Polybrominated diphenyl ethers in the suspended matter and sediments of the St. Lawrence River

Background

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants since the 1960s, in a wide range of products such as plastics, resins, electronics, textiles, paints, adhesives and sealants. Demand for them increased between 1980 and 1990, and they were even used in the production of car parts and toys. Similar to polychlorinated biphenyls (PCBs) in both structure and form, they can leach from finished products during production processes, during use or after disposal, and then enter the environment through effluents or in the form of atmospheric fallout. PBDEs are persistent because of their resistance to degradation and because they are sparingly water soluble but are fat soluble. Because of their lipophilic character and their strong affinity to organic material, these substances are bioaccumulable in aquatic organisms. PBDEs produce toxic effects, including the development of cancers and endocrine disruption. They are found not only in different trophic levels, but also in breast milk, blood and fatty tissues.


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The water in the St. Lawrence River and its tributaries has not been spared from PBDE contamination. A study carried out by Quebec's Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP) using a dozen sampling sites throughout Quebec shows the presence of relatively high concentrations of PBDEs in drinking water before treatment. The concentrations measured in Terrebonne, Lavaltrie and downstream from Granby might even have harmful effects on aquatic fauna. Fortunately, once treated, the water intended for human consumption does not seem to present a risk. The treatment systems that eliminate most of the suspended matter and combined with the hydrophobicity of the PBDEs make it possible to reduce the concentrations observed before treatment by 90% (Berryman *et al.*, 2009).

This report presents the results of the PBDE analyses obtained as part of the Quebec Water Quality Monitoring and Surveillance program for suspended matter in water and sediments. The results pertain to the spatial distribution of PBDEs between Cornwall and Québec (Quebec City), and the temporal variations over several decades.

Overview of the Situation

Sampling and analysis

In order to paint a spatial picture of the suspended matter contamination by PBDEs in the St. Lawrence River, several stations were sampled between 2004 and 2008, so as to cover the major water masses and the river's sedimentation zones. Suspended matter samples were taken at five characteristic stations along the St. Lawrence River's water masses: Wolfe Island near Kingston (green water from Lake Ontario), Carillon station (brown water from the Ottawa River), Lavaltrie station (brown water from the Ottawa River affected by the metropolitan region of Montréal), Bécancour station (green water from the Great Lakes affected by agricultural tributaries from the St. Lawrence Lowlands and by urban regions such as Drummondville, Sherbrooke, Saint-Hyacinthe and Granby) and finally the Québec station, which represents the mixed water at the mouth of the St. Lawrence (Figure 1). These samples were collected using a fibreglass membrane filter with a diameter of 240 mm that can retain particles > 0.7 µm (see photo). Several suspended matter samples taken at the Québec station between 1995 and 2005 (frozen at –20°C) were analyzed in 2006, while those sampled between 2006 and 2008 were analyzed in the weeks following their collection. All of these analyses allow us to describe the temporal variation in PBDE contamination at the mouth of the St. Lawrence River and to evaluate the variations in PBDE concentrations on a seasonal basis.

The spatial portrait of the sediment contamination was performed using samples collected in Lake Saint-Louis and Lake Saint-Pierre in fall 2003 and analyzed between 2004 and 2006 (Pelletier, 2008 and 2009); in Lake Saint-François, they were collected and analyzed in fall 2008 (Pelletier, 2010) (Figures 2 and 3). These samples were collected using Shipek or Ponar grab samplers, which can be used to take largely undisturbed samples at a depth of a dozen centimetres. Only the upper portion comprised of between 0 and 5 cm was saved and frozen at –20°C (see photo). Given that the sedimentation rate of the different fluvial lakes is approximately 1.5 cm per year, these surface sediment samples represent the environmental conditions of the five years prior to sampling. Two sediment cores were also collected in order to create a temporal profile of the evolution of PBDE concentrations since the 1960s. The sediment cores were taken using a percussion corer in the main sedimentation zones of Lake Saint-François and Lake Saint-Pierre in summer 2004 (see photo). The subsampling of cores was performed at intervals of two centimetres for the upper portion of the cores.

