with some arsenic species being much more toxic than others. Of the inorganic forms, arsine is highly

toxic, being absorbed through the lungs, and has been related to the deaths of some notable historical figures including Napoleon (Jones, 1982), Tchaikovski (Stuttaford, 1993) and James Maybrick, a chief Jack-the-Ripper suspect (Sunday Times, 1993) [See Section 3.2.3]. However, arsenic tolerance in man and some other animals can be induced through gradual habituation (Luh et al, 1973).

The toxicity of the organoarsenical compounds also varies; those with natural origins tend to be non-toxic or of low toxicity (with the exception of the arsines), whilst those of a synthetic origin, particularly those containing As(III) [such as the chemical warfare agents described in Section 3.2.8] are highly toxic. It is generally observed that compounds containing As(III) display a higher toxicity than those containing As(V), be they inorganic or organic (Peters et al, 1996).

The duration of exposure to arsenic compounds is another important variable in toxicity studies. A single (common) dose is usually not very dangerous, but continuous uptake over an extended period of time is potentially much more harmful.

5.9.1 *Essentiality*

Arsenic has been shown to be essential to the red algae *Asparagopsis* (Bowen, 1979). However, it is also known that organisms may adapt to survive under conditions normally poisonous to that organism. Arsenic has been demonstrated to be essential in some other animals experimentally (goats, hamsters, rats and minipigs), but the biological role in plants, in farm livestock and in humans remains to be established (Pontius et al, 1994). The rat, for example, shows a deficiency for As(III) below a dietary concentration of 0.003mg/day, with a toxic threshold of around 0.6mg/day; lethal doses are in the range 1.3-4mg/day. Humans however, show deficiency with less then 0.07mg/day, a toxic threshold range of 5-50mg/day and a lethal range of 50-340mg/day (Bowen, 1979). While different mammals have different sensitivities, comparing the species dose per unit body weight is a fairly constant parameter.

Arsenic is an element whose supply is of little or no importance for plant growth, but whose concentration in the plant is important for the health of animals or humans consuming the plant, although trace concentrations have been suggested as slightly stimulating plant growth (Bowen, 1979). In terrestrial plants, As(III) is found to be toxic if present in the nutrient solution at concentrations above about 0.02-7.5mg/l, whilst in

leaves, concentrations of 1-1.7μg/g shows no effect, and 5-20μg/g results in toxic effects (Fergusson, 1990).

On a more positive side, arsanilic acid and related compounds are used as growth promoting factors and used as food additives in poultry and swine feeds (See Section 3.2.5).

5.9.2 *Arsenic Toxicity*

The Japanese National Institute for Occupational Safety and Health (NIOSH) has shown that the LD_{50}'s (dose which caused death to 50% of the tested population) of rats through oral administration were as follows for the arsenic compounds shown in Table 5.2 (note the changes in concentration between the various arsenic compounds).

Considering the fact that As(V) compounds are usually less toxic than As(III), the toxicity is expected to decrease in the order As(III)>As(V)>MMAA>DMAA. LD_{50}'s are also shown in Table 5.3, but in this case for mice (Hamasaki et al, 1995).

Table 5.2. Rat LD_{50}'s for some arsenic compounds.

As Compound	LD_{50}[1]	LD_{50}[2]
Sodium arsenite	41mg/kg	-
Sodium methyl arsenate	0.79g/kg	-
Sodium dimethyl arsenate	2.6g/kg	-
Arsenite	-	1.5mg/kg
Arsenate	-	5.0mg/kg
MMAA	-	50.0mg/kg
DMAA	-	0.5g/kg

From [1]Hamasaki et al, 1995; [2]Peters et al, 1996.

Table 5.3. Mouse LD_{50}'s for some arsenic compounds.

As Compound	LD_{50}
Arsenobetaine	>100g/kg
Arsenocholine	6.5g/kg
Trimethylarsine oxide	10.6g/kg
Tetramethylarsonium iodide	0.89g/kg
Dimethylarsonous (AsIII) acid	1.2g/kg
Dimethylarsinic (AsV) acid	1.8g/kg
Arsenous oxide	0.0345g/kg

From Hamasaki et al, 1995.

It is interesting to note the higher toxicity of dimethylarsonous acid [DMAA(III)] compared with that of DMAA and that comparing with arsenous oxide, the acute toxicity of methylated arsenicals is very much weakened, especially in

trimethylated forms. It has also been reported that both MMAA(III) and DMAA(III) are more toxic than inorganic As(III) [Hasegawa et al, 1995], although this is not seen in Table 5.3.

The toxic dose of arsenic for various animals is given in Table 5.4. While this table is useful in giving an idea of the amount of arsenic which will probably cause death in that animal, it makes no reference to the arsenic species used in any of the testing, although it is probably safe to assume it to be an arsenate. For comparison, birds can tolerate up to 4.8g/l of lead arsenate in drinking water for up to 60 days without harm (Luh et al, 1973).

Table 5.4. Toxic dose of arsenic for various animals.

Animal	Toxic dose (g)
Fowl	0.05-0.10
Dog	0.10-0.20
Swine	0.50-1.00
Sheep, goat, horse	10.0-15.0
Cow	15.0-30.0

From Luh et al, 1973.

To humans, As(III) is 20 to 60 times more toxic than As(V), and several hundred times more toxic than methylated arsenicals (Korte and Fernando, 1991), with acute poisoning occurring with the ingestion of only 20mg of arsenic (Luh et al, 1973). Pontius et al (1994) estimate that the LD_{50} for humans is in the order of 1-4mg/kg for an adult. Chronic arsenic poisoning has been reported as a result of drinking contaminated water containing arsenic in the ranges 0.21-10.00mg/l, although water containing 0.05-0.25mg/l has been reported as causing no ill-effects (Korte and Fernando, 1991). A lethal range of 50-340mg/day of arsenic for humans has also been reported (Bowen, 1979). The actual pattern of toxic effects observed in an individual is a function of dose (often poorly characterised), host response, or susceptibility, and therapeutic interventions that might modify the response (Franzblau and Lilis, 1989).

With respect to the lower forms of aquatic life, arsenic toxicity is variable. Aquatic insects can tolerate much higher arsenic concentrations than many fish. To minnows, As(III) is toxic at concentrations between 1.0 and 45mg/l, while As(V) is only toxic at concentrations in excess of 230mg/l (Ferguson and Gavis, 1972). Certain mayflies can tolerate 3-14mg/l, whilst 10-20mg/l causes certain dragon and damsel flies no harm. In comparison, the application of 4mg/l of sodium arsenite caused a great

reduction in the population of rotifers, and wiped out all the microcrustacea. The toxic threshold for the flatworm *Polycelis nigra* has been reported as being as high as 361mg/l, although the immobilisation of *Dapnia magna* only required 4.3-7.5mg/l of arsenic. Algae were not killed at As(V) concentrations of 10^3mg/l, and 10^4mg/l of potassium arsenate did not affect bacteria, although sodium arsenite has been reported as toxic at concentrations of 35-46mg/l and 290mg/l to the algal genus *Scenedesmus* and the bacterium *Escherichia coli* respectively (Luh et al, 1973).

In the marine environment, it is clear that there are large, species specific differences in sensitivity to arsenic, probably caused by a varying affinity to phosphate and As(V) [Sanders and Riedel, 1989]. While sensitivity to arsenic is not restricted to plants, animals are, in general, less sensitive. Indeed, phosphorus concentrations play a part in the arsenic uptake by phytoplankton, this is not the case for invertebrates (Lindsay and Sanders, 1990).

4.9.3 *Routes of exposure*

Exposure can be defined in three ways (Zielhuis, 1981):

i) exposure in the general sense: concentration (C) in for example air, food and water, taking into account the duration of exposure (T);

ii) amount offered to various routes of exposure, i.e. the intake (I) = C × T × volume or weight;

iii) amount absorbed, i.e. the uptake (U) = I × fractional absorption factors.

In toxicology, the probability of an effect depends not upon concentration, but rather on the intake (I) and, even more on the uptake (U) per unit of time over what is often a long period. Zielhuis (1981) goes on to state that looked at scientifically, air, water, soil and food quality standards (such as those set down by the UK Department of the Environment, the US-EPA and the EEC, and briefly mentioned in Appendix C) based upon acceptable concentrations are non-sensical, although in practice they indirectly serve their objective. Indeed, although individual limits are set on drinking water and foodstuffs determined by 'ambient monitoring', measurement and assessment of agents or their metabolites and health risk or 'biological monitoring' is a much better reflection of the total individual uptake and internal exposure than an assessment of concentration. To take this one step further, there are two sets of 'limits'. Health-based

recommended limits, which take into account prevention of adverse health risk, and quality standards, which also take into account cost-benefit considerations, and which are used as regulatory measures. The former are similar to the standards laid out under the Dutch concept of multifunctionality (Moen, 1988), while the second might include the old UK ICRCL guidelines (ICRCL, 1983), and those introduced by the EEC.

The primary routes of potential human exposure to arsenic and certain arsenic compounds are inhalation, ingestion, and through contact with the skin (although this last pathway is considered insignificant [Pontius et al, 1994]). Higher than average exposure may occur during the smelting of ores containing arsenic, during pesticide application and wood preservation, although recent reductions in emissions and improved industrial hygiene have substantially reduced occupational exposures.

Direct consumer exposure may occur through the consumption of food, which is estimated to provide an intake per person of about 20-70μg/day, although the true figure may lie anywhere in the range <10-1000μg/day, depending on diet (Fergusson, 1990; US-NTP, 1994; Pontius et al, 1994; Vahter, 1994). Zielhuis (1981) quotes daily arsenic intakes of 10-20μg/day for the USA, and 22μg/day for the Netherlands. These figures refer to total arsenic daily intake, the relative proportions of inorganic to organic arsenic vary widely. Meats and cereals contain 65-75% inorganic arsenic, whilst fruits and fish contain <10% inorganic arsenic, and it has been estimated that about 20% of total dietary arsenic intake is in the inorganic form (Pontius et al, 1994), although the true figure may lie anywhere between 5 and 50% (Hering, 1996).

Potential consumer exposure also occurs through the consumption of water containing arsenic (see Table 2.14). Absorption of inorganic compounds from the gut is subject to their solubility varying from 5-25% and even up to 100% in the case of some organoarsenicals. Additionally, the general population is potentially exposed to arsenic compounds through air emissions from pesticide and glass manufacturing plants, smelters, cotton gins, burning of fossil fuels and other sources. Additional exposure might also arise from old wallpapers (Jones, 1982) or the taking of arsenic containing medicines (Luh et al, 1973; Fergusson, 1990; US-NTP, 1994). Fergusson (1990) suggests that in relatively uncontaminated environments, the daily intake of arsenic from inhalation and drink is around 5μg, although cigarette smoking can add a lot more if arsenic pesticides have been used on the tobacco plants.

Once ingested, arsenic is metabolised. In humans, this involves two processes; reduction and methylation. As discussed in Section 5.3.1, As(V) is reduced to As(III), which is subsequently methylated to MMAA and DMAA. In humans, this process occurs primarily in the liver (Pontius et al, 1994).

4.9.4 *Rate of excretion*

The rate of excretion of arsenic compounds is inversely proportional to its toxicity, i.e. arsine is the most rapidly excreted and organoarsenicals the slowest (Puttemans and Massart, 1982), although more recent study suggests that the reverse might be true for airborne arsenic (EPRI, 1995). Vahter (1994) and Hamasaki et al (1995) state that arsenic compounds are rapidly excreted after intake, and that the excretive rate of methylated arsenicals is higher than that of inorganic arsenicals, with the main output being in urine. Thus, the intake of marine food, in which the arsenic compounds are present at concentrations of several tens of mg/kg in trimethylated forms, does not affect human health, being excreted without being biotransformed (Vahter, 1994). The metabolism of AsC in mammals is thought to involve oxidation to AsBe, but the metabolism of the arsenosugars found in various edible seaweeds is not known (Vahter, 1994).

An estimate put forward by Bowen (1979) suggests an average residence time of arsenic in the human body at between 200 and 400 days. This is a very crude estimate, using data on arsenic intake, multiplied by an estimate of the fraction absorbed across the gut wall and a knowledge of the average arsenic concentration of 'reference man'. It does not take into account the different effects and absorbencies of the different arsenic species, nor their mode of entry into the body (orally, via inhalation or skin absorption). Fergusson (1990), however, gives a biological half life for arsenic in the human body of 10-30 days, and Franzblau and Lilis (1989) suggest a figure of less than one day. This is again a crude figure, although acknowledgement is given to the fact that arsenic removal time will vary with the tissue type; generally it takes longer from hard tissue compared with soft, and usually longer from soft tissue than from fluids.

The metabolism of ingested arsenicals from poultry and swine feed additives has been investigated by a number of researchers over the years. Arsanilic acid is excreted by chickens largely unchanged, with no evidence that it underwent conversion to inorganic arsenic or any other organoarsenical. Four-nitrophenylarsonic acid, however,

was partly converted to arsanilic acid and 3-nitro-4-hydroxyphenylarsonic acid was partly converted to 3-amino-4-hydroxyphenylarsonic acid (roxarsone) [see Appendix B for structures], with no evidence for inorganic arsenic generation (Calvert, 1975). Cullen and Reimer, however, report that although arsanilic acid and roxarsone are excreted essentially unchanged, their presence in animal wastes affects the performance of anaerobic and aerobic waste digestors by diminishing methane production. The rate of arsenic excretion by both poultry and swine has been reported both as being very rapid and accounting for a large proportion of the ingested arsenic. In experiments involving sheep, around 87% of the administered arsenic was excreted within 5 days (Calvert, 1975).

5.9.5 *Method of action*

The toxic effects of arsenic in animals are generally:

i) systemic vascular poisoning, a paralytic action on smooth and cardiac muscle and leading to haemorrhage;

ii) mitotic poisoning, blockage of chromosonal mitotic metaphase during cellular division;

iii) protoplasmic poisoning, a combination with certain enzymatic sulphydryl groups, which causes inhibition of various oxidative systems requisite in tissue respiration (Luh et al, 1973; Cox, 1975);

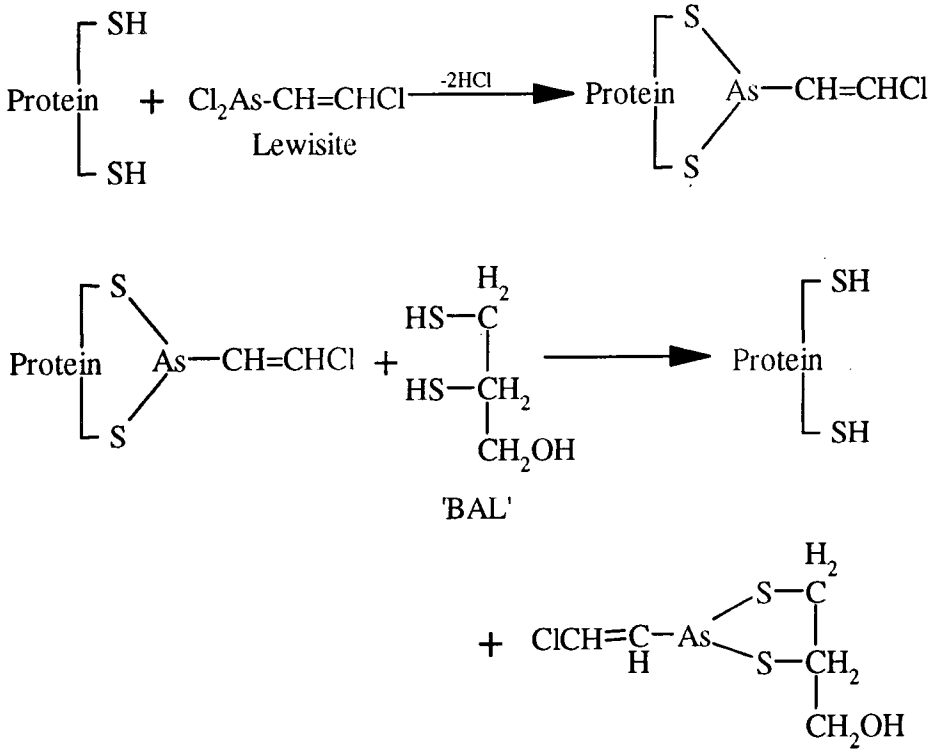
iv) possibly a fourth mechanism of arsenic toxicity exists in which a single toxicant is formed from metabolism of the various arsenicals (Cox, 1975).

In mammals, arsenic's toxicity comes mainly from protoplasmic poisoning, with the more toxic As(III)'s ability to react with sulphydryl groups (thiol or -S-H groups) of cysteine in proteins, so causing coagulation of the proteins, forming complexes with co-enzymes and inhibiting the production of ATP in essential metabolic processes (Luh et al, 1973; Cox, 1975; Peoples, 1975; Fergusson, 1990; Lindsay and Sanders, 1990; Manahan, 1991; Thompson, 1993). The resulting compounds are thermodynamically unstable, but persistent. Arsenates do not react with sulphydryl groups, but may be reduced to inorganic As(III) in organisms, and may compete for binding sites with other metabolites. The strong bond between As(III) and sulphur may explain why arsenic accumulates in the hair and nails which are keratin tissues. The stability of the arsenic sulphur compound is enhanced if a heterocyclic ring is formed. This helps account for

the ability of 2,3-dimercaptopropanol, or 'BAL' to counteract the toxic effects of arsenicals such as Lewisite, as is shown in Figure 5.5. Other dithiols such as dimercaptopropanesulphonic acid (DMPS) and 2,3-bis-(acetylthio)-propanesulphonamide (BAPSA) have also been shown to be effective chelation therapy agents in the treatment of acute arsenic exposures (Thompson, 1993).

As(V) may also be disruptive by competing with phosphate. For example, As(V) uncouples oxidative phosphorylation, which is the process by which adenosine triphosphate (ATP) is produced, while at the same time nicotinamide adenine dinucleotide (NADH) is oxidised. As(V) disrupts this process by forming an As(V) ester of adenosine diphosphate (ADP, a precursor of ATP), which is unstable and undergoes hydrolysis non-enzymatically, inhibiting energy metabolism. Arsenic may also replace phosphorus in DNA, and this appears to affect the DNA repair mechanism (Fergusson, 1990; Brown and Fan, 1994). It has also been reported that phosphate addition may relieve As(V) and As(III) toxicity in microorganisms, although this is not the case when DMAA is the arsenical involved [reasoning unresolved] (Cox, 1975).

Figure 5.5. Detoxification of arsenic poisoning with 'BAL' (Cullen et al, 1984).



In plants, in addition to competition for metabolite binding sites, arsenic is also known to affect the transpiration process (Fergusson, 1990).

Arsine (AsH_3) is a more toxic form if it is absorbed through the lungs, and is lethal to small mammals in the concentration range of 0.01-0.1mg/l (Bowen, 1979). To humans, arsine concentrations of 3-10ppm may cause toxic symptoms in several hours, 10-60ppm may be dangerous in 30-60 minutes, and 250ppm may be lethal in 30 minutes (Sandberg and Allen, 1975). TMA ($As(CH_3)_3$) may be formed by microorganisms (Ferguson and Gavis, 1972), and is highly toxic under certain circumstances, usually through inhalation. The same basic rule of toxicity has also been shown to apply to aquatic organisms.

5.9.6 *Effects of arsenic intoxication*

The principle consequences of intoxication induced by chronic exposure to arsenic in farm animals are incoordination, appetite failure and respiratory distress, with a maximum tolerable concentration of 50mg/kg dry diet (unspecified inorganic arsenic) and 0.2mg/l in drinking water (Bowie and Thornton, 1985). High concentrations of arsenic (23-2,500mg/kg) occur in some soils of the Tamar Valley in Cornwall, exceeding the threshold values (1000mg/kg of dry soil) found in localities in New Zealand which cause chronic arsenic poisoning in ruminants. The incidence of arsenic intoxication in such areas has been attributed to either direct ingestion of the soil or ingestion of water with arsenic concentrations greater than 0.2mg/l (Bowie and Thornton, 1985; Xu and Thornton, 1985). Indeed, Xu and Thornton (1985) estimate that cattle intake of arsenic from pastures grown on soils as contaminated as those in parts of Cornwall might be as high as 50mg per day, with 60-70% of this being ingested with soil particles, a result of bovine feeding behaviour.

Other studies have shown that the susceptibility of cattle to arsenic intoxication was higher when the streams or soil deposits included limonite (a form of hydrated iron oxide) containing arsenic, but substantially less if orpiment (As_2S_3) or realgar (As_3S_3) were ingested. Reducing conditions promoting a low redox potential in soils increased incidents due to the dominant arsenic species under such conditions being the more toxic As(III). Arsenic intoxication from natural sources is as yet unknown in Britain, but the possibility that high arsenic anomalies, such as those found in the Tamar Valley and other areas could induce an outbreak of chronic poisoning cannot be ruled out (Bowie and Thornton, 1985).

The proportion of arsenic in the soil used to grow vegetables that is actually available for plant uptake is generally small, even in areas with high (up to 2,500ppm) arsenic concentrations. Xu and Thornton (1985) suggest that vegetables grown in soils containing high arsenic concentrations act as 'geochemical barriers' in the environment, and consequently only make a small contribution to man's exposure. This contribution must, however, be assessed in relation to other pathways of arsenic into man through water supplies, air and direct ingestion albeit through food or contaminated dusts and airborne soil particles.

The possibility that arsenic may in some way be related to iodine deficiency has not been fully explored (Bowie and Thornton, 1985), although with mammals in general, arsenic deficiency is thought to cause an enlarging of the spleen and poor hair growth. Excess arsenic results in stomach pains, convulsions, and if a more chronic exposure persists, goitre (Bowen, 1979).

In humans the symptoms of acute arsenic poisonings depend upon whether the arsenic was taken as an organic or inorganic compound. Generally, symptoms appear within 12 hours, initially with sharp crampy abdominal pains, vomiting and diarrhoea. The severe gastro-enteritis is associated with cardiovascular collapse. Chronic poisoning is associated in the first stage with the digestive symptoms of vomiting and diarrhoea. Later, conjunctivitis, rhinitis, laryngitis and bronchitis are common. Together with these, various skin eruptions occur. These are followed by neurological disorders, muscular tension is often noted, and mental confusion may be observed. The skin is characterised by pigmentation and hyperkeratosis, and such discoloration gives the endemic Blackfoot disease of Taiwan its name (Oster, 1988; Fergusson, 1990). A similar outbreak of chronic poisoning resulting from the drinking of arsenic contaminated water (25mg/l) was reported in Reichenstein, Silesia (western Poland) in 1898. This resulted in the development of skin cancers in some of the 60 people affected, and was referred to as Reichensteiner's disease (Peters et al, 1996). More recently, a large area of West Bengal (India and Bangladesh) has become affected by arsenic contaminated drinking water. An estimated 200,000 people already have arsenic induced skin lesions, with many also showing hyperkeratosis. The potential for tens of millions of people being affected has yet to be ruled out (Lee, 1996; Bagla and Kaiser, 1996). The province of Córdoba in Argentina also has an endemic disease called HACRE (hidroarsenocismo crónico régional endemico, chronic endemic regional hydroarsenicism) resulting from arsenic

contaminated drinking water. In places, the occurrence of theis disease is so common it is called 'Belle Ville disease' (Nicolli et al, 1989).

Arsine intoxication is different due to arsine's high toxicity. Initial symptoms are of a general constitutional nature (e.g. headache, malaise, weakness, etc.) accompanied by gastrointestinal disturbances, with abdominal pain and vomiting. A dark red urine frequently occurs 4-6 hours after inhalation. After 24-28 hours, jaundice is present. An important laboratory finding is a haemolytic anaemia with low whole blood haemoglobin and increased free haemoglobin in the plasma due to a rapid hemolysis of the erythrocytes (Oster, 1988).

Epidemiological studies have suggested that arsenic is teratogenic (causing malformation of embryos), mutagenic (mutation causing) and carcinogenic (cancer causing) [Oster, 1988; Fergusson, 1990], although the evidence is not universally accepted, since certain cases of carcinogenesis, involving occupational exposure to arsenic, are complicated by exposure to other potentially harmful materials. It is further possible that not all forms of arsenic are carcinogenic and that the type of arsenical involved may play a role in the carcinogenesis (Luh et al, 1973).

In humans, chronic arsenic poisoning has been reported as a result of drinking contaminated water containing arsenic in the ranges 0.21-10.00mg/l, although water containing 0.05-0.25mg/l has been reported as causing no ill-effects. The result of drinking water containing greater than 0.1mg/l is believed to lead to neurological damage (Clement and Faust, 1981; Korte and Fernando, 1991), especially of the peripheral nervous system (Franzblau and Lilis, 1989; Fergusson, 1990). Much higher (9,000-10,000μg/l) concentrations of arsenic in drinking water have led to severe gastrointestinal disorders, impairment of bone marrow function, cirrhosis of the liver, tubular dysfunction in the kidneys and neurological abnormalities. It is interesting to note, however, that low doses of arsenic have been reported as stimulating the formation of red blood cells in the bone marrow (Rochow, 1966). A brief discussion relating arsenic in drinking water to the incidence of cancers is to be found in Section 5.9.8.

Chronic poisoning has also come via some more obscure pathways. In 1900, thousands of beer drinkers in Lancashire fell sick due to what was eventually diagnosed as chronic arsenic poisoning. The arsenic source was finally traced to the sulphuric acid used in refining the sugar used in the brewing process (Rochow, 1966). More recently, there have been suggestions that arsine, released from mattresses by the action of fungi

on flame retarding chemicals might be contributory to the so-called 'cot death' phenomenon. Although nothing conclusive has yet been proven either way, many manufacturers of cot mattresses have completely removed the arsenic, together with the antimony and phosphorus also used in the flame retardants and coverings (Stuttaford, 1994; Braidwood, 1996).

5.9.7 *Phytotoxicity*

The relationship between the amount of arsenic in the soil and plant growth has been briefly discussed in Section 2.6.7. As(III) is generally regarded as being more toxic than As(V) and has been suggested as the most toxic element to seed plants, with toxic effects being noted with As(III) concentrations in the range of 0.02-7.5mg/l (Bowen, 1979). Arsenic has been shown to be correlated to rice yield, with depression of growth being dependent on the amount of As(III) in the soil. Arsine damages rice roots, resulting in the inhibition of nutrient uptake (Huang, 1994).

The addition of large amounts of high phosphate content fertilisers has been shown to increase the release of adsorbed arsenic through the process of competitive anion exchange (see Sections 4.8.1 and 4.10.2). Such a release may temporarily create undesirable arsenic release possibly resulting in phytotoxic effects (Davenport and Peryea, 1991).

The visual symptoms of arsenic phytotoxicity are only apparent at the highest application level of soluble arsenic (60ppm), when the youngest and most succulent tissues start to wilt slightly and other tissues show veinal necrosis. Experiments by Huang (1994) have shown that arsenic levels of 45-60ppm caused significant reductions in plant weight, and most aznki beans grown on orchard-surface soil suffered severe arsenic injury. The yield of oats was reduced when 20ppm of arsenic was added to the soil, while no reduction in alfalfa yield was observed at arsenic concentrations of 80ppm. However, in soil with >200μg of soluble arsenic, 90% of Scots pine died within 50 days. Cotton and soyabean yields were reduced when arsenic tissue concentrations reached 44.0 and 1.0ppm respectively (Huang, 1994).

Phytotoxicity experiments have shown that 1ppm soluble arsenic causes adverse effects to cowpeas, 7ppm affects rice, 2ppm to barley and 9ppm to peas, beans and barley (Huang, 1994). While the lethal arsenic concentration in tomatoes, is 120 to 150mg/l in the nutrient solution or 100mg/l in the plant, lower concentrations result in

normal but smaller plants. In the cases of Sudan grass and beans, As(III) is found to be ten and four times more toxic than As(V), respectively (Luh et al, 1973).

The toxicity of arsenic to plants is dependent upon the arsenic species present, and it thus stands to reason that different arsenic concentrations will affect the same plant species differently if they are growing in different soils due to each soil having different chemical and redox conditions controlling arsenic speciation (Sandberg and Allen, 1975; Walsh and Keeney, 1975; Bhumbla and Keefer, 1994). An example of this is given in Table 5.5, where rice was grown in pots containing different paddy soils and subsequently treated with varying amounts of arsenic.

Subsequent to this work, a working group in China has developed a multi-index, multi-system method for determining the critical arsenic concentrations for a variety of soil types Huang, 1994). It has also been reported that arsenic is antagonistic (the combined effect of the two elements is less than the sum of their separate effects) towards phosphate, manganese and zinc in plant tissues, and to manganese outside the plant and close to the roots (Fergusson, 1990).

Table 5.5. Critical arsenic concentration (ppm) in soil leading to toxicity in rice plants.

Soil	50% Reduction		No Tilling		Death	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Paddy soil	130	160	170	210	210	310
Stanogleyed paddy	75	85	110	115	169	269
Red sandy paddy	47	52	69	77	109	157

From Hwang, 1994.

5.9.8 *Carcinogenicity?*

There is evidence for the carcinogenicity of arsenic and the following arsenic compounds in experimental animals: arsenic pentoxide (As_2O_5), arsenic trioxide (As_2O_3) calcium arsenate ($Ca_3(AsO_4)_2$), calcium arsenite ($Ca_3(AsO_3)_2$), disodium hydrogen arsenate (Na_2HAsO_4), lead arsenate ($Pb_3(AsO_4)_2$), potassium arsenate (K_3AsO_4), potassium arsenite (K_3AsO_3), sodium arsenate (Na_3AsO_4) and sodium arsenite (Na_3AsO_3). Various introductions to rats, through injections or food additions of these compounds have led to a wide range of effects, ranging from lung adenomas (glandlike tumours) and carcinomas, renal tumours, and carcinomas, adenomas, papillomas (wartlike tumours) and adenomatoid lesions of the respiratory tract (US-NTP, 1994).

It has also been established that there is sufficient evidence for the carcinogenicity of inorganic arsenic in humans. Many cases of skin cancer have been reported among people exposed to arsenic through medical treatment with inorganic trivalent arsenic compounds. In some instances, skin cancers have occurred in combination with other cancers such as liver angiosarcoma, intestinal and urinary bladder cancers and meningioma. Epidemiological studies of cancer after medical treatment with arsenic have shown an excess of skin cancers, but no clear association with other cancers has been obtained. No relation was found between prostatic cancer and treatment for syphilis with arsenicals (US-NTP, 1994).

An association between environmental exposure to arsenic through drinking water and skin cancer has been widely observed and confirmed. Epidemiological studies in areas where drinking water contained between 0.35mg/l and 1.14mg/l arsenic indicated elevated risks for cancers of the bladder, kidney, skin, liver, lung and colon in both men and women (US-NTP, 1994). This supersedes the work of Franzblau and Lilis (1989), who state that there is no link between lung cancer and the ingestion of arsenic contaminated drinking water. Unlike most substances classified as carcinogens, the classification of arsenic is based on human data; animal data are inadequate. Indeed, the precise mechanism of action of arsenic in the development of cancer is not known (Brown and Fan, 1994), but evidence suggests that arsenic acts as a promoter, rather than an initiator (Pontius et al, 1994), although Murphy et al (1989), suggest that it acts in the progression of precancerous cells to malignant cells.

Occupational exposure to inorganic arsenic, especially in mining and copper smelting, has quite consistently been associated with an increased risk of cancer. An almost tenfold increase in the incidence of lung cancer was found in workers most heavily exposed to arsenic, and relatively clear dose-response relationships have been obtained with regard to cumulative exposure. Other smelter worker populations have been shown to have consistent increases in lung cancer incidence, as well increases in the region of 20% in the occurrence of gastrointestinal cancer and 30% for renal cancer and haematolymphatic malignancies (US-NTP, 1994).

5.9.9 *Risk Assessment*

The US EPA has calculated the unit cancer risk from inhaled arsenic at 0.00429/μg/m^3 (for drinking water, the risk is estimated to be in the order of 0.002-0.0053/μg/kg/d [Brown and Fan, 1994]). This figure (for inhaled arsenic) is based on the results of two studies of workers exposed to copper smelter dust, which is thought to contain arsenic [most probably as As(III)] (see Sections 2.5.1 and 2.7.1). In a recent study, the US Electric Power Research Institute (EPRI, 1995) claim that this figure is in error, being too high by a factor of about three. The EPRI suggest a lower unit risk value of 0.00143/μg/m^3, having used further data from Sweden. The EPRI also suggest that the risk figures must be viewed with caution due to a number of significant assumptions made during their calculation.

a) Regarding the arsenic oxidation state; As(V) is the major arsenic species present in coal fly ash (mainly as calcium arsenate), whilst As(III) species (particularly As_2O_3) are thought to predominate in smelter dusts (Andreae, 1980; Bhumbla and Keefer, 1994; EPRI, 1995). This suggests that, as most arsenic detected in airborne particulates is in the pentavalent form, then if coal and smelting are the dominant anthropogenic sources, then oxidation of the As(III) to As(V) must be fairly rapid. The processes involved are discussed in Section 2.5.1 and Chapter 4.

b) EPRI' laboratory studies suggest that lung retention is slightly higher for the arsenic in copper smelter dust than that associated with fly ash, and that excretion of the copper smelter dust arsenic appears to be slower than the arsenic associated with the fly ash. This is, however contrary to previous studies which generally indicate that As(III) is excreted faster than As(V). See Section 4.9.4, for a discussion on this subject.

c) Regarding linearity of the arsenic exposure-response relationship, there might be significant differences between the health impact of arsenic at low doses and that of arsenic at high doses. It has been suggested that the capacity of individuals to detoxify arsenic may be inhibited after high exposures. This will cause non-linearity in the exposure-response relationship (Murphy et al, 1989; EPRI, 1995).

In addition, Murphy et al (1989) point out that previous research has indicated that arsenic may neither be an initiator nor a promoter of cancer, but rather that it acts in

the progression of precancerous cells to malignant cells. This has important implications, because older people have a higher probability of the initiation and promotional stages of cancer being complete, thus making doses of arsenic later in life more significant in determining risk than doses earlier in life (Murphy et al, 1989).

It has also been suggested that the essential differences in toxicokinetics and toxicodynamics between different compounds of the same element (arsenic in this case) should be taken into account when setting environmental quality objectives, and that from the health protection viewpoint, the differences should be noted between water-soluble, water-insoluble and organic arsenic compounds present in food, particularly in marine food (Hamasaki et al, 1995; Mushak and Crocetti, 1995). This point is taken further by Mushak and Crocetti (1995), who state that arsenic cancer risk assessments have been made largely on the basis of epidemiological studies of a large population exposed to arsenic contaminated water in Taiwan. Critics have pointed out a number of potential failings in this course of action:

i) that cancer incidence among the Taiwanese was amplified by a number of host and environmental factors not applicable elsewhere;

ii) the cancer dose response curve (see Figure 5.4) may not be linear at the lower exposures found elsewhere;

iii) there is a toxicokinetic and metabolic threshold that was exceeded by the Taiwanese.

The components of diet must be looked at carefully when assessing the amount of arsenic being incorporated through oral ingestion. The Taiwanese, for example are not only exposed to arsenic in food and in drinking water, but also through the methods of food preparation. For example, water is used to make tea and rice is boiled in water. A volume of only 450-550ml used to boil rice is about 25% of the EPA generic drinking water intake of 2l/day and around 10% of the 4.5l/day used by the EPA in its current Integrated Risk Information System (IRIS) computer file for estimating the cancer risk from inorganic arsenic (Mushak and Crocetti, 1995). It is important to note that only part of the daily human water requirement is derived from drinking water consumed directly, the fraction depending upon age, climatology, activity patters, and dietary habits. The conclusion is that there is little current basis for a large well water intake of 4.5l/day in the Taiwanese, or any values above the EPA's generic intake value of 2.5l/day for adults, itself an arbitrary figure.

Hering (1996) has recently indicated that it is the health risk associated exposure rising from the consumption of arsenic in drinking water that is the driving force behind the proposals for lowering maximum contaminant levels, as indicated in Table 1.1. However, because the risk to health comes mainly from inorganic arsenic, and because the inorganic arsenic concentration in diet is relatively constant, then the only way to reduce risk is to reduce the concentration of arsenic in drinking water. However, with a conservative estimate of the daily intake of inorganic arsenic, consumption of food and of drinking water are calculated to contribute equally to exposure to inorganic arsenic at a concentration of arsenic in drinking water of 1μg/l. As a consequence, the minimum achievable risk level is dominated by the dietary intake of inorganic arsenic and becomes independent of the concentration of arsenic in drinking water (Hering, 1996).

Other arguments have also been made that levels of carcinogenic arsenic in diet can be significant and must be taken into account, rather than using drinking water alone. The quantitative role of dietary inorganic arsenic in the generation of a cancer risk assessment is far from being established and may not be significant, given the overall uncertainty and variability in the cancer risk characterisations reported for inorganic arsenic. Arguments have been put forward that carcinogenic risk from inorganic arsenic is quantitatively linked to biomethylation of inorganic arsenic in humans, with the Taiwanese population being in the reduced methylation portion of the dose curve. However, there is no concrete evidence to show that there is a reduction in biomethylation with increasing arsenic loading of the system (Mushak and Crocetti, 1995), with Vahter (1994) indicating man to have a reasonably high methylating capacity. It is therefore clear that great care must be exercised in the development of cancer risk values based on either drinking water or dietary arsenic intake concentrations. The use of data, albeit highly detailed data, must be used with great care if it is to be applied to a population with a different age distribution, dietary habit, climate and activity pattern.

The risk of contracting cancer from ingesting arsenic must be extrapolated from epidemiological data. However, little is known definitively about the excess cancer risk posed by arsenic concentrations below about 100μg/l, which also encompasses the concentrations at which essentiality and a threshold effect are postulated. The analysis is further complicated by the fact that each cancer site (e.g. bladder, skin, lung) will likely have a different and unique dose-response relationship, and current knowledge is

inadequate to state conclusively which cancer site presents the greatest risk. The strongest evidence is for a relationship between arsenic and skin cancer, with the US-EPA calculating a unit cancer risk of 5×10^{-5}/μg/l, estimating a 1.5:10,000 (or 10^{-4}) individual risk of skin cancer at 2μg/l arsenic (Pontius et al, 1994). However, it is also noted that uncertainties are such that the skin cancer risk estimates could be lower by as much as an order of magnitude, relative to the risk estimates associated with most other carcinogens. The formulation of cancer risk in developing internal cancers as a result of arsenic exposure has not yet been done. This is because of uncertainties over the suitability of existing data for making extrapolations about low-dose risks (Pontius et al, 1994).

CHAPTER 6

SAMPLE COLLECTION

6.1 Introduction

In aquatic systems, where there is a good supply of organic material, as frequently occurs in lakes, rivers, estuaries and coastal waters, the sediment-water interface is characterised by marked chemical changes. Nutrient and metal ions may be released from the rapidly oxidising organic material, and the consequent supply of electrons and the reduction of further organic materials can produce a sharp redox boundary. In some cases, this boundary extends over only 1-2mm (Davison et al, 1994), whilst in water it may extend for several metres (Davison, 1993). The spatial position of this narrow zone would be expected to be fairly constant in low energy relatively stable environments such as lakes, but is expected to be more variable within more dynamic environments such as the intertidal zone. To be able to understand the linkages of the various chemical changes in and around this zone, whether biologically mediated or not, it is essential that the sources and sinks of all the components can be precisely defined spatially. This requires the development of a sampling method which will give adequate resolution and so allow the detection of localised vertical heterogeneity within the sediment system, as already demonstrated in coastal marine sediments for the consumption of oxygen (Gundersen and Jørgensen, 1990), and for iron in lake sediments (De Vitre et al, 1991; Belzile et al, 1989; Davison, 1993, Davison et al, 1994). This would allow for the comparison of porewater phase concentrations with those of the 'parental' sediments, so enabling an understanding of the local solid-solution interactions within the sediment (Davison et al, 1994). It would also allow for changes in porewater concentrations with time to be determined, so helping in the understanding of how intertidal porewater chemistry changes in the short period of a single tidal cycle, or other dynamic environments whilst also allowing the development of a seasonal model.

The biggest single problem in the sampling of sediments to be used for trace analysis is the procurement of a representative sample. In undisturbed, low energy conditions, such as at the bottom of a lake, it is relatively easy, with care, to take reasonable samples. In stark contrast, the intertidal zone is one of the most disturbed and

active portion of any water body, rendering representative sampling almost impossible (Cowgill, 1994).

The measurement of arsenic concentrations in the surrounding environment prior to any localised investigation is essential to fix background levels. These background levels then form the yardstick against which investigative results may be compared, allowing development of the conceptual local cycling of arsenic.

Representative samples must therefore be collected from all of the individual system components. These components include the soil (in the engineering sense), rock, groundwater (including sediment porewater), seawater, and possibly rainwater from the local surround. In this discussion, there will, however, be a greater focus on the presence of the differing arsenic species present within the porewaters of sediments over time, and their procurement will be considered first. Any field sampler must, however, recover the target metals quantitatively and should be rugged and not require excessive set-up procedures in the field.

6.2 Porewater sampling methods

The study of arsenic dynamics in surficial sediments is a prerequisite to the understanding of its behaviour in the whole aquatic system. In their recent reviews, Carignan et al (1985), Ankley and Schubauer-Berigan (1994) and Bufflap and Allen (1995a; 1995b), compared several pore water sampling techniques, including the *ex situ* methods of centrifugation and squeezing and the *in situ* methods of vacuum filtration, and in situ dialysis. Each method was found to have both advantages and disadvantages, as might be expected. A recent and new technique involving *in situ* sampling using thin-film gels (Davison et al, 1991, 1994; Davison and Zhang, 1994; Krom et al, 1994; Zhang and Davison, 1995; Zhang et al, 1995a, 1995b) is also discussed.

Because it is impossible to know the 'true' composition of sediment interstitial water, the characteristics of the porewater isolated using any of the methods discussed below are operationally defined. For this reason, it is impractical to expect one porewater isolation method to be useful for all applications. Due to the ease by which the reduced species of arsenic [As(III)] may be oxidised, it is highly desirable, although not always completely practicable to conduct all sampling and subsequent sample handling under anoxic conditions. Aside from these problems, it is not possible to collect replicate samples of porewater, indeed, it is possible to take two sets of samples in

exactly the same way, handle and analyse in the same way; the results will show variations due to sampling and/or subsampling techniques, but the heterogeneity of the sediments will still affect the chemical results (Cowgill, 1994).

6.2.1 *Centrifugation*

This method has been applied by a number of workers, with varying degrees of reproducibility and reliability. Based on work carried out on an artificial sediment system spiked with cadmium, Bufflap and Allen (1995b) found the recovered concentrations, after filtration, to be slightly lower than expected, although the reasons for this are unclear. They found no difference between polycarbonate and polysulfone centrifuge tubes. Carignan et al (1985), suggest that centrifugation followed by filtration may be prone to artefacts resulting from sample oxidation and temperature variation. Their study, performed on natural sediments, concentrated on Ca, Mg, Fe, Mn, Cr, Co, Ni, Cu, Zn and organic carbon, was found to give fairly reliable results provided that care is taken to avoid precipitation or contamination from colloidal sediment particulates. Bufflap and Allen (1995a) point out that oxidation due to the extra sample handling required for filtration after centrifugation can be eliminated either by using a centrifuge tube with an in-built changeable filter, which has found success with coarse, sandy sediments and sandstone aquifer samples, or by using a dense inert solvent displacement method, also within the centrifuge tube.

Watson and Frickers (1990) quote past work where the concentrations of several components in pore fluids have been dependent upon time and speed of rotation, the precise location of sediment particles in the centrifuge vessel, and the centrifugal crushing of macrophyte roots in productive sediments [which may release dissolved organic carbon and precursors to such compounds as dimethylsulphide (Howes et al, 1985)]. Ankley and Schubauer-Berigan (1994), working with natural sediments, found that low speed (2,500g) centrifugation resulted in higher Cu, Pb and Zn concentrations than high speed (10,000g) centrifugation, a point earlier made by Carignan et al (1985), who used speeds of 5,000g and 11,000g, finding that lower speeds gave higher Cu and Zn levels. Peterson and Carpenter (1986) used a speed of 12,000 rpm for a 10 minute at 5°C duration for the separation of arsenic contaminated porewaters, whilst Aggett and Kriegman (1987) used 12,000rpm, at 4°C for 35 minutes, but later used 15,000rpm for 20minutes at 4°C, not stating a reason for the change in conditions. Aggett and Kadwani

(1983) used a refrigerated centrifuge to separate interstitial porewaters from sediments utilising a speed of 10,000 rpm for 15 minutes and a speed of 15,000 rpm was utilised for one hour for extracting samples from lake weeds. Haswell et al (1985) centrifuged soil samples on site at 3,000rpm (1000g) for one minute prior to filtering, also on site. Iverson et al (1979) ensured minimal oxidation of freshwater sediment samples by ensuring all the centrifuge tube was filled and by limiting centrifuging time (12,000 rpm) to 15 minutes. Subsamples of the recovered porewaters were then filtered (0.45μm), while others were used for rapid Eh measurement. All samples were then returned to the laboratory and stored at 4°C until analysis. The use of glass fibre filters is not recommended due to the apparent adsorption of non ionic organic compounds (Ankley and Schubauer-Berigan, 1994). Indeed, Braman et al (1977) report that inorganic arsenic may be completely trapped by this type of filter.

In conclusion, centrifugation generally requires more equipment, sample handling and time than some other methods, although an adequate sample volume may be readily procured. This method has been used by a number of other studies: Andreae (1978, 1979); Bender et al, (1987); Jahnke, (1988); Belzile and Tessier, (1990); Parametrix Inc. (1994), with a good deal of success.

6.2.2 *Squeezing*

A large number of different designs have been implemented in the extraction of porewater from sediment samples by squeezing. Some of these squeezers use an inert gas such as nitrogen or argon (to avoid oxidation artefacts) under a high pressure (in excess of 140MPa), others low pressure (maximum of 1MPa), applied to a rubber diaphragm which in turn applies a force to the sediment which is confined within a suitable non-metallic inert material lined container (Reeburgh, 1967; Robbins and Gustinis, 1976; Reimer and Thompson, 1988; Reimer, 1989; Crecelius et al, 1994; Bufflap and Allen, 1995a; 1995b; Bright et al, 1996). Although this design is in theory very good for collecting samples for trace metals, no work has been performed on the potential adsorption of trace metal species onto the rubber diaphragm. Earlier designs simply applied a gas pressure directly to the sample with no separating rubber diaphragm. At high gas pressure in this type of design, however, there is the possibility that 'channelling' may be created while squeezing the sediment and if this method is used, then carbon dioxide must not be utilised as it can dissolve in the porewater and thus

lower the pH (Bufflap and Allen, 1995a). Typically, the squeezing method will recover in the order of 50%-60% of the sediment porewater (Robbins and Gustinis, 1976; Presley and Trefry, 1980).

