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Chapter 17

Atmospheric contamination of a national forest near a copper smelter in Northern Michigan

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Abstract

The Copper Range Smelter in White Pine, Michigan, was a significant source of copper for the Ottawa National Forest. Air dispersion modeling (ISC3 model) accurately predicted the pattern of peak, half-peak, and near-background smelter particulate deposition. However, the model significantly underestimated total copper loading at the medium and high deposition sites due to incomplete emissions information. Excessive copper accumulation occurred under both eastern hemlock (*Tsuga canadensis* (L.) Carr.) and sugar maple (*Acer saccharum* Marsh.) forest types in the litter layer and to a depth of 0–10 cm in mineral soils at the peak and half-peak deposition sites. Mean copper concentrations at the peak deposition sites ranged from 2260–3050 mg/kg in the forest litter and 360–875 mg/kg in the 0–10 cm mineral soil layer. The retention of copper in the organically enriched upper horizons minimized movement of copper to the 10–20 cm mineral soil layer. Copper concentrations (range 17–47 mg/kg) in the 10–20-cm soil samples were similar to background values for Great Lakes region northern hardwood forests.

1. Introduction

The Upper Peninsula of Michigan has been an important source of copper for centuries. The indigenous peoples of the Great Lakes region traded the native copper extensively with other tribes of central North America. After European settlement in the 1830s, the region developed into a significant copper mining district. The Copper Range Company constructed the largest mine-smelter facility in this mining district near the village of White Pine, Michigan, in the

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mid 1950s. Smelter emissions exceeded air permit limits and contributed significant amounts of copper-rich particulates to adjacent forest ecosystems. The mine and smelter ceased operation in 1995.

Numerous studies from Europe and North America have documented significant, adverse impacts in local terrestrial ecosystems from smelting activities. Notable examples include Sudbury, Ontario (Freedman and Hutchinson, 1980a, 1980b, 1981; Cox and Hutchinson, 1981; Hutchinson and Whitby, 1974, 1977); Gusum, Sweden (Bengtsson and Rundgren, 1984; Folkeson, 1984; Folkeson and Anderson-Brinkmark, 1988; Ruehling et al., 1984; Tyler, 1984); Harjavalta, Finland (McEnroe and Helmisaari, 2001); and Arizona (Dawson and Nash, 1980; Wood and Nash, 1976). The effects noted in these studies included acute toxicity to flora and fauna, soil acidification, heavy metal accumulation in soil, and loss of species diversity. Much of the gross contamination at these sites occurred before modern mining regulations were implemented and before air pollution control devices were made mandatory.

This study was undertaken in the fall of 1996 and spring of 1997, approximately 18 months after the smelter ceased operation. An air-quality dispersion model was used to predict particulate deposition patterns and guide the soil contamination assessment efforts. Sampling efforts focused on the predicted peak, half-peak, and low (near-background) deposition sites under mature coniferous and deciduous cover types. Study objectives were threefold:

- Assess the accuracy of the predicted deposition pattern—i.e., peak, half-peak, and near-background deposition;
- Determine whether copper deposition or accumulation/retention rates in forest litter and mineral soils were influenced by forest type:
  - coniferous (eastern hemlock—*Tsuga canadensis* (L.) Carr.) and
  - deciduous (sugar maple—*Acer saccharum* Marsh.);
- Evaluate copper concentrations and loadings in the forest floor, 0–10 cm and 10–20 cm soils.

2. Methods

2.1. Air dispersion and particulate deposition modeling

The air dispersion/deposition model used was the Industrial Source Complex 3 or ISC3 (Environmental Protection Agency, 1995b). Because of a lack of information on smelter particulate density and chemical composition, four main modeling assumptions were made to calculate particle deposition. First, smelter particles less than 10 microns in diameter were assumed to have a density of 1.83 g/cm^3 and particles larger than 10 microns were assumed to have a density of 6.56 g/cm^3. Second, the particle size distribution provided in a 1992 smelter stack test report (TRC, 1992) was assumed to have occurred throughout the life of the project. Third, each particle, regardless of particle diameter and density, was assumed to have the same percent copper. Fourth, predicted deposition depends upon the stack discharge height ($\sim$ 167 meters above ground level), plume characteristics (e.g., temperature and velocity), height of the terrain, and the roughness of the surface (i.e., topography and vegetation cover).

