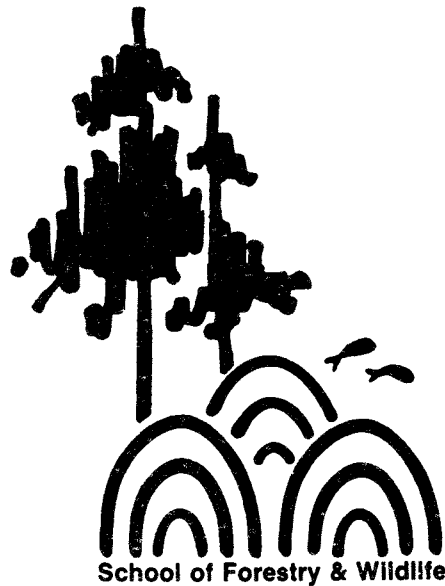


**Atmospheric Deposition of Heavy Metals  
and Forest Health:  
An Overview and a Ten-Year Budget  
for the Input/Output of Seven Heavy Metals  
to a Northern Hardwood Forest**



**A lecture by**

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**for**

**Distinguished Lectureship Program  
School of Forestry and Wildlife Resources  
Virginia Polytechnic Institute and State University  
Blacksburg, Virginia 24061 U.S.A.**

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AN OVERVIEW AND A TEN-YEAR BUDGET  
FOR THE INPUT/OUTPUT OF SEVEN HEAVY METALS  
TO A NORTHERN HARDWOOD FOREST

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## INTRODUCTION

Approximately 90 elements constitute the inorganic component of forest soils. Eighty-nine percent of these elements are present in concentrations less than  $1000 \mu\text{g g}^{-1}$  (1000 ppm), or less than 0.1 percent, and are designated trace elements. Trace metals with a density greater than  $6 \text{ g cm}^{-3}$  are "heavy metals."

Heavy metals are input to forest soils via both natural and anthropogenic processes. Natural sources include *in situ* soil weathering and atmospheric deposition of metals via soil processes, oceanic processes, and volcanic eruptions. Anthropogenic sources include fossil-fuel combustion for electricity generation, industrial processes, motor vehicle use, and agricultural activities.

Some heavy metals are biologically essential for normal plant growth and development, while others are biologically nonessential (Table 1). At sufficient concentration or dose, *all* heavy metals are toxic to plants.

### Anthropogenic Heavy Metal Sources

Galloway et al. (1982) have provided a comprehensive review of trace metal deposition from the atmosphere. These authors examined metal-emission rates (mobilization factors), ratios of metal concentrations in the atmosphere (enrichment factors), and historical trends in metal deposition to evaluate the relative source strength of natural versus human sources. One or more of these techniques indicated that human activities caused moderate or large increases in heavy metal deposition from the atmosphere for antimony, cadmium, chromium, copper, lead, molybdenum, nickel, silver, tin, vanadium, and zinc. Small increases caused by human activities were indicated for cobalt, manganese, and mercury.

The processes associated with human release of heavy metals are varied and range from combustion activities to agricultural activities. Particularly important combustion

Table 1. Heavy metals are essential and nonessential for plant health and have natural and pollution sources. Capitalized metals are thought or known to be especially significant for considerations of forest ecosystem health risk.

Essential	Nonessential	
COPPER (Cu)	antimony (Sb)	SILVER (Ag)
IRON (Fe)	bismuth (Bi)	THALLIUM (Tl)
MANGANESE (Mn)	CADMIUM (Cd)	tellurium (Te)
molybdenum (Mo)	CHROMIUM (Cr)	thorium (Th)
ZINC (Zn)	cobalt (Co)	tin (Sn)
	LEAD (Pb)	uranium (U)
	MERCURY (Hg)	VANADIUM (V)
	NICKEL (Ni)	

processes include coal burning, solid waste incineration, iron and steel industry burning, metal smelting, and motor vehicle combustion. Coal combustion is an especially important source of heavy metal input to the atmosphere. Trace metal content of coal is site and coal bed specific. Antimony, cadmium, lead, mercury, and molybdenum, however, are commonly more abundant in coal than in the average heavy metal composition of the earth's crust. At the beginning of this decade, annual consumption of coal in the United States was about 600 million metric tons. By 1990 this consumption is projected to double (National Research Council 1980). Coal pretreatment (washing), where major amounts of mineral matter are separated, can reduce the heavy metal content of coal. Current best-available technology for emissions management can collect more than 99 percent of the solid residues of coal combustion. Tall stacks, emissions management associated with new plants, and coal washing has reduced heavy metal deposition to forest, aquatic, and agricultural ecosystems in the local environments of these point sources. Older coal-burning plants, however, will continue to release heavy metals to the atmosphere in large amounts until they are closed or required to install best-available technology for emissions reduction. In addition, however, some fraction of gaseous emissions and sub-micron-size particles will continue to escape emission-control devices of all coal-burning plants and enter the atmosphere. Currently, soil disturbance by cultivation is the most significant agricultural heavy metal source; historically it has been pesticide applications.

Parekh and Husain (1981) attempted to characterize the heavy metal deposition in rural New York State during the growing season by human source. They suggested an association of: antimony and zinc deposition with refuse incineration; chromium, iron, and manganese deposition with iron and steel industrial activity; and iron and manganese deposition with soil disturbance.

