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Metal Content in Soil and Black Spruce (*Picea mariana*) Trees in the Sudbury Region (Ontario, Canada): Low Concentration of Arsenic, Cadmium, and Nickel Detected near Smelter Sources

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Abstract Several studies have reported high metal concentrations in soil within the vicinity of smelters in the Sudbury (Ontario) region. Continued investigation and monitoring of soil and vegetation are essential to the understanding of ecosystem recovery following the reduction of emissions from smelters and the establishment of a reforestation program. The concentrations of Cd, Co, Cu, Fe, Ni, and Zn, found in the present study were within the limits set by Ontario Ministry of Environment and Energy (OMEE) guidelines even in sites within the vicinity of the Falconbridge Smelters. The levels of these elements in black spruce (*Picea mariana*) tissues were much lower and far below the toxic levels for vegetation. This is the first documented report of metal content in black spruce populations in the Sudbury region.

Keywords Metal content · Soil · Black spruce trees · Sudbury

The Sudbury region Ontario, Canada has the best known deposits of nickel, copper, cobalt and iron ores in the world. This area is also one of the most ecologically disturbed regions in Canada (Backor and Fahselt 2004). During the past 80 years of mining and smelting, more than 100 million tonnes of sulphur dioxide and tens of thousands of tonnes of copper, nickel and iron have been released from the open roast beds and smelters. Sulphur dioxide fumigations, along with particulates containing heavy metals, devastated forests for kilometres and greatly reduced the diversity of vascular plants (Backor and Fahselt 2004). Several studies have reported high metal concentrations in soil within the vicinity of smelters and a high correlation between concentrations of certain metals in plants with distance from the source of pollution (Bagatto et al. 1993; Gratton et al. 2000).

The impoverished plant communities that are currently found in the Sudbury area are not only structurally and floristically different from plant communities found in uncontaminated areas in the basin, but they appear to have a different genetic make-up. During the last 20 years, the production of nickel, copper and other metals has remained at high levels, however industrial sulphur dioxide emission has been reduced by about 90%. This has allowed for a certain degree of recovery to occur (Backor and Fahselt 2004). This recovery has been sustained by the Sudbury reforestation program that has reached over 7 million trees planted in the Greater Sudbury Region. Most of the trees planted were conifers including Jack pine (*Pinus banksiana*), red pine (*Pinus resinosa*) and black spruce (*Picea mariana*). Estimates of the times for a naturally recovering contaminated site to reach a stable quasi – natural community structure and floristic composition are not easy to make. Progress toward complete recovery needs to be continually monitored and strategies adjusted to new analyses and information.

The objective of the present study is to determine the level of metal content in soil and various tissues from black spruce populations in Greater Sudbury region. This study will report for the first time relatively low levels of metal content in soil and plant tissues within the Sudbury region.

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Materials and Methods

Black spruce needles, branches and soil samples were collected from four separate sampling sites located at different distances from Falconbridge Smelter along a Northwest transect corresponding to prevalent wind directions (Fig. 1). One site located approximately 80 km from Sudbury was used as a reference site. For each sampling site, 25 g of needles and 50 g of branches were collected randomly from 10 individual trees. These samples were rinsed with deionized distilled water, oven dried for 16 h and homogenized. Three soil samples were also taken from each site by collection of materials from topsoil in intervals of 10–20 cm depth. Soil samples were air dried, lightly grounded with ceramic mortar and pestle, sieved to 2 mm, and stored prior to further analysis.

All analyses were performed at TESTMARK Laboratories Ltd. Sudbury, Ontario, Canada. The laboratory, ISO/IEC 17025 certified and member of the Canadian Council of Independent Laboratories (CCIL) and the Canadian Association of Environmental Analytical Laboratories (CAEAL) is accredited by the Standards Council of Canada (SCC). The laboratory employs standard QA/QC procedures, involving blank and replicate analyses and with recovery rates of 98 ± 5% in analyses of spiked samples depending on element selected, in their ICP/MS analyses reported on here. The minimum detection limits (MDL), following microwave digestion of plant tissue (Aqua Regia digestion of soil samples), for elements reported here, were: Al 0.05 µg/g (0.5 µg/g), As 0.05 µg/g (0.5 µg/g), Cd 0.05 µg/g (0.5 µg/g), Co 0.05 µg/g (0.5 µg/g), Cu 0.05 µg/g (0.5 µg/g), Fe 1.0 µg/g (10 µg/g), Pb 0.05 µg/g (0.5 µg/g), Mg 0.2 µg/g (2.0 µg/g), Mn 0.05 µg/g (0.5 µg/g), Ni 0.05 µg/g (0.5 µg/g), and Zn 0.05 µg/g (0.5 µg/g). These MDLs reflect actual sample weights and dilutions; instrument detection limits were lower.

