

DATE ISSUED JUL 2 1979

ORNL/TM-6674

78113

ORNL

Mechanisms and Rates of Atmospheric Deposition of Selected Trace Elements and Sulfate to a Deciduous Forest Watershed

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ENVIRONMENTAL SCIENCES DIVISION
Publication No. 1299

OAK RIDGE NATIONAL LABORATORY
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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$16.25; Microfiche \$3.00

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Contract No. W-7405-eng-26

MECHANISMS AND RATES OF ATMOSPHERIC DEPOSITION
OF SELECTED TRACE ELEMENTS AND SULFATE
TO A DECIDUOUS FOREST WATERSHED¹

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David S. Shriner, and Dale D. Huff

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¹Submitted as a thesis by Steven E. Lindberg to the Graduate Council
of the Florida State University in partial fulfillment of the
requirements for the degree of Doctor of Philosophy.

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Date Published: June 1979

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ACKNOWLEDGEMENTS

Coordinating the field, analytical, and data processing work involved during the past three years would not have been possible without the help of many individuals. I wish to acknowledge the field assistance of Linda Mann, Maxine Levin, and Jay Story; the analytical assistance of Ken Talbott, Francis Ball, Marion Ferguson, Juel Emory, and Les Hulett; the statistical help of John Beauchamp; and the assistance with computer graphics of Connie Begovich, Dick Raridon, Keith Penny, Jerry Jones, and Julia Watts. I wish to acknowledge the assistance given by Jim Meagher and staff of the Tennessee Valley Authority Air Quality Branch. Without their help the cooperative in-plume sampling of the Cumberland Steam Plant would have been impossible.

In addition, several individuals both within and outside of the Laboratory have acted as sounding boards at various times. In many instances, these discussions have provided the incentive to interpret a given data set in a new light, resulting in some interesting hypotheses. I wish to thank Walt Culkowski, Ray Hosker, and Detlef Matt of the Atmospheric Turbulence and Diffusion Laboratory (NOAA), Bruce Hicks (Argonne National Laboratory), Bill Hoffman (Denison University), Lenny Newman and the Atmospheric Sciences Group at Brookhaven National Laboratory, Tom Theis (Notre Dame University), and Brian Murphy (Oak Ridge National Laboratory).

I am also grateful to several individuals for both informal discussions and formal review of this manuscript. These include Dr. John Winchester, Dr. Tom Vickers, Dr. Ray Staley, and Dr. Andy Clewell in the Departments of Oceanography, Biology and Chemistry, Florida State University.

Editorial production of this document was a bearable task largely as a result of the guidance and considerable help of Linda Littleton, Natalie Millemann, Jenny Merritt, Sherry Ward, and the entire Publications Office staff.

ABSTRACT

LINDBERG, S. E., R. C. HARRISS, R. R. TURNER, D. S. SHRINER, and D. D. HUFF. 1979. Mechanisms and rates of atmospheric disposition of selected trace elements and sulfate to a deciduous forest watershed. ORNL/TM-6674. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 550 pp.

The critical links between anthropogenic emissions to the atmosphere and their effects on ecosystems are the mechanisms and rates of atmospheric deposition. The objective of this research has been to quantify the atmospheric input of several trace elements and sulfate to a deciduous forest canopy and to determine the major mechanisms of deposition. The study area was Walker Branch Watershed (WBW) in eastern Tennessee. Precipitation samples were collected on an event basis at sites above the forest canopy, at ground level in the open, and beneath the canopy. Dry deposition was measured using inert, flat surfaces situated in the upper canopy, and laboratory leaching of sequentially collected leaves from the same locations. Aerosols were collected above the forest canopy using standard filter and cascade impactor methods. Laboratory leaching procedures were applied to all particulate samples to extract the water soluble and the dilute acid leachable trace element and sulfate fractions.

Substantial amounts (> 75%) of the dilute acid leachable fraction of Mn, Zn, Cd, and Pb in aerosols were soluble in water. The water soluble to available element ratio increased with decreasing particle size and with the duration of atmospheric water vapor saturation during the sampling period. Relationships between aerosol chemistry and

meteorological parameters suggest that atmospheric chemistry over WBW is the result of regional air transport phenomena rather than the direct result of local source emissions.

Smaller amounts (< 75%) of the dilute acid leachable trace element fraction of dry deposited particles were water soluble, suggesting a larger particle size, which was confirmed by scanning electron and light microscopy of biological and inert deposition surfaces. The presence of a significant quantity of fly ash and dispersed soil particles on upward-facing leaf and flat surfaces suggested sedimentation to be a major mechanism of dry deposition to upper canopy elements. The agreement for deposition rates measured to inert, flat surfaces and to leaves was good for Cd, SO_4^- , Zn, and Mn (within a factor of 2) but poor for Pb (an order of magnitude higher rate measured to the inert surfaces). Leaf surface absorption of soluble Pb could be a factor. Calculated deposition velocities to individual upper canopy surfaces indicated that the generally used value of 0.1 cm/sec was an underestimate in the case of Cd, Zn, Mn, and possibly sulfate.

The precipitation concentrations of H^+ , Pb, Mn, and SO_4^- reached maximum values during the summer months in response to synoptic meteorologic conditions. A model applied to the relationship between elemental concentrations in rain and rainfall amount indicated that, on an annual basis, ~ 90% of the wet deposition of Pb and SO_4^- was attributable to scavenging by in-cloud processes while for Cd and Mn, removal by in-cloud scavenging accounted for 60 to 70% of the deposition.

The interception of incoming rain by the forest canopy resulted in a net increase in the concentrations of Cd, Mn, Pb, Zn, and SO_4^- but a net decrease in the concentration of H^+ , suggesting both a cation exchange and leaching process. Net exchange increased with increasing free acidity of the incoming rain and with increasing residence time of the rain on the leaf surface. The source of these elements in the forest canopy was primarily dry deposited aerosols for Pb, primarily internal plant leaching for Mn, Cd, and Zn, and an approximately equal combination of the two for SO_4^- .

Significant fractions of the total annual elemental flux to the forest floor in a representative chestnut oak stand were attributable to external sources for Pb (99%), Zn (44%), Cd (42%), SO_4^- (39%), and Mn (14%), the remainder being related to internal element cycling mechanisms. On an annual scale the dry deposition process constituted a significant fraction of the total atmospheric input of Cd and Zn ($\sim 20\%$), SO_4^- ($\sim 35\%$), Pb ($\sim 55\%$), and Mn ($\sim 90\%$). Over short term periods however, the ratio of dry/total deposition for any element ranged over an order of magnitude.

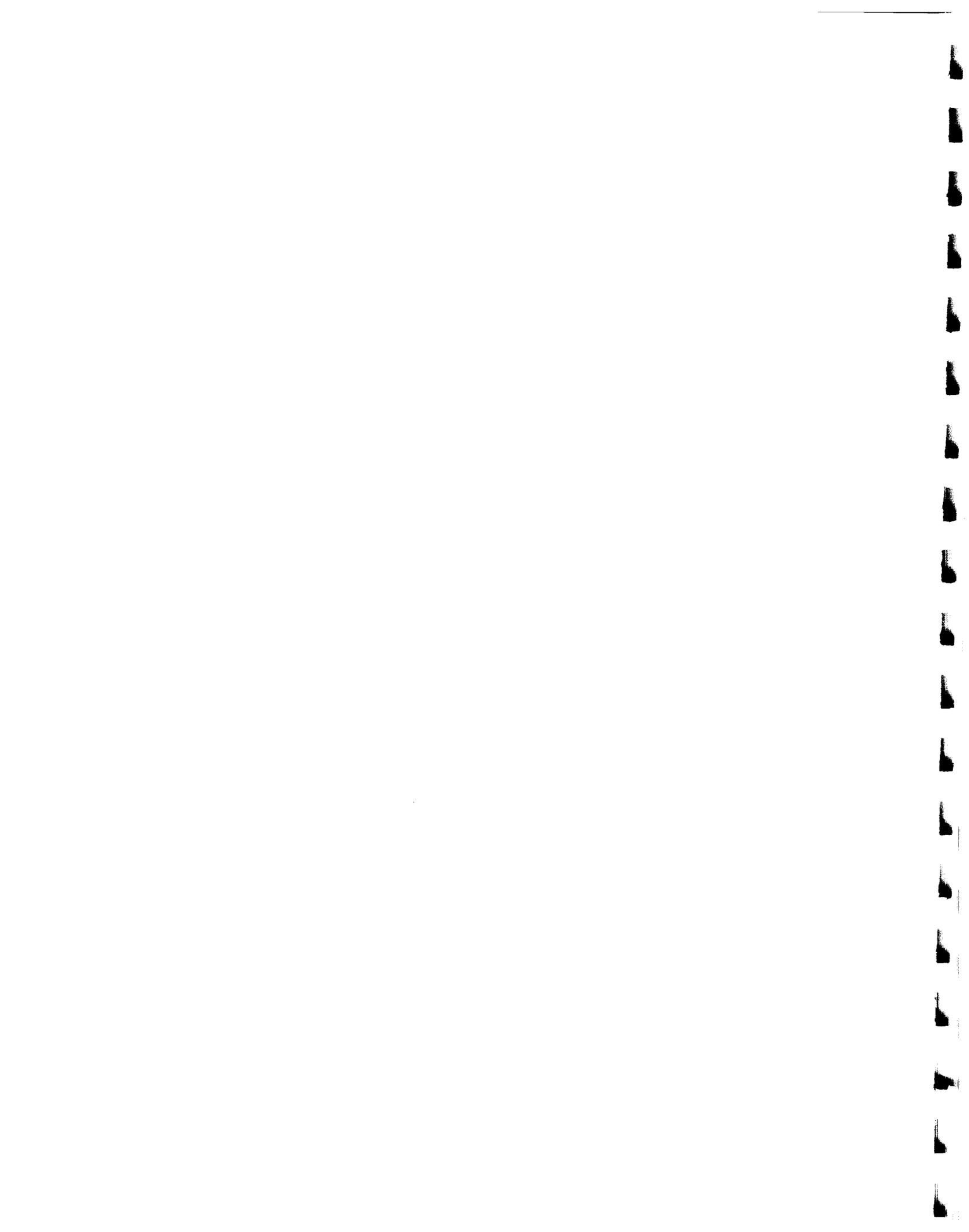


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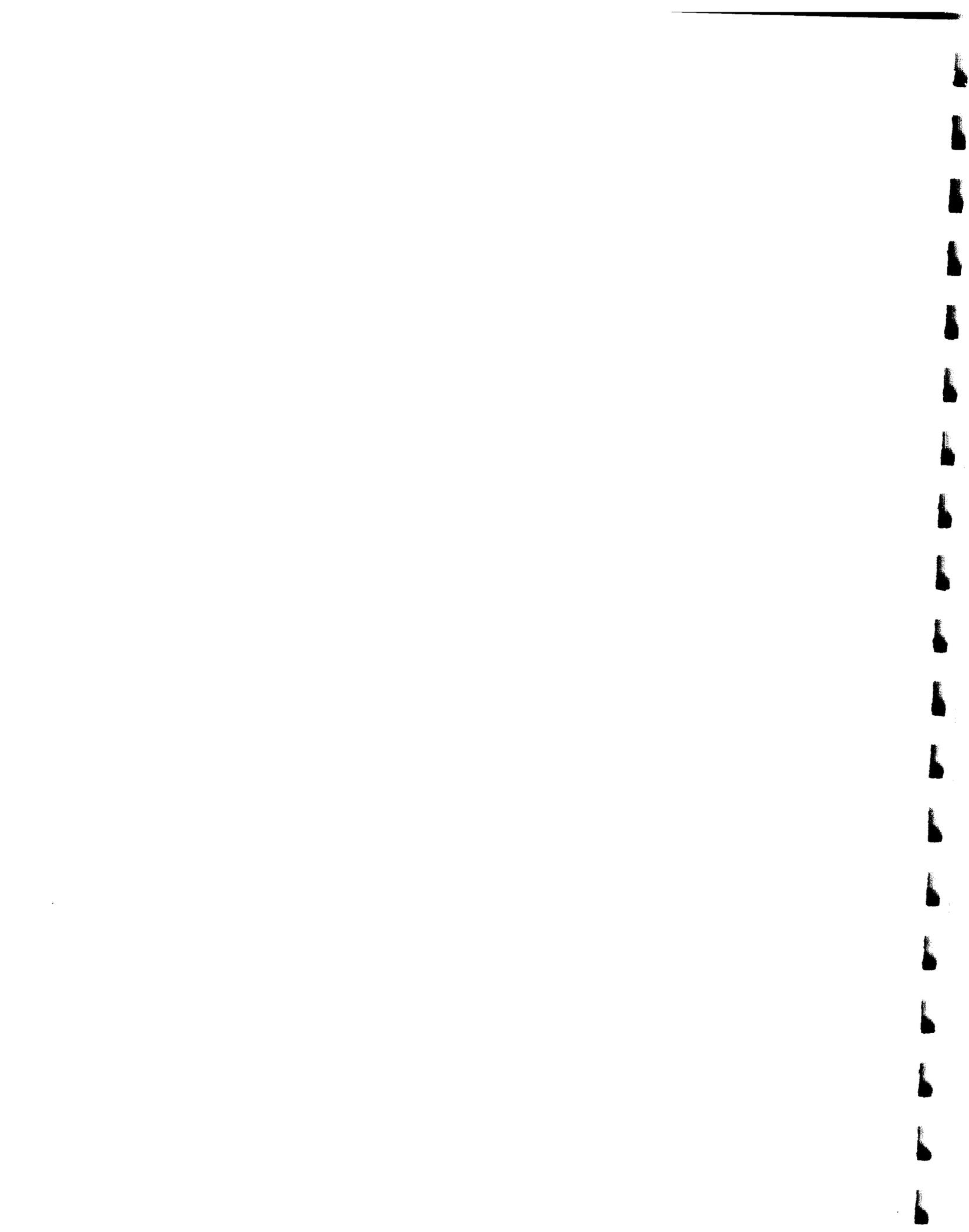
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EXECUTIVE SUMMARY

It is becoming increasingly apparent that the greatest potential for human impact on the geochemical cycle of several elements is related to their atmospheric chemistry, transport, and deposition. The critical links between increased atmospheric emissions and effects on terrestrial and aquatic ecosystems are the rates at which, and mechanisms by which, atmospheric species are transported to the earth's surface. Material is removed from the atmosphere by two general processes: wet deposition (precipitation scavenging of particles and gases, occurring within and below the cloud) and dry deposition (convective diffusion, inertial impaction, and sedimentation), where the relative importance of any mechanism is highly dependent on particle size and solubility characteristics. Perhaps the most important aspect of aerosol chemistry, from the standpoint of atmospheric deposition, geochemical cycling, and potential effects to the bioreceptor is the water solubility of aerosol-associated elements. This parameter is critical in determining the mobility of particle-associated elements in a given environment. Elements which are transported to vegetation surfaces in an insoluble form may be of little consequence. However, a particle-associated element of relatively high solubility residing on the vegetation surface can be mobilized (1) during precipitation, (2) by formation of a moisture layer on the vegetation, or (3) by reaction with leaf exudate, all of which may be readily followed by direct plant absorption or incorporation into various element cycling pathways. Wet deposition is

of particular importance due to both its episodic nature and the fact that originally gas- or particle-associated elements are delivered to the forest canopy partly in solution, thereby enhancing the possibility of absorption by vegetation surfaces and generally increasing the mobility of the element in the landscape.

The objective of this research has been to accurately quantify the atmospheric input of the environmentally mobile fraction of several trace elements and sulfate to a deciduous forest canopy and to determine the critical mechanisms of deposition. The research was performed at Walker Branch Watershed (WBW), a 97.5 ha intensively monitored forested catchment on the Oak Ridge National Laboratory reservation. The watershed provides an ideal field laboratory for study of the deposition and accumulation of coal combustion derived effluents, since it is situated within 20 km of three power plants (annual coal consumption $\sim 7 \times 10^6$ tons) and within 260 km of eight major coal-fired power plants (total electric capacity $> 14,000$ MW).

The problems involved in the sampling and analysis of both wet and dry deposition are well known. In precipitation collection these involve the efficiency of the sampler to collect a representative sample, postdepositional chemical alterations of the sample, sample contamination, sampling and analytical precision, and event definition. Accordingly, a modified version of the HASL collector was developed. The unit was modified with respect to construction materials and arrangement of components to minimize trace level contamination. Precipitation samples were collected on an event basis

over a two-year period at sites above the forest canopy (on a 46 m meteorological tower), at ground level in the open, and at four sites directly beneath the canopy. All samples were collected using individual funnel/bottle arrangements, a procedure amenable to different container washing, sample preservation, and analytical methods. The measurement of dry deposition presents a far more complex problem because of the many interrelated processes involved, all of which are somewhat dependent on the surface characteristics of the receptor. Two methods were utilized, one involving inert, flat surfaces situated in the upper canopy and the other involving laboratory leaching of material from sequentially collected leaves from the same locations. Dry deposition samples were collected over 4- to 7-day intervals during a 10-week intensive sampling period in the 1977 growing season. Concurrent with these experiments, aerosols were collected above the forest canopy using standard filter and impactor methods. To assure comparability between element fractions in suspended, deposited, and precipitation-scavenged material, laboratory leaching procedures were applied to all samples to extract the water soluble (pH \sim 5.6) trace element and sulfate fraction, followed by the dilute acid leachable fraction (pH \sim 1.2), both of which (termed the available fraction) were considered to represent environmentally mobile material. Analyses involved standard methods (graphite furnace AAS for trace elements; automated colorimetry for sulfate), with emphasis on sampling reproducibility, trace level contamination, and quality control.

Investigations of the parent aerosol population at the atmosphere-canopy interface led to several interesting conclusions. Substantial amounts (> 75%) of the available fraction of Mn, Zn, Cd, and Pb in aerosols were soluble in water, as were significant fractions (> 65%) of the total Mn and Cd but smaller fractions (< 30%) of the total Pb and Zn. The solubility and the water soluble-to-available-element ratio (termed relative solubility) both increased with decreasing particle size and with the duration of atmospheric water vapor saturation during the sampling period. Ambient aerosols exhibited considerably higher relative solubilities than aerosols collected in the stack of a coal-fired power plant, but relative solubilities of plume aerosols did increase during plume aging (measured by plume travel from 0.25 - 7 km) to levels measured for ambient aerosols. These observations suggest the importance of aerosol hydration in controlling elemental solubility. Relationships between aerosol chemistry and meteorological observations indicated the following: (1) elemental air concentrations and size distributions at WBW did not reflect a significant influence of local coal combustion, being more similar to concentrations measured at remote and rural locations than at urban or industrialized areas; (2) as regional air stagnation increased, the concentrations of Cd, Pb, Zn, and $\text{SO}_4^{=}$ increased while Mn decreased; (3) particle size distributions and concentrations of each element, and the manner in which they were influenced by various atmospheric parameters, suggested a soil source

for Mn, secondary atmospheric particle and combustion sources for Pb and $\text{SO}_4^{=}$, and both small particle combustion and large particle dispersion sources for Cd and Zn; and (4) the lack of any apparent wind direction effects on elemental mass median diameters and the slight increase in concentrations with winds from "other than local source" directions suggested that atmospheric chemistry over WBW was more likely the result of regional air transport phenomena rather than the direct result of local source emissions.

Compared to the ambient aerosols, smaller amounts (< 75%) of the available trace element fraction of dry deposited particles were water soluble, suggesting a larger particle size. This was confirmed by scanning electron and light microscopy of biological and inert deposition surfaces, which indicated the presence of a significant fraction of relatively large (> 10 μm) fly ash particles and dispersed soil fragments. An interesting observation from several scanning electron photomicrographs was the association of submicrometer- to micrometer-sized fly ash with considerably larger (5-20 μm) fly ash and scoriaceous particles, and the agglomeration of several submicrometer fly ash particles into large aggregates. The removal of these large particles from the atmosphere is primarily controlled by sedimentation, which may account for the often high concentrations of small particle-associated elements (Pb, $\text{SO}_4^{=}$) in dry deposited material. The presence of a significant quantity of such material on upward-facing leaf and inert, flat surfaces suggested particle sedimentation to be an important mechanism of dry deposition to upper canopy elements. The dry deposition rates of Cd, Pb, Zn, and $\text{SO}_4^{=}$

to the upper canopy were correlated with air stagnation frequency, concentrations of each element in the total aerosol fraction, and the frequency of winds from directions other than those influenced by local sources. Thus, dry deposition rates, as well as air concentrations, were not detectably enhanced by local emissions. Other possible sources of the large-particle fly ash were determined by calculating upper level air mass backward trajectories for time intervals comparable to large-particle tropospheric residence times. These trajectories were found to traverse two major regional urban centers and five major regional coal-fired power plants with sufficiently rapid air mass travel times to account for the large-particle transport.

The circumstances of sampling provided only one period (7 days) for which dry deposition to inert, flat surfaces could be compared with dry deposition estimated from sequential leaf washing. The agreement in deposition rates was good for Cd, $\text{SO}_4^{=}$, Zn (within 30%), and Mn (within a factor of 2) but poor for Pb (an order of magnitude higher rate measured to the inert surface). Leaf surface absorption of soluble Pb could be a factor. Comparing these deposition rates to air concentrations allowed calculation of deposition velocities (V_d) for the available element fraction to individual upper canopy surfaces. The mean V_d values reflected the general particle size distribution of each element such that elements characterized by larger mass median diameters exhibited higher deposition velocities. The V_d data indicated that the generally used value of 0.1 cm/sec is an

underestimate in the case of Cd, Mn, Zn, and perhaps sulfate (Cd = 0.05-0.87 cm/sec, Mn = 1.7-17 cm/sec, Pb = 0.04-0.10 cm/sec, Zn = 0.24-0.66 cm/sec, $\text{SO}_4^{=}$ = 0.07-0.24 cm/sec).

The precipitation concentrations and the wet deposition of H^+ , Pb, Mn, and $\text{SO}_4^{=}$ reached maximum values during the summer months. This was in response to synoptic meteorologic conditions which result in elevated aerosol concentrations due to air stagnation, and in generally lower rain volumes per event and hence less dilution of the scavenged material. These dilution phenomena were indicated by significant negative correlation coefficients between element concentrations in rain and rainfall amount, storm duration, and intensity. The expected positive correlations between rain concentrations and time since previous rainfall were not apparent, suggesting the local atmospheric reequilibration with the regional air mass to be relatively rapid. A simple model was applied to the empirical relationship between rain concentration and rainfall volume in an attempt to estimate the relative importance of in-cloud vs below-cloud scavenging to the wet deposition of each element. The model was based on the assumption that as precipitation continues at a sufficient rate, the below-cloud layer is depleted of its readily scavengeable particles and gases, and material still present in rain can be largely attributed to in-cloud scavenging. The calculations indicated that, on an annual basis, ~ 90% of the wet deposition of the primarily small particle atmospheric constituents, Pb and $\text{SO}_4^{=}$, was attributable to scavenging by in-cloud processes while for the large

particle-associated elements, Cd and Mn, removal by in-cloud scavenging was relatively less important, accounting for 60 to 70% of the deposition.

The interception of incoming rain by the forest canopy resulted in a net increase in the concentrations of Cd, Mn, Pb, Zn, and SO_4^- but a net decrease in the concentration of H^+ . The mean annual elemental enrichments were as follows: Mn (factor of 160); Cd(4); Zn and SO_4^- (3); Pb(2.7). The uptake of H^+ and concomitant loss of several elements by the canopy suggests a combination of cation exchange and leaching processes. The net exchange was seen to increase with increasing free acidity of the incoming rain and with increasing residence time of the rain on the leaf surface. On an equivalent basis, the hydrogen exchange could easily account for the trace cation leaching from the canopy, but accounts for less than 10% of the total cation leaching from the canopy during the growing season, indicating the importance of other processes. Leaf washing experiments and dry deposition analyses suggested the source of these elements in the forest canopy on an annual basis to be primarily dry deposited aerosols for Pb, primarily internal plant leaching for Mn, Cd, and Zn, and an approximately equal combination of the two for SO_4^- . However, these proportions were highly variable with time.

The above observations were integrated into an estimate of the annual atmospheric flux to the landscape. The wet deposition flux was determined from the product of the annual precipitation volume and from the annual precipitation volume-weighted mean concentration in rain

collected above the forest canopy. The dry deposition flux was estimated by multiplying the mean dry deposition rates measured to individual upper-canopy surfaces by suitable leaf area and scavenging indices for several canopy levels during the growing and dormant seasons. The estimated total annual atmospheric deposition to WBW of the elements of interest was similar to values reported in the literature for remote and rural locations. These rates were as follows (in g/ha/yr): $\text{SO}_4^{2-}\text{-S} = 19 \times 10^3$, Mn = 350, Pb = 150, Zn = 93, and Cd = 5.2. On an annual scale the dry deposition process constituted a significant fraction of the total atmospheric input of Cd and Zn (~20%), increasing in relative importance for SO_4^{2-} (~35%), Pb (~55%), and Mn (~90%). However, when measured during short-term periods (days), the ratio of dry/total deposition for any element ranged over an order of magnitude.

The importance of wet deposition to the bioreceptor as an episodic inundation of the leaf surface was seen from a comparison of wet and dry deposition rates on a comparable unit time basis (i.e., wet deposition rate calculated for the duration of an individual storm). Wet deposition rates expressed in this manner were 2 to 3 orders of magnitude greater than measured short-term dry deposition rates. The potential for plant effects can be further illustrated by calculating the deposition to an individual leaf during one event and over the growing season relative to the total leaf internal pool of the element. A single dry/wet event was seen to deposit a quantity of Pb to the leaf surface equal to ~70% of the internal pool. Deposited quantities of Cd and SO_4^{2-} were equal to 11 and 5%, respectively,

while quantities of Mn and Zn were $\sim 1\%$ of the internal pool. During the growing season, the leaf surface was exposed to 1 to 2 orders of magnitude more Cd and Pb, and nearly equal amounts of Zn and $\text{SO}_4^{=}$, relative to that contained within the leaf.

The total annual flux to the forest floor beneath a representative stand of chestnut oaks was attributable, to a significant extent, to external sources (atmospheric deposition by wet and dry processes) for Pb (99%), Zn (44%), Cd (42%), $\text{SO}_4^{=}$ (39%), and Mn (14%), the remainder attributable to internal element cycling mechanisms (leaffall plus foliar leaching). The pathways of highest relative importance to the total flux of each element to the forest floor were varied: foliar leaching for Cd (55% of the total) and Mn (49%), dry deposition for Pb (67%), wet deposition for Zn (36%), and leaffall for $\text{SO}_4^{=}$ (31%).

CHAPTER I

GENERAL INTRODUCTION AND OBJECTIVES

Statement of the Problem

It is becoming increasingly apparent that the greatest potential for human impact on the geochemical cycle of several elements concerns their atmospheric chemistry, transport, and deposition. Recent emphasis on intermittent control strategies, and the use of tall stacks, has resulted in dilution of concentrated emissions near the source, which is likely to improve urban air quality. However, the potential for degradation of the regional atmosphere by long-range transport of heavy metal vapors and fine particles known to escape conventional emission control techniques is increased. In addition, for trace elements currently estimated to be mobilized by coal combustion at rates from 0.1 to 0.5 or more times natural rates (e.g., Ni, Zn, As, Se, Hg and Pb; Vaughan et al., 1975), projected increases in coal combustion by the National Energy Plan will result in emission rates approaching those associated with natural processes.

The critical links between increased atmospheric emissions and effects on terrestrial and aquatic ecosystems are the rates at which, and mechanisms by which, atmospheric gases and particles are transported to the earth's surface and made available to receptor

organisms. Perhaps the most important aspect of aerosol chemistry, from the standpoint of atmospheric deposition, geochemical cycling, and potential effects to the bioreceptor is the water solubility of aerosol-associated elements. This parameter is critical in determining the mobility of particle-associated elements in a given environment. Elements which are transported to vegetation surfaces in an insoluble form may be of little consequence. However, a particle-associated element of relatively high solubility residing on the vegetation surface can be mobilized (1) during precipitation, (2) by formation of a moisture layer on the vegetation, or (3) by reaction with leaf exudate, all of which may be readily followed by direct plant absorption or incorporation into various element cycling pathways.

Material is removed from the atmosphere by two general processes: wet deposition (precipitation scavenging of particles and gases, occurring within and below the cloud) and dry deposition (convective diffusion, inertial impaction, and sedimentation). Slinn (1976) has presented a theoretical argument that dry deposition of "pollutant" materials to a forest from ground-based sources appears to be comparable in magnitude to wet deposition. The dry deposition flux can be estimated from the empirical relationship between pollutant flux to a surface (F_d) and its air concentration (C): $F_d = V_d \cdot C$. The term C is any representative value for a pollutant's air concentration while V_d , defined as the deposition velocity, can be estimated from literature data to be as follows: $0.1 \leq V_d \leq 1$ cm/sec. A similar estimate for wet deposition flux can be calculated using the concept of washout ratios, defined as the ratio of a contaminant's concentration

in surface level precipitation (k) to its concentration in surface level air (C). Wetfall flux (F_w) is then as follows: $F_w = \left(\frac{k}{C}\right) \cdot (pC)$, where p = precipitation rate. From theory and further data presented in Slinn (1976) it can be estimated that the washout ratio ($\frac{k}{C}$) is on the order of 10^5 . Using these assumptions, F_d and F_w can be estimated considering an annual time scale and applying the 23 year mean annual precipitation rate at Walker Branch Watershed, 130 cm/yr ($= p$), resulting in:

$$\frac{F_d}{F_w} = \frac{V_d C}{(\sim 10^5) p C} = 0.7 - 7.0 \quad .$$

Thus, within an order of magnitude, wet and dry deposition are of comparable importance to forest systems. Of these two mechanisms, wet deposition is of particular importance due both to its episodic nature and the fact that originally gas or particle-associated elements are delivered to the forest canopy partly in solution, thereby enhancing the possibility of absorption by vegetation surfaces and generally increasing the mobility of the element in the landscape.

Although the literature contains information on the atmospheric concentration of many elements data for their removal has not been readily available until quite recently. A critically important property of suspended particulate matter is its atmospheric size distribution. This largely determines the degree of respiratory system penetration and, hence, human toxicity, as well as governing atmospheric residence times and transfer efficiencies to various

surfaces (see the reviews by Chamberlain, 1975; Hosker and Lindberg, 1979). Thus, elements associated primarily with aerosols of a certain particle size may be more effectively removed from the atmosphere by any of several mechanisms involved in the wet and dry deposition process. Accordingly, this research has concentrated on a group of elements, some of which (1) have a significant vapor phase chemistry in the atmosphere and whose particulate forms exist primarily in the finest size range (Pb and S); (2) have been found to exhibit bimodal particle size distributions in aerosols (Cd and Zn), and (3) exhibit a more uniform size distribution in atmospheric particles, tending to occur on larger particles compared to the above elements (Mn).

Organization

It is the intent of this research to determine the critical mechanisms involved in the deposition of airborne materials to a deciduous forest in eastern Tennessee, and the rates at which these processes occur for the environmentally mobile fractions of Cd, Mn, Pb, Zn, and soluble S in the +6 oxidation state ($\text{SO}_4^{=}$). This report is divided into six chapters dealing with aerosol chemistry, measurement of dry deposition rates, precipitation chemistry, geochemical relationships between material deposited by several processes, a brief chapter describing the study area, and a final chapter which summarizes the results of each phase of the research into a coherent picture of the potential role of atmospheric deposition in element cycling and vegetation effects in Walker Branch Watershed (WBW).

Objectives

1. The overall objective of this study is the qualitative determination of the role of a forested landscape in the scavenging of atmospheric material, including transfer by dryfall processes, transfer by wetfall processes, and the role of water soluble aerosol components in the overall deposition process to WBW.
2. Specific objectives of the various subprojects are as follows:
 - (a) Characterize the composition and variability in the aerosol population at the atmosphere-forest interface,
 - (b) Determine the relative importance of various environmental factors which contribute to the variability of aerosol composition and particle size distribution,
 - (c) Determine the degree of water solubility of selected elements associated with aerosols in various size classes,
 - (d) Develop and apply techniques to measure the transport of particle associated trace elements and sulfate from a passing air mass to biological and inert upper canopy elements.
 - (e) Characterize the input of Cd, Mn, Pb, Zn, $\text{SO}_4^{=}$, and H^+ to the forest canopy by wet deposition on time scales commensurate with the identification of meteorologic and other factors regulating the magnitude of episodic element inputs.

- (f) Determine the extent to which and mechanisms by which the chemistry of incoming rain is influenced by forest canopy interception.
- (g) Determine the physical and chemical relationships between particles in coal combustion plumes, in ambient air, and deposited to the landscape by wet and dry processes.
- (h) Integrate the results of the short term, intensive field experiments into an estimate of the seasonal and annual atmospheric flux of elements to the landscape.

The following hypotheses were tested during the course of this research: (1) dry deposition, including the processes of gravitational settling and impaction, is a significant input mechanism to the Walker Branch Watershed landscape, (2) there is a need to expand aerosol chemistry studies beyond total element analysis to concentrate on the environmentally mobile fractions of particle associated elements, (3) some particles deposited on certain leaf surfaces may be physically tightly bound to the surface and available for incorporation into element cycling pathways only after leaf fall, (4) application of enrichment factor and elemental ratio calculations using the composition of particles dislodged from vegetation surfaces and collected from ambient air, combined with similar data from potential sources (i.e., coal-fired steam plant emissions and fugitive dust) can be used in the identification of trace element sources, (5) the operational status of the local (within 20 km) TVA coal-fired power plants has a significant effect on the trace element concentrations in the air mass over WBW, and material deposited to the landscape,

(6) elements associated with particles having certain characteristics (size and shape) may be more efficiently scavenged by the forest canopy than others, (7) the parameter having the most significant influence on elemental concentrations in precipitation is rainfall volume, (8) the fully developed forest canopy has a significant influence on the trace element chemistry of intercepted rain, (9) the most significant flux of the non essential elements (Cd, Pb) to the forest floor will be due to external, atmospheric sources; while the flux to the forest floor of the essential elements (Mn, Zn, SO_4^{2-}) will be more equally divided between internal and external sources.

CHAPTER II

THE STUDY AREA, WALKER BRANCH WATERSHED, AND SOURCES
OF ATMOSPHERIC EMISSIONS

Walker Branch Watershed (WBW) is located on the Department of Energy's Oak Ridge National Laboratory (ORNL) Reservation in eastern Tennessee (latitude $35^{\circ} 58'N$, longitude $84^{\circ} 17'W$, Figure 1). The ORNL Reservation consists of 15,000 hectares, $\sim 40\%$ of which is devoted to environmental research and management. The watershed is roughly centered within the reservation boundary. Walker Branch Watershed has been maintained in a relatively undisturbed state since 1942. The biogeochemical cycling program, initiated in 1969, has resulted in the establishment of several instrumented facilities which are of critical importance in a study such as this. Briefly, these include a 46 m meteorological tower (further discussed in Chapters III and V), a multi-site continuously recording raingauge network (Chapter V), two continuously recording stream gauging stations, and one permanent and several mobile field laboratories.

The watershed is a 97.5 ha, primarily deciduous forested catchment comprised of two sub-basins of 59.1 and 38.4 ha each. The area is typical of the oak forests of the Ridge and Valley Topographic Province, ranging in elevation from 265-360 m. The canopy is approximately 93% deciduous with oaks, hickories, and yellow poplar the predominant species. The catchment terrain is underlain by dolomitic

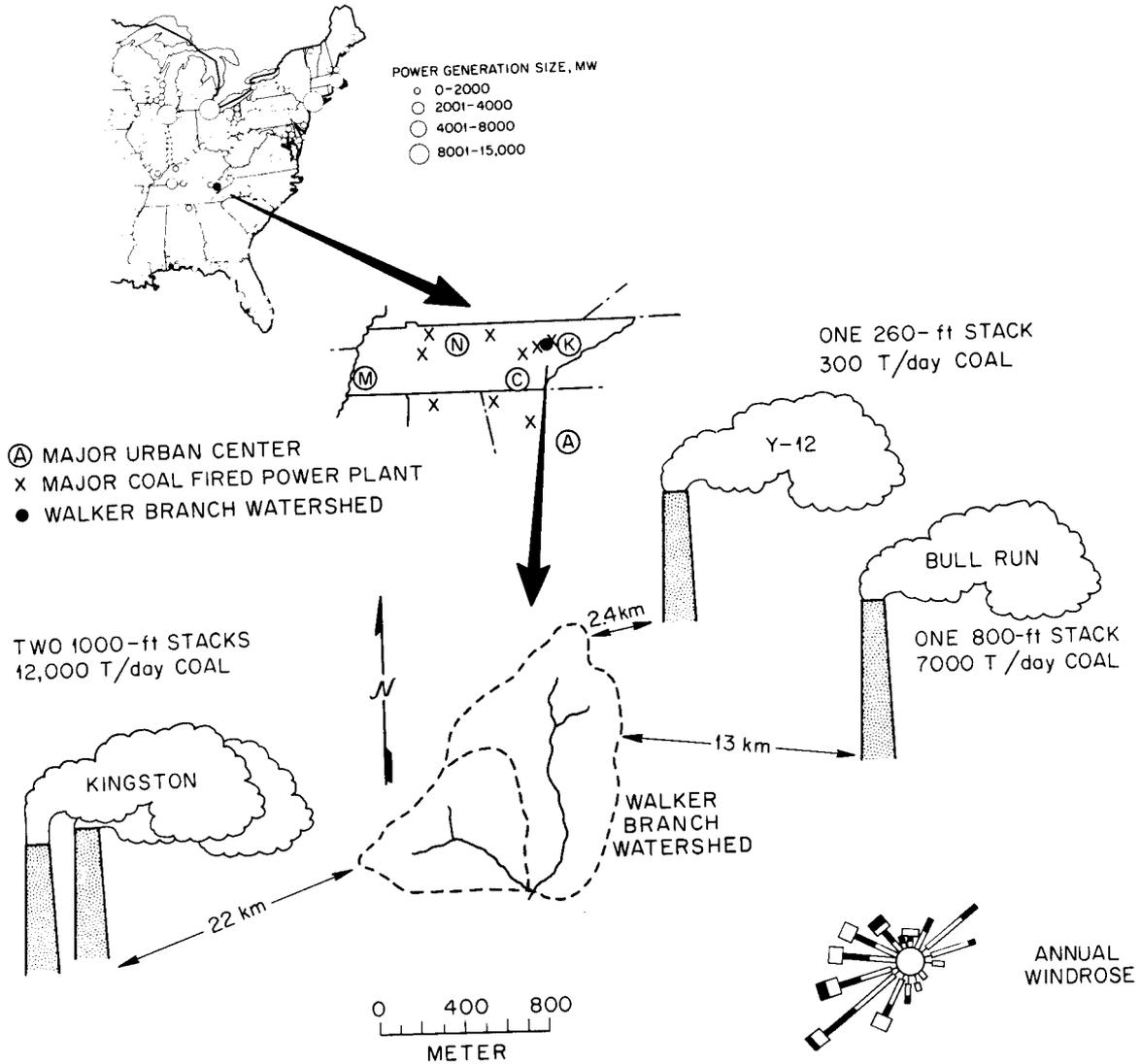


Fig. 1. Geographical location of Walker Branch Watershed in relation to continental, regional, and local sources of atmospheric emissions due to fossil fuel utilization. Shown are the spatial distribution of centers of coal and oil-fired steam electric generation capacity in the eastern U.S., the location of specific regional coal-fired power plants and major urban centers, and the proximity of three local power plants to the watershed.

formations, including several sinkholes. Soils of the Fullerton and Bodine series comprise ~ 90% of the watershed area, with the predominant clay mineral in the soils being kaolinite. The watershed receives an average of 130-150 cm precipitation annually, being generally evenly distributed throughout the year with small peaks in the late winter/early spring period and dry periods generally occurring during late summer/early fall. Precipitation as snow is considered negligible. Rain days occur with an approximate frequency of 33%, 55% of these days receiving < 1 cm rain and 90% receiving < 3 cm (Henderson et al., 1977). Earlier and continuing studies on the watershed provide correlative information on meteorology, hydrology, chemistry, and biology which are essential to the interpretation of the experiments conducted as a part of this research (e.g., see Harris, 1977, for a more detailed physical description of the watershed and a discussion of the research scope of the Walker Branch Watershed research project; see also Henderson et al., 1977; Comisky et al., 1977; Huff et al., 1977; Lindberg et al., 1977; Turner et al., 1977; Van Hook et al., 1977; Elwood and Henderson, 1975; and Shriner and Henderson, 1978).

Further descriptions of several characteristics of the watershed and surrounding area which are pertinent to the deposition research have been integrated into various sections of this manuscript. These include a description of the meteorological tower (Chapter III, V) and the rain gauge and sampling network (Chapter V), a further discussion of variations in seasonal and annual precipitation volume (Chapter V), some consideration of seasonal development and morphology of the forest

canopy (Chapter IV, V), and a discussion of general air quality and wind direction frequency during the 1977 growing season (Chapter III).

The watershed provides an ideal field laboratory in which to examine deposition and cycling of airborne trace contaminants derived from atmospheric emissions related to energy technology. The catchment is located within ~ 20 km of two major and one small coal fired power plants (Figure 1). As indicated by the annual windrose, these point sources are frequently upwind of the watershed. The Tennessee Valley Authority (TVA) operates the Kingston power plant 22 km to the west-southwest. This facility consumes 12,000 tons of coal daily, generating 1200 Mw of electricity. The plant was recently (1976) upgraded by the addition of two 330 m stacks and "best available technology" electrostatic precipitators. To the east-northeast of the watershed, ~ 13 km, TVA operates the Bull Run power plant. This facility, built in 1962, was originally constructed with a single 270 m stack and has been recently (1977) upgraded by the construction of new, high efficiency (99.9% mass removal efficiency), electrostatic precipitators. The Bull Run plant consumes 7000 tons of coal daily, generating 890 Mw of electricity. The third plant is a much smaller unit operated by the Department of Energy on the Oak Ridge Reservation, ~ 2.4 km to the northeast of the watershed. This unit is equipped with an 87 m stack and somewhat older, less efficient (98%) precipitators. The facility burns 300 tons of coal daily for steam production only.

In addition, there are several other sources of atmospheric emissions within ~ 35 km of the watershed. These have been recently

characterized for Roane County which includes the watershed and extends ~ 50 km to the southwest, in a generally upwind direction (Miller et al., 1977). Approximately 50% of the labor force in this area is employed in manufacturing industries, with such development being primarily centered in the Tennessee River Valley around the Rockwood-Harriman Industrial Corridor, ~ 35 km to the west-southwest. The industrial corridor includes facilities for the production of steel, wood, paperboard, and textile products. The TVA Kingston power plant is also located in this corridor. Sources in this direction from the watershed may be particularly important because of the influence of the topography which is dominated by parallel ridges. These ridges run WSW to ENE and act as a strong influence in channelling winds through the parallel valleys. The annual windrose in Figure 1 indicates this industrial corridor to be frequently upwind of the watershed. Miller et al. (1977) have estimated the total annual emissions related to coal combustion for Roane County as follows (in metric tons per year): suspended particulates = 35.6×10^3 , sulfur oxides = 157×10^3 , nitrogen oxides = 30×10^3 . Of these totals, the authors estimated the contributions due to the Kingston steam plant to be 97%, 98%, and 99%, respectively. Of the total annual emissions in the county due to combustion of all fossil fuel types (coal, fuel oil, natural gas, and gasoline) the relative contribution of the Kingston power plant was 97% of the suspended particulates and sulfur oxides, and 94% of the nitrogen oxides. The potential influence of this one point source on local air quality is obvious.

The possibility of regional effects on local air quality must not be neglected, however. In addition to these local sources, the watershed is located ~ 20 km west of Greater Knoxville, and within 260 km of three major regional urban centers (Chattanooga and Nashville, TN, and Atlanta, GA) and 8 major coal fired electric generating stations with a combined generating capacity of > 14,000 Mw (Figure 1). The potential of such regional sources to contribute to the atmospheric load and deposition in Walker Branch Watershed is considered in Chapter VI.

CHAPTER III

TRACE CHEMISTRY AND PARTICLE SIZE DISTRIBUTION OF THE
WATER SOLUBLE AND DILUTE ACID LEACHABLE FRACTIONS OF
AEROSOLS IN WALKER BRANCH WATERSHED

Introduction

Suspended particles represent a class of airborne materials which are extremely complex due to wide variations in origin, chemical and physical properties, and elemental composition. One of the most important properties of suspended particulate matter, whether liquid or solid, is particle size distribution. This property largely determines the degree of respiratory system penetration (Lee, 1972), and hence human toxicity (Natusch and Wallace, 1974), as well as governing the atmospheric residence times and transfer efficiencies to various surfaces (Cawse and Peirson, 1972).

Perhaps an equally important aspect of aerosol chemistry, from the standpoint of atmospheric deposition, elemental cycling, and potential effects to the bioreceptor is the water solubility of aerosol associated elements. It is well known that the hygroscopicity of atmospheric particles is very important from the point of view of cloud physics (Junge, 1963). However, the degree of water solubility, in addition to the size distribution, of aerosols is also a critical factor in atmospheric chemistry, particularly as related to origin, transport, and removal of particles from the air. This factor is critical in

determining the mobility of an element in a given environment. Elements which are transported to vegetation surfaces in a highly insoluble form may be incorporated into the plant only through the chance occurrence that the parent aerosol happens to directly enter an open stoma during deposition. However, a particle associated element of relatively high solubility residing on the vegetation surface can be mobilized, (1) during precipitation events, (2) by the formation of a moisture layer on the vegetation (i.e., dew), or (3) by reaction with leaf exudate. Direct plant absorption may or may not follow all of these. Alternatively, elements associated with particles deposited on vegetation can be removed from these surfaces by wetfall and, if in a soluble form, are more readily incorporated into various element cycling pathways than an insoluble particle.

Particle solubilities have been reported in the literature to a limited extent for major aerosol constituents such as $\text{SO}_4^{=}$, NH_4^+ , and Cl^- (Meszaros, 1968), but not for many trace constituents. Hodge et al. (1978) recently reported on the sea water leachability of several aerosol associated elements and found that substantial amounts of metals in the solid phase were leachable. Because of the indication that aerosol solubility may be related to wetfall scavenging efficiencies, surface retention of particles following dry deposition, and element cycling in general, this aspect of aerosol chemistry was studied during an intensive sampling period including 10 intervals of 4 to 7 days duration during the summer of 1977. Also sampled during these 10 experimental periods were incident precipitation and throughfall (discussed in Chapter V), and dry

deposition of particles to natural and artificial surfaces (discussed in Chapter IV).

The overall objectives of this aspect of the work were:

(1) Characterize the composition and variability in the aerosol population at the atmosphere-forest interface,

(2) Determine the relative importance of various environmental factors which contribute to the variability of aerosol composition and particle size distribution,

(3) Determine the degree of water solubility of selected elements associated with aerosols in various size classes,

(4) Compare characteristics of ambient aerosols to possible source materials including fly ash and combustion plume particles, and

(5) Compare chemical and physical characteristics of ambient aerosols to particles deposited on leaf surfaces and inert surfaces and to material scavenged by precipitation. The geochemical and physical relationships between suspended, deposited, and rain scavenged particles is the topic of discussion in Chapter VI and will not be discussed here.

Materials and Methods

Aerosol Collection

All of the aerosol samples collected during this study were made from the top of a 46 m meteorological tower at the western edge of WBW approximately 23 m above the forest canopy (see Figures 20 and 21 in Chapter V). The bulk or total aerosol fraction was sampled continuously during each of the 10 periods using a 0.4 μm Nuclepore

polycarbonate membrane in a Millepore stainless steel filter holder. The relationships between retention efficiency and particle size and membrane pore size have been tabulated by the Nuclepore Corporation. These data indicate that particles $> 0.2 \mu\text{m}$ in diameter are retained by this filter material with a $\sim 50\%$ efficiency. The efficiency of such samplers to collect relatively large particles ($> 10 \mu\text{m}$) has recently been discussed by Pattenden and Wiffen (1977) to be on the order of 5% at high wind speeds. Simultaneous with the collection of the total aerosol fraction, ambient aerosols were also fractionated into 9 particle size classes using a standard Anderson cascade impactor, model #20-800, operated at $\sim 28 \text{ lpm}$ ($\sim 1.0 \text{ SCFM}$). Nuclepore polycarbonate film was used as the impaction surface on each stage and as the backup filter ($0.4 \mu\text{m}$ pore size) in the impactor. The utility of this material as the collection surface lies in its inherent low trace constituent concentrations (Andren et al., 1975), its non-hygroscopicity, its hydrophillic nature, and its low absorption and adsorption losses (Nuclepore Incorporated, Catalogue 20). These properties allowed for determination of the tare weight on all impactor surfaces prior to and following sampling so that this total filter load (total suspended particulate load, TSP, per size class) could be compared to the trace element concentrations. From these measurements the elemental concentrations could be compared on both a particulate concentration (ppm) and an air concentration (ng/m^3) basis. Tests on the efficiency of this material to act as impaction surfaces are discussed in a following section.

Sample collection devices were prepared in the laboratory immediately prior to placement in the field. Sampler components were hand washed using polyethylene gloves and double distilled water (2XDW), leached briefly in dilute NH_3 , washed with profuse amounts of 2XDW, dried in a convection oven, and stored in sealed polyethylene bags. New polycarbonate membranes were placed into the samplers after taring, all components being handled with teflon forceps and polyethylene gloves and all work being done in a laminar flow clean bench using HEPA absolute filtered air (high efficiency particle air filters, rated efficiency is 99.97% removal of particles $> 0.3 \mu\text{m}$). Filters and impaction surfaces were used directly from the original storage containers without prewashing. Prewashing steps, including combinations of dilute Ultrex ultrapure HNO_3 and 2XDW, were generally found to result in unchanged or even slightly higher blank levels. The impaction membranes were placed on the standard glass impaction plates provided with the impactor after first exposing the glass plates to steam from heated 2XDW. The moisture film resulted in a positive seal between the polycarbonate membrane and the glass plate.

Samples were then transported to the field in sealed polyethylene bags and mounted atop the tower using rain shields fabricated from 2 liter polypropylene bottles. Each sample was attached to a separate carbon vane air pump located at the base of the tower by means of large diameter tubing to minimize friction induced pressure drop in the 43 m tube. Flow was monitored continuously using in-line rotameters at the pump end of the system, correcting for pressure drop prior to flow rate calculation. In addition, flow rate was checked frequently using a

cleaned rotometer placed momentarily at the intake of the impactor or filter sampler. Flow through the impactor averaged $1.53 \text{ m}^3/\text{hr}$ (± 0.11) while flow through the total filter averaged $0.96 \text{ m}^3/\text{hr}$ (± 0.23) during the 10 sampling periods.

Two additional sets of samples were collected for supportive information. These were precipitator ash samples collected at the local Bull Run Power Plant and at the TVA Cumberland Power Plant. Post precipitator fly ash samples were also collected by hand from the deflection plate at the base of the exhaust stack while the units were down for maintenance. In addition, during a cooperative study with the TVA Air Quality Branch plume samples were collected at three distances from the stack of the Cumberland Plant using a TVA helicopter with a sampling port designed for isokinetic plume sampling beyond the influence of the prop wash. Particulate samples were collected using total filters and modified Anderson impactors designed for isokinetic flow under these conditions. The impactor modification involved removing several lower stages after calculating the critical flow velocities and impaction parameters for the conditions of sampling (flow rate of $4.6 \text{ m}^3/\text{hr}^{-1}$) needed to maintain isokinetic flow through the plume probe and impactor.

Analytical Techniques

Extraction Procedure and Operational Definitions

At the end of each sampling period the collectors were returned to the laboratory where the impaction plates and total and backup filters were removed using teflon forceps and polyethylene gloves in the clean

bench. These filters were weighed on a 5 place balance with a resolution of 0.01 mg, sealed in acid washed polypropylene petri dishes and stored in glass dessicators until analysis or extraction. To simplify interpretation of the impactor data and to assure sufficient material in each particle size range for analysis, the impaction plates were combined in pairs for extraction as follows: stages 0 + 1 (designated as particle size class 1), stages 2 + 3 (class 2), stages 4 + 5 (class 3), stages 6 + 7 (class 4), while the backup filter (class B) was treated separately. The aerodynamic particle diameters for each stage, assuming an impaction efficiency of 50%, were calculated from relationships between flow rate, impaction efficiency, and particle diameter supplied by C. H. Erickson, Director of Engineering, Anderson 2000 Inc.

On several occasions duplicate total filter samplers and impactors were prepared in the laboratory, stored in the clean bench during field sampling, and dismantled along with the field samplers as described above, including both weighing steps. These filters and impaction surfaces were carried through the laboratory leaching procedure, as described below, and used for blank determinations.

The laboratory leaching experiments were designed to result in the complete extraction of the water soluble component of the ambient aerosols in the first step and in the extraction of the dilute acid leachable component in the second step. On one occasion, the residue remaining after the water and dilute acid extraction was subjected to an additional acid leaching at 10 times the original acid concentration. On another occasion the residue was subjected to a

complete digestion procedure. The details of the various leaching procedures were as follows: (1) Water extraction- filters or impaction surfaces were placed into prewashed (washing procedure as described in Appendix A) 250 ml polyethylene bottles with 50 ml 2XDW (water quality and distillation procedure for the 2XDW also described in Appendix A). These bottles were tightly capped, sealed in clean polyethylene bags, and shaken on a reciprocating shaker at high speed (240 oscillations per minute) for two hours. This leachate was filtered through a standard 0.4 μm Nuclepore filter, and the filtrate, termed the water soluble fraction, saved for analysis. The details of the filtration procedure, including types of filter apparatus, washing procedures, and contamination checks, are described in Turner et al. (1977) and briefly discussed in Chapter IV; (2) Dilute acid leach- the original filter or impaction surface was retained in the polypropylene washing bottle from step 1 and the 0.4 μm nuclepore membrane used to filter the water extract was added to this bottle. These filters were then shaken on the reciprocating shaker for 2 hours with 50 ml of 0.08 N (pH = 1.1) Ultrex ultra pure HNO_3 . The reasons for the choice of this pH and the trace element levels in the Ultrex acid are discussed in Appendix A. Following the shaking step, the samples were stored at ambient temperature in the dark for 7 days prior to analysis; (3) Occasional 1N acid leach- the sample from step 2 was acidified to 1.0 N with Ultrex HNO_3 and carried through step 2 again; (4) Occasional "total" wet digestion- the sample from step 2, including both filters, was slowly taken to dryness on a steam plate. The residue was leached with 10 ml Ultrex concentrated HNO_3 + 10 ml

Ultrex concentrated HCl + 10 ml 2XDW as suggested by Anderson (1974). This solution was shaken on the shaker for 2 hours, stored in the dark for 7 days, and heated to 90°C for 12 hours prior to analysis. Extraction efficiency or recovery was checked using small quantities of NBS Standard Fly Ash (discussed in a following section).

In the following discussions certain operational definitions will apply to the use of the terms "soluble" and acid "leachable" components. These will be as follows:

Soluble fraction = quantity of material removed by the distilled water extraction in step 1, expressed in air concentration or particle concentration terms.

Acid leachable fraction = quantity of material removed by 0.08 N HNO₃ leach in step 2, expressed similarly.

Environmentally mobile or available fraction = soluble fraction plus acid leachable fraction, expressed similarly.

Relative solubility = [soluble fraction/available fraction] · 100, expressed as percent soluble.

Extraction Efficiency

The extraction method was tested to determine the completeness of the water and dilute acid extractions. A series of sequential samples were collected over a given time period during the water leaching and during the dilute acid leaching. These samples were analyzed for the element of interest to determine the optimum extraction times and solution volumes. The data for two representative tests for the leaching rates of Cd and Pb from a total aerosol filter is summarized

in Figure 2. The patterns of Zn and Mn release were nearly identical to those of Cd. The release of $\text{SO}_4^{=}$ was similar to the metals tested for the 2XDW leach but very little additional $\text{SO}_4^{=}$ was removed in the acid leach step. After the initial 2 hours of leaching 98% of the Cd and Pb were in solution (assuming the 24 hour values to represent 100% of the water extractable material). Following the 24 hr leaching, the solution was acidified to $\text{pH} = 1.1$ (at a rate of 5 ml Ultrex $\text{HNO}_3/1$). This resulted in an additional rapid release of the acid leachable metal fraction during the following 2 hours, followed by a very gradual release over the next 36 to 48 hours. The amount released during the initial 2 hours of dilute acid leaching represented 95% of the Cd and 97% of the Pb present in solution following 9 days of continued leaching while the amount in solution after 7 days was essentially 100% of that present at 9 days. Thus the 2XDW leaching was terminated after 2 hours while the dilute acid leaching was terminated after 7 days.

As described above, two aerosol samples were further extracted by an additional 1N HNO_3 leach in one case, and a "total" wet digestion in another. These samples were not analyzed for a $\text{SO}_4^{=}$ because of the previous indication that very little (approximately an additional 1%) $\text{SO}_4^{=}$ was removed by the dilute acid leach step. This is in agreement with results reported by Dams et al. (1975). The results of the additional 1N acid leach can be expressed as the ratio of the total metal removed by the 2XDW leach plus dilute acid leach plus 1N acid leach to the amount removed by the first 2 steps alone. Results for a total aerosol filter were as follows: Cd = 1.05, Mn = 1.01, Pb = 1.11,

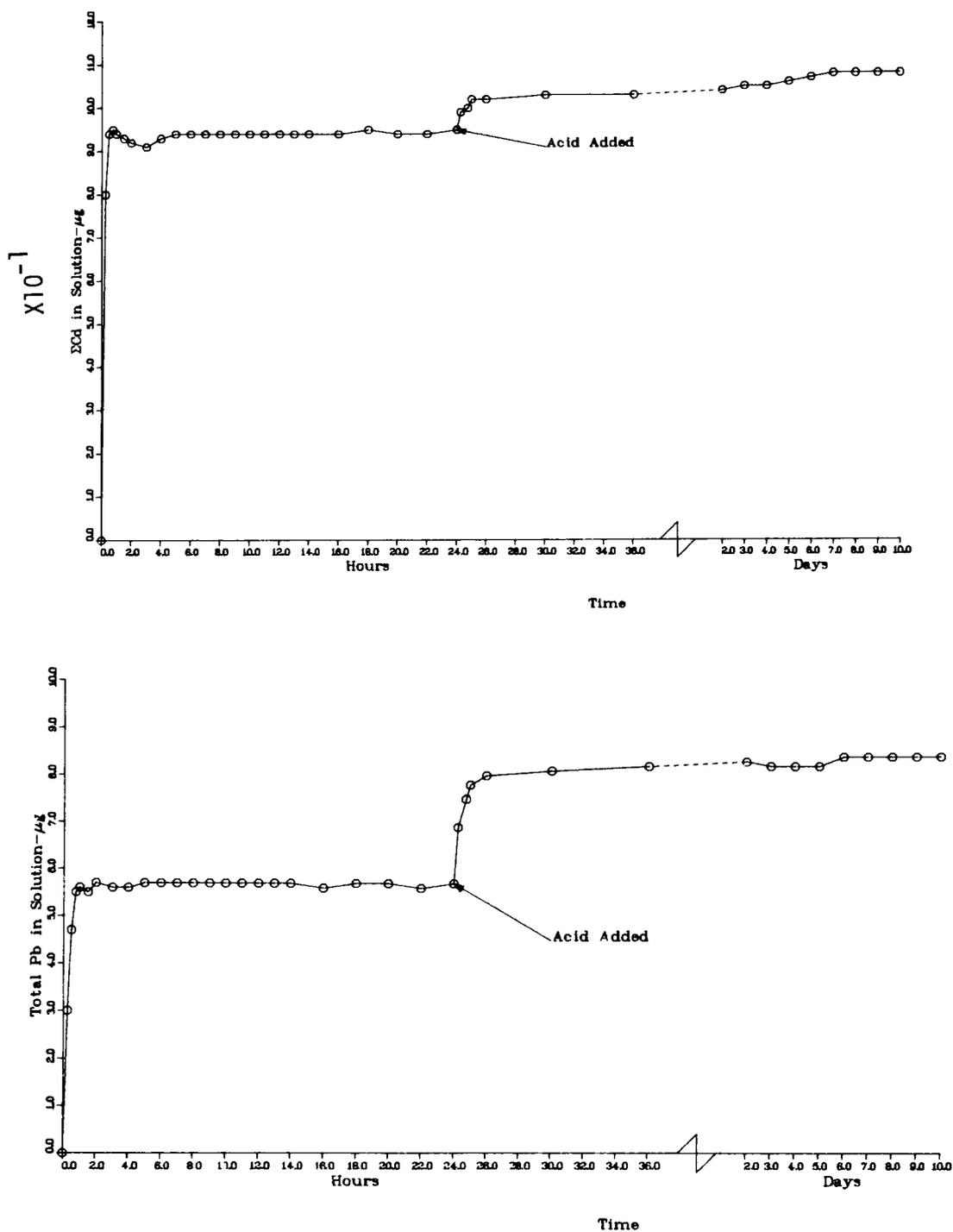


Fig. 2. Temporal variations in Cd (upper plot) and Pb (lower) concentrations in solution during the leaching of a total aerosol filter. Extraction solution was double distilled water ($\text{pH} \approx 5.6$) until acidified to $\text{pH} \approx 1.2$ (nitric acid).

Zn = 1.11, while results for a single impaction surface were:
Cd = 1.00, Mn = 1.01, Pb = 1.12, Zn = 1.01. Thus, with the possible exceptions of Pb and Zn, a negligible amount of additional metal was removed by the 1N acid leach relative to a 0.08 N acid leach, lending support to the routine use of the more dilute acid leaching step described above.

One full set of impaction plates was carried through the "total" wet digestion procedure. Because of the refractory nature of fly ash and its suspected presence in aerosol samples in WBW (Lindberg et al., 1975), the digestion procedure was tested using milligram quantities (similar in mass to the amount of aerosol generally collected on aerosol filters) of Standard NBS Fly Ash.

The results of the NBS ash digestion and the digestion of ambient aerosols are summarized in Table 1. The ratios of analyzed NBS ash content to certified content for 3 replicate samples indicate that the wet digestion of the NBS ash resulted in excellent recovery for Cd and generally good, but erratic, recoveries for Pb and Zn. Only in the case of Mn were the recoveries consistently low, perhaps due to the inclusion of Mn within the acid resistant ash residue to some extent. For this reason, the "total" wet digestion concentrations of Cd, Pb, and Zn in aerosols were used without correction while the "total" digestion concentrations of Mn were corrected for an apparent 80% recovery. The second section of Table 1 indicates the ratios of available metal concentrations to total metal concentrations for large and small particle fractions of the total aerosol. The largest particles (stages 0 plus 1, size class 1) were the least efficiently

Table 1. Comparison of measured to certified concentrations in NBS standard fly ash digested by the HNO_3 -HCl wet method. Also, comparisons of the amount of metal removed from various aerosol size fractions by distilled water and dilute acid leaching techniques relative to the total digestible metal present

Sample	Cd	Mn	Pb	Zn
	[analyzed/certified concentration ratio ($\bar{X} \pm \sigma$)]			
NBS Standard Fly Ash (#1633) (n=3)	0.97±0.09	0.80±0.04	0.89±0.17	0.89±0.17
	<u>Available^a/total digestible^b concentration ratio</u>			
Anderson Stages 0-1 ^c	0.81	0.80	0.20	0.002
Stages 6-7 ^d	1.03	0.83	0.26	0.15
Backup filter ^e	1.23	0.99	0.23	0.59
Total aerosol fraction	1.02	0.93	0.46	0.40

^aAvailable = distilled water leach plus dilute acid leach.

^bDigestible = available plus wet digestible (HNO_3 -HCL).

^cAerodynamic diameter $> \sim 7.2 \mu\text{m}$ (size class 1).

^dAerodynamic diameter $\sim 0.44 \mu\text{m}$ (size class 4).

^eIdeally should capture $< \sim 0.44 \mu\text{m}$ material (size class B).

leached by the 2XDW plus dilute acid steps, yielding < 1% of the Zn, 20% of the Pb and ~ 80% of the Mn and Cd. The fraction of the material removed by the water and dilute acid leaching procedures relative to the "total" material generally increased as the particle size decreased (from size class 1 to 4 to B). This increasing availability of trace metals associated with smaller particles is related to their known increased concentration on the surfaces of smaller particles (Natusch et al., 1974; Natusch and Wallace, 1974; Keyser et al., 1978), and is discussed further in a following section.

For the total aerosol material the available fraction represents 50% of the Pb and Zn, but nearly all of the Cd and Mn. This should be kept in mind when "relative solubility" of the aerosol associated metals is discussed in the following sections. The operational definition of "relative solubility" discussed earlier will yield values for Mn and Cd in all particle size classes within 20% of the value commonly termed water-solubility (e.g., water leachable fraction divided by the total metal originally present). Similarly the relative solubility will most closely approximate the water-solubility for the small particle fractions of Pb and Zn. However, it should be kept in mind that the operational definition will overestimate the water-solubility of Pb and Zn in large particle fractions and in the total aerosol. Similarly, discussions of the available or environmentally mobile concentrations of elements in the atmosphere should be read with this in mind. However, since such harsh extraction procedures ($5.3 \text{ N HNO}_3 + 4 \text{ N HCl}$) are rarely encountered in the environment, the consideration of available metal concentrations is

valid, especially as related to element cycling and mechanisms of both wet and dry deposition. In addition, the operational definition remains useful for all elements for the purpose of sample to sample comparisons.

Analytical Procedure

All samples for trace metal determinations were analyzed using graphite furnace atomic absorption spectrophotometry (GFAAS), employing the standard additions method on each sample. The details of the technique, including considerable discussion of quality control, are described in Appendix A, while results of a four laboratory intercalibration study are described in Turner and Lindberg (1976).

Sulfate was determined using an automated colorimetric procedure employing the improved method of McSwain et al. (1974). A detailed discussion of the technique and an evaluation of its accuracy and precision are described in Appendix A. The sulfate technique resulted in a mean accuracy of $\pm 1\%$ and a mean precision of $\pm 4\%$ for samples in the 1-5 mg/l range (most commonly encountered concentration in extraction samples). The GFAAS technique resulted in mean accuracies generally between ± 1 to $\pm 3\%$ with precision ranging from ± 4 to $\pm 10\%$ for concentrations in the $\mu\text{g/l}$ range.

Sampling Reliability and Reproducibility

Efficiency of Impaction Surface

A number of experiments were run during the developmental period of this research to test the reliability of the sample collection design and to determine overall sampling plus analytical precision.

Prior to checking the overall reproducibility between replicate impactor runs, total aerosol runs, and between the concentrations determined by the total filter compared to the sum of the impactor stages, it was necessary to evaluate the utility of the nuclepore membranes as impaction surfaces. The problem of particle bounce in cascade impactors is well known but not easily solved (Dzubay et al., 1976). In several applications glass slides or stainless steel impaction plates have been used for sample collection when covered by an additional impaction surface such as polyethylene foils or films (Heindryckx, 1976; Martens et al., 1973). As previously discussed, because of the need to maintain low blank levels, and to find a substrate of low tare weight which was amenable to the leaching procedures, Nuclepore membranes were chosen.

Various membrane films have previously been used in particle size analysis, but were generally coated with a sticky material (Berg, 1976; Dzubay et al., 1976). Since the sticky substance could obviously not be used in this application, it was necessary to compare untreated Nuclepore membranes with sticky membranes. An experiment was designed wherein 2 samplers were operated simultaneously above the forest canopy for 96 hours. One sampler contained untreated membranes as described above while the other contained similar membranes coated with a thin layer of Apiezon L, a hydrocarbon grease previously used by Berg (1976). The atmospheric conditions during this experiment were characterized by low relative humidities (< 50%) and strong, persistent westerly winds. These conditions should have enhanced the possibility of particle bounce because of the relatively high suspended loads and

significant large particle fractions associated with turbulent winds, in addition to the low humidities (Winkler, 1974). The samples were analyzed directly by neutron activation analysis, primarily for aluminum, using the methods described in Bate et al. (1976). This element was chosen because of its ubiquity in both soil dust and fly ash, its tendency to occur on larger particles, and its low density, all characteristics conducive to increased particle bounce. The results of the experiment may be represented by the uncoated/coated impaction plate aluminum concentration ratios for each particle size class as follows:

0.94 (8.2 μm , aerodynamic diameter), 0.84 (5.4 μm), 1.09
(3.8 μm), 0.86 (2.4 μm), 1.15 (1.2 μm), 1.0 (0.76 μm).

This data suggests a somewhat lower collection efficiency for the large particle stages with uncoated slides and somewhat higher collection efficiency for smaller particle stages with uncoated slides. Thus there is some evidence of particle bounce, but these 10 to 15% differences were not judged sufficient to sacrifice the solubility experiments by using the treated surfaces. In addition the major experimental work with the impactors was performed during the summer months when the mean relative humidity ranged from 65 to 90%, values conducive to enhanced particle retention by impaction surfaces, especially for the water soluble fraction of aerosols (Winkler, 1974).

Comparability of Sampling Techniques

The overall reproducibility of the sampling plus analytical techniques was determined by two methods. The air concentration determined by analysis of the total air filter was compared with the sum of the impactor stages. These values are summarized in Table 2 as the ratio of the sum of the impactor stages to the total aerosol concentrations for each experiment. Although for any given element in any given sampling period the sum of the impactor stages can either under- or overestimate the concentration measured by the total filter, the ratios of these values show an overall average close to 1 for the total suspended particulate load (TSP), SO_4^{2-} , Mn, and Pb. A similar agreement was recently reported by Lawson and Winchester (1978) for the major aerosol constituents S, K, Fe, and Ca, although such comparisons are not routinely reported in the literature. However, the elements Cd and Zn show a tendency toward concentration overestimates by the sum of the Anderson stages relative to the total filter, although there was not a consistent bias such as might be indicative of a systematic contamination. For this reason the impactor data will be used primarily as an indication of the relative size distribution of each element, the total filter data being considered a better measure of the air concentration.

The reproducibility of replicate impactor runs was determined on two occasions. However, more than simple reproducibility was actually assessed. Immediately prior to the aerosol experiments a series of papers appeared in the literature pertaining to the large particle collection efficiency of the standard 8 stage Anderson impactor

Table 2. Comparison of total air concentrations determined from the sum of the individual impactor stage concentrations and from the total aerosol filter sample.

Sample	$\frac{B}{1}$ (concentration per impactor stage)/total aerosol filter concentration)					
	TSP ^a	SO ₄ ⁼	Cd	Mn	Pb	Zn
W1	1.2	1.1	2.1	0.3	0.9	1.6
2	1.2	0.9	1.1	2.1	0.8	1.3
3	0.8	0.8	1.1	0.6	0.8	1.3
4	0.7	0.7	1.0	0.6	0.7	2.3
5	0.7	0.7	1.6	1.1	0.8	2.2
6	1.3	1.1	1.6	0.6	1.2	1.6
7	0.9	1.6	2.3	0.8	1.7	3.2
8	0.7	1.2	0.3	0.8	1.0	1.0
9	1.0	1.4	2.9	0.5	0.8	1.0
10	-	-	-	-	-	-
11	1.0	1.0	1.5	0.7	0.7	1.5
11M	0.9	0.8	1.3	0.5	0.6	1.5
12	0.7	0.8	2.1	0.8	0.6	1.2
12M	0.7	0.8	2.1	0.8	0.7	1.3
Mean	0.9	1.0	1.6	0.8	0.9	1.6
Standard Error	0.1	0.1	0.2	0.1	0.1	0.2

^aTotal suspended particulates.

(Wedding et al., 1977; McFarland, 1977). The basic conclusion of these authors was that the standard impactor operating under certain conditions was subject to low collection efficiencies ($\sim 2\%$) for relatively large particles ($> 5 \mu\text{m}$). Our initial contact with the Anderson Corporation ultimately resulted in procurement of modified (based on the suggestions of Wedding et al., 1977) upper impaction stages, impaction plates, and all-weather sampling inlets for two impactors, but not until the final weeks of our experiments. The new samplers were outfitted with the usual impaction surfaces and operated simultaneously with standard impactors during the final two sampling periods (W11, 12). The results of these 4 impactor runs are summarized in Figure 3, which illustrates the concentration ratio for each element calculated from the sum of the impaction stages (standard/modified), and the relative particle size distributions in each sample (percent of total concentration found in each size class). In general there were no clear trends in the data suggesting more efficient collection by either sampler. The concentration ratios during W11 were all > 1 except for Zn (≈ 1), indicating that the standard impactor actually collected more material. For TSP the ratio for experiment W11 was 1.07 supporting the conclusion. For W12 all the ratios were ≈ 1 (Cd, Pb, $\text{SO}_4^{=}$) or < 1 (Mn, Zn) suggesting a somewhat greater trace element collection by the modified sampler. However the TSP ratio was > 1 , as during W11. Thus, it is more likely that the differences in absolute collection between the two samples (generally $\pm 15\%$) is related as much to analytical precision as to sampler reproducibility.

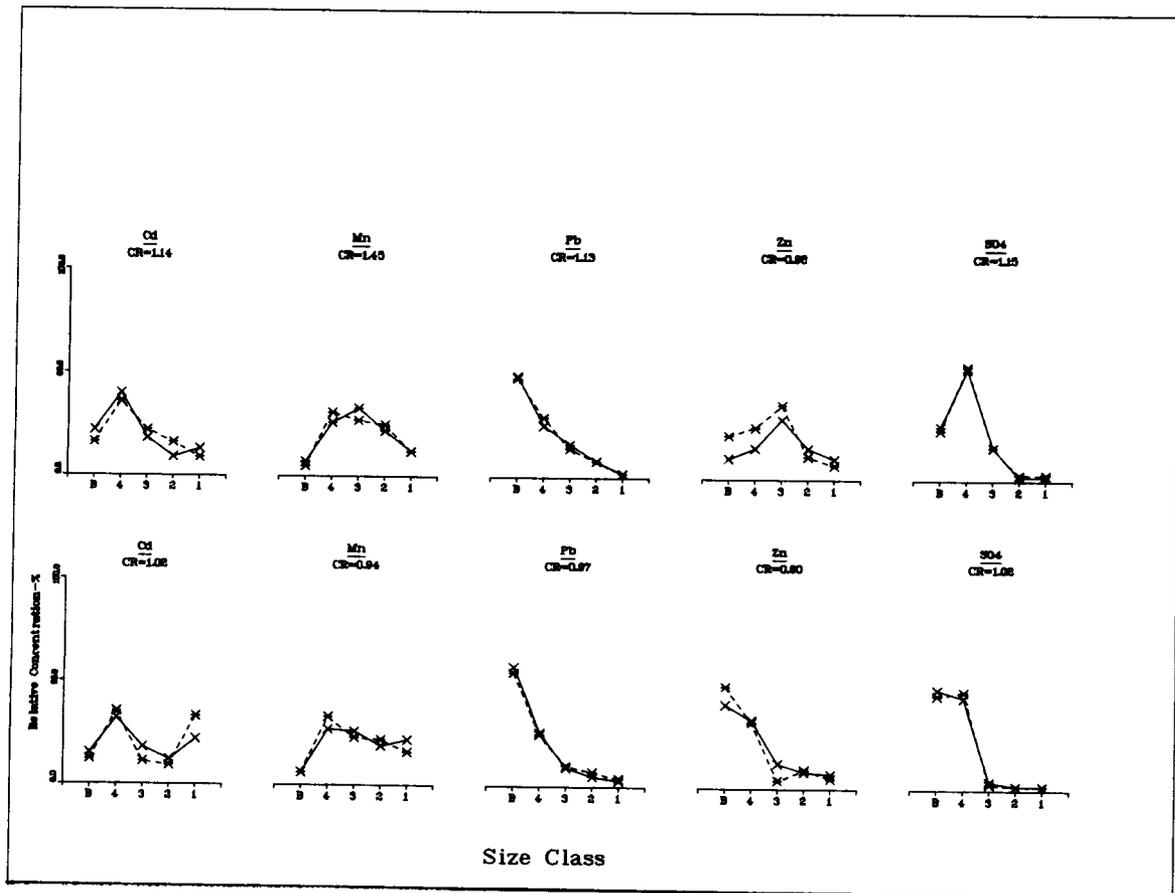


Fig. 3. Comparison of total air concentrations and relative concentrations in five size classes of the available fraction (water soluble plus dilute acid leachable) of several elements in aerosols collected simultaneously with a standard (*, dashed line) and a modified (x, solid line) Andersen impactor. Relative concentration is expressed as percent of the element collected on any one stage with respect to the total quantity of the element collected on all stages (i.e., $[\Delta C \cdot 100 / \Sigma C] / \Delta d_p$). Particle size classes are approximated by the following aerodynamic diameters (assuming a 50% impaction efficiency): B, $< 0.44 \mu\text{m}$; 4, $0.44 \mu\text{m}$; 3, $1.1 \mu\text{m}$; 2, $3.4 \mu\text{m}$; 1, $> 7.2 \mu\text{m}$. CR = concentration ratio = sum of the impactor stage concentrations for the standard Andersen divided by the sum of the impactor stage concentrations for the modified Andersen impactor. The upper 5 plots are for data collected during experimental period W11; the lower 5 plots are for data collected during W12.

The agreement between the particle size distributions determined from each sampler was reasonable as indicated in Figure 3. If the modified sampler does collect aerosols in the 5 μm size range with a considerably greater efficiency than the standard impactor, one would have expected to see relatively higher concentrations of some elements in size class 1 (impaction stages 0 + 1, aerodynamic diameter $> \sim 7 \mu\text{m}$) and somewhat lower concentrations on the succeeding stages. This trend was illustrated to some extent by the Cd and Zn data during W11 and by Mn and $\text{SO}_4^=$ during W12, in that size class 1 and sometimes class 2 exhibited higher relative concentrations in the modified impactor compared to the standard model. However it is apparent that beyond the initial 2 size classes the trends for each element are complex. For Cd during W11 the material gained by the increased efficiency of size class 1 of the modified impactor appears to have been collected in size classes 2 + 3 by the standard impactor. For Zn during W11 classes 1 + 2 of the modified collector retained material apparently collected in size class 3 of the standard sampler. For Mn during W12 the material collected in size class 1 of the modified samples was collected in size class 2 of the standard sampler, while for $\text{SO}_4^=$ during W12 the modified impactor collected relatively more material in classes 1, 2, and 3 but relatively less in classes 4 and B. Thus there were no consistent differences for any one element and it is possible that the minor differences seen are related to sampling and analytical reproducibility and not the result of sampler design differences. Of most importance from this experiment was the fact that replication between duplicate particle size collections and analyses was sufficient

to indicate that differences in size distributions on the order of 20% or more between sampling periods can be distinguished using the methods employed here.

Results and Discussion

General Atmospheric Conditions and Regional Air Quality

The general air quality and weather characteristics of the periods of aerosol sampling during this study are summarized in Table 3. Since it was the intent of these experiments to relate aerosol chemistry and size distributions to the chemistry and deposition rates of particles removed by both wet and dry processes it is informative to consider the sampling periods in terms of their general meteorologic and air quality characteristics. As anticipated, intensive sampling during the summer months resulted in a variety of such conditions being encountered. Three parameters are useful in characterizing these periods according to atmospheric conditions. Three parameters are quantity and duration of precipitation, which are also generally related to atmospheric stability, and wind direction frequency. Data relating to precipitation characteristics was taken from the 5 site, continuously recording rain gauge network at Walker Branch Watershed (Chapter V), as well as from a recording wetness sensor operated at the sample collection site (described in a following section and in Chapter IV). The frequency distribution of wind speed and direction was determined from data collected at a 110 m meteorological tower located ~ 10 km WSW of the watershed. Observations at the tower included a continuous record of wind speed and direction at 10 m and 110 m heights, and are

Table 3. Air quality and atmospheric conditions during the study period

	Experimental period												
	W1	W2	W3	W4	W5	W6	W7	W9	W11	W12			
GENERAL													
Dates	5/9-16/77	5/16-20/77	5/30-6/6/77	6/6-13/77	6/20-27/77	7/12-18/77	7/18-22/77	8/11-17/77	9/12-19/77	10/12-17/77			
Duration (days)	6.94	4.17	7.0	6.92	7.0	6.0	4.0	5.95	6.94	4.99			
AIR QUALITY CONDITIONS													
Measured TSP at MBW ($\mu\text{g}/\text{m}^3$)	45.5	64.0	38.1	31.4	26.0	36.3	31.5	28.9	23.6	23.0			
Fine particle contribution to TSP ^a (%)	32	24	34	51	11	21	24	34	24	32			
MMD ^b of TSP (μm)	2.2	0.9	0.6	0.5	0.9	0.6	0.6	0.6	0.7	0.6			
Photooxidant violations ^c (%)	19	23	30	16	5	24	10	10	6	0			
ATMOSPHERIC CONDITIONS													
Precipitation amount (cm)	0.00	0.13	0.30	1.50	11.80	0.20	0.20	1.40	8.36	0.38			
Number of events	0	1	1	2	7	1	1	5	6	1			
Precipitation duration (hr)	0	0.17	0.50	0.42	17.25	0.20	0.42	14.33	15.0	2.0			
Relative time of event ^d													
First event	-	0.6	0.2	0.02	0.06	0.01	0.8	0.5	0.1	0.7			
Last event	-	-	-	0.9	0.9	-	-	1.0	0.9	-			
Wind direction and frequency (%)													
Primary	ENE-24	SW-13	WSW-20	NNW-15	SW-27	ENE-23	SW-33	SW-21	ESE-21	SW-16			
Secondary	E-16	ENE-12	SW-15	SW-13	WSW-24	NE-13	WSW-19	WSW-16	SW-16	N-14			
Frequency (%) of winds from:													
KSP ^e	12	22	42	25	51	15	57	40	30	25			
BRSP + Y12SP ^f	37	18	12	20	8	36	8	9	8	13			
Other	51	60	46	55	41	49	36	51	62	62			
Atmospheric stability ^g (%)	47	51	52	40	40	41	45	36	39	26			
Air stagnation ^h (%)	29	100	0	0	0	33	0	0	0	40			
Relative Humidity ⁱ (%)	65	76	71	69	85	79	82	87	90	72			

^aFine particles ≤ 0.44 TSP = total suspended particulate load.

