United States
Department of
Agriculture

Forest
Service

North Central
Forest Experiment
Station

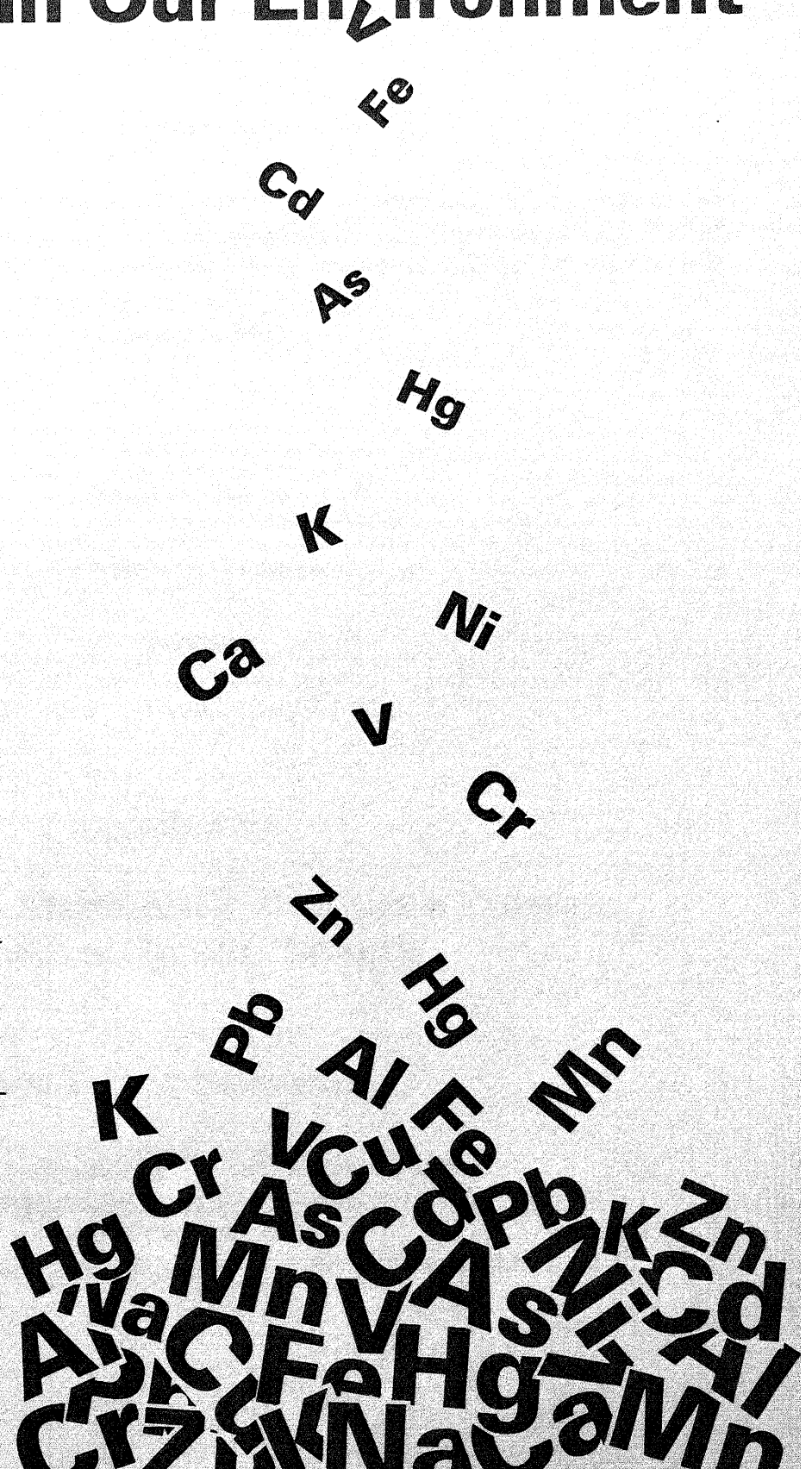
General Technical
Report **NC-150**

The Deposition and Fate of Trace Metals in Our Environment

Symposium Proceedings

Philadelphia, PA
October 8, 1991

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/
NATIONAL TRENDS NETWORK



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North Central Forest Experiment Station
Forest Service -- U.S. Department of Agriculture
1992 Folwell Avenue
Manuscript approved for publication March 19, 1992
1992

The Deposition and Fate of Trace Metals in our Envrionment

Philadephia, Pennsylvania
October 8, 1991

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Organized by:

The National Atmospheric Deposition Program
National Trends Network

Published and Distributed by:

USDA-Forest Service
North Central Forest Experiment Station

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FORWARD

It is the business of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) to define the chemical climate of America. Since 1978, we have built a consistent, high quality record of the major anions and cations in precipitation nation-wide. A record used by scientists to better understand acid rain processes and impacts and used by legislators to define our national policy. Our chemical and data analysis is streamlined to deliver information in a timely and quality-controlled manner. The network has matured in area coverage and data management. We now seek to explore the addition of other critical environmental measurements. Among which are ultraviolet beta light, herbicides, and trace metals.

On October 8, 1991, in Philadelphia, the NADP/NTN Technical Committee hosted a symposium on the deposition and fate of trace metals in our environment. Fourteen papers were prepared by 37 authors with a breadth of experience in trace metal ecology over the last decade. These proceedings are meant to inform our members of the analytic and collection methods for trace metals in precipitation, and the processing of trace metals in the landscape and its biota. It is a solid review of trace metals designed to facilitate an informed discussion about the addition of trace metals to the NADP/NTN network.

We realize that rapid change in our world society and change in our environment is, in fact, the order of our world. However, this symposium helps us to see that change does not separate us from our past. Indeed, we have the opportunity to mold the future if we can interpret our historical legacy and monitor our present. The cycling of trace metals is part and parcel of our society and our environment. A recent vision of ecology in the 21st century[1] captures the need to understand the ecology of trace metals in our environment too.

> **"To treat Nature as a partner, people must learn, and learn well, the principles of ecology..., and see [the] implications not only for natural ecosystems but also for our own artificial and intensely human societies."**

NADP/NTN is well prepared to provide new services in a changing world. John Masefield in his poem "The Ending" from *The Wanderer* looks well beyond the end of the traveled road.

> **"Adventure on, for from the littlest clue**
> **Has come whatever worth man ever knew;**
> **The next to lighten all men may be you."**

Elon S. Verry

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[1]Eville Gorham, 1990. An ecologist's guide to the problems of the 21st century. The American Biology Teacher. 52(8):480-483.

THE DEPOSITION AND FATE OF TRACE METALS IN OUR ENVIRONMENT: A SUMMARY[1]

Elon S. Verry and Stephen J. Vermette[2]

A GLOBAL PERSPECTIVE

The actions of our global society now dominate the natural biogeochemical cycle of some trace metals in the atmosphere and many receiving ecosystems. The ratios of anthropogenic to natural fluxes of trace metals to the atmosphere are currently estimated at 28 for lead (Pb), 5 for cadmium (Cd), 3 for zinc (Zn) and vanadium (V), 2 for nickle (Ni) and arsenic (As), and about 1 for mercury (Hg), and copper (Cu). Energy production, and mining (including smelting and refining) are significant sources for all trace metals. Waste incineration also accounts for about half the amount of Hg emitted. Lead emissions are dominated by volatile losses from gasoline, but even without leaded gasoline, the ratio for Pb is 7. The magnitude of emissions and deposition rates are closely related, creating profound regional differences across the globe. The greatest perturbation of the natural trace metal cycle is in the northern hemisphere where most industries are located. The maximum difference in deposition is between the North Atlantic and South Pacific oceans. The most striking trend is a sharp rise in emissions and ambient environmental concentrations in developing countries, as opposed to declines in developed counties (See Nriagu).

THE LEGISLATIVE PERSPECTIVE

The 1970 Clean Air Act dealt primarily with national ambient air quality standards (NAAQS) for particulate matter, lead, sulfur dioxide, nitrogen oxides, ozone, and carbon monoxide. These standards are directed at threshold levels below which there are no adverse human health effects in populated urban areas. The 1990 Clean Air Act continues to focus on urban areas, but expands the need for ambient air quality measurements by mandating research in rural areas, and by extending the initial focus on human health to include effects on water, soils, forests and crops. Characterization of the spatial and temporal impacts of trace metal and toxic compounds on rural ecosystems is a significant part of the 1990 Clean Air Act Amendments. Title III,

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[1]Many of the words in this summary are paraphrased from the authors' manuscripts published in this proceedings. In this summary they are recognized for all or part of each paragraph.

[2]USDA-Forest Service, 1831 Highway 169 East, Grand Rapids, MN 55744; and Illinois State Water Survey, 2204 Griffith Dr. Champaign, IL 61820.

Section 112 (k)(2) calls for research to monitor metals, pesticides and many other hazardous air pollutants, and to characterize their sources and risks to public health in urban areas. Section 112 (m) requires EPA and NOAA to extend research and monitoring programs to the rural watersheds of the "Great Waters" including the Chesapeake Bay and coastal waters, and Lake Champlain, as well as the Great Lakes. Title IX, Section 901 of the 1990 Clean Air Act Amendments identifies new environmental and ecosystem measurement and monitoring research objectives on a national network basis. These objectives include evaluating the effects of air pollution on water quality, forests, materials, biological diversity, soils and crops. (See Pahl, et al.).

AN HISTORICAL PERSPECTIVE

PRIOR TO THE TWENTIETH CENTURY

The extraction and dating of lake sediment and peat cores suggests that rates of Pb deposition in the United States accelerated in the mid 1800's (See Norton and Kahl); however, ice cores from Greenland are longer and extend further back in time. They suggest that low rates of anthropogenic lead deposition in North America began in the mid 1700's. Lake and peat core analyses from Scotland, Norway, Finland, and Denmark suggest that trace metals released from industries in Britain and central Europe were reaching remote areas of Scandinavia by the mid 1600's . While local metal contamination of the environment existed near the silver mines of ancient Greece, long range transport of trace metals in the atmosphere probably began in the mid 1500's with the development of large smelting furnaces and tall stacks (see Nriagu).

THE TWENTIETH CENTURY

The highest rates of Pb accumulation in sediments began about 1960 in the United States. Norton and Kahl's analyses point out many of the problems associated with the interpretation of Pb chemistry in dated lake and peat cores. These include: uncertainties in sediment dating, coring difficulties, bulk or extractable methods of preparing sediments for chemical analysis, area-variable sedimentation processes, and sediment mixing by worms. Other problems include relocation of trace elements within the sediment, deposition of metals in sediment not of the same age, loss of trace metals from sediments caused by changes in oxidation state etc., and retention of metals within the catchment. For these reasons, the correspondence between measured air quality, atmospheric deposition, and sediment accumulation is useful for identifying historic changes and trends in only the broadest way (See Norton and Kahl).

Lead in the forest floor (organic material lying over the mineral soil) has been used to estimate Pb deposition directly. This method assumes that, once deposited, Pb is retained in the forest floor, and that there is no uptake or cycling of the Pb by vegetation. During the period of the mid 1960's to the mid 1980's, Pb deposition in the northeastern U.S. was estimated at 175 to 600 $g\ m^{-2}\ yr^{-1}$ increasing as elevation increased from about 500 m to 1000 m. However, repeated

measures of Pb in the forest floor, over the same period and in the same locations, show lower amounts of Pb at the end of the period. The amounts are even lower than that expected from reduced Pb deposition rates as unleaded gasoline replaces leaded gasoline. This leads to speculation that Pb is lost from the forest floor. The mechanism of loss is not confirmed, but may relate to the export of Pb bound with organic carbon in tea-stained leachate waters. Nonetheless, forest floor estimates of Pb deposition are similar to total (wet plus dry) Pb deposition measured at the mid-Atlantic coast in the early 1980's (400 g m^{-2} yr^{-1}) (See both Friedland, and Church, et al.).

Trace metals in the atmosphere are delivered to and are partially retained in receiving ecosystems. The work by Nater, et al. clearly shows a significant correlation between the deposition of S, and its concentration in various components of forest ecosystems from northwestern Minnesota to Michigan's Lower Peninsula . Sulfur in the forest floor, surface mineral soil, and in tree wood follows the increasing deposition of sulfur from west to east. The concentrations of Pb, Cd, and Hg in the soil components follow a similar gradient trend as S in those components. Trace metals and sulfur are often derived from the same industrial sources, and rural as well as urban ecosystems must process these elements along with sulfur. In present-day ecosystems trace metals are not merely sequestered in depositional sediments, but occur in the major ecosystem components in a dynamic fashion that corresponds with site specific atmospheric deposition from long range transport. (See Nater, et al., and Nriagu).

MEASURING REGIONAL TRACE METAL DEPOSITION

The Ontario Ministry of the Environment has measured Cu, Ni, Pb, Mn, Zn, Cd, Fe, Al, V, and As in wet-only deposition since 1981. High concentrations are located around and south of the lower Great Lakes. Annual loadings of Pb, Mn, Zn, and Cd to Lakes Ontario, Erie, and Huron show an annual rate of decrease from 1981 to 1988, averaging about 6%. This is true for Zn and Cd over Lake Superior as well, but annual Pb and Mn loading to Lake Superior has increased by 2%and 6% respectively (See Orr, et al.). With the exception of Ca and Na, similar trends are shown for the Great Lakes in the EPA GLAD network for the period 1982-1989. The most dramatic decrease in Pb deposition occurs near urban sites (See Klappenbach).

Trace elements have been measured in precipitation and aerosols at several mid-Atlantic coastal sites since 1982 by the University of Delaware as part of the NOAA-WATOX program. These data for 13 trace metals suggest common emission sources from the midwest and southeast U.S. with efficient precipitation scavaging after long-range transport. The atmospheric flux of most trace metals dominate the input of metals to coastal watersheds, and the export of metals from estuaries to coastal waters. Wet-only deposition accounts for 85% to 98% of the total atmospheric deposition of Cu, Zn, Ni, and Cd, and 47% to 55% of the total atmospheric deposition of Cr, Pb, and Fe. (See Church, et al.).

ACCURACY OF TRACE METAL MEASUREMENTS

Most of the trace metal concentrations reported for precipitation prior to 1980 are compromised by gross contamination, or conversely, by irreversible losses of certain metals to container walls. The accurate determination of trace metals in precipitation at the nanogram level requires: 1) the use of specific collection materials, 2) exacting cleaning of materials prior to use, 3) careful sample handling, 4) sample acidification for preservation, 5) very careful or Clean-Lab analysis techniques, and 6) exacting QA/QC protocols. The use of Teflon® is recommended for most trace metals. Low density polyethylene (virgin LDPE polymerized directly from ethylene gas) is a low cost alternative for most trace metals because its porous surface can be easily leached to remove adsorbed metals. High density clear polyethylene (Rubbermaid® No. 2618) is currently being satisfactorily used in the University of Delaware studies. Ultra-high purity HCl or HNO_3 and Milli-Q® equivalent water are required cleaning and preserving agents. Unfortunately the Aerochem Metric white bucket is not "virgin" polyethylene and significantly leaches Cd, Cu, and especially Zn. At the same time, it absorbs half the Pb in rain water. Automatic operation of the Aerochem Metric sampler (with an HDPE bucket) gives comparable concentrations to manual operation suggesting that between-event contamination does not occur. (See Scudlark et al.)

Preliminary analyses of an NADP/NTN trace metals network at three locations are reported (Vermette, et al.). The modification of the Aerochem Metrics sampler to incorporate all Teflon® surfaces and the use of an inductively coupled plasma mass spectrometer (ICP-MS) for analysis is well adapted to the routine analysis of As, Cd, Cu, Mn, Pb,and Zn at the ng L^{-1} level. However, Teflon® adsorbs more than 90% of the Hg in precipitation samples if not properly "pretreated" and "conditioned". Pre-baked borosilicate glass in combination with cold vapor atomic florescence spectroscopy (CVAFS) analysis is best adapted for the routine analysis of Hg in precipitation at the ng L^{-1} level. Analysis of field and laboratory quality assurance blanks and inter-laboratory comparisons, suggests that careful field handling, and careful lab procedures can produce analyses equal to Clean-Lab, and clean-dressed operator procedures (Vermette et al.).

IMPACTS ON PLANTS AND FISH

SOIL MEDIATION

Low-level accumulation of trace metals in soils causes subtle, and potentially more far reaching problems than direct smelter impacts; these include 1) uptake by plants and movement in the food chain, 2) disappearance of metal-intolerant species, and 3) overall reduction in plant growth. Trace metals in soils are made unavailable to plants via precipitation as metal carbonates, phosphates, sulfides, and silicates; and by complexation with organic matter and hydrous oxides of Fe, Al, and Mn. The thermodynamics of soil solutions favor the precipitation and complexation of trace metals, particularly in soils high in clays and organic matter. Although this capacity is large, continuous trace metal accumulation yields immobilized forms that are

increasingly more soluble and more available to plants. Acid soils and well oxidized soils increase the availability of most trace metals to plants.

Subtle impacts on plant growth may be indirect. The toxicity of trace metals to mycorrhizal fungi may reduce mycorrhizal activity, and suppress root colonization. In turn, these can lead to plant nutrient deficiency, root disease and drought stress. It is clear that host plant response to metals in soils is closely related to fungal tolerance. Dosskey and Adriano's review of soil/metal interaction, and their application of Bradley, et al.'s (1981) hypothesis of fungal mediation suggests that plants which form ectomycorrhizae with large hyphal masses outside the root surface may be capable of sustaining greater metal inputs before experiencing adverse impacts than those forming vesicular-arbuscular (VA) mycorrhizae with hyphae inside the root. Thus VA mycorrhizae-forming herbaceous plants (e.g. beans) and deciduous trees would be more sensitive to metal contamination of soil than conifers with their more tolerant ectomycorrhizae. Net sensitivity to plants is the result of soil physical and chemical properties, trace metal load, and mycorrhizal ecology. These factors cause great spatial variation in plant stress from trace metals (See Dosskey and Adriano).

MERCURY IN LAKE WATER AND FISH

Almost all atmospheric Hg is elemental Hg°. In precipitation and lake water it occurs at nanogram L^{-1} (one billionth of a gram per liter) concentrations. Thus, as with the earlier analyses of trace metals in precipitation, lake water concentrations determined prior to 1980 are grossly contaminated. Blank concentrations of 0.5 ng L^{-1} must be determined in order to measure ambient levels of 1-3 ng L^{-1}. Roughly 6 billion grams of Hg circulate through the atmosphere each year. Mercury is important because the most toxic form, methyl-Hg accumulates in fish tissue at 10^6 to 10^7 times ambient levels . Birds, humans, and mammals that consume aquatic organisms with high Hg concentrations may incur increased risks to health (See Porcella, et al.).

An investigation of Hg cycling in northcentral Wisconsin lakes demonstrates the importance of atmospheric Hg to the geochemical cycling and bioaccumulation of Hg in temperate seepage lakes and the potential linkage between modest increases in atmospheric Hg loading and enhanced Hg levels in biota. The Hg speciation data suggest that atmospheric deposition of methyl-Hg is very small. Instead, the bioaccumulation of methyl-Hg in fish is directly related to the in-lake Hg(II) substrate available for methylation. Some elemental Hg (Hg°) escapes to the atmosphere, particularly in acid waters. The Hg(II) substrate consists of labile inorganic associations (e.g. Hg^{2+} ; $Hg(OH)^2$), organic associations (e.g. simple amino acid Hg complexes), and labile particulate Hg complexes. The annual accumulation of methyl-Hg in fish tissue (0.15 g in Little Rock Lake) is < 10% of the annual net input of elemental Hg°, yet this constant input maintains the Hg(II) substrate available for methylation. (See Fitzgerald, et al.). The concentration of methyl-Hg in fish tissue has resulted in state advisories against eating fish in thousands of lakes in Minnesota, Wisconsin, Michigan, Illinois, New York, and Florida, as well as many of the eastern provinces in Canada.