The samples of suspended matter were extracted using a soxhlet with toluene as a solvent, whereas the sediments were dried in a microwave oven and extracted with a mix of acetone-hexane (1:1) solvents. The extracts were concentrated and then purified on a multilayer column and a Florisil® column. The concentrations of 24 PBDE congeners were determined using a gas chromatograph coupled with

Suspended matters filter

Shipek grab

Ponar grab

a high-resolution mass spectrometer (GC–HRMS) in the lab at the Centre d'expertise en analyse environnementale du Québec (CEAEQ) between 2004 and 2008. The measured concentrations were corrected in order to recover the overlapping standards added at the beginning of handling. The analyzed PBDEs included the following 24 congeners: 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207 and 209. A quality control of the analyses was performed by using 10% lab blanks and 10% certified reference material (CRM), as well as by adding duplicates. The acceptable deviation for CRM analysis and duplicates remained under 25%.

In general, congeners 28, 47, 49, 66, 85, 99, 100, 153, 183 and 209 were the most detected in all the samples of suspended matter and sediments, whereas the other congeners were only occasionally detected. In order to facilitate understanding and simplify the presentation of results, all the congeners other than congener 209 (BDE 209) were grouped together to form the sum total of all congeners (∑PBDE). The reason for doing this is tied to both the composition of the blend of congeners in the commercial products pentaBDE, octaBDE and decaBDE and the fact that the concentrations of BDE 209 are markedly higher than those of the other congeners in the St. Lawrence River (Table 1).

Table 1 Median concentrations (standard deviation) of PBDE congeners in suspended matters and surface sdeiments of the St. Lawrence River

Station	Interval years	n	BDE 28 ng/g	BDE 47 ng/g	BDE 49 ng/g	BDE 66 ng/g	BDE 99 ng/g	BDE 100 ng/g	BDE 153 ng/g	BDE 15 ng/g	BDE 183 ng/g	BDE 209 ng/g	∑PBDE ng/g
Suspended matters													
Québec	1995–1997	16	0.02 (0.04)	3.07 (0.99)	0.15 (0.06)	0.07 (0.07)	4.68 (1.83)	0.93 (0.32)	0.64 (0.27)	0.41 (0.23)	0.34 (0.69)	12.93 (6.71)	11.38 (3.56)
	1998–2000	25	0.03 (0.05)	2.53 (1.52)	0.21 (0.10)	0.09 (0.06)	3.33 (2.53)	0.78 (0.50)	0.50 (0.41)	0.32 (0.26)	0.20 (0.28)	13.89 (15.78)	8.16 (5.44)
	2001–2003	18	–	2.45 (1.97)	0.21 (0.11)	–	3.24 (2.75)	0.72 (0.58)	0.42 (0.42)	0.23 (0.23)	0.02 (0.20)	34.30 (43.49)	8.44 (6.02)
	2004–2006	21	–	1.73 (1.14)	0.12 (0.10)	–	2.00 (1.82)	0.45 (0.35)	–	–	–	50.00 (27.19)	4.51 (3.64)
	2007–2009	17	1.84 (0.72)	5.71 (1.43)	0.44 (0.25)	–	2.32 (0.80)	0.54 (0.25)	0.22 (0.20)	–	–	50.65 (45.52)	13.24 (3.08)
Carillon	2004–2005	7	–	1.90 (1.88)	–	–	1.98 (2.36)	–	–	–	–	13.18 (18.27)	8.04 (4.28)
Wolfe Island	2004–2006	8	–	0.18 (1.26)	–	–	0.23 (1.59)	–	–	–	–	13.92 (16.61)	1.35 (2.73)
Lavaltrie	2007–2009	24	2.49 (1.81)	11.91 (5.40)	0.71 (0.47)	0.29 (0.18)	5.26 (3.34)	1.27 (0.71)	0.60 (0.39)	0.52 (0.26)	0.12 (0.53)	34.68 (129.83)	25.37 (11.23)
Bécancour	2006–2008	24	1.63 (5.07)	4.54 (10.66)	0.28 (0.97)	0.02(0.01)	1.25 (1.64)	0.33 (0.57)	–	–	–	29.60 (56.19)	9.12 (19.03)
Surface sediments													
Lake Saint-François	2008	30	–	0.05 (0.13)	0.03 (0.07)	–	0.06 (0.12)	–	–	–	–	2.40 (7.46)	0.18 (0.41)
Lake Saint-Louis	2003	20	0.02 (0.02)	0.26 (0.55)	0.08 (0.11)	0.08 (0.02)	0.24 (0.52)	0.08 (0.15)	0.06 (0.10)	0.05 (0.08)	0.08 (0.16)	4.05 (3.24)	0.85 (1.54)
Lake Saint-Pierre	2003	45	0.02 (0.05)	0.63 (1.73)	0.02 (0.06)	0.09 (0.28)	0.62 (2.30)	0.14 (0.45)	0.07 (0.27)	0.08 (0.19)	0.03 (0.14)	2.50 (11.21)	1.65 (5.40)

