

Regional distribution and mobility of copper and lead in soils near the Horne copper smelter at Rouyn-Noranda, Quebec

P.J. Henderson¹ and R.D. Knight¹

Henderson, P.J. and Knight, R.D., 2005: Regional distribution and mobility of copper and lead in soils near the Horne copper smelter at Rouyn-Noranda, Quebec; in Metals in the Environment Around Smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and Conclusions of the GSC MITE Point Sources Project, (ed.) G.F. Bonham-Carter; Geological Survey of Canada, Bulletin 584, 23 p.

Abstract: Regional sampling of the humus, B, and C horizons of glacial soils from 106 sites within a 100 km radius of the copper smelter at Rouyn-Noranda, Quebec, has provided an extensive database on soil geochemistry and other physical properties both from sites within the area of metal contamination and from sites showing little anthropogenic enrichment. Using this database, the distribution and mobility of two smelter-derived trace metals, copper and lead, was examined with respect to parent material, soil horizon, and wind patterns for the area. Copper is the primary smelter product and is concentrated in local mineralized deposits. Lead is a smelter emission with low concentrations in the local bedrock and soils. Geochemical results indicate that both emitted metals are enriched in humus in the vicinity of the smelter and decrease in concentration with distance and that a higher percentage of emitted copper is retained in humus than lead. Sequential analyses of humus show that chemical phases in which the metals are retained vary depending on the element and distance from the smelter, but both copper and lead are retained primarily in the labile phase associated with soluble organic material at sites within 10 km. Leaching from humus into lower compartments of the soil horizon depends on parent material and distance from the smelter. At sites near the smelter, evidence supports metal retention in the B horizon of soils developed on glaciolacustrine sediment and metal migration downward through the C horizon for soils on diamicton.¹

Résumé : Le prélèvement régional d'échantillons dans l'humus et dans les horizons B et C de sols glaciaires, dans 106 sites situés dans un rayon de 100 km de la fonderie de cuivre de Rouyn-Noranda (Québec), a permis de produire une vaste base de données sur la géochimie du sol et d'autres propriétés physiques de sites se trouvant dans la zone contaminée par des métaux et de sites ne présentant qu'un faible enrichissement anthropique. À l'aide de cette base de données, on a examiné la répartition et la mobilité de deux métaux à l'état de traces émis par la fonderie, soit le cuivre et le plomb, en tenant compte des matériaux d'origine, des horizons pédologiques et des vents de la région. Le cuivre, qui est le principal produit de la fonderie, est concentré dans des gisements minéralisés locaux. Le plomb est une émission de la fonderie qui est présent localement en faibles concentrations dans le socle rocheux et les sols. Les données géochimiques obtenues indiquent que ces deux métaux émis par la fonderie sont enrichis dans l'humus aux environs de la fonderie, que leurs concentrations diminuent en s'éloignant de cette dernière et qu'un plus fort pourcentage d'émissions de cuivre que de plomb est piégé dans l'humus. Des analyses séquentielles de l'humus montrent que les phases chimiques des métaux piégés varient selon l'élément et la distance par rapport à la fonderie. Toutefois, le cuivre et le plomb sont tous deux principalement piégés en phase labile, cette dernière étant associée à la matière organique soluble des sites situés à moins de 10 km. La lixiviation depuis l'humus jusque dans les parties inférieures de l'horizon pédologique est fonction des matériaux d'origine et de la distance par rapport à la fonderie. Dans les sites situés à proximité de la fonderie, des indices témoignent du piégeage des métaux dans l'horizon B des sols formés sur des sédiments glaciolacustres, ainsi que de la migration descendante des métaux à travers l'horizon C des sols reposant sur du diamicton.

¹ Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8

INTRODUCTION

Variations in trace-metal concentrations were examined in glacially derived soils collected near the Horne smelter at Rouyn-Noranda, Quebec (Fig. 1). This project is part of the GSC Metals in the Environment (MITE) initiative, a multidisciplinary program designed to examine the distribution and fate of smelter emissions in various sample media (Bonham-Carter, 2005). The soil study focused on 1) mapping the areal and vertical variations in trace-metal concentrations; 2) characterizing the form and association of metals in soils through physical methods and geochemical analyses; 3) assessing the factors and processes that control the distribution and fate of elements in the environment; and 4) developing criteria to distinguish anthropogenic from geogenic metal enrichment.

Rouyn-Noranda is located in the Abitibi Greenstone Belt, one of the richest mineralized areas of the world (Veillette et al., 2005). The Horne smelter is located on the edge of the city and is the main source of atmospheric pollution to the surrounding environment. It is a custom copper smelter, owned and operated by Noranda Inc., and has been in operation since 1927. Smelter emissions include arsenic, cadmium, copper, lead, and zinc (Noranda, Inc., pers. comm., 1997).

Metal smelters are known to be sources of metal contamination in surficial materials (e.g. Davies, 1983; Reimann et al., 1998a; McMartin et al., 1999).

Emission sources obviously include the smelter stack, as well as the less obvious fugitive sources, such as windblown dust from metal concentrate piles and tailings, which have been reported as major contributors to contamination within 5 km of smelters (Jennett et al., 1977). Metals derived from these atmospheric sources accumulate in humus, primarily through absorption on and complexation with organic matter and oxides of iron and manganese, and clay minerals (Adriano, 2001). Near smelters, concentrations of smelter-derived metals in humus decrease with increasing distance from the source (Paquet, 1987; Dumontet et al., 1992; McMartin et al., 2002). This metal loading is attributed to atmospheric fallout of metal-rich particulate; however, difficulties arise in distinguishing smelter-related metal loading from natural (geogenic) metal enrichment. This is particularly true in highly mineralized areas such as Rouyn-Noranda (Veillette et al., 2005), since soil geochemistry is a function of sediment provenance, including mineralization.

The regional distribution of smelter-derived metals in soils addresses only one aspect of smelter-related input to the environment. Knowledge of the chemical and mineralogical forms of emitted metals is equally important, since it provides information on the mobility and bioavailability of the metals. Various researchers have addressed the mobility problem, although results are contradictory (Karczewska, 1996). Depending on the research method, some authors indicate metal stability and limited mobilization in soil horizons (Dumontet et al., 1992; Wang et al., 1995), whereas others emphasize the high potential for metal mobilization into other compartments of the environment (Hazlett et al., 1984; McBride, 1989; Greinert, 1993). Differences in interpretation

are related primarily to variations in the factors influencing metal solubility and the sorption capacity of soils. These factors are related to soil characteristics (i.e. pH, organic matter, cation exchange capacity, and clay content), soil genesis (depositional and soil-forming processes), and the extent, nature, and form of emissions contributing to soil contamination (Colbourn and Thornton, 1978; Åyräs et al., 1995; Henderson et al., 1998).

This paper summarizes results from the geochemical analysis of samples collected at 106 sites within 100 km of the Horne smelter at Rouyn-Noranda and is based on data reported in Henderson et al. (2002). The soil-sampling program focused on establishing metal concentrations related to the main factors affecting soil geochemistry, including bedrock provenance, parent material, and distance from the smelter. Samples represent contaminated and 'background' sites, as well as vertical geochemical variation in soil profiles. Using copper and lead as examples, the distribution of these emitted metals is examined with the following objectives: 1) to infer the extent of anthropogenic metal loading, through relationships between concentration levels at contaminated and background sites, and 2) to assess metal mobility resulting from metal loading through sequential and selective geochemical analyses.

PROTOCOLS AND METHODS

Sampling design

The study area was centred on the Horne smelter at Rouyn-Noranda, Quebec, with sample density decreasing with distance from the smelter to an approximately 100 km radius (Fig. 1). This sampling protocol is based on results from previous studies near smelters, which showed that soil contamination occurs primarily within 30 to 40 km of the source (Paquet, 1987; McMartin et al., 1999). The 106 site locations were chosen on the basis of site-specific and regional criteria, which include 1) sample integrity — the absence of identifiable anthropogenic sources of soil contamination (other than the smelter); 2) program integration — proximity to sample sites of other sample media used in the MITE program (e.g. peat, lake-bottom sediment); 3) sample diversity — various parent material (till and glaciolacustrine sediment) overlying various bedrock terrains; 4) regional coverage — an areal distribution with site density decreasing with increasing distance from the smelter; and 5) sediment thickness — sediment accumulation more than 1 m thick with established soil profile.

Sampling procedures

At most sites, samples were collected from three soil horizons, i.e. humus (total thickness, ~0–5 cm) and the B (5–25 cm depth) and C (80–90 cm depth) soil horizons (Fig. 1; Henderson et al., 2002). Humus comprised the well decomposed, dark organic part of the uppermost soil horizon. It consisted primarily of the decay products of surface organic material (i.e. plants, leaves, roots); however, both partially decomposed forest litter and mineral soil constitute part of

the sample in areas where organic soil horizons are thin. The soils were collected from pits approximately 1 m deep and from cleaned natural exposures. At each site, 1 to 2 kg of humus and 5 to 10 kg of mineral soil samples were placed in thick polyethylene bags, which were tightly fastened. Observations were recorded on site and sample characteristics (*see* Henderson et al., 2002, Appendix A1 and A2). Humus was stored in coolers and kept refrigerated prior to analyses; all other samples were stored in pails at room temperature.

Analytical procedures

All samples (both humus and B- and C-horizon soils) were air dried and sieved to <2 mm using a stainless steel screen. The <2 mm fraction was analyzed for a broad suite of elements (Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, P, Pb, Sr, Ti, V, Zn) by inductively coupled plasma atomic emission spectrometry (ICP-AES) following partial digestion in aqua regia (HNO₃-HCl) and, for Hg, cold-vapour atomic absorption spectrometry (CV-AAS). In addition,

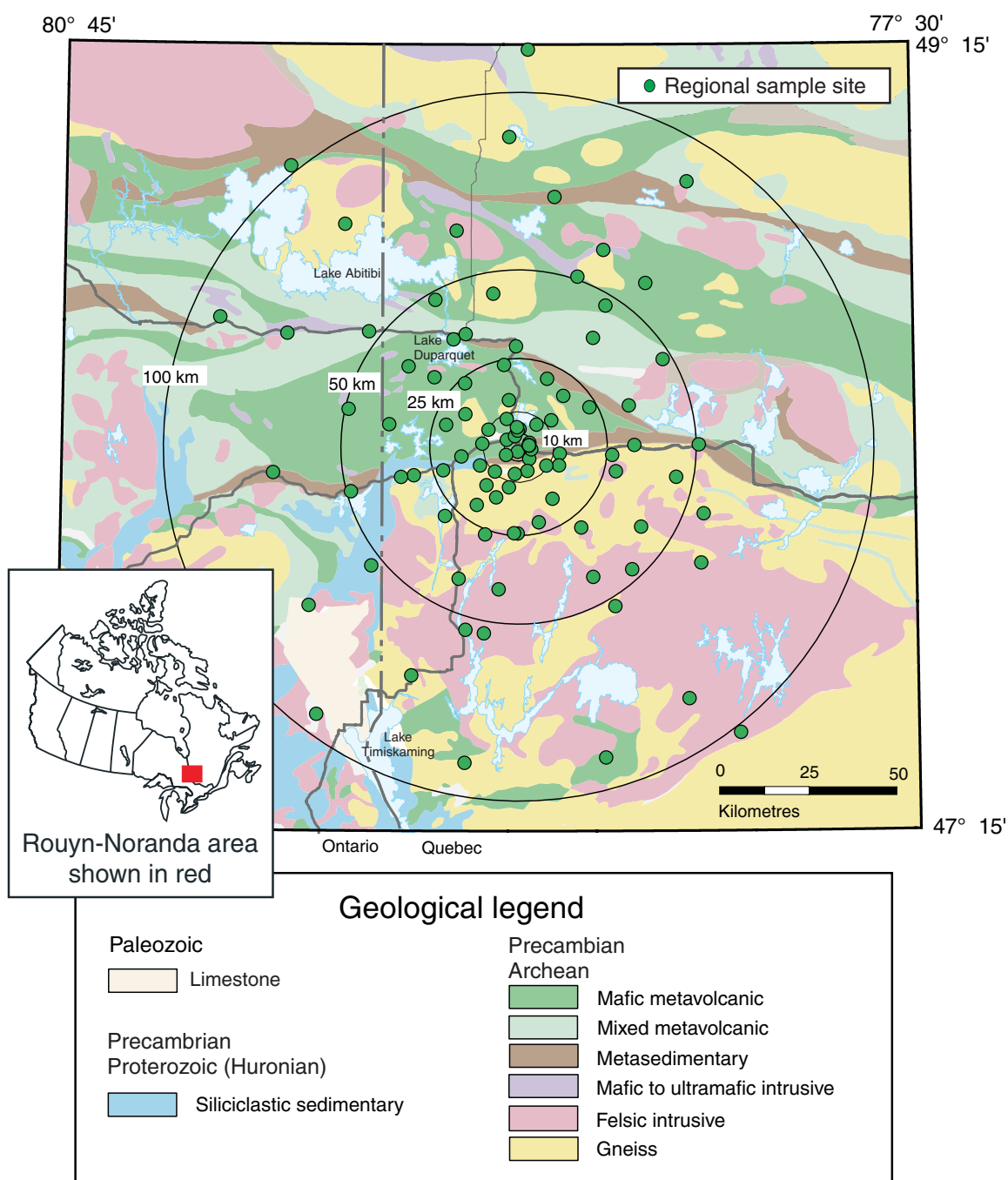


Figure 1. Sample locations, Rouyn-Noranda area (geology modified from MERQ-OGS, 1984). Circles represent approximate radii of 10, 25, 50, and 100 km from the smelter.

the organic-matter content was characterized using the loss-on-ignition (%LOI) method at 550°C (Sheldrick, 1984). Soil pH was determined using methods outlined by Sheldrick (1984) and Thomas (1996) and described in Knight et al. (2000). Grain size was determined for all mineral soil samples using a two-step process, involving a sieve stack and particle size analyzer (Lectotrac LT-100; R.A. Klassen, I. Girard, R.R. LaFramboise, and P.J. Lindsay, unpub. rept., 2000).