The data for the metal levels in soil and plant samples were analyzed using SPSS 7.5 for Windows. All the data were transformed using a $\log_{10}$ transformation to achieve a normal distribution. ANOVA followed by Tukey HSD multiple comparison analysis were performed to determine significant differences ($p < 0.05$) among the five sites (SPSS 1996).

Results and Discussion

The Canadian Environmental protection act (CEPA) has scheduled lead, mercury, inorganic arsenic and cadmium compounds, and oxidic, sulphidic and soluble inorganic nickel compounds as toxic substances. Some of these substances are carcinogenic to humans and may also be endocrine disrupters, as well as strong chemical poisons (Ogilvie 2003). In 1998, INCO Limited in Sudbury met its

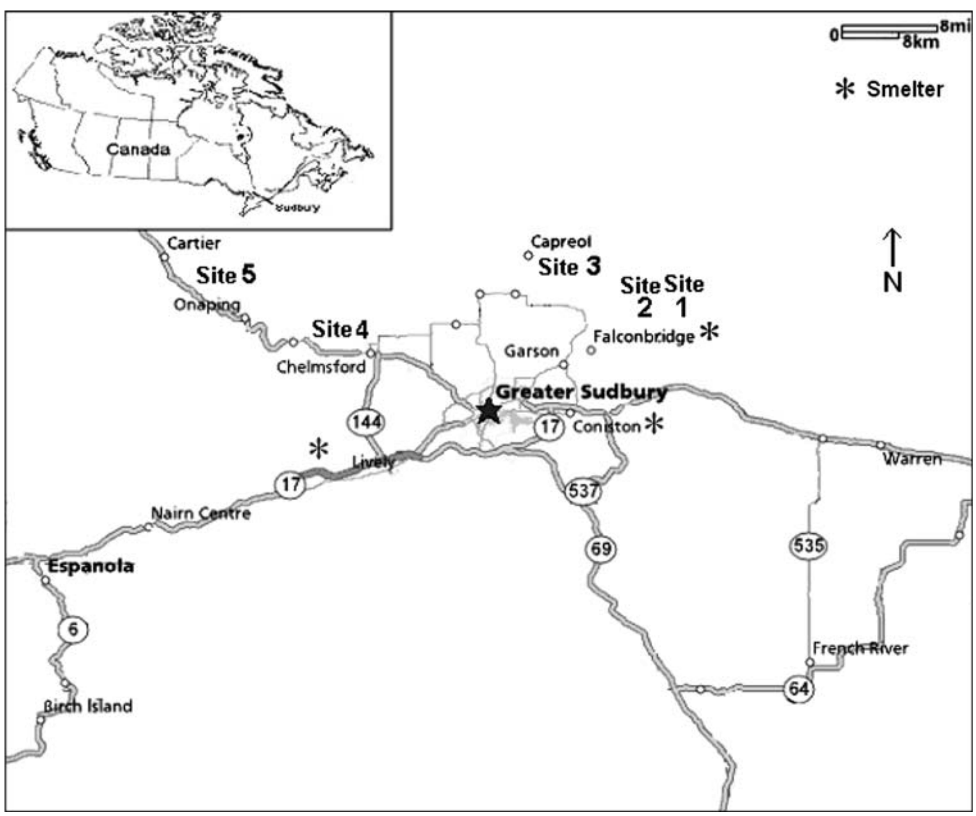

Fig. 1 Location of soil and vegetation sampling sites within the Sudbury region

Table 1 Metal concentrations in black spruce (*Picea mariana*) needles from the Sudbury region sites (mg kg^{-1}, dry wt)*