Note: Numbers in parentheses represent the standard deviation.

Spatial distribution of the PBDE concentrations

Suspended matter in the water

The median concentrations of PBDE congeners as well as ∑PBDE in the suspended matter of the St. Lawrence are presented in Table 1, by two-year interval (approx.) for each station. In addition, Figure 1a presents the spatial variation (upstream-downstream) of the median concentrations of PBDEs between 2004 and 2008. These results show that the median concentration of BDE 209 at each of the stations is higher than the median concentration of ∑PBDE. At Wolfe Island and Québec, BDE 209 is 10 and 6 times higher than ∑PBDE, respectively. However, the median concentration of BDE 209 is only 1.4 times higher than ∑PBDE at Lavaltrie, showing that the BDE 209 input does not match that of the other PBDE congeners. Moreover, this input variation is highlighted by the spatial variation of the congeners. The median concentration of BDE 209 is 3 to 4 times higher at the mouth of the river at Québec (50 ng/g) than at the outflow of Lake Ontario (14 ng/g) or the mouth of the Ottawa River (14 ng/g). While the median concentration of ∑PBDE also increased from upstream to downstream, going from 1.4 ng/g at Wolfe Island to 8.4 ng/g at Québec, it is highest at Lavaltrie station, with 25.4 ng/g, which characterizes the water in the Ottawa River. Moreover, the median concentration at Carillon (4.8 ng/g) is approximately 3 times higher than at Wolfe Island, showing a sharp distinction between the brown water of the Ottawa River and the St. Lawrence River's green water. These observations indicate that there are significant sources of PBDEs in the freshwater reach between Carillon and Lavaltrie, including the urban outfalls of Montréal and its northern suburbs. The results also show that the BDE 209 might also come from sources other than the outfalls since it has a different spatial behaviour than the ∑PBDE.

