Monitoring the State of the ST. LAWRENCE RIVER

Water quality of the fluvial sector

Transport of Contaminants in the St. Lawrence River

Background

The St. Lawrence River has been exposed for a long period of time to numerous sources of contamination originating from urbanization and from industrial and agricultural activities within its watershed. These inputs have contributed to the degradation of the water quality of the river, thereby putting the health of this unique ecosystem at risk. To monitor this issue, Environment Canada has set up reference stations in the fluvial sector that are used to assess the status of water contamination by recording seasonal and interannual fluctuations, and long-term trends in contaminant concentrations. Three sampling stations operated by Environment Canada were selected as representative of the main water masses of the St. Lawrence River by establishing a system with two inlets and one outlet (Figure 1). One station, located at Wolfe Island at the outlet of Lake Ontario, assesses the water quality at the outlet of Lake Ontario and estimates contaminant inputs from this lake to the St. Lawrence River. One station,

Quebec bridge © Thinkstock

sampled in 1995 and 1996 and in continuous operation since 2004, is located near the mouth of the Ottawa River at Carillon. It allows scientists to assess contaminant inputs of the largest tributary of the St. Lawrence River. The waters from this river are strongly coloured and cover a large portion of the north shore of the St. Lawrence River. These waters, referred to as brown waters, can be easily identified up to Trois-Rivières. The last station, in operation since 1995 in the Quebec City region, is used to assess contaminant inputs exported towards the St. Lawrence estuary. The water collected at this location integrates contamination from the various water masses that make up the St. Lawrence River upstream and that are mixed under the effect of tides.

The contaminants analyzed at these stations were selected from the lists of priority substances from Environment Canada, the U.S. Environmental Protection Agency and the International Joint Commission. Due to the strong affinity of many contaminants for suspended solids in water and their distinct behaviour in the dissolved and particulate phases at the time of their transport in the aquatic environment, these two phases were analyzed separately for many contaminants. The use of clean sampling methods and analysis techniques produced accurate results for substances occurring at the trace and ultra-trace levels. This sheet presents the results for the analysis of suspended solids, nutrients, metals, pesticides and PBDEs (polybrominated

