

**PRELIMINARY DOCUMENT: NOT FOR CIRCULATION**

# **Canadian Environmental Protection Act**

**Technical Background document for  
Priority Substances List  
Assessment Report No.**

## **ARSENIC AND ITS COMPOUNDS**

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## Section 1. Executive Summary

### *Identity*

Arsenic is a metalloid, belonging to Group 5 of the Periodic Table. It has an atomic number of 33, a molecular weight of 74.92, and valences -3, 0, +3 and +5. Arsenic occurs naturally in the elemental state, but is found more often in compounds with sulphur, either alone or in combination with various metals. Common arsenic-containing minerals include arsenopyrite ( $\text{FeAsS}$ ), realgar ( $\text{AsS}$ ), orpiment ( $\text{As}_2\text{S}_3$ ) and niccolite ( $\text{NiAs}$ ).

### *Analytical Chemistry*

Recent advances in sample handling and analytical techniques have made it possible to accurately measure arsenic at concentrations in the sub- $\mu\text{g/L}$  range. Methods commonly used in environmental monitoring include neutron activation analysis, and atomic emission and atomic absorption spectrometry. With the exception of neutron activation analysis, these methods can be combined with liquid or gas chromatography, or an ion exchange technique, to distinguish individual arsenic species.

### *Production and Uses*

In Canada, arsenic is produced mainly as arsenic trioxide, obtained from the treatment of arsenious gold ores. Demand for arsenic has fallen sharply since the early 1980's because of concerns about its environmental safety. Because of low prices, current Canadian arsenic trioxide production is being stockpiled for future sale. In 1990, about 70% of the world's arsenic production was used in wood preservatives, 22% in agricultural chemicals (herbicides, insecticides and plant defoliants), 4% in glass manufacturing, 2% in nonferrous alloys and 2% in other uses.

### *Releases*

Arsenic is released naturally into the aquatic and terrestrial environments by weathering and erosion of rock and soil. If bedrock is arsenic-enriched, background arsenic concentrations in local soils and waters can be significantly elevated. Arsenic is released naturally into the atmosphere by volcanic eruptions, and escape of volatile methylarsines from soil.

On a world-wide basis, anthropogenic releases of arsenic result mostly from base-metal production, pesticidal uses of arsenicals, production and use of arsenical wood preservatives, coal-fired power generation and disposal of domestic and industrial wastes. Gold mining and roasting are additional sources of local importance in Canada.

## Transformations and Fate

Arsenic can undergo a variety of chemical and biochemical transformations which affect its mobility and fate. For example,  $\text{As}_2\text{O}_3$  vapour is introduced into the atmosphere, with other high temperature gases, by smelters, fossil fuel combustion and roasters. After release it can be trapped on suspended particulate matter by adsorption or complexation reactions, or condense directly to a solid upon cooling.  $\text{As}_2\text{O}_3$  can react with atmospheric water to form the arsenite anion ( $\text{AsO}_3^{3-}$ ), which can in turn be oxidized to arsenate ( $\text{AsO}_4^{3-}$ ). It is removed from the atmosphere by either dry deposition or rainfall, rates of deposition typically being highest closest to sources.

When  $\text{As}_2\text{O}_3$  is deposited directly into aerobic surface waters the resultant arsenite ( $\text{AsO}_3^{3-}$ ), being thermodynamically unstable, and tends to oxidize to arsenate ( $\text{AsO}_4^{3-}$ ). Although this oxidation is relatively slow, it can be accelerated by chemical oxidizing agents such as manganese oxide, or by the action of certain bacteria. Although thermodynamically unfavourable, phytoplankton can reduce some arsenate to arsenite, and produce methylated arsenicals such as monomethylarsonic acid (MMAA;  $(\text{CH}_3)_2\text{AsO}_3$ ) and dimethylarsinic acid (DMAA;  $(\text{CH}_3)_2\text{HAsO}_2$ ), in oxygenated surface waters. Arsenate is chemically reduced to arsenite in anaerobic conditions like those found in some deep lacustrine and marine waters, sediment pore waters, ground waters, and waterlogged soils. Relatively large amounts of dissolved arsenate have been reported in some anoxic sediment pore waters, however, and this has been variously attributed to slow reaction kinetics or possibly the formation of soluble arsenate-sulphide complexes.

Arsenic can be removed from solution by biotic uptake, adsorption onto iron and manganese hydroxides or clay particles, fixation by organic matter, or less frequently by precipitation or coprecipitation. As a result of these processes, dissolved arsenic is rapidly removed from most surface waters and deposited with settling organic and inorganic particulates. Once in the sediment it can be re-released into pore waters, however, with the decomposition of organic matter, or the dissolution of Fe/Mn hydroxides in anaerobic conditions resulting from sediment burial. Although some of the arsenic released in subsurface sediment likely diffuses downward and is immobilized with precipitating sulphides, some can also diffuse upward and escape, at least in part, into the overlying surface water. Sediment is therefore not necessarily an arsenic "sink".

Soils can be contaminated with inorganic arsenic ( $\text{AsO}_3^{3-}$  and  $\text{AsO}_4^{3-}$ ) or methylated arsenicals such as the herbicides monosodium methylarsenate (MSMA;  $(\text{CH}_3)\text{NaHAsO}_3$ ) and disodium methylarsenate (DSMA;  $(\text{CH}_3)\text{Na}_2\text{AsO}_3$ ). Some of this arsenic (20% or more) could be lost to the atmosphere as a result of production of volatile

methylarsines, such as monomethylarsine ( $\text{MMA}$ ;  $\text{CH}_3\text{AsH}_2$ ) and dimethylarsine ( $\text{DMA}$ ;  $(\text{CH}_3)_2\text{AsH}$ ), by soil microorganisms. MSMA and DSMA are furthermore thermodynamically unstable and, depending upon soil conditions, can be completely oxidized to  $\text{CO}_2$  and arsenate within a few years.

In soil, most forms of dissolved arsenic can be quickly removed from pore waters, principally by adsorption onto Fe/Mn oxides, and to a lesser extent clay minerals. These processes can significantly reduce the amount of arsenic reaching ground water, or which is available for absorption by plant roots. They also account for the long residence time of arsenic in most subsurface soils. They are most effective in well drained heavy textured soils, but are less effective in light textured acidic poorly drained soils. Adsorbed arsenic can be remobilized when Fe/Mn oxides dissolve after soils become anaerobic due to an extended period of flooding.

Arsenic is bioaccumulated from water by various aquatic organisms but is not biomagnified through the either aquatic or terrestrial food chains.

In freshwater aquatic plants, arsenic is present mainly as lipid and water soluble "lipid-related" compounds; lesser amounts of arsenite and methylated As (V) species are also present. Although little is known about the behaviour of arsenicals in terrestrial plants, methylation has been reported in some plants grown in nitrate- and/or phosphate-deficient conditions. Methylated arsenicals (methylarsonate and dimethylarsinate) are also produced in a variety of terrestrial animals including humans. Arsenosugars, arsenic containing lipid compounds, as well as methylated arsenicals have been found in marine plants. Arsenobetaine ( $(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{COO}^-$ ) is the principal arsenic compound in marine animals.

### *Concentrations in the Environment*

#### *Air*

Arsenic concentrations in air over land have been estimated to typically be about  $1 \text{ ng/m}^3$ . Recent (1985-87) surveys of arsenic in inhalable ( $<10 \text{ }\mu\text{m}$  diameter) particulates in air of 15 major Canadian cities revealed concentrations of from  $<0.5$  up to  $11 \text{ ng As/m}^3$ . These relatively low values contrast with much higher concentrations (up to  $3910 \text{ ng As/m}^3$ ) reported near gold roasters at Yellowknife in the early 1970's, prior to the installation of effective emission controls.

### *Precipitation*

Typical arsenic concentrations in rainwater and snow are reported to be about 1 µg/L. Concentrations ranging between <0.1 and 2.5 µg As/L were found in precipitation in the Great Lakes region in the mid-1970's. Much higher levels were reported, however, near a copper smelter at Noranda Quebec (32 µg As/L in rain, in 1976), and a gold roaster at Yellowknife NWT (up to 11,400 µg As/L in surface snow in the mid-1970's).

### *Surface Water*

Results of recent studies suggest that, partly because of short residence times in the water column, arsenic levels in fresh surface waters are typically relatively low (< 2 µg/L). From <0.1 - 2.5 µg As/L were reported in surface waters in the Canadian Great Lakes region in the mid-1970's. Low levels (range 0.2 - 0.6 µg As/L) were also found in lakes near the copper/nickel smelters at Sudbury in 1978. Higher arsenic concentrations (up to 20 µg/L) were reported, however, in lake water near a copper smelter at Noranda, Quebec in the mid-1970's.

Highest arsenic concentrations were detected in waters affected by gold mining and roasting. Up to 5.8 µg As/L were detected in 1983 in Lake Thomas receiving outflow from a former tailings pond near an abandoned gold mine at Waverley, Nova Scotia. Even higher levels (up to 250 µg As/L) were reported in the Moira River in 1977, downstream from Deloro, Ontario, a site of past gold mining, and silver and cobalt smelting. Arsenic levels in several lakes near the Yellowknife gold mines and roasters were likewise elevated (typically >100 µg/L, and up to 3000 µg/L in Kam Lake) in the mid-1970's.

### *Ground Water*

Although ground water normally contains more arsenic than surface waters, levels in most parts of Canada are likely to be below the Federal Government's guideline of 50 µg As/L for raw drinking water. Well waters containing 50 - 700 µg As/L were reported, however, in parts of New Brunswick and Nova Scotia, in areas of past gold mining, where bedrock is naturally arsenic-enriched. Much higher concentrations (up to 11,000 µg As/L) were detected in ground water in the vicinity of an abandoned arsenical wood preservative facility near Vancouver, British Columbia.

### *Sediment*

In part because of post-depositional remobilization, arsenic levels are typically higher in surface than subsurface sediment. In Canada, background concentrations in relatively uncontaminated surface (0-10 cm) sediment are generally less than 20 mg As/kg; arsenic levels in deeper sediment are typically only a few mg/kg.



Arsenic enrichment has been reported in contaminated Hamilton and Halifax harbour sediments (up to 50 and 65 mg/kg, respectively), and near base and precious metal mining and smelting/roasting facilities. From 100 - 200 mg/kg of weak acid-extractable arsenic was found in river sediment downstream from a Pb/Zn mine near Bathurst, New Brunswick, and in lake sediment near a Cu/Pb/Zn mine near Buchans, Newfoundland. Arsenic concentrations in the 100 to 650 mg/kg range were detected in surface sediments from lakes near base metal smelters at Sudbury Ontario, Noranda Quebec and Flin Flon Manitoba. Sediment from a former gold mine tailings pond at Waverley, Nova Scotia, contained up to 1750 mg As/kg, while sediments near an abandoned gold mine and precious metal refinery at Deloro, Ontario, contained up to 1695 mg As/kg. Sediment in Back Bay, adjacent to one of the major Yellowknife area gold mines, was found to contain up to 3000 mg As/kg.

### Soil

Normal soils in Canada likely contain an average of less than 10 mg As/kg. An average of only about 9 mg As/kg were reported in surface soil near the Cu/Ni smelters at Sudbury, Ontario, and a Cu smelter at Noranda Quebec. Up to 2000 mg As/kg were found, however, in surface soil near a secondary lead smelter in Toronto. As much as 170 mg As/kg were reported in soil at the site of a former wood preservative facility near Vancouver, British Columbia. Arsenic concentrations as high as 290 mg/kg were detected in soil from an apple orchard in Ontario that had been sprayed with arsenical pesticides. Peat samples obtained within a few kilometres of a former gold roasting plant at Duparquet, Quebec, contained up to 1000 mg As/kg. Soils in the city of Yellowknife contained up to 600 mg As/kg, while concentrations as high as 7600 mg/kg were reported near the gold mines and roasters.

### Biota

In unpolluted or mildly contaminated waters, levels of arsenic in freshwater fish tissue generally range from  $<0.1-0.4 \mu\text{g As/g}$  fresh weight (fw). Concentrations in fish samples in Lakes Erie and Ontario in the mid-1970's, and in base-metal and gold mining areas in Atlantic Canada in 1984/85 were typically within these limits. Higher levels (up to  $3.2 \mu\text{g As/g fw}$ ) were reported in the mid-1970's in fish from Kam Lake, near the gold roasting facilities at Yellowknife, NWT. Even higher concentrations (up to  $13.2 \mu\text{g As/g fw}$ ) have recently been found in Canadian marine fish.

Arsenic accumulation was also reported in aquatic macrophytes (max.  $3700 \mu\text{g As/g dry weight (dw)}$ ), zooplankton (max.  $2400 \mu\text{g As/g dw}$ ), and other invertebrates (up to  $1300 \mu\text{g As/g dw}$ ) from two Yellowknife area lakes in the mid-1970's.

Arsenic concentrations in tissue from Canadian (mostly

Ontario) waterfowl were generally low ( $< 1 \mu\text{g/g}$  fw) in 1988/89. Some of the highest levels (up to  $9.0 \mu\text{g/g}$  fw) were attributed to ingestion of arsenic-contaminated lead shot. Liver and muscle samples from several species of seabirds in Lancaster Sound, NWT, contained relatively large amounts of arsenic ( $1.1$  to  $91 \mu\text{g As/g dw}$ ) in the mid-1970's. Low arsenic levels (average  $0.067 \text{ mg/kg dw}$ ) were found in liver samples from polar bear (*Ursus maritimus*) of the western and central Canadian Arctic in the mid-1980's.

Population Exposures  
Kinetics and Metabolism  
Mammalian Toxicology  
Effects on Humans

(These four sections are being prepared by Health and Welfare Canada)

Effects on Aquatic Ecosystems: Dissolved Arsenic

Algae

Among aquatic organisms, algae are the most sensitive to dissolved arsenic ( $\text{As}^{+3}$  and  $\text{As}^{+5}$ ), with reduced growth occurring in such species as *Skeletonema costatum*, *Scenedesmus obliquus*, and *Chlamydomonas* sp. at concentrations ranging between  $5$  and  $75 \mu\text{g As}^{+3}$  and  $\text{As}^{+5}/\text{L}$ . Harmful effects of arsenic can be reduced, however, in the presence of phosphate.

Aquatic Invertebrates

Adverse effects on marine aquatic invertebrates have been reported at arsenic levels of  $100 \mu\text{g/L}$  and above. A 15-day exposure to sodium arsenate at  $100 \mu\text{g As/L}$  reduced the survival of juvenile *Eurytemora affinis* (copepod) by about 25%, while adult survival was reduced at  $1000 \mu\text{g As/L}$ . The 96-h LC50 of arsenic trioxide for zoea larvae of the Dungeness crab, *Cancer magister*, was  $232 \mu\text{g As/L}$ , while the 48-h EC50 of sodium arsenite for embryos of the Pacific oyster, *Crassostrea gigas*, was found to be  $326 \mu\text{g As/L}$ .

Toxic effects have been observed in freshwater invertebrates exposed to over  $500 \mu\text{g As/L}$ . Sodium arsenate at a concentration of  $520 \mu\text{g As/L}$  for three weeks caused a 16% reproduction impairment in *Daphnia magna*, while the three week LC50 was  $2850 \mu\text{g As/L}$ . The 48-h EC50 of arsenic trioxide to the midge, *Chironomus tentans*, was  $680 \mu\text{g As/L}$ , while the 96-h LC50 of sodium arsenate to the cladoceran, *Bosmina longirostris*, was  $850 \mu\text{g As/L}$ .

## Fish

A six-month exposure to arsenic trioxide resulted in a small but statistically significant reduction in smolt out-migration (from 91% to 80%) of coho salmon, Oncorhynchus kisutch, exposed to at a concentration of 300  $\mu\text{g As}^3/\text{L}$ . The 7-d LC50 for goldfish, Carassius auratus, eggs was found to be 490  $\mu\text{g As}^3/\text{L}$ , while the 21-d LC50 for rainbow trout, Oncorhynchus mykiss, eggs was 540  $\mu\text{g As}^3/\text{L}$ . LC50's for other fish species (both young and adults) have been reported in the 1100 to 28,500  $\mu\text{g As}^3/\text{L}$  range.

## Amphibians

Amphibians may be quite sensitive to arsenic, with concentrations as low as 40  $\mu\text{g As}^3/\text{L}$  causing death in embryo-larvae of the toad Gastrophryne carolinensis. An LC50 of 4450  $\mu\text{g As}^3/\text{L}$  was reported for embryo-larvae of the marbled salamander Ambystoma opacum.

## Effects on Aquatic Ecosystems: Sediment-Bound Arsenic

### Microorganisms

A decline in sediment microbial populations has been observed at concentrations exceeding 100 mg  $\text{As}^3/\text{kg}$ . Using an Apparent Effects Threshold (AET) approach, reduced luminescence was noted in the marine bacterium Photobacterium phosphoreum, at concentrations above 700 mg  $\text{As}/\text{kg}$  in sediment from Puget Sound, in Washington State.

### Benthic Invertebrates

A Screening Level Concentration approach, was used to evaluate sediment toxicity to freshwater benthos in the Great Lakes region. For arsenic the Severe Effect Level, considered to be detrimental to majority of the 92 benthic species recognised, was estimated to be 33  $\mu\text{g}/\text{g dw}$  of sediment. Using the AET approach, depressions in total abundance of higher level benthic infauna (Polychaeta, Mollusca, Crustacea) were noted in sediment from Puget Sound at concentrations above 57 mg  $\text{As}/\text{kg dw}$ . Increased amphipod (Rhepoxynius abronius) mortality and oyster (Crassostrea gigas) larvae abnormalities were reported in Puget Sound sediment at concentrations above 93 and 700 mg  $\text{As}/\text{kg dw}$ , respectively.

## Effects on Terrestrial Ecosystems

### Microorganisms

Arsenic was shown to reduce population densities of bacteria and actinomycetes by over 50% at 20 mg  $\text{As}^5/\text{kg soil}$ . Sodium arsenate at 100  $\mu\text{g As}/\text{L}$  caused a reduction in the activity of the

nitrifying bacteria, Nitrobacter sp.

#### Terrestrial Invertebrates

Earthworms have been found to be sensitive to soil arsenic. One study reported a total absence of earthworms in soil containing 150 to 165 mg As/kg, while another study reported 100% mortality in Eisenia fetida exposed to sodium arsenite for 14 days at a concentration of 200 mg As/kg.

#### Terrestrial Plants

Some plants are quite sensitive to soil arsenic. Reduced growth has been demonstrated in the stinging nettle, Urtica dioica, green beans, Phaseolus vulgaris, and spinach, Spinacia oleracea, for example, after as little as 1.0 to 26 mg As<sup>5</sup>/kg were added to soil. Adverse effects were more highly correlated with "plant-available" than with total soil arsenic contents.

#### Wildlife

Birds are most sensitive to arsenic in early life stages. For example, sodium arsenite was found to be extremely toxic in chicken (Gallus gallus) eggs, reducing hatchability by 65% at injected concentrations of 0.001 mg/L, and causing 100% mortality at 1.0 mg/L. Teratogenicity was observed when eggs were dosed at or above 0.05 mg/L.

Inorganic arsenite poisoning in nestlings and adult birds is marked by muscular debilitation and incoordination, fluffed and huddled position, immobility and seizures. For example, one-day-old Mallards (Anas platyrhynchos) fed a diet containing 300 mg As/kg added as sodium arsenate for ten weeks showed increased resting times, which could increase susceptibility to predators in the wild. Oral LD<sub>50</sub> values for sodium arsenite were reported to be 47.6, 323 and 386 mg/kg bw for the California Quail (Lophortyx californicus), Mallard Duck and Ring-necked Pheasant (Phaisianus colchicus), respectively.

Arsenic exposure has been shown to produce teratogenic effects in mammals such as rats, ewes and hamsters. In addition, arsenic ingestion can adversely impact some hormonally-mediated behaviours. For example, when administered as monosodium methylarsenate in the drinking water at a concentration of 477 mg As/L, nest building in the White-footed mouse (Peromyscus leucopus) was impaired to the point where survival of offspring could be reduced in cold weather. Mortalities were recorded in white-tailed deer (Odocoileus virginianus) following consumption of browse contaminated with an arsenical pesticide.

## *Regulations, Guidelines and Standards*

Ambient air quality criteria and point of impingement standards established by the Province of Ontario range from 0.3 to 1.0  $\mu\text{g As}/\text{m}^3$  and from 5 to 10  $\mu\text{g AsH}_3/\text{m}^3$ . British Columbia has set ambient air quality objectives for arsenic of from 0.1 to 1.0  $\mu\text{g}/\text{m}^3$ .

Under the Federal Fisheries Act effluent from metal mines can contain no more than 1.0 mg As/L in a grab sample, 0.75 mg As/L in a composite sample and a monthly arithmetic mean of 0.5 mg As/L. Alberta, British Columbia and Newfoundland have additional regulations limiting arsenic levels in waste water effluent from various industrial and municipal sources to from 0.05 to 1.9 mg/L.

The Canadian government has established a water quality guideline of 50  $\mu\text{g}/\text{L}$  of total arsenic for the protection of freshwater aquatic life. This is the same as the guideline for Canadian raw drinking water. For irrigation waters, the Canadian government has proposed a guideline of 100  $\mu\text{g As}/\text{L}$  for continuous use on all soils and 2000  $\mu\text{g As}/\text{L}$  for use on fine-textured neutral to alkaline soils for up to 20 years. A guideline of 500  $\mu\text{g As}/\text{L}$  has been established for water used for livestock watering in Canada.

British Columbia, Alberta, Ontario and Quebec have established soil quality guidelines for arsenic ranging from 5 mg/kg, the "threshold for investigation" for residential, recreational and agricultural land use set by British Columbia, to 50 mg/kg, a threshold for remedial action in commercial and industrial areas in Ontario and British Columbia.

The Province of Ontario has proposed Sediment Quality Guidelines for arsenic establishing a Lowest Effect Level, which can be tolerated by the majority of benthic organisms, at 6  $\mu\text{g}/\text{g}$ , and a Severe Effect Level, where pronounced disturbance of the benthic infaunal community is likely, at 33  $\mu\text{g As}/\text{g}$ .

### *Risk Assessment Recommendations*

(These two sections are in preparation.)

## Section 2. Introduction

The *Canadian Environmental Protection Act (CEPA)* requires the Ministers of the Environment and of National Health and Welfare to prepare and publish a Priority Substances List that identifies substances, including chemicals, effluents and wastes which may be harmful to the environment or constitute a danger to human health. The Act requires the federal Ministers of the Environment and of National Health and Welfare to assess these substances and determine whether they are "toxic" as defined in Section 11 of the Act, which states:

"A substance is toxic if it is entering, or may enter, the environment in a quantity or concentration, or under circumstances:

- a) having, or that may have, an immediate or long-term harmful effect on the environment;
- b) constituting, or that may constitute, a danger to the environment on which human life depends;  
or
- c) constituting, or that may constitute, a danger in Canada to human life or health."

While research and information collection may be undertaken, the primary objective is to determine whether these substances are "toxic" according to the definition under the Act, in which case they are to be placed on Schedule I of the Act, which allows for the making of regulations to control any aspect of their life cycle, from the research and development stage through manufacture, use, storage, transport and ultimate disposal.

This report assesses the "toxicity" of arsenic and its compounds.

## Section 3. Identity

Arsenic is a metalloid, belonging to Group 5 (N, P, As, Sb, Bi) of the Periodic Table. It has an atomic number of 33, and a molecular weight of 74.92.

Valences -3, 0, +3 and +5 are commonly assigned to arsenic (NRCC, 1978). The validity of the -3 valence depends on the assumption that arsenic is more electronegative than some of the elements with which it combines. Assigning arsenic the oxidation number -3 in arsine ( $\text{AsH}_3$ ), for example, assumes that arsenic is more electronegative than hydrogen. As Cullen and Reimer (1989) have noted, however, because of uncertainty about the relative

magnitude of the electronegativities of these two elements, it is not clear that this assumption is correct. Furthermore the other elements with which arsenic typically combines - carbon, oxygen and sulphur - are generally acknowledged to be more electronegative than arsenic. If it is assumed that arsenic is more electropositive than hydrogen, as Cullen and Reimer (1989) have done, then arsenic would not normally exist in the -3 valence state. Thus, following the suggestion of Cullen and Reimer (1989), in this review arsenic will be considered to have only three possible valences states; 0, +3 and +5.

Arsenic occurs naturally in the native (elemental) state, but is found more often in compounds with sulphur or with metals such as copper, cobalt, silver, lead and zinc. Common arsenic-containing minerals include realgar ( $\text{AsS}$ ), orpiment ( $\text{As}_2\text{S}_3$ ), arsenopyrite ( $\text{FeAsS}$ ) and niccolite ( $\text{NiAs}$ ) (Boyle and Jonasson, 1973).

### 3.1 Terminology

A wide variety of natural and synthetic arsenic complexes and compounds are recognised because of the multiple oxidation states and reactivity of the element. The situation is further complicated by lack of a consistent nomenclature in the literature for, in particular, methylated arsonic and arsinic acids and associated salts. To minimize possibility of misinterpretation, when summarizing results of individual studies for this document, it was decided to use the terminology of the original authors of studies cited. To avoid ambiguity, however, a list of the principal arsenic species mentioned in the text, and associated formulas, is presented in Table 1.

When reporting arsenic levels in water, soil and sediment terms such as "total", "dissolved", "extractable" and "available" can have different meanings for different authors. Care has been taken to specify, wherever possible, sample pretreatment or digestion procedures used. Generally, in this review the terms "dissolved" and "total" as applied to waters, mean that concentrations were measured on filtered (typically  $0.45 \mu\text{m}$ ), and unfiltered samples after addition of a strong oxidant (eg. nitric acid), respectively. When applied to soils and sediments, the term "total" arsenic indicates that levels were estimated after digestion in an acid mixture containing HF, or that a non-destructive instrumental method such as neutron activation was used.