Sasseville et al (1974), designed and used a large (800cm^3) piston squeezer, based on a standard U100 tube, for soft lake sediments. The drawback of this device is the exposure of the sediment to the atmosphere during sample loading, that the porewater only escapes from the bottom of the squeezer, and the fact that there is no in-line filtration, so the eluent porewater is also exposed to the atmosphere. Another technique involves the use of the sampling tube (thus negating exposing the sample to any atmosphere), and two plungers which squash both ends of the sample simultaneously (Kalil and Goldhaber, 1973; Azcue et al, 1994a). The porewater is recovered at each end, through holes drilled in the plunger, so discrete porewater recovery is only possible if the recovered core is sliced thinly.

It has been shown (Sasseville et al, 1974) that this type of sampler can recover quite large volumes of porewater in a relatively short period of time (75ml from 200cm^3 of sediment in 15mins). Ankley and Schubauer-Berigan (1994), using a sampler identical to that of Sasseville et al (1974) but incorporating an in-line 1μm glass fibre filter, recovered approximately 30% of the original volume of sediment. The results gained from their study showed dissolved oxygen concentrations similar to those gained from low speed centrifugation (2,500g) for an organic rich sediment, and similar to both low and high speed (10,000g) centrifugation for a primarily sandy sediment. Metal recoveries (Cu, Cr, Pb and Zn) were low in both cases when compared with centrifugation. Ankley and Schubauer-Berigan (1994), give no indication of the applied pressures used with respect to squeezing.

Bufflap and Allen (1995a) report other designs which generally use gas pressures of between 100psi (690kPa) and 200psi (1,380kPa), although one design was designed for use at up to 5,000psi (34.5MPa). In their investigation, Bufflap and Allen (1995b), used a design based on that of Reeburgh (1967), with applied gas pressures of between 20psi and 40psi (138kPa to 276kPa), which is similar to that used by Reimer and Thompson (1988) and Reimer (1989) who used pressures of between 138kPa and 207kPa. Bright et al (1994, 1994) used a system similar to that of Reimer (1989), applying a pressure of 345kPa, recovering between 26.7 and58% of the original volume of the sediment. Bufflap and Allen (1995b) found that the recovered concentrations

from an artificial sediment spiked with cadmium, to be much higher than expected. This was thought to be due to errors caused by poor seals during filtration.

A major potential problem with sediment squeezing for the analysis of trace metals is that of solid-solution interaction (Bender et al, 1987). It is suggested, and perfectly reasonable to assume that, as pore waters travel through the sediment in a whole core squeezer, they will come into contact with sediment particles which have previously been in equilibrium with porewater of a different composition. Exchange kinetics between the sediment and the porewater can be more rapid than the rate of squeezing, so re-equilibration of trace metal concentrations are only to be expected. The problem can be lessened in two ways without over modification of the squeezer. Either the pressure of squeezing is increased (which is sometimes physically impossible), or the sample must be small enough for complete extraction before reaction kinetics override.

Closely spaced holes drilled in the sample tube or core barrel lining may partially negate this problem (Jahnke, 1988), and can give quite high degrees of resolution. The holes act as sampling ports and as the sample is squeezed the porewater is collected from these. Howes et al (1985) used an inert gas pressure squeezing technique which included the predrilled core barrel aspect of the later Jahnke (1988) design, but which relied on the head space of the core being gas pressurised directly, using pressures in the order of <0.1atm (<10kPa).

Bender et al (1987) suggest that whole core squeezing is not a suitable method for the extraction of porewaters for trace metal analysis for three main reasons:

i) contamination of porewaters with overlying bottom waters;

ii) internal mixing of porewaters during extrusion;

iii) solid-solution reactions as porewater is expressed through the overlying sediment.

However, in a series of experiments, they compared whole core squeezing, using a 63mm diameter core, with core sectioning and centrifugation. It was found that whole core squeezing can be used to accurately define interfacial profiles of particulate unreactive porewater constituents, including NO_3^- and O_2 and other gases, and anions such as I, IO_3^- and SO_4^{2-}. Although SiO_2 is particle reactive, it appears that reaction kinetics are sufficiently slow that its interfacial gradient can be defined by this method. In defining profiles, it has the advantage over the 0.1mm horizontal radial dimension of a microelectrode by using 63mm diameter core samples.

6.2.3 *Vacuum filtration*

The first reported use of this technique was by Sayles et al (1973). A harpoon shaped drop sampler was constructed with a trip valve releasing the piston of a pre-pressurised cylinder. This then applies suction to the probe interior and porewater is drawn into the sampler through holes drilled in its sides. The porewater is collected in capillary tubes (15ml storage capacity), which are closed off before the sampler is recovered. Results of tests performed on samples collected in this manner were shown to agree well with squeezed samples obtained from a core taken adjacent to the sample site (Sayles et al, 1973).

Watson and Frickers (1990), developed a more complex device capable of sampling at 10mm intervals. This sampler is operated by applying a vacuum to chambers machined in a Perspex or Plexiglass block. These chambers are connected to the outside via porous polytetrafluoroethylene (PTFE or Teflon) inserts, and by way of PTFE (3.2mm o.d., 1.5mm i.d.) tubing to sample collection tubes held within a sample storage jar. When a vacuum is applied to the storage jar, porewaters are drawn into the sample chambers, from where they may be collected. The original design was for a five-level sampler, but a ten-level sampler has also been constructed and successfully tested (Watson and Frickers 1990). The useful aspect of this design is the capacity to take sequential samples from the same location with good vertical resolution, a feature not possible with replicate core samples. The possible effect of drawdown of over- and underlying porewater into a single sample port has also been looked into. This effect is thought to be negligible below 100mm depth (~0.4mm), but may be of importance in the uppermost 75mm (amounting to 3-4mm), with the boundary of the sampling zone intersecting the surface in the top 25mm.

Bufflap and Allen (1995b) tested a vacuum filtration apparatus built according to Watson and Frickers (1990) design, with a few minor modifications. They found that this method gave results exceeding those expected. These high results are thought to be due to errors caused by poor seals during filtration, as with the squeezing method. This type of sampler has also been used successfully in an investigation into arsenic speciation in North Sea sediments (Millward et al, 1997).

A similar but cheaper version loosely based on Watson and Frickers' (1990) design is described by Hursthouse et al (1993). This comprises a polythene tub in which a number of holes are drilled in a descending spiral. These are initially stoppered with

solid rubber bungs which are replaced after the pot is bedded in a pre-dug hole in the sediment. The replacement pre-drilled bungs support 350mm of PTFE tubing with the 'sediment' end being capped with PTFE high-performance liquid chromatography solvent filters and fittings. The filters are pushed approximately 50mm into the sediment, an action designed to lessen the possibility of contamination from surface water percolating down the side of the pot, and also aids in the stability of the device in the sediment. The free ends of the sampling tubes are sealed and the device is weighted and left to bed-in for at least a tidal cycle. Interstitial water samples are collected in the same way as described by Watson and Frickers (1990).

6.2.4 *Dialysis*

This was first described by Beneš and Steinnes (1974) for the sampling of trace metals in rivers, lakes and seawater. They compared the concentration of a number of elements (not including arsenic) collected by dialysis with samples collected and subsequently filtered and found that the method of dialysis was much less susceptible to contamination effects because of the simplicity of the device, and that any impurities released from the dialysis membrane could diffuse out into the surrounding solution. They found that anion diffusion was quite slow, probably due to the negative charge of cellulose membranes at pH>3, which repels the diffusing anions and so decreases the effective diameter of the pore in the membrane. They also found that the quality of the water inside the dialysis bag (either filtered double distilled water, or deionised water) had little influence on the results although it is important to ensure that the water must not contain colloidal impurities. Such impurities could lead to inaccurate results due to their trace metal content, or due to the adsorption of trace elements on them during dialysis.

Mayer (1976), employed a very simple method of sampling sediment porewaters, utilising small dialysis bags filled with distilled water held within a perforated Lucite (a form of acrylic plastic) tube, with a removable cone to aid sediment penetration. A similar device has been used more recently by Bottomley and Bayly (1984), involving stacked vials with membrane covered ports held within a perforated Lucite probe. These 'stackers' were emptied by inserting a syringe through a rubber septum in the end. Equilibration times in high salinity (500 to 1000mg/l) have been shown to take place in

seven to eight hours at 25°C (Mayer, 1976) and about one week in a Norwegian river (Glomma river) in November (Beneš and Steinnes 1974).

In water, computer modelling of Fick's second law of diffusion:

$$C = \left(\frac{C_o}{2}\right) \mathrm{erfc}\left[\frac{x}{2}(Dt)^{1/2}\right]$$

where: C is the concentration at a point *x*,
C_o is its original concentration,
erfc is the error function complement,
D is the diffusion coefficient, and
t is time,

yields a roughly linear, inverse correlation of equilibration time with D (Mayer, 1976). Thus, decreases in temperature will increase equilibration time due to the temperature effect on diffusion. In sediments, however, equilibration times will vary much more than in the water column. This is because the diffusivities in sediments are subject to the variables of molecular size, porosity, tortuosity, adsorption and ion exchange reactions in addition to those of ion type, temperature and the area/volume ratio of the sample compartment (Mayer, 1976; Hesslein, 1976; Carignan, 1984; Carignan et al, 1985; Fetter, 1994; Bufflap and Allen, 1995a). It is therefore easy to see that equilibration times will be much greater in clays and other low permeability sediments. Carignan (1984), gives a range of between 3 and 20 days for equilibration, depending on the particular site and dissolved species investigated. Bottomley and Bayly (1984) reported an equilibration time of 10 days in anoxic sediments. At the porosities encountered in most recent sediments, 20 days for cold (4°-6°C) and 15 days for warm (20°-25°C) sediments have been suggested as safe equilibration times for major ions and nutrients (Carignan, 1984). More recent work (Carignan et al, 1985) has shown that, at room temperature, Fe, Mn, Zn, Ni, Co, Cr ,Cu and dissolved oxygen all reach equilibrium or near equilibrium within one week. However, it should be noted that this is not directly applicable to species which may adsorb to the solid phase, since adsorption and desorption do not always proceed at the same rate, although porewater species

interacting with a relatively large adsorbed pool can reach equilibrium much quicker than species exhibiting little or no adsorption (Carignan et al, 1985).

Hesslein (1976), also designed a useful dialysis sampler, capable of 1cm resolution. This device comprises two pieces of Plexiglass (one about four times thicker than the other) into which are machined a series of compartments at 1cm centres. The sampler is prepared for use by filling the compartments in the thicker half with deionised distilled water, carefully laying a piece of dialysis membrane over the full compartments. The thinner acrylic sheet is then laid over the membrane, and acrylic screws introduced into previously drilled and threaded holes. The sampler is then suspended in a container of degassed distilled water, or distilled water bubbled through with nitrogen (Carignan, 1984; Azcue et al, 1994b) until use, when it is carefully inserted into the sediment and allowed to equilibrate for around a week. Samples are recovered using a syringe.

Carignan (1984, Carignan et al, 1985) has investigated the effects of different construction materials and membrane filter types and pore sizes on the results gained from sediment studies, using a dialyser similar to that of Hesslein (1976). Polycarbonate dialysers always gave lower concentrations of dissolved reactive phosphorus, Fe and Mn than those constructed from Plexiglass, even if both types were treated identically. In all the sediments tested, polycarbonate dialysers always induced ferric hydroxide precipitation in the compartments, even after equilibration time of up to one month. Since all plastics are more or less permeable to oxygen, this type of artefact is probably due to the diffusion of oxygen initially present out of the plastic body once it is placed in anoxic sediments. Oxygen diffusion into the compartments has also been shown to be fairly rapid (4μM/min), although this can be minimised by reducing the time the device is exposed to the atmosphere (Carignan, 1984).

Membrane selection is also an important consideration. The membrane must be able to exclude sediment particles, allow the chemical species in the porewater to diffuse into the sampler, retain the dialysis water in the sampler, and maintain its integrity while in the sediment (Bufflap and Allen, 1995a). Cellulose-based membranes have been shown to deteriorate with time (under 5 days), and, while a cellulose acetate membrane give results comparable with a polyvinyl chloride membrane, marked membrane deformation was noticed after 25 days (Carignan, 1984). A combination of 0.45μm plus a 0.03μm membrane gave essentially identical results to that simply using a 0.45μm membrane, suggesting that the Brownian diffusion of colloidal metal species through the

relatively large pores of the 0.45μm membrane is not a likely source of artefact (Carignan et al, 1985).

Carignan et al (1985), compared this technique with that of centrifugation and filtration and found the recovered concentrations to be in fair agreement. This finding has subsequently been verified by Bufflap and Allen (1995b), although the results were slightly lower than expected. Ankley and Schubauer-Berigan (1994) used a dialysis technique similar to that of Hesslein (1976), but as they were performing toxicity tests upon aerobes, no precautions were taken to preclude oxygen. In their study, dialysis gave the lowest metal concentrations when compared to high and low speed centrifugation, sediment squeezing and syringe extraction. This is thought to be due to the oxidation and precipitation of dissolved metal species, resulting in the discovery that the recovered samples contained particles with a mean size of 3.7μm, even though the apparatus was fitted with a 0.45μm membrane.

6.2.5 *Thin film gels*

This describes the relatively new techniques of diffusive equilibrium and defined diffusive gradients in polyacrylamide gels to provide measurements of porewater components (Davison et al, 1991; Davison and Zhang, 1994; Davison et al, 1994; Krom et al, 1994; Zhang and Davison, 1995; Zhang et al, 1995a, 1995b). The diffusive equilibrium method relies on a similar equilibration principle to that of the dialysis samplers, but rather than confining the solution to compartments, it uses a thin film gel to provide the medium for solution equilibrium, and allows for sub-millimetre interval sampling. Concentrations of less common species may be measured using this method with the slight modification of backing the gel with an ion-exchange resin or organic absorbents, which creates a constant diffusive gradient within the gel layer.

6.2.5.1 *Diffusive equilibrium*

The polyacrylamide gel used in the initial investigation into iron and manganese concentrations comprised 15% by volume of acrylamide and 0.3% by volume of AcrylAide crosslinker, and was cast between two glass plates separated by plastic spacers to give the required final dimensions. The setting time is controlled by the proportion of initiator and crosslinker added and a typical time of 30-45 minutes is appropriate (Davison et al, 1994), although Krom et al (1994) placed their mould in an

oven (30-40°C) for 15-20 minutes. The gel was then fully hydrated by insertion in a deionised water bath for 24 hours, during which time the gel swelled by a factor of 2.2, and after which no further swelling will occur if the gel is stored in deionised water. Once this is complete, the gel is sandwiched between two thin Perspex (or some other suitably inert material) sheets. The top sheet has a central front window and is held in place with clips or with acrylic screws. In the initial experiments this was then inserted into sediment system for 24 hours, after which time it was removed and rinsed briefly in distilled water, before immersion in 1 mmol/l sodium hydroxide solution (Davison et al, 1991) [or 10mmol/l sodium hydroxide solution (Davison et al, 1994; Krom et al, 1994)] which oxidised the mobile Fe(II) to immobile Fe(III). To prevent particles adhering to the gel, a 0.45μm pore size membrane can be used as a barrier to them, but still allowing free movement of dissolved species (Davison and Zhang, 1994). The gel is then washed, peeled from the backing plate, pressed between either Teflon or acrylic sheets before drying at 60°C.

The iron and manganese concentrations in the gel were determined using proton induced X-ray emission (PIXE), which does not require the gel to be sectioned. Concentrations in the sediment porewaters were calculated from the measured volumetric concentration factor and the density of the gel, assuming that 90% of the wet gel consisted of water capable of equilibrating with the porewaters (Davison et al, 1991). An alternative analytical method is extraction of the iron and manganese into concentrated nitric acid followed by graphite furnace atomic absorption spectroscopy (GF-AAS) (Davison et al, 1994), a method also applied successfully to the determination of chloride, nitrate, sulphate and ammonia nitrogen (Krom et al, 1994). The drawback with the AAS method is that the gel must be sectioned prior to the extraction step in the procedure, which may induce errors through lateral diffusion unless carried out quickly.

Fick's laws indicate that for a typical dialysis cell (10mm deep), complete equilibrium is established in 3 days [assuming a diffusion coefficient of $10^{-5}cm^2/s$ (no temperature reported)]. Using a 1mm thick gel with the same diffusion coefficient, complete equilibration would take only 42 minutes (Davison et al, 1991). It is estimated that the pore size of the polyacrylamide gel is not less than 2-5nm, so hydrated cations or anions with radii of 0.2-0.3nm can be expected to move readily through the gel

provided that there is no interaction between the ions and the gel (Davison et al, 1994). When the gel is exposed to a solution containing a known concentration of ions and left to equilibrate for a set time, the change in concentration of the ion with distance in the gel should be described by Fick's diffusion equation:

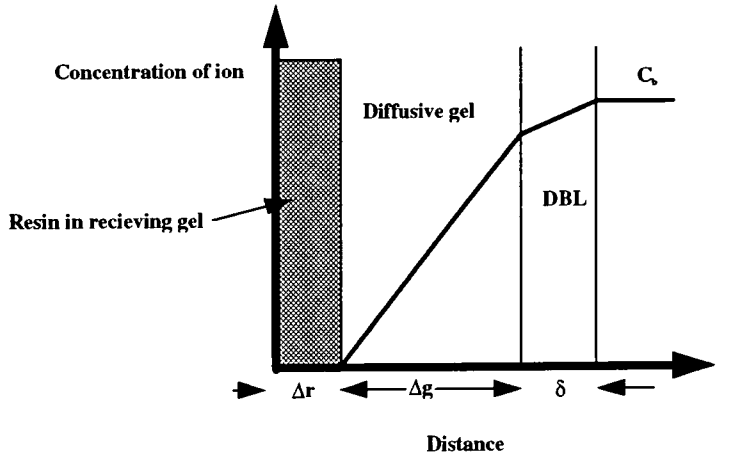
$$\frac{\delta C}{\delta t} = D_s \frac{\delta^2 C}{\delta x^2}$$

Where C is concentration, t is time, x is distance and D_s is the salt diffusion constant. Comparison of concentration as a function of distance as measured, with that calculated using the salt diffusion coefficient in a dilute aqueous solution (from the procedure of Li and Gregory, 1974) gives a good agreement, suggesting that the diffusion of ions within the gel is effectively the same as in water (Davison et al, 1994).

6.2.5.2 *Diffusive gradient*

Concentrations of less common species may be measured using this method with the slight modification of backing the gel with an ion-exchange resin or organic absorbents (Davison and Zhang, 1994). This material is close packed in a single layer of 75-150μm spheres and this arrangement relies on measuring a flux of metal over a given time. It depends on establishing a defined diffusion gradient in a thin film, in contrast to diffusive equilibrium in a thin film which depends on equilibrium being established. Within the resin layer (see Fig. 6.1) of thickness Δr, the concentration of the free metal

Fig. 6.1. Schematic representation of the free concentration of ionic species in a gel assembly in contact with natural water, (Cb - concentration; DBL - diffuse boundary layer).



From Davison and Zhang, 1994.

in solution is effectively zero, owing to its complexation with the resin. The bulk solution has a concentration of free metal of C_b. The gel layer is assumed to be separated from the bulk solution by a diffuse double layer (DBL) of thickness δ, in which metal transport occurs only by molecular diffusion. Metal ions must therefore diffuse across the DBL, and then through the gel, with a thickness of Δg. Small ions may diffuse freely through the pores of polyacrylamide gel with effective diffusion coefficients, D, indistinguishable from those in water (Li and Gregory, 1974). If it is assumed that $\delta << \Delta g$, then Fick's laws may be used to define the flux of a given metal ion:

$$\text{flux} = DC_b/\Delta g \qquad (1)$$

The mass per unit area of resin, M_a, after time t is then:

$$M_a = DC_b t/\Delta g \qquad (2)$$

and the concentration in the resin layer, C_r is given by:

$$C_r = M_a/\Delta r \qquad (3)$$

After a given time, the concentration in the resin layer can be measured (by HNO_3 extraction and atomic absorption spectroscopy) and the concentration in the bulk solution quantified by:

$$C_b = C_r \Delta g \Delta r/Dt \qquad (4)$$

Given a 24 hour immersion, a gel layer thickness of 1mm, a resin layer of 0.1mm thickness and a diffusion coefficient, D, of $10^{-5}cm^2/s$ the concentration in the resin layer will be 864 times the concentration in the bulk solution (Davison and Zhang, 1994).

Equations 1-4 depend on the thickness of the DBL being negligible. It has been estimated that the DBL is in the order of 1mm in thickness in the bottom waters of stratified lakes or deep-sea locations. This diminishes to an estimates 0.1-0.01mm in faster moving waters such as rivers and the surface waters of lakes and seas (Davison and Zhang, 1994). It is not known, however, how thick this layer is in a buried sediment

environment. If the gel layer is 1mm thick, variations in δ between 0.1mm and 0.01mm could at most result in a change in flux to the resin of an estimated 10%. By ensuring that the gel layer is sufficiently thick, this method can in principle control the mass transfer of metal ions irrespective of changes in the velocity of water in the bulk solution.

6.2.6 *Proposed porewater sampling device*

All of the sampling methods for the collection of sediment porewaters discussed have both their advantages and disadvantages. These are listed in Table 6.1. It is obvious that for trace metal sampling, the chosen method should be simple, both in design and in use, it should avoid unnecessary sample handling, and it should be relatively inexpensive. The *ex situ* methods of centrifugation and squeezing suffer from the disadvantages of the potential for oxidation and temperature artefact effects caused by the quite high degrees of sample handling involved, although the methods for avoiding some of these problems have been quite extensively discussed in the literature. The *in situ* methods of vacuum filtration, dialysis and thin film gels each have their own problems. Vacuum filtration suffers from the general problem of construction expense and also that it has depth limitations. Dialysis' main problem is that of equilibration time; and both this method and the thin film gel method suffer problems with placement and retrieval, although for an environment such as the intertidal zone, this is a problem for all the methods, both *ex* and *in situ*, especially at high tide, when the area of interest is under water.

Table 6.1. Advantages and disadvantages of porewater sampling methods.

Method	Advantages	Disadvantages
Centrifugation	Rapid, simple	Potential for oxidation and temperature artefacts
Squeezing	Simple, inexpensive, immediate filtration	Potential for oxidation and temperature artefacts
Vacuum filtration	Limited potential for artefacts, continuous monitoring	Expensive, depth limitations, potential loss of volatiles
Dialysis	Limited potential for artefacts	Equilibration times, placement and retrieval
Thin film gels	Limited potential for artefacts, rapid equilibration	Placement and retrieval

For sampling at times of high tide, the *ex situ* methods would require either the remote triggering of a sampling device or the construction of a pontoon from which

sampling could be undertaken. The use of a boat is not desirable due to the open nature of the coastline and the often rough nature of the sea. As a consequence, the use of *ex situ* methods is not considered appropriate for the sampling of sediment porewaters under these circumstances. There thus remains the choice of *in situ* techniques. Dialysis is ruled out on the grounds of slow equilibration times, whilst the construction of a new vacuum filtration unit is close to prohibitive in terms of machining costs. This leaves thin film gels as the only viable option both financially and practically. Thin film gels have been used to gain fine degrees of resolution and are not depth limited, but have not been used under the conditions anticipated in this study. To overcome the problems posed by these conditions, a new design of sampler is proposed, which allows continuous sampling of porewaters over a time period long enough to include a complete tidal cycle. This thus negates having to use remotely triggered sampling devices, or the construction of structures from which sampling could take place.

A number of sampler designs have been considered, based on the review of current samplers. These designs are described below, together with the reasoning behind the selection of one, and the rejection of the remainder, as a feasible sampler. The four designs are simply referred to in the text as sampler Nos.1-4 respectively. Primarily, design No.1 was to be used for diffusive equilibrium sampling, whilst the remainder are for sampling using the diffusive gradient principle. The principles of both methods are described in Section 6.2.5.

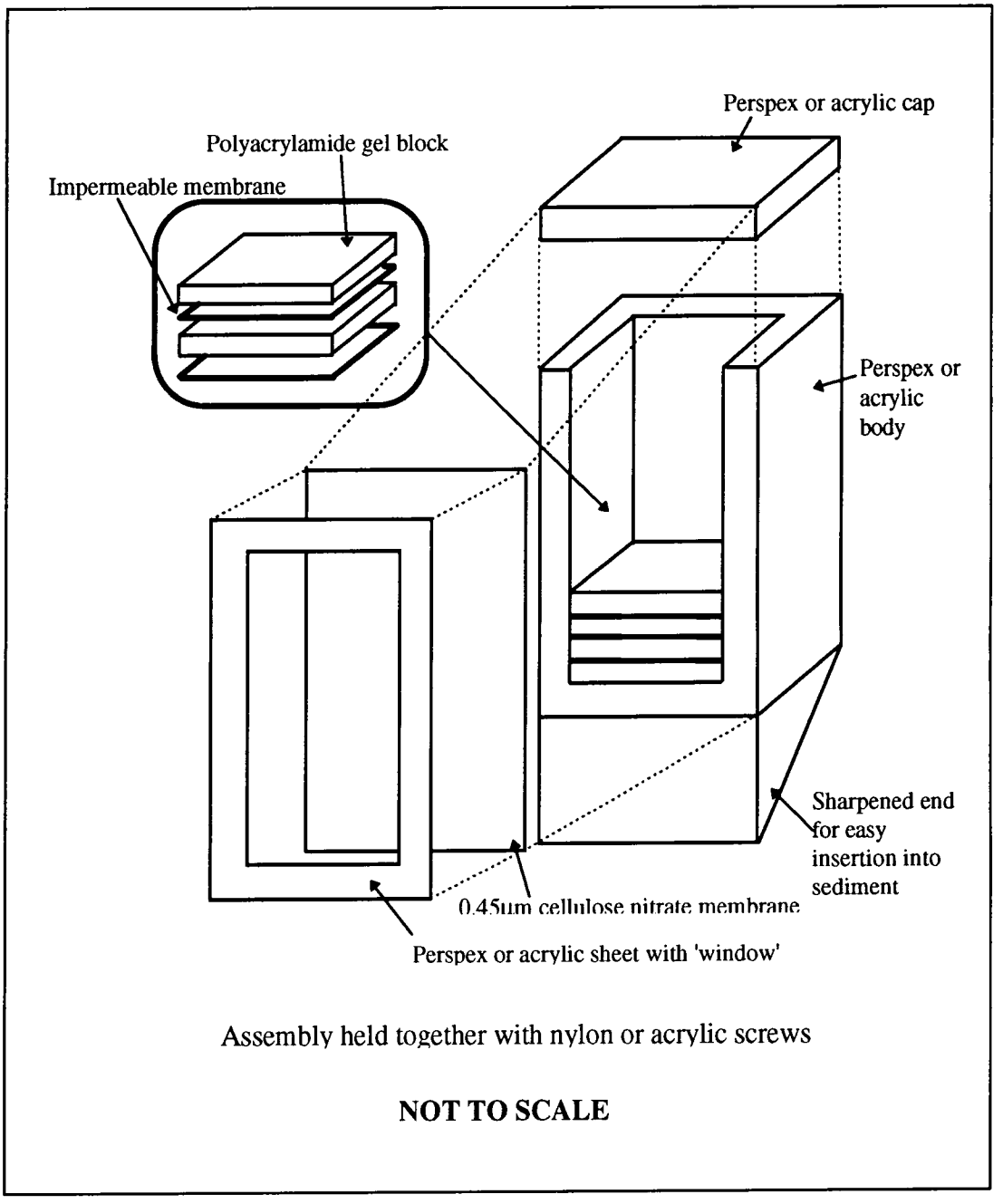
The basic design of proposed sampler No.1 is presented as Figure 6.2. The main body, cap and fronting 'window' are constructed of Perspex and it is easy to see that two samplers could easily be mounted back to back, or stacked vertically with only simple modification.

The precise dimensions are fairly flexible, although, obviously the larger the apparatus, the greater the likelihood of sediment disturbance, although this could be balanced (in the lateral dimension) by a sample homogenising effect. It is unlikely that the compartment in the main body will exceed 15-20mm in depth, but may be up to 50mm in width. The polyacrylamide gel blocks, each around 5mm to 10mm in thickness, would be stacked in the compartment, separated by layers of an impermeable membrane. Thus, each gel block would act as a single sampling compartment, analogous to the milled compartments in Hessleins' (1976) dialysis sampler, and giving vertical resolution of 5 to 10mm. This design negates the problem of internal diffusion were a single large

gel block used. A greater degree of resolution is theoretically possible, using thinner gel layers, but great care would be needed in handling the gel layers (to ensure they do not tear), ensuring total elimination of oxygen and maintaining individual gel layer isolation.

Once the main compartment is filled with alternating layers of gel and impermeable membrane, and the cap placed in position, a 0.45μm pore size filter membrane is added as a barrier to prevent particles adhering to the gel, but still allowing

Figure 6.2 Exploded view of proposed sampling device No.1.

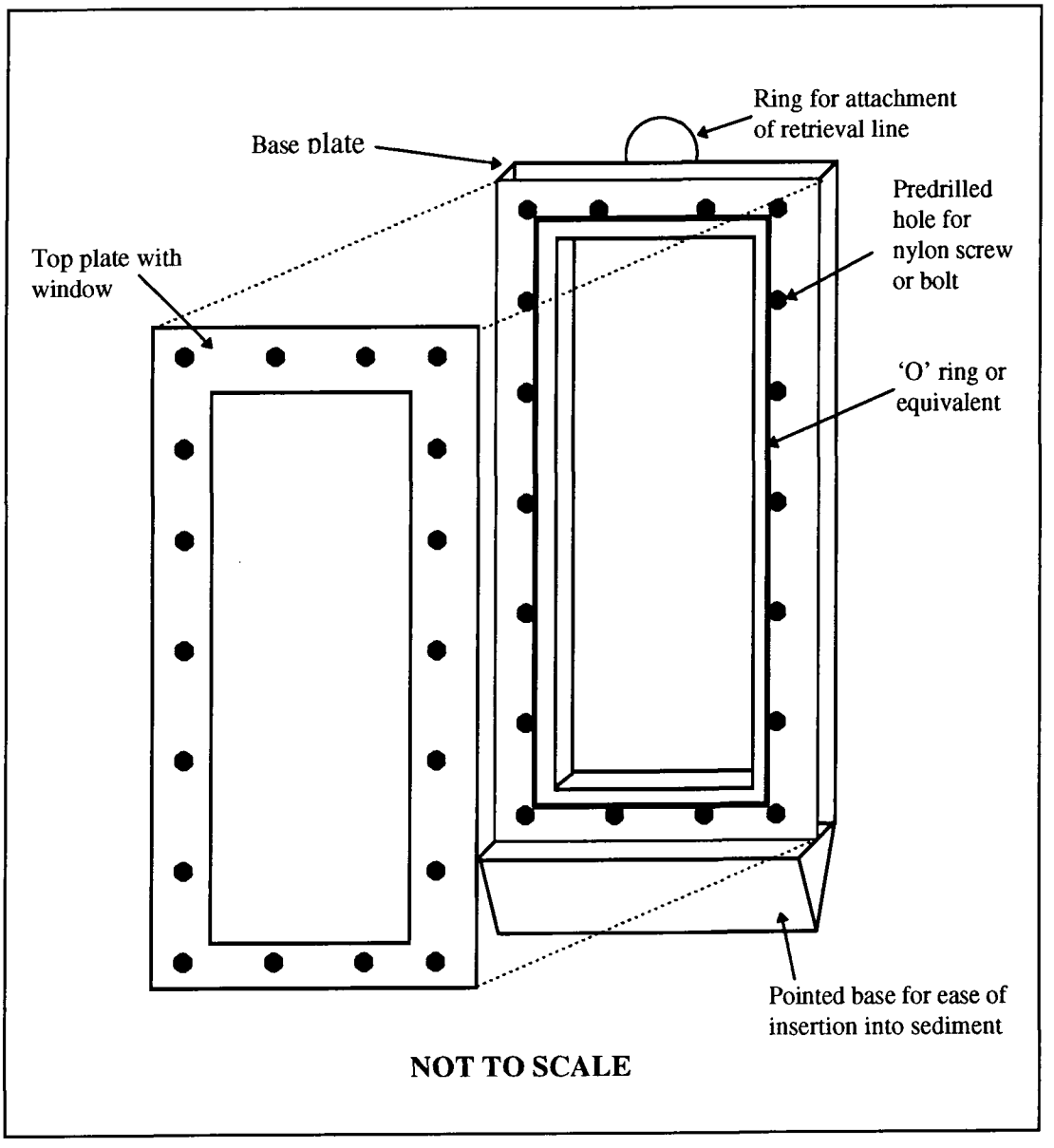


free movement of dissolved species (Davison and Zhang, 1994). The membrane also acts as a support to the gel layers, and in turn is held in place by a thin sheet of Perspex, in which a suitable shaped hole has been cut, so allowing maximum exposure of the membrane protected gel to the surrounding sediment. The cap and fronting sheet, are both held in place with acrylic or nylon screws in pre-drilled and threaded holes. In addition, a thin (in the order of 1mm) solid facing plate may be used to protect the filter membrane during insertion into the sediment. The actual placement into the sediment may be facilitated by the use of a tight fitting removable sampler sleeve. The sleeve is pushed into the sediment and the sediment then contained is removed. The sampler is inserted, and the sleeve withdrawn, leaving the sampler embedded in the sediment.

Proposed sampler design No.2 is shown in Figures 6.3 and 6.4. Figure 6.3 shows an exploded view of the sampler. This design differs markedly from that of design No.1, in that the gel simply lies as a single undivided sheet in a recess in the main body. The gel layer is held in place partly by the filter membrane as with design No.1, but mainly by the windowed top plate, which has a protruding lip which mates with the recess in the main body, the design of this sampler is very similar to those used by Davison et al (1991, 1994), Davison and Zhang (1994); Krom et al (1994), Zhang and Davison (1995) and Zhang et al (1995a, 1995b). This is clearly seen in Figure 6.4 which shows the longitudinal and transverse cross sections of this design. The advantage of this design is that various thicknesses of the acrylamide gel may be utilised, the changes in gel thickness being accommodated by the use of O-rings of different thickness, or 'stiffness'. Again the main body and fronting 'window' are constructed of Perspex or another suitably inert material. The fronting sheet, is held in place with acrylic or nylon screws in pre-drilled and threaded holes as with sampler design No.1, and rests against a lip machined near the base of the main body. This lip forms part of the sharpened tip of the sampler, allowing for easier insertion into the sediment. the main disadvantage of this design is in the construction, with the milling of the recess in the main body, the lip near the base and the lip in the front sheet being difficult to machine with the degree of precision required. This design of sampler enables it to be used more easily with the DGT method described in Section 6.2.5.2. If it is to be used with the DET method, then the gel must be either quickly sectioned on retrieval, or the diffused ions must be rapidly immobilised to prevent internal diffusion and consequent loss of vertical resolution. The

immobilisation may be accomplished by either immersion in a sodium hydroxide solution, or quick frozen as described in Chapter 7.

Figure 6.3. Exploded view of proposed sampling device No.2.



Proposed sampler design No.3 is shown in Figures 6.5 and 6.6. Figure 6.5 shows an exploded view of the sampler. This design is similar to that of design No.2, in that the gel simply lies as a single sheet but in this design there is no recess in the main body, and the windowed front plate has no lip. This is more clearly seen in Figure 6.6 which shows the longitudinal and transverse cross sections of the proposed sampling device. The absence of the recess allows gel sheets to be used without precise cutting to fit the size of the recess. The O-rings are sunk into the main body of the sampler, and stand proud

by about 0.5-0.8mm. Any gel layer thinner than this will be trapped by the fronting plate and filter membrane by tightening the retaining screws. Thicker gels may also be used, but it may be preferable to use O-rings with greater diameters thus necessitating the machining of larger O-ring recesses. The fronting sheet is held in place with acrylic or nylon screws in pre-drilled and threaded holes as with the previous sampler designs, and again rests against a lip machined into the sharpened tip of the sampler, allowing for easier insertion into the sediment.

Proposed sampler design No.4 is shown in Figures 6.7 and 6.8. Figure 6.7 shows an exploded view of the sampler. This design is almost identical to that of design No.3, but in this design both the main body, and the windowed front plate are machined in such a way as to form a point when the sampler is assembled. This is more clearly seen in Figure 6.8. There is one particular problem found with this design which is not found with those described earlier, namely, the small gap found between the two halves at the

Figure 6.4. Longitudinal and transverse cross sections of proposed sampling device No.2.

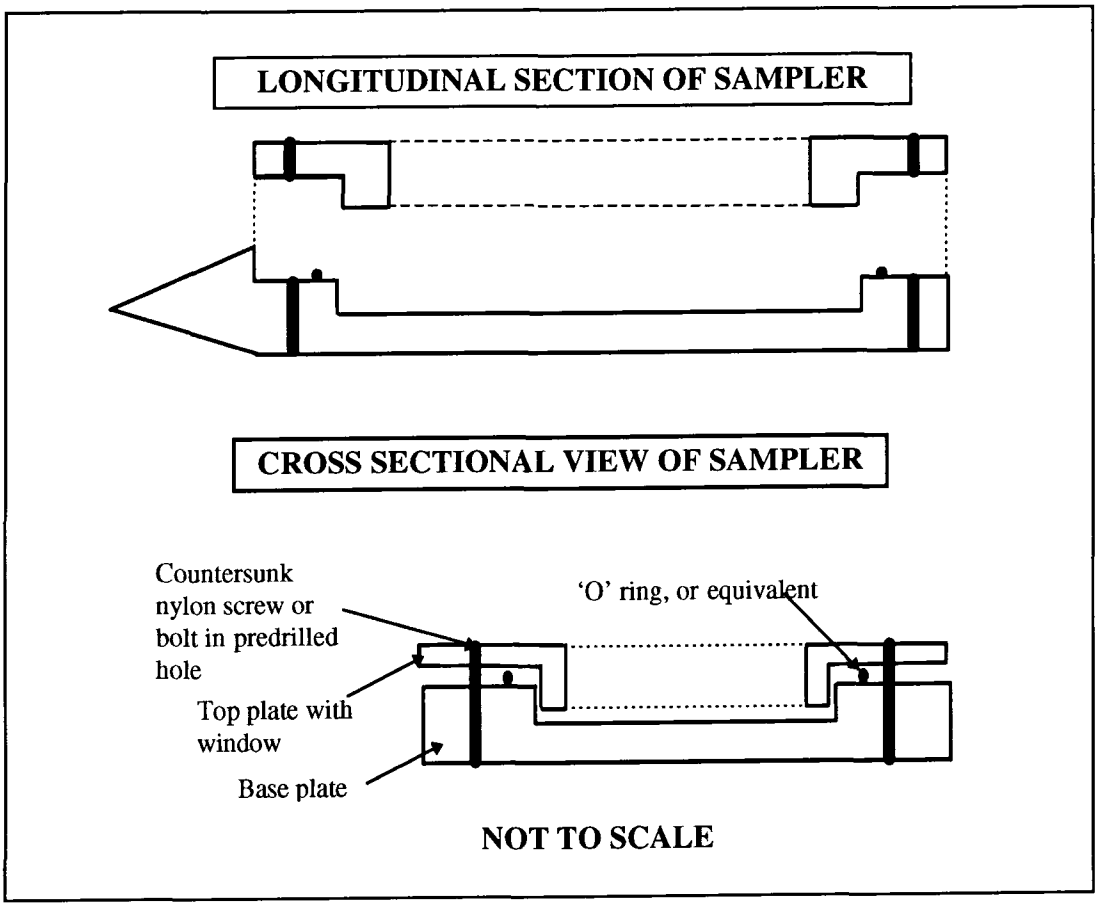


Figure 6.5. Exploded view of proposed sampling device No.3.

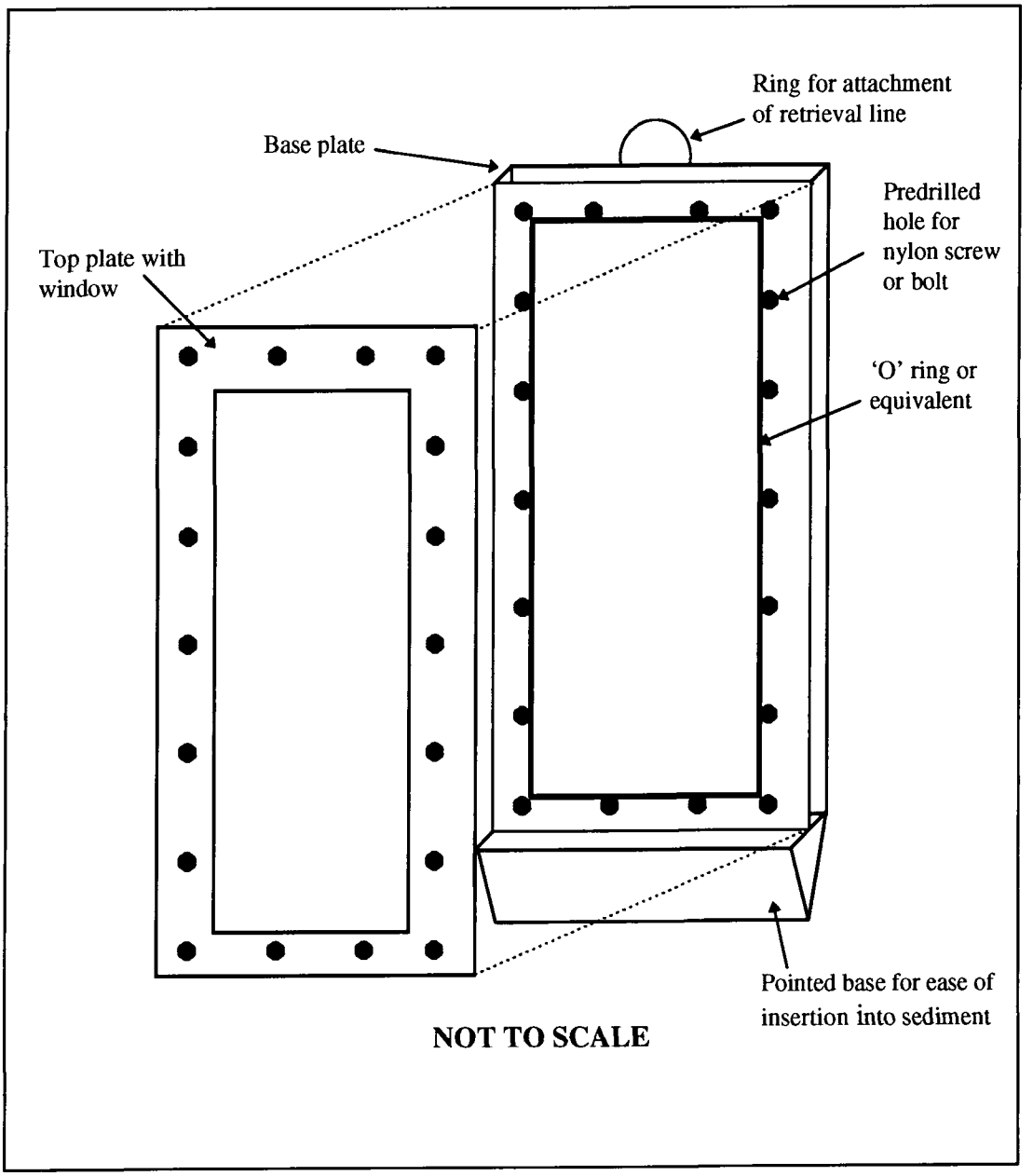
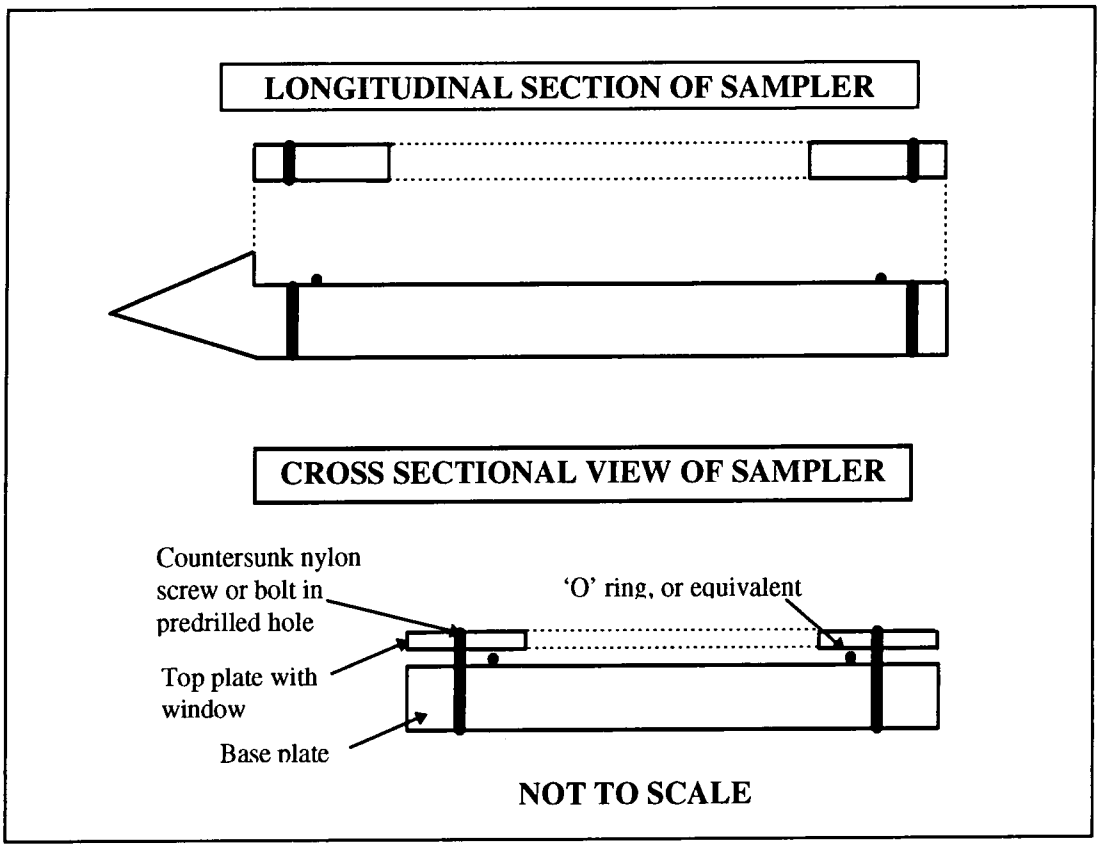


Figure 6.6. Longitudinal and transverse cross sections of proposed sampling device No.3.



sampler tip. This gap could give rise to unnecessary sediment disturbance during sampler placement, although this might be minimised by the use of suitably sized inserts, or by sacrificial tips, such as that shown in Figure 6.9, although numerous other variations of this are easy to invisage. Sampler design No.4, together with design Nos.2 and 3, are much easier to push into the sediment than sampler No.1. Like sampler No.1, design Nos.2, 3 and 4 may all have a protective plate attached, although the extra sampler thickness would have a greater relative disturbing affect on the sediment than with sampler design No.1. The greatest problem with these latter three thinner designs is the potential for sampler deformation during placement, especially if the sediment is particularly heterogeneous, with consequent sediment disturbance. The choice of design must therefore take this into consideration, and so the choice of material or materials used in the sampler construction is another highly important aspect of sampler design. The materials must be very carefully selected, with the materials potential reactivity, easy of machining and rigidity all being of great importance.

Figure 6.7. Exploded view of proposed sampling device No.4..

