

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

P. J. Henderson · I. McMartin · G. E. Hall · J. B. Percival · D. A. Walker

Abstract Trace element geochemistry of humus (<0.425 mm) and till (<0.002 mm) collected in the Flin Flon-Snow Lake area, northern Manitoba and Saskatchewan, provides a regional context for assessing smelter contamination in the environment. The area includes a Cu-Zn smelter known to discharge As, Cd, Cu, Fe, Hg, Pb, and Zn. In this study, sequential extraction analyses, scanning electron microscopy and x-ray diffraction analyses were used on a suite of samples to determine: (1) the chemical and physical characteristics of heavy metals in surficial sediments related to distance from the smelter, (2) criteria for assessing the relative contribution of these metals from natural and anthropogenic sources, and (3) the potential of these metals for remobilization in the environment. Humus geochemistry reflects the anthropogenic and natural component of heavy metal concentrations. Smelter-related elements show anomalously high values adjacent to the smelter, decreasing with distance until background values are reached at 70–104 km, depending on the element. In humus, Zn is associated primarily with labile phases; Hg with non-labile phases. Adjacent to the smelter, high proportions and concentrations of Zn and Hg in non-labile phases, indicative of smelter-derived particulates, are confirmed by SEM examination. The particles occur as spheres, irregular grains, and with organics. With increasing distance from the smelter, the geochemical response to bedrock composition is more obvious than the anthropogenic input. Till geochemistry reflects the natural variation imposed by bedrock composition. At highly contami-

nated sites (<3 km from the smelter), increased percentages of smelter-related elements in labile phases suggests heavy metals are leached from humus to the underlying sediment.

Key words Heavy metals · Base metals · Smelter Anthropogenic contamination · Chemical partitioning · Soil · Particulate emissions

Introduction

Interest in the distribution of heavy metals in soils is based on environmental concerns associated with the effects of high concentrations on human and animal health. Variations in the abundance of these metals in the surficial environment can be related to both natural and anthropogenic sources (Kabata-Pendias and Pendias 1983; Rasmussen 1996). Distinguishing between these two sources is difficult; however, the information is essential for the formulation of realistic industrial emission standards and environmental controls. One method of addressing the problem is to examine the chemical and physical signature of heavy metals in areas where anthropogenic emission is known to be the primary source of metal enrichment. In this paper, the extent and nature of heavy metal distribution will be examined in soils affected by smelter contamination.

Metal smelters and thermal electric plants are well known as point sources of heavy metal contamination with metals emitted from these facilities decreasing in concentration with distance from the source (Davies 1983). This distribution pattern has been mapped in foliage, and organic and surface mineral soils of forested areas (Freedman and Hutchinson 1980; Hogan and Wotton 1984); in peat (Zoltai 1988); and lake sediments (Jackson 1978; Jackson and others 1993). There are few comprehensive detailed studies, however, on the physical and chemical characteristics of heavy metals derived from industrial contamination and on their potential availability to biota. In this study, the forms of Zn, Hg, and Ni will be examined in humus and till collected at varying distances from

Received: 5 November 1996 · Accepted: 31 March 1997

P. J. Henderson (✉) · I. McMartin · G. E. Hall
J. B. Percival · D. A. Walker
Geological Survey of Canada, 601 Booth St., Ottawa,
Ontario, K1A 0E8, Canada
E-mail: phenderson@gsc.nrcan.gc.ca
Geological Survey of Canada contribution no. 1996356

the base metal smelting complex operated by Hudson Bay Mining and Smelting Corporation at Flin Flon, Manitoba (55°N, 102°W), as a basis for assessing metal mobility and outlining criteria for the recognition of smelter-related contamination in the terrestrial environment. The study area (Fig. 1) is ideally suited for examining the distribution of smelter contamination because it has been subjected to atmospheric deposition of particulate emissions for nearly 60 years and is remote from any significant industrial center. In addition, a comprehensive geochemical database for humus and till is available for the region as a result of a surficial geological mapping and geochemical prospecting project conducted in the Flin Flon-Snow Lake area, northern Manitoba and Saskatchewan (99° W–103° W longitude; 54°N–55°15' N latitude) by the Geological Survey of Canada and Manitoba Department of Energy and Mines (Fig. 1; Henderson 1995; McMartin and others 1996; McMartin and others 1998). Humus and the underlying sediment, predominantly till, were sampled at more than 2000 sites over 36 000 km² and analysed geochemically for a suite of major and trace elements. This database provides the context to assess the effects of prolonged smelter emission contamination in

the terrestrial environment, in an area where the natural geological variation in heavy metal concentrations is well known.

To characterize dispersal from the smelter, humus and till samples collected at varying distances from the stack, as well as from several soil profiles, were subjected to chemical partitioning through the application of sequential extraction techniques. In addition, the mineral composition of the non-organic portion of both humus and till was determined by x-ray analyses, and the size, composition and morphology of metal bearing particulates were characterized with a scanning electron microscope (SEM).

Regional setting

The area is situated at the margin of the Precambrian Shield (Figs. 1 and 2). It is underlain by rocks of four distinct geological terranes (Ashton 1987; Syme and others 1993; Stern and Lucas 1995). Slightly metamorphosed volcanic and sedimentary rocks and associated intrusions of the Flin Flon-Snow Lake greenstone belt outcrop in the central part of the area. The Attitti Block, which forms the northwestern extension of this belt, is composed of the highly metamorphosed equivalent of greenstone belt lithologies (Ashton and others 1995). In the north, the area is underlain by rocks of the Kisseynew Domain which consist of gneisses and associated intrusions. To the west, the greenstone belt is in tectonic contact with a geologically complex association of generally highly metamorphosed supracrustal and plutonic rocks that range widely in composition, the Hanson Lake Block. Unmetamorphosed Paleozoic dolostones and minor sandstones unconformably overlie the Precambrian rocks in the southern half of the area.

The area has a high potential for gold and base metal mineralization, particularly within the Flin Flon-Snow Lake greenstone belt. Gold occurs in sulphide-bearing fracture zones that may or may not be quartz-filled. Base metal deposits are essentially of two types: volcanic massive sulphide (VMS) deposits of Cu-Zn, and porphyry-style Cu mineralization in a volcanic vent setting. In the Flin Flon area, mines have been developed in large Zn deposits and smaller Cu or Cu-Zn deposits. Extensive Cu and Zn mineralization has also been exploited in the Snow Lake area.

The area has been glaciated by ice flowing from two dispersal centers: one located in the District of Keewatin, the other located in Hudson Bay (Dyke and Prest 1987). The dominant ice flow indicators in the northern and western part of the area indicate flow to the south-southwest from the Keewatin dispersal centre (Fig. 1). In the southeastern part of the study area, ice flowed west-southwestward from the Hudson dispersal centre. Tills deposited by these glaciers primarily reflect local bedrock composition (Henderson 1995; McMartin and others 1996). During ice retreat, the entire area was inundated

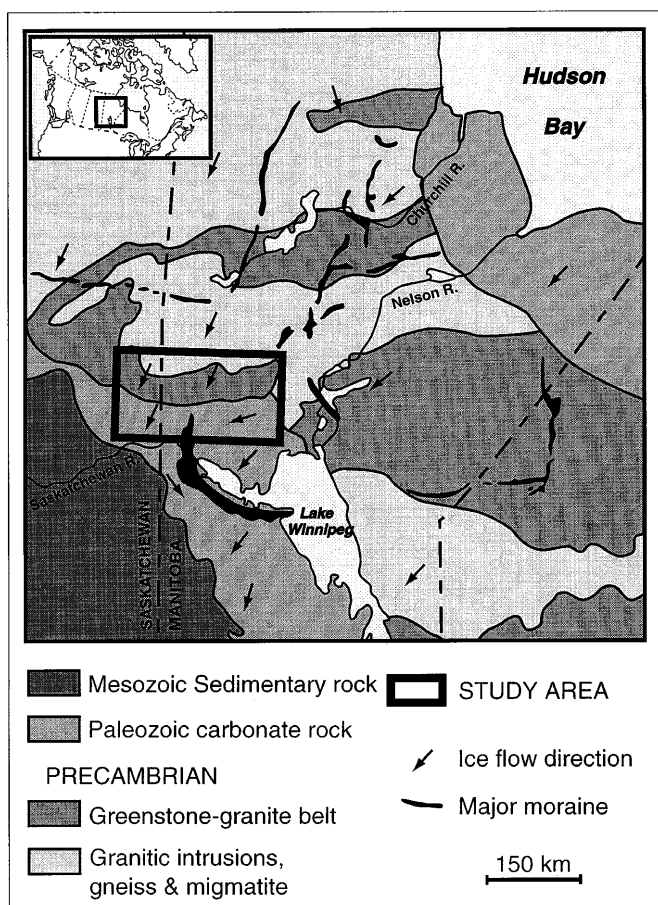


Fig. 1

Location map of the regional study area showing generalized bedrock geology, major glacial landforms and ice flow directions

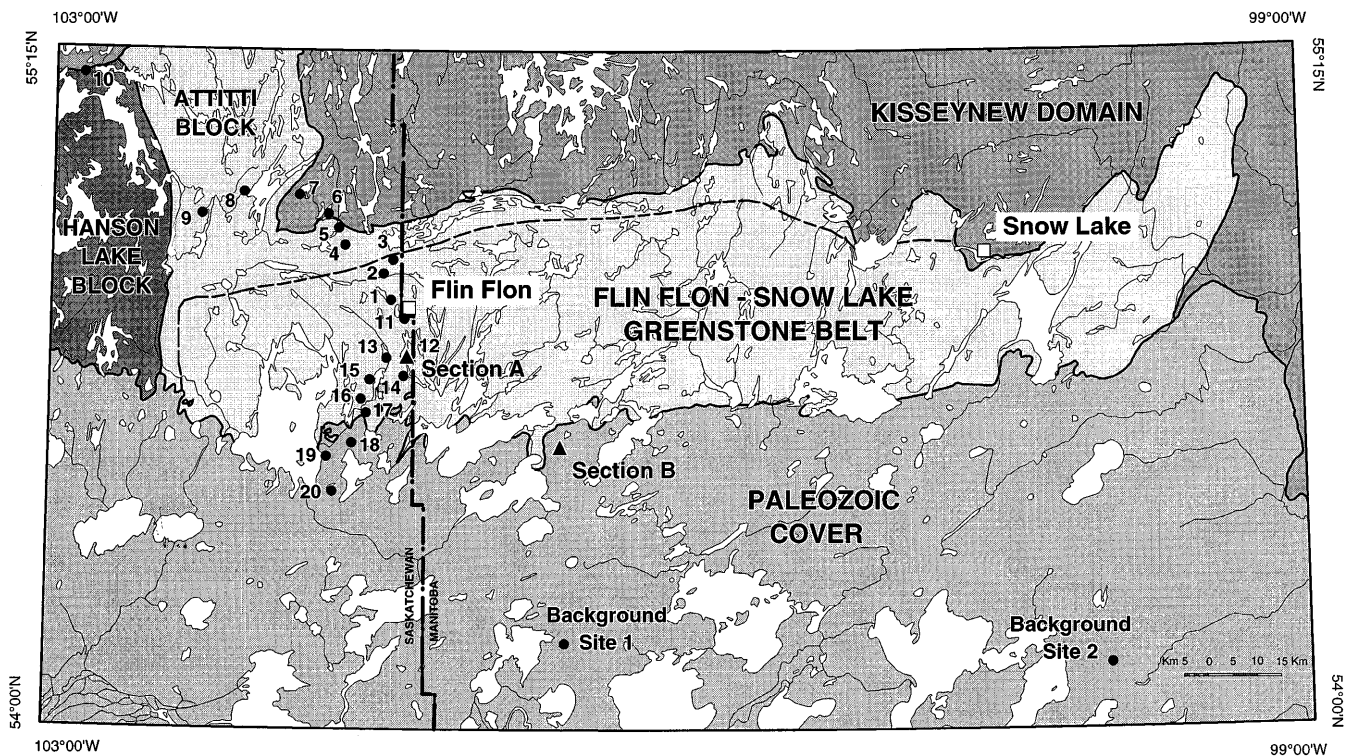


Fig. 2

Location of transect sites, sections, and background sites. Bedrock geology simplified from Broome and others (1995)

by proglacial Lake Agassiz (Teller and Clayton 1983; Schreiner 1984). As a result, deposits of glaciolacustrine clay occur in topographic depressions of the Shield and as thick blankets, overlain by peat, in Paleozoic terrane. The area is forested by a mixed coniferous deciduous boreal community comprising jack pine, black spruce, white spruce, trembling aspen, balsam poplar and speckled alder (Hogan and Wotton 1984). At Flin Flon, the dominant winds are southeastward and southwestward, with strong north-northwestward and southward components (Environment Canada 1990).