METAL TOXICITY TO FISH

There is a well-documented response of fish to trace metal toxicity. This has been developed primarily by studies of gross anatomical abnormalities in fish found in streams, estuaries, and bays receiving trace metals from point sources. The early life stages of fish are the most sensitive to trace metal toxicity. Responses of fish embryos and larvae to trace metals include death, development of teratogenic abnormalities, slowed motility and egg development, reduced or inhibited enzyme activity, and reduced growth. Specific mechanisms of fish toxicity include failure of the skeletal system to develop fully (curved, or no spine), stunting, circulatory stasis (failure of the heart tube to bend and edema of the pericardial cavity), and failure of the optic system to develop fully. It is not the developmental arrest itself but the continuous exposure to a teratogen at that critical life stage that causes the anomalies once development resumes. Aqueous metal concentrations that elicit these responses are relatively high compared to concentrations in precipitation, and various fish species respond at different levels (Weis and Weis).

Salmonids are most sensitive to elevated metal concentrations. Developmental toxicity from Zn begins at 1,400,000 ng L^{-1} for brook trout, at 500,000 ng L^{-1} of Cu for northern pike, at 250,000 ng L^{-1} of As for rainbow embryos, and at 37,000 ng L^{-1} of Cu for rainbow trout. Selenium causes mortality in rainbow trout embryos at 10,000 ng L^{-1}, and Cd concentrations of 10,000 ng L^{-1} cause cardiac malformations in rainbow trout. Hg concentrations of 1,000 ng L^{-1} cause weight loss in salmonid embryos. Adult rainbow trout exposed to water with as little as 200 ng L^{-1} of Hg and subsequently placed in clean water, produce larvae with only half the 4-day survival as larvae from non-exposed adults. Those larvae that survive have many abnormalities. For adult trout themselves, exposure to 200 ng L^{-1} of Hg significantly reduces reproductive success, increases mortality and the occurrence of abnormalities (Weis and Weis).

In contrast to these toxic metal concentrations in lake, stream or esturary water, only Hg approaches direct toxic levels in precipitation. The higher concentrations of trace metals found in precipitation are estimated from Nriagu (p. 18), or the original work of Vermette et al.. They are associated with urban precipitation, and are given below as about 3X average concentrations (This is often equivalent to the mean plus two standard deviations).

Element	As	Cd	Cu	Mn	Pb	Zn	Hg
ng L^{-1}	5000	5500	9000	35000	18000	25000	200

In mammalian teratology, a field much more intensively studied than fish teratology, it has become clear that functional deficiencies are a more subtle response to toxicants than the production of gross anatomical abnormalities. It is likely that exposure of fish embryos to low concentrations of trace metals also results in (difficult to measure) abnormal behavior in anatomically normal individuals after their birth (Weis and Weis).

CONCLUSIONS

Trace metal concentrations in the atmosphere and in precipitation have been above background levels for some 400 years. Increases above background became pronounced from 1850 to 1950 and acute from 1950 to the early 1970's. Decreases in trace metals in wet deposition have occurred since enactment and implementation of the Clean Air Act of 1970, with an annual decrease averaging 6 % over the Great Lakes. Decreases in Pb have been most dramatic approaching a total 33% reduction in parts of the northeastern United States as seen in some lake sediment cores. However, precipitation measures of Pb loading to the Great Lakes show annual decreases of 3% over L. Huron, 4% over L. Erie, and 9% over L. Ontario. In contrast, Pb deposition over Lake Superior has increased 2%annually from 1981 to 1988. The 1990 Clean Air Act amendments expands the focus of air pollution monitoring and standards from urban areas to rural areas and includes trace metals as a major item. It further extends our national concern for air pollution from impacts on human health to include impacts on ecosystem integrity, fish, and plant health.

The measurement of trace metals in precipitation, aerosols, and lake and stream waters has been seriously compromised by contamination, such that analyses prior to 1980 ehibit large positive biases. New sampling and analysis techniques developed and refined over the last 12 years have made the analysis of trace metals in all ecosystem components accurate at the microgram L^{-1} and nanogram L^{-1} levels, and, for some metals, even the sub-ng L^{-1} level. It is demonstrated that trace metal accumulation in rural ecosystems parallels the deposition of sulfur in those ecosystems. Long range transport of trace metals from fossil fuel energy production, metal mining and refining, and waste incineration dominates the geochemical cycle of trace metals in the atmosphere by factors of 2 to 28 times natural sources.

Soils are generally well-adapted to the sequestering of trace metals in both inorganic and organic precipitates, and plants can be protected from high levels of trace metals in soils by sequestering trace metals in the hyphae of fungal mycorrhizae. Spatial variation in soils that support plants impacted by trace metals is likely to be high. Soils susceptible to acidification by sulfur and nitrogen loading (low base saturation, low organic matter, coarse fractions, well oxidized, and low pH) are also likely to have plants with a low tolerance to metal toxicity. Thus the occurrence of serious trace metal impacts on plants is not likely to exceed more than 5 to 10 % of the landscape.

Lake waters can pass atmospheric Hg^{o} to lake sediments (but availability to the water column may increase under conditions of frequent change between aerobic and anaerobic states). Reactive Hg (HgII) in lake water provides a substrate for methylation. Virtually all of the methyl Hg produced accumulates in fish tissue reaching concentrations high enough to invoke fish-eating advisories for thousands of lakes. Toxicity of trace metals to fish at critical life stages is well documented for physical abnormalities. The concentration of trace metals in precipitation is not generally great enough to directly elicit physical abnormalities in fish with the exception of the higher concentrations of Hg found in urban precipitation. Just as our ability to measure

small concentrations of metals accurately has dramatically improved, our ability to measure behavioral disabilities rather than gross physical abnormalities is also improving and will likely provide greater insight to trace metal and fish health interactions.

The study of trace metal ecology is both miniscule and immense. The concentration levels are extremely small, yet we now realize that biogeochemical cycling at the ng L^{-1} level operates just as precisely as plant nutrient cycling at the mg L^{-1} level. In the United States, the longest record of atmospheric deposition of trace metals is limited to shoreline stations at the mid-Atlantic coast and around the Great Lakes. Yet we now know that trace metal deposition is tied to fossil fuel combustion, waste incineration, metal mining, and metal refining and processing. The spatial, and temporal distribution of trace metals in atmospheric deposition is information that an environmentally concerned society should have. It is information that NADP/NTN is well suited to provide at a reasonable cost.

ACKNOWLEDGEMENTS

We and the members of NADP/NTN are indebted to the symposium authors for their willingness to share a decade of rigorous research and monitoring experience. We also thank V. Bowersox, C. Simmons, and L. Ohmann for helpful reviews of this summary.

WORDWIDE CONTAMINATION OF THE ATMOSPHERE WITH TOXIC METALS

Jerome O. Nriagu[1]

ABSTRACT.--The contamination of the atmosphere with toxic metals from industrial sources has become a global phenomenon. The cumulative emissions of Pb, Zn, Cu, Ni and Cd have been estimated to be 23, 17, 2.6, 1.3 and 0.38 million metric tonnes respectively. Industrial inputs now dominate the natural biogeochemical cycle of trace metals in the atmosphere and many other receiving ecosystems. Two opposing trends have recently become evident in the anthropogenic generation of toxic metals: the developing countries where the emissions are still rising sharply and the developed countries with a downward trend in both emissions and ambient environmental concentrations. Unfortunately, most of the available databases on trace metals in rainfall are compromised by severe sample contamination and only yield confusing insights on the human influence on the atmospheric trace metal cycle.

INTRODUCTION

The atmosphere is a key medium in the dispersal of anthropogenic generated metals and as such plays an important role in the global contamination of environmental compartments with toxic metals. It now represents the dominant pathway by which trace elements get into many ecosystems, such as the oceans and the Great Lakes (Gatz et al. 1989, Patterson and Duce 1991). The identification of the sources of atmospheric metal pollution and the determination of their emission rates are essential steps in any program aimed at controlling or reducing the levels of toxic metals in the environment. Proper inventory of atmospheric emissions are also basic to our understanding of the global biogeochemical cycles of the trace metals and in assessing the impacts of human activities on such cycles. Furthermore, the emission of toxic metals is closely linked to the most controversial air quality issue of recent years. Trace metals and S are often derived from the same industrial sources and, to some extent, the rains owe their toxicity to their trace metal burden. And the anthropogenerated metals often catalyze the oxidation of SO_2 to sulfuric acid. Thus, the human influence on the atmospheric metal cycle thus is of considerable interest because of the causal relationships that exist between the emissions of trace metals and (i) the concentrations and effects of trace metals in ambient air, (ii) the toxicity of rainfall, (iii) the deposition of toxic metals into fragile ecosystems and their effects on sensitive fauna and

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flora as exemplified by forest decline. This reports examines the perturbation of the global atmospheric cycle of trace metals by emissions from natural and industrial sources.

HISTORICAL

Contamination of the environment with toxic metals is an old human pursuit. Before the Industrial Revolution, mining and smelting operations represented the major source of trace metals in the environment, and the available records leave no doubt as to the severity of pollution in some of the classical mining regions. Xenophon (Book 3, Verse 6), for example, noted that the district around the famous ancient silver mines of Laurion (in Greece) was too contaminated [unhealthy] to warrant a visit by Ariston's son, Glaucon. The ancient Greek poet Lucretius (*De rerum natura*, Book VI) was particularly concerned about the health effects of the noxious emissions from precious metal mines:

> **And when there is mining for veins of gold and silver**
> **Which men will dig for deep down in the earth**
> **What stenches arise, as at Scaptensula!**
> **How deadly are the exhalations of gold mines!**
> **You can see the ill effects in the miners' complexions.**
> **All these exhalations come from the earth**
> **And are breathed forth into the open light of day.**

Vitruvius (Bk 8, verse 3) spoke about extensive water pollution around mines, while Pliny (Bk 33, verse 31) noted that emissions from mines and smelters were dangerous to all animals and especially to dogs. Del Mar (1880) maintained that the concern for environmental quality was as important as the social and economic factors in the interdiction of mining operations near ancient cities, a perfect example being the Roman edict forbidding any mining activities in Italy. Will Durant shared the same sentiments and in his highly acclaimed work, *The Story of Civilizations*, aptly observed that "Laurion pays the price of wealth it produces, as mining always pays the price for metal industry; plants and men wither and die from furnace fumes, and the vicinity of the works becomes a scene of desolation".

In ancient times, the dispersion of trace metals from polluting sources was local, or at most regional, in scope. The mine workings were done on a small scale but the uncontrolled smelting in open fires often resulted in severe local contamination (as noted above). Evidence of pollution in ancient times comes from the trace metal profiles of peats in the mining district of Giordano Valley near Bristol which show elevated concentrations suggesting that the Roman smelting operations produced measurable flux of pollutants to the local environment (Livett 1988). Elevated Pb concentrations in the Featherbed Moss also attest to the environmental impacts of Roman exploitation of the Derbyshire Pb deposits (Lee and Tallis 1973).

During the 16th Century, the development of large furnaces equipped with tall stacks (see Agricola 1555) forever changed the sphere of influence of the smelters. Increased trace metal deposition dating back to the Middle Ages which has been recorded in peat profiles at Gordano Valley, Featherbed Moss, Glenshieldaig (northwest Scotland) and in Lake Windermere sediment

suggests that emissions from smelters in Britain were already affecting the regional environment (Livett 1988). Furthermore, the profiles of trace metals in peat at Dravel Mose, Denmark, the ice cores from Jatunheimen Mountains, southern Norway, and lake sediments from southern parts of Norway and Finland (Livett 1988, Verta et al 1989) all point to the fact that by the middle of the 17th century, the pollutant trace metals released from industries in Britain and central Europe were reaching the most remote regions of Scandinavia. In their study of ice cores from Greenland, Murozumi et al. (1969) also found that accelerated deposition of Pb from anthropogenic sources began in the middle of the 18th Century.

The health effects of high levels of toxic metals in the air were of some concern even during the Middle Ages. In his 1661 tract entitled Fumifium, John Evelyn condemned air pollution from coal combustion:

> **"New Castle cole, as an expert Physician affirms, causeth consumptions, phthisicks, and indisposition of the lungs, not only by the suffocating abundance of smoke, but also by its virulency: for all subterrany fuel hath a kind of virulent or arsenical vapor rising from it" (cited in Lenihan 1988, p.123).**

In John Evelyn's days, As was synonymous with poison, and his perception of the dangers of toxic metal pollution from coal combustion was remarkable.

Analyses of recent layers of peat, ice and aquatic sediments have provided historical records, dating back to the early 1800s, of ubiquitous trace metal pollution of increasing severity especially in the northern hemisphere (see MARC 1985, Levitt 1988). Since the middle of the last century, the production and discharge of trace metals in the environment have been increasing almost at a logarithmic scale (Nriagu 1979). It has been estimated that between 1850 and 1900, the worldwide industrial emissions of Cd, Cu, Pb, Ni and Zn to the atmosphere averaged about 380, 1800, 22000, 240 and 17000 tonnes respectively (Nriagu 1979). Between 1900 and 1980, the industrial emission rates for Cd, Cu, Pb, Ni and Zn increased by 8-, 6-, 9-, 51-, and 8-fold respectively (Table 1). Between 1980 and 1990, there was a 20% decline in rates of industrial emissions (compared to those of the preceeding decade) due to legislative initiatives and pollution control in the developed countries. The cumulative all-time emissions from industrial sources have been estimated to be 0.37, 2.6, 23, 1.3 and 17 million metric tonnes for Cd, Cu, Pb, Ni and Zn (Table 1). The quantities of the anthropogenerated metals clearly dwarfs the reservoirs of the trace elements in the atmosphere and many other target ecosystems and leave no doubt that mankind has become a key agent in the global redistribution of toxic metals. The short lifetime of pollutant metals in the atmosphere ensures that there is no inexorable build-up of toxic metals in the atmosphere. Nevertheless, the pervasive nature of trace metal pollution in the atmosphere is well documented in a large number of published reports (for instance, see Nriagu and Davidson 1986).

Table 1.--Historical changes in the emissions of trace metals to the atmosphere. Units: x 10^6 kg (from Nriagu, 1979).

Period	Cd	Cu	Pb	Ni	Zn
Pre-1850	63	319	2420	-	2804
1850-1900	19	92	1100	12	841
1901-1910	9	53	471	8	392
1911-1920	11	80	493	21	493
1921-1930	14	96	1120	21	622
1931-1940	17	116	1693	49	746
1941-1950	22	169	1672	80	959
1951-1960	34	230	2694	140	1514
1961-1970	54	435	3704	257	2372
1971-1980	74	585	4265	415	3252
1981-1990	59	468	3412	332	2602
TOTAL	376	2643	22990	1335	16597

GLOBAL EMISSIONS OF TRACE METALS INTO THE ATMOSPHERE

The following discussions are based on global inventories of emissions of trace metals from natural and anthropogenic sources that have recently been published (Nriagu and Pacyna 1988, Nriagu 1989). The data lead to the sgestion that mankind has destabilized the steady-state (pretechnological) atmospheric cycles of the trace metals and that the various components of the biosphere are gaining large quantities of toxic metals via the aerial route.

The summary of annual emissions from natural sources (Table 2) shows that volatile and particulate material derived from biogenic processes account for over 50% of the Se and Hg and for about 30% of the As that would have been released in prehistoric times. Volcanoes and fumaroles account for over 40% of the Cd, Hg and Ni and for 20-40% of the As, Cr, Cu, Pb, Sb, V and Zn released naturally. Volcanic eruptions are episodic in nature and the values listed should be regarded as the average source strengths. Spikes of elevated metal concentrations have been reported in the polar ice layers which can be related to major volcanic eruptions (Boutron et al. 1984). Soil-derived dusts are responsible for over 60% of the Cr, Co and Mn, for about 40% of the Mo and Zn and for 20-40% of the As, Cu, Pb and Sb emitted to the atmosphere from

natural sources. Forest fires and seasalt sprays represent minor sources of airborne trace metals, each source representing <10% of the global baseline flux (Table 2). It should be noted that the data in Table 2 over-represent the natural fluxes into the pre-industrial atmosphere since anthropogenerated metals are now being mobilized by the natural processes.

Table 2.--Emissions of trace metals from natural sources to the atmosphere ($x10^6$ kg yr^{-1}; from Nriagu 1989).

Element	Soil-derived dust	Seasalt sprays	Volcanoes	Forest fires	Biogenic sources	TOTAL
As	2.6	1.7	3.8	0.19	3.9	12
Cd	0.21	0.06	0.82	0.11	0.24	1.4
Cr	27	0.07	15	0.09	1.1	43
Co	4.1	0.07	0.96	0.31	0.66	6.1
Cu	8.0	3.6	9.4	3.8	3.3	28
Hg	0.05	0.02	1.0	0.02	1.4	2.5
Mn	221	0.86	42	23	30	317
Mo	1.3	0.22	0.40	0.57	0.54	3.0
Ni	11	1.3	14	2.3	0.73	29
Pb	3.9	1.4	3.3	1.9	1.7	12
Sb	0.78	0.56	0.71	0.22	0.29	2.6
Se	0.18	0.55	0.95	0.26	8.4	10
V	16	3.1	5.6	1.8	1.2	45
Zn	19	0.44	9.6	7.6	8.1	45

Most industrial processes release one trace metal or the other into atmosphere. The three principal contributors to worldwide trace metal pollution, however, are the burning of fossil fuels, the pyrotechnical recovery of metals from their ores and the production and use of metallic commercial products (Table 3). The burning of fossil fuels to generate energy is the dominant source of atmospheric V (98%), Ni (81%), Hg (64%) and Se (60%). Most of the V is released from the burning of fuel oil and the Mn/V ratios have been used with success for identifying air parcels from this particular source (Rahn and Lowenthal 1984). The ratios of the concentrations of Ni to metals can also be used to fingerprint any air masses released from coal-fired power

plants while Se would not be a prefered choice for normalizing other metals in atmosheric source apportionment.

The mining and smelting of base metals represent the principal industrial sources of airborne Cd (71%), Cu (66%), As (63%), Cr (55%), and Zn (54%) (see Table 3). Since As, Cd, Sb and Se are by-products in the beneficiation of base metal ores, they are often allowed to go into the "smoke" unless the concentrations are high enoh to warrant their economic recovery. This method of getting rid of unwanted accessory metals in the smelted ores is environmentally ill-advised and should be discouraged especially in the developing countries.

The automobile remains the single largest source of lead in the atmosphere, accounting for about 75% of the total Pb emission (Table 3). The contribution from this source is declining rapidly, however, in response to the reduced use of lead additives in gasoline in North America and Europe (Nriagu 1990). Secondary non-ferrous metal plants represent the principal source of

Table 3.--Worldwide emissions of trace metals from industrial sources. Units: $x10^6$ kg yr^{-1} (from Nriagu and Pacyna 1988).

Process	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Se	Sn	V	Zn	Ti
Energy Production	2.2	.79	13.	8.0	2.3	12.	42.	13.	1.3	3.8	3.3	84.	17.	1.1
Mining	.06	-	-	.42	-	.62	.80	2.6	.10	.16	-	-	.46	-
Smelting and Refining	12.	5.4	-	23.	.13	2.6	4.0	46.	1.4	2.2	1.1	.06	72.	-
Manufacturing Processes	-	.60	17.	2.0	-	15.	4.5	16.	-	-	-	.74	33.	4.0
Commercial Applications	2.0	-	-	-	-	-	-	4.5	-	-	-	-	3.2	-
Waste Incineration	.31	.75	.84	1.6	1.2	8.3	.35	2.4	.67	.11	.81	1.2	5.9	-
Transportation	-	-	-	-	-	-	-	248	-	-	-	-	-	-
TOTAL	19.	7.6	3.1	35.	3.6	38.	52.	332	3.5	6.3	5.1	86.	132	5.1

atmospheric Mn pollution while the iron and steel mills account for about 55% of the anthropogenerated chromium (Table 3). Refuse incineration is currently responsible for over 30% of the Hg and for 10-20% of the Cd, Sb, Mn and Sn from industrial sources. The contribution from this source is expected to rise in future as incineration becomes increasing attractive as a strategy for municipal waste management. Burning of fuel wood and agricultural wastes is the major source of trace metals in villages and remote areas of the developing countries (Nriagu 1991).