Table 1. Names, formula and properties of some arsenic species.

<u>Chemical Species/Synonym</u>	<u>Formula</u>	<u>Properties</u>
ARSENIC (0)		
arsenic, native	As	grey solid, insol. in water, sol. in $\text{HNO}_3$ , sublimes at $615^\circ\text{C}$
ARSENIC (+3)		
arsenic (III)	$\text{As}^{+3}$	
arsenic, trivalent "arsenite"		
arsine	$\text{AsH}_3$	colourless gas (b.p. $-55^\circ\text{C}$ ), odour, sol. in cold water (20 ml/100 cc)
arsine, methyl/MMA	$(\text{CH}_3)\text{AsH}_2$	volatile at room temp., sol. in organic solvents
arsine, dimethyl/DMA	$(\text{CH}_3)_2\text{AsH}$	volatile at room temp., sol. in organic solvents
arsine, trimethyl-/TMA	$(\text{CH}_3)_3\text{As}$	volatile at room temp., sol. in organic solvents
arsenite	$\text{AsO}_3^{-3}$ , $\text{AsO}_2^{-}$	
arsenite, sodium	$\text{NaAsO}_2$	grey-white powder, very sol. in water
arsenite (meta-), potassium	$\text{KAsO}_2$	white powder, sol. in water



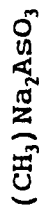
Table 1. cont'd.

<u>Chemical Species/Synonym</u>	<u>Formula</u>	<u>Properties</u>
<u>ARSENIC (+3) cont'd</u>		
trioxide, arsenic	$\text{As}_2\text{O}_3$	colourless solid, sublimes at $193^\circ\text{C}$ , m.p. $278^\circ\text{C}$ , b.p. $465^\circ\text{C}$ , sol. cold water 1.2 g/100 cc.
<u>ARSENIC (+5)</u>		
arsenic (V) arsenic, pentavalent "arsenate"	$\text{As}^{+5}$	
arsenate	$\text{AsO}_4^{3-}$	
arsenate, aluminum	$\text{AlAsO}_4 \cdot 8\text{H}_2\text{O}$	white powder, insol. in water, slightly sol. in acid
arsenate, barium	$\text{Ba}_3(\text{AsO}_4)_2$	m.p. $1605^\circ\text{C}$ , sol. in cold water 0.055 g/100 cc
arsenate, calcium <sup>2</sup>	$\text{CaHAsO}_4$ , $\text{Ca}(\text{H}_2\text{AsO}_4)_2$ , $\text{Ca}_3(\text{AsO}_4)_2$ , $2\text{CaO}-\text{As}_2\text{O}_5$ , $\text{Ca}_3(\text{AsO}_4)_2$ , $\text{Ca}_5\text{OH}(\text{AsO}_4)_3$	colour-less powder, sol. in cold water 0.013 g/100 cc
arsenate, ferric	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	green solid, insol. in water and $\text{HNO}_3$ , sol. in $\text{HCl}$
arsenate, lead	$\text{Pb}_3(\text{AsO}_4)_2$	white crystalline, very slightly sol. in cold water, sol. in $\text{HNO}_3$

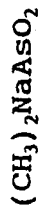
Table 1. cont'd.

<u>Chemical Species/Synonym</u>	<u>Formula</u>	<u>Properties<sup>1</sup></u>
ARSENIC (+5) cont'd		
arsenate, sodium <sup>2</sup>	$\text{NaH}_2\text{AsO}_4$ , $\text{Na}_2\text{HASO}_4$ , $\text{Na}_3\text{AsO}_4$	colourless solid, sol. in water ( $\text{Na}_2\text{HASO}_4 \cdot 12\text{H}_2\text{O}$ 56 g/100 cc)
arsenate, dibasic sodium arsenate, di-sodium <sup>2</sup>	$\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$ $\text{Na}_2\text{HASO}_4$	
acid, arsenic	$\text{H}_3\text{AsO}_4 \cdot 1/2\text{H}_2\text{O}$	white crystalline, sol. in cold water 16.7 g/100 cc.
acid, (4-amino-phenyl-) arsanilic	$(\text{NH}_2)(\text{C}_6\text{H}_4)\text{H}_2\text{AsO}_3$	
acid, monomethylarsonic/MMAA	$(\text{CH}_3)\text{H}_2\text{AsO}_3$	
acid, methylarsonic/MMAA		
acid, methanearsonic/MMAA		
methanearsonate methylarsonate	$(\text{CH}_3)\text{AsO}_3^{2-}$ , $(\text{CH}_3)\text{HASO}_3^-$	
acid, dimethylarsinic/DMAA	$(\text{CH}_3)_2\text{HASO}_2$	
acid, cacodylic/DMAA cacodylate/DMAA		
dimethylarsinate	$(\text{CH}_3)_2\text{AsO}_2^-$	
acid, methanearsonic	$(\text{CH}_3)\text{H}_2\text{AsO}_2$	
methanoarsonate, monosodium/MSMA	$(\text{CH}_3)\text{NaHASO}_3$	
methanearsonate, monosodium/MSMA		
methylarsenate, monosodium/MSMA		

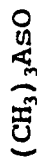
Table 1. cont'd.

Chemical Species/Synonym<sup>1</sup>FormulaProperties<sup>1</sup>ARSENIC (+5) cont'dmethanoarsonate, disodium/DSMA<sup>2</sup>  
methaneearsonate, disodium/DSMA<sup>2</sup>  
methylarsenate, disodium/DSMA<sup>2</sup>

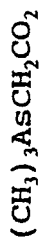
dimethylarsenate, sodium/SDMA



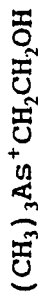
trimethylarsine oxide/TMAO



arsenobetaine



arsenocholine



pentoxide, arsenic

white solid, decomposes  
at 315°C, sol. in water  
150 g/100 cc; sol. in  
alkali, acid and alcoholSULPHIDES

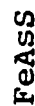
sulphide, arsenic/realgar

red-brown solid, m.p.  
267-307°C, b.p. 565°C,  
insol. in water

sulphide, arsenic/orpiment

yellow-red solid, m.p.  
300°C, b.p. 707°C, insol.  
cold water, sol. alkali

arsenopyrite

ARSENIDES

arsenide, nickel/niccolite

solid, insol. in water,  
sol. in aqua regia<sup>1</sup> Principal source Weast (1988); b.p. = boiling point; m.p. = melting point; sol. =  
soluble, insol. = insoluble.<sup>2</sup> Some forms of these compounds can be hydrated (see for example, BIBRA, 1990)

### 3.2 Physical and Chemical Properties

Physical and chemical properties of some of the more common arsenic species are also given in Table 1.

On heating, native arsenic oxidizes to arsenic trioxide ( $\text{As}_2\text{O}_3$ ). Arsenic trioxide sublimates at  $193^\circ\text{C}$ , and arsenic vapours can be removed from the hot gases, such as those generated during metal roasting or smelting, by cooling them below this temperature (Weisenberg et al., 1979).

Arsine and its methylated derivatives are all volatile at room temperatures. They are unstable in the presence of oxygen, but according to Parris and Brinkman (1976), the oxidation of trimethylarsine proceeds relatively slowly.

The water solubility of arsenite and arsenate salts varies from negligible (aluminum arsenate, ferric arsenate) to very high (sodium arsenite, sodium arsenate). In the case of sodium arsenate, 56 g of this compound will dissolve in 100 cc of cold water (Weast, 1988). The solubility of arsenic pentoxide is even higher - 150 g/100 cc in cold water. The arsenic sulphides are all essentially insoluble in water, but are dissolved by strong oxidizing acids such as  $\text{H}_2\text{SO}_4$ .

## Section 4. Analytical Chemistry

Although a complete review of the analytical chemistry of arsenic is beyond the scope of this document, several of the more popular methods of arsenic measurement are briefly described. More detailed information can be found in reviews by Talmi and Feldman (1975), Irgolic et al. (1983), and most recently, Korte and Fernando (1991).

Recent advances in analytical instrumentation, and the development of "clean lab" and "clean sampling" techniques, have made possible the determination of both "total" arsenic and individual arsenic species with greater accuracy and at much lower concentrations than were previously possible. The impact of these advances has been greatest in the field of water analysis. As a result, arsenic concentrations recently measured in freshwater are often lower than those previously reported (Leger, 1991), suggesting that currently accepted average arsenic levels in freshwater may have to be revised significantly downwards (Nriagu, 1983).

#### 4.1 Pretreatment and Dissolution

Unfortunately there are no universally accepted procedures for handling water samples for measurement of individual arsenic species. For example, if arsenite is to be measured, Andreae (1977) has recommended storage of water samples in a freezer below  $-15^{\circ}\text{C}$ . Korte and Fernando (1991), however, have described an alternate procedure involving refrigeration to  $2^{\circ}\text{C}$ , acidification to pH 2, and exclusion of air from the sample. Furthermore, according to Andreae (1977), if methylated arsenicals are to be identified, losses can be prevented by adding a small amount of HCl to the water sample after collection. Cullen and Reimer (1989) have pointed out, however, that acidification could result in the hydrolysis of organoarsenicals bound to microorganisms, thus increasing the concentration of methylated arsenicals in the original water. As Cullen and Reimer (1989) have noted, although it is likely that postsampling changes have influenced results of some speciation studies, it is not possible to determine the extent of this problem.

The measurement of "total" arsenic in water samples is more straightforward. Normally unfiltered waters are digested in a strong acid, such as  $\text{HNO}_3$ , to ensure breakdown of organo-arsenic compounds.

Acid digestion is the most common dissolution procedure for biological and geological samples, although dry ashing and fusion are also sometimes used. Depending upon the sample matrix, a variety of mineral acids ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ ) can be employed to attack samples with minimal arsenic losses (Talimi and Feldman, 1975). HF must be used with caution, however, due to the possible formation of volatile arsenic fluorides (Hall, 1991). Dry ashing in the  $550$ - $650^{\circ}\text{C}$  range with  $\text{MgO}/\text{Mg}(\text{NO}_3)_2$  can be applied to organic samples, with good arsenic recovery (Talimi and Feldman, 1975). Also, geological samples can be safely brought into solution by fusion with NaOH (Talimi and Feldman, 1975).

#### 4.2 Measurement

Methods commonly used to measure arsenic in environmental materials include colorimetry, neutron activation analysis, and atomic emission and atomic absorption spectrometry. With the exception of neutron activation analysis, these methods can be combined with liquid or gas chromatography, or an ion exchange technique, to determine concentrations of individual arsenic species. Other methods, such as voltammetry and mass spectrometry, although described in the recent literature (see for example, Stojanovic et al. (1990) and Hall (1991)), are as yet rarely used for environmental samples.

Colorimetric methods involve formation of coloured arsenic complexes with silver diethyldithiocarbamate or ammonium molybdate, and spectrophotometric estimation of colour intensity (Irgolic et al. 1983). Although they were the methods of choice in the 1950's and 1960's, today they have been largely supplanted by more advanced instrumental techniques.

Neutron activation analysis generally involves bombarding a sample with thermal neutrons and measuring the intensity of gamma radiation produced by the resultant radioactive isotopes. Although only total arsenic can be measured, this method has the advantage of being relatively interference free, and well suited to determining small concentrations of arsenic in environmental media (Talmi and Feldman, 1975). It is not in common usage however, probably because of the need for access to a neutron source, typically a reactor.

Atomic absorption spectrometry is among the most popular analytical methods at present, likely because of its high sensitivity and comparatively low capital cost. In this procedure arsenic is normally atomised in either a heated quartz tube or a graphite furnace, and then excited by absorption of radiant energy from an arsenic-containing light source. The amount of energy absorbed is measured and is proportional to the concentration of the absorbing atoms.

In the case of the quartz tube atomizer, arsenic must be introduced as a gas. Thus only volatile arsenic species such as arsine, or those that can be easily transformed into volatile forms with a reducing agent, can be determined with this system. By controlling the pH of the sample solution during the reduction/arsine generation step, this method can be used to distinguish arsenite from arsenate (Aggett and Aspell, 1976). Also, after a gas chromatographic separation, methylarsonate, diemethylarsinate and trimethylarsine oxide can be measured (Andreae et al., 1983). Glaubig and Goldberg (1988) have reported detection limits for As (III) of less than 0.4  $\mu\text{g/L}$  using this apparatus. As both Hall (1991) and Korte and Fernando (1991) have noted however, care must be taken to avoid interferences during the reduction step.

Samples are normally introduced into the graphite furnace atomizer as liquids. Although only a small amount (5-50  $\mu\text{L}$ ) of solution can be atomized at one time, detection limits of about 0.5  $\mu\text{g/L}$  can be achieved (Irgolic et al., 1983). When used in conjunction with high pressure liquid chromatography, concentrations of nonvolatile organo-arsenic species such as arsenobetaine can be determined (see for example, Lawrence et al. (1986)). Korte and Fernando (1991) have described a method of separating As (III), As (V), monosodium methylarsenate (MSMA) and disodium methylarsenate (DSMA) using a single ion exchange column containing both cation and anion exchange resins, followed by a

graphite furnace finish.

Finally, inductively coupled plasma emission spectrometric (ICP-ES) methods are now finding more frequent application. In this case sample atoms are excited by an argon plasma heat source, and the intensity of radiation emitted is measured with the aid of a monochromator. According to Irgolic et al. (1983), although ICP-ES is almost interference free, detection limits of only 10-80 µg/L are achievable when samples are introduced as liquids. However, the sensitivity of the method can be increased dramatically when it is combined with an arsine generation attachment, like that used for quartz tube atomic absorption. With this increasingly popular system, reducible arsenic compounds are measurable at sub-µg/L levels (Irgolic et al., 1983).

## Section 5. Production, Uses and Sources

### 5.1 Production

In Canada, arsenic production occurs mainly as arsenic trioxide, obtained from the treatment of arsenious gold ores. Demand for arsenic has fallen sharply since the early 1980's, because of environmental concerns about its use in agriculture. Canadian production of arsenic trioxide in 1986 amounted to approximately 5100 tonnes, down from about 8400 tonnes produced in 1985 (Law-West 1987). Because of weak demand and low prices, current Canadian arsenic trioxide production is being stockpiled for future sale (Ignatow et al., 1990). World production of arsenic trioxide amounted to about 56,000 tonnes in 1990, up from about 37,000 tonnes in the early 1980's (Ignatow et al., 1990; Law-West 1987).

### 5.2 Uses

In 1990, about 70% of world arsenic production was used in wood preservatives (such as chromated copper arsenate (CCA) and ammoniacal copper arsenate (ACA)), 30% was used in agricultural chemicals (monosodium and disodium methanearsenate (MSMA and DSMA), used as herbicides to control grassy and broad-leaved weeds, being the most common), 4% was used in glass manufacturing, 2% was used in nonferrous alloys, and 2% was used for other applications (Ignatow et al., 1990). The United States uses more than 50% of the world production of arsenic.

The most recent overview of arsenic usage in Canada covered the year 1974. At that time 240 tonnes of arsenic were used, 67% for glassmaking, 32% in metal rolling, casting and extruding, and the rest in other chemical industries (CCREM 1987). Patterns of use have no doubt changed since then, however. Konasewich and Henning (1988), for example, have stated that in 1984, 5000 tonnes

of 50% CCA concentrate (about 550 tonnes of arsenic) were used in Canada for wood preservation.

Nriagu and Azcue (1990) cited data showing that by 1974 about 5 million kg of arsenic were used globally in wood preservation, and that this use has been increasing at a rate of about 10-25% per year.

Wauchope and McDowell (1984) have noted that the use of herbicides containing MSMA, DSMA and dimethylarsinic acid (cacodylate) has grown rapidly since the mid-1970's. These replaced inorganic arsenical pesticides, such as calcium and lead arsenate, which had been popular previously. Nriagu and Azcue (1990) have cited recent U.S. data indicating that usage of MSMA + DSMA as herbicides amounted to about 10 million kg, while usage of arsenic acid was 3.3 million kg, and of cacodylate, 269,000 kg.

### 5.3 Sources

#### 5.3.1 Natural Release

Although arsenic occurs in nature in a wide variety of forms, the principle carrier of arsenic in rocks is pyrite ( $\text{FeS}_2$ ), in which it occurs as an impurity at concentrations of up to 6,000 mg/kg (Boyle and Jonasson 1973). Although most rocks contain on average only 1 - 3 mg/kg total arsenic, concentrations in shales (especially dark pyritiferous types), phosphorites and some coal deposits can be enriched by a factor of 10 or more (Boyle and Jonasson 1973). Arsenic levels in mineral soils can be over 1000 mg/kg, depending upon that of the parent bedrock, but are typically in the 3 - 7 mg/kg range (Boyle and Jonasson 1973).

Weathering of arsenic-enriched bedrock, and associated soil and overburden, can result in the release of significant amounts of soluble arsenic to both ground and surface waters. Ferguson and Gavis (1972) estimated the total quantity of arsenic weathered and transported to the oceans to be about  $45 \times 10^6$  kg/year.

Estimates of natural atmospheric emissions vary. For example, Walsh et al. (1979) determined that about  $7.8 \times 10^6$  kg As/yr are released to the atmosphere naturally, principally from volcanoes. Chilvers and Peterson (1987), on the other hand, estimated that mean annual atmospheric releases amount to about  $45 \times 10^6$  kg As/year, of which about  $17.7 \times 10^6$  kg come from volcanoes and  $26.2 \times 10^6$  kg from low temperature release of volatile di- and trimethylarsine from soils and sediments. As Cullen and Reimer (1989) have noted, it would appear that better data are required, particularly on low temperature release rates for methylarsines, before reliable atmospheric arsenic budgets can be developed.



### 5.3.2 Release Related to Human Activities

Nriagu and Pacyna (1988) have estimated that worldwide anthropogenic emissions of arsenic to the atmosphere are about 12 to  $26 \times 10^6$  kg/yr, with release from pyrometallurgical non-ferrous metal production being by far the largest source, amounting to about 9.5 to  $15 \times 10^6$  kg/yr.

Worldwide additions of arsenic to land amount to about  $98 \times 10^6$  kg/yr according to Nriagu and Azcue (1990), with the major sources being wastage of commercial products ( $38.5 \times 10^6$  kg/yr), coal fly ash and bottom ash ( $21.91 \times 10^6$  kg/yr), atmospheric fallout ( $13.2 \times 10^6$  kg/yr), mine tailings ( $9.1 \times 10^6$  kg/yr), and smelter slags and wastes ( $6.8 \times 10^6$  kg/yr).

Input of arsenic into the world's aquatic ecosystems was estimated in Nriagu and Azcue (1990) to be about  $41 \times 10^6$  kg/yr (median), with the main sources being domestic waste water ( $9.15 \times 10^6$  kg/yr), steam electric generating plants ( $8.2 \times 10^6$  kg/yr), non-ferrous smelting and refining ( $7.0 \times 10^6$  kg/yr), and atmospheric fallout ( $5.65 \times 10^6$  kg/yr).

In the United States, the US EPA (1976), using both empirical data and dispersion models, concluded that copper smelters emitted 2990 tons of arsenic in 1974 - 61.1% of the estimated total of anthropogenic emissions for that year. As is noted in Section 6.3.1, arsenic levels in the ambient air near these smelters were typically elevated. Coal-burning power plants, were estimated to account for 580 tons, or 11.9% of the total, while application of inorganic arsenical pesticides and emissions from glass production released 440 tons and 400 tons of arsenic (9.0 and 8.2% of the total), respectively, in 1974.

The total amount of arsenic released into the atmosphere in Canada in 1972 from anthropogenic sources was estimated to be about 4,100 tons (Gagan, 1979). Gold roasting accounted for nearly half of this amount, while primary base metal (Cu, Ni, Pb and Zn) and iron and steel production contributed about 25% each. By 1982, after the installation of more effective emission controls, atmospheric releases of arsenic in Canada had fallen to about 470 tonnes, most of which came from base metal (71%) and iron and steel (22%) production (Jaques 1987). Gold roasting accounted for less than 4% of the arsenic emitted to the atmosphere in 1982. By province, atmospheric emissions of arsenic in 1982 were estimated to be 192 tonnes in Ontario, 160 tonnes in Quebec, 61 tonnes in Manitoba, 32 tonnes in British Columbia, and less than 10 tonnes in each of the other provinces and territories.

Arsenic occurs naturally at relatively high concentrations in most gold-bearing ores, and may thus be released to local ground and surface water by rock crushing and subsequent weathering of

mine tailings and waste rock materials (Kay 1985). Locations of producing gold mines in Canada is shown in Figure 1. Using data from a 1921 Province of Nova Scotia report, Trip and Skilton (1985) calculated an average arsenic concentration of 0.4% in tailings from the Waverley gold mining operations, where ground water contamination with arsenic has been demonstrated (Bottomley, 1984).

As noted previously, in the 1970's gold roasting operations were major source of atmospheric arsenic contamination. Gagan (1979) estimated that in 1972, about 1930 tons of arsenic were emitted into the atmosphere by four Canadian gold roasting operations - at Yellowknife, NWT, and Red Lake and Virginiatown Ontario. At present only the Giant Mine at Yellowknife operates a roaster. Data of McCaig and Cianciarelli (1984) indicate that, as a result of the installation of effective emission controls, only about 8.8 tonnes of arsenic were released annually to the atmosphere by this facility in the early 1980's.

Arsenic is also a constituent of all base-metal sulphide deposits, and mining and processing of these ores can likewise release significant amounts of arsenic. The location of the principal base metal smelters and refineries in Canada is given in Figure 2. According to data gathered by MacLatchy (1991) in 1988, there were 5450 metric tons of arsenic in the sulphide ores processed at 11 of these facilities (Table 2). Of that, 2110 tonnes went into useable products, and 1790 tonnes of arsenic went as waste into air (280 tonnes), water (840 tonnes) or soil (670 tonnes). Some of the slag (which contained 1040 tonnes of arsenic) was likely disposed of on land as solid waste, and some was also probably used, for example, as fill in road bed construction.

Table 2. Inputs and outputs of arsenic from Canadian sulphide-based metal smelters and refineries in 1988<sup>1</sup>.

<u>Inputs</u> (Tonnes of arsenic)		<u>Outputs</u> (Tonnes of arsenic)	
Copper concentrates	1830	Products	2110
Lead concentrates	1280	Slags	1040
Zinc concentrates	475	Liquid Effluents	840
Nickel concentrates	60	Solid Wastes	670
Other inputs	<u>1805</u>	Air Emissions	<u>280</u>
Total Inputs <sup>2</sup>	5450	Total Outputs <sup>2</sup>	4940

<sup>1</sup> Source: MacLatchy (1991)

<sup>2</sup> The discrepancy between total inputs and total outputs is attributable partly to fugitive emissions not included in the output estimates.

