

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231291240>

Sources and Fluxes of Mercury in the St. Lawrence River

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · FEBRUARY 1999

Impact Factor: 5.33 · DOI: 10.1021/es980400a

CITATIONS

56

READS

21

5 AUTHORS, INCLUDING:



Bernadette Quemerais

University of Alberta

25 PUBLICATIONS 309 CITATIONS

SEE PROFILE



Daniel Cossa

University Joseph Fourier - Grenoble 1

176 PUBLICATIONS 3,727 CITATIONS

SEE PROFILE

Sources and Fluxes of Mercury in the St. Lawrence River

BERNADETTE QUÉMERAIS,[†]
 DANIEL COSSA,^{*,‡} BERNARD RONDEAU,[†]
 THANH T. PHAM,[†]
 PIERRE GAGNON,[†] AND BENOÎT FORTIN[†]
*St. Lawrence Centre, Environment Canada, 105 McGill,
 Montréal, Quebec, H2Y 2E7, Canada, and Institut français de
 recherche pour l'exploitation de la mer (Ifremer), BP 21105,
 F.44311 Nantes Cedex 3, France*

A mass balance approach, based essentially on the reconstruction of daily fluxes and circumscribed by strict error calculations, was designed to quantify the main mercury sources for the St. Lawrence and its tributaries, which constitute a large river system. High-frequency samplings were performed over an 18-month period (1995–1996) at the main water inputs and the mouth of the river. Minor tributaries and the Montreal effluent were also sampled. This strategy allowed models to be obtained that relate mercury concentrations in solution and in particles to the hydrological regime. The calculated budget was balanced relative to the calculated errors of the estimates. Gross mercury export from the river was found to be 5.9 kmol yr^{-1} (73% as particulate). Tributaries and internal erosion of the river contributed equally for a total of 75% of this gross load, whereas the Upper St. Lawrence River, which is almost exclusively composed of Lake Ontario waters, accounted for less than 10%, and inventoried anthropogenic point sources accounted for about 5%. Dissolved mercury was mainly from north shore tributaries, and particulate mercury was largely from erosion of the river bed and banks. On the basis of the present results as well as estimates of atmospheric deposition from the literature it can be inferred that at least 88% of deposited mercury was retained in the watersheds.

Introduction

Chemical mass balances are useful tools for estimating the relative importance of contamination sources in an aquatic system. They provide complementary information to the monitoring of concentration levels and trend analyses of chemical contaminants for assessments of the quality of aquatic environments. The significance of the data provided by this method is limited by existing knowledge of the biogeochemical cycle of the substance or element of interest, which is crucial to working out the main sources and sinks. Current understanding of the mercury cycle in continental waters is sufficiently developed to permit reasonable global, regional, or local mass balance calculations (e.g., refs 1–4). The factor limiting the quality of the information is the accuracy and associated error in estimations of various fluxes, which depends on taking natural and man-made variability

into account and using adequate statistical techniques. In rivers, rapid changes in water discharges make it difficult to obtain a representative data set for annual flux calculations. Short floods and unforeseeable storm events often constitute a large part of the annual transport of suspended particulate matter and associated chemicals (e.g., ref 5). This is particularly true for small drainage basins under temperate and oceanic climatic conditions. In colder environments, where the temperature remains below 0 °C for several months, the effect of precipitation variations is smoothed within a prolonged melting season. In addition, the large size of the watersheds, due to an increase in water and sediment retention times, lessens the effects of abrupt water pulses. In these latter cases, it is reasonable to suppose that precise mass balance calculations can be performed. Such was the purpose of this tentative mercury budget, which has been designed on the scale of one of the world's largest drainage areas, the St. Lawrence River basin ($1.34 \times 10^6 \text{ km}^2$). Because of the variety in the geology, superficial deposits, and land use of the different subunits of the drainage basin, this study may be regarded as an experimental model which could eventually be generalized to other large riverine systems of the sub-boreal and cold-temperate regions.

This study provides time-series data on mercury in waters and suspended particles of the St. Lawrence River system that allow rating curves (relationships between Hg concentrations and water or solid discharge) to be determined in major water bodies. The rating curves and flow-weighted concentrations were used for flux calculations, and error estimations were computed using a combination of classical parametric methods and bootstrap techniques. This budget, which balances within two standard errors of the estimate, allows the major mercury sources for both dissolved and particulate species to be identified and quantified.

Environmental Setting

The St. Lawrence River ranks 13th in the world for its watershed surface area and 15th for its mean annual discharge (6). It drains a basin comprising the crystalline rocks of the Canadian shield on the north shore and carbonated material deposited as Champlain Sea sediments during the last marine invasion on the south shore. While the north shore tributary basins are occupied by forest, the banks of Lake Ontario and the St. Lawrence River are largely used for agriculture. The chemical characteristics of the waters are strongly controlled by the geology of the catchment basins (7, 8). The water of the tributaries draining the Canadian shield has very low dissolved major ions and high iron and dissolved organic carbon concentrations. Waters from Lake Ontario and the tributaries from the south shore are more mineralized but differ with respect to their particulate matter content. The Upper St. Lawrence River waters at Cornwall have the typical composition of the outflow of Lake Ontario for numerous chemical compounds (7, 8). At that point, the waters are crystal clear, since the lake constitutes a sedimentary basin, whereas the south shore tributaries carry high sediment loads. In addition, the bed and banks of the St. Lawrence River itself are currently eroding and are thought to constitute the largest source of the suspended particulate matter transported downstream (9). The main urban and industrialized areas are located around the Great Lakes and in the Montreal area. The total population of the basin is around 40 million inhabitants, with 5 million in the St. Lawrence River valley itself, mainly concentrated in Montreal and its suburbs. Human activities on the watershed have deteriorated the water quality of the river (10). Until the mid-1970s, the St.

* Corresponding author phone: (33) 2 40 37 41 76; fax: (33) 2 40 37 40 75; e-mail: dcossa@ifremer.fr.

[†] St. Lawrence Centre.

[‡] Ifremer.