Humus samples were also analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using a sequential leach method modified from Hall et al. (1996; Table 1). The leaches are operationally defined to extract labile soluble organic phases using sodium pyrophosphate and non-labile phases using hydroxylamine hydrochloride to digest crystalline iron oxides, potassium chloride to digest sulphides and 'less soluble' organic phases, and a multi-acid leach to digest residual mineral phases.

The <2 mm fraction of B- and C-horizon soils was also analyzed using two selective extraction methods (non-sequential; Hall et al., 1996), one defined to extract amorphous iron and manganese oxides and hydroxides (labile phases) after digestion by hydroxylamine hydrochloride (0.25M in 0.25M HCl) at 60°C for 2 hours, and the other defined to extract all phases including most silicates and resistant minerals after multi-acid digestion (HF-HClO₄-HNO₃). Extracted solutions were analyzed by ICP-MS.

The accuracy and precision of geochemical data were monitored using control samples, both duplicates and reference standards, and are presented in detail in Henderson et al. (2002). The precision (as measured by the relative standard deviation) for ICP-AES (aqua regia) analyses is <5% for both Cu and Pb. For the sequential analyses of humus, the precision for Cu is <15% and for Pb, <10%, for each of the first three leaches. The precision for geochemical analyses of mineral soils using the hot hydroxylamine digestion is <10% for both Cu and Pb, and using the multi-acid digestion, <10% for Cu and ~20% for Pb, as concentrations are at or near the lower detection limits.

SOIL CHARACTERISTICS

Soil parent materials in the Rouyn-Noranda area include glacial sediment (till) deposited during the latest continental glaciation (Wisconsin) and postglacial glaciolacustrine sediment (Veillette, 1989; Veillette et al., 2005). Till is characteristically a grey to grey-brown sandy diamicton (averaging 57% sand, 40% silt, 3% clay), commonly stony and generally loosely compacted. Where it has been reworked by glaciolacustrine processes, it can appear as poorly sorted gravel, lacking the finer grain sizes. Glaciolacustrine sediment consists of grey, fine-grained, clayey silt (averaging 10% sand, 68% silt, 22% clay). It varies from massive to varved and may contain local pebbles, cobbles, or sandy lenses. The deposits formed offshore of postglacial Lake Barlow-Ojibway, from fine-grained material derived directly from the glacier.

Since drainage of the postglacial lake at approximately 8000 BP (Vincent and Hardy, 1979; Veillette, 1996), the soils have been subjected to weathering. Soil profiles that developed on the parent materials in the area include the following: 1) Humo-Ferric Podzol (Fig. 2a), developed primarily on till and reworked till. These soils have a brownish, well developed B horizon in which the dominant accumulation product is amorphous material composed mainly of humified organic matter combined in varying degrees with Al and Fe. Typically, podzolic soils occur in coarse- to medium-textured, acid parent materials, under coniferous, mixed, and deciduous forest vegetation (Agriculture Canada Expert Committee on Soil Survey, 1987). Under similar conditions, more immature brunisols may develop in the area; however, field characteristics are similar and brunisolic soils can only be differentiated from podzolic soils through chemical analysis; 2) Grey Luvisol (Fig. 2b), developed primarily on glaciolacustrine silty deposits. These soils characteristically occur in well to imperfectly drained sites in sandy loam to clay, base-saturated parent materials, under forest vegetation (Agriculture Canada Expert Committee on Soil Survey, 1987).

Table 1. Sequential extraction scheme (*modified from Hall et al., 1996*).

	Extractant	phase dissolved
1	0.1M Na ₄ P ₂ O ₇ (sodium pyrophosphate) 1g sample/100 ml 1 hour (h) extraction	'soluble organic' component metals adsorbed, complexed, or chelated by organics (humics and fulvics)
2	1M NH ₂ OH.HCl (hydroxylamine hydrochloride) in 25% acetic acid 30 ml at 90°C 3 h extraction	Crystalline iron oxides (eg. hematite, goethite, magnetite)
3	KClO ₃ /HCl 15 ml for 0.5 h with mixing; followed by 4M HNO ₃ (10 mL) at 90°C	Sulphides and 'less soluble' organic matter
4	HF-HClO ₄ -HNO ₃ -HCl 10 mL, to dryness	Silicates, residual crystalline fraction

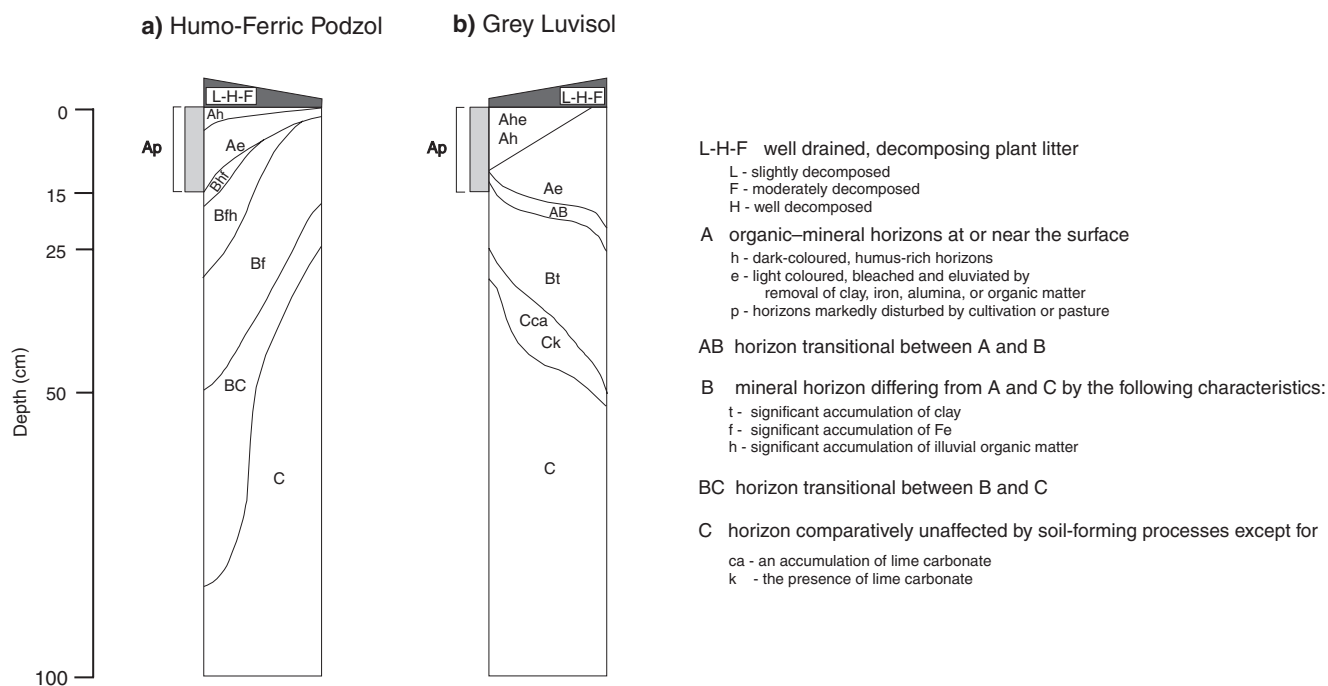


Figure 2. Characteristics of soil profiles developed in the Rouyn-Noranda area. a) Humo-Ferric Podzol; b) Grey Luvisol (modified from Agriculture Canada Expert Committee on Soil Survey, 1987).

METAL DISTRIBUTION IN SOILS

Henderson et al. (2002) provide the complete database for the soil component of the MITE program in the Rouyn-Noranda area. The report presents site and sample descriptions as well as results of all geochemical analyses, including quality assurance and control, in Microsoft® Excel format. Geochemical maps and statistics are presented for Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, P, Pb, Sr, Ti, V, Zn. Geochemical data for humus, B-horizon, and C-horizon soils are provided in the GIS Mite database (<2 mm fraction; ICP-AES, following aqua regia digestion).

In this paper, only results for Cu and Pb will be discussed. Both elements are emitted from the smelter. Copper occurs in massive sulphide deposits of the Rouyn-Noranda area (Sangster, 1972; Veillette et al., 2005) and is the main smelter product. Approximately 70 tonnes of copper were emitted from the stack as particulate matter in 1998 (Noranda, Inc., pers. comm., 2000). Over 150 tonnes of particulate lead were emitted from the smelter stack that same year. Although lead can be associated with massive-sulphide deposits, it is not present in high concentrations in either the rocks or unweathered glacial soils of the Rouyn-Noranda area (Henderson et al., 2002).

Copper and lead distribution

Geochemical maps for Cu and Pb are shown as dot maps and interpolated surfaces for humus, B-, and C-horizon soils (Fig. 3, 4). Dot maps are created using MAPINFO™ Professional, with dot symbols centred over sample locations. Symbol shapes reflect the underlying parent materials, which are characterized, for this study, by the C soil horizon and are

either diamicton (till and other sandy sediment) or clay (glaciolacustrine silty sediment). The symbols are colour-coded to correspond with the 100th, 95th, 90th, 75th, and 50th percentile intervals, based on the total population. For humus only, the background value (Table 2) is used in place of the 50th percentile. Geochemical data are rendered as a contoured surface using the natural-neighbour interpolation in Vertical Mapper™ within the MapInfo® platform. This method is appropriate for data that are both sparsely distributed and clustered. For interpolated maps, coloured intervals correspond to the same percentile breaks as are used on dot maps.

Humus

In humus, the bulk of Cu and Pb is retained within 20 km of the smelter for both elements, with the pattern forming a bull's-eye skewed in the direction of the dominant winds, as indicated by a wind rose (Fig. 3, 4, 5). The average wind direction is to the east-northeast, with strong components, in terms of both frequency and velocity, to the north, northeast, east, southeast, and south (Fig. 5).

Maximum concentrations of both elements are anomalously high near the smelter and decrease with distance, regardless of parent material. On the basis of background values determined from the median concentration of humus samples more than 40 km from the smelter (Table 2), humus is enriched up to 180 times background for Cu and 96 times for Pb. Concentrations above background value are present at sites beyond 50 km, predominantly in the downwind areas east, north and south of the smelter site.

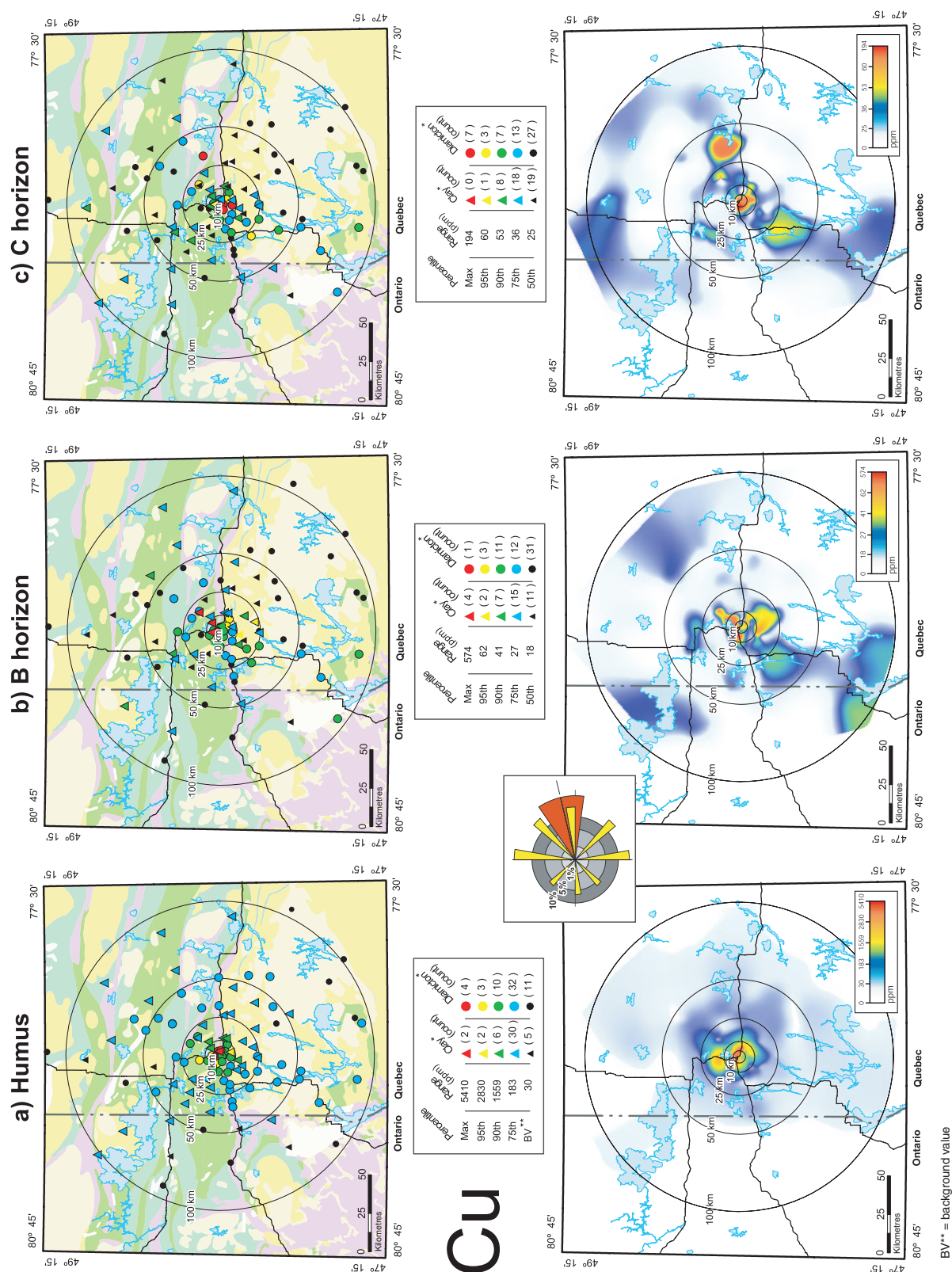
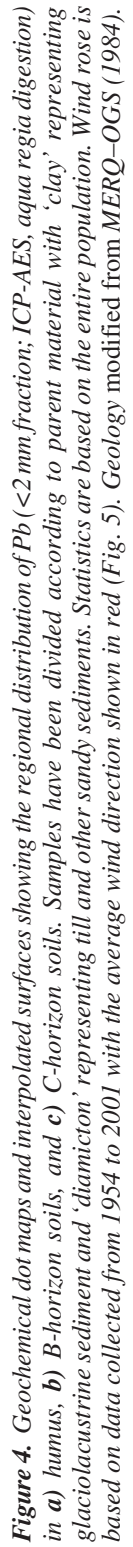