The isopleths of air particulate concentrations were initially derived assuming all receptor sites were at the same elevation as the base of the stack. These initial modeling results were superimposed on United States Geological Survey quad maps to identify potential impact areas. The actual elevations for each of the sample areas were then used to recalculate deposition rates.

2.2. Study area

The smelter was located in the western Upper Peninsula of Michigan (46° 45′ N, 89°35′ W), approximately 10 km south of Lake Superior at an elevation of 305 meters. The mean annual temperature is 5.4 °C, with an average annual precipitation is 85.9 cm.

The sample sites were located on a gently sloping, well-dissected glacial lake plain within the Porcupine Mountains Wilderness State Park on the west and the Ottawa National Forest to the southwest and south of the smelter, respectively. The forest type is northern hardwoods dominated by second-growth sugar maple-hemlock forests, with most of the trees less than 60 years old. The most common tree species are sugar maple, eastern hemlock, birch (*Betula* spp.), aspen *(Populus* spp.), balsam fir (*Abies balsamifera* L. Mill.), ash (*Fraxinius americana* Marsh.), elm (*Ulmus* spp.) and cedar (*Thuja occidentalis*). The soils in the area have not been mapped, but isolated descriptions suggest a Spodosol classification with loamy to sandy loam textures in the upper pedons. Spodosols are common under the northern hardwood forests in the Great Lakes region (Frelich et al., 1993; Hix and Barnes, 1984; MacDonald et al., 1991). The depth of forest litter beneath sugar maple and hemlock in the region is often similar (Hix and Barnes, 1984). Bedrock geology is dominated by Precambrian sandstones, shales, and conglomerates.

2.3. Field sampling protocol

Sampling sites were selected based on forest type, age, and lack of disturbance. All sites were located on public lands: near-background deposition near Union Springs in the Porcupine Mountain Wilderness State Park, and the peak and half-peak deposition sites were located on US Department of Agriculture—Forest Service lands in the Ottawa National Forest.

Table 1. Field sampling design

	Low deposition						Half-peak deposition						Peak deposition					
	Maple			Hemlock			Maple			Hemlock			Maple			Hemlock		
	FI	S1	S2	FI	S1	S2	FI	S1	S2	FI	S1	S2	FI	S1	S2	FI	S1	S2
#	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
∑		15			15			15			15			15			15	
∑			30						30						30			
∑									90									

∑ = sum of samples for FI = forest litter; S1 = soil 0–10 cm; S2 = soil 10–20 cm; # = number of sample points.

Three types of samples were collected at each sample point: forest litter and mineral soil from depths of 0–10 cm and 10–20 cm (Table 1). Five samples of each type were collected beneath the drip line of mature sugar maple and eastern hemlock at each of the three deposition regimes. Samples were stored in plastic bags and kept in a chilled cooler in the field. All forest litter material within a 30×30^2 cm plot was collected and processed at the lab. The mineral soil samples were collected directly beneath the forest floor sampling area.

All five samples within a given cover type for a specific deposition regime were collected within an area of about 300 m^2 to minimize spatial variability. The topographic surface at the sample sites was approximately level to minimize erosional and depositional processes.

All coarse materials were removed from the forest floor samples in the laboratory and weighed separately. Only the leaves, needles, and fine twigs (less than 2 mm diameter) were dried and divided into two subsamples; one for physical and chemical analysis and the other for archival purposes. At the lab, all samples were stored at 2 °C until processing and analysis.

2.4. Physical and chemical analysis

All samples were analyzed at the University of Wisconsin Soil and Plant Analysis Lab in Madison, Wisconsin within 2 weeks of collection using methods described in UW Extension Publication (Schulte et al., 1987). All samples were dried at 55 °C for 7 days. After drying, the samples were ground to pass through a 12-mesh screen. Total copper concentrations were determined by ICP.

2.5. Statistics

Systat Windows (version 7.0) was used to calculate all regressions, pair-wise comparisons and ANOVAs. The probabilities for the comparisons were computed using Fisher's LSD test.

