Metal distribution in peat hummocks and hollows within 100 km of the copper smelter, Rouyn-Noranda, Quebec

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Abstract: Profile samples were collected from peat hummocks and hollows from 37 peatlands within a 100 km radius of the Horne copper smelter, to investigate the value of peat as an historical record of smelter metal emissions. Splits of 630 samples were digested with HNO_3–$HClO_4$ prior to analysis for smelter-related (Cu, Pb, Zn) and non-smelter (Ni) elements. Twenty-four samples were subjected to a four-step sequential extraction analysis to identify the main metal residence sites. Peat age was constrained from ^{137}Cs, bulk density, and vertical growth rate data.

Concentrations of Cu, Pb, and Zn were relatively low in the uppermost 20 cm of the hummocks and increased markedly between depths of 20 and 45 cm. In the tallest hummocks, metal concentrations decreased again below 50 cm depths and, by 60 to 75 cm depth, reached values less than those in the uppermost 20 cm. This pattern was most pronounced within 25 km of the smelter but was still discernible in hummocks at distances of more than 60 km. A similar pattern of increased and decreased concentrations was found in hollows, but it was compressed over the uppermost 20 cm of the hollow peat sequence. In hummocks 10 km and more from the smelter, about 25% of the Cu and 75% of the Pb and Zn resided in the labile phases, whereas closest to the smelter, in the 7 km hummock, even larger amounts of these elements were labile. In contrast to the smelter-derived elements, Ni concentration in hummocks and hollows varied.

Résumé : Des échantillons du profil ont été prélevés dans des buttes de tourbe et des dépressions situés dans 37 tourbières réparties dans un rayon de 100 km autour de la fonderie de cuivre Horne et ce, afin de déterminer dans quelle mesure la tourbe renseigne sur l'histoire des émissions de métaux de la fonderie. Les sous-échantillons de 630 échantillons ont été dissous dans une solution de HNO_3-$HClO_4$ avant leur analyse visant à détecter des éléments issus de la fonderie (Cu, Pb et Zn) ou non (Ni). On a soumis 24 échantillons à une analyse d'extraction séquentielle en quatre étapes pour relever les principaux sites renfermant des métaux. L'âge de la tourbe a été délimité d'après une datation au ^{137}Cs, la masse volumique apparente et des données sur le taux de croissance vertical.

Les concentrations de cuivre, de plomb et de zinc étaient relativement faibles à des profondeurs de 20 cm et moins sous les buttes, mais elles augmentaient nettement à une profondeur allant de 20 à 45 cm. Dans les buttes les plus élevées, les concentrations de métaux diminuaient à nouveau à plus de 50 cm de profondeur pour atteindre, entre 60 et 75 cm de profondeur, des valeurs inférieures à celles relevées à 20 cm et moins de profondeur. C'était à moins de 25 km de la fonderie que ces variations étaient les plus apparentes, mais elles demeuraient discernables dans les buttes situés à plus de 60 km de la fonderie. Des variations similaires ont été observées dans les dépressions, mais elles étaient concentrées à 20 cm et moins de profondeur dans la séquence de tourbe. Dans les buttes se trouvant à 10 km ou plus de la fonderie, environ 25 % du cuivre et 75 % du plomb et du zinc étaient en phase labile, tandis que dans la butte qui se trouvait le plus près de la fonderie, soit 7 km, ces pourcentages étaient encore plus élevés. Contrairement aux concentrations d'éléments issus de la fonderie, celles du nickel variaient dans les buttes et les dépressions.

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INTRODUCTION

In 1997, the Geological Survey of Canada initiated research on heavy metal concentrations in peatlands surrounding the Horne copper-zinc smelter (Fig. 1) at Rouyn-Noranda, Quebec. This work was carried out as part of an integrated Metals in the Environment (MITE) project to investigate and compare the records of smelter particulate emissions in different types of surficial media (till, soil, lake sediment, snow, lake water, peat, and tree rings) and to evaluate anthropogenic loading in these natural systems. Samples were collected from peat hummocks and adjacent hollows (flat part of the peatland) in 37 peatlands within a 100 km radius of the Horne smelter. The main objective of the peatland study was to investigate the value of peat as an historical record of smelter metal emissions. This was accomplished by 1) constraining the age of near-surface peat; 2) searching for physical evidence of smelter particulate emissions in peat; and 3) generating geochemical records of smelter-related metals in peat, paying attention to regional- and site-scale variations in metal distribution with depth in the peatlands and at varied distances from the smelter. A second project objective was to generate baseline data on metal residence sites in peat at varied distances from the smelter, through a series of sequential geochemical extractions on selected samples. These data are useful for determining the sources and assessing the potential bioavailability of the metals contained in peat. This report summarizes the results of the research undertaken to meet these two objectives. A third project objective — to compare the record of smelter-related metals in peat with other surficial materials (humus and surficial lake sediments) — is considered only briefly in this paper but is covered in Bonham-Carter et al. (2005).

The remote but accessible Rouyn-Noranda area is an excellent location for investigating the atmospheric deposition of metals around a smelter. It has only one major point source of atmospheric pollution, wind patterns are well documented, and there is a continuous emissions record since the smelter opened in 1927. In addition, the influence of the copper-nickel smelter at Sudbury is not discernible as the smelter is located upwind and about 250 km to the southwest.

Peatlands have massive organic deposits at least 40 cm thick and most commonly take the form of bogs or fens (Zoltai, 1988a). They are abundant in the Rouyn-Noranda area where they cover approximately 20 to 30% of the land area (Tarnocai et al., 2000). Fens, dominated by sedges and grasses, are influenced to varying degrees by regional groundwaters carrying nutrients from the surrounding mineral sediments (Zoltai, 1988a). In places, fens become weakly minerotrophic or evolve into ombrotrophic bogs when the decaying organic materials they are composed of have accumulated to the point that they become isolated from the effects of groundwater transport. Bog surfaces are acid, nutrient-poor, and unlike most other types of surficial materials, nourished almost entirely by atmospheric inputs (Zoltai, 1988a).

Surface vegetation in bogs and nutrient-poor fens is dominated by *Sphagnum*, a genus with properties that make it useful for bioenvironmental monitoring (Fig. 2a). *Sphagnum* plants are rootless, grow from the apex, and have stems that grade from live to dead material, with no clear demarcation between the two (Andrus, 1980; Clymo and Hayward, 1982). The plants act as cation exchangers, releasing hydrogen ions in exchange for dissolved cations, and have a chemical composition that slows down decomposition (Kalviainen and Karuenen, 1984).

Sphagnum is a colonizer that may accumulate in mounds on the peatland surface; the elevated mounds alternate with topographically lower, flatter, and wetter areas, referred to as 'hollows' (Fig. 2b). Among the *Sphagnum* species, those associated with hummocks decay more slowly than hollow species, retain their physical structure longer, and, hence, allow for greater peat accumulation than those found in hollows (Johnson et al., 1990; Ohlson and Dahlberg, 1991; Johnson and Damman, 1993). These differences, and the resulting slower hydrological transmissivity in the hollows, account in part for the formation and long-term maintenance of hummocks and hollows over hundreds to even thousands of years (Nungasser, 1997). In addition, hummocks have been shown to become hydrologically isolated from the minerotrophic waters in the areas that they occupy, which essentially turns each hummock into a miniature ombrotrophic bog (Bellamy and Rieley, 1967)

Peat is commonly used to monitor airborne pollution in North America and Europe following two general approaches, 1) the use of actively growing vegetation and 2) the measurement of metal concentrations of old growth *Sphagnum* with depth (Glooschenko et al., 1986). In Canada, work has focused on monitoring metal deposition in the vicinity of the major metal smelters (Glooschenko and Capoblanco, 1978, 1982; Glooschenko et al., 1981; Azzaria and Frechette, 1987; Zoltai, 1988b; Dumontet et al., 1990), whereas in the Nordic countries, determining regional patterns of metal loading has been emphasized (Aaby and Jacobsen, 1979; Parkinen, 1981; Steinnes, 1997; Jensen, 1997). The use of peat for monitoring smelter emissions is especially attractive in northern Canada because widespread peatlands are found in Archean Greenstone Belt areas where several smelters are located.

PREVIOUS WORK

Glooschenko et al. (1986) sampled surface *Sphagnum* and peat profiles at depth in 10 bogs located within 70 km of the Horne smelter. Some results from this study are discussed later in this report. Dumontet et al. (1990) examined the distribution of metals in peat in peat-bearing swamps at 11 sites along transects oriented north-northeast and east-southeast from the smelter. They noted a decrease in average pH values and ash content for the whole peat profiles with increasing distance from the smelter. They found high concentrations of all metals in the 0 to 15 cm layer at sites near the smelter, with Cu having the highest concentration (5525 ppm), followed by Pb and Zn, and limited concentrations of Cd and Ni. They suggested that there had been some migration of metals down into the peat profiles and some accumulation in the sublayers at sites close to the smelter.
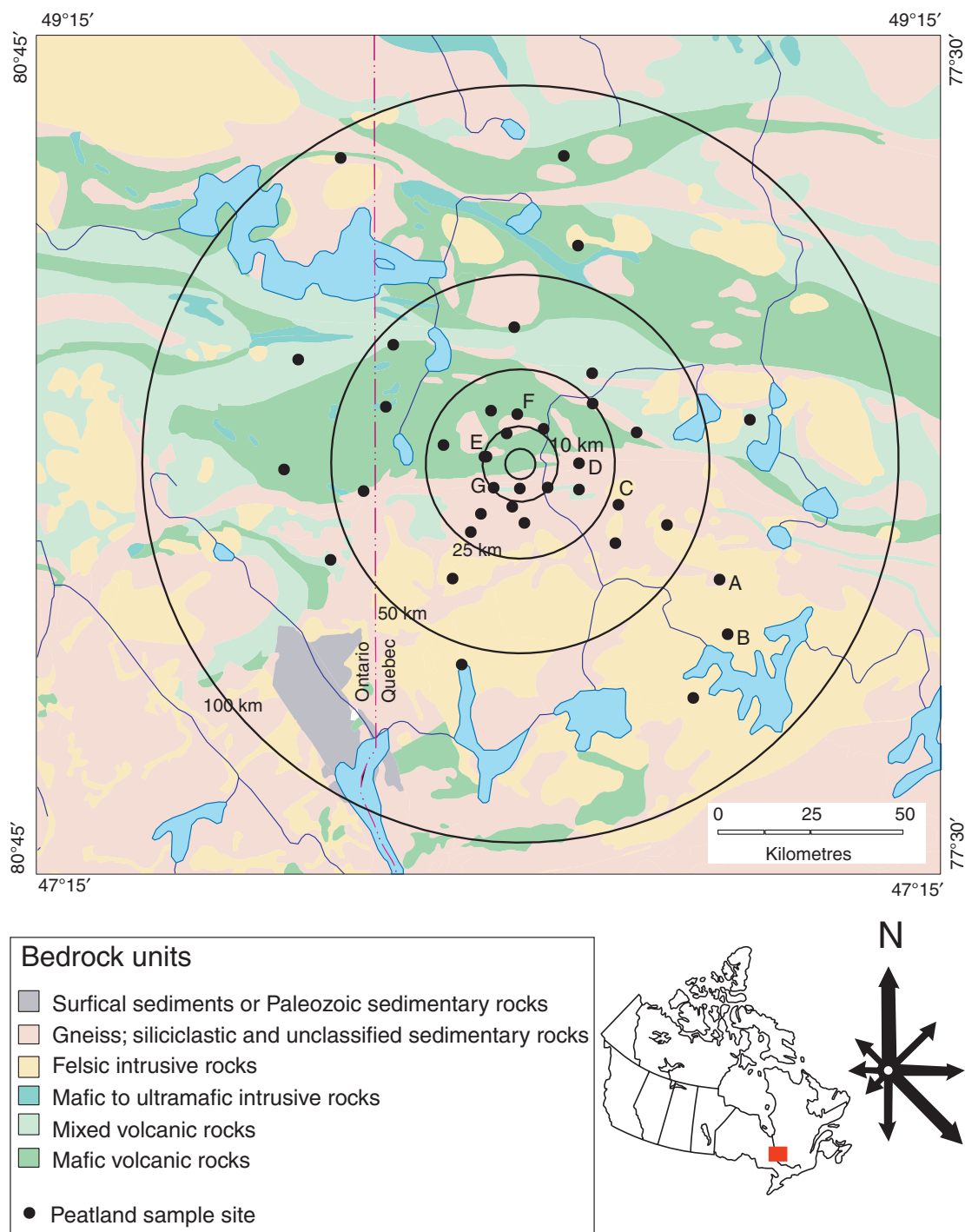
Figure 1. Diagram showing underlying bedrock (modified from MERQ–OGS, 1984) and locations of 37 peatland study sites in the Rouyn-Noranda area, Quebec. The city of Rouyn-Noranda is at the centre of the circles. Letters denote sites with detailed hummock and hollow sampling and analysis (A, site 3520; B, site 3522; C, site 3525; D, site 3527; E, site 3533; F, site 3536; G, site 3540). The wind rose diagram shows the frequency (length) and strength (width) for eight directions, based on 54 year annual averages (1954–1993) (Noranda Mines, unpub. data, 1996). Inset map shows study location in Canada.
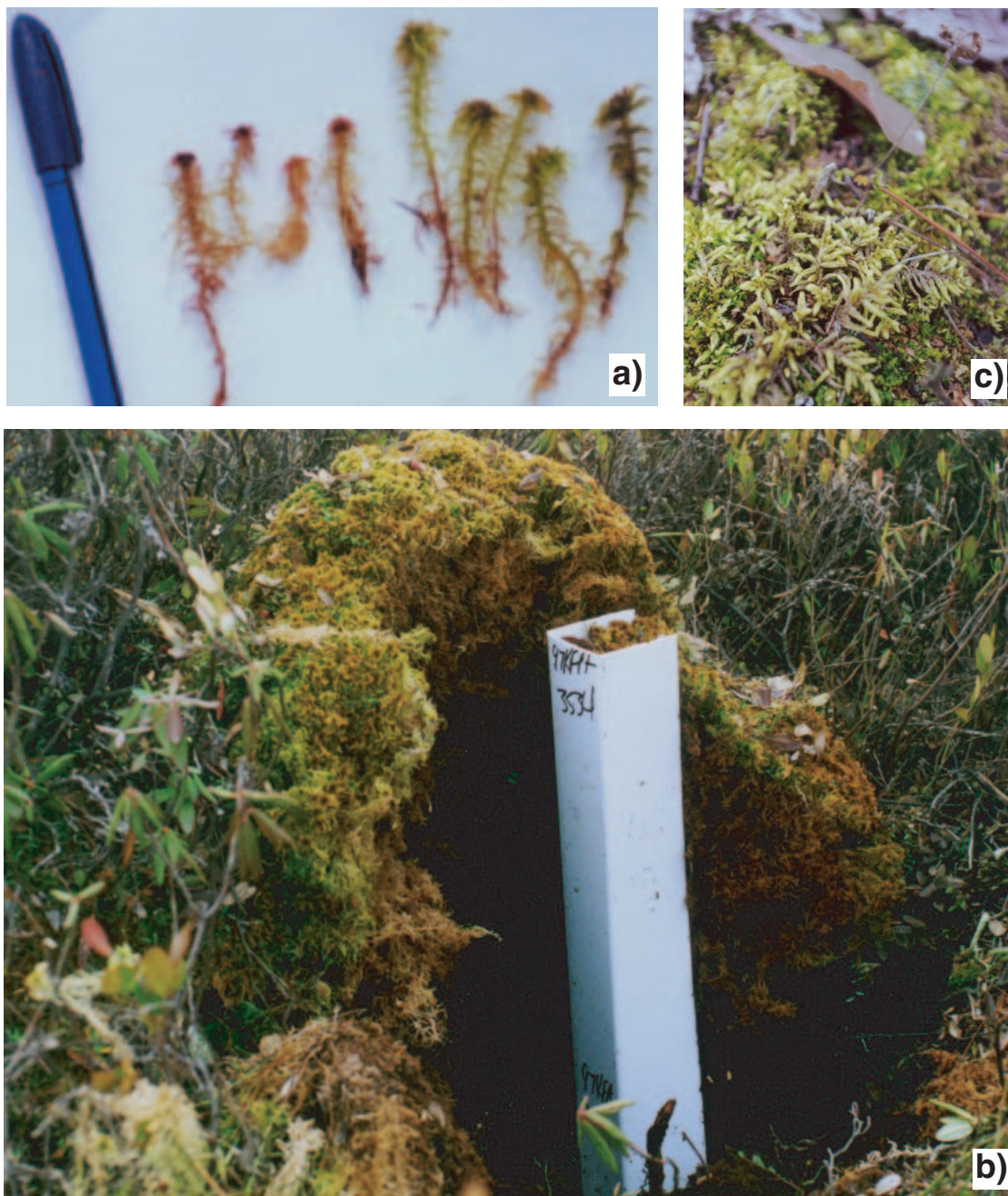
Figure 2. Photograph of a) Sphagnum *species; b) a* Sphagnum *hummock with PVC tube used for coring; and c)* Pleurozium scherberi *(feather moss).*

At least two precipitation studies have been carried out in the Rouyn-Noranda area. Lalonde (1978) measured metals levels in snow 2, 10, and 20 km from the smelter and in rain samples from Rouyn-Noranda and from LaSarre 65 km from the smelter. As part of this MITE program, Kliza et al. (2000) determined the levels of smelter-related and other elements in snow collected in 1998 around the Horne smelter.