Sampling sites	Elements										
	Aluminium	Arsenic	Cadmium	Cobalt	Copper	Iron	Lead	Magnesium	Manganese	Nickel	Zinc
1	25.13 a	0.15 d	0.04 a	0.25 d	2.95 bc	59.67 bc	0.41 bc	908.17 a	1231.67 c	16.95 bc	27.85 abc
	(±9.33)	(±0.02)	(±0.01)	(±0.04)	(±0.36)	(±28.55)	(±0.1)	(±43.44)	(±60.160)	(±0.16)	(±8.15)
2	24.03 a	0.21 e	0.04 a	0.12 bc	2.32 abc	19.78 abc	0.33 abc	1451.67 b	371.83 a	20.48 bcd	12.28 ab
	(±2.62)	(±0.01)	(±0.02)	(±0.01)	(±0.21)	(±9.01)	(±0.03)	(±91.02)	(±23.66)	(±1.26)	(±3.22)
3	47.20 b	0.06 bc	0.01 a	0.04 ab	1.40 ab	0.40 ab	0.13 ab	998.67 a	353.67 a	20.97 cd	11.68 ab
	(±6.9)	(±0.01)	(0)	(±0.002)	(±0.17)	(0)	(±0.02)	(±87.18)	(±71.42)	(±1.25)	(±4.6)
4	24.87 a	0.05 abc	0.01 a	0.08 abc	2.58 bc	1.62 ab	0.27 abc	1117.83 a	606.00 b	21.08 cd	32.67 bc
	(±2.38)	(±0.004)	(±0.003)	(±0.02)	(±0.56)	(±1.24)	(±0.12)	(±71.71)	(±78.61)	(±1.95)	(±7.53)
5	20.83 a	0.02 ab	0.01 a	0.03 ab	1.43 ab	12.83 ab	0.11 ab	1133.33 a	1330.00 c	3.48 a	59.63 d
	(±1.71)	(±0.001)	(±0.001)	(±0.006)	(±0.14)	(±10.63)	(±0.02)	(±94.92)	(±20.81)	(±0.17)	(±6.93)

* Means in columns with a common subscript are not significantly different based on Tukey multiple comparison test ($p \geq 0.05$)

target of 50% reduction in toxic metal releases, reducing its combined metal emissions of arsenic, copper lead and nickel by 67%. Falconbridge Limited has achieved almost a 75% reduction in SO_2 emissions using a continuous improvement philosophy, including certification of all of its sites and facilities worldwide to the ISO 14001 Environmental Management System standard. Its emissions in Sudbury of the CEPA substances are reasonable, but the nickel emission is still somewhat high (Ogilvie 2003). Monitoring of metal content in Sudbury ecosystems is needed to assess the level of recovery following the abatements procedures by industries and the land reclamation program of the Greater of Sudbury. In the present study the level of metal content in soils, black spruce branches and needles was measured.

The measured levels of metal content in different sites are illustrated in Tables 1, 2, and 3. The highest concentration of metals was detected in soils followed by branch and needle samples, respectively. Copper concentrations in black spruce needles ranged from 3.48 to 20.97 mg kg^{-1}. These values were equal or below the Ontario Ministry of Environment and Energy (OMEE) guidelines of 20 mg kg^{-1} of Cu in vegetative tissue. Only the copper content in branches from sites 1 and 2 within the vicinity of the Flaconbridge smelter were higher and exceeded the OMEE upper limit guidelines. Overall the content of copper in black spruce tissue were within normal levels found in vegetation (Kabata-Pendias and Pendias 1992) and comparable or lower than, those previously determined in gymnosperms and angiosperm species located within proximity of smelters (Freedman and Hutchinson 1980; Hutchinson and Whitby 1977; Negusanti and McIlveen 1990; Gratton et al. 2000).

The nickel concentrations in needles and branches were below the OMEE upper limit guidelines of 30 mg kg^{-1} of Ni in plant tissue for all the sites with the exception of site two that had the nickel content in branches of 36.37 mg kg^{-1}.

Table 2 Metal concentrations in black spruce (*Picea mariana*) branches from the Sudbury region sites (mg kg^{-1}, dry wt)*

