Regional Characterization of Water Quality (Proceedings of the Baltimore Symposium, May 1989).
IAHS Publ.no.182, 1989.

Chemical composition of the St. Lawrence River and its controlling factors

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ABSTRACT The hydrochemistry of the St.Lawrence River is primarily controlled by rock weathering. The total dissolved load of St.Lawrence River to the Atlantic ocean is estimated to be 73.31 * 10^6 t $year^{-1}$ which accounts 2% of the fluvial input into the world oceans. The flux of individual dissolved species of St.Lawrence River water to the Atlantic are in the following order : HCO_3 > Ca > SO_4 > Cl > Na > Mg > SiO_2 > K. The high solute yield (71 t km^2 $year^{-1}$), in comparison with the global average, suggests that the St.Lawrence River is a highly active environment. The average heavy metal concentrations in total (unfiltered) St.Lawrence river water (except Fe) agrees well with the earlier published data and were below the limits for safe drinking water.

INTRODUCTION

The annual river water discharge to the ocean is estimated to be about 37.4 * 10^3 km^3 (Berner & Berner 1987), which is 2.7 * 10^{-3}% of the total volume of seawater in the world ocean. With a mean annual water discharge of 447 km^3, the St.Lawrence River ranks thirteen among the world rivers which accounts for about 1.2% of the total discharge to the oceans. The St.Lawrence River receives water from the Great lakes and from its tributaries such as the Ottawa, Richelieu and Saguenay rivers. A great variety of bedrock type is exposed in the drainage basin.The River drains an area of about 1.03 * 10^6 km^2 largely comprising the crystalline rocks of the Canadian Shield. The surficial cover of much of the area immediately bordering the Great lakes and St.Lawrence River to the north and the south is composed of sedimentary material deposited as Champlain Sea sediments during the marine invasion of the valley following the glacial retreat of the quaternary period (Yeats & Bewers 1982). The River is now coming under pressure from the increasing industrial activities and the population of the basin is about thirty million. Subramanian & d'Anglejan (1976) and Meybeck (1979) reported on hydrochemistry and Yeats & Bewers (1982) reported on heavy metals of the St.Lawrence River based on limited observations near the river mouth and estuary region. In this report, water quality data obtained from the National Water Quality Data Storage and Retrieval System (NAQUADAT) for the period 1950 to 1980 are analyzed and the factors controlling the water chemistry of St.Lawrence are highlighted. Results from the present study confirm and expand the initial observations and provide a more reliable data base for examining the hydrochemistry and metal pollution of the River.

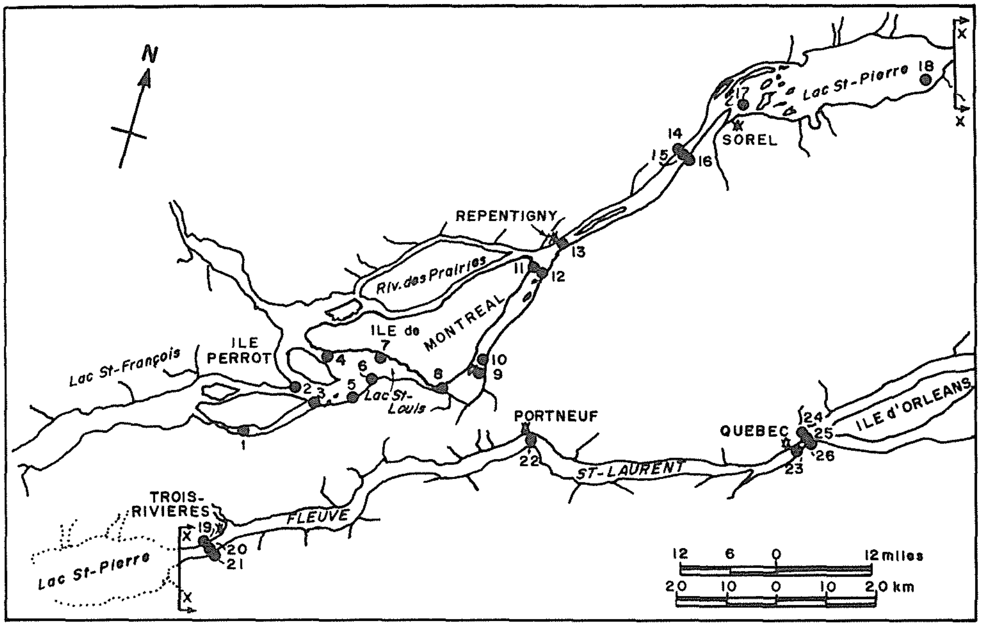

Figure 1. Location of sampling stations along the St.Lawrence River.Number 1 to 26 corresponds to sampling locations.