Figure 3. Geochemical dot maps and interpolated surfaces showing the regional distribution of Cu (<2 mm fraction; ICP-AES, aqua regia digestion) in **a**) humus, **b**) B-horizon soils, and **c**) C-horizon soils. Samples have been divided according to parent material with 'clay' representing glaciolacustrine sediment and 'diamicton' representing till and other sandy sediments. Statistics are based on the entire population. Wind rose is based on data collected from 1954 to 2001 with the average wind direction shown in red (Fig. 5). Geology modified from MERQ-OGS (1984).



B-horizon soils

Maximum Cu and Pb concentrations in B-horizon soils are lower than in humus (Fig. 3b, 4b). Copper concentrations exceeding the 90th percentile value are concentrated at sites within 25 km of the smelter (Fig. 3b), particularly in areas northeast and southeast of Rouyn-Noranda. Lead concentrations exceeding the 90th percentile value are present throughout the area and are largely associated with glaciolacustrine parent material (Fig. 4b). Within the 25 km radius, Pb enrichment occurs in two zones, one extending northeast and the

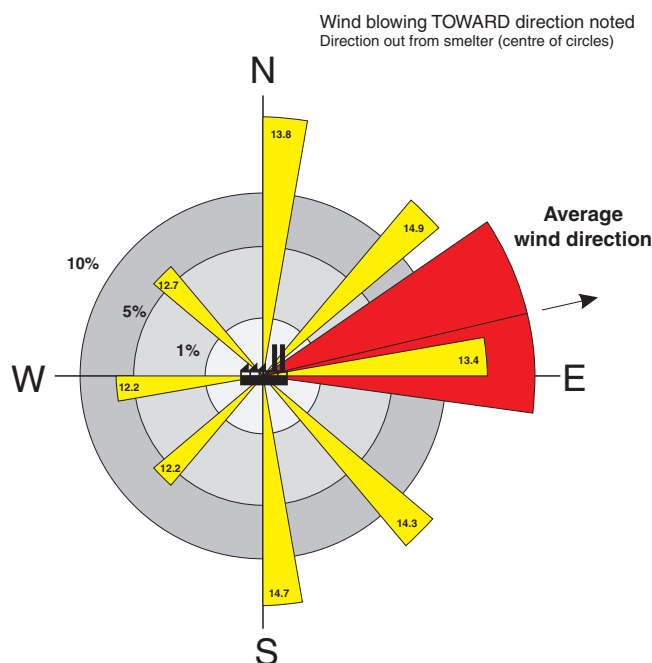


Figure 5. Wind rose for the Rouyn-Noranda area based on historical data collected by Environment Canada from the Rouyn airport (1954–2001). Sector length for eight principal wind directions is proportional to the per cent time the direction is downwind from the smelter (Baas, 2000). Average wind direction is shown in red.

Table 2. Background concentrations of Cu and Pb in humus. Estimates used for geochemical maps are based on the median concentration in humus at sites more than 40 km from the smelter. Values are also shown for median concentrations in humus for sites more than 10, 20, 30, 40, and 50 km from the smelter and for calculated values using a three-parameter, non-linear, radial decay model (Bonham-Carter and McMartin, 1997).

Distance	Cu (ppm)	Pb (ppm)
> 10 km	43	100
> 20 km	39	90
> 30 km	36	68
> 40 km	30	56
> 50 km	30	52
Calculated background	26.1	52.5

other, southeast from Rouyn-Noranda. This distribution does not appear to be smelter related, since Pb concentrations within 10 km are generally low, with values exceeding the 90th percentile occurring at only three sites. Three other sites with Pb enrichment occur beyond the 25 km radius in the northeast, south, and southwest near Lake Duparquet, a former mining and smelting area (Sangster, 1972).

C-horizon soils

The concentration range for Cu and Pb in C-horizon soils is less than in humus and B-horizon soils (Fig. 3c, 4c). Maximum Cu values occur at sites within 10 km of the smelter and are associated with diamicton parent material (Fig. 3c). Enriched Cu values (>90th percentile value) are also present within the 50 km radius in areas south-southwest, east-northeast, and northwest of Rouyn-Noranda at Lake Duparquet. With two exceptions, Pb concentrations exceeding the 95th percentile value occur at sites >25 km from the smelter (Fig. 4c) in areas north, northwest, and south-southwest of Rouyn-Noranda. High (>13 ppm) Pb values are associated primarily with glaciolacustrine parent material.

Discussion and interpretation of copper and lead distribution in soils

Two major factors influence Cu and Pb distribution in humus — distance from the smelter and wind patterns (Fig. 3, 4). For B- and C-horizon soils, the primary factor appears to be parent material. The two parent materials in the Rouyn-Noranda area (diamicton, predominantly till or reworked till, and glaciolacustrine sediment) are fundamentally different in composition and texture because of differences in sedimentation. The composition of unweathered till (diamicton parent material) is related to the mechanical process of glacial erosion, transport, and deposition and, consequently, is dependent on up-ice geology (commonly within several kilometres) and the degree of sediment reworking by wave action associated with the postglacial lake. A real variation in till geochemistry is related primarily to bedrock geology, including mineralization (i.e. Cu-Zn deposits near Rouyn-Noranda (Veillette et al., 2005)). Consequently, diamicton parent material is both compositionally and texturally heterogeneous within the area. In contrast, glaciolacustrine sediments are likely to be compositionally and texturally homogeneous, and regional variations in the composition of C-horizon soils are less than in till. As with till, the composition reflects regional bedrock geology; however, the textural sorting and depositional environment associated with glaciolacustrine sedimentation results in compositional averaging over a broad region.

Geochemical data (<2 mm fraction; aqua regia digestion) for Cu and Pb in the three soil horizons are discussed in terms of three dominant factors that influence their distributions, i.e. distance from the smelter, wind direction, and parent material (Fig. 6, 7). Sites have been separated into those downwind and those upwind from the smelter. Downwind

Table 3. Correlation matrix for Cu and Pb concentrations in humus, distance from the smelter, humus thickness, humus pH, and %LOI. Correlation coefficients >0.5 are shown in bold.

	Distance to smelter	Cu (ppm)	Pb (ppm)	%LOI	Humus pH
Distance (km)	1.00				
Cu (ppm)	-0.49	1.00			
Pb (ppm)	-0.52	0.89	1.00		
% LOI	-0.14	0.24	0.34	1.00	
Humus pH	-0.05	0.03	0.05	-0.17	1.00
n = 105					

sites are those lying in the eastern half of the study area, with respect to the smelter; upwind sites lie in the western half of the area (Fig. 5).

Humus

The distribution of Cu and Pb in humus is interpreted as directly related to atmospheric deposition of metal-rich smelter particulate on the basis of the following observations:

1. A regional dispersal pattern indicating decreased concentrations with distance from the source, which is skewed in the dominant wind directions (Fig. 6, 7). For both elements, regardless of parent material, the relationship is described by the power equation $y = ax^{-b}$, where y is the metal concentration, x is the distance from the smelter, and a and b are variables of the specific trendline. Metal values in the downwind direction are higher farther from the smelter than those in the upwind direction at comparable distances.
2. The distribution patterns of Cu and Pb are unrelated to soil variables, such as parent material, organic matter content (%LOI), or soil pH (Table 3). The strongest correlation is between Cu and Pb (0.89) and inversely between Cu, Pb, and distance from the smelter (-0.49 and -0.52, respectively). These correlations indicate strongly that smelter emissions are the main factor controlling the metal distribution in humus.
3. Both elements are known to occur as particulate smelter emissions (Noranda, Inc., pers. comm., 1997; see Table 1; Henderson et al., 2002; Bonham-Carter, 2005).
4. Smelter particles derived from dust emissions are present within the humus; their number and size decrease with distance from the smelter (Knight and Henderson, 2005).

B- and C-horizon soils

In areas affected by smelter fallout, B-horizon concentrations reflect the combined influence of geogenic and anthropogenic factors, and C-horizon concentrations, primarily geogenic factors (Reimann et al., 1998a). The geogenic component refers to the mineralogy of the soil. During postglacial weathering, minerals in soils are subjected to natural pedogenic processes that break down less stable minerals, resulting in the liberation of the elements and a vertical differentiation of metals with depth. In podzols (Fig. 2a), metals released by weathering can remain in solution to be

taken up by plants or leached into the groundwater, and/or be retained in the B horizon, adsorbed, precipitated, or sequestered in compounds that have a high sorption capacity, such as clay-sized phyllosilicates, organic matter, or secondary oxides and/or hydroxides (Räisänen et al., 1997; McMartin et al., 2002). In less mature podzols and brunisols, B horizons may show stable or depleted metal concentrations.

Smelter emissions deposited on the soil surface through direct deposition or incorporated into the soil through biogeochemical cycling are also subject to pedogenesis. Previous studies in areas affected by smelter emissions report downward leaching of metals to 10 to 15 cm depth in contaminated soils (e.g. Dumontet et al., 1992; Henderson et al., 1998), depending on the quality and thickness of the surface organic horizons, solubility of the metal constituents, and the degree of anthropogenic metal loading. Therefore, the response to smelter-related metal loading, if present, will be observed in the geochemical make-up of B-horizon soils. Metal concentrations in the essentially unweathered C-horizon soils represent the geological background at a site, provided there are no facies changes within the soil profile. For soils developed on till, C-horizon elemental concentrations commonly range widely because of compositional variations related to bedrock geology. The composition of glaciolacustrine sediment has less regional variation and the range is commonly more limited than for diamicton parent materials.

Diamicton parent material

Copper concentrations in both B- and C-horizon soils developed on diamicton vary and decrease with increasing distance from the smelter. The trendline for B-horizon soils downwind from the smelter shows the best fit to the data ($R^2 = 0.61$) (Fig. 6). The geogenic background, as defined by C-horizon values, ranges from 3 to 194 ppm, with average concentrations higher in the western half of the project area. Copper concentrations in B-horizon soils average 24 ppm and are generally lower than in the C horizon. The high geogenic background in the Rouyn-Noranda area, as expressed by C-horizon soil concentrations, is most likely a function of mineralization (Veillette et al., 2005).