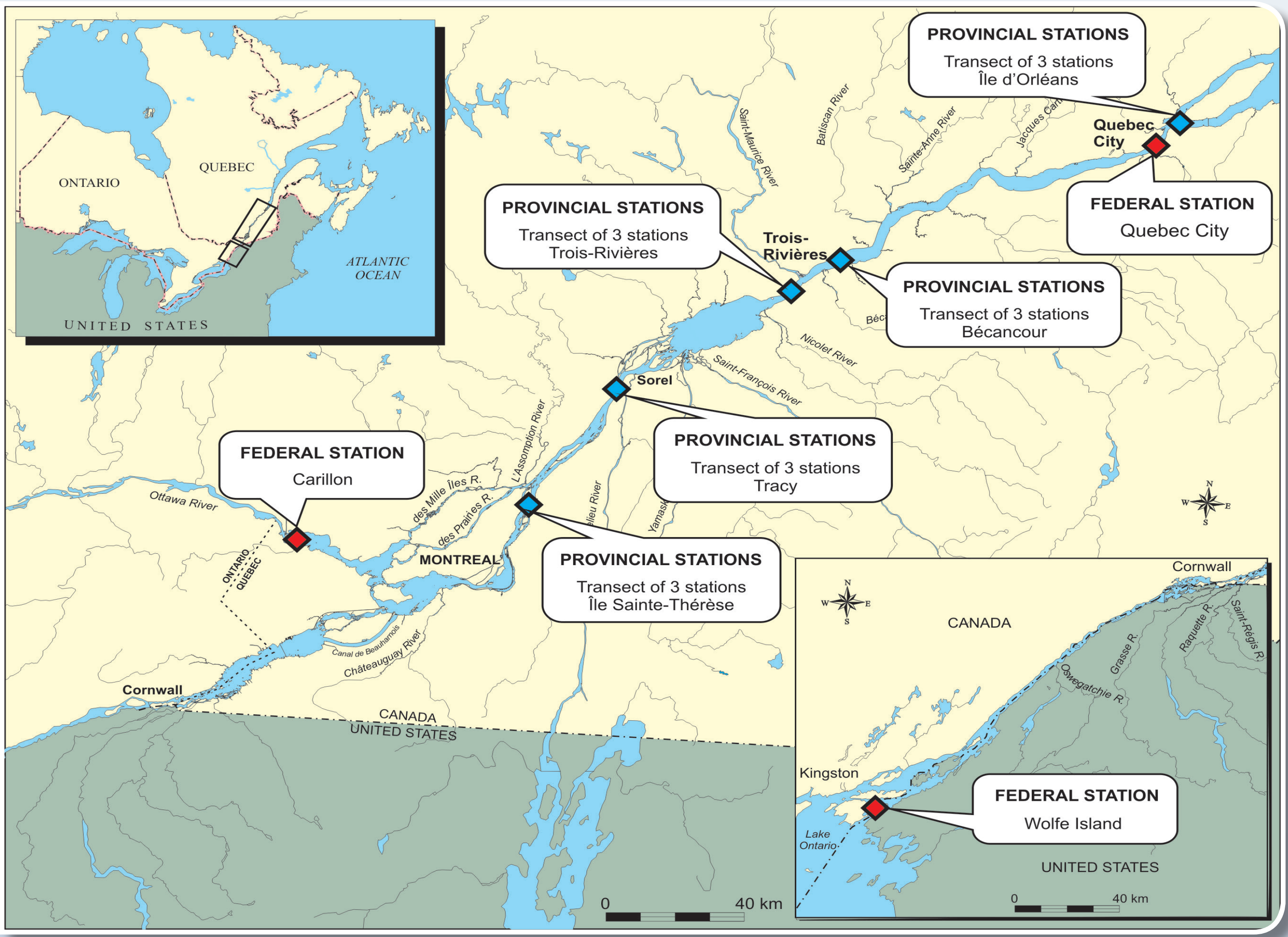

Figure 1. Location of sampling stations

diphenyl ethers) at the three federal stations. A spatial representation of the contamination of the river by metals, based on results from Quebec's Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques (MDDELCC) will also be presented (see metals).

Overview of the situation

The quantity of a contaminant released into an ecosystem directly affects the concentration of that contaminant in the aquatic environment. The origin of a contaminant also partly determines variations in its concentration in the aquatic environment. These variations are amplified or weakened by hydrological events such as dilution, sedimentation and flow of waters, which fluctuate with episodes of flood and low flow. On an overall annual basis, 60% of the flow of the St. Lawrence River at Quebec City originates from the Great Lakes, while 15% comes from the Ottawa River, the largest tributary of the St. Lawrence. By contrast, at certain times of year, such as the spring, the Ottawa River accounts for up to 50% of the water flowing at Quebec City. In order to account for these variations, the sampling frequency at the three stations was modulated based on the sites, flow rates and contaminants; it ranges from one sampling event every two days during the flood period to a monthly sampling event during the low flow period. In an attempt to determine the origin of St. Lawrence River contaminants, we have calculated contaminant loadings that correspond to the quantity of the contaminant transported during a given time period at the three stations (Wolfe Island, Carillon and Quebec City). This approach, called "mass balance," is a preferred tool for relating and comparing different sources of contaminants in the St. Lawrence River.

Suspended solids (SS): Although concentrations of SS are known to be relatively low in the St. Lawrence River compared with the other large rivers of the world, SS nonetheless play a very important role in the transportation of contaminants. There are numerous sources of SS. They can originate from shoreline erosion along streams or from farmland but can also come from urban and industrial effluents. Annual loadings of SS calculated at the two inlet stations of the St. Lawrence River (Wolfe Island and Carillon) account for less than 10% of the loadings at the outlet of the river (Figure 2). Only 2% of SS loadings at Quebec City originate from Lake Ontario because the lake acts as a large settling basin. A previous study demonstrated that the main source of SS to the St. Lawrence River (60%) was erosion of the shoreline and riverbed (Rondeau et al. 2000). Although no increasing or decreasing trend in loadings was observed between 1995 and 2009 at the Quebec City station, there was an observable strong interannual variability related to the water levels of the St. Lawrence River. During years of low hydraulicity (1999 and 2001), the St. Lawrence River exported only 4 million tons of sediment towards its estuary, while it transported almost double this amount in 1996 and 1997.