FIGURE 1. PRINCIPAL CANADIAN GOLD MINES 1990

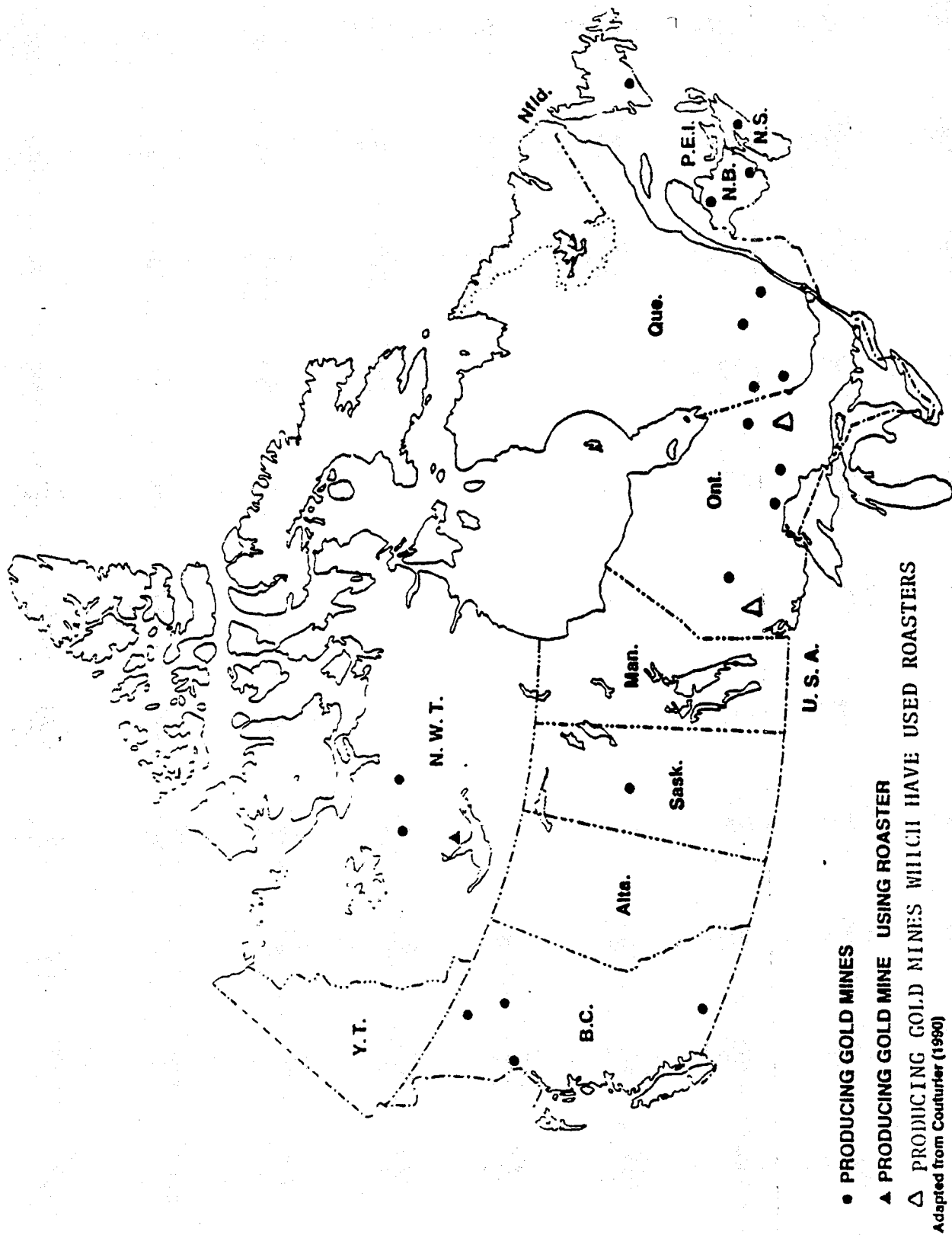
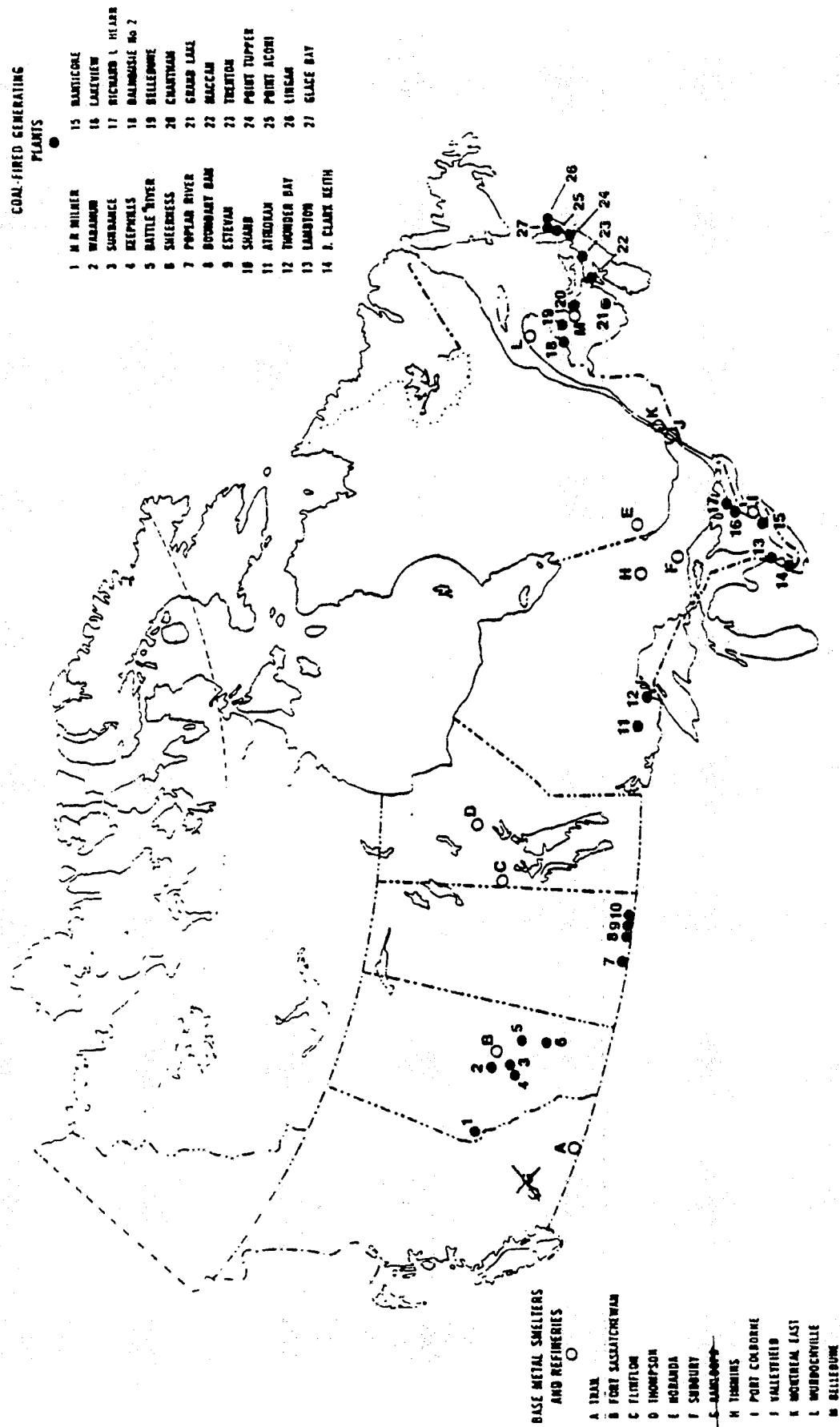


FIGURE 2  
MAP OF CANADA SHOWING THE LOCATION OF THE BASE-METAL SMELTERS AND  
REFINERIES AS WELL AS THE COAL-FIRED GENERATING PLANTS



Of the 280 tonnes of arsenic emitted into the atmosphere in 1988 by Canadian sulphide-based metal smelters and refineries, the copper smelter at Noranda, Quebec, released the largest amount, 110 tonnes. This value is about half of a previous estimate (207 tons/yr) for the late 1970's (Azzaria and Frechette, 1987), and likely reflects improved emission controls. Output estimates in Table 2 include data on atmospheric releases from only the smaller of the two copper/nickel smelting facilities at Sudbury, Ontario. Chan and Lusi (1986) have noted, however, that for the period 1973-1981, about 120 tonnes of arsenic were emitted annually from the larger Sudbury facility.

Atmospheric emissions of arsenic from the combustion of coal at electrical generating stations in Canada were estimated to be about 12 tonnes in 1982 (Jaques, 1987), and 13.6 tonnes in 1986 (Doiron, 1990). Furthermore, according to Doiron (1990) in 1986, 675-700 tonnes of arsenic were retained in fly and bottom ashes, and subsequently disposed of as solid waste. Locations of Canadian coal-fired power plants are shown in Figure 2.

Evans et al. (1985) and Van Voris et al. (1985) have investigated the fate of a variety of pollutants, including arsenic, at four Canadian coal-fired power plants (Battle River Alta., Langan Nova Scotia, Poplar River Saskatchewan, Nanticoke Ontario; Fig. 2). These stations were selected to represent a variety of coal types, ranging from western lignite to eastern bituminous varieties. Estimated atmospheric releases at the four plants ranged from 0.02 tonnes As/yr for the Battle River plant to 8.5 tonnes As/yr for the Langan facility. Emissions varied depending upon the arsenic content of the input coal (range 4.8 - 94 mg/kg), and inversely with its calcium content. Using an atmospheric model, arsenic deposition rates were calculated to be highest (range 0.001 to 1  $\mu\text{g}/\text{m}^2/\text{yr}$ ) within a few kilometres of the source plants (Van Voris et al. 1985). Assuming a 30-year operating life for these stations, no more than about 30  $\mu\text{g}$  As/ $\text{m}^2$  would therefore be expected to be added to local soils by atmospheric emissions.

Evans et al. (1985) estimated that 87 to 94% of the arsenic contained in the coal burned at these plants was trapped as fly ash by electrostatic precipitators. This ash can be transported to storage areas by either dry process or sluicing. If sluiced, there is a possibility of significant arsenic release to the transport waters. At the Nanticoke plant, for example, the ash slurry is discharged to a holding pond, and after most of the ash settles out the water is released into Lake Erie. Evans et al. (1985) concluded that about 1% of the arsenic input to this facility (i.e. between 8 and 9 kg/yr) was lost in this way.

Evans et al. (1985) also measured arsenic concentrations in coal pile drainage waters at the Langan, Poplar River and Nanticoke

plants. Values ranged from <1 (Nanticoke) to 240 µg As/L (Lingan), but no attempt was made to estimate totals amounts released by this pathway.

Reviewing the results of Evans et al. (1985), Van Voris et al. (1985) and others, Doiron (1990) concluded that, in view of the strong enrichment of arsenic in coal fly ash, ash disposal should be regarded as the principal potential pathway to the environment. As Doiron (1990) has noted, however, additional monitoring data are required to adequately assess the impact arsenic leaching from fly and bottom ashes on the environment in Canada.

In a study of landfill leachate discharges to sewer systems in the Greater Vancouver area (Anonymous 1988), the concentrations of arsenic in leachate ranged from an average of 0.003 mg/L, in Port Mann Landfill leachate (calculated loading 0.002 kg As/day), to an average of <0.3 mg/L in Cottonwood Landfill leachate (calculated loading <0.2 kg As/day). The same report cited a study in which 51 samples of leachate from a westcoast landfill contained arsenic concentrations ranging from <0.001 to 0.011 mg/L, with an average level of 0.003 mg As/L.

The Ontario Ministry of the Environment (1988) reported the results of a pilot monitoring study on "hazardous contaminants" from 37 water pollution control plants. The detection limit for arsenic in this study was relatively high (30 µg/L). Arsenic (unfiltered, total) was detected in only 3 of 308 samples of raw waste water at a maximum concentration of 60 µg/L. Arsenic was not detected in effluents from any of the seven primary treatment plants nor in the effluents of the two lagoons included in the study. Arsenic was detected in 3 of 252 samples of effluent from secondary treatment plants, again at a maximum concentration of 60 µg/L. Arsenic was not reported in the effluents of the one tertiary treatment plant included in the study.

The Ontario Ministry of the Environment (1988), detected arsenic in 50 of 51 samples of raw sewage sludge at a maximum concentration of 41.5 mg/kg dry weight and a mean of 6.13 mg/kg. Arsenic was also found in 49 of 50 samples of treated sludge at a maximum concentration of 23.56 mg/kg dry weight and a mean of 5.4 mg/kg. Such sludges are often disposed of on Canadian agricultural lands (Webber and Shamess, 1987).

The Petroleum Association for Conservation of the Canadian Environment (PACE 1983) reviewed levels of trace metals in various petroleum sludges which are disposed of on land. As indicated in Table 3, concentration ranged up to several hundred mg As/kg in some of these sludges.

Table 3. Summary of arsenic in petroleum industry sludges.

Type of Sludge	Concentration Range (mg As/kg)
Refinery Biosludges	0 - 123
API Separator Sludge	0 - 310
Cooling Water Sludge	0.1 - 18
Non-Leaded Product Tank Bottoms	Trace
Crude Tank Bottoms	<0.003 - 53
Pond, Lagoon Sludge	105
DAF Float	<0.006 - 10.5
Slop Oil Emulsion Solids	2.5 - 24

The manufacture and use of arsenic-containing pesticides can also result in the build-up of significant arsenic burdens in the environment. Inorganic arsenical pesticides have been applied in orchards, and to a lesser extent vegetable growing areas, in Canada since the early 1900's at rates of up to 2.7 kg As/ha (Frank et al., 1976a). Although by the early 1970's the popularity of inorganic arsenicals had decreased markedly, that of organic arsenicals began to rise (Walsh and Keeney, 1975). Organic arsenicals are typically applied at a lower rate, however, and are currently used in the forest industry for the thinning of young conifer stands, and for control of mountain pine and spruce beetles (E.D. Brien, Environment Canada, pers. comm.).

With the recent increase in popularity of arsenic-containing wood preservatives, wood treatment facilities have also become potentially significant sources of local soil and ground water contamination (Henning and Konasewich, 1984). In addition there is the potential for the release of arsenic from pressure-treated lumber. Warner and Solomon (1990), for example, found that arsenic was leached from jack-pine (*Pinus banksiana*) lumber pressure-treated with chromated copper arsenate (CCA). After a 40-day exposure, 68% and 9% of the arsenic pentoxide originally present in new pressure-treated wood had leached out in leaching baths with pH's of 3.5 and 8.5, respectively. After 40 days, the concentration of arsenic in the leaching solutions reached 16,000 µg/L and 2,200 µg/L, respectively, for pH 3.5 and pH 8.5.

## Section 6. Environmental Fate and Levels

### 6.1 Transport and Transformation

Arsenic is affected by a variety of chemical and biochemical processes in nature, such as oxidation, reduction, methylation, adsorption and precipitation, which affect its form, distribution

and mobility. Principal arsenic species expected in the environment in the dissolved, solid and vapour phases, are listed in Table 4. A comprehensive review of arsenic speciation in environmental media was recently published by Cullen and Reimer (1989).

Table 4. Principal arsenic species expected in dissolved, solid and vapour phases in the environment.

Phase	Arsenic Species	
<u>Dissolved</u> <sup>1</sup> : in surface water and soil and sediment pore waters	AsO <sub>4</sub> <sup>-3</sup> AsO <sub>3</sub> <sup>-3</sup> (CH <sub>3</sub> ) <sub>2</sub> AsO <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> HAsO <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> AsO	arsenate arsenite methylarsonic acid dimethylarsinic acid [trimethylarsine oxide] <sup>2</sup>
<u>Solid</u> : in biota, soil, sediment, and suspended particulates in air and water	"dissolved" species, plus various organo-arsenicals like arseno-sugars, arsenobetaine, arsenocoline, in tissues of biota "dissolved" species, adsorbed onto Fe and Mn oxyhydroxides, clays or organic matter sulphides, such as FeAsS (arsenopyrite) and As <sub>2</sub> S <sub>3</sub> (orpiment), in sediment As <sub>2</sub> O <sub>3</sub>	arsenic trioxide, in air (T < 193°C)
<u>Vapour</u> : mostly in air	(CH <sub>3</sub> ) <sub>3</sub> As (CH <sub>3</sub> ) <sub>2</sub> AsH (CH <sub>3</sub> )AsH <sub>2</sub> AsH <sub>3</sub> As <sub>2</sub> O <sub>3</sub>	trimethylarsine dimethylarsine methylarsine [arsine] <sup>2</sup> [arsenic trioxide] <sup>2</sup> (T > 193°C)

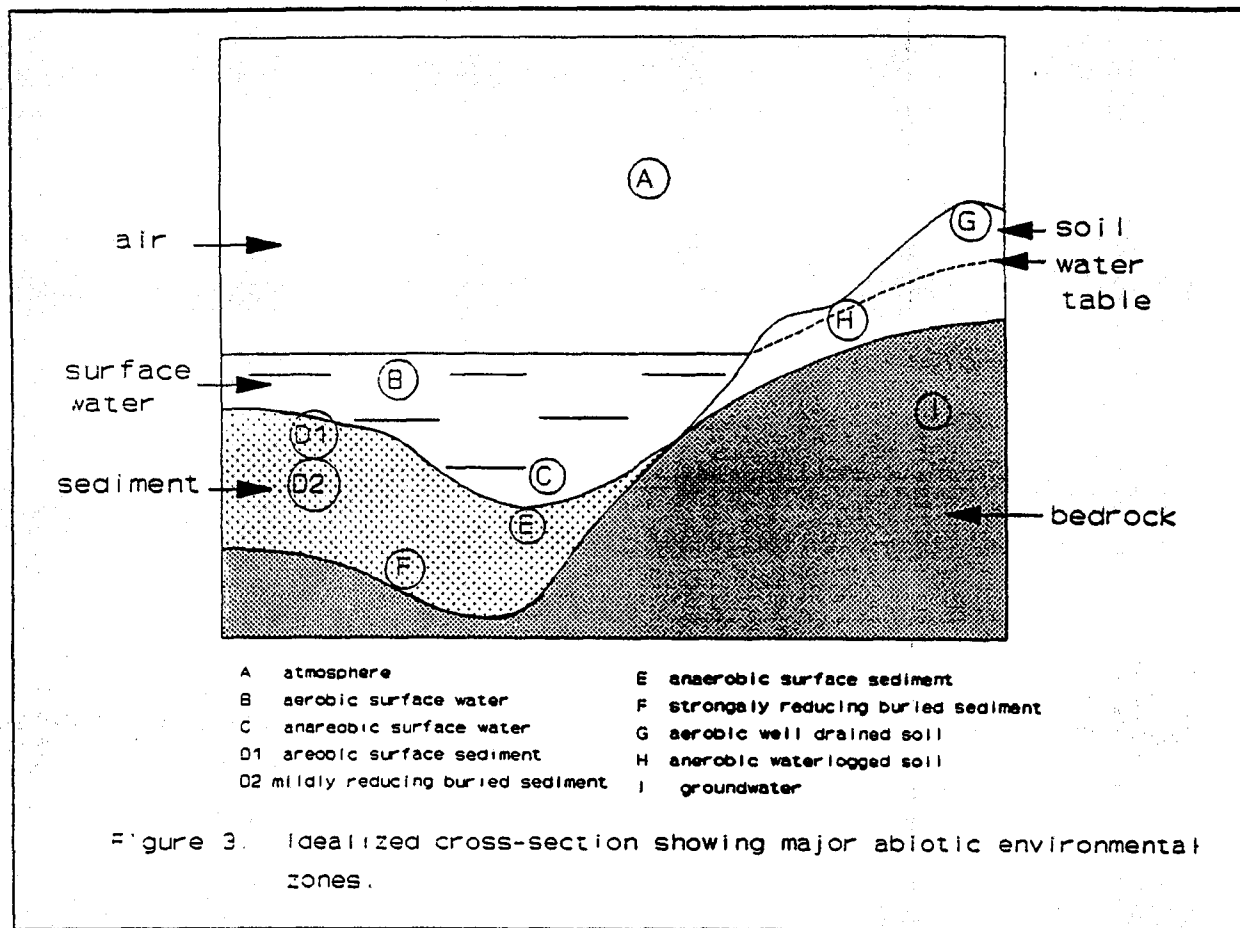
<sup>1</sup> Only inorganic arsenic species have been reported in ground waters.

<sup>2</sup> Species in square brackets are likely to occur in only very limited amounts.

As Woolson (1983) has noted, the ultimate sink for most environmental arsenic is ocean sediment. However, because of its reactivity and mobility, arsenic can cycle extensively through both biotic and abiotic components of local aquatic and terrestrial systems. In the following discussion processes affecting the transformation and movement of arsenic in individual abiotic environmental "zones" - (A) the atmosphere, (B) aerobic-surface



water, (C) anaerobic bottom water, (D & E) aerobic and mildly reducing surface sediment, (F) strongly reducing buried sediment, (G & H) well drained and waterlogged soil and (I) ground water - (Figure 3), will be considered.



$\text{As}_2\text{O}_3$  vapour is the main arsenic species introduced into the atmosphere (Zone A, Figure 3), with other high temperature gases, by smelters, fossil fuel combustion (Cullen and Reimer, 1989) and roasters (Gagan, 1979). Since less than 10% of the arsenic in the atmosphere is in the vapour phase (Walsh et al., 1979), most  $\text{As}_2\text{O}_3$  likely quickly condenses to a solid on cooling, or is trapped on suspended particulate matter by adsorption or complexation reactions (Cullen and Reimer, 1989). It is removed from the atmosphere by either dry deposition or rainfall, rates of deposition typically being highest closest to the source.

As Cullen and Reimer (1989) have observed, inorganic  $\text{As}^{+3}/\text{As}^{+5}$  ratios in the condensed phase are expected to vary, depending upon the concentrations of reducing agents such as  $\text{SO}_2$ , or oxidizing agents like  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ . Although methylarsenic species have also been detected in the atmosphere, these probably result mostly from

the natural release of volatile methylarsines by soil microorganisms. According to calculations of Parris and Brinkman (1976) one microbially produced methylarsine,  $(\text{CH}_3)_3\text{As}$ , is oxidized very slowly and can likely be transported for considerable distances without undergoing chemical change. Eventually, however, methylarsines will be oxidized to methylarsonic acid, dimethylarsinic acid and trimethylarsine oxide, or undergo other reactions, possibly on the surface of particles (Cullen and Reimer, 1989).

Andreae et al. (1983) studied arsenic speciation in the Tego River Estuary in Portugal, which received some 1000 - 2000 tons/year of arsenic, about half as atmospheric fallout from a near-by pyrite roasting plant. As (III) was found to comprise from 2.9% to 20% of the total inorganic arsenic found in the surface waters of the estuary (the remainder was  $\text{As}^{+5}$ ). Highest percentages were found nearest the emission source, indicating that a significant proportion of the  $\text{As}_2\text{O}_3$  released by the plant had not oxidized to  $\text{As}^{+5}$  species at the time of deposition.

In their review of the arsenic cycle in water, Ferguson and Gavis (1972) pointed out that inorganic arsenate ( $\text{AsO}_4^{3-}$ ) is the thermodynamically stable form of dissolved arsenic in most aerobic waters (Zone B, Figure 3). The oxidation of arsenite to arsenate is reportedly "slow" at neutral pH (Ferguson and Gavis, 1972), but it can be catalyzed in various ways. For example, the rate of oxidation has been shown to increase with initial arsenite concentration, temperature, salinity and exposure to sunlight (Cullen and Reimer, 1989). Also, Oscarson et al. (1981) have reported that 100 mg of Mn (IV) oxide oxidised about 7 mg As (III) (dissolved in 70 ml of water) to As (V) after only 72 hours, whereas in the absence of Mn oxide no detectable As (III) was oxidized. Furthermore bacteria capable of oxidizing arsenic - at rate of about 5 times normal rates of chemical oxidation - have been found in fresh and marine waters of high productivity (Cullen and Reimer, 1989).

At pH and Eh conditions typical of most waters arsenite anions typically hydrolyse to form  $\text{H}_2\text{AsO}_3$  and, less commonly,  $\text{H}_2\text{AsO}_3^-$  (Ferguson and Gavis, 1972). Hydrolysis of arsenate produces species such  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ . Equilibrium modelling suggests that arsenic forms few additional aqueous complexes with typical water constituents (Cullen and Reimer, 1989).

As Cullen and Reimer (1989) have noted, based on thermodynamic criteria alone, the calculated  $\text{As}^{+5}/\text{As}^{+3}$  ratio for uncontaminated surface water is  $10^{15}$ - $10^{26}$ , however the actual value for most marine waters is about  $10^{+1}$ . Andreae (1978, 1979), for example, found an  $\text{As}^{+5}/\text{As}^{+3}$  ratio of from about  $10^3$ - $10^{-1}$  in United States fresh and coastal marine waters. These authors observed that ratios tended to be lowest in productive algae-rich waters, and concluded that

arsenite was derived from the reduction of arsenate by phytoplankton in response to high arsenate stress. These results, and those of others such as Johnson and Burke (1978), suggest that thermodynamic equilibrium is rarely achieved in productive surface waters, largely because of arsenite generated by phytoplankton (Cullen and Reimer, 1989).

Andreae (1978, 1979), have found small amounts ( $<0.01 - 0.56 \mu\text{g/L}$ ) of methylated arsenicals (methylarsonic and dimethylarsinic acids) in United States near-surface fresh and coastal marine waters (Zone B, Figure 3). Concentrations of these thermodynamically unstable species did not exceed 20% of the total dissolved arsenic, and were typically much lower. Although methylarsenicals are used as herbicides, they are immobilized in most soils, and thus are not generally transferred to aquatic systems in large amounts (Andreae, 1986). Andreae (1978, 1979) observed that, as with arsenite, methylarsonic and dimethylarsinic acid concentrations tended to be highest in eutrophic waters, and concluded that they were also produced by phytoplankton. Other workers have reported similar findings (Cullen and Reimer, 1989).

In deep anoxic basins (Zone C, Figure 3), dissolved arsenate should be reduced to arsenite. Consistent with this expectation, Peterson and Carpenter (1983) found an arsenate/arsenite ratio of 15/1 in surficial oxygenated water in Saanich Inlet, British Columbia, and only 1/12 in deep ( $> 150 \text{ m}$ ) anoxic waters. As Cullen and Reimer (1989) have remarked, however, more residual arsenate is often present in these deep anoxic waters than would be expected on thermodynamic grounds.

Near-surface sediment can be either oxic (Zone D<sub>1</sub>, Figure 3) or anoxic (Zone E, Figure 3) depending upon the oxygen status of the overlying waters. Even when in contact with oxygenated waters (Zone D<sub>1</sub>, Figure 3), however, aerobic conditions normally persist for only a short distance below the sediment surface (see for example Belzile, 1988). In mildly reducing buried and surface sediment (Zone D<sub>2</sub> and E, Figure 3) the production and persistence of arsenite in pore water is favoured. Thus Peterson and Carpenter (1986) found no detectable  $\text{As}^{+5}$  in sediment pore water in Saanich Inlet when bottom waters were anoxic. However, the same authors reported  $\text{As}^{+3}/\text{As}^{+5}$  ratios of only 0.1 to 0.6 in pore waters of Washington State coastal sediments, and ratios in the 1.0 to 4.0 range in interstitial waters of Lake Washington and Puget Sound sediment. Similarly, Andreae (1979) found  $\text{As}^{+3}/\text{As}^{+5}$  ratios from about 0.02 - 0.2 in pore waters in sediment from the northeast Pacific and off the southern California coast. The cause of the "excess" arsenate in some anoxic pore and surface waters is uncertain (Cullen and Reimer, 1989), but it has been suggested that it could be kinetically controlled or that soluble thioarsenates ( $\text{AsO}_3\text{S}^{3-}$ ) may be forming in some anoxic  $\text{S}^{2-}$ -enriched environments.

Recently methylarsonic acid, dimethylarsinic acid and trimethylarsine oxide were found in pore waters of sediments from two British Columbia coastal sites - Rupert Inlet and Alice Arm (Reimer and Thompson, 1988). Crecelius (1975) has also reported finding dimethylarsinic acid ( $1 \mu\text{g As/L}$ ) in pore water of arsenic contaminated Lake Washington. According to Andreae (1986) these results are most likely explained by the decomposition of deposited algal material. Cullen and Reimer (1989) have questioned Andreae (1986)'s conclusion, however, and consider that *in situ* bacterial methylation of inorganic arsenic is at least a possibility.