Smelter history and nature of emissions

The base metal mining and smelting complex at Flin Flon produces Zn, Cu and Cd metals on site, in addition to Pb concentrates and Au, Ag, Se, and Te by-products which are recovered and refined off-site (Franzin and others 1979). Since the early 1930's, the complex has processed ore from local mines, undergoing many changes during that time to improve processing and comply with environmental standards. As a result, particulate stack emissions have decreased from an average of 13.983 tons/day in 1985 to 0.914 tons/day in 1995 (Hudson Bay Mining and Smelting Company 1995). Nevertheless, the cumula-

tive effects of emissions up to several kilometers from the smelter has resulted in high tree mortality, reduced growth, reduction in species diversity and soil erosion (Hogan and Wotton 1984).

Presently, the majority (90%) of stack dust escapes from the smelter baghouse (Salomon de Friedberg 1993), however, prior to recent modifications, emissions were derived equally from the Zn precipitator (48%) and smelter baghouse (48%; R. Tardiff, HBMS, pers. comm.). Chemical analyses of these smelter dusts indicate high concentrations of Zn, Fe, Cu, Pb, Cd, and As, with low to trace amounts of Hg, Cr, Co, Ni, and Mn (Hudson Bay Mining and Smelting Company 1995). Analyses of archived dusts from the smelter baghouse and Cu and Zn precipitators indicate that retained particles are predominantly in the fine to medium silt size range (0.002–0.031 mm). These dusts vary in composition, but consist largely of angular and spherical particles of Cu, Zn, Fe sulphates and, to a lesser extent, oxides and sulphides commonly containing trace amounts of Pb, As and/or Cd. These results differ from those of Chen and Pint (1980) who report that more than 97% of the dust from the smelter baghouse contains <0.001 mm sized grains of ZnO, and possibly hydrous (Zn, Pb, Fe, Cu) sulphates/arsenates. The remaining 2–3% consists of 0.001–0.02 mm spherules of Cu metal (frequently with a Cu₂S rim), sulphides containing Cu, Fe and/or Zn, silicates [for example: (Fe), (Fe, Zn, Cu), (Fe, Zn, Cu, Ca), (Fe, Zn, Pb, Al, K) and (Fe, Zn, Cu, Al, K)], and oxides of Zn, Fe, Cu, and/or Pb, in addition to angular grains of SiO₂, CuFeS₂, Cu₅FeS₄, (Zn,Fe)S, PbS, and silicates of varying composition [for example: (Zn, Al, Ca), (Fe, Zn, Cu), (Ca, Al), and (Fe, Zn, Ca, Mg)] (Chen and Pint 1980).

Previous work

The regional distribution and deposition of smelter emissions in the surface terrestrial environment near Flin Flon has been examined using differing sampling media. By analysing rain and snow collected over several seasons, Franzin and others (1979) showed that the smelter at Flin Flon is a source of airborne Zn, Cd, Pb, As, and Cu. Zoltai (1988) showed that peat collected in bogs and fens was enriched in these smelter-related elements up to 100 km SSE from the smelter. Both studies concluded that the maximum radius of deposition varied depending on the element. Franzin and others (1979) calculated distances of contamination ranging from 33 to 217 km, such that the radius of Zn>Pb>As>Cu, while Zoltai (1988) concluded that the radius of Cu = As>Zn>Pb. Henderson and McMartin (1995) showed that Hg enrichment in humus was related to smelter emissions and extended over 40 km from the stack. Hogan and Wotton (1984) also found elevated values of Cu, Pb and Zn in the upper organic layers of material on the forest floor (LFH layer) more than 40 km south and southeast from the smelter stack with 50–60% Zn and 20–35% Cu retained in a bio-available form.

The regional geochemical data and geochemical maps for humus and till collected in the Flin Flon-Snow Lake area (Fig. 2) have been published in Henderson (1995) and McMartin and others (1996). Geochemical maps for humus exhibit a “bull’s eye” pattern, centered on the Flin Flon smelter, for As, Cd, Cu, Hg, Pb, and Zn. For these elements, concentrations are anomalously high at the center of the area, and decrease with distance from the smelter, such that the log-concentration of the heavy metal decreases directly with the log-distance from the smelter until regional background concentrations are reached (McMartin and others 1998). Estimates of re-

gional background determined statistically as the median value after the elimination of most contaminated samples (Table 1; Column C) indicate that distance-to-background ranges from 70 to 104 km, with the radius of As>Cu>Hg>Zn>Pb>Cd. These results are similar to those of Zoltai (1988) and represent the maximum distance for recognition of smelter-related contamination, associated with each element, assuming an annular distribution pattern. It is evident from the geochemical maps, however, that the radius of recognizable contamination in humus varies with direction, extending further in the southeast, southwest, and northwest, consistent with the prevailing winds in the area (McMartin and others 1998). These maps also show that concentrations of trace elements less evident in smelter emissions (Ni, Co, Cr) were generally lower in humus than till and that the distribution in humus did not form a “bull’s eye” pattern. In the clay-sized fraction (<0.002 mm) of till, concentrations of all smelter-related elements were commonly lower than in humus with the distribution pattern relating primarily to bedrock composition modified by the effects of glacial erosion, transport, and deposition (Henderson 1995; McMartin and others 1996; McMartin and others 1998).

Methods

Field procedures

Based on distance from the smelter and stratigraphic context, humus and till samples from 23 sites in the regional geochemical survey were selected for detailed mineralogical, geochemical and physical analyses. On a regional basis, 3-kg till samples were collected from below the B soil horizon either from exposed sections or pits hand dug to bedrock or 1 m maximum depth. In addi-

Table 1

Distance to background (km) for smelter-related elements in humus. Using various estimations for background values, distances for columns B–D are calculated following the regression trendline $y = cx^{-b}$, where y is the estimated background concentration, x the distance from the smelter, and c and b variables of the specific trendline for that element (McMartin and others 1996)

[A – background estimated visually from trendline plot of all samples (McMartin and others 1996); B – background taken as median value of geochemical results for all humus samples in database ($n = 1624$); C – background taken as median value for all samples >50 km from smelter (eliminates highly contaminated samples) ($n = 829$); D – background taken as median value for all samples >75 km from smelter (eliminates most contaminated samples) ($n = 538$)]

Element	A		B		C		D	
	Background (estimated)	Distance to background	Median value (all samples)	Distance to background	Median value (>50 km)	Distance to background	Median value (>75 km)	Distance to background
As (ppm)	4	64	6	42	2.5	104	2.5	104
Cd (ppm)	1	70	1.5	51	1	70	0.5	121
Cu (ppm)	30	66	36	58	20	90	17	101
Hg (ppb)	200	81	300	51	190	85	180	91
Pb (ppm)	50	54	56	49	34	76	28	90
Zn (ppm)	150	56	172	51	84	84	68	97
		$x = 65.2$ km		$x = 50.4$ km		$x = 84.8$ km		$x = 100.5$ km

tion, two excavated till exposures were sampled vertically at 10–50-cm intervals.

Approximately 50–100 g humus was collected from directly over or adjacent to the till sample (Henderson 1995; McMartin and others 1996). The well decomposed, dark organic part of the soil horizon (H) was preferentially sampled for humus (Agriculture Canada 1987). At some sites, however, partially decomposed forest litter and mineral soil (Ah) may constitute part of the sample, since organic soil horizons in the region are generally thin (5–7 cm). In this paper, the term “humus” will be used to represent all samples from the upper organic-rich part of the soil horizon, although those containing <30% organic matter cannot strictly be regarded as humus (Agriculture Canada 1987).

Analytical procedures

Sample preparation

Humus samples were air-dried and sieved to <0.425 mm; the clay-sized fraction (<0.002 mm) of till was separated by centrifugation and decantation (Lindsay and Shilts 1995). In addition, the silt and clay-sized fraction (<0.063 mm) of till for some samples was separated by dry sieving (Henderson 1995).

Standard geochemical analyses

All size fractions were analysed geochemically for Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Sr, Ti, V, and Zn using inductively coupled plasma atomic emission spectrometry (ICP-AES), following nitric-aqua regia digestion. Mercury in humus (<0.425 mm) and the clay-size fraction (<0.002 mm) of till was analysed by cold vapour atomic absorption spectrometry (CV-AAS) following aqua regia digestion. Analyses of duplicate samples and laboratory standards were used to monitor analytical accuracy and precision (Henderson 1995; McMartin and others 1996).

Loss-on-ignition (percent LOI)

The total organic content of humus (<0.425 mm) was determined by heating a small portion of the oven dried sample to approximately 550 °C for one hour. The resulting weight loss, expressed as a percentage of the dry weight, provides an estimate of the amount of organic matter in the sample (Sheldrick 1984). A correlation ($r=0.52$) exists between percent LOI and total soluble organic content determined geochemically using the sodium pyrophosphate leach (see section below, Sequential extraction analyses).

X-ray diffraction (XRD)

The mineralogy of till (<0.002 mm) and the inorganic fraction of humus (<0.425 mm) was determined using a Philips PW1710 automated powder diffractometer equipped with a graphite monochromator, $\text{CoK}\alpha$ radiation at 40 kV and 30 mA. The samples were also x-rayed following saturation with ethylene glycol and heat treatment (550 °C). To remove organic material from humus prior to analyses, samples were pre-treated with 30 percent hy-

drogen peroxide, washed with distilled water, and dried at room temperature (Sheldrick 1984).

Sequential extraction analyses

The sequential extraction scheme used to analyse the <0.425 mm fraction of humus and the <0.002 mm fraction of till is summarized in Table 2. A detailed description of methodology and quality control is presented by Hall and others (1996). Humus samples were initially leached with sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) to extract the “soluble organic” component (humic and fulvic complexes) prior to sequential extraction of the “insoluble residue” (humic and mineral matter). Solutions derived from the application of the leaches were analysed by flame atomic absorption spectrometry (AAS) for Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn; Hg was analysed by vapour generation (ICP-MS); As by quartz tube AAS after hydride generation.

Sequential extraction has been used in exploration and environmental geochemistry to determine element residence sites (Chao 1984). The technique differentiates between elements held in “labile” or secondary phases [soluble organic matter, adsorbed/exchangeable/carbonate (AEC), and amorphous Fe/Mn oxyhydroxide phases] from those more strongly held in “non-labile” phases (crystalline Fe oxide, sulphide/“less soluble” organic, and silicate/residual crystalline phases; Table 2]. Selectivity is not perfect and extraction efficiencies vary depending on the chemicals employed, the length of treatment, and sediment-to-extractant ratio (Hall and others 1996).

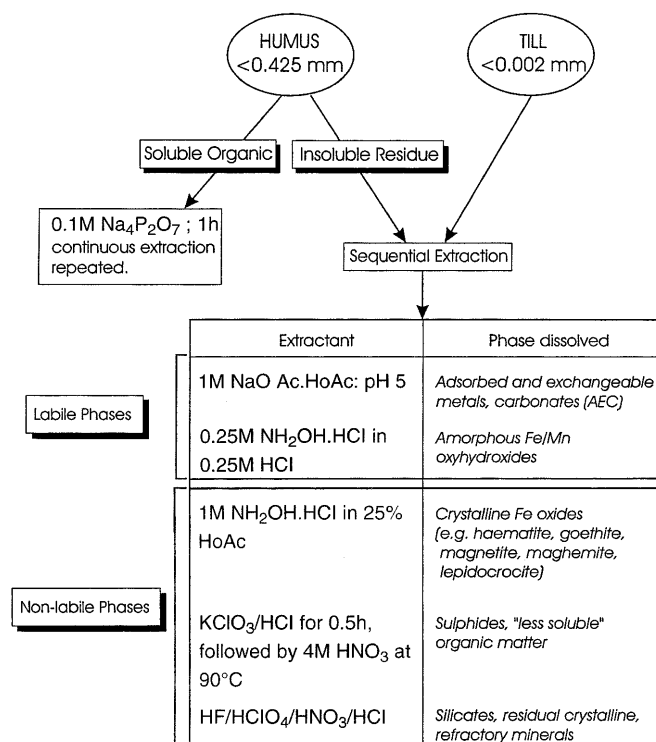


Table 2

Sequential extraction scheme (modified from Kaszycki and Hall 1996)

Scanning electron microscope

Humus (<0.425 mm fraction) and till (<0.002 mm and <0.063 mm fraction) samples were examined under the scanning electron microscope (SEM) using grain mounts prepared by sprinkling sample material onto a carbon-impregnated tape. Grain mounts were carbon-coated prior to examination. A Leica Cambridge Stereoscan S360 SEM equipped with an Oxford/Link eXL-II energy-dispersion x-ray analyzer, Oxford/Link Pentafet Be window/light element detector, and an Oxford/Link Tetra back-scattered electron detector was used. Samples were scanned using the backscattered electron imaging mode specifically to identify grains with elements of high atomic number.

