

Arsenic in the St. Lawrence River Ecosystem

Bernadette Quémerais
Contamination of the Aquatic Environment

St. Lawrence Centre
Environmental Conservation
Environment Canada - Quebec Region

November 1996

READERS' COMMENTS

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This document should be cited as follows:

Quémerais, B. 1996. *Arsenic in the St. Lawrence River Ecosystem*. Environment Canada - Quebec Region, Environmental Conservation, St. Lawrence Centre. Scientific and Technical Report ST-40E, 28 pages.

© Minister of Supply and Services Canada 1996
Catalogue No. En153-72/1996E
ISBN 0-662-25179-2

Management Perspective

Recent results of a project in the Sainte-Anne River showed that arsenic concentrations in some Atlantic tomcod there are very high. Arsenic concentrations in the St. Lawrence River (data from the Environment Canada monitoring network) are also high relative to water quality criteria established by MENVIQ (the Quebec environment ministry). Furthermore, Environment Canada considers arsenic to be a priority contaminant. It would thus appear important to understand the dynamics of arsenic in the aquatic ecosystem, especially in the St. Lawrence River. This paper presents all available information on arsenic in the aquatic environment of the St. Lawrence River and in other international water bodies.

Perspective de gestion

Lors d'un projet sur les poulamons de la rivière Sainte-Anne, les analyses ont montré que les teneurs en arsenic pouvaient être élevées dans la chair de certains poissons. De plus, les concentrations en arsenic dans le fleuve Saint-Laurent (données du réseau de suivi du Ministère) sont relativement élevées si l'on considère les critères de qualité du MENVIQ. Enfin, l'arsenic a été jugé comme contaminant prioritaire par Environnement Canada. Il paraît donc important de connaître la dynamique de l'arsenic dans l'écosystème aquatique et particulièrement dans le Saint-Laurent. Ce rapport présente toutes les informations disponibles sur l'arsenic en milieu aquatique, à l'échelle du Saint-Laurent ainsi qu'à une échelle globale.

Abstract

Arsenic concentrations in water and fish from the St. Lawrence River are relatively high, and Environment Canada considers arsenic a priority contaminant. This paper looks closely at the latest information on the behaviour of arsenic in the aquatic environment, including its sources, its biogeochemical cycle, its concentration levels in various aquatic media and its toxicity. This report also deals with existing knowledge on contamination levels observed in the St. Lawrence River, and looks at the analytic techniques available to determine total arsenic as well as its various chemical species.

Résumé

Les teneurs en arsenic dans l'eau et les poissons du Saint-Laurent sont relativement élevées et ce contaminant est jugé prioritaire par Environnement Canada. Ce document présente en détail les connaissances les plus récentes sur le comportement de l'arsenic en milieu aquatique, incluant ses sources, son cycle biogéochimique, ses niveaux de concentrations dans les diverses matrices environnementales et sa toxicité. La deuxième partie du rapport traite des connaissances actuelles sur les niveaux de contamination observés dans le Saint-Laurent. Enfin, la dernière partie traite des techniques analytiques actuellement disponibles aussi bien pour la mesure de l'arsenic total que pour la détermination de ses différentes espèces chimiques.

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1 Introduction

Arsenic, though commonly considered a poison, is in fact a substance that is naturally present in the environment. Its toxicity is highly dependent on its chemical form, inorganic compounds being more toxic than organic compounds (Blais-Ladouceur, 1979; Goyer, 1980; Messier, 1981). In general, arsenic in water and sediment is in the inorganic form, mainly As(V) (Ferguson and Gavis, 1972), but traces of methylated arsenic may also be found (Andreae and Klumpp, 1979; Anderson and Bruland, 1991; Michel et al., 1992). In aquatic organisms, arsenic is more commonly found in the form of organic complexes. In brown algae, for example, it is essentially found in the form of arsenoribosides (Edmonds and Francesconi, 1981; Edmonds and Francesconi, 1993), while in fish, about 95% of arsenic takes the form of arsenobetaine (Beauchemin et al., 1988; Shibata and Morita, 1989; Michel, 1993).

Concentrations of arsenic observed in marine organisms are generally high, with levels up to 100 µg/g (wet weight) (Bohn, 1975; Michel, 1993). In freshwater organisms, concentrations are usually lower, often less than 1 µg/g (Lawrence et al., 1986).

Environment Canada considers arsenic to be a priority contaminant (Government of Canada, 1993). As such, it is important that a report be prepared on our current level of knowledge of this element in the St. Lawrence ecosystem. This report contains information on arsenic in the aquatic environment, both in the St. Lawrence and in other water bodies of the world. It also reports on the various analytical techniques used to quantify arsenic in various matrices.

2 Arsenic in the Environment

2.1 USE AND PRODUCTION

Arsenic is a non-metallic mineral, long known for its medicinal and toxic properties. It was already being used as a poison and in therapeutic applications 2000 years before Christ (Ferguson and Gavis, 1972; Goyer, 1980). It is currently used to make pigments, medicinal products, glass and alloys of lead and copper. Very pure arsenic is used in the manufacture of semi-conductors (CCREM, 1987). Arsenic compounds (calcium and lead arsenates and sodium arsenate) are also used as pesticides, herbicides, defoliants and preservatives (CCREM, 1987).

In 1974, about 67% of the arsenic used in Canada went to make glass and 32% for the lamination, moulding and extrusion of metals. The remaining 1% was used by other chemical industries (CCREM, 1987). Canada produced 34 tonnes of arsenic in 1971. This figure has since fallen to near zero. In 1981, Canada imported 518 t of arsenic and arsenic compounds, a figure which fell to 317 t in 1982 (CCREM, 1987).