3. Results

3.1. Deposition modeling

The modeling predicted a striking southwest to northeast pattern that was strongly influenced by the unique meteorological conditions created by the Porcupine Mountains and the cold waters of Lake Superior. A substantial majority of the airborne particulates were deposited northeast of the smelter on company lands or in Lake Superior (Fig. 1). Significant deposition was also predicted southwest of the smelter in the Ottawa National Forest. The modeling predicted a doubling of the deposition between the low and half-peak sites and a fourfold increase between the low and peak deposition regimes (Table 2) over public lands.

Using copper concentrations from literature values and low deposition site forest floor and soil physical characteristics, a background copper load of approximately 29 kg/ha was calculated. The measured accumulation was significantly greater than the modeled deposition plus background, indicating enrichment at all sites. The estimated background copper is about half the measured load at the low deposition sites, fourfold less than the half-peak sites and thirteen-fold less than the peak sites. Potential reasons for the discrepancies between the modeled and measured loads are described in the Discussion section.

3.2. Forest type

Tables 3, 4 and 5 summarize the copper concentrations, loadings, and statistical comparisons for the soils within and between forest types and deposition regimes, respectively. The copper concentrations and loads in the forest floors

Table 2. Comparison of estimated background plus predicted copper deposition with measured soil load[a]

Low deposition		Half-peak deposition		Peak deposition	
Soil background plus deposition	Soil load kg/ha	Soil background plus deposition	Soil load kg/ha	Soil background plus deposition	Soil load kg/ha
$29 + 6.6 = 35.6$	63	$29 + 12 = 41$	178	$29 + 27 = 56$	759

[a]Average of both cover types.
Low (near-background) deposition $= 0.164$ kg Cu ha^{-1} yr^{-1} of copper $\times$ 40 yr $= 6.6$ kg Cu ha^{-1}. Half-peak deposition $= 0.296$ kg Cu ha^{-1} yr^{-1} of copper $\times$ 40 yr $= 12$ kg Cu ha^{-1}. Peak deposition $= 0.664$ kg Cu ha^{-1} yr^{-1} of copper $\times$ 40 yr $= 27$ kg Cu ha^{-1}. Estimated soil background Cu load of 29 kg/ha (assuming 20 mg/kg Cu in forest floor, 15 mg/kg Cu in the mineral soils and low deposition forest floor and soil bulk densities and thickness represented background conditions).

