Suivi de l'état du
SAINT-LAURENT

Contamination of water by toxic substances

Highlights

Status: According to the results of recent analyses of water quality in the St. Lawrence, concentrations of polybrominated diphenyl ethers (PBDEs) have been declining steadily since 2010. Levels of other contaminants are stable or low, with copper being the only contaminant of concern.

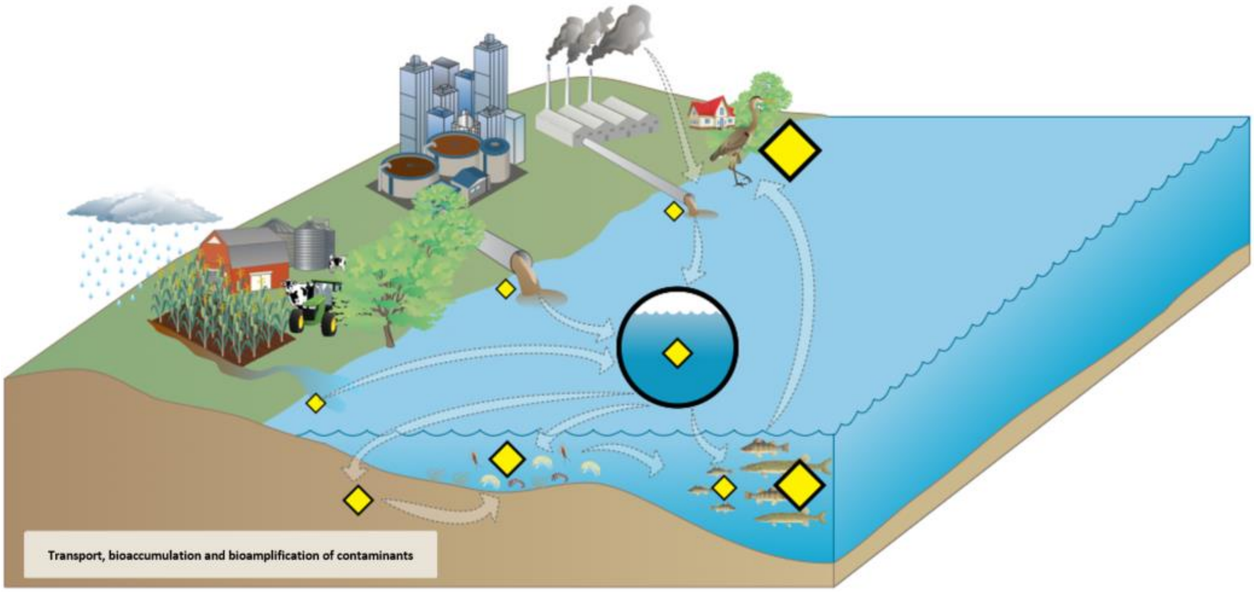

Figure 1 – Conceptual diagram showing the transport, bioaccumulation and biomagnification of toxic contaminants in fresh water

Issues

Over the last century, urban development, industrial activities and farming have unleashed a massive load of toxic substances into our watercourses. These contaminants bioaccumulate and biomagnify in the food chain (figure 1) These inputs have contributed to degrading the water quality in the immense Great Lakes–St. Lawrence Basin and have adversely affected a number of species living there. Metals, nutrients and pesticides have been detected in water at concentrations that are sometimes cause for concern.

New classes of pesticides, which cause significant effects at different levels, are appearing in the environment, including neonicotinoid pesticides.

Four fluvial monitoring stations are used to assess the water quality in the St. Lawrence River, by recording seasonal and interannual fluctuations and long-term trends in the concentrations of several contaminants (figure 2).