## Transport and Deposition of Anthropogenic Heavy Metals

Human activities introduce heavy metals to the atmosphere primarily in particulate form. Only cadmium and mercury are thought to enter the troposphere in the vapor phase. During high-temperature combustion (coal, industrial, or motor vehicle), metal elements and their oxides become volatilized. The elements of high volatility--for example, cadmium, chromium, nickel, lead, thallium, and zinc--show a pronounced concentrating effect as they condense on fine particle surfaces. The concentrations of these elements in fly ash from coal-fired power plants increase greatly with decreasing particle size (Davison et al. 1974). Due to large surface-to-volume ratios, particles with diameters approximately  $1\ \mu\text{m}$  or less contain as much as 80 percent of their total elemental mass on the surface (Linton et al. 1976).

Preferential association of heavy metals with small particles is not only significant because these small particles may escape emissions control, but because these small particles have the longest atmospheric residence times and, therefore, can be carried long distances. Depending on climatic conditions and topography, fine particles may remain airborne for days or weeks and be transported 100-1000 km or more from their source. This long-distance transport and subsequent deposition qualify heavy metals as regional-scale air pollutants (Smith 1985). Ecosystems downwind of major power-generating, industrial, or urban complexes receive atmospheric deposition that has accumulated and integrated heavy metals from fossil-fuel electric power plants, metal smelters, foundries, steel mills, incinerators, and motor vehicles.

Heavy metal particles are deposited to forests by both wet and dry processes (Swank 1984). Dry deposition is presumed more effective for large particles and elements such as iron and manganese, while wet deposition is presumed more effective for fine particles and elements such as cadmium and lead (Galloway et al. 1982). Galloway et al. (1982) have provided an excellent inventory of heavy metal deposition rates ( $\text{kg ha}^{-1}\ \text{yr}^{-1}$ ) for urban, rural, and remote environments. Evidence from studies in the eastern United States indicates that wet deposition of certain heavy metals--for example, cadmium, lead,

manganese, and zinc--is highest during the growing season (warmest months) (Lindberg 1982).

In 1973 the senior authors of this paper initiated a detailed study of the biogeochemistry of selected heavy metals at the Hubbard Brook Experimental Forest in central New Hampshire. Our goal was to accumulate information on the input/output of heavy metals to/from the forest to complement the information being accumulated on the macro- and micro-elements important in forest nutrient cycles and to evaluate the potential toxicity of heavy metals to this northern hardwood forest ecosystem. Hubbard Brook was judged to be an excellent site to do this work because of the potential for quantifying input/output relationships (small watershed technique), the accumulation of related information on other elements, and the long-term research plans for the study site (Likens et al. 1977). The Hubbard Brook Experimental Forest is a 3160 ha reserve, located in the White Mountain National Forest of north central New Hampshire, dedicated to the long-term study of forest and stream ecosystems. The forest is approximately 120 km northwest of Boston and relatively distant from major sources of heavy metal emission. It has been shown, however, that due to continental air mass movement, storm tracks that have passed over centers of industrial and human activity also frequently pass over northern New England, resulting in heavy metal deposition potential that is higher than might be expected based on the distance of the experimental forest from industrial and urban centers (Schlesinger et al. 1974, Johnson et al. 1972). We presently have 10 years of data on the bulk precipitation input (dry plus wet deposition, winter and summer periods) and streamwater outputs of cadmium, copper, iron, lead, manganese, nickel, and zinc.

## METHODS

Bulk precipitation was collected at two meteorological instrument clearings, at 490 m and 750 m elevations, on reference watersheds of the Hubbard Brook Experimental Forest, West Thornton, New Hampshire. The lower site was at a lower reach of a monitored watershed and the higher site on a level ridge summit at the upper reach of a

watershed. After two years of operation, no difference in input was detected between the two collection sites, and subsequent collections were made only at the lower site. From May through November (summer period), monthly bulk collections were made in one-liter plastic bottles connected by a loop of plastic tubing to plastic funnels mounted on wooden frames of a design similar to that described by Likens et al. (1977). From December through April (winter period), precipitation was collected in 95-liter plastic barrels. The winter collectors were left open at the sampling sites for one month, covered and bagged in the field, and returned to the laboratory to thaw. A sample of melt water was poured into a one-liter plastic bottle. Streamwater samples were obtained monthly from reference watershed 6. Samples were collected in one-liter polyethylene bottles by the standard procedure used at Hubbard Brook (Likens et al. 1977). The time of sampling was recorded to enable subsequent correlation with streamflow rate from the stream gauge recorder. Notes on stream conditions, such as ice, turbidity, and unusual flow conditions caused by snowmelt or heavy rain, were recorded at the time of sampling.

Total monthly precipitation input to the various watersheds of the Hubbard Brook Forest was calculated by the USDA Forest Service from a network of precipitation gauges. Total monthly heavy metal input can be calculated as the average concentration obtained in our two collectors for a given month, times the total precipitation for that month. Heavy metal output in streamwater was calculated by multiplying total monthly water output (provided by the USDA Forest Service water records) times monthly streamwater heavy metal concentrations. Output calculations are element-specific because concentration in streamwater is differentially responsive to streamflow rate. For some elements concentration is independent of flow, while for others strong linear or curvilinear correlative relationships occur (Table 2). For those elements which were strongly related to flow, equations were developed that related concentration to flow. The flow rates from the daily-continuous hydrograph record were calculated and the equations applied to calculate the concentration expected at that flow rate. The amount of water which leaves the watershed at each flow rate was then calculated and the concentration multiplied by that rate, summing for appropriate time periods across all the flow rates. In cases where



Table 2. Functions employed to calculate streamwater losses of heavy metals from Watershed 6, Hubbard Brook Experimental Forest, New Hampshire. For elements whose loss was independent of streamflow rate, a mean concentration was used to calculate loss. For elements whose loss was dependent on streamflow rate, an equation relating loss to flow rate was used to calculate export.