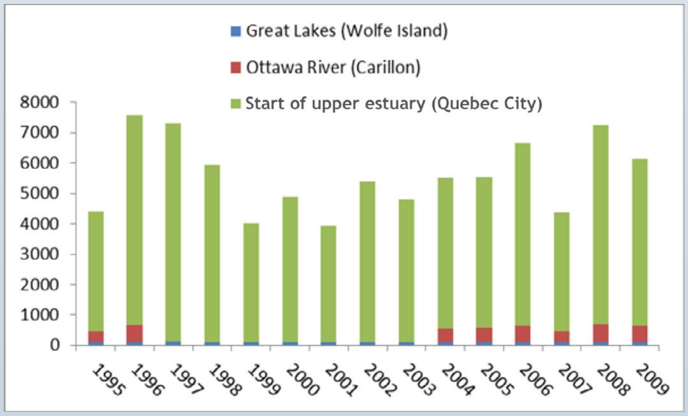

Figure 2. Quantity of suspended solids at the three main stations (thousand tons/year)

Nutrients: The occurrence of excess nutrients in the waters of the St. Lawrence River can cause some eutrophication problems and potentially result in hypoxia issues in the estuary. As is the case for ss, there are many sources of nutrients to the St. Lawrence River, but the anthropogenic portion originates in large part from agricultural and urban activities. Calculated loadings for nitrates and nitrites at the three stations (Figure 3) display a very different pattern from that of SS. Inputs originating from Lake Ontario account for up to 60% of the loadings estimated at the mouth of the St. Lawrence River (Quebec City), which corresponds to the same proportion as the water discharged from the lake. Nitrates and nitrites are not associated

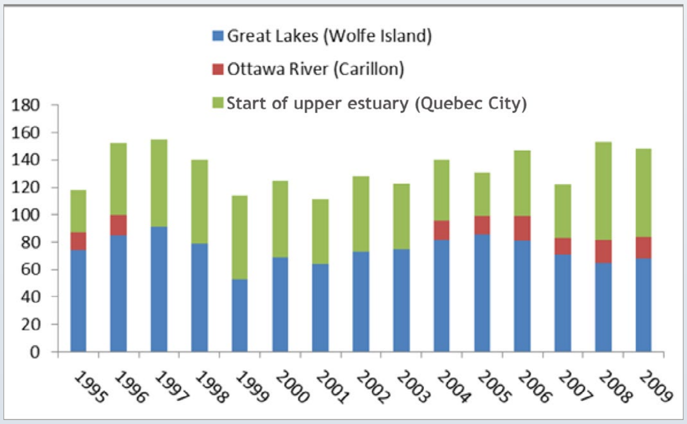

Figure 3. Quantity of nitrates-nitrites at the three main stations (tons/years)”

with SS; they are therefore not affected by sedimentation in the lake. Total phosphorus lies between SS and nitrates and nitrites (Figure 4). At the outlet of the St. Lawrence River (Quebec City), a significant portion of phosphorus (about 60%) is associated with SS. In addition, we observe the same temporal variation as for SS between 1995 and 2009. If the proportion of phosphorus originating from the Great Lakes is greater than that of SS, it is due to the fact that a large quantity of phosphorus (90%) at the exit of Lake Ontario is in the dissolved phase. The large proportion of phosphorus added between Wolfe Island and Quebec City (Figure 4) could originate from the tributaries of the St. Lawrence lowlands and could be partly related to agricultural activities but also to erosion and urban effluent.