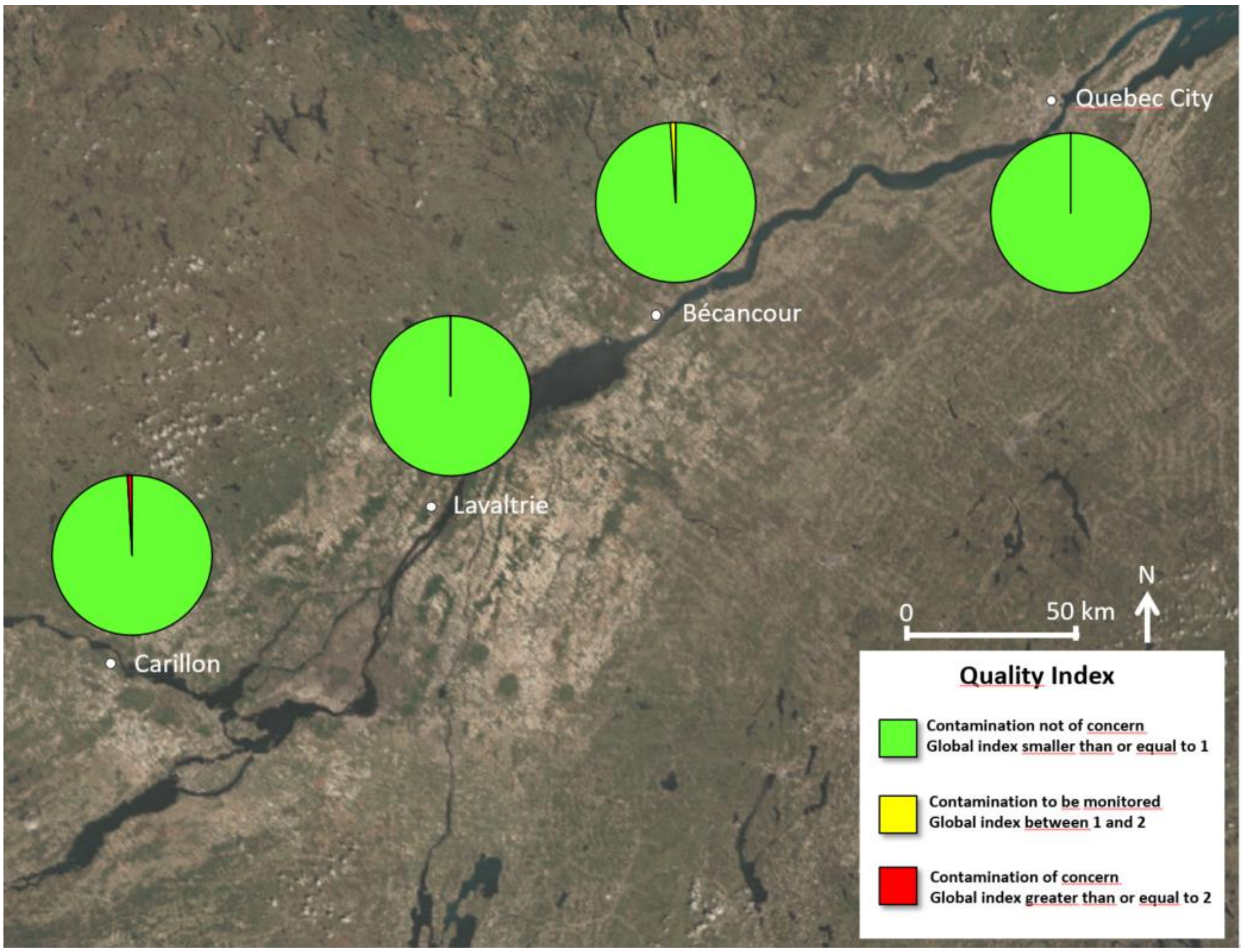

Figure 2 – Levels of contamination at four fluvial stations during the 2012–2020 period: Carillon, Lavaltrie, Bécancour and Quebec City

Water quality criteria

Water quality criteria serve as reference levels for assessing the health of aquatic ecosystems. These criteria are values associated with a safe threshold at which a water use is protected from all possible deleterious effects.

Among these criteria, water quality guidelines (WQG) for the protection of aquatic life are used to measure chronic toxicity to aquatic life. A WQG is the highest concentration of a substance to which aquatic organisms (and their progeny) can be exposed daily over their lifetime without suffering adverse effects. Any concentration in the environment that exceeds these criteria for a long enough period is likely to have an undesirable effect. The criteria stem from various sources, including recommendations made by Environment and Climate Change Canada (ECCC), the Canadian Council of Ministers of the Environment (CCME), and the Ministère de l'Environnement et de la Lutte contre les Changements Climatiques (MELCC), depending on the substance in question.

The frequency with which a criterion is exceeded is used to issue findings at the scale of the individual contaminant, group of contaminants, water quality station or the river as a whole.

Water quality between 2012 and 2019

This monitoring sheet presents the results of analyses of metals, pesticides, and polybrominated diphenyl ethers (PBDEs) in samples taken at four stations in the river between 2012 and 2019. The same parameters were not measured at all the stations (figure 3). Some sampling campaigns included analyses designed to target activities that take place near the stations. The latest sampling and analysis techniques were used to obtain results for substances present at trace and ultratrace levels.