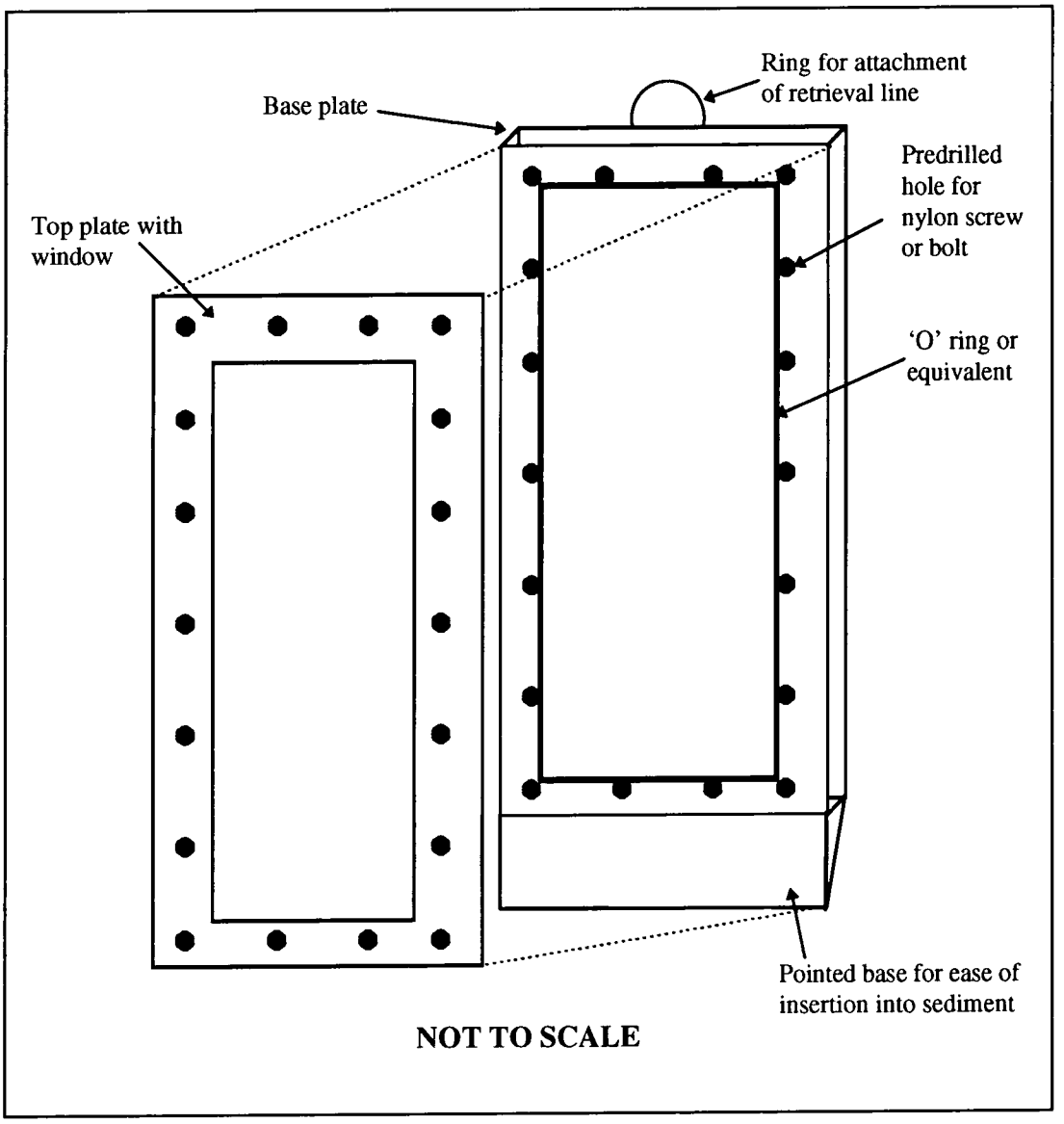


Figure 6.8. Longitudinal and transverse cross sections of proposed sampling device No.4.

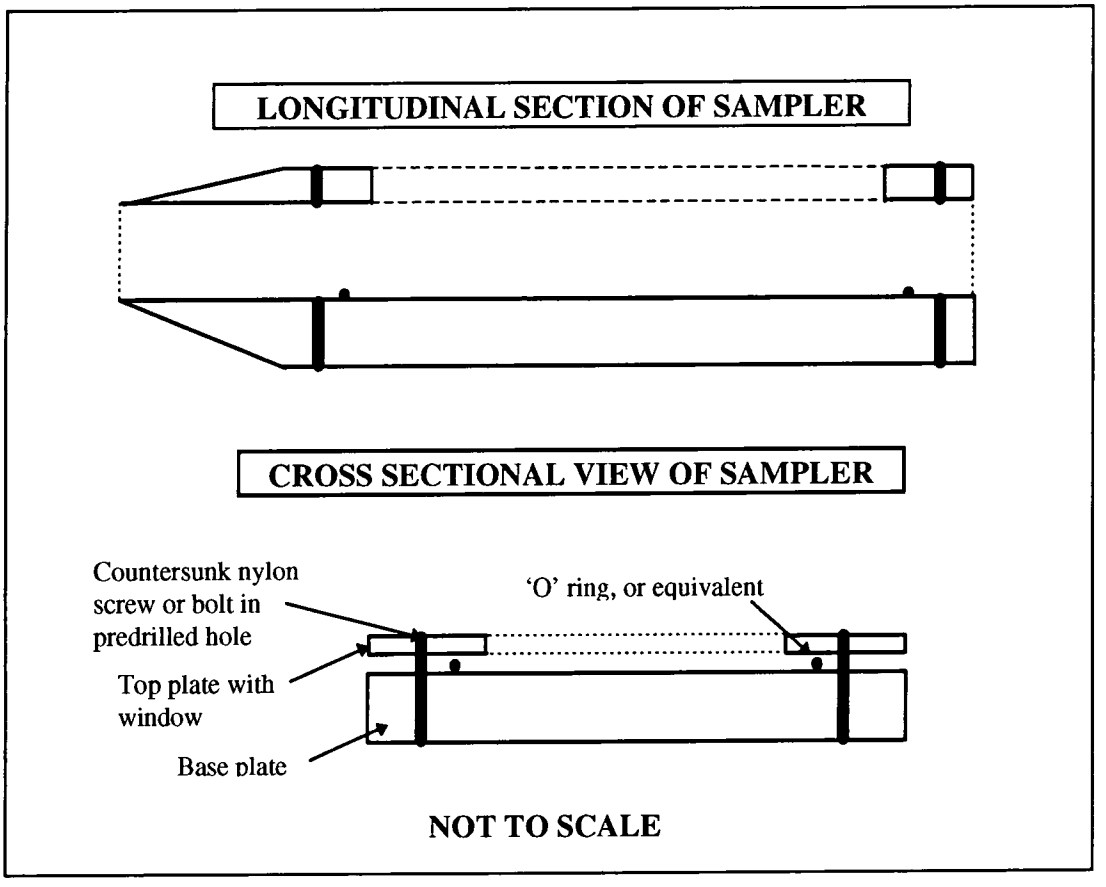
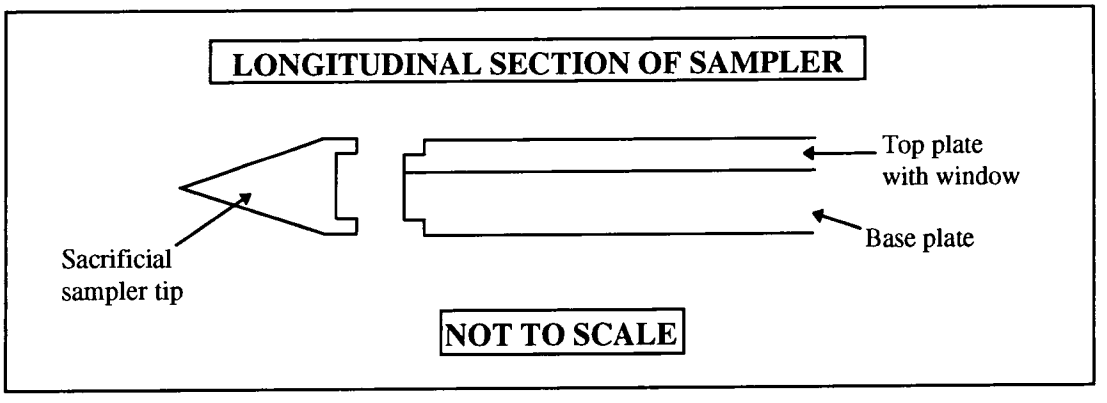


Figure 6.9. Longitudinal sectional view of proposed sacrificial tip for sampling device No.4.



6.2.6.1 *Sampler materials*

Teflon (PTFE) is not a suitable material for use in construction due to the difficulty in machining and lack of rigidity, caused by PTFE's physical properties. Teflon is not contaminated with trace metals and does not adsorb dissolved trace metals either, but it is quite an expensive material to purchase. However, Teflon has been used as a sampling substrate (by surface deposition) for the collection of both iron and manganese oxyhydroxides in situ, and arsenic has been shown to be preferentially adsorbed by iron oxyhydroxides (Belzile et al, 1989; De Vitre et al, 1991).

Polycarbonate has been reported as being moderately oxygen permeable (Carignan, 1984), an undesirable property. Plexiglass has been shown to collect the least amount of iron oxyhydroxides on its surface than either glass, polyvinylchloride, polystyrene or Teflon (see Table 6.2), although the ability of the surfaces to collect iron oxyhydroxides is inversely correlated with their reported surface energies (Belzile et al, 1989).

Table 6.2. Mean deposition of iron oxyhydroxides on various materials.

Materials	Glass	Plexiglass	Polystyrene	Polyvinylchloride	Teflon
Fe deposit* ($\mu g/cm^2$)	0.6±0.1	0.4±0.1	1.3±0.2	0.9±0.3	3.6±0.3

*N = 3 samples; ±1 uncertainty is one standard deviation. From Belzile et al, 1989.

A single gram of polyethylene has been shown (reported in Creed et al, 1995b) to release 0.5µg of manganese when treated with 8N nitric acid, and in a separate experiment (reported in Creed et al, 1995b) $1cm^2$ of linear polyethylene was also shown to release 8ng of zinc and 0.4ng of copper when treated with 1:1 nitric acid for one week, although the leaching of sampling containers during cleaning using 0.5% nitric acid (pH~1-2) is not expected to have such an effect. Essentially, the same care must be taken with sampler materials as with sample container materials, as discussed in Section 7.8.1, with the choice being based upon these considerations and the nature of the sediment being investigated.

6.3 Soil and water sampling

6.3.1 *Soil sampling*

In this case, the term 'soil' is taken to mean the uncemented results of weathering above bedrock. This includes residual soils, alluvial soils, boulder clay and glacial drift, together with all the beach sediments and anthropogenic deposits. Sampling is generally carried out by hand, with samples being collected using hand driven U100 tubes, or in suitably cleaned plastic bags or bottles. It is important to note that many of the porewater sampling methods require the procurement of sediment samples from which the porewaters are then extracted using one of the methods discussed above. A novel and interesting technique, which does not use any conventional ideas for sediment retrieval has been successfully employed by Siami et al (1987), who obtained continuous samples of loose and unconsolidated lake sediments. The samples were obtained by freezing the sediments onto the exterior surface of metal tubing containing dry ice. As the core was removed from the sediments, the zone between the frozen and unfrozen portions was smeared; once out of the water, this was stripped away and the cores returned to the laboratory. Were this method to be used for the sampling of arsenic species, rather than for total arsenic, then it would be recommended that the metal tube either be replaced with one of a suitably inert plastic, or similarly coated. The frozen sediment was removed by filling the tube with warm water. The doughnut shaped core could then be sectioned, with the surface that had been in contact with the tube also being removed. The porewater can then be recovered from such samples by centrifugation, or squeezing, although Siami et al (1987) were only interested in the arsenic content of the sediment itself.

6.3.2 *Surface water sampling*

Sturgeon and Berman (1987) state that sampling at or near the surface is normally carried out by hand, this leading to a minimising of potential contamination. The sampling bottles should be emptied of storage water (usually a dilute acid) just prior to being used. Sample collection should take place at arms length and shoulder length plastic gloves should be worn. The bottle should only be uncapped below the surface(~0.5m) and recapped whilst submerged so as to avoid contamination from the surface layers. Samples should then be wrapped in clean polyethylene bags for transport.

An alternative is to use a 'sampling pole' to the end of which is attached a holder in which the sampling bottle rests.

Remotely triggered sampling devices normally associated with deep sea sampling have also been applied successfully to surface water sampling for arsenic (Grasshoff, 1983a; Sturgeon and Berman, 1987).

Iverson et al (1979) divided samples, collected and stored in acid washed polyethylene bottles, in two. One subsample was filtered (0.4μm) on site and the remaining subsample acidified to pH 1 with HNO_3 to prevent bacterial oxidation of MMAA and DMAA.

6.3.3 *Groundwater sampling*

Groundwater samples may be procured from boreholes by means of a bailer, although if more than one borehole is to be sampled then great care must be taken in thoroughly cleaning both the bailer and retrieval chord between holes. Alternatively, bailers may be assigned to specific boreholes, one being used for that one borehole only. Again, these bailers must be cleaned between visits and stored in clean conditions.

An alternative and altogether preferable method to using a bailer is pumping, either with a down hole submersible pump, or with a surface pump. In these cases, care must be taken to ensure sediment is not included within the sample, although the fitting of a filter to the intake may alleviate this problem. Contamination from pump construction materials is another cause for care and bladder and diaphragm pumps are a way around this problem. It is good practice to store dilute acid (1N HCl) in the pump system between sampling stations and to ensure adequate flushing of the line prior to sampling (Sturgeon and Berman, 1987; Dick, 1994). The flushing may be completed adequately in low production wells by using a sampling tube of small internal diameter.

More of a problem is ensuring that the sample retrieved from the well is actually representative of the groundwater, and not just what is in the borehole, since the water in the borehole casing is open to oxygen and other gases. Many workers initially over-pump wells, and allow the well to recover before sampling, although this is not without its problems (Dick, 1994). This is problematic in wells sunk in low permeability materials. If money is no object, then the well could be maintained under an inert atmosphere during initial pumping and subsequent recovery and sampling, although this

could be extremely time consuming. If the well was not hidden or fenced off securely, then vandalism might be another problem.

A potential way around this is, and one that concurrently allows for discreet sampling at specific levels within the well, is to use a variation of the dialysis sampling method described in Section 6.2.4, or a variation on the vacuum filtration method, described in Section 6.2.3.

More of a problem is one highlighted by Bjerg and Christensen (1992), who found very large differences in groundwater quality over depth in a shallow unconfined essentially homogenous sandy aquifer. The observed depth variation was found to be much more significant than short-term (months) temporal variations. Additionally, a surprisingly large horizontal variation was found over short distances; a variation much larger than could be ascribed to either uncertainty in sampling or chemical analysis. Indeed, the horizontal correlation ranges were very short (5-10m) and essentially negligible. The conclusions reached were that horizontally distributed samples are preferred to repeated sampling in the same well, since the horizontal variation found is much larger than the temporal variation, and that well-defined depth specific groundwater sampling is paramount in characterising such aquifers (Bjerg and Christensen, 1992). One way around such a problem is to install a multi-level monitoring well capable of continuous sample collection, similar in design to that constructed by Ayers and Gosselin (1995). This well had several pumps at different depths and was succesfully used as part of the monitoring of the movement of nitrate-nitrogen during the pumping of a nearby irrigation water supply well.

CHAPTER 7

SAMPLE PRESERVATION

7.1 Introduction

Prior to any sampling, a protocol must be defined with the aim of ensuring that all equipment used prior to, during and after sampling is, and remains arsenic free. A brief discussion on the choice of materials used in sample bottle construction, and the cleaning procedures used are given in Sections 7.8.1 and 7.8.2.

Once the required samples have been procured, they must then be transported to the laboratory for suitable analysis, or analysed on site. For the analysis to be of any value, then the relative proportions of the arsenic species present in the medium sampled must be preserved as closely as possible. Water samples may undergo changes with regard to their physical, chemical or biological state at varying rates from their time of sampling (Sturgeon and Berman, 1987). This then requires the sample to be preserved either in as close to a natural state (i.e. temperature, etc.) as possible, or, as this is generally very difficult to achieve, then treating the sample in such a way as to maintain any disturbance at an absolute minimum. A great number of methods of preservation are available to maintain arsenic speciation, varying with the arsenic containing phase, the arsenic species of interest and the facilities available. The literature is almost exclusively dedicated to the preservation of either water samples, be they of fresh or salt water, groundwaters, sediment porewaters, or sediments themselves. There is no literature on the preservation of arsenic species held in polyacrylamide gels or other preconcentrating sampling media. The following summary briefly examines the effects of filtering samples and then goes on to look at preservation techniques associated with each of the sampled media. There then follows brief discussion on the selection of the preservation method applicable to that medium, and the problems associated with each.

7.2 Filtration and filter membrane characteristics

A number of recent papers (Grasshoff, 1983b; Sturgeon and Berman, 1987; Horowitz et al, 1992, 1996; Puls, 1994; Hall et al, 1996), have highlighted a limitation of using the operationally defined definition of the term 'dissolved'. It is generally accepted that the term dissolved refers to that fraction of water and its constituents that pass through a 0.45μm pore size membrane filter. This does not, however, prevent the passage of a large range of metal species, including: metals bound in colloids (considered to be finer than 1μm) with clay, Fe and Mn oxides and humic acids, metal organic complexes, inorganic complexes and free inorganic ions. Indeed, previous work (Horowitz et al, 1992; 1996) has shown that a number of factors influence the concentrations of dissolved phase metals (the work was carried out initially on Fe and Al, and later on a broader range of metals, not including arsenic). These factors include: filter type; filter diameter; filter pore size (the expressed pore size is often an average); method of filtration; dilution by entrained water used to condition the filters; suspended sediment concentration; suspended sediment grain size distribution; concentration of colloids and colloidally-associated trace elements; degree of sorption/desorption of trace metals to/from the filter itself or to/from the solids retained by it, the volume of sample processed (due to suspended sediment quantity, size and chemistry), and in samples from oxic or reduced systems, the oxidation of iron or managnese (for example) may result in precipitation prior to filtration and result in the removal from solution of previously dissolved species due to instantaneous adsorption by the precipitate (Grasshoff, 1983b; Sturgeon and Berman, 1987; Horowitz et al, 1992; 1996; Puls, 1994; Hall et al, 1996).

A wide variety of filter types are commercially available, including those made from cellulose esters, Teflon, nylon, polycarbonate, PVC, polyamide, silver foil, glass and glass fibre. Polycarbonate and cellulose ester are most commonly used for trace metal analysis with preference generally being given to the polycarbonate types due to their superior retention powers for submicron sized particles, small salt retention, lower

intrinsic trace metal impurities (see Tables 7.1 and 7.2) and the relative ease of obtaining reproducible filter weights.

However, although there are differences between filter types (brand, composition and filtration method [sieve or tortuous path]), not all elements (28 elements in 5 natural water samples) behave similarly, and differences are more marked in some samples than others. Indeed, it is not possible to predict filtration artifacts according to the type or diameter of membrane, and although elemental recoveries do show a correlation with the particular filter used, the magnitude of change in elemental concentration across the filter systems studied is not great (Hall et al, 1996).

Filtration may be performed under partial vacuum or under pressure. With either technique, it is important to use low pressures since phytoplankton cells rupture at pressures greater than 20mm Hg (Sturgeon and Berman, 1987). Partial vacuum filtration, however, must be completely avoided if the sample is suspected to contain volatile compounds such as arsine. Vacuum filtration also suffers from the fact that it is inherently an off-line process, whereas pressure filtration allows filtration directly from the sampler under an inert atmosphere, so minimizing potential oxidation and airborne contamination. The only drawback of the on-line pressure filtration is that settling of suspended particles takes place which is detrimental to the collection of representative suspended particle samples if so desired (Sturgeon and Berman, 1987).

The filtration of water samples, like any other sample manipulation is a possible source of contamination, with the possibility of elemental or compound retention (adsorption) or release (desorption) by the filter. In addition, if some particles are of biological origin (such as plant cells), then mechanical damage may lead to cell destruction and will lead to the release of intercellular fluid into the sample. If the sample is to be frozen, then filtration must take place if there are biological particles, as these almost always rupture on freezing.

In practice, therefore, filtration procedures are a compromise, not only with respect to the separation of the truly dissolved matter from the particulates, but also with respect to the extent of unavoidable undesirable artifacts (Grasshoff, 1983b;

Sturgeon and Berman, 1987). Indeed, if seasonal data on dissolved trace element concentrations are derived from filtered water samples, it might be impossible to differentiate between true environmental changes and those superimposed or created by sample processing procedures. Thus, in some cases, although suspended particles may contaminate samples during prolonged storage through sorption processes or biological action, removal of particulates by filtering may pose a greater hazard to sample integrity than leaving them unfiltered.

Unfortunately, there does not seem to be a way to evaluate sample processing effects/contributions relative to true environmental changes, for dissolved trace metal concentrations (Horowitz et al, 1992). With the elimination of contamination as a possible cause of the observed chemical differences in the various studies on filtrates, the justification for the common practice of accepting the lowest concentrations determined for a particular sample or site as being the most representative is no longer valid, and could lead to underestimations of ambient trace metal concentrations or to negatively biased data (Horowitz et al, 1996).

There then lies the question as to when samples should be filtered, and does the source of the sample affect this decision?

The majority of workers investigating freshwater environmental arsenic concentrations filter their samples immediately after procurement (Aggett and O'Brien, 1985; Faust et al, 1987a, b, c; Thornton, 1988; Seyler and Martin, 1989; van Elteren et al, 1991; Aurillo et al, 1994; Webster et al, 1994; Hunt and Howard, 1994; Azcue et al, 1994a; Azcue and Nriagu, 1995), almost all using 0.45μm filters, although other workers (Kuhn and Sigg, 1993; Boult et al, 1994), have left up to eight hours before filtration. Bright et al (1994) transported their samples to the laboratory prior to filtration. Cheam and Agemian (1980), compared a variety of preservation techniques on artificial samples and a Great Lakes harbour water, with arsenic concentrations in the range 1-10μg/l. On the basis of their study, they recommended that samples be unfiltered, a view shared by Navarro et al (1993). Crecelius et al (1986) and Howard and Comber (1992) suggest that only if <u>total</u> inorganic arsenic and methylated (MMAA

and DMAA) species are to be determined, should the samples be filtered. Iverson et al (1979), immediately filtered river water samples if they were to be analysed for As(III) and As(V), but sample were simply acidified for organoarsenical analysis. Andreae (1980) preserved rainwater samples by acidification, but only if they were to be stored for long periods of time. Otherwise, they were left unfiltered and simply analysed as soon as possible after collection.

With investigations of seawater arsenic concentrations, there is a similar range of opinions. Andreae (1978, 1979) and a number of other workers (Bodewig et al, 1982; Howard and Comber, 1992; Riedel, 1993; Kitts et al, 1994; Santosa et al, 1994) suggest filtering samples immediately, whilst Navarro et al (1993), did not filter their samples, but simply acidified them, and Peterson and Carpenter (1983), neither filtered nor acidified their samples, but ensured they were stored for no longer than 24 hours. Howard and Apte (1989) and De Battencourt et al (1994) filtered collected samples on arrival at the laboratory.

Probes into the arsenic concentrations of groundwater seem to be less beset with confusion as to when filtration takes place with seemingly all workers filtering their samples on site (Holm and Curtiss, 1989; Chatterjee et al, 1992; Yokoyama ,1993; Davis et al, 1994; Chen et al, 1994).

Aggett and Kriegman (1987), produced a fairly comprehensive review of the problem of preserving environmental sediment porewater samples containing the various arsenic species and recommend that samples taken for the determination of As(III) and As(V) should be filtered, presumably on site.

Haswell et al (1985), who filtered on site found that this enabled samples to maintain a stable As(III):As(V) ratio for up to 5 hours, with a loss of ~20% As(III) over the same time if the sample is unfiltered. MMAA and DMAA losses are reduced to <10% if the samples are filtered on site and stored for up to 5 hours. They suggest that any sample preservation techniques will modify the natural species equilibrium, and consequently recommend that analysis be performed as soon as possible after sampling.

Aggett and O'Brien (1985), Moore et al (1988), also filtered their samples on site.

Reimer and Thompson, 1988; Reimer 1989; Bright et al (1994) transported their samples back to the laboratory prior to nitrogen displacement and filtration

Tessier et al (1985) preserved samples collected by dialysis (essentially an in situ filtration method) by sealing them and returning them to the laboratory for analysis.

Azcue and Nriagu (1994) stored their samples in acid leached polyethylene vials.

7.3 Sediments and Soils

Elkhatib et al (1984a; 1984b), found no oxidation of As(III) to As(V) in soil extracts containing 5-500mg/l arsenite over time periods of between 30 minutes and 24 hours. Millward et al (1993) and Kitts et al (1994) stored intertidal sediments frozen in acid washed plastic containers. Reimer (1989) stored marine samples in plastic bags at -20°C until analysis, while Holm et al (1979) simply stored river sediments in plastic vials at 4°C until use. Crecelius et al (1986) experimented with various storage strategies for the preservation of arsenic containing freshwater lake sediments. They came to the conclusion that there is no significant loss of arsenic speciation if the samples are placed in polythene bags, sealed, and stored at 0-4°C or frozen at -18°C for up to 30 days, but recommend that samples be analysed as soon as possible after procurement. Azcue et al (1994a) stored lake sediments in prewashed plastic vials at 4°C in the field, freeze drying them on return to the laboratory. Navarro et al (1993) dried soil and sludge samples for 2 weeks at room temperature before sieving (340μm) and storing at -18°C until analysis. de Magalhães and Pfeiffer (1995) sieved their marine sediment and soil samples (<63μm) prior to drying at less than 60°C to prevent volatilisation of arsenic compounds. Bischoff et al (1970), illustrated the need to squeeze sediment samples at the in situ temperature, as changes in ion-exchange selectivity occur as a function of temperature, leading to misleading results.

7.4 Freshwaters

Aurillo et al (1994) and Hunt and Howard (1994) simply placed their on site filtered samples on ice and ensured that analysis took place within 24 hours, although other workers (Kuhn and Sigg, 1993; Boult et al, 1994), have left up to eight hours before filtration. Bright et al (1994) transported their samples to the laboratory prior to filtration and subsequent freezing over dry ice. Webster et al (1994), filtered their samples on site and then acidified them with 2ml of HNO_3/250ml of sample. Azcue et al (1994a) also filtered samples on site, acidified them with HNO_3 (to a final concentration of 0.4%), and then stored them at 4°C until analysis. Johnson and Thornton (1987) and van Elteren et al (1991) recommend filtering samples on site, but acidified them with HCl, before storing at 4°C until analysis. Azcue and Nriagu (1995) stored their filtered samples frozen under dry ice in the dark until analysis. Seyler and Martin (1989) immediately filtered samples, but did not acidify them prior to storage in the dark at 4°C, subsequently ensuring that analysis took place within 72 hours.

Cheam and Agemian (1980), compared a variety of preservation techniques on artificial samples and a Great Lakes harbour water, with arsenic concentrations in the 1-10μg/l range. On the basis of their study, they recommended that samples be unfiltered, acidified with 0.2% V/V H_2SO_4 (pH 1.5) and stored at room temperature in polyethylene bottles. Navarro et al (1993), did not filter their samples, but simply acidified them by the addition of 2ml of HNO_3/100ml of sample in the polyethylene storage bottles. Crecelius et al (1986, 1994) stored lake water samples in acid washed polyethylene bottles prior to freezing. They suggest that if only total inorganic arsenic and methylated (MMAA and DMAA) species are to be determined, then the samples should be filtered into polyethylene bottles and stored at 0-4°C until analysis, with no addition of any preservative. If, however, the As(III):As(V) ratio is to be maintained, then the sample should be quick frozen to -196°C in liquid nitrogen and stored at least -80°C until analysis. Even with storage at -18°C after quick freezing, a loss of around 25% of the As(III) from a sample in 4 days was found. Simply freezing to -18°C led to a loss of 90% of As(III) in 4 days.

Aggett and O'Brien (1985), preserved lake water As(III) by filtering, acidifying to pH2 and flushing with nitrogen. They showed that both arsenic and iron were oxidised more or less immediately at room temperature if no preservation was implemented and concluded that refrigeration (without freezing) to 2°C, acidification to pH2 (with HCl) and exclusion of air was the best way to preserve samples, a finding verified by Faust et al (1987a, b, c).

Feldman (1979), reported that complete oxidation of the As(III) present in artificial samples containing 1-10µg/l took place within 4 days. For 100ng/ml this occurred in just under 8 days, with 1µg/l taking 18 days. Feldman suggests the addition of 1mg/ml of ascorbic acid as a preservative for solutions as dilute as 1ng/ml As(III), providing that this does not interfere with any other chemical species present, a test relatively easily performed.

Iverson et al (1979), working with river water samples with relatively low arsenic levels, concentrated the arsenic prior to GC analysis by evaporation. Arsenic volatility during evaporation was eliminated by adjusting the pH of the sample to 10 before evaporation thus ensuring that all arsenic species (inorganic As, MMAA and DMAA) were in their ionic states.

Andreae (1980) preserved rainwater samples for arsenic species determination by acidification with 4ml concentrated HCl/1000ml sample, but only if they were to be stored for long periods of time. Otherwise, they were simply analysed as soon as possible after collection.

7.5 Sea and estuarine waters

Andreae (1977, 1979), reported the loss of 0.05µg/l of As(III) after one week of storage, with acidification increasing the rate of oxidation, a finding also reported by Aggett and Kriegman (1987), who found that in oxygenated samples, As(III) is more rapidly oxidised to As(V) at pH1 than at pH2. This is in disagreement with the findings of van Elteren et al (1991) who found that at pH 3.37, As(III) oxidation proceeded at a rate about half of that at pH 3.98. They also found that higher initial As(III)

concentrations resulted in lower oxidation rates, and that although decreasing the temperature of storage increases storage times, almost 70% of As(III) is oxidised in 17days, with a 20% loss in the first two days. Andreae (1977) suggested storing samples containing As(III) in a freezer below -15°C or under dry ice, in which case an initial loss of As(III) corresponding to about 0.02ppb is experienced, after which the sample remains unchanged with prolonged storage. In later publications, Andreae (1978, 1979), suggests filtering the samples into polyethylene bottles, acidifying with 1ml conc. HNO_3/250ml of sample (to prevent loss of methylated species) prior to storing at about 4°C with analysis taking place within a week. For the preservation of As(III) and As(V), the sample is stored unacidified at around 4°C with analysis taking place within a week (Andreae, 1978, 1979). Otherwise, samples may be quickly (within 5-10 minutes) frozen under dry ice or kept in the dark for up to 5 days at natural pH (Andreae, 1977, 1979; Peterson and Carpenter, 1986). Santosa et al (1994) immediately filtered samples and then stored them at 0°C in the dark. Navarro et al (1993), did not filter their samples, but simply acidified them by the addition of 2ml of HNO_3/100ml of sample whereas Peterson and Carpenter (1983), neither filtered nor acidified their samples, but ensured they were stored for no longer than 24 hours at 6°C. Riedel et al (1993), and Kitts et al (1994) filtered samples immediately and then froze them, using either liquid nitrogen or a dry-ice/isopropanol mixture, keeping the samples at -18°C in the dark. Andreae (1983) suggests storing samples in acid washed polyethylene bottles. To preserve the As(III):As(V) ratio the sample should be 'quick frozen' using liquid nitrogen and subsequently stored at a temperature below -30°C. This method does not affect the stability of As(V) or methylarsenicals. If the separation of As(III) and As(V) is not required, then the sample may be acidified with 4ml concentrated HCl/1000ml of sample. Under these circumstances, As(III) will be oxidised to As(V), but total inorganic arsenic and the methylarsenic compounds will be stable for several months. Methylarsenicals undergo unpredictable changes in untreated samples. Howard and Comber (1992) also suggest that where As(III) is the major arsenic species present, then samples should be filtered and immediately stored in liquid nitrogen. Where this is not

the case, then filtration with subsequent storage at around -20°C is deemed satisfactory. De Bettencourt et al (1994) collected samples in acid washed bottles which were kept in cold boxes until arrival at the laboratory, where they were filtered, acidified with purified HCl (up to 0.05M) and stored at 4°C until analysis. Bodewig et al (1982) also used HCl to acidify samples to pH2, after filtration. The samples were then stored in thoroughly cleaned polyethylene bottles at 4°C. Howard and Apte (1989) also collected samples in acid washed bottles, but which were filtered at the laboratory and then frozen (-20°C) until analysis.

7.6 Groundwater

Tallman and Shaikh (1980) reported that oxidation of arsenate to arsenite in groundwater samples is slow with no oxidation after 3 weeks. Sandhu et al (1978) collected their samples in Pyrex glass jars with Teflon lids. These were then stored on ice until the night before analysis, when they were stored at 4°C. Chatterjee et al (1992) added either nitric acid (1.0ml/l) or ascorbic acid (100mg/l) to the samples in pre-washed (HNO_3:water, 1:1) polythene bottles. Chen et al (1994) used a similar system, filtering the samples on site into pre-washed (10% HNO_3 then rinsed with water) Teflon bottles, prior to acidification with sulphuric acid (2ml/1000ml sample) to a pH<2 with subsequent storage at 4°C, a method similar to that of Holm and Curtiss (1989) and Yokoyama (1993). In highly alkaline groundwaters, any acidification will result in a serious alteration of sample chemistry, so filtration but not acidification is the only pre-treatment recommended (Davis et al, 1994).

7.7 Sediment and soil porewaters

Aggett and Kriegman (1987), produced a fairly comprehensive review of the problem of preserving environmental sediment porewater samples containing the various arsenic species and performed experiments with varying pH, temperature and exposing the samples to either oxygen or oxygen free environments for periods of between 3 hours and 4 weeks. They recommend that samples taken for the determination of As(III) and As(V) should be filtered, acidified to pH2 with concentrated HCl and refrigerated close to 0°C without freezing. Under these conditions, deoxygenation is not necessary, but is a wise precaution. Haswell et al (1985), found oxidation of up to 90% of arsenite

present in both aerobic and anaerobic soil pore water samples (stored at room temperature and in the light) at nanogram per litre concentrations took place within 12 hours of sampling with a concurrent 10-15% loss of MMAA and DMAA. Filtration on site enabled samples to maintain a stable As(III):As(V) ratio for up to 5 hours, with a loss of ~20% As(III) over the same time if the sample is unfiltered. MMAA and DMAA losses are reduced to <10% if the samples are filtered on site and stored for up to 5 hours. They suggest that any sample preservation techniques will modify the natural species equilibrium, and consequently recommend that analysis be performed as soon as possible after sampling. Crecelius et al (1986, 1994) found a loss of around 30% of As(III) in 5 hours and suggest that quick freezing to -196°C with subsequent storage at -80°C is necessary, whilst Andreae (1977) suggests that samples be frozen under dry ice and stored in a freezer until analysis. Aggett and O'Brien (1985), preserved sediment interstitial water by filtering, acidifying to pH2 and flushing with nitrogen, although this was not sufficient for preventing the oxidation of arsenite. They showed that both arsenite and iron (Fe^{2+}) were oxidised more or less immediately at room temperature if no preservation was implemented and concluded that refrigeration (without freezing) to 2°C, acidification to pH2 (with HCl) and exclusion of air was the best way to preserve samples, a finding also verified by Faust et al (1987a, b, c). Tessier et al (1985) preserved samples collected by dialysis by sealing them in acid leached pre-acidified (2N HNO_3) polyethylene vials at room temperature. Belzile and Tessier (1990) used prewashed and preacidified (1N HNO_3, final pH<2.5) Teflon vials for the storage of samples at room temperature. Azcue and Nriagu (1994) stored their samples at 5°C in acid leached but unacidified polyethylene vials. Moore et al (1988), procured porewater from core samples by gas displacement, then simply filtered them directly into acidified containers, with bottling either under a nitrogen atmosphere, or in the weak vacuum of the filtration apparatus. Bright et al (1994) transported their samples to the laboratory prior to nitrogen displacement, filtration and subsequent freezing over dry ice.

Reimer and Thompson (1988) preserved marine and estuarine porewaters (extracted from sediment cores nitrogen displacement) by freezing using dry ice (-20°C), after filtration. No acidification was used for samples to be used for arsenic species determination (Reimer and Thompson, 1988; Reimer 1989).

7.8 Contamination and interferences

Preventing environmental water samples from becoming contaminated during the sampling and analytical process, constitutes one of the greatest difficulties encountered in arsenic speciation studies. Much past work has reported results for trace metals which are erroneously high as a result of the reported concentrations reflecting contamination from sampling and analysis rather than the ambient levels (Fergusson, 1990; Nriagu et al, 1993; US-EPA, 1995a, 1995b, 1996a, 1996d). It is imperative, therefore, that extreme care be taken to avoid all possible sources of contamination when collecting and analysing environmental water samples for any trace metal, especially so when speciation information is the desired goal. Because contamination is a factor during every step of sampling and handling water, rigorous analytical protocols are required since every extraneous object or environment which contacts the sample may positively or negatively affect it (Sturgeon and Berman, 1987; Nriagu et al, 1993). Positive contamination involves the release of trace metals into the sample from any surface or atmosphere which results in concentrations that are biased high. Negative contamination entails loss of trace metals from the sample, generally by adsorption onto surfaces, leading to concentrations that are biased low.

Samples may become contaminated by numerous routes. Potential sources of contamination during sampling and subsequent sample handling include:

i) metallic or metal-containing labware (e.g.: talc gloves that contain high zinc levels), containers, sampling equipment, reagents and reagent water;
ii) improperly cleaned and stored equipment, labware and reagents;
iii) atmospheric inputs such as dirt and dust.

Even human contact can be a source of trace metal contamination.

The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place, where avoidance means performing operations in an environment known to be free of contamination, such as a clean room or glove box/bag. This degree of caution also applies to the apparatus that will contain samples, blanks or standard solutions, which should only be opened or exposed in a clean environment, so that exposure to an uncontrolled environment is minimised. Any gloves worn should be of a clean, non-talc variety (polyethylene, for example), and should be changed if an object or substance which may contaminate the work is touched.

It is therefore clear that the philosophy behind contamination control is to ensure that any substance or object that contacts the sample is metal free and free from any metal containing materials, that an awareness of potential sources of contamination exists, and that strict attention is paid to any work being done. This philosophy, however, will continue to cause financial problems, due to the high cost involved in running a clean room and ensuring all sample handling procedures are 'sterile'. As a consequence, a compromise decision must be made taking both financial and investigative aims into consideration.

7.8.1 *Sample container materials*

The majority of field samples must be returned to the laboratory for subsequent analysis. Where this involves a water sample, then the transfer of the sample from the sampling bottle directly to the storage container (with or without filtration) should be considered. Water samples may undergo changes with regard to their physical, chemical or biological state at varying rates from their time of sampling (Johnson and Pilson, 1975; Sturgeon and Berman, 1987).

Changes in metal concentrations can occur as a result of sorption processes between the metals, container walls and suspended particles; chemical changes such a precipitation or colloid formation; and by bacterial growth or degradation.. Included among the many factors which influence the stability of a specific metal in solution are the type of storage container, element, concentration, pH, temperature, concentrations of other salts, the presence or absence of organic compounds, the particulate material content (Sturgeon and Berman, 1987; US-EPA, 1996a), and the presence or absence of oxygen. Additional problems arise when preserving a sample for speciation studies, as alteration of any one of the numerous equilibria within an environmental sample may result in erroneous results, especially if the initial concentrations are low.

The apparatus used for water sample storage, like that used in the initial procurement of the sample, must be non-metallic, free of material which may contain metals, or both. Only fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene containers should be used for samples that will be analysed for arsenic (US-EPA, 1995a, 1996a). PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious

memory effects. A comparison of the trace metal contents of common labware materials is given in Tables 7.1 and 7.2.

Table 7.1. Trace metal contents of common labware materials.

	Concentration Range (μg/g)			
Material	**0.001-0.01**	**0.01-0.1**	**0.1-10**	**10-100**
Polyethylene & polypropylene	Hg, Cu, Sb, Co	Ni, Cr, Mn, Al, Se, As	Cd, Pb, Sr, Fe	Zn (Ti, Al)*
Polyvinylchloride		Cu, Co, As, Sb	Zn, Pb, Sn, Cd, Ni, Cr, Mn	(Sn, Al)*
Teflon	Pb, Co, Cs, As	Cu, Cd, Mn, Cr, Fe, Ni, Zn, Co	Al, W	
Polycarbonate		Cd, Cu, Cr, Pb, Ni, Zn, Co, As	Fe, Al, Mn	
Glass	Tl, Y, U, Sc, Hg, Ag, Se	La, Au, Rb, As, Co, Se	Cd, Pb, Cu, Ni, Zn, Cr, Ti, Fe	Mn, Al
Silica	Hg, As, Mn, Cd, Mo, Co, Sb, Se	Ni, Cu, Cr	Pb, Zn , Fe	

*Some types only. From Nriagu et al, 1993.

High-purity plastics have distinct advantages over glass with respect to weight, cost, durability and cleanliness. However, a considerable variation in both the composition and trace metal content may be present in a particular material depending upon the manufacturing process. This is clearly seen in Table 7.2 where the differences between both forms of PVC and polyethylene are obvious. It is also widely known that Teflon TFE (tetrafluoroethylene) products often suffer from Fe, Cr and Ni contamination due to particulate inclusions within the vessel walls as a consequence of the sintering and moulding processes involved during their manufacture.

Polycarbonate has been reported as being moderately oxygen permeable (Carignan, 1984), an undesirable property. Plexiglass has been shown to collect the least amount of iron oxyhydroxides on its surface than either glass, polyvinylchloride, polystyrene or Teflon (see Table 7.3.), although the ability of the surfaces to collect iron oxyhydroxides is inversely correlated with their reported surface energies (Belzile et al, 1989). Teflon is not contaminated with trace metals, although some problems have been encountered as mentioned above, and does not adsorb dissolved trace metals. However, Teflon has been used as a sampling substrate (by surface deposition) for the collection of both iron and manganese oxyhydroxides in situ, and arsenic has been shown to be preferentially adsorbed by iron oxyhydroxides (Belzile et al, 1989; De Vitre et al, 1991), although such sampling strategies require long periods of time (days to weeks) [Belzile

et al, 1989; De Vitre et al, 1991]. A single gram of polyethylene has been shown (reported in Creed et al, 1995b) to release 0.5µg of manganese when treated with 8N nitric acid, and in a separate experiment (reported in Creed et al, 1995b) 1cm^2 of linear polyethylene was also shown to release 8ng of zinc and 0.4ng of copper when treated with 1:1 HNO_3 for one week.

Table 7.2. Trace metal contents of common trace metal sampling and storage materials.

	Metals (ng/g)										
Materials	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ag**	**Sb**	**Pb**	**Hg**
Polystyrene	<6	3.8	<1000	2.0	-	6.1	50	-	<0.2	-	<3
Polypropylene	-	20	-	40	-	-	-	-	600	-	-
Polycarbonate	-	-	-	6	-	-	-	-	-	-	-
Polyvinylchloride											
structural	2	-	2.7×10^5	45	-	630	7100	<5	2700	-	-
tygon	6000	2000	5×10^4	-	2×10^5	1×10^4	5000	600	-	2×10^5	-
Polyethylene											
high -pressure	15-300	<10	600-2100	5	-	4	90	20	<5	200	-
low pressure	180-1500	-	-	10-370	-	-	300	<10	<10	-	-
Plexiglass	<10	-	<140	<0.05	-	<10	<10	<0.03	<0.01	-	-
Nylon (structural)	-	-	-	1.4×10^6	-	-	-	-	-	-	-
Teflon	20	-	35	1	-	22	8	<0.3	0.4	-	-
Surgical (rubber) tubing	4.2×10^5	-	<100	7500	-	-	4.1×10^7	<700	360	-	-
Neoprene rubber	-	-	-	2300	-	-	1.8×10^7	<1000	290	-	-
Quartz tubing	6.5	-	395	0.44	-	2.0	1.5	0.05	0.05	-	-
Vitreous silica	30	<20	<200	0.1	-	<1000	<100	-	100	-	<100
Borosilicate glass	-	1×10^6	3×10^6	81	-	-	730	<0.001	2900	-	-
Millipore (HA) filters	1.8×10^4	-	330	13	-	-	2400	<0.5	39	-	<0.015
Nucleopore filters	2000	130	2.8×10^4	25	-	1800	2300	-	<20	-	-

From Sturgeon and Berman, 1987.

Table 7.3. Mean deposition of iron oxyhydroxides on various materials.

Materials	Glass	Plexiglass	Polystyrene	Polyvinylchloride	Teflon
Fe deposit* (µg/cm^2)	0.6±0.1	0.4±0.1	1.3±0.2	0.9±0.3	3.6±0.3

*N = 3 samples; ±1 uncertainty is one standard deviation. From Belzile et al, 1989.

Massee et al (1981) conducted a series of experiments to determine the amount of arsenic lost during sample (As spiked distilled water and artificial seawater) storage in a range of container materials. They found no significant loss of arsenic (total As) to borosilicate glass, high pressure polyethylene and PTFE (Teflon), when these were stored for up to 28 days in the dark, at room temperature and with gentle agitation. From this study of arsenic and several other metals, they concluded that the various

factors involved in sorption losses may be classified into four categories, any one of which can cause sample losses (or even gains). The first is concerned with the analyte itself, especially chemical form and concentration. The second category includes the characteristics of the solution, such as the presence of acids (pH), dissolved material (e.g. salinity and hardness), complexing agents, dissolved gasses (especially oxygen), suspended matter (further potential sorption sites) and micro-organisms (potential uptake). The third category comprises the properties of the container, such as its chemical composition, surface roughness and cleanliness, and specific surface (internal surface to volume ratio). The history of the container is also of importance (such as its age, previous samples, methods of cleaning and exposure to sunlight and heat) as this may affect both the type and number of sorption sites available, and if previous cleaning has not been rigorous, then relic of previous samples may lead to inaccurate results. The fourth category consists of external factors such as temperature, contact time, presence or absence of light and occurrence of agitation. Similar findings were reported in an earlier study perfomed by Johnson and Pilson (1975), who reported that 'aged' glassware produced less variable results than did 'new' glass.

The extent of improvement afforded by the use of plastic materials is dependent upon the meticulousness of the cleaning procedure prior to their use.

7.8.2 *Labware cleaning procedure*

As stated above it is imperative that all equipment is free of contamination prior to use. To ensure this, all equipment which will contain samples or reagents to be used in experimentation must be rigorously cleaned before use. As with sample preservation, there is a variation with attitudes towards the cleaning of labware prior to use. Nriagu et al (1993) recommend a nine-step procedure, as detailed below for the sampling of general trace metals in Great Lakes waters. All the times given are the minimum normally employed.

1) Degrease in soap bath for 24h, rinse well with reverse osmosis (RO) 'distilled' water, shake off excess water.
2) Fill bottle or soak piece in bath of reagent grade acetone for 1h, drain off acetone and allow to air dry and then rinse with RO-water, shake off excess water.