2.2 SOURCES IN THE AQUATIC ENVIRONMENT

2.2.1 Natural sources

Arsenic is contained in commonly found minerals, most often mispickel or arsenopyrite (FeAsS). It is also present in realgar (As_2S_2) and orpiment (As_2S_3). In its pure state, arsenic oxidizes quickly to form arsenic trioxide, commonly used as rat poison (*Handbook of Chemistry and Physics*, 1986; Blais-Ladouceur, 1979).

The arsenic content of igneous rocks is estimated at about 2 $\mu\text{g/g}$, that of schist and marine sediment at about 10 $\mu\text{g/g}$ and that of sandstone and limestone at 1.5 $\mu\text{g/g}$ (Ferguson and Gavis, 1972). Arsenic input to the aquatic environment results from the erosion of arseniferous rocks and volcanic activity. It would appear that most of the arsenic accumulated in ocean sediment over geological time is essentially the result of direct volcanic activity, but current natural input is the result of the erosion of non-marine rock (Ferguson and Gavis, 1972). On a

global scale, the input of arsenic as a result of erosion has been estimated at 45 000 t/year (Ferguson and Gavis, 1972).

2.2.2 Anthropogenic sources

Total worldwide inputs of arsenic from anthropogenic sources to the environment have been estimated at 99 800 t/year, or about twice the amount produced by soil erosion (CCREM, 1987). The most recent data on atmospheric emissions of arsenic in Canada date back to 1972, when they totalled 4073 t (Environment Canada, 1976). The mining and iron industries were responsible for 98.9% of inputs, 47.5% of which was attributable to the metallurgical processing of gold, 25.6% to the primary smelting of iron and steel and 16.2% to the primary smelting of copper and nickel (Environment Canada, 1976). Other sources were the combustion of heavy metals and coal (0.9%), and the application of arsenical pesticides (0.2%) (Environment Canada, 1976).

2.3 SPECIATION AND FATE IN THE AQUATIC ENVIRONMENT

2.3.1 Arsenic in water

Arsenic exists in various degrees of oxidation: 0 (metallic), -3 and +3 (trivalent As(III)) and +5 (pentavalent As(V)). The two species most commonly found in natural waters are As(III) and As(V) (Ferguson and Gavis, 1972; CCREM, 1987; Pettine et al., 1992). The stability of the different species depends on the oxidation-reduction potential (E_H) and the pH of the water (Ferguson and Gavis; 1972, Pettine et al., 1992). In oxygenated water with high E_H values, the predominant species are pentavalent arsenates (H_3AsO_4 , $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) (Ferguson and Gavis, 1972). In neutral pH, the $H_2AsO_4^-$ and $HAsO_4^{2-}$ species are important, while at pH levels over 9, $HAsO_4^{2-}$ predominates (Pettine et al., 1992). At lower E_H values, characteristic of reducing conditions, the trivalent arsenate forms (H_3AsO_3 , $H_2AsO_3^-$ and $HAsO_3^{2-}$) become stable. At low pH levels and in the presence of sulphide, $HAsS_2$ predominates (Ferguson and Gavis, 1972). Metallic arsenic is stable when the oxidation-reduction potential is low, and arsine (AsH_3) when the oxidation-reduction potential is very low (Ferguson and Gavis, 1972). Most of these

compounds are soluble and As(III) species are more mobile than As(V) species. The As(V)/As(III) ratio varies according to the chemical composition of the water (Ferguson and Gavis, 1972; Pettine et al., 1992). In a study of dissolved arsenic in the Po River, Pettine et al., 1992 found that the ratio of the oxidated (pentavalent) form to the reduced (trivalent) form varied from 1.5 to 8.5. This ratio increased significantly with increases in iron and manganese oxides.

Dissolved inorganic arsenic can adsorb to iron and alumina hydroxides and co-precipitate with them (Ferguson and Gavis, 1972; Crecelius and Carpenter, 1973; CCREM, 1987; De Vitre et al., 1991). This association with iron oxides seems to be an important mechanism for the fixation and retention of arsenic in sediment (Lowell and Farmer, 1983). In addition, studies on arsenic speciation in sediment demonstrate that this element is largely associated with oxides of iron and manganese (Oscarson et al., 1981; Belzile and Tessier, 1990; Azcue and Nriagu, 1993). The total arsenic content in fresh water is highly variable, between 1 and 40 $\mu\text{g/L}$ (Michel, 1993). Concentrations of dissolved As generally vary from 0.1 to 10 $\mu\text{g/L}$ and about 25% of arsenic is transported in the dissolved phase in rivers (Michel, 1993).

Arsenic has difficulty combining with organic ligands such as humic and fulvic acids, so the organic fraction of arsenic in most rivers is therefore negligible (Pettine et al., 1992). However, inorganic arsenic may be methylated by phytoplanktonic activity and, in sediment, by micro-organisms, becoming methylarsonic acid (MMA), dimethylarsinic acid (DMA) or trimethylarsine oxide (TMAO) (Andreae, 1978; Andreae and Klumpp, 1979; Reimer and Thompson, 1988; Anderson and Bruland, 1991; Michel et al., 1992; Millward et al., 1993; Sanders and Riedel, 1993). Concentrations of these biomethylated forms vary from trace levels to a few micrograms per litre in surface water (Michel et al., 1992) and marine interstitial water (Reimer and Thompson, 1988). Concentrations of arsenite, MMA and DMA vary seasonally and methylated arsenic (essentially DMA) is most often found during periods of strong phytoplankton growth in coastal areas (Sanders, 1985; Sanders and Riedel, 1993; Riedel, 1993). In addition, these concentrations are largely dependent on the species of phytoplankton present in the environment (Andreae and Klumpp, 1979; Sanders, 1985; Sanders and Riedel, 1993). Lastly, molecules with the highest molecular weight synthesized by aquatic organisms -

arsenoribosides, arsenolipids, arsenobetaine, etc. – may be found in water. These molecules may represent up to 25% of all other organic and inorganic arsenic compounds (Michel, 1993).

