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Heavy Metal Accumulation in Soil and Jack Pine *(Pinus banksiana)* Needles in Sudbury, Ontario, Canada

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The Sudbury region in Ontario, Canada is known for the mining and smelting of high sulphide ores containing nickel, copper, iron, and precious metals. Early practice of open roast-yard mining, followed by the construction of smelters, released large quantities of sulphur dioxide and heavy metal particulates into the atmosphere. Years of intense fumigation of more than 100 million tonnes of sulphur dioxide and tens of thousands of tonnes of metal particulates created barren and semi-ban-en land near smelters (Amiro and Courtin 1981). Elevated accumulations of metal concentration in soil and vegetation have been documented more than 15 years ago within short distances of smelters (Freedman and Hutchinson 1980; Hutchinson and Whitby 1974).

There are signs of recovery as emissions have been reduced, but continued investigation and monitoring of soil and vegetation is essential to the understanding of ecosystem recovery. The present study is the first detailed report on the levels of accumulation of heavy metals in jack pine foliage from trees colonizing the semi-barren landscape of the Sudbury region. The current levels of metals in soil were also investigated and the degree of interaction among elements was determined. Such biological monitoring is needed to evaluate current abatement procedures.

MATERIALS AND METHODS

Jack pine needle and soil samples were collected from eight separate sampling plots within 15 km of smelters in Sudbury, Ontario from September 1995 to October 1995 (Fig. 1). Two other sites, each located approximately 100 km North-West and North-East from Sudbury were used as reference sites. For each sampling site, 25 g of 1 yr old needles were collected randomly from 10 individual trees. Needles were rinsed with deionized distilled water, oven dried for 16 hours and homogenized. Three soil samples were also taken from each individual site by collection of material from topsoil in intervals of 5 cm to a 15 cm depth. Soil samples were air dried, lightly grounded with a ceramic mortar and pestle, sieved to 2 mm, and stored prior to further analysis.

Metal analysis was performed as described by Carter (1993) with some modifications. Subsamples of 0.2 g of homogenized soil were digested using a combination of hydrofluoric, perchloric, and hydrochloric acids. Subsamples of 0.5 g of needle tissues were oven dried at 400 °C and digested using a modified nitric

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acid-30% hydrogen peroxide procedure (Jones *et al.* 1991) with the resultant solutions being analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for total metal concentration.

Soil and needle sample digests were analyzed for concentrations of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn. Metal analysis was performed at the Geoscience Laboratories of the Ministry of Northern Development and Mines, Sudbury, Ontario. Data quality was assessed by digestion and analysis of certified reference material for vegetation NIST 1575 (NBS 1575) and soil (Till 1, CANMET) and analytical and method duplicates. The total QA/QC (quality assurance/ qualilty control) analyzed was 25%

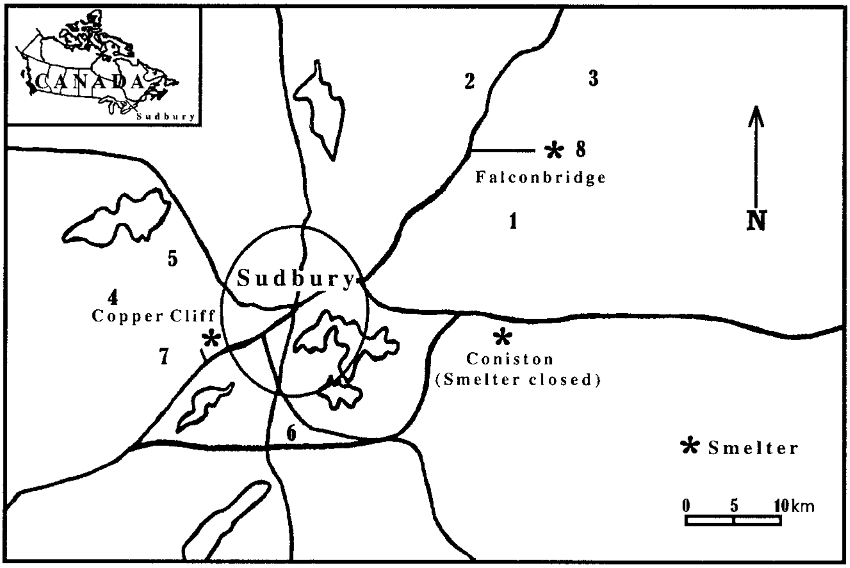

Figure 1. Location of soil and vegetation sampling sites within the Sudbury region.