Charts legend

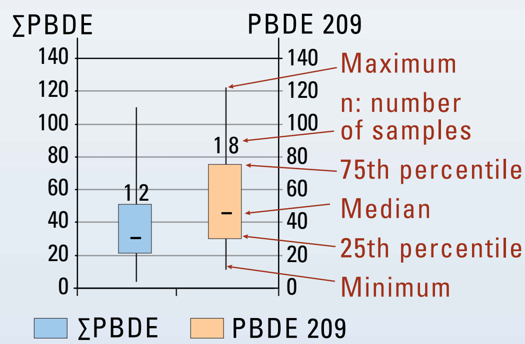
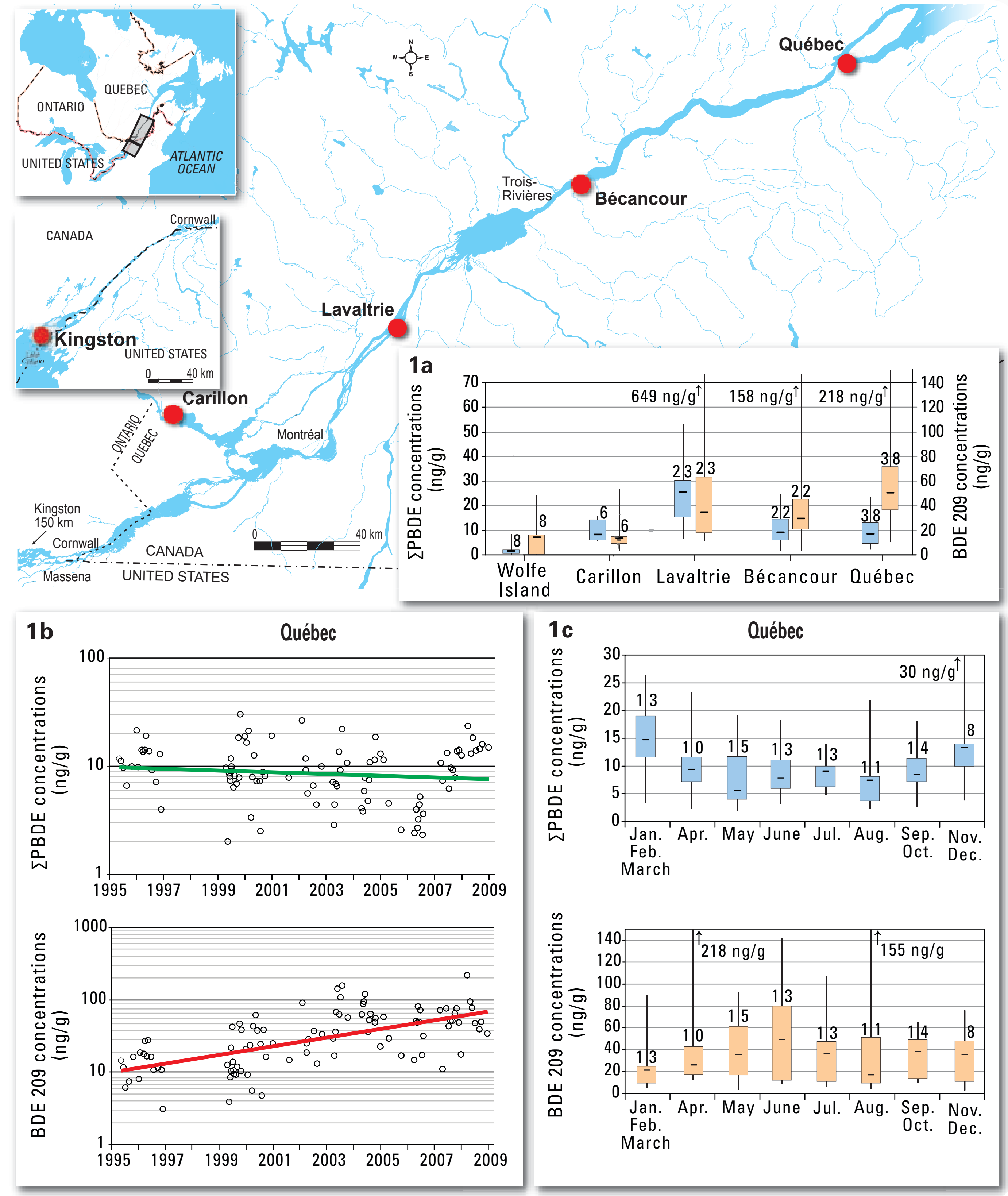


Figure 1 Spatial distribution and temporal evolution of PBDEs in suspended matter of the St. Lawrence River



Sediments in the fluvial lakes

The median values of the surface sediments in each of the fluvial lakes are presented in Table 1 and Figure 2a. The median value of ∑PBDE is nine times higher in Lake Saint-Pierre (1.65 ng/g) than in Lake Saint-François (0.18 ng/g), with an intermediate value of 0.85 ng/g in Lake Saint-Louis. On the other hand, the median values of BDE 209 vary little. The variation of the median values of ∑PBDE shows that the concentrations tend to increase from upstream to downstream, probably because of the local sources located along the St. Lawrence River. However, unlike the results obtained for the suspended matter, BDE 209 does not tend to rise significantly.

