Water chemistry of the freshwater section of St. Lawrence River and its major tributaries

Prepared for Olivier Morissette, Biologist, Ministry of Wildlife, Forestry and Parks (Québec, Canada)

By John Farver, Bowling Green State University, USA

March 30, 2020

Objectives: This project aims to characterise water chemistry (trace metal concentrations) of the St. Lawrence River's freshwater water mainstream as well as its major tributaries. Those tributaries are important spawning ground for numerous important fish species (i.e., walleye (*Sander vitreus*), lake sturgeon (*Acipenser fulvescens*)). They also represent highly-probable habitats for aquatic invasive species, namely grass carp (*Ctenopharyngodon idella*), of which one specimen has been captured in the St. Lawrence mainstream in May 2016.

This project aim to test three main hypotheses, 1) element fingerprints of St. Lawrence River mainstream are discernible from the tributaries, 2) inter-tributaries variability are sufficient to discriminate between them and 3) element fingerprint are stable within a single season.

Data collection: Water samples were collected by hired collectors, members of diverse non-governmental organisms located in each tributaries' draining basin (i.e. *Organismes de bassin versant*). For each river, two sampling sites were visited 5 time during the summer (from May to September). The first sampling site was located near the mouth of the river and the second site about 20-40km further upstream (see table 1). If an impassable barrier was identified on the river, the second site was just downstream of the barrier. Additionally to river sampling sites, St. Lawrence mainstream were sampled on the same temporal frequency (figure 1). St. Lawrence River sites were situated in the "brown water" (flowing from the Ottawa River) and the "green waters" (flowing from the Great Lakes).

Water Sampling: Water sampling kits were provided by Bowling Green State University. The water sampling kits consisted of acid-washed 65 ml polypropylene bottles that contained 1 ml of metals-grade nitric acid. The water sampling kits also contained sterile Luer-Lok tip syringes along with 0.45 μm nylon syringe filters. A water sampling guidelines sheet (see below) was included with the water sampling kits. The guidelines outlined that the surface water samples (50 mL) were to be collected using the Luer-Lok Tipped sterile syringe and filtered through a 0.45 μm nylon

syringe filter into the acid washed, polypropylene Nalgene bottle that contained 1 ml of metals-grade nitric acid to acidify the water samples to 2% vol/vol following USEPA method 3015. After collection, the filtered and acid stabilized samples were stored in a refrigerator and shipped in bulk to Bowling Green State University at the end of the field season.

Analyses: The water samples were analyzed using a ThermoElectron iCAP 6500 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) following USEPA Method 6010C – Inductively Coupled Plasma-Atomic Emission Spectrometry. The water analysis was done in radial plasma view. Multiple wavelengths were monitored for each element and the reported element concentrations are for the wavelengths recommend in USEPA method 6010C (see table below). The samples were introduced to the ICP-OES using a Cetac ASX-520 autosampler.

Standards were prepared using SPEX CetriPrep™ AA/ICP-AES Plasma Grade standard solutions and MilliQ™ ultrapure (>18.2 MΩ·cm) water. Standards and rinse waters were acidified to 2% vol/vol with metals-grade nitric acid to matrix match the water samples. The standards were analyzed twice at the beginning of each set of unknowns to insure plasma stability. Each unknown sample was analyzed in triplicate with a 60-second sample flush time and 35-second autosampler rinse time between samples.

Standardized intensity ratios were plotted against concentration using a linear fit. Quality of fit was determined from the correlation coefficient which was 0.999 or better for all elements.

Precision of the ICP-OES analysis was calculated (minimum detection limits) based on blanks and the standards prepared using SPEX CetriPrep™ AA/ICP-AES Plasma Grade standard solutions. The minimum detection limit for each element is noted in the table below. Potential instrument drift during analysis was monitored by running a quality control sample after every ten unknown samples. QC failure was set to ±10% of stated concentration. The accuracy of the ICP-OES analysis was checked using a SPEX CetriPrep™ Multi-element solution 2 certified standard that was randomly included in each set of thirty unknowns.

Results: Results are tabulated in a separate excel file. Samples with element concentrations below detection limits are indicated with gray shading.