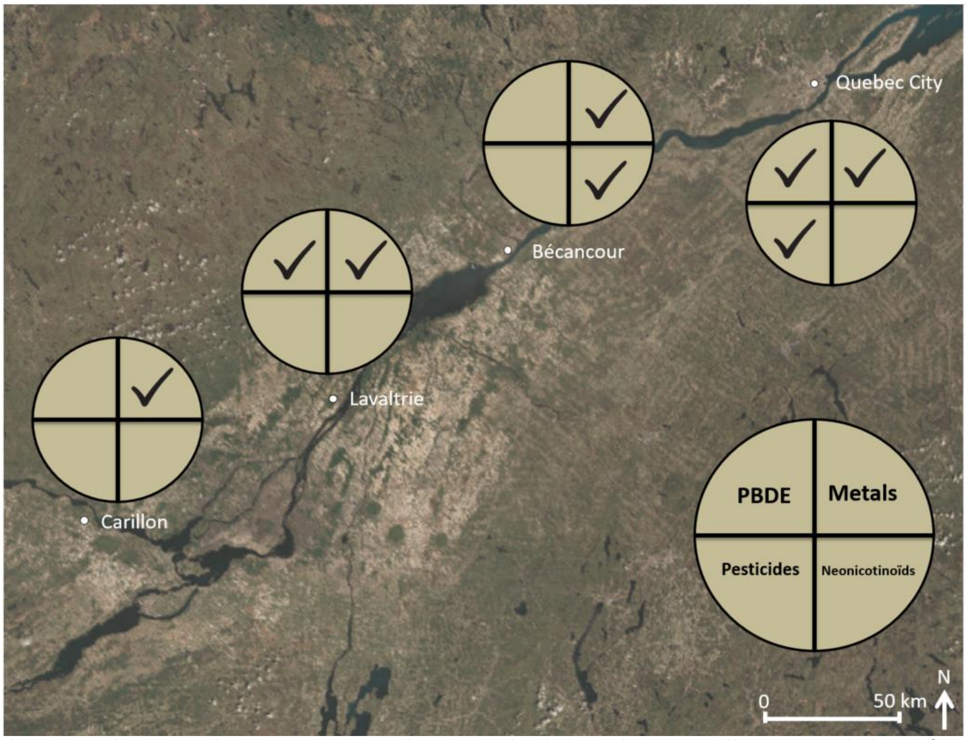

Figure 3 – Classes of contaminants measured at four fluvial stations: Carillon, Lavaltrie, Bécancour and Quebec City

Metals

The metal concentrations measured at the stations complied in large part with water quality criteria for the protection of aquatic life (Table 1). Any exceedances observed were generally associated with high concentrations of suspended solids, which occur, for example, during the spring freshet. The origin of these metals is sometimes difficult to determine, since metals are naturally present in all watercourses. Only when concentrations exceed a certain threshold can we conclude that anthropogenic inputs are involved. Increased metal concentrations in the brown-water massbetween the Carillon and Lavaltrie stations may be associated with anthropogenic inputs of metals from the Montreal and Laval urban area. Water sampled at the Bécancour station is affected by metal inputs that likely come from the tributaries on the south shore of Lake Saint-Pierre. These rivers have high levels of suspended solids, with which metals are associated.

A total of 11 different metals were evaluated: arsenic, silver, cadmium, copper, iron, molybdenum, nickel, lead, selenium, zinc and mercury. They were chosen because WQG for the protection of aquatic life were available.

For most of the metals measured, the frequency of exceedance (%) of the WQG was below 5% at the four fluvial stations (Table 1). The frequency of exceedance varied between 1.8% and 9.6% for lead and between 3.6% and 9.6% for zinc, depending on the station. However, for copper the corresponding values ranged from 9.1% to 38.3%; copper is therefore a contaminant of concern that requires monitoring.