Metal	Function
cadmium	$\text{ppb} = 0.15068 + 0.00937 [\log (\text{liters sec}^{-1})] + 0.01435 [\log (\text{liters sec}^{-1})]^2$
copper	ppb = 0.54443 (mean)
iron	
(> 10 liters sec <sup>-1</sup> )	$\log \text{ppb} = 0.8967 - 0.8658 [\log (\text{liters sec}^{-1})] + 0.7509 [\log (\text{liters sec}^{-1})]^2$
(< 10 liters sec <sup>-1</sup> )	$\text{ppb} = 4.726 - 1.235 [\log (\text{liters sec}^{-1})] + 1.883 [\log (\text{liters sec}^{-1})]^2$
lead	ppb = 0.5636641 (mean)
manganese	$\log \text{ppb} = 1.592 + 0.1017 [\log (\text{liters sec}^{-1})] + 0.09104 [\log (\text{liters sec}^{-1})]^2$
nickel	ppb = 1.1184 (mean)
zinc	ppb = 14.073 + 1.8178 [\log (liters sec <sup>-1</sup> )]

there was no correlation, the mean metal concentration was multiplied by the total water leaving in the appropriate time periods.

Particulate matter eroded and transported from the reference watershed was collected in the ponding basin at the wier in 1975 and 1976, and subsamples were totally digested and analyzed for each element. Functional relationships as calculated by Likens et al. (1977) for estimating particulate losses from flow rates were applied to the water record, and total annual output for each year was calculated. Total outputs were multiplied by the concentrations to obtain annual total outputs of each metal via particulate matter erosion.

Heavy metal concentrations in the unfiltered, acidified water samples (one ml Ultrex nitric acid per sample bottle) was determined by atomic absorption spectrophotometry using a graphite furnace at the Environmental Trace Substances Research Center, University of Missouri, Columbia.

## RESULTS

The heavy metal mass budgets for reference watershed 6 are presented in Table 3. These results suggest that, over the past decade, the northern hardwood forests of central New Hampshire have received via atmospheric deposition a very slight net gain of cadmium and copper; a large net gain of lead; a large net loss of manganese; and an uncertain net gain or loss of iron, nickel, and zinc caused by yearly variation in input/output relationships.

Lead had the most impressive net gain. Examination of the input of this element on an annual basis reveals variable concentrations in bulk precipitation but a consistent decrease in input of approximately 70 percent over the study period (Fig. 1). This decrease in lead input to the forest correlates extremely well with the decrease in national urban lead levels (Fig. 2) and with the decrease in lead consumed in gasoline (Fig. 3) over the same time period.

Table 3. Mass budgets for 1975-1984 for reference watershed number six of the Hubbard Brook Experimental Forest, White Mountain National Forest, New Hampshire, for cadmium, copper, iron, lead, manganese, nickel, and zinc. The symbols ( ) represent incomplete data set and - no data available, respectively. Mean of complete data sets provided.

Cadmium (Cd)				
Year	Input	Output (dissolved)	Output (particulate matter)	Net Gain
(g ha <sup>-1</sup> )				
1975	2.5	1.6	0.01	0.89
1976	3.0	1.8	0.01	1.19
1977	40.0	1.5	0.02	38.48
1978	11.0	1.2	0.01	9.79
1979	16.0	1.9	0.01	14.09
1980	-	-	-	-
1981	(7.4)	(0.5)	-	(6.90)
1982	8.0	1.2	0.01	6.79
1983	8.0	1.5	0.01	6.49
1984	(2.6)	(0.2)	-	(2.40)
Mean	12.6	1.5	0.01	11.1

Copper (Cu)				
Year	Input	Output (dissolved)	Output (particulate matter)	Net Gain
(g ha <sup>-1</sup> )				
1975	18.2	5.2	0.1	12.9
1976	11.6	5.9	0.1	5.6
1977	10.0	4.8	0.3	4.9
1978	26.0	3.7	0.2	22.1
1979	16.0	5.8	0.2	10.0
1980	-	-	-	-
1981	(4.4)	(1.6)	-	(2.8)
1982	14.0	4.0	0.1	9.9
1983	17.0	4.9	0.1	12.0
1984	(0.9)	(0.7)	-	(0.2)
Mean	16.1	4.9	0.2	11.1

Iron (Fe)					
Year	Input	Output (dissolved)	Output (particulate matter)	Net Gain	Net Loss
(g ha <sup>-1</sup> )					
1975	832.4	279.6	54.7	498.1	
1976	1214.0	343.4	99.2	771.4	
1977	372.0	745.8	368.7		-742.5
1978	234.0	629.6	306.1		-701.7
1979	207.0	505.3	298.6		-596.9
1980	-	-	-	-	
1981	(45.0)	(40.2)	-	(4.8)	
1982	178.0	175.9	68.5		-66.4
1983	206.0	175.6	63.4		-33.0
1984	(25.9)	(11.0)	-	(14.9)	
Mean	463.3	407.9	179.9	634.8	-428.1

