

**Stream water, stream sediment, and vegetation geochemistry of the Restigouche -
Murray Brook area, Bathurst Mining Camp, New Brunswick (parts of NTS 2107,
2108, 2109 and 21010)**

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Abstract

A detailed hydrogeochemical, stream sediment and biogeochemical survey was carried out in the northwestern part of the Bathurst Mining Camp as part of the EXTECH-II program. The purpose of the survey was 1) to evaluate the mineral potential of a belt of Ordovician rocks in the Bathurst Mining Camp; 2) to test the effectiveness of detailed multiparameter geochemical techniques in mineral exploration, and; 3) to provide valuable baseline geochemical data for evaluating natural and anthropogenic contributions of metals to the surface environment. The purpose of this report is to release this multi-media, multi-element geochemical data set.

Within the survey area (approximately 400 km²) there are several known mineral occurrences, a past producing mine (Murray Brook deposit) and a presently inactive mine (Restigouche deposit). Samples were collected around the Restigouche deposit prior to open pit operations. The survey area was chosen because it allows the characterization of anomalies from known sulphide deposits (e.g. the Restigouche deposit) as well as the assessment of the influence of past mining activity on the composition of stream sediments and waters (e.g., Murray Brook deposit). Samples were collected at 500 m spacings along all streams within the survey area. Additional samples were taken from seepage zones encountered during stream traverses.

Surface water anomalies are most consistently developed for Zn, but in many cases, Pb, As and Cu anomalies are consistent with known mineral occurrences. Stream water Zn anomalies define dispersion trains up to 4 km downstream from the Restigouche deposit (< 2 km for Pb) but are more restricted at other massive sulfide occurrences in the study area. Total and partial extraction stream sediment compositions show similar anomaly patterns as surface waters around known mineralization. The partial extraction data allows identification of the most labile phases (adsorbed and bound to amorphous Mn and Fe oxyhydroxides) and yields greater anomaly contrast for some metals (e.g. Pb, Zn, Tl) than the total sediment data but reveals essentially the same anomalies. At elevated metal contents, Zn, Pb, and Tl are primarily hydromorphically dispersed. In contrast, total stream sediment compositions show anomalous Bi, In, and Sn contents where mineralization is at

or near surface with respect to drainage, whereas these elements do not show systematic anomalies in the partial extraction data, indicating that they are dispersed mechanically. For many elements, balsam fir needles show significant anomalies around known mineralization.

The type and magnitude of the metal anomalies are controlled by a) the extent of oxidation of massive sulfides, b) the composition of ground and surface waters which interact with massive sulfides, and c) the local hydrology which controls the depth of recharge of oxygenated waters and the discharge of groundwaters into the stream system. The distance of dispersion is controlled by water pH, adsorption on to precipitating Mn- and Fe-oxyhydroxides, and dilution by unmineralized base-flow (groundwater discharge). The results of this study are important for mineral exploration in the Bathurst Mining Camp and suggest: 1) surface waters are an effective exploration tool in this mining camp; 2) base metal dispersion is generally restricted (typically less than 1- 2 km) indicating that sampling should be carried out at a detailed scale (500 m intervals or less); 3) the local hydrology may determine whether a concealed target has a surficial expression.

Introduction

The Bathurst Mining Camp (BMC) is a mature mining camp with several active and recently active mines (Brunswick #12, Heath Steele, Caribou and Restigouche deposits), several past producing mines (Wedge, Brunswick #6 and Austin Brook deposits), and over 30 other significant occurrences. All of these deposits, however, occur at or near surface and were discovered in the 1950's and 1960's using standard geochemical (soil, stream sediment) and geophysical exploration methods (McCutcheon, 1992). Because groundwaters penetrate deeply into the earth's crust, hydrogeochemistry offers the potential to explore into the third dimension and detect more deeply buried mineralization. The purpose of this study was to use hydrogeochemical methods (surface water geochemistry, complemented by total and partial stream sediment compositions) and biogeochemistry (balsam fir needles) in the BMC to test the efficacy of these techniques (and recent advances in analytical methods) in a mature mining camp.