Data were statistically analyzed using SPSS 7.5 for Windows (SPSS Inc.,1996). Nonparametric analysis of variance and Tukey-type multiple comparison (Zarr 1996) were performed since data transformations were unsuccessful to satisfy criteria of normality and homogeneity. Spearman rank correlation coefficients were determined to evaluate relationships among different metal concentrations.

RESULTS AND DISCUSSION

Recovery and precision for all elements in reference pine needles were within acceptable range. Copper, Ni and Pb were elevated in needle samples of trees within the Sudbury region (Table 1). The concentrations of these elements were 3-10 times higher in samples from Sudbury compared to those from control sites.

In the present study, Cu concentration in jack pine needles of trees at Sudbury ranged from 12.3 to 28.6 mg kg^{-1} (Table 1). Although, significantly different in comparison to control sites, values were within normal levels found in vegetation (Kabata-Pendias and Pendias 1992; Jones *et* al. 1991) and comparable, or lower than, those

Tablel. Metal concentrations (±SEM) in jack pine needles (n=100) from the Sudbury region and uncontaminated sites (mg kg^{-1}, dry wt)

	Sampling sites[a]									
Elements	1	2	3	4	5	6	7	8	9	10
Cd	0.22 (±0.02)bc	0.26 (±0.02)c	0.31 (±0.03)c	0.25 (±0.04)c	0.29 (±0.02)c	0.29 (±0.04)c	0.23 (±0.01)bc	0.26 (±0.03)c	0.14 (±0.02)ab	0.05 (±0.01)a
Co	0.73 (±0.03)c	0.94 (±0.05)cd	0.82 (±0.05)cd	0.45 (±0.03)b	1.29 (±0.11)d	0.43 (±0.04)b	0.88 (±0.06)cd	0.96 (±0.07)cd	0.62 (±0.08)bc	0.18 (±0.01)a
Cu	16.7 (±0.8)cd	18.8 (±1.0)d	12.3 (±1.0)bc	10.5 (±0.7)b	28.6 (±3.9)d	10.3 (±0.6)b	18.4 (±1.2)d	18.5 (±1.2)d	3.1 (±0.15)a	3.4 (±0.05)a
Fe	253 (±7)d	268 (±15)d	206 (±16)bc	145 (±7)ab	342 (±24)d	130 (±10)ab	272 (±15)d	259 (±14)d	222 (±26)cd	107 (±13)a
Mn	145 (±17)a	331 (±53)ab	879 (±125)c	808 (±146)c	746 (±43)c	313 (±59)ab	230 (±43)a	515 (±121)bc	645 (±63)c	125 (±15)a
Ni	39.8 (±2.2)bc	49.3 (±2.0)c	35.3 (±1.8)b	28.9 (±2.9)b	50.8 (±1.9)c	34.7 (±2.1)b	41.9 (±2.2)bc	50.4 (±1.8)c	4.5 (±0.4)a	3.3 (±0.25)a
Pb	4.8 (±0.2)c	5.9 (±0.3)c	4.6 (±0.5)bc	2.5 (±0.2)b	5.5 (±0.8)c	1.8 (±0.2)a	5.4 (±0.4)c	4.6 (±0.3)bc	0.5 (±0.1)a	0.6 (±0.1)a
Zn	13 (±0.8)ab	10.4 (±1.1)a	18.8 (±1.2)bcd	15.3 (±1.6)abc	15.3 (±1.6)abc	20.7 (±1.2)cd	14.1 (±0.35)abc	12.7 (±2.0)abc	66.4 (±6.4)e	43 (±2.0)e

Means in rows with common subscripts are not significantly different as indicated by Kruskal-Wallis test followed by nonparametric comparison ($p \geq 0.05$).

