FACT SHEET ON THE STATE OF

THE MARINE ENVIRONMENT OF THE ST. LAWRENCE

MAURICE LAMONTAGNE INSTITUTE • MARINE SCIENCES RESEARCH CENTRE

PAHs IN THE SAGUENAY FJORD

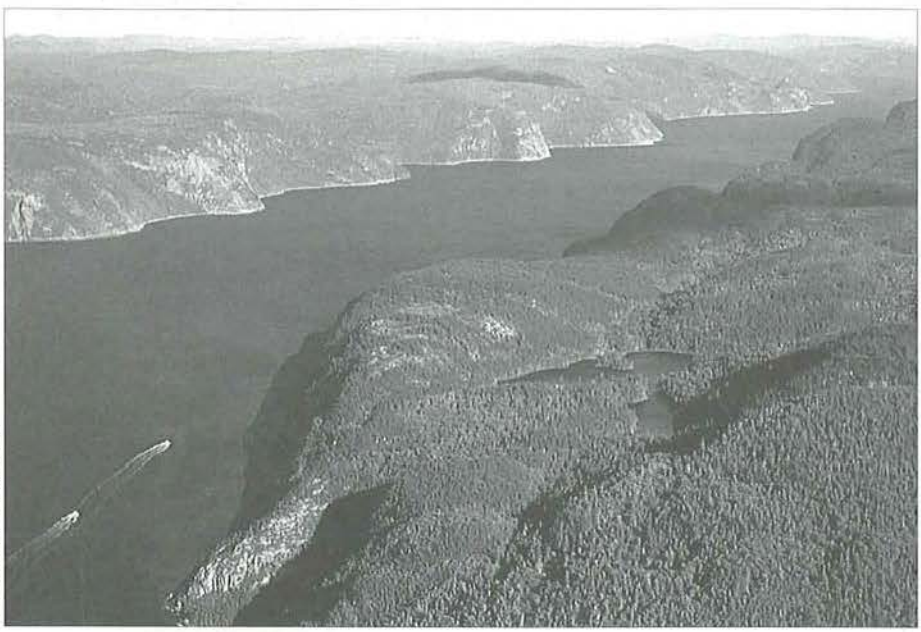

Photo : J. Beardsell /Parks Canada

The Saguenay Fjord, the main tributary of the Lower St. Lawrence Estuary, is an area of environmental concern, particularly because of its contamination by polycyclic aromatic hydrocarbons, better known as PAHs. The concern regarding PAHs is mainly related to the fact that some of them are carcinogenic. However, following the establishment of clean-up measures and changes in industrial processes, PAH concentrations in the environment of the Saguenay Fjord have decreased considerably in recent years.

DESCRIPTION AND PROPERTIES OF PAHs

Polycyclic aromatic hydrocarbons (PAHs) are a family of chemical compounds made up of carbon and hydrogen atoms, with a molecular structure consisting of at least two fused aromatic rings, each with five or six carbon atoms. The PAH family includes about 100 substances, differing in the number and position of their rings. The *total PAH* designation is generally used to identify a group of 12 to 21 PAHs found in the environment. Thus, the number of PAH compounds measured in the environment varies between studies, and consequently, care must be taken in comparing results from different scientific studies. PAHs may be subdivided into two groups: low molecular weight PAHs, with less than four rings, and high molecular weight PAHs, with four or more rings. Low molecular weight PAHs are water soluble, with a low affinity for particle adsorption. PAHs with high molecular weights are generally not very water soluble, and have a strong affinity for adsorption onto particle surfaces which are suspended in air and water.