Two divergent trends have become evident in the emissions to toxic metals in the environment. As a result of pollution control measures, the discharge of metals by industries has been curtailed and the concentrations of toxic metals in the ambient environment of many developed countries

are now declining. The reduction in atmospheric metal burden is nicely demonstrated by the the Pb, Zn and Cd concentrations in the Greenland ice layers which have declined by factors of 7.5, 2.5 and 2.5 respectively since the late 1960s (Boutron et al. 1991). By contrast, the emissions of toxic metals in the developing countries continues to rise sharply (Nriagu 1991). In fact, the highest ambient concentrations of many toxic metals in the environment are now being reported in the developing countries.

PERTURBATION OF THE ATMOSPHERIC METAL CYCLE

From the inventories in Tables 2 and 3, the ratios of anthropogenic to natural fluxes of trace metals to the atmosphere have been estimated to be 28 for Pb, 5.4 for Cd, 2.9 for Zn, 3.1 for V, 1.6 for As, 1.4 for Hg, 1.8 for Ni, 1.3 for Sb, 1.2 for Cu, 0.72 for Cr, 0.63 for Se and 0.12 for Mn. Thus, with the exception of Mn, the fluxes from industrial sources either exceed or are comparable to the emissions from natural sources implying that mankind has become the key element in the global and regional atmospheric cycling of the trace elements. Numerous field studies demonstrate causal relationships between emissions and ambient concentrations of trace metals in air in many parts of the world, thereby confirming the over-riding importance of anthropogenic inputs on the regional and global atmospheric fluxes of the trace elements (see Nriagu and Davidson 1986). For instance, the atmospheric concentrations of Pb, Cd, Cu and Fe in urban areas typically fall in the range of 100-500, 1.0-5.0, 10-60, and 50-400 ng m-3 (see Nriagu and Davidson 1986). These values are well over 1000-fold higher than the concentrations in the Antarctic Peninsula (Table 4), and large fractions of the aerosols in the Antarctica come from industrial sources (Boutron and Patterson 1987, Suttie and Wolff 1991). The long-range atmospheric transport of metal pollution is shown dramatically by the high concentrations of toxic metals in the Arctic winter haze (Table 4) which can cover up to 8% of the surface area of the earth.

Most of the industries are located in the northern hemisphere and the pertubation of the trace metal cycles in this region should be more profound. The big difference in the levels of trace metals in the Arctic and Antarctic regions is noted in Table 4. Regional differences in the anthropogeneration of trace metals are also well documented in the deposition of metals into the seas and oceans (Table 5). For most of the metals, the average atmospheric fallout follows the pattern: N. Atlantic>N. Indian>N. Pacific>S. Atlantic>S. Indian>S. Pacific. This sequence is closely related to the intensities of trace metal emissions in different regions of the world. The fact that most of the emissions currently occur in the Northern Hemisphere is clearly highlighted. The maximum disparity in metal fluxes is between the North Atlantic (most polluted) and the South Pacific (least polluted); the differences in the deposition rates between the two oceans is over 50-fold for most metals (Table 5). A recent study shows that atmospheric fallout of Pb exceeds 1000 $\mu g\ m^{-2}yr^{-1}$ of the coasts of Western Europe, eastern North America, West Africa and around Japan (GESAMP 1989); these high deposition areas are adjacent to countries where the use of Pb is very intensive. The fluxes of metal pollution into the seas in Europe make the deposition rates into the oceans look small however (Table 5).

Table 4.--Atmospheric trace metal concentrations (pg m^{-3}) in the polar regions

Element	Antarctic Penninsula 1984-1985[1]	Kap Tobin,Greenland[2] March 1979-80	Kap Tobin,Greenland[2] March 1979-80
Pb	4.7	370	3210
Cu	1.0	70	500
Zn	6.1	350	37900
Cd	0.06	-	0.11[3]

[1] Dick, 1991; [2] Heidam, 1986; [3] Spitsbergen, Dec. 1973-Mar. 1974, Wiersma and Davidson, 1986.

As to be expected, industrial emissions have drastically changed the concentrations of trace elements in the rainfall. The average concentrations of trace metals in rainfall can be estimated by assuming that 70% of the natural plus anthropogenic emissions to the atmosphere (Tables 2 and 3) are deposited on the terrestrial environment, and that the volume of rainfall on land is $1.1x10^{17}$ liters (Berner and Berner 1987). It has also been assumed that rainfall accounts for 60% of the total atmopsheric fallout. The calculated average concentrations of the trace elements in wet precipitation are shown in Table 6. It would seem reasonable that the calculated concentrations fall between the values observed in rural and remote locations. A notable feature in Table 3 is that the concentrations of trace metals in some urban areas now exceed the levels considered unsafe in drinking water and shown to be injurious to some aquatic organisms. This should be a matter of some concern in developing countries where rain water is consumed by a large number of people in the urban areas.

The average concentrations of trace metals in rainwater shown in Table 6 are much lower than those one typically finds in the literature (see Galloway et al. 1982 for good compilation). The lower concentrations are more consistent with (a) the emission inventories in Tables 2 and 3, and (b) the low ambient air concentrations of trace metals in rural and remote areas (for instance, see Wiersma and Davidson 1986, Patterson and Duce 1991). The low concentrations implies that the rainwater samples are highly prone to being contaminated during collection, treatment and analysis. Few laboratories that monitor the chemistry of atmospheric deposition employ ultra-clean laboratory techniques or have the capability for measuring trace metal concentrations in the ng l^{-1} range. Most of the available databases on trace metal concentrations in rainfall are compromised by severe sample contamination and thus provide veryconfusing insight on the question of atmospheric metal pollution. Our understading of the human influence on the distribution, fate and effects of toxic metals in the atmosphere has thus far been twarted by lack of credible data obtained using rigorous ultra-clean methods (see, for instance, Tramontano et al. 1987).

Table 5.--Fluxes of trace metals ($\mu g\ m^{-2}yr^{-1}$) into the seas and oceans (from GESAMP, 1989).

Ocean/Sea	As	Cd	Cu	Hg	Ni	Pb	Zn
N. Atlantic	67	36	400	7.6	291	1030	1600
S. Atlantic	5.4	2.9	31	1.8	24	80	127
N. Pacific	13	7.1	77	6.5	57	200	312
S. Pacific	1.3	0.73	7.8	3.0	6.0	20	31
N. Indian	21	12	125	4.9	97	330	514
S. Indian	2.1	1.5	17	3.7	13	50	69
North Sea	650	300	2700	-	1200	14000	14000
Black Sea	460	140	2900	-	-	2400	11000
NW Mediter.	<1000	<1000	4200	-	-	29000	34000

The levels of trace metals in rainfalls (Table 6) now exceed the dissolved concentrations in many aquatic ecosytems, and there is considerable evidence to suggest that the aerial inputs now dominate the biogeochemical cycling of the trace metals in such environments (Nriagu and Pacyna 1988). For instance, the atmospheric inputs are now several times higher than the riverine delivery of dissolve trace metals to the oceans (Table 7). Other evidence for the perturbation of the marine cycle of Pb by atmospheric inputs include (a) there is a 15-fold increase in Pb content of recent coral growth layers compared to those of a century ago; (b) the marked change in the form of Pb profiles in ocean water column reflects the strong atmospheric source intensity; (c) a 26-fold difference in the Pb concentrations in mixed surface layers has been noted between the North Atlantic (polluted) and the South Pacific (relatively unpolluted); and (d) a measurable shift in the isotopic signature of Pb in surface waters towards the isotopic ratio of airborne industrial Pb has also been reported (see Patterson and Settle 1987 for detailed discussion of oceanic Pb pollution). A recent analysis of the Atlantic Ocean sediments show a sharp increase in the Pb content of the surficial layer which has been attributed to increased influx of anthropogenic Pb (Veron et al. 1987).

Table 6.--Concentrations (ng L^{-1}) of trace metals in wet deposition

Element	Urban1[1]	Rural[1]	Remote[1]	Predicted[2]
As	900	240	10	120
Cd	350	50	4	33
Cr	1200	380	25	340
Cu	2800	450	20	270
Pb	6000	1400	80	1320
Hg	65	25	2	22
Ni	1500	500	35	330
V	2000	700	50	440
Zn	3500	800	75	705

[1]Compiled from recent literature.
[2] Predicted using the emission data in Tables 2 and 3.

Several studies have shown that aquatic ecosystems respond rather quickly to changes in anthropogenic inputs of trace metals. For example, the surface ocean waters off the northeastern United States have shown a 30-40% decline in Pb concentration due to the phase-out of leaded gasoline. The isotopic composition of Pb in the surface waters of the Great Lakes is very similar to the isotopic signature of the ambient aerosol (Flegal et al., 1989); the close correlation stems from the fact that the life-time of Pb in the epilimnion is only a few days and the Pb concentration is controlled by recent atmospheric inputs. Also, there has been a drastic shift in the isotopic composition of Pb in Lake Erie sediments which reflects the declining role of atmospherically derived automotive Pb (Mueller 1988). The installation of a tall stack at the Cu/Ni smelters in Sudbury (Ontario) has reduced the rates of accumulation of trace metals in the local lake sediments (Nriagu and Rao 1987), while the reduced consumption of leaded gasoline has engendered the recent decline in Pb accumulation in aquatic sediments which has been documented in many parts of the world (Levitt 1988).

Table 7.--Atmospheric versus riverine inputs of trace metals into the oceans

Element	Dissolved in Rivers ($ng\ L^{-1}$) [1]	River Input ($x10^9\ g\ yr^{-1}$) [2]	Atomospheric Input ($x10^9\ g\ yr^{-1}$) [3]
As	47	1.6	5.8
Cd	2.1	0.07	3.2
Cr	172	5.8	-
Cu	115	4.0	34
Hg	0.82	0.03	1.7
Mo	12	0.41	-
Ni	135	4.6	25
Pb	8.5	0.29	88
Sb	14	0.48	-
Se	35	1.2	-
Zn	165	5.6	136

[1] Based on published data obtained using the ultra-clean laboratory proceedures.
[2] Assuming total discharge of water by rivers to be $3.4 \times 10^{16}\ L\ yr^{-1}$.
[3] From GESAMP, 1989.

These studies clearly emphasize the strong influence of atmospheric pollution on the trace metal economy of many ecosystems and the need for emission controls as a critical means of reducing the levels and effects of toxic metals not only in the air but in our water, soils and foods as well.

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CLEAN AIR ACT REQUIREMENTS FOR TRACE METALS INFORMATION

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ABSTRACT.--The Clean Air Act Amendments of 1990 have expanded the requirements for trace metal and air toxics information in urban areas and added new requirements for this information in rural areas and ecosystems. Specific provisions germane to trace metals and other air toxics compounds are found in Title III, Section 112 and in Title IX, Section 901. In response to these provisions, the United States Environmental Protection Agency (EPA) plans to conduct research in atmospheric monitoring networks in urban areas, in the Great Lakes watershed, and in regional components of a national Clean Air Act status and trends network.

INTRODUCTION

Historically, the Clean Air Act has included requirements for the acquisition and assessment of information about trace metals and other air toxics compounds. This has resulted in research and regulatory assessment that included measurements of trace metals and associated atmospheric toxic compounds from stationary sources and the ambient air. This paper reviews the legislative framework of the Clean Air Act relevant to trace metals, discusses specific provisions of the recent 1990 Clean Air Act Amendments that are germane to trace metals and air toxics compounds, and identifies research plans for meeting these provisions.

LEGISLATIVE FRAMEWORK

The provisions for attainment and maintenance of national ambient air quality standards (Sections 108 and 109 of the Clean Air Act and subsequent Amendments) have formed the cornerstone of the national strategy to reduce and control air pollution. The fundamental concept underlying these national ambient air quality standards (NAAQS) is that they represent threshold levels of air pollution below which the best scientific evidence and judgement indicates that humans experience no adverse health effects.

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The NAAQS have been established to regulate levels of "criteria" air pollutants: particulate matter, lead, sulfur dioxide, nitrogen dioxide, ozone, and carbon monoxide. Establishing and revising these standards has required a scientific determination of the relation between ambient concentrations of these pollutants, their sources, and associated health effects. This in turn has required the deployment and operation of national monitoring networks to measure the concentrations of these pollutants and to identify their sources. The primary focus of these networks has been urban areas. However, since the NAAQS apply only to a relatively small number of air pollutants, additional legislative mechanisms were needed to establish regulations for the large number of stationary sources of trace metals and toxic emissions not covered by these standards.

Thus, Sections 107 and 110 of the Clean Air Act of 1970 provided for the establishment of metropolitan statistical areas (formerly air quality control regions), the determination through statistical analysis of whether and by how much air pollution in each region exceeds the relevant NAAQS, and the development of strategies and regulations known as State Implementation Plans (or SIP's) to achieve compliance with the NAAQS.

These SIP's typically mandated control of categories of "existing" stationary sources of air pollution and were less stringent than federal standards for categories of "new" stationary sources. Sections 111 and 112 of the 1970 Clean Air Act Amendments required EPA to promulgate New Source Performance Standards (NSPS) and National Emission Standards for Hazardous Air Pollutants (NESHAPs), respectively. Stationary source control regulations promulgated under sections 111 and 112 have been largely responsible for improvements since 1970 in ambient air quality, which have occurred for all criteria pollutants except ozone.

An additional legislative mechanism was employed for lead and other compounds emitted from motor vehicles. Ambient concentrations of this trace metal are generally attributed to mobile sources and a limited number of stationary sources. Thus, Section 211 of the 1970 Clean Air Act and subsequent Amendments has reduced tailpipe lead emissions by mandating a gradual phase-down of lead in gasoline used in motor vehicles.

In summary, prior to 1990, Clean Air Act legislation has managed the impact of air pollutants on human health through implementation of national ambient air quality standards. Determination of the relationship between ambient air quality and human health has been accomplished primarily through atmospheric measurements to characterize spatial and temporal concentrations of air pollutants in populated urban areas. Ambient air quality has been improved largely through stationary source control regulations which have required short term source emissions measurements.

RECENT REQUIREMENTS FOR TRACE METAL INFORMATION

In contrast to this historical legislative framework, the Clean Air Act Amendments of 1990 include new provisions of particular relevance to the need for trace metal and toxic compound information. Although continuing the historic focus on urban areas, the 1990 Clean Air Act expands the need for ambient air measurements beyond urban areas by mandating significant research to characterize the spatial and temporal impacts of trace metal and toxic compounds on rural ecosystems. These new legislative provisions are found in Title III, Section 112 and Title IX, Section 901 of the 1990 Clean Air Act Amendments.

In establishing new provisions for trace metals and other hazardous air pollutants in Section 112 (k), Congress determined that emissions of hazardous air pollutants from area sources may present significant risks to public health in urban areas. Area sources consist of small, unregulated stationary and mobile sources. This determination was based in part on the large number of potentially exposed individuals in urban areas as well as the risk of carcinogenic and other adverse health effects from hazardous air pollutants.

Thus, Section 112 (k)(2) requires a program to conduct research that will characterize and identify the sources of hazardous air pollutants in urban areas. To meet these objectives, the Environmental Protection Agency (in consultation with State and local air pollution control agencies) will design a program that will: (1) conduct ambient monitoring for a broad range of hazardous air pollutants (including volatile organic compounds, metals, pesticides, and products of incomplete combustion) in a representative number of urban areas; (2) characterize the sources of these compounds and determine those contributing area sources as well as their contribution to public health risks; and (3) consider factors which can elevate public health risks from these sources such as atmospheric transport and transformations.

Section 112 (k)(2) requires the development of a national strategy based on this research that would control emissions of hazardous air pollutants from area sources. The national strategy must identify at least 30 hazardous air pollutants that pose the greatest threat to public health in the largest number of urban areas; source categories which, individually or in the aggregate, present a threat of adverse effects to human or environmental health; source categories which represent 90 percent or more of the area source emissions of the 30 pollutants mentioned above; and additional research needs in monitoring, analytical and measurement methodology, modeling, or pollution control technology. A report of this national strategy is to be transmitted to Congress in 1995.

Section 112 (m) of the 1990 Clean Air Act Amendments requires EPA, in cooperation with the National Oceanic and Atmospheric Administration, to conduct a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants to the Great Lakes, Chesapeake Bay, Lake Champlain, and coastal waters (hereafter, this group is referred to as the "Great Waters"). As a part of this program, EPA will conduct atmospheric measurements and monitoring of these Great Waters; investigate the sources, concentrations, and deposition rates of these pollutants; conduct research to develop and improve monitoring methods and source attribution techniques; evaluate adverse effects to public and environmental health, including

ecosystem health; and sample biota in Great Waters ecosystems and characterize the sources of any identified pollutants.

Section 112 (m) contains additional requirements that are specific to the Great Lakes. These requirements mandate the establishment and operation of a Great Lakes atmospheric monitoring network to characterize trace metals and other hazardous air pollutants and to estimate atmospheric deposition of these substances. This network is to be coordinated with the Integrated Atmospheric Deposition Network called for in the Great Lakes Water Quality Agreement between the United States and Canada. Moreover, EPA is to establish by December 31, 1991 at least one facility on each of the five Great Lakes capable of monitoring hazardous air pollutants in both wet and dry conditions. The trace metal and hazardous air pollutant information collected by both United States and Canadian participants in this monitoring network is to be comparable (from a measurement and analytic perspective) and compatible with appropriate integrated databases from both countries.

The focus of these Great Lakes provisions in Section 112 (m) is on the largely rural watershed of the lakes and on the ecosystems contained in the watershed. The measurements acquired through the monitoring network will be used to identify and track the movement of hazardous air pollutants to the lakes and to determine the portion of total loadings to the watershed attributable to the atmospheric pollution and sources. To the extent that atmospheric sources are significant, the monitoring data will be essential in developing strategies for regulations, remedial action plans, and pollution prevention.

Section 112 (n) of the 1990 Clean Air Act also requires the acquisition and assessment of trace metal and air toxics data. In contrast to the Great Lakes and Great Waters focus of the previous provisions, this requirement focuses specifically on electric utility steam generating units. Section 112 (n)(1) requires EPA to conduct a study of the hazards to public health reasonably anticipated to occur or remain as a result of utility emissions after the imposition of the various provisions of the 1990 Clean Air Act. In a separate study required under Section 112 (n)(2), EPA is to study mercury emissions from electric utility steam generating units, municipal waste combustion units, and other sources, including area sources. This study is to characterize not only the mercury emissions but also the human and environmental health impacts of these emissions.

The second group of legislative provisions that require trace metal and air toxics information is found in the Title IX, Section 901, clean air research provisions of the 1990 Clean Air Act Amendments. These provisions identify broad new environmental and ecosystem measurement and monitoring research objectives.

Sections 901 (a), (b), and (c) direct EPA to conduct a research and development program that would include research, testing, and development of methods for sampling, measurement, monitoring, analysis, and modeling of air pollutants. This program is to include the establishment of a national network to monitor, collect, and analyze data (with quantification of certainty) on the status and trends of air emissions, deposition, air quality, surface water quality, forest condition, and visibility impairment. Similar research is to be done to increase understanding of the sources of ozone precursors, formation, and transport.

Section 901 (e) directs EPA to conduct ecosystem research to improve the understanding of the short- and long-term causes, effects, and trends in damage from air pollutants. This research is to include: identification of regionally representative and critical ecosystems; characterization of the causes and effects of chronic and episodic ecosystem exposures to air pollutants; development of improved atmospheric models and monitoring systems for evaluating exposures and effects of the multiple environmental stresses associated with air pollution; and evaluation of the effects of air pollution on water quality, forests, materials, biological diversity, soils, and crops.