Table 1. Localization of sampling stations

Rivers	Sites	Latitude	Longitude
Nicolet	Near mouth	46,22143	-72,61259
	Upstream	46,05476	-71,96702
Nicolet Sud-Ouest	Upstream	46,11188	-72,56640
Saint-François	Near mouth	46,10227	-72,90594
	Upstream	45,88560	-72,48160
Du Loup	Near mouth	46,22774	-72,92563
	Upstream	46,39846	-72,95908
Yamachiche	Near mouth	46,26464	-72,80875
	Upstream	46,44780	-72,82275
Yamaska	Near mouth	46,05644	-72,94190
	Upstream	45,62165	-72,94975
L'Assomption	Near mouth	45,74829	-73,47077
	Upstream	46,02115	-73,43568
Châteauguay	Near mouth	45,35197	-73,74190
	Upstream	45,25330	-73,79978
Richelieu	Near mouth	46,04117	-73,11789
	Upstream	45,47545	-73,27216
Fleuve Saint-Laurent	Brown waters	45,95708	-73,21621
Fleuve Saint-Laurent	Green waters	45,95385	-73,20139
Lac des deux Montagnes	Brown waters	45,45919	-74,09561
Beauharnois	Green waters	45,23558	-74,16223

Table 2. Elements Analyzed with Wavelength used and Corresponding Minimum Detection Limit

Element	Wavelength (nm)	Minimum Detection Limit (ppb)
Arsenic	193.7	14.7
Barium	455.4	0.37
Calcium	318.1	45.95
Cadmium	226.5	0.77
Cobalt	228.6	2.60
Chromium	267.7	5.91
Copper	324.7	3.57
Iron	259.9	3.66
Potassium	766.4	49.53
Magnesium	285.2	2.80
Manganese	257.6	0.636
Molybdenum	202.0	4.17
Sodium	588.9	27.5
Nickel	231.6	3.52
Lead	220.3	10.47
Strontium	407.7	0.155
Zinc	213.8	0.650

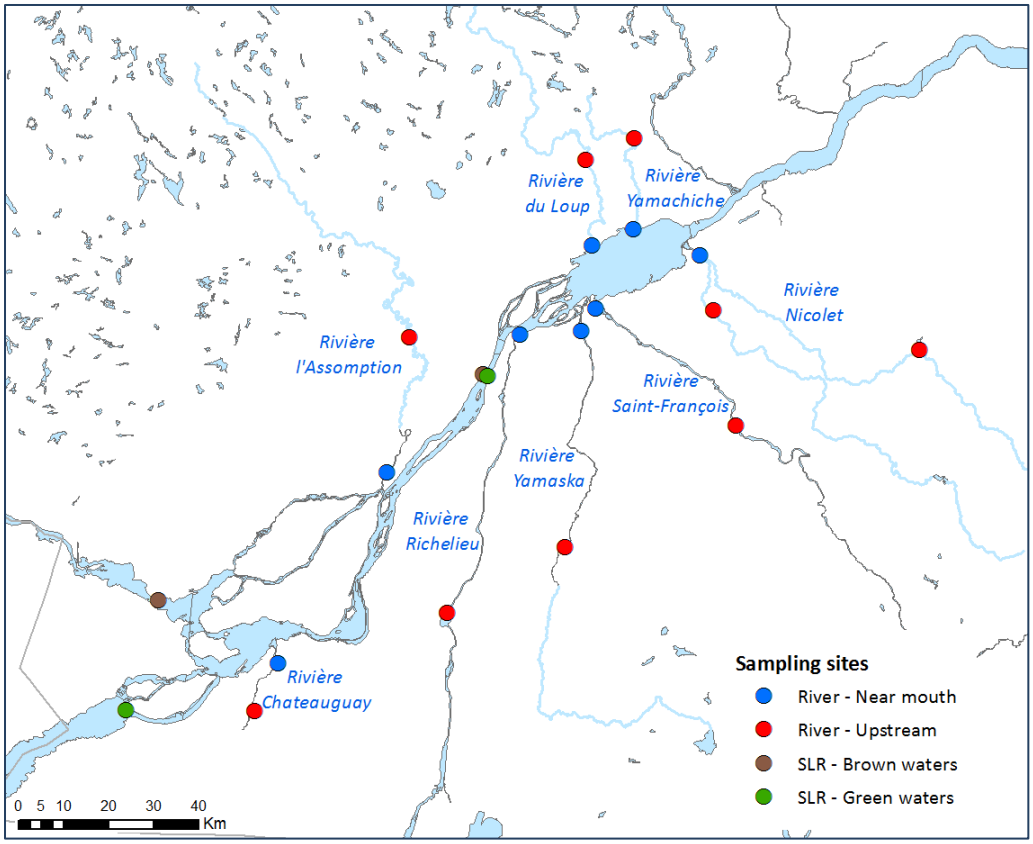

Figure 1. Map of sampling site within the St. Lawrence River freshwater mainstem and their tributaries. Blue points are near mouth sampling sites and red are upstream sites.