Parameter	Threshold ng/L	Measurements	Carillon	Lavaltrie	Bécancour	Quebec City
Arsenic	5,000	Median (ng/L)	450	450	760	735
		No. of samples	110	94	94	108
		Exceedance (%)	**0.9**	0	0	0
Silver	2,500	Median (ng/L)	5	6.5	5	5
		No. of samples	110	94	94	108
		Exceedance (%)	0	0	0	0
Cadmium	90	Median (ng/L)	10	20	19	10
		No. of samples	110	94	94	108
		Exceedance (%)	**3.6**	**2.1**	**1.1**	**0.9**
Copper	2,000	Median (ng/L)	1,300	1,800	1,700	1,500
		No. of samples	110	94	94	108
		Exceedance (%)	**9.1**	**38.3**	**35.1**	**15.7**
Iron	See formula*	Median (ng/L)	396	730	656	588
		No. of samples	108	92	91	106
		Exceedance (%)	0	0	**1**	**2**
Molybdenum	73,000	Median (ng/L)	240	330	735	840
		No. of samples	110	94	94	108
		Exceedance (%)	0	0	0	0
Nickel	25,000	Median (ng/L)	880	1,325	1,685	1,270
		No. of samples	110	94	94	108
		Exceedance (%)	0	0	0	0
Lead	1,000	Median (ng/L)	210	455	445	355
		No. of samples	110	94	94	108
		Exceedance (%)	**1.8**	**7.5**	**9.6**	**3.7**
Selenium	1,000	Median (ng/L)	90	100	120	130
		No. of samples	110	94	94	108
		Exceedance (%)	**1.8**	0	0	0
Zinc	7,000	Median (ng/L)	1,800	3,550	3,150	2,800
		No. of samples	110	94	94	108
		Exceedance (%)	**3.6**	**9.6**	**8.5**	**5.6**
Mercury	26	Median (ng/L)	1.79	2.32	1.79	2.1
		No. of samples	110	93	94	108
		Exceedance (%)	0	0	0	0

*The threshold is specific to each sample. Measurements of dissolved organic carbon (DOC) and pH make up part of the formula that is used to determine the threshold: $\exp(0.671(\ln(DOC))+0.171(pH)+5.586)$. Ref.: FEQG, ECCC 2019

Table 1 – Median concentrations of metals and frequency of exceedance (%) of the water quality guidelines for the protection of aquatic life established by CCME, at the four fluvial stations, 2012 to 2019

Polybrominated diphenyl ethers (PBDEs)

In the past, these products were used as flame retardants in familiar items such as carpets, fabrics, computers and paint. PBDEs in these products can be released during manufacturing or use and even after disposal making their way into the environment through effluents or atmospheric deposition. The manufacture, import, use and sale of commercial products intentionally containing pentaBDE and octaBDE has been prohibited in Canada since 2008.

The presence of PBDEs in suspended particulate matter in the St. Lawrence was monitored at the Lavaltrie and Quebec City stations; 24 PBDE congeners were analyzed individually to measure their concentrations in suspended solids. Median concentrations of total PBDE congeners (excluding congeners BDE-99 and BDE-100) are shown in Table 2. At each station, the median concentration of congener BDE-209 was higher than the total concentrations of all other detected congeners combined. However, pentabromodiphenyl ethers (congeners BDE-99 and BDE-100), also commonly detected in the St. Lawrence, are recognized to be more toxic than congener BDE-209. The highest PBDE concentrations were measured at the Lavaltrie station, which confirms the significant contribution from urban sources in the Montreal region. However, no WQG exceedances were observed among the eight congeners or congener families. Furthermore, concentrations declined over time at both stations (figure 4), showing that the various regulations that have been enacted since 2008 have had an impact.

Parameter	Threshold pg/L	Measurements	Lavaltrie	Quebec City
TriBDE	46,000	Median (pg/L)	2.25	1.27
		No. of samples	88	85
		Exceedance (%)	0	0
TetraBDE	24,000	Median (pg/L)	47.5	16.9
		No. of samples	88	85
		Exceedance (%)	0	0
Congener BDE-99	4,000	Median (pg/L)	37.5	11
		No. of samples	88	85
		Exceedance (%)	**2.1**	**0.9**
Congener BDE-100	200	Median (pg/L)	8.55	3.1
		No. of samples	88	85
		Exceedance (%)	0	0
PentaBDE	200	Median (pg/L)	6.45	4.5
		No. of samples	88	85
		Exceedance (%)	0	0
HexaBDE	1,200	Median (pg/L)	17.45	9.1
		No. of samples	88	85
		Exceedance (%)	0	0
HeptaBDE	17,000	Median (pg/L)	5.85	3.6
		No. of samples	88	85
		Exceedance (%)	0	0
OctaBDE	17,000	Median (pg/L)	13.45	9.4
		No. of samples	88	85
		Exceedance (%)	0	0

Table 2 – Median concentrations of PBDEs and frequency of exceedance (%) of the water quality guidelines for the protection of aquatic life established by CCME, at Lavaltrie and Quebec City, 2012 to 2020

