Application of GIS to a Study of Mercury in the Environment, Kejimkujik Park, Nova Scotia, Canada

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Abstract

A Geographic Information System (GIS), in concert with statistical analysis tools, are used to study the statistical and spatial relationships between mercury (Hg) and dissolved organic carbon (DOC) concentrations in a variety of media in Kejimkujik Park, south-central Nova Scotia, where high Hg concentrations have been found in loons and fish. The sampled media includes soil, humus, till, vegetation and water.

Humus and the Ah soil horizon exhibit the highest concentrations of Hg, followed by till and water. The GIS analysis of the various media and the integration of Hg anomaly maps using a simple boolean additive model, has established that anomalous Hg concentrations occur in specific areas within the park. The area around Big Dam Lake over the contact zone between leucogranites and Goldenville rocks, and an area around Big Red Lake over biotite/muscovite-bearing granitoid rocks especially high in K, appear to be anomalous. Anomalous Hg and DOC concentrations in water primarily occur southeast of Kejimkujik Lake over sulphide-bearing Halifax Formation slates. These rocks may be a preferential source of Hg (biotite and sulphides as a sink for Hg). More importantly, the granitoids and slates may be more conducive to the formation of wetland environments that are characterized by lower pH and increased DOC. These factors are, perhaps, the main drivers in the bioaccumulation of Hg in the park.

Résumé

Un système d'information géographique (SIG) et des outils d'analyse statistique sont utilisés de concert dans l'étude des relations statistiques et spatiales entre les concentrations de Hg et de matière organique dissoute (MOD) dans une variété de milieux du parc Kejimkujik, la Nouvelle-Écosse sud-centrale, où de fortes concentrations de Hg ont été trouvées dans le corps de huards et de poissons. Les milieux échantillonnés comprennent le sol, l'humus, le till, la végétation et l'eau.

Ce sont les échantillons d'humus et d'horizon de sol Ah qui renferment les plus hautes concentrations de Hg, suivis par ceux de till et d'eau. L'intégration des résultats d'analyse des divers milieux et des cartes d'anomalies dans le SIG, selon un modèle simple d'addition booléenne, a révélé que les concentrations anomalies de Hg ne sont présentes qu'en certaines zones du parc. Semblent anomalies, la zone entourant le lac Big Dam au-dessus de la zone de contact entre les
INTRODUCTION

The application of Geographic Information Systems (GIS) in environmentally relevant work is thriving. An increase in the use of GIS for environmental work began in the early 1990s and continues to increase yearly (Figure 1). Much of today’s research in the field of environmental geochemistry is focused on trying to understand complicated environmental processes within ecosystems. Of principal importance are the factors influencing the chemistry of different media (soil, water, vegetation), the relationships between these media and predictions of impacts on ecosystems. The advent of user-friendly GIS software packages has facilitated the spatial analysis of multiple ecosystem variables.

A diversity of uses for GIS technology can be found in the published environmental literature. Skinner and Vance (2001) combined GIS data for geology, soils and vegetation in an attempt to determine if soil-geology relationships were contributing to Se distribution and transport in disturbed and native ecosystems. Hanset et al. (1996) combined a biogeochemical model and GIS databases to evaluate N, P, Si and C fluxes to San Francisco Bay from the urban watershed. Zhang and Selinus (1998) examined the function and limitations of statistics and GIS in environmental geochemistry. The Geological Survey of Canada has recently used GIS to investigate Hg movement in Kejimkujik Park, Nova Scotia. Spatial characterization of Hg concentration is important to assist in determining possible sources of Hg, and to identify areas of high Hg content within the park.

This study presents the results of using a GIS to characterize the spatial and statistical distribution of Hg from a variety of sampling media, within the Kejimkujik Park in southwestern Nova Scotia. Spatial characterization of Hg concentration is important to assist in determining possible sources of Hg, and to identify areas of high Hg content within the park.

Biogeochemical Cycle of Mercury

The Hg biogeochemical cycle (Figure 2) is particularly dynamic, which makes it an ideal candidate for a large scale multidisciplinary study. Elemental mercury (Hg0) is the predominant form of Hg in the atmosphere and inorganic mercury (Hg2+) is the predominant form in lakes (Watras and Huckabee, 1994). A number of atmospheric reactions can result in the oxidation of atmospheric elemental Hg and its subsequent deposition, by precipitation. Once Hg is dissolved in lake water it is available to undergo many other species conversions, the most important being its conversion to methyl mercury (MeHg) through biotic or abiotic reactions (Rudd, 1995). Once in the form of methyl mercury, it can efficiently bioaccumulate and biomagnify through the food chain. Other important areas of Hg cycling that have received less attention in the past include Hg volatilization from rocks and soils, and Hg uptake in vegetation and its subsequent re-volatilization (Watras and Huckabee, 1994).

In the terrestrial environment, uptake of metals by vegetation and the decomposition of plant material play an important role in metal and nutrient cycling, e.g., the decomposition of plant material directly results in the enrichment of metals in the organic-humus layer of surface soils. In addition to deposition from the atmosphere, runoff from the terrestrial environment will affect the concentration of metals in surface waters. Physical properties (temperature, flushing rate) and chemical properties (pH, dissolved organic carbon (DOC)) of surface waters will influence the bio-availability of metals to aquatic species, such as zooplankton and fish, which
will in turn affect the availability of metals to waterfowl and terrestrial species. Surface water properties will also influence the rate of sedimentation, and oxidation-reduction conditions will determine the breakdown or redistribution of metals from sediments. The research at Kejimkujik Park incorporated detailed sampling and analyses of metals within various reservoirs and exchange pools namely: soils, vegetation, surface waters, sediments, as well as the various pathways by which metals transfer between pools (microbial speciation, redox reactions, transpiration). It is for multidisciplinary studies, like Kejimkujik, that GIS are useful, not only for assembling and representing data in a spatial context, but for statistically and empirically examining spatial and statistical relationships among the data and producing models reflecting those relationships.

