

RESULTS

The site descriptions recorded during the soil-sampling program and for the chemical analysis of the sampled soils are documented in Appendix I and II. All chemical data listed in the Appendices are averages of duplicate samples on an oven dry weight basis. The data are presented for soil samples for all depths, 0-5cm, 5-10cm, 10-20cm and parent material. The data in Appendix III, the interactive database, are also mean data from the field replicate samples.

Metal Distribution in Soil Profiles

A series of pedons formed in stable landscape position were sampled by genetic horizon adjacent to the principal areas of industrial activity within the Sudbury region, namely Copper Cliff, Falconbridge and Coniston. The pedons were located within 5 km of either the active or decommissioned smelters, respectively.

The EMMA data listed in Table 7 for a site approximately equidistant the Copper Cliff and Coniston smelter areas illustrate the relatively high concentrations of the metal(loid)s As, Co, Cu, Fe, Mn, Pb, Se and Zn in the LFH horizons of the sampled soils relative to the concentrations measured in the sub-soil or parent material. The data in Table 7 document total concentration of the individual analytes.

The localization of airfall materials in the surface horizons is indicative of particulate fallout, with the LFH layers effectively acting as a filter retaining the airfall and preventing translocation to underlying mineral horizons, an observation also described for the Kola region of Russia (Nikonov *et al.*, 1999; Koptsik *et al.*, 2003). The retention of the anthropogenic metals in this filter zone is further suggestive of a relatively low solubility and bioavailability of metals in the high temperature particulates. In contrast to our observations, however, the study of Nikonov *et al.*, (1999) considered the aerial contaminants to be soluble and retained as metal-organic complexes, not as particulates such as illustrated in Figure 9.

In order to evaluate if the metal(loid) content of the LFH is derived from natural or anthropogenic sources, an approximate enrichment factor (EF) was calculated for the above elements using the following equation: $EF = ((M) / (Ti)_{LFH}) / ((M)_{pm} / (Ti)_{pm})$. Enrichment factors ranging between 0.5 and 2 can be considered in the range of natural variability,

whereas ratios greater than 2 indicate enrichment from anthropogenic inputs (Hernandez *et al.*, 2003; Shotyk *et al.*, 2000).

The enrichment factors calculated in this study are normalized to Ti as a reference element because Ti is relatively immobile in the solum, and there is minimal indication of additions to the soils from the industrial sector. This approach could be utilized, with analyses of appropriate reference elements such as Sc, Ti, Y or Zr for the entire regional sample dataset, to indicate the potential zone of anthropogenic influence within the Sudbury smelter footprint if data for total elemental concentrations were available.

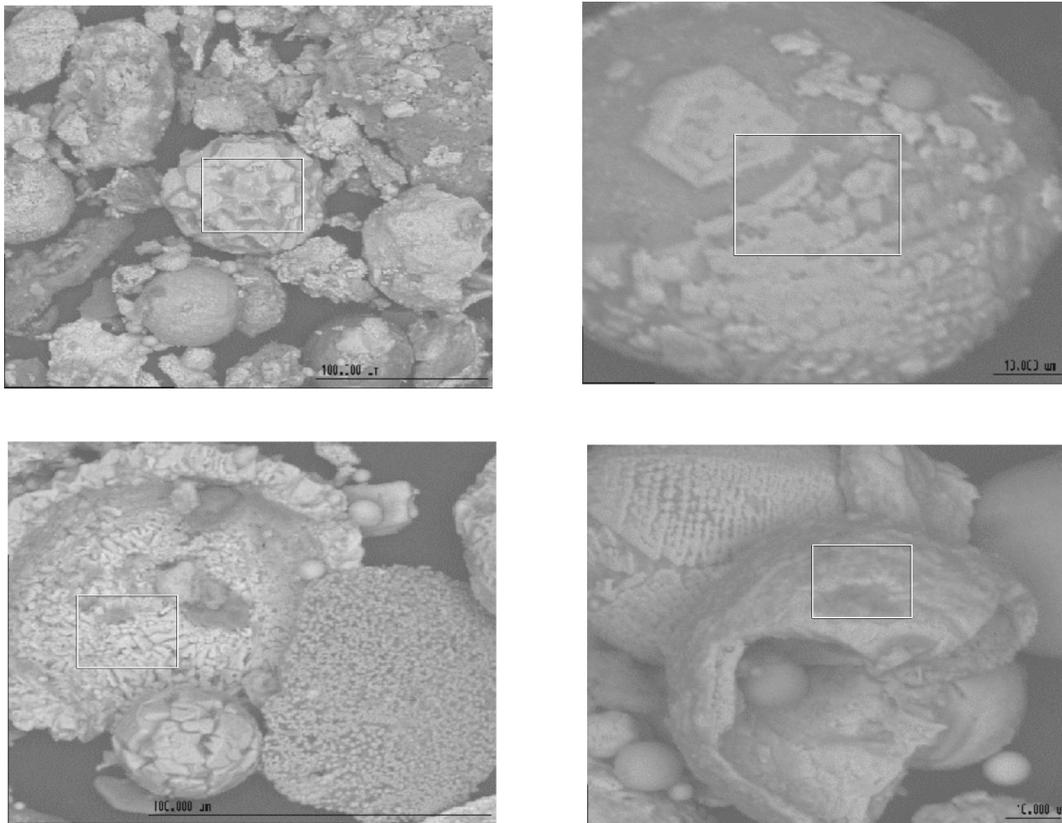


Figure 9: Examples of weathered aerosolic particles retained in the LFH horizons of a forested soil from the Sudbury region.

Iron, an element suggested in some studies (Shotyk *et al.*, 2000), is unsuitable as a reference element in the Sudbury region because of the amounts found in modern smelter emissions. The effective use of Al as a reference element in the current regional data set is also limited

because of the incomplete dissolution of Al-bearing phases in both the soils and parent materials by *Aqua regia*. The calculated EF values do, however, suggest a strong anthropogenic influence in the concentrations of the metal(loid)s As, Cu, Fe, Mn, Pb, Se and Zn in the LFH horizons. The lack of enrichment for Cr in the surface (LFH) horizon suggests that there has been minimal anthropogenic output of this element from the industrial activity within the region. This enrichment of specific elements in the LFH horizons suggests that these organic-rich layers act a filter preventing the translocation of the aerosol particles to the deeper soil horizons. There is also evidence for the possible solubilization and translocation of Mn, Ni and Zn in dissolved phases to the Bf1 horizon lower in the profile, an indication of potential bioavailability of these metals to soil fauna and flora.

However, copper, known to be chelated by soil the potentially mobile soil humic acids, is only translocated to the Ae horizon of the pedon. Arsenic exhibits the same profile distribution pattern as copper. These observations indicate the importance of sampling the genetic horizons of soils to the parent material to enable the determination of potential impacts of anthropogenic emissions in relatively undisturbed sites. The possibility of vertical translocation of specific elements also supports the conjecture of Ngriau *et al.*, (1998) that the release of anthropogenic metals from regional sola may affect metal levels in regional lakes for perhaps hundreds of years. The evidence for translocation also points to the potential slow solubility and bioavailability of the anthropogenic metals retained in the surface organic layers of regional soils.

Metal Distribution in Regional Parent Materials

The sites selected for this study were sampled to a depth of greater than 80cm wherever possible using bucket augurs to obtain soil samples assumed to unaffected by recent industrial activities. These samples, referred to as parent material samples, were obtained from over 70% of the sites visited during the sampling program. The analytical data obtained from these samples represent the first known attempt to establish the pre-industrial levels of metals in regional soils, with the data providing an excellent indication of regional backgrounds levels of *Aqua Regia* extractable metal(loid)s. As the textures of the soil-forming parent materials in the region are variable, with the clay fraction commonly being

enriched in many of the transition metals, the lack of textural data does limit interpretation of the regional background concentration data.

The summary statistics of the individual elements in the soil parent materials of the region are shown in Table 8. The statistical data indicate that all the elements measured in this study show some deviation from statistical normality, an observation that would normally indicate the need to subject the data to a log-normal transformation.

Similar observations with soil chemical compositional data in previous studies (Spiers *et al.*, 1984) has, however, indicated that the log transformation of the data did not significantly affect any of the general interpretations, the multivariate calculations discussed later in this report use standardized data. The variability in textures of the soils, together with the wide range of igneous and metamorphic minerals inherited in the diamictons from the regional bedrock, should balance the usual log-normal distribution of minor and trace elements in minerals in natural systems.

The mean values of the individual elements in the soil parent materials of the region in Table 8 are compared with values for mean crustal abundance, for granite as a major rock type common to region, for the soils of the conterminous United States (Shacklette *et al.*, 1971), and for soils of the Canadian Shield (McKeague *et al.*, 1979) for comparative purposes. Values for the individual elements are discussed below. In the following discussion the values obtained are compared with data for soils parent materials from a variety of sources, including those documented by MOE in the *Guidelines for Use at Contaminated Sites in Ontario* (MOE, 1997).

Direct comparison with the latter data must be tempered by the fact that the ranges documented by the MOE are for soils in the pH range 5.0-9.0. In the current study, soil pH values were determined on a sub-set (35) only of the samples, with a pH range from slightly alkaline (7.78) to acidic (3.69) being reported. The lower pH values are trending northeast from Copper Cliff, with the highest pH values between 6.5 and 7.78 being obtained for samples from an area of calcareous soils formed on silt loam glaciolacustrine materials in the Verner area.

Table 8: Distribution of Aqua Regia extractable levels of 19 major and trace elements in parent materials ▲ of the Sudbury Smelter footprint region.

Element	Arithmetic Mean	Minimum	Maximum	Standard error	Standard Deviation	Skewness	Kurtosis	Granite*	Crustal Abundance (%)	U.S. Soils	Shield Soils**
Al	1.78	0.21	9.10	0.067	1.07	1.84	8.26	7.7	8.2	6.6	6.7
Ca	0.78	0.10	5.80	0.067	1.11	3.11	8.94	1.6	4.1	2.4	1.8
Fe	2.27	0.21	7.80	0.068	1.09	0.96	1.81	2.7	5.6	2.5	2.5
Mg	0.67	0.04	3.80	0.034	0.54	2.47	9.57	0.16	2.3	0.92	0.53
			($\mu\text{g gm}^{-1}$)						($\mu\text{g gm}^{-1}$)		
As	1.11	nd	29	na	6.8	12	166			7.4	na
Ba	98	13	390	na	80.2	1.2	0.61			580	
Be	0.15	nd	1.1	na	0.29	1.57	0.86			0.92	
Cd	na	na	na	na	na	na	na			na	
Cr	56.4	12	130	1.63	26.04	0.53	-0.47	4	100	53	19
Co	8.9	2	38	0.29	4.64	1.73	7.11	1	25	10	19
Cu	26.4	nd	270	1.73	27.65	4.61	32.12	10	55	25	12
Mn	293	23	1800	11.35	180.8	2.66	17.86	400	950	560	417
Mo	0.11	nd	3.1	0.03	0.46	4.14	16.45			2	na
Ni	36.1	8.5	163	1.32	21.0	2.39	9.77	<1	75	20	12
Pb	5.9	1	47	0.24	3.85	5.12	50.97	20	12.5	20	20
Se	0.06	nd	2.0	0.02	0.31	5.51	29.92			na	0.18
Sr	43.8	11	80	1.08	17.27	-0.08	-1.09	285	375	240	409
V	43.3	6.7	220	1.29	20.61	2.63	19.21	20	135	76	na
Zn	29.7	5.4	160	1.16	18.5	1.98	9.07	40	70	54	57

Notes:

Average values (Total) of the elements in the earth's crust, in the major rock type common to the region and in soils of the Canadian Shield are listed for comparison.

▲ Based on values for 254 sample sites

* Values for Taylor (1964)

** Values for conterminous US soils (Shacklette et al. 1971, Gough et al. 1988)

** Values for soils of the Canadian Shield (McKeague et al. 1979)

The maximum value for aluminum in parent material was 9.1%, with a minimum reported value of 0.21%. The mean value for Shield soils listed by McKeague *et al.*, (1979) is 6.7% and for U.S. soils by Shacklette *et al.*, (1971) is 6.6%, considerably higher than the arithmetic mean of 1.78% of this study. The data are, however, similar to the 2.32% documented for coarse textured soils of Shield glacial and glaciofluvial origin in North East Alberta (Spiers *et al.*, 1989). Although there is no MOE Table F value for aluminium in surface materials, the OTR₉₈ value was exceeded in 28 of the 254 sites sampled; these sites are apparently random within the area (see Appendix III), with aluminum levels obtained perhaps reflecting the chemistry and mineralogy of the underlying bedrock.

Arsenic

The maximum value for arsenic in the parent samples was 98 µg/g, with minimum values below detection limits. The arithmetic mean concentration of arsenic in the parent materials of the Sudbury region is 1.1 µg/g. Of the 285 parent material samples analyzed, only 24 have an arsenic concentration above detection limits by the methodology used in this study. The MOE Table F background concentration limit for arsenic (17 µg/g) for all non-agricultural use for surface materials was exceeded in 6 samples, centered on the Copper Cliff smelter, with an outlier in Val Caron. Although comparative data for the levels of arsenic in Shield soil materials is not available, mean levels for uncontaminated soils of Southern Ontario are documented at 5.2 µg/g, whilst that for U.S. soils is 7.4 µg/g, with a range from 1-97 µg/g (Shacklette *et al.*, 1971; Gough *et al.*, 1988). For comparison, Henderson *et al.*, (2002) estimate the background level of arsenic for soils of the Rouyn-Noranda area approximately 250 km north east of Sudbury at 6 µg/g. In a similar study of background concentrations for 1366 soils formed in tills underlain by Precambrian bedrock formations in the Flin Flon region of Manitoba, McMartin *et al.*, (1999) document arsenic mean concentration as 20 µg/g.

Barium

The arithmetic mean barium concentration documented in this study is 98 µg/g, a content much lower than that documented by Shacklette *et al.*, (1971; Gough *et al.*, 1988) for conterminous U.S. soils (500 µg/g), with the range for Sudbury soil forming materials being at

the lower end of the documented range for U.S. soils. The MOE Table D limit is 210 µg/g for surface materials used for non-agricultural uses for surface materials in the pH range of 5.0 to 11.0, with the Table F level being 210 µg/g.

Beryllium

The arithmetical mean regional soil beryllium concentration is 0.15 µg/g, actually below Ontario Table F background concentration limits of 1.2 µg/g. The highest concentration documented in the soil parent materials of the region is 1.1 µg/g. Although comparative data for the levels of beryllium in Shield soil materials is not available, mean levels for nickel-contaminated soils in Port Colborne, Southern Ontario are documented at 1.0 µg/g (MOE, 2002). The documented beryllium concentration level for U.S. soils is 7.4 µg/g, with a range from 1-97 µg/g (Shacklette *et al.*, 1971; Gough *et al.*, 1988).

Cadmium

Cadmium was below method detection levels for the 285 samples of regional soil parent materials. Henderson *et al.*, (2002) estimate the background level of cadmium for soils of the Rouyn-Noranda area at 1 µg/g, a level in contrast to a measured mean background concentration of 0.3 µg/g for soils formed in tills in the Flin Flon region of Manitoba, (McMartin *et al.*, 1999).

Calcium

The arithmetic mean calcium concentration documented in this study is 0.78%, a content median to that documented by McKeague *et al.*, (1979), Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples for Shield (2.4%) and conterminous U.S. soils (1.8%), respectively. The parent material sites with calcium concentrations at the higher end of the range (0.22% – 5.8%) are all at the eastern edge of the study area. These data reflect the fact that only about 15% of the soils sampled in the Sudbury region are developed on calcareous parent materials, specifically the medium textured glaciolacustrine sediments of the Warren-Verner area. The OTR₉₈ value for calcium is 5.5 %, with no Table F limit. In a similar study of background concentrations for 1366 soils formed in tills underlain by Precambrian bedrock formations in

the Flin Flon region of Manitoba, McMartin *et al.*, (1999) document calcium mean concentration as 0.32 %. The OTR₉₈ value for calcium reflects the dominance of data from the calcareous soils of southern Ontario used in the production of the advisory tables.

Chromium

The regional mean for chromium concentration of the soil parent materials is 56.4 µg/g, with a range of 12 - 130 µg/g. These data are in fairly close agreement with the Canadian (45 µg/g) mean soil parent material chromium content, but significantly higher than that documented for Shield soils (19 µg/g). Several sample sites in the Sudbury area have concentrations above the Ontario MOE Table F background chromium concentration limit of 71 µg/g for all non-agricultural uses for surface materials. The data of Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for the less than 75 µm fraction of subsurface soils of the conterminous U.S.A. (51 µg gm⁻¹) indicate that the levels of this study are about normal background for surficial soil forming sediments. Interestingly, the higher chromium values in the regional parent materials are primarily to the south of the major industrial region. The measured mean background concentration of chromium in soils formed in tills in the Flin Flon region of Manitoba was 135 µg/g (McMartin *et al.*, 1999).

Cobalt

With a range in concentration from 2-38 µg/g, the arithmetic mean cobalt levels (8.9 µg/g) in soil parent materials of the Sudbury region are lower than those described by McKeague *et al.*, (1979) for Shield soils. However, the mean value is similar to that defined for U.S. soils (10 µg/g) by Shacklette *et al.*, (1971) and Gough *et al.*, (1988). Several sample sites in the Sudbury area have concentrations above the Ontario MOE Table F background cobalt concentration limit of 21 µg/g for all non-agricultural uses for surface materials.

Copper

The overall mean level of copper (26.4 µg gm⁻¹) is similar to that defined for U.S. soils (25 µg/g) by Shacklette *et al.*, (1971) and Gough *et al.*, (1988), but double that documented by McKeague *et al.*, (1979) for samples for Shield soils. One site in the Kelley Lake delta, with a

level of copper at 270 µg/g, skewed the data for the regional distribution of Cu. This site is probably enriched with copper as a result of erosion from the mining and smelter operations further up the Junction Creek watershed. This is also the only site in the region with soil copper levels above the MOE Table F guidelines (85 µg/g) for surface materials.

Interestingly, the data obtained in the current Sudbury study are similar to the estimation of background concentration of copper at 30 µg/g for soil forming materials of the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). The measured mean background concentration of copper in soils formed in tills in the Flin Flon region of Manitoba was 122 µg/g (McMartin *et al.*, 1999).

Iron

The mean iron concentration documented in this study is 2.27 %, essentially identical to the values documented by McKeague *et al.*, (1979), Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples for Shield and conterminous U.S. soils, respectively. The OTR₉₈ value for iron is 3.5 %, with no Table D limit. There were 40 samples that exceeded the OTR₉₈ values for surface material. The samples are dominantly in the area to the south of the 3 smelters, and reflect the local bedrock influence (see later). In comparison, the measured mean background concentration of iron in soils formed in tills in the Flin Flon region of Manitoba was 5.28% (McMartin *et al.*, 1999).

Lead

The mean regional value for lead (5.9 µg/g) in Sudbury area soil parent materials is much below that documented by Dudas and Pawluk (1980) for Prairie soils, by McKeague *et al.*, (1979) for soils of the Shield region and by Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for soil forming materials of the conterminous U.S. (20 µg/g). The lead levels for all parent material sample sites in this Sudbury area study have concentrations below the Ontario MOE Table D background lead concentration limit of 1000 µg/g for all non-agricultural uses for surface materials. Furthermore, the data obtained in the current Sudbury study are much lower than the estimate of background concentration of lead at 80 µg/g for soil forming materials of the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002).

The measured mean background concentration of lead in soils formed in tills in the Flin Flon region of Manitoba was 8 µg/g (McMartin *et al.*, 1999).

Magnesium

The arithmetic mean magnesium concentration documented in this study is 0.62%, a content median to that documented by McKeague *et al.*, (1979), Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples for Shield (0.53%) and conterminous U.S. soils (0.92%), respectively. The OTR98 value for magnesium is 2.0 %, with no Table F limit. The parent material sites with magnesium concentrations at the higher end of the range (0.04% – 3.8%) are all at the eastern edge of the study area. These soils at these sites are probably developed on calcareous medium textured glaciolacustrine sediments. In comparison, the measured mean background concentration of magnesium in soils formed in tills in the Flin Flon region of Manitoba was 1.89% (McMartin *et al.*, 1999).

Manganese

The arithmetic mean manganese concentration documented in this study is 293 µg/g, with a range of 23 – 1800 µg/g. No samples exceed the OTR₉₈ values of 2200 µg/g for manganese for surface materials. The manganese levels described in this study are lower than those documented elsewhere (McKeague *et al.*, 1979; Shacklette *et al.*, 1971; Spiers *et al.*, 1989) for background soil levels in North America.

Molybdenum

With a mean of 0.11 µg/g, levels of molybdenum are lower than those documented by Shacklette *et al.*, (1971) for U.S. soils (0.98 µg/g) and Gough *et al.*, (1988) for Alaskan soils (1.3 µg/g), with no comparable data being readily available for Canadian Shield soil parent materials, with the exception of the data of Pawluk and Bayrock (1969) who describe a background level of 1-2 µg/g molybdenum for the clay-rich soils Northeastern Alberta. No sampling sites exceed the MOE Table F guideline of 2.5 µg/g molybdenum for all non-agricultural uses for surface materials. The data obtained in the current Sudbury study are similar to the estimation of background concentration of molybdenum at 1 µg/g for soil

forming materials of the Rouyn-Noranda area approximately 15 km north east of Sudbury (Henderson *et al.*, 2002).

Nickel

The arithmetic nickel levels (36 µg/g) for the Sudbury region in this region are higher than those levels documented in the review by McKeague *et al.*, (1971) for agricultural soils of the Shield region (12 µg/g) and in the USGS documented levels for soils (20 µg/g) of the conterminous U.S. soils (Shacklette *et al.*, 1971; Gough *et al.*, 1988). The range in parent material nickel concentrations is from 9 to 163 µg/g, with the higher concentrations being in the soil parent materials in the vicinity of the Kelly Lake delta that is the receiver of the sediment load from the major mineral extraction operations of the region. The high values are, however, below the MOE Table D guideline of 710 µg/g for surface materials where soil pH is 5.0 to 11.0. The measured mean background concentration of nickel in soils formed in tills in the Flin Flon region of Manitoba was 67 µg/g (McMartin *et al.*, 1999), approximately twice as high as in the soils of the Sudbury region. The data obtained in the current Sudbury study are much lower than the estimation of background concentration of nickel at 1 µg/g for the humus layer of soils of the Rouyn-Noranda area approximately 15 km north east of Sudbury (Henderson *et al.*, 2002).

Selenium

The arithmetic selenium levels (0.06 µg/g) for the Sudbury region in this region are lower than documented in the review by McKeague *et al.*, (1971) for agricultural soils of the Shield region (0.18 µg/g). The reports of Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for soils of the conterminous U.S. soils do not document levels for selenium. The values documented in this study are considerably below the potentially toxic levels of the MOE Table D guideline of 2500 µg/g for surface materials where soil pH is 5.0 to 11.0.

Strontium

The arithmetic strontium levels (44 µg/g) for the Sudbury region in this region are considerably lower than documented both in the review by McKeague *et al.*, (1971) for

agricultural soils of the Shield region (409 µg/g) and in the USGS documented levels estimated from 563 soil profiles (240 µg/g) of the conterminous U.S. soils (Shacklette *et al.*, 1971; Gough *et al.*, 1988). The values documented in the latter studies are similar to those documented for both granite and the estimated mean crustal abundance (Taylor, 1964). The range in parent material strontium concentrations is from 11 to 80 µg/g. The lower concentrations in this study compared to those listed above is a reflection of the non-calcareous nature of the soil forming materials of the Sudbury region. Similar levels are, however, documented for soil parent materials formed on glaciofluvial materials of North East Alberta (Spiers *et al.*, 1989). There are no soil remediation criteria listed in the MOE Table D guideline for surface materials where soil pH is 5.0 to 11.0. However, the OTR₉₈ value for strontium is 64 µg/g.

Vanadium

The arithmetic mean vanadium level for the Sudbury region is 43 µg/g, with a range of 6 to 220 µg/g. The mean value in this region is lower than documented for soils in the USGS study estimated from 563 soil profiles (76 µg/g) of the conterminous U.S. (Shacklette *et al.*, 1971; Gough *et al.*, 1988), and for soils of North East Alberta (Spiers *et al.*, 1989). The low level of vanadium found in the current study may reflect the relatively high proportion of granite incorporated in the regional glaciogenic sediments that form the soil parent materials. There values documented for soil parent materials in this study are below the level of 910 µg/g listed in the MOE Table D guideline for surface materials where soil pH is 5.0 to 11.0 where soil remediation is an issue.

Zinc

The arithmetic mean zinc concentration for soil parent materials in the Sudbury region is 30 µg/g, with a range from 5.4 to 160 µg/g. The mean value is lower than that documented for both Shield soils (57 µg/g) by McKeague *et al.*, (1979) and the conterminous U.S. soils (54 µg/g) and Alaskan soils (79 µg/g) in the USGS studies of Shacklette *et al.*, (1971) and Gough *et al.*, (1988), respectively. Pawluk and Bayrock (1969) document levels of 40 - 50 µg g⁻¹ for the North East of Alberta for coarse textured soils formed in glaciogenic materials

primarily of Shield source. Elevated concentrations are to the west, south and east of the three smelters. The background zinc levels obtained in this study are lower than estimates of background concentration of zinc at 80 µg/g for soil forming materials of the Rouyn-Noranda area approximately 150 km north east of Sudbury (Henderson *et al.*, 2002).

Regional Geochemical Maps

Overlain on regional bedrock maps (Figure 1), the regional elemental concentration maps display geochemical data as proportional dots illustrating concentrations of individual elements in the soil parent materials of the Sudbury region (Figure 10 to 27). The geochemical maps indicate that metal concentrations in the parent materials of the Sudbury region vary with underlying bedrock composition. The apparent associations between concentrations of metals extracted by *Aqua Regia* from soil parent materials and the regional bedrock geology will be briefly developed in the following section.

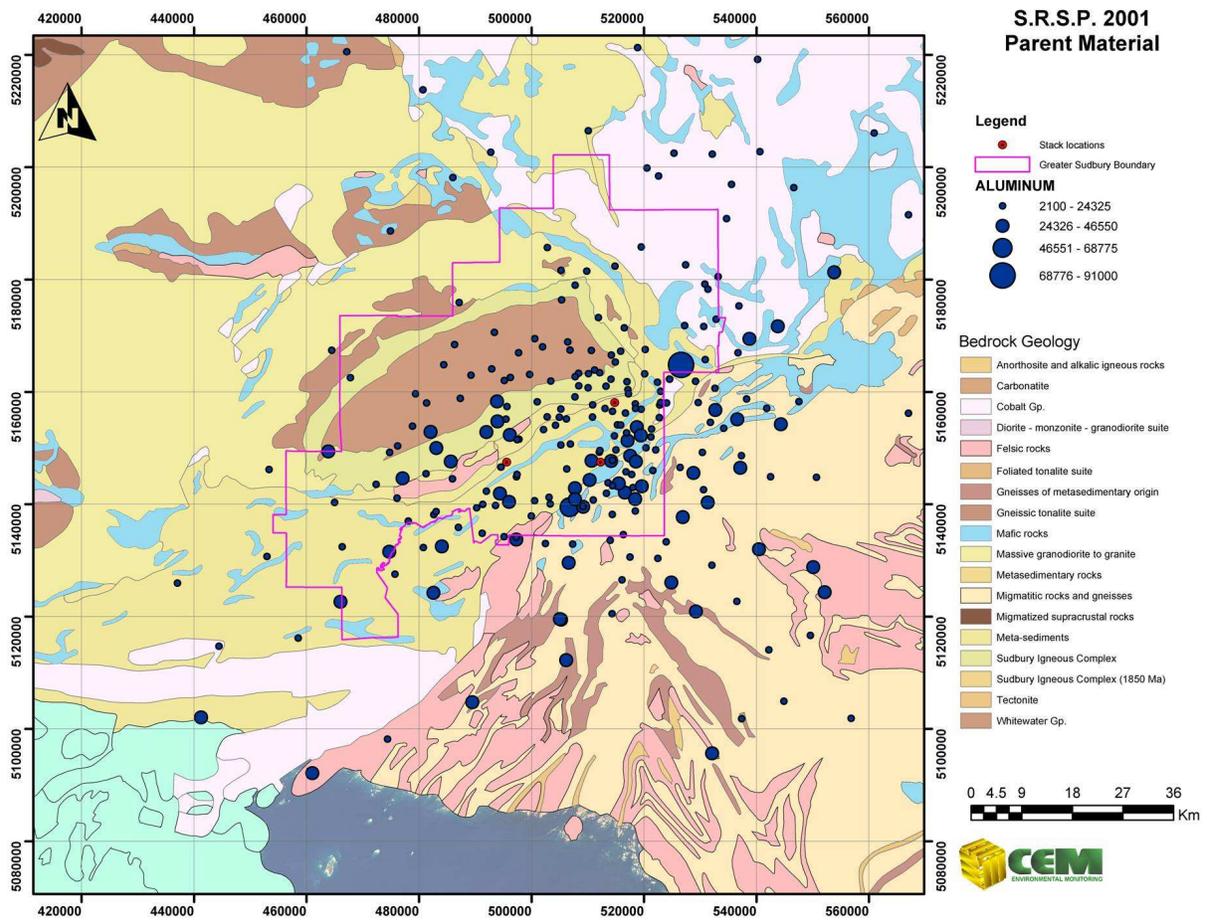


Figure 10: Distribution of aluminium in the soil parent materials of the Sudbury Region.

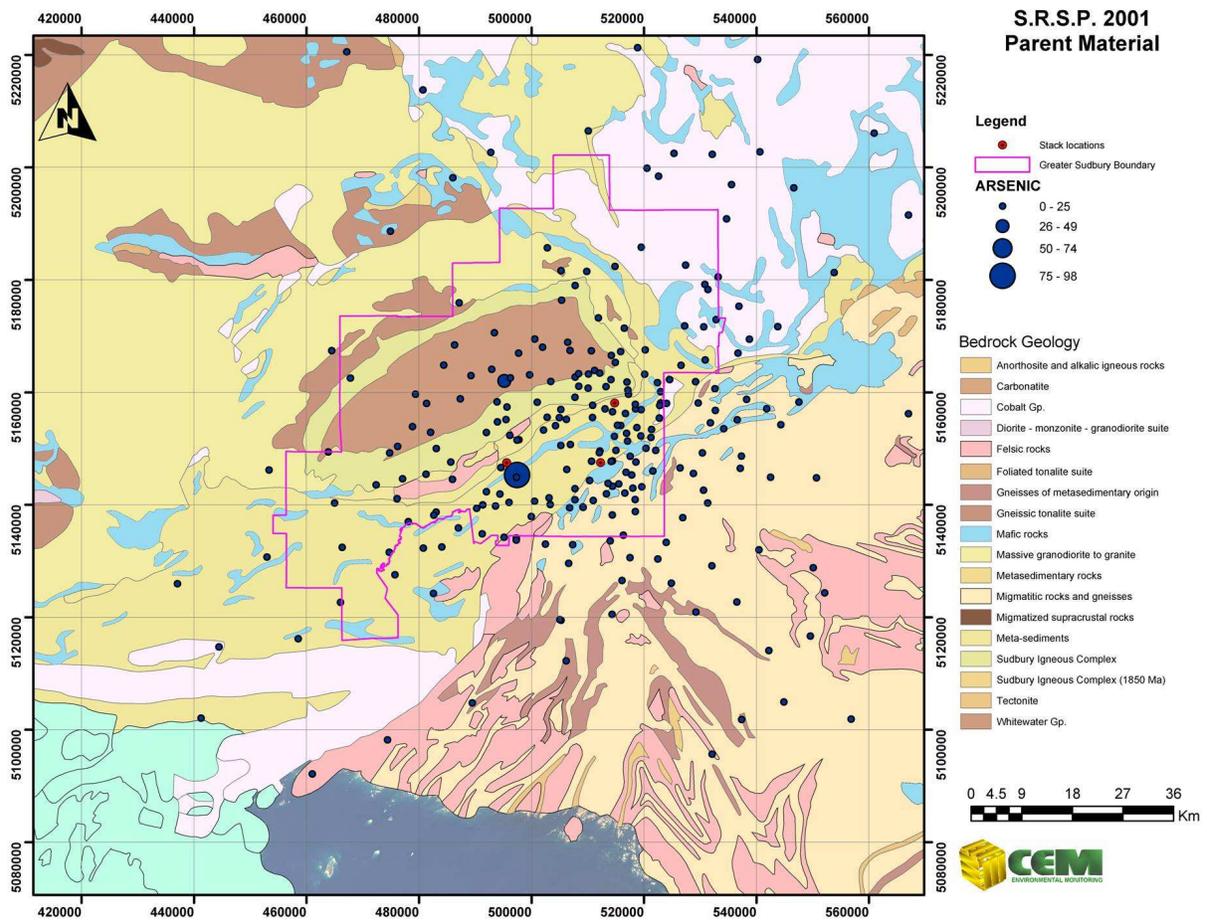


Figure 11: Distribution of arsenic in the soil parent materials of the Sudbury Region.