The toxicity of the different chemical species is highly variable (Table 1). In general, inorganic compounds are more toxic than organic compounds and trivalent compounds are more toxic than pentavalent compounds (Blais-Ladouceur, 1979; Goyer, 1980; Messier, 1981). However, the toxic effect varies significantly according to various biotic and abiotic factors, such as water temperature, pH, E_H , organic matter, phosphate, suspended matter and the presence of other contaminants (Eisler, 1994).

Table 1
Toxicity of arsenical compounds

Arsenic compound	LD ₅₀ (mg/g) Administered orally to mice
Arsenobetaine	>10.0
Arsenocholine	6.5
Trimethylarsine oxide	10.6
Dimethylarsinic acid	1.2
Methylarsonic acid	1.8
Arsenic trioxide (As(III))	0.0345

Source: Shiomi, 1994.

2.3.2 Arsenic in aquatic organisms

Like most contaminants, arsenic bioconcentrates in aquatic organisms. The arsenate As(V) is chemically similar to phosphate and is easily assimilated by phytoplankton and algae, which reduce it to soluble methylated species (Andreae and Klumpp, 1979; Anderson and Bruland, 1991; Michel et al., 1992; Millward et al., 1993; Sanders and Riedel, 1993). This biomethylation is the preferred detoxication method for inorganic arsenical compounds (Eisler, 1994).

Total concentrations of arsenic in freshwater algae and phytoplankton are on the order of 1 to 10 µg/g (dry weight) (Seydel, 1972; Reay, 1972, Goyer, 1980; Messier, 1981;

Government of Canada, 1991) and from 1 to 100 $\mu\text{g/g}$ (dry weight) in marine algae and plankton (Lunde, 1973; Bohn, 1975; Kennedy, 1976; Bohn and McElroy, 1976; Millward et al., 1993) (Table 2). Accumulated arsenic may be essentially inorganic (Maeda et al., 1993) or methylated (Millward et al., 1993). The major arsenic compounds in brown algae have been determined to be arsenoribosides (Edmonds and Francesconi, 1981; Shibata et al., 1987; Jin et al., 1988; Edmonds and Francesconi, 1993) (Table 3). It would appear that the differences observed in the percentage of arsenic forms depend essentially on the species of algae being considered.

Table 2
Arsenic concentrations in algae and plankton

Type of sample	Location	Species	Concentration ($\mu\text{g/g}$, dry weight)	Reference
Freshwater algae	New Zealand	<i>Ceratophyllum demersum</i>	1.4	Reay, 1972
		<i>Elodea canadensis</i>	3.0	Reay, 1972
	North America Lake Michigan	Phytoplankton	3.7 - 9.6	Seydel, 1972
		Zooplankton	4.1 - 7.9	Seydel, 1972
	Lake Superior	Phytoplankton	3.2 - 4.3	Seydel, 1972
		Zooplankton	1.2 - 4.4	Seydel, 1972
Marine plankton	Canadian Arctic	Copepoda	5.6 - 7.3	Bohn and McElroy, 1976
		Amphipods	7.9	Bohn and McElroy, 1976
		<i>Sagitta</i> sp.	7.6	Bohn and McElroy, 1976
	Greenland	Copepoda	6.0	Bohn, 1975
		Newfoundland	Copepoda	0.9 - 1.7
	Euphausiids		1.5 - 2.3	Kennedy, 1976
	Hyperiid		2.3 - 2.8	Kennedy, 1976
		Gammarids	4.4 - 8.9	Kennedy, 1976
Marine algae	Greenland	<i>Fucus vesiculosus</i>	35.6	Bohn, 1975
	Norway	<i>Laminaria hyperborea</i>	142.0	Lunde, 1973
	Australia	<i>Ecklonia radiata</i>	50 - 145	Maher, 1983
		<i>Sargassum bracteolosum</i>	64 - 123	Maher, 1983
	England	<i>Fucus vesiculosus</i>	14.8	Millward et al., 1993
		<i>Fucus serratus</i>	27.9	Millward et al., 1993
<i>Ascophyllum nodosum</i>		3.6	Millward et al., 1993	

Table 3
Percentage of arsenic forms found in various species of algae

Species	Inorganic As (%)	MMA (%)	DMA (%)	Arseno-ribosides	Reference
<i>Nostoc</i> sp.	97.5 - 100	nd - 0.5	nd - 2.0	-	Maeda et al., 1993
<i>Fucus vesiculosus</i>	3	1	96	-	Millward et al., 1993
<i>Fucus serratus</i>	3.1	0.3	96.4	-	Millward et al., 1993
<i>Hizikia fusiforme</i>	50	-	-	50	Edmonds et al., 1987
<i>Sphaerotruchia divaricata</i>	-	-	-	75	Jin et al., 1988

In terms of toxicity, it would appear that phytoplankton are much more sensitive than zooplankton (Michel, 1993). Arsenic concentrations of from 5 to 10 $\mu\text{g/L}$ in water inhibit primary production (Sanders, 1979; Sanders and Cibick, 1985). The effect on zooplankton is considered negligible when concentrations are below 100 $\mu\text{g/L}$ (Sanders, 1986). Growth of the freshwater algae *Scenedesmus obliquus* was reduced by 40% following a two-week exposure to a concentration of 10 $\mu\text{g/L}$ (Vocke et al., 1980).