^bMMD = mass median diameter.

^cPercent of total sampling period during which $[\text{O}_3] \geq 0.08\text{ppm}$.

^dTime from start of sampling to initiation of precipitation \div duration of sampling.

^eKSP = Kingston Power Plant.

^fBRSP, Y12SP = Bull Run Power Plant and Y-12 Steam Plant.

^gPercent of time stable conditions (classes D, E, and F) prevailed.

^hPercent of time air stagnation conditions were recorded.

ⁱHourly mean.

used to calculate mean hourly wind speed and direction and standard deviation of the hourly mean wind direction. The data is logged, coded, verified, and summarized by the Tennessee Valley Authority Air Quality Branch, Muscle Shoals, Alabama. Frequency plots of wind speed and direction were produced for each of the 10 experimental periods, as illustrated in Figures 4 and 5 in the form of windroses. Each experimental period was then classified according to the frequency of winds from the direction of any of the local coal fired plants (located in two general directions from the watershed, as illustrated in Figure 1, Chapter II), or from directions not directly influenced by local sources.

A summary by similar precipitation characteristics is presented in Table 4. Two periods were characterized by considerably rainfall volumes (W5 and 11, both > 8 cm), two by moderate amounts (W4 and 9, ≤ 1.5 cm) and the remainder by traces of rain (0.24 ± 0.10 cm). The wettest periods were also characterized by multiple events and long durations of continuous rain, $\sim 10\%$ of the total sample period. In addition, the precipitation began near the start of each period ($< 10\%$ of the time since initiation of sampling) and continued, at least intermittently, until the end of the sampling period (within 10% of the time before sampling completion). In general the mean relative humidity during these periods reflected these conditions.

Atmospheric stability was also related to the precipitation characteristics as indicated by the frequency of occurrence of stable or unstable conditions. For purposes of simplification the six standard stability classes were grouped into two general types of

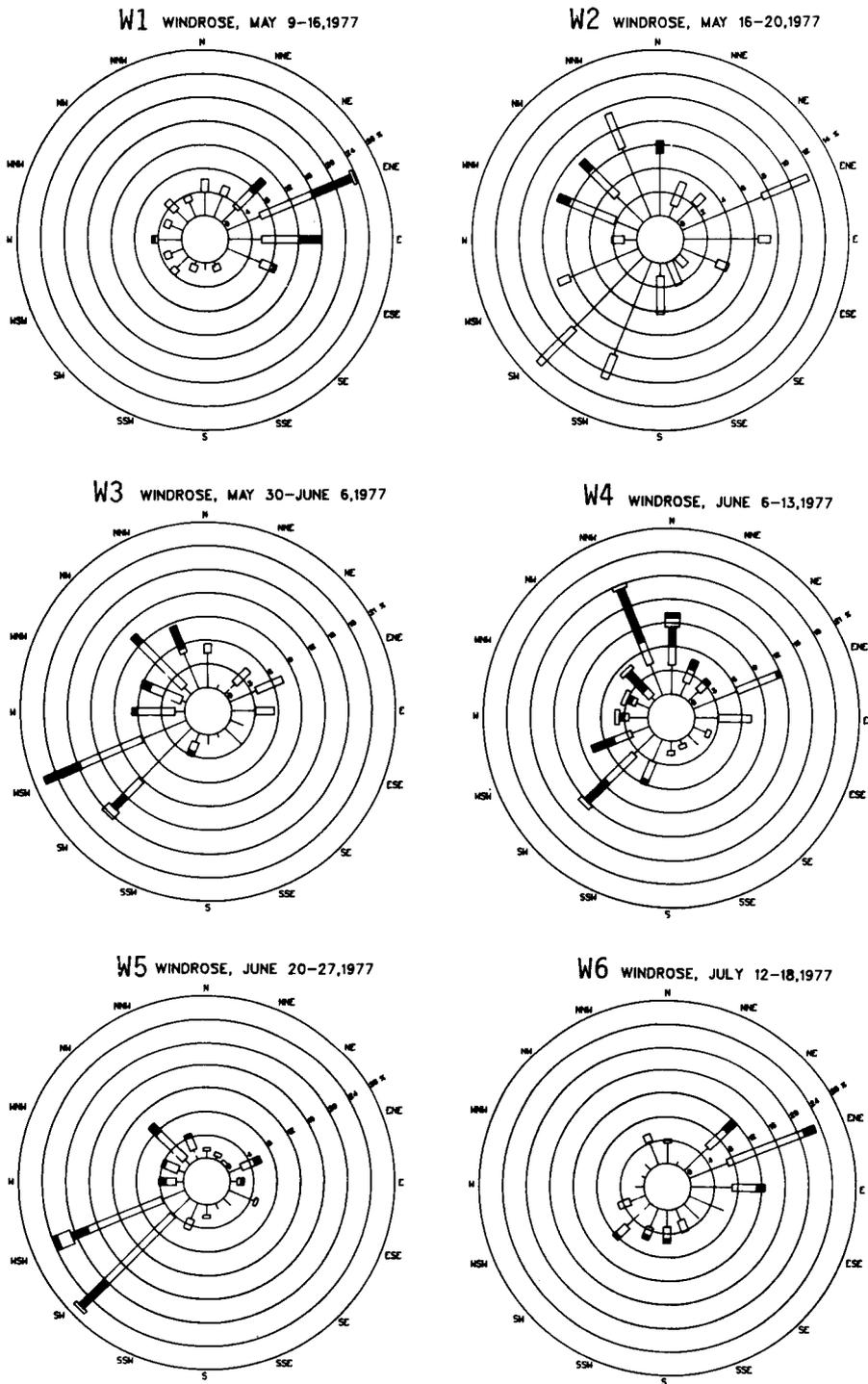


Fig. 4. Windroses for experimental periods W1-W6. See Figure 5 for key to scale.

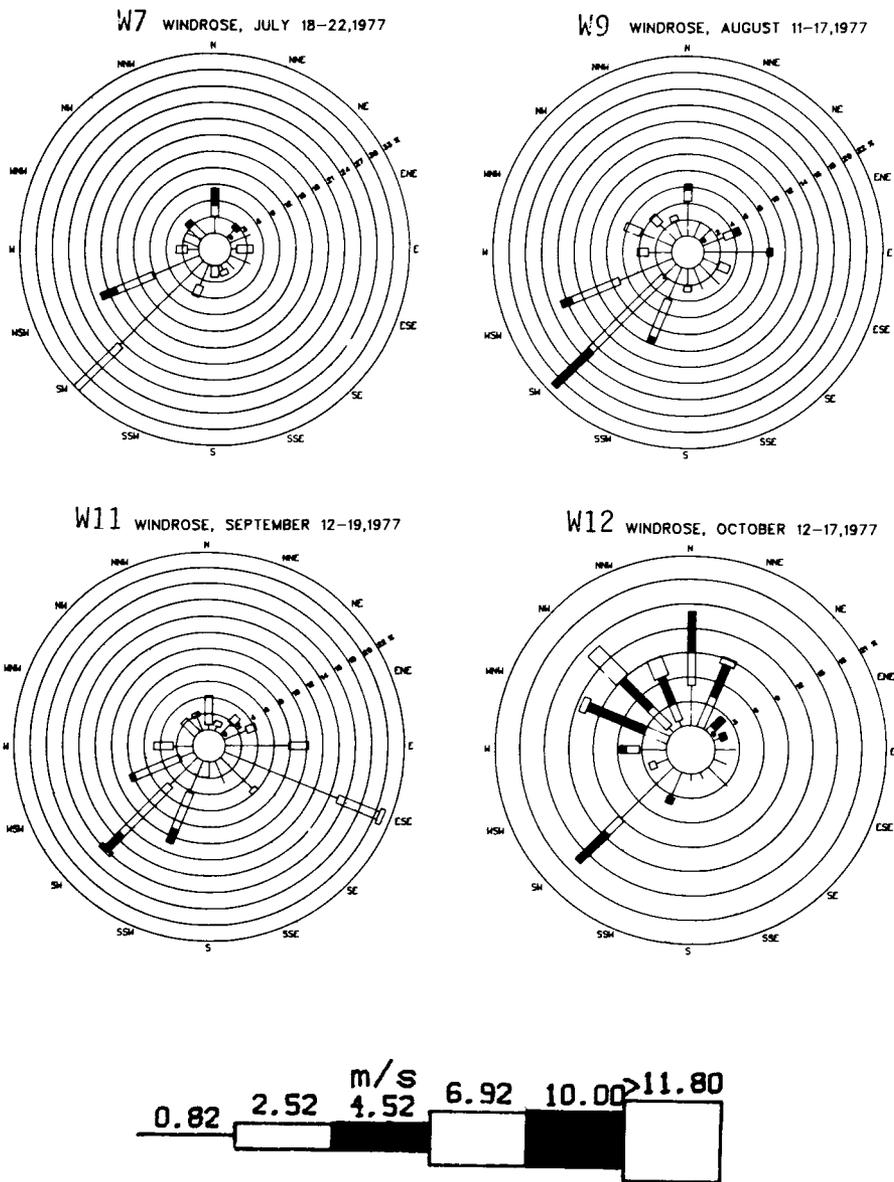


Fig. 5. Windroses for experimental periods W7, W9, W11, W12.

Table 4. Characteristics of experimental periods grouped by precipitation amount and duration. Shown are mean values (or ranges) of each parameter for each grouping.

Period	Precipitation amount (cm)	Precipitation duration (%)	Number of precipitation events	Relative humidity (%)	Frequency of stable conditions (%)	TSP ($\mu\text{g}/\text{m}^3$)	Fraction of fines (%)	MMD (μ)	Frequency of photooxidant concentration violations (%)
W5+11	10	10	6-7	88	39	25	17	0.8	6
W4+9	1.4	5	2-5	78	38	30	42	0.6	13
W1, 2, 3, 6, 7, & 12	0.2	0.4	0-1	74	48	39	28	0.9	21

conditions, unstable (Classes A, B, C) and stable (D, E, and F). The classes were determined from the standard deviation of the mean hourly wind direction (Slade, 1968).

The rain volume and stability conditions were reflected to some degree by the general air quality. The least stable, highest precipitation periods were characterized by the lowest TSP and lowest frequency of photooxidant concentration violations. Both of these parameters increased consistently as rain volume and duration decreased. These observations relate to the increased atmospheric mixing and dispersion during unstable conditions and to the ability of precipitation to scavenge particles and gases from the atmosphere. Wet conditions also result in a general decrease in ground level dust resuspension.

Classifying the periods by air flow patterns revealed few clear relationships. The periods were grouped by frequency of winds from any directions not influenced by the three local power plants. This method resulted in 3 classes: high (W2, 4, 11; $x = 60\%$); moderate (W1, 6, 9; $x = 50\%$); and low (W3, 5, 7; $x = 40\%$) frequency of winds from quadrants other than those influenced by the local sources. An effect of wind direction on TSP was not apparent, the mean TSP for each group ranging between 37 - 40 $\mu\text{g}/\text{m}^3$. Wind direction did not influence the frequency of photo-oxidant conditions, with mean values ranging from 15 to 18%.

Concentrations and Particle Size Distributions
of Available Metal and Sulfate Fraction:
Relationships to Atmospheric Conditions

The air concentration and relative size distribution data for the available element fractions of Cd, Mn, Pb, Zn, and $\text{SO}_4^{=}$ in aerosols collected during each of the 10 sampling periods is summarized in Table 5. For the initial purpose of comparing the concentrations measured at WBW with those determined for other areas, the arithmetic mean and standard deviation, the geometric mean and standard deviation (the log normal distribution of trace elements in aerosols is well established; e.g., see Lee et al., 1975), and the range of concentrations for each component in the total aerosol fraction were calculated and are presented in Table 6. It is apparent that sulfate forms a significant fraction of the total aerosol composition, comprising $\sim 25\%$ of the material by weight. Of the remaining elements only Pb approaches 1% of the aerosol composition (0.33%) followed by Mn and Zn (0.03%) and Cd (0.0004%). These values are in excellent agreement with those determined by an earlier neutron activation analysis (NAA) of aerosols collected in WBW (Andren and Lindberg, 1977) with the exception of Cd (0.01% in the 1977 paper). This difference relates primarily to the relatively poor sensitivity of NAA for Cd, leading to a possible overestimate due to the reporting of "less than" values. Interestingly, the earlier multielement approach accounted for an additional 8% of the aerosol composition attributed to Al, Fe, Cl, Ca, and Na, and another 1% due to 28 trace constituents. Combined with the data in Table 6 this leaves $\sim 65\%$ of the aerosol which must be

Table 5. Summary of "available" metal^a and sulfate air concentrations in WBW during the intensive sampling experiments. Shown are the total filter concentrations in mass per unit volume and the relative particle size distributions in percent of total concentration per impactor stage.

Experimental period	Impactor stage	Aerodynamic diameter ^b (µm)	TSP	Cd	Mn	Pb	Zn	SO ₄ ²⁻
W1	total		45.5 µg/m ³	0.12 ng/m ³	10.5 ng/m ³	92 ng/m ³	3.5 ng/m ³	11.8 µg/m ³
	1	>8.0	17%	18%	20%	2%	14	2
	2	3.7	25	33	36	7	16	2
	3	1.2	12	18	21	8	19	3
	4	0.50	13	18	11	16	18	22
	B	<0.50	32	13	11	67	35	71
W2	total		64.0 µg/m ³	0.24 ng/m ³	2.0 ng/m ³	170 ng/m ³	7.4 ng/m ³	18.0 µg/m ³
	1	>7.8	18%	6%	22%	1%	8%	1%
	2	3.7	17	16	27	4	7	2
	3	1.2	12	23	22	8	11	8
	4	0.48	30	10	13	33	8	48
	B	<0.48	24	44	16	53	66	42
W3	total		38.1 µg/m ³	0.13 ng/m ³	11.4 ng/m ³	85 ng/m ³	3.4 ng/m ³	10.7 µg/m ³
	1	>7.2	14%	8%	8%	1%	1%	2%
	2	3.3	18	11	28	7	1	2
	3	1.1	7	13	23	11	18	6
	4	0.44	27	28	11	31	49	47
	B	<0.44	34	40	30	49	32	43
W4	total		31.4 µg/m ³	0.16 ng/m ³	18.0 ng/m ³	78 ng/m ³	2.9 ng/m ³	6.88 µg/m ³
	1	>7.8	10%	11%	45%	2%	2%	1
	2	3.7	13	25	14	4	6	1
	3	1.2	8	6	16	8	31	4
	4	0.48	17	7	16	20	30	23
	B	<0.48	51	52	8	66	31	72
W5	total		26.0 µg/m ³	0.063 ng/m ³	7.2 ng/m ³	63 ng/m ³	2.9 ng/m ³	6.60 µg/m ³
	1	>7.0	6%	25%	15%	2%	3%	2%
	2	3.3	18	16	31	7	22	3
	3	1.1	21	24	39	14	22	12
	4	0.43	43	24	11	46	35	64
	B	<0.43	11	10	4	31	18	19
W6	total		36.3 µg/m ³	0.10 ng/m ³	10.0 ng/m ³	97 ng/m ³	3.7 ng/m ³	11.0 µg/m ³
	1	>7.8	9%	19%	20%	1%	3%	2%
	2	3.7	16	19	31	5	14	3
	3	1.2	11	10	27	11	14	6
	4	0.49	45	27	15	30	25	61
	B	<0.49	21	25	6	53	44	28
W7	total		31.5 µg/m ³	0.05 ng/m ³	13.0 ng/m ³	98 ng/m ³	3.2 ng/m ³	7.00 µg/m ³
	1	>7.1	11%	13%	17%	1%	0%	2%
	2	3.3	14	6	30	6	23	2
	3	1.1	9	6	17	5	20	4
	4	0.44	43	18	13	15	19	39
	B	<0.44	24	57	23	72	39	52
W9	total		28.9 µg/m ³	0.22 ng/m ³	12.0 ng/m ³	130 ng/m ³	226 ng/m ³	5.10 µg/m ³
	1	>7.8	8%	13%	21%	1%	17%	2%
	2	3.7	14	27	23	4	24	2
	3	1.2	11	19	24	9	10	5
	4	0.48	33	26	23	20	32	52
	B	<0.48	34	16	9	65	17	38
W11	total		23.6 µg/m ³	0.29 ng/m ³	9.8 ng/m ³	172 ng/m ³	32 ng/m ³	7.1 µg/m ³
	1	>7.3	7%	9%	12%	2%	7%	3%
	2	3.4	12	16	25	8	11	3
	3	1.1	16	22	27	14	36	16
	4	0.45	41	36	31	29	25	55
	B	<0.45	24	16	5	48	21	24
W12	total		23.0 µg/m ³	0.29 ng/m ³	9.5 ng/m ³	138 ng/m ³	30 ng/m ³	5.3 µg/m ³
	1	>7.1	16%	33%	16%	4%	5%	2%
	2	3.3	17	9	22	7	9	2
	3	1.1	6	11	23	10	4	3
	4	0.44	29	35	33	25	32	47
	B	<0.44	32	12	6	55	49	45

^a"Available" metal = distilled leachable plus dilute acid leachable, as defined in text.

^bAssuming a 50% particle collection efficiency, data supplied by Andersen 2000, Inc.

Table 6. Statistical summary of air concentration data (10 sample periods, May to October, 1977), for leachable sulfate and available metals in the total aerosol.

Component	Arithmetic mean concentration	Standard deviation	Range	Geometric mean concentration	Geometric standard deviation
TSP	34.8 $\mu\text{g}/\text{m}^3$	12.4	23.0-64.0	33.2	1.4
Cd	0.17 ng/m^3	0.09	0.05-0.29	0.14	1.8
Mn	9.4 ng/m^3	5.1	2.0-18.0	9.2	1.8
Pb	112 ng/m^3	38	63-172	107	1.4
Zn	34.6 ng/m^3	72.7	2.9-(226) ^a	8.5	4.4
SO ₄ ⁻	9.0 $\mu\text{g}/\text{m}^3$	4.0	5.1-18.0	8.3	1.5

^aThe value 226 ng/m^3 was 7 times greater than the next highest Zn concentration.

attributed primarily to the light elements H, C, N, O, and Si (Dams et al., 1975).

In comparing the elemental concentrations of aerosols in WBW no attempt will be made at an exhaustive literature survey of aerosol composition, this having been done elsewhere (Harris, 1976). Rather, representative concentrations from various airshed types are summarized in Table 7 along with our data (keep in mind that the WBW concentrations are for the available element fractions only, these being comparable to total element air concentrations for Cd, Mn, and $\text{SO}_4^=$, but underestimates for Pb and Zn, as discussed earlier). The atmospheric concentrations at WBW are what might be expected given the general location of the area, although the influence of the three local coal fired power plants is not readily apparent. The concentration of Cd is considerably below that seen for several other rural and urban areas. In fact the concentration range of Cd at WBW falls within that reported by Duce et al. (1975) at remote locations in the N. Atlantic. A similar situation exists for both Mn and Zn with WBW concentrations more comparable to remote and rural locations than urban areas. The levels of both Pb and $\text{SO}_4^=$ in WBW air are considerably enriched over those measured at remote locations but are similar to concentrations reported for rural areas.

From this brief comparison it is clear that any general effect of the three local coal fired plants on WBW air quality is not manifested in the elemental concentration data in a straightforward manner. This is an interesting conclusion in light of the fact that these elements are believed to represent various sources to the WBW aerosol. For

Table 7. Summary of representative aerosol composition studies at diverse locations

Location	Airshed type	Concentrations (ng/m ³)				
		Cd	Mn	Pb	Zn	S
South Pole ^a	remote	-	0.01	0.63	0.03	-
Bolivia ^b	remote	-	0.8-3.4	3.6-7.1	1.2-5.3	65-182
White Mtn., CA ^c	remote	-	-	8.0	-	-
Squaw Mtn., CO ^d	remote	-	BD	BD	BD	121-429
Gulf of Mexico ^e	marine	-	-	-	-	1730
N. Atlantic ^f	marine	0.003-0.62	0.05-5.4	0.10-64	0.3-27	-
Chadron, NB ^g	rural	0.57	5.7	45	16	-
New York State ^h	rural	-	-	-	-	300-24,900
Belgium ⁱ	rural	6-16	-	212-594	218-799	-
WBW ^j	rural to suburban	0.14	9.2	107	8.5	3000
Pasadena, CA ^k	suburban	-	-	2140	76	-
Cleveland, OH ^l	suburban	1.6	66	451	264	~17,000
New York State ^h	urban	-	-	-	-	500-16,700
Cleveland, OH ^l	urban	3.9	148	759	413	~25,000
St. Louis ^m	urban	-	-	~300	~150	~2500
Belgium ⁱ	industrial	14-50	-	791-975	618-3054	-
N. W. Indiana ⁿ	industrial	-	63-390	400-3700	100-1540	-

^aZoller et al, 1974.

^bAdams et al, 1977.

^cChow et al, 1972.

^dLawson and Winchester, 1978. BD described as "less than a few ng/m³ by the authors.

^eBerg, 1976.

^fDuce et al, 1975.

^gStruempfer, 1975.

^hGalvin et al, 1978.

ⁱKretzschmar et al, 1977.

^jThis study (mean values). Metal concentrations are for the available fraction only, not total. Sulfur concentration is for the leachable sulfate fraction (expressed as S).

^kHammerle and Pierson, 1975.

^lKing et al, 1976.

^mWinchester et al, 1974.

ⁿHarrison et al, 1971.

example, earlier work has suggested soils as the primary source of Mn, automobile exhaust as the Pb source, and coal combustion as the primary SO_4^- source and an important Zn source, while Cd could not readily be attributed to any single source (Andren et al., 1975; Lindberg et al., 1975; Andren and Lindberg, 1977).

The relative size distribution of these elements in the atmosphere has been used as an indication of source types (Eisenbud and Kneip, 1975). Elements originating indirectly from atmospheric gas-particle reactions or directly from combustion sources are generally characterized by high concentrations of small particles ($< \sim 1 \mu\text{m}$). Material introduced into the atmosphere by dispersion of surface soil dust or by industrial grinding and milling processes is generally characterized by predominance of larger particles ($> 1 \mu\text{m}$). Although the relative particle size distributions were somewhat variable from period to period (Table 5) the average elemental concentrations in each particle size class are useful as indicators of the general size distribution type characterizing any given element. Figure 6 summarizes the mean concentrations (\pm standard deviation) in each particle size class for the 10 experiments. These generalized size distributions suggest that the five constituents studied fall roughly into three categories; (1) monomodal size distribution with a maxima in the coarse particle mode represented by size classes 1 and 2 (Mn); (2) monomodal size distribution with a maxima in the fine particle mode, represented by classes 4 and B (Pb and SO_4^-); and (3) bimodal size distribution with maxima in both modes (Cd and Zn). The dominance of the coarse particle mode for Mn confirms the expectation of a surface

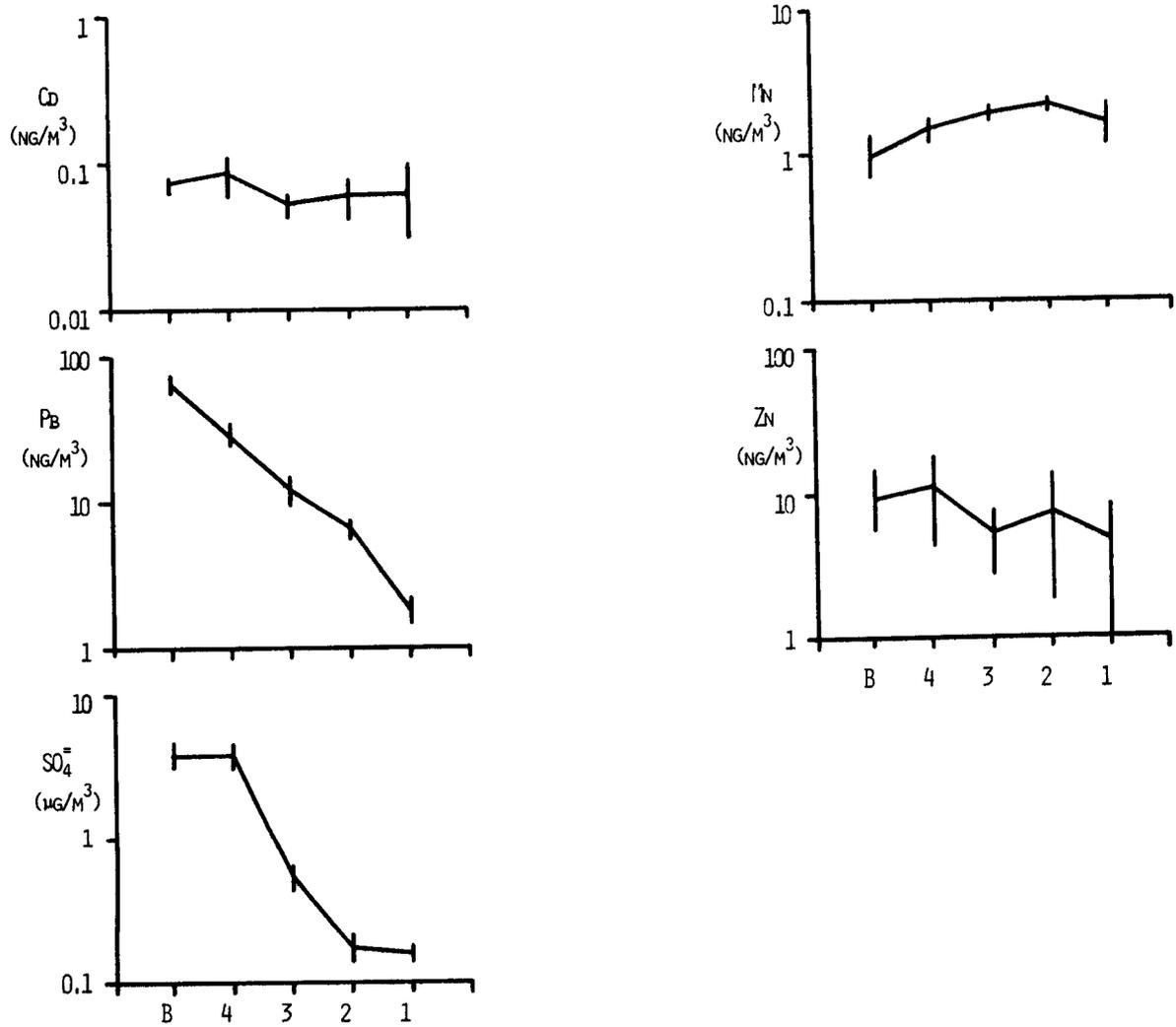


Fig. 6. Mean (\pm standard error) air concentration of the available element fraction in five particle size classes for the ten experiments. Aerodynamic diameters range from B, $< \sim 0.44 \mu\text{m}$, to 1, $> \sim 7.2 \mu\text{m}$.

soil dust source. The strong fine particle modes for Pb and $\text{SO}_4^{=}$ are expected if the primary sources of each constituent are combustion processes and/or secondary particle formation in the atmosphere. The bimodal distributions Cd and Zn suggest two general source types. Because of the co-geochemical occurrence of both elements (Rankhama and Sahama, 1950) this similarity in behavior does not seem unusual. Both elements are known to be emitted during coal combustion and ore roasting processes, resulting in primarily submicron particles (Van Hook and Shultz, 1977), and during ore grinding and automobile tire wear processes, both mechanisms resulting primarily in coarse particles (Huntzicker and Davidson, 1975). The general multimodal size distribution of aerosols has been well established (Junge, 1963; Whitby et al., 1972), while considerable published data exists confirming the size distributions of the individual elements measured in this study (e.g., see the review by Harris, 1976; also Lee, 1972; Lee et al., 1968; Martens et al, 1973; Whitby et al, 1975; Davidson, 1977).

The atmospheric concentrations of each element in 5 particle size fractions measured during the 10 periods are illustrated in Figures 7 to 9. In general these distributions conform to those of the mean concentrations just discussed. However, it is apparent from these figures that there are numerous atmospheric processes influencing the size distributions of any element during the 10 sample periods. For example, Cd deviates from a clearly bimodal distribution only during W11 and perhaps W1, while Zn exhibits other than a bimodal distribution during W3, 6, and 11. Although Cd and Zn are generally bimodally distributed, the peak concentrations don't always occur in the same

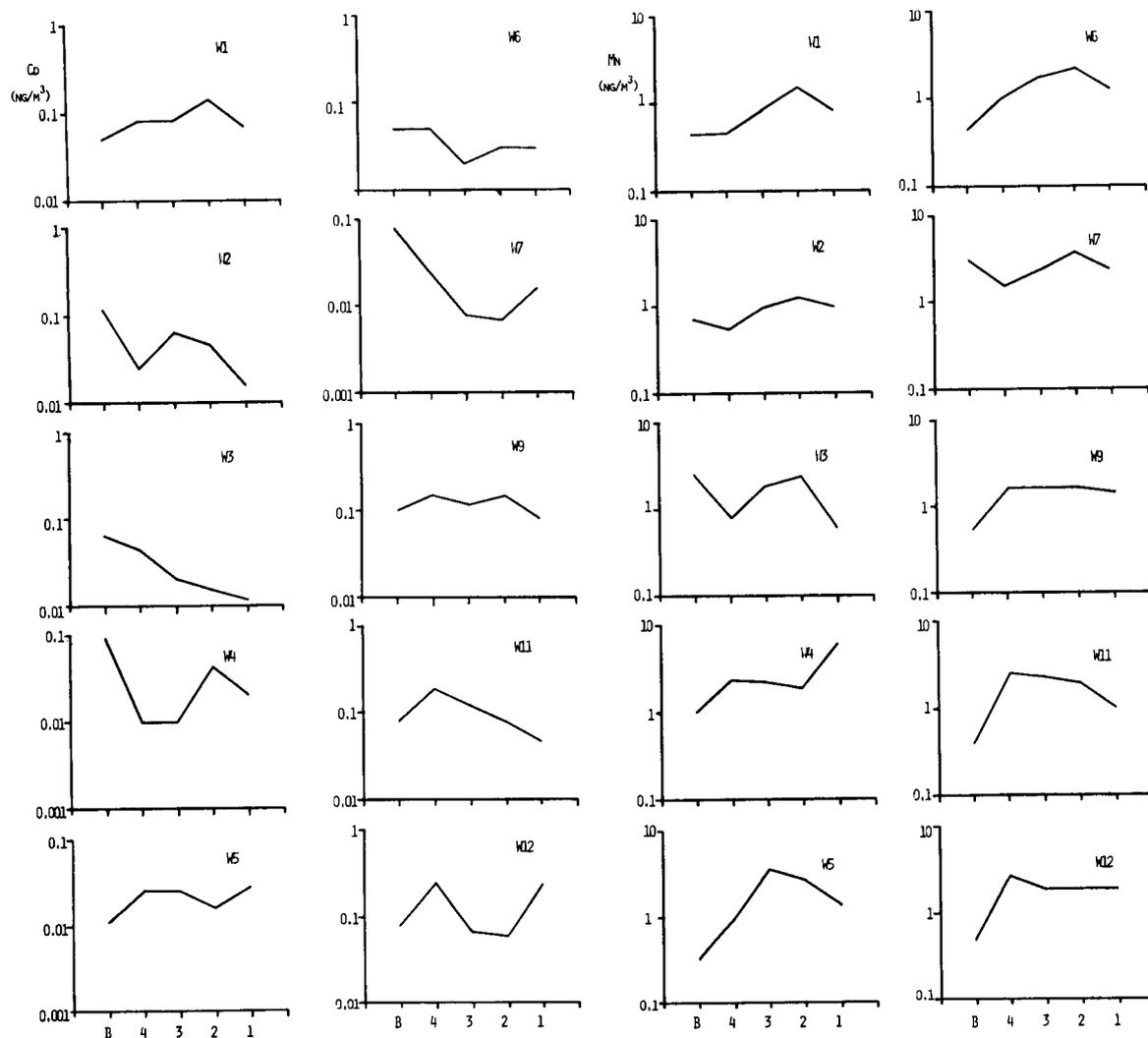


Fig. 7. Air concentration of the available element fraction of Cd (left two columns) and Mn (right two columns) in five particle size classes during each of the ten experimental periods. Aerodynamic diameters range from B, $\sim 0.44 \mu\text{m}$ to 1, $\sim 7.2 \mu\text{m}$.

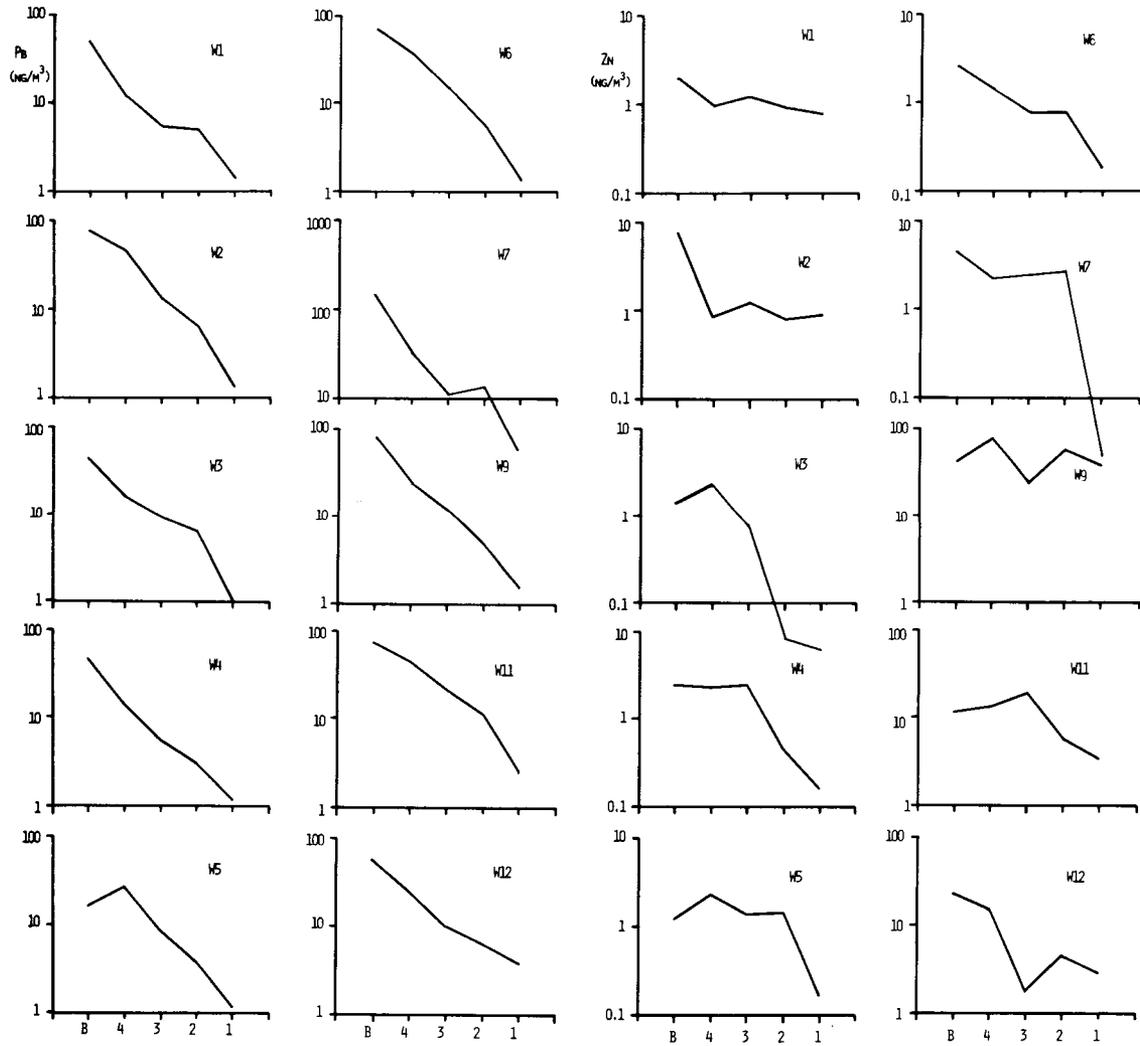


Fig. 8. Air concentration of the available element fraction of Pb (left two columns) and Zn (right two columns) in five particle size classes during each of the ten experimental periods. Aerodynamic diameters range from B, $\sim 0.44 \mu\text{m}$ to 1, $> 7.2 \mu\text{m}$.

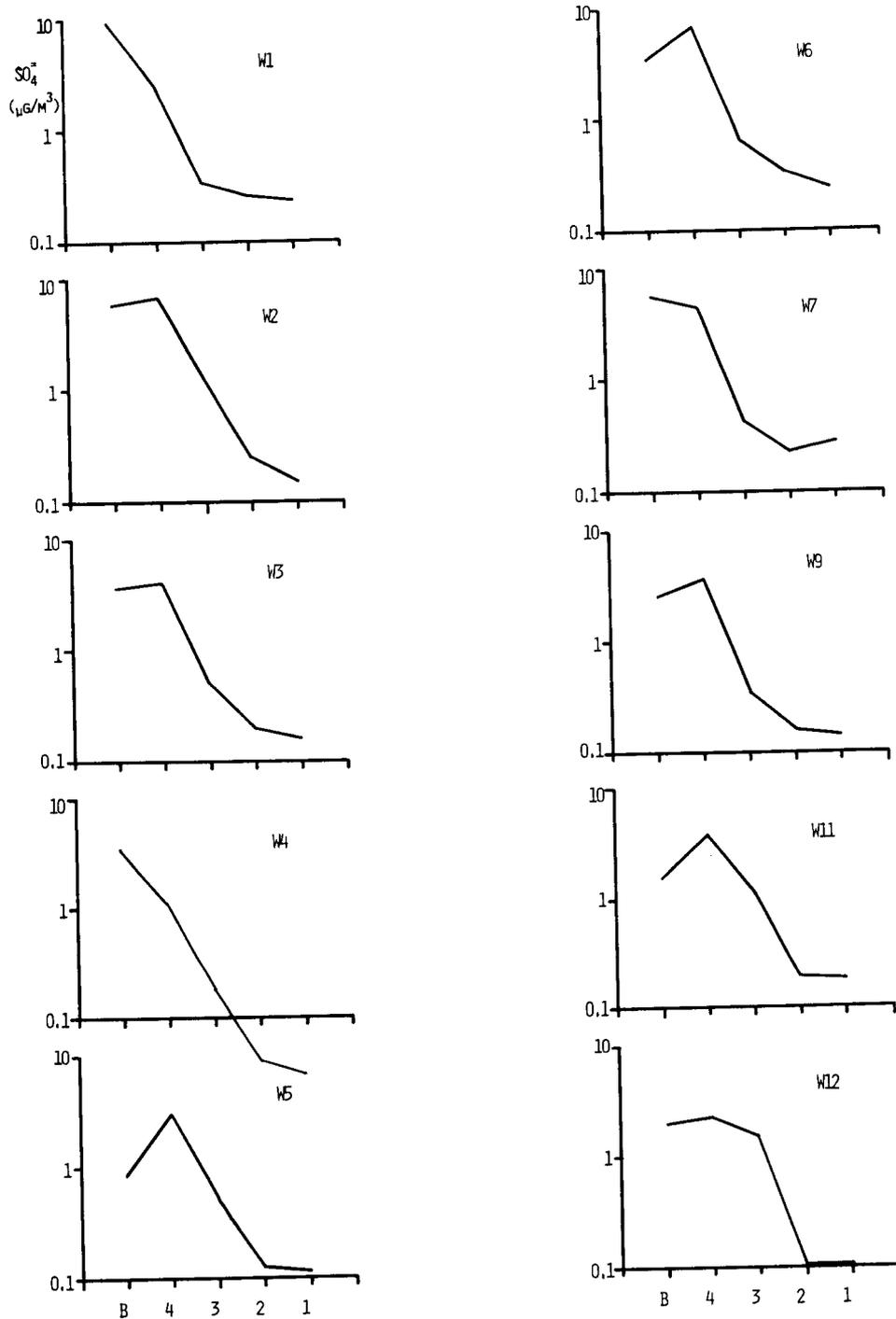


Fig. 9. Air concentration of water leachable sulfate in five particle size classes during each of the ten experimental periods. Aerodynamic diameters range from B, $\sim 0.44 \mu\text{m}$ to 1, $\sim 7.2 \mu\text{m}$.

size class, generally shifting between classes B and 4 at the low end and 2 and 1 at the high end. This suggests that, although the primary sources of Cd and Zn probably generate aerosols with a relatively constant, characteristic size distribution over the experimental period, other factors involved during aerosol aging such as gravitational sedimentation and particle coagulation also influence the size distributions at the receptor. A similar situation exists for Mn and $\text{SO}_4^{=}$, and, to a lesser extent, for Pb. Manganese is dominated by the large particle mode for 6 of the periods but also exhibits a significant small particle mode during W2, 3, 7, and 12. Sulfate is dominated by the fine particle fraction, occurring primarily in size class B during W1, 4, 7 but primarily in size class 4 during the remainder of the periods. Lead is also clearly concentrated in the smallest particle size mode for every sampling period except W5 when it occurs primarily in class 4.

Despite these variations two sampling periods exhibit interesting similarities in the particle size distributions of each element. During W5 all elements are characterized by relatively low concentrations in the smallest size class (B), primary concentration peaks generally occurring in the next larger size range (4). This period was characterized by relatively high humidities and the largest amount and longest duration of rainfall occurring during the 10 experiments (Table 3). The period also exhibited the lowest fine particle contribution to the TSP load (11%). Particle scavenging by nucleation as well as particle growth by water vapor sorption and by coagulation could account for the apparent upwards displacement in size

of the fine particle mode. In contrast during W7, all elements exhibited significant concentration peaks in size class B. This could imply a strong influence of a nearby source of fine particle emissions, a source close enough so that significant particle growth and coagulation has not occurred by the time the plume has reached the WBW area. As indicated in Table 3 this period was characterized by very little precipitation and by the highest wind frequency from the direction of the three local coal fired power plants (65%). However, the wet period W5, discussed above, exhibited a similar wind pattern, having the second highest wind frequency (59%) from the direction of these 3 power plants. This suggests that precipitation or general atmospheric moisture conditions may be a critical factor controlling the size distribution of all of these elements during this period. This point will be considered in more detail in the following discussion. The lack of any other obvious generalization again suggests that several factors control the concentrations and size distributions during any given period. These factors which include relative humidity, wind direction, atmospheric stability, and precipitation conditions do not necessarily influence the concentration and size distributions of the various elements in a similar manner. This is apparent from Figure 6.

In a further attempt to determine the role of various meteorologic factors in controlling atmospheric concentrations and size distributions, the data from Tables 3 and 5 were grouped by several classifications. For ease of comparison the data are also illustrated in Figure 10, which shows the temporal variability in rainfall amounts,

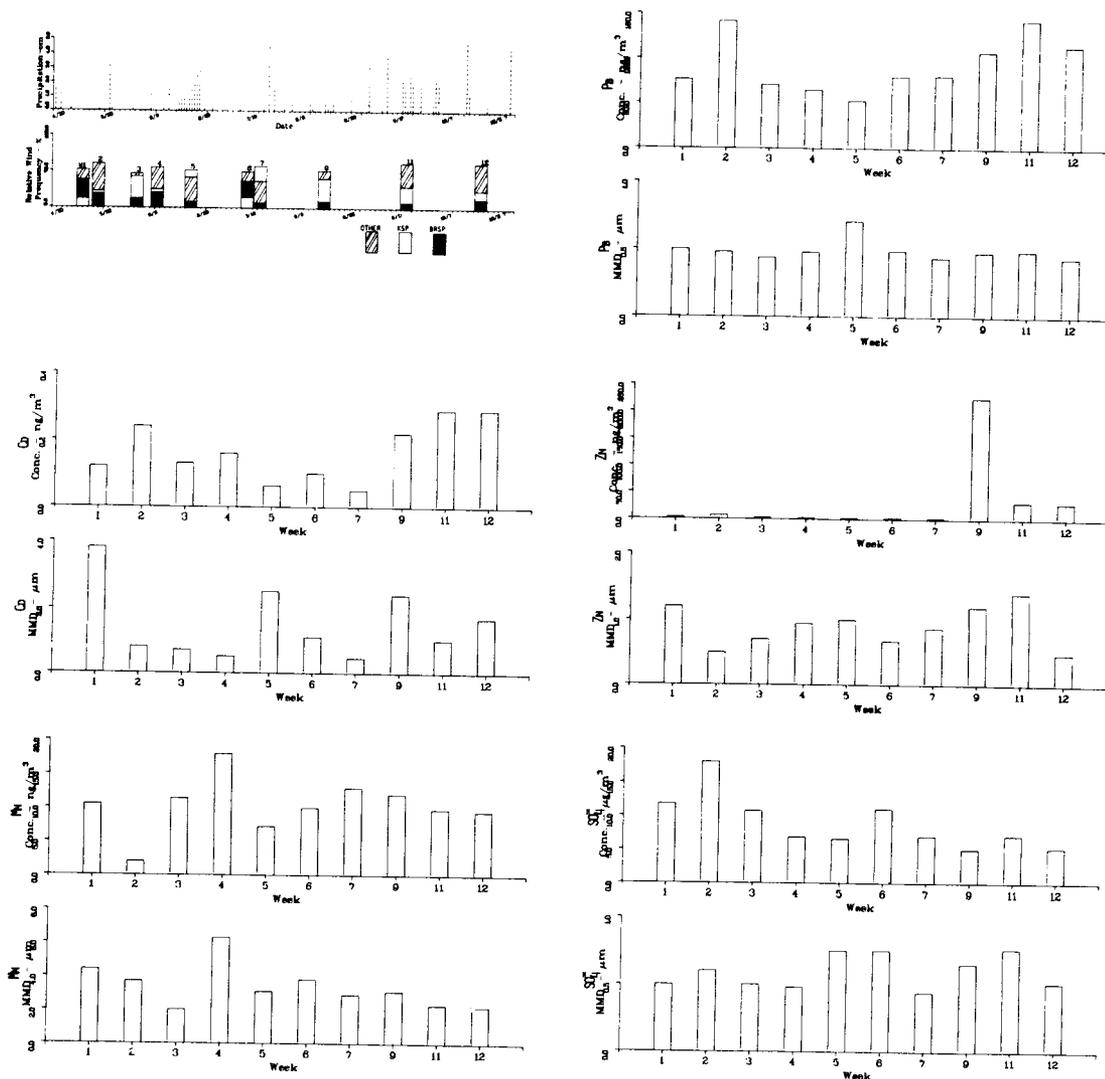


Fig. 10. Meteorological and atmospheric chemistry characteristics of the ten experimental periods during the 1977 growing season. Illustrated are the daily precipitation volumes from 4/30 to 10/30/77, the relative wind frequency during each experimental period from the direction of the local coal fired power plants (KSP = Kingston Power Plant; BRSP = Bull Run Power Plant and Y-12 Power Plant), the relative wind frequency from directions not directly influenced by the three local power plants (other), and the total air concentrations and mass median diameters (MMD) of the available fraction of Cd, Mn, Pb, Zn, and sulfate during each experimental period.

wind direction frequency, and weekly elemental air concentrations and MMD's. The data were grouped generally into 3 classifications for each atmospheric parameter, those exhibiting the highest values of a parameter (e.g., atmospheric stability), periods with moderate values, and periods with relatively low values. For each parameter this method resulted in well defined classes with little overlap in the mean values. This technique was discussed earlier for rainfall amount and duration in Table 4. For each classification the mean total air concentrations and MMD's were determined for each element.

Classification by atmospheric stability, precipitation amount and duration, and wind direction all resulted in apparent relationships with either MMD's or atmospheric concentrations. The parameter resulting in the most consistent trends in the elemental data was air stagnation. Table 8 summarizes the mean concentrations and MMD's for 3 air stagnation classifications. These classifications are based on the frequency of the issuance of regional air dispersion statements and air stagnation alerts by the National Weather Service. These statements are issued when both vertical stratification and horizontal dispersion of the atmosphere are such that particles and gases will tend to build up in concentrations in the atmosphere near ground level. Although it is difficult to determine significant differences with this limited data set, several interesting trends are apparent. For the small particle, combustion source elements Pb and SO_4^{2-} there is a general decrease in atmospheric concentration as air stagnation decreases. This is the result of increased atmospheric dilution during the periods characterized by more efficient atmospheric mixing. Interestingly the

Table 8. Classification of elemental air concentrations and mass median diameters (MMD) by air stagnation conditions. Shown are mean values (\pm SE).

Air stagnation class and value ^a (%)	Experimental periods	Parameter	Cd	Mn	Pb	Zn	SO ₄ ⁻
1 - 100	W2	concentration	0.24 ng/m ³	2 ng/m ³	170 ng/m ³	7.4 ng/m ³	18.0 µg/m ³
		MMD	0.8 µm	3.7 µm	<0.48 µm	<0.48 µm	0.6 µm
2 - 34±6	W1, 6, 12	concentration	0.17±0.06	10±0.5	109±25	12±15	9.4±3.5
		MMD	2.2±1.4	3.5±1.1	<0.48±.03	0.77±.38	0.59±0.14
3 - 0	W3, 4, 5, 7, 9, 11	concentration	0.15±.09	11.9±3.6	104±40	^b	7.2±1.8
		MMD	1.3±0.9	3.3±1.5	0.51±.10	1.02±0.25	0.60±0.14

^aClassified according to relative duration of air stagnation conditions; (in percent of total sampling period) class 1>2>3.

^b8.9±12.9 ng/m³ excluding W9 and 45±89 including W9.

air stagnation conditions had little effect on the particle size distributions, as evidenced by the similar MMD's for Pb and $\text{SO}_4^{=}$ in each class. This supports the contention made earlier that both of these elements are dominated by similar source types, each characterized by a relatively narrow size distribution at the point of emission. The generally accepted sources of Pb and $\text{SO}_4^{=}$, auto exhaust and fossil fuel combustion, conform to these size distributions (Lee et al., 1968; Gordon 1975).

The behavior of Mn during these periods supports the hypothesis of a soil source. The air concentration increases sharply as air stagnation decreases while the MMD shows relatively little change. As air stagnation decreases the chances for resuspension of surface dusts rapidly increase due to generally increasing horizontal wind speeds and increased vertical dispersion (Slade, 1968). The fact that the MMD shows little change reflects the importance of the soil source of Mn under varying degrees of atmospheric stability. Although Cd and Zn are both characterized by bimodal size distributions, they behaved differently with respect to air stagnation conditions. This difference provides some evidence of the relative importance of the small and large particle sources for each element. The concentration of Cd decreases as air stagnation decreases implying a somewhat greater importance of the small particle source. As expected there is a trend of increasing MMD's for Cd as air stagnation decreases and as large particle material is more efficiently mixed into the atmosphere. Zinc, on the other hand shows a slight increase in both concentration and MMD as air stagnation decreases. (Note: the Zn concentration data is

somewhat difficult to interpret because of the order of magnitude higher air concentration measured during W9. For these comparisons the data for W9 was eliminated. Study of the meteorological and general air quality parameters characterizing W9 revealed no apparent reason for the high concentrations measured by both the total filter collector and the Anderson impactor. Since both of these samples were carried through the laboratory leaching procedure at the same time, (contamination is a possibility). The behavior of Zn concentrations and MMD's with respect to air stagnation implies that the large particle source may be somewhat more important relative to the small particle source over a long time period. In general the trends revealed by classification of the data according to air stagnation were also manifested when the data was classified by atmospheric stability frequencies and mean daily wind speed for each period.

Although variations in precipitation duration and amount did correlate with some other regional meteorological and air quality parameters, no general relationships were noted between rain characteristics and elemental concentrations. The wettest period, W5, was characterized by relatively lower air concentrations than the other periods (Table 5), but period W11, similar in rainfall amount and duration to W5, exhibited considerably higher concentrations. The expected general decrease in elemental air concentrations during heavy precipitation periods was seen only marginally for Cd, there being no consistent trends for the other elements. Precipitation scavenging efficiencies, discussed in more detail in Chapter V, are highest for very small and very large particles. Thus, rainfall effects on the air

concentrations of Mn, Pb, and $\text{SO}_4^=$ were expected. However, it is likely that these effects were not seen because of the relatively low time resolution of our sampling (~ 10 times longer than the duration of the precipitation events). For example, Lawson and Winchester (1978) recently reported decreased sulfate concentrations during a snowfall when time sequence samples were collected prior to, during, and following the event.

Despite the failure to identify consistent air concentration trends with increasing precipitation amounts there were some interesting effects on MMD. Except for Mn, all elements exhibited a general increase in MMD as quantity and duration of precipitation during a period increased. Thus wet conditions resulted in somewhat larger particles in the atmosphere, implying relatively efficient nucleation scavenging of small particles and enhanced particle growth and coagulation. The role of impaction scavenging in the removal of large particles was only weakly reflected by a slight decrease in the MMD for Mn as rainfall amount increased. The data presented by Lawson and Winchester (1978) did not address the effect of the snowfall on particle size distributions.

The indication that general atmospheric moisture status has an influence on particle size distribution was not unexpected. The growth of aerosols by hydration is well known (Junge, 1963). Rahn et al. (1971) reported that the occurrence of nocturnal fog was correlated with a measurable decrease in the concentrations of several elements, likely by increased settling during particle growth. To investigate this effect in more detail correlation coefficients were calculated for

the relationships between the fraction of the total concentration of each element in the smallest size class (B) and the general atmospheric moisture status during each experimental period. The atmospheric moisture condition was previously estimated by the precipitation amount and duration during each sample period (Table 3). A more accurate measure is that provided by the atmospheric water vapor saturation as manifested by the occurrence of radiative fogs. A surface wetness sensing device was constructed to monitor the degree of leaf wetness as a measure of particle retention efficiency during the deposition experiments (Chapter IV). Since the wet sensor records fog, dew and precipitation wetness, it was necessary to correct the "wetness duration" measurements to reflect only fog. This was done by matching the continuous wetness record with simultaneously collected wet and dry bulb readings and with the continuous record of precipitation duration determined with both weighing and tipping bucket rain gauges. Since the shape of the wet sensor trace was indicative of the source of the induced wetness, only periods following the end of active precipitation needed to be corrected. If wetness was recorded, the wet/dry bulb temperatures indicated water vapor saturation, and active precipitation was no longer occurring, the conditions were assumed to indicate atmospheric water vapor saturation. The duration of these conditions, expressed as the percent of the total sampling period were taken as a general indication of the atmospheric moisture status during the period. The indicated periods of atmospheric saturation were in excellent agreement with regional radiative fogs recorded by personal

observation. In addition atmospheric saturation frequency was significantly correlated with mean relative humidity (Table 3).

The values of atmospheric moisture status and the relative elemental concentrations in the backup filter size class (B - also termed "fine" particle size range) are summarized in Table 9. Also shown are the correlation coefficients between these two variables. There is a consistent negative correlation between atmospheric saturation and fine particle relative concentrations indicating a general decrease in the fraction of an element in the fine particle size class ($< \sim 0.5 \mu\text{m}$) as duration of atmospheric saturation increases. The correlation coefficients were statistically significant only for Pb and $\text{SO}_4^=$, the two elements with the highest relative concentration in the fine particle range. A plot of this relationship for $\text{SO}_4^=$ is in Figure 11. The data define a relatively smooth decrease in the contribution of fine particles to the total $\text{SO}_4^=$ concentration as frequency of atmospheric saturation increases, reaching an apparent asymptote at $\sim 25\%$. This could suggest a kinetically controlled particle growth mechanism where the rate determining step is not necessarily the physical growth rate of the particles but the rate of supply to the atmosphere of parent ($< 0.5 \mu\text{m}$) material. Thus in this case, the rate of fine particle formation exceeded that of particle growth and coagulation under high moisture conditions leading to what appears to be a constant minimum fine particle contribution to the $\text{SO}_4^=$ load. Although this is speculative without further data, it is interesting hypothesis

Table 9. Correlations between atmospheric water vapor saturation and the fraction of the total air concentration of each element collected on the backup filter ($<0.44\mu\text{m}$)

Period	Atmospheric water vapor saturation frequency ^b (%)	Relative elemental concentration in backup filter size class ^a				
		Cd (%)	Mn (%)	Pb (%)	Zn (%)	SO _x (%)
W1	3	12	11	67	34	70
W2	10	41	16	53	66	40
W3	8	41	31	49	32	40
W4	1	53	8	66	31	70
W5	55	10	3	29	19	18
W6	40	28	7	53	44	28
W7	6	55	23	73	39	51
W9	17	16	9	65	18	37
W11	67	16	5	48	22	23
W12	16	12	6	55	48	44
Correlation coefficients ^c		-0.53	-0.55	-0.71*	-0.40	-0.83**

^aExpressed as: $[\text{air concentration on backup filter} / \text{total air concentration}] \cdot 100$.

^bExpressed as percent of total sampling period during which saturated conditions occurred.

^cFor the relationship between saturation frequency and relative concentration in the backup filter size class; * = (P<0.05), ** = (P<0.01).

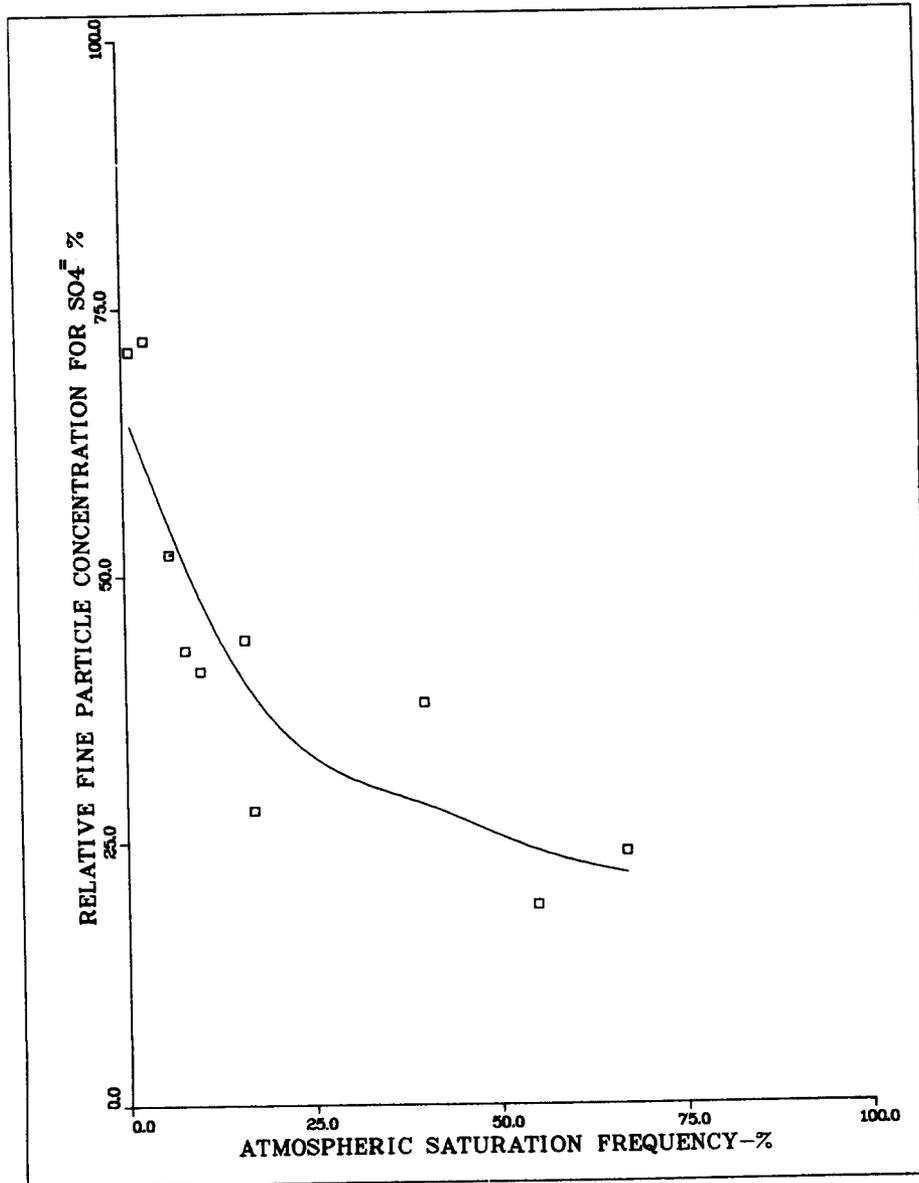


Fig. 11. Relationship between the fraction of the total aerosol sulfate collected on the backup filter (fine particle sulfate) and the atmospheric water vapor saturation frequency. Saturation frequency is the relative duration of saturated atmospheric conditions during a given experimental period.

concerning mechanisms controlling particle size distributions and, hence, atmospheric residence times.

One aspect of this relationship which should be noted is its similarity to a relationship previously presented by Mezaros (1968). Mezaros studied the correlation between the relative contribution of water soluble $\text{SO}_4^=$ particles in the Aitken size range to the total sulfate air concentration and relative humidity. The plot of these variables was very similar to Figure 11. The author suggested that the inverse relationship was a strong indication that $\text{SO}_4^=$ particles were hygroscopic in nature, increasing in size out of the Aitken range by hydration as relative humidity increased. This conclusion is supported by our determination that essentially all of the sulfate in atmospheric particles is readily water soluble. The relationship between this aspect of particle chemistry and atmospheric conditions is the subject of a following section. Implicit in the above discussion is the assumption that the Anderson cascade impactor is able to separate particles efficiently into several size ranges based on aerodynamic diameters regardless of atmospheric conditions. There has been and continues to be considerable debate on this subject (Hu, 1971; Dzubay et al., 1976; Wedding et al., 1977). If the impactors are subject to severe particle bounce and wall losses one might expect these problems to be minimized when sampling a relatively "wet" aerosol (Winkler, 1974). If this is the case, sampling during wet periods might lead to better upper stage retention, less particle bounce to lower stages, and better overall size separation thus resulting in an apparently larger MMD during the wet period. However particle growth

during wet periods is a well known phenomenon (Junge, 1963) which could explain these same observations. Without further laboratory and wind tunnel studies, such as those by Winkler (1974) and Dzubay et al. (1976), this problem will remain unresolved.

As discussed earlier, these experimental periods can also be characterized according to frequency of winds from the direction of the TVA Kingston coal fired power plant (~ 20 km SW), the TVA Bull Run plant (~ 14 km NE), and the DOE Y12 Plant (~ 2 km NE), and from all other directions (see Table 3). The 10 periods were grouped into classes of high, medium, and low frequency of winds from each of these directions. Unexpectedly there was no clear influence of the three local sources on air concentrations. In fact, when grouped according to frequency of winds from directions other than the local coal fired generating stations, the air concentrations of Cd, Pb, Zn, and $\text{SO}_4^{=}$ increased as the frequency of "other" direction winds increased. There was little effect on Mn concentrations as expected for a predominantly soil dust associated element. Classification by wind direction did not result in any clear trends in the elemental MMD's, although it did have an influence on the overall TSP MMD, as discussed earlier. This was surprising for the bimodally distributed elements Cd and Zn. Since a large fraction of the fine particle mode for these elements is expected to have a combustion source, a high frequency of winds from the direction of the local power plants might be expected to result in a downward shift in the MMD's. The lack of any apparent influence of wind direction on elemental MMD's coupled with the unexpected influence of wind direction on concentrations, discussed above, implicates the

more distant sources (as manifested by regional air quality) as influencing atmospheric concentrations and size distributions over WBW. This hypothesis is in general agreement with the results of an earlier multielement study of aerosols in WBW (Andren and Lindberg, 1977). A model based on a chemical mass balance approach (Miller et al., 1972; Friedlander, 1973; Gatz, 1975) was used to estimate the local coal combustion contribution to the aerosol composition in WBW. The model accounted for < 1% of the Cd and Pb, 2% of the Mn, and 12% of the Zn as arising from local coal-fired generating plants. The calculations indicated that, for the period July, 1974, no more than 5% of the aerosol load in WBW could have been attributed to local coal combustion. A similar conclusion was drawn by Gordon et al. (1975) in their studies at the Chalk Point Generating Station. The authors found that for most species the concentrations measured upwind and downwind of the plant were the same. It was assumed that much of the "coal component" of the aerosol chemistry was probably transported long distances and was not the result of local emissions.

Briefly summarizing the above observations leads to several interesting conclusions: (1) elemental air concentrations at WBW do not reflect a significant influence of local coal combustion, being more similar to concentrations measured at remote and rural locations than at urban or industrialized areas, (2) increasing precipitation volume and duration has the effect of increasing the MMD's of Cd, Pb, Zn, and $\text{SO}_4^{=}$ while decreasing that of Mn, (3) as regional air stagnation increases, the concentrations of Cd, Pb, Zn, and $\text{SO}_4^{=}$

increase, while Mn decreases, (4) elemental size distribution and concentrations and the manner in which they are influenced by various atmospheric parameters suggest a soil source for Mn, secondary atmospheric particle and combustion sources for Pb and $\text{SO}_4^{=}$, and both small particle combustion and large particle dispersion sources for Cd and Zn, and (5) the lack of any apparent wind direction effects on MMD and the slight increase in concentrations with winds from "other than local source" directions suggests that atmospheric chemistry over WBW is more likely the result of regional air transport phenomena rather than the direct result of local source emissions.

The Water Soluble Nature of Aerosol Associated Trace Metals

General Considerations

The water solubility of atmospheric particles has apparently been infrequently studied. Yet the property has been regarded as an important characteristic related to physical growth, nucleation efficiency, and atmospheric residence times of aerosols. As seen in the previous discussion there is evidence for particle growth of aerosol associated $\text{SO}_4^{=}$ and Pb in the fine particle size range (size class B). It is possible that this phenomenon is related to the degree of water solubility of these elements. This has been suggested by Meszaros (1968) in a study of the size distributions of water soluble $\text{SO}_4^{=}$, NH_4^{+} , and Cl^{-} in the atmosphere. Part of the intent of this discussion will be to determine the relationship between aerosol solubility and particle size. In addition to physical and chemical aspects of the suspended particles, water solubility is also

related to the efficiency of aerosol capture and retention during sedimentation and impaction processes (Winkler, 1974; see also the review by Hosker and Lindberg, 1979) and is thus of interest as related to mechanisms of dry deposition. Finally the solubility of certain elements associated with submicrometer particles has received considerable attention (but little study) from the standpoint of human health effects. Elements which are highly soluble in lung fluids are expected to be potentially more hazardous than elements bound within the aerosol matrix in an insoluble or unavailable form (Morrow, 1972). Particle solubility has also been suggested as an important characteristic affecting lung deposition and retention of aerosols (Desadalier and Winchester, 1975).

A considerable quantity of the metals studied in air particulates collected in WBW were soluble in the water-aerosol leachate. Before considering the data in detail some further discussion regarding the laboratory procedures is necessary. The distilled water leaching solution is termed the water-aerosol leachate above for an important reason. It is obviously not possible to extract any sample as complex and heterogeneous as a natural mixture of ambient aerosols without significantly altering the initial leaching solution chemistry. Of most importance from the standpoint of trace metal leaching would be the simultaneous leaching of strong acid anions, dissolved organic matter, and free hydrogen ion. Table 10 summarizes typical characteristics of the initial 2XDW leaching solution and the resultant distilled water aerosol leachate. It is obvious that there are substantial changes in the concentrations of these components. The

Table 10. Major constituent chemistry of initial double distilled water (2XDW) leachate and typical resultant aerosol - 2XDW solutions

Sample	Specific conductance ($\mu\text{mhos}/\text{cm}^2$)	DOC ^a (mg/liter)	H ⁺ ($\mu\text{eq}/\text{liter}$)	SO ₄ ⁻ (mg/liter)	NO ₃ ⁻ (mg/liter)	Cl ⁻ (mg/liter)
2XDW	2	0.08	2.5	<0.2	0.008	<0.05
Aerosols in size class:						
1	3	0.1	2.5	0.2	0.008	0.1
2	3	0.1	2.5	0.3	0.008	0.1
3	3	0.3	4.7	1.5	0.03	0.1
4	6	1.1	31	4.3	0.09	0.1
B	13	1.5	20	4.1	0.2	0.1

^adissolved organic carbon.

extent to which these materials influence the extraction of metals from the aerosol is unknown. Metal salts of strong acid anions or metal-organic complexes may form during the extraction, thus increasing the apparent solubility of the metals in question. Similarly H^+ may exchange with surface sorbed metals or react with surficial metal oxides to increase apparent solubilities. The assumption must be made in this type of extraction that a quasi-equilibrium is reached (see Figure 2), a situation approaching that occurring under natural conditions. Interestingly the highest major element concentrations measured in the aerosol-water leachate are very similar to typical precipitation concentrations in this area.

The second point which must be considered is the meaning of the term relative solubility (RS). As discussed earlier the distilled water and dilute acid extraction procedures do not result in complete recovery of the total metal originally present. Thus when the solubility is expressed in relative terms ($RS = \text{water soluble concentration} \cdot 10^2 / \text{available concentration}$) this value may in some cases overestimate the solubility defined in more conventional water-solubility terms ($WS = \text{water soluble concentration} \cdot 10^2 / \text{total metal originally present}$). When internal consistency is maintained comparisons are valid within the sample set. However, for the purpose of external comparability, the samples which were additionally subjected to the "total" wet digestion procedure, as previously discussed in reference to Table 1, can be used to compare the water leachable to available metal ratios (RS) with the water leachable to total metal ratios (WS). These data are summarized in Table 11 for one

Table 11. Comparison of trace metal solubilities in aerosols and fly ash expressed in terms of relative solubility (RS) and water-solubility (WS)

Sample	Cd		Mn		Pb		Zn	
Aerosols ^a in size class:	<u>RS</u> ^b	<u>WS</u> ^c	<u>RS</u>	<u>WS</u>	<u>RS</u>	<u>WS</u>	<u>RS</u>	<u>WS</u>
1	77	64	68	55	22	4.3	0	0
2	83	59	75	68	13	2.4	97	54
3	77	55	75	61	39	7.7	71	11
4	56	43	91	76	76	19	97	65
B	79	79	86	86	77	64	96	65
Stack ash ^d	32	6	51	18	10	1.2	0	0
	RS/WS Ratios							
	<u>Cd</u>		<u>Mn</u>		<u>Pb</u>		<u>Zn</u>	
1	1.2		1.2		5.1		-	
2	1.4		1.1		5.5		1.8	
3	1.4		1.2		5.1		6.5	
4	1.3		1.2		4.0		9.7	
B	1.0		1.0		1.2		1.5	
Stack ash	5.3		2.8		8.3		-	

^a Aerosols collected during W7.

^bRS = (water soluble metal/available metal) •(100) = relative solubility.

^cWS = (water soluble metal/total metal) •(100) = water-solubility.

^d"Fly" ash collected in the stack of a large-scale coal-fired power plant.

set of aerosol samples and one set of stack ash samples collected at a nearby coal fired generating station. As expected the RS overestimates the WS in nearly every case. However, the RS is a reasonable approximation of the WS for both Mn and Cd in all particle size classes. The solubilities of Pb and Zn in the larger size classes are overestimated by factors of 2 to 10 by the RS. Conventional solubilities are best estimated by the relative solubility term for all elements in the backup filter size class. The metal solubilities in the stack ash samples were overestimated to the greatest extent using the RS term, by factors of 3 to 8. When the samples are considered in terms of their particle size, there is a relationship between size and RS/WS ratios such that the largest particles reflect the highest ratios. The possible relationship between elemental solubility and particle size will be further considered as this discussion continues.

Relative Solubility of Metals in Ambient Aerosols

The air concentrations and relative solubilities measured for the total aerosol fractions over the 10 week sampling period are summarized in Table 12. Substantial amounts of each of the available metal fractions are leachable in DW. Zinc exhibited the largest relative solubility of the metals followed by Mn, Cd, and Pb. All indications are that essentially 100% of the available $\text{SO}_4^{=}$ is water soluble as would be expected given the generally accepted hypotheses that aerosol sulfate exists largely as $(\text{NH}_4)_2\text{SO}_4^{=}$ and acid sulfate (Meszaros, 1968; Weiss et al., 1977). The pattern of relative trace metal solubilities ($\text{Zn} > \text{Mn} > \text{Cd} > \text{Pb}$) is similar to the general order

Table 12. Air concentrations and relative solubilities of the distilled water leachable fractions of the total aerosol

Parameter	Element	\bar{X}	σ	Range
Air concentration of water-leachable fraction (ng/m ³)	Cd	0.14	0.08	0.04-.25
	Mn	8.6	3.8	1.7-17
	Pb	84.0	34	43-140
	Zn	8.9	11	2.5-30 ^a
	SO ₄ ⁼ (μg/m ³)	8.9	4.0	5.1-18
Relative solubility (%)	Cd	82	14	47-91
	Mn	83	6	70-92
	Pb	76	10	55-88
	Zn	89	6	74-95
	SO ₄ ⁼	~100	1	98-100

^aZn concentrations for W9 were not included (see text).

of the solubilities of the most probable salts of these elements occurring in airborne particles (i.e., $\text{SO}_4^{=}$, NO_3^- , and Cl^- salts; Dams et al., 1975). Although the general relationships between the elemental relative solubilities is not geochemically unusual, the indication that Pb exhibits a similar relative solubility to the other elements is surprising. This is particularly true since the more soluble salts of Pb are believed to account for only a few percent of the Pb in aged aerosol. Ter Haar and Bayard (1971) identified $\sim 77\%$ of the Pb in an aerosol sample collected at a rural location as oxides, carbonates, and oxycarbonates, all of which are less soluble than the strong acid anion salts of Pb. The reported chemical solubilities of the possible occurring Pb salts are 5 to 10 times lower than those for Cd, Mn, and Zn.

Unfortunately, there are no literature values with which the results in Table 12 are directly comparable. However by applying a factor to these values to account for the difference between relative and conventional solubility (Table 11) these results may be compared with recent studies by Hodge et al. (1978) and Eisenbud and Kneip (1975). The normalization factors were determined by calculating a mass weighted mean RS/WS ratio from the data in Table 11 and the average relative concentrations of each element in the five size classes (Table 5). These factors were as follows:

$$WSc_d = RSc_d/1.2 ,$$

$$WSMn = RSMn/1.1 ,$$

$$WSpb = RSpb/2.6 , \text{ and}$$

$$WSZn = RSZn/4.7 .$$

The resulting water-solubilities were as follows:

$$Mn (75\%) > Cd (68\%) > Pb (28\%) > Zn (19\%).$$

The aerosol leaching studies by Hodge et al. (1978) involved a water extraction step similar to that used in the present study but followed by a wet digestion involving an $HNO_3 - HClO_4$ extraction followed by $HCl - HF$ digestion of the residue. The values are thus expressed in water-solubility terms. Samples were collected at Scripps Institute and at Ensenoda, Mexico. The mean water soluble element concentrations at Scripps Pier were (in ng/m^3): $Pb = 220$, $Zn = 17$, $Mn = 5.2$, $Cd = 0.21$, while those at the remote coastal site in Ensenada were: $Pb = 20$, $Mn = 16$, $Zn = 4.4$, $Cd = 0.16$. The water soluble concentrations measured at WBW (Table 12), when compared to the above support the earlier indication that atmospheric trace metal levels are generally in line with those measured in rural or remote areas. The concentrations of soluble Pb , Mn , and Zn are between the two mean values reported by Hodge et al. while Cd is somewhat lower than both. The means and ranges in aerosol elemental solubilities reported for the Scripps Pier station were as follows: Cd 84% (69-91%); Zn 68% (44-82%); Mn 47% (32-54%); and Pb 39% (17-54%). The solubilities at the Ensenada station were generally lower, averaging 80% (63-90) for

Cd, 35% (23-58) for Mn, 24% (10-60) for Zn, and 17% (6-29) for Pb. It is apparent that there are considerable differences in the solubilities between the marine aerosols collected by Hodge et al. and the continental aerosols collected over WBW, although the soluble aerosol concentrations are similar.

Eisenbud and Kneip (1975) recently reported the results of similar leaching experiments on aerosols collected in New York City. The aerosol filters were extracted with hot distilled water for 24 hrs in a Soxhlett apparatus followed by a HNO_3 - HClO_4 digest of the residue; as such the reported solubilities are directly comparable to the water solubilities reported here and by Hodge et al. The results of these extractions on several samples collected over a 2 year period indicate the following order of water-solubilities (means and ranges): Cd 85% (68-100); Zn 64% (41-100); Mn 62% (55-68); Pb 9.4% (5-13). Once again both the measured solubilities and their relative ranking are different from those measured at WBW. Both the marine aerosols collected by Hodge et al. and the urban aerosol collected by Eisenbud and Kneip showed Cd to be considerably more soluble ($\sim 85\%$) than the next most soluble metal Zn ($\sim 65\%$), followed closely by Mn ($\sim 55\%$) which was considerably more soluble than Pb ($\sim 10-40\%$). However it is apparent from the ranges reported for each element that there is considerable variability at each site. With the exception of Mn, the solubility ranges of the marine and urban aerosols encompass the values measured at WBW. Since the water-solubilities values were originally determined for only one set of WBW aerosols, these differences are not surprising.

The considerably higher apparent solubility of Mn in WBW aerosols suggests both a source and particle size effect. Although the solubility data was not discussed in any detail by Hodge et al., Eisenbud and Kneip did speculate that the considerable range in Zn solubilities reflected variable sources over the 2 year study period. Because of the indication from the data in Table 11 that solubility, expressed in both relative and water-solubility terms, may be a function of particle size, it is possible that the differences between the water-solubilities of aerosols in WBW and those collected elsewhere are simply related to differences in particle size distributions. Size distributions were not measured by Hodge et al., nor were solubilities of various particle size ranges reported by Eisenbud and Kneip. The latter authors did, however, discuss size distributions for a limited number of samples for Mn, Pb, and Zn. The relative concentrations of these three elements were determined for the following size ranges: $> 4 \mu\text{m}$, $2.5-4 \mu\text{m}$, $1.5-2.5 \mu\text{m}$, $0.5-1.5 \mu\text{m}$, and $< 0.5 \mu\text{m}$, which roughly correspond to the size classes 1, 2, 3, 4, and B, respectively, as reported here. To simplify comparison, the relative concentrations were grouped by size classes 4 and B ($< \sim 1.5 \mu\text{m}$) and classes 1, 2, and 3 ($> \sim 1.5 \mu\text{m}$), for both sets of samples. The results for the relative concentration of each metal in the $< 1.5 \mu\text{m}$ size range are as follows:

urban: Mn 16%, Pb 47%, Zn 27%

WBW: Mn 30%, Pb 82%, Zn 62%

Both Mn and Pb in WBW had considerably higher small particle fractions compared to the urban aerosols. This observation and the indication

that solubility increases for these two elements as particle size decreases (Table 11) could explain the higher Pb and Mn solubilities measured for the WBW aerosols. However, this does not explain the lower solubility of Zn in WBW aerosols for which a higher proportion also occurred in the small particle size range. The difference in Zn may be more strongly related to differences in the sources of both submicron and supermicron Zn containing particles. One possible Zn source in the WBW area is a Zn mining and milling facility which may release large quantities of highly insoluble ZnS dust.