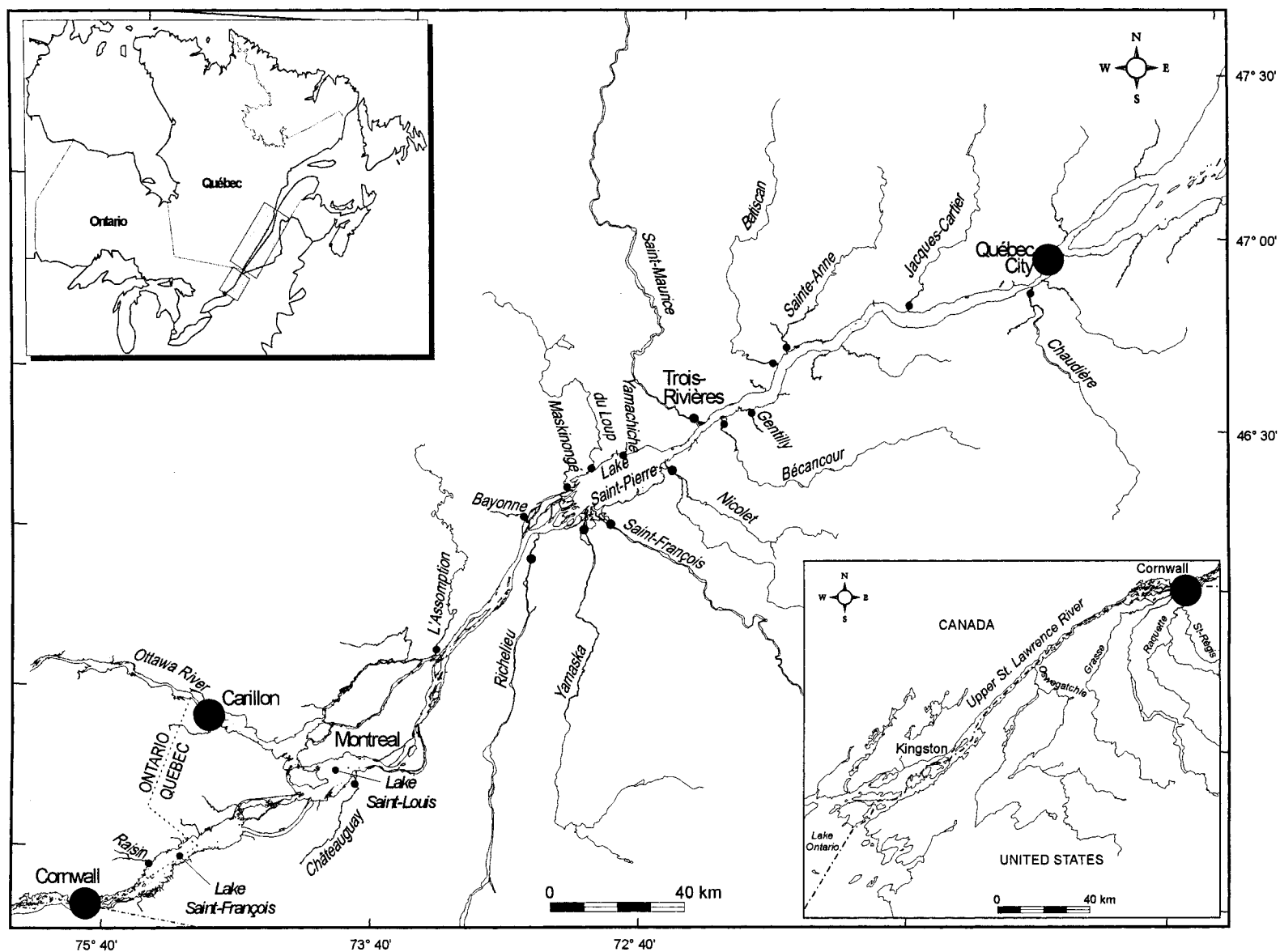


FIGURE 1. The St. Lawrence River drainage basin. Dots are for the main stations sampled for the determination of dissolved and particulate mercury (Cornwall, Carillon, Quebec City, St. Maurice, and the municipal sewage effluent of the city of Montreal). Minor tributaries indicated on the figure have been sampled only for particulate mercury determinations.

Lawrence River received mercury mainly from effluents of chlor-alkali plants. Government regulations and plant shut-downs reduced the direct discharge of mercury effluents into Canadian waters 10-fold between 1975 and 1985 (11). This trend is reflected in the sediment profiles of Lake St. Louis and downstream in the Laurentian Trough (12, 13) where surface sediments are considerably less contaminated than layers deposited during the 1960s and 1970s.

Methodology. Sample Collection and Analysis. Surface water samples were collected at three stations along the river (Figure 1): (i) Cornwall, representing the water mass from the Upper St. Lawrence River (almost exclusively composed of Lake Ontario waters); (ii) Carillon, at the mouth of the Ottawa River, the major St. Lawrence tributary; and (iii) Quebec City, the furthest downstream point before the water becomes brackish. The first two stations were sampled on a twice-monthly basis and the last one weekly from spring 1995 to fall 1996. In addition, the effluent of the wastewater treatment plant of the Montreal Urban Community (MUC) was sampled once a month from late spring 1995 to spring 1996 and then twice a month from spring 1996 to spring 1997. The St. Maurice River was sampled at its confluence with the St. Lawrence River three times in spring 1995 and twice a month from July to October 1996. Analysis of the particulate phase was also carried out on samples collected during spring 1995 in minor tributaries at their confluence with the St. Lawrence River.

Water samples were collected with a pneumatic all-Teflon pump (ASTI, PSP-2) and filtered through 0.5- μ m Teflon filters (LCR membranes from Millipore) under a laminar flow hood. Filtrates were collected in Teflon bottles, acidified (HCl 1% v/v, Seastar), and kept in two polyethylene bags until analysis. All material in contact with samples was acid-washed and rinsed beforehand. Filtrates were analyzed using the BrCl and SnCl₂ method described by Bloom and Creclius (14) for total filtered (HgD) mercury determination. Particulate Hg (HgP) was determined after digestion of the material on filters using HNO₃:HCl (9:1 v/v) in Teflon reactors (90 °C; 3 h). Mercury was determined by atomic fluorescence detection (AFS-Merlin, PSA analytical Ltd.) after preconcentration by gold amalgamation (15). Accuracy for HgP determinations was checked regularly using Certified Reference Material from the National Research Council of Canada (BEST-1). For HgD, an intercomparison exercise was performed in conjunction with Frontier Geosciences (Seattle, WA), the University of Connecticut (Groton, CT), and the University of Maryland (Solomon, MD) on a freshwater sample. These results were consistent and have been detailed in a previous report (16). Reproducibility was below 10% for both phases. Detection limits (3 SD of the blank), calculated for each day of analysis, ranged from 0.05 to 0.5 pM for filtered water and from 0.01 to 0.1 nmol·g⁻¹ for the particulate phase. The sampling and analytical methods have been fully detailed elsewhere (15, 16). Ancillary parameters, i.e., suspended particulate matter (SPM) and dissolved (DOC) and particulate organic carbon (POC), were obtained using standard methods described elsewhere (8).

Calculation of Fluxes. Instantaneous fluxes F_i were determined using $F_i = C_i Q_i$, where C_i is the instantaneous concentration and Q_i the instantaneous discharge. In theory, the total flux over a given period of time t is the integration of instantaneous fluxes F_i , which would require continuous determination of both discharge and concentration. As this is difficult to perform, especially for trace elements such as mercury, total flux is generally estimated. Various calculation methods are available in the literature (17–20) which, together with the errors (precision and accuracy) associated with the estimation of fluxes, have been intensively discussed (19, 21, 22). Meybeck (22) recommends the use of a rating

