CONTAMINATION OF SOILS NEAR A COPPER SMELTER BY ARSENIC, ANTIMONY AND LEAD

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Abstract. Stack dust from a large Cu smelter near Tacoma, Washington has contaminated soil with As, Sb, and Pb. Within 5 km of the smelter 380 ppm (dry weight) As, 200 ppm Sb, and 540 ppm Pb have been measured in the surface soil (0–3 cm). Plants grown in these soils may be affected and also the consumption of plants coated with this heavy metal rich dust may be of concern.

1. Introduction

A large copper smelter, located near Tacoma, Washington, on Puget Sound, releases approximately 300 metric tons of particulate material into the atmosphere per year. This stack dust is composed of approximately 30 to 40% As, 20 to 30% Pb, 2% Sb and smaller amounts of Zn, Cu, Hg, and other metals (Puget Sound Air Pollution Control Agency). The Tacoma-Pierce Country Health Department has noted elevated levels of As and Pb in children living in areas near the smelter. Also the Seattle-King County Health Department has reported elevated levels of As in children and cattle on Vashon and Maury Islands which are located 10 km to the north and northeast of the source.

In order to better delineate the surrounding area affected by the smelter emissions, soil samples were collected by the Department of Oceanography, University of Washington, the Seattle-King County Department of Public Health and the Puget Sound Air Pollution Control Agency, and analyzed for As, Sb, and Pb. The aim of this note is to present all available data on As and Pb in soils near the smelter. The data should be of value in planning future studies involving trace metal pollution from the smelter.

2. Methods

The sampling grid was based on meteorological and topographical conditions which affect the decomposition of particulate emissions from the smelter. Soil samples were

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collected from areas where the soil had not been recently disturbed. Samples were not collected near highways, buildings or from recently cultivated land. The upper 3 cm of soil were placed in a polyethylene container and stored until analyzed. Rocks and large organic fragments were removed from the samples. The samples included material from the 0 soil horizon and/or the upper A horizon. A few samples were taken from only the lower A and/or upper B horizon to compare with the surface samples. Because Douglas fir (Pseudotsuga menziesii) commonly contain 10 to 100 times more As than other trees usually associated with them (Warren *et al.*, 1968) soil samples were not collected in the vicinity of these species. All soil samples were collected during 1972.

The soil samples collected by the Department of Oceanography, University of Washington were analyzed by neutron activation analysis. Samples were dried at 80 °C for 48 h, cooled, and 0.3 to 0.8 g were weighed and sealed in $\frac{2}{5}$ g polyethylene vials. Samples were then irradiated with suitable standards for 1 to 2 h in a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} at the University of Washington Nuclear Reactor. After cooling for 2 to 4 days, the samples were counted 0.5 to 2 h on a high resolution Ge(Li) diode detector with an energy resolving capability of 2.56 keV FWHM at 1333 keV. The ^{76}As 559 keV and the ^{122}Sb 564 keV γ-ray peaks were used for the determinations.

Samples collected by the Seattle-King Country Department of Public Health and the Puget Sound Air Pollution Control Agency were analyzed by the Western Area Occupational Health Lab., U.S. Dept. HEW, Salt Lake City, Utah (Hammer *et al.*, 1971).

Standard Orchard Leaves (National Bureau of Standards Reference Material 1571) and U.S. Geological Survey W-1 rock standard were analyzed to determine the accuracy of the neutron activation technique and the standard deviation of replicate analyses of homogeneous samples. The following mean concentrations and standard deviations were determined: Orchard Leaves 10.5 ± 0.5 ppm As, 3.5 ± 0.5 ppm Sb; W-1 2.2 ± 0.2 ppm As, 1.1 ± 0.1 ppm Sb. Recommended or certified values for As and Sb in these standards are: Orchard Leaves 10 ppm As, 2.9 ppm Sb (Bertine and LaFleur, 1972) and W-1 2.4 ppm As, 1.1 ppm Sb (Fleischer, 1965). The standard deviations for replicate analysis of several soil samples from the same location (1 m apart) were 9% for As and 12% for Sb.

3. Results and Discussion

The concentrations of As, Sb, and Pb in the soil samples are shown in Table I. The distribution of As in soils surrounding the smelter is shown in Figure 1. This distribution is of interest for three reasons: (1) The high As and Pb concentrations near the tall smelter stack (1 to 2 km) indicate that either the tall stack does not prevent dust from accumulating near the smelter and/or ground level emission from the smelter buildings or other stacks contribute a significant amount of As and Pb to the soils immediately surrounding the smelter; (2) The high levels of As, Sb, and Pb in the soils of southern Vashon and Maury Islands, indicate the stack dust is transported at least

TABLE I

The concentration of As, Sb, and Pb in soils from Vashon Island, Maury Island and the Tacoma and Seattle area. Concentrations in ppm dry weight basis

As ppm	Sb ppm	Pb ppm
Vashon Island		
43[a]	8	
13[b]		20
20[b]		70
9[b]		37
18[b]		31
4[b]		18
23[b]		21
62[b]		200
9[b]		49
19[b]		51
186[a]	61	
10[b]		38
120[b]		540
93[b]		160
Maury Island		
29[b]		72
10[b]		69
232[a]	49	
87[b]		250
338[a]	72	
100[b]		350
266[a]	204	
39[b]		23
Tacoma Area		
250[c]		410
380[c]		330
67[c]		51
85[c]		38
80[a]	31	
61[c]		84
89[c]		125
<1[c]		59
East of Tacoma		
244[a]	65	
109[a]	109	
West of Tacoma		
166[a]	63	
33[a]	12	
26[a]	11	
North of Seattle (not shown on Figure 1)		
17[a]	5	
26[a]	3	
32[a]	5	
28[a]	4	

[a] Soil samples collected by the University of Washington.
[b] Soil samples collected by the Seattle-King County Department of Public Health.
[c] Soil samples collected by the Puget Sound Air Pollution Control Agency.

