

UNIVERSITÉ DU QUÉBEC À MONTRÉAL

SUIVIS ISOTOPIQUES (^2H & ^{18}O) DU FLEUVE SAINT-LAURENT ET DE LA
RIVIÈRE DES OUTAOUAIS ENTRE 1997 ET 2003 – RELATIONS AVEC LA
VARIABILITÉ HYDROCLIMATIQUE À L'ÉCHELLE SAISONNIÈRE ET
INTERANNUELLE

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ISOTOPIC MONITORING (^2H & ^{18}O) OF THE ST. LAWRENCE AND OTTAWA
RIVERS FROM 1997 TO 2003 – LINKAGES WITH SEASONAL AND
INTERANNUAL HYDROCLIMATIC VARIABILITY

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ABSTRACT

Isotopic compositions ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of the St. Lawrence and Ottawa rivers have been monitored since 1997 as a contribution to the project on *Isotope tracing of hydrologic processes in large river basins* of the International Atomic Energy Agency of Vienna [1]. Sampling of St. Lawrence waters has been performed on a biweekly to weekly basis at Montreal (representing waters outflowing from the Great Lakes) and Quebec City (at the head of the St. Lawrence estuary), whereas waters from the Ottawa River, the most important tributary, were sampled near its outlet into the St. Lawrence River. Seasonal isotopic variability has been examined in relation with major hydrologic processes occurring in the watershed and head Great Lakes, notably evaporation and snow-melt. Interannual climatic variability has been examined in relation with hydrological budgets and long term climate trends.

Waters outflowing from the Great Lakes display relatively enriched isotopic compositions with mean weighted annual values of -55‰ for $\delta^2\text{H}$ and -7.1‰ for $\delta^{18}\text{O}$. Ottawa River waters display a more heavy-isotope depleted signature (-80‰ for $\delta^2\text{H}$ and -10.7‰ for $\delta^{18}\text{O}$). Finally, as the isotopic composition of water sampled at the outlet of the St. Lawrence River (Quebec City) depends primarily upon the contribution from the two previous sources, it exhibits intermediate values (-64‰ for $\delta^2\text{H}$ and -8.4‰ for $\delta^{18}\text{O}$).

The seasonality of river water isotopic signal is partly driven by the varying isotopic input from local precipitation. This input signal gets further dampened and de-phased by the residence time of water in the basin, its evaporation and the isotopic evolution of snow cover during Winter and early Spring. The melting of heavy-isotope depleted Winter snow during Spring accounts for most of the seasonal isotopic variations in the Great Lakes (1.3‰ for $\Delta\delta^{18}\text{O}$ and 8‰ for $\Delta\delta^2\text{H}$) and the Ottawa River (1.1‰ for $\Delta\delta^{18}\text{O}$ and 6‰ for $\Delta\delta^2\text{H}$). At the outlet of the St. Lawrence River (Quebec City), seasonal variations are modulated by the prominent contribution from the heavy-isotope enriched water from the Great Lakes during Summer, and heavy isotope depleted tributary waters during Spring (2.4‰ for $\Delta\delta^{18}\text{O}$ and 19‰ for $\Delta\delta^2\text{H}$).

The interannual isotopic variability of surface water in the St. Lawrence River basin appears to be relatively small. From year to year, the outflowing waters from the Great Lakes display relatively stable isotopic compositions ($\Delta\delta^{18}\text{O} = 0.5‰$ and $\Delta\delta^2\text{H} = 2‰$) although a slight increase in the heavy isotope-enrichment of late Summer–Early Fall waters was observed between 1997 and 2003. No similar trend could be identified in precipitation thus suggesting that both warmer overall summer conditions and enhanced evaporation could be responsible for the isotopic

enrichment of surface water. The Ottawa River isotopic signal displays the largest important interannual variability ($\Delta\delta^{18}\text{O} = 1\text{‰}$ and $\Delta\delta^2\text{H} = 8\text{‰}$) and seems to reflect the interannual isotopic variations of local precipitation at Ottawa, but with a somewhat lower amplitude. The interannual isotopic variations of the St. Lawrence River at Quebec City ($\Delta\delta^{18}\text{O} = 0.7\text{‰}$ and $\Delta\delta^2\text{H} = 3\text{‰}$) differ from a simple mixing of Great Lakes and Ottawa River waters. The contribution of smaller tributaries between Montreal and Quebec City might be responsible for this enhanced variability. In fact, the interannual isotopic variations observed at Quebec City show a better agreement with hydrological conditions and isotopic inputs from the smaller tributary basins.

[1] Gibson et al., 2002. EOS 83: 613 et p.

Keywords: stable isotopes, river basin, hydrology, hydroclimatic variability.

RÉSUMÉ

Les compositions isotopiques ($\delta^{18}\text{O}$ et $\delta^2\text{H}$) du Fleuve Saint-Laurent et de la Rivière des Outaouais ont fait l'objet d'un suivi depuis 1997 dans le cadre d'une contribution au projet de l'Agence Internationale de l'énergie atomique portant sur le traçage isotopique des processus hydrologiques dans les grands bassins. L'échantillonnage des eaux du Saint-Laurent a été réalisé sur une base hebdomadaire à bimensuelle à la station de Montréal (représentant les eaux des Grands Lacs à leur sortie du Lac Ontario) et de Québec (à l'entrée de l'estuaire maritime). Les eaux de la Rivière des Outaouais, le plus important tributaire, ont été échantillonnées à l'embouchure de la rivière à Carillon. Une attention particulière a été portée à la variabilité saisonnière en relation avec les processus hydrologiques (l'évaporation et la fonte des neiges) dans les bassins des tributaires et des Grands Lacs. La variabilité interannuelle a également été analysée en relation avec les bilans hydrologiques et les tendances climatiques à long terme.

Les eaux à la sortie des Grands Lacs présentent des compositions isotopiques relativement enrichies en isotopes lourds avec des moyennes annuelles pondérées de -55‰ pour $\delta^2\text{H}$ et -7.1‰ pour $\delta^{18}\text{O}$. La Rivière des Outaouais se démarque par sa signature isotopique plus appauvrie (-80‰ pour $\delta^2\text{H}$ et -10.7‰ pour $\delta^{18}\text{O}$). Finalement, puisque le contenu isotopique de l'eau à la sortie du Fleuve Saint-Laurent dépend en grande partie de l'apport des deux sources précédentes, ce dernier est caractérisé par des valeurs intermédiaires (-64‰ pour $\delta^2\text{H}$ et -8.4‰ pour $\delta^{18}\text{O}$).

La saisonnalité du signal isotopique de l'eau de surface provient en partie de la variation de l'apport isotopique des précipitations. Toutefois, le signal des précipitations est tamponné et déphasé par le temps de séjour de l'eau dans le bassin, l'évaporation et l'évolution du tapis nival pendant l'hiver et le début du printemps. Au printemps, la fonte des précipitations hivernales appauvries en isotopes lourds est responsable pour la plus grande partie des variations saisonnières dans les Grands Lacs (1.3‰ pour $\Delta\delta^{18}\text{O}$ et 8‰ pour $\Delta\delta^2\text{H}$) et la Rivière des Outaouais (1.1‰ pour $\Delta\delta^{18}\text{O}$ et 6‰ pour $\Delta\delta^2\text{H}$). À la sortie du Fleuve Saint-Laurent à Québec, les variations saisonnières sont dictées par l'apport massif des eaux enrichies en isotopes lourds des Grands Lacs pendant l'été ainsi que par la contribution appauvrie en isotopes lourds des tributaires pendant la période de fonte des neiges (2.4‰ pour $\Delta\delta^{18}\text{O}$ et 19‰ pour $\Delta\delta^2\text{H}$).

La variation isotopique interannuelle de l'eau dans le bassin du Fleuve Saint-Laurent est relativement faible. D'année en année, l'eau à la sortie des Grands Lacs présente des compositions isotopiques assez stables ($\Delta\delta^{18}\text{O} = 0.5\text{‰}$ et $\Delta\delta^2\text{H} = 2\text{‰}$). Il nous a toutefois été possible d'observer un faible enrichissement isotopique de l'eau entre la fin de l'été et le début de l'automne entre 1997 et 2003. Puisqu'un tel

enrichissement n'est pas observé dans les précipitations, il pourrait être attribué à l'augmentation des températures moyennes annuelles induisant une évaporation accrue dans les Grands Lacs. Les variations interannuelles de la Rivière des Outaouais ont été les plus importantes ($\Delta\delta^{18}\text{O} = 1\text{‰}$ et $\Delta\delta^2\text{H} = 8\text{‰}$) et semblent être reliées de près aux variations observées dans les précipitations à Ottawa avec une moindre amplitude. La variabilité interannuelle à l'embouchure du Fleuve, à Québec, ($\Delta\delta^{18}\text{O} = 0.7\text{‰}$ et $\Delta\delta^2\text{H} = 3\text{‰}$) ne peut être entièrement expliquée par un simple mélange des eaux des Grands Lacs et de la Rivière des Outaouais. L'apport des plus petits tributaires entre Montréal et Québec pourrait expliquer cette différence. En effet, les variations isotopiques interannuelles à Québec semblent être reliées de près aux conditions hydrologiques et à l'apport isotopique provenant des bassins des plus petits tributaires.

[1] Gibson et al., 2002. EOS 83: 613 et p.

Mots clé: Isotopes stables, bassin fluvial, hydrologie, variabilité hydroclimatique.

1. INTRODUCTION

Efforts have been made over the past few years to develop a global network monitoring the isotopic composition of large rivers, coordinated by the International Atomic Energy Agency (IAEA). This coordinated research project on “isotope tracing of hydrological processes in large river basins” involves many research groups studying the world’s major rivers. The project is concerned with “developing and testing isotope methods for quantitative analysis of water balance and related processes, tracing environmental changes, and ultimately establishing an operational Global Network for Isotopes in Rivers” (Gibson et al., 2002). Preliminary results have already been presented and are very promising. Ultimately, as a sufficient number of reliable, long-term records of the isotopic composition of large rivers will become available, these results could be incorporated into the next generation of climate models using stable isotopes of water (^{18}O and ^2H) to study the global water balance (Hoffman, 2000). The isotopic monitoring undertaken in this study of the St. Lawrence River and its largest tributary, the Ottawa River, is part of this IAEA project.

The St. Lawrence River in south-eastern Canada ranks 16th in the world with regard to its freshwater discharge. Its importance relates to environmental, economic, social and political factors. The great volume of water delivered to the northern Atlantic Ocean via the St. Lawrence is controlled by the presence of the Laurentian Great Lakes located at the head of the river. Since 1960, water flow has been actively controlled to assure safe navigation for transport ships into the harbours on the American and Canadian sides of the Great Lakes. The anticipated long-term changes in the hydrological balance in response to climate warming raise questions about water supplies over the next few decades.

The St. Lawrence and Ottawa rivers have already been the subject of a detailed isotopic monitoring by Hélie et al. (2002). Their goals were to determine the carbon

cycling and fluxes in the St. Lawrence River system in relation to hydrologic and climatic changes. The St. Lawrence Centre from Environment Canada is also actively monitoring the physical and chemical properties of the St. Lawrence River and its tributaries. Until recently, only a few studies examined the oxygen-18 and deuterium systematic of the St. Lawrence River (Mook, 1982; Brown, 1970; Yang et al., 1996; Telmer, 1997; Barth and Veizer, 2000;). Although data from these studies are sparse and were not collected on a regular basis, they illustrate the heterogeneity of the oxygen-18 and deuterium content of water in the Great Lakes, the St. Lawrence River. This study is the first attempt to establish a detailed monitoring of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the St. Lawrence and Ottawa River. The time resolution of our survey was higher than in previous studies and covered a longer period of time (more than 6 years). Seasonal isotopic variability has been studied in relation to major hydrologic processes occurring in the watershed and headwater Great Lakes, notably evaporation and snow-melt. Interannual climatic variability was examined in relation with hydrological budgets and long-term climate trends.

The sampling was initiated in mid-1997 at three stations. One, upstream in the Montreal area, provides information in the water outflowing from the Great Lakes; a second, near Quebec City, allowed the isotopic monitoring of the St. Lawrence River water at the head of the estuary; the third, at Carillon, near the mouth of the major tributary, the Ottawa River. The sampling network and strategies were established to characterize the different water sources contributing to total discharge at the outlet of the St. Lawrence River. The sampling locations were chosen to allow regular, relatively easy and representative sampling of the whole water column.

2. LOCAL HYDROLOGY AND SAMPLING

This project was undertaken as part of a collaborative project with the St. Lawrence Centre (Environment Canada), to determine carbon cycling and fluxes in the St. Lawrence River system in relation to hydrologic and climatic changes (Hélie et al., 2002). The sampling network and strategies were established to characterize the different water sources contributing to total discharge at the outlet of the St. Lawrence River. The sampling locations were chosen to allow regular, relatively easy and representative sampling of the whole water column.

The St. Lawrence can be qualified as a lacustrine river owing to the fact that Great Lakes water represents more than half of the water discharged from the outlet of the river near Quebec City. The relatively high outflow rates at the mouth of the river (mean value of 7066 m³/s at Montreal, based on unpublished data from Environment Canada for the 1997-2003 period) limits mixing of Great Lakes water with incoming water from north shore and south shore tributaries such as the Ottawa River (figure 1). These water masses with different physical and chemical characteristics flow northward with limited mixing until they reach Quebec City, where the narrowness of the river and the effects of tide induce efficient mixing. Water at Quebec City is thus composed of a combination of water from the Great Lake, the Ottawa River and water from smaller tributaries. During this study, no synoptic survey was conducted in the St. Lawrence itself between the outlet of the Great Lakes at Montreal and Quebec City because of incomplete mixing of the different water masses. Instead, sampling stations were positioned to characterize the isotopic input into the St. Lawrence River and the outflow from the river at its estuary.

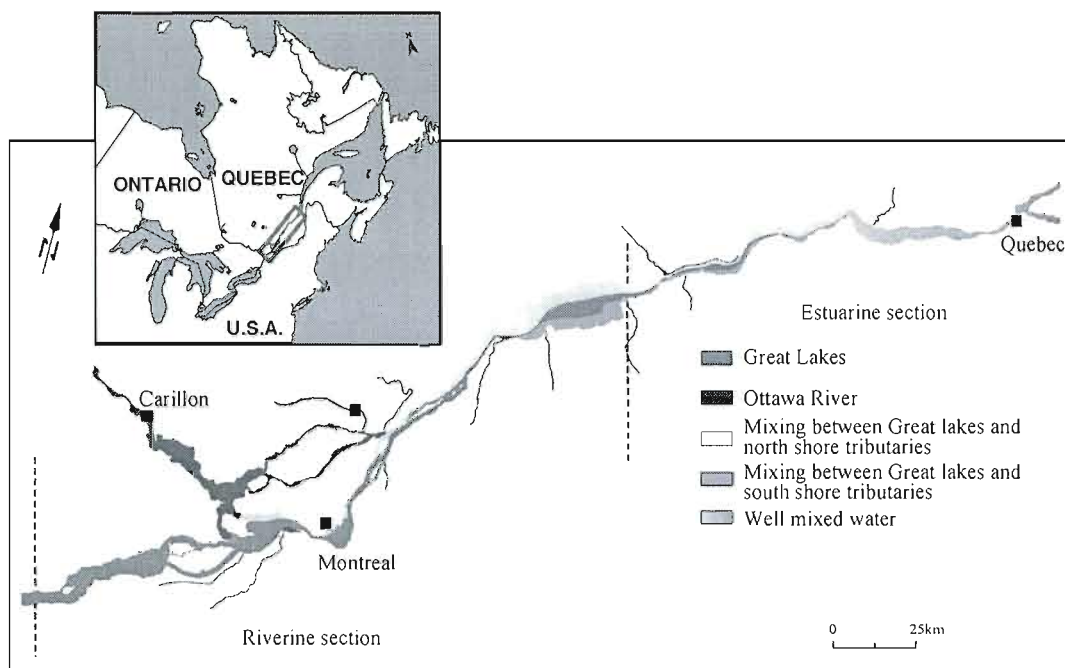


Figure 1. The location of the three sampling stations that were visited on a bimonthly to weekly basis. The different water masses of the St. Lawrence River are identified. The upper part of the river is dominated by water outflowing from the Great Lakes whereas the contribution from tributaries becomes greater as water flows northward. (Modified source: St. Lawrence Center, http://www.qc.ec.gc.ca/csl/inf/inf010_f.html)

Lake	Area ² km ²	Datum ² m	Volume ³ km ³	Mean depth ³ m	Hydraulic residence time ¹ Year
Superior	82100	182.88	12110	148	190
Michigan	57800	175.81	4920	85	100
Huron	59600	175.81	3540	59	20
St. Clair	1114	174.25	6	5	<1
Erie	25700	173.31	484	19	3
Ontario	18960	74.01	1640	86	8

Table 1. Hydrologic and physical characteristics of the Great Lakes. Data are from (1) Quinn (1992), (2) Coordinating Committee (1977) and (3) by the division of lake volume by lake surface area.

The Great Lakes annually supply 62% of the water outflowing from the St. Lawrence River (based on unpublished data from Environment Canada for June 1997 to April 2004). The chain of lakes is composed of several lakes connected by

ivers, rapids and falls. Lake Superior, the deepest and largest lake, discharges into Lake Huron. After they merge with Lake Michigan, Lake Huron waters flow into Lake St. Clair, the shallowest lake, and then into Lake Erie. Waters of Lake Erie finally flows into Lake Ontario over the Niagara Falls. The different hydrologic and physical characteristics of these lakes are listed in table 1.

The Great Lakes contain 22 690 km³ of fresh water; their mean depth varies from 147 m for Lake Superior to 5 m for Lake St. Clair. The cumulative residence time of water in these lakes is very long. All the lakes develop thermal stratification during winter and summer, whereas overturning of water column occurs during fall and spring.

Since this study focuses on the riverine portion of the St. Lawrence River, no sampling was conducted directly in the Great Lakes. Due to time and cost considerations, water outflowing from the Great Lakes was sampled at the southern tip of Montreal Island using the facilities of the Charles J.-des-Baillets water treatment plant (figure 1). Water was sampled from a pipe collecting water in the middle part of the river channel. Sampled water is thought to be representative of water outflowing from Lake Ontario. In fact, even though contributions from smaller tributaries between Cornwall and Montreal Island are expected (mainly from the Châteauguay River), the middle part of the channel is considered to carry only water from the Great Lakes. This assumption is supported by a comparison of water conductivity data from measurements conducted at the outlet of Lake Ontario and at the Charles J.-des-Baillets pumping station (Hélie et al., 2002). Great Lakes water could thus be sampled more easily and at much lower cost at the Montreal station than directly at the outlet of Lake Ontario. The hydrologic and isotopic properties of water outflowing from the Great Lakes will provide us with the initial signal of the St. Lawrence River and should thus, as a whole, be representative of hydrologic and climatic conditions prevailing over the Great Lakes basin.

The Ottawa River is the largest tributary of the St. Lawrence River, with a mean discharge rate of $1810 \text{ m}^3/\text{s}$ (based on unpublished data from Hydro-Québec for the 1997-2002 period). It drains a catchment of $146\,300 \text{ km}^2$ and is more than 1130 km long. The river is characterized by a succession of lakes as well as 30 storage reservoirs and dams used for hydroelectric generation and flow control. Human regulation of the Ottawa River tends to alter the natural variability of runoff but contributions from numerous smaller unregulated tributaries partly counter this effect (Telmer, 1997). The watershed is located within the Laurentian Mountains at an altitude ranging from 46 to 406 m (masl, Meteorological Service of Canada, http://www.msc-smc.ec.gc.ca/contents_e.html?). With such an altitudinal range, climatic conditions over the subbasins can differ significantly. Telmer (1997) observed that smaller rivers draining subbasins of the Ottawa River located at different altitudes presented different hydrological characteristics. The Carillon station located on the Quebec-Ontario border used here was also used by Telmer (1997) to characterize the overall hydrologic and isotopic signal of the Ottawa River prior to our study. It is located near the mouth of the river, before it merges into the main channel of the St. Lawrence River downstream of Montreal Island.

Sampling was conducted on the Hydro-Quebec hydroelectric dam facing the city of Carillon. Sampling was done on the lower part of the dam where water exits the turbines. Water is thus well mixed and remains unfrozen all year long. The water that is diverted through the turbines is collected at mid-depth approximately in the middle of the dam and should be representative of the whole water column. In one exceptional case, water was sampled on a ferry located a 100 m downstream of the dam. Surface water was then sampled in the middle part of the river.

Finally, water outflowing from the St. Lawrence River was sampled at the end of its riverine portion at Quebec City, where salty water begins to dominate the hydrology of the river. Using the facilities of the City of Lévis water filtration plant, the

sampling was done two hours before low tide to avoid mixing with estuarine waters. Water was collected in a hole that is hydraulically connected to the river via a pipe located 7 meters below the surface and a few tenths of meters from the south shore. Rondeau (1999) validated the use of this sampling station to characterize the entire water column whereas Désilet and Langlois (1989) identified a single water mass based on physical and chemical characteristics in the Quebec City vicinity. The cumulative discharge at Quebec City averaged $11559 \text{ m}^3/\text{s}$ for the 1997-2003 period (based on unpublished data, Environment Canada).

Other smaller tributaries draining into the St. Lawrence River were not sampled directly. These tributaries discharge into the St. Lawrence River between the outlet of Lake Ontario up to and beyond Quebec City. Their headwaters are located on either side of the river in the Appalachian or Laurentian Mountains. The south shore tributaries also drain an important part of the St. Lawrence Lowlands. The mean annual discharge rates of these tributaries vary from $33 \text{ m}^3/\text{s}$ to $700 \text{ m}^3/\text{s}$ (St-Laurent Vision 2000, http://www.slv2000.qc.ca/St_Laurent_facettes/pdf/Carre_tributaires_f.pdf), and their cumulative contribution to the total discharge at Quebec City is greater than that of the Ottawa River alone. Their overall input and properties will be estimated based on a comparison of outflowing water at Quebec City vs. incoming water from the Great Lakes (Montreal) and the Ottawa River (Carillon).

3. METHODOLOGY AND SAMPLING PROCEDURES

3.1 Water levels and discharge rates

Discharge rates at Quebec City, Trois-Rivières, Sorel and Montreal were provided by Environment Canada. The discharge rates for Quebec City were calculated by adding together the values measured at Lasalle (Montreal), the St. Lawrence Seaway canal at Saint-Lambert, the Milles-Îles and Des Prairies rivers and all the smaller tributaries discharging into the St. Lawrence River between Montreal Island

and Quebec City. Data from the outlet of Lake Ontario (at Cornwall) were provided by Ontario Power Generation (unpublished data). Discharge rates for the Ottawa River were provided by Hydro-Québec. Discharge was measured on the Carillon hydroelectrical dam where our own sampling was conducted. To estimate the contribution of smaller tributaries to the total discharge at Quebec City, we subtracted the mean monthly discharge recorded at Carillon (Ottawa River) and at Cornwall (outlet of Lake Ontario) from that measured at Quebec City.

For intercomparison between the different stations, we decided to use monthly discharge data to avoid the introduction of errors associated with the transit time of water between the outlet of the Great Lakes and Quebec City. The time lag between Montreal and Quebec City is thought to be 4 days on average (pers. comm. Guy Morin, Environment Canada). The fact that the transit time of water between Montreal and Quebec City is in fact shorter than our sampling frequency is forcing us to consider the inputs from the Great Lakes and the Ottawa River to be synchronous.