TABLE 1. Equations Used for Mercury Flux Calculations C_i Is the Daily Mercury Concentration Q_i the Daily Water Discharge, M_i the Daily Suspended Particulate Matter Concentration, and \bar{Q} and \bar{M} Are the Mean Annual Water and Solid Discharges

	flux		variance	
	dissolved	particulate	dissolved	particulate
Cornwall	$C_i = 1.15 \times 10^{-7.91} \sum_{j=1}^{366} C_j Q_j$	$Q_i^{2.06} \bar{Q} \sum_{j=1}^n C_j M_j Q_j / \sum_{j=1}^n Q_j$	$\sigma^2_{\text{bootstrap}} \quad (25)$	$((n - m)/n) [\overline{OM^2} / (\sum_{j=1}^n Q_j M_j)^2] [\sum_{j=1}^n (Q_j M_j)^2 \sigma_C^2 + \sum_{j=1}^n (Q_j C_j)^2 \sigma_M^2]$
Carillon	$C_i = 1.41 + 0.0011 Q_i$	$C_i = 10^{-0.075 M_i - 0.22} \sum_{j=1}^{366} C_j M_j Q_j$	$\sigma^2_{\text{bootstrap}} \quad (25)$	$\sigma^2_{\text{bootstrap}} + ((n - m)/n) [\text{flux} / (\sum_{j=1}^n Q_j M_j C_j)]^2 \sum_{j=1}^n Q_j^2 \sigma_{MC}^2$
Quebec City	$C_i = 1.15 \times 10^{-10.16} Q_i^{2.59} \sum_{j=1}^{366} C_j Q_j$	$\bar{Q} \sum_{j=1}^n C_j M_j Q_j / \sum_{j=1}^n Q_j$	$\sigma^2_{\text{bootstrap}} \quad (25)$	$((n - m)/n) [\overline{OM^2} / (\sum_{j=1}^n Q_j M_j)^2] [\sum_{j=1}^n (Q_j M_j)^2 \sigma_C^2 + \sum_{j=1}^n (Q_j C_j)^2 \sigma_M^2]$
St. Maurice River	$\bar{Q} \sum_{j=1}^n C_j Q_j / \sum_{j=1}^n Q_j$	$\bar{Q} \sum_{j=1}^n C_j M_j Q_j / \sum_{j=1}^n Q_j$	$((n - m)/n) [\bar{Q}^2 \sum_{j=1}^n Q_j^2 / (\sum_{j=1}^n Q_j)^2] \sigma_C^2$	$((n - m)/n) [\overline{OM^2} / (\sum_{j=1}^n Q_j M_j)^2] [\sum_{j=1}^n (Q_j M_j)^2 \sigma_C^2 + \sum_{j=1}^n (Q_j C_j)^2 \sigma_M^2]$
MUC effluent	$\bar{Q} \sum_{j=1}^n C_j Q_j / \sum_{j=1}^n Q_j$	$\bar{Q} \sum_{j=1}^n C_j M_j Q_j / \sum_{j=1}^n Q_j$	$((n - m)/n) [\bar{Q}^2 \sum_{j=1}^n Q_j^2 / (\sum_{j=1}^n Q_j)^2] \sigma_C^2$	$((n - m)/n) [\overline{OM^2} / (\sum_{j=1}^n Q_j M_j)^2] [\sum_{j=1}^n (Q_j M_j)^2 \sigma_C^2 + \sum_{j=1}^n (Q_j C_j)^2 \sigma_M^2]$

^a Expressed per unit of volume dissolved and per unit of solid for particulate. ^b n is the number of days, m is the number of measurements of the studied period, and σ_C^2 , σ_M^2 , and σ_{MC}^2 are the variances of the m measurements.

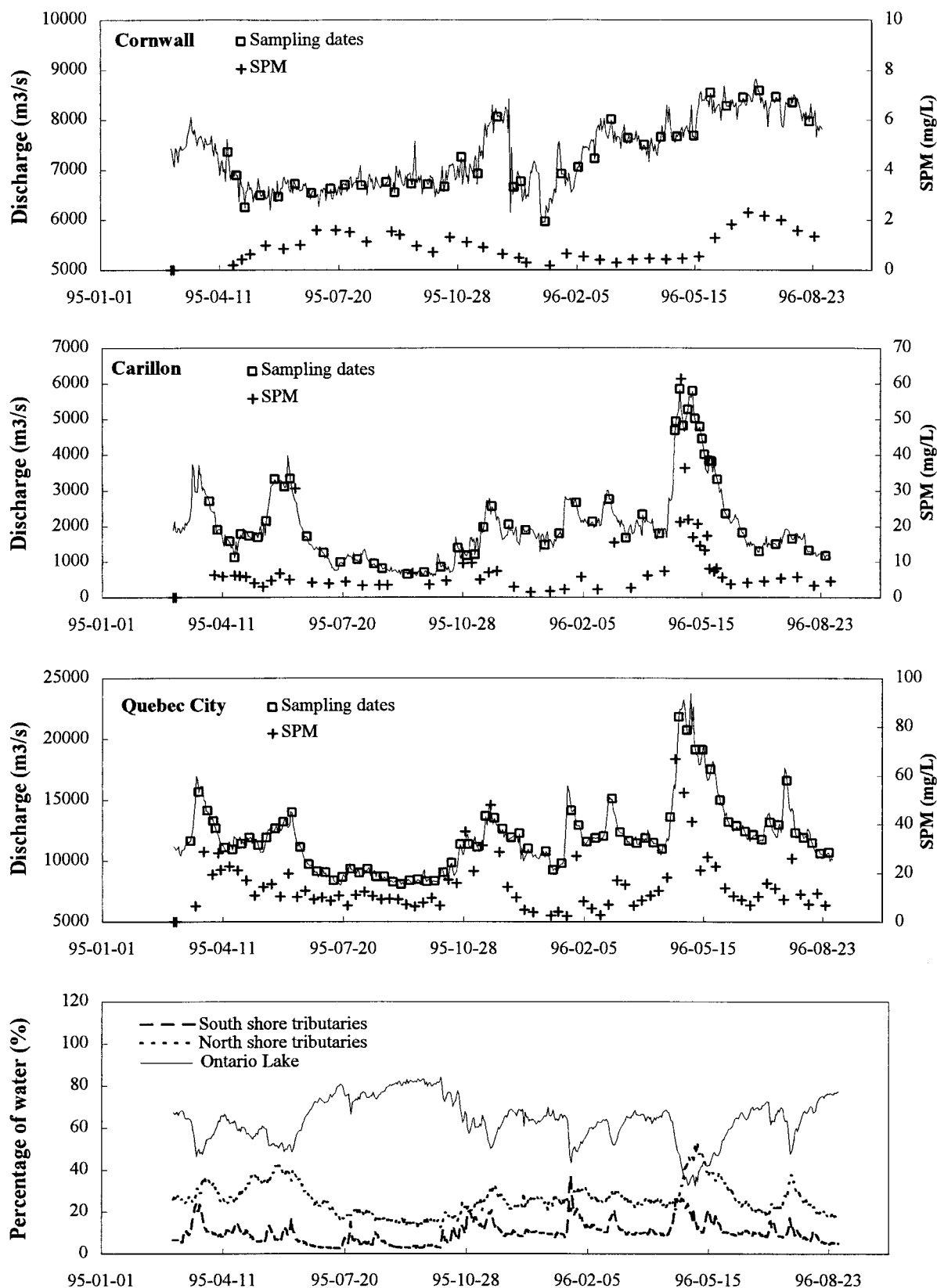


FIGURE 2. Variations of water discharge and suspended particulate concentrations (SPM) at the main sampling stations.