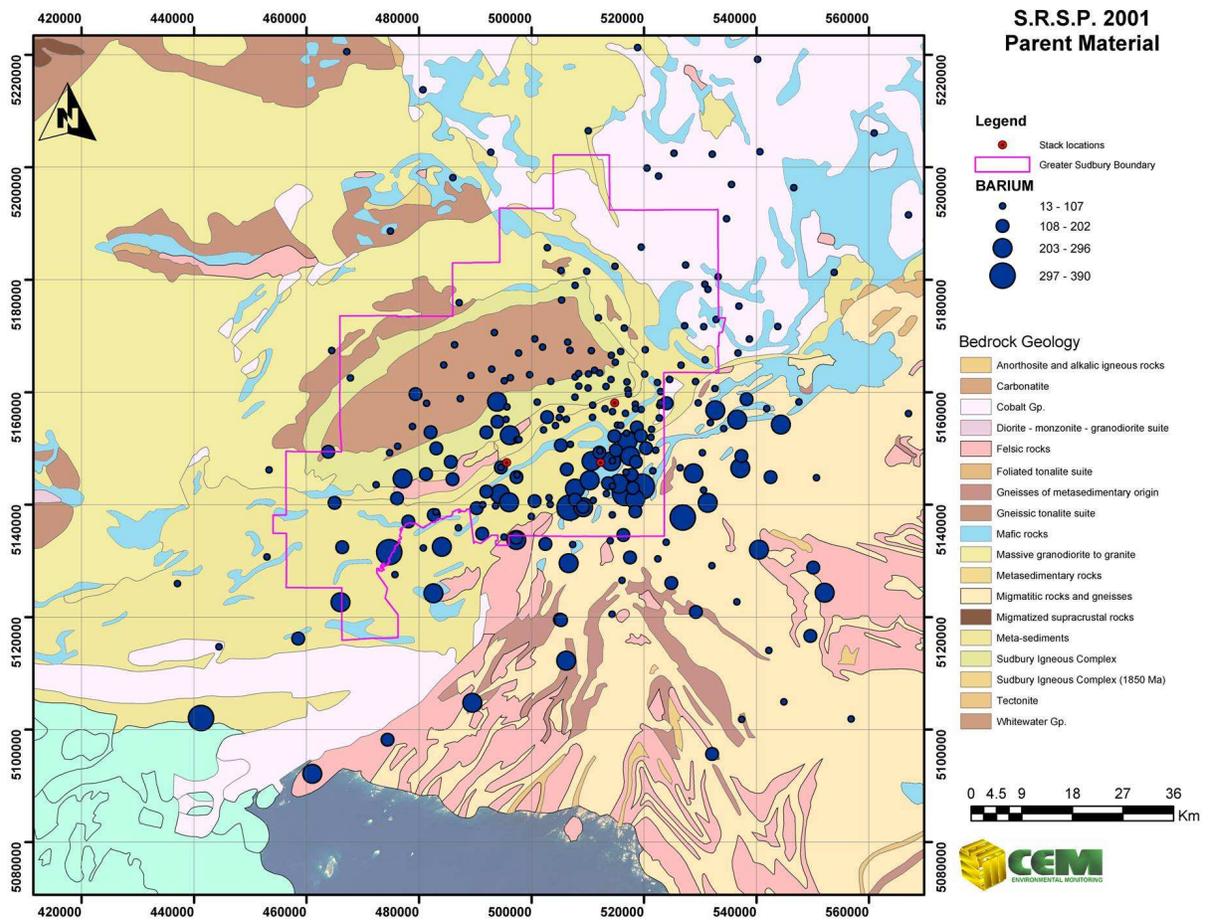


Figure 12: Distribution of barium in the soil parent materials of the Sudbury Region.

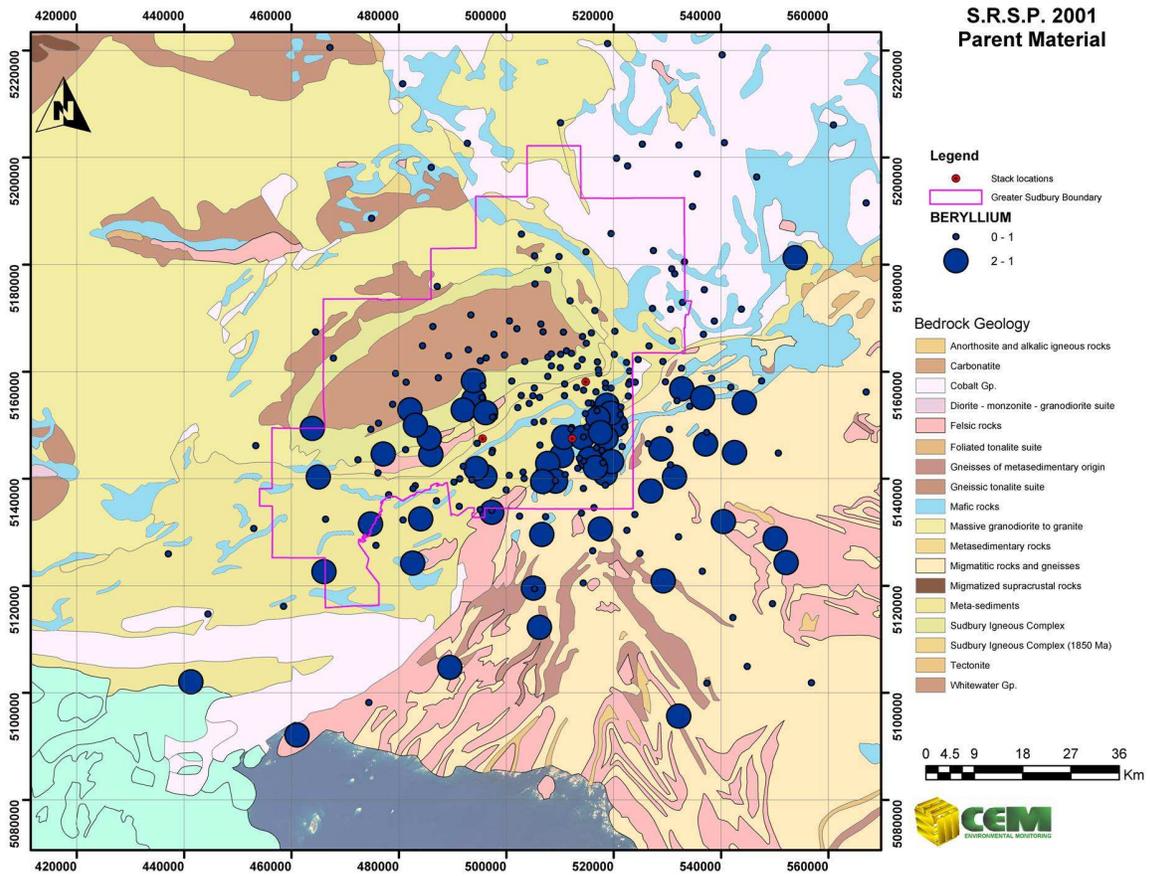


Figure 13: Distribution of beryllium in the soil parent materials of the Sudbury Region.

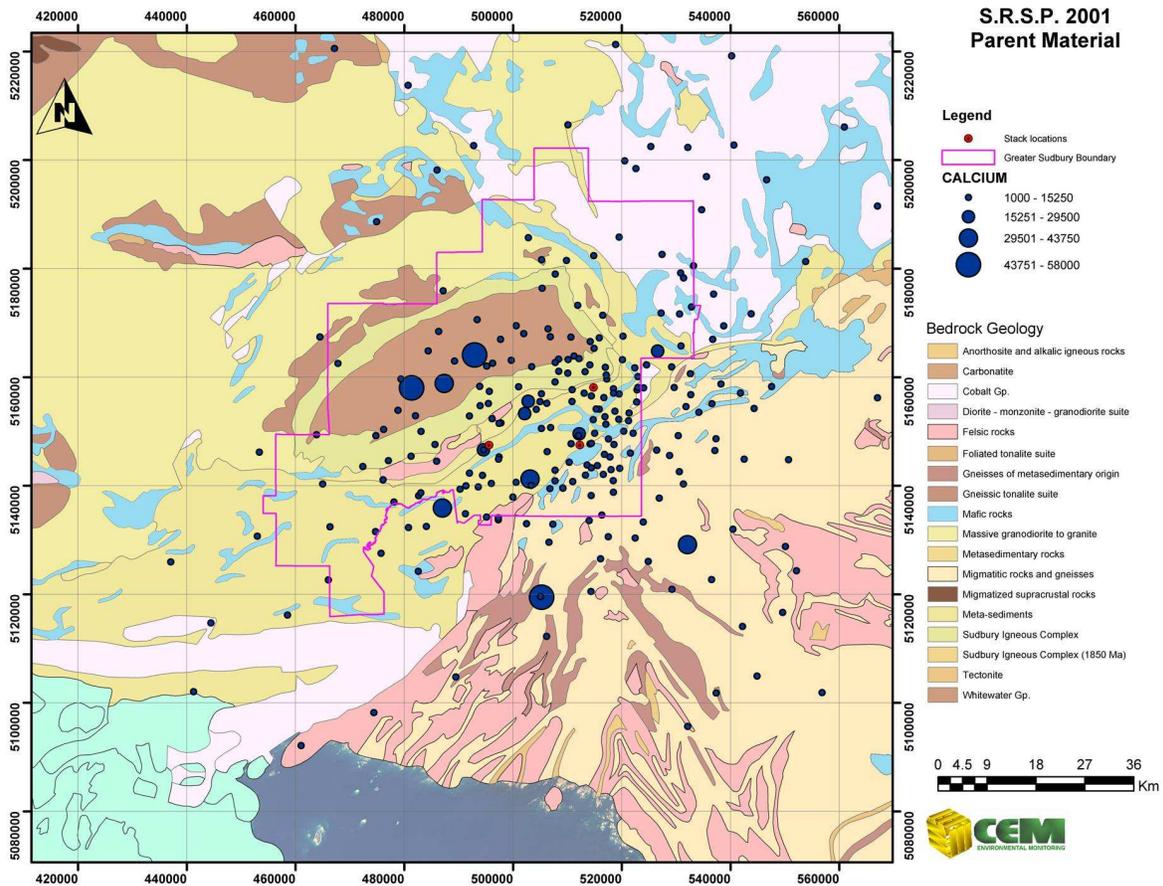


Figure 14: Distribution of calcium in the soil parent materials of the Sudbury Region.

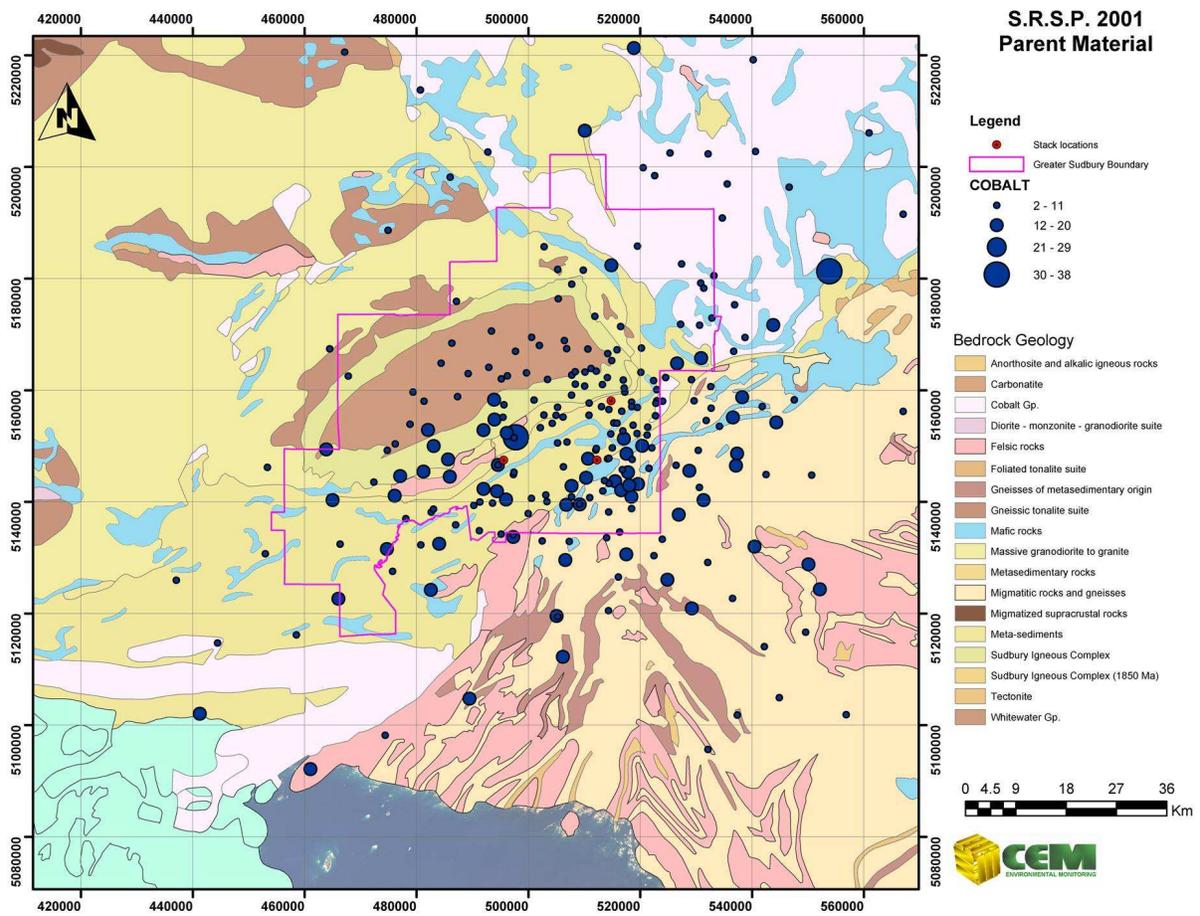


Figure 15: Distribution of cobalt in the soil parent materials of the Sudbury Region.

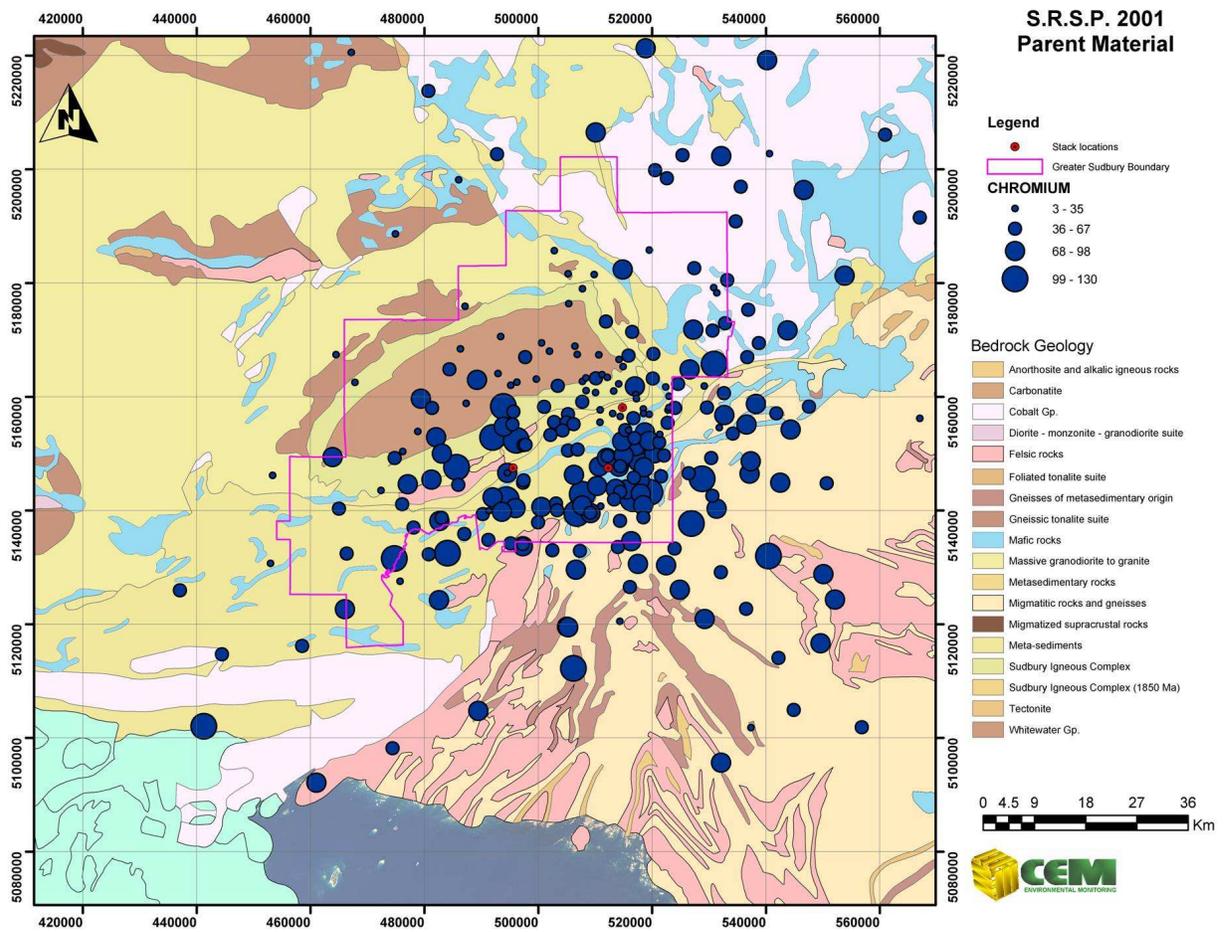


Figure 16: Distribution of chromium in the soil parent materials of the Sudbury Region.

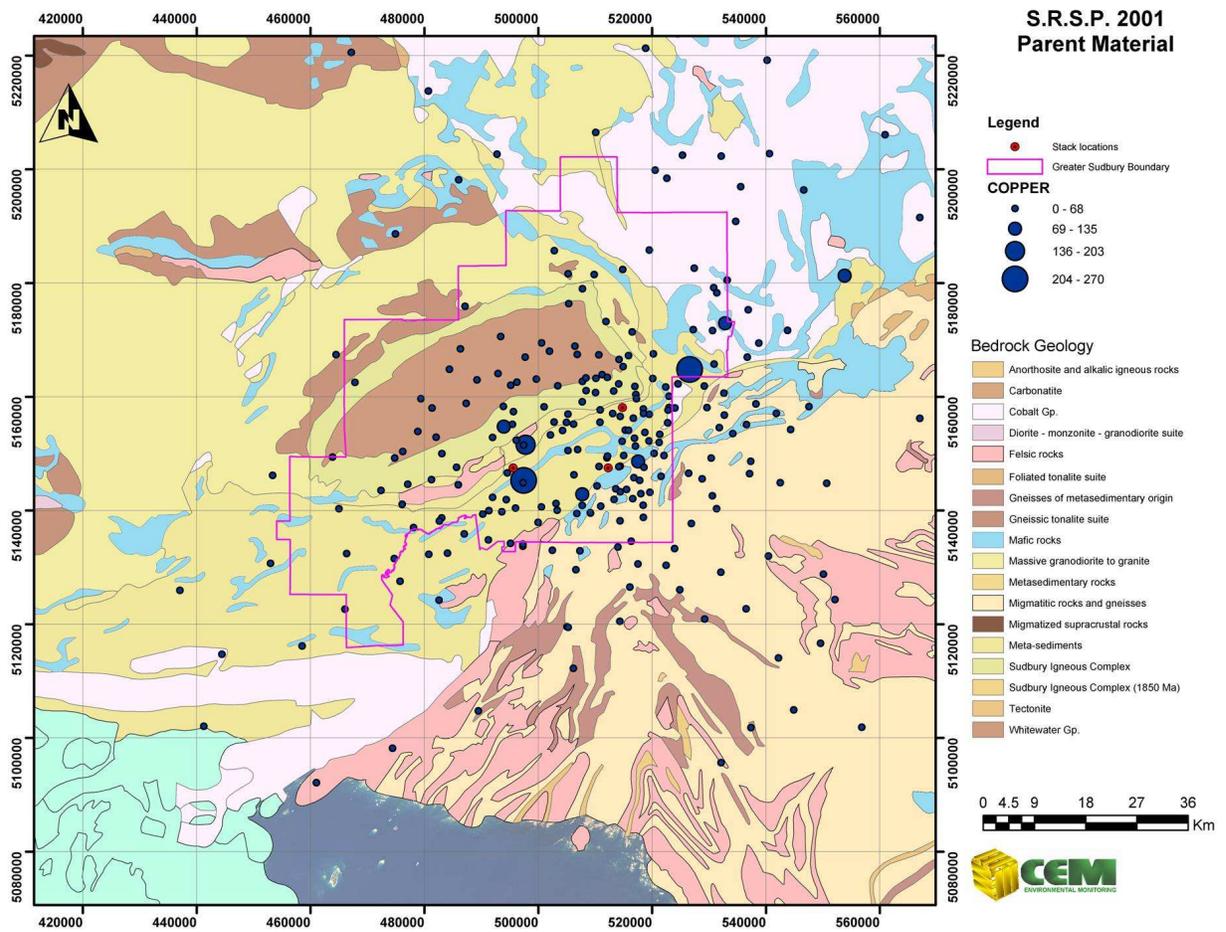


Figure 17: Distribution of copper in the soil parent materials of the Sudbury Region.

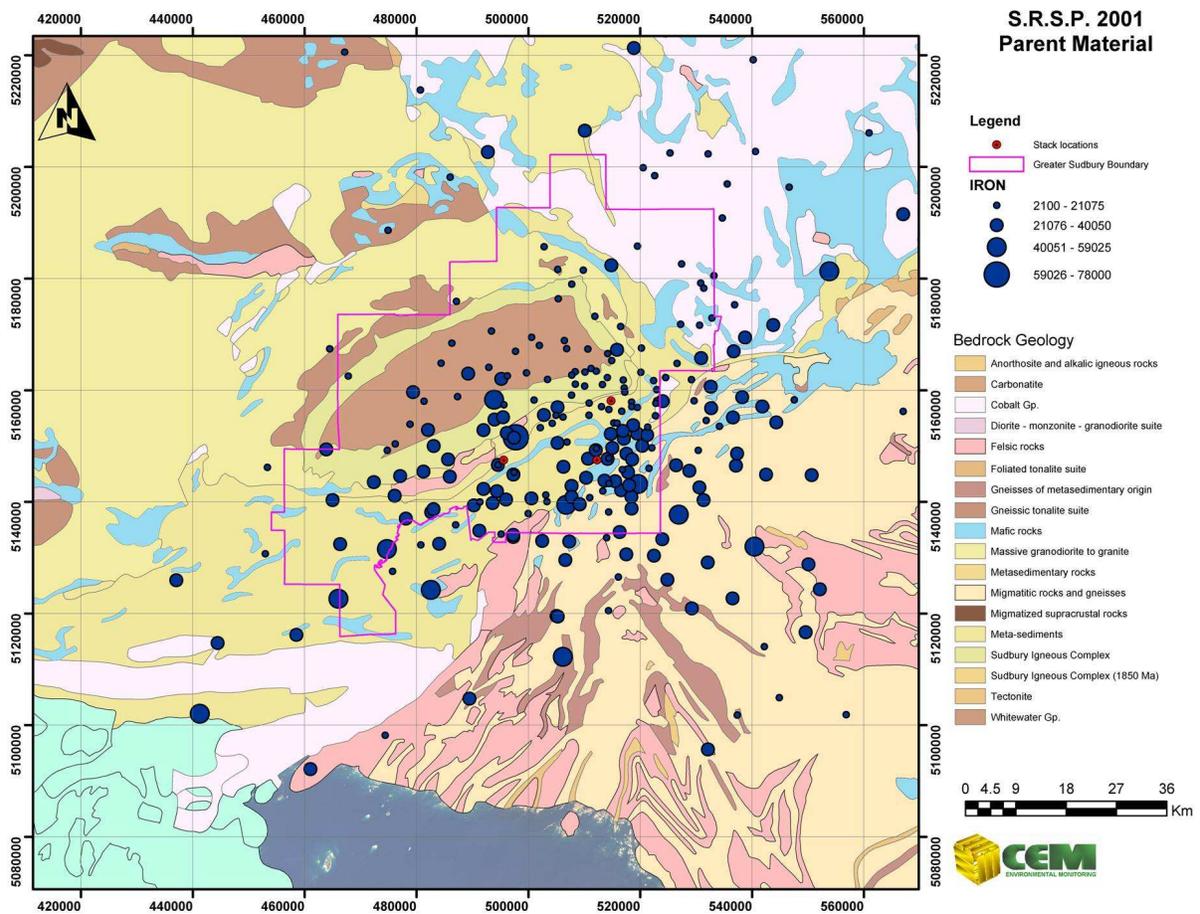


Figure 18: Distribution of iron in the soil parent materials of the Sudbury Region.

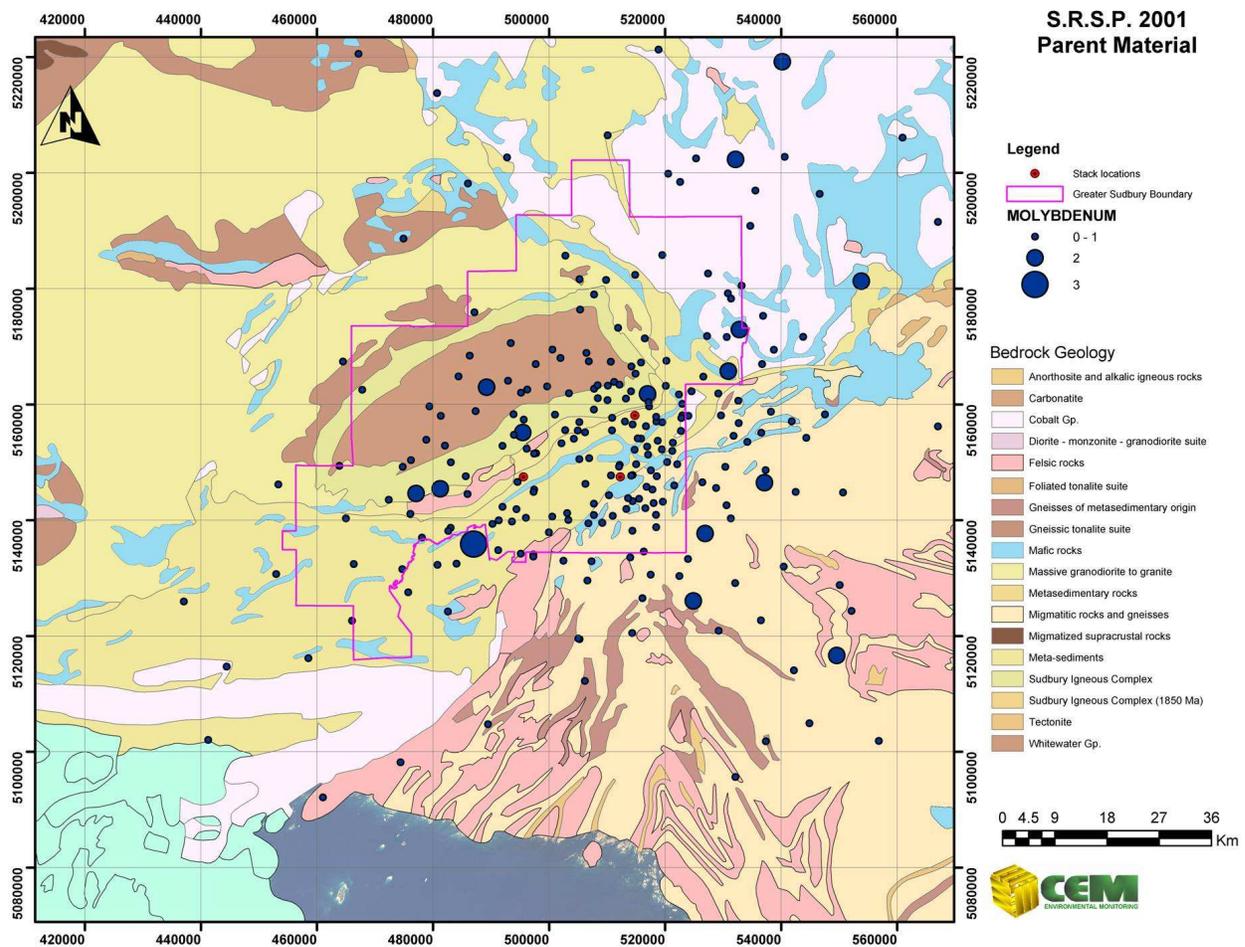


Figure 19: Distribution of molybdenum in the soil parent materials of the Sudbury Region.