3.2 Stable isotopes analyses

Water was analyzed for its oxygen-18 and deuterium content at the GEOTOP-UQAM-McGILL research centre on water sampled in 60 ml plastic bottles entirely filled and stored at 4°C. 100 µl of unfiltered water were equilibrated with 50 to 100 µl of CO₂ gas at 40°C in vials previously purged with He gas. Equilibration time ranged from 12 to 24 hours. Equilibrated CO₂ gas was then sampled and diverted through the isotope ratio mass spectrometer. The resulting isotopic values were corrected for any apparent drift and corrected to their absolute values using international standards (V-SMOW and SLAP) and/or with internal lab standards calibrated against international standards. Data were also temperature corrected and equilibration isotope effect was taken into account. Every water sample was

equilibrated in three different vials and the mean isotopic value was calculated. The overall analytical uncertainty was $\pm 0.1\%$.

The analysis of the deuterium content of the water was done by pyrolysis of water over hot chromium (Donnelly et al., 2001; Kelly et al., 2001). 1 μ l of filtered water was injected into a hot (1300°C) chromium furnace to create H₂ gas that was then diverted through an isotope ratio mass spectrometer. The same sample was injected three times and the mean value was calculated. The resulting isotopic values were corrected for any apparent drift (Nelson and Dettman, 2001) and corrected to their absolute isotopic value with international standards (V-SMOW and SLAP) and/or with internal lab standards calibrated against international standards. Care was taken to avoid any memory effect by subtracting the first result of the series of three injections if it appeared to be obviously affected by previous injections. The overall analytical uncertainty for $\delta^2\text{H}$ measurements was equal to or better than 1‰.

All isotopic values are reported against VSMOW international standard and are defined by the following equation:

$$\delta (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) * 1000$$

where R is the ratio $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$.

The deuterium excess parameter (Dansgaard, 1964) was calculated using the following equation:

$$D_{\text{xs}} = \delta^2\text{H} - 8 * \delta^{18}\text{O}$$

The propagation of overall analytical uncertainty from oxygen-18 and deuterium measurements yields a systematic error of 1.8‰ for deuterium excess values.

3.3 Precipitation data

Climatic parameters (air temperature and amount of precipitation) were extracted from the MSC (Meteorological Service of Canada) database. Data from the

Toronto, Ottawa, Drummondville and Saint-Jérôme stations were chosen for the consistency of their time records to characterize the different geographical regions of the St. Lawrence watershed (see figure 4).

Stable isotopic data from precipitation were downloaded from the CNIP (Canadian Network for Isotopes in Precipitation, <http://www.science.uwaterloo.ca/~twdedwar/cnip/cniphome.html>) web site and complementary data were provided by Jean Birks (unpublished data from the CNIP) for the Ottawa and Egbert stations.

4. RESULTS

4.1 Isotopic signature of water in the St. Lawrence River basin

The effectiveness of our sampling program in measuring short-term isotopic variability in river water can be estimated by comparing discharge rates and stable isotopic data. There is a relatively strong correlation between discharge and isotopic compositions at Quebec City from 1997 to 2002 ($R^2=0.55$ for $\delta^{18}\text{O}$ values and $R^2=0.59$ for $\delta^2\text{H}$ values). Correlation coefficients (R^2) vary from 0.51 to 0.88 for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values when individual years are considered (years with poor correlation coefficient generally have more missing data points).

Assuming a significant correlation between discharge and isotopic data, we can estimate the error introduced by our bimonthly to weekly sampling in comparison to the results that would have been obtained by a daily sampling. Average annual discharge values were calculated using daily discharge measurements and values corresponding to the sampling dates. For each individual year, a systematic error of 0 to 5% is observed as the average values calculated from the bimonthly to weekly data were systematically higher than those calculated using daily measurements. It is therefore probable that the average isotopic signature of the St. Lawrence River calculated from biweekly sampling also suffers from a 0 to 5% overestimation. It

was not possible to do the same calculation for the Montreal and Carillon stations because the correlation between delta values and discharge rates was not significant.

4.1.1 Surface waters

Great Lakes water sampled at Montreal exhibits the most enriched isotopic compositions. $\delta^{18}\text{O}$ values range from -6.3‰ to -9.8‰ , with a mean value of -7.1‰ , whereas $\delta^2\text{H}$ values range from -50‰ to -71‰ , with a mean value of -54‰ . The correlation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values yields the following equation: $\delta^2\text{H} = 5.8 \pm 0.2 * \delta^{18}\text{O} - 13 \pm 2$, $R^2 = 0.87$. Deuterium excess values are relatively low: 0‰ to 5‰ (mean: 3‰).

Sampling done between the Fall of 1991 and the Spring of 1992 by Yang et al. (1996) between the outlet of Lake Huron and Montreal Island gave similar values between -6.1‰ to -7.4‰ for $\delta^{18}\text{O}$ and between -45‰ to -54‰ for $\delta^2\text{H}$. The more enriched $\delta^2\text{H}$ values observed by Yang et al. may result from the fact that the meltwater pulse during the spring of 1992 was not accurately sampled, thus creating a bias toward more enriched values. The isotopic values of water sampled during the fall of 1991 appear to be more heavy-isotope enriched than those observed during our seven year survey. Great Lakes water sampled by Barth and Veizer (2004) from May 1995 to June 1996 yielded $\delta^2\text{H}$ values ranging from -47‰ to -61‰ . These values are also more ^2H -enriched than the values from our dataset.

The Ottawa River water also displays small variations in its isotopic compositions around more heavy-isotope depleted values than in the Great Lakes. $\delta^{18}\text{O}$ values vary from -9.6‰ to -12.2‰ , with a mean value of -10.7‰ , whereas $\delta^2\text{H}$ values range from -73‰ to -88‰ , with a mean value of -80‰ . The correlation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values is: $\delta^2\text{H} = [(4.9 \pm 0.4) * \delta^{18}\text{O}] - (28 \pm 4)$, $R^2 = 0.73$. The deuterium excess parameter shows a wide range of values, from 1‰ to 12‰ , with a

mean value of 7‰. Sampling conducted by Telmer (1997) at the Carillon station in 1993 and 1994 yielded isotopic values falling within the interval defined by the present dataset.

Water sampled at the outlet of the St. Lawrence River exhibits intermediate isotopic compositions between two major end-members, the isotopically enriched Great Lakes water and the more depleted water from the Ottawa River. Depending on the amount of water contributed by these sources, the isotopic content of water at Quebec City fluctuates over a wide range of values. The oxygen-18 content of water varies from -7.2‰ to -11.2‰ (mean values of -8.4‰) whereas the deuterium content of water ranges from -55‰ to -90‰ (mean value of -64‰). The correlation between the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values is described by the following equation: $\delta^2\text{H} = [(6.0 \pm 0.1) * \delta^{18}\text{O}] - (13 \pm 1)$, $R^2 = 0.95$. This equation represents in fact a mixing line between the contribution from the Ottawa River and all the other tributaries and the Great Lakes. Deuterium excess values at Quebec City vary between -1‰ and 10‰, with a mean value of 5‰.

The contribution of smaller tributaries to the isotopic composition of water at the outlet of the St. Lawrence can be estimated through a simple mass balance equation (assuming negligible evaporation losses in the St. Lawrence River from Montreal to Quebec City):

$$\delta_{\text{Tributaries}} = (\delta_{\text{Qc}} * Q_{\text{Qc}} - \delta_{\text{MTL}} * Q_{\text{MTL}} - \delta_{\text{CAR}} * Q_{\text{CAR}}) / Q_{\text{Tributaries}}$$

where δ is the weighted monthly isotopic composition of water at each station and Q is the mean monthly discharge rate. In that calculation, the use of monthly isotopic and discharge values was necessary in order to reduce the impact of the transit time of water between Montreal and Quebec City. Moreover, on rare occasions, sampling has been conducted monthly at the three stations. To facilitate the calculation of discharge weighted monthly isotopic values, bimonthly to weekly isotopic time series have been integrated and isotopic values were generated at a 15-

day time interval. As a result, each month of the year was represented by two to three isotopic values. The weighting procedure was carried using discharge values corresponding to the same 15-day time interval.

Isotopic values for the smaller tributaries draining into the St. Lawrence are more variable than those of the St. Lawrence and Ottawa rivers. Oxygen-18 values range from -7.8‰ to -14.3‰ (mean value of -10.7‰) whereas deuterium values vary from -52‰ to -105‰ (mean value of -75‰). Deuterium excess values show great variability, ranging from -12‰ to 30‰, with a mean value of 10‰. $\delta^{18}\text{O}$ values are poorly correlated to $\delta^2\text{H}$ values: $\delta^2\text{H} = [(4.0 \pm 0.7) * \delta^{18}\text{O}] - (33 \pm 7)$, $R^2 = 0.37$.

Synoptic monitoring was carried out by Yang et al. (1996) during the fall of 1991 and spring of 1992 in several tributaries draining into the St. Lawrence River. Oxygen-18 and deuterium values all fall within the interval defined by our set of values. During 2004, several samples from the St. Francis and Yamaska rivers (two smaller tributaries draining into the St. Lawrence River) were collected by collaborators from the GEOTOP-UQAM-McGill research center. These samples displayed isotopic values similar to those calculated for the smaller tributaries.

4.1.2 Precipitation and groundwater

Because the St. Lawrence River drains a very large portion of Central and Eastern Canada, precipitations and their isotopic compositions are most likely to be affected by regional scale climatic processes. The Canadian Network for Isotopes in Precipitation (CNIP) operates several stations in Canada, and stable isotopic data from these stations were used to estimate the heterogeneity of precipitation over the St. Lawrence River basin. Long-term records are available for Simcoe station located within the Great Lakes basin, whereas the Ottawa and Ste. Agathe stations cover the Ottawa River basin. Isotopic records span different time periods but are extensive enough to reliably characterize the isotopic signature of precipitation over

the basins (1976-1981 for Ste. Agathe, 1976-1994/1999-2002 for Ottawa and 1975-1980 for Simcoe, figure 2).

The Ste. Agathe and Ottawa stations, located at higher altitudes in the Ottawa River basin, display a more depleted isotopic signature ($\delta^{18}\text{O} = -12.7\text{‰}$, $\delta^2\text{H} = -89\text{‰}$ and $\delta^{18}\text{O} = -11.1\text{‰}$, $\delta^2\text{H} = -77\text{‰}$, respectively) than the Simcoe station, located near Lake Erie ($\delta^{18}\text{O} = -9.5\text{‰}$, $\delta^2\text{H} = -63\text{‰}$). Therefore, it seems possible to distinguish the isotopic input of precipitation in the two watersheds.

The isotopic content of precipitation within the Ottawa River basin is also heterogeneous. A comparison of the oxygen-18 and deuterium content of precipitation during the 1976-1982 period at the Ottawa and Ste-Agathe stations revealed that for both isotopes, although monthly variations appear to be correlated from one station to the next ($\delta^{18}\text{O}_{\text{Ottawa}} = 0.88 * \delta^{18}\text{O}_{\text{Ste.agathe}} + 0.001$, $R^2 = 0.81$ and $\delta^2\text{H}_{\text{Ottawa}} = 0.85 * \delta^2\text{H}_{\text{Ste.agathe}} - 2.15$, $R^2 = 0.78$), absolute isotopic values are less depleted in heavy isotopes at the Ottawa than at the Ste. Agathe station.

Monthly composites samples are also available for the Ottawa and Egbert stations for the time length of this study (CNIP dataset, unpublished data for the 1997-2002 period). This dataset will be useful to estimate propagation time of climatic signals and post-rain modification of water isotopic composition. Results are displayed in figure 2. The oxygen-18 and deuterium values recorded at the Ottawa station from 1997 to 2002 slightly differ from long-term averages whereas those from the Egbert station appear to be more depleted than those recorded at Simcoe from 1975 to 1980. Despite small differences, the more recent isotopic data still display the same heterogeneity characterizing older time records.

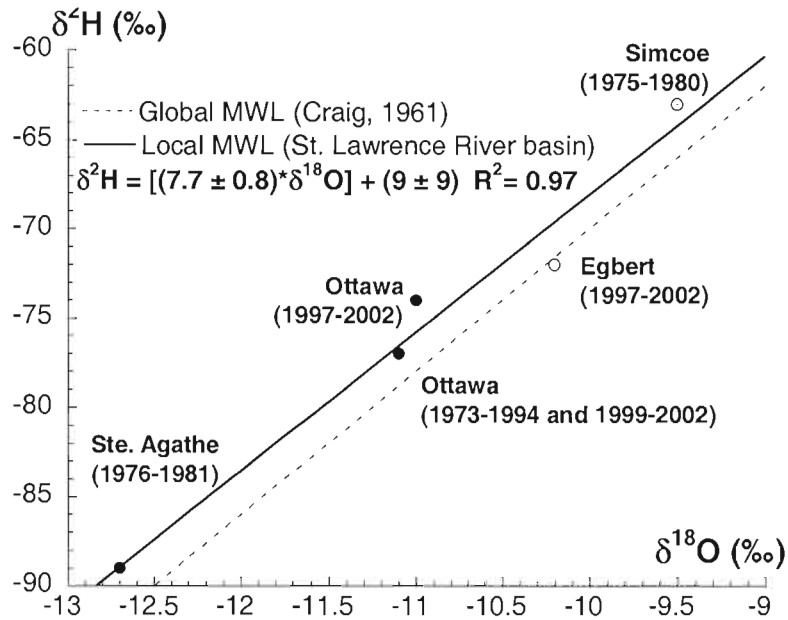


Figure 2. Weighted annual isotopic compositions of precipitation in the St. Lawrence River basin from the CNIP dataset. Solid points are data from stations located within the Ottawa River basin, while empty points represent data from the Great Lakes basin. All data fit onto a local meteoritic water line close to the Global Meteoritic Water Line (Craig, 1961).

The isotopic composition of groundwater is thought to be representative of the mean weighted annual composition of precipitation (Clark and Fritz, 1997). However, this assumption depends on the period of recharge and on the extent of post-rain modification of water isotopic composition prior to recharge. In eastern Canada, Fritz et al. (1987) observed a significant correlation between the mean annual composition of precipitation and groundwater isotopic content. This correlation is due to the period of recharge that takes place in late spring before the loss of water through evapotranspiration becomes important. Recharge also occurs during late fall when air temperature drops thereby limiting surface water and soil evaporation and plant transpiration. Summer rains should not contribute significantly to recharge because the water can be affected by evaporation in soil and/or interception by vegetation. In the same way, winter- or early spring-depleted water should have limited infiltration in frozen soils. The mixture of late-Spring depleted water and late-Fall enriched water in the recharge zone should thus plot near the average annual isotopic values of precipitation over the recharge area.

Moreover, annual seasonal variations of either precipitation or runoff are greatly dampened in shallow groundwater and even more at greater depths (Clark and Fritz, 1997).

To our knowledge, no recent large-scale study of stable isotopes in groundwater has been conducted in southwestern Quebec since the contribution of Fritz et al. (1987). Their $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data of groundwater across Canada will serve as an estimate of the isotopic content of groundwater in the studied area. These data show a clear northwestern gradient toward more depleted values across southern Quebec. This gradient is not paralleled by latitude and is thought to be representative of continental progression of air masses (Fritz et al., 1987). $\delta^{18}\text{O}$ values of -9‰ to -11‰ are observed in the Great Lakes region, whereas values between -12 and -13‰ characterize the Ottawa River basin. These results are in agreement with data compiled by Simard (1977) in the Eaton River and Mirabel aquifer. $\delta^{18}\text{O}$ values of -12.2‰ and between -10.5‰ to -11.9‰ were obtained for these two aquifers, respectively (values for modern samples dated using ^{14}C measurements). Cloutier et al. (2001) reported similar $\delta^{18}\text{O}$ values (-11.3‰ , 0.6‰ standard deviation from several measurements) for groundwater located north of Montreal Island up to the Laurentian Mountains.

Contribution to discharge from groundwater in the St. Lawrence River itself should be limited because of the near constant volume of water delivered annually by the Great Lakes. On the other hand, groundwater contribution could be substantial in tributaries draining the St. Lawrence Lowlands.

4.2 Discharges rates

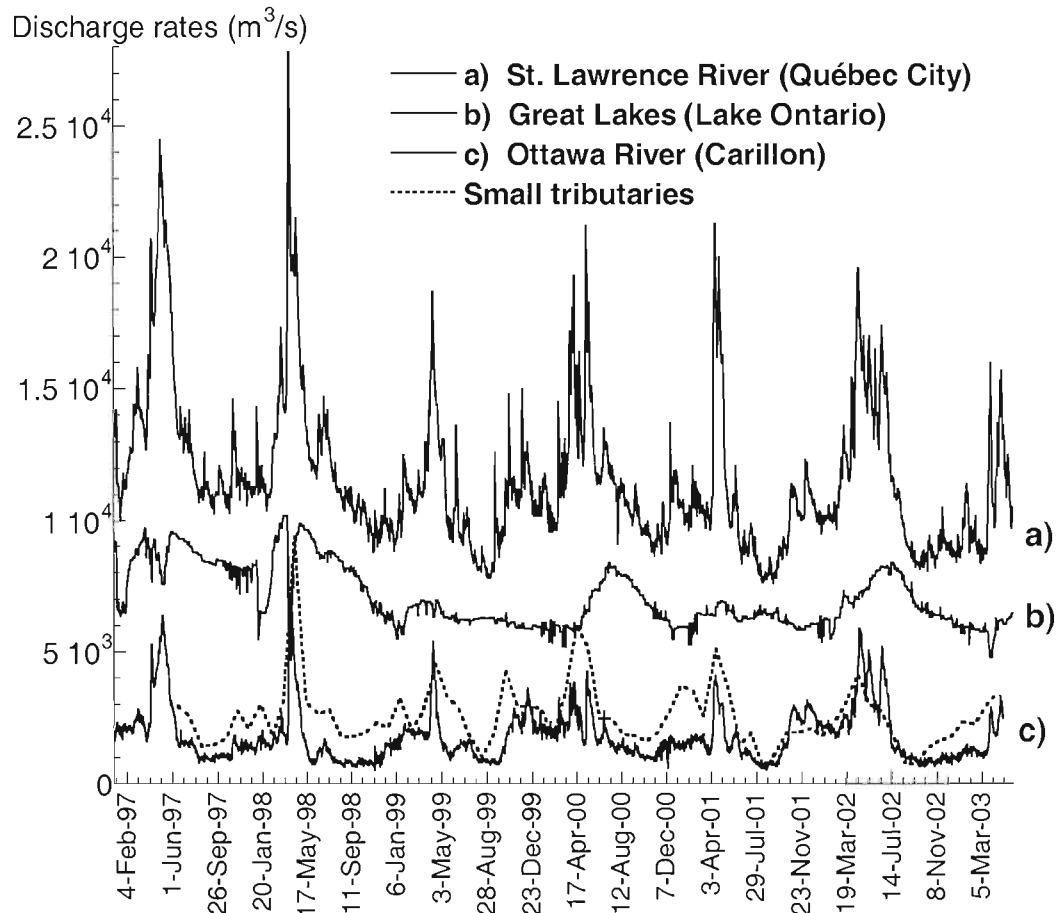


Figure 3. Daily discharge rates for the St. Lawrence and Ottawa rivers. Calculated average monthly values for smaller tributaries are also shown (dashed lines). Note the high frequency variability at Quebec City in comparison with the smoothed signal of the Great Lakes.

The large volume of water contained within the Great Lakes and the mechanical regulation associated with the St. Lawrence Seaway are responsible for the low annual variations observed at the outlet of Lake Ontario. Discharge rates at Cornwall oscillated between 4690 and $10200 \text{ m}^3/\text{s}$, with a mean value of $7066 \text{ m}^3/\text{s}$, from 1997 to 2003. Highest values were observed during the spring of 1998.

The annual contribution from the Ottawa River to the St. Lawrence River is in the order of $1810 \text{ m}^3/\text{s}$, with the highest value of $7239 \text{ m}^3/\text{s}$ recorded during the spring

of 1998 and the lowest value of 535 m³/s during the winter of 2000-2001. The Ottawa River is also highly regulated by the presence of several hydroelectric dams, but the contribution of numerous unregulated tributaries attenuates the dampening effect of human regulation (Telmer, 1997). Consequently, the attenuation of natural discharge variability occurs, but not as intensively as in the Great Lakes.

The volume of water at the outlet of the St. Lawrence River at Quebec City varies according to the different contributions from the Great Lakes and the river's tributaries. During low water levels, baseflow is sustained by the contribution from the Great Lakes but can be as low as 7950 m³/s, whereas in the spring, the meltwater peak is characterized by a greater contribution from smaller tributaries and the Ottawa River, with discharge rates as high as 23251 m³/s. Average discharge for the 1997-2003 period was 11429 m³/s.

Contributions from smaller tributaries have been estimated by subtracting discharge values at Cornwall and Carillon stations from Quebec City values. Their cumulative contribution is of the same order of magnitude as that of the Ottawa River. It can vary from 648 m³/s to 9383 m³/s (average value of 2555 m³/s). Mean monthly values are displayed in figure 3. Discharge variability is similar to that of the Ottawa River.

4.3 Climatic parameters

Data from the Toronto, Ottawa and Saint-Jérôme stations were extracted from the MSC database. These stations were chosen because of the consistency of their time records to characterize the different geographical regions. Mean air temperature and weighted annual values are listed in table 2 for the 1971-2000 and 1997-2002 periods. Long term values slightly differ from that of the study period (1997-2002) thus raising concerns about the regional impact of global warming on precipitation.

		1971-2000		1997-2002		
		Air temperature	Precipitation	Air temperature		Precipitation
	Altitude	Mean	Annual	Mean	Weighted mean	Annual
	meter	°C	mm	°C	°C	mm
Toronto*	112,5	9,2	834	10,5	10,8	743,3
Ottawa*	114	6	943,5	7,7	9,1	843,3
Saint-Jerôme	169,5	5	1064	6,1	7,2	970,6
Drummondville*	82,3	5,9	1125	7,2	7,6	962,9

Table 2. Air temperature and precipitation data for stations located in the St. Lawrence River basin.

* Station that meets the standards of the World Meteorological Organization.