Figures 2b, 2c and 2d present the spatial distribution maps of ∑PBDE, and Figures 3a, 3b and 3c those of BDE 209. From upstream to downstream, we observed both a relative increase of the number of stations containing BDEs other than BDE 209 (∑PBDE) and an increase in their maximum concentrations, ranging from 1.5 ng/g at Lake Saint-François to 26 ng/g at Lake Saint-Pierre. This increase in ∑PBDE concentrations may be associated with urban outfalls. Moreover, at Lake Saint-Louis, you can observe a local increase in the ∑PBDE concentrations in the branch of the Ottawa River between île Perrot and Vaudreuil-Dorion, into which flow the outfalls of local cities. Similarly to Lake Saint-Pierre, the concentrations increase in the Sorel islands sector, which receives the wastewater from the city of Montréal and its northern suburbs.

While BDE 209 is also associated with the urban outfalls, its spatial distribution does not match that of ∑PBDE. We observe high concentrations in Lake Saint-François, even though there are no significant outfalls upstream. In Lake Saint-Louis and Lake Saint-Pierre, the highest concentrations of ∑PBDE are in the sedimentation zones, whereas BDE 209 concentrations are not necessarily associated with these zones. This difference could be tied to the water mass differentiation and possibly to the sedimentation process, which varies considerably in Lake Saint-Pierre (Pelletier, 2008; Morin and Champoux, 2006).

St. Lawrence River fluvial lakes: Lake Saint-François, Lake Saint-Louis and Lake Saint-Pierre