3) Fill bottle or soak piece in plastic bath of reagent grade concentrated HCl for 1h, rinse with RO-water, shake off excess water.
4) Fill bottle or soak piece in plastic bath of reagent grade concentrated HNO_3 for 1h, rinse with RO-water, shake off excess water.
5) Fill bottle or soak piece in small plastic bath of reagent grade 6M HNO_3 for 72h, drain off the acid and rinse with RO-water, shake off excess water.
6) Soak in warm (40-50°C) 2M reagent grade 2M HNO_3 bath for 72h.
7) Rinse inside with 0.5% reagent grade HNO_3 then rinse entire piece with quartz distilled water.
8) Place piece(s) in heavy polyethylene bag, rinsed inside and out with quartz distilled water for transfer to the clean room.
9a) For bottles, volumetric flasks, jars, separatory funnels, and other containers rinse inside with low metal content multiply distilled water (such as MQ-water) and then fill with 0.2% ultrapure grade HNO_3 until use.
9b) For beakers, AA vials, pipette tips, watch-glasses, volumetric cylinders and other small items either rinse with MQ-water and store in PE bags until use or place in a small tub containing 0.2% ultrapure grade HNO_3 until use.

This treatment is recommended for all new and unknown bottles and materials. Once they have gone through this treatment, they need only be subjected to steps 5-9 during subsequent cleanings. The sample bottles are taken into the field still containing the final cleaning solution.

The large HDLPE containers used to store the MQ distilled waters, are cleaned first with dilute soap solution, filled for at least a week with 6M then 2M HNO_3, after which they are rinsed thoroughly with MQ-water. The heavy polyethylene bags in which the sample bottles are transported to the field are soaked in either the 2M or 6M HNO_3 baths for 24h and are then rinsed with quartz distilled water.

The US-EPA standard for determination of arsenic in water (Method 1632, 1996a), states that cleaning should be as follows:

1) Bottles cleaned with liquid detergent and then thoroughly rinsed with reagent water.

2) Bottles are then immersed in a bath of concentrated reagent grade HNO_3 at 50-60°C for at least 2h and rinsed thoroughly.
3) Bottles are then immersed in a bath of trace metal grade 1M HCl at 50-60°C for at least 48h and rinsed thoroughly.
4) Bottles are then filled with 0.1% (v/v) ultrapure HCl and double bagged in new polyethylene zip-type bags until needed.

7.8.3 *Preparation of standards*

Standard solutions containing a known amount of arsenic are used to ensure that errors are not being introduced into the analytical procedure. These errors may be due to contamination from somewhere within the sampling, sample handling or preparative stages of analysis, or possibly to instrumental 'drift'. The US-EPA (1996a) suggest either procuring a certified standard from a supplier and verifying its arsenic content by comparing it with a second standard from a second source, or by careful preparation in the laboratory.

Instead of estimating the purity of reagents used in their experiments, Yokoyama et al (1993) determined the base line levels of their chromatograms every measurement, so maintaining a constant monitoring of procured results. As the base line remained stable constant during these measurements, they were able to deduce that no arsenic was lost during analysis.

7.8.3.1 *Arsenite [As(III)]*

The arsenite standard may be prepared from 'primary standard' grade arsenic trioxide. 989.2mg As_2O_3 is dissolved with a few pellets of NaOH in about 100ml of water, the solution is then neutralised with HCl and a glass electrode and brought to a volume of 1000ml to give a 0.01mol/l As(III) standard. Fresh dilutions may be made when required, as the stock solution is stable for several months. Care must be taken that the water used for the dilution is of high purity, and contains no free chlorine or hypochlorite (this sometimes happens with faulty de-ionising systems), or oxidation of As(III) to As(V) may occur within a very short time (Andreae, 1983).

Crecelius et al (1986) used 1.73g of reagent grade $NaAsO_2$ dissolved in 1.0 litres of deionised water containing 0.1% ascorbic acid, to produce a 1000mg/l standard. The

solution is then kept in an amber bottle and diluted with 0.1% ascorbic acid solution to prepare suitable working standards.

Yokoyama et al (1993) used a commercial standard solution of 1000ppm As for AAS, prepared by dissolving As_2O_3 in 0.1mol/l NaOH and then adjusting to pH 5 with HCl.

The US-EPA (1996a) suggest making up a 1000mg/l standard by dissolving 1.320g of As_2O_3 in 100ml of reagent water containing 4g NaOH. This is then acidified with 20ml of concentrated HCl and diluted to 1000ml. The primary dilution standard (1.0mg/l) and standard arsenic solution (10µg/l) are then made up by dilution. Al-Sibaai and Fogg (1973) and Van Elteren et al (1991), both used the same method as the US-EPA, but diluted to a standard of 20µg/l and used a 1000µg/l stock solution, respectively for their investigations into the stability of standards.

7.8.3.2 *Arsenate [As(V)]*

Arsenate standard solution is prepared from the commercially available salt. This is not usually completely pure and/or stoichiometric. 3.120g $Na_2HAsO_4.7H_2O$ is dissolved in 1000ml of water to give a 0.01mol/l As(V) standard. The As(III) content should be checked and the arsenic content verified by comparison with the As(III) standard. The stock solution is stable for several months but should be checked periodically for As(III) [Al-Sibaai and Fogg, 1973; Andreae, 1983]. Yokoyama et al (1993) also used this method. 4.17g $Na_2HAsO_4.7H_2O$ is dissolved in 500ml of water; 10ml of this is then diluted to 1 litre to give 20µg/ml of arsenic (Al-Sibaai and Fogg, 1973). Van Elteren et al (1991) simply dissolved 1.000g of As_2O_5 in 1l of 1mol HCl to give a stock solution of 1000µg/l As, whilst Crecelius et al (1986) used 4.16g of $Na_2HAsO_4.7H_2O$ to produce a 1000mg/l solution.

7.8.3.3 *Monomethylarsonic (MMAA) and dimethylarsinic (DMAA) acids*

Stock solutions of methylarsonate and dimethylarsinate are also prepared from commercially available standards. The monomethylarsonic acid standard is prepared from the disodium methylarsonic ($CH_3AsO(ONa)_2.6H_2O$) salt; for a 0.01mol/l standard, 2.920g of this salt is dissolved in a few hundred ml of water, 4ml concentrated HCl added and the solution made up to 1000ml. The 0.01mol/l dimethylarsenous acid standard is made up in the same way, using 1.380g hydroxydimethylarsine oxide.

Crecelius et al (1986) dissolved 3.90g of $CH_3AsO(ONa)_2.6H_2O$ in 1 litre of water to produce a 1000mg/l MMAA solution and 2.86g of $(CH_3)_2AsO_2Na.3H_2O$ to give a standard of the same concentration.

The methylarsenicals are not usually very pure, and the compositions of the standards and their titre need to be checked. Alternatively, the standard compounds can be purified using the method described by Dietz and Perez (1976). In slightly acid solution (~4ml concentrated HCl/1000ml), the methylarsenical standards are stable for many months (Andreae, 1983).

Commercial or laboratory synthesis of MMAA and DMAA generally rely on the Meyer reaction:

$$Na_3AsO_3 + CH_3X \rightarrow NaX + CH_3AsO(ONa)_2$$

where X + Cl^- or Br^-.

$$CH_3AsO(ONa)_2 \xrightarrow[3)\ CH_3X]{1)\ SO_2/HCl,\ 2)\ NaOH} Na_2SO_4 + NaX + (CH_3)_2AsO(ONa).$$

Acidification of these reaction mixtures with HCl or H_2SO_4 followed by appropriate isolation steps provides impure MMAA and DMAA. The acids thus obtained nay contain NaCl (or NaBr), Na_2SO_4, and arsenous acid; DMAA contains MMAA as an additional component. Arsenic acid is also present in both products because of air oxidation of As(III) or from an intentional oxidation step conducted during commercial manufacture (Dietz and Perez, 1976).

Total arsenic analyses or acid titrations may provide an estimate of purities, but these methods are only accurate if the arsenical contaminants in the respective samples have been removed. Dietz and Perez (1976) purified MMAA and DMAA using a strong-acid cation exchange resin [AG 50W-X8 (100-200mesh, hydrogen form)], using water as the eluent, and finished with 99.94-100.23% pure MMAA samples, having started with samples of 95.29-99.57% purity. DMAA samples started with purities of 99.02-99.51% but were purified to 99.98-100.96%.

7.8.3.4 *Preservation of standards*

Al-Sibaai and Fogg (1973) report that artificial samples (dilute standards) were made up by dissolving As_2O_3 in NaOH solution and neutralised, giving solutions in the range 4-20µg/ml arsenic. These solutions maintained full titre for 56 days in borosilicate

glass, soda glass and polyethylene containers, in both light and dark. Although there was no actual loss of arsenic, it was found that As(III) had fallen to 50% of its original concentration in 33 days as a result of oxidation to As(V), although Andreae (1983) states that such solutions are stable for several months. Solutions of $Na_2HAsO_4.7H_2O$ showed no loss of arsenic for 100 days under the same conditions.

Due to the oxidising effect of deionised water, dilute As(III) standards should be prepared daily (Andreae, 1983; Crecelius et al, 1986).

It has been reported that As(V) is reduced to As(III) in about a week when diluted with deionised water (van Elteren et al, 1991). After investigating this phenomenon, which is contrary to thermodynamic data which predict As(V) to be stable at the pH and Eh values normally associated with deionised water, they concluded that the reduction was probably due to the water being contaminated with small <2μm particles released from the ion exchange resins used in the deionised waters' preparation, although they could not completely rule out the possibility of the leaching of a reducing agent from sample storage container walls.

7.8.4 *Quality assurance and quality control*

Once a sample has been taken, each container should be properly labelled and packaged. This makes the tracking of samples accurate and simple, maintaining an uninterupted chain of custody from sampling site through to analysis. Samples should then be transported to the laboratory immediatley (Dick, 1994; Puls, 1994), so as to avoid any of the problems mentioned earlier in this chapter. Additionally, constistency must be imposed upon the sampling, preservation and sample handling (Puls, 1994), ensuring that although samples come from the same site, the results are comparable, due to them having been sampled and subsequently handled in exactly the same way.

The apparatus used throughout should be indelibly marked, and a record kept of which piece of apparatus was used for what purpose at what time, so that any contamination may be traced back to source and eliminated. It is useful to dedicate separate sets of labware to specific sample types (e.g. receiving waters vs. effluents) although it is important that the apparatus used in processing blanks and standards is mixed with the apparatus used for samples, so that contamination of all labware may be detected.

7.9 Summary

It is evident that the preservation of samples for the determination of arsenic species is dependent upon a number of factors ranging from the origin and composition of the sample to whether the sample was stored in the dark or in the light. These variable factors help in explaining why one particular preservation technique was successful for one set of circumstances, yet failed for another under similar environmental conditions (Korte and Fernando, 1991). For example, Oscarson (1981a), suggests that one reason for the variable As(III) oxidation rates may be the presence of manganese which is likely to be present in many samples of reducing groundwater. As with the sampling method, the sample preservation methods for the various different sample types discussed have both their advantages and disadvantages. It is obvious that for arsenic species preservation, the chosen method should be simple, avoid unnecessary sample handling, and be relatively inexpensive. It should also be reemphasised that pre-treatment (e.g. cleaning) of the sample containers is also of vital importance.

The freezing of samples may be a good method in the absence of other ionic species, however, there must be a considerable doubt over its ability to maintain readily oxidised species such as Fe(II) and Mn(II) in solution during thawing and oxidation of these is likely to affect the concentration of both As(III) and As(V) [Aggett and Kriegman (1987)] due to precipitation (Sturgeon and Berman, 1987). However Crecelius et al's (1986) work was performed on porewater extracts from colliery spoil, a material expected to have fairly high iron [albeit Fe(III)] contents.

The main advantage in low temperature storage (4°C or below) is that bacterial activity is reduced, although deep freezing is generally accepted as being more suitable. However, as well as the problems associated with precipitation, a major problem arises when samples require transportation, as suitably insulated containers can be bulky and are awkward to handle.

The preservation method utilised by Feldman (1979) [Addition of ascorbic acid], may well prove to be a more suitable method than freezing as there is no time wasted in thawing the sample before pre-treatment and analysis.

Ultraviolet radiation has been reported (Howard and Comber, 1989) as photo-oxidising arsenic compounds such as AsBe, AsC and quaternary arsonium ions

[$(CH_3)_4As^+$] to As(V) and Brockbank et al (1988) found that, under a mercury lamp, the half-life for the oxidation of arsenite [As(III)] to arsenate [As(III)] was about 5mins for seawater and 2mins for distilled water. It would therefore be prudent to ensure that samples are not exposed unnecessarily to sunlight, and should preferably be kept in the dark. However, it may also be noted that Al-Sibaai and Fogg (1973) reported that artificial samples (dilute inorganic arsenic standards) maintained full titre for 56 days in borosilicate glass, soda glass and polyethylene containers, in both light and dark. While there was no actual loss of arsenic, it was found that As(III) had fallen to 50% of its original concentration as a result of oxidation to As(V), although it was assumed that oxygen alone caused this oxidation. Solutions of $Na_2HAsO_4.7H_2O$ remained unchanged for 100 days under the same conditions. Johnson and Pilson (1975) reported that they found no obvious relationship between initial As(III) oxidation rate and the surface area to volume ratio of the storage containers used in their experiments. Additionally, although they found no observable difference in As(III) oxidation rate between experimental flasks kept under laboratory lighting and those kept in the dark, sunlight increased the As(III) oxidation rate by 5 to 10 times.

CHAPTER 8

ARSENIC SPECIES SEPARATION

8.1 Introduction

Element speciation has been defined as the identification and quantification of the individual physicochemical forms of an element in a sample (Le et al ,1994). These chemical forms include inorganic compounds of elements in various oxidation states and organometallic compounds. Speciation studies are very important because the toxicity and availability of a metal often depend upon its chemical form. Arsenic is a typical example, being ubiquitous, and exhibiting varying degrees of toxicity with different oxidation states and chemical forms. It is a combination of these factors that render traditional approaches to environmental studies, based upon the determination of total element concentration, obsolete.

Early methods of speciation merely distinguished between the two oxidation states of inorganic arsenic. Later methods determined simple methylated arsenic compounds in addition to inorganic arsenic. More recently, work has been directed towards quantifying more complex arsenic compounds that occur mainly in marine organisms (Francesconi et al, 1994).

Analytical methods for determining arsenic are employed considering the target arsenic species, available instruments, detection limits, ease of handling and degree of contamination. Briefly described below are a variety of techniques, including methods for determining total arsenic concentration in a sample, and a description of the various speciation procedures.

8.2 Total arsenic determination

In aqueous solution, total arsenic concentrations may be determined by any one of a wide range of analytical methods. These methods are also all used to identify specific arsenic species, and descriptions of each are found in Chapter 9.

If total arsenic is to be determined, then the sample must be mineralised to transform all the arsenic into inorganic forms prior to analysis. The treatment chosen should be the mildest which will result in this complete conversion, so as to minimise

both losses and potential contamination (Talmi and Feldman, 1975; Greschonig and Irgolic, 1992). This is achieved by using one of the following:

i) wet ashing;

ii) dry ashing;

iii) fusion;

iv) oxygen combustion.

8.2.1 *Wet ashing*

This method employs concentrated acids to digest the material of interest, usually at an elevated temperature. All materials may be treated in this manner, although it is obvious that stronger treatment will be needed to digest organic materials high in lipids than vegetation or animal muscle, and that minerals might need extreme treatment. Talmi and Feldman (1975) reviewed a number of works which employed wet ashing, and most of the 'gentle' techniques employed nitric or sulphuric acids at various concentrations and temperatures.

For more aggressive digestion, more concentrated nitric, sulphuric and perchloric acids (sometimes fuming) are used, often with refluxing. This method is commonly performed as part of the sample preparation for the determination of total arsenic in sediments and whole rock samples. Crecelius et al (1986) digested a dried sediment sample by first forming a slurry with water, and then adding a mixture of concentrated H_2SO_4 and HNO_3 (1:4) and heating at 80 to 90°C for 2 hours. On cooling the sample is diluted and analysed. Other researchers have used much more aggressive methods to extract arsenic from samples. Seyler and Martin (1989), for example, heated sediment samples in a Teflon bomb with a mixture of $HClO_4$ and HNO_3, and subsequently dissolved in HF, evaporated to dryness and then diluted in relatively weak (0.6M) HCl. Bowell et al (1994) extracted arsenic from 10g soil samples by digestion in 15ml of HNO_3 (70%) with 15ml of $HCLO_4$ (70%). Breslin and Duedall (1983) compared the efficiencies of a number of acids and acid mixtures in extracting arsenic from fly ashes. They found that HCl digestion was the most accurate and precise method, giving 100% recovery. Both the HF - H_3BO_3 - HNO_3 and HNO_3 acid digests yielded 90% recoveries. Since HNO_3 is an oxidising agent, the accuracy of this method may be limited due to HNO_3 competing with sodium borohydride ($NaBH_4$) if hydride generation is used in the detection process (see Section 8.4.5). The HF - H_3BO_3 acid

digestion yielded only 59% recovery, possibly due to the formation of volatile AsF_3, which is lost during the digestion process (Talmi and Norvell, 1975; Breslin and Duedall, 1983).

8.2.2 *Dry ashing*

Various methods have been described which involve the use of $MgO/Mg(NO_3)_2$ to dry ash vegetable and animal tissues. Generally, the method involves heating the sample to which MgO has been added, after which $Mg(NO_3)_2$ is added and the mixture again heated to high temperature. Good recovery has been reported for samples spiked with 1-2ppm arsenic (Talmi and Feldman, 1975).

8.2.3 *Fusions*

Minerals are usually fused with NaOH in a silver or nickel crucible. Essentially all of the arsenic is recovered in the leach liquid, even when a residue is present. James and Richards (1955) used this method to separate and isolate arsenic impurities in silicon semiconductors. The silicon was first dissolved in NaOH in the presence of H_2O_2, with arsenious [As(V)] oxide added as a carrier. The solution was then acidified with HCl and reduced in volume under oxidising conditions. The arsenic was then reduced with HBr, followed by distillation of the trichloride into water. This was then acidified and the arsenic again reduced to its elemental form through the addition of ammonium hypophosphate. Separation is then performed via centrifugation. Recovery is in the order of 80-90%.

8.2.4 *Oxygen combustion*

This method involves the combustion of a sample in a closed flask containing oxygen and an absorbing solution, although for biological and some other samples mineralisation may be achieved at low temperatures by using electrically excited oxygen (Talmi and Feldman, 1975).

8.3 Arsenic speciation

The term 'separation' is employed in two contexts within modern analytical chemistry. In inorganic analysis, it is used to denote the process of isolating an analyte (or analytes) from a matrix and is often inherently combined with preconcentration. In organic chemistry, the term is generally used to include chromatography and electrophoresis. Being an interfacial field between inorganic and organic analysis, speciation analysis employs the term in both senses. The analytes are first isolated from the matrix and then subject to refined separation procedures (Szpunar-Lobinska et al, 1995).

The prerequisite for a valid speciation is the ability to discriminate among the different chemical forms of the same element, both organic and inorganic. This should allow for the determination of each form, or species, in one analytical run. A variety of techniques have been used to obtain speciation data for the different forms of arsenic at trace levels, and these generally fall into one of two main approaches. The first is applied to determine the structure of hitherto unknown compounds' structures, whilst the second combines a separation method with a sensitive detection system.

The first method involves separating the arsenic species from a large quantity of starting material, and then purifying and isolating them before determining their structure by one of the following methods:

a) X-ray crystallography;
b) NMR spectroscopy;
c) IR spectroscopy;
d) Mass spectrometry;
e) UV visible spectroscopy; and
f) elemental analysis.

This method generally requires a large amount of initial sample (several tens of micrograms) and considerable time, but has the advantage of providing unequivocal species identification. Because of this, it is rarely used quantitatively, but in a more qualitative context (Morita and Edmonds, 1992; Francesconi et al, 1994).

The second method involves the combination of separation with detection, such as a combination of hydride generation and gas chromatography-mass spectrometry (GC-MS) or graphite furnace-mass spectrometry (GFAA) detection system. This is widely used to identify and quantify the volatile arsenic compounds (such as the

methylarsines) because of its non-destructive, high detection limit and species identifying ability, although more recently, a high performance liquid chromatography-inductively coupled-mass spectrometry (HPLC-ICP-MS) system has become the state-of-the-art procedure. These methods are selective and sensitive if appropriate combinations are made, and are suitable for both quantitative and qualitative determinations if standard arsenic compounds are available (Morita and Edmonds, 1992; Pickering, 1995; Greenway, 1995). There is, however, the possibility of mis-identification in some methods: for example if the only information on a compound is its retention time in a chromatographic system.

8.4 Separation systems

Both of these methods may be 'in-line', in which case the separation and identification/detection systems are interfaced, or the two systems may be kept separate. It is obvious that an in-line system requires much less sample handling once the sample has been introduced into the system, and is consequently less prone to potential contamination.

Separation systems are generally based on one of the following methods, some of which are based on arsenic's association with specific particle size, but the majority of which are aimed at identification of specific arsenic species. Few can do both usefully due to the large numbers of handling steps involved, each of which may alter the samples' chemical equilibrium.

1) *Fractionation of species based on selective sizing:*

a) sieving;
b centrifugation;
c) ultrafiltration;
d) dialysis;
e) gel permeation chromatography.

2) *Differentiation on the basis of charge and size effects:*

a) electrophoresis (flat bed and capillary);
b) ion exchange columns;
c) chelating resins;
d) adsorption columns;

e) liquid-liquid extraction;

f) field flow fractionation.

3) *Chromatographic methods of separation:*

a) open column chromatography;

b) high performance liquid chromatography (HPLC);

c) ion chromatography;

d) gas chromatography, including sequential volatilisation;

e) supercritical fluid chromatography;

f) planar chromatography.

4) *Selective chemical extraction.*

5) *Hydride generation techniques.*

Detection systems

The subsequent detection systems, which may or may not be in-line, include:

a) atomic spectrometry;

b) elctrothermal atomic absorption spectrometry;

c) colorimetry or molecular absorption spectophotometry;

d) electron capture and flame ionisation detection;

e) electro-analytical speciation techniques;

f) microwave-emission spectrometry;

g) X-ray fluorescence and atomic fluorescence spectrometry;

h) mass spectrometry;

i) neutron activation analysis;

j) proton-induced X-ray emission;

k) DC discharge spectral emission;

l) kinetic methods,

and are discussed in the next chapter.

8.4.1 Fractionation of species based on selective sizing

8.4.1.1 *Sieving*

The process of physically sieving a sample prior to any subsequent analysis, enables the determination of the proportion of the total amount of a chemical species associated with any particular particle size. The highest levels of trace elements are usually associated with the clay (<2μm) fraction. As particle size increases through silt to sand, grade, the dominant mineral is usually quartz, with which few trace elements are associated. Yamamoto (1975), conducted a small investigation on the clay fraction of two farm pond sediment samples which he artificially spiked with As(V), MMAA and DMAA. The method used to extract the three arsenic species from the sediments is discussed in Section 4.4.4.

8.4.1.2 *Centrifugation*

Sub-division of particulate matter such as the extraction of denser particles from colloids may be effected by the use of centrifugation. The efficiency of the process depends very much upon the size and density of the particles, and the speed and duration of the centrifugation itself. Watson and Frickers (1990) quote past work where the concentrations of several components in pore fluids have been dependent upon the time and speed of rotation, the precise location of sediment particles in the centrifuge vessel, and the centrifugal crushing of macrophyte roots in productive sediments [which may release dissolved organic carbon and precursors to such compounds as dimethylsulphide (Howes et al, 1985)].

8.4.1.3 Ultrafiltration

This method involves applying a constant pressure of inert gas to a filtration cell containing the sample, an agitation device, and a supported membrane disc. Filtrate passes through the membrane, and is collected for analysis. The membranes are usually composed of a thin film of polymeric hydrous gel supported on a porous polyethylene or cellulose ester base. The membranes have pore diameters of 1-5nm, and are normally classified in terms of the nominal molecular weight of the species they retain. This method has been used recently (Chen et al, 1994) to characterise the distribution of dissolved arsenic species in well waters.

8.4.1.4 Dialysis

Dialysis membranes are generally composed of cellulose acetate, collodin or gelatin, and also have pore diameters in the order of 1-5nm. Fractionation in this case is, however, based on differential rates of diffusion across the membrane. Anion (negatively charged particles) diffusion can be quite slow, probably due to the negative charge of cellulose membranes at pH>3, which repels the diffusing anions and so decreases the effective diameter of the pore in the membrane. Some metal complexes dissociate at the membrane surface. The rate of diffusion (for small ions) is based on the concentration gradient that exists across the membrane, and if this is not maintained at a high level, then the process will be quite slow. Dialysis has been used fairly extensively as a selective method of sampling, and many designs have been used to sample sediment porewaters (Beneš and Steinnes, 1974; Hesslein, 1976; Mayer, 1976; Bottomley and Bayley, 1984; Carignan, 1984; Carignan et al, 1985; Fetter, 1994; Ankley and Schubauer-Berigan, 1994; Bufflap and Allen, 1995a, 1995b) for a wide range of trace metals, including arsenic. A detailed discussion on the use of dialysis samplers is given in Section 6.2.4. Another variation of the dialysis technique involves the use of polyacrylamide gels as the medium to generate a diffusive gradient, and is also used in the sampling of trace metals in sediment interstitial waters or in water bodies (Davison et al, 1991; Davison et al, 1994; Krom et al, 1994). The use of such gels is described more fully in Section 6.2.5.

8.4.1.5 *Gel permeation chromatography*

This method, also known as gel filtration and size-exclusion chromatography, also separates species based on their molecular size. The sample is introduced into the top of a column filled with solvent-swelled, uncharged, cross-linked macro-molecular gel. On elution with a suitable solvent, the solutes are partitioned between the mobile and stationary phases, with separation being based on steric (reactions with the stationary phase are controlled by the size and arrangement of groups on the molecules in the solute) effects, hence, larger molecules are those least retarded. Again, the gels are normally classified in terms of the nominal molecular weight of the species they retain, or a range of species weights. Separation by size exclusion should be independent of the analyte's charge, but in practice the stationary phase surface has charge properties, so the separation is rarely unaffected. Gel permeation chromatography has

recently been used in close conjunction with high performance liquid chromatography (HPLC) [Shibata and Morita, 1989a, b; Edmonds et al, 1992; Szpunar-Lobinska et al, 1995]. Whilst not generally applied to arsenic species, AsBe has been separated using this method (Szpunar-Lobinska et al, 1995).

8.4.1.6 *Field flow fractionation.*

Field flow fractionation is an elution method which takes place in a thin rectangular open channel. A gravitational field is applied across the thin dimension of the channel, which compresses sample particles or molecules against the accumulation channel wall where they form equilibrium clouds (groups of particles suspended by Brownian motion) whose average thickness is usually related to particle size or mass. Carrier fluid is simultaneously pumped down the channel, causing each sample species to travel at a characteristic velocity which is directly related to the average cloud thickness. On emerging from the channel, the sample clouds pass through a detector which enables the sample elution volume or time to be recorded. Since the elution mechanism is purely a physical process, the measured elution volume can be directly to the sample particle size or mass by relatively simple equations (Szpunar-Lobinska et al, 1995).

Field flow fractionation is well suited to the separation of sub- and supermicrometer particles of various types into specific size fractions with a high degree of resolution. Sedimentation field flow fractionation has been used to size and separate colloids in the range 0.05-1μm. Flow field flow fractionation has been used to size and separate different humic substances and to fractionate colloids and macromolecules in the 1-100nm range. Again, this is potentially a useful method to determine arsenic distribution in relation to specific sized particles, although there are no reports of it having been used in this context.

8.4.2 *Differentiation on the basis of charge and size effects*

8.4.2.1 Electrophoresis (flat bed and capillary)

This method separates chemical species on the basis of their overall charge, sign, and to a lesser extent, size. In the horizontal bed procedure, differential migration is promoted by applying an electrical potential along the length of a sheet of porous, conducting polymer, such as a cross-linked polyacrylamide gel (supported on an inert base). The ends of the sheet are held in reservoirs of the buffer solution which controls the pH and conductance of the system. When an aliquot of the sample is placed in the centre of the conducting sheet and a current applied, cations and anions move in opposite directions at a rate determined by each analyte's characteristic electrophoretic activity. Neutral molecules remain in the centre. Neutral elements may be analysed since they can be trapped in the micelles of an ionic surfactant, and can thus migrate in an aqueous solution by electrophoresis, a technique called micellar electrokinetic chromatography (Szpunar-Lobinska et al, 1995).

Gels made of polyacrylamide can be formed with well defined molecular sieving properties. The polyacrylamide gel electrophoresic technique has been applied to the separation of proteins, after they have undergone denaturing. This imparts all proteins, regardless of their identity, with the same free solution mobility, so their separation is based solely on size, with smaller proteins migrating through the gel faster than the larger ones.

High performance capillary electrophoresis (HPCE or CE) uses a length of fused silica capillary tubing (25-200μm i.d.) in place of the porous conducting polymer sheet. This tube has a port for the introduction of a small (<1μl) sample, and (together with the end reservoirs) is filled with a suitable electrolyte. On application of a high potential across the tube, sample component molecules move at different rates along the capillary tube. The inherently high surface area to volume ratio in the capillary results in highly efficient separation of both small species (such as ions) and large molecules (such as proteins). This method has been successfully applied to separate As(III), As(V), MMAA, DMAA, AsC, AsBe and phenylarsenic acid in standard solutions using an Na_2HPO_4-NaH_2PO_4 buffer.

8.4.2.2 *Ion exchange columns*

Since the electrical charge on metal species can vary from positive (cations), through neutral to negative (anions), passage of water samples sequentially over anion and cation exchange resins should serve to separate the differently charged forms. In practice, dissociation of unstable complexes, retention (by way of the filtering effect) of particulate metal forms and adsorption of some neutral species to the polymer base, may cause distortion of species distribution patterns. Despite these limitations, however, the results may still be informative, and this has been widely used to separate the four common arsenic species As(III), As(V), MMAA and DMAA, provided that care is taken to regulate the pH of the system being used. This method is really a form of chromatography, since the exchanged species may be sequentially eluted by controlling the solutions being added to the column. Both pellicular and porous microparticles have been adopted for use with this method by coating the rigid silica particles with a thin layer of relatively non-porous ion-exchange resin. The simplest methods are based on affinity differences of the native analytes for the column, with separation being controlled by pH and ionic strength of the eluent, which competes with sample species for exchange sites and elutes the sample from the column (push mechanism). The efficiency is increased by adding a complexing agent to the eluent, which changes the form of the sample species allowing it to move down the column more easily (weaker retention - pull mechanism). The complexing agent controls the amount of ion species available to compete with the eluent for the exchange resin sites.

Eluents in ion exchange are aqueous solutions, containing an ionic solute in the mobile phase. A proton source (supplied by acids) is a favoured eluting agent for the separation of cations because its binding capability can easily be controlled by the use of pH buffers. The ion exchange resin will bind all chemical ion species of opposite charge type. The range of application can be increased by converting metal cations to anions by complexation with a negatively charged ligand, so making a simultaneous separation of anions and cations possible (Szpunar-Lobinska et al, 1995).

Cation exchange resins

Korte and Fernando (1990), compared the two cation exchange methods proposed by Yamamoto (1975) and Iverson et al (1979) which separate As(V), MMAA and DMAA (in that order of elution), the method also employed by Holm et al (1979). However, whilst successfully using the strong-acid cation exchange resin Dowex® AG 50W-X8 to separate and purify MMAA and DMAA, both Dietz and Perez (1976) and Pacey and Ford (1981) point out that whilst As(III), As(V), MMAA and DMAA all have different retention volumes when passed through a sulphonic acid resin chromatographic column, no true ion exchange mechanism can prevail. In fact, all four of these protonic acids should elute from the column after one void displacement. However, many non-ion exchange processes may occur when a solute passes through a resin bed. Dietz and Perez (1976) suggest that the separation of these arsenic species is possible due to protonation reactions resulting in the formation of positively charged species and it is the functioning of these arsenicals as bases toward the very acidic resin particle which results in their observed resin sorption, a view shared by Pacey and Ford (1981). For DMAA, an equilibrium constant of 37 has been established for the protonation reaction:

$$(CH_3)_2AsO_2H + H^+ \rightarrow ((CH_3)_2AsO_2H_2)^+$$

Although MMAA is also amphoteric, its basicity is no doubt less than that of DMAA, as it is not retained so strongly (Dietz and Perez, 1976). Although non-polar sorption of solutes is also common, it is not thought to be significant in the case of arsenic species. If a non-polar sorption of MMAA and DMAA predominated, then the sodium salts of the arsenicals would be retained to the same extent on the Na-form of the resin; this has been found not to be the case (Dietz and Perez, 1976).

This system of cation exchange chromatography (where solutes with higher charge are eluted faster than those with lower charge due to electrostatic repulsion between resin matrix and solutes) later became known as ion-exclusion chromatography (Yokoyama et al, 1993).

Dietz and Perez (1976) simply used water as the eluent for the ion exchange column. They collected the following eluent fractions for analysis: 80-120ml for As(V), 200-450ml for MMAA and 750-1000ml for DMAA. Yamamoto (1975) however, used a

number of different eluents. These were, after the addition of the sample to the column [Dowex® AG 50W-X8 (but 20-50 mesh)], in order of addition: trichloroacetic acid (40ml of 0.2M at pH 1.7), sodium acetate (30ml of 1.8N at pH 6.5) and another batch of sodium acetate (50ml of 1.0N at pH 11.8) all at a rate of about 1ml/min. These additions result in much more rapid elution (0-25ml for As(V), 25-70ml for MMAA and 70-120ml for DMAA) of the arsenic species, which like Dietz and Perez's (1976) work come out in the order As(V), MMAA and finally DMAA.

Iverson et al (1979) used a modification of the method used by Yamamoto (1975), eluting the Dowex® AG 50W-X8 (100-200 mesh) resin with 30ml of 0.2M trichloroacetic acid followed by 70ml of 1M NH_4OAc, and the eluents collected in 5ml vials for subsequent analysis. The arsenic species were eluted in the order As(V), MMAA and then DMAA. The column was conditioned with ammonium hydroxide and HCl prior to use, so that the resin was in the ammonium form at a pH of less than 1.5. The samples were acidified to pH<2 before loading onto the column, which led to better separation of inorganic arsenic and MMAA than at pH 4 as used by Yamamoto (1975), so allowing the use of shorter columns. Additionally, because the eluents were of a relatively low ionic strength, major cations such as Na^+, K^+, Mg^{2+} or Ca^{2+} could also be retained on the resin, thus eliminating some of the major interferents in flameless atomic absorption spectrometry, which was used for analysis. Analysis was also performed using hydride generation with gas chromatography/mass spectrometry.

Yokoyama et al (1993) used the cation exchange resin SP-Sephadex® C-25 to successfully separate As(III) and As(V) in geothermal waters. The sample solution was introduced into the column in a carrier stream of 0.1M NH_3-NH_4Cl, having been previously adjusted to pH 9 by addition of ammonia water. The flow rate was maintained at 5ml/min and As(V) was eluted before As(III). The detection system in this case was an in-line continuous hydride generation from which the arsines were swept by an argon carrier gas into a quartz cell atomiser fitted in an atomic absorption spectrometer.

Larsen et al (1993) used the cation exchange column Ionosphere-C with a mobile phase of pyridinium ion buffered at pH 2.65 with HCOOH to separate the cations AsBe, AsC, TMAO and TMAs (tetramethylarsonium).

Anion exchange resins

Ricci et al (1981) used a Dionex anion exchange column to separate, in order of elution: unresolved DMAA and As(III), MMAA, *p*-aminophenyl arsonate and As(V). The mobile phase used for this was a mixture of 0.0024M $NaHCO_3$, 0.0019M Na_2CO_3, and 0.001M $Na_2B_4O_7$. The resolution of DMAA was obtained by selection of a lower ionic strength eluent, 0.005M $Na_2B_4O_7$. The pH is not reported for either elution solution. All five species were separated in one analysis using a gradient elution, but it is very time consuming and complete separation is easier and quicker with two separate runs, one for DMAA and As(III) and one for the rest. Due to the low specific conductivities of the arsenic species in solution, the presence of anions such as Cl^-, PO_4^{3-}, Br^-, NO_3^-, and SO_4^{2-} results in unresolved elution of all the arsenic species, making conductivity detection useless. Detection of the arsenic species was performed using hydride generation followed by quartz furnace ETAAS (Ricci et al, 1981).

Aggett and Kadwani (1983) used anion chromatography alone to separate, in order of elution, As(III), DMAA, MMAA and As(V), in sediment interstitial waters and aquatic plant extracts, reporting that cation exchange alone was not successful in separating inorganic As(III) and As(V). Larsen et al (1993) successfully used this method to separate the anions As(III), As(V), MMAA and DMAA utilising the ION 120 anion-exchange resin, with a mobile phase of NH_4HCO_3 buffered at pH10.3 with NH_4OH. Jiang et al (1994), also used this method to preconcentrate and separate As(III), As(V), Selenium Se(IV) and Se(VI) in spring waters, using the strong Dowex® AG 1-X8 (100-200 mesh) resin. Separation of As(III) and As(V) was possible as long as the pH of the column was carefully controlled, with As(V) being recovered quantitatively in the pH range 9-13, whist As(III) was recovered quantitatively in the pH range 8-13. Recovery was followed by detection using an ICP-MS.

Slightly more recently, Kawabata et al (1994) and Inoue et al (1994), have gone further with the separation of As(III), MMAA, DMAA, TMAO and arsenobetaine (AsBe) in rat urine. Both groups used two columns in series, packed with Excelpak® ICS-A35 resin with tartaric acid as the mobile phase. The pH was varied between 3 and 6 by addition of NH_4OH. Increasing the pH delayed the elution of MMAA, DMAA and TMAO, whilst not affecting that of the inorganic arsenic species or AsBe. This suggests that As(III) and AsBe do not fully exchange with the stationary phase, as As(III)'s pK_a (see Appendix A) has not quite been reached, and AsBe is a cationic compound within

this pH range. It is thought that the As(III) is retained by hydrophilic interaction with the hydrophilic groups on the packed resin materials. Higher tartaric acid concentrations greatly reduced the retention of MMAA and slightly reduced the retention of AsBe, whilst DMAA was unaffected and that for As(III) increased. Recovery was followed by detection using an ICP-MS.

Combination exchange resins

Another method (Grabinski, 1981), uses a single ion-exchange column containing both anion and cation exchange resins, allowing the separation of As(III), DMAA, MMAA and As(V) in that order of elution. The two resins used in this procedure were the cation exchange resin Dowex® AG 50W-X8 and the anion exchange resin Dowex® A1-X8 (both 100-200 mesh).

Both Henry and Thorpe (1980) and Pacey and Ford (1981) used the cation exchange resin Dowex® AG 50W-X8 and the anion exchange resin Dowex® A1-X8 (both 50-100 mesh) for the determination of total arsenic, DMAA, MMAA, As(III) and As(V), but in both cases the anion and cation columns in parallel.

Henry and Thorpe (1980) utilised four equal volumes of sample, one for each species with As(V) being determined by difference, whilst Pacey and Ford (1981) used three sample aliquotes to determine DMAA, MMAA and total arsenic, with As(III) being determined by difference. DMAA was isolated using the cation exchange resin, with As(V) and MMAA being separated using the anion exchange resin. Henry and Thorpe (1980) determined As(III) directly using differential pulse polarography. In contrast to the cation exchange methods used by Yamamoto (1975) and Iverson et al (1979), acetic acid (1.0ml of 1.75M was mixed with 100ml of sample, initially) was used as the eluent (70ml of 0.02M) to ensure complete separation. The DMAA was then stripped by passing 1.0M ammonia solution through the column at a flow rate of 1.0ml/min. The flow-rate is critical for successful stripping. To isolate MMAA, 100ml of sample was mixed with a pH 4.7 ammonium acetate/acetic acid buffer (total acetate concentration of 0.01M) and passed through the anion exchange column followed by 50ml of the same 0.01M buffer at the same pH. As(III) and DMAA are not retained and MMAA and As(V) are stripped using a 0.5M or 1.0M buffer at a pH of 4.7, MMAA being stripped first. The separated species concentrations were then determined using a graphite furnace atomic absorption spectrophotometer.

8.4.2.3 Chelating resins

The addition of chelating functional groups into polymer beads gives a product with a high affinity for metal ions, but which excludes large molecules and colloidal particles. It thus also has the effect of filtering out the smaller metal ions. Columns of chelating resin (e.g. Chelex 100®) have been used to preconcentrate metal ions in water samples. The precision of the operation can vary with the choice of counter ion in the column packing. Some of the best results have been obtained when the resin is first converted to either the Na^+ or NH_4^+ forms. In this state, the resin is capable of retaining most of the hydrated metal ions and/or labile metal complexes present in the sample. Colloidally associated metals are not retained, and in seawater, any metals not retained are probably present as species adsorbed on or contained within colloidal particles. Compared with techniques such as ultrafiltration, dialysis or solvent extraction, chelating column separations may be quicker, simpler and cheaper. Indeed, a variation of this technique using chelating resin embedded within a polyacrylamide gel has been successfully used to sample trace metals in sediment porewaters in situ (Davison et al, 1991; Davison and Zhang, 1994; Davison et al, 1994; Krom et al, 1994; Zhang and Davison, 1995; Zhang et al, 1995a, 1995b). This is described fully in Section 6.2.5.

8.4.2.4 *Adsorption columns*

Columns packed with uncharged adsorbents (such as hydrophobic copolymers) have been used to separate trace levels of organic molecules in waters. Isolation and preconcentration of organic complexes of metals has been achieved through adsorption on a non-polar substrate. The retained species may be retrieved by eluting the column with organic solvents, although (in seawater) the recovery of metal organics is not always quantitative.

Chelating groups may be grafted into cellulose, and cellulose based polymers acting as ion-collecting filters for preconcentration from aqueous solutions, offer a simple separation step and have been recommended for their mechanical and chemical suitability for batch or column procedures, especially for combination with neutron activation analysis and similar techniques (Sarzanini and Mentasti, 1991). Arsenic (together with Se, Sb and Te) have been extracted from water using 'thiol cotton', cotton impregnated with thioglycolic acid, and helped give detection limits in the ng-pg/l range. The recovery from the aqueous phase is generally in the range 90-100%, making

this an efficient method, although there seems to be no data as to whether this method may be extended to speciation studies.

Silica or controlled pore beads have also been used to preconcentrate ions, essentially through one of three routes. Siliceous materials are impregnated with ligand solutions and the solvent is removed, chelating functional groups able to retain metal groups are chemically attached to the surface of silica, or C18 chemically bonded silica gels are used. The last two materials act essentially as chromatographic supports able to retain specific ions or their complexes. The procedures based on these materials are suitable for instrumental techniques requiring either solid samples i.e. X-ray fluorescence, or elution of the adsorbate by solvent or acid solution, i.e. GFAAS, ICP-MS techniques (Sarzanini and Mentasti, 1991). This method has been used to trap arsenic in seawater using mercapto-modified silica, with a 91-98% recovery, and allowing detection in the µg/l range. Arsenic(III) and As(V) have both been concentrated from seawater and other unspecified samples using thiol-silica, again allowing detection in the µg/l range (Sarzanini and Mentasti, 1991).

8.4.2.5 *Liquid-liquid extraction*

If an aqueous solution is shaken with a volume of immiscible organic solvent, uncharged species tend to be extracted into the organic layer. This method has some application to speciation studies, but extraction efficiencies are not always high. This may be low due to the following reasons:

i) charged complexes not being transferred between phases; and
ii) the metal adsorbed on organic colloids being only partially extracted (particles tend to collect at phase boundaries).

Extraction of polar metal ions may be achieved by transforming them into an uncharged complexes (for example by adding a chelating agent such as dithizone or diethyldithiocarbamate). By applying a chelate extraction process before and after the destruction of the organic content of a water (using an appropriate oxidation method), an estimate of the amount of metal initially associated with the organic material can be made. If the stability of the metal chelate species is not great enough to ensure total dissociation of the original organometallic complexes, then this procedure can underestimate the amount of organically bound metal fraction present.

It is generally known that As(III) forms arsenic trichloride when treated with a strong HCl solution; As(V) does not. The $AsCl_3$ may then be either separated from the resulting mixture by distillation, or by extracting the $AsCl_3$ into toluene or benzene, the arsenic later being recovered using an acidified KI solution.

Seawater arsenic speciation may be performed by way of extraction of diethyldithiocarbamate complexes into chloroform. The first report of this method is over 40 years old (Talmi and Feldman, 1975), and only As(III) was precipitated with ammonium pyrolidinedithiocarbamate (APDC), as well as other dithiocarbamates in the pH range 2-6. As(III) may be selectively extracted over As(V) with APDC into organic solvents at a controlled pH, but in strongly acidic mediums, both As(III) and As(V) are extracted from sulphuric acid into the organic layer (Chen et al, 1994; Francesconi et al, 1994). Mok et al (1986), however, selectively extracted As(III) at pH1, with As(V) being extracted after reduction to As(III) using sodium thiosulphate. Sodium diethyldithiocarbamate is not recommended as an extractant for arsenic species as it is unstable in acid solution and consequently may give only partial extraction (Mok et al, 1986), although it has been successfully applied to the determination of other trace metals in the low µg/l range using a pH of 4.5 (Chakraborti et al, 1987), and Chatterjee et al (1993) used it as the chelating agent for As(III) and then used chloroform with hexamethelene-tetramine (*sic*) as the absorbing solution for the arsenic.

Puttemans and Massart (1982) used the fact that only As(III) is extracted from acidic media to successfully separate As(III) and As(V). They used both APDC and *O*, *O*-diethyldithiophosphate (HDEDTP) as chelating agents for the quantitative extraction of As(III) into chloroform, followed by back extraction into an aqueous phase containing some (between 200 and 1000ppm) Cu(II) chloride. Reduction of As(V) to As(III) using a mixture of hydrogen sulphite and thiosulphate allows the determination of total inorganic arsenic, and hence by difference, the concentration of As(V). The back extraction uses the Cu(II) chloride because the APDC has a greater affinity for Cu(II) ions than for As(III) ions, resulting in the quantitative release of the As(III). The resulting back extracted solution may then be analysed using a suitable method, such as GF-AAS.

As(III) has been reported (Chakraborti et al, 1986) as being quantitatively and selectively extracted into carbon tetrachloride in the presence of As(V), MMAA and DMAA by a 0.5%(w/v) aqueous solution of ammonium sec-butyldithiophosphate with a

2.5%(w/v) aqueous solution of sodium diethyldithiocarbamate. The As(III) containing extract thus isolated may then be evaporated to dryness, mineralised with concentrated HNO_3, reduced to arsine and determined using a suitable detection system. These researchers found that the extraction procedure gave good preconcentration, allowing absolute detection limits in the region of 0.1-0.3ng of arsenic when used in conjunction with hydride generation, with an actual detection limit of around 0.6ng/l using a dc discharge emission technique.