**STUDY AREA**

Kejimkujik National Park (Figure 3a) is situated in south-central Nova Scotia, approximately 90 km southwest of Halifax. It provides a good example of an area where GIS can play an important role in environmental geochemistry research.

**Bedrock Geology**

The bedrock of Kejimkujik Park is typical of rocks of the Meguma Terrane found throughout about half of the landmass of southwestern Nova Scotia (Keppie, 2000). The area is underlain by two main rock sequences, each of which could be a source of Hg: 1) the Meguma Group of Cambro-Ordovician age and 2) the South...
Mountain Batholith and related intrusive rocks of Devonian-Carboniferous age (Figure 3b).

The Meguma Group consists of a lower greywacke unit (Goldenville Formation) and an overlying black, organic carbon-rich sulfidic slate (Halifax Formation) that underlies the southern and eastern parts of Kejimkujik Park, as well as most of the Atlantic shore of Nova Scotia. Rasmussen et al. (1997) indicated that the bedrock lithology, age and abundance of sulfide mineralization are very important to understanding Hg distribution in bedrock. In particular pyritic/pyrrhotitic black shales and Hg bearing sphalerite (ZnFeS) are implicated as important in complexing Hg. Meguma Group rocks collected on surface in Kejimkujik Park were generally low in Hg ranging from <1 ppb to 16.4 ppb in samples form sulfidic slates of the Halifax Formation. However, similar Meguma Group rocks collected from drill core outside the Kejimkujik Park area, contained higher average Hg values, to a maximum of 242 ppb in Zn-bearing sulfidic slate (Sangster et al., 2003).

The South Mountain Batholith, which occupies most of the western part of the park, is locally comprised of two intrusions, the Davis Lake leucomonzogranite and Kejimkujik monzogranite (Horne and Corey, 1994). These rocks contain abundant biotite that may have associated mercury. The granitic rocks contain an average of 1.5 ppb Hg contained mainly in easily alterable biotite that averages 13.7 ppb (Sangster et al., 2003).

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Recent studies by Siciliano et al. (2003, 2005) showed that bedrock lithology influences MeHg concentration in wetlands within the park. In particular, it was found that MeHg concentration in wetlands over the Kejimkujik monzogranites was 2 to 10 times greater than in lakes over other rock types.

Surficial Geology

The park is mainly covered by stony till plain deposits. These tills were formed under local ice caps that were prevalent in Nova Scotia during the advance of the last ice age. These tills are characterized by a loose texture, sandy matrix, and abundant, locally derived, angular cobbles and boulders. In places, the boulders are large, measuring up to 20 m in diameter. Over most of the park area, glacial debris is relatively thin (<1 m). The area has low relief with a strong southeastward grooving that recorded the last main movement of the ice sheet that crossed Nova Scotia. The southern third of the park area features very elongate streamlined hills of glacial debris (drumlins) on average 1 to 2 km long. They record the main southeastward course of the ice sheet across Nova Scotia and give the terrain a strong southeast fabric.

Vegetation

The forest cover of the park is representative of the Atlantic Uplands forest region, and is composed of mixed coniferous and deciduous vegetation. There is a mixture of tree species but the dominant trees include: white pine (Pinus strobus), eastern hemlock (Tsuga canadensis), white birch (Betula papyrifera) and red maple (Acer rubrum). While past logging has disturbed much of the forest in the region, there is no logging within the park. Forests in the park are generally less than 100 years old, due to the effects of forest fires and logging. However, a few stands of eastern hemlock have survived for more than 300 years. Figure 4 shows a series of photos taken from a helicopter which show characteristic geomorphic and vegetation conditions in the park.

DATA

Over a three-year period, samples were collected from numerous types of media within the park and were analyzed for a suite of elements. These samples represent point data in the GIS database.
Figure 4. Photographs (taken from a helicopter) of typical geomorphology and vegetation of the Park.

**Drumlin landscape**
A common feature of Kejimkujik National Park are the numerous streamlined elliptical hills of glacial debris called drumlins. The low tapering tail points in the direction of ice flow; their trend records the main southeastward course of the ice sheet across Nova Scotia. Carved by strong glacial action from a thick blanket of drift, the drumlins form islands and peninsulas in many lakes.

**Esker along Stewart Brook, near Frozen Ocean Lake.**
The narrow ridge winding across the view is an esker. It is composed of gravel that was deposited by glacial meltwater coursing through a tunnel at the base of the ice sheet. The bog, Burnaby Meadow, occupies depressions left by melted ice blocks.

**Rogen moraine with hummocks, Cobrielle Lake.**
Long drumlinoid ridges (seen in the distance) are overlaid with transverse ribs, here trending obliquely from the lower left. The ribs, called rogen moraine, are pushed up as the ice sheet thins, slows, and tends to plough the underlying drift rather than mould it. During stagnation and disintegration, the ice sheet deposited till hummocks mounds which here form islands and shoals.
(Table 1). Lithogeochemical data for the area exists however a decision was made not to use the data as Hg concentrations were generally very low (close to the analytical detection limit). Lake sediment data are also available but were not used due to suspect analyses (P. Friske, pers. comm., 2002).