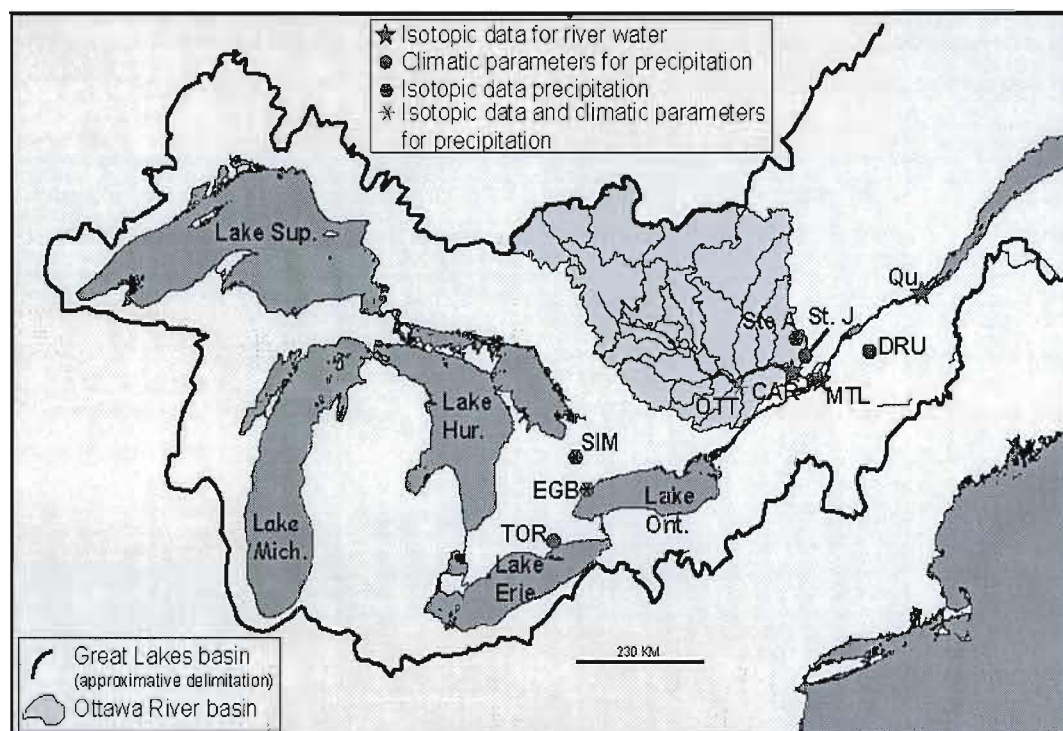


Figure 4. Location of the three river sampling stations and other stations where isotopic and climatic data were collected by the CNIP and MSC. (CAR: Carillon; OTT: Ottawa; DRU: Drummondville; MTL: Montreal; Ste A: Ste Agathe; St J: St Jerome; Qu: Quebec City; SIM: Simcoe; EGB: Egbert; TOR: Toronto)

5. DISCUSSION

5.1 Isotopic signature of water in the St. Lawrence River basin

5.1.1 Precipitation

Because this study focuses on processes occurring in the basin, climatic and isotopic processes occurring prior to precipitation will only be briefly addressed. Basic information about these processes can be found in Clark and Fritz (1997), Yurtsever and Gat (1981) and Kendall and McDonnell (1998)

The St. Lawrence River drains a large portion of North America with contrasting geographic features, including large water bodies, mountainous terrains and lowlands. Fritz et al. (1987) showed that the isotopic content of precipitation varies significantly over Eastern Canada, mainly because of the loss of heavy isotopes by condensation in air masses as they move across the continent. The survey conducted by these authors was not precise enough to capture small-scale physiographic features, such as the local effect of the Appalachian Mountains. Nevertheless, their findings agree with the more recent data from the CNIP dataset, which show a significant difference in the isotopic content of precipitation falling over the Great Lakes and the Ottawa River basin. Because this basin is located at an altitude ranging from 46 to 406 m (masl, Meteorological Service of Canada), it might be expected that the isotopic composition of precipitation will be more depleted in heavy isotopes due to large variations in mean air temperature (see table 2). This variation can be attributed not only to the difference in elevation, but also to the higher latitude of the Ottawa River basin.

Air masses that reach the St. Lawrence River basin originate mostly from either the Pacific or Atlantic Ocean; however, during winter, the penetration of Arctic air masses can also be relatively significant (Bryson and Hare, 1964). During summer,

precipitations over the basin are influenced by warm, humid air masses from the Gulf of Mexico. As the air masses move over North America, they gradually become depleted in heavy isotopes by a rainout process known as Rayleigh-type distillation (Machavaram and Krishnamurthy, 1994). This is in agreement with the map of average distribution of oxygen-18 in mean annual precipitation in Canada produced by the CNIP (<http://www.science.uwaterloo.ca/~twdedwar/cnip/cniphome.html>). This map clearly shows that the Great Lakes basin is located in a more heavy isotope-enriched region (from -10‰ to -6‰) while the Ottawa River basin is incorporated in a more ^{18}O -depleted region (-14‰ to -10‰). Figure 5 shows the local meteoric water lines (LMWL) for the Ottawa River and the Great Lakes basin. The slope of the $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ relationship is significantly different in the two basins and is smaller than that observed by Fritz et al. (1987) for Canada ($\delta^2\text{H} = \delta^{18}\text{O} * 7.75 + 9.83$).

The influence of the Great Lakes on the isotopic content of precipitation has been discussed in a few studies (Machavaram and Krishnamurthy, 1995; Bowser et al. 1994). They found that during summer, 9 to 21% (Machavaram and Krishnamurthy, 1995) and 4.6 to 15.7% (Gat et al., 1994) of the total vapour load over the Great Lakes basin originates from evaporation of lake water. This contribution was detected by changes in the deuterium excess values of precipitation downwind of the Great Lakes, where monitoring stations all show average deuterium excess values above 10, which is the theoretical value for the global meteoric water line (Dansgaard, 1994). It was not shown if this additional moisture significantly affected the absolute isotopic values of precipitation or their relationship with climatic parameters (air temperature and/or amount of precipitation).

It was not possible to characterize the isotopic input or precipitation over the St. Lawrence Lowlands and the Appalachians Mountains. It might be expected that only small differences exist between the isotopic composition of precipitation at the

Ottawa and Drummondville stations, since they are located at relatively similar altitudes (114 and 82 meters, respectively).

5.1.2 Surface water

The isotopic content of surface water is significantly different in the Great Lakes, the Ottawa River and the smaller tributaries (table 3). The isotopic heterogeneity of precipitation in these basins is partly responsible for this difference. Post-rain hydrological processes affecting the isotopic content of water, such as evaporation and isotopic enrichment of snow in the snow blanket, could also account for this difference. Depending on local climatic conditions (relative humidity and air temperature) and the hydrologic properties of the basin (water/land surface ratio, residence time of water), these hydrologic processes will have a more or less significant effect on the isotopic signature of water.

	Montreal			Carillon			Quebec			Tributaries		
	$\delta^{18}\text{O}$	$\delta^2\text{H}$	Dxs	$\delta^{18}\text{O}$	$\delta^2\text{H}$	Dxs	$\delta^{18}\text{O}$	$\delta^2\text{H}$	Dxs	$\delta^{18}\text{O}$	$\delta^2\text{H}$	Dxs
	‰	‰	‰	‰	‰	‰	‰	‰	‰	‰	‰	‰
<i>Weighted annual</i>	-7.1	-54	3	-10.8	-80	6	-8.6	-65	4	-10.8	-78	8
Mean annual	-7.1	-54	3	-10.8	-80	6	-8.4	-64	3	-10.6	-75	11
S.D.	0.5	3	2	0.6	3	3	0.9	7	2	2	10	10

Table 3. Isotopic compositions of the St. Lawrence (Montreal and Quebec) and Ottawa (Carillon) rivers from 1997 to 2003 along with calculated values for smaller tributaries. Mean annual values are almost identical to discharge-weighted values. Standard deviations provide an estimate of the relative variability of isotopic data. Deuterium excess values show little variation from one station to another. Tributaries display the most variable isotopic compositions.

Table 3 displays the average and weighted average isotopic values at the three sampling stations and the calculated values for the smaller tributaries. Discharge-weighted values are only slightly different from if not identical to average values underlying the buffered nature of these hydrologic systems. The isotopic values of Great Lakes water are more enriched than those of all the tributaries draining into the St. Lawrence River.

The discrepancy between the isotopic content of precipitation and that of surface water is a common feature of most watersheds and is often caused by evaporation of open-surface and soil water. In the St. Lawrence River basin, deuterium excess values show significant signs of evaporation, since they are systematically lower than local precipitation values (10‰ at Egbert and 15‰ at the Ottawa station). Water evaporation tends to decrease the content of deuterium relative to that of oxygen-18, thus decreasing the deuterium excess value ($D_{xs} = \delta^2H - 8 \cdot \delta^{18}O$) in remaining water. Evaporated water is also recognizable when its $\delta^{18}O$ and δ^2H values are plotted. The slope of the regression line fitted through the isotopic cluster will be lower than that defined by equilibrium fractionation (with a slope equal to 8).

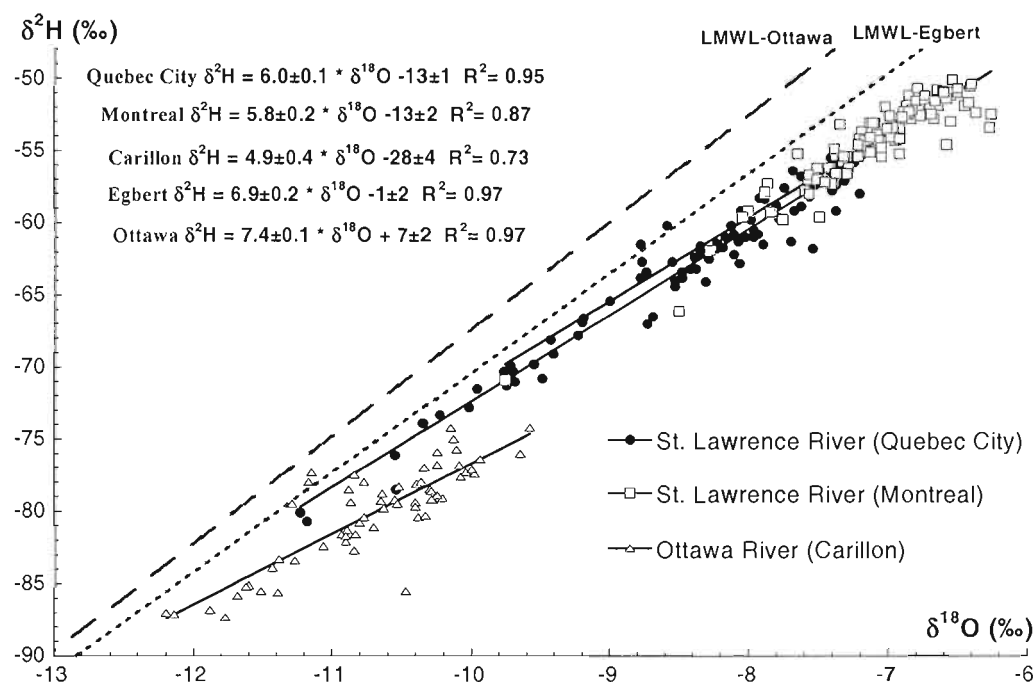


Figure 5. Bimonthly to weekly values of the stable isotope systematic of water in the St. Lawrence and Ottawa rivers. Deuterium and oxygen-18-enriched values are observed at Montreal (located at the outlet of the Great Lakes), whereas more negative isotopic compositions characterize the Ottawa River water. Quebec City samples display an intermediate signature closer to that of the Great Lakes. The slope of 4.9 defined by the Ottawa River samples underlines the incidence of evaporation in the corresponding catchment basin compared with a lesser influence in the Great Lakes basin (as illustrated by St. Lawrence River water at Montreal). Local meteoric water lines are presented for precipitation at Ottawa and Egbert stations, respectively located in the Ottawa River and the Great Lakes basins.

5.1.2.1 Water in the Great Lakes

Outflowing waters from the Great Lakes display isotopic compositions typical of large bodies of high-residence time waters. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values define a dense cluster and represent the most ^{18}O - ^2H enriched values observed in the St. Lawrence system (figure 5). The density of the isotopic cluster indicates the low seasonal and interannual variations observed at the outlet of the Great Lakes. The fact that mean annual $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values do not differ from weighted annual values illustrates the low seasonal variations of both isotopic composition and discharge (table 3). The discrepancy between the delta values of precipitation at the Egbert station and those of water outflowing from the Great Lakes can be attributed to the dilution of precipitation in the large volume of lake water and to the evaporation of surface water. The weighted annual $\delta^{18}\text{O}$ ($\delta^2\text{H}$) values for Great Lakes water between 1997 and 2003 was -7.1‰ (-54‰), compared to -10.1‰ (-71‰) for precipitation at the Egbert station. The difference represents a 3‰ (17‰) enrichment. This isotopic enrichment is noticeable when $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data are compared (Figure 6). The linear regression fitted through the isotopic cluster has a slope of 5.8 ± 0.2 , compared to a slope of 6.9 ± 0.2 for precipitation samples. This lower slope for river samples is the result of evaporative isotopic enrichment associated with kinetic fractionation occurring during evaporation and, to a lesser extent, to enrichment processes in the snowcover (due to the scale of the observation).

The regression line fitted through Montreal samples intercept within standard deviation the weighted annual isotopic input of precipitation at the Egbert station ($\delta^{18}\text{O} = -10.1\text{‰}$ and $\delta^2\text{H} = -71\text{‰}$). Observed isotopic values at the outlet of the Great Lakes are thus closely related to the isotopic input from precipitation that took place during the same period. The weighted average isotopic compositions of precipitation could be used to represent the main input to the Great Lakes system instead of using values from small rivers draining into the lake (Yang et al. 1995). This close relationship between isotopic values of lake waters and precipitation also

raises some interrogations about the use of the theoretical residence time for water in the Great Lakes (ca. more than 200 years, Quinn, 1992). A more detailed isotopic monitoring of Great Lakes waters could be done to assess the effective residence of water in this system.

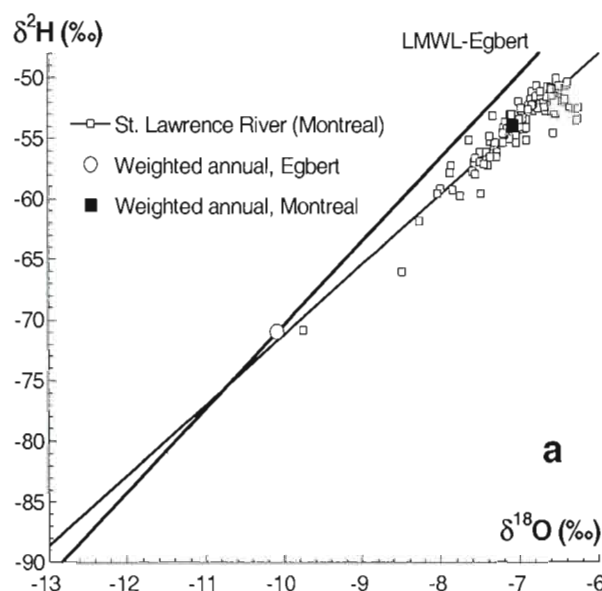


Figure 6. Relationship between isotopic values of river water and precipitation in the Great Lakes basin. Bimonthly to weekly data (1997 to 2003) are displayed for the Montreal station along with the weighted annual isotopic input of precipitation at the Egbert station (CNIP). The linear regression fitted through river samples is prolonged to highlight its interception with the LMWL.

Due to the hydrological nature of the Great Lakes basin, outflowing water sampled at Montreal is an integration of all the precipitation falling over the five major lakes and the surrounding catchment and of the evolution of water as it circulates through the chain of lakes. One important aspect to consider is the spatial variability of the isotopic content of water in the chain of lakes. One would think that water would become more isotopically enriched due to evaporation as it flows from lake to lake. Gat (1995) presented examples of such an isotopic build-up in different hydrologic systems, the so-called “string-of-lakes” effect. In the case of the Laurentian Great Lakes, Gat argued that the isotopic build-up is perturbed by meteoritic and drainage inputs of different isotopic compositions, which increase the complexity of the system and make it difficult to treat it with a simple isotopic model.

Results from previous studies showed however that the isotopic composition of water within the Great Lakes basin undergoes minimal changes along the chain of lakes. A synoptic survey conducted in October 1967 by Brown (1970) showed that the isotopic content of water remains fairly constant from Lake Superior to the outlet of Lake Huron. An enrichment of 1‰ in $\delta^{18}\text{O}$ was observed between the inflow and outflow of both Lakes St. Clair and Erie (Yang et al., 1996 and Brown, 1970), possibly because these are the shallowest lakes and therefore favour evaporation the most. Some estimates of evaporation in the Great Lakes from Derecki (1981) showed that annual evaporation from downstream lakes (Lakes Erie and St. Clair) is greater than for upstream lakes such as Lake Superior (676 mm, 569 mm and 483 mm, respectively).

Stable isotopic data from Yang et al. (1996) were used to estimate an overall annual evaporation in the Great Lakes. An estimate of a 7% loss of lake water through evaporation was obtained by these authors. This value is very small considering the fact that the inflow values used in the calculations are those of the Grand and Thames rivers, which are isotopically enriched compared to their precipitation input. The fact that the authors applied this 7% loss to the entire volume of water contained within the five Great Lakes is questionable. Thermal stratification of the water column that occurs during summer and winter limits exchanges between epilimnion and hypolimnion water. Since Yang et al. (1996) divided the 7% value by the theoretical residence time of water in all the Great Lakes, this calculation is questionable.

It can be expected that the isotopic content of upper lakes is more influenced by tributaries and precipitation input whereas in the lower lakes, the isotopic content of water is dictated by the massive input from upstream lakes. The isotopic signature at the end of the chain of lakes could thus greatly depend on the hydrology of the larger lakes upstream.

Some attention has been given to the effect of thermal stratification of the water column on the isotopic compositions of Great Lakes water. Bennett (1978) characterized some aspects of the thermal regime of Lake Superior and identified two periods of stratification in the water column. The summer stratification takes place from mid-July to late November whereas the winter stratification develops in early January and vanishes in mid-April. The overturning occurs at the end of the stratification period (late Fall and Spring) with a surface mixed layer often as deep as the lake depth. The overturning is thought to happen earlier for shallower lakes, such as lakes Ontario and Erie (Bennett, 1978).

During the late Fall overturning period, isotopically enriched water is moved to great depths. It will remain there until the following overturning (in early Spring) mixes deep water with the spring-depleted surface water. At that moment, depleted Spring water is stored at great depth until late Fall overturning brings it into contact with enriched surface water. Sampling done in Lake Ontario by Torgensen (1977) yielded interesting results. ^3H - ^3He ages were measured in the water column at several stations in June and August 1974. In the last week of June, ^3H - ^3He ages of 30 to 50 days were found throughout the water column, indicating that vertical mixing was still occurring and that deep water had not lost all its ^3H excess. At the end of August, surface samples had an age approaching 0 days while hypolimnion water was 110 days old. This indicates that hypolimnion water was brought down approximately at the beginning of May, when overturning is thought to occur. Similar results were obtained for Lakes Erie and Ontario, where hypolimnion water showed ^3H - ^3He ages of 160 days in mid-October 1974, which places the overturning in mid-May.

It is not known how this overturning/stratification phenomenon affects the isotopic composition of outflowing water sampled at Montreal. One would think that it should attenuate the isotopic depletion of Spring melt-water and deplete Fall-

enriched surface water. Such a result was modelled by Gat (1970) in Lake Tiberias. When incorporating stratification and overturning into his model instead of assuming a fully mixed water column, Gat observed a shorter depleted Winter signal and a less enriched Summer peak. The Great Lakes situation is quite different from that of Lake Tiberias because winter isotopic signal is retained in the snow blanket and released later in the Spring. Sampling water at the outlet of the chain of lakes did not allow us to capture short-term variations specific to each lake.

The enriched isotopic compositions observed at the outlet of the Great Lakes are thus the result of a low but steady enrichment due to evaporation, particularly in the downstream shallower lakes and. In addition, the precipitation falling over the Great Lakes are the most enriched observed in the St. Lawrence River basin.

5.1.2.2 Water in the Ottawa River

The water sampled from the Ottawa River displays the most depleted isotopic values observed in our survey but also seems to be the most affected by evaporative enrichment. Its $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ slope of 4.9 ± 0.4 is typical of water having been affected by substantial evaporation (Figure 7). Seasonal isotopic variations are as low as those observed in the Great Lakes and mean annual isotopic values are identical to weighted annual values. This highlights the overall buffered hydrology of the Ottawa River.

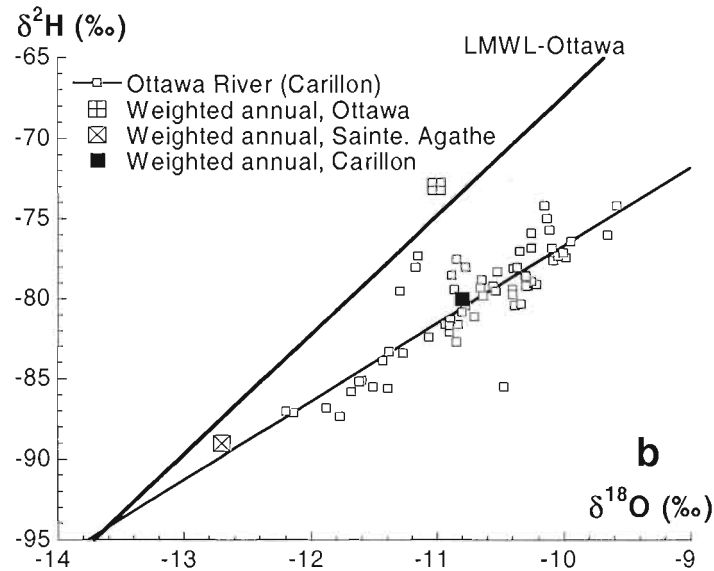


Figure 7. Bimonthly to weekly isotopic values for the Ottawa River and weighted annual values for river water and precipitation in the Ottawa River basin. Precipitation over the basin are characterised by the Ottawa (1997-2002) and Sainte-Agathe (1975-1981) stations. The isotopic signature of the Ottawa River shows a good agreement with the isotopically depleted precipitation recorded at Sainte-Agathe.

The relationship between the isotopic composition of runoff and that of precipitation at Ottawa is not direct. The linear regression fitted through the river samples intercept the LMWL (defined by Ottawa station samples) at $\delta^{18}\text{O} = -13.6\text{‰}$ and $\delta^2\text{H} = -94\text{‰}$. These values are isotopically lighter than the weighted annual input of precipitation at Ottawa ($\delta^{18}\text{O} = -11.0\text{‰}$ and $\delta^2\text{H} = -73\text{‰}$). This could be due to the fact that the Ottawa station (located at an altitude of 114 meters) is not representative of the mean input of precipitation over the basin, which has an altitude ranging from 46 to 406 m (masl, Meteorological Service of Canada). The difference in altitude has a direct impact on mean annual air temperature, which, for the Ottawa station, is 6.0°C , whereas for the Sainte-Agathe station, at 395 meters in altitude, it is 3.1°C (Meteorological Service of Canada, data from 1971 to 2000). The isotopic composition of precipitation over more elevated parts of the Ottawa River basin could thus be more depleted in oxygen-18 and deuterium at the Ottawa station. Telmer (1997) estimated the isotopic compositions of precipitation in the Ottawa River basin to be of -14.5‰ for $\delta^{18}\text{O}$ and -103.8‰ for $\delta^2\text{H}$ between 1991-

1994. These numbers were obtained by extrapolating the regression line fitted through a set of data from the Ottawa River at Carillon until its interception with the local meteoric water line defined by Fritz et al. (1987) and are quite similar to the results obtained within this study.

Data from the Sainte-Agathe station for the 1976-1981 period are reported in figure 7. The weighted annual values are more ^2H & ^{18}O -depleted than those observed at the Ottawa station. The regression line fitted through Ottawa River samples shows better agreement with isotopic values at the Sainte-Agathe station, which could be more representative of the mean isotopic composition of precipitation in the Ottawa River basin. Such an altitude effect has been demonstrated in several studies which reported a gradient of -0.15‰ to -0.5‰ in $\delta^{18}\text{O}$ per 100 meters of elevation (Clark and Fritz, 1997). The difference in elevation between Ottawa and the rest of the Ottawa River basin could cause precipitation to be 0.5‰ to 1.5‰ lighter than the values observed at Ottawa.