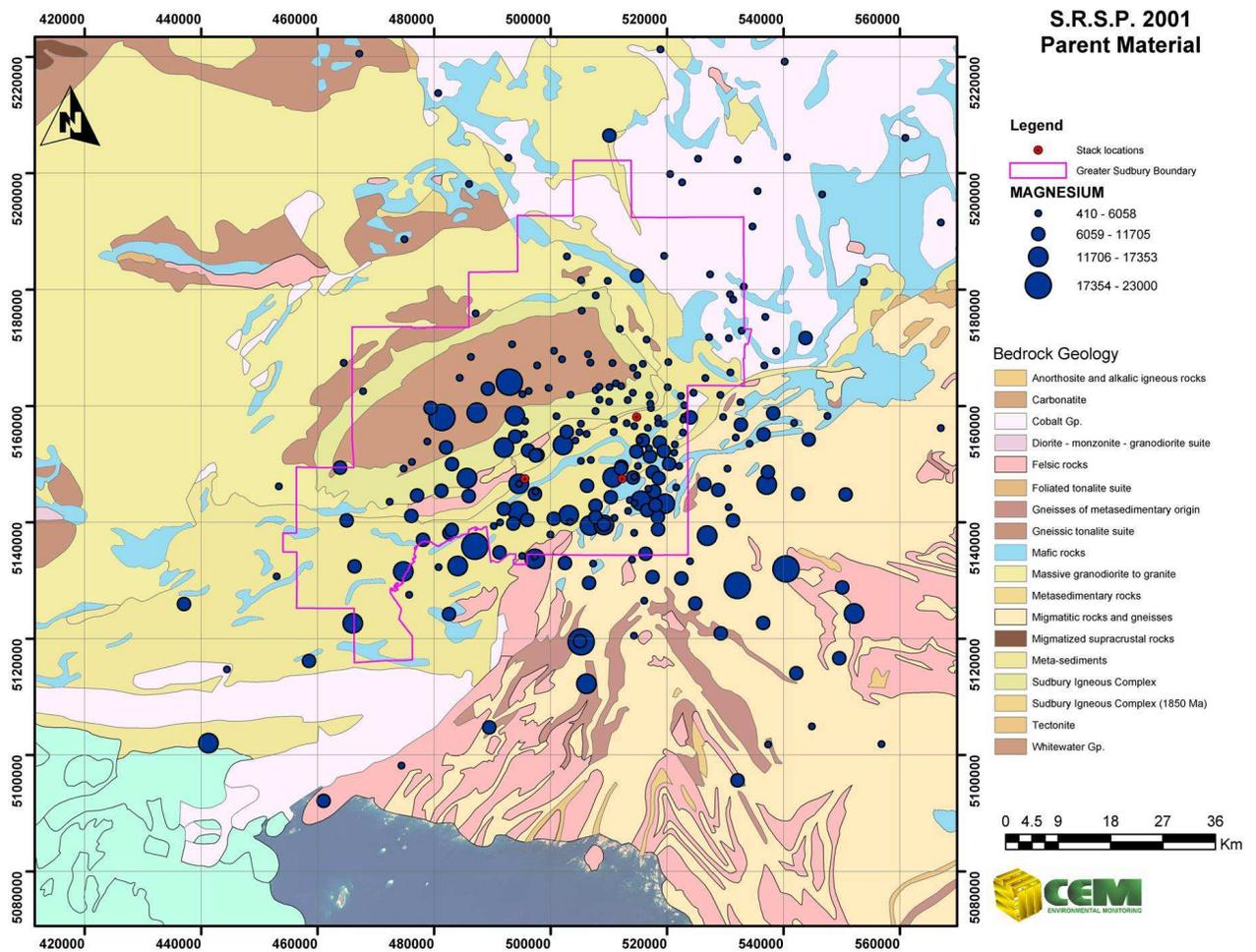


Figure 20: Distribution of magnesium in the soil parent materials of the Sudbury Region.

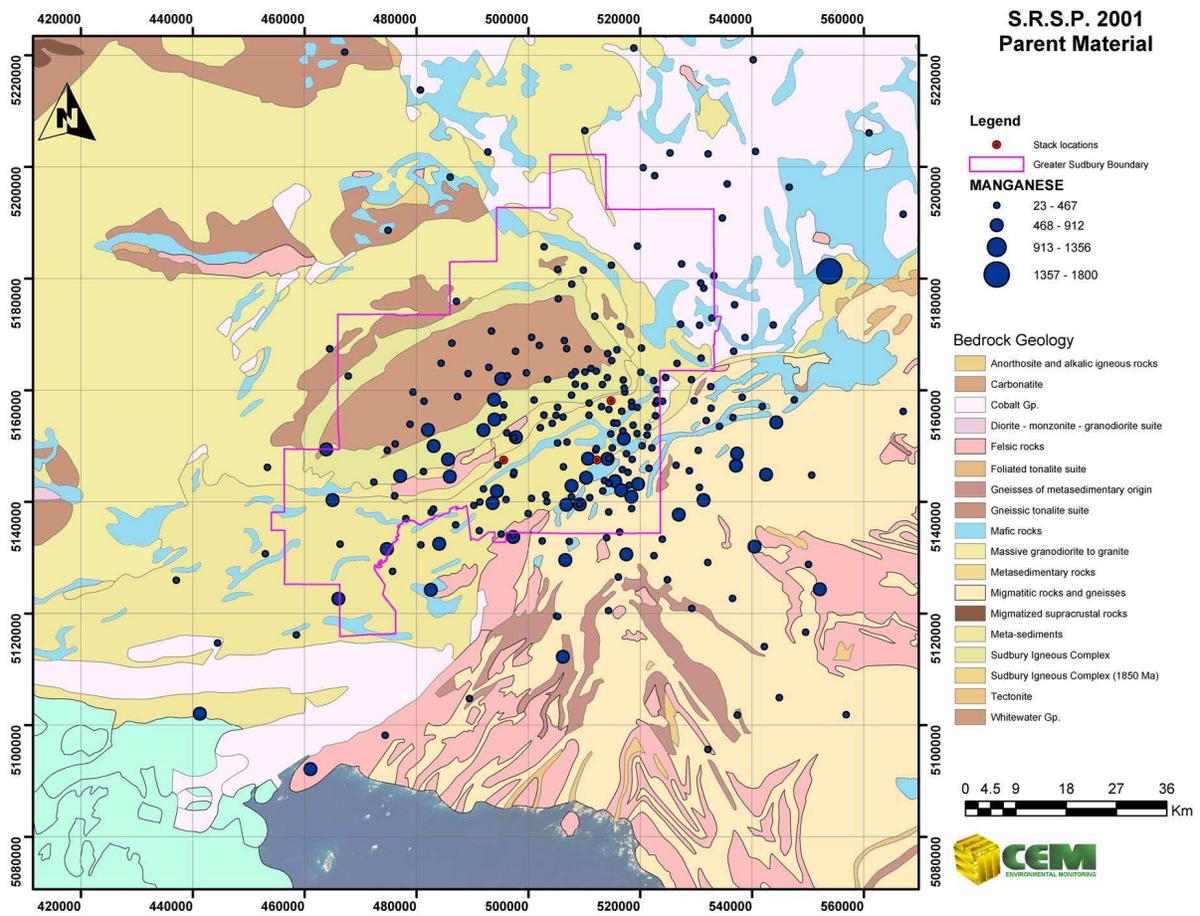


Figure 21: Distribution of manganese in the soil parent materials of the Sudbury Region.

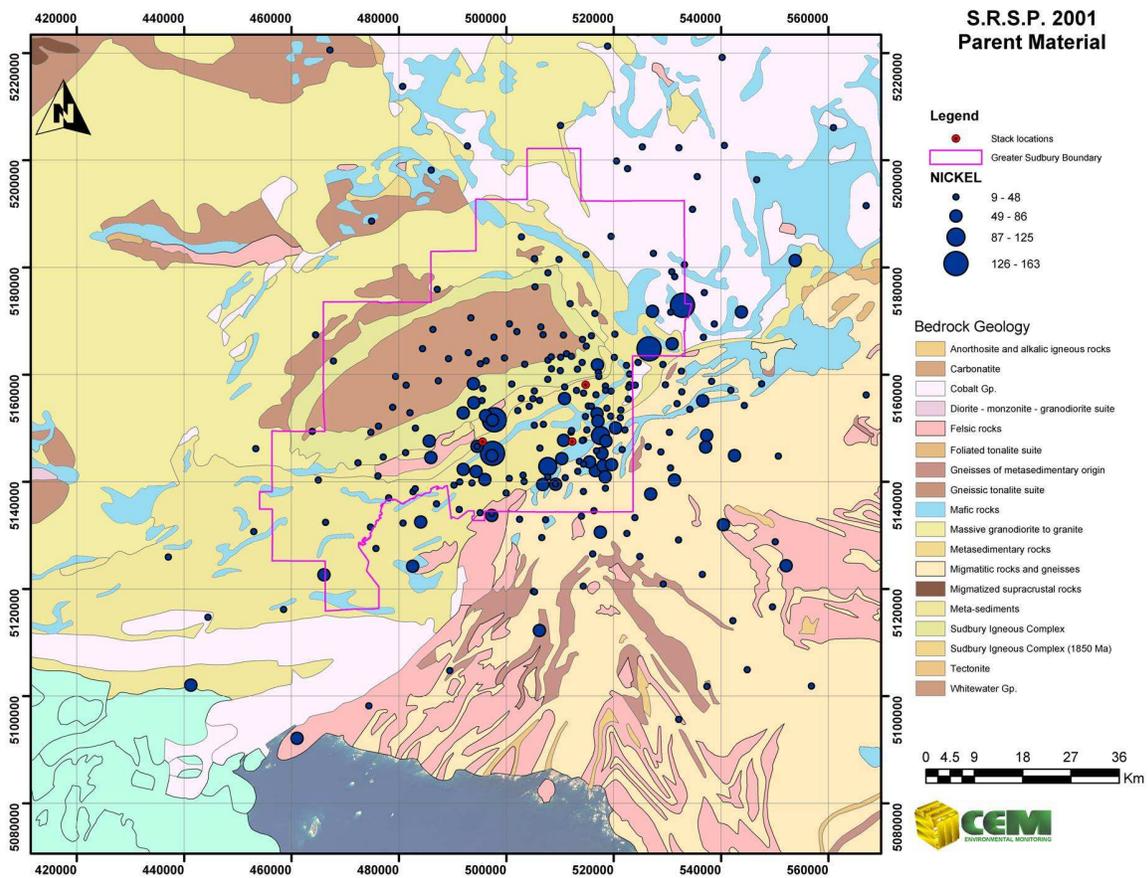


Figure 22: Distribution of nickel in the soil parent materials of the Sudbury Region.

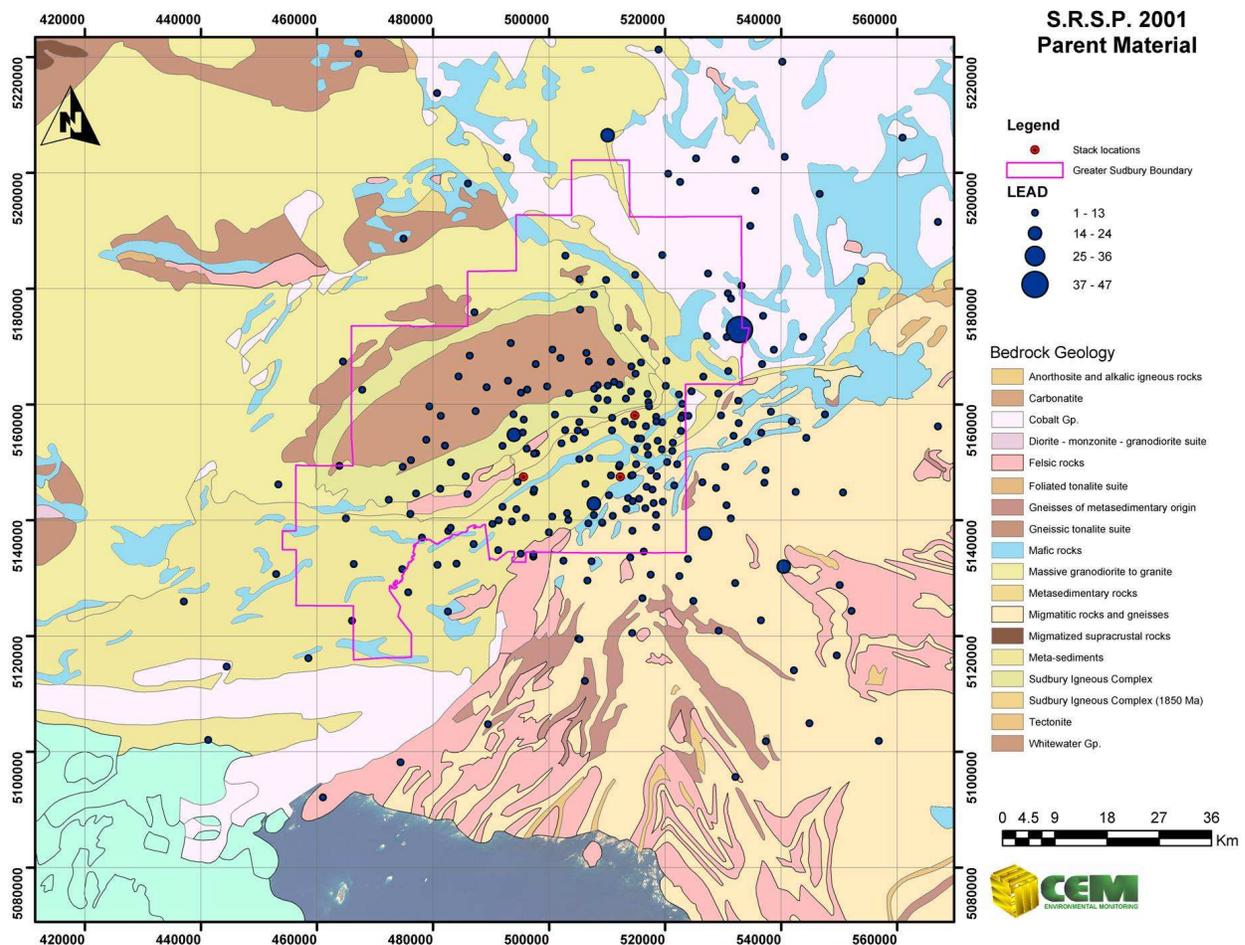


Figure 23: Distribution of lead in the soil parent materials of the Sudbury Region.

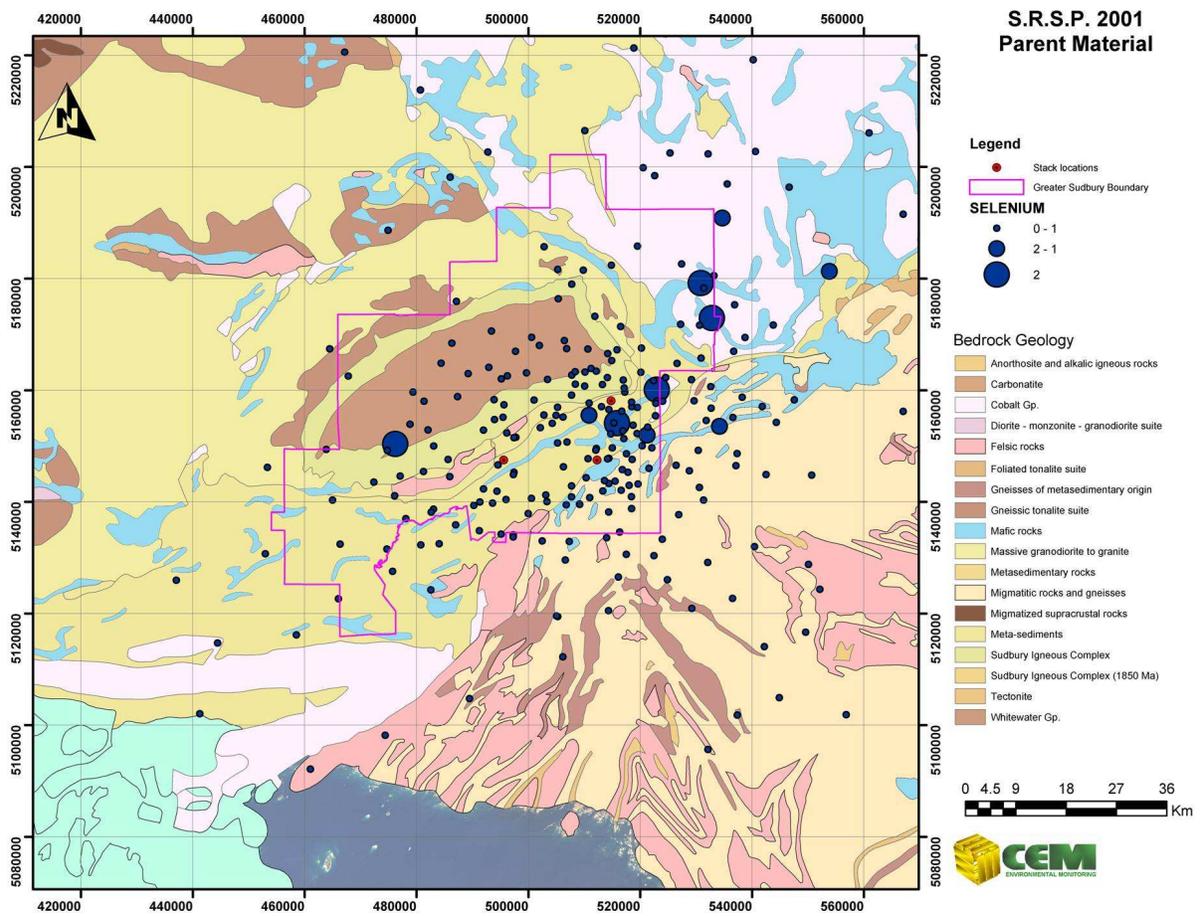


Figure 24: Distribution of selenium in the soil parent materials of the Sudbury Region.

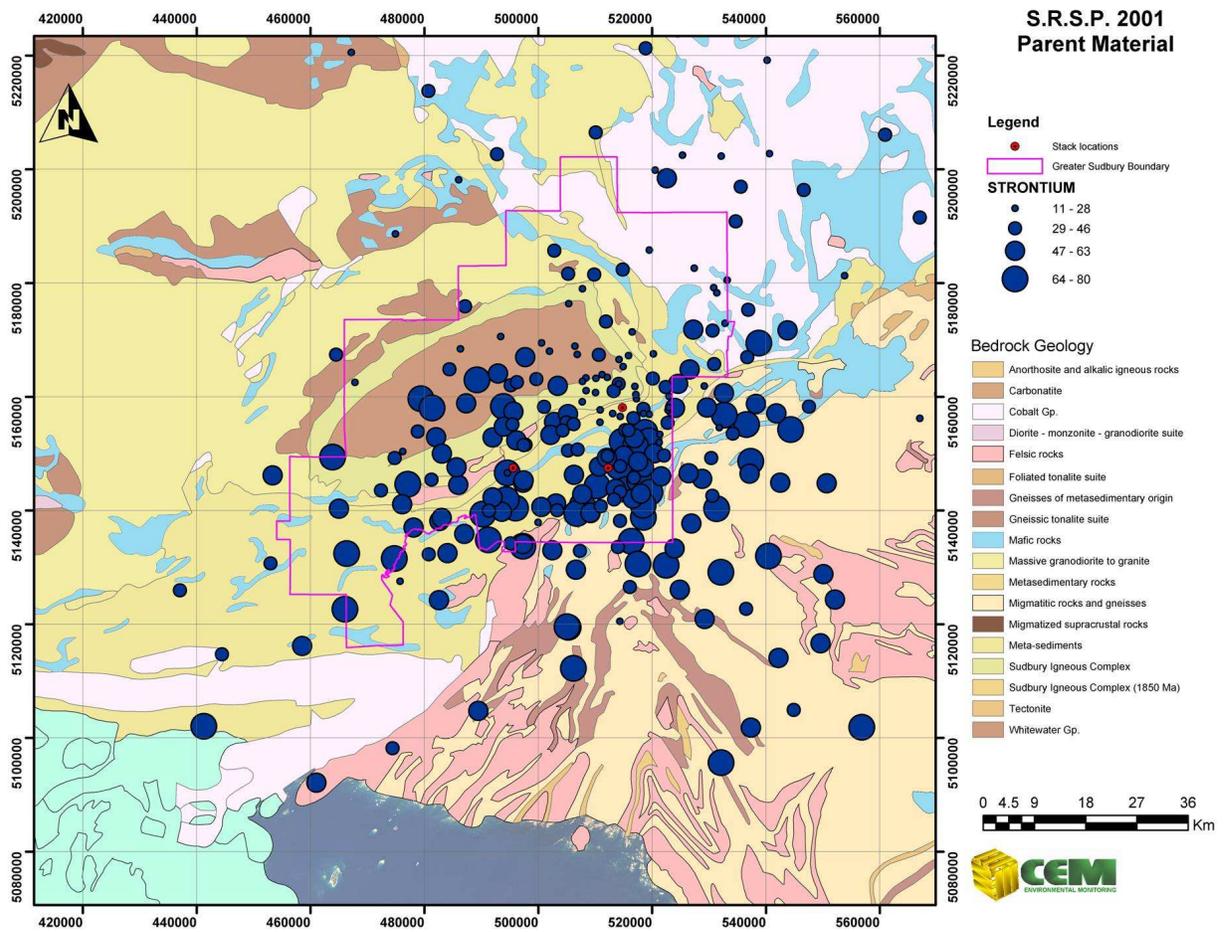


Figure 25: Distribution of strontium in the soil parent materials of the Sudbury Region.

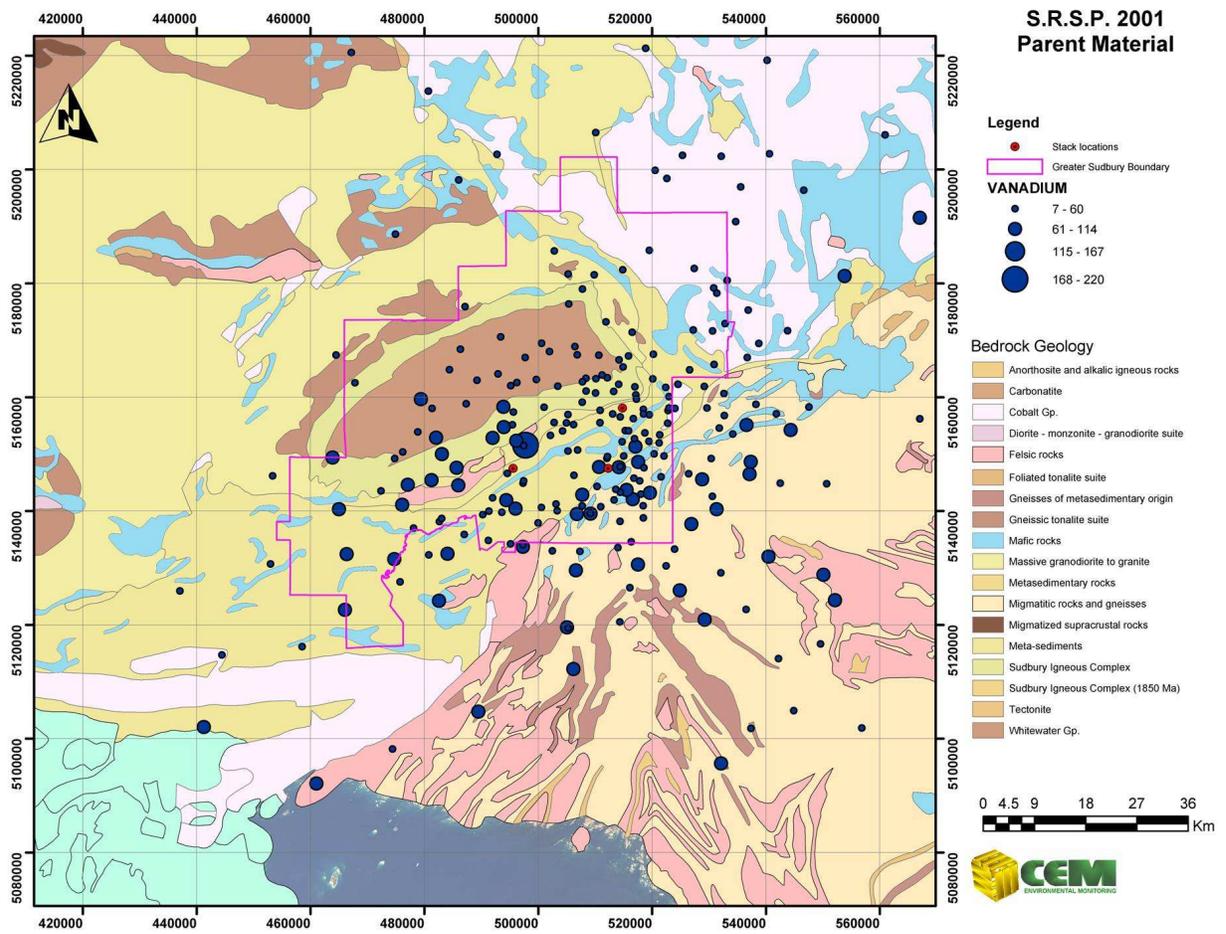


Figure 26: Distribution of vanadium in the soil parent materials of the Sudbury Region.

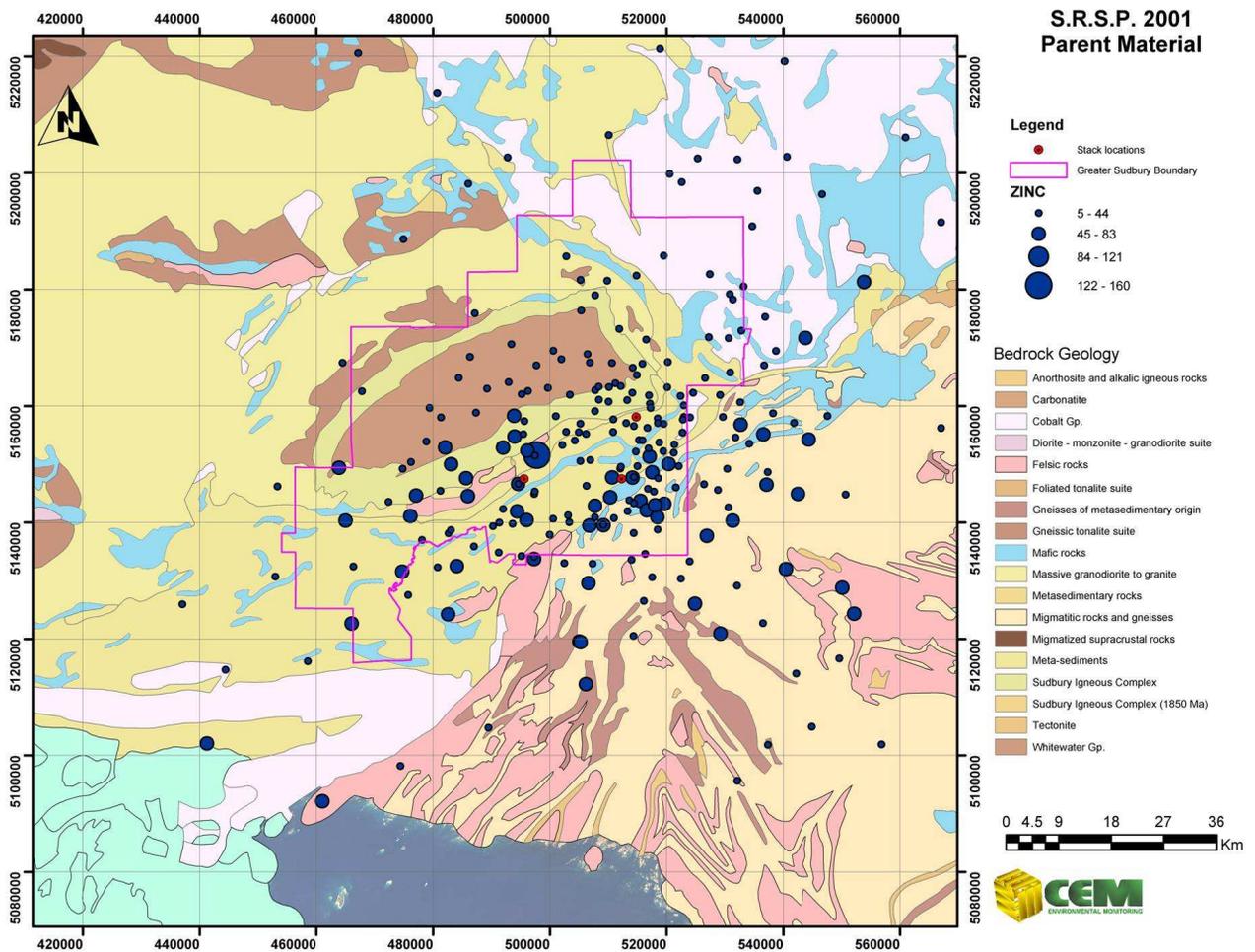


Figure 27: Distribution of zinc in the soil parent materials of the Sudbury Region.

Metal Correlations in Regional Parent Materials

The relationships between the individual elements extracted from the regional soil parent material samples with *Aqua Regia* are listed in the Pearson correlation matrix (Table 9) calculated using SPSS™ with a correlation value of $r < 0.5$ being highly significant at the 0.01 level. The major elements, aluminium, iron, magnesium and manganese, are all strongly positively correlated, probably reflecting the abundance of ferromagnesian minerals partially digested by the *Aqua Regia* extractant from the soil matrix. These minerals would have been incorporated from the underlying basic metavolcanic bedrock by glacial activity.

Table 9: Pearson Correlation for the Aqua Regia extracted metals for all samples from parent materials sampled within the study region (n = 255 samples).

	Arsenic	Barium	Beryllium	Calcium	Chromium	Cobalt	Copper	Iron	Lead	Magnesium	Manganese	Molybdenum	Nickel	Selenium	Strontium	Vanadium	Zinc
Aluminium	0.01	0.80 ^b	0.74 ^b	0.16 ^b	0.82 ^b	0.76 ^b	0.56 ^b	0.79 ^b	0.51 ^b	0.60 ^b	0.62 ^b	0.07	0.86 ^b	-0.12 ^a	0.86 ^b	0.68 ^b	0.74 ^b
Argon		0.02	0.02	0.01	0.02	0.07	0.57 ^b	0.03	0.14 ^a	-0.03	0.08	0.08	0.38 ^b	0.02	0.04	0.03	0.05
Barium			0.87 ^b	0.11	0.85 ^b	0.71 ^b	0.40 ^b	0.84 ^b	0.56 ^b	0.70 ^b	0.68 ^b	0.06	0.57 ^b	-0.13 ^a	0.74 ^b	0.71 ^b	0.77 ^b
Beryllium				0.05	0.74 ^b	0.64 ^b	0.34 ^b	0.75 ^b	0.49 ^b	0.60 ^b	0.68 ^b	0.04	0.46 ^b	-0.07	0.54 ^b	0.63 ^b	0.72 ^b
Calcium					0.14 ^a	0.13 ^a	0.08	0.13 ^a	0.04	0.72 ^b	0.20 ^b	0.07	0.11	-0.06	0.41 ^b	0.11	0.15 ^a
Chromium						0.79 ^b	0.42 ^b	0.84 ^b	0.54 ^b	0.67 ^b	0.68 ^b	0.22 ^b	0.88 ^b	-0.15 ^a	0.71 ^b	0.73 ^b	0.76 ^b
Cobalt							0.60 ^b	0.90 ^b	0.54 ^b	0.63 ^b	0.80 ^b	0.15 ^a	0.73 ^b	-0.08	0.57 ^b	0.86 ^b	0.90 ^b
Copper								0.48 ^b	0.52 ^b	0.28 ^b	0.41 ^b	0.11	0.84 ^b	0.07	0.30 ^b	0.49 ^b	0.54 ^b
Iron									0.57 ^b	0.70 ^b	0.83 ^b	0.11	0.60 ^b	-0.13 ^a	0.70 ^b	0.96 ^b	0.96 ^b
Lead										0.38 ^b	0.47 ^b	0.26 ^b	0.66 ^b	0.20 ^b	0.40 ^b	0.54 ^b	0.58 ^b
Magnesium											0.66 ^b	0.09	0.43 ^b	-0.14 ^a	0.71 ^b	0.61 ^b	0.67 ^b
Manganese												0.16 ^a	0.44 ^b	-0.04	0.61 ^b	0.75 ^b	0.80 ^b
Molybdenum													0.19 ^b	0.10	0.00	0.09	0.09
Nickel														0.03	0.42 ^b	0.58 ^b	0.64 ^b
Selenium															-0.22 ^b	-0.14 ^a	-0.08
Strontium																0.63 ^b	0.61 ^b
Vanadium																	0.94 ^b

b Correlation is significant at the 0.01 level (2-tailed).
a Correlation is significant at the 0.05 level (2-tailed).