The relationships between particle size and relative solubility in the WBW aerosols are illustrated in Figure 12, showing the mean RS of each particle size class and its associated standard deviation. As originally noted in Table 11 there is a trend of decreasing relative solubilities with increasing particle size as well as an increase in the variance of the data as particle size increases. This trend does not appear to be related to the particle size distribution of the specific elements since similar patterns in RS occur for Mn, Pb, and Zn, which exhibit a monomodal large particle size distribution, a monomodal small particle size distribution, and a bimodal size distribution, respectively. However, in the case of Cd, the RS does behave similarly to the concentration of Cd, showing a bimodal distribution with a lower solubility for the material in size class 3. Because of the large degree of variability in the solubilities for each size class, it is tenuous to generalize without seeing the individual distributions of RS for each sampling period, which are summarized in Figure 13. The decrease in RS with increasing particle size is most

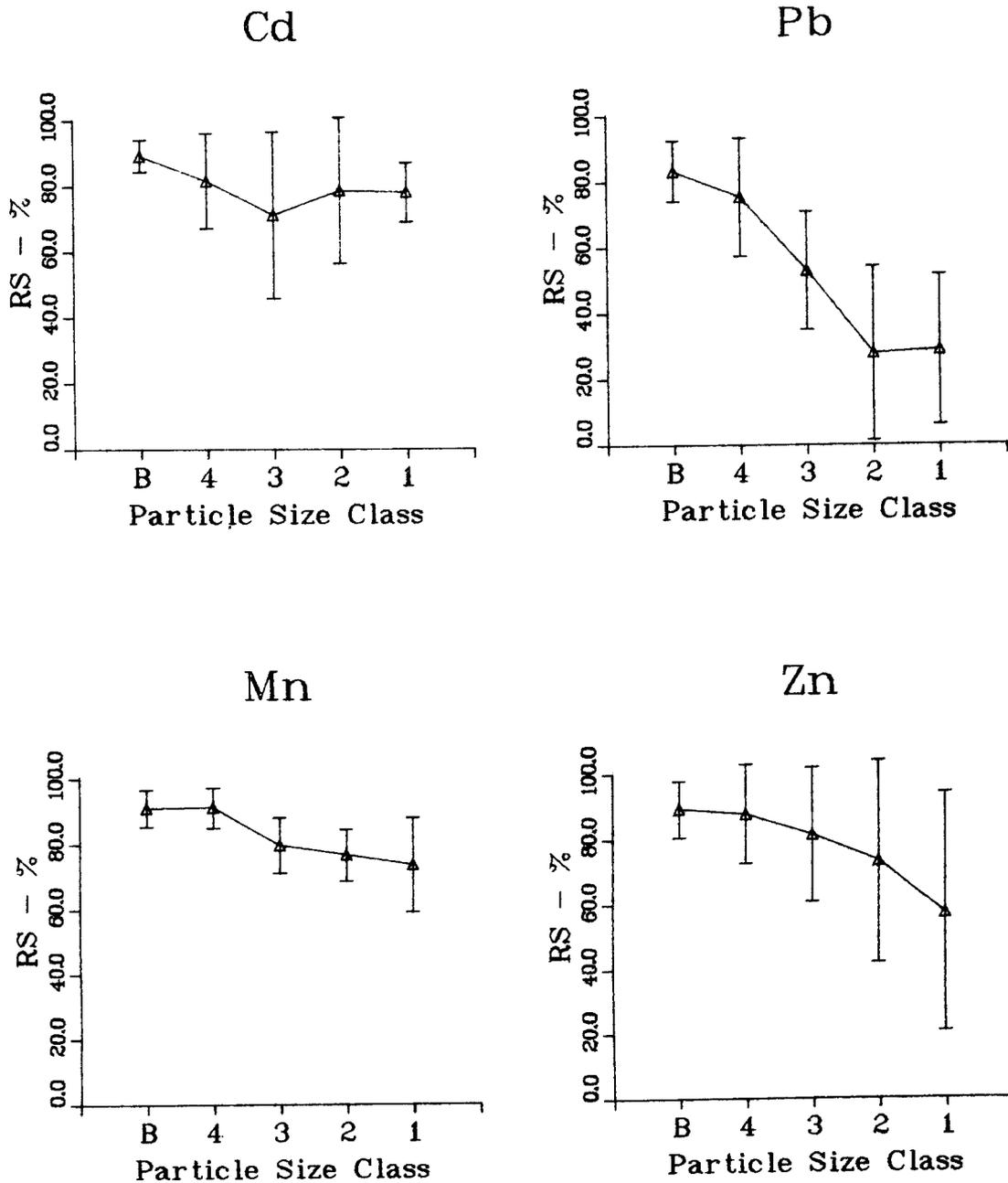


Fig. 12. Relationship between relative solubility (RS = water soluble concentration \cdot 100/available element concentration) and particle size class. Mean values for the ten experimental periods are plotted with associated standard deviations. Aerodynamic diameters range from B, \sim 0.44 μ m to 1, \sim 7.2 μ m.

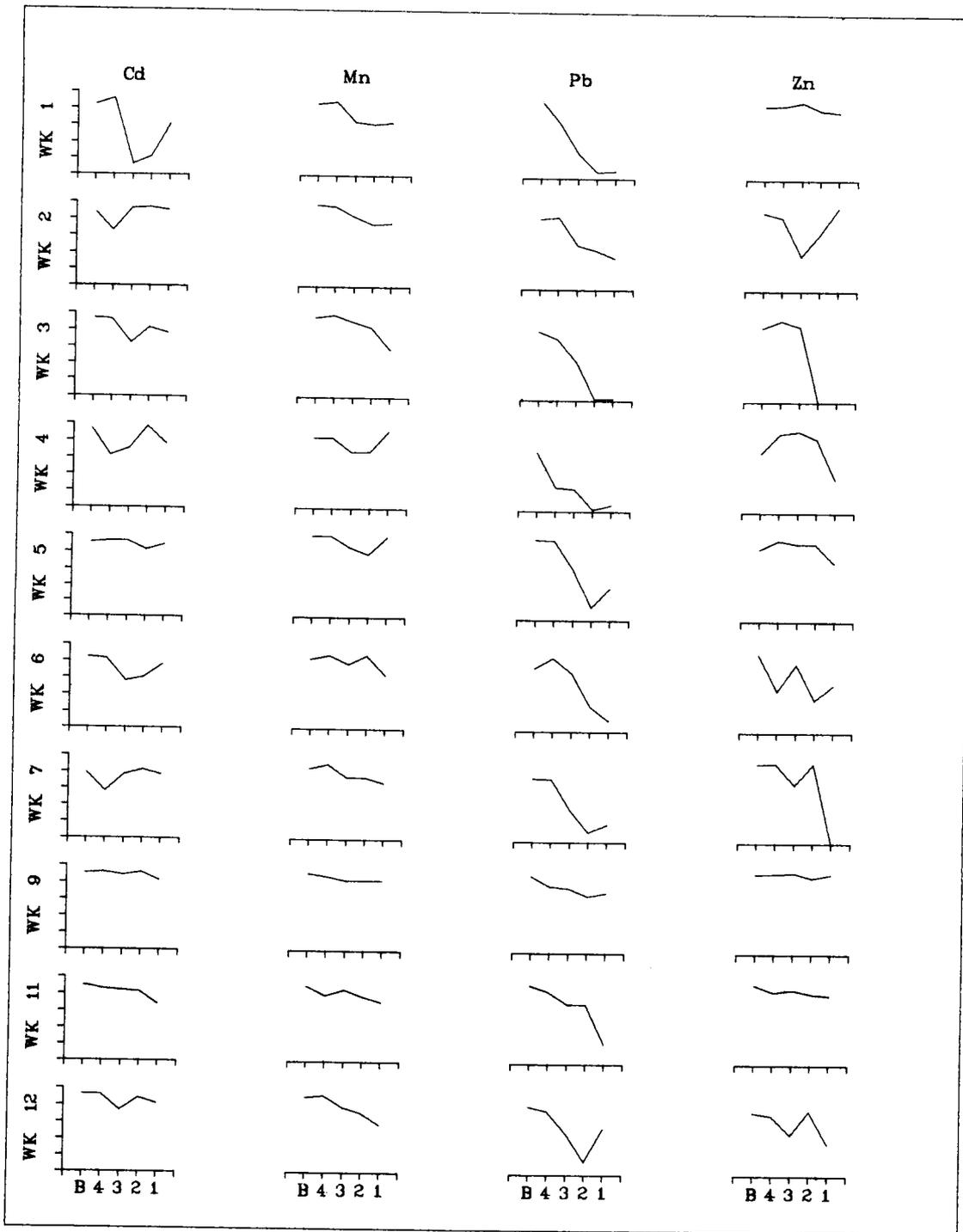


Fig. 13. Relative solubility (RS) of trace elements in five particle size classes for the ten experimental periods. The scale on the ordinate is RS in percent while the abscissa represents aerodynamic diameters ranging from B, $\sim 0.44 \mu\text{m}$ to 1, $\sim 7.2 \mu\text{m}$.

pronounced and consistent in the case of Pb, strongly suggesting two different sources of aerosol Pb, characterized by both particle size and water solubility. Manganese also decreases in RS as particle size increases except for periods W4 and W5. Cadmium generally shows a minimum solubility in the middle of the size range with the exception of W9 and W11. The most striking feature of the RS distributions for Zn is the large degree of variability in the solubility of Zn associated with the large particle fraction. These values range from essentially 0% (W3, W7) to nearly 100% (W2, W9), again suggesting considerably different large particle sources, dominant during different periods.

The general trend of higher elemental solubilities associated with smaller particles may be explained by three possible phenomena: (1) a basic difference in the chemistry of the source material contributing to each size fraction; (2) the greater surface area to volume ratio of smaller particles and the previously discussed surface predominance and elevated concentrations of metals on small particles, thus effectively increasing the relative availability of certain elements (this hypothesis should also consider the more effective atmospheric hydration of small particles), and (3) the increase in the water leachable free H^+ and strong acid anion component with a decrease in particle size (Table 10). The most likely explanation is a combination of the three factors, in addition to other, more subtle, phenomenon. The latter two phenomena are probably related since much of the small particle fraction is composed of secondary aerosols, originating from gas/particle reactions in the atmosphere. These particles are the

primary source of neutral sulfates (highly soluble as parent aerosols) and acid sulfates (the obvious source of the free hydrogen ions) in the atmosphere (Cunningham and Johnson, 1976). The phenomenon of increased water solubility of atmospheric particles with decreasing particle size was previously reported by Meszaros (1968) who found the major fraction of airborne water soluble particles in the size range of $0.1 \mu\text{m} < r \leq 0.3 \mu\text{m}$. The ratio of total soluble to insoluble material in the Aitken size range was 0.2 while the ratio in the larger ranges was 0.07 - 0.08.

Some evidence for the possible importance of the three factors above may be extracted from an examination of the temporal variations in the elemental solubilities in the total aerosol fraction and the distribution of elemental solubilities with particle size over the 10-week sampling period. Figure 13 indicates that the only period characterized by a similar distribution in the relative solubilities with particle size for all elements was W9. Each element showed relatively little effect of particle size on solubility and each element exhibited the highest relative solubility measured during the 10 sampling periods. The general atmospheric characteristics of W9 do not completely distinguish this period from any other (Table 3), there being other periods with similar wind patterns, relative humidities, and precipitation amount. However combining the precipitation volume and duration to calculate the rain intensity (volume/duration) does indicate this period to be characterized by the lowest intensity, long duration rain measured. Aerosol hydration during such events is likely and could result in increased relative solubilities.

To further investigate the possible relationship between relative solubility and atmospheric moisture, correlation coefficients were calculated between the elemental relative solubilities and the atmospheric saturation frequency (previously discussed in Table 9) during each sample period. The resulting correlation coefficients were as follows:

$$\begin{aligned} \text{Pb, } r &= 0.77 \text{ (} P \leq 0.05 \text{); Cd, } r = 0.41, \text{ (} P \geq 0.05 \text{);} \\ \text{Zn, } r &= 0.31 \text{ (} P \geq 0.05 \text{); and Mn, } r = 0.17, \text{ (} P \geq 0.05 \text{).} \end{aligned}$$

Although the correlation is significant only for Pb, all elements exhibit a trend of increasing solubility as the duration (frequency) of atmospheric water vapor saturation increases. The relationship between solubility and atmospheric moisture is illustrated in Figure 14 for Pb. The figure indicates the relative solubility of Pb in the total aerosol fraction to gradually increase from $\sim 55\%$ to $\sim 85\%$ as the atmospheric saturation frequency increases from 0% to $\sim 70\%$, reaching an apparent asymptotic maximum solubility of $\sim 85\%$. The remaining $\sim 15\%$ of the aerosol associated Pb may represent an occluded fraction or a matrix compound not readily available. Interestingly Ter Haar and Bayard (1971) estimated $\sim 20\%$ of the Pb in aged aerosols (collected at sites remote from automotive sources) was present as the highly insoluble PbO.

The trends in the relative solubilities of the other elements with atmospheric moisture are summarized in Table 13 showing the mean relative solubility for each element calculated after separating the 10 experimental periods into three groups according to general moisture

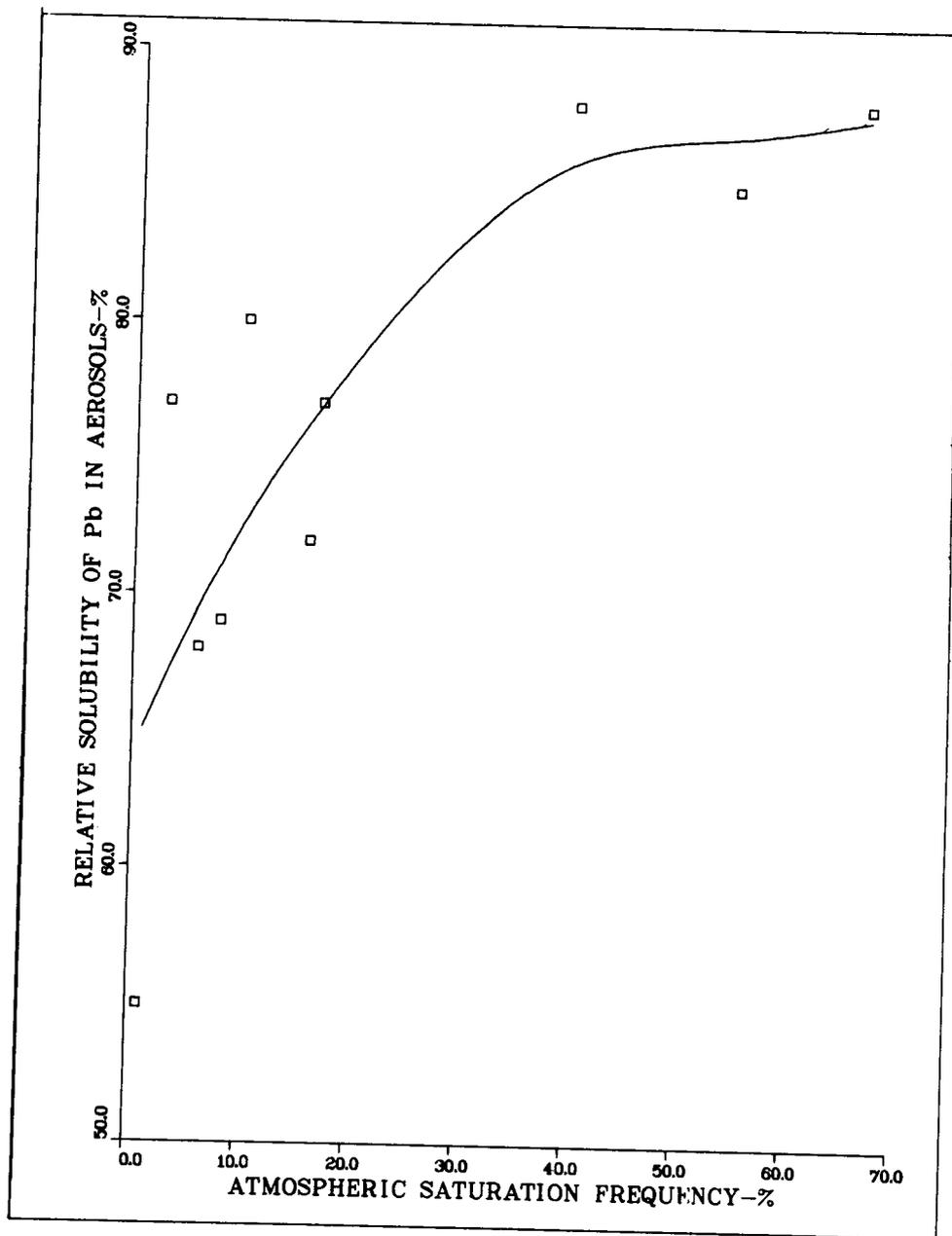


Fig. 14. Relationship between the relative solubility of Pb in the total aerosol fraction and atmospheric water vapor saturation frequency.

Table 13. Mean relative solubilities of trace metals in aerosols during experimental periods divided into three classes of atmospheric water-vapor saturation frequency

Class	Saturation frequency (%)	Experimental periods	Relative solubility				
			Cd	Mn	Pb	Zn	
						Total aerosol fraction	
1	54	5, 9, 11	88	85	87	94	
2	14	2, 6, 12	85	81	76	84	
3	4	1, 3, 4, 7	73	82	67	90	
						<u>Backup filter aerosol fraction^a</u>	
1	54	5, 9, 11	91	94	96	94	
2	14	2, 6, 12	89	91	81	84	
3	4	1, 3, 4, 7	88	89	81	87	
						<u>Size class 1 aerosol fraction^b</u>	
1	54	5, 9, 11	80	85	46	85	
2	14	2, 6, 12	83	66	36	66	
3	4	1, 3, 4, 7	73	71	11	31	

^aSize class B, aerodynamic diameter $\approx 0.44\mu\text{m}$.

^bAerodynamic diameter $\approx 7.2\mu\text{m}$.

conditions. Although there is considerable scatter in the solubility data (Figure 13), the relative solubilities generally decrease with decreasing atmospheric saturation frequency for Cd and Mn in the total aerosol and size class B fractions, Pb in all fractions, while the trend is best defined for Zn in the largest particle size fraction.

An examination of the relative solubilities for the total aerosol fraction in the context of the other atmospheric conditions discussed previously (precipitation amount, air stagnation, atmospheric stability, wind direction) revealed very few clear trends. Solubilities generally increased as precipitation amount and duration increased but not as consistently as the increase with atmospheric water vapor saturation frequency, although the two are necessarily related. No clear, consistent relationships between relative solubility and atmospheric stability or air stagnation were apparent. There was also no apparent dependence of relative solubility on wind direction. Solubility thus does not appear to be influenced by the increased concentration of material below the mixed layer under poor dispersion conditions nor the resuspension of surface dusts during periods of strong vertical mixing. Similarly the solubilities do not appear to be strongly influenced by emissions from the three local coal-fired generating plants. When wind directions were grouped according to frequency from the local source quadrants, the mean solubility of each element during the periods of high frequency winds from the local sources was similar to the solubility during periods of very low frequency winds from these sources.

Combustion Plume Aerosol Solubility Experiments

Based on the relative solubilities of stack ash summarized in Table 11 one might expect a decrease in solubilities during periods with a high frequency of "local source" winds. The relative solubilities of Cd, Mn, and Pb in stack ash were 25 to 65% of the values measured for ambient aerosols, while the solubility of Zn in fly ash was < 1% compared to ~ 90% in the aerosol. This was not reflected in the ambient aerosol data collected during periods dominated by winds from the directions of the local power plants, as described above. However, even though the characteristics of the ambient aerosol over WBW are reflective of regional rather than specific local sources, there is considerable evidence for the presence of "fly ash" in all ambient air samples collected (see Chapter VI). A possible explanation for this apparent contradiction comes from the work of Gordon et al. (1975) who made a similar observation during studies on the solubility of several elements associated with precipitator ash collected at the Chalk Point power plant. Detailed in-plant studies led to the conclusion that the general chemical nature of in-plume aerosols may be quite different from that of fly ash collected in the precipitator. The authors suggested that future studies concentrate on leaching experiments using fine suspended material collected on backup filters following in-stack or plume impactor samples. A set of experiments was designed to investigate this phenomenon.

A cooperative agreement between the Environmental Sciences Division and the Tennessee Valley Authority resulted in our participation in a series of in-plume sampling studies under the

direction of J. Meagher of the TVA Air Quality Branch. This work was part of a comprehensive study of plume oxidation rates of SO_2 . Two sets of aerosol samples were collected in the plume of a TVA 2600 MW coal fired power plant with a stack height of 305 m. Collections were made from a helicopter fitted with an intake probe, using a modified high flow Anderson cascade impactor as described earlier. Samples were collected at altitudes ranging from 250 to 450 m at two distances from the stack. Collections progressed early in the morning under hazy atmospheric conditions before the plume began to disperse and was still relatively well defined at distances of ~ 10 km. The plume was identified both visually and by continuous readout of SO_2 and condensation nuclei data. Collections were made during horizontal passes perpendicular to the wind in an attempt to sample similarly aged aerosols.

Because of the difference in relative solubilities between ambient aerosols (containing fly ash) and fly ash collected in the power plant stack, the two experimental runs were performed at, (1) a distance as close to the stack as possible (250 m), and (2) a distance on the order of that of the local power plants from WBW; the distance chosen was 7 km where the plume was still well defined). The purpose of choosing these two distances was to determine whether large changes occurred in the aerosol solubility during the period when the plume is subjected to the most rapidly varying ambient conditions. The stack gas exits the precipitator at $\sim 160^\circ\text{C}$ but varies little in temperature during travel through the stack, exiting at $\sim 135^\circ\text{C}$. However the largest temperature change occurs during the initial few minutes of mixing with

the ambient air, a time period comparable to a plume travel distance of ~ 1 km. It is during this period that many condensation reactions or other gas - particle reactions may be occurring. Thus the sample at 250 m should represent the in stack material as it begins to experience a series of condensation reactions. The 7 km sample should represent the plume material after it has reached ambient temperature and has mixed and interacted with the background aerosol to some extent.

The total aerosol plume concentrations at the two distances were as follows:

0.25 km- Cd 27 ng/m³, Mn 47 ng/m³
 Pb 820 ng/m³, Zn 990 ng/m³, and SO₄⁼ 400 μg/m³;
 7 km- Cd 8.2 ng/m³, Mn 10.3 ng/m³
 Pb 290 ng/m³, Zn 270 ng/m³, SO₄⁼ 115 μg/m³.

Comparing these concentrations with the mean aerosol concentrations in ambient air at WBW (Table 6) indicates that at 7 km the elements previously considered as having possible significant coal combustion sources (Cd, Zn, SO₄⁼) are present at concentrations 10 to 50 times those in WBW, while the concentrations of elements considered to be derived primarily from other sources (Mn, Pb) are comparable to those of the ambient aerosol. The particle size distributions of each element were as expected for direct emissions from a combustion source, the more volatile elements Cd, Pb, Zn, and S being strongly small particle associated while the possible matrix element, Mn was relatively uniformly distributed. At the 0.25 km distance the geometric mass weighted mean diameters (GMWMD) were as follows:

Cd 0.16 μm , Mn 0.23 μm , Pb 0.14 μm ,
Zn 0.17 μm , and $\text{SO}_4^=$ 0.12 μm .

These values are in close agreement with those presented by Whitby et al. (1976) for the total aerosol geometric mean diameter (GMD) for plume samples collected at 2 to 4 km from the stack of a major coal fired plant (GMD = $0.20 \pm 0.01 \mu\text{m}$). As the plume aged during travel from 0.25 - 7.0 km there was an increase in the GMWMD for Cd to 0.34 μm while the GMWMD of the other elements did not change significantly. An increase in the mean particle size would be expected from the work of Whitby et al. (1973). Particles in the size range $< 0.1 \mu\text{m}$ are referred to as transient nuclei since they have short half lives due to rapid coagulation with each other and with larger particles. These particles tend to grow into the 0.1 - 2 μm range or the so called accumulation mode. A slight increase in the GMD was seen by Whitby et al. (1976) in plume travel from 2 to 4 km with no subsequent change during travel from 4 to 18 km. There is no ready explanation for the large shift in the Cd size distribution with no significant change in the size distribution of Mn, Pb, Zn, or $\text{SO}_4^=$.

The results of the solubility experiments are illustrated in Figure 15 which describes the relative solubility for each element in 4 particle size classes and in the total aerosol fraction, and for comparison, the relative solubilities measured for stack ash and ambient aerosols. The relative solubilities for each element in the total aerosol fraction exhibit a similar trend with distance from the source. Taking the stack ash to represent the unaltered source

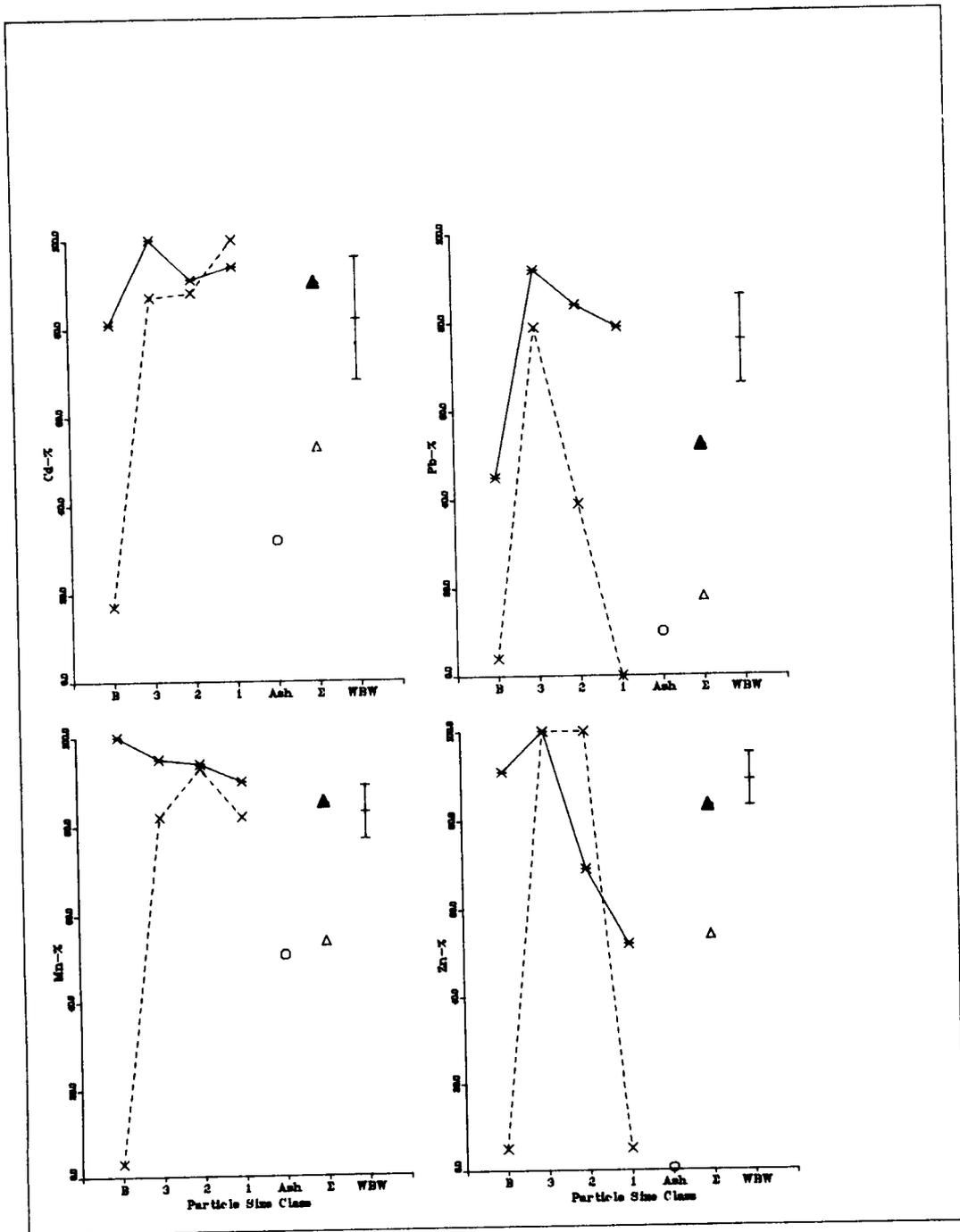


Fig. 15. Relative solubilities of aerosol-associated trace metals in the plume of a major coal fired generating plant at two distances from the stack, 0.25 km (---) and 7 km (—). Also shown for comparison are relative solubilities of the stack ash, the total (Σ) aerosol fraction in the plume (Δ = 0.25 km, \blacktriangle = 7km), and ambient aerosols collected in Walker Branch Watershed ($\bar{X} \pm \sigma$).

aerosol, each element increases in relative solubility with increasing distance, and hence plume aging and its associated gas - particle interactions. The relative solubilities of Mn and Pb are similar but slightly higher at the 0.25 km distance compared to the stack ash while the solubilities of Cd and Zn are considerably elevated above those of the stack ash. Plume travel from 0.25 to 7 km results in a similar increase in the total aerosol relative solubilities of each element, by factors of $\sim 2-3$. The relative solubilities of Cd, Mn, and Zn at the 7 km distance are within 1σ of the values measured in WBW while that for Pb is a factor of ~ 1.5 lower. Recall that coal combustion derived Pb apparently contributes only a minor fraction to the ambient air in WBW (Andren and Lindberg, 1977).

It is difficult to compare directly the variations in relative solubility with particle size for the plume samples with those measured in WBW because of the modifications made to the cascade impactor used in the plume sampling. However, the trend of increasing relative solubilities with decreasing particle size seen for the ambient aerosols does not exist for the 0.25 km plume samples and is exhibited only marginally by Zn in the 7 km plume samples. It is also apparent that it is the smallest particle fraction which is the most reactive from the standpoint of relative solubility during plume aging, both because of the higher elemental concentrations associated with this fraction and the large increase in relative solubilities from the 0.25 km to 7 km samples. In most cases it is the increase in the relative solubility of the material in size class B which is responsible for the overall increase in the relative solubility of the

total aerosol fraction. The origin of the initially high relative solubilities of the larger particle classes is difficult to explain. One useful set of data would have been collection and solubility analysis of the stack ash by particle size to determine whether this "larger" material exhibits high relative solubilities before leaving the stack. The total stack ash sample is characterized by low relative solubilities. However, because of the expected small contribution of larger particles to the total stack ash sample, these large particles could have initially exhibited high relative solubilities as well. These higher relative solubilities are not inconsistent with the lower "large" particle relative solubilities measured for ambient aerosols because of the different size spectrum collected by the modified impactor used in the plume studies. In general the "large particle" fraction of the plume material (stages 1 & 2) corresponds to the "small particle" fraction (stages 4 & B) of the ambient aerosol, which was characterized by higher relative solubilities.

Summary and the Role of Particle Hydration in the Solvation Process

Summarizing the data on elemental relative solubilities in both plume and ambient samples leads to an interesting hypothesis. The relative solubility of each element in ambient aerosols collected over WBW was seen to increase with the length of time the atmosphere was saturated with water vapor during the sampling period. No other atmospheric conditions showed apparent effects on relative solubility. In the ambient aerosol, relative solubilities tended to increase with decreasing particle size while absolute elemental concentrations in

each particle size class had little effect. Ambient aerosols exhibited considerably higher solubilities compared with aerosols collected in the stack of a coal fired power plant. However, distilled water extraction of samples collected in the power plant plume indicated that relative solubilities increased during plume aging (as measured by plume travel from 0.25 to 7 km) from values similar to those measured for stack material to values representative of ambient aerosols.

The process of aerosol hydration can be used to explain all of these observations. The problem may be viewed in terms of the solvating effects involved during hydration using the approach of the James and Healy (1972) model of adsorption of hydrolyzable metal ions at the oxide-water interface. The phenomenon of metal dissolution into aqueous media can be considered in terms of two reactions between three physico-chemical states. The solid state is represented by a metal cation associated with an anion or anionic surface by chemical bonding or adsorption; the intermediate state is represented by the metal hydrate still associated with the anion; and the aqueous state is represented by the metal cation in solution. The free energy of solvation of each state is directly proportional to the ionic charges and the electronic charge and inversely proportional to the cation-anion separation and the dielectric constant (ϵ). Considering the change in free energy (ΔG) between states as a measure of the spontaneity of a reaction, it can be shown, by neglecting constants and considering the published values of ϵ for water and possible representative aerosol matrices (SiO_2 , MnO_2 , Al_2O_3), that since the ΔG term is inversely proportional to the dielectric constant, the

two intermediate steps in the solvation process are both favorable reactions (James and Healy, 1972; T. Theis, personal communication). Since the sum of the two steps represents the complete dissolution reaction, the more completely hydrated the metal cations become (in step 1), the more readily the second step of the solvation process will proceed.

A typical monolayer of hydration is thought to consist of approximately 6 water molecules while hydration double layers are also believed to exist. As these layers form, energy is utilized in displacing the metal cation from its associated anion to some extent. When the cation is fully hydrated the necessary energy to completely displace it from the anion surface is far less than that needed for the entire dissolution process. In addition, solution pH determines the surface charge and potential of the oxide, thus controlling the coulombic interactions between the ions and the surface. A decrease in pH results in an increase in the dielectric constant of the interfacial region which will, in turn, further enhance the initial hydration reaction. Thus the relationship between atmospheric water vapor saturation frequency and elemental relative solubilities can be considered in the following terms: ambient aerosols collected during periods with a longer exposure to an atmosphere saturated with water vapor will include particles more completely hydrated and which more readily yield metal cations to solution. Similarly during the initial cooling of a combustion plume the stack gases, saturated with water vapor, begin to condense on the submicron particles, hydrating all available surfaces. This would explain the low relative solubilities

associated with in-stack material and the general increase in the relative solubilities of the metals in the total aerosol fraction during the initial period of plume aging.

CHAPTER IV

EMPIRICAL DETERMINATION OF DRY DEPOSITION TO A FORESTED LANDSCAPE

Introduction

Although the literature contains considerable information on the atmospheric concentration of many elements in aerosols (briefly reviewed in Chapter III), data on their mechanisms and rates of removal have not been readily available until quite recently (e.g., see the recent reviews by Chamberlain, 1975; also Hosker and Lindberg, 1978).

Aerosols are removed from the atmosphere by (1) wet deposition, (2) sedimentation, and (3) impaction on obstacles, all three processes being highly dependent on particle size characteristics. Wet deposition will be considered in detail in Chapter V. Sedimentation involves falling particles which accelerate until their terminal velocity is reached. This speed depends on the density, gravitational acceleration, and aerosol diameter as well as the viscosity of the air. Calculated terminal velocities for rigid spheres of unit density in air are well documented (Israel and Israel, 1974). From these calculations and the observed particle diameter of aerosols from a wide range of sources (Lee et al., 1975) it is evident that sedimentation should be most important relatively close to major emission sources. Impaction involves processes of wind advection and turbulence wherein particles suspended in air are able to strike the surface of

vegetation, soil, or water. This mechanism is thus strongly dependent on meteorological conditions as well as the configuration of the depositional surface.

Chamberlain (1955), Chamberlain and Chadwick (1966), and Cawse and Peirson (1972) have used an expression relating deposition flux to the air concentration: $V_d = F/c$, where F = rate of dry deposition ($\text{ng}/\text{cm}^2/\text{sec}$), C = concentration in air above the depositional surface (ng/m^3), and V_d = deposition velocity (cm/sec). As discussed earlier, Slinn (1976) has recently presented a theoretical argument that dry deposition of "pollutant" materials to a forest from ground-based sources appears to be comparable in magnitude to wet deposition. Comparing the assumptions of Slinn's calculations ($V_d \approx 0.3\text{-}3 \text{ cm}/\text{sec}$) with some limited field data further emphasizes the potential importance of dry deposition to a forest canopy. Chamberlain (1953) estimated that the maximum deposition velocity due to impaction in a forest could be as high as $5 \text{ cm}/\text{sec}$. Cawse and Peirson (1972), however, measured V_d values for 29 elements to an artificial surface that averaged less than $0.38 \text{ cm}/\text{sec}$. In a more recent paper Cawse (1974) again determined deposition velocities for minor and major aerosol-associated elements at seven open field locations over a two-year period and found an overall range of 0.04 to $5.9 \text{ cm}/\text{sec}$ with interlocation variations for any single element of $\pm 86\%$ of the mean. Of importance in the work is the fact that all V_d values were determined utilizing an entirely artificial but reproducible surface (Whatman 541, $25 \times 20 \text{ cm}$ filter paper) that neither corresponded to any natural surface (soil, grass, or other

vegetation) nor to any other type of collection surface routinely in use by other researchers (e.g., Wong, HASL, or Finnish wet/dry deposition collectors). A similar experiment was performed by White and Turner (1970) over a woodland canopy. Using artificial collection discs at various locations and levels within a canopy the authors determined deposition velocities for major cations on a monthly basis. Mean values for 12 months varied from 3.0 to 7.1 cm/sec and indicated the increased potential of a forest system to scavenge aerosols.

The influence of meteorological conditions, particle size distribution, and surface characteristics on wet and dry deposition including particle impaction has been often discussed (Sehmel and Hodgson, 1974; Slinn, 1975 and 1976; Clough, 1973; Scriven and Fisher, 1975) but few measurements exist outside of wind tunnel experiments. Through the use of radioactively tagged spores and various inorganic particles Chamberlain (1970) studied the effects of surface characteristics and wind speed on particle transport to rough surfaces both in wind tunnel experiments and in the field over grassland areas. The author concluded the following: surface stickiness is important in controlling V_d for particles of $> 10 \mu\text{m}$ diameter while for particles of 1 to 5 μm deposition is dependent on the presence of micro-roughness on surfaces, and stickiness is no longer important; $V_d \approx V_s$ (terminal velocity) for very small wind speeds but at higher speeds deposition by impaction on roughness elements becomes progressively more important; and all surfaces are particularly efficient scavengers when wet. In a more recent paper Raynor et al. (1975) reported on the measured dispersion of pollens and spores from in-forest releases.

Their data indicated that deposition predominates over impaction in forest regimes and that most particles were lost to the foliage rather than the ground. However, the major shortcoming in these experiments was the choice of particles and associated size ranges. In both studies larger particles (10 to 50 μm range) were primarily used and, where smaller aerosols were included, no attempt was made to approximate previously measured particle size distributions.

Under the controlled conditions of a wind tunnel, Wedding et al. (1975) simulated Pb aerosol impaction onto vegetation with results that substantiated the above field measurements. However, the particles used were relatively uniform in size, $6.77 \pm 0.02 \mu\text{m}$ diameter, while various researchers have measured the mass median diameter of Pb in ambient air to be on the order of $0.45 \mu\text{m}$ with 50 to 90% of Pb particles in urban air less than $1 \mu\text{m}$ (NRC-NAS, 1971).

Actual field measurements of particle deposition onto various types of foliage have primarily involved whole leaf analyses, use of indicator species or artificial foliage, or analyses of leaf dislodgable residue. Schlesinger et al. (1974) compared total deposition of major cations by using artificial foliar and open-bucket collectors in a montane area of New England. Although limited, their data suggested that under conditions of high wind and frequent fog, interception contributed significantly to total elemental deposition. Little (1973) utilized leaf washing experiments to measure the effect of a local Pb and Zn smelter on trace element deposition. Results indicated a large fraction of the metal burden on leaves was readily removed as soluble (8% Pb, 13% Cd, and 27% Zn) or particulate (87% Pb,

62% Cd, and 67% Zn) material by distilled water. Although no attempt was made to relate the results to ambient air particulate data, the proximity of the area to the smelter suggests the particles involved were predominantly in larger size fractions than generally expected for these trace elements. In a recent study Sheline et al. (1975) analyzed samples of the epiphyte Tillandsia usenoides L. (Spanish moss) and compared the results to the composition of the ambient aerosol in forests as a function of particle size. Although absolute concentrations were not determined, elemental ratio comparisons between the aerosols and the moss suggested the following: moss composition approaches the composition of the aerosol group in the $> 5 \mu\text{m}$ size range for nine soil and pollution-derived elements; element enrichments in the moss relative to the ambient aerosol occurred for K, Ca and associated elements and not for pollution-derived elements; the moss may exhibit a particle uptake cutoff of $< 5 \mu\text{m}$ in diameter and can serve as an indicator of time average aerosol composition for large particle pollution-derived elements.

The purpose of this chapter is to describe the development and application of techniques to experimentally measure dry deposition in Walker Branch Watershed. A similar discussion concerning wet deposition is the topic of Chapter V while comparison of all input mechanisms on an annual scale is the subject of Chapter VII.

A General Consideration of the Problems Involved In
Measuring Dry Deposition to a Forested Canopy

The problems involved in field measurement of dry deposition have been considered in detail in two recent reviews (Galloway and Parker, 1978; Hosker and Lindberg, 1978). The determination of dry deposition onto natural surfaces presents particularly difficult problems. It is not a straightforward task to relate deposition on an artificial surface to that on living vegetation. With few exceptions most deposited particle collection devices currently in use detect primarily the fall of relatively large, sedimenting particles. Small particles and gases transferred via turbulence and deposited via impaction processes require different methods and techniques. For evaluation of the overall mass transfer to the forest canopy, there seems little alternative to the task of direct in-canopy sampling. Conventional methods involving artificial sampling devices such as open buckets, sheets of filter paper, or other exposed materials generally suffer not only from artificiality of the surfaces, but also from their common use at ground level. Deposition measurements using the above techniques are useful, however, for providing comparative data on relative temporal and spatial variability, but are less useful in estimating absolute mass transfer because of the different turbulent regime developed around the artificial surfaces compared to vegetation components (Munn and Bolin, 1971). These problems relate to the typical ground level bucket collector and may not apply to the use of artificial surfaces mounted in the canopy.

Many of the difficulties involved in the measurement of dry deposition are further confounded when trace elements are of interest. This is due to the generally lower trace element concentrations in the atmosphere, and hence transport to the atmosphere - canopy interface, and the well known problems of contamination in trace analysis. These constraints necessitate relatively long term sampling (days) to provide sufficient material for analysis. With the above constraints in mind the decision was made to develop and modify two previously, but only occasionally, applied techniques for the measurement of dry deposition. Basically these two methods involved the use of pre washed inert surfaces, in one case, and actively growing vegetation, in the second, to collect dry deposited material at the atmosphere-canopy interface. The use of both inert surfaces and growing leaves provides the critical comparison between artificial and vegetative surfaces recommended in the reviews discussed above (Galloway and Parker, 1978; Hosker and Lindberg, 1978).

Materials and Methods

Collection of Deposited Particles on Inert, Flat Surfaces in the Forest Canopy: Deposition Plates

The device used for the collection of dry deposition on an inert surface was a modification of the standard bucket technique (Volchok et al., 1974) and the teflon disc technique recently described by Elias et al. (1976). The standard bucket collector is complicated by several problems: (1) large side wall to bottom surface area ratio making the choice of true exposed surface area difficult, (2) considerable volumes

of solution are required for leaching the sample from the container, both increasing the chances of contamination while also diluting the sample, (3) the buckets are too large to be easily amenable to ultra clean laboratory procedures, and (4) the buckets are too bulky to be easily used in the tree canopy. The teflon disc technique is a far better choice but still has some problems: (1) heavy dew can cause wash-off of some deposited materials, and (2) the entire disc must be leached in the laboratory for complete removal of the deposited particles, thus also exposing the backside of the disc (which must be used to attach the disc to a mounting platform in the field) to the leachate solution. The choice in these experiments was polyethylene petri dishes, henceforth termed deposition plates. These dishes are inert, exhibit low background contamination during leaching, are amenable to several small scale laboratory leaching techniques, are small and lightweight (diameter = 9.3 cm), have a large bottom to side surface area ratio, yet have a large enough rim to prevent dew runoff even during moderate wind disturbance, are easily handled and mounted in the field without touching the deposition surface, and are readily available in large quantities.

The deposition plates were rigorously acid washed and rinsed with profuse amounts of double distilled water according to procedures described in Appendix A, covered with similarly cleaned petri dish cover, and sealed in polyethylene bags. Plates were handled during all procedures using polyethylene gloves. The plates were transferred to the field immediately prior to an experimental period and mounted in aluminum clamps which had been previously coated with polystyrene and

sprayed with a fluorocarbon coating. The deposition plates were mounted in the forest canopy around a mature chestnut oak (Quercus prinus) at the four cardinal directions at the approximate point of canopy closure, such that the plates were not covered by overhanging leaves but were within the framework of the vegetative canopy. The plates were attached to terminal branches in a horizontal position when the branches were at rest. A typical arrangement of the deposition plates is illustrated in Figure 16. The site used for the deposition plate collections was location T4 in Figure 20 (Chapter V), ~ 45 m NW of the meteorological tower described in the previous chapter. The general canopy type at this site is oak-hickory. The four deposition plates ranged in height from 16 to 18 m above the ground. In addition, deposition plates were also placed at two levels within the canopy of the same tree, one ~ 2/3 of the distance between the tree trunk and canopy edge beneath ~ 6 m of leaf canopy and 12 m above the ground, and the other ~ 1/3 of the distance between the trunk and canopy edge beneath ~ 10 m of leaf canopy and ~ 8 m above the ground. On selected occasions plates were also placed 1 m above the ground beneath this chestnut oak tree, and 48 m above the ground on top of the meteorological tower.

Deposition plates were used as described above during two experimental periods. The initial utilization was for long term collection during the preliminary field experimental and developmental stage of the research (7/76 - 4/77) when the plates were in place for periods ranging from 9 to 40 days. These periods included forest canopy conditions ranging from barren (12/76) to partial leaf opening

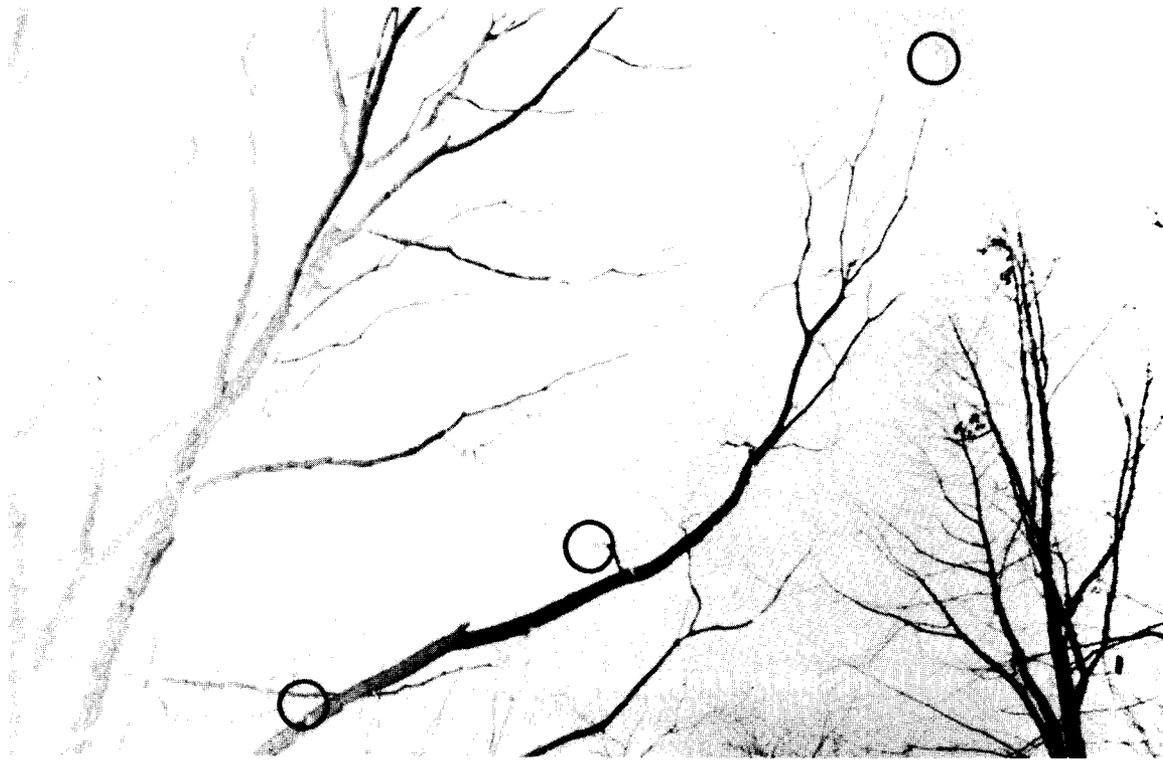


Fig. 16. Location of deposition plates (flat, inert surfaces) in the chestnut oak canopy. Top photo illustrates the positions (circled) of deposition plates in the upper, middle, and lower canopy. Lower photo shows the position of one upper canopy deposition plate during full canopy development.

(4/77) to maximum canopy development. The bulk of the deposition plate collections, however, were of a short term nature, corresponding to the intensive sampling periods during the growing season of 1977 described in detail in Chapter III. The deposition plates were in place during the ten experimental periods of aerosol sampling at the meteorological tower which ranged in duration from 4 to 7 days. At the end of each experimental period the plates were retrieved by hand, covered with a clean polypropylene lid, and sealed in plastic bags for transport to the laboratory. In the laboratory, the dishes were stored in sealed, pre cleaned dessicators, as described in Chapter III, prior to extraction (generally < 48 hours).

Deposition Plate Extraction and Efficiency of Extraction

The leaching of the deposition plates was done using a technique similar to that described in Chapter III for the aerosol samples. This was done to assure comparibility between the available element fractions and relative solubilities of the aerosols and deposited particles. The available element fraction is the sum of the water soluble plus dilute acid leachable fractions, using similar solid to solution ratios and acid concentrations as used for the aerosol filters. The overall extraction method involved the following:

- (1) distilled water extraction - 50 ml of 2XDW were added to each deposition plate, all work being done in the laminar flow clean bench and using polyethylene gloves; an acid washed and rinsed 2 cm teflon stirring bar was placed in each deposition plate and the petri dish cover replaced; the covered plates were then placed on a magnetic

stirring apparatus and stirred at moderate speed (a speed fast enough to keep particulate material in suspension but slow enough to allow the stirring bar to circulate around the full surface area of the deposition plate). Using this method up to four plates could be stacked on one magnetic stirrer. The circular "travelling" motion of the stir bar around the deposition plate was found to be very efficient in scraping deposited material from the plate and keeping it in suspension; this stirring continued for two hours after which time the solution was carefully decanted, using an acid washed funnel, into a pre-cleaned membrane filter apparatus and filtered through a 0.4 μm nuclepore polycarbonate membrane as described in Chapter III. The filtrate from the deposition plates at the four cardinal directions were occasionally analyzed separately, but generally composited. The water extractions were preserved until analysis with Ultrex ultra pure HNO_3 as described in Appendix A. (2) dilute acid leach procedure - the nuclepore membrane used to filter the water extract was placed into the now dry deposition plate after rinsing down the sides of the filter apparatus to insure collection of all particulate material; 50 ml of 0.08 N (pH = 1.1) Ultrex HNO_3 were added to each deposition plate, the lids replaced, and the plates stirred as above for an additional 2 hours after which time the plates were stored, still filled with the acid solution, in clean dessicators, in the dark, for 7 days. Following this period the samples were decanted into acid washed polyethylene bottles and held for analysis. During each set of extractions clean deposition plates were carried through the entire process to generate blanks for each step.

A similar set of experiments to those described for the aerosol filters in Chapter III were performed using the deposition plates. These involved collection of a series of sequential samples throughout the water extraction and dilute acid leach steps for a period of 10 days to determine the efficiency of the extraction procedure to remove the available metal fraction. Since similar experiments were described in detail in Chapter III (see Figure 2) only the pertinent results are summarized here. The time series patterns of trace element release during the two extractions of the deposition plates were very similar to those shown in Figure 2, although the absolute concentrations were not the same. The release of the water soluble fractions of Cd and Mn were ~ 100% complete after one hour (relative to 24 hours) while the amount of Pb and Zn in solution following 2 hours of water extraction were 87 and 91% of the quantity in solution at 24 hours. Following acidification, ~ 98 to 100% of the metals in solution after 10 days of leaching were in solution after 36 hours for Pb and after 3 to 4 days for Cd, Mn, and Zn.

As described in the previous chapter, selected samples were also exposed to additional dilute acid leaching and strong acid digestion. The results of an additional 1N acid leach can be best expressed as the ratio of the total metal removed by the water extraction and dilute acid leach plus 1N acid leach steps divided by the amount removed by the water plus dilute acid leach alone. These were as follows:
Cd = 1.04, Mn = 1.02, Pb = 1.24, Zn = 1.01. With the exception of Pb, the 1N acid leach removed an insignificant additional amount of each element. The results for Pb agree with those discussed in Chapter III

regarding the recovery of Pb from aerosol samples. The results of the additional wet acid digest can be similarly expressed as the ratio of the total metal concentration to the available metal concentration. These values were as follows: Cd = 8.6, Mn = 5.7, Pb = 8.1, Zn = 55. All of the elements were inefficiently extracted by the available metal extraction procedures, yielding 2% of the total Zn, 12% of the Cd and Pb, and 18% of the Mn. Comparing these values with those in Table 11, Chapter III for aerosols in several size classes suggests the possible predominance of larger particles in the deposition plates, a point which will be further considered this chapter. Recall that in the leaching experiments with the aerosols, the largest particles were least effectively leached by the distilled water and dilute acid steps.

Collection of Vegetation Components

Actively growing vegetation was sampled sequentially at specific locations over relatively short (days) and long (weeks) time periods with the intent of comparing the temporal variations in the quantity of material washed from a known surface area of leaves in the laboratory. Several techniques of leaf collection were attempted during the developmental phase of this research, including the use of Swedish portable climbing ladders to access tree tops, projectiles to shear young branches situated at the point of canopy closure, and extension pole pruners to remove outer canopy branches. These methods were used only on occasions during the initial year of sampling, at 9 of the 10 permanent collection sites across the watershed. These sites transected the watershed as illustrated in Figure 17. Each site

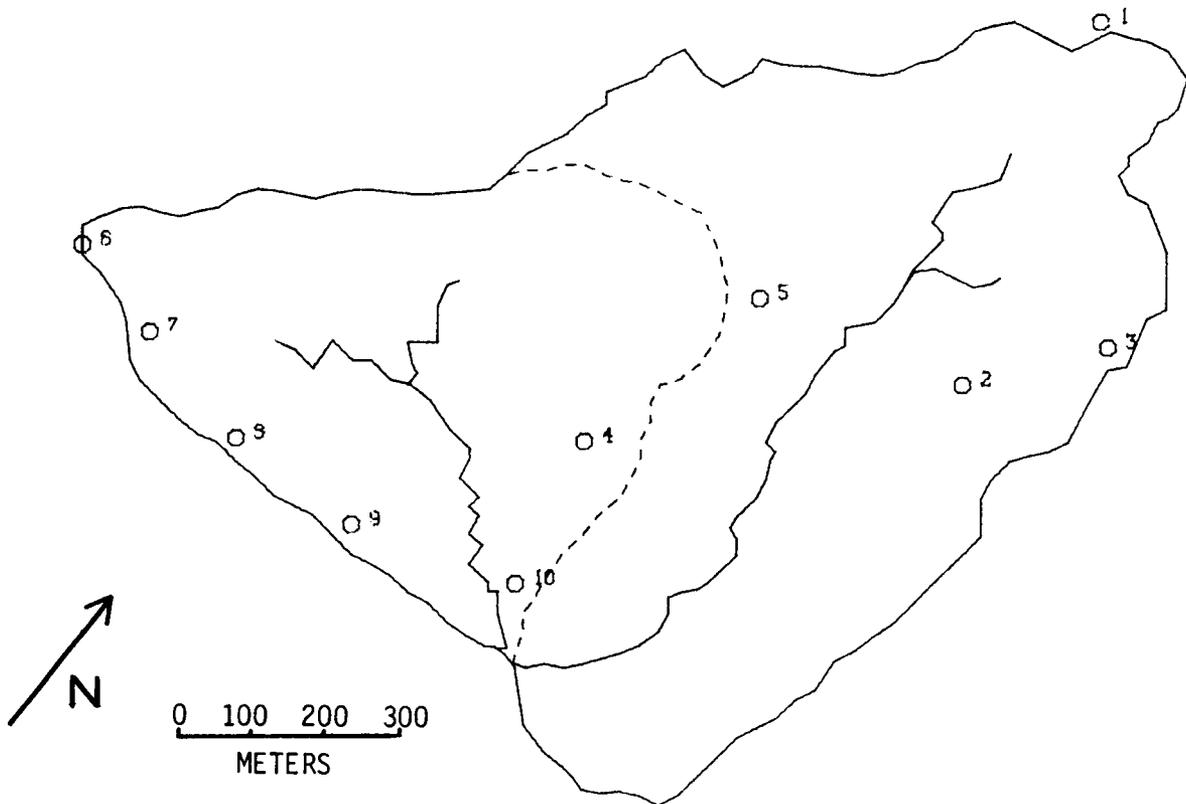


Fig. 17. Location of ten experimental plots for the collection of upper and lower canopy foliage of chestnut oak and mockernut hickory for analysis of leaf surface area concentration.

included a pair of plots containing one canopy dominant chestnut oak and one canopy dominant mockernut hickory (Carya tomentosa). These two species represent opposite extremes in surface texture, the oak having a smooth surface and the hickory having a pubescent surface. These species each represent ~ 20% of the total basal area of the watershed. Site 6 corresponds to site T4 discussed above, the site of the intensive deposition plate experiments. Because of the accessibility of the chestnut oak at this site, it was also chosen for several short term developmental experiments during the 1976 growing season.

The vegetation at site T4 was also sampled simultaneously with the deposition plate and aerosol collections during the intensive 10 week experimental period during the 1977 growing season. All leaf collections at the T4 site were done by hand using the following technique. At each predetermined location in the tree canopy (adjacent to the deposition plates when they were in use) leaves were removed by hand from the outer canopy immediately above the point of canopy closure using polyethylene gloves and handling the leaves only by the base of the stem. Four well-developed and undamaged (by abrasion, tears, insect grazing, or air pollution) leaves from each location were placed in 200-ml acid washed and rinsed (described in Appendix A) polyethylene bottles, the bottles capped and returned to the laboratory. Washing of the intact leaves (by methods described in the following section) was always begun immediately upon return to the laboratory (generally < 2 hours following collection).

During the initial period of the research another collection and washing technique was tested because it afforded a method of increasing

the sample size for each location: four branches of five or more leaves each were removed from each location in the canopy, and sealed in a clean polyethylene bag (this same sample handling procedure was utilized during mechanical collection of leaves at the 9 watershed transect plots). In the laboratory a single disc of 15 mm diameter was cut from the center base of each leaf and all 20 of the discs placed into a polyethylene bottle for washing. This method, although it afforded a "representative" sampling of 20 leaves at each canopy location, and hence 80 from the full sample of 4 cardinal directions, was abandoned for several reasons relating to contamination, excessive foliar leaching, and leaf surface heterogeneity.

Leaf Washing Experiments

Physical washing of leaves has been used in previous studies of pesticide residue on leaves (Gunther et al., 1974), fluoride toxicity to foliage (McHenry and Charles, 1961; Cook et al., 1976), and Pb particle mobility on vegetation surfaces (Carlson et al., 1976). The major problem of these techniques is maximization of surface deposit removal and minimization of internal leaf leaching. As described above an early attempt in this research involved washing of leaf discs so as to allow a larger, presumably more representative, sample size per analysis. This assumed that a disc cut from the center of a leaf was representative of the entire surface with respect to particle accumulation. This method suffered from two major problems:

(1) considerable scanning electron microscopy (SEM) of leaf surfaces indicated a large degree of heterogeneity in particle residence on the

surface of freshly collected leaves such that a 2 cm disc could be very non-representative of the surface as a whole (see Chapter VI), and (2) freshly cut discs were far more susceptible to internal cell leaching (as determined by dissolved organic carbon concentrations in the leaching solutions of whole leaves vs discs with the same surface area, as well as observation of both chlorophyll and a large quantity of leaf fragments in the disc washing solution).

The decision to wash whole leaves was followed by several experiments to determine optimum washing times, solution volumes, and volume to leaf surface area ratios. Briefly, these involved sequential collection and analysis of the leachate solution in a manner similar to the experiments previously described for aerosol filters and deposition plates, sequential gravimetric analysis of the dislodged particulate material, and microscopic examination of a series of leaves before and after washing by various procedures. The results of these experiments led to the following leaf washing techniques: (1) Water soluble fraction - immediately upon return from the field 100 ml of 2XDW was added to the four whole leaves collected in polypropylene bottles as described earlier; these bottles were capped, sealed in polyethylene bags, and secured in a reciprocating shaker. Following 1 hour of agitation at 240 oscillations per minute, another 100 ml of 2XDW was added to each bottle. Following an additional 1 hour of shaking, the bottles were removed and the solution decanted into a prewashed membrane filter apparatus and filtered through a 0.4 μ m Nuclepore membrane directly into an acid-washed polyethylene bottle as described earlier. The filtrate was acidified and stored for analysis at 4°C.

(2) Dilute acid leachate fraction - the leaves and bottle were rinsed with an additional 50 ml of 2XDW onto the filter used above, then the leaves were carefully removed and stored at 4°C for surface area determination or future SEM analysis (surface area was measured using a Lambda leaf-area-meter which operates on a light attenuation principle. With practice one can achieve a precision in leaf area determination of $\pm 5\%$). The membrane filter was placed into the original polypropylene washing bottle using teflon foreceps, and 50 ml of 0.08 N Ultrex HNO_3 were added. Thus, the leaves themselves were never exposed to the acid leaching step, rather only the particulate material which was removed from the leaf surfaces by the initial washing procedure was acid leached. This solution was agitated on the shaker for 2 hours to remove particulate material from the filter surface and the bottle stored in the dark in clean dessicators for 7 days. Following this period the samples were decanted into acid washed polyethylene bottles for analysis.

Using this method, tests of extraction efficiency yielded the following results. Sequential elemental analysis of the leachate indicated that after 2 hours $\sim 100\%$ of the soluble Cd and Mn and 90 to 95% of the soluble Pb and Zn were in solution (relative to the amount in solution after 24 hours). Addition of dilute acid to the particulate material removed from the leaf surface resulted in a rapid initial release of all metals such that $\sim 100\%$ of the Cd and Zn was in solution after 4 days, Mn after 2 days, and Pb after 36 hours (relative to the amount in solution after 10 days). The effectiveness of the agitation technique to remove deposited particulate material from leaf

surfaces was tested by two experiments. A series of sequential leaf washes were done wherein the same set of four leaves was washed in 200 ml of 2XDW as above but replacing the wash solution every 15 minutes. Each successive wash solution was filtered through a pre-weighed nuclepore 0.4 μm filter and the net weight per washing determined. On several occasions these experiments yielded similar results: $\sim 90\%$ by detectable weight (using a conventional balance with a readability of 10 μg) of the material removed after 3 hours of washing was removed during the first 30 minutes and $\sim 100\%$ during the first 90 minutes. Because of the relatively low resolution of this gravimetric analysis, particle removal was also studied using SEM. In some cases adjacent leaves were used and in other cases the same leaf was divided in half. In each case one sample was washed as usual, the other held as a control. These results must be considered as semi-quantitative at best since particle residence on the leaf surface is non uniform. Representative scanning electron photomicrographs are illustrated in Figure 18 for two locations on the leaf surface. Photos A (after washing) and B (before) are 200X magnification of the surfaces near the leaf base adjacent to the vein while C (after washing) and D (before) are 50X magnifications of the vein at mid leaf. It was apparent that the washing procedure was removing some material from the results presented above. This is also indicated by the photographs. However, there always remained some fraction of the original particle load lodged in crevices of the leaf surface generally near the central vein. For this reason the material removed during the washing

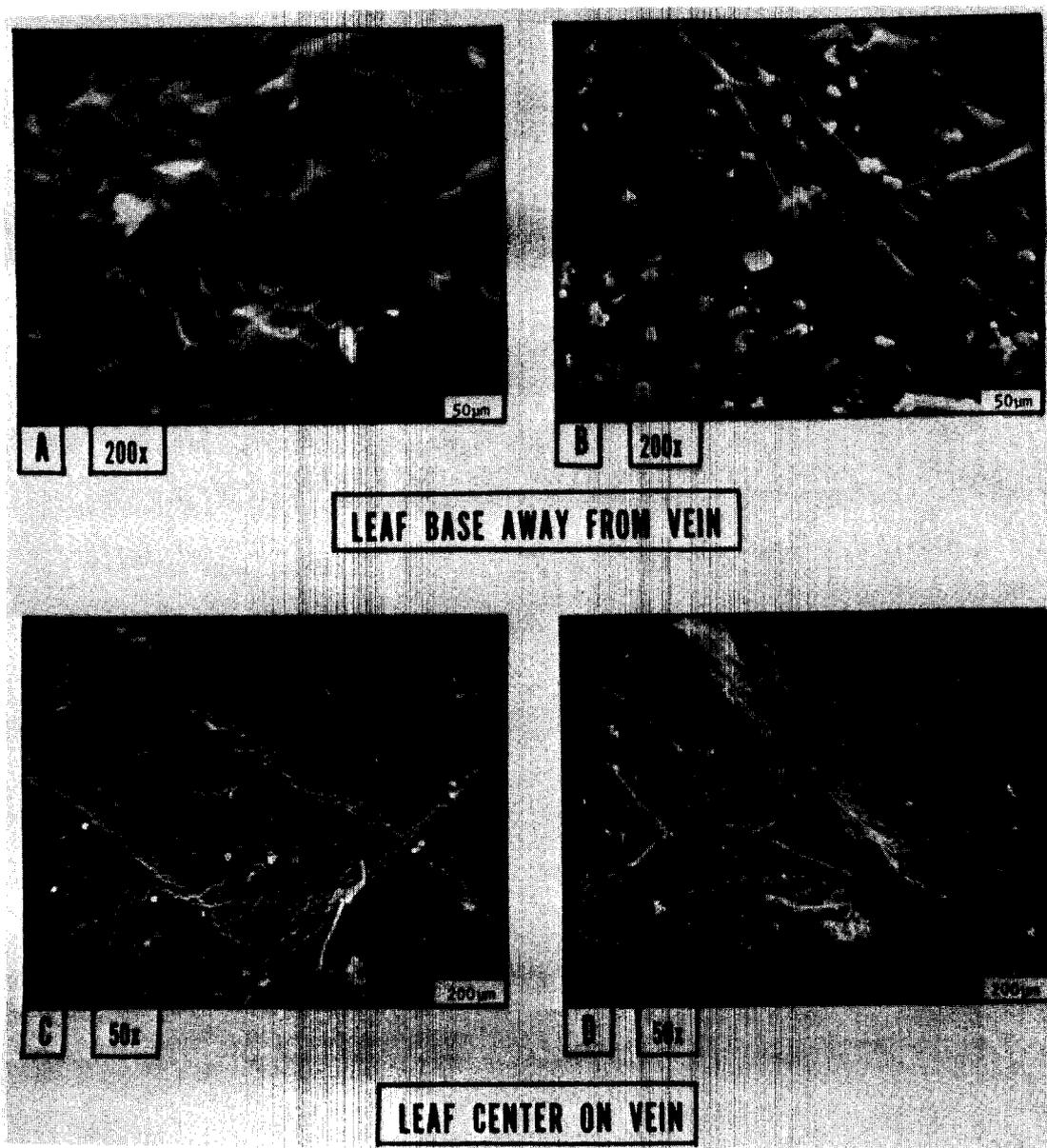


Fig. 18. Scanning electron photomicrographs of washed (A and C) and unwashed (B and D) chestnut oak leaf surfaces .

procedure must be operationally defined as the water soluble plus loosely bound particulate fraction.

Analytical Methods and Precision

The analytical techniques employed in this phase of the research were identical to those used in the aerosol experiments. These were briefly described in Chapter III and are considered in detail in Appendix A.

Precision, determined from replicate analyses of the same sample were $\pm 4\%$ for $\text{SO}_4^{=}$ in deposition plate leachate and $\pm 8\%$ for $\text{SO}_4^{=}$ in leaf wash. The increased organic content of the leaf wash solutions was responsible for the poorer precision of these analyses (discussed in Appendix A). The actual precision of any trace element analysis is related to the concentration range encountered, as follows: concentrations of $> 1 \mu\text{g/l}$, precision of replicate injections into the graphite furnace = 4 to 10% (this range included 100% of all Mn analyses, $\sim 50\%$ of Pb and Zn, and none of the Cd analyses); concentrations between 0.1 to 1.0 $\mu\text{g/l}$, precision 10 to 15% ($\sim 15\%$ of Cd analyses, $\sim 50\%$ of Pb and Zn analyses); concentration range $< 0.1 \mu\text{g/l}$, precision = 20 to 25% (includes $\sim 85\%$ of all Cd analyses). Because of the nature of these samples it is difficult to determine an overall procedural precision for field collection and analysis. However, samples of leaf wash from one extraction were occasionally split into three replicates and filtered and analyzed separately. Because of the extra steps involved in filtration, these samples would be expected to illustrate maximum values for the overall precision of

the extraction and analytical procedures. The result of typical experiments were as follows: (mean extraction concentrations \pm standard deviation) Cd = 0.20 ± 0.005 $\mu\text{g/l}$, Mn = 130 ± 38 $\mu\text{g/l}$, Pb = 0.23 ± 0.07 $\mu\text{g/l}$, Zn = 2.2 ± 1.1 $\mu\text{g/l}$, $\text{SO}_4^{=}$ = 1.4 ± 0.3 mg/l ; these result in precisions of 20% for Cd, 30% for Mn, 30% for Pb, 50% for Zn, and 20% for $\text{SO}_4^{=}$. The non filtered, dilute acid leachable fraction in all cases exhibited better overall reproductivity, generally 15 to 20% for Cd, 10 to 15% for the other constituents. In addition, when the above experiments were repeated for the apparently less complex matrix of the deposition plate leachate the overall reproductibility was on the order of 10 to 15% for all constituents.

Results and Discussion

Preliminary Vegetation Experiments

The Problem of Spatial Heterogeniety

In any research involving the collection and analysis of living vegetation, variability must be accepted as a natural phenomenon. The analysis of leaf wash solution is no exception. The preliminary phases of the research involved several experiments to determine the degree of variability on both large and small spatial scales for the leaf surface-area concentrations of Cd, Mn, Pb, Zn, and $\text{SO}_4^{=}$. These included the following: watershed wide intersite variability ($n = 10$, see Figure 17) in the surface-area concentration associated with upper canopy leaves of the chestnut oak and mockernut hickory and subcanopy leaves of the chestnut oak; variability in surface-area concentrations of chestnut oak leaves collected at 8 equally spaced compass orientations around

the same tree; variability in surface-area concentrations for chestnut oak leaves collected at different heights above the ground in the same tree; variability in surface area concentrations for chestnut oak leaves collected from adjacent positions in the same tree; and variability in surface-area concentrations associated with various locations on a leaf.

Beginning with the smallest spatial scale, surface-area concentrations were determined for discs cut from four locations on a leaf (collected 5/24/76): leaf tip, base (just above stem, including central vein), midrib (center of leaf, including central vein), and margin (leaf edge, away from vein). The mean whole leaf surface-area concentrations and coefficients of variation were calculated from the four samples as follows: Cd = $0.45 \mu\text{g}/\text{m}^2 \pm 110\%$, Mn = $1.13 \text{ mg}/\text{m}^2 \pm 15\%$, Pb = $76 \mu\text{g}/\text{m}^2 \pm 51\%$, Zn = $32 \mu\text{g}/\text{m}^2 \pm 110\%$, $\text{SO}_4^- = 265 \text{ mg}/\text{m}^2 \pm 19\%$. It is apparent that the elements fall into two groups, those with coefficients of variation $< 20\%$ and those $> 50\%$. The two elements exhibiting the smallest degree of variability, Mn and SO_4^- , are both micronutrients known to exist in the leaf tissue in an available, and hence leachable, form (see the discussion in Chapter V). Thus, the relative importance of internal leaf vs external surface-deposited sources of these elements in the leaf wash solution might be inferred from this data. This is a point of considerable interest if throughfall, collected by precipitation filtering through the canopy (the field analogy to laboratory leaf washing, see Chapter V), is to be used to estimate dry deposition. The

nonuniformity of surface deposited elements is related to the differences in leaf micro-surface characteristics as related to position (i.e., the abundance of leaf hairs in some areas, or the larger surface crevisses associated with veinations). This is visible to some extent in the photographs in Figure 18, and has been illustrated and discussed in detail in the review edited by Preece and Dickinson (1971). These irregularities in surface topography are known to influence the efficiency of a leaf surface to retain deposited particulate material (e.g., see the review by Hosker and Lindberg, 1978). Another reason for aerial variability of surface deposited elements relates to the effectiveness of leaf moisture layers (dew, light rain) to mobilize surface deposited material causing it to collect in concave areas on the leaf surface (i.e., cup-shaped depressions). During two years of leaf sampling it became apparent that this was a very important mechanism in controlling the distribution of particulate material on the leaf surface. Depressions near the base and tip of the leaves were often visibly discolored as if material were collected and deposited by the surface tension at the edge of an evaporating water droplet. Examination of the discolored areas by light microscopy indicated considerably heavier concentrations of particles, including large fly ash and soil fragments (20-80 μm diameter), relative to the rest of the leaf.

The pattern of surface-area concentration on the leaf reflected this phenomenon. All 5 elements occurred with the highest surface area concentration at the leaf tip ($\text{Cd} = 1.1 \mu\text{g}/\text{m}^2$, $\text{Mn} = 1.2 \text{mg}/\text{m}^2$, $\text{Pb} = 120 \mu\text{g}/\text{m}^2$, $\text{Zn} = 82 \mu\text{g}/\text{m}^2$, and $\text{SO}_4 = 320 \text{mg}/\text{m}^2$; compare

with the whole leaf average concentrations above) followed generally by base or midrib concentrations, with the lowest concentrations consistently measured at the leaf margin ($Cd = 0.04 \mu\text{g}/\text{m}^2$, $Mn = 0.97 \text{ mg}/\text{m}^2$, $Pb = 47 \mu\text{g}/\text{m}^2$, $Zn = 4 \mu\text{g}/\text{m}^2$, and $SO_4^{=} = 200 \text{ mg}/\text{m}^2$). The fact that even the possibly internal source elements Mn and $SO_4^{=}$, exhibit these patterns suggest that some surface deposited material contributes to the leaf wash concentration of these elements, but that both elements are influenced by a relatively large and constant internal source. These experiments illustrate two important points: (1) extrapolation of leaf disc surface area concentrations to whole leaf surface area concentrations can over or under estimate the surface area concentrations of some elements by a considerable amount, and (2) patterns in concentration variations from different areas of a single leaf surface may be useful in determining the extent to which an element is leached internally from the leaf or externally from surface deposited particles.

The remaining experiments all involved collection of intact leaves over spatial scales ranging from a few meters to hundreds of meters. The collections within the same tree were made at location 6 and involved adjacent leaves on the same branch, leaves growing at 8 heights above the ground, and leaves growing at 8 directions around the tree. The large scale collections were done across the watershed at the 10 sites illustrated in Figure 17 and included chestnut oak and hickory upper canopy leaves and chestnut oak subcanopy leaves. Since the major purpose of these experiments was to determine spatial variability on different scales, all of the data is summarized in

Table 14. Also, included for comparison are the leaf position variabilities just discussed, as well as variability for one set of whole leaves collected during the intensive sampling experiments during the 1977 growing season using the collection, washing, and analytical technique of final choice (as described earlier).

Manganese and $\text{SO}_4^{=}$ again stand out as exhibiting considerably less variability than the other elements, the coefficient of variation (CV) of Mn ranging from 15 to 55%, generally increasing with spatial scale, and the CV of $\text{SO}_4^{=}$ ranging from 15 to 35% with no clear trend. This lends further support to a large internal leaf source for these elements. There are few clear trends in the CV of Cd, Pb, or Zn although Cd and Zn were generally more variable than Pb. Two important points should be made concerning this data. It is clear that the sample collected in 1977 from the four cardinal directions on the same tree, using the techniques of ultimate choice, is characterized by some of the lowest CV. It is gratifying that the technique developed following the initial year's work and used throughout 1977 resulted in less variability in the surface area concentrations. This may be related to the larger number of leaves composited per sample and the use of only whole leaves in the washing technique. The second point is that the spatial variability in surface area concentrations is comparable over a wide range of scale (mm to ~ 0.1 km). Thus, from the standpoint of assessing temporal changes, the following points are apparent: (1) samples may be collected over a relatively small spatial scale (single tree), thus allowing for a more intensive sampling effort, and still yielding surface area concentrations comparable to

Table 14. Variability of leaf surface-area concentrations of the available fraction of sulfate and trace metals over a range of spatial scales. Shown are mean surface area concentrations, standard deviations, and coefficients of variation.

Sample	Spatial Scale	Surface area concentrations ($\bar{X} \pm \sigma$, C.V.)				
		Cd ($\mu\text{g}/\text{m}^2$)	Mn (mg/m^2)	Pb ($\mu\text{g}/\text{m}^2$)	Zn ($\mu\text{g}/\text{m}^2$)	SO_4 (mg/m^2)
<u>SAME TREE (chestnut oak)</u>						
Positions on one leaf ^a	mm	0.45±0.50 110%	1.13±0.17 15%	76±39 50%	32±35 110%	265±49 20%
Adjacent leaves ^b	cm	3.0 ±3.5 115%	0.91±0.12 15%	180±92 50%	19±16 80%	120±29 25%
Different heights ^c	m	0.96±1.0 110%	1.5 ±0.4 25%	6.0±8.5 130%	370±480 140%	166±43 25%
Different compass directions ^d	m	0.55±0.64 120%	2.3 ±0.7 30%	17±30 175%	260±550 220%	328±75 25%
Four cardinal directions ^e	m	0.35±0.20 60%	1.5 ±0.6 40%	10±3 30%	15±5 35%	17±4 25%
<u>DIFFERENT TREES (10 sites)</u>						
Chestnut oak, canopy ^f	~0.1km	0.86±0.90 105%	3.7 ±2.0 55%	210±130 60%	170±350 205%	155±35 25%
Hickory, canopy ^f	~0.1km	0.50±0.57 115%	9.8 ±4.2 45%	380±400 105%	40±48 120%	140±48 35%
Chestnut oak, subcanopy ^f	~0.1km	3.4 ±9.9 290%	2.1 ±0.9 45%	130±50 40%	54±51 95%	90±14 15%

^aCollected 5/24/76, site 8.

^bCollected 6/17/76, site 6.

^cCollected 7/6/76, site 6.

^dCollected 6/14/76, site 6.

^eCollected 10/17/77, site 6.

^fCollected 10/11/76, all sites.

those collected on a larger scale, and (2) temporal variations in surface area concentrations must be quite large to result in meaningful calculations of net changes in surface area concentrations. Related to this second point, it is useful to compare the spatial variability in surface area concentrations measured at the four cardinal directions of the chestnut oak at location 6 during 1977 with the temporal variability in leaf surface-area concentrations measured at the same tree during the intensive sampling period from 5/9/77 to 10/24/77. The temporal variability in leaf surface-area concentrations for 23 sets of samples collected at site 6 during this period were as follows: Cd $0.28 \pm 0.42 \mu\text{g}/\text{m}^2$, CV = 150%; Mn $0.54 \pm 0.32 \mu\text{g}/\text{m}^2$, CV = 60%; Pb $7.1 \pm 6.2 \mu\text{g}/\text{m}^2$, CV = 85%; Zn $24 \pm 61 \mu\text{g}/\text{m}^2$, CV = 250%; SO_4^- $49 \pm 55 \text{mg}/\text{m}^2$, CV = 115% (compare with the values in Table 14). In each case it is apparent that the temporal variability in surface area concentrations exceeded the spatial variability at the same site, satisfying the above condition.

Although the experiments designed to collect the data in Table 14 were intended primarily to develop the optimum foliage sampling technique, they did provide some other interesting results. This data has been presented elsewhere (Lindberg et al., 1976) and will be only briefly discussed here. Although leaf surface area concentrations measured at any one point in time are not directly related to dry deposition rates, they provide some insight into deposition processes. For example, the patterns of surface-area concentrations with height above ground indicate higher concentrations of each element at the outer canopy within 2 m of the tree top. Lead and Cd also exhibit high

concentrations on leaves in the inner canopy ~ 13 m below the tree top. This suggests that the initial point of contact between aerosols and surfaces at the canopy - atmosphere interface is a point of accumulation of deposited particles. The secondary concentration peaks at the canopy base may be due to particle resuspension from upper canopy elements both by wind and canopy drip followed by recapture at the canopy base.

The distribution of surface-area concentrations on leaves collected at 10 sites across the watershed showed no consistent patterns. Despite the location of one sampling site much nearer the closest coal fired power plant (within 2.4 km) there was no apparent affect on the leaf surface-area concentrations at this location. There were, however, some consistent trends between the sample types. Understory chestnut oak leaves exhibited generally lower surface-area concentrations of all elements relative to both upper canopy chestnut oak and hickory leaves for samples collected near the beginning (5/24/76) and end (10/11/76) of the growing season. The highest surface-area concentrations were expected to be associated with the more pubescent hickory leaves because of the greater surface roughness (as reviewed in Hosker and Lindberg, 1978). This was true in the case of Mn for samples collected during the early, mid, and late growing season, but surface area concentrations of $\text{SO}_4^{=}$ were consistently lower for hickory compared to upper canopy chestnut oak during these periods. However, the concentrations of Cd, Pb, and Zn were highly variable between the two species, showing no consistent trends. The fact that the species differences were apparent only for the two

essential elements Mn and $\text{SO}_4^{=}$ again suggests the possibility that these two elements are derived primarily from internal processes, the concentration differences being related to physiological differences. The surface-area concentrations of elements believed to be primarily of external origin did not indicate the presence of more material on the "hairy" hickory leaves relative to the smooth chestnut oak leaves.