Several reports and papers have been published based on peat data from this study. These include 1) a release of field and geochemical data from the 1997 reconnaissance sampling survey (Kettles and Dion, 2000); 2) modelling metal dispersal from the Horne smelter, using geochemical and other data for the hummock surface (Kettles and Bonham-Carter, 2002); 3) exploring the data error effects on the resultant estimates of metal tonnages using a Monte Carlo simulation (Bonham-Carter and Kettles, 2001); and 4) some comparisons of the peat and humus metal records (Kettles et al., 2001).

SETTING

The Rouyn-Noranda area lies on the Canadian Shield within the boreal forest (Ecoregions Working Group, 1989). Rocks of the Abitibi Greenstone Belt underlie the region and consist of Archean metasedimentary and metavolcanic units and associated intrusions (Stockwell et al., 1970; Fig. 1). At elevations below 300 m above sea level, large areas are covered at the surface by glaciofluvial sands and gravels or by extensive clay plains (Veillette, 1996); above 300 m, bedrock is covered predominantly by till. Till generally forms a discontinuous veneer 0 to 1.5 m thick that mantles and reflects the underlying bedrock topography. Peatlands have developed in poorly drained areas of the clay plains and in undrained depressions in the knobby shield terrane.

Development of the Rouyn-Noranda area followed the opening of the Horne mine in 1925 and the Horne smelter in 1927 (Roberts, 1956). Since that time, extensive urban and industrial development, farming, and logging have occurred in the surrounding region. The Horne smelter has two stacks, 161 and 127 m high, respectively, but since the 1990s the shorter stack has seen the most use (Noranda Mines, Ltd., unpub. data, 1996). The amount of particulate material discharged into the atmosphere increased steadily over time (except during the war years), increasing six-fold from 1928 to the peak year 1965. Since 1965, the emission levels have decreased steadily, being about 25% of peak zinc levels and 14% of copper and lead levels since 1990. The prevailing winds are to the north and to the southeast, but winds to the northeast, east, and south are also common (Noranda Mines, Ltd., unpub. data, 1996; Fig.1). The influence of the copper-nickel smelter at Sudbury is not discernible as the smelter is located upwind and about 250 km to the southwest.

METHODS

Field sampling of peat

In late September–early October 1997, profile peat samples were collected from *Sphagnum* hummocks in 37 peatlands located from 7 to 92 km from the smelter (Fig. 1; Table 1). The sample sites were selected on the basis of peatland distribution, dominant wind directions, and road access. Wherever possible, the sites selected for sampling were bogs dominated by *Sphagnum* species, with ericaceous shrubs such as *Chamaedaphne calyculata*, *Ledum groenlandicum*, and *Kalmia polifolia.* However, in places, the hummocks sampled were growing on the surface of more nutrient-rich peatlands or on a thin veneer of organic materials.

One of the best developed hummocks at each site was cut open near its highest point to expose a vertical face for sampling (Fig. 2b). Sampled hummocks ranged in height from 30 to 65 cm above the flat part of the peatland, with most having a height of at least 40 cm. Profile samples were collected at about 3 to 8 cm intervals from top to bottom and, where possible, sample volumes were estimated. The samples were cut using stainless steel knives and clippers and stored in plastic ziplock bags. For reference purposes, a small core of continuous intact material was also collected from the vertical face by inserting a three-sided PVC channel and carefully removing the material around it (*see* Fig. 2b).

In order to gain insight into peat composition at greater depths in the peatland, peat profile samples were also collected in 1997 from the hollow adjacent to and within 1 to 2 m of each sampled hummock, where peat accumulations above the mineral sediment were at least 50 cm thick. In the hollow, blocks of peat were hand cut to depths of about 30 cm; below this, a 4 cm diameter core was collected using a stainless steel macaulay corer (Jowsey, 1966) and subsampled at 15 to 50 cm intervals. Mineral sediments from the base of these cores were also sampled and analyzed (Table 2; Kettles and Dion, 2000). New growth from *Pleurozium schreberi* (red-stemmed feather moss) growing on the surface of the hollows was also sampled at 14 of the peatland sites (Fig. 2c). Using methodology described by Rasmussen (1994), 2 to 4 cm long segments were clipped from the ends of the moss branches using stainless steel clippers. Geochemical data for this species, known to be an effective metal bioindicator, have been published (Table 3; Kettles and Dion, 2000).

In May 1999 and September 2000, additional sampling was undertaken at three of the original peatland sites in order to examine hummock metal distribution patterns in more detail and to assess intrasite variability. The sites (3533, 3540, and 3525) were located 10, 12, and 30 km, respectively, from the smelter. They were chosen because they were known to contain tall, well developed hummocks, based on the 1997 sampling. Profile samples were collected at 1 to 2 cm intervals from three hummocks, along with the surface 30 to 100 cm of two or three hollows at each of the three sites.

Sample analysis

HNO$_3$–HClO$_4$ digestion and ICP-AES analysis

Peat samples from hummock and hollow sequences and feather moss were digested with HNO$_3$–HClO$_4$ prior to inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis by ALS Chemex Ltd., Vancouver (Table 1; Kettles and Dion, 2000; Kettles and Bonham-Carter, 2002). Data from hummock surface, hollow surface, and feather moss samples were used for modelling the geographical distribution of metals, whereas data from hummock and hollow profiles were used to investigate temporal changes in element accumulation.

Analytical error was estimated on the basis of data from blind duplicates and a vegetation (uncertified) reference sample used at the Geological Survey of Canada. These data were plotted using a method devised by Thompson and Howarth (1978) to estimate precision. Precision was estimated at 30% for Cu, 40% for Pb, 30% for Zn, 40 % for Ni, and 25 % for Ca.

Sequential extraction analysis

A total of 24 samples selected from sites 3533, 3540, and 3525 as well as from site 3520 (15 km from the smelter) were subjected to a four-step leaching analysis modified from

Table 1. Peatland site locations, peat depth, and sample types.

Site	Hummock surface	Hollow surface	Hummock sequence	Hollow sequence	Sector	Distance from smelter (km)	Latitude (°N)	Longitude (°N)	Hollow peat depth* (cm)
3500	x				SE	17.2	48.1704	78.8093	45
3501	x	x	x		SE	44.2	48.0835	78.4883	70
3503	x				W	20.7	48.2789	79.2894	210
3504	x	x	x	x	NW	14.9	48.3572	79.1155	60
3505	x				NE	9.6	48.3127	78.9364	< 30
3506	x				SW	24.5	48.0706	79.1945	< 30
3507	x	x		x	SW	18.9	48.1132	79.1608	153
3508	x	x		x	S	18.4	48.0897	78.9951	98
3509		x			S	14.6	48.1280	79.0474	65
3510	x	x		x	N	11.1	48.3497	79.0250	200
3511	x	x		x	N	33.1	48.5545	79.0383	169
3512	x				W	38.4	48.1635	79.5703	< 30
3513	x	x		x	SW	57.6	48.0072	79.6950	400
3514	x	x		x	W	63.1	48.2228	79.8555	92
3515	x	x		x	NW	44.9	48.5153	79.4684	74
3516	x				NW	64.9	48.4820	79.8078	42
3517	x				NW	37.9	48.3665	79.4977	unknown
3518	x	x	x	x	E	32.6	48.3095	78.6061	107
3519	x		x		E	61.9	48.3387	78.1941	< 30
3520	x		x		SE	62.6	47.9606	78.3043	< 30
3521	x				SE	78.8	47.6720	78.4031	unknown
3522	x	x	x	x	SE	73.2	47.8258	78.2824	106
3523	x				S	58.1	47.7548	79.2166	35
3524	x		x		SW	37.9	47.9603	79.2564	358
3525	x	x	x (3)	x (2)	SE	29.5	48.1366	78.6685	129
3526	x				SE	35.4	48.0419	78.6734	60
3527	x	x		x	E	15.2	48.2292	78.8142	< 30
3528	x	x	x	x	N	57.6	48.7489	78.8190	96
3529	x	x		x	N	80.8	48.9652	78.8641	147
3530	x	x	x	x	NW	91.7	48.9575	79.6546	144
3531	x	x			NE	29.5	48.4491	78.7557	< 30
3532	x	x		x	NE	23.2	48.3741	78.7578	178
3533	x	x	x (3)	x (3)	W	9.8	48.2475	79.1412	242
3534	x		x	x	W	8.6	48.2554	79.1296	166
3536	x		x (2)		NW	7.1	48.3075	79.0620	< 30
3537	x	x	x	x	SE	11.9	48.1713	78.9168	140
3538	x				S	9.6	48.1703	79.0268	< 30
3540	x	x	x (3)	x (2)	SW	11.6	48.1702	79.0998	249

*depth of peat to underlying mineral sediment in sequence sampled from flat part of peatland adjacent to hummock

Hall et al. (1996) (Table 4). The first two sequential extractions (Ch_3COONa and $Na_4O_7P_2$) selectively digested the labile phases and the last two (aqua regia and a nearly total multi-acid leach), the non-labile phases. Analysis was undertaken using inductively coupled plasma mass spectroscopy.

Analysis of ^{210}Pb, ^{226}Ra, and ^{137}Cs

Homogeneous portions of 22 samples from the tallest hummock sampled at site 3540 and 7 samples from a hummock at site 3525, including two sets of replicates, were analyzed at the National Water Research Institute, Burlington, Ontario, for ^{210}Pb. Using a method modified from Appleby and Oldfield (1978), the ^{210}Pb content of samples was derived from measurements of the activity of ^{209}Po, a closely related and more accurately measured decay product of ^{210}Pb (Turner and Delorme, 1996; Turner, 1999).

Peat was subsampled to 0.2 g and mixed with approximately 10 d/m/mL (disintegrations per minute per millilitre) of a previously prepared ^{209}Po spike. The peat was digested first in concentrated HNO_3 under reflux to destroy organic material, and later with two HCl treatments to remove any remaining traces of HNO_3. Polonium from the remaining solution was plated onto a finely polished silver disk used for the counting process in an alpha spectrometer; ^{209}Po was identified by its 4.88 MeV alpha particle and ^{210}Po, by its 5.305 MeV alpha particle. The ^{210}Po counts obtained from the spectrometer, measured as disintegrations per minute per gram, were compared to the ^{210}Po counts (of known activity) to determine the activity of ^{210}Po in the peat sample.

Seven peat samples from the site 3540 hummock were analyzed at Flett Research, Winnipeg, for ^{226}Ra activity in order to determine indirectly (using ^{222}Rn) background ^{210}Po activity. A peat sample of known weight was digested with HNO_3 and the residue purged with He at 200 mL/min for 1 h to remove any pre-existing radon. The remaining solution

Table 2. Concentration of Cu, Pb, Zn, Ca, and Ni in mineral sediments underlying peatland hollow sample sites.

Site number	Sector	Distance (km)	From (cm)	To (cm)	Sediment type	Lat (°N)	Long (°N)	Cu ppm	Pb ppm	Zn ppm	Ca %	Ni ppm
3501	SE	44.2	70	74	sand/gravel	48.083467	78.488317	5	2	<2	0.06	2
3503	W	20.7	175	198	gyttja	48.278866	79.289400	123	8	58	0.75	35
3503	W	20.7	198	210	gyttja	48.278866	79.289400	71	4	62	0.66	35
3507	SW	18.9	153	166	clay; blue grey	48.113200	79.160800	40	10	94	0.71	50
3508	S	18.4	98	100	silt; grey	48.089700	78.995100	60	4	94	0.45	76
3509	S	14.6			mineral sed; undiff.	48.128033	79.047433	68	90	76	0.09	5
3510	N	11.1			clay	48.349667	79.025000	50	8	80	1.29	42
3511	N	33.1	169	174	silty clay; grey	48.554517	79.038317	20	6	62	0.28	30
3513	SW	57.6	475	500	clayey silt; grey	48.007233	79.694967	32	8	72	3.71	43
3513	SW	57.6	450	475	clayey silt; grey	48.007233	79.694967	35	12	72	2.95	43
3514	W	63.1	92	100	mineral sed; undiff.	48.222800	79.855500	15	2	12	0.38	17
3515	NW	44.9	74	78	silt	48.515250	79.468400	30	14	60	0.60	25
3516	NW	64.9	42	70	sand	48.482000	79.807817	5	10	8	0.17	7
3519	E	61.9	30	40	mineral sed.; undiff	48.338650	78.194133	7	6	12	0.16	25
3522	SE	73.2	106	110	clay; grey	47.825800	78.282400	8	2	10	0.18	15
3523	S	58.1	30	36	silt/clay	47.754833	79.216600	14	6	24	0.43	21
3524	SW	37.9	350	358	clay; grey blue	47.960267	79.256400	69	4	92	0.90	46
3524	SW	37.9	358	375	clay; grey blue	47.960267	79.256400	31	10	78	0.64	43
3525	SE	29.5	129	132	silty sand	48.136617	78.668533	4	<2	6	0.16	6
3526	SE	35.4	83	90	sand	48.041900	78.673417	8	<2	22	0.25	18
3528	N	57.6	96	100	clay; grey	48.748867	78.819033	23	10	108	0.91	44
3529	N	80.8	140	150	mineral sed; undiff.	48.965183	78.864133	18	2	38	0.87	20
3530	NW	91.7	54	84	clay; blue	48.957450	79.654633	29	10	80	0.64	39
3531	NE	29.5	40	50	mineral sediment	48.449133	78.755683	6	<2	16	0.41	20
3532	NE	23.2	194	200	silty clay; blue	48.374050	78.757767	29	6	62	1.57	35
3533	W	9.8	238	242	clay; blue	48.247533	79.141150	31	4	94	1.20	34
3533	W	9.8	242	272	clay; blue	48.247533	79.141150	21	6	72	1.24	37
3534	W	8.6	198	200	clay	48.255367	79.129550	33	8	78	0.60	42
3536	NW	7.1	45	58	till	48.307500	79.061983	86	8	176	0.54	37
3537	SE	11.9	120	140	clay	48.171250	78.916817	32	6	56	0.72	35
3537	SE	11.9	140	150	clay	48.171250	78.916817	40	6	82	0.82	48
3540	SW	11.6	249	272	clay; blue grey	48.170233	79.099750	21	6	48	0.85	33

Note: <0.063 mm fractionof samples digested with aqua regia and analysed using the ICP-AES method

Table 3. Concentration of Cu, Pb, Zn, Ca, and Ni in new growth from feather moss growing on the hollow surface in 14 peatlands.