Calcium is only correlated strongly with magnesium, perhaps reflecting the association of these two elements in the small area of slightly calcareous soils formed on lacustrine sediments both in the Valley area, and in the materials to the east of the study area. The correlation between magnesium and strontium may further support this suggestion (McKeague and Wolynetz, 1979). The Group II metals, barium, beryllium and strontium are all strongly correlated, indicative of a common mode of occurrence in the soil parent materials.

The strong positive correlations between arsenic, cobalt, copper, lead, nickel and zinc is indicative of a strong mineralogical relationship in mode of occurrence of these elements in the soil parent materials. Also strongly correlated with iron and manganese, these elements are probably to be found primarily in either sulphides or as minor inclusions in the weathered iron and manganese (oxy)hydroxides of the glaciogenic sediments. Chromium, on the other hand, being strongly correlated with the major elements aluminium, iron, magnesium and manganese, as well as with the other trace elements such as barium, beryllium, cobalt, lead, nickel, strontium, vanadium and zinc, is to be found in a different mineral assemblage associated with the metasedimentary rocks to the south of the study area. Neither molybdenum nor selenium are highly correlated with any other element, with selenium being

the only element exhibiting a significant inverse relationship with other elements such as aluminium, barium, chromium, iron, lead and strontium.

The interrelationships between minor and major elements indicated by the correlation matrix are probably related to chemical substitution in the various minerals comprising the soil matrix. The sources of data variation described by the correlation matrix were examined by Principal Component Analysis (Harman, 1967) using the Systat™ 10 program. The data were standardized prior to analysis to give a mean of zero and a standard deviation of unity, a technique that has been successfully applied to soils data by Stynes *et al.*, (1979). The initial factor extracted by Principal Component Analysis tends to be a general factor, which means that it loads significantly on every variable. The second factor tends to be bipolar, as do the remaining factors. This makes factor interpretation difficult, especially as every variable tends to be decomposed into positive and negative factors. Examination of plots of orthogonal factors generally indicates grouping of the variables in two-dimensional factor space.

Rotation of the original axis, however, produces completely different factor loadings. This rotation causes the clustered variables to load heavily on one factor only, thus producing a simplification of the factor structure, and produces factor loadings that are conceptually simpler than those on the unrotated factors. Thus Varimax rotation was utilized in an attempt to arrive at “Simple Structure” (Harman, 1967). Principal components were extracted (Table 10), and a Varimax rotation was performed. The Varimax rotated loading matrix results of this analysis is described in Table 11.

The importance of individual variables (elements) as members of a component are indicated by the magnitude of their loadings, with these components being generally interpreted in the earth sciences as factors describing geochemistry, mineralogy, hydrology or provenance. The four component analysis defined in Table 10 to explain the variability of the data matrix lists Component I explaining 53 %, Component II explaining 11 %, Component III explaining 7 % and Component IV explaining 6 % of the variance in the initial correlation matrix respectively.

Examination of the resultant Varimax rotated factor matrix, in which a simplified geometric structure is defined, indicates that the first factor, explaining the major proportion of the variance, reflects high loadings (<0.6) by zinc, barium, vanadium, chromium, cobalt, beryllium and strontium in the minor elements, and aluminium, iron, magnesium and manganese in the major elements.

Table 10: Principle component analysis describing the relationship between the compositional chemistry of Aqua Regia extracted metal(loid)s in the soil parent materials of the soils of the Sudbury smelter footprint.

	1	2	3	4
Iron	0.954	0.088	0.148	0.004
Zinc	0.925	0.012	0.125	0.002
Cobalt	0.909	-0.072	0.093	0.001
Chromium	0.896	0.078	0.082	-0.040
Barium	0.887	0.146	0.142	0.024
Vanadium	0.883	0.045	0.155	0.035
Aluminum	0.863	0.027	0.077	0.069
Manganese	0.826	0.096	0.036	-0.092
Beryllium	0.800	0.121	0.236	-0.018
Magnesium	0.768	0.384	-0.432	-0.101
Strontium	0.756	0.313	-0.213	0.106
Nickel	0.744	-0.511	-0.136	0.092
Lead	0.658	-0.360	0.049	-0.304
Copper	0.608	-0.650	-0.198	0.237
Arsenic	0.120	-0.671	-0.380	0.399
Calcium	0.241	0.369	-0.861	-0.122
Selenium	-0.107	-0.404	0.009	-0.647
Molybdenum	0.154	-0.254	-0.166	-0.611
Percent of Total Variance Explained				
	1	2	3	4
	53.640	10.778	7.587	6.454

Table 11: Varimax rotated loading matrix for Aqua Regia extracted metal(loid)s in the soil parent materials of the soils of the Sudbury smelter footprint.

	1	2	3	4
Iron	0.958	0.110	0.101	0.005
Zinc	0.913	0.171	0.084	0.039
Barium	0.901	0.058	0.114	-0.041
Vanadium	0.885	0.137	0.059	-0.009
Chromium	0.884	0.110	0.147	0.051
Cobalt	0.877	0.245	0.074	0.078
Beryllium	0.843	0.005	0.008	-0.005
Aluminium	0.841	0.190	0.112	-0.027
Manganese	0.808	0.073	0.187	0.090
Strontium	0.695	0.061	0.461	-0.165
Magnesium	0.658	0.002	0.708	0.009
Lead	0.594	0.298	-0.028	0.463
Nickel	0.590	0.675	0.047	0.191
Arsenic	-0.102	0.869	0.034	-0.036
Copper	0.420	0.835	0.000	0.117
Calcium	0.034	0.035	0.973	0.037
Selenium	-0.137	0.016	-0.131	0.747
Molybdenum	0.079	0.042	0.136	0.680
Percent of Total Variance Explained				
	1	2	3	4
	48.879	12.117	10.045	7.419

The elements lead and nickel exhibit intermediate loadings (<0.5) on this first Varimax rotated factor. These elements are generally associated with the ferromagnesian and micaceous minerals, and thus this first factor is related to mineralogical variability in the parent materials. The higher concentrations of aluminium and beryllium display a similar pattern in the soil parent materials of the Sudbury region (Figure 10 and 13), and are commonly in glacial sediments overlying the mafic and metasedimentary rocks to the southeast of the Sudbury basin. The pattern for barium is similar, with the highest concentrations associated with parent materials overlying the mafic units. The regional distribution of iron and manganese has the highest concentration zones in soil parent materials overlying the mafic rocks along the Grenville boundary (Figures 18 and 21), with intermediate concentrations in the parent materials overlying the rocks of the Sudbury Igneous Complex.

The distribution for the higher concentrations of the minor elements chromium, cobalt, vanadium and zinc extracted by *Aqua Regia* display similar broad regional patterns to the other elements loading highly on the first Varimax rotated factor (Figure 16, 15, 26 and 27). The highest concentrations of all four elements are generally in the glacial parent materials over the mafic rocks, and over members of the Sudbury Igneous Complex. The concentration of lead in soil parent materials (Figure 23), which also has a loading of 0.46 on the fourth factor, does not appear to have a strong association with any of the major rock types underlying the Sudbury region.

The second factor has high loadings by arsenic, nickel and copper. These latter elements are commonly associated with sulphides minerals, perhaps inherited in the tills by sub-glacial erosion from base-metal rich regional deposits. With the exception of the high extremes in the Kelly Lake delta and in the centre of the Sudbury basin, levels of arsenic (Figure 11) do not appear to display any major pattern in the soil parent materials of the region. The higher concentrations of copper and nickel are in the sediments overlying the mafic rocks of the region (Figures 17 and 22).

The only three elements to load significantly on the third Varimax rotated factor are the major elements calcium and magnesium, together with the minor element, strontium. These three elements are commonly associated in carbonate minerals, and are especially enriched in calcareous soil parent materials (McKeague and Wolynetz, 1979). This factor suggests that approximately 10% of the regional parent material variability may be associated with the minor area of calcareous glaciolacustrine sediments. The higher concentrations of calcium (Figure 14) are generally associated with the pockets of lacustrine sediments in the region, whereas higher levels of magnesium (Figure 20) are also associated with glacial sediments overlying the mafic rocks to the east of the City of Greater Sudbury. The distribution pattern for strontium shows all soil forming materials to the south east of the Sudbury Basin to be generally similar in concentration (Figure 25).

Only two trace elements, molybdenum and selenium, have significant loadings (<0.68) on the fourth Varimax rotated factor. Lead, with no apparent strong association between soil parent material concentrations (Figure 23) and the regional basement geology, is also

important in this fourth factor. The first two elements appear to be associated with the glacial sediments overlying the mafic rocks of the region (Figures 19 and 24).

Hierarchical classification techniques were used to produce natural groupings based on numerical similarities between both individuals and variables. The cluster analysis using Ward's method similarity coefficients produced four major groupings. These groupings of soil parent materials based on partial chemical composition using the concentrations of individual elements extracted from the original soils materials using *Aqua Regia* form a broad pattern reflecting the provenance of the glacial sediments in which the soils have been developing for the past 10,000 years.

Metal Distribution in Regional Surface Soils

The sites selected for this study were sampled in specific depth increments as defined by MOE in the *Guidelines for Sampling Contaminated Sites in Ontario* (MOE, 1997). The depth increments were 0 – 5 cm, 5 –10 cm and 10 – 20 cm. Samples from a depth of greater than 80cm have been discussed in the previous sections of this report. As the textures of the soil-forming materials in the region are variable, with the clay fraction commonly being enriched in many of the transition metals, the lack of textural data does limit interpretation of the regional metal(loid) concentration data.

The summary statistics of the individual elements in the individual soil layers from all sites sampled in the region are shown in Table 12, 13 and 14. The statistical data indicate that all the elements measured in this study show some deviation from statistical normality, an observation that would normally indicate the need to subject the data to a log-normal transformation. A similar observation with soil chemical compositional data in previous studies (Spiers *et al.*, 1984) has, however, indicated that the log transformation of the data did not significantly affect any of the general interpretations. The multivariate calculations discussed in this report use standardized data. The variability in textures of the soil profiles, together with the wide range of igneous and metamorphic minerals inherited in the diamictons from the regional bedrock, should balance the conventional use of log-normal distribution of minor and trace elements in minerals in natural systems.

Table 12: Summary statistics describing the Aqua Regia extractable concentrations for 20 elements in the 0 to 5 cm depth of soils within the Sudbury area.

STATISTICS	Aluminum	Calcium	Iron	Magnesium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Copper	Lead	Manganese	Molybdenum	Nickel	Selenium	Strontium	Vanadium	Zinc	
	%				µg																
Mean	1.00	0.31	1.59	0.18	0.13	14.8149	89.44	0.01	0.36	38.72	12.45	261.40	49.98	306	0.30	263.05	2.19	32.90	31.13	39.00	
Standard Deviation	0.45	0.20	0.60	0.12	0.28	21.2601	36.60	0.12	0.54	13.34	10.30	313.91	24.99	286	0.62	296.27	2.11	12.38	8.87	20.63	
Min	0.24	0.05	0.46	0.04	0.00	0	16.50	0.00	0.00	10.00	2.00	6.10	3.50	43	0.00	14.00	0.00	0.00	10.05	0.00	
Max	3.10	2.45	4.30	0.62	1.20	305	215.00	1.77	3.20	98.00	78.50	3850.00	194.00	2200	4.55	2900.00	17.00	62.50	61.50	115.00	
Range	2.87	2.40	3.85	0.58	1.20	305	198.50	1.77	3.20	88.00	76.50	3843.90	190.50	2157	4.55	2886.00	17.00	62.50	51.45	115.00	
Median	0.92	0.28	1.55	0.15	0.00	9	85.00	0.00	0.00	36.50	9.00	145.00	48.00	200	0.00	165.00	2.00	32.00	30.50	35.00	
Kurtosis	2.21	39.33	1.97	1.25	2.97	95.7272	0.51	164.27	2.55	1.06	9.01	46.59	3.37	9.80	7.84	18.81	8.24	-0.42	0.50	1.24	
Skew	1.26	4.54	0.92	1.25	2.01	7.46556	0.69	12.03	1.55	0.80	2.35	4.80	1.14	2.60	2.50	3.25	2.17	0.19	0.55	1.02	
Mode																					
Count	365	365	365	365	355	362	365	365	365	365	365	365	365	365	365	365	365	365	365	365	365
ND	0	0	0	0	282	89	0	357	230	0	0	0	0	0	282	0	49	2	0	2	
Blank/Not Analysed	4	4	4	4	14	7	4	4	4	4	4	4	4	4	4	4	4	4	4	4	
Value above 0	365	365	365	365	73	273	365	8	135	365	365	365	365	365	83	365	316	363	365	363	

Table 13: Summary statistics describing the Aqua Regia extractable concentrations for 20 elements in the 5 to 10 cm depth of soils within the Sudbury area.

STATISTICS	Aluminum	Calcium	Iron	Magnesium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Copper	Lead	Manganese	Molybdenum	Nickel	Selenium	Strontium	Vanadium	Zinc
	%				µg															
Mean	1.34	0.28	1.68	0.23	0.04	5.72	61.77	0.02	0.01	38.88	7.17	101.22	14.56	232	0.13	81.50	0.60	34.58	37.81	31.61
Standard Deviation	0.48	0.13	0.50	0.13	0.17	15.61	33.32	0.08	0.08	14.03	5.38	128.56	14.54	168	0.54	110.93	1.14	13.32	9.19	19.72
Min	0.43	0.05	0.63	0.05	0.00	0.00	20.00	0.00	0.00	15.00	1.80	5.15	3.00	95	0.00	7.50	0.00	0.00	17.00	0.00
Max	3.45	1.04	3.00	0.78	1.50	150.00	250.00	0.78	0.80	85.50	38.80	945.00	119.50	1250	3.60	738.50	6.50	56.50	65.50	146.00
Range	3.02	0.99	2.37	0.72	1.50	150.00	230.00	0.78	0.80	71.50	37.00	939.85	116.50	1155	3.60	731.00	6.50	56.50	48.50	146.00
Median	1.25	0.27	1.65	0.20	0.00	7.50	54.25	0.00	0.00	31.50	6.00	57.25	11.25	175	0.00	45.75	0.00	34.75	37.00	27.50
Kurtosis	2.25	55.1	0.44	1.97	31.87	94.77	6.00	47.54	50.85	0.96	7.16	12.45	25.57	7.71	25.58	15.56	3.92	1.79	0.04	6.12
Skew	1.19	1.50	0.26	1.32	5.11	8.47	1.87	6.78	7.12	0.76	2.21	3.07	4.57	2.24	4.50	3.67	2.82	0.27	0.41	1.72
Mode																				
Count	150	150	150	150	157	150	150	150	150	150	150	150	150	150	150	150	150	150	150	150
ND	0	0	0	0	173	46	0	184	195	0	0	0	0	0	174	0	116	4	0	3
Blank/Not Analysed	179	179	179	179	152	179	179	179	179	179	179	179	179	179	179	179	179	179	179	179
Value above 0	150	150	150	150	14	144	150	6	4	150	150	150	150	150	16	150	74	155	150	157

Values for the individual elements are discussed below, with a focus on the data obtained for the 0 – 5 cm layer in which the aerosolic fallout particles rich in metal(loid)s has been shown earlier in this report to be concentrated. The data obtained in this study are similar to that documented in the OMOE report released in 2001 (OMOE, 2001), with a greater degree of internal consistency because the data in the current study were all obtained using identical sampling protocols and analytical methodology. In the following discussion the values

obtained are compared with data for soil materials from a variety of sources, including those documented by MOE in the *Guidelines for Use at Contaminated Sites in Ontario* (MOE 1997), for the soils of the conterminous United States (Shacklette *et al.*, 1971), and for surface mineral soils (equivalent approximately to the 5 to 10 cm layer in this study) of the Canadian Shield (McKeague *et al.*, 1979) for comparative purposes. Direct comparison with the MOE data must be tempered by the fact that the ranges documented by the MOE are for soils in the pH range 5.0-9.0. In the current study, soil pH values were determined on a subset (35) only of the samples, with a pH range from slightly alkaline (7.78) to acidic (3.69) being reported. The lower pH values are trending northeast from Copper Cliff, with the highest pH values between 6.5 and 7.78 being obtained for samples from an area of calcareous and/or agricultural soils formed on silt loam glaciolacustrine materials in the Verner and Valley East areas.

Table 14: Summary statistics describing the Aqua Regia extractable concentrations for 20 elements in the 10 to 20 cm depth of soils within the Sudbury area.

STATISTICS	Aluminum	Calcium	Iron	Magnesium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Copper	Lead	Manganese	Molybdenum	Nickel	Selenium	Strontium	Tungsten	Zinc	
	%				µg																
Mean	1.72	0.32	1.92	0.32	0.04	3.80	63.45	0.01	0.00	44.04	7.30	49.67	8.90	215	0.11	50.57	0.17	38.04	40.29	33.70	
Standard Deviation	0.54	0.13	0.50	0.17	0.16	10.14	32.81	0.07	0.04	16.16	3.25	75.05	8.37	105	0.45	55.18	0.49	11.07	8.90	15.82	
Min	0.41	0.07	0.64	0.07	0.00	0.00	21.50	0.00	0.00	18.00	2.50	3.15	3.00	4.3	0.00	10.00	0.00	0.00	10.20	10.50	
Max	3.65	1.26	3.70	0.96	0.90	88.50	185.00	0.67	0.40	115.00	20.00	510.00	74.00	697	3.80	485.00	3.00	65.00	66.00	84.00	
Range	3.24	1.18	3.07	0.89	0.90	88.50	163.50	0.67	0.40	97.00	17.50	505.85	71.00	654	3.80	475.00	3.00	65.00	55.80	73.50	
Median	1.70	0.31	1.90	0.27	0.00	0.00	65.50	0.00	0.00	42.00	6.50	24.50	7.00	185	0.00	33.00	0.00	38.00	40.00	32.00	
Kurtosis	0.93	14.53	0.53	1.60	13.30	38.60	2.20	72.45	82.95	3.17	1.65	13.37	27.15	2.57	38.78	23.92	13.67	0.42	0.65	0.13	
Skew	0.61	2.48	0.24	1.31	3.76	5.65	1.45	8.45	9.16	1.34	1.16	3.45	4.70	1.38	5.75	4.38	3.56	-0.23	0.14	0.79	
Mode																					
Count	171	171	171	171	171	171	171	171	171	171	171	171	171	171	171	171	171	171	171	171	171
ND	0	0	0	0	159	106	0	168	169	0	0	0	0	0	157	0	145	1	0	0	0
Blank/Not Analyzed	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198
Value above 0	171	171	171	171	12	65	171	3	2	171	171	171	171	171	14	171	25	170	171	171	

Soil Layer 0-5 cm

Aluminum

The maximum value for aluminum in 0 – 5 cm layer was 3.1%, with a minimum reported value of 0.235%. The mean value for Shield surface mineral soils listed by McKeague *et al.*, (1979) is 6.28% and for U.S. surface soils by Shacklette *et al.*, (1971) is 6.6%, considerably higher than the arithmetic mean of 1.00% of this study. The data are, however, similar to the

2.32% documented for coarse textured soils of Shield glacial and glaciofluvial origin in North East Alberta (Spiers *et al.*, 1989). Although there is no MOE Table F value for aluminium in surface materials, the OTR₉₈ value was exceeded at 1 of the 254 sites sampled.

Arsenic

The maximum value for arsenic in the 0-5 cm samples was 305 µg/g, with minimum values below detection limits. The regional arithmetic mean value is 14.8 µg/g, which compares with an upper crustal average of 4.8 µg/g (Rudnick and Gao, 2003). Although there is no OTR₉₈ value for arsenic, the OMOE Table F limit is 17µg/g and the MOE Table A limit is 20 µg/g. The Table A limit was exceeded in 113 samples. The elevated arsenic concentrations are centred on the Coniston, Inco and Falconbridge smelters (Figure 29), with the maximum values in the vicinity of the Falconbridge smelter.

Barium

With a mean concentration of 89.4 µg/g, barium levels are substantially below the expected upper crustal average of 628 µg/g (Rudnick and Gao, 2003) and the level documented in the surface soils of the conterminous States (Shacklette *et al.*, 1971). Although there is no OTR₉₈ value, the MOE Table A guideline is 750 µg/g and the Table F value is 210 µg/g, values again substantially greater than any concentration measured in this study.

Beryllium

Beryllium, potentially very toxic if ingested in excess, exists at very low concentrations in surface soils of the region with a mean content of 0.01 µg/g, below the mean concentration (0.92 µg/g) documented for U.S. soils (Shacklette *et al.*, 1971). Although there is no OTR₉₈ value for beryllium, the MOE Table A and Table F guideline of 0.2 µg/g was exceeded in one instance at site 82 in the south east of the study region, with a measured concentration of 1.77 µg/g.

Cadmium

With a mean concentration of 0.36 µg/g, and a maximum concentration of 3.2 µg/g, cadmium did not exceed the MOE Table F limit of 12 µg/g at any site within the study region.

Henderson *et al.*, (2002) estimate the background level of cadmium for soils of the Rouyn-Noranda area at 1 µg/g, a level in contrast to a measured mean background concentration of 0.3 µg/g for soils formed in tills in the Flin Flon region of Manitoba, (McMartin *et al.*, 1999).

Calcium

The arithmetic mean calcium concentration documented in this study is 0.31%, a concentration lower than that documented by McKeague *et al.*, (1979) for samples for Shield surface soils (2.05 %) and conterminous U.S. soils (1.8%), respectively (Shacklette *et al.*, 1971). The surface soils sites with calcium concentrations at the higher end of the range (1.5 – 2.7%) are all at the eastern and southern edges of the study area. These data reflect the fact that only about 15% of the soils sampled in the Sudbury region are developed on calcareous parent materials, specifically the medium textured glaciolacustrine sediments of the Warren-Verner area. The OTR₉₈ value for calcium is 5.5 %, with no Table F limit. The OTR₉₈ value for calcium reflects the dominance of data from the calcareous soils of southern Ontario used in the production of the advisory tables. In a similar study of background concentrations for 1366 soils formed in tills underlain by Precambrian bedrock formations in the Flin Flon region of Manitoba, McMartin *et al.*, (1999) document calcium mean concentration as 0.32 %.

Chromium

The regional mean for chromium concentration of the 0 to 5 cm layer is 38.7 µg/g, with a range of 10 - 98 µg/g. These data are in fairly close agreement with the Canadian (45 µg/g) mean soil parent material chromium content, but significantly higher than that documented for Shield surface soils (24 µg/g). Thus some sample sites in the Sudbury area have concentrations above the Ontario MOE Table F background chromium concentration limit of 71 µg/g for all non-agricultural uses for surface materials, but well below the Table F value of 750 µg/g. The data of Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for the less than 75 µm fraction of

subsurface soils of the conterminous U.S.A. ($54 \mu\text{g gm}^{-1}$) indicate that the levels of this study are about normal background for surficial soil forming sediments. Interestingly, the higher chromium values in the surface soil layer reflect the pattern displayed for regional parent materials, being highest to the south of the major industrial region. For comparison, the measured mean background concentration of chromium in soils formed in tills in the Flin Flon region of Manitoba was $135 \mu\text{g/g}$ (McMartin *et al.*, 1999).

Cobalt

With a range in concentration from 2-78 $\mu\text{g/g}$, the arithmetic mean cobalt levels ($12.5 \mu\text{g/g}$) in soil surface layers of the Sudbury region are slightly lower than those described by McKeague *et al.*, (1979) for the surface mineral horizon of Shield soils. However, the mean value is similar to that defined for U.S. soils ($10 \mu\text{g/g}$) by Shacklette *et al.*, (1971) and Gough *et al.*, (1988). Several sample sites in the Sudbury area have concentrations above the Ontario MOE Table F background cobalt concentration limit of $21 \mu\text{g/g}$ for all non-agricultural uses for surface materials. The distributional map for cobalt (Figure 34) shows the effect of regional aerosolic fallout, with the higher concentrations being around the centroid area of the regional smelters.

Copper

The overall mean level of copper ($261.4 \mu\text{g gm}^{-1}$) for the 0 to 5 cm layer of Sudbury region surface soils is substantially greater than those defined for U.S. soils ($25 \mu\text{g/g}$) by Shacklette *et al.*, (1971) and Gough *et al.*, (1988), and for surface layers of Canadian Shield soils ($11 \mu\text{g/g}$) as documented by McKeague *et al.*, (1979). With a range from 6 to $3850 \mu\text{g/g}$, the distribution of copper in surface soils as illustrated in Figure 36 shows a classic wind driven ellipsoidal pattern centred on the regional smelter complex. The highest levels of copper at $270 \mu\text{g/g}$ are on treed landscapes adjacent the mining and smelter operations in the Junction Creek watershed. Interestingly, the data obtained in the current Sudbury study are considerably higher than that documented for humus copper at $43 \mu\text{g/g}$ for in the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). The measured mean humus concentration of copper in soils formed in tills within 5 km of the Flin Flon region of

Manitoba was 1970 µg/g (McMartin *et al.*, 1999). With no OTR₉₈ value, the Table A limit is 225 µg/g. Of the analyzed surface samples 145 exceeded the MOE Table A guideline.

Iron

The mean iron concentration documented for the 0 to 5 cm layer in this study is 1.59 %, with a range from 0.46 to 4.3 %. These values are almost identical to those documented by both McKeague *et al.*, (1979) for surface mineral layers of Shield soils, and by Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples from the conterminous U.S. soils. The OTR₉₈ value for iron is 3.5 %, with no Table A or F limit. There were 5 samples that exceeded the OTR₉₈ values for surface material. The samples include: site 269, 35500 µg/g; site 293, 40500 µg/g; site 304, 36500 µg/g; site 308, 35500 µg/g; and site 332, 43000 µg/g. In comparison, the measured mean background concentration of iron in soils formed in tills in the Flin Flon region of Manitoba was 5.28% (McMartin *et al.*, 1999).

Lead

With a range in concentrations from 3.5 to 194 µg/g , the mean regional value for lead (50 µg/g) in Sudbury area soil 0 to 5 cm layers is higher than that documented by Dudas and Pawluk (1980) for Prairie soils, by McKeague *et al.*, (1979) for soils of the Shield region (20 µg/g) and by Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for soil forming materials of the conterminous U.S. (20 µg/g). The lead levels for all surface layers sample sites in this Sudbury area study have concentrations below the Ontario MOE Table A background lead concentration limit of 200 µg/g for all non-agricultural uses for surface materials. Furthermore, the data obtained in the current Sudbury study are lower than the estimate of background concentration of lead at 80 µg/g for soil forming materials of the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). In comparison, the measured mean background concentration of lead in soils formed in tills in the Flin Flon region of Manitoba was 8 µg/g (McMartin *et al.*, 1999).

Although some of the high concentrations of lead in surface layers of soils of the Sudbury region are found in the vicinity of the smelter complexes, a series of regional high levels to

the south of the industrial area are centred on the above the boundaries of Cobalt group (Figure 41), reflecting a parent material influence on concentrations in the surface layers.

Magnesium

With a concentration range of 0.04 to 0.62 %, the arithmetic mean magnesium concentration documented for the 0 to 5 cm layers in this study is 0.18%, a content below that documented by both McKeague *et al.*, (1979) and Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples for Shield (0.51%) and conterminous U.S. soils (0.92%), respectively. The OTR98 value for magnesium is 2.0 %, with no Table F limit.

The sites with magnesium concentrations at the higher end of the range (0.2% – 0.8%) are all in southern half of the study area where soils are formed on tills and sediments overlying the felsic and diorite members of the Grenville Province. These soils with highest concentrations of magnesium are probably developed on calcareous medium textured glaciolacustrine sediments. In comparison, the measured mean background concentration of magnesium in soils formed in tills in the Flin Flon region of Manitoba was 1.89% (McMartin *et al.*, 1999). The mean humus magnesium content in the Rouyn area is 0.28 %, with a range from 0.02 to 0.89 % (Henderson *et al.*, 2002).

Manganese

The arithmetic mean manganese concentration documented in this study is 306 µg/g, with a range of 43 – 2200 µg/g. No samples exceed the OTR₉₈ values of 2200 µg/g for manganese for surface materials. The manganese levels described in this study are lower than those documented elsewhere (McKeague *et al.*, 1979; Shacklette *et al.*, 1971, ; Spiers *et al.*, 1989) for background soil levels in North America. In comparison, the measured mean concentration of manganese in the humus layers of soils formed in tills in the Rouyn area is 800 µg/g with a range from 25 to 3190 µg/g (Henderson *et al.*, 2002).

Molybdenum

With a mean of 0.3 µg/g, levels of molybdenum are lower than those documented by Shacklette *et al.*, (1971) for U.S. soils (0.98 µg/g) and Gough *et al.*, (1988) for Alaskan soils

(1.3 µg/g), with no comparable data being readily available for Canadian Shield soil parent materials, with the exception of the data of Pawluk and Bayrock (1969) who describe a background level of 1-2 µg/g molybdenum for the clay-rich soils Northeastern Alberta. Some sampling sites exceed the MOE Table F guideline of 2.5 µg/g molybdenum for all non-agricultural uses for surface materials. In comparison, the measured mean concentration of molybdenum in the humus layers of soils formed in tills in the Rouyn area is 2.32 µg/g with a range from 0.5 to 29 µg/g (Henderson *et al.*, 2002).

Nickel

The arithmetic nickel levels (263 µg/g) for the Sudbury region in this region are much higher than those levels documented in the review by McKeague *et al.*, (1971) for agricultural soils of the Shield region (12 µg/g) and in the USGS documented levels for soils (20 µg/g) of the conterminous U.S. soils (Shacklette *et al.*, 1971; Gough *et al.*, 1988). The range in the 0 to 5 cm soil layer nickel concentrations is from 14 to 2900 µg/g, with the higher concentrations being in the soil parent materials in the vicinity of the regional smelter operations (Figure 42). The nickel distribution around the smelter centroid zone forms an ellipsoid centred on the Copper Cliff operations of INCO Ltd, with the long axis in a SW to NE direction. The nickel concentrations for the 0 to 5 cm layers of the sola in the core of the study area are considerably above the MOE Table A (43 µg/g) and F (150 µg/g) guidelines for surface materials where soil pH is 5.0 to 11.0. For comparison, the measured mean background concentration of nickel in the humus layers if soils formed in tills in the Flin Flon region of Manitoba was 7 µg/g (McMartin *et al.*, 1999). In Rouyn, on the other hand, Henderson *et al.*, (2002) report levels of nickel in the humus layers of 20.55 µg/g, with a range of 7 to 82 µg/g, levels much lower than in the soils of the Sudbury region.

Selenium

The arithmetic selenium levels (2.19 µg/g) for 0 to 5 cm layer of undisturbed soils the Sudbury region in this region are higher than documented in the review by McKeague *et al.*, (1971) for agricultural soils of the Shield region (0.18 µg/g). The reports of Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for soils of the conterminous U.S. soils do not document

levels for selenium. The values documented in this study are considerably below the potentially toxic levels of the MOE Table A guideline of 10 µg/g for surface materials where soil pH is 5.0 to 11.0, with some sites above the Table F guideline of 1.9 µg/g for soils with a pH between 5.0 and 11.0.