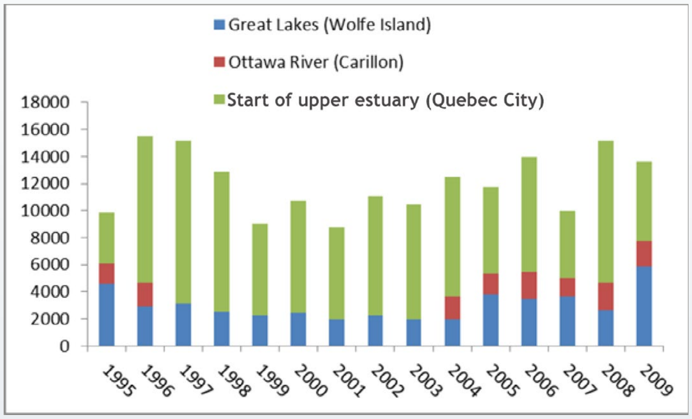

Figure 4. Quantity of phosphorus at the three main stations (tons/years)

Metals: It is sometimes difficult to determine the origin of metals, because they occur naturally in streams. Only when concentrations exceed a certain threshold can we conclude that human activities have made a significant contribution. Data for metals collected in the St. Lawrence River do not exceed the water quality criteria for the protection of aquatic life (see metals). The comparison of loadings calculated at the two inlets (Wolfe Island and Carillon) and at the outlet into the estuary (Quebec City) for copper, zinc and mercury, however, shows that there are large sources of metals within the territory of Quebec (Figure 5). The computation of loadings, performed for the dissolved and particulate fractions, shows that Lake Ontario is a significant source of dissolved metals in the St. Lawrence River. By contrast, metals associated with SS originate mainly from within Quebec and seem to have the same source as SS. In addition, concentrations of metals adsorbed onto SS are very close to those measured in the Earth’s crust (Rondeau et al. 2005). Inputs of metals from tributaries and of particles resulting from shore line and riverbed erosion are hypothesized to be the major source of metal inputs to the St. Lawrence River.

Pesticides: Atrazine and metolachlor are herbicides used in agriculture, and in corn and soya production in particular. A mass balance performed in 1995 and 1996 demonstrated the importance of Lake Ontario as a source of these herbicides in the St. Lawrence River (Pham et al. 2000). In general, the concentrations measured in the St. Lawrence River are of the same order of magnitude as those measured at Wolfe Island, at the outflow of Lake Ontario. However, at the Quebec City station, higher concentrations are observed during the summer, likely due to the spraying of pesticides on crops located in the St. Lawrence lowlands. Pesticides are not routinely monitored in the Ottawa River at Carillon. A previous study (Cossa et al. 1998) revealed the virtual absence of these contaminants, considering the low level of agricultural activity in the watershed. Annual loadings calculated for these two herbicides at the Quebec City station for 1995–2012 (Figure 5) show a net decrease (in the order of 50%) in inputs toward the estuary. This decrease is not observed in the Great Lakes (Burniston et al. 2012), but it is significant in the Quebec tributaries (Giroux and