Sample number	Sample sector	Distance (km)	Lat (°N)	Long (°W)	Cu ppm	Pb ppm	Zn ppm	Ca pct	Ni ppm
97KFA3520fm	SE	62.6	47.960550	78.304250	10	10	44	0.29	3
97KFA3522fm	SE	73.2	47.825800	78.282400	9	21	265	0.34	6
97KFA3524fm	SW	37.9	47.960267	79.256400	15	14	83	0.35	2
97KFA3525fm	SE	29.5	48.136617	78.668533	12	12	173	0.27	2
97KFA3526fm	SE	35.4	48.041900	78.673417	12	14	77	0.21	2
97KFA3528fm	N	57.6	48.748867	78.819033	14	16	94	0.34	6
97KFA3529fm	N	80.8	48.965183	78.864133	8	6	70	0.31	3
97KFA3530fm	NW	91.7	48.957450	79.654633	6	4	42	0.36	3
97KFA3531fm	NE	29.5	48.449133	78.755683	11	12	39	0.36	2
97KFA3532fm	NE	23.2	48.374050	78.757767	17	26	76	0.49	2
97KFA3533fm	W	9.8	48.247533	79.141150	31	56	49	0.4	1
97KFA3534fm	W	8.6	48.255367	79.129550	66	75	87	0.38	3
97KFA3535fm	W	8.6	48.136617	78.668533	78	237	144	0.38	9
97KFA3537fm	SE	11.9	48.171250	78.916817	78	117	226	0.33	4
97KFA3540fm	SW	11.6	48.170233	79.099750	33	119	164	0.29	4

Note: Samples digested with aqua regia and analyzed using the ICP-AES method

Table 4. Sequential extraction scheme for peat hummock and hollow samples (*after* Hall et al., 1996).

Extraction step	Digestion method	Targeted mineral phases
1.	1 M sodium acetate (0.5 g/20 mL) for 2 hours at room temperature	easily extractable component (adsorbed and exchangeable material; carbonates, some phosphates)
2.	0.1 M sodium pyrophosphate (0.5 g/40 mL) for 1 hour at room temperature	soluble organic component (humic and fulvic component)
3.	Aqua regia digestion	refractory organic materials; sulphides; crystalline iron oxides (e.g. hematite, goethite, magnetite)
4.	Near total multi-acid digestion	resistant mineral phases; residual crystalline fraction; (some refractory crystalline material such as chromite may not be digested)

was set aside for at least four days to allow accumulation of measurable amounts of radon, then analyzed using a method devised by Mathieu et al. (1988); the concentration of radium was calculated.

Ten samples from each of the site 3525 and 3533 hummocks and twelve samples from the site 3540 hummock were analyzed for ^{137}Cs at Flett Research. Peat samples were dried overnight at 60°C and placed in 56 mm diameter aluminium foil planchettes, compressed to about 2000 PSI (14 MPa) and their height was measured. Each planchette was placed on a 3 in. by 3 in. (7.62 cm by 7.62 cm) NaI(Tl) gamma detector contained within 2 in. (5.08 cm) of lead shielding. The gamma spectrum was acquired for a minimum of 24 h. Counting efficiency was calculated by comparing results with a graded height series of ^{137}Cs spiked clay standards (NBS) of the same diameter as the samples. The signal was acquired using a Canberra 8180 MCA with a 1000 channel window.

Annual vertical accumulation rate

An average annual vertical accumulation rate at the hummock surface was estimated by observing changes in growth direction of individual *Sphagnum* plants caused by pressure from the snow cover, after a method developed by Parkinen and Tolonen (1977) (Kettles and Bonham-Carter, 2002). It was possible to distinguish and measure one or two annual increments on the uppermost part of 59 *Sphagnum* plants extracted from nine of the reference cores, for a total of 93 individual measurements (Kettles and Bonham-Carter, 2002). The 93 values were then averaged to obtain a mean annual rate of vertical growth at the hummock surface.

Peat bulk density, ash content, and colour determinations

Hummock and hollow peat samples were assigned a laboratory number, coded using a Munsell soil colour chart (Munsell Color Company, 1971), weighed, and oven dried at 37°C. The dried samples were reweighed and the bulk densities were calculated (Kettles and Dion, 2000; Kettles and Bonham-Carter, 2002). The ash content of selected peat samples from the 1997 sampling had been determined previously after burning at 500°C (Kettles and Dion, 2000).

Scanning electron microscope analysis

Ash remaining from the ash-content analysis of eight hummock and hollow samples from site 3540 (12 km from the smelter) was mounted on aluminium scanning electron microscope (SEM) stubs using double-sided carbon tape. Scanning electron microbeam images and X-ray spot detection chemistry were generated using a Cambridge S-360 SEM connected to an energy dispersive X-ray spectroscopy beam (Oxford-Link eXL11 EDS). Digital TIFF backscattered electron images were captured at various magnifications.

RESULTS

Geochemical and other data for peat hummock and hollow samples

Geochemical and other data for peat samples are included in the GIS database that is included on the CD-ROM. Sample and site descriptions, the results of ICP-AES analysis after aquaregia digestion for 23 elements including Cu, Pb, Zn, Ni, and Ca, and, where available, bulk density, ash content measurements, and Munsell colour information are presented for 1) a total of 338 peat hummock profile samples (including surface growth) for the 15 sites with the tallest and best developed hummocks, 2) a total of 272 peat hollow profile samples (including surface growth) from 20 sites, 3) hummock surface growth from an additional 22 peatland sites, and 4) hollow surface growth from an additional 2 peatland sites (*see* Table 1). Files with duplicate and control data and Thompson-Howarth plots for the aqua regia–ICP-AES data accompany the database. Also listed in the database are the data from the sequential extraction analysis of 20 hummock and 4 hollow peat samples.

Physical properties of hummock and hollow peat

Sphagnum hummocks in the Rouyn-Noranda area ranged in height from 35 to about 60 cm and were usually oval or subrounded. In most hummocks, *Sphagnum* plants were almost intact to depths of about 30 cm, with the uppermost 10 cm being composed of living or recently dead, light-coloured plants. Samples collected above 30 cm had low bulk density

(0.01–0.02 g/cm³) and were yellow, yellowish brown, or light olive-brown. The most common species identified from the hummock surface samples were *Sphagnum russowii*, *S. fuscum*, *S. capillifolium*, and *S. magellanicum* (D. Bastien, Botalys Ltd., pers. comm., 1998). Below depths of 25 to 30 cm, the hummock peat was brown to dark brown and consisted of moderately decomposed materials, including, in places, sedge peat. Bulk density was generally about 0.03 to 0.05 g/cm³ in *Sphagnum* peat and higher in sedge peat near the base. Ash content of most *Sphagnum* samples from the hummocks ranged from 0.5 to 5% (Kettles and Dion, 2000).

In the hollows, there was more variation in the decomposition state, bulk density, and colour of the *Sphagnum* or other plant material composing the uppermost 10 to 15 cm of the sequence. Samples were dark reddish or yellowish brown to very dark brown and had bulk density values that ranged from 0.01 to 1.00 g/cm³. Below 10 to 15 cm, peat samples were dark brown to black and composed of partially to well decomposed *Sphagnum* or sedge with bulk density values greater than 1.00 g/cm³. The ash content of the hollow samples was more varied, with values ranging from 1.5% to more than 30% and averaging 10% (Kettles and Dion, 2000).

Distribution of metals in vertical hummock and hollow profiles

When geochemical profile data were plotted for hummocks sampled to depths of over 50 cm and the associated hollow sequences from peatlands located 7 to 92 km from the Horne smelter, a strong and consistent pattern of metal distribution emerged (Kettles and Dion, 2000; Kettles and Bonham-Carter, 2002). Figure 3 shows the distribution patterns for smelter-related metals (Cu, Pb, and Zn) and, for comparison, for Ni (Ni is emitted in low concentrations) in profiles from the tall hummocks. Figure 4 shows metal distribution in the adjacent hollows at three of the four sites and in another hollow 63 km southeast of the smelter. In the hummock profiles, Cu, Pb, and Zn levels are consistently low in the uppermost 30 cm and also below depths of 60 cm. Between depths of 35 and 60 cm, a pattern is seen first of systematic increase and then decrease of the levels. This pattern is most pronounced within 35 km of the smelter and, although weak, is still discernible in the hummock sampled at 63 km (Fig. 3; Kettles and Bonham-Carter, 2002) and in others to the maximum distance of 92 km (Kettles and Dion, 2000).

The metal distribution pattern for peat from the hollows is similar to that for peat from the hummocks but is compressed over a lesser depth in the uppermost part of the hollows (Fig. 4). Concentrations of smelter-related metals systematically increase and decrease with increasing depth in the uppermost 25 cm and are low below 25 cm. In places, Cu, Pb, and Zn are also enriched in basal peat from the hollows (not shown), although to a much lesser extent than in hollow surface peat close to the smelter. In contrast, no systematic variation in the distribution pattern of Ni was found in the hollows or hummocks sampled.

At three of the sites, geochemical profiles were generated for two or more separate hummocks and hollows in order to test the intrasite variation. The results of these analyses are shown in Figure 3. For hummock profiles, there was little observable intrasite variation for Cu and a small amount of variation for Pb and Zn. Smelter-related metal distribution varied more in hollow profiles from the same site, but the trends were strong and similar. No discernible relationship was recognized between the patterns of metal distribution in the hummock peat and the position of the water table or the nutrient status of the peatland. The consistently low levels of Ca in peat at sites 3525, 3520, and 3522 (Fig. 3, 4) indicate a nutrient-poor (bog) environment for peat formation. In contrast, at sites 3533 and 3540, the higher levels of Ca in the hollows and peat hummocks below 50 cm indicate that these hummocks developed in a more nutrient-rich peatland (poor fen to fen).

Physical record of metal-bearing particulates in peat hummocks and hollows

Ashed peat from a hummock at site 3540 (12 km southwest of the smelter) at sample intervals of 4.5 cm, 20 cm, 39 cm, 47 cm, and 55 cm (mid-depths) and from the adjacent hollow at 41 cm, 158 cm, and 230 cm were analyzed using the SEM. In the samples from the hummock (Fig. 5a, b, c, d, e) and the uppermost sample from the hollow (not shown), angular to subrounded or spherical particles of metal-bearing dust with diameters ranging from 1.5 to 50 µm were observed. The angular dust took the form of iron-enriched particles with pitted or layered surfaces (Fig. 5b, c, d), one of which was rod shaped (Fig. 5c). The spherical dust had plated, tubular, or etched surfaces (e.g. Fig. 5c, e) and appeared similar to particles observed in humus (Knight and Henderson, 2005). The only metal-bearing particles detected at depth in the hollow contained S, Ca, and Zn residing within the plant matter cells (Fig. 5f).

Regional distribution of smelter-related metals in peat

To examine more closely regional-scale patterns of metal distribution in peat, Cu, Pb, Zn, and Ni concentrations in peat from the hummock surface (approximately 0–3 cm), peat from the hollow surface (approximately 0–5 cm), and feather moss from the hollow surface were plotted against distance from the smelter and the best-fit trendlines were determined (Fig. 6; Table 5). Prior to plotting, the samples were divided into two groups, on the basis of wind direction (*see* wind rose diagram in Fig. 1). The first group consisted of 'upwind' samples collected southwest, west, and northwest of the smelter and the second, of 'downwind' samples collected north, northeast, east, southeast, and south of the smelter. Hummock surface data were sufficient to generate separate fits for the upwind and downwind models.