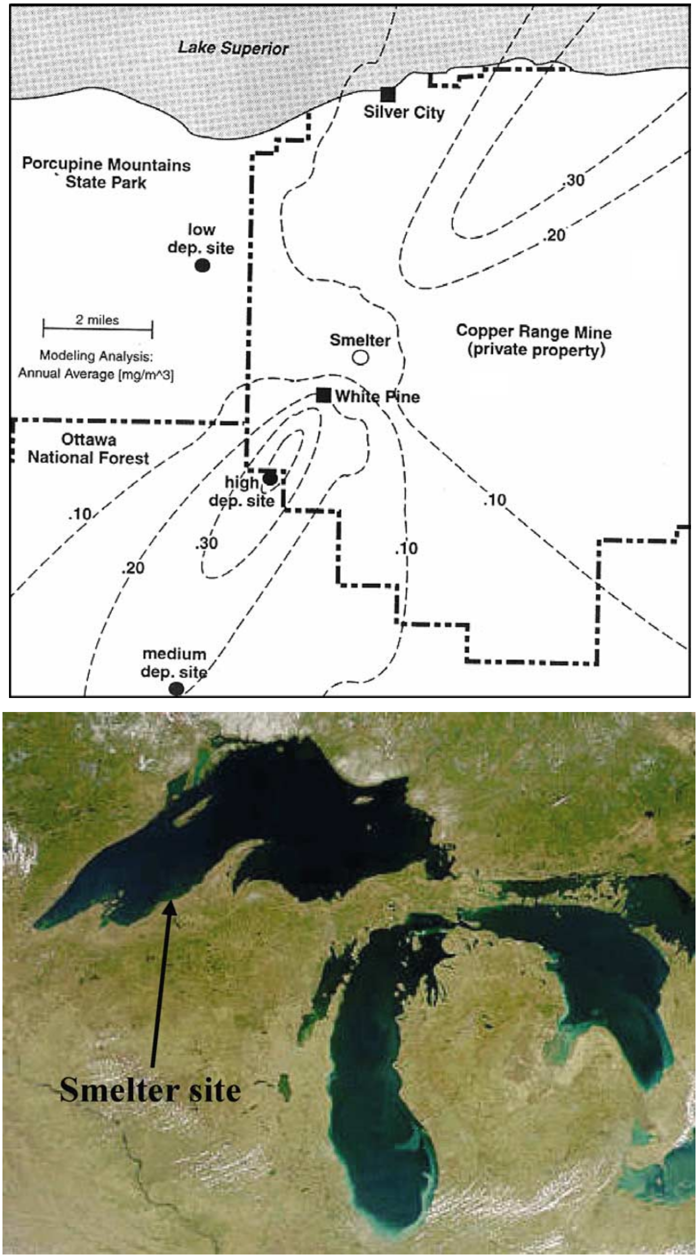

Figure 1. Predicted annual particulate deposition isopleths (mg/m^3) for the Copper Range smelter.

Table 3. Copper concentration forest floor and mineral soil layers mean (SE)

	Sugar maple			Eastern hemlock		
	Forest floor [mg/kg]	Soil: 0–10 cm [mg/kg]	Soil: 10–20 cm [mg/kg]	Forest floor [mg/kg]	Soil: 0–10 cm [mg/kg]	Soil: 10–20 cm [mg/kg]
Low	91 (9.8)	47 (2.6)	17 (1.5)	122 (7.1)	54 (3.6)	20 (2.7)
Half-peak	297 (49)	149 (29)	18 (2.2)	412 (48)	199 (42)	17 (3.8)
Peak	2260 (254)	875 (438)	47 (17)	3050 (55)	360 (89)	20 (5.9)

Table 4. Total copper accumulation in leaf litter and soil layers mean (SE)

	Sugar maple			Hemlock			Grand
	Forest floor [kg/ha]	Soil: 0–10 cm [kg/ha]	Soil: 10–20 cm [kg/ha]	Forest floor [kg/ha]	Soil: 0–10 cm [kg/ha]	Soil: 10–20 cm [kg/ha]	total
Low	0.21 (0.1)	33 (2)	21 (2)	0.72 (0.1)	49 (3)	23 (3)	127
Half-peak	0.75 (0.1)	136 (27)	26 (3)	2.2 (0.4)	169 (35)	21 (5)	355
Peak	29 (4.5)	876 (483)	76 (28)	66 (8)	449 (111)	23 (7)	1519
Total	30	1045	123	69	667	67	

Note: Forest floor loading calculations only include leaf and fine twig litter mass. Coarse branches, bark, and seed material excluded.

Table 5. ANOVA probabilities for differences in copper loading between forest types by soil depth

		Leaf litter	Soil: 0–10 cm	Soil: 10–20 cm
Low deposition	*n*	10	10	10
	p	0.001	0.003	0.522
Half-peak deposition	*n*	10	10	10
	p	0.004	0.470	0.403
Peak deposition	*n*	10	10	10
	p	0.003	0.372	0.104

n = number of samples; p = probabilities.

under hemlock were significantly greater than sugar maple in all deposition regimes. However, the hemlock forest floor (0.037 g/cm^3) was significantly ($p = 0.05$) more dense than that of the sugar maple (0.014 g/cm^3) and, adjusting for this difference, it indicates copper accumulation within the forest types was roughly similar. Copper concentrations and loads in the 0–10 and 10–20 cm mineral soils also increased with increasing deposition, but the standard errors increased substantially too. This increased variability resulted in no significant interaction between copper accumulation and/or atmosphere–canopy linkage.

3.3. Soil copper distribution

Highly significant differences ($p = 0.000$) in copper concentrations and loads existed between deposition regimes and soil layers. Copper accumulations varied greatly between the forest litter and the 0- to 10-cm soil layers. The 0–10 cm mineral soil layer contained the vast majority of the copper relative to either the forest floor or the 10–20 cm soil layer. The loading analysis results were similar to the concentration data trends with low $<$ half peak $\ll$ peak deposition for the forest floor and 0–10 cm soils.