RESULTS AND DISCUSSION

Major-ion chemistry

Figure 1 shows the locations of the sampling stations that are scattered from Cornwall to Quebec city. Table 1 summarizes the average major ion composition for the selected locations that are representative of the entire river. Table 2 summarizes the average chemical composition of St.Lawrence River water and compares the values to other North American (Mackenzie, Mississippi), South American (Amazon), African (Zarie, Nile) and Asian (Bhrmaputra, Ganges) rivers. Also given for comparison are the average composition of St.Lawrence river published by Meybeck (1979) , the Indian and World average rivers composition. The available data on the chemical composition of St.Lawrence River water are generally lower than the results of the present study except HCO_3. Meybeck's report is based on old (pre-1900) data and are questionable.

Table 1. Major ion chemistry (mg l^{-1}) of St.Lawrence River*

Loc.	pH	HCO_3	Cl	SO_4	Ca	Mg	Na	K	SiO_2	TDS
1	7.8	90.5	26	27	39	7.9	13	1.5	4.1	209
2	7.8	90.5	25.2	27	39	7.8	13	1.4	4.2	208
3	7.8	86.8	25	26	37	7.5	12	1.4	2.1	198
14	7.2	34.9	8.8	15	16	3.5	5.5	1.1	4.1	89
22	7.4	47.1	13	17	21.9	3.9	7.3	1.1	2.6	114
23	7.6	70.6	19	23	30.4	6.3	9.2	1.3	4.3	164

* data presented in the order of downstream direction.
Loc.-Location, corresponds to Figure 1.

The St.Lawrence River is slightly alkaline (p^H range, 7.2-7.8). The River water shows erratic downstream variation for all the major anions and cations except K (Table 1). Such variations are widely reported for all the river basins in the world : Amazon - (Stallard & Edmond, 1983); Mekong - (Carbonnel & Meybeck, 1975); Ganges - (Sarin & Krishnaswami, 1984); Krishna (Ramesh & Subramanian, 1988).There is very little variation in K concentration within the basin (Table 1) as well between major rivers of the world (Table 2). The conservative behaviour of K in major world rivers may be due to several factors. For example, 1) the average concentration of K in sedimentary rocks and in crystalline rocks are almost similar (2 to 3.2% K_2O; Holland 1978), so the lithology of various drainage basins should be less important. 2) K is released much more slowly and less completely during weathering than many other dissolved ions (Berner & Berner 1987).

The chemical composition of St.Lawrence River water (Table 1) shows HCO_3 is the most abundant anion (varies from 39 to 43% of the total dissolved solids (TDS), and Ca is the most abundant cation (varies from 18 to 19% of the TDS). High content of HCO_3 and Ca in St.Lawrence confirms the fact that 98% of all river waters was of the calcium carbonate type (Meybeck 1979).Ca, Mg and HCO_3 concentrations are higher when compared to Amazon, Zarie, Bhramaputra and global average. Ca, Mg and HCO_3 are contributed to river water mostly by rock weathering and the pollution contribution is less significant (2 to 9% - Meybeck, 1979).This provides evidence that rock weathering may be a predominant factor in St.Lawrence. It can be seen from Table 2 that the St.Lawrence River is depleted in silica compared with most of the world rivers. The presence of diatoms in the Great lakes may reduce the amount of silica that reaches the St.Lawrence River.

Cl varies from 10 to 12% ; Na varies from 5 to 6% and SO_4 varies from 13 to 17% of the TDS. All the three ions are enriched in St.Lawrence when compared to most

Table 2. Average chemical composition (mg l^{-1}) of St.Lawrence and other major world rivers.