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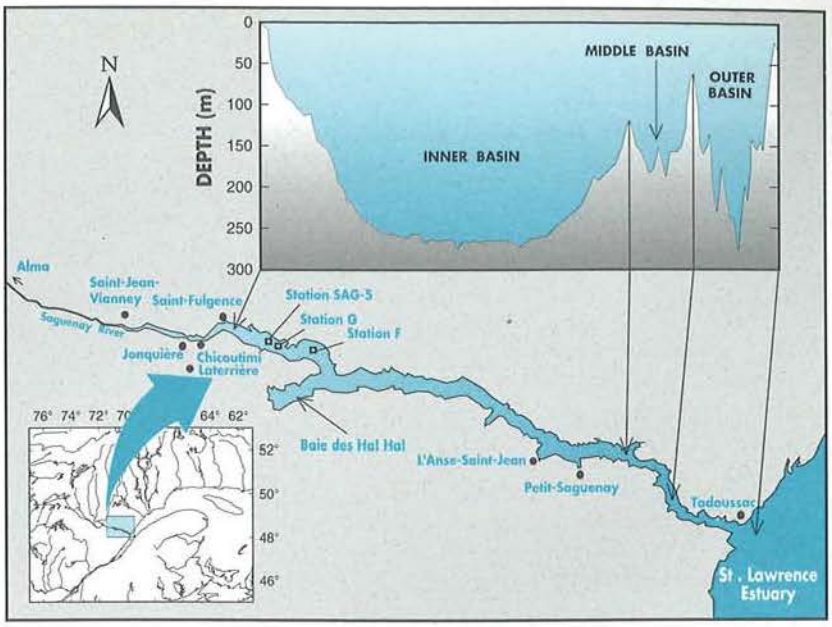
THE SAGUENAY FJORD

The Saguenay Fjord extends over nearly 100 kilometres between Saint-Fulgence and Tadoussac, and is located approximately 160 km northeast of Quebec City. It fills an ancient glacial valley and discharges into the Lower St. Lawrence Estuary. The upper part of the Fjord is "Y"-shaped, with the southern arm forming Baie des Ha! Ha! and the northern arm, the main branch of the Fjord, extending upstream to the end of the Saguenay River. Three sills, which form underwater mountains, delimit three deep basins. The Inner Basin, located furthest upstream, is 275 metres deep and covers three quarters of the Fjord's area. The Middle and Outer Basins have maximum depths of 180 and 275 metres respectively.



WHERE DO PAHs COME FROM?

PAHs are generally formed from the incomplete combustion of organic matter. They can be natural and are widespread in the environment; they are formed as a result of forest and grass fires and volcanic activity. PAHs are also naturally present in coal and petroleum products. Today, most of the PAHs present in the environment come from human activities. PAHs can enter the aquatic environment directly, through industrial and municipal effluents, accidental crude oil spills and PAH emissions from creosote treated materials used in water (for example, on pilings). Groundwater and runoff from urban and industrial areas can also be non-point sources of PAHs in the marine environment. Finally, nearly all types of organic fuel combustion can produce PAHs. The most important sources are the incomplete combustion of fossil fuels from domestic heating systems and transportation (car exhaust fumes), garbage incineration, alumina reduction smelting for aluminum production, catalytic cracking of crude oil and coal liquefaction and gasification. All these human activities release PAHs into the atmosphere, where they tend to adhere to particles in suspension, some of which will enter the aquatic environment through atmospheric fallout.

TABLE 1

Main sources of PAH in Quebec in1990.

Sources	PAH	
	QUANTITY (tonnes)	PROPORTION (%)
Aluminum smelters	858	71
Residential wood heating	162	14
Forest fires	148	12
Transportation (diesel and gasoline)	33	3
Total	1201	100

Source: Germain *et al.*, 1994.

THE SITUATION IN QUEBEC AND IN THE SAGUENAY AREA

In Quebec in 1990, an inventory of PAH sources (see Table 1) showed that primary aluminum production ranked first among the sectors of activity in terms of PAH emissions released annually into the atmosphere (71 %). The highest PAH concentrations in the air were measured at Jonquière (0.457 µg of PAH/m³), where one smelter using Söderberg cells for the electrolysis of alumina is still in operation. The horizontal-stub Söderberg process generates 2.05 kg of PAH per tonne of aluminum produced, while the new prebaked-anode process generates only 0.0013 kg of PAH per tonne of aluminum.