Sampling sites	Elements										
	Aluminum	Arsenic	Cadmium	Cobalt	Copper	Iron	Lead	Magnesium	Manganese	Nickel	Zinc
1	121.77 abc	0.17 a	0.36 d	1.38 b	25.20 bcd	313.33 b	7.78 bcd	494.00 ab	493.67 b	27.27 b	47.00 cde
	(±23.62)	(±0.04)	(±0.05)	(±0.28)	(±5.02)	(±109.77)	(±1.65)	(±34.48)	(±23.91)	(±4.92)	(±4.72)
2	149.50 bc	0.30 b	0.18 bc	1.21 b	27.57 cd	284.33 b	8.45 cd	854.33 bc	199.33 a	36.37 c	36.67 abc
	(±18.37)	(±0.02)	(±0.01)	(±0.12)	(±2.31)	(±55.78)	(±1.03)	(±35.62)	(±18.41)	(±1.76)	(±0.33)
3	107.63 abc	0.12 a	0.08 ab	0.39 a	11.00 ab	75.77 a	3.40 ab	815.67 bc	220.67 a	19.80 b	30.33 ab
	(±14.64)	(±0.03)	(±0.01)	(±0.05)	(±1.98)	(±9.09)	(±1.08)	(±144.82)	(±20.28)	(±1.19)	(±1.45)
4	100.57 abc	0.15 a	0.11abc	0.43 a	16.63 abc	74.23 a	5.04 abc	676.00 abc	280.33 a	20.47 b	41.33 bcd
	(±10.64)	(±0.03)	(±0.01)	(±0.03)	(±1.66)	(±17.11)	(±0.66)	(±49.68)	(±35.46)	(±1.39)	(±1.76)
5	88.87 ab	0.08 a	0.06 ab	0.21 a	17.97 abc	38.03 a	2.80 ab	524.67 ab	442.33 b	7.56 a	52.33 de
	(±20.33)	(±0.02)	(±0.01)	(±0.04)	(±2.71)	(±17.96)	(±0.6)	(±40.64)	(±59.03)	(±1.22)	(±4.66)

* Means in columns with a common subscript are not significantly different based on Tukey multiple comparison test ($p \geq 0.05$)

Table 3 Metal concentrations in soil from the Sudbury region sites, concentrations are in mg kg^{-1}, dry wt*

Sampling sites	Elements										
	Depth (cm)	Aluminum	Arsenic	Cadmium	Cobalt	Copper	Iron	Lead	Magnesium	Manganese	Nickel	Zinc
1	0–5	8260.00 b	24.70 cd	1.16 abc	7.47 bc	390.67 bcd	11600.00 a	81.70b c	830.67 bcd	113.67 a	0.47 a	17.70 a
		(±1722.79)	(±11.32)	(±0.37)	(±4.87)	(±202.12)	(±7123.43)	(±38.92)	(±290.46)	(±48.90)	(±0.03)	(±9.23)
	5–20	5520.00 abc	17.90 a	1.59 abc	16.36 a	193.70 a	5200.00 a	27.13 ab	1263.33 abc	73.93 bc	0.37 a	46.60 a
		(±190.78)	(±9.04)	(±0.97)	(±9.93)	(±154.84)	(±1205.54)	(±20.77)	(±129.91)	(±16.95)	(±0.08)	(±22.43)
2	0–5	1166.67 a	19.33 bcd	1.50 abc	8.66 abc	370.53 cd	4333.33 a	63.67 bc	695.67 abc	46.63 a	0.47 a	20.33 a
		(±49.10)	(±2.96)	(±0.23)	(±1.67)	(±192.97)	(±1369.10)	(±26.91)	(±94.96)	(±10.88)	(±0.033)	(±5.81)
	5–20	1179.00 ab	15.60 a	1.06 abc	7.77 a	172.00 a	5090.00 a	36.43 ab	737.67 ab	60.83 abc	0.43 a	23.00 a
		(±105.04)	(±5.54)	(±0.26)	(±2.7)	(±94.88)	(±3769.14)	(±24.15)	(±115.62)	(±11.54)	(±0.03)	(±2.51)
3	0–5	9263.33 b	19.33 abc	0.99 ab	2.05 ab	156.67 ab	4000.00 a	50.67 ab	100.67 ab	12.57 a	0.47 a	11.20 a
		(±1532.97)	(±2.18)	(±0.21)	(±1.08)	(±8.81)	(±2059.93)	(±1.79)	(±49.67)	(±2.7)	(±0.03)	(±2.8)
	5–20	6206.67 bcd	9.67 a	0.75 abc	0.46 a	94.17 a	2966.67 a	29.70 abc	163.67 ab	13.17 ab	0.47 a	13.30 a
		(±399.26)	(±2.16)	(±0.06)	(±0.37)	(±63.45)	(±688.79)	(±16.89)	(±24.36)	(±2.16)	(±0.03)	(±4.44)
4	0–5	3613.33 a	14.00 abc	1.79 bc	2.11 abc	152.00 abc	4600.00 a	60.20 abc	349.00 abc	20.35 a	0.43 a	24.33 a
		(±1952.38)	(±3)	(±0.63)	(±1.08)	(±70.17)	(±1069.26)	(±27.57)	(±185.37)	(±10.82)	(±0.03)	(±4.05)
	5–20	11740.00 cd	13.67 a	1.57 ac	10.60 a	65.13 a	18366.67 b	27.03 ab	2899.67 bc	186.33 bc	0.43 a	64.13 a
		(±5557.42)	(±2.33)	(±1.17)	(±3.81)	(±33.12)	(±6856.22)	(±16.04)	(±1247.36)	(±53.29)	(±0.03)	(±23.12)
5	0–5	1654.00 a	8.48 ab	1.01 ab	5.03 abc	68.77 abc	9553.33 a	47.07 ab	1440.00 cd	98.90 a	38.50 b	54.07 a
		(±357.33)	(±2.16)	(±0.48)	(±0.72)	(±24.64)	(±3384.38)	(±5.79)	(±190.78)	(±19.14)	(±6.25)	(±8.06)
	5–20	1383.33 ab	6.56 a	0.88 ab	2.78 a	46.40 a	3100.00 a	50.60 bc	1021.67 abc	56.43 abc	37.33 b	34.67 a
		(±102.68)	(±0.94)	(±0.19)	(±0.36)	(±10.54)	(±508.95)	(±7.41)	(±63.92)	(±8.63)	(±8.38)	(±0.33)