Sarzanini and Mentasti (1991), in their review, mention an extraction process using APDC and DBADBDDC (dibenzylammonium-dibenzyldithiocarbamate) as the dithiocarbamates to extract arsenic (unspecified oxidation state) and 13 trace elements from lake waters into 2-ethylexylacetate (*sic*), with detection limits in the µg/l range.

Hasegawa et al (1994) used diethylammonium diethyldithiocarbamate (DDDC) to successfully separate inorganic As(III), MMAA(III) and DMAA(III) from their pentavalent counterparts, both in laboratory and environmental samples. Once these had been back extracted, they were determined using HG-ETAAS. The pentavalent species were determined by measuring the amount of As(III) + As(V) species present, the As(V) species present then being determined by difference (Hasegawa et al, 1994).

It may be difficult to distinguish the two forms of inorganic arsenic in a natural sample using liquid-liquid extraction due to the presence in the sample of reducing species capable of reducing As(V) to As(III) [Francesconi et al, 1994]. Errors may be reduced if all the arsenic is first reduced to As(III), although, of course, this is undesirable if speciation data is required.

Liquid extraction has also been used as part of the hydride generation analytical procedure in arsenic determination, with arsines being absorbed into toluene or *n*-heptane. This is detailed in Section 8.4.6.

8.4.3 Chromatographic methods of separation

8.4.3.1 *Open column chromatography*

In this method, the sample is added to the top of a column packed with an adsorbent material (e.g. alumina, silica gel, polymer gel or a fine grained substrate coated in an organic compound). Separation of the sample components is effected by gravity feeding of an aqueous or organic eluent. Identification of the separated components is achieved by analysis of the emerging fractions. This technique has been used in the separation of both volatile and non-volatile inorganic species, but the process is time consuming, and is not suitable for species which are easily oxidised.

8.4.3.2 *High performance liquid chromatography (HPLC)*

Many trace element compounds, including arsenic containing lipids, are not volatile and cannot be converted to volatile derivatives without loss of information on their original chemical nature. In this technique, small (e.g. 50µl) samples are introduced into the top of a column packed with a fine adsorbent, and a liquid eluent is pumped through at a rate of Xml/min. With suitable packing the components of the test sample can be separated in a few minutes. To achieve separation of different types of sample, both the stationary and mobile phases may be varied.

In normal phase operation, the stationary phase is usually silica or alumina with a highly polar stationary phase liquid retained on the solid support by physical adsorption. The eluent is a relatively non-polar solvent such as phosphate, borate, Tris-HCl tributylammonium phosphate and aqueous NaCl solutions. The least polar solute is the first to be eluted, whereas retention times decrease with increasing polarity of the mobile phase. Speciation separation applications are mainly limited to stable natural chelates, and care must be taken to maintain constant pH and temperature as variations may cause variations in retention times (Edmonds et al, 1992).

In reversed phase operation HPLC, the stationary phase is composed of a non-polar material, and the eluent is a polar solvent. Polar substances prefer the mobile phase and are eluted first, followed by the non-polar substances. In addition to separation of metal chelates and organometallic species, reversed-phase operation may also be used to separate inorganic cations and anions, but in this application, the mobile phase contains a

charge neutralising species. In modern methods, the molecules comprising the stationary phase are covalently bonded to a silica or silica-bases support particle.

Ion pair or ion-interaction chromatography is based on the distribution of an ion-pair (analyte-counter ion) between a non-polar stationary phase and polar mobile phase. In this, it is vary similar to reversed phase HPLC, but includes in the mobile phase an ion-pairing reagent, and acid-base buffer, a complexing agent and sometimes an organic solvent. Two modes of operation are possible. The first involves column conditioning with the ion-pairing agent which is adsorbed onto the mobile/stationary phase interface and thus omitted from the mobile phase. The second, and more popular mode, involves addition of the ion-pairing agent to the mobile phase and thus dynamically coating the stationary phase. Both cationic and anionic species may be separated by these methods, with large anions or cations used as counter-ions, although in some cases, a chelating agent is used to form a negatively charged complex of the analyte species which forms an ion-pair with a suitable cation. In arsenic speciation, the common ion-pairing agents include sodium dodecylsulphonate, heptyltriethylammonium phosphate, tetramethylammonium hydroxide, tetrabutylammonium phosphate and tetrabutylammonium hydroxide (Szpunar-Lobinska et al, 1995).

HPLC applications in speciation studies have included the separation of inorganic arsenic and organoarsenic compounds. In addition, there are also procedures for the separation of mixtures of oxyanions of nitrogen, sulphur or phosphorus.

The use of HPLC for the separation of arsenic compounds was first reported by Brinkman et al (1977). Reece et al (1984) describe a separation of As(III), As(V), MMAA, DMAA and TMAO found in soil extracts. Altering the HPLC chromatographic conditions by utilising gel permeation and ion pairing has allowed the technique to be extended to the determination of As(III), As(V), DMAA, MMAA and a further eleven organoarsenic compounds (Shibata and Morita, 1989a), in artificial samples, although this was later extended to a dogfish muscle reference material (Shibata and Morita, 1989b). Edmonds et al (1992) detected seventeen arsenic compounds in artificial samples and lobster digestive gland extracts. HPLC techniques incorporating a hydride generating step have also been reported (Haswell et al, 1985; Hunt and Howard, 1994; Bowell, 1994; Bowell et al, 1994; Hwang and Jiang, 1994) sometimes with gas chromatography following the hydride generation.

A wide range of detection techniques have been interfaced with HPLC units, but most only provide elution rate information. As with other forms of chromatography, for component identification, the retention parameters have to be compared with the behaviour of known chemical species, and it is therefore very important to ensure that appropriate standards are available against which experimental results may be compared. For organometallic species, element specific detectors have proved quite useful as they tend to eliminate sample matrix effects, and the combination of HPLC and AAS has been attempted for HPLC-flame AAS (HPLC-FAAS) and HPLC-electrothermal AAS (HPLC-ETAAS) detection of arsenic (Morita and Edmonds, 1992). However, the ETAAS can not be used on-line due to its discrete mode of operation (unlike FAAS which simply requires a length of Teflon tubing [Larsen et al, 1993]). HPLC can be directly interfaced to ICP-AES, allowing continuous monitoring of arsenic, and has been used to separate selected arsenic compounds, using ion-exchange and gel permeation techniques (Morita et al, 1981; Morita and Edmonds, 1992). The state-of-the-art HPLC detection system is an ICP-MS detector, due to it being an on-line, real-time chromatographic detector that is highly sensitive to both anionic and cationic arsenic species (Shibata and Morita, 1989a, 1989b: Edmonds et al, 1992; Jiang et al, 1994;).

The problems encountered when interfacing HPLC with ETAAS arise due to the stepwise operational characteristics of the commercially available atomisers and because only a small volume of sample can be injected into them. Methods for reducing these problems are briefly detailed in Section 8.3.

Morita et al (1981) used both cation and anion HPLC to separate As(III), As(V), MMAA, DMAA and AsBe with ICP-AES as the detector. With the anion exchange chromatography, the strongly basic resin Nagel®-N-$(CH_3)_3$ was used with a 0.05M phosphate buffer. The cation exchange was performed with Nagel®-SO_3H-10. Since arsenate is a stronger acid than arsenite, As(V) is more negatively charged than As(III). Arsenobetaine may be neutral or weakly positive. These ionic characteristics may explain the elution sequence: AsBe→As(III)→As(V) in anion exchange chromatography, and As(III), As(V)→AsBe in cation exchange chromatography. At the same time however, hydrophobic interactions may also need to be taken into consideration. DMAA eluted later than MMAA on both columns, indicating the affinity of methyl groups on arsenic for the alkyl groups of the column packing.

Larsen et al (1993) also used both anion (to separate As(III), As(V), DMAA, and MMAA) and cation exchange (to separate AsBe, TMAO, AsC and TMA) successfully. For the anion exchange column, an ION 120 column was used with a mobile phase consisting of 0.10M of NH_4HCO_3 at pH 10.3 with NH_4OH, whilst the cation exchange system comprised an Ionosphere-C column with a mobile phase of 0.1M of pyridinium ion at pH 2.65 with HCOOH. The high pH of the anion mobile phase results in the ionisation of arsenous acid (see Appendix A), which is not retained on most chromatographic systems. TMAO, is thought to exhibit its cationic character as a result of the protonation of the As=O bond at the low pH (pH 2.65), resulting in the formation of the cationic compound $(CH_3)_3As^+OH$ [or its corresponding salt $(CH_3)_3As^+O^-$ (*sic*)], which is analogous to the protonation of DMAA at low pH (Larsen et al, 1993).

Shibata and Morita (1989a, 1989b) and Edmonds et al (1992) separated the anionic arsenic species using tetraethylammoniun hydroxide as the pairing ion buffer at neutral pH, cationic species by using 1-butane sulphonate and tetramethylammoniun hydroxide as the pairing ion buffer at pH3, and gel permeation (see Section 8.4.1.5) for large molecular sized arsenic compounds.

Hwang and Jiang (1994) used reversed phase HPLC to separate As(III), As(V), MMAA and DMAA, before generating their corresponding arsines and subsequent detection using ICP-MS. The separation was achieved using a tetrabutylammonium salt as the ion-pairing reagent. Le et al (1994) used tetramethylammonium hydroxide and malonic acid at pH6.8 as the ion pairing agents to separate arsenosugar derivatives on a C18 ODS-2 column; and another C18 column (10μBondclone C18) with sodium heptanesulphonate and tetramethylammonium hydroxide at pH3.5 as the ion pairing agents to separate arsenobetaine. Detection was performed using on-line ICP-MS.

8.4.3.3 *Ion chromatography*

Ion chromatography uses two ion exchange columns in series followed by a conductivity monitor. The first column separates the solutes and the second suppresses the eluent electrolyte by converting ions to water or carbon dioxide so that the conductivity measured is that of the solute only. For anions, the separation column is packed with pellicular strong base anion-exchange resin in hydrogen carbonate form. The second column is a porous polymeric ion exchange column in acid form, which

converts sodium hydrogen carbonate and sodium carbonate to water and carbon dioxide. Columns have a limited capacity, but run very fast due to the pellicular beads. As the membrane becomes depleted of protons (by exchange with the sodium ions in the mobile phase) they are replaced by more protons from an external regeneration solution which accumulates sodium ions. Ion chromatography, is used mainly for the separation of inorganic ions such as halides, sulphate, nitrate, but separation of other anions and transition metal cations has also been achieved. An alternative detection system of comparable sensitivity negates the use the second column, by using ultraviolet detection of a strongly absorbing phthalate ion which gives a constant high baseline against which the eluting samples appear as negative peaks. A variation of this technique has been used by Yokoyama et al (1993), who used a single cation exchange resin packed column to separate As(III) and As(V), prior to introduction into a hydride generation detection system.

8.4.3.4 *Gas chromatography (GC)*

In this method, a stream of gas (such as He, Ar or N_2) is used to aid in the separation of small (μl) volumes of volatile liquids or vapours introduced into one end of a column packed with fine particles of an inert solid that has been coated with an organic 'liquid' film such as a silicone oil. Separation of the introduced compounds is achieved by using stationary phases (packing) of different polarities for different compounds. The operating conditions are determined by the sample type and the variables which can be adjusted including the column packing (both the solid and 'liquid' phase), temperature and gas flow rate. Contrary to liquids, the sample is transported to the detector almost quantitatively (no nebulisation necessary), and the carrier gas itself brings only a low background contribution to the detector.

Both packed and capillary (or open-tube) columns have been used for speciation studies. Capillary columns are open tubes of small diameter with a polymethoxysilane coating on the inner surface and have the advantage of superior separation and the utilisation of low mobile phase flow rates which are advantageous for direct interfacing with a detector. The main disadvantage is that they can only cope with a small amount of sample (in the order of 1μl), so limiting the sensitivity. Packed columns GC may be regarded as an advanced form of thermal desorption chromatography, can use a much

larger sample, and can be more easily cleaned if a 'dirty' sample is introduced. Packed columns tend to be the GC columns used for the separation of arsenic compounds.

The separated sample components are detected as they emerge from the column at different time intervals. Gas chromatography has been used extensively for the separation and determination of volatile organic molecules, but in the detection of trace inorganic species fewer compounds possess the required volatility. However, arsenic is one of the elements capable of forming stable volatile species of low molecular weight (including the methyl derivatives, hydrides, chlorides and fluorides). A detailed description of the generation of arsenic's volatile hydride compounds is described in Section 8.4.6. Talmi and Feldman (1975) state that GC has potential advantages over selective thermal volatilisation of arseno-hydrides, including:

a) GC separation is less ambiguous, better controlled and more reproducible;
b) sharp well resolved peaks are obtained and thus peak heights, rather than integrated peak areas are used for measurements.

The most common detectors used in conjunction with GC have been atomic absorption spectrometry, microwave-induced plasma spectrometry and mass spectrometry, although others have been used (such as direct current plasmas, alternating plasmas, capacity coupled plasmas, flame ionisation, thermal conductivity and electron capture). The reasoning behind the choice of detector is mainly on elemental selectivity, which allows less sample preparation and less demanding separation (Greenway, 1995).

Talmi and Bostick (1975) used a 6 foot long, 3.5mm i.d. Pyrex column packed with 5% Carbowax 20M on 80/100 mesh Chromosorb 101 packing. The column was held at 175°C and the argon carrier gas flowed at a rate of 100ml/min. It was found that the column operated best at a pressure slightly below that of atmospheric, and was used to successfully separate seven arsenic species using microwave emission plasma spectrometry as the detection method.

Odanaka et al (1983) used a similar 2m long, 3.0mm i.d. Pyrex column packed with 5% PEG-20M on 80/100 mesh Chromosorb 101 packing. The column was held at 160°C and the helium carrier gas flowed at a rate of 30ml/min. This system was used to successfully separate four arsenic species using multiple ion detection mass spectrometry as the detection method.

Andreae (1977) used a 4.8mm o.d., 6m long stainless steel column, packed with 16.5% silicone oil DC-550 on 80/100 mesh Chromosorb W AW DMCS packing with a helium carrier gas flow rate of 80ml/min to successfully separate arsine, MMA, DMA and TMA.

Talmi and Norvell (1975) [and Talmi and Feldman, 1975] formed triphenylarsine from the arsenic in environmental samples [once all had been reduced to As(III)] and then used GC successfully to separate the triphenylarsine from the solution for detection. They used a 3 foot long, 3.5mm i.d. Pyrex column packed with 4% FFAP on 80/100 mesh Gas Chrom Q packing. The column was held at 220-240°C and the argon carrier gas flowed at a rate of 100-129ml/min. The detection method again was microwave emission plasma spectrometry.

8.4.3.5 *Supercritical fluid chromatography (SFC)*

SFC may be regarded as a hybrid of the gas and liquid chromatographic techniques. The mobile phase is a supercritical fluid (i.e. a fluid at pressures and temperatures above its critical point, whose physical properties are intermediate between those of gases and liquids) and so far, only carbon dioxide has been extensively used, since the pressures required can be handled by HPLC pumps. The separation is carried out on a packed (usually 1mm microbore) or a capillary (i.d. 50-100μm) column. Prior to detection the carrier is decompressed to a gas which is conveyed to the detector. Packed columns may accept larger injection volumes, but the larger surface area packings often exhibit some adsorption and/or catalytic decomposition of some compounds, leading to lower sensitivities and unreliable reproducibility. The stationary phases are similar to those used in GC, but a higher degree of deactivation is necessary. The major advantage of this method is its ability to use much lower temperatures than those utilised in gas chromatography, coupled with the pressures of HPLC. Consequently, thermally labile, non-volatile and high molecular weight compounds which are not easily gas chromatographed can be separated with shorter analysis time and lower solvent consumption than required for liquid chromatography (Szpunar-Lobinska et al, 1995). However, this is offset by the high cost and by the fact that applications have so far been limited to organic compounds. The detection systems used may be the same as those used by any of the other chromatographic techniques

(Pickering, 1995), although as yet this method has not been applied to studies involving arsenic.

8.4.3.6 *Planar chromatography*

Planar chromatography is basically a combination of paper and thin layer chromatography. Both of these methods exploit the differential partition of solutes between stationary and mobile phases. In paper chromatography, this tends to be cellulose based, while the thin layer method utilises a thin film of silica gel coating a glass plate or aluminium foil plates. The sample is placed at one end of a strip of paper or TLC plate. This is then placed with the lower end in a reservoir containing the mobile phase. Capillary action draws the mobile phase up the paper or plate. When the solvent front has almost reached the far end, then the paper/plate is removed and developed in some way so as to enable detection of the spots (if they are not coloured). To count as non-destructive, detection would have to be restricted to UV fluorescence or by the use of radioactive traces. When the spots have been located, then they may be leached from the paper or plate for analysis. These methods are not commonly used in the separation of arsenic species, but have been employed (Morita and Edmonds, 1992).

8.4.4 Selective chemical extraction

Sediments and soils may have their total element concentrations sub-divided in terms of a number of operational parameters:

a) physical size fractions (as may be based on selective sizing using sieving, centrifugation, etc.);
b) detrital and non-detrital fractions (rock fragments and weathered material);
c) relative solubility (i.e. solubility of different species in acid or alkaline solutions);
d) 'species distribution patterns', which describe the proportion of each trace metal associated with specific components of the soil or sediment. These are often described in terms of mode of bonding such as physically sorbed, co-precipitated, ion-exchangeable, complexed or metal bonded in inert positions within mineral crystal lattice, and are outlined in Table 8.1.

Separation of each element from each of the different sample phases may be achieved by treating the solid with a number of different chemical solutions having a range of chemical reactivities. The sample of interest may be analysed in two different ways:

i) by sub-dividing the solid sample, with a separate analysis being performed on each aliquot, or;

ii) by a sequence of selective extractions on the same sample.

With the latter approach, it is debatable as to which fraction should be attacked first. In many cases, metal release from hydrous oxides and carbonates precedes oxidation of sulphides and destruction of organic material, whilst in others, oxidation is one of the early steps. It is also argued that many of the inorganic components may be coated with organic material, which should be removed first. It is thus important to determine the dominant 'coating' (if there is one) before embarking on a selective extraction procedure.

Table 8.1. Metal ion associations in soil and sediment samples.

Soil/sediment component	Metal content source	Release mechanism
Precipitated compounds		
Carbonates (incl. shell fragments)	Physically sorbed Co-precipitated Pseudo-morphosis	Reduction of ρCO_2 Dissolution in weak acids
Sulphides	Co-precipitated metal sulphides	Oxidation of S
Fe/Mn hydroxides and oxides	Physically sorbed Co-precipitated Chemi-sorbed	Reduction of Fe/Mn to lower valency
Organic acid compounds	Sparingly soluble metals salts Metal complexes	Lowering of pH; Destruction of organic material
Residual organics		
Lipids and humic substances	Physically sorbed Chemi-sorbed Metal complexes	Destruction of organic material; displacement by ligands (e.g. EDTA)
Rock fragments	Crystal lattices	Destruction of basic lattice

From Pickering, 1995.

It must also be noted that few reagents are completely 'selective' in their attacks on specific bonding modes or component species, and the amount of any particular element being selected is highly dependent upon the conditions under which the procedure is being performed, including extractant concentration; system pH; temperature; time of interaction; mode of mixing; particle size; matrix composition; competing chemical reactions; level of illumination, and resorption of released ions. It is

easy to see why the choices open must all be carefully considered, as errors could easily be compounded if a mistake was made early in the procedure.

Yamamoto (1975), successfully extracted As(V), MMAA and DMAA from the sub-2μm fraction of a farm pond sediment spiked with the above arsenic species. The treated samples were shaken for an hour with a number of extractants (soil:extractant = 1:10), which were 0.1M solutions of Na_2HPO_4 at pH 9.1, Na_2HPO_4/NaH_2PO_4 (3:2) at pH 7.0, NaH_2PO_4 at pH 4.5, and H_3PO_4 at pH 1.6. Phosphate was selected as the extractant because its chemical and physical reactions in soils are very similar to those of arsenic. After centrifugation (15,000 rpm for 30 mins) the supernatants were stored for some time before being analysed. Recoveries of the three species was found to be most efficient using H_3PO_4 at pH 1.6, and when combined with an ion exchange separation, followed by arsine generation and detection using SDDC colorimetry (see Section 9.4.1). Recovery of arsenate was the highest (94-98%), while MMAA was the lowest (80-86%), and DMAA was intermediate (86-90%). Recoveries were slightly higher (98%, 86% and 90% respectively for arsenate, MMAA and DMAA) when only one species was in the soil.

Iverson et al (1979) used a series of 1M solutions of NH_4Cl, NH_4OH, acid ammonium oxalate and HCl applied to dried sediment solids, and equilibrated for 24 hours at room temperature in a slow inversion mixer to speciate inorganic As(III), As(V), MMAA and DMAA. The fractions were operationally defined as water-soluble As, Fe and Al-As, occluded As, and Ca-As respectively. Although sediment solid extracts could be accurately speciated, the data were not considered to be an accurate representation of the actual solid-phase due to incomplete extraction.

Crecelius et al (1986) determined 'leachable' As(III) by adding 0.1 M H_3PO_4 (pH 1.5) to wet sediment samples held in centrifuge tubes. These are agitated for up to 24 hours before being centrifuged at 2,500rpm for 30 minutes. 'Leachable' As(V), MMAA and DMAA samples were treated in the same physical manner as above, but were treated with a 0.1 M Na_3PO_4 (pH 12) solution. The sample is then analysed using pH controlled hydride generation, which will ensure that only As(V) is generated.

Moore et al (1988) performed their experiments on subsamples of freeze dried sediments. First, a 0.25M hydroxylamine hydrochloride in 25% acetic acid (V/V) solution was used to remove the metals and arsenic bound to oxyhydroxides of iron and manganese, and also those bound in carbonates (although in this case, the carbonate

phase was regarded as being insignificant). This slurry was shaken for 12 hours before centrifugation, the supernatant being filtered and analysed. The remaining sediment was rinsed with distilled, deionised water and the organically bound fraction extracted over 12 hours using 0.1M sodium pyrophosphate at pH10. The sediment was again rinsed and the sulphide phase dissolved using potassium chlorate with HCl. The total arsenic content of the sediment was also determined by HF-perchloric acid digestion of separate freeze dried sediment subsamples.

Azcue et al (1994a) used the sequential extraction scheme outlined in Table 8.2, to determine the total arsenic content of a lake sediment. It should be noted, however, that some refractory minerals, such as spinel, tourmaline and zircon are not dissolved effectively using this digestion. Later work has been done using a similar method (Azcue and Nriagu, 1995).

Bowell (1994) used a three step extraction on tropical soils. The soils were treated successively with $MgCl_2$, citrate-dithionate-bicarbonate and ethandioic acid, which release arsenic from the exchangeable, amorphous, and crystalline iron oxyhydroxides and oxides respectively.

Table 8.2. Sequential extraction scheme of Azcue et al (1994a).

Extractant	Phase Dissolved
1.0 M NaOAc. HOAc pH5 (1g sediment/20ml; 2×6 hours shaking over about 2 days)	Carbonates, adsorbed metals, exchangeable metals
0.25 M $NH_2OH.HCl$ in 0.25 M HCl (At 60°C, first leach for 2 hours, second for 0.5 hour over about 0.5 days)	Amorphous oxyhydrates of Fe and Mn. Hydroxylamine hydrochloride is preferred to oxalate reagent as its attack on organic material is minimal.
1.0 M $NH_2OH.HCl$ in 25% HOAc (At 90°C, first leach for 3 hours, second for 1.5 hour over about 1 day)	Crystalline Fe oxides (such as haematite, goethite, magnetite etc.)
$KClO_3$/HCl for 0.5 hours, followed by 4 M HNO_3 at 90°C, first leach for 30 mins, second for 20 mins over about 0.5 days	Sulphides, organic matter
HF/$HClO_4$/HNO_3/HCl evaporation (about 1 day)	Silicates, residual crystalline fraction

Ac - acetate/acetic.

De Magalhães and Pfieffer (1995) only differentiated between mobile and residual arsenic in sediments. They recovered the mobile phase (the arsenic associated with Fe and Mn oxides) by extraction of 0.25g of sediment with 10ml of 1.0 M HCl for 24 hours. The strongly bound residual fraction was determined by taking 0.1g of sediment and extracting the arsenic using 10ml of concentrated HCl in a closed bomb for

15 hours at 130°C. It is not clear, however, if the extractions were performed sequentially on the same sediment sample, or whether separate sediment samples were used.

Other sequential extraction schemes have been applied to the removal of metals other than arsenic from sediment samples. An example of this is outlined in Table 8.3, which was used by Förstner and Carstens (1989) to extract manganese, copper and cadmium from natural and artificial soil and sediment samples. A similar, but more involved procedure was devised by Ross (1980) to investigate the concentrations of a range of metals associated with each soil fraction with increasing depth in an experimental study of landfill leachate migration within the unsaturated zone of the British Lower Greensand.

More recently, there has been an attempt to standardise sequential extraction procedures for a number of metals (not including arsenic) in sediments using a three step procedure (Quevauviller et al, 1994). This method is based on an acetic acid extraction (step 1), hydroxylammonium chloride extraction (step 2) and hydrogen peroxide/ammonium acetate extraction (step 3). This method, was primarily developed to aid in the production of sediment reference material to be certified for its contents of extractable trace metals, and to help establish the sequential scheme described as an international standard method.

Table 8.3. Sequential extraction scheme of Förstner and Carstens (1989).

Extractant	Phase Extracted
1.0 M NH_4OAc, pH7	Exchangeable ions
1.0 M NaOAc, pH5, with HOAc	Carbonates
0.01 M $NH_2OH.HCl$ with 0.01 M HNO_3	Easily reducible metals (e.g. Mn and Fe oxides)
0.1 M oxalate buffer at pH3	moderately reducible metals (e.g. amorphous Fe oxides)
30% H_2O_2 with 0.02 HNO_3 at pH2. Extracted with 1.0 M NH_4OAc in 6% HNO_3	Sulphides together with organic matter
Hot concentrated HNO_3	Residual crystalline fraction

A recent and valid comment on the use of extraction procedures has been made by Kersten and Förstner (1995), who point out that there are three basic factors which may influence the success in selective extraction, namely (i) the chemical properties of the extractant chosen, (ii) its extraction efficiency, and (iii) experimental parameter effects. In applying sequential extraction schemes, another four factors may be involved: (iv) the sequence of the individual steps, (v) specific 'matrix effects' such as cross

contamination and readsorption, (vi) heterogeneity as well as physical associations (such as surface coatings) of the various solid fractions, and (vii) particle size distribution. In exaluating the suitability of an extractant chosen for a specific investigation, all of these factors must be critically evaluated. Not doing this would probably result in data of doubtful validity. Whatever the extraction procedure chosen, the validity of the selective extraction results will, however, be primarily dependent upon the sampling collection and subsequent preservation methods carried out prior to analysis (Kersten and Förstner, 1995).

8.4.5 *Hydride generation (HG) techniques*

In this method, often used in conjunction with some of the previously described methods, the arsenic species in solution are reduced using a suitable reductant to their corresponding arsines: arsenate and arsenite to arsine (AsH_3), MMAA(III) and MMAA(V) to methylarsine (MMA, CH_3AsH_2), DMAA(III) and DMAA(V) to dimethylarsine (DMA, $(CH_3)_2AsH$), and TMAO to trimethylarsine (TMA, $(CH_3)_3As$). The arsines are purged from the solution by an inert carrier gas stream and either collected by one of the methods described below or fed directly into the detection system. Other dimethyl and trimethyl organoarsenicals such as some of the arsenoribosides are also reduced under such conditions, but generally exhibit insufficient volatility to be separated using this technique (see Section 8.4.5.9). Hydride generation is especially useful for the determination of trace amounts of arsenic because the high efficiency of analyte introduction to the atomiser leads to an increase of sensitivity compared to liquid nebulisation techniques, together with the possibility of preconcentration and speciation.

It is, however, very important to note that not all arsenic compounds form volatile arsines, and if more arsenic species are though to be present, then another separation technique will have to be employed. This is especially true with more complex arsenic compounds such as arsenobetaine, which make up the majority of the arsenic content in marine organisms, and which must first be converted to hydride forming compounds if this method is to be used in their detection.

8.4.5.1 *pH dependency and reduction*

It has been extensively reported that the reduction reaction whereby arsenic compounds are transformed into their respective hydrides is pH dependent, and related to the pK (dissociation constant) of the arsenic acids. The pK's of the common arsenic compounds are given in Appendix A, and it is easy to see that at a pH of 4-7, arsenous acid [As(III)] (pK_a ~9) will be reduced, but arsenic acid [As(V)], MMAA and DMAA (pK_a ~2.2, 2.6 and 6 respectively), will not, and a pH of 1-2 is needed for these arsenicals (Braman and Foreback, 1973; Braman et al, 1977; Andreae, 1977, 1978, 1983; Howard and Arbab-Zaver, 1981; Breslin and Duedall, 1983; Crecelius et al, 1986; Chakraborti et al, 1986; Reimer and Thompson, 1988; Reimer, 1989; Korte and Fernando, 1991; Howard and Comber, 1992; Campbell, 1992).

Although sodium borohydride ($NaBH_4$) is able to reduce As(V) [in acidic conditions] to As(III) and then through to arsine, the resultant signal is generally depressed by 20-30% relative to As(III). The sequence of reactions (Breslin and Duedall, 1983) is:

$$As(V) + NaBH_4 \rightarrow As(III)$$

$$2As(III) + 18BH_4 \rightarrow 2AsH_3 + 6H_2 + 9B_2H_6 \ (sic)$$

It is preferable to carry out hydride generation with $NaBH_4$ on As(III), and KI-ascorbic acid is an efficient prereductant for any As(V) present (Azcue et al, 1994a). Sodium thiosulphate has been found to quantitatively reduce As(V) to As(III) within a few minutes at pH1 (Mok et al, 1986). At pH4, As(V) is poorly reduced by $NaBH_4$ and this property may be used to obtain information on speciation. Alternatively As(III) may be selectively reduced by adding dimethylformamide [$HCON(CH_3)_2$] to the sample which suppresses As(V) reduction (Clement and Faust, 1973).

Sodium borohydride is the commonly used reductant, although potassium borohydride (KBH_4) has also been used (Reimer and Thompson, 1988; Reimer, 1989; Bright et al, 1994, 1996). Tin and HCl has been used successfully (Clement and Faust, 1973; Korte and Fernando, 1990), and zinc and HCl, and both magnesium and aluminium powder in acid have also been used (Melton et al, 1973; Clement and Faust, 1973; Talmi and Feldman, 1975; Korte and Fernando, 1991; Francesconi et al, 1994) but only with regard to total arsenic determination (the arsenic first being reduced to As(III) with $SnCl_2$ and/or KI). The arsines thus generated may then be swept

immediately to the detection system, separated in a gas chromatograph, or collected by one of the methods described below and subsequently analysed.

8.4.5.2 *Other arseno-hydrides*

Occasionally, workers have used phenylarsine as the volatile arsenic derivative for determination. Talmi and Norvell (1975) reduced all the arsenic in environmental samples to As(III) by wet ash digestion followed by addition of ascorbic acid and boiling with a pH of about 1. The arsenic was then co-crystallised out of solution with thionalid (thioglycolic-β-amino-naphtalide), which, in excess amounts, serves as both the complexing and crystallising agent, forming water insoluble complexes with submicrogram quantities of arsenic. The precipitate was separated by filtration and subsequently reacted with phenylmagnesium bromide, resulting in the formation of the phenylarsine, which is absorbed into ether to which thioglycolic acid had been added to prevent oxidation. The sample was then centrifuged, and aliquots of the organic layer were injected directly into a GC column.

8.4.5.3 *Interferences*

The determination of methylarsenicals by this method does require a degree of care. Researchers have found that various parameters including temperature, pH, presence of oxygen and carbon dioxide, and the initial concentration of both acids and $NaBH_4$ (Talmi and Bostick, 1975; Braman et al, 1977; Odanaka et al, 1983; Campbell, 1992), in addition to affecting the rate and efficiency of the reduction (and hence their removal and efficient collection), also determine the degree to which the undesirable side reactions of arsine molecular rearrangement take place.

Interference effects have been revealed in both the hydride generating and atomisation processes. These effects, resulting in an alteration (usually a reduction) of instrumental sensitivity, are usually expected to occur in real samples, as opposed to those manufactured in the laboratory for the purposes of methodological investigation. In general, certain metals interfere with the hydride generation reaction, but those elements which also form volatile hydrides (such as antimony, germanium, lead, selenium, and tin) are more likely to interfere in the atomisation process, although the hydride forming bismuth and tellurium are reported as interfering during the hydride generation phase as well (Campbell, 1992).

A wide range of transition and heavy metals, and nitrate are known to affect the signal (Braman et al, 1977; Pierce and Brown, 1977; Brown et al, 1981; Howard and Arbab-Zaver, 1981; Odanaka et al, 1983), but in many cases, the cause of the signal change has not been correctly assigned (Morita and Edmonds, 1992). The reasons behind the damaging effect of copper(II), cobalt(II) and nickel(II), in particular, upon arsine generation are numerous. The favoured explanation revolves around the reduction process, with some reduced metal ions reacting with the generated arsines, so eliminating a proportion before their release into the carrier gas. This suggestion supports the observation of increased interference occurring when elevated concentrations of $NaBH_4$ are used, and the decrease in interference when the hydrides are rapidly removed from the matrix. In addition, it is thought that some metal ions (such as iron(III), cobalt(II), nickel(II) and platinum metals) catalyse the decomposition of $NaBH_4$ with the formation of metal borates and hydrogen, thus leading to a suppressed hydride formation. These suppressions are much less marked if the $NaBH_4$ concentration is kept low (addition as an aqueous solution rather than in pellet form) and reagent addition is slow, ensuring thorough mixing (Campbell, 1992). Another problem may arise where the sum of two interferents isolated separately do not account for the total interference seen and under such conditions a synergistic interaction must be in operation. This has been reported by Brown et al (1981), who found that copper catalysed the $NaBH_4$ reduction of NO_3^- (once the copper itself had also been reduced) to produce NO_2^-, NO_2, NO ,etc. and that it was these catalytically produced species which caused the large observed interference, even though the initial copper and NO_3^- concentrations were low.

Attempts to circumvent the deleterious effects of dissolved metals include extraction of the metals with 8-quinolinol immobilised on glass beads, masking then with thiosemicarbazide, 1, 10-phenathroline, tellurium, or a 'cocktail' containing pyrogallol, thiosemicarbazide, 1, 10-phenathroline and cup-ferron, or co-precipitation with lanthanum or ferric hydroxides prior to the primary hydride evolution reaction (Brown et al, 1981). Boampong et al (1988) successfully used a 3% solution of L-cysteine in 5M HCl to reduce interferences for a wide range of transition and platinum group metals a finding also supported by Huang et al (1995). The catalytically produced NO_2^- mentioned above is much less easily treated, and Brown et al (1981) suggest removal of the copper catalyst prior to hydride generation.

Pierce and Brown (1977) found that interferences caused greatest problem when an automated hydride generation method was used in conjunction with a graphite furnace AAS, followed by manual hydride generation in conjunction with an argon-hydrogen flame atomisation, and the least interference was associated with an automated hydride generation with detection using a flameless quartz tube atomiser. The relative sensitivities offered by the automated hydride evolution technique and quartz tube (0.5µg/l - detection limit, 0.2µg/l) is about the same as for the flameless graphite furnace atomisation technique (0.8µg/l - detection limit, 0.2µg/l). The manual hydride evolution technique is somewhat less sensitive than the other two (2µg/l -detection limit, 1µg/l). Andreae (1977), simply suggests that if interfering metals are thought to be present, then standard additions should be used to check the reduction yields. Howard and Arbab-Zaver (1981) found that an addition of ethylenediaminetetraacetic acid (EDTA) with the sample adjusted to pH 3.0 masked the majority of interferences, bar antimony, gold(III) and nitrate; and that passing the sample through a column of chelating resin Chelex 100 at pH 4.0 removed all cationic interferents except for iron(II) and iron(III).

Additionally, the large excesses of carbon dioxide, water vapour and other gases generated in the reduction process (often dependent upon the origins of the sample) may cause interferences with the optimal operation of the detection system (mainly due to carryover of reagents into the detector, or from memory effects), and their elimination using various traps is to be encouraged, but only where necessary, and if it can be shown that they trap none of the arsines. Odanaka et al (1983) tested for arsine loss when NaOH, $CaCl_2$, $Mg(ClO_4)_2$ and a U-tube cooled with dry ice-acetone were used as a carbon dioxide or water vapour absorber. No loss of any arsenic species was noted for the NaOH, $Mg(ClO_4)_2$ and a U-tube, while a 15-20% decrease of DMA and TMA was noted for $CaCl_2$. Andreae (1977) tried drying the gas stream coming from the reaction vessel using a number of compounds ($CaCl_2$, K_2CO_3, $Mg(ClO_4)_2$ silica gel and Drierite) none of which were found to be effective, either not removing the water vapour or irreversibly trapping the evolved arsines. Effective drying was obtained by using a short Pyrex U-tube immersed in a dry ice-isopropyl alcohol bath.

8.4.5.4 *Carrier gas*

Both argon and nitrogen may be used as the carrier gas and under most circumstances either may be used with no significant loss of sensitivity. However, to

avoid condensation of liquid argon, either helium or nitrogen is the preferred carrier gas when using a liquid nitrogen trap (see Section 8.4.5.9). A mixture of 1%V/V oxygen in argon is reported to give enhanced optical absorbence compared to nitrogen, and a trace of oxygen increases the efficiency of atomisation (Campbell, 1992). It has also been noted that the carrier gas flow rate influences both the sensitivity and resolution of analysis by affecting the steady-state arsenic concentration in the detector and the rate of arsenohydride volatilisation. The optimum flow rate for a continuous flow generation method has been determined to be around 150ml/min (Howard and Arbab-Zaver, 1981; Howard and Comber, 1992).

8.4.5.5 *Sodium borohydride*

The use of pelletised $NaBH_4$ was at one time the preferred method of introduction to the reaction medium, but it gives undesirably high localised reagent concentrations. Consequently, a freshly prepared solution is now preferred and is the obvious reagent for continuous flow systems. The concentration of this reagent must be optimised for efficient and complete reduction, and usually lies in the range of 5-50g/l in aqueous solution made alkaline with potassium or sodium hydroxide. After filtration (0.45μm filter), this is sufficiently stable for up to three weeks (Campbell, 1992). The concentration and mode of introduction of $NaBH_4$ into the reagent mixture has been shown to be important in ensuring minimisation of potential interferences and this is outlined in Sections 8.4.5.3, 8.4.5.6 and 8.4.5.7.

8.4.5.6 *Acid concentrations*

Arsines are most effectively generated from an HCl matrix (Francesconi et al, 1994; Hasegawa et al, 1994). The concentration of the HCl added has a considerable effect on the yield of arsines, with DMA and TMA yields dropping rapidly with increasing HCl concentrations above about 0.4N, although the degree of molecular rearrangement reported was small (Odanaka et al, 1983). Pahlavanpour and Thompson (1981), in a slight contrast to Odanaka et al, found that maximum MMAA reduction efficiency was unaffected by HCl concentration up to a concentration of 1M. As(III) reduction efficiency is generally unaffected by variations in acid concentration. The optimum acid concentration is therefore best determined by a set of trials, although there is considerable evidence to support the use of higher concentrations (Campbell, 1992).

At higher HCl concentrations (3-5mol/l), the interference from transitions metals is much less marked (Campbell, 1992), although the addition of the acids in themselves appears to cause light to massive suppression of arsenic, depending upon the acid used, the acid concentration and the method of detection used (Pierce and Brown, 1977).

Pahlavanpour and Thompson (1981), suggest the use of citric acid (1% W/V) to enhance arsine production from As(III) [using $NaBH_4$], with 0.5M HCl being used to aid both As(V) and MMAA, and with 5M HCl with KI (0.1% W/V) for total inorganic arsenic determination.

Hwang and Jiang (1994) and Huang et al (1995) first reduced all arsenic species present with L-cysteine (rather than with KI) prior to the addition of $NaBH_4$, thus negating using HCl at all, a decision also taken so as to help to prevent the formation of $^{40}Ar^{35}Cl^+$ an interferent in ICP-MS determinations.

The rapid reaction between $NaBH_4$ and HCl sometimes causes foaming, which can be reduced by the addition of antifoaming reagents, although care must be taken to ensure their non-reactivity with any of the reagents or sample constituents (Braman et al, 1977; Campbell, 1992).

Nitric acid additions have been used with a degree of success in preventing the precipitation of transition metal reduction products, but may give rise to other problems, particularly in the batch method of generation. This is thought to be as a result of the nitric acid acting as an oxidising agent, counter to the reduction by $NaBH_4$ (Breslin and Duedall, 1983). Continuous flow methods appear to be more tolerant of nitric acid additions, which are also thought to cause problems through the formation of various volatile nitrogen oxides (Brown et al, 1981), although it has been reported that acidification of the sample solution prior to the $NaBH_4$ addition results in much less interference from oxidising anions including those arising from the use of nitric acid (Campbell, 1992). Another method is to remove all traces of the nitric acid before proceeding with hydride generation. The sample may be heated until the nitric acid is deemed to be no longer present, although this will only remove reduced forms of nitric acid (leaving unreacted NO_3^- behind), or sulfamic acid (HSO_3NH_2) may be added to the sample. This has the effect of reducing NO_2^- (regarded as the dominant interferent) to nitrogen gas.

8.4.5.7 *Molecular rearrangement*

Molecular rearrangements can lead to the formation of small amounts of AsH_3, DMA and TMA in addition to MMA during the reduction of MMAA. The reduction of DMAA resulted in the formation of small amounts of MMA (Talmi and Bostick, 1975; Talmi and Feldman, 1975; Odanaka et al, 1983). The rearrangements are almost completely eliminated if oxygen is excluded from the reaction (the alkylarsines are highly reactive and easily oxidised) and when the rate of reduction is increased by lowering the pH and increasing the concentration of $NaBH_4$.

8.4.5.8 *Generation methods*

One of the initial attractions of this method was the simplicity of the equipment which allowed interfacing with conventional AAS. Subsequent developments include automation, elimination of various interferences and increases in sensitivity and an increasing of detection limits. It must be stressed, however, that all equipment must be maintained scrupulously clean and condensation of water vapour on tubing surfaces must be avoided as it gives rise to peak broadening and memory effects (Campbell, 1992). There are several modes of operation of hydride generation 'instruments'.

i) *Batch type.* There are three variations of this type of operation. In its simplest form, the generated arsines are swept immediately to the atomiser, normally in a carrier gas. In equipment using the 'stopped flow' method, the sweep of the arsines from the reaction vessel is delayed to allow the generation reaction to proceed to completion. Care must be taken due to the instability of the hydrides. The last method uses a low temperature trapping device to concentrate the arsines so that the large volume of generated hydrogen is not transported into the detection instrument (Campbell, 1992).

ii) *Continuous flow.* These methods use peristaltic pumps for both the sample and for the reagents, and so have the advantage of intimate mixing of the participating reactants, with better pH control and also appear to be more tolerant of elements normally regarded as interferents in hydride generation. However, they usually have a lower detection limit compared with the batch systems, though this must be balanced against more rapid analysis (Campbell, 1992), and is the main method used in arsenic speciation analysis.

8.4.5.9 *Arsine collection methods*

i) *Liquid nitrogen cold trap*

The arsines may be trapped in a liquid nitrogen cold trap filled with a gas chromatographic packing, or simply a U-tube (usually packed with chromatographic quality glass wool, or glass beads, which are sometimes HF etched) held in a liquid nitrogen bath. A number of researchers (Andreae, 1983; Crecelius et al, 1986; Reimer and Thompson, 1988 and the US-EPA, 1996a) suggest 15% OV-3 on Chromosorb W-AW-DCMS 45/60 or 60/80 mesh be used if a chromatographic packing is to be used, while Reimer (1989) used a rigorously salinised Poropak P-S chromatographic packing and Hasegawa et al (1994) suggest 15% OV-3 on Chromosorb W-AW-DWCS 60/80 mesh. Either way, once the collection is complete, the trap is carefully heated (to around 80°C) and the arsines elute in the order of their boiling points as chromatographic peaks (Braman and Foreback, 1973; Talmi and Feldman, 1975; Braman et al, 1977; Edmonds and Francesconi, 1977; Andreae, 1977, 1983; Howard and Arbab-Zaver, 1981; Crecelius et al, 1986; Reimer and Thompson, 1988; Howard and Apte, 1989; Howard and Comber, 1989, 1992; Reimer, 1989; Szpunar-Lobinska et al, 1995; Hasegawa et al, 1994; US-EPA, 1996a). They are then swept by the carrier gas (such as helium or argon) into a burner mounted in the beam of a detector such as an atomic absorption spectrophotometer and the atom populations resulting from the combustion of the arsines result in transient atomic absorption signals which are monitored. On warming of the simple U-tube cold trap, the arsines may also be separated by gas chromatography (Talmi and Bostick, 1975; Andreae, 1977, 1978) although it is important that heating should be instantaneous to ensure adequate chromatographic resolution. The drawback of this method is that the large volume of the trap is disproportionate to the quantity of the hydride being trapped and the large surface area favours losses by adsorption processes unless care is taken.

ii) *Extraction*

In this method, described by Talmi and Bostick (1975), the acidified sample (pH1) had 10ml of either toluene or benzene added prior to the addition of a pellet of $NaBH_4$. The extraction vessel (a long test tube) was left open to allow the H_2 formed to escape. To ensure an efficient extraction of the generated arsines into the organic layer, the test tube was constantly shaken during the reaction period. The two layers were then

allowed to separate before aliquots of the organic layer were taken for analysis, separation being by gas chromatography. Arsine, however is too volatile to be collected by this method and escapes with the generated H_2. The quantitative collection of the various arsines depends on their volatility and solubility in the organic solvent. Unlike DMA, MMA was not extracted efficiently due to its lower boiling point (see Appendix A) and other solvents, such as ethanol and diethyl ether are not always compatible with GC columns.

iii) *Cold trap extraction*

In this method, the reaction vessel is airtight and the generated arsines escape via a glass frit bubbler in a test tube containing toluene. The test tube is suspended in an ethylene-glycol-ice cold bath (-5°C). In this method, the efficiency of collection of the various arsines depends on both the efficiency of the arsine flushing from the sample and the collection of these by the cold toluene. Both MMA and DMA are efficiently collected, and although MMA collection is not as efficient due to its lower boiling point, the overall collection recoveries are highly reproducible (Talmi and Bostick, 1975).

A variation of this method was developed by Odanaka et al (1983), who used *n*-heptane as the absorbing material. The *n*-heptane has a lower boiling point than toluene, and was used successfully to trap arsine as well as MMA, DMA and TMA, when kept immersed in a dry ice-acetone bath at -80°C.

iv) *Solid adsorbent trap*

The generated arsines are passed through a column packed with the same material as that utilised in GC so as to adsorb all the arsines. The adsorption efficiency has been found to be 100% (Talmi and Bostick, 1975). After collection, the column is heated and the desorbed arsines are flushed (either argon or helium) into a cold toluene trap, so providing a relatively simple preconcentration step.

v) *Membrane gas-liquid separator*

This type of separator is used mainly in conjunction with continuous flow systems and involves the use of a microporous membrane. Compared with membrane film separators, the membrane tube separator provides a larger surface area and is therefore able to separate a large amount of gas quantitatively from the solution.