This study includes surface waters and stream sediments collected from an approximately 400 km² survey area in the western part of the BMC (Fig. 1). The surface waters include seeps and stream waters, primarily first and second order streams. For the most part the surface waters represent base flow conditions as confirmed by the similarity between stable isotope values of surface and shallow ground waters (Leybourne, 1998). This result is an important point because the efficacy of surface water hydrogeochemical exploration will depend on the extent to which deeper groundwaters are being expressed at the surface. The survey area also includes a previously exploited deposit (Murray Brook) to provide quantification of anthropogenic impacts on survey design and results. The result of this study is a comprehensive data set of surface water and stream sediment (total and partial extraction) geochemical and biogeochemical data at a detailed sample spacing. This open file report presents this multi-media and multi-element data set along with some preliminary interpretations.

Regional Setting

The study area is located in the BMC which comprises part of the Miramichi terrane of northern New Brunswick, Canada (Fig. 1). Tetagouche Group rocks host the volcanogenic massive sulfide (VMS) deposits and are interpreted to have formed within an Ordovician (465-471 Ma) ensialic rift basin (van Staal et al., 1992; van Staal and Sullivan, 1992). The survey area includes the Restigouche deposit, the Murray Brook deposit, and several known mineral occurrences (Fig. 2). The geology of the study area consists of Cambro-Ordovician Miramichi Group metasediments (COMG; Fig. 2), that are conformably overlain by Tetagouche Group rocks including felsic volcanic and associated volcanoclastic rocks (Nepisiguit Falls Formation, ON; Flat Landing Brook Formation, OF; Mount Brittain Formation, OMB; Camel Back Formation, OCB) and mafic volcanic and volcanoclastic rocks (Little River Formation, OL). The western and northwestern margins of the study area are dominated by Siluro-Devonian metasedimentary cover rocks (SDs).

Massive sulfides at the Restigouche deposit are characterized by elevated contents of Zn, Pb,

Cu, Ag, Cd, In, Mo, Sn, and Tl compared to unaltered host lithologies. Cobalt and Ni are not enriched in the Restigouche deposit. Mafic volcanic rocks and cross cutting dykes typically have higher Co and Ni than massive sulfides (Leybourne, 1998). The Murray Brook deposit is a larger deposit (21.5 Mt of 2.81% combined Zn and Pb) with a well-formed gossan (1.9 Mt with 1.53 g/t Au and 65.9 g/t Ag) capping a supergene Cu zone and Zn-Pb massive sulfides (Boyle, 1995; Rennick and Burton, 1992). The gossan was mined between 1989 and 1992 for Ag and Au using a cyanide vat-leach process. Within the study area there are 27 other mineral occurrences, most of which are of Zn-Pb-Cu VMS-type. At the time of sampling, the Restigouche deposit was undisturbed with the exception of exploration drilling undertaken since the 1950's. Subsequent to sampling in 1995 and 1996, the Restigouche deposit was put into open-pit production. The primary land use in the study area is logging for wood pulp. The study area is generally forested and dominated by boreal forest type vegetation including black and red spruce, jack pine, balsam fir and birch. Alders are common in swampy areas of valley bottoms.

Sample Collection

A total of 429 sites were sampled during the summer of 1997 (210-971xxx, stream sediments; 210-972xxx, surface waters; 210-3xxx, balsam fir needles), with an additional 136 sites from around the Restigouche deposit which were sampled during the summers of 1995 and 1996 (MLW, water and MLS, sediment samples). Samples were located using hand-help GPS units and topographic maps. Samples were collected at ~500 m intervals (100 and 200 m intervals around the Restigouche deposit) and were located at least 50 m upstream of roads and culverts in order to minimize anthropogenic contamination. Surface waters were collected in 125 ml prewashed Nalgene bottles (cations and anions) and an acid-washed 60 ml Nalgene bottle (Hg). Cation and anion samples were filtered in situ through 0.45 µm filters, refrigerated and acidified (cations) with ultrapure nitric acid (to 0.4%) at the base camp. The Hg sample was unfiltered, collected with plastic gloves and individually bagged to prevent contamination. The Hg was preserved with BrCl

reagent and refrigerated. Sediments were collected from the active part of the stream in kraft paper bags, air dried and sieved to -80 mesh ($< 177 \mu\text{m}$). For the 1995 and 1996 sites around the Restigouche deposit, Hg and balsam fir needles were not collected.