curve for both dissolved and particulate contaminants, provided that the relationship between solute or suspended particulate matter and discharge is well-known. In general, the concentrations of these contaminants are a power function of discharge. In some cases, linear regressions may be used since they give a better fit with data. However, it has been found that the use of rating curves underestimates real

fluxes (19, 23, 24), requiring the use of bias correction factors (23, 24). Cohn (24) determined that all of these methods lead to the same result if the regression model is correct and if it has been calibrated with a large range of data. For data in our study, mercury fluxes were estimated using the equations provided by Ferguson (23) and Bradu and Mundlack (25). These two methods gave similar results (a difference of less

TABLE 2. Average, Standard Deviation, Number of Samples and Range of Variation of Mercury Concentrations in Water Samples Collected from the St. Lawrence River, the Ottawa River, the St. Maurice River, and the MUC Waste Water Treatment Plant Effluent between March 1995 and September 1996

	filtered Hg (pM)				particulate Hg (nmol g ⁻¹)			
	mean	SD	range	n	mean	SD	range	n
Cornwall	1.3	0.9	0.4–5.8	39	1.1	0.5	0.3–2.6	39
Carillon	4.0	2.3	0.8–10.2	53	0.6	0.2	0.2–1.1	56
Quebec City	3.0	2.3	0.5–12.9	81	0.7	0.3	0.2–1.5	79
St. Maurice River ^a	8.8	3.0	2.5–13.2	11	2.4	1.4	0.6–5.2	11
MUC effluent ^b	10.9	4.8	5.2–22.0	27	3.9	1.5	0.8–8.4	29

^a The St. Maurice River was sampled in spring 1995 and from July to October 1996. ^b The MUC effluent was sampled from spring 1995 to spring 1997.

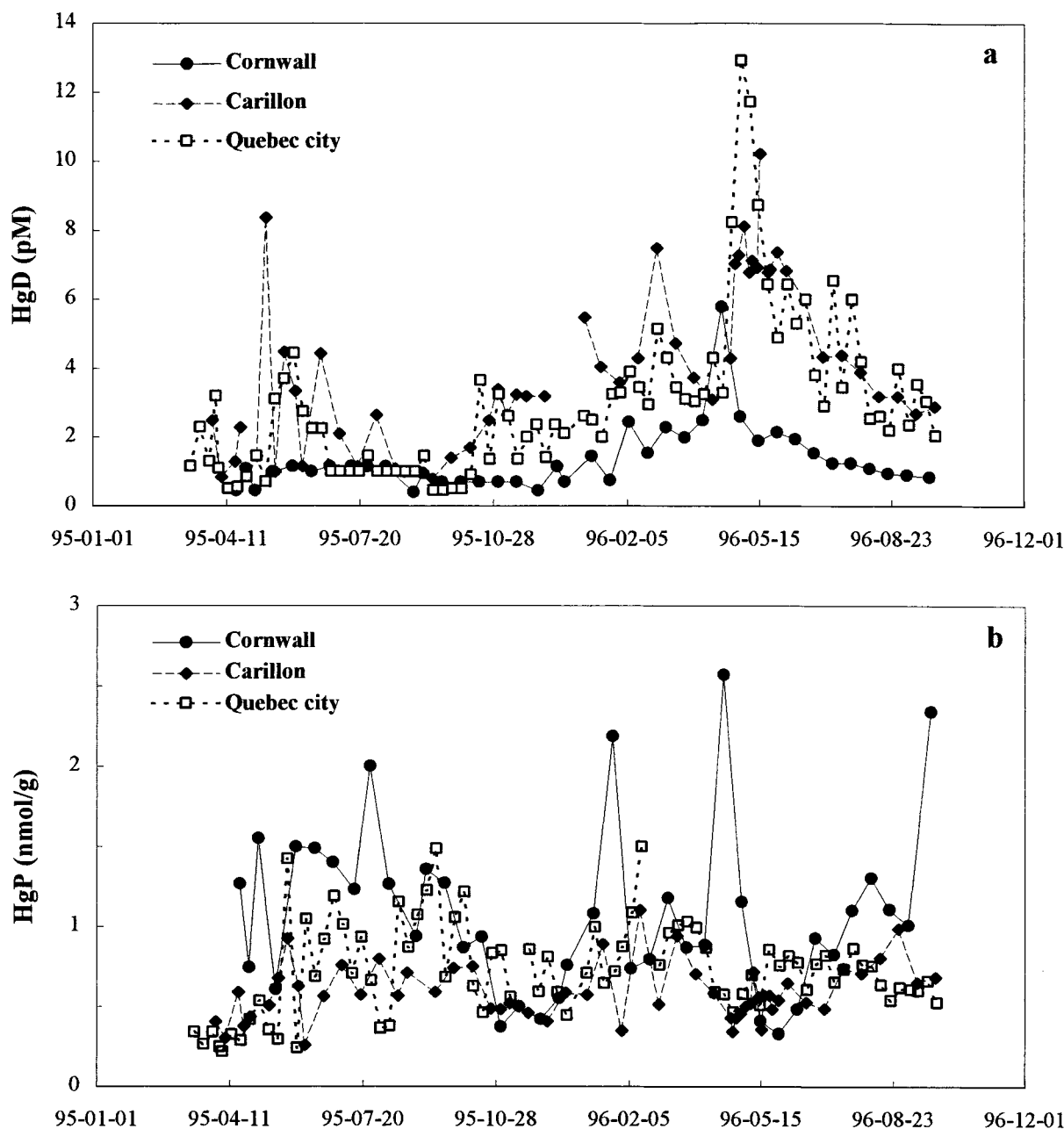


FIGURE 3. Time variations of dissolved (HgD) and particulate mercury (HgP) concentrations at the main sampling stations. The transit time for water between Cornwall and Quebec City is 3–4 days (8).

than 10%), which is indicative of the accuracy of the regression models. Another type of calculation, based on flow-weighted concentrations, was used for stations that showed no relationship between HgD concentrations and water dis-

charge or HgP and suspended particle concentrations. All equation fluxes are shown in Table 1. Load estimate standard errors were computed using a combination of classical parametric methods and bootstrap techniques (26). Sampling

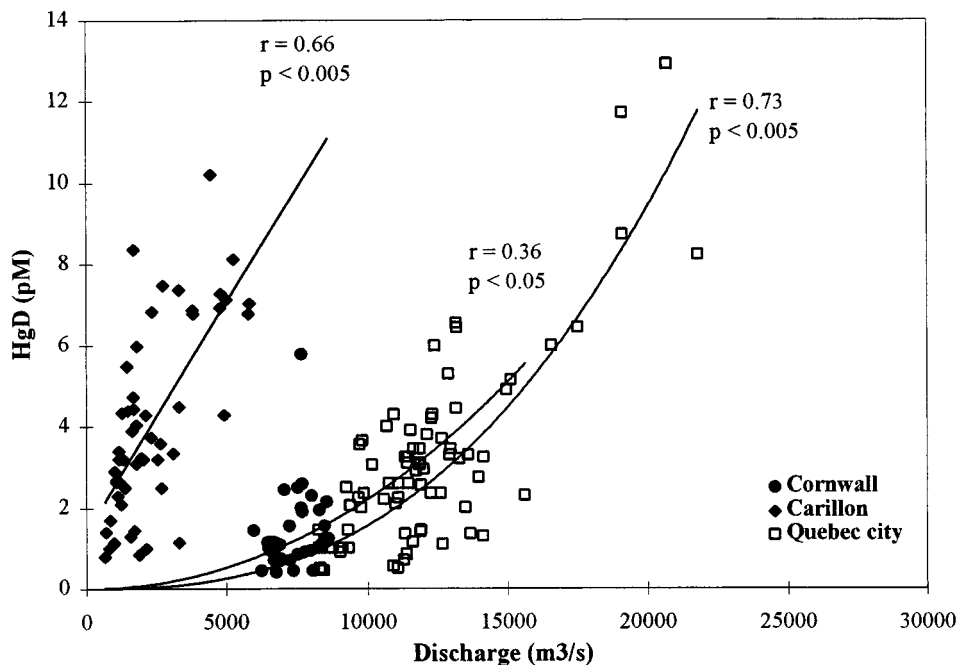


FIGURE 4. Relationships between dissolved mercury (HgD) and water discharge at the main sampling stations. The equations of the best fit models are given in Table 1.

variability and uncertainty in regression model estimates are reflected in these standard errors (Table 1).