The Problem of Internal Leaf Leaching

The use of washing procedures with living vegetation to estimate dry deposition is obviously subject to the problem of foliar leaching. The work of Tukey (1970) and several others (see the discussion in Chapter V) suggests that leaching of elements from within the leaf requires little more than a cursory wetting of the leaf surface. This was emphasized in the recent review by Galloway and Parker (1978) who stated that experiments involving leaf surface washing must include strict controls on internal leaching. This problem is expected to be most severe in the case of elements with a known biological role and hence a higher tissue concentration and often a higher internal mobility. As discussed in Chapter V the total concentration of the elements of interest were determined in pre-washed chestnut oak leaves as occurring in the following order of abundance: $\text{SO}_4^{=}$ >> Mn >> Zn >> Pb > Cd. As expected the micronutrients are present in the highest concentrations. Although little data exists concerning Zn mobility, $\text{SO}_4^{=}$ and Mn are known to exist in relatively mobile forms in leaf tissue and are regarded as easily leached elements (see the discussion in Chapter V).

There are other lines of evidence indicating that the concentrations of Mn and $\text{SO}_4^{=}$ in leaf wash solutions reflect primarily internal sources in addition to some external surface deposited material while Pb appears to arise primarily from surface material. Zinc and Cd likely have an important source both internal and external to the leaf. Recall that the spatial variabilities discussed above (Table 14) indicated Mn and $\text{SO}_4^{=}$ to exhibit the lowest coefficients of variation for surface area concentrations over small and large spatial scales. The lack of any significant difference between different positions on a leaf suggests any spatial trends in surface deposition to be "smoothed out" by a relatively large, less variable internal source. In another preliminary experiment, six sets of adjacent chestnut oak leaves were collected at site 6 and washed using the disc method in one case and the whole leaf method in another. The discs were cut from several portions of each leaf to assure a representative sampling of the whole leaf area. Elements subject to internal leaching are expected to be lost more readily from freshly cut leaf surfaces, such as the discs, than from whole, intact leaves. The analysis of the wash solutions indicated the following: Pb was somewhat, but not significantly, higher in the whole leaf solutions; Cd and Zn were higher in the disc wash solution by a factor of ~ 2 ; Mn and $\text{SO}_4^{=}$ were both an order of magnitude higher in the disc wash solutions ($\text{Mn} = 3.2 \pm 0.2 \text{ mg/m}^2$, $\text{SO}_4^{=} = 120 \pm 20 \text{ mg/m}^2$) than in the whole leaf leachate ($\text{Mn} = 0.24 \pm 0.03 \text{ mg/m}^2$, $\text{SO}_4^{=} = 13 \pm 6 \text{ mg/m}^2$).

The method of calculating deposition from washings of sequentially collected leaves circumvents the internal leaching problem to some extent since deposition is calculated as the net difference between surface area concentrations at two points in time:

$$DR_L = (LSAC_2 - LSAC_1)/\Delta t,$$

where DR_L = deposition rate to the leaf surface, $LSAC_1$ = initial leaf surface area concentration, $LSAC_2$ = final leaf surface area concentration, and Δt is the interval between leaf collections, resulting in typical units of $\mu\text{g}/\text{m}^2$ day. If leaf collections are made over relatively short time intervals the assumptions of stable internal leaching levels may be valid. However there is considerable data in the literature which indicates that several major and some minor elements show either a steady increase or decrease in leaf concentration and leaching on a monthly time scale during the growing season (see the discussion in Chapter V), making the use of the above equation over longer time scales tenuous.

Since a similar consideration of the variability in leaf concentrations and leaching of trace constituents on a shorter time scale (4 to 7 days) apparently does not exist in the literature, an experiment was designed to develop an internal leaching control. This involved artificially isolating branches of leaves, left intact on the tree which was being sampled sequentially. A set of leaf samples was collected and washed on 10/12/77. At the same time small branches at the four cardinal directions were sealed in large polyethylene bags in such a manner that several leaves were centered in the enclosure away

from the bag edges. The reasons for performing this experiment late in the growing season were two-fold: (1) it is during this period in leaf development that changes in internal leaching of cations are most apparent as discussed in Chapter V, and (2) elevated temperature and relative humidity and depleted CO_2 within sealed bags of living leaves are known to adversely affect leaf physiology; thus this experiment was done under optimum atmospheric conditions in an attempt to minimize any adverse effects. The experimental period was characterized by relatively low temperatures, overcast skies, and calm winds. By isolating these leaves, the assumption is that at the time of the subsequent collection any changes in leaf surface-area concentrations would be due to change in internal leaching alone since dry deposition had been excluded. Thus, on 10/15 the bagged leaves were collected and washed along with another set of exposed leaves. The results were as follows: exposed leaves collected on 10/12, $\text{Cd} = 0.14 \mu\text{g}/\text{m}^2$, $\text{Mn} = 0.66 \text{ mg}/\text{m}^2$, $\text{Pb} = 5.2 \mu\text{g}/\text{m}^2$, $\text{Zn} = 6.9 \text{ g}/\text{m}^2$, $\text{SO}_4^{=}$ = $6.7 \text{ mg}/\text{m}^2$ (composited samples from each direction); leaves bagged on 10/12 and collected 10/15, $\text{Cd} = 0.34 \mu\text{g}/\text{m}^2$, $\text{Mn} = 0.56 \text{ mg}/\text{m}^2$, $\text{Pb} = 4.8 \mu\text{g}/\text{m}^2$, $\text{Zn} = 6.4 \mu\text{g}/\text{m}^2$, $\text{SO}_4^{=}$ = $7.5 \text{ mg}/\text{m}^2$, and exposed leaves collected on 10/15 - $\text{Cd} = 0.35 \mu\text{g}/\text{m}^2$, $\text{Mn} = 1.5 \text{ mg}/\text{m}^2$, $\text{Pb} = 10 \mu\text{g}/\text{m}^2$, $\text{Zn} = 15 \mu\text{g}/\text{m}^2$, $\text{SO}_4^{=}$ = $17 \text{ mg}/\text{m}^2$. The agreement in surface-area concentrations between the exposed leaves collected 10/12 and the leaves bagged on 10/12 and collected 10/15 was quite good with the concentrations of Mn, Pb, Zn, and $\text{SO}_4^{=}$ in the protected leaves within 7 to 15% of the levels measured prior to enclosure. However,

the concentration of Cd increased by a factor of ~ 2.5 , apparently due to internal leaching. The surface-area concentrations measured for the leaves exposed from 10/12 - 10/15 were detectably higher than both of the control levels, by factors of 2 to 2.5 for Mn, Pb, Zn, and SO_4^- . However, the surface-area concentration of Cd was essentially the same as that measured for the bagged leaves, again suggesting an increase in internal leaching as the primary cause. The results of this set of leaf collections could be used to estimate the increase in surface-area concentrations of SO_4^- , Mn, Pb, and Zn attributed to deposition. However, the data for Cd suggests no deposition could be detected. The assumption that large changes in internal leaf leaching do not occur over periods of a few days is supported by this experiment for the elements Mn, Pb, Zn, and SO_4^- .

The Calculation of Atmospheric Deposition Rates: Some Operational Definitions and Limitations

The initial assumption for using leaf leaching data to calculate atmospheric deposition rates is that the washing technique is relatively efficient in removing surface deposited material. This is probably valid for relatively large, easily dislodgeable particles, but not necessarily for fine particles retained in leaf crevices. On the other hand, trace metals associated with these smaller particles occur in relatively soluble forms, as discussed in Chapter III, and may be efficiently removed even though some residual, insoluble material is retained by the leaf surface.

Deposition rates calculated from the measured increase in leaf surface area concentrations over a given period of time may, in some

cases, reflect a change in internal leaching as well. This is particularly true if time intervals between leaf collections are long. The data discussed above suggest this could be a problem with Cd on a short time scale as well. In addition, the leaf washing technique may be less useful with the essential elements, which have a large internal pool, than with metabolically inactive trace elements. Manganese and $\text{SO}_4^{=}$, for example, may be leached from the leaves to such a degree as to make difficult the detection of a small increment in surface-area concentration due to atmospheric deposition over short collection intervals.

Because of the constraints of analytical sensitivity, it is often necessary to compromise short sampling duration for sample quantity. When sampling over the period of a few days, the deposition surface (flat plate or leaf) is subject to variable atmospheric phenomena. The sample obtained at the end of this period is the integration of several processes which act to both deliver material to and remove it from the surface. These processes include dry deposition of particles by impaction and sedimentation mechanisms, dry deposition and uptake of gases by adsorption and absorption mechanisms, wet deposition and precipitation washoff, and particle resuspension. The comparison of flat, inert collection surfaces with leaf surfaces is complicated by the non-comparability in surface microstructure, electric charge, wettability, chemical dynamics, and associated micrometeorological boundary layer resistance.

In the following discussion the deposition rates measured by the sequential leaf washing and deposition plate techniques will be

discussed and compared in detail using the data collected during the intensive 10 weeks of experimentation described in Chapter III. For the above reasons and for the sake of clarity and simplicity in the following discussions several operational definitions will be used. The available metal fraction of ambient aerosols and the associated relative solubility were defined in Chapter III. These terms retain their meaning when applied to deposited material. In addition, the following definitions will be applied to deposition determined by various means: (1) net leaf retention (NLR) is the net change in leaf surface area concentration of an element divided by the interval between sample collections. A positive value of NLR calculated during a period of no recorded precipitation is attributed to dry deposition and is equivalent to a dry deposition rate. Similarly a negative value measured during a dry period represents element absorption by the leaf or particle resuspension loss. Values of NLR calculated during wet periods represent either total deposition retention (wet and dry) if positive, or material wash-off if negative, and (2) deposition plate retention (DPR) is the blank corrected surface-area concentration in the exposed plate divided by the exposure time. Only positive values (or values below the detection limit) of DPR can occur. These are interpreted in a similar manner to the NLR values above depending on atmospheric conditions during the sampling period.

Estimation of Atmospheric Deposition to Biological Receptors

As part of the intensive sampling during the 1977 growing season, upper canopy chestnut oak leaves were collected at 5- to 10-day

intervals as discussed previously. Deposition rates were calculated as the net change in leaf surface-area concentration divided by the collection interval. Since several of the sampling periods included both wet and dry deposition many of the calculated net changes in concentration were negative, presumably indicating element loss due to surface wash-off during rain. These values were not included in the analysis of net retention rates, although it should be clear to the reader from the plots of temporal variations in leaf surface-area concentrations (Figure 19), during which periods net losses were recorded. Because of the need to collect leaves at the initiation and end of each experimental period it was also possible to estimate leaf retention rates for intervals between experimental periods. Thus, there were actually 21 periods for which leaf deposition could be estimated, comprising 22 leaf collections from 5/9/77 to 10/24/77. In addition to period W1, one other period was sampled during which no rain occurred (10/17-10/24).

The temporal variations in the leaf surface area concentrations for each of the elements are illustrated in Figure 19. Also illustrated are the daily total precipitation volumes. It is apparent from the plots that processes influencing leaf surface area concentrations do not affect all of the elements similarly. Cadmium and Zn exhibit the most similar behavior with several of the fluctuations in Pb concentrations following the same pattern. Variations in Mn concentration are similar to the above mentioned elements only during a few experimental periods while variations in $\text{SO}_4^{=}$ concentrations are considerably different from the other

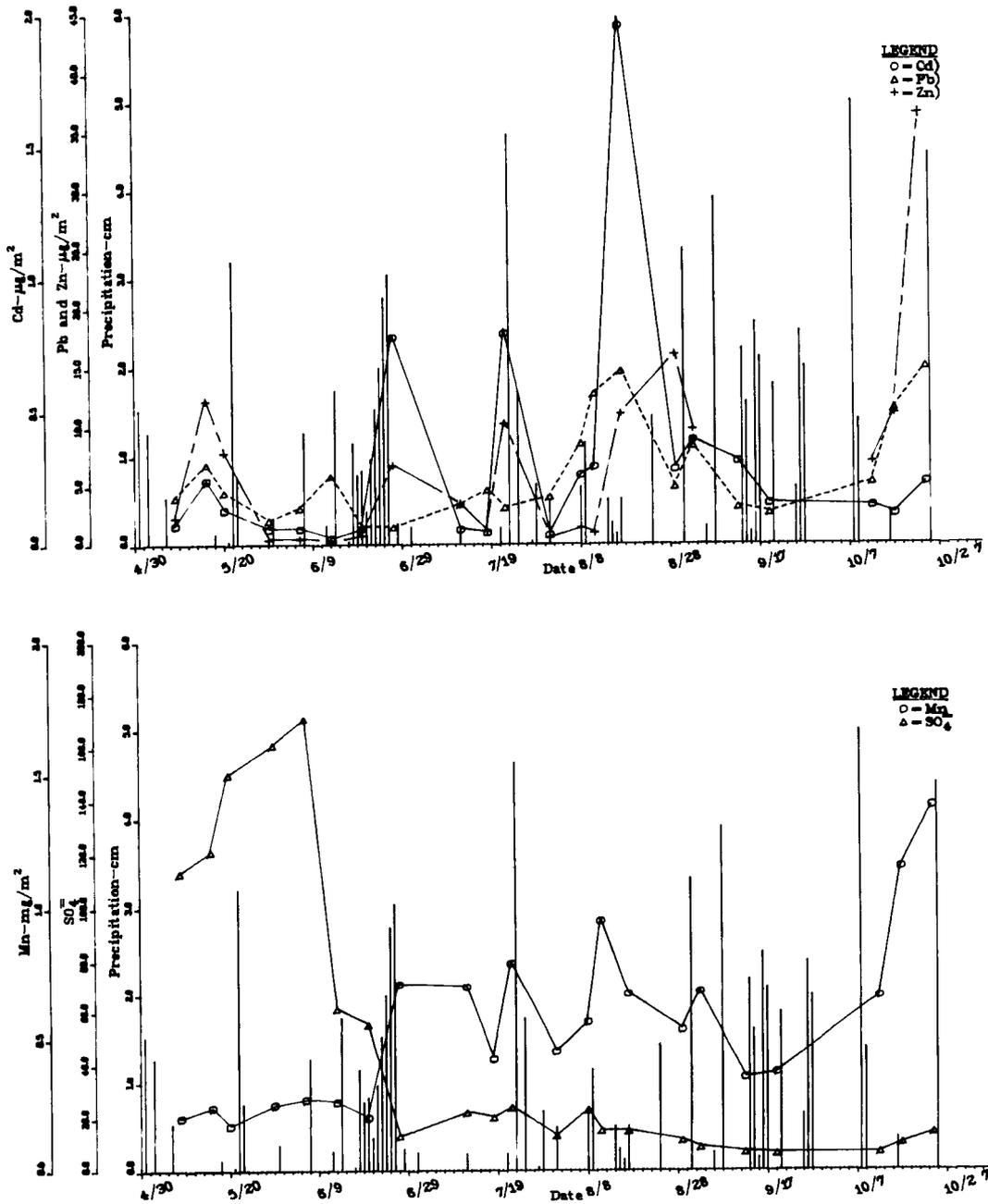


Fig. 19. Temporal variations in leaf surface area concentrations of the available fractions of Cd, Pb, and Zn (top graph), and Mn and sulfate (bottom graph), and daily rainfall volume during the intensive experimental period of the 1977 growing season.

elements studied. For example, the surface-area concentrations of all elements increased during the dry period from 5/9-5/16 and all but SO_4^- decreased during the following week, although only a brief shower was recorded. Cadmium, Pb, and Zn continued to decrease during the following week which included a relatively large storm while Mn and SO_4^- increased. During the next few weeks the concentrations of Mn, Cd, and Zn remained relatively constant while Pb peaked and decreased and SO_4^- decreased considerably. Despite the variability, several trends are apparent in the behavior of each element. Concentration peaks were recorded for all elements during the early growing season, during mid July, mid August, and again at the end of the growing season. Manganese surface-area concentrations were characterized by a general increase throughout the growing season toward peaks just prior to leaf-fall. On the other hand, SO_4^- exhibited a clear peak in concentration during the early growing season then decreased sharply to a relatively constant value.

The behavior of both Mn and SO_4^- concentrations with time may be indicative of strong internal sources. The pattern of variations in Mn concentrations may be divided into two additive curves. One is a general increase in leachable Mn during the growing season while the other is composed of a series of shorter term peaks in surface-area concentration presumably related to wet and dry deposition and surface washing by rain. The increase in leachability during the growing season has been reported for several nutrient elements, with leachability generally highest during leaf senescence (see the discussion in Chapter V). In addition, Guha and Mitchell (1965) have

documented the seasonal changes in trace element content of leaves from three deciduous species. Manganese was described as generally showing a continuous increase in concentration until near the end of the growing season, similar to Ca and Mg. For an element as leachable as Mn (see the discussion in Chapter V) an increase in whole leaf concentration would be expected to result in a similar increase in surface-area concentrations if the primary source to the leaf surface is internal leaching.

The variation in $\text{SO}_4^{=}$ concentrations over the growing season is different from those of the other elements. The concentration of $\text{SO}_4^{=}$ washed from the leaf surface increased consistently during the first 30 days of sampling to a peak concentration in early June then decreased sharply over the following 21 days remaining relatively constant or decreasing slightly during the remainder of the growing season. This relatively well defined behavior was also reflected in the net leaching of $\text{SO}_4^{=}$ by precipitation passing through the forest canopy, as discussed in detail in Chapter V. Unfortunately, the work by Guha and Mitchell (1965) did not include analysis of temporal variations of $\text{SO}_4^{=}$ concentrations. However, Carlisle et al. (1966) found exceptionally high leaching of P from leaves during the weeks directly following leaf emergence as compared to the remainder of the growing season, with no peak in leaching during leaf senescence as seen for many elements. The data of Guha and Mitchell (1965) for P in leaf tissue indicated a similar pattern of P concentration. Since sulfur and phosphorous are closely related in plant systems one might infer

internal sulfur leaching to behave similarly. Turner et al. (1977) recently studied the relationship between N and S in foliage of Douglas Fir. Because of the known biochemical relationship between N and S in protein and the necessity for adequate foliar $\text{SO}_4^{=}$ concentrations for N utilization, any S in excess of that required to balance N was found to be accumulated as inorganic $\text{SO}_4^{=}$. Thus, it is possible that during the early growing season when maximum leaf growth occurs, S and N are actively accumulated with any excess S available for leaching as $\text{SO}_4^{=}$. As growth diminishes, active uptake decreases resulting in less leachable $\text{SO}_4^{=}$. The obvious complication with this explanation is the additional influence of dry deposition. The period during which $\text{SO}_4^{=}$ surface-area concentrations were increasing were characterized by high atmospheric suspended loads, frequent air stagnation, and some of the highest total aerosol $\text{SO}_4^{=}$ concentrations measured (see Chapter III, Table 3). In addition, these periods were also characterized by the highest deposition plate retention rates measured. Thus, it is likely that the temporal variation in the surface-area concentration of $\text{SO}_4^{=}$ is the end result of both internal and external processes at the leaf surface.

Guha and Mitchell (1965) also analyzed the variation in Pb and Zn concentrations in whole leaves during the growing season. The concentration of Pb decreased rapidly from May to June and then increased gradually toward the end of the growing season with a somewhat more rapid increase during leaf senescence. The measured variations in Pb surface-area concentrations in chestnut oak leaves (Figure 19) did not behave similarly except perhaps near the end of the

growing season. Guha and Mitchell found the concentration of Zn to behave differently among the 3 species studied. In beech leaves the concentration was relatively constant throughout the growing season while the concentration in horse chestnut and sycamore leaves decreased gradually during the early growing season but increased considerably during October. Again the surface-area concentrations in chestnut oak leaves collected in WBW exhibited a similar change only at the end of the growing season. If the results of Guha and Mitchell's research are any indication of trace element behavior in other deciduous species, they suggest that the shorter term variations in surface area concentrations of Pb and Zn may be attributed to surface deposition, although this assumption may be questionable when applied to periods near the end of the growing season.

The positive net leaf retention values calculated for sequential differences in leaf surface area concentrations are summarized in Table 15 along with the amount of precipitation recorded per period. As in the case of the deposition plate measurements, only two periods were sampled during which no precipitation was recorded, and thus provide estimates of dry deposition alone (W1, W13; at the beginning and end of the growing season respectively). One of these corresponds to a period during which deposition plates were also in use W1. A comparison of leaf and inert surface deposition be considered at the end of this chapter. The deposition rates of Cd and Pb differed by < 25% between the two periods (W1 and W13) lending some support to the relatively small effect of internal leaching on the surface area concentration of these two elements. On the other hand the deposition

Table 15. Net retention rates for upper canopy chestnut oak leaves determined from sequential surface area concentrations.

Period	Dates (1977)	Precipitation volume (cm)	Net retention rate ($\mu\text{g}/\text{m}^2\text{-day}$)					SO_4
			Cd	Mn	Pb	Zn		
W1	5/ 9- 5/16	0	0.024	6.8	0.4	1.4	1300	
W2	5/16- 5/20	0.13					7000	
W3	5/20- 5/30	4.02		8.3			1000	
W4	5/30- 6/6	0.30	0.003	2.4	0.96	0.014	1500	
	6/ 6- 6/13	1.50			0.39			
W5	6/13- 6/20	4.26	0.005	73		0.075		
	6/20 -6/27	11.60	0.10			0.84		
	6/27 -7/12	0.46			0.13		620	
W6	7/12- 7/18	0.20			0.20			
W7	7/18- 7/22	0.20	0.25	118		2.6		
	7/22- 8/1	7.59						
W8	8/ 1- 8/8	0.11	0.032	15	0.09			
	8/ 8- 8/11	1.80	0.012	137	0.63	0.12	1400	
W9	8/11- 8/17	1.40	0.28		1.5			
	8/17- 8/29	2.56			0.31	1.7		
W10	8/29- 9/2	2.92	0.028	39	0.89	0.39		
	9/ 2- 9/12	4.12						
W11	9/12- 9/19	8.41		3.2				
	9/19-10/12	13.22		12	0.11			
W12	10/12-10/17	0.38		97	1.2	0.82	680	
	10/17-10/24	0	0.018	32	0.50	4.2	590	

rate of Mn was ~ 4.7 times higher during W13 than W1, some of the increase possibly due to increased internal leaching during leaf senescence. Similarly the calculated dry deposition rate of Zn increased by a factor of ~ 3 for perhaps the same reason. The dry deposition rate of $\text{SO}_4^=$ was within a factor of ~ 2 of the rate during W1 but was lower. The reason for the difference may be the same since $\text{SO}_4^=$ leaching is apparently higher during the early growing season.

When the leaf retention rates were paired with the meteorological and air quality parameters discussed in Chapter III for each of these periods no significant correlations were found. The only consistent trends in the data were indicated by positive correlation coefficients between net leaf retention and total air concentration of each element (ranging from $r = 0.07$ for Mn to $r = 0.89$ for $\text{SO}_4^=$). However, it is apparent that accumulation rates of all elements but Zn are highest during periods of some measurable precipitation. The highest measured retention rates of Cd, Mn, and Pb occurred during periods with 1 to 2 cm of precipitation, while the highest value for $\text{SO}_4^=$ occurred during W2 which included a brief shower of 0.13 cm. It is also apparent from the time series plots of leaf surface-area concentration that precipitation events do not always result in a net decrease in surface-area concentrations. There were occasions during the 1977 growing season where the same rain event was accompanied by an increase in the concentration of some elements and a decrease in others, while other events resulted in entirely different changes, further emphasizing the complexity of the leaf surface - atmosphere interaction.

Deposition of Trace Metals and Sulfate
to Inert Surfaces at the Canopy-Atmosphere
Interface: Short Term Intensive Sampling Experiments

As discussed in detail in Chapter III a series of 10 experiments of 4 to 7 days duration were performed during the 1977 growing season during which, in addition to the aerosol collections and solubility experiments previously discussed, both leaf and deposition plate collections were performed. Samples were extracted and analyzed for available element concentrations, and relative solubilities were determined. Several samples were examined in detail with both light and scanning electron microscopy to estimate particle size ranges for comparison with ambient aerosols. The comparison of physical and geochemical properties of suspended, deposited, and precipitation scavenged materials is the topic of Chapter VI.

Variations in Deposition Plate Retention

Since the decision in the planning of the deposition experiments was to work in the field under ambient conditions it was expected that precipitation would occur on some occasions before the deposition plates could be retrieved. Thus, some fraction of the collected material would represent wet deposition, the amount of which could be estimated based on incident precipitation chemistry. Of the 12 experimental periods (2 were aborted due to electric power loss at the field site related to storm activity) only one (W1) was completed during a period of no recorded precipitation. Another 5 periods (W2, 3, 6, 7, 12) were characterized by single storm events with amounts < 30% of the depth of the deposition plates (~ 1.4 cm) while the

remainder (W4, 5, 9, 11) included precipitation amounts greater than or equal to the deposition plate depth (precipitation volume/plate depth ratios ranged from 1.0 to 8.3). Thus, one experiment is a useful indication of dry deposition alone, 5 include wet plus dry deposition but small enough quantities of wetfall such that no deposition plate overflow occurred (splash-off may be a problem, however), while the remaining 4 were dominated by wet deposition to such an extent that plate overflow occurred. Any deposition rates estimated from these last four periods must be considered in light of the operational definitions discussed above as being a measure of net deposition plate retention and do not warrant rigorous analysis. Because of the possibility of rain-drop splash the periods of intermediate wetfall amounts should perhaps also be interpreted with some restraint. This is especially true if the storm was relatively intense and occurred near the end of the sampling period. Of these 5 periods two (W7 and W12) were characterized by somewhat more intense storms which occurred late in the sampling period. Periods W3 and W6 included early, less intense storms, while period W2 included one event of relatively low intensity which occurred at the approximate midpoint of the sampling interval.

The quantity of material captured and retained by the deposition plates at several locations is summarized in Table 16 for the 10 experimental periods. The deposition plate retention is expressed in terms of the mean rate of accumulation on the deposition plate over the full sampling interval, normalized to unit surface area and time, in other words in terms of a deposition rate. These values are raw data,

Table 16. Deposition plate retention of the available metal and sulfate fraction at various locations sampled during each of the 10 intensive sampling periods. Also indicated are the precipitation characteristics of each period.

Period	Precipitation Volume (cm)	Location of Deposition Plates	Deposition plate retention				
			Cd	Mn	Pb ($\mu\text{g}/\text{m}^2\text{-day}$)	Zn	$\text{SO}_4^{=}$
W1	0	UC ^a	0.034±0.014 ^b	15±5	3.7±0.6	2.0±2.0	900±110
W2	0.13	LC ^c	0.047±0.011	24±4	3.3±0.3	1.4±0.9	1200±400
		UC	0.29 ^d	37	16	3.2	8700
W3	0.30	LC	0.19	140	18	2.4	9800
		UC	0.20	51	6.2	1.6	4300
W4	1.50	LC	0.07	62	7.1	1.4	4700
		UC	0.16	40	10	0.29	2300
W5	11.60	LC	0.028	73	16	1.6	4300
		UC	0.10	1.9	6.7	0.20	780
W6	0.20	LC	0.030	5.9	4.2	0.02	670
		UC	0.069	22	6.3	1.8	3100
W7	0.20	LC	0.056	80	8.1	2.3	4600
		FF ^e	0.150	270	8.3	13	8000
		TT ^f	0.069	7.0	8.4	0.97	2100
		UC	0.085	6.1	5.4	0.94	1200
W9	1.40	LC	0.10	120	16	2.2	3000
		FF	0.15	230	20	10	6200
		TT	0.066	3.9	9.6	0.82	1200
		UC	0.23	6.8	5.5	9.9	1900
W11	8.41	LC	0.51	102	9.3	28	2400
		FF	0.55	132	8.7	45	5700
		TT	0.23	1.1	3.6	4.5	1100
		UC	0.090	2.5	2.6	3.6	620
W12	0.38	LC	0.095	25	9.2	7.3	1900
		FF	0.085	32	5.6	8.6	3000
		TT	0.059	1.4	4.1	4.1	830
		UC	0.081	5.9	3.8	3.9	1300
		LC	0.14	40	9.1	8.2	1400
		FF	0.12	50	7.8	29	2400
		TT	0.052	4.9	5.7	1.9	1000

^aUC = upper canopy.

^b $\bar{x} \pm \sigma$, n=4.

^cLC = lower canopy.

^dComposite analysis of deposition plates at four cardinal directions.

^eFF = forest floor.

^fTT = tower top (meteorological tower, 23 m above the forest canopy).

not "corrected" for any possible wetfall input. Also indicated are the precipitation amounts measured during each period. Note that during W1 the deposition plates were analyzed separately rather than being composited to provide some indication of spatial variability while during the remaining periods the samples were composited. When the standard deviations for the W1 data are expressed relative to the means, the resulting coefficients of variation for upper and lower canopy plates are as follows: Cd 25-40, Mn 20-35, Pb 10-15, Zn 65-100, and $\text{SO}_4^{=}$ 10-35. The deposition plate values are generally lower those for the leaf surface area concentrations discussed above. Once again the point is that for temporal differences to be meaningful they must be on the same order as the degree of spatial variability.

It is apparent from the data in Table 16 that the temporal variations are in general large, in many cases ranging over an order of magnitude for samples collected at any one location. For further comparison the data is summarized in Table 17 in groups of experiments during which deposition plates were used in various locations. Because of the problems concerning large rainfall volume, the periods W4, W5, W9, and W11 were eliminated from the data set. Thus, upper and lower canopy accumulation rates can be compared for all remaining experiments (i.e., W1, 2, 3, 6, 7, and 12), while upper, lower, forest floor, and above canopy can be compared for periods W6, W7, and W12. Differences in deposition measured at the various deposition plate locations may provide some insight into the processes controlling element accumulation on the inert surfaces. For the full data set a

Table 17. Statistical summary of deposition plate retention of the available metal and sulfate fraction for various sampling locations. Shown are mean values, $\pm \sigma$.

Location of deposition plates	Periods averaged	Deposition plate retention ($\mu\text{g}/\text{m}^2\text{-day}$)				
		Cd	Mn	Pb	Zn	SO_4^-
Upper canopy	W1,2,3,6,7,12	0.13 \pm 0.10	23 \pm 18	6.9 \pm 4.6	2.2 \pm 1.1	3200 \pm 3000
Lower canopy	W1,2,3,6,7,12	0.10 \pm 0.05	78 \pm 45	10 \pm 6	3.0 \pm 2.6	4100 \pm 3200
Tower top	W6,7,12	0.06 \pm 0.01	5.3 \pm 1.6	7.9 \pm 2.0	1.2 \pm 0.6	1400 \pm 600
Upper canopy	W6,7,12	0.08 \pm 0.01	11 \pm 9.2	5.2 \pm 1.3	2.2 \pm 1.5	1900 \pm 1100
Lower canopy	W6,7,12	0.10 \pm 0.04	80 \pm 40	11 \pm 4	4.2 \pm 3.4	3000 \pm 1600
Forest floor	W6,7,12	0.14 \pm 0.02	180 \pm 120	12 \pm 7	17 \pm 10	5500 \pm 2800

non-parametric test was applied to test for significance of the difference between the accumulation rates in the upper and lower canopy. Wilcoxon's distribution-free signed rank test (Hollander and Wolfe, 1973) was applied to the following null hypothesis: H_0 , the difference between the lower and upper canopy accumulation rates ($LC-UC = \theta$) is such that $\theta > 0$, implying higher accumulation rates in lower canopy samples. The results of the tests indicate that the null hypothesis could not be rejected for Mn, Pb, and SO_4^{2-} , but could be rejected for Cd and Zn.

The greater accumulation rate of Mn, Pb, and SO_4^{2-} in the lower canopy can be related to a number of possible explanations: the primary particle source may be ground level soil dust resuspension; particle resuspension from upper canopy elements may result in accumulation on lower canopy elements; or external particle washoff and internal element leaching from upper canopy leaves may transport more material to the lower canopy. The first mechanism is unlikely in a forest landscape because of the limited areas of exposed soil and the attenuation of turbulent mixing near the forest floor because of the presence of the canopy. Some indication of the relative influence of the latter two processes can be seen from the ratios of lower canopy to upper canopy accumulation rates during periods with different quantities of precipitation. During the dry period (W1), the lower to upper canopy ratios are > 1 for Cd, Mn, and SO_4^{2-} and < 1 for Pb and Zn but all values are within 40% of 1.0 except for Mn (1.6). For the wet periods both the quantity of precipitation and time of the event had an effect on the ratios. These ratios are summarized in Table 18

Table 18. Ratios of lower canopy (LC) to upper canopy (UC) accumulation rates measured with inert surfaces (deposition plates).

Period	Precipitation		Deposition plate retention ratio (LC/UC)				
	Volume	Occurrence ^a	Cd	Mn	Pb	Zn	SO ₄ ⁼
1	0 cm	---	1.4	1.6	0.9	0.7	1.3
6	0.3	0.01	0.8	3.6	1.3	1.3	1.5
3	0.3	0.18	0.4	1.2	1.1	0.9	1.1
2	0.13	0.64	0.7	3.8	1.1	0.8	1.1
12	0.38	0.72	1.7	6.8	3.2	3.0	10.8
7	0.20	0.82	1.2	20	3.0	2.3	2.5

^aRelative time of occurrence of precipitation event, expressed as interval from initiation of sampling to the precipitation event ÷ total duration of sampling period.

with the volume of rain per period and the relative time of occurrence of the rain event. It is clear from the variability in the data that several processes must be influencing the relative quantity of material retained by each deposition plate. There does appear to be a trend of increasing lower/upper canopy ratios as the relative time of occurrence of the rain event increases. This suggests that precipitation washing of upper canopy leaves is more important in regulating the downward flux of material through the forest canopy than is turbulent resuspension from upper canopy elements and recapture by lower canopy elements during dry periods. This agrees with results of laboratory and wind tunnel experiments reported by Carlson et al. (1976) for Pb particles on plant leaves. Assuming a ratio of ≥ 2 to be significant (since many of the coefficients of variation are ~ 50 to 100%) the accumulation of Pb, Zn, and $\text{SO}_4^{=}$ are significantly increased on deposition plate surfaces in the lower canopy only during W7 and W12 when the precipitation was preceded by relatively long dry periods (~ 70 -80% of the sampling duration). A similar situation exists for Mn, although the ratios during W6 and W2 are anomalously high. There are no clear relationships between precipitation volume and lower/upper canopy retention ratios, indicating that element removal from leaves proceeds rapidly following initial wetting of the surfaces. This has been previously reported by Tukey et al. (1965) for elements leached internally and by Carlson et al. (1976) for micron sized Pb particles deposited on leaf surfaces. The lower/upper canopy ratios for Cd indicate a relatively small effect of the removal of upper canopy deposited material during wet or dry periods. Since this is true even

during periods W7 and W12, which experienced precipitation late in the sampling period, it suggests that dry deposition is relatively unimportant in the total deposition of Cd. This point is considered further in Chapter VII.

The effect of an increased number of upper canopy elements on below canopy accumulation can be seen in the data in Table 17 for the three experimental periods when deposition was also measured at the tower site above the canopy and on the forest floor at site 6. The accumulation rates of all elements follow a trend of increasing from upper canopy to lower canopy to forest floor, or as depth of canopy elements over the deposition plates increases. However, the accumulation rates of Pb show little additional increase from lower canopy to forest floor.

Also presented in Table 17 are the accumulation rates measured at the tower top, ~ 23 m above the forest canopy. This location is of interest for two reasons; it is far removed from any canopy element influence such as splash off from adjacent leaves, and is in a generally more accessible location. If accumulation rates are comparable with those measured at the canopy-atmosphere interface, it would allow the approach to be more easily utilized at other forested sites where towers are often available and more accessible than the equipment necessary for intensive upper canopy sampling. As indicated in Table 17 the accumulation rates are in fairly good agreement. Because of the variability, they are more easily compared as the mean above canopy/upper canopy ratio for the 5 experimental periods as follows: Cd = 0.81 ± 0.18 , Mn = 0.50 ± 0.26 , Pb = 1.4 ± 0.4 ,

$Zn = 0.84 \pm 0.37$, $SO_4^{2-} = 0.87 \pm 0.30$. The two methods appear surprisingly comparable for all elements. The ratios are significantly different from 1 only for Mn, but the somewhat lower values for Cd, Zn, and SO_4^{2-} , as well as Mn, may indicate a leaf splash effect for these elements at the upper canopy location. The fact that Mn is most susceptible to this problem, as evidenced by the factor of ~ 2 difference, agrees with the high leachability of this element from chestnut oak leaves. The reason for the higher rate of Pb accumulation in the above canopy deposition plates is unknown.

Some indication of the parameters influencing upper canopy deposition plate accumulation rates can be seen by comparing the deposition plate retention data in Table 16 with the meteorological and atmospheric conditions characterizing each of the experimental periods as summarized in Table 3, Chapter III. Bulk deposition rates might be expected to correlate with precipitation amount and atmospheric particle load (TSP). Since both wet and dry deposition were involved during all of the experimental periods except W1, this period was not included in the analysis. Correlation coefficients were determined for the relationships between deposition plate accumulation rates and precipitation volume and TSP. Although none of the correlation coefficients with rain volume were significant, they were all negative indicating more efficient cleansing of the deposition surface or dilution of the deposited material during large storms. However, when the two periods of considerable quantities of rain (W5, W11) were removed from the data set, the recomputed correlation coefficients were positive or within 5% of zero on the negative side. Thus, it is

difficult to define any strong trends between precipitation volume and deposition plate retention. The correlation coefficients with TSP concentration were positive and significant ($P \leq 0.05$) for Cd, Pb, and $\text{SO}_4^=$, but insignificant for Mn and Zn. Thus, all of the atmospheric conditions related to increased TSP loads, discussed in Chapter III, also result in increased deposition plate retention. These parameters include precipitation amount and duration, atmospheric stability, and frequency of air stagnation events. However, except for $\text{SO}_4^=$, the deposition plate accumulation rates are not simply related to the total elemental concentrations in the air. The correlation coefficients between elemental concentration in the total aerosol fraction and deposition plate retention were all positive and insignificant for Cd, Pb, Mn, and Zn, but highly significant for $\text{SO}_4^=$ ($P \leq 0.01$). This high correlation coefficient is a reflection of the fact that $\text{SO}_4^=$ is a major, and relatively constant, component of the total aerosol load ($\text{SO}_4^=/\text{TSP}$ ranging from 0.22 to 0.31).

Dry Deposition to Upper Canopy Elements

As discussed above only period W1 of the intensive experiments was completed without the complication of precipitation. However, for certain of the remaining periods it was possible to subtract the wet deposition input from the measured deposition plate retention to yield the input due to dry deposition alone. Thus, average daily dry deposition rates were calculated as follows:

$$DDR = \frac{SAC_{DP} - (C_{IP} \cdot V_{IP})}{t} ,$$

where DDR = dry deposition rate in $\mu\text{g}/\text{m}^2\text{day}$, SAC_{DP} = surface area concentration of an element retained in the dry deposition plate at the end of the sampling period in $\mu\text{g}/\text{m}^2$, C_{IP} = concentration of the element in incident precipitation in $\mu\text{g}/\text{l}$, V_{IP} = volume of incident precipitation occurring in mm, Δt = duration of sampling period in days. Wet deposition was sampled above the canopy at the meteorological tower using automatic wetfall only collectors described in detail in Chapter V. The data required for these calculations and the resulting dry deposition rates are summarized in Table 19 for periods W1, 2, 3, 6 and one preliminary experiment of relatively short duration (W0, 8.8 days). Although there were two other experimental periods with moderate amounts of rain (W7, W12), these storm events were somewhat more intense and occurred near the end of the experimental period. When the deposition plate net retention rates for these two periods were corrected for wetfall input, negative values resulted for some elements. Since this suggested significant splash-off removal during these events, this data was not included in this analysis.

A statistical summary of the dry deposition rates of both the available element fraction and water soluble fraction is presented in Table 20. The mean deposition rates for the water soluble fraction are based only on the two deposition experiments during which no precipitation was recorded, since the material deposited during wetfall was characterized by an unknown, but presumable high, relative

Table 19. Dry deposition rates of available metal and sulfate fractions determined from deposition plate surface area concentrations

Period	Constituent	Deposition plate surface area concentration ^a ($\mu\text{g}/\text{m}^2$)	Precipitation amount (cm)	Incident precipitation concentration ($\mu\text{g}/\ell$)	Total wet deposition ^b ($\mu\text{g}/\text{m}^2$)	Dry deposition ^c ($\mu\text{g}/\text{m}^2$)	Dry deposition rated ($\mu\text{g}/\text{m}^2\text{-day}$)
W0 ^e	Cd	1.1	0	---	0	1.1	0.12
W1		0.24	0	---	0	0.24	0.034
W2		1.2	0.13	0.35	0.46	0.74	0.18
W3		1.4	0.30	0.45	1.35	0.05	0.006
W6		0.41	0.20	0.15	0.30	0.11	0.019
W0	Mn	120	0	---	0	120	14
W1		100	0	---	0	100	15
W2		150	0.13	24	31	120	29
W3		360	0.30	12	36	320	46
W6		130	0.20	3.8	7.6	120	21
W0	Pb	47	0	---	0	47	5.3
W1		26	0	---	0	26	3.7
W2		67	0.13	3.1	4.0	63	15
W3		43	0.30	7.7	23	20	2.9
W6		38	0.20	2.1	4.2	34	5.7
W0	Zn	8.8	0	---	0	8.8	1.0
W1		14	0	---	0	14	2.0
W2		13	0.13	2.9	3.8	9.2	2.3
W3		11	0.30	1.9	5.7	5.3	0.78
W6		11	0.20	3.1	6.2	4.8	0.77
W0	SO_4	8500	0	---	0	8500	970
W1		6200	0	---	0	6200	900
W2		36000	0.13	16000	21000	15000	3700
W3		30000	0.30	8600	26000	4000	600
W6		19000	0.20	5700	11000	8000	1200

^aSurface area concentration of the available metal fraction of the particulate material retained in the deposition plate following exposure in the field.

^bWet deposition = precipitation volume (mm) \cdot precipitation concentration ($\mu\text{g}/\ell$).

^cCalculated as the difference between deposition plate retention and wet deposition.

^dDry deposition measured for the full experimental period \div duration of experiment.

^ePeriod W0 was a preliminary experiment from 4/4 - 4/13/77, duration = 8.8 days.

Table 20. Statistical summary of experimentally measured dry deposition rates of water soluble and available metal fractions to upper canopy inert surfaces^a.

Statistic	Dry deposition rate ($\mu\text{g}/\text{m}^2\text{-day}$)				
	Cd	Mn	Pb	Zn	$\text{SO}_4^{=}$
	Available fraction ^b				
Mean	0.072	25	6.5	1.4	1500
Standard deviation	0.075	13	4.9	0.73	1300
Minimum	0.006	14	2.9	0.77	600
Maximum	0.18	46	15	2.3	3700
Coefficient of variation (%)	104	52	75	52	86
	Water soluble fraction ^c				
Mean	0.053	10	1.1	0.94	1500

^aPeriods W 0, 1, 2, 3, 6.

^bAvailable fraction = water soluble plus dilute acid leachable.

^cPeriods during which no precipitation was recorded, W0 and W1 only.

solubility which could not be factored into these calculations. Over the 5 periods sampled the variability in deposition rates of Mn and Zn were surprisingly low, with coefficients of variation $\approx 50\%$. Any conclusions regarding the variations in Zn dry deposition rates between the 5 experimental periods must be considered tenuous since the single tree spatial variability in dry deposition rates measured during W1 (Table 16) actually exceeded the temporal variability over the 5 periods.

The temporal variability of the dry deposition rate of Mn was somewhat larger than the single tree spatial variability, while for the remaining elements the temporal variabilities were considerably larger than the spatial variabilities. The dry deposition rate of $\text{SO}_4^=$ was considerably higher than those of the trace constituents as would be predicted from the air concentrations (Chapter III). The relative order of dry deposition input was $\text{SO}_4^= \gg \text{Mn} > \text{Pb} > \text{Zn} \gg \text{Cd}$ in the ratio of 21000 : 350 : 90 : 20 : 1. This does not reflect the relative abundance of these elements in the total aerosol fraction which was as follows: $\text{SO}_4^= \gg \text{Pb} > \text{Mn} > \text{Zn} \gg \text{Cd}$ in the ratio of 86000 : 740 : 55 : 30 : 1. However the relative order of input does coincide with the atmospheric abundance of these elements in the largest particle size class sampled (class 1, aerodynamic diameter ~ 7 to $8 \mu\text{m}$), which occurred in the following order and relative abundance: $\text{SO}_4^= = 13000 \gg \text{Mn} = 85 > \text{Pb} = 50 > \text{Zn} = 20 > \text{Cd} = 1$. The abundance ratios for $\text{SO}_4^=$, Pb and Zn in dry deposition agree to within $\sim 40\%$ of these values. The relative input of Mn is ≈ 4 times higher than its large particle atmospheric abundance would indicate, however. This could

be related to the capture of internally cycled organic material (frass) by the deposition plates, the leaching of which would be expected to release relatively more Mn than the other elements of interest. However deposition plates obviously contaminated with leaf fragments were either excluded from the leaching procedure or, if possible, the organic material removed prior to leaching. A more probable explanation is that the atmospheric concentration of Mn in the large particle mode was underestimated by the Andersen cascade impactor. As discussed in Chapter III, these samplers have been the subject of recent criticism regarding their efficiency to collect "large particles" ($\geq 10 \mu\text{m}$). The experimental comparison between the two impactors during period W12 did indicate an $\sim 35\%$ higher Mn concentration in size class 1 as measured by the modified impactor relative to the standard impactor. Davidson (1977) has recently presented experimental evidence that an Anderson impactor, modified to provide isokinetic sampling, resulted in collection of a considerably greater (2 to 3 times) mass of particles $> 10 \mu\text{m}$ aerodynamic diameter for the bimodally distributed elements Cd and Zn and for the predominantly small particle element, Pb.

The indication that dry deposition of the available element fraction is related to the large particle atmospheric concentration suggests that the material collected by the deposition plates results primarily from sedimentation mechanisms, or large particle impaction processes. Although the captured particles could not be aerodynamically sized, some indication of the general particle size range was determined by a combination of light and scanning electron

microscopy of deposition plate surfaces prior to leaching. The results of these semi-quantitative analyses are summarized elsewhere (Table 44, Chapter VI) along with a similar analysis of particles collected on several stages of the Anderson impactor. The size distributions of both recognizable fly ash and unrecognizable "particles" retained by deposition plates are strongly influenced by particles of $\geq 10 \mu\text{m}$ in diameter, such that the number median diameter of fly ash is $\sim 5\text{-}10 \mu\text{m}$ and that of nondescript particles is $> 10 \mu\text{m}$. Although several small ($< 1 \mu\text{m}$) fly ash particles were observed, they were generally in aggregates. Whether the material was deposited in this form or aggregation occurred during wet/dry cycles on the deposition surface is unknown. This point is considered further in Chapter VI. The size range of material collected by the upper stages of the impactor was somewhat narrower than that collected in the deposition plates, the major difference occurring the diameter of the large fly ash particles collected. The impactor collected nondescript particles of a similar diameter to those deposited on the inert surfaces. However fly ash, of generally greater density, was less efficiently collected by the impactor as evidenced by the large difference in the diameters of the largest particles collected. This lends evidence to the contention of Davidson (1977) that further modification of the Andersen impactor is necessary for more efficient collection of large particles. The smallest particles collected by the upper impactor stages were smaller in diameter than predicted by theory; however, these particles were few in number and generally occurred in aggregates.

The observed particle size distribution of material retained by the deposition plates provides further evidence for the importance of the mechanisms of sedimentation and large particle impaction. Because falling particles accelerate until reaching a terminal velocity it is possible to estimate the particle size range most likely to be influenced by sedimentation removal. The terminal velocity depends on particle density, aerodynamic diameter, and air viscosity, but has been estimated for rigid spheres of unit density by Israel and Israel (1973). These velocities are as follows for particles of radii 0.1, 1.0, and 10 μm : 2.3×10^{-4} cm/s, 1.3×10^{-2} cm/s, and 1.2 cm/s. It is apparent that particles on the order of 5 to 10 μm in diameter or larger are most likely to be removed by sedimentation processes. This is in agreement with experimental results of Sehmel (1973) who has shown that for a smooth surface and at relatively low windspeeds, sedimentation governs deposition. Further evidence of the importance of sedimentation in deposition to flat surfaces is presented in the work by Davidson (1977). From measured particle size ranges of Pb, Cd, and Zn using the modified Anderson cascade impactor, Davidson calculated the total deposition due to particle sedimentation by integrating over 15 particle size classes. The calculated fluxes were compared with those measured to flat teflon discs exposed simultaneously with the impactor collections. Measured sedimentation was determined by subtracting the measured flux to downward facing plates (which presumably collect particles only by impaction) from the flux to upward facing plates. The results of calculated and measured sedimentation were in reasonable agreement (within 15% for Pb and Zn,

within a factor of 2 to 3 for Cd). The measured fluxes to top and bottom plates indicated that the sedimentation process was responsible for 64 to 78% of the deposition. Optical microscopic examination of the top and bottom surfaces revealed that the ratio of large particles ($> 10 \mu\text{m}$) in the top plate to those in the bottom plate was ~ 23 , leading to the conclusion that trace metal deposition to bottom plates was primarily due to small particles.

There have been several measurements of particle deposition in both rural and urban areas, with the element Pb of primary interest. For comparison several of these "dry" deposition rates are summarized in Table 21 (many of the original references did not specify whether precipitation occurred during exposure of the deposition collectors). It is difficult to compare absolute deposition rates between these studies due to different methodologies in particle collection, surface leaching, and analysis. However, there is a general trend of increasing trace metal deposition associated with increasing human activity. Most of the reported deposition rates are for acid digestible fractions although the particles are often removed from the deposition surface by a distilled water wash prior to digestion. The deposition rates of the available trace metal fraction to WBW can be modified to reflect total metal deposition using the total metal/available metal ratios discussed earlier. These values are as follows: Cd = $0.60 \mu\text{g}/\text{m}^2\text{day}$, Mn = $140 \mu\text{g}/\text{m}^2\text{day}$, Pb = $53 \mu\text{g}/\text{m}^2\text{day}$, Zn = $77 \mu\text{g}/\text{m}^2\text{day}$. Given these deposition rates it is apparent that trace metal deposition to WBW is comparable with the higher values measured at remote sites and lower values measured at suburban sites.

Table 21. Dry deposition to inert surfaces measured at diverse locations

Location	Surface	Airshed type	Dry deposition rate ($\mu\text{g}/\text{m}^2\text{-day}$)				
			Cd	Mn	Pb	Zn	SO_4^{2-}
Pacific Ocean offshore buoy	a	marine	0.08-0.38	---	4-50	1.2-20	---
French Congo	b	remote continental	---	---	0.53	---	---
San Gabriel Mountains	a	remote continental	0.07-1.0	---	22-40	23-25	---
Central Wales, U.K.	c	remote continental	BD	5	30	40	---
Shetland Is., U.K.	c	remote coastal	BD	BD	40	50	---
Catalina, Is.	a	remote coastal	---	---	3-690	0-1700	---
Ensenada, Mexico	d	remote coastal	---	160	29	39	---
S. W. France	b	rural	---	---	7.4	---	---
Oslo, Norway	e	rural	---	---	75	---	5300
Central S. England	c	rural	BD	8	50	40	---
W B W	f	rural to suburban	0.07±0.07	25±13	6.5±4.9	1.4±0.7	1500±1300
Toulouse, France	b	residential	---	---	24	---	---
LaJolla, Calif.	d	suburban	---	27	76	65	---
Los Angeles Basin	a	suburban	0.7-3.6	---	280-810	73-340	---
Los Angeles Suburbs	a	suburban	1.1-2.0	---	47-330	23-400	---
Los Angeles Coastal	a	suburban	0.27-1.6	---	25-140	6-160	---
Pasadena	a	suburban	0.7-3.6	---	280-810	73-340	720
Central Los Angeles	a	urban	1-2.4	---	1000-22,000	240-1500	---
New York City	g	urban	20	270	1500	2600	---

^aTeflon plates (Davidson, 1977).

^bPluviometer (Servant, 1976).

^cFilter paper (Cawse, 1975).

^dPolyethylene buckets (Hodge, et al, 1978).

^eSnow surface (Doveland and Eliasson, 1976).

^fPolyethylene plates (this study). Values given are for the available element fractions only. (mean ± standard

^gPolypropylene buckets (Eisenbud and Kneip, 1975).

This is an agreement with the conclusions presented in Chapter III regarding the aerosol concentrations over WBW. When the soluble metal deposition rates measured in WBW (Table 20) are compared with those reported in the study by Hodge et al. (1978) at Ensenada, Mexico and LaJolla, California, the conclusion is similar. The soluble metal concentrations measured by Hodge et al. were as follows: (in $\mu\text{g}/\text{m}^2\text{day}$): LaJolla, Cd = 0.31, Mn = 16, Pb = 38, Zn = 41; Ensenada, Cd = 0.03, Mn = 15, Pb = 2, Zn = 2. Thus the WBW deposition rates for the soluble trace metal fractions are more similar to those measured at the remote coastal site than those measured at the suburban coastal site.

The data discussed to this point suggest the proximity of WBW to the three local coal fired power plants apparently has little effect on the dry deposition rates of trace metals to flat surfaces. Given the large number of parameters which can influence dry deposition rates it will be difficult to isolate the atmospheric and surface characteristics having the most significant effect on this limited data set. Unfortunately supportive meteorological and air quality data was not evaluated during the preliminary experiments, further limiting the data to the four periods during the 1977 growing season (W1, 2, 3, 6). As described in Chapter III these periods were characterized by several parameters, of which the following might be expected to influence dry deposition rates: leaf surface wetness, air stagnation frequency, TSP load, fraction of TSP $> 7 \mu\text{m}$ in aerodynamic diameter, atmospheric saturation frequency, atmospheric stability, wind direction frequency

from local sources, elemental mass median diameter, elemental air concentration, and fraction of the air concentration of an element occurring on particles $> \sim 4 \mu\text{m}$ aerodynamic diameter. Many of these parameters were summarized in Tables 3 in Chapter III, the remainder are presented in Table 22. Consistent relationships between dry deposition rates and the parameters discussed above were identified using correlation analyses. Because of the limited data, these relationships should be regarded cautiously, but may be useful indicators from a mechanistic standpoint. Despite these limitations several consistent relationships were revealed, as summarized in Table 23. Parameters not included in the table did not produce any correlation coefficients with absolute values > 0.70 (an arbitrary cutoff).

The most consistent trends appear to be related directly or indirectly to atmospheric loading. The dry deposition rates of Cd, Pb, Zn, and $\text{SO}_4^{=}$ all increase with increasing air stagnation frequency, which was shown in Chapter III to have a significant effect on atmospheric concentration in the total aerosol fraction. Related to this effect, these same elements also show an increase in dry deposition rate during periods characterized by higher TSP levels. As anticipated this relationship is also reflected in the elemental air concentration of the total aerosol fraction, being significant for Cd, Pb, and $\text{SO}_4^{=}$. Thus dry deposition of 4 of the 5 elements studied appears to be determined principally by atmospheric concentrations of the total aerosol fraction. This would imply that the same mechanisms which influence aerosol loading also influence dry deposition rates.

Table 22. Further air quality and meteorological parameters characterizing the experimental periods of dry deposition measurement (see also Table 3, Chapter III)

Period	Surface wetness frequency (%)	Fraction of TSP ^a > ~3.4 μm aerodynamic diameter (%)	Elemental ^b fraction associated with particles > ~3.4 μm aerodynamic diameter (%)				
			Cd	Mn	Pb	Zn	SO ₄ ⁼
W1	7	42	51	56	9	30	4
W2	10	35	22	49	5	15	3
W3	1	32	19	36	8	2	4
W6	17	25	38	51	6	17	5

^aTSP = total suspended particle load.

^bAvailable metal and soluble sulfate fractions.

Table 23. Correlation coefficients between elemental dry deposition rates and various meteorological and air quality parameters^a

Dry deposition rate of:	Leaf surface wetness	Air stagnation frequency	TSP	Wind direction frequency			Elemental air concentration	Elemental aerosol fraction > ~ 3.4 μm aerodynamic diameter
				KSP ^b	Y-12 and BRSP ^c	Other		
Cd	---	0.97*	0.97* ^d	---	---	0.98*	0.96*	---
Mn	---	---	---	0.99*	-0.93*	---	---	0.99*
Pb	---	0.97*	0.89	---	---	0.95*	0.99*	0.83
Zn	---	0.75	0.89	---	---	0.85	0.70	---
SO ₄ ⁼	0.74	0.98*	0.92	---	---	0.96*	0.98*	0.72

^aOnly coefficients shown are those for which $|r| \geq 0.70$.

^bKingston coal-fired power plant quadrant.

^cBull Run and Y-12 coal-fired power plants quadrant.

^d* = significant correlation coefficients ($P < 0.05$).

This conclusion is supported by the work of Eisenbud and Kneip (1975). In their measurement of the dustfall of 9 trace elements in New York City, monthly dry deposition was strongly related to ground level air concentrations.

The dry deposition rate of Mn in WBW is not influenced by any factor related to atmospheric loading. The correlation coefficients in each case were very near zero. Manganese deposition did increase with the frequency of winds from the west and southwest directions. Since Mn is believed to be derived primarily from surface soil dust resuspension, this deposition is presumably unrelated to power plant emissions. However, during the study period forest clearing activities, involving 400 to 500 acres, were prevalent in this general direction from the watershed. Site preparation in these areas involved considerable disturbance of the soil surface as well as burning of slash, all of which result in suspension of large Mn bearing particles. The relatively low efficiency of the Andersen impactor to collect very large particles, such as would be generated and resuspended during soil abrasion and which would be primarily subject to sedimentation deposition, would account for the lack of a relationship between Mn deposition and air concentration.

There does appear to be some relationship between deposited and suspended Mn however, as reflected by the correlation coefficient between Mn deposition and the relative concentration of Mn-bearing particles of $\geq \sim 4 \mu\text{m}$ aerodynamic diameter. Periods characterized by high Mn dry deposition rates are also characterized by low fractions of aerosol Mn in the larger particle size classes collected by the upper

impactor stages. Lead and sulfate exhibited this same trend of lower relative concentrations of the large particle fractions during periods of high dry deposition rates, although the correlation coefficients were not significant. Although Mn deposition apparently increased with the frequency of W - SW winds, the dry deposition rates of the other elements all increase as the frequency of winds from "other" directions increase. This is related to the associated increase in air concentration of these elements with these winds and lends further support to the lack of any strong local source effect on the atmospheric loading and dry deposition of this group of elements.

The lack of any apparent local source influence on deposition rates and the indication that much of the deposited mass is in the $\geq 10 \mu\text{m}$ size range may seem contradictory. However, there are reports in the literature of the apparently long-range transport of particles of this size. Lindgren and Paulus (1973) detected a significant number of particles as large as $100 \mu\text{m}$ in an area with no obvious local source. Dustfall plates at the same location collected particles primarily in the size range 25 to $120 \mu\text{m}$ comprising $\sim 90\%$ of the total mass deposited. Further reports of large particles have included Johnson's (1976) detection of particles up to $55 \mu\text{m}$ at heights 300 m above St. Louis, evidence of large particle Pb in the atmosphere by Gillette and Winchester (1972), and the measurement of up to 17% of the Pb, 38% of the Zn, and 37% of the Cd in urban aerosols associated with particles of $> 10 \mu\text{m}$ aerodynamic diameter by Davidson (1977).

The work of Chamberlain (1975; see also the recent review by Montith, 1975) indicated the increased efficiency of particle capture

by wet or sticky surfaces. However there was no indication in this data set that dry deposition rates of trace metals increased as relative duration of surface wetness increased. Although there were no strong relationships between surface wetness and trace metal deposition rates, there was a significant positive correlation between $\text{SO}_4^=$ deposition and surface wetness duration. However, the reason that the dry deposition rate of $\text{SO}_4^=$ increased during periods of extended leaf wetness may have been related to SO_2 deposition. Oxides of S may be incorporated into fog droplets during nucleation and be deposited on surfaces with high efficiency (Chamberlain 1975; Fowler and Unsworth, 1974). In addition, the ability of a dew covered surface to rapidly accumulate $\text{SO}_4^=$ was recently reported by Brimblecomb (1978). The mechanism involved was absorption of SO_2 by the droplets followed by oxidation to $\text{SO}_4^=$ with the rate limiting step being turbulent transfer of SO_2 to the moisture surface for alkaline solutions, diffusion across the liquid-air boundary layer for acid solutions, and a combination of the two for intermediate pH values (i.e., those most frequently encountered in leaf surface moisture).

The occurrence of precipitation during the deposition experiments complicated the interpretation of the relative solubility data. It is not possible to modify the calculated relative solubilities of the material collected in the deposition plates during periods of measurable wetfall in a manner similar to the calculation of dry deposition rates. Thus there are two types of relative solubility data, that related to dry deposited material and that related to bulk deposition. Because of this complication, only the periods will be

considered during which no precipitation occurred, W0 and W1. These values were as follows (in % relative solubility): W0, Cd = 73, Mn = 73, Pb = 24, Zn = 61; W1, Cd = 52, Mn = 70, Pb = 27, Zn = 63. The relative order of solubilities of deposited material is similar to that for the suspended aerosol fraction. However, the relative solubilities are lower for deposited particles by ~ 10% for Mn, ~ 20% for Cd ~ 35% for Zn, and ~ 60% for Pb compared to the suspended material (compare Table 11 in Chapter III). This again suggests the predominance of larger particles in deposited material because of the general decrease in relative solubility with an increase in particle size seen for suspended material (Table 11, Chapter III). This same trend is apparent in the data from period W1 alone which included simultaneous collection of dry deposition and suspended particles.

Apparently very little data on elemental solubilities of deposited material has been collected. As described in Chapter III, Hodge et al. (1978) have presented unpublished data on water-solubilities of several elements associated with both suspended and deposited particles. Solubilities were expressed as: water soluble fraction/total element concentration, which is not directly comparable with the relative solubility determined in this work. Using the total-acid-leachable metal/available metal concentration ratios discussed in the methods section above, the relative solubility values for W0 and W1 can be expressed in water-solubility terms as follows: Cd = 6-8%, Mn = ~ 13%, Pb = ~ 4%, Zn = 1%. Comparing these values with those reported by Hodge and Goldberg (1978) for a set of samples collected at La Jolla, California (Cd = 89% soluble, Mn = 59%, Pb = 50%, Zn = 59%) and in

Ensenada, Mexico (Cd = 11%, Mn = 9%, Pb = 7%, Zn = 5%) again indicates the WBW samples to be more similar to the remote coastal samples from Ensenada than the suburban-coastal samples collected at La Jolla. This was also the case for the suspended particle water-solubilities as discussed in Chapter IV. The authors speculated that the lower water-solubilities associated with the Ensenada samples may reflect a smaller, more leachable anthropogenic fraction at the remote site, or a strong non leachable association of the metals with higher amounts of Fe and Al in the Ensenada samples. However, there is no evidence that anthropogenic aerosols or deposited particles are any more or less leachable than natural materials other than as related to particle size. The WBW data suggests the differences seen by Hodge and Goldberg are more likely related to particle size effects. The higher concentrations of Al and Fe, generally large-particle soil-derived elements, found by Hodge and Goldberg in the Ensenada samples tend to support this hypothesis.

Summary and Comparison of Dry Deposition
and Net Accumulation Rates to Inert
and Biological Surfaces

With a working knowledge of the generally accepted problems involved in the empirical determination of dry deposition rates, several laboratory and field experiments were designed to develop and test various sampling techniques using inert and biological surfaces. The techniques of final choice involved: (1) artificial surfaces (deposition plates, see Figure 16) situated in the upper canopy of a mature chestnut oak tree for intervals of 4 to 7 days, and (2) the

sequential collection of upper canopy leaves from the same site over similar time intervals. In each case extraction techniques were developed using agitation with distilled water and dilute acid in sequence to remove water soluble $\text{SO}_4^{=}$ and water soluble plus acid leachable trace element fractions. The sum of the two trace element fractions represents the quantity of any given trace element which is likely to be relatively available in various element cycling pathways. Preliminary experiments indicated that these techniques resulted in the removal of $\sim 12\%$ of the total Cd, 18% of the total Mn, 12% of the total Pb, and 2% of the total Zn from dry deposited particles captured by the inert surface.

Two major problems encountered in the use of leaves to estimate deposition rates involved spatial heterogeneity and internal leaching. For example attempts to obtain a larger, more representative leaf sample for each extraction involved cutting uniform circular discs from the center of 20 leaves and washing these discs as one sample. However, spatial variability, even on the scale of a single leaf, as well as increased internal leaching from the freshly cut leaf discs made this technique of questionable utility. When whole leaves were sampled, the spatial variability in elemental surface area concentrations (Table 14) were similar over scales of 10's of cm (adjacent leaves) to 100's of m (watershed wide) indicating that equally useful estimates of leaf deposition may be determined from sampling that is concentrated at one easily accessible site rather than sampling uniformly across the watershed.

Several lines of evidence indicated that a considerable fraction of the Mn and $\text{SO}_4^=$ washed from the leaves represented internally leached material, while some of the Zn and Cd may have a similar source but most of the Pb appeared to originate from the leaf surface. Thus deposition rates calculated from sequential increases in the quantity of an element washed from the leaves may be subject to overestimation in the case of the micronutrients. This was particularly true during the early growing season for $\text{SO}_4^=$ and the late growing season for Mn and Zn and possibly Cd to some extent.

The two techniques for collection of deposited material were utilized throughout the 10 week intensive sampling period described in Chapter III. Since most of the sampling periods experienced wet as well as dry deposition and because of the constraints of sampling over relatively long time intervals to collect sufficient material for analysis, several operational definitions were applied to the data. For both inert and leaf surfaces the net increase in the surface area concentration of an element over a given time period represents the integration of several processes acting to both increase and decrease surface area concentrations (wet and dry deposition, wash off and resuspension, and additionally, internal leaching and absorption in the case of leaves). Since deposition to the leaf surface is calculated from the net difference in surface area concentrations over time it is also possible that a net loss of an element can occur. Thus deposition rates to both leaf and inert surfaces measured by sequential difference are best termed net retention or accumulation rates.

The deposition plates were utilized at several canopy locations with the intent of comparing surface retention as influenced by density of overstory vegetation. Plates situated on the meteorological tower well above the influence of any canopy elements generally resulted in accumulation rates comparable with those measured for plates in the upper canopy. The rates for Mn were ~ 2 times higher at the upper canopy site presumably due to leaching and splash off from adjacent leaves. Similarly the rates of the other micronutrients $\text{SO}_4^{=}$ and Zn were slightly higher at the upper canopy site, while Cd was comparable and Pb was somewhat lower. The generally good agreement between these sites has important implications for the use of the deposition plate technique at other, more remote, forested areas where towers are often available and more accessible than the upper canopy. In addition to these sites, plates were situated in the lower canopy and on the forest floor. Accumulation rates generally increased with increasing canopy density over the plates, with the increases larger during wet periods, indicating the accumulation to be primarily due to particle wash off and leaching from upper canopy elements. The net accumulation rates at the upper canopy location were not simply related to precipitation volumes or air concentrations. However, they did tend to increase as the TSP load increased suggesting accumulation rates to be enhanced by meteorological and atmospheric conditions which were responsible for elevated TSP levels (as discussed in Chapter III).

Dry deposition was calculated from deposition plate samples during 5 of the experimental periods (W0, 1, 2, 3, 6; Table 19) while dry deposition to the leaf surface could only be determined for two of the

periods (W1, W13; Table 15). The relative order of dry deposition rates generally followed the order of atmospheric concentrations: $\text{SO}_4^= > \text{Mn} > \text{Pb} > \text{Zn} > \text{Cd}$. When these rates were compared with similar data in the literature (Table 21) it was apparent that deposition rates measured at WBW were more similar to those measured at remote and rural locations than in urban environments. A substantial amount of the available metal fraction captured in the deposition plates was present in a water soluble phase (in relative solubility terms: $\sim 72\%$ of the Mn, ~ 50 to 70% of the Cd, $\sim 62\%$ of the Zn, and $\sim 26\%$ of the Pb). However, these relative solubilities were generally lower than for the corresponding total aerosol fraction, reflecting a larger particle size than in the suspended particles. Scanning electron and light microscopy of the deposited material substantiated the presence of generally larger particles (Table 44, Chapter VI), suggesting sedimentation to be an important particle deposition process to these surfaces.

The dry deposition rates of Cd, Pb, Zn, and $\text{SO}_4^=$ measured to upper canopy plates were correlated with air stagnation frequency, TSP, and the air concentration of each element in the total aerosol fraction, and the frequency of winds from directions other than those influenced by local sources. Thus the dry deposition of Cd, Pb, Zn, and $\text{SO}_4^=$ was apparently not enhanced by local source emissions. Manganese deposition was not correlated with any of these parameters but did increase with frequency of west and southwest winds suggesting the influence of resuspended surface dust related to forest clearing and site preparation activities to the west-southwest of the watershed

during the sampling period. Only the dry deposition rate of SO_4^- was correlated with surface wetness, suggesting that scavenging of SO_2 by fog and dew droplets followed by oxidation may be an important SO_4^- deposition mechanism to these surfaces.

For comparison, the various measurements of dry deposition and short-term net retention by leaf and deposition plate surfaces are summarized in Table 24 as the mean and standard error for all observations. The dry deposition rates have been estimated from short term deposition plate and sequential leaf collection experiments during experimental periods with no measured precipitation (W0, 1, 13) or during periods for which the deposition plate total input could be corrected to reflect dry deposition alone (W2, 3, 6). The short term surface net retention rates include all data from the intensive experimental periods during the 1977 growing season. It is apparent from the data that the choice of a given method for the estimate of dry deposition rates can have a significant influence on the value ultimately determined. The overall range for Pb is over an order of magnitude while the values for Cd and Mn range over a factor of ~ 8 , and SO_4^- and Zn over a factor of ~ 5 . Perhaps the most interesting aspect of this data is the one period (W1) for which dry deposition estimated by deposition plate retention and net leaf retention can be compared for the same sampling interval. Given the operational problems discussed above, the agreement is very good for Cd, Zn, and SO_4^- . The dry deposition rates of Cd and Zn to the leaf surface were $\sim 30\%$ lower than the dry deposition rates to the inert surface while being $\sim 30\%$ higher for SO_4^- . The rate of dry deposition of

Table 24. Comparison of mean deposition rates of available metal fractions to surfaces at the upper canopy (including S.E. where appropriate)

Sampling period	Deposition surface	Deposition rate ($\mu\text{g}/\text{m}^2\text{-day}$)				
		Cd	Mn	Pb	Zn	$\text{SO}_4^{=}$
DRY DEPOSITION						
W1 ^a	Plates	0.034	15	3.7	2.0	900
W1	Leaves	0.024	6.8	0.4	1.4	1300
W1,13	Leaves	0.021±0.003	19±13	0.4±0.1	2.8±1.4	950±350
WO,1	Plates	0.077±0.043	14±1	4.5±0.8	1.5±0.4	940±35
WO,1,2,3,6 ^b	Plates	0.072±0.034	25±6	6.5±2.2	1.4±0.3	1500±600
SURFACE NET RETENTION: SHORT TERM ^c						
W1-13	Leaves	0.075±0.032	45±14	0.56±0.12	1.2±0.4	1800±750
WO-12 ^d	Plates	0.13 ±0.03	19±6	6.6 ±1.2	2.7±0.9	2500±790

^aThe only dry period during which leaves and plates were both sampled.

^bIncludes deposition rates corrected for wetfall.

^cShort term experiments were those of <9 days duration. Surface net retention reflects the end result of both wet and dry deposition processes.

^dNot including periods W8 and W10 during which sampling was prematurely terminated due to power failures, thus n = 10.

Mn estimated from the inert surface is approximately twice that estimated to the leaf surface, which may reflect the increased efficiency of the deposition plates to retain larger particles.

Only for Pb was the difference between the two estimates of dry deposition very larger factor of 10. Since there is only one observation offering this direct comparison, in-depth analysis of the difference is not warranted. However, even though the other estimates of dry deposition by plates and leaves are not directly comparable in time (periods W1, W13 for leaves and W0, W1 for plates) the same order of magnitude difference exists for Pb. In addition, the short term surface net retention rates of Pb also are a factor of 10 lower for the leaf surfaces compared to the deposition plates over approximately the same time interval. For these same periods the agreement between inert and leaf surface retention for Cd, Mn, Zn, and $\text{SO}_4^{=}$ was generally within a factor of two. There are two possible explanations for this phenomenon: (1) Pb containing particles are more efficiently captured and retained by the inert surface than the leaf surface, or (2) Pb is captured with similar efficiency by both surfaces but is absorbed through the leaf surface resulting in less surface available Pb when the leaves are washed. The first explanation could account for the difference only to the extent that a considerable fraction of the atmospheric Pb exists in relatively large particles ($> 10 \mu\text{m}$). As discussed above the Pb particle size distribution during these experiments was predominantly submicrometer as determined by the Anderson impactor. However, because of the known inefficiency of this impactor to capture large particles, this explanation should not be ruled out.

There is conflicting evidence in the literature regarding Pb absorption by the leaf surface. Krause and Kaiser (1977) dusted leaves of various crop plants with a metal oxide mixture containing PbO_2 (particle size $< 50 \mu m$). Their results indicated that Pb uptake through leaves occurred even when applied as PbO_2 and that the Pb was translocated downward into the roots by basipetal transport. Rabinowitz (1972) has reported foliar absorption and translocation of Pb halide aerosols by oats and lettuce grown near a freeway. Hemphill (1974) reported similar results for leaves of Sycamore trees. On the other hand, Carlson et al. (1976) found no evidence of absorption of topically applied Pb either as a solution or as a dry aerosol by soybean leaves. In studies using isolated plant cuticle, Arvick and Zimdahl (1974) found that the cuticle acts as a nearly perfect barrier against Pb ion penetration. However, even if deposited particle Pb can be absorbed, the relative solubility data suggests that only a small fraction of the Pb would be involved ($\sim 4\%$ of the total Pb and $\sim 30\%$ of the available Pb) if the absorption process involved a water solubilization step. Thus, without further study it is difficult to account for the order of magnitude lower dry deposition rates estimated for the biological surfaces relative to the inert surfaces.

Although the remaining estimates of dry deposition are not from entirely comparable sampling intervals they do, nevertheless, indicate a relatively good agreement between the two methods, except for Pb (Cd agreed within a factor of ~ 4 , Mn ~ 1.5 , Zn ~ 2 , and $SO_4^{=}$ ~ 1.5). Because of the indication that the inert surfaces apparently provide a

reasonable estimate of the available metal and soluble SO_4^- dry deposition to the leaf surface, the mean dry deposition values calculated from deposition plate retention during periods W0, 1, 2, 3, and 6 will be taken as the best estimates of dry deposition rates to upper canopy surfaces in WBW (with the understanding that the value for Pb dry deposition may be an overestimate). The use of these experimental values to estimate longer term dry deposition rates to the watershed as a whole for comparison with wet deposition rates is the subject of Chapter VII.

CHAPTER V

TRACE ELEMENT, SULFATE, AND HYDROGEN ION CHEMISTRY
OF INCIDENT PRECIPITATION AND THROUGHFALL
IN WALKER BRANCH WATERSHED

Introduction and Statement of the Problem

As discussed in the previous chapter, Slinn (1976) has presented a theoretical argument that wet and dry deposition of pollutants to a forest from ground based sources are comparable in magnitude. Of these two suspended particle removal mechanisms, wet deposition is of particular importance due both to its episodic nature and the fact that particle and gaseous-associated elements are delivered to the forest canopy partly in solution, thereby enhancing the possibility of absorption by vegetation surfaces. In addition, wetfall may simultaneously remove previously deposited or impacted material from the canopy, hence increasing the mobility of particle-associated trace elements. The physical processes by which precipitation removes impurities from the atmosphere were briefly summarized in a recent report by Gatz and Changnon (1976). Gases are scavenged with an efficiency roughly proportional to their water solubility. Soluble gases are incorporated into precipitation either within or below clouds by three mechanisms: simple dissolution in a rain droplet, dissolution followed by hydration or dissociation, or dissolution followed by chemical reaction with other dissolved or particulate species in the

water droplet. This latter process occurs with SO_2 leading to formation of various sulfite and sulfate salts in rain. Particle scavenging is comprised of processes which predominate either within or below the cloud base with efficiencies dependent on particle size. The interception of particles of $\sim 0.1 \mu\text{m}$ diameter with cloud water through Brownian motion is termed Brownian capture, a process whose effectiveness increases with decreasing particle size. Partially water soluble particles of $\sim 0.1 - 1 \mu\text{m}$ can be removed by nucleation scavenging, individual droplets nucleate on hygroscopic particles. Finally for particles $\sim 5 \mu\text{m}$ in diameter impaction scavenging predominates as the removal process, occurring both within and below the cloud and involving particles captured by falling raindrops. Thus, elements associated primarily with aerosols of a certain particle size may be more effectively removed by either dry or wet processes including the various wet scavenging mechanisms.

The importance of precipitation in nutrient and major element cycling on a watershed scale has been well documented (Fisher et al., 1968; Johnson and Swank, 1973; Likens et al., 1967; Swank and Henderson, 1976). Nutrients are removed from the canopy and transported to the forest floor in throughfall, which is precipitation intercepted by the canopy but still reaching the forest floor by canopy drip. Dissolved and suspended constituents in throughfall are derived not only from the incident precipitation but also from material leached internally from the vegetation as well as from the vegetative surface. In addition, there are both physical and chemical reactions between

material on the leaf surface and that dissolved in incident precipitation leading to element exchange at the surface.

Previous watershed scale investigations of the chemistry of incident precipitation and throughfall have concentrated on major element and nutrient cycling as influenced by canopy leaching (Eaton et al., 1973; Henderson et al., 1977). However these studies have involved primarily bulk sampling on weekly or monthly time scales as opposed to wetfall only sampling on an event basis, a sampling scheme often cited as one providing the most accurate quantitative information on the chemical composition of rain (Galloway and Likens, 1976, 1978). The relatively few studies concerned with trace chemistry of both throughfall and incident precipitation (Heirichs and Mayer, 1977; McColl and Bush, 1977) have involved sampling on a small scale or have utilized bulk samples collected either on an event basis or over fixed time periods. The same has generally been true for previous investigations of the trace chemistry of rain alone (Hallsworth and Adams 1973; Schlesinger et al., 1974; Ruppert, 1975; Harrison et al., 1975; Struempfer, 1976; Beavington, 1977; Andren and Lindberg, 1977). However, few studies have combined the unique sample collection design and possessed the analytical sensitivity required for trace analysis of wetfall with the facilities of a calibrated watershed. These considerations have prompted this investigation of the precipitation input of selected trace elements into Walker Branch Watershed (WBW), including the interaction between incoming rain and the deciduous forest canopy. The primary objective of this section is to characterize the input of Cd, Mn, Pb, Zn, and SO_4^{2-} -S to the

watershed by wet deposition on time scales commensurate with the identification of meteorologic and other factors regulating the magnitude of episodic trace element inputs.