Balsam fir sample sites were all close to those at which stream sediments and waters were collected. At each sample location 200 - 250 g of fresh twigs and needles were snipped from a single balsam fir tree using standard anvil-type, teflon-coated, garden pruning snips. Usually 5 - 7 twigs, each comprising 5 - 7 years of growth, provided the required amount of material, which were placed in aerated sample bags. Within the survey area this amount of growth was commonly 35 - 40 cm length of twig. At some sites, where forest growth was more dense and annual growth increments were shorter, approximately 10 years of growth was collected. Although there is annual variation in the metal uptake and storage of many chemical elements (some accumulating near the twig ends), the over-riding factor for consideration in a biogeochemical sampling programme is the diameter of the twig. It is important to maintain a consistent ratio of twig bark to twig wood, because many of the heavy metals are located in the bark, and not in the woody tissue of the twig. If this ratio changes substantially, then variations in element content may be attributable to mixing thick with thin twigs, providing false anomalies. In light of the variability in size and the low volume of some twig samples obtained for this survey (i.e. low ash yield) a decision was made to analyse only the needles. For most elements, concentrations in needles are commonly lower than in twigs, but for surveys of the type reported here it is the relative spatial variation in composition are more significant rather than absolute concentrations.

Balsam fir samples were air-dried for several weeks in a greenhouse. Needles were then separated from the twigs, because balsam fir needles have a different chemical composition from the twigs. The ratio of needle to twig may vary among sample locations, so if twigs are not separated from needles some false biogeochemical anomalies may be generated which are simply a function of different twig to needle ratios. Approximately 50 g of dry needles was weighed into aluminium trays. The trays were placed in a pottery kiln, and the temperature slowly raised (over 2

- 3 hours) to 470°C. After a further 12 hours no charcoal remained, and the needles were reduced to 1 - 2 g of ash.

Water Analysis

For surface waters collected during 1997, only pH was measured in the field. For the 1995 and 1996 waters collected around the Restigouche deposit, pH, Eh, conductivity and dissolved oxygen were measured. Major and minor elements were analyzed by inductively-coupled plasma emission spectrometry (ICP-ES; Si, Ti, Al, Fe, Mg, Ca, Na, K, B, Ba, Be, Cd, Co, Cr, Cu, Li, Ni, Pb, Sc, Sr, V and Zn), trace elements by ICP-MS (mass spectrometry; Ag, Bi, Co, Cr, Cs, Ga, In, Mn, Pb, Rb, Sb, Tl, U, V, Al, As, Ba, Cd, Cu, Mo, Ni, Be, Se and Zn), anions by ion chromatography (SO₄, Cl, F, Br, PO₄, NO₃, NO₂), and alkalinity by titration at the Geological Survey of Canada. Rare earth elements (REE) and selected trace elements (Sc, V, Co, Ni, Cu, Ga, Y, Mo, Cd, Bi, Th and U) were analyzed by ICP-MS following 5x pre-concentration and chelation, using the method of Hall et al. (1995). Detection limits are presented in Table 1 and surface water data are presented in Table 2.

Stream Sediment Analysis

Sediments were analyzed by ICP-MS (REE, Cs, Tl, U, Th, Hf, In, Nb, Rb, Ag, Ga, Cd, Mo, Ta, Bi, Sn, Zr and Pb), ICP-ES or XRF (Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K) and wet chemical methods (Fe, H₂O, CO₂, C, S) following total dissolution (Table 3). For ICP-ES, analysis is completed by fusing the sample with a mixed lithium metaborate - lithium tetraborate flux with dissolution of the fusion melt, typically with nitric acid. ICP-MS determinations are based on the total dissolution of the sample using nitric, perchloric and hydrofluoric acids followed by a lithium metaborate fusion of any residual material. Stream sediments were also analyzed by ICP-MS (REE, Cs, Tl, U, Th, Hf, In, Nb, Rb, Ag, Ga, Cd, Mo, Ta, Bi, Sn, Zr and Pb) and ICP-ES (Fe, Mn, Ag, Be, Co, Cr, Cu, La, Mo, Ni, Pb, Sc, Sr, V, Y, Yb, Zn and Zr) following partial

extraction by 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.05 M HCl , using the methods outlined in Hall et al. (1996) (Table 4). For the partial extraction, 1 g of sample was added to 20 ml of 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride). The resultant solution was heated to 60°C for two hours and vortexed every 30 minutes, following which the samples were centrifuged for 10 minutes at 2800 rpm. The supernatant was then decanted for analysis. All analyses were performed at the Geological Survey of Canada.

