CEM
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Metal Levels in the Soils of the Sudbury Smelter Footprint

A Report To:

Safety, Health and Environment,
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and

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EXECUTIVE SUMMARY

Metals constitute a natural component of soils, with contents dependent on soil mineral composition and geochemical history. Man has added metals to soils through atmospheric deposition from industrial processes, or by fertilizing with manure and fertilizers in amounts that add more metal to the soil matrix than is removed by plant uptake. Localized, strongly enhanced metal concentrations have been created in surface soils by atmospheric deposition in the neighbourhood of metal extraction plants.

With the release of the OMOE report describing the distribution of metals in soil and vegetation in the Sudbury area in 2001, the need was recognized for an extensive statistically defensible regional soil sampling programme to enable accurate delineation of any metal loadings to the soils ecosystem from anthropogenic activities. The necessity of obtaining a reliable estimate of pre-industrial background levels in surficial sediments was paramount so that reasonable loading estimates to surface soils could be calculated.

This data is necessary to study the fate of, or to determine the environmental health risk posed by, metals added to soils by atmospheric deposition or by other sources. An understanding of the natural physicochemical processes in the soil-plant system that govern and regulate the behaviour of their natural metal content is also necessary in estimating the potential ecological or human health risk of anthropogenic metals in the Sudbury environment. Crucial in the development of the understanding of these processes is knowledge of the geological history, of the glacial history and of the soil mineralogical and background elemental composition.

The objectives of the study described in this report are to:

- Describe the planning and sampling program the Sudbury Regional Soil Sampling Programme;
- Document the background levels for selected metal concentrations in regional soil parent materials extracted with *Aqua Regia*; and
- Document the regional distribution of selected metal concentrations in defined depth increments for regional soil materials extracted with *Aqua Regia.*

This report describing the study consists of two main sections, namely:

- A detailed narrative report documenting a summary of the geology and soil chemistry, with a summary of the data obtained during this study, with overview maps describing the elemental distribution in both surface soils and their parent materials. The metadata describing the individual sampling sites, together with the analytical data for a series of elements of environmental interest are documented in two appendices;
- An interactive electronic map and database which combines all the meta- and chemical data in the written narrative in a friendly interactive form which can, by following simple installation instructions, be installed on any desktop computer data. This interactive database also contains images of all sites sampled for analysis in study.

ACKNOWLEDGEMENTS

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The principal author of this report is Graeme Spiers. Caroline Hawson, as well as completing the data quality control analyses, prepared the first draught of the review segments of the report. Francois Prevost completed much of the statistical analyses, the maps and the interactive display for Appendix III. Dr. David Pearson provided thoughtful insight in reviewing the report.

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INTRODUCTION

Metals constitute a natural component of soils, with concentrations dependent on soil mineral composition and geochemical history. Man has added metals to soils through atmospheric deposition from industrial processes, or by fertilizing with manure and fertilizers in amounts that add more metal to the soil matrix than is removed by plant uptake. Localized, strongly enhanced metal concentrations have been created in surface soils by atmospheric deposition in the neighbourhood of metal extraction facilities. Soils, more than any other sampling medium, reflect the total historical metal accumulation from the point source, but modified to varying degrees by soil forming processes and erosion.

The metals originating from anthropogenic sources in a soil do not behave differently from the natural metal ions present. Therefore, to study the fate of, or to determine the environmental health risk posed by, metals added to soils by atmospheric deposition or by other sources, an understanding of the natural physicochemical processes in the soil-plant system that govern and regulate the behaviour of their natural metal content is necessary. Crucial in the development of the understanding of these processes is knowledge of the geological history, of the glacial history and of the soil mineralogical and background elemental composition.

In Sudbury, home of one of the world’s largest copper–nickel mining camps, the mining and processing of mineral deposits for over a century has raised concern about the potentially high levels of heavy metals in the soil environment. Identification of chemical contamination of Sudbury soils thus requires an understanding of the natural processes involved in the formation of the regional soils, of the inherent heavy metal content of underlying rock units, of the potential increased metal content of surficial materials through mineralizing processes. The anthropogenic processes, such as mining and smelting, have released metal-rich aerosols that have been washed from the atmosphere by meteorological events to be deposited on the landscape surface. Locally, leaching of heavy metals from rock piles and tailings ponds, together with fugitive emissions from ground sources and smelter sites, may prove significant.

The Sudbury Regional Soils Project is a sampling, analytical and interpretative program designed to provide detailed information describing metal levels in parent materials and soils within the footprint of the Sudbury smelter region as a pre-requisite to the initiation and development of one of the largest and comprehensive ecological and human risk assessment projects ever completed on this sensitive planet.

Industrial History

The first industry in the Sudbury area developed around the rich forests (Gunn, 1995). After the great fire of Chicago in 1871, Sudbury area lumber helped rebuild the city. The transcontinental railway development also put demands on the local forests because of the need for railway ties and trestles. Denudation of the forests resulted in the faster spread of man made and natural fires. Lumbering remained dominant until the 1920s (Winterhalder, 1995). A major consequence of the increased acreage being felled was an increase in regional soil erosion, especially on the shallow soils of the steeper slopes.

The first Cu-Ni discovery was made in 1856 (Murray, 1857). The Canadian Copper Company commenced production at Copper Cliff in 1886 at the Murray Mine, discovered in 1883. Heap roasting began the same year. Although several companies have been involved in the development of the Sudbury mining camp, there are now only two producers, Falconbridge Limited and INCO Limited. Peak production occurred in 1974 when 209,000 tonnes of nickel were produced, decreasing to 128,558 tonnes of nickel (21% of the world's nickel production) in 1988. In 2000 Sudbury operations for the two companies produced 113,945 tonnes nickel and 301,987 tonnes copper (MNDM Information and Marketing Services Section, unpublished data, 2002).

Smelter emissions from Sudbury area smelters have decreased dramatically from their maximum in the late 1960s. In 1995 total SO_2 emitted from the INCO and Falconbridge smelters was 281,000 tonnes; the Residual Discharge Information System (Environment Canada, unpublished data, 1995) places the total of suspended particulate matter discharged to the atmosphere for the INCO Copper Cliff smelter at 7050 tonnes per year and for the Falconbridge smelter 1180 tonnes per year (Table 1). The data in Table 1 are from National Pollution Release Inventory 2002 (Environment Canada, unpublished data, 2002).

Table 1: Heavy metal and sulphur discharges for 2001 for Inco Limited and Falconbridge Limited.

Location	Cu	Zn	Ni	Pb	Cd	As	H_2SO_4	H_2S
					tonnes			
Inco Central Mills	37.76	3.84	195.80	0.91	0.36	0.12	27.26	--
Copper Cliff Nickel Refinery	5.98	--	12.42	6.68	--	3.94	--	--
Copper Cliff Smelter Complex	109.64	18.96	64.19	63.40	4.84	52.91	1271.08	--
Inco Copper Refinery	43.42	1.20	0.50	2.92	0.05	2.54	0.99	--
Falconbridge Smelter	10.66	5.32	11081	6.24	1.70	0.27	24.87	21.20

NB: Data from National Pollution Release Inventory 2002 (Environment Canada, unpublished data, 2002).

GEOLOGY OF THE SUDBURY AREA

Introduction

This overview places Sudbury soils into a regional geological context. The geology and chemistry of the bedrock, the Quaternary history, and especially the provenance, transportation and metal chemistry of the glacial units are summarized. These processes influence soil chemistry and generate the normal background levels of individual elements. Knowledge of this background data enables a review of the chemical composition of the soils to ascertain the presence and level of anthropogenic contamination. A synopsis of previous soil regional published and unpublished soil studies, with an emphasis on limitations of the analytical methods used, is presented. Limited analytical data for vegetation and dustfall-rainfall-snowfall processes is also reviewed.

Geological Setting

PRECAMBRIAN GEOLOGY

The Sudbury Structure (Figure 1) is an elliptical unit produced by a meteorite colliding with the southern part of the Superior Province at 1.85 Ga. The impact melted rocks to form the world's largest impact-related melt sheet. The melt sheet of Sudbury Igneous Complex is composed, from base to top, of norite, quartz gabbro and granophyre. Above the Sudbury Igneous Complex is the Whitewater Group composed from base to top of the Onaping, Onwatin and Chelmsford formations. The Onaping Formation is a series of fallback breccias

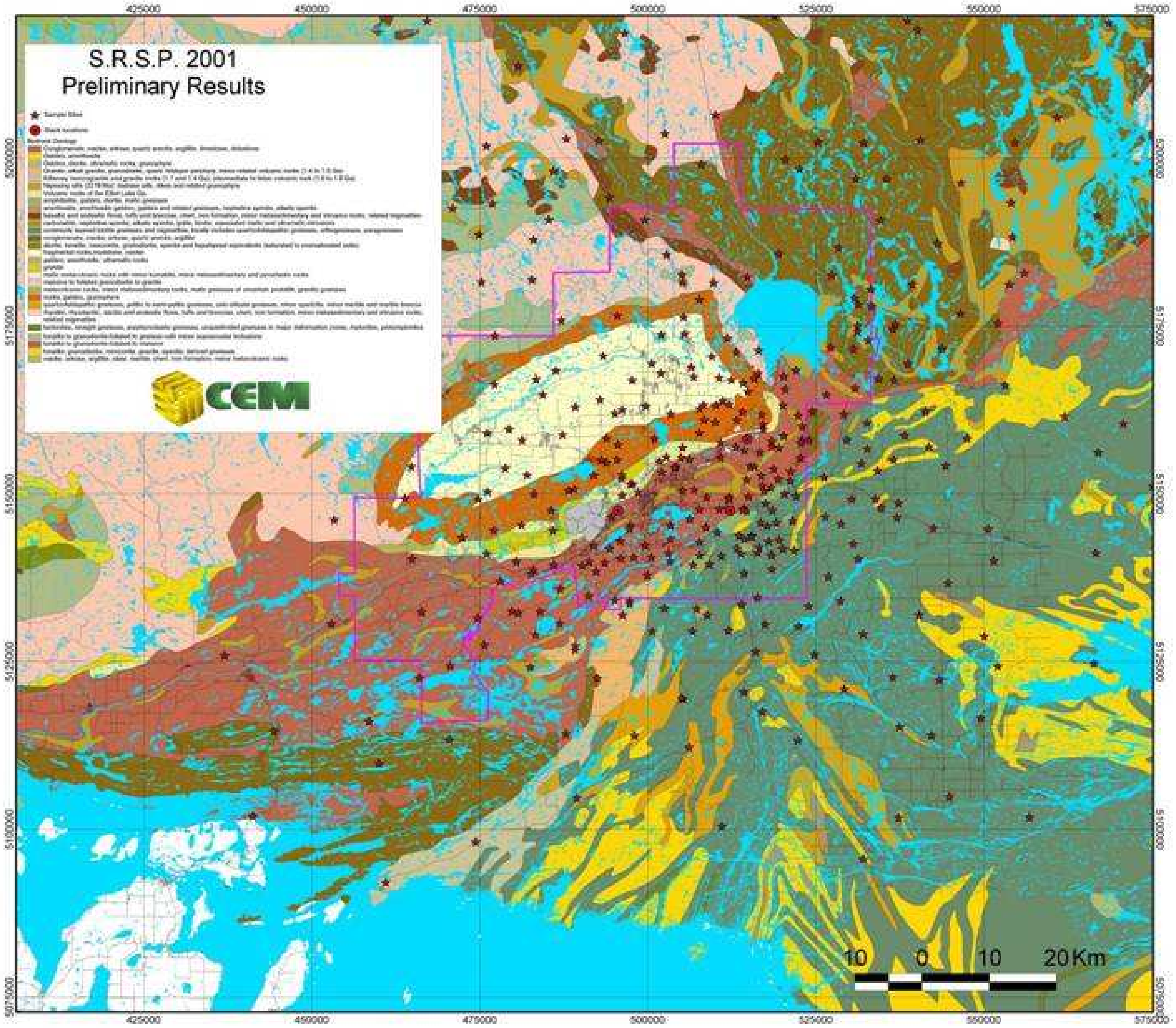

Figure 1: Regional geology of the Sudbury area.

overlain by Chelmsford and Onwatin formations. The Onaping Formation represents impact-related volcanism.