Results

The samples selected for detailed chemical, mineralogical and physical analyses are from 23 sites in the regional geochemical survey. These sites are located at varying distances from the smelter and represent two transects extending from the point source, and two "background" locations (Fig. 2). The first transect (Sites 1–10) extends 82 km NNW from the smelter across metasedimentary and metavolcanic rocks of the Flin Flon greenstone belt (Sites 1–3), the Attitti Block of the Flin Flon terrane (Sites 4, 5, 8, and 9), gneisses and associated intrusive rocks of the Kisseynew Domain (Sites 6 and 7), and

gneissic and supracrustal rocks of the Hanson Lake Block (Site 10). The second transect (Sites 11–20) extends 40 km SSW from the smelter. Sites 11–17 are underlain by rocks of the Flin Flon greenstone belt and Sites 18–20 by Paleozoic carbonate rocks.

The two background sites overlie Paleozoic bedrock (Fig. 2). Background site 1 is located 74.8 km SSE from the smelter, humus overlies glaciolacustrine clay and a locally derived, moderately calcareous till. Background site 2 is located 160.4 km southeast of Flin Flon in an area of highly calcareous till.

Mineralogy and organic content

Humus represents the organic-bearing mineral-rich surface horizon of the soil profile and includes varying amounts of material derived from the smelter through atmospheric deposition. The relative proportion and composition of the organic and mineral component will affect humus geochemistry since certain phases have a tendency to scavenge trace metals (Rose and others 1979; Varskog and others 1993). In this study, the total organic content (percent LOI) of humus (<0.425 mm fraction) varies from 22.72 to 92.15 percent (Table 3; Fig. 3). The inorganic component of the samples consists primarily of common rock-forming minerals (quartz, plagioclase, potassium feldspar), with trace amounts of amphibole, mica and chlorite, particularly at sites in the Flin Flon greenstone belt. Dolomite is abundant at sites overlying Paleozoic bedrock.

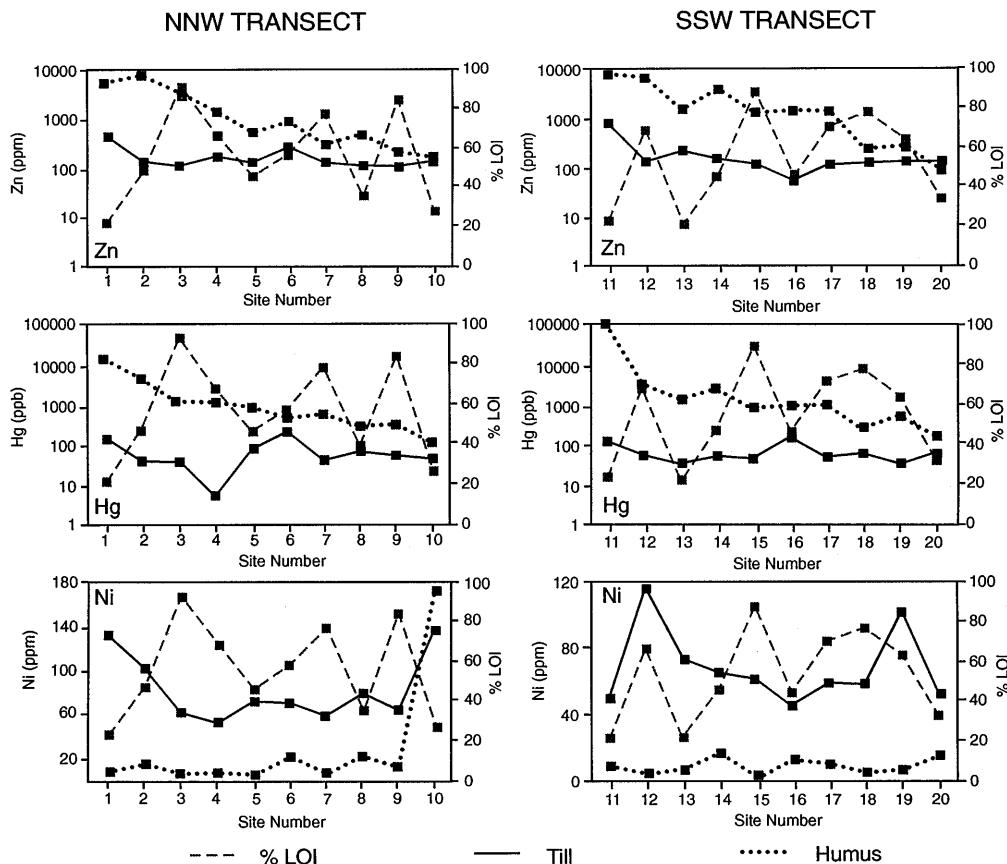


Fig. 3 Total organic content (percent LOI) of humus and total concentrations of Zn, Hg and Ni in humus and till collected from transect sites. Transects extend 82 km NNW and 40 km SSW from the smelter at Flin Flon

Table 3
Distribution of heavy metals in humus and till from transect and background sites. Carbonate content is determined by atomic absorption spectrometry on the <0.063 mm size fraction (Henderson 1995; McMartin and others 1996)

Site no.	Distance (km)	% LOI (Humus)	% CO ₃ (Till)	As (ppm)		Cd (ppm)		Cu (ppm)		Hg (ppb)		Pb (ppm)		Zn (ppm)		Ni (ppm)		Cr (ppm)		
				Humus	Till	Humus	Till	Humus	Till	Humus	Till	Humus	Till	Humus	Till	Humus	Till	Humus	Till	Humus
North-northwest Transect																				
1	3.1	22.72	2.20	112	42	31.5	<0.5	1877	155	12800	140	1004	16	5666	426	8	130	30	460	
2	5.1	47.81	3.21	84	2	42.5	<0.5	1671	144	4500	40	920	4	7908	132	16	102	47	465	
3	11.2	92.15	1.93	32	48	12.0	<0.5	496	87	1200	40	314	4	3364	102	7	60	5	131	
4	17.5	68.00	0.80	50	136	8.5	<0.5	363	87	1150	50	458	14	1348	170	6	51	9	99	
5	21.2	46.07	1.42	20	<2	6.0	<0.5	160	102	800	80	198	16	510	118	4	71	12	146	
6	24.8	57.71	2.08	50	22	9.0	0.5	250	709	440	190	174	8	830	260	21	69	21	133	
7	31.0	77.07	2.61	12	22	3.5	<0.5	95	114	600	40	198	1	302	124	5	58	9	147	
8	40.5	34.63	2.43	12	4	3.5	<0.5	67	88	280	70	94	1	426	96	19	77	17	188	
9	46.4	83.52	2.55	<2	<2	2.0	<0.5	34	92	300	50	56	1	196	100	12	63	14	154	
10	82.0	26.69	1.75	<2	<2	0.5	<0.5	294	364	100	40	30	18	134	124	169	136	107	250	
South-southwest Transect																				
11	1.75	23.21	1.34	558	4	39.0	<0.5	2670	89	100000	110	1692	12	7428	756	14	52	20	142	
12	8.75	68.64	1.75	48	32	32.5	<0.5	1234	229	2800	50	1100	8	5612	124	8	118	21	264	
13	10.00	21.71	2.59	32	6	9.0	<0.5	453	271	1200	30	426	4	1458	206	10	74	22	164	
14	14.40	46.84	8.48	22	116	14.0	<0.5	390	184	2200	50	232	2	3722	136	19	65	41	151	
15	15.10	87.74	2.84	42	30	8.0	<0.5	387	94	720	40	534	10	1192	106	4	62	9	153	
16	19.40	44.5	6.74	12	<2	6.0	<0.5	135	263	850	130	64	6	1372	52	15	46	33	77	
17	21.80	70.76	7.13	16	<2	8.0	<0.5	297	112	900	40	182	2	1320	102	13	60	24	131	
18	29.00	76.94	10.59	16	8	2.0	<0.5	58	125	220	50	48	2	196	106	7	59	12	147	
19	33.60	63.29	3.65	8	6	2.5	<0.5	66	96	460	30	154	1	256	112	9	102	15	231	
20	39.30	32.38	23.65	8	4	0.5	<0.5	29	71	140	50	8	2	74	106	17	52	26	139	
Background																				
1	74.80	64.64	66.47	16	4	1.0	<0.5	51	38	200	60	72	12	172	70	20	33	31	65	
2	160.40	59.32	76.07	2	<2	0.5	<0.5	10	22	140	50	18	6	24	20	9	27	19	36	

The clay-size fraction (<0.002 mm) of till comprises quartz, plagioclase, potassic feldspar, and abundant to moderate amounts of mica, chlorite, kaolinite, and smectite (possibly montmorillonite). Locally, trace to moderate amounts of amphibole occur in samples overlying greenstone belt rocks. As with humus, dolomite and calcite are present in tills overlying Paleozoic terrane.

Geochemical composition

All transect sites and Background Site 1 lie within the zone of recognizable smelter contamination in humus for smelter-related elements defined by the regional database, except for Cd and Pb (Table 3; cf. Table 1, column C). In humus, total concentrations near or less than background values occur at Site 9 for As, Site 10 for As and Hg, Site 20 for Hg and Zn, and Background Site 1 for Hg. On a site-to-site basis, differences between actual heavy metal concentrations and those predicted from the regional distribution (McMartin and others 1998) are to be expected given the complex interplay of factors controlling atmospheric deposition of smelter emissions and humus geochemistry (Rose and others 1979).

In humus, total concentrations of all smelter-related elements decrease with distance from the smelter (Table 3) and, as illustrated by the distribution of Zn and Hg (Fig. 3), are independent of total organic content (percent LOI) (Zn, $r=0.23$; Hg, $r=0.33$). In the case of Zn, samples collected within 5 km from the smelter are enriched to a maximum of 94 times the regional background value, at 10 km approximately 40 times, at 20 km 16 times,

at 40 km 5 times, and at 80 km only 1.6 times regional background. Mercury, on the other hand, is enriched in humus as much as 500 times the regional background value at sites <5 km from the smelter and drops to approximately 6 times at 10 km; 4 times at 20 km; and 1.5 times at a distance of 40 km from the smelter (Table 3; cf. Table 1, Column C). In general, concentrations of all smelter-related elements in humus exceed those in till, although exceptions are present for As, Cu, and Zn at several sites (Table 3). Concentrations of trace elements unrelated to smelter emissions (Ni, Cr) are consistently lower in humus than till, with the exception of Ni at Site 10 (Fig. 3). This site is located in the Hanson Lake Block and anomalous values in both humus and till may be associated with the presence of Ni-rich mafic dykes throughout the area (Ashton 1989).

In till, concentrations of smelter related elements show no direct relationship to distance from the smelter (Fig. 3). Values are less variable than in humus, fluctuating around regional background (McMartin and others 1996).