HISTORY OF PAH CONTAMINATION IN THE FJORD

Due to high sedimentation in the northern arm of the Saguenay Fjord and high inputs of organic matter from pulp and paper mills and sawmills, a relatively accurate chronology of PAH inputs has been determined from sediment cores collected in this area. PAH concentrations in Saguenay Fjord sediments illustrate the main events in the aluminum industry development in the Chicoutimi region. PAH concentrations in pre-industrial layers are generally below 0.5 µg/g (see Figure 1, Station F). During the 1930s, PAH concentrations in the Fjord's sediments double, probably as a result of the Jonquière aluminum smelter opening in 1926. Later, in response to the growing demand for aluminum, the Jonquière plant expands and converts to the Söderberg process, while a new plant, also using the Söderberg process, is built in Alma. To limit air pollution, air filtration systems are installed in the pot rooms. Between 1956 and 1976, liquid effluents from these systems, containing substantial amounts of PAH, are discharged directly into the Saguenay River, resulting in a major increase of PAH inputs in the Saguenay Fjord sediments. PAHs in sediments of the Saguenay Fjord's northern arm reached concentrations of more than 16 µg/g during the 1960s (see Figure 1, Station G) and more than 20 µg/g in the mid-1970s (see Figure 1, Station SAG-5). Low concentrations measured in the early 1970s, at Stations G and SAG-5, reflect a dilution caused by the input of uncontaminated sediments from the Saint-Jean-Vianney landslide in 1971.

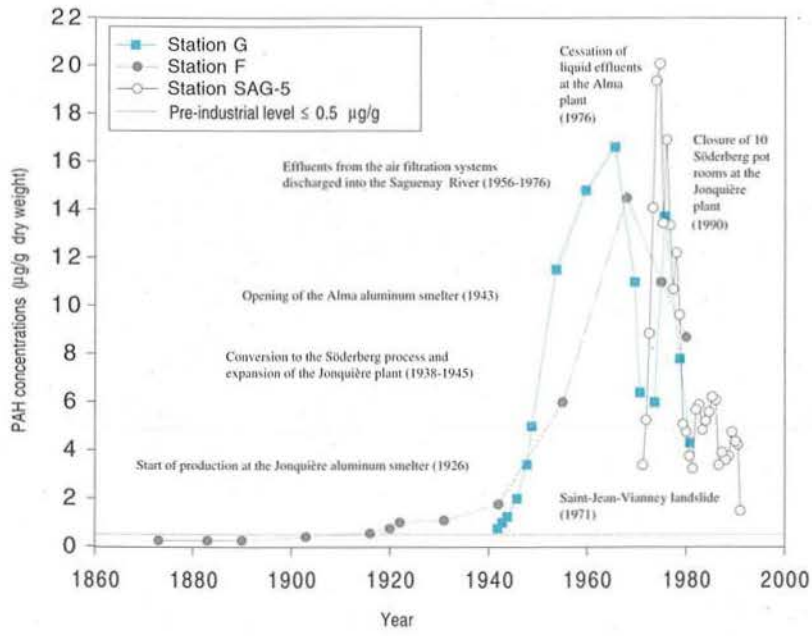


Figure 1 Temporal variations of PAH concentrations in sediments of the northern arm of the Saguenay Fjord. The location of the samples are indicated on the map of the Saguenay Fjord.

Sources: Stations F et G: Martel *et al.*, 1987. Station SAG-5: unpublished data 1992, É. Pelletier, INRS-Océanologie, Rimouski. The years were estimated by using the sedimentation rate.

From this point, the situation greatly improves. Between 1976 and 1981, PAH concentrations in Fjord sediments declined by about 70 % when the Alma smelter, among others, stopped discharging liquid effluents into the Fjord in 1976. In 1990, 10 Söderberg pot rooms were closed at the Jonquière plant and were replaced by prebaked-anode cells. The latter eliminated the generation of PAH at the source (no PAH liquid effluent) and were installed in a new and more modern smelter at Laterrière. In addition, liquid effluents with a high PAH content were virtually eliminated in all smelters and PAH emissions have continuously declined since 1976. More recently, analysis of a sediment core collected in 1992 showed PAH surficial sediment concentration to have fallen to the 1940 level (see Figure 1, Station SAG-5).

