

# Natural and Human Signals in the Ottawa River, Canada, and its Tributaries: GIS and Statistical Analysis

Kevin Telmer and Jan Veizer

Department of Earth Sciences, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada  
(613) 562-5800 ext.6461; FAX: (613) 562-5192  
e-mail: Telmer@geol.uottawa.ca

## Abstract

Chemical and stable isotope analyses of the Ottawa River's tributaries are linked to the spatial entities of their catchment basins by overlaying maps of the various entities on maps of the catchments utilizing a Geographic Information System. The main inputs are bedrock geology, surficial geology, forest type, soil type, organic carbon content of soils, nitrogen content of soils, land use, elevation, total precipitation, and temperature. A principal components analysis and Pearson correlation based on the results of the overlays show that the chemical and isotopic compositions of the waters are controlled primarily by the geology and population density within the basins, and secondly by the photosynthesis/respiration cycle within the tributaries. A cluster analysis of the same results characterizes individual tributaries of the river system as more or less sensitive to the controlling factors.

**Keywords:** Biogeochemistry, Stable Isotope, Ottawa River, GIS, Principle Components, Cluster Analysis.

## Introduction

Chemical evolution of river water in space (down-stream) and in time is a result of an interaction of geogenic and anthropogenic factors. Polluted rivers acquire higher loads of dissolved salts and an excess of dissolved CO<sub>2</sub> down-stream. It is believed that anthropogenic input of nutrients may stimulate organic productivity, which, in turn, is oxidized to CO<sub>2</sub> that evades into the atmosphere and contributes to the "greenhouse" effect. Yet, similar trends are evident also in relatively unpolluted rivers, such as the Amazon, where the respiration and evasion can be attributed mostly to recharge from floodplains. The Ottawa river is an example of a river in a relatively unaltered natural state, evolving from a "pristine" shield stream at its headwaters into a moderately industrialized and polluted river that is buffered by carbonate-rich sedimentary rocks down-stream.

## Sampling And Analytical Procedures

The main river and its largest tributaries were sampled during low water stand in the fall of 1991 and high water stand in the spring of 1992. All sampling bottles were cleaned following the procedure recommended by the Environment Canada (1974). Temperature, conductivity, total dissolved solid (TDS), pH, alkalinity, dissolved O<sub>2</sub>, chloride, nitrate and sulfate were measured immediately in the field using a Hach field chemistry kit. After being filtered through a 0.45μ Millipore membrane, duplicate samples were collected and stored at 4°C for chemical and isotope analysis. Samples collected for anion analysis needed no further

treatment. The samples for determination of cations and Sr isotopes were acidified with strong HNO<sub>3</sub>. For carbon isotopes, samples were collected in brown glass bottles and poisoned with HgCl<sub>2</sub> to eliminate bacterial growth. For sulfur isotopes, each sample was treated with HCl and BaCl<sub>2</sub> to precipitate BaSO<sub>4</sub> which was then collected by filtering through 0.45μ Millipore ashless filter paper.