No trend is evident in the distribution of Pb in B- and C-horizon soils with respect to distance from the smelter. Concentrations in samples from both horizons are low (<20 ppm) with a high proportion below the detection limit (2 ppm) for the analytical method. There is no to very little enrichment in either soil horizon at sites near the smelter,

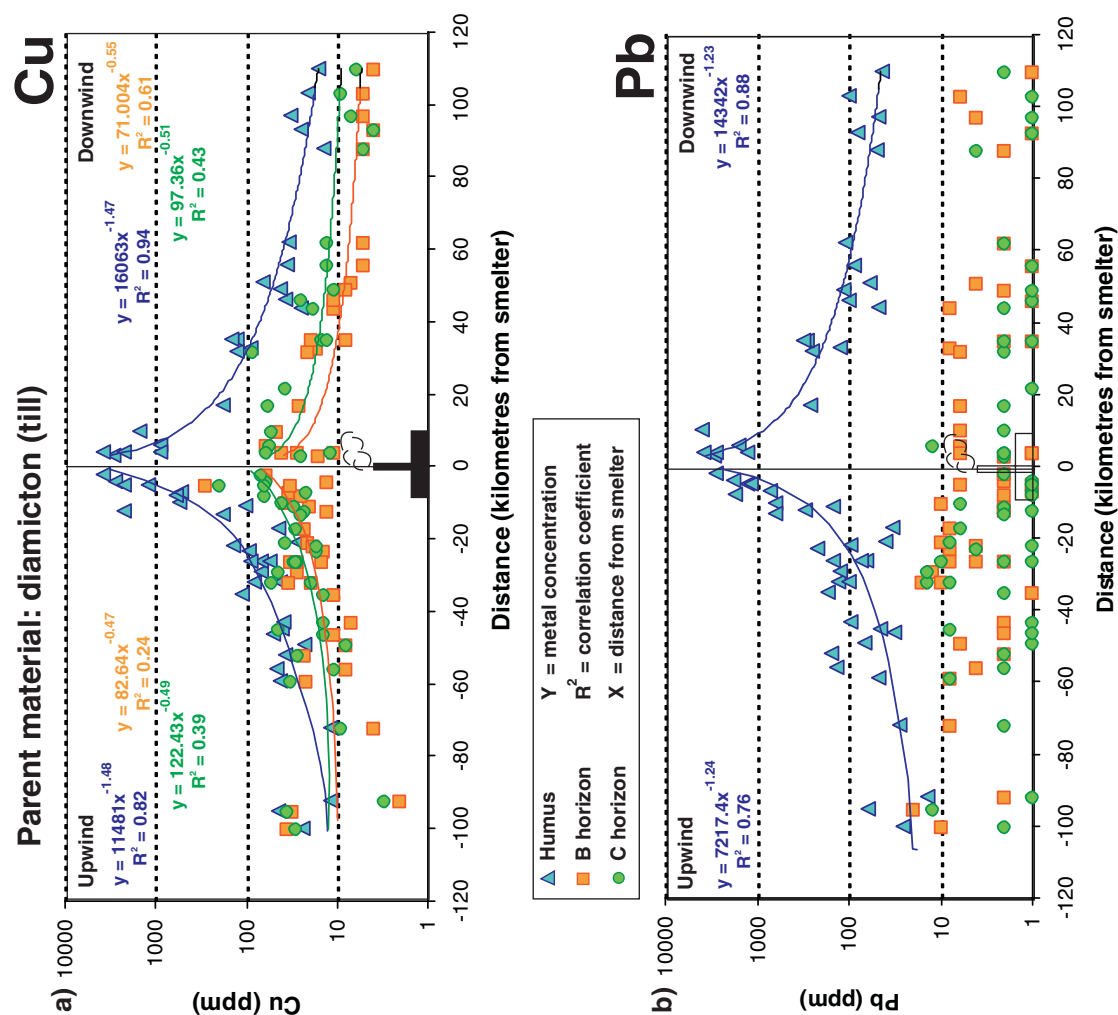
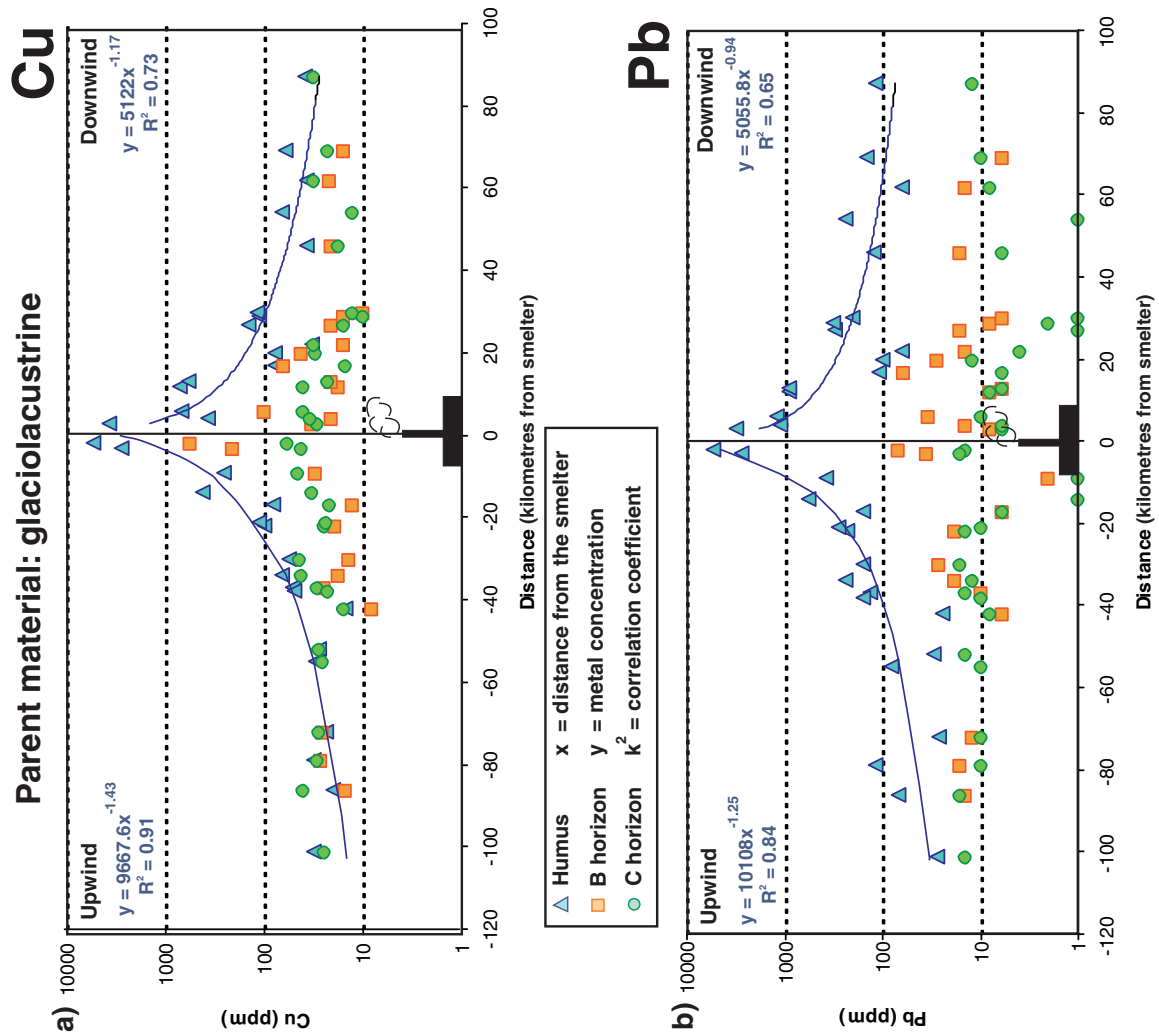


Figure 6. Descriptive statistics and distance vs. concentration plots (<2 mm fraction; ICP-AES, aqua regia digestion) for humus, B₁, and C-horizon soils developed on diamicton as parent material. Sites are subdivided into downwind (east half of area) and upwind (west half) directions. **a)** copper (Cu); trendlines are given for humus, B₁, and C-horizon data and colour-coded to point data; **b)** lead (Pb); trendlines are given for humus data.

10



Descriptive statistics for Cu in glaciolacustrine sediment

	Humus	B horizon	C horizon
Mean	484.35	53.65	28.82
Standard error	199.56	22.25	1.86
Median	72	21	28.5
Mode	38	21	29
Standard deviation	1163.65	113.44	10.86
Sample variance	1 354 076.42	12 869.60	118.03
Kurtosis	11.10	19.30	0.19
Skewness	3.34	4.26	0.47
Range	5395	566	48
Minimum	15	8	10
Maximum	5410	574	58
Sum	16 468	1395	980
Count	34	26	34
Confidence level (95.0%)	406.02	45.82	3.79

Descriptive statistics for Pb in glaciolacustrine sediment

	Humus	B horizon	C horizon
Mean	582.62	18.23	8.68
Standard error	188.48	3.24	0.82
Median	160	14	10
Mode	160	6	10
Standard deviation	1099.04	16.53	4.78
Sample variance	1 207 890.67	273.38	22.83
Kurtosis	11.36	4.26	-0.98
Skewness	3.24	2.07	-0.21
Range	5346	68	15
Minimum	24	2	1
Maximum	5370	70	16
Sum	19 809	474	295
Count	34	26	34
Confidence level (95.0%)	383.47	6.68	1.67

Figure 7. Descriptive statistics and distance vs. concentration plots (<2 mm fraction; ICP-AES, aqua regia digestion) for humus, B-, and C-horizon soils developed on glaciolacustrine sediment as parent material. Sites are subdivided into downwind (east half of area) and upwind (west half) directions. a) copper (Cu); trendlines are given for humus data only; b) lead (Pb); trendlines are given for humus data only.

Table 4. Correlation matrix for B- and C-horizon soil Cu and Pb concentrations, pH, %LOI, and distance from the smelter for soils developed on a) diamicton and b) glaciolacustrine sediment as parent material. Correlation coefficients >0.5 are shown in bold.

a) Diamicton parent material													
	Distance to smelter	Cu (humus)	Pb (humus)	%LOI (humus)	pH (humus)	Cu (B horizon)	Pb (B horizon)	%LOI (B horizon)	pH (B horizon)	Cu (C horizon)	Pb (C horizon)	%LOI (C horizon)	pH (C horizon)
Distance to smelter		1.00											
Cu (humus)	-0.53	1.00											
Pb (humus)	-0.53	0.80	1.00										
%LOI (humus)	0.01	0.20	0.35	1.00									
pH (humus)	-0.05	-0.03	0.03	-0.39	1.00								
Cu (B horizon)	-0.48	0.37	0.49	-0.05	0.09	1.00							
Pb (B horizon)	0.22	-0.20	-0.19	-0.35	0.09	0.22	1.00						
%LOI (B horizon)	0.38	-0.06	0.05	-0.09	0.03	0.18	0.51	1.00					
pH (B horizon)	0.11	-0.35	-0.29	-0.15	0.27	-0.17	0.05	-0.34	1.00				
Cu (C horizon)	-0.56	0.36	0.43	0.01	0.13	0.72	0.15	-0.04	0.03	1.00			
Pb (C horizon)	0.06	-0.20	-0.20	-0.31	0.05	0.26	0.79	0.11	0.07	0.19	1.00		
%LOI (C horizon)	0.35	-0.09	-0.07	-0.26	0.06	0.29	0.66	0.73	-0.14	0.11	0.38	1.00	
pH (C horizon)	0.06	-0.19	-0.11	0.06	0.25	-0.22	-0.30	-0.28	0.65	-0.03	-0.30	-0.34	1.00

= 42

n = 42

b) Glaciolacustrine sediment parent material													
	Distance to smelter	Cu (humus)	Pb (humus)	%LOI (humus)	pH (humus)	Cu (B horizon)	Pb (B horizon)	%LOI (B horizon)	pH (B horizon)	Cu (C horizon)	Pb (C horizon)	%LOI (C horizon)	pH (C horizon)
Distance to smelter	1.00												
Cu (humus)	-0.47	1.00											
Pb (humus)	-0.52	0.99	1.00										
%LOI (humus)	-0.13	0.34	0.39	1.00									
pH (humus)	0.10	0.09	0.06	0.02	1.00								
Cu (B horizon)	-0.35	0.84	0.87	0.21	0.05	1.00							
Pb (B horizon)	-0.34	0.53	0.56	-0.13	0.14	0.76	1.00						
%LOI (B horizon)	0.33	-0.10	-0.11	0.10	-0.26	-0.06	-0.05	1.00					
pH (B horizon)	0.37	-0.07	-0.10	0.05	0.22	-0.09	-0.05	0.07	1.00				
Cu (C horizon)	-0.22	0.51	0.55	0.34	0.45	0.58	0.41	-0.09	-0.02	1.00			
Pb (C horizon)	0.14	0.23	0.23	0.15	0.47	0.33	0.39	0.29	-0.11	0.58	1.00		
%LOI (C horizon)	0.06	0.18	0.15	0.10	0.40	0.23	0.37	0.29	-0.23	0.52	0.85	1.00	
pH (C horizon)	0.36	0.08	0.08	0.21	0.11	0.07	-0.11	0.42	0.54	0.28	0.08	-0.02	1.00

= 26

n = 26

which is a reflection of low Pb concentrations in bedrock (Sangster, 1972). The highest values in C-horizon soils occur at sites near and in the western half of the project area.

Other factors that may control B- and C-horizon metal concentrations are indicated by the correlation matrix relating distance from the smelter, Cu and Pb concentrations, %LOI, and pH in humus, B-, and C-horizon soils for sites with diamicton as parent material (Table 4a). A relationship appears to exist between Cu in B and especially C soil horizons and distance from the smelter, and between Cu concentrations in humus and those in both B and C horizons. These relationships are also evident in Figure 6 and may result from Cu leaching downward from contaminated humus and/or geogenic enrichment in the C horizon. No relationship was found between Pb concentrations in B and C horizons and smelter distance (Table 4a), and metal concentrations in humus do not affect Pb concentrations in the B horizon. Both Cu and Pb concentrations in B-horizon soils show a strong correlation with corresponding values in C-horizon soils, as might be expected from weathering of the parent material. Lead concentrations in B-horizon soils correlate positively with the organic matter content (%LOI) and lead is known to form stable metal-organic bonds in soils (Adriano, 2001).

Glaciolacustrine sediment as parent material

Copper concentrations in C-horizon soils developed on glaciolacustrine sediment (Fig. 7) lack the broad fluctuation in geogenic background associated with soils developed on diamicton. Values range from 10 to 58 ppm and average 29 ppm. B-horizon samples have a much greater range (8–574 ppm) because of elevated Cu concentrations at some sites within 25 km of the smelter, primarily in the downwind direction.