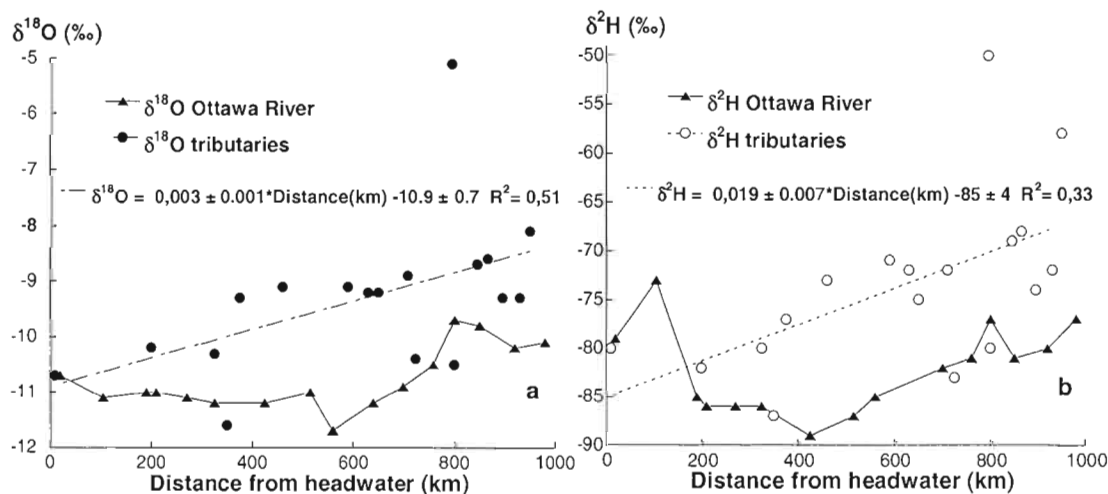


Figure 8. Spatial evolution of the isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of the Ottawa River and its tributaries. Distance is calculated from Dozois Reservoir to the end of the river at Carillon. Samples were taken during September and October of 1991 (data from Telmer, 1997). The input from the Gatineau River which display the most heavy isotopes enriched values ($\delta^2\text{H} = -50\text{‰}$ and $\delta^{18}\text{O} = -5.1\text{‰}$) is clearly noticeable. These values have not been used to calculate the regression line.

Telmer (1997) estimated the evaporation in the Ottawa basin. The total volume of water contained in the basin is unknown but considering a water residence time

greater than 1 year for groundwater reservoirs, Telmer found that 8.1% of the total precipitation volume was lost via evaporative processes in 1994, representing roughly 10 000 km³. This could explain the heavy isotope enriched signature of water at the mouth of the river.

This evaporated signature could be the result of heavy isotope enrichment occurring in open-surface water (lakes and reservoirs) as in a string-of-lakes effect (Gat, 1995). Numerous dams and reservoirs located on the Ottawa River are likely to increase water losses through evaporation. A synoptic survey of the Ottawa River conducted in 1991 by Telmer (1997) did show a low but steady enrichment in oxygen-18 and deuterium from the upland reservoir to the mouth of the river at Carillon (figure 8). This spatial trend could also be attributed to changes in the isotopic content of precipitation, and thus of input from tributaries, corresponding to an increase in altitude and a decrease in mean air temperature. Such an altitude pattern in precipitation was previously discussed and data from Ottawa River tributaries sampled in the fall of 1991 and spring of 1992 by Telmer (1997) seem to support this pattern. Figure 8 illustrates the evolution of both the tributaries and the main river towards isotopically heavier values from the head of the catchment to the mouth of the river. These results suggest that the tributaries dictate the isotopic composition of the main river channel. Moreover, the fact that they display heavier ²H & ¹⁸O values than the main river itself also indicates that most of the evaporation occurs during the transit of water in the smaller tributaries rather than in the Ottawa River.

Deuterium excess values of the Ottawa River remain fairly constant from the head of the catchment to the mouth of the river and are similar to those of its tributaries. This leads us to conclude that the evaporated signature of the Ottawa River is inherited from the isotopic composition of its tributaries having been affected by evaporation prior to their mixing with the main river channel. The relatively heavy-

isotope depleted isotopic signature of the Ottawa River can thus be attributed to the isotopically depleted input from the river's tributaries draining the elevated part of the basin.

5.1.2.3 Water in the smaller tributaries

The calculated monthly isotopic values for smaller tributaries display a wide range of values because small rivers are less affected by dilution due to the small size of their reservoirs (small rivers, shallow groundwater). This is illustrated by the large scatter of values in the $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ graph (Figure 9). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the whole dataset do not show a strong correlation ($R^2 = 0.37$). As will be seen later, isotopic values for individual years show a much more linear $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ relationship. Most of the isotopic values plotted on the local meteoric water line defined by precipitation samples at Ottawa, whereas the weighted annual isotopic values of runoff and precipitation are relatively similar (Figure 9).

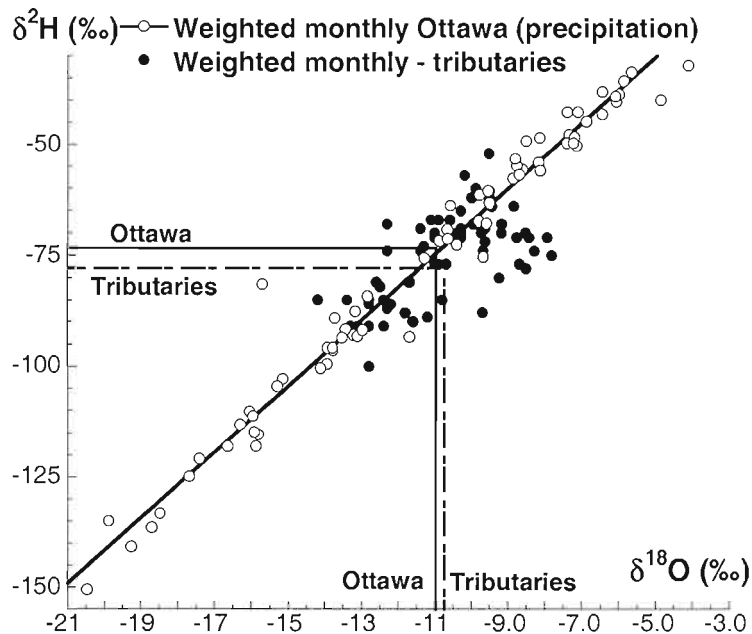


Figure 9. Calculated weighted monthly isotopic values for smaller tributaries and weighted monthly values for precipitation at Ottawa. Weighted annual values for precipitation and runoff are similar (represented by solid and dashed lines, respectively) and most of the isotopic values for smaller tributaries plotted on the LMWL at Ottawa. Some data points located below the LMWL indicate that heavy isotopes enrichment of surface water by evaporation occurred.

These observations suggest that the isotopic signature of small rivers might be closely related to the input of the weighted annual precipitation. Deuterium excess values are the highest observed in the St. Lawrence River basin but remain lower than those for precipitation at the Ottawa station, which suggests that water in smaller tributaries may be slightly affected by non-equilibrium fractionation processes (evaporation).

The catchment basins of the smaller tributaries of the St. Lawrence River are located either in the Laurentians or in the Appalachians and the St. Lawrence Lowlands. Due to differences in altitude and mean air temperature, it may be expected that these tributaries have different isotopic signatures that depend on the location of their headwaters. Although the lack of direct measurements in tributaries prevents us from validating this assumption, a synoptic monitoring conducted by Yang et al. (1995) in the fall of 1991 and spring of 1992 in several tributaries draining into the St. Lawrence River yielded interesting information about the isotopic signature of these tributaries. When plotting $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values from spring grab samples, it was possible to distinguish between values from the south and north shore tributaries and rivers draining into the Great Lakes basin (Figure 10). When mean discharge rates for all the tributaries are considered (St. Lawrence Center, http://lavoieverte.qc.ec.gc.ca/CSL/inf/images/inf016_001_e.jpg), the contribution from rivers draining the north shore and that of tributaries draining the St. Lawrence Lowlands and the Appalachian Mountains is roughly equal. The composite isotopic signatures of smaller tributaries are thus expected to present values intermediate between those of the south shore and north shore tributaries.

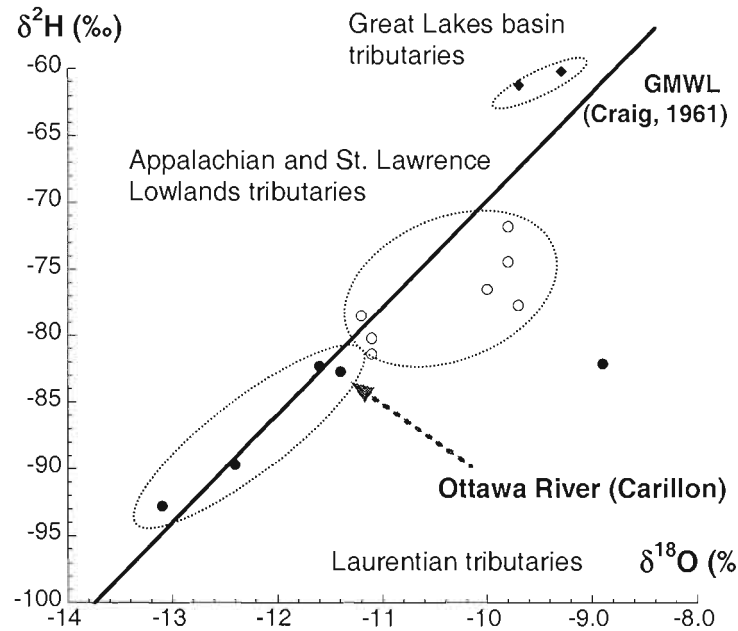


Figure 10. Isotopic compositions of water sampled in tributaries of the St. Lawrence River during the Spring of 1992 (data from Yang et al., 1995). Isotopic data are separated into different groups according to the location of their headwaters. The Batiscan River is clearly affected by evaporation as its isotopic values stand out of the isotopic clusters defined by all tributary samples.

5.1.2.4 Water in the St. Lawrence River

The isotopic composition of water at the outlet of the St. Lawrence River (Quebec City) depends upon contributions from all sources considered above, namely the Great Lakes, the Ottawa River and numerous smaller tributaries. Each of these sources has a distinct isotopic signature. The dampened isotopic input of the Great Lakes is the most heavy-isotope enriched one and accounts for a great portion of the Quebec City signal because of the near-constant volume of water delivered throughout the year ($7066 \pm 1112 \text{ m}^3/\text{s}$). As the largest tributary, the Ottawa River, with its more depleted signature, contributes to a substantial portion ($1800 \text{ m}^3/\text{s}$ on average). Smaller tributaries draining the surrounding mountains and lowlands contribute significantly to the composite signal at the outlet of the river with an isotopic composition not unlike that of the Ottawa River (figure 11a and b).

The weighted sum of all these distinct sources accounts for the final signature observed at Quebec City. To estimate the true contribution of each source, we can calculate the weighted isotopic input of this source:

$$\text{Weighted isotopic input} = \delta_{\text{station}} * (Q_{\text{station}}/Q_{\text{Quebec City}}).$$

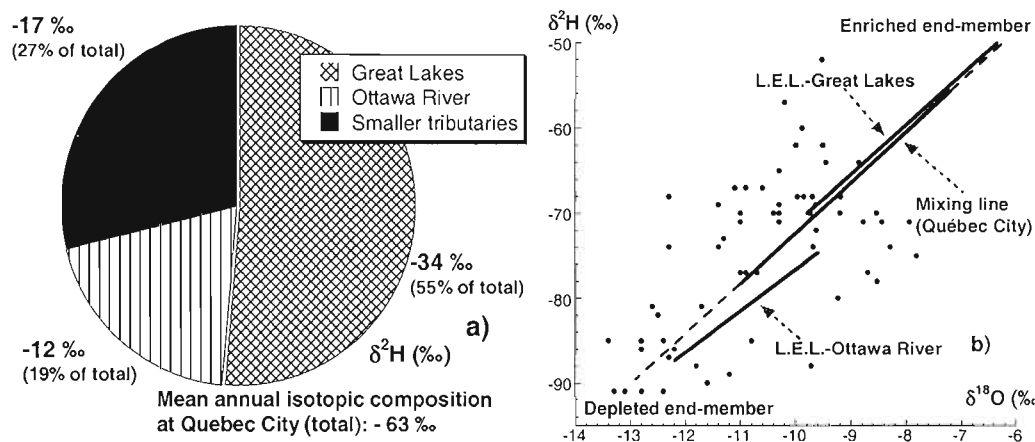


Figure 11 a). Weighted isotopic input to the isotopic signature of water at Quebec City ($\delta^2\text{H} = -63\text{‰}$). The following calculations were done using weighted monthly isotopic and discharge data from June 1997 to March 2003. With its high discharge rates and enriched isotopic signature, Great Lakes water accounts for more than half of the final -63‰. The input from smaller tributaries is slightly greater than that of the Ottawa River due to higher discharge rates. Figure 11b). Local evaporative lines (LEL) for the Great Lakes and the Ottawa River basin are also plotted. The regression line fitted through Quebec City samples is a mixing line between spring-depleted values of tributaries (including Ottawa River) and summer-enriched Great Lakes water. Monthly composite data from smaller tributaries are shown to highlight their contributions to the Quebec City signal during spring.

Because discharge rates at the outlet of the Great Lakes are twice greater than those of all the tributaries combined, their heavy isotope enriched compositions account for a greater portion of the Quebec City signal (Figure 11a). Although the tributaries and the Ottawa River each deliver a smaller volume of water, their heavy-isotope depleted compositions increase their weighted isotopic input. The percentages of the Quebec City signal associated with the smaller tributaries and the Ottawa River input are 27% and 19%, respectively, even though they deliver only 22% and 15%, respectively, of the water outflowing from the St. Lawrence River at Quebec City.

Figure 11b illustrates the local evaporative lines for the Great Lakes and the Ottawa River. Monthly weighted isotopic values for smaller tributaries are also shown. The regression line fitted through Quebec City isotopic values is derived from the seasonally changing contributions from the Great Lakes and the tributaries. The regression line is prolonged (dashed line) to illustrate the two major end-members of the mixing equation, namely spring meltwater from the Ottawa River and the smaller tributaries and summer-enriched water from the Great Lakes. During the snowmelt period (April), the contribution from all the tributaries increases to up to 54% whereas during summer (August), the Great Lakes account for 78% of the discharge at the outlet of the St. Lawrence River. Consequently, isotopic values at Quebec City oscillate between these two end-members, summer isotopic compositions being influenced primarily by Great Lakes-enriched water and spring-depleted values, depending on the contribution from all tributaries.

5.2 Seasonal variability

5.2.1 Discharge rate and water levels

Seasonal variations of discharge in the St. Lawrence River are clearly related to the melting of snow during spring and the low water levels during summer months (figure 12). In tributaries, discharge rates during spring are three times those of August and September. At the outlet of the Great Lakes (Cornwall), discharge values display a contrasting pattern: the highest values are observed in the summer (June) and the lowest values in the Winter (November to January). Water level variations in Lake Ontario are dictated mostly by regulation practices. Variations in discharge rates at the outlet of the St. Lawrence River incorporate the small variability of the Great Lakes with that of the tributaries and the Ottawa River. Discharge rates at Quebec City show better agreement with those of all the tributaries, with the highest values in April and the lowest values in August and September.

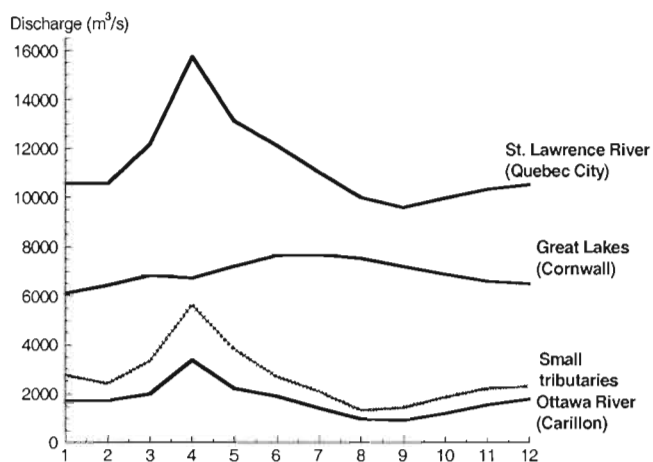


Figure 12. Average monthly discharge rates in the St. Lawrence River basin. Seasonal variability at Quebec City is inherited from the contributions of its tributaries.

5.2.2 Isotopic compositions

The seasonal isotopic variability of surface water in the St. Lawrence River system is driven by two major factors: the seasonally varying input of precipitation and post-rain hydrologic processes that further modify this input. The isotopic composition of precipitation over the St. Lawrence basin shows a good correlation with monthly air temperature and no correlation with the amount of precipitation. Summer precipitations are the most ^2H & ^{18}O enriched, whereas snow precipitating during winter displays the most heavy-isotope depleted compositions (figure13).

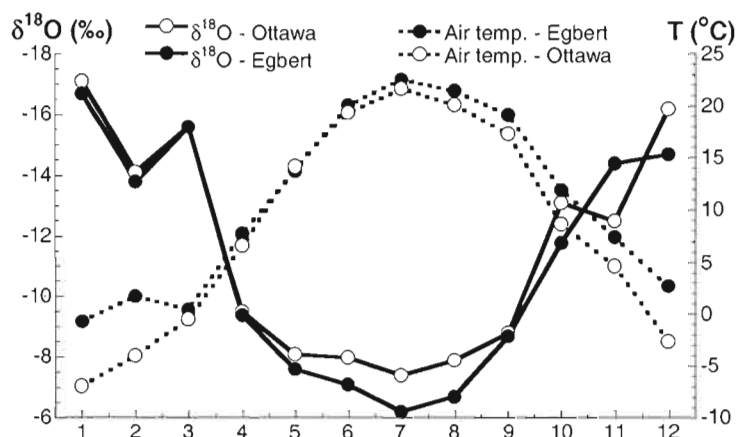


Figure13. Amount-weighted $\delta^{18}\text{O}$ and air temperature values for precipitation at Egbert and Ottawa stations. Note the close relationship between delta values and air temperature.

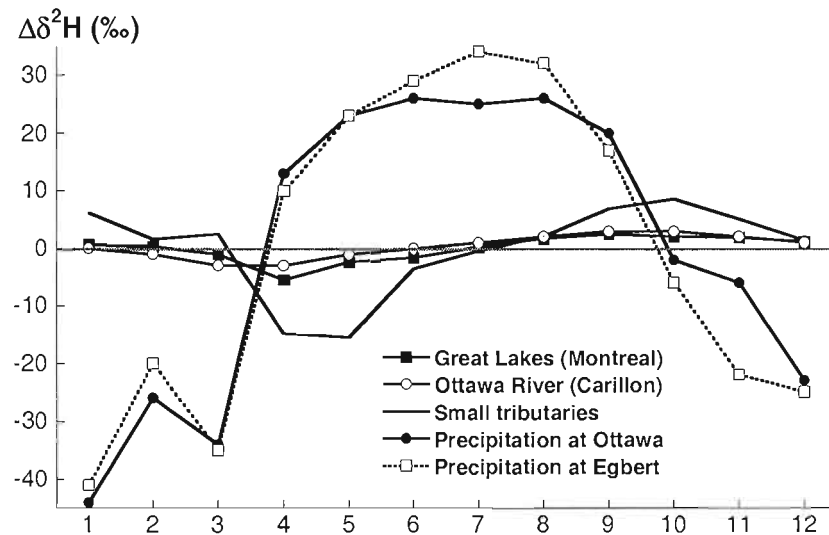


Figure 14. Deviation from weighted annual $\delta^2\text{H}$ values for river water and precipitation. Phase shift and the dampening of the isotopic signal of precipitation are clearly seen. The seasonal cycle seems more buffered in lake water (Great Lakes) and reservoir-dominated rivers (Ottawa River) than in the smaller tributaries.

This seasonal pattern is driven by temperature-dependent fractionation occurring during condensation of water in air masses. Theoretical basis for temperature effects on isotopic fractionation have been discussed by Dansgaard in 1964.

This seasonal cycle is also observed in runoff but with greatly reduced amplitude (figure 14). The seasonal isotopic variability of water is known to be higher in precipitation, reduced in river water and even more reduced in groundwater (Clark and Fritz, 1997). Burgman et al. (1987) observed a significant correlation between the dampening of seasonal variations in river and the percentage of lakes on the river course. Dilution, water residence time and evaporation increase as water passes through lakes and reservoirs. The dampening may also be related to the contribution from groundwater, which has a longer residence time, and a buffered isotopic signal. In such a case, the mean annual isotopic value of surface water should not be significantly different from that of precipitation. Small rivers draining shallow groundwater would be a perfect example of this. On the other hand, if dampening is related to the transit time of water in rivers and lakes and to

evaporation, the mean annual isotopic composition of surface water should be more enriched in heavy isotopes than that of precipitation. The discrepancy between isotopic values of precipitation and surface water in the Great Lakes and Ottawa River basin leads us to conclude that the latter scenario is applicable for most of the St. Lawrence River watershed.

Extensive isotopic monitoring of precipitation and runoff in Sweden (Burgman et al., 1987) showed that the seasonal isotopic variability of river water can be described as an almost perfect sinusoidal function in southern areas of Sweden, where accumulation of snow is low to nonexistent and evaporation is minimal. On the contrary, in areas where major snowmelt occurs during spring, the Fourier expansion used by Burgman et al. (1987) underestimated the amplitude of seasonal isotopic variations in river water. Peak discharge of snowmelt water during spring is responsible for the transformation of the signal, which cannot be described as a sinusoidal function. In figure 14, we observe a significant time lag between the seasonal isotopic variations of precipitation and that of surface water. The peak discharge of depleted snowmelt water during spring is the primary cause of this de-phasing.

As illustrated by the case of the Great Lakes basin in figure 15, the minimum delta values are measured in January in precipitation when air temperature is the lowest. In runoff, the most heavy-isotope depleted compositions are recorded in April, when the melting of snow (winter precipitation) occurs. The Summer heavy-isotope enriched signal is observed in July in precipitation. In runoff, the most isotopically heavy values are recorded in September, November and October. This is probably due to the transit time of water in the catchment but also to the fact that a large portion of summer precipitation is intercepted by active vegetation growth. This was observed in the Arno and Era rivers in Central Italy by Gonfiantini et al. (1963). The $\delta^{18}\text{O}$ content of water in these rivers showed a good correlation with

the input of December rains but did not respond at all to fall precipitations (September to November), which were thought to be intercepted by evapotranspiration and by the recharge of groundwater reservoirs that were depleted in the summer.