The forest floor at the half-peak and peak sites had significantly greater copper concentrations than the mineral soils. The high concentrations were offset by the lower bulk density of the forest floors and their thinness (Table 6). There were significant increases in the soil organic matter at the half peak and peak deposition sites (Table 7) in the 0–10 cm soils. Mineral soil bulk densities increased with depth at all sites (e.g., 0.70–1.25 g/cm^3 for the 0–10 cm and 1.17–1.6 g/cm^3 for the 10–20 cm soils). There were no significant differences in bulk density for the mineral soil samples in the sugar maple and hemlock stands. As a result, the overall contribution of the forest floor to the total copper loading was substantially diminished.

The 10–20 cm soil layers had similar copper loads regardless of deposition regime. Only the peak deposition sugar maple site displayed a significant relative increase in both copper concentration and load. However, this increase was within the range reported for other non-polluted sites.

Table 6. Forest floor thickness (cm) mean (SE)

	Low	Half-peak	Peak
Hemlock	1.5 (0.16)	1.7 (0.2)	5.0 (0.27)
Sugar maple	1.7 (0.2)	2.0 (0.16)	6.0(0.7)

Table 7. Soil organic matter (kg/m^2) mean (SE)

	Sugar maple 0–10 cm	Sugar maple 10–20 cm	Hemlock 0–10 cm	Hemlock 10–20 cm
Low	8 (0.9)	3.8 (0.6)	9 (0.5)	4.5 (0.1)
Half-peak	23 (1.2)	4.1 (0.3)	24 (4.1)	4.2 (0.6)
Peak	37 (2.2)	6.5 (1.9)	30 (9.7)	4.7(1.0)

4. Discussion

4.1. Deposition modeling

The ISC3 dispersion model accurately predicted the location of peak, half-peak and low (near-background) deposition areas near the smelter. The copper concentration and loading results from the field sampling strongly confirmed the pattern predicted by the model. However, the model significantly underestimated copper loading at the half-peak and peak sites. The differences between the deposition estimates and the measured amounts can be attributed to two factors.

- Modeling results could have been improved if the physical and chemical characteristics of the particulate matter had been better defined (e.g., particle size distribution and the chemical composition and density of each size class).
- Particulate information used in the model was based on stack emissions test results from the early 1990s. The smelter operated for a number of years without any form of air pollution control in the 1950s to the mid-1960s. Deposition can be considered to have occurred in two phases—one before control and another after an electrostatic precipitator was placed in operation. Significantly greater emissions and deposition probably occurred during the pre-precipitator phase.

4.2. Forest type

Deciduous and coniferous species have distinctly different crown architectures and leaf characteristics. Factors such as longevity of the leaf-on season, leaf shape and orientation, and leaf chemistry can affect tree crown–atmosphere interactions, thus influencing particle deposition phenomena and long-term retention of copper in the forest ecosystem. According to Burton et al. (1991), Fassnacht (1995, 1996), and Miller and Lin (1985) sugar maple stands in the northern hardwood forests typically have leaf area index values (LAIs) between 6–8. Tucker et al. (1993) reported LAIs of 5–6 for dominant sugar maple trees with heights between 15–20 m. LAI values obtained from University of Wisconsin-Madison Forestry staff indicate LAIs of 5–8 for hemlock would be reasonable. The similarities in LAI values between these species suggest LAI would not have been a significant variable influencing deposition.

Comparing the substantial copper loadings in the 0–10 cm soil layers relative to the forest litter and the 10–20 cm soils does not support the contention that forest type significantly influenced deposition phenomena. The differences in copper concentrations between forest types did not significantly influence loading estimates after bulk density and organic matter factors were taken into account. The hemlock stands with year-round foliage and similar growing season LAIs were not more efficient at capturing smelter particulates than sugar maple. Particle aerodynamic and density characteristics were more influential than tree crown variables on deposition rates at these sites.