Overview of Montreal © Thinkstock

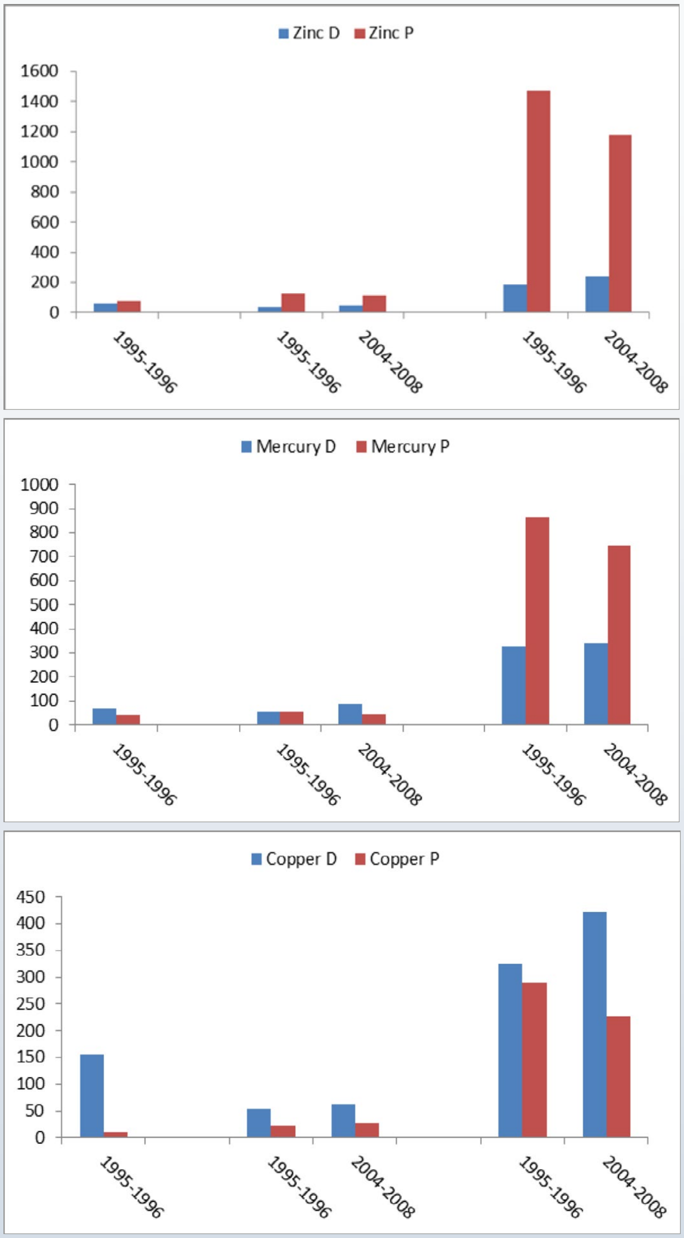

Figure 5. Quantity of zinc, mercury and copper at the three main stations (tons/year, except for Hg – kilograms/year)

Pelletier 2012), suggesting that the observed decrease in the St. Lawrence River at Quebec City could possibly stem from a decrease in the Quebec tributaries.

Polybrominated Diphenyl Ethers (PBDEs): These compounds are used as flame retardants in many everyday objects such as carpets, fabrics, computers and paints. PBDEs can escape from manufactured products during production processes, product use or after product disposal, to subsequently end up in the environment via effluents or in the form of atmospheric emissions. Monitoring of PBDEs in SS of the St. Lawrence River was performed at the Quebec City station between 1995 and 2010 (except for the years 1997 and 1998). PBDE loadings show a net increase over the last 10 years (Figure 7). This increase is, however, not obvious for light PBDEs, for which loadings remain constant for the period under study. A detailed description of results for PBDEs in particles and sediments from the St. Lawrence River can be found in the sheet on the monitoring of the state of the St. Lawrence River (Pelletier and Rondeau 2013).

Outlook

Although the waters of the St. Lawrence River originate mainly from Lake Ontario (60%), it is not necessarily the case for contaminants. In the case of the St. Lawrence River, the affinity of contaminants for SS (hydrophobic) largely dictates the source of the contaminants. Since Lake Ontario acts as a large sedimentation basin, contaminants associated to particles will tend to remain in the lake in the form of sediments. In the St. Lawrence River, SS and contaminants associated to sediment (metals, phosphorus and PBDEs) do not originate from the Great Lakes but rather are the result of erosion or urban or industrial effluents, and come from tributaries of the St. Lawrence River. In contrast, more soluble contaminants such as nitrates and pesticides originate in large part (often in the same proportion as the water inputs) from Lake Ontario.

Due to recent technological developments, it is now possible to detect new contaminants of concern, and surveillance and monitoring programs have been implemented to learn more about their chemical behaviour and fate in the aquatic environment. Many of these substances (surfactants, steroids, medications, hormones, etc.) are linked to disruptions of the endocrine system in aquatic organisms. Information on the occurrence and sources of such contaminants will help improve water quality monitoring in the St. Lawrence River. In addition, the flow rate of the St. Lawrence River is an important factor regulating the transportation of contaminants. Changes to the flow regime of the St. Lawrence River resulting from climatic change or regulation of water levels in the Great Lakes will have consequences that will need to be documented.