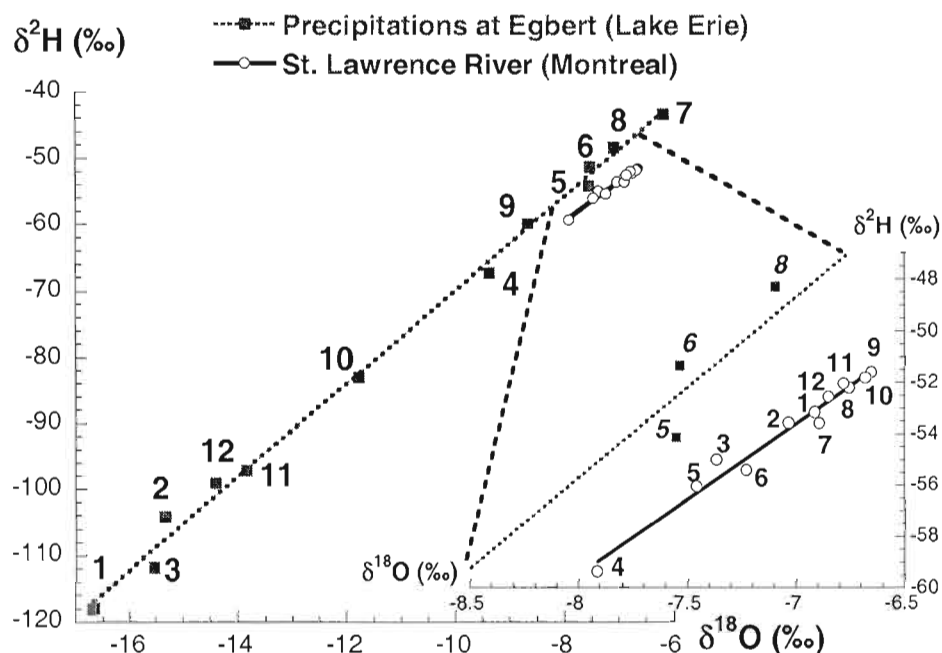


Figure 15. Average weighted monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation at Egbert and surface water outflowing from the Great Lakes. The timing of maximum and minimum values is not the same for precipitation and river samples. The Montreal dataset is enlarged to increase resolution. The numbers correspond to the twelve months of the year, starting with January.

The fact that precipitation displays more heavier isotopic values than summer runoff could be caused here by the dilution of precipitation input in pre-event water, particularly in the case of the Great Lakes basin. In addition to being diluted, dampened and de-phased, the isotopic signal of precipitation is further modified by hydrological processes that enrich surface water in heavy isotopes. Evaporation and heavy isotope enrichment of the snow cover are the two major processes by which the isotopic composition of surface water is altered. Because these processes take place at different times of the year, their isotopic effects contribute to the isotopic seasonality of surface water.

The snowmelt period is very important in the hydrology of the St. Lawrence River basin because, from November to March, precipitation falls almost exclusively as snow. Taylor et al. (2001) demonstrated that no isotopic correlation can be expected between snow precipitation and snowmelt water, whereas only a weak correlation can be observed between snow precipitation and snow layers in the snowpack. They found evidence of isotope redistribution in the snowpack caused by percolation of meltwater and, to a certain extent, by vapour transport causing some isotopic homogenization of the snowpack.

The isotopic content of the snowpack can also be altered by the sublimation of snow and recondensation of atmospheric vapour at the surface layer of the snow blanket. Moser and Stichler (1970, 1974) observed considerably enriched isotopic compositions in the surface layer, even when air temperature remained well below 0°C. Evaporation of snow is maximal during the day, when solar insulation causes an increase in air temperature and, recondensation occurs when air temperature drops below 0°C at night. The evaporation of the surface layer of the snow will concentrate heavy isotopes in the remaining snow but, because the snowpack has relatively high water content, fractionation can occur nearer to isotopic equilibrium than during water evaporation. This results in a steeper $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ slope ($s = 5.75$) for snow samples, as demonstrated by Moser and Stichler (1975).

When major snowmelt begins, an enrichment of the snowpack caused by the preferential removal of light isotopes via snowmelt percolation is observed (Unnikrishna et al., 2002). Meltwater is thus more depleted in heavy isotope than the remaining snow. In the second part of the major snowmelt, the heavy isotopically enriched snowpack begins to melt and the meltwater becomes isotopically heavier. At that time, the isotopic content of the snowpack is also modified by the addition of late spring-enriched rain. Taylor et al. (2001) monitored the evolution of the isotopic composition of meltwater and observed a ^2H & ^{18}O

depleted signature for the first meltwater (melting of the first 5-10% of the snowpack) and a constant enrichment in these isotopes for the rest of the meltwater. On a daily scale, they observed a significant relationship between melt flow rate and the isotopic content of meltwater. Using a physically based one-dimensional model, Feng et al. (2002) also observed a significant relationship between the melting rates and the isotopic enrichment of the snowpack. Typically, their model yielded a variation of 1 to 4‰ of the $\delta^{18}\text{O}$ values of meltwater as the snowpack melted. These experiments, which were conducted on melt pans, laboratory columns and small-scale catchments, all showed a systematic enrichment of the snowpack as the melting occurred, causing the meltwater to gradually become enriched in heavy isotopes.

The isotopic composition of snowmelt input, then, depends significantly upon ^{18}O - ^2H enrichment processes (driven by climatic parameters) within the snowpack. It is therefore difficult, if not impossible, to retrieve a climatic signal from the melting of winter precipitation. Unnikrishna et al. (2002) also highlighted the need for a high-resolution sampling during the snowmelt period, since they observed major daily variations in $\delta^{18}\text{O}$ in snowmelt (up to 3‰). Laudon et al. (2002) improved the separation of event and pre-event water during snowmelt by accounting for both the temporal change in snowmelt isotopic signal and the temporary storage of meltwater in the catchment. Laudon et al. (2002) suggested that the general assumption that spring flood is composed of 30 to 60% pre-event water (Rhodes et al. 1998) could be too conservative and that a greater portion of the spring isotopic signal of water could be attributed to the mobilization of pre-event water during snowmelt.

Our weekly sampling was successful in characterizing the main meltwater event but was not precise enough to capture such short-term variations in the snowmelt isotopic budget. Because it is difficult to conduct hydrograph separation at the basin

scale, it was impossible for us to evaluate the proportion of meltwater contributing to the spring-depleted signal in the Ottawa River or the Great Lakes and to determine the importance of isotopic enrichment of water in the snowpack.

Evaporation of surface water can also alter the isotopic signal of precipitation by concentrating heavy isotopes in residual water. Evaporation during the Summer and Fall months enriches surface water in heavy isotopes and thus increases and/or prolongs the summer-enriched peak in rivers and lakes. Part of the Summer ^{18}O - ^2H -enriched values observed in surface water could thus be related to the evaporative enrichment, whereas another part would be inherited from Summer isotopically heavier precipitation inputs. This assumption seems to be supported by the fact that river samples for Summer and Fall months plot below the local meteoric water on the $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ graph (Figure 15). This could mean that their ^{18}O - ^2H enriched values are related to non-equilibrium enrichment processes such as evaporation rather than to equilibrium fractionation, which causes the ^{18}O - ^2H -enriched values observed in precipitation during Summer.

As seen in the previous section, water from the Ottawa River and the Great Lakes seems to be affected by evaporative enrichment in heavy isotopes to different degrees. For a typical catchment such as the Ottawa River basin, evaporation is thought to be maximal during the Fall, when lower air temperature inhibits vegetation growth and limits water inception by plants (Gat, 1996). In the Great Lakes basin, because almost half of the catchment is occupied by open water, the systematic of evaporation differs significantly, since it is driven by air/water temperature differences throughout the year.

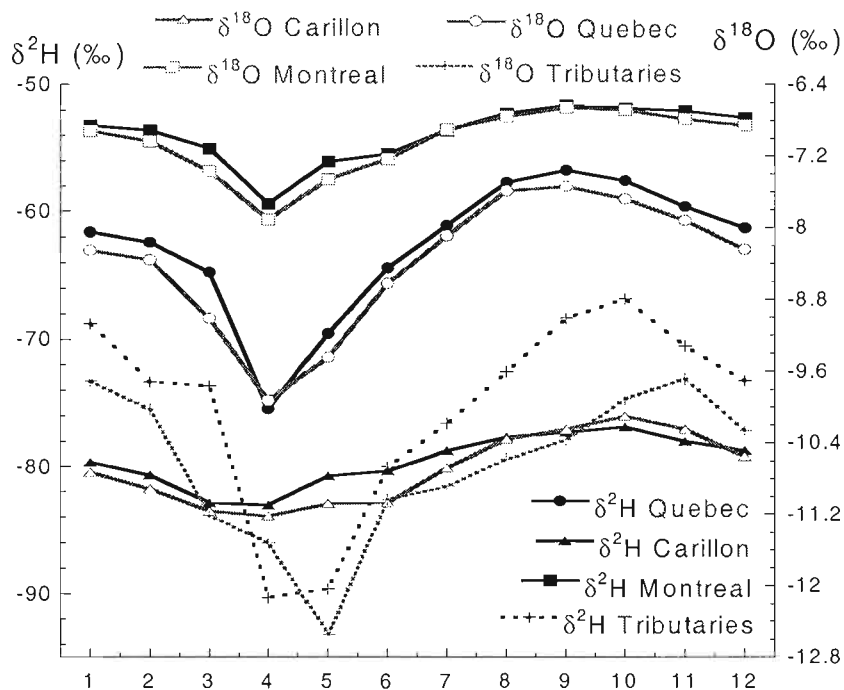


Figure 16. Average weighted monthly $\delta^2\text{H}$ values for the St. Lawrence and Ottawa Rivers (1997-2003). Notice the dampened signature of the Ottawa River in comparison to that of the St. Lawrence River at Quebec City, where the contribution of small, unregulated tributaries is evident. The fact that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ do not vary simultaneously is a sign of non-equilibrium fractionation occurring during evaporation and the melting of the snow blanket.

5.2.2.1 Water in the Great Lakes

The relatively small seasonal isotopic variations observed in water sampled at Montreal may be related to the buffering effect of the large volume of water contained within the Great Lakes (22684 km^3 , Yee and Lloyd, 1985). Between 1997 and 2002, the amplitude of seasonal variations was almost 10 times smaller than that of precipitation at Egbert (Lake Erie), the standard deviation for monthly composite values being 0.4‰ and 2.4‰ ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) at Montreal and 4.2‰ and 30‰ ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) at Egbert station.

Yang et al. (1996) did not observe any seasonal changes between Fall 1991 and Spring 1992 in the St. Clair and Detroit Rivers connecting Lake Huron to Lake Ontario or in the Niagara River, located between Lake Erie and Lake Ontario,

possibly because spring meltwater pulse is less intense in lake water-dominated streams. Another explanation could be that the survey conducted by Yang et al. (1996) missed the meltwater pulse and sampled typical winter baseflow water, which should have isotopic compositions similar to those of water sampled during the Fall. Huddart et al. (1999) reported oxygen-18 and deuterium variations of 0.8‰ and 11‰, respectively, for a 21-month period in Lake Erie.

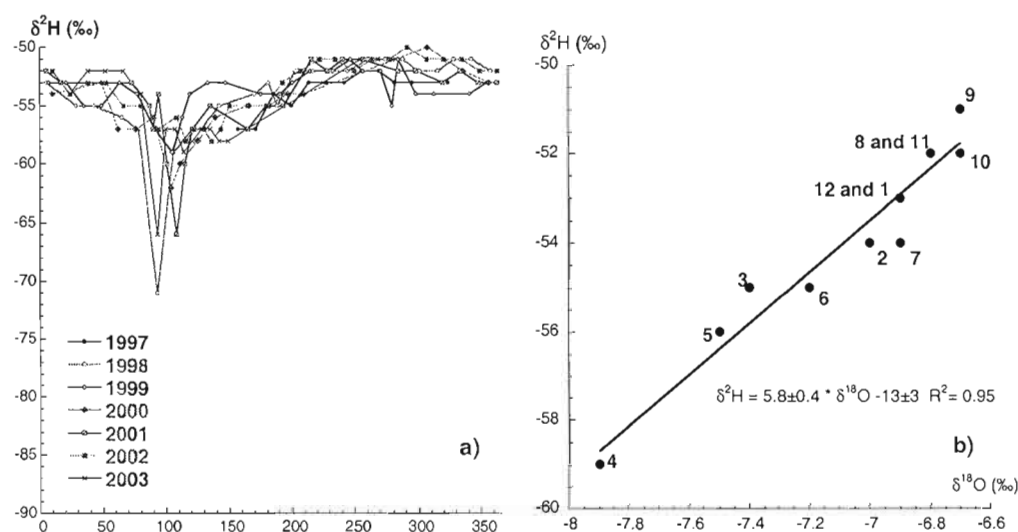


Figure 17 a) Bimonthly to weekly $\delta^2\text{H}$ values at Montreal station. The spring meltwater pulse is responsible for most of the seasonal isotopic variability. b) Average monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values at Montreal station. Variations in deuterium and oxygen-18 values are closely related by a regression line with a slope smaller than 6.

Although dampened, an annual isotopic cycle can be recorded from year to year at the outlet of the Great Lakes (figure 16). The seasonal variations are driven mostly by the depleted signature of the meltwater peak that begins in March and culminates in April. Its influence lingers until June. During the rest of the year (July to February), isotopic compositions remain fairly stable. The Summer heavy isotope-enriched peak is recorded during September but is not as clearly defined as the meltwater peak (Figure 17a). One possible explanation is that in the Great Lakes basin, evaporation is controlled by temperature differences between water and air (Derecki, 1981). The heavy isotope enrichment of surface water through evaporation can thus also occur during winter, when air temperature is lower than

water temperature. This assumption is supported by deuterium excess values that remain stable from June to February, which suggests that heavy isotope enrichment is not strictly limited to Summer and Fall months. The figure 18 shows estimated monthly values for evaporation in lakes Superior, St. Clair and Erie (Derecki, 1981). For lakes Erie and St. Clair, which are the smallest and shallowest lakes, evaporation is maximal from July to December, while for Lake Superior, which has a high heat storage capacity due to its larger volume of water, evaporation is maximal from September to February/March. These are the most extreme cases, and lakes Michigan and Huron, which are smaller than Lake Superior but larger than Lake Erie, show intermediate behaviours, whereas Lake Ontario behaves not unlike Lake Erie. In the chain of lakes, evaporation can significantly affect surface water almost all year long. This could partly explain the smoothed seasonal cycle, which is almost exclusively driven by the meltwater peak during Spring. The seasonality of precipitation input does not seem to play an important role in determining seasonal variability in lake water, possibly because of extensive dilution of precipitation signal in surface water and mixing with hypolimnion water.

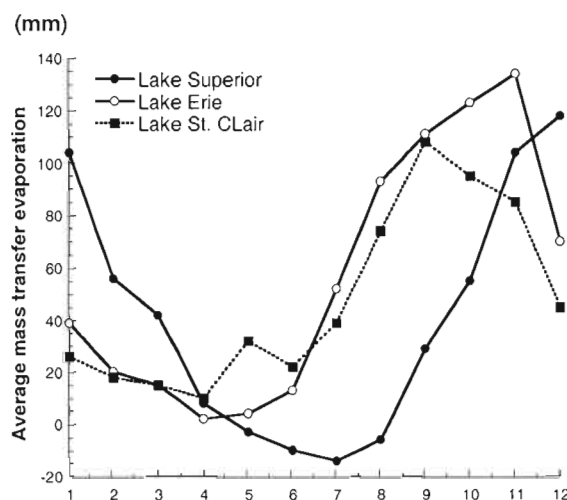


Figure 18. Average mass transfer through evaporation in the Great Lakes. The time lag between values of the smallest and the largest lakes is due to the great heat storage capacity of the largest lake. Negative values represent a net flux toward the lake via condensation. Data: Derecki (1981).

5.2.2.2 Water in the Ottawa River

The Ottawa River displays even smaller seasonal variations than the Great Lakes. This reduced variability may be related to the buffering effect of the high volume of water retained for hydroelectricity generation diluting the isotopic signal of precipitation and the contribution of groundwater that is thought to be significant throughout the year (30-35%; pers. comm. M. Slivitzky, INRS-ETE).

The spring meltwater pulse seems to occur earlier in the Ottawa River than it does in the Great Lakes, possibly because of the fact that, prior to the Spring freshet, excess water from the reservoir is released to recharge these reservoirs in the Spring (pers. comm. Marc Bisson, Ottawa River Regulation Planning Board). This would raise the expected winter low water levels by adding water from reservoirs located at higher altitudes, thereby accounting for the depleted ^{18}O - ^2H values observed prior to the Spring meltwater pulse. The peak of low deuterium excess values associated with the Spring freshet that is recorded in May and June appears to be delayed and is not synchronous with the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ depleted values of March and April (figure 19a).

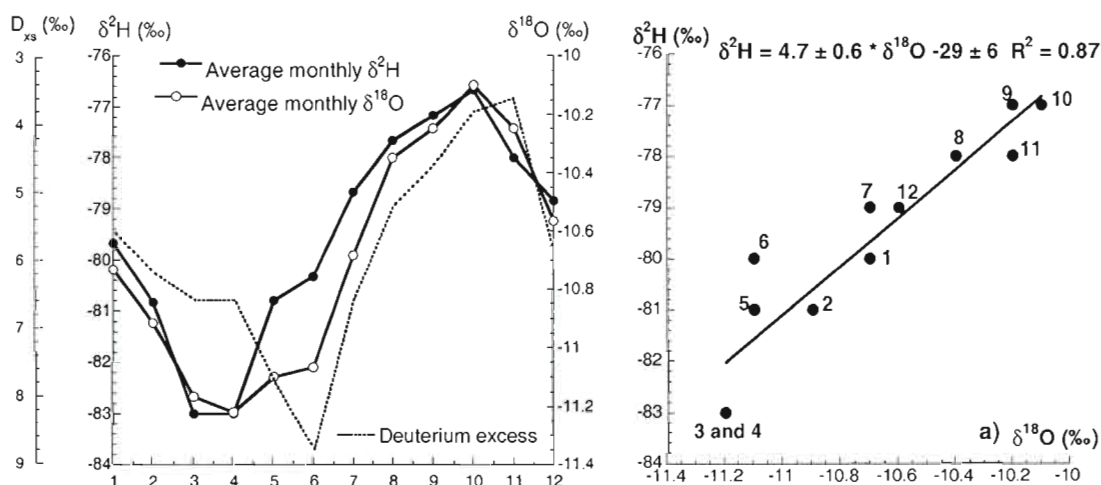


Figure 19. a) Average monthly $\delta^2\text{H}$, $\delta^{18}\text{O}$ and D_{xs} values of the Ottawa River at Carillon. Deuterium excess values indicate that the spring meltwater pulse is not synchronous with the depletion in oxygen-18 and deuterium values. b) Linear relationship between average weighted monthly oxygen-18 and deuterium values. The value of the slope is significantly low and suggests that evaporation plays an important role in seasonal isotopic variability.

The cause of this delay could be that most of the basin is at a higher altitude, where snow is expected to melt later in the Spring. Regulation practices could also cause the snowmelt event to be delayed in attempts to achieve flood control in the lower reach of the basin. Heavy isotope-depleted waters would thus be kept in headwater reservoirs and released later due to water control for avoiding the flooding of downstream areas. This delayed release would also cause the meltwater heavy isotope-depleted signal to be diluted by later precipitations.

The amplitude of the Summer heavy-isotope enriched peak is relatively small (figure 16). Average monthly isotopic values for the Summer months are only slightly higher than the mean annual values. Although the Summer shift appears to be limited, it is synchronous with a peak of low deuterium excess values, which suggests that the ^{18}O - ^2H -enriched summer signal is related to non-equilibrium enrichment processes that occur during evaporation. The regression line fitted in the data from Carillon also suggests that evaporation plays a key role in determining the seasonal isotopic variability of the river, which has a slope value of less than 5 (figure 19b). Although evaporation seems to significantly influence the isotopic content of the Ottawa River, the river still displays the smallest seasonal variability, possibly due to the dilution of the evaporative signal in reservoir waters on the river itself. As has been shown earlier, evaporative ^{18}O - ^2H enrichment of water occurs mostly in the tributaries of the Ottawa River.

Transpiration of plants also acts as an outflow term in the regional water balance, but without significantly modifying the isotopic composition of the water as there is no significant isotopic fractionation occurring during water uptake by vegetation (Gat, 1996). Part of the ^2H & ^{18}O enriched isotopic signal of precipitation could thus be lost during Summer when plant growth is maximal. Telmer (1997) postulated that in the Ottawa River basin, evapotranspiration prevents a large portion

of summer precipitation from contributing to runoff without major incidence on isotopic budgets.

The mean annual evapotranspiration in the Ottawa River basin has been estimated by Telmer (1997) to be 51% of annual precipitation. This finding is in agreement with Environment Canada's estimate of 50% (Environment Canada, 1978). This water loss is attributed to surface water evaporation but also to transpiration and interception by plants. Telmer (1997) took into account the difficulty of evaluating the proportion of evaporation to transpiration in calculating the 51% loss.

The seasonal variations observed in the isotopic composition of the Ottawa River water thus seems to be controlled mainly by regulation practices and, to a lesser extent, by evaporative enrichment that occurs mostly in the Ottawa River's tributaries.

5.2.2.3 Water in the smaller tributaries

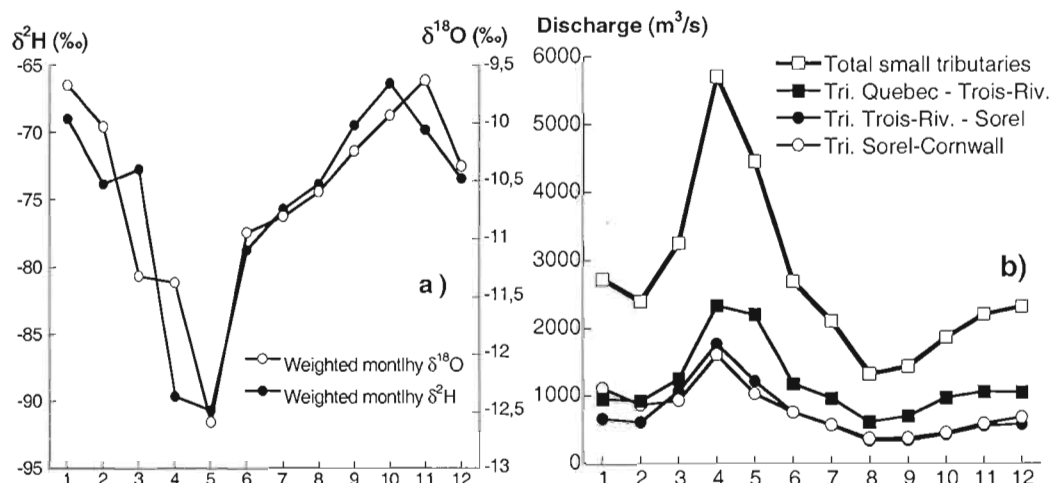


Figure 20 a) Average weighted monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are displayed in the smaller tributaries. Seasonal variations are greater than in the St. Lawrence River and are not as smoothed. This reflects the composite nature of tributaries' isotopic signal, since they all drain different types of catchments. b) The seasonal variations of discharge in the tributaries merging into the St. Lawrence River at different locations between the outlet of the Great Lakes and Quebec City. Tributaries draining into the main river between Trois-Rivières and Quebec City display a more complex meltwater peak.

Monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of smaller tributaries are much more variable than those of the St. Lawrence River, both on the seasonal and interannual scales. In figure 20a, the seasonal variations of ^{18}O and $\delta^2\text{H}$ values do not always appear to be synchronous. In fact, the duration of the meltwater-depleted signal is greater for $\delta^2\text{H}$ values, and the depleted peak occurs mostly in May. On the contrary, discharge values indicate that the meltwater event is maximal in April (figure 20b). This time lag could be explained by the fact that a portion of the smaller tributaries drain mountainous catchments at higher altitudes. The meltwater event could thus be delayed and/or prolonged until May by lower air temperatures in the Spring.

To investigate this hypothesis, we divided the smaller tributaries into three groups. The first group represents the tributaries draining mostly the St. Lawrence Lowlands on the south shore and merging into the main river between the outlet of the Great Lakes at Cornwall and Sorel (figure 21). The second group includes tributaries draining the Appalachians and joining the main river between Sorel and Trois-Rivières. Finally, the last group represents the rivers that drain the Laurentians and Appalachians and then merge in the St. Lawrence River between Trois-Rivières and Quebec City. Figure 20b illustrates the discharge contribution of these three groups along with the cumulative contribution from all the tributaries combined. The last group, which includes the St. Maurice River (the largest of the smaller tributaries), displays a prolonged meltwater pulse that lasts until May. These rivers all drain more elevated catchments than the other smaller tributaries. This could explain the more complex seasonal cycle defined by the isotopic values calculated for all the smaller tributaries (figure 20a).

It is probable that a more detailed monitoring of all the tributaries would have yielded slightly different seasonal variations for each tributary, depending on the location of its headwaters. Our theoretical calculation of the average isotopic signal of smaller tributaries thus integrates different seasonal signals.

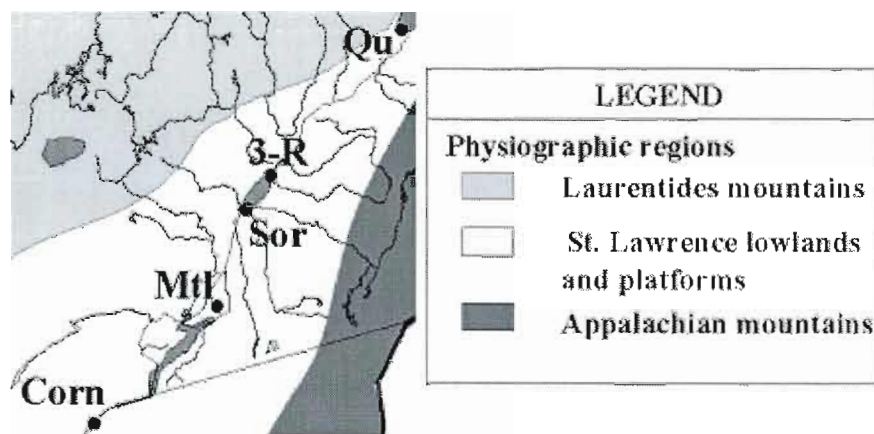


Figure 21. Geographic distribution of the smaller tributaries draining into the St. Lawrence River between the outlet of the Great Lakes and Quebec City. Most of the tributaries that drain into the main river downstream of Sorel have their headwaters in the Appalachians and Laurentians (Source St. Lawrence Center, http://www.qc.ec.gc.ca/csl/pro/images/pro028br_001_e.jpg).

Nevertheless, it clearly appears that the seasonal isotopic variations in these rivers are the largest observed in the St. Lawrence River basin. This is due to the smaller size of their catchments in comparison to those of the Great Lakes and the Ottawa River. The isotopic variability of precipitation is therefore less diluted and dampened.

Isotopic values of smaller tributaries present significant interannual variability (figure 22b). This limits the calculation of reliable monthly averages. Consequently, it is difficult to estimate the influence of the isotopic enrichment of snow and evaporation on the seasonality of the isotopic signal in these rivers.

Nevertheless, the relatively high slope value for the regression line of figure 22a suggests that most of the seasonal isotopic variations observed in tributary water can be attributed to the seasonality of the isotopic input of precipitation without much influence from evaporation. But then again, the high uncertainty on the slope and the intercept prevents us from drawing solid conclusions.

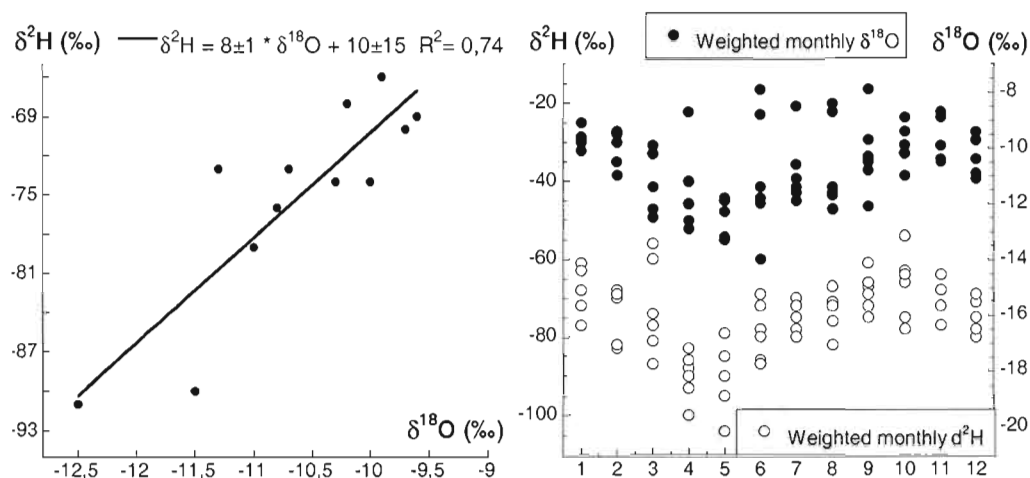


Figure 22 a) Relationship between calculated weighted monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the smaller tributaries. The deuterium and oxygen-18 variations do not show as strong a correlation as in the Great Lakes or the Ottawa River. The slope of the correlation is steeper than in the other basin but the uncertainty on the slope and the intercept is significant. b) Weighted monthly average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the smaller tributaries. The high interannual variability of monthly isotopic values makes it difficult to calculate reliable average values for each month.

5.2.2.4 Water in the St. Lawrence River

The seasonal isotopic variability observed at the outlet of the St. Lawrence River at Quebec City mirrors that of surface water in the rest of the basin and also displays a spring ^{18}O - ^2H -depleted meltwater pulse and summer heavy-isotope enriched isotopic composition. The amplitude of these variations is greater than in the Great Lakes but smaller than in the smaller tributaries (figure 16).

The discharge contributions from these sources also vary on a seasonal basis. The contribution from Great Lakes water is maximal in August (78% of discharge at Quebec City) whereas the heavy isotope depleted contribution from the tributaries is greater in April (54%). The predominance of isotopically light contributions during Spring and ‘‘ heavy ‘‘ contributions during Summer also contributes to the seasonal isotopic variability of water at the outlet of the St. Lawrence River. Figure 23 illustrates the influence of the isotopic and discharge contributions from each source to the isotopic variability at Quebec City. In the first scenario, we assume constant $\delta^{18}\text{O}$ values in the Great Lakes, the Ottawa River and the smaller

tributaries (mean annual $\delta^{18}\text{O}$ value). Only discharge rates vary annually. In the other scenario, we use the true seasonal isotopic cycle of each source with unvarying discharge rates (mean annual values). The two different scenarios do not account for all the isotopic variability observed in the true $\delta^{18}\text{O}$ values. The combination of both varying isotopic compositions and discharge rates is responsible for the seasonal variations at the outlet of the St. Lawrence River.

Because the isotopic seasonality of the St. Lawrence River depends upon the volumetric contribution from its tributaries and the Great Lakes, isotopic values at Quebec City show good agreement with discharge variations on a seasonal basis:

$$\delta^{18}\text{O} = -0,00036 \pm 0,00003 * Q(\text{m}^3/\text{s}) - 4.2 \pm 0.3 \quad R^2 = 0.94$$

$$\delta^2\text{H} = -0,0026 \pm 0,0001 * Q(\text{m}^3/\text{s}) - 32 \pm 1 \quad R^2 = 0.98$$

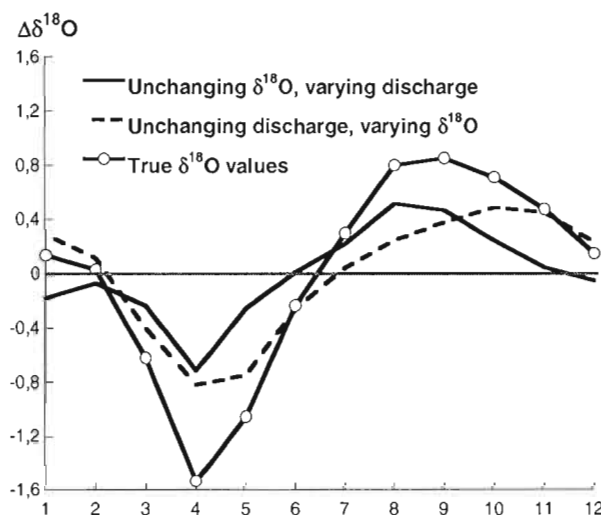


Figure 23 Seasonal $\delta^{18}\text{O}$ variations of the St. Lawrence River at Quebec City. Theoretical values are also displayed and have been calculated assuming either constant discharge or constant isotopic values. Neither of these two scenarios reproduces the overall seasonal variability of the St. Lawrence River.

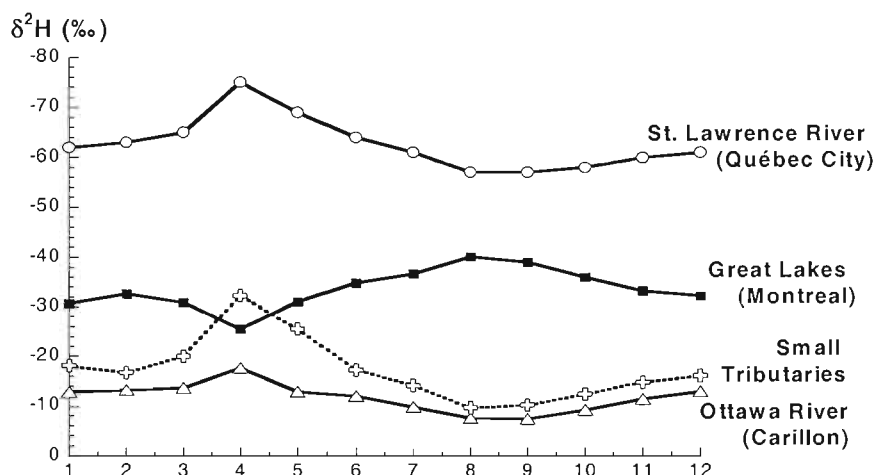


Figure 24. Weighted isotopic input from different water sources to the isotopic signal at the outlet of the St. Lawrence River (Quebec City). The smaller tributaries and the Ottawa River contribute greatly to the Spring snowmelt event, while the Great Lakes contribution dominates Summer isotopic signal.

Figure 24 illustrates the weighted isotopic input from different sources to the isotopic signal at Quebec City. Due to the dephasing between discharge variations in the Great Lakes and the Ottawa River, the addition of the weighted isotopic input from these two sources results in only small seasonal variations. Consequently, it is the smaller tributaries that account for most of the seasonal variations at Quebec City. There is a very good relationship between the weighted isotopic input from smaller tributaries and monthly $\delta^2\text{H}$ values at Quebec City ($R^2 = 0.98$).

5.3 Interannual variability

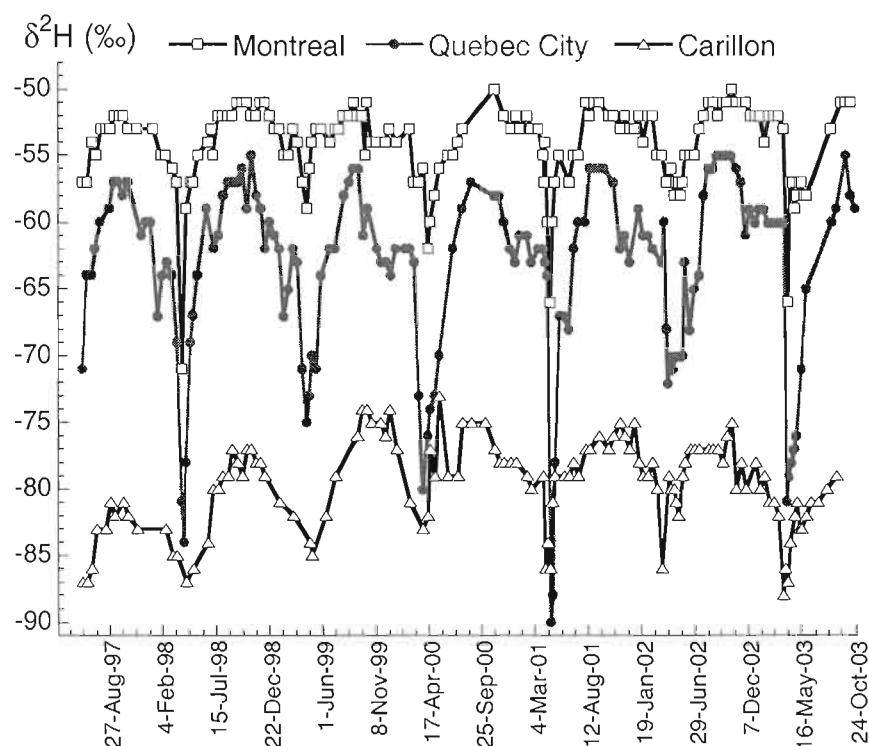


Figure 25. Bimonthly to weekly $\delta^2\text{H}$ values for the three sampling stations. Most of the interannual variability seems related to the isotopic signature of the Spring meltwater pulse. A shift towards more ^{18}O - ^2H -enriched values is observed in the Ottawa River from 1997 to the beginning of 2000.

When looking at bimonthly to weekly isotopic values (figure 25), the interannual isotopic variability seems more or less controlled by the isotopic composition of the spring meltwater pulse. Data from the Montreal and Quebec City stations illustrate relatively stable $\delta^2\text{H}$ values during the Summer months, whereas the variability is much higher for values during Spring months. This could be due to either the isotopic content of Winter precipitation, the climatic parameters that control the heavy isotope enrichment of snow, or the effect of human regulation in the part of the basin where natural discharge is disturbed. The variability of the Ottawa River appears to be more important and is not limited to certain months of the year.

One major factor influencing the interannual isotopic variability of surface water is, of course, the varying input from precipitation. On a certain time scale (decadal to centennial), it can be estimated that the isotopic signature of surface water varies similarly to that of regional precipitation. The difference between absolute values then may be due to the loss of water through evaporation (Gibson, 2003), rivers and lakes being significantly ^{18}O - ^2H -enriched in comparison to the isotopic input of precipitation. This assumption seems to be validated by results from long-term isotopic records, notably of European rivers. Rank et al. (1998) observed a similar interannual relationship between precipitation in Vienna and in the Danube River. Their 1969-1994 $\delta^{18}\text{O}$ chronicle demonstrated that interannual variations in the isotopic content of precipitation were transmitted into runoff with a one-year lag time. The situation should differ significantly here due to the relatively high residence time of water in the Great Lakes system.

Nevertheless, on a shorter time scale (interannual to decadal), the variability of hydrological processes could significantly affect the isotopic signature of surface water. Variations in the intensity of evaporation and/or isotopic enrichment of the snowpack might be responsible for part of the interannual isotopic variability. Discharge regulation in certain parts of the basin could also alter the transmission of the climatic signal of precipitation. In cases where the influence of these factors is small to nonexistent, large rivers can absorb the interannual isotopic variability of regional precipitation. Frederickson et al. (1999) demonstrated that the Meramec River system in central Ohio closely followed the interannual isotopic variations of precipitation linked to climatic fluctuations (1997-1998 El Nino). In that particular case, the isotopic variability of precipitation, even dampened, was transmitted into runoff with a near 100 days time lag. The situation of the Meramec basin differs from that of the St. Lawrence River since no regulation is affecting its natural flow. Moreover, the smaller size of the catchment made it easier to estimate the response of the system to a precipitation event and to partition the contribution of

groundwater and overland flow. Finally, the absence of snow accumulation during Winter and its subsequent isotopic alteration make the isotopic correlation between precipitation and river water more unequivocal. As such, regulation practices, the presence of snow, and its melting during spring present further challenges when trying to identify the factors controlling the interannual isotopic variability in large surface water systems.

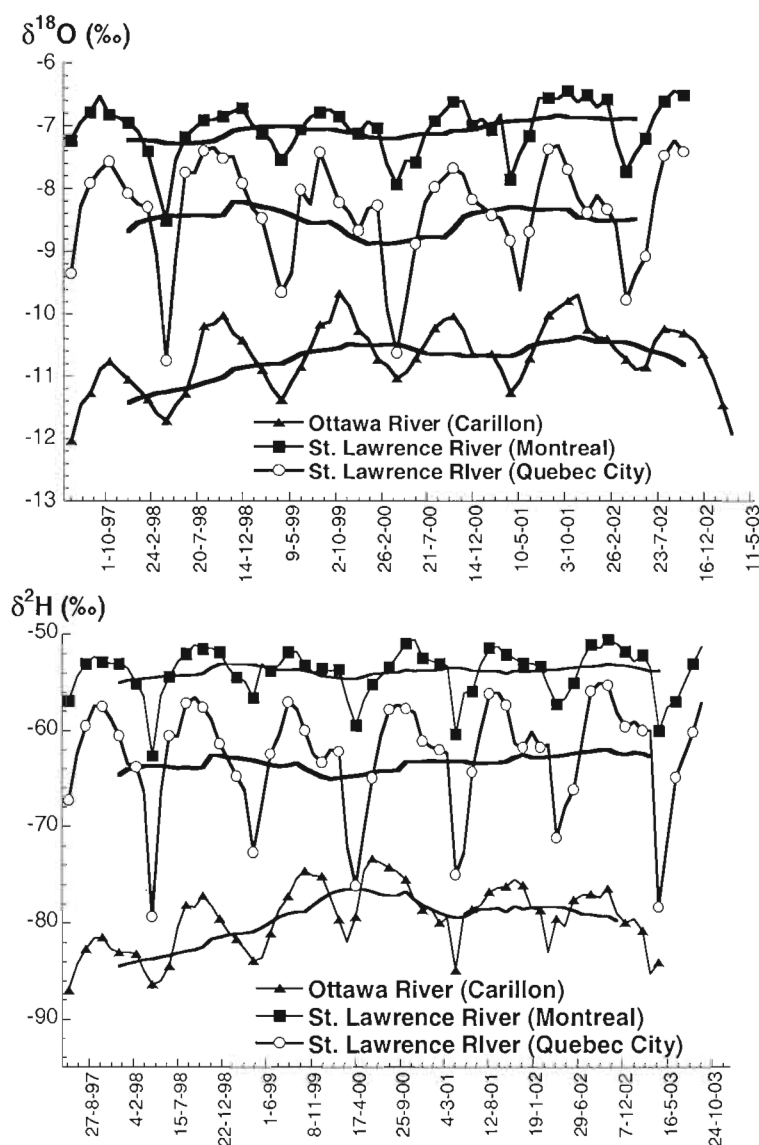


Figure 26. Weighted 12-month running averages of weighted monthly $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values at the three stations. In comparison to the almost unchanging isotopic values of Great Lakes water, the isotopic signal at Quebec City provides evidence of short to mid-term fluctuations that cannot be attributed to the isotopic input from the Ottawa River.

5.3.1 Isotopic compositions

5.3.1.1 Water in the Great Lakes

Due to the hydrological properties of the basin, the isotopic composition of Great Lakes water was not expected to vary significantly from year to year. Indeed, the amplitude of the interannual variations from 1997 to 2003 was only of 2.11‰ for $\delta^2\text{H}$ and 0.46‰ for $\delta^{18}\text{O}$ values (highest difference between 12-month weighted running average values).

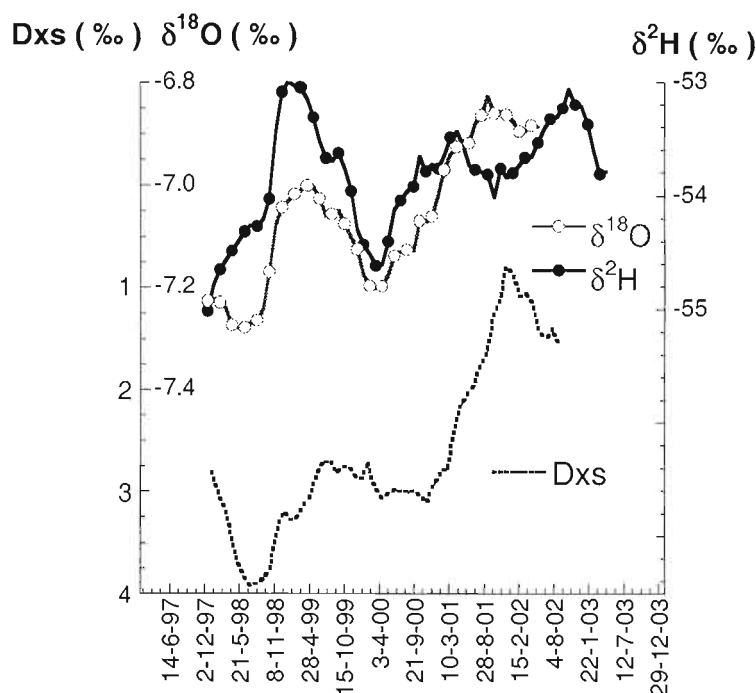


Figure 27. 12-month weighted running averages of $\delta^{18}\text{O}$, $\delta^2\text{H}$ and Dxs values at Montreal station. There is a small but significant increase of the delta values between 1997 and 2003. The fact that deuterium excess values present a similar increase suggests that it is primarily related to evaporative enrichment.

As seen in figure 27, despite the fact that 12-month weighted annual values vary only little, they seem to depict a trend towards isotopic enrichment with time. Where the increase of deuterium is more or less equal to the overall analytical uncertainty of deuterium analyse, the increase in $\delta^{18}\text{O}$ values appears to be more

significant and seems to be paralleled by a decrease of the deuterium excess values. Variations of these two parameters are related by the following equation:

$$\delta^{18}\text{O}_{(\text{MTL})} = [(-0.145 \pm 0.009) * \text{Dxs}_{(\text{MTL})}] - (6.68 \pm 0.03), R^2 = 0.83$$

The correlation leads us to believe that most of the interannual variations of the $\delta^{18}\text{O}$ values in the Great Lakes are related to changes in the evaporative term of the water balance.

To test this hypothesis, we have isolated the late Summer/Fall signal which is most representative of the evaporative signal in the Great Lakes to calculate interannual isotopic variations. Values from August to December were amount-weighted to calculate a single value for each year. Values from certain months were subtracted from the calculation when it was obvious that the isotopic compositions were not representative of the summer evaporative signal and to obtain a relatively stable isotopic signal for the summer period (s.d. < 0.1‰ for $\delta^{18}\text{O}$ and 1‰ for $\delta^2\text{H}$). There is a small but significant heavy-isotope enrichment of the late Summer/Fall signal between 1997 and 2002 (0.3‰ for $\delta^{18}\text{O}$ and 1.8‰ for $\delta^2\text{H}$). Unfortunately, because there is too much variation of the deuterium excess values, we can not tell if this parameter is showing a similar trend. If we consider the Great Lakes to have a relatively stable isotopic signal on an interannual basis with only small variations during the Spring meltwater period, it is possible to consider the observed increase of oxygen-18 and deuterium values as a slow but steady response to an enhancement of evaporation in relation to the general increase of mean air temperature over the past decades. In addition, the fact that no similar trend could be observed in the isotopic content of precipitation indicates that the heavy isotopes enrichment of surface water can be attributable to evaporation.