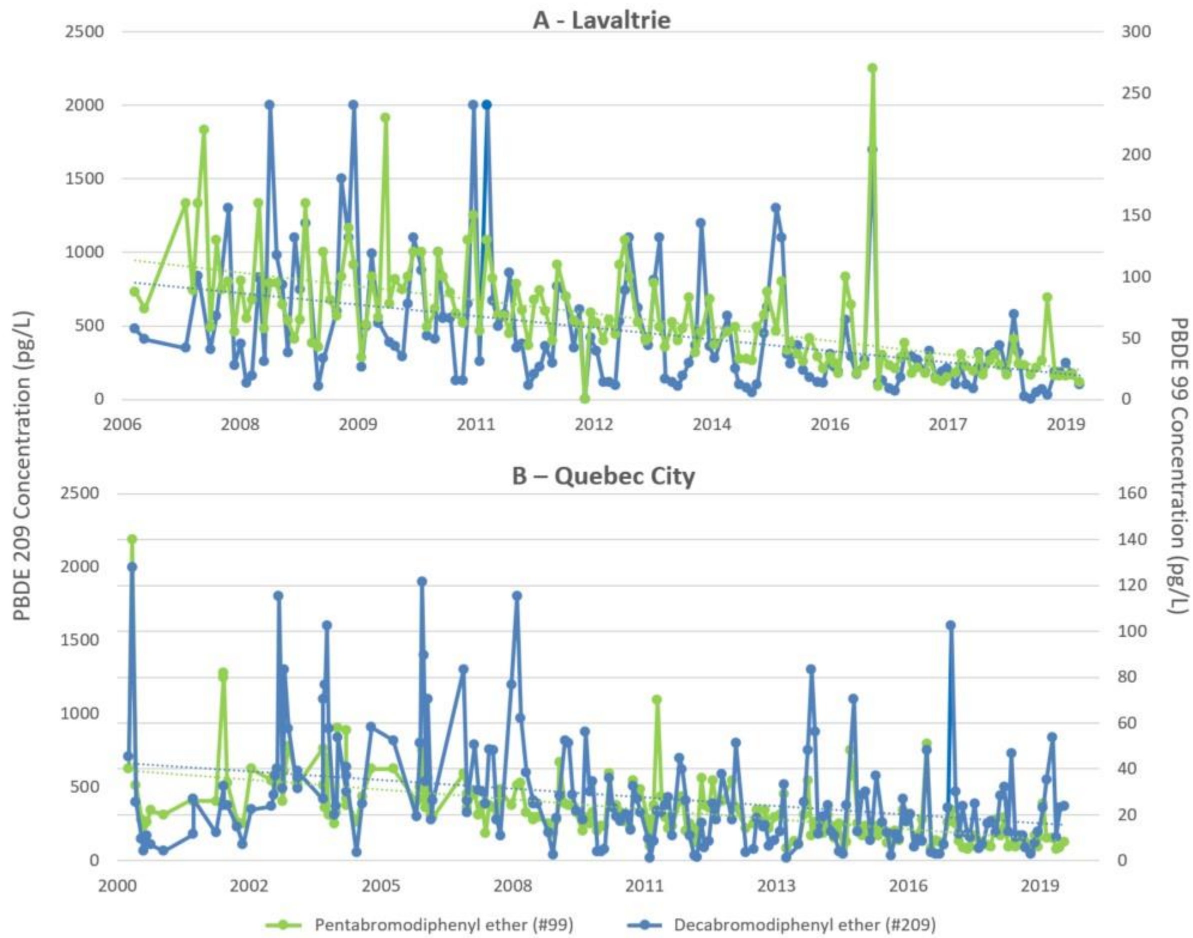

Figure 4 – Concentrations of congeners BDE-209 and BDE-99 at Lavaltrie (A) (2006 to 2019) and at Quebec City (B) (2000 to 2019)

Pesticides

The pesticides analyzed in the water quality monitoring program for the St. Lawrence were chosen based on the intensity of their use in the St. Lawrence Lowlands. Herbicides such as atrazine and metolachlor, widely used on corn and soybean crops, were the pesticides most commonly detected in the St. Lawrence.

Pesticide concentrations were measured at the Quebec City station. Median concentrations did not exceed WQG values (Table 3). However, major seasonal variations were found in these contaminants. At the Quebec City station (figure 5), higher concentrations were observed in summer, likely because of pesticide applications on crops.