Lead concentrations in C-horizon soils developed on glaciolacustrine sediment are low, averaging 9 ppm, and vary within a range up to 15 ppm over detection limit (2 ppm — concentrations at detection limit are plotted as 1 ppm; Fig. 7). Concentrations in B-horizon

soils are generally higher (averaging 18 ppm) than in C-horizon soils, likely due to the higher organic matter content (%LOI) and the strong relationship between Pb and organic matter content (McMartin et al., 2002). As with Cu, B-horizon Pb concentrations at some sites within 25 km from the smelter are elevated compared to values from sites more than 40 km away.

In glaciolacustrine parent material (Table 4b), Cu and Pb are interrelated in all soil horizons. The strongest correlations are between Cu and Pb in a particular soil horizon (i.e. Cu in the B horizon with Pb in the B horizon) and between soil horizons (i.e. Cu in the B horizon with Cu in the C horizon). Concentrations of both metals in B-horizon soils correlate positively with Cu and Pb values in humus; Cu concentrations in C-horizon soils also correlate positively with Cu and Pb concentrations in humus. The only relationship between metal concentrations and organic matter content (%LOI) is evident in the C horizon, where both metal concentrations and organic matter content are lowest. From these data, it appears that metal concentrations in humus are the main factors influencing B-horizon Cu and Pb concentrations in soils developed on glaciolacustrine parent material, which suggests metal leaching downward from humus with high metal loads.

B:C-horizon metal ratios

Assuming that smelter-related metal loading is ubiquitous in areas within at least 30 km of the smelter, several questions arise based on regional distribution patterns:

1. Why is B-horizon Cu and Pb enrichment not evident at all sites or at sites developed on diamicton?
2. How can the smelter-related metal load be differentiated from geogenic metal enrichment in the B horizon of the soil profile?

B-horizon metal loading related to a smelter source can be inferred by using ratios comparing metal concentrations in B and C horizons with respect to distance from the source (Colbourn and Thornton, 1978; McMartin et al., 2002). Ratios established at background sites (more than 45 km from the smelter) would essentially determine the natural value for the weathering profile in the area, particularly in glaciolacustrine sediment, since the composition and texture are fairly homogeneous within the region. An increase in B-horizon enrichment over the background ratio at sites near the smelter indicates probable anthropogenic metal loading. In diamicton, regional variations in mineralogy and texture affect the weathering profile in more complex ways and weathering processes vary depending on site-specific factors. Nevertheless, the B:C-horizon ratio should minimize the effects of geogenic metal loading, since C-horizon concentrations essentially establish the geogenic signal at a site and emphasize anthropogenic or other B-horizon metal enrichment.

For soils developed on diamicton parent material, the B:C-horizon concentration ratio for Cu data varies widely, ranging from approximately 0.2 to 1.5 (Fig. 8a). The ratio is generally <1, with an average ratio of 0.75 for sites more than 45 km from the smelter. Although sites with B-horizon

enrichment are mainly within 45 km of the smelter, no definitive pattern is evident. Sites at any distance may or may not show B-horizon enrichment (B:C-horizon ratio >0.75). Results are similar for Pb data. B:C-horizon Pb ratios also range widely, varying from 0.5 to 6, and show no pattern of B-horizon enrichment with distance from the smelter (Fig. 8b). Because B-horizon Pb enrichment may be associated with organic matter content (%LOI (B horizon): range 1.2–24%, average 6.8%) (Table 4), B-horizon Pb content was normalized to %LOI and the resulting ratio plotted (Fig. 8c). Again, no regular pattern of B-horizon enrichment was evident with respect to distance from the smelter, on the basis of an average ratio of 0.45 for sites more than 45 km from the smelter, although the higher ratios (>0.45) are commonly within 60 km from the smelter. From these results, it is unjustifiable to attribute B-horizon Cu or Pb enrichment in diamicton soils near the smelter to the smelter, given the range and variation in ratio values within the area.

For soils developed on glaciolacustrine sediment as parent material, the average B:C-horizon concentration ratio for Cu data from sites more than 45 km from the smelter is 0.8 (Fig. 9a). All sites with B-horizon enrichment (B:C ratio >0.8) are located within 45 km of the smelter in the downwind direction, although many sites within the same area show no B-horizon enrichment. For Pb, the average background B:C-horizon concentration ratio is 1.5 (Fig. 9b). Ratios exceeding this value occur at sites near the smelter and within 60 km downwind from the smelter. When B-horizon Pb concentrations are normalized to %LOI, Pb ratios >0.1 (estimated background ratio) are obtained at sites near the smelter and within approximately 40 km from the smelter in the downwind direction (Fig. 9c). These results suggest that B-horizon metal enrichment is smelter related, although the validity of using B:C-horizon Pb concentration ratios is questionable since metal values for both horizons are commonly low and at, or near, detection limit at many sites.

B-horizon Cu and Pb enrichment at sites near the smelter suggests metal retention in the B horizon of glaciolacustrine sediment that is likely related to metal loading from the smelter. Approximately 60% of all sites within 10 km of the smelter and within 50 km in the downwind direction have B:C-horizon concentration ratios greater than those of background sites, and ratios tend to decrease with distance from the smelter (Fig. 9). It remains unclear as to why B-horizon metal enrichment is not present at all sites with contaminated humus. Correlations between humus variables and B:C-horizon concentration ratios for Cu and Pb suggest that B-horizon Cu enrichment is directly related to metal (Cu, Pb) concentrations in humus and, possibly, inversely related to humus thickness (Table 5). For Pb, only humus pH appears to inversely influence Pb ratios. This relationship suggests that acidity in humus may increase metal mobility and result in downward leaching of the metal into the B-horizon soil.

Reimann et al. (1998a) propose that B-horizon soils in the Kola Peninsula form a natural trap for heavy metals moving down the soil profile in cases where the overlying humus layer (the initial trap) is poorly developed. In the Rouyn-Noranda area, parent material, not humus thickness, appears to be the main factor controlling smelter-related metal retention in B-horizon

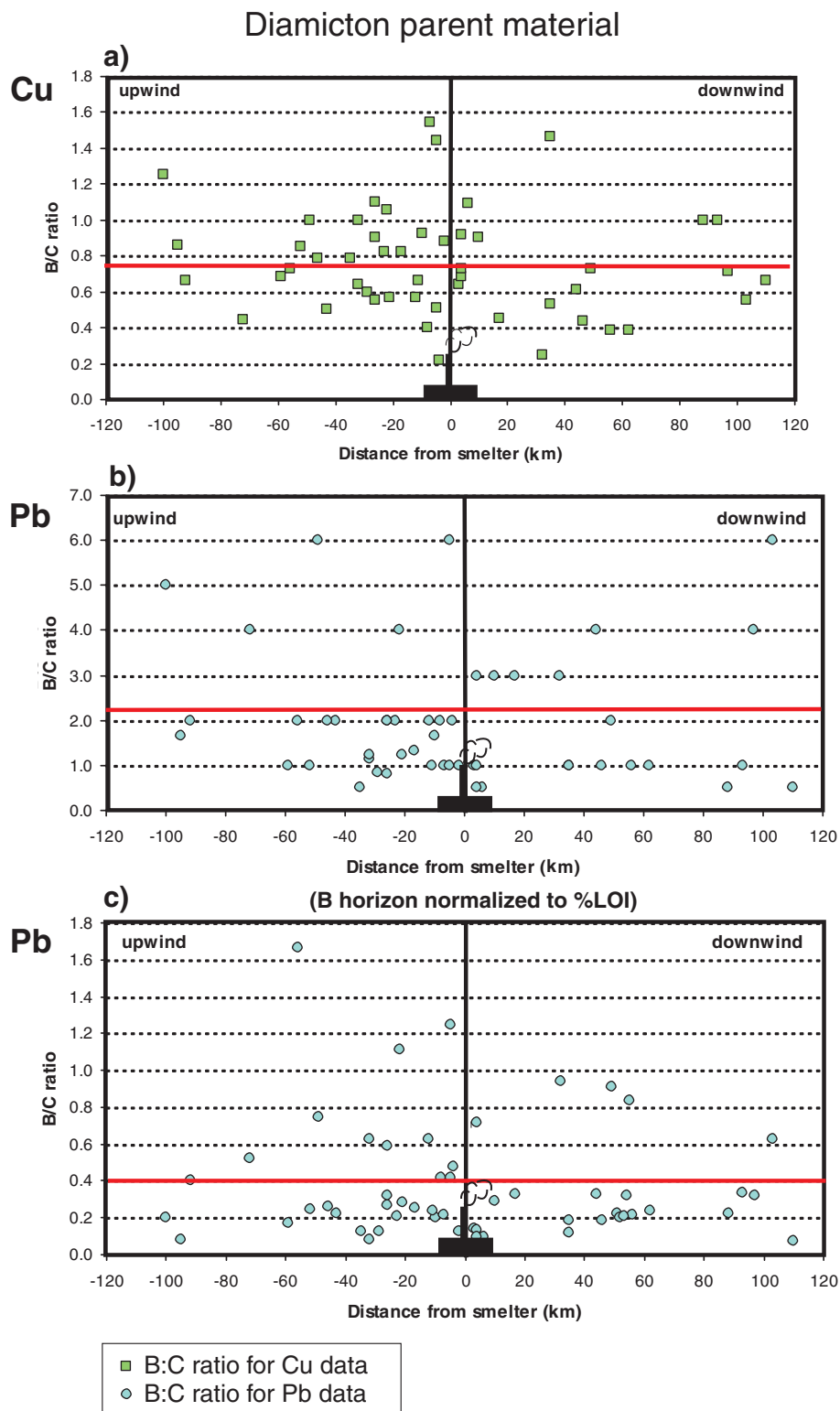


Figure 8. Ratio of B- and C-horizon metal concentrations (<2 mm fraction; ICP-AES, aqua regia digestion) vs. distance from the smelter for soils developed on diamicton as parent material. For all graphs, the red line represents the average ratio for sites more than 45 km from the smelter. **a)** copper; **b)** lead; **c)** lead: B-horizon values normalized to %LOI.

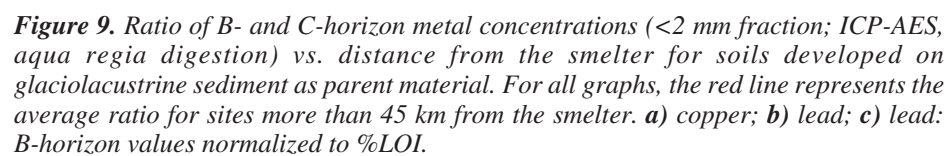


Table 5. Correlation matrix for Cu and Pb B:C-horizon ratios, Cu and Pb concentrations in humus, humus pH, humus thickness, and %LOI for humus for soils developed on glaciolacustrine sediment as parent material. For metal ratios, correlation coefficients >0.5 are shown in bold and those >0.3 and <0.5 are in italics.

	Humus Cu (ppm)	Humus Pb (ppm)	Humus LOI (%)	Humus pH	Humus thickness (cm)	B-horizon LOI (%)	B-horizon pH	B:C (Cu)	B:C (Pb)
Humus Cu (ppm)	1.00								
Humus Pb (ppm)	0.99	1.00							
Humus LOI (%)	0.34	0.38	1.00						
Humus pH	0.11	0.08	0.04	1.00					
Humus thickness (cm)	0.10	0.10	0.45	-0.12	1.00				
B-horizon LOI (%)	-0.10	-0.11	0.11	-0.27	-0.05	1.00			
B-horizon pH	-0.03	-0.06	0.13	0.14	0.13	0.10	1.00		
B:C ratio (Cu)	0.78	0.80	0.09	0.00	-0.32	-0.22	-0.03	1.00	
B:C ratio (Pb)	0.02	0.04	-0.13	-0.44	-0.07	-0.01	0.17	0.30	1.00
n = 26									

soils. Copper and lead retention is evident only in soils developed in glaciolacustrine fine-grained soils. For diamictos, such as till and reworked till, little evidence exists for Cu and Pb enrichment in the soil profile that can be directly related to smelter emissions. Assuming that smelter particulate is deposited throughout the area, it is hypothesized that metal from contaminated humus may be leached through the sandy diamicton soils into the B and C horizons, and possibly to depths beyond those sampled in this study.

METAL MOBILITY

In environmental research, selective leaches are used to establish the form of an element in the surficial environment and to describe its source, mobility, and bioavailability (Henderson et al., 1998; Reimann et al., 1998b). The effect of metals in the natural system may be higher (or lower) than predicted by total concentrations, depending on the chemical (and mineralogical) species in which the element occurs.

Humus

Sequential analyses were used to characterize the chemical species or mineral phases of elements in humus as a means of assessing metal mobility and bioavailability (Bernard et al., 1986; Hall et al., 1996; Henderson et al., 1998; Adamo et al., 2002). Results for humus show that the average concentration and relative proportion of metal extracted using the four digestions (outlined in Table 1) vary depending on the element and distance from the smelter (Fig. 10; Table 6; Henderson et al., 2002, Appendix B1:4). In Table 6, smelter distance is divided into four subgroups (0–10, 10–30, 30–50,

and more than 50 km from the smelter), based on the patterns of metal contamination in humus (Fig. 3, 4, 6, 7). Descriptive statistics for Cu and Pb for each distance group show that average metal concentrations for all digestions decrease with increasing distance from the smelter, with the exception of Pb extracted using the KCl-HCl (3) digestion. Lead concentrations in the last two digestions (3 and 4) of the sequence commonly approach detection limit, resulting in increased analytical uncertainty.