10 km and accumulates in the soil; and (3) The distribution of these three metals indicates the prevailing winds are from the southwest, which is the case.

The same pattern was observed for the concentration of Pb and Cu in fir trees in this area (Crecelius and Piper, 1973) and Heilman (1973) found that As concentrations and distribution in acid soluble soil fractions from this area were very similar to our results. Also marine sediment samples from Quartermaster Harbor are enriched in both As and Sb (Crecelius *et al.*, 1974).

Although no data are available on the natural levels of As, Sb, and Pb in soils from Puget Sound, results from this survey indicate that natural levels should be approximately 1 to 30 ppm, 3 to 5 ppm and 20 ppm, respectively. These levels are somewhat above the world average for soils. Soil samples collected at depth (lower A and/or upper B horizon) near the smelter contained lower concentrations of the trace metals

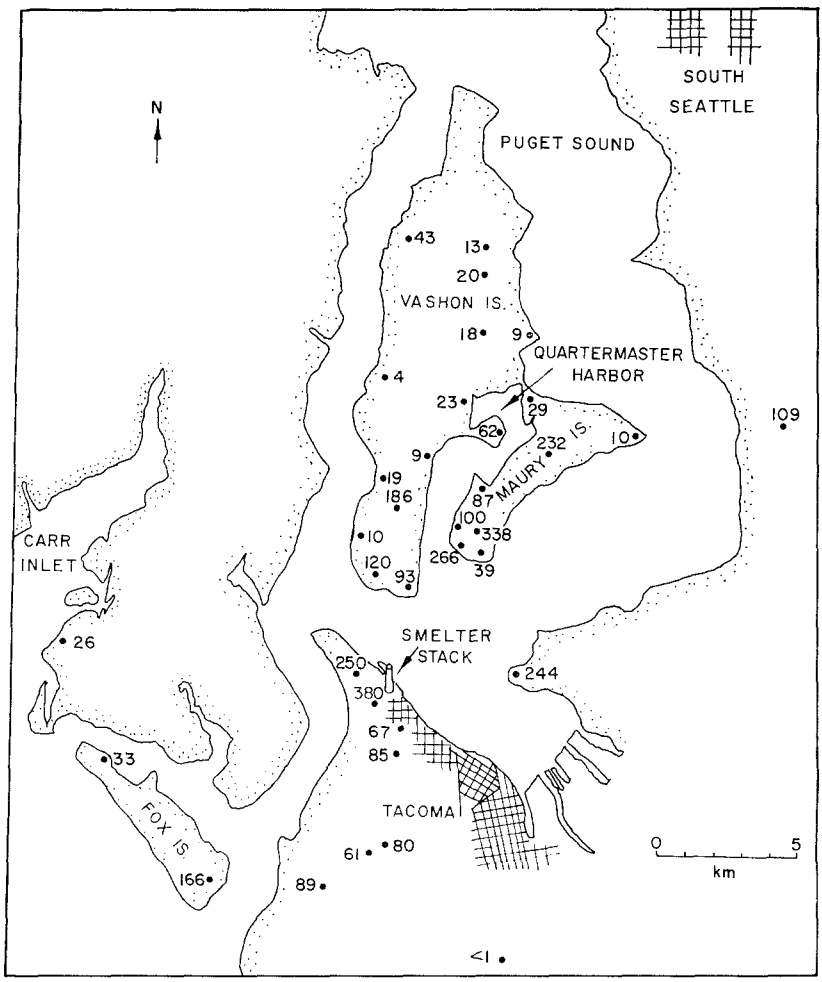

Fig. 1. The concentration of As (ppm dry weight) in surface soils (0 to 3 cm).

than the surface soils indicating the trace metals tend to remain and accumulate in the surface soil. The soil samples from depth were also well above natural levels. None of our samples may represent natural levels of these trace metals even though four samples collected north of Seattle (Table I) were 50 to 70 km downwind of the smelter. HiVol air filter dust samples collected in Seattle, 40 km downwind of the smelter, often have extremely high concentrations of As (>2000 ppm) and Sb (>300 ppm). These dust samples indicate that some smelter dust may reach to and beyond the Seattle area. The Pb concentrations in most Puget Sound soils are probably affected more by Pb from automobile exhaust than by Pb from the smelter stack dust. Lead analyses of fir tree needles by Crecelius and Piper (1973) indicated that only within 10 km of the smelter is the Pb output from the smelter greater than that from automobiles. Because automobiles in the Seattle-Tacoma area release more Pb into the atmosphere than the smelter, As and Sb are the best tracers of the smelter stack dust. We do not have any reason to believe that there are other significant atmospheric sources of As or Sb in the Seattle-Tacoma area.

Peach trees and different kinds of legumes have been shown to be adversely affected by As contaminated soils (Lindner, 1943; Overley, 1950). The toxicity of As to plants also depends on the type of soil, the chemical form of the As and the amount of rainfall or leaching (Arnott and Leaf, 1968; Woolson, 1969). One field experiment has shown that for one soil treated with $NaAsO_2$ the As gradually disappeared with a half-life of 6.5 yr (Tammes and DeLint, 1969).

Most plants do not concentrate As to a great extent (Williams and Whetstone, 1940) so the primary danger for humans and animals, including insects, is from consuming plants coated with As rich dust. There is also the possibility of harm from the inhalation of air-borne trace metals.

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