Figure 2 Spatial distribution of ∑PBDEs in surface sediments of fluvial lakes

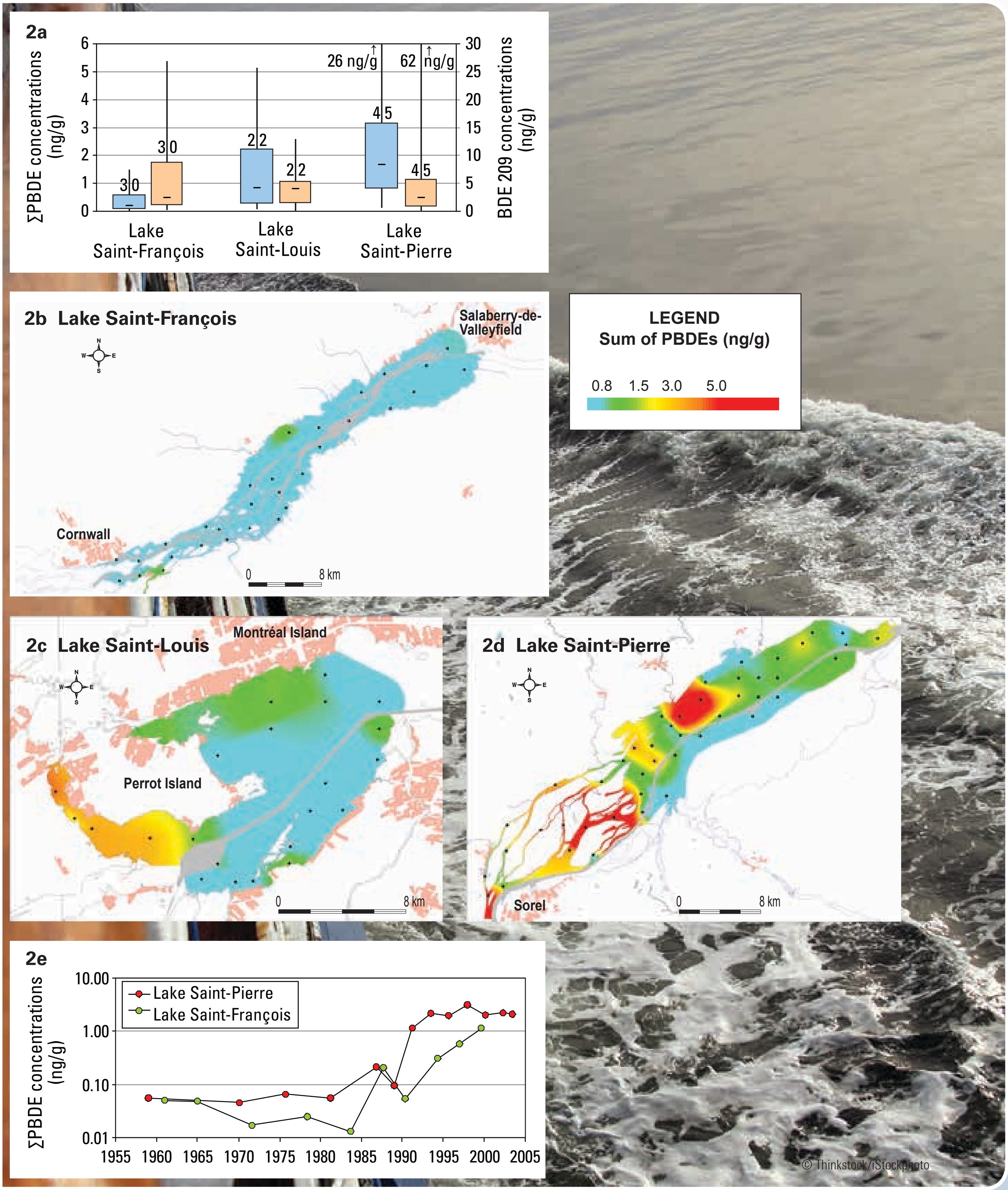
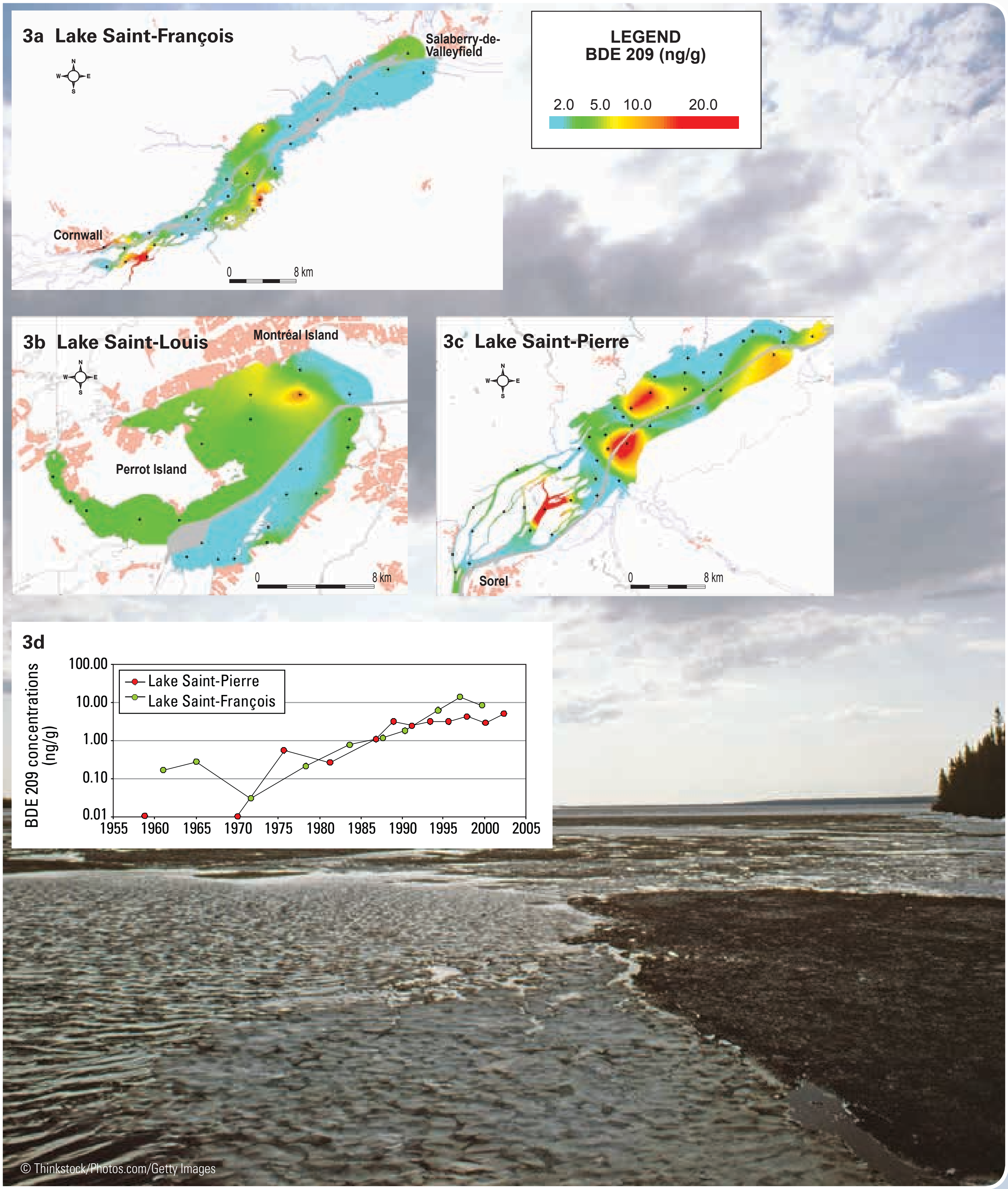