EXTENT OF CONTAMINATION IN THE FJORD

A study of the PAH spatial distribution in the Saguenay Fjord's surface sediments was conducted in 1983. Since several PAHs adhere to particles, the sedimentation rate of the suspended material in the water column is used to explain the variations in PAH concentrations observed in the Fjord's surface sediments. In the Saguenay River, where sedimentation is low, concentrations are weak, with the exception of samples taken near smelters. In the upper part of the Inner Basin, sedimentation rates are high (approximately 7 cm per year), and PAH concentrations in surface sediments of this sector are the highest in the Fjord (see Figure 2). PAH concentrations gradually decline as we move toward the St. Lawrence Estuary. Near the Estuary, where the Fjord becomes less deep, currents are stronger and the sediment particle size is larger, the concentrations are the lowest. Nevertheless, higher concentrations were measured in the Saguenay Fjord as far as 60 km downstream of Chicoutimi. It should be noted that the slight reduction observed at the head of the Fjord (between stations 18 and 10) can be explained by a dilution of PAHs caused by the large inputs of particulate matter from Baie des Ha! Ha!, the location of a pulp and paper plant. Finally, these results clearly show that the main sources of PAHs are confined to the upper part of the Fjord. Today, if the same study was repeated, it is very likely that the same pattern would be repeated, but with lower concentrations. Moreover, following the considerable input of new sediments during the major floods in July 1996, PAH levels in affected areas in the upstream part of the Fjord may have dropped in surface sediments.

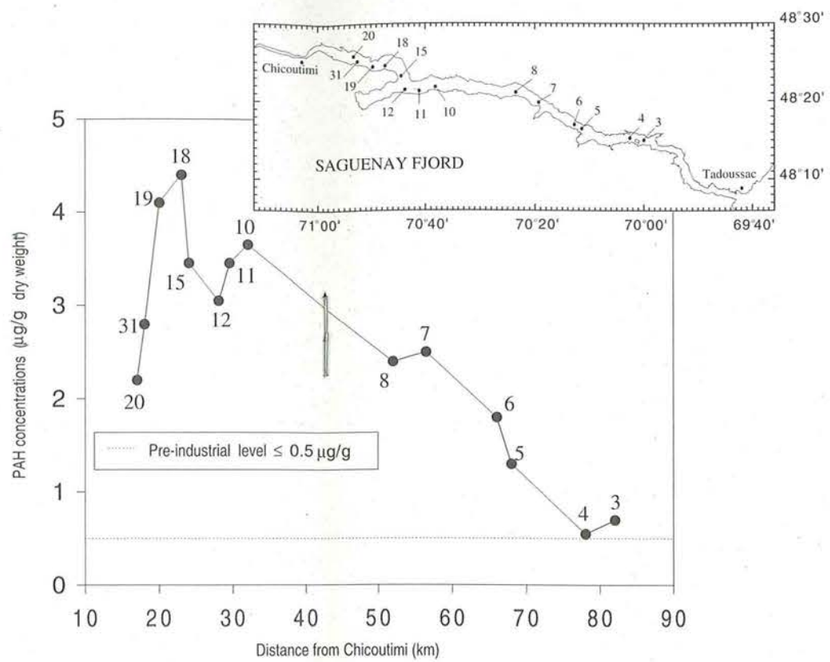


Figure 2

Spatial distribution of PAH concentrations (sum of 21 compounds) in surface sediments of the Saguenay Fjord in 1983. Numbers on the line correspond to sampling stations indicated on the map.

Source: Martel *et al.*, 1986.