Chemical speciation

Chemical partitioning in humus and till was achieved through selective, sequential extraction analyses. For the purposes of discussion, phases determined through the application of this technique, are grouped: for humus, into the soluble organic phase (humic and fulvic complexes), and the relatively labile and non-labile components of the insoluble humus residue (humins and mineral

Table 4

Relative distribution of heavy metals in various phases of humus and till

Humus	Soluble organic phase (% of total concentration)		Insoluble residue			
			% Labile		% Non-labile	
	Average	Max-Min	Average	Max-Min	Average	Max-Min
As	16	34- 6	43	68-23	57	77-32
Cd	45	73- 7	63	89-14	37	86-11
Cu	32	50-16	50	68-30	50	68-32
Hg	18	40- 5	2	4- <1	98	100-96
Ni	24	60- 0	38	75- 6	62	94-25
Pb	49	75- 9	65	83-51	35	49-17
Zn	54	78- 9	23	49- 7	77	93-51

Till	Insoluble residue			
	% Labile		% Non-labile	
	Average	Max-Min	Average	Max-Min
As	19	30- 9	81	91-74
Cd	64	88- 5	36	95-12
Cu	33	54-15	67	85-49
Hg	14	27- 5	86	95-73
Ni	17	35- 6	83	95-65
Pb	42	100-14	58	86- 0
Zn	31	75-18	69	83-25

matter), and for till, the labile and non-labile phases (Table 2).

Partitioning effects differ depending on the element and the sample medium (Table 4). Based on the phase distribution of trace elements in humus in relation to organic content, three broad categories have been recognized:

1. Smelter-related elements having a strong correlation between the proportion associated with the "soluble organic" phase and the total organic content (percent LOI) (Zn, Pb, Cd, and Cu);
2. Smelter-related elements having no such correlation (As, Hg); and
3. Non-smelter-related elements for which concentrations in humus are low for all phases (Co, Ni).

Sequential analytical results are discussed for three elements representative of each category (Zn, Hg, Ni): Zn and Hg are of environmental significance, whereas Ni is not characterized as an important trace metal emitted from the Flin Flon smelter (Table 5).

Zinc Partitioning

Humus Zinc concentrations in all phases decrease generally with distance from the smelter (Fig. 4a). The highest percentage of Zn is associated with the soluble organic phase, for most sites (Table 4; Fig. 4b), and a correlation is present between the percent Zn in that phase and percent LOI (Fig. 5a). A significant component of Zn in humus must also reside in the insoluble residue, however, because no correlation exists between total Zn concentrations and percent LOI (Fig. 5b).

In the insoluble humus residue, the ratio of Zn in labile to non-labile phases increases generally with distance from the smelter (Figure 4b). Close to the smelter, the relative proportion of Zn in the non-labile phases is high (Table 5), attaining >90% at sites within 3 km from the smelter (Sites 1 and 11). This spatial distribution suggests that Zn concentrations near the smelter are strongly influenced by smelter-derived particulates, such as Zn-rich silicates and Fe-oxides (Chen and Pint 1980), which

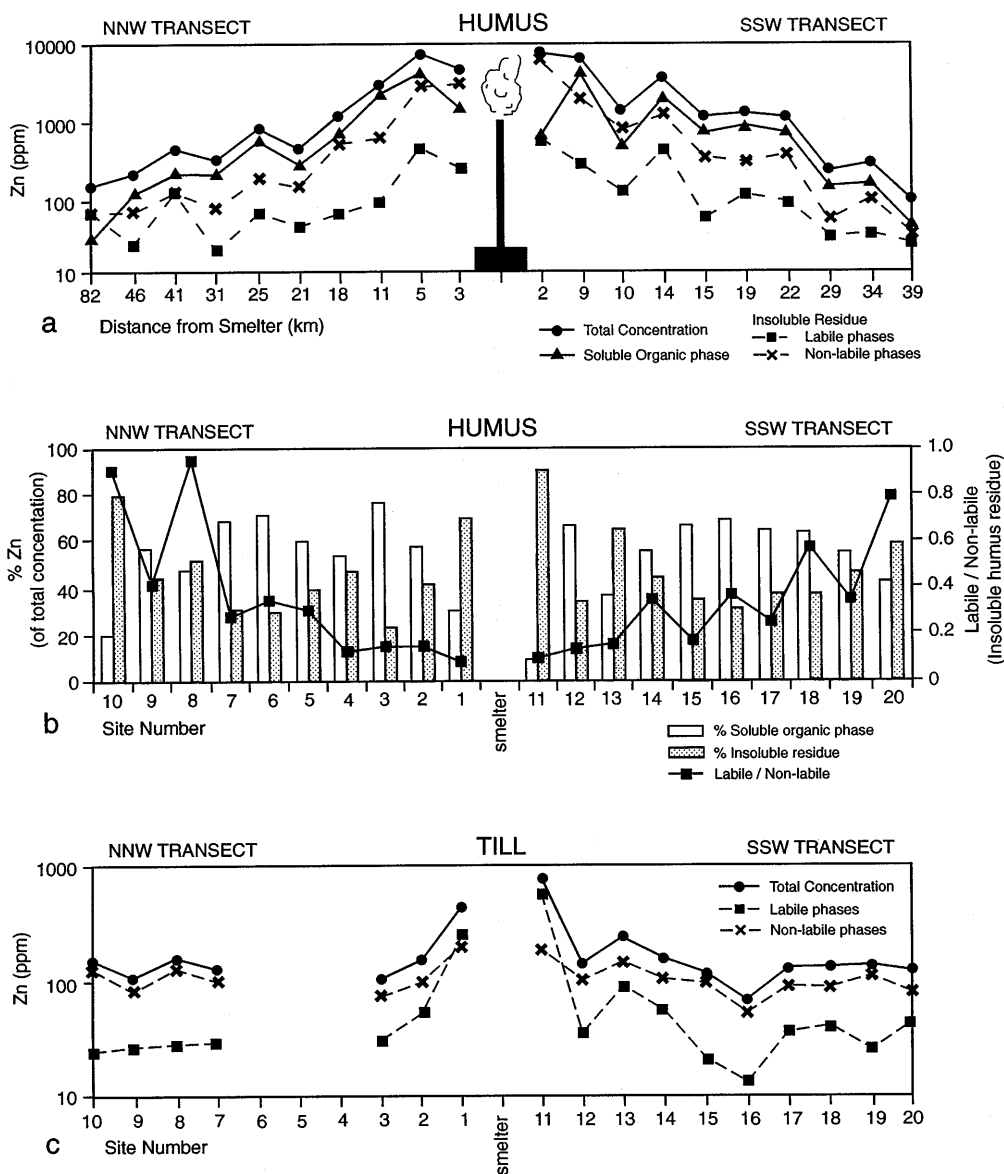


Fig. 4 Partitioning of Zn in samples collected from transect sites: a total concentration in various phases of humus; b percent total Zn in soluble organic phase and insoluble humus residue and ratio between labile and non-labile components in insoluble humus residue; c total concentration in various phases of till

Table 5

Relative proportion of Zn, Hg and Ni in the soluble organic phase of humus and the insoluble portion of humus and till collected from transect and background sites

Humus Transect Site no	Zn partitioning			Hg partitioning			Ni partitioning		
	% Soluble organic	Insoluble residue		% Soluble organic	Insoluble residue		% Soluble organic	Insoluble residue	
		% Labile	% Non-labile		% Labile	% Non-labile		% Labile	% Non-labile
NNW Transect									
1	30.7	6.6	93.4	6.0	2.9	97.1	15.0	5.9	94.1
2	58.1	13.0	87.0	6.0	1.0	99.0	12.0	18.2	81.8
3	77.5	12.4	87.6	10.0	1.3	98.7	60.0	76.0	25.0
4	53.8	10.5	89.6	16.4	2.0	98.0	40.0	33.3	66.7
5	60.7	23.4	76.6	24.6	2.9	97.1	57.1	33.3	66.7
6	71.4	25.5	74.6	23.9	2.1	98.0	38.1	46.2	53.8
7	69.1	22.0	78.0	19.9	3.2	96.8	0.0	50.0	50.0
8	47.7	49.1	50.9	23.2	2.7	97.5	31.6	53.8	46.2
9	56.2	27.0	72.9	9.8	1.7	98.4	0.0	62.5	37.5
10	19.9	47.7	52.3	26.1	5.4	94.7	20.5	62.1	37.9
SSW Transect									
11	8.5	8.2	91.8	39.3	3.8	96.2	0.0	10.0	90.0
12	67.0	12.0	88.0	15.5	1.7	98.3	35.0	23.1	76.9
13	35.4	13.0	87.0	17.0	2.1	97.9	16.7	30.0	70.0
14	56.0	25.8	74.2	5.4	0.6	99.4	0.0	30.0	70.0
15	66.9	13.4	86.6	20.6	2.1	97.9	57.1	33.3	66.7
16	69.3	26.7	73.3	9.4	1.0	99.0	6.7	35.7	64.3
17	63.7	19.5	80.4	18.7	2.0	98.0	11.1	50.0	50.0
18	64.3	36.5	63.5	16.1	4.0	96.0	0.0	40.0	60.0
19	54.2	25.0	75.0	16.0	3.1	96.5	47.1	44.4	55.6
20	41.9	44.0	56.0	30.9	4.4	95.6	30.4	31.2	68.8
Background									
1	43.7	40.5	95.5	10.7	3.4	96.6	5.3	44.4	55.6
2	30.0	28.6	71.4	18.4	1.9	98.1	0.0	20.0	80.0
Till									
Transect Site no.	Zn partitioning		Hg partitioning		Ni partitioning				
	% Labile	% Non-labile	% Labile	% Non-labile	% Labile	% Non-labile			
NNW Transect									
1	54.9	45.1	5.4	94.6	13.4	86.6			
2	35.1	64.9	8.3	91.7	26.0	74.1			
3	29.2	70.8	19.5	80.6	13.1	86.9			
4	insufficient sample material for analyses								
5	insufficient sample material for analyses								
6	insufficient sample material for analyses								
7	22.7	77.3	13.6	86.5	7.8	92.2			
8	17.9	82.1	14.0	86.0	6.6	93.4			
9	24.8	75.2	24.5	75.5	8.2	91.8			
10	16.9	83.1	20.9	79.1	10.4	89.6			
SSW Transect									
11	75.3	24.7	11.2	88.8	35.3	64.7			
12	25.7	74.3	10.0	90.0	19.1	80.9			
13	38.6	61.4	20.2	79.8	24.2	75.8			
14	35.0	65.0	12.6	87.4	27.8	72.2			
15	17.8	82.2	27.3	72.7	5.5	94.5			
16	19.1	80.9	4.6	95.4	17.3	82.7			
17	27.9	72.1	12.0	88.0	9.0	91.0			
18	31.3	68.7	5.9	94.1	28.4	71.6			
19	18.2	81.8	14.6	85.4	9.9	90.1			
20	35.5	64.5	8.5	91.5	28.3	71.7			
Background									
1	23.3	76.7	6.9	93.1	6.2	93.8			
2	22.9	77.2	11.0	89.1	25.6	74.4			

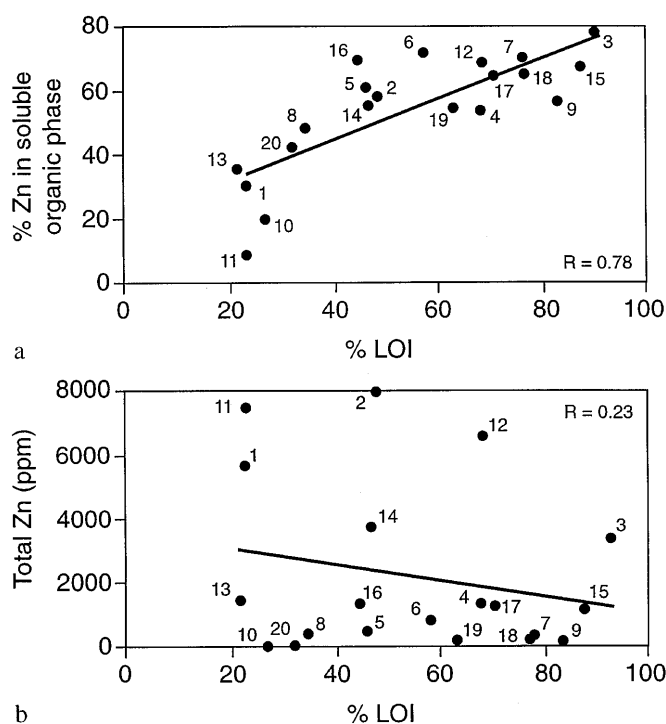


Fig. 5 Relationship between Zn concentrations and total organic content (percent LOI): **a** % Zn in soluble organic phase, **b** Total Zn (ppm)

would be expressed geochemically in the residual crystalline and crystalline Fe-oxide phases of the non-labile component of the insoluble humus residue. Definitive linkages between this component and smelter-derived particulates through geochemical analyses is difficult, especially at sites more removed from the smelter, since naturally occurring minerals also contain these trace elements. Chemical partitioning in humus from the Snow Lake area, >120 km from the smelter (Fig. 2), where total Zn concentrations approximate regional background (Table 1), also shows a high proportion of Zn in non-labile phases (Kaszycki and Hall 1996). There, partitioning in the insoluble humus residue is interpreted to reflect the mineralogy of underlying till.