* Means in columns with a common subscript are not significantly different based on Tukey multiple comparison test ($p \geq 0.05$)

Cobalt concentration in needles and branches were 3–20 times higher in the two sites close to the Falconbridge smelter than the other three sites. Nevertheless, the levels of cobalt in black spruce tissues were within normal levels found in vegetation (Kabata-Pendias and Pendias 1992).

The concentrations of cadmium in needles were very low varying from 0.01 mg kg^{-1} to 0.04 mg kg^{-1} with no significant differences among sites (Table 1). The cadmium concentrations in branches were greater in samples from sites one and two compared to other sites (Table 2). All the values recorded for cadmium contents in black spruce tissue were well below toxic levels. Likewise, the concentration of arsenic was higher in needles and branches samples from sites one and two than samples from sites 3, 4, and 5 located over 15 km from the smelters. But all the values were below toxic levels. Similar trend was also observed for iron and lead where the concentration in needles and branches were higher in samples from sites one and two compared to samples from sites three, four, and five. No particular trend was observed for magnesium, manganese, and zinc.

Overall, arsenic and copper, content in soil was significantly higher in the top 0–10 cm compared to the 10–20 cm in the two sites close to the Smelter (Table 3). Most of the sampling sites showed no significant differences between individual soil depths for all the elements tested. The aluminum levels in sites 1, 3, and 4 were extremely high compared to other sites. Iron concentrations in the present study were much higher than those reported in previous studies (Hutchinson and Whitby 1977; Hutchinson and Witby 1974; Gratton et al. 2000). All the tests showed that the concentrations of iron in the samples analyzed were within the normal guidelines of 3.5% Fe in soil established by the OMEE. Fe is naturally present in fairly high concentration in Sudbury soils and is also emitted in fairly large quantities from smelters.

Over all, the soil content in main CEPA substances (arsenic, cadmium, and nickel) that we tested were relatively low compared to previous studies (Grattons et al. 2000). The concentrations of these elements in the soil profiles analyzed were below OMEE guidelines and/or background levels. The level of mercury, a harmful CEPA substance in soil was not analyzed since it is not released from the Sudbury smelters.

In conclusion, atmospheric deposition of metals due to anthropogenic activity has been an important contributor to contaminant metal levels within the Sudbury region. A significant reduction of atmospheric metal deposition in the last 30 years has shown a declined in metal levels in soils. The present study reported much lower soil content for the main CEPA substances and other elements than previous studies. The concentrations of Cd, Co, Cu, Fe, Ni, and Zn were within the limits set by OMEE even in sites within the vicinity of Falconbridge Smelters. The levels of these elements in black spruce tissues were much lower and far below the toxic levels for vegetations. The continued revegetation of the Sudbury greater Sudbury should help improve the Sudbury terrestrial ecosystems.

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