For Cu, Pb, and Zn in hummock and hollow surface growth and Cu and Pb in feather moss, an inverse relationship was noted for the smelter-related metals, i.e. the element concentration decreases with distance from the smelter on a log-log plot. Near the smelter, concentrations were two to
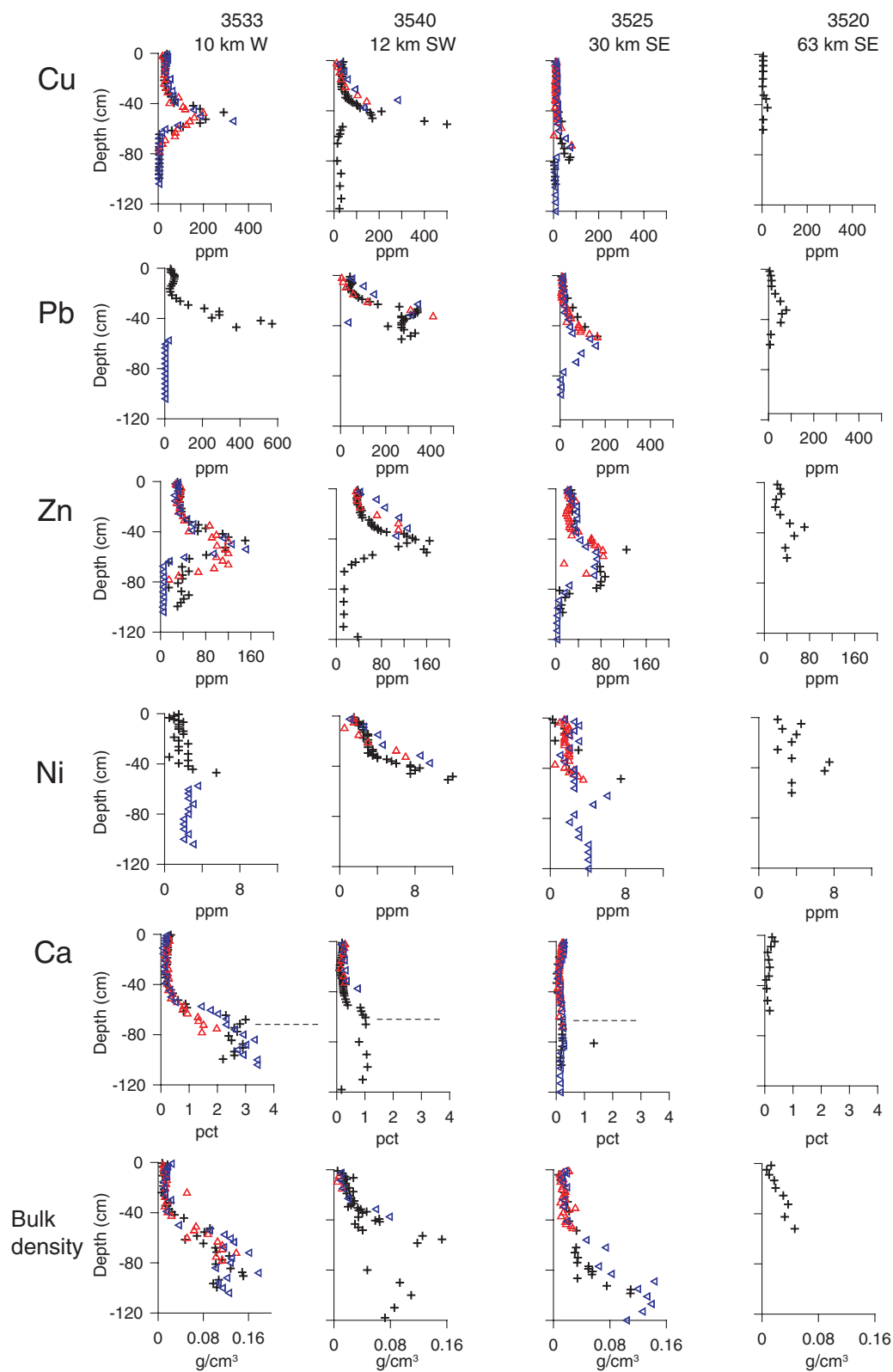
Figure 3. *Distribution of Cu, Pb, Zn, Ca, and Ni in profile samples from tall hummocks at four peatland sites. Samples were analyzed by ICP-AES after HNO_3–$HClO_4$ digestion. At three of the sites, geochemical profiles were generated for two or more separate hummocks, indicated using different symbols. The dashed line on the Ca graphs represents the position of the water table.*
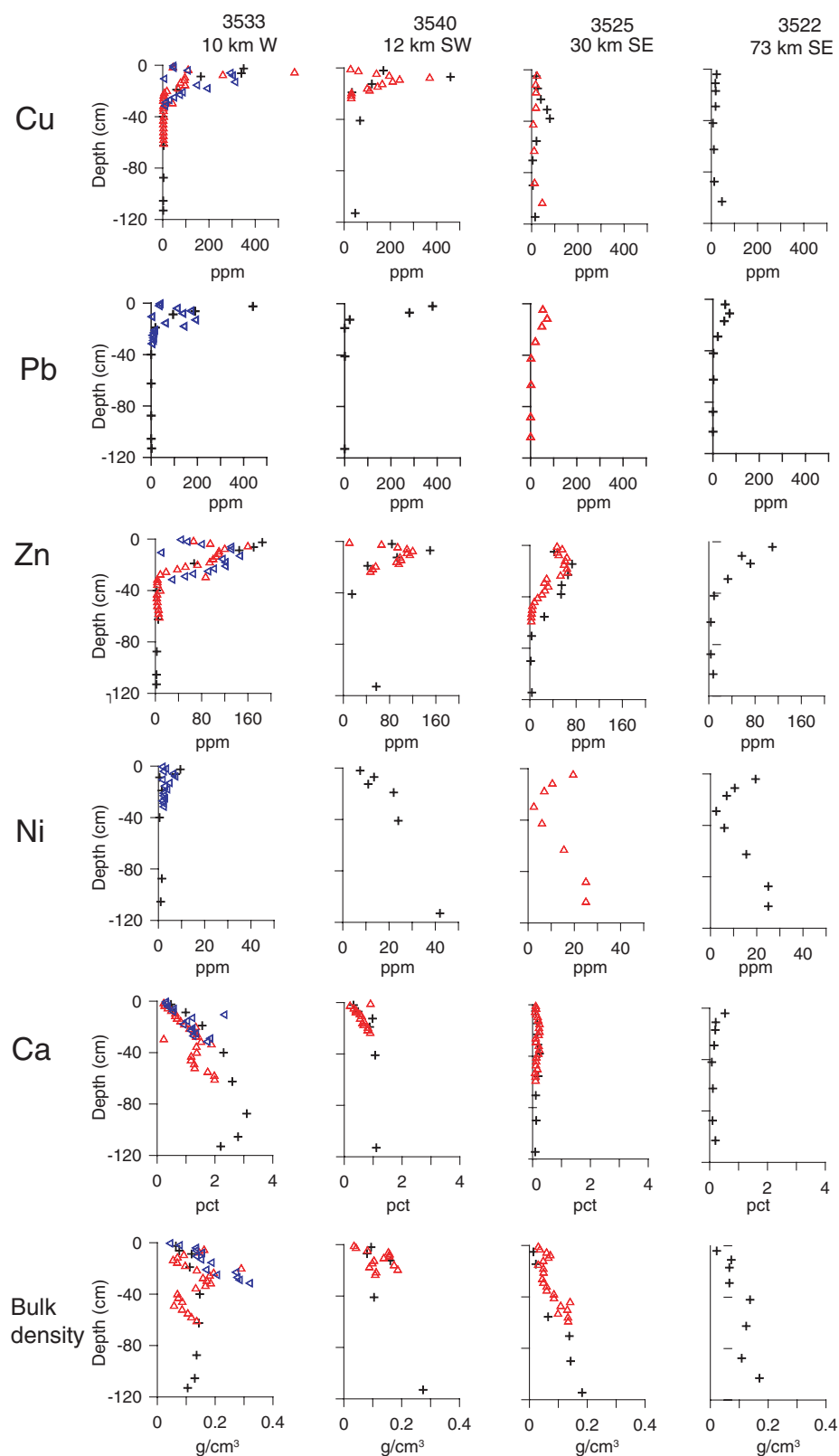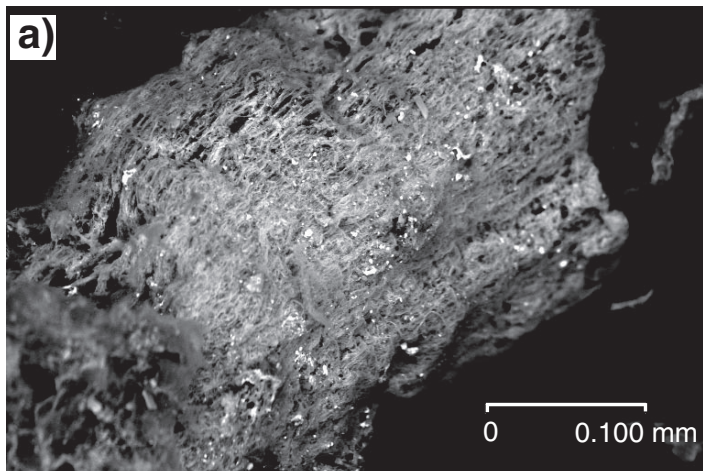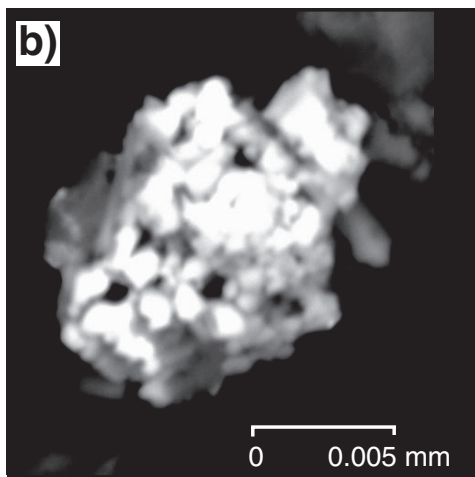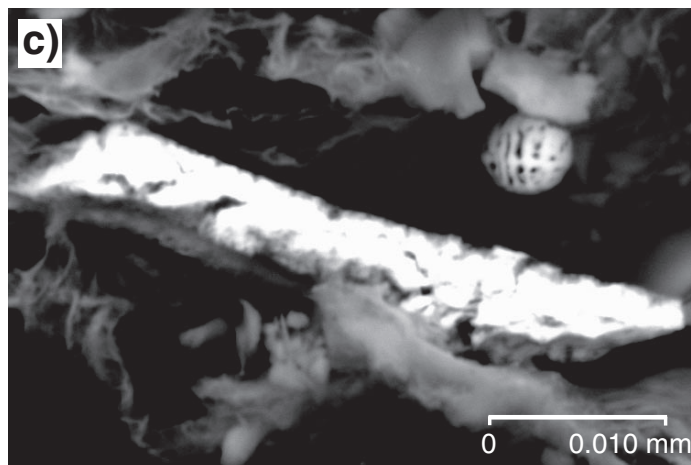
Figure 4. Distribution of Cu, Pb, Zn, Ca, and Ni in profile samples from the uppermost 2 m of hollow sequences at four peatland sites. Samples were analyzed by ICP-AES after HNO_3–HCl digestion. At three of the sites, geochemical profiles were generated for two or three hollow sequences, indicated using different symbols.

hummock 4.5 cm

hummock 15–20 cm

hummock 30–39 cm

hummock 44–50 cm
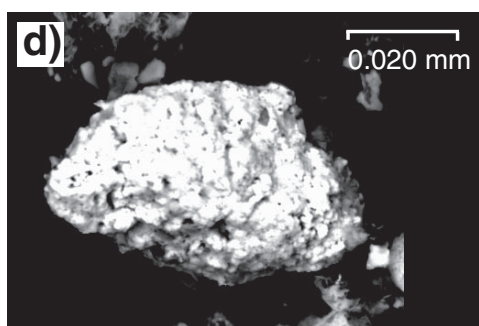
hummock 44–50 cm
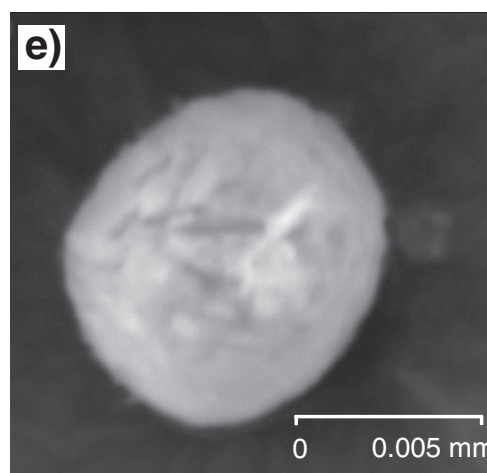
hollow 220–240 cm
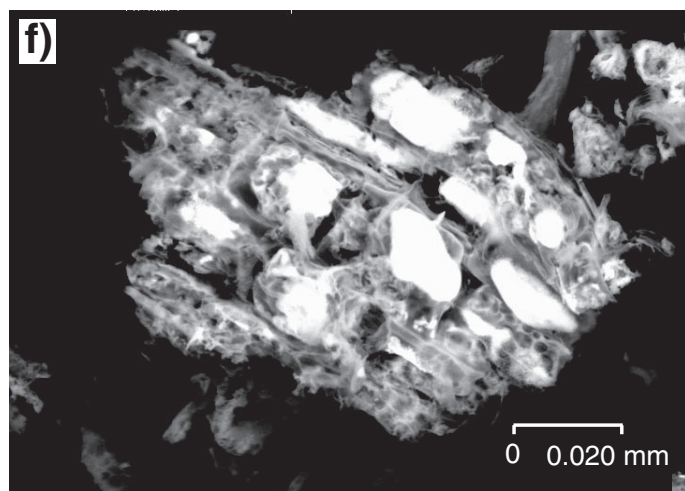
Figure 5. *Backscattered electron images from the SEM analysis of ashed peat samples from a hummock and hollow at site 3540, 12 km from the smelter.* ***a)*** *Metal-bearing particles (light-coloured specks) within a mass of organic matter at 4.5 cm in the hummock;* ***b)*** *iron-enriched particles from 15 to 30 cm in the hummock;* ***c)*** *rod-shaped and spherical particles, enriched in iron, from between 30 and 39 cm in the hummock;* ***d)*** *and* ***e)*** *iron-enriched spherical particles from between 44 and 50 cm in the hummock;* ***f)*** *particles of sulphur, calcium, and zinc residing within the plant matter cells between 220 and 240 cm in the hollow.*
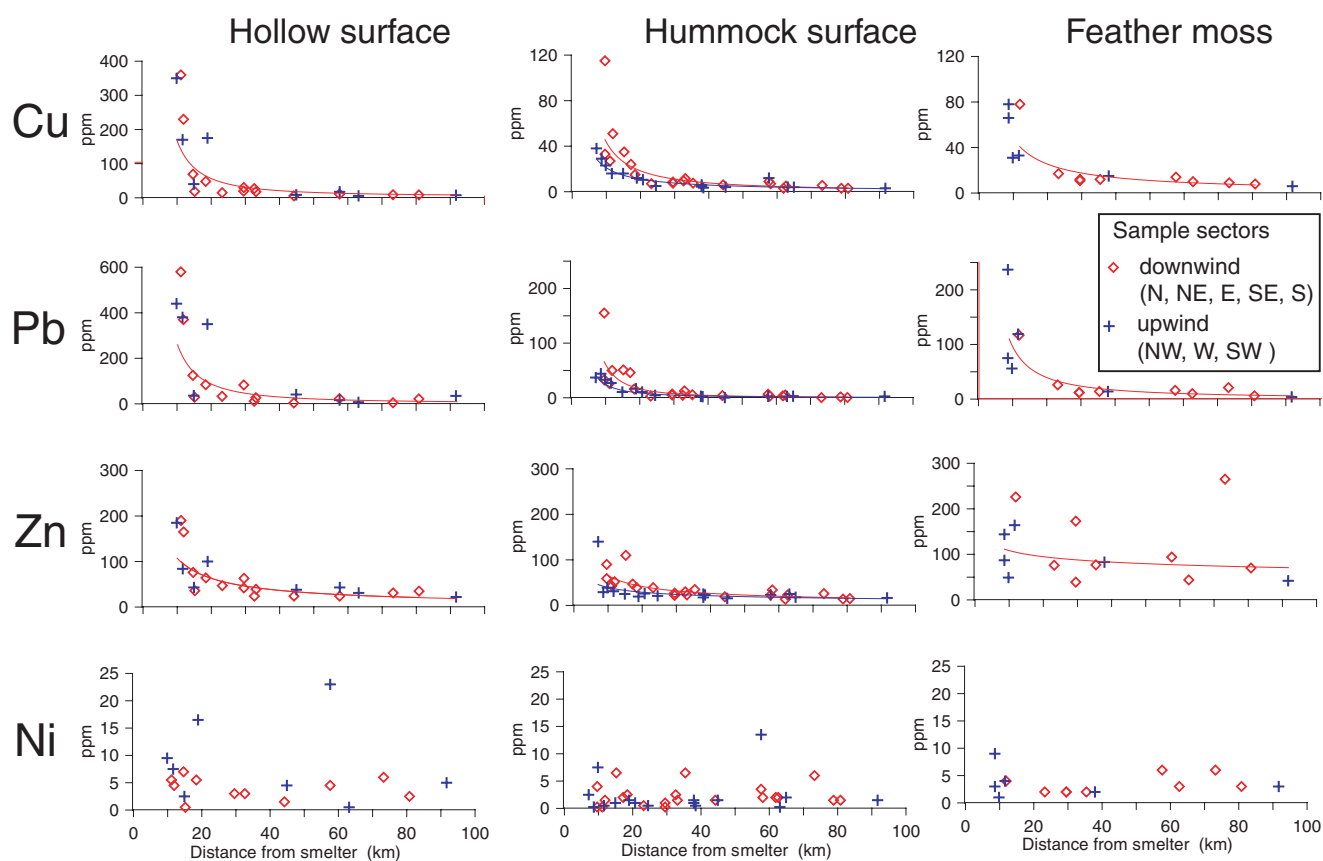
Figure 6. *Distance vs. element concentration for hummock surface, hollow surface, and feather moss samples, grouped according to wind direction. Equations for the trendlines shown are presented in Table 5. Sufficient hummock surface data were collected to fit trendlines to the 'upwind' and 'downwind' groups of data.*

Table 5. Equations for best-fit trendlines in distance vs. element concentration for hummock surface, hollow surface, and feather moss samples at peatland sites between 7 and 92 km from the smelter.