Two major, cross cutting types of breccia are present 1) Sudbury Breccia and 2) Footwall Breccia. Sudbury Breccia is a heteolithic breccia forming bodies from several metres to kilometres in size that cross cut all pre-impact units up to 80 km from the Sudbury Igneous Complex. Footwall Breccia occurs along the contact between the Sudbury Igneous Complex and country rocks and in both radial and concentric “offset dikes”. This latter breccia unit consists of quartz diorite and various other Sudbury Igneous rock types and is host to most of the Sudbury ore bodies, both where it is subjacent to the Sudbury Igneous Complex and in "offset dikes". As host to the ore deposits, its mineralogy and geochemistry are important in discriminating between anthropogenic contamination and influences of bedrock in the geochemistry of soils. Note an endogenic origin has also been proposed for the origin of the Sudbury Igneous Complex (Muir, 1984). The Sudbury Igneous Complex has been divided into the Main Mass (norite, quartz gabbro, and granophyre) and Sublayer (Contact Sublayer and Offset Sublayer) (Dressler *et al.,* 1991). Mineralization of importance occurs in the sublayer and the offset dikes.

QUATERNARY GEOLOGY

Quaternary and minor Holocene deposits form the soil parent material of the Sudbury region (Figure 2). An understanding of these deposits is therefore important in any interpretation of soil geochemistry. Quaternary deposits and features preserved within the Sudbury area are almost certainly Wisconsinan. Tills found in the area likely correlate to the Adam Till of the Hudson Bay Lowland (Skinner, 1973) and the Matheson Till of the Timmins and Kirkland Lake areas (Hughes, 1959, 1965). No nonglacial sediments attributed to the last interglacial period occur in the Sudbury area (Barnett and Bajc, 2002).

The Laurentide Ice Sheet covered Ontario, extending into the northern United States of America about 20,000 years ago. This ice sheet had three main centres of growth: 1) the interior uplands of Labrador and Quebec, 2) the Keewatin area in the Northwest Territories and 3) Baffin Island. Ice of the Labrador Sector covered the Sudbury area and generally flowed to the south-southwest (Boissoneau, 1968). Boissoneau (1968) describes an eastern lobe that flowed southwest and a western lobe that flowed more southerly both meeting near Sudbury.

During deglaciation, glacial lakes formed against the receding ice margin within the Great Lakes Basin. Glacial Lake Algonquin occupied the Lake Huron, Lake Michigan and part of the Lake Superior basins including the Sudbury area (Barnett and Bajc, 2002). Deglaciation of the Sudbury area occurred 10,500 to 10,000 years ago. There is much evidence of the glaciation, ranging from striae on bedrock to kilometre-scale roche moutonées and whalebacks, to large erratic, far-travelled boulders littering the surface and many stony soils, attesting to the presence of continental glaciers.

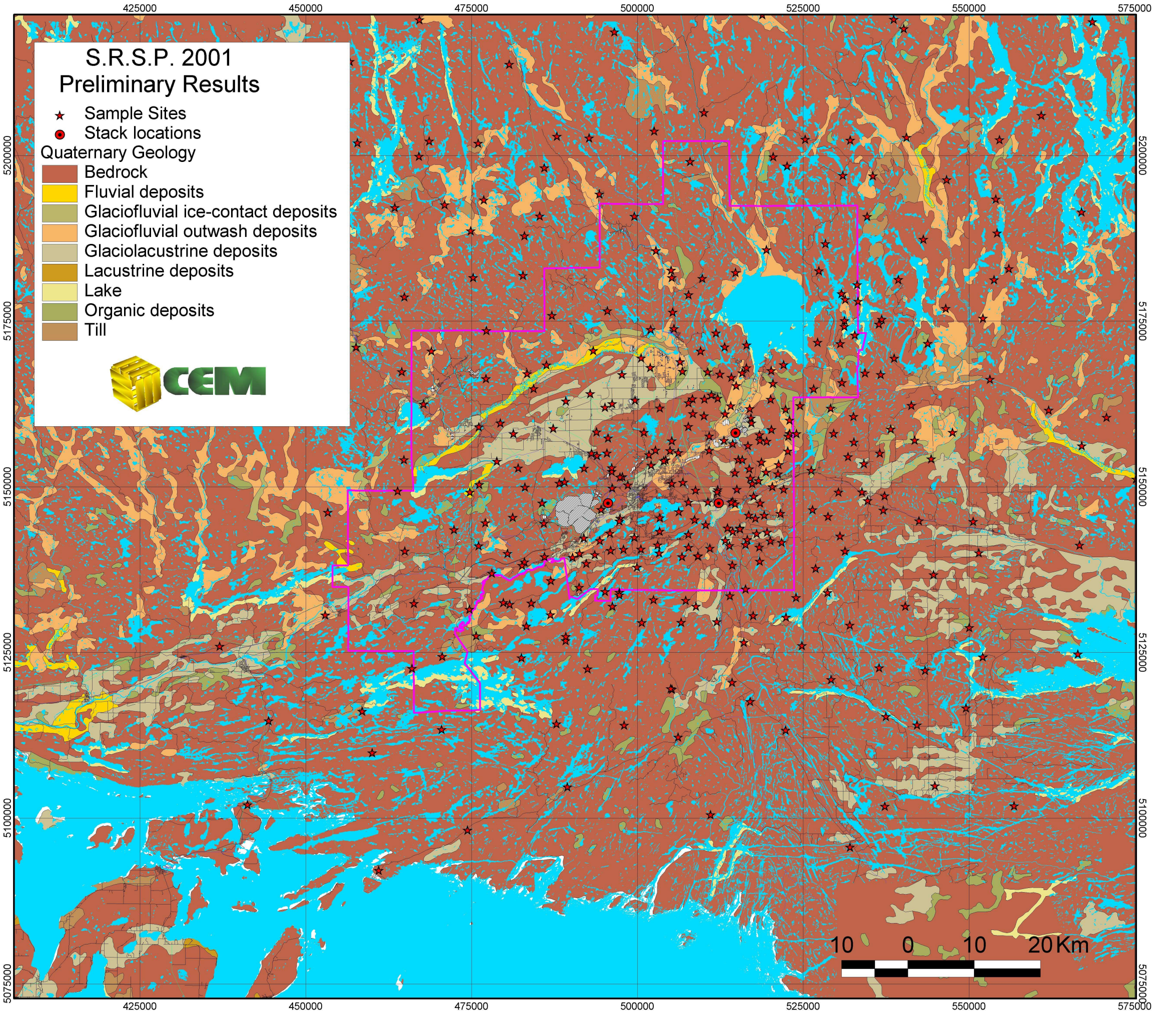

Figure 2: Quaternary geology of the Sudbury region.

Ice Flow Direction

Ice-flow directional indicators define an ice-flow pattern that was strongly influenced by regional topography. Ice-flow across the Abitibi Uplands and the north edge of the Sudbury Basin was north to south (170° to 210°). Within the Valley, a shift in flow was recorded at between 220° and 245°. South of the Sudbury Basin, ice flowed at 205° to 225°. Evidence of an earlier ice flow event is recorded along the north rim; however, the magnitude of glacial dispersal associated with this older event is not known (Barnett and Bajc, 2002).

Till

Till is “sediment deposited directly by a glacier with little or no subsequent reworking” (Dreimanis, 1988). There are two main types of till 1) subglacial till deposited by lodgement and melt-out processes and 2) supraglacial tills deposited by flow from the upper surface of glaciers. Debris within the glacier can move between the various transport zones (Barnett, 1992). Tills are poorly sorted, sheet-like deposits that contain clay to boulder sized particles. Till appears massive but may contain discontinuous lenses or layers of stratified sediment.

Landforms

Landforms created by a continental ice sheet influence pedological development. Landforms include: 1) linear features parallel to flow, 2) linear features transverse to flow and 3) features lacking consistent orientation. Linear features formed parallel to ice-flow include drumlins, crag-and-tail features and interlobate moraines. Linear features that form transverse to ice flow include Rogen and de Geer moraines. Landforms lacking in orientation are ground moraine and hummocky ground moraine (Barnett, 1992) are common in the Sudbury region.

Sedimentary Deposits

Sediments deposited from glacial meltwater streams form glaciofluvial sediments, which are sorted, stratified gravel and/or sand. As a result of being deposited in contact with the glacier, abrupt changes in grain size and stratification occur vertically and laterally. Glaciofluvial outwash deposits are generally more consistent laterally and tend to become finer grained in a down-flow direction (Barnett and Bajc, 2002). Glaciolacustrine deposits are commonly stratified sediments deposited directly from the glacier into a standing body of water. Coarse-grained glaciolacustrine sediments of sand and gravel form beaches, deltas and subaqueous fans. Fine-grained glaciolacustrine sediments, silt and clay, are deposited in deeper water basinal settings. The dominant depositional environments for glacial sediments in the Sudbury area are: the subglacial environment, the proglacial lake, and braided streams.

There are many erosional features on the bedrock of the Sudbury area; these were produced by abrasion due to the dragging of glacial debris at the base of a glacier and/or by plucking as a result of pressure gradients. Subglacial meltwater also modified the bedrock surface by aiding the plucking process and sculpting the bedrock surface leaving a suite of elaborate erosional forms.

Till forms the most widespread glacial sediment in the Sudbury area, forming a thin discontinuous layer above bedrock (<1 m thick), with thicker accumulations along the slopes of bed rock knolls and ridges. In some areas, such as along the west shore of Lake Wahnapitae, there is extensive continuous till masking the bedrock.

Transportation, depositional history, and postdepositional weathering processes all influence the appearance of till. Glacial debris transported subglacially contains striated and faceted clasts. Debris transported englacially or supraglacially tends to be more angular and striated clasts are rare. The process of deposition, for example, lodgement, subsole-deformation, melt-out or flow processes will also influence the appearance of till. Bedrock type, either immediately beneath or up-ice, influences the overall appearance and chemistry of the till. Local topography affects the depositional setting and postdepositional processes affect the colour, texture and structure of the till. There have been three distinct till facies identified in the Sudbury area (Bajc and Hall, 2000): subglacially deposited till forming ground moraine, ice-marginal flow till forming recessional moraine, and supraglacial meltout till forming hummocky terrain.

The properties of these tills were described from shallow test pits, road cuts and exploration trenches. At shallow depths, the tills are generally loose and exhibit an orangey-brown to brownish-grey colour. Typically, Sudbury area tills contain less than 1% total carbonate, (Bajc personal communication, 2002) suggesting that till provenance is several tens of kilometres to the north, but not as far north as the Hudson Bay Lowlands or the Cobalt Embayment. The subglacially deposited till varies widely across the region, reflecting the diversity of source materials. Tills from areas dominated by coarse crystalline rocks (e.g., Sudbury Igneous Complex, Levack gneiss) have, in general, a sand-rich matrix and contain a high proportion of boulders, cobbles and pebbles. Tills from regions underlain by the Huronian metasedimentary rocks generally have a finer grained matrix, with a lower proportion of boulders, cobbles and pebbles (Bajc and Hall, 2000).

Although glacial deposits are generally thin and discontinuous within the Sudbury Basin (Barnett and Bajc, 2002), isolated areas with thicknesses of 120 m are reported (Burwasser, 1979). In the rock dominated Abitibi Uplands, Penokean Hills and the Cobalt Plain, Quaternary sediments are thin (<1 m), except along valley bottoms where thicknesses of over 60 m have been reported in water well records.

PHYSIOGRAPHY OF THE SUDBURY AREA

The Sudbury area includes parts of the Abitibi Uplands, Penokean Hills and Cobalt Plain of the James Physiographic Region and a small part of the Laurentian Highlands within the Laurentian Physiographic Region (Barnett and Bajc, 2002). The Abitibi Uplands north of Sudbury are underlain by Archean crystalline rocks and comprise broad, rolling, bedrock-controlled surfaces rising gently towards the Abitibi Uplands southern boundary to a maximum elevation of 450 m. Locally, relief may be as much as 90 m along deeply incised canyons (Dredge and Cowan 1989). The Penokean Hills southwest of Sudbury comprise the folded metasedimentary rocks of the Huronian Supergroup with quartzite ridges reaching elevations of 240–300 m above sea level. Locally, relief may be as much as 100 m (Dredge and Cowan, 1989). The Cobalt Plain, northeast of Sudbury, is underlain by nearly flat lying clastic metasedimentary rocks with some ridges and hills formed by gabbro sills (Nipissing gabbro) or older Archean rocks forming inliers (Dredge and Cowan, 1989). The Laurentian Highlands is an old erosion surface consisting of low, rounded knobs and ridges, locally, relief may be as much as 30 to 50 m. Elevation of this area is up to 300 m (Barnett and Bajc, 2002).