[a] Sites 1,2,3 = sites located around Falconbridge Ltd. smelter, sites 4,5,6 = sites located around Inco Ltd. smelter, site 7 = Inco Ltd. tailing, site 8 = site located on Falconbridge Ltd. property, site 9 = Temagami (control site) and site 10 = Low water lake (control site).

previously determined in gymnosperms and angiosperm species located within proximity of smelters (Freedman and Hutchinson 1980; Hutchinson and Whitby 1977; Negusanti and McIlveen 1990). Only one site, located north of the copper cliff smelter, exceeded Ontario Ministry of Environment and Energy (OMEE) guidelines of 20 mg kg^{-1} of Cu in vegetative tissue (Table 1). This higher concentration is presumably due to the close proximity to the Copper Cliff smelter in combination with the summer prevailing winds from the south west and south. Soil pH was measured and found not to be an important factor in variation of metal accumulations among sites.

In contrast, Ni concentration in jack pine needles of trees at Sudbury continues to be elevated. Concentrations ranged from 28.9 to 50.8 mg kg^{-1}, exceeding both typical background levels and control sites values by 7 to 10 fold. Normal concentrations of Ni in plants seldom exceed 5 mg kg^{-1} (Kabata-Pendias and Pendias 1992). Concentrations observed in Sudbury fall within excessive or toxic levels reported in vegetation, and exceed the OMEE upper limit guidelines of 30 mg kg^{-1} of Ni in plant tissues for nearly all sampling sites (Table 1)(Kabata-Pendias and Pendias 1992; Negusanti and McIlveen 1990).

Particulate emissions have decreased since the early 1970's (Negusanti and McIlveen 1990). But the present study showed that total Ni concentration is as high as those found in other species more than 15 years ago (Freedman and Hutchinson 1980). This higher concentration of Ni indicates possible continued elevated deposition in pine species surrounding smelter operations and/or higher availability for plant root uptake from soil as a result of historical deposition.

Significant correlation between Cu and Ni concentrations were found ($r = 0.82$, $p \leq 0.05$) suggesting a uniform deposition and plant uptake patterns (Table 2). This is consistent with previous studies conducted by the Ministry of Environment and Energy reporting that Cu and Ni are the major elements emitted by smelters within the region (Negusanti and McIlveen 1990). Lead concentrations in needles from trees at Sudbury were three to lo-fold higher than the control sites. But these values did not exceed the normal concentrations guidelines of 30 mg kg^{-1} of samples (Table 1)(Negusanti and McIlveen 1990).

Table 2. Spearman correlation coefficients of total metal concentrations in jack pine needles (n=100).

	Spearman correlation coefficients							
	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.00							
Co	0.44*	1.00						
Cu	0.46*	0.77*	1.00					
Fe	0.33*	0.87*	0.76*	1.00				
Mn	0.50*	0.36*	0.09	0.27*	1.00			
Ni	0.49*	0.74*	0.82*	0.57*	0.12	1.00		
Pb	0.44*	0.70*	0.86*	0.69*	0.02	0.80*	1.00	
Zn	-	-	-0.63*	-0.33*	0.10	-0.69*	-0.70*	1.00

* Correlation is significant at the 0.05 level

Iron is also considered a major element emitted from Sudbury smelters operations. Its concentrations in needles from trees at Sudbury were within normal concentration guidelines of 500 mg kg^{-1} of samples. Nonparametric analysis of variance of Cd concentrations in needles from the Sudbury region showed significant differences in comparison to the control site at Low water lake (Table 1). These values were well below toxic levels and slightly higher than normal levels found in foliage (Kabata-Pendias and Pendias 1992). Cobalt concentrations in jack pine needles at Sudbury were similar to those recorded at Temagami and only significantly different than the control site of Low water lake (Table 1). All the Co concentrations were within normal levels found in vegetation (Kabata-Pendias and Pendias, 1992). Interestingly, significant positive correlations between copper and cobalt ($r = 0.77$, $p \leq 0.05$) and nickel and cobalt ($r = 0.74$, $p \leq 0.05$) were observed (Table 2). Manganese levels were elevated in needles at some sampling sites from Sudbury and the Temagami control site. These high concentration data exceed typical values found in foliage.