Parameter	Threshold ng/L	Measurements	Quebec City
Atrazine	1,800	Median (ng/L)	41
		No. of samples	101
		Exceedance (%)	0
Bentazon	510*	Median (ng/L)	9.8
		No. of samples	13
		Exceedance (%)	0
Dicamba	10,000	Median (ng/L)	3.8
		No. of samples	13
		Exceedance (%)	0
Metolachlor	7,800	Median (ng/L)	8
		No. of samples	101
		Exceedance (%)	0
Metribuzin	1,000	Median (ng/L)	0.905
		No. of samples	92
		Exceedance (%)	0
Simazine	10,000	Median (ng/L)	3.9
		No. of samples	101
		Exceedance (%)	0

* Thresholds established by MELCC

Table 3 – Median concentrations of pesticides and frequency of exceedance (%) of the water quality guidelines for the protection of aquatic life established by CCME, unless otherwise indicated, as measured at Quebec City, 2012 to 2020

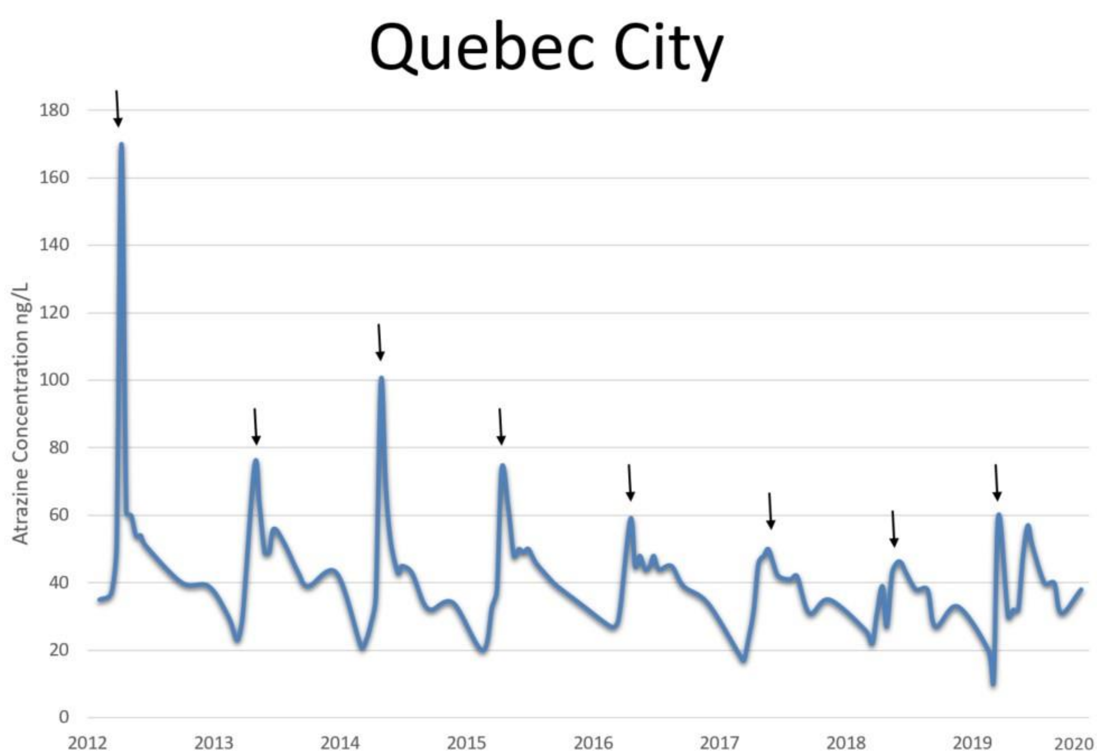

Figure 5 – Annual variation in atrazine concentrations at the Quebec City station between 2012 and 2020

Neonicotinoids

Neonicotinoids are a class of insecticides used primarily for corn and soybean crops. However, instead of being sprayed on crops, they are applied as seed coatings (seed treatment). Neonicotinoids are transported through the air (during sowing with pneumatic seed drills), in surface runoff, and in stagnant water on the ground (precipitation). Consequently, higher concentrations are detected in summer (Chrétien et al. 2017).

Five substances were selected to monitor this family of pesticides: imidacloprid (a first-generation product), thiamethoxam (a second-generation product), clothianidin (a degradation product), dinotefuran (a third-generation product; no WQG) and chlorantraniliprole. Clothianidin, a degradation product of thiamethoxam, is much more persistent in the environment: clothianidin has a half-life of 545 days in the soil, compared with 50 days for thiamethoxam (PPDB; Pesticide Properties DataBase, University of Hertfordshire 2020). Chlorantraniliprole, a ryanoid-class insecticide, is one of the replacement products for neonicotinoids.

Neonicotinoids were monitored at the Quebec City station in 2018, for a full year. However, since all concentrations detected were below the detection limit, monitoring was halted at this station; the following year, neonicotinoids were measured at the Bécancour station instead, where WQG exceedances for thiamethoxam and clothianidin had been observed in 2014 (Giroux I. 2015). Therefore, only the 2019-2020 data (nine samples) were used in the analyses.