<table>
<thead>
<tr>
<th>Media</th>
<th>Data Available</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface water</td>
<td>Chemistry, pH, DOC, temp, conductivity</td>
</tr>
<tr>
<td>Groundwater</td>
<td>Chemistry, DOC</td>
</tr>
<tr>
<td>Well water</td>
<td>Chemistry, DOC</td>
</tr>
<tr>
<td>Lake sediments</td>
<td>Chemistry</td>
</tr>
<tr>
<td>Zooplankton</td>
<td>Mercury</td>
</tr>
<tr>
<td>Fish</td>
<td>Mercury</td>
</tr>
<tr>
<td>Soil</td>
<td>Chemistry</td>
</tr>
<tr>
<td>Soil gas</td>
<td>Mercury</td>
</tr>
<tr>
<td>Till</td>
<td>Chemistry</td>
</tr>
<tr>
<td>White Pine</td>
<td>Chemistry</td>
</tr>
<tr>
<td>Red Maple</td>
<td>Chemistry</td>
</tr>
</tbody>
</table>

Two water sampling surveys (lakes and rivers) were included in this study; one completed by Rencz (2001) and the other by A.L. Sangster (pers. comm., 2003). Rencz (2001) sampled waters from 50 lakes, mostly within the boundaries of Kejimkujik National Park, over a three-day period in October of 1997. Samples were passed through 0.45 μ filters and stored at 4°C for subsequent chemical analyses (total Hg, methyl mercury, anions, cations, and trace elements - Telmer and Veizer, 1999; Cai et al., 1996; Rencz et al., 2003). The Sangster survey involved the collection of samples from all types of surface drainages (lakes and rivers) with a bias toward headwaters and surface water sources. Samples were collected during 5 periods of differing water flows over a 3 year period (1999-2001). Analyses were carried out for total Hg, DOC, anions, and cations. Figure 5 shows proportional dot plots of total Hg in water (Figure 5a) and DOC (Figure 5b) from both water surveys.

Samples of leaf and twig tissue from the dominant tree species were collected in and around Kejimkujik Park. Dominant trees included red maple (Acer rubrum), white pine (Pinus strobus), eastern hemlock (Tsuga canadensis) and white birch (Betula papyrifera). Samples were placed in paper bags and air-dried. They were then sorted into leaf and twig tissue, ground to ensure homogeneity prior to analysis for trace elements (including Hg - Hall and Pelchat, 1997). Figure 6 shows proportional dot maps of Hg in red maple analysed at ACME Analytical Laboratory Ltd. (Figure 6a) and analysed at the Geological Survey of Canada (Figure 6b).

Soil samples were collected from three different soil horizons, O (humus), Ah and the C-horizon. Samples were placed in plastic bags and returned to the lab for air-drying, sieving and analyses (Hall and Pelchat, 1997). Figure 7 show proportional dot maps of Hg in various soil horizons (analyzed by Acme analytical).

Burgess et al. (1998b) collected the fish chemistry dataset used in this study. They sampled 678 yellow perch (Perca flavescens) from 24 different lakes in Kejimkujik Park and prepared their samples according to Environment Canada guidelines (Environment Canada, 1982). Figure 8 shows the mean Hg concentration (μg/g on a wet weight basis) in perch habitating lakes from which the samples were acquired.

During the 2000 and 2001 field seasons, the Nova Scotia Department of Mines collected a total of 97 till samples at 500 m intervals along 8 northwest–southeast traverse lines of variable length (Goodwin, 2005). The traverse lines were carefully selected to ensure they crossed all dominant till and bedrock types. Approximately 500 g of till were collected at each site and all organic material and large clasts were removed in the field. Relatively unoxidized samples were collected from an average sampling depth of 1 m having a minimum sampling depth of 45 cm and a maximum sampling depth of 4 m. A 1 to 2 g subsample was digested with aqua regia and analyzed for Hg (total) by Cetac Cold Vapour - Atomic Absorption (Cetac CV-AA) with a detection limit of 0.2 ppb by ACME Analytical Laboratories Ltd. of Vancouver, British Columbia. Figure 9 shows a proportional dot map of Hg in till.

The digital elevation data used in this project was provided by the Centre for Topographic Information (CTI), Natural Resources Canada (NRCan), in Canadian Digital Elevation Data (CDED) format. This data is derived from the 1:50,000 National Topographic Database (NTDB). Figure 10a shows the digital elevation model (DEM) and Figure 10b shows a shaded relief rendition of the DEM.

Landsat TM data was obtained from Radarsat International and included seven channels of information in the visible and near infrared portion of the electromagnetic spectrum. Figure 11a shows a Landsat 7, band 4 (infrared) image of the park area.

Airborne spectrometer data was also collected over the park by the Geological Survey of Canada primarily to provide lithologic information and to distinguish the different phases of the South Mountain Batholith.

Data Processing Using the GIS

All data were compiled into a georeferenced GIS database using a Universal Transverse Mercator projection (UTM Zone 20) with NAD 27 datum. Data compilation and processing was undertaken using ArcGIS 8.2™ and ArcView 3.2™, both Environmental Systems Research Institute (ESRI) software products.