Yamamoto et al (1987) used a membrane tube separator successfully to separate arsine from the effluent from a flow injection manifold using hydride generation for arsenic determination.

In addition to MMAA and DMAA, the $NaBH_4$ reduction method may be applied to the determination of some other alkylarsenicals. Where toluene and GC are used, however, then the method is limited to those arsines with a retention time not exceeding that of toluene, thus excluding those arsenoacids with an alkyl group of greater than C_5. The collection of these heavier molecules again depends upon their volatility. Ethylarsine ($C_2H_5AsH_2$) may be collected by any of the above methods as its volatility is close to that of DMA. The low volatility *n*-propylarsine (*n*-$C_3H_7AsH_2$) and *n*-butylarsine (*n*-$C_4H_9AsH_2$) are only partially volatised (50% retained in water) and therefore are only quantitatively collected by the extraction method (Talmi and Bostick, 1975).

The extraction method and cold trap extraction methods have the advantage over the liquid nitrogen trap in that every sample may be analysed several times, and since arsine-toluene solutions are stable for up to 24 hours, a large number of samples may be first collected and then analysed (Talmi and Bostick, 1975). The major disadvantage is that arsine is not efficiently trapped due to its volatility.

Compounds such as arsenobetaine, arsenocholine and the more complex arsenoribosides do not form hydrides on treatment with $NaBH_4$. Samples containing these compounds must therefore be pretreated in such a way as to form hydride forming compounds still retaining speciation information, otherwise other speciation methods are employed. Arsenobetaine may be converted by hot NaOH to TMAO which may be reduced to TMA with $NaBH_4$. Arsenocholine, however, cannot be digested using the same method. UV radiation has been used to photo-oxidise a variety of arsenic compounds [AsBe, AsC and quaternary arsonium ions {$(CH_3)_4As^+$}] to inorganic As(V), although potentially significant speciation information is again lost (Howard and Comber, 1989), and it is thought that this process also occurs naturally to a certain extent. Howard and Comber (1992) found that monophenylarsine derived from monophenylarsonate compounds can be resolved using the hydride generation method.

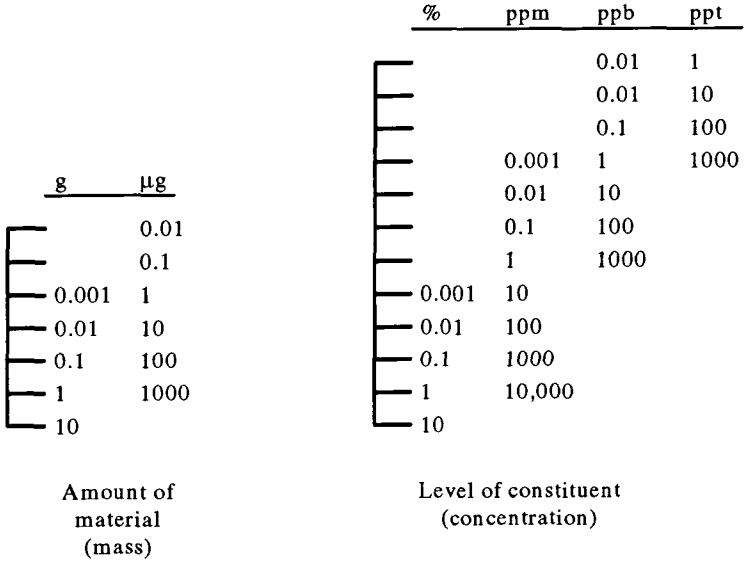
CHAPTER 9

ARSENIC SPECIES DETERMINATION

9.1 Introduction

Once the arsenic species have been separated, they must then be identified and quantified. A number of detection systems have been used for arsenic speciation studies, some for a considerably longer period than others, reflecting the continuing development of new techniques and the refinement of existing ones. The terms utilised in analytical chemistry have also changed. In the 1970's, the term 'trace' was equivalent to μg/g (mg/kg, or ppm), and 'ultra-trace' to ng/g (μg/kg ppb), although of course the same applies to aqueous samples. Now, and in the near future, 'trace' will mean ppb, and 'ultra-trace' will mean pg/g (ng/kg or ppt) or less (Pais, 1994). The relationship between these various concentrations and material masses is shown in Figure 9.1.

Figure 9.1. Log scale of amounts and concentrations in trace element analysis.



From Fergusson, 1990.

The detection systems used in the determination of arsenic in environmental samples include, but are by no means restricted to:

a) flame atomic absorption and emission spectrometry;

b) electrothermal atomic absorption spectrometry;

c) colorimetry or molecular absorption spectophotometry;

d) electron capture and flame ionisation detection;

e) electro-analytical speciation techniques;

f) microwave-emission spectrometry;

g) X-ray fluorescence;

h) mass spectrometry;

i) neutron activation analysis;

j) proton-induced X-ray emission;

k) dc discharge spectral emission;

l) kinetic methods;

and each is described in turn below. First it is important to briefly discuss what is meant by the term 'detection limit'. The detection limit for an analytical method is expressed either as an absolute detection limit (in μg, ng or pg) or as a relative limit (μg/ml or μg/l, ng/ml or ng/l, etc.). The limit of detection is the lowest amount or concentration of the element or compound of interest that can be reliably estimated, and has been defined as:

$$(x - x_b)_{min} = k\sqrt{(2\sigma_b)}$$

where x = sample mean, x_b = blank mean, k is a constant = 1.96 for the 95% confidence level and ≈ 3 for the 99% level, and σ_b = standard deviation for the blank. For k = 1.96,

$$(x - x_b)_{min} \approx 3\sigma_b$$

which gives the minimum level of detection as

$$x = x_b + 3\sigma_b$$

A problem in emphasising the detection limit is that it is sometimes mistakenly believed that the limit represents the level that can be accurately or precisely measured (Fergusson, 1990). Most of the systems described here, reduce the arsenic introduced into the system to its atomic state, which is then detected. As such, this tells us nothing of the chemical nature of the arsenic compound being analysed. For example, the use of

high performance liquid chromatography - atomic absorbance atomic spectroscopy (HPLC-AAS) only gives the different chromatographic retention times for the various compounds under investigation. It is therefore important to compare the retention times on different columns under a variety of conditions and comparison with authenticated samples is necessary to ensure the correct identification.

9.2 Atomic spectrometry

Spectrometric determinations of arsenic are troubled by scattering and molecular absorption of the light (because the useful resonance line of arsenic lies below 200nm) by air, matrix species present in the combustion cell and by the optical components of the instrument. Thus, improvement in these techniques are made by either operating in an inert atmosphere (vacuum, N_2 or a noble gas), by using a more efficient spectrometric excitation source such as electrode or electrodeless discharge plasmas, or both (Talmi and Feldman, 1975). However, improvements made over the years, have made this method quite a sensitive and reliable method for arsenic determination, although its sensitivity is not as good as some of the more modern methods. It is used as one of the reference methods for the determination of arsenic in testing samples with respect to EEC Directive 75/440/EEC (concerning the quality required of surface waters intended for the abstraction of drinking water) [EEC Directive 79/869/EEC].

9.2.1 *Atomic emission spectrometry* (AES)

Generally, flame emission techniques are not thought to provide adequate sensitivity for analysis of environmental samples, due to the inadequate excitation energies provided by flames. Both direct current (DCP) and inductively coupled plasmas (ICP) have been employed and are found to be much more efficient excitation sources and therefore more sensitive. Microwave-induced plasma AES has an achievable arsenic detection limit of 0.1μg/ml when monitored at the 228.8nm spectral line (Bostick and Talmi, 1975) and this is discussed in Section 9.7. Braman et al (1972) used a direct current plasma AES (DCP-AES) system following arsine generation. This gave an absolute detection limit of 0.5ng (for inorganic As(III) and As(V), and 1.0ng for methylarsenicals) and has been adapted for speciation studies (Braman et al, 1977; Sanders and Windom, 1980). Morita et al (1981) compared Ar/H_2 flame AAS and DCP-AES with ICP-AES as an HPLC detector. With the Ar/H_2 flame AAS and monitoring of

the 193.7nm line, the sensitivity was about 1/20th of ICP-AES, whilst the sensitivity of the DCP-AES was about 1/5th that of ICP-AES.

ICP-AES is an optically thin emission source formed by coupling radio-frequency power to a stream of argon gas. The argon is constrained into three concentric streams in a plasma torch fabricated from fused silica. A toroidal shaped plasma is formed and the sample is injected through the central tunnel, heated to around 8000K and thereby atomised to a large extent. Emission from the excited atoms is observed approximately 10-20mm above the load coil using a conventional spectrometer system. Morita et al (1981) calculated the detection limit for arsenic to be around 2.6ng (by taking a signal to noise ratio of 2), if all operational conditions were optimised.

The coupling of HPLC to ICP-AES is simple, using a short length of Teflon tubing, and has enabled continuous monitoring of selected arsenic compounds (Francesconi et al, 1994). Both ion exchange and gel permeation chromatography HPLC have been interfaced with detection limits in the region of 19-41ng.

The monitoring of arsenic takes place at the strong 189.0nm emission line, but only when vacuum or gas purge type detectors are utilised (Morita and Edmonds, 1992). The emission line at 193.7nm gives greater sensitivity than either the 197.2nm or the 228.8nm lines, but is affected by the carbon content of the solution because of the carbon emission line at 193.1nm. The 228nm line is the least sensitive but is not affected by carbon interference. The 197.2 line is intermediate both in terms of sensitivity and carbon interference. Thus the 193.7nm line or the 197.2nm line is used for aqueous phase ion exchange chromatographic separation, and the 228.8nm or the 197.2nm line are used for reversed phase, ion pair chromatography that employ organic solvents (Morita and Edmonds, 1992).

The determination of arsenic with ICP was initially not possible as arsenic is commonly found at concentrations too low to be detected when conventional ICP sample introduction techniques such as nebulisation are employed (Francesconi et al, 1994). However, one of the main advantages of the hydride generation technique for sample introduction is the increase in sensitivity gained over liquid sample nebulisation because of its high transport efficiency of the hydride and the possibility of preconcentration, although it is important to adopt an experimental technique which eliminates the adverse effect on plasma stability of the large volume of hydrogen produced in the hydride forming reaction. It also has the advantage over flame AAS

because arsenic's useful atomic resonance line is below 200nm, a region where there is considerable interference from radicals in flame AAS. An improvement in the arsenic detection limits using hydride generation methods over those found for conventional ICP nebuliser systems can be expected to be in the order of one to two orders of magnitude. Detection limits 30-700 times better (0.1ng/ml compared with 70ng/ml, using the 189.05nm line) than those found with pneumatic nebulisation have been achieved for a number of hydride forming elements (Hwang et al, 1989) and it is also apparent that gas flow rate is critical and very much less (about 40% less) than for conventional ICP so as to prevent carry-over effects.

The response of ICP-AES was initially thought to be a constant function of the amount of arsenic injected, irrespective of the compound due to the ICP's ability for complete atomisation (due to the high temperatures). However it was shown that the peak area response was a function of the nature of the compound, and that detection limits depended on peak heights not peak areas, thus showing a chemical form dependency (Morita et al, 1981; Morita and Edmonds, 1992).

Interferences are caused by emissions from other elements, and are dependent upon several parameters including the wavelength of the arsenic emission line, the resolution of the spectrometer, the ICP operating conditions and the major solutes in the HPLC solvent if this is the speciation method used. For example, with the arsenic 228.8nm line, cadmium interference may be a serious problem if it is present in the effluent, as it shares the same emission line (Morita and Edmonds, 1992). With hydride generation techniques, most problems are associated within the generation step, as mentioned in Section 8.4.5.3 in the previous chapter.

The use of HPLC-ICP-AES only gives the different chromatographic retention times for the various compounds under investigation. It is therefore important to compare the retention times on different columns under a variety of conditions and comparison with authenticated samples is necessary to ensure the correct identification. Morita et al (1981), using ion exchange HPLC-ICP-AES, achieved a practical detection limit of 30, 19, 41 and 30ng, respectively, for As(III), MMAA, DMAA and As(V), taking the limit at a signal to noise ratio of 2.

9.2.2 *Atomic absorption spectrometry (AAS)*

Atomic absorption is comparatively easy to use and is dependable, but a detection limit of 0.5-1.0μg/l limits its application with environmental samples (Lemmo et al, 1983; Morita and Edmonds, 1992). Conventional atomic absorption spectroscopy involves nebulisation into a flame, above which the non excited atoms absorb electromagnetic radiation at characteristic wavelengths. Arsenic has two absorption lines and these are at 193.7nm or the less sensitive arsenic resonance line at 197.2nm.

The interfacing of HPLC and flame AAS is another method used in arsenic analysis, requiring only a short piece of Teflon tubing to connect the two instruments. When the HPLC flow rate is not the same as the AAS uptake (they should be about the same), two kinds of device have been proposed (Morita and Edmonds, 1992). The first is the employment of a three way connector, allowing for an auxiliary liquid flow to compensate for the deficiency in the HPLC flow rate. The other is to use a Teflon funnel micro-sampling cup attached directly to the nebuliser. The HPLC effluent is added dropwise and analysed without dilution. There are, however problems: when arsenic species are dissolved in organic solvents, such as those used in reversed phase and ion pair chromatography, sensitivity falls, mainly due to suppressed atomisation. This low sensitivity makes it difficult to apply HPLC-flame AAS to the speciation of arsenic at the low concentrations found in most environmental and biological samples. Usually, the use of HPLC-flame AAS is restricted to those samples containing relatively high concentrations (>100μg/ml) and separated by aqueous phase or isocratic organic phase chromatography. For the analysis of real samples, it may be necessary to use the standard addition method by co-injecting known amounts of authentic samples (Morita and Edmonds (1992). Enhancement of sensitivity has been improved by the inclusion of a hydride generation step between HPLC and flame AAS.

Usually, arsenic analyses are conducted utilising volatile hydride generation (as described in Section 8.4.5), where the arsenic can be injected as a gas phase (covalent hydride) - which gives greatly improved sensitivity (mainly because of the greater rate at which the analytes can be injected - due to the greater efficiency of hydride formation) over pneumatic nebulisation, or by graphite furnace atomic absorption techniques. The drawback is that the arsenic resonance line is less than 200nm and consequently highly susceptible to interferences from flame radical absorption. The detection limit for the

hydride generation method is in the order of 1.0ng and around 0.2ng for the graphite furnace method (Lemmo et al, 1983).

There are several commonly used determination methods employed in conjunction with hydride methods:

1) Nitrogen is used to sweep the generated arsines directly into a hydrogen/argon flame. Morita and Edmonds (1992) suggest a detection limit in the order of 1μg/ml.
2) Once generated, the arsines are swept into an air-acetylene heated quartz tube. The detection limit of this method is around 0.25ng of arsenic as As(III), As(V), MMAA and DMAA (Howard and Arbab-Zavar, 1981). Sweeping the arsines directly into an air-acetylene flame has also been used successfully, with detection limits for total arsenic of 20ppb in water, and 1ppm in soils (Melton et al, 1973). This was also used successfully by Le et al (1994) for the detection of total arsenic in some marine organisms down to 0.2μg/g.
3) Separated nitrous oxide-acetylene flames have also been used in the determination of arsenic (Kirkbright and Ranson, 1971; Talmi and Feldman, 1975), with detection limits in the order of 1.0ppm.
4) Andreae (1977, 1978, 1983), Crecelius et al (1986), Reimer and Thompson (1988) and Reimer (1989) used a H_2-rich hydrogen/air flame in a quartz burner cuvette. Andreae achieved a detection limit for arsine of 0.05ng As, whilst Reimer and Thompson (1988; and Reimer, 1989) report absolute detection limits of 0.12ng (of arsenic) for As(III) and 0.25ng for As(V), MMAA and DMAA.

Both (1) and (2) yield reliable results in complex matrices, but only if the arsine generation is preceded by a closed acid digestion process. Both methods mentioned above may be applied to speciation studies if the arsines are separated prior to introduction into the detector, but methods are prone to interferences from common ions when cool flames are used (due to incomplete vaporisation of the other elements present in the sample solution), although separating the oxidising secondary reaction zone of the air-acetylene flame using nitrogen results in slightly lower background

absorption and noise levels (Kirkbright and Ranson, 1971). Morita et al (1981) used an Ar/H_2 flame for arsenic speciation studies, but found that the sensitivity of the AAS was about $1/20^{th}$ of that obtained using ICP-AES as the HPLC detector.

The pre-mixed nitrous oxide-acetylene flame (3, above) however, is effective for the atomisation of elements which form refractory oxides due to the low concentration of oxygen in the internal zone of the fuel rich flame, resulting in low background absorption and noise levels, especially after separation of the secondary reaction zone by inert gas (Kirkbright and Ranson, 1971). The sensitivity attainable is less than either the hydrogen/argon or air-acetylene flames, presumably due to the higher gas flow rates necessary to support this flame. However, due to the low flame background absorbance and noise, the detection limit is somewhat superior to air-acetylene and possibly also to the hydrogen/argon flame where complex matrices such as glass, metals and alloys are being investigated.

The H_2-rich hydrogen/air flame used by Andreae (1977, 1978, 1983) and Reimer (1989) requires great care in its operation due to the nature of the gases utilised. Optimal sensitivity is attained with an H_2/O_2 ratio of about 5, and this is tolerant of variations of up to 20% in gas flow rates. The detection limit for arsine is 0.05ng using the 193.7nm line and peak integration. When a 100ml sample is used, this translates into a relative detection limit of 0.5ppt.

Of the two available wavelengths for arsenic, the 193.7nm line in the short wavelength UV region offers almost 100% more sensitivity at small absorbancies than the 197.2nm line. Since the absorbancies for both lines are highly non-linear, and the 193.7nm line gives a shorter dynamic range than the 197.2nm line, the useful range and reproducibility can be greatly improved by using peak area response rather than peak height. As a light source, an electrodeless discharge lamp should be used, which provides significant improvement in detection limits and linear range over hollow cathode lamps for arsenic (Kirkbright and Ranson, 1971; Andreae, 1983), due to their greater signal intensity. The sensitivity can be similar for arsine and the methylated arsines from chromatographic separation techniques, but the increased peak width of the higher substituted arsines gives a reduction of detection limit. The detection limit for arsine is about 0.05ng As using the 193.7nm line and peak integration. When a 100ml sample is used, this translates into a relative detection limit of 0.5ppt (Andreae, 1977).

The use of flames in the detection of arsenic, although very convenient, is not ideal as they only partially fill the requirements of the following:

1) total sample utilisation,
2) efficient and reproducible atomisation,
3) low degree of ionisation,
4) inert atmosphere,
5) long residence time to prolong observation time,
6) capability of atomising solids, liquids and gasses,
7) fast routine analysis, and
8) low cost and simple operation.

Other atomisers have been used in an effort to meet the above criteria or to minimise interferences. The use of a long tube absorption cell with argon, helium or nitrogen air-hydrogen flames achieves a long optical path in an almost inert atmosphere, and although sensitivity is improved (6ng/ml) and absorption by air is reduced, the technique suffers from multiple interferences requiring careful preparation of both samples and standards.

9.3 Electrothermal atomic absorption spectrometry (ETAAS)

Flameless atomic absorption (FAAS) using a graphite (GF-AAS) or quartz tube or furnace has been employed, yielding a detection limit for arsenic of 1.0-5.0µg/l under optimum conditions. The absolute detection limit for the HG-ETAAS method is in the order of 0.2ng for the graphite furnace method (Lemmo et al, 1983), with detection limits for the quartz tube lying in the range 19 to 61ng/l (Howard and Comber, 1992). The use of these technique for determining arsenic species of unknown chemical form in crude environmental extracts should be viewed with caution (Francesconi et al, 1994).

The advantage with this technique over the flame methods is the greater sensitivity due to the lower background absorbency. Problems include the fact that the graphite atomiser tube continually deteriorates, may be prone to complex interference effects, and can also be slower, whilst the electrically heated quartz tube has been reported as suffering from devitrification and to sensitive catalytic surfaces on the quartz tube itself (Campbell et al, 1992). Also, the atomisation process is quenched by the presence of traces of organic solvents, although Brinkman et al (1977) state that this method is comparatively little affected by solvent matrix effects. Another problem in the

determination of arsenic by GF-AAS is the loss of arsenic during the ashing stage (arsenic sublimes at 613°C). This may be overcome by the use of nickel salts as matrix modifiers (stabilisers) which prevent this loss through the formation of nickel arsenate (mp, 968°C). Palladium has also been used as a matrix modifier, the arsenic absorption being 30% greater than in the presence of nickel. A mixture of palladium and magnesium nitrates has also been used to good effect (Belzile and Tessier, 1990; Francesconi et al, 1994). To overcome matrix effects inherent in the determination of arsenic by GF-AAS, cleaning of the sample by using one of the previously described speciation techniques is often carried out.

Most of these phenomena associated with the quartz tube may be explained by a mechanism of catalytic decomposition of the hydrides by hydrogen radicals. Hydrogen has been recognised as being essential in the quartz tube atomisation process. At 900°C pure arsine in argon gives no absorption, but the expected signal is achieved if hydrogen is introduced into the carrier stream. The hydride decomposition is also assisted by the presence of a small amount of oxygen (Campbell, 1992). Various designs of quartz tubes have been tried and all give slightly differing results, although the nature of the surface of the tube is extremely important, and mist carryover from the hydride generation must be avoided by the use of a suitable trapping device (such as those described in Section 8.4.5.9). Generally, due to the continuous deterioration of the graphite, the quartz furnaces have the advantage of longevity although they are generally operated at lower temperatures and this may lead to incomplete atomisation if care is not taken.

It is also important to note, however, that these devices generally use very small samples (1-50µl) which is attractive as the sensitivities are high, although this is not quite so attractive if expressed in terms of relative sensitivity. Additionally, the sensitivity and reproducibility also depends on the variation of the sample location within the atomisation chamber. The performance of the atomiser tube generally deteriorates continuously with time (especially if samples with high salt concentrations are used) and the fact that the very small volume in which the vaporised sample is confined results in very high non-specific spectral interferences compared to the flame methods. Replacement of a damaged cuvette does not necessarily produce the same result as one subjected to a number of analysis cycles, necessitating the frequent use of standards (Morita and Edmonds, 1992).

Different arsenic compounds produce different ETAAS responses for the same quantity of arsenic, with less volatile species giving a more intense signal than those of greater volatility. Atomisation processes are likely to be different for each compound and a greater loss of the volatile compounds from the cuvette during atomisation is a probable cause of this observation. It is also probable that organic materials eluted at the same chromatographic positions will reduce the atomic absorption signals. In this case, it may be necessary to use the standard addition method by co-injecting known amounts of authentic samples (Morita and Edmonds, 1992). The addition of nickel to the sample solution has been reported to eliminate the species dependency of the signal, and also prevents the loss of arsenic during the ashing stage of ETAAS.

Iverson et al (1979) separated inorganic arsenic, MMAA and DMAA using a cation exchange resin, but by using eluents of a relatively low ionic strength, major cations such as Na^+, K^+, Mg^{2+} or Ca^{2+} could also be retained on the resin, thus eliminating some of the major interferents in GF-AAS, before detection using an electrodeless arsenic discharge lamp as the source. Detection limits using 10µl samples resulted in a linear working range of 10-300µg of As/l, while optimum conditions using dilute standards (2-20µg of As/l) lowered the detection limit to 2µg of As/l (with a signal to noise ratio of 2).

Puttemans and Massart (1980) used a graphite furnace atomiser with an arsenic electrodeless discharge lamp to determine arsenic concentrations in back extracted solutions from a liquid-liquid extraction procedure (see Section 8.4.2.5). The samples injected were 50µl and were followed by 50µl of nickel nitrate solution as a stabilising solution. They report no detection limits, but worked with standard solutions of 10ng/ml.

Pacey and Ford (1981) separated As(V), MMAA and DMAA using cation and anion exchange columns before introducing the eluents into a GF-AAS, fitted with a hollow cathode arsenic lamp. Purified and dried argon was used as the carrier gas. By the use of large samples, DMAA could be determined at concentrations as low as 0.02ng/ml with an absolute detection limit of 0.01ng. For MMAA and As(V) the minimum concentrations determinable were 2.0ng/ml and 0.4ng/ml with absolute detection limits of 0.5ng and 0.2ng respectively. Grabinski (1981) also used this method and gained an overall analytical detection limit of 10ppb for each of As(III), As(V), MMAA and DMAA respectively.

Ricci et al (1981) developed an automated system using an anion exchange column to separate the five arsenic species (see Section 8.4.2.2), before arsine generation and detection using a quartz tube AAS. Detection limits were 6ng/l for As(V), 7ng/l for DMAA, 8ng/l for As(III) and *p*-aminophenyl arsonate, and 9ng/l for MMAA.

Howard and Comber (1992) used hydride generation to separate inorganic arsenic, MMAA and DMAA and subsequently determined their concentrations using an electrically heated quartz tube atomiser. Detection limits were 19ng/l for arsine, 45ng/l for MMA and 61ng/l for DMA. Yokoyama et al (1993) also successfully used a quartz tube atomiser connected to an AAS to measure inorganic arsenic hydride in the concentration range 0.01-10ppm arsenic. The measurable concentration depended on the injected sample volume and was monitored at 193.7nm.

Hasegawa et al (1994) were the first workers to find and measure trivalent methylarsenicals in natural waters, using a quartz tube ETAAS detector. Because they used a liquid-liquid extraction procedure prior to HG (see Sections 8.4.2.5 and 8.4.5) the detection limits for the trivalent arsenicals were better by a factor of 10 than those for the pentavalent arsenicals. The detection limit for As(III), MMAA(III) and DMAA(III) were 0.015, 0.017, and 0.013nM respectively, whilst those for As(V), MMAA and DMAA were 0.14, 0.18 and 0.11nM respectively. The sensitivity and reproducibility were the same for both the trivalent and pentavalent arsenic species.

The coupling of HPLC to ETAAS instruments involves a number of problems as mentioned in Section 8.4.3.2, due to its discrete mode of operation (Larsen et al, 1993). Two interfacing methods have been proposed (Morita and Edmonds, 1992). Firstly, on-stream sampling, in which 10-50µl of the effluent sample is sampled periodically (e.g. every 40s) from the effluent stream. Secondly, off-stream sampling, in which the automatic sampler of the ETAAS spectrometer is used as a fraction collector. The on-stream sampling method sacrifices the resolution of the HPLC by the relatively low frequency of the sampling caused by the heating cycles of the atomisers. In the off-stream method, the resolution of the HPLC is lost to a lesser extent, but the total time for analysis is increased.

The use of HPLC-ETAAS only gives the different chromatographic retention times for the various compounds under investigation. It is therefore important to

compare the retention times on different columns under a variety of conditions and comparison with authenticated samples is necessary to ensure the correct identification.

9.4 Colorimetry or molecular absorption spectophotometry

This technique utilises relatively simple instrumentation, involves low cost and gives acceptable accuracy and precision. The two commonly used reagents used for the formation of coloured arsenic derivatives are silver-diethyldithiocarbamate [SDDC] (Dietz and Perez, 1976; Korte and Fernando, 1991) and ammonium molybdate (Johnson and Pilson, 1972; van Elteren et al, 1991). Spectophotometry was the most widespread technique for the determination of arsenic during the 1970's (Talmi and Feldman, 1975), mainly because of its inherent methodical and technical simplicity and its low cost, although for separation of arsenic species, several other techniques are generally better suited. Indeed, it is the main reference method to be used for the determination of arsenic in testing samples with respect to EEC Directive 75/440/EEC (concerning the quality required of surface waters intended for the abstraction of drinking water) [EEC Directive 79/869/EEC]. It is not suitable for the determination of organoarsenicals without prior treatment to reduce then to suitable inorganic species (Braman, 1975).

9.4.1 *Silver-diethyldithiocarbamate (SDDC)*

The limit for detection for SDDC is near 1 ppb (Clement and Faust, 1981), and has been used in the determination of As(III), As(V) and MMAA (Yamamoto, 1975; Dietz and Perez, 1976). Initially, the method was used to determine total inorganic arsenic, with all arsenic being reduced to arsine and then bubbled through a 0.5% SDDC solution in pyridine with the intensity of the red coloured complex being measured at 533nm. As(III) may be determined by adding dimethylformamide [$HCON(CH_3)_2$] to the sample which prevents As(V) reduction to As(III) and arsine by both the tin/potassium iodide and zinc/HCl methods, but which does not interfere with the production of arsine from As(III) [Clement and Faust, 1973].

MMAA may be reduced to methylarsine, which also forms a coloured complex on treatment with SDDC. The absorption bands of the two complexes (arsine and MMA) are well separated (by about 40nm) in the visible range, so a distinction may be made, although DMAA interferes with the method (Yamomoto, 1975; Korte and Fernando, 1991). Yamamoto (1975) successfully used cation exchange as a method to

separate As(V), MMAA and DMAA prior to reducing the effluents with zinc and HCl to their respective arsines, which were reacted with SDDC in chloroform to give the coloured complexes, the absorbancies of which were measured at 520nm.

This method can suffer some interference from other metal ions. These interferences have been reported as being reduced by digesting aqueous samples with potassium permanganate and then passing the digest through an anion exchange resin (Francesconi et al, 1994), or other pretreatments or procedural changes (Clement and Faust, 1973).

9.4.1 *Ammonium molybdate*

The arseno-molybdate complex is considered more suitable by many workers due to its sensitivity, reliability and general freedom from interferences, although large amounts of sample are required (in excess of 40ml). Arseno-molybdic acid, formed by the reaction of arsenate (any As(III) may first be oxidised by a suitable agent, such as potassium iodate, as it does not form the coloured complex) with modified molybdate, is reduced to the blue complex (molybdenum blue), the absorption of which is measured spectophotometrically at 865nm (Johnson and Pilson, 1972), 840nm (Al-Sibaai and Fogg, 1973) or at 866nm (Talmi and Feldman, 1975). A variety of compounds have been used for the molybdate reduction. $SnCl_2$ has been used, but gives an unstable colour, while hydrazine sulphate is slow. The rate of molybdoarsenate formation has also been shown to be faster in the presence of phosphate, than when phosphate is absent (Johnson and Pilson, 1972). Total arsenic is determined by ensuring all the arsenic present in the sample is oxidised to As(V), with As(III) being determined through the difference between this 'oxidised' sample and an 'untreated' sample. Van Elteren et al (1991) separated As(III) and As(V) using a variation of this method. As(III) was first removed from solution by coprecipitation with Na-DBTBC (sodium dibenzyldithiocarbamate) in methanol, followed by filtration. This precipitate was then analysed, with recoveries being calculated by comparison with references (i.e. filters spiked with the respective references). As(V) was then complexed with sodium molybdate and analysed as before. Johnson and Pilson (1972) determined that this method was suitable for the determination of As(III) and As(V) in seawater and most other natural waters where the arsenic concentration is less than about 3×10^{-6}M. Where higher arsenic concentrations are expected, they recommend sample dilution.

9.4.2 *Other complexes*

Arsenite forms a yellow complex with N-phenylbenzohydroxamic acid at pH 4.5-5.2 that can be extracted into chloroform and measured spectophotometrically, although other methods have also been used (Francesconi et al, 1994).

Stará and Starý (1970) report that As(III) is selectively extracted from a sulphuric acid (3.5-4.5M) solution containing potassium iodide into carbon tetrachloride or other non-polar organic solvents. The addition of 8-mercaptoquinoline (in carbon tetrachloride) results in the formation of a strongly coloured yellow complex, with a maximum absorbance at 380nm. This method is reported as being more rapid then either the molybdenum blue or SDDC methods, although the presence of some other metals requires a preliminary arsenic separation step to minimise interference. Calibration curves prepared using this method were linear up to 6μg/ml (30μg for a 5ml solution).

Peters et al (1996) report the use of ethyl violet in the presence of sodium nitrite, as a method to oxidise As(III) to As(V), and also to remove some interferences. The As(V) so formed may then be selectively detected by reaction with potassium iodide in the presence of sulphuric acid. The product has a characteristic pink colour in carbon tetrachloride solution.

9.5 Electron capture and flame ionisation detection

This detection method has been used successfully by Andreae (1977) in conjunction with gas chromatography for the determination of arsenic. In this case the electron capture device was mounted in parallel with a flame ionisation detector. The reasoning behind this parallel system is that peak height ratios together with retention time are highly characteristic for a given compound, allowing for positive peak identification. This is especially useful because if the electron capture detector is overloaded (see below), then the flame ionisation detector signal may be used to measure the methylarsines (Andreae, 1977).

9.5.1 *Electron capture detection*

The sensitivity of the electron capture detector is a function of the electron capture cross-section of a given molecule and of the operating conditions of the detection unit. The most important variables are pulse interval, quench gas flow rate, and temperature. Andreae (1977), used a ^{63}Ni source with a pulse interval of 50μs with

helium carrier gas supplied at 30ml/min and P-10 (10% methane in argon) at 25ml/min. Under these conditions (no temperature specified), the detection limits for mono- di- and trimethylarsine are 0.4, 0.2 and 15.0ng arsenic. However, because of the inherent non-linearity of the device, the useful range of electron capture extends only to about 20 to 50 times the detection limit of the analyte (Andreae, 1977).

9.5.2 *Flame ionisation detection*

The flame ionisation detector shows much less sensitivity for MMAA and DMAA than the electron capture device, but has a dynamic range of about five orders of magnitude. It can therefore be used where high concentrations of organoarsenicals would overload the electron capture detector. Andreae (1977) used 25ml/min helium carrier gas, 28ml/min hydrogen, 240ml/min air and 30ml/min helium as an auxiliary. For TMA, it is a more sensitive device than the electron capture detector, giving a detection limit in the order of 1.0ng, although it is less sensitive than electron capture for the detection of MMA and DMA (Andreae, 1977).

9.6 Electro-analytical speciation techniques

This group of techniques has been used extensively in the studies of natural waters. Electro-analytical techniques and their applications include: ion-selective electrodes, polarography, stripping voltammetric studies and amperometric titrations. These are briefly outlined below.

Environmental samples may contain both inorganic and organic arsenic compounds. For the determination of inorganic arsenic compounds by electrochemical methods, the various compounds must be converted to As(V), or preferably As(III) [Greschonig and Irgolic, 1992]. Solid samples and samples containing complex organoarsenicals must first be mineralised using one of the methods described in Section 8.2. Aqueous samples or those containing no complex organoarsenicals need not be digested. As(III) is the preferred oxidation state for electrochemical determinations (usually differential pulse polarography) and so a prereductant is required that will give a quantitative reduction with no products that could interfere with the determination. Several reducing agents are available, including potassium iodide, copper(I) chloride, hydroxylamine, hydrazinium sulphate, sodium sulphite and sulphur dioxide, although for these determinations, best results were achieved using sodium sulphite and sulphur

dioxide in an acidic solution (Greschonig and Irgolic, 1992). If the samples contain arsenic only as As(III) and As(V), then the As(V) may be reduced to As(III) or the As(III) may be oxidised to As(V). The determination of total arsenic may be performed by the polarographic reduction of As(III) or As(V) using any electrochemical technique responsive to these inorganic arsenic compounds. Organoarsenicals may be determined polarographically. This is briefly described in Section 9.6.2.

In addition, these methods are also, like any analytical method, prone to interferences, particularly from heavy metal ions whose reduction signals overlap that of arsenic. Cathodic scans receive problems from metals such as lead(II), tin(II), thallium(III), bismuth(III) and antimony(III); while anodic scans are influenced by elemental mercury or copper. To minimise these effects, attempts are often made to remove the arsenic from the sample prior to analysis. A number of these methods have been described in Chapter 8 and include organic extractions, arsine generation and ion exchange. Naturally occurring organic compounds such as humic, fulvic and amino acids also appear to interfere with the determination of As(III) and total arsenic in surface waters. These may be destroyed by UV irradiation of the acidified samples (Greschonig and Irgolic, 1992).

9.6.1 *Ion-selective electrodes*

Ion-selective electrodes allow the measurement of the activity of free hydrated ions in solution. When the electrode is immersed in the test solution, a potential develops, which should be directly related to the logarithm of the activity of the specific hydrated ion for which the electrode has been constructed and calibrated. Responses can, however, be distorted due to interaction with other ions in the test sample. The detection limits of most commercially available electrodes usually fall in the range 10^{-6}-10^{-7}mol/dm^3, and so generally lack the degree of sensitivity required for arsenic speciation studies. In addition, in many natural systems, a significant proportion of the element of interest may be present as, for example, complexes which will not give a potential to the same degree as a free hydrated ion, and, if As(V) is regarded as electrochemically inactive, then only As(III) would be detected, unless pre-reduction of any As(V) present was carried out.

9.6.2 *Polarography*

This non-destructive technique uses a dropping mercury cathode and a comparably larger nonpolarisable anode immersed in the sample. The dropping mercury cathode consists of a narrow tube through which mercury is slowly passed into the solution so as to form small drops at the end of the tube, which fall away. In this way the cathode can have a small surface area, and always remain clean. A variable potential (generally increasing) is applied to the cell, and a plot of current against potential is made. As each chemical species is reduced at the cathode (in order of their electrode potentials) a step-wise increase in current is obtained, which is in direct proportion to the concentration of that species being reduced. This is dependent upon the initial concentration of the species of interest being relatively low (10^{-4}-10^{-7}mol/dm^3), while the supporting solution should be deoxygenated, and contain an excess of non-reducible electrolyte salt (e.g. KCl). As(V) is electrochemically inactive under conditions used in the electrochemical determination of As(III). If, however, As(V) is dissolved in 11.5mol HCl, then polarographic signals may be obtained, although only at fairly high arsenic concentrations (above 0.004mol/l) [Greschonig and Irgolic, 1992]. As(V) may, however, become electroactive if phenols are added to 2mol/l perchloric acid solutions of As(V), and as a result be determined by this method. The exact mechanism for this activation is not known, although ligation to or condensation of the hydroxyl groups with arsenic acid is the probable cause (Greschonig and Irgolic, 1992).

Organoarsenicals may be determined by polarography, although pH and composition of the supporting electrolyte are critical. Adsorption processes at the electrode surfaces, especially at higher concentrations, make it difficult to measure peak currents reliably and the electrode reactions are irreversible.

Differential pulse polarography is a slight modification on this method, with a small potential pulse being applied for short intervals as the overall potential is being increased steadily. This allows direct measurement of the signal derivative (d*i*/dV) and a plot of this value against applied potential, gives graphs having sharp peaks on a fairly flat baseline. Because polarography is a non-destructive technique, any change in sample concentration may be continuously monitored on the same sample. This has been successfully used to show the oxidation of Fe^{2+}, with time, on recovery of anoxic interstitial waters (Davison et al, 1982). Detection limits for metals, depend on the potential ramp modification used, but generally lie in the range 10^{-5}-10^{-7}mol/dm^3

(Pickering, 1995), although Greschonig and Irgolic (1992) state that As(III) may be determined in the range 20μg/l to 50mg/l.

Aqueous solutions of MMAA and DMAA, may be analysed using this method, but the poor resolution and wave maxima make it unreliable. Neither MMAA nor DMAA are electroactive in non-aqueous media (such as methanol and acetonitrile) because of poor availability of protons. However, if an acid supporting electrolyte such as guanidinium perchlorate is added, then both MMAA and DMAA exhibit well-defined, diffusion-controlled polarographic waves (Elton and Geiger, 1978) although the precise reduction mechanism was unknown. The detection limit for MMAA was not determined in aqueous solution due to the poor resolution, but was in the region of 0.1μg/ml in the non-aqueous media. DMAA was not detectable at concentrations below 3μg/ml in aqueous solution, but detection limits were greatly improved using non-aqueous solvents, with the limit being in the order of 2.5μg/ml. Although the peak potentials of both MMAA and DMAA are sufficiently different in non-aqueous media to allow identification of each acid in pure solutions, simultaneous determination of both acids in these solvents is not possible, hence separation of the species prior to determination is necessary (Elton and Geiger, 1978).

Henry and Thorpe (1980) used this method successfully to determine arsenic after separation of the individual species by ion exchange chromatography. The detection limits were reported as being 18ppb for MMAA, 8ppb for DMAA; no limit was given for As(III). As(V) may be determined using this method if present in the range 20μg/l to 160mg/l, although under certain conditions As(III) will interfere with As(V) determination. Oxidation of the As(III) with chlorine eliminates this interference and allows the determination of total inorganic arsenic as As(V) [Greschonig and Irgolic, 1992]. If a phenol is present (such as D-manitol) then a simultaneous differential-pulse polarographic determination of As(III) and As(V) is possible at As(III) concentrations of 20 to 200μg/m^3 and if As(V) concentrations exceed those of As(III). If these conditions are not fulfilled, then the reduction peaks interfere with each other, giving a difficult interpretation. Differential pulse polarography has also been used successfully to give a linear calibration curve from the detection limit of about 0.4mg/l to 80mg/l for phenylarsonic acid and to 25mg/l for other arylarsonic acids. It has also been reported that the peak potential of alkylarsonic acids increases with increasing numbers of methyl groups, and that this corresponds to a decrease in detection limit

(Greschonig and Irgolic, 1992). These methods are not as sensitive in their detection of organoarsenicals as many of the other methods described in this chapter, and are generally unsuitable for environmental applications.

Square wave polarography gives a detection limit of 1.0-10.0μg/g, whilst differential pulse polarography has an operating range of 0.3μg/l to 50.0mg/l under optimised conditions (Talmi and Bostick, 1975).

9.6.3 *Stripping voltammetric studies*

9.6.3.1 *Anodic stripping voltammetry (ASV)*

In this process, the metal ions of interest are first electro-deposited on a mercury cathode (either a hanging drop or a thin film on an inert carbon electrode), or, in the case of arsenic, platinum and gold electrodes have also been used successfully (Forsberg et al, 1975; Bodewig et al, 1982). One of the advantages of this method is that it can be used to distinguish between As(III) and As(V), since the latter is not electroactive and has to be reduced by chemical means prior to its determination. Care must be taken with the reduction of As(V) to As(III) as a quantitative reduction is desired, and excess reductant or the by-products of the reduction reaction should not interfere with the determination of As(III). Forsberg et al (1975) used a heated acid solution with Na_2SO_3 as a suitable reduction matrix. As(V) has been reduced to elemental arsenic on some electrodes, but poor (high) detection limits, bad reproducibility and low selectivity make it unsuitable for analytical applications (Greschonig and Irgolic, 1992).

The number of metals being deposited can be restricted by varying the magnitude of the applied potential present (Bodewig et al, 1982) used a potential of -0.3V), and the time of the deposition (seconds or minutes) can be varied to suit the concentration of electro-active species (the lower the concentration, the greater the allowed time of deposition. Deposition into the small volume of mercury (the commonest electrode), in the presence of Cu^{2+} or Se(IV) acts as a preconcentration step, despite the short electrolysis periods removing only a small fraction of the element. If a platinum electrode is used, then Cu^{2+} also aids preconcentration. These additions of copper or selenite are necessary due to the otherwise low solubility of elemental arsenic in mercury (Greschonig and Irgolic, 1992); forming mercury selenide with which arsenite reacts to form arsenic selenide which is reduced to arsine, and similarly, copper(II) produces copper arsenide which dissolves in the mercury.

In the second phase of the procedure the potential of the mercury electrode is gradually made more positive, and the deposited metals are stripped out successively in the reverse order of their standard potential. The resultant current flows, recorded as peaks, reflect the amount of electro-reducible species initially present. Greater sensitivity (and flatter baselines) may be achieved by superimposing small pulses of voltage (say 50 mv) across the electrodes during the stripping scan (differential pulse ASV). The size of the peaks can be affected by a number of experimental parameters including the deposition potential used, the rate of stirring, the mercury drop diameter, the prehistory and pre-treatment of platinum or gold electrodes, the pulse frequency, the stripping solution composition, the system pH, the temperature and the presence of dissolved organic matter (Forsberg et al, 1975; Bodewig et al, 1982).

Interferences, as with all determination schemes, also occur with this method. Copper, although in some cases acting to aid preconcentration, has also been reported as being an interferent because in addition to having overlapping oxidation peaks, copper and arsenic strongly combine and in the presence of even a slight excess of copper (in acid mine drainage, for example) greatly reduces electrode response to arsenic (Forsberg et al, 1975). Dissolved organic matter has also been reported as an interferent (Bodewig et al, 1982). Oxygen is also a serious interferent and must be completely removed from the system by nitrogen flushing (Pickering, 1995), although Greschonig and Irgolic (1992), report an earlier study in which oxygen appeared to increase the precision of the determination, and speed up the electrode reactions.

In speciation studies, the ASV method has been used in the following ways:

i) as an analytical technique for determining the total metal content of a sample fraction obtained through sequential extraction;

ii) to discriminate between 'labile' and 'bound' metal species, and

iii) to evaluate the stability of metal complexes present (Pickering, 1995).

The position of the peak on the voltage scan reflects the nature of the ion being reduced, and for complex ions the peak position moves to more negative potentials as stability increases. The ASV technique is mainly used, but not restricted to, the determination of metals that form amalgams with mercury. Detection limits below 10ng/l have been achieved for some metals, although Bodewig et al (1982) report a detection limit for arsenic of about 0.2µg/l for a deposition time of 4 minutes. Greschonig and Irgolic (1992) report the results of two studies which used this method successfully to

determine As(III) in prepared solutions, natural waters (lake and river waters), seawater and wastewater and gave working ranges in the order of 0.15-700µg/l, although they also report a study claiming a detection limit of 0.3ng/l for As(III) in a non-aqueous solution. Forsberg et al (1975) reported an absolute detection limit of 0.002µg/l using gold working electrodes and 0.14µg/l using platinum ones.

9.6.3.2 *Potentiometric stripping voltammetry*

This is similar to the ASV method, but here addition of a known amount of chemical oxidant solution is used to oxidise the metals deposited on the mercury cathode in place of the potential sweep used in ASV. The potential of the system is then monitored as a function of time. Each metal, as it is oxidised, controls the electrode potential for time periods which reflect the amount of that metal originally present. In this method, oxygen does not have to be removed from the system prior to analysis. The detection limit for arsenite, estimated from potential vs time curves, is around 0.3µg/l (Greschonig and Irgolic, 1992).

9.6.3.3 *Cathodic stripping voltammetry*

In this method, an insoluble film (usually the mercury salt of the analyte ion) is deposited on the working electrode by application of a positive potential. This salt is then stripped by the anode being made more positive (a cathodic stripping cycle). Applications include the determination of As(III) in the presence of the higher valency As(V). As(III) has been determined using this method in prepared aqueous samples in the range 0.2-20µg/l (Greschonig and Irgolic, 1992).

9.6.4 *Amperometric titrations and electro-chemical detectors*

In amperometric titrations, a potential is applied across a pair of electrodes, and its value is adjusted so that current flows when either analyte or titrant is present in excess. This method has been used only to a limited extent in speciation studies, and is used more in distinguishing between classes of compounds (without identifying the alkyl groups) in organometallic titrations, due to the relatively high solution concentrations required. Amperometric titration has been used to analyse for total arsenic, with suitable titrants being iodine, morpholine-4-carbodithioate, potassium iodate and potassium permanganate. Errors of 1% and concentration ranges of 0.02-100.0mg/l are common

(Talmi and Feldman, 1975), although Greschonig and Irgolic (1992) give a working range of 1.5-100mg/l.