No exceedances were observed for substances for which a WQG value has been established (Table 4). As the table shows, the median value for clothianidin is higher than that for thiamethoxam, probably because of its greater persistence (linked to its half life in the soil). In addition, higher levels of chlorantraniliprole were detected, which suggests that this replacement chemical is now in use

Parameter	Threshold ng/L	Measurements	Bécancour
Imidacloprid	230	Median (ng/L)	0.396
		No. of samples	9
		Exceedance (%)	0
Clothianidin	83*	Median (ng/L)	0.783
		No. of samples	9
		Exceedance (%)	0
Thiamethoxam	83*	Median (ng/L)	0.337
		No. of samples	9
		Exceedance (%)	0
Dinotefuran	-	Median (ng/L)	0.05
		No. of samples	9
Chlorantraniliprole	220*	Median (ng/L)	1.37
		No. of samples	9
		Exceedance (%)	0
***Thresholds established by MELCC**			

Table 4 – Median concentrations of neonicotinoids (pesticides) and frequency of exceedance (%) of the water quality guidelines for the protection of aquatic life established by CCME, unless otherwise indicated, as measured at Bécancour, 2012 to 2020

Calculation of indices

To limit biases resulting from the selection and use of only certain contaminants in the analyses, all contaminants for which water quality criteria have been established were included in the calculation of the key measurements.

A five-step calculation method was used to integrate the various water quality indices for each station (figure 6).

<u>Step 1 – Targeted contamination index</u>: The index was calculated for each substance analyzed (e.g., each metal individually). To do this, the ratio between the concentration of the substance in the water and the WQG was calculated for each sample.

<u>Step 2 – Index by contaminant class</u>: This represents the average of all indices calculated for a sample. For example, for metals, the average of the 11 metals analyzed was used to represent the index.

<u>Step 3 – Integrated overall index</u>: The purpose of this calculation was to obtain an index for each station by integrating all the measurements made at the station. To achieve this, all the indices calculated in step 2 were used. An average value for each station was then calculated to integrate all the indices (e.g., metals and PBDEs at Lavaltrie versus metals only at Carillon).

<u>Step 4 – Integrated overall index (%)</u>: Once the integrated overall indices were calculated, the level of contamination was evaluated. Indices were classified in three groups — uncontaminated, contaminated or heavily contaminated — which were defined as follows:

- Uncontaminated sample: integrated overall index ≤1
- Contaminated sample: integrated overall index > 1 and < 2
- Heavily contaminated sample: integrated overall index ≥ 2

The percentage of each group was then evaluated.

<u>Step 5 – State of the river index</u>: The percentages of each of the three groups obtained in Step 4 were weighted to obtain an index per station. Weighting was done as follows:

- % of uncontaminated samples multiplied by 2
- % of contaminated samples multiplied by 0
- % of heavily contaminated samples multiplied by –2.

The sum of the values obtained after weighting was then divided by 100. This value therefore represents the index for the station.

The average of the integrated overall indices obtained for each station was then used to characterize the state of the St. Lawrence based on five possible status designations (Good, Moderate-Good, Moderate, Moderate-Poor or Poor).