Geochemical Data

The geochemical data in the form of Excel™ spreadsheets were imported directly into the GIS for analysis. With respect to visualization, the various geochemical data collected for this study were not of sufficient spatial density to warrant interpolation to continuous surfaces. Therefore, four approaches were used to visualize and analyze the data: (1) establishing a zone of influence (1 km) around each sample point by buffering, (2) delineating drainage basins from the Digital Elevation Model (DEM) which were used as discrete areas in spatial analysis, (3) using lakes as a zone of influence for Hg data collected from fish and, (4) using lithology for spatial analysis units (Figure 12).
Method 1 involved buffering each sample point using the GIS to a distance of 1 km to facilitate overlay analysis. A one kilometre radius was arbitrarily chosen as a maximum zone of influence to establish polygons which are required for overlay analysis. With respect to method 2, drainage basins were automatically derived from the DEM using the hydrologic functionality of the GIS (see below). A GIS point-in-polygon procedure was then undertaken to append each sample to the underlying drainage basin and a mean value for selected geochemical elements was calculated for each drainage basin. The drainage basins were then colour-coded by geochemical concentration for each element analyzed. The same point-in-polygon approach was used in geochemical analysis using lakes and lithologic units (methods 3 and 4) as a spatial analysis unit.

**Digital Elevation Model (DEM)**

The DEM was imported into the GIS directly and was enhanced by hillshading using GIS software (Figure 10b). The ArcInfo Grid module was used to automatically generate drainage basins from the DEM. The Grid BASIN function delineates drainage basins by identifying ridge lines between basins. BASIN analyzes the flow-direction grid to find all sets of connected cells that belong to the same drainage basin. Grid's FLOWDIRECTION function uses a DEM grid as input and creates a grid of flow direction from each cell to its steepest downslope neighbour. The FLOWDIRECTION function can be the argument to the BASIN function so the computation of the basin grid is computed using the following grid statement:

```
basins = BASIN ( FLOWDIRECTION ( dem ) )
```

Figure 10c shows the drainage basins that were automatically extracted from the DEM using the above function.

**Landsat TM**

The Landsat data were georeferenced (NAD 27, UTM Zone 20) and enhanced (contrast stretched) to produce images suitable for visual interpretation. Wetland areas (possible sinks for Hg) were visually and automatically extracted from the infrared band (Band 4) using a histogram thresholding technique (Figure 11b). Hirtle and Rencz (2003) have found that wetlands are important predictors of higher Hg levels within the park.

**DATA INTEGRATION AND ANALYSIS**

First, individual Hg and pathfinder (for Hg) anomaly maps were produced using proportional dot maps (Figures 5 to 9) in which the dot size is proportional to element concentration. Second, anomalous concentrations were identified by plotting the data on normal probability maps and selecting upper thresholds to divide the element into anomalous and background concentrations. Grunsky
(1997) and Harris et al. (1999, 2000) provide more details on this method for identification of geochemical anomalies. The anomalous points for each media were then buffered creating a 1 km zone (area of influence) around each anomalous point. All the binary maps were then simply overlaid (added together) in the GIS producing an anomaly map that shows the coincidence between anomalous Hg concentrations in the various media. Correlation and regression analysis were also applied to the data to study the statistical relationships between Hg, DOC and, in some cases, pH, between the various media.

RESULTS

Reliability of Hg Analyses

Soil/Humus and Vegetation Data

In any geochemical study the precision and accuracy of the analyses must be assessed to ensure that reliable results are achieved. In this study, because Hg was analyzed at two different labs (GSC and ACME) a comparison of Hg analyses was undertaken to assess data quality. This involved statistically evaluating each analysis for each media using correlation analysis, and statistical procedures for testing the differences between population means (t-tests), medians (Mann-Whitney U) standard deviations (F-test) and frequency distributions (Kolmogorov-Smirnov test). Table 2 shows the results of these tests applied to Hg.

 Generally, these results are acceptable as the correlation coefficients are high although some analytical variability exists with the vegetation and soil data by virtue of slightly lower correlations. However, this analysis only tests for the global statistical similarity between datasets and not spatial variability. It is still possible to get spatial differences with respect to high (anomalous) concentrations of Hg throughout the study area. Figure 13 is a series of Hg maps that show anomalous concentrations for Hg in humus, soil (<63 μm) and red maple analyzed at two different labs (analyzed at ACME and GSC). Note that there are areas that are anomalous on both datasets but there are also anomalous areas that are not coincident, which may reflect variability in the analysis of the samples by the different labs. Anomalous Hg concentrations were identified by looking at upper breakpoints on normal probability plots (Harris et al., 1999, 2000; Grunsky, 1997). Generally, these breakpoints coincided with values between the 80th and 90th percentiles, depending on media. As a result of this comparison the data analyzed at ACME were used for further analysis largely because of a greater number of samples.

Till Data

To ensure the integrity of the analytical results, strict quality control (QC) protocols were employed during all stages of the till sampling program (including planning, sample collection, sample preparation and sample analysis). Duplicates were collected during the field sampling phase and preparation splits, certified reference standards and in-house reference standards were routinely inserted prior to geochemical analysis (T. Goodwin, pers. comm., 2003).

As a further test of analytical precision, ACME re-ran the first 34 samples submitted during the 2000 sampling program for Hg by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) as a check against Hg values reported by the Cetac CV-AA method.

Total Hg – Total Concentration in Each Media

Table 3 summarizes Hg concentration in the various media sampled. Humus and the Ah soil horizon exhibit the highest concentra-
Figure 7. Proportional dot plots of Hg in surficial media (a) Ah soil - <63 μm, (b) Ah soil - >63 μm, (c) C soil <63 μm, (d) C soil >63 μm, (e) humus – lithological contacts are overlayed – see Figure 3 for lithologic unit names.
Figure 8. Mean Hg concentration in perch colour-coded by lake – see Figure 3 for lake names and lithological unit names.

Figure 9. Proportional dot plot of Hg in till – see Figure 3 for lithological unit names.