Unlike mercury, arsenic does not biomagnify in the food chain (Eisler, 1994). It would appear, in fact, that higher organisms such as fish are less exposed to bioaccumulation than are invertebrates and algae. In a study by Maeda et al. (1993), total arsenic content in freshwater shrimp varied from 19 to 33 $\mu\text{g/g}$ (dry weight), with 68 to 91% of the arsenic being in the inorganic form, while total As content in carp, which feed on these shrimp, varied from 2 to 12 $\mu\text{g/g}$ (dry weight), with 59.2 to 94.7% being in the inorganic form and the rest of the arsenic in the methylated form. In general, the higher up the food chain, the lower the total arsenic content. However, the low toxicity methylated and organic complex forms (Table 1), increase (Maeda et al., 1993). Maher (1983) found higher total arsenic content in algae, crustaceans and molluscs than in fish. It would appear that dissolved arsenic is not directly bioaccumulable, but that the methylated compounds produced by phytoplankton are (Michel, 1993). However, a study on shrimp and carp showed that these two species accumulate inorganic arsenic directly from the water and that this accumulation increases as the arsenic content of the water increases (Maeda et

al., 1993). However, a number of authors have noticed that bioconcentration can also be produced through food transfer (Maeda et al., 1993; Michel, 1993).

In aquatic invertebrates, total arsenic content varies from 1 to 70 µg/g (dry weight) (LeBlanc and Jackson, 1973; Bohn, 1975; Shinagawa et al., 1983; Maher, 1983; Michel, 1993) (Table 4). The chemical forms of arsenic in invertebrates seem to differ between species. Edmonds and Francesconi (1981) found arsenic in the form of arsenobetaine in lobster flesh, while, in a more recent study, Le et al. (1994a) found arsenobetaine to be the predominant form in shrimp and bivalves, although they also found arsenoribosides in bivalves.

Table 4
Arsenic concentrations in aquatic invertebrates

Location	Species	Concentrations (µg/g)	Reference
Greenland (ocean)	<i>Pandalus borealis</i>	52.5 - 70.6	Bohn, 1975
	<i>Mytilus edulis</i>	0.8 - 16.7	Bohn, 1975
Australia (ocean)	<i>Penaeus latisulcatus</i>	11.4 - 23.1	Maher, 1983
	<i>Mytilus edulis planulatus</i>	12.6 - 22.0	Maher, 1983
	<i>Sepioteuthis australia</i>	3.9 - 8.8	Maher, 1983
Japan (ocean)	<i>Penaeus orientalis</i>	41.3	Shinagawa et al., 1983
	<i>Turbo cornutus</i>	15.0	Shinagawa et al., 1983
	<i>Illex argentinus</i>	9.5	Shinagawa et al., 1983
France (ocean)	<i>Mytilus edulis</i>	4.9 - 43.3	Michel, 1993
	<i>Crassostrea gigas</i>	14.4 - 27.0	Michel, 1993
St. Lawrence (Canada)	<i>Elliptio complanata</i>	3.43	Metcalf-Smith et al., 1995
	<i>Lampsilis radiata radiata</i>	5.43	Metcalf-Smith et al., 1995
	<i>Elliptio complanata</i>	1.8 - 3.8	de Lafontaine, 1995
	<i>Dreissena polymorpha</i>	1.9 - 4.1	de Lafontaine, 1995

Aquatic invertebrates are less sensitive to arsenic than aquatic plants. For example, Rodrigues-Capitulo (1984) found mortalities in a shrimp species at concentrations of over

100 µg/L. In general, toxic effects appear at concentrations on the order of 0.5 to 1 mg/L of arsenic (Eisler, 1994).

Total arsenic content in fish is generally much lower in freshwater species than in marine fish. Concentrations on the order of 0.05 µg/g (dry weight) have been found in Lake Tanganyika in Burundi (Sindayigaya et al., 1994). These values are similar to those obtained (0.03 µg/g, wet weight) in rivers and lakes in Tennessee (Blevins and Pancorbo, 1986). Concentrations measured in fish flesh, however, seem to be higher in the St. Lawrence and the Great Lakes (on the order of 0.6 µg/g, wet weight) (Sloterdijk, 1976; Sloterdijk, 1977; Blais-Ladouceur, 1979; Langlois and Sloterdijk, 1989, Government of Canada, 1991). In marine fish, arsenic content is much higher, reaching as much as several hundred micrograms per gram (wet weight) (Bohn, 1975; Bebbington et al., 1977; Michel, 1993) (Table 5).