In general, Co and Pb distribution patterns were similar to Ni and Cu, with sites 2, 5, and 8 adjacent to Falconbridge Ltd. and Inco Ltd. smelters, respectively, having the highest concentration. The high metal level pattern in foliage north and north west of the smelters seems to be influenced by the dominant regional wind vector from the south west and south. Surprisingly, Co concentration measured in needles from trees at Temagami control site were as elevated as in other samples from contaminated sites. The analysis of Cd concentrations in jack pine foliage revealed no remarkable difference among contaminated sites.

In contrast to the observed elevated metal concentration of Ni, Cu, and Pb, Zn concentrations were lower in jack pine needles from the Sudbury region. Indeed, Zn concentration in jack pine needles collected from the Sudbury region were three to four times lower than controls and below normal concentration ranges usually found in vegetation (Kabata-Pendias and Pendias 1992; Jones *et al.* 1991). Zinc is an essential trace element necessary for numerous enzyme activities and its uptake is influenced by many parameters. In this study significant negative correlation between Cu and Zn (r=-0.63, $p \leq 0.05$), Ni and Zn (r=-0.69, $p \leq 0.05$), and Pb and Zn (r=-0.70, $p \leq 0.05$) were found suggesting a possible antagonistic interaction (Table 2). Zinc foliar deficiency in birch leaves found around a Cu-Zn smelter in Russia was also suggested as a result of possible antagonistic interaction between Cu and Zn (Kozlov *et al.* 1995). Other cases of antagonistic interactions between anthropogenic elements Cu, Ni and Pb with Zn have been reported (Kabata-Pendias and Pendias 1992). In general, metal uptake and accumulation in plants vary with species (Lobersli and Steinnes 1988).

Recovery and precision for all elements in reference soil samples were within acceptable range. Elevated concentrations of Ni, Cu, Pb and Cd were found in Sudbury. Soil metal concentrations were highest close to smelters (Table 3). In general, sampling sites surrounding smelters had concentrations of Pb and Cd 4 to 10 times higher in the upper soil profile in comparison to lower soil depths. Greatest metal accumulations occurred at sampling sites located along the dominant wind vector having the highest surface concentration. Both Cd and Pb concentrations were frequently higher in the first 5 cm of soil in these sampling sites exceeding background levels and ministry guidelines.

Table 3. Total mean metal concentrations in soil from the Sudbury regionand uncontaminated sites; concentrationsare in mg kg^{-1},dry wt.

		Sampling sites[a]									
Elements	Depth (cm)	1	2	3	4	5	6	7	8	9	10
Cd	0-5	0.09a	1.29a	0.69a	0.25a	1.21a	0.80a	0.26a	0.27a	0.22a	0.18a
	6-10	0.11a	0.15b	0.08b	0.13a	0.26b	0.22b	0.15ab	0.22a	0.09a	0.07a
	11-15	0.08a	0.07b	0.11b	0.13a	0.33b	0.22b	0.09b	0.14a	0.08a	0.02a
Co	0-5	10a	29a	20a	7a	29a	16a	37a	31a	15a	3a
	6-10	6a	6b	7b	9a	15b	5b	35a	30a	18a	5a
	11-15	7a	6b	11b	9a	12b	10ab	12a	31a	20a	5a
Cu	0-5	93a	866a	673a	146a	808a	528a	245a	355a	48a	35a
	6-10	96a	70b	51b	34a	206b	100b	266a	310a	43a	11a
	11-15	55a	21b	36b	35a	144b	80b	135a	295a	49a	7a
Fe[b]	0-5	1.65a	2.36a	2.33a	2.28a	3.37a	2.06a	3.49a	8.48a	3.01a	0.82a
	6-10	1.29a	2.21a	1.93a	2.98a	3.72a	2.04a	3.06a	8.63a	4.44a	1.66a
	11-15	1.50a	2.08a	2.60a	3.07a	3.95a	3.49b	2.30a	9.27a	4.16a	1.55a
Mn	0-5	207a	129a	232a	464a	697a	181a	361a	1032a	516a	129a
	6-10	206a	181ab	309ab	490a	800ab	207a	361a	1084a	542a	232a
	11-15	232a	232 b	438b	464a	955b	336a	431a	1109a	542a	232a
Ni	0-5	96a	841a	410a	128a	675a	306a	229a	356a	42a	26a
	6-10	50a	69b	30b	43 a	120b	37b	183ab	335a	54a	17a
	11-15	35a	28b	37b	44 a	72b	42b	45b	320a	59a	12a
Pb	0-5	29a	202a	180a	33a	158a	85a	46a	53 a	29 a	34a
	6-10	17a	14b	15b	17a	29b	21 b	45a	51 a	14 a	11a
	11-15	14a	10b	12b	17a	30b	23 b	11a	53 a	13 a	8a
Zn	0-5	23a	38a	60a	40a	83a	52a	38a	80a	56a	22a
	6-10	17a	15b	24a	60b	68a	52a	38a	78a	48a	20a
	11-15	21a	20ab	35a	59b	65a	95a	42a	78a	46a	17a