Element	Variable	Hummock surface – downwind	Hummock surface – upwind	Hollow surface – all sites	Feathermoss – all sites
Cu	number	21	16	22	15
	equation	$\ln(y) = -1.25 \ln(x) + 6.64$	$\ln(y) = -0.92 \ln(x) + 5.16$	$\ln(y) = -1.63 \ln(x) + 8.86$	$\ln(y) = -0.91 \ln(x) + 5.95$
	coef. det. (R^2)	0.83	0.79	0.75	0.84
Pb	number	21	16	21	15
	equation	$\ln(y) = -1.90 \ln(x) + 8.50$	$\ln(y) = -1.50 \ln(x) + 6.63$	$\ln(y) = -1.59 \ln(x) + 9.20$	$\ln(y) = -1.25 \ln(x) + 7.39$
	coef. det. (R^2)	0.76	0.62	0.60	0.80
Zn	number	21	16	22	15
	equation	$\ln(y) = -0.66 \ln(x) + 5.70$	$\ln(y) = -0.44 \ln(x) + 4.70$	$\ln(y) = -0.74 \ln(x) + 6.39$	$\ln(y) = -0.18 \ln(x) + 5.13$
	coef. det. (R^2)	0.70	0.48	0.64	0.06
Ni	number	21	16	21	15
	equation	$\ln(y) = 0.41 \ln(x) - 0.94$	$\ln(y) = 0.09 \ln(x) - 0.12$	$\ln(y) = -0.18 \ln(x) + 1.72$	$\ln(y) = 0.03 \ln(x) + 0.98$
	coef. det. (R^2)	0.09	0.00	0.01	0.00

four times higher in hollow surface material than in hummock surface growth and feather moss. The element levels in each dropped rapidly out to about 25 km; beyond this, they decreased gradually to background levels. The effects of wind were evident, especially in the case of hummock surface material, for which downwind samples had higher metal concentrations than upwind samples both near the smelter and farther away. Using the 1997 hummock surface-growth data and an empirical model fitted to the data, distances to background levels were calculated to be 50 to 55 km for Cu, Pb, and Zn for downwind samples and 40 km for Cu and Pb and 12 km for Zn for upwind samples (Kettles and Bonham-Carter, 2002). For Zn in feather moss and Ni in all three types of material, no discernible relationship was recognized between concentrations and distance.

Hummock surface data were sufficient to show concentration levels in map view (Fig. 7). These show approximately circular patterns of elevated smelter-related metal levels around the smelter (skewed somewhat because of the prevailing wind pattern), which decrease with radial distance eventually to approach a background value far away from the smelter. Nickel, which is present in the emissions only in trace amounts, does not show such a smelter-centred pattern.

Metal residence sites in peat

Figure 8 shows Cu, Pb, Zn, and Ni data from the sequential leaching of peat samples from selected sites plotted as pie charts along with the geochemical profiles (from ICP-AES analysis after HNO_3–$HClO_4$ digestion) for the selected hummocks and hollows. Three or four samples were analyzed
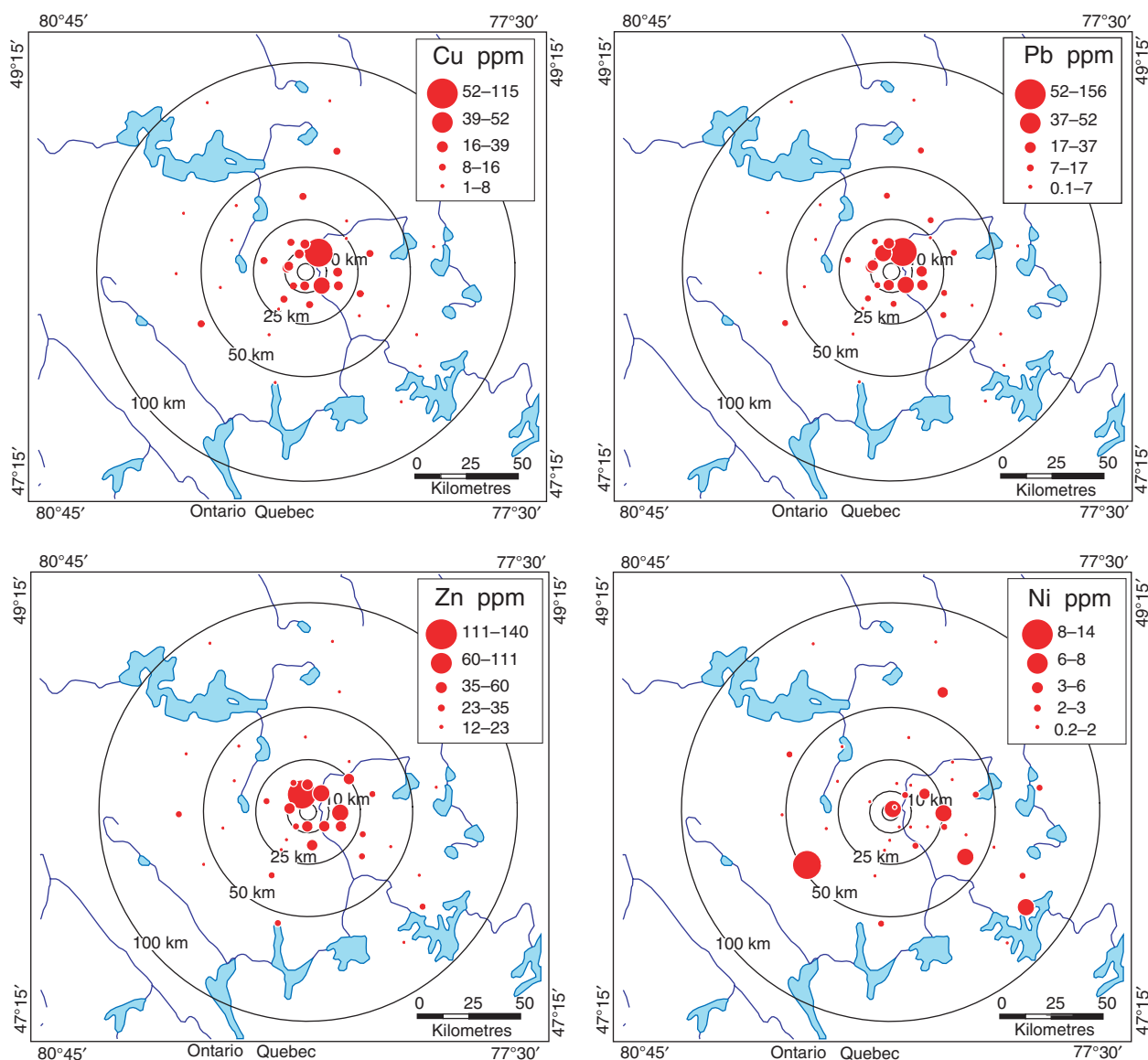

Figure 7. Spatial variation of Cu, Pb, Zn, and Ni concentrations in hummock surface growth samples around the smelter. Dot sizes are proportional to elemental concentrations.
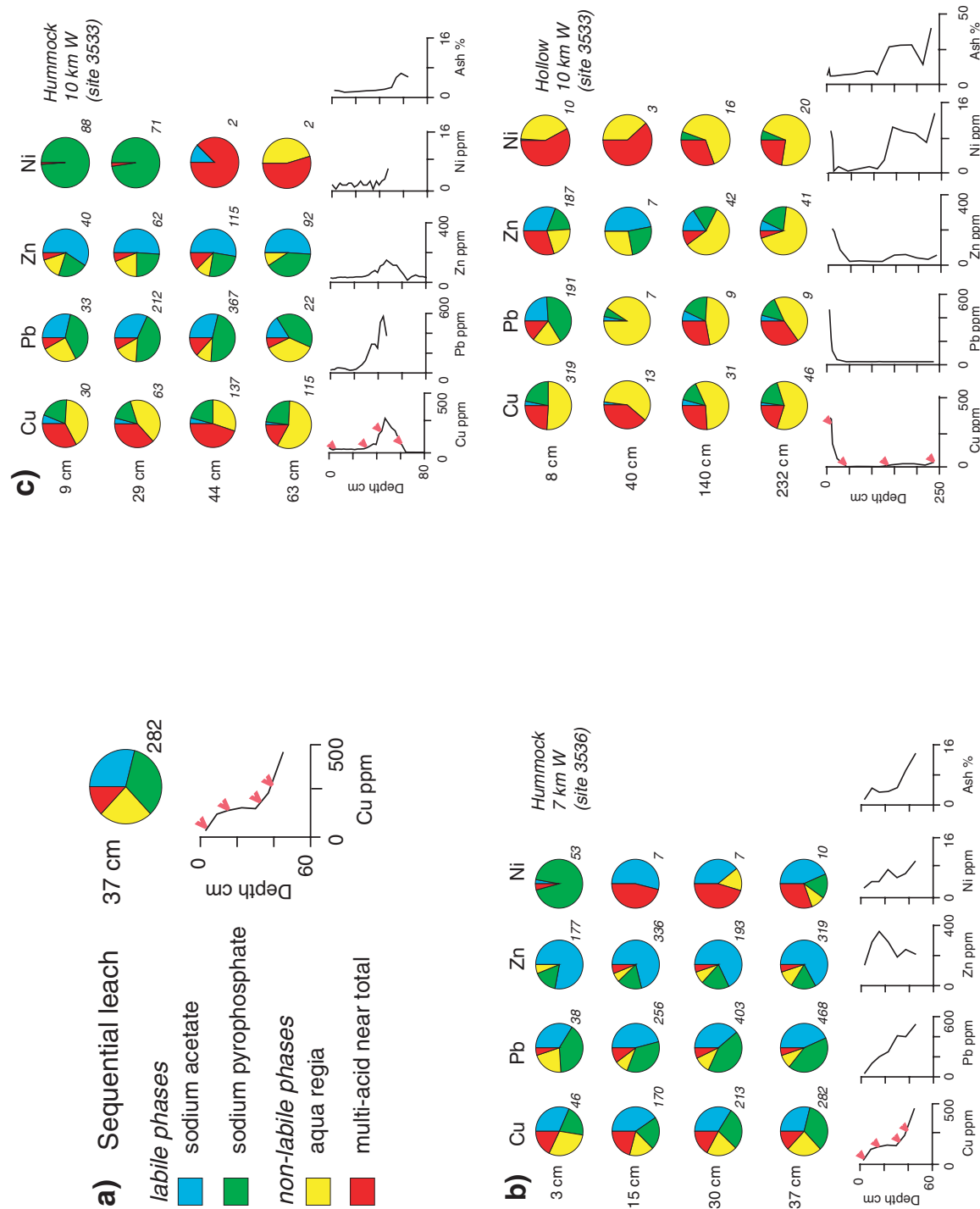
Figure 8. *Metal residence sites in peat hummock and hollow samples.* ***a****) Legend for Figure 8b to f. Sequential extractions are based on Hall et al. (1996) and are explained in Table 4. Extractants were analyzed using the ICP-MS method. The four-colour-coded segments of the pie diagram show the relative proportion of total metals extracted by the four leaches in samples selected for analysis from different depth intervals. The labile phases were selected with 1) CH_3COONa and 2) $Na_4O_7P_2$ and the non-labile phases, with 3) aqua regia and 4) a multi-acid nearly total leach. The sum of the metal extracted is shown in italics in parts per million (ppm); when concentrations were below detection limit, they were set arbitrarily at zero. Geochemical profiles, based on ICP-AES analysis after an $HCl–HNO_3$ digestion, and ash content are also shown (after Kettles and Bonham-Carter, 2002). Red arrows indicate the position of samples selected for sequential extraction analysis.* ***b****) Site 3536 hummock, 7 km west of the smelter;* ***c****) site 3533 hummock and hollow, 10 km west of the smelter.*
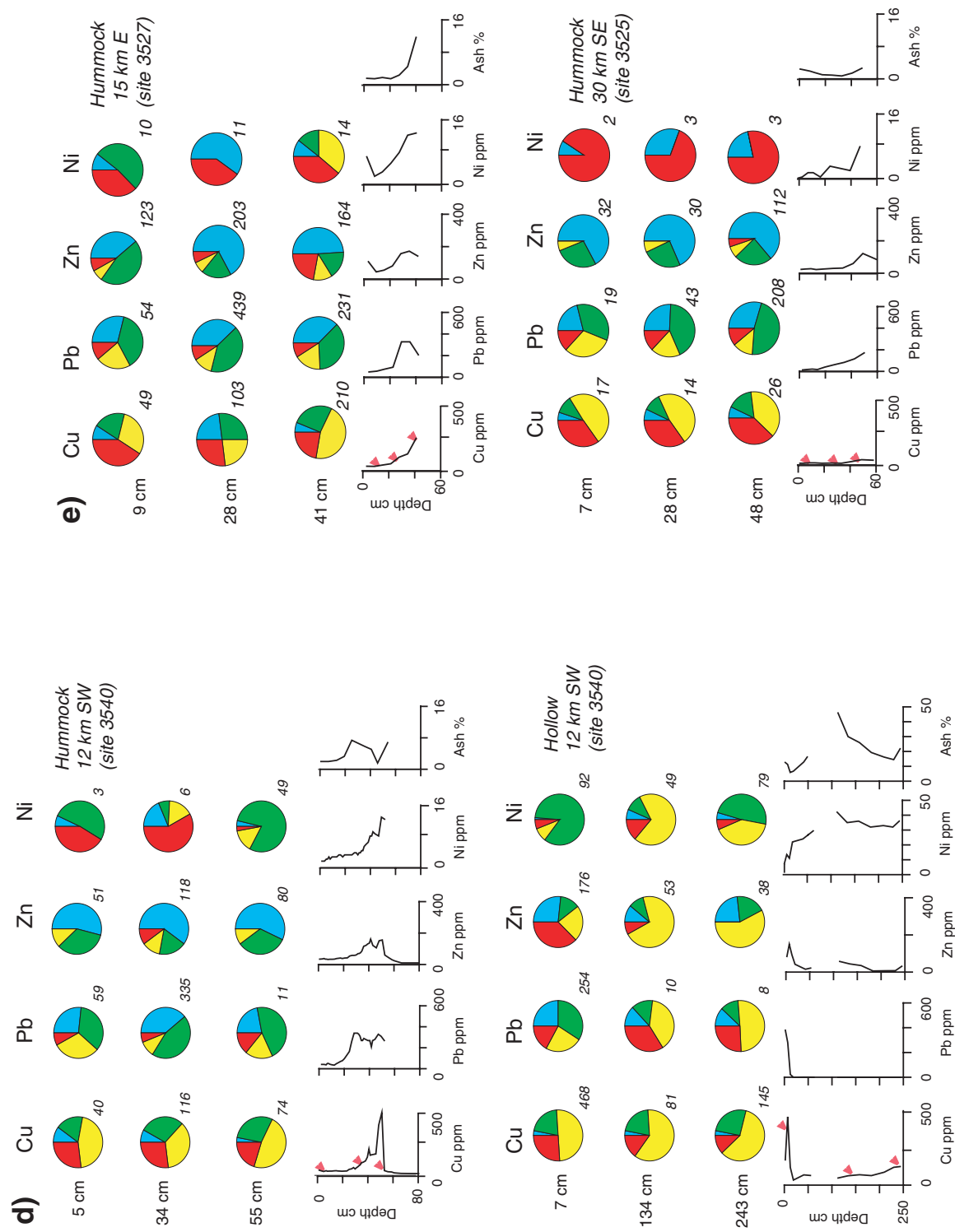
Figure 8. (cont.) d) *site 3540 hummock and hollow, 12 km northwest of the smelter;* **e)** *site 3527 hummock, 15 km east of the smelter;* **f)** *site 3525, 30 km east of the smelter.*

from progressively deeper depths in the hummocks located 7, 10, 12, 15, and 30 km from the smelter and from the hollows in the peatlands 10 and 12 km from the smelter. Results shows that the relative proportion of metals in the different components of the peat sample is consistent at sites 10 km and more from the smelter. At all depths in these hummocks, only about 33% of the Cu resides in the labile phases (CH_3COONa and $Na_4O_7P_2$), whereas about 66% of the Pb and about 75% of the Zn reside in the labile phases. Within the labile fraction, about 66% of the Zn was easily extracted (CH_3COONa), compared to less than 50% of the Pb and about 10% or less of the Cu. In peat from the hummock closest to the smelter (7 km), the pattern of metal apportionment was different. In the samples from 7 km, more than 50% of the Cu and 80 to 90% of the Pb and Zn were labile and retained primarily in the easily extracted phases.

The patterns of Cu and Pb apportionment in the near-surface samples from the two hollows were similar to those from the hummocks. Zinc distribution patterns at the hollow surface were transitional between those of the hummocks and those of peat collected at depth in the hollow. In the more decomposed peat from deeper in the hollow, about 66% or more of the smelter-related metals were non-labile (aqua regia and multi-acid nearly total phases). In contrast to the smelter-related metals, the apportionment of Ni varied in the hollow samples and in the hummock samples.