Table 5
Arsenic concentrations in fish

Location	Species	Concentrations (µg/g)	Reference
Burundi (Lake Tanganyika)	<i>Lates stappersii</i>	0.04 (dry weight)	Sindayigaya et al., 1994
	<i>Stolothrissa tanganyikae</i>	0.06 (dry weight)	Sindayigaya et al., 1994
Lakes and rivers in Tennessee	Various species	<0.03 - 0.03 (wet weight)	Blevins and Pancorbo, 1986
St. Lawrence River	Various species	<0.05 - 0.34 (wet weight)	Langlois and Sloterdijk, 1989
	Burbot (flesh)	2.08 (wet weight)	Langlois and Sloterdijk, 1989
	Burbot (liver)	1.39 (wet weight)	Langlois and Sloterdijk, 1989
Lake Erie	Walleye	0.35 (wet weight)	Government of Canada, 1991
	American smelt	0.2 (wet weight)	Government of Canada, 1991
Lake Superior	Various species	0.25 - 0.35 (wet weight)	Government of Canada, 1991
Lake Ontario	Lake trout	0.5 - 0.65 (wet weight)	Government of Canada, 1991
Greenland (ocean)	<i>Gadus ogac</i>	23.9 - 152 (dry weight)	Bohn, 1975
	<i>Anarhichas minor</i>	17.1 - 195 (dry weight)	Bohn, 1975
Greenland	<i>Hippoglossoides platessoides</i>	17 - 290 (dry weight)	Bohn, 1975

Location	Species	Concentrations ($\mu\text{g/g}$)	Reference
Australia (ocean)	Yellowfin bream	0.1 - 2.4 (wet weight)	Bebbington et al., 1977
	Sea mullet	0.1 - 3.8 (wet weight)	Bebbington et al., 1977
	Snapper	0.4 - 4.4 (wet weight)	Bebbington et al., 1977
	Australian salmon	0.1 - 0.5 (wet weight)	Bebbington et al., 1977
France (ocean)	<i>Dicentrarchus labrax</i>	3.1 - 12.3 (dry weight)	Michel, 1993
	<i>Conger conger</i>	58.4 - 210 (dry weight)	Michel, 1993
	<i>Scomber scombrus</i>	2.1 - 27.1 (dry weight)	Michel, 1993
	<i>Scyliorhinus canicula</i>	39 - 609.5 (dry weight)	Michel, 1993

In fish, arsenic mainly takes the form of arsenobetaine. This non-toxic compound accounts for about 95% of total arsenic in fish (Beauchemin et al., 1988; Shibata and Morita, 1989; Larsen et al., 1993; Michel, 1993). Arsenobetaine is synthesized by means of another organic complex, arsenocholine (Norin et al., 1983; Andreae, 1986). But the presence of arsenocholine in fish and other aquatic organisms is the subject of some dispute (Norin et al., 1983; Lawrence et al., 1986; Le et al., 1994a). Organic arsenic compounds are metabolized and excreted very quickly by fish. The accumulation of arsenic in fish is likely a function of biological rhythms and local and seasonal variations in diet (Michel, 1993). This would explain the major variations observed in different studies.

Toxic effects have been detected in juvenile salmon exposed to arsenic concentrations of 300 $\mu\text{g/L}$ (Nichols et al., 1984). In general, the chronic toxicity level of arsenic is about 1 mg/L and acute toxicity on the order of 10 to 15 mg/L (CCREM, 1987).

2.3.3 Recommendations relative to arsenic concentrations in water (Quebec and Canada)

The recommendations made by Quebec and Canada with regard to toxicity levels are shown in Table 6.

Table 6
Recommendations relative to arsenic concentrations in water
(Quebec and Canada)

Toxicity level	Parameter	Recommendation	Reference
Raw water - Human consumption (Quebec)	Total As	2.2 ng/L	MENVIQ, 1990
Aquatic life forms - Acute toxicity (Quebec)	As (III)	360 µg/L	MENVIQ, 1990
	As (V)	850 µg/L	MENVIQ, 1990
Aquatic life forms - Chronic toxicity (Quebec)	Total As	50 µg/L	MENVIQ, 1990
Protection of aquatic life forms (Canada)	Total As	50 µg/L	CCREM, 1987

Recommendations vary considerably, depending upon water use. The criterion for raw water is very low, since it takes into consideration the consumption of both water and aquatic organisms. Given the high natural concentration (1 to 40 µg/L; Michel, 1993), this criterion does not seem very attainable. Criteria for acute toxicity are much higher than those for chronic toxicity and correspond to toxic effect levels in fish. The recommendation of 50 µg/L for chronic toxicity is essentially based on fish toxicity data. However, according to toxicity studies, it would appear some algae would not be protected if they were exposed to this concentration on a continual basis (CCREM, 1987). At present, there is no recommendation with regard to arsenic concentrations in fish intended for consumption.

3 Arsenic in the St. Lawrence Ecosystem (Cornwall-Quebec City Section)

3.1 ARSENIC IN WATER

Few studies have been carried out on arsenic concentrations in the water of the St. Lawrence River, and the Ottawa River is the only one of its tributaries to have been studied. Most available data comes from Environment Canada's National Water Quality Data Base. So far, concentrations have been measured only in the total phase in the freshwater section of the St. Lawrence (Table 7). In the Cornwall-Quebec City stretch (data from 1985 to 1990), arsenic concentrations vary from 0.2 to 2.5 µg/L (Rondeau, 1993) (Table 7). There is little spatial variability. Mean concentrations, however, are higher in the green waters of the Great Lakes (0.7 µg/L in Lake Saint-Francois and 0.6 µg/L in the Montreal region) than in the brown waters of the Ottawa River (0.4 µg/L). The median for all data is 0.6 µg/L (Rondeau, 1993), which is equal to the average obtained by Neilson (1983) in the Great Lakes. As concentrations vary little spatially and as they are similar to those in the Great Lakes, Rondeau (1993) concluded that arsenic concentrations in St. Lawrence waters corresponded to geochemical background rather than to direct or indirect anthropic sources. However, green water which has passed through the area of the Port of Montreal has much higher arsenic levels (2.5 µg/L).