The Sudbury Basin consists of an oval central low, the “Valley”, rimmed by a zone of high relief ridges to the north, east and south. The rocks of the Sudbury Igneous Complex and the Onaping Formation form these ridges. The Valley floor is dominantly Quaternary glaciolacustrine, glaciofluvial and fluvial sediments. Rocks of the Chelmsford and Onwatin formations underlie these Quaternary sediments. Rocks of the Onaping Formation can be found at the northeastern end of the basin underlying the Quaternary sediments. The Valley is a plain exhibiting low relief interrupted by bedrock ridges caused by the broad folding of the Chelmsford Formation. The plain slopes to the southwest with a drop in elevation of about 40 m over 39 km (Barnett and Bajc, 2002). Local relief in the Valley is about 15 m and in places as much as 30 m. Some bedrock ridges reach 320 m above sea level

Drainage

The Sudbury area is drained southward by rivers and streams that flow into Georgian Bay (Pearson *et al.,* 2002). Most of the region is drained by the Spanish River in the west; the French River in the east drains a small part of the region. The river courses are largely bedrock controlled, although the Vermillion River where it cuts unconsolidated sediments of the Sudbury Basin has well developed meander patterns. Surface drainage influences transportation of glacial material and contaminated materials from tailings ponds, ore heaps and other industrial sites. Pearson *et al.,* (2002) have produced a watershed map of the region from which it is possible to deduce the probable path of any surface runoff.

SOILS OF THE SUDBURY AREA

The characteristics of soil are greatly influenced by the nature of the parent material, together weathering and erosion processes. The soil mineralogical and chemical composition in the

Sudbury area will, therefore, reflect the bedrock geology of the region, the up-ice geology, the organic input from the flora and fauna of the region, and exogenous materials such as particulate matter from both long and short-range transport processes. Sudbury area soils belong to five orders of the Canadian Soil Classification System (Agriculture Canada Expert Committee on Soil Survey, 1987): Luvisolic, Gleysolic, Podzolic, Brunisolic, and Organic (Gillespie *et al.,* 1983).

Luvisolic soils occur on calcareous or high base status soil parent materials. They have light coloured eluvial horizons and an illuvial B-horizon in which silicate clay has accumulated. Luvisols develop in well to imperfectly drained sites on sandy loam to clay textured parent materials under forest vegetation. Luvisols of the Sudbury area belong to the Gray Luvisol Great Group, due primarily to the effect of climate and parent material on soil development. These soils have developed on glaciolacustrine sediments.

Gleysols are poorly drained and their profile is indicative of long periods of water saturation and reducing conditions. Two groups of Gleysols are described in this area 1)

Humic Gleysols with a high base status and a thick organic rich Ah horizon underlain by a gleyed mottled Bg or Cg horizon; 2) Gleysol Great Group developed on mineral soils of low base status. The Ahg horizon is either absent or less than 10 cm thick. These soils have commonly developed on glaciolacustrine, glaciofluvial or fluvial sediments.

Podzols occur in coarse to medium textured low-base parent materials under forest or heath vegetation in cool to very cold humid to perhumid climates. Podzolic soils can also develop in strongly leached calcareous materials.

Brunisols exhibit a lack of horizon development compared to the other soils groups. The two Brunisols mapped in the Sudbury area are Melanic Brunisols and Sombric Brunisols. Melanic Brunisols have a high base status and develop on calcareous parent materials, whereas Sombric Brunisols have a relatively low base saturation. These soils commonly form on coarser textured morainal and outwash parent materials

Organic soils have developed from organic deposits of mosses, reeds, or woody vegetation. The three groups recognized in the area are Fibrisol, Mesisol and Humisol depending on the degree of decomposition of the organic material. Organic soils are commonly found in enclosed basins, or on the margins of lake basins.

As the focus of this study was on well to imperfectly drained soils developed on the regional glaciogenic sediments, the organic or wetland soils were not sampled in this study. However, as the ombrotrophic peat soils are only fed by atmospheric sources, these organic soils are excellent archives of historical aerosolic inputs (Shotyk *et al.,* 2000, 2001, 2002; Zoltai, 1988) that must be critically sampled and studied to enable currently non-available emissions histories to be reconstructed.

MINING AND SMELTING EMISSIONS

Sudbury has been home to mining, smelting and refining of nickel-copper ores since the late nineteenth century. The early methods of refining included the use of roast beds, and later, roast yards. Layering sulphide ore with locally cut timber that was then ignited to heat the ore until the sulphide minerals ignited formed the roast beds. The resultant nickel and copper concentrates were gathered for further refining (Winterhalder, 1995). The roasting process generated dense plumes of smoke, including sulphur dioxide (Freedman and Hutchinson, 1980). Thus the local forests were denuded by felling for use as fuel and for construction of the railway, and also by the noxious gases emanating from the roast beds. Rapid, severe erosion of the barren soils ensued, resulting in exposure of the bedrock that has, in turn, been subject to intense acid weathering.

Estimates suggest that as much as 2.7×10^5 tonnes of SO_2 were emitted annually, together with many tonnes of heavy metal particulates (Holloway, 1917), at the peak of the ore roast yard era between about 1895 and 1928. In 1928 the use of open roast beds was forbidden by an order from the Ontario Legislature. The open roast beds were supplemented with more efficient smelter facilities with smoke stacks. The three smelters in the Sudbury region were located at Copper Cliff, Coniston and Falconbridge. In the mid 1970s, Ni and Cu emissions from the three smelters were estimated at 1100 tonnes per year (Cox and Hutchinson, 1981). The Coniston Smelter was decommissioned in 1972 when the “Super Stack” (381 m) was brought on line at INCO Limited’s Copper Cliff smelter. Today all smelting in the region is carried out at the Copper Cliff (INCO Limited) or Falconbridge (Falconbridge Limited) smelter. The INCO stack emitted 1.1×10^6 tonnes of SO_2 and 1.2×10^6 tonnes in 1977 (Freedman and Hutchinson, 1980). This represented a reduction from the 2.5×10^6 tonnes reported in 1970. Emissions from the Falconbridge smelter totaled approximately 2.0×10^5 tonnes in 1977, about 17% of the Copper Cliff total (Freedman and Hutchinson, 1980). In 1976 Total Canadian SO_2 emissions were 6.0×10^6 tonnes (Air Pollution Control Directorate, 1976), with emissions from the Sudbury area representing about 25% of the national inventory.

In addition to sulphur-rich emissions, large quantities of metal-containing particulate materials are vented through the stacks. In 1976 and 1977 emissions from the Copper Cliff stack amounted to 1.0×10^4 tonnes, a reduction from the total INCO emissions of 3.4×10^4 tonnes in 1970 (Freedman and Hutchinson, 1980). The particulate material emitted primarily comprises of iron oxides, with significant amounts of nickel and copper emissions. The majority of the particulates sampled were less than 7 μm as the Cotrell dust collectors in use at the Copper Cliff smelter did not efficiently trap these small particles (Freedman and Hutchinson, 1980). Total Canadian emissions for all particulates in 1972 were 2.12×10^6

tonnes with 1.42 x 10^6 tonnes originating from industrial processes (Air Pollution Control Directorate, 1976). Thus, particulate emissions from the Copper Cliff smelter complex account for approximately 0.5% of the total Canadian emissions from all sources.

Smelter emissions from the Sudbury area smelters have decreased over the years. In 1995 total SO_2 emitted from the INCO Copper Cliff and the Falconbridge smelters totaled 281,000 tonnes per year. Annual metal emissions, in 1995, were approximately; 140 tonnes Cu, 10 tonnes Zn, 87 tonnes Ni, 52 tonnes Pb, 10 tonnes Cd, and 48 tonnes As (Air Pollution Control Directorate, 1976). The Residual Discharge Information System (Ministry of Environment, unpublished data, 1995) places the annual total of suspended particulate matter emitted to the atmosphere for the Copper Cliff smelter at 7050 tonnes and for the Falconbridge smelter 1180 tonnes. The 2001 data for the INCO and Falconbridge operations in Sudbury are presented in Table 1.

The amount of trace elements released during smelter operations is a function several factors. These factors include the mineralogy of the ores being processed, the tonnage processed, the temperature of the smelting process, with the more volatile elements (e.g., As, Cd, Hg, Pb, Sb, Se, Tl, Zn) emitted at lower temperatures than the less volatile elements (e.g., Cu, Fe, Mn, Ni), and the efficiency of the emission control equipment at the facility (e.g., multi-cyclones, electrostatic precipitators or bag houses).

Although there is limited data on the size of particles released, the particulate matter released by the INCO smelter is dominantly fine grained (80% by mass) with particles <3 µm, and particles from fugitive emissions (dust from roads, wind erosion of exposed surfaces, releases from material handling and on site storage) are relatively coarse grained at >2 µm (Environment Canada, unpublished data, 1999). Metals such as Cu and Ni may be primarily associated with coarse particle sizes (>2.5 µm) with mass median diameters <9 µm (Chan and Lusis, 1986). These authors further reported that Pb, Zn and As are most frequently associated with fine particles (<2.5 µm), typically with mass median diameters closer to 1 µm. Cumulative plots for coarse particle distributions of Cu indicate that 60-95% of Cu was associated with particles greater than 2.5 µm.

Regional rainfall contains both particulate and soluble phase emissions from smelting operations. Rainfall close to the smelters in the Sudbury region is acidic, containing high levels of soluble metallic ions. In 1970 the conductivity of rainwater collected 1.6 km from the Coniston smelter was 450 µmhos and at 13.5 km was still 64 µmhos. The fallout of Ni dissolved in rainwater decreased from 271 m g^{-2} $month^{-1}$ at 1.6 km to 8.1 m g^{-2} $month^{-1}$ at, 19.3 km (Cox, 1975).

Snow sampling provides a means of examining deposition over the duration of the winter period of elements of interest. Snow sampling in the Sudbury area was carried out in 1972 (McGovern and Balsillie, 1973), with samples being analyzed for total S, Cd, Cl, Co, Cu, Fe, Ni, Zn and pH. Three sets of samples were collected 1) after significant snowfall in January and 2) February and 3) during freeze-thaw in April. The values for April were significantly lower than the other two sets of samples, suggesting that metals were removed by run-off to regional lakes, streams or groundwaters, or they percolated or leached out during the thaw. Levels of all elements except Cl decreased with increasing distance from Sudbury, indicative of the influence of smelting operations on regional precipitation chemistry.

Metal Particulate Deposition

Metals, deposited from the atmosphere by wet and dry depositional processes, can accumulate in a variety of environmental media including soil, water and sediment. Concentrations of emitted metals typically decrease exponentially with distance from the source. Particulate matter is generally subdivided into a fine fraction (<2.5µm) and a coarse fraction (>2.5 µm). Particulate matter may be primary or secondary. Primary particulate matter is emitted directly into the atmosphere, whereas secondary is formed in the atmosphere through chemical and physical transformations. The principal gases involved in secondary particulate formation include SO_2, NO_x, volatile organic compounds and NH_3.

Primary particles are present in both the coarse and fine fractions, while secondary particles are dominantly in the respirable fine fraction. Particulate matter may include elemental and organic carbon compounds, aluminium, iron and silicon oxides, trace metal rich spheres, metal sulphates, and metal nitrates.

Extremely fine particles (<0.1 µm) are formed mainly from the condensation of hot vapours during high temperature combustion processes and the nucleation of atmospheric species. These tiny particle nuclei mode have a short atmospheric residence time as they nucleate and coagulate to yield larger particles. Particles 0.1-2.0 µm in diameter result from the coagulation of particles in the nuclei mode, and from the condensation of metal-rich vapours onto previously existing particles. Thus the growth of these particles may be continuous. This group of particles accounts for much of the particle mass in the atmosphere. Atmospheric removal processes are least efficient in this size range. These fine particles can remain in the atmosphere for days to weeks. Eventually, these particles are removed from the atmosphere by dry deposition and precipitation. Scavenging by precipitation accounts for 80-90% of the mass of particles in the accumulation mode (Wallace and Hobbs, 1977).

Particles larger than 2.5 µm, the sedimentation or coarse mode, are typically associated with mechanical processes such as wind erosion and grinding operations. These particles are generally removed by gravitational settling. Quantitatively, these particles are not particularly numerous, however, they contribute significantly to mass, especially immediately downwind of major industrial sites.

SOIL

Soil is “the top layer of the earth’s surface, consisting of rock and mineral particles mixed with organic matter” (Concise Oxford Dictionary, 1982) formed by the interaction of parent material, climate, relief, vegetation over time (Jenny, 1994). Soil is chemically stable with a strong buffering of elemental availability, with variable H_2O availability, with ion rich soil solutions, an active microbial and inorganic catalysis, a source and sink of all the elements essential to living organisms, with a high P content, but low P availability, with a variable ratio of biomass/unit area and photosynthesis/unit area. Bohn *et al.,* (2001) further state that

> “plant uptake and decay, plus the strong retention of transition metals by inorganic and organic soil components, lead to a slight accumulation of trace metal ions near the soil surface. Total concentrations in the surface layers or horizons of untilled soil can be several times the concentration shown in the subsoil”.