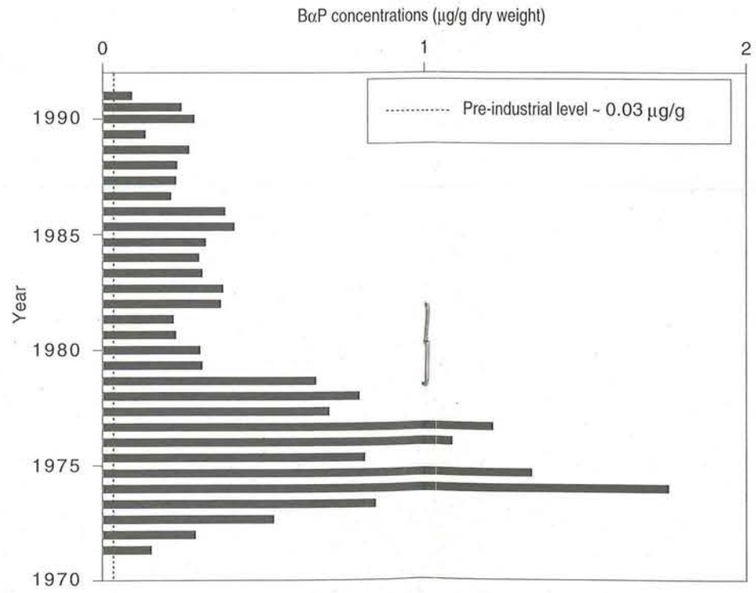


Figure 3

BαP concentrations measured in a sediment core collected at station SAG-5 in 1992.

Source: Unpublished data 1992, É. Pelletier, INRS-Océanologie, Rimouski. The years were estimated by using the sedimentation rate. Pre-industrial level: Martel *et al.*, 1987.

THE MOST WORRISOME PAH: BENZO[α]PYRENE

Benzo[α]pyrene (BαP), a 5-cycle PAH with known carcinogenic properties, accounts for 3 % of PAHs emitted by smelters. Because of its toxicity and that of its metabolites, BαP is the PAH which causes the most environmental concern and has therefore received a great deal of attention from scientists. Given its low water solubility and strong affinity for adsorption onto particle surfaces, concentrations of BαP in water solutions are relatively low (less than 0.008 µg/L). In order to assess the Fjord's sediment quality, we can compare BαP concentrations measured in a sediment core collected in 1992 with the BαP concentration measured in deep sediment layers deposited before the industrial era (see Figure 3). Results indicate that BαP concentrations in sediments from the north arm of the Saguenay Fjord, particularly during the 1970s, were considerably higher than the pre-industrial level. However, concentrations in recent sediments had decreased by a factor of 18 in comparaison with the observed maximum and were approximately 0,09 µg/g before the July 1996 floods.

Recently, researchers have developed a mathematical model to predict quantities, concentrations, as well as transportation and transformation rates of BαP in water and sediments of the Saguenay Fjord. The model's results indicate that only 40 % of the total BαP in the northern arm of the Fjord is associated with the sediments, while the rest (60 %) is found in the water column, associated with suspended particles or in a dissolved form. However, despite a higher contaminant load, concentrations of BαP are lower in the water column than in the sediments because of a higher dilution factor in the water column. Approximately 43 % of BαP inputs to the Fjord are predicted to remain there, while the majority (57 %) would be transported by currents to the St. Lawrence Estuary, this would make Saguenay Fjord a source of BαP for the Estuary.

IS BαP FOUND IN MARINE ORGANISMS?

The blue mussel (*Mytilus edulis*), often used as an indicator of contamination levels in the marine environment, lends itself very well to a study of BαP levels in a coastal environment because, like other marine invertebrates (shrimp, clams, polychaete worms, etc.), it accumulates this contaminant. Indeed, the absence of mixed-function oxidases (MFOs) enzyme systems prevents marine invertebrates from effectively metabolizing and eliminating PAHs, which explains why these compounds tend to accumulate in their tissues. Scientists measured BαP concentrations in blue mussels in the St. Lawrence Estuary and Gulf between 1977 and 1979. Analyses carried out at 27 sampling stations showed that only mussel samples from the two stations located on either side of the mouth of the Saguenay had high BαP levels–29 and 24 µg/kg (dry weight).