Vegetation Analysis

Ashed balsam fir needles were analyzed by ICP-ES and ICP-MS. All values quoted are for total concentrations in ash. The ash yield from the dry tissue was 3-4%. Determinations for 10 major elements and Ba, Be, Co, Cr, Cu, Ni, Sc, Sr, V, and Zn were done by ICP-ES. Additional determinations by ICP-MS provided data for REE (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb), Ag, Bi, Cd, Cs, Ga, Hf, In, Mo, Nb, Pb, Rb, Ta, Th, Tl, U, and Zr. Balsam fir needle analytical data is presented in Table 5.

Analytical Quality Control

One standard was included within each group of 20 samples prepared for analysis. For waters the standard was a field sample collected at the end of the season and prepared in the same manner as the other samples. For the sediments, an in house standard was used, and for the vegetation an ash standard was used (V6c). In addition, each group of twenty samples included a field duplicate as well as duplicate analytical analyses. These provided quality controls on accuracy (standards) and precision (duplicates), respectively (Table 1).

Data Presentation

Selected data are presented as proportional circle maps, with data subdivided on the basis of percentiles (98-100, 95-98, 90-95, 75-90, 50-75, 25-50, and <25). For data below the detection

limit, a value of half the detection limit has been used in the plots. In this study, threshold and background values were chosen based on analysis of probability plots and on spatial associations of water and stream sediment compositions in areas of known mineralization at the Restigouche deposit [Leybourne, 1998 #3895]. Statistical methods of threshold selection (e.g. mean + one standard deviation) are less applicable given that a significant proportion of samples were collected close to known mineralization. For many elements in both waters and sediments, several populations are evident based on log-normal probability plots. In these cases, there are two anomalous populations, and background is interpreted to be all values less than the lower threshold.

Data Presentation and Preliminary Interpretation - Surface Waters

Most of the surface waters are Ca-HCO_3 type waters, with less common $\text{Ca-HCO}_3\text{-SO}_4$ and Ca-SO_4 types. Surface waters in the study area are generally fresh, ranging from < 10 to 150 mg/L total dissolved solids (TDS) (Fig. 4). Waters with high TDS values are concentrated in the northern and northwestern part of the study area where streams drain mafic volcanic and metasedimentary rocks, dacitic to felsic volcanic rocks of the Mt. Brittain Formation and Silurian metasedimentary cover rocks. Low TDS waters occur in streams which primarily drain Cambro-Ordovician metasediments and felsic volcanic and volcanoclastic rocks of the Nepisiguit Falls and Flat Landing Brook formations (Fig. 4). Surface waters with elevated HCO_3 , Ca and Mg contents coincide with elevated TDS, consistent with the strong correlation between TDS and HCO_3 ($r = 0.99$) and Ca ($r = 0.99$). Sulfate is also not well correlated with TDS ($r = 0.39$), although surface waters with elevated SO_4 are also concentrated in the northern and northwestern parts of the study area (Fig. 5). The majority of the surface waters have near-neutral pH values (pH between 6.5 and 7.5) (Table 2).

The most elevated SO_4 contents occur downstream from the Murray Brook deposit and in several seeps close to the Restigouche deposit (Fig. 5). High SO_4 contents are also evident in

several streams draining to the south and southeast of the Restigouche deposit, over Miramichi group metasediments. There is only one sulfide showing in this area, the Upsalquitch Lake showing (Fig. 2). Most of the streams in the southern half of the study area which drain felsic volcanic and volcanoclastic rocks have low SO_4 contents (Fig. 5). However, for many of these streams, although the SO_4 contents are low, SO_4 comprises 20-30% of the anions, whereas surface waters draining Silurian metasedimentary rocks in the northwest corner of the study area have elevated SO_4 , but the SO_4 typically represents < 10% of the total anions.