As Boyle and Jonasson (1973) have pointed out, in addition to inorganic and methylated species, "dissolved" arsenic can be present in a variety of organic complexes, or adsorbed to hydrous iron oxide, silicate and humic colloids. Complexes with dissolved organic matter may be particularly important in the transport of arsenic. Waslenchuk (1979), for example, has reported a close relationship between dissolved organic carbon and arsenic levels in ten major southeastern United States rivers. The author also noted that significant amounts of arsenic can be carried by the suspended particulates in these rivers.

Arsenic can be removed from solution in various ways: (i) uptake by biota, (ii) adsorption onto iron, manganese and aluminum hydroxides or clay particles (Klaassen et al., 1986), (iii) fixation by non-living organic matter, or less frequently by (iv) precipitation or coprecipitation. Processes (i) and (ii) are principally responsible for the removal of dissolved arsenic from surface waters (Zones B and C, Figure 3), and their eventual deposition in sediment. The effectiveness of these processes is reflected in the relatively short residence time for arsenic in most surface waters (see for example, Seydel (1972)). Processes (ii) to (iv) remove arsenic from solution in sediment, soil and rock pore waters (Zones D to I, Figure 3).

Amorphous iron hydroxide has an extremely high capacity for adsorbing arsenic (Pierce and Moore, 1982). Adsorption is also very fast. Pierce and Moore (1982) found that, in rates of adsorption experiments, more than 50% of the arsenic was adsorbed before a sample could be taken. Adsorption of arsenate tended to decrease with increasing pH (range 4-10). pH variations had a different effect on arsenite. In the 50-1000  $\mu\text{g/L}$  concentration range arsenite adsorption increased as pH rose, to reach a maximum at pH 7, after which adsorption decreased. These authors noted that arsenate was more efficiently adsorbed than arsenite at concentrations found in natural waters.

Frost and Griffin (1977), studying As (V) adsorption from municipal landfill leachate solutions by kaolinite and montmorillonite, found that maximum adsorption occurred in the pH range 4 to 6, and concluded that  $\text{H}_2\text{AsO}_4^-$  was the primary species

being adsorbed. As (III) was less efficiently adsorbed by these clays than As (V). In general adsorption of As (III) tended to increase as pH rose from 3 to 9.

Using sediments from streams and lakes of the Mississippi alluvial flood plain, Wauchope and McDowell (1984) showed that adsorption of arsenate ( $\text{H}_2\text{AsO}_4^-$ ), methanearsonate ( $\text{HASO}_3\text{CH}_3^-$ ), and dimethylarsinic acid ( $\text{HASO}_2(\text{CH}_3)_2$ ) was strongly correlated with Fe and clay content of the sediments, and less strongly correlated with Al content. The sediments had a stronger affinity for arsenate and methanearsonate than for dimethylarsinic acid. Organic matter content of the sediments ranged from 10 to 80 g/kg, but no significant correlation was found between adsorption of the various arsenic compounds and sediment organic matter content.

After removal from solution in surface water, arsenic is deposited in sediment with settling organic and inorganic particulates. Surface sediments (Zone D, and E, Figure 3) are not necessarily arsenic sinks, however. Byrd (1988), for example, found that dissolved arsenic concentrations varied seasonally on the continental shelf off Georgia and South Carolina. During periods of high winds and sediment resuspension in the spring, dissolved arsenic was adsorbed onto suspended particles and/or removed by phytoplankton and incorporated into nearshore sediments, resulting in dissolved arsenic concentrations as low as 20% of typical open ocean concentrations. In August, the arsenic that had been removed by suspended sediment was released into the overlying waters, and the concentration of dissolved arsenic in the nearshore zone may be elevated to levels up to 50% greater than the concentration in the open ocean.

Various workers, including Andreae (1979), have suggested that sediment-bound arsenic can be released by both decomposing organic matter and the reduction and consequent dissolution of arsenic-bearing iron and manganese hydroxides with burial in subsurface sediment. In the Gulf of St. Lawrence, Edenborn et al. (1986) and Belzile (1988) have proposed that arsenic associated with iron oxyhydroxides follows a redox pattern of dissolution in suboxic sediment (Zone D, Figure 3), with release of both arsenic and iron into pore waters, followed by upward and downward diffusion of both elements along concentration gradients. Arsenic moving upward through pore waters may eventually be trapped (adsorbed or coprecipitated with iron hydroxides) in the surface oxic layer (Zone D, Figure 3), or if the oxic layer is thin, escape to the water column above. Belzile and Tessier (1990) concluded that very little arsenic was escaping through the surface oxic layer of littoral (near-shore) sediments of several small eastern Canadian lakes. Nriagu et al. (1987), on the other hand, have estimated that relatively large amounts of arsenic ( $6.8 \text{ mg As/m}^2/\text{yr}$  or about half of the amount being deposited) were diffusing from sediment into the overlying water at a site in the Central basin of Lake Erie.

Arsenic migrating downward (into Zone F, Figure 3) can coprecipitate with iron sulphides, formed by the reaction of downward diffusing  $\text{Fe}^{+2}$  with sulphide ions produced by sulphate reduction, or it can react directly with sulphide ions to produce compounds such as  $\text{As}_2\text{S}_3$  (Cullen and Reimer, 1989). These reactions are favoured in organic-rich sediment. Once precipitated as a sulphide in sediment, arsenic is not easily remobilized.

Soils (Zones G and H, Figure 3) can be contaminated with arsenic in a variety of ways, such as from atmospheric fallout (arsenate, arsenite and smaller amounts of methylated arsenicals), pesticide applications (principally mono- and disodium methanearsenates, and historically, inorganic arsenates), use and production of wood preservatives (inorganic arsenates), and leaching of materials in waste storage sites.

As in the aquatic environment, arsenic movement in soil is largely controlled by adsorption by iron and manganese oxides and clay minerals. In some heavier soils with higher clay and hydrous oxide contents, added arsenic can thus be effectively immobilized within a short distance of its point of entry. Veneman et al. (1983), for example, found that 35 years after application of lead arsenate pesticides had ceased, no significant leaching of arsenic residues had occurred below a depth of about 20 cm in a silty, mildly acidic (pH about 6.0), former apple orchard soil. The highest concentrations of arsenic occurred in the upper 10 cm, while no secondary accumulations of arsenic were evident below a depth of 25 cm.

Woolson (1973) studied changes in available ( $0.05 \text{ N H}_2\text{SO}_4/0.025 \text{ N HCl}$ -extractable) arsenic levels with time after spiking two clay- and iron-bearing soils and one sandy soil with 10, 50, 100 and 500  $\mu\text{g/g}$  sodium arsenate. After only four months available arsenic levels fell (in comparison to values measured after 1 month) by between about 40 and 70% in the clay- and iron-bearing soils which had received the two highest arsenic treatments. In the sandy (clay- and iron-poor) soil, available levels fell by only from 2-27% after four months. Results of testing after 19 months were roughly comparable to those for the 4 month tests. These findings support Woolson (1983)'s observation that, in orchards where arsenical pesticides were applied, a significant proportion of soil arsenic can be so tightly bound that it is no longer available for plant uptake.

Arsenic in organoarsenical pesticides takes the form of the univalent anion of methanearsonate in most soils (Hiltbold, 1975). Like inorganic arsenic, methanearsonate can be removed from solution by adsorption onto soil clays and iron hydroxides (Wauchope and McDowell, 1984). Results of field studies reported by Hiltbold (1975) suggested that in agricultural soils methylarsenicals are rarely transported to depths below about 30

cm. Methanearsonate is thermodynamically unstable, however, and eventually it is oxidized to  $\text{CO}_2$  and inorganic arsenate. Hiltbold (1975) has estimated that in light textured soils of low organic matter content, about 80% of the added methanearsonate could be broken down in this fashion after one year. The rate of decomposition would be reduced in organic clay-rich soils.

It should be noted, however, that the adsorption capacity of a soil for arsenic is finite, and if it is exceeded the "excess" soluble arsenic will remain in soil solution (NRCC, 1978). Furthermore adsorption by iron and manganese oxides is reduced in acidic soils, due to the instability of these phases (NRCC, 1978).

High phosphate levels can also reduce arsenic adsorption. Roy et al. (1986), for example, showed that adsorption of arsenate by Cecil clay was reduced by the presence of phosphate and, to a lesser extent, molybdate. At pH 4.5 and an equilibrium arsenic concentration of 1600  $\mu\text{moles/L}$  (about 120,000  $\mu\text{g As/L}$ ), absorption of arsenic was reduced from about 50  $\mu\text{moles/g}$  (about 3,750  $\mu\text{g As/g}$ ) at 0  $\mu\text{moles/L}$  phosphate to about 19  $\mu\text{moles/g}$  (approximately 1,425  $\mu\text{g As/g}$ ) at a phosphate concentration of 3229  $\mu\text{moles/L}$ . The authors speculated that all three anions are adsorbed by hydrous oxides in soils by some type of ligand exchange reaction, and hence may compete with each other for sorption sites.

Studies of the speciation of arsenic in soil pore waters have indicated that, consistent with thermodynamic predictions, in aerobic soils (Zone G, Figure 3) on which no organoarsenical pesticides have been used, arsenate is typically the predominant species (Haswell et al., 1985). Conversely, in waterlogged soils (Zone H, Figure 3) where reducing conditions occur, the major species is reported to be arsenite.

Masscheleyn et al. (1991), for example, have examined arsenic speciation and solubility in a soil which had been exposed to arsenic contamination from a wood preservation facility for over 20 years. The soil was loamy at the surface and had a pH of 5.6, and a total arsenic content ( $\text{HCl/HNO}_3$ -extractable) of 555 mg/kg. Using selective extraction techniques it was determined that the major part of the arsenic present was associated with amorphous iron oxides. After flooding for only one day the oxidation potential was still high (Eh 250 - 350 mV) and the  $\text{As}^{+3}/\text{As}^{+5}$  ratio in near-surface soil was  $\leq 1.0$ . After 35 days, however, the Eh had fallen to about zero, and the  $\text{As}^{+3}/\text{As}^{+5}$  ratio had increased to about 3.0. These authors also reported a large ( $> 10$  fold) increase in the total soluble arsenic concentrations in this soil after 35 days, which they attributed to reduction and dissolution of the arsenic-bearing iron oxides.

In naturally arsenic enriched aerobic soils Haswell et al. (1985) have found methylarsonic acid (comprising up to 10% of total

dissolved arsenic), but not dimethylarsinic acid, in soil pore waters. The absence of detectable methylarsonic acid in aerobic soils with normal arsenic contents led Haswell et al. (1989) to suggest that there may be a threshold concentration of arsenite at which methylarsonic acid is microbially produced. These authors also found methylarsonic acid in pore waters of anaerobic soils with normal arsenic contents however. Haswell et al. (1989)'s results are consistent with those of Woolson (1983), who reported finding small amounts of methylarsonate and dimethylarsinate in soil 26 weeks after it had been treated with inorganic arsenic.

A variety of fungi, aerobic and anaerobic bacteria, have been shown to be capable of producing volatile methylarsines from both inorganic and organoarsenic species (Cullen and Reimer, 1989). McBride and Wolfe (1971), for example, have shown that Methanobacterium can produce dimethylarsine from arsenate under anaerobic conditions. Similarly, Cox and Alexander (1973) have demonstrated that Cabdida humicola can produce trimethylarsine from arsenite, arsenate, and methylarsonic and dimethylarsinic acids at pH 5. When the initial arsenic species is inorganic (arsenite or arsenate) it is likely that methylarsonic and dimethylarsinic acids are formed as intermediates in these processes (Cullen and Reimer, 1989), thus perhaps accounting for their detection in some soils. Detection of both dimethyl- and trimethylarsines in air above soil treated with various arsenicals (Woolson, 1983) has led to the suggestion that considerable amounts (20 to 60 %) of arsenic applied to soils may be lost to the atmosphere (NRCC, 1978). Dudas (1987), for example, considered that the apparent loss of arsenic from the surface of an acidic naturally arsenic-enriched soil in Alberta, could have been due to the formation of volatile arsines. As Cullen and Reimer (1989) have noted, however, there is still controversy about the quantitative importance of these microbially mediated volatilization processes.

Terrestrial ground waters (Zone I, Figure 3) can be either oxic or anoxic, depending in part upon their depth, age and the type of aquifer, and thus either As (V) or As (III) can be thermodynamically stable. Korte and Fernando (1991) noted that the influence of biological processes on arsenic speciation in ground waters has not been studied, but considered that they are likely of only minor importance. Otherwise, processes affecting arsenic speciation and movement in ground waters would be expected to be similar to those described for soils.

Results of studies of the transformation of arsenicals after absorption by higher organisms have been reviewed by Cullen and Reimer (1989). These authors noted that the herbicide monosodium methylarsonate (MSMA) can be absorbed by either leaves or roots of terrestrial plants, and that at least some of the compound persists unchanged after absorption.

Freshwater algae are capable of synthesizing considerable



amounts of arsenic-lipid, as well as unidentified water-soluble lipid-related arsenic compounds, methylated intermediates and arsenite, when incubated with arsenic in the form of arsenate (Nissen and Benson 1982). Studies of other freshwater plants have produced similar results (Cullen and Reimer, 1989). In terrestrial plants Nissen and Benson (1982) found that arsenate was readily reduced to arsenite, but methylation of arsenic only occurred in plants grown in phosphorus-deficient or phosphorus and nitrogen-deficient conditions. Methanearsonic acid, dimethylarsinic acid, and possibly methanearsonic acid were detected in roots, stems and leaves of arsenate-exposed N- and P-deficient plants. No arsenic-lipid was detected in extracts of leaves from these terrestrial plants. Nissen and Benson (1982) suggested that terrestrial plants may not have evolved mechanisms to detoxify arsenic because the normally high P/As ratios in soil would render arsenic uptake insignificant. Aquatic plants, on the other hand, are occasionally exposed to relatively high arsenic concentrations and therefore have evolved mechanisms to detoxify the substance.

In a range of animal species, inorganic arsenic compounds are metabolized by methylation to dimethylarsinic acid and methylarsonic acid (Cullen and Reimer, 1989).

Marine plants and algae have been shown to contain significant amounts of methanol-soluble arsenic-containing sugar derivatives and lipid-soluble arsenic compounds (Cullen and Reimer, 1989). Most of the arsenic in marine animals is in water-soluble organic form, the major compound being arsenobetaine (Kaise et al. 1987). In an attempt to understand the circulation of arsenic in marine ecosystems, Kaise et al. (1987) investigated the fate of arsenobetaine in tissues after death. They identified trimethylarsine oxide as one of the metabolites produced by marine microorganisms. Hanaoka et al. (1987) observed three arsenic metabolites, indicating the conversion of arsenobetaine into other arsenic compounds by microorganisms occurring in bottom sediments of coastal waters. The metabolites were not identified, however.

## 6.2 Bioaccumulation and Biomagnification

### 6.2.1 Aquatic Systems

Arsenic is bioaccumulated from water by various aquatic organisms but is not biomagnified through the food web (CCREM 1987, Eisler 1988). The degree of bioaccumulation depends upon the species, age of organism, arsenic concentration and water temperature (NRCC 1978, US EPA 1979, Demayo et al. 1979). Lower forms of aquatic life may accumulate greater amounts of arsenic than do fish. The fish most likely to concentrate arsenic are bottom feeders (CPHA 1977).

Andreae (1986) noted that arsenate and phosphate have similar

chemical properties. He examined arsenic/phosphorus ratios at different levels in the food chain and reported a biotransformation of arsenic. For example, Andreae (1986) indicated that at the surface of the ocean the arsenic level is  $0.0015 \mu\text{g/g}$  and the phosphorus level is  $0.016 \mu\text{g/g}$ . This results in a P:As ratio of 11. There was a marked increase in the estimated P:As ratio from ocean surface water (11) to marine algae (170) to crustacea (6,000) to fish (10,600) to mammals (215,000). Andreae (1986) suggested that the biochemical depletion of arsenic relative to phosphorus and its conversion to relatively harmless forms represents a natural control on As toxicity up the food chain.

Using a three-step freshwater food chain, Maeda et al. (1990) found that the green alga Chlorella vulgaris accumulated arsenic concentrations as high as  $2850 \mu\text{g As/g}$  dry weight following a 14-day exposure to  $\text{Na}_2\text{HAsO}_4$  at  $100,000 \mu\text{g As/L}$ . The zooplankton, Moina macrocopa, accumulated arsenic levels as high as  $225 \mu\text{g As/g}$  dry weight when fed for seven days on Chlorella containing  $2850 \mu\text{g As/g}$ . When exposed to arsenic only through the water at a concentration of  $2,000 \mu\text{g/L}$ , Moina accumulated only  $17.9 \mu\text{g As/g}$ . Goldfish, Carassius carassius auratus, fed for seven days on Moina containing  $225 \mu\text{g As/kg}$  accumulated arsenic concentrations of  $37 \mu\text{g/g}$ , while fish exposed only through the water, at a concentration of  $1,000 \mu\text{g/L}$ , accumulated slightly higher concentrations,  $51.3 \mu\text{g As/g}$ . Most of the accumulated arsenic in Chlorella (99.2%) was in the form of non-methylated arsenic. Moina feeding on the algae accumulated 83.5% of the arsenic in the non-methylated form, but also contained 9.6% of this arsenic as monomethyl arsenic and 6.9% as dimethyl arsenic. Only 63.5% of the arsenic burden of Carassius was in the non-methylated form, while 18.6% existed as monomethyl arsenic, 3.5% as dimethyl arsenic, and 14.3% as trimethyl arsenic.

Lindsay and Sanders (1990) exposed three species of phytoplankton, Thalassiosira pseudonana, Dunaliella tertiolecta and Skeletonema costatum, to arsenate concentrations of 0, 10, and  $25 \mu\text{g As/L}$  (as added arsenic; natural river water ( $0.71 \mu\text{g As/L}$ ) was used as the diluent). After a 48-hour exposure all three species contained significant concentrations of arsenic, ranging from  $6.82 \mu\text{g/g}$  dry weight in T. pseudonana exposed to ambient levels, to  $92.2 \mu\text{g/g}$  in D. tertiolecta exposed to  $25 \mu\text{g/L}$  added arsenic. Brine shrimp, Artemia sp. exposed only to waterborne arsenic contained slightly increased arsenic concentrations after a 72-hour exposure to  $25 \mu\text{g/L}$  added arsenic ( $17.8 \mu\text{g/g}$  dry weight, compared to  $16.8 \mu\text{g/g}$  for the controls). Artemia exposed only to arsenic-loaded phytoplankton did not exhibit statistically significant increases in arsenic content. Grass shrimp, Palaemonetes pugio, exposed to elevated waterborne arsenic or to arsenic-dosed Artemia for 28 days did not exhibit significant increases in arsenic content compared to the control groups (which contained 6.12 and  $6.19 \mu\text{g As/g}$ ).

In an experiment using the freshwater diatom, Asterionella formosa, Conway (1978) found that the cellular arsenic content appeared to reach an equilibrium value of approximately  $0.03 \mu\text{g As}/10^9 \mu\text{m}^3$  after a 22-day exposure to arsenate at about  $60 \mu\text{g As/L}$  and after a 5-day exposure to about  $160 \mu\text{g As/L}$ . The sorption of arsenic by the diatoms appeared to be a linear function of the ambient arsenic concentration. The bioconcentration factor was about 150 at the higher exposure level and about 350 at the lower level. Fractionation experiments showed that 48% of the arsenic taken up by the diatoms was associated with the organic coating of the diatom frustules, while 16% was associated with the siliceous frustules and 36% with the cell contents (Conway 1978).

Spehar et al. (1980) exposed five species of invertebrates and rainbow trout to four arsenic compounds (arsenic trioxide, arsenic pentoxide, sodium dimethyl arsenate and disodium methyl arsenate) at concentrations of approximately 100 and  $1000 \mu\text{g As/L}$  for 28 days. The concentration (dry weight basis) of accumulated arsenic in relation to the water concentration was as high as 131 for the stonefly, Pteronarcys dorsata, (exposed to  $89 \mu\text{g As/L}$  as arsenic pentoxide), 99 for the snail, Helisoma campanulata, (exposed to  $89 \mu\text{g As/L}$  as arsenic pentoxide), 92 for the snail, Stagnicola emarginata (exposed to  $89 \mu\text{g As/L}$  as arsenic pentoxide) and 219 for Daphnia magna (exposed to  $96 \mu\text{g As/L}$  as arsenic trioxide). The amphipod, Gammarus pseudolimnaeus and rainbow trout contained arsenic residues similar to those found in the control groups. Other workers, such as Isensee et al. 1973 and Nichols et al. (1984), have similarly noted a lack of arsenic accumulation in fish exposed to both inorganic and methylated arsenic species.

Finally, Furr et al. (1979) compared the content of a number of elements in sediment and biota from two ponds. One pond was contaminated by fly ash from a coal-burning power-generating plant, while the other pond was non-contaminated. The arsenic concentration in sediment from the fly-ash pond was significantly higher than in sediment from the control pond (Table 5), however, arsenic was elevated only in pondweeds and, to a lesser degree, fish (bullhead) liver from the contaminated pond. There was no evidence of arsenic biomagnification in this system.

Table 5. Arsenic in bottom sediments, plant material and aquatic animals from a fly-ash contaminated and non-contaminated pond.

Type of Sample	Concentration ( $\mu\text{g As/g dry weight}$ )	
	Fly-ash Pond	Control Pond
Sediment	103	9.8
Pondweeds <sup>1</sup>	84	9.6
Algae <sup>2</sup>	9.6	27
Dragonfly <sup>3</sup> nymphs	-	0.8
Newts <sup>4</sup>	0.6	0.8
Bullhead <sup>5</sup> liver	0.4	0.0

<sup>1</sup> Potamogeton pectinatus

<sup>4</sup> Notophthalmus viridescens

<sup>2</sup> Zygnema sp.

<sup>5</sup> Ictalurus nebulosus

<sup>3</sup> Platemis lydia

### 6.2.2 Terrestrial Systems

Comparison of typical arsenic levels in terrestrial plants (1-2 mg/kg, dry weight; NRCC, 1978) with typical total soil levels (7.2 mg/kg; Boyle and Jonasson, 1974), indicates that arsenic is not normally bioaccumulated from soil by vegetation. Arsenic uptake by plants varies with the type of arsenical, and whether absorption is by roots or foliar. For example, Sachs and Michael (1971) reported that sodium arsenate and sodium arsenite were more readily absorbed by the root system of beans (Phaseolus vulgaris) than monosodium methanoarsonate (MSMA) and cacodylic acid. Uptake also varies with plant species (NRCC, 1979), and with plant-available (i.e. water-soluble and loosely bound) soil arsenic concentrations. According to NRCC (1978) highest arsenic levels typically occur in plant roots followed by those in plant tops, and lastly by those in edible seeds and fruits. Furthermore, the edible parts of plants seldom accumulate very high levels of arsenic as most plant growth is severely retarded prior to this occurrence (NRCC, 1978).

Ingestion is the most likely route of uptake of arsenic by animals (NRCC, 1978). The amount absorbed depends, in part, upon the solubility of the arsenical.

Earthworms consume soil directly, and are consumed by both birds and small mammals. Beyer and Cromartie (1987) reported a statistically significant but low positive correlation ( $r = +0.45$ ) between concentrations of arsenic in soil and in earthworms in natural (uncontaminated), mining and industrial areas in eastern United States. Soil arsenic concentrations ranged from 0.77 to 3.5 kg/kg dry soil at "natural" sites, 1.1 to 24 mg/kg at the mining sties, and 2.8 to 33 mg/kg at industrial sites. Earthworms contained consistently less arsenic than associated soils; from

< 0.05 to 1.5 mg As/kg dry weight at "natural" sites, < 0.05 to 10 mg As/kg at mining sites and < 0.05 to 0.81 mg As/kg at industrial sites.

In most animals highest arsenic levels are found in the liver, kidney, spleen and lung (NRCC, 1978). For example, Vreman et al. (1986) reported that cows fed 33 mg arsenic (as arsenic pentoxide) per day for 15-28 weeks had only 0.03 mg As/kg (fresh weight) in muscle, compared to 0.10 and 0.16 mg As/kg in liver and kidney.

As in aquatic systems, arsenic levels do not appear to be biomagnified through the terrestrial food chain. Sharma and Shupe (1977), for example, compared arsenic levels in soil, unwashed vegetation and rock squirrel (Spermophilus variegatus) livers from 18 different localities in a semi-arid part of the United States.  $\text{HNO}_3/\text{HClO}_4$  extractable soil concentrations ranged from 7.5 to 655 mg As/kg, while levels in vegetation ranged from only 0.6 to 94 mg/kg dry weight, and those in squirrel livers from 0.1 to 9.4 mg/kg dry weight. Similarly in a controlled experiment, lambs fed for 3 months on a diet containing 2 mg As/kg dry weight (as arsenic trioxide) had arsenic levels of only 0.014, 0.024 and 0.041 mg As/kg fresh weight, in muscle, liver and kidney, respectively (Veen and Vreman, 1986).

Studies have shown that inorganic and organic arsenic compounds are generally not excreted into milk of cows (Vreman et al. 1986; Hesse et al. 1990), although a slight elevation, to 0.022 and 0.019 mg As/kg, occurred after five days in milk from cows fed 3.2 mg As/kg body weight from arsanilic acid or 3-nitro-4-hydroxyphenylarsonic acid, respectively. Milk arsenic levels returned to background concentrations of 0.013 and 0.004 mg As/kg after a seven-day withdrawal period (Calvert, 1973).