Figure 10. Digital Elevation Model (DEM), (a) raw DEM displayed in black and white, (b) shaded-relief rendition of the DEM (from the NW at 40° elevation), (c) drainage basins automatically extracted from the DEM using GIS software.
Figure 11. LANDSAT data, (a) band 4 – infrared channel, (b) wetlands extracted from the band 4 channel using a histogram thresholding technique – lithological contacts have been overlayed – see Figure 3 for lithological unit names.

Table 2. Results of statistical significance tests between samples analysed at ACME and GSC (Y = significant difference, N = not a significant difference)

<table>
<thead>
<tr>
<th>Medium</th>
<th># of samples</th>
<th>Correlation (spearman rank)</th>
<th>Means Test</th>
<th>Median test</th>
<th>Standard deviation test</th>
<th>Distribution test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veg (rm)</td>
<td>28</td>
<td>.87</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Soil_Ah_gt63</td>
<td>8</td>
<td>.94</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Soil_Ah_lt63</td>
<td>15</td>
<td>.92</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Humus</td>
<td>37</td>
<td>.96</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>Soil_C_gt63</td>
<td>11</td>
<td>.98</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Soil_C_lt63</td>
<td>11</td>
<td>.96</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

Table 3. Hg concentration in various media – humus, Soil – A-horizon (Ah) (> and < 63 μm, Soil – C-horizon (< and > 63 μm), till, vegetation, water (Rencz dataset), water (Sangster dataset)
tions for Hg, and have maximum values of 466 and 42.8 ppb, respectively. The high concentrations in these media reflect the high percentage of organic matter and its strong affinity to bind mercury. The decreasing trend of Hg content with depth continues to the unweathered till below the C-horizon. The lower levels of Hg at lower levels in the soil column reflect the lower levels of organic matter.

Presumably, the lower Hg concentrations in the larger size soil fraction in the C-horizon reflect a reduced CEC (cation exchange capacity). It would be expected that there would be more binding sites for Hg with the increased clay content in the smaller grain size fraction. Mercury concentrations in red maple ranged from 5 to 41, ppb and levels in white pine ranged from 5 to 58 ppb, dry weight. Concentrations of total Hg were found to be significantly higher in epiphytic lichens (maximum of 660 ppb) and in feather mosses.

Hg Correlation with Other Elements – Identification of Pathfinders

In this analysis, it is not possible to statistically compare Hg concentrations by media on a point-to-point basis because the data were
not sampled at the same geographic location. However, two possible solutions can be invoked to allow for such a comparison; (1) interpolation of the Hg concentrations and, (2) summing Hg concentration by a zone of influence, which in this case, is a drainage basin. Interpolation was not employed as the sample density was not sufficient and the pattern of points was heterogeneous and sporadic (see Figures 5 to 9). However, as mentioned above, drainage basins were automatically generated from the DEM and the geochemical points were intersected with each drainage basin using a point-in-polygon operation. This operation attaches the drainage basin ID in which the sample data resides to each geochemical sample point. From this, an average Hg concentration can be calculated from the points within each drainage basin.

Correlation analysis was also conducted between Hg and other metal elements (pathfinders) and also U, K and Th, to determine whether airborne gamma ray spectrometer data can be used as a vector for high Hg levels. Table 4 shows the results of Spearman rank correlation analysis. All correlations are significant at the 95% confidence interval. Spearman correlation was used because of the non-normal distributions of the geochemical elements being compared.

Moderate to strong correlations are found between Hg in soil (Ah horizon) and humus and Pb, S, Sb and K. The positive correlation with K is noteworthy because it indicates that airborne gamma ray spectrometer data (%K) may be useful as a pathfinder for high Hg levels within the study area, and also suggests that K-bearing granitoid rocks may, in part, be a source of Hg. Mercury also shows a moderate correlation with P, Pb and S in the C-horizon of soil and Al, S and Pb in till.

Phosphorous has a moderately strong to weak correlation with several media (Table 4). High concentrations of P have been linked to increased MeHg production through its affect on eutrophication. Eutrophication may enhance the level of MeHg through a variety of factors including increased microbial activity and fulvic acid concentrations (Vaithiyanathan et al., 1996). However,
Vaithiyanathan et al. (1996) noted that the correlation between Hg and P was associated with enhanced peat accretion rates and not a change in the mobilization of Hg. Therefore, phosphorus may be related to the amount of peat present in the wetlands surrounding the lakes in Kejimkujik Park. This may result in an increase in DOC export and a resulting increase in Hg transport from wetlands to lakes.

**Hg Correlation with LOI (Organic Matter)**

Correlation analysis between Hg and loss-on-ignition (LOI) was also undertaken for samples having coincident geographic locations as various researchers (Watras and Huckabee, 1994; Clair et al., 1998; Renz et al., 2003; Siciliano et al., 2003) have found a relationship between high Hg levels and organic matter. LOI can be used as a proxy for organic matter content in a geochemical sample because organic matter is driven off easily, when subjected to low levels of heat and is measured as a loss-on-ignition. Table 5 shows the results of the correlation analysis. These results suggest a strong positive correlation between Hg and organic matter supporting the hypothesis that wetlands may contain higher than normal Hg levels within the park (Clair et al., 1998). However, the statistical robustness of these results must be questioned due to the low number of samples. Figure 14 shows an average LOI map created by selecting