This biodynamic accumulation of metals (van Tilbourg, 1998) supports the suggestion by Bohn *et al.,* (2001) that normal concentration of Ni and Cu in surface soils can range from 10 to 1000 mg kg^{-1} and 2 to 100 mg kg^{-1}. Complexation by soluble organic anions increases the concentration of Cu and Zn in the surface soil.

Natural levels of metals in soils are in equilibrium with the inorganic and organic components of a soil. Due to soil processes, these metals are not biologically available. This is also valid for metals added to soils, given time to reach the same equilibrium position. Time decreases the availability of ions added to soils. Recent experiments have shown, for example, that the ecotoxicity of added zinc decreases with time (Smit, 1997) as the applied zinc becomes incorporated in soil organic matter or soil secondary minerals. Time allows ions to diffuse through the soil solution to the strongest sorptive sites on weathered soil particles (Bohn *et al.,* 2001). Time leads to the aging of soil solids, with smaller reactive phases evolving into larger, less reactive phases and less plant-available phases. Leaching of toxic ions through the solum is generally negligible in undisturbed sites. Potentially toxic elements generally remain within a few centimetres of where they first come into contact with the soil matrix unless stirred by cultivation. If retained at the immediate soil surface, they may be above the active portion of the root zone and may, therefore, be relatively unavailable to plants unless active acidic dissolution processes are dominant.

MINERALOGY OF SUDBURY SOILS

Minerals formed by igneous or metamorphic processes are commonly unstable at the surface of the Earth. The minerals undergo weathering, with the products being re-equilibrated with the current dynamic system. The Precambrian bedrock, in this area, is above global background levels in nickel and copper in sulphide minerals that are the major ore minerals; also as trace elements in silicate minerals, for example, olivine and pyroxene, and the oxide minerals, for example, magnetite (Deer *et al.,* 1966). Copper is an incompatible element with a partition coefficient of <1.0 for minerals such as olivine, orthopyroxene and clinopyroxene and amphibole, whereas, Ni is a compatible element with partition coefficients >1.0 for the same minerals (Rollinson, 1993; Earthref, 2002). Hosted within the silicate mineral phases of the Quaternary sediments forming the parent materials of the region will also be immiscible mineral phases such as blebs of sulphide minerals (Sposito, 1989).

There is minimal information in the open literature on Sudbury soils describing relict silicate mineralogy, clay mineralogy, and soil solution composition (Costescu and Hutchinson, 1972; McGovern and Balsillie, 1973; Whitby and Hutchinson, 1974; Cox, 1975; Dreisinger, 1976; Dreisinger and Buchannan, 1977, 1979; Dreisinger, 1978; Rutherford and Bray, 1979; Hazlett *et al.,* 1983; Taylor and Crowder, 1983; Chan and Lusis, 1986; Negusanti and McIlveen, 1990; Heale, 1993; Dudka *et al.,* 1995, 1996; Gundermann and Hutchinson, 1995; Adamo *et al.,* 1996; Chuan *et al.,* 1996; Dudka and Adriano, 1997; Bajc and Hall, 2000; Morra and McIlveen, 2001; Adamo *et al.,* 2002). Therefore, speculation about the bioavailability of metals is difficult. Metals within the lattice of resistant minerals are not readily available for uptake by biologic processes whereas heavy minerals absorbed on clay minerals are more readily available, whilst those existing as either free ions or ionic complexes in the soil solution are perhaps most readily bioavailable (Sposito, 1989). There is, however, a voluminous literature on the bedrock geology and mineralogy of the area (Pye *et al.,* 1984; Lightfoot and Naldrett, 1994).

Silicate Minerals

Adamo *et al.,* (2002) used scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) for the analysis on iron oxides and sulphides in the soil, both before and after sequential extractions. They observed the results of incomplete dissolution of the mineral phases at the second and third stages of the sequential extraction. Microchemical analysis indicated the presence of Ni, Cu and Zn in some of the particles along with Al, Si, K, Ca, Mn, Fe, ±Zr and ±S. In the fine sand fraction Adamo *et al.,* (1996) observed numerous spherical particles containing encapsulated Fe and Ni metallic or oxide phases in a matrix rich in Si, Ca, and Fe. These particles were formed from molten materials during the smelting process, and were deposited on the sampled soils following emission from the regional smelters. Hollow spheres containing particles rich in Cu and S, with smaller amounts of Fe and Ni, were also observed. Trace amounts of Cu and Ni were observed in the clay fraction (Adamo *et al.,* 1996). Elemental maps of crushed soil materials indicated that Cu to be diffused throughout the soil matrix, whereas Ni was concentrated in zones. These researchers did not attempt to identify the specific minerals species by X-ray diffraction.

The residue remaining from the sequential leaching experiments contained silicate and clay minerals, as well as Fe containing micro-aggregates. These micro-aggregates sometimes also contained P, Cu and Ni, with isolated 20-40 µm diameter framboids of pyrite also being identified. Hollow spherical particles were found to exist in the residue from the sequential leaching experiments. The residue, after "total digestion", contained particles with C and S contents, as well as measurable concentrations of Si, Al, Fe, Ca, Ti, Zr, Cr, ±Mg, ±K, ±Ni, and ±Cu. These particles were insoluble in HF (Adamo *et al.,* 1996). Adamo *et al.,* (1996) found Cu to be more readily extractable than Ni from the Sudbury soil samples studied, suggesting that Cu may be more mobile. Alloway (1990) suggests that adsorption of heavy metals to soil particles follows the order Cd < Ni < Co < Zn << Cu < Pb < Hg. The few Sudbury soil studies utilizing SEM/EDX indicate that Cu is strongly associated with organic matter and homogeneously distributed on the surfaces of the clay fraction, whereas Ni was associated with Fe oxides and in the spherical silicate particles. This observation may indicate the Cu is associated with mineral phases that are more easily weathered than the Ni-rich mineral phases.

Clay Mineralogy

The minerals of the clay fraction (< 2µm) have a major influence upon the variability of soil chemistry (Bohn *et al.,* 2001). The sand (50-200 µm) and silt (2-50 µm) fractions are much less chemically active and are commonly composed largely of chemically inert quartz. Primary minerals do occur in the clay fraction of weakly weathered soils but are generally minor constituents of the clay fraction of most soils. Clay minerals are largely secondary, formed by low temperature reactions, and are either inherited from sedimentary rocks or formed directly in the soil by weathering. The authigenic clay-sized minerals include layer silicates, Al and Fe hydroxides, carbonates and sulphur compounds.

The free oxides range from gels of short-range order to crystalline and are often found as the weathered, or precipitated, outer layer of soil mineral grains (Bohn *et al.,* 2001). This layer is commonly found on quartz, feldspar and mica grains in soils. Allophane and imogolite are aluminosilicate gels of short-range order, having a very high cation exchange capacity that is pH and hydration dependent (Bohn *et al.,* 2001), common in podzolic soils (Farmer, 1982). These gels of short-range order have been documented to retaining phosphate and sulphate in

Solonetzic soils (Spiers *et al.,* 1984), a mechanism that may be very important in controlling the effects of acid deposition on the soils of the Sudbury region. Secondary iron oxide minerals, common in the orange coloured B-horizons of the Podzolic and Brunisolic soils of the Sudbury region, have been described as important sinks for arsenic in Boreal soils of Northern Alberta (Dudas *et al.,* 1988).

An understanding of the clay mineralogy of regional soils is crucial. The secondary or authigenic minerals of the clay fraction, when exposed to metal ions in the soil solution, show ion exchange properties at their surface that are very important in controlling the bioavailability of the soluble metal phases. On longer exposure not only is the surface of the mineral particle involved, but the dissolved phase metal may penetrate the lattice layers or tubes of these minerals, or exchange ions with the surface oxide layers. Once thus fixed in the mineral structure, the metal ion cannot easily escape. Such processes must limit the availability of the metal ions to the biota. Thus the soluble metal ion may be transformed from a bioavailable free ion form into a bio-inert soil mineral complex.

Kodama (1979), in a literature survey of the clay mineralogical data of Canadian soils, related the distribution of various clay fraction compositional assemblages to the soil-physiographic regions of Canada. He indicated the subsoils of the Shield regions of Canada to have a clay mineral assemblage dominated by clay mica, followed in order by mixed-layer minerals, vermiculite, kaolinite and smectite. The smectite tended to be found in soils on the western border of the Shield region, or in areas impacted by the draining of Glacial Lake Agassiz. In 1993 clay mineralogical data from 461 publications were integrated with the Soil Map of Canada to produce a clay mineralogical map for the surface soils of Canada at a 1:10 million scale (Kodama *et al.,* 1993). Although the region of the Sudbury smelter footprint is conspicuous by the absence of data, the clay mineralogy soils to the north of the region are dominated by an admixture clay mica, chlorite and kaolinite. Bajc and Hall (2000) noted that labile minerals such as sulphides and carbonates are slowly dissolved in a neutral to acid soil environment, with the associated chemical constituents either removed in solution to the water table, or scavenged locally by clay-sized phyllosilicates and secondary oxides/hydroxides. Minor amounts of secondary carbonate minerals have been observed in the finer textured subsoils immediately south of the abandoned Coniston smelter (Spiers, personal observation).

Evans (1980, 1982) and Evans and Wilson (1985), in studies examining development of podzolic soils west of the Sudbury region, documented presence of clay mica, chlorite and kaolinite in the clay fraction of the loamy sand and sandy loam soils of the Chapleau area. These studies, together with that of Jensen (1988), also provided extraction chemistry evidence for presence of allophone and imogolite in the B-horizons of the Podzolic and Brunisolic soils of the same area. Cruickshank *et al.,* (1990), in micromorphological and microchemical study of podzolic Ae and Bhf horizons documented the presence of carbon-rich allophone-like layers encapsulating sand grains. The presence of a mineral with an imogolite-like structure, observed with scanning electron microscopy and energy dispersive spectroscopy, was also documented. As these latter studies have all been on soils formed on similar parent materials in the same climate and vegetation zones as Sudbury, the presence of the same inherited and authigenic clay mineral suite is probable in the soils of the Sudbury smelter footprint.

Although there is no clay mineralogical data presented, Adamo *et al.,* (2002) report the content of the clay fraction as ranging from 30-209 $\mu g\ g^{-1}$ with a mean value of 109 $\mu g\ g^{-1}$ for the soils studied in the Sudbury area, with the highest content of clay-sized particles in the finer textured soils of the Copper Cliff area. Acidification in soil environments adjacent to sulphur piles has been shown to dissolve chlorite, micaceous and smectitic minerals (Warren and Dudas, 1992; Warren *et al.,* 1993), a result possible in the study region with historic emissions of sulphurous gases in the hundreds of thousands of tonnes from the Sudbury smelters. The weathering of soil clay minerals also causes solubilization and translocation of the dissolved trace metals released from the mineral structures.

Organic Horizons

The well to imperfectly drained undisturbed soils of the Sudbury region are characterized by having organic (LFH) horizons ranging in thickness from 2 to 15 centimetres. The designation LFH refers to the fresh plant detritus (L=litter) on the soil surface, the partially decomposed organic layer (F=fermentation) and the well-decomposed organic layer

(H=humus). These poorly studied LFH horizons, initially composed almost entirely of organic matter, are crucial sinks for the aerosolic particles (Spiers *et al.,* 2002) from both local and long-range sources, acting both as filters to prevent particle translocation to lower horizons, and as exchange surfaces to absorb dissolved metals in precipitation and throughflow. Colloidal soil organic matter, for example, strongly adsorbs Cu, Zn, Fe and other transition metal ions, by acting as a chelating agent (Bohn *et al.,* 2001).

In a study in the Falconbridge area, Golder Associates Ltd. (2001) reported total C content ranges from a low of 0.16% to high of 10.1% in the 0-5 cm layer of the sampled soils. The study documented carbonate contents to range below detection limit to a high of 0.89% in the same 0-5 cm layer, with the higher levels being in areas which were either landscaped or limed. Gundermann and Hutchinson (1995) reported that the organic C content of soils in the 0-5 cm layer in the Coniston smelter area decreased over the period between 1972 and 1992, probably because of soil erosion. The latter study also reported a concomitant decrease in water extractable metal content from 74, 33 and 52 µg g^{-1} Ni, Cu, and Al to 2, 2, and 3 µg g^{-1}, Ni, Cu and Al, respectively, suggesting that the decrease is strongly linked to the erosion of surface organic matter. Hazlett *et al.,* (1983) report organic C content of soils around the Coniston smelter in the range 0.1% to 19.4%, with the high values being for the LFH horizons and the lowest values for C-horizons. A recent study, for samples collected for the 0-20 cm layer from throughout the Sudbury region some 12 years ago, documented organic carbon content ranges from about 0.5% to 2.1% (Adamo *et al.,* 2002).