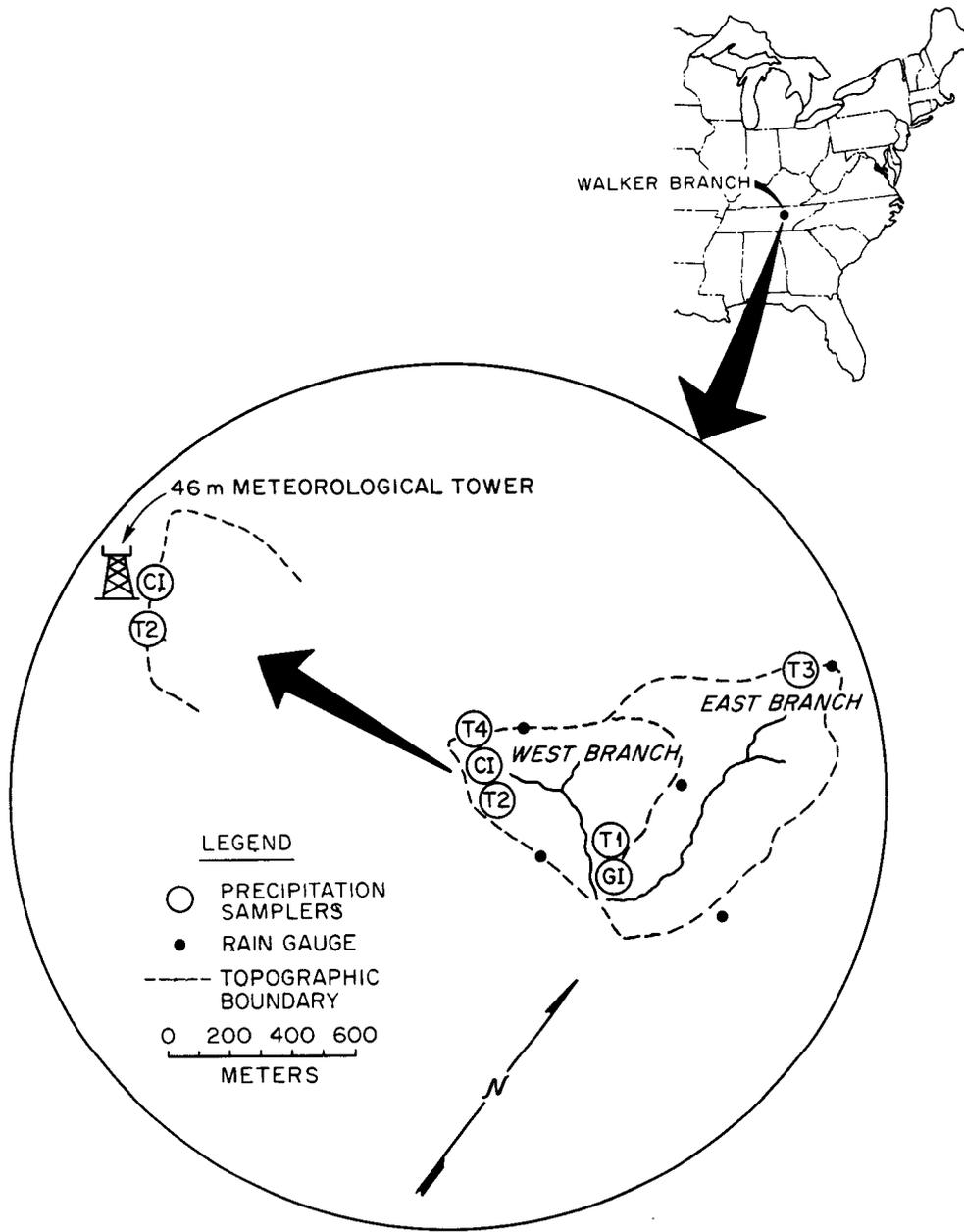
Sampling and Analysis

Precipitation Collector Design and Sampling Procedures

Many problems have been associated with the collection of rainfall for major element and nutrient chemistry and were recently reviewed by Galloway and Likens (1976, 1978). Briefly these involve efficiency of the sampler to collect a representative sample, postdepositional chemical alterations of the sample, sample contamination, sampling and analytical precision, and event definition. These difficulties are, in general, compounded when trace analysis is intended due to both the high probability of sample contamination and possibility of element loss to container surfaces (e.g., see the recent review paper by Morgan, 1975). All of these problems were considered during the development of the precipitation sampling network on Walker Branch Watershed. The utility of using wet/dry or wet only samplers (automatic devices designed to expose the collector surfaces only during precipitation) for collection of rain for chemical analysis has been well established. Accordingly the HASL (U. S. Department of Energy, Health and Safety Laboratory, Volchock et al., 1974) design was chosen, a reportedly reliable (Galloway and Likens, 1976) wet/dry sampler which was modified to minimize contamination from metal components of the sampler itself or from spurious dry deposition into the wetfall samples.

The unit as modified for our studies is described in considerable detail and illustrated in Lindberg et al. (1977; reproduced in Appendix A; see also Figures 25 and 29 following). Briefly, all components of the sample cover have been replaced with polyethylene, teflon, or stainless steel; the cover has been fitted with a polyethylene-covered foam sealing surface which is removable for cleaning, and the metallic wet sensor grid has been relocated on a separate post mounted 2 m from and below the level of the collector. For the results reported here only the wetfall side of the collector was utilized. The collector efficiency of the HASL samplers was tested by two methods on an event basis. The expected volume of catch was calculated given the exposed funnel surface area and measured quantity of rain at the site, or by comparison of the catch of plastic wedge type rain gauges placed one inside and one outside the collector. Both methods yielded efficiencies ranging from 1% low to 3% high, averaging 1% low for the HASL sampler relative to the rain gauge. When checked for longer periods of time over several events the discrepancies ranged from 16% low to 18% high, still averaging 1% low.

The location of the individual samplers and the recording raingauge network is indicated in Figure 20. The present network, which has been in operation since 1/76, consists of 6 HASL samplers, 4 of which are located at permanent, paired throughfall and incident sites, the other 2 of which are permanent throughfall sites. The paired sites consist of a ground level incident collector (GI) and throughfall collector (#T1), within 50 m of each other, at one location, and an above canopy incident collector (CI, atop a 46-m



Walker Branch Watershed Deposition Network.

Fig. 20. Walker Branch Watershed (WBW) study area indicating the location of incident precipitation and throughfall collectors.

meteorological tower) and ground level throughfall collector (#T2), within 50 m of each other, at another. All throughfall collectors are situated beneath mixed hardwood stands (predominantly oak; beech, poplar in one case, #T1). These sites are illustrated and discussed in detail in a following section.

Rainfall volume is monitored continuously at 5 ground level rain gauge sites (see Figure 20) by Fisher-Porter automatic recorders which allow calculation of the weighted average rainfall input to the entire watershed on a daily or an event basis (Henderson et al., 1977). In addition, located at each HASL sampler site is a portable wedge type rain gauge which is read on an event basis giving an indication of intersite variability rainfall.

The rationale for our sampling methodologies, including technical details, is described elsewhere (Lindberg et al., 1977; Appendix A). In practice, the collection procedure is designed (1) to minimize the chance of contamination of the sample container in the field prior to the occurrence of rainfall and to the sample itself during precipitation and prior to retrieval from the field; and (2) to reduce the chance of chemical alteration of the original sample by evaporation, degassing, biological action, and sorption phenomena.

Samples were collected on an event basis with the HASL samplers being double distilled water washed and rinsed and prepared for service in the field prior to initiation of rainfall (generally within 24 hrs) and all samples retrieved soon after precipitation had ceased (< 24 hrs). In addition, a limited number of storms were sampled sequentially for both incident precipitation and TF. This involved

manual replacement of sample bottles following collection of sufficient sample for analysis.

All samples were collected using a polyethylene funnel/bottle arrangement placed inside the HASL sampler prior to initiation of rainfall. The advantages of this technique are discussed in detail in Appendix A. The funnels used in throughfall collectors were covered with 105 mesh polyethylene screen to exclude coarse organic debris. Bottles and funnels for trace metal samples were leached with 2N HNO₃ for 16 hours double distilled water for 8 hours, and rinsed profusely with Millepore Milli-Q[®] double distilled water prior to use. Bottles and funnels for sulfate and pH samples were similarly washed omitting the acid leach. The levels of metals in the leach water were 1 to 2 orders of magnitude below the levels measured in rain (Lindberg et al., 1977).

For sampling purposes an event was defined as any measurable precipitation (0.25 mm of rain in an hour's time) preceded and followed by 6 continuous hours of no measurable rain. Using this definition generally led to sampling well defined events for which correlative meteorological parameters could be measured.

Table 25 summarizes the characteristics of the precipitation events sampled during a 2-year period. Using the procedures and event definition described above 72% of the precipitation input by volume was sampled while minimizing the length of time the sample bottles remained in the field. Of the samples collected, 64% represented "single storm" events, 30% were multiple events with a total sampling duration of < 7 days, and only 8% represented multiple events with a sampling time

Table 25. Characteristics of individual precipitation periods sampled during 1976-1977

Season ^a	Number of events sampled (A) and samples collected (B) A/B	Fraction of total precipitation which was sampled	Fraction of samples representing individual events	Statistic	Precipitation amount sampled per period (cm)	Precipitation amount occurring per event (cm)	Duration ^b of events sampled (hr)
Dormant ^c	34/32	47%	70%	\bar{X} range	2.4 0.5 - 8.4	1.3 0.03 - 7.6	18 5-58
Budbreak ^d	16/18	86%	60%	\bar{X} range	4.3 0.5 - 19.2	1.5 0.05 - 19.2	32 8-89
Maxgrowth ^e	61/68	84%	59%	\bar{X} range	3.1 0.2 - 11.8	1.2 0.03 - 7.0	12 1-43
Senescent ^f	28/30	74%	72%	\bar{X} range	4.3 0.4 - 8.4	1.7 0.05 - 7.9	20 1-46
Total two year period	139/148	72%	64%	\bar{X}	3.1	1.4	19

^aExpressed in terms of deciduous canopy condition.

^bLength of time of continuous measurable precipitation.

^cNovember - February.

^dMarch - April.

^eMay - August.

^fSeptember - October.

exceeding the 7 day maximum sample collection period suggested by Galloway and Likens (1976, 1978).

On a seasonal basis we sampled 47 to 86% of the precipitation by volume, the lowest sampling efficiency occurring during the winter (dormant) period. This largely reflects our inability to effectively sample freezing rain or snow. The fraction of samples representing individual events were seasonally evenly distributed, ranging from $\sim 60-70\%$. The most disturbing problem encountered was the inability to consistently sample minor storm events (< 0.5 cm). This related both to an inability to predict such events and, when sampled, to collect sufficient volume for analysis. Comparison of the data in in Table 25 of the mean precipitation amount sampled with the mean amount which occurred illustrates this point. Since such storms were only infrequently sampled the mean precipitation volume of the storms sampled, exceeded that which occurred by a factor of two to three. According to Henderson et al. (1977), daily precipitation of < 0.5 cm accounts for only 6% of the annual rainfall input to WBW but occurs with a frequency of $\sim 37\%$. During the two year study period storms of < 0.5 cm occurred with a frequency of $\sim 40\%$ but accounted for only 7% of the hydrologic input. We were able to sample such storms with a frequency of $\sim 10\%$. Since these events comprise a minor component of the input to WBW the effect of under representative sampling of small events is insignificant in the calculation of wetfall deposition to the watershed. The frequency distribution of rainfall volume for all events sampled is described in further detail in a following section.

Analytical Methods

The parameters pH and specific conductance were measured immediately upon return to the laboratory on samples allowed to reach room temperature. Hydrogen ion concentration was determined by standard methods on samples equilibrated with atmospheric CO₂ using a combination reference-pH electrode (Galloway et al., 1976). Free and total acidity were determined by titration of selected samples as described in detail in Hoffman et al. (1979). An aliquot for sulfate was transferred into a prewashed polyethylene bottle and stored at 4 °C in the dark until analysis (< 7 days).

Sulfate was determined using an improved methylthymol blue colorimetric procedure with a Technicon Auto Analyzer II system. The method has been described in detail by McSwain et al. (1974) and its application to our studies including information on analytical precision, accuracy, spike recoveries, and intermethod calibration is described in Lindberg et al. (1977; Appendix A).

Samples for trace metal analysis were stabilized by addition of concentrated Ultrex ultra pure HNO₃ to pH = 1.1 in the laboratory immediately following collection. The decision not to use preacidified bottles in the field was based on several tests of both methods involving blank determination, matrix effects, container contamination, and solution adsorption (Lindberg et al., 1977; Subramanian et al., 1978). Thus we routinely analyzed for "total acid leachable" metals; in general acid leachable trace metal concentration would be greater than water soluble metals levels for any given sample. However, occasional samples were fractionated by filtration (0.4 μ Nuclepore®

membrane) in the lab or by a method of "in situ" membrane filtration in the field as the rain was collected.

All metal analyses were performed using a Perkin Elmer[®] Model 503 atomic absorption spectrometer with deuterium background corrector in conjunction with a P.E. H.G.A. 2100 graphite furnace. Standard conditions as specified by the manufacturer were employed in all analyses, and all solutions were analyzed directly without preconcentration by the method of standard additions. Specific details of this methodology including matrix effects, limits of detection, interlaboratory quality control, accuracy, and precision are discussed in Turner and Lindberg (1976) and Lindberg et al. (1977). Analytical accuracy for the sulfate technique, based on blind standards, was $\pm 3\%$ while precision, based on replicate analysis of standards and samples was ± 2 to 4% . Similarly for trace metals, accuracy, based on blind analyses of EPA check samples, was generally $\pm 5\%$ while precision ranged from ± 4 to $\pm 10\%$. In addition we recently cooperated with the Department of Energy Environmental Measurements Laboratory (E.M.L.) in a blind analytical quality control test using "standard" rain samples prepared by E.M.L. for the MAP3S precipitation network. The results of this test involving 15 laboratories are presented elsewhere (Bogen et al., 1978). For the 8 samples analyzed for 18 constituents, including H^+ , SO_4^- , Cd, Mn, Pb, and Zn, our analyses were consistently in the middle of the ranges reported by all laboratories.

The goal of identifying mechanistic relationships between precipitation trace element chemistry and meteorologic, spatial, temporal, and air quality parameters cannot be reached unless natural

variations can be resolved from procedural variations. Accordingly we collected replicate samples of 4 storms from a single HASL collector resulting in a measure of the overall procedural precision as influenced by sample collection, handling, preservation, and analysis. The reproducibility of each parameter measured for each storm is presented in Lindberg et al. (1977). Summarizing this data leads to an average overall precision of pH and sulfate determinations of $\pm 2\%$. Average precision for trace element analyses ranged from $\pm 5\%$ for Pb to $\pm 11\%$ (Mn), $\pm 15\%$ (Zn), and $\pm 16\%$ for Cd. In each case, these values are on the same order as the precision of the analytical methods alone.

Results and Discussion

Element Distribution in Incident Precipitation and Throughfall

Table 26 is a statistical summary of Cd, Mn, Pb, Zn, $\text{SO}_4^{=}$, and H^+ concentrations observed in rain and throughfall for the two year period 1976-1977. The observations from which Table 2 was compiled are presented in Appendix B. The information listed in Table 26 includes arithmetic means, standard deviations, coefficients of variation, concentration ranges, and number of observations. Precipitation volume weighted means are considered in a following section. The data for incident precipitation includes the above canopy and exposed ground level sampling sites while the throughfall data is a summary of the four ground level subcanopy collection sites.

Table 26. Statistical summary of selected elements in incident precipitation and throughfall in Walker Branch Watershed for the period 1976-1977

Constituent	Arithmetic mean	Standard deviation	Range	Coefficient of variation	Number of observations
INCIDENT PRECIPITATION					
Cd	0.44 µg/l	0.53	0.003 - 2.60	121%	64
Mn	3.46	4.72	0.03 - 24	137	64
Pb	6.85	5.45	0.62 - 24	80	64
Zn	6.13	6.36	0.44 - 37.2	104	64
$\text{SO}_4^{=}$	3.6 mg/l	2.7	0.4 - 16.5	75	66
H^+	74 µeq/l	38	6 - 178	52	68
(as pH)	4.13	—	3.75 - 5.22	—	—
Conductance	32.4 µmhos/cm	19.3	7.2 - 112	60	66
THROUGHFALL					
Cd	1.41 µg/l	2.36	0.03 - 13.0	170	73
Mn	135	135	5.8 - 733	100	73
Pb	11.8	10.8	1.00 - 54.0	91	73
Zn	15.4	15.6	0.71 - 86.0	101	73
$\text{SO}_4^{=}$	9.1 mg/l	7.6	0.84 - 37.5	84	78
H^+	55	43	7 - 151	78	80
(as pH)	4.26	—	3.82 - 5.15	—	—
Conductance	48.5 µmhos/cm	28.3	9.9 - 158	58	77

Of the trace constituents in incident precipitation, Pb and Zn are comparable in concentration, are somewhat more abundant than Mn, and are an order of magnitude higher than Cd in concentration. However $\text{SO}_4^{=}$ and H^+ are far more dominant constituents in the rain in WBW, both present at from 1 to 3 orders of magnitude higher concentrations than the above. When compared to the annual average concentration of major elements in WBW rain (Swank and Henderson, 1976; Henderson et al., 1977) on an equivalent basis, H^+ constitutes $\sim 50\%$ of the cationic strength while the trace element group accounts for only 0.2%. For the anions, $\text{SO}_4^{=}$ comprises $\sim 65\%$ of the anionic strength, occurring on an equivalent basis at a level 3.5 times higher than the next most abundant anion, NO_3^- . Similarly, H^+ is 2 times more abundant than Ca^{++} , the second cation in relative importance. Thus, as in the case for rain collected in the Hubbard Brook experimental forest (Likens et al., 1977), incident precipitation in WBW during this 2 year period can be described as a dilute mineral acid solution, primarily H_2SO_4 , at a pH ~ 4.2 containing a relatively minor amount of various trace element salts.

The chemistry of precipitation reaching the forest floor is considerably different from that collected above the canopy or at ground level but removed from the influence of the canopy. Mean concentrations of all elements in throughfall except H^+ are elevated over those in incident rain. The increases range from a minimum of 1.3 times for Pb to a maximum of 53 times for Mn. Hydrogen, on the other hand, shows a decreased concentration by a factor of 1.2. With the exception of Mn, the relative abundance of the elements is similar to

that in rain with Pb and Zn being comparable in concentration and both exceeding Cd by ~ 10 times. Manganese has increased in abundance to ~ 10 times that of Pb and Zn and is now comparable with H^+ . Sulfate remains 1 to 3 orders of magnitude higher than the other constituents. The comparison between major element throughfall chemistry and the concentration of the trace constituents cannot be done as readily as for incident precipitation. This relates both to the known influence of overstory vegetation type on throughfall chemistry (Eaton et al., 1973; Henderson et al., 1977), and the scarcity of such data. However, combining the available data for cations in throughfall in WBW (Henderson et al., 1977) with that for anions in throughfall in a northern hardwood forest (Eaton et al., 1973; NB., the cation data indicated comparability between the two data sets) results in the following comparison. Sulfate comprises $\sim 60\%$ of the total anions on an equivalent basis, exceeding the next most abundant anion (NO_3^-) by ~ 3 times, while H^+ now comprises only 15% of the cationic budget and is exceeded by Ca^{++} and NH_4^+ by factors of 1.5 to 2, is comparable to K^+ , and exceeds Mg by a factor of 2. The combined trace elements now account for slightly greater than 1% of the total cations. Thus, throughfall appears to be a more dilute solution of H_2SO_4 than rain, with pH ~ 4.5 , containing a relatively higher concentration of alkaline earth salts of $SO_4^{=}$ and NO_3^- , in addition to somewhat higher levels of trace elements. A comparison between the levels of the above elements in rain and throughfall in WBW and precipitation chemistry at remote, rural, and urban locations is presented in a following section.

An important complicating factor in the attempt to describe the "typical" chemistry of rain or throughfall is the considerable variability of all constituents listed in Table 26, especially Cd, Mn, Zn and to a lesser extent Pb. The coefficients of variation for Cd, Zn, and Mn equal or exceed 100%, while those for Pb range from 82 to 92%. Sulfate and hydrogen ion show less variability than the trace elements with coefficients of variation between 52 to 84%. With the exception of Mn, the variability in the data is somewhat higher for throughfall than incident precipitation. Despite this trend, the ranges in concentration are comparable or higher for incident precipitation compared to throughfall. Cadmium and Mn range over ~ 3 orders of magnitude in rain and 2 orders of magnitude in throughfall, Pb and Zn range over ~ 2 orders of magnitude for both rain and throughfall, and sulfate ranges over a factor of ~ 40 in both mediums. On the other hand, H^+ ranges over an order of magnitude in rain but increases in range to 2 orders of magnitude in throughfall.

In the study of trace chemistry of precipitation it must be acknowledged that large concentration variations do occur naturally. Figures B1 to B12 in Appendix B illustrate this point by showing the temporal variations over the two year period of elemental concentrations in rain and throughfall. As described above the coefficients of variation of all parameters exceed 50% while those for Cd, Mn, and Zn are $\geq 100\%$. In all cases the observed variabilities, exceed the overall procedural reproducibilities described above, by approximately an order to magnitude (ranging from 7 to 40 times

higher). Thus there is little doubt that these variabilities are real and not analytically imposed.

In general the variability of rain chemistry has not been considered in great detail, especially in the case of trace constituents. In many cases the time variability has been minimized by the collection of periodic rain samples comprised of < 1 to several events and ranging in collection period from weeks to months, as opposed to event samples. Also the variabilities have been complicated by the collection of bulk precipitation instead of wetfall alone. In still other cases only the monthly or annual mean values are presented.

The concentrations of Mn, Ni, Pb, and Fe in monthly samples were reported by Drozdova and Makhonko (1970) to range over factors of 2 to 48 during a 2-year study. However it was not clear whether these samples represented bulk precipitation or wetfall. For bulk precipitation collected on a weekly basis, several investigators have reported data with ranges in variation over 1 to 2 orders of magnitude (Schlesinger et al., 1974; Ruppert, 1975; Harrison et al., 1975). In a recent study of bulk precipitation collected in the southeastern U. S. over periods ranging from < 1 to 18 days, the metals Cd, Mn, Cu, and Pb exhibited coefficients of variation up to 140% and ranges over 2 orders of magnitude (Wiener, 1978). Beamish and Van Loon (1977) reported limited data on trace element concentrations in bulk precipitation collected both on a periodic and an event basis over a two year period. For the metals Zn, Cu, Ni, and Fe the coefficients of variation ranged from 42 to 106% for periodic samples and from 25 to 120% for event samples. A recent paper by Granat (1977) concentrated

on the problem of rainwater composition variability and its effect on wet deposition estimates. Although much of the data consisted of monthly collections of bulk deposition, the results of a multisite event study were also presented. A network of from 32 to 100 bulk samplers located within a 60 km radius was used to sample 7 individual events for major element chemistry. Coefficients of variation ranged from 12 to 51% for $\text{SO}_4^{=}$, 61 to 114% for NH_4^+ , and 57 to 77% for Ca. The general problem of spatial variability in concentration fields was described as a significant contributions to the uncertainty in wet deposition estimates. To our knowledge similar considerations of rain composition variability in precipitation and throughfall collected on an event basis do not exist for trace constituent chemistry and are sparse for major element composition.

Because of the large variation in the composition of precipitation and throughfall for both trace and major constituents, the mean and standard deviation do not adequately describe the distribution of elemental concentrations. Figures 21 and 22 include frequency histograms for each element in rain and throughfall. With the exception of H^+ , all histograms reflect strong skewness toward lower concentrations with a well defined tail of few observations with very high concentrations. The histogram concentration classes represent 20 equally sized concentration ranges from minimum to maximum values for each constituent. In the case of Cd in rain, 56% of its concentration values fall into the lower two concentration classes or the lowest 10% of the range. In throughfall, 73% of the Cd values fall into this range. Similarly for Mn and Zn in rain the values are 60% and 50%

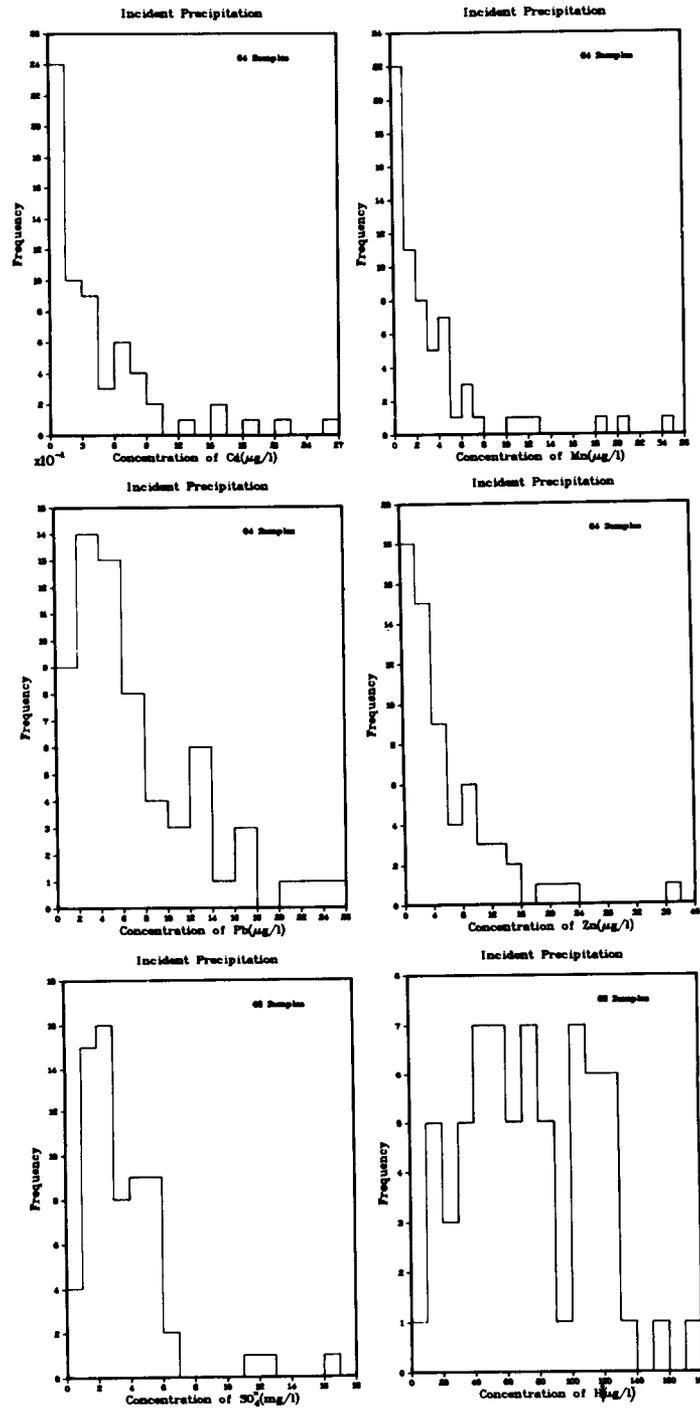


Fig. 21. Frequency distribution of trace element, sulfate, and hydrogen ion concentrations in incident precipitation.

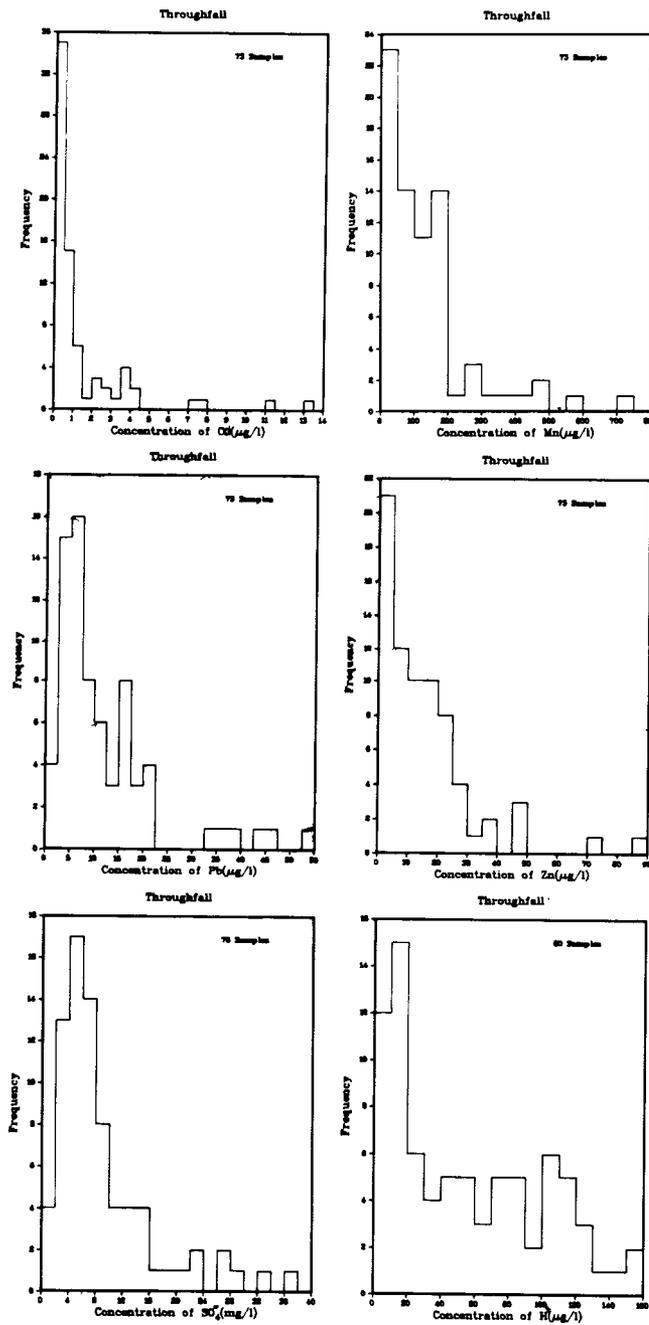


Fig. 22. Frequency distribution of trace element, sulfate, and hydrogen ion concentrations in throughfall.

respectively while in throughfall 45% of the Mn and 47% of the Zn levels fall into this range. For Pb and $\text{SO}_4^{=}$ the skewness is somewhat less acute with 27 and 36% of the Pb and 27 and 21% of the $\text{SO}_4^{=}$ values in the lowest 10% of the range in rain and throughfall respectively. For H^+ in rain the distribution is considerably more uniform while in throughfall the distribution appears bimodal and somewhat skewed toward the lower end (30% of the values in the lowest 10% of the range).

The positive skewness of many of the histograms indicates significant departure from normal distributions normality for these parameters and suggests the possibility of lognormality. The lognormal distribution of atmospheric data has been indicated for heavy metals in aerosols (Kretzschmar et al., 1977) and in bulk precipitation (Weiner, 1978). Figures 23 and 24 are lognormal plots for concentrations of Cd, Mn, Pb, Zn, and $\text{SO}_4^{=}$ in incident precipitation and throughfall. The hydrogen ion concentration data is illustrated with a normal probability plot. The figures illustrate that the lognormal distribution approach is reasonable for all elements other than hydrogen. If significant deviations from linearity occur they are generally at the upper end of the distribution where the histograms indicated a low frequency of high concentration observations.

The original data and the log transformed data were tested for significant deviations from normality with the following results (test for normality using the 3rd and 4th moments of the distribution; also using KSL test of normality): (1) Cd, Mn, Pb, Zn, and $\text{SO}_4^{=}$ in incident precipitation do not depart significantly ($P \leq 0.01$) from a

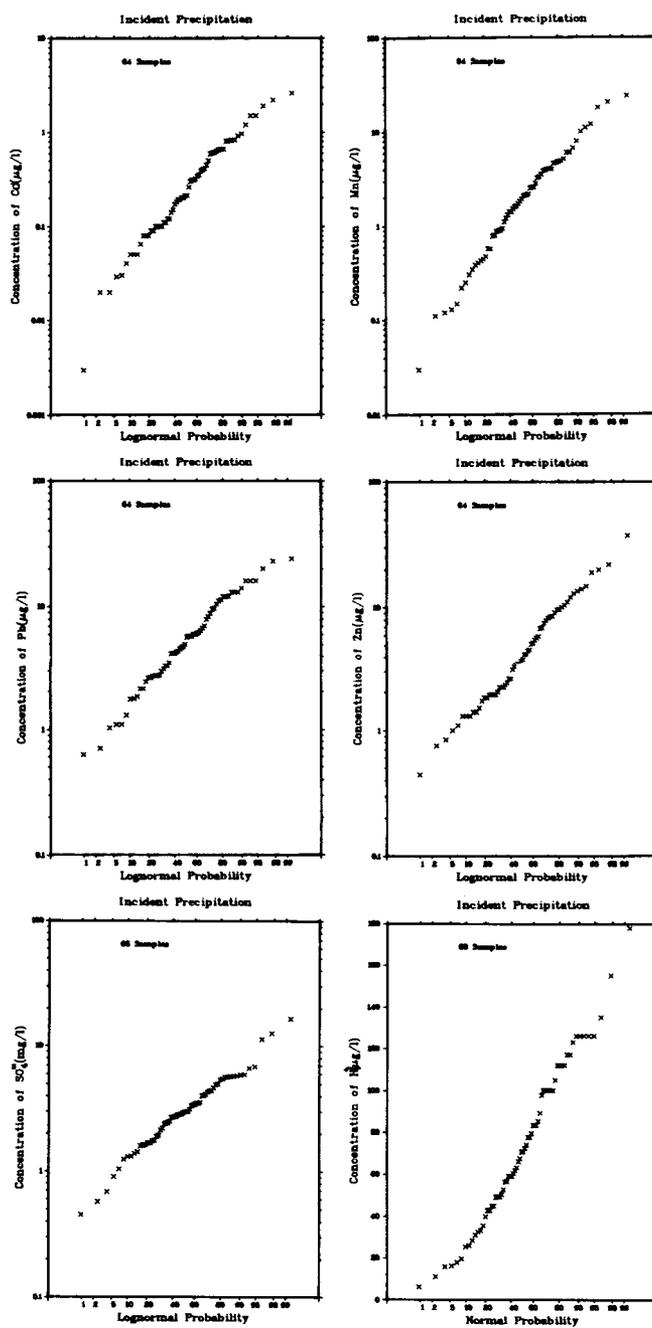


Fig. 23. Lognormal probability plots of trace metal and sulfate concentrations and a normal probability plot of hydrogen ion concentration in incident precipitation.

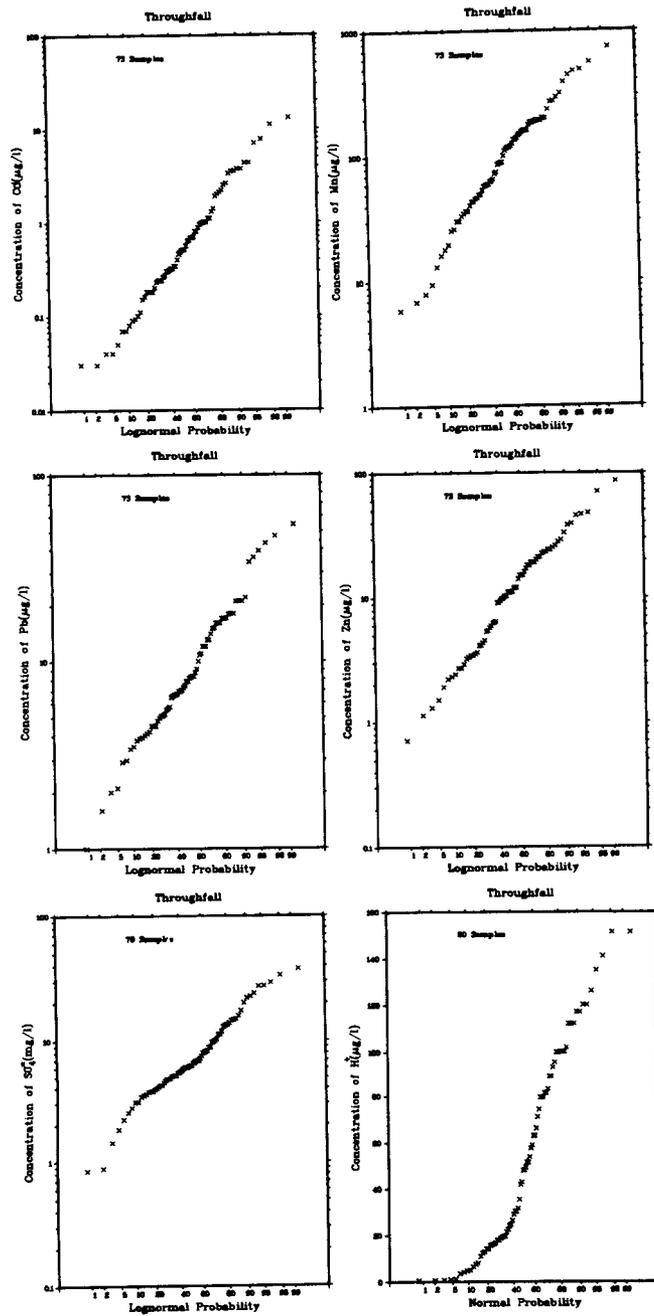


Fig. 24. Lognormal probability plots of trace metal and sulfate concentrations and a normal probability plot of hydrogen ion concentration in throughfall.

lognormal distribution, (2) Cd, Pb, Zn, and $\text{SO}_4^{=}$ in throughfall do not depart significantly from log normality, (3) Mn in throughfall cannot be defined by a normal or log-normal distribution, and (4) H^+ in both I and TF does not depart significantly from a normal distribution.

For the elements fitting the lognormal distribution, it is of interest to compare the frequency plots for rain and throughfall. The effect of the forest canopy on precipitation chemistry is manifested by the upward displacement of the throughfall curves with respect to the incident rain curves in each case. For Cd 50% of the rain concentration values are $< 0.21 \mu\text{g/l}$ and 95% are $< 1.5 \mu\text{g/l}$ while in throughfall 50% of the values are < 0.73 and 95% are $< 4.8 \mu\text{g/l}$. The parallel nature but upward displacement of the throughfall curve compared to that for incident precipitation suggests the two populations to differ primarily in numeric location but each exhibiting a similar spread in values. This is also true for Pb where 50% of the rain concentrations are < 5.5 and 95% are $< 11.5 \mu\text{g/l}$ and 50% of the throughfall concentrations are < 8.2 and 95% are $< 26 \mu\text{g/l}$. For Zn the populations differ somewhat in both spread and location with 50% of the Zn concentrations in rain $< 4.3 \mu\text{g/l}$ and 95% $< 16 \mu\text{g/l}$ while in throughfall 50% of the concentrations observed are < 10.4 and 95% $< 4.5 \mu\text{g/l}$. For Mn the two populations differ considerably in both location and spread with the median Mn concentration in rain at $20 \mu\text{g/l}$ and median concentration in throughfall at $74 \mu\text{g/l}$. Similarly for $\text{SO}_4^{=}$ the plots indicate considerable difference between the two populations, the forest canopy influencing both the location and spread

of the concentration distributions. The median $\text{SO}_4^{=}$ concentration in rain is 3.2 mg/l and the 95th percentile is 6.25 mg/l. The median throughfall $\text{SO}_4^{=}$ concentration is 7.2 mg/l and the 95th percentile is 26 mg/l. The two H^+ populations are normally distributed but differ in both location and spread with the displacement of the throughfall curve in this case to a point below that of the rain curve. Incident precipitation reflects a median pH of 4.15 and a 95th percentile of 3.84 while in throughfall the median pH is 4.30 and the 95th percentile is 3.86.

Temporal and Spatial Effects on Rain Chemistry

Much of the variability associated with the composition of rain and throughfall in WBW may be attributed to three major factors, (1) location effects, (2) temporal or seasonal effects, and (3) rainfall volume effects. The influence of precipitation volume will be considered in detail in a following section but is an integral part of these effects.

There are numerous complexities associated with this data set, including non normality of some parameters, lognormality of others, and the inability to consistently maintain a balanced sampling design when dealing with somewhat unpredictable, event situations. Hence several statistical methods were employed to define the significant variations related to location and seasonal effects on rain and throughfall chemistry. These included non parametric tests, analysis of variance using log transformed data from certain subsets of the data which represented balanced designs, Duncan's new multiple range tests on log

transformed data sets, and analysis of covariance to account for precipitation volume effects on seasonal variability in element concentrations. The applications of these tests to the incident precipitation and throughfall chemistry data is described in detail in Appendix C. Also included in this appendix are plots of percentiles for the concentrations of Cd, Mn, Pb, Zn, SO_4^- , and H^+ during the four seasons and at the six collection sites. These plots provide a simple, visual summary of the distribution of the data in space or time. The results of the statistical considerations presented in the appendix are summarized in the following two sections.

Spatial Variability

A major incentive in the establishment of multi-site rain chemistry sampling networks is assessment of location differences in incident precipitation and throughfall chemistry over a relatively small area. Although spatial differences in rain chemistry have been previously reported, these have generally involved studies on regional scales (Schlesinger et al., 1974, Swank and Henderson, 1976). In the case of throughfall, investigations of spatial differences have generally involved studies of the chemistry as influenced by various canopy types (i.e., coniferous vs hardwood or one hardwood species vs another; e.g., see Eaton et al., 1973; Henderson et al., 1977).

The WBW data provides the opportunity to test for statistically significant location effects among the four throughfall sites and also between the two incident precipitation stations for storms which were sampled simultaneously. The major difference between the two incident

sites is in their watershed elevation and location relative to the forest canopy. As described earlier the CI site (Figure 20) is located on the western ridge of WBW at an elevation of 336 m (MSL) and, additionally, atop a 46-m meteorological tower approximately 23 m above the forest canopy (Figure 25). The GI site, on the other hand, is a ground level incident precipitation station located adjacent to the stream bed at an elevation of 268 m (~ 110 m in height below the CI site) in a clearing which is ~ 18 m below the edges of the surrounding forest canopy (Figure 26). The composition of rain at the GI site thus exhibits the additional effects of particle and gas washout from the air mass within the watershed compared to the composition of precipitation above the canopy (CI site). In addition, there exists the possibility of infrequent canopy effects on rain chemistry at the ground level station resulting from wind blown rain being intercepted by the edges of the canopy prior to collection by the incident precipitation sampler. This may be possible since the lateral distance from the sampler to the canopy edge is generally < 20 m (Figure 26).

As described earlier, throughfall samples were collected beneath chestnut oak (Quercus prinus) canopies at three of the four sites. Site T1 was situated along the stream bank, near the GI station, beneath a beech-poplar canopy (Fagus grandifolia, Liriodendron tulipifera; Figure 20) while sites T2, T3, and T4 were located on ridge tops surrounding the watershed beneath exclusively chestnut oak canopies. As indicated in Figures 27-30, (which illustrate the location of the samplers at each site, and the canopy during early spring for sites T1, T2, and T4) T2 was characterized by two moderately

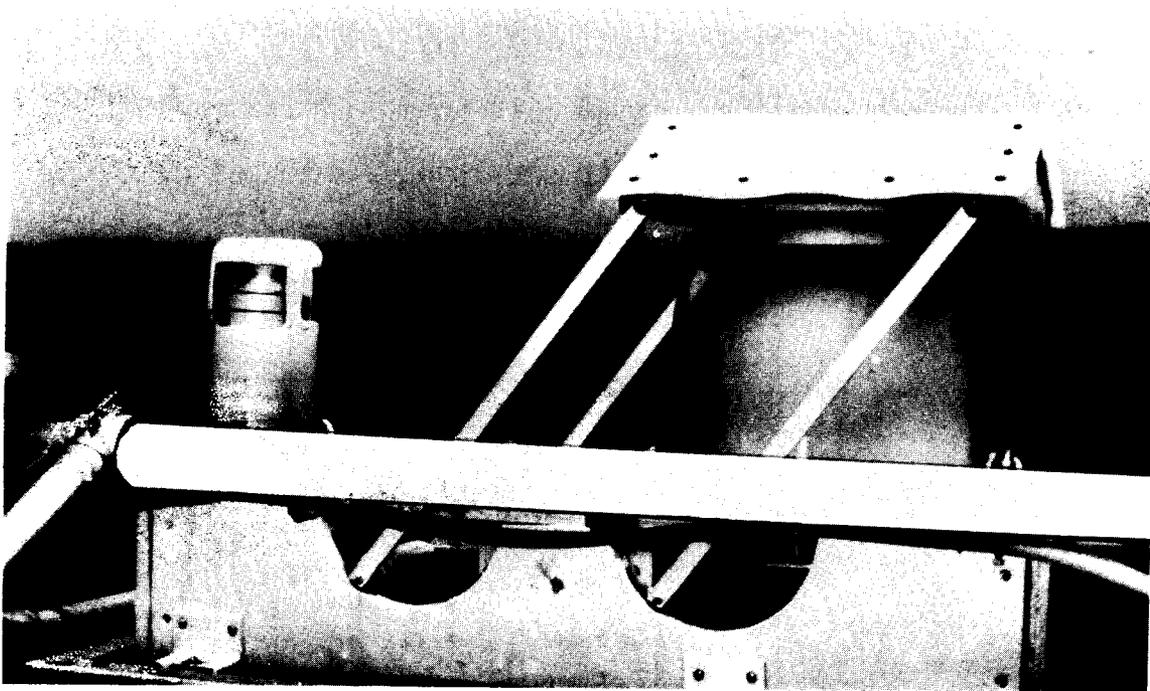
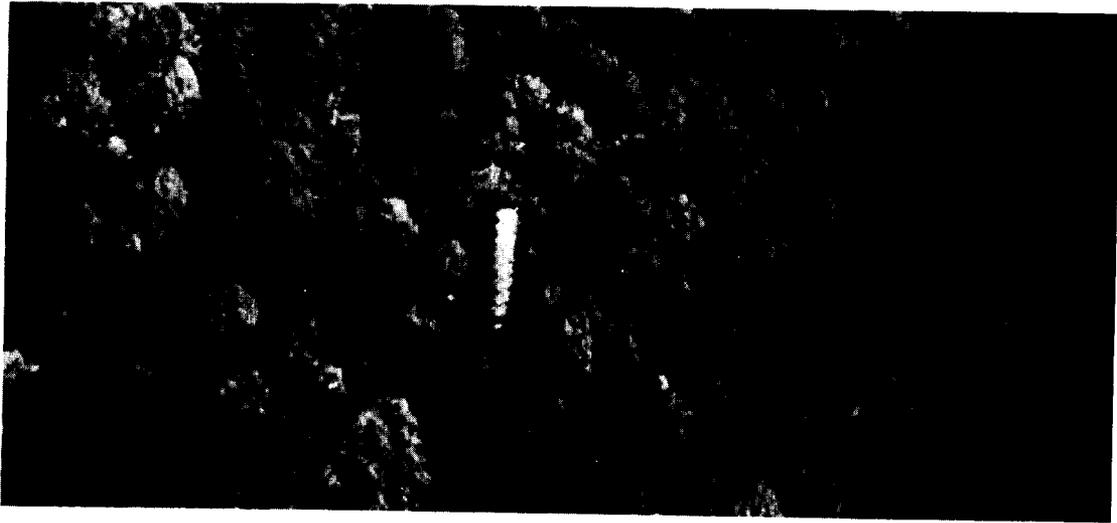


Fig. 25. Above canopy (CI) incident precipitation collection site at the 46 meter meteorological tower (upper photo) indicating deployment of the modified HASL rain sampler.

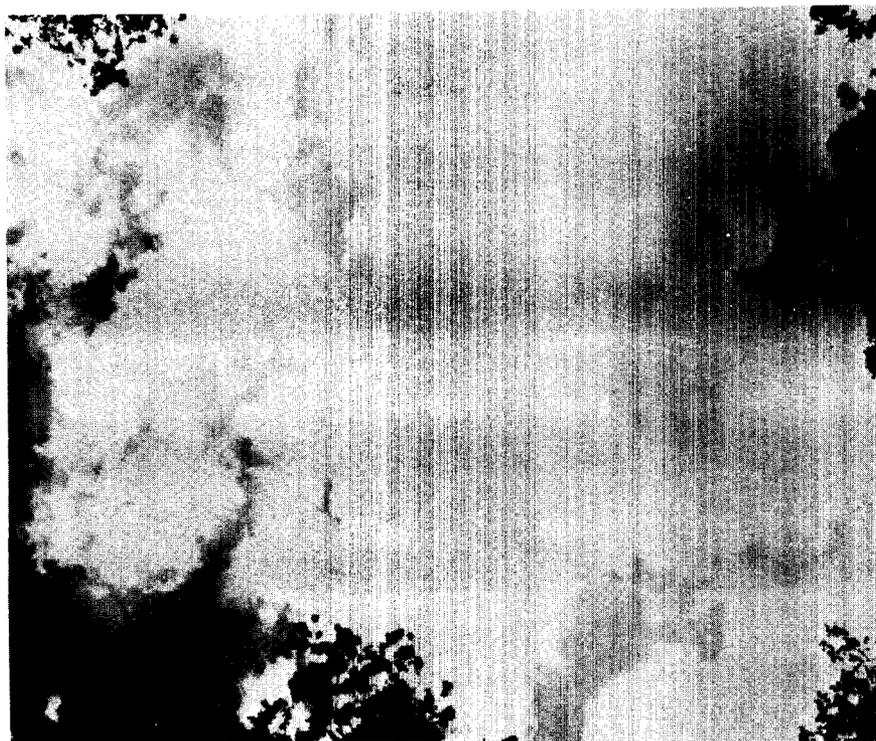


Fig. 26. Ground level (GI) incident precipitation collection site indicating the location of the HASL sampler with respect to the surrounding canopy. The photo to the right is the air space immediately above the sampler. Vertical distance from the sampler to the nearby branches is ~ 18 m while the horizontal distance between the left- and right-most branches is ~ 30 m.

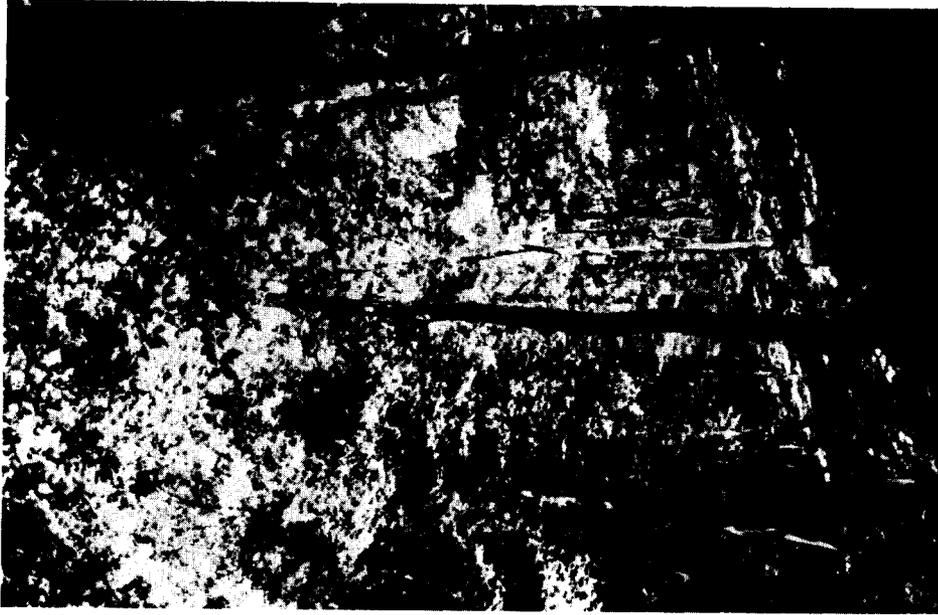


Fig. 27. Throughfall collector site #11. The left photo shows the canopy morphology shortly following budbreak. The right photo illustrates the location of the HASL wetfall collector in relation to the beech/poplar canopy. This site is paired with site GI.



Fig. 28. Throughfall collector site #T2. The left photo shows the canopy morphology shortly following budbreak. The right photo shows the location of the HASL collector in relation to the chestnut oak canopy. This site is paired with site CI.



Fig. 29. Throughfall collection site #T3. Left photo shows the typical deployment of a modified HASL wetfall collector beneath the forest canopy. The right photo illustrate the HASL collector at site T3 in relation to the chestnut oak canopy.



Fig. 30. Throughfall collector site #T4. The left photo shows the canopy morphology shortly following budbreak. The right photo shows the location of the HASL wetfall collector in relation to the chestnut oak canopy.

sized, but tall oaks, T3 was characterized by several smaller oaks, and T4 was dominated by one, large chestnut oak. Thus, storms sampled simultaneously at all sites offer the opportunity to test for significant differences in TF chemistry beneath similar canopy types separated by distances ranging from 260 to 3500 m, as well as to test for differences in chemistry as influenced by forest type.

As described in Appendix C, nonparametric tests (Wilcoxon signed rank and Friedman's rank sum tests; Hollander and Wolfe, 1973) were applied to a data set comprised of storm events sampled simultaneously at all throughfall or both incident precipitation sites. The results of the nonparametric tests are summarized in Figure 31 which presents a comparison of the mean values, standard errors of the means, and statistical significance of differences between sites. Differences were tested at both the 0.01 and 0.05 probability levels of significance and are so indicated on the figure. Only for Mn was there a highly significant ($P \leq 0.01$) difference in rain chemistry between the GI and CI sites. In addition there were somewhat less significant ($P \leq 0.05$) location effects on Cd concentration and on H^+ concentration. It is worth noting that the significance of the station differences for Mn and H^+ is difficult to discern from Figure 31 ($\bar{X} \pm SE$) above. However, although the differences between CI and GI were small, the arithmetic sign of the differences was consistent. In every event sampled the GI concentration of Mn exceeded the concentration at CI while in the case of H^+ every storm but one exhibited equal or lower H^+ concentrations at the GI site relative to the CI site. The differences in Mn and H concentrations between the

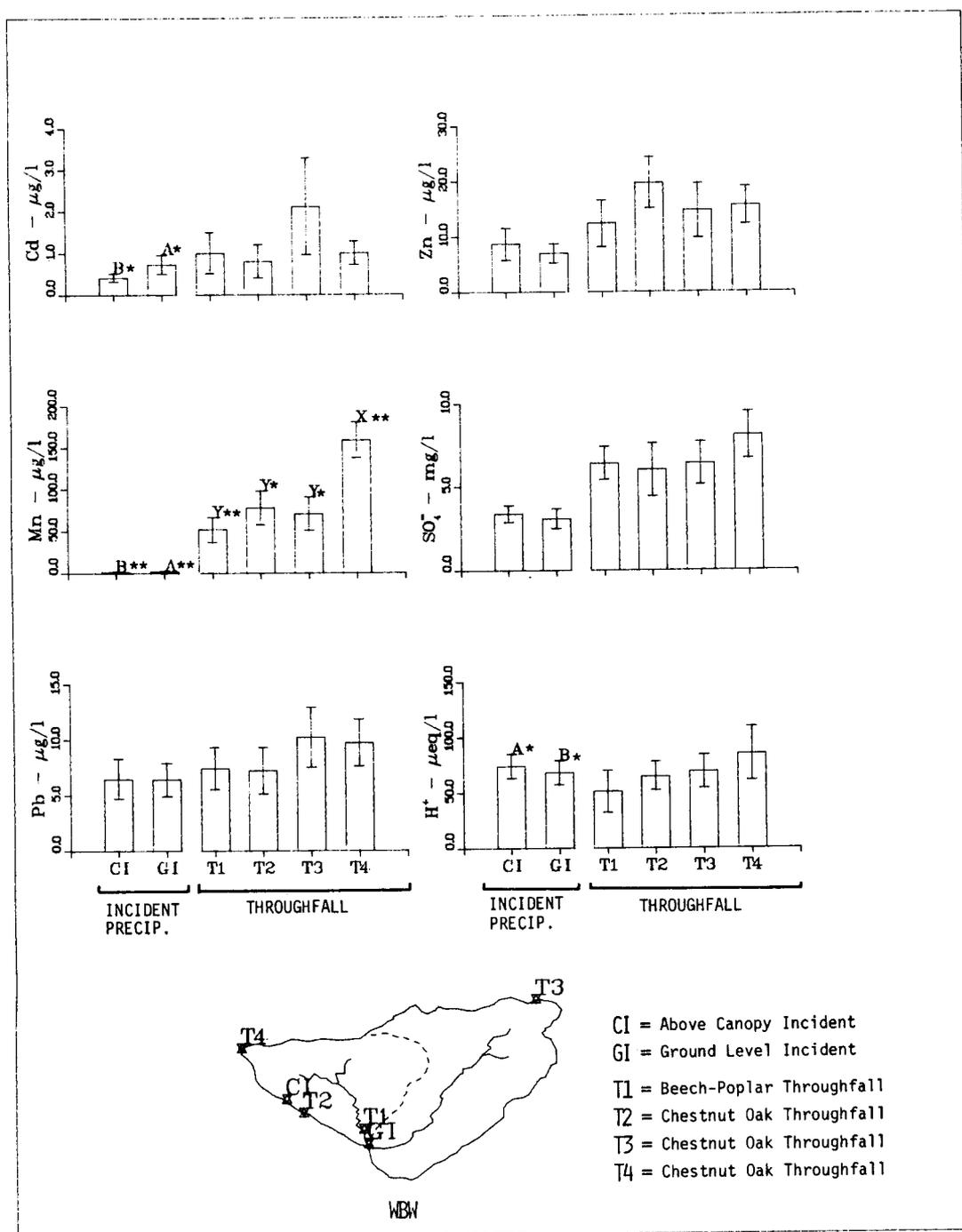


Fig. 31. Comparison of mean concentrations (\pm standard error) in rain and throughfall for events sampled simultaneously at both incident or all throughfall stations, indicating statistically significant differences. Letters over each bar indicate difference between sites for either rain or throughfall; values with the same or no letter are not significantly different, asterisks indicate level of significance (*, $P \leq 0.05$; **, $P \leq 0.01$; Wilcoxon signed rank and Friedman's rank sum tests were used).

ground level and above canopy incident precipitation sites is most likely related to the possible canopy interception effects described above for the GI site. Rain marginally interacting with the edges of the canopy before being collected by the GI sampler would be expected to show enrichment in the element whose concentration is most strongly influenced by canopy interception, Mn, and show depletion in the only element of this group which is removed by the canopy, H^+ .

Studies of small spatial differences in incident precipitation are few and generally involve bulk collections on a non-event basis. Harrison et al. (1975) sampled rain at several sites near London, collecting weekly, bulk samples. Two stations were located within 1 km of each other in areas of different land use. Nonetheless the differences found between the sites for Pb, Cd, and pH were small (Pb was 0.17 vs 0.11 mg/l; Cd 0.006 vs 0.006 mg/l; and pH 5.67 vs 5.12) although no statistical treatment was attempted. Weiner (1978) has recently compared the trace chemistry of rain collected at two adjacent sites (100 m apart) in the southeastern U.S. Over a two year period the sites yielded a significant difference in rain chemistry only for Pb, although between site coefficients of variation for Cd, Cu, and Mn were also high (17 to 44%). Reasons for inter-site variability were not discussed.

Figure 31 also illustrates the differences in mean throughfall concentrations for storms sampled simultaneously at all 4 sites. The nonparametric tests (Appendix C) indicated only one series of significant site effects, those for Mn. Site T4 produced throughfall with a significantly greater Mn concentration than T1 ($P \leq 0.01$), T2

and T3 ($P \leq 0.05$), although there were no significant differences between T1, T2, and T3 ($P > 0.05$). Although there is a trend of somewhat lower throughfall concentrations for all elements beneath the beech-poplar canopy (T1) compared to the chestnut oak canopies, these differences were not significant. It is interesting that the element whose concentration is most strongly influenced by interaction with the forest canopy, Mn, is the only element to exhibit significant location effects in throughfall. It appears from this discussion and data presented in Chapters IV and VII that Mn is the only element of the group studied here whose concentration in throughfall results primarily from internal leaf leaching and only to a minor extent from surface associated dry deposition. Thus, Mn might be the most likely of the elements studied to exhibit differences in throughfall concentrations beneath different canopy types or between different age class trees of the same species.

In a previous study of the major element chemistry of throughfall in WBW, Henderson et al. (1977) reported significant differences between concentrations of N, P, K, and Mg in throughfall beneath 4 different forest types. The differences were such that a mixed oak-hickory stand resulted in consistently higher throughfall concentrations than a pine stand, poplar-beech stand, and chestnut oak stand. Only in the case of Mg was there a significant difference between the poplar-beech and chestnut oak canopies with the concentration of Mg in throughfall higher beneath the poplar-beech canopy. The authors stated that the reasons for the differences in throughfall chemistry were unclear but that they were only weakly

related to differences in foliar concentration. Eaton et al. (1973) reported similar differences between TF chemistry collected beneath sugar maple, yellow birch, and beech canopies in a northern hardwood forest. The sugar maple canopy resulted in throughfall significantly enriched in Na, $\text{SO}_4^{=}$ and Cl compared to the other two. In addition, they reported that tree size influenced leachate loss of elements from the canopy with significantly greater amounts lost from large trees compared to small on a unit area basis, apparently in agreement with the results reported here for Mn. Nihlgard (1970) studied major element chemistry of rain and throughfall collected in beech and spruce stands 100 m apart in southern Sweden using bulk collectors operated on a continuous non-event basis. The author found large differences between the average concentration in throughfall beneath the two forest types with spruce greater than beech by factors of ~ 2 for Mn and ~ 3 for $\text{SO}_4^{=}$. In addition the mean pH of spruce throughfall was 4.5 compared to 5.7 in the beech forest and 5.2 in incident precipitation. The author concluded that the variability resulted from differences in internal leaf/needle leachability of the elements in the forest types. He found no indication of the spruce canopy being more aerosol-adherent than the beech canopy. Heinrichs and Mayer (1977) reported trace element concentrations in an annual composite of bulk samples collected beneath beech and spruce canopies in central Germany. As such, the values reported are not amenable to statistical analysis, representing only one actual analysis in each case. However for the elements reported in our study, the authors reported large differences in throughfall concentrations between the

two canopy types, with the spruce forest consistently yielding throughfall of higher concentration. The enrichment of throughfall concentrations in the spruce forest compared to the beech forest ranged from ~ 2 for Cd, Pb, and S to ~ 3 for Mn to ~ 5 for Zn. The authors did not discuss reasons for the forest type differences but, contrary to the conclusions of Nihlgard, did speculate that the source of all elements studied in throughfall, with the exception of K, was primarily "filtering of atmospheric particles by the tree canopy" with subsequent washoff by rain.

Temporal Variability

Seasonal effects on concentration are likely to be influenced by differences in rainfall volume and, thus may not be amenable to simple interpretation. For this reason several approaches were used to assess the significance of seasonal variability in rain and throughfall chemistry. These are discussed in detail in Appendix C. As in the case of spatial variability, previously published discussions of temporal effects have largely involved sample sets complicated by the collection procedures used (i.e., bulk samples including wet plus dryfall and samples collected over long time periods). However, seasonal effects whether related to synoptic meteorological conditions, seasonal storm characteristics, forest canopy development, or other phenomena including variable anthropogenic emissions have been previously identified (Swank and Henderson, 1976; Henderson et al., 1977; Eaton et al., 1973).

Analysis of variance (ANOVA) was used to determine significant seasonal effects on rain and throughfall chemistry. Because of the lognormal distribution of most of the data, the possible effect of rain volume, and the previously discussed effect of station location on some of the parameters a number of statistical methods were applied. These are described in detail in Appendix C. Briefly, seasonal and annual effects on elemental concentrations were determined using a log transformed data set for Cd, Pb, Zn, and SO_4^- and the nontransformed H^+ data, replacing every group of "replicate" observations of concentrations in either incident precipitation or throughfall for each event by a single concentration equal to the mean of the "replicate" concentrations, since no highly significant location effects were found for these elements. These transformations were necessary to satisfy the requirements for the use of ANOVA. In the case of Mn which exhibited significant station effects, the ANOVA tests were run on log transformed data from individual stations. If ANOVA yielded highly significant effects for any given element in rain or throughfall, ($P \leq 0.01$), Duncan's new multiple range test (Duncan) was used to distinguish significant differences between seasonal or annual concentrations. The results of these comparisons are summarized in Table 27. In addition, the seasonal distributions of concentrations for each element are illustrated in Figures C3 and C4 in Appendix C. These are in the form of percentile plots. The table presents annual and seasonal average concentrations and standard errors for the modified data set indicating significant differences as determined by

Table 27. Mean annual and seasonal concentrations (\pm standard error) in incident precipitation and throughfall^a

	1976	1977	Dormant ^b	Budbreak ^b	Max. growth ^b	Senescence ^b
INCIDENT PRECIPITATION						
Cd $\mu\text{g/l}$	0.30 \pm 0.12	0.49 \pm 0.08	0.55 \pm 0.19	0.41 \pm 0.22	0.41 \pm 0.10	0.28 \pm 0.08
Pb	5.78 \pm 0.54	7.67 \pm 1.11	5.66 \pm 1.31	3.81 \pm 1.14	8.52 \pm 1.23	5.34 \pm 1.45
Zn	5.91 \pm 1.06	5.77 \pm 1.13	4.79 \pm 1.10 B	1.12 \pm 0.13 B	4.07 \pm 0.68 B	13.1 \pm 2.5 A
SO ₄ ⁼ mg/l	3.1 \pm 0.3	4.1 \pm 0.6	2.52 \pm 0.29 B	1.73 \pm 0.50 B	5.22 \pm 0.70 A	2.26 \pm 0.29 B
H ⁺ $\mu\text{eq/l}$ (as pH)	0.075 \pm 0.007 4.12	0.076 \pm 0.007 4.12	0.067 \pm 0.008 AB 4.17 AB	0.043 \pm 0.011 B 4.37 B	0.093 \pm 0.008 A 4.03 A	0.051 \pm 0.007 B 4.29 B
THROUGHFALL						
Cd $\mu\text{g/l}$	0.85 \pm 0.26	1.69 \pm 0.45	1.70 \pm 0.57	1.45 \pm 1.14	1.81 \pm 0.70	0.91 \pm 0.50
Pb	7.12 \pm 1.07	13.2 \pm 2.1	8.71 \pm 1.91 AB	6.54 \pm 1.13 B	17.6 \pm 3.3 A	6.72 \pm 1.43 B
Zn	14.5 \pm 4.6	14.6 \pm 2.8	15.8 \pm 5.2 A	3.72 \pm 1.05 B	14.7 \pm 4.3 AB	22.6 \pm 4.3 A
SO ₄ ⁼	6.9 \pm 1.9	10.7 \pm 1.4	5.4 \pm 1.1 B	7.0 \pm 2.1 B	14.4 \pm 2.1 A	6.0 \pm 1.0 B
H ⁺ $\mu\text{eq/l}$ (as pH)	0.031 \pm 0.014 4.51	0.062 \pm 0.007 4.21	0.084 \pm 0.013 4.08	0.043 \pm 0.014 4.37	0.063 \pm 0.011 4.20	0.028 \pm 0.006 4.55

^aValues followed by the same or no letter are not significantly different ($P \leq 0.01$; Duncan's New Multiple Range Test).

^bDormant = November through February; budbreak = March and April; max. growth = May through August; senescence = September and October.

ANOVA and Duncan. Annual or seasonal mean values followed by the same or no letter are not significantly different ($P > 0.01$).

The seasons listed in the tables and figures are related to conditions of the deciduous forest canopy and roughly correspond to the natural seasonal cycle with "dormant" comprising the months of November to February; "budbreak" includes the months of March and April and is the period during which all major deciduous forest species are forming new leaves; "maximum growth" runs from May to August and represents the period of maximum leaf growth and canopy development; and "senescence" which includes September and October and is the period during which deciduous species are in the process of losing their leaves. Although the "seasons" defined here relate to obvious canopy effects on throughfall chemistry, they are as useful as any other definitions of season in assessing temporal effects on rain chemistry as well.

Concentrations of each element in rain and throughfall, with the exception of Zn, exhibited the trend of higher concentrations in 1977 compared to 1976, although in no cases were the differences significant. Similarly for Mn, which had to be considered for each individual station (summarized in Table 28), there were higher concentration levels during 1977 at all stations except T2. However, only for the two incident stations were the between year differences significant.

Significant seasonal effects ($P \leq 0.01$) were found for all elements except Cd and Pb in rain and Cd and H^+ in throughfall. Although the seasonal variations for each element were different, in general the seasonal trends for any element in rain were reflected by

Table 28. Mean annual and seasonal concentrations (\pm standard error) of Mn in incident precipitation and through-fall for each sampling station^a

	1976	1977	Dormant	Budbreak	Max. growth	Senescence
<u>Incident precipitation^b</u>						
CI	0.94 \pm 0.29 B	4.68 \pm 0.99 A	2.02 \pm 0.72	5.65 \pm 4.35	4.55 \pm 1.21	1.23 \pm 0.41
GI	1.08 \pm 0.62 B	4.72 \pm 1.45 A	2.19 \pm 1.02	3.61 \pm 1.57	6.36 \pm 2.58	1.55 \pm 0.31
<u>Throughfall</u>						
T1	36.4 \pm 10.7	45.1 \pm 10.9	48.7 \pm 9.4	15.8 \pm 8.2	35.7 \pm 5.5	88.3 \pm 31.9
T2	105 \pm 20	98.4 \pm 21.0	85.6 \pm 22.0	109 \pm 81	104 \pm 29	105 \pm 27
T3	39.8 \pm 17.2	105 \pm 24	84.0 \pm 18.6	98.4 \pm 91.6	79.6 \pm 42.3	112 \pm 36
T4	— ^c	260 35	136 \pm 10	— ^b	319 \pm 47	156 \pm 15

^aValues followed by the same or no letter are not significantly different ($P \leq 0.01$; Duncan's New Multiple Range Test).

^bAll concentrations in $\mu\text{g/l}$.

^cStation not operational.

similar trends in throughfall. The relationship between the chemistry of rain and throughfall is the subject of considerable discussion in the following section. Maximum concentrations of Pb and $\text{SO}_4^{=}$ in both rain and throughfall occurred during the maximum growth period, when the deciduous canopy was fully developed. The levels of $\text{SO}_4^{=}$ during maximum growth were significantly different from all other seasonal concentrations in both incident precipitation and throughfall. The seasonal differences for Pb were not significant in rain but were in throughfall ($P \leq 0.01$). Hydrogen ion in rain exhibited highest concentrations during maximum growth period, these concentrations being significantly different from those during budbreak and senescence but not dormant. The ability of the fully developed canopy to scavenge hydrogen ions was evident in the considerably decreased concentration of H^+ in throughfall during the maximum growth period. However, during the dormant, leafless period the incident and throughfall H^+ levels were comparable, with the peak concentration in throughfall occurring at the time. Zinc in both rain and throughfall occurred in highest concentrations during the senescence period with the incident rain concentration being significantly different from all other seasons. In throughfall the concentrations of Zn during this period was significantly different only from the budbreak concentration. Cadmium in rain and throughfall did not exhibit any significant seasonal effects although the trend was for highest concentrations in rain to occur during dormant and highest throughfall concentrations during maximum growth.

For Mn, which had to be considered on an individual site basis (Table 28) the above canopy site (CI) experienced somewhat higher concentrations during budbreak while at the ground level incident site the highest concentrations occurred during the maximum growth period. This is related to the canopy interception effect at the station, as described above, which is expected to be more pronounced during full canopy development. In the case of the throughfall sites, the beech-poplar canopy (T1) yielded highest Mn levels during leaf senescence, the multiple tree chestnut oak sites (T2, T3) showed relatively little seasonal variations in Mn levels, while the single tree chestnut oak site (T4) exhibited considerably higher Mn concentration during the maximum growth period. It is apparent that the station differences in throughfall, Mn concentrations discussed above are further manifested in seasonal behavior of Mn concentrations in throughfall beneath various canopies.

As a final test of the validity of the above seasonal effects a second ANOVA model was used which included the effect of rainfall volume per event for each sample since rain volume varies seasonally as described earlier. The inclusion of the rain volume covariate did not substantially alter the conclusions of the ANOVA models discussed above. However, the analysis of covariance models did indicate a significant influence of precipitation volume on nearly all elemental concentrations. These relationships are the topic of a following section.

In general, previous attempts to explain seasonal effects have been complicated by collection of bulk samples, influenced by both wet

and dry deposition, collected over multiple events. In the case of TF beneath a deciduous canopy the seasonal trends relate to some extent to the presence or absence of leaves or to the physiological status of the leaves (Eaton et al., 1973; Henderson et al., 1977). However, few have attempted to include in their analyses the effect of seasonal variations in rainfall volume. Previous research in WBW, for wetfall only samples collected on a weekly basis, has suggested that maximum concentrations of several elements occur during periods roughly corresponding to the maximum growth period. Seasonal trends of Ca, Mg, and K concentration in rain indicated generally higher levels during the period March to June and lower concentrations during December-February. Similar trends were reported for a second southern Appalachian watershed (Swank and Henderson, 1976). In a recently completed study Shriner and Henderson (1978) reported trends of H^+ and $SO_4^{=}$ in incident precipitation in WBW indicating highest concentrations of both elements to occur during the period June-September.

Hornbeck et al. (1976) found trends in H^+ concentration in bulk precipitation collected in the northeastern U. S. which indicated highest levels during summer and fall and lowest levels during spring and winter, similar to the trend in Table 3 for WBW. Few studies have involved detailed analysis of seasonal effects on trace metal levels in rain, although some trends have been reported. Hallsworth and Adams (1973) found higher levels of Cu and Cd in monthly bulk precipitaton during the summer quarter. Drozdova and Makhonko (1970) collected rain samples during warm and cold periods in the USSR and reported higher

concentrations of Mn, Ni, and Pb concentrations during the warm period and higher levels of Fe during cold periods. Struempfer (1976) reported higher concentrations of Cd and Pb in snow compared to rain but comparable levels of Al, Cu, Mn, and Zn. However, it is not clear from the paper whether the samples represented bulk precipitation or wetfall only. In a statistical treatment of bulk rain chemistry collected over a 2 year period in the Southeast, Weiner (1978) found significant seasonal effects on Mn and Pb concentrations but not on Cd concentrations. Manganese concentrations were highest in summer, Pb in spring-summer.

Seasonal trends in throughfall chemistry have generally been considered only for major elements. In WBW Henderson et al. (1977) found little difference in concentrations of K, Ca, and Mg in bulk rain between the growing season and dormant period while in throughfall the elements were considerably elevated in concentration during the growing season. Eaton et al. (1973) reported higher levels of K, Ca, and Mg in throughfall in fall than summer but comparable concentrations of $\text{SO}_4^{=}$.

For major cations and primarily crustally derived metals, seasonal fluctuations in agricultural activities resulting in increased resuspension of surface soil material have been indicated as possibly influencing rain chemistry (Swank and Henderson, 1976). Seasonal trends of trace element concentrations in precipitation have often been ascribed to similar fluctuations in anthropogenic emissions, such as increased fossil fuel combustion during winter months (Struempfer, 1974; Bertine and Goldberg, 1971). However, in a region where the

primary utilization of fossil fuels is coal combustion for electrical production or consumption of gasoline by automobiles, such as East Tennessee, there are no clearly defined seasonal fluctuations in combustion emissions.

The summer maximum discussed above for $\text{SO}_4^{=}$ and H^+ in rain apparently exists across the eastern U. S. Galloway (1978) has recently summarized the initial results of the multi-site precipitation chemistry network (samples are wetfall only collected on an event basis) operated as part of the Department of Energy's MAP3S program (Multi-state Atmospheric Power Production Pollution Study). The sulfur data presented by Galloway for the four original MAP3S sites, in the eastern and north-eastern U. S., have been plotted in the form of monthly weighted mean concentrations of sulfate in incident rain during 10/76-10/77 (Figure 32). Also included in this plot are weighted mean concentrations of sulfate in rain collected during this same period in WBW. The comparability of the temporal variations in concentration at these five sites situated across the eastern U. S. is striking. The regional nature of the wetfall deposition of sulfate is apparent. Interestingly the peak summer concentrations of sulfate in rain at WBW are considerably lower than those measured at Ithaca, New York, Pennsylvania State University, and Charlottesville, VA., being comparable to those measured at the more remote Whiteface Mountain, New York site. Galloway speculated the summer maxima to be related to increased emission rates of S into the atmosphere in the summer and a concurrent faster rate of oxidation of SO_2 to $\text{SO}_4^{=}$ due to higher temperature and humidity. An alternative, perhaps additional,

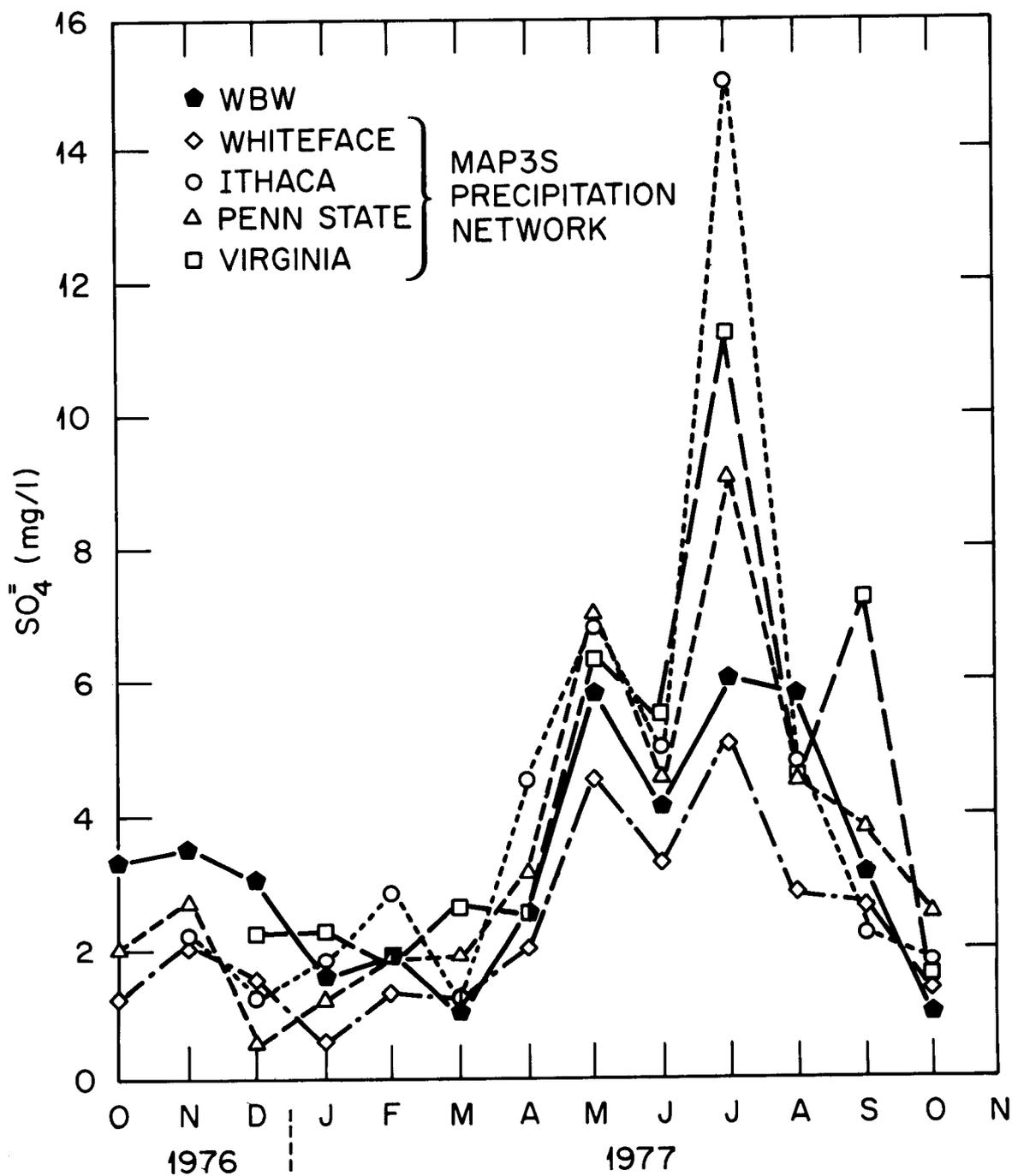


Fig. 32. Comparison of weighted mean monthly concentrations of sulfate in incident precipitation collected in Walker Branch Watershed (WBW) and four MAP3S precipitation chemistry monitoring stations in New York (\diamond), Pennsylvania (Δ), and Virginia (\square). Adapted from Galloway (1978).

explanation for the trends seen in the WBW data is that the summer maxima is in response to synoptic meteorologic conditions which result in elevated pollutant gas and aerosol concentrations due to air stagnation, and in generally lower rain volumes per event, and hence less dilution of precipitation scavenged material. Discussion with K. Whitby (1978) have confirmed this to be a viable explanation.

The Relationship Between the Chemistry of Rain and Throughfall

The chemistry of throughfall is the result of the interaction between incoming precipitation and the vegetation-surface. This interaction can be primarily with leaves and secondarily with branches (i.e., during budbreak, to some extent, and during maximum growth and senescence) or with branches alone (during dormant and the initial period of budbreak). In a fully developed canopy, precipitation generally interacts with 3 tiers of leaves before exiting the canopy (Tukey, 1970). Depending on season and forest type, a measurable fraction (generally 10 to 20%) of the incident precipitation never reaches the forest floor, being evaporated from or absorbed directly by the leaf surface of initial contact. That which reaches the ground occurs primarily as throughfall with only ~ 5% as stemflow (Likens et al., 1977). Stemflow was not considered in this study because of inherent problems in contamination free sampling and its relatively minor contribution to the total water flux.

In a recent study of the quantity of throughfall beneath different forest types in WBW, Henderson et al. (1977) noted that, although there were differences in the amount of throughfall between seasons and

years, there were no significant differences in the throughfall amount beneath the various canopy types regardless of season or year. Two of the canopy types studied were chestnut oak (~ 50% Quercus prinus L. by basal area) and poplar-beech (~ 50% Liriodendron tulipifera L., ~ 4% Fagus grandifolia Ehrh.), corresponding to the throughfall stations in this study. During the growing season 84 to 87% of the incident rain passed through the poplar-beech canopy and reached the ground, while for the chestnut oak the amount ranged from 83 to 84%. During the leafless period there was an insignificant difference from the above values (~ 85% in each case).