Lead (Pb)				
Year	Input	Output (dissolved)	Output (particulate matter)	Net Gain
(g ha <sup>-1</sup> )				
1975	351.9	4.6	0.43	346.7
1976	359.0	5.2	0.51	353.3
1977	195.0	4.2	1.44	189.2
1978	141.0	3.3	1.20	136.5
1979	155.0	5.1	1.20	148.7
1980	-	-	-	-
1981	(28.0)	(1.4)	-	(26.6)
1982	70.0	3.6	0.42	66.0
1983	57.0	4.3	0.40	52.3
1984	(9.2)	(0.6)	-	(8.6)
Mean	189.8	4.3	0.8	184.7

Manganese (Mn)				
Year	Input	Output (dissolved)	Output (particulate matter)	Net Loss
(g ha <sup>-1</sup> )				
1975	100.0	481.2	3.3	-384.5
1976	199.0	539.0	4.2	-344.2
1977	39.0	446.0	12.7	-419.7
1978	74.0	342.7	10.5	-279.2
1979	172.0	550.0	10.3	-378.0
1980	-	-	-	-
1981	(25.0)	(140.0)	-	(-115.0)
1982	49.0	369.8	3.4	-324.2
1983	52.0	445.3	3.1	-396.4
1984	(4.3)	(60.3)	-	(-56.0)
Mean	97.9	453.4	6.8	-362.4

Nickel (Ni)					
Year	Input	Output (dissolved)	Output (particulate matter)	Net Gain	Net Loss
(g ha <sup>-1</sup> )					
1975	29.4	10.8	0.1	18.5	-
1976	18.0	12.0	0.1	5.9	-
1977	8.0	9.8	0.4	-	-2.2
1978	13.0	7.6	0.3	5.1	-
1979	12.0	12.0	0.3	-	-0.3
1980	-	-	-	-	-
1981	(15.0)	(3.2)	-	(11.8)	-
1982	13.0	8.3	0.1	4.6	-
1983	7.5	10.0	0.1	-	-2.6
1984	(0.8)	(1.4)	-	-	(-0.6)
Mean	14.4	10.1	0.20	8.5	-1.7

Zinc (Zn)					
Year	Input	Output (dissolved)	Output (particulate matter)	Net Gain	Net Loss
(g ha <sup>-1</sup> )					
1975	175.0	153.2	0.8	21.0	
1976	182.0	171.4	0.8	9.8	
1977	116.0	140.7	2.0		-26.7
1978	95.0	108.7	3.6		-17.3
1979	278.0	172.5	1.6	103.9	
1980	-	-	-	-	-
1981	(24.0)	(45.2)	-		(-21.2)
1982	54.0	117.9	0.7		-64.6
1983	76.0	142.2	0.7		-66.9
1984	(13.2)	(19.6)	-		(-6.4)
Mean	139.4	143.8	1.5	44.9	-43.9