Analysis of ^{210}Pb, ^{226}Ra, and ^{137}Cs

No systematic pattern was recognized of decreasing ^{210}Po activity with increasing depth in the hummock profiles from sites 3540 and 3525, indicating unsuitable conditions for peat dating using the ^{210}Pb method (Fig. 9). Seven samples from the site 3540 hummock were further analyzed for ^{226}Ra activity in order to determine background levels of ^{210}Pb activity. Low levels of ^{226}Ra activity, ranging from 0.28 to 1.08 d/m/mL, indicate that the background levels of ^{210}Pb are low in these samples and that most of the ^{210}Pb activity is due to atmospheric input (G. Flett, pers. comm., 1999).

The profiles of ^{137}Cs activity for the sites 3533, 3540, and 3525 hummocks show peaks at depths of 45 to 50 cm (Fig. 9). The highest ^{137}Cs activity is expected in surficial materials that formed during the time of maximum nuclear testing (1963). In the case of Rouyn-Noranda, the time of maximum testing coincides with the period of maximum smelter emissions (Fig. 9). In the three hummocks analyzed for ^{137}Cs, the ^{137}Cs peak occurs in that part of the peat hummock profile with high concentrations of smelter-related elements.

DISCUSSION

Metal accumulation within peat hummocks and hollows

Peat hummocks and hollows all show a consistent pattern of smelter-related metal variation with depth, with the levels of enrichment decreasing with increasing distance from the smelter. In the geochemical profiles, metal levels first increase then decrease systematically with increasing depth over the uppermost 60 cm of the hummock and 25 cm of the hollow. The differences in the depths of enrichment are thought to reflect the higher vertical accumulation and lower decomposition rates that characterize peat in hummocks compared to hollows (Johnson et al., 1990; Ohlson and Dahlberg, 1991; Johnson and Damman, 1993). In a study of Swedish peatlands, Ohlson and Dahlberg (1991) calculated vertical accumulation rates in hummocks and hollows by measuring, on small pine trees growing on hummocks and hollows, the vertical distance between the stem base and the peat surface and counting the tree rings at these two points on the excavated tree. They determined 1) that the average depth at which peat from *Sphagnum fuscum* hummocks was 25 years old ranged from 15 to 35 cm and 2) that 25 to 100 year old peat in the hummocks occurred at twice the depth as peat of similar age found in the peatland hollow. The pattern of increasing and decreasing smelter-related metal concentrations with increasing depth from the surface is similar in the hummocks and hollows in the Rouyn-Noranda area, but is compressed over a depth of 25 cm in the hollows compared to about 60 cm in the tallest hummocks. These differences are consistent with the differences in the growth patterns of hummock and hollow species determined from the Swedish study.

In the Rouyn-Noranda area, *Sphagnum* in the hummocks is loose and poorly decomposed and has low bulk density. Except very near the surface, *Sphagnum* or other plant material in the hollows was more decomposed and its bulk density was commonly two or more times higher. Although no near-surface peat from the hollows was dated, peat in the uppermost tens of centimetres in the hollows likely formed over a much longer time period than peat at similar depths in the hummocks. As a result, peat from hummocks generates more highly resolved geochemical records than peat from hollows. Each 1 to 2 cm thick vertical segment in the hummock sample profile represents a short enough period of time so that, when it is analyzed, it reveals smaller scale changes in metal distribution in the resulting geochemical profile.

Estimating the age of hummock peat

To evaluate the distribution of metal with depth in hummock profiles in relation to smelter history, it is necessary to know the age of the peat that accumulated in the hummock. Historical trends in atmospheric deposition of airborne pollutants have been reconstructed in detail using metal profiles through ombrotrophic peat accumulations and radionuclide-derived chronologies (e.g. Shotyk et al., 1998; Renberg et al., 2000). Hummock peat samples from sites 3533 and 3540 were analyzed using the ^{210}Pb method in an attempt to produce detailed chronological records for the hummock sequences from these sites.

Lead-210 is a naturally occuring radioactive element that is part of the ^{238}U decay series (Faure, 1986; Flett Research, 2001). Included in the ^{238}U series is ^{226}Rn, which produces the radioactive inert gas ^{222}Ra. Low but fairly constant quantities of radon gas produced at the soil surface–air contact escape to the atmosphere before the radon decays to the next
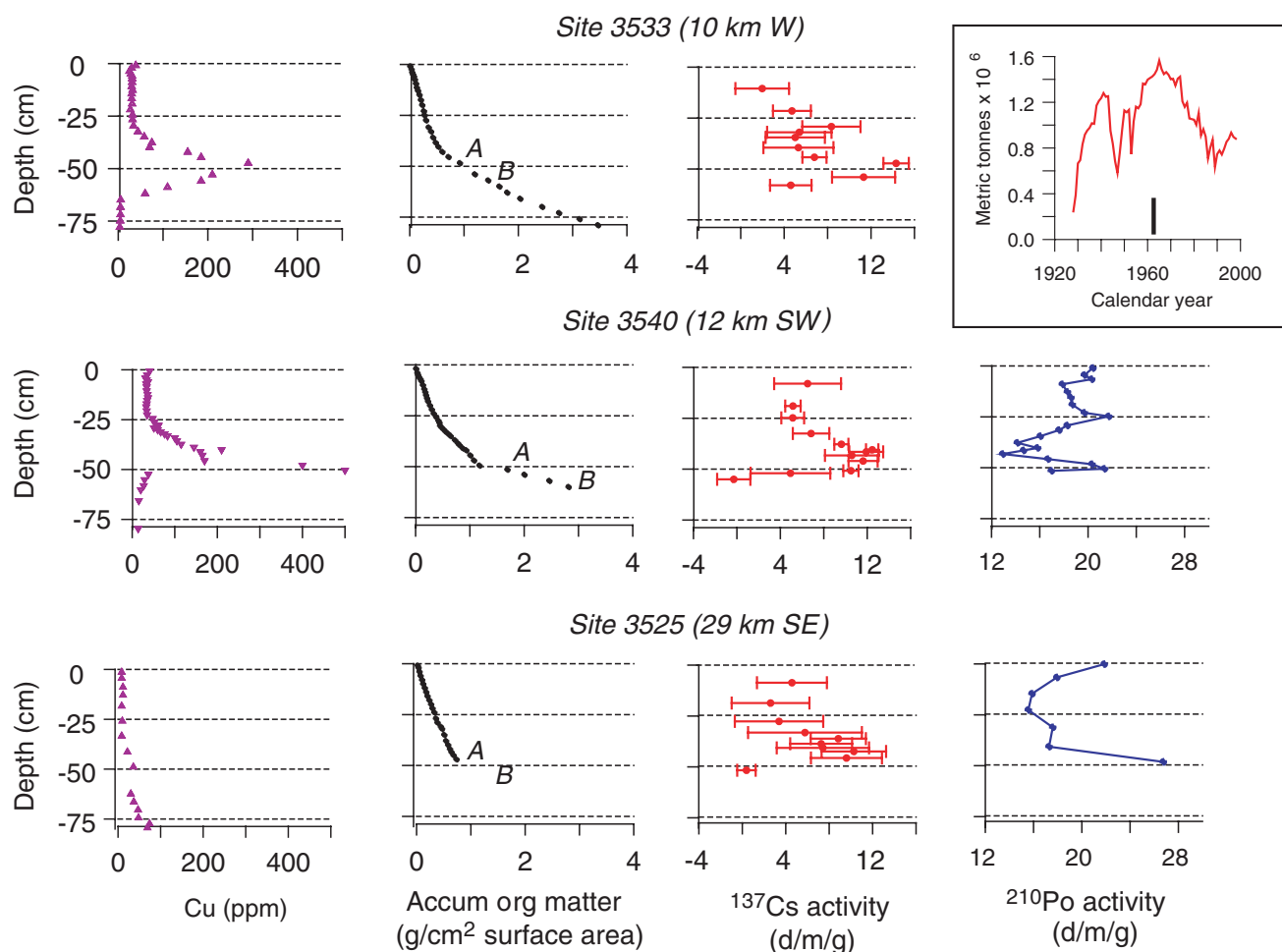
Figure 9. Copper distribution (ppm), accumulated organic matter with depth, ^{137}Cs activity, and [210]Po activity for hummock samples from sites 3533, 3540, and 3525. The ^{137}Cs and [210]Po activity was measured in disintegrations per minute per gram (d/m/g). Copper content (ppm) was determined from ICP-AES analysis after HNO_3–HCl digestion (after Kettles and Bonham-Carter, 2002). Smelter particulate emission levels between 1927 and 2000 (Noranda Mines, unpub. data, 1996) are shown top right. The estimated organic matter cumulative accumulation in 73 years, based on average rates for Sphagnum balticum *(A) and* Sphagnum fuscum *(B) hummocks from Wallen and Malmer (1995), are 0.72 and 1.46 g/cm² of surface area, respectively (after Kettles and Bonham-Carter, 2002).*

non-volatile element in the decay series. Within the atmosphere, [222]Ra decays to [218]Po, which falls to the surface in dust and rain and later decays to [210]Pb (half-life of 22.3 years). The ^{210}Pb becomes permanently fixed onto sediment particles or organic matter, where it decays to the more easily measured [210]Po, coming into secular equilibrium with ^{210}Pb within two years.

Peat also contains ^{210}Pb produced from the decay of the [226]Ra retained in the soils and transported by groundwater and surface water (Flett Research, 2001). The watershed-derived [210]Po tends to be of constant activity throughout the length of the core and represents the background or 'supported' [210]Pb.

In sufficiently long peat cores, [210]Po activity decreases with depth to a consistent low level (Clymo et al., 1990; Appleby and Oldfield, 1992). This low-level activity is

subtracted from the total [210]Po activity and the difference or 'unsupported' [210]Po is used to determine peat ages. The data for the hummock profile samples from sites 3533 and 3540 did not show an exponential decay pattern of [210]Po with increasing depth (Fig. 9) and, as a result, it was impossible to calculate the age of peat in the samples from these sequences. These results differed from those obtained for a northern Ontario peatland, where profile samples collected from a hummock of *Sphagnum* peat with higher bulk density (about 0.05 g/cm³), analyzed at the same laboratory, produced data that showed an exponential decay pattern of [210]Po with increasing depth (Turner and Kettles, 2000; Kettles et al., 2000).

Other researchers have reported atypical decay curves and, as a result, the reliability of the ^{210}Pb method for dating peat has been questioned. Norton et al. (1997) described two hummock peat cores from Maine that had nearly constant

^{210}Pb activity down to the water table; they interpreted this pattern as resulting from comparable rates of biological accumulation and decay and radioactive decay. Disparate patterns have also been attributed to postdepositional mobility of ^{210}Pb caused by water-table fluctuations or other water movement (Damman, 1978; Urban, 1990). Vile et al. (1999) experimentally evaluated lead mobility and the chemical forms in which lead is stabilized in peat profiles and, in contrast to the studies critical of ^{210}Pb dating, interpreted their results as lending credence to ^{210}Pb dating. Mackenzie et al. (1997) also determined that ^{210}Pb chronologies in Scottish ombrotrophic peat in contrasting locations coincided with historical trends in known lead input. The reasons for uncharacteristic decay patterns for samples from sites 3540 and 3525 are unknown but the poor correspondence between total Pb (Fig. 3) and ^{210}Po distribution profiles (Fig. 9) at each site suggests that ^{210}Pb remobilization is not a strong controlling factor.

Peat samples from hummock profiles collected at sites 3533, 3540, and 3525, were also analyzed for ^{137}Cs activity. As previously stated, the highest ^{137}Cs activity is expected at about the time of maximum nuclear testing (1963) when emissions from the Horne smelter were also at their maximum. For each of the three hummock profiles, the ^{137}Cs peak occurred at depths of 45 to 47 cm and coincided with that part of the profile with pronounced Cu, Pb, and Zn enrichment (Fig. 9).

Results from the analysis of ^{137}Cs for the three hummocks appear to be reliable, but some problems with ^{137}Cs mobility in peat have been reported. MacKenzie et al. (1997) found that ^{137}Cs was more mobile in peat cores with low (3%) mineral matter content than in a core with 6% mineral matter, and noted that these results were consistent with earlier observations on the influence of clay minerals on ^{137}Cs mobility in peat soils. Hummock peat from site 3540 had about 2% mineral matter to a depth of 30 cm and 5% below that level, whereas peat from sites 3533 and 3525 had about 2% at all depths; however, in all three cases, the peat overlies glaciolacustrine clay or silt and the mineral matter present may be enriched in clay minerals.

In this study, the age of hummock peat was also estimated using bulk density and annual vertical accumulation rate data (Kettles and Bonham-Carter, 2002), as well as information from an earlier study in Sweden. Wallen and Malmer (1995) determined that peat hummocks with *Sphagnum fuscum* (a species also common in the Rouyn-Noranda area) in one bog in Sweden accumulated an average of 0.019 g/cm²/a of dry mass over 14 years, and *Sphagnum balticum* hummocks in two bogs, about 0.01 g/cm²/a. As described earlier in this paper, hummock surface growth for the sampling year (1997) was calculated as having an average vertical accumulation of 2.5 cm of *Sphagnum* with an average bulk density of 0.009 g/cm³, indicating the formation, on average, of 0.022 g of dry mass per square centimetre of surface area on the hummock surface. At this average rate of dry-mass accumulation and assuming no decomposition, 1.60 g of dry mass would be expected to have accumulated for every square centimetre of hummock surface between 1927 and 2000. In the hummocks at sites 3533 and 3540, this amount of dry mass has accumulated

by depths of about 60 and 50 cm, respectively (Fig. 9). Although *Sphagnum* plant material forming the hummocks in the Rouyn-Noranda area was only slightly decomposed, usually appearing virtually intact to depths of at least 30 cm, some loss of dry mass due to decomposition is expected each year and also some variation in annual growth rates. On the basis of the *Sphagnum fuscum* accumulation rate from the Swedish study, hummock peat between 54 and 57 cm at site 3533 and at about 50 cm at site 3540 is estimated to have formed near the time the smelter opened in 1927, whereas peat at about 30 cm and 25 cm, respectively, formed in the 20 years between 1980 and 2000 (Fig. 9).

It was impossible to produce a detailed chronological record for peat in hummock profiles from the Rouyn-Noranda area because of the poor results obtained from ^{210}Pb analysis. However, the results of ^{137}Cs analysis for peat from hummock profiles and estimates of peat age based on bulk-density data provide some constraints on the time of peat formation in hummocks. These data suggest that peat between the surface and depths of about 60 cm in hummocks formed since the opening of the Horne smelter, whereas peat at a depth of about 45 cm in the three hummocks sampled in detail (sites 3525, 3533, and 3540) formed in the mid-1960s.

Changes in metal dstribution in peat over time and distance

The changes in smelter-related metal levels over the hummock and hollow profiles are considered to reflect most strongly the changing patterns of smelter particulate emissions over time and with distance from the smelter. Smelter metal emissions are known to have increased steadily from the opening of the smelter until the early 1940s, dropped to low levels over the war years, and increased again steadily from 1950 until they peaked in the mid-1960s (Noranda Mines, Ltd., unpub. data, 1996). With the use of new equipment and procedures, levels dropped markedly to the late 1980s and continued to drop during the 1990s. For example, since 1967, copper emissions decreased from about 3000 t to less than 300 t in 1989; they have been below 80 t since 1990.

