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Cadmium, Copper, and Lead in Soils and Garden Produce near a Metal Smelter at Flin Flon, Manitoba

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Towns in the vicinity of base metal smelters are subject to contamination from atmospheric fallout containing heavy metals. Many smelters have been in operation for decades, and have resulted in substantial accumulation of metals in the surrounding soils. Metal contamination of edible vegetation near mines and smelters has been the source of health concerns in a number of countries (Jennett et al. 1977).

One smelter that has operated for more than half a century is located at Flin Flon, Manitoba. Smelting activities in Flin Flon have been associated with a decline in the native vegetation surrounding the town. Deer mice trapped near the smelter have been shown to contain increased tissue levels of copper, lead and arsenic, and elevated hemoglobin concentrations. Background levels of these elements in tissues were not reached until approximately 40 km from the stack (Manfreda and Sabesky 1987). However even at this distance, background levels in blueberries have been reported to exceed the average Canadian level of 0.05 µg/g wet weight (McEachern and Phillips 1983).

Many Flin Flon residents utilize home vegetable gardens year after year. However little is known regarding heavy metal contamination of locally grown garden produce. Since food can contribute as much as 90% of total body uptake of metals (Ewing and Pearson 1974), it is important to identify any sources which may account for a disproportionate share. The objective of the present study was to examine concentrations of cadmium, copper and lead in soils and garden produce in the vicinity of the Flin Flon smelter.

MATERIALS AND METHODS

Flin Flon (population ca. 8,000) is located on the Manitoba-Saskatchewan boundary at approximately 55°N, 102°W. The area lies on the Precambrian Shield and surface soil is thin and patchy. Sulphide ores of copper, zinc, silver and gold have been mined and smelted in the Flin Flon region since 1930. The smelter is located on the west side of the town. A 250 m stack was constructed in

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1974. Prior to this time, emissions were discharged from a stack <30 m high. Average atmospheric emissions of sulphur dioxide between 1950 and 1985 have varied from 724 to 872 tons per day, whereas particulate emissions ranged from an annual average of 11.5 to 43.4 tons per day between 1981 and 1985 (Manfreda and Sabesky 1987). The composition of the latter is dominated by zinc, followed by iron and lesser quantities of lead, copper, aluminum, magnesium, arsenic, cadmium, manganese, selenium, nickel, chromium and cobalt. Wind in the area predominates from the northwest to northeast directions at an average annual speed of 11.1 km/hr, and prevails from the smelter toward the town 34% of the time (Manfreda and Sabesky 1987).

Samples were harvested from home gardens at the end of the 1989 growing season at 12 locations ranging from 0.29-12.8 km northeast to southwest of the smelter (Fig. 1). The variety of produce grown in the area is small, and samples consisted of crops that were available in each particular garden. The samples were washed thoroughly in Flin Flon drinking water (which originates from Cliff Lake, 1 km north of the town), then frozen and freeze-dried. The tissues were pulverized using plastic and stainless steel utensils. For root crops, only interior portions were used. Samples of the top 10 cm of garden soil were collected in plastic containers and freeze-dried.

Values for each sample were means of 3 replicates of 1.0 g each. Each replicate was digested by heating below boiling for 1 hr with 7.5 mL concentrated nitric acid and 1.5 mL 70% perchloric acid, then cooling and adding 10 mL 1% nitric acid. The material was filtered through Whatman No. 541 hardened ashless filter paper, and the filtrate was made up to 30 mL with 1% nitric acid, and aspirated into a lean air-acetylene flame in an atomic absorption spectrophotometer (Model IL151, Instrumentation Laboratory Inc., Wilmington, Mass.). The standard additions method was used for all samples in order to compensate for matrix absorption effects. Additions of certified metal standards (Fisher Scientific Co., Ottawa, Ontario) were made prior to initiation of digestion. Controls consisted of all steps and reagents in the procedure less the sample material. All glassware was acid-washed prior to use.