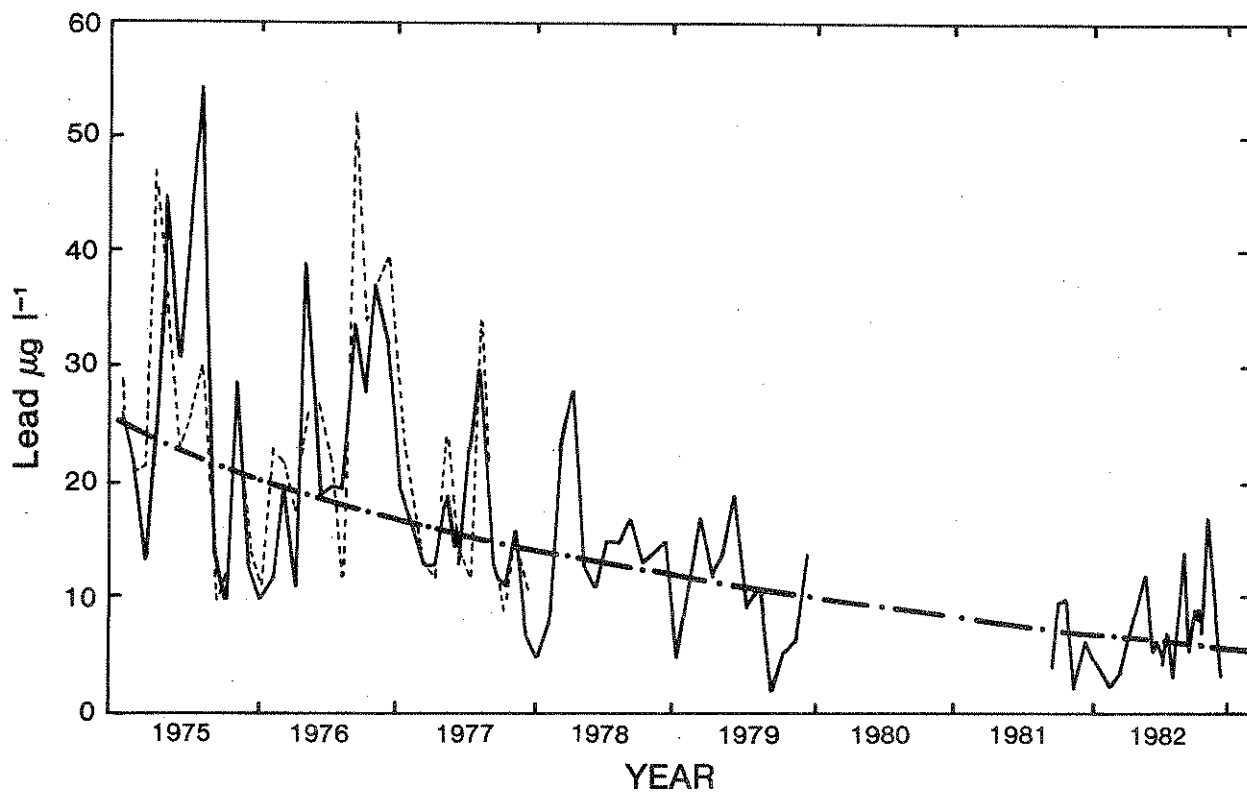


Fig. 1. Lead concentration in bulk precipitation collected at the Hubbard Brook Experimental Forest, White Mountain National Forest, New Hampshire, from 1975-1984. The regression line,  $Y = ae^{-bx}$ , has coefficients for  $a$  of 25.53 and  $b$  of -0.01589, where  $Y = \mu\text{g Pb l}^{-1}$  and  $x = \text{months}$ . The dashed line is for a collector near the ridge top (750 m) and the solid line is for a collector at 490-m elevation in the south-facing experimental watersheds. The break in the data occurred because of an interruption in funding for the study.

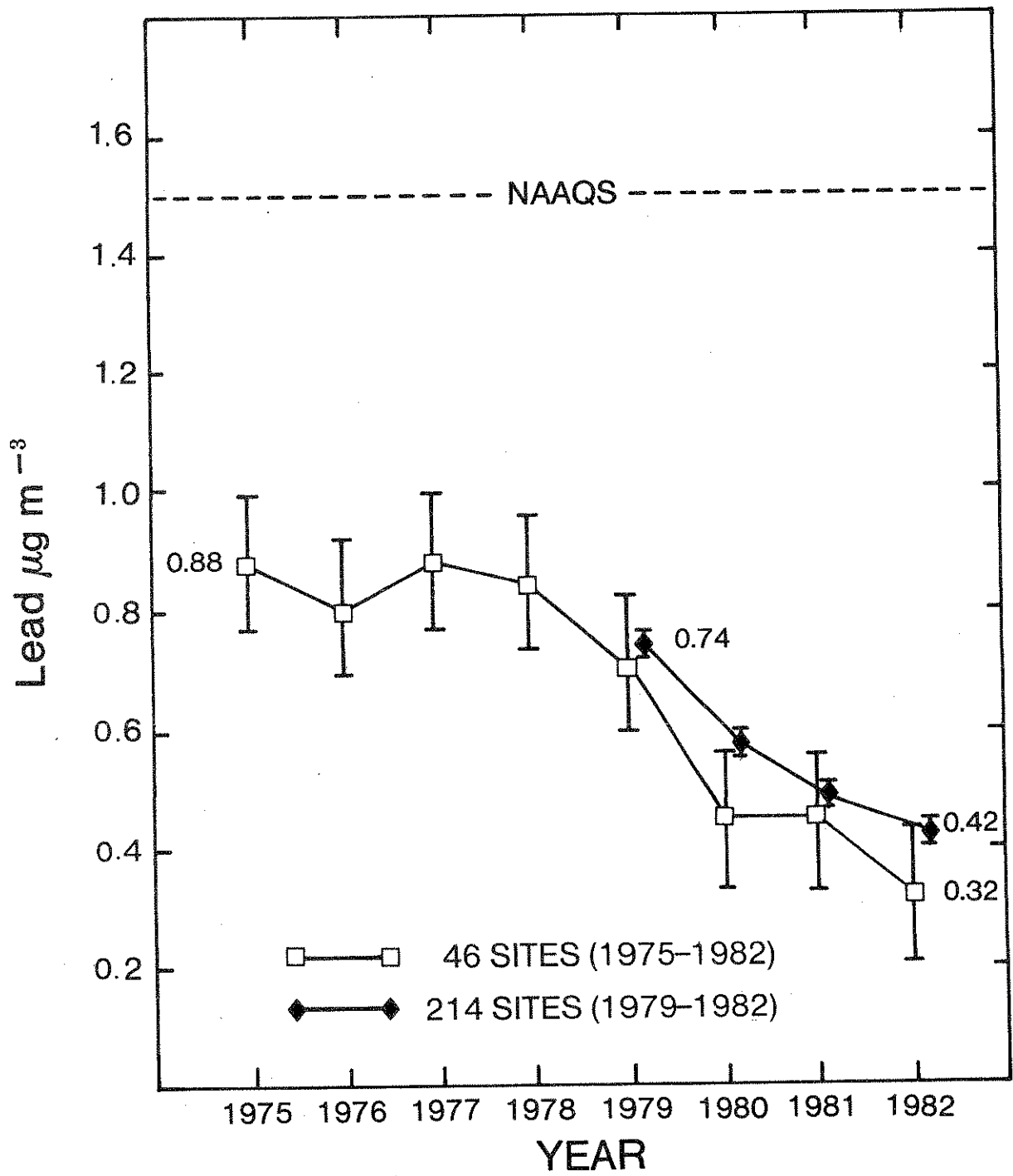


Fig. 2. National trend in maximum quarterly average lead levels with 95% confidence intervals at 46 urban sites (1975-1982) and 214 urban sites (1979-1982) (from U.S.E.P.A. 1984).