Figure 3 **Spatial distribution of BDE 209 in surface sediments of fluvial lakes**



Temporal evolution of PBDE concentrations

Suspended matter in the water

The temporal evolution of PBDE concentrations observed in the suspended matter at the Québec station between 1995 and 2008 is presented in Figure 1b. During these years, the concentrations of ∑PBDE and BDE 209 went from approximately 10 ng/g to 7 ng/g and from 10 ng/g to 50 ng/g in the waters of the St. Lawrence River. The highest concentrations were observed in November 1999 for ∑PBDE with 22 ng/g, and in April 2008 for BDE 209 with 218 ng/g. These results show that the PBDE concentrations remained relatively stable for ∑PBDE, unlike the concentrations of BDE 209, which increased quickly. This divergence in the evolution of the concentrations of different congeners again suggests that the PBDE inputs in the river come from several sources.

The monthly variations in the median values of ∑PBDE and BDE 209 (Figure 1c) tend to confirm the hypothesis that BDE 209 and the other PBDEs come from distinct sources or at least have a different geochemical behaviour. The median concentrations of ∑PBDE are higher in colder periods (fall and winter) and lower during the hottest period whereas the median concentrations of BDE 209 are high during winter and reach their lowest values in winter. The work of Gouin and Harner (2003) shows that the PBDEs are more volatile in warm weather than in cold weather, that they are affected by light and that vegetation may be a significant confounding factor. Thus, in the St. Lawrence River, the winter concentrations of ∑PBDE are high, probably due to the cold water temperature that leads to low volatilization, and because of the ice cover and a lower dilution of concentrations because of limited erosion processes during winter. During the warmer period, concentrations are lower, probably because of the effect of the spring dilution. Then, during the summer, there is probably a stronger volatilization. The behaviour of BDE 209 is the opposite, which seems to confirm that the sources of the PBDEs are different. Thus, it is possible that the increase in concentrations during the warm months is linked to a greater atmospheric input during summer, an input that is limited in the winter because of the snow and ice cover.

Sediments in the fluvial lakes

The temporal evolution of PBDE concentrations in the sediments in Lake Saint-François and Lake Saint-Pierre is presented in Figures 2e and 3d. The results show a precipitous increase in PBDE concentrations since the beginning of the 1980s for ∑PBDE, and since the beginning of the 1970s for BDE 209. In 2000, the median concentrations of ∑PBDE and BDE 209 were 0.7 ng/g and 7.6 ng/g in Lake Saint-François and 2.4 ng/g and 3.9 ng/g in Lake Saint-Pierre, respectively. Thus, the concentrations of ∑PBDE were at least 3.0 times higher in Lake Saint-Pierre than in Lake Saint-François, whereas the concentrations of BDE 209 were 4.0 times higher in Lake Saint-François than in Lake Saint-Pierre. These results suggest that there is a relatively significant input of congeners other than BDE 209 between Lake Saint-François and Lake Saint-Pierre, thus connecting them firmly with the urban outfalls of the city of Montréal and its northern suburbs. The low variation of BDE 209 between the two lakes suggests that the input of this congener to the St. Lawrence River sediments is different from that of the other PBDEs, thus confirming the observations made regarding the suspended matter.