4.3. Soil contamination

Table 8 provides estimates of relatively non-polluted copper concentrations for northern hardwood forests in the Great Lakes region. Copper values were approximately 15 mg/kg (range 3–60 mg/kg) in the forest floor and 20 mg/kg (range 5–100 mg/kg) in mineral soils. The United States Environmental Protection Agency has established a maximum acceptable copper concentration in soils of 769 mg/kg for land disposal of sewage sludge on cropland (Environmental Protection Agency, 1995a). Canadian soil guidelines for residential/park land recommend mineral soil copper concentrations not exceed 63 mg/kg (CCME, 1997). These values suggest slight enrichment of the forest floors, and perhaps the 0–10 cm soils, may have occurred at the low-deposition sites. The 10–20 cm soils at the high-deposition maple site had a statistically greater accumulation of copper than the other deposition regimes, but it also had a statistically greater organic matter content. Based on these comparisons, the low-deposition site values and the 10–20 cm soils under all deposition regimes were similar to literature estimates of background copper concentrations and loadings.

Copper concentrations and loadings in the forest floor and 0–10 cm soils at the peak-deposition sites were grossly in excess of those at the low-deposition sites the background data references and most samples exceeded soil protection guidelines. Forest litter depths and soil organic matter accumulation at the peak sites were significantly greater than the low-deposition sites. At the half-peak deposition sites, copper loadings in the forest litter and 0–10 cm soils

Table 8. Background soil concentrations of copper

Freedman & Hutchinson (1)	Freedman & Hutchinson (2)	Hutchinson & Whitby (3)	Grigal & Ohmann (4)	Jepsen (5)
mean 20 mg/kg range 2–100 mg/kg	60 mg/kg	26 mg/kg	mean 11 mg/kg range 3–27 mg/kg	FF 5–20 mg/kg (0–10): 3–18 mg/kg

(1): Mineral soils; no information about specific horizons or depth. (2): Data from 1981 Sudbury study; samples of forest litter 76 km away from the stack. (3): Data from 1974 Sudbury study; soil samples (0–10 cm) 50 km away from the stack. (4): Data from a mid-1980s survey of selected Great Lake region FIA plots; forest floor samples. (5): Data from soil survey of trembling aspen plots in 1993. FF = forest floor; (0–10) = mineral soil.

were elevated and the soil standards were also exceeded. Litter depth at the half-peak sites was similar to the low-deposition sites, while organic matter in the 0–10 cm soil was significantly higher.

Copper forms strong bonds with chelate complexes (Alloway, 1995; Friedland et al., 1986). This can result in copper accumulation in the forest floor and the organically enriched upper soil horizons, with rapid decreases in concentrations to near-background levels in the underlying soil horizons. The accumulation of organic matter near smelters may be related to elevated copper concentrations adversely affecting litter decomposition rates (Freedman and Hutchinson, 1980b; McEnroe and Helmisaari, 2001). Both cover types had significantly thicker forest floors at the peak-deposition sites compared with the other deposition regimes. Soil organic matter content in the 0–10 cm soil layer increased with increasing copper deposition, regardless of cover type. The patterns of anthropogenic enrichment of copper in this study were similar to those reported in the literature.

5. Conclusions

The ISC3 air dispersion model proved to be an extremely useful tool for assessing deposition patterns and focusing sampling efforts. A lack of significant disturbance in the forested areas and the magnitude of the smelter emissions relative to other sources contributed to the success of the terrestrial verification of the model predictions. The spatial distribution predictions were exceptionally accurate, but total deposition and accumulation were significantly underestimated at the medium- and high-deposition sites. The underestimation was believed to be related to the particle density and chemistry assumptions, as well as to changes in air pollution control equipment, rather than an inherent flaw in the ISC3 model.

Excessive copper concentrations occurred under both hemlock and sugar maple in the forest litter and 0–10 cm soil layer at the peak and half-peak deposition sites in the Ottawa National Forest. Several of the sites exceeded soil guidelines established to protect plants and animals. However, the excessive accumulation was restricted to the upper soil layers, with copper concentrations in the 10–20 cm soils at these sites near background levels regardless of deposition regime or forest type. The copper concentrations for all soil layers sampled in the low (i.e., near-background) deposition stands were within acceptable soil guidelines.

In general, there were no significant differences in overall copper accumulation between hemlock and sugar maple stands. Forest type did not appear to have a significant effect on deposition phenomena or on copper movement beyond the 0–10 cm soil layer. The excessive copper in the forest floor and

0–10 cm soil layer at the higher deposition sites appears to adversely affect organic matter decomposition processes.

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