The chemistry of incident precipitation is altered to various degrees in passing through the forest canopy, the extent of change being related to the element of interest and stage of canopy development (as previously discussed with respect to the data in Table 26). Canopy interception influences the chemistry of rain by various means including sorption, ion exchange, chemical reactions, and leaching. Elements in throughfall thus result from: (1) material originally present in incoming rain and not scavenged or altered at the leaf/branch surface through cellular uptake mechanisms or interactions with material present at the leaf surface, (2) material residing superficially on the leaf/branch surface and subsequently washed off, and or (3) material originally present within the vegetative tissue and leached by rain at the leaf surface. The origin of elements in this last phase could be root uptake and translocation, gaseous uptake at the leaf, or dissolution and uptake of particulate associated elements at the leaf surface prior to the precipitation event (Wittwer and

Teubner, 1969). Alternatively some elements initially in rain may occur in somewhat lower concentrations in throughfall because of absorption by the leaf or adsorption onto the leaf surface or adhering particles (Wittwer and Teubner, 1969).

To describe the relationship between incident precipitation and throughfall chemistry in WBW most accurately, the 2-year data set was subsampled by selecting only those events for which there existed analyses of both rain and throughfall collected simultaneously at one of the paired rain and throughfall stations (Figure 20). This data set was comprised of 60% of the total number of events sampled and included samples collected during each season and for events ranging in precipitation volume from 0.13 cm - 11.4 cm.

Figures 33 to 35 graphically summarize the relationship between incident rain and throughfall chemistry for each of the simultaneously sampled event during 1976-1977. The effect of the forest canopy on the element concentrations in throughfall relative to incoming rain is obvious, being most pronounced in the case of Mn. For every event sampled, regardless of canopy condition, the throughfall concentrations of Cd, Pb, Mn, Zn, and $\text{SO}_4^{=}$ equalled or exceeded the concentration in incoming rain, although the difference was generally most pronounced during the period of maximum canopy development (\sim May to October). The relationship between incident rain and throughfall hydrogen ion concentrations was more complex, with the pH of rain generally lower than that of throughfall during the growing season (budbreak + max. growth + senescence) and higher during the dormant season, with some exceptions. The relationship between rain and throughfall

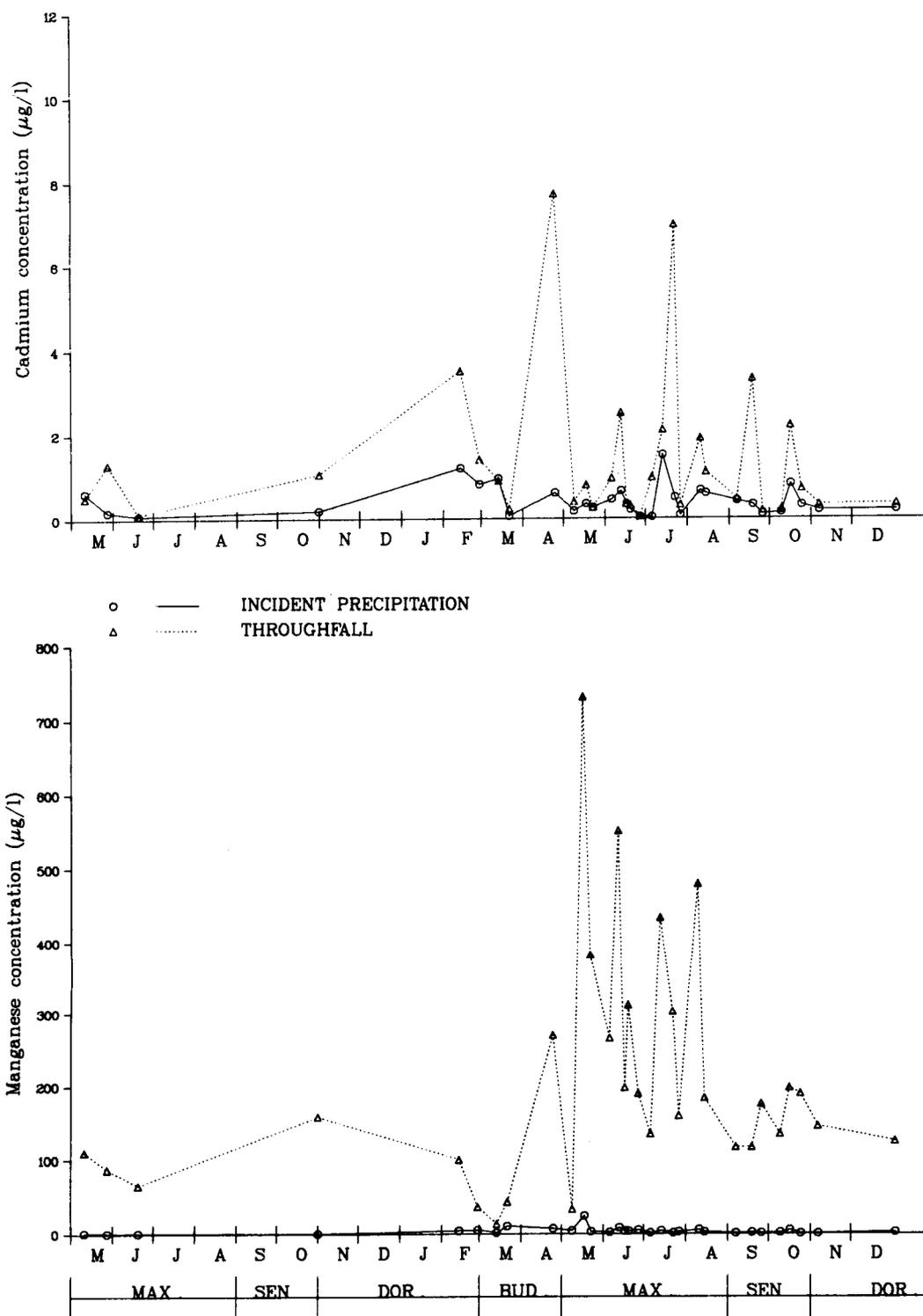


Fig. 33. Temporal variations in Cd (upper plot) and Mn (lower plot) concentrations in rain and throughfall for events sampled simultaneously from May 1976 to December 1977.

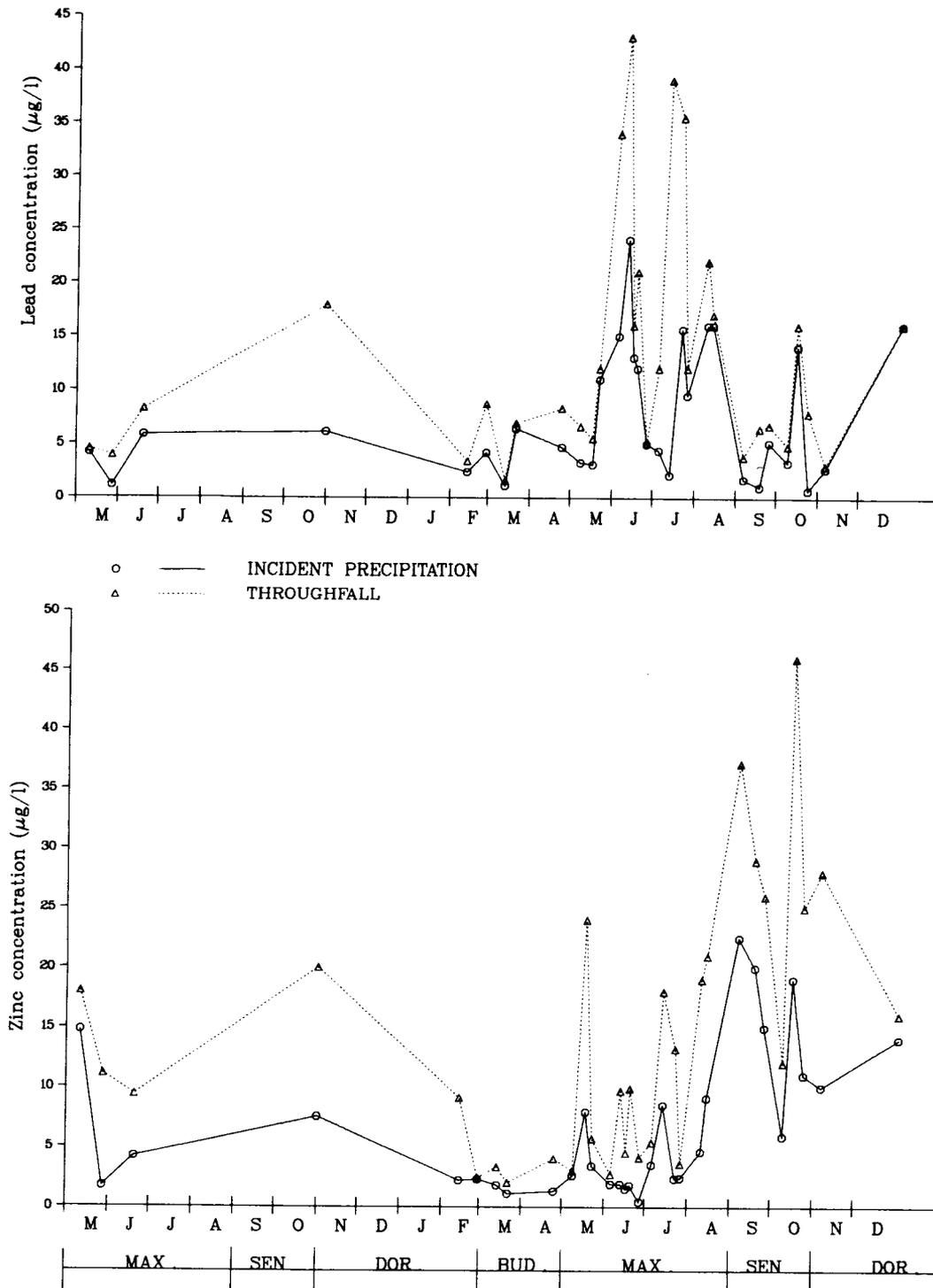


Fig. 34. Temporal variations in Pb (upper plot) and Zn (lower plot) concentrations in rain and throughfall for events sampled simultaneously from May 1976 to December 1977.

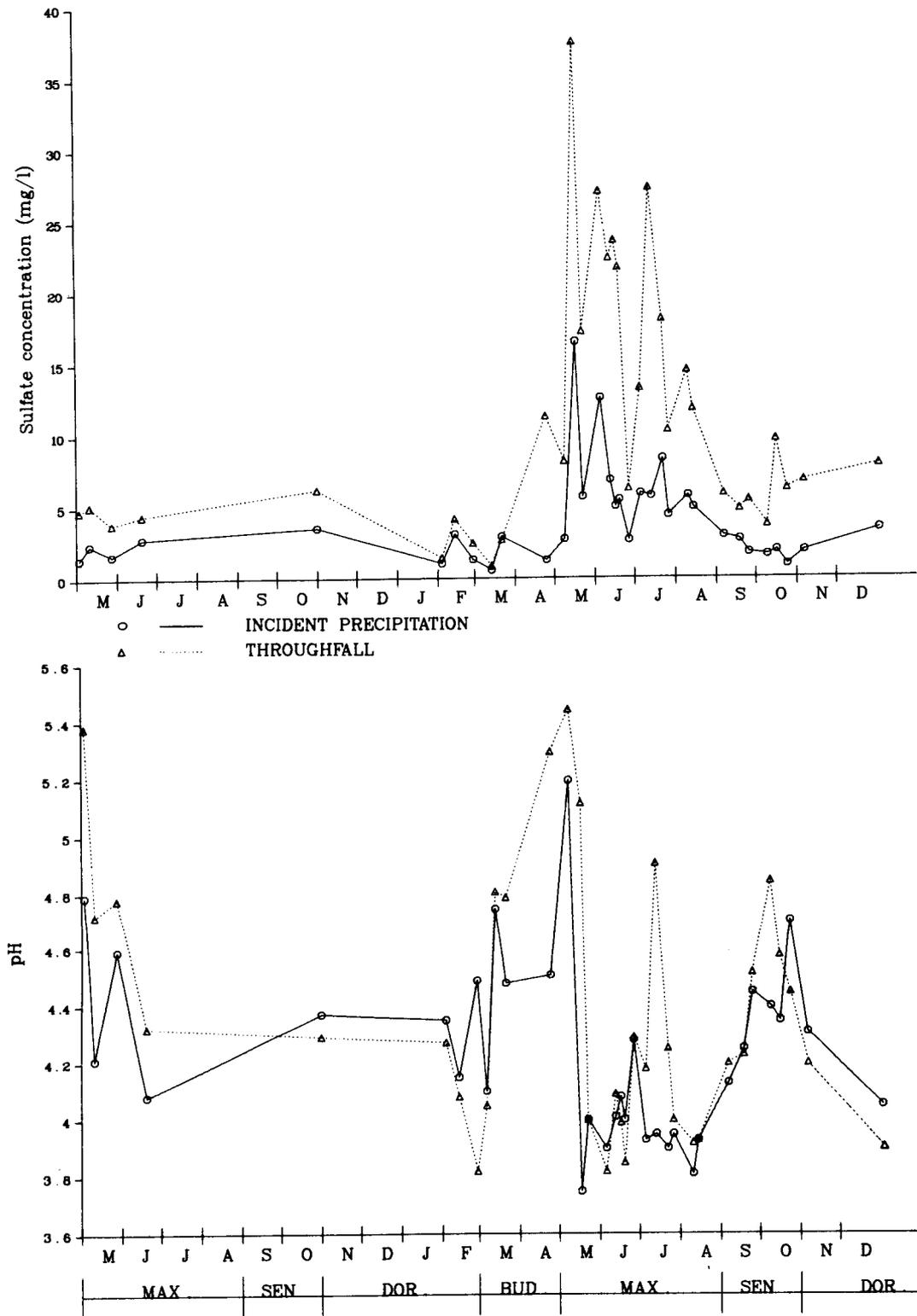


Fig. 35. Temporal variations in sulfate (upper plot) and pH (lower plot) concentrations in rain and throughfall for events sampled simultaneously from May 1976 to December 1977.

concentrations of Pb, Zn, and $\text{SO}_4^=$ indicates a certain degree of dependence, since temporal variations in rain concentrations are reflected by similar fluctuations in throughfall levels, regardless of canopy status.

The data comprising the paired observations are summarized in Table 29 which presents mean concentrations (± 1 S.E.) in rain and throughfall, rain event characteristics, and ratios of throughfall/rain concentrations. A comparison of the mean concentrations in this table with those for the complete data set in Table 26 gives an indication of the representativeness of the paired data set. The mean values are within 20% of those for the complete data set, except for Mn in throughfall. This difference relates to the significant location effect on Mn in throughfall discussed in the previous section, since this data group includes observations only from one or two of the four throughfall sites. Comparing the mean rain volume in this table with that for the overall data set in Table 25, and with that actually occurring during the period of sampling, indicates a similar comparability.

The numerical relationship between the rain volume above the canopy and below, on an event basis, was determined using ordinary least squares linear regression analysis to be as follows:

$$T = 0.94I - 0.05 \text{ (coefficient of determination} = 0.97\text{),}$$

where T = throughfall and I = incident precipitation volume in cm. This is similar to the generalized equation of Helvey and Patric (1965) where the relationships were considered on a seasonal basis:

Table 29. Statistical summary of the relationship between incident precipitation and throughfall concentrations for storm events sampled simultaneously above and below the canopy

Combined data, 2 years			
	Incident precipitation	Throughfall	T/I ^a
Cd	0.42 ± 0.06 µg/l	1.57 ± 0.45 µg/l	4.4 ± 1.2
Mn	3.40 ± 0.79	211 ± 29	160 ± 40
Pb	7.69 ± 1.14	13.9 ± 2.2	2.7 ± 0.6
Zn	6.52 ± 6.22	14.2 ± 11.3	2.9 ± 0.3
SO ₄ ²⁻	4.1 ± 0.6 mg/l	11.0 ± 1.6 mg/l	2.9 ± 0.3
H ⁺	73 ± 7 µeq/l	62 ± 8 µeq/l	0.93 ± 0.13
(as pH)	4.14	4.21	---
Precipitation volume	2.59 ± 0.46 cm	2.46 ± 0.43 cm	---

^aThroughfall to incident precipitation ratio.

$T = 0.90I - 0.08$ for the growing season

$T = 0.91I - 0.04$ for the dormant season.

However, the generalized equations would underestimate the amount of throughfall in WBW for this data set, to some extent. Henderson et al. (1977) applied these equations to WBW daily precipitation data for 1971-1973 and found good agreement, except during periods of heavy precipitation, when the generalized equations overestimated throughfall volumes. As pointed out in Rutter et al. (1975), the frequency of observations is very critical when calculating canopy interception, with errors in prediction increasing with decreasing frequency of observations. Thus, in some cases, better agreement might be expected when using hourly or event rainfall data rather than daily totals.

The throughfall to incident ratios in Table 29 provide an indication of the relative effect of the canopy in altering the concentration of various components in throughfall. The canopy has a considerably larger influence on the chemistry of Mn than on the other elements studied, increasing the incoming rain concentration by a factor of 160. Next in order of canopy influence was Cd (factor of 4.4), followed by Pb, Zn, and $SO_4^{=}$ (approximately a factor of 3 for each). Only in the case of H^+ did the mean ratio indicate a negative effect. However, this ratio is misleading because of the apparent ability of the canopy to either add or remove H^+ from incident precipitation (Figure 35), depending on season. Similar ratios for each element were calculated by season and by general leaf status of the canopy, and are summarized in Figure 36. Canopy leaf status

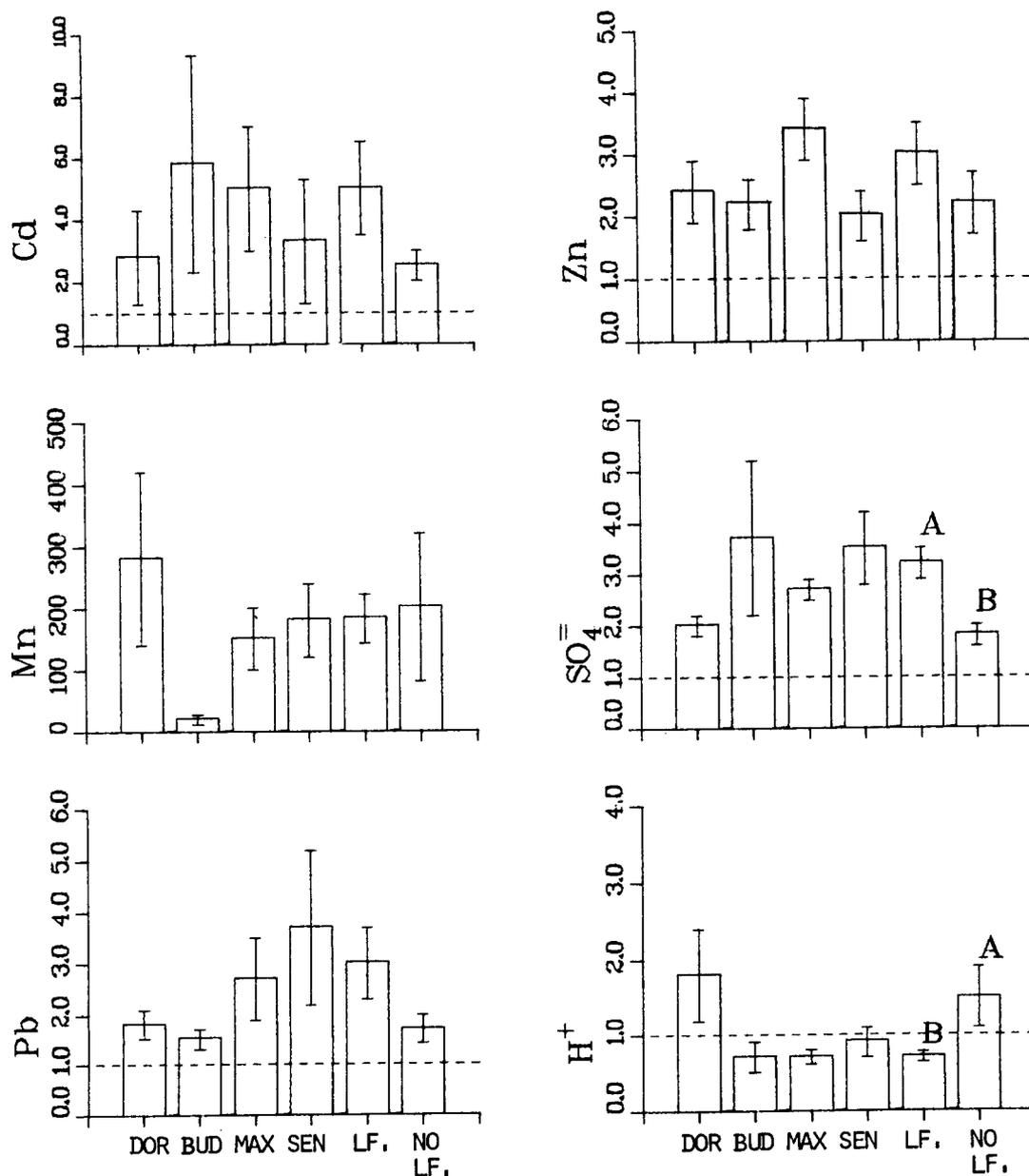


Fig. 36. Variations in mean (\pm standard error) throughfall/incident precipitation concentration ratios during four seasons and two leaf status periods. Values with the same or no letter over the histogram bar are not significantly different ($P > 0.05$, Duncan's new multiple range test). The significance of differences applies only within the four seasons or two leaf status periods.

relates to the presence or absence of leaves, the "no leaves" period including November-March (dormant and the first half of budbreak) and the "leaves" period, or growing season, including April to October.

Analysis of variance of seasonal effects (including precipitation volume as a covariate, in conjunction with Duncan's new multiple range test as discussed in the previous section) failed to reveal any significant ($P \leq 0.05$) differences in seasonal throughfall to incident concentration ratios for any elements. As indicated in the figure any seasonal differences may have been obscured by the variability in the data, in particular due to the small size of the seasonal subsets of this more limited data set. However, the trends in the seasonal means do suggest a difference between the growing seasons (budbreak, max. growth, and senescence) and dormant season. By combining the seasonal data into periods of contrasting canopy development (leaves vs no leaves) it was possible to increase the size of the subsets. The mean concentration ratios during these periods are also summarized in Figure 36. For Cd, Pb, Zn, and $\text{SO}_4^{=}$ the effect of the canopy on throughfall chemistry was more pronounced during the leaves period than during the no leaves period, although there was a significant difference only for $\text{SO}_4^{=}$ ($P \leq 0.05$). The relative influence of the canopy on Mn concentrations was substantial, but similar during both periods. Hydrogen ion concentration, as described above, is depressed by canopy interactions during the growing season but is somewhat enhanced during the dormant season with the throughfall/incident ratios significantly different ($P \leq 0.05$). These trends indicate the presence of leaves to be important in enhancing the levels of Cd, Pb, Zn, and

SO_4^- in throughfall, that both leaf and bark (twig) interactions are important in increasing the concentration of Mn in throughfall, and that leaves act to scavenge H^+ from incoming rain while the leafless canopy tends to slightly increase the H^+ concentration of throughfall relative to incident rain. Note, however, that this generalization for H^+ was not applicable throughout the entire 1977 growing season since, during a short period, the interaction between incoming rain and the fully developed canopy resulted in an increase in H^+ concentration (Figure 35). This will be considered in more detail.

Linear Regression Analysis of the Throughfall - Rain Concentration Relationship

To further examine the relationship between throughfall and incident precipitation chemistry on a storm by storm basis, linear regression analyses were applied to the paired observations. As above, the data were treated separately according to canopy leaf status. Using this method it is also possible to statistically test the slope of the regression line for a significant difference from 1, a value which would imply no effect of the canopy on incoming rain. Plots of the ordered pairs for each element are presented in Figures 37 and 38, along with the regression lines and equations (if highly significant, $P \leq 0.01$) for the two leaf status periods (indicated by L = leaves or N = no leaves). Although there is considerable scatter in the data, the trends of increasing throughfall concentrations with increasing rain concentrations are apparent, as was suggested by the temporal variation plots in Figures 33 to 35. As indicated by the plotted regression lines for the "leaves" data, the linear approximations were

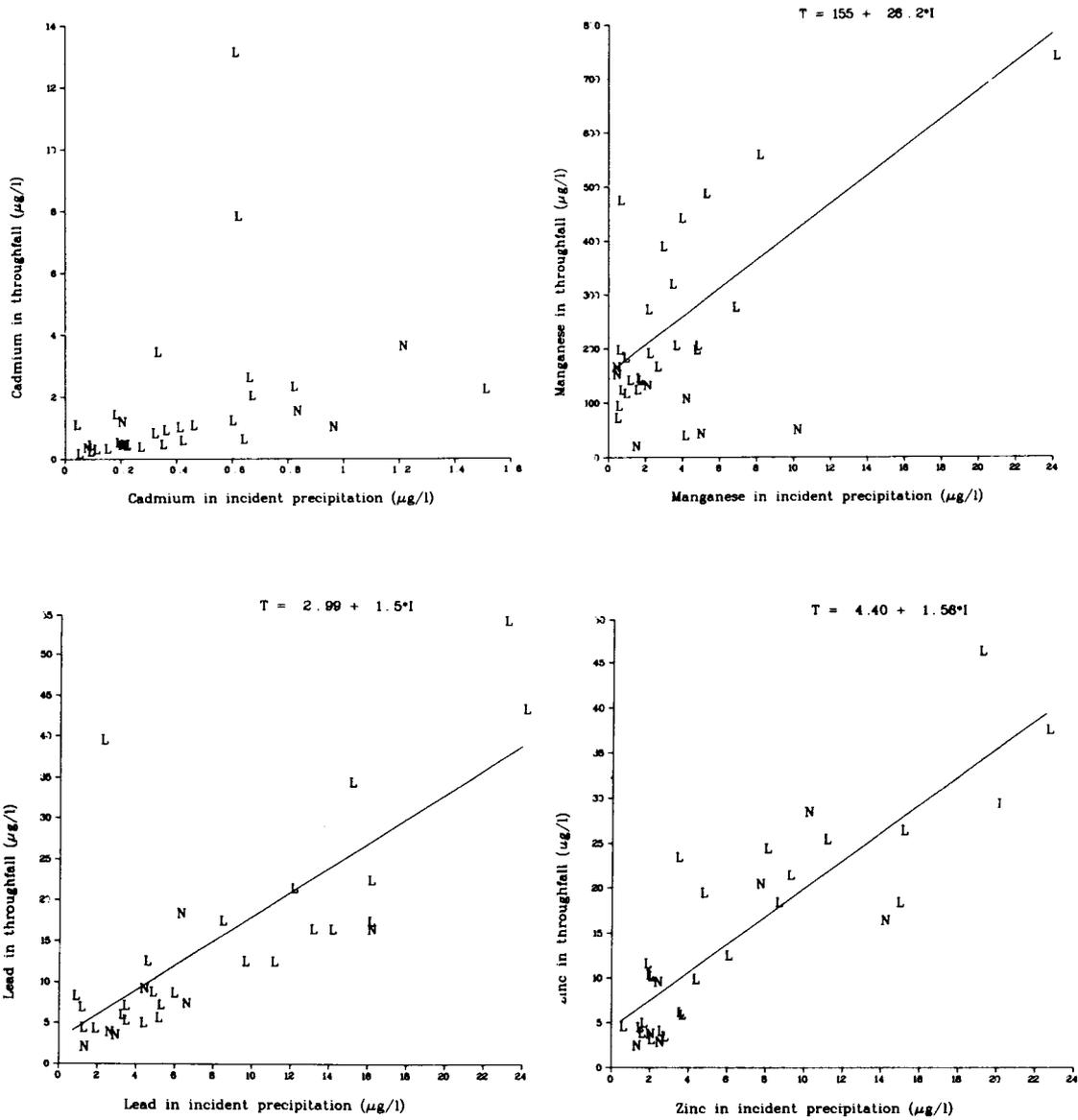


Fig. 37. Relationships between throughfall and incident precipitation concentrations of trace elements during the growing season (L = leaves) and the dormant period (N = no leaves). Also illustrated are the results of the regression analyses if significant.

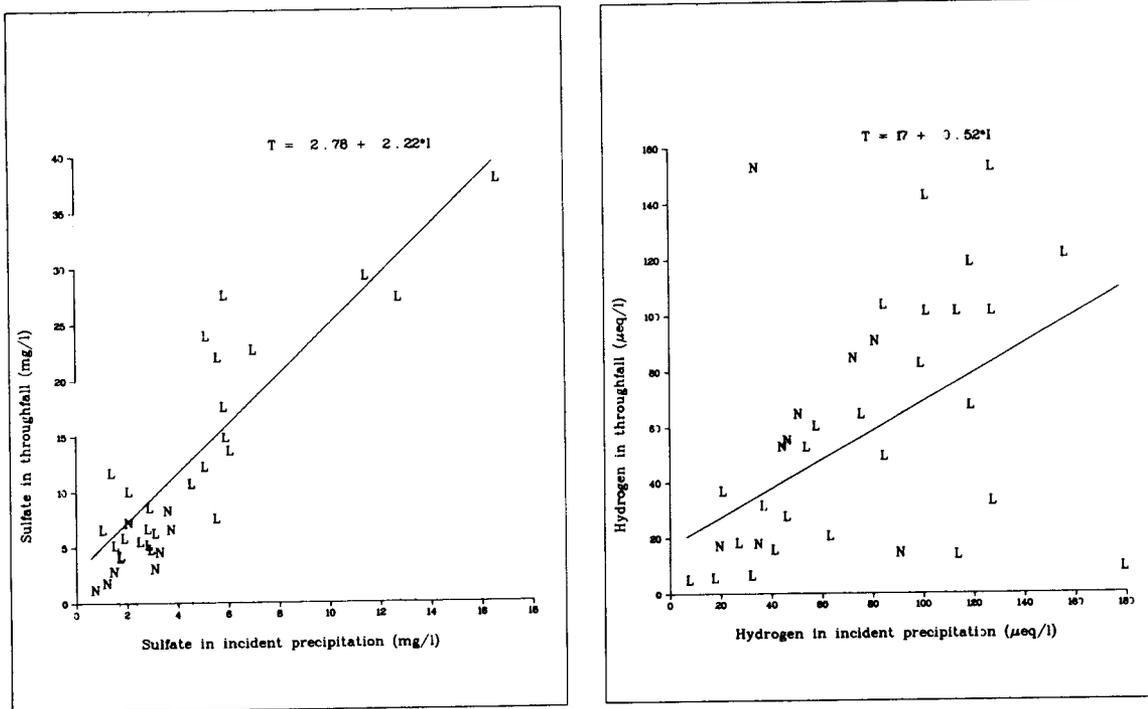


Fig. 38. Relationships between throughfall and incident precipitation concentrations of sulfate and hydrogen ion during the growing season (L = leaves) and the dormant period (N = no leaves). Also illustrated are the results of the regression analyses if significant.

highly significant ($P \leq 0.01$) for Mn, Pb, Zn, $\text{SO}_4^{=}$, and H^+ during the growing season (L). In addition, these approximations were somewhat less significant ($P \leq 0.05$) for Cd, Pb, and Zn during the dormant season (equations not plotted, see Table 30 for coefficients).

Table 30 summarizes the statistics for the regressions, including slopes and intercepts of the models, correlation coefficients, coefficients of determination (r^2), F ratios of the regression model and its significance level, and t statistics for testing the significance of the differences of the intercepts from 0, the slopes from 1, and the mean throughfall (μ_T) and incident (μ_I) concentrations from each other. During the period when the deciduous canopy is barren of leaves, the results of the interaction between incoming rain and the canopy on throughfall concentrations is poorly defined. The simple linear approximation was valid only for Cd, Pb, and Zn, meaning that the computed regression slopes were significantly different from 0. However, in each case the regression constants were not significantly different from what would be predicted from a simple 1 to 1 relationship between throughfall and incident precipitation (slope = 1, intercept = 0). This indicates that the barren canopy has a relatively minor influence on the concentration of Cd, Pb, and Zn in throughfall. This was also suggested by the throughfall/incident ratios summarized in Figure 36. This same simple relationship is also suggested by the plots of $\text{SO}_4^{=}$ and H^+ during the dormant period (N), though there is considerable scatter. This being the case, the throughfall and incident precipitation mean concentrations were also compared using Student's paired t test. During the dormant period the

Table 30. Statistical summary of linear regression analysis using throughfall (TF) concentrations as the dependent variables and incident (I) concentrations as the independent variables to conform to the general equation: $TF = a_0 + a_1 \cdot I$.

Element	a_0 (intercept)	a_1 (slope)	r^a	D^b	F^c	t statistic ^d for $H_0: a_0 = 0$ vs. $a_0 \neq 0$	t statistic ^e for $H_0: a_1 = 1$ vs. $a_1 \neq 1$	t statistic ^f for $H_0: \mu_T = \mu_I$ vs. $\mu_T > \mu_I$ ($\mu_T < \mu_I$ for H^+)
CANOPY STATUS = LEAVES								
Cd	— ^g	—	NS ^g	NH	NS	—	—	2.3 *
Mn	155	26.2	0.72 ***	0.52	25 ***	5.1 ***	4.8 ***	2.3 *
Pb	2.99	1.50	0.75 ***	0.57	30 ***	1.0	1.8 *	2.4 *
Zn	4.40	1.56	0.88 ***	0.77	77 ***	2.6 *	3.1 **	3.1 **
$SO_4^{=}$	2.78	2.22	0.88 ***	0.77	75 ***	1.8 *	4.8 ***	4.2 ***
H^+	17	0.52	0.52 **	0.27	8 **	1.0	2.6 *	1.8 *
CANOPY STATUS = NO LEAVES								
Cd	0.07	2.01	0.81	0.65	9 *	0.15	1.4	1.3
Mn	—	—	NS	NS	NS	—	—	3.9 **
Pb	2.86	0.96	0.75	0.56	6 *	1.0	2.2	0.9
Zn	2.74	1.58	0.79	0.62	8 *	0.68	2.2	1.4
$SO_4^{=}$	—	—	0.67	0.45	NS	—	—	1.8
H^+	—	—	0.52	0.27	NS	—	—	1.2

^aCorrelation coefficient and significance.

^bCoefficient of determination.

^cF value of regression equation and its significance.

^dF test applied to the null hypothesis that the intercept term is equal to 0; a significant t statistic indicates rejection of the null hypothesis.

^eF test applied to the null hypothesis that the slope is equal to 1; a significant t statistic indicates rejection of the null hypothesis.

^ft test applied to the null hypothesis that the mean throughfall concentration (μ_T) is equal to the mean incident precipitation concentration (μ_I); the alternative hypothesis for Cd, Mn, Pb, Zn, and $SO_4^{=}$ was $\mu_T > \mu_I$, while for H^+ the alternative hypothesis was $\mu_I < \mu_T$. A significant t statistic indicates rejection of the null hypothesis.

^g— or NS indicates no significant regression equation was found, or that the statistic was not significant.

^hLevels of significance as follow: *** ($P \leq 0.001$), ** ($P \leq 0.01$), * ($P \leq 0.05$).

throughfall concentrations were significantly greater than the rain concentrations only in the case of Mn. Applying this test to the data collected during the growing season revealed significantly greater throughfall concentrations compared to rain for all elements except H^+ . The H^+ concentration in throughfall was significantly decreased by canopy interaction, relative to incoming rain.

The differences revealed by the t tests were, in general, confirmed by the regression analyses since the equations for Mn, Pb, Zn, $SO_4^{=}$, and H^+ were highly significant ($P \leq 0.01$). Only for Cd was the linear regression model not statistically significant ($P > 0.05$). The regression coefficients and interaction plots reveal three general types of relationships between throughfall and incident precipitation concentrations: (1) intercept > 0 and slope > 1 (Mn, Zn, and $SO_4^{=}$); (2) intercept not significantly different from 0 but slope > 1 (Pb); and (3) intercept not different from 0 but slope < 1 (H^+). Although the regression equation was not significant in the case of Cd, the plot of Cd in throughfall vs Cd in rain suggested it to behave similarly to group (2). These relationships may be thought of as corresponding to canopy effects characterized by (1) (corresponding to 1 above) greater rate of increase of throughfall concentration relative to concentrations in incoming rain with an apparent "lower limit" for the concentration in throughfall, (2) greater rate of increase of throughfall concentrations relative to rain, but with a minimum concentration not significantly different from that in rain, and (3) a significantly slower rate of concentration increase in throughfall

relative to rain with a lower limit concentration not significantly different from that in rain.

It is apparent from the coefficients of determination in Table 30 that the variances in the rain concentrations alone account for a considerable fraction of the variance in throughfall concentrations, $\sim 75\%$ for Zn and $\text{SO}_4^{=}$, $\sim 50\%$ for Mn and Pb, and $\sim 25\%$ for H^+ . The large fraction of the variance accounted for by concentrations of Zn and $\text{SO}_4^{=}$ in incident precipitation suggests that the effect of the foliated canopy on throughfall concentrations is relatively constant over the full range of conditions sampled. This is also reflected in the small standard errors of the mean throughfall/incident ratios in Table 29 (2.9 ± 0.3 for each element). However, for Mn, Pb, and particularly H^+ there are obviously additional factors unrelated to incident precipitation chemistry which account for at least 50% of the variability in throughfall concentrations.

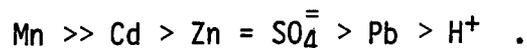
The Role of the Deciduous Canopy in Throughfall Chemistry

The three types of relationships discussed above, and the fact that they are valid over a wide range of precipitation volumes, lend some insight into the processes occurring at the leaf surface during canopy interception of incoming rain. The relationships may reflect a dependence of both throughfall and incident precipitation concentrations on rain volume such that both are simultaneously effected by dilution with increasing rain volumes. This question is considered in detail in the following section. Despite this possibility it is apparent that Mn is removed from the canopy at a

considerably greater rate (factor of ~ 26) than it is supplied by incoming rain, and that, regardless of precipitation volume, there appears to be a minimum increment in Mn concentration in throughfall relative to the concentration in rain (represented by the significant intercept term in the regression equation). During the leafless period the canopy interaction between twigs and rain is less well defined but still results in a significantly higher throughfall concentration of Mn. Zinc and SO_4^- appear to behave similarly to Mn, but only during the growing season, and with a considerably smaller rate of increase. Interestingly these three components are the only members of the plant nutrient/micronutrient group of those elements studied here. The interaction between rain and the leafless canopy did tend to increase the concentration of Zn and SO_4^- (Figure 36), but not significantly. Lead and perhaps Cd are removed from the foliated canopy at a slightly greater rate than that at which they are delivered (~ 1.5 times for Pb) but not at a greater rate from the leafless canopy. In both cases the throughfall concentrations tended to go to 0 with no apparent "residual" throughfall concentration. Free H^+ is removed from the leafy canopy at a lower rate ($\sim 0.5x$) than that of delivery in rain, indicating a neutralization or uptake at the leaf surface. This was not true for the leafless canopy.

As previously discussed the contribution of an element to throughfall by canopy leaching requires presence of the element within or upon the leaf surface. Elements available within the leaves originate either from a biological requirement or passive uptake by the plant via roots or surface absorption. Elements available on the leaf

surface originate either from within the leaf, being leached by surface moisture and deposited during evaporation, or they originate from external sources, being transferred to the leaf surface as gases, liquids, or solids by atmospheric deposition processes. The absolute amount of an element leached from the canopy may be related to its concentration within the foliage although this is not always true (Eaton et al., 1973). Recall from Table 29 that the relative effect of the foliated canopy on throughfall concentrations was greatest in the case of Mn, decreasing in the order:



A similar conclusion was reached by Nihlgard (1970) in a study of throughfall collected beneath both beech and spruce canopies. However he had also studied the major plant nutrient elements, finding the relative increase in Mn concentrations beneath the canopy to be much greater than those for S, K, Ca, Mg, Na, N, and P. Both Mn and S were hypothesized to originate from internal leaf leaching. In the beech forest the relative increase of Mn compared to S was by a factor of 10 while in our case for the chestnut oak canopy this factor was ~ 50 . Tukey (1970) compared the leaf leaching of the radioisotopes ^{54}Mn and ^{65}Zn concluding that Mn was > 25 times more leachable than Zn.

Eaton et al. (1973) used the ratio between foliar concentrations of an element during the growing season and the absolute net leaching from the canopy as a measure of the "relative leachability" from a hardwood canopy. Net leaching is defined as the difference between the concentration of an element in throughfall and the concentration in

incoming rain (usually expressed as the ratio of areal biomass contents to areal fluxes, in kg/ha/yr for each component). This gives a measure of the net addition (or loss) of an element resulting from canopy interception of rain and is a useful indication of the absolute influence of the canopy on throughfall chemistry. The mean net leaching concentrations from the chestnut oak canopy are summarized in Figure 39 on a seasonal and leaf status basis. Significant seasonal and leaf status effects were determined as above using ANOVA and Duncan's new multiple range test. As expected, all elements, with the exception of H^+ , showed higher net leaching during the growing season than during the dormant period, with the differences for Mn and $SO_4^{=}$ between growing and dormant periods significant ($P \leq 0.01$ and $P \leq 0.05$, respectively). Hydrogen ion exhibited a significant difference between mean net leaching during the two periods, with a net loss during the growing season and a slight net gain during the dormant period. Seasonal differences were significant only for Zn and $SO_4^{=}$. Zinc exhibited a significantly higher net leaching during the period of leaf senescence. Sulfate net leaching was significantly higher during the maximum growth period when Pb and Mn leaching also reached a maximum, although not significantly so. Because of the variability in Cd leaching there were no clear seasonal differences.

The reasons for these seasonal and leaf status differences are related both to the variable efficiency of the canopy to scavenge atmospheric material depending on the stage of canopy development, and to the variability of element mobility in plant tissue. The former relationship may be as simple as a direct increase in scavenging

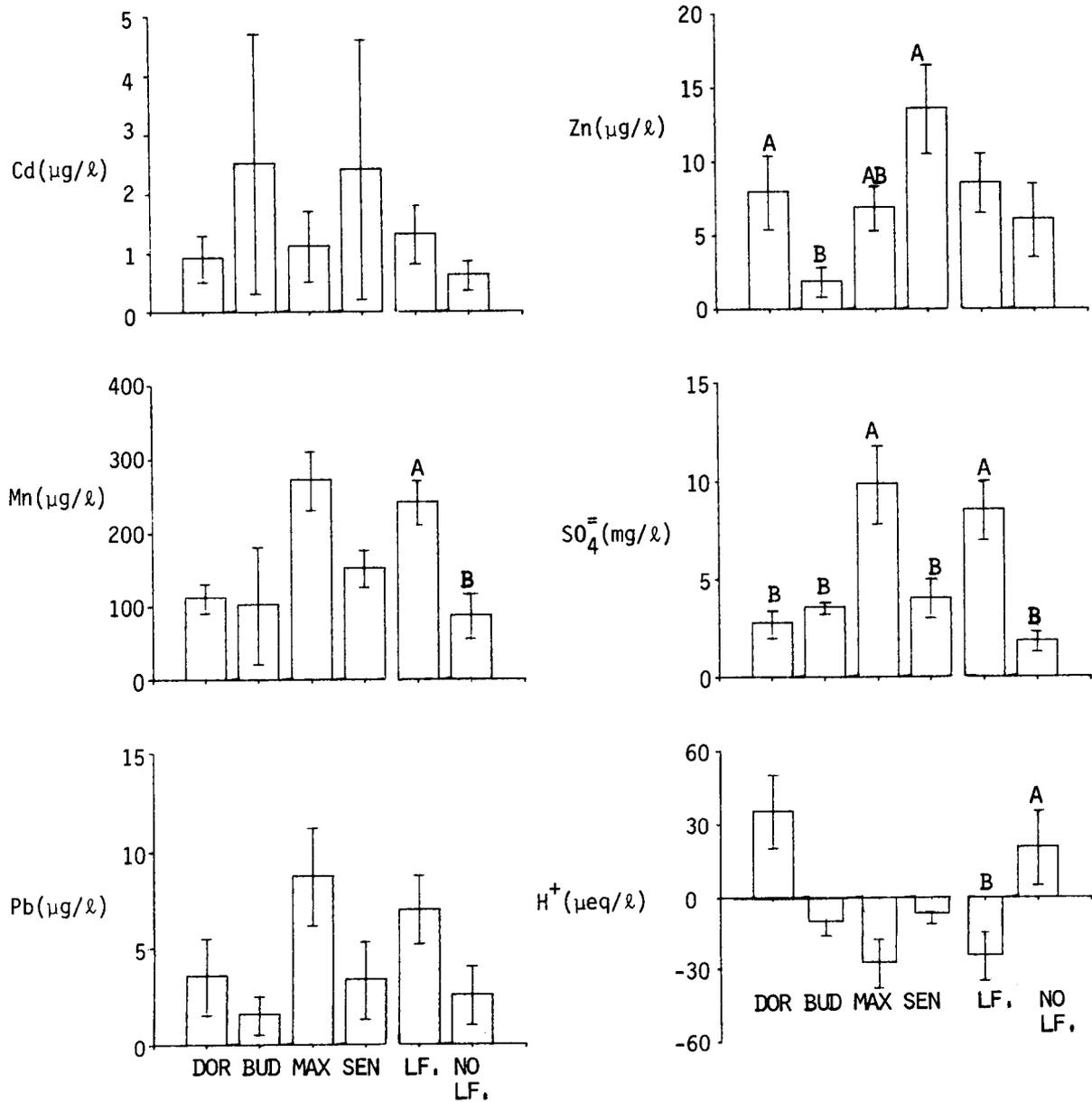


Fig. 39. Variations in mean (\pm standard error) throughfall net leaching concentrations (throughfall concentration minus incoming rain concentration) during four seasons and two leaf status periods. Values with the same or no letter over the histogram bar are not significantly different ($P > 0.05$, Duncan's new multiple range test). The significance of differences applies only within the four seasons or two leaf status periods.

efficiency with increasing quantity and size of leaves in the canopy. The latter explanation would be expected to have a greater influence on the elements with a known biological requirement (Mn, Zn, and $\text{SO}_4^{=}$).

From Figure 39 the mean net leaching concentrations for the growing season were as follows (in $\mu\text{g/l}$): $\text{SO}_4^{=}$ (8500) \gg Mn (242) \gg Zn > (8.2) > Pb (7.2) > Cd (1.3) > H^+ (-23). As expected, the essential components dominate the net leaching chemistry, although much less so in the case of Zn. To compare the relative leachability with respect to foliar concentrations, the ratios between net leaching and foliar concentrations of the elements were calculated. These are summarized in Table 31. The foliar concentrations are the mean of 16 samples of chestnut oak leaves collected in October near the end of the growing season, while the net leaching is for the growing season as given in Figure 39 (metal concentrations in leaves were determined by wet ashing of freshly washed leaves, as described in Chapter IV, using NBS standard orchard leaves as a procedural check. Soluble sulfate was determined following sonification of whole, freshly washed leaves in distilled water). In addition, the ratio of concentrations has been modified by a factor of 0.88 to convert the ratio to terms of areal biomass content and areal flux (i.e., standing crop of an element in chestnut oak foliage in kg/ha during the growing season divided by the growing season net leaching in kg/ha). These terms are then comparable to those given in Henderson et al. (1977) for major cations and nutrients for the chestnut oak canopy in WBW.

The high ratios for Pb and Cd indicate either that these elements are far more leachable from foliage than are the micro-nutrients or

Table 31. Relationship between net leaching from the chestnut oak canopy and foliar elemental concentrations during the growing season

Component	Mean foliar concentration ^a	Net leaching concentration ^b	Relative leachability ratio ^c
Cd	0.11	1.3	11
Mn	230	242	0.9
Pb	0.40	7.2	16
Zn	12.5	8.2	0.6
SO ₄ ²⁻	11,000	8500	0.7

^aμg/g dry weight.

^bμg/l.

^c(net leaching concentration/foliar concentration) · (0.88). The factor converts the ratio of concentrations to one of areal loadings (kg/ha / kg/ha).

that the net leaching concentrations result primarily from external surface deposited material and not from internal leaf leaching. Eaton et al. (1973) attributed "extremely high" net leaching to standing crop ratios of Na (5.6) and S (3.7) to "contamination" of the forest canopy from the atmosphere. As suggested by the data discussed in Chapter IV and as will be discussed in Chapter VII, this is the case for Pb but not Cd. For the essential elements the order to relative leachability is Mn (0.9) > SO_4^- (0.7) > Zn (0.6). The ratios were considered by Eaton, et al. (1973) to be somewhat indicative of the mobility of the elements within a tree during the growing season. Thus, it is interesting to compare the above ratios with those determined by Henderson et al. (1977), for a chestnut oak stand in WBW:

$$\text{K (0.21)} > \text{Ca (0.19)} > \text{Mg (0.09)} > \text{P (0.04)} > \text{N (0.03)} .$$

According to this, the micronutrients Mn and Zn are more mobile or comparable in mobility to several macronutrients. The data of Eaton et al. (1973) for a northern hardwood forest revealed a similar same trend in relative leachability of macronutrients, with the addition of Na and SO_4^- , both of which were more leachable than K.

Summary: Mechanisms of Precipitation - Foliar Interactions

At this point it is helpful to summarize the throughfall-incident rain relationship for each element and consider in detail the mechanisms of precipitation interactions with the leaf surface.

Cadmium - The concentration of Cd in throughfall is significantly ($P \leq 0.05$) enriched by the interaction between rain and the fully

developed forest canopy. However, the relationship is not significantly approximated by a linear expression, there being considerable scatter in the data. The fact that the relationship is not a simple linear one suggests that the leaching of Cd from the canopy, internally or externally, is dependent on numerous factors related to season and meteorological conditions as well as other unknown factors. The interaction between rain and the leafless canopy results in an insignificant increase in the concentration of Cd in throughfall. The mean throughfall to incident ratio indicates that, on an annual basis, the concentration of Cd is increased by a factor of ~ 4 by canopy interactions. Published throughfall/incident ratios for Cd are scarce with the only available data indicating concentration increases of 1.5 and 3 times due to precipitation passing through a beech and a spruce canopy, respectively (Heinrichs and Mayer, 1977). As will be discussed in Chapter VII, the source of Cd in throughfall in WBW is both foliar leaching and surface deposited aerosols which contain Cd in a water soluble form.

Lead - Like Cd, Pb is significantly enriched in throughfall relative to rain only during the growing season. Unlike Cd, however, the rain - throughfall chemistry relationship during this period can be approximated by a linear expression:

$$TF = 3.0 + 1.5 I \text{ (for concentrations in } \mu\text{g/l) ,}$$

in which the variance in rain concentrations (I) accounts for $\sim 60\%$ of the variance in throughfall (TF) concentrations. Since the intercept term was not significantly different from 0, the equation implies a

nearly constant 150% increase in throughfall concentrations with respect to incoming rain levels over the range of seasons and rain volumes studied. However, there is a trend in the seasonal net leaching data indicating higher levels during the period of maximum canopy development. As discussed in Chapters IV and VII this relates to the increased scavenging efficiency of the fully foliated canopy for aerosols, and to the increased atmospheric loading of Pb during this period, since the primary source of Pb in throughfall is atmospherically deposited particles on the leaf surface. Heinrichs and Mayer (1977) reached a similar conclusion regarding the atmospheric deposition source, reporting throughfall/incident ratios similar to the 2.7 reported in Table 29, ranging from 1.3 to 2.6 for beech and spruce canopies.

Manganese - Of the elements studied, the chestnut oak canopy has the greatest influence on the concentration of Mn, significantly increasing the concentration regardless of canopy leaf status. The effect of the foliated canopy on the Mn concentration in throughfall can be represented by the linear expression:

$$TF = 1.55 + 26 I \quad .$$

Although throughfall concentrations are enriched in Mn throughout the year, the net leaching from the fully developed canopy is significantly higher than from the leafless canopy, with a tendency for a peak in net leaching to occur during the maximum growth period. The seasonal trends in Mn enrichment in throughfall are apparently related to changes in plant physiology since, as discussed in Chapters IV and VII,

the primary source of Mn in throughfall is internal leaching. Tukey et al. (1965) considered foliar leaching of cations to involve a process of exchange and diffusion at the leaf surface. Nutrients in newly formed growing tissue are quickly metabolized and less susceptible to leaching loss (Tukey, 1970). However in aged tissue these compounds may be in more exchangeable or soluble forms and thus easily leached. This is suggested by the seasonal trend of Mn net leaching (Figure 39) which indicates lowest net leaching during budbreak and highest during maximum growth.

When compared with other essential elements, on a relative scale, Mn is apparently as leachable from the chestnut oak canopy as K, an element considered highly mobile within plant systems (Tukey, 1970). Manganese is known to be quite mobile in acid soils and is rapidly released in dissolved form from decomposing litter, as well as from living leaves (Witkamp and Ausmus, 1975; Lindberg, unpublished data). It is also known to be present in relatively high concentrations in WBW soils (Fortesque et al., 1973; Turner et al., 1977). Thus Mn may very rapidly cycle through the plant/soil system in a reduced form (Mn^{+2}) easily complexed by the plant (Tiffin, 1977), or as an organic complex (Rankhama and Sahama, 1950) being assimilated and rapidly translocated via the root system (Tiffin, 1977). The mechanism of uptake may be passive, with Mn essentially following the flow of water through the plant and into the twigs and leaves (R. J. Luxmoore, personal communication). Presumably the loss during the dormant period is unrelated to active uptake but must occur from a storage pool, such as from the bark. Bark leaching is a complex process involving large

populations of mosses, lichens, and microflora which may alter the true leaching by various exchange or sorption processes (Eaton et al., 1973). In contrast to Mn, Ca is not readily leached from barren dogwood trees relative to foliated trees (Thomas, 1969). Manganese leaching concentration from the chestnut oak canopy is comparable to that reported for a beech canopy in Germany (net leaching in $\mu\text{g/l}$, ~ 250 from beech, ~ 240 from chestnut oak) but considerably less than that reported for a spruce forest in Germany ($\sim 980 \mu\text{g/l}$; Heinrichs and Mayer, 1977). However, these authors speculated that the source of Mn in throughfall was atmospheric deposition and not internal leaching. Interestingly, Nihlgard (1970) studying similar forest types in Sweden, reported contrasting data in that the net leaching concentration from the beech canopy ($\sim 730 \mu\text{g/l}$) was considerably greater than that from the spruce ($\sim 280 \mu\text{g/l}$) when calculated from the tabulated data. Nihlgard (1970) concluded the Mn in throughfall to result from internal leaching, also in contrast to the conclusions of Heinrichs and Mayer (1977).

Zinc - The concentration of Zn in throughfall is significantly increased during the interception of rain by the developed canopy but not by the barren chestnut oak canopy. The degree of canopy influence as indicated by throughfall/incident ratios was considerably less than in the case of Mn but comparable to Pb. During the growing season the relationship followed the linear expression:

$$\text{TF} = 4.4 + 1.6 \text{ I} \quad .$$

As was true for Mn, both regression coefficients in the Zn equation were significantly greater than the "no effect" values of 0 for intercept and 1 for slope. Thus the concentration of Zn in throughfall increased at a rate $\sim 160\%$ of that for incident rain concentration, with an apparent lower limit concentration of $\sim 4 \mu\text{g/l}$ in throughfall. The concentration of Zn in throughfall during the dormant canopy period varied in direct response to the concentration in incoming rain but was not significantly higher. The seasonal variability in Zn net leaching is very similar to that previously reported for K (Eaton et al., 1973). There is a steady increase in Zn net leaching throughout the growing season with a significant peak during leaf senescence. Numerous investigators have observed similar seasonal patterns in the removal of other essential elements from the forest canopy (e.g., see the review by Tukey, 1970), attributing the trends to leaf aging. Leaf growth and aging involves physiological changes and physical surface deterioration both of which increase the leachability of cations such as K^+ (Fogg, 1947).

Potassium is widely distributed in plants, occurring primarily in ionic form, or as charged particles on colloidal surfaces, is concentrated by an active transport process, is not generally associated with a specific compound within the cells or with a specific part of the cell, and is thought to act as a catalyst or cofactor in enzymatic reactions (Broda, 1965). Zinc is also thought to play a catalytic role in plant enzyme reactions (Bogorad, 1965; Broda, 1965). However, its behavior in plant uptake and translocation systems contrasts sharply with that of K. The uptake of Zn is predominantly

passive, not requiring a metabolic process. The uptake is nonspecific in that many similar and dissimilar ions compete heavily, and it appears to exist within the plant as an anionic complex to some extent (Broda, 1965; Tiffin 1977). Experiments by Timperley et al. (1973), using differential centrifugation on tree leaf extracts, indicated Zn to be distributed nearly equally between supernatant (soluble) and chloroplast (including cell wall fragments) fractions. While the soluble form was as an anionic complex the state of the bound form was not considered. However, a certain fraction of the Zn is believed to exist as a cation bound to the cell wall by ion exchange (Broda, 1965). Thus Zn, like K, may be leached by the process of cation exchange (Tukey, 1970). This is considered further in the discussion of the interaction between the canopy and H^+ in rain. The leaching of Zn from the chestnut oak canopy is complicated by the fact that a significant fraction of the net leaching is attributable to atmospheric deposition (see Chapter VII). This may account for the fact that on a relative scale Zn shows a somewhat higher net leachability (0.6) than that given for K (0.2) by Henderson et al. (1977).

Sulfate - During the growing season the concentration of SO_4^- in throughfall increases due to the interaction between rain and the forest canopy according to the relationship

$$TF = 2.8 + 2.2 I \text{ (for } SO_4^- \text{ concentration in mg/l) ,}$$

This indicates that throughfall concentrations increase at approximately twice the rate of increase of incident rain levels with a significant "lower limit" throughfall concentration of ~ 3 mg/l as the

concentration in rain approaches zero. Interception by the leafless canopy also results in a small but insignificant increase in throughfall sulfate concentrations. During the growing season there is a significant seasonal trend such that the highest net leaching occurs during maximum growth, while budbreak and senescence are approximately equal. Thus $\text{SO}_4^{=}$ tends to behave similarly to Mn. However, unlike Mn, the seasonal variability in net sulfate leaching is not solely related to physiological changes since a significant fraction of the net leaching is attributable to atmospheric deposition (Chapter VII). Sulfur occurs both within the leaf and associated with particles deposited on the leaf surface as a readily soluble, highly mobile, $\text{SO}_4^{=}$ salt. Thus the maximum growth period peak in net leaching may relate to increased efficiency of atmospheric scavenging, increased air concentrations of both SO_2 and $\text{SO}_4^{=}$, and increased uptake, translocation and leachability of sulfate within the leaves.

Numerous contrasting reports exist on the source of sulfate in throughfall. Eaton et al. (1973) reported a tendency for $\text{SO}_4^{=}$ to occur at higher concentrations in throughfall beneath a hardwood forest during July and September than during June and October although net leaching data was not presented on a seasonal basis. The ratio of throughfall/incident concentrations during the growing season ranged from 3.4 to 9.0 and was dependent on tree size and type (compared to 3.2 for WBW chestnut oak, Figure 36). The relative leachability (net removal/standing crop) during the growing season was 3.7 or ~ 5 times that seen here. The high ratio was not thought to be explained by rapid cycling of S but was tentatively attributed to atmospheric

deposition. Similarly Heinrichs and Mayer (1977) measured throughfall/incident ratios of 2 to 4.6 beneath beech and spruce canopies and stated that leaching of metabolic substances was of minor importance in the increase in throughfall concentrations. McColl and Bush (1977) reported a throughfall/incident ratio of 4.4 for $\text{SO}_4^{=}$ beneath a eucalyptus canopy for a 5-month period. Interestingly for 14 storms sampled on an event basis they found no significant correlation between $\text{SO}_4^{=}$ concentrations in throughfall and incident rain ($r = 0.02$ compared to $r = 0.88$ for WBW), although this may relate to the fact that bulk precipitation was collected and not wetfall only. The authors concluded that the larger amount of $\text{SO}_4^{=}$ in throughfall was attributable to impaction of particles on leaf surfaces rather than leaf leaching. If this were true, it would support the lack of correlation between throughfall and rain concentrations because of the non-comparable scavenging efficiencies for atmospheric particles by the developed canopy and the funnels used to collect bulk rain and throughfall.

In contrast Nihlgard (1970) reported dissimilar ratios of throughfall/incident beneath a beech (1.2) and spruce (5.7) forest and attributed the increase beneath the spruce canopy to the leaching process. This conclusion was based on a related experiment wherein the composition of rain above and below an inert plastic net was measured to determine the sulfate in throughfall due to particle deposition. The below/above $\text{SO}_4^{=}$ ratio was intermediate between those of the two forest canopies (3.9). This tends to support the hypothesis that $\text{SO}_4^{=}$ in throughfall results from both leaching and particle

deposition, depending on canopy type. Raybould (1977) recently reported that 90% of the sulfur gain in TF below a wheat canopy was due to internal leaching and that only a small fraction of the $\text{SO}_4^{=}$ dry deposited onto the leaves could be washed off. However, the authors made some tenuous assumptions and neglected some very important points. In order to estimate the amount of dry deposition sulfate the authors assumed the composition of throughfall and stemflow to be equal, an invalid assumption at least for forest trees (Eaton et al., 1973; Nihlgard, 1970; Patterson, 1975). The authors considered only the dry deposition of SO_2 in the calculation of foliar surface deposited sulfate, neglecting active or passive plant uptake of SO_2 and, most importantly, dry deposition and impaction of aerosol sulfate. If these considerations had been included in their calculations the ratio of leached $\text{SO}_4^{=}$ to dry deposited $\text{SO}_4^{=}$ would have been reduced.

Hydrogen ion and the cation exchange process - Hydrogen ion, unlike the other components, is decreased in concentration by the interaction between incident precipitation and the foliated forest canopy. Although the relationship between rain and throughfall H^+ concentrations is not as clear as in the case of the cations Mn, Pb, and Zn, it roughly follows the expression:

$$\text{TF} = 17 + 0.52 \text{ I (for } \text{H}^+ \text{ in } \mu\text{eq/l) } .$$

The intercept term is not significantly different from 0 implying that approximately 50% of the hydrogen entering the canopy is removed before reaching the ground. There is considerable scatter in the data with

the variance in incident rain concentrations accounting for only 27% of the variance in throughfall concentrations. The relatively poor fit of the regression line suggests the H^+ - canopy interaction to be strongly influenced by several other factors including meteorological conditions and seasonal leaf status. Although the seasonal differences are not significant they suggest the highest degree of removal to occur during the period of maximum growth with less during budbreak and senescence. During the leafless canopy period the concentration of H^+ in throughfall is increased, but not significantly, relative to incoming rain.

The potential effects of increased leaching of macronutrients as related to H^+ uptake at the leaf surface has been discussed in general in the recent review by Tamm and Cowling (1976) and for some individual cases in the recent symposia volume edited by Dochinger and Seliga (1976). However the interaction between leaching solutions of low pH (acid rain) and trace element chemistry at the leaf surface has not been widely considered. The interaction between H^+ in rain and the leaf surface is thought to involve exchange reactions at the cuticle. This has been demonstrated for Ca (Tukey et al., 1965) and hypothesized for K, Rb, and Sr (Tukey, 1970), suggesting a simple cation exchange process. Cations, such as Ca, are translocated from roots to leaves by a process involving various exchange reactions (Tukey et al., 1965). The distribution of Ca within leaves and movement through the cuticle also occurs via exchange processes involving sites on cell walls and pectinaceous material penetrating the cuticle (Mecklenberg et al., 1966). Calcium can then be leached from

the leaf by cation exchange between H^+ in the leaching solution (rain) and Ca on the cell wall exchange site, followed by outward diffusion through the cuticle. Alternately direct exchange of Ca on cuticle exchange sites external to the leaf may occur. Since both Ca and Mn are believed to occur and be transported within plants as divalent cations (Bowen, 1966; Epstein, 1965; Tiffin, 1977) this process may also account for foliar Mn leaching. As discussed above, Mn is apparently more readily leached from the chestnut oak canopy than is Ca.

A similar process may not occur in the case of Zn and sulfate because of their anionic nature in plant solutions, as discussed above. Tukey and Morgan (1964) have suggested that leaching of SO_4^- and PO_4^- are not affected by experimental treatments to the same degree as cation leaching and may be related to a different mechanism. Zinc, although it does occur in plant solutions as an anionic complex, may reside at exchange sites as Zn^{++} and thus its leaching may be partially controlled by exchange with H^+ . This may explain the slight difference in net leachability of Zn (0.7) compared with Mn (0.9, Table 31).

Reports of increased leaching related to increasing H^+ levels in leaching solutions have generally involved major cations. Wood and Borman (1975) treated tree seedlings under controlled conditions with artificially applied mist and reported increased leaching of cations as mist pH decreased. Fairfax and Lepp (1975) leached leaves of tobacco plants with pH = 6.7 and pH = 3.0 artificial precipitation, acidified with dilute H_2SO_4 . They found increasing H^+ concentrations to

significantly increase the Ca leaching (by a factor of ~ 4), significantly decrease the K loss (by a factor of ~ 4), and not effect Mg leaching. The decrease in K leaching was speculated to be the decreased efficiency of the selective root uptake mechanism for K caused by acid application, leading to a decreased uptake and, hence, availability for leaching. A similar analysis of the WBW data suggests that both cations and anions are leached from the chestnut oak foliage during the growing season in increased quantities in response to decreased pH levels of the incoming rain. Linear regression analysis of the relationship between element net leaching and incident rain H^+ concentrations revealed statistically significant positive slopes for both $SO_4^{=}$ and Mn (Mn, $r = 0.65$, $P \leq 0.01$; $SO_4^{=}$, $r = 0.56$, $P \leq 0.01$). The remaining elements also exhibited a trend of increased net leaching with increased H^+ concentrations in rain, although, the regression analysis did not yield slopes significantly different from zero.

Eaton et al. (1973) considered the H^+ exchange phenomenon in the context of element cycling in a northern hardwood forest. The authors found that during the growing season, $\sim 90\%$ of the H^+ was removed from incoming rain by the canopy. On an equivalent basis, this hydrogen exchange accounted for at least 27% of the cation leaching which occurred from the canopy during the growing season. A similar calculation can be done for the data collected in WBW. Precipitation weighted mean concentrations (see Chapter VII) were calculated for the paired observation data set for two growing seasons and combined with the hydrologic input, yielding a net H^+ exchange loss at the canopy

of 6.6×10^{-6} meq/ha. During this period the net trace cation leaching was 4.0×10^{-6} meq/ha, or less than 60% of the H^+ exchanged. However, the estimated growing season major cation leaching (primarily K and Ca) from the chestnut oak canopy was $\sim 80 \times 10^{-6}$ meq/ha, for a total of 84×10^{-6} meq/ha. This indicates that simple H^+ exchange may account for only 8% of the net cation leaching from the canopy and that other processes of foliar loss must be involved.

The role of strong and weak acids in hydrogen ion chemistry - Some of our recent work on rain chemistry, presented elsewhere (Hoffman et al., 1979) has explored the role of strong and weak acids in rain above and below the chestnut oak canopy. The contribution to the free acidity as measured by a standard pH electrode is from all protons in solution, regardless of source. Strong acids completely dissociate in solution while weak acids, both organic and inorganic, partially dissociate. The degree of weak acid dissociation increases with increasing pH such that at the pH of most acid precipitation samples (< 5.6) they contribute negligibly to the free acidity and primarily to the total acidity (Galloway et al., 1976). For 11 storms sampled in WBW during the 1977 growing season we found weak acids to account for $\sim 30\%$ of the total acidity in incident rain ($\bar{x} \pm SE = 33 \pm 3\%$). This is similar to the early data published on weak acids in rain by Galloway et al. (1976) who reported a contribution of 32% weak acids to the total acidity in one storm sampled during July in the Northeast.

The contribution of weak acids to throughfall chemistry has not been previously quantified. In throughfall collected beneath the chestnut oak canopy for the period described above, we found weak acids

to contribute approximately twice as much to the total acidity ($57 \pm 4\%$) than was the case for incoming rain ($\sim 30\%$). In general the contribution of the weak acids to the free acidity was negligible in both rain and throughfall. On a concentration basis the average net loss of strong acids from the incoming rain to the canopy was $\sim 30 \mu\text{eq/l}$ while the average net gain in weak acids was $\sim 40 \mu\text{eq/l}$. It is apparent that the role of weak acids in cation leaching in throughfall must be considered. Although the composition of leaf cuticle is not well known, it is thought to be a polyester of $C_{16} - C_{18}$ acids (Albersheim, 1965). The action of this material as an exchange site could be expected to result in some degree of structural alteration (Garrells and Christ, 1965) such that some components of the negative framework would dissolve into the surrounding solution. Thus the interaction between H^+ in rain and the canopy may be responsible for both cation displacement and weak acid leaching. This is discussed in more detail in Hoffman et al. (1979).

With this background it is useful to reconsider the event by event variations in rain and throughfall pH as shown in Figure 35. During the maximum growth period in 1976 the influence of the H^+ exchange process was apparent, yielding consistently higher pH values in throughfall. At the end of the senescence period, following leaf fall, and up to the start of the budbreak period, the throughfall pH values were similar to but consistently lower than the incident rain pH values. This is attributed to leaching of primarily weak organic acids and, in some cases, strong acids from bark and twigs (Hoffman et al., 1979). Following budbreak and canopy refoliation, the pH again

reverses such that the throughfall pH exceeds that of incoming rain, indicating H^+ exchange at the newly formed leaf surface. However this trend was not maintained throughout the growing season, as it was during the previous year. For five successive storms in May - June the throughfall pH values were less than or comparable to those in rain above the canopy, with one exception. This suggests that the fully developed canopy had temporarily lost the ability to remove H^+ from incoming precipitation. This phenomenon did not coincide with a concomitant decrease in net leaching of other cations, however (Figures 33 and 34). The indication is that leaching during this period must have involved some other mechanism than the cation exchange process described above, or that the H^+ ions, once at exchange sites, were not retained by the leaves.

We have found that this phenomenon of higher throughfall acidity relative to incident rain during full canopy development is caused by increases in both strong and weak acids in throughfall (Hoffman et al., 1979). This indicates increased weak acid leaching from the leaves and solubilization of particles on the leaf surface having a strong acid reaction. Aerosols with a strong acid nature are abundant both in ambient air and deposited on various surfaces (see Chapters III and IV). Interestingly the above "pH reversal" period was preceded by 15 days of no precipitation (except for a brief 10 minute shower of 0.1 cm on the 5th day preceding the start of this period) during which time several local air stagnation bulletins were issued. The period was characterized by calm, hazy conditions, and frequent inversion/fumigation events (see Chapter III), during which time the

O_3 , SO_2 , TSP, and NO_x concentrations in ambient air exceeded air quality standards (Knoxville - Knox County Air Quality Board, personal communication).

The interaction of the strong oxidant O_3 at and internal to the leaf surface is known to attack double bonds and affect membrane permeability (Mudd and Kozlowski, 1975). The esterified $C_{16} - C_{18}$ acids, which comprise the cuticle, include free carboxyl groups which would be likely sites of cation exchange. If these groups are points of reaction with O_3 , as would be predicted by a strict chemical consideration, their ability to behave as H^+ exchange sites would be significantly impaired. This may partially explain the subsequent pH reversal. The storm events occurring during this period (every event was sampled) were generally small in volume (< 2.5 cm). However the first major storm following this period (> 11 cm) resulted in return of the throughfall/rain pH relationship to that expected for the developed canopy (throughfall pH \geq rain pH). It may be speculated that this large volume of rain efficiently cleansed the leaves and in some way restored the exchange nature of the surfaces, since the storms following this resulted in considerably higher throughfall pH's relative to incoming rain. This "normal" relationship was maintained throughout the remainder of the growing season, although there were two more events where the pH of rain was essentially unchanged following canopy interception (Figure 35). During the period following leaf fall (approximately October 20) throughfall pH was consistently less than that of the incident precipitation. Detailed information on the

strong and weak acid character of precipitation collected during maximum growth and senescence (1977), and dormant and budbreak (1978), is given in Hoffman et al. (1979).

Meteorological Effects: Element Concentrations
in Incident Precipitation and Throughfall as a
Function of Amount and Type of Precipitation

A General Background of Rainfall
Type - Concentration Relationships

The relationship between elemental concentrations in incident precipitation and the quantity of rainfall is well known and has been discussed for several major constituents (Eriksson, 1952; Junge, 1963; Wolaver and Leith, 1972). However, the relationships between trace constituents in rain and various precipitation characteristics have not been considered in detail, particularly in the case of wetfall only samples, nor have the concentrations of trace constituents in throughfall been similarly investigated. The most often presented relationship is the inverse nature of the precipitation volume - concentration interaction. Several mechanisms have been suggested to explain this feature. Huff and Stout (1964) have implicated the evaporation effect when raindrops at the leading edge of a storm fall through relatively dry air leading to higher concentrations during the initial part of a storm and thus higher concentrations in smaller storm volumes. Also implicated was the scavenging of below cloud dust during the initial period of a storm. Gatz and Dingle (1971) studied the concentration variations during individual convective rains and concluded that variations in rain concentrations were the result of

individual changes within moving rain cells in conjunction with horizontal and vertical advection of concentration gradients in the rain field leading to generally inverse relationships between rainfall rate and concentration, but occasionally also to direct relationships. However, their data supported the hypothesis that the initial precipitation of the largest and most easily scavenged nuclei result in higher concentrations in smaller showers and low concentrations in the heaviest rain. Bleeker et al. (1966) suggested a combination of the processes of diffusive aerosol capture, initial rain evaporation, and dilution of trace substances by heavy rain to explain inverse relationships.

As suggested by Englemann (1971), the process of the cleansing of the air by precipitation is perhaps easiest to predict when considered as two mechanisms, the so called "rainout" and "washout" processes. As recently reviewed by Slinn (1977) this terminology is subject to misuse and should be replaced by the full expressions relating to each. Rainout is more properly termed in-cloud scavenging and refers to precipitation scavenging initiated during the formation and growth of cloud particles resulting in removal of material from within the cloud followed by deposition on the earth's surface. Washout refers to below cloud scavenging and involves precipitation scavenging by fully developed hydrometeors resulting in wet deposition of material from beneath the cloud to the ground.

The theory of precipitation scavenging is well developed in the literature and will be briefly discussed here to serve as an introduction to some empirical considerations. Several early and

recent reviews on the subject may be consulted for more detailed discussions of the theory involved (Engelmann, 1968; Facy, 1962; Junge, 1963). The scavenging process involves repeated exposure of particles and gases to condensation or precipitation elements with some chance of collection at each exposure. In-cloud scavenging primarily involves the collection mechanisms of nucleation and condensation related phenomena. These in turn are dependent on electrical effects, coalescence, diffusiophoresis, Brownian motion, and velocity gradients. Various simplified considerations of in-cloud scavenging efficiency have resulted in values ranging from 0.1 to 1.0 (depending on cloud type, age, and residence time of air parcel within the cloud), all values which were considered significant by Engelman (1968). Below-cloud scavenging primarily involves collection due to inertia. The falling raindrop sweeps out a volume of air but because of inertia, electrical attraction, and molecular diffusion some fraction of the particles below the cloud will cross the falling drop streamlines and intersect the rain drop. Since contact does not imply collection, the fraction carried away by the droplet is termed the retention efficiency. This fraction multiplied by the fraction of the total material intercepting the raindrop path is the collection efficiency, values of which range from 0.2 to 1.0 and are dependent on drop diameter (Engelmann, 1965). Both the in- and below-cloud scavenging processes are also strongly related to the size distribution of particles in the air. Since the below cloud mechanism is largely an inertial process the scavenging efficiency is directly proportional to the particle size, as stated by Engelmann (1968): $E = f(a^2 \rho, D)$

where E = below cloud scavenging efficiency, a = particle radius, ρ = particle density, D = rain droplet diameter. Particles smaller than $1 \mu\text{m}$ are very inefficiently removed by falling drops, indicating that washout may be restricted to giant particles (Junge, 1963), although Engelmann warns that the theory must be cautiously regarded because of the uncertain electrical effects which may enhance small particle washout. Collection due to inertia is much less significant for smaller raindrops and submicron particles in viscous flow such as in clouds. For these materials the attachment of particles to cloud elements by Brownian motion or the water vapor gradient and consumption of particles as condensation nuclei also results in a dependence of in cloud scavenging efficiency on particle radius (Jung, 1963). The combination of these processes results in a bimodal distribution of scavenging efficiencies with particle size (Junge, 1963; Englemann, 1968; see also the example given by Dana and Hales, 1977). This distribution indicates increased scavenging of particles less than approximately $0.05 \mu\text{m}$ and greater than approximately $0.1 \mu\text{m}$. The considerable complexities of these scavenging processes have been discussed in detail in a recent paper by Slinn (1977) including several theoretical and empirical approaches to the problems of assessing collision efficiency, below cloud rain and snow scavenging, scavenging from within clouds and industrial plumes, and washout ratios.

The observed relationships between rainfall volume and elemental concentrations appear to depend on the predominance of one of the two scavenging processes during a particular storm type or during a given period in the course of a storm. For example, Junge (1963) reported

that, based on his own work and data of others, concentrations in relatively small rain events showed considerable scatter of values but decreased as rain volume increased. One example cited was the decrease in the maximum/minimum concentration ratios from > 20 for events of ≤ 1 mm, to 10 for storms of ~ 10 mm, and to ~ 5 for events of ~ 20 mm. The decrease in the ratio was in each case due primarily to a decrease in the maximum concentrations, the minimum values being generally unaffected. The increased concentration variability for smaller rain volumes was attributed to the predominant influence of below-cloud scavenging and particularly rain drop evaporation which can significantly increase precipitation concentrations. For larger amounts of rainfall both of these factors become less important since in-cloud scavenging becomes the dominant factor and the increased humidity associated with larger storms will decrease evaporation. The minimum values are less affected by storm volume since they are controlled within certain limits by the maximum water content and minimum elemental air concentrations associated with a particular rain event. The overall result of these influences is a decrease in the average concentration in rain as the amount of precipitation increases (Junge, 1963).

Some attempts have been made to separate the effects of within and below cloud scavenging. Georgii and Weber (1966) collected precipitation in Frankfurt and in a remote control area near Frankfurt. Because of the geographical location of the sites, the authors assumed in cloud scavenging to be similar between sites but that below cloud processes would be more important in Frankfurt which

is influenced by the considerably higher pollution levels. The data for NH_4^+ , NO_3^- , and Cl^- indicated higher concentrations in rain at Frankfurt for events of < 6 mm but comparable concentrations for larger storms. The authors suggested below-cloud scavenging of the constituents to be essentially completed for storms of > 5 mm and that the influence of local emissions was much less obvious for larger rainfall volumes. However, for $\text{SO}_4^{=}$ the Frankfurt concentrations were consistently higher for larger volumes as well. The authors attributed this effect to below-cloud scavenging of SO_2 in addition to scavenging of $\text{SO}_4^{=}$ aerosols.

Classification of Event Parameters Measured

Before considering the details of the concentration - precipitation relationships it is useful to define the storm parameters observed, calculated, or measured for each event. Table 32 describes the major parameters which were considered relevant to characterizing any given rainfall event in this study; these were rainfall volume, duration of event, length of antecedent period, precipitation intensity, and number of individual events per sampling period. The methods for determining each parameter were described in detail earlier. Briefly precipitation volume was measured using portable plastic wedge type rain gauges at each sample site. These values were compared for each event with those of the 5 site rain gauge network operating continuously at WBW. Whenever evaporation from the exposed plastic gauges was significant the values were replaced by those measured over the network. This correction was necessary on fewer than 5% of the samples. The data

Table 32. Definitions of precipitation event characteristics determined for each rain period sampled

Terminology	Symbol ^a	Definition
Rainfall volume, Measured precipitation	V, Rainclass Measppt	The total amount of precipitation measured at the site of sample collection, during the time samples were being collected (expressed in cm).
Precipitation event	No. event	An event was defined as any period of measurable precipitation (>0.25 mm) preceded and followed by six continuous hours of no precipitation. No. event signifies the number of events sampled during a given period.
Event duration	Dur, Duratn	Total period of time of measurable precipitation, or length of storm event (expressed in fractional days).
Storm intensity	Int, Intensty	Event averaged precipitation intensity or rainfall rate as volume per unit time (expressed in mm/hr).
Antecedent conditions	Ant, Antecedt	Length of time between initiation of a given precipitation event and the end of the previous measurable quantity of precipitation (expressed in days).

^aRefers both to computer abbreviations used in Appendix B and to names of class variables where appropriate.

collected by the continuous recorders was used in conjunction with NOAA data collected for the Oak Ridge site for determination of the number of events occurring during each sampling period, the duration of each event, the intensity, and time since previous rain.