The proportion of Zn in the labile component of the insoluble humus residue generally increases with distance from the smelter (Figure 4b; Table 5). The higher relative influence of these labile phases in partitioning indicates that Zn concentrations are increasingly affected by secondary chemical processes (such as weathering, alteration, etc.) at sites removed from the stack. These secondary processes may only be recognizable with distance from the smelter when the rate of chemical weathering exceeds the rate of clastic deposition from the smelter. Low Zn concentrations (24 ppm; Table 3) at Background Site 2 are characteristic of humus overlying Paleozoic terrane (McMartin and others 1996; McMartin and others 1998). Geochemical differences among phases cannot be

distinguished at these low concentrations, due to analytical imprecision near lower detection limits.

Till Zinc partitioning in till appears to be related, at least in part, to distance from the smelter (Fig. 4c). Near Flin Flon (Sites 1 and 11), total Zn concentrations are elevated compared to other transect samples, with Zn residing primarily in labile phases (Table 5). The Zn enrichment and its phase distribution may result from:

1. Geological enrichment associated with the greenstone belt near Flin Flon. Sites along the SSW transect lie down-ice from Zn-Cu mines, and Zn enrichment in labile phases may result from oxidation of sulphide minerals derived from mineralized zones.
2. Smelter contamination. Sites near the smelter are characterized by poorly developed humus (LOI averages 23%) with anomalously high Zn concentrations. Zn enrichment in labile phases of till may result from downward leaching because of the lack of a well developed organic horizon or, more directly because of the high level of contamination in humus at these sites. This possibility will be considered further by examining vertical sections through till.

The relative proportion of Zn in labile phases of till is also higher than average at other sites close to the smelter (2, 3, 13, and 14), and in carbonate-rich tills (18 and 20) near the southern end of the transects. Since an average of 69% Zn in humus is retained in easily leached forms at distances >3 km from the smelter, the phase distribution at these sites may also result, at least in part, from leaching from contaminated humus. In general, however, Zn partitioning in till is similar to that observed in the Snow Lake area (Kaszycki and Hall 1996) where it has been interpreted to represent the geochemical response to bedrock composition and glacial erosion and transport.

Mercury partitioning

Humus Mercury concentrations in all phases of humus decrease with distance from the smelter (Fig. 6a). Unlike Zn, Hg concentrates primarily (>95%) in the non-labile component of the insoluble humus residue (Table 5; Fig. 6a) and, consequently Hg partitioning in humus is related either to Fe-oxide, sulphide, and silicate minerals, such as those emitted from the smelter, and/or bound with "less soluble" organic material (Table 2). The probable influence of smelter-derived particulates on total Hg concentrations is particularly apparent at sites within 3 km of the smelter (1 and 11), where Hg concentrations exceed 10000 ppb in non-labile phases. At all sites, however, the strong association of Hg with this non-labile component indicates that Hg is less mobile in the surface environment than Zn.

The ratio between labile and non-labile components of the insoluble humus residue is low because of the overwhelming proportion of total Hg associated with non-labile phases. With the exception of sites <3 km from the smelter (Fig. 6b), the relative proportion of Hg in the labile component tends to increase with distance from the

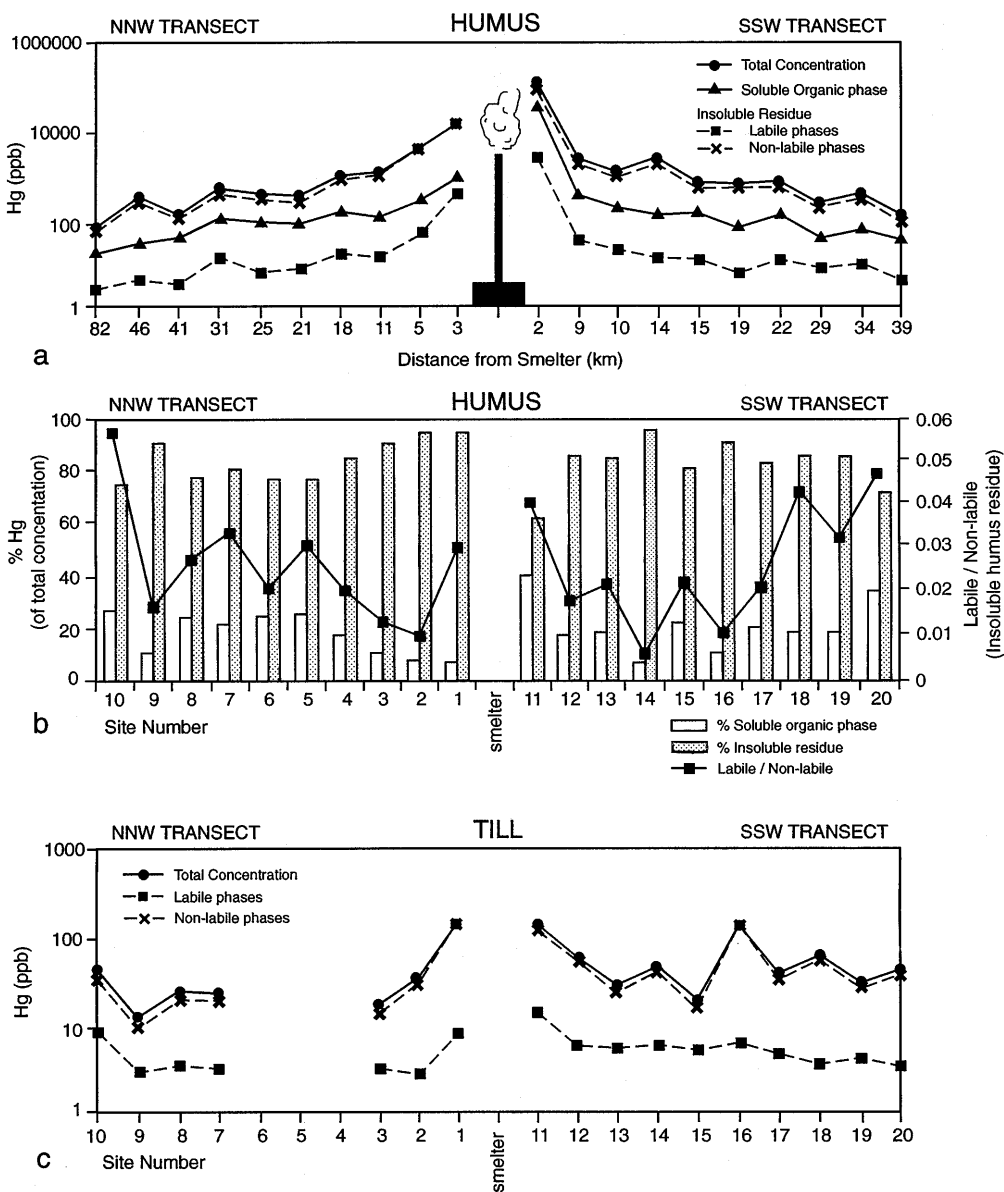


Fig. 6 Partitioning of Hg in samples collected from transect sites: a total concentration in various phases of humus, b percent total Hg in soluble organic phase and insoluble humus residue and ratio between labile and non-labile components of insoluble humus residue; c total concentration in various phases of till

smelter, following the relationship seen with Zn. At those sites within 3 km (Sites 1 and 11), however, the proportion of Hg in the labile component of the insoluble residue is relatively high, with associated concentrations of 443 and 2590 ppb. This indicates that significant amounts of Hg may be bio-available adjacent to the smelter, in areas of high contamination.

The proportion of Hg in the soluble organic phase of humus is low, varying from 6 to 40% (Table 5; Fig. 6b), and no correlation exists between percent LOI and percent Hg in the soluble organic phase (Fig. 7). In the NNW transect, the percent of total Hg in this phase increases before stabilizing at distances >20 km from the smelter. This stabilisation may reflect a decrease in the influence of smelter-derived particulate matter associated with the non-labile component of the insoluble humus residue with distance from the smelter, however, no similar trend is evident in the SSW transect. High total Hg concentra-

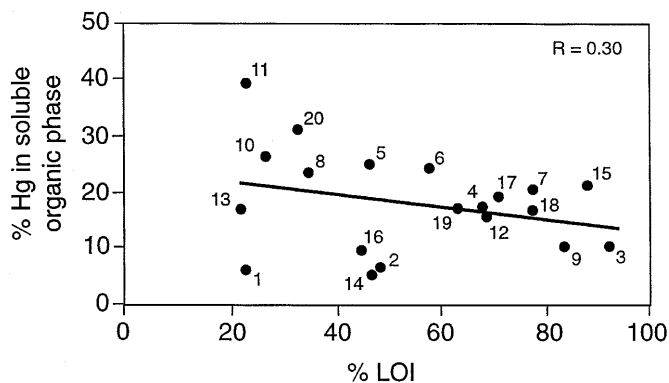


Fig. 7 Relationship between % Hg in soluble organic phase and total organic content (percent LOI)

tions (>1000 ppb) in the soluble organic phase at Site 11 (<2 km from the smelter) augment concentrations in the labile component of the insoluble humus residue, and further indicate the potential for significant amounts of Hg to become mobile in those highly contaminated areas adjacent to the stack.

Till - Total Hg concentrations in till are low (Table 3; Fig. 6c). As with Zn, Hg enrichment in labile phases is present at sites near the smelter (Sites 1 and 11) possibly as a result of downward leaching of heavy metals from anomalous concentrations in humus, and/or geological enrichment associated with mineralization near Flin Flon.

Over 73% Hg is held in the non-labile component of till (Table 5), particularly the crystalline Fe oxide (average 65%) and the sulphide/"less soluble" organic (average 21%) phases. In the latter phase, Hg is likely bound with either phyllosilicate minerals or organic material since sulphide minerals are absent in till due to weathering (Kaszycki and others 1996). The proportion of Hg in the labile component varies from 5 to 27% and is unrelated to total Hg concentrations.

Ni partitioning

Humus - No evidence of smelter-related contamination is indicated by Ni distribution in humus because of low total concentrations (Table 3) and the inherent analytical imprecision (Table 5). In general, Ni resides primarily in the non-labile component of the insoluble humus residue. At Site 10, total Ni values exceed 160 ppm reflecting a similar enrichment in till (Table 3). Nickel in humus at this site is predominantly in the labile component of the insoluble humus residue, which suggests that enrichment may result from geological and biological factors associated with Ni-rich mafic dykes in the area.

Till - Nickel concentrations in till are higher than in humus (Table 3) and primarily reflect clastic dispersal from bedrock sources. An average of 83% of total Ni in transect and background samples is associated with the non-labile component, particularly the sulphide/"less soluble" organic phase. With some exceptions, the percentage of Ni in the more labile component is higher in till samples overlying the Flin Flon greenstone belt and the Hanson Lake block (Site 10). This may be a function of the generally elevated trace element concentrations associated with these rocks (McMartin and others 1996) and the resulting effects of weathering of sulphides and other Ni-rich minerals derived from greenstone belt lithologies.

Partitioning in soil profiles

Two soil profiles, varying in distance from the smelter and in geological context (Fig. 2), were examined in order to assess the geochemical effects of soil forming processes, and the extent of downward leaching of smelter-related elements (Fig. 8). Section A represents a shallow hole (1 m) dug to bedrock (Site 12) 8.75 km SSW of the smelter stack. The area is underlain by mafic volcanic

rocks of the Flin Flon greenstone belt which contain gold mineralization. Section B is a 5.3-m-high section overlying Paleozoic dolostone, 42.5 km SE of Flin Flon, in an area where heavy metal concentrations in humus approach background values. Both sections represent a single till unit.