RESULTS AND DISCUSSION

Ranges of soil concentrations are summarized in Table 1. Concentrations decreased significantly with increasing distance from the smelter for cadmium ($r = -0.76$, $p = 0.008$), copper ($r = -0.74$, $p = 0.011$) and lead ($r = -0.78$, $p = 0.006$). Soils known to have been supplemented from outside the Flin Flon area were excluded. The best fit was achieved when both distance and metal concentrations were log transformed. All metals were strongly intercorrelated in soil (Cd-Cu $r = 0.98$, $p<0.001$; Cd-Pb $r = 0.95$, $p<0.001$; Cu-Pb $r = 0.99$, $p<0.001$).

The observed gradient in soil concentrations supported the findings of McEachern and Phillips (1983), who found an exponential decrease

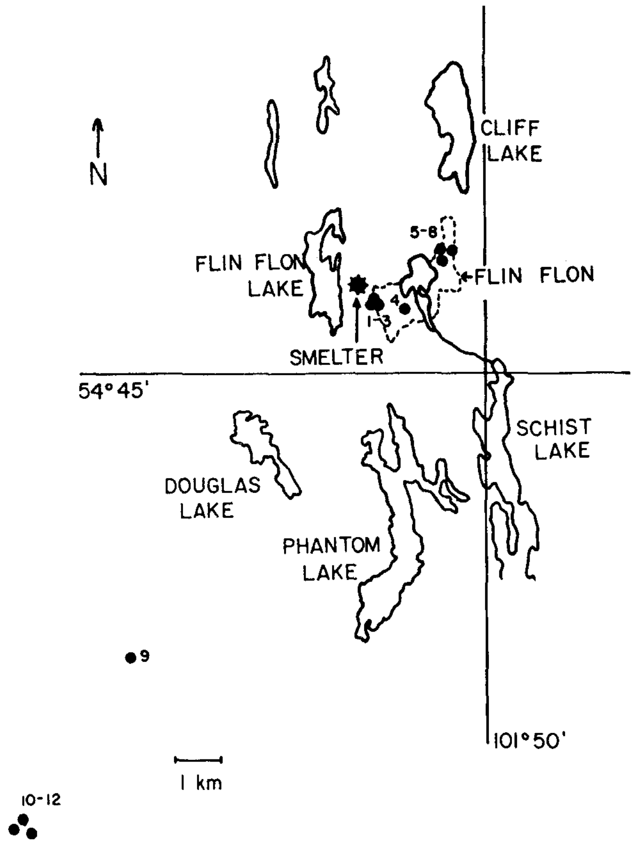

Figure 1. Distribution of home gardens sampled with respect to the location of the smelter at Flin Flon, Manitoba.

of lead concentrations in the surface soil with increased distance from the Flin Flon smelter, and of related studies on deposition of a number of metals on snow in the region (reviewed in Manfreda and Sabesky 1987). Van Loon and Beamish (1977) reported similar exponential relationships for zinc, copper and sulphate in the surrounding lakes.

In some instances, gardeners had replaced or augmented their native soil with material imported from outside the area, and the dilution effect on metals was apparent. For example, a garden located 0.29 km from the smelter yielded values of 13, 332, and 538 µg/g dry weight for cadmium, copper, and lead respectively in unreplaced native soil, and 5, 29, and 84 µg/g in an adjacent plot where soil had been brought in from The Pas area (located about 110 km to the southeast) 10 years previously.

Produce samples showed substantial variation in metal concentrations (Table 1), and such variation has been noted in other smelter town studies as well (e.g. Jennett et al. 1977). When all produce

Table 1. Summary of metal concentrations in the samples. Values are µg/g dry weight.