Water Sampling Guidelines

NOTE: SAMPLE BOTTLES CONTAIN 1 ml of CONCENTRATED NITRIC ACID – **BE CAREFUL** when opening them as there may be FUMES.

In the Kit you should find:

Acid-washed polypropylene sample bottles each containing 1.0 ml of concentrated nitric acid.

Sterile syringes (60 ml with Luer-Lok tip)

Syringe filters (0.45 micron nylon)

Nitrile gloves

Sharpie permanent marker

Bags to put bottles in for transport

Sample site selection / collection method:

Sampling method is dictated by the physical location of the individual when collecting a sample. The surface sample should be collected away from the shoreline where the stream is flowing (not in stagnant backwaters, etc). Depending upon accessibility, the most common sample collection methods are:

1. Using a sample container attached to a long handled dipper from off of a dock or pier (upstream side)
2. Using a sample container attached to a rope and dropped from a bridge (be careful of traffic)
3. Dipping a sample container into the stream from a boat (upstream side).

In all cases, the sampling container should be plastic (cup or beaker is fine) and should be rinsed several times with the water being collected.

Sampling Procedure:

1. Wearing nitrile gloves (or other gloves of your choosing), remove the sterile syringe from its plastic sleeve.
2. Rinse the syringe by drawing up a full syringe of the water from the sampling container and expelling the water. Then draw up **50** ml of water from the sampling container.
3. Attach a syringe filter to the syringe using a twisting motion (the filters have a slight thread on them).
4. Empty the syringe through the filter into an acid-washed sample bottle. **NOTE: SAMPLE BOTTLES CONTAIN 1 ml of CONCENTRATED NITRIC ACID – BE CAREFUL** when opening them as there may be FUMES and BE CAREFUL not to SPILL the acid. Emptying the syringe may require some force depending upon the amount of suspended sediment in the water. If the filter becomes clogged, remove it and replace with a new one. **NOTE**: if filtering is too difficult, 25 ml of water is enough but you should note the amount on the bottle.
5. Securely cap and label the sample bottle using a Sharpie permanent ink marker. Please include the date, location (GPS), your name or initials, and any other information necessary to uniquely identify the source. Fill out the field data sheet (see below).
6. If possible, refrigerate the water samples before sending them to BGSU. Note, it is not critical that the water samples are refrigerated as the nitric acid will stabilize them, however, it is best if they remain

cool. Please place the sample bottles into ziplock bags (double bagging is best) for transport in case the caps leak.

7. Used syringes and filters can be discarded.

Entries for Field Data sheet

River:	Name of river
Date/time:	Date and time collected. Please use 24-hour time, e.g., 1300
Location:	Brief description of where sample was collected, e.g., Hwy 20 bridge
Lat/Long:	Decimal degrees is preferred. If a different system is used specify in Notes e.g., dd mm ss, dd mm.mmm, etc.
Collector:	Name of person who collected the field sample
Agency:	Agency of the person who collected the sample. These will be used to ensure proper acknowledgement of collaborators for communication purposes
Notes:	Any seemingly relevant detail about the sample. Was it raining? Was the water turbid? Any unusual odors or colors? Etc…

Thank you for your help with this project. If you have any questions please contact:

John Farver, Professor and Chair
Department of Geology
Bowling Green State University
Bowling Green, OH 43403

Phone 419.372.7203, or email jfarver@bgsu.edu

Field Data Sheet for Surface Water Samples

River_____

Date/time_____ Location_____

Latitude_____ Longitude_____

Collector_____

Agency_____

Notes_____
_____
_____
_____
_____
_____
_____

Samples can be shipped immediately, refrigerated, or frozen until the end of field season if desired.

Send to: Dr. John Farver
Bowling Green State University
190 Overman Hall
Bowling Green, OH USA 43403-0211
Phone: 419-372-2886
Fax: 419-372-7205
jfarver@bgsu.edu