The highest mean Cu concentrations are associated with the sodium pyrophosphate digestion at sites within 10 km of the smelter, and with the KCl-HCl digestion at sites more than 10 km from the smelter (Table 6). The relative proportion of Cu extracted by the sodium pyrophosphate leach, selective for the labile soluble organic phase, decreases with distance from the smelter, as indicated in the box-and-whisker plot (Fig. 10). An average of 40% Cu is held in the labile phase at sites within 10 km of the smelter, the area of highest smelter-related contamination in humus. With distance, an increasingly higher proportion of the metal is associated with the KCl-HCl digestion, selective for insoluble organic phases. The relative proportion of Cu associated with the hydroxylamine (2) and multi-acid (4) digestions remains fairly stable with distance from the smelter.

Lead is primarily extracted using the sodium pyrophosphate digestion (1) associated with the labile soluble organic phase of humus, and secondarily by the hydroxylamine digestion (2) associated with non-labile iron- and magnesium-oxide phases, regardless of distance from the smelter (Fig. 10; Table 6). Approximately 70% of Pb is associated with the labile phase at sites within 10 km and approximately 43% at sites 50 to 110 km from the smelter. The relative proportion of Pb extracted by the last two digestions is low, although the

relative percentages tend to increase at sites over 50 km from the smelter where total Pb concentrations in humus are relatively low.

Results show that a high proportion of both Cu and Pb in humus is retained in labile phases at sites within 10 km from the smelter, where total metal concentrations may exceed the 90th percentile values (Fig. 6, 7). Consequently, a significant amount of metal may be mobile and leached into the underlying soils in this area. The proportion of Pb in the labile phase

extracted by sodium pyrophosphate digestion (1) is highest (of all digestions) at all distances from the smelter. Near the smelter, this proportion represents a significantly higher percentage of the total concentration than sites beyond 10 km distance. Colbourn and Thornton (1978) also observed an increase in the percentage of extractable Pb (by dilute nitric acid) near a smelter, which they attributed to the presence of more soluble Pb species (oxides) associated with the smelting process.

Table 6. Descriptive statistics for Cu and Pb concentrations reporting to each of the various sequential extractions outlined in Table 1. Statistics have been subdivided with respect to site distances from the smelter of 1 to 10 km, 10 to 30 km, 30 to 50 km, and more than 50 km.

Copper in humus (ppm)				
0–10 km	1	2	3	4
	Na Pyro	Hydrox	KCl-HCl	Multi-acid
Mean	789.9	505.6	304.6	102.2
Standard error	207.6	118.7	64.1	47.5
Median	514.5	408.5	225.5	46.0
Standard deviation	719.1	411.1	222.1	164.4
Range	1956.8	1201.4	698.9	595.0
Minimum	43.2	63.6	8.2	17.0
Maximum	2000	1265	707	612
Count	12	12	12	12

Copper in humus (ppm)				
10–30 km	1	2	3	4
	Na Pyro	Hydrox	KCl-HCl	Multi-acid
Mean	38.6	40.6	44.5	11.7
Standard error	8.9	7.7	8.6	3.1
Median	24.3	30.9	30.0	7.0
Standard deviation	42.5	36.7	41.5	15.1
Range	161.6	146.9	160.1	56.0
Minimum	5.9	10.7	9.0	1.0
Maximum	167.5	157.5	169.0	57.0
Count	23	23	23	23

Copper in humus (ppm)				
30–50 km	1	2	3	4
	Na Pyro	Hydrox	KCl-HCl	Multi-acid
Mean	12.9	14.1	18.7	5.2
Standard error	2.7	2.0	2.7	1.0
Median	8.9	11.2	16.0	4.0
Standard deviation	11.9	8.9	11.6	4.5
Range	42.8	36.6	40.3	13.0
Minimum	4.6	3.9	4.1	1.0
Maximum	47.4	40.4	44.4	14.0
Count	19	19	19	19

Copper in humus (ppm)				
50–110 km	1	2	3	4
	Na Pyro	Hydrox	KCl-HCl	Multi-acid
Mean	6.2	8.4	11.5	2.5
Standard error	0.8	0.9	1.0	0.4
Median	4.9	7.5	10.1	2.0
Standard deviation	4.1	4.8	5.3	2.2
Range	19.0	19.3	21.8	8.5
Minimum	1.9	1.6	3.2	0.5
Maximum	20.9	20.9	24.9	9.0
Count	29	29	29	29

Lead in humus (ppm)				
0–10 km	1	2	3	4
	Na Pyro	Hydrox	KCl-HCl	Multi-acid
Mean	2159.4	831.8	16.0	109.3
Standard error	383.9	158.7	6.5	62.9
Median	1812.5	633.5	7.4	26.8
Standard deviation	1329.7	549.9	22.6	217.9
Range	4726	1988	77	761.5
Minimum	274	192	6.5	6.5
Maximum	5000	2180	83.5	768
Count	12	12	12	12

Lead in humus (ppm)				
10–30 km	1	2	3	4
	Na Pyro	Hydrox	KCl-HCl	Multi-acid
Mean	190.0	117.3	8.1	7.0
Standard error	48.9	16.6	0.4	0.8
Median	111.5	87.0	7.5	5.5
Standard deviation	234.4	79.5	1.8	3.7
Range	927.6	320.5	7.4	13.5
Minimum	7.4	27.5	6	3.5
Maximum	935	348	13.4	17
Count				23

Lead in humus (ppm)				
30–50 km	1	2	3	4
	Na Pyro	Hydrox	KCl-HCl	Multi-acid
Mean	105.1	66.8	8.0	6.0
Standard error	19.6	10.0	0.8	1.4
Median	78.7	48.7	7.1	4.5
Standard deviation	85.6	43.7	3.6	6.0
Range	300.2	157.5	16.5	28
Minimum	10.8	16.5	6	2
Maximum	311	174	22.5	30
Count	19	19	19	19

Lead in humus (ppm)				
50–110 km	1	2	3	4
	Na Pyro	Hydrox	KCl-HCl	Multi-acid
Mean	59.0	42.3	8.7	4.2
Standard error	10.6	4.9	0.5	0.4
Median	37.1	43.1	7.3	4.0
Standard deviation	57.0	26.4	2.9	2.1
Range	229.1	109.9	10.8	9.5
Minimum	4.9	7.1	6	0.5
Maximum	234	117	16.8	10
Count	29	29	29	29

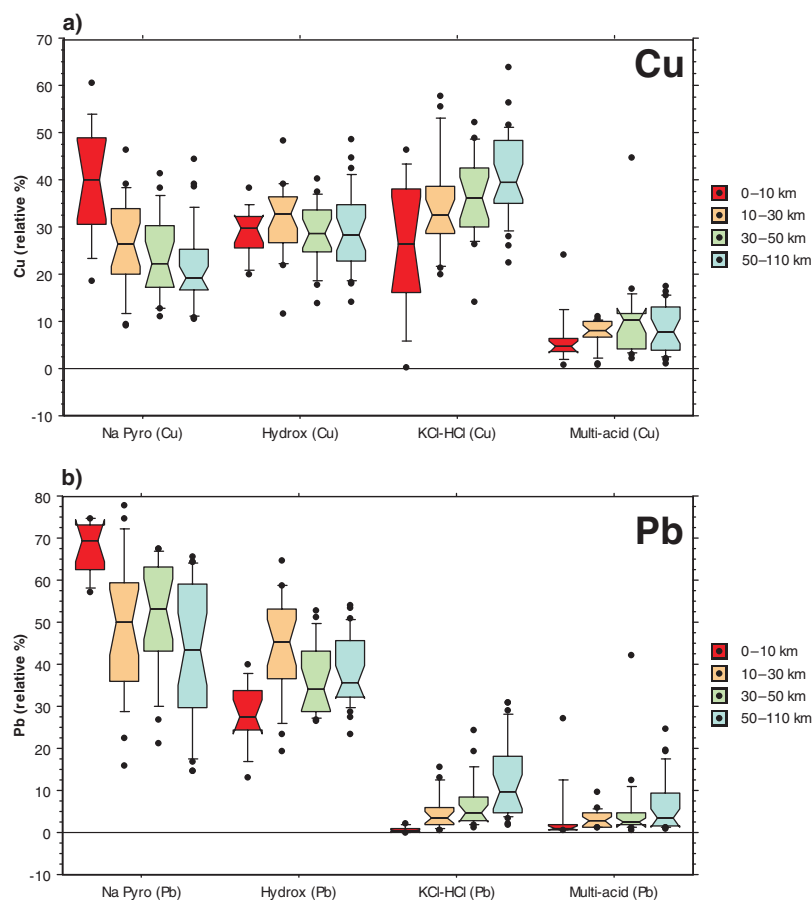


Figure 10. Box-and-whisker plot summarizing the results of sequential extraction analyses of humus samples with respect to distance from the smelter. These data are presented as the relative proportion of metal residing in each extracted phase based on the four-step sequential analytical protocol outlined in Table 1. Sites have been subdivided into groups according to distance from the smelter. The box plot is composed of five horizontal lines that show the 25th, 50th, and 75th percentile values as the bottom, middle, and top of the coloured box, respectively. The lowest line represents the 10th percentile value and the highest, the 90th percentile. All values above the 90th percentile and below the 10th percentile values are plotted separately. Notches represent the 95th percentile confidence interval for the median. **a)** copper; **b)** lead.

B- and C-horizon soils

The regional distribution of Cu and Pb in glaciolacustrine sediment as parent material indicates B-horizon enrichment at some sites within 20 km of the smelter, which may result from metal migration from contaminated humus into the underlying mineral soil (Fig. 7, 9). In the coarser grained soils, such as those developed in diamicton parent material, B-horizon enrichment is limited (Fig. 6, 8) and metals mobilized from humus may, in fact, be transported lower into the soil profile or carried in solution to other compartments of the surficial environment.

Diamicton parent material

No sequential analyses were undertaken on B- and C-horizon soils; however, two selective extractions were applied to a subset of samples: 1) a hot hydroxylamine extraction selective for labile metal concentrations associated with amorphous iron and manganese oxides and hydroxides; and 2) a multi-acid extraction selective for ‘total’ metal concentrations. The ratio between labile (hot hydroxylamine extraction) and total (multi-acid extraction) metal concentrations for B- and C-horizon samples was calculated for diamicton sites located at various distances from the smelter (Fig. 11).

For these samples, the relative proportion of Cu held in labile phases varies with distance from the smelter (Fig. 11). B- and, to a lesser extent, C-horizon Cu enrichment is evident in the labile phase at sites more than 20 km from the smelter. The relationship follows the trendline shown in Figure 11 for B-horizon hydroxylamine:multi-acid concentration ratios ($R^2 = 0.52$) and indicates a decrease in the proportion of labile Cu with increasing distance from the smelter. C-horizon ratios are more inconsistent and no definitive trend was established. Within 20 km of the smelter, the ratio in B-horizon soils is higher than in C-horizon soils; however, beyond this distance, the C-horizon ratio is equal to or greater than that of B-horizon soils (Fig. 11). In general, the relative proportion of labile Cu in B-horizon soils at sites near the smelter, where anthropogenic metal loading has been recognized in humus, is higher than at sites where humus concentrations approach background values.

Lead concentrations in B- and C-horizon soils near Rouyn-Noranda are low, commonly approaching the analytical detection limit (Henderson et al., 2002; Fig. 4, 6, 7). At these concentration levels, analytical errors can be significant and magnified when dealing with ratios. Nevertheless, results show that B-horizon ratios are greater than C-horizon ratios at most sites, regardless of distance from the smelter

(Fig. 11), which suggests a greater proportion of labile metal in B-horizon soils. As with Cu, the ratio for Pb in B-horizon soils decreases with distance from the smelter. No such trend is evident in C-horizon soils, with the exception of one site near the smelter.

On the basis of B:C-horizon concentration ratios (Fig. 8), no definitive metal enrichment was recognized in diamicton soils in relation to distance from the smelter. In contrast, results from the examination of resident sites for metals in these sandy soils indicate that the relative proportion of Cu

and Pb retained in the labile phase, particularly in B-horizon soils, differs with distance from the smelter (Fig. 10). Thus, smelter emissions may influence metal mobility in these soils, but, in the case of Cu, other factors may also be involved. Near the smelter (less than 20 km), in the area of extensive metal loading, the relative proportion of labile Cu in B-horizon soils exceeds that in C-horizon soils. In this same area, Cu enrichment in diamicton soils has been associated with mineralization (Fig. 6), and the weathering of sulphide minerals would also result in a relatively higher proportion of metal retained in labile phases in both B- and C-horizon soils (Fig. 11a). A similar geochemical response could result from the leaching of Cu from contaminated humus (less than 20 km from the smelter) into the B and C horizons. This latter interpretation is supported by Pb data. Since there is no known Pb mineralization in area, labile Pb in B-horizon soils (and possibly C-horizon soils) is most likely of anthropogenic origin.