Zinc values above 3 $\mu\text{g/L}$ are considered anomalous, with a highly anomalous population above 20 $\mu\text{g/L}$ (Fig. 6). Areas of anomalous Zn (> 3 $\mu\text{g/L}$) include the Restigouche deposit, particularly several seeps close to the deposit and downstream from the deposit (Fig. 6). Zinc contents are low upstream from the Restigouche deposit (< 1 $\mu\text{g/L}$), whereas, surface waters immediately downstream from the deposit have Zn contents of 7 - 8 $\mu\text{g/L}$. With increasing distance downstream, Zn contents decrease to around 2 $\mu\text{g/L}$ four kilometers from the Restigouche deposit. Anomalous Zinc contents also occur in the headwaters of a stream draining west of the Dungannon showing (Figs. 2, 6). However, the showing is in a different catchment basin. In the northwest corner of the study area, waters from Simpsons Brook show anomalous Zn values over a length of several km (Fig. 6), although there is no associated Pb anomaly (Fig. 7). There is a single Zn anomaly on Little Elbow Brook adjacent to the Little Elbow Brook occurrence. A stream draining to the NE of the Little Elbow Brook occurrence also has Zn values above threshold (Fig. 6). West of the Restigouche deposit, several small streams drain into the Portage Lakes and display anomalous Zn values (as well as elevated SO_4 and As). These anomalies are north of two small occurrences and upstream from the Portage Lakes mineral occurrence.

Lead has a lower threshold at 1 $\mu\text{g/L}$ and a higher threshold at the 98th percentile (1.7 $\mu\text{g/L}$; Fig. 7). Lead in surface waters close to the Restigouche deposit display patterns similar to Zn (Fig. 7). Lead contents are low upstream from the deposit (background values around 0.5 $\mu\text{g/L}$), increase immediately downstream from the deposit (up to 2.4 $\mu\text{g/L}$) and ultimately reach

background values two kilometers downstream from the deposit. Lead values decrease more rapidly than Zn and generally coincide with a rapid decrease in dissolved Fe contents downstream from the deposit.

Copper is generally a poor indicator of proximity to the main Restigouche deposit (Fig. 8). Most anomalous values occur along the small stream adjacent to the Restigouche deposit and in streams draining south and southeast of the Restigouche deposit. However, surface waters downstream of the Restigouche deposit have higher Cu contents than most other surface waters in the study area with the exception of Gossan Creek downstream from the Murray Brook deposit (Fig. 8).

Arsenic tends to be elevated in BMC massive sulfides over host lithologies, and is hosted primarily in arsenopyrite, pyrite and sulfosalts. Anomalous As ($> 1 \mu\text{g/L}$; 90th percentile) contents are associated with the Restigouche and Murray Brook deposits and the Little Elbow Brook showing (Fig. 9). Arsenic is anomalous in streams close to the Upsalquitch Lake gold showing (Fig. 9).

The open pit and gossan tailings pile at the Murray Brook deposit are located at the headwaters of Gossan Creek. This stream has the highest sulphate and the highest metal contents of all surface waters in the study area with up to $11,000 \mu\text{g/L}$ Zn, $29 \mu\text{g/L}$ Pb, $15,000 \mu\text{g/L}$ Cu and $15 \mu\text{g/L}$ Cd (e.g. sample 210-972115 in Table 2). In addition, this stream has the most elevated Hg contents in the study area (Fig. 10). Most surface waters have Hg contents close to natural background values which for fluvial systems are considered to be from 0.1 to 20 ng/L , with most values $< 5 \text{ ng/L}$ (Mastrine et al., 1999).

Data Presentation and Preliminary Interpretation - Stream Sediments

High Mn (and Fe) contents in stream sediments are concentrated in the northwestern part of the study area, around the Restigouche deposit, and particularly in streams draining east and west of the deposit and draining Miramichi Group metasedimentary rocks south of the Restigouche deposit

(Fig. 11).

Areas of anomalous Zn (> 500 ppm) include the Restigouche deposit, Gossan Creek at the Murray Brook deposit, Simpsons Brook, streams draining south of the Restigouche deposit and small streams east and west of the Restigouche deposit (Fig. 12). Zinc and Pb are anomalously high (> 500 and > 60 ppm, respectively) in some streams away from the Restigouche deposit. Zinc is anomalous (up to 1600 ppm) near the top of the small stream adjacent to the Restigouche deposit and decreases towards the Restigouche deposit). Elevated Zn contents (1500 to 1600 ppm) also occur in stream sediments 4 km to the northeast of the Restigouche deposit (Fig. 12). These sediments also have the highest Cd contents in the Restigouche deposit area. In addition, Little Elbow Brook has a single Zn anomaly that coincides with that seen in the surface waters (cf Figs. 6, 12). Similarly, stream sediments west of the Dungannon showing in the central part of the study area are anomalous in Zn that is coincident with Zn anomalies in the surface waters.