River	Disch -arge*	Drainage@	HCO_3	Cl	SO_4	SiO_2	Ca	Mg	Na	K	TDS	Reference
St.Lawrence	447	1.03	70.06	19.5	22.5	3.56	30.55	6.15	10	1.3	164	present study
St.Lawrence	337	1.02	75	6.6	14.2	2.4	25	3.5	5.3	1	133	Meybeck (1979)
Mackenzie	304	1.8	111	8.9	36.1	3	33	10.4	7	1.1	211	Meybeck (1979)
Mississippi	580	3.27	118	19.3	50.3	7.6	39	10.7	17	2.8	265	Meybeck (1979)
Amazon-upper	1512	-	68	6.5	7.0	11.1	19	2.3	6.4	1.1	122	Stallard (1980)
Amazon-lower	7245	6.3	20	1.1	1.7	7.2	5.2	1	1.5	0.8	38	Stallard (1980)
Cango(Zarie)	1230	4.0	11	2.9	3	9.8	2.4	1.3	1.7	1.1	33	Meybeck (1979)
Nile	83	3.0	134	7.7	9	21	25	7	17	4	225	Meybeck (1979)
Brahmaputra	603	0.58	54	3.8	9.6	7.3	17	2.9	3.7	3.1	101	Ming-Hui et al (1982)
Ganges	493	0.975	100	5.6	9.4	3.1	40.4	6	8.7	3.9	178	Abbas & Subramanian (1984)
Indian rivers	1700	3.99	74	15	13	7	30	7	12	3	159	Subramanian (1983)
Global average	31400	101	62.2	3.7	9.2	12.4	16	4	4.4	1.5	115	Sarin & Krishnaswami(1984)

* Discharge in 10^9 m^3 $year^{-1}$
@ Drainage area in 10^6 km^2

Table 3. Average chemical flux (million tonnes) in St.Lawrence and other world rivers.

River	HCO_3	Cl	SO_4	SiO_2	Ca	Mg	Na	K	annual flux	erosion rate*	Average fluxes calculated from
St.Lawrence	31.32	8.72	10.06	1.59	13.66	2.75	4.47	0.58	73.31	71.17	present study
St.Lawrence	25.28	2.22	4.79	0.81	8.43	1.18	1.79	0.34	44.82	43.94	Meybeck (1979)
Mackenzie	33.74	2.71	10.97	0.91	10.03	3.16	2.13	0.33	64.14	35.63	Meybeck (1979)
Mississippi	68.44	11.19	29.17	4.41	22.62	6.21	9.86	1.62	153.7	47	Meybeck (1979)
Amazon-upper	102.82	9.83	10.58	16.78	28.73	3.48	9.68	1.66	184.46	-	Stallard (1980)
Amazon-lower	144.9	7.97	12.32	52.16	37.67	7.25	10.87	5.8	275.31	43.7	Stallard (1980)
Cango(Zarie)	13.53	3.57	3.69	12.05	2.95	1.6	2.09	1.35	40.59	10.15	Meybeck (1979)
Nile	11.12	0.64	0.75	1.74	2.08	0.58	1.41	0.33	18.68	6.23	Meybeck (1979)
Brahmaputra	32.56	2.29	5.79	4.4	10.25	1.75	2.23	1.87	60.9	105	Ming-Hui et al (1982)
Ganges	49.3	2.76	4.63	1.53	19.92	2.96	4.29	1.92	87.75	90	Abbas & Subramanian (1984)
Indian rivers	125.8	25.5	22.1	11.9	51	11.9	20.4	5.1	270.3	67.74	Subramanian (1983)
Global average	1953.08	116.18	288.88	389.36	502.4	125.6	138.16	47.1	3611	35.75	Sarin & Krishnaswami (1984)

* erosion rate in $t.km^2$ $year^{-1}$

of the world rivers (Table 2). Pollution can be an important source for such high concentrations. Meybeck (1979) Berner & Berner (1987) estimated that about 30% of Cl, 28% of Na and 43% of SO_4 in river water arises from pollution. The high content of Na and Cl in St.Lawrence may also be due to addition through Champlain Sea sediments.