<table>
<thead>
<tr>
<th>Media</th>
<th># of samples</th>
<th>Elements that are moderately correlated with Hg (&gt; .6)</th>
<th>Elements with weaker (.4-.6) and negative correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veg (red maple)</td>
<td>28</td>
<td>None</td>
<td>Pb (.3), Cr (.41), Zn (?)</td>
</tr>
<tr>
<td>Soil (Ah &gt; 63 μm)</td>
<td>47</td>
<td>Pb (.7), K (.65), S (.8), Sb (.64)</td>
<td>Ag (.48), Au (.48), P (.5), Zn (.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Neg corr with U (-.67), Th (-.6)</td>
</tr>
<tr>
<td>Soil (AH &lt; 63 μm)</td>
<td>47</td>
<td>Pb (.79), K (.64), S (.8)</td>
<td>Au (.49), Cu (.51), P (.48)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Th (-.74), U (-62), Fe (-.46)</td>
</tr>
<tr>
<td>Humus</td>
<td>44</td>
<td>Pb (.7), S (.61), Sb (.6)</td>
<td>K (.47), P (.45), Fe (.42), As (.33)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Th (-.7), U (-.68)</td>
</tr>
<tr>
<td>Soil (C &gt; 63 μm)</td>
<td>50</td>
<td>P (.63)</td>
<td>Pb (.45), S (.43), Cr (.4)</td>
</tr>
<tr>
<td>Soil (C &lt; 63 μm)</td>
<td>49</td>
<td>Ag (.69), P (.6)</td>
<td>Cr (.58), Fe (.55), Pb (.54), S (.54), Zn (.54), As (.41)</td>
</tr>
<tr>
<td>Till</td>
<td>97</td>
<td>Al (.66)</td>
<td>S (.48), Pb (.23)</td>
</tr>
</tbody>
</table>

**Table 4.** Correlation between Hg in various media and potential pathfinder

![Mean LOI content calculated from soil and humus and wetlands from LANDSAT and NTDB data.](image-url)
LOI values > 0 for all soil (Ah and C-horizons) and humus. Interpolated maps of LOI (using an inverse-distance-weighted (IDW) algorithm) for each media and each separate horizon and fraction (total of 5 maps) were created and the average of these maps was calculated. Wetlands extracted from the Landsat data (see Figure 11b) and from the NTS topographic data (NTS sheet 21A/06) have been included on this map for comparison purposes.

Three areas of high LOI (high organic matter) are noteworthy; Area A around Big Dam Lake which is found over Goldenville rocks and is coincident with swamp areas derived from the NTS sheets and Landsat image, Area B southeast of Loon Lake also over Goldenville rocks and, Area C over biotite bearing monzogranite rocks in the central portion of the study area. Areas A and C are coincident with Hg anomalies in other media (see discussion later in the paper). This suggests that organic matter may be acting as a sink for Hg within the study area. Generally, no apparent spatial association between density of wetlands and areas of high organic content can be seen visually, except in the vicinity of Loon Lake.

Analysis of Hg in Water

It is important to look at the spatial variations between Hg and DOC and pH in lakes within the study area as researchers have found a moderate to strong positive correlation between Hg concentration and DOC and a negative correlation between Hg and pH (Rudd 1995; Clair et al., 1998). In this study, a moderate correlation between DOC and Hg in waters was found (0.72 – Spearman correlation coefficient – average of the two water datasets - 0.78 for Rencz and 0.7 for Sangster), whereas a weak negative relationship between Hg and pH (-0.51) was found. This suggests that acidic lakes with high DOC are good predictors of high Hg levels within the park. Hickey et al. (2005) and Clair et al. (2005) provide more detailed discussions on the relationship between DOC and pH in lakes within Kejimkujik National Park.

Figure 15 shows normal probability plots for Hg and DOC in water for the Rencz dataset. Breakpoints (thresholds) which separate the populations into anomalous and background levels have been labelled on these plots. Figure 16a shows a map of anomalous samples from the Rencz water dataset (Hg ≥ 5 ppb and DOC ≥ 12.5 ppm). A number of samples may have both anomalous Hg and DOC levels. These occur in Big Red Lake over the Kejimkujik monzogranite and in the northern portion of the park (around the Twin Lakes) over biotite monzogranites. High Hg levels are found in Luxton Lake (at least for the period sampled – August, 2000) over the Kejimkujik monzogranites and in the vicinity of Frozen Ocean Lake over Goldenville greywackes. Given the moderately strong correlation between Hg and DOC and that the presence of high DOC levels are associated with high Hg levels, these samples may be more representative of bedrock concentrations and less dependent on local sources of DOC (i.e., wetlands). However, more research on this matter is required to determine whether most of the lake chemistry is wetland or lithologically driven. High DOC levels are found in a stream draining Minard Lake over Halifax Formation rocks and in the vicinity of Big Dam Lake.

The water dataset collected by Sangster et al. (2003) was divided into different seasonal periods as previously discussed. Figure 17 shows a plot of mean and median Hg and DOC concentrations over the five sampling periods. DOC concentrations are highest in November 1999 and 2001, whereas Hg is highest in November, 1999. The higher levels of Hg and DOC in the fall may be related to lower water levels (higher flushing rate) and higher decomposition rates. Figures 16b and c show anomalous Hg and DOC levels by sampling period. Anomalies in this case were standardized using greater than the 95th percentile value for each population. Many of the samples with anomalous Hg concentrations, particularly those collected in the summer, are located south of Kejimkujik Lake over Halifax Formation rocks. One sample with anomalous Hg concentrations in three sampling periods occurs in a small creek south of Luxton Lake within the Kejimkujik monzogranite. A number of samples with high DOC levels in more than one sampling period again occur to the southwest of Kejimkujik