Lead displays two major and one minor population, with highly anomalous values above 300 ppm (up to 2000 ppm) and background values below 60 ppm (Fig. 13). For two kilometers downstream from the Restigouche deposit Pb contents are greater than Zn contents. Maximum Zn contents occur between 500-900 meters downstream from the Restigouche deposit, shifted slightly further downstream compared to the Pb peak. Both Zn and Pb show generally decreasing concentrations beyond one kilometer from the deposit, but do not reach background levels at the limit of this data set (3 km downstream from the deposit; Figs. 12, 13).

As with the surface waters, Cu in stream sediments is anomalous close to the Restigouche and Murray Brook deposits, but is also elevated in Mn-rich stream sediments south of the Restigouche deposit (Fig. 14). Copper accumulation in these latter sediments is probably due to Mn-oxyhydroxide scavenging.

Tin, In, and Bi show patterns similar to Zn with respect to proximity to the Restigouche deposit although they decrease more rapidly to background values (e.g., Figs. 15, 16) approximately 2 km downstream from the deposit. Bismuth and In are typically enriched in BMC massive sulphides

and typically have low abundances in the major lithologies in the BMC (Boyle, in prep.). The rate of decay of anomalous values to background levels is more rapid than is the case for Pb. However, although Sn, Bi and In display strong anomalies over the Restigouche deposit, there is little relationship with other known occurrences in the study area (e.g., Sn and Bi; Figs. 15, 16).

Data Presentation and Preliminary Interpretation - Partial Sediments

Comparison of the total and partial sediment data shows that typically < 20% of the total Fe is released during partial extraction, whereas on average 90% of the total Mn is released (c.f. Tables 3, 4). Manganese in the partial extractions shows similar distribution patterns to Mn in the total sediments (c.f. Figs. 11, 17). For Zn, the partial extraction technique recovers around 56% of the total Zn and the percent Zn recovered increases with increasing Zn content. Anomalous areas indicated by Zn and Cd contents are similar. Significant anomalies are associated with the Restigouche and Murray Brook deposits. The streams draining Miramichi Group rocks south of the Restigouche deposit are anomalous in both Zn (Fig. 18) and Cd, confirming surface water and total sediment anomalies for this area. Overall, elements partially extracted show similar spatial relationships to those measured in the total sediment (Figs. 17-20). Note that for very Cu-rich sediments from Gossan Creek downstream from the Murray Brook deposit, essentially 100% of the Cu is labile (c.f. Figs. 14, 20).

Data Presentation and Preliminary Interpretation - Balsam Fir Needles

A review of the analytical data showed that 26 elements exhibit concentrations above detection levels and sufficient data variability to warrant plotting their distribution patterns. These 26 elements could be divided into two equal sized groups of interest based on their geochemical relief with respect to the data set:

High interest: Cu, Ni, Ag, Cd, Zn, Ga, Cs, Th, Rb, Pb, Nb, Tl and U;

Moderate interest: Al, Fe, Mn, Mg, K, P, Ba, Sr, Ce (to represent the light REE), Yb (to

represent the heavy REE), Hf, Mo and Zr.

Zinc is essential for carbohydrate and protein metabolism, therefore differences of a few 100 ppm Zn in ash are probably related to the health of the tree rather than subtle changes in substrate chemistry. However, the Zn maps (Figs. 21, 22) show a range in concentration of almost 4000 ppm Zn indicating that the regional pattern of Zn distribution is reflecting broad differences across the area. Of note are enrichments related to base metal mineralization at Murray Brook; northwest from Restigouche; and several areas to the east.

Despite the known toxic effects of Pb, it occurs naturally in all plants, and in small traces Pb may even be an essential element (Broyer et al., 1972). It is taken up mainly by root hairs and stored as a pyrophosphate in cell walls. With few exceptions Pb concentrations throughout the survey area are close to normal background levels (<20 ppm Pb). Figures 23 and 24 show the distribution of lead and subtle enrichments near several known base metal deposits.