EPA RESEARCH PLANS

FOR HAZARDOUS AIR POLLUTANTS AND TRACE METALS

The brief review of the 1990 Clean Air Act Amendments presented above illustrates the increased importance of research to characterize hazardous air pollutants and trace metals and their human and environmental health effects in both urban and nonurban environments. Also illustrated is the significance of the new emphasis on the need for information about these air pollutants and their impacts on predominantly nonurban ecosystems. This review further indicates that the provisions of Section 901 have more ambitious environmental implications than those of Section 112 because of the number of air pollution and ecosystem research objectives included.

Currently, EPA is planning an integrated series of new and existing atmospheric and ecosystem monitoring networks designed to achieve many of these research objectives. This Clean Air Act status and trends network, operated through the Environmental Monitoring and Assessment Program (EMAP), is being designed and implemented by a team of environmental scientists that includes representatives from EPA, State air pollution control agencies, other federal agencies, corresponding Canadian federal and provincial agencies, and universities. The details of this design, which is too complex to describe in the limited context and space of this paper, will be the subject of final scientific peer review and journal publication later this year.

This atmospheric and ecosystem network will include a Great Lakes trace metals and air toxics monitoring component. Designed to achieve the Section 112 (m) schedule of establishing at least one site on each of the Great Lakes by December 31, 1991, these sites will be a part of the United States and Canadian Integrated Atmospheric Deposition Network.

A separate ambient monitoring network will be established to achieve the urban area source provisions of Section 112 (k). This urban air toxics research network, which will measure trace metals and air toxics compounds, will be a part of the Enhanced Ozone Monitoring Network required under Title I of the 1990 Clean Air Act Amendments. The current plan for this network is that one site in each of twenty five metropolitan areas that have been identified as serious, severe, or extreme ozone nonattainment areas will characterize volatile organic compounds and aldehydes. A subset of these sites will be selected for supplemental measurements of trace metals, pesticides, and other toxic compounds. Additional measurements will be made at these

sites to assist in the identification of sources contributing these air pollutants to the ambient air in the urban environment.

ANALYSIS AND DEPOSITION OF TRACE METALS IN ONTARIO

Daniel B. Orr, Michael J. Shaw and Neville W. Reid[1]

ABSTRACT.--Results of monitoring for selected trace metals in wet deposition in Ontario are presented. Spatial trends indicate a decreasing gradient from south to north, consistent with the location of the main emission sources in and to the south of the province. Anomalies in this typical deposition pattern are associated with local emission sources. Mass loadings to the Laurentian Great Lakes have been calculated. Loadings of the selected metals into the Great Lakes have decreased over time, with the exception of increased lead and manganese inputs into Lake Superior. Special studies complementing the regular monitoring program are described.

INTRODUCTION

Direct atmospheric deposition is now recognized as a significant input pathway of toxic trace metals into the Laurentian Great Lakes and their drainage basin. For instance, the International Joint Commission (1988) estimates that more than 90% of the lead entering Lakes Superior, Huron and Michigan is input from the atmosphere. The proportions estimated for other critical pollutants and the other lakes in the Great Lakes system are smaller, but are always significant.

The ramifications of trace metals deposition in the Great Lakes system are realized in more pragmatic terms. In Ontario, for example, annual consumption advisories are issued for top predator fish species based upon muscle mercury concentrations (Ontario Ministry of the Environment 1991). Similarly, an advisory warning against the consumption of moose and deer liver and kidneys is in effect because of their elevated cadmium levels (Glooshenko et al. 1988). With the exception of localized effects, no widespread phytotoxological injury to cash crops has been reported in Ontario. However, vegetable crops grown on soils in regions of high trace metals deposition and no local sources rapidly take up and assimilate these metals (Czuba and Hutchinson 1980).

This paper describes the spatial and temporal trends of selected trace metals wet-only deposition monitored by the Ontario Ministry of the Environment (OME), under the auspices of the Acidic Precipitation in Ontario Study (APIOS). The wet-only deposition trends stated in this paper update a previous report by Reid et al. (1989), by using data for the period 1981-1988. Special studies and new initiatives complementing the regular monitoring program are discussed also.

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NETWORK OPERATIONS

Trace metals wet-only deposition is monitored in Ontario in the APIOS Cumulative Network. The density of samplers is greatest in the southern part of the province, where the highest concentrations are expected. Network operations have been described by Chan et al. (1985). Briefly, an integrated precipitation sample is collected over a 28-day period, commencing every fourth Tuesday, using an M.I.C. Type A wet-only collector, fitted with a polyethylene bag insert. No preservative solution is added to the sample. The implications associated with this particular sampling scheme have been described by Chan et al. (1983) and Tang et al. (1987).

An aliquot of each cumulative precipitation sample is acidified with a 1% ultrapure nitric acid solution. The empty bag is leached for 24 hours in a 5% ultrapure nitric acid solution, then both portions are analysed for copper (Cu), nickel (Ni), lead (Pb), manganese (Mn), zinc (Zn), cadmium (Cd), iron (Fe), aluminum (Al), vanadium (V), and arsenic (As) by graphite furnace atomic absorption spectrometry.

Wet deposition is calculated directly as the product of precipitation concentration and precipitation depth. Mass loadings into the Great Lakes are calculated directly as the product of wet deposition and the respective surface areas of the lakes.

RESULTS

The spatial trends described are based upon results from thirty-three sites in operation during the study period. The temporal trends and estimates of mass loadings into the Great Lakes stated are based upon results from selected sites located within 20 km of the shoreline of the Great Lakes. Discussion of results is limited to the elements Pb, Mn, Zn and Cd.

SPATIAL TRENDS

The pattern of wet deposition for lead is presented in Figure 1. This figure shows a strongly decreasing gradient in the annual wet deposition from south to north, a pattern typical for the other pollutants considered here and for most pollutants monitored in Ontario (Tang et al. 1986). This observation is consistent with the fact that pollutant sources are mainly located in and to the south of the province. The annual wet deposition of Pb ranges from greater than 60 g ha^{-1} in the south to less than 30 g ha^{-1} in the north. For Mn the range is from greater than 45 g ha^{-1} to less than 20 g ha^{-1}. For Zn the range is from greater than 60 g ha^{-1} to less than 20 g ha^{-1}, while Cd deposition ranges from greater than 2.0 g ha^{-1} to less than 0.5 g ha^{-1}.

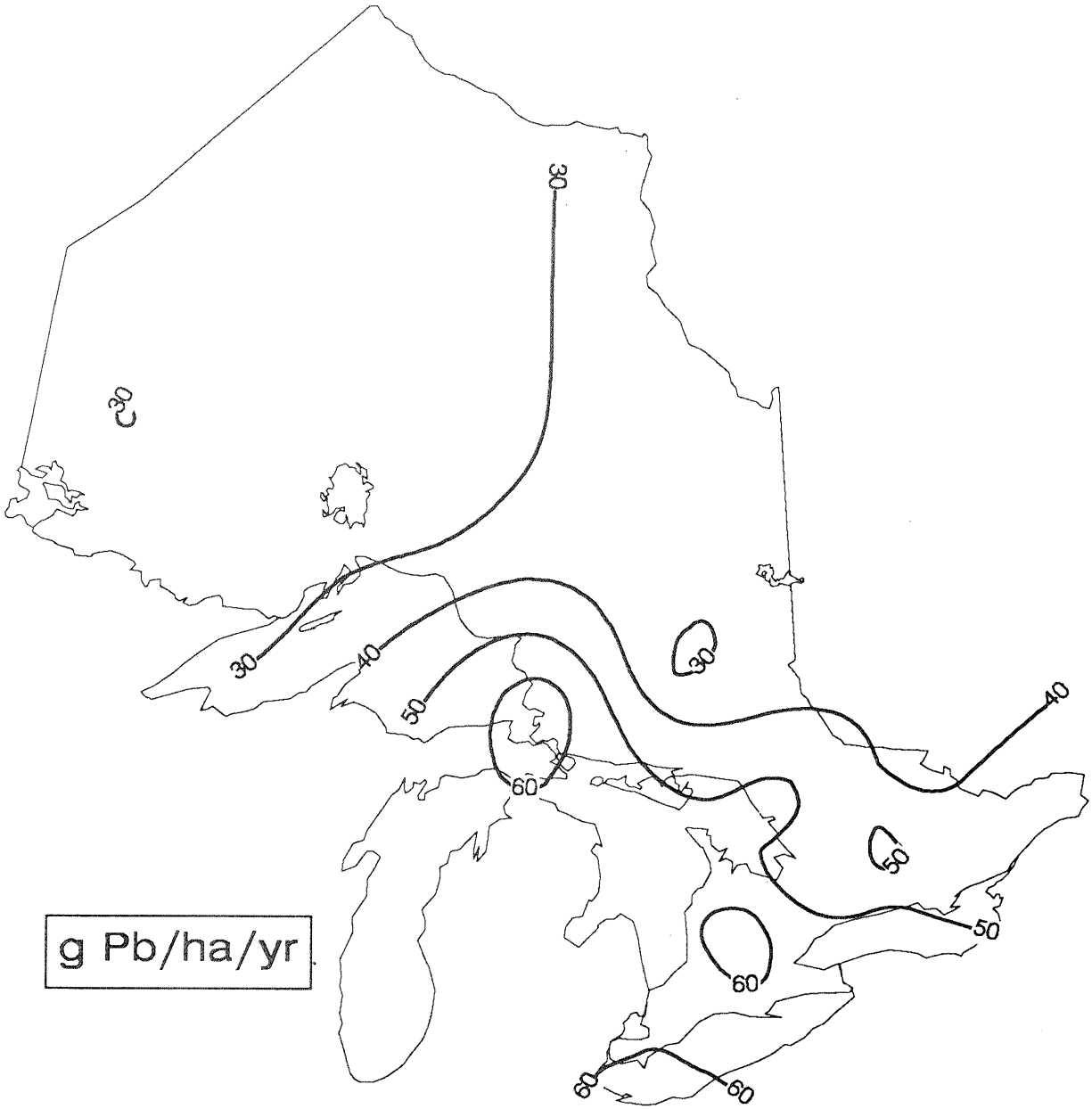

Figure 1.--Annual wet deposition (g ha^{-1}) for Pb in Ontario, 1981-1988.

Figure 1 also illustrates a deposition feature typical of the northern portion of the province. This is the occurence of localized, elevated levels of Pb, Mn, Zn and Cd. Hot spots for Mn and Pb can be readily associated with emissions from steel mills in Sault Ste. Marie and an iron-ore sintering plant in Wawa. Zinc and Cd anomalies can be attributed to emissions from the non-ferrous smelters in Sudbury.

TEMPORAL TRENDS

The temporal trend of Pb mass loading is shown in Figure 2.

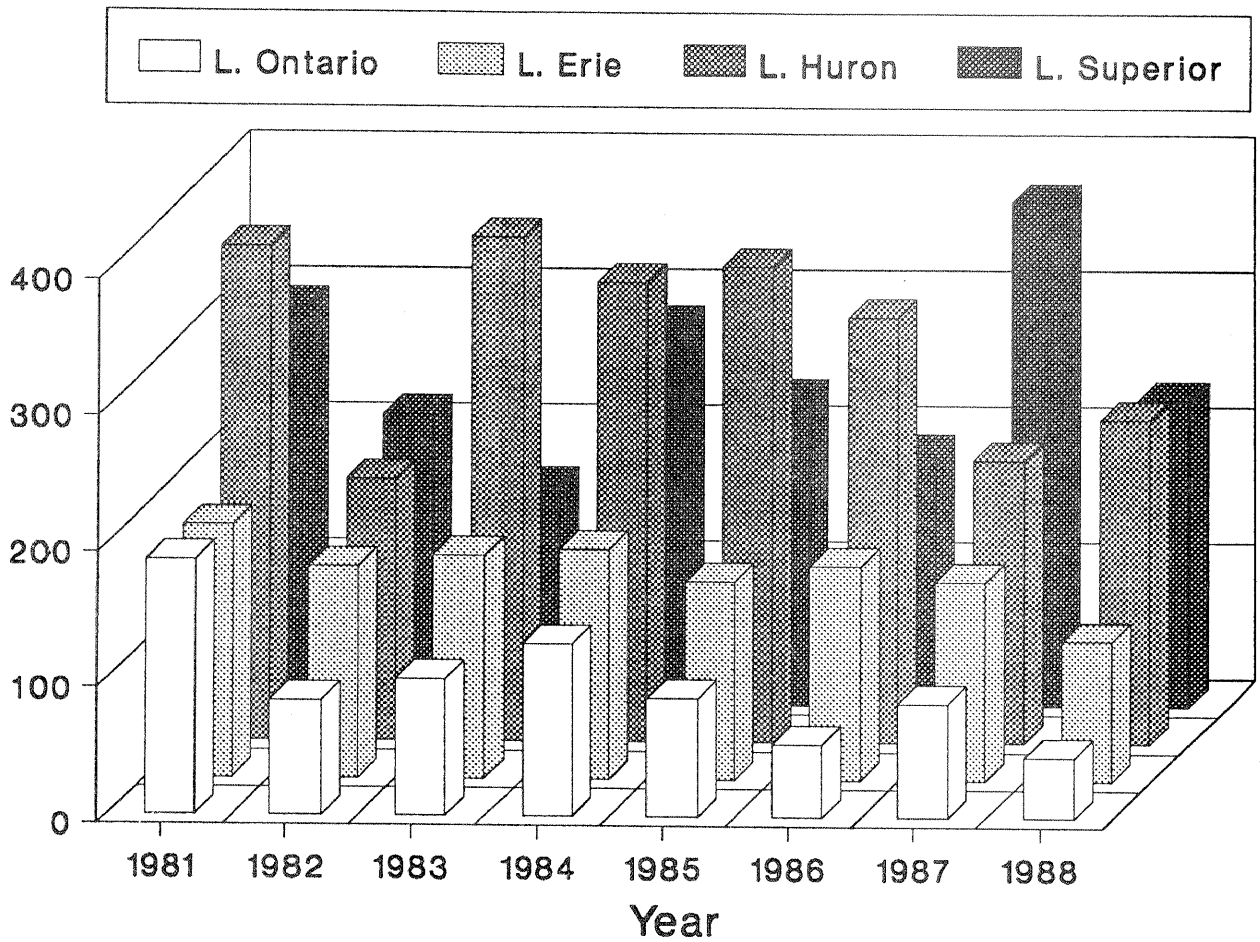

Figure 2.--Mass loading of Pb (x 10^3 kg) to the Laurentian Great Lakes, 1981-1988.

The temporal profiles for Mn, Zn and Cd loading are similar to the pattern observed for Pb, that is, there is considerable variability from year to year. It may be noted that during 1982 the non-ferrous smelting operations in Sudbury were shut down for most of the year because of a labour strike. Despite the annual variability, it is possible to discern decreasing temporal trends for each of the selected metals into the lakes using classical time series analysis (for example, Reinmuth 1977). The notable exceptions to this observation are for Pb and Mn loading into Lake Superior, where a slight increase is seen over the study period. The average mass loadings and annual per cent change for the study period are summarized in Table 1.

Table 1.--Estimated average mass loadings (x 10^3 kg) to the Laurentian Lakes, 1981-1988. The annual per cent change in temporal trend appears in parentheses.

Element	L. Ontario	L. Erie	L. Huron	L. Superior
Pb	96.3 (-8.8)	153.4 (-4.3)	296.8 (-3.3)	244.1 (+1.8)
Mn	61.0 (-0.7)	129.1 (-2.2)	167.4 (-0.9)	177.3 (+5.6)
Zn	87.5 (-10.0)	140.0 (-4.0)	220.9 (-3.7)	244.2 (-5.5)
Cd	1.5 (-6.3)	5.1 (-11.7)	4.9 (-11.3)	5.0 (-9.8)

The decreasing trend in Pb loading for several lakes is to be expected, following the phase-out of Pb in gasoline in North America. The increasing trend for Lake Superior suggests that other sources, presumably mining, dominate in this area.

SPECIAL STUDIES AND NEW INITIATIVES

ANALYTICAL MEASUREMENTS

Since September, 1990 all APIOS cumulative precipitation samples have been analysed by inductively-coupled plasma/mass spectrometry (ICP/MS). This method achieves more sensitive limits of detection and enables the determination of more exotic elemental tracers, such as In, Sb, Se, and Ge.

DAILY PRECIPITATION SAMPLING

Daily precipitation samples are collected at the APIOS Dorset event site in south-central Ontario for trace metals analysis. Samples are collected in Aerochem Metrics precipitation collectors fitted with polyethylene bag inserts. The samples are analysed by ICP/MS. Residence time analysis (Poirot and Wishinski 1986) is able to delineate the boundaries of implied source areas using this data, as shown in Figure 3.

In this example, air parcel trajectories were calculated for 1989 daily samples with high V deposition, that is, values greater than the 75th percentile. The amount of time an air parcel spent over a source area was calculated, with the results depicted as isolines of probability. Heaton et al. (1990) postulate that non-crustal V is a useful tracer for regional pollution sources, notably oil combustion. The results illustrated in Figure 3 substantiate this premise, implicating midwest sources.

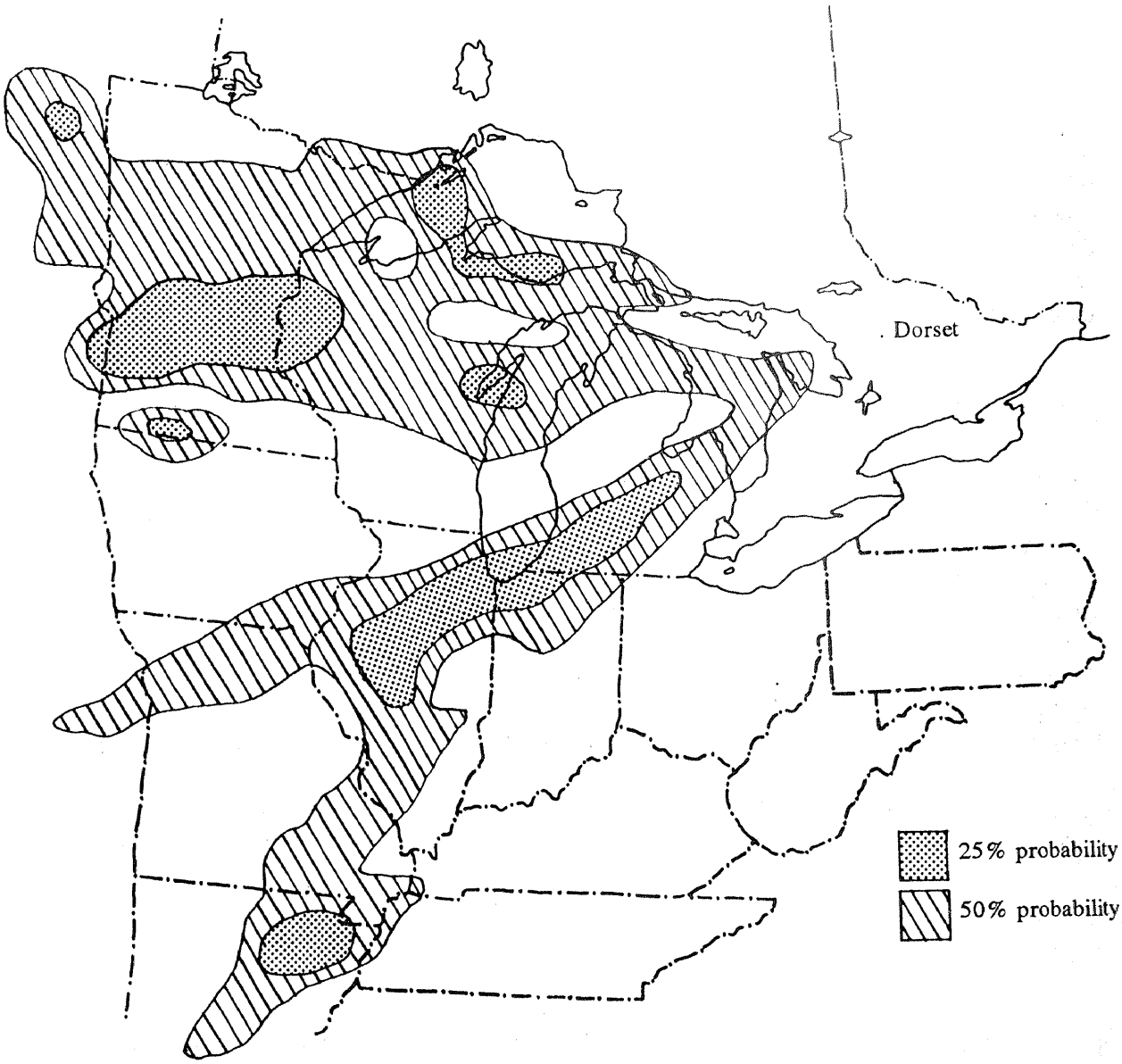

Figure 3.--Residence time analysis plot for high V deposition in daily precipitation samples collected at Dorset, Ontario.