Results and Discussion

Variation of Water Discharge. The hydrological regimes for the St. Lawrence River and its tributaries are those of a temperate/boreal climate, i.e., influenced by the spring snowmelt and autumn rains. However, as a result of flow regulation upstream at the Moses-Saunders Dam, the water discharge from the Upper St. Lawrence River at Cornwall shows only a few variations (Figure 2). Discharge of the main tributary, the Ottawa River, at Carillon is more seasonally marked (Figure 2). At Quebec City and the mouth of the St. Lawrence River, the discharge is the result of a mixture of tributary inputs (Figure 2). The influence of the north shore tributaries is evident, especially in spring when they account for up to 50% of the total discharge of the river (Figure 2). Our procedure allowed representative sampling of the various discharge situations encountered at the three stations. In particular, all flood situations were adequately sampled (Figure 2).

Variation of Suspended Particulate Matter Discharge. Variations in SPM concentrations measured during the sampling period at Cornwall, Carillon, and Quebec City are shown in Figure 2. High SPM concentrations were observed at Carillon and Quebec City during the spring and fall. SPM concentration levels in the outflow waters of Lake Ontario were very low. The higher concentrations at Quebec City indicate that other SPM sources probably exist within the river. A recent study of suspended particulate transport in the St. Lawrence River (9) found that the Upper St. Lawrence River contributes only 2% of the sediment load of the river and the north and south shore tributaries 13 and 19%, respectively. The evidence provided by these authors indicates that 65% of the suspended load in the St. Lawrence River originates from erosion of its bed and banks.

Mercury in Filtered Water Samples. Summary statistics on mercury concentrations in filtered samples (HgD) at the three sampling stations are shown in Table 2. Average concentrations were significantly ($p > 0.001$) higher at Carillon than at Quebec City and Cornwall. The low average concentration of HgD at Cornwall was the same as that

observed for Lake Michigan (the only other source of data for the same drainage basin) where concentrations ranged from 1.15 to 1.90 pM (27). Higher HgD concentrations were found for the Ottawa River (Carillon) and the St. Maurice River, which, like the other north shore tributaries of the St. Lawrence River, drain boreal forest soils (Table 2). In a previous paper (16), we considered the significance of these observed differences and discussed the biogeochemical behavior of mercury in relation to iron, manganese, and organic carbon dynamics. We concluded that Hg is probably stabilized in solution by complexation or sorption with dissolved and/or colloidal humic-hydrous oxide associations (16).

The temporal variations of HgD for the three main stations showed the lowest concentrations during low water months, with peaks corresponding to flood periods (Figure 3a). Higher Hg concentrations have also been found during flood events in Wisconsin rivers (28). At the exit of the system (Quebec City) the high concentrations measured during the flood (Figure 3a) were associated with a larger proportion from tributary waters, which represented up to 50–70% during the spring runoff (Figure 2).

At the Cornwall, Carillon, and Quebec City stations, HgD was correlated with water discharge (Figure 4). With increasing flow, a positive relationship between dissolved element concentrations is uncommon. Dilution at high discharge is the usual situation when the source of the solute is rock weathering (21). A “concentration effect” at high discharge is occasionally found for compounds and for rivers in which solute concentration is low and atmospheric fallout is the dominant source (e.g., ref 29), which is the case for mercury in the St. Lawrence River basin. Indeed, seven snow samples collected in Montreal during the winter of 1996 gave a mean total mercury concentration of 32.9 pM (SD: 14.5 pM), and rain samples collected in the Quebec region in 1995 and 1996 showed a mean total mercury concentration of 34.9 pM (30). These concentrations are 1 order of magnitude higher than those in the St. Lawrence or Ottawa River.

Particulate Mercury. Particulate Hg concentrations (HgP) were significantly different ($p < 0.001$) from one station to another. Upper St. Lawrence River water gave the highest concentrations, and the Ottawa River the lowest (Table 2).