The distributional map for selenium (Figure 43) also illustrates the classic ellipsoidal nature characteristic of aerosolic deposition of point source origin, with a locus in the vicinity of the Copper Cliff smelting operations. The highest concentration zone is immediately to the northeast of the Copper Cliff operations.

Strontium

The arithmetic strontium levels (32.9 µg/g) for the 0 to 5 cm layer of the surface soils of the Sudbury region in this region are considerably lower than documented both in the review by McKeague *et al.*, (1971) for surface mineral layers of agricultural soils of the Shield region (402 µg/g) and in the USGS documented levels estimated from 563 soil profiles (240 µg/g) of the conterminous U.S. soils (Shacklette *et al.*, 1971; Gough *et al.*, 1988). The values documented in the latter studies are similar to those documented for both granite and the estimated mean crustal abundance (Rudnick and Gao, 2003). The range in the 0 to 5 cm layer strontium concentrations is from 10 to 62 µg/g. The lower concentrations in this study compared to those listed above is a reflection of the non-calcareous nature of the soil forming materials of the Sudbury region. Similar levels are, however, documented for soil parent materials formed on glaciofluvial materials of North East Alberta (Spiers *et al.*, 1989). There are no soil remediation criteria listed in the MOE Tables A or F guidelines for surface materials where soil pH is 5.0 to 11.0. However, the OTR₉₈ value for strontium is 64 µg/g. None of the samples collected and analyzed in the 0-5 cm exceed the OTR₉₈ value of 64 µg/g. For comparison, the measured mean concentration of strontium in the humus layers of soils formed on glacial sediments in the Rouyn-Noranda region of Quebec at 37 µg/g, with a range of 7 to 96 µg/g, levels similar to the surface layers of the soils of the Sudbury region (Henderson *et al.*, 2002).

The distributional map for strontium (Figure 44) indicates no relationship with historical smelting operations. The distribution pattern illustrates the relationship between strontium levels in surface soils and the glaciolacustrine sediments of the region. The highest concentration zones are associated with soils formed in the glacial sediments immediately overlying the metasediments of the Grenville Province.

Vanadium

The arithmetic mean vanadium level for 0 to 5 cm layer of undisturbed soils of the Sudbury region is 31 µg/g, with a range of 10 to 62 µg/g. The mean value in this region is lower than documented for soils in the USGS study estimated from 563 soil profiles (76 µg/g) of the conterminous U.S. (Shacklette *et al.*, 1971; Gough *et al.*, 1988), and for soils of North East Alberta (Spiers *et al.*, 1989). The low level of vanadium found in the current study may reflect the relatively high proportion of granite incorporated in the regional glaciogenic sediments that form the soil parent materials. The measured mean concentration of vanadium in the humus layers of soils formed on glacial sediments in the Rouyn-Noranda region of Quebec at 19 µg/g, with a range of 3 to 63 µg/g, levels similar to the surface layers of the soils of the Sudbury region (Henderson *et al.*, 2002).

The values documented for all surface soil materials in this study are below the level of 200 and 91 µg/g, respectively, listed in the MOE Table A and F guidelines for surface materials where soil pH is 5.0 to 11.0 where soil remediation is an issue. The distributional map for vanadium (Figure 45) indicates no relationship with historical smelting operations. The distribution pattern illustrates the relationship between vanadium levels in surface soils and the finer textured glaciolacustrine sediments of the region, with the highest concentration zones associated with soils formed in the glacial sediments immediately overlying the metasediments of the Grenville Province.

Zinc

The arithmetic mean zinc concentration for the 0 to 5 cm layer of undisturbed soils of the Sudbury region is 39 µg/g, with a range from <1 to 115 µg/g. The mean value is lower than that documented for both the surface mineral layers of Shield soils (54 µg/g) by McKeague

et al., (1979) and the conterminous U.S. soils (54 µg/g) and Alaskan soils (79 µg/g) in the USGS studies of Shacklette *et al.*, (1971) and Gough *et al.*, (1988), respectively. Pawluk and Bayrock (1969) document levels of 40 - 50 µg gm⁻¹ for the North East of Alberta for coarse textured surface soils formed in glaciogenic materials primarily of Shield source. Elevated concentrations are to the west, south and east of the three smelters. The background zinc levels obtained in this study are lower than estimates of background concentration of zinc at 80 µg/g for soil forming materials of the Rouyn-Noranda area approximately 150 km north east of Sudbury (Henderson *et al.*, 2002).

There is no OTR₉₈ value, and no samples exceed the MOE Table A or F guidelines of 600 and 160 µg/g, respectively. The distributional map for zinc (Figure 46) indicates no relationship with historical smelting operations, rather illustrating the relationship between zinc levels in surface soils and the glaciogenic sediments of the region. The highest concentration zones are associated with soils to the south west of the study region formed in the glacial sediments immediately overlying the rocks of the Cobalt Group.

Soil Layer 5-10 cm

Aluminum

The maximum value for aluminum in 5 – 10 cm layer was 1.34%, with a minimum reported value of 0.43% and a maximum value of 3.45%. The mean value for Shield surface mineral soils listed by McKeague *et al.*, (1979) is 6.28% and for U.S. surface soils by Shacklette *et al.*, (1971) is 6.6%, considerably higher than the arithmetic mean of 1.00% of this study. The data are, however, similar to the 2.32% documented for coarse textured soils of Shield glacial and glaciofluvial origin in North East Alberta (Spiers *et al.*, 1989). The OTR₉₈ value is 3.0 % for surface materials. There is neither a Table F nor a Table A limit for aluminum.

Arsenic

The maximum value for arsenic in the 5 to 10 cm samples was 190 µg/g, with minimum values below detection limits. The regional arithmetic mean value is 9.7 µg/g, which compares with an upper crustal average of 4.8 µg/g (Rudnick and Gao, 2003). Although there is no OTR₉₈ value for arsenic, the OMOE Table F limit is 17µg/g and the MOE Table A limit

is 20 µg/g. The elevated arsenic concentrations are centred on the Coniston, Inco and Falconbridge smelters, with the maximum values in the vicinity of the Falconbridge smelter.

Barium

With a mean concentration of 61.8 µg/g barium levels of the 5 to 10 cm layer of the regional soils are substantially below the expected upper crustal average of 628 µg/g (Rudnick and Gao, 2003) and the level documented in the surface soils of the conterminous States (Shacklette *et al.*, 1971). Although there is no OTR₉₈ value, the MOE Table A guideline is 750 µg/g and the Table F value is 210 µg/g, values again substantially greater than any concentration measured in this study.

Beryllium

Beryllium, potentially very toxic if ingested in excess, exists at very low concentrations in surface soils of the region with a mean content of 0.01 µg/g, below the mean concentration (0.92 µg/g) documented for U.S. soils (Shacklette *et al.*, 1971). Although there is no OTR₉₈ value for beryllium, the MOE Table A and Table F guideline of 0.2 µg/g was exceeded in one instance at site 82 in the south east of the study region, with a measured concentration of 0.78 µg/g.

Cadmium

With a mean concentration of 0.001 µg/g, and a maximum concentration of 0.8 µg/g, cadmium did not exceed the MOE Table F limit of 12 µg/g at any site within the study region. Henderson *et al.*, (2002) estimate the background level of cadmium for soils of the Rouyn-Noranda area at 1 µg/g, a level in contrast to a measured mean background concentration of 0.3 µg/g for soils formed in tills in the Flin Flon region of Manitoba, (McMartin *et al.*, 1999). There is no OTR₉₈ value, the MOE Table F limit is 12 µg/g for surface materials, this was not exceeded.

Calcium

The arithmetic mean calcium concentration documented in this study for the 5 to 10 cm layer is 0.28 %, a concentration lower than that documented by McKeague *et al.*, (1979) for samples for Shield surface soils (2.05 %) and conterminous U.S. soils (1.8%), respectively (Shacklette *et al.*, 1971). The OTR₉₈ value for calcium is 5.5 %, with no Table F limit. The OTR₉₈ value for calcium reflects the dominance of data from the calcareous soils of southern Ontario used in the production of the advisory tables. In a similar study of background concentrations for soils formed in tills underlain by Precambrian bedrock formations in the Flin Flon region of Manitoba, McMartin *et al.*, (1999) document calcium mean concentration as 0.32 %.

Chromium

The regional mean for chromium concentration of the 5 to 10 cm layer is 38.9 µg/g, with a range of 15 - 86 µg/g. These data are in fairly close agreement with the Canadian (45 µg/g) mean soil parent material chromium content, but significantly higher than that documented for Shield surface soils (24 µg/g). Thus some sample sites in the Sudbury area have concentrations above the Ontario MOE Table F background chromium concentration limit of 71 µg/g for all non-agricultural uses for surface materials, but well below the Table F value of 750 µg/g. The data of Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for the less than 75 µm fraction of subsurface soils of the conterminous U.S.A. (54 µg gm⁻¹) indicate that the levels of this study are about normal background for surficial soil forming sediments. Interestingly, the higher chromium values in the surface soil layer reflect the pattern displayed for regional parent materials, being highest to the south of the major industrial region. For comparison, the measured mean background concentration of chromium in soils formed in tills in the Flin Flon region of Manitoba was 135 µg/g (McMartin *et al.*, 1999).

Cobalt

With a range in concentration from 1.5 to 38.5 µg/g, the arithmetic mean cobalt levels (7.2 µg/g) in soil 5 to 10 cm layers of the Sudbury region are slightly lower than those described by McKeague *et al.*, (1979) for the surface mineral horizon of Shield soils. However, the mean value is similar to that defined for U.S. soils (10 µg/g) by Shacklette *et al.*, (1971) and Gough *et al.*, (1988). Several sample sites in the Sudbury area have concentrations above the Ontario MOE

Table F background cobalt concentration limit of 21 µg/g for all non-agricultural uses for surface materials.

Copper

The overall mean level of copper (101.2 µg gm⁻¹) for the 5 to 10 cm layer of Sudbury region surface soils is substantially greater than those defined for U.S. soils (25 µg/g) by Shacklette *et al.*, (1971) and Gough *et al.*, (1988), and for surface layers of Canadian Shield soils (11 µg/g) as documented by McKeague *et al.*, (1979). The range in concentrations of copper is from 5 to 545 µg/g, with the distribution of copper being highest in the soils closer to the regional smelter complex. The highest levels of copper at 545 µg/g are on treed landscapes adjacent the mining and smelter operations in the Junction Creek watershed. Interestingly, the data obtained in the current Sudbury study are considerably higher than that documented for B-horizon copper levels of 31 µg/g for in the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). The measured mean B-horizon concentration of copper in soils formed in tills within 5 km of the Flin Flon region of Manitoba was 155 µg/g (McMartin *et al.*, 1999). With no OTR₉₈ value, the Table A limit is 225 µg/g, with 19 samples analyzed exceeding the latter limits for surface materials. These samples are largely trending south of the Copper Cliff smelter with some elevated values around the Coniston and Falconbridge smelters.

Iron

The mean iron concentration documented for the 5 to 10 cm layer in this study is 1.68 %, with a range from 0.63 to 3.0 %. These values are similar to those documented by both McKeague *et al.*, (1979) for surface mineral layers of Shield soils, and by Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples from the conterminous U.S. soils. The OTR₉₈ value for iron is 3.5 %, with no Table A or F limit. There were no samples exceeding the OTR₉₈ values for surface material. In comparison, the measured mean background concentration of iron in soils formed in tills in the Flin Flon region of Manitoba was 5.28% (McMartin *et al.*, 1999).

Lead

With a range in concentrations from 3.0 to 119 µg/g , the mean regional value for lead (15 µg/g) in Sudbury area soil 5 to 10 cm layers is higher than that documented by Dudas and Pawluk (1980) for Prairie soils, by McKeague *et al.*, (1979) for soils of the Shield region (20 µg/g) and by Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for soil forming materials of the conterminous U.S. (20 µg/g). The lead levels for all surface layers sample sites in this Sudbury area study have concentrations below the Ontario MOE Table A background lead concentration limit of 200 µg/g for all non-agricultural uses for surface materials. Furthermore, the data obtained in the current Sudbury study are lower than the estimate of background concentration of lead at 80 µg/g for soil forming materials of the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). In comparison, the measured mean background concentration of lead in soils formed in tills in the Flin Flon region of Manitoba was 8 µg/g (McMartin *et al.*, 1999).

Magnesium

With a concentration range of 0.06 to 0.78 %, the arithmetic mean magnesium concentration documented for the 0 to 5 cm layers in this study is 0.23%, a content below that documented by McKeague *et al.*, (1979), Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples for Shield (0.51%) and conterminous U.S. soils (0.92%), respectively. The OTR98 value for magnesium is 2.0 %, with no Table F limit. The soils with highest concentrations of magnesium are probably developed on calcareous medium textured glaciolacustrine sediments. In comparison, the measured mean background concentration of magnesium in soils formed in tills in the Flin Flon region of Manitoba was 1.89% (McMartin *et al.*, 1999). The mean B-horizon magnesium content in the Rouyn area is 0.76 %, with a range from 0.06 to 2.32 % (Henderson *et al.*, 2002).

Manganese

The arithmetic mean manganese concentration for the 5 to 10 cm layers in regional soils documented in this study is 232 µg/g, with a range of 55 to 1250 µg/g. No samples exceed the OTR₉₈ values of 2200 µg/g for manganese for surface materials. The manganese levels described in this study are lower than those documented elsewhere (McKeague *et al.*, 1979;

Shacklette *et al.*, 1971; Spiers *et al.*, 1989) for background soil levels in North America. In comparison, the measured mean concentration of manganese in the B-horizons of soils formed in tills in the Rouyn area is 410 µg/g with a range from 20 to 3110 µg/g (Henderson *et al.*, 2002).

Molybdenum

With a mean of 0.13 µg/g, levels of molybdenum levels in the 5 to 10 cm layer of regional soils are lower than those documented by Shacklette *et al.*, (1971) for U.S. soils (0.98 µg/g) and Gough *et al.*, (1988) for Alaskan soils (1.3 µg/g). There is no comparable data readily available for Canadian Shield soil materials, with the exception of the data of Pawluk and Bayrock (1969) who describe a background level of 1-2 µg/g molybdenum for the clay-rich soils Northeastern Alberta. Some sampling sites exceed the MOE Table F guideline of 2.5 µg/g molybdenum for all non-agricultural uses for surface materials. In comparison, the measured mean concentration of molybdenum in the C-horizon of soils formed in tills in the Rouyn area is 2.1 µg/g with a range from 0.5 to 9 µg/g (Henderson *et al.*, 2002).

Nickel

The arithmetic nickel levels (81.5 µg/g) for 5 to 10 cm layers of soils of the Sudbury region are much higher than those levels documented in the review by McKeague *et al.*, (1971) for agricultural soils of the Shield region (12 µg/g) and in the USGS documented levels for soils (20 µg/g) of the conterminous U.S. soils (Shacklette *et al.*, 1971; Gough *et al.*, 1988). The range in the 5 to 10 cm soil layer nickel concentrations is from 7.5 to 739 µg/g, with the higher concentrations being in the soil parent materials in the vicinity of the regional smelter operations. The nickel concentrations for the 5 to 10 cm layers of the soils in the core of the study area are considerably above the MOE Table A (43 µg/g) and, in some cases, F (150 µg/g) guidelines for surface materials where soil pH is 5.0 to 11.0. For comparison, the measured mean concentration of nickel in the B-horizon of soils formed in tills in the In Rouyn-Noranda region of Quebec was 34 µg/g (Henderson *et al.*, 2002), with a range of 9 to 347 µg/g, levels much lower than in the soils of the Sudbury region.

Selenium

The arithmetic selenium levels (0.6 µg/g) for 5 to 10 cm layer of undisturbed soils the Sudbury region in this region are higher than documented in the review by McKeague *et al.*, (1971) for agricultural soils of the Shield region (0.18 µg/g). The reports of Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for soils of the conterminous U.S. soils do not document levels for selenium. The values documented in this study are considerably below the potentially toxic levels of the MOE Table A guideline of 10 µg/g for surface materials where soil pH is 5.0 to 11.0, with some sites above the Table F guideline of 1.9 µg/g for soils with a pH between 5.0 and 11.0.

Strontium

The arithmetic strontium levels (35 µg/g) for the 5 to 10 cm layer of the surface soils of the Sudbury region in this region are considerably lower than documented both in the review by McKeague *et al.*, (1971) for surface mineral layers of agricultural soils of the Shield region (402 µg/g) and in the USGS documented levels estimated from 563 soil profiles (240 µg/g) of the conterminous U.S. soils (Shacklette *et al.*, 1971; Gough *et al.*, 1988). The range in the 5 to 10 cm layer strontium concentrations is from < 1 to 96 µg/g. The lower concentrations in this study compared to those listed above is a reflection of the non-calcareous nature of the soil forming materials of the Sudbury region. Similar levels are, however, documented for soil parent materials formed on glaciofluvial materials of North East Alberta (Spiers *et al.*, 1989). There are no soil remediation criteria listed in the MOE Tables A or F guidelines for surface materials where soil pH is 5.0 to 11.0. However, the OTR₉₈ value for strontium is 64 µg/g. A few of the samples collected and analyzed in the 5 to 10 cm layer exceed the OTR₉₈ value of 64 µg/g. For comparison, the measured mean concentration of strontium in the B-horizon of soils formed on glacial sediments in the Rouyn-Noranda region of Quebec is 24 µg/g, with a range of 9 to 65 µg/g, levels similar to the surface layers of the soils of the Sudbury region (Henderson *et al.*, 2002).

Vanadium

The arithmetic mean vanadium level for 5 to 10 cm layer of undisturbed soils of the Sudbury region is 37.8 µg/g, with a range of 17 to 67 µg/g. The mean value in this region is lower

than documented for soils in the USGS study estimated from 563 soil profiles (76 µg/g) of the conterminous U.S. (Shacklette *et al.*, 1971; Gough *et al.*, 1988), and for soils of North East Alberta (Spiers *et al.*, 1989). The measured mean concentration of vanadium in the B-horizon of soils formed on glacial sediments in the Rouyn-Noranda region of Quebec at 53 µg/g, with a range of 9 to 155 µg/g, levels relatively similar to the surface layers of the soils of the Sudbury region (Henderson *et al.*, 2002). The values documented for all surface soil materials in this study are below the level of 200 and 91 µg/g, respectively, listed in the MOE Table A and F guidelines for surface materials where soil pH is 5.0 to 11.0 where soil remediation is an issue.

Zinc

The arithmetic mean zinc concentration for the 5 to 10 cm layer of undisturbed soils of the Sudbury region is 31.6 µg/g, with a range from <1 to 149 µg/g. The mean value is lower than that documented for both the surface mineral layers of Shield soils (54 µg/g) by McKeague *et al.*, (1979) and the conterminous U.S. soils (54 µg/g) and Alaskan soils (79 µg/g) in the USGS studies of Shacklette *et al.*, (1971) and Gough *et al.*, (1988), respectively. Pawluk and Bayrock (1969) document levels of 40 - 50 µg g⁻¹ for the North East of Alberta for coarse textured surface soils formed in glaciogenic materials primarily of Shield source. The background zinc levels obtained in this study are lower than estimates of B-horizon concentrations for zinc at 60 µg/g for soil forming materials of the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). There is no OTR₉₈ value, and no samples exceed the MOE Table A or F guidelines of 600 and 160 µg/g, respectively.

Soil Layer 10-20 cm

Aluminum

The maximum value for aluminum in 10 – 20 cm layer was 1.72 %, with a minimum reported value of 0.41 % and a maximum value of 3.65 %. The mean value for Shield surface mineral soils listed by McKeague *et al.*, (1979) is 6.28% and for U.S. surface soils by Shacklette *et al.*, (1971) is 6.6%, considerably higher than the arithmetic mean of 1.00% of

this study. The data are, however, similar to the 2.32% documented for coarse textured soils of Shield glacial and glaciofluvial origin in North East Alberta (Spiers *et al.*, 1989). The OTR₉₈ value is 3.0 % for surface materials. There is neither a Table F nor a Table A limit for aluminum.

Arsenic

The maximum value for arsenic in the 10 to 20 cm samples was 88.5 µg/g, with minimum values below detection limits. The regional arithmetic mean value for the 10 to 20 cm layer is 3.8 µg/g, which compares with an upper crustal average of 4.8 µg/g (Rudnick and Gao, 2003). Although there is no OTR₉₈ value for arsenic, the OMOE Table F limit is 17µg/g and the MOE Table A limit is 20 µg/g. The highest arsenic concentration is found in the sediments of the Junction Creek delta, probably reflecting modern sedimentation as a result of erosion of mining lands in the watershed. The secondary region of high concentration is on the soils of the Falconbridge area, again probably reflecting the detrital arsenic in the shallow weathered overburden materials.

Barium

With a mean concentration of 63.5 µg/g barium levels of the 10 to 20 cm layer of the regional soils are substantially below the expected upper crustal average of 628 µg/g (Rudnick and Gao, 2003) and the level documented in the surface soils of the conterminous States (Shacklette *et al.*, 1971). Although there is no OTR₉₈ value, the MOE Table A guideline is 750 µg/g and the Table F value is 210 µg/g, values again substantially greater than any concentration measured in this study.

Beryllium

Beryllium exists at very low concentrations in surface soils of the region with a mean content in the 10 to 20 cm soil layers of 0.01 µg/g, below the mean concentration (0.92 µg/g) documented for U.S. soils (Shacklette *et al.*, 1971). Although there is no OTR₉₈ value for beryllium, the MOE Table A and Table F guideline of 0.2 µg/g was exceeded in one instance at site 82 in the south east of the study region, with a measured concentration of 0.67 µg/g.

Cadmium

With a mean concentration of $<0.01 \mu\text{g/g}$, and a maximum concentration of $0.67 \mu\text{g/g}$ in the 10 to 20 cm layer of the Sudbury region soils, cadmium did not exceed the MOE Table F limit of $12 \mu\text{g/g}$ at any site within the study region. Henderson *et al.*, (2002) estimate the background level of cadmium for soils of the Rouyn-Noranda area at $1 \mu\text{g/g}$, a level in contrast to a measured mean background concentration of $0.3 \mu\text{g/g}$ for soils formed in tills in the Flin Flon region of Manitoba, (McMartin *et al.*, 1999). There is no OTR₉₈ value, the MOE Table F limit is $12 \mu\text{g/g}$ for surface materials, this was not exceeded.

Calcium

The arithmetic mean calcium concentration documented in this study for the 10 to 30 cm layer is 0.32% , a concentration lower than that documented by McKeague *et al.*, (1979) for samples for Shield surface soils (2.05%) and conterminous U.S. soils (1.8%), respectively (Shacklette *et al.*, 1971). The OTR₉₈ value for calcium is 5.5% , with no Table F limit. The OTR₉₈ value for calcium reflects the dominance of data from the calcareous soils of southern Ontario used in the production of the advisory tables. In a similar study of background concentrations for soils formed in tills underlain by Precambrian bedrock formations in the Flin Flon region of Manitoba, McMartin *et al.*, (1999) document calcium mean concentration as 0.32% . The mean calcium content of soils in the Rouyn-Noranda area is documented at 0.37% for B-horizon soils.

Chromium

The regional mean for chromium concentration of the 10 to 20 cm layer is $44 \mu\text{g/g}$, with a range of 18 to $115 \mu\text{g/g}$. These data are in fairly close agreement with the Canadian ($45 \mu\text{g/g}$) mean Shield soil parent material chromium content, but significantly higher than that documented for Shield surface soils ($24 \mu\text{g/g}$). Thus some sample sites in the Sudbury area have concentrations above the Ontario MOE Table F background chromium concentration limit of $71 \mu\text{g/g}$ for all non-agricultural uses for surface materials, but well below the Table F value of $750 \mu\text{g/g}$. The data of Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for the less than 75 μm fraction of subsurface soils of the conterminous U.S.A. ($54 \mu\text{g gm}^{-1}$) indicate that the levels of this

study are about normal background for surficial soil forming sediments. For comparison, the measured mean background concentration of chromium in soils formed in tills in the Flin Flon region of Manitoba was 135 µg/g (McMartin *et al.*, 1999), and for B-horizon soils in the Rouyn-Noranda area was 78 µg/g (Henderson *et al.*, 2002).

Cobalt

With a range in concentration from 2.5 to 20 µg/g, the arithmetic mean cobalt levels (7.3 µg/g) in soil 10 to 20 cm layers of the Sudbury region are slightly lower than those described by McKeague *et al.*, (1979) for the surface mineral horizon of Shield soils. However, the mean value is similar to that defined for U.S. soils (10 µg/g) by Shacklette *et al.*, (1971) and Gough *et al.*, (1988). No sample sites in the Sudbury area have concentrations above the Ontario MOE Table F background cobalt concentration limit of 21 µg/g for all non-agricultural uses for surface materials. There is no OTR₉₈ value, the MOE Table A limit is 40 µg/g for surface materials, no samples exceeded this value. In comparison, B-horizons in the Rouyn-Noranda region have a mean cobalt concentration of 12 µg/g (Henderson *et al.*, 2002).

Copper

The overall mean level of copper (49.7 µg gm⁻¹) for the 10 to 20 cm layer of Sudbury region surface soils is substantially greater than those defined for U.S. soils (25 µg/g) by Shacklette *et al.*, (1971) and Gough *et al.*, (1988), and for surface layers of Canadian Shield soils (11 µg/g) as documented by McKeague *et al.*, (1979). The range in concentrations of copper is from 3 to 510 µg/g, with the distribution of copper being highest in the soils closer to the regional smelter complex. The highest levels of copper at 510 µg/g are on treed landscapes adjacent the mining and smelter operations in the Junction Creek watershed. Interestingly, the data obtained in the current Sudbury study are considerably higher than that documented for B-horizon copper levels of 31 µg/g for in the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). The measured mean B-horizon concentration of copper in soils formed in tills within 5 km of the Flin Flon region of Manitoba was 155 µg/g (McMartin *et al.*, 1999). With no OTR₉₈ value, the Table A limit is 225 µg/g, with 10 samples analyzed

exceeding the latter limits for surface materials. These samples are from sites trending south of the Copper Cliff smelter.

Iron

The mean iron concentration documented for the 10 to 20 cm layer in this study is 1.92 %, with a range from 0.64 to 3.7 %. These values are similar to those documented by both McKeague *et al.*, (1979) for surface mineral layers of Shield soils, and by Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples from the conterminous U.S. soils. The OTR₉₈ value for iron is 3.5 %, with no Table A or F limit. There were no samples exceeding the OTR₉₈ values for surface material. In comparison, the measured mean concentration of iron in soils formed in tills in the Flin Flon region of Manitoba was 5.28% (McMartin *et al.*, 1999), and 2.82 % for the B-horizons of soils formed in glaciogenic sediments in the Rouyn-Noranda area (Henderson *et al.*, 2002).

Lead

With a range in concentrations from 3.0 to 74 µg/g , the mean regional value for lead (8.9 µg/g) in Sudbury area soil 10 to 20 cm layers is lower than that documented by Dudas and Pawluk (1980) for Prairie soils, by McKeague *et al.*, (1979) for soils of the Shield region (20 µg/g) and by Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for soil forming materials of the conterminous U.S. (20 µg/g). The lead levels for all surface layers sample sites in this Sudbury area study have concentrations below the Ontario MOE Table A background lead concentration limit of 200 µg/g for all non-agricultural uses for surface materials. Furthermore, the data obtained in the current Sudbury study are lower than the estimate of background concentration of lead at 80 µg/g for soil forming materials of the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). In comparison, the measured mean background concentration of lead in soils formed in tills in the Flin Flon region of Manitoba was 8 µg/g (McMartin *et al.*, 1999).

Magnesium

With a concentration range of 0.07 to 0.96 %, the arithmetic mean magnesium concentration documented for the 10 to 20 cm layers in this study is 0.032 %, a content below that documented by McKeague *et al.*, (1979), Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for samples for Shield (0.51%) and conterminous U.S. soils (0.92%), respectively. The OTR98 value for magnesium is 2.0 %, with no Table F limit. The soils with highest concentrations of magnesium are probably developed on calcareous medium textured glaciolacustrine sediments. In comparison, the measured mean background concentration of magnesium in soils formed in tills in the Flin Flon region of Manitoba was 1.89% (McMartin *et al.*, 1999). The mean B-horizon magnesium content in the Rouyn area is 0.76 %, with a range from 0.06 to 2.32 % (Henderson *et al.*, 2002).

Manganese

The arithmetic mean manganese concentration for the 10 to 20 cm layers in regional soils documented in this study is 215 µg/g, with a range of 43 to 697 µg/g. No samples exceed the OTR₉₈ values of 2200 µg/g for manganese for surface materials. The manganese levels described in this study are lower than those documented elsewhere (McKeague *et al.*, 1979; Shacklette *et al.*, 1971; Spiers *et al.*, 1989) for background soil levels in North America. In comparison, the measured mean concentration of manganese in the B-horizons of soils formed in tills in the Rouyn area is 410 µg/g with a range from 20 to 3110 µg/g (Henderson *et al.*, 2002).

Molybdenum

With a mean of 0.11 µg/g, levels of molybdenum levels in the 10 to 20 cm layer of regional soils are lower than those documented by Shacklette *et al.*, (1971) for U.S. soils (0.98 µg/g) and Gough *et al.*, (1988) for Alaskan soils (1.3 µg/g). There is no comparable data readily available for Canadian Shield soil materials, with the exception of the data of Pawluk and Bayrock (1969) who describe a background level of 1-2 µg/g molybdenum for the clay-rich soils Northeastern Alberta. Some sampling sites exceed the MOE Table F guideline of 2.5 µg/g molybdenum for all non-agricultural uses for surface materials. In comparison, the

measured mean concentration of molybdenum in the C-horizon of soils formed in tills in the Rouyn area is 2.1 µg/g with a range from 0.5 to 9 µg/g (Henderson *et al.*, 2002).

Nickel

The arithmetic nickel levels (50.6 µg/g) for 10 to 20 cm layers of soils of the Sudbury region are much higher than those levels documented in the review by McKeague *et al.*, (1971) for agricultural soils of the Shield region (12 µg/g) and in the USGS documented levels for soils (20 µg/g) of the conterminous U.S. soils (Shacklette *et al.*, 1971; Gough *et al.*, 1988). The range in the 5 to 10 cm soil layer nickel concentrations is from 10 to 485 µg/g, with the higher concentrations being in the soil parent materials in the vicinity of the regional smelter operations. The nickel concentrations for the 10 to 20 cm layers of the sola in the core of the study area are considerably above the MOE Table A (43 µg/g) and, in some cases, F (150 µg/g) guidelines for surface materials where soil pH is 5.0 to 11.0. For comparison, the measured mean concentration of nickel in the B-horizon of soils formed in tills in the In Rouyn-Noranda region of Quebec was 34 µg/g (Henderson *et al.*, 2002), with a range of 9 to 347 µg/g, levels much lower than in the soils of the Sudbury region.

Selenium

The arithmetic selenium levels (0.17 µg/g) for 10 to 20 cm layer of undisturbed soils the Sudbury region in this region are lower than documented in the review by McKeague *et al.*, (1971) for agricultural soils of the Shield region (0.18 µg/g). The reports of Shacklette *et al.*, (1971) and Gough *et al.*, (1988) for soils of the conterminous U.S. soils do not document levels for selenium. The values documented in this study are considerably below the potentially toxic levels of the MOE Table A guideline of 10 µg/g for surface materials where soil pH is 5.0 to 11.0, with some sites above the Table F guideline of 1.9 µg/g for soils with a pH between 5.0 and 11.0.