Copper plays a fundamental role in plant metabolism. It assists in respiration, photosynthesis, nitrogen fixation and valence changes, and it is present in many micro-components of plants (small and large molecules, chloroplasts, mitochondria etc.). As a consequence, the background concentration of Cu in ash of the needles (median 110 ppm) is high compared to many trace elements. The interpretation of Cu distribution patterns in tree tissues should be approached with caution, since laboratory studies report numerous antagonistic and synergistic interactions with both major and minor elements. Kabata-Pendias and Pendias (1984) review these briefly. However, despite the essentiality of Cu and the complex metabolic roles that it may play, substantial differences among the survey samples are more likely to reflect significant differences in the Cu content of the substrate than the relatively small differences attributable to micronutrient functions. Areas of copper enrichment (Figs. 25, 26) are quite large and low in magnitude, yet there is general enrichment near several of the base metal deposits.

Of particular interest is the distribution pattern for thallium (Figs. 27, 28). Thallium is not known to be an essential element for plant growth and can be quite toxic. Typically, plant tissues

contain considerably less than 1 ppm Tl in ash, although it is known to concentrate to extraordinary levels in certain species growing on Pb/Zn mine tailings at Les Malines (Les Avinières), near Montpellier in southern France (Leblanc et al., 1999, in press). A maximum concentration of 1.5% Tl is recorded in dry tissue of the brassicaceous plant *Biscutella daevigata* L., and 0.4% Tl in *Iberis intermedia* Guersent (candytuft) (Anderson et al., 1999 in press).

In the present data set the median value is 0.25 ppm, yet in the Murray Brook area (centre north) there are concentrations up to 49 ppm Tl with high concentrations continuing downstream to the north. Work by Warren and Horsky (1986) has shown a near perfect correlation between Tl and Au contents of various plants from British Columbia. Gold was not determined by the analytical method employed for this study and so this relationship has not been tested, but from the observations of others the implication is that the Tl is associated with base metals and perhaps some Au enrichment at Murray Brook. Although samples were not obtained from the Restigouche area, it is noteworthy that there is a subtle enrichment of Tl immediately to the south. Similar weak enrichments occur in the southeast part of the survey area near Devil's Elbow, and to the east of Little Elbow. Thallium could prove to be a useful pathfinder element for certain styles of mineralization in the Bathurst Camp.

Silver is not known to be essential to plant life, and can become toxic to plants by substituting for K in membranes and thereby inhibiting the absorption of other cations by roots (Hendrix and Higinbotham, 1974). Silver concentrations are close to those expected for plant tissues in general. However Figures 29 and 30 show areas of relative silver enrichment, and outlines an area to the south of Murray Brook. The implication is that there is geochemical zoning of Ag peripheral to the Murray Brook Deposits.

Although there is a strong geochemical association between Cd and Zn in many geochemical environments, this is not evident in plant tissues because of the *requirement* that plants have for Zn but not for Cd. However, Cd is easily absorbed by plants and may therefore be expected to reflect relative Cd concentrations in the soils and groundwater. Absolute concentrations differ among

plant species because Cd can be captured by a variety of organic compounds in cell walls and therefore not all will be transported to the tree extremities. In general the Cd concentrations in the survey area are fairly low (Figs. 31, 32), with a typical median concentration of 2-3 ppm Cd, yet reaching a maximum of 15 ppm Cd near several of the known zones of mineralization – Murray Brook, 44 Mile Brook, northeast of Restigouche, and Upsalquitch. Modest enrichment in the south central part of the survey area, remote from known mineralization, is similar in magnitude to concentrations near known base metal deposits.

Seasonal Variation During Sampling

In order to test for variation in all sample media during the sampling program, five sites were selected and were sampled every five days, or more frequently following major rain events. Site one was sampled for balsam fir needles only, sites four and five for stream sediments (total and partial analyses), and sites two to five for stream waters. Site three was from a major stream (Nepisiguit River), site two from a third order stream (Eighteen Mile Brook), site four from a first order stream draining an Fe-oxide rich seep system, and site five from a second order stream (see Fig. 2 for site locations). Data for the different monitoring sites are presented in Tables 6 (waters), 7 (total stream sediments), 8 (partial stream sediments) and 9 (balsam fir needles).