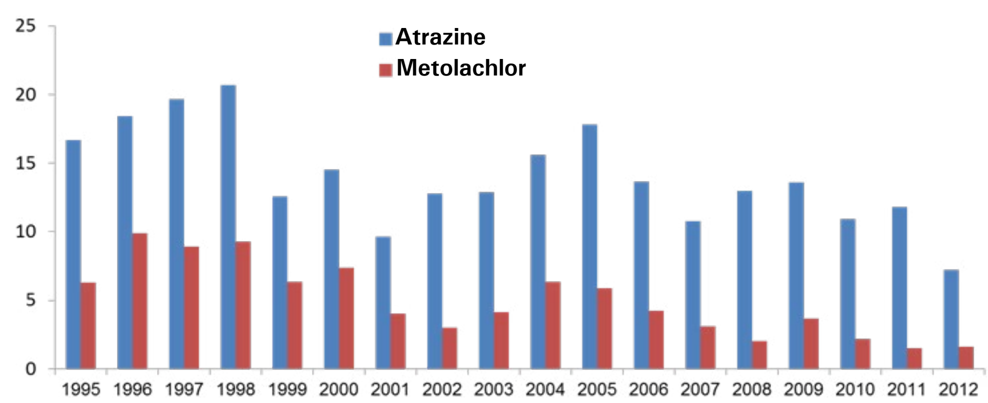

Figure 6. Quantity of atrazine and metolachlor exported to the St. Lawrence estuary (tons/year)

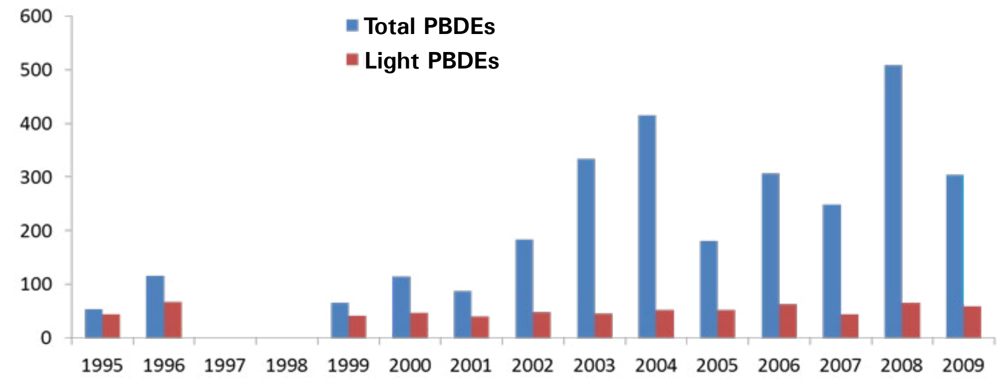

Figure 7. Quantity of PBDEs exported to the St. Lawrence estuary (kilograms/year)

Key Variables

Quality criteria

Thresholds or guidelines assess whether different uses of water, such as swimming, livestock watering and aquatic life, are impaired by the occurrence of a substance. Water quality criteria are not standards. These values are not enforceable. They are integrated into management procedures, where they are used as reference levels to assess the health of aquatic ecosystems. The quality criteria are values associated with a safety threshold that protects a use from any type of possible deleterious effect: toxicity, organoleptic properties or aesthetic impairment. Among these criteria, the one pertaining to chronic toxicity for aquatic life used here is the highest concentration of a substance that will not produce any deleterious effect on aquatic organisms (and their offspring) when they are exposed daily during their whole lifetime. Any environmental concentration exceeding this criterion, when it is continuously maintained, is likely to cause a deleterious effect. Considerations of the health of the ecosystem, the cumulative effects of several substances—for aquatic life as well as human health—or the occurrence of a specific use can necessitate additional requirements.

Metals

In 2009 and 2011, concentrations of some 20 metals were measured at 15 provincial sampling stations distributed between Îles de Boucherville and Île d'Orléans (Figure 1). Twelve sampling rounds were conducted during these 2 years. No exceedances of the quality criteria for the protection of aquatic life were recorded (Table 1). Despite the low concentrations for all metals analyzed, there is an observable increase in concentrations, from upstream to downstream, for most of them (beryllium, cadmium, chromium, cobalt, copper, iron, manganese, nickel, lead, vanadium and zinc), which indicates that the territory of Quebec and the activities carried out therein are a significant source of inputs for these metals.