Strontium

The arithmetic strontium levels (38 µg/g) for the 10 to 20 cm layer of the surface soils of the Sudbury region in this region are considerably lower than documented both in the review by

McKeague *et al.*, (1971) for surface mineral layers of agricultural soils of the Shield region (402 µg/g) and in the USGS documented levels estimated from 563 soil profiles (240 µg/g) of the conterminous U.S. soils (Shacklette *et al.*, 1971; Gough *et al.*, 1988). The range in the 10 to 20 cm layer strontium concentrations is from < 1 to 65 µg/g. The lower concentrations in this study compared to those listed above is a reflection of the non-calcareous nature of the soil forming materials of the Sudbury region. Similar levels are, however, documented for soil parent materials formed on coarse textured glaciofluvial materials of North East Alberta (Spiers *et al.*, 1989). There are no soil remediation criteria listed in the MOE Tables A or F guidelines for surface materials where soil pH is 5.0 to 11.0. However, the OTR₉₈ value for strontium is 64 µg/g. No samples collected and analyzed in the 10 to 20 cm layer exceed the OTR₉₈ value of 64 µg/g. For comparison, the measured mean concentration of strontium in the B-horizon of soils formed on glacial sediments in the Rouyn-Noranda region of Quebec is 24 µg/g, with a range of 9 to 65 µg/g, levels similar to the surface layers of the soils of the Sudbury region (Henderson *et al.*, 2002).

Vanadium

The arithmetic mean vanadium level for 10 to 20 cm layer of undisturbed soils of the Sudbury region is 40 µg/g, with a range of 10 to 66 µg/g. The mean value in this region is lower than documented for soils in the USGS study estimated from 563 soil profiles (76 µg/g) of the conterminous U.S. (Shacklette *et al.*, 1971; Gough *et al.*, 1988), and for soils of North East Alberta (Spiers *et al.*, 1989). The measured mean concentration of vanadium in the B-horizon of soils formed on glacial sediments in the Rouyn-Noranda region of Quebec was 53 µg/g, with a range of 9 to 155 µg/g, levels relatively similar to the surface layers of the soils of the Sudbury region (Henderson *et al.*, 2002). The values documented for all surface soil materials in this study are below the level of 200 and 91 µg/g, respectively, listed in the MOE Table A and F guidelines for surface materials where soil pH is 5.0 to 11.0 where soil remediation is an issue.

Zinc

The arithmetic mean zinc concentration for the 10 to 20 cm layer of undisturbed soils of the Sudbury region is 33.7 µg/g, with a range from 10 to 84 µg/g. The mean value is lower than that documented for both the surface mineral layers of Shield soils (54 µg/g) by McKeague *et al.*, (1979) and the conterminous U.S. soils (54 µg/g) and Alaskan soils (79 µg/g) in the USGS studies of Shacklette *et al.*, (1971) and Gough *et al.*, (1988), respectively. Pawluk and Bayrock (1969) document levels of 40 - 50 µg gm⁻¹ for the North East of Alberta for coarse textured surface soils formed in glaciogenic materials primarily of Shield source. The background zinc levels obtained in this study are lower than estimates of B-horizon concentrations for zinc at 60 µg/g for soil forming materials of the Rouyn-Noranda area approximately 250 km north east of Sudbury (Henderson *et al.*, 2002). There is no OTR₉₈ value, and no samples exceed the MOE Table A or F guidelines of 600 and 160 µg/g, respectively.

Regional Geochemical Maps for Surface Soils

Overlain on regional bedrock maps (Figure 1), the regional elemental concentration maps for the non-anthropogenic metal(loid)s display geochemical data as proportional dots illustrating concentrations of individual elements in the soil parent materials of the Sudbury region (Figures 28 to 46).

These geochemical maps indicate that the non-anthropogenic metal(loid)s concentration in the 0-5 cm layer of the Sudbury region vary with underlying bedrock composition. There is an apparent association between concentrations of these metal(loid)s extracted by *Aqua Regia* from the 0-5 cm layer of the Sudbury region soils and the regional bedrock geology. This relationship was discussed in more detail in an earlier section of this report describing the regional distribution of metal(loid)s in soil parent materials of the region.

The associations apparent in the regional maps, especially for the anthropogenic metal(loid)s, will be discussed on an individual metals basis in the following section. The concentrations of the elements arsenic, cobalt, copper, nickel, lead and selenium all display an ellipsoidal distribution, with the long axis in the approximate SW-NE trend of the dominant vector of the annual wind rose diagram, approximately centred on the smelter area.

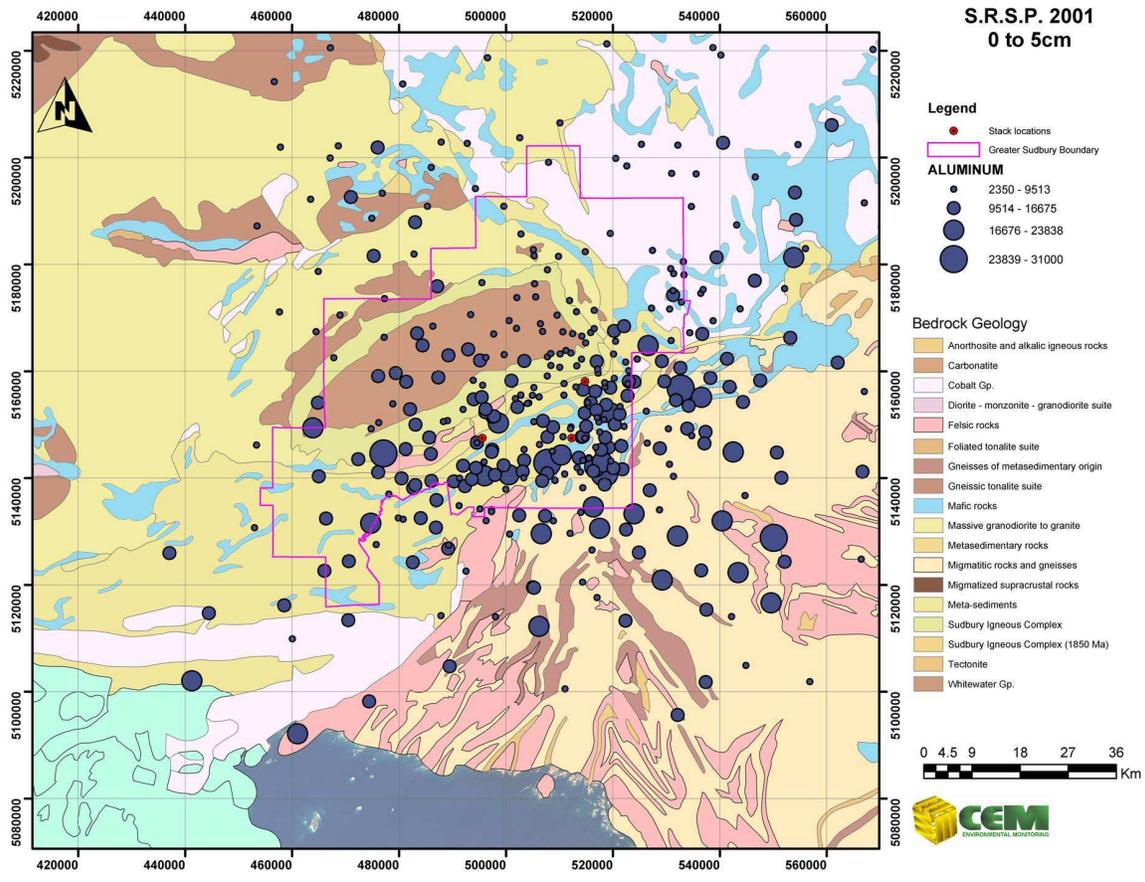


Figure 28: Distribution of aluminium in the 0-5 cm layer of soils of the Sudbury Region.

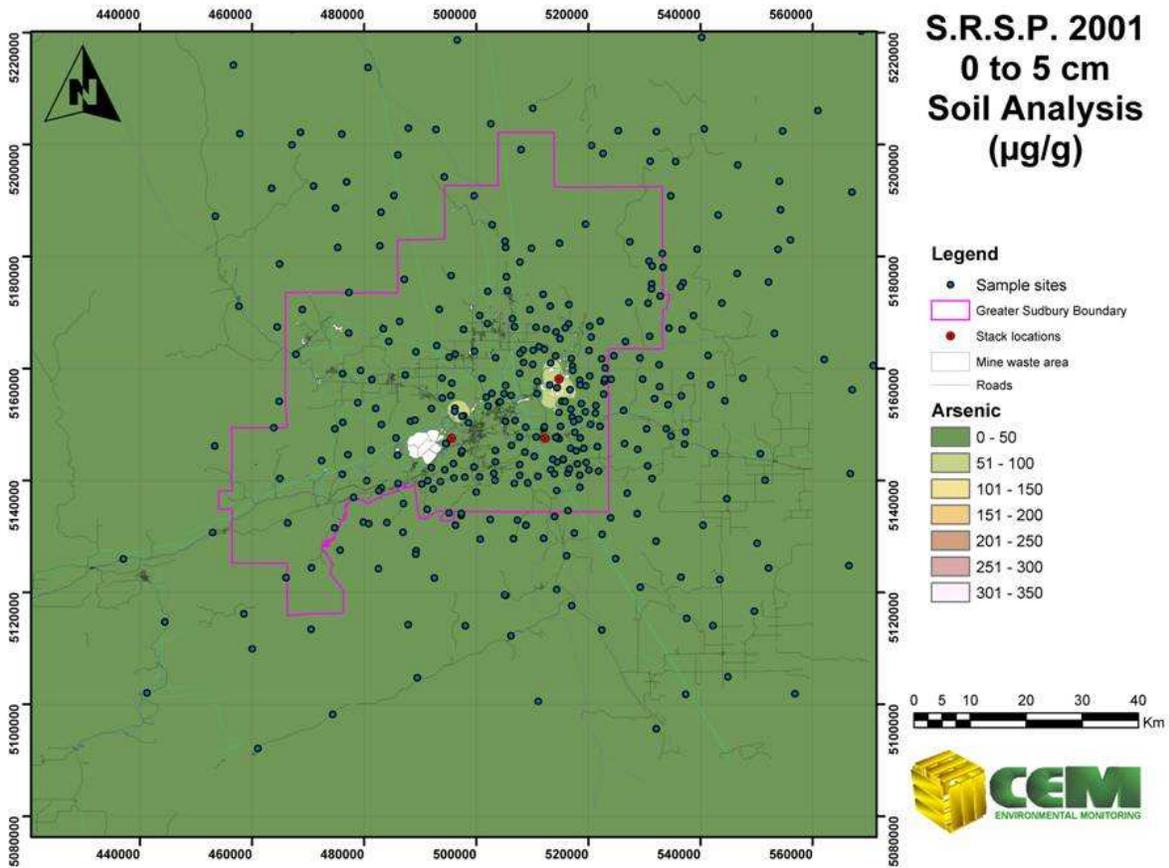


Figure 29: Distribution of arsenic in the 0-5 cm layer of soils of the Sudbury Region.

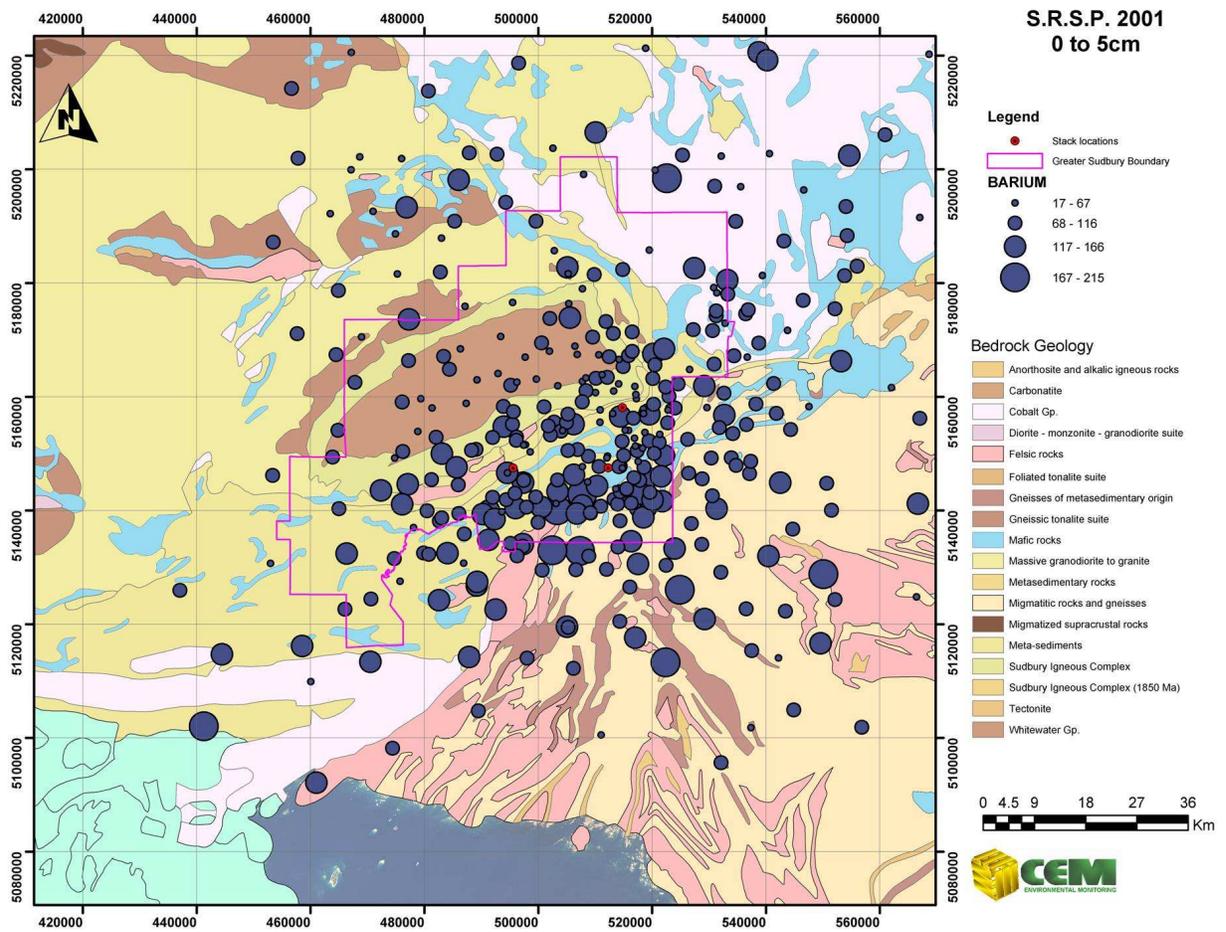


Figure 30: Distribution of barium in the 0-5 cm layer of soils of the Sudbury Region.

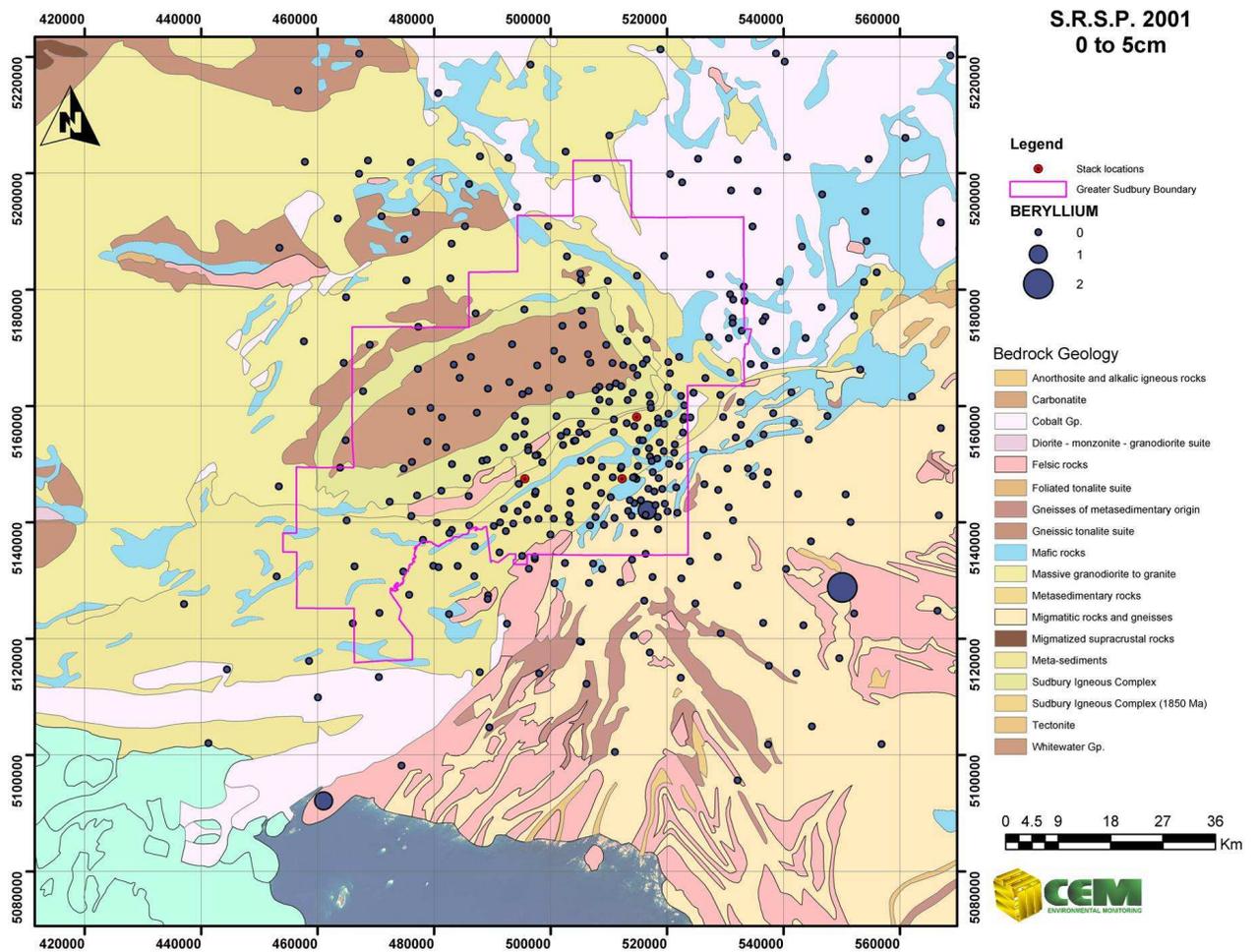


Figure 31: Distribution of beryllium in the 0-5 cm layer of soils of the Sudbury Region.

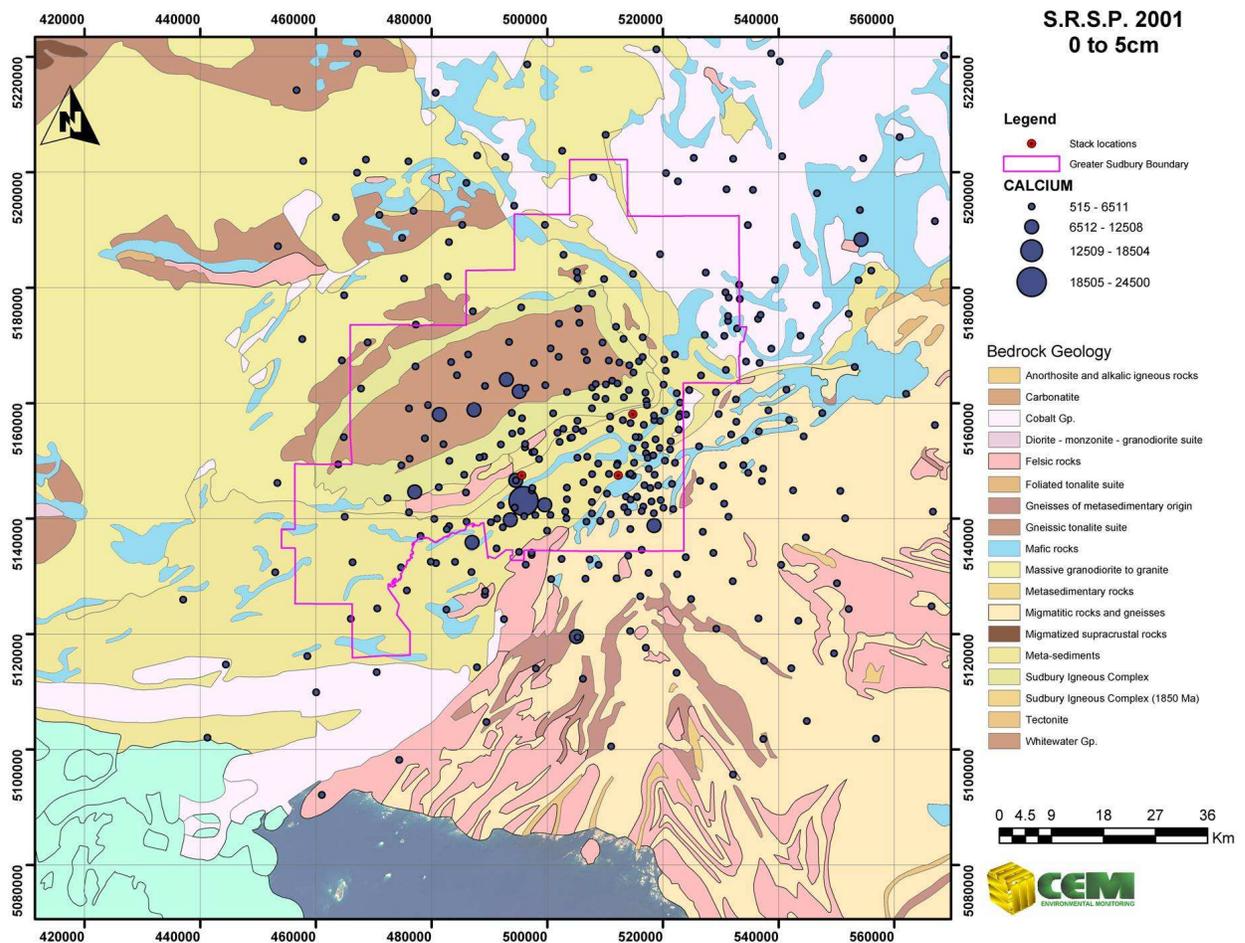


Figure 32: Distribution of calcium in the 0-5 cm layer of soils of the Sudbury Region.

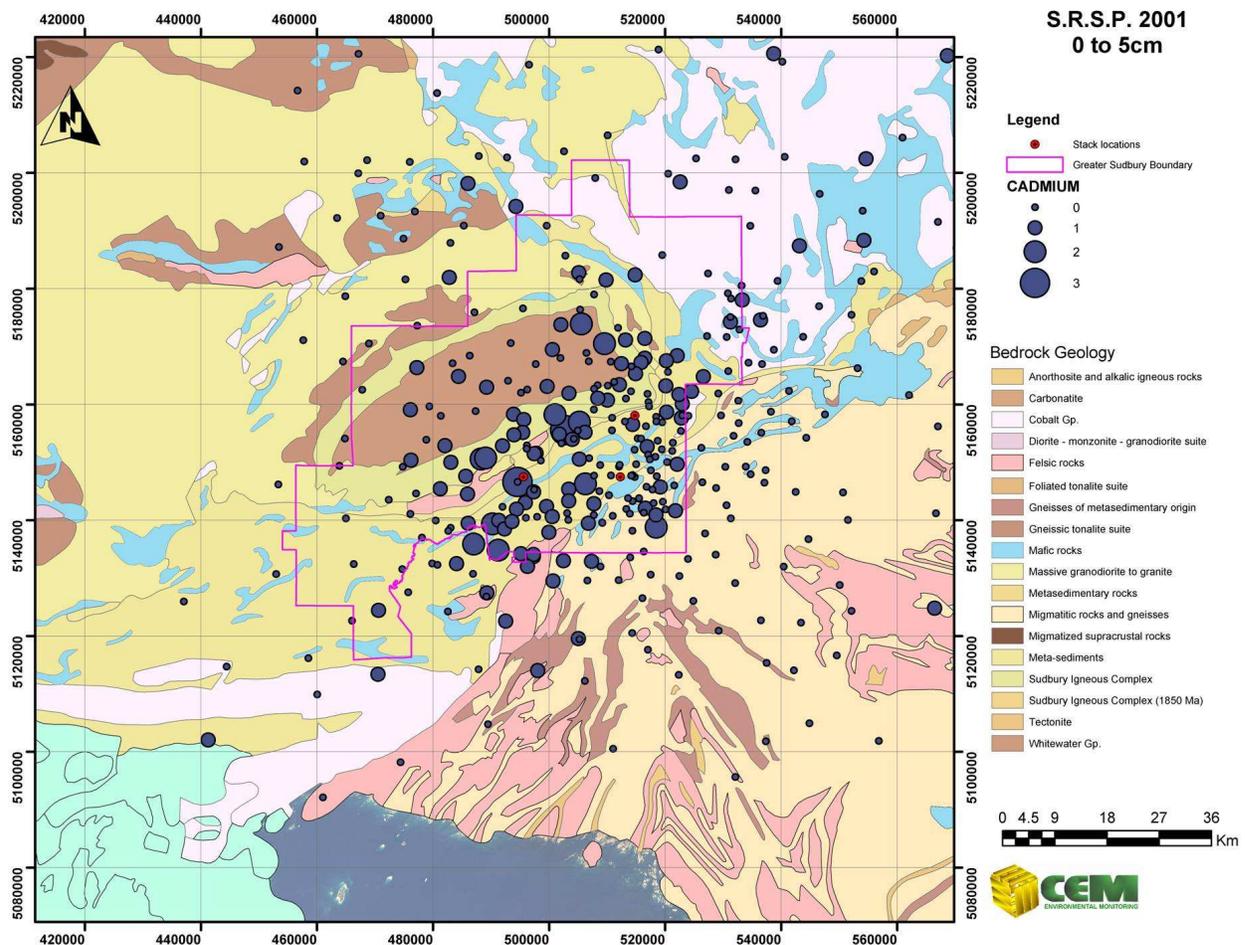


Figure 33: Distribution of cadmium in the 0-5 cm layer of soils of the Sudbury Region.

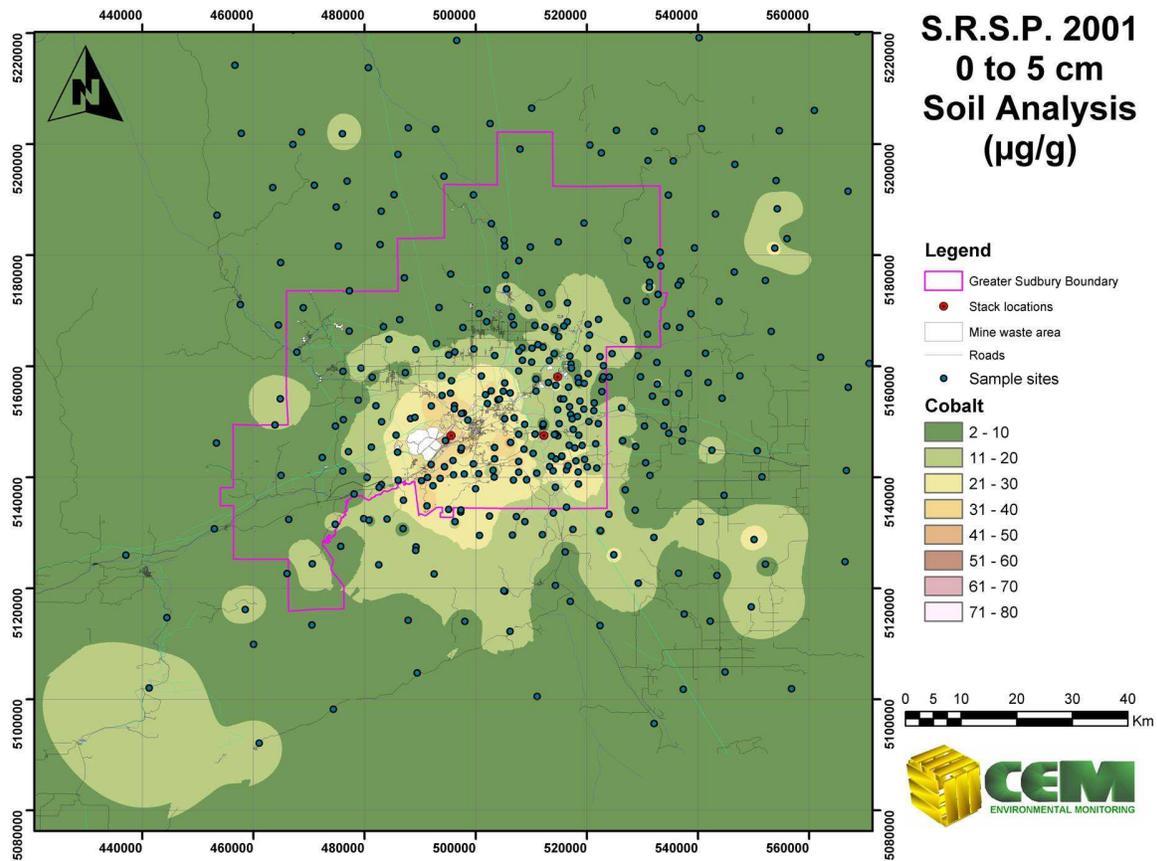


Figure 34: Distribution of cobalt in the 0-5 cm layer of soils of the Sudbury Region.

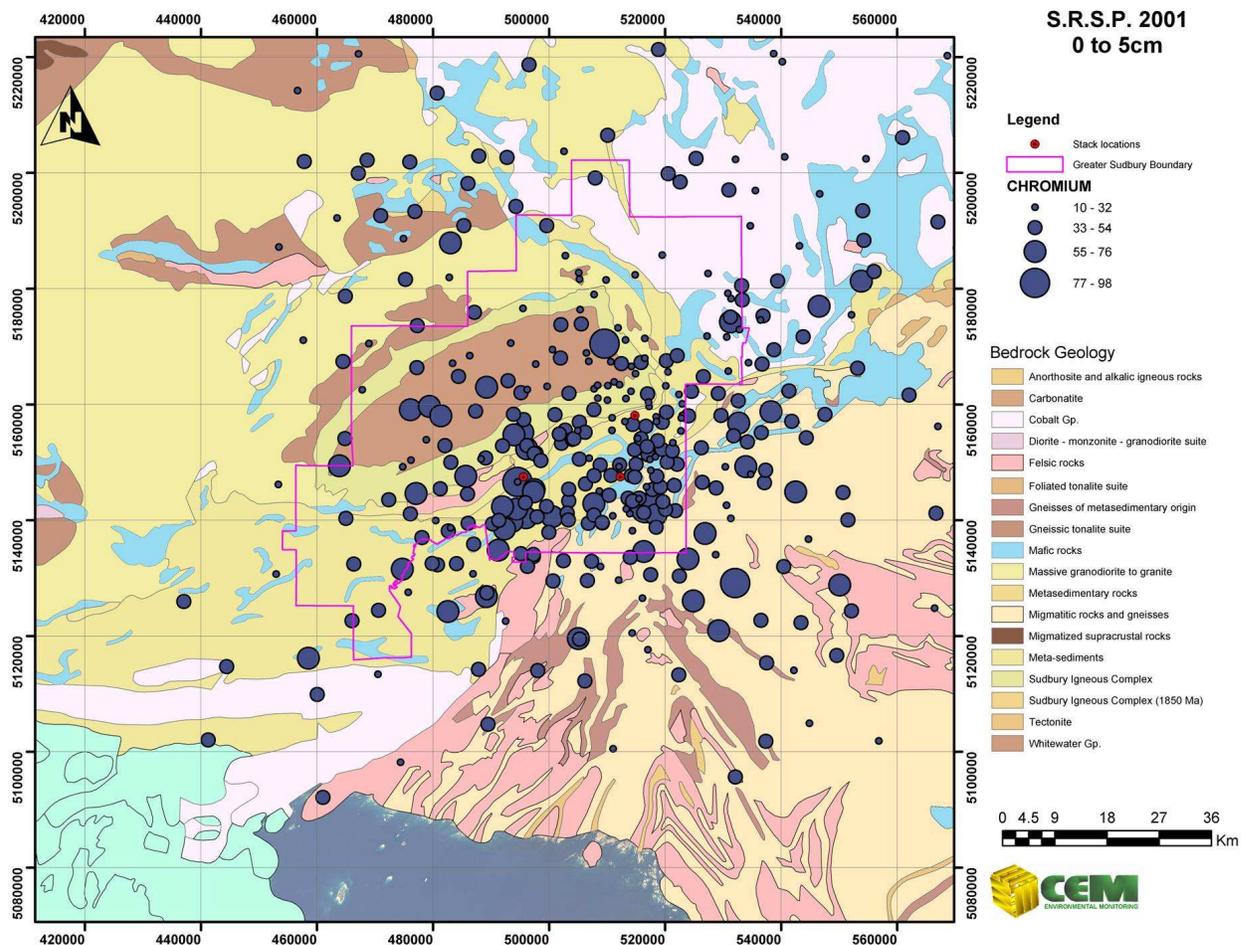


Figure 35: Distribution of chromium in the 0-5 cm layer of soils of the Sudbury Region.