MERCURY IN PRECIPITATION SAMPLING

Mercury concentrations in northwestern Ontario daily precipitation on the order of 1 microgram L^{-1} have been reported (Glass et al. 1986). These results are considered qualitative only because the preservative solution of 0.06% potassium dichromate and 1% nitric acid was ineffective in preventing wall losses and volatilization. Mercury in cumulative precipitation is being re-investigated, with method development focussing on the use of bromine monochloride or hydrogen peroxide as stabilizing agents, and analysis by cold vapour atomic absorption.

SUMMARY

The deposition of trace metals in Ontario generally decreases spatially from south to north. Deposition in the province and mass loadings to the Great Lakes have also generally decreased over time since 1981. The substantial trace metals deposition data base generated by routine monitoring and special studies activities has enabled the Ontario Ministry of the Environment to develop considerable expertise in the analysis and interpretation of trace metals data - a resource which other deposition monitoring agencies could draw upon when they consider trace metals for their chemical target list.

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ANALYSIS & DEPOSITION OF TRACE METALS AROUND THE GREAT LAKES

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ABSTRACT.--The Great Lakes Atmospheric Deposition (GLAD) network is designed to collect precipitation samples around the shoreline of the Great Lakes. Calculations of the annual volume weighted means and loadings for selected metals to each of the Great Lakes are estimated through the subsequent analysis of the wet deposition samples taken at various sites around the lakes. Both precipitation and loadings to the Great Lakes are variables. Site variations in annual precipitation amounts, especially in and around urban areas such as southern Lake Michigan and western Lake Ontario, influence the loadings to each lake. This paper examines the annual volume weighted means (VWM) of metals around the Great Lakes.

INTRODUCTION

The Great Lakes of North America collectively comprise the largest area (244,007 km^2) of fresh water on the surface of the earth as reported by Herdendorf (1982) and represent a great natural resource to both the United States and Canada. Under the Great Lakes Water Quality Agreement of 1972 these two nations developed surveillance, monitoring, and research activities to protect and reclaim, if necessary, the chemical and physical quality of the Great Lakes Basin. The importance of atmospheric deposition to these lakes was recognized in the 1970s by Shiomi and Kuntz (1973).

The problems of precipitation measurement over the Great Lakes using data from shoreline sites were addressed by Changnon and Huff (1966), Wilson (1977), and Bolsenga (1979). In 1981 the United States Environmental Protection Agency established an atmospheric deposition network consisting of thirty five (35) wet-only precipitation samplers along the shoreline of the Great Lakes. In January 1986 the size of the network was reduced from 35 sites to 20 sites because of funding reductions. The sites are located in both rural and urban locations. A rural site is any site at least 40 km from a metropolitan center of population greater than 15,000. Urban sites are all sites falling within 40 km of any metropolitan area with a population greater than 15,000.

The purpose of this network is to determine the annual volume weighted means (VWM) and loadings of metals, nutrients, and other inorganic compounds to each of the lakes. In addition,

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this monitoring program is designed to determine spatial and temporal trends in deposition, to identify emerging problems in atmospheric pollution in the Great Lakes Basin, and to provide source information for regulatory action. This report examines the metals data obtained from the Great Lakes Atmospheric Deposition (GLAD) network from 1982 through 1989. Annual loadings are calculated for these metals at each site based upon the product of the annual volume weighted means (VWM) and their annual precipitation amounts. Investigations into the loadings of metals from precipitation have been performed by Barrie et al. (1987), Eisenreich (1980), Gatz et al. (1989), Reid et al. (1989), and Ross (1987).

WET DEPOSITION SAMPLING METHODOLOGY

To obtain wet deposition concentrations of metals, the samples must be handled very carefully by each site operator and also by the chemist performing the analysis in the laboratory. The sampling period has an effect on the wet deposition of metals as indicated by de Pena et al. (1985). Investigations done by Chan et al. (1983) and Ross (1986) point out the problems encountered when collecting precipitation samples in polyethylene buckets or bags for analyses of heavy metals. As pointed out by Barrie (1988) metals may yield an aerosol signature from a region that is sufficiently distinct that its presence at a distant receptor can be distinguished from that of other source regions.

LOADINGS TO THE LAKES

As reported by Barrie (1986) the measurement of metal species concentrations were more suited to special intensive research than to routine network monitoring. However, total concentrations of many metals can be measured routinely by networks following proper sample collection, handling, and analysis procedures.

Precipitation samples are collected at the GLAD sites in polyethylene bag liners on a weekly interval (each Tuesday) provided a minimum of 500mL of precipitation (1/8 inch of water or 1 1/4 inches of snow) is in the Aerochem Metrics sampler. Both the liners and the 500mL bottles in which the precipitation samples are sent to our laboratory are checked for contaminants prior to shipment to the field site operators. All site operators are properly clothed to ensure that sample contamination is kept to a minimum. The volume of the sample is measured by the respective GLAD site operator, and then a 500mL sample is mailed to our laboratory.

Each precipitation sample is analyzed for twenty two (22) metals. They are aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). Seven (7) of these metals (Na, K, As, Cr, Cd, Pb, and Ni) are analyzed using atomic adsorption (AA) spectrophotometry. The other fifteen (15) metals are analyzed by inductively coupled argon plasma (ICP) spectrophotometry.

Instructions regarding the sample collection and laboratory analysis are described in the station operator's manual (1990a) for the Great Lakes National Program Office and the quality assurance project plan for the Bionetics Corporation (1990b), respectively. The limit of detection (LOD) of these metals by our contractor laboratory are given in Tables 1 and 2. The concentrations of these metals are expressed in mg L^{-1}. A report of site visits and evaluations of the GLAD sites was made by Murphy (1985). This report identified siting problems which were corrected. In some cases a change in sampler location was necessary.

Table 1.--ICP detection limits for metals in precipitation.

Metal	Detection Limits (mg L^{-1})	Range (mg L^{-1})
Al	0.02	0.020 - 2
B	0.008	0.008 - 2
Ba	0.002	0.002 - 2
Be	0.001	0.001 - 2
Ca	0.05	0.050 - 2
Co	0.0025	0.003 - 2
Cu	0.0025	0.003 - 2
Fe	0.005	0.005 - 2
Li	0.005	0.005 - 2
Mg	0.005	0.005 - 2
Mn	0.002	0.002 - 2
Sr	0.001	0.001 - 2
Ti	0.004	0.004 - 2
V	0.004	0.004 - 2
Zn	0.004	0.004 - 2

Each year the annual VWM for these metals are calculated using the following equation:

$$VWM = \sum_{i=1}^{n} X_i Y_i \; / \; \sum_{i=1}^{n} X_i$$

where X_i represents the sample volume in mL and Y_i is the concentration of the metal in mg L^{-1} collected at that respective site.

Precipitation is variable from year to year and from site to site, and the Great Lakes influence this precipitation variability as described by Changnon and Jones (1972) and Eichenlaub (1979). The annual precipitation amounts, calculated using a method developed by Barnes (1964) and modified by Achtemeier (1987), are furnished by the Illinois State Water Survey. Examination of this 8-year annual precipitation amount (1982-1989) compared to the 30-year mean (1951-1980) mean precipitation at the GLAD sites around the Great Lakes shows the 1982-1989 precipitation amounts to be greater than the 30-year average at 30 of the 35 sites.

After the annual VWM and the annual precipitation data are available, the annual loadings, expressed in kg km^{-2}, for all metals at all sites are then calculated. The sites have been grouped into either rural or urban sites according to the guidelines explained in the Introduction. A comparison of the VWM and annual loadings for the urban and rural sites has been completed. In addition the 8-year average monthly VWM for the sites was compiled to examine the monthly variation in metals data.

Table 2.--Atomic adsorption (AA) detection limits for metals in precipitation.T

Metal	Detection Limits (mg L^{-1})	Range (mg L^{-1})
As	0.00007	0.000007 - 0.0025
Cd	0.00013	0.00013 - 0.001
Cr	0.00007	0.00007 - 0.003
K	0.015	0.015 - 1.0
Na	0.010	0.010 - 1.0
Ni	0.00025	0.00025 - 0.003
Pb	0.0007	0.0007 - 0.010

RESULTS

The combined monthly 1982-1989 VWM data were examined for ten (10) metals (Pb, Fe, Ca, Zn, Cu, Cd, K, Mg, Na, and Ni). Except for Ca, Zn, and K the rural VWMs were less than those from the urban sites. Cd did not exhibit any pattern, and the urban maximum found in November is questionable.

The loadings trends of metals were variable. Sodium and Ca showed an increase in annual trends while Cd increased most notably at rural sites except for Lake Michigan. Potassium, Cu, Fe, Ni, and Zn loadings decreased from 1982 to 1989 while Mg loadings showed a general decrease during this same time period.

Lead is the metal which has shown the most noticeable reductions in loadings to the Great Lakes during this 8-year time period. The reason for the reduction in lead loadings is the mandatory use of unleaded fuel by automobiles in the United States as was pointed out by Eisenreich et al. (1986). Figure 1 is a plot of the annual lead loadings at three sites: Put-In-Bay (a downwind urban site) in western Lake Erie and Beaver Island (a rural site) and Evanston (an urban site) both on Lake Michigan. Data for lead is available from 1983-1989. This lead analysis was done by atomic adsorption (AA) spectrophotometry whereas in 1982 the precipitation samples were analyzed by inductively coupled argon plasma (ICP) spectrophotometry. The ICP had a much higher limit of detection, and therefore the data values were usually below minimum instrument detection limits.

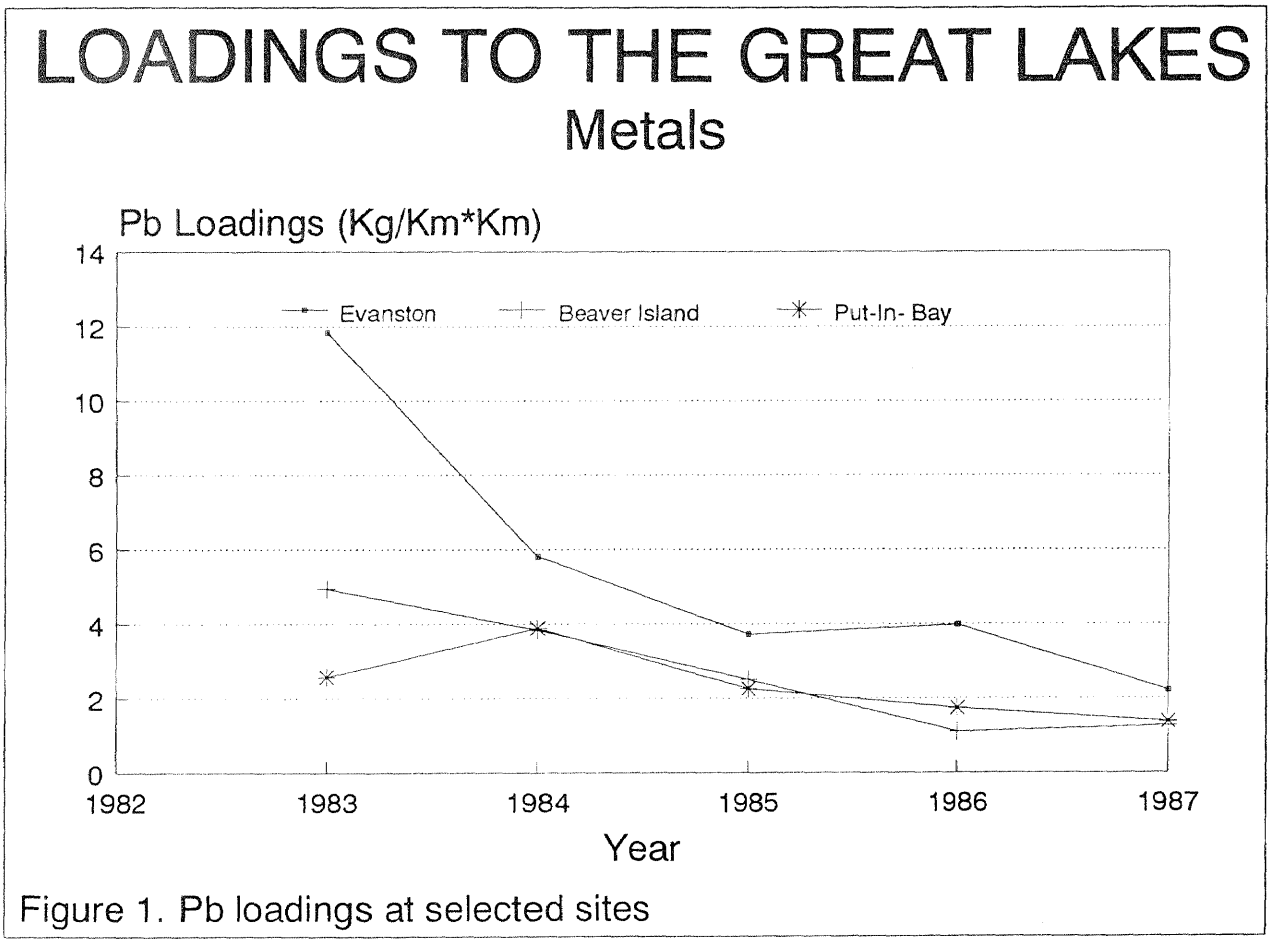

Figure 1. Pb loadings at selected sites

Figure 1.--Pb loadings at selected sites

CONCLUSIONS

Both the rural and urban 8-year VWMs for Pb, Fe, Zn, Cu, and Na show a maximum in the winter months and a minimum in the summer months. Potassium, Mg, and Ca, however, show maximums in the spring and summer while Ni and Cd show no significant pattern from month to month.

ACKNOWLEDGEMENTS

I wish to thank Messrs. D. K. Salisbury and C. H. O'Leary of Computer Sciences Corporation (CSC) for providing the programming assistance necessary to compute the volume weighted means and loadings to the lakes. I am also indebted to Mr. Van C. Bowersox of the Illinois State Water Survey for providing the mean weighted annual precipitation data to me.

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TRACE ELEMENTS IN PRECIPITATION AT THE MIDDLE ATLANTIC COAST: A SUCCESSFUL RECORD SINCE 1982

T. M. Church and J. R. Scudlark[1]

ABSTRACT.--The trace elements Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se and Zn have been successfully measured in atmospheric precipitation events at Lewes, Delaware on the mid-Atlantic coast since 1982 as part of the NOAA-WATOX program. This constitutes probably the longest and most comprehensive trace element precipitation record in the United States. The concentrations exhibit large event and seasonal variation according to remote sources and local meteorology. This necessitates long and continual records for accurate analysis of concentration and flux trends. The patterns of enrichment relative to crustal elements are concordant with local and remote aerosol records suggesting common emission sources and scavenging after long range transport. The long-term average fluxes are consistent over the region and document the continual decline of some emission enriched elements such as lead over the past decade. The atmospheric fluxes of most trace elements, while a minor direct input term for estuaries, can dominate on the basis of the entire watershed. The atmospheric fluxes of many emission trace elements dominate the exported estuarine fluxes to coastal waters of the middle Atlantic region.

INTRODUCTION

Many atmospheric trace elements are co-emitted with sulfur and nitrogen during high temperature combustion. This results in the potential for the significant atmospheric mobilization and deposition of other elements in acid precipitation which may have equally important ecological implications.

Trace elements include both natural and anthropogenically derived metals such as Al, Cr, Fe, Mn and Ni which can have both mineral and metallurgical sources; As, Cd, Cu, Pb, Se, and Zn which can have primarily high temperature emission sources over industrialized continents from fossil fuel burning and industrial manufacturing.

Trace elements emitted and transported as micron-size aerosols largely fall out in the boundary layer near continental sources. However, many emission derived trace metals occur as submicron size aerosols which are scavenged from the troposphere primarily by precipitation. Thus trace metals in precipitation can be and are pervasive constituents of acid precipitation. Their transport

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and direct atmospheric deposition can constitute effective fluxes into continental or coastal watersheds with important ecological implications.

RATIONALE AND HISTORY OF COLLECTION

We initiated trace element collection at Lewes, Delaware in 1982 in an effort to expand our DOE-MAP3S major ion collections to other elements. Figure 1 is a map of the site, which is located within the semi-remote confines of Cape Henlopen State Park, in a sandy clearing among scrub pines a couple miles west of the Atlantic ocean beach.

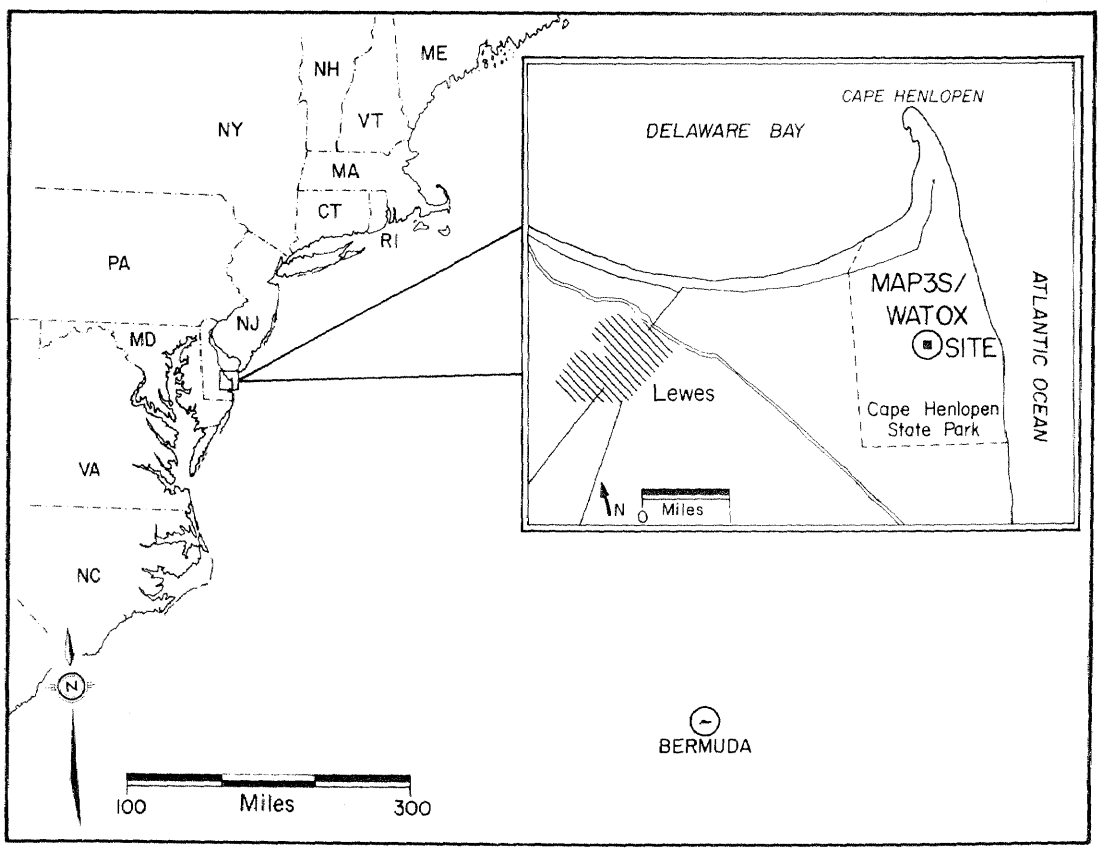

Figure 1.--Location of the atmospheric research station at Lewes, Delaware for the sampling of major and trace elements in precipitation.