Means in columns with common subscripts are not significantly different as indicatedby Kruskal-Wallis test followedby nonparametric comparison ($p \geq 0.05$).

[a]Sites 1,2,3 = sites located around Falconbridge Ltd. smelter, sites 4,5,6 = sites located around Inco Ltd. smelter, site 7 = Inco Ltd. tailing, site 8 = site located on Falconbridge Ltd. property, site 9 = Temagami (control site) and site 10 = Low water lake (control site).

[b]Fe concentrations are expressed in percentage of Fe in the samples (Fe%)

High concentration of Ni and Cu were found in surface horizons around the smelting operation, decreasing with both depth and distance (Hutchinson and Whitby 1974). Copper and Ni concentrations obtained in this study near both the Inco and Falconbridge smelters were also extremely elevated. Concentrations of Cu and Ni were three to eight times higher in the upper 5 cm of soil relative to both lower soil depths and control sites, respectively. Concentration on average were higher in the upper soil layers sampled than those reported previously from surveys of Sudbury and Garson regions (Negusanti and McIlveen 1990). All upper soil profile samples collected from Sudbury exceeded ministry guidelines for uncontaminated sites of 60 mg kg^{-1} of Cu or Ni in soil. In previous studies, extensive sampling of topsoil (O-20 cm) by Dudka *et al.* (1995) indicated that only 25% and 38% of 73 locations in Sudbury had concentration of Cu and Ni, respectively, below ministry guidelines.

In general the results of soil analysis showed a high spatial variability in soil metal concentration. Significant differences between soil depths for Cu, Co Mn, and Pb were found primarily at sampling sites 2, 3 (around Falconbridge Ltd. smelter) and 5, 6 (around Inco Ltd. smelter) (Table 3). Furthermore, both Cu and Ni concentrations were highest at these sites. All metal concentrations values for the upper soil profiles of these sampling sites exceeded OMEE guidelines and/or background levels (Negusanti and McIlveen 1990; Spiers *et al.* 1989). Manganese concentration exceeded background levels only at site 5 (adjacent to Inco Ltd. smelter).

In contrast, nearly all sampling sites showed no significant differences between individual soil depths for Zn and Fe concentrations. Overall, Zn was not elevated in soil in Sudbury and previous air analysis indicated that Zn is emitted only in small quantities from the smelters (Freedman and Hutchinson 1980; Hutchinson and Whitby 1977) whereas Fe is emitted in large quantities. Although Fe is naturally present in fairly high concentration in Sudbury area soils, the levels of concentration measured in the present study were comparable to those reported in previous studies (Hutchinson and Whitby 1977; Hutchinson and Whitby 1974) and were within normal guidelines of 3.5% Fe in soil established by the OMEE.

In conclusion, atmospheric deposition of heavy metals due to anthropogenic activity is still an important contributor to contaminant metal levels within the Sudbury region. Although a reduction of atmospheric metal deposition in the last 30 years has shown a decline in metal levels in soils, element concentrations within the region continue to exceed OMEE upper limit guidelines for uncontaminated soils. Elevated soil concentration of Cu, Ni Pb and Cd were frequently observed. The range of values of these metals indicates a strong impact of metal deposition from smelters within the Sudbury region. Sites adjacent to both Falconbridge Ltd. and Inco Ltd smelters showed increases between 3 to 8 times for metal concentrations in the first 5 cm profile. Spatial distribution of metal concentration indicates that study sites located primarily within dominant wind vector had higher concentration of metal contaminants compared to other sampling sites. Further studies are required to understand the possible antagonistic interaction between Cu, Ni, and Pb with Zn.

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