SOIL CHEMISTRY

Parent Materials

McKeague *et al.,* (1979) compiled much of the published data in conjunction with their studies of background levels of minor and trace elements in Canadian soils. They describe levels for 53 profiles both on a national and regional basis. The mean levels (µg g^{-1}) documented are: Cr 43, Mn 520, Co 21, Ni 20, Cu 22, Zn 74, Sr 210, Hg 0.06, Pb 20. Their data compare closely with data reported for levels in soils of the U.S.A. (Shacklette *et al.,* 1971). However, McKeague *et al.,* (1979), with data for only 12 sites for the entire Canadian Shield region, document no sites within the present study region, and base the prediction of levels on a small sample base. Webb and Howarth (1979) point out that extrapolation of the results of detailed studies from such type localities ignores the often significant differences in composition within single stratigraphic formations that are lithologically different in space.

Ginocchio *et al.,* (2004), in a recent study describing micro-spatial variation in metal contamination in the vicinity of a Chilean copper smelter, document a wide range of variability in soil metal concentrations at the micro-site level having a dramatic influence on plant recruitment. Such observations tend to temper the statement of Dudas and Pawluk (1980) that predictions of elemental status of soil material can be based on average values of parent rocks, even in glaciated terrains. Such prediction is complicated, even if the parent lithology is uniform, by changes in composition owing to sedimentary source variations and/or selective mobilization and redeposition of individual elements during weathering processes (Webb and Howarth, 1979). Prediction of soil elemental status is further compounded by the vagaries of glacial/fluvial/aeolian processes on surficial materials within the Sudbury region.

The approach investigated by the U.S. Geological Survey, in conducting a reconnaissance geochemical survey of Missouri State, was based on random sampling of previously mapped broad geological, pedological, vegetational and hydrological units at different densities (Tidball, 1978; Miesch, 1976; Erdmann *et al.,* 1976). Analyses of variance were used to study geochemical variation between each selected unit, and it was found, for many of the 30 to 40 analyzed elements, that significant differences occurred between the previously mapped surficial units. These techniques were deemed suitable for regions containing relatively homogeneous pedologic units, such as may be associated with glaciated terrain.

McKeague *et al.,* (1979) used the data obtained in their compilation to calculate prediction equations for minor elements based on more easily determined parameters such as clay, organic C and the major elements (Al, Fe, Ca, Mg) as independent variables. They were able to account for more than 50% of the variability of Mn, Cu, Pb, Co, Ni, Cr, Sr and Se in this for manner for different sample groupings. Such relationships are obviously based on the ability of the minor elements to proxy for the major elements in the crystal lattices of various minerals (Dudas and Pawluk, 1980). They were able to predict Sr levels based on Ca alone for noncalcareous samples, probably because Sr can proxy for Ca in plagioclase feldspars (McKeague and Wolynetz, 1980).

Geochemical exploration work has produced a vast body of data in regions of known mineralization, much of which is not pertinent to this study because the determinations are made on a range of size fractions, rather than only <2mm material. Data of relevance to the 2 µm (clay size) fraction will be mentioned here. Shilts (1977), in a study of till samples from the Keewatin region, describes the content of the following in the clay separate: Zn 100 µg g-1, Cu 100 µg g-1, Ni 80 µg g-1. Bajc and Hall (2000), in a study of till geochemistry to the immediate north of the area of Sudbury, stated that, intuitively, the underlying bedrock should have a direct relationship with the composition of both the overlying till (C-horizon) and the soils developed on them. Thus, in their study, various till facies were investigated to determine whether distinct background concentrations of metals could be associated with different till types. They also sampled the local vegetation to ascertain whether different forest types partitioned metals differently, which would, in turn, influence the background geochemical signature of the resulting humus. Factors such as slope and drainage were directly linked to the soil-forming processes, thus affecting the A- B- horizon geochemistry. The Bajc and Hall (2000) study did not, however, document the aqua-regia extractable trace metal contents of the tills and soils examined.

McMartin *et al.,* (1999) documented the influence of the smelter emissions on soils in the Flin Flon area of Manitoba. They concluded that the humus layers contained a record of historical smelter airfall additions, with the degree of contamination with As, Cd, Cu, Hg, Pb and Zn decreasing with increasing distance from the smelter. The levels of these metals in the parent tills or C-horizons reflect complete absence of any significant contamination. In a recent survey in the Rouyn–Noranda area within a 100 km radius of the Horne Smelter Henderson et al (2002) described the metal concentrations of soil parent materials. The study provides geochemical maps and summary statistics for the <2 mm fraction of soils analyzed by ICP-AES following aqua-regia digestion for both diamicton and clay deposits. Diamicton includes all poorly sorted to unsorted clastic sediments, primarily till, which, at a few sites, may be significantly reworked. Clay includes all fine-grained clastic glacial lake sediment such as clay, silt and silty clay. The study documents parent material concentrations for As, Cd, Cu, Pb and Zn as 3.95 ± 0.17, 0.67 ± 0.22, 26.07 ± 0.12, 52.5 ± 0.14, 79.74 ± 0.2, respectively. These values are considerably higher than those documented by McKeague *et al.,* (1979), possible reflecting the inclusion of underlying metal-rich bedrocks in the diamicton deposits forming the parent materials of the regional soils. The Geological Survey of Canada completed a broad regional sampling and analytical program for much of Ontario to approximately to lower half of the current study region as a component of a National Geochemical mapping initiative in the 1990s (Garret, personal communication), with data analysis and report publication currently in a preliminary stage only.

This brief overview has shown that, although there is a considerable amount of site-specific data on levels of minor elements in soils in Canada, there are very few studies describing regional variation of major, minor and trace elements. Studies relating concentrations of specific elements to parent material variation are similarly sparse, and there is only one detailed study of elemental partitioning among the various particle size fractions of soils, although this does, admittedly, discuss the data with genetic overtones.

SUDBURY SOILS

McKeague *et al.* (1979) compiled much of the published data in conjunction with their studies of background levels of minor and trace elements in Canadian soils, describing levels for 53 profiles both on a national and regional basis (Table 2).

Table 2: Distribution of major and trace elements in Canadian soil parent materials.

Element	Granite	Shale	Crustal Abundance	Canadian Shield Soils
		Major elements %		
Al	7.7	8.0	8.2	6.7
Ca	1.6	2.5	4.1	1.8
Fe	2.7	4.7	5.6	2.5
K	3.3	2.3	2.1	na
Mg	0.16	1.34	2.3	0.53
Na	2.8	0.66	2.4	na
		Trace elements ($\mu g/gm^{-1}$)		
As				na
Cr	4	100	100	19
Co	1	20	25	19
Cu	10	57	55	12
Mn	400	850	950	417
Ni	< 1	95	75	12
P	700	770	1050	na
Pb	20	20	12.5	20
Se				0.18
S	285	450	375	409
V	20	130	135	na
Zn	40	80	70	57
		(ng/gm^{-1})		
Hg				107

Notes:

1) Values from Taylor (1964)
2) Values for soils from the Canadian Shield (McKeague, 1979)

They also document levels for surface horizons of Canadian soils which are similar in range to those documented for surface soils worldwide, namely for Ni, Cu and As are 40 µg g^{-1}, 30-20 µg g^{-1} and 5 µg g^{-1} respectively (Dreisinger, 1976; Alloway, 1990). Maximum values of 2300 µg g^{-1} Ni for soil in the Sudbury area before the construction of the super stack, in Copper Cliff, are documented as decreasing to 1715 µg g^{-1} after the introduction of the super stack (Dreisinger, 1976). For Cu, these values are essentially unchanged at 1750 µg g^{-1} and 1738 µg g^{-1}, both results obtained from samples taken at Copper Cliff (Dreisinger, 1976).

Maximum pre-Super Stack S values of 0.38% were reported in samples from the Sudbury area and maximum post-stack S values of 0.36% (Dreisinger, 1976). MOE acceptable level for S in soil is 0.1% (Table 3; Heale, 1993). Iron levels in soils in the Sudbury region have on the whole increased since the construction of the Super Stack from 4.7% up to 5.30%. Zinc levels declined from 416 µg g^{-1} to 313 µg g^{-1}, with a concomitant increase in As levels from 50 µg g^{-1} to 63 µg g^{-1}. These levels contrast greatly with maximum Cu and Ni values reported by Taylor and Crowder (1983), 6912 µg g^{-1}, and 9372 µg g^{-1}, respectively, close to the Copper Cliff smelter, decreasing with distance. The differences reported over time by the above authors may merely reflect the natural site variability of the region, or be a product of site micro-topographic variation which leads to micro-zones of enrichment because of snow-melt or runoff translocation of aeolian materials.

Table 3: MOE guidelines for the upper normal limit for metals in Ontario soils (from Heale, 1993).

Parameter	Soil (0-5 cm)	
	Urban (µm/g dry weight)	Rural (µm/g dry weight)
As	20	10
B	15	10
Cd	4	3 or 4
Cr	50	50
Co	25	25
Cu	100	60
Fe (%)	3.5	3.5
Hg	--	0.5
Mg (%)	--	1
Mn	700	700/1000
Ni	60	60
Pb	500	150
Sb	8	1
Se	2	2
S (%)	0.1	0.1
V	70	70
Zn	500	500

The maximum values for NH_4OAc extractable metals are Cu 2243 µg g^{-1}, Ni 6730 µg g^{-1}. The maximum DTPA (diethylenetriaminepentaacetic acid) extractable metals are Cu 717 µg g^{-1}, and Ni 1013 µg g^{-1}. Taylor and Crowder (1983) report that Cu and Ni concentrations in wetland soil-sediment material are comparable to Sudbury area lake sediments (Semkin and Kramer, 1976) and are comparable to concentrations measured in regional forest soils by Freedman and Hutchinson (1980).

The 1978 the Ontario Ministry of the Environment (MOE) documented the guidelines for maximum acceptable Ni, Cu, As and Co content in soils between pH 5.0 and 8.0 (0-10 cm depth) at 100 µg g^{-1} Ni, 100 µg g^{-1} Cu, 25 µg g^{-1} As and 25 µg g^{-1} Co. Data collected from a sparse sample set collected adjacent regional roads and highways in 1977 indicated that the MOE guideline for surface soils were exceeded in an area of over 930 square kilometres for Ni, 580 square miles for Cu, 65 square miles for As, and 43 square miles for Co (Heale, 1993), with no data being documented describing the soil pH. The information on analytical procedures is not provided, but the data being reported as total concentrations of metals. As the standard analytical procedure used by MOE is based on an aqua regia extraction of dried and ground soil materials, the data cannot be described as total concentrations. By 1993 MOE guidelines for upper normal limits for heavy metal content of soils had been changed as shown in Table 3 (Heale, 1993). In 1988 Ni levels in soil were up to 9 times background level, As levels were 7 times greater than background levels, Cu levels were up to 14 times above background levels (Heale, 1993), although the source for regional background concentration data was not documented.

Hutchinson and Whitby (1974) describe the pH, electrical conductivity, LOI (loss on ignition) and metal content of soil samples collected around the Coniston smelter impact zone. The reported pH values ranged from 2.19 at 0.8 km from the smelter up to pH 3.39 about 50 km from the smelter on the surface. At 10 cm depth, pH ranged from 2.5 to 4.19 at a distance of, 19.3 km, increasing to 3.42 about at 50 km. Generally, pH increased with depth in the soil profile. Electrical conductivity decreased both with distance away from the smelter and with depth in the soil profile.

The variability in LOI, whilst apparently showing no correlation with soil type, is probably a function of increasing organic content away from the smelter and decreasing sulphur compounds with distance. Hutchinson and Whitby (1974) also analyzed homogenized samples taken from the upper 10 cm of soil for metal content by atomic absorption spectrometry following digestion with a mixture of HF:H_2SO_4, with the digestate being dissolved in HNO_3 prior to analysis. The results indicated a trend of decreasing metal content in soil with increased distance from the smelter (Table 4).

Adamo *et al.,* (2002) analyzed pH of 20 samples collected from the east and northeast of the 3 Sudbury area smelters in 1992. They reported a mean pH of 4.5, which is within the range

(3.8-4.8) for unpolluted podzolic soils of the Sudbury area; however 40% of the samples had a pH<4.0, perhaps indicative of acidification as a result of SO_2 emissions. The mean S content of soils in the same study (Adamo *et al.,* 2002) was 3.3 µg g^{-1}; however almost half the samples had a total S content of >10 µg g^{-1}, which exceeds the OMOE (Negusanti and McIlveen, 1990) guideline of 10 µg g^{-1}.