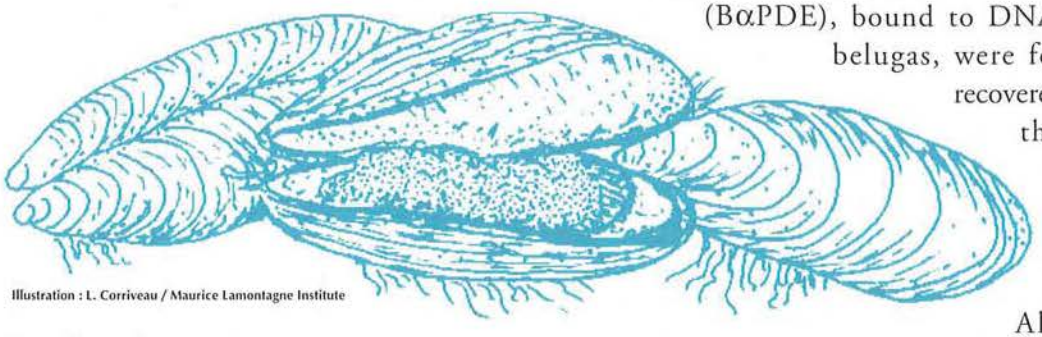


Illustration : L. Corriveau / Maurice Lamontagne Institute

For the other stations,
PAH concentrations were below detection levels of the analytical method (0.15 µg/kg) and seem to reflect natural levels. Researchers wondered if this contamination was related to discharges from the aluminum smelters located in the Chicoutimi area.

Since natural populations of mussels are very limited in the Fjord, researchers collected mussels with a PAH content of less than 0.15 µg/kg from the Gulf of St. Lawrence and transplanted them to various locations in the Saguenay Fjord. After a month, the transplanted mussels in the Fjord had average BαP concentrations of more than 200 times the level measured prior to transplant.

This experiment showed that: 1) a BαP contamination from human sources spread to the entire Fjord; 2) this contaminant was bioavailable; and 3) it can be accumulated in some marine invertebrates. In addition, researchers were able to conclude that this pollution was related to the aluminum industry. However, in light of recent data for sediments, one can assume that BαP levels have also considerably declined in invertebrates.

Unlike invertebrates, vertebrates such as fish and mammals don't accumulate PAHs in their tissues. They have an enzyme system which enables them to eliminate PAHs or to metabolize them into a variety of water solvable metabolites, which can link to proteins or DNA (adducts) of living organisms. It is believed that some metabolites can interfere with biochemical processes of cells, which could lead to developmental abnormalities, or could cause cancers by altering genetic and cell division processes during DNA combination. Concentrations of adducts specific to BαP (BαPDE), bound to DNA in brain cells of belugas, were found in carcasses recovered on the shores of the St. Lawrence Estuary, which suggests that these individuals had ingested BαP. Although a high prevalence of malignant tumours observed in belugas, which could hinder the re-establishment of the beluga population, has been associated with these results, this hypothesis is highly controversial. In fact, the establishment of a causal link between a specific contaminant and beluga health is a difficult task. In addition, the malignant tumours were, in most cases, found in older belugas whose reproduction capacity was limited. Finally, recent data indicate that the population may even be increasing slightly.

WHAT IS THE PRESENT SITUATION?

In recent decades, the ecosystem of the Saguenay Fjord has been highly contaminated by PAHs, including one of the most toxic, BαP. Fjord sediments remain a reservoir of PAHs from human sources, with concentrations generally higher than those measured in sediments from the St. Lawrence Estuary and Gulf, where PAH concentrations are generally low (0.5-1 µg/g). On the other hand, changes in the industrial processes have resulted in significant decreases in PAH concentrations in the Saguenay Fjord sediments.

In addition, since 1993, the *St. Lawrence Vision 2000* action plan (SLV 2000) continues the efforts of the *St. Lawrence Action Plan* (SLAP) to further reduce atmospheric emissions and liquid toxic effluents discharged into the environment. Lastly, the effects of PAHs on the aquatic environment are not fully understood and should be given further attention.