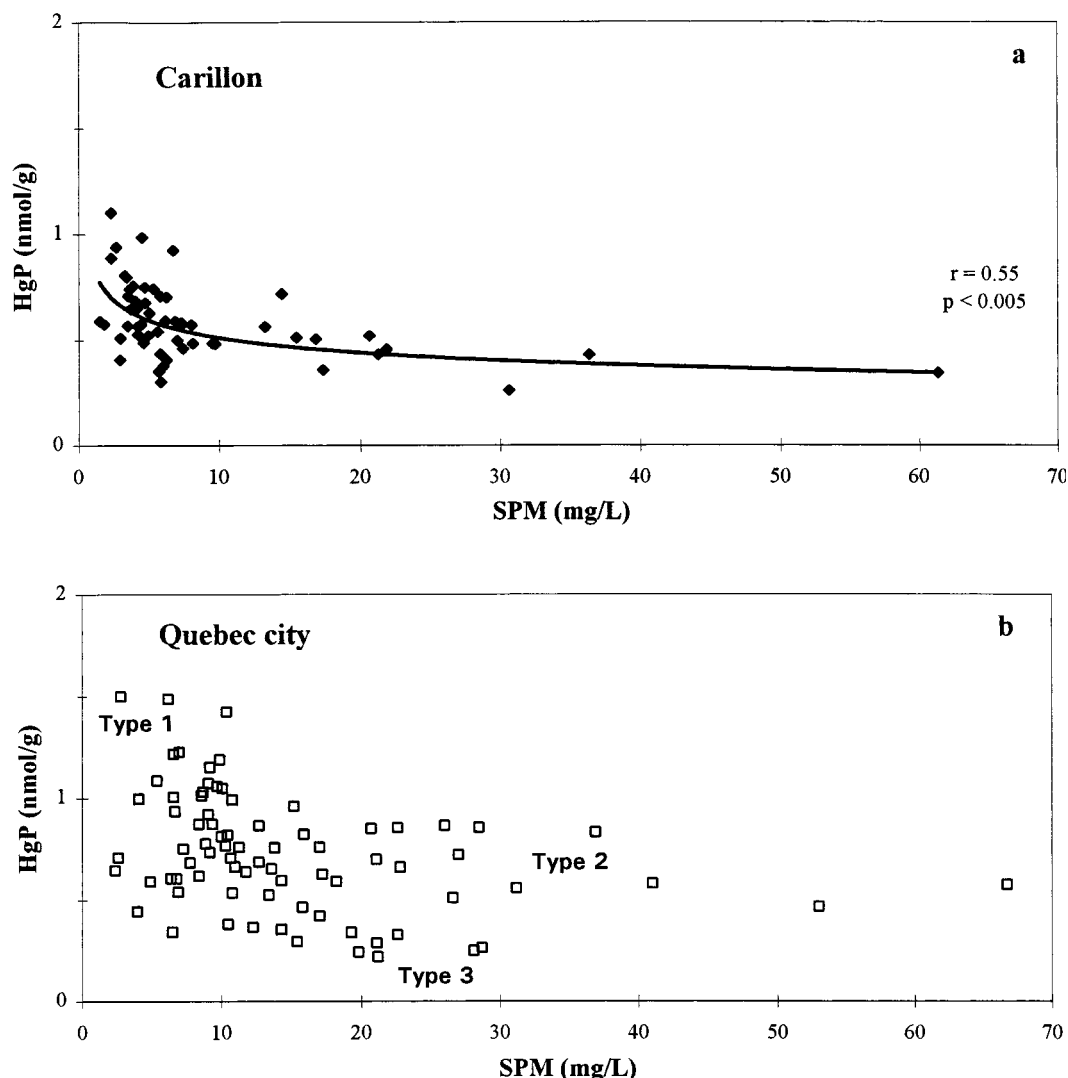


FIGURE 5. Relationships between particulate mercury (HgP) and suspended particulate matter (SPM) at Carillon and Quebec City. The equation of the best fit model is given in Table 1.

Particles at Quebec City showed intermediate concentrations. HgP in particles from the Upper St. Lawrence River was in the upper range of concentrations measured in Lake Michigan [$0.4\text{--}1.1\text{ nmol g}^{-1}$ according to Mason and Sullivan (27)]. These relatively high mercury concentrations may result from the very small size and high organic content of the particles outflowing from Lake Ontario via the Upper St. Lawrence River (8).

Time variations of mercury in particles from the three stations showed a trend toward low concentrations during high discharge periods, i.e., spring and fall (Figure 3b). In addition, at Carillon and Quebec City, particulate mercury concentrations decreased with increasing particulate matter concentrations (Figure 5). At Carillon, the relationship followed a significant power function (Figure 5a). A close examination of Figure 5b shows that the dilution-type relationship between HgP and the SPM concentration at Quebec City was probably the result of a variable mixture of particles from different origins. Mercury-rich particles ($0.8\text{--}1.5\text{ nmol g}^{-1}$, associated with the high organic and manganese fraction (16); type 1 according to Figure 5b) were diluted by particles characterized by a medium mercury content ($0.6\text{--}0.8\text{ nmol g}^{-1}$, type 2 according to Figure 5b) or by mercury-poor particles ($0.2\text{--}0.4\text{ nmol g}^{-1}$, type 3 according to Figure 5b). Type 2 particles had a mercury composition close to that of tributary flood particles (Tables 2 and 3 and Figure

5a), and type 3 particles reflected the composition of the earth's crust or uncontaminated sediments accumulated in the St. Lawrence Trough before the industrialized era (13). The former were observed when the proportion of SPM from tributaries was maximum, and the latter when the ancient marine sediments eroded from the St. Lawrence River bed (9) were predominant.

Budget. The mercury budget for the St. Lawrence River is based on calculated and estimated fluxes from data in the literature (Table 4). The calculated values are from three origins: (i) the main sources (the Upper St. Lawrence River and the Ottawa River, Table 2) and the sink (the St. Lawrence estuary, Table 2), as monitored on a high-frequency basis; (ii) low-frequency measurements (the St. Maurice River and the Montreal Urban Community sewage effluent, MUC, Table 2); and (iii) discrete measurements of HgP performed for minor tributaries (Table 3). High- and low-frequency measurements provided the data for calculations based on the equations in Table 1. The HgP flux calculations for minor tributaries are from Table 3. Other fluxes are estimates from data in the literature given in the caption of Table 4.

The estimated fluxes for anthropogenic sources, erosion, and air/water exchanges require special comment. The calculated fluxes of the MUC wastewater plant were 0.01 and 0.08 kmol yr^{-1} for dissolved and particulate mercury, respectively, accounting together for 1.5% of the total mercury

TABLE 3. Particulate Mercury Concentrations, Estimated Particulate Matter Annual Loads and Estimated Particulate Mercury Loads from Northern and Southern Tributaries of the St. Lawrence River

	SPM loads (10 ³ t yr ⁻¹)	HgP (nmol g ⁻¹)	Hg loads (mol yr ⁻¹)
North shore			
St. Maurice	108 ^a	model (Table 1)	300
Ottawa River	435 ^a	model (Table 1)	270
Raisin	0.02 ^b	0.7	0.01
Rivière du Loup	2.5 ^b	0.6	1.5
Assomption	82 ^a	0.8	65.6
Yamachiche	1.1 ^b	0.2	0.22
Maskinongé	2 ^b	1.2	2.4
Bayonne	3 ^b	0.3	0.9
Batiscan	51 ^a	0.9	45.9
St. Anne	62 ^a	0.3	18.6
Jacques Cartier	21 ^a	0.7	14.7
other minor tributaries	136.2 ^a	0.5 ^c	68.08
total	904		788
South Shore			
Raquette	0.06 ^b	1.3	0.08
St. Régis	2 ^b	1.8	3.6
Châteauguay	38 ^a	0.4	15.2
Bécancour	14 ^b	0.6	8.4
Gentilly	1 ^b	0.4	0.4
Chaudière	156 ^a	0.5	78
Nicolet	59 ^a	0.7	41.3
Yamaska	255 ^a	0.4	102
Richelieu	265 ^a	0.9	238.5
St. François	245 ^a	1.6	392
other minor tributaries	246.4 ^a		123.2
total	1281		1003

^a Data from ref 9. ^b St. Lawrence Centre, unpublished data. ^c This value was chosen as the overall average HgP for the entire St. Lawrence River system. ^d The Ottawa and St. Maurice River fluxes were calculated using the model from Table 1, and others by multiplying the annual SPM load by the HgP concentration.

load exported at Quebec City. For estimations of total urban mercury inputs, we chose to double this load. In fact, during

the period of intense rain or snowmelt, the MUC wastewater treatment plant cannot handle all the water arriving at the station, so that a part is rejected directly into the St. Lawrence River without treatment (34). Since the influent wastewaters have high average mercury concentrations (HgD = 16.9 pM, HgP = 548 pM, $n = 27$; St. Lawrence Centre, unpublished data), dissolved mercury inputs from the MUC are probably quite underestimated. In addition, most of the other municipalities along the St. Lawrence River discharge their sewage effluent directly into the waters.

Erosion of the bed and banks is assumed to be the most important single source of particles within the St. Lawrence River between Cornwall and Quebec City, according to Rondeau et al. (9) who found that 4.6×10^6 t yr⁻¹ of suspended sediments at Quebec City originated from river bed and river bank erosion. If we assume an average HgP concentration of 0.3 nmol g⁻¹ for these eroded particles [which corresponds to the background concentration of pre-industrial sediments deposited at the head of the St. Lawrence Trough (13)], a flux of 1.38 kmol yr⁻¹ is obtained (Table 4). This natural input is the largest single source of particulate mercury in the system.