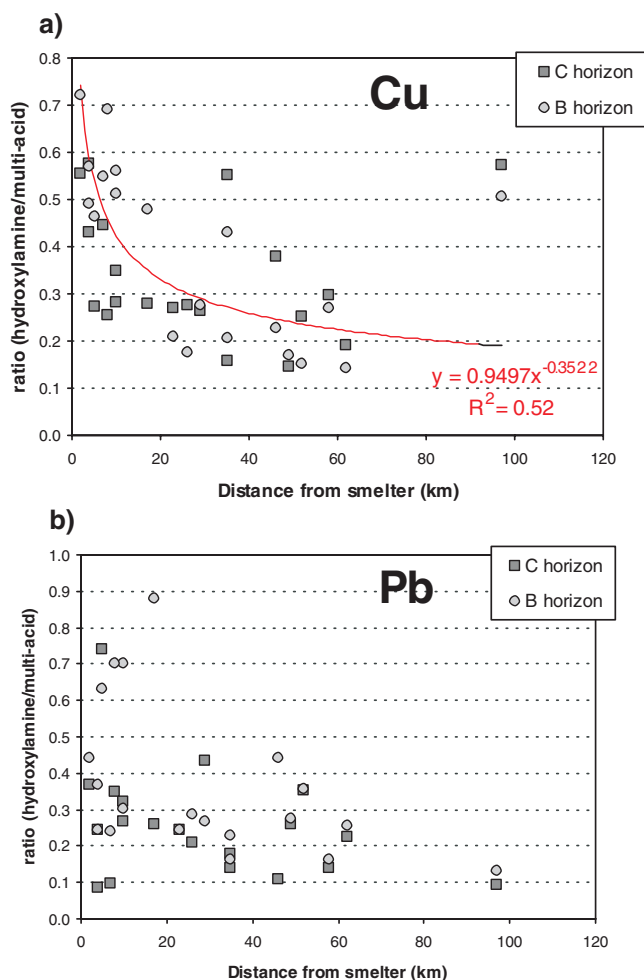


Figure 11. Ratio of metal concentrations (<2 mm fraction) in labile phase (hydrogen hydroxylamine digestion) and total concentration (multi-acid digestion) in B- and C-horizon soils developed on diamicton parent material vs. distance from the smelter. The trendline for B-horizon Cu data is shown in red. a) copper; b) lead.

Glaciolacustrine sediment parent material

Selective leach data are available for only one site developed on glaciolacustrine sediment as parent material (Fig. 12). The site lies 13 km east (downwind) of the smelter and was sampled at intervals of 5 cm to 85 cm, although selective leaches were not applied to all samples. Copper and lead concentrations in bulk humus at the site are 528 and 1100 ppm, respectively. Results from ICP-AES analyses, following aqua regia digestion (Fig. 12a), indicate both Cu and Pb enrichment at the top of the soil profile with concentrations decreasing with depth to approximately 30 cm for Cu and 50 cm for Pb. Below these depths, metal values essentially stabilize at values lower than in the upper B horizon. From regional data (Fig. 7), site geochemistry is characteristic of sites near the smelter showing B-horizon metal enrichment. At sites more than 20 to 30 km from the smelter, B- and C-horizon concentrations are nearly equal and, in the case of Cu, C-horizon concentrations may be slightly higher.

The relative proportion of metal held in labile phases, extracted by the hydroxylamine leach, is consistently higher for Pb than for Cu (Fig. 12b). Soil profile patterns are similar with ratios generally decreasing from a maximum at the top of the section. This pattern shows little relationship with the organic matter content (Fig. 12b). Ratios above approximately 25 cm for Cu and 45 cm for Pb are higher than ratios from samples at the base of the profile, which, theoretically, represent the natural or background geochemical signature. Consequently, it is proposed that the labile portion of metal (over background) in the upper part of the profile represents smelter-related metal loading. In the uppermost sample, the labile metal portion attributed to smelter contamination is small and amounts to 24 ppm Cu (26% total Cu concentration) and 6 ppm Pb (33% total Pb concentration).

Discussion on metal mobility

Near smelters, enhanced metal accumulation in humus results from atmospheric fallout of stack emissions and fugitive dust, and the decomposition of plant material. Because Cu is an essential element for plant growth, it is naturally enriched in humus through the biogeochemical cycle. On the basis of speciation studies, Stevenson and Fitch (1981) concluded that anthropogenic Cu is retained primarily in the organically bound component of humus as a result of complexation of organic matter with fluvic and humic acid. Copper is known to be one of the least mobile trace metals in soils (Adriano, 2001) and, in unpolluted areas, only a very small fraction of the total metal is present in labile species (Bernard et al., 1986). In the Rouyn-Noranda area, Cu is retained primarily in non-labile phases of humus except at sites within 10 km of the smelter, where the metal is largely held in the labile soluble organic phase extracted using sodium pyrophosphate digestion (Fig. 10). Other researchers have found that the relative proportion of Cu retained in soluble phases of humus increases with increasing total concentration; they have concluded that considerable downward leaching of Cu can occur in acidic mineral soils with high total concentrations in humus (Räsänen et al., 1997; Sauvé et al., 1997).

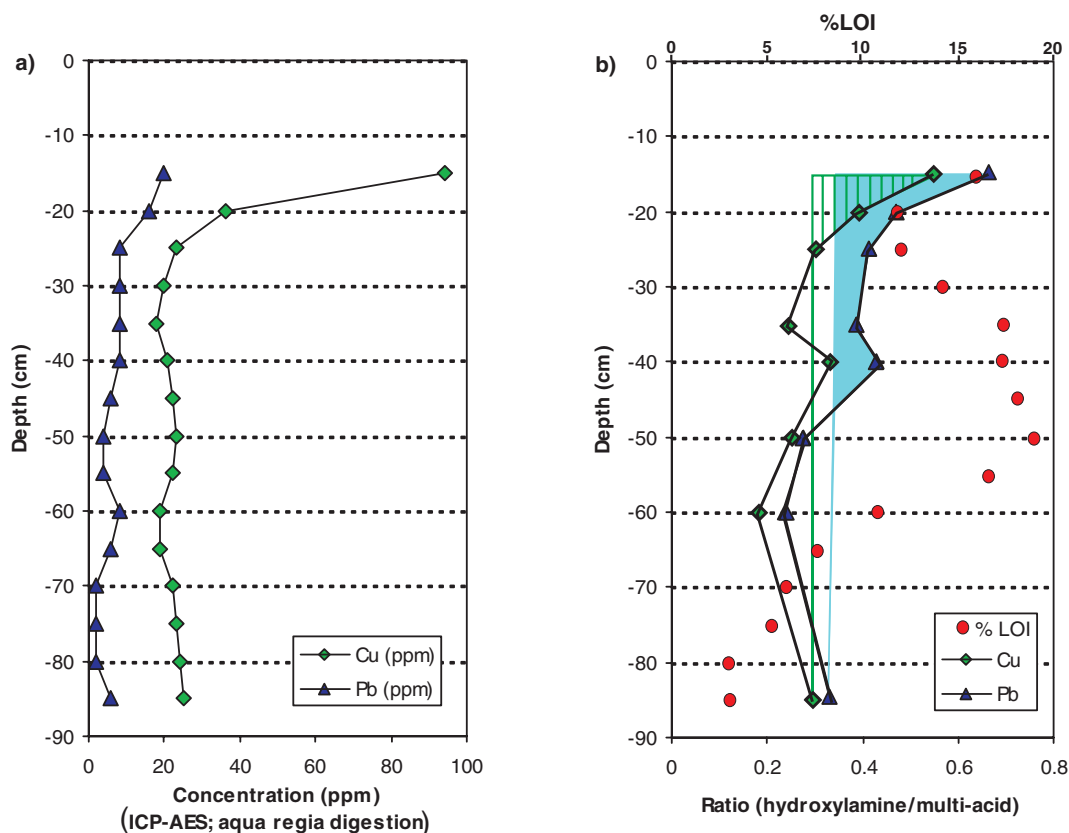


Figure 12. Geochemical profile in soil developed on glaciolacustrine sediment. **a)** Cu and Pb concentrations determined from ICP-AES analyses following aqua regia digestion for the <2 mm fraction; **b)** Cu and Pb ratios for concentrations extracted using hydroxylamine hydrochloride (labile phase) vs. multi-acid ('total' concentration) digestions followed by ICP-MS analyses on <2 mm fraction of sediment. The organic matter content (%LOI) is also shown.

At polluted sites, the relative percentage of Pb retained in soluble phases of humus varies directly with total Pb concentrations (Fig. 10; Colbourn and Thornton, 1978; Kabala and Singh, 2001). Underlying mineral soil horizons are presumed to be the final sink for Pb due to re-immobilization by adsorption on amorphous organo-mineral grain coatings or accumulated colloidal organic matter (Wang and Benoit, 1996). This hypothesis is supported by the speciation studies of soils in the Rouyn-Noranda area. Here, results indicate that the relative percentage of mobile Pb in B-horizon diamicton soils decreases with increasing distance from the smelter (Fig. 11), suggesting that labile Pb is derived primarily from contaminated humus. In soils developed on glaciolacustrine sediment, the relative percentage of mobile Pb decreases with depth to approximately 45 cm (Fig. 12), implying anthropogenic metal accumulation associated with the B horizon only. On the other hand, Semlali et al. (2001) hypothesized that Pb may migrate to deeper horizons as fine organic and organo-mineral constituents associated with the clay-sized fraction and may ultimately be leached out of the soil.

SUMMARY

The regional distribution of trace elements in soils near the Horne smelter at Rouyn-Noranda, Quebec, indicates metal loading in humus and B-horizon soils resulting from smelter-related particulate emissions. In humus, the level of enrichment decreases with distance from the point source depending on the element and dominant wind directions, with maximum enrichment up to 180 times background for Cu and 96 times background for Pb. The total smelter-derived metal load for Cu and Pb was calculated using a three-parameter non-linear radial decay model (Bonham-Carter and McMartin, 1997), based on background values given in Table 2. Assuming an average humus depth of 5 cm and density of 0.2 gm/cm³, total Cu and Pb in humus (to 1000 km) is estimated to be 7940 and 10 696 tonnes, respectively. Data provided by Noranda, Inc. (see Henderson et al., 2002, Table 1) indicate that 5080 tonnes of copper and 40 102 tonnes of lead were emitted from the smelter stack between 1965 and 1998. This represents only a fraction of the total historical emissions,

as the facility has been in operation since 1927. Nevertheless, it does indicate that a much larger proportion of emitted copper is retained within humus compared to lead, and suggests that lead is either more readily mobilized to lower soil horizons, including other compartments of the environment, and /or subjected to long-distance transport (Banic et al., 2002).

At increasing depth in the soil profile, the anthropogenic input becomes more difficult to differentiate from local variations in metal content due to site-specific factors. This is especially true for soils developed on diamicton where, even near the smelter, geogenic factors, such as bedrock mineralization, may enrich metal concentrations above normal background values. Using B:C-horizon concentration ratios to minimize geogenic factors, B-horizon Cu and Pb enrichment, likely smelter related, is most convincingly evident in soils developed in glaciolacustrine sediment (Fig. 8, 9). In these soils, B-horizon Cu and Pb enrichment near the smelter can be over 10 times background. The level of enrichment for both metals decreases with depth in the soil profile and distance from the smelter; however, some sites near the smelter show no enrichment (Fig. 9). From these results, it is evident that factors influencing B-horizon smelter-related metal loading include parent material and metal concentrations in humus (i.e. distance from smelter).

Metal mobility was assessed using sequential extraction analyses on humus and selective extractions for B- and C-horizon soil samples. In humus, Cu is held primarily in non-labile phases (extracted using the KCl-HCl digestion) and Pb resides in soluble phases (extracted using a sodium pyrophosphate digestion) (Table 1). The relative proportion of both Cu (~40%) and Pb (~70%) retained in the soluble phases of humus is higher within 10 km of the smelter than at sites more removed from the source, which suggests that total metal concentration in humus is a factor affecting metal mobility.

Labile metal in humus is presumed to be mobile and, consequently, easily leached to lower soil horizons. Ratios between metal concentrations extracted using various selective leaches (hydroxylamine hydrochloride: multi-acid digestion) in B-horizon diamicton soils support this hypothesis. The ratios indicate that the relative proportion of Cu and Pb retained in the labile phases of B-horizon soils decreases with distance from the smelter, following the trend toward decreasing labile Cu and Pb concentrations in humus (Fig. 11). Conversely, no direct relationship is evident between B-horizon metal enrichment (as seen in B:C-horizon concentration ratios based on aqua regia digestion) and distance from the smelter for soils developed on diamicton as parent material (Fig. 6, 8). These data imply that although the relative proportion of labile metal in B-horizon soils is enhanced by smelter-related metal loading, B-horizon metal enrichment in diamicton soils is not entirely smelter related. For Cu, B-horizon enrichment and metal mobility may be the result of both anthropogenic loading and geogenic factors related to local known copper mineralization. The geochemical response to weathering of sulphide minerals derived from mineral deposits or smelter particulate would likely be similar. For Pb, enrichment near the smelter is due to anthropogenic sources, since the geogenic Pb component is low in both bedrock and soils of the area.

In soils developed on glaciolacustrine sediment, local bedrock mineralization is not a significant influence on metal concentrations. Elevated Cu and Pb values in the B horizon, at sites within 40 km of the smelter, indicate smelter-related metal retention up to 10 times background (Fig. 7, 9). Concentration ratios, determined from hydroxylamine hydrochloride and multi-acid digestions, for samples from a glaciolacustrine soil profile 13 km from the smelter, indicate a higher proportion of labile Cu and Pb in the upper 25 and 45 cm, respectively, of the profile than at the base (Fig. 12). The labile portion of metal in the upper part of the section is attributed to smelter emissions.