Section A Brunisolic soils are the commonest soils in the study area, developing mainly on glaciofluvial and glacial till deposits (Acton and Padbury 1984). From the results of Fe analyses, the B-horizon can be seen to extend to approximately 45 cm depth (Fig. 8a). Humus is enriched in Hg and Zn compared to till. In till, Hg and Zn concentrations are elevated near the top of the soil profile, decrease with depth in the B-horizon, and stabilize below this zone. Nickel concentrations, on the other hand, are depleted in humus and the B-horizon of till. Below 45-cm depth, values for all elements approach background levels for Shield-derived till (McMartin and others 1998).

In Section A, over 70% Zn (4624 ppm) and 16% Hg (473 ppb) in humus is retained in an easily leached form and, consequently, may be mobilized within the soil profile. The high proportion of Zn associated with the labile component of till at 5-cm depth (Fig. 8a) suggests downward leaching occurs to that depth, at least. Below 25 cm, however, the distribution of Zn among phases does not change with depth. Because Ni partitioning is similar to Zn, and Hg partitioning shows no variation with depth, there is no evidence to support downward leaching below 25 cm, based on the results of sequential extraction analyses. Based on total concentrations, however, the enrichment of Zn and Hg, as opposed to the depletion of Ni, in B-horizon tills suggests that Zn and Hg contamination may occur within the section to a depth of 45 cm, at least. Soil profiles from geologically similar terrane in the Snow Lake (Kaszycki and others 1996) and Naosap Lake areas (McMartin and others 1996), located >120 and >40 km from the smelter, respectively, are characterized by a depletion in most trace element concentrations in the B-horizon relative to the underlying material.

Section B In Section B, till is enriched in Paleozoic carbonate detritus and, consequently, the concentrations and distribution of trace elements differ from the previous section (Fig. 8a). Because the section is located >40 km from the smelter, Zn and Hg concentrations in humus are only slightly enriched compared to regional background (McMartin and others 1996) and the underlying till. The upper 20 cm of the soil profile is leached of carbonate, and metal concentrations tend to be enhanced; from 30- to 100-cm depth carbonate is reprecipitated, and trace metal concentrations are relatively depleted; below 100 cm, till is essentially unweathered (Fig. 8b). The B-horizon extends to approximately 40-cm depth. No evidence for downward leaching of smelter-related elements is provided by sequential extraction analyses. Above 80-cm depth, less than 20% of the total metal concentration of all elements resides in the labile component

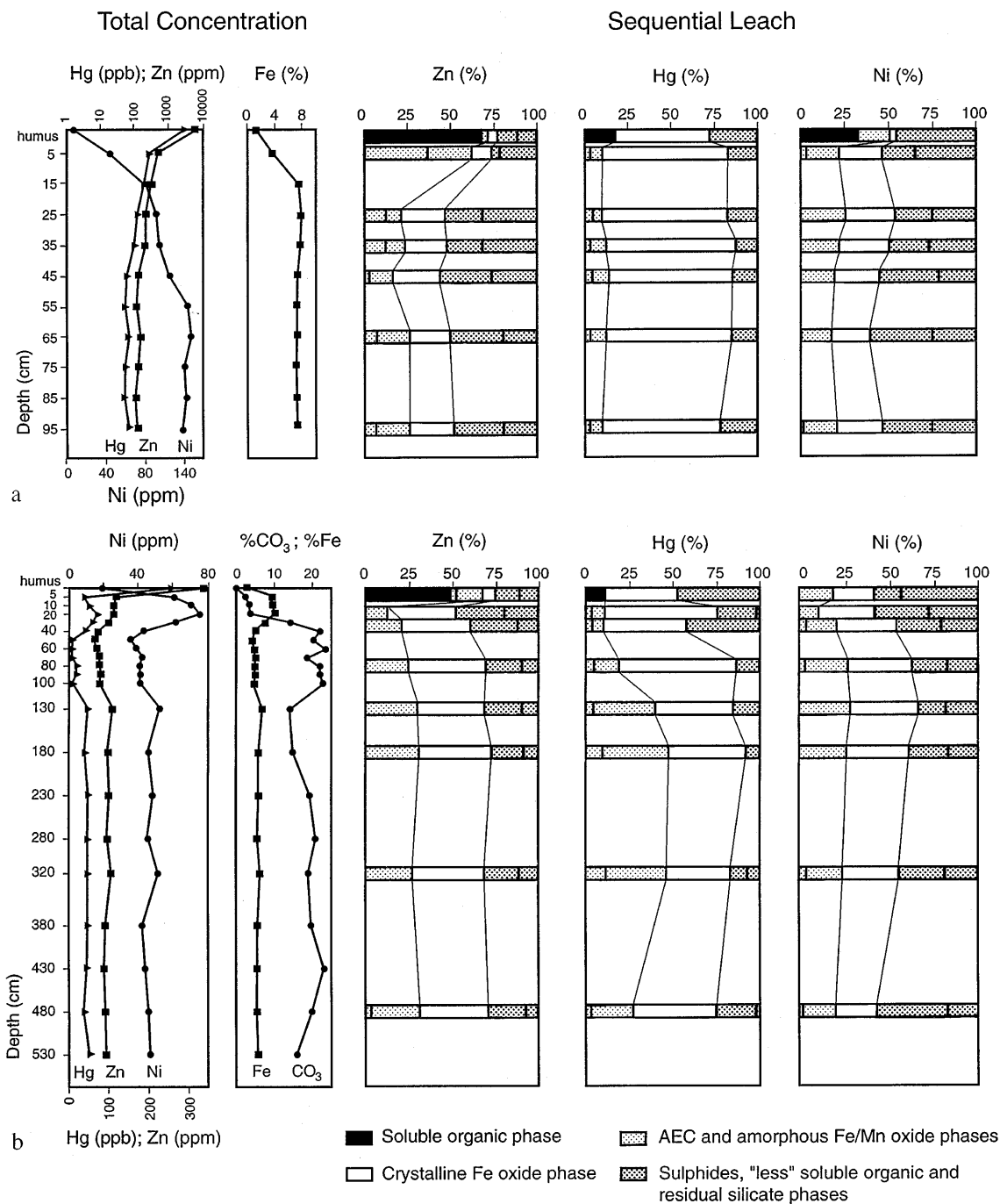


Fig. 8

Trace element concentrations and partitioning of samples from vertical profiles: Section A Shield-derived till; Section B Paleozoic-derived till (Fig. 2)

of till (Fig. 8b), whereas below 80 cm, the percent associated with these phases increases and partitioning among phases stabilizes, particularly for Zn. At the base of the section, the percent Hg and Ni associated with the non-labile component of till increases as might be expected in the essentially unweathered C-horizon.

From the profiles, vertical variations in trace metal concentrations appear to result primarily from soil-forming processes, although evidence for downward leaching of smelter-related elements from humus is indicated in the B-horizon of Section A. More extensive leaching may occur at those heavily contaminated sites (sites 1 and 11, see previous section) within 3 km from the smelter, based on the high proportions of Zn and Hg in the labile component of till (Figs. 4 and 6). Similar conclusions were reached by Hogan and Wotton (1984) and Freedman and Hutchinson (1980).

SEM examination of particulate matter

Humus and till samples were examined qualitatively under the scanning electron microscope to determine the size, morphology and composition of particles enriched in heavy metals and to validate the results of metal speciation studies by sequential leaching. Samples from Sites 1, 7, 10–12, and 17 of the transects, Background Site 2 and Section B were examined.

Humus

In humus, smelter-related heavy metal particles were found at all sites. These particles occur as spheres, amalgamations of spheres, angular grains, and within organic material. Heavy metals may also occur as grain coatings. All particles examined were >0.001 mm diameter. Results

of SEM examination of samples from the NNW transect and Background Site 2 are summarized in Table 6.

Spherical particles The formation of spherical particles has been associated with natural geological processes, such as volcanism (Meeker and Hinkley 1993), lightning strikes (Essene and Fisher 1986) and cosmic dust (Murrell and others 1980; Blanchard and others 1980; Bi and Morton 1995), as well as anthropogenic processes, such as smelting activities (Dunn and others 1993). In general, spheres formed by natural processes differ in composition, texture and size from those observed in humus in the Flin Flon area. The composition of spherical particles examined in this study closely approximates smelter dust from the local plant (Chen and Pint 1980) and, conse-

Table 6

Size and composition of particulate matter enriched in heavy metals in humus from selected sites along the NNW transect and Background Site 2 (Fig. 2)

Site	Particle type					
	Spherical particles			Discrete grains		
	Size (μ)	Composition	Comments	Size (μ)	Composition	Comments
NNW Transect						
1	20	Fe, Si, Al, O; minor Zn, Cu; trace Pb		47	Fe, Zn, O	rectangular, angular grns; Rice crispy texture
	26	Fe, O; minor Cu		18.5	Fe, Si, O; minor Zn, Al	irregular, discrete grain
	27	Zr, Si, O		2.5	Ag	
	2.5	Fe, Zn, Si, Al, O	attached to large sphere	4	Fe, Cr	
	9.7	Si, Al, O; minor K; trace Zn, Fe		2.25	Ba, S, Pb	with large grain
	35	Si, Al, O		2.5	Fe, O	
	20	Si, Al, O; minor Zn		1.75	Pb, Si, O; minor Al, Mg	
7	80	Si, O, Al	fragmented crust	6.5 × 15	Pb, Ba, S	
	45	Zn, Si, Al, O; minor Pb, Cu, Fe		12	Fe, O	
	36	Si, Al, O; minor Na, Ca			Fe, Si, Ca, Al; minor K	
	43	Si, Al, O; minor Ca, K, Fe, Na, Si, O			Si, Al, K, O	in agglutinated mass
				Fe, O		
				Si, Ca, Mg, Fe, O		
				Fe, Ti, O		
				Ce, La, Si, O (x2)	monazite	
				Si, Al, Mg, Fe, Ca, O		
10	6	Si, Al; minor O			Si, Al, O; minor Fe, Ca, K, Mg	
	6.4	Si, O; minor Al				
	4.75	Si, O			Si, O, Zn	
	5.5	Fe, Si, O			Fe, O; trace Cr	
	4.5	Si, O; Fe (x2)			Zr, Si, O (x2)	zircon
	4	Si, O; trace Al (x2)			Ce, La, P, O; Si, Al	monazite
				Fe, Si, O		
Background Site						
2	5.3	Si, O				
	5	Si, O	organic coating			
	8	Si, O; minor Al, C, K; trace Mg, Fe				
	4.5	Si, O; minor Al, Ca, Fe; trace Mg				

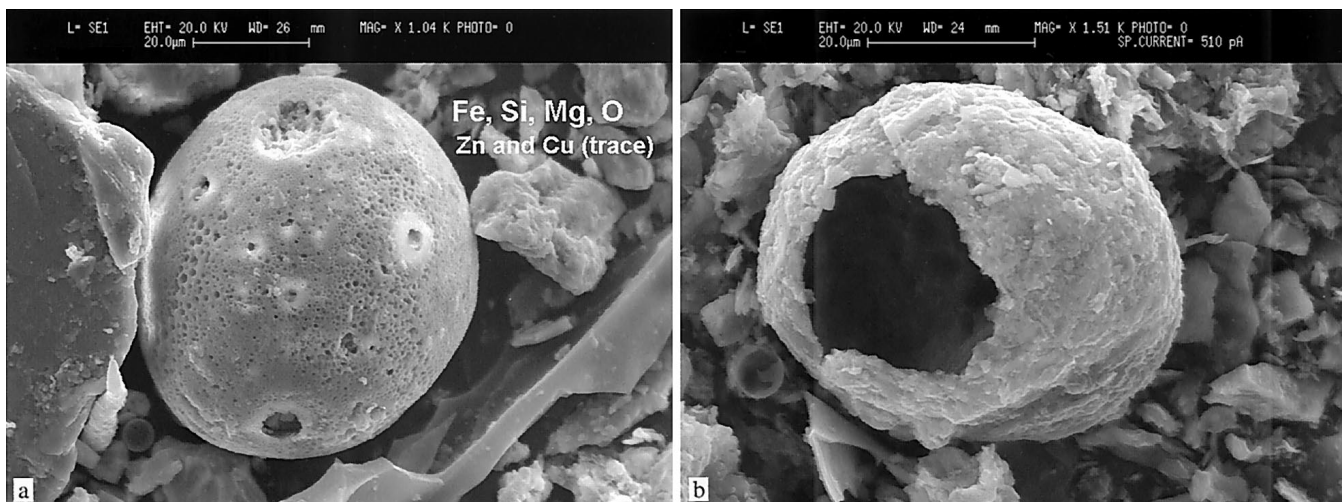


Fig. 9

SEM secondary electron images showing morphology and composition of spherical particles in humus collected at varying distances from smelter:

a Heavy metal rich particle collected approximately 2 km SSW from smelter. Note microsphere (5 μ diameter) in lower left corner of photo.

b Hollow sphere composed of Si, Al O, with minor Mg, Fe, Na and Mn collected 82 km NNW of stack. Note microsphere (5 μ diameter) in SW quadrant of photo

quently, they are interpreted as originating from the smelting process in the Flin Flon area.