Direct atmospheric deposition on the river surface and evasion were estimated to be smaller than 0.1 kmol yr⁻¹ (Table 4): dissolved load was calculated to be 0.05 kmol yr⁻¹ and particulate load 0.03 kmol yr⁻¹. Evasional flux, when related to Hg supply, was quite low (less than 0.2% of the Hg loading) compared to observations made in lakes (several tens of percents) (40). However, the flux used in the calculation (Table 4) was in the range of evasional fluxes calculated for temperate lakes (40, 41), which is obviously a result of the short residence time of water in the river section studied (less than 5 days according to ref 16).

The present mercury budget in the St. Lawrence River balances within two standard errors of the estimates (Table 4). The main results can be summarized as follows: North and south shore tributaries and internal erosion of the river contribute equally for three-quarters of the total mercury input into the St. Lawrence River. The Upper St. Lawrence River (including Lake Ontario inputs) contributes only 9%, and inventoried direct anthropogenic point sources con-

TABLE 4. Dissolved, Particulate and Total Mercury Fluxes and Standard Errors (SE) from the Various Sources

	dissolved load (kmol yr ⁻¹)	SE	particulate load (kmol yr ⁻¹)	SE	total load (kmol yr ⁻¹)
Upper St. Lawrence River	0.35	0.05	0.21	0.04	0.56
north shore tributaries:					
Ottawa River	0.28	0.01	0.27 ^f	0.03	0.55
St. Maurice River	0.20	0.02	0.30 ^f	0.15	0.50
other rivers	0.12 ^{a,b}		0.22 ^f		0.34
total	0.60		0.79 ^f		1.39
south shore tributaries	0.45 ^{a,c}		1.00 ^f		1.45
net direct atmospheric deposition ^h	0.05		0.03		0.08
erosion			1.38 ^{a,d}		1.38
total urban sewage ^g	0.02	0.002	0.16	0.01	0.18
industries ^e	0.14				0.14
Quebec City	1.62	0.10	4.31	0.34	5.93
difference	-0.01	0.11	-0.74	0.38	-0.75

^a The contributions of the minor tributaries were estimated by multiplying the HgD or HgP concentrations by mean annual water or solid discharges, respectively. ^b Because they drain the same boreal forest soil as the St. Maurice and the Ottawa Rivers, the average HgD concentrations of these two rivers (6.5 pM) were used. ^c A value of 10 pM was chosen for the HgD concentration for the south shore tributaries as it corresponds to the median of the range found for North American rivers from the same latitude running through drainage basins also covered by agriculture and forest (28). ^d Based on an HgP concentration of 0.3 nmol g⁻¹ corresponding to the pre-industrial level in the area (13); see text. ^e Since the shut down of the chlor-alkali plant in May 1995, the known direct industrial mercury discharge of 0.14 kmol yr⁻¹ (35) is assumed to be dissolved. ^f According to Table 3. ^g Twice the MUC fluxes; see text. ^h Wet deposition values were estimated using HgD of 25.9 pM and HgP of 9.0 pM in rain (29), a surface of 1.74×10^9 m² for the St. Lawrence River (36), and a total precipitation of 1.125 m yr⁻¹ (data from Atmospheric Environment Services, Environment Canada). Dry deposition from the vapor phase was estimated in Poissant and Casimir (33). Particulate dry deposition was estimated using a mean particulate mercury concentration of 0.05 pmol m⁻³ (37), the equation described in Eisenreich and Strachan (38), and a deposition velocity of 0.5 cm s⁻¹ (39). Loss of elemental mercury in the atmosphere (5 pmol m⁻² h⁻¹), as estimated by Poissant and Casimir (33), gave an evasion of 0.01 kmol yr⁻¹. ⁱ The Upper St. Lawrence River, Ottawa and St. Maurice Rivers, municipal sewage effluent (MUC) and Quebec City fluxes were calculated using the model from Table 1.

TABLE 5. Mercury Deposition and Evasion in the Watershed

	forested land		agricultural land	
	deposition	evasion	deposition	evasion
wet (pmol m ² d ⁻¹)	224 ^b		110 ^a	
(kmol yr ⁻¹)	19.75 ^{b,e}		1.1 ^{a,e}	
dry (pmol m ² d ⁻¹)	289 ^b	239 ^c	20 ^a	214 ^d
(kmol yr ⁻¹)	25.48 ^{b,e}	21.07 ^{c,e}	0.2 ^{a,e}	2.14 ^{d,e}

^a Wet and dry depositions on open fields were calculated using a mercury level of 35 pM in precipitation (30) and a particulate mercury concentration of 0.05 pmol m⁻³ (37). ^b Wet and dry depositions on forested land were estimated using data from Hultberg et al. (42). ^c Evasion for forested land was estimated using data from Lindberg et al. (43). ^d Evasion for agricultural land was calculated from ref 33. ^e The St. Lawrence River watershed is 269 × 10⁹ m² (8), with 241 × 10⁹ m² as forested land and 27.42 × 10⁹ m² as agricultural land.

tribute around 5%. The proportion of inputs associated with dissolved and particulate phases depends on the sources. The ratios between the particulate and dissolved loads increase in the following order: Upper St. Lawrence River (0.7) < north shore tributaries (1.3) < south shore tributaries (2.2). Essentially, this reflects the relative importance of particulate matter in the various sources. The main source for dissolved mercury in the St. Lawrence River is the north shore tributaries which drain the Canadian shield covered by boreal forest. For particulate mercury, the main source is the erosion of river bed and banks, consisting of Quaternary marine sediments. Even though the atmosphere is the overall main source of mercury for continental waters, this budget indicates that direct atmospheric deposition on the River is quite low, which raises the issue of mercury retention in the watershed.

Mercury Retention in the Watershed. Wet and dry depositions and evasion on the St. Lawrence River watershed were evaluated. The results and the details of the calculation are given in Table 5. For the whole watershed (Great Lakes basin excluded), mercury deposition was estimated to be 46.5 kmol yr⁻¹ and evasion 23.2 kmol yr⁻¹. Thus, net deposition on the watershed is estimated to be 23.3 kmol yr⁻¹. The total mercury (HgD + HgP) flux from north and south shore tributaries was estimated to be 2.8 kmol yr⁻¹ (Table 4), which indicates that at least 88% of the deposited mercury is retained in the watersheds. Humic soil of the boreal forest may actually favor the retention of mercury. In addition, the north shore watershed includes many lakes whose sediments may retain mercury. The value of 88% retention in the watershed is very similar to that calculated for other high latitudinal areas (e.g., refs 42, 44–46).

Acknowledgments

The authors are grateful to M. Arseneau, D. Labonté, B. Isernhagen, D. Many and A. Tremblay for their help in the field and the laboratory, and to L. Lapierre from the Ministère de l'Environnement et de la Faune du Québec for providing samples for the St. Maurice River. This work is a part of the St. Lawrence Action Plan, Vision 2000.