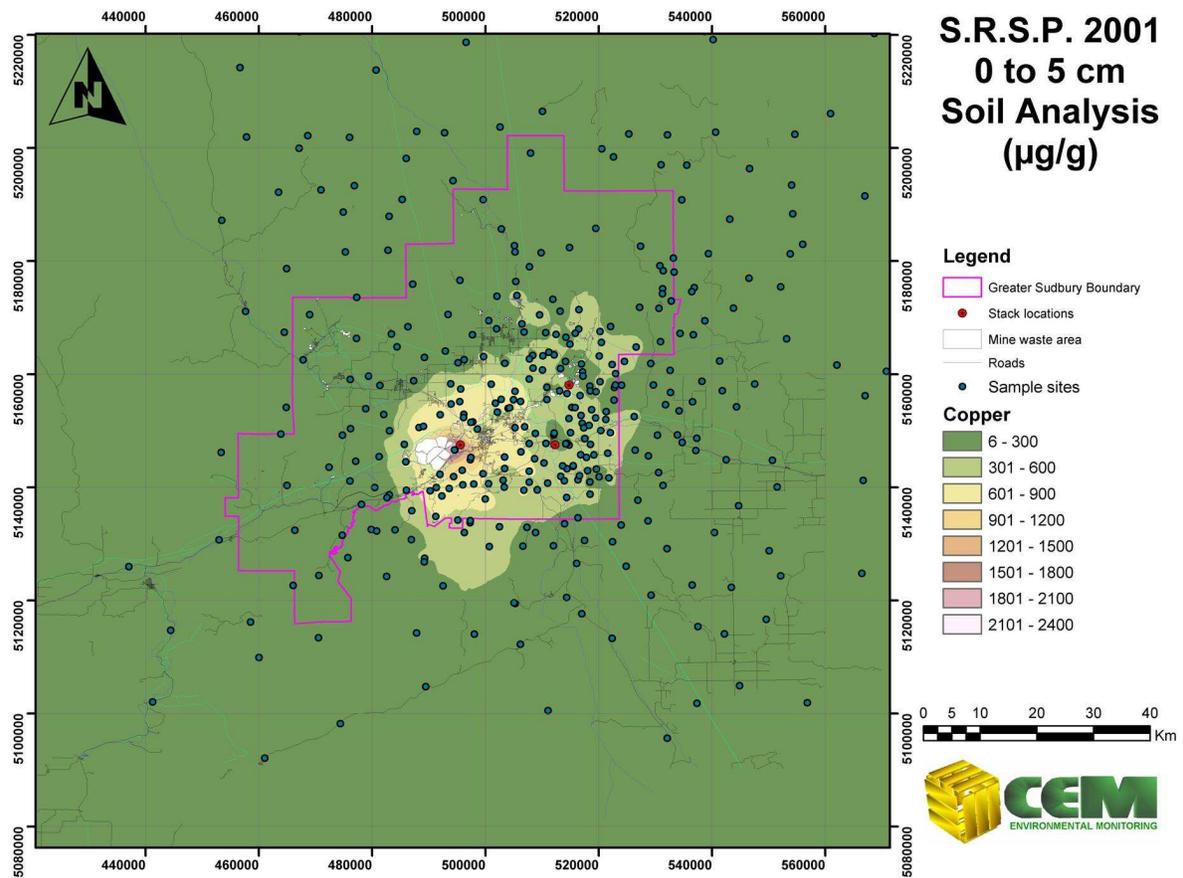


Figure 36: Distribution of copper in the 0-5 cm layer of soils of the Sudbury Region.

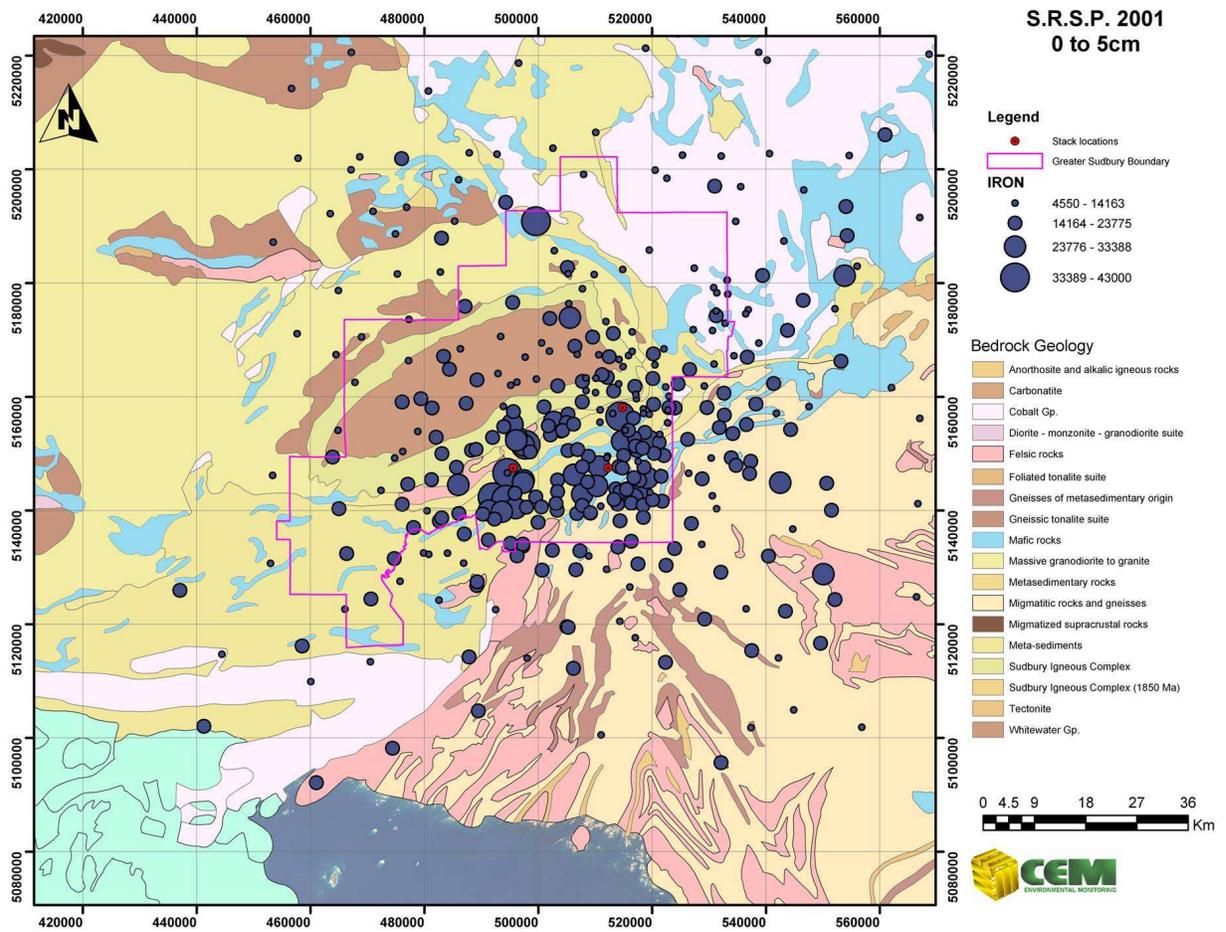


Figure 37: Distribution of iron in the 0-5 cm layer of soils of the Sudbury Region.

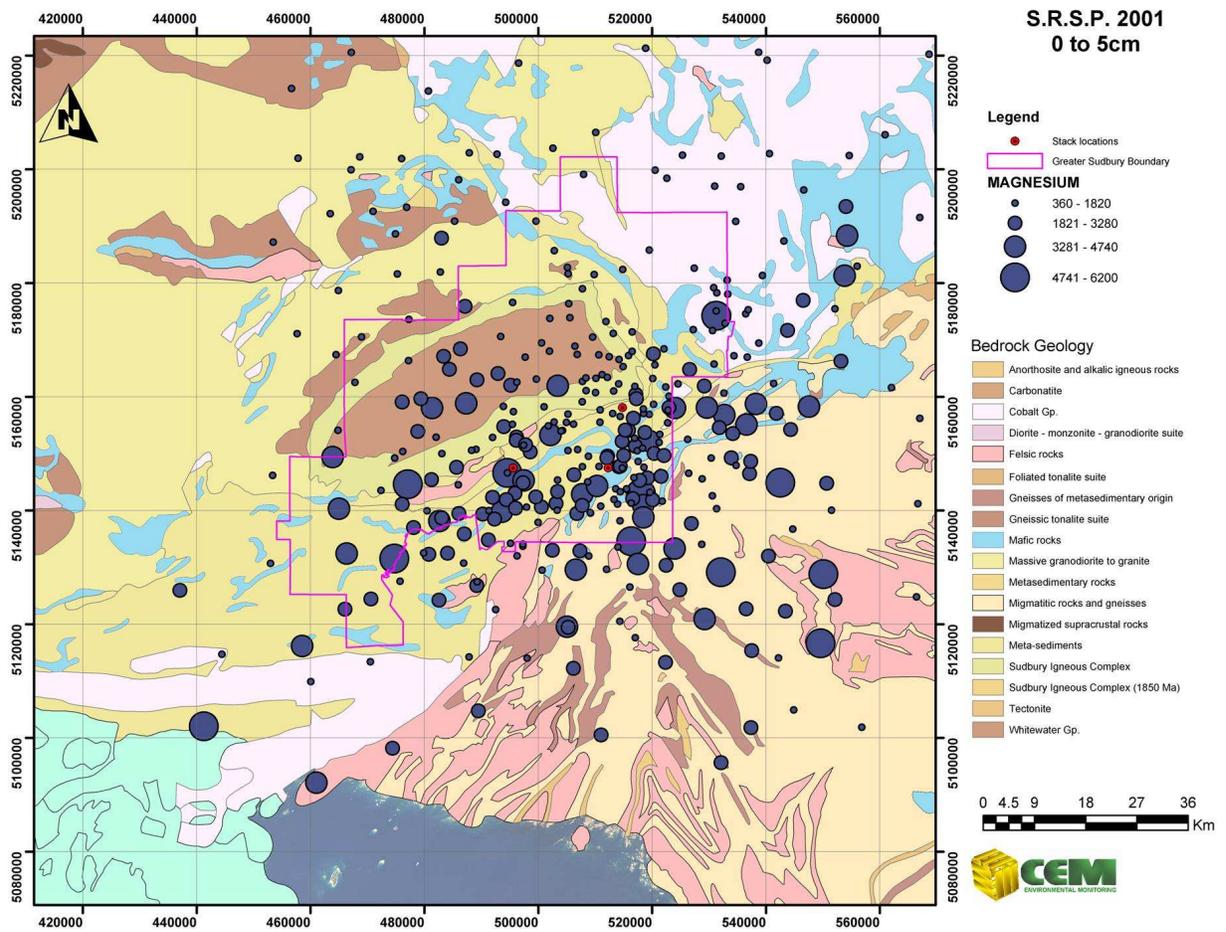


Figure 38: Distribution of magnesium in the 0-5 cm layer of soils of the Sudbury Region.

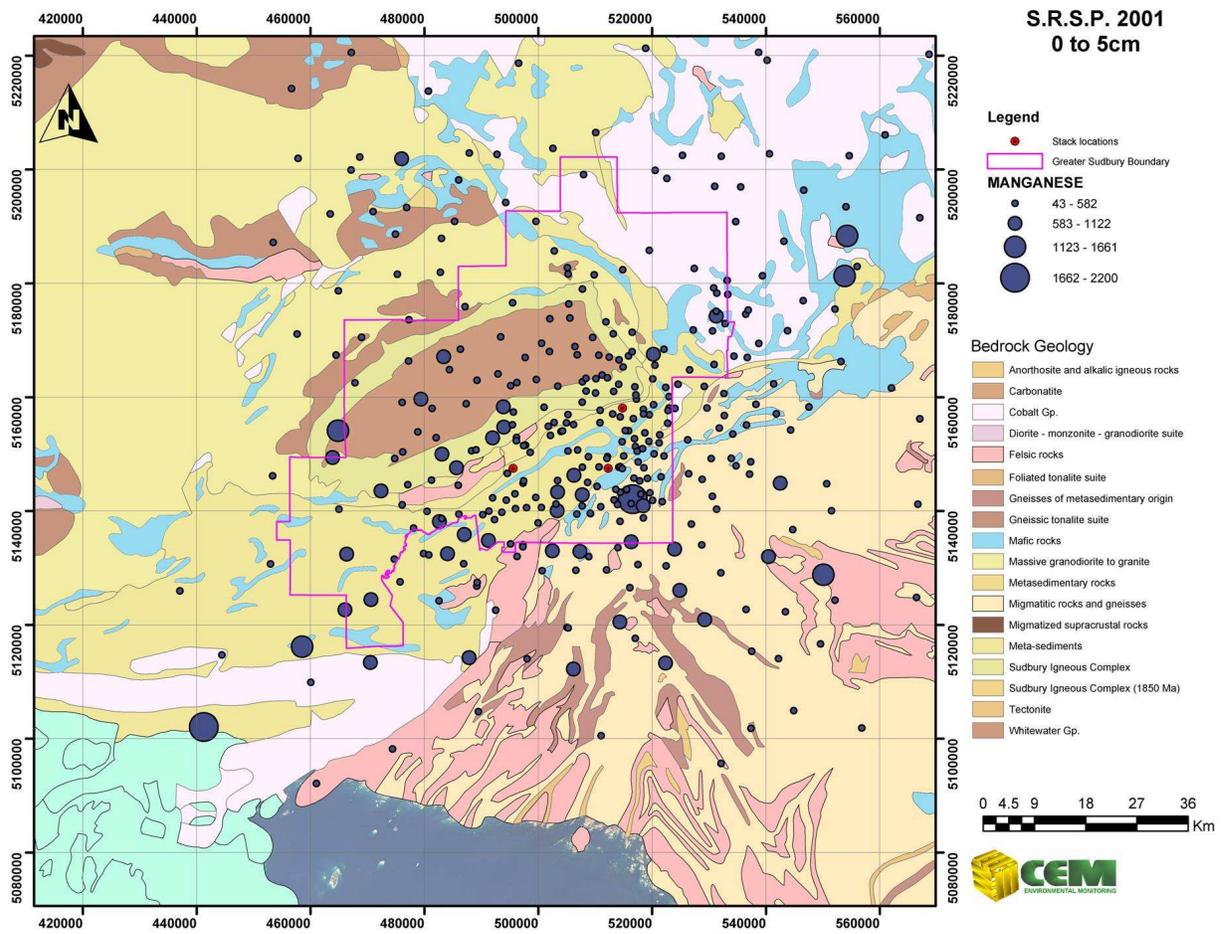


Figure 39: Distribution of manganese in the 0-5 cm layer of soils of the Sudbury Region.

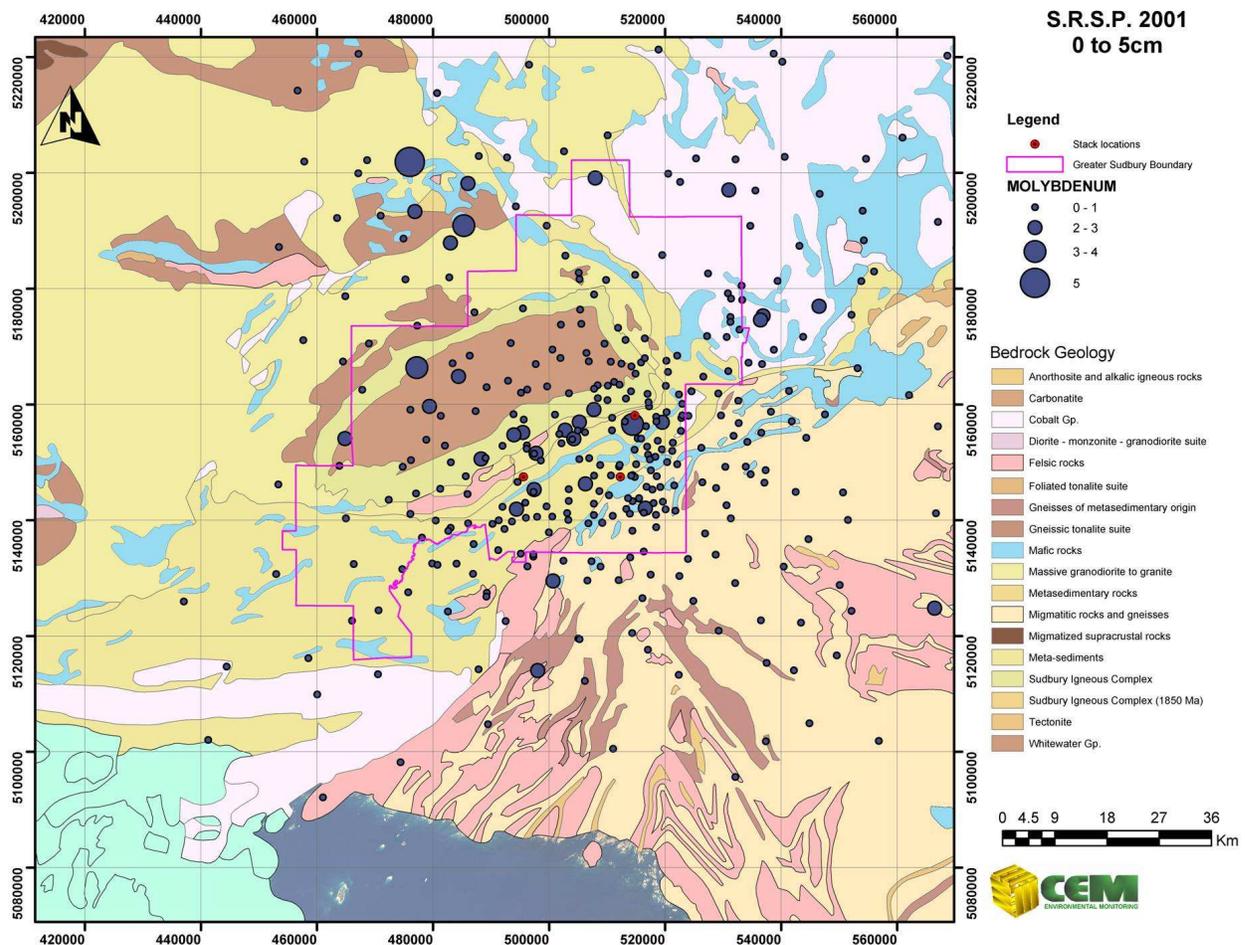


Figure 40: Distribution of molybdenum in the 0-5 cm layer of soils of the Sudbury Region.

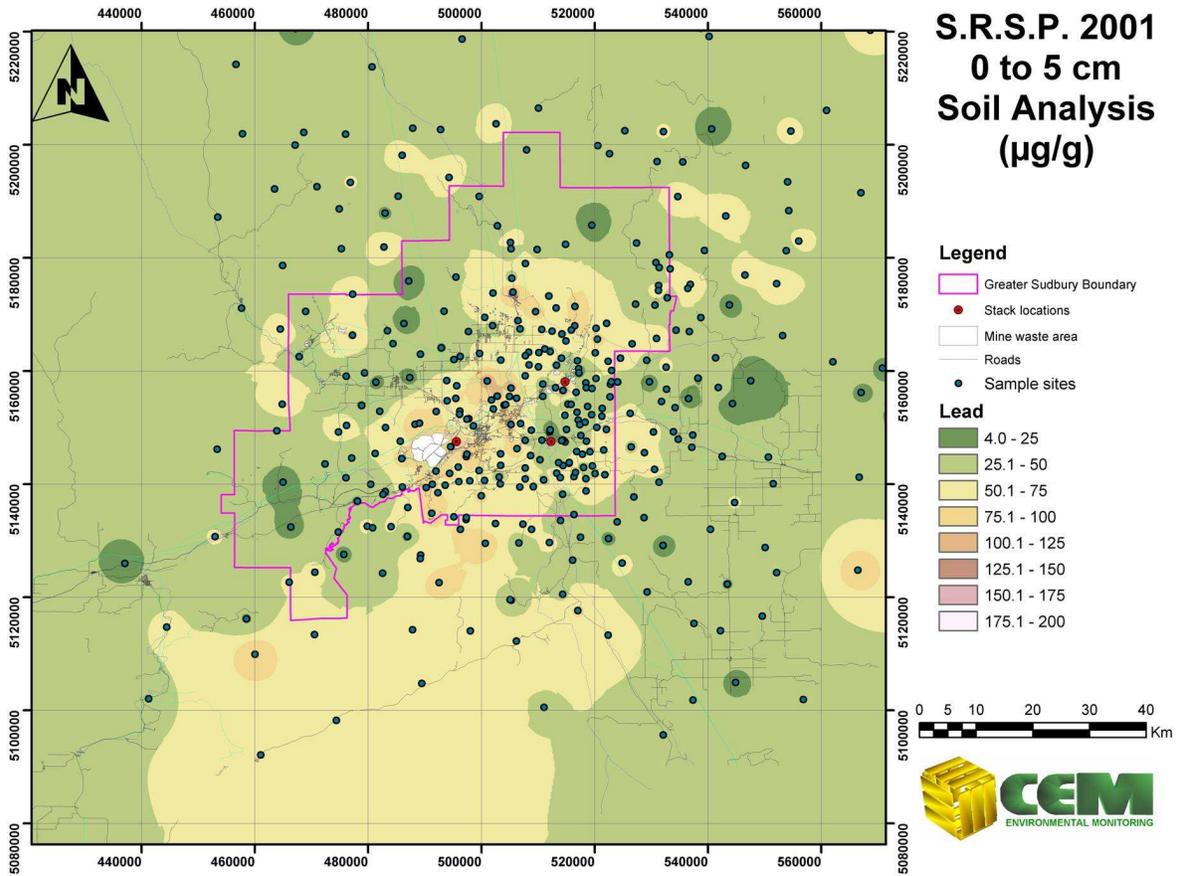


Figure 41: Distribution of lead in the 0-5 cm layer of soils of the Sudbury Region.

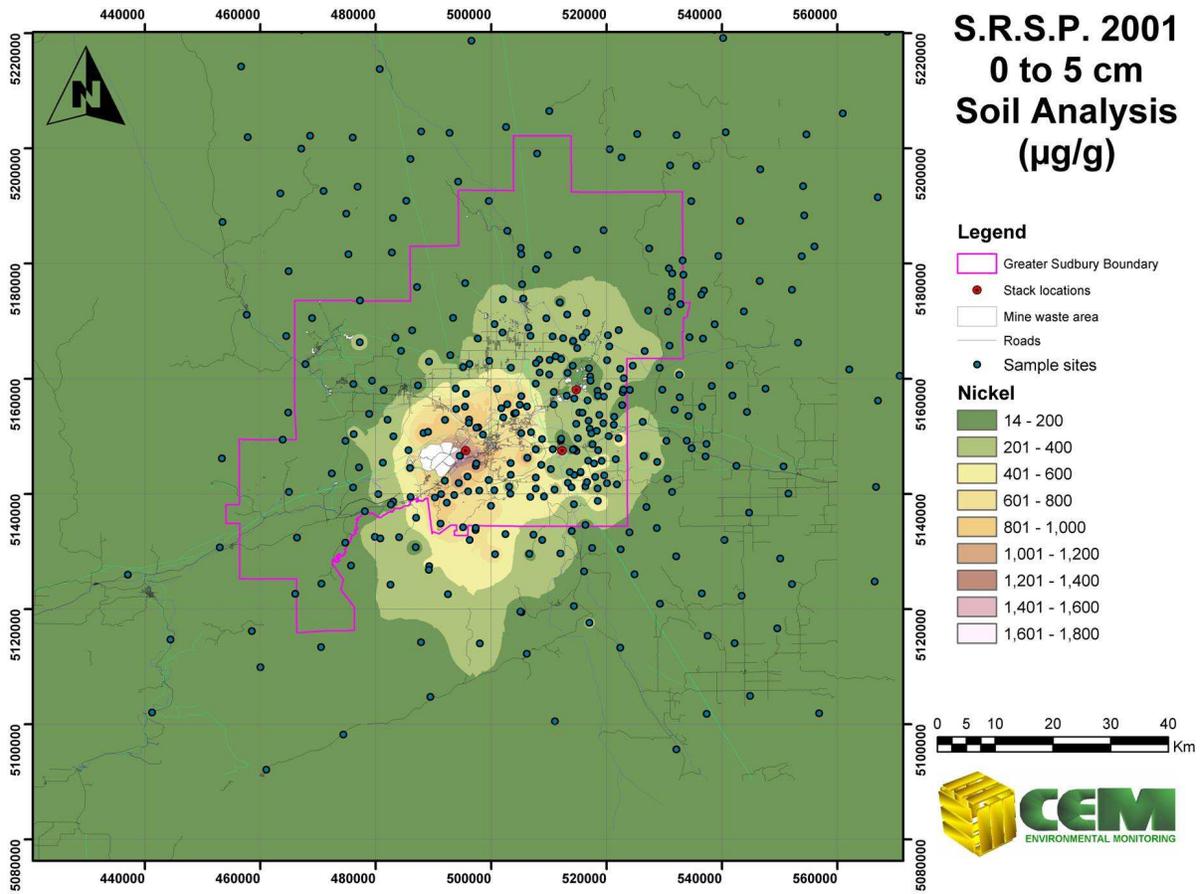


Figure 42: Distribution of nickel in the 0-5 cm layer of soils of the Sudbury Region.

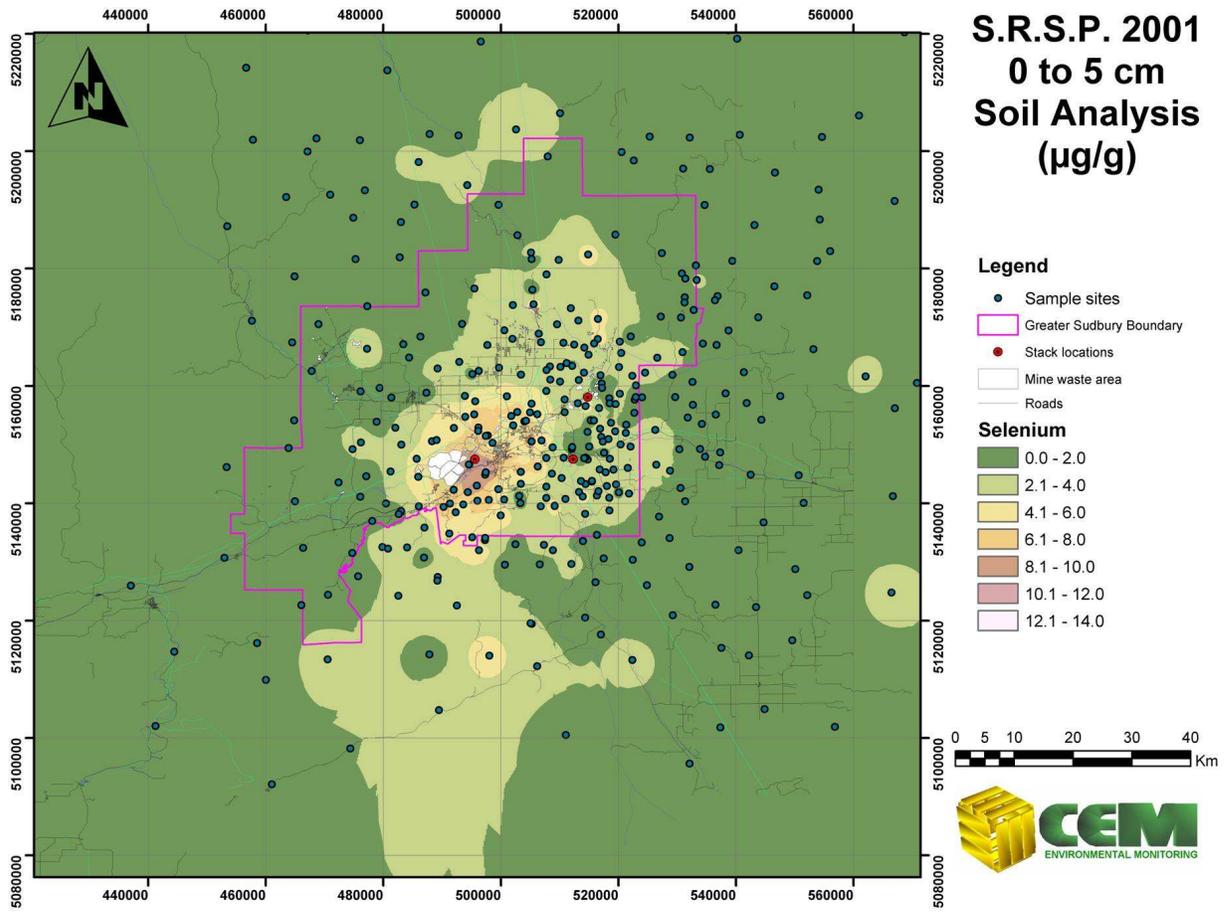


Figure 43: Distribution of selenium in the 0-5 cm layer of soils of the Sudbury Region.