Distinctive spherical particles were present in all humus samples examined. The particles tend to decrease in size and vary in composition with distance from the smelter (Table 6). Heavy metals, particularly Fe and Zn, and to a lesser extent Cu, are the major components of those spheres found closest to the smelter (Fig. 9a). At these sites, there is a broad inverse relation between sphere size and heavy metal content. Over 30 km from the stack, sphere composition is similar to glass (Si, O, Al) and trace metals occur as minor or trace constituents. At sites >40 km from the smelter, hollow and/or partially disintegrated (or malformed prior to deposition) (Fig. 9b) spheres and glassy microspheres (averaging 0.005 mm diameter) are common. Microspheres are also present in humus >160 km from the smelter, although they are rare and depleted in heavy metals. The general relationship between size, composition, and distance from the smelter indicates density sorting of spherical particles from the smelter stack.

Angular grains Grains in humus include metal particulates, oxides and sulphides similar in composition to those observed in smelter dust (Chen and Pint 1980). Although quantitative studies have not been made, the number of heavy metal grains in humus appears highest at sites within 30 km of the stack. At sites <3 km from the stack, heavy metal grains dominate the proportion of all particles in humus attributed to smelting activities.

Few angular grains with the composition and/or texture that could be linked to smelter emissions were found in humus at distances >30 km from the stack.

The distribution, size, and composition of angular grains enriched in heavy metals is summarized in Table 6. Iron occurs as an oxide, either solely or with Zn or Ti, as a sulphide with Cu, and, less commonly, as a silicate with Zn or Cu. At several sites (1, 11 and 12), distinctive Zn, Fe-oxide grains characterized by a regular geometric surface pattern (Fig. 10) and Zn-sulphide grains exhibiting a rough, spongy texture and, in one instance, a definite rim or coating, were observed. Lead occurs, at sites closest to the smelter, as a sulphide with Ba and/or Fe and Zn, in regular, prismatic crystal forms. Mercury, in combination with Se and, in one case, Fe and S, was also observed at Site 11, closest to the smelter. The Hg-rich grains are small (<0.01 mm), appear spongy, and may occur as coatings or crusts on larger grains, or as part of composite particles consisting of an amalgamation of grains differing in composition. No particles exhibiting the compo-

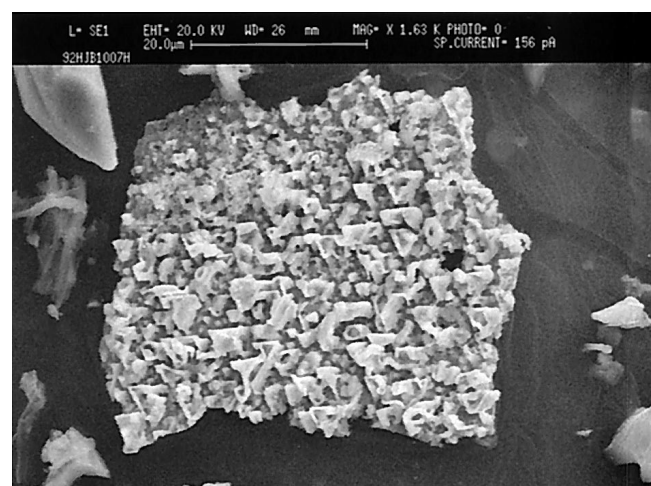


Fig. 10

SEM secondary electron image of smelter-derived Zn-rich particle observed in humus collected 3 km NNW of stack

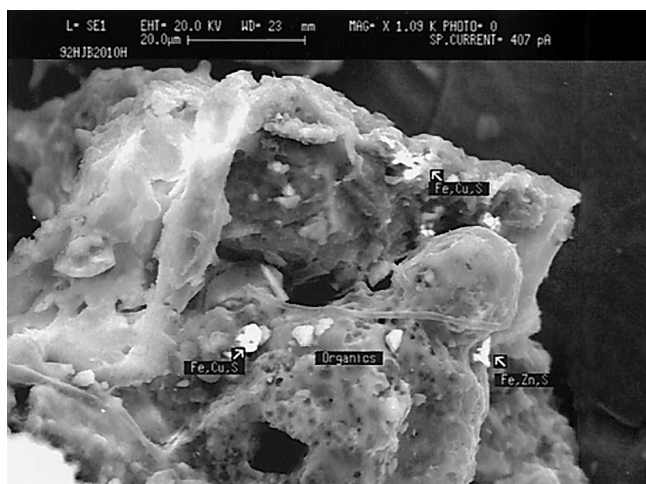


Fig. 11

SEM mixed secondary and backscattered image showing metal rich particles and organic material in humus 17 km SSW of stack

sition, surface texture, and morphology of these grains were found in till in any size fraction. Common rock-forming minerals, however, were recognized in both sample media.

Organic associations Trace elements associated with organic matter occur primarily as oxides (Fe, O; Fe, Zn, O with minor Cu) or sulphides (Fe, Cu, S; Fe, Zn, S; Fe, S) and form particles ranging from 0.002 to 0.005 mm diameter (Fig. 11). Because oxides and sulphides of similar chemical composition have not been observed in till, these grains are interpreted as smelter related.

Till

No smelter-related particles were observed in the <0.002 mm size fraction of till. Their absence may be a function of grain size because heavy metal particles observed in humus exceed 0.002 mm diameter. One sphere was observed in the <0.063 mm fraction of till collected at 0.7-m depth at Site 11, located within 2 km of the stack. The size and composition of the sphere is similar to those from humus at the same site, and indicates the possibility of sediment reworking, or, more likely, the incorporation of heavily contaminated surface material during sample collection.

Discussion and conclusions

The distribution of smelter-related heavy metals in humus observed in the vicinity of Flin Flon represents the historical record of contamination from mining and smelting activities in the region. Organic soils surrounding the smelter serve as a sink for heavy metals released to the environment as gases, aerosols or dusts from the smelter stack, ore stock piles and tailings, or during

transport. The nature and extent of soil contamination is the net result of all primary depositional processes, including atmospheric fallout resulting from smelting activities, as well as secondary processes related to chemical and biochemical reactions associated with the atmospheric transport and deposition of smelter emissions, the decomposition of plant material, and the weathering of soils.

The nature and extent of smelter contamination in the region has varied through time depending on the size and density of emitted particles, ore composition, emission control technologies, and wind strength and direction. Once deposited or incorporated into the terrestrial environment, however, trace elements derived from mining and smelting activities in the area become part of the complex assemblage of soil materials, and are subject to modification by biological, hydrological, and geological agents associated with soil-forming processes. Emitted smelter particles, like primary rock-forming minerals, are chemically weathered, and their elemental components precipitate in secondary minerals, form complexes with inorganic and organic surfaces, or remain temporarily in the soil solution (Sposito 1983).

In the vicinity of Flin Flon, the distribution of smelter-derived heavy metals in humus forms a bull's eye pattern centered on the smelter, with concentrations decreasing with distance from the smelter. Contaminant pathways in humus vary with the element and distance from the smelter, as indicated by the chemical speciation of Zn and Hg. Zinc partitioning is controlled by several factors including the total organic content of humus and the rate of deposition of smelter-derived particulates. Zinc is held primarily in an easily leached (labile) form, with an average of 54% in the soluble organic phase of humus at sites within 50 km of the smelter stack. The remaining Zn is held in the insoluble humus residue which consists of a labile and non-labile component. For Zn, the relative proportion in these components indicates that non-labile phases associated with smelter particulate emissions dominate the insoluble humus residue within 30 km from the stack (NNW transect), and decrease in significance with increasing distance. This geochemical response is supported by SEM observations indicating density sorting of smelter-derived particulates from the smelter source. With distance from the smelter, the relative increase in Zn in the labile component of the insoluble humus residue reflects the effects of processes associated with chemical leaching and alteration. This suggests that near the stack the rate of clastic input of smelter-derived particulates exceeds the rate of chemical weathering. Partitioning in humus at sites >30–40 km from the smelter primarily reflects bedrock control on till geochemistry such that the absolute contribution of smelter contamination on total concentrations of heavy metals becomes harder and harder to distinguish with distance.

In humus, Hg partitioning is largely controlled by the composition of the non-labile component of the insoluble humus residue. An average of 80% of total Hg is retained in this component and, consequently, Hg is less mobile

than Zn. The concentration, and, in part, the proportion of Hg in the non-labile phases decreases with distance from the smelter suggesting a decreased input of smelter-derived particulate matter with distance, as confirmed from SEM observations. Adjacent to the smelter (<2 km), however, elevated Hg concentrations (>1000 ppb) in the soluble organic phase, and the labile component of the insoluble humus residue, indicate the potential for significant amounts of Hg to be mobilized at highly contaminated sites.

On a regional scale, the geochemistry of till is a reflection of bedrock geology, modified by glacial erosion and transport (McMartin and others 1998). At sites <3 km from the smelter, however, elevated concentrations of Zn and Hg in labile phases of till may reflect downward leaching from humus in areas with high levels of contamination and poorly developed humus, in addition to the geochemical expression of the mineralization which established mining in the Flin Flon area. In a soil profile located 9 km SSW of the smelter, vertical variations in total Hg and Zn concentrations provide evidence for the downward leaching of heavy metals from humus to the B-horizon (approximately 45-cm depth).

The results of Ni partitioning in this study differ from those reported from areas adjacent to Cu-Ni smelting facilities (Adamo and others 1996; Niskavaara and others 1996). In the Flin Flon area, Ni is not associated with smelter emissions and concentrations in humus are depleted compared to till. Ni exists primarily in a non-labile form in both sample media. In Ni-contaminated areas, Ni is retained in labile phases of the A_o-horizon (Niskavaara and others 1996), and the non-labile residual phases (60%) of mineral soils (0–20-cm depth) (Adamo and others 1996).

Possible criteria for distinguishing anthropogenic from natural sources of heavy metal enrichment

Humus has been regarded as one of the best sampling media for mapping regional environmental contamination because of the strong geochemical contrast between anomalous and background concentrations resulting from its capacity to accumulate high levels of trace metals (Steinnes 1984; Niskavaara and others 1996). Determining the relative proportion of heavy metals in humus derived from anthropogenic sources, however, requires an appreciation for the 'natural' or geogenic component of the sample medium.

One method of estimating the geogenic component is based on the calculation of regional background values for humus (Table 1). These background values vary depending on the element and represent the median concentration for the data set after the elimination of most

contaminated samples, ostensibly the natural background for humus in the Flin Flon area. The value is subjective because actual concentrations fluctuate over wide ranges depending on biological, chemical, and geological factors, and assumptions are made on the maximum extent of anthropogenic contamination (McMartin and others 1997). Near the smelter, where concentrations of smelter-related elements are anomalously high, regional background values serve as good approximations for natural concentrations, but, with increasing distance from the source, deviations from background values become more difficult to interpret. At those sites where total concentrations in humus approach calculated regional background values, both anthropogenic and natural components of the surficial material are subjected to weathering processes with the accompanying formation of secondary minerals and complexes having indistinguishable geochemical signatures. SEM observations have shown that smelter-related particles are present in humus at sites >160 km from the source, and, undoubtedly, gaseous smelter emissions and particles <0.001 mm diameter are subjected to transport for greater distances, well beyond the recognizable zone of smelter contamination defined in the regional study. Consequently, the relative proportion and maximum extent of anthropogenic contamination in humus will be difficult to estimate on the basis of humus geochemistry alone, especially at sites at or near regional background values.