Table 4: Distribution of selected major and trace elements within the surface layers of selected soils at various distances from the Coniston smelter.0

	Distance from smelter	
Element	1.1 km	50 km
	(µg/g)	
Cu	2892	26
Ni	5104	35
Co	200	22
Zn	97	84
Ag	7.9	1
Pb	83	20
Mn	255	168
V	103	23
	(%)	
Fe	7.75	1.15
Al	1.1%	0.22

Values from Hutchinson and Whitby (1988).

Adamo *et al.,* (2002), using air-dried, crushed by hand and sieved soil samples from 0-20 cm depth, analyzed for metal content by ICP-AES following acid digestion (HF/HNO_3). A four-step chemical extraction procedure (Singh *et al.,* 1998; Ure *et al.,* 1993) was also used to fractionate the chemical forms of the heavy metals into the following fractions: 1) soluble and exchangeable, 2) occluded in iron and manganese oxides, 3) organically bound or in the form of sulphides, and 4) present mainly in mineral structures. These four fractions are extractible with increasing difficulty: 1) easily extractible, 2) reducible, 3) oxidizable and 4) residual. The concentration of Cu, Ni, Fe, Mn, Zn, Pb Cr and Cd in the various extracts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), with the analytical results summarized in Table 5.

Adamo *et al.,* (2002) used scanning electron microscope (SEM) and energy dispersive X-ray (EDS) spectroscopic analysis to examine the heavy mineral separate of the fine sand fraction of the soils before and after sequential extraction treatments. Iron oxide and sulphide phases, with associated Cr, Cu, Ni, Mn and Zn were associated with the Fe phases, with some iron oxide and sulphide particles being still visible after the various sequential extraction procedures. The results suggested that some of the soil Cu may be in potentially more mobile phases in the soils, with Ni being dominantly (average 64%) in the inorganic residual phase. Unfortunately, detailed mineralogical examination of the various metal-rich phases was not documented.

Table 5: Metal proportions in the various fractions from selected soils of the Sudbury region using the European Union extraction procedure.

	HOAc	**Reducing**	**Oxidizing**	**Residue**	**Mean Total**
		(% total metal)			
Cu	27	17	26	31	433±474
Ni	2-46	2-24	2-20	17-92	410±410
Fe	0.1-2.2	7.9	2.8-14.7	85	2.6±0.85%
Mn	0.3-18.1		0.6-8.4	52	389±195
Zn	1.8-34.6	1.2-25.7	15.6	29.1-90	57±34.4
Pb	5	2.4-46.7	14	15.1-96.6	30±23.8
Cr				78.2-92-4	63±24
Cd	3.8	3.7	13.9%		2.7±0.8

Notes: Adamo et al. (2002)

In an examination of regional surficial material geochemistry, Bajc and Hall (2000) noted that concentrations of Cu and Ni in humus are significantly higher than concentrations in B- and C-horizon soils, an observation supported by Spiers *et al.,* (2002) (*see* Table 7). However, Bajc and Hall (2000) attribute the higher content in the humus layer to the scavenging and binding properties of fulvic and humic acids in complexing soluble airfall metals, thus recognizing the possibility of anthropogenic sources being possibly responsible for the elevated concentrations. Bajc and Hall (2000) report that the absolute concentration of Cu in the B-horizon is lower than in the C-horizon, attributing the distribution to the dissolution and hydromorphic dispersion under acidic soil conditions in the zone of pedogenic weathering. Nickel shows a similar distribution in the horizons of the sampled pedons (Bajc and Hall, 2000), suggestive of Ni being less affected by hydromorphic processes. The authors do not attribute the differing distributions of Cu and Ni in the sola to the different affinity of the elements to the mobile dissolved organic acids in the pedologic system.

In analyzing the control of bedrock geology on humus-form chemistry, Bajc and Hall (2000) noted only slight variations in the Ni and Cu ranges. However, definite trends were observed in the B- and C-horizon data. The contents of Cu and Ni from samples collected over norite and Levack gneiss were consistently higher than samples collected over other bedrock units. The C-horizon also showed elevated Cu and Ni concentrations in samples collected over quartz diorite and mafic extrusive rocks. The lower limit of concentration is similar to those obtained from other bedrock domains.

Bajc and Hall (2000) sampled the pedogenic mineral horizons of soil profiles at several geochemically anomalous sites to examine the vertical variation in Ni and Cu. The postdepositional, low-temperature geochemical processes that occur in the porous and permeable Quaternary sediments in an oxidizing environment may modify the chemistry of mineral phases originally sorted into grain size fractions on the basis of resistance to glacial abrasion. In an oxidizing environment, for example, fine carbonates and sulphide minerals are dissolved (Bajc and Hall, 2000), with the dissolved products either translocated in solution to be either reprecipitated in an authigenic phase, or absorbed by phyllosilicates and secondary oxides/hydroxides. The translocation of the dissolved ions or ionic complexes may result in elevated concentrations of the elements at depths. The samples from the Ae horizon, the B- and C-horizons were size fractionated prior to analysis (Bajc and Hall, 2000), with <63 µm fraction being analyzed by ICP-AES and ICP-MS following both *aqua regia* and a hydroxylamine hydrochloric acid extractions, with <2µm fraction being analyzed following an aqua regia digestion. The results from the Bajc and Hall (2000) study are summarized below:

- The Ae-horizon is usually depleted in the elements present in the underlying B-horizon. The authors attribute this depletion to the hydromorphic dissolution of metals from this horizon by humic and fulvic acids originating in the overlying organic horizons.

- The B-horizon is usually depleted in the elements present in the C-horizon, with the depletion attributed to the destruction of labile minerals by oxidation and the hydromorphic dispersion of the contained metals within the profile. There are some instances where Ni is enriched in the B-horizon, usually coincident with an increase in Fe in either the clay and/or silt and clay fraction.

- Concentration of elements generally increases downward through the C-horizon. Bajc and Hall (2000) are not sure whether this is a primary or secondary signature.

- The proportion of Ni and Cu extracted with the hydroxylamine hydrochloric acid leach in the –63 μm fraction is quite high relative to that of the aqua regia digest. This is indicative of a large proportion of Ni and Cu being potentially mobile in the pedologic environment and not tightly bound as sulphide minerals.

The study provided data for mineral soil horizons only. The surface organic (LFH) horizons were not sampled and analyzed.

Dudka *et al.,* (1995) using ICP-AES (HNO_3 and $HClO_4$ acid digestion) present metal content for 73 soil samples (Table 6). Gundermann and Hutchinson (1995) found concentrations of Cu, Ni and H ions have decreased significantly in the surface soil horizons at the site of the Coniston smelter, over the period, 1972-1992. As there was a concomitant reduction in the organic carbon content in the soils over the same period, they suggested the reduction was a result of surface horizon leaching and erosion, effectively removing metals from the top 5 cm of the soil profile. Water extraction of metals indicated a high of 75 μg g^{-1} Ni in 1972 and in 1992 this value was about 5 μg g^{-1}, together with about 30 μg g^{-1} Cu in 1972 and in 1992 about 2 μg g^{-1} Cu. Although the water extraction may be indicative of the bioavailability of Ni and Cu, the values obtained cannot be readily compared to other regional studies because of the variability in digestion methods.

Plants are the integrator of bioavailability of metals in soils, and various species have different levels of tolerance for high levels of anthropogenic contaminant metals in soils. Bowen (1966) documents, for example, normal levels of Ni and Cu in vegetation as 3 μm/g and 14 μm/g, respectively, compared with values of 45 μg g^{-1} and 98 μg g^{-1} in Coniston area vegetation for samples analyzed by Hutchinson and Whitby (1974). Hutchinson and Whitby (1974) sampled foliage from *Vaccinium augustifolium* (low sweet blueberry), *Acer rubum* (red maple) and *Deschampsia flexuosa* (wavy hair grass).

Table 6: Distribution of selected major and trace elements within the surface layers of selected soils of the Coniston airshed. From Dudka *et al.,* (1995).

Element	Geometric mean	Geometric deviation	Observed range	95% expected range
		%		
Ca	0.41	2.15	0.06-2.5	0.09-1.9
Fe	2.08	1.43	0.70-4.5	1.0-4.3
Mg	0.39	1.83	0.08-1.5	0.1-1.3
Na	0.04	2.74	0.004-0.2	0.005-0.3
		µg/g		
B	17.93	1.73	1.6-56.2	6.0-53.7
Cd	0.29	4.67	<0.06-10.1	0.01-6.3
Co	10.50	2.45	0.9-113.3	1.7-63.0
Cr	49.29	1.66	4.0-131.6	17.9-135.8
Cu	116.20	2.81	11.4-1891.0	14.7-917.5
Mn	260.70	2.06	63.6-4714.0	61.4-1106.3
Ni	104.80	3.04	5.3-2149.0	11.0-994.2
S%	0.13	4.53	0.008-7.3	0.006-2.7
V	52.25	1.36	25.9-97.9	28.2-96.9
Zn	34.80	2.64	1.5-336.1	5.0-242.0

These regionally widespread species are fairly tolerant of SO_2 pollution. In all three species, analysis was carried out on washed, dried and ground samples. Further, these authors noted that Cu and Ni concentrations decreased markedly with increased distance from the smelter zone. More detailed descriptions of levels of metals in vegetation in the Sudbury area may be found in papers McIlveen and Nagusanti (1994).

REGIONAL SOIL STUDIES IN THE SUDBURY AREA

A series of large-scale studies on the effects of smelter metal emissions on soils and vegetation in the Sudbury area have been carried out in the past, starting in the, 1970s. The results of these studies are documented the publications of Dreisinger (1975, 1976, 1978); Dreisinger and Buchannan (1977, 1979); Heale (1993); Negusanti and McIlveen (1990);

Morra and McIlveen (2001). The timing of these studies is related to aspects of regional smelting operations and changes as follows:

In 1971–1972, prior to the installation and operation of the super stack, 60 permanent sampling stations were established throughout the Sudbury area to determine background levels of SO_2 and various other contaminants in snow, soil and vegetation. Sampling of soil and vegetation was also carried out at 22 long distance transport sites. The results of these investigations are found in Dreisinger (1976) and Dreisinger and Buchanan (1979).

In 1973–1975, following the commencement of operation of the Superstack, the soil and vegetation sampling program was carried out during 3 consecutive growing seasons at 90 stations up to 280 km from Copper Cliff. The results are presented in Dreisinger and Buchanan (1979).

In 1976–1978, soil and vegetation sampling was repeated at 90 stations. Analyses for Ni. Cu, Fe, S, Zn, As and Co were carried out to determine on a yearly basis, existing levels and distribution patterns of these elements in the Sudbury area. Soil pH was also determined throughout the 7 seasons of this report (Dreisinger and Buchanan, 1979). In 1988, soil and vegetation was sampled at 59 stations within an 80 km radius of Copper Cliff. Data are presented in Heale (1993). In 2001 Morra and McIlveen described the metal concentrations of 21 widely distributed sample sites were selected in 1971 to comprise the Sudbury Regular Survey. Sporadic sample collection at these sites commenced in 1971. This report also included the results of the Sudbury Special Survey, also initiated in 1971. In the latter study, 92 sample locations were established along cardinal compass directions at increasing distances from the three smelting centres of Copper Cliff, Coniston and Falconbridge. Sites extended up to 30 km distance from the smelters. In 2000 a soil survey of an expanded sample set containing 11 additional sites was completed.

The data described in all these studies is inconsistent, both in terms of sampling, documentation of actual sample location, and description of analytical methodology. Most of the sample sites, for example, are dotted within metres of major highways leaving large regions completely unrepresented in the resultant databases. There is minimal discussion of the quality program with these reports, and samples were frequently not archived to enable external, or future, checking of analytical accuracy. The data do, however, provide a broad picture of the major impact of anthropogenic metal additions to the surface layers of regional soils, although whether the data are for extractable or total metal concentrations in soils is often unknown. Unfortunately, the data provide no indication of the actual horizon of metal loading, and are essentially useless for providing any insight into metal bioavailability into the food webs of the Sudbury smelter footprint, especially as the data are generally for a strong acid digestion, the results from which do not have any relationship to an available metal pool (Prokop *et al.,* 2003).