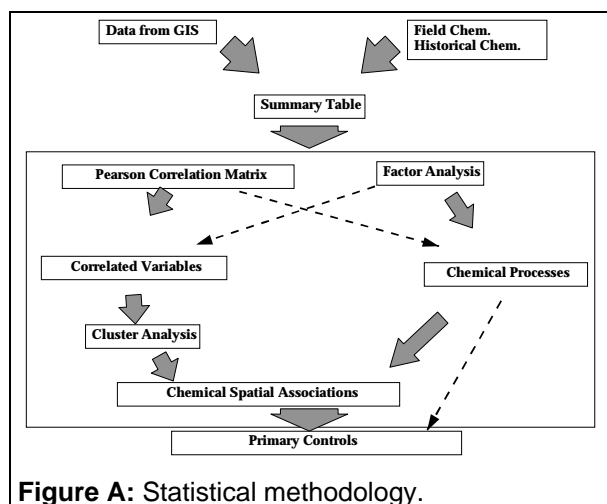
In the laboratory major cations were analyzed by a Thermo Jarrell Ash Atomscan 25 Argon ICP. The D/H ratio was determined by mass spectrometry on H<sub>2</sub> gas. Water was converted to hydrogen by oxidation with hot zinc. The <sup>18</sup>O/<sup>16</sup>O ratio was determined by equilibrating a small amount of CO<sub>2</sub> with 3ml of sample and analyzing the resulting CO<sub>2</sub> on a mass spectrometer. The <sup>13</sup>C/<sup>12</sup>C compositions were determined by mass spectrometry on CO<sub>2</sub> gas liberated by adding concentrated H<sub>3</sub>PO<sub>4</sub> to the samples under vacuum. Sulfur isotopes were determined by combusting BaSO<sub>4</sub> under vacuum with an oxidizing agent (CuO) to release SO<sub>2</sub>, which was then measured on a mass spectrometer. The δD, δ<sup>18</sup>O, δ<sup>13</sup>C and δ<sup>34</sup>S are reported relative to SMOW, Chicago PDB, and to Canyon Diablo Troilite, respectively, with a precision of ±0.1‰. All these measurements were carried out at the Department of Geology, University of Ottawa. Sr isotope measurements were determined on a five collector Finnigan MAT 262 solid source mass spectrometer at the Institute for Geology, Ruhr University, Bochum (Buhl et al., 1991). The partial pressure of CO<sub>2</sub> and the saturation index of calcite and dolomite in the river were calculated using the WATEQ computer program

(Truesdell and Jones, 1974). The concentration of dissolved inorganic carbon (DIC) was calculated from alkalinity and pH (Skirrow, 1975).

### GIS and Statistical Procedures

Geology, hydrology, watersheds, population density and hydroelectrical parameters such as reservoir size and generating capacity were entered into the GIS manually by digitizing from existing maps. Forestry data such as dominant and subdominant tree species, watershed boundaries, and agricultural intensity were obtained from Environment Canada's Environmental Information System (EIS). Landuse, classified AVHRR data, was obtained from the Manitoba Centre for Remote Sensing. Soil features such as carbon content in the upper 15 cm of soil was obtained from the Canadian Soil Information System (CANSIS) at Agriculture Canada. Geochemistry of lake and river waters was obtained from the National Geochemical Reconnaissance Program (NGR) at the Geological Survey of Canada. Geochemistry of glacial tills in the Ottawa basin was obtained from Geological Survey of Canada Open File # 643 by Inez Kettles. Meteorological data was obtained from the Atmosphere and Environmental Service (AES) at Environment Canada. This data was imported into a database where it was then summarized for the purposes of the study. Digital Elevation was obtained from the United States Geological Survey (USGS). Discharge records were obtained from Environment Canada's hydrometric database (HYDAT).

The above data layers and the watershed boundaries of the Ottawa river's major tributaries were



**Figure A:** Statistical methodology.

“area-cross-tabulated” to determine the proportion of each entity in each tributary subbasin. This data and the field chemistry were then appended into a large summary table which was subsequently used for the statistical analyses. Figure 1 depicts this procedure. A

good explanation of the statistical techniques used can be found in Davis, (1986).

### Conclusions

The chemical and isotopic compositions of the waters are controlled primarily by the geology, and population density within the subbasins, and secondly by the photosynthesis/respiration cycle within the tributaries. Low-elevation-low-latitude tributaries, draining carbonate terrains, and containing areas with relatively high population density and intense agricultural land use, are characterized by: 1) high concentrations of total dissolved solids (TDS),  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ , and low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, representing a geogenic signal; and 2) high concentrations of  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{K}^+$ , representing an anthropogenic signal. Conversely, tributaries draining the relatively sparsely populated Canadian Shield are characterized by very low TDS,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Sr}^{2+}$  higher Si and  $\text{Fe}_{\text{total}}$  and high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and their anthropogenic signal is subdued. The chemistry of the Ottawa River itself falls between these two end-members.

This technique is useful for determining the basic controls on river water quality and their location; whether they are induced naturally or by humans; and as a guide for policy makers to make development and remediation decisions.

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