### 6.3 Levels in the Environment

Arsenic levels in air, water, sediment, soil and biota were reviewed. Except in the case of biota for which Canadian data are lacking, only a limited amount of non-Canadian data are discussed in this Section. Data for air, water, sediment and soil from more severely contaminated Canadian sites, and some non-Canadian locations, are summarized in Tables 6 and 7, respectively. Data for biota are presented in Table 9.

#### 6.3.1 Air

Measurements of Walsh et al. (1979) suggested that average arsenic concentrations in air over land were about  $1.0 \text{ ng/m}^3$ . Levels over oceans were found to be much lower (typically  $< 0.2 \text{ ng/m}^3$ ). Most of this arsenic was associated with fine ( $< 5 \text{ }\mu\text{m}$  diameter) suspended particulates. The residence time of arsenic in

Table 6. Concentrations of arsenic in air, water, sediment and soil at some contaminated Canadian sites.

<u>Media</u>	<u>Concentration</u> mean (max. or range)	<u>Location</u>	<u>Reference</u>
Air µg/m <sup>3</sup>	(1.68)	Giant Yellowknife Mine, NWT <sup>1</sup>	Gemmill, 1977
	(0.38) monthly geom. mean	Con Mine, NWT <sup>1</sup>	Gemmill, 1977
	(3.91)	Yellowknife, NWT <sup>1</sup>	Gemmill, 1977
	(32)	Noranda, Que <sup>s</sup>	Azzaria and Frechette 1987
Precipitation µg/L			
Snow (on ground) µg/L	(85% >50) (11,400)	Yellowknife, NWT <sup>1</sup> Near Giant	CPHA, 1977
	(31,000)	Yellowknife smelter <sup>1</sup> Giant Yellowknife Mine tailings effluent <sup>1</sup>	CPHA, 1977; Gemmill, 1977 Gemmill, 1977
Spring runoff µg/L			
Liquid Effluent µg/L	(10,000 - 22,000)	Giant Yellowknife Mine, NWT <sup>1</sup>	CPHA 1977
	(1,000 - 17,000)	Con Mine, NWT <sup>1</sup>	CPHA 1977
River water µg/L	(250)	Moirs R., Ont <sup>1</sup>	Mudroch and Capobianco 1980
	(<0.2-47)	Shubenacadie R. Waverley, NS <sup>3</sup>	Clair 1985
	(<20 - 100)	Baker Cr., NWT, above Giant	Gemmill, 1977
	(19,800)	Yellowknife mine <sup>2</sup> Mouth of Baker Cr., NWT <sup>1</sup>	CPHA, 1977

Table 6 cont'd.

<u>Media</u>	<u>Concentration</u> mean (max.or range)	<u>Location</u>	<u>Reference</u>
Lake water µg/L	(<1) (20) (15)	Sudbury, Ont' Noranda, Que' Bay of Quinte, Lake Ontario <sup>1</sup>	Nriagu 1983 Azzaria and Frechette 1987 Mudroch and Capobianco 1980
	(<5 - 20) (320)	Yellowknife Bay Back Bay, Yellowknife, NWT <sup>1</sup>	CPHA, 1977 CPHA, 1977
	(2,000 - 3,000)	Kam Lake, NWT <sup>1</sup>	CPHA, 1977
Tap water µg/L	(6 - 24)	Yellowknife, NWT	Gemmill, 1977
Ground water µg/L	(365) (11,000)	Waverley, NS <sup>3</sup> Vancouver, BC <sup>4</sup>	Bottomley 1984 Henning and Konasewich 1984
Sediment mg/kg, dw	(50) (15 - 65) (15 - 22) (30 - 34) (146)	Hamilton Harbour, L. Ontario Halifax Harbour Nova Scotia Rupert Inlet, B.C. <sup>6</sup> Alice Arm, B.C. <sup>6</sup> S. Tomogonops R., Bathurst, NB <sup>6</sup>	Krantzberg and Boyd 1991 Tay et al. 1991 Reimer and Thompson 1988 Reimer and Thompson 1988 Bailey 1988
	(100 - 196) (650)	Red Indian L. NFLD <sup>6</sup> Sudbury area lakes, Ont <sup>5</sup>	Bailey 1988 Palmer et al. 1989
	(>100) (206)	Noranda area lakes, Que <sup>5</sup> lakes near Flin Flon, Man. <sup>5</sup>	Azzaria and Frechette 1987 Franzin 1984

Media      Concentration  
mean (max.or range)

- 1 Area affected by gold mining/smeltering
- 2 Yellowknife area, not believed to be affected by mining/smeltering
- 3 Area affected by gold mining
- 4 Area affected by arsenical pesticides
- 5 Area affected by base metal mining/smeltering
- 6 Area affected by base metal mining
- 7 Area affected by municipal incinerator
- 8 Area affected by fossil fuel-burning power plant



Table 7. Concentrations of arsenic in water and sediment at some non-Canadian locations.

<u>Media</u>	<u>Concentration</u> mean (max.or range)	<u>Location</u>	<u>Reference</u>
Fresh water: lakes and rivers µg/L	1 (0.15-1100)	USA <sup>1</sup>	Durum et al. 1971
rivers µg/L	0.4 (0.065-9.4)	N.A., Asia	Byrd 1990
	As(V) (4.72) As(III) (0.34)	Tejo River, Portugal <sup>2</sup>	Andreae et al. 1983
Ocean water µg/L	2 (0.15-6)	world	Ferguson and Gavis 1972
	arsenate (1.79) arsenite (0.15) trimethyl- arsenic (0.29)	off SE coast, USA	Waslenchuk 1978
Estuary µg/L	As(V) (6.39) As(III) (0.94)	Portugal <sup>2</sup>	Andreae et al. 1983
Sediment mg/kg	(6-16)	San Francisco Bay & river delta	Johns and Luoma 1990

<sup>1</sup> Includes samples from contaminated sites.

<sup>2</sup> Arsenic emissions from local industrial area estimated to be 1,000 - 2,000 tonnes/year, with a pyrite roasting plant a major source.

Traversy et al. (1975) found arsenic levels of from  $<0.1$  to  $2.5 \mu\text{g/L}$  (mean  $0.72 \mu\text{g/L}$ ) in 53 samples of precipitation from the Great Lakes region in the mid-1970's. The highest level found was from a station at Toronto Island. Traversy et al. (1975) noted that these levels were higher than those found in lake and river water in the region (overall mean  $<0.40 \mu\text{g/L}$ ), and suggested that they may have reflected atmospheric contamination from various urban/industrial sources.

In 1976, a single rain sample collected near the copper smelter at Noranda Quebec was found to contain  $32 \mu\text{g As/L}$  (Azzaria and Frechette, 1987). A sample taken two years earlier at a control site, about 80 km to the north, contained only  $3 \mu\text{g As/L}$ .

Gemmill (1977) reported from 20 to  $11,400 \mu\text{g As/L}$  in surface snow within a few kilometres of the gold smelter at Yellowknife in the mid-1970's.

#### 6.3.3. Surface Water

Improvements in sample handling and analysis procedures in the past decade have resulted in a lowering of detection limits for arsenic in waters into the  $\text{ng/L}$  range. Coincident with these analytical improvements, there has been a significant drop in typical arsenic levels found in unpolluted surface waters (see for example Leger (1991)). It has therefore been suggested that some earlier estimates of background arsenic concentrations in surface fresh waters - particularly lakes - are erroneously high (J.O. Nriagu, CCIW, Burlington Ontario, pers. comm.).

Data presently available suggest that total arsenic levels in uncontaminated fresh surface waters are generally less than about  $2 \mu\text{g/L}$  (see for example Nriagu, 1983). Background concentrations typically vary, depending upon the nature of local rock and soil (Waslenchuk, 1979). Marine waters are higher in arsenic than freshwaters (average  $2-3 \mu\text{g/L}$ ), reflecting desorption from particulate matter (Moore and Ramamoorthy, 1984).

A nationwide survey of rivers and lakes in the U.S. was carried out in October of 1970 (Durum et al. 1971). Of the 727 samples, only 2% had more than  $50 \mu\text{g/L}$  dissolved arsenic. One sample in South Carolina (Table 7), which was downstream from an industrial complex, had an arsenic content of  $1,100 \mu\text{g/L}$  (Durum et al. 1971).

According to Traversy et al. (1975), total arsenic concentrations in Canadian Great lakes water in the mid-1970's ranged between  $<0.10$  and  $1.40 \mu\text{g/L}$ , with highest levels occurring in Lake Ontario. Similar levels were reported by Seydel (1972) in Lake Superior water. Traversy et al. (1975) found up to only  $2.50 \mu\text{g As/L}$  in rivers in the Great Lakes region; the average for the St

Lawrence River was 0.61  $\mu\text{g As/L}$ .

Tremblay and Gobeil (1990) found that the concentration of dissolved ( $<0.45 \mu\text{m}$ ) arsenic increased from 6.3 nmoles (0.47  $\mu\text{g/L}$ ), the mean concentration in the St. Lawrence River, to 18.9 nmoles/L (1.42  $\mu\text{g/L}$ ) in the St. Lawrence Estuary. The concentration of arsenic ranged from 1.1 nmoles (0.08  $\mu\text{g/L}$ ) in the Saguenay River (mean concentration) to 18.7 nmoles (1.40  $\mu\text{g/L}$ ) in the Saguenay Fjord. In both areas, arsenic concentration was linearly correlated with salinity, which implies that these water bodies were receiving natural, rather than anthropogenic, inputs of arsenic.

Similarly low dissolved arsenic levels (1.6-6.8 nmoles, or 0.13-0.52  $\mu\text{g/L}$ ) were reported by Byrd (1990) in water samples from the Medway River, Nova Scotia, and the St John River, New Brunswick. Bailey (1988) reported  $< 0.2 \mu\text{g/L}$  total arsenic in surface water from the Salmon/Mira River Basin in Nova Scotia downstream from an active lead mine.

From 0.2 to 0.6  $\mu\text{g/L}$  total arsenic were measured by Nriagu (1983) in 1978 in unfiltered water samples from representative lakes around the base-metal smelters at Sudbury. These low levels reflected relatively high deposition rates (up to 8.3  $\text{mg/m}^2/\text{yr}$ ) and consequent short residence times for arsenic in these waters. Azzaria and Frechette (1987) presented data indicating that up to 20  $\mu\text{g/L}$  total arsenic occurred in surface waters within a 10 km radius of the Noranda copper smelter in the mid-1970's.

In a study on the Shubenacadie River headwaters, Nova Scotia, Clair (1985) detected arsenic concentrations as high as 47.0  $\mu\text{g/L}$  in a sample of unfiltered outflow collected in 1983 from Muddy Pond, which served as a tailings pond for a gold mining operation near Waverley during the 19th century and at the beginning of the 20th century. Arsenic concentrations in Lake Thomas, into which Muddy Pond drains, ranged from 2.4 to 5.8  $\mu\text{g/L}$ .

Mudroch and Capobianco (1980) examined the impact of past gold mining and silver and cobalt smelting activities near Deloro Ontario, on water quality in the Moira River Basin. The lowest concentration of total arsenic for obviously unpolluted water collected in 1977 was 6.0  $\mu\text{g/L}$ ; the highest level, 250  $\mu\text{g/L}$ , was found in a sample taken from the Moira River, about 15 km downstream from Deloro. Arsenic levels in water were observed to decrease progressively downstream, presumably due to adsorption of arsenic onto river sediment and dilution by tributaries. 15  $\mu\text{g As/L}$  were reported in Bay of Quinte water, where the Moira River empties into Lake Ontario.

Gemmill (1977) reported that arsenic levels in several lakes near the Yellowknife gold mines and smelters exceed 100  $\mu\text{g/L}$  in the mid-1970's. In Back Bay (Great Slave Lake) which borders on the

community of Yellowknife, concentrations of up to 320  $\mu\text{g/L}$  were measured in surface waters. In Kam Lake, located adjacent to a mine tailings pond, CPHA (1977) reported from 2,000 to 3,000  $\mu\text{g As/L}$ .

#### 6.3.4 Ground Water

In general ground waters are higher in arsenic than surface waters (Boyle and Jonasson, 1973). Near arseniferous mineral deposits ground waters may be greatly enriched in arsenic. Michel (1990) explained that liberation of arsenic from primary sulphide minerals occurs during oxidation. One would therefore expect to see elevated arsenic concentrations in shallow ground waters with detectable dissolved oxygen where arsenic-bearing sulphides occur. In addition, one would expect to find elevated iron and sulphate values due to the breakdown of sulphides like arsenopyrite ( $\text{FeAsS}$ ).

Although Boyle and Jonasson (1973) indicated that ground waters near sulphide deposits can contain over 10,000  $\mu\text{g/L}$  arsenic, most ground waters in Canada probably contain less than 50  $\mu\text{g/L}$ . In Michel (1990)'s study of uncontaminated ground water in southeastern Ontario, for example, only 16 of nearly 200 water samples were reported to contain arsenic in concentrations equal to or greater than 1  $\mu\text{g/L}$ ; the highest level was 8.7  $\mu\text{g/L}$ . Ground waters containing more than 50  $\mu\text{g/L}$  are known to occur, however, in parts of southwestern New Brunswick and southern Nova Scotia, often in association with arsenopyrite-bearing gold deposits (Bottomley, 1984).

Meranger et al. (1984) found that of 94 well water samples taken from residences in Halifax County - an area of past gold mining - 66 samples contained concentrations of arsenic above the Canadian Drinking Water Guideline of 0.05 mg/L. Concentrations of arsenic in acidified, unfiltered samples, ranged from about 1.0 to approximately 700  $\mu\text{g/L}$ .

In a more extensive study, Grantham and Jones (1977) reported that of 642 water wells sampled from areas designated as gold districts in Nova Scotia, 83 (13%) contained arsenic concentrations above the Canadian Drinking Water Guideline of 0.05 mg/L. A further 51 wells (8%) contained arsenic concentrations between 0.04 and 0.05 mg/L. In areas where no gold mineralization was recognized, 22 of 183 wells (12%) contained arsenic levels in excess of 0.05 mg/L, while a further 6 wells (3%) contained concentrations of arsenic between 0.04 and 0.05 mg/L.

Because bedrock in most gold mining areas is arsenic-enriched (Boyle and Jonasson, 1973), contamination resulting from gold mining activities is often difficult to distinguish from natural anomalies. Detailed geochemical studies by Bottomley (1984) near

Table 8. Arsenic in lake and stream sediments in the Geological Survey of Canada's ORACLE data base, May 1991 (source: P. Friske, GSC, pers. comm.).

<u>Statistic</u>	<u>As (mg/kg)<sup>1</sup></u>	
	<u>Lake<sup>2</sup></u>	<u>Stream</u>
Arith. mean	2.4	13.3
Minimum conc.	<1	<1
50th %tile	1	5
95th %tile	5	38
99th %tile	13	125
Maximum conc.	10,000	11,200
No. samples	23,744	18,467

<sup>1</sup> Concentrations represent total or strong acid-extractable values.

<sup>2</sup> Lake sediment samples typically exclude the top 5 cm.

Johnson (1987) examined HNO<sub>3</sub>/HClO<sub>4</sub>-extractable arsenic levels in sediment cores from 14 relatively remote Ontario lakes. Concentrations ranged from <1.0 to about 20 mg As/kg, with highest values generally occurring in the top 10 cm of sediment. Although Johnson interpreted this surface enrichment to be indicative of regional atmospheric arsenic contamination, as Edenborn et al. (1986) and others have noted, natural diagenetic processes can produce similar surface anomalies.

H<sub>2</sub>SO<sub>4</sub>/HClO<sub>4</sub>-extractable arsenic concentrations were reported for 11 lakes in central and southern Saskatchewan by Huang and Liaw (1978). Levels ranged from 2.7 to 13.2 mg As/kg. Lakes in areas where arsenical pesticides had been extensively used in potato farming had highest values.

Arsenic levels have been measured in river, reservoir and lake sediment near three western coal-fired generating stations. Allan and Richards (1978) found only 1-14 mg/kg HNO<sub>3</sub>/HClO<sub>4</sub>-extractable arsenic in lake and reservoir sediment near the Wabamun (Alberta) and Boundary (Saskatchewan) power stations. Van Voris et al. (1985) reported similarly total arsenic contents (8-11 mg/kg) in river and reservoir sediment downstream from the Battle River power plant in Alberta.

In the United States, Furr et al. (1979) reported arsenic concentrations of 103 mg/kg dry weight in sediment of a pond contaminated with fly ash from a coal-fired power-generating plant,

Arm. Monomethylarsonic acid, dimethylarsinic acid and trimethyl arsine oxide were also found in small amounts (typically < 0.5  $\mu\text{g/L}$ ) in interstitial waters in both areas. Arsenic was calculated to be diffusing into the overlying waters at three control sites (rates 0.10 - 0.53  $\mu\text{g/cm}^2/\text{yr}$ ) and in the tailings disposal area at Alice Arm (rate 0.13  $\mu\text{g/cm}^2/\text{yr}$ ). The calculated arsenic flux between sediment and overlying waters in the active tailings disposal area in Rupert Inlet was, however, negligible.

Bailey (1988) measured 0.5 N HCl-extractable arsenic concentrations in minus 80 mesh (< 177  $\mu\text{m}$ ) river and lake sediment in three river basins in Atlantic Canada influenced by base-metal mining. Levels ranged from <2 to about 200 mg As/kg. Concentrations were particularly high (> 100 mg/kg) in sediment of the South Tomogonops River, downstream from a Pb/Zn mine near Bathurst, New Brunswick, and Red Indian Lake near a Cu/Pb/Zn mining area at Buchans, Newfoundland. Although not determined, total whole-sediment arsenic contents would likely be higher than the extractable levels reported.

Palmer et al. (1989) reported total arsenic concentrations in surface sediments of lakes near Sudbury, Ontario, ranging as high as about 650 mg/kg dry weight, although most sediment samples contained less than 400 mg/kg. Concentrations in the sediments of the 72 lakes studied tended to decrease with distance from the Sudbury smelters. Similar total arsenic levels were found in Sudbury area lake sediment cores by Nriagu (1983). Belzile and Tessier (1990) measured up to about 45  $\mu\text{g/L}$  of total dissolved arsenic in pore waters of surface littoral sediment from several Sudbury area lakes. Comparison of the vertical distribution of arsenic in the sediment to information on the history of nickel and copper production in the district, lead Nriagu (1983) to conclude that, in this area, surface arsenic enrichment reflected recent input of arsenic from local smelters and not diagenetic processes.

$\text{HNO}_3/\text{HClO}_4$ - extractable arsenic levels were shown to be elevated (10 - >100 mg/kg) in lake sediment over an area of about 6,000  $\text{km}^2$  centred on the copper smelter at Noranda, Quebec (Azzaria and Frechette, 1987). Somewhat lower concentrations (9-206 mg As/kg) were found by Franzin (1984) in lake sediment near the base metal mining and smelting facilities at Flin Flon, Manitoba.

Mudroch (1985) collected sediment cores from three lakes near the site of a former gold mine at Waverley, Nova Scotia. The highest concentration of arsenic (1750 mg/kg, dry weight) was found at the 10 to 15 cm sediment depth in the core from Muddy Pond which once served as a tailings pond for the mine. Levels of up to 800 mg/kg were found in Thomas and Powder Mill Lakes. Arsenic concentrations of 4 and 43  $\mu\text{g/g}$  in the surface sediments of two control lakes in the area suggest that background levels in sediment in this region are naturally elevated.

Mudroch and Capobianco (1980) measured total arsenic levels in surface river and lake sediment in the Moira River Basin, downstream from the site of a former gold mine and refinery at Deloro, Ontario. Concentrations decreased from 1695 mg/kg in the river near the abandoned mine, to 15 mg/kg in the Bay of Quinte, about 80 km downstream.

At the site of a former gold mine and roasting operation at Duparquet Quebec, Azzaria and Frechette (1987) have reported from 10 to over 400 mg/kg  $\text{HNO}_3/\text{HClO}_4$ -extractable arsenic in lake sediment over an area of about 1,500 km<sup>2</sup>. Sediments in Back Bay, adjacent to one of the major Yellowknife area gold mines, were found to contain up to 3,000 mg As/kg Gemmill (1977).

#### 6.3.6 Soil

According to Boyle and Jonasson (1973) normal soils from various sites throughout the world contain an average of 7.2 mg As/kg. Although these authors estimated that the maximum arsenic content of normal soil is 55 mg/kg, they reported levels of up to 8,000 mg/kg in soils and tills near arseniferous mineral deposits. Concentrations in surface A horizons were indicated to be somewhat depleted, and those in B horizons somewhat enriched, relative to levels in unweathered C horizons.

Frank et al. (1976b) measured arsenic concentrations in a total of 296 Ontario soils (0-15 cm depth), selected to include most types of crop production in the province. There were 207 soil samples where no actual or potential for arsenic contamination was recognized, and these soils contained from 1.1 to 16.7 mg/kg of  $\text{HNO}_3$ -extractable arsenic with a mean of 6.3 mg/kg. Arsenic content increased slightly with increasing clay content. Sandy soils had the lowest arsenic levels (mean of 5.8 mg/kg). The background levels in organic soils in Ontario were difficult to determine as past farming practices could not always be ascertained, but a mean of about 6.5 was estimated for uncontaminated sites.

Webber and Shames (1987) found only low levels of strong acid-extractable arsenic (3.7-8.1 mg/kg) in 57 samples of municipal sludge-treated soil from Halton Region, in southern Ontario.

Boyle and Jonasson (1973) reported levels in old apple orchards sprayed with arsenical pesticides in Nova Scotia and southwestern Ontario of 10-124 and 45-290 mg/kg, respectively. Frank et al. (1976a) found similarly high  $\text{HNO}_3$ -extractable arsenic levels in samples of Ontario agricultural soils (0-15 cm depth) where lead arsenate had been used for pest control. Highest concentrations occurred in samples from apple orchards (3-126 mg/kg), followed by those from cherry orchards (6-63 mg/kg) and potato fields (8-29 mg/kg).

Although no Canadian data were found, Noris et al. (1983) reported no significant build-up of arsenic in forest floor soils in Washington State after thinning with MSMA.

McGovern and Balsillie (1975) found from 3 to 47 mg As/kg (average 8.5 mg As/kg) in acidic surface (0-10 cm) soil within a 26 km radius of the Sudbury nickel and copper smelters. The maximum arsenic concentration at two control sites was 4.4 mg/kg (average 2.9 mg/kg).

Azzaria and Frechette (1987) reported that average arsenic content of humus within a 15 km radius of the Noranda copper smelter was only 9 mg/kg. This was, however, over 5 times the estimated background arsenic level of 1.9 mg/kg. Much higher levels (mean 110 mg/kg) were measured in humus near the site of the former gold roasting plant at Duparquet, Quebec. Peat samples obtained within a few kilometres of the roasting site contained up to about 150 mg As/kg.

Up to 2,000 mg As/kg (mean about 70 mg/kg) were found in surface (0-5 cm) soil near a secondary lead smelter in Toronto (Temple et al. 1977). As the authors of this study pointed out, this plant recovered lead from scrap storage batteries, and small amounts of arsenic are alloyed with lead in the production of battery plates and grids. The mean concentration in a Toronto urban background area was estimated to be only 9.8 mg As/kg (range 2.7-41). No significant arsenic build-up was found in soils near a major Toronto expressway (3.0-24 mg/kg) or near a sewage sludge incinerator (4.2-20 mg/kg). Some arsenic enrichment was observed, however, in surface soils around a power plant (mean 25 mg/kg; range 6.8-114 mg/kg), and to a lesser degree, a municipal incinerator (mean 16 mg/kg; range 3.0-49 mg/kg). Temple et al. (1977) speculated that high levels near the power plant were related to a previous period of coal burning.

More recent studies by Van Voris et al. (1985), however, suggested that arsenic releases from modern fossil-fuel burning power stations - with emission controls improved over those in previous decades - are comparatively small. Van Voris et al. (1985), for example, predicted (using an atmospheric model) that net accumulations of arsenic in the top 15 cm of soils around four Canadian power stations (Battle River, Poplar River, Nanticoke and Lingan), over their expected 30 year lifespans, will be  $\leq 1.33 \times 10^{-4}$  mg/kg.

Van Voris et al. (1985) measured total arsenic concentrations in litter, humus, surface and subsurface (15 cm depth) soil in ten aspen groves along a 120 km transect centred on the coal-fired Battle River Generating Station in Alberta. The highest arsenic concentration, 22 mg/kg, was found in subsurface soil about 3.5 km from the station on the downwind side. No more than 12 mg/kg of



Table 9. Concentrations of arsenic in biota.

<u>Media</u>	<u>Concentration</u> mean (max. or range) µg/g fw (unless dw specified)	<u>Location</u> (* signifies Canadian data)	<u>Reference</u>
<b><u>AQUATIC ORGANISMS:</u></b>			
<u>Potamogeton sp.</u>	(3,700 dw)	*Keg Lake, Yellowknife, NWT <sup>1</sup>	Wagemann et al., 1978
	(6-8 dw)	*Likely Lake, Yellowknife, NWT <sup>2</sup>	Wagemann et al., 1978
Zooplankton	(700-2,400 dw)	*Keg and Kam Lakes, Yellowknife, NWT <sup>1</sup>	Wagemann et al., 1978
	(21-38 dw)	*Likely and Grace Lakes, NWT <sup>2</sup>	Wagemann et al., 1978
Bivalves:			
( <u>Corbicula</u> sp.)	(5.5-11.5 dw)	San Francisco Bay & river delta	Johns and Luoma, 1990
( <u>Macoma balthica</u> )	(7.6-12.1 dw)	San Francisco Bay	Johns and Luoma, 1990
Snails	(79.7)	*Keg Lake, NWT <sup>1</sup>	Gemmill, 1977
Fish:			
marine	(0.31-13)	*Canada	Lawrence et al., 1986
freshwater			
0.07	(0.01-0.24) (0.03-0.12) ( $<0.001$ ) (0.067)	*Canada *Lakes Erie, Ontario *Red Indian L. Nfld <sup>5</sup> *Tomogonops R., N.B. <sup>3</sup>	Lawrence et al., 1986 Traversy et al., 1975 Bailey, 1988 Bailey, 1988
0.040	(0.009-0.261)	*Shubenacadie R., Waverley, NS <sup>3</sup>	Eaton and Clair, 1985
pike	(3.22)	*Kam Lake, NWT <sup>1</sup>	Gemmill, 1977
pike	(2.23) in liver	*Kam Lake, NWT <sup>1</sup>	Gemmill, 1977
whitefish	(0.77)	*Yellowknife Bay <sup>1</sup>	CPHA, 1977

Table 9 cont'd.