THE SUDBURY REGIONAL SOILS PROJECT

The 2001 Sudbury Regional Soils Project was developed following discussions between INCO Ltd., Falconbridge Ltd., MIRARCO's Centre for Environmental Monitoring at Laurentian University (CEM), the Ontario Ministry of the Environment (OMOE), the Sudbury Health Unit and the City of Greater Sudbury following a review of the historical data described above, together with data from the OMOE 2000 Regular and Special Soil Surveys. Significant geographic gaps were recognized within the data sets, generating a need for a comprehensive sampling program to provide the required input for an upcoming detailed Regional Risk Assessment Project. These data gaps prevented the preparation of an accurate geochemical map of the Sudbury smelter footprint to describe the impacts of anthropogenic metals on regional soils, waters, vegetation or sediments.

The CEM designed the regional soil sampling survey, and OMOE designed the urban soil sample program. The CEM and Golder Associates, with the OMOE sampling in intensive detail the public parks, schoolyards, private gardens and yards, completed the regional sampling project. INCO Ltd. and Falconbridge Ltd funded the project.

Regional Sampling Plan

The sampling program was developed using a randomized stratified sampling plan with modifications to remove, wherever possible, the potential effects of infrastructure. Previously existing "historical" sites sampled by INCO personnel on a regular basis since 1972 were included in the appropriate grid cell for this study to enable possible utilization of the historical data for time series analyses. The nested sampling grid, covering an area 200 km by 200 km, was centred on the three smelters, Copper Cliff, Coniston and Falconbridge. The centroid was in the vicinity of the Copper Cliff smelter.

The cells of the stratified sampling plan ranged in size, with the smallest cells being in the zones of historically known high smelter impact. The cells were 2, 4, 8 and 16 km square, respectively. The irregular 2 km grid cells extended approximately 8 km in each direction from the individual smelters. The 4 km grid cells extended 12 km out from the edge of the 2 km grid cells, with the 8 km grid cell area being squared off and designed to encompass the rest of the Greater City of Sudbury. The 16 x 16 km border grid was only one cell deep. The design of this survey will allow systematic expansion in any direction should a detailed examination of the resultant chemical data indicate a significant emissions impact of the smelting operations outside of the immediate region as already sampled. The details of the final sampling grid and sample locations are illustrated in Figure 3.

Within each cell one proposed sampling point was selected using a random lookup table in ArcView. A series of sampling exclusion zones were developed to minimize any resultant data bias from contamination by recent erosion, sedimentation or flooding, as well as from non-smelting anthropogenic activities such as effects of road construction, road salt drift, and railway traffic fugitive dust. These exclusion zones included:

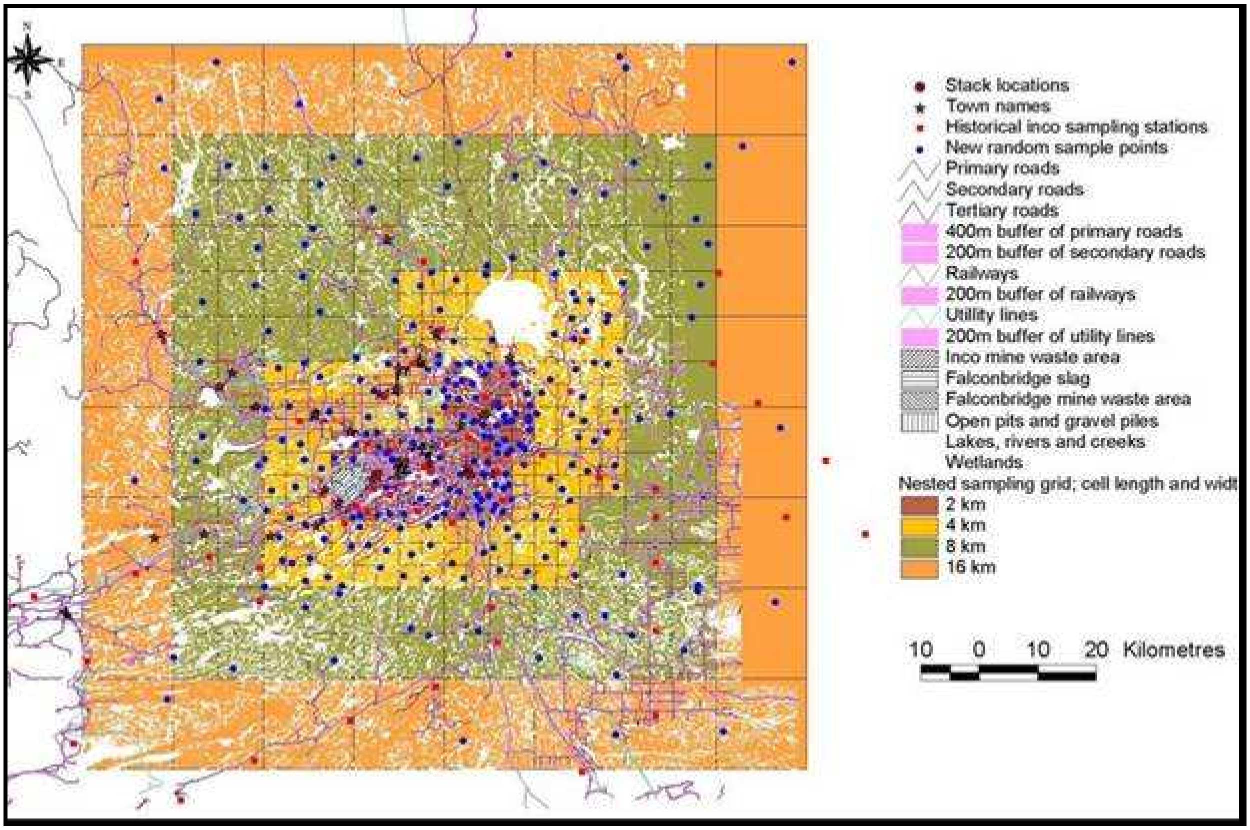

Figure 3: Sampling program for the regional soil study, with sampling exclusion zones delineated.

Industrial lands, such as tailings ponds, slag heaps, open pits

- Wetlands

- Lakes
- Rivers and streams
- 200 m of the centre line on primary roads
- 100 m of the centre line on secondary roads
- 100 m of railway lines
- 100 m of major utility lines.

In the 8 and 16 km outer cells, a replacement point was randomly reassigned if the initial sample location fell within an exclusion zone. The distribution of exclusion zones is illustrated in Figure 2. In the 2 and 4 km grid cell zones, sampling density was deemed sufficient to minimize the requirement of selecting a replacement point if the initial selection was in an exclusion zone, especially given the extreme density of the parallel urban program being completed by OMOE. The final number of sites sampled in the Regional Soils Project was 386.

SOIL SAMPLING PROTOCOL

Soil samples were collected according to standard protocol in the OMOE publication "*Field Investigation Manual, Part 1, General Methodology*" (OMOE, May, 1993). All sites for the survey were in stable landscape positions, with minimal evidence of erosion and with a full stable vegetation cover. Limed sites from the regional regreening program were not selected as core sites for the sampling program. In the wooded areas, sampling was conducted within a 10 m quadrat, with the duff (leaf/grass litter) being lightly scraped away with a boot or hand, even though this procedure would naturally remove recent airfall material from the solum to be sampled. The UTM coordinates of the stake at the quadrat corner were taken with a GPS unit and recorded on standard site description forms. On the form, the sample name and location were recorded, a sketch of the area and the sample location drawn and sample labels for the laboratory were recorded. Each site was also photographed (Figure 4).

Soil cores were collected using Star Quality Soil Sampler that was cleaned between sample locations. The soil was cored by pushing the auger into the soil to at least 20 cm or the maximum attainable depth, rotating to the right to break off the core, enlarging the hole slightly and removing the auger from the soil taking care to maintain the bottom of the sample. At each sampling site, a digital photo of a representative core was taken (Figure 5), together with written description of a representative sample core. According to OMOE procedure, a large “W” pattern was walked and cores collected along this pattern until a full sample of 30 cores was collected. Duplicate samples were collected from an adjacent quadrat.

Figure 4: Photograph of vegetation at a representative soil sampling site.

Figure 5: Typical soil sample in the Sudbury area.

These samples or field ‘duplicates’ are not a split from the first sample, but rather a separate sample, or replicate, collected from the same area. Each core was sectioned according to MOE depth protocol: from 0 to 5 cm depth, from 5 to 10 cm depth and from 10 to 20 cm depth. Cores were sectioned using stainless steel spatulae, with each depth interval being placed in a plastic bag together with an MOE tracking label. Additional field notes recorded for each site provide descriptions of the dominant vegetation, slope, topography, outcrop, weather, location and directions (see Appendix III).

The sampling procedure, originally developed for contaminated industrial sites and contaminated brownfields within municipal environments, is not ideally suited for sampling undisturbed soils in natural soilscapes within relatively pristine ecosystems. The pedogenic horizons of undisturbed soils have undulating boundaries sub-parallel to the land surface. For example, the potential of mixing the pedogenic horizons using the defined 0-5, 5-10 and 10-20 cm depth increment sampling protocol required by OMOE is illustrated in Figure 6. The sampling at uniform depth increments as in this study may lead to variable mixing of the natural soils horizons, thus leading to a loss of any pedogenic overprint which could aid in understanding the natural geochemical and weathering processes responsible for translocation of soluble and colloidal materials. The mixing of soil horizons that is inevitable in following such a protocol will also lead to the field replicate composite samples possible exhibiting a high degree of variability in chemical and textural composition.

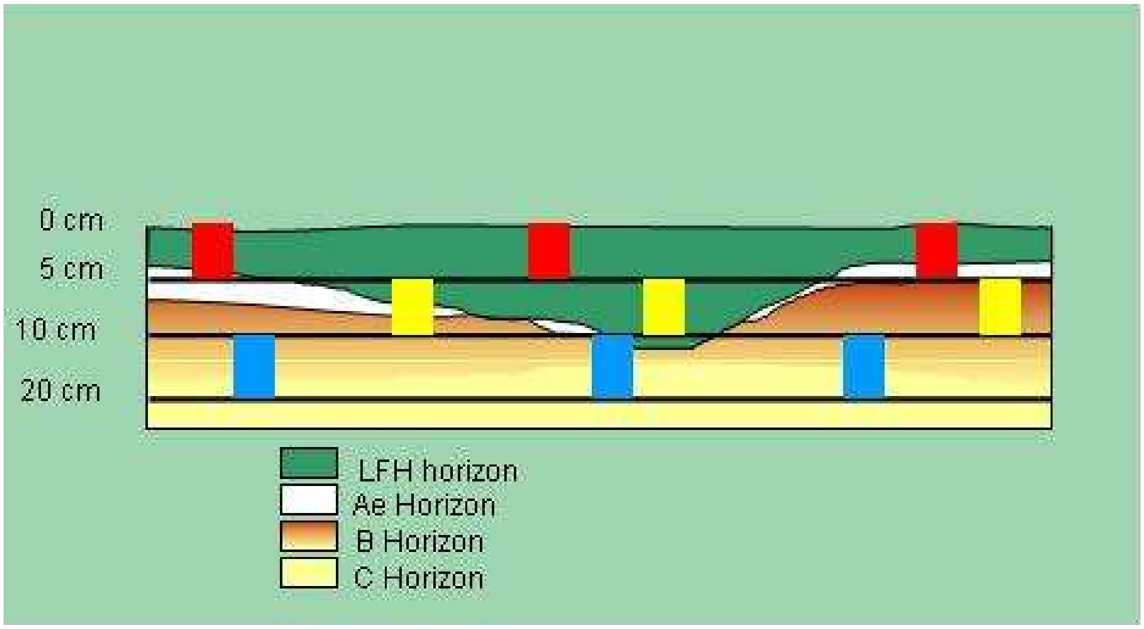

Figure 6: Diagram illustrating the variability of horizons, horizon boundaries in undisturbed soils at forested sites. Coloured boxes indicate the difficulty in obtaining homogeneous samples of any one layer unless sampling is completed on a horizon basis.

Parent Material Sampling

Soil parent material was collected to determine “normal” background levels on the contaminants-of-concern. Soil for parent/background material is collected using a bucket auger. A Dutch auger is first used to remove the top 60-80 cm of soil, with a bucket auger with an enclosed liner being used to collect 25 to 30 cm depth of soil (Figure 7). The soil sampling depth was noted (e.g., between 85 and 112 cm). A field identification number is placed in the sample bag, with the material being characterized and photographed.

Figure 7: Collection of a soil parent material sample with Dutch augur.

Soil Profile Sampling

In order to better define the localization of anthropogenic materials in the solum, a series of pedons formed on undisturbed sites adjacent the regional smelters were sampled by genetic horizon. Soil pits were excavated to a depth of approximately 1.5 metres, taking care to preserve one face of the pedon for sampling by genetic horizon. A 2 kg composite horizon sample was collected from across the exposed pit face. A typical pedon is illustrated in Figure 8, with the genetic horizon boundaries indicated by the sub-horizontal lines.