Table 7
Arsenic concentrations in the water of the St. Lawrence River
(total phase)

Sampling site	n	Range of concentrations (µg/L)	Mean (µg/L)
Great Lakes (Lake Saint-Francois)	65	0.3 - 1.1	0.7
Ottawa River	74	0.2 - 1.0	0.4
Green water (Montreal region)	193	0.2 - 2.5	0.6
L'Assomption River	40	0.3 - 1.8	0.5
South shore (Lake Saint-Pierre)	10	0.4 - 0.8	0.6
Mixed water (Quebec City)	43	0.3 - 0.8	0.6

Source: Rondeau, 1993.

Sampling carried out at 26 stations in Lake Saint-Pierre between May 1986 and February 1987 (Langlois and Sloterdijk, 1989) showed that arsenic concentrations varied from 0.2 to 0.9 $\mu\text{g/L}$, with a mean value of 0.5 $\mu\text{g/L}$. These values are equivalent to those reported by Rondeau (1993) and to those obtained for Lake Ontario (Neilson, 1983).

The above data refer to concentrations in the total phase (non-filtered water). None of the studies deal with concentrations in the dissolved and particulate phases. Recent data for the Great Lakes indicate total phase concentrations of 0.25 to 0.98 $\mu\text{g/L}$ for total As, with 80 to 100% of the arsenic being in dissolved form (Government of Canada, 1991). In a study on the St. Lawrence Estuary and the Saguenay Fjord, Tremblay and Gobeil (1990) found that total dissolved arsenic concentrations varied from about 0.5 $\mu\text{g/L}$ (at Quebec City) to 1.4 $\mu\text{g/L}$ in the estuary. Consequently, a large part of the arsenic in the St Lawrence River would be transported in the dissolved phase.

3.2 ARSENIC IN SEDIMENT

The results of different studies on sediment (Table 8) showed that, in general, total arsenic concentrations vary from 0.3 to 11.1 $\mu\text{g/g}$ from Lake Saint-Francois to Lake Saint-Pierre, with a mean of roughly 3 $\mu\text{g/g}$. These values are similar to those obtained for the Great Lakes, where total arsenic concentrations vary from 2 to 11 $\mu\text{g/g}$. They are also close to the geochemical norm, which is 8 $\mu\text{g/g}$ for this type of sediment. However, concentrations are higher in the Lesser La Prairie Basin, where they vary from 4 to 27.2 $\mu\text{g/g}$, with a mean of 9.8 $\mu\text{g/g}$. In this basin, the distribution of arsenic concentrations is uniform, with the exception of one station, where the concentration is 27.2 $\mu\text{g/g}$. Since there is no other known source of arsenic in the area, it would appear to be the result of the Candiac municipal sewer outfall (Hardy et al., 1991). In Lake Saint-Louis, higher concentrations were also found in the northern part of the lake, near Valois Bay (Champoux and Sloterdijk, 1988). These authors found no known source of arsenic in this area.

Table 8
Arsenic concentrations in surface sediment

Location	Range of concentrations (µg/g)	Mean (µg/g)	Reference
Lake Saint-Francois	0.5 - 8.7	3.7	Lorrain and Jarry, 1994
Beauharnois Canal/Lake Saint-Louis	0.4 - 6.9	-	Deschamps, 1979
Lake Saint-Louis	<0.2 - 32.7	4.9	Champoux and Sloterdijk, 1988
Beauharnois Canal	3.8 - 5.8	-	Champoux and Sloterdijk, 1988
Lake des Deux Montagnes	1.5 - 11.1	-	Champoux and Sloterdijk, 1988
Lesser La Prairie Basin	4 - 27.2	9.8	Hardy et al., 1991
Lake Saint-Pierre	0.3 - 5.7	2.6	Langlois and Sloterdijk, 1989; Hardy et al., 1991
Great Lakes	2 - 11	-	Government of Canada, 1991

3.3 ARSENIC IN AQUATIC INVERTEBRATES

With regard to invertebrates, a study was carried out to determine arsenic concentrations in zooplankton and zoobenthos (Messier, 1981), and two additional studies were conducted on various species of mussel (Metcalf-Smith et al., 1995; de Lafontaine, 1995). The results of the first study are shown in Table 9 and compared to the values obtained in the Great Lakes and for marine invertebrates. The arsenic levels measured in St. Lawrence River zooplankton are similar to those observed in the Great Lakes and to levels in marine zooplankton. In general, there does not seem to be any variation in arsenic concentrations in zooplankton throughout the drainage basin. Concentrations observed in freshwater mussels are on the same order of magnitude as those obtained for zooplankton (Table 9), but clearly lower than those found in marine mussels (see Table 4).

Table 9
Total arsenic concentrations in invertebrates

Location	Species	Concentrations ($\mu\text{g/g}$)	Reference
St. Lawrence River	Zooplankton	0.3 - 8.6 (d. w.)	Messier, 1981
	Zoobenthos	0.04 - 1.26 (w. w.)	Messier, 1981
Lake Ontario	Zooplankton (<i>Mysis</i> sp.)	3 - 4 (d. w.)	Government of Canada, 1991
Lake Michigan	Zooplankton	4.1 - 7.9 (d. w.)	Seydel, 1972
Lake Superior	Zooplankton	1.2 - 4.4 (d. w.)	Seydel, 1972
Canadian Arctic (ocean)	Zooplankton	5.6 - 7.3 (d. w.)	Bohn and McElroy, 1976
Newfoundland (ocean)	Zooplankton	0.9 - 1.7 (d. w.)	Kennedy, 1976
St. Lawrence River	<i>Elliptio complanata</i>	3.43 (d. w.)	Metcalf-Smith et al., 1995
	<i>Lampsilis radiata radiata</i>	5.43 (d. w.)	Metcalf-Smith et al., 1995
	<i>Elliptio complanata</i>	1.8 - 3.8 (d. w.)	de Lafontaine, 1995
	<i>Dreissena polymorpha</i>	1.9 - 4.1 (d. w.)	de Lafontaine, 1995

NOTE: (d. w.) = dry weight; (w. w.) = wet weight.