There are some estimations of the overall evaporation occurring in the Great Lakes. These estimates are based on temperature differences between water and air and on several other factors (NOAA, <http://www.glerl.noaa.gov/data/pgs/hydrology.html>).

As such, the interannual variations of evaporation show a good agreement with interannual variations of mean annual air temperature over the Great Lakes. Our survey is still too short to allow a precise comparison between the isotopic compositions of water and the amount of evaporation over the lakes on an interannual time scale. In addition, an important lag time might be expected between variations in evaporation and the isotopic signal recorded at the outlet of the Great Lakes (at Montreal).

5.3.1.2 Water in the Ottawa River

The Ottawa River provided a more variable isotopic signal. Between mid-1997 and 1999, a trend of increasing $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values developed, followed by a stabilisation of the delta values between the spring of 2000 and the end of 2002 (figure 26).

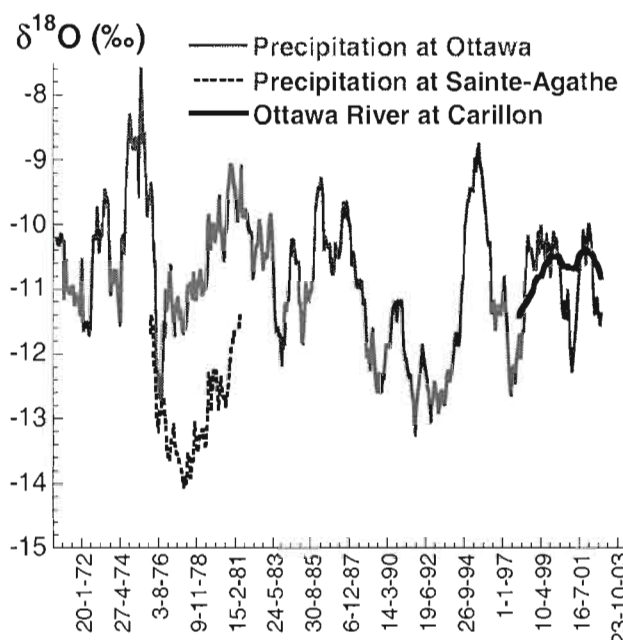


Figure 28. Weighted 12-month running average of monthly $\delta^{18}\text{O}$ values for precipitation and river water in the Ottawa River basin. There is a similarity between the long-term variability of the Ottawa River and that of precipitation at Ottawa. Even if absolute isotopic values differ in precipitation at Ottawa and at Sainte-Agathe, long-term changes seem to be synchronous.

When looking at the 12-month running average of monthly $\delta^{18}\text{O}$ values (figure 28) we observe a relatively good correlation between the interannual variability of precipitation at Ottawa and that of the Ottawa River. Data from Sainte-Agathe station are also shown in figure 28. Even if $\delta^{18}\text{O}$ values are more negative at Sainte-Agathe, their interannual variability seems similar to that recorded at Ottawa Station. Unfortunately, the isotopic monitoring at Saint-Agathe ended in the early 1980s.

Figure 29 provides isotopic values for precipitation and river water between 1997 and 2002, along with air temperature data recorded at Ottawa Station. There is a significant correlation between air temperature and the oxygen-18 content of precipitation at Ottawa. ($R^2=0.64$). The relationship between air temperature and the isotopic content of precipitation at Ottawa station has been assessed elsewhere. Rozanski et al. (1992) observed only a weak correlation ($R^2=0.14$) between these two parameters over a two decades period (1970-1990). As it has been mentioned by Fritz et al. (1987), the Ottawa station is located in the a mixing zone of different continental air masses systems, namely, the tropical air coming from the Gulf of Mexico and arctic air that penetrates deeper south during Winter. Some of the long-term fluctuations of the isotopic content of precipitation over central eastern Canada could thus be related to mixing proportion of these different air masses displaying distinct isotopic signals.

Although the relationship between the isotopic compositions of precipitation and air temperature is relatively good ($R^2=0.64$), the correlation between the isotopic content of the Ottawa River and air temperature is much less robust ($R^2=0.30$). There still seems to be some similarity between the interannual isotopic variability of the Ottawa River and that of precipitation at Ottawa even though there is no strong statistical evidence of it (figure 29). Evaporative heavy isotopes enrichment, which is thought to be significant in the basin, might be significantly altering the

precipitation signal along with regulation practices that could have modified the residence time of water in the basin. These factors could explain the poor relationship observed.

In addition, the close relationship between weighted 12-month running averages of $\delta^{18}\text{O}$ and the $\delta^2\text{H}$ values at Carillon:

$$\delta^2\text{H} = 7.5 \pm 0.5 * \delta^{18}\text{O} + 1 \pm 5, R^2 = 0.82$$

indicates that deuterium and oxygen-18 variations occur simultaneously and are related by a near equilibrium fractionation ratio (slope of 8). This tells us that long-term isotopic variations in the Ottawa River are most likely to be related to equilibrium fractionation processes, such as those recorded in precipitation during condensation. Non-equilibrium fractionation processes do not seem to play an important role in determining the interannual isotopic variability of the Ottawa River.

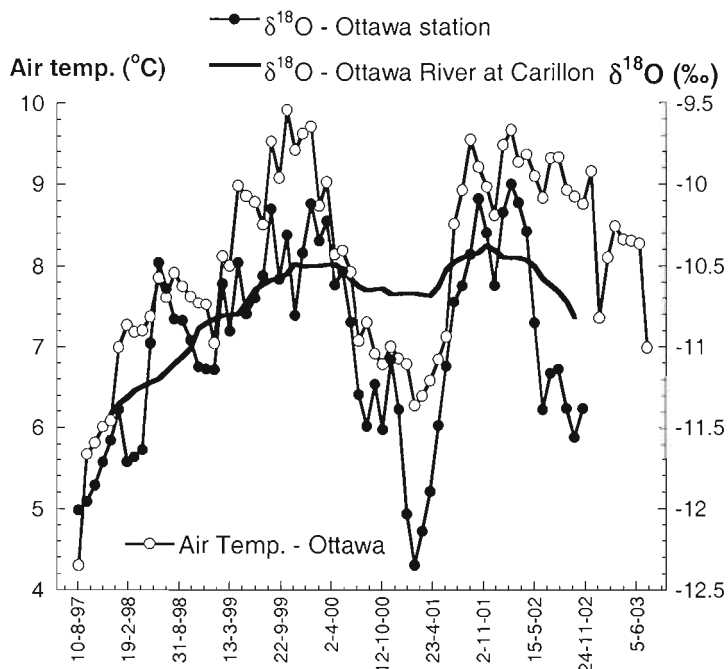


Figure 29. Weighted 12-month running average of $\delta^{18}\text{O}$ values for precipitation and river water in the Ottawa River basin. There is a similarity between the long-term variability of the Ottawa River and that of precipitation at Ottawa. Even if absolute isotopic values differ in precipitation at Ottawa and at Sainte-Adathe, long-term changes seem to be synchronous.

Consequently, despite the lack of statistical evidence and the importance of evaporative processes, the interannual isotopic variability of the Ottawa River could be considered to be representative of that of precipitation over its drainage basin. This hypothesis would have to be tested and validated as soon as a longer isotopic series becomes available for precipitation and surface water in the Ottawa River basin.

5.3.1.3 Water in the smaller tributaries

The isotopic compositions of smaller tributaries provided the most significant interannual variability. The smaller size of the groundwater and surface reservoirs of these tributaries might explain this higher variability. Figure 30 shows calculated monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the smaller tributaries, as well as weighted 12-month running averages. ^2H & ^{18}O values seem to vary in a different and contradictory way. This results in significant variability of the deuterium excess parameter, which can be associated to non-equilibrium isotopic fractionation of water. There is a negative correlation between interannual variations of $\delta^{18}\text{O}$ and deuterium excess values ($R^2=0.80$) and a positive correlation between D_{xs} and $\delta^2\text{H}$ values ($R^2=0.57$). As such, it appears that deuterium and oxygen-18 values are differently affected by the same processes and may deliver different information. It is important to remember that the calculated isotopic values for smaller tributaries represent the sum of different seasonal (and possibly interannual) isotopic signals specific to the different catchments being drained by these tributaries. The summation of these different signals increases the complexity of the composite signal and makes it difficult to compare with the isotopic input of precipitation.

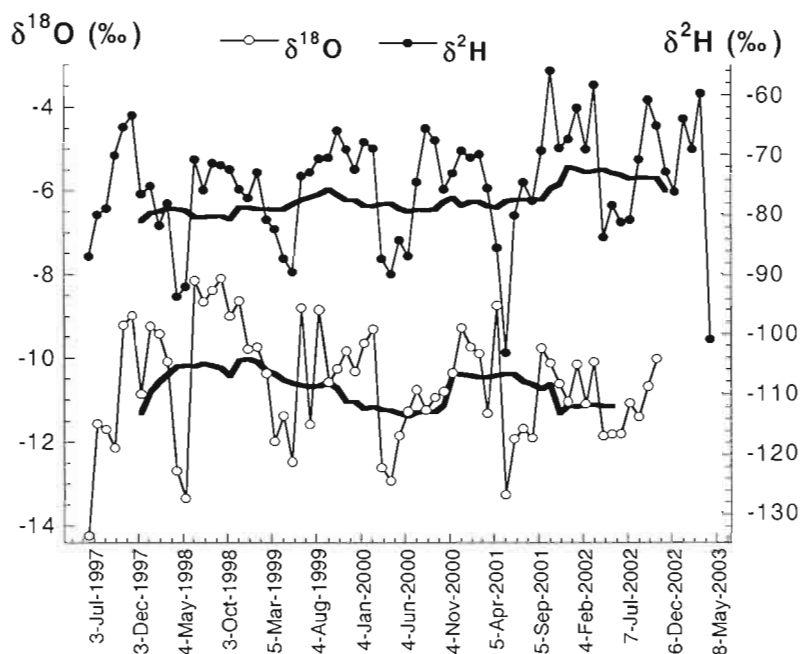


Figure 30. Monthly composite $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for smaller tributaries. Bold and dashed lines represent weighted 12-month running averages. Although seasonal variations are similar for deuterium and oxygen-18 values, long-term fluctuations present some contrasting patterns.

Nevertheless, changes towards more $\delta^{18}\text{O}$ enriched values appear to be paralleled by a decrease of deuterium excess values. This tells us that non-equilibrium enrichment processes could play an important role in determining the interannual isotopic variability of the water in the smaller tributaries.

5.3.1.4 Water in the St. Lawrence River

The isotopic composition of water at the outlet of the St. Lawrence River shows greater interannual variability than in the Great Lakes, but smaller than in the tributaries (including the Ottawa River). Part of this variability is due to changes in the mixing proportion of the different water sources.

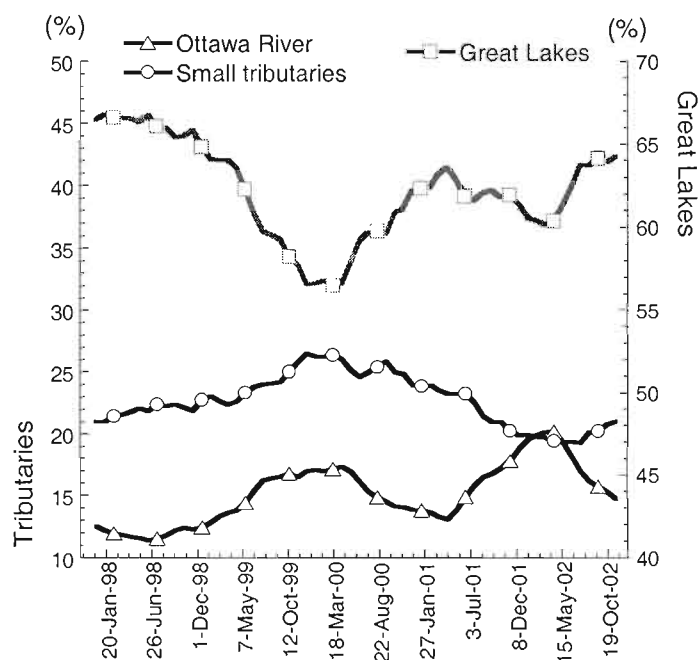


Figure 31. Relative input of water from different sources to total discharge at the outlet of the St. Lawrence River. Values are 12-month running averages of the percentage of discharge at Quebec City. If Great Lakes water generally represents more than 55 % of the water outflowing from the St. Lawrence River, this contribution has varied in relative intensity by up to 10 %.

Figure 31 provides 12-month running averages of the relative contribution of each source (percentage of discharge at Quebec City). If the Great Lakes remain the most important source of water to the total flow at the outlet of the St. Lawrence, its relative importance has varied in comparison to the input of the Ottawa River and the smaller tributaries. The contribution from all the tributaries was maximal during 1999 and 2000. Considering the fact that the Great Lakes and the tributaries provide very distinct isotopic inputs, changes in the relative contribution of these sources might have been responsible for the isotopic variability observed at the outlet of the St. Lawrence River.

These sources also showed long-term isotopic fluctuations (especially in the case of the smaller tributaries and Ottawa River), and part of the total isotopic variability of the St. Lawrence River is due to the isotopic variability of these sources. To estimate the proportion by which these two factors have influenced the isotopic

composition of the river, we compared the deuterium and oxygen-18 content of water at Quebec City to the discharge rates and isotopic values at each station. Table 4 illustrates the results from these comparisons.

Variations in the isotopic content of water at Quebec City do not show much similarity to those recorded in other parts of the basin. The interannual isotopic variability at Quebec City seems to be more or less correlated to that of the Great Lakes recorded at Montreal ($R^2=0.62$), probably because of their greater contribution to total discharge at the outlet of the St. Lawrence River. On the other end, when considering the variations of discharge recorded at each station, the isotopic variability of water at Quebec City is better correlated with the input of water from the smaller tributaries ($R^2=0.78$) while there is no correlation at all with the input from the Great Lakes or the Ottawa River.

	Montreal	Carillon	Smaller tributaries
	R^2	R^2	R^2
Vs. Delta values at Quebec City	$\delta^2\text{H} (\delta^{18}\text{O})$	$\delta^2\text{H} (\delta^{18}\text{O})$	$\delta^2\text{H} (\delta^{18}\text{O})$
Discharge rates : Q_{station}	0.01 (0.02)	0.01 (0.26)	0.78 (0.51)
Relative discharge contribution : $Q_{\text{station}} / Q_{\text{Quebec City}}$	0.16 (0.48)	0.02 (0.14)	0.54 (0.34)
Weighted isotopic contribution : $(Q_{\text{station}} / Q_{\text{Quebec City}}) * \delta_{\text{station}}$	0.12 (0.43)	0.03 (0.22)	0.72 (0.79)
Isotopic compositions : δ_{station}	0.62 (0.19)	0.01 (0.05)	0.41 (0.63)

Table 4. Correlation coefficients between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values at Quebec City and four different sets of parameters from each station on an interannual basis. The Ottawa River values do not correlate with those at Quebec City, whereas the smaller tributaries seem to significantly influence the isotopic signal at the outlet of the St. Lawrence River. All correlation are defined between 12-month running averages of each parameters.

To truly estimate the impact of each source on the isotopic variability of water in the St. Lawrence River, we can look at the weighted isotopic input as follow:

$$Q_{\text{station}}/Q_{\text{Quebec City}} * \delta_{\text{station}}$$

which represents the true input of each source to the overall isotopic content of the St. Lawrence defined by the mass balance equation :

$$\delta_{\text{Quebec city}} = (\delta_{\text{Mtl}} * Q_{\text{Mtl}} + \delta_{\text{Car}} * Q_{\text{Car}} + \delta_{\text{Tri.}} * Q_{\text{Tri.}}) / Q_{\text{Quebec city}}$$

The good correlation between interannual variations of ^2H & ^{18}O values at Quebec City and both the weighted isotopic input and the discharge contribution from the smaller tributaries highlight the importance of these rivers in determining the interannual isotopic variability of the St. Lawrence River. On the contrary, the Great Lakes and the Ottawa River waters do not seem to have much influence on the isotopic variability of water at Quebec City. Considering that the smaller tributaries might respond more quickly to climatic and hydrologic forcing than other parts of the basin that are affected by regulation and/or by the high residence time of water, it might be expected that the isotopic signal of the St. Lawrence River will be affected in a similar way.

6. CONCLUSION

The goal of the present study was to determine seasonal and interannual isotopic variability of the St. Lawrence River in relation to hydroclimatic variability based on a relatively long term time series of isotopic composition of the river water. By comparing the river isotopic compositions to climatic parameters such as air temperature and the amount and isotopic composition of precipitation, it has indeed been possible to observe significant relationships.

They include:

- i) The heterogeneity of isotopic compositions in the St. Lawrence River basin (in both the surface water and precipitation) and the importance of evaporative heavy isotope enrichment affecting the isotopic content of rivers and lakes.
- ii) The influence of mechanical regulation and hydroclimatic factors (evaporation, ^2H & ^{18}O enrichment of snow and its melting) on the seasonal isotopic variability of surface water.
- iii) The diverse factors affecting the interannual isotopic variability of water; evaporative enrichment in the Great Lakes, precipitation variability in the Ottawa River, and water contribution from the smaller tributaries in the St. Lawrence River at Quebec City

The sampling at Montreal, Carillon and Quebec City stations was reliable, relatively easy, and representative of the water outflowing from the Great Lakes, the Ottawa River and the St. Lawrence River itself. Unfortunately, the lack of direct measurements of smaller tributaries between Montreal Island and Quebec City hampered our understanding of the hydrology of this important component of the St. Lawrence River system. Calculated isotopic values for smaller tributaries between Montreal and Quebec provided some insights into their overall hydrology.

Nonetheless, direct information on some of these tributaries would be useful. We thus recommend, for the continuing monitoring program of the St. Lawrence system, bimonthly sampling and weekly sampling, during the spring meltwater period, of three additional stations located on the St. Maurice River draining the Laurentides, the Chaudière and the Richelieu rivers, draining the Appalachians and the St. Lawrence Lowlands, respectively. These additional stations should be located near the mouths of these rivers before they merge into the St. Lawrence. Such an addition to the sampling network would provide us with a better understanding of runoff from these contrasting sub-basins.

The isotopic monitoring of the St. Lawrence River and its tributaries should be maintained over more than a decade in order to compare trends and relationships observed in this study with climate oscillations such as the AO/NAO.

7. REFERENCES

Barth, J. A. C. and J. Veizer. 2004. « Water mixing in a St. Lawrence River embayment to outline potential sources of pollution ». *Applied geochemistry*, vol. 19, p. 1637-1641.

Bennett, E. B. 1978. « Characteristics of the thermal regime of Lake Superior ». *Journal of Great Lakes Research*, vol. 4, nos 3-4 (December), p. 310-319.

Brown, R. M. 1970. « Distribution of hydrogen isotopes in Canadian waters ». In *Isotope Hydrology*, International Atomic Energy Agency, Vienna (Austria), p. 3-21, SM-192/1.

Burgman, J.O., B. Callesand, F. Westman. 1987. « Conclusions from a ten year study of oxygen-18 in precipitation and runoff in Sweden ». Symposium on Isotope Techniques in Water Resources Development, International Atomic Energy Agency, Vienna (Austria), 30 March-3 April 1987, IAEA-SM-299/107. SM-299/107 PP. 579-590

Clark, I. and P. Fritz. 1997. *Environmental isotopes in hydrology*. Lewis Publisher, New York, 328 p.

Cloutier, V., E. Bourque, R. Lefebvre, M. M. Savard, M. Nastev, R. Martel and R. Therrien. 2001. « Regional groundwater hydrogeochemistry of fractured rock aquifer in south-western Québec ». *Odyssée de la Terre*, p. 1068-1077.

Désilet, L. and C. Langlois. 1989. *Variabilité spatiale et saisonnière de la qualité de l'eau du fleuve Saint-Laurent*, Environnement Canada. Inland Water Branch, Quebec region, 90 pp + appendixes.

Derecki, J. A. 1981. « Stability effects on Great Lakes evaporation ». *Journal of Great Lakes research*, vol. 7, no4, p. 357-362.

Donnelly, T., S. Waldron, A. Tait, J. Dougans, and S. Bearhop. 2001. « Hydrogen isotope analysis of natural abundance and deuterium-enriched waters by reduction over chromium on-line to a dynamic dual inlet isotope-ratio mass spectrometer ». *Rapid communication in mass spectrometry*, vol. 15, p. 1297-1303.

Feng, X., S. Taylor, C. E. Renshaw and J. W. Kirchner. 2002. « Isotopic evolution of snowmelt 1. A physically based one-dimensional model ». *Water Resources Research*, vol. 38, no 10, 1217

Friedman, I., A. C. Redfield, B. Schoen and J. Harris. 1964. « The variation of the Deuterium content of Natural waters in the hydrological cycle ». *Reviews of Geophysics*, vol. 2, no 1, p. 177-224.

Fritz P., Drimmie R. J., Frape S. K. and O'Shea K. 1987. « The isotopic composition of precipitation and groundwater in Canada ». In *Isotope Techniques in Water Resources Development*, International Atomic Energy Agency, Vienna (Austria), p. 539-550.

Gat, J. R. 1970. « Environmental isotope balance of Lake Tiberias ». In *Isotope Hydrology*, International Atomic Energy Agency, Vienna (Austria), p. 109-127.

Gat, J. R., C. J. Bowser and C. Kendall. 1994. « The contribution of evaporation from the Great Lakes to the continental atmosphere: estimate based on stable isotope data ». *Geophysical Research Letters*, vol. 21, no 7 (April 1), p. 557-560.

Gat, J. R. 1995. « Stable isotopes and the water balance of fresh and saltwater lakes. » In: *Physics and chemistry of lakes*, 2nd Edition. Springer-Verlag, Berlin, p. 139-166.

Gat, J. R. 1996. « Oxygen and hydrogen in the hydrologic cycle ». *Annual Review of Earth and Planetary Sciences*, vol. 24, p. 225-262.

Gibson, J. J., P. Aggarwal, J. Hogan, C. Kendall, L. A. Martinelli, W. Stichler, D. Rank, I. Goni, M. Choudhry, J. Gat, S. Bhattacharya, A. Sugimoto, B. Kekete, A. Pietroniro, T. Maurer, H. Panarello, D. Stone, P. Seyler, L. Mauricie-Bourgoin and A. Herceg. 2002. « Isotopes studies in large river basins : a new global research focus ». *Eos, Transactions, American Geophysical Union*, vol. 83, no 52 (24 Decembre), p. 615-617.

Hélie, J.-F., C. Hillaire-Marcel and B. Rondeau. 2002. « Seasonal changes in the source and fluxes of dissolved inorganic carbon through the St. Lawrence Rivers— isotopic and chemical constraint ». *Chemical Geology*, vol. 186, p. 117-138.

Laudon, H., H. F. Hemond, R. Krouse and K. H. Bishop. 2002. «Oxygen 18 fractionation during snowmelt: Implications for spring flood hydrograph separation ». *Water Resources Research*, vol. 38, no 11, 1258.