Electro-chemical detection systems, which measure the current flowing between pairs of electrodes carrying an applied potential, can be used to monitor eluents from chromatography columns. The detector can measure specifics of the mobile phase, such as the number of species undergoing electron transfer reactions, or a more general property, such as electrical conductance. Few applications have been described for inorganic species.

9.7 Microwave-emission spectrometry

The microwave-emission plasma (MEP) or microwave-induced plasma (MIP) spectrometer is a low power excitation source for emission spectrometry. In this measurement technique, used mainly with gas chromatography (GC), the sample is introduced into the excitation source, where it is broken down into atoms which are then excited by the energy of the source and emit radiation. The plasma, a partially ionised gas, is sustained in a quartz torch held in a microwave cavity. The plasma gas may be either helium or argon, although helium is preferred due to its high excitation energy (even though it is low powered), its capability of exciting a wider range of elements and the fact that the plasma can operate at atmospheric pressure rather than at a reduced pressure. In addition, the helium plasma has a better shape, a small torus, for sample introduction (Greenway, 1995).

The wavelength of the radiation emitted is characteristic of the element and the intensity of the radiation is proportional to the concentration of the element present. In the case of arsenic, the emission intensity response, measured as peak height at the 228.8nm resonance line is proportional to the analyte concentration in the range 0.01-1.0µg/ml used in the study by Talmi and Norvell (1975), although the range was later increased to 0.01-20.0µg/ml in a slightly later study (Talmi and Bostick, 1975).

In early work with GC, where packed columns were used, large sample volumes necessitated the use of high levels of solvents, which had to be vented before introduction into the spectrometer. The introduction of capillary columns overcame this problem, however, because the sample size and carrier gas flow rates were more compatible with stable plasma operation. The capillary column could be passed down the heated line and the end of the column placed in the plasma torch just before the

plasma, which prevented any sample loss. Volatile organic impurities can impair the capillary, and periodic cleaning is necessary to ensure no deterioration in performance. Additionally, it was the development of more advanced microwave cavities that allowed helium plasmas to be operated at atmospheric temperature, allowing a simpler interface with the GC column (Greenway, 1995).

Arsenic has been detected using this method (interfaced with GC), using an argon plasma with the emission intensity being measured at 228.8nm (Talmi and Norvell, 1975; Talmi and Bostick, 1975). The detection limit in these cases was approximately 20pg for arsenic, with water samples and solid samples being determined with relative sensitivities of 50ng/l and 30ng/l respectively. Although this detection method appears to be equally sensitive to all arsines, regardless of their molecular structure a single calibration curve cannot be used due to differing collection efficiencies for the various generated arsines (Talmi and Bostick, 1975).

The detection system may make use of either a single channel, detecting one element, or multiple element where a polychromator detects several elements simultaneously. GC-MIP detectors were not popular for many years due to plasma instability and carbon and polymer deposition on the quartz capillary walls, resulting in short life-times. Recently, however, Hewlett Packard have introduced a commercial hybrid GC-MIP system which operates at atmospheric pressure with a helium plasma and is capable of detecting single elements or fixed sets of elements simultaneously.

The limits of detection for GC-MIP are generally an order of magnitude better than for GC-AAS, but the use of capillary columns necessitating small samples is restrictive.

9.8 X-ray fluorescence and atomic fluorescence spectrometry (XRF)

When high energy radiation hits an atom, it can eject an electron from an inner electron shell. An electron from an outer shell can then descend to fill the gap, emitting X-rays as it does so. This X-ray energy corresponds to the energy difference between the shells and each element has a characteristic value. Each element has only one or two X-ray fluorescences strong enough to be detected, and the outer 'bonding' electrons are not affected, so the sample is unaffected by the procedure. However, this method only provides a relative elemental concentration and so the use of calibration standards is essential, and can lead to errors if great care is not taken. It is an excellent multi-element

technique if simple preparation methods for X-ray samples are available. The technique has been applied to arsenic determination in solid samples (maximum sample size is in the order of 10μg) with only simple preconcentration required, but is not sufficiently sensitive for water analysis without the employment of more complex isolation and preconcentration steps (Bostick and Talmi, 1975; Talmi and Feldman, 1975). These methods include evaporation, precipitation, ion exchange and solvent extraction. The relative sensitivity after preconcentration can be in the 20-50ng/l range, although more recent work appears promising. Prange (1996) reports detection limits for arsenic of 20-100ng/l for freeze dried rainwater; 20-3500ng/filter for rainwater; 1.0-3.0μg/l for river water (25μl direct measurement); 3-25mg/kg for HNO_3 digested suspended particulate matter; 5-30mg/kg for HNO_3/HF digested sediment, and 0.1-1.0mg/kg for mussel tissue. Additionally, this method has been applied to the analysis of reference materials and the results show that it is a reliable method for the determination of arsenic. This method shows great promise as an alternative to PIXE in the determination of arsenic sampled using DGT or DET gel samplers (see Section 6.2.5).

9.9 Mass spectrometry

There are a number of mass spectrometric methods of determination used in arsenic analysis. Of these, multiple ion detection and inductively coupled-plasma mass spectrometry are the methods put to most use in speciation studies. Molecular mass spectrometry is another method used for arsenic speciation, but can also provide additional structural information. A general detection limit for arsenic using MS is in the order of 0.0006μg/g (ppm) [Pais, 1994].

9.9.1 *Multiple ion detection (MID)*

Multiple ion detection MS (MID-MS) was used successfully in conjunction with GC to analyse arsines formed by a hydride generation technique (Odanaka et al, 1983). The arseno-hydrides identified using this method were arsine, MMA, DMA and TMA. However, simultaneous determination of all four arsenicals could not be done due to the limited range of detectable mass spectra in the MID system used. The calibration curves generated during analysis are linear for this method in the range 0.2ng/ml to 2000ng/ml As in 50ml aqueous samples, with an absolute detection limit of 30pg for arsine and TMA and 20pg for MMA and DMA. When the arsines have been collected from an

initial 50ml sample in 3ml of heptane (see Section 8.4.5.9 for a description of the method) and 5µl is used for analysis, then the relative detection limits are 0.4ng/ml for inorganic arsenic and TMAO and 0.2ng/ml for MMAA and DMAA (Odanaka et al, 1983).

9.9.2 Inductively coupled-plasma mass spectrometry (ICP-MS)

Inductively coupled-plasma mass spectrometry (ICP-MS), which uses high temperature plasma as an ionisation source, is the most commonly used up to date analytical method where arsenic compounds are found at extremely low concentrations, combining the characteristics of inductively coupled-plasma for atomising and ionising injected material with the sensitivity of mass spectrometry. Since the temperature of the plasma is very high (over 6000K), arsenic compounds are decomposed completely to their constituent ions, which means that the sensitivity of an arsenic compound as arsenic does not depend upon its structure. Thus, when the concentrations of the arsenic compounds as arsenic are the same, then each compound produces the same sensitivity at 75amu, giving the same area on a chromatogram. Any discrepancy from this is likely to indicate a degree of compound decomposition, or a lack of material purity (Kawabata et al, 1994; Inoue et al, 1994). This method has been used with great effect, especially when used in conjunction with a HPLC system (Shibata and Morita, 1989a; Larsen et al, 1993; Le et al, 1994), although LC-HG (Hwang and Jiang, 1994), flow injection-HG (Huang et al, 1995), direct HG (Santosa et al, 1994), ion chromatography (Inoue et al, 1994; Kawabata et al, 1994; Jiang et al, 1994) and ultrasonic nebulisation (Creed et al, 1995a) techniques have also been employed successfully. Indeed, so useful a method for multiple element determination is ICP-MS, that the US-EPA has adopted it as the standard detection method for the analysis of antimony, cadmium, copper, lead, nickel, selenium, silver, thallium and zinc (US-EPA, 1996b, 1996c).

ICP-MS is a relatively new technique, and as such still has a number of operational limitations, particularly when it is realised that in order to achieve accurate, reliable and sensitive results, preconcentration and separation are needed when the concentrations of analysed elements are too small to be determined directly by mass spectrometry, or when matrix effects interfere with the determination (Jiang et al, 1994).

The ultrasonic nebuliser produces a response difference between the As(III) and As(V) oxidation states, with As(III) giving the lower response. This lower response can

be eliminated by the addition of HCl to the sample prior to analysis, although with ICP detection this is not advantageous due to the isobaric or polyatomic interference at the mass-to-charge ratio (*m/z*) of 75 caused by the recombined molecular ion $^{40}Ar^{35}Cl^{+}$ generated by the plasma argon gas (Shibata and Morita, 1989a; Creed et al, 1995a; Larsen et al, 1993; Kawabata et al, 1994; Jiang et al, 1994; Inoue et al, 1994; Francesconi et al, 1994). Interference correction software may compensate for this, but the correction adds variability, resulting in an elevation in detection limit. The response difference can be almost eliminated by the addition of 1µg/l Cl_2 (as sodium hypochlorite) to the sample prior to analysis. This oxidises all the As(III) to As(V), and has the advantage that the amount of Cl_2 added does not adversely effect the variability induced by the $^{40}Ar^{35}Cl^{+}$ correction (Creed et al, 1995a). Addition of a few percent of nitrogen to the argon plasma has also been reported as successfully suppressing the formation of $^{40}Ar^{35}Cl^{+}$ (Larsen et al, 1993; Francesconi et al, 1994), although in the study by Larsen et al (1993) [utilising both anion and cation HPLC], chloride interference was not found to be a problem with the arsenic anions, even though the sample matrix was urine, a substance with a naturally high chloride content. Chloride interference with the cations was not a problem as the chloride was eluted with the void volume from the cation-exchange chromatographic system.

Flow injection incorporating a L-cysteine hydride generation step reduces the $^{40}Ar^{35}Cl^{+}$, interference but only if it utilises a mild HNO_3 condition, not HCl (reported as having been used in Huang and Jiang [1994]). Additionally, the use of L-cysteine reduces the interfering effects of a range of transition metals, notably Ni and Cu. Compared to conventional methods, the deposition of solids (particularly where high salt content samples are being analysed) on the sampling orifice may be minimised if the sample is injected by flow injection. The sample is nebulised directly, without the use of a gas-liquid separator, and this process alone is a very effective way to purge arsine from the liquid carrier (Hwang and Jiang, 1994; Huang et al, 1995). This method gave an absolute arsenic detection limit of 0.6pg, corresponding to a relative value of 3pg/ml (Huang et al, 1995), although Hwang and Jiang (1994) reported detection limits of 11ng/l for As(III), 51ng/l for As(V), 29ng/l for MMAA, and 28ng/l for DMAA, with absolute detection limits in the range of 2.2-10pg.

Ion chromatography, using anion exchange resins (Jiang et al, 1994) allows preconcentration and separation of As(III) and As(V)and also chloride. Care has to be

taken in controlling the pH of the column elution matrix (HNO_3), as nebulisation is difficult with concentrated acids due to their density and viscosity, and matrix effects have been observed when high concentration acids have been nebulised. Jiang et al (1994) achieved a detection limit of 2ng/l using this technique, although $^{40}Ar^{35}Cl^+$ interference can still be a problem. Kawabata et al (1994) and Inoue et al (1994) achieved the separation of 5 arsenic species using anion chromatography, and achieved detection limits of 0.39µg/l for As(III), 0.44µg/l for MMAA, 0.28µg/l for DMAA, 0.25µg/l for TMAO, and 0.22µg/l for AsBe.

Shibata and Morita (1989a), successfully separated 15 arsenic species in artificial samples using ion pairing and gel permeation techniques. Using ICP-MS as the detection system, they achieved absolute detection limits of 20-50pg for the separation of the cations, and anions, and 100-150pg for the larger organoarsenicals separated using gel permeation. The HPLC was connected directly to the ICP-MS nebuliser by way of a short length of Teflon tubing. They then successfully applied this method to a dogfish muscle reference material, resulting in the first report of tetramethylarsonium ion in fish (Shibata and Morita, 1989b). Edmonds et al (1992) used the same method as Shibata and Morita (1989a) but extended it so a further two organoarsenical species could be identified.

Larsen et al (1993), using both anion and cation HPLC as the speciation method, achieved detection limits of 2.3, 2.6, 2.0 and 1.6ng/cm^3 for each of the arsenic anions As(III), As(V), MMAA and DMAA respectively; and 1.5, 0.8, 0.7 and 0.7ng/cm^3 for each of the arsenic cations AsBe, AsC, TMAO and TMA respectively, when the HPLC was connected directly to the ICP-MS nebuliser, again using Teflon tubing.

9.9.3 *Molecular mass spectrometry (MMS)*

Molecular mass spectrometry (MMS) utilises electron impact, chemical ionisation, field desorption ionisation, or neutral atom collision for ionisation. Both field desorption (FD) and fast atom bombardment (FAB) mass spectrometry have played a part in the identification of AsBe in marine organisms, although interfering components and matrix effects in the sample extracts often prevent the acquisition of good quality spectra (Francesconi et al, 1994).

9.10 Neutron activation analysis

In principle, neutron activation analysis (NAA) is a non destructive analytical technique, although radiochemical separation techniques are almost always required to avoid overlapping of various photo-peaks (Talmi and Feldman, 1975), and the need for specialised equipment has limited its use in arsenic analysis (Francesconi et al, 1994; Peters et al, 1996).

The separation schemes are generally based on one, or a combination of distillation, precipitation, cocrystallisation, solvent extraction or ion exchange. Shreedhara Murthy and Ryan (1983), for example, coprecipitated As(V) with hydrous iron (III) oxide. It is also obvious, that if speciation studies are to be undertaken, then separation of the various species is highly desirable *prior* to irradiating the sample.

With the advent of high resolution solid state detectors, it was hoped that a direct instrumental approach would have been possible. Unfortunately, the high activity of ^{24}Na ($t_{1/2}$ = 15h) and ^{81}Br ($t_{1/2}$ = 36h) induced in many environmental samples prevents the determination of arsenic at low (a few ppm) concentrations, because the γ-activity of these samples would have to decay for 4-5 days before measurement. The induced γ-activity of ^{76}As is measured by monitoring the 559KeV photopeak, and because of the short half life of ^{76}As (around 26.5 hours, see Appendix A), must be performed as soon as possible after irradiation (Mok et al, 1986). The 657KeV photopeak for ^{76}As, although much less sensitive, has also been used when matrix interferences are high (Francesconi et al, 1994). NAA has been reported (Talmi and Feldman, 1975) as being one of the most sensitive techniques at that time with a detection limit of 0.1ng using a thermal neutron flux of 10^{12}neut/cm^2/sec. and having accuracy and precision generally in the range of 3-10%. Shreedhara Murthy and Ryan (1983) reported an absolute detection limit for arsenic of 0.06μg, which is in close agreement with the figure of 0.0006μg/g (ppm) suggested by Pais (1994), although Francesconi et al (1994) report detection limits in the region of 0.001μg/l. The method is useful at the sub-ppm concentration level, and requires much smaller sample volumes than techniques such as colorimetry.

For useful speciation results, this method must, however, be combined with one of the previously described speciation systems. Mok et al (1986) used a liquid-liquid extraction procedure followed by back extraction into nitric acid, prior to irradiation, to

separate As(III) from solution. Total arsenic was determined by first reducing all As(V) to As(III), with As(V) subsequently being determined by difference. With the conditions used by Mok et al (1986), they estimated the absolute detection limit to be in the order of 1ng. However, if a preconcentration factor of 20 can be obtained with the liquid-liquid extraction, and a further concentration factor of 5 can be achieved in the back extraction (as reported), then detection limits as low as 0.1µg/l in natural waters could be theoretically obtained.

9.11 Proton-induced X-ray emission

This method involves the detection of characteristic X-rays emitted following inner electron shell bombardment by projectile ions. The technique is analogous to electron probe analysis, but instead of bombarding the material of interest with electrons, more dense protons are used. A complimentary technique, Rutherford backscattering, involves measuring the energy loss of projectile ions recoiling out of the sample following elastic collision with the sample nuclei. The optimum mass resolution for this method occurs for light elements. Whilst these methods have not been directly applied to the determination of arsenic, they have been used in conjunction with thin-film sampling techniques (see Section 6.2.5) to determine iron, manganese and potassium (Davison et al, 1991, 1994; Zhang et al, 1995b) and there seems no reason why this method cannot be utilised in arsenic detection.

9.12 DC discharge spectral emission

In this method, initially described by Braman and Dynako (1968) for detection of mercury and subsequently for arsenic by Braman et al (1972, 1977), arsines are first generated using sodium borohydride. The arsines are swept out of the solution using a helium carrier gas, then through a calcium sulphate drying tube or a NaOH carbon dioxide trap, and through the dc discharge detector. The 228.81nm or 234.98nm arsenic emission line intensity is monitored using a conventional type photometric system (scanning manochromator), and the detection limit is in the order of 1ng (as arsenic), although Sanders and Windom (1980) report absolute detection limits of 0.5ng for As(III) and As(V), and 1ng for the methylarsenicals (using 40ml samples, these give minmum detectable concentrations of 0.01ng/l and 0.03ng/l respectively). Initially, samples were added to a solution containing the $NaBH_4$, and consequently, the solution

pH had to be maintained at neutral to slightly alkaline to prevent decomposition of the $NaBH_4$, so preventing the reuse of the $NaBH_4$ solution for the subsequent analysis (Braman et al, 1972). This initial system did not allow separate arsenic species to be detected, but the simple alteration of adding $NaBH_4$ to the sample solution, and controlling the sample solution pH enables separation of the generated arsines, as described above (Sections 8.4.3.4 and 8.4.5) [Braman et al, 1977]. Concentration limits of detection calculated using 50ml samples range from 0.004 to 0.002ppb (as arsenic). Interferences for this detection method are minimal, but Ag^+ and Cu^{2+} inhibit arsine evolution by 10% or more at concentrations of around 20ppm or greater (Braman et al, 1972, 1977).

Morita et al (1981) also used this method, but found the sensitivity to be about one-fifth that of ICP-AES. Chakraborti et al (1986) used this method in conjunction with liquid-liquid extraction-hydride generation preconcentration steps to successfully gain an absolute detection limit of 0.1-0.3ng of with an actual detection limit of around 0.6ng/l.

9.13 Kinetic methods

In principle, maximum sensitivity in analytical methods involving chemical reactions are those in which the component of interest acts as a catalyst, rather than a reactant (Tarumoto and Freiser, 1975). Arsenic is known to act as a catalyst in the formation of the complex between osmium and thiourea, presumably because the As(III) facilitated the reduction of the Os(VIII)→Os(III), the oxidation state of the osmium in the complex. Osmium is also the catalyst of the redox reaction of bromide-iodide. Arsenic may therefore be determined kinetically as it acts as an auxiliary catalytic agent in the Os-catalysed bromide-iodide reaction in a linear fashion, the concentration of arsenic directly controlling the rate of reaction.

The procedure involves mixing the solution (25ml) containing the As(III) with a mixture of acetate buffer solution (5ml, pH 4.85-5.0), potassium bromate solution (2ml, 0.025M), starch solution (1ml, 1%) and an excess of potassium iodide (in relation to the potassium bromate, 0.25M). The osmium (VIII) [5ml, 10^{-4}M] is added last and thoroughly mixed, the absorbency is measured after about four minutes at 580nm with water as a reference. The arsenic concentration is read from a calibration curve prepared using specific arsenic standard solutions (Tarumoto and Freiser, 1975).

Arsenic (V) behaves differently to As(III), though not sufficiently to allow a reliable determination without prior separation. For the determination of total inorganic arsenic, all As(V) must first be reduced to As(III).

CHAPTER 10

DISCUSSION

The toxicity of arsenic and its long history of use in human culture has resulted in widespread concern about the natural and anthropogenic levels of arsenic in the environment. The location and state of arsenic in the environment is primarily controlled by three major processes: oxidation and reduction, adsorption and precipitation, and methylation and volatilisation (Peters et al, 1996). In aquatic environments these processes are themselves controlled by differences between the temporal and equilibrium concentrations and hydraulic gradients.

The precise mechanisms and pathways involved in the cycling of arsenic in the environment are not fully understood, either on a global macro-scale, or on a much more local micro-scale. The speciation of arsenic has been extensively studied in soils, surface waters and to a lesser extent in groundwaters, freshwater sediments, seawater, marine sediments and estuarine waters. Very little work has been carried out on the chemistry of intertidal sediments or intertidal sediment porewaters, and none with specific regard to arsenic.

It is expected that some sediments within the intertidal zone experience a flushing through with fresh water at low water and are then subjected to a reversal of this flow as the tide floods to a point where they become saltwater saturated. This should be recognised by a change in porewater chemistry, with a change from the Ca^{2+} and HCO^{-} dominated freshwater to the Na^{+} and Cl^{-} dominated seawater. Additionally, at low water there are sediment zones that are unsaturated, which become saturated as the tide floods. As a result, it is expected that through the tidal cycle, both horizontal and vertical variations in Eh and pH will occur causing complex variations in environmental conditions and changes in the relative proportions of numerous important nutrients, metal and organic complexes and inorganic arsenic species present. There is also the probability of detecting various organoarsenical species, both through the degradation of continually deposited and buried organic debris, and by the action of burrowing organisms. It is also recognised that there will be no single model that can be applied to all intertidal sediments, with quieter, low energy salt marsh environments obviously

being easier to sample and monitor compared with high energy open sea sand and shingle beaches.

The adsorption of arsenic on solid phases is related to the chemical speciation which is highly dependent upon pH as well as Eh and microbiological activity. High adsorption of As(V) at low pH is related to electrostatic interactions between the As(V) anions and the solid surface. The adsorption of As(V) is generally higher than that of As(III) and the organoarsenicals. The presence of humic acids can further decrease arsenic adsorption (Xu et al, 1991).

A reduced pH in combination with reducing conditions will enhance the As(III)/As(V) ratio which in turn increases the leaching of arsenic from solid phases to overlying or interstitial waters. A decrease of pH (from 6-7 down to around 4) under oxidising conditions could reduce arsenic concentrations due to an increase in As(V) adsorption by the solid phase. Reduced biological activity due to the decrease in pH would also effect a change in arsenic speciation due to a decrease in organoarsenic formation.

Acidification thus has a complex but significant effect upon arsenic mobility in the environment. Under reducing conditions, the predominance of As(III) over As(V) and the concurrent release of arsenic from iron hydroxides would lead to increased arsenic mobility and dissolved concentrations with decreasing pH. Under oxidising conditions, however, a slight reduction in pH would reduce arsenic mobility due to enhanced adsorption, perhaps coupled with precipitation/coprecipitation with iron. However, a large decrease in pH (to 4 or lower) would enhance arsenic's mobility, even under oxidising conditions (Xu et al, 1991).

The use of Eh/pH diagrams (such as those included in Appendix D), while they provide valuable thermodynamic information, do not permit insight into kinetic and other factors influencing the measurement As(III)/As(V) ratio. Thus, although both iron and manganese oxides should be able to oxidise As(III) to As(V) in freshwater sediments (for example), manganese appears to be the more efficient oxidiser (Oscarson et al, 1981b). The situation is further complicated by the contradictory evidence regarding the apparent redox stability of As(III) and As(V) in aqueous systems (Feldman, 1979; Tallman and Shaikh, 1980). In marine waters especially, both heterogeneous and microbiological factors conspire to control the observed

As(III)/As(V) ratios. These factors are particularly important in determining the arsenic impact upon anthropogenically modified sediments (Reimer et al, 1988).

The biological controls of arsenic speciation are also a complex and involved subject, with different organisms showing different methylating pathways, with different end products. Indeed, while some organisms may use arsenic as a potential energy source, the sole reason for methylation in a wide range of organisms and plants is one of detoxification. The ingestion of organoarsenicals, subsequent methylation or incorporation into metabolic pathways may also result in the formation of quite exotic organic species analogous to known organonitrogen and organophosphorus compounds.

In aquatic systems, many of the organoarsenical species have been identified, either *in-vivo* or as a result of *in-vitro* laboratory experiments. A similar, but slightly reduced number have also been identified in natural waters as dissolved species. The distribution of organoarsenicals in sediment porewaters is another topic for debate, with arguments for in situ methylation and occurrence as a result of biological degradation being put forward with equal enthusiasm. It seems likely that the truth will lie somewhere in the middle!

The seasonality associated with the occurrence of organoarsenic species has been widely researched in marine and estuarine waters, with different organoarsenic species being linked to blooms of different microalgae. Efforts into recognising similar phenomena in freshwaters seem to be very few and far between, with efforts generally being concentrated on the elucidation of the structures of non-$NaBH_4$ reducible marine organoarsenic species.

Toxicological studies are generally aimed at determining the detoxification and/or arsenic assimilatory pathways in mammals and other organisms and plants. These studies (especially those with mammals) are themselves used subsequently in refining the role of arsenic in initiating, promoting or acting in the progression of precancerous cells to malignant cells. Generally, these results have then been applied towards assessing the potential risk associated with inhalation, ingestion or dermal contact with arsenic. There is much debate regarding the application of local epidemiological studies to global risk assessment, most revolving around the differences in lifestyle, age distribution, climatology, activity patters, and dietary habits of those in the study group with those for whom the risk is being calculated.

However, before any of these studies mentioned so far can take place, there must have been experimentation involving the taking of samples and the subsequent analysis of such samples. The initial intention of this study was to investigate the speciation of arsenic in intertidal sediments, consequently, the emphasis on sampling techniques has focused on this area. Due to the lack of literature dealing with the sampling of intertidal sediments for interstitial trace metal sampling, a general review of porewater sampling techniques was made. There are five general methods for the extraction of porewaters from sediments, each with its advantages and disadvantages as set out in Section 6.2.6. Essentially, the problem to be overcome both cheaply, effectively and with minimal disturbance is the insertion and removal of the sampling device from the sediment. These can all be minimised, but the skimping on one may well compromise the efficiency of the others, a 'Catch-22' situation.

Further problems arise when the samples have been procured; they must be transported back to the laboratory for analysis as soon as is practicably possible to minimise temperature, pH and Eh changes that will affect the sample's representativness. It must be remembered that porewater samples cannot be replicated. The preservation of samples may thus involve splitting an already small sample into still smaller samples, each with a different preservation method, so as to allow each sub-sample to be analysed for a (or a limited number of) specific arsenic species. One way around the preservation problem is to analyse on-site, a very expensive option not usually practicable.

Once preserved samples have been transported back to the laboratory, they may then be analysed. It is clear that there is a wide variety of methods for the determination of both total arsenic and the various arsenic species. The problem therefore lies in deciding which method(s) is best suited to the program of study being undertaken. This last comment includes the anticipated arsenic concentration, together with the environment under study, the sampling method used, and to a lesser extent (as it should have no discernible effect upon concentration) the sample preservation method. In the earlier years of speciation studies, it was the lack of instrumental sensitivity which held back investigation into environments with only trace and ultra-trace quantities of arsenic. As time has passed and techniques have improved (with a parallel improvement

in detection limits), so the importance of rigorous laboratory protocols to eliminate potential contamination (be it positive or negative contamination) has come increasingly to the fore. Concurrent with this is the inevitable increase in laboratory costs. The steps involved in thoroughly cleaning all equipment that might come into contact with any samples are described in Section 7.8, which also discusses the choice of materials used in sample container construction. The detection limits for arsenic for a variety of determination methods are set out in Table 10.1. It should be stressed, however, that the detection limits given were generally acquired under optimum operating conditions, a luxury not always available to those dealing with 'real' samples.

Table 10.1. Arsenic detection limits for the various determination methods.

	Absolute detection limit, ng	Detection limit, ng/ml
Colorimetry	1	-
FAAS	25	100-300
GF-ETAAS	0.008-0.03	0.6-2.0
Electron capture[4]	0.2-15	-
FID[4]	1.0	-
Polarography	-	0.02-20
ASV	-	100
DC Emission[8]	0.1-0.3	0.6
XRF[5]	-	0.02-0.05
DCP-AES[1]	500	2.5ppm
ICP-AES[1]	2.6	0.1
F-AES[2]	0.5-1.0	-
MIP-AES[3]	20	0.03-0.05
MIP[6]	0.02-0.03	0.2-0.4
ICP-MS[7]	0.0006	0.03
MS	0.06	-
NAA	0.1-0.6	-
Atomic fluorescence	-	100

From Fergusson, 1990; [1]Morita, 1981; [2]Braman et al, 1977; [3]Bostick and Talmi, 1975; [4]Andreae, 1977; [5]Talmi and Bostick, 1975; [6]Odanaka et al, 1983; [7]Huang et al, 1995; [8]Chakraboti et al, 1986.

Additionally, with time considerable improvements have evolved in the various speciation schemes described in Chapter 8. Early methods of speciation merely distinguished between the two oxidation states of inorganic arsenic. Later methods determined simple methylated arsenic compounds in addition to inorganic arsenic. More recently, work has been directed towards quantifying more complex arsenic compounds that occur mainly in marine organisms (Francesconi et al, 1994), with the identification of so-called 'hidden' or refractory arsenic compounds now being at the fore of arsenic research.

Detection of methylated arsenic species can be dependent on a variety of factors including salinity, temperature, nutrient availability, and plant species present in the water (Comber and Howard, 1989; Millward et al, 1993). A brief comparison of detection limits for various systems is set out in Table 10.2.

Table 10.2. Techniques for measuring organoarsenic compounds.

Technique	Detection limit (ng/l)
HG-AES	4-20
HG-GC-EC/FID	2-4
HG-AAS	10-100
FI-ICP-MS[1]	28
HPLC-AAS	50,000

Based on Turner, 1984; [1]Hwang and Jiang, 1994.

The past and continuing research into the cycling of arsenic in the environment is an extremely important one if engineers are to have any chance in successfully remediating soils or water bodies that have in the past, or might in the future, be contaminated by arsenic or some compound of arsenic.

Inorganic arsenicals were banned from use on nearly all vegetable and agronomic crops in the United States in 1968 (Walsh and Keeney, 1975). Since then, several ways have been sought to restore arsenic contaminated soils to their optimal levels of production. Concurrent with this has been a large amount of research into methods of safely removing arsenic from water systems, particularly those used for potable water supply.

There are four primary categories into which arsenic removal techniques may be classified. These include oxidation, precipitation/coagulation, ion exchange, and adsorption. As will become clear, oxidation of As(III) to As(V) is a necessary precursory step regardless of chosen method (Peters et al, 1996). There is an underlying assumption in the literature that organoarsenicals will not be encountered in groundwater, although the potential exists (see Section 4.6). Consequently, there is no information regarding large scale removal of organoarsenical species from water. It is generally accepted that the remediation of aquifers contaminated with reactive chemicals is mechanistically difficult, largely due to rate-limited adsorption and desorption (Kuhlmeier, 1997), which result in very slow removal of arsenic from aquifer solid phase.

Water remediation

Oxidation

Due to the slow kinetics of the As(III)/As(V) oxidation reaction described in Section 4.5, the usefulness of this approach to large scale water treatment is severely limited (Peters et al, 1996). The effective removal of arsenic from water requires the complete oxidation of As(III), especially if the drinking water standard is low. There are various means of oxidation available, but in drinking water treatment, there are important considerations such as the limited list of chemicals, the residuals of the oxidants, oxidation of by-products, and the oxidation of other water constituents (Jekel, 1994). Catalytic methods successfully used include activated carbon, and UV irradiation. In the oxidation process with dosing of chemicals, effective oxidants include free chlorine, hypochlorite, ozone, permanganate and hydrogen peroxide/Fe^{2+} (Fenton's reagent). All of these methods, however, have their individual drawbacks. For example, UV irradiation requires large amounts of power and chlorine and ozone both produce undesirable by-products with natural organic matter (Jeckel, 1994; Peters et al, 1996).

Precipitation/coagulation

The common use of aluminium and ferric salts in drinking water treatment is primarily for coagulation of particles and colloids in the water. Both metal salts undergo hydrolysis to various products, but can be reduced to a very low level if the poorly soluble hydroxides are formed at the correct pH, and can be filtered off completely. Dissolved substances can also be bound to the precipitate by adsorption or coprecipitation (Jekel, 1994). Arsenic removal by metal ions is the best known and most frequently used technique. Best removal conditions for arsenic are with ferric ions and arsenic as As(V) at a pH of below 7.2 to 7.5. Less than 2ppm added ferric ions will remove more than 95% (initial concentration about 135ppb) of the arsenic present if As(III) is oxidised, by chlorination for example (Jekel, 1994). The use of aluminium ions (as Al^{3+}) is almost as effective at a pH of between 6 and 7, with 80-90% removal of arsenic as As(V). Aluminium precipitation will not remove As(III) from solution, necessitating an oxidation step, prior to aluminium addition (Jekel, 1994).

Lime treatment (water softening) to reduce or remove carbonate hardness is another efficient As(V) removal process, especially if the pH is above 10.5, with the majority of As(III) being removed if the pH exceeds 11. The mechanism of removal may

be adsorption onto calcium carbonate and magnesium hydroxide, or it may be a direct precipitation of calcium arsenate, similar to the phosphate precipitation that occurs under the same conditions (Jekel, 1994).

Adsorption

Activated aluminium oxide is a commercially available porous oxide, which, when used as a filter shows much promise as a tool in large scale water treatment due to the high volumes of water that can be treated before renewal, or regeneration with dilute NaOH (Jekel, 1994; Peters et al, 1996). The optimum pH for As(V) removal is in the order of 5.5 to 6, as the aluminium oxide is protonated, but the anions of the acid added (to lower the pH) are not yet competitors in adsorption. As(III) will not be removed from solution using this method, and the presence of competing anions such as phosphate, sulphate and fluoride will diminish the efficiency of the system.

Amorphous ferric hydroxide has been shown, on laboratory scale, to be a more effective adsorptive material, with capacities 3 to 10 fold greater than activated aluminium oxide. Again, the adsorption is much more efficient for As(V) than for As(III), but there are no granular activated ferric oxides with high specific surface on the market (Jekel, 1994).

Other adsorbents that have been suggested for arsenic removal include activated carbon, powdered coal, crushed coconut shells, and sand (Jekel, 1994; Peters et al, 1996).

Ion exchange

Anion exchange resins have been used with some success for the removal of As(V), As(III) is not retained, however. The difference in retention between the two inorganic arsenic species is so pronounced that it has been used as a separatory tool in analytical studies (see Section 8.4.2.2). Chelating resins (see Section 8.4.2.3) have also been used with some success for both As(III) and As(V), but optimum pH for effective removal is different for each species [pH 3-6 for As(V); pH 8-9 for As(III)]. This last problem is the real stumbling block when trying to apply this method on the large scale (Jekel, 1994; Peters et al, 1996).

Soil remediation

Many workers have used soil amendments with iron, aluminium, or calcium compounds to overcome high arsenic levels in soils. However, the success of ameliorating arsenic phytotoxicity varies from soil to soil, the pH of the soil under investigation being of prime importance, as it controls the stability of many metal arsenate complexes (Sadiq et al, 1983).

Molar P/As ratio

The addition of sufficient phosphate to the system should, in theory, depress the uptake of arsenate by plants. This has been shown to be a viable option in laboratory studies, with a molar P/As ratio of at least 5 required to protect wheat from arsenic toxicity. In practice, however, other problems may ensue. If the soil being treated has a high capacity for phosphate, then the amount of available phosphate may not increase appreciably. A worse situation may arise if the phosphate displaced sorbed and previously unavailable arsenic, resulting in increased arsenic toxicity (Walsh and Keeney, 1975).

Addition of Fe or Al compounds

Since arsenic is sorbed by the iron and aluminium components of soils, then addition of iron and/or aluminium salts is another approach. The addition of iron sulphate or ferrous sulphate (5 to 10 tonnes/ha.) have been reported as reducing arsenic toxicity, while the addition of aluminium sulphate occasionally actually increased toxicity (Walsh and Keeney, 1975).

Cultural practices

Deep ploughing results in the dilution of arsenic through soil mixing, and exposing more sites for arsenic fixation. Similarly, the growing of arsenic tolerant plant species such as rye and Sudan grass and subsequently ploughing the crop under has the same effect (Walsh and Keeney, 1975).

Leaching

In soils where phosphate desorbs arsenate, then deliberate leaching will wash the arsenic down into the soil, away from plant root zones. Other potential leaching agents might include chelating agents such as humic acids, although with compounds such as these, all ions capable of binding with such agents will be stripped from the soil. In addition, there may be more of a compound with a stronger affinity for binding with a humic acid in the soil than arsenic. A major drawback of this idea, however, is the potential for underlying aquifer contamination (Walsh and Keeney, 1975).

The observation that arsenic solubilisation is enhanced at both high and low pH, and under reducing conditions is significant (see Chapter 4). On a regional scale, acid rain is probably an important factor affecting the mobility of arsenic and other metals (Mok and Wai, 1994). In the case of acid mine drainage treatment, the use of excessive quantities of lime to reduce the waters' pH, is not necessarily a good idea either, due to the potential arsenic release from sediments which come into contact with the high pH treated waters. Anaerobic conditions also lead to much higher arsenic concentrations [(principally as As(III)], than under aerobic conditions. It is therefore considered that conditions of high Eh and near neutral pH should be maintained when protection against arsenic solubility and mobilisation from arsenic containing wastes is required (Mok and Wai, 1994).

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APPENDIX A

PROPERTIES OF ARSENIC

Sources (unless otherwise stated): Rochow, 1966; Powell and Timms, 1974; Tennent, 1983; Montgomery and Welkom, 1989; Daintith, 1990; Fergusson, 1990.

Arsenic: Atomic No.: 33

Atomic mass: 74.992

Moh hardness: 3.5

Density: 5.73g/cm^3

Isotopes: ^{76}As, Half life 26.8 hours (other values include: 26.5 hrs. (Talmi and Feldman, 1975), 26.3 hrs. (Shreedhara Murthy and Ryan, 1983); 26.4 hrs. Mok et al, 1986).

Electron configuration: $1s^1\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4$

First ionisation energy: 946.57kJ/mol

Second ionisation energy: 1797.90kJ/mol

Third ionisation energy: 2736kJ/mol

Where the ionisation energy is the enthalpy change for the process:

$$A_{(gas)} \rightarrow A^+_{(gas)} + e^- \quad \text{or} \quad A^+_{(gas)} \rightarrow A^{2+}_{(gas)} + e^-$$

Atomisation energy: 302kJ/mol

Electron affinity: ~60kJ

Where the electron affinity is defined as the enthalpy change when the A^- atom losses an electron:

$$A^- \rightarrow A_{(gas)} + e^-$$

Allred-Rochow type electronegativity: 2.20

Pauling type electronegativity: 2.00

Electronegativity is a measure of the relative attractive power for electrons of the atoms forming a chemical bond. This may be taken as being in proportion to the arithmetic mean of its ionisation energy and electron affinity, or they may be derived from atomic radii and Coulomb's law. In the Pauling method an empirical equation using

the electronegativities of the two atoms forming the bond is used for the derivation. Low values indicate the element loses electrons easily, gaining them with difficulty, while the reverse is true for elements with high electronegativities. The closer the electronegativities of two elements forming a compound, the more covalent the bonding between them will be.

Atomic radius: 139pm (10^{-12}m)

Covalent radius: 121pm

Trivalent state covalent radius: 58pm

Pentavalent state covalent radius: 46pm

Trivalent state ionic radius: 58pm

Pentavalent state ionic radius: 46pm

van der Waals radius: 200pm

The size of an atom should be considered in terms of both bonding and non-bonding situations. Half the length of a single bond A-A is equal to the bonding or covalent radius of the atom A. Half the distance of the closest approach of one atom to another in the solid element, where no chemical bonding takes place between these two atoms, is equal to the non-bonding or van der Waals radius of A.

Arsenic is stable in four oxidation states: -3, 0 +3, and +5 under Eh conditions occurring in aquatic systems. Arsenic metal is rarely found and As^{3+} only occurs under extremely reducing conditions. In addition, realgar (a covalent compound AsS) and orpiment (As_2S_3) are stable at low pH and moderately reducing conditions.

Melting points of arsenic compounds

Table A1. Melting points of various arsenic compounds.

Molecular Form	Melting Point °C
As (elementel)	814 (36 atm); 1090 (28 atm)
MMAA	160-161
DMAA	199-200
AsBe	203-210[1]
TMA	-87[2]
AsF_3	-8.5[3]
AsF_5	-80[3]
$AsCl_3$	-18[3]
As_2O_3	315[3]
As_2O_5	315dec.[3,4]
AsH_3	-113.5[3] 116.3[4]
As_4O_6	278[2] 193sbl.[4]

Dietz and Perez, (1976); [1]Edmonds et al (1977); [2]Fergusson (1990); [3]Rochow (1966); [4]Daintith (1990).

Boiling points of arsenic compounds

Table A2. Boiling points of various arsenic compounds.

Molecular Form	Boiling Point °C
As (elemental)	613subl.
Arsine AsH_3	-55 [1,2,5,6]
MMA CH_3AsH_2	2[1] -2[2]
DMA $(CH_3)_2AsH$	35.6[1] 36[2]
TMA $(CH_3)_3As$	70 50[3]
Phenylarsine $C_6H_5AsH_2$	148
As_2O_3	457.2[4]
AsF_3	63[5]
AsF_5	-53[5]
$AsCl_3$	130[5]
As_2O_3	193subl.[5]

Braman et al (1977); [1]Crecelius et al (1986); [2]Talmi and Bostick (1975); [3]Fergusson (1990); [4]Powell and Timms (1974); [5]Rochow (1966); [6]Daintith (1990).

Dissociation constants of arsenic species

In an aqueous solution, an acid (HA) will dissociate into an anion (A^-) and a hydrogen ion (H^+), and may be represented by the following equation:

$$HA_{(aq)} \leftrightarrow H^+ + A^-$$

At equilibrium, the ratio of the products (ions) to the reactant (non-ionised electrolyte) may be represented by the following equation:

$$K_a = \frac{[H^+][A^=]}{[HA]}$$

Where K_a is the dissociation constant. This expression shows that K_a increases if there is an increase in ionisation and vice versa. A strong acid such as HCl ionises readily and has a large K_a, whereas a weak acid such as benzoic acid ionises to a lesser extent and so has lower K_a. The dissociation constant is usually expressed as pK_a, which is:

$$pK_a = -\log_{10}K_a$$

When the pH of a solution and the pK_a are equal, 50% of the acid will have dissociated into ions. While it would seem that dissociation constants would remain

'constant' there seems to be some variation in their exact values, as may be seen in the examples below, although many of these are not the result of original work aimed specifically at determination of dissociation constants, and many researchers have simply cited other work. Unless stated, it is assumed that these values refer to 25°C.

Arsenic acid [(As(V): H_3AsO_4]

Table A3. Dissociation constants for arsenic acid.

pk_{a1}	pk_{a2}	pk_{a3}	Reference
2.5	7.2	12.5	Powell and Timms (1974)
2.25	-	-	Braman et al (1977)
2.19	6.94	11.50	Onishi (1978)
2.24	6.94	11.50	Sadiq et al (1983)
3.60	7.26	12.47	Lemmo et al (1983)
2.25	7.25	12.30	Aggett and Kadwani (1983)
2.2	6.9	11.5	Cullen and Reimer (1989)
3.60	7.26	12.47	Blank et al (1989)
2.20	6.97	11.53	O'Neill (1990)
2.2	6.9	11.5	Korte and Fernando (1991)
2.26	-	-	Yokoyama et al (1993)
2.19	6.94	11.50	Jekel (1994)
2.20	6.97	11.53	Bowell et al (1994)
2.24	7.04	11.50	Lumsdon and Evans (1995)

Arsenous acid [As(III): H_3AsO_3]

Table A4. Dissociation constants for arsenous acid.

pk_{a1}	pk_{a2}	pk_{a3}	Reference
9.2	12.0	-	Powell and Timms (1974)
~9	-	-	Dietz and Perez (1976)
9.23	-	-	Braman et al (1977)
9.22	-	-	Onishi (1978)
9.23	12.13	12.71	Sadiq et al (1983
9.21	-	-	Lemmo et al (1983)
9.21	12.1	13.4	Cullen and Reimer (1989)
9.22	12.13	13.40	O'Neill (1990)
9.2	-	-	Korte and Fernando (1991)
9.2	12.1	12.7	Xu et al (1991)
9.2	-	-	Yokoyama et al (1993)
9.23	-	-	Larsen et al (1993)
8.78	-	-	Inoue et al (1994)
9.20	-	-	Jekel (1994)
9.22	12.13	13.40	Bowell et al (1994)
9.29	-	-	Lumsdon and Evans (1995)

Monomethylarsonic acid [MMAA: $CH_3AsO(OH)_2$]

Table A5. Dissociation constants for MMAA.

pk_{a1}	pk_{a2}	Reference
3.61	8.24	Hiltbold (1975)*
3.60	-	Dietz and Perez (1976)
2.60	-	Braman et al (1977)
4.26	8.25	Aggett and Kadwani (1983)
4.1	8.7	Lemmo et al (1983)
4.19	8.77	O'Neill (1990)
3.6	8.2	Xu et al (1991)
4.1	8.7	Korte and Fernando (1991)
4.19	8.77	Bowell et al (1994)
3.60	8.22	Bowell (1994)

*at 18°C

Dimethylarsonic acid [DMAA: $(CH_3)_2AsOOH$]

Table A6. Dissociation constants for DMAA.

pk_{a1}	Reference
6.19	Hiltbold (1975)
6.2	Dietz and Perez (1976)
6.19	Braman et al (1977)
6.25	Aggett and Kadwani (1983)
6.2	Lemmo et al (1983)
6.27	O'Neill (1990)
6.2	Xu et al (1991)
6.2	Korte and Fernando (1991)
6.27	Bowell et al (1994)
6.20	Bowell (1994)

Arsine [AsH_3]

Table A7. Dissociation constant for arsine.

pk_{a1}	Reference
19.0	Powell and Timms (1974)

Phenylarsonic acid [(As(V): $C_6H_5AsO(OH)_2$]

Table A8. Dissociation constant for phenylarsonic acid.

pk_a	Reference
3.59	Braman et al (1977)

Free energies of formation of arsenic compounds

Changes in Gibbs free energy, ΔG, are useful in indicating the conditions under which a chemical reaction will occur. If a ΔG is positive, the reaction will only occur if energy is supplied to force it away from the equilibrium position (i.e. when $\Delta G = 0$). If ΔG is negative, the reaction will proceed spontaneously to equilibrium. The value of ΔG for the formation of unit amount of a compound from its elements, with all the components in their standard states is then called the standard molar Gibbs function of formation of that compound, and written $\Delta G_f°$.

Table A9. Free energies of formation $\Delta G_f°$ for various arsenic compounds.