Other proposed methods for estimating the geogenic component of humus are based on the geochemical composition of the underlying, essentially unweathered, till or C-horizon material (Steinnes and Njåstad 1993; Niskavaara and others 1996). In the Flin Flon area, the till (>45-cm depth) reflects the natural distribution of trace metals as it relates to bedrock geology, modified by glacial erosion, transport, and deposition. The geochemistry of humus, on the other hand, results from the complex interaction between geochemical, biogeochemical and atmospheric processes and, consequently, reflects both the geogenic and the anthropogenic component. Simple comparisons, such as ratios between trace metal concentrations in humus and till, highlight areas of anomalous anthropogenic enrichment, but become less sensitive indicators for distinguishing between the anthropogenic and geogenic input with distance from the smelter. The difficulty is related primarily to site specific variations in the composition of the two sample media, since site-to-site correlations between elemental concentrations in humus and till are poor to lacking in areas removed (>120 km) from the immediate effects of smelter contamination (Henderson 1994; Kaszycki and others 1996).

A realistic estimate of the anthropogenic component of humus is fundamental to mass balance studies focused on determining the proportion of total known smelter emissions that is represented by contaminated soil in the Flin Flon area. A meaningful calculation would require knowledge of the distribution of heavy metals within the organic horizon, an assessment of the rate of weathering of smelter-derived particles and knowledge of the envi-

ronmental pathways of elements held in easily leached forms, in order to determine the proportion of material removed or recycled in the soil horizons. Studies addressing these issues are presently underway.

Acknowledgements The authors would like to acknowledge the significant contribution of Erik Nielsen, Manitoba Energy Mines; Janet Campbell, Saskatchewan Research Council; and Christine Kaszycki, Ontario Geological Survey, who were responsible for sample collection over large parts of the area, and Hudson Bay Mining and Smelting Corporation for their co-operation throughout the project, particularly in providing archived smelter dust. We are also grateful to Patty Lindsay and Judy Vaive, Geological Survey of Canada, who supervised the geochemical analyses. This paper has been significantly improved by reviews from Inez Kettles and Rod Klassen, Terrain Sciences Division, Geological Survey of Canada.

References

- ADAMO P, DUDKA S, WILSON MJ, MCHARDY WJ (1996) Chemical and mineralogical forms of Cu and Ni in contaminated soils from the Sudbury mining and smelting region, Canada. *Environ Pollut* 91:11–19
- Agriculture Canada Expert Committee on Soil Survey (1987) The Canadian system of soil classification, 2nd edn Agriculture Canada Publication 1646
- ASHTON KE (1987) Preliminary geological map of the Kisseynew gneisses between the Sturgeon-Weir River and Kisseynew Lake, Saskatchewan, scale 1:50 000. Geological Survey Canada Open File 1410
- ASHTON KE (1989) The southern flank of the Kisseynew Gneiss Belt in Saskatchewan and its boundaries with the Flin Flon Volcanic Belt and the Hanson Lake Block. Geological Survey Canada Open File 2133, pp 17–20
- ASHTON KE, BALZER SS, TRAN H (1995) Geology of the Galbraith-Attititi Lakes area, Attititi Block (part of 63 M/1 and /2). Saskatchewan Energy and Mines Miscellaneous Report 95–4, pp 23–29
- BI D, MORTON RD (1995) Magnetic spherules from recent fluvial sediments in Alberta, Canada; characteristics and possible origins. *Can Jour Earth Sci* 32:351–358
- BLANCHARD MB, BROWNLEE DE, BUNCH TE, HODGE PW, KYTE FT (1980) Meteoroid ablation spheres from deep-sea sediments. *Earth Planet Sci Lett* 46:178–190
- BROOME J, VILJOEN D, NATMAP Digital Working Group (1995) Preliminary release of selected geoscience data for the NATMAP Shield Margin Project, Flin Flon area, Manitoba and Saskatchewan; CD-ROM Release. Geological Survey Canada Open File 2743
- CHAO TT (1984) Use of partial dissolution techniques in geochemical exploration. *J Geochem Explor* 20:101–135
- CHEN TT, PINT P (1980) Mercury in Canadian non-ferrous metals extraction circuits: Part 1 - Hudson Bay Mining and Smelting Company, Limited, Flin Flon, Manitoba. CANMET, Min. Res. Program, Min. Sci. Lab., Rept 80–9
- DAVIES BE (1983) Heavy metal contamination from base metal mining and smelting: implications for man and his environment. In: Thornton I (ed) *Applied Environmental Geochemistry*, 425–462
- DUNN JG, MACKAY LC, SMITH TN, STEVENSON IR (1993) Mineralogical study of products collected following pilot-scale smelting of some western Australian nickel sulphide concentrates. *Trans Inst Min Metall* 102:C75–C82
- DYKE AS, PREST VK (1987) Late Wisconsinan and Holocene history of the Laurentide Ice Sheet. *Geogr phys Quaternaire* 41:237–264
- Environment Canada (1990) Canadian climate normals, 1988–1990. Flin Flon area, vol 5, Environmental Canada, Ottawa
- ESSENE EJ, FISHER DC (1986) Lightning strike fusion: extreme reduction and metal-silicate liquid immiscibility. *Science* 234:189–193
- FRANZIN WG, MCFARLANE GA, LUTZ A (1979) Atmospheric fallout in the vicinity of a base metal smelter at Flin Flon, Manitoba, Canada. *Environ Sci Technol* 13:1513–1522
- FREEDMAN B, HUTCHINSON TC (1980) Pollutant inputs from the atmosphere and accumulations in soils and vegetation near a nickel-copper smelter at Sudbury, Ontario, Canada. *Can J Bot* 58:108–132
- HALL GEM, VAIVE JE, BEER R, HOASHI M (1996) Phase selective leaches for use in exploration geochemistry. In: Bonham-Carter GF, Galley AG, Hall GEM (eds) *Extech I: a multidisciplinary approach to massive sulphide research in the Rusty Lake-Snow Lake Greenstone Belts, Manitoba*. Geological Survey Canada Bulletin 426, pp 169–200
- HENDERSON PJ (1994) Surficial geology and drift composition of the Bissett-English Brook area, Rice lake Greenstone Belt, southeastern Manitoba. Geological Survey Canada Open File 2910
- HENDERSON PJ (1995) Surficial geology and drift composition of the Annabel Lake-Amisk Lake area, Saskatchewan (NTS 63L/9, L/16, and part of 63 K/12 and K/13). Geological Survey Canada Open File 3026
- HENDERSON PJ, McMARTIN I (1995) Mercury distribution in humus and surficial sediments, Flin Flon, Manitoba, Canada. *Water Air Soil Pollut* 80:1043–1046
- HOGAN GD, WOTTON DL (1984) Pollutant distribution and effects in forests adjacent to smelters. *J Environ Qual* 13:377–382
- HUDSON BAY MINING AND SMELTING COMPANY (1995) Compliance testing report. Environmental Control Programs, Manitoba Environmental Management Division, Winnipeg, Canada
- JACKSON TA (1978) The biogeochemistry of heavy metals in polluted lakes and streams at Flin Flon, Canada, and a proposed method for limiting heavy-metal pollution of natural waters. *Environ Geol* 2:173–189
- JACKSON TA, KLAVERKAMP JF, AND DUTTON MD (1993) Heavy metal speciation and its biological consequences in a group of lakes polluted by a smelter, Flin Flon, Manitoba, Canada. *Appl Geochem* 2:285–289
- KABATA-PENDIAS A, PENDIAS H (1983) Trace elements in soils and plants. CRC Press, Inc., Boca Raton, Fla.
- KASZYCKI C, HALL GEM (1996) Application of phase selective and sequential extraction methodologies in surficial geochemistry. In: Bonham-Carter GF, Galley AG, Hall GEM (eds) *Extech I: a multidisciplinary approach to massive sulphide research in the Rusty Lake-Snow Lake Greenstone Belts, Manitoba*. Geological Survey Canada Bulletin 426, pp 155–168
- KASZYCKI C, NIELSEN E, GOBERT G (1996) Surficial geochemistry and response to volcanic-hosted massive sulphide mineralization in the Snow Lake region. In: Bonham-Carter GF, Galley AG, Hall GEM (eds) *Extech I: a multidisciplinary approach to massive sulphide research in the Rusty Lake-Snow Lake Greenstone Belts, Manitoba*. Geological Survey Canada Bulletin 426, pp 139–154

- LINDSAY PJ, SHILTS WW (1995) A standard laboratory procedure for separating clay-sized detritus from unconsolidated glacial sediments and their derivatives. Drift exploration in the Canadian Cordillera. British Columbia Geological Survey Paper 95-2, pp 165-166
- MCMARTIN I, HENDERSON P, NIELSEN E, CAMPBELL J (1996) Surficial geology, till and humus composition across the Shield margin, north-central Manitoba and Saskatchewan: geospatial analysis of a glaciated environment. Geological Survey Canada Open File 3277
- MCMARTIN I, HENDERSON P, NIELSEN E (1997) Impact of base metal smelter on the geochemistry of soils of the Flin Flon region, Manitoba and Saskatchewan. *Can J Earth Sci* in press
- MEEKER GP, HINKLEY TK (1993) The structure and composition of microspheres from the Kilauea volcano, Hawaii. *Am. Mineral* 78:873-876
- MURRELL MT, DAVIS JR PA, NISHIZUMI K (1980) Deep-sea spherules from Pacific clay: mass distribution and influx rate. *Geochim Cosmochim Acta* 44:2067-2074
- NISKAVAARA H, REIMANN C, CHEKUSHIN V (1996) Distribution and pathways of heavy metals and sulphur in the vicinity of the copper-nickel smelters in Nikel and Zapoljarnij, Kola Peninsula, Russia, as revealed by different sample media. *Appl Geochem* 10:1-10
- RASMUSSEN PE (1996) Trace metals in the environment: a geological perspective. Geological Survey Canada Bulletin 429
- ROSE AW, HAWKES HE, WEBB J S (1979) *Geochemistry in mineral exploration*, 2nd edn. Academic Press, London
- SALOMON DE FRIEDBERG AM (1993) Impurities at HBM&S' Flin Flon copper smelter. *Can Inst Min Metall Bull* 86:119-125
- SCHREINER BT (1984) Quaternary geology of the Precambrian Shield, Saskatchewan. Saskatchewan Energy and Mines Report 221
- SHELDRICK BH (ed) (1984) *Analytical methods manual*, 1984. Research Branch, Agriculture Canada, LRRRI Contribution No. 84-30
- SPOSITO G (1983) The chemical forms of trace metals in soils. In: Thornton I (ed) *Applied environmental geochemistry*, pp 123-170
- STEINNES E (1984) Heavy metal pollution of natural surface soils due to long-distance atmospheric transport. In: Yaron B, Dagan G, Goldschmid J (eds) *Pollutants in porous media*. Springer, Berlin Heidelberg New York, pp 115-122
- STEINNES E, NJÅSTAD O (1993) Reasons for enrichment of metals in the organic surface layer of natural soils. In: RJ Allan, JO Nriagu (eds) *Proceedings of the ninth international conference on heavy metals in the environment*, Toronto, Canada. CEP Consultants Ltd, Edinburgh, UK (1993) 2:226-229
- STERN RA, LUCAS SB (1995) Geochemistry and geochronology of volcanic and plutonic rocks, central Flin Flon Belt, Saskatchewan (NATMAP Shield Margin Project). In: DG Richardson (ed) *Investigations completed by the Saskatchewan Geological Survey and the Geological Survey of Canada under the Geoscience Program of the Canada-Saskatchewan Partnership Agreement on mineral development (1990-1995)*. Geological Survey Canada Open File 3119, pp 99-110
- SYME EC, THOMAS DJ, BAILES AH, REILLY BA, SLIMMON WL (1993) Geology of the Flin Flon area, Manitoba and Saskatchewan (parts of NTS 63 K and 63L), scale 1:50 000. Geological Survey Canada Open File 2658
- TELLER JT, CLAYTON L (1983) Glacial Lake Agassiz. Geological Association Canada Special Paper 26
- VARSKOG P, FLATEN TP, STEINNES E (1993) Relations between elemental concentrations and soil organic matter content in Norwegian forest soils. In: RJ Allan, JO Nriagu (eds) *Proceedings of the ninth international conference on heavy metals in the environment*, Toronto, Canada. CEP Consultants Ltd, Edinburgh, UK (1993) 2:167-169
- ZOLTAI S (1988) Distribution of base metals in peat near a smelter at Flin Flon, Manitoba. *Water Air Soil Pollut* 37:217-228