Literature Cited

- Mason, R. P.; Fitzgerald, W. F.; Morel, F. M. M. *Geochim. Cosmochim. Acta* **1994**, *58*, 3191.
- Hudson, R. J. M.; Gherini, S. A.; Watras, C. J.; Porcella, D. B. In *Mercury as a Global Pollutant: Towards Integration and Synthesis*; Watras, C. J., Huckabee, J. W., Eds.; Lewis Publishers: Chelsea, MI, 1994; pp 473–526.
- Fitzgerald, W. F.; Mason, R. P. In *Global and Regional Mercury Cycle: Sources, Fluxes and Mass Balances*; Baeyens, W. et al., Eds.; Kluwer Academic Publishers: The Netherlands, 1996; pp 85–108.
- Watras, C. J.; Morrison, K. A.; Back, R. C. In *Global and Regional Mercury Cycle: Sources, Fluxes and Mass Balances*; Baeyens, W. et al., Eds.; Kluwer Academic Publishers: The Netherlands, 1996; pp 329–358.
- Walling, D. E.; Webb, B. W. In *Recent Developments in the Explanation and Prediction of Erosion and Sediment Yield*, IAHS Publication No. 164, 1982; pp 313–329.
- St. Lawrence Centre. *St. Lawrence Update: The River at a Glance. Info-Flash series on the state of the St. Lawrence River*; Environment Canada, 1993.
- Yang, C.; Telmer, K.; Veizer, J. *Geochim. Cosmochim. Acta* **1996**, *60*, 851.
- Cossa D.; Pham, T. T.; Rondeau, B.; Quémérais, B.; Proulx, S.; Surette, C. *Mass Balance of Chemical Contaminants in the St. Lawrence River*; Environment Canada, Environment conservation, St. Lawrence Centre, Scientific and Technical Report ST-163, 1998; p 258.
- Rondeau, B.; Cossa, D.; Gagnon, P.; Bilodeau, L. *Hydrological Proc.* In press.
- Government of Canada. *State of the Canadian Environment*; Ottawa, Ontario, Canada, 1991.
- Cossa, D. In *Coastal and Estuarine Studies*, El-Sabih, M. I., Silverberg, N., Eds.; Springer-Verlag: New York, 1990; pp 239–258.
- Rukavina, N. A.; Murdoch, A.; Joshi, S. R. *Sci. Total Environ.* **1990**, *97/98*, 481.
- Gobeil, C.; Cossa, D. *Can. J. Fish. Aquat. Sci.* **1993**, *50*, 1794.
- Bloom, N. S.; Creclius, E. A. *Mar. Chem.* **1983**, *14*, 49.
- Quémérais, B.; Cossa, D. *Procedures for sampling and analysis of mercury in natural waters*; Environment Canada, Environment conservation, St. Lawrence Centre, Scientific and Technical Report ST-31E, 1997; p 34.
- Quémérais, B.; Cossa, D.; Rondeau, B.; Pham, T. T.; Fortin, B. *Sci. Total Environ.* **1998**, *213*, 193.
- Ongley, E. D. *Can. J. Earth Sci.* **1973**, *12*, 1555.
- Verhoff, F. H.; Yaksich, S. M.; Melfi, D. A. *J. Environ. Eng. Div. ASCE* **1980**, *10*, 591.
- Walling, D. E.; Webb, B. W. In *Erosion and sediment transport measurement*; IAHS: 1981; Vol. 133, p 177.
- Rodda, J. C.; Jones, G. N. *J. Inst. Water Eng. Sci.* **1983**, *37*, 529.
- Walling, D. E.; Webb, B. W. In *Dissolved Load of Rivers and Surface Waters Quality/Quality Relationship*; IAHS: 1983; Vol. 141, p 3.
- Meybeck, M.; Pasco, A.; Ragu, A. *4^{ème} Rencontres ARPE-PACA*; Toulon, 1993; pp 55–67, ISSN 1148-0815.
- Ferguson, R. I. *Water Resources Res.* **1986**, *22*, 74.
- Cohn, T. A. *Rev. Geophys.* **1995**, *33*.
- Bradru, D.; Mundlack, Y. J. *Am. Stat. Assoc.* **1970**, *65*, 198.
- Efron, B. *The jackknife, the bootstrap and other resampling plans*; CBMS-NSF Regional Conference Series in Applied Mathematics, SIAM: 1982; Vol. 38.
- Mason, R. P.; Sullivan, K. A. *Environ. Sci. Technol.* **1997**, *31*, 942.
- Hurley, J. P.; Benoit, J. M.; Babiarz, C. L.; Shafer, M. M.; Andren, A. W.; Sullivan, J. R.; Hammond, R.; Webb, D. A. *Environ. Sci. Technol.* **1995**, *29*, 1867.
- Foster, I. D. L. *Catena* **1979**, *6*, 145.
- Poissant, L.; Pilote, M. *Sci. Total Environ.* In press.
- Webb, B. W.; Walling, D. E. In *Remediation and Management of Degraded River Basins*; Novotny, V., Somlyódy, L., Eds.; NATO ASI Science Series, 2. Environment, Springer-Verlag: New York, 1995; Vol. 3, pp 73–100.
- Grieve, I. C. Scotland. *Hydrological Proc.* **1990**, *4*, 231.
- Poissant, L.; Casimir, A. *Atmos. Environ.* **1998**, *32*, 883–893.
- Hudon, C.; Sylvestre, A. *Water Quality Downstream Montreal Island, 1994–1996*. Preliminary Report, St. Lawrence Centre, Environment Canada.
- Environnement Canada. *Assessment of the Elimination of Eleven Priority Toxic Substances*. Preliminary Report, Environment Canada.
- Bouchard, H. St. Lawrence Centre, Environment Canada, Montréal, Qué., Canada.
- Burke, J.; Hoyer, M.; Keeler, G.; Scherbatskoy T. *Wat. Air Soil Pollut.* **1995**, *80*, 353.
- Eisenreich, S. J.; Strachan, W. M. J. *Estimating atmospheric deposition of toxic substances to the Great Lakes – An update*; Environment Canada, Canada Center for Inland Waters, 1992.
- Fitzgerald, W. F.; Mason, R. P.; Vandal, G. M. *Water Air Soil Pollut.* **1991**, *56*, 745.
- Vandal, G. M.; Fitzgerald, W. F.; Rolphus, K. R.; Lamborg, C. H. *Water Air Soil Pollut.* **1995**, *80*, 529.
- Amyot, M.; Mierle, G.; Lean, D.; McQueen, D. J. *Geochim. Cosmochim. Acta* **1997**, *61*, 975.

- (42) Hultberg, H.; Munthe, J.; Iverfeldt, A. *Water Air Soil Pollut.*, **1995**, *80*, 415.
- (43) Lindberg, S. E.; Kim, K.-H.; Munthe, J. *Water Air Soil Pollut.* **1995**, *80*, 383.
- (44) Mierle, G.; Ingram, R. *Water Air Soil Pollut.* **1991**, *56*, 349.
- (45) Swain, E. B.; Engstrom, D. R.; Brigham, M. E.; Henning, T. A.; Brezonik, P. L. *Science* **1992**, *257*, 784.

- (46) Mason, R. P.; Lawson, N. M.; Sullivan, K. A. *Atmos. Environ.* **1997**, *31*, 3531.

Received for review April 17, 1998. Revised manuscript received December 14, 1998. Accepted January 5, 1999.

ES980400A