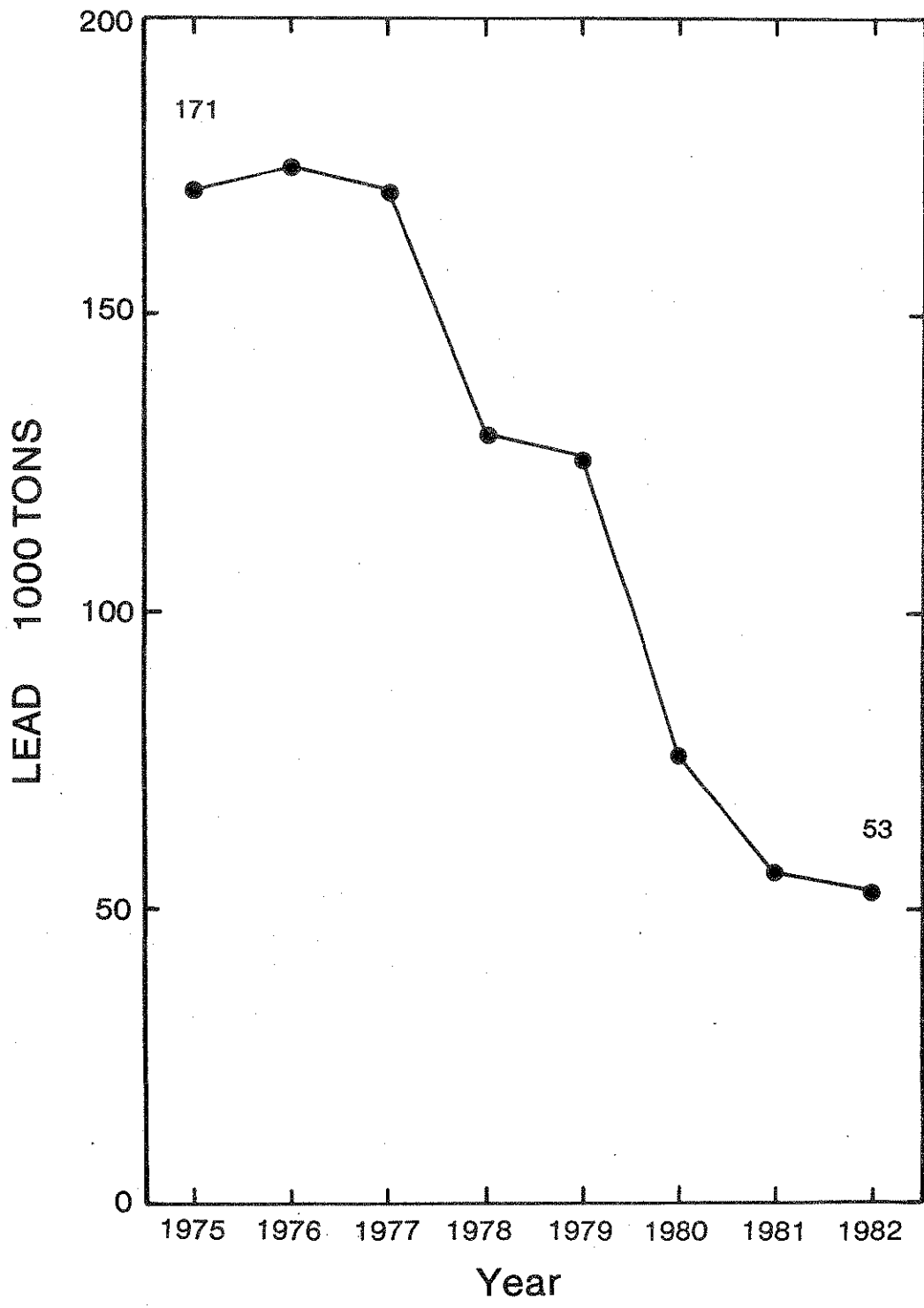


Fig. 3. Lead consumed in gasoline, 1975-1982. Sales to the military excluded (from U.S.E.P.A. 1984).

## DISCUSSION

Extensive evidence is available to support the suggestion that heavy metals deposited from the atmosphere to forest systems are accumulated in the upper soil horizons or forest floors (Andresen et al. 1980, Friedland et al. 1984a, Friedland et al. 1984b, Miller and McFee 1983, Page and Change 1979, Siccama et al. 1980, Smith and Siccama 1981). Since this accumulation is commonly in the soil horizons with maximum root activity and maximum activity of the soil micro- and macro-biota, it is appropriate to consider the potential for heavy metal toxicity to tree roots and other biotic components of the soil ecosystem. Many studies provide detail on the biochemical and physiological toxicity of heavy metals to higher plants (e.g., Antonovics et al. 1971, Bowen 1966, Energy Research and Development Administration 1975, Foy et al. 1978, Foy 1983) and to microorganisms (e.g., Jernelov and Martin 1975, Somers 1961, Summers and Silver 1978). It is not necessary to review this information, but it is appropriate to summarize selected aspects of our understanding of direct tree toxicity and toxicity to the soil biota caused by heavy metal loading of the upper forest soil profile.

### Direct Tree Toxicity

All of the heavy metals, biologically essential or nonessential, can be toxic to forest trees at some threshold level of dose. Only a few metals, however, have been documented to cause direct phytotoxicity in actual field situations. Copper, nickel, and zinc toxicities have occurred frequently. Cadmium, cobalt, and lead toxicities have occurred less frequently and under more unusual conditions. Chromium, silver, and tin--in solution culture under experimental conditions--have not been demonstrated to be phytotoxic in field situations even at high dose (Foy et al. 1978).

Direct heavy metal phytotoxicity will result only if the metal can move from the soil to the root or from the plant surface to the plant interior. Movement via diffusion or mass flow of heavy metals from soils to roots, from roots to shoots, or from plant exteriors (leaf

surfaces) to plant interiors remains poorly characterized under natural conditions. Heavy metals that do enter plants and cause abnormal physiology do not cause unique or specific symptoms that are useful in field diagnoses.