<u>Media</u>	<u>Concentration</u> mean (max. or range) µg/g fw (unless dw specified)	<u>Location</u> (* signifies Canadian data)	<u>Reference</u>
<b>TERRESTRIAL PLANTS:</b>			
Lichen	(10,000 dw?)	*Yellowknife, NWT <sup>1</sup>	CPHA, 1977
Black spruce needles and willow leaves	(100 dw?)	*Yellowknife, NWT <sup>1</sup>	CPHA, 1977
Tree and shrub leaves	(33 dw)	*Toronto, Ont <sup>6</sup>	Temple et al., 1977
Grass	(139 dw) (62 dw)	*Yellowknife, NWT <sup>1</sup>	Gemmill, 1977
Vegetables		*Toronto, Ont <sup>6</sup>	Temple et al., 1977
lettuce	(2.65)	*Yellowknife, NWT <sup>1</sup>	Gemmill, 1977
beets	(0.61)		
carrots	(0.45)		
Moss ( <u>Sphagnum</u> <u>fuscum</u> )	(110)	*Noranda, Que <sup>4</sup>	Glooschenko, 1986
<b>BIRDS:</b>			
Brown Pelican ( <u>Pelicanus</u> <u>occidentalis</u> )	<0.3 in eggs	Corpus Christi <sup>6</sup> , TX	King et al., 1983
Brown Pelican	0.31 in eggs (0.23-1.02) in liver	S. Carolina	Blus et al., 1977
Western Grebe ( <u>Aechmophorus</u> <u>occidentalis</u> )	2.7 in liver	Commencement Bay, Washington <sup>6</sup>	Henny et al., 1990
Royal Tern ( <u>Sterna maxima</u> )	<0.16	Corpus Christi <sup>6</sup> , TX	King et al., 1983

Table 9 cont'd.

<u>Media</u>	<u>Concentration</u> mean (max. or range) µg/g fw (unless dw specified)	<u>Location</u> (* signifies Canadian data)	<u>Reference</u>
Dunlin ( <u>Calidris alpina</u> )	0.5 in eggs	Dutch Wadden Sea	Goede et al., 1989
Dunlin	6.6 in kidney	Dutch Wadden Sea	Goede and deBruin, 1985
Greater Yellowlegs ( <u>Tringa melanoleuca</u> )	0.05 in liver+kidney (0.05 - 1.5)	"	"
Least Sandpiper ( <u>Calidris minutilla</u> )	in liver+kidney (0.05 - 0.42)	"	"
Lesser Yellowlegs ( <u>Tringa flavipes</u> )	in liver+kidney (0.05 - 1.23)	Corpus Christi, TX	White et al., 1980
Sanderling ( <u>Calidris alba</u> )	in liver+kidney (0.05 - 1.12)	"	"
Western Sandpiper ( <u>Calidris mauri</u> )	in liver+kidney (0.05 - .26)	"	"
Avocet ( <u>Recurvirostra americana</u> )	in liver+kidney	"	"
Red Knot ( <u>Calidris canutus</u> )	1.85 in feathers	Dutch Wadden Sea	Goede and deBruin, 1984
Bar-tailed Godwit ( <u>Limosa lapponica</u> )	1.75 in feathers	"	"
Dovekie ( <u>Alle alle</u> )	(2.84-50.34 dw) in muscle (6.55-64.13 dw) in liver	*Lancaster Sound, N.W.T.	Renewable Resources Consulting Services, 1977
Black-legged Kittiwake ( <u>Rissa tridactyla</u> )	(1.41-13.02 dw) in muscle (1.10-20.50 dw) in liver	"	"
Thick-billed Murre ( <u>Uria lomvia</u> )	(2.36-26.03 dw) in muscle (5.80-90.87 dw) in liver	"	"

Table 9 cont'd.

<u>Media</u>	<u>Concentration</u> mean (max. or range) $\mu\text{g/g}$ fw (unless dw specified)	<u>Location</u> (* signifies Canadian data)	<u>Reference</u>
Northern Fulmar ( <u>Fulmaris glacialis</u> )	(5.64-35.98 dw) in muscle (3.00-8.75 dw) in liver (4.11-24.37 dw) in muscle (4.20-50.14 dw) in liver <1.5 in liver (0.05-2.0) in kidney not detected	*Lancaster Sound N.W.T.	Renewable Resources Consulting Serv., 1977
Black Guillemot ( <u>Cepphus grylle</u> )		"	"
Osprey ( <u>Pandion haliaetus</u> )		Eastern United States	Wiemeyer et al., 1980
Greater Scaup ( <u>Aythya fuligula</u> ) White-winged Scoter ( <u>Melanitta fusca</u> ) Bufflehead ( <u>Bucephala albeola</u> ) Mallard ( <u>Anas platyrhynchos</u> ) Black Duck ( <u>Anas rubripes</u> ) Canvasback ( <u>Aythya valisineria</u> ) Canada Goose ( <u>Branta canadensis</u> )	" " " " " " " "	New York State " " " " " "	Baker et al., 1976 " " " " " "
Gadwall ( <u>Anas strepera</u> ) Green-winged Teal ( <u>Anas crecca</u> )	(5.9) in bone (14.6) in bone (44.2) in feather (8.1) in feather	Chambers Co., TX "	Hall and Fisher, 1985 "

Table 9 cont'd.

<u>Media</u>	<u>Concentration</u> mean (max. or range) $\mu\text{g/g}$ fw (unless dw specified) Canadian data)	<u>Location</u> (* signifies Canadian data)	<u>Reference</u>
Lesser Scaup ( <u>Aythya affinis</u> )	(11.4) (62.8) in bone in feather	Chambers Co., TX	Hall and Fisher, 1985
Pintail ( <u>Anas acuta</u> )	(12.2) (12.0) in bone in feather	"	"
Mottled Duck ( <u>Anas fulvigula</u> )	(10.3) (13.0) in bone in feather	"	"
Shoveler ( <u>Anas clypeata</u> )	(11.8) (5.2) in bone in feather	"	"
Black Duck	0.18 in eggs	Atlantic Flyway	Haseltine et al., 1980
Pacific Black Duck ( <u>Anas superciliosa</u> ) in wing	0.39 (0.14-1.24)	New South Wales	Olsen, 1984
Starling ( <u>Sturnus vulgaris</u> ) in whole body	(<0.05-1.40)	Continental U.S.	White et al., 1977
Willow Ptarmigan ( <u>Lagopus lagopus</u> ) in whole body	0.45 (<0.1-0.75)	*Yellowknife, NWT <sup>1</sup>	Gemmill, 1977
<b>MAMMALS:</b>			
Fin Whale ( <u>Balaenoptera physalis</u> ) in blubber oil	(1.8)	-----	Jenkins, 1980
Pilot Whale ( <u>Globicephala melaena</u> )	(0.1-1.49) in muscle (0.22-1.8) in liver (0.16-1.8) in kidney	Faroe Islands, Norway	Julshamn et al., 1987

Table 9 cont'd.

<u>Media</u>	<u>Concentration</u> mean (max. or range) $\mu\text{g/g}$ fw (unless dw specified) Canadian data)	<u>Location</u> (* signifies Canadian data)	<u>Reference</u>
Walrus ( <u>Odobenus rosmarus</u> )	0.01 in liver 0.13 in kidney	Bering Sea	Taylor et al., 1989
Polar Bear ( <u>Ursus maritimus</u> )	0.067 dw. in liver	*Canadian Arctic	Norstrom et al., 1986
Coyote ( <u>Canis latrans</u> )	0.23 in hair 0.1 in liver 0.1 in kidney	Wisconsin	Smith and Rongstad, 1981
White-tailed Deer ( <u>Odocoileus virginianus</u> )	18.96 in liver 17.78 in kidney 22.5 in rumen 102	Tennessee <sup>7</sup>	Swiggart et al., 1972
White-tailed Deer ( <u>Odocoileus virginianus</u> )	in liver 56 in kidney	New York <sup>7</sup>	Mathews and Porter, 1989
Rock Squirrel ( <u>Spermophilus</u> <u>variegatus</u> )	(0.1-9.4 dw) in liver	Utah	Sharma and Shupe, 1977

Table 9 cont'd.

<u>Media</u>	<u>Concentration</u> mean (max. or range) $\mu\text{g/g}$ , fresh weight (unless dw specified) Canadian data)	<u>Location</u> (* signifies Canadian data)	<u>Reference</u>
Bushy-tailed Wood Rat ( <u>Neotoma cinerea</u> )	(7.0-7.4 dw) in liver	Utah	Sharma and Shupe, 1977
Meadow Vole ( <u>Microtus pennsylvanicus</u> )	(0.05-0.63) in whole body	New York <sup>7</sup>	Elfving et al., 1979
Pine Vole ( <u>Pitymus pinetorum</u> )	(0.16-0.96) in whole body	"	"
White-footed Mouse ( <u>Peromyscus leucopus</u> )	(0.08-0.59) in whole body	"	"
Snowshoe hare	(1.44) in whole body	*Giant Yellowknife Mine dump, NWT <sup>1</sup>	Gemmill, 1977

- <sup>1</sup> Area contaminated by gold mining and smelting
- <sup>2</sup> Area relatively unaffected by gold by mining and smelting
- <sup>3</sup> Area contaminated by gold mining
- <sup>4</sup> Area contaminated by base metal mining and smelting
- <sup>5</sup> Area contaminated by base metal mining
- <sup>6</sup> Area contaminated by base metal smelting
- <sup>7</sup> Area contaminated by arsenical pesticides
- <sup>8</sup> Some individuals contaminated by ingestion of lead shot

Lawrence et al. (1986) reported that the concentrations of arsenic in several species of freshwater fish muscle from Ontario and Alberta ranged from 0.01-0.24  $\mu\text{g/g}$ . Johnson (1987) found similar arsenic levels ( $<0.05$ -0.8  $\mu\text{g/g}$ ) in whole-fish from 14 relatively uncontaminated lakes in across Ontario. Forty-three whole-fish samples collected by Traversy et al. (1975) in the mid-1970's in Lakes Erie and Ontario contained an average of 0.07  $\mu\text{g/g}$ , (range 0.03-0.12  $\mu\text{g/g}$ ). Bailey (1988) reported  $<0.001$  - 0.067  $\mu\text{g As/g}$  in whole-fish samples obtained from three river basins in Atlantic Canada that had been influenced by base-metal mining activities.

Eaton and Clair (1985) found only from 0.01-0.26  $\mu\text{g As/g}$  in 25 samples of fish muscle taken from lakes near the arsenic-contaminated Waverley gold mining area, in Nova Scotia. Much higher arsenic levels were detected in fish muscle (up to 3.22  $\mu\text{g/g}$ , in 1973) from Kam Lake, near the gold mines and smelters at Yellowknife (Gemmill, 1977).

The concentrations of total arsenic in Canadian Atlantic and Pacific marine fish (including haddock, halibut, cod, herring, mackerel and sole) muscle were found to be 0.31-13.2  $\mu\text{g/g}$  (Lawrence et al. 1986). These relatively high values are consistent with data reported for marine fish in other areas (NRCC, 1978).

In the mid-1970's Wagemann et al. (1978) found high arsenic concentrations in macrophytes (150-3,700  $\mu\text{g As/g, dw}$ ), zooplankton (700-2,400  $\mu\text{g As/g, dw}$ ) and other invertebrates ( $<1$ - 1,300  $\mu\text{g As/g, dw}$ ) from arsenic contaminated lakes in the Yellowknife area (Table 9).

Elevated arsenic levels ( $> 10$   $\mu\text{g/g, dw}$ ) have also been reported in tree leaves and grass near gold mining/smeltering facilities at Yellowknife and secondary lead smelters in Toronto (mid-1970's data), and in moss close to the copper smelter at Noranda, Quebec (Table 9).

Arsenic concentrations were measured in 688 waterfowl tissues collected and analyzed by the Canadian Wildlife Service (Laird Schutt, Environment Canada, pers. comm.). The majority of these were breast muscle tissue from adult birds collected in the province of Ontario, between September and October, 1988 and 1989 as part of the wildfoods contaminants monitoring program. Eighty-one percent of the Ontario samples contained less than 0.3  $\mu\text{g/g As}$ , and only 3% exceeded 1.0  $\mu\text{g/g As}$ . In British Columbia, 29% of the duck breast muscle samples exceeded the 0.3  $\mu\text{g/g As}$  level. Birds collected in Saskatchewan were relatively low in As; 7% had tissue levels greater than 0.3  $\mu\text{g/g As}$ . Arsenic levels in birds from the North West Territories were similarly low. Ducks collected in Quebec were more contaminated; 12% of the breast muscle samples analyzed contained over 6.0  $\mu\text{g/g As}$ .



Quebec and nine states on the east coast of the U.S. Arsenic was present in 18 of 20 eggs sampled along the Atlantic flyway, with an average level of  $0.18 \pm 0.02$  mg/kg As. Eggs collected contained comparably low levels throughout the sample area.

Royal Tern (Sterna maxima) eggs were collected from nesting colonies along the central Texas coast in 1976 (King et al. 1983). Corpus Christi and Nueces Bays are heavily contaminated with As from nearby a copper smelter and runoff from agricultural use of arsenic-containing pesticides. However, the eggs sampled at both colonies contained relatively little arsenic ( $<0.16$  mg/kg).

Several species of seabirds were sampled in Lancaster Sound, N.W.T. (Renewable Resources Consulting Services Ltd, 1977). Liver and muscle concentrations of arsenic frequently occurred at levels  $>10$   $\mu\text{g/g}$  dw. Arsenic was found to be very high in the pectoral muscle of the Northern Fulmar (Fulmarus glacialis glacialis); mean  $14.84$   $\mu\text{g/g}$  dw, range  $5.6$ - $36$   $\mu\text{g/g}$ . Thick billed Murre (Uria lomvia lomvia) livers contained an average of  $35.64$   $\mu\text{g As/g dw}$  (range  $5.8$ - $91$   $\mu\text{g/g}$ ). Liver and muscle of the Dovekie (Platus alle alle) contained on average  $23.64$   $\mu\text{g/g dw}$  (range  $6.6$ - $64$   $\mu\text{g/g}$ ) and  $16.21$   $\mu\text{g/g dw}$  (range  $2.8$ - $50$   $\mu\text{g/g}$ ) As respectively. Liver concentrations of arsenic in the Black Guillemot (Cepphus grylle) were  $20.38$   $\mu\text{g/g dw}$  (range  $4.2$ - $50$   $\mu\text{g/g}$ ).

According to NRCC (1978), animal tissues generally contain less than  $0.3$   $\mu\text{g As/g}$ . In most test animals arsenic levels are highest in liver, kidney, spleen and lung.

Small mammals consume plants, insects, organic debris and traces of soil. Mice and voles trapped on soils from a New York orchard that had received yearly applications of inorganic arsenic were analyzed for whole body burdens of arsenic (Elfving et al., 1979). Eighty percent of arsenic absorbed was stored in the following tissues; liver, abdominal viscera, skin, and particularly, bone and hair. Animals showed  $1.2$  to  $13.6$   $\mu\text{g As/total body concentration}$ . Control species from an unsprayed orchard showed  $0$  to  $0.8$   $\mu\text{g As/total body}$ . Soil in the contaminated orchard ranged from  $31$ - $94$  mg As/kg, with control orchards containing  $2.4$  mg As/kg.

The danger to wildlife consuming vegetation in areas that have been treated with MSMA-containing herbicides is evident from results of a study by Mathews and Porter (1989). These authors noted that White-tailed Deer (Odocoileus virginianus) were attracted to the salty taste of debarking agents made from MSMA. Deer mortalities were recorded following consumption of MSMA-contaminated browse (Mathews and Porter 1989). Necropsies revealed severe blood fluid loss and plasma clots in haemorrhagic lungs. The arsenic concentration in deer liver was  $102$  mg/kg; the level in kidney was  $56$  mg/kg.

Arsenic is monitored in polar bears (Ursus maritimus) in the Canadian Arctic annually, by sampling bear harvested in native peoples hunts. The bears eat Ringed (Pusa hispida) and Bearded (Erignathus barbatus) seals exclusively, which, in turn, feed on crustaceans and Arctic Cod (Boreogadus saida), creating a simple food chain study. Bear livers averaged 0.067 mg As/kg dry weight; 10 fold lower than seals and man (Norstrom et al., 1986). This indicates no apparent biomagnification in bear tissue.

## **Section 7. Population Exposures**

(This section is being prepared by Health and Welfare Canada.)

## **Section 8. Kinetics and Metabolism**

(This section is being prepared by Health and Welfare Canada. Some pertinent information is also presented at the end of Section 6.1)

## **Section 9. Mammalian Toxicology**

(This section is being prepared by Health and Welfare Canada.)

## **Section 10. Effects on Humans**

(This section is being prepared by Health and Welfare Canada.)

## **Section 11. Effects on the Ecosystem**

A thorough review of the literature on the toxicity of arsenic was recently presented in BIBRA (1990). In the following discussion attention is focused primarily on studies suggesting particular sensitivity to arsenic. Results of these and other studies are summarized in Table 10.

### **11.1 Toxicity**

The mechanisms of arsenic toxicity differ greatly among chemical species, although all cause similar signs of poisoning. Biochemical toxicity of arsenic appears to be related to its close resemblance to phosphorus (NRCC 1978). Arsenic enters cells via an active transport mechanism normally used in phosphate transport (NRCC 1978) and may uncouple oxidative phosphorylation. Inorganic arsenic ( $\text{As}^{+3}$  and, to a lesser extent,  $\text{As}^{+5}$ ) causes enzyme inhibition by reacting with protein sulfhydryl groups (Eisler 1988), ultimately resulting in decreased cellular respiration. Biomethylation is the preferred detoxification mechanism for

Table 10. Response levels of biota (grouped phylogenetically) to arsenic.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
<b>Microorganisms:</b>			
Soil bacteria & actinomycetes	20 mg As/kg soil as calcium arsenate	>50 % population growth inhibition	Zonglian et al. 1987
sediment	>100 mg/kg sediment As(III), 3-d	reduction in colony forming units (CFU's)	Huysmans and Frankenberger 1990
<u>Photobacterium phosphoreum</u>	700 mg/kg sediment 15-min	AET: reduced luminescence	Tetra Tech Inc. 1986
<u>Nitrobacter</u> sp.	0.1 mg As/L sodium arsenate	reduction in activity	Holm and Cox 1978
agricultural drainage water	>1.0 mg/L, 3-d As (III)	reduction in CFU's	Huysmans and Frankenberger 1990
lake	3 mg As/L, as arsenate & arsenite	50% red. degrad. of organic matter (winter only)	Brunskill et al. 1980
<u>Pseudomonas putida</u>	18 mg As/L disodium arsenate	reduced growth	Bringmann and Kuhn 1980
<u>Photobacterium phosphoreum</u>	24.2 mg As/L 15-min, sodium arsenate	EC50: reduced luminescence	Williams et al. 1986
fungus <u>Coniophora olivacea</u>	45 mg As/L as potassium arsenite	no growth	Da Costa 1972

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
bacteria (soil)	270 mg/L, 24-h sodium arsenite <sup>2</sup>	LC50	Anderson and Abdelgani 1980
mixed bacteria	290 mg/L, arsenite	pop. reduction	Peoples 1975
<b>Algae:</b>			
alga <u>Skeletonema costatum</u>	5 µg As/L, as sodium arsenite & arsenate	growth inhibition	Sanders 1979
<u>Scenedesmus obliquus</u>	10 µg/L, As(V), 14-d	42% reduced growth	Vocke et al. 1980
phytoplankton	15 µg As/L, 21-d, as sodium arsenate	species shift	Sanders 1986
<u>Chlamydomonas</u> sp.	75 µg As/L, 25-d, as dibasic sodium arsenate	29% reduced growth	Christensen and Zielski 1980
red alga <u>Champia parvula</u>	95 µg As/L, 14-d, as sodium arsenite with 0.45 µM phosphate	prevented maturation of cystocarps	Thursby and Steele 1984
	145 µg As/L, 14-d, as sodium arsenite with 0.45 µM phosphate	10-20% growth inhibition	Thursby and Steele 1984
	10,000 µg As(V)/L, 14-d sodium arsenate with 0.45 µM phosphate	no growth inhibition	Thursby and Steele 1984

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
red alga <u>Champia parvula</u>	56 µg As(V)/L, 14-d phosphate-free water	growth red. 40%	Thursby and Steele 1984
<u>Ankistrodesmus</u> <u>falcatus</u>	As(V), 14-d, 100µg/L	28% reduced growth	Vocke et al. 1980
<u>Selenastrum</u> <u>capricornutum</u>	As(III), 4-d, 2,320µg/L	50% growth inhibition	CESARS 1988
<u>Cladophora</u> sp. <u>Spirogyra</u> sp. <u>Zygnema</u> sp.	As(III), 2-wk, 2320µg/L " " " " " "	100% kill	CESARS 1988
<u>Selenastrum</u> <u>capricornutum</u>	As(V), 14-d, 25,000µg/L	50% reduced growth	Vocke et al. 1980
<u>Microcoleus</u> <u>vaginatus</u>	As(V), 14-d, 100,000µg/L	no effect	Vocke et al. 1980
<u>Chlorella vulgaris</u>	100,000µg As/L, 14-d, Na <sub>2</sub> HAsO <sub>4</sub>	survival	Maeda et al. 1990
<b>Pondweed:</b> <u>Potamogeton</u> sp.	As(III), 1-mo., 2320µg/L	95% kill	CESARS 1988
<b>Aquatic Invertebrates:</b>			
Cladoceran <u>Daphnia magna</u> (fed)	520 µg/L, 3-wk, As(V)	16% reprod. impairment	Biesinger and Christensen 1972

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
<u>Daphnia pulex</u>	sodium arsenite, 48-h 1,800 µg/L <sup>2</sup>	EC50	Sanders and Cope 1966
<u>Daphnia pulex</u>	sodium arsenate, 48-h 49,600 µg As/L	LEC50	Passino and Novak 1984
<u>Ceriodaphnia dubia</u> (unfed)	sodium arsenite, 48-h 1,448 µg As/L	LC50	Spehar and Fiantdt 1986
<u>Ceriodaphnia dubia</u> (Young/female)	sodium arsenite, 7-d 1,140 µg As/L	max. acceptable tox. concentration	Spehar and Fiantdt 1986
Amphipod <u>Rhepoxynius</u> <u>abronius</u>	93 mg/kg sediment	AET: increased mortality	Tetra Tech Inc. 1986
<u>Gammarus</u> <u>pseudolimnaeus</u>	874 µg As/L, 96-h, as sodium arsenite	EC50	Lima et al. 1984
<u>Gammarus</u> <u>pseudolimnaeus</u>	As(III), 7-d, 961 µg As/L (arsenic trioxide)	80% decrease of survival	Spehar et al. 1980
<u>Gammarus</u> <u>pseudolimnaeus</u>	As(III), 14-d, 961 µg As/L (arsenic trioxide)	100% decrease of survival	Spehar et al. 1980
<u>Eurytemora affinis</u> (juveniles)	100 µg As/L, 15-d, as sodium arsenate	reduced survival	Sanders 1986
<u>Eurytemora affinis</u> (adults)	arsenate, 15-d, 50 µg As/L	no effect	Sanders 1986

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
<u>Eurytemora affinis</u> (adults)	arsenate, 15-d, 1000µg As/L	reduced survival	Sanders 1986
<u>Eurytemora affinis</u> (adults)	arsenate, 26 to 33-d 25 µg As/L	no effect: survival or reproduction	Sanders 1986
<u>Pteronarcys dorsata</u> (stonefly)	As(III), 28-d, 961 As µg/L (arsenic trioxide)	no effect: survival	Spehar et al. 1980
<u>Pteronarcys dorsata</u>	As(V), 28-d, 973 µg As/L (arsenic pentoxide)	no effect: survival	Spehar et al. 1980
<u>Pteronarcys dorsata</u>	disodium methyl arsenate 28-d, 970 µg As/L	no effect: survival	Spehar et al. 1980
<u>Pteronarcys dorsata</u>	sodium dimethyl arsenate 28-d, 846 µg As/L	no effect: survival	Spehar et al. 1980
<u>Helisoma campanulata</u> (snail)	As(III), 28-d, 961 µg As/L (arsenic trioxide)	no effect: survival	Spehar et al. 1980
<u>Helisoma campanulata</u>	As(V), 28-d, 973 µg As/L (arsenic pentoxide)	no effect: survival	Spehar et al. 1980
<u>Helisoma campanulata</u>	disodium methyl arsenate 28-d, 970 µg As/L	no effect: survival	Spehar et al. 1980
<u>Helisoma campanulata</u>	sodium dimethyl arsenate 28-d, 846 µg As/L	no effect: survival	Spehar et al. 1980