Under the NOAA-WATOX program our general objectives were to document the source, transport, deposition and fate of North American atmospheric pollutants exported to the North Atlantic Ocean (Galloway et al. 1986). The collections at Lewes represented the coastal boundary end member for this effort, and the earlier results are published elsewhere (Church et al. 1982, Church et al. 1984). During this period (Table 1), several other researchers and programs took advantage of our site and research at Lewes to carry on related atmospheric studies at a semi-remote coastal location.

Table 1.--Chronology of atmospheric research at the Lewes, Delaware site located at Cape Henlopen state park on the mid-Atlantic coast-sponsoring agencies.

Dates	Research Activities
8/77-3/78	Initial site evaluations
3/78	Precipitation collections for major ions commenced (MAPBS)-DOE
4/81	OSCAR study (primary and 4 satellite stations) - DOE
5/82	Precipitation collections for trace metals started - (WATOX) - NOAA
8/82 & 2/83	WATOX Intensives--pollutant aerosols and gases (with General Motors, U. Miami, RSMAS, NRL)
8/23	Metalloid (As and Se) speciation study with G. Cutter (ODU)
2-4/85	WATOX Winter Intensive (AES Canada, NOAA-ARL, U.Wash., U. Virginia, NRL, York Univ.
2-3/86	GALE Extended Precipitation Network Site-
6/86	Tidal Wetlands Study NASA
9/87	AEROCE (NSF) Study commences - NSF
4 & 10/89	AEROCE related cruises (R/V Cape Hartteras)
7/89	Precipitation aerosol scavenging intensive, G. Gordon, (U. MD) - Md. Power Plant Res. Prog.
6/90	Chesapeake Atmospheric Toxics Deposition Network initiated - EPA

The rationale and procedures of our collection protocols and analytical techniques were published previously (Tramontano et al. 1987), and are updated in the companion paper by Scudlark et al. (1992, this volume). The analytical method is derived largely from our associated work in local salt marsh, estuarine and coastal waters. Here our objectives have been to evaluate the source and transport of trace metals from the land to the sea, and specifically to include atmospheric processes.

OBJECTIVES

The specific research objectives of our Delaware laboratory by collecting precipitation for trace elements in the Middle Atlantic region are to:

(1) determine the continental or marine source of trace elements and associated acid species using local meteorological and air mass trajectory information

(2) assess the short and long-term variability relative to atmospheric sources and fluxes

(3) measure the wet and estimate the dry atmospheric fluxes of trace elements to local estuarine and coastal waters relative to the mass balance from other fluvial sources

(4) provide a precipitation record useful for other state and federal projects interested in the possible environmental, health or ecological implication for the atmospheric deposition of trace elements in precipitation.

Application of the early part of the trace element precipitation record to these objectives has been published elsewhere (Church et al. 1986, Church 1986, Church 1988, Church et al. 1988) and will be updated in this paper. Generally, the early results showed that although trace element concentrations in coastal precipitation were greater than local rivers, estuaries, and bays, their direct atmospheric influx was minor in amount yet significant in proportion. However, considering the larger catchment areas of drainage basins and the indirect inputs to coastal waters, atmospheric trace element deposition primarily from precipitation was major and significant.

RESULTS AND DISCUSSION

CONCENTRATIONS

The average volume weighted concentrations and corresponding wet flux of trace elements from precipitation at the Lewes site for the eight year record (1982-1989) are shown in Table 2. While crustal elements (Al, Fe) dominate, non-crustal elements (e.g. Zn) are nearly as abundant, and generally most all trace elements are significantly more concentrated in precipitation than other continental surface waters. A limited (one year) data record at sites on the upper eastern and western shores of Chesapeake Bay (Scudlark and Church, unpublished data) show very similar concentrations suggesting long range sources and transport of most precipitation trace elements to the mid-Atlantic region.

The range of the monthly concentration of most elements (e.g., Al; Fig. 2) over the past eight years at Lewes is quite large (1-2 orders of magnitude) and show some cyclic trends. Aluminum generally peaks in spring coincident with regional agricultural tilling.

Table 2.--The long-term volume weighted average concentration and flux of trace elements in precipitation at Lewes, Delaware from 1982-1989.

	Concentrations		Wet Flux (110 cm H_2O yr^{-1})	
Element	ppb ($\mu g\ L^{-1}$)	n Molar	ng cm^{-2} yr^{-1}	μmoles m^{-2} yr^{-1}
Al	26.2	970	2880	1070
Cd	0.098	0.87	10.8	9.61
Co	0.510	9.81	56.1	10.8
Cu	0.760	12.3	83.6	13.2
Fe	15.3	273	1680	301
Mn	1.24	22.6	137	25
Ni	1.12	19.0	123	21
Pb	1.9	9.17	209	10.1
Zn	5.16	78.9	568	86.9

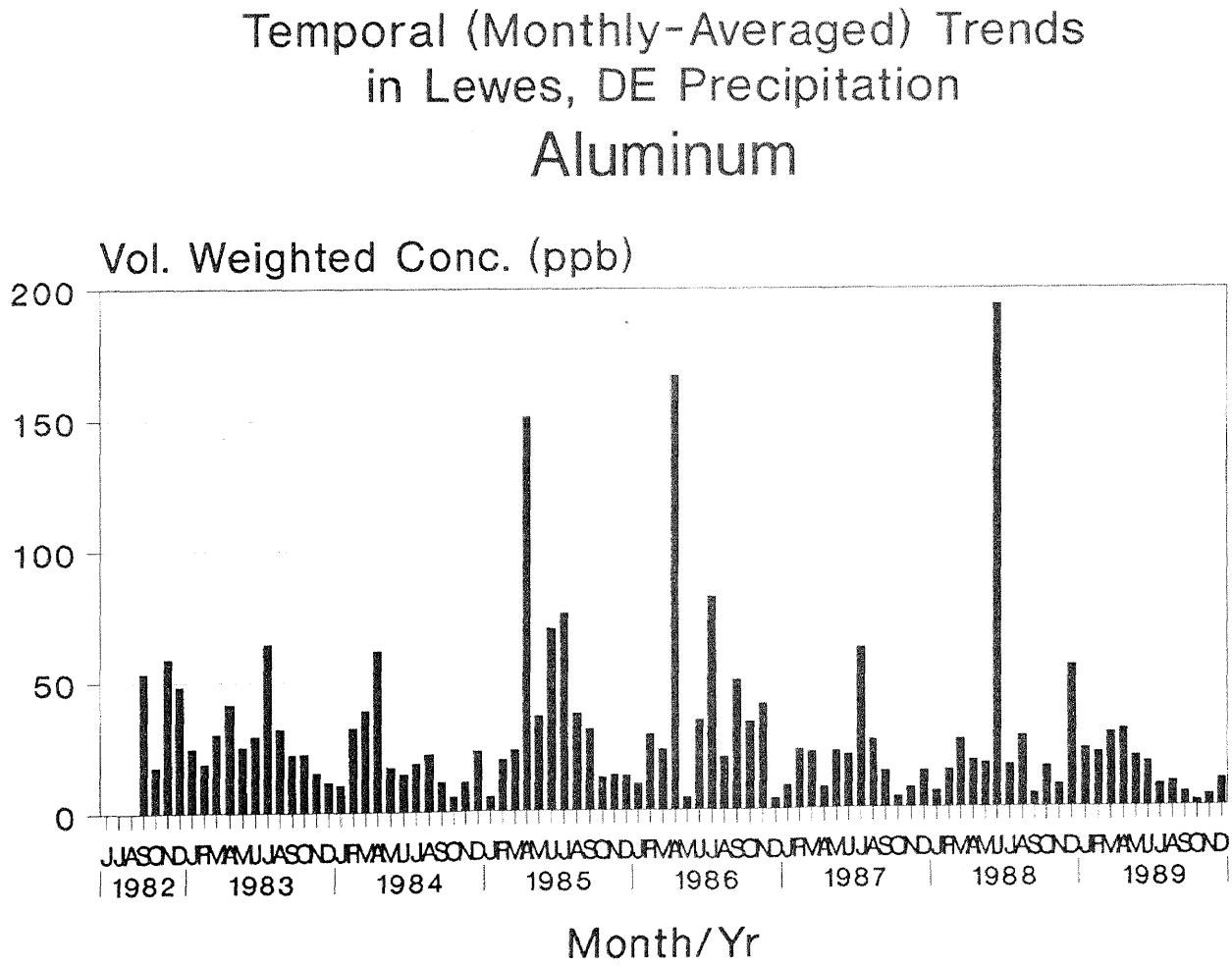

Figure 2.--Monthly volume weighted mean concentration of Al in Lewes, Delaware precipitation.

The yearly volume weighted mean concentrations of Cu is level, while Pb shows a gradual long-term decline coincident with the phasing out of leaded gasoline in the U.S. (Figure 3).

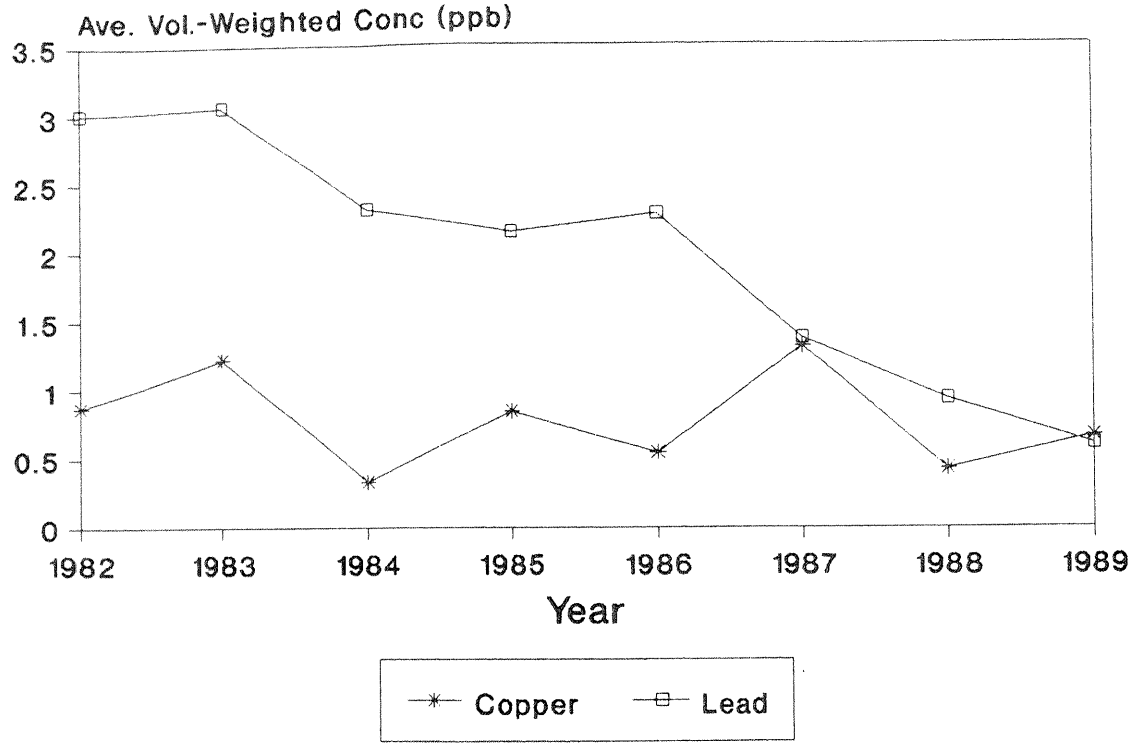

Figure 3.--Yearly volume weighted mean concentration of Cu and Pb in Lewes, Delaware precipitation.

An alternative way to present precipitation and aerosol concentration data is to use the enrichment factor (EF), the ratio of an element in the precipitation over a crustal reference (e.g. Se) to the same ratio in the reference material (e.g. crustal rock). The precipitation enrichment factors at Lewes (Scudlark and Church 1988) are nearly identical to those found in local aerosol, or in even more remote marine areas. This globally pervasive sequence in aerosols and precipitation bears witness to the common volatility, transport and deposition via precipitation of most atmospheric trace elements.

The good correlation of some trace elements to acid species in Lewes, Delaware precipitation points to a common source of some metals and acid species. By example, Figure 4 shows arsenic versus protons. Similar correlation of the metalloids Se and As with sulfate and nitrate respectively identifies coal combustion as a primary source (Cutter and Church 1986, Scudlark and Church 1988). In addition the redox species of these elements can act as effective probes of the redox conditions for those reactions coincident with cloud scavenging. For example the

oxidation of S (IV) to S (VI) is analogous to the oxidation of Se(IV) to Se(VI). Likewise the oxidation potential for NO_x conversion is coincident with that for As(III) oxidation.

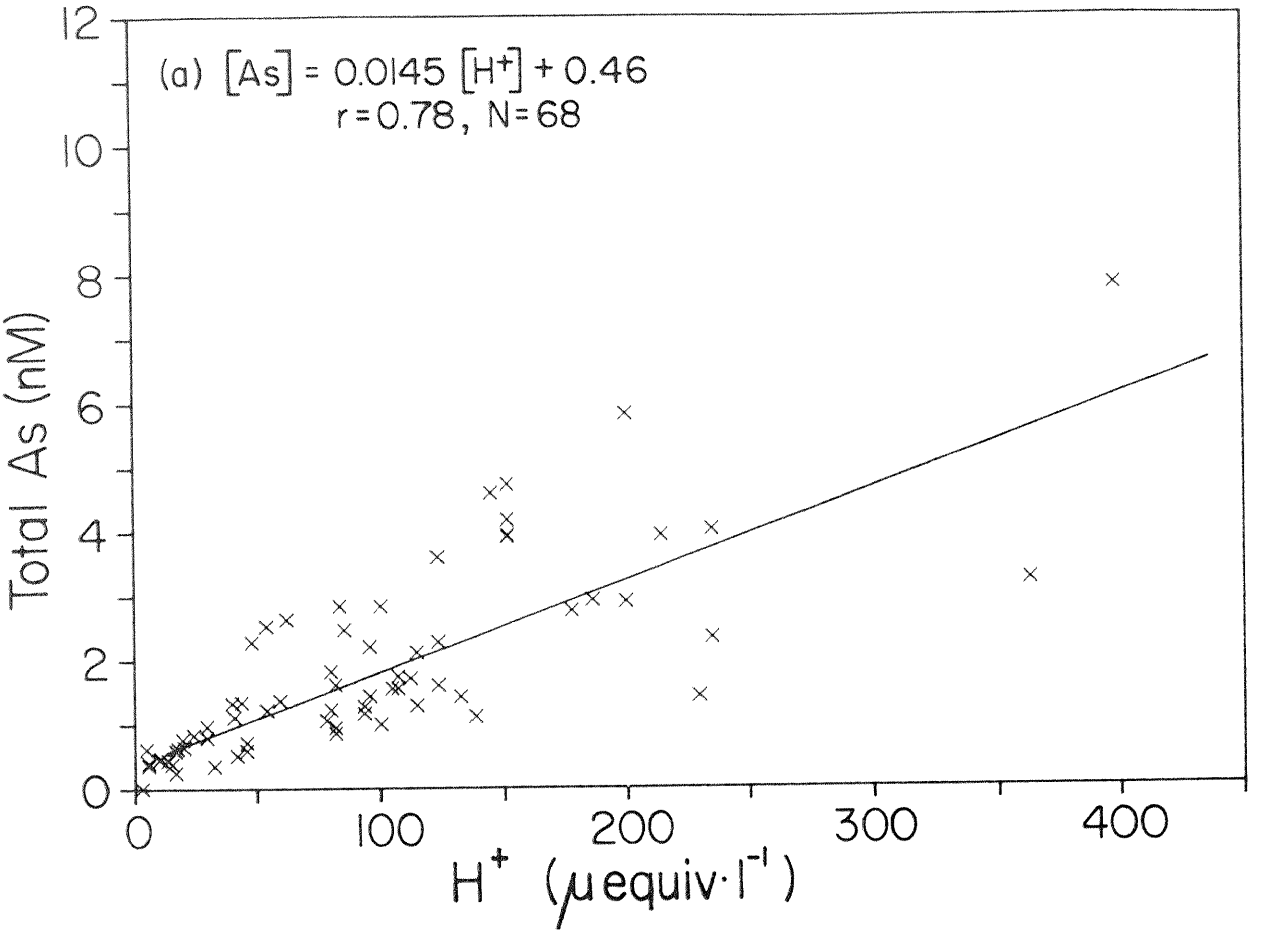

Figure 4.--Correlation of As and protons in Lewes, Delaware precipitation.

FLUX SOURCES

It is instructive to stratify wet deposition trace element data at Lewes, Delaware according to sectors of air mass trajectory during the events. The NOAA-ARL isobaric trajectory analysis corresponds to marine, southeast, midwest, and northeast sectors. Many coastal storms cannot be sectored and remain undefined. In Figure 5, the concentration and flux sectors for Se are given as an example.

Generally the sector flux patterns are similar for most trace elements, whereby the marine sector contributes the lowest flux while the southwest or midwest sectors contribute the most. Anthropogenic combustion and industrial sources are concentrated to the west and southwest, primarily from coal fired electrical power production and metal refinement.

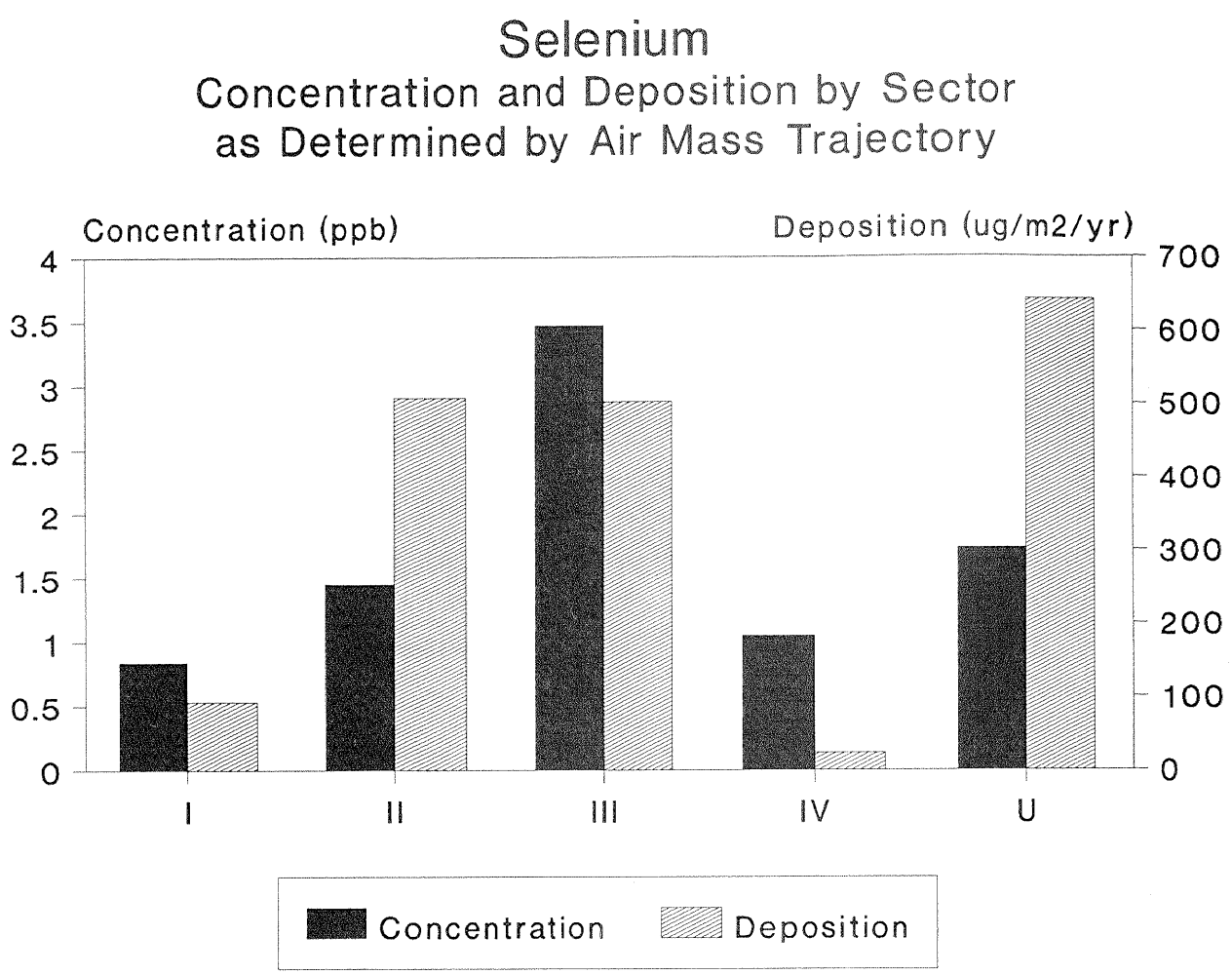

Figure 5.--Concentration and flux of Se in Lewes, Delaware precipitation sectored according to air mass origin I (marine), II (southeast), III (midwest), and IV (northeast), and U (undefined).