General metal toxicity symptoms include hypotrophy (growth suppression - stunting) and chlorosis (yellowing). Metal-induced hypotrophy may result from toxicity to one or more specific metabolic pathways, uptake antagonism with one or more required nutrients, and/or inhibition of root growth and development. Initial symptoms of heavy metal stress are frequently associated with root tips. Lateral root development may be acutely restricted. Root length restriction may cause the uptake of phosphorus, potassium, and iron to drop below levels necessary to sustain normal metabolism. Chlorosis caused by heavy metal toxicity appears symptomatically similar to iron-deficiency chlorosis. Evidence is available to link chlorosis due to excess cadmium, copper, nickel, and zinc with interference with foliar iron metabolism (Foy 1983, Foy et al. 1978).

Direct and acute heavy metal toxicities have been described for forest trees only in the immediate vicinity of point sources (Smith 1981). Lower heavy metal doses associated with regional-scale deposition are linked primarily with demonstrated and potential interactions with nutrient cycling processes as reviewed by Smith (1981, 1984, 1985) and summarized in the following section.

### **Direct and Indirect Soil Ecosystem Toxicity**

The high productivity of forest ecosystems is achieved and maintained through efficient nutrient cycling. For most forests essential elements required to maintain productivity cannot be sustained by annual increments from precipitation and mineral substrates alone. Organic matter decomposition, mineralization, and efficient nutrient uptake by roots are additional essentials. Increasing evidence is available to indicate that heavy metals have the potential to interfere with nutrient cycling mechanisms in forest ecosystems. Some of the most important hypotheses follow.

The decomposition rate of forest floor organic matter by the soil biota may be retarded by heavy metal contamination of soil. Binding of heavy metal ions with colloidal organic matter may increase the resistance to decomposition and/or exert a toxic effect directly on an important decomposing microorganism or arthropod (Jackson and Watson 1977, Jordan and Lechevalier 1975, Tyler 1972, Williams et al. 1977).

A large number of soil enzymes have been shown to participate in important extracellular soil processes, including free extracellular enzymes and enzymes bound to inert soil components as well as active enzymes within dead cells and others associated with nonliving cell fragments. It is well established that heavy metals have potential for enzyme interference. Metal ions may inhibit enzyme reactions by complexing the substrate, by combining with the active group of the enzyme, or by reacting with the enzyme-substrate complex. Evidence has been presented that link at least 10 forest soil enzymes with heavy metal interference (Burns 1978, Smith, 1981, Spalding 1979).

Evidence also indicates heavy metal reduction in soil processes. Numerous studies have documented reduction in rates of soil respiration associated with cadmium, copper, mercury, nickel, lead, and zinc (Babich et al. 1983, Bond et al. 1976, Doelman 1978, Ebreget and Boldewijm 1977, Spalding 1979). The process of nitrification is important in forest soils and other soil types (Duggin 1984). Under experimental conditions, cadmium, chromium, iron, lead, mercury, nickel, silver, and tin have been demonstrated capable of reducing nitrification (Liang and Tabatabai 1977, Morissey et al. 1974, Tyler et al. 1974, Wilson 1977).

Symbiotic microorganisms have roles of great importance in nutrient relations in forest ecosystems. Forests frequently flourish in regions of low, marginal, or poor soil nutrient status. In addition to nutrient conservation and tight control over nutrient cycling, trees have evolved critically significant symbiotic relationships with soil fungi and bacteria that enhance nutrient supply and uptake. Ectomycorrhizal- and endomycorrhizal-forming fungi are extremely important and varied. It is presumed that the response of these fungi to heavy metal stress is also very variable. Tolerance (Bowen 1966) and toxicity (McIlveen

et al. 1975) to zinc, for example, have been shown. Fixation of nitrogen by members of the *Rhizobium* genus may be influenced by heavy metal availability. In nonwoody species, cadmium, copper, nickel, and zinc have been demonstrated to reduce the number and size of nodules and/or quantity of nitrogen fixed (Doberciner 1966, Huang et al. 1974, Vesper and Weidensaul 1978). The endophyte of *Alnus* nodules has been identified as *Frankia*, an actinomycete. Cadmium has been shown to be toxic to actinomycetes over a wide range of concentrations *in vitro*. Nickel is generally toxic above 10 ppm, while lead and vanadium appear to be relatively nontoxic (Waksman 1967).

## **Availability of Heavy Metals in Forest Soils and Potential Interactive Effects with Acid Deposition**

Direct toxicity to trees and direct and indirect toxicity to other biotic components of the forest soil by heavy metals are dose-dependent. Dose is a function of both deposition from the atmosphere and chemical availability. Heavy metals not available for ready exchange from binding sites or in solution are not available for root or microbial uptake. More than 90 percent of certain heavy metals deposited from the atmosphere may be biologically not available.

Heavy metals may be adsorped or chelated by organic matter (humic, fulvic acids), clays and/or hydrous oxides of aluminum, iron, or manganese. Heavy metals also may be complexed with soluble low-molecular weight compounds. Soluble cadmium, copper, and zinc may be chelated in excess of 99 percent. Adsorped heavy metals remain in equilibrium with chelated metals (Foy 1983). Heavy metals may also be precipitated in inorganic compounds of low solubility such as oxides, phosphates, or sulfates. Miller and McFee (1983), for example, have suggested that lead may be present in the soil profile in the following forms: bound to organic matter, 43 percent; bound to ferro-manganese hydrous oxides, 39 percent; as insoluble precipitates, 10 percent; and biologically available (exchangeable), 8 percent.