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
<u>Stagnicola emarginata</u> (snail)	As(III), 28-d, 961 µg As/L (arsenic trioxide)	no effect: survival	Spehar et al. 1980
<u>Stagnicola emarginata</u>	As(V), 28-d, 973 µg As/L (arsenic pentoxide)	no effect: survival	Spehar et al. 1980
<u>Stagnicola emarginata</u>	disodium methyl arsenate 28-d, 970 µg As/L	no effect: survival	Spehar et al. 1980
<u>Stagnicola emarginata</u>	sodium dimethyl arsenate 28-d, 846 µg As/L	no effect: survival	Spehar et al. 1980
Cladoceran <u>Simocephalus serrulatus</u>	1400 µg/L, 48-h, sodium arsenite <sup>2</sup>	EC50	Sanders and Cope 1966
<u>Nitocra spinipes</u>	1.45 mg As/L, 30-min disodium arsenate	EC50	Tarkpea et al. 1986
<u>Nitocra spinipes</u>	7.86 mg As/L, 30-min sodium arsenite	EC50	Tarkpea et al. 1986
Mud Snail <u>Nassarius obsoletus</u>	>2000 µg As/L, 72-h, as sodium arsenite	O <sub>2</sub> rate depression, abnormal behaviour	MacInnes and Thurberg 1973
<u>Mytilus edulis</u> (bay mussel)	arsenic trioxide, 48-h >3000 µg As/L	EC50- abnormal development	Martin et al. 1981
<u>Scylla serrata</u> (Indian marine crab)	arsenic trioxide, 96-h 17,000 µg As/L	LC50	Krishnaja et al. 1987



Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
Oyster			
<u>Crassostrea gigas</u> (larvae)	700 mg/kg sediment	AET: increased abnormalities	Tetra Tech Inc. 1986
Dungeness crab(zoea)	232 µg As/L, 96-h, as arsenic trioxide	LC50	Martin et al. 1981
<u>Cancer magister</u>			
Pacific oyster	326 µg As/L, 48-h, as sodium arsenite	EC50	Martin et al. 1981
<u>Crassostrea gigas</u> (embryo)			
midge			
<u>Tanytarsus dissimilis</u>	As(III), 48-h, 97,000µg/L	LC50	Holcombe et al. 1983
midge			
<u>Chironomus tentans</u>	680 µg As/L, 48-h, as arsenic trioxide	EC50	Khangarot and Ray 1989
<u>Bosmina longirostris</u>	sodium arsenate, 96-h 850µg As/L	LEC50	Passino and Novak 1984
Fish:			
<u>Chelon labrosus</u> (grey mullet)	arsenic trioxide 96-h 27,300µg As/L	LC50	Taylor et al. 1985
Rainbow trout eggs			
<u>Salmo gairdneri</u>	540 µg As/L, 28-d, as sodium arsenite	LC50	Birge, 1978
Rainbow trout			
<u>Salmo gairdneri</u>	10 mg As/kg diet, 8-wk	haemoglobin 86% of control	Oladimeji et al. 1984

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
<u>Rainbow trout</u> <u>Salmo gairdneri</u>	30 mg As/kg diet, 8-wk	weight gain 69% of control	Oladimeji et al. 1984
<u>Rainbow trout</u> <u>Salmo gairdneri</u>	961 µg As/L, 28-d, arsenic trioxide	no effect: survival	Spehar et al. (1980)
	973 µg As/L, 28-d, arsenic pentoxide	no effect: survival	Spehar et al. (1980)
	970 µg As/L, 28-d, disodium methyl arsenate	no effect: survival	Spehar et al. (1980)
	864 µg As/L, 28-d, sodium dimethyl arsenate	no effect: survival	Spehar et al. (1980)
<u>Pink Salmon</u> <u>Oncorhynchus</u> <u>gorbuscha</u>	3,787 µg As/L, 10-d, as arsenic trioxide	LC50 or EC50	Holland et al. 1964
<u>Coho Salmon</u> <u>Oncorhynchus</u> <u>kisutch</u>	300 µg As/L, 6-mo, as arsenic trioxide	reduction in smolt out-migration	Nichols et al. 1984
<u>Brook trout</u> <u>Salvelinus</u> <u>fontinalis</u>	sodium arsenite 27,800 µg As/L	LC50	Cardwell et al. 1976
<u>Muskellunge</u> <u>Esox masquinongy</u> (swim-up fry)	1,100 µg As/L, 96-h sodium arsenite	LC50	Spotila and Paladino 1979

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
Marbled salamander <u>Ambystoma opacum</u> (embryo, larva)	4450 µg As/L, 8-d, as sodium arsenite	LC50	Birge et al. 1978
Toad (tadpole) ( <u>Bufo arenarum</u> )	25,000 µg As/L, as potassium arsenate	increased malformations	Vega and Pisano 1983
<b>Soil Invertebrates:</b>			
Earthworm <u>Eisenia fetida</u>	200 mg As/kg substrate sodium arsenite, 14-d	100% mort.	Bouche et al. 1987
<b>Terrestrial Plants:</b>			
<u>Allium cepa</u> Onion	2 mg/L, 7-d As(V)	growth inhibition of bulb roots	Pepper et al. 1988
Stinging nettle <u>Urtica dioica</u>	1 µg As/g soil, as lead arsenate & sodium cacodylate	significant growth reduction	Otte et al. 1990
Green beans <u>Phaseolus vulgaris</u>	10 µg As/g soil as disodium arsenate	42% reduced growth in loamy sand	Woolson 1973
Spinach <u>Spinacia oleracea</u>	10 µg As/g soil as disodium arsenate	41% reduced growth in loamy sand	Woolson 1973
Green beans <u>Phaseolus vulgaris</u>	26 µg As/g soil H <sub>2</sub> SO <sub>4</sub> /HClO <sub>4</sub> - extractable	56% reduced yield in sandy soil	Jacobs et al. 1970
Lima beans <u>Phaseolus linensis</u>	50 µg As/g soil as disodium arsenate	99% reduced growth in loamy sand	Woolson 1973

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
<u>Tomato</u> <u>Lycopersicon</u> <u>esculentum</u>	50 µg As/g soil as disodium arsenate	42% reduced growth in loamy sand	Woolson 1973
Pea <u>Pisium sativum</u>	68 µg As/g soil H <sub>2</sub> SO <sub>4</sub> /HClO <sub>4</sub> - extractable	54% reduced yield in sandy soil	Jacobs et al. 1970
Sweet corn <u>Zea mays</u>	68 µg As/g soil H <sub>2</sub> SO <sub>4</sub> /HClO <sub>4</sub> - extractable	53% reduced yield in sandy soil	Jacobs et al. 1970
Potato <u>Solanum tuberosum</u>	250 µg As/g soil H <sub>2</sub> SO <sub>4</sub> /HClO <sub>4</sub> - extractable	76% reduced yield in sandy soil	Jacobs et al. 1970
Sweet corn <u>Zea mays</u> (4-wk-old)	100 µg As/g soil Na <sup>+</sup> , Al <sup>+</sup> , or Ca arsenate	>50% reduced growth in loamy sand	Woolson et al. 1971
<b>Birds:</b> Chicken embryos ( <u>Gallus gallus</u> )	1-20 µg/egg, on day 14 as sodium arsenite	increased malformations	Gilani and Alibhai 1990
	9 µg/egg, on day 14 as sodium arsenate	LD50	"
Chicken (embryos)	.001-50 mg As/kg, as sodium arsenite in the yolk	100% mortality at 1.0 mg/kg; TL50 at 0.05 mg/kg; hatchability reduced to 65% at 0.001 mg/kg	Birge and Roberts, 1976

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
Chicken (4-8 day old embryos)	0.2 mg/egg, at day 4 Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O <sup>2</sup>	50% growth inhibition and limb defects.	Ridgway and Karnofsky, 1952
Chicken	18 mg As/kg body wt.	unspecified tox.	Hesse et al. 1990
Chicken (1 day old)	8 mg/kg Se, 15 mg/kg sodium arsenate <sup>2</sup> feed additive	As decreased embryo mortality caused by selenium	Arnold et al. 1973
Mallard ducklings <u>Anas platyrhynchos</u>	300 mg/kg As, 10-wk as sodium arsenate	decreased brain ATP, altered growth	Camardese et al. 1990
Mallard	323 mg As/kg bw as sodium arsenite	LD50; single dose	Hudson et al. 1984
Ring-necked Pheasant <u>Phasianus colchicus</u>	386 mg/kg bw sodium arsenite <sup>2</sup>	LD50; single dose	Hudson et al. 1984
Ring-necked Pheasant	1403 mg/kg copper acetoarsenate <sup>2</sup> 4989 mg/kg lead arsenate <sup>2</sup>	LC50.	Heath et al., 1972
Bobwhite Quail <u>Colinus virginianus</u>	480 mg/kg copper acetoarsenate <sup>2</sup>	LC50	"

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
Japanese Quail	1204 mg/kg copper acetoarsenite <sup>2</sup>	LC50	"
California Quail ( <u>Lophortyx californicus</u> )	47.6 mg/kg bw sodium arsenite <sup>2</sup>	LD50; single dose	Hudson et al. 1984
Cowbird <u>Molothrus ater</u>	99.8 mg/kg, 11-day, copper acetoarsenite <sup>2</sup>	50% mortality	NAS 1977
<b>Mammals:</b>			
Holtzman rat	1.0 mg As/kg as sodium arsenite; 0.5 mg/kg Se	enhanced hepatic clearance of Se	Levander and Bauman 1966
Wistar rat	1 mg/kg arsenic acid IV, .5 mg/kg As acid oral dose <sup>2</sup>	increased dimethylated As in blood	Odanaka et al. 1980
hamster	20 mg/kg injected as sodium arsenate <sup>2</sup>	malformations in CNS, uro-genital abnormalities	Ferm and Carpenter, 1968
Sprague-Dawley rat (livers <u>in vitro</u> )	sodium arsenite and sodium arsenite, 10-3 molar	altered regulation of heme metabolism	Woods et al., 1981
White-footed mouse <u>Peromyscus leucopus</u>	monosodium methane arsenate, (MSMA) 477 mg/kg As in drinking water	negative changes in hormone-mediated behaviour	Lopez and Judd, 1979

Table 10. cont'd.

Species	Concentration/exposure period producing response <sup>1</sup>	Response	Reference
rabbit	50 mg/kg MSMA <sup>2</sup> in food for 52 weeks	toxic hepatitis in weeks 7 - 12	Exon et al. 1974
White-tailed deer <u>Odocoileus virginianus</u>	241-337 mg As/kg bw as monosodium methanearsonate (estimated dose)	mortality	Mathews and Porter 1989
sheep	45.6 mg As/kg body weight, 60-d	unspecified tox.	Hesse et al. 1990
Gray seal <u>Halichoerus grypus</u>	arsenic trioxide 0.45 mg/kg <sup>2</sup>	altered biosynthesis of steroids in testes and adrenals <u>in vitro</u>	Freeman and Sangalang, 1977

<sup>1</sup> These values can only be compared on an approximate basis, as water characteristics, especially hardness, are known to influence the acute toxicity of heavy metals for aquatic organisms (Khangarot and Ray 1989).

<sup>2</sup> Concentration expressed in terms of the compound and not elemental arsenic.

absorbed inorganic arsenicals; methylated arsenicals usually clear from tissues within a few days (Eisler 1988).

## 11.2 Factors Affecting Aquatic Toxicity

Various factors, besides form and dose, influence the expression of arsenic toxicity in aquatic organisms. These have been previously reviewed (NRCC 1978) and are summarized as follows:

- (i) pH, as more acidic aqueous conditions favour the formation of lower and often more toxic arsenic oxidation states (Ferguson and Gavis, 1972).
- (ii) Eh, as decrease in dissolved oxygen content of water will lead to an increased prevalence of the lower and more toxic oxidation states, particularly As(III).
- (iii) the duration of exposure is a factor to consider, as an extended exposure to arsenic leads to enhanced toxicity (eg. Sorensen, 1976).
- (iv) sensitivity to arsenic varies with species. Aquatic insects, for example, are generally less sensitive to arsenic than are fish, algae, worms or bacteria. As a general rule, arsenic toxicity occurs at lower concentrations in immature specimens.
- (v) the volume of water in the test system can also influence the expression of toxicity. Test fish in large holding tanks or using a flow-through system give acceptable results, but in small tanks, the arsenic may be depleted by absorption and false low toxicity readings can result.
- (vi) increasing water temperature is known to promote greater arsenic uptake by fish and also to increase the intrinsic toxicity of a given amount of absorbed arsenic.

In both freshwater and seawater environments phosphate concentration has been found to affect the toxicity of arsenate but apparently not of arsenite. There is also evidence to suggest that the presence of other toxicants may reduce still further the thresholds for arsenic toxicity (BIBRA 1991).

In view of these factors, response levels for aquatic organisms given in Table 10 should be understood as being relative, approximate effect levels.

## 11.3 Effects on Microorganisms

Zonglian et al. (1987) reported that population densities (measured as number of cells/gm dry soil) of bacteria and actinomycetes were reduced by over 50% when soil was treated with 20 mg As/kg (as calcium arsenate), relative to controls with no



arsenic added.

Huysmans and Frankenberger (1990) isolated and enumerated arsenic-resistant microorganisms from agricultural drainage water and sediments from an evaporation pond (used for disposal of agricultural waste water) in California. The evaporation pond sediments showed a decline in total colony forming units (CFU's) with supplemented As(III) concentrations >100 mg/kg. At a concentration of 1000 mg As(III)/kg sediment, no CFU's were observed. Water samples showed a rapid decline in CFU's with a concentration of As(III) exceeding 1.0 mg/L. By contrast, there were no effects on CFU's in sediment or water samples when As(V) was added, even at a concentration of 1,000 mg/kg and 1,000 mg/L, respectively. Addition of methylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) to the minimal medium at concentrations above 25 mg/kg promoted the microbial population counts of the sediment samples, but had no effect on the microbial populations from the water samples. MMAA was shown to be a better carbon source for the CFU production than DMAA.

Tetra Tech Inc. (1986) used the Microtox test in their evaluation of sediment quality in Puget Sound. This toxicity bioassay uses the luminescent marine bacteria Photobacterium phosphoreum as the test organism, and response is measured as the reduction in light emitted by the bacteria after a 15 minute exposure. The Apparent Effects Threshold (AET, defined as the concentration above which statistically significant adverse effects are always expected relative to appropriate reference conditions) was estimated as 700 mg As/kg for Puget Sound sediment. No data were given on arsenic speciation in this study.

Sodium arsenate reduced the activity of the nitrifying microorganisms Nitromonas sp. and Nitrobacter sp. at concentrations of 100 mg As/L and 0.1 mg As/L, respectively (Holm and Cox 1978). Arsenite and arsenate at concentrations of 40  $\mu$ moles/L (approximately 3 mg As/L) reduced by 50% the ability of lake microbial populations to degrade organic matter in winter, when nutrient levels were low, but not in summer when nutrient levels were higher (Brunskill et al., 1980). Growth of Pseudomonas putida was reduced by exposure to disodium arsenate at a concentration of 18 mg/L (Bringmann and Kuhn, 1980).

The fungi Coniophura olivacea, and Poria monticola, exhibited no growth when exposed to potassium arsenate at concentrations as low as 0.005 moles/L (375 mg As/L) or to potassium arsenite at concentrations as low as 0.0006 moles/L (45 mg As/L) (C. olivacea) and 0.04 moles/L (3,000 mg As/L) (P. monticola) (Da Costa, 1972). The 24-h LC50 values for three species of bacteria, Citrobacter frundii, Aeromonas sp., and Klebsiella sp. were reported to be 1300 mg/L for sodium arsenate and 270 mg/L for sodium arsenite (Anderson and Abdelghani 1980). Peoples (1975) cited data showing that As(III) caused a significant reduction in mixed bacterial

populations at a concentration of 290 mg/L, while As(V) has little effect up to 10,000 mg/L.

#### 11.4 Effects on Algae and Aquatic Plants

Some species of aquatic algae are quite sensitive to arsenic. Levels as low as 10  $\mu\text{g As(V)/L}$  (as sodium arsenate) caused 42% reduced growth in one species of algae (Scenedesmus obliquus) in a 14 day experiment (Vocke et al., 1980). The EC50 for this species was 48  $\mu\text{g As(V)/L}$ . Growth was also reduced (by 29%) in Chlamydomonas sp. when exposed to 75  $\mu\text{g As(V)/L}$  for 25 days (Christensen and Zielski, 1980).

Sanders (1979) found that arsenate and arsenite at concentrations as low as 67 nmoles/L (about 5  $\mu\text{g As/L}$ ) significantly inhibited the photosynthesis and  $^{14}\text{C}$  uptake of Skeletonema costatum when tested with low concentrations of phosphate. Enrichment with 20  $\mu\text{moles phosphate/L}$  (about 620  $\mu\text{g P/L}$ ) eliminated the arsenate inhibition of  $^{14}\text{C}$  uptake. Dimethylarsinic acid at concentrations of up to 340 nmoles/L (approximately 25.5  $\mu\text{g As/L}$ ) did not significantly affect the algae.

Arsenic is a chemical analogue of phosphate, and as such is indiscriminately taken up by phytoplankton (Sanders and Windom 1980). Once inside the cell, small quantities can inhibit oxidative phosphorylation and growth. Chronic arsenic stress commonly results in the replacement of dominant species by others that are more resistant to arsenate or can better discriminate between arsenate and phosphate (Sanders and Vermersch 1982, Sanders and Cibik 1985).

In a series of experiments, Sanders (1986) exposed natural phytoplankton assemblages to sodium arsenate (As V) at a concentration of 15  $\mu\text{g As/L}$  for 21 days. By day 10 there was a diversion in the proportion of dominant species between the treated and control groups, which continued to grow so that by day 21, flagellate species comprised more than 75% of the total algal density in the controls, but less than 25% in the arsenic-treated groups. Zooplankton assemblages also differed in the two groups, as the altered species composition of phytoplankton affected normal predator-prey relationships, greatly reducing zooplankton grazing, survival and reproductive success. By day 21, the density of adult copepods, Acartia tonsa, was about 120 individuals/L in the control group, but only about 50 individuals/L in the arsenic-treated groups. This was believed to have been caused by the differences in the phytoplankton assemblages, rather than by the added arsenic.

Giddings and Eddlemon (1978) studied the effect of arsenic on the photosynthesis/respiration ratio in an aquatic microcosm. Initial arsenic concentrations of 66, 11500, and 143000  $\mu\text{g As/L}$

experienced a 16% reproductive impairment at 520  $\mu\text{g As(V)/L}$  and a 50% reproductive impairment at 1400  $\mu\text{g As(V)/L}$ . The difference between survival (LC50) and 50% reproductive impairment was more than two-fold. This difference was more striking for arsenic and six other elements (Sn, Cr, Au, Pb, Pt, Cd) than for 14 additional elements which were tested at the same time.

Lima et al. (1984) also studied the acute and chronic toxicities of arsenic (sodium arsenite) to daphnids. They obtained 96-h EC50 estimates of 4340 and 1500  $\mu\text{g/L}$  for fed and unfed daphnids, respectively. In the 28-d chronic test, the highest exposure tested having no adverse effect was 633  $\mu\text{g/L}$ . The lowest tested exposure concentration having an adverse effect was 1320  $\mu\text{g/L}$ .

A large variability in the response of amphipods to  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ , MSMA and DSMA, prevented tabulation of results in a study conducted by Spehar et al. (1980). None of the arsenic forms examined significantly affected the survival or production of young in Daphnia magna exposed for 14 days at concentrations of about 1000  $\mu\text{g As/L}$ . Results for the full 28 days were not obtained because of high mortality in the control groups.

Tetra Tech Inc. (1986) studied effects of variations in Puget Sound sediment quality on benthic invertebrates. This study used several approaches to evaluate sediment toxicity including the Apparent Effects Threshold (AET; see definition in Section 11.3) method, which according to Chapman (1989) is one of the more reliable techniques. AET were developed for three aquatic invertebrate effects indicators: amphipod (Rhepoxynius abronius) mortality, oyster (Crassostrea gigas) larvae abnormality, and depressions in total abundance of higher level (Polychaeta, Mollusca, Crustacea) benthic infauna. Estimated AET values for these indicators were, 93, 700 and 85 mg As/kg (strong acid-extractable; dw), respectively. Subsequent re-evaluation of the Tetra Tech data by Barrick et al. (1988) resulted in a lowering of the benthic infaunal community AET for Puget Sound sediments from 85 to 57 mg/kg. As Chapman (1989) has noted, one of the criticisms of results of this type is that they can be site-specific. However results for Puget Sound are generally consistent with those of similar studies conducted in San Francisco Bay, California, and Commencement Bay, Washington (Long and Morgan, 1990).

The Province of Ontario used a somewhat different, Screening Level Concentration (SLC), approach in evaluating the toxicity of sediment-bound chemicals to 92 species of benthic invertebrates in and around the Great Lakes basin (Jaagumagi, 1990). In this procedure the sediment arsenic levels at all locations at which a given species was present are plotted in order of increasing concentration, and the 90th percentile of this concentration distribution determined. The 90th percentile, referred to as the

Species SLC, is chosen to provide a conservative estimate of the tolerance range of the species in question. The 90th percentiles for all of the species present are next plotted in order of increasing concentration, and from this plot the 5th and 95th percentiles are calculated. The concentration at the 5th percentile is defined as the Lowest Effect Level, at which majority of benthic infauna are unaffected. The 95th percentile is defined as the Severe Effect Level, which is considered to be detrimental to majority of benthic organisms. In the case of arsenic (strong acid-extractable), the Lowest and Severe Effect Levels were estimated to be, 6 and 33  $\mu\text{g/g}$  of sediment, respectively.

Results of other studies on aquatic invertebrates are given in Table 10.

#### 11.6 Effects on Fish

Nichols et al. (1984) studied the effects of arsenic trioxide on the parr-smolt transformation in coho salmon, Oncorhynchus kisutch. A six-month exposure to 300  $\mu\text{g As(III)/L}$  caused a delay in the onset of the normal increase in plasma thyroxine levels and a transient reduction in gill  $\text{Na}^+, \text{K}^+$ -ATPase activity. Out-migration of the smolts was significantly reduced ( $p < 0.05$ ) from 91% in the controls to 80% in fish exposed to 300  $\mu\text{g As(III)/L}$ .

Twenty-two elements found in coal were run through aquatic bioassays by Birge (1978). He exposed eggs of goldfish (Carassius auratus) and rainbow trout (Salmo gairdneri) to coal elements from fertilization through four days post-hatching, giving treatment periods of 7 days for goldfish and 28 days for trout. LC50's were 490 and 540  $\mu\text{g As/L}$  (as sodium arsenite), for goldfish and trout eggs, respectively.

Hughes and Davis (1967) tested the effects of 15 aquatic herbicides on the bluegill sunfish (Lepomis macrochirus). They obtained a 48-h median tolerance limit for sodium arsenite of 500  $\mu\text{g/L}$ . Unfortunately, it is not clear from their description, whether LC50 concentration was expressed in terms of the compound or elemental arsenic.

Spotila and Paladino (1979) reported that the tolerance of muskellunge fry (Esox masquinongy) to arsenic (as sodium arsenite) changed considerably with age. Mortality rates for fry up to 7 days old were low, and no LC50 concentration could be determined. The 96-h LC50 for swim-up fry (beginning at an age of 8 days) was 1,100  $\mu\text{g As/L}$ . Tolerance to arsenic then increased with the age of the fry, with a 96-h LC50 of 2,600  $\mu\text{g/L}$  for 5 week old fry and 16,000  $\mu\text{g As/L}$  for 12 week old fish.

Lima et al. (1984), using sodium arsenite, reported chronic

limits (NOEC-LOEC) of 2,130-4,300  $\mu\text{g As(III)/L}$  for fathead minnows, based on reduced mean wet weight and mean standard length over a 29-day exposure period. The chronic limits for flagfish were reported as 2,130-4,120  $\mu\text{g As(III)/L}$ , based on reduced wet weight and standard length over a 31-day exposure period (Lima et al., 1984). Spehar and Fiantt (1986) reported a maximum acceptable toxicant concentration (MATC) (calculated as the geometric mean of the highest no effect and lowest effect concentrations) of 3,330  $\mu\text{g As/L}$  and an EC50 of 7,079  $\mu\text{g As/L}$  for fathead minnows, based on growth reduction over a 32-d exposure to sodium arsenite. Spehar et al. (1980) reported that the survival of rainbow trout (likely adults, but age was not mentioned in their paper) was not affected by 28-d exposures to arsenic trioxide (961  $\mu\text{g As/L}$ ), arsenic pentoxide (973  $\mu\text{g As/L}$ ), disodium methyl arsenate (970  $\mu\text{g As/L}$ ), or sodium dimethyl arsenate (846  $\mu\text{g As/L}$ ).

For results of other studies of arsenic toxicity to fish, the reader is referred to Table 10, and Section 11.11 "Toxicity of Mixtures of Chemicals".

#### 11.7 Effects on Amphibians and Reptiles

Only a limited amount of data were found on arsenic toxicity to amphibians (Table 10), and none were found on toxicity to reptiles.

In Birge (1978)'s study the LC50 for toad (Gastrophryne carolinensis) eggs, was estimated to be 40  $\mu\text{g As (III)/L}$ . Birge et al. (1978) also reported that Marbled salamander eggs, (Ambystoma opacum), had an LC50 of 4450  $\mu\text{g As (III)/L}$ .

#### 11.8 Effects on Soil Biota and Insects

There are limited data on the effects of arsenic on non-target soil biota and insects. Honeybees (Apis mellifera) were accidentally killed by arsenite spray dusting. Dead bees contained 4-5  $\mu\text{g}$ , equivalent to 21-31 mg/kg bw (Jenkins 1980).