Gibbs (1970) classified the world rivers on the basis of surface-water chemistry into three types : 1) atmospheric precipitation 2) rock weathering and 3) evaporation and fractional crystallization. A boomerang-shaped diagram resulted when he plotted Na/(Na+Ca) versus TDS. Gibbs also found an identical location for almost all rivers if a similar diagram was plotted using $Cl/(Cl+HCO_3)$ in place of Na/(Na+Ca). The plot of St.Lawrence water data, not shown in this paper, falls in the middle portion of the boomerang indicating that the chemical composition is controlled by rock weathering. Most of the major world rivers falls in this category (Berner & Berner 1987). Thus, most rivers are dominated by rock weathering and are mainly Ca and HCO_3 waters derived from carbonate minerals.

Fluxes

The transport of major ions by the St.Lawrence River has been calculated using the mean discharge rate of 447 * 10^9 m^3 $year^{-1}$ (Meybeck, 1984). Table 3 gives the annual flux of individual ions for the St.Lawrence river together with other major world rivers and the global flux. The St.Lawrence River delivers annually 73.31 million tonnes of dissolved load to the Atlantic ocean. This accounts to 2% of the world's dissolved transport. The approximate contribution of each dissolved species by St.Lawrence to the Atlantic ocean are as follows : HCO_3,43% ; Cl,12% ; SO_4% ; SiO_2, 2% ; Ca,17% ; Mg, 4% ; Na, 6% and K, 1%.

In comparison to North American rivers, the Nile and the Zarie have a very low chemical flux and reflects the closed nature of nutrient cycling in the African rain-forest environment. The water discharge and the chemical load of the Ganges and St.Lawrence appears to be more or less similar in spite of their diverse environmental factors (Table 3). The erosion rate of the St.Lawrence is higher when compared to other world rivers (except Asian rivers) and it is two times higher than that of global average.

Heavy Metals

Table 4 summarizes the average concentrations of Fe, Mn, Cu, Ni and Zn in the St.Lawrence unfiltered water sample. Also shown are the published values for St.Lawrence, major world rivers, global average and EPA limits for water quality. Eventhough the published data on heavy metal content in St.Lawrence river (Yeats & Bewers, 1982) is based on two stations at its river

Table 4. Heavy metal concentrations (ug l^{-1}) in St.Lawrence River water compared with other major rivers.

River	Fe	Mn	Cu	Ni	Zn
St.Lawrence[a] (unfiltered)	477	18	3.46	2.35	11.38
St.Lawrence[b] (unfiltered)	705	23	3.67	2.26	10.4
St.Lawrence[b] (dissolved)	55	6.3	2.5	1.5	8.6
Mississippi[c] (dissolved)	10	10	2	1	0.16[h]
Amazon[d] (dissolved)	-	-	1.52	0.29	0.13[h]
Orinoco[d] (dissolved)	-	-	0.64	0.24	0.13[h]
Niger[e] (unfiltered)	-	-	0.14	0.45	0.31
Yangtze[d] (dissolved)	-	-	1.08	0.17	0.07[h]
Global average[f] (dissolved)	40	8.2	1.5	0.5	30
Water quality criteria[g]	300	50	60	100	-

a-This study, average of 26 samples
b-Yeats & Bewers (1982); c-Presley et al (1980)
d- Grant et al (1982); e- Nriagu (1986)
f-Martin & Whitfield (1983); g- E.P.A.(1973,1976)
h-shiller & Boyle (1985)

mouth (Quebec city), it agrees well with the present values for all the metals except Fe. The heavy metal concentrations in St.Lawrence River water are several orders of magnitude higher than those of reported major world rivers. The available data on St.Lawrence River (Table 4) shows that the total (unfiltered) samples are enriched about 2 to 13 times than those of dissolved metals. Thus, the results of this study become quite comparable to the dissolved concentrations that have been reported for the other major rivers of the world. But, the average concentrations of Zn reported by Shiller & Boyle (1985) for Mississippi, Amazon, Orinoco and Yangtze rivers are in general much lower than the results of the earlier studies (Table 4). The discrepancies may be attributed, at least in part, to difficulties in measuring low levels of the dissolved constituents in these natural waters. The average concentration of Cu in Niger river is among the lowest in a major river (Table 4). It may be due to the absence of Cu-bearing minerals in the Precambrian bedrock of West Africa (Nriagu, 1986). All the metal concentrations (except Fe) in St.Lawrence River water proved to be considerably below the EPA limits for safe drinking water.

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