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Figure Captions

Figure 1. General geology of the Bathurst Mining Camp, New Brunswick (modified from van Staal and Rogers, in prep.). Also shown is survey study area and the locations of the two main deposits in the study area, the Restigouche and Murray brook deposits.

Figure 2. Geology of the study area including locations and names of known massive sulfide deposits and other mineral occurrences.

Figure 3. Digital elevation model of the study area showing the location of the Restigouche (RG) and Murray Brook (MB) deposits.

Figure 4. Distribution of total dissolved solids (TDS) in surface waters. Numbers in parentheses are the number of samples.

Figure 5. Distribution of sulfate in surface waters. Proportional circles subdivided by percentile (given in parentheses).

Figure 6. Distribution of zinc in surface waters. Proportional circles subdivided by percentile (given in parentheses).

Figure 7. Distribution of lead in surface waters. Proportional circles subdivided by percentile (given in parentheses).

Figure 8. Distribution of copper in surface waters. Proportional circles subdivided by percentile (given in parentheses).

Figure 9. Distribution of arsenic in surface waters. Proportional circles subdivided by percentile (given in parentheses).

Figure 10. Distribution of mercury in surface waters. Proportional circles subdivided by percentile (given in parentheses).

Figure 11. Distribution of manganese in stream sediments (total dissolution). Proportional circles subdivided by percentile (given in parentheses).

Figure 12. Distribution of zinc in stream sediments (total dissolution). Proportional circles subdivided by percentile (given in parentheses).

Figure 13. Distribution of lead in stream sediments (total dissolution). Proportional circles subdivided by percentile (given in parentheses).

Figure 14. Distribution of copper in stream sediments (total dissolution). Proportional circles subdivided by percentile (given in parentheses).

Figure 15. Distribution of tin in stream sediments (total dissolution). Proportional circles subdivided by percentile (given in parentheses).

Figure 16. Distribution of bismuth in stream sediments (total dissolution). Proportional circles subdivided by percentile (given in parentheses).

Figure 17. Distribution of manganese in stream sediments (partial extraction). Proportional circles subdivided by percentile (given in parentheses).

Figure 18. Distribution of zinc in stream sediments (partial extraction). Proportional circles subdivided by percentile (given in parentheses).

Figure 19. Distribution of lead in stream sediments (partial extraction). Proportional circles subdivided by percentile (given in parentheses).

Figure 20. Distribution of copper in stream sediments (partial extraction). Proportional circles subdivided by percentile (given in parentheses).

Figure 21. Distribution of zinc in balsam fir needles. Proportional circles subdivided by percentile (given in parentheses).

Figure 22. Distribution of zinc in balsam fir needles. Contour plot.

Figure 23. Distribution of lead in balsam fir needles. Proportional circles subdivided by percentile (given in parentheses).

Figure 24. Distribution of lead in balsam fir needles. Contour plot.

Figure 25. Distribution of copper in balsam fir needles. Proportional circles subdivided by percentile (given in parentheses).

Figure 26. Distribution of copper in balsam fir needles. Contour plot.

Figure 27. Distribution of thallium in balsam fir needles. Proportional circles subdivided by

percentile (given in parentheses).

Figure 28. Distribution of thalium in balsam fir needles. Contour plot.

Figure 29. Distribution of silver in balsam fir needles. Proportional circles subdivided by percentile (given in parentheses).

Figure 30. Distribution of silver in balsam fir needles. Contour plot.

Figure 31. Distribution of cadmium in balsam fir needles. Proportional circles subdivided by percentile (given in parentheses).

Figure 32. Distribution of cadmium in balsam fir needles. Contour plot.

Tables

Table 1. Detection limits.

Table 2. ICP-ES and ICP-MS data for surface waters

Table 3. XRF, ICP-ES and ICP-MS data for stream sediments, total dissolution

Table 4. XRF, ICP-ES and ICP-MS data for stream sediments, partial extraction

Table 5. ICP-ES and ICP-MS data for balsam fir needles

Table 6. Monitoring station data, surface waters

Table 7. Monitoring station data, total sediments

Table 8. Monitoring station data, partial sediments

Table 9. Monitoring station data, balsam fir needles