There was a complete absence of earthworms in soil containing between 150-165 mg As/kg (NRCC 1978). This was supported in another study where there was 100% death rate in earthworms, Eisenia fetida, exposed for 14 days to sodium arsenite at a concentration of 200 mg As/kg of an artificial substrate, whereas no deaths were observed at 100 mg As/kg (Bouche et al., 1987).

53, and 76%, respectively) when grown in sodium arsenite-treated Plainfield sand with  $H_2SO_4/HClO_4$  extractable soil arsenic concentrations as low as about 26, 68, 68, and 250  $\mu g/g$ , respectively. Arsenic concentrations in potato tubers and peelings increased with increasing arsenic concentrations in the soil, reaching as high as 0.5 and 83.0  $\mu g/g$ , respectively in soil with an arsenic concentration of 250  $\mu g/g$ .

Woolson (1973) grew six vegetable crops in three Maryland soils treated with disodium arsenate at nominal soil concentrations ranging from 10 to 500 mg/kg As. Phytotoxicity was generally highest on the loamy sand and lowest on the silty clay loam soil. For example, with a nominal soil concentration of 10 mg/kg As growth of green beans, Phaseolus vulgaris, the most sensitive of the six species tested, was reduced by 42% in Lakeland loamy sand, but only by 11% in Hagerstown silty clay loam. "Available" (0.05 N  $H_2SO_4$ /0.025 N HCl extractable) arsenic ranged from 1.4 to 3.0 mg/kg soil in the loamy sand, but only from <0.1 to 1.2 mg/kg soil in the silty clay loam. Cabbage, Brassica oleracea var. capitata, was the least sensitive crop tested. Growth in Hagerstown silty clay loam was not significantly affected by a nominal arsenic concentration of 100 mg/kg (available arsenic 5.7 to 18.3 mg/kg). Growth of cabbage in the Lakeland loamy sand was reduced by 68% at a nominal arsenic concentration of 100 mg/kg (available arsenic 27.9 to 55.0 mg/kg). Results of tests of other vegetables in the Lakeland soil are given in Table 10.

Woolson et al. (1971) showed that the addition of 100 mg As/kg from sodium, aluminum and calcium arsenate to soil already containing 8 mg As/kg resulted in >50% growth reduction of 4-wk-old corn plants, while the addition of 100 mg As/kg as ferric arsenate caused no growth reduction. As was the case in the Woolson (1973) study, growth reduction was more highly correlated with measures of "available" than with total soil arsenic. - - -

#### 11.10 Effects on Birds and Mammals

Although wildlife populations may be exposed to arsenic via inhalation of aerosols or ingestion of particulates while preening, the principal route of exposure is through ingestion of contaminated forage.

##### 11.10.1 Birds

Metal compounds may adversely affect avian reproduction (Birge and Roberts 1976). Even at subacute levels, they are well known inhibitors of reproduction. Ingested metals may concentrate in eggs and show a high degree of toxicity to the developing embryo.

The embryopathic effects of sodium arsenite were studied by Birge and Roberts (1976). White Plymouth Rock chicken (Gallus gallus) eggs were injected with  $\text{NaAsO}_2$  at concentrations ranging from 1.0  $\mu\text{g/kg}$  to 50.0  $\text{mg/kg}$ . Sodium arsenite was extremely toxic, reducing hatchability by 65% at 0.001  $\text{mg/kg}$ , and causing 100% mortality at 1.0  $\text{mg/kg}$ . The approximate TL50 (level of exposure producing 50% malformations) was 0.05  $\text{mg/kg}$ . Teratogenicity and defective survivors were seen in appreciable levels when eggs were dosed at or above the TL50. Defects of hatchlings included: brain deficiencies, absent eyes, skeletal abnormalities, unabsorbed yolk sacs and severe motor impairment. The frequency of teratogenesis showed striking concentration dependence that correlated inversely with survival.

Sodium ortho arsenate ( $\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$ ), a pentavalent arsenical used as a wood preservative and fungicide, was found to inhibit growth, produce abdominal edema and micromelia (limb bud defects) in 50% of the treated four day old White Leghorn chicken embryos which were injected with 0.20  $\text{mg}$  of the salt (Ridgway and Karnofsky 1952).

Recently, Gilani and Alibhai (1990) injected White Leghorn embryos with 1 to 20  $\mu\text{g/egg}$  of sodium arsenate salt ( $\text{NaHASO}_4$ ). The  $\text{LD}_{50}$  value was determined to be 9  $\mu\text{g/egg}$   $\text{NaHASO}_4$ . Observed malformations were approximately 64%; micromelia 27%, decreased body size 24% and haemorrhage 32%. Abnormalities in defective hatchlings were: neck and limb defects, everted viscera, reduced body size and body haemorrhage. Sodium arsenate salt is similar to sodium arsenite in that both are used as herbicides in non-crop areas, such as ditches and forest edges, where the risk of exposure to wildlife is high.

Inorganic arsenite poisoning in nestlings and adult birds is marked by muscular debilitation and incoordination, fluffed and huddled position, unkempt appearance, lack of reflexes, immobility and seizures. These symptoms, however, are similar to those of many other toxicants and not unique to arsenic (Eisler 1988).

Nestlings of several avian species were fed grasshoppers which had been poisoned with As trioxide. Nestling Bobwhites (Colinus virginianus), Mockingbirds (Mimus polyglottus) and American robins (Turdus migratorius), as well as several other songbird species, exhibited no toxic symptoms after consuming up to 40  $\text{mg As}$  per bird (NAS 1977).

Hudson et al. (1984) determined oral  $\text{LD}_{50}$  values for a single dose of sodium arsenite. The California Quail (Lophortyx californicus) was found to be the most sensitive, 47.6  $\text{mg/kg bw}$ , followed by the Mallard (Anas platyrhynchos) and Ring-necked Pheasant (Phasianus colchicus), 323 and 386  $\text{mg/kg bw}$  respectively.

Sodium arsenate, a constituent of agricultural irrigation drainwater, may have an impact on the survival, growth and physiology of ducklings. One day old Mallards were fed a diet containing 0, 30, 100 and 300 mg As/kg added as sodium arsenate for ten weeks (Camardese et al., 1990). Survival of exposed young was not directly affected. The 300 mg/kg dose, however, decreased brain ATP production rates. This lack of ATP resulted in altered behavioral patterns and increased the birds' resting times which may decrease survival in the wild. Decreased overall growth and lowered growth rates were present in females. Growth of male ducklings was affected at the 300 mg/kg level only. The observed effects on growth could lead to reproductive impairment in adults.

Heath et al. (1972) reported LC50's of 480 and 1403 mg copper acetoarsenate/kg in Bobwhites (Colinus virginianus) and Ring-necked Pheasants (Phasianus colchicus). Results of other studies on birds are given in Table 10.

#### 11.10.2 Mammals

As noted in a previous Section (6.1), in a range of animal species inorganic arsenic compounds are metabolized by methylation to dimethylarsinic acid and monomethylarsonic acid (Cullen and Reimer, 1989). The methylated products being less strongly bound to the tissues than arsenite, are more readily eliminated in the urine (BIBRA 1990). Methylation is thus considered a detoxification mechanism (Braman and Foreback 1973).

Chronic exposure of mammals to arsenic rarely results in a toxic response, since it is detoxified and rapidly excreted from the body (Woolson 1975). Chronic organic arsenosis in mammals is characterized by demyelination of optic and sciatic nerves, decreased growth and immune responses. Chronic inorganic toxicosis is illustrated by weakness, paralysis, conjunctivitis, dermatitis, decreased growth and liver damage (Klevay 1976, NRCC 1978).

Metals are known to be potent teratogens and embryo toxins. Arsenic is the only member of the group V elements that produces teratogenic effects in mammals. In rats, ewes and hamsters its effects on embryos include: cleft palate, exencephaly, eye defects, malformations in the anterior central nervous system, renal agenesis with severe uro-genital abnormalities (Ferm and Carpenter, 1968; Kurzel and Cetrulo 1981). Mice exposed to As produce broods with a higher than expected proportion of males. Hood et al., (1987) exposed fetal mice to pentavalent As via oral dosing and injection. Results indicate that the accumulation of arsenicals by the fetus may be similar to those measured in the dam.

Arsenic is known to accumulate in the placenta, without signs of fetotoxicity (Ferm and Carpenter, 1968; Kurzel and Cetrulo 1981). Anionic and organic arsenic cross the placenta to some



cattle. The calculated LD<sub>50</sub> for deer was 241.1-336.6mg As/kg body wt. The assimilation rate in deer was found to be higher than that reported for cattle.

Misuse of arsenic acid has also resulted in the death of White-tailed Deer (Swiggart et al., 1972). Arsenic acid is approved for use as a herbicide principally on crabgrass (Digitaria sanguinalis), but was improperly applied at higher than directed concentrations. Deer were aerially exposed to rates of 5 gal/acre of a solution containing 52.3% arsenic trioxide. Lethality in man is 0.2-0.3 grams of arsenic trioxide. Eleven animals were found dead after the spray episode. Necropsies performed on the animals found 19 mg/kg As in the liver and 18 mg/kg in the kidneys. Death was caused by acute arsenic poisoning.

#### 11.11 Toxicity of Mixtures of Chemicals

Thursby and Steele (1984) studied the effect of phosphate on the toxicity of arsenic to the red alga Champia parvula. Phosphate did not alter the effect of arsenic(III) on the vegetative growth over the range of phosphate tested (up to 9  $\mu$ moles/L (850  $\mu$ g/L)). Arsenic (V) toxicity was inhibited by the presence of phosphate. Plants died when exposed to all arsenic concentrations tested (1,290 - 9,330  $\mu$ g As(V)/L) in phosphate-free water, while growth in all treatment levels was not significantly different from that of controls with a phosphate concentration of 4.5  $\mu$ moles/L (430  $\mu$ g/L). Phosphate also inhibited the effects of arsenic(V) and, to a lesser extent, of arsenic(III), on sexual reproduction in the alga. With 1.1  $\mu$ moles/L (105  $\mu$ g/L) phosphate, no cystocarps were produced with 1,290  $\mu$ g As(V)/L, while with 9.1  $\mu$ moles/L (860  $\mu$ g/L) phosphate, production of mature cystocarps was inhibited only at 9,330  $\mu$ g As(V)/L. Growth of C. parvula was reduced by about 40% at 56  $\mu$ g As(V)/L in phosphate-free water.

Sanders (1979) reported that with phosphate concentrations above 0.3  $\mu$ moles/L (approximately 29  $\mu$ g/L), concentrations of As(V) less than 340 nmoles/L (about 26  $\mu$ g/L) did not inhibit cell growth of Skeletonema costatum. At arsenate concentrations of greater than 340 nmoles As(V)/L (26  $\mu$ g/L) some inhibition was noted even at phosphate concentrations exceeding 30  $\mu$ moles/L (approximately 2,850  $\mu$ g/L).

Lee et al. (1991) studied the effect of phosphate on arsenic uptake in an aquatic plant, hydrilla (Hydrilla verticillata Casp.). Phosphate from 12 to 160 mg/L inhibited the uptake of arsenic, whereas 5 mg/L phosphate did not effectively influence the uptake.

Selenium (Se) and arsenic are known to have antagonistic interactive effects when administered to mammals (Levander 1972),

chickens (Arnold et al., 1973; Howell and Hill, 1978) and ducklings (Camardese et al., 1990). The underlying mechanisms of toxicity are not fully understood, however it appears that the biological effects of arsenic and selenium are modified in the presence of each other (Frost, 1967). Poultry exhibit arsenic protection from selenium poisoning when arsenic is placed in the drinking water and selenium in the feed (NRCC 1978). Howell and Hill (1978) noted that 10 mg/kg As overcame growth retardation and mortality caused by 25 mg/kg Se in domestic chicken diets. Arnold et al. (1973) also reported that chickens exposed to As overcame weight depressions caused by selenium.

In most polluted environments, aquatic organisms are likely to be exposed to a wide variety of toxicants simultaneously. An investigation into the additive or synergistic effects of a mixture of six metals (Cu, Cd, Cr, Pb, Hg and As) commonly found together as mixtures in sewage and industrial wastes, was conducted by Spehar and Fiantt (1986). Metals combined at the U.S. criterion maximum concentration for protection of the environment (140 µg/L for As (III)) caused nearly 100% mortality in rainbow trout (Salmo gairdneri) and daphnids during acute exposures, and when combined at the criterion average concentrations (72 µg/L for As(III)) the metals significantly ( $p < 0.05$ ) reduced production of daphnid young and growth of fathead minnows (Pimephales promelas) after 7 and 32 days, respectively. The contribution of arsenite to these effects was not ascertained, but the investigators point out that single-chemical water quality criteria may not sufficiently protect some species when other toxicants are also present.

Spehar and Fiantt (1986) found that arsenic, cadmium, chromium, copper, mercury and lead in combination had a more than additive effect in acute toxicity tests with Pimephales promelas, compared with the toxicities of the individual metals, but in 32-day tests on effects on growth, these chemicals had a less than additive effect on the same species. For Ceriodaphnia dubia, the joint action of these metals was nearly additive in both acute and 7-day chronic (growth) tests.

## Section 12. Other Pertinent Data

Recently Environment Canada's Water Quality Branch summarized arsenic data generated between 1966 and 1989 in the Atlantic Region (Leger, 1991). Concentrations were reported in a variety of media, including stream, lake, ground and mine waste waters, sediments and fish.

Nearly all stream, lake and estuary waters (2370, 598 and 85 samples, respectively) had total, dissolved or extractable (i.e. waters unfiltered, with HCl added) arsenic levels of less than 50 µg/L. Typical concentrations in lake and stream waters dropped 10-fold between 1980 and 1981 - from about 10 to < 1 µg As/L. This

decline was found to correspond exactly to the period when the analytical method was changed from colorimetry to atomic absorption spectrometry - with a corresponding 10-fold drop in the detection limit. The author concluded that pre-1981 results for surface waters were in general an overestimation of "true" arsenic levels.

Of the 311 ground water samples analyzed all but five, measured in 1971, had levels less than 50  $\mu\text{g As/L}$ . It should be noted, however, that none of these samples were from Halifax and Guysborough Counties, where both Grantham and Jones (1977) and Meranger et al. (1984) have reported a relatively high proportion of wells with > 50  $\mu\text{g As/L}$  (see Section 6.3.4).

Arsenic concentrations in 83 samples of mine waste water from New Brunswick ranged from 5  $\mu\text{g/L}$ , up to 1,900  $\mu\text{g/L}$ .

Of the 133 sediment samples analyzed, most had arsenic levels of less than 10 mg/kg. Samples showing the highest concentrations (up to 260 mg As/kg) were those near mining areas. Although these sediment concentrations are low in relation to levels reported near some base and precious metal mining and smelting areas elsewhere in Canada (see Table 6), this is likely partly due to the weak acid attack (cold 0.5 N HCl) used for sample digestion.

Most of the 98 fish samples analyzed contained less than about 0.27 mg As/kg (fw ?). The highest level found in fish flesh was 2.68 mg/kg (fw ?).

### **Section 13. Regulations, Guidelines and Standards**

Standards relating to arsenic levels in Canadian waste water effluent are summarized in Table 11. Metal Mining Liquid Effluent Regulations were approved by the Canadian Government in February, 1977, under the *Fisheries Act* to limit the concentrations of several deleterious substances that may be discharged in effluents from new, expanded, and reopened metal mines (Environment Canada 1988). Guidelines for Liquid Effluents from Existing Metal Mines were published at the same time. For arsenic, these regulations and guidelines specify a maximum monthly arithmetic mean concentration of 0.5 mg/L; a maximum concentration in a composite sample of 0.75 mg/L; and a maximum concentration in a grab sample of 1.0 mg/L. In 1986 only two existing mines - out of about 30 for which arsenic release data were reported - failed to meet the authorized levels for arsenic (Environment Canada 1988).

Since 1973 Alberta's *Clean Water Act* has limited arsenic levels in waste water effluent from gas processing plants to 0.25 mg/L. In Newfoundland, the *Department of the Environment Act* sets the maximum acceptable arsenic concentration in effluent discharged into a body of water at 0.5 mg/L. British Columbia's *Waste*

Table 11. Summary of standards pertaining to arsenic in Canadian waste water effluent<sup>1</sup>.

Jurisdiction	Legislation/Date	Description	As (mg/L)
Federal Government	<i>The Fisheries Act, 1977</i>	maximum authorized concentrations in effluent from metal mines: (i) monthly arithmetic mean (ii) composite sample (ii) grab sample	0.5 0.75 1.0
Alberta	<i>Clean Water Act, 1973</i>	standard for waste water effluent from gas processing plants	0.25
British Columbia	<i>Waste Management Act, 1974</i>	effluent quality objectives for release of As III from chemical industries other than petroleum refineries: Level A <sup>2</sup> - marine and fresh water Level B <sup>2</sup> - marine and fresh water Level C <sup>2</sup> - marine - fresh water	0.05 0.05 0.08 0.05
	<i>Waste Management Act, 1975</i>	objectives for total As in municipal type waste discharges to all receiving water and to ground: Level AA Level BB	0.05 0.25
	<i>Waste Management Act, 1975</i>	objectives for the discharge of effluent to marine and fresh waters from metal-finishing plants and industries discharging heavy metals: Level A <sup>2</sup> Level C <sup>2</sup>	1.0 1.9
	<i>Waste Management Act, 1979</i>	objectives for discharge to marine and fresh waters from mining, smelting and related industries: As III Total dissolved As	0.05-0.25 0.10-1.0
Newfoundland	<i>Department of the Environment Act, 1980</i>	maximum acceptable concentration in effluent discharged into a body of water	0.5

<sup>1</sup> Information obtained from IRPTC (1991)

<sup>2</sup> All new or proposed discharges should meet Level A objectives. All existing discharges should meet Level C, either immediately or within the shortest possible time feasible to do so. Existing discharges should be upgraded to interim Level B, and ultimately Level A by a staged program of improvement.

Table 12. Summary of standards, criteria and objectives pertaining to arsenic (As) and arsine (AsH<sub>3</sub>) in Canadian air.

Jurisdiction	Legislation/Date	Description	Level (µg/m <sup>3</sup> )
British Columbia	Waste Management Act, 1979 <sup>1</sup>	ambient air control objectives	0.1-1.0 As
Ontario	Environmental Protection Act, 1991 <sup>2</sup>	interim ambient air quality criteria; 24 hr average	0.3 As & compounds 5.0 AsH <sub>3</sub>
		standard at point of impingement from a source of contamination; half-hour average	1.0 As & compounds 10.0 AsH <sub>3</sub>
	Environmental Protection Act, 1991 <sup>2</sup>		

<sup>1</sup> Information obtained from IRPTC (1991)

<sup>2</sup> Source: Ontario Ministry of the Environment (1991)

Management Act defines objectives for the total arsenic and As (III) content of waste water discharges ranging from 0.05 - 1.9 mg/L (see Table 11), depending upon the type of source, and whether it is new or existing.

As indicated in Table 12, only British Columbia and Ontario have established objectives, or criteria and standards for arsenic in ambient air. Ontario's *Environmental Protection Act* sets an interim ambient air quality criterion of 0.3  $\mu\text{g As}$  and its compounds per cubic metre, except for  $\text{AsH}_3$ , for which the criterion is 5  $\mu\text{g/m}^3$  (24-hr averages). Standards at the point of impingement from a source of contamination are 1.0  $\mu\text{g/m}^3$  and 10  $\mu\text{g/m}^3$ , respectively, for arsenic and its compounds and arsine (half-hour averages). In British Columbia, the *Waste Management Act* sets ambient air control objectives at from 0.1 to 1.0  $\mu\text{g As/m}^3$ . The same Act establishes objectives for gaseous and particulate emissions from copper smelting at 0.1 kg As/tonne Cu, and from lead smelting and refining at 0.1 kg As/tonne Pb.

Guidelines and objectives pertaining to arsenic in Canadian waters are summarized in Table 13. The Federal Government guidelines were developed by a Task Force of the Canadian Council of Resource and Environment Ministers (CCREM), and were intended to harmonize water quality guidelines across the country. A guideline of 0.05 mg/L of total arsenic has been established by CCREM (1987) for the protection of freshwater aquatic life. This is the same as the guideline for Canadian raw drinking water. For irrigation waters, the Council has set a guideline of 0.1 mg As/L for continuous use on all soils and 2.0 mg As/L for use on fine-textured neutral to alkaline soils for up to 20 years (CCREM 1987). The Federal guideline for water used for livestock watering is 0.5 mg As/L. Ontario's Water Management Guidelines and Saskatchewan's Surface Water Quality Objectives are similar to Federal guidelines.

Angus Environmental Ltd. (1991) recently reviewed soil quality criteria of various jurisdictions including British Columbia, Alberta, Ontario and Quebec (Table 14). The Alberta Government has a two "Tier" system of classification (Alberta Environment, 1990). Tier I values represent approximate acceptable concentrations of soil contaminants for all site conditions and land uses. Tier II criteria offer an alternative. They consider site specific risks to human health or the environment, and must be developed by a proponent. In the case of arsenic, a Tier I value of 10 mg As/kg has been established.

The British Columbia and Quebec Governments use the "ABC" format (Angus Environmental Ltd, 1991). In general, A Levels represent soil of good quality. Levels B suggests some contamination with the potential for harmful effects on human health or the environment, and indicates the need for further investigation. Level C represents concentrations above which

Table 13. Summary of guidelines and objectives pertaining to arsenic in Canadian waters<sup>1</sup>.

Jurisdiction	Description	As (mg/L)
Federal Government	Canadian Water Quality Guidelines, 1987	0.05
	guideline for protection of aquatic life	
	guideline for irrigation waters used	
Ontario	(i) on all soils	0.1
	(ii) on fine textured neutral-alkaline soils for 20 yr	2.0
	guideline for protection of livestock	0.5
	Ontario Water Management Guidelines, 1984	0.1
	objective for the protection of aquatic life	
Saskatchewan	maximum concentration in irrigation waters used	
	(i) on all soils	0.1
	(ii) on fine textured neutral-alkaline soils for 20 yr	2.0
	criteria for livestock watering	0.2
	Surface Water Quality Objectives, 1988	0.05
	objective for the protection of aquatic life and wildlife	
	objective for the protection of irrigation use	0.1
	objective for the protection of use of water for livestock watering	0.5

<sup>1</sup> Information obtained from IRPTC (1991)

Table 14. Summary of guidelines pertaining to arsenic in Canadian soil<sup>1</sup>.

Jurisdiction	Description		As (mg/kg)
Alberta	Tier I (draft)	approximate acceptable concentration	10
British Columbia and Quebec	Level A	soil of good quality	5
	Level B	some contamination; further investigation indicated	30
	Level C	remedial investigation and/or clean-up are needed	50
Ontario	agricultural/ residential/ parkland uses	a) medium-fine textured soil	25
		b) coarse textured soil	20
	commercial/ industrial uses	a) medium-fine textured soil	50
		b) coarse textured soil	40
	sludged agricultural soils <sup>2</sup>	maximum recommended concentration	14

<sup>1</sup> Information from Angus Environmental Ltd. (1991), unless otherwise noted.

<sup>2</sup> From Frank et al. (in preparation).



remedial investigations and/or clean-up are needed. The B.C. Ministry of the Environment further specifies that for residential, recreational and agricultural land uses, Level A is the threshold for investigation, and Level B the threshold for remedial action. For commercial and industrial land uses, Level B is the threshold for investigation and Level C the threshold for remedial action. Both Quebec and British Columbia have established A, B and C Levels of 5, 30 and 50 mg As/kg, respectively.

The Ontario Ministry of the Environment has included consideration of soil texture in its soil clean-up guidelines. In agricultural, residential and parkland areas the provisional guideline for arsenic is 20 mg/kg for coarse soils, and 25 mg/kg for medium and fine textured soils. In commercial and industrial areas the guidelines are 40 and 50 mg/kg for coarse and finer textured soils, respectively.

Frank et al. (in prep.) have proposed a somewhat lower maximum recommended concentration (14 mg As/kg) for Ontario agricultural soils receiving applications of sewage sludge. In establishing this criterion they noted that arsenic is a direct phytotoxicant at relatively low levels, and that the average arsenic concentration in uncontaminated Ontario agricultural soils is about 7 mg/kg.

With regard to sediment quality, the Province of Ontario is presently preparing a comprehensive set of Sediment Quality Guidelines for a variety of potentially toxic substances, including arsenic (Jaagumagi, 1990; Persaud et al., 1991). The Lowest Effect Level, which can be tolerated by the majority of benthic organisms, was estimated at 6  $\mu\text{g}$  As/g; the Severe Effect Level, where pronounced disturbance of the benthic infaunal community can be expected, was set at 33  $\mu\text{g}$  As/g. These levels were derived using a "Screening Level Concentration" approach, using information on both arsenic content and the presence (or absence) of 92 benthic species in sediment from 442 sites in and adjacent to the Great Lakes region.

MacDonald et al. (in preparation) have compiled sediment quality guidelines for several pollutants from a variety of jurisdictions. They noted that the Ontario Ministry of the Environment currently has a dredge spoil guideline of 8 mg As/kg for open water disposal and that the U.S. EPA (Region VI) has proposed a similar guideline (5 mg As/kg). According to Persaud et al. (1991), Ontario's Open Water Disposal Guidelines will be superseded by the Province's new Sediment Quality Guidelines, when the latter officially come into effect.

#### **Section 14. Risk Assessment**

(This Section is currently being prepared)

## Section 15. Recommendations

(This Section is currently being prepared)

## Section 16. References

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