	Cadmium		Copper		Lead	
Sample group	x̄ (S.E.)	range	x̄ (S.E.)	range	x̄ (S.E.)	range
Fruiting parts						
Tomato	2.57 (0.50)	1.8–3.5	11.0 (1.0)	9.8–12.9	23.5 (2.6)	20.0–28.5
String bean	2.54 (1.42)	0.9–4.8	10.4 (3.5)	7.7–16.4	6.9 (2.8)	2.6–17.7
Other[1]	3.65 (0.79)	2.6–6.0	16.8 (2.9)	11.4–25.1	46.6 (6.2)	28.2–55.6
Total	2.92 (0.39)	0.9–6.0	12.7 (1.4)	7.7–25.1	24.3 (5.6)	2.6–55.6
Below ground parts						
Potato	2.80 (0.27)	1.9–3.8	9.5 (0.8)	7.2–13.5	15.2 (4.0)	4.0–25.4
Carrot	3.06 (0.31)	2.3–4.7	7.5 (0.7)	5.1– 9.9	14.8 (6.1)	3.3–47.0
Beet[2]	2.80	–	12.0	–	20.9	–
Total	2.92 (0.19)	1.9–4.7	8.8 (0.6)	5.1–13.5	15.4 (3.3)	3.3–47.0
Leaves						
Rhubarb stalk	2.45 (1.15)	1.3–3.6	10.3 (1.1)	9.2–11.4	25.8 (4.9)	20.9–30.6
blade[3]	6.80	–	127	–	278	–
Lettuce/chard[4]	3.75 (0.05)	3.7–3.8	12.9 (0.5)	12.4–13.3	42.1 (12.0)	30.1–54.0
Other[5]	4.20 (0.88)	2.5–5.5	55.6 (24.0)	10.2–92	110 (37.4)	40.6–168
Total	4.17 (0.65)	1.3–6.8	47.2 (18.1)	9.2–127	101 (36.2)	20.9–278
Soil	5.19 (0.59)	3.2–13.1	78.1 (25.1)	10.4–332	159 (49.9)	21.0–538

1 apple and raspberry, blueberry and honeysuckle berries
2 2.4 km from smelter
3 0.29 km from smelter
4 12.8 km from smelter
5 leaves of carrot, asparagus, honeysuckle

samples were pooled, significant positive correlations were observed among all three metals in plant tissue as a whole (Cd-Cu $r = 0.67$, $p<0.001$; Cd-Pb $r = 0.63$, $p<0.001$; Cu-Pb $r = 0.97$, $p<0.001$). Distance from the smelter (log transformed) was related significantly and inversely in pooled samples with plant concentrations (untransformed) of cadmium ($r = -0.44$, $p = 0.004$) and lead ($r = -0.37$, $p = 0.015$), while copper yielded a slightly better fit when both concentrations and distance were log transformed ($r = -0.52$, $p = 0.001$).

When samples were grouped into below ground and fruiting parts respectively (Table 1), relationships between metal concentrations and distance within each group were inverse but not significant, due to the large variation of values, with the exception of a significant ($r = -0.45$, $p = 0.045$) inverse correlation between cadmium and distance for below ground parts (both variables log transformed). Leafy parts showed a significant inverse correlation with distance for copper ($r = -0.67$, $p = 0.049$).

Other workers have found decreasing levels of lead with increasing distance in native blueberry plants (McEachern and Phillips 1983) and immature pine (*Pinus banksiana*) cones (Hogan and Wotton 1980 *in* Manfreda and Sabesky 1987) in the Flin Flon area.

In below ground parts, none of the metals were significantly correlated with each other in the group as a whole, nor were they correlated in individual crops, where sufficient numbers of samples were available for comparison (i.e. potatoes and carrots). In fruiting parts, cadmium and copper were significantly correlated with each other ($r = 0.86$, $p<0.001$), as were copper and lead ($r = 0.64$, $p = 0.012$). However in leaves, all three metals were intercorrelated (Cd-Cu $r = 0.82$, $p = 0.011$; Cd-Pb $r = 0.83$, $p = 0.011$; Cu-Pb $r = 0.99$, $p<0.001$).