Strong and consistent patterns of increase and decrease in metal concentrations have been recognized from the same peatland and from one peatland to the next. The observed patterns of increase and decrease in metal concentrations above depths of 60 to 70 cm within hummocks and high Cu, Pb, and Zn levels coincident with the ^{137}Cs peak are broadly similar to the patterns of smelter emissions over the lifetime of the Horne smelter (Fig. 9). In peat that formed before the opening of the smelter (below depths of 70 cm in the hummocks and 30 cm in the hollows), individual smelter-related elements have similar low levels close to and at large distances from the smelter (Fig. 3, 4). Peat at depths of about 50 cm contains high levels of metals in hummocks that are close to the smelter and relatively low levels in hummocks that are farther away. In addition, smelter dust was observed in hummock samples but not in samples collected at depth in the hollows.

Concentrations of Cu, Pb, and Zn in the hummock and hollow surface growth and of Cu and Pb in feather moss growing on hollow surfaces are higher near the smelter and decrease with distance, such that the log concentration is inversely proportional to the log distance from the smelter. Near the smelter, levels of these elements are about two or three times higher in the hollow surface material than in the hummock surface material or the feather moss. The levels dropped rapidly to distances of about 25 km, beyond which they decreased gradually to background levels. For unknown reasons, this relationship does not exist for Zn in feather moss. The effects of wind are most noticeable in the hummock surface growth samples, i.e. the sample type with the most data (n = 37). Hummock surface samples collected 'downwind' or north, northeast, east, southeast, and south of the smelter have higher levels of smelter-related metals close to and at intermediate distances from the smelter than those collected 'upwind' or northwest, west, and southwest of the smelter.

Results from hummock sampling work undertaken in 1982 around Rouyn-Noranda (Glooschenko et al., 1986) provide additional evidence for linking the patterns of hummock metal distribution and smelter emissions. Glooschenko et al. (1986) sampled the surface 5 cm of *Sphagnum fuscum* hummocks in peatlands 9 to 69 km from the Horne smelter, selecting the site locations on the basis of the most common downwind directions. Although the chemical digestions used on the 1982 samples differed from those used in the present study, both were strongly oxidizing and, hence, the results

should be comparable. Comparisons of hummock surface data from the two studies indicate that within 20 km of the smelter, the concentrations of Cu, Pb, and Zn (Fig. 10) are markedly higher in the 1982 samples than in the 1997 samples. Reported emissions of copper, lead, and zinc were respectively 120 t, 1200 t, and 1000 t in 1982 and 50 t, 197 t, and 55 t in 1997. The decrease in metal levels in peat between 1982 and 1997 is therefore consistent with the decrease in emission levels over the same period. Levels of Cu and Zn from the most distant 1982 sample sites (about 70 km from the smelter) were nearly similar to levels found in the 1997 samples at similar distances; however, Pb levels were slightly higher in the 1982 samples than in the 1997 samples.

Smelter-related element data for the hummock surface growth have been used previously to estimate the rate of decrease in concentration with radial distance and the background metal level far away from the smelter (Bonham-Carter and Kettles, 2001; Kettles and Bonham-Carter, 2002). Results showed that for Cu, Pb, and Zn, the smelter-related anomaly is statistically indistinguishable from background levels at about 50 km from the smelter. Using the average annual vertical accumulation rate of 2.5 cm for Rouyn-Noranda hummock surface growth and the average bulk density of 0.009 g/cm³ for Rouyn-Noranda surface hummock peat determined from this study, the amount of metal in the smelter-centred anomaly was calculated by integration. The Cu anomaly can account for about 30% of reported emissions in the sampling year (1996–1997) whereas the Pb and Zn anomalies account for about 10% and 26% of reported
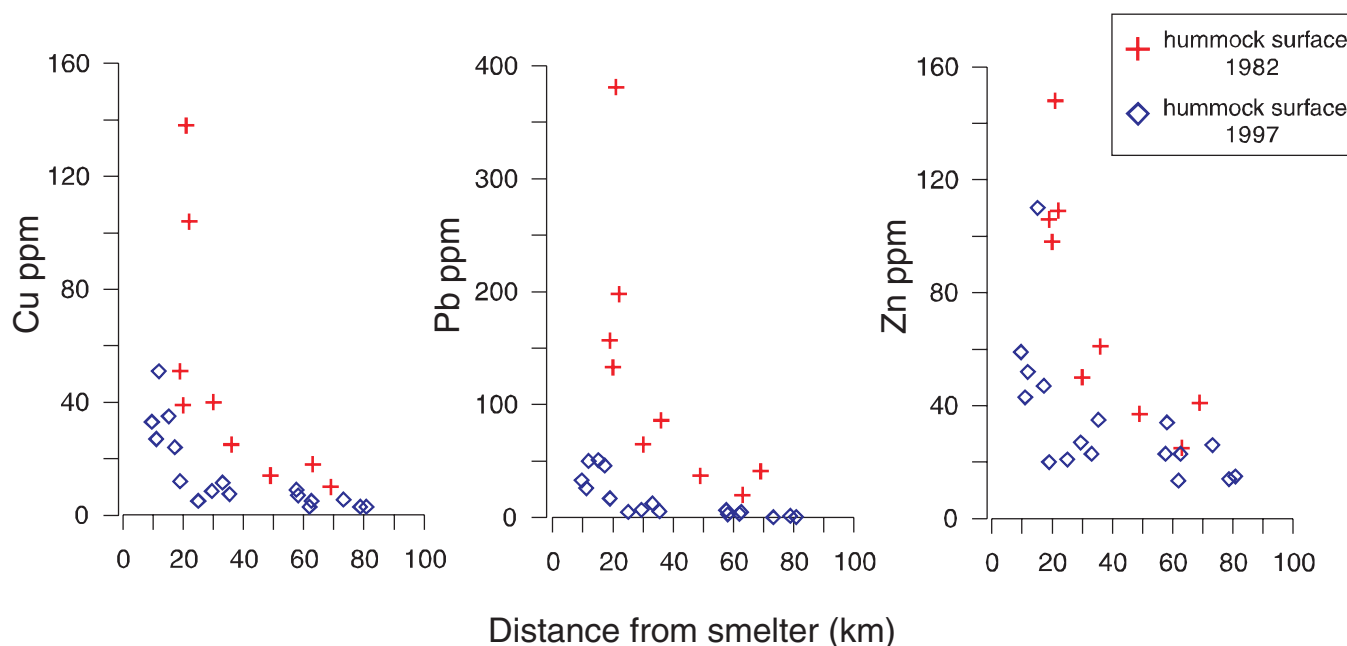

Figure 10. *Distribution of Cu, Pb, and Zn in surface* Sphagnum *hummock samples from the downwind (north, northeast, east, southeast, and south) sectors of the study area. The 1982 samples were collected by Glooschenko et al. (1986) (n = 9). The 1997 samples were collected as part of this study (n = 17). The Glooschenko composite samples were made from the surface 5 cm from 30* Sphagnum fuscum *hummocks at each site. These samples were digested with 2:1 HNO₃–H₂SO₄ and H₂O₂ and analyzed using atomic absorption spectrophotometry.*

emissions, respectively. The discrepancy between the peat-derived metal anomaly and the reported emissions is attributed mostly to long-range transport of atmospheric emissions, particularly during dry weather periods, and possibly to incomplete physical trapping and chemical fixation of metal in the peat hummocks.

Other, likely minor, sources of error include the modelling process and the reported emissions. Other sources of error relate to the capacity of the *Sphagnum* for 'fixing' metals and may also account for some intersite and intrasite variation Cu, Pb, and Zn in hummock and hollow profiles. These include the effects of 1) interspecies variation between hummocks (Aulio, 1982); 2) annual growth rate variation from site to site; 3) differences in deposition patterns at the hummock surface in heavily wooded to open peatland areas; 4) variations in pH and redox conditions at the hummock surface; 5) the effect on metal composition of leaves or fragments of non-*Sphagnum* species in some samples; 6) some metal transport from soil or minerotrophic peat deposits by *Sphagnum* leaves or by root uptake in higher plants and subsequent transfer to the *Sphagnum* by leaching from living or dead plant material (Steinnes, 1995); and 7) the loss of metalliferous particles trapped by the *Sphagnum* in solution or washed off in the snowmelt.

Comparison of the record of smelter-related metals in peat and in other surficial materials

Figure 11 shows a plot of Cu in hummock surface growth, hollow surface growth, and feather moss from this study and in surficial lake sediments (Kliza et al., 2000) and humus (Henderson et al., 2002) from other Rouyn-Noranda area studies. The decay pattern of Cu concentration is consistent for all materials with log concentration of Cu being inversely proportional to log distance from the smelter. Similar plots for Pb and Zn show similar decay patterns, except, as noted previously, for Zn in feather moss.

Large differences in the range of concentrations exist among some types of sample materials at similar distances from the smelter (Fig. 11). For example, at 7 to 10 km from the smelter, Cu concentrations are about 200 ppm in humus and lake sediment and about 200 ppm in hollow surface growth, whereas they are about 30 to 50 ppm in hummock surface growth and feather moss. At 70 km from the smelter, Cu levels have dropped to about 40 to 60 ppm in lake sediment and humus and to 3 to 10 ppm in hummock and hollow surface growth and feather moss. High metal concentrations in humus and surficial lake sediments, compared to peat and feather moss, likely reflect the stronger influence of mineralized groundwaters on these sediments and the higher content of mineral matter in them. The mineral matter content, derived primarily from underlying and surrounding soils, is about 25% in humus and over 30% in surficial lake sediments. Background levels of smelter-related elements in the underlying till or glaciolacustrine sediments at most sites (Table 2) are higher than those in peat. (*See* element concentrations at depths below 65 cm in the hummock profiles in Figure 3 and at depths below 25 cm in the hollow profiles in Figure 4.) In addition, metal levels in the 1997 hummock
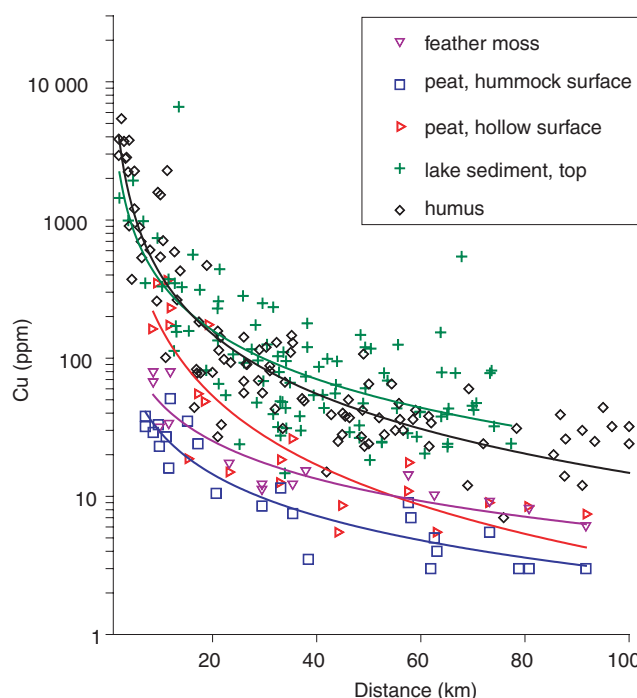

Figure 11. *Distribution of Cu in hummock surface growth, hollow surface growth, feather moss, surficial lake sediment (Kliza and Telmer, 2001), and humus (Henderson et al., 2002) around the smelter at Rouyn-Noranda, Quebec.*

surface growth samples, most of which were about 3 cm thick, and in the new-growth feather moss samples represent a few years of accumulation; those is the hollow surface growth samples represent an accumulation period that is about double that of the hummocks. In contrast, the lake sediments in the surface samples took tens to hundreds of years to form and the humus samples, thousands of years. The relatively high Cu and Pb concentrations in feather moss compared to the hummock surface material, both of which are composed of recent-growth materials, likely reflect metal uptake from the hollow surface, which is metal-rich compared to the hummock surface, as well as some interspecies differences. As noted previously, the feather moss species (*Pleurozoium schreberi*) is recognized as an effective metal bioindicator (Rasmussen, 1994).

Metal apportionment in hummock and hollow peat

Hummock samples from sites 3536, 3533, 3540, 3527, and 3525, located 7, 10, 12, 15, and 30 km, respectively, from the smelter, and hollow samples from sites 3533 and 3540 were subjected to a series of sequential extractions and analyzed for their Cu, Pb, Zn, and Ni content. The hummock samples collected 10 km or more from the smelter gave a consistent pattern of Cu, Pb, and Zn apportionment — a pattern that persisted whether total concentrations were 15 ppm or up to several hundred parts per million. Most Zn within the labile fraction was easily extracted (CH_3COONa leach), whereas Pb in the mobile fraction was about evenly distributed between

the easily extractable and the soluble organic ($Na_4O_7P_2$) phases. Within the non-labile phases (aqua regia and nearly total multi-acid leaches) of hummock peat samples, more Cu, Pb, and Zn was extracted using the partial extraction (aqua regia) than the nearly total digestion. The lower proportion of Cu in the labile phases compared to Pb and Zn may explain the less 'noisy' and the stronger systematic distribution pattern observed for Cu with increasing depth in the hummock profiles (Fig. 3) and in hummock surface growth with increasing distance from the smelter (Fig. 6). The more noisy patterns for Pb and Zn may reflect a greater (but still small) amount of postdepositional mobility of these elements. The apportionment patterns for Cu, Pb, and Zn were similar in the labile and non-labile phases in humus in the Rouyn-Noranda area (Henderson and Knight, 2005).

Of the four samples of hollow peat analyzed from the 12 km site, the metals in the uppermost sample collected at a depth of 7 cm were apportioned between the labile and non-labile phases in a manner similar to that seen for the hummock samples. The Cu distribution at depth in the hollow was similar to that seen in the hummock; however, a larger proportion of Pb and Zn resided in the non-labile phases.

The retention of about 66% of the Cu in the non-labile phases of peat samples at less contaminated sites (10 km or more from the smelter) is well documented and consistent with the behaviour of this element (Kabata-Pendias and Pendias, 2001). Copper is known to be one of the least mobile of the soil micronutrients, being specifically adsorbed by iron and manganese oxides and more strongly bonded to organic matter than other trace elements (McBride, 1981). The relatively large proportion of Pb in the labile phases compared to Cu was unexpected, since Pb is reported as being immobile (Kabata-Pendias and Pendias, 2001) and associated mainly with clay minerals, manganese oxides, iron and aluminium hydroxides, and organic matter. Recent studies have shown that lead in surface soil occurs in mobile, dissolved, colloidal, and/or particulate forms that can be transferred to lower soil horizons (Miller and Friedland, 1994; Johnson et al., 1995) and, as previously noted, problems with lead mobility have been encountered during ^{210}Pb dating. Zinc is considered to be readily soluble relative to the other heavy metals in soils and is known to be highly soluble in acid peaty soils (Kabata-Pendias and Pendias, 2001).

A higher proportion of Cu, Pb, and Zn was easily extractable in hummock samples from the most contaminated site (site 3536), located 7 km from the smelter, than from sites farther from the smelter. These results are comparable to those from earlier studies in which higher metal solubility was noted in soils sampled near smelters and attributed to metal loading. Colborn and Thornton (1978) reported that the percentage of Pb extracted with weak leaches increased with an increase in total Pb. Greinert (1993) determined that the relative solubility of Cu was higher in polluted soils, but he found that unlike the results for site 3536, the relative solubility of most other heavy metals was almost the same in both polluted and unpolluted soils. Henderson and Knight (2005) found a higher proportion of labile metals in humus sites sampled closest to the Horne smelter; these results are similar to those from the site 3536 hummock samples. Also, Karczewska

(1996) found a high proportion of exchangeable Cu, Pb, and Zn in the surface soil layer in the vicinity of the smelter, with Zn being more mobile than Cu.

CONCLUSIONS

1) Strong patterns of metal distribution are found in peat hummocks and hollows; they change consistently with depth and distance from the smelter. Vertical distributions of smelter-related metals in peat hummocks at various distances from Rouyn-Noranda are consistent with temporal changes in metal emissions from the smelter. Differences between metal levels in hummocks at the same site are minor and, although more variation exists among hollows, smelter-related metal-distribution trends are similar.