3.4 ARSENIC IN FISH

Historical data obtained by analysing 1600 fish caught at 17 sites between Cornwall and Quebec City in 1975 and 1976 revealed that total arsenic concentrations in the flesh of St. Lawrence River fish vary from 0.05 to 0.9 $\mu\text{g/g}$ (wet weight), with a mean of 0.2 $\mu\text{g/g}$ (Sloterdijk, 1977). Arsenic concentrations are higher at stations downriver of Trois-Rivières and fish caught at Quebec City were the most contaminated. Blais-Ladouceur (1979) noted that arsenic concentrations in the flesh of fish in the Beauharnois Canal and Lake Saint-Louis varied from 0.04 to 0.14 $\mu\text{g/g}$ (wet weight) in Yellow perch and from 0.06 to 0.2 $\mu\text{g/g}$ (wet weight) in Pumpkinseed and Rock bass. In Lake Saint-Pierre, concentrations in fish varied from “undetected” to 0.34 $\mu\text{g/g}$ (wet weight), with a mean of 0.14 $\mu\text{g/g}$; concentrations in juvenile fish vary from “undetected” to 0.53 $\mu\text{g/g}$ (wet weight), with a mean of 0.1 $\mu\text{g/g}$ (Langlois and Sloterdijk, 1989). Arsenic concentrations are especially variable in fish tissue. For example, in Burbot (*Lota lota*), mean concentrations are 2.1 $\mu\text{g/g}$ (wet weight) in flesh, 1.5 $\mu\text{g/g}$ (wet weight) in gonads, 0.7 $\mu\text{g/g}$ (wet weight) in eggs, and 1.4 $\mu\text{g/g}$ (wet weight) in liver (Langlois and Sloterdijk, 1989). In the Atlantic tomcod (*Microgadus tomcod*), de Lafontaine et al. (1994) obtained mean concentrations of 1.5 $\mu\text{g/g}$ (wet weight) in carcasses, 10 $\mu\text{g/g}$ (wet weight) in

liver and 0.5 $\mu\text{g/g}$ (wet weight) in gonads. Because the species is anadromous, these high values could be associated with the estuarine habitat used by tomcod.

In general, the total arsenic concentrations measured in fish from the St. Lawrence River are equivalent to those found in the Great Lakes (Sloterdijk, 1976). They are, however, much lower than those found in ocean fish, which can be as high as 50 $\mu\text{g/g}$ (wet weight) (Ferguson and Gavis, 1972; Bohn, 1975; Bohn and McElroy, 1976; Michel, 1993).

3.5 SUMMARY OF AVAILABLE DATA ON ARSENIC IN THE ST. LAWRENCE

Data currently available on arsenic in the various compartments of the St. Lawrence ecosystem are summarized in Table 10. This table points up our many knowledge gaps. There is no data available on the dissolved and particulate phases of arsenic in water, with the exception of concentrations in the dissolved phase obtained by Tremblay and Gobeil (1990), and there is no data on the tributaries. No studies have been carried out on algae. With regard to aquatic invertebrates, only zooplankton and zoobenthos have been studied. Information on mussels and crustaceans would be desirable. Lastly, no data is available on the speciation of arsenic in the various compartments, despite the fact that the toxicity of arsenic is very dependent upon its chemical form.

Table 10
Data available on arsenic in the St. Lawrence River

Compartment	Data available
Water	Total arsenic in the total phase and for the St. Lawrence only
Sediment	Total arsenic throughout the St. Lawrence
Algae	No data
Aquatic invertebrates	Total arsenic in zooplankton and zoobenthos in part of the St. Lawrence
Fish	Total arsenic in whole fish and fish organs throughout the St. Lawrence

4 Analysis Methods

Various methods are described in the literature for analysing total arsenic content and concentrations of the various chemical species in the matrices studied. This chapter covers only the methods currently in use; they are recapitulated in Table 11.

4.1 ANALYSIS OF ARSENIC IN WATER (DISSOLVED PHASE)

The analytical technique most commonly used to determine total arsenic in the dissolved phase is hydride generation combined with atomic absorption spectroscopy (Tremblay and Gobeil, 1990; Seyler and Martin, 1990). The main method is based primarily on reducing pentavalent arsenic to trivalent arsenic with NaBH_4 , and transforming As(III), methylarsonic acid and dimethylarsinic acid into their respective hydrides using NaBH_4 . The hydrides so formed are volatile and may be degassed by bubbling helium through the solution. The components are fed by the helium to the atomic absorption spectrophotometer, where they are analysed. This technique has the advantage of being simple and quite sensitive. It attains detection limits on the order of $0.075 \mu\text{g/L}$ for a 40-mL sample (Tremblay and Gobeil, 1990) and is currently available at the St. Lawrence Centre. Total arsenic can also be determined directly by ICP-AES or ICP-MS.