<table>
<thead>
<tr>
<th>Media</th>
<th># samples</th>
<th>Spearman Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veg</td>
<td>Too few samples (&lt;5)</td>
<td></td>
</tr>
<tr>
<td>Soil (Ah horizon &gt; 63μm)</td>
<td>8</td>
<td>.74</td>
</tr>
<tr>
<td>Soil (Ah horizon &lt; 63μm)</td>
<td>8</td>
<td>.92</td>
</tr>
<tr>
<td>Humus</td>
<td>11</td>
<td>.81</td>
</tr>
<tr>
<td>Soil (C horizon &gt; 63μm)</td>
<td>11</td>
<td>.9</td>
</tr>
<tr>
<td>Soil (C horizon &lt; 63μm)</td>
<td>11</td>
<td>.91</td>
</tr>
</tbody>
</table>

Table 5. Correlation between Hg in various media and LOI (organic matter)

Figure 15. Normal probability plots from Rencz water dataset showing thresholds used for identifying anomalous concentrations (a) Hg, (b) DOC.
Figure 16. Symbol plots of Hg and DOC anomalies derived from water datasets, (a) Hg and DOC from Renz dataset, (b) Hg from Sangster dataset, (c) DOC from Sangster dataset – anomalies for (b) and (c) based on Hg and DOC ≥95th%.

- Water (Renz dataset) - DOC > 125 ppm
- Water (Renz dataset) - Hg > 5 ppm

+ Water (Sangster dataset) - Hg > 95th% ppm - Nov. 2001
★ Water (Sangster dataset) - Hg > 95th% ppm - Aug. 2000
▲ Water (Sangster dataset) - Hg > 95th% ppm - June 2000
● Water (Sangster dataset) - Hg > 95th% ppm - Nov. 1999
○ Water (Sangster dataset) - Hg > 95th% ppm - Aug. 1999

- shear zone
- - Limit of effects of shearing (cleavage)
○ Water (Sangster dataset) - DOC > 95th% ppm - Aug. 1999
● Water (Sangster dataset) - DOC > 95th% ppm - Nov. 1999
▲ Water (Sangster dataset) - DOC > 95th% ppm - June 2000
□ Water (Sangster dataset) - DOC > 95th% ppm - Aug. 2000
+ Water (Sangster dataset) - DOC > 95th% ppm - April 2001
★ Water (Sangster dataset) - DOC > 95th% ppm - Nov. 2001
Lake within Halifax Formation rocks. A northeast-trending shear zone has been mapped in this vicinity (Figure 16c) which imparts a strong cleavage on the rocks in this area. Whether a causal relationship between high Hg and DOC levels and shearing in this area exists is not known at this time.

Moderate but significant correlations are found between Hg and Fe, Pb, Al, U and Cr in water (Table 6). This analysis is statistically more robust due to larger sample sizes (>30). The reason for this is because most metals complex with DOC, which is a major controlling factor on metal transport in water.

**Analysis of Hg in Perch**

Table 7 shows the results of correlation analysis between Hg in water, DOC and Hg levels in perch. The correlation analysis was undertaken on a lake-to-lake basis involving 18 lakes within the study area. When more than one sample was present for a lake, the average value of the total number of samples was calculated. The number of samples per lake ranged from 1 to 23. The Spearman correlations shown in brackets are based on a subset of the 10 largest lakes within the study area. The correlation is moderate at best (0.35) between Hg in water and Hg in perch but higher between DOC and Hg in perch (0.7) and pH and Hg in perch.

**Hg and Pathfinder Anomaly Maps**

Figure 19a shows a Hg anomaly map produced by identifying anomalous concentrations on probability plots for each surficial medium (humus, soil, till – all fractions) and vegetation (red maple), buffering the points to one km and then adding all the bina-
ry Hg anomaly maps (total of 7) to produce a map that shows coincident Hg anomalies in the various media. Mercury anomalies in rock were not included due to suspect results as discussed earlier. Figure 19b shows a pathfinder anomaly map in which all elements that showed a moderately strong correlation with Hg (>0.6 correlation coefficient – Table 4). Table 9 summarizes the geochemical maps used to produce the Hg anomaly maps and the thresholds used to define Hg anomalies.

Figure 19c is a total anomaly map representing the additive result of the Hg and pathfinder anomaly maps (Figures 19a and b). Figure 19d shows the Hg concentration in perch by lake (Figure 8) and is included here for comparison purposes.

Based on the above maps with high levels of Hg are found in the vicinity of Luxton Big Red and Ben lakes within the Kejimkujik (biotite/muscovite) monzogranite and around Big Dam Lake within the contact zone between Goldenville rocks and leucomonzogranite rocks. A secondary area occurs in a northwest striking zone in the vicinity of North Cranberry Lake.

The highest Hg levels in yellow perch are found in Big Red Lake and in several of the surrounding lakes such as Luxton and Little Red (all of which are headwater lakes). Concentrations of 0.72 ppm Hg at Big Red Lake and 0.54 ppm at Luxton Lake represent the highest yellow perch concentrations and values 3 to 4 times higher than Pebbleloggitch Lake, which is <10 kms away. Mercury concentrations in red maple from around Big Red Lake represent the highest Hg values (76 ppm) and again concentrations decrease over a short distance to "background" levels of around 10 ppb in the watershed basin for Kejimkujik Lake. Mercury concentrations in the soil are also high in the Big Red Lake area and the values in the Ah horizon (<63 μm) are in excess of 400 ppb.

There are also coincident anomalies in Hg for all media around North Cranberry Lake. While the Hg content in yellow perch at North Cranberry Lake and George Lake are similar (0.4997 and 0.4686 ppm, respectively) the Hg concentrations in the lake waters are elevated at George Lake relative to North Cranberry (4.4 ppt and 1.93 ppt respectively). Similarly, Hg concentrations in red maple and the soil, particularly the Ah horizon is also high in the area (Figures 6 and 7).