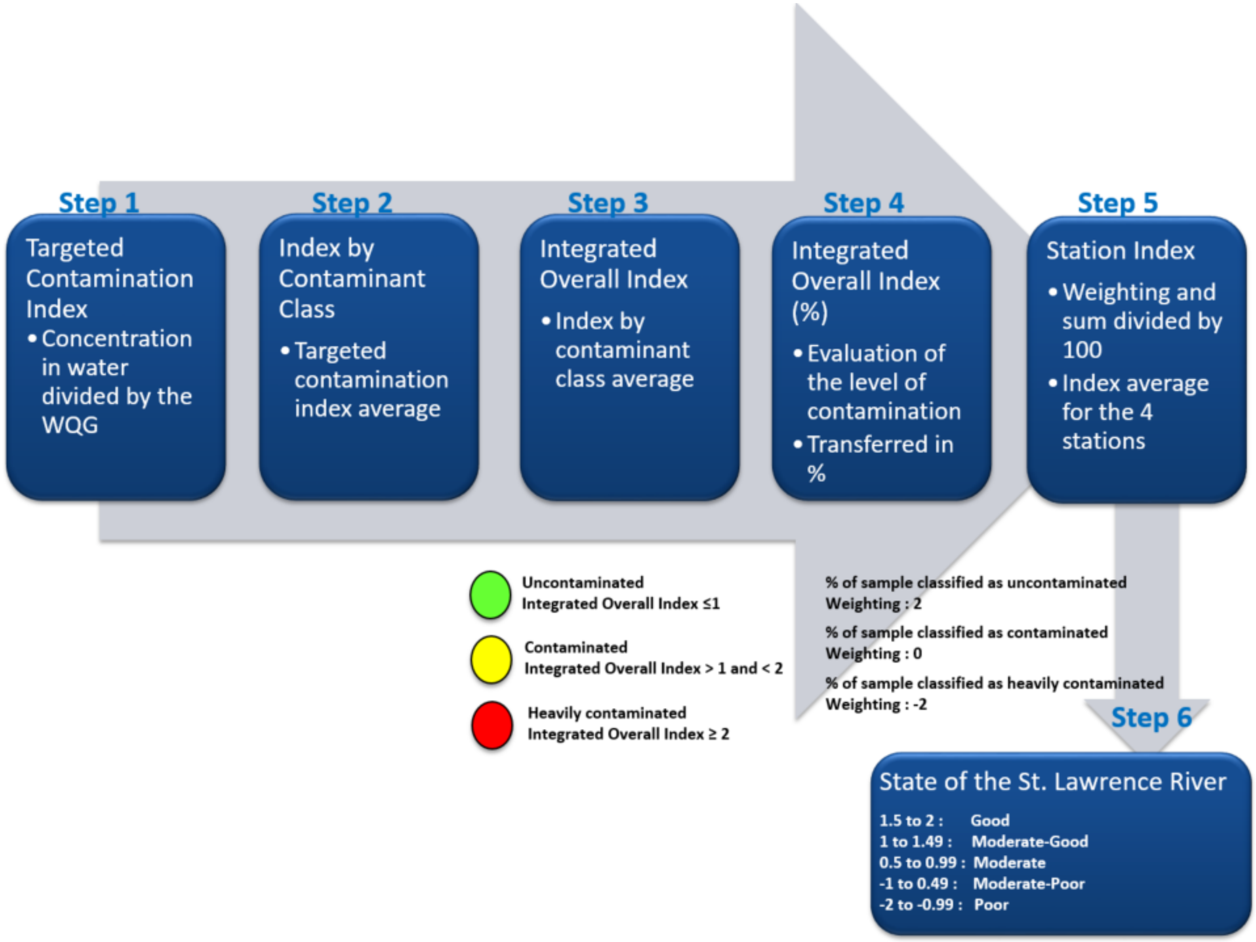

Figure 6 – Overview of method for calculating water quality indices

Outlook

Although PBDE concentrations have been declining since the 2000s, these substances must be carefully monitored to ensure that the situation continues to improve. Unfortunately, the industrial sector has been very quick to replace these compounds with new substances that are just as harmful to the environment. It is important to continue monitoring efforts to detect the presence of these new substances in the water. Various emerging substances such as pharmaceuticals and pesticides as well as other compounds associated with urban effluents must be evaluated under the Water Quality Monitoring and Surveillance program.

References

Chrétien, F., Giroux, I., Thériault, G., Gagnon, P. and Corriveau, J. 2017.
Surface runoff and subsurface tile drain losses of neonicotinoids and companion herbicides at edge-of-field, Environmental Pollution, Vol. 224, Pages 255-264

MELCC's water quality criteria for the protection of aquatic life [in French only]:
http://www.environnement.gouv.qc.ca/eau/criteres_eau/index.asp

CCME's Canadian Water Quality Guidelines for the Protection of Aquatic Life:
http://st-ts.ccme.ca/en/index.html

Toxic substances list: PBDEs: https://www.canada.ca/en/environment-climate-change/services/management-toxic-substances/list-canadian-environmental-protection-act/polybrominated-diphenyl-ethers.html

Environment and Climate Change Canada. 2019. Federal Environmental Quality Guidelines - Iron. 9 p.

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Giroux, I. (2015). *Présence de pesticides dans l'eau au Québec : Portrait et tendances dans les zones de maïs et de soya – 2011 à 2014*, Québec, Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques, Direction du suivi de l'état de l'environnement, ISBN. 978-2-550-73603-5, 47 p. + 5 app. [Online] http://www.mddelcc.gouv.qc.ca/eau/flrivlac/pesticides.htm

Pesticide Properties DataBase (PPDB), University of Hertfordshire (updated 2020-03-03):
http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm

State of the St. Lawrence Monitoring Program

Five government partners—Environment and Climate Change Canada, Fisheries and Oceans Canada, Parks Canada, the Quebec Ministère de l'Environnement et de la lutte contre les Changements Climatiques and the Ministère des Forêts, de la Faune et des Parcs du Québec 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, and long-term changes in, the St. Lawrence.

For more information on the State of the St. Lawrence Monitoring Program, please consult our website: http://planstlaurent.qc.ca/en/state_monitoring.html

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