Key Measures

Regulations and guidelines for PBDEs

Several voluntary reduction initiatives and new regulations made it possible to initiate a relatively important change in the use of PBDEs since 2001. The manufacturing, import, use and sale of the commercial products pentaBDE and octaBDE have been prohibited in Canada since 2008, thus meeting the virtual elimination criteria of the *Canadian Environmental Protection Act, 1999*. More than a dozen American states have prohibited pentaBDE and octaBDE, and a few states have even prohibited decaBDE in the aim of voluntarily eliminating it before the end of 2012. The European Union reacted promptly to the danger represented by PBDEs by prohibiting pentaBDE and octaBDE in 2004 and by limiting the concentration of PBDEs in electrical and electronic equipment.

In general, it is difficult to evaluate the impact of a contaminant on aquatic fauna in the absence of quality criteria. Long ecotoxicological studies and environmental data gathering are needed to develop quality criteria for sediments. However, an initial guideline for PBDEs was established in 2010 by Environment Canada's National Guidelines and Standards Office (CMP, 2011). This guideline includes the guide concentrations for the following congeners: BDE 28 (43.1 ng/g), BDE 47 (39.4 ng/g), BDE 99 (0.38 ng/g), BDE 100 (0.35 ng/g), BDE 153 (436 ng/g) and BDE 209 (18.9 ng/g). These values were derived based on the observed effects on fish and may serve as a basis for the evaluation of the quality of sediments and suspended matter, but must not be considered as quality criteria for the protection of benthic organisms. Detailed studies on chronic and acute effects should be performed in order to be able to derive criteria for the aquatic environment.

Outlook

PBDEs are increasingly present in the aquatic system of the St. Lawrence River. Since 1995, the concentrations of BDE 209 have increased five-fold in the suspended matter at Québec, and since 1985, they have doubled in the sediments of fluvial lakes. At Québec, the highest concentrations of BDE 209 in suspended matter were observed in spring and summer, whereas the highest concentrations of the other PBDE congeners were observed in winter. The analytical results observed in surface sediments of Lake Saint-Pierre and Lake Saint-Louis and in the suspended matter at the Lavaltrie and Québec stations show a significant input of PBDEs in the St. Lawrence River stemming from the urban outfalls of Montréal and its northern suburbs. Currently the most contaminated sediments are found in Lake Saint-Pierre, where they reach a contamination level similar to those observed in the Great Lakes. The input of PBDEs other than BDE 209 into the river probably comes from the outfalls in the Montréal and Laval islands and in Montréal's northern suburbs. The BDE 209 input cannot be explained only by the input of these outfalls. The results suggest the presence of other sources that bring very fine organic particles. The seasonal geochemical behaviour of BDE

209 leads us to believe that this source may be partially atmospheric in nature. However, it is possible that a significant amount of fine and organic particles comes from the Great Lakes Basin, as seen in the results obtained in Lake Saint-François. The results show the scope of the PBDE contamination of suspended matter and sediments in the St. Lawrence River and suggest that significant amounts of PBDEs are carried to the St. Lawrence Estuary.

In light of these results, it appears essential to continue monitoring the PBDEs at different stations for the water component of the St. Lawrence River. In addition, the high concentrations of PBDEs observed in the suspended matter at Lavaltrie and in the sediments in Lake Saint-Pierre point to the need to continue documenting knowledge regarding the freshwater reach between Montréal and Lake Saint-Pierre. Sampling sediments along the freshwater reach will make it possible to draw up a description of sediment PBDE concentrations and, what is more, will make it possible to sample the suspended matter in the plume of the Montréal outfall for a year so as to document the seasonal variations and estimate the importance of this PBDE source.

To Know More

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State of the St. Lawrence Monitoring Program

Four government partners – Environment Canada, Fisheries and Oceans Canada, Parks Canada Agency, and the Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs du Québec – and 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 evolution. To this end, environmental indicators have been developed on the basis of data collected as part of each organization's ongoing environmental monitoring activities.

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 Web site at **www.planstlaurent.qc.ca**.

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Aussi disponible en français sous le titre : *Les polybromodiphényl-éthers (PBDE) dans les matières en suspension et les sédiments du fleuve Saint-Laurent*