Adsorption, chelation, and precipitation are strongly regulated by soil pH. As pH decreases and soils become more acid, heavy metals generally become more available for biological uptake. Natural forest soils generally become more acid as they mature. Acidification in excess of natural processes is possible, especially in soils with a pH greater than 5. Under this circumstance, soil acidification associated with acid deposition may result in increased biological availability of heavy metals in the forest floor.

Rhizosphere processes also may transform heavy metals from an unavailable pool to an available pool. The single most important zone of the soil ecosystem for forest tree health and growth is the rhizosphere. This zone, while only extending approximately 2 mm from root surfaces, is a unique environment and has extraordinary significance for nutrient dynamics and root metabolism. Microorganisms are stimulated in the rhizosphere because of the ready availability of organic nutrients from plant mucilages, mucigel, lysates, secretions, and root exudates. While bacteria and fungi exhibit the greatest stimulation, a large number of additional organisms are also enhanced. Chemical and physical properties of rhizosphere soil also differ from these properties in soil devoid of roots. Typically, rhizosphere soil has lower pH, lower water potential, lower osmotic potential, lower redox potential, and higher bulk density than soil away from roots (Table 4). These characteristics enable the rhizosphere to exert dominant regulation over element uptake by forest tree roots, root disease resulting from biotic agents, and microbial root symbiont and saprophyte ecology. Atmospheric deposition may alter rhizosphere regulation of heavy metal uptake. It is generally assumed that heavy metals accumulated from the atmosphere in forest floors are retained in bulk soil in largely insoluble form as hydroxide, sulfide, or other low solubility precipitates or strongly chelated by humic acids. In this form the heavy metals are not available for root or microbial uptake and the potential for toxicity is presumed low. The rhizosphere processes of pH regulation, protonation, solubilization, reduction, and complexation, however, may transform unavailable metals to available metals. Rhizosphere processes that may be particularly important in lead uptake include pH, hydrogen ion availability, organic acid availability, and phosphate availability. Organic acids capable of complexing copper and zinc in the rhizosphere may be important in root

Table 4. Biological, chemical, and physical differences of bulk soil (soil devoid of roots) and rhizosphere soil (soil in the immediate vicinity of roots).

Attribute	Soil		
	Bulk	Rhizosphere	
			(G <sup>-1</sup> )
<i>Biological</i>			
Organisms	Less: Bacteria Actinomycetes Fungi Protozoa Algae	More: Bacteria Actinomycetes Fungi Protozoa Algae	(10 <sup>9</sup> ) (10 <sup>7</sup> ) (10 <sup>6</sup> ) (10 <sup>3</sup> ) (10 <sup>3</sup> )
Respiration	Lower	Higher	
Mycorrhizas	-	+	
<i>Chemical</i>			
Organic Compound Source	Microflora Microfauna OM decomposition	Root exudates Secretions Mucilage Mucigel Lysates	
Organic acids	Humified	Nonhumified	
pH	Higher	Lower	
Negative water potential	Smaller	Larger	
Osmotic potential	Higher	Lower	
Redox potential	Higher	Lower	
<i>Physical</i>			
Bulk density	Lower	Higher	

uptake. Manganese reduction to the divalent form may allow excess uptake of this heavy metal. Complexing agents and reduced rhizosphere pH may also facilitate cadmium uptake. Again, any alteration of rhizosphere processes caused by chemical changes induced by air pollution could easily alter availability and uptake of these potential toxic elements (Smith 1987).

## SUMMARY

Deposition of heavy metal-contaminated particles from the atmosphere is an important regional-scale air pollution stress potential for forest ecosystems. Increased coal burning for energy production in the United States, combined with the high cost of gaseous heavy metal and fine-particle source reduction, will increase heavy metal input to the atmosphere over the next several decades.

A 10-year perspective on the heavy metal mass balance budget for a New Hampshire northern hardwood forest reveals net gains for cadmium, copper, and lead via atmospheric deposition. Cadmium and copper inputs have remained stable over the study decade. Lead deposition, on the other hand, has dramatically decreased, presumably due to reduced combustion of lead-containing gasoline. As long as input exceeds output, however, accumulation of a heavy metal by a forest ecosystem can be anticipated.

Acute, direct toxicity caused by heavy metal deposition probably does not occur in forest trees located outside of urban, roadside, or point source industrial and electrical generating environments. Indirect and subtle effects of heavy metal deposition on forest ecosystems have highest risk potential in association with nutrient cycling processes.

The three most important mechanisms for heavy metal interference with nutrient cycling are represented by the following hypotheses.

1. Heavy metals cause abnormal root physiology and restrict the uptake and translocation of water and essential nutrients.



2. Heavy metals reduce available nutrients by reducing the activity of soil microorganisms associated with decomposition, mineralization, nitrification, or symbiotic root associations.
3. Heavy metals may restrict nutrient cation availability by precipitating nutrient anions in insoluble forms or by antagonizing the uptake of nutrient cations.

The potential for heavy metal interaction with other regional-scale air pollutants in forest ecosystem stress is significant. Acid deposition may alter heavy metal availability by changing soil pH or other soil chemical parameters. Alteration of foliar physiology resulting from ozone exposure may alter root physiology, resulting in altered heavy metal uptake by roots.

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