Reference		Rochow (1966).	Ferguson and Gavis (1972)	Fergusson (1990)	Bowell et al (1994)
Species	**State**	**$\Delta G_f°$ (kcal/mol)**	**$\Delta G_f°$(kcal/mol)**	**$\Delta G_f°$(kcal/mol)**	**$\Delta G_f°$(kcal/mol)**
H_3AsO_4	aq.	-	-184.0	-183.7	-183.8
$H_2AsO_4^-$	aq.	-	-181.0	-178.8	-178.9
$HAsO_4^{2-}$	aq.	-	-171.5	-168.9	-169.0
AsO_4^{3-}	aq.	-	-155.8	-151.9	-152.0
H_3AsO_3	aq.	-	-154.4	-152.8	-152.9
$H_2AsO_3^-$	aq.	-	-141.8	-140.3	-140.4
$HAsO_3^{2-}$	aq.	-	-125.3	-	-125.31
AsO_3^{3-}	aq.	-	-	-	-107.0
$HAsO_2$	aq.	-	-	-96.2	-
AsO_2^-	aq.	-	-	-83.6	-83.7
AsO^+	aq.	-	-	-39.1	-
$HAsS_2$	aq.	-	-11.61	-	-
AsS_2^-	aq.	-	-6.56	-	-
AsS	s.	-	-16.81	-	-
As_2S_2	c.	-	-	-32.1	-
As_2S_3	s.	-	-40.25	-40.3	-
As	s.	-	0	-	0
AsH_3	aq.	-	23.8	-	-
AsH_3	g.	-	16.5	-	-
AsH_3	-	43.5	-	-	-
As_2O_3	s.	-	-140.8	-	-275.36
As_2O_3	-	147.9	-	-	-
As_2O_5	s.	-	-186.9	-184.5	-
As_2O_5	-	217.9	-	-	-
As_4O_6	c.	-	-	-275.2	-
$AsCl_3$	liq.	-	-	-61.4	-
$AsCl_3$	-	72.4	-	-	-

The data of Fergusson (1990) was converted from kJ using 1kJ/mol = 0.2389kcal/mol (Tennent, 1983)

Reduction reactions of arsenic compounds

Table A10. E° values for various redox reactions of arsenic compounds.

Reaction	E° (Volts at 25°C
$H_3AsO_4 + 3H^+ + 2e^- \leftrightarrow AsO^+ + 3H_2O$	0.550
$H_3AsO_4 + 2H^+ + 2e^- \leftrightarrow HAsO_2 + 2H_2O$	0.560
$H_3AsO_4^- + 3H^+ + 2e^- \leftrightarrow HAsO_2 + 2H_2O$	0.666
$HAsO_4^{2-} + 4H^+ + 2e^- \leftrightarrow H_2AsO_2 + 2H_2O$	0.881
$HAsO_4^{2-} + 3H^+ + 2e^- \leftrightarrow AsO_2^- + 2H_2O$	0.609
$AsO_4^{3-} + 4H^+ + 2e^- \leftrightarrow AsO_2^- + 2H_2O$	0.977
$As_2O_{3(s)} + 6H^+ + 6e^- \leftrightarrow 2As + 3H_2O$	0.234
$As_2O_{3(s)} + 10H^+ + 10e^- \leftrightarrow 2As + 5H_2O$	**0.429**
$As_2O_{5(s)} + 10H^+ + 10e^- \leftrightarrow 2As + 5H_2O$	0.429
$As_2O_{5(s)} + 4H^+ + 4e^- \leftrightarrow As_2O_{3(s)} + 2H_2O$	0.721
$AsO^+ + 2H^+ + 3e^- \leftrightarrow As + H_2O$	0.254
$HAsO_2 + 3H^+ + 3e^- \leftrightarrow As + 2H_2O$	0.248
$AsO_2^- + 4H^+ + 3e^- \leftrightarrow As + 2H_2O$	0.429
$AsO_4^{3-} + 8H^+ + 5e^- \leftrightarrow As + 4H_2O$	0.648
$2\ H_3AsO_4 + 4H^+ + 4e^- \leftrightarrow As_2O_{3(s)} + 5H_2O$	0.580
$2H_2AsO_4^- + 6H^+ + 4e^- \leftrightarrow As_2O_{3(s)} + 5H_2O$	0.687
$2HAsO_4^{2-} + 8H^+ + 4e^- \leftrightarrow As_2O_{3(s)} + 5H_2O$	0.901
$2AsO_4^{3-} + 10H^+ + 4e^- \leftrightarrow As_2O_{3(s)} + 5H_2O$	1.270
$As + 4H^+ + 3e^- \leftrightarrow AsH_{3(g)}$	-0.608
$O_2 + 4H^+ + 4e^- \leftrightarrow H_2O$	1.229
$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$	-0.826

Lemmo et al (1983). The equation in bold appears as it does in the original reference.

APPENDIX B

ARSENIC COMPOUNDS

Inorganic Arsenic Acids

$HAsO_2$ or H_3AsO_3

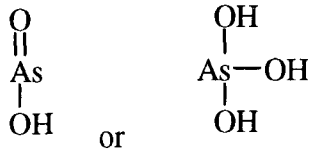
Name and arsenic oxidation state:

Arsenous acid As(III)

$HAsO_2$: Dietz and Perez, 1976; Lemmo et al, 1983; Aggett and Kadwani, 1983; Korte and Fernando, 1990.

H_3AsO_3: McBride and Wolfe, 1971; Yokoyama et al, 1993.

Structural formula:

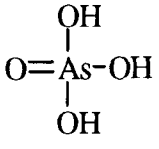


$HAsO_3$ or H_3AsO_4

Name and arsenic oxidation state:

Arsenic acid As(V)

Structural formula:



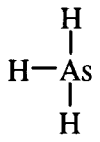
Arsenic Hydrides and Oxides

AsH_3

Name and arsenic oxidation state:

Arsine As(-III)

Structural formula:

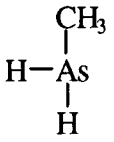


CH_3AsH_2

Name and arsenic oxidation state:

Monomethylarsine (MMA) As(III)

Structural formula:

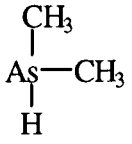


$(CH_3)_2AsH$

Name and arsenic oxidation state:

Dimethylarsine (DMA) As(III)

Structural formula:



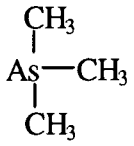
Spontaneously combustible (Peoples, 1975).

$(CH_3)_3As$

Name and arsenic oxidation state:

Trimethylarsine (TMA) As(III)

Structural formula:

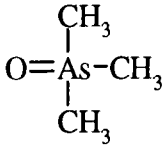


$(CH_3)_3As^+\text{-}O^-$

Name and arsenic oxidation state:

Trimethylarsine oxide (TMAO) As(V)

Structural formula:



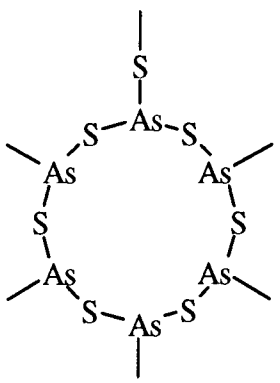
Sulphides

As_2S_3

Name and arsenic oxidation state:

Orpiment As(III)

Structural formula:

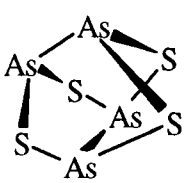


As_4S_4

Name and arsenic oxidation state:

Realgar As(II)

Structural formula:



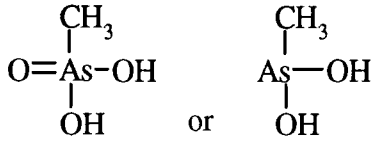
Common Methylarsenicals

$CH_3As^{V}O(OH)_2$ or $CH_3As^{III}(OH)_2$

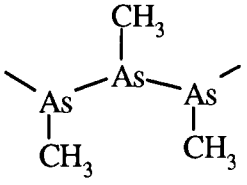
Name and arsenic oxidation state:

Methane arsinic acid	As(III)	Matisoff et al, 1982.
Methylarsonous acid	As(III)	Thompson, 1993.
Methylarsenic acid	As(III)	Wood, 1974.
*Monomethylarsonous acid	As(III)	Hasegawa et al, 1994.
Monomethylarsonic acid	As(III)	Holm, et al, 1979; Lemmo et al, 1983; Welch et al, 1988;Szpunar-Lobinska et al, 1995.
Methanearsonic acid	As(V)	Ferguson and Gavis, 1972; Elton and Geiger, 1978; Holm et al, 1979; Pontius et al, 1994.
Methylarsonic acid	As(V)	McBride and Wolfe, 1971; Cox, 1975; Dietz and Perez, 1976; Braman et al, 1977; Andreae, 1978, 1983; Cullen and Reimer, 1989; Morita and Edmonds, 1992; Thompson, 1993; Edmonds et al, 1993.
*Monomethylarsonic acid	As(V)	Talmi and Bostick, 1975; Yamamoto, 1975; Andreae, 1977; Iverson et al, 1979; Aggett and Kadwani, 1983; Reimer, 1989; Howard and Comber, 1992; Riedel, 1993; Davis et al, 1994; Hasegawa et al, 1994.
Monomethylarsenic acid	As(V)	Millward et al, 1993.
(Mono)Methylarsonoate	Protonated As(V), ($CH_3AsO(OH)O^-$)	Cox, 1975; Morita et al, 1981; Andreae, 1983; Cullen and Reimer, 1989; Larsen et al, 1993 Aurillo et al, 1994; Mok and Wai, 1994.

Structural formula:



As(V) As(III)



Methylarsonous-acid anhydride
$(CH_3AsO)_x$

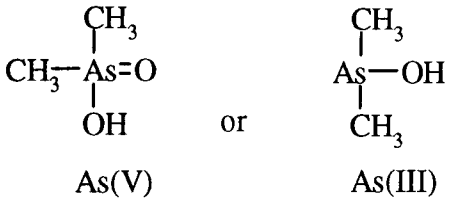
$\underline{(CH_3)_2As^{V}OOH \text{ or } (CH_3)_2As^{III}OH}$

Name and arsenic oxidation state:

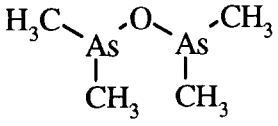
*Dimethylarsinic acid	As(I)	Holm et al, 1979.
	As(III)	Welch et al, 1988; Szpunar-Lobinska et al, 1995.
	*As(V)	Cox, 1975; Talmi and Bostick, 1975; Andreae, 1977, 1978, 1983; Elton and Geiger, 1978; Iverson et al, 1979; Matisoff et al, 1982; Odanaka et al, 1983; Aggett and Kadwani, 1983; Cullen and Reimer, 1989; Reimer, 1989; Howard and Comber, 1992; Edmonds et al, 1993; Riedel, 1993; Davis et al, 1994; Hasegawa, 1994.
Dimethylarsenic acid	As(V)	McBride and Wolfe, 1971; Wood, 1974; Braman et al, 1977; Morita and Edmonds, 1992.
Cacodylic acid	As(V)	Ferguson and Gavis, 1972; Wood, 1974; Yamamoto, 1975; Dietz and Perez, 1976; Holm et al, 1979; Pontius, 1994.

Hydroxydimethyl arsine oxide	As(V)	Yamamoto, 1975; Dietz and Perez, 1976; Holm et al, 1979.
Hydroxydimethylarsinic acid	As(?)	Pontius, 1994.
*Dimethylarsenous acid	As(III)	Hasegawa, 1994.
Dimethylarsinate	Protonated As(V), $[(CH_3)_2AsO(O^-)]$	Yamamoto, 1975; Cox, 1975; Morita et al, 1981; Andreae, 1983; Cullen and Reimer, 1989; Larsen et al, 1993; Aurillo et al, 1994; Mok and Wai, 1994.

Structural formula:



As(V) or As(III)

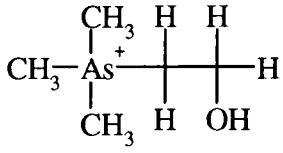


Tetramethylarsinous-acid anhydride
As(III)

$\underline{(CH_3)_3As^+(CH_2)_2OH}$

Name and arsenic oxidation state:

Arsenocholine (AsC)	As(V)

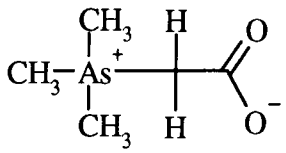


$(CH_3)_3As^+CH_2OO^-$

Name and arsenic oxidation state:

Arsenobetaine (AsBe) As(V)

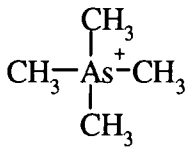
Trimethylarsinoacetate As(V)



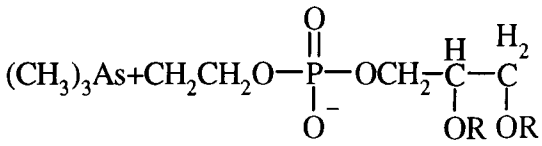
$(CH_3)_4As^+$

Name and arsenic oxidation state:

Tetramethylarsonium ion As(V)

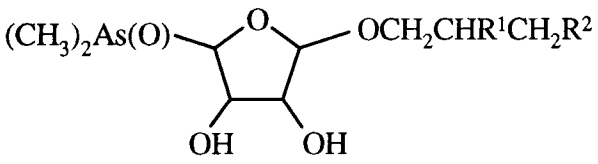


Arsenolipids



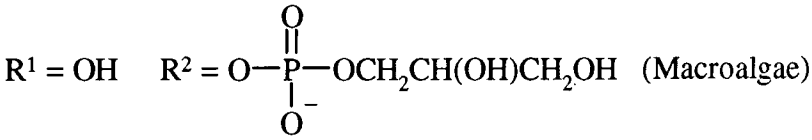
R = H (Glycerylphosphorylarsenocholine)
R = $CO(CH_2)nCH_3$ (Phosphatidylarsenocholine)

Dimethylarsenoribosides

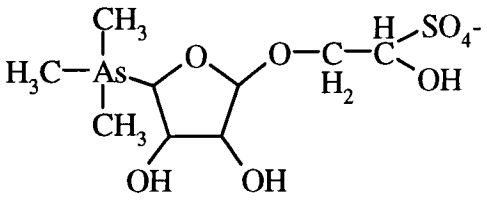


Where

$R^1 = OH$	$R^2 = SO_3H$	(Macroalgae)
$R^1 = OH$	$R^2 = OH$	(Giant clams and algae)
$R^1 = OH$	$R^2 = OSO_3H$	(Giant clams and *Hizikia fusiforme*)
$R^1 = NH_2$	$R^2 = SO_3H$	(*Hizikia fusiforme* only)
$R^1 = OH$	$R^2 = OC(O)CH_2CH_2(CH_2)_{12}CH_3$	(*Undaria pinnatifida*)



(Macroalgae)



(*Sargassum thunbergii*)

Chemical Warfare Agents

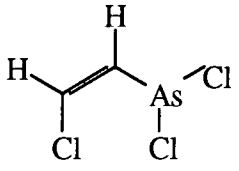
$C_2H_2AsCl_3$

Name and arsenic oxidation state:

Lewisite As(III)

(2-chloroethenyl)arsonous dichloride; β-chlorovinyldichloroarsine; L.

Structural formula:



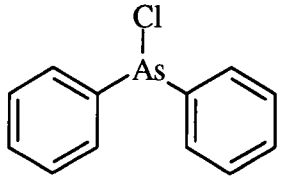
$(C_6H_5)_2AsCl$

Name and arsenic oxidation state:

Diphenylchloroarsine As(III)

DA; Clark I; diphenylarsonous chloride.

Structural formula:



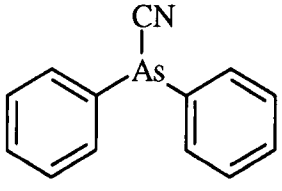
$(C_6H_5)_2AsCN$

Name and arsenic oxidation state:

Diphenylcyanoarsine As(III)

DC; Clark II; diphenylarsonous cyanide.

Structural formula:



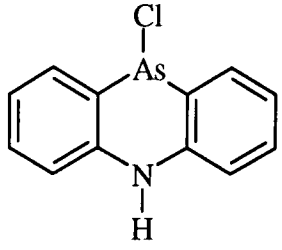
$C_{12}H_9AsClNH$

Name and arsenic oxidation state:

10-chloro-5, 10-dihydrophenarsazine As(III)

DM; Adamsite.

Structural formula:



Medicinal Organoarsenicals

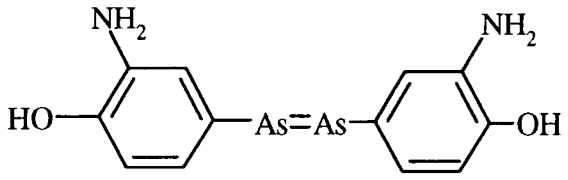
Note: although the formulas show double bonds between arsenic atoms, it is not known whether these are really involved in the classical way (as with, for example, ethane), but rather are somewhat metallic in nature (Rochow, 1966).

$(C_6H_3(OH)(NH_2)As)_2$

Name and arsenic oxidation state:

Arsphenamine (Salvarsan)	As(III)
3,3'-diamino-4,4'dihydroxyarsenobenzene	As(III)

Structural formula:

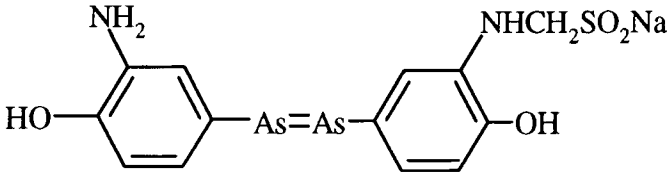


$(C_6H_3(OH)(NH_2)As)(AsC_6H_3(OH)(NHCH_2SO_2Na)$

Name and arsenic oxidation state:

Neoarsphenamine	As(III)

Structural formula:



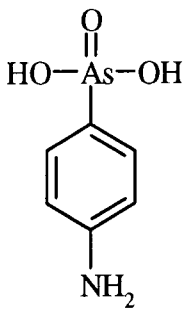
Agricultural Feed Additives

$C_6H_4NH_2AsO(OH)_2$

Name and arsenic oxidation state:

Arsenilic acid	As(V)

Structural formula:

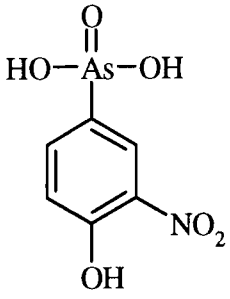


$C_6H_3(NO_2)(OH)AsO(OH)_2$

Name and arsenic oxidation state:

3-nitro-4-hydroxyphenylarsonic acid	As(V)
Roxarsone	As(V)

Structural formula:

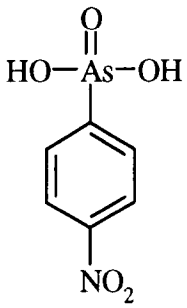


$C_6H_4NO_2AsO(OH)_2$

Name and arsenic oxidation state:

4-nitrophenylarsonic acid	As(V)

Structural formula:

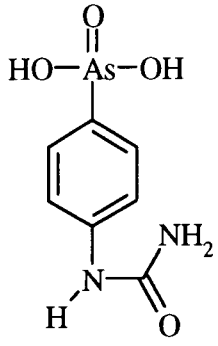


$C_6H_4(NHCONH_2)AsO(OH)_2$

Name and arsenic oxidation state:

p-ureidobenzenearsonic acid	As(V)

Structural formula:



APPENDIX C

UK and EEC Legislation

Within the EEC, there exists a legislative framework to prevent the contamination of surface waters, groundwaters and near coastal waters, by a wide range of metals (including arsenic) and other potential contaminants. The main directives relating to water are briefly described below, together with the relevant UK, Department of the Environment Circulars, which implement the EEC Council Directives, making them law in this country. A review of the legislation pertaining to the US equivalents is not addressed here. It is extremely important to note, however, that all the legislation published relating to arsenic makes NO distinction as to the prevalent oxidation state present, nor whether the arsenic present is of an inorganic or organic nature. As described in Chapters 2 and 5 the oxidation state of the arsenic is a crucial factor determining the potential hazard associated with it.

The 1978 EEC Directive 78/319/EEC was drawn up on toxic and dangerous waste, where waste is defined as 'any substance or object which the holder disposes of pursuant to the provisions of national law in force'. The substances covered (i.e. toxic and dangerous waste, meaning any waste containing or contaminated by the substances or materials listed, of such a nature, in such quantities, or in such concentrations as to constitute a risk to human health or the environment) include arsenic and arsenic compounds, together with a wide range of other metals and compounds. However, this Directive does not cover other toxic or dangerous waste covered by other specific Community rules, nor other substances such as radioactive waste, effluents discharged to sewers and water courses, emissions to the atmosphere and mining wastes. This last case (relating to mines) is discussed in slightly more detail in Section 4.10.3. Arsenic was thus defined as a potential toxic and dangerous waste in law, although this was already the case in many countries, and in fact arsenic had already been incorporated into some previously existing EC legislation.

Surface Waters

The EEC Directive 75/440/EEC concerning the 'quality required of surface waters intended for the abstraction of drinking water', relates to surface fresh water used or intended for use in the abstraction of drinking water. This Directive DOES NOT apply to groundwater, brackish water or water intended to replenish aquifers. Waters are divided into three groups corresponding to the appropriate standard method of treatment and relates to the respective physical, chemical and microbiological characteristics, with mandatory (I) and guide (G) limits for the parameters in each group. This is set out with respect to arsenic in Table C1.

Table C1. Arsenic concentrations permitted in surface waters intended for the abstraction of drinking water.

Treatment Method	A1 G	A1 I	A2 G	A2 I	A3 G	A3 I
Concentration (mg/l)	0.01	0.05	-	0.05	0.05	0.1

Where G is guide limit and I is mandatory limit;

A1 Simple physical treatment and disinfection;
A2 Normal physical treatment, chemical treatment and disinfection;
A3 Intensive physical and chemical treatment.

Groundwater

The UK Department of the Environment (DoE) Circular 4/82 (Welsh Office 7/82) initially implemented EEC Directive 80/68/EEC, the 'Groundwater Directive' but has been more recently superseded by DoE Circular 20/90 (Welsh Office 34/90) which again implements the EEC Directive 80/68/EEC, but also includes later EEC directives relating to specific substances and provides a revised and more specific procedure for determining those substances as belonging to 'List I' or 'List II'. The EEC Directive outlines two groups of 'certain dangerous substances' ascribing each to one of either List I or List II, depending upon their potential effects upon the environment; List I being elements and compounds deemed to pose the most serious risk to groundwater quality. Arsenic is denoted as a member of List II, and consequently, rules on arsenic discharges are not quite as stringent as if it was a List I substance. However, there is a caveat that states that List II substances may be classed as List I if it is shown to possess 'carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment', which arsenic does under certain circumstances (see Section 5.9). It also allows substances from List I families and groups to be treated (exceptionally) as List II

substances on the basis of low risk of toxicity, persistence or bioaccumulation. It is also important to note that 80/68/EEC does not set specific standards for concentrations in discharges or the receiving environment, but leaves the setting of such standards to the individual EEC Member States.

The Directive (and subsequent DoE Circular) state that:

List I discharges only need to be controlled where there is evidence of toxicity, persistence or bioaccumulation, and List II only where they could have a harmful effect on groundwater.
In addition, the following are things to which the Directive does not apply:

a) discharges of List I substances into groundwater which is found to be permanently unsuitable for other uses, provided that other aquatic systems or ecosystems cannot become polluted by these substances and that mineral exploitation is not impeded;
b) discharges due to the reinjection into the same aquifer of water used for geothermal purposes, water pumped out of mines and quarries or water pumped out for civil engineering purposes;
c) aquifer recharge for the purpose of groundwater management may be carried out subject to special authorization, provided that there is no risk of the groundwater becoming polluted.

This Directive does not cover:

a) domestic effluent from certain isolated dwellings;
b) discharges containing substances in List I or List II in very small quantities and concentrations, on account of the low risk of pollution and the difficulty of controlling the discharge of such effluent;
c) discharges of matter containing radioactive substances;
d*) discharges of List I substances into groundwater which is found to be permanently unsuitable for other uses, provided that other aquatic systems or ecosystems cannot become polluted by these substances and that mineral exploitation is not impeded;
e*) discharges due to re injection into the same aquifer of water used for geothermal purposes, water pumped out of mines and quarries or water pumped out for civil engineering purposes;
f*) aquifer recharge for the purpose of groundwater management may be carried out subject to special authorization provided that there is no risk of the groundwater becoming polluted.

* Taken from DoE Circular 4/82 on the implementation of this Directive.

Due to inherent problems in monitoring groundwater quality, the emphasis of this Directive is on imposing control measures on discharge rather than on setting a standard that the receiving water (the groundwater) has to achieve. The requirements of this Directive are to avert the pollution of groundwater by providing for the prevention of discharge of List I substances and the limitation of discharges of List II substances, unless prior investigation can establish that pollution of groundwater will not occur. The method of control for List I substances is to prohibit their discharge directly into groundwater and, if necessary, prevent or regulate via authorizations any disposal of the substances or other operation that might lead to them entering the groundwater after percolation through the ground or subsoil (known as indirect discharge) so as to prevent such a discharge. Control of List II substances is by means of investigating all direct

discharges and disposal or other operations which may lead to indirect disposal, and regulating such activities via authorizations. In England and Wales, limiting inputs of List II substances is governed by the NRA's consent system.

The Dutch government has published a set of reference values that groundwater should meet. These values, the so-called 'T' and 'I' values are regarded as 'trigger' and 'threshold' values for soil contaminants, but for groundwater an absolute value for arsenic is set at 10μg/l (Moen, 1988).

Water for Human Consumption

The 1982 DoE Circular 20/82 (Welsh Office 33/82), implemented the EC Directive relating to the quality of water intended for human consumption: "EEC Directive 80/778/EEC relating to the Quality of Water Intended for Human Consumption". As with DoE Circular 4/82, implementation was achieved through administrative means and the use of existing legislative powers, including those contained within the Public Health Act (1936), the Water Act (1945), the European Communities Act (1972) and the Water Act (1973), although these involved minor amendments to clauses dealing with the statutory obligation of water undertakings to soften water in some areas.

This EEC Directive applies to water intended for human consumption meaning all waters used for that purpose, either in their original state or after treatment, regardless of origin, whether supplied for consumption or whether used in food production or substances intended for human consumption, and affecting the wholesomeness of the food in its finished form. The maximum admissible concentration for arsenic is currently set at 50μg/l.

The DoE Circular modifies the EEC definition slightly, so that it covers:

a) water for consumption supplied by a statutory water undertaker;
b) water for consumption supplied by a non-statutory water undertaker, including private supplies and bottled water not covered by the exclusions below;
c) water supplied for use in food production undertakings.

The DoE Circular does not apply to:

d) natural mineral waters as defined by the EEC, and recognized as such by MAFF;

e) medicinal water recognized as such by the Department of Social Services (DSS), and licensed under the Medicines Act (1971);
f) water used in a food production undertaking that does not affect the wholesomeness of the foodstuff in its finished form.

Aquatic Environment

The 1989 DoE Circular 7/89 (Welsh Office 16/89), implements the EC Directives on pollution caused by certain dangerous substances discharged to the aquatic environment, including EEC Directive 76/464/EEC "on pollution caused by certain dangerous substances discharged into the aquatic environment of the community".

This EEC Directive, the so called 'Framework Surface Water Directive' applies specifically to inland surface waters, territorial waters and internal coastal waters (NOT groundwater), setting out List I (Black List) and List II substances with the limit values for each set out in 'daughter' directives. The List I and List II substances associated with this Directive, are not to be confused with those contained in List I and List II of the 'Groundwater Directive' (80/68/EEC) because each Directive deals with different water bodies. In this Directive, List I substances are those which comprise: "of certain individual substances selected mainly on the basis of their toxicity, persistence and bioaccumulation, with the exception of those which are biologically harmless or which are rapidly converted into substances which are biologically harmless". List II on the other hand "contains substances which have a deleterious effect on the aquatic environment, which can, however, be confined to a given area and which depend on the characteristics and location of the water into which they are discharged".

Through this Directive, Member States to required to eliminate pollution of the above mentioned waters by all List I substances and to reduce the pollution caused by those in List II. Arsenic is classed as a List II substance, although, as arsenic has yet to risk assessed, it may yet be classified as a List I substance. In addition, List I includes substances in respect of which it has been proved they possess carcinogenic properties in or via the aquatic environment, so again, arsenic might be included on the basis of this caveat.

As such, not all List I are banned, but are 'controlled' by standards set out in the Groundwater Directive (80\68\EEC), while List II substances standards are set by individual member states according to national requirements, as with the Groundwater

Directive. There is an obligation on each member state to illustrate that the standards set represent a progressive program of reduction of the use and presence of the substances. The procedure for setting standards may take two paths:

i) limit values - absolute standards in terms of concentration discharged:

ii) Environmental Quality Objectives approach, whereby standards are set according to the environmental receiving capacity of the particular stretch of water.

Therefore all discharges can be set at different levels, as long as the Environmental Water Quality Objective (WQO) is achieved. This is the system used in the UK implementation by the NRA, now the Environment Agency. Arsenic currently has a range of maximum admissible concentrations in the UK as may be seen in Table C2, depending upon the nature of the receiving water.

Table C2. UK, MAC's for arsenic in the aquatic environment.

Receiving Water	Arsenic MAC	Arsenic State
Direct abstraction to potable supply	50µg/l both A1 and A2[1]	Total arsenic
Protection of sensitive aquatic life (e.g. salmonid fish)	50µg/l	Dissolved arsenic
Protection of other aquatic life (e.g. cyprinid fish)	50µg/l	Dissolved arsenic
Protection of salt water life	25µg/l	Dissolved arsenic

[1] Refer to treatment method defined by 75/440/EEC.

The NRA (1992) criticizes EEC Directive 80/68/EEC, and the subsequent DoE implementation, stating: "..impact of this Directive has been limited. Only a limited number of substances are controlled. It did not address either diffuse pollution or the essential links to the management of abstraction and did not establish a comprehensive system for the monitoring of groundwater". This document went on to point out that the variability of geology and soils, of hydrogeology, of waters in the natural environment and of the various preventative measures which might be taken can result in groundwater protection decisions being complex, dependent on local circumstances, and NOT capable of prescription within a general policy.

Soil

The Dutch government has introduced in its 1987 Soil Protection Act a system of soil quality reference values (with the term soil including groundwater, soil organisms and the gaseous portion of the soil, together with the bottom of lakes, rivers and other

water bodies) which partly replace the former A, B, C values used in soil (in the Dutch sense) remediation. These new values go some way to taking particle size and the organic content of the soil into consideration when determining what is and what is not contaminated. Arsenic reference values for soils are calculated using the formula:

$$(As) = 15 + 0.4(L + H)$$

where:

(As) is the As concentration in mg/kg on a dry matter basis;

L is the weight percentage of the soil clay (<2μm) fraction;

H is the weight percentage of organic matter in the soil.

If the value determined in the soil exceeds the value calculated using the equation, then appropriate action should be taken to maintain multifunctionality. Groundwater, however, does not come under this 'formula method', and the arsenic reference value is 10μg/l irrespective of the soil type, as described above (Moen, 1988).

Based on the equation above, a table has been produced on the basis of a standard Dutch soil (10% organic matter and 25% dry content) in which two values have been calculated for a wide range of both organic and organic pollutants. These values, the so-called 'T' and 'I' values are regarded as 'trigger' and 'threshold' values, and for arsenic are set at 29 and 55mg/kg respectively (Moen, 1988). Although in common usage within the UK, it should be noted that these guidelines have no regulatory status outside the Netherlands. While broadly based on risk criteria, they include elements of ecological risk and country specific groundwater use factors which render them conservative for most UK industrial (for example) situations.

A 'similar' system was drawn up in the UK by the Interdepartmental Committee on the Redevelopment of Contaminated Land in 1983 (ICRCL 59/83), but rather than the policy of multifunctionality favored by the Dutch, the British trigger concentrations depend upon acceptable levels of contaminant applicable for the *planned use* of the area under examination and NOT for the land in its current use. The threshold values for arsenic are 10mg/kg (air dried soil) for domestic gardens and allotments, and 40mg/kg for parks, playing fields and open spaces. There is as yet no action limit for arsenic for either of these two groups of uses, so it is a matter of judgment and specific conditions, as to whether action is needed.

APPENDIX D

ARSENIC Eh/pH AND pH/pE DIAGRAMS

Figure D1. Eh-pH diagram for arsenic at 25°C and one atmosphere with total arsenic 10^{-5} mol/l and total sulphur 10^{-3} mol/l. Solid species are enclosed in parethases in cross hatched area, which indicates solubility less than $10^{-5.3}$ mol/l. From Ferguson and Gavis (1972).

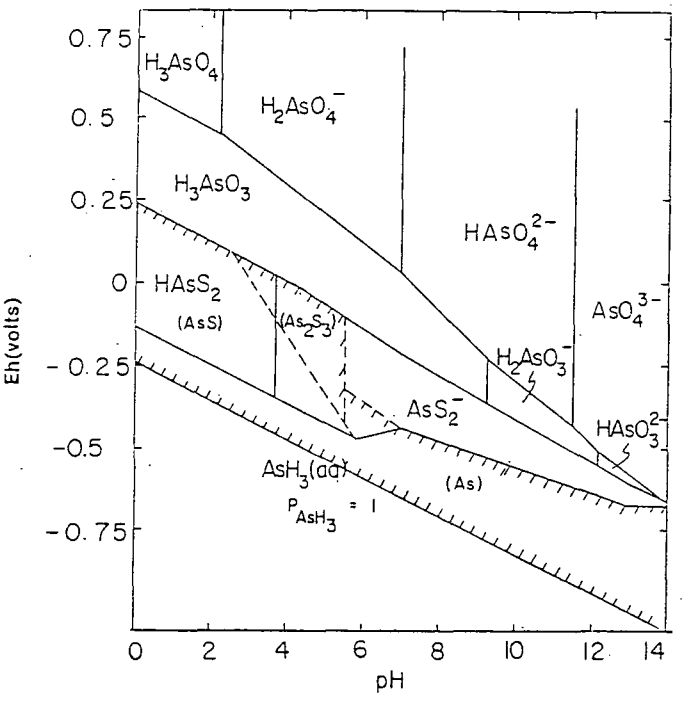


Figure D2. Eh-pH diagram for arsenic at 25°C and one atmosphere with total arsenic 10^{-5} mol/l, total sulphur 10^{-3} mol/l and total barium 2.2×10^{-7}. Dashed lines define domains for species enclosed in parenthases. From Wagemann (1977).

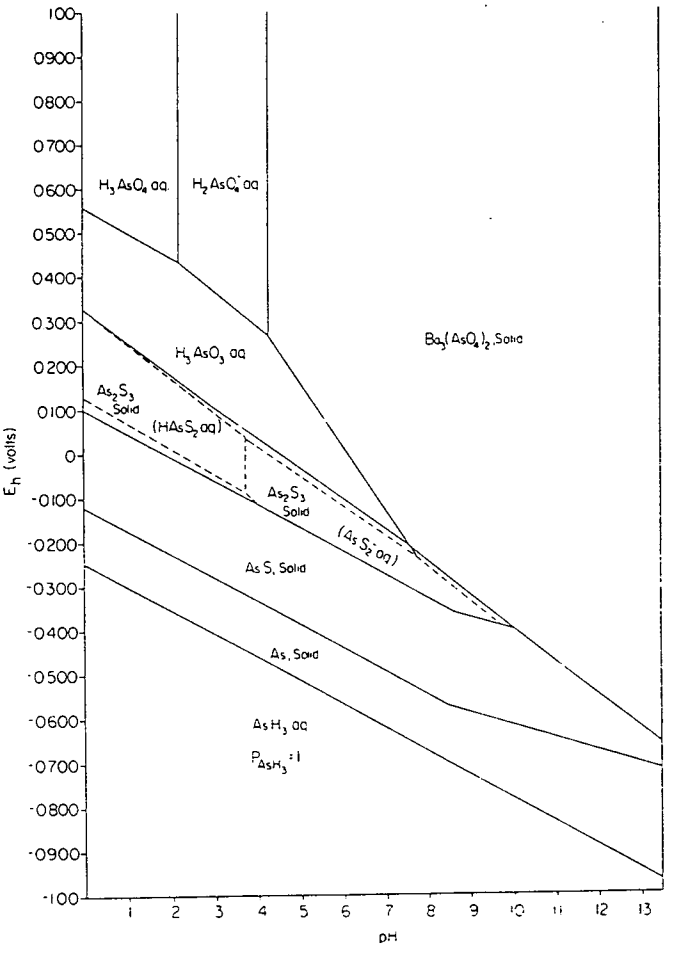


Figure D3. pH-pE diagram for the As-H_2O system at 25°C. Total dissolved arsenic species is set at $10^{-6.176}$ mol/l (50μg/l). The area within the vertical bars represents the common pH-pE domains for natural waters. From Cherry et al (1979); Cullen and Reimer (1989).

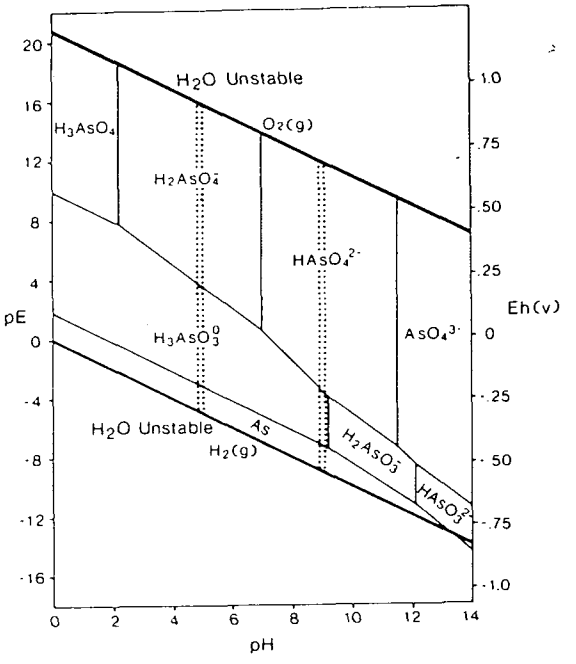


Figure D4. pH-pE diagram for the As-S-H_2O system at 25°C. Total dissolved arsenic species is set at $10^{-7.176}$ mol/l (5μg/l) and S species is set at 10^{-3} mol/l (32μg/l). The area within the hatched lines denotes that the solid phases are predominant (total dissolved As species are present at less than $10^{-7.176}$ mol/l (5μg/l). From Cherry et al (1979); Cullen and Reimer (1989).

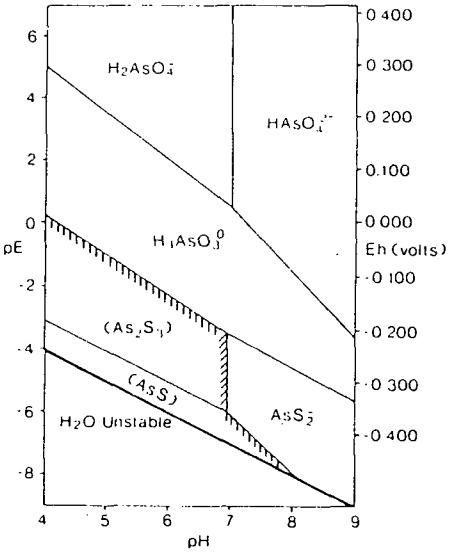


Figure D5. Eh-pH diagram for arsenic aqueous species. The cross hatched region represents oxygenated natural waters. From Crecelius et al (1986).

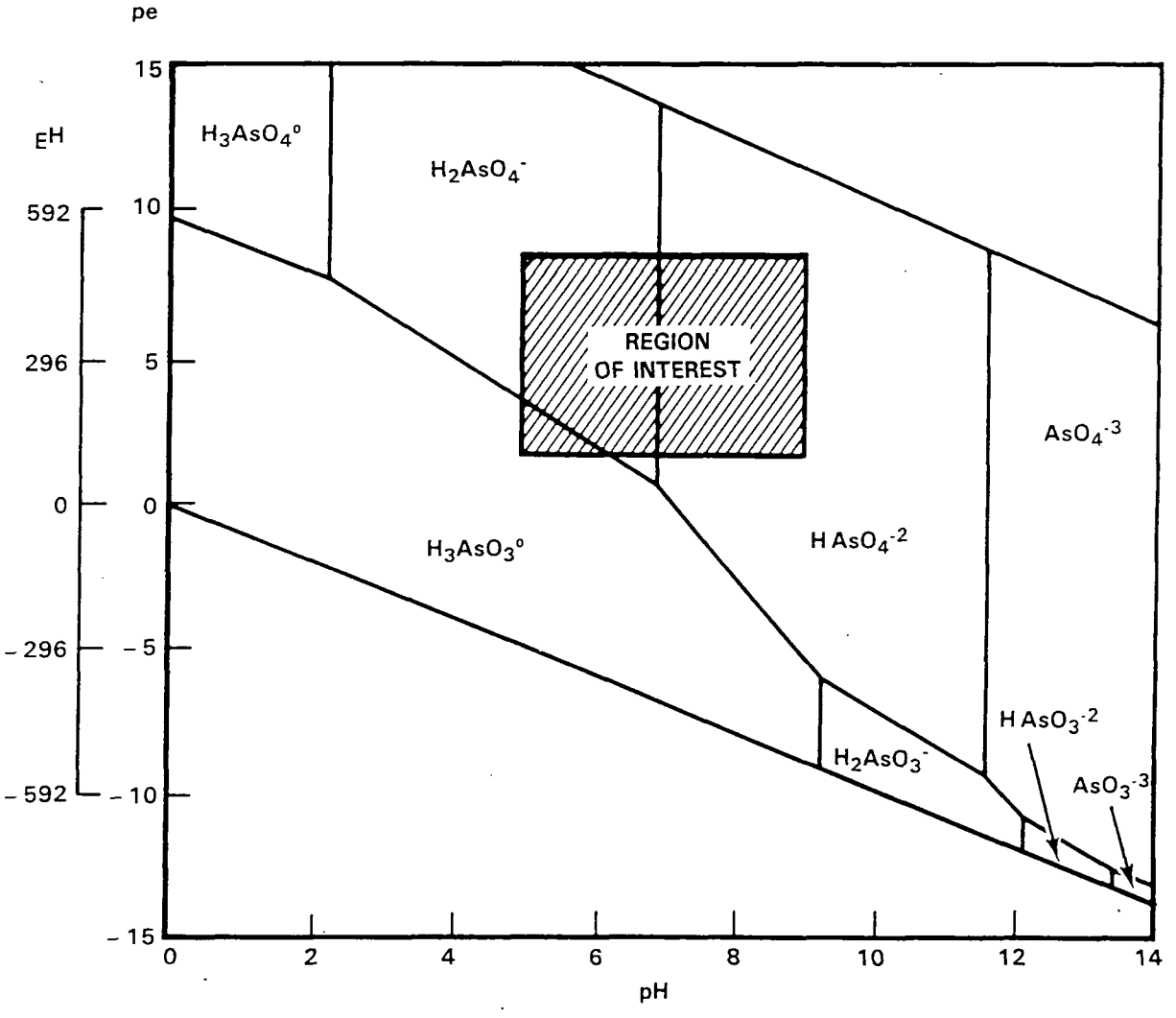


Figure D6. pH-pE diagram for the As-H_2O system. From Fergusson (1990).

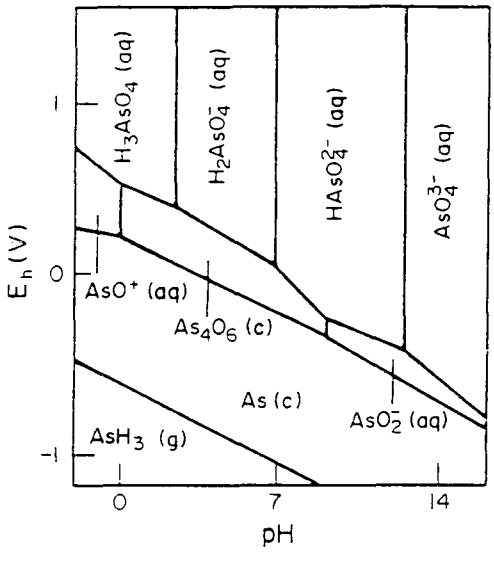


Figure D7. pH-pE diagram for the As-Ba-H_2O system. The broken line represents the boundary line for barium arsenate. From Fergusson (1990).

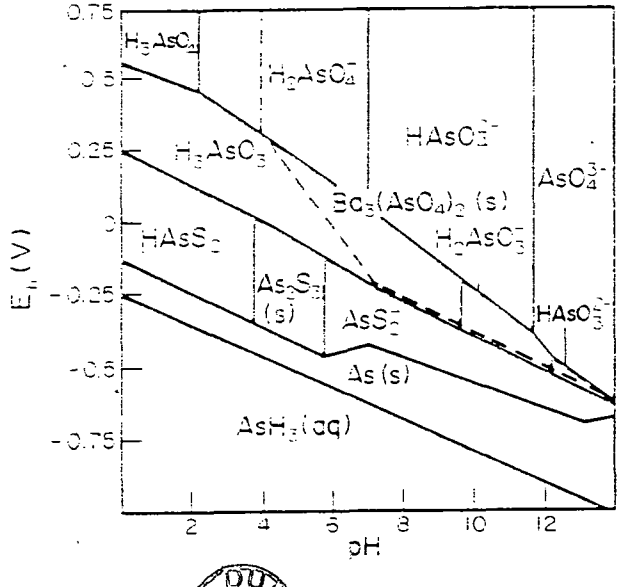


Figure D8. Eh-pH diagram for arsenic at 25°C and one atmosphere with total arsenic 10^{-6} mol/l, total sulphur 10^{-3} mol/l. From Xu et al (1991).

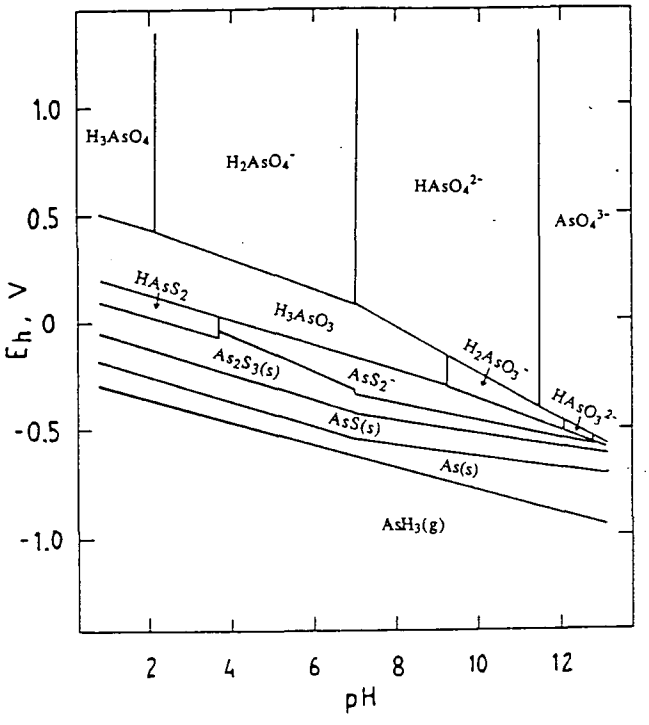


Figure D9. Eh-pH diagram for the As-O-H system at 25°C and one bar (one atmosphere) with total arsenic 10^{-5} mol/l. From Bowell ert al(1994).