The values of these characteristics are summarized in Table 33 for the events sampled during 1976-1977. Indicated are the mean, standard deviation, and range for the continuous variables and, additionally, median and mode for the class variable "number of events" (which could take on only whole number values). The storms sampled exhibited a wide range of values for each parameter with measured precipitation, antecedent period, and intensity ranging over 2 orders of magnitude and duration over a factor of 50. The coefficients of variation for each of the continuous parameters exceeded 70% indicating a wide scatter in their distributions. This suggests that some of these parameters might be expected to account for the large variance in the elemental concentrations to some extent. The non-continuous variable "number of events" ranged from 1 to 6 with a mean of 2 but the mode and median values were both equal to 1 indicating the predominance of single event sample periods.

For several reasons it is helpful to describe more completely the distribution of precipitation volume for the events sampled (because of the known relationships described above, its large range and coefficient of variation, and its inherent relationship with the other storm parameters). Figure 40 describes the full distribution of values for measured precipitation for all events sampled. As in the

Table 33. Characteristics of all rain events sampled during 1976-1977

Precipitation characteristic	Mean	Standard deviation	Range	Coefficient of variation		
Rainfall volume	3.10 cm	3.15	0.13-19.18	102%		
Antecedent period	5.0 days	4.0	0.2-16.5	80		
Storm duration	0.72 days	0.54	0.04-2.38	75		
Storm intensity	2.15 mm/hr	1.53	0.06-6.47	71		
	<u>Mean</u>	<u>Median</u>	<u>Mode</u>			
Number of events per sample	2	1	1	1	1-6	--

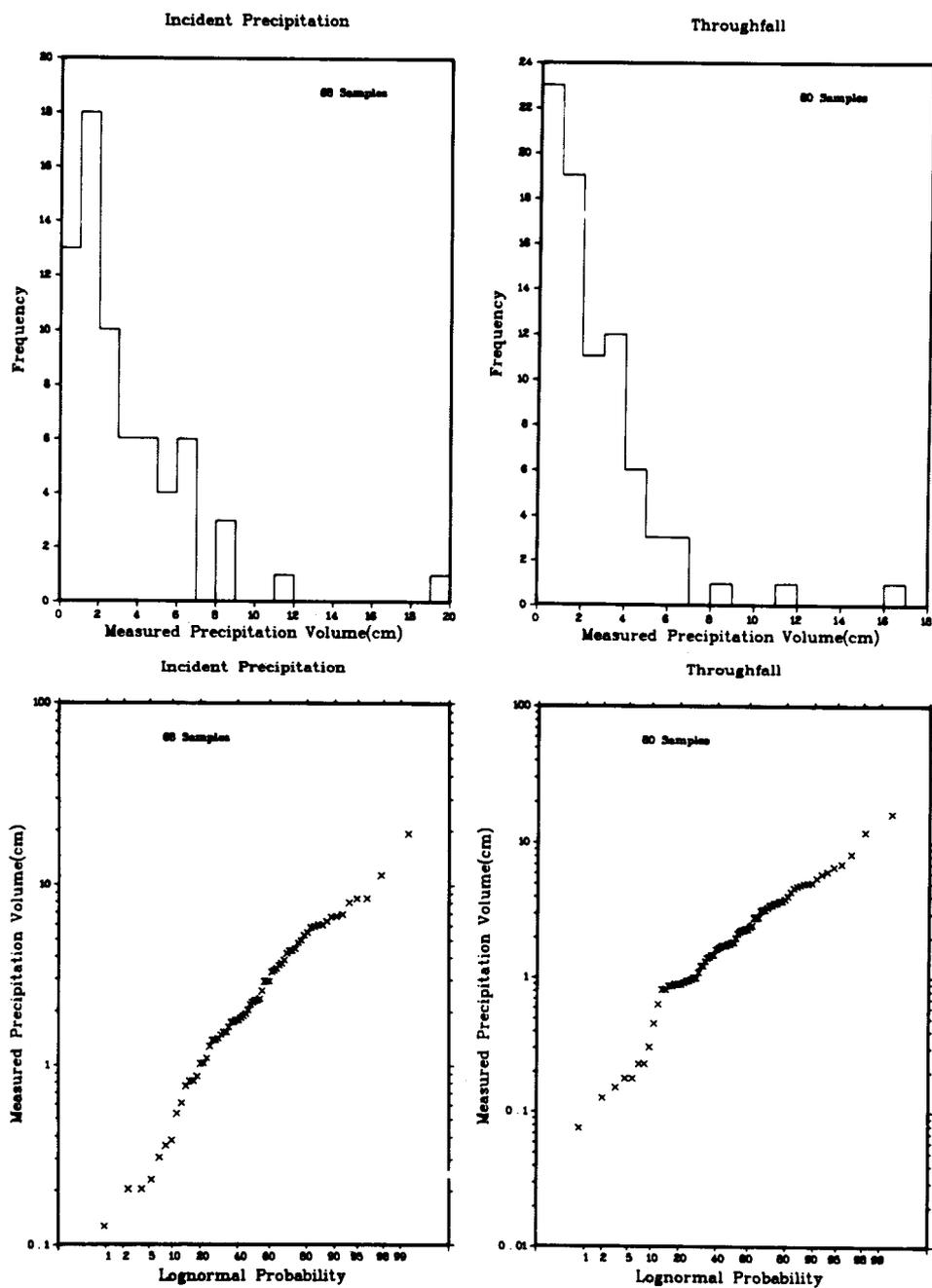


Fig. 40. Frequency distribution and lognormal probability plots of measured rain volume in incident precipitation and throughfall.

case of most chemical constituents, the frequency plots are skewed toward lower values with incident rain volumes between 1 or 2 cm occurring with the highest frequency in the sample set ($\sim 25\%$ of the values) and volumes of < 1 cm occurring with the highest frequency, $\sim 30\%$, for throughfall. In both cases, the log transformed data did not significantly deviate from a normal distribution. The log normality of rainfall volume is a well known phenomenon (Essenwanger, 1959). Similar analysis indicated that antecedent period and storm duration did not significantly deviate from log normality. However, storm intensity could not be significantly defined by either a normal or log normal distribution.

The interdependence of these characteristics is illustrated by the simple correlation matrix in Table 34. Shown are the correlation coefficients with the highest absolute values for any given variable pair, the type of relationship for which the $|r|$ value was largest, and the significance level of the r values. As expected both storm intensity and duration are significantly correlated with rain volume, with the largest r values occurring for the log transformed data. Thus more rainfall generally is associated with storms of longer duration and for storms of higher intensity, not a surprising conclusion. However, the important point is that further analysis of the effects of these parameters on rain and throughfall chemistry must consider this interrelation. The variable antecedent period was not correlated with any other variable nor were the variables intensity and duration correlated with each other.

Table 34. Correlation coefficients between transformed and non-transformed precipitation event characteristics. Shown are the coefficients of largest absolute value for each possible pair of variables, if significant at the 95% level ($P \leq 0.05$).

	Measured precipitation	Duration	Antecedent	Intensity
Measured precipitation	---	0.57 ^a	N ^b	0.61 ^a
Duration		----	N	N
Antecedent			---	
Intensity				----

^aBoth of the correlation coefficients were highest in absolute value for the log-log relationships.

^bNot significant ($P > 0.05$).

The Relationship Between Precipitation
Characteristics and Concentrations

Preliminary considerations - In an initial screening effort to identify significant relationships between various storm parameters and concentrations of trace and major constituents in rain and throughfall, the previously discussed modified data set (one observation for each storm) was used to calculate simple correlation coefficients between log transformed and nontransformed characteristic storm parameters and concentrations. The results of these calculations are presented in Tables 35 and 36 including the significant ($P \leq 0.05$) correlation coefficients of highest absolute value for any combination of transformed and nontransformed variables. All of the significant relationships are negative with one exception, the relationship between throughfall hydrogen ion levels and storm intensity. Thus as precipitation volume, storm duration and intensity increase, there are associated decreases in precipitation concentrations. The parameter having the greatest influence on concentrations appears to be rain volume, as evidenced by the generally higher correlation coefficients compared with those of the other storm characteristics. This parameter exhibits statistically significant inverse relationships (best described as semilogarithmic in nature) with all elements in rain except Zn. In throughfall the relationships are similar (semilogarithmic, insignificant for Zn) except for H^+ . This lack of a significant H^+ - volume relationship in throughfall is thought to be due to the ability of the developed canopy to act as both source and sink for H^+ ions.

Table 35. Correlation coefficients between elemental concentrations in incident precipitation and storm characteristics for log-transformed and non-transformed data. Numerical values shown are those with the largest absolute value for any combination of transformed and non-transformed data; the superscript indicates the type of relationship.

	Precipitation volume	Duration	Antecedent period	Intensity
Cd	-0.55 ^a	-0.48 ^b	NS ^c	NS
Mn	-0.63 ^d	-0.56 ^b	NS	-0.30 ^d
Pb	-0.39 ^a	-0.31 ^b	NS	NS
Zn	NS	NS	NS	NS
SO ₄ ⁼	-0.59 ^d	-0.33 ^d	NS	-0.42 ^d
H ⁺	-0.40 ^d	-0.30 ^d	NS	NS

^aLog-linear concentration vs. storm characteristic relationship.

^bLog-log relationship.

^cNS = no significant relationship was found (P > 0.05).

^dLinear-log relationship.

Table 36. Correlation coefficients between elemental concentrations in throughfall and storm characteristics for log-transformed and non-transformed data. Numerical values shown are those with the largest absolute value for any combination of transformed and non-transformed data; the superscript indicates the type of relationship.

	Precipitation volume	Duration	Antecedent period	Intensity
Cd	-0.55 ^a	-0.41 ^b	NS ^c	-0.36 ^d
Mn	-0.52 ^d	-0.42 ^d	NS	-0.34 ^d
Pb	-0.64 ^d	-0.43 ^b	NS	-0.46 ^d
Zn	NS	NS	NS	NS
SO ₄ ⁼	-0.64 ^d	-0.43 ^d	NS	-0.47 ^d
H ⁺	NS	NS	NS	+0.28 ^a

^aLog-linear concentration vs. storm characteristic relationship.

^bLog-log relationship.

^cNS = no significant relationship was found (P > 0.05).

^dLinear-log relationship.

Somewhat unexpectedly none of the constituent concentrations in rain or throughfall showed significant correlations with antecedent conditions. This parameter, a measure of the length of the dry period preceding each event, might be expected to show a positive correlation with rain concentrations and definitely with throughfall concentrations. The calculated coefficients, not shown, were actually equally distributed on either side of zero, all $|r| < 0.15$. The expectation for this relationship for incident rain was based on the assumption that the reequilibration of the relatively clean "washed out" atmosphere below the cloud base with the surrounding unaffected air following a rain event is the rate limiting step in controlling the concentration of material removed by the subsequent event. However, the atmospheric mixing of material below the cloud base is thought to be fairly rapid, particularly following convective storms, so as not to be a concentration-controlling factor (except, perhaps, during a rapid sequence of events) (Gatz and Dingle, 1971). This conclusion is supported by a set of field experiments involving collection of sequential samples during a single event (Lindberg and Turner, unpublished data). Interestingly, previous reports of positive correlations between antecedent conditions and rain chemistry have involved only bulk samples (Weiner, 1978; Gascoyne, 1977). In each case the relationships were attributed to the accumulation of dry deposition on the exposed funnels prior to a precipitation event, and unambiguous relationships between wetfall only and antecedent period were not identified in either study.

Throughfall would be expected to show a positive correlation with antecedent conditions since a longer dry period would imply increased dry deposition of aerosols to the canopy surface, available for leaching during subsequent precipitation events. This hypothesis might also apply to the elements in throughfall which originate to some extent from internal leaf leaching (Mn and SO_4^{2-}) because of the requirement and ability of the plant to reestablish a pool of readily leached elements following foliar leaching (Tukey, 1970). However it seems reasonable that the strong inverse relationship between rain volume and concentration could easily mask any such positive effects of antecedent period. An attempt was made to normalize for the volume effect by calculating correlation coefficients between concentration and antecedent period for several limited classes of rain volume. No significant relationships were found, perhaps because of the limited sample size or because the effects of duration and intensity could not also be removed. This problem points to the critical need for large scale programs of sequential precipitation and throughfall collection to further study controlling mechanisms. If an initial constant volume fraction of each storm were collected separately the effect of antecedent period might be more clearly identified. Such experiments have been proposed for continued study of rain chemistry at WBW but will entail highly specialized collection equipment such as a noncontaminating wetfall only modification of the sequential bulk collector designed by Gascoyne (1977). A similar program of sequential sampling has been recently initiated by Raynor and Haynes (1977) for

major constituents in incident precipitation but not for trace constituents nor for elements in throughfall.

Because of the previously discussed relationships between intensity, duration and rain volume it is necessary to explore the possibility that any significant correlations between either of these parameters and elemental concentrations in rain or throughfall are artefacts due to interdependence. An indication of such an artefact would be similar behavior between concentration and both rain volume and either duration or intensity. This is apparently true for storm duration. In both incident precipitation and throughfall, each element exhibits a very similar relationship between duration and concentration as between rain volume and concentration. For this reason the relationships between duration and concentration were judged to be too similar to the rain volume relationships to warrant further investigation. However the relationships between intensity and concentration are not similar to those between volume and concentration, nor are they similar in nature between incident precipitation and throughfall. This relationship appears to be worthy of some additional consideration.

The influence of rainfall intensity on throughfall chemistry - As indicated in Table 35, only Mn and $\text{SO}_4^{=}$ in incident precipitation appear to show a possible relationship with storm intensity. However, in throughfall, apparent relationships exist between storm intensity and concentrations of Cd, Mn, Pb, $\text{SO}_4^{=}$ and H^+ . Interestingly, the correlation coefficients are negative for Cd, Mn, Pb, and

SO_4^- while the relationship between H^+ concentration and storm intensity is of a positive nature. The validity of these relationships is best tested statistically by transforming the data to fit a linear function, a semilogarithmic approach being indicated by the data in Table 36. Once transformed, the significance of the relationship can be determined by testing the hypothesis that the slope of the linear regression line is equal to zero. The results of these tests are summarized in Table 37. For incident precipitation, only SO_4^- shows a significant negative slope for the concentration - intensity line, although the indication is that all elements show inverse relationships between concentration and intensity. Several researchers have considered the variations of element concentrations in rain as influenced by storm intensity (e.g., Gatz and Dingle, 1971; Müller and Beilke, 1975). The relationships reported were generally inverse in nature, although the former authors pointed out that for certain storm types and during certain phases of a storm the concentration could increase with intensity. The most often used relationship in the study of rain chemistry, however, is that between concentration and volume (Gambell and Fisher, 1964; Makhonko, 1967; Munn and Rohde, 1971; Gascoyne, 1977; Raynor, 1977). As indicated in Table 11 the effect of precipitation volume on rain concentrations is also significant for the WBW data set and will be considered in detail in the following section.

Table 37 indicates that the slopes of the linearized relationships between throughfall concentrations during the growing season and storm intensity are significantly negative for Cd, Mn, Pb, and SO_4^- and significantly positive for H^+ . The relationship for Zn is also of an

Table 37. Linearized relationships between storm intensity (mm/hr) and concentration for incident precipitation and throughfall

Element	Linearized expression: Concentration = $A_0 + A_1 \cdot \log(\text{intensity})$	
	Intercept = A_0	Slope = A_1
<u>Incident precipitation</u>		
Cd ($\mu\text{g/l}$)	0.44* ^a	-0.07
Mn	4.0 *	-3.1
Pb	7.6 *	-2.3
Zn	5.9 *	-0.28
SO_4^- (mg/l)	4.5 *	-3.3 *
H^+ ($\mu\text{eq/l}$)	-80	-20
<u>Throughfall</u>		
Cd ($\mu\text{g/l}$)	2.08*	-2.17*
Mn	-106 *	-97 *
Pb	-15.4 *	-12.9 *
Zn	-15.1 *	-2.0
SO_4^- (mg/l)	-11.9 *	-9.6 *
Log (H^+) ($\mu\text{eq/l}$) ^c	-1.27*	+0.11*

^a* signifies a significant t statistic in the test of the hypothesis that the coefficient = 0. A significant t statistic indicates rejection of this hypothesis.

^bMn in incident precipitation calculated for data from CI only, Mn in throughfall calculated for data from combined (T1, T2, T3).

^cBest fit equation for this variable was $\log(\text{H}^+) = A_0 + A_1(\text{intensity})$.

inverse nature, although the slope is not significantly different from zero. Characterizing the parameter "storm intensity" as a class variable resulted in three well defined intensity classes, $I_1 \leq 1$ mm/hr, $1 < I_2 \leq 5$, $I_3 > 5$ mm/hr. The variation in element concentration between intensity classes is illustrated in Figure 41. Shown are mean element concentrations (\pm SE) for each intensity class with significant differences between means (determined by Duncan's new multiple range test) indicated by uncommon letters over each column. The effect of increasing intensity of the incident rain is to result in significant decreases in throughfall concentrations of Cd, Mn, Pb, and $\text{SO}_4^{=}$ but significant increases in the throughfall concentration of H^+ .

The opposite effect of intensity on H^+ compared to the other constituents leads to an interesting hypothesis concerning residence time of rain water on the leaf surface as controlled by precipitation intensity. Storms characterized by relatively high intensities would necessarily result in short residence times of the incoming rain on the leaf surface. This is a function of increased splash-off of the larger drops associated with intense rains, increased leaf flutter exposing less surface area to the incoming rain, and the shorter leaf surface saturation time during high intensity rainfall. All of these factors would contribute to shorter leaf surface - precipitation contact time. Given less equilibration time at the leaf surface, the incident rain would be expected to remove less rain-soluble material, resulting in lower throughfall concentrations. Based on the previous discussion of the role of leaf leaching and aerosol solubilization in the

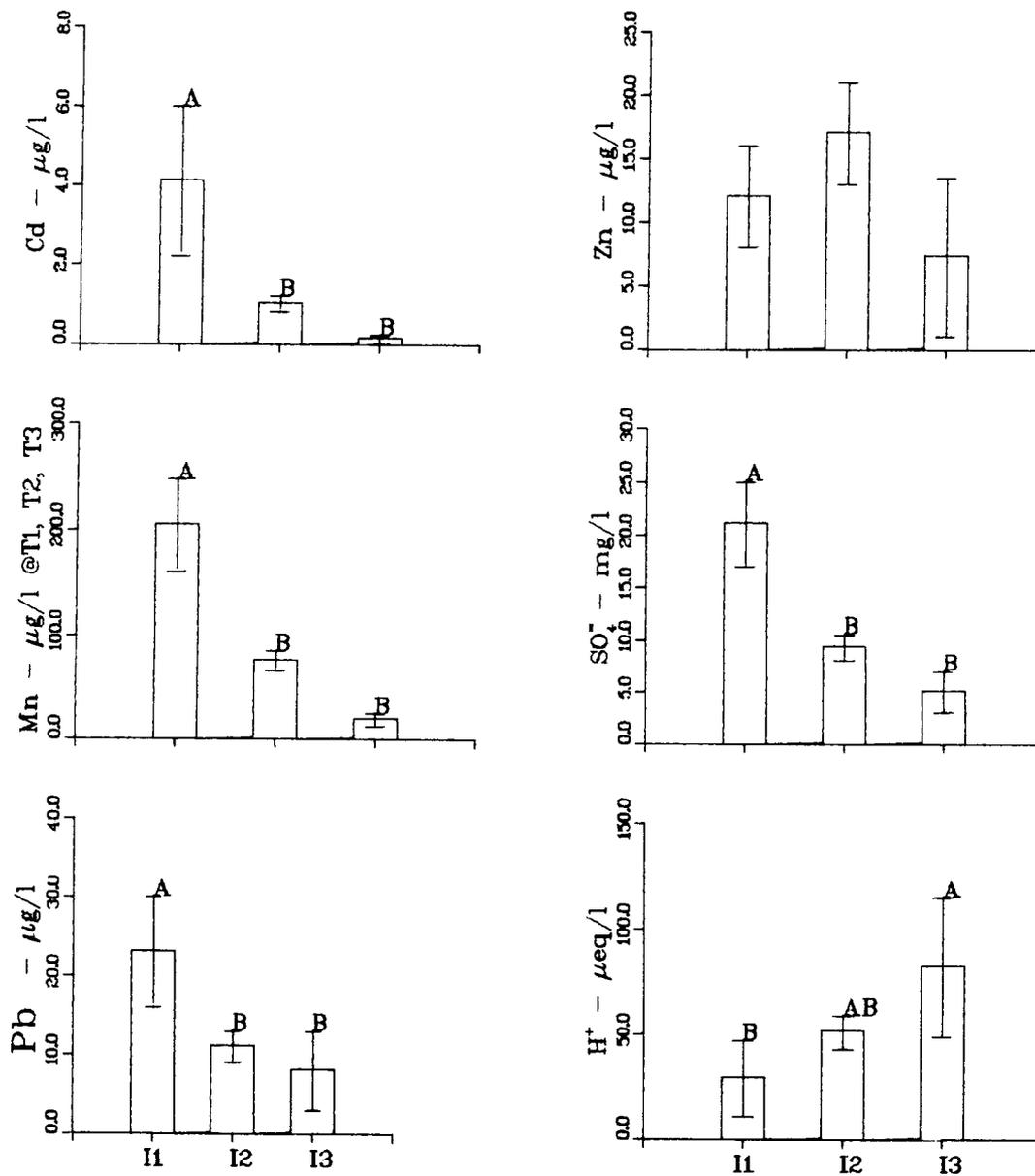


Fig. 41. Relationship between concentrations in throughfall and intensity of precipitation per event. Shown are mean concentrations (\pm standard error) for three intensity ranges (I1 \leq 1 mm/hr, 1 < I2 \leq 5 mm/hr, I3 > 5 mm/hr). Values with the same or no letter are not significantly different ($P > 0.05$, Duncan's new multiple range test).

relationships between incident rain and throughfall chemistry, decreased residence times should result in lower throughfall concentrations Cd, Mn, Pb, and $\text{SO}_4^{=}$. However because of the importance of the H^+ - cation exchange process, decreased residence times at the leaf surface should also result in less H^+ loss while rain passes through the canopy, resulting in higher concentrations of H^+ in throughfall. The linear relationships between concentration and storm intensity in Table 37 and the variation in mean concentrations between each intensity class in Figure 41 support these conclusions for data collected during the growing season. When the data collected during the "no leaves" periods was similarly analyzed, no significant relationships were found. Several other investigations of this phenomenon have been reported for the leaching of nutrients (Tukey et al., 1965; Attiwill, 1966; see also several papers discussed in the review by Tukey, 1970). In each case the authors concluded that rain falling in a light drizzle, continuously bathing the foliage, removed considerably more metabolites than heavy rain of short duration.

The influence of rain volume on incident precipitation chemistry: empirical and theoretical approaches - The trend of decreasing concentrations of various constituents in rain with increasing precipitation volume appears to hold true for the WBW data as evidenced by the correlation matrix (Table 35). The nature of this relationship will be considered using a number of approaches, involving theoretical calculations and investigation of the empirical data using both continuous and class variables. The advantage of class variables is to

decrease the overall variability of the data by segregating the concentrations into confined groups of similar rain volume. Two rain volume classification schemes were devised, one each for rain and throughfall (because of the previously described relationship between rain volume above and below the canopy) and each containing four subgroups. These classifications are as follows: (1) incident precipitation class $R1 \leq 1.1$ cm, $1.1 < R2 \leq 2.1$ cm, $2.1 < R3 \leq 5.1$ cm, $R4 > 5.1$ cm; and (2) throughfall class $R1 < 0.9$ cm, $0.9 < R2 \leq 1.8$ cm, $1.8 < R3 \leq 3.5$ cm, $R4 > 3.5$ cm. The rain class trends are illustrated for concentrations in both incident precipitation and throughfall using percentile plots of the complete data set (Figures 42 to 43). Because the complete data set contains "replicate" observations it will be briefly discussed and is presented for the purpose of allowing the reader to judge the strength of the trends through a visual presentation of all observations. Although there is considerable scatter and overlap in the data the trends are clear. Nearly all elements show both a decreasing central tendency in concentration and a generally decreasing variability (as indicated by interquartile range) as rain class increase in volume. This decrease in concentration variance with increasing rainfall amounts was described by Junge (1963) for major constituents in rain; but it has not been demonstrated for trace elements in rain or for other constituents in throughfall, particularly for wetfall only event samples. Zinc does not appear to exhibit a clear trend with rain volume. There is a tendency for generally lower concentrations to occur in the highest rain class relative to the lowest class but the trend is not consistent

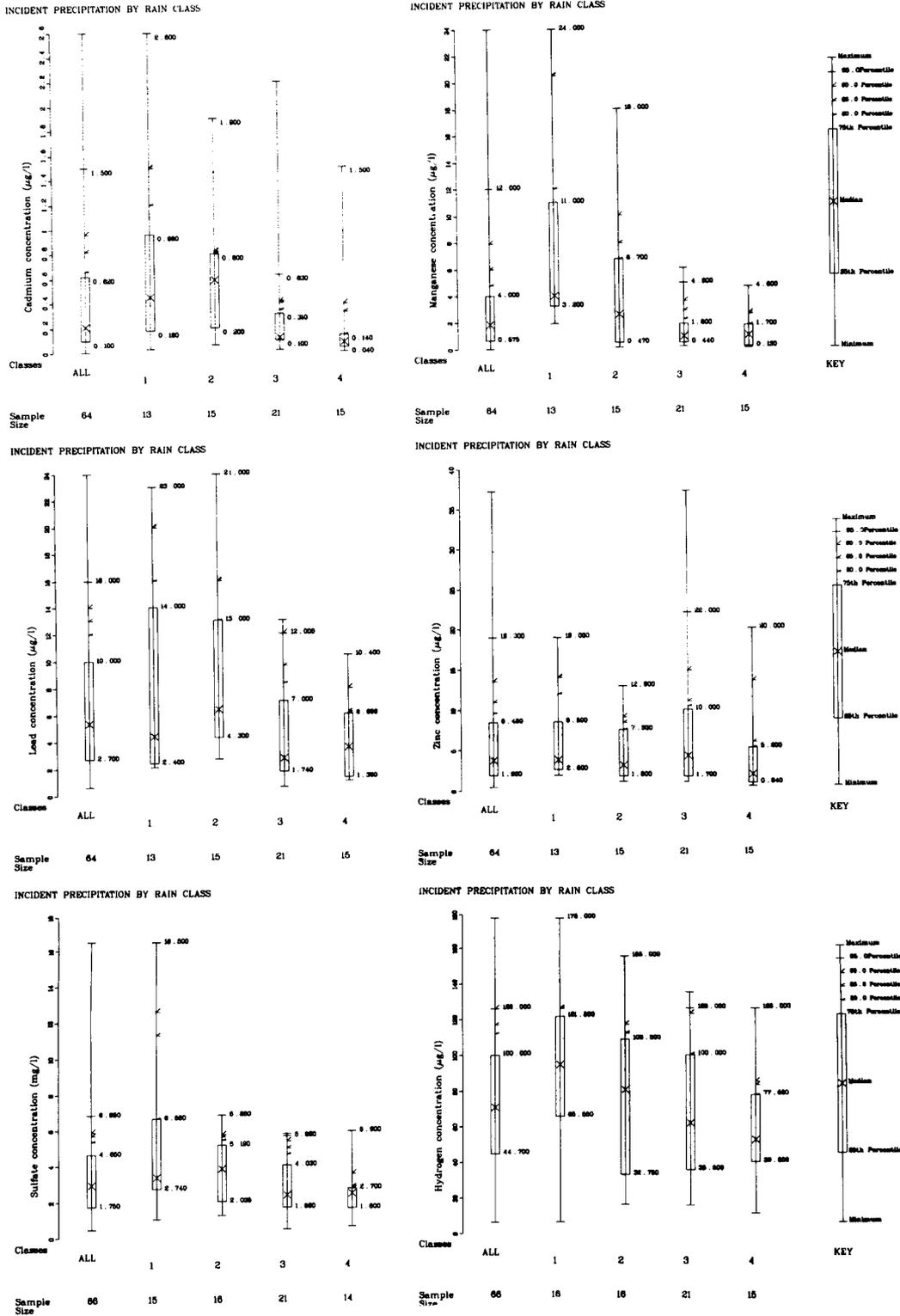


Fig. 42. Plots of percentiles of concentrations in incident precipitation within four classes of measured precipitation volume ($R1 \leq 1.1$ cm, $1.1 < R2 \leq 2.1$ cm, $2.1 < R3 \leq 5.1$ cm, $R4 > 5.1$ cm).

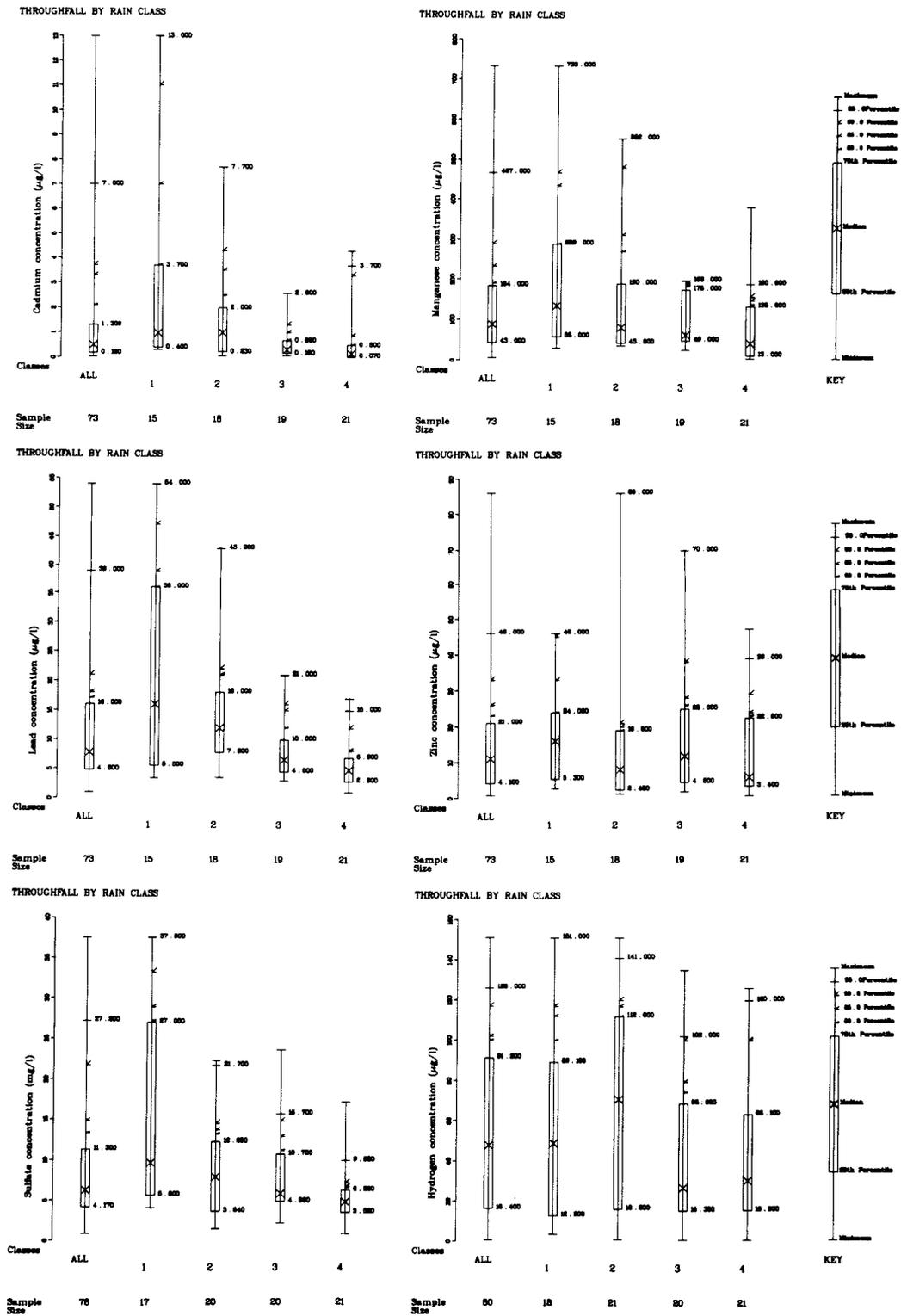


Fig. 43. Plots of percentiles of concentrations in throughfall within four classes of measured precipitation volume ($R1 \leq 0.9$ cm, $0.9 < R2 \leq 1.8$ cm, $1.8 < R3 \leq 3.5$ cm, $R4 > 3.5$ cm).

between the extremes, nor does the variability decrease as rain volume increases. The same situation is manifested by H^+ concentrations in throughfall which are complicated by the source and sink nature of the forest canopy as previously discussed. The situation for Zn is further considered later in this section using a nonlinear approach.

Figures 44 and 45 summarize the trends in mean element concentrations and standard errors of the mean for each rain volume class for rain and throughfall. The data comprising these figures was developed from the modified data set by combining replicate observations as described earlier. As previously discussed Mn must be considered by station and is presented for the one incident and the 3 combined throughfall stations with the largest number of observations (CI, and combined T1, T2, and T3). The statistical significance of the differences in means for each rain class were determined by applying Duncan's new multiple range test to the log transformed data (since all constituents are best approximated by log normal distributions) but the results are presented as arithmetic means for ease of comparison. As suggested by the percentile plots of the full data set, all elements except Zn and H^+ (H^+ in throughfall only) exhibit significant differences in mean concentrations between rain classes, the greatest differences occurring between the extremes ($R1 < \sim 1$ cm and $R4 > \sim 3$ to 5 cm).

The validity of these relationships over the full range of concentration and precipitation volume may be assessed using linear regression analysis on the transformed data (as described for intensity in the previous section). The rain volume - concentration relationship

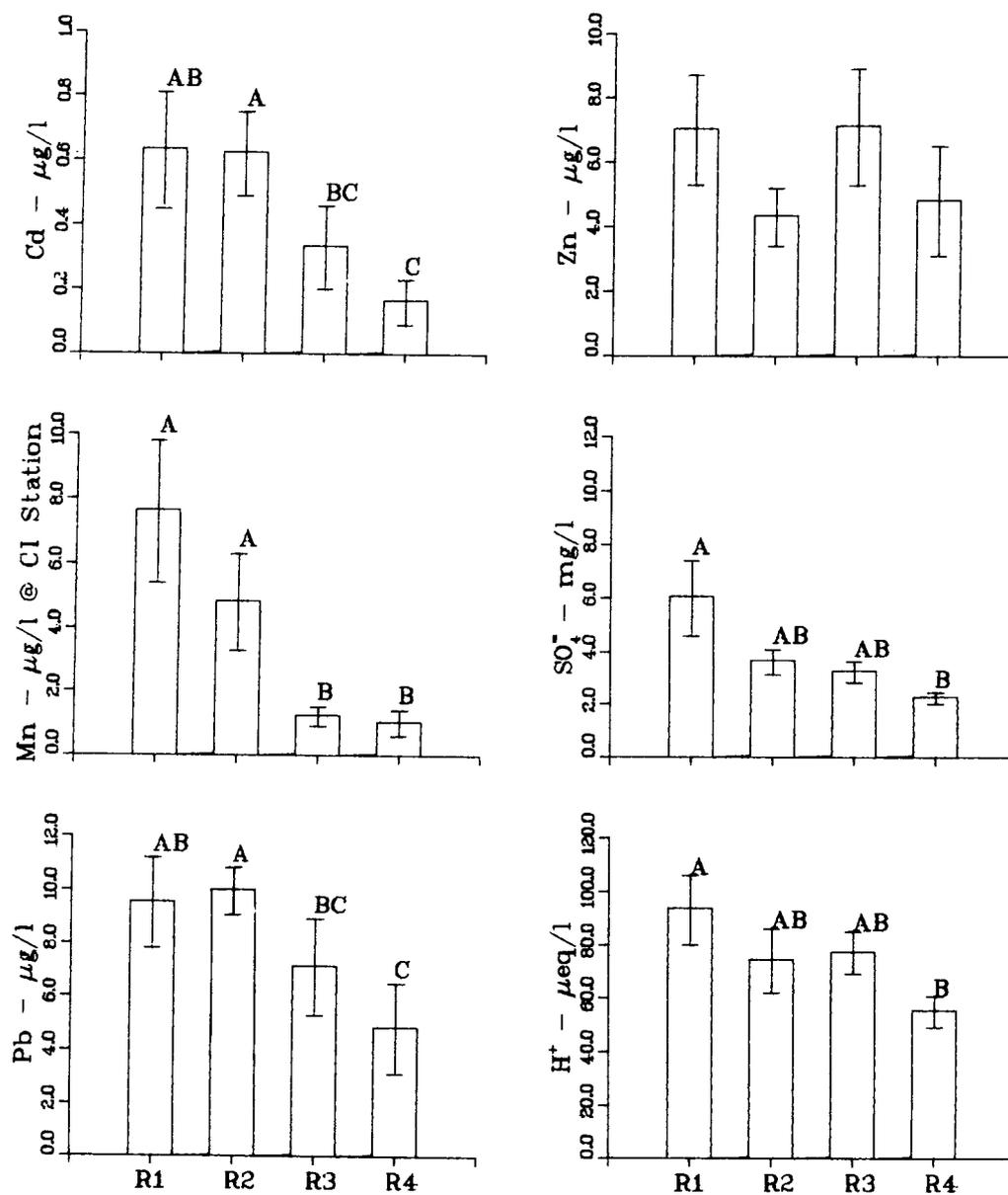


Fig. 44. Relationship between concentrations in incident precipitation and volume of rainfall per event. Shown are mean concentrations (\pm standard error) in four rain volume classes (R1 \leq 1.1 cm, 1.1 < R2 \leq 2.1 cm, 2.1 < R3 \leq 5.1 cm, R4 > 5.1 cm). Values with the same or no letter are not significantly different ($P > 0.05$, Duncan's new multiple range test).

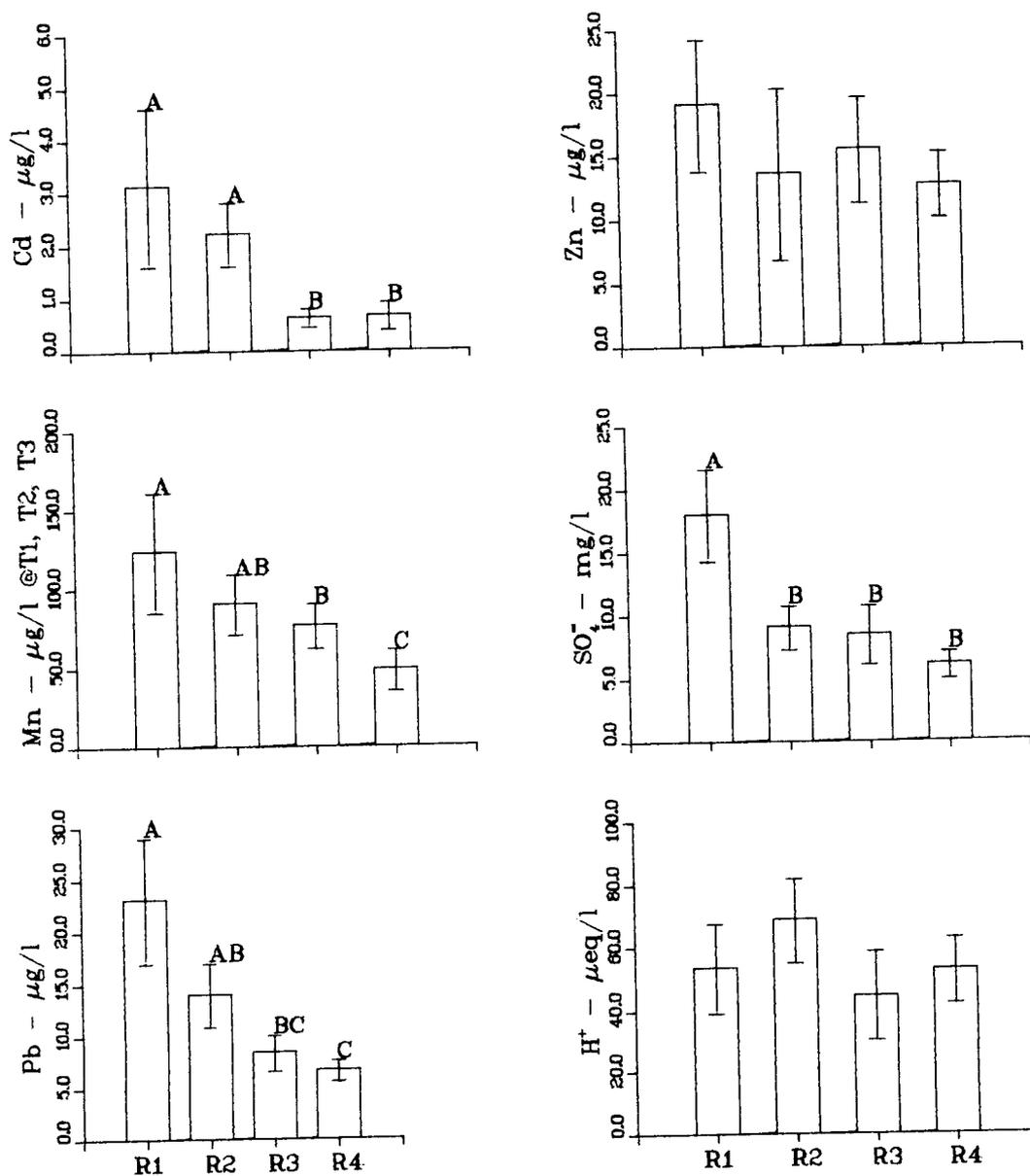


Fig. 45. Relationship between concentrations in throughfall and volume of rainfall per event. Shown are mean concentrations (\pm standard error) in four rain volume classes (R1 \leq 0.9 cm, $0.9 < \text{R2} \leq 1.8$ cm, $1.8 < \text{R3} \leq 3.5$ cm, R4 > 3.5 cm). Values with the same or no letter are not significantly different ($P > 0.05$, Duncan's new multiple range test).

has been considered in the past as one of a linear nature (Bromfield, 1974), of a semilogarithmic nature (Makhonko, 1967; Munn and Rodhe, 1971) and of a nonlinear nature (Wolaver and Leith, 1972). For the purpose of this investigation the semilogarithmic approach appears most useful, although as will be discussed shortly, the nonlinear approach will also be quite useful although not as statistically straightforward. The results of the best fit linearized models are presented in Table 38. Shown are the slope, intercept, and significance level of each for the expression: $10^Y = a_0 X^{A_1}$, linearized to $Y = A_0 + A_1 \log X$, where Y = elemental concentration, X = rain volume (cm), and $A_0 = \log(a_0)$. The results of these analyses confirm the trends discussed above. In incident precipitation the concentrations of Cd, Pb, Mn SO_4^- and H^+ all exhibit a significant inverse relationship with rain volume. The slopes of the regression lines (given by A_1 , for the log transformed data) provide an indication of the magnitude of concentration decreases associated with increases in rain volume. For comparison the slopes must be normalized to a constant volume change and expressed on a relative concentration scale (i.e., by determining the concentration decrease relative to the initial "undiluted" concentration over a given range of volumes). In terms of the generalized linear expression above the relative dilution factor (RDF) is expressed as:

$$\text{RDF} = \frac{A_1 \log \frac{X_1}{X_2} \cdot 10^3}{x A_0 - A_1 \log (X_1)} ,$$

Table 38. Linearized relationships between precipitation volume (cm) and concentration for incident precipitation and throughfall

Element	Linearized expression: Concentration = $A_0 + A_1 \log$ (measured precipitation)	
	Intercept = A_0	Slope = A_1
<u>Incident precipitation</u>		
Cd ($\mu\text{g/l}$)	0.55* ^a	-0.37* ^a
Mn ^b	5.4 *	-6.1 *
Pb	8.5 *	-4.4
Zn	6.2 *	-1.2 *
SO ₄ ⁼ (mg/l)	4.9 *	-3.7 *
H ⁺ ($\mu\text{eq/l}$)	85.7 *	-32.7 *
<u>Throughfall</u>		
Cd ($\mu\text{g/l}$)	2.1 *	-2.2 *
Mn ^b	108 *	-89.8 *
Pb	15.7 *	-13.9 *
Zn	16.2 *	-6.8
SO ₄ ⁼ (mg/l)	12.3 *	-10.6 *
H ⁺ ($\mu\text{eq/l}$)	57.1 *	-3.1

^a* signifies a significant t statistic in the test of the hypothesis that the coefficient = 0. A significant t statistic indicates rejection of this hypothesis.

^bMn in incident precipitation calculated using CI data, Mn in throughfall calculated using combined (T1, T2, T3) data (see text).

where X_1 and X_2 = the lower and upper limits to the rain volume range respectively, $\Delta X = X_2 - X_1$, A_1 = regression equation slope, A_2 = regression equation intercept. The rain volume range chosen for this comparison was $X_1 = 0.1$ cm to $X_2 = 7$ cm, a range including 90% of all the volumes measured in WBW (Figure 40). This equation results in the following order of RDF's for incident precipitation (summarized in Table 39:

$$\text{Mn} > \text{Cd} > \text{SO}_4^{2-} > \text{Pb} > \text{H}^+.$$

Since, during the precipitation scavenging process, the below-cloud material is thought to be depleted first, these RDF values provide an indication of the relative importance of below-cloud scavenging. Elements with higher RDF's are likely to be more strongly influenced by below-cloud scavenging mechanisms compared to elements with lower RDF's. This does not imply that the below cloud mechanism dominates the precipitation chemistry or deposition of an element relative to the in-cloud process, a question which will be considered shortly, but that some elements are more strongly influenced by the below-cloud process than others. In a theoretical approach to this same question Muller and Beilke (1975) calculated the relative influence of "washout" and "rainout" on Pb and Mn scavenged in an urban and a remote area, concluding that the washout process was relatively more important in influencing the rain chemistry of Mn than of Pb. Because of the previously discussed influence of particle size on in and below-cloud scavenging efficiencies, it seems reasonable to relate the RDF's to particle size distribution of these elements in the atmosphere over

Table 39. Relative dilution factors (RDF) for the rainfall volume dilution of element concentrations in rain

Element	RDF ^a Incident precipitation
Cd	-110
Mn	-140
Pb	-90
SO ₄ ⁼	-120
H ⁺	-70

$${}^a\text{RDF} = \frac{A_1 \cdot \log\left(\frac{X_2}{X_1}\right) \cdot 10^3}{\Delta X[A_0 - A_1 \log(X_1)]}$$
, where X_1 and X_2 are the upper and lower limits to the rain volume range, respectively, $\Delta X = X_2 - X_1$, A_1 and A_2 are the regression equation slope and intercept, respectively.

WBW. Elements with higher RDF's, and presumably more strongly influenced by below-cloud processes, would thus be expected to occur in the air to a greater degree on relatively large ($> 1 \mu\text{m}$) particles. The aerosol size spectrum of the "available fraction" of trace elements and sulfate in WBW was considered in detail in Chapter III. Table 40 summarizes some of this information for comparative purposes. It is apparent that Cd and Mn exhibit considerably different size distributions in the ambient air compared to Pb and $\text{SO}_4^{=}$ (unfortunately little data was collected for the size distribution of leachable H^+ in aerosols; on one occasion when it was determined the distribution was nearly identical to that of $\text{SO}_4^{=}$). As expected the distribution of Pb and SO_4 are dominated by the smallest size fractions while for Cd and Mn 50 to 72% of the material is present on "giant" particles ($> 1 \mu\text{m}$).

Quantifying the contribution of in-cloud and below-cloud scavenging mechanisms: A nonlinear approach to the empirical data -
Assessing the relative importance of the processes of in and below cloud scavenging to the ultimate chemistry of precipitation reaching the ground is a difficult problem. The results of early work, primarily concerning the scavenging of bomb debris, have led to the general notion that the in-cloud process dominates the removal of material from the atmosphere by precipitation (Junge, 1963). However, since bomb debris are introduced initially into the stratosphere their removal process would be expected to be dominated by in-cloud processes. The vertical distribution of bomb nuclides has been well characterized as increasing in concentration with height above the

Table 40. Summary of particle size distributions of water leachable components of trace elements in air over WBW. Shown are the mean (\pm SE) relative contribution of material within each size class to the total atmospheric concentration of each element, in percent.

Element	Giant particles ^a	Large particles ^b	Aitken particles ^c
Cd	50% (± 3) ^d	24% (± 3)	27% (± 5)
Mn	72% (± 2)	17% (± 2)	11% (± 3)
Pb	19% (± 1)	27% (± 3)	53% (± 4)
SO ₄	11% (± 1)	47% (± 4)	42% (± 5)

^aTerminology used for ease of comparison. Giant corresponds to particles collected by stages 0-5 of an Anderson cascade impactor (aerodynamic diameter $> \sim 1 \mu$).

^bLarge corresponds to particles collected by stages 6-7 (aerodynamic diameter $\sim 0.44 - 1 \mu$).

^cAitken corresponds to particles collected by backup filter (aerodynamic diameter $< \sim 0.44 \mu$).

^dStandard error of the mean of 10 impactor runs over a 22-week period.

surface (e.g., Hintzpeter, 1959; as cited in Junge, 1963). In a recent review paper Slinn (1977) challenged the propagation of this generalized statement stating that the relative importance of either mechanism depended on numerous factors such as vertical distribution of the material to be scavenged, and the particle size distribution, and that the statement could be erroneous when applied to the removal of particles from urban or industrial sources. Several approaches have been used to determine the relative importance of each process in the total wetfall removal of various elements. Although the question is far from being resolved, the general opinion is that the in-cloud process is the more important when considering the removal of fine particulates (P. Krey, L. Newman, personal communications). The approaches presented in the literature have ranged from strict theoretical applications (Slinn, 1977), to similar theory applied to field data (Müller and Beilke, 1975), to controlled laboratory scavenging experiments (Dahl and Corrin, 1977) to considerations of empirical data only (Gatz, 1977; Krey and Toonkel, 1977; Wolaver and Leith, 1972). Concerning individual elements the conclusions have supported the greater importance of the in-cloud scavenging process for Co, Br, V, Cd, Pb, Mn and SO_2 (Dahl and Corrin, 1977; Müller and Beilke, 1975; Krey and Toonkel, 1977; Bogen, 1974; Barrie et al., 1977) and the below-cloud process for Sm, Sc, Fe, K, Na, Ca, Cl^- , NH_4^+ , NO_3^- , and SO_4^{2-} (Bogen, 1974; Wolaver and Leith, 1972).

In addition to the interpretation presented above that the slopes of the linearized concentration - volume relationships provide some indication of the relative importance of below-cloud scavenging, two

further approaches, one empirical and one theoretical, will be applied to the WBW data. The intention is to determine the relative importance of local ground level industrial and urban sources relative to regional or longer range transported material on the chemistry of incident precipitation as manifested by dominance of either below cloud or in cloud scavenging. Wolaver and Leith (1972) took an empirical approach in examining the data from the National Precipitation Sampling Network. The data, which consisted of 4 years of observations of monthly wetfall only samples collected at 33 stations across the U.S. was analyzed with the purpose of (1) determining the processes causing the negative exponential relationship between concentration and volume, (2) developing mathematical expressions for the relationships between 7 major constituents in rain and monthly rain volume, and (3) calculating and producing contour maps of "washout" and "rainout" concentrations across the U.S. Although this approach as originally presented involved some tenuous oversimplifying assumptions it does provide an interesting starting point for interpretation of the WBW data. Since this approach relies heavily on interpretations of the shape of the volume - concentration curve, it is useful to briefly consider the origin of this relationship.

The results of several approaches to the sampling of individual storm events on a sequential basis have confirmed the idea of a general decrease in concentration with an increase in volume. Concentrations in individual events also decrease approximately exponentially as time since storm initiation, or cumulative volume of rainfall, increase (Müller and Beilke, 1975; Gatz and Dingle, 1971; Gambell and Fisher,

1964; Makhonko, 1967; Gascoyne, 1977; Raynor, 1977; Lindberg and Turner, unpublished data from WBW). Below-cloud scavenging is generally considered to occur primarily during the early stages of precipitation when particles and gases are scavenged by both in- and below-cloud mechanisms. Thus below cloud scavenging is generally associated with smaller rainfall volumes. As precipitation continues, if a sufficient rate is maintained, the below-cloud layer will be depleted of its readily scavengeable particles and gases, and material still present in rain can be largely attributed to in-cloud scavenging processes (Raynor, 1977). In most of the cases cited above the authors attributed the concentrations of elements in early rain periods, or in low volume events, to within- and below-cloud scavenging and the nearly steady concentrations in the later periods of rain, or in high volume events, to primarily in cloud processes. For example, Georgii and Weber (1966) stated that "washout" was more or less completed for rainfalls of 5 mm for NH_4^+ , NO_3^- , and Cl^- .

Figure 46 is patterned after the approach taken by Wolaver and Leith (1972) with several additions and changes. The precipitation concentrations occurring within Region I are the result of in- and below-cloud scavenging, concentrations being increased by drop evaporation and decreased by dilution. Concentrations in Region III result primarily from in-cloud processes generally being decreased by dilution. Region II encompasses the transition zone between below-cloud and in-cloud dominance and both mechanisms must be considered. The general form of this line can be described by:

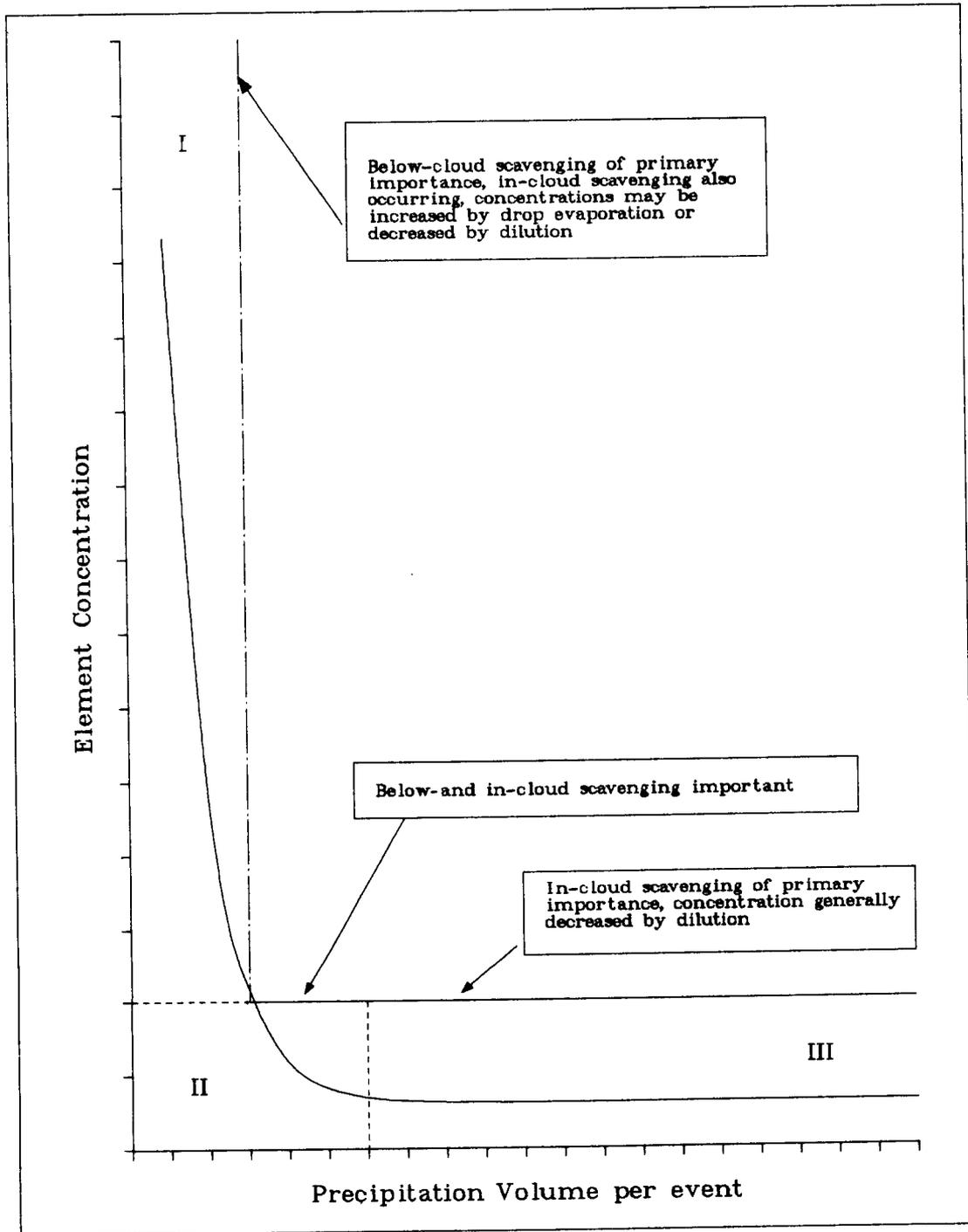


Fig. 46. Simplified general relationship between the concentration of a constituent in rain and the volume of rainfall; also applies to the time series variation of constituent concentration in an individual event vs event time or vs cumulative rain volume. The concentrations within each region are the result of various combinations of in- and below-cloud scavenging as indicated.

$$Y = A_0 + A_1 e^{A_2 X},$$

where Y = elemental concentration, and X = measured precipitation volume. The parameter A_0 represents the concentration corresponding to the asymptote along the X axis, or the minimum predicted concentration as $X \rightarrow \infty$, while the sum $A_0 + A_1$ represents the Y intercept, or maximum predicted concentration as $x \rightarrow 0$. These coefficients were estimated using nonlinear regression techniques (Barrett et al., 1976). This equation includes the negative exponential (i.e., $A_0 = 0$, $A_2 < 0$) and the straight line (i.e., $A_1 = 0$) in its family of curves. Wolaver and Leith separated the relationships obtained for the 7 elements studied on the basis of the general range of values of the predicted coefficients. Four graphical models were hypothesized which were found to explain the variations in the basic equation as related to physical and meteorological differences. Concentrations in precipitation from relatively clean areas (e.g., Grand Island, Nebraska) resulted in concentration - volume curves shaped like that in Figure 46, that is both tails and inflection point well defined ($0 \leq A_2 \leq 1$, $|A_0| \leq 1$). Precipitation collected near major urban areas (e.g., Chicago and St. Louis) resulted in curves with one of two tails less well defined and the inflection point less obvious and tending to occur further away from the origin at a 45° angle ($A_2 \rightarrow 0$ and $|A_1| \gg 1$, or $A_2 < 0$ and $|A_1| > 1$). Finally in areas of extreme precipitation amounts (very arid or extremely wet) the curves were essentially linear along the ordinate (arid areas) or abscissa (wet areas).

The application of this approach to the WBW data is illustrated by Figures 47 and 48. Shown are nontransformed plots of element concentrations in rain vs amount of rainfall for each event and the best fit nonlinear regression curve. The coefficients for each equation are also summarized in Table 41 with their 67 and 95% confidence intervals. As indicated in Figure 48 the plot for Zn shows considerably more scatter than seen for the other constituents. Table 41 indicates that a nonlinear regression equation could not be developed for Zn within the constraints of the approach used here. This agrees with the earlier indication that significant relationships between Zn and precipitation volume could not be found. Thus although the Zn concentration data does suggest the expected relationship with volume, it will not be further considered in this analysis.

Wolaver and Leith stated that the most significant result of the development of the quantitative relationships between concentration and volume was the ability to differentiate between the processes of "washout" and "rainout". This statement must be considered with some skepticism both because of the scatter in the concentration vs. volume relationships presented by these authors and because of the method used to determine the importance of these mechanisms. The authors apparently estimated rainout as the average of the two lowest values of monthly precipitation concentrations measured. This value was subtracted from the remaining concentrations to "correct" for the "rainout" contribution. Weighted mean "washout" concentrations, corrected for "rainout" were calculated and compared to the rainout concentrations with the conclusion that washout dominated the removal

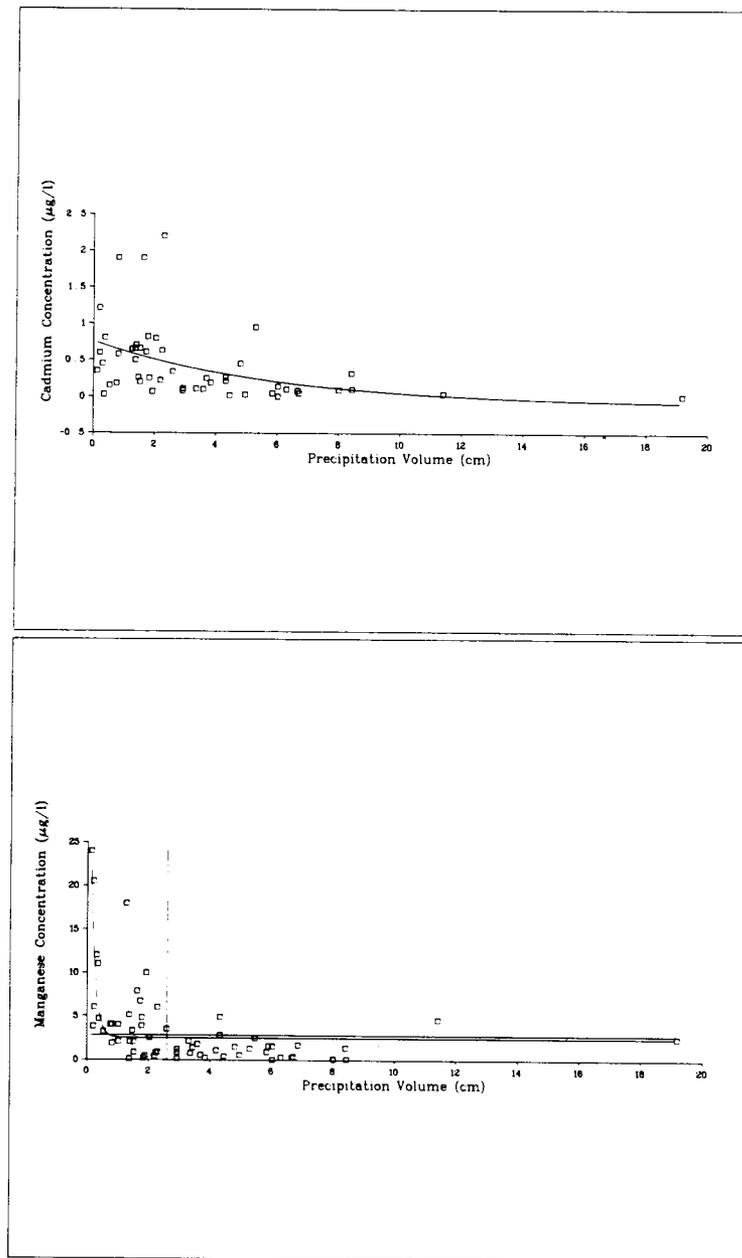


Fig. 47. Relationship between measured precipitation volume and Cd (top) and Mn (bottom) concentrations in incident precipitation. Also indicated are the results of the nonlinear regression analyses, the parameters for which are summarized in Table 41. Illustrated on the plot of Mn concentrations are the outlines of the three regions of in- and below-cloud scavenging dominance as described in the generalized model in Figure 46.

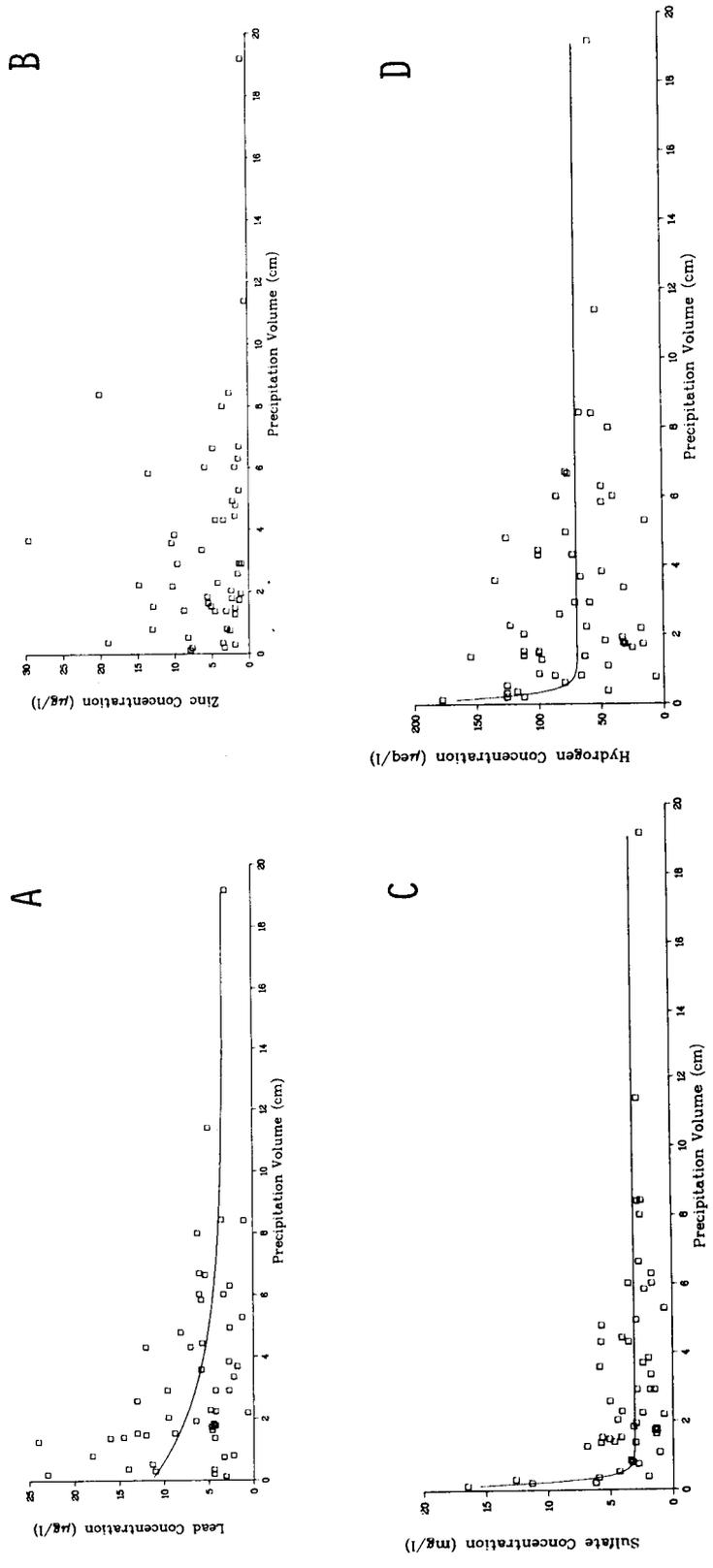


Fig. 48. Relationship between measured precipitation volume and Pb (plot A), Zn (B), sulfate (C), and hydrogen ion (D) concentrations in incident precipitation. Also indicated are the results of the nonlinear regression analyses, the parameters for which are summarized in Table 41.

Table 41. Estimated parameters for the nonlinear model of the relationships between precipitation concentration and rainfall volume^a

Element	A ₀	A ₁	A ₂
Cd	-0.103	0.858* ^b	-0.174
Mn	2.49** ^c	48.3** ^c	-7.26** ^c
Pb	3.28* ^b	8.20** ^c	-0.322* ^b
Zn	DID NOT CONVERGE ^d		
SO ₄ ⁼	3.04** ^c	28.7** ^c	-6.59** ^c
H ⁺	69.3** ^c	201* ^b	-5.70* ^b

^aGeneralized model is: $Y = A_0 + A_1 C^{A_2 X}$, where Y = concentration in µg/l (Cd, Mn, Pb, Zn), mg/l (SO₄⁼), or µeq/l (H⁺) and X = rain volume per event in cm.

^b* signifies that the asymptotic 67% confidence interval did not include zero.

^c** signifies that the asymptotic 95% confidence interval did not include zero.

^dNonlinear regression residual sums of squares failed to converge in 50 iterations.

of the 7 constituents studied. This conclusion is in disagreement with the general feeling about the washout contribution to precipitation chemistry, especially in the cases of $\text{SO}_4^{=}$, NO_3 , and $\text{NH}_4^{=}$. It seems that a better approach, and that which will be used here, would be to rely more heavily on the visible trends in the actual data rather than the predicted trends of the nonlinear regression models.

In the case of the WBW data a visual approach was employed to separate each of the concentration volume plots into the 3 components of the generalized relationship in Figure 46. This approach is illustrated in Figure 47 using Mn as an example. Region I of the plot, during which below cloud processes and drop evaporation are believed to dominate, was fairly well defined as including those observations with rain volumes < 2.6 cm. The concentrations in this region, which were similar in magnitude to those asymptotic along the x axis ($< 2.8 \mu\text{g/l}$), were taken to represent values influenced equally by in- and below-cloud scavenging (Region II). Region I then, was defined for Mn as including all observations for volumes < 2.6 cm and concentrations $> 2.8 \mu\text{g/l}$. Region III, thus, includes all observations for rain volumes > 2.6 cm. The results of similar inspections of the relationships for Cd, Pb, and $\text{SO}_4^{=}$ are summarized in Table 42. These relationships reveal an interesting trend in the rain volume ranges in which the below-cloud scavenging process apparently predominates. For Pb and $\text{SO}_4^{=}$ the washout process appears to be essentially complete for rain volumes > 1.7 cm while for Cd and Mn the process influences the rain concentrations up to volumes of ~ 3 cm. This is in good agreement with the particle size distribution data

Table 42. Estimated concentration and rain-volume class limits related to the three regions of precipitation scavenging defined in the generalized concentration - rain volume relationship for incident precipitation in Figure 46

Element	Parameter	Concentration and rain volume range in:		
		Region I ^a	Region II ^b	Region III ^c
Cd	concentration	>0.4 µg/l	<0.4	NL ^d
	volume	<2.9 cm	<2.9	>2.9
Mn	concentration	>2.8 µg/l	<2.8	NL
	volume	<2.6 cm	<2.6	>2.6
Pb	concentration	>6.5 µg/l	<6.5	NL
	volume	<1.6 cm	<1.6	>1.6
SO ₄ ⁼	concentration	>4.0 mg/l	<4.0	NL
	volume	<1.7 cm	<1.7	>1.7

^aConcentrations in this region are believed to be primarily influenced by below-cloud scavenging and drop evaporation, secondarily by in-cloud scavenging and dilution.

^bConcentrations in this region are influenced by below- and in-cloud scavenging as well as dilution and evaporation.

^cConcentrations in this region are influenced primarily by in-cloud scavenging and dilution.

^dNo limit, but concentrations seldom exceed the upper limits of Region II.

summarized in Table 16 which indicated Pb and $\text{SO}_4^{=}$ to have a considerably smaller giant particle fraction in the atmosphere compared to Mn and Cd. These larger particles are preferentially scavenged during small rain events or early stages of continuous precipitation and would be expected to be more rapidly depleted in the below-cloud layer during active precipitation, leading to a more rapid removal of the available Pb and $\text{SO}_4^{=}$ in the below-cloud layer (Dahl and Corrin, 1977). The plot of hydrogen ion activity does yield itself to this visual analysis even though a nonlinear regression line was not determined. The scatter in the data is too large to permit a detailed analysis, however. One might infer that the behavior of H^+ should closely follow that of $\text{SO}_4^{=}$. Recall that H^+ (free acidity) and not total acidity is measured here. The reason for the inability to clearly define the H^+ relationship may be related to the large number of atmospheric reactions which can either increase or decrease free H^+ through neutralization, hydrolysis, or gas dissolution reactions.

Once each element - volume relationship was classified as above, the relative contribution of the in- or below-cloud scavenging processes were estimated as follows: (1) the weighted mean "rainout" concentration was calculated using all observations falling in Region III from the relationship

$$R = \frac{\sum_{i=1}^n (C \cdot V)}{\sum_{i=1}^n (V)},$$

where C = elemental concentration, V = rainfall volume, n = number of observations within Region III, (2) the weighted mean value "R" was subtracted from each observation occurring in Regions I and II to yield individual precipitation washout concentrations with the influence of the rainout concentration removed, (3) the total precipitation input of any element resulting primarily from below-cloud scavenging was calculated as the sum of the products of the washout concentrations and associated precipitation volumes in regions I and II (washout is assumed to be a relatively minor fraction of the input in Region III), and (4) the total precipitation input resulting primarily from in-cloud scavenging of material was calculated as the sum of the products of the rainout concentrations and their respective precipitation volumes (for Regions I and II the rainout concentrations were taken as the weighted mean rainout concentration calculated from Region III, while in Region III each individual observation was considered as a rainout concentration). One complication of using weighted mean rainout concentrations in the calculations is the inability to easily assign confidence intervals to the resulting concentrations (Turner, 1976). Thus weighted mean concentrations were compared to the arithmetic mean concentrations for each element using the Region III data. Because the observations in the region are hypothesized to reach an asymptote along the volume axis one would not expect a significant difference between the weighted means and arithmetic means since the utility of a weighted mean is to account for a dependence between concentration and volume (further discussed in Chapter VII). This expectation is confirmed by the following comparison of means (arithmetic $\bar{X} \pm S.E.$, weighted \bar{X}):

Cd (0.16 ± 0.04 , 0.14), Mn (1.37 ± 0.23 , 1.49), Pb (4.99 ± 0.50 , 4.67), $\text{SO}_4^=$ (2.7 ± 1.4 , 2.7). The lack of a substantial difference between the two means confirmed the absence of a strong concentration-volume relationship for the observations in Region III.

Table 43 summarizes the results of this approach to the incident precipitation data. Shown are the estimated mean concentrations of 56 storm events attributed to both in- and below-cloud scavenging, total precipitation inputs on an areal basis, and the fraction of the total input attributed to in cloud scavenging. For Cd and Mn the estimated mean washout concentrations exceed the rainout concentrations by factors of ~ 3 confirming the importance of the giant particle class in below cloud scavenging. For the small particle elements $\text{SO}_4^=$ and Pb, the washout concentrations exceed the rainout levels by only $\sim 20\%$. The relatively high concentrations caused by in-cloud scavenging processes for these two elements are understandable in light of the moderately long in-cloud contact time ($10^3 - 10^4$ seconds) compared to the contact time of a falling raindrop ($< 10^2$ seconds) (Junge, 1963). However, when the influence of each scavenging process is considered individually in relation to the volume of rain with which it is associated, the actual contribution of the below cloud process becomes quite clear. Although the concentration of material removed primarily from the below-cloud layer is relatively high, these concentrations are associated with smaller amounts of rainfall resulting in relatively lower amounts of material input to the system from this process. For storms of longer duration and larger volumes the initial below-cloud material is diluted with precipitation of lower

Table 43. Estimated contributions of in-cloud (rainout) and below-cloud (washout) scavenging processes to the wet deposition of trace elements and sulfate to WBW

Element	Washout concentration ^a	Rainout concentration ^b	Total washout input	Total rainout input	Total input	Rainout/washout ratio	Rainout fraction of total input (%)
	(μg/l metals, mg/l sulfate) (g/ha metals, kg/ha sulfate)						
Cd	0.52 ± 0.11	0.16 ± 0.02	1.91	2.63	4.54	1.4	58
Mn	3.90 ± 1.08	1.60 ± 0.21	8.58	20.7	29.3	2.4	71
Pb	6.72 ± 1.55	4.76 ± 0.34	10.7	82.4	93.1	7.7	89
SO ₄ ⁻	2.9 ± 0.8	2.7 ± 0.1	3.36	46.9	50.3	14	93

^a($\bar{X} \pm SE$), not weighted by volume since each input value was calculated from individual concentration-volume pairs.

^b($\bar{X} \pm SE$), values calculated by the model, not a weighted mean.

concentration. This larger volume of diluent derives its composition primarily from in cloud processes resulting in relatively higher quantities of material input to the system from this process. Thus for the large particle dominated elements, Cd and Mn, the total input of below-cloud scavenged material approaches that resulting from in-cloud processes. For Cd the two processes are of approximately equal importance with the input attributed to in-cloud scavenging ~ 1.4 times more important. Similarly for Mn this process is 2.4 times more effective in removing atmospheric material by precipitation. However for the small particle elements Pb and S (as SO_4^-) the in-cloud process clearly dominates being nearly an order of magnitude more important in each case (~ 8 times more effective for Pb, 14 times for SO_4^-).

The contribution attributable to in-cloud processes on a relative scale ranged from a low of $\sim 60\%$ for the input of Cd to $\sim 70\%$ for Mn and $\sim 90\%$ for both Pb and SO_4^- . The ability of the above approach to predict the relatively larger contribution of below-cloud processes to the input of Cd and Mn (which predominate in the giant particle range in the atmosphere above WBW), and to predict the smaller contribution of these processes to the input of SO_4^- and Pb, (which predominate in the submicrometer size range) is very encouraging. It is clear that, although it would be difficult to assess the actual contribution of in-cloud and below-cloud processes to the element concentrations in individual events without sequential sampling of each event, this approach does provide a reasonable approximation of the relative importance of the two major scavenging mechanisms.

The greater importance of the in-cloud scavenging process for the wetfall removal of Pb and $\text{SO}_4^{=}$ in WBW implies that the concentrations of both elements are fairly uniform in the mixed layer. This hypothesis is derived from experimental and theoretical evidence that the raindrop collection efficiency or impaction scavenging below the cloud layer is very small for particles in the 0.05 - 0.5 μm range (e.g., see Slinn, 1977). For materials routinely released from near ground level sources some physical mechanism must exist to promote upward mixing into the cloud layer in order for in-cloud scavenging to dominate. Slinn (1977) recently presented an interesting argument that this upward mixing may occur prior to and during both convective and frontal storms, being caused by rain shaft induced upward mixing of industrial or urban plumes.

Concerning this vertical mixing of ground level source material, Gatz (1977) presented a summary of precipitation scavenging studies in the METROMEX program at St. Louis, including some interesting results of vertical profiles of Aitken nuclei within and downward of the city. The data indicated that these small particles were very rapidly mixed into the vertical. Further, the deposition rates were measured for Pb and Zn with distance from the city revealing patterns not generally consistent with impaction scavenging but suggesting that in-cloud processes must have been involved in the scavenging of the cities effluents. Recent studies of stable Pb deposition in New York indicated no apparent trend in wet deposition of Pb per month and rain volume per month (Krey and Toonkel, 1977). The authors hypothesized that some process other than in- or below-cloud scavenging above

accounted for deposition rates, concluding that in-cloud scavenging was the primary removal mechanism but that this process was rate limited by diffusion of the surface Pb aerosol to the cloud base. The authors also failed to find rain volume-deposition relationships for V and Cd, thus suggesting they behaved similarly to Pb. Recent discussions (P. Krey, personal communication) have led to the conclusion that the relative importance of in- or below-cloud scavenging for many materials is still unresolved.

A simple theoretical approach to quantifying the in-cloud and below-cloud scavenging of trace elements - A recent paper by Müller and Beilke (1975) considered the wet removal of heavy metals from the atmosphere using a straightforward theoretical approach developed by Junge (1963). Application of this theory to the WBW data provides a means of confirming the results of the empirical approach above. The authors used the relationship:

$$K = \frac{\epsilon \cdot C}{L} \quad (\text{Junge, 1963}),$$

where K = concentration of a component in cloud water ($\mu\text{g/ml}$),
 C = concentration in air ($\mu\text{g/m}^3$), L = liquid water content of cloud (g/M^3) = LWC, ϵ = rainout coefficient (coefficient for incorporation of condensation nuclei and coefficient of diffusional incorporation). This equation was applied to data collected for a clean continental area near St. Moritz, Switzerland and for a polluted area in Frankfurt, Germany. Measured parameters entered into the calculation include the mass ratios of the metals Mn and Pb to total atmospheric particulate

matter and the approximate particle size distribution of these metals in giant, large, and Aitken size ranges. To complete the required data the authors applied some simplifying assumptions including rainout coefficients of 0.9, cloud base height of 2000 M, LWC of stratus clouds of 0.1 g/M^3 and for cumulus clouds of 1 g/M^3 , literature values of estimated particle concentrations near ground in background and polluted areas and their distribution with altitude, constant rain and particle parameters during the course of an event, theoretical dependence of rain drop radius on precipitation intensity, and collision efficiencies for below cloud scavenging of 0.5 for giant particles, 0.05 for large, and 0.005 for Aitken particles. The equation is integrated over the three size ranges and over height intervals of 2000 M resulting in a relationship between precipitation intensity and the concentration of Pb or Mn in precipitation, attributable to either in- or below-cloud scavenging. Unlike the empirical approach above these calculations result in an estimate of the contribution of each scavenging process to the concentration in individual events.