Table 1: Maximum concentration measured and water quality criteria for the protection of aquatic life

Metal	**Extractible fraction** Maximum concentration measured[1] (µg/l)	**Dissolved fraction** Maximum concentration measured[1] (µg/l)	**Quality criteria** (chronic effect)[3] (µg/l)
Antimony	0.17	0.16	240
Arsenic	1.00	0.99	150
Barium	27	23	440[2]
Beryllium	0.039	0.014	2.4[2]
Boron	24	24	5000
Cadmium	0.031	0.015	0.270[2]
Chromium	2.0	0.25	11
Cobalt	0.57	0.30	100
Copper	7.3	3.3	9.3[2]
Iron	1200	130	1300
Lead	0.66	0.16	3.2[2]
Manganese	54	6.7	1900[2]
Molybdenum	1.4	1.3	3200
Nickel	2.0	0.95	52[2]
Selenium	0.3	0.2	5
Silver	0.015	0.007	0.100
Strontium	200	200	8300
Uranium	0.39	0.35	14[2]
Vanadium	2.1	0.71	12
Zinc	7.9	2.0	120

[1] For all 15 stations
[2] Criterion calculated for hardness of 100 mg/L $CaCO_3$
[3] MDDELCC criterion

To know more

Burniston, D., P. Klawunn, S. Backus, B. Hill, A. Dove, J. Waltho, V. Richardson, J. Struger, L. Bradley, D. Mcgoldrick, C. Marvin. 2012. Spatial distributions and temporal trends in pollutants in the Great Lakes 1968–2008. *Water Quality Research Journal of Canada* 46:269-289.

Cossa, D., T.-T. Pham, B. Rondeau, S. Proulx, C. Surette, B. Quémerais. 1998. *Bilan massique des contaminants chimiques dans le fleuve Saint-Laurent.* Environnement Canada – Région du Québec, Conservation de l'environnement, Centre Saint-Laurent. Rapport scientifique et technique ST-163. 258 pages.

Giroux, I. and L. Pelletier. 2012. *Présence de pesticides dans l'eau au Québec : bilan dans quatre cours d'eau de zones en culture de maïs et de soya en 2008, 2009 et 2010*. Québec, ministère du Développement durable, de l'Environnement et des Parcs, Direction du suivi de l'état de l'environnement. ISBN 978-2-550-64159-9 (PDF). 46 p. and 3 annexes.

Pham, T.-T., B. Rondeau, H. Sabik, S. Proulx, D. Cossa. 2000. Lake Ontario: The predominant source of triazine herbicides in the St. Lawrence River. *Canadian Journal of Fisheries and Aquatic Sciences* vol. 57: 78-85.

Pelletier, M. and M. Rondeau. 2013. Les polybromo-diphényléthers (PBDE) dans les matières en suspension et les sédiments du fleuve Saint-Laurent.

Rondeau, B., D. Cossa, P. Gagnon, L. Bilodeau. 2000. Budget and sources of suspended sediment transported in the St. Lawrence River. *Hydrological Processes 14: 21-36*.

Rondeau, B., D. Cossa, P. Gagnon, T.t. Pham, C. Surette. 2005. Hydrological and biogeochemical dynamics of the minor and trace elements in the St. Lawrence River. *Applied Geochemistry* 20: 1391-1408.

State of the St. Lawrence Monitoring Program

Five government partners—Environment Canada, Fisheries and Oceans Canada, Parks Canada, Quebec's Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques and the Ministère des Forêts, de la Faune et des Parcs—in collaboration with Stratégies Saint-Laurent, a non-governmental organization that works actively with riverside communities, are pooling their expertise and efforts to provide Canadians with information on the state of the St. Lawrence and its long-term changes.

To this end, environmental indicators have been developed on the basis of data collected as part of each organization's ongoing environmental monitoring activities over the years. These activities cover the main components of the environment, namely water, sediments, biological resources, uses and shorelines.

For more information on the State of the St. Lawrence Monitoring Program, please visit our website at **www.planstlaurent.qc.ca/**.

Written by:
Myriam Rondeau
Science and Technology Branch
Environment Canada

ISBN 978-1-100-25939-0
Cat. No.: En154-79/2015E-PDF

Photo Credits: Some symbols in this document were graciously provided by the Integration and Application Network site at the University of Maryland Center for Environmental Science (ian.umces.edu/ symbols/).

Également publié en français sous le titre :
La qualité de l'eau du secteur fluvial.