FLUX MODELING

The atmospheric flux of trace elements by precipitation can be put in perspective with other fluxes to coastal water bodies. First, however, the wet fluxes measured in Lewes, Delaware precipitation (Table 2) must be added to dry fluxes which have not been measured. Dry fluxes can be estimated from aerosol concentration at Lewes, Delaware measured during WATOX intensive experiments (summarized in Wolff et al. 1987). These aerosol concentrations represent the average of nearly 70 samples collected over two six week periods during August 1982 and February 1983. The aerosol concentrations can be partitioned into crustal components using Al as a normalizer, with the excess constituting the non-crustal component. The crustal component is assigned a deposition velocity typical of soil dusts (0.3 cm/sec) and the non-crustal component one typical of accumulation mode aerosols (0.1 cm/sec). The calculated total dry deposition of

trace elements is added to the measured wet deposition to give an estimate of the total atmospheric deposition (Table 3).

Table 3.--Dry and total atmospheric flux (ng $cm^{-2}yr^{-1}$) at Lewes, Delaware.

	Aerosol	----------Dry Flux----------			Wet	Total
Element	(ng m^{-3})	Crustal	Non-crustal	Total	Flux[1]	Flux
Al	432	4040	--	4040	2880	6920
Cd	<1	--	<1	<1	10.8	11
Cr	12	7.7	55	63	56.1	119
Cu	4.5	1.9	13	15	83.6	98.6
Fe	149	1390	0	1390	1680	3070
Mn	4.7	43	0.4	43	137	180
Ni	5.4	3.7	5.6	9.3	123	132
Pb	63	1	197	198	209	407
Zn	32	4.7	83	88	568	656

[1] From Table--2.

The dry deposition component is only comparable to the wet component for the crustal elements (Al, Cr and Fe) which is consistent with their super-micron soil mode. However, the wet flux clearly dominates the total flux for all non-crustal dominated elements (Cd, Cu, Ni and Zn) which is consistent with their sub-micron accumulation mode as emission derived elements. We know the dry component for Pb is too high from inaccurate aerosol concentrations.

The wet flux of trace elements to the Delaware watershed (DEW) can be estimated using the Lewes, Delaware precipitation data and comparing it to that entering the Delaware Bay estuary from the river at Trenton (Church et al. 1988). The result shows that precipitation can contribute far more trace elements (except Mn) to the watershed than are needed to account for that entering its estuarine portions. The excess is evidently taken up in the watershed soils and ecosystems by aquatic reactions during run off.

The direct wet deposition flux of trace metals from precipitation falling into open waters of the Delaware Bay estuary (DEB) itself is minor to that entering from fluvial and tidal sources (Church 1986). This may be unrealistic when one considers that the fresh and tidal sources themselves may be directly derived from atmospheric deposition to their watersheds, or indirectly from chemical reactions of digenesis within their soils.

Table 4 summarizes by percentage the mass balance contributions of trace elements from wet and total atmospheric deposition at Lewes, Delaware.

The direct total atmospheric deposition to coastal waters of the Middle Atlantic Bight (MAB) can be compared to that estimated from the net tidal flux of the large estuarine river systems Chesapeake, Delaware and Hudson (Church 1988). These earlier estimates have been updated in Table 4 from the more recent seven year record presented in Tables 2 and 3. The percentage atmospheric input to the Middle Atlantic bight, while minor for some elements such as Cu and Mn, can be dominate for other elements such as Pb and Zn. Atmospheric delivery of trace elements to coastal waters is as important as delivery of major nutrients such as N.

Table 4.--The corresponding atmospheric percentages of trace metal deposition at Lewes, Delaware.

	----------Fluxes (%)----------		--------Atmospheric component (%)---------		
Element	Wet[1]	Dry[1]	DEW[2]	DEB[3]	MAB[4]
Al	42	58	--	--	--
Cr	98	2	--	--	--
Cd	47	53	--	--	--
Cu	85	15	41	4	18
Fe	55	45	64	2	--
Mn	70	24	-58	0.1	4
Ni	93	7	43	2	30
Pb	51	49	--	--	96
Zn	87	13	32	4	64

[1] Relative percentage of the total flux.
[2]Percentage wet flux surplus of the Deleware watershed (DEW) to the fluvial component entering Deleware Bay (DEB).
[3]Direct atmospheric input to the total including all fluvial and tidal sources to Delaware Bay (DEB)
[4]Direct atmopsheric input to the total including net estuarine flux to coastal waters of the Middle Atlantic Bight (MAB). See text for details.

CONCLUSIONS

As for acid components, the concentration of trace elements in continental precipitation can be substantial. The range of concentrations can be very large depending on remote sources and local meteorology. The enrichments relative to crustal rocks and the sectoring of air mass sources suggest long range transport and deposition from emission sources to the south and midwest. The magnitude of the concentrations largely exceeds that of other surface waters suggesting that their atmospheric contribution from wet flux may be important. Indeed, mass balance calculations show that atmospheric deposition indirectly to the watersheds of Middle Atlantic estuaries or directly to the waters of the shelf is significant. This may have important implication to the ecosystems of these water bodies.

Future monitoring of trace elements in precipitation must be taken with considerable caution. The protocols for collection and the challenges of analysis will be demanding in dedication and resources. The places of collection must be well chosen and maintained; and, the collection maintained for a number of years to accurately average the variability of event fluxes. Nevertheless, the potential importance of the atmospheric wet deposition of trace elements will demand such monitoring.

ACKNOWLEDGEMENTS

This research was supported by funding from DOE, USGS, EPA and by NOAA Office of Sea Grant, Department of Commerce, under Grant No. NA16RG0162-02 (Project No. R/ME-7). We gratefully commend S. Moore, K. Conko, and A. Konizer (posthumously) for their dedication in the field and laboratory which has been responsible for our successful measurement of trace elements in precipitation.

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A METHOD FOR THE AUTOMATED COLLECTION, PROPER HANDLING AND ACCURATE ANALYSIS OF TRACE METALS IN PRECIPITATION

J.R. Scudlark, T.M. Church, K.M. Conko, and S.M. Moore[1]

ABSTRACT.--A method is described for the accurate determination of trace metals in precipitation, which has been successfully utilized for ten years at diverse rural and remote locations. The accurate determination of trace metals in precipitation at the nanomolar level (generally 3 or more orders of magnitude less than major ion constituents), requires the use of specific materials and exacting cleaning, handling, preservation and collection procedures. The total atmospheric wet deposition of trace metals is apportioned between dissolved and particulate phases, which varies spatially and temporally for each metal. The application of proper collection and analysis techniques insures quantification of the total (dissolved plus particulate) concentration.

INTRODUCTION

Within the past decade, atmospheric trace elements have come under increased scrutiny from a number of perspectives. The importance of the atmospheric transport and deposition of trace metals to aquatic and terrestrial systems has been well documented. Atmospheric trace metals have also been identified as important redox catalysts for aqueous phase S(IV) oxidation (Graedel and Weschler 1981, Conklin and Hoffmann 1988). Additionally, recent approaches have utilized atmospheric trace elements for emission source identification, using a variety of source-receptor modeling approaches (as reviewed by Gordon 1988).

In 1980, our laboratory began to address the routine monitoring of trace metals in precipitation as part of the MAP3S (DOE) and WATOX (NOAA) programs. For this we required a simple, automated, accurate procedure applicable to both rural continental and semi-remote island locations. Reviews of the historical data on the concentration of trace metals in continental precipitation (Galloway et al. 1982a, Barrie et al. 1987) cast considerable doubt on the reliability of reported values and the efficacy of the techniques utilized. In many of these studies, it was apparent that the authors failed to observe proper sampling and handling precautions (Batley and Gardner 1977, Ross 1986), resulting in either gross contamination, or conversely, irreversible losses of certain metals to container walls (Chan et al. 1983).

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On the other hand, we did not know if the meticulous precautions utilized in studies at remote locations (e.g. Arimoto et al. 1987) were necessary or practical for application in a long-term, routine monitoring mode. Thus, we proceeded to develop and test a technique for the automated collection, handling and analysis of trace metals in precipitation.

The procedures reported in this paper represent the ongoing evolution of our methodology as previously published (Tramontano et al. 1987). These methods have been successfully employed under a variety of conditions, including a continual (since 1982) record of trace metals in precipitation at the mid-Atlantic coast of the U.S. (Lewes, DE), reported by Church et al. in this volume and an ongoing study of the wet depositional flux of potentially toxic trace metals to Chesapeake Bay. The same technique has also been used in more remote locations such as Bermuda (Church et al. 1984) and Ireland.

PROCEDURES

The principal challenge in determining trace metals in precipitation is to minimize contamination of the sample during sampling, handling and analysis. Compared with acid rain protocols (e.g. Galloway 1978), this is considerably more difficult since trace metals are typically present at concentrations lower by 3 or more orders of magnitude than major ions, generally in the nmole/L range for most elements in continental precipitation. Thus, fastidious collection and handling procedures must be strictly adhered to; even contamination by airborne dust must be minimized. We emphasize the following two specific precautions to insure trace metal-clean techniques:

(1) All operations involving sample manipulation (collection, acidification, partitioning and analysis) must be performed wearing clean, powder-free polyethylene gloves. As a general rule, a new pair of gloves is donned when the surface to be touched is cleaner than the previously-handled surface.

(2) Sample manipulation, plasticware cleaning, and analyses should be performed in a clean area; we strongly recommend use of a Class 100 clean bench. Regardless, precautions should be taken to minimize exposure of the sample to airborne contamination.

PLASTICWARE

Materials only made of polyethylene, Teflon^{R} (Reg. TM E.I. duPont de Nemours & Co.) and polypropylene should be used for sampling, storage and laboratory manipulation. Of these, Teflon^{R} is the preferred material for trace metals studies (Batley and Gardner 1977), but is prohibitively expensive for large-scale use. "Virgin" LDPE (low density polyethylene polymerized directly from ethylene gas) is a practical alternative for transition metals, as the comparatively permeable plastic matrix allows for efficient metal leaching during cleaning and sample desorption steps (Batley and Gardner 1977, Subramanian et al. 1978). However, for the metalloids (Se, As, Sb etc.), which in contrast to most metal cations are in theory present in

precipitation as oxy-anions, irreversible losses to the container walls have been reported for LDPE (G. Cutter, pers. communication); for these elements, less pervious HDPE is the preferred plastic, (although, this artifact is probably insignificant at concentrations typical of most U.S. continental precipitation).

The standard white polyethylene bucket used in acid rain studies is absolutely not suited for trace metals studies. To demonstrate the inaccuracy resulting from samples obtained in standard white acid rain buckets, we conducted a side-by-side comparison of samples from 26 events, collected according to standard major ions protocols and our trace metals methods as presented here. (Samples from the major ions collector could obviously not be acidified until partitioned into storage bottles). A comparison of the mean concentrations calculated from samples collected by each method (Table 1) shows that Cd and Zn were severely contaminated (>100%) and Cu moderately contaminated in the major ion sampler. In contrast, Pb exhibited significant adsorptive loss in the major ions bucket. Thus, it is clear that except for Fe and Mn (which are of little interest from a toxicological perspective), samples collected according to standard major ions procedures cannot be utilized for trace metal determinations.

Table 1.--Comparison of mean trace metal concentrations from simultaneous collections utilizing major ions/acid rain protocols with trace metal methods as presented in this paper.

Collector	Cd	Cu	Fe	Mn	Pb	Zn
			mean concentration ($\mu g\ L^{-1}$)			
Major Ions	0.320	1.20	10.24	1.79	1.46	15.66
Trace Metals	0.116	0.78	11.59	1.63	3.14	4.57

For sample collection, we currently utilize a clear, 17 liter HDPE bucket and snap-fitting lid (Rubbermaid #2618), cleaned according to the procedures outlined in Table 2 (which are subsequently discussed). This bucket has a slightly larger effective capture area compared with the white major ions bucket (730 vs 682 cm^2), but is compatible with the ACM collector without modification.

In the past, we have also utilized an appropriately cleaned, heavy gauge (4 mil), 10 x 8 x 24 in. round-bottomed, LDPE bucket liner (Associated Bag Co., Milwaukee, WI) for sample collection (Good and Schroeder 1984). For installation, the top of the bag is folded over the lip of a major ions bucket, and the air under the bag is evacuated by applying a vacuum via a small hole near the bottom corner of the bucket. Although bucket liners are inexpensive, expendable and easy to ship to remote collection sites, we found them to be difficult to properly clean and install according to trace metal protocols, as evidenced by blank levels which were consistently higher

than buckets. In addition, we found that bag liners were not always reliable in the field, due to leakage (resulting from manufacture, cleaning or puncture by post-depositional ice formation) and the tendency of the bag to blow out of the bucket in high winds.

REAGENT ACIDS

To prevent (or reverse) the adsorptive loss of trace metals from the precipitation sample onto the plastic surfaces of collector bucket and storage containers, standard laboratory practice is to acidity samples to a pH <2 (Struempler 1973; Subramanian et al. 1978). HNO_3 is the most commonly used acid for this purpose, but its use might be discouraged where cross-contamination with parallel acid rain collections poses a potential problem. To avoid any possible contamination, we have substituted HCl. Regardless of the acid employed, it is imperative to utilize ultra-high purity acid (i.e. low trace metal content). This can either be prepared in-house by doubly re-distilling reagent grade acid in a Teflon^R or quartz sub-boiling still, or purchasing a commercially-available equivalent. With our doubly-distilled acid (which we refer to as Qz-HCl), acidification to 0.4% (v/v) results in a 0.05 N solution, which is sufficient to lower the pH of poorly-buffered precipitation below 2. It should be noted however, that with few exceptions (e.g. Se), acidification precludes metal speciation studies.

CLEANING

To minimize sample contamination from metals introduced via manufacture (impurities from catalysts, promoters or metal dies) or prior use, all plasticware must be rigorously cleaned. Such impurities can exist adsorbed onto the plastic surface or within the plastic matrix (Karin et al. 1975). Although many variations on trace metal cleaning procedures have been reported, all involve leaching with acid (HCl and/or HNO_3) of varied strengths and duration. The cleaning procedure we utilize is outlined in Table 2. Ultrapure rinse water (ASTM/CAP/NCCLS Type I, having a resistivity consistently in the 18 megohm/cm range) should be used throughout. In our laboratory we utilize Milli-Q^R (Reg. TM Millipore Corp.) reagent grade water, and subsequently refer such water as Q-H_20. To preserve the activated adsorption sites on the freshly-cleaned plastic surface, we store sample bottles with a small amount of 0.1% Qz-HCl (enough to cover the bottom).

Due to their relatively high cost (ca. $10), we reuse trace metal buckets by either recleaning them on site or alternatively, recycling them back to the centralized laboratory for re-cleaning. For on-site recleaning between precipitation events, a less rigorous procedure is required (Table 2, steps 1, 2, 9-12); however, we recommend periodically (semi-annually) returning the buckets to the central laboratory for a more thorough cleaning.

Table 2.--Cleaning procedure for plasticware utilized for the collection, storage and analysis of trace metals in precipitation.

1.	wash with soapy water
2.	rinse 3 times with Q-$H_2$0
3.	rinse with reagent grade acetone
4.	shake off excess acetone and rinse 3 times with Q-$H_2$0
5.	soak in 6N reagent/ACS grade HNO_3 for 3 days
6.	rinse 3 times with Q-$H_2$0
7.	soak in 10% reagent/ACS grade HCl for 3 days
8.	rinse 3 times with Q-$H_2$0
9.	soak in 0.4% Qz-HCl for 3 days
10.	rinse 3 times with Q-H_2O
11.	fill sample bottles with a small amount (enough to cover bottom) of 0.1% HP-HCl and cap tightly
12.	seal all plasticware in doubly-bagged, clean LDPE bags

PRECIPITATION COLLECTOR

For trace metals sampling, the collector siting criteria utilized for any precipitation chemistry study should be adhered to. To further minimize "splash-off" from the collector into the bucket during sampling, we orient the wet bucket to face upwind relative to the prevailing wind direction (west) during typical precipitation events at our site.

It is necessary to dedicate a separate collector for trace metals studies due to several significant collector modifications, and incompatibilities in collection buckets and handling protocols with major ions (acid rain). However, trace metals collections can otherwise be conducted in parallel with acid rain sampling. We have utilized the Aerochem Metrics (ACM) Model 301 (Aerochem Metrics, Inc. Bushnell, FL) wet-only collector. Since the ACM collector is widely used in acid rain studies, most site operators are familiar with its operation and repair, and it is convenient to keep an inventory of spare parts on hand which can be used with either collector. Additionally, use of identical major ions and trace metal samplers insures comparable collection (capture) efficiencies, which is an important consideration for subsequent data comparisons. In fact, it is advisable and relatively simple to connect both collectors to a single rain sensor.

For trace metals determination, the ACM collector must be factory-equipped with the following important modifications:

(1) Teflon^R-coated lid support arms, to minimize contamination from "splash-off" during rain events;

(2) polycarbonate lid, for the same purpose as above. A peaked polycarbonate snow roof is also available where necessitated by the amount of snowfall.

(3) "old" style (about 26 cm. high) bucket holder, which accommodates the required collection buckets without further modification; and

(4) removal of the dry side bucket, which prevents contamination of the lid seal and "carry-over" of dry deposited trace metals from the rim of the dry bucket to the clean wet bucket (we remove the entire bucket holder).

As an independent verification of collection efficiency and accuracy of the automated collector, we used a side-by-side manually deployed (MD) collector. The MD sampler was carefully covered and exposed to achieve a high (>99%) collection efficiency and to avoid the inadvertent capture of dry fallout during non-precipitating periods. This collector consists of a HDPE funnel (surface area 600 cm^2) screw fitted with a watertight, threaded Teflon^R (TFE) coupling to a 1-L Teflon^R (FEP) bottle. This sampler design has been used in the NOAA Global Precipitation Chemistry Project (Galloway et al. 1982b). Comparisons of concentrations from the two collection methods were made on 25 occasions at Lewes, DE and High Point, Bermuda. For all metals, the data were highly correlated (r^2>0.88) with slopes close to 1.0; the volume-weighted average concentrations from each collector (Table 3) were also in accord. Thus, we believe that precipitation collected with the modified ACM collector accurately reflects the wet depositional flux of trace metals.