The method most commonly used for speciation studies is that described by Braman et al. (1977). It is based on the above-described method: the formation of hydrides using NaBH_4 and analysis through atomic absorption, plus separating hydrides by cryogenic trapping. A U-shaped glass tube, half-filled with glass beads, is installed between the reactor and the spectrophotometer. During the formation of hydrides, the tube is plunged into liquid nitrogen to trap all the compounds formed before they reach the atomic absorption spectrophotometer. Separation is carried out by the successive volatilization of the various compounds, which have different volatilization temperatures. Volatilization is carried out slowly, either by leaving the tube at room temperature or by heating it with a heating wire. The detection limits provided by Braman et al. (1977) vary from 0.004 to $0.02 \mu\text{g/L}$, depending on the compounds and for a

Table 11
Methods for analysing arsenic in various matrices and detection limits

Matrix	Chemical species	Method	Detection limits	Reference
Water: dissolved phase	Total As	Hydride generation/ atomic absorption	0.075 µg/L for a 40-mL sample	Tremblay and Gobeil, 1990
Water: dissolved phase	As(III), As(V), MMA, DMA	Hydride generation / chromatography/ atomic absorption	0.004 - 0.02 mg/L for a 50-mL sample	Braman et al., 1977
Sediment/ particulate phase	Total As	Digestion/graphite furnace/ atomic absorption	0.05 mg/g	Reimer and Thompson, 1988
Biota	Total As	Digestion with magnesium nitrate/ graphite furnace/atomic absorption	5 ng	Maeda et al., 1993
Biota	Various species	Extraction/HPLC/ICP-MS	0.3 ng for arsenobetaine	Beauchemin et al., 1988

50-mL sample. However, this technique has the inconvenience of not separating the two inorganic species As(III) and As(V). This problem can be solved by controlling the pH at the hydride formation stage (Braman et al., 1977; Andreae, 1977; Andreae and Andreae, 1989). The initial pH is adjusted to 6, using a buffer solution, which permits the degassing of As(III). The pH is then adjusted to 1, using HCl 6N to allow for the degassing of other arsenites (Andreae, 1977).

The sensitivity of these two methods may be increased by using an atomic fluorescence detector (Cossa, 1995). The British manufacturer PS Analytical provides an atomic fluorescence spectrophotometer with a detection limit of 0.02 µg/L, while atomic absorption has a detection limit of 0.075 µg/L for a 40-mL sample (Tremblay and Gobeil, 1990).

4.2 ANALYSIS OF ARSENIC IN SEDIMENT AND IN THE PARTICULATE PHASE

In sediment and suspended particles, only total arsenic is analysed. With this method, the sediment or particles are digested on filters, and a graphite furnace atomic absorption assay of arsenic concentrations is then carried out (Reimer and Thompson, 1988; Belzile, 1988). This technique is now available at the St. Lawrence Centre and has a detection limit of 0.05 µg/g.

4.3 ANALYSIS OF ARSENIC IN BIOTA

The most frequently used technique for determining total arsenic in algae, seafood and fish involves digesting the sample and conducting an atomic absorption assay using either hydride generation or a graphite furnace (Siu et al., 1984; Blevins and Pancorbo, 1986; Petersen and Krog Mortensen, 1994; Environment Canada, 1994). This technique is currently available at the St. Lawrence Centre. The difficulty with this method lies in obtaining total digestion of the sample. Organic arsenic compounds such as arsenobetaine are very difficult to digest and do not form hydrides with NaBH₄ in hydride generation analysis. In graphite furnace analysis, the sulphuric acid contained in the digested matter attacks the graphite and very quickly damages the furnace. To overcome these problems, some authors advise that the samples be mineralized in a

muffle furnace in the presence of magnesium nitrate prior to digestion (Siu et al., 1984; Lopez et al., 1993; Maeda et al., 1993).

The determination of the various chemical species of arsenic may be carried out using a variety of methods. The latest technique is HPLC combined with ICP-MS (Beauchemin et al., 1988; Shibata and Morita, 1989; Larsen et al., 1993; Le et al., 1994b). It allows for the analysis of all the chemical species present in the samples, including organic complexes. The samples are extracted using a mixture of solvents, generally methanol-water-chloroform. The extracts obtained contain a variety of arsenical compounds, which are then separated using HPLC and detected by ICP-MS. The use of various types of HPLC columns (C-18, ion exchange, cation exchange) allows for different separations of the compounds being examined. This technique, however, is quite costly, since it requires ICP-MS, but it has the advantage of determining both the inorganic and organic arsenic present in the samples. It is not available at the St. Lawrence Centre, but is being developed by the Chemistry Department of the University of Montreal, in the laboratory of Professor Joseph Hubert.

5 Conclusion

Arsenic is a very common element of the Earth's crust and it is present in various environmental compartments. Its cycle in the aquatic environment appears very complex and brings many intermediary molecules into play. While the studies currently available deal mainly with the marine environment, the cycle of arsenic in marine organisms remains in many ways unknown. We do not know the precursor of arsenobetaine in marine invertebrates and fish, and the presence or non-presence of arsenocholine in these organisms is still highly controversial. However, few studies have been carried out on arsenic in fresh water. In the case of the St. Lawrence River (Cornwall-Quebec City sector), only concentrations in the total phase have been studied, and nothing is known regarding concentrations in the dissolved and particulate phases. A study by Tremblay and Gobeil (1990), however, sets the concentration in the dissolved phase at Quebec City at 0.5 µg/L. Some work has been done on aquatic invertebrates and fish, but most of it dates back to the 1980s. Few recent results are available on organisms in the St. Lawrence. Moreover, there is no data concerning the link between arsenic and primary producers in the River. Lastly, no speciation study has so far been done on water or organisms in the St. Lawrence River. The Government of Canada (1993) estimates that inorganic arsenic compounds form a highly toxic group of substances which constitute a health risk, whatever the degree of exposure. In light of these considerations, more information on the behaviour and fate of arsenic in the St. Lawrence River would be desirable.

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