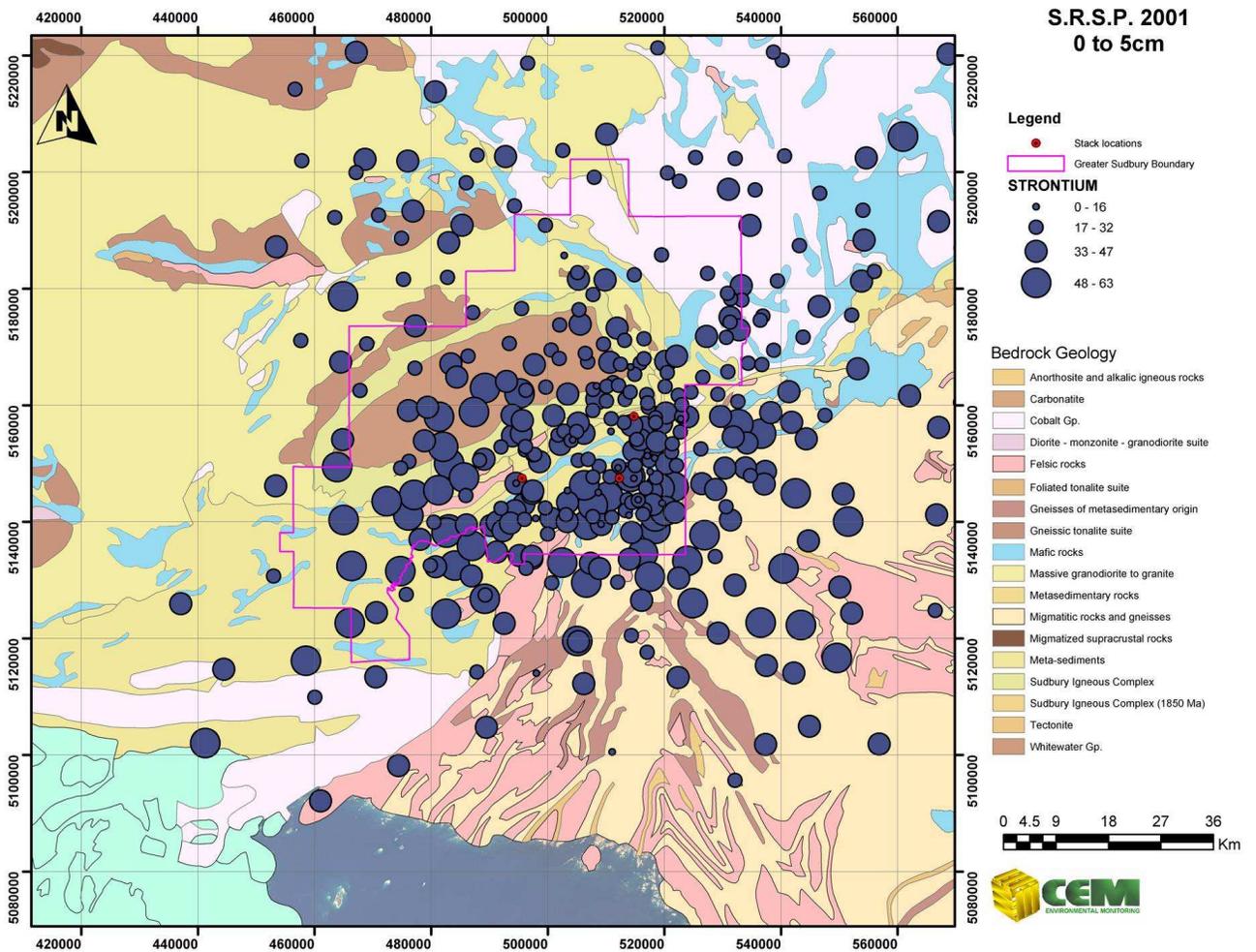


Figure 44: Distribution of strontium in the 0-5 cm layer of soils of the Sudbury Region.

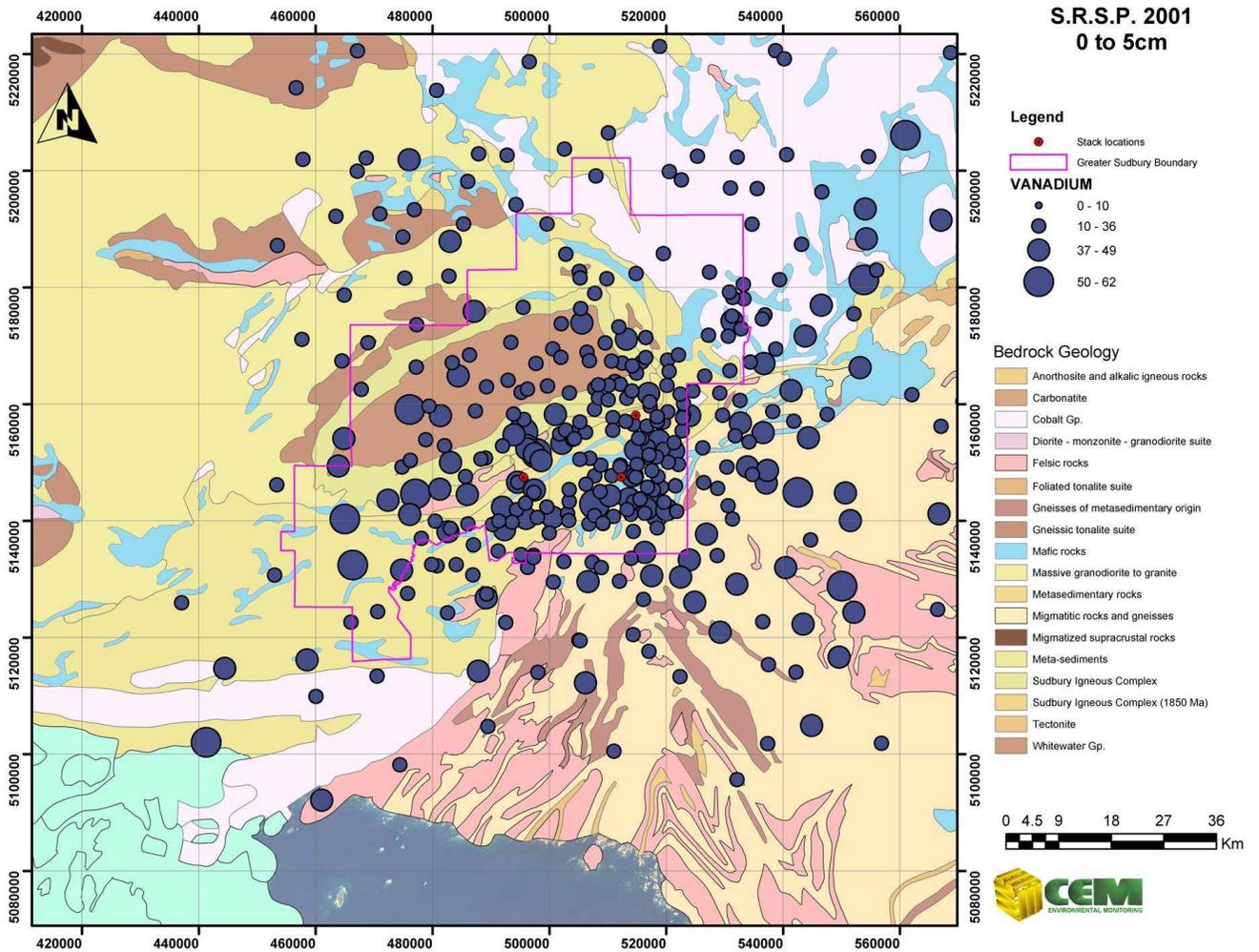


Figure 45: Distribution of vanadium in the 0-5 cm layer of soils of the Sudbury Region.

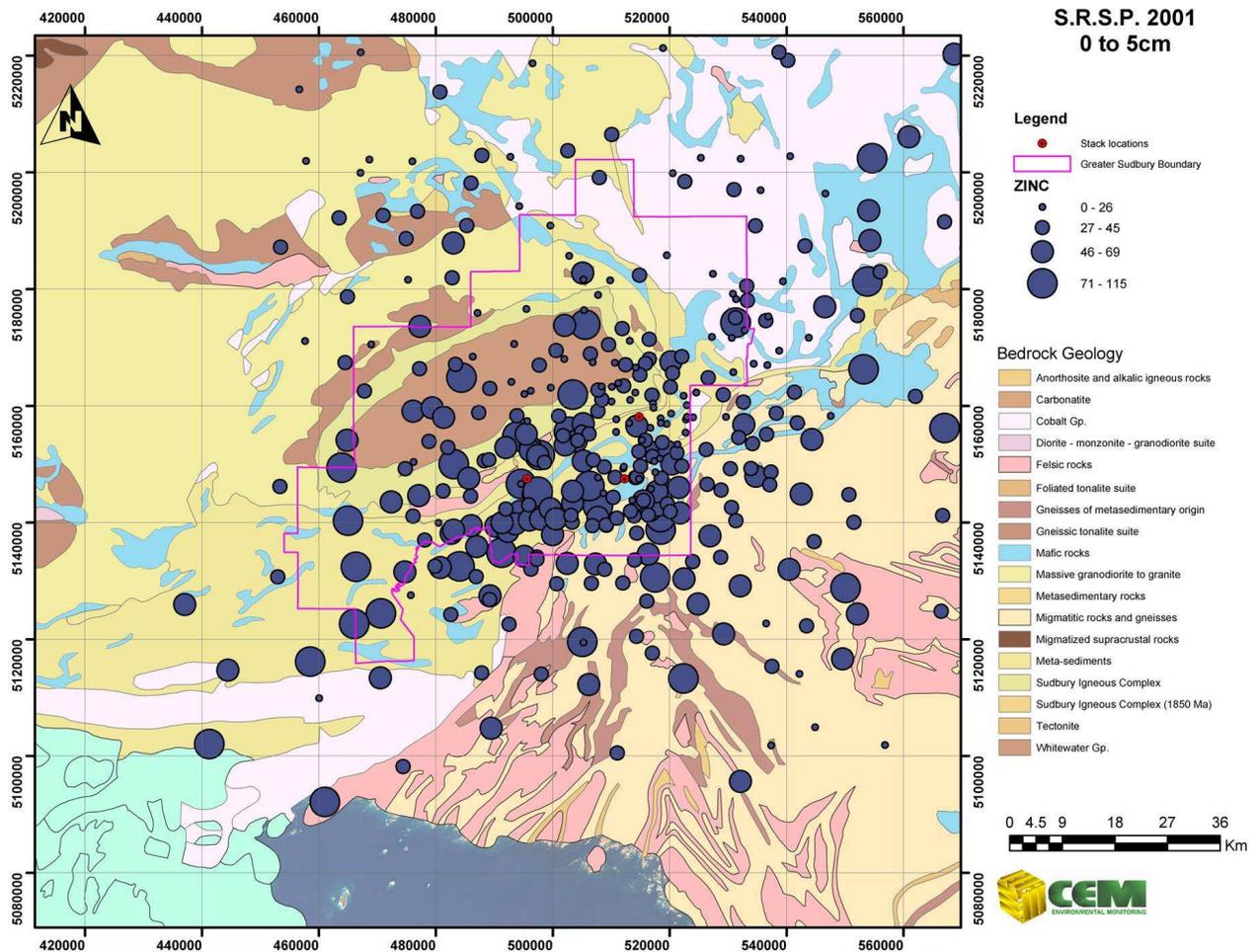


Figure 46: Distribution of zinc in the 0-5 cm layer of soils of the Sudbury Region.

Metal Correlations in Regional Surface Soil Layers

The relationships between the individual elements extracted from the individual sampled layers of the regional soil samples with *Aqua Regia* are listed in the Pearson correlation matrix (Table 15) calculated using SPSS™ with a correlation value of $r < 0.5$ being highly significant at the 0.01 level. The major elements, aluminium, iron, magnesium and manganese, are all strongly positively correlated, probably reflecting the abundance of ferromagnesian minerals partially digested by the *Aqua Regia* extractant from the soil matrix. These minerals would have been incorporated from the underlying basic metavolcanic bedrock by glacial activity. The trace elements of non-anthropogenic origin, namely

chromium, strontium, vanadium and zinc are also strongly correlated with the major elements in the regional soils.

Table 15: Pearson Correlation for the Aqua Regia extracted metal(loid)s for all samples from the 0 to 5 cm layer within the study region (n = 387 samples).

	ARSENIC	BARIUM	BERYLLIUM	CADMIUM	CALCIUM	CHROMIUM	COBALT	COPPER	IRON	LEAD	MANGANESE	MOLYBDENUM	NICKEL	SELENIUM	STRONTIUM	VANADIUM	ZINC	
ALUMINIUM	0.004	0.443 ^a	0.330 ^a	-0.017	0.418 ^a	0.730 ^a	0.297 ^a	0.008	0.698 ^a	-0.164 ^a	0.821 ^a	0.528 ^a	-0.006	0.044	-0.046	0.634 ^a	0.776 ^a	
ARSENIC		0.033	-0.028	0.290 ^a	-0.091	0.098	0.802 ^a	0.541 ^a	0.498 ^a	0.546 ^a	-0.000	-0.080	0.231 ^a	0.474 ^a	0.952 ^a	-0.143	0.088	
BARIUM			0.219 ^a	0.330 ^a	0.236 ^a	0.473 ^a	0.348 ^a	0.141 ^a	0.228 ^a	0.334 ^a	0.338 ^a	0.590 ^a	0.086	0.196 ^a	0.141 ^a	0.910 ^a	0.328 ^a	
BERYLLIUM				-0.004	0.011	0.233 ^a	0.228 ^a	-0.026	0.134 ^a	-0.000	0.217 ^a	0.090	0.016	-0.017	0.016	0.134 ^a	0.176 ^a	
CADMIUM					0.210 ^a	0.197 ^a	0.626 ^a	0.579 ^a	0.308 ^a	0.703 ^a	0.026	0.207 ^a	0.231 ^a	0.647 ^a	0.578 ^a	0.096	-0.012	
CALCIUM						0.427 ^a	0.175 ^a	0.099	0.246 ^a	-0.073	0.880 ^a	0.334 ^a	0.020	0.062	0.603 ^a	0.364 ^a	0.419 ^a	
CHROMIUM							0.443 ^a	0.208	0.606 ^a	0.082	0.717 ^a	0.474 ^a	0.246 ^a	0.274 ^a	0.173 ^a	0.854 ^a	0.690 ^a	
COBALT								0.828 ^a	0.720 ^a	0.609 ^a	0.314 ^a	0.361 ^a	0.239 ^a	0.283 ^a	0.768 ^a	0.102	0.204 ^a	
COPPER									0.887 ^a	0.687 ^a	0.086	-0.046	0.226 ^a	0.953 ^a	0.828 ^a	-0.115 ^a	0.026	
IRON										0.338 ^a	0.085	0.180 ^a	0.609 ^a	0.516 ^a	0.266 ^a	0.626 ^a	0.548 ^a	
LEAD											-0.202 ^a	0.002	0.389 ^a	0.700 ^a	0.752 ^a	-0.136 ^a	-0.109 ^a	
MANGANESE												0.002	-0.091	0.105 ^a	-0.017	0.688 ^a	0.607 ^a	
MOLYBDENUM													0.033	0.025	-0.076	0.498 ^a	0.443 ^a	
NICKEL														0.230 ^a	0.329 ^a	0.062	0.137 ^a	
SELENIUM															0.884 ^a	-0.049	0.026	
STRONTIUM																-0.160 ^a	-0.030	
VANADIUM																	0.576 ^a	
ZINC																		0.528 ^a

b Correlation is significant at the 0.01 level (2-tailed).
a Correlation is significant at the 0.05 level (2-tailed).

The elements, namely copper, cobalt, iron, lead, nickel and selenium, enriched in the surface layer (0-5 cm) of the soils of the Sudbury smelter footprint zone are all significantly correlated at the 0.01 level. This correlation (not shown) is not as strong at the 5-10 and 10-20 cm depths, indicating that there is may be minimal solubilization and translocation of the anthropogenic metal(loid)s to lower depths of the solum. This lack of consistent correlation of the anthropogenic metals in the slightly deeper soil layers may indicate that there is minimal bioaccessibility and/or bioavailability of these metal(loid)s within the region, an observation not necessarily consistent with the conjecture of Nriagu *et al.*, (1998) about long term release of metal(loid)s to regional waters as a result of soil weathering.

Metal Enrichment in Regional Soil Surface Layers

Table 16 summarizes the mean concentrations from all sites of *Aqua Regia* extractable metal(loids) for all soil layers sampled during the regional survey program. Although this data summary does not account for the potential decrease anthropogenic in metal(loid) concentration with distance form the smelter foci, the enrichment of antimony, arsenic, cobalt, copper, lead, molybdenum, nickel, selenium and zinc in the surface layers (0 to 5 cm) may be indicative of particulate fallout from regional smelting operations. The surface

organic soil layers (LFH horizons) effectively act as a filter retaining the airfall and preventing translocation to underlying mineral horizons, an observation also described for the Kola region of Russia (Nikonov *et al.*, 1999; Koptsik *et al.*, 2003). The retention of the anthropogenic metals in this filter zone is further suggestive of a relatively low solubility and bioavailability of metals in the high temperature particulates.

In order to evaluate if the metal(loid) content of the 0 – 5 cm layer is derived from natural or anthropogenic sources, an approximate enrichment factor (EF) was calculated for the above elements using the following equation: $EF = ((M) / (Al)_{LFH}) / ((M)_{pm} / (Al)_{pm})$. Enrichment factors ranging between 0.5 and 2 can be considered in the range of natural variability, whereas ratios greater than 2 indicate enrichment from anthropogenic inputs (Hernandez *et al.*, 2003; Shotyky *et al.*, 2000). The enrichment factors calculated in this study are normalized to Al as a reference element because Al is relatively immobile in the solum, and there is minimal indication of Al additions to the soils from the industrial sector. This approach in use Al as a reference element must, however, be interpreted with caution because of the incomplete dissolution of Al-bearing phases in both the soils and parent materials by *Aqua regia*. Such enrichment estimates are more rigorous if based on total elemental concentrations using analytical techniques such as XRF, or analyzing solutions by ICP-AES or ICP-MS following either hydrofluoric acid digestion or fusion with acid digestion of the resultant glass.

The calculated EF values do, however, suggest a strong anthropogenic influence in the concentrations of the metal(loid)s Sb, As, Cu, Pb, Mo, and Se in the 0 – 5 cm layers of regional soils. Cadmium, although at concentrations below detection limits for many of the soil parent material samples may also be enriched in the surface (0 – 5 cm) layers of the regional soils. The lack of enrichment for elements such as Cr, Co and Zn in the surface layers (0 – 5 cm) suggests that there has been minimal anthropogenic output of these elements from the industrial activity within the region. This enrichment of specific elements in the 0 – 5 cm depth layers suggests that the LFH horizons which dominate 0 – 5 layer act a filter preventing the translocation of the aerosol particles to the deeper soil horizons.

Table 16: Mean concentration of Aqua Regia extractable metal(oids) from the individual layers of all sites sampled in the Sudbury region, along with calculated enrichment factors for the surface (0 - 5 cm) layer calculated using aluminium as an immobile element.

Depth	Aluminum	Calcium	Iron	Magnesium	Antimony	Arsenic	Barium	Beryllium	Cadmium	Chromium	Cobalt	Copper	Lead	Manganese	Molybdenum	Nickel	Selenium	Strontium	Vanadium	Zinc
	%				$\mu\text{g gm}^{-1}$															
0 - 5 cm	1.00	0.31	1.59	0.18	0.13	14.81	89.44	0.01	0.36	38.72	12.45	261.4	49.98	306	0.30	263.1	2.19	32.90	31.13	39.09
5 - 10 cm	1.34	0.28	1.68	0.23	0.04	9.72	61.77	0.02	0.01	38.88	7.17	101.2	14.96	232	0.13	81.5	0.60	34.98	37.81	31.61
10 - 20 cm	1.72	0.32	1.92	0.32	0.04	3.80	63.45	0.01	0.00	44.04	7.30	49.7	8.90	215	0.11	50.6	0.17	38.04	40.29	33.70
Parent Material	1.78	0.58	2.28	0.62	0.02	1.11	98.37	0.15	na	56.37	8.97	26.4	5.91	293	0.11	36.13	0.06	43.86	45.31	29.75
0 - 5 / Parent	0.56	0.53	0.70	0.29	7.96	13.34	0.91	0.09		0.69	1.39	9.92	8.46	1.04	2.65	7.28	37.09	0.75	0.69	1.31
EF _(C-0-5)	0.6	0.5	0.7	0.3	8.0	13.3	0.9	0.1		0.7	1.4	9.9	8.5	1.0	2.6	7.3	37.1	0.8	0.7	1.3

Enrichment factor $EF = ((M) / (Al)_{LH}) / ((M)_{pm} / (Al)_{pm})$

However, copper, known to be chelated by soil the potentially mobile soil humic acids, appears to be slightly translocated to the 5-10 cm layer in these undisturbed forested soils of the Sudbury region. Arsenic and lead exhibit a similar depth distribution pattern to copper, an observation in agreement to the data describing total metal concentrations in soil horizons documented in Table 9. The possibility of vertical translocation of specific elements further supports the conjecture of Nriagu *et al.*, (1998) that release of anthropogenic metals from regional sola may affect dissolved metal levels in regional lakes for perhaps hundreds of years. The evidence for translocation also points to the potential slow solubility and potential bioavailability of the some anthropogenic metals currently stored as particulates in the surface layers of regional soils.

Zonation of Metal Enrichment in the Sudbury Smelter Footprint

The regional geochemical maps (Figure 28 to 46) indicate that the loading of the aerosolic particular fallout from the regional smelters follows an ellipsoid, with a dominant SW – NE axis. The graphs in Figure 47 illustrating the concentrations of the individual anthropogenic metal(oid)s along a gradient from the smelter zone centroid indicate the impact of the smelter ejecta tends towards regional background approximately 120 km from the heart of Sudbury. This estimate of regional impact of smelter emissions agrees well with those estimated using metal accumulation on lichen thalli as deposition indices (Tomassini et al,

1976), although the latter study could not provide an estimate of regional soil background because the lichens grow on a rock substrate. This estimate also compares with a calculated distance to regional background in humus of between 50 and 110 km (Henderson *et al.*, 2002; McMartin *et al.*, 1999; Zoltai, 1988) for the smelter in the Flin Flon area of Manitoba , and a zone of 40 to 50 km for the Horne Smelter in the Rouyn-Noranda area of Quebec (Henderson *et al.*, 2002). Goodarzi *et al.*, (2001, 2002) documented enrichment of a series of six elements (As, Cd, Cu, Hg, Pb and Zn) in soils of the Trail area to a distance of 26 km from the smelter, concluding that, using associated moss bag studies, the enrichment of mercury and arsenic in the regional soils was not attributed to smelter activity. These authors emphasized the need for high quality atmospheric deposition data to supplement, and help to explain, data obtained from regional soil survey data.

The data in Table 17 document the mean concentration of the 20 *Aqua Regia* extracted elements in the 0 to 5 cm layer of the soils of this study in a series of circular zones around the centroid of smelter activity in the Sudbury region. The circular zonation does not exactly mimic the ellipsoidal zone suggested by wind rose and extrapolated map concentration data (Figures 21 to 40), but does provide an indication of the decrease in anthropogenic metal concentration in the surface soils with distance, to a final distance of 100 km at the borders of the current study zone.

The non-smelter emitted elements (aluminium, calcium, magnesium manganese, barium, beryllium, chromium, strontium, vanadium and zinc) tend to generally exhibit a similar concentration in the surface layer throughout the zones of the region, with no obvious enrichment pattern in the 0 to 5 cm layer. Some of these elements (calcium, manganese, and strontium) actually are depleted in the surface layer nearer to the smelter zone centroid. This depletion perhaps reflects the effects of earlier higher levels of soil acidification from the high sulphur dioxide washout to regional soils prior to the implementation of the modern control systems. These control systems have resulted in the sulphur dioxide from the smelting process being converted into sulphuric acid, a valuable by-product of the mineral extraction process.

The metal(loid)s which are influenced by anthropogenic or smelter processes, on the other hand, show distinct concentration drops in the 0 to 5 cm layer with distance from the smelter zone centroid, a characteristic response to point source emissions documented in most studies (eg. Goodarzi *et al.*, 2001, 2002; Henderson *et al.*, 2002; Koptsik *et al.*, 2003; McMartin *et al.*, 1999; Nikonov *et al.*, 1999; Zoltai, 1988). The last zone (60 to 100 km) may exaggerate the drop in concentration with distance because the data are predominantly from the outer portion of the survey region with the 16 km cells at the extreme corners of the square.

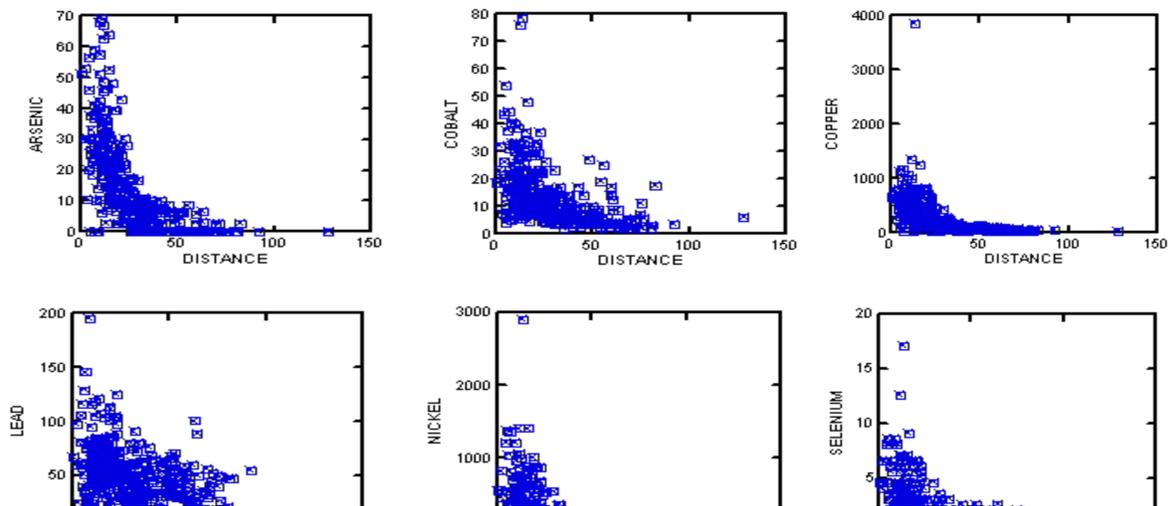


Figure 47: Graphs illustrating the concentrations of the individual anthropogenic metal(loid)s along a gradient from the smelter zone centroid indicate the impact of the smelter tends towards regional background approximately 120km from the heart of the Sudbury metallurgical region.

Table 17: Mean concentration of metal(loid)s in the 0 to 5 cm layer of sampled soils within concentric zones around the Sudbury smelter region. The centre of the circular zones is at the centroid of the three smelters in the region.

Parent Material Influence Metals										
Aluminum	Calcium	Magnesium	Manganese	Barium	Beryllium	Chromium	Strontium	Vanadium	Zinc	
<i>(ug gm)</i>										
0 to 5 km	8564	2036	1510	220	80	0.03	37	23	26	35
5 to 15 km	9980	2649	1918	265	81	0.02	38	28	31	39
15 to 30 km	10054	3286	1853	308	91	0.00	40	35	31	40
30 to 60 km	9730	3154	1773	344	92	0.02	38	35	32	39
60 to 100 km	8720	3025	1556	343	87	0.02	36	33	29	41
Anthropogenic Influence Metal(loid)s										
Antimony	Arsenic	Cadmium	Cobalt	Copper	Iron	Lead	Molybdenum	Nickel	Selenium	
<i>(ug gm)</i>										
0 to 5 km	0.24	30	0.52	23	545	19145	62	0.40	582	4.4
5 to 15 km	0.18	30	0.41	19	511	19352	58	0.33	450	3.3
15 to 30 km	0.14	14	0.52	14	283	16205	53	0.23	307	2.3
30 to 60 km	0.09	3.1	0.19	7.2	82	13789	43	0.29	104	1.1
60 to 100 km	0.13	0.57	0.17	4.6	33	11620	40	0.19	47	0.7
Parent Material	0.02	1.11	na	8.9	26	22800	5.9	0.11	36	0.06

RECOMMENDATIONS

The following are a series of recommendations for further study to provide key data to further develop an understanding of the effects of anthropogenic emissions on the soils, landscapes and watersheds of the Sudbury smelter. Several key data gaps in the following areas became apparent during the course of the study.

Area Sampled

The key data gap relates to the actual area sampled in this study. Relative to studies in both Flin Flon and Rouyn-Noranda conducted by the Geological Survey of Canada researchers, the current survey only samples to a distance of approximately one half (50 km) from the smelter zone centroid. As the other studies indicate that the impact is still detectable to in excess of 100 km, the sampling design should be further extended by selecting random points within another four (4) series of 16 km cells to a distance some

95km from the smelter centroid. Two (2) 32 km cells should then bound the study area. This extension will give the outer zone of sampling at approximately 160 km from the smelter centroid. This sampling design may lead to impact zone overlaps with the mining operations of the Timmins and Rouyn-Noranda areas, but the true extent of the Sudbury operations would be much better defined.

Clay Mineralogy

To date, there has been no research describing the clay mineralogy of the soils of the Sudbury region, aside from two studies to the northwest in the Chapleau area. Acidification of soils has been demonstrated to cause accelerated weathering of clay minerals in the smectite-rich soils of western regions of Canada. Given the importance of clay-sized minerals in trace metal and nutrient retention in soils, detailed mineralogical determinations on a series of pedons within the Sudbury smelter footprint are crucial to determine the effects acidification and metal loading on the individual minerals. This knowledge is also needed to enable accurate prediction of the long-term effects of the liming and fertilization program, which is key to the regional re-greening initiatives, on metal absorption by clay mineral species and on metal retention within the sola. The information will help predict present and future bioavailability and mobility of metals if the pH and physicochemical properties of the soils are changed with revegetation processes, or with enhanced land management programs.

Chemical and Mineralogical Nature of Emissions

A detailed mineralogical, micro-chemical and release study of the particulate matter trapped in the bag-houses of the smelter complexes would positively identify the materials currently emitted by the smelters, and provide insight into their potential availability to the biosphere. The results from this study, if coupled with longitudinal data from analyses at a series of aerosol sampling stations with the region, would provide data invaluable for the prediction of potential ecological and human health risk. A series of column experiments, especially if linked with freeze-thaw capabilities, will provide crucial information on the sequential availability of metalloids and metals layered in the aerosol particles for transport through the sola to groundwater and/or surface water systems.

Solid Phase Speciation

There is no detailed information on the solid phase speciation of metal(loid) compounds within the soils of the Sudbury area. The actual form of the metals within the surface and subsoils of the Sudbury region can only be ascertained by detailed chemical and mineralogical studies. The results of such studies will provide information on the potential solubility, and hence availability, of the soil-borne metals to vegetation, animals and humans.

There is also a need to understand the mechanics and chemistry of the land reclamation program to ensure that process does not cause more problems than are resolved by modifying the availability of the complexed and adsorbed metals currently retained in the humus layers of the regional soils. These metals could potentially become more bioavailable as the pH of the soils changes over time as a result of either climate change events, or as the effects of the liming activities, so crucial in the regreening program, are minimized through the weathering of the surface applied limestone.

Bioavailability and/or Bioaccessibility of Metals

There has been no published research assessing the bioavailability and/or bioaccessibility of metals in Sudbury area soils. The large-scale projects provide concentrations of either total or acid-extractable metals within the soil matrix but have not assessed bioavailability of the metals. There is a need to study 1) speciation, 2) localization, and 3) bioavailability of metals. These studies could provide answers to crucial questions such as:

- What is the form and site of the metals in the soils of the region?
- Is any vegetation in the agricultural food chain a bioaccumulator, and are the metals stored in a form potentially available to humans through animal uptake?
- Is any vegetation directly in the human food chain a metal bioaccumulator, and are the metals accumulated in the vegetation in a form that is bioavailable to humans?

The latter question may be, in part, answered by the detailed Sudbury area local 'food-basket' survey being completed during the summer of 2003. This survey will not, however, provide any information on the availability of any metal(loids) in the vegetables and fruit to humans.

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