CONCLUSION

Results from the study indicate that smelter-derived metals are retained primarily in humus. Both Cu and Pb are mobilized from the contaminated humus to lower soil horizons at sites near the smelter at Rouyn-Noranda. As the degree of metal loading in humus decreases with distance from the smelter, so does the relative proportion of metal retained in labile phases of B- and, possibly, C-horizon sandy soils (Fig. 11). For Pb, this relationship suggests downward leaching of metal from the contaminated humus throughout the soil profile. For Cu, similar leaching processes must be occurring, but it is more difficult to differentiate the anthropogenic component from geogenic sources related to local mineralization. Both metals are retained in B-horizon soils developed on fine-grained glaciolacustrine sediment at some highly contaminated sites (Fig. 7, 9). This enrichment must be anthropogenic, since no direct relationship exists between sediment composition and the underlying bedrock. In the Rouyn-Noranda area, the main factors influencing smelter-related metal loading in soils include the soil horizon, parent material, distance from the smelter source, chemical states of the metals in soil horizons, and related factors such as soil pH and organic matter content.

ACKNOWLEDGMENTS

The authors would like to thank the following people: Drs. Gwendy Hall, Conrad Gregoire, and Bob Garrett for their advice on geochemical analyses, analytical techniques and quality assurance and control; Isabelle Girard and Patty Lindsay for handling sample preparation and arranging and monitoring analyses with commercial laboratories; and Dr. Rod Klassen for an excellent review of an earlier version of this paper. Marc Lapointe provided assistance in the field in 1998. We would also like to thank Stéphane Robert and Robert Laprairie of Noranda, Inc. for their interest in the project and specific data and information on the Horne smelter. Dr. Graeme Bonham-Carter modelled metal loading in humus and encouraged the completion of this paper. Finally, we would like to acknowledge the input, through discussions and presentations, of our colleagues in the GSC MITE project, particularly Deb Kliza, Inez Kettles, Isabelle McMartin, Alain Plouffe, and Rod Klassen.

REFERENCES

- Adamo, P., Dudka, S., Wilson, M.J., and McHardy, W.J.**
2002: Distribution of trace elements in soils from the Sudbury smelting area (Ontario, Canada); *Water, Air, & Soil Pollution*, v. 137, p. 95–116.
- Adriano, D.C.**
2001: *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals* (2nd edition); Springer-Verlag, New York, New York, 866 p.
- Agriculture Canada Expert Committee on Soil Survey**
1987: The Canadian system of soil classification (2nd edition); Agriculture Canada, Publication 1646, 164 p.
- Äyräs, M., De Caritat, P., Chekushin, V.A., Niskavaara, H., and Reimann, C.**
1995: Ecogeochemical investigation, Kola Peninsula: sulphur and heavy metal content in snow; *Water, Air, & Soil Pollution*, v. 85, p. 749–754.
- Baas, J.H.**
2000: EZ-ROSE: a computer program for equal-area circular histograms and statistical analysis of two-dimensional vectorial data; *Computers & Geosciences*, v. 26, no. 2, p. 153–166.
- Banic, C., Daggupaty, S., Leaith, W.R., Wong, H., Campbell, I., Nejedly, Z., Skeaff, J., Packtunc, D., Strawbridge, K., Gariepy, C., Chatt, A., Lamoureux, M., MacPherson, J.I., Gaonach, H., and Michelangeli, D.**
2002: Study of the physical and chemical evolution of aerosols in smelter and power plant plumes; Addendum to the Programme, National Conference of the Toxic Substances Research Initiative, Ottawa, p. 45.
- Bernard, M., Brinckman, F.E., and Irgolic, K.J.**
1986: Why 'speciation'; in *The Importance of Chemical 'Speciation' in Environmental Processes*, (ed.) M. Bernard, F.E., Brinckman, and P.J. Sadler; Springer-Verlag, Berlin, p. 7–14.
- Bonham-Carter, G.F.**
2005: Introduction to the GSC MITE Point Sources project; in *Metals in the Environment Around Smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and Conclusions of the GSC MITE Point Sources Project*, (ed.) G.F. Bonham-Carter; Geological Survey of Canada, Bulletin 584.
- Bonham-Carter, G.F. and McMartin, I.**
1997: Calculations on metals in humus around the base-metal smelter at Flin Flon, Manitoba, Canada; in *Proceedings, Third Annual Conference of the International Association for Mathematical Geology (IAMG'97)*, (ed.) V. Pawlowsky-Glahn; International Center for Numerical Methods in Engineering (CIMNE), Barcelona, Spain, p. 262–267.
- Colbourn, P. and Thornton, I.**
1978: Lead pollution in agricultural soils; *Journal of Soil Science*, v. 29, p. 513–526.
- Davies, B.E.**
1983: Heavy metal contamination from base metal mining and smelting; implications for man and his environment; in *Applied Environmental Geochemistry*, (ed.) I. Thornton; Academic Press, New York, New York, p. 425–462.
- Dumontet, S., Dinel, H., and Lévesque, M.**
1992: The distribution of pollutant heavy metals and their effect on soil respiration and acid phosphatase activity in mineral soils of the Rouyn-Noranda region, Quebec; *The Science of the Total Environment*, v. 121, p. 231–245.
- Greinert, H.**
1993: The solubility and plant availability of heavy metals in soils contaminated with industrial dusts and sludges; in *Integrated Soil and Sediment Research. A Basis for Proper Protection*, (ed.) H.J.P. Eijssackers and T. Hamers; Kluwer, Dordrecht, The Netherlands, p. 257–260.
- Hall, G.E.M., Vaive, J.E., Beer, R., and Hoashi, M.**
1996: Phase selective leaches for use in exploration geochemistry; in *EXTECH I: A Multidisciplinary Approach to Massive Sulphide Research in the Rusty Lake–Snow Lake Greenstone Belts, Manitoba*, (ed.) G.F. Bonham-Carter, A.G. Galley, and G.E.M. Hall; Geological Survey of Canada, Bulletin 426, p. 169–200.
- Hazlett, P.W., Rutherford, G.K., and Van Loon, G.W.**
1984: Characteristics of soil profiles affected by smelting of nickel and copper at Coniston, Ontario, Canada; *Geoderma*, v. 32, p. 273–285.
- Henderson, P.J., Knight, R.D., and McMartin, I.**
2002: Geochemistry of soils within a 100 km radius of the Horne Cu smelter, Rouyn-Noranda, Quebec; Geological Survey of Canada, Open File 4169 (CD ROM).
- Henderson, P.J., McMartin, I., Hall, G.E.M., Percival, J.B., and Walker, D.A.**
1998: The chemical and physical characteristics of heavy metals in humus and till in the vicinity of the base metal smelter at Flin Flon, Manitoba, Canada; *Environmental Geology*, v. 34, no. 1, p. 39–58.
- Jennett, C.J., Wixson, B.G., Lowsley, I.H., Purushothaman, K., Bolter, E., Hemphill, D.D., Gale, N.L., and Tranter, W.H.**
1977: Transport and distribution from mining, milling, and smelting operations in a forest ecosystem; Chapter 7 in *Lead in the Environment*, (ed.) W.R. Boggess; National Science Foundation, Washington, D.C., p. 135–178.
- Kabata-Pendias, A. and Pendias, H.**
1984: *Trace Elements in Soils and Plants*; CRC Press, Boca Raton, Florida, 315 p.
- Kabala, C. and Singh, B.R.**
2001: Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter; *Journal of Environmental Quality*, v. 30, p. 485–492.
- Karczewska, A.**
1996: Chemical speciation and fate of selected heavy metals in soils strongly polluted by copper smelters; in *Geochemical Approaches to Environmental Engineering of Metals*, (ed.) R. Reuther; Springer, Berlin, Germany, p. 55–79.
- Knight, R.D. and Henderson, P.J.**
2005: Characterization of smelter dust from the mineral fraction of humus collected around Rouyn-Noranda, Quebec; in *Metals in the Environment Around Smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and Conclusions of the GSC MITE Point Sources Project*, (ed.) G.F. Bonham-Carter; Geological Survey of Canada, Bulletin 584.
- Knight, R.D., LaPointe, M., Kyer, T., and Henderson, P.J.**
2000: Some observations on the effects of length of sample storage, sample type, and sample depth on the determination of pH in soils collected in the vicinity of the Horne smelter at Rouyn-Noranda, Quebec; Geological Survey of Canada, Current Research 2000-C24, 7 p.
- McBride, M.B.**
1989: Reactions controlling heavy metal solubility in soils; in *Advances in Soil Science*, v. 10; Springer, Berlin, Germany, p. 1–56.
- McMartin, I., Henderson, P.J., and Nielsen, E.**
1999: Impact of a base metal smelter on the geochemistry of soils of the Flin Flon region, Manitoba and Saskatchewan; *Canadian Journal of Earth Science*, v. 36, p. 141–160.
- McMartin, I., Henderson, P.J., Plouffe, A., and Knight, R.D.**
2002: Comparison of Cu-Hg-Ni-Pb concentrations in soils adjacent to anthropogenic point sources: examples from four Canadian sites; *Geochemistry: Exploration, Environmental, Analysis*, v. 2, p. 57–74.
- MERQ-OGS**
1984: Lithostratigraphic map of the Abitibi Subprovince; Ontario Geological Survey / Ministère de l'Énergie et des Ressources, Québec, catalogued as 'Map 2484' in Ontario and 'DV 83-16' in Quebec, scale 1:500 000.
- Paquet, A.**
1987: Influence des contaminants aéroportés sur la planification et l'interprétation des travaux de prospection géochimique. Région de Rouyn-Noranda; ministère de l'Énergie et des Ressources du Québec; DP 87-03, 83 p.
- Räisänen, M.L., Kashulina, G., and Bogatyrev, I.**
1997: Mobility and retention of heavy metals, arsenic and sulphur in podzols at eight locations in northern Finland and Norway and the western half of the Russian Kola Peninsula; *Journal of Geochemical Exploration*, v. 59, p. 175–195.
- Reimann, C., Äyräs, M., Chekushin, V., Bogatyrev, I., Boyd, R., de Caritat, P., Dutter, R., Finne, T.E., Halleraker, J.H., Jäger, O., Kashulina, G., Lehto, O., Niskavaara, H., Pavlov, V., Räisänen, M.L., Strand, T., and Volden, T.**
1998a: *Environmental Geochemical Atlas of the Central Barents Region*; NGU-GTK-CKE Special Publication, Grytting AS, 745 p.

Reimann, C., de Caritat, P., Niskvaara, H., Finne, T.E., Kashulina, G., and Pavlov, V.

1998b: Comparison of elemental contents in O- and C-horizon soils from the surroundings of Nickel, Kola Peninsula, using different grain size fractions and extractions; *Geoderma*, v. 84, p. 65–87.

Sangster, D.F.

1972: Precambrian volcanogenic massive sulphide deposits in Canada; a review; Geological Survey of Canada, Paper 72-22, 44 p.

Sauvé, S., McBride, M.B., Norvell, W.A., and Hendershot, W.

1997: Copper solubility and speciation of in situ contaminated soils: effects of copper level, pH and organic matter; *Water, Air, & Soil Pollution*, v. 100, p. 133–149.

Semlali, R.M., Van Oort, F., Denaiz, L., and Loubet, M.

2001: Estimating distribution of endogenous and exogenous Pb in soils by using Pb isotopic ratios; *Environmental Science and Technology*, v. 35, p. 4180–4188.

Sheldrick, B.H.

1984: Analytical methods manual, 1984; Research Branch, Agriculture Canada, LRR Contribution no. 84-30.

Stevenson, F.J. and Fitch, A.

1981: Reactions with organic matter; in *Copper in Soils and Plants*, (ed.) J.F. Loneragan, A.D. Robson, and R.D. Graham; Academic Press, New York, New York, p. 69–95.

Thomas, G.W.

1996: Soil pH and soil acidity; in *Methods of Soil Analysis; Part 3, Chemical Methods*; (ed.) J.M. Bartel; Soil Science Society of America, Agronomy, Madison, WI, p. 475–490.

Veillette, J.J.

1989: Ice movements, till sheets and glacial transport in Abitibi-Timiskaming, Quebec and Ontario; in *Drift Prospecting*, (ed.) R.N.W. DiLabio and W.B. Coker; Geological Survey of Canada, Paper 89-20, p. 139–154.

1996: Géomorphologie et géologie du Quaternaire du Témiscamingue, Québec et Ontario; Commission géologique du Canada, Bulletin 476, 269 p.

Veillette, J.J., Paradis, S.A., and Buckle, J.

2005: Bedrock and surficial geology of the general area around Rouyn-Noranda, Quebec and Ontario; in *Metals in the Environment Around Smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and Conclusions of the GSC MITE Point Sources Project*, (ed.) G.F. Bonham-Carter; Geological Survey of Canada, Bulletin 584.

Vincent, J.-S. and Hardy, L.

1979: Evolution of Glacial Lakes Barlow and Ojibway, Quebec and Ontario; Geological Survey of Canada, Bulletin 316, 18 p.

Wang, E.X. and Benoit, G.

1996: Mechanisms controlling the mobility of lead in the Spodosols of a northern hardwood forest ecosystem; *Environmental Science and Technology*, v. 30, p. 2211–2219.

Wang, E.X., Bormann, F.H., and Benoit, G.

1995: Evidence of complete retention of atmospheric lead in the soils of northern hardwood forested ecosystems; *Environmental Science and Technology*, v. 29, p. 735–739.