MLI'S CONTRIBUTION TO PAH RESEARCH

Scientists of the Maurice Lamontagne Institute (MLI) from the Department of Fisheries and Oceans (DFO) are conducting several research projects on the quality of the marine environments of the Saguenay Fjord, the St. Lawrence Estuary and the Gulf of St. Lawrence, notably on the contamination by PAHs. The main projects through which PAHs are studied focus on: modelling of the transportation of residual PAHs found in the Saguenay Fjord, monitoring of contaminants in sediments and fish of the St. Lawrence Estuary and the Saguenay Fjord, fish contamination in the vicinity of industrial effluents, sediment quality and forecasting bioaccumulation of fish contaminants, effects of contaminants on fish health and reproduction, and monitoring of environmental quality by the development of marine microbiotests. These studies are conducted within the framework of *St. Lawrence Vision 2000* action plan and the *DFO Toxic Chemicals Program.*

GLOSSARY

Aromatic: term designating an organic compound which has physical and chemical properties resembling those of benzene.

Bioaccumulation: process whereby some aquatic organisms accumulate chemicals directly from ambiant water and sediments or through food containing chemicals.

Bioavailability: portion of a contaminant present in the environment that can be assimilated by a living organism.

DNA: material which determines heredity in all living organisms.

Metabolite: any organic substance which is formed during metabolic reactions in an organism.

Sediment core: column composed of many layers of sediment, the analysis of which shows the vertical, or chronological, breakdown of the physical and chemical characteristics of sediment (as example, the concentration of a contaminant).

µg/g: microgram (one millionth of a gram = 0.000001 grams) of a substance per gram of sediment or biological mass.

µg/m³: microgram (one millionth of a gram = 0.000001 grams) of a substance per meter cube of substance.

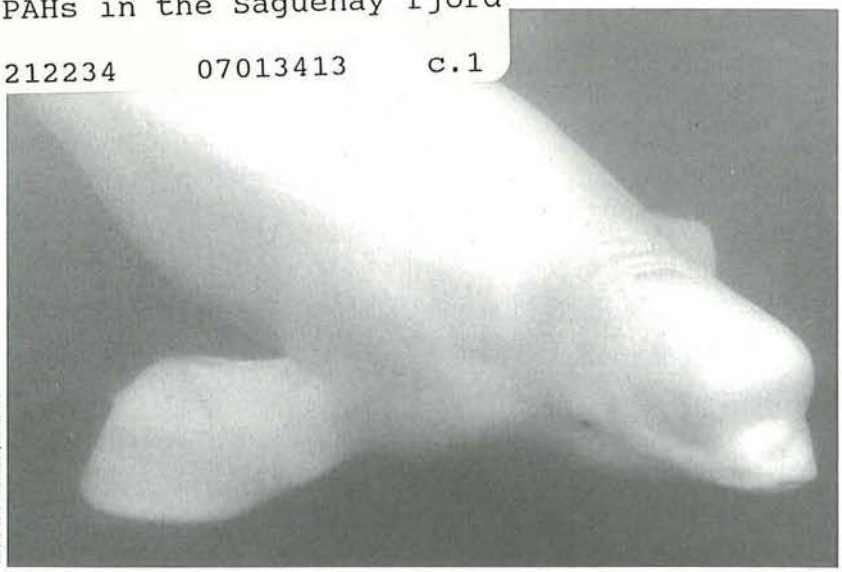


Photo : R. Michaud / GREMM

The beluga, *Delphinapterus leucas*

This fact sheet is intended to provide information and disseminate the results of scientific research on the state of the marine environment of the St. Lawrence. The fact sheets present specific environmental issues or the results of environmental research conducted by the MLI. They are intended for environmental managers and decision-makers, non-government organizations (NGOs), industry, the media and the general public. They are published on an ad hoc basis.

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FOR MORE INFORMATION...

For more information on PAH contamination in the Saguenay Fjord, please refer to the bibliography or contact the Communications Service of the Maurice Lamontagne Institute at (418) 775-0526.

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