Also of interest are areas where there are high levels of Hg in one media but not in other media. For example, it was observed that the area around Pebbleloggitch Lake has relatively high concentrations of Hg in soil and red maple but concentrations in fish were the lowest in the 24 lakes sampled (0.1854 ppm). Pebbleloggitch Lake was also characterized by relatively high levels of Hg (4.75 ppt) in the lake.
Figure 19. Anomaly maps, (a) total Hg in all surficial media (soil, till, humus and vegetation), (b) anomaly map based on Hg pathfinders, (c) total anomaly map comprising Hg and pathfinders, (d) Hg anomalies in perch colour-coded by lake.
waters and moderate DOC (7.06 ppm). This 'exception' to the pattern illustrates the complexity of Hg cycling in the area.

### Analysis of Hg by Drainage Basins

Analysis of Hg by drainage basin was restricted to only four basins in which Hg was sampled from all media (surficial, water, vegetation and fish). Figure 20 shows the four drainage basins ranked from highest to lowest mean Hg concentrations calculated from all surficial media (soil, humus, till) and vegetation. The total Hg anomaly map (Figure 19c) and associated pathfinders are overlaid over the drainage basins as is average Hg in perch (ppm) by lake. Drainage basin 1 has the highest Hg concentrations in humus, soil (Ah > 63 μm fraction) and till whereas drainage basin 4 has the highest Hg concentration in soil (C > 63 μm fraction (silt + clay)).

### SUMMARY AND CONCLUSIONS

The elemental concentrations from a variety of media at Kejimkujik National Park, Nova Scotia illustrate that the levels of Hg in various components of the ecosystem (vascular plants, soil, till, humus, water and rocks) have a broad concentration range of values but the maximum values are not unusually higher than other ecosystems (Vaidya et al., 2000). In the soil, the highest levels of Hg are found...
in humus, followed by the Ah soil horizon in both fractions (>63 μm and <63 μm). Part of the Hg content of the Ah soil horizon may have been leached from humus. The other media (soil C-horizon and till) have much lower Hg concentrations perhaps reflecting lower cation exchange capacity. Mercury concentrations in all media evaluated showed moderate positive correlations with Pb, S, Sb and P indicating that the presence of sulfides (acting as an Hg sink) may be valuable predictors for high levels of Hg. Phosphorus may be associated with enhanced peat accretion (increased production of organic matter) which also can act as a sink for Hg.

DOC and pH play fundamental roles in the control of Hg levels in Kejimkujik National Park. The importance of DOC and pH in Hg cycling has been observed in other wetland environments (Rudd, 1995). Results of this study provide further evidence that wetland environments will typically be fundamental to the cycling of Hg. In these areas, the combination of low pH, and high DOC provide an environment conducive to retention of Hg and transport to lakes. The importance of the terrestrial ecosystem in Hg cycling and its interaction with wetland-dominated ecosystems is a growing area of interest in Hg research.

The results of this study indicate that the Hg content of the water is directly correlatable with DOC at a ratio of approximately 1 ppt Hg per 4 ppm DOC (Sangster et al., 2003). Values are highest in the smaller, boggy, source areas and lowest in streams draining lakes where solar radiation results in degradation of DOC and release of Hg to the atmosphere. Bedrock control on Hg occurrence may involve several factors but perhaps the most important is the weathering hardness of the rocks with some rock types, slates in particular, producing a terrain amenable to the production of bogs.

Sangster et al. (2003) noted that many of the higher Hg values in water occur in streams over the sulfidic-carbonaceous Halifax Formation rocks or in very low pH (3.8 to 5.0) streams draining the Kejimkujik monzogranite. In this study, anomalous Hg in water were found primarily in lakes over Halifax Formation rocks and the Kejimkujik (biotite/muscovite bearing) monzogranite.

The occurrence of background levels of Hg in yellow perch (despite the presence of relatively high values of Hg (total) in lake waters, soils and red maple leaf tissue) for several lakes may indicate that in certain lakes Hg is not in a bioavailable form and therefore is not readily available to enter the aquatic food chain. This emphasizes the dual role of DOC in acting both as a transporter of Hg species from wetlands but also as a ligand for Hg species in lakes. It is possible that the methyl Hg is bound to DOC and is not bioavailable.

Although concentrations of Hg in yellow perch are unrelated to Hg levels in terrestrial vegetation and soil, phosphorus levels in vegetation and in the soil were strongly correlated (positive) with Hg in fish. While there is no known link between P in vegetation and Hg in fish there are several possible explanations. Phosphorus and Hg may be linked through a third parameter such as the oxygen content of the lake and surrounding wetland, which will affect microbial activity and MeHg production. It is also possible that soil characteristics such as buffering capacity may play a role in phosphorus dynamics and affect the vegetation-perch correlation. While this requires more study before any conclusions can be drawn, it is clear that multidisciplinary work, such as this, is essential to understanding the Hg cycle and links between terrestrial and aquatic processes.

The GIS analysis of the various media and integration of Hg anomaly maps using a simple Boolean additive model, has established that anomalous Hg concentrations occur in specific areas within the park. The area around Big Dam Lake over the contact zone between leucogranites and Goldenville rocks and an area around Big Red Lake over the Kejimkujik monzogranites (which is especially high in K on the gamma ray spectrometer data), appear to be anomalous. Anomalous Hg and DOC concentrations in water primarily occur southeast of Kejimkujik Lake over sulphide-bear- ing Halifax Formation slates. These rocks may be a preferential source of Hg (biotite and sulfides as a sink for Hg).

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REFERENCES