Table 3.--Comparison of volume-weighed mean concentrations from a manually-deployed (MD) and automated (ACM-TM) collector, sampled in parallel.

COLLECTOR	Cd	Cu	Fe	Mn	Pb	Zn
Lewes, DE						
ACM-TM	0.172	1.18	16.4	1.40	3.17	5.39
MD-TM	0.133	0.81	18.2	1.62	2.80	4.69
High Point, Bermuda						
ACM-TM	0.041	0.223	6.21	1.10	0.48	1.30
MD-TM	0.043	0.261	7.56	1.08	0.50	1.62

COLLECTOR DEPLOYMENT, RECOVERY AND SAMPLE PROCESSING

While retrieving samples or deploying collection buckets, we recommend standing downwind from the bucket to minimize potential contamination from the site operator. Wearing clean gloves, the bucket (with lid attached) is removed from its bag, and placed in the holder on the collector. As the collector lid moves back to cover the bucket, the bucket lid is removed, returned to its bag and sealed with a twist-tie. This process is then reversed for sample retrieval, with a clean bucket deployed at the same time. We also recommend cleaning the underside of the collector lid (which contacts the bucket) with a clean, wetted Precision Wipe^{R} (Reg. TM Scott Paper Co.), or equivalent low-lint, low-trace metal lab wipe.

In the designated clean area in the laboratory, the sample weight is determined by subtracting the tare weight of the empty bucket and lid. Uncovering the bucket only slightly (1/2"), the appropriate amount of Qz-HCl is added with an adjustable auto-pipette and acid-cleaned disposable tip to make the final concentration 0.4% (v/v), i.e. 4 mL of acid per liter of sample. As previously discussed, this step insures the quantitative desorption of metals from the collection bucket walls back into solution. It is not advisable to pipette directly from the primary acid supply, but rather, to utilize a small sub-aliquot for day-to-day use. Where appropriate clean facilities and/or high purity acids are not available, it is possible to freeze precipitation samples directly in the collection bucket, for subsequent acidification and processing at the centralized laboratory.

After a 24-hr. desorption period, the sample is homogenized by swirling the bucket, and partitioned into pre-cleaned, triply-rinsed storage bottles. (The 0.1% Qz-HCl storage solution should be first discarded). It should be noted that when volume limited, three small rinses are more efficient than one large rinse of equal volume. The bottles should be tightly capped, and doubly sealed in plastic bags pending analysis. Depending on the inventory of elements to be analyzed, the minimum volume requirements for trace metals analysis is similar to major ions (ca. 50 mL for the suite of standard transition metals). For metalloids and/or other elements with larger analysis requirements, we save a maximum of 2 liters of sample. Samples should be refrigerated, or preferably frozen, until analysis.

ANALYSIS

The two most commonly-employed methods for trace element analysis of natural waters are graphite furnace atomic absorption spectrophotometry (GFAA) and inductively-coupled plasma emission spectroscopy (ICP). Except for a few elements (Al, Fe, Mn, Zn), only GFAA exhibits adequate detection limits for the direct determination of trace metals in precipitation at concentrations typical of rural U.S. regions. However, with sample preconcentration by evaporation (-20X), ICP offers a viable alternative to GFAA (Keller et al. 1988, Jickells et al. 1991). In fact, as is subsequently discussed, for elements derived predominantly from crustal sources (Fe, Al), ICP may yield more accurate results.

Some elements of interest from a toxicity perspective (e.g. As, Se, Hg) are present in precipitation at concentrations well below the detection limits of commercially available atomic absorption/hydride techniques. For example, the average As concentration in Lewes, DE precipitation (1.3 nmole L^{-1}) is significantly less than both atomic absorption (~7 nmole L^{-1}) and ICP (~20 nmole L^{-1}) hydride detection limits. Accurate quantification of these elements requires the application of state-of-the-art analytical techniques (e.g. Cutter et al. 1991) and larger minimum sample volume requirements.

Our laboratory has routinely utilized GFAA for the determination of Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn in wet deposition. Although the relatively simple chemical matrix of precipitation greatly facilitates GFAA analyses, for some elements specialized techniques are required to compensate for chemical interferences. For example:

(1) the Pb signal is significantly suppressed by salts, thus requiring analysis using a L'vov platform (which eliminates matrix suppression by delaying atomization);

(2) since we utilize HCl for sample acidification, the char/ash step is limited to 170°, to prevent volatilization of $AlCl_3$ (b.p. 185°);

(3) increased analytical sensitivity for Al and Fe is achieved by the addition of cirtic acid as a matrix modifier.

QA/QC PROTOCOLS

A strict adherence to a rigorous quality assurance / quality control (QA/QC) program is essential to establish and maintain data accuracy. Elements of this program include the use of:

(1) externally certified reference solutions (e.g. EPA, NIST) which are included in every analytical session;

(2) inter-lab analytical comparisons;

(3) operational blanks on a regular (bi-monthly) basis and/or if there is a significant change in methods, reagents (e.g. a new batch of acid), land use around the site (e.g. excavation) or personnel (a new or substitute site operator).

OPERATIONAL BLANKS

In order to accurately quantify background trace metal levels and to identify and remedy sources of contamination, we strongly advocate the use of procedural blanks. We use three types of additive blanks to identify, quantify and remedy any source of contamination:

(1) A process blank, which consists of a 250 mL sample bottle containing Q-H_2O and Qz-HCL only. This is a measure of the trace element contribution derived from the acid spike, leaching from the storage bottle, and analytical procedures.

(2) A laboratory blank, which consists of a 250 mL Q-H_2O spike added to a clean sample bucket in the laboratory, acidified, and decanted into a sample bottle after a 24-hr. desorption period. The lab blank gauges the trace metal contribution from all sources embodied in the process blank, as well as metal leached from the collector bucket and airborne contamination during partitioning.

(3) A field blank, which is conducted identically to the lab blank, but using a bucket which was previously deployed in the collector during a non-precipitating period for a representative sampling interval (e.g., 2-5 days for event sampling or 7 days for weekly integrated sampling). The field blank includes trace metal input from all sources included in the lab blank, plus metal contribution from field operations such as the input of fugitive dust to the sample bucket during transport, deployment and recovery.

For most metals, the majority of the blank contribution is from materials and reagents, as represented by the laboratory blank. For Al, Fe, and to some degree Mn, which have predominant crustal sources, the field activities provide the major blank contribution. However, since the field blank is the most representative of sampling conditions, it is used to correct apparent precipitation concentrations. This correction is usually only required when the blank contribution exceeds 10% of the average metal content in corresponding precipitation (an approximate limit of analytical confidence).

A comparison of absolute blank levels and relative blank contributions to precipitation [(nmoles blank/nmoles in average precipitation sample) x 100%] at three sites using the sampling protocols under varying conditions is presented in Figure 1. For the Lewes site, sampling on a daily basis under optimal conditions and with an experienced operator, the field blank is only utilized qualitatively for diagnostic purposes. At Bermuda, also sampled daily, the blank levels are lower for most elements (probably due to cleaner environmental conditions), although the very low precipitation concentrations require that the field blanks be used quantitatively for some elements (Pb, Cd, and Zn) to accurately determine true rainwater concentrations. At the Chesapeake Wye site, precipitation is sampled in parallel (weekly integrated) with the NADP collector. However, without an available clean bench for sample processing or the same level of operator expertise as the Bermuda and Lewes sites, the blank levels are significant for a number of metals (Cd, Cu, and marginally Zn).

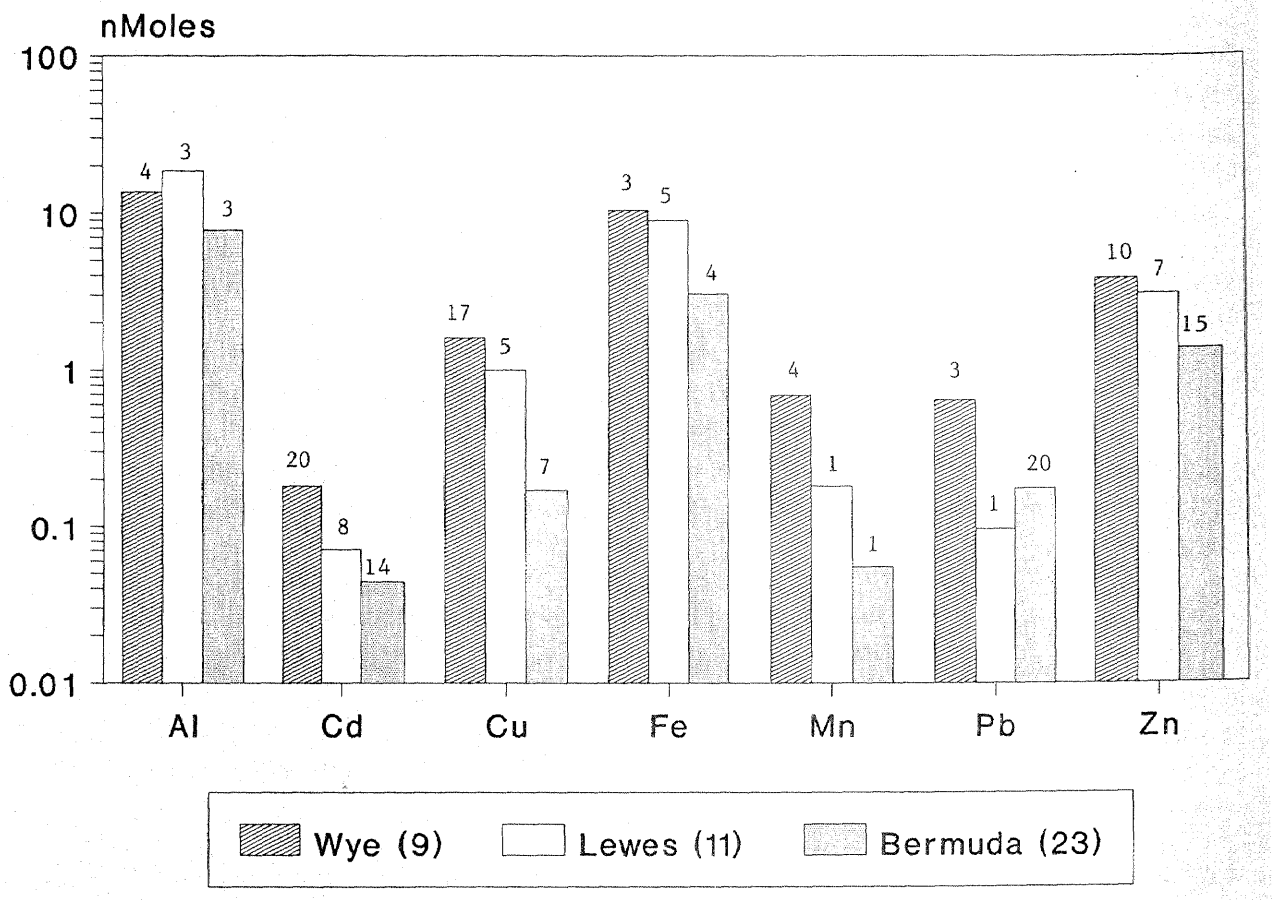

Figure 1.--A comparison of absolute field blank levels (nmoles) at three sites. Numbers above each bar refer to the average field blank contribution (%) to precipitation at each site.

This is probably representative of typical blank levels that could be expected under these conditions, and underscores the critical importance of determining accurate blanks under variable field and meteorological conditions at each site.

It is important to bear in mind that whether sampling or conducting blanks, the objective is both to minimize contamination as well as maintain it at a consistent level for accurate blank correction. This emphasizes the need to utilize uniform reagents, materials and sample handling procedures. Thus, to maintain constancy, blanks should be conducted with the same degree of caution as normal sampling.

TRACE METAL SOLUBILITY IN PRECIPITATION

Trace metals may be introduced into the atmosphere via resuspended soil and from high temperature emissions of both natural (e.g. volcanism) and anthropogenic origin. Crustally-derived trace metals are generally encountered in the "coarse " (>2.5μ) size fraction, and are largely subjected to dry deposition near the source. Under unique conditions, however, aeolian transport of resuspended soil can occur over long (1000's of km) distances (Duce et al. 1980, Prospero 1987). During high temperature combustion processes, trace metal oxides are vaporized and consequently condense on or form fine sub-micron aerosols (Smith et al. 1979, Natusch et al. 1974). Thus, most atmospheric trace metals are present in association with particles, although some (e.g. Hg and Se) may exhibit significant vapor-phase sources.

Such particulate metals are subsequently entrained in precipitation via two processes: (1) in-cloud nucleation, and (2) below-cloud scavenging by falling hydrometeors. Depending on the associated precipitation chemistry, particulate phases are solubilized to varying degrees before, during or after deposition. Thus, in terms of evaluating deposition, the total wet atmospheric flux of trace metals includes both dissolved and particulate forms. However, from an ecological perspective, the dissolved component is of most interest as it is the most readily available.

Based on a review of recent data reported at worldwide locations (Nguyen et al. 1979, Nurnberg et al. 1984, Gatz and Chu 1986, Lim and Jickells 1990, this work), the phase distribution of trace metals in precipitation appears to be highly variable. In general, the solubility is dependent on the element, the ambient pH, and the chemical properties of the parent aerosol which has been scavenged. For example, these data indicate that under ambient pH, mineral aerosols such as Al are generally insoluble (< 50%), while high temperature combustion condensates such as Pb are highly (>80%) soluble. Furthermore, the prescribed sample acidification will post-depositionally solubilize many elements, although this acid-leachable fraction may underestimate the total concentration of some mineral elements bound in crustal lattices (Lim and Jickells 1990).

Recent experiments in our laboratory support this observation. Filtration (0.2 μ pore size, acid-washed Nuclepore^{R}) of freshly-collected, acidified rainwater samples removed an average of 54% of the "GFAA-analyzable" Fe; in contrast, filtration removed less than 5% of the Zn. Furthermore, a comparison of GFAA with ICP analysis of unfiltered samples (Fig. 2a) indicates that about 1/2 of the total Fe is not detected by GFAA techniques. Even the filtered samples (Fig. 2b) exhibit an apparent underestimation (ca. 40%) by GFAA. (Similar results at both ICP analytical wavelengths insures that this difference is not due to a matrix effect or spectral interference). For both filtered and unfiltered samples, the discrepancy appears to be non-linear, i.e. is proportionately larger at higher Fe concentrations.

Conversely, for Zn we observe excellent agreement between analytical methods for both filtered and unfiltered treatments (Figs. 2c and 2d). Presumably, the Fe phase not detected by GFAA is a refractory micro-colloidal form (probably of local crustal origin) which is detected by ICP due to: (a) higher atomization temperatures in the ICP plasma (6000°C) compared with the GFAA furnace (2500°C) and/or (b) the settling of particles which results in sample heterogeneity. This

effect is largely compensated for by ICP methodology (where the analyte is continuously aspirated) than for GFAA (where a small volume of analyte is discretely sampled). Thus, for some elements, analysis by ICP appears to more accurately reflect the total (wet and particulate) wet depositional flux.

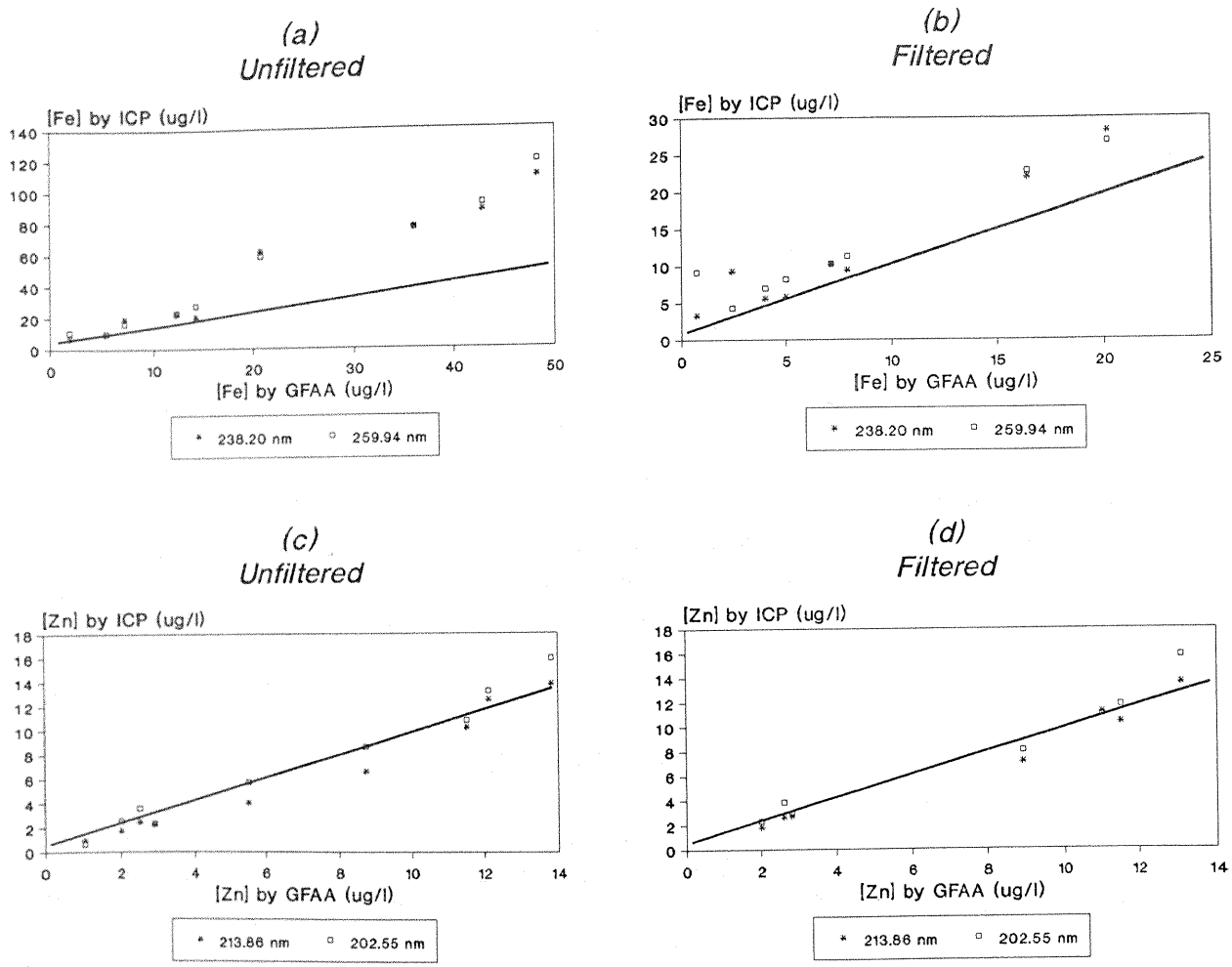

Figure 2.--Acomparison of Fe and Zn concentrations (µg L^{-1}) in filtered and unfiltered precipitation at Lewes, DE, analyzed by GFAA vs. ICP-AES. The line is a 1:1 correlation.

CONCLUSIONS

According to the procedures reported in this paper, the accurate determination of the total (dissolved and particulate) trace metals concentration in precipitation is accomplished by:

(1) meticulous sample handling and processing procedures;

(2) exclusive use of acid-washed plasticware;

(3) utilizing a modified ACM collector equipped with HDPE collection bucket;

(4) sample acidification with ultra-high parity acid (HNO_3 or HCl);

(5) analysis by GFAA and ICP;

(6) strict adherance to a QA/QC program.

ACKNOWLEDGEMENTS

We are grateful to Anna Quisel for her contribution on dissolved/particulate partioning, to Jack Tramontano for his early methods development work, and to site operators Patti Salevan and Skip Konizer for field assistance. This research was conducted under support from the MAP3S (DOE) and WATOX (NOAA) programs. This paper is dedicated in the memory of Skip Konizer.

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