In most cases, metal concentrations in soil were higher than in plant tissue. Any exceptions were consistently with leaf tissue. Tissue/soil ratios showed much variation among sites and crops. For cadmium, these ratios varied from 0.26 to 0.95, copper 0.03 to 0.64, and lead 0.01 to 0.72. Differences in ratios were not significant among different plant parts, although leaves showed the highest average ratios. When all plant samples were pooled, metal levels in tissue were correlated significantly with soil concentrations for cadmium ($r = 0.51$, $p = 0.008$), copper ($r = 0.46$, $p = 0.017$) and lead ($r = 0.36$, $p = 0.05$).

Plant-soil correlations have also been noted for some crops by Koeppe (1977) and Wiersma et al. (1986). While cadmium and copper showed well-defined relationships with distance in the present study, lead, although significant, was less rigorously correlated because of other potential sources for this element, for example vehicle emissions, which were superimposed on the underlying gradient from the smelter.

It is interesting that tissue/soil ratios tended to increase with increasing distance, and these relationships were significant for pooled plant samples for copper ($r = 0.46$, $p = 0.016$) and lead ($r = 0.67$, $p<0.001$). Similarly, when plant parts were examined as groups, fruiting and below ground parts each showed the same trend for copper ($r = 0.92$, $p = 0.006$; $r = 0.62$, $p = 0.029$) and for lead ($r = 0.87$, $p = 0.012$; $r = 0.86$, $p = 0.001$) respectively. Leaves did not show a significant trend. No significant patterns were seen for cadmium tissue/soil ratios. The increases with distance for copper and lead tissue/soil ratios in fruiting and below ground parts suggested that proportinately less uptake occurred at higher soil concentrations. Cadmium was taken up to a greater extent than lead in relation to soil concentration.

Analysis of variance indicated that copper concentrations showed significant differences ($F = 8.31$, $p = 0.001$) among plant parts (leaves, below ground structures, and fruits), and a similar result was obtained for lead ($F = 9.40$, $p<0.001$). Student-Neuman-Keuls multiple range tests showed that fruiting and below ground parts each showed significantly lower concentrations than leaves. While fruiting structures showed lower values than below ground parts for both copper and lead, this difference was not significant. For cadmium, differences among parts were less pronounced ($F = 2.98$, $p = 0.065$), but leaves still showed significantly greater concentrations than below ground parts. Within individual groups, t-tests showed no significant differences among various crops.

The high metal values and lack of consistent pattern for leaves with respect to soil concentrations may have been related in large part to aerial deposition and the large surface area/volume ratio of leaves. In rhubarb, leaf blades showed much greater concentrations than the petioles. That metal concentrations tend to be highest in leafy vegetables or leafy parts of plants, and low in fruiting parts, has also been reported elsewhere (e.g. Ewing and Pearson 1974, Fuchs et al. 1976, Jennett et al. 1977, Barudi and Bielig 1980, Wolnik et al. 1983, Wiersma et al. 1986). Wotton (1979) and McEachern and Phillips (1983) found that native blueberries in the Flin Flon area contain substantially lower concentrations in the fruits than in stems, leaves, or roots, and that woody perennial parts show the greatest accumulations.

Studies suggest that lead is not translocated readily from leaves, and no decline in lead content is observed after exposure and initial deposition (Carlson et al 1976). For this reason, Jennett et al. (1977) suggested that tree leaves are suitable agents for monitoring extent of lead pollution near smelters, particularly if collected at the end of the season when maximum deposition has occurred.

While differences in accumulation among various crops have been reported (Wolnik et al. 1985), such differences were not evident in the present study, as the effects of distance and soil concentration appeared to be the most important. Additional factors may have contributed towards the great variability in metal content. For example, different cultivars of the same crop may show different uptake rates under the same conditions (Koeppe 1977, Wolnik et al. 1983), while different environmental conditions may cause uptake to vary in a given crop, for example phosphorus availability, soil pH, capacity of the soil to sorb metals (Koeppe 1977) and stress such as disease and drought.

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