2) The physical record of smelter dust found in the hummock samples analyzed using the SEM method was consistent with particles observed in humus from the Rouyn-Noranda area.

3) Except for Zn in feather moss, the geographical patterns of metals in hummock and hollow surface growth and feather moss around the smelter are spatially consistent and are predictable within a regional context. For these materials and for surficial lake sediments and humus, the log concentration of Cu, Pb, and Zn was determined to be inversely proportional to log distance from the smelter. The wind effect is most noticeable for Cu, Pb, and Zn in hummock surface growth and skews the concentration patterns in the direction of the predominant winds. This effect is most noticeable for samples collected at less than about 30 km from the smelter.

4) Results from earlier peat sampling undertaken by Glooschenko et al. (1986) in the same area in 1982 gave substantially higher metal concentrations than in 1997. Metal levels in hummock surface growth decreased substantially over the last 20 years, mirroring a reduction in emissions over the same period.

5) The hummock sequences are most useful for providing an historical record of smelter emissions. The differences in the distribution patterns of smelter-related elements in peat from the hummocks and peat from the hollow surfaces are thought to reflect the higher vertical accumulation rates of hummock peat compared to hollow peat. When sampling the upper part of the hollow peat sequence (0–35 cm), it is difficult to divide the sequence into vertical segments that are small enough so that the resulting profile shows the small-scale geochemical variations in peat that formed since the opening of the smelter. In addition, in comparison to the hummocks, more variation was seen in the plant species growing on the hollow surface and in the decomposition state, bulk density, and mineral content of the organic materials composing the uppermost part of the hollow sequences.

6) In hummocks at 10 km and more from the smelter, only about 25% of the Cu is labile, compared to about 66% of the Pb and about 75% of the Zn. In the hummock sampled

closest to the smelter (7 km), larger proportions of the three elements were found in the labile phases, much of which was easily extracted with the CH$_3$COONa leach. The change was greatest for Cu with about 60% of the total content residing in the labile phases. These results suggest that a significant portion of the three metals, but especially Pb and Zn, are labile and, hence, potentially bioavailable. The much larger proportion of Cu, compared to Pb and Zn, in the non-labile phases of the peat sampled at distances of 10 km and more from the smelter likely explains why Cu has the most consistent and least 'noisy' pattern of systematic change with increasing depth in the geochemical profiles for the hummocks and in its distribution in hummock surface growth with increasing distance from the smelter.

ACKNOWLEDGMENTS

REFERENCES

Aaby, B. and Jacobsen, J.
1979:   Changes in biotic conditions and metal deposition in the last millenium as reflected in ombrotrophic peat in Draved Mose, Denmark; Geological Survey of Denmark, Yearbook 1978, p. 5–43.

Andrus, R.E.
1980:   Sphagnaceae (peat moss family) of New York state; New York State Museum Bulletin 442, 89 p.

Appleby, P.G. and Oldfield, F.
1978:   The calculation of ^{210}Pb dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment; Catena, v. 5, p. 1–8.
1992:   Application of lead-210 to sedimentation studies; in Uranium Series Disequilibrium (2nd edition), (ed.) M. Ivanovich and R.S. Harnmon; Oxford University Press, Oxford, United Kingdom, p. 731–778.

Aulio, K.
1982:   Nutrient accumulation in Sphagnum mosses. II. Intra- and interspecific variation of four species from ombrotrophic and minerotrophic habitats; Annales Botanica Fennici, v. 17, p. 93–101.

Azzaria, L.M. and Frechette, G.
1987:   Natural and industrial sources of trace elements, Rouyn-Noranda-Val d'Or mining area, Quebec, Canada; in Practical Applications of Trace Elements and Isotopes in Environmental Biogeochemistry and Mineral Resources Evaluation, (ed.) R.V. Hurst, T.E. Davis, and S.S. Augustithis; Theophrastus Publications, S.A., Athens, Greece, p. 3–26.

Bellamy, D.J. and Rieley, J.
1967:   Some ecological statistics of a miniature bog; Oikos, v. 13, p. 33–40.

Bonham-Carter, G.F. and Kettles, I.M.
2001:   Estimating the size of a metal anomaly around a base-metal smelter in Quebec, Canada, using peatland data: a Monte Carlo error analysis; in Geologic Modeling and Simulation: Sedimentary Systems, (ed.) D.F. Merriam and J.C. Davis; Kluwer-Plenum Publishers, New York, New York, p. 303–326.

Bonham-Carter, G.F., Henderson, P.J., Kliza, D.A., and Kettles, I.M.
2005:   Smelter emissions deposited in the environment around the Horne smelter, Quebec: comparison of regional snow, peat, soil, and lake-sediment and lake-water surveys; 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.

Clymo, R.S. and Hayward, P.M.
1982:   The ecology of Sphagnum; in Bryophyte Ecology, (ed.) A.J.E. Smith; Chapman and Hall, London, United Kingdom, p. 229–289.

Clymo, R.S, Oldfield, F., Appleby, P.G., Person, G.W., Ratnesar, P., and Richardson, N.
1990:   The record of atmospheric deposition on a rainwater dependent peatland; Royal Society of London, Philosophical Transactions, Series B., v. 327, p. 105–112.

Colborn, P. and Thornton, I.
1978:   Lead pollution in agricultural soils; Journal of Soil Science, v. 29, p. 513–426.

Damman, A.W.H.
1978:   Distribution and movement of elements in ombrotrophic peat bogs; Oikos, v. 30, p. 480–495.

Dumontet, S., Levesque, M., and Mathur, S.P.
1990:   Limited downward migration of pollutant metals (Cu, Zn, Ni, and Pb) in acidic virgin peat soils near a smelter; Water, Air, & Soil Pollution, v. 49, p. 329–342.

Ecoregions Working Group
1989:   Ecoclimatic regions of Canada, first approximation; Environment Canada, Canadian Wildlife Service, Conservation and Protection, Ecological Land Classification Series, No. 23, 118 p.

Faure, G.
1986:   Principles of Isotope Geology (2nd edition); John Wiley & Sons, New York, New York, 589 p.

Flett Research
2001:   Understanding the Pb-210 method; Flett Research (Winnipeg, Manitoba) (http://www.flettresearch.ca/Webdoc4.htm).

Glooschenko, W.A. and Capoblanco, J.A.
1978:   Metal content of Sphagnum mosses from two northern Canadian bog ecosystems; Water, Air, & Soil Pollution, v. 10, p. 215–220.
1982:   Trace element content of northern Ontario peat; Environmental Science and Technology, v. 16, p. 187–188.

Glooschenko, W.A., Holloway, L., and Arafat, N.
1986:   The use of mires in monitoring the atmospheric deposition of heavy metals; Aquatic Botany, v. 25, p. 179–190.

Glooschenko, W.A., Sims, R., Gregory, M., and Mayer, T.
1981:   Use of bog vegetation as a monitor of atmospheric input of metals; in Atmospheric Pollutants in Natural Waters, (ed.) S.J. Eisenreich; Ann Arbor Science, Ann Arbor, Michigan, p. 389–399.

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. Eijsackers and T. Hamers; Kluwer Academic Publishers, 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.

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.

Henderson, P.J., Knight, R.D., and McMartin, M.
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).

Jensen, A.
1997: Historical deposition rates of Cd, Cu, Pb, and Zn in Norway and Sweden estimated by ^{210}Pb dating and measurement of trace elements in cores of peat bogs; Water, Air, & Soil Pollution, v. 95, p. 205–220.

Johnson, C.E., Siccama, T.G., Driscoll, C.T., Likens, G.E., and Moeller, R.E.
1995: Changes in lead biogeochemistry in response to decreasing atmospheric inputs; Ecological Applications, v. 5, p. 813–822.

Johnson, L., Damman, A.W.H., and Malmer, N.
1990: *Sphagnum* macrostructure as an indicator of decay and compaction in peat cores from an ombrotrophic south Swedish peat-bog; Journal of Ecology, v. 78, p. 633–647.

Johnson, L.C. and Damman, A.W.H.
1993: Decay and its regulation in *Sphagnum* peatlands; Advances in Bryology, v. 5, p. 249–296.

Jowsey, P.C.
1966: An improved sampler; New Phytologist, v. 65, p. 245.

Kabata-Pendias, A. and Pendias, H.
2001: Trace Elements in Soils and Plants (3rd edition); CRC Press, Boca Raton, Florida, 413 p.

Kalviainen, E. and Karuenen, P.
1984: On the growth, senescence, and decay-resistance of *Sphagnum* mosses; *in* Proceedings, 7th International Peat Congress, Dublin, Ireland, v. 4, p. 263–275.

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.

Kettles, I.M. and Bonham-Carter, G.F.
2002: Modelling dispersal of metals from a Cu-Zn smelter at Rouyn-Noranda (Quebec, Canada) using peatland data; Geochemistry: Exploration, Environment, Analysis, v. 2, no. 2, p. 99–110.

Kettles, I.M. and Dion, K.M.
2000: Geochemical composition of hummock and hollow peat and feather moss in the vicinity of the Horne Smelter, Rouyn-Noranda, Quebec; Geological Survey of Canada, Open File 3882, 185 p.

Kettles, I.M., Garneau, M., and Jetté, H.
2000: Macrofossil, pollen, and geochemical records of peatlands in the Kinosheo Lake and Detour Lake areas, northern Ontario; Geological Survey of Canada, Bulletin 564, 24 p.

Kettles, I.M., Henderson, P.J., and Knight, R.D.
2001: Comparison of the metal record in peat and humus near the Cu-Zn smelter at Rouyn-Noranda, Quebec, Canada; *in* Proceedings, 6th International Conference on the Biogeochemistry of Trace Elements, (ed.) K. Bolton; University of Guelph, Guelph, Ontario, SP306, p. 535.

Kliza, D.A. and Telmer, K.
2001: Phase I. Lake sediment studies in the vicinity of the Horne smelter in Rouyn-Noranda, Quebec; Geological Survey of Canada, Open File D2952 (CD-ROM).

Kliza, D.A., Telmer, K., Bonham-Carter, G.F., and Hall, G.E.M.
2000: Geochemistry of snow from the Rouyn-Noranda region of western Quebec: an environmental database; Geological Survey of Canada, Open File 3869.

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.

Lalonde, J.P.
1978: Étude et implications des éléments traces dans les précipitations de la région de Rouyn-Noranda; Service de la géochimie, ministère des Richesses naturelles du Québec, DPV-643, 38 p.

Mackenize, A.B., Farmer, J.G., Sugden, C.L.
1997: Isotopic evidence of the relative retention and mobility of lead and radiocaesium in Scottish ombrotrophic peats; Science of the Total Environment, v. 203, p. 115–127.

Mathieu, G.G., Biscaye, P.E., Lupton, R.A., and Hammond, D.E.
1988: System for measurement of [222]Rn at low levels in natural waters; Health Physics, v. 55, p. 989–992.

McBride, M.B.
1981: Forms and distribution of copper in solid and solution phases of soil; *in* Copper in Soils and Plants, (ed.) J.F. Loneragan, A.D. Robson, and R.D. Graham; Academic Press, New York, New York, p. 25–43.

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.

Miller, E.K. and Friedland, A.J.
1994: Lead migration in forest foils: response to changing atmospheric inputs; Environmental Science and Technology, v. 28, p. 662–669.

Munsell Color Company
1971: Munsell Soil Color Charts; Munsell Color Company, Baltimore, Maryland.

Norton, S.A., Evans, G.C., and Kahl, S.
1997: Comparison of Hg and Pb fluxes to hummocks and hollows of ombotrophic Big Heath Bog and to nearby Sargent Mt. Pond, Maine, USA; Water, Air, & Soil Pollution, v. 100, p. 271–286.

Nungasser, M.K.
1997: Stability and resilience in bog hummocks and hollows; Ph.D. Dissertation, Department of Environmental Sciences, University of Virginia, Charlottesville, Virginia, 136 p.

Ohlson, M. and Dahlberg, B.
1991: Rate of peat increment in hummock and lawn communities on Swedish mires during the last 150 years; Oikos, v. 61, p. 369–378.

Parkinen, P.
1981: Metal content of ombrotrophic *Sphagnum* mosses in NW Europe; Annales Botanica Fennici, v. 18, p. 282–292.

Parkinen, P. and Tolonen, K.
1977: On the growth rate and dating of surface peat; Suo, v. 28, p. 19–24 (in Finnish, English summary).

Rasmussen, P.
1994: Mercury in vegetation of the Precambrian shield; *in* Mercury Pollution: Integration and Synthesis, (ed.) C.J. Watras and J.W. Huckabee; Lewis Publishers, Boca Raton, Forida.

Renberg, I., Brannvall, M.L., Bindler, R., Emteryd, O.
2000: Atmospheric lead pollution history during four millennia (2000 BC to 2000 AD) in Sweden; Ambio, 2000, v. 29, p. 150–156.

Roberts, L.
1956: Noranda; Irwin & Co., Toronto, Ontario, 223 p.

Shotyk, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., and Van Der Knaap, W.O.
1998: History of atmospheric lead deposition since 12,370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland; Science, v. 281, p. 1635–1640.

Steinnes, E.
1995: A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals; The Science of the Total Environment, v. 160/161, p. 243–249.

1997: Trace element profiles in ombrogenous peat cores from Norway: evidence of long range atmospheric transport; Water, Air, & Soil Pollution, v. 100, p. 405–413.

Stockwell, C.H., McGlynn, J.C., Emslie, R.F., Sanford, B.V., Norris, A.W., Donaldson, J.A., Fahrig, W.F., and Currie, K.L.
1970: Geology of the Canadian Shield; *in* Geology and Economic Minerals of Canada, (ed.) R.J.W. Douglas; Geological Survey of Canada, Economic Geology Report, No. 1, p. 45–150.

Tarnocai, C., Kettles, I.M., and Lacelle, B.
2000: Peatlands of Canada; Geological Survey of Canada, Open File 3484, scale 1:6 500 000.

Thompson, M. and Howarth, R.J.
1978: A new approach to the estimation of analytical precision; Journal of Geochemical Exploration, v. 9, p. 23–30.

Turner, L.J.
1999: [210]Pb analysis of two peat cores from the Rouyn-Noranda region (cores 221 and 222), Quebec; National Water Research Institute, Report no. 99-09, 15 p.

Turner, L.J. and Delorme, L.D.
1996: Assessment of ^{210}Pb data from Canadian lakes using the CIC and CRC models; Environmental Geology, v. 28, p. 78–87.

Turner, L.J. and Kettles, I.M
2000: Data for the ^{210}Pb dating of four cores from the vicinity of Detour Lake and Kinosheo Lake, Ontario, and Fort Simpson, Northwest Territories; Geological Survey of Canada, Open File 3858, 78 p.

Urban, N.R.
1990: Mobility and diagenesis of Pb and ^{210}Pb in peat; Geochimica et Cosmochimica Acta, v. 54, p. 3329–3346.

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

Vile, M.A., Wieder, R.K., and Novak, M.
1999: Mobility of Pb in *Sphagnum*-derived peat; Biogeochemistry, v. 45, p. 35–52.

Wallen, B. and Malmer, N.
1995: Rate of carbon accumulation in hummocks and hollows; *in* Northern Peatlands in Global Climate Change, (ed.) R. Laiho, J. Laine, and H. Vasander; Academy of Finland, EDITA Helsinki, Finland, p. 262–268.

Zoltai, S.
1988a: Wetland environments and classification; *in* Wetlands of Canada, (ed.) National Wetlands Working Group; Environment Canada, Ecological Land Classification Series, no. 24, p. 1–26.
1988b: Distribution of base metals in peat near a smelter at Flin Flon, Manitoba; Water, Air, & Soil Pollution, v. 37, p. 217–2