SOIL SAMPLE PREPARATION

Samples were delivered to the laboratory within 12 hours of collection. The sample bags were opened immediately, and the soil material was disaggregated to initiate air-drying in order to minimize chemical alteration consequent to the development of anaerobic conditions within the sealed bags. The samples were then homogenized and further dried in weighed plastic containers to constant moisture, and weighed to enable bulk density calculation in order to quantify actual metal loadings to soils is subsequent data analysis. The soil sample was then passed through a 2 mm mesh Fritsch Pulveriser, with the coarse material (>2mm fraction) being weighed and stored for future analysis. The pulverized soil was split, using a stainless steel sample splitter, with a 200 g split being ground and sieved to 45 mesh and stored in labeled 250 ml plastic jars ready for shipment to the analytical facility.

Figure 8: Typical Podzolic pedon developed under mixed birch and coniferous vegetation in the Sudbury region.

Samples were shipped to Lakefield Research (Peterborough, Ontario) for analysis. All remaining <2mm soil material was archived.

SAMPLE ANALYSIS

The prepared soil samples were analyzed at the Environmental Analytical Services Division of Lakefield according to Method #9-2-37 (June 2000). The sample was mixed thoroughly to ensure sub-samples would be homogenous. Between 0.5 and 0.505 g of the sample was weighed into a Teflon sleeve and was treated with 5 ml each of concentrated HNO3 and HCl (*Aqua Regia)*. The vessels were placed in a MARS 5 MAW2 Microwave Oven, put through a heat cycle and allowed to cool to less than 60 C. The contents were poured into 50 ml volumetric flasks and diluted to volume with deionized water. The solutions were analyzed by a combination of Inductively-Coupled Plasma-Optical Emission Spectrometry (ICP-AES), Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS) and hydride generation atomic emission spectrometry (HG-AAS).

The soil profile samples were analyzed by energy dispersive X-ray fluorescence spectrometry using the EMMA system in the CEM laboratories (Cheburkin and Shotyk, 1996). Approximately 5 g of the 45-mesh sample was placed in a plastic tube sealed with a Mylar sheet and irradiated for 120 seconds. Data reduction was completed with propriety software, with data accuracy and precision being checked with selected NIST SRM materials.

Quality Program

The samples were analyzed at Lakefield, which is certified by the Standards Council of Canada (accredited ISO/IEC Guide 1725 level) and the Canadian Association of Environmental Analytical Laboratories. The calibration and testing activities at Lakefield follow the requirements of the ISO/IEC 9000 series standards. According to the Lakefield Research Analytical Services Description of Quality Control and Accreditation, quality control measures include duplicate samples, spiked blanks, spiked replicates, reagent/instrument blanks, preparation control samples, certified reference material analysis and instrument control samples. The Lakefield SOP required that, internally, at least 20% of samples analyzed are quality control samples.

In addition to the laboratory QA/QC procedures, the CEM quality control program included submission of periodic splits of soil samples, and an analytical drift-monitoring sample collected from within the Sudbury region. This Internal Reference Material (IRM) was prepared from a 100kg air-dried surface soil sample by sieving through the 2 mm mesh Fritsch Pulveriser, then through a 45 mesh sieve. The IRM sample was then tumbled for 24 hours to ensure homogenization, and bottled in 250 ml plastic jars for storage and submission for analysis. Blind CEM IRM samples were submitted for every thirty samples. Reported laboratory values are considered accurate if their reported value is ±10% of the "target" value of the blind reference material established by the analytical program.

Table 7: Distribution of selected major and trace elements within the solum for a pedon equidistant from the Copper Cliff and Coniston smelters. The EMMA data provide total concentrations of the analyte elements within the soil samples.

Horizon	K	Ca	Ti	Fe	As	Cr	Cu	Ni	Pb	Se	Zn
	(%)				($\mu g\ gm^{-1}$)						
LFH	1.27	0.66	0.26	5.12	59.7	99.3	4551	2563	416	23.8	187
Ae	1.87	0.45	0.35	1.26	17.3	41.6	105	40.4	12.1	1.22	32.0
Bhf1	2.1	0.66	0.36	3.09	6.6	82.3	12.9	62.3	11.5	1.3	116
Bhf2	1.66	0.61	0.3	2.12	4.44	66.5	14.0	31.8	6.22		46.3
C	1.94	0.59	0.28	2.19	6.54	55.4	16.9	22.6	7.71	1.06	36.6
$EF_{C\text{-}LFH}$	0.7	1.2	1.0	2.5	9.9	1.9	289	122	58.2	24.2	5.5

EF = Enrichment factor EF = $((M) / (Ti)_{LFH}) / ((M)_{pm}/(Ti)_{pm}))$

Blind duplicates of the field samples were submitted every twenty samples. Reported laboratory values of the blind duplicate samples were considered precise and accurate if the values were within the 95% confidence intervals when plotted, with a slope of the regression line of the plotted data being between 0.95 and 1.05. The field duplicate accuracy and precision was evaluated in the same manner as the blind sample duplicates. The overall QA/QC requirements of the Sudbury Soils project meant that approximately 40% of all samples digested and analyzed were for data quality assessment and assurance, exclusive of the field duplicates which were required to allow for an assessment of landscape homogeneity.

All IRM samples and duplicates were submitted in a randomized sequence relative to their duplicate, their geographic location, and their order of field collection. The laboratory analyses of duplicated splits of soil samples indicate very good reproducibility (precision). In general, there is also good agreement between the CEM laboratory analysis values and the reported values for the IRM. For the elemental analyses of the soil IRM, the majority analyses fell within the ±10% criterion.

NUMERICAL ANALYSIS TECHNIQUES

The chemical data obtained in this study were subjected to analysis by techniques described as numerical classification by Webster (1979). The purpose of numerical classification is to produce groups that are as homogeneous as possible within the groups, but are as distinct as possible between the groups. To achieve this purpose, a measure of similarity is used to objectively evaluate the similarity or dissimilarity between the individuals; then another measure of similarity, called a sorting strategy, is applied to form groups. This process of grouping individuals on the basis of similarity or dissimilarity is called classification (Sokal, 1966).

Studies that examine relationships between variables are called R$^-$mode analyses, whereas investigations of between individual relationships are called Q-mode analyses. Classification can be utilised to identify generic units for mapping purposes (Volland and Connelly, 1978). The classification phase may be hierarchical or reticulate, and may also be divisive or agglomerative in the way groups of similar individuals are formed. Finally, the classification may be based on monothetic or polythetic procedures. Webster (1979) indicates that hierarchical agglomerative procedures, although they may not perform optimally on poorly structured populations such as soils, are the most popular in pedological studies and are, by nature, polythetic.

The coefficients used in numerical classification can be grouped into three categories (Williams and Dale, 1964), namely information statistics, Euclidean distances and disjoint - space functions. Information statistics are used in conjunction with either presence-absence or continuous data, and are considered non-metric and non-Euclidean. Euclidean distance statistics are metric, and measure the distance in space between two individuals, or between a cluster of individuals and other individuals. Use of Euclidean distance metrics requires an assumption that the variables are uncorrelated, an assumption not necessarily valid with geochemical data unless the sources of variation are a result of varying lithology or provenance. Pyott (1972) notes that Euclidean distance is biased towards attributes that are highly variable across the data set, and the resulting classification will be regulated by the more abundant rather than the diagnostic attributes. This tendency may be alleviated by data standardization. Disjoint-space functions use a probabilistic approach to classification in which a null hypothesis is required, and thus an assurance that the data follows some known probability distribution is required (Williams and Dale, 1964).

In a study of soil trace element data, Moore and Russell (1967) indicate that Euclidean distance coefficients possess the following advantages: 1. They are metric; 2. They are likely to separate groups with aberrant attributes; 3. They provide models that may be grasped mentally with comparative ease. For these reasons the Euclidean distance coefficients are used in this study.

Cluster Analysis

Cluster analysis is a term applied to a host of methods used to combine either individuals or groups in either a hierarchical or a reticulate classification. As hierarchical classification optimizes a route between a population and its individuals (Volland and Connelly, 1978), it is used in this study. Different classifications result from the application of different clustering techniques to the same transformation matrix (Williams, 1971). The most common hierarchical clustering strategies as outlined by Webster (1979) are: single linkage grouping (nearest neighbour); centroid method; weighted centroid method; group average method; complete linkage grouping (farthest neighbour); flexible grouping; and Ward’s method. As is indicated by Webster (1979), it was necessary to perform analyses by several of the above methods to ascertain the degree of clustering exhibited by the data generated in the course of this study.

Factor Analysis

Factor analysis or, more correctly, principal components analysis is a procedure used to interpret relationships within the variance - covariance matrix of a standardized multivariate data set (Davis, 1973). Rummell (1970) describes factor analysis as taking numerous measurements and resolving them into distinct patterns of occurrence, with no particular assumption of underlying variable structure being required. Principal Components Analysis can be separated into two steps:

- Computation of a correlation matrix of variables as a measure of associations;

- Extraction of initial components from the correlation matrix as eigenvalues and eigenvectors, with these components being orthogonal or independent of each other.

The first of these composite variables or components represents the linear combination of variables accounting for more of the variance within the data set than any other combination. The second component is defined as the second linear combination of variables, conditionally orthogonal to the first, accounting for most residual variance in the data following removal of the first component. Subsequent components are defined similarly until all variance in the data is exhausted.

The Principal Components Analysis routine within Systat™ program was used to determine the interrelationships present among geochemical variables of the 0-5, 5-10 and 10-20 cm soil samples, as well as for the soil parent materials. The chemical variables were standardized prior to analysis so that each variable had a mean of zero and unit variance to allow comparison between variables when units of measurement differ in type or relative order of magnitude as was found with the chemical compositional data of this study (Davis, 1973).

DATA PRESENTATION

The written report is primarily focused on the results of the chemical analyses of the soil samples collected by CEM and Golders personnel during the summer and fall of 2001 for the Sudbury Soils Study project. The fundamental purpose is to provide an overview of the regional distribution of analyzed metals in surficial materials, and to provide a structured database that will serve as the foundation for the Sudbury Regional Risk Assessment project. The data is interpreted to provide an assessment of the regional influence of smelting operations within the Sudbury smelter footprint.

Contour maps were produced for all analyzed elements using both the surface (0-5 cm), subsurface (5-10, 10-20 cm) and the soil parent material extraction chemistry data. The regional metal distributional maps were produced using the Inverse Distance Weighted interpolation (IDW) in ARCVIEW GIS (version 8.13). IDW interpolation explicitly implements the assumption that sites close to one another are more alike than those that are farther apart. To predict a value for any unmeasured location, IDW will use the measured values surrounding the prediction location. Those measured values closest to the prediction location will have more influence on the predicted value than those farther away. Thus, IDW assumes that each measured point has a local influence that diminishes with distance, thus weighting the points closer to the prediction location greater than those farther away, hence the name inverse distance weighted.

The regional maps provided with this report are designed to illustrate the predicted distribution zones of effect of both anthropogenic metal inputs and parent material zonation, rather than to provide **exact** concentration contours at any specific soil depth. The concentrations of extracted metal(loids) are known with certainty **only** at the sampled sites, with values between the sites being mathematical interpolations estimated using the IDW algorithms. The maps are designed to provide visual interpretative tools **ONLY**.

The database for the Sudbury Soils project is organized into a series of Appendices, with all data keyed to GPS location and site number. These appendices list the site and sample metadata, as well as the *Aqua Regia* soluble concentrations, reported on 105 C dry weight, of aluminum, arsenic, barium, beryllium, cadmium, calcium, cobalt, copper, chromium, iron, lead, magnesium, manganese, molybdenum, nickel, selenium, strontium, vanadium and zinc. The *Aqua Regia* digestion does not produce a total digest of soil organic materials and minerals. As aluminosilicate minerals and some oxide minerals are not totally digested, quantitative concentration values are NOT obtained for recalcitrant elements such as Al, Cr, Ti and Zr. The incomplete digestion also leads to poor precision in data for the recalcitrant metals. The analytical results in Appendices I, II, and III are arranged on a site basis, with the data for the replicate samples from all sites being in Appendices I and II only.

The Appendix tables are organized by sample depth, with the GPS location for each site being listed in the first column of the file. The Appendix contains the averaged raw data from the field duplicates, as well as the full vertical sequence data for all sampled soils. Appendix III (on CD) is an interactive database of all the site metadata, the soil description, and the MEAN analytical data from the replicate sites referenced to individual sample points on a regional map display. The data associated with the individual sites are accessed in the HTML files by clicking on the point of interest. Navigation throughout the entire sampled area is possible.