Hoffmann, G., J. Jouzel and V. Masson. 2000. « Stable water isotope in atmospheric general circulation models ». *Hydrological processes*, vol. 14, p.1385-1406.

International Atomic Energy Agency. 1981. *Stable isotopes hydrology : Deuterium and Oxygen-18 in the water cycle*. Technical reports series no. 210. Elsevier, Vienna, 339 p.

Kelly, S. D., K. D. Heaton and P. Brereton. 2001. « Deuterium/hydrogen isotope ratio measurements of water and organic samples by continuous-flow isotope ratio mass spectrometer using chromium as the reducing agent in an elemental analyser ». *Rapid Communication in mass spectrometry*, vol.15, p. 1283-1286.

Kendall, C. and J. J. McDonnell. 1998. *Isotope tracers in catchment hydrology*. Elsevier, Amsterdam, 839 p.

Kendall, C. and T. B. Coplen. 2001. « Distribution of oxygen-18 and deuterium in river waters across the United States ». *Hydrological Processes*, vol. 15, p. 1363-1393.

Machavaram, M. V. and R. V. Krishnamurthy. 1994. « Survey of factors controlling isotope ratios in precipitation in the Great Lakes region ». 1994. *Israel Journal of Earth Sciences*, vol. 43, p.195-202..

Machavaram, M. V. and R. V. Krishnamurthy. 1995. « Earth surface evaporative process: A case study from the Great Lakes region on the United States based on deuterium excess in precipitation ». *Geochimica et Cosmochimica Acta*, vol. 59, no 20, p. 4279-4283.

Nelson, S. T. and D. Dettman. 2001. « Improving hydrogen isotope ratio measurements for on-line chromium reduction systems ». *Rapid communication in mass spectrometry*, vol. 15, p. 2301-2306.

Quinn, F. H. 1992. « Hydraulic residence times for the Laurentian Great Lakes ». *Journal of Great Lakes Research*, vol. 18, p. 22-28.

Rank, D., A. Adler, L. Araguas-Araguas, K. Froellich, K. Rozanski and W. Stichler. 1998. « Hydrological parameters and climatic signals derived from long term tritium and stable isotope time series of the river Danube ». In *Isotope Techniques in the Study of Environmental Change*, International Atomic energy Agency, Vienna (Austria), p. 191-207

Rondeau, B. 1999. « Validation d'une station de référence pour le suivi de la qualité des eaux dans le fleuve Saint-Laurent à Québec ». Scientific and Technical Report. Environment Canada, Quebec region, Environmental Conservation, St. Lawrence Centre, 58 pp.

Rozanski, K., L. Araguas-Araguas and R. Gonfiantini. 1992. « Relation between long-term trends of oxygen-18 isotope composition of precipitation and climate ». *Science*, vol. 258, 6 November, p. 981-985.

Sklash, M. G., R. N. Farvolden and P. Fritz. 1976. « A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer ». *Canadian Journal of Earth Sciences*, vol. 13, p. 271-283.

Simard, G. 1977. « Carbon 14 and tritium measurements of groundwaters in the Eaton River basin and in the Mirabel area, Quebec ». *Canadian Journal of Earth Sciences*, vol. 14, p. 2325-2338.

Taylor, S., X. Feng, M. Williams and J. McNamara. 2002. « How isotopic fractionation of snowmelt affects hydrograph separation ». In *59th Eastern Snow Conference*, Stowe, Vermont (USA), p. 285-293.

Telmer, K. H. 1997. Biogeochemistry and water balance of the Ottawa River basin. PhD thesis, Ottawa-Carleton Geoscience Centre, University of Ottawa, 240 p.

Unnikrishna, P. V., J. J. McDonnell and C. Kendall. 2002. « Isotope variations in a Sierra Nevada snowpack and their relation to meltwater ». *Journal of Hydrology*, vol. 260, p. 38-57.

Yang, C., K. Telmer and J. Veizer. 1996. « Chemical dynamics of the «St. Lawrence» riverine system: δD_{H_2O} , $\delta^{18}O_{H_2O}$, $\delta^{13}DIC$, $\delta^{34}S_{sulfate}$, and dissolved $^{87}Sr/^{86}Sr$ ». *Geochimica et Cosmochimica Acta*, vol 60, no5, p. 851-866.

Yee, P. and J. Lloyd. 1985. Great Lakes water levels. Environment Canada.

Yurtsever, Y. and J. R. Gat. 1981. « Atmospheric waters », In: Stable isotope hydrology, deuterium and oxygen-18 in the water cycle. International Atomic Energy Agency, Vienna (Austria), p. 103-139.

ANNEXE A

A1 Table of results for bimonthly to weekly $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurements...75

Montreal station N 45 25,511 W 073 37,113

Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰	Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰
06-06-97	-7,3		-57	-57	04-03-99	-7,0		-53	
20-06-97			-57	-57	18-03-99	-7,2	-7,4	-54	
04-07-97			-54	-54	01-04-99	-7,4	-7,7	-57	
18-07-97	-6,9	-6,9	-55	-55	15-04-99	-8,0		-59	
01-08-97			-53	-53	23-04-99	-7,3	-7,6	-56	
15-08-97	-6,8	-6,8	-53	-53	29-04-99	-7,2		-54	
29-08-97			-53	-53	13-05-99	-7,4		-53	
12-09-97	-6,4	-6,4	-52	-52	27-05-99			-53	
26-09-97			-52	-52	10-06-99				
08-10-97	-6,9	-6,9	-53	-53	24-06-99	-7,0		-54	
22-10-97	-6,8	-6,8	-53	-53	09-07-99	-6,9		-54	
05-11-97					19-07-99			-53	
19-11-97	-6,9	-6,9	-53	-53	02-08-99	-6,8	-6,8	-52	-52
04-12-97					20-08-99	-6,8	-6,8	-52	-52
17-12-97					03-09-99	-6,7	-6,7	-51	-51
05-01-98	-7,0	-7,0	-53	-53	13-09-99	-6,6	-6,6	-52	-52
19-01-98					27-09-99	-6,9	-6,9	-52	-52
29-01-98	-7,4		-55	-56	06-10-99			-55	
12-02-98			-55	-55	11-10-99	-6,6	-6,6	-51	-51
06-03-98	-7,4		-56	-57	25-10-99	-7,1		-54	
19-03-98			-57	-56	08-11-99	-7,0		-54	
03-04-98	-9,8		-71	-71	22-11-99				
16-04-98	-7,9		-59		06-12-99	-7,2	-7,1	-54	
01-05-98			-57	-57	20-12-99			-53	
08-05-98	-7,6		-57		10-01-00	-6,9		-54	
22-05-98	-7,3		-55	-56	04-02-00				
05-06-98					18-02-00	-7,0		-53	
19-06-98	-7,1	-7,2	-54		02-03-00	-7,4		-57	
30-06-98	-7,1	-7,3	-53		16-03-00	-7,9		-57	
07-07-98	-7,1	-7,3	-55		30-03-00	-7,3		-56	
21-07-98	-7,0		-52	-52	13-04-00	-8,3		-62	
04-08-98			-52	-52	20-04-00	-8,1		-60	
20-08-98	-6,9	-6,9	-52	-52	04-05-00	-7,6		-58	
01-09-98	-6,9	-6,9	-52	-52	18-05-00	-7,5		-56	
17-09-98			-51	-51	13-06-00	-7,7		-55	
01-10-98	-6,9	-6,9	-51	-51	29-06-00	-7,3	-7,4	-55	
15-10-98			-51	-51	14-07-00	-7,1	-7,0	-54	
27-10-98			-52	-52	27-07-00	-7,0	-6,9	-54	
11-11-98	-6,8	-6,8	-52	-52	24-08-00				
24-11-98	-6,8	-6,8	-51	-51	08-09-00				
08-12-98	-6,6	-6,6	-51	-51	21-09-00				
23-12-98			-52	-52	05-10-00				
07-01-99			-53		19-10-00				
21-01-99	-7,0	-6,9	-53		02-11-00	-6,5	-6,5	-50	-50
04-02-99			-55		16-11-00				
18-02-99	-7,2		-55		30-11-00	-6,9	-6,9	-52	-52

Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰	Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰
21-12-00	-7,1		-53	-53	09-08-02	-6,7	-6,7	-51	-51
05-01-01	-6,7	-6,7	-52	-52	22-08-02	-6,5	-6,5	-51	-51
17-01-01	-6,9	-6,9	-53	-53	06-09-02			-52	-52
07-02-01			-53	-53	20-09-02	-6,4	-6,4	-51	-51
21-02-01	-7,1	-7,0	-53	-53	04-10-02	-6,6	-6,6	-51	-51
14-03-01	-6,6		-53	-53	18-10-02	-6,4	-6,4	-50	-50
28-03-01	-7,4		-55		31-10-02	-6,6	-6,6	-51	-51
31-03-01	-7,6		-57		18-11-02			-51	-51
04-04-01	-7,1	-7,4	-54		29-11-02			-51	-51
11-04-01	-7,5		-60		13-12-02			-52	
18-04-01	-8,5		-66	-64	28-12-02			-52	
25-04-01	-7,8		-60		10-01-03			-52	
01-05-01	-7,5		-57		24-01-03			-54	
15-05-01			-55		07-02-03			-52	
31-05-01					21-02-03			-52	
14-06-01	-7,3		-57		07-03-03			-52	
28-06-01	-7,1		-55		21-03-03			-54	
12-07-01	-6,6	-6,6	-55		28-03-03				
03-08-01	-6,5	-6,5	-51	-51	04-04-03			-66	
16-08-01	-6,5	-6,5	-52	-52	11-04-03			-57	
28-08-01	-6,6	-6,6	-51	-51	18-04-03			-57	
13-09-01	-6,6	-6,6	-51	-51	25-04-03			-59	
11-10-01			-52	-52	02-05-03			-58	
25-10-01	-6,4	-6,4	-52	-52	09-05-03			-57	
15-11-01			-53		16-05-03			-57	
29-11-01	-6,7		-52		23-05-03			-58	
13-12-01	-6,3		-53		30-05-03			-58	
28-12-01	-6,7		-53		12-06-03				
10-01-02			-52		19-06-03				
24-01-02			-54		04-07-03				
07-02-02	-6,7		-53		15-07-03				
21-02-02	-6,3		-53		30-07-03				
07-03-02	-7,1		-55		12-08-03			-53	
21-03-02			-55		28-08-03				
04-04-02	-7,4		-57		11-09-03			-51	-51
11-04-02					25-09-03			-51	-51
18-04-02			-56		09-10-03			-51	-51
26-04-02	-7,9		-58						
02-05-02	-7,5		-57						
10-05-02			-57						
16-05-02	-7,6		-58						
23-05-02			-57						
30-05-02	-7,2		-55						
14-06-02			-55						
28-06-02	-7,2		-55						
11-07-02			-53						
25-07-02	-6,7	-6,7	-52	-52					

Carillon station N 45 34,096 W 074 23,003

Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰	Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰
06-06-97	-12,1	-11,7	-87		04-03-99			-82	
20-06-97	-11,9		-87		18-03-99				
04-07-97	-11,5		-86		01-04-99	-11,3	-11,3		
18-07-97			-83		15-04-99	-11,4			
01-08-97					23-04-99	-11,4		-84	
15-08-97	-11,3		-83		29-04-99			-85	
29-08-97			-81		13-05-99	-11,1			
12-09-97	-10,9	-10,7	-82		27-05-99				
26-09-97	-10,7				10-06-99	-10,9		-82	
08-10-97			-81		24-06-99				
22-10-97	-10,8		-82		09-07-99	-10,6		-79	
05-11-97					19-07-99				
19-11-97			-83		02-08-99				
04-12-97					20-08-99	-10,1			
17-12-97					03-09-99				
05-01-98	-11,2				13-09-99	-10,1		-76	
19-01-98					27-09-99	-10,2		-74	-86
29-01-98					11-10-99	-9,6		-74	
12-02-98	-11,4	-11,4	-83		25-10-99			-75	
06-03-98	-11,6		-85		08-11-99	-9,8			
19-03-98	-11,6		-85		22-11-99			-75	
03-04-98					06-12-99	-10,3		-76	
16-04-98	-11,8		-87		20-12-99			-74	
01-05-98	-11,3				10-01-00	-10,3		-77	-77
08-05-98	-11,7		-86		04-02-00				
22-05-98					18-02-00	-10,8			
05-06-98					28-03-00	-10,8		-83	
19-06-98			-84		13-04-00	-11,1			
30-06-98					20-04-00	-11,2		-77	
07-07-98			-80		04-05-00			-79	
21-07-98	-10,8		-80		18-05-00			-73	
04-08-98	-10,3		-79		13-06-00				
20-08-98	-10,2		-79		29-06-00				
01-09-98			-77		14-07-00				
17-09-98	-10,1	-10,1	-78		27-07-00				
01-10-98	-10,3		-79		24-08-00	-10,1			
15-10-98	-10,0		-77		08-09-00				
27-10-98	-10,0		-77		21-09-00				
11-11-98			-78		05-10-00			-75	
24-11-98	-10,4		-78		19-10-00				
08-12-98	-10,3		-79		02-11-00	-10,0		-77	-76
23-12-98	-10,5				16-11-00			-78	
07-01-99					30-11-00	-10,9	-10,5		
21-01-99	-10,7		-81		21-12-00	-10,3		-79	
04-02-99					05-01-01	-11,2		-78	-78
18-02-99	-10,9				17-01-01	-10,5			

Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰	Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰
07-02-01	-10,7		-79		04-10-02			-76	
21-02-01	-10,6		-80	-78	18-10-02			-75	
14-03-01	-11,0				31-10-02	-10,3		-80	-77
28-03-01	-10,9		-79		16-11-02			-78	
04-04-01	-11,4		-86		29-11-02	-10,5		-80	
11-04-01			-84	-86	13-12-02				
18-04-01			-86		28-12-02	-10,8			
25-04-01			-81		10-01-03			-80	
01-05-01			-79	-81	24-01-03			-79	
15-05-01					07-02-03			-81	-79
31-05-01			-79	-80	21-02-03			-81	
14-06-01			-79		07-03-03			-82	-80
28-06-01			-78		21-03-03			-88	
12-07-01	-10,6		-79		28-03-03			-86	
03-08-01	-10,1		-77		04-04-03	-12,2		-87	
16-08-01			-77		11-04-03			-84	
28-08-01					18-04-03				
13-09-01	-9,9		-76	-75	25-04-03			-82	
11-10-01			-77		02-05-03			-81	
25-10-01			-76	-78	09-05-03			-83	
15-11-01			-75	-77	16-05-03			-83	
29-11-01	-9,7		-76	-76	23-05-03				
13-12-01	-10,3		-77		30-05-03			-82	
28-12-01			-75		12-06-03			-81	
10-01-02	-10,4		-78	-76	19-06-03				
24-01-02	-10,4		-79		04-07-03			-81	
07-02-02	-10,3		-79		15-07-03			-80	
21-02-02	-10,5		-78		30-07-03				
07-03-02	-10,4		-80		12-08-03			-79	
21-03-02	-10,5		-86	-79					
04-04-02	-11,2								
11-04-02			-79	-79					
18-04-02	-11,3	-11,0	-80						
26-04-02	-10,4		-80						
02-05-02	-10,9		-81						
10-05-02	-10,9		-82						
16-05-02									
23-05-02			-79						
30-05-02			-78						
14-06-02			-77						
28-06-02	-10,8		-78						
11-07-02			-77						
25-07-02	-10,2			-80					
09-08-02			-77						
22-08-02			-77						
06-09-02			-77						
20-09-02			-78						

Quebec City station N 46 48,378 W 071 11,304

Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰	Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰
04-06-97	-9,8		-71		17-02-99			-65	-64
18-06-97			-64		03-03-99	-8,3		-63	-62
02-07-97	-8,5		-64		03-03-99	-8,3		-63	-62
16-07-97			-62		17-03-99			-63	
30-07-97	-8,0		-60		31-03-99	-9,5		-71	
13-08-97					14-04-99			-75	-75
27-08-97	-7,8		-59		21-04-99			-73	
10-09-97			-57		28-04-99	-9,7		-70	-70
24-09-97	-7,6		-57		12-05-99	-9,7		-71	-72
08-10-97			-58		26-05-99			-64	-64
22-10-97	-7,5		-57		09-06-99				
05-11-97					22-06-99	-7,6		-62	-61
19-11-97					07-07-99	-8,8		-62	
03-12-97	-8,2		-61		21-07-99				
18-12-97	-8,0		-60		04-08-99	-7,4		-58	
29-12-97			-60		18-08-99			-57	
21-01-98			-67		01-09-99	-7,4		-56	
04-02-98	-8,5		-64	-64	15-09-99			-56	
18-02-98	-8,1		-63		29-09-99	-8,1		-61	
04-03-98			-64		13-10-99			-59	
18-03-98	-9,4		-69		09-11-99			-62	
01-04-98	-11,2		-81		23-11-99	-8,4	-8,8	-63	
08-04-98			-84		08-12-99			-63	
15-04-98			-78		21-12-99	-8,8		-64	
29-04-98			-69		05-01-00	-8,4		-62	
06-05-98	-9,2		-67		19-01-00				
20-05-98			-64		02-02-00	-8,2		-62	
03-06-98					16-02-00	-8,2	-8,4	-62	
17-06-98	-7,4		-59		01-03-00	-8,6		-63	
02-07-98					15-03-00	-10,0		-73	
08-07-98	-7,9		-62		29-03-00	-11,2		-80	
22-07-98	-7,7	-8,1	-61		12-04-00	-10,6	-10,7	-76	
05-08-98	-7,8		-58		19-04-00	-10,4		-74	
19-08-98	-7,3		-57		03-05-00	-10,2		-73	
02-09-98			-57		17-05-00	-9,7	-9,7	-70	
16-09-98	-7,4		-57	-58	14-06-00				
30-09-98	-7,3		-56		28-06-00	-8,4	-8,6	-62	
14-10-98	-7,6		-59	-58	12-07-00				
28-10-98	-7,4		-56	-58	26-07-00	-8,1		-59	
12-11-98	-7,2		-58	-58	23-08-00			-57	
25-11-98	-7,7		-59		07-09-00				
09-12-98			-62		20-09-00				
22-12-98	-8,0		-61		04-10-00				
06-01-99	-7,9	-7,9	-61		18-10-00				
20-01-99			-62	-61	01-11-00	-7,6		-58	
03-02-99	-8,7		-67		15-11-00	-7,9	-8,0	-58	

Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰	Date	$\delta^{18}\text{O}$ ‰	replica $\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	replica $\delta^2\text{H}$ ‰
29-11-00	-8,0		-60		10-07-02	-8,3		-64	-62
19-12-00	-8,3	-8,4	-62		24-07-02	-7,9		-58	
03-01-01	-8,7		-63		07-08-02			-56	
17-01-01	-8,1		-61	-61	21-08-02	-7,4		-56	
07-02-01	-8,0		-61		04-09-02			-55	
21-02-01	-8,8		-63	-62	18-09-02			-55	
14-03-01	-8,4		-62	-62	02-10-02	-7,2		-55	
28-03-01	-8,3		-62		16-10-02			-55	
04-04-01	-8,4		-63		30-10-02	-7,7		-56	
10-04-01	-8,5	-8,7	-64		13-11-02			-57	
19-04-01			-90		27-11-02			-61	
25-04-01			-88		11-12-02			-59	
02-05-01	-10,5		-79	-79	27-12-02			-60	
16-05-01	-9,2		-67		08-01-03			-59	
30-05-01	-8,7		-67		21-01-03			-59	
13-06-01	-9,2		-68		04-02-03			-60	
27-06-01	-8,3		-62		18-02-03			-60	
11-07-01	-8,1		-60		04-03-03			-60	
01-08-01	-7,8		-60		18-03-03			-60	
15-08-01	-7,4		-56		24-03-03			-60	
29-08-01			-56		31-03-03			-81	
12-09-01	-7,3		-56		07-04-03			-79	
26-09-01	-7,3		-56		14-04-03			-78	
10-10-01					23-04-03			-77	
24-10-01			-57		29-04-03			-76	
14-11-01	-8,1		-62		14-05-03			-71	
28-11-01	-8,2		-61		29-05-03			-66	
12-12-01	-8,5		-63	-62	13-06-03				
29-12-01					18-06-03				
09-01-02			-59		02-07-03				
23-01-02	-8,0		-61		16-07-03				
06-02-02			-61		29-07-03				
20-02-02			-62		13-08-03			-60	
06-03-02	-8,5				27-08-03			-59	
20-03-02			-63		10-09-03				
27-03-02	-8,6		-60		24-09-03			-55	
03-04-02	-9,4		-68		08-10-03			-59	
10-04-02	-10,0		-72		22-10-03			-59	
17-04-02	-9,8		-70		05-11-03				
24-04-02			-71						
01-05-02	-9,6		-70						
08-05-02			-70						
15-05-02			-70						
22-05-02			-70						
29-05-02			-63						
12-06-02			-68						
26-06-02	-9,0		-65						

Calculated values for small tributaries

Date	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰
15-06-97	-14,2	-87
15-07-97	-11,6	-80
15-08-97	-11,7	-79
15-09-97	-12,1	-70
15-10-97	-9,2	-65
15-11-97	-9,0	-63
15-12-97	-10,9	-77
15-01-98	-9,2	-75
15-02-98	-9,4	-82
15-03-98	-10,1	-78
15-04-98	-12,7	-94
15-05-98	-13,3	-92
15-06-98	-8,2	-71
15-07-98	-8,7	-76
15-08-98	-8,4	-71
15-09-98	-8,1	-72
15-10-98	-9,0	-73
15-11-98	-8,6	-76
15-12-98	-9,8	-77
15-01-99	-9,7	-73
15-02-99	-10,4	-81
15-03-99	-12,0	-83
15-04-99	-11,4	-87
15-05-99	-12,5	-90
15-06-99	-8,8	-74
15-07-99	-11,6	-73
15-08-99	-8,9	-71
15-09-99	-10,6	-71
15-10-99	-10,3	-66
15-11-99	-9,8	-69
15-12-99	-10,3	-72
15-01-00	-9,7	-68
15-02-00	-9,3	-69
15-03-00	-12,6	-87
15-04-00	-12,9	-90
15-05-00	-11,8	-84
15-06-00	-11,3	-87
15-07-00	-10,8	-75
15-08-00	-11,2	-66
15-09-00	-10,9	-68
15-10-00	-10,8	-76
15-11-00	-10,4	-73
15-12-00	-9,3	-69
15-01-01	-9,7	-70
15-02-01	-9,9	-70
15-03-01	-11,3	-76

Date	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰
15-04-01	-8,7	-86
15-05-01	-13,3	-103
15-06-01	-11,9	-80
15-07-01	-11,7	-75
15-08-01	-11,9	-78
15-09-01	-9,8	-69
15-10-01	-10,1	-56
15-11-01	-10,6	-69
15-12-01	-11,0	-67
15-01-02	-10,2	-62
15-02-02	-11,1	-69
15-03-02	-10,1	-58
15-04-02	-11,9	-84
15-05-02	-11,8	-79
15-06-02	-11,8	-81
15-07-02	-11,1	-81
15-08-02	-11,4	-71
15-09-02	-10,7	-61
15-10-02	-10,0	-65
15-11-02		-73
15-12-02		-76
15-01-03		-64
15-02-03		-69
15-03-03		-60
15-04-03		-101