The relationship developed by Müller and Beilke was modified for the WBW data to calculate input (not simply concentrations) and then applied to the storms sampled with known intensities over the two-year period. As an approximation of the ability of this relationship to predict precipitation concentrations the ratio of the predicted total concentration (predicted rainout plus predicted washout) to the measured total concentration was calculated. For Pb this ratio had a mean value of 1.4 (SE = 0.2), while for Mn it was 1.8 (SE = 0.5) for 51

events, overpredicting the rain concentrations in nearly every case. The equation also predicted relatively higher rainout to washout concentration ratios compared to the empirical approach (~ 2.5 times higher for each element than those estimated in Table 43), but not unreasonable given the number of simplifying assumptions involved. Most importantly, this approach predicted the greater relative importance of the in-cloud scavenging process in the wet removal of both Mn and Pb and also predicted that the in-cloud scavenging process was ~ 3 times more effective for Pb than Mn, a value in excellent agreement with that estimated earlier (Table 43). The application of this equation to the data collected by the authors resulted in the following: in Frankfurt, where the concentration of below-cloud particles was considerably elevated above the levels at the background area, the rainout process was ~ 2 times more effective than washout for Mn scavenging and ~ 5 times more effective for Pb (for rain intensities on the order of 1 to 2 mm/hr). Both of these rainout to washout ratios are very similar to those estimated for WBW by the empirical approach (Table 43). The data from the background area indicated that, with a lower below cloud particle concentration, the in cloud removal process clearly dominated, by a factor of ~ 7 for Mn and ~ 20 for Pb.

Some limited work has been performed on wet scavenging under controlled conditions which supports this hypothesis for Pb. Dahl and Corrin (1977) measured wet removal of Pb aerosols from automotive exhaust, with the conclusion that the prime mechanism for precipitation scavenging of automotive Pb involved in-cloud processes. Further they

demonstrated that the particle size distribution of Pb was altered by the below-cloud scavenging of layer particles. With this information the authors calculated the expected deposition of Pb due to washout for the city of Denver. The calculated rain drop concentration due to below-cloud scavenging was 1.4 $\mu\text{g/l}$. Assuming the total Pb concentration in precipitation in Denver to be similar to that in WBW (Table 16) leads to the approximation that $\sim 20\%$ of the Pb in rain results from below-cloud scavenging processes, a value in reasonable agreement with that estimated for WBW.

There appear to be several current theories concerning the removal of $\text{SO}_4^=$ by precipitation, none of which are universally accepted. The wet scavenging of $\text{SO}_4^=$ is complicated by the major gas phase component of atmospheric sulfur, SO_2 . Dana et al. (1975) measured scavenging rates of S near a power plant and found that washout of sulfate could be 1 to 5 times greater than that of SO_2 , on a molar basis. This is due, in part, to the decreased solubility of SO_2 in acid precipitation and the apparent fast initial rate of SO_2 $\text{SO}_4^=$ oxidation in rainy conditions. Kramer and Snyder (1977), on the other hand, studied deposition of S near Sudbury and concluded that the appearance of S in precipitation occurred with little or no oxidation of SO_2 in the atmosphere. The conclusion for the WBW data that $\text{SO}_4^=$ in precipitation results primarily from in cloud processes is supported by recent work of Easter and Hobbs (1977) and Barrie et al. (1977). As previously stated dominance of in cloud scavenging implies efficient upward mixing of ground level source material. This process for SO_2 is well known. Once in the cloud,

however, the removal of SO_2 may be rate limited by diffusion or chemical kinetics. If the SO_2 remains dissolved as SO_2 in cloud water there is a good chance that it will be lost from the rain drop during descent and prior to ground level deposition (Dana et al., 1975). On the other hand, if the SO_2 is rapidly oxidized to SO_4^- , in-cloud removal is more complete. Easter and Hobbs (1977) calculated that the in-cloud production of $(\text{NH}_4)_2\text{SO}_4$ particles was a very significant source of this material on a global basis, this material being efficiently scavenged by rainout mechanisms. Barrie et al. (1977) and Beilke et al. (1977) concluded that the rate determining step for the transformation of dissolved $\text{SO}_2 \rightarrow \text{SO}_4^-$ in cloud water was the oxidation of the initially and rapidly formed SO_3^- ion by molecular oxygen but that the oxydation was promoted by O_3 , NH_3 , and heavy metal ions. In studies of the influence of heavy metals the authors reported that Mn^{+2} in cloud water could account for significant SO_2 removal rates, on the order of 1 to 5% per hour. If this reaction is critical in the removal of S by precipitation a relationship between precipitation concentrations of Mn and SO_4^- might be expected. This is the case for the WBW data as will be discussed in the following chapter.

Summary

The distribution of Cd, Mn, Pb, Zn, and SO_4^- in throughfall do not depart significantly from log normality. The distributions of H^+ concentrations in rain and throughfall do not depart significantly from normality. Nonparametric statistical analysis of the multisite

precipitation/throughfall data indicated that only one element, Mn, exhibited significant inter-site differences in concentration in both incident precipitation and throughfall. The significant internal foliage source of Mn undoubtedly accounted for the difference between throughfall sites, with concentrations at one site beneath a single mature chestnut oak consistently higher than at all other sites. Leaching of Mn apparently also contributed to the difference between incident precipitation sites. The site at ground level, in a clearing surrounded by trees, yielded consistently higher Mn concentrations than the site atop a 46-m tower, above the canopy. Rain intercepted by the canopy margin and subsequently blown into the nearby ground level collector would be expected to show an enrichment in the easily leachable element Mn. Analysis of variance and covariance procedures were applied to the data to reveal seasonal effects on chemistry of rain above and below the canopy. For elements exhibiting significant seasonal effects, the maximum concentrations of Pb, $\text{SO}_4^{=}$, and H^+ in rain occurred during the summer while the peak for Zn occurred in the fall. In throughfall the highest concentrations of Pb and $\text{SO}_4^{=}$ occurred during summer, Zn during fall, and H^+ during winter when foliar interception of rain is at a minimum. Although Cd and Mn did not exhibit significant seasonal effects, concentrations in rain also tended to increase in summer. The summer maxima may be in response to synoptic meteorologic conditions which result in elevated aerosol concentrations due to air stagnation, and in generally lower rain volumes per event and hence less dilution of scavenged material.

The interception of incoming rain by the forest canopy resulted in a net increase in the concentrations of Cd, Mn, Pb, Zn, and $\text{SO}_4^{=}$, but a net decrease in the concentration of H^+ . The elemental enrichments on an annual basis were as follows: Mn (factor of 160), Cd (4), Zn and $\text{SO}_4^{=}$ (3), Pb (2.7), H^+ (0.9). Simple linear regression models were applicable in the prediction of throughfall concentrations of Mn, Pb, Zn, $\text{SO}_4^{=}$, and H^+ during the growing season based on concentrations in incoming rain. The variances of concentrations in incoming rain accounted for the following fractions of the variances in throughfall: $\text{SO}_4^{=}$ and Zn ($\sim 80\%$), Pb and Mn ($\sim 55\%$), H^+ (27%). The uptake of H^+ and concomitant loss of several elements by the canopy suggests a cation exchange process, with the net exchange seen to increase with increasing free acidity of the incoming rain and with increasing residence time of the rain on the leaf surface. On an equivalent basis, the hydrogen exchange can easily account for the trace cation leaching from the canopy, but for $< 10\%$ of the estimated total cation leaching from the canopy during the growing season, indicating the importance of other processes as well. In throughfall collected beneath the chestnut oak canopy during the growing season, weak acids were responsible for approximately twice as much of the total acidity ($57 \pm 4\%$ as weak acids) than was the case for incoming rain ($33 \pm 3\%$; mean \pm standard error), although the contribution of weak acids to free acidity (H^+) was generally negligible. The leaching of weak acids from the canopy may be related to the uptake of H^+ and consequent cation displacement suggesting some degree of physiological alteration of the leaf surface.

Dilution phenomena in incident precipitation were indicated by significant negative correlation coefficients between element concentrations and rainfall amount, storm duration, and intensity. The expected positive correlations between rain concentrations and time since previous rainfall were not apparent, suggesting the local atmospheric reequilibration with the regional air mass to be relatively rapid. A simple model was applied to the empirical relationship between rain concentration and rainfall volume in attempt to estimate the relative importance of in-cloud vs below-cloud scavenging to the wet deposition of each element. The calculations indicated that, on an annual basis, ~ 90% of the wet deposition of the primarily small-particle atmospheric constituents Pb and $\text{SO}_4^{=}$ was attributable to scavenging by in-cloud processes, while for the large particle-associated elements, Cd and Mn, removal by below-cloud scavenging was somewhat more important, accounting for 30 to 40% of the deposition. Theoretical calculations of scavenging efficiencies confirmed the greater importance of the in-cloud processes in Pb deposition relative to Mn deposition.

CHAPTER VI

GEOCHEMICAL AND PHYSICAL RELATIONSHIPS BETWEEN SUSPENDED,
DEPOSITED, AND PRECIPITATION-SCAVENGED MATERIAL

Particle Morphology and Geometric Size Distribution

The Occurrence of Fly Ash in Suspended and Deposited Particles

Although the data discussed in the preceding chapters has not indicated a clear relationship between deposited material collected in the watershed and emissions from the three local coal fired power plants, it has become evident throughout this research that fossil fuel combustion residues are present in nearly every sample collected in WBW. These combustion residuals take the form of spherical particles, more commonly called fly ash, and have been previously identified as typical of atmospheric emissions from coal combustion processes (Gordon, 1975; Bolton, 1973; 1974; Lindberg et al., 1975; Fisher et al., 1976). During the course of this research 120 leaf samples, 20 aerosol samples, 13 filtered precipitation samples, and 12 deposition plate samples were examined by scanning electron microscopy (SEM). Fly ash was present in every sample analyzed, generally uniformly distributed in the aerosol and precipitation samples but very heterogeniously distributed (i.e., clumped) on the leaf or deposition plate surfaces. For comparison, several representative SEM photographs are presented in Figures 49 to 52. Figure 49 shows three Anderson

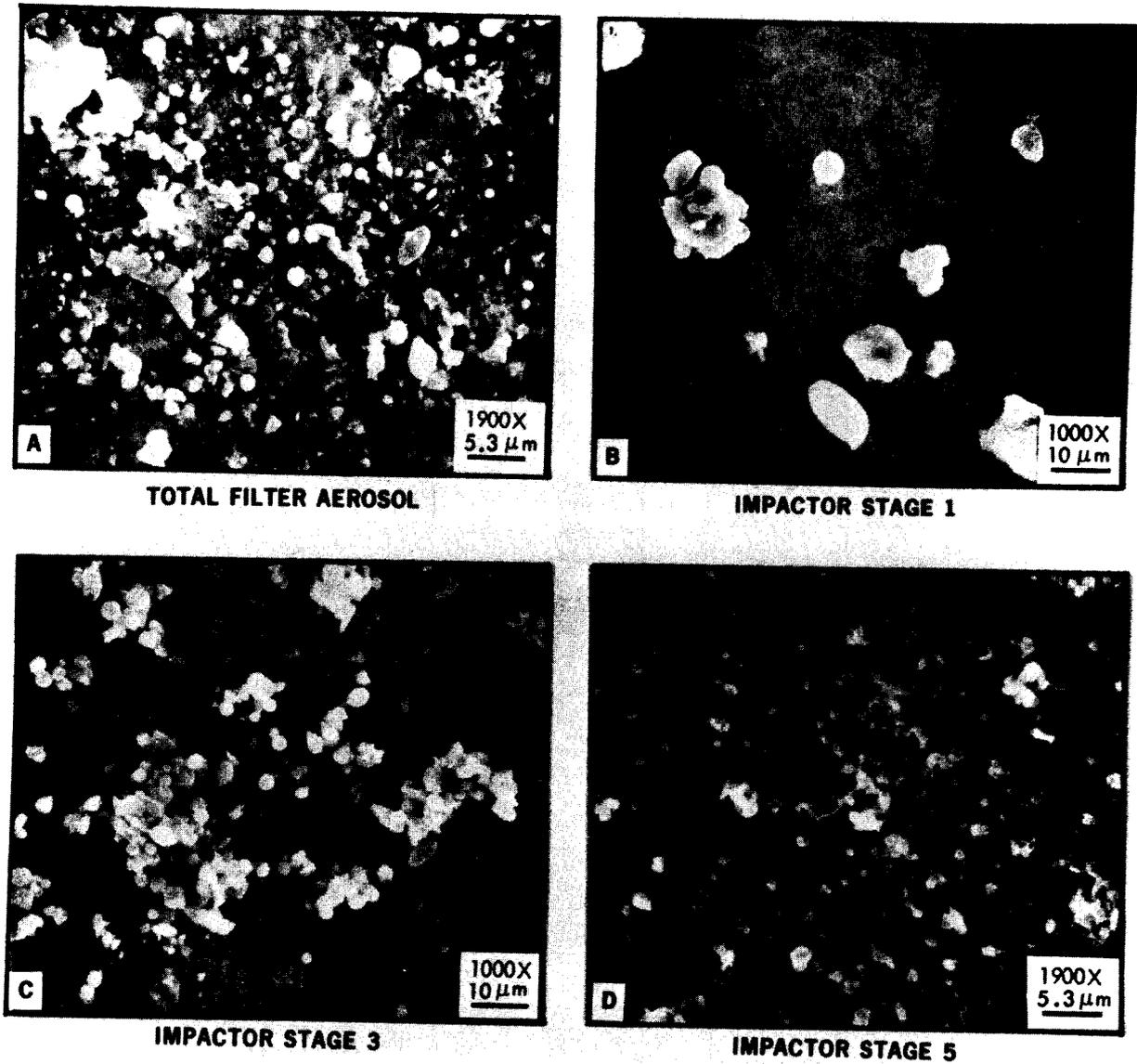


Fig. 49. Scanning electron photomicrographs of particles captured by a total aerosol filter (A) and several impactor stages (B, C, D). Theoretical aerodynamic diameters for an impaction efficiency of 50% were as follows: Stage 1 = 7 μm , Stage 3 = 3.3 μm , and Stage 5 = 1.1 μm .

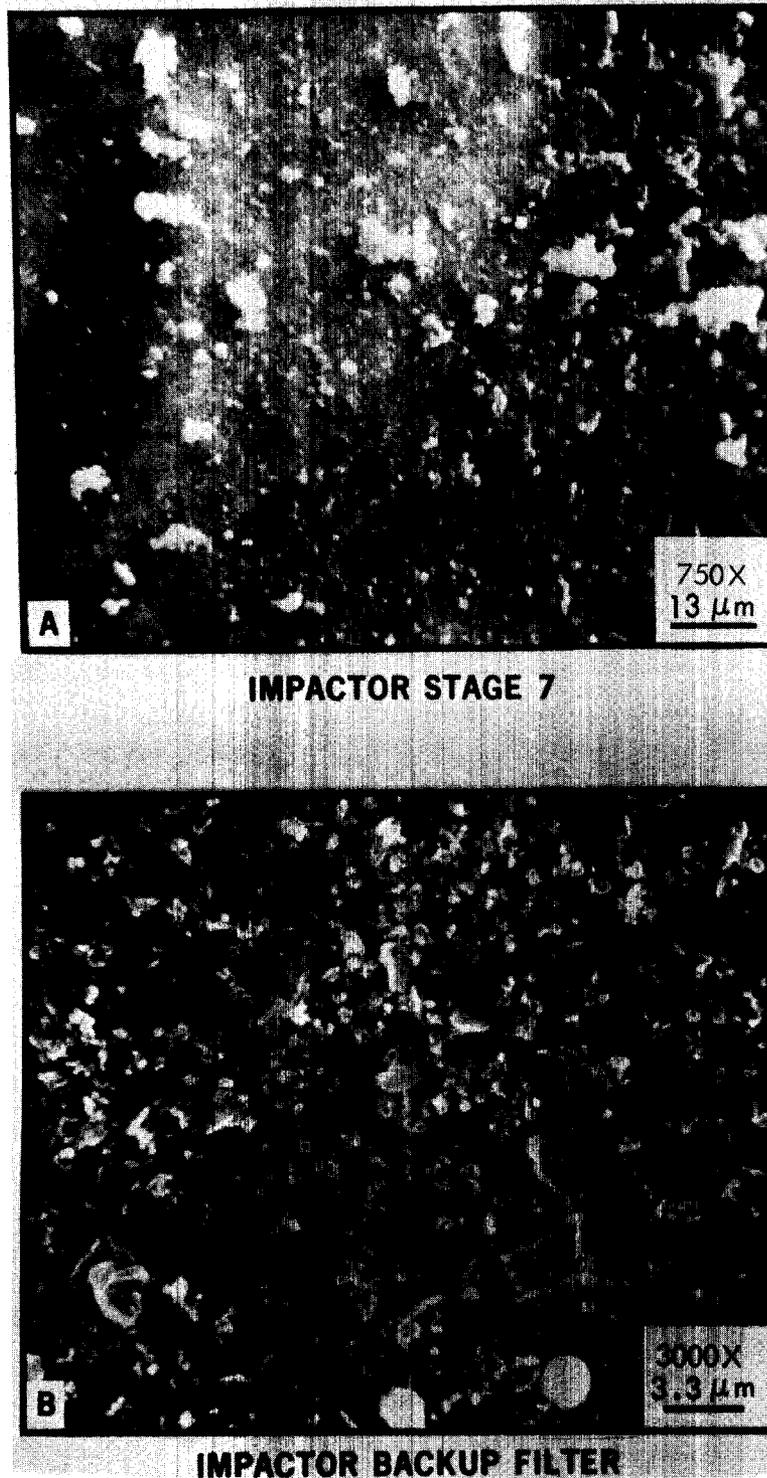
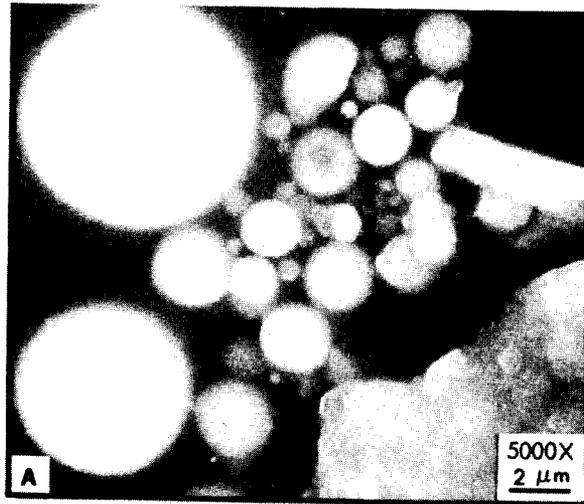
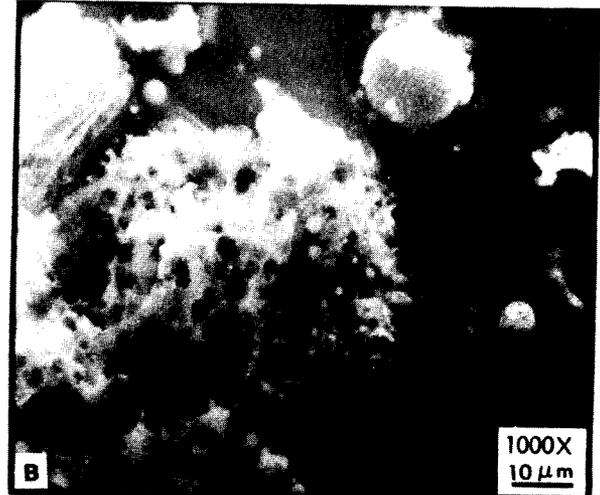


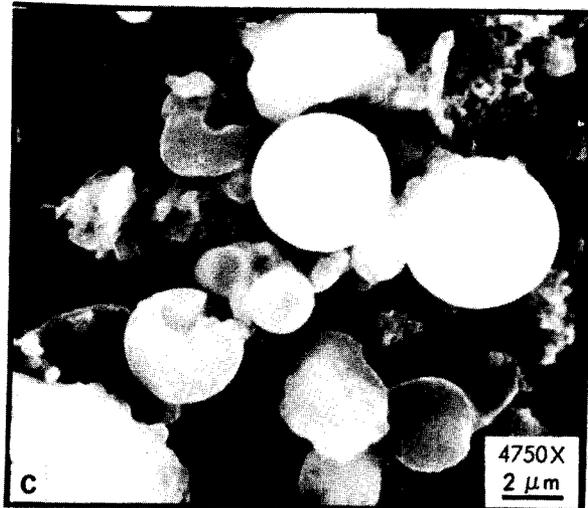
Fig. 50. Scanning electron photomicrographs of particles captured by one impactor stage (A) and the backup filter (B). Theoretical aerodynamic diameters were as follows: Stage 7 = $0.43 \mu\text{m}$, Backup filter = $< 0.43 \mu\text{m}$ (ideally).



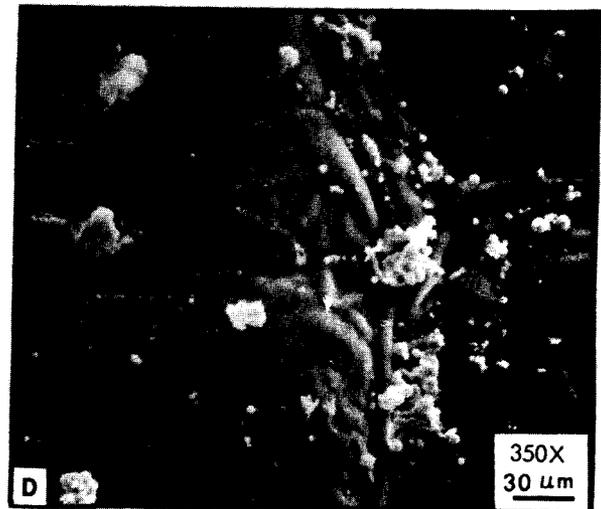
INERT HORIZONTAL SURFACE 1



INERT HORIZONTAL SURFACE 2



TOTAL FILTER AEROSOL



CHESTNUT OAK LEAF 1

Fig. 51. Scanning electron photomicrographs of particles retained on flat, inert surfaces (A, B), and on a chestnut oak leaf (D), and captured by a total aerosol filter (C).

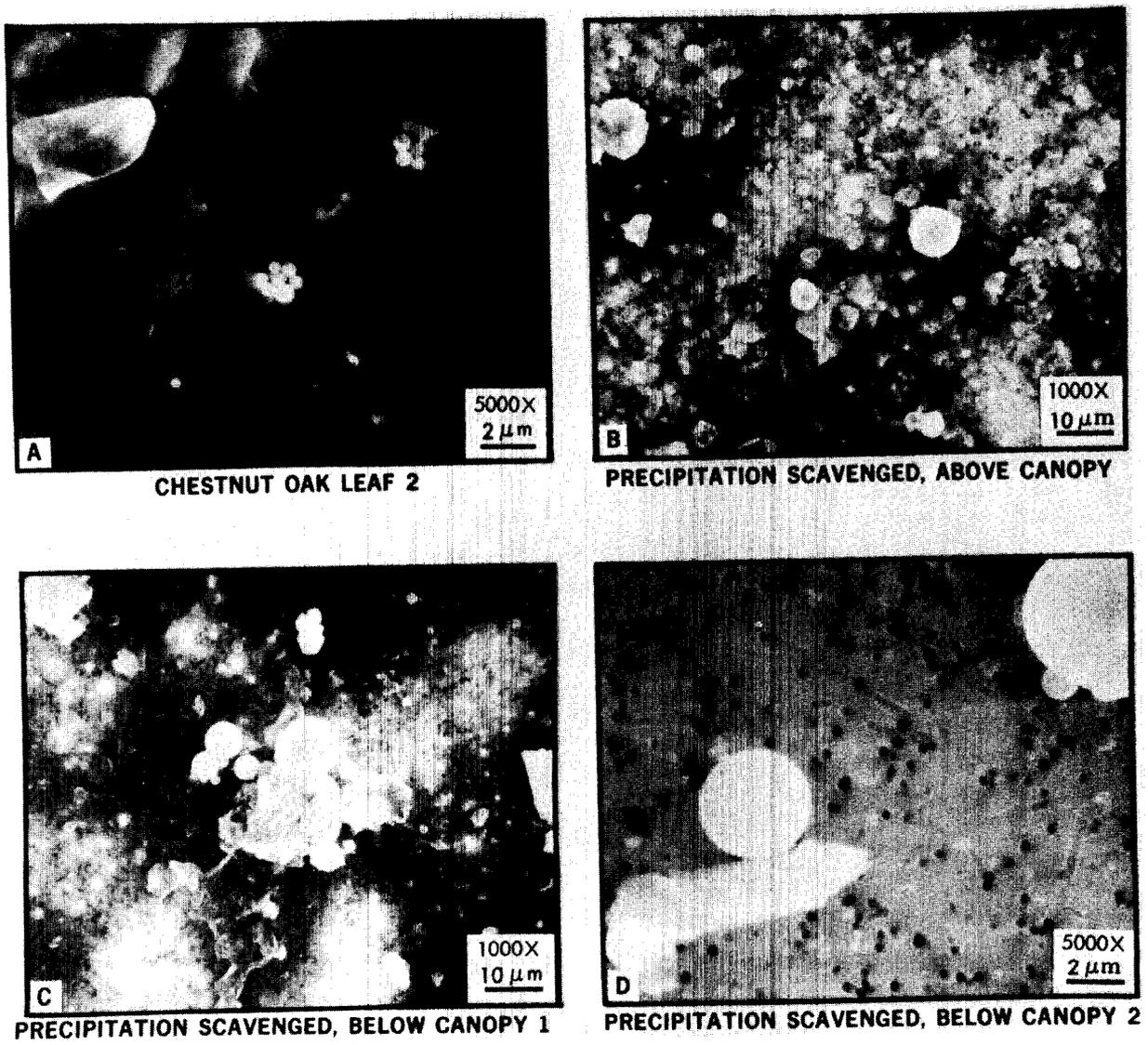


Fig. 52. Scanning electron photomicrographs of particles retained on a chestnut oak leaf (A), and scavenged by precipitation collected above the canopy (B), below the fully developed canopy (C), and below the leafless canopy (D).

impactor stages (1, 3, and 5), and the total aerosol filter for samples collected 8/29-9/2/77. Figure 50 shows one impactor stage (7) and the backup filter for the same set of samples. The impactor stages illustrated represent the lower particle size cutoff of each grouped size class as described in Chapter III (e.g., stage 1 was combined with the next larger stage 0 prior to analysis to comprise particle size class 1, thus the stage with the smaller particle diameter cutoff is illustrated). Figures 51 and 52 indicate several environments of particle deposition including inert surfaces, chestnut oak leaves, incident precipitation, and throughfall, as well as an additional total air filter.

For ease of description, particles were characterized as belonging to one of two general groups, easily recognizable fly ash or nondescript "particles" (i.e., that not recognizable as fly ash). This latter group of particles included primarily dispersed soil material [recognizable by the typical platelet structure attributable to various clay minerals (Rosinski and Langer, 1974), such as the leftmost particle in stage 1, Figure 49-B, and the central particle in the photograph of below canopy rain scavenged material in Figure 52-C), and scoriaceous material with a spongy appearance suggestive of cinder ash and often integrally associated with fly ash (such as the particle near the upper left hand corner of the total aerosol filter, Figure 49-A, and the large particle in the middle and left of the photograph of the horizontal inert surface in Figure 51-A). These particles were generally relatively large ($> 5 \mu\text{m}$), occurring in the upper impactor stages. Semi-quantitative elemental analysis by

SEM-induced X-ray fluorescence (XRF) of individual "particles" indicated high concentrations of Si, Al, and K in the soil material with lesser amounts of Fe and Ti; while the scoreaceous material was characterized by high concentrations of Si, Al, S, Ca, Fe, and lesser amounts of Zn and Cu and generally presented an XRF spectrum very similar to individual fly ash particles. Other large particles in the shapes of hollow tubules were investigated by electron spectroscopy for chemical analysis (ESCA) and found to contain N in the form of amides and amines, indicative of a biological origin, possibly fungi (L. D. Hulett, personal communication). On several occasions, generally during the spring, various types of pollen grains were readily identifiable in samples of both suspended and deposited material.

Nondescript particles in the lower impactor stages included some material with the platelet structure, and fragments of the scoreaceous material, but more often included an amorphous material with a puffy appearance such as that seen throughout the field of the photo of stage 7, Figure 50-B. The fact that these particles are ~ 25 times larger than the theoretical size predicted for this impactor stage ($\sim 10 \mu\text{m}$, compared to a predicted aerodynamic diameter of $\sim 0.4 \mu\text{m}$) suggests a very low density, or formation in situ during or after collection by the impactor. X-ray fluorescence of this material collected on stage 7 and also on the backup filter indicated S to be the overwhelmingly predominant element followed by Ca, Si, Fe, Pb, and Zn. Analysis by ESCA indicated S to be present in the +6 oxidation state. It is likely that this material represents $(\text{NH}_4)_2\text{SO}_4$ or

(NH₄) HSO₄, some of which may have been formed in situ (Dingle and Joshi, 1974).

The most interesting aspect of the occurrence of fly ash, besides its ubiquity, was the association of submicrometer size particles with much larger fly ash particles and with the scoriaceous material. This phenomenon is seen in stage 1, Figure 49-B and horizontal inert surface (Figure 51-B), chestnut oak leaf (Figure 51-D), and the total air filter material (Figure 51-C). A similar phenomenon is the occurrence of aggregates of similarly sized fly ash particles such as seen in the total aerosol filter, Figure 49-A, and horizontal inert surface (Figure 51-A), and the chestnut oak leaves in Figures 51-D and 52-A. While it is difficult to state positively that such aggregates form prior to capture by deposition surfaces, their occurrence in samples of suspended particles is suggestive of this contention. This is particularly true for the fly ash particles on impactor stage 1 because of the predicted inability of the smaller fly ash particles to come into contact with the impactor surface, and hence the large fly ash particles, during sample collection. Fly ash agglomerates have been previously reported to occur in samples collected in precipitator hoppers (Fisher et al., 1976). Recall also from the discussion in Chapter III that aerosol samples collected in the plume of a major coal fired power plant by Whitby et al. (1976) were seen to exhibit a slight increase in geometric mean diameter during plume aging, attributed to coagulation with each other and with larger particles. This phenomenon was also seen for Cd in the plume samples collected during this research at a TVA power plant (Chapter III).

The association of submicrometer size material with both larger fly ash and larger nondescript particles (both of which are seen on the horizontal inert surface in Figure 51-A) has important implications regarding the mechanisms of deposition which influence the atmosphere to surface transfer of various elements to inert and biological receptors. Interestingly, one conclusion reached in Chapter IV was that sedimentation was an important process of particle deposition to various surfaces. Yet most of the atmospheric burden of Cd, Pb, Zn, and SO_4^- was associated with particles of aerodynamic diameters in the submicron to micron size range. For example, XRF analysis of two particles on the total air filter sample in Figure 51-C yielded interesting results. One large ($\sim 5.5 \mu\text{m}$ diameter) and one small ($\sim 0.6 \mu\text{m}$) fly ash particle were analyzed for S and Al. The S/Al ratio on the surface of the large particle was ~ 0.1 , while the ratio for the small particle (which was associated with a much larger fly ash particle of $\sim 4 \mu\text{m}$ in diameter) was ~ 40 times higher. Aggregation of small particles with other small particles or with large particles could result in parent particles in a size range for which the deposition is primarily influenced by sedimentation. Upon sedimentation to a surface, these aggregates would be expected to retain their configuration. However, when impacted onto the collection surface in a cascade impactor, these aggregates may fragment, with the aerodynamically smaller particles subject to resuspension and impaction on lower impactor stages, as previously reported for soil particles by Rosinski and Langer (1974).

This phenomenon of particle aggregation also has important implications related to possible effects at the receptor surface. As discussed in Chapter III these smallest particles generally contain the highest concentrations of strong acids and toxic trace elements. Such material may be concentrated on small areas of a leaf surface during sedimentation of aggregates, as well as individual particles which are often concentrated by the increased retention of various surface roughness features of the leaf (as indicated by the buildup of particles on the chestnut oak leaf in Figure 51-D). When these deposits come into contact with small quantities of surface moisture, resulting concentrations of soluble material are highly localized on the leaf surface increasing the potential for adverse effects.

As briefly discussed in Chapter IV particle size analyses were performed for several samples of deposited and suspended material by optical means. Particle sizes were classified by hand counting of several photomicrographs of known magnification (50-5000 X, resolution $\sim 0.1 \mu\text{m}$) or by hand counting particles sized using an ocular micrometer (resolution $\sim 1 \mu\text{m}$) within several randomly selected grids. The results of these analyses are summarized Table 44 for several of the samples described in Figures 49 to 52, with the addition of impactor stage 0. Shown are the range in diameters for individual particles in each sample for both recognizable fly ash and nondescript particles. In addition, several samples were further analyzed to determine average geometric diameter of the largest and smallest particles found ($\bar{X} \pm \sigma$), the number frequency of particles in 5 size classes, the calculated number median particle diameter, and the

Table 44. Optical analysis of the particle size distribution of material retained by deposition plates, leaves, cascade impactor surfaces, total air filters, and material scavenged by precipitation above and below the canopy

Type of particles	Parameter	Anderson impactor ^a					Backup filter	Total air filter ^a	Inert, flat surface ^b		Leaf surfaces ^c		Precipitation scavenged ^d		
		0	1	3	5	7			Horizontal-1	Horizontal-2	Set 1	Set 2	Above canopy 1	Below canopy 1	Below canopy 2
Fly ash	Maximum diameter (µm)	25	25	5	1.2		2	6	90	75	38	40	9	7	8
Fly ash	Minimum diameter (µm)	5	2	2	0.9		0.4	0.2	0.3	0.4	1	0.5	1	0.4	1
Fly ash	Large particle mean diameter (±σ) (µm)	22±2	22±1	- ^e	-	-	-	7±1	42±15	24±22	23±10	26±12	5±4	4±3	6±1
Fly ash	Small particle mean diameter (±σ) (µm)	6±1	5±3	-	-	-	-	0.4±0.2	1±0.5	0.4±0.2	1±0.5	1±0.5	1±0.5	5±0.2	1±0.5
Fly ash	Number frequency (%) in size ranges of:														
	<0.5 µm	-	-	-	-	-	-	63	1	15	1	7	0	11	0
	0.5 ≤ x < 1 µm	-	-	-	-	-	-	22	10	18	4	5	22	11	13
	1 ≤ x < 5 µm	-	-	-	-	-	-	4	20	49	47	35	67	67	60
	5 ≤ x < 10 µm	-	-	-	-	-	-	11	10	25	41	45	11	11	13
	≥ 10 µm	-	-	-	-	-	-	0	46	8	7	7	0	0	0
Fly ash	Number median particle diameter (µm)	-	-	-	-	-	-	0.5	5-10	1-5	1-5	1-5	1-5	1-5	1-5
Fly ash	Mean particle diameter (±σ) (µm)	-	-	-	-	-	-	2±3	14±12	5±5	5±5	7±10	3±4	3±2	4±3
Non-descript	Maximum diameter (µm)	80	80	6	4		2	15	100	100	30	80	12	32	10
Non-descript	Minimum diameter (µm)	5	3	2	0.8		0.4	0.2	2	1	1	1	0.3	1.1	1
Non-descript	Large particle mean diameter (±σ) (µm)	45±22	47±32	-	-	-	-	11±6	55±19	63±31	27±5	58±21	8±3	18±9	9±2
Non-descript	Small particle mean diameter (±σ) (µm)	6±1	4±2	-	-	-	-	0.4±0.2	3±1	1±1	1±0.5	3±2	0.4±0.1	1.3±0.3	1±0.5
Non-descript	Number frequency (%) in size ranges of:														
	<0.5 µm	-	-	-	-	-	-	53	0	0	0	0	11	0	0
	0.5 ≤ x < 1 µm	-	-	-	-	-	-	13	0	6	0	0	11	0	29
	1 ≤ x < 5 µm	-	-	-	-	-	-	28	2	16	37	40	37	33	21
	5 ≤ x < 10 µm	-	-	-	-	-	-	3	2	35	37	25	37	24	50
	> 10 µm	-	-	-	-	-	-	3	96	48	26	35	4	43	0
Non-descript	Number median particle diameter (µm)	-	-	-	-	-	-	0.5	10	5-10	5-10	5-10	1-5	5-10	1-5
Non-descript	Mean particle diameter (±σ) (µm)	-	-	-	-	-	-	2±3	24±22	22±30	12±10	23±20	4±5	10±12	6±5

^aTheoretical aerodynamic diameters for an impaction efficiency of 50% were as follows: stage 0 = 11 µm, 1 = 7 µm, 3 = 3.3 µm, 5 = 1.1 µm, 7 = 0.43 µm. Impactor and total air filter samples collected 8/29 - 9/2/77.

^bHorizontal-1 collected in the upper canopy of a chestnut oak from 8/29 - 9/2/77. Horizontal-2 collected at ground level 2/14 - 2/24/75.

^cChestnut oak leaves collected in the upper canopy on 10/2/75 (set 1) and on 9/2/77 (set 2).

^dFiltered rain samples collected above the canopy for a storm occurring 6/6 - 6/8/78 (above canopy 1) and filtered throughfall samples collected below the canopy for storms occurring during the full canopy development period, 6/6 - 6/8/78 (below canopy 1), and during the "no leaves" or dormant period, 2/11 - 2/14/77 (below canopy 2).

^e--- = not determined.

calculated overall average particle size ($\bar{X} \pm \sigma$). Generally four different photographs of each sample were analyzed, containing from 10 to 200 particles of any one type.

The inefficiency with which the impactor and total air filter collected large ($> 10 \mu\text{m}$) particles was discussed in Chapter III by a comparison of the mass-determined particle size distribution (calculated from the weights of the impactor surfaces) with the geometric size distribution of the material retained by the deposition plates. This same difference in the sizes of suspended and deposited particles is apparent from the optically determined geometric size distributions shown in Table 44. As discussed above this may relate to some extent to the fragmentation of aggregated particles upon collection by the impactor surface. The largest fly ash particles collected by the impactor and total filter are considerably smaller than those collected by the inert surfaces but more comparable to those collected on leaf surfaces. The total air filter was apparently less efficient in collecting large particles, since the material collected exhibited a large particle mean diameter $\sim 1/3$ that collected by the upper stages of the impactor. These same differences were generally also reflected by the nondescript particles which occurred in even larger diameters than the fly ash. Comparing the data with the predicted aerodynamic diameters of each stage, it is apparent that the true geometric diameters of particles collected on each stage are not always reflective of the theoretical aerodynamic diameters, as has been reported elsewhere (Dingle and Joshi, 1974). This is especially true for the nondescript particles which are heterogeneous in both shape and

density, or which, in some cases, may arise as artefacts of the sampling system as discussed above. However, it is encouraging that the more uniformly shaped fly ash is relatively efficiently separated by size in the impactor. Although there is evidence of particle bounce and reentrainment on each stage, the ranges in geometric size of fly ash collected on stages 3, 5, and 7 are quite small and centered about the theoretical aerodynamic diameter predicted for a 50% collection efficiency.

The size distribution of particles retained by the inert surfaces was discussed in some detail in Chapter IV, although the data was not compared with that collected from leaf surfaces. Although there is considerable overlap in the size distributions, mean diameters, and ranges in diameter for particles collected on the leaves and on inert surfaces, the two samples collected at comparable times (horizontal inert surface (Figure 51-A) and chestnut oak leaf (Figure 52-A) indicate that the inert surface retained generally larger particles relative to the leaves, an observation consistent with theory (see the discussion in Chapter IV). However, since this sampling period also included some precipitation, the difference may be related to the efficiency of each surface to retain large particles during rain wash-off. Unfortunately replicate samples for SEM analysis were not collected during the experiments with no precipitation.

The size distribution of fly ash scavenged by precipitation is remarkably similar for all three samples with the presence of the forest canopy not indicating the expected result of increasing the size of fly ash particles scavenged, presumably from leaf surface wash off.

However, this effect was manifested by the size distributions of the nondescript particles. The particles filtered from the below canopy sample, (Figure 52-C) collected during full canopy development, were measurably larger than those filtered from a sample collected above the canopy during the same event, or the other below canopy sample (collected during the leafless dormant period). It would be difficult to compare these size distributions in any detail with those of suspended or dry deposited particles because of the incomparability in the sample collection periods.

Sources of Fly Ash Deposited in Walker Branch Watershed

The widespread occurrence of fly ash in nearly all samples collected in WBW over a 2-year period was initially considered as evidence that the 3 local coal-fired power plants had a significant influence on the atmospheric chemistry and deposition of elements in the watershed. However, analysis of the chemical and meteorological data in Chapters III and IV did not support this contention, but rather implied the importance of regional sources. This was particularly surprising given the large physical and aerodynamic size of some of the suspended material and much of the deposited material. However, recall from these discussions that a number of references appear in the literature which support the phenomenon of relatively long range transport of large particles. For example, Johnson's (1976) report of particles $\sim 50 \mu\text{m}$ diameter at heights 300 m above St. Louis provides evidence that urban-industrial areas may serve as potential large particle sources to more remote areas. In addition, the recent trend

in the electric generation industry to utilize tall stacks (~ 300 m) on new, and in some cases existing, power plants further increases this potential.

To assess the potential of regional sources to contribute to WBW, the N.O.A.A. air mass trajectory computer program described by Heffter and Taylor (1975) was used to determine air mass trajectories backward in time over a 4-day period taking WBW as the origin. The period 9/16-9/20/75 was chosen for two reasons; the upper level wind data necessary to run the program was readily available for 1975, and during this period preliminary experiments were being conducted at WBW to determine the utility of portable ground level (3 m) wind direction and velocity indicators (Thorntwaite Model 104 Wind System). Back trajectories were calculated for two durations in time, 15 and 24 hours, with the depth of the transport layer taken as 100 to 3000 m. The time intervals were chosen to represent the approximate tropospheric residence times of large particles. Residence times were calculated from the data in Junge (1963) assuming sedimentation as the primary removal mechanism, ignoring eddy diffusion, assuming a mean particle density of 2 g/cm^3 , and assuming the aerosol to be contained within a layer of 5000 m with a homogeneous distribution. Given these simplifying assumptions, residence times were calculated for three particle diameters to be as follows: $10 \text{ }\mu\text{m}$, $t_r = 50 \text{ hr}$; $15 \text{ }\mu\text{m}$, $t_r = 23 \text{ hr}$; $20 \text{ }\mu\text{m}$, $t_r = 14 \text{ hr}$. The air mass trajectories of interest (not all are shown to simplify interpretation) and ground level wind rose for the 4 day period are presented in Figure 53 along with the locations of several possible regional emission sources in the

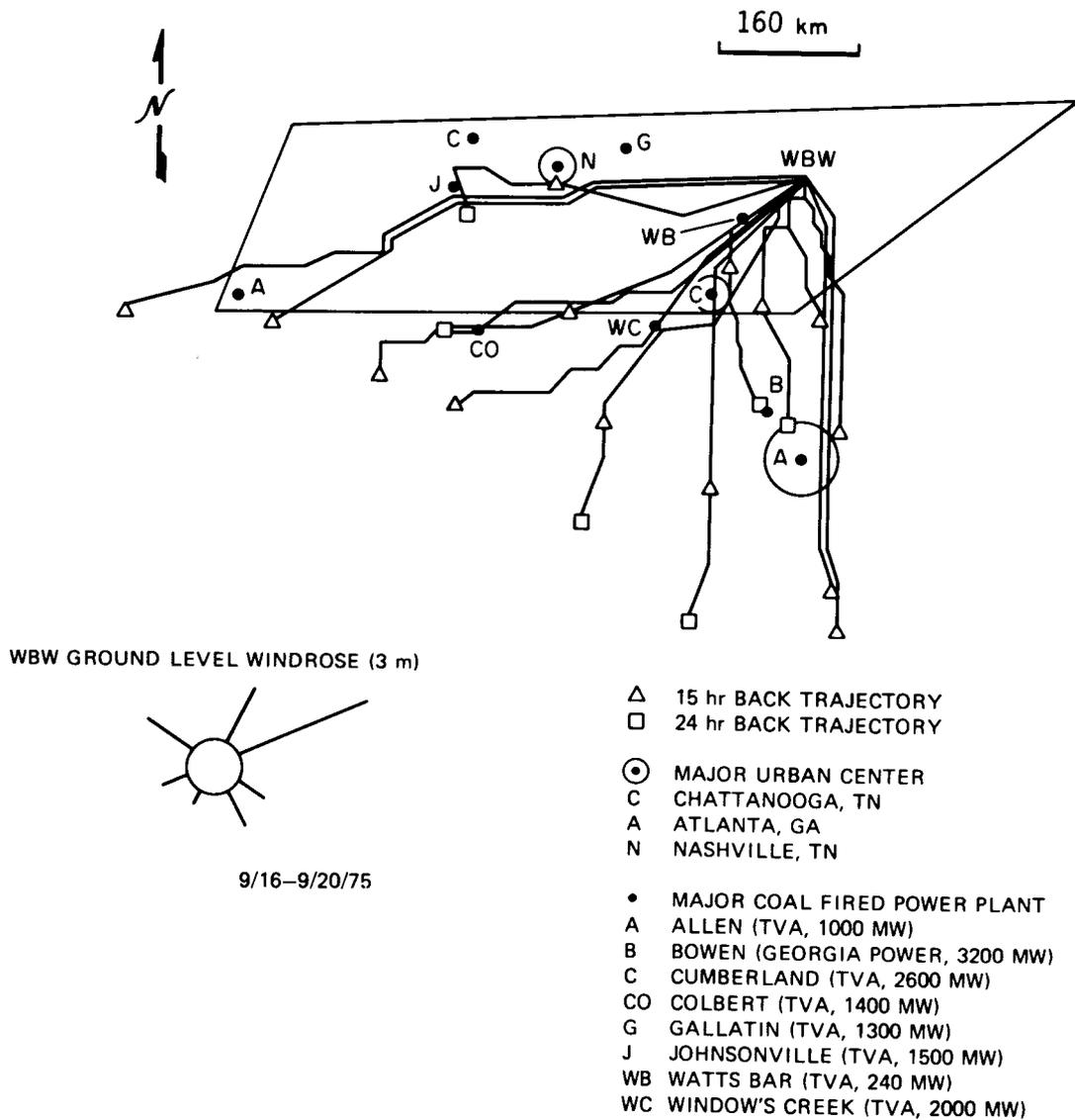


Fig. 53. Air mass back-trajectories from Walker Branch Watershed (WBW) for the period 9/16-9/20/75. Transport layer taken as 100-3000 m. Shown are major coal fired power plants and urban centers in the Tennessee Valley region.

Tennessee Valley area. Interestingly, the ground level wind rose indicated predominantly ENE winds, from the approximate direction of the local Bull Run Power Plant (BRSP, see Figure 1, Chapter II). However, the upper level trajectories were dominated by transport from the SW quadrant. These upper level transport directions were also reflected by the wind rose (not shown) determined from data collected at a local 110-m tower near the BRSP (this is the same tower from which the data was collected to calculate the windroses in Figures 4 and 5, Chapter III). As indicated in Figure 53 the region to the south and southwest of the watershed includes two major urban-industrial centers, Chattanooga and Atlanta, as well as 4 major coal-fired power plants (240-3200 MW). At some point during the 4-day period, air mass trajectories passed through or very near to each of these potential sources, as well as some to the west, with travel times less than or on the same order as the large particle tropospheric residence times. Thus, accepting the simplifying assumptions above, it is apparent that several regional sources can contribute to the large particle load and deposition in WBW.

Each of the above assumptions had the effect of increasing the atmospheric residence times (Junge, 1963). The occurrence of precipitation will rapidly deplete the large particle source. Also choice of a lower mixing height will decrease the residence times proportionally. The assumption of no precipitation is certainly valid over limited time periods. However, if the mixing layer is reduced by approximately an order of magnitude to the stack height of many major power plants and to the height at which Johnson (1976) found very large

particles over St. Louis (~ 300 m), the residence time is drastically reduced such that the largest particles which could still reach WBW are ~ 6 to $8 \mu\text{m}$ in diameter. As described in Table 44, particles in this size range and smaller constitute a significant fraction of the material captured on total air filters, deposited on leaf and inert surfaces, and scavenged by precipitation. It is probable that a significant fraction of the particles in the atmosphere and deposited on various surfaces in the watershed could have originated from several regional sources. The chemical and meteorological data indicated that local source effects were relatively poorly defined, leading to the conclusion that the regional influence was more important. It is difficult to hypothesize a very distant source, however, for some of the largest fly ash particles collected in the watershed. It seems logical to assume that under most conditions, fly ash on the order of 20 to $100 \mu\text{m}$ diameter must originate relatively close to the receptor. However, without the aid of combustion plume tagging experiments (e.g., using SF_6) it will be an extremely difficult task to positively identify specific sources of particles captured by the forest canopy in WBW or to accurately quantify the local source input to the watershed.

Geochemical Relationships

Elemental Ratios and Correlations as Indicators of Sources and Mechanisms of Removal

Having established the presence of fly ash in samples of suspended, deposited, and scavenged materials it is of interest to compare the chemical composition of these samples in an attempt to

further define mechanistic and geochemical relationships. An approach which has been applied in several studies and which avoids the complications and errors of absolute predictions is normalization of the concentration data using element ratios (Gordon, 1975; Zoller et al., 1974; Lawson and Winchester, 1978; Andren and Lindberg, 1977). Since much of the material in the atmosphere is derived from natural processes resulting in suspended soil and rock dust, the choice of the reference element should reflect this fact. The most widely used are relatively common lithophile elements which are generally sparingly soluble and non volatile, thus minimizing chemical and physical fractionation. These include Al, Fe, Sc and several rare earths. Ratios of the elements of interest to the reference element are further normalized by comparison with similar ratios in surface soils or crustal material. This double normalization technique results in an enrichment factor (EF, Zoller et al., 1974):

$$EF = (X/\text{reference element})_{\text{air}} / (X/\text{reference element})_{\text{crust or soil}}$$

Enrichment factors within an order of magnitude of unity are taken as suggestive of a crustal or surface soil source while values much greater indicate a non soil related source. The use of the EF is generally associated with multi-element studies in which total Al, Fe or rare earth concentrations are determined by neutron activation analysis. Since such an approach was not practicable in this research, it was necessary to develop the case for another reference element. The data discussed in Chapters III and VI suggested the primary source of Mn in the atmosphere and deposited on surfaces in the watershed to

be resuspended surface soil dust. To test the utility of using Mn as a reference element, enrichment factors relative to Al were calculated for the samples subjected to the total wet digestion procedure (experimental period W7 for the aerosols and deposition plate retention samples, the precipitation samples were collected 9/29-10/10/77). These values are summarized in Table 45. The soil concentrations were taken from data compiled in Andren and Lindberg (1977). The enrichment factors for Mn indicate it to behave similarly to Al in all aerosol size fractions as well as in dry deposited material collected in the upper canopy and on the forest floor. This is in agreement with the previous work of Struempfer (1975) who compared aerosol enrichment factors calculated using both Al and Mn as reference elements and found no significant difference between the two methods.

The elements Pb and Zn are apparently present in suspended and deposited particles in concentrations too high to be derived from a crustal weathering source. The enrichment factors increase considerably as particle size decreases, suggesting a combustion - condensation source for these relatively volatile elements. The lower EF values for the deposited material reflect the influence of the particle sedimentation process in diluting the trace metals with relatively high concentrations of crustally derived Al as well as large fly ash particles which exhibit lower trace metal to Al ratios because of their small surface area to volume ratios relative to submicron fly ash (Natusch et al., 1974). The enrichment factors of Cd in the upper three aerosol size classes indicate a possible soil source while the smaller particles exhibit a higher enrichment, as expected of a

Table 45. Enrichment factors of trace metals in suspended, deposited, and precipitation scavenged materials collected during experimental period W7 (based on total metal concentrations)

Sample	Enrichment factor ^a			
	Cd	Mn	Pb	Zn
Aerosols: ^b				
Size class 1	4	1	76	14
Size class 2	3	2	190	36
Size class 3	7	3	630	250
Size class 4	17	2	2400	390
Size class B	23	4	13,000	170
Deposited Particles: ^c				
UC	10	1	100	30
FF	4	2	120	25
Precipitation Scavenged: ^d				
Above canopy	670	40	6500	2800
Below canopy	110	750	1500	1600

^aEF = (X/A1) sample / (X/A1) soil.

^bSize class 1 aerodynamic diameter (for 50% collection efficiency) \approx 7 μ m, class 2 \approx 3.4 μ m, class 3 \approx 1.1 μ m, class 4 \approx 0.4 μ m, class B \approx backup filter (< \approx 0.44 μ m).

^cParticles retained by inert surfaces in the upper canopy (UC) and on the forest floor (FF).

^dIncludes only the available metal fraction, not total. These samples were not collected during period W7, but from 9/29-10/10/77.

volatile element released in a combustion process. Because of the greater concentrations of soil derived material on the upper canopy deposition plates, it is difficult to determine the extent to which Cd deposition is of crustal origin, the enrichment factor being 10.

The enrichment factors for elements leached from precipitation indicate some enrichment of Mn in incident precipitation, considerable enrichment of Cd, Pb, and Zn in incident precipitation and throughfall, but also considerable enrichment of Mn in throughfall. The last observation is related to the much higher solubility of particulate associated Mn compared to Al (Hodge et al., 1978) and the strong internal dissolved Mn source within the forest canopy (Chapter V). Thus there is a potential problem in comparing ratios of total element concentrations such as in soil, or suspended and deposited particles, with ratios of dissolved element concentrations such as in rain. Because of the indication that Mn is largely of crustal derivation, such comparisons are valid when using the soluble and available element ratios. However, because of the complication of the internal Mn source in leaves, element ratios to Mn in samples of throughfall or leaf leachate will be difficult to interpret.

Ratios of the available trace element and soluble $SO_4^{=}$ concentrations to the available Mn concentrations were calculated for the samples collected during the 1977 intensive sampling experiments, as well as for some precipitator ash, stack ash, and in-plume ash samples from coal fired power plants. These ratios were calculated for the experimental periods during which dry deposition rates were calculated (Chapter IV) and for periods during which well defined,

single precipitation events were sampled. This data is summarized in Figures 54 and 55 for each element. Indicated on the plots are the mean values (\pm S.E. for sample sets of multiple observations) of the element to Mn ratios for the fly ash, plume samples and ambient aerosols in several particle size classes, incident precipitation, and dry deposition captured on inert, flat surfaces. Shown for comparison are representative soil ratios for WBW taken from the data in Fortesque et al. (1973), Andren and Lindberg (1977), and Van Hook et al. (1977) and corrected to reflect available element fractions according to the data of Tyler (1978). These ratios indicate the trace elements to behave somewhat similarly with respect to Mn in fly ash and aerosol samples. Since Mn apparently behaves as a matrix element during coal combustion, showing little enrichment in fly ash compared to coal or slag (Kaakinen et al., 1975; Klein et al., 1975), variations in the element to Mn ratio generally reflect the behavior of the element in question with respect to the parent particle. There was an enrichment of Pb and $\text{SO}_4^{=}$ in ash collected in the stack relative to precipitator ash, while Cd and Zn reflected little change. All elements exhibited a substantial enrichment in combustion plume aerosols compared to in-stack material, further supporting the conclusions discussed in Chapter III relative to the importance of the initial stages of plume cooling and associated gas-particle interactions on aerosol chemistry. The increase in ratios with decreasing particle size for each element are also indicative of vapor condensation reactions since the smallest particles with the largest surface area to volume (and hence surface area to matrix element)

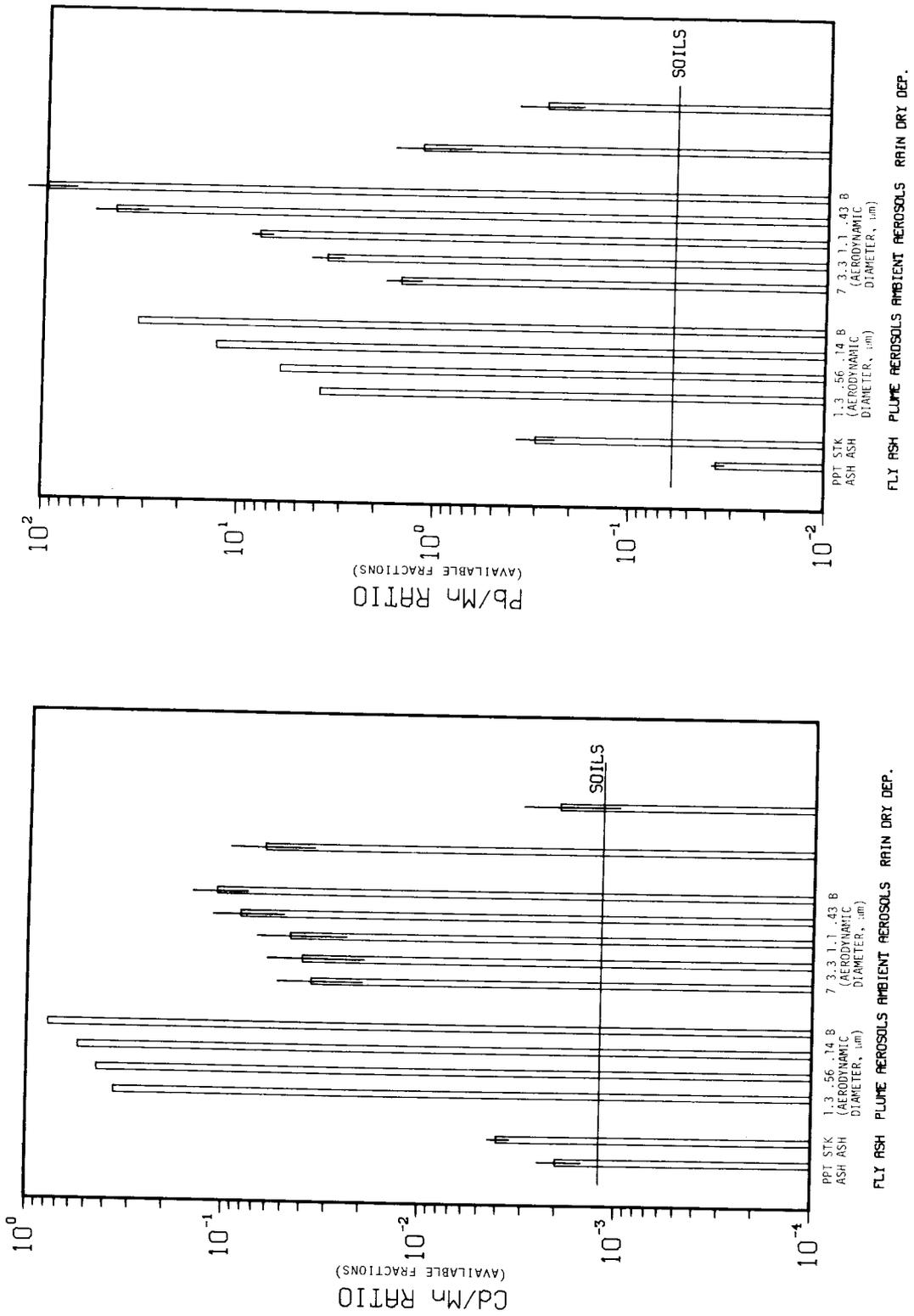


Fig. 54. Mean available Cd/Mn (left) and Pb/Mn (right) ratios in fly ash and in-plume aerosols from a major coal fired power plant, and in ambient aerosols, rain, dry deposition, and soils collected in Walker Branch Watershed. Error bars represent ± 1 standard error of the mean.

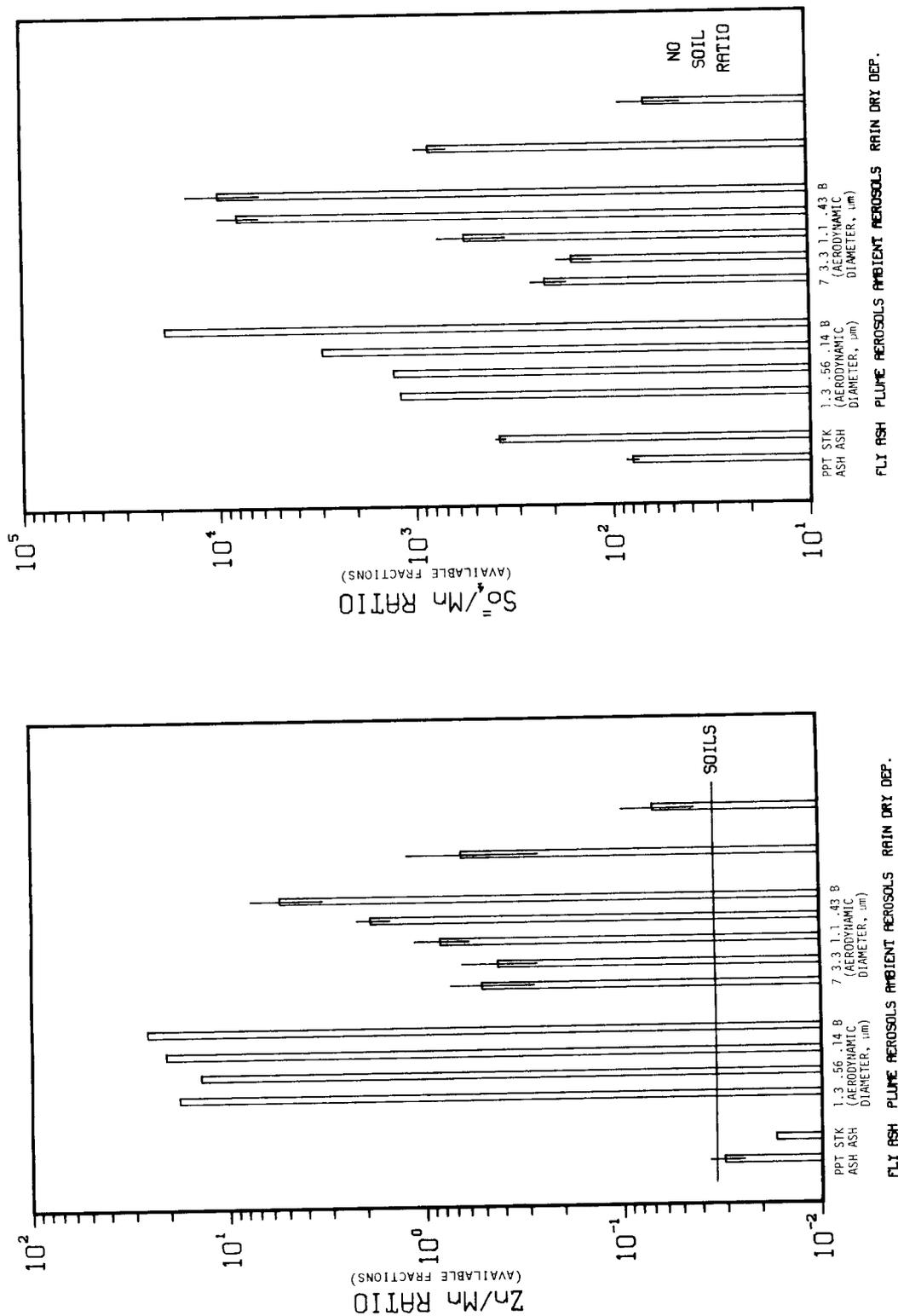


Fig. 55. Mean available Zn/Mn (left) and sulfate/Mn (right) ratios in fly ash and in-plume aerosols from a major coal fired power plant, and in ambient aerosols, rain, dry deposition, and soils collected in Walker Branch Watershed. Error bars represent ± 1 standard error of the mean.

ratios will act as preferential sites of vapor condensation resulting in the highest volatile element to Mn ratios.

As the combustion plume mixes with the background air mass, the surface associated elements are effectively diluted by regional aerosols including relatively Mn rich soil dust. This results in a decrease in the ratios for those elements for which coal combustion is a major source to the regional aerosol load. This is apparently the case for Cd, Zn, and $\text{SO}_4^{=}$. However, Pb/Mn ratios in the ambient aerosol are 2 to 4 times higher than the ratio in combustion plume aerosols, reflecting the importance of automobile emissions to the regional aerosol composition, as expected (Chow and Earl, 1970). Despite the physical and chemical interactions between the plume and the background aerosols each of the elements retains the pattern of increasing element/Mn ratios with decreasing particle size.

The ratios for deposited material indicate further dilution of the ambient aerosol with crustally derived particles with lower trace element and higher Mn concentrations. In each case the element ratios in rain are more reflective of the composition of supermicron particles than of submicron particles. The indication of a more efficient wetfall removal of particles $> \sim 1 \mu\text{m}$ diameter is supported by the longer residence time of small particles in the atmosphere as well as the theoretical collection efficiency of precipitation for polydisperse aerosols (discussed in Chapter V). The importance of large particle sedimentation in aerosol deposition to flat, inert surfaces is reflected by still lower element to Mn ratios in dry deposited material. Interestingly, at this point in the geochemical cycle of

aerosols the element ratios to Mn are on the same order as those of surface soils, making the link between deposited particles and emissions from coal combustion plants, on a chemical basis, somewhat tenuous. However, the physical presence of fly ash in all samples leaves little doubt of the general source of much of the deposited material. This may indicate a serious shortcoming of the application of elemental ratios and enrichment factors to the identification of sources for very heterogeneous surface deposited particles.

In a further attempt to relate deposition by both wet and dry mechanisms with suspended particle chemistry, correlation coefficients were calculated between precipitation concentrations or dry deposition rates and concentrations in the total aerosol fraction, size class 1 fraction ($> \sim 7 \mu\text{m}$), and size class B fraction ($< \sim 0.4 \mu\text{m}$). The correlation coefficients between dry deposition and air concentrations were previously discussed in Chapter IV (Table 23) as indicating a significant, direct relationship between the air concentrations and dry deposition rates of Cd, Pb, and SO_4^{2-} and possibly Zn. Similar relationships between precipitation concentrations and atmospheric concentrations are complicated by the strong interdependence between rain concentrations and rain volume, as discussed in Chapter V. For the periods of intensive deposition sampling during which well defined, single precipitation events occurred ($n = 5$, see Table 3, Chapter III), Cd exhibited a marginally significant correlation coefficient with precipitation concentration and with the air concentration in the large particle size class; Zn exhibited a significant positive correlation coefficient between wet deposition rate and air concentration in the

fine particle size class; Pb and $\text{SO}_4^=$ exhibited marginally significant correlation coefficients between rain concentration and air concentration in the fine particle size class, and Mn exhibited no significant correlation coefficients. The relationship between Cd in rain and large particle Cd in air supports the hypothesis developed in Chapter V that below cloud scavenging (of primarily large particles) is an important mechanism of Cd wet deposition. The absence of a similar relationship for Mn, the precipitation concentration of which was also strongly related to below cloud scavenging processes, may be explained by the relatively poor efficiency of the aerosol samplers to collect large particle Mn (as discussed in Chapter III). The relationships between the concentration of Pb and $\text{SO}_4^=$ in rain and in the fine particle mode in air would also have been predicted from the calculations in Chapter V which suggested in cloud scavenging (of primarily small particles) to be the major mechanism controlling the concentrations of these constituents in rain.

Several authors have utilized correlation analysis to identify common source elements in samples of both suspended and deposited particles (Struempfer, 1975, 1976; Winchester, 1973; Cause, 1974). Large correlation coefficients between any element pair are assumed to be indicative of a common source and similar behavior. However, a point often neglected is that significant correlation coefficients can be indicative of similar behavior alone, regardless of source. This is particularly important when considering the interrelationships between two elements each of which, in turn, is known to be related to a common parameter (such as simultaneous dilution of 2 elements in precipitation

by increased rain volume). In addition, chemical interactions in the atmosphere following release from different sources are largely ignored (such as between NH_4^+ and $\text{SO}_4^{=}$). Interelement correlation coefficients were calculated for the various data sets discussed in the preceding chapters, the results being summarized in Table 46. To simplify comparison, only those element pairs for which the correlation coefficients were significant ($P \leq 0.05$) are included (the coefficients are in parentheses). The dry deposition and air concentration data sets resulted in few significant correlations, which may have been due to the limitations of the data in both time and number of observations. However, both of the significant relationships provide good examples of possible misinterpretation which can result from such analyses. In the total aerosol fraction Cd and Pb concentrations were significantly correlated and yet, according to the discussions in Chapter III, they do not appear to have a common source or a similar particle size distribution (and hence possibly a similar behavior). An artifact is suggested. Similarly, the concentrations of Pb and $\text{SO}_4^{=}$ in dry deposition are highly correlated, although they do not share a common primary source, other than fossil fuel combustion in general. However, because of their similar size distribution in suspended particles their deposition rates to flat surfaces may be controlled by similar processes (i.e., small-particle deposition mechanisms would be relatively more important for these elements than for those with larger mass median diameters).

The significant correlation coefficients in the precipitation related samples provide an interesting group of common source and

Table 46. Correlation coefficients between elements in various sample types

Sample type	Cd	Mn	Pb	Zn	SO ₄ ⁻	H ⁺
Incident precipitation (n = 50)	-- ^a	Pb (0.43) SO ₄ ⁻ (0.75) H ⁺ (0.39)	Mn (0.43)	--	Mn (0.75) Pb (0.44) H ⁺ (0.79)	Mn (0.39) Pb (0.48) SO ₄ ⁻ (0.79)
	Pb (0.47)	Pb (0.50) Zn (0.39) SO ₄ ⁻ (0.83) H ⁺ (-0.60)	Cd (0.47) Mn (0.50)	Mn (0.39)	Mn (0.83) Pb (0.61) H ⁺ (-0.45)	Mn (-0.60) SO ₄ ⁻ (-0.45)
	--	--	SO ₄ ⁻ (0.96)	--	Pb (0.96)	--
Dry deposition (n = 5)	--	--	--	--	--	--
Total aerosol fraction (n = 10)	Pb (0.84)	--	Cd (0.84)	--	--	--

^aOnly those coefficients are indicated for which r was significant ($P \leq 0.05$).

^bCanopy net leachate is calculated as the difference between throughfall and rain concentrations for samples collected above and below the canopy simultaneously.

similar behavior relationships. The H^+ - $SO_4^{=}$ correlation is suggestive of the scavenging of acid sulfate aerosols or the production of H^+ during SO_2 oxidation. The Pb - $SO_4^{=}$ correlation may be related to the similarity in aerosol size distribution and importance of in cloud scavenging for these elements. However, it is difficult to apply the same explanation to the $SO_4^{=}$ - Mn correlation because of the considerable difference in both particle size distribution and importance of in-cloud vs below-cloud scavenging. It is more likely that this correlation is related to recently proposed atmospheric interactions between S species and dissolved Mn in rain droplets and cloud water. The dissolution of SO_2 and subsequent oxidation to $SO_4^{=}$ is a major source of $SO_4^{=}$ in rain, in addition to direct particulate $SO_4^{=}$ scavenging (Bielke and Georgii, 1968). The mechanism of SO_2 oxidation in water has been described in detail by Scott and Hobbs (1967) while its application to rain chemistry has been discussed by several authors (Hutcheson and Hall, 1975; Dana et al., 1975; Miller, 1972). The oxidation process involves production of the intermediate species HSO_3^- which dissociates to produce $SO_3^{=}$. The rate of oxidation to $SO_4^{=}$ is controlled by the concentration of sulfite which is, in turn, controlled by pH. Beilke et al. (1975) measured the rate of oxidation in a pure system and concluded that at $pH \leq 6$ oxidation is too slow to be of importance in the atmosphere. However, in addition to the well known role of NH_3 in increasing the solution pH and hence allowing increased oxidation of $SO_4^{=}$ (Junge, 1963) heavy metal ions are known to act as catalysts to accelerate the oxidation reaction. The reaction mechanism of catalytic oxidation has

been described by Schmidkunz (1963; as cited by Barrie and Georgii, 1976) and further investigated by Barrie and Georgii (1976). Their research indicated that, of several metals, Mn^{+2} was the most effective catalyst, forming an intermediate, regenerable complex with sulfite. Since the oxidation rate was reported to increase with increasing Mn^{+2} concentration, one would expect a positive relationship between Mn and $SO_4^{=}$ in precipitation if this is indeed an important atmospheric SO_2 oxidation mechanism as suggested by the authors. The remaining significant correlations, Pb - Mn, Pb - H^+ , and Mn - H^+ are likely artifacts of the correlations between $SO_4^{=}$, Mn, H^+ , and Pb. The interelement correlation coefficients for the canopy net leachate samples, which include material both washed from the leaf surface and leached from the foliage, represent source and behavior relationships for Mn and $SO_4^{=}$ but primarily behavior relationships for the other elements. Manganese and $SO_4^{=}$ are highly positively correlated while each is significantly negatively correlated with H^+ . These two elements in net leachate reflect a strong internal leaf source, as discussed in Chapters IV and V, from which leaching increases in response to certain storm parameters which also result in increased H^+ scavenging by the canopy and hence lower H^+ concentrations in canopy leachate. Several discussions in Chapter V considered these interactions in detail. The correlations between the element pairs Mn - Pb, Cd - Pb, Mn - Zn, and $SO_4^{=}$ - Pb most likely reflect similar behavior of these elements with respect to various meteorological parameters while some of the correlations may be

artifacts due to correlations of two actually unrelated elements with a common element.

Predictive Utility of Concentration Ratios
Between Suspended and Deposited Particles:
Deposition Velocities and Scavenging Ratios

Measurement of both wet and dry deposition of airborne materials has often been oriented toward predictive needs of various disciplines. The ecologist is interested in estimating particle or gas flux to biological receptors for the purpose of predicting possible physiological effects; the meteorologist is interested in the dynamic physical processes at the atmosphere-surface interface and how these processes alter atmospheric transport; and the geochemist is interested in the role of the atmosphere in element cycling, particularly as influenced by man's activities. Two types of relationships between deposited and suspended material have been in relatively wide use in recent years, generally for predictive purposes. These are the relationships between dry deposition rates and air concentrations and between precipitation concentrations and air concentrations. The former relationship is represented by the deposition velocity (V_d), defined as the vertical flux of an element to a surface (F) divided by the mean concentration of the element in the air at some height above the surface (C), expressed in cm/sec (Chamberlain, 1953). Comparisons of element concentrations in rain and air are based on the scavenging ratio, W , defined as the ratio of the product of precipitation concentration of an element (k) and the density of air (ρ) divided by the concentration in air (C) (Engelmann, 1971; Gatz, 1977).

Some of the theory behind these relationships was discussed in Chapter V. Thus in terms of the measured values reported in this research, these parameters are expressed as follows:

$$V_D \text{ (cm/sec)} = [F(\mu\text{g}/\text{m}^2\text{day}) / C \text{ (ng}/\text{m}^3)] \cdot 1.16, \text{ and}$$
$$W = k \text{ (\mu g/l)} \cdot \rho \text{ (= } 1200 \text{ g}/\text{m}^3 \text{ @ } 20^\circ\text{C, } 760 \text{ mm)} / C \text{ (ng}/\text{m}^3) .$$

Deposition velocities and scavenging ratios were calculated for the summer, 1977 experimental periods for which interelement correlations, ratios, and enrichment factors were calculated in the previous section. These results are summarized in Table 47 for each sample period. There are widely recognized to be several problems with the concept and use of the deposition velocity (Droppo and Hales, 1976; Sehmel and Hodgson, 1977). One recently reported, but previously unconsidered, complication is the possibility that some plant canopies may act as both sources and sinks for atmospheric particles. This phenomenon has been reported in the laboratory for the release of Zn and Pb containing particles by mature pea and bean plants, and pine tree seedlings (Beauford et al., 1975, 1977). In a series of recent short term, intensive experiments, Hicks and Wesely (1978) measured net upward fluxes of particulate SO_4^- from a pine forest canopy during certain times of the day. The result of such releases may lead to overestimates of deposition velocity since much of the deposited material may actually represent internally cycled particles. Nonetheless, the concept of deposition velocity is still widely used and perhaps of most use from a comparative, as well as a predictive, standpoint.

Table 47. Dry deposition velocities (V_d) and precipitation scavenging ratios (W) in WBW for several experimental periods during the summer of 1977

Period ^a	Cd	Mn	Pb	Zn	$SO_4^{=}$
DRY DEPOSITION VELOCITY (cm/sec)					
1	0.33	1.7	0.047	0.66	0.09
2	0.87	17	0.10	0.36	0.24
3	0.05	4.7	0.040	0.27	0.07
6	0.22	2.4	0.068	0.24	0.13
PRECIPITATION SCAVENGING RATIO					
2	1800	14000	22	470	1100
3	4200	1300	110	670	960
6	1800	460	26	1000	620
7	14000	1900	280	1200	1900
12	3300	600	122	760	430

^aDetails of each experimental period are described in Chapter III, particularly in Table 3.

The importance of sedimentation in the dry deposition of particles to the inert, flat surfaces is reflected by the deposition velocities. With the exception of Zn, the highest deposition velocities calculated were for period W2 which experienced the highest frequency of air stagnation of the 4 experimental periods. Under these meteorologic conditions sedimentation would be expected to be a more important deposition process than impaction because of the low wind speed and incomplete atmospheric mixing. Periods of higher wind speed and increased atmospheric mixing increase the relative contribution of particle impaction and convective diffusion to the deposition process while under stagnant conditions sedimentation may dominate (Sehmel and Hodgson, 1976). The correlation coefficients between air stagnation frequency and deposition velocities were significant ($P \leq 0.05$) for Cd ($r = 0.98$), Pb (0.96), and $SO_4^{=}$ (0.98), marginally significant ($P \leq 0.10$) for Mn (0.86) but insignificant for Zn. Zinc on the other hand, was the only element with a large correlation coefficient between MMD and V_d (0.85). Despite the lack of a strong correlation between the periodic variations in MMD and V_d for each of the other elements, the general order of deposition velocities ($Mn > Cd > Zn > SO_4^{=} > Pb$) was strongly related to the MMD of each element. The correlation coefficient between the mean deposition velocity and mean MMD of each element for these experimental periods was 0.95 ($P \leq 0.05$). This increase in V_d with MMD is expected for particles in the size range $\sim 0.6 - 10 \mu m$ where gravitational settling and inertial impaction are the primary deposition mechanisms at low and high wind speeds respectively (Sehmel and Hodgson, 1976; Slinn, 1976).

Table 48 compares the deposition velocities determined at WBW with several literature values (also compares precipitation scavenging ratios). It should be kept in mind that the values measured in WBW are expressed on an individual upper canopy element surface area basis and do not reflect the overall effect of the fully developed canopy, which could effectively increase the deposition velocities by as much as a factor of 6 (see the discussion in Chapter VII). In general the WBW data compare rather favorably with the work of others. The deposition velocities for Mn in WBW are somewhat higher than those measured elsewhere for two possible reasons. The data presented for the U.K. are annual averages of monthly composite samples, a method expected to minimize extremes in the data. In addition any problems in the underestimation of the atmospheric large particle Mn burden in WBW, as previously discussed, would result in a positive bias in the calculated deposition velocities. The Pb data collected in the California experiments provides an interesting comparison of source effects on deposition velocity. Near the source (freeway) a wide spectrum of Pb particles are released ranging from $< 1 \mu\text{m}$ to $> 10 \mu\text{m}$ (Davidson, 1977). These largest particles have the highest deposition velocities due to efficient removal by sedimentation and inertial impaction processes (Sehmel and Hodgson, 1976). As distance from the source increases, as from the freeway shoulder, to Pasadena (samples collected ~ 300 m from the nearest street) to the remote wilderness area site, the particle size distribution is altered by continuing deposition to reflect increasingly smaller aerosols with lower deposition velocities.

Table 48. Comparison of dry deposition velocities and precipitation scavenging ratios at several locations

Location	Cd	Mn	Pb	Zn	SO ₄ ⁼
DRY DEPOSITION VELOCITY (cm/sec)					
N. C. Pine Forest ^a	--	--	--	--	0.42-1.27
Wilderness Area, CA ^b	--	--	0.07	--	--
Pasadena, CA ^c	--	--	0.29	--	--
Freeway Shoulder, L.A. ^d	--	--	1.8	--	--
U. K., rural ^e	--	0.55-0.71	0.23-0.43	0.41-0.97	--
U. K., remote coastal ^e	--	< 0.05-1.4	< 1-1.5	0.64-3.3	--
U. K., remote continental ^e	--	0.35-0.55	0.57-0.69	0.50-0.71	--
U. K., industrial ^e	--	0.60-0.76	0.19-0.39	0.45-1.2	--
U. S., west ^f	--	--	--	--	0.1-0.3
WBW ^g	0.05-0.87	1.7-17	0.04-0.1	0.24-0.66	0.07-0.24
PRECIPITATION SCAVENGING RATIO					
N. Y. City ^h	--	--	20-280	--	--
St. Louis ⁱ	--	120-3500	25-450	30-4200	--
U. K., rural ^e	--	500-630	290-340	370-720	1500
U. K., remote coastal ^e	--	6000-11,000	870-1100	2700-9000	24,000
U. K., remote continental ^e	--	145-160	57-140	190-220	520
U. K., industrial ^e	--	230-440	290-360	120-210	1050
WBW ^g	1800-14,000	460-14,000	22-280	470-1200	430-1900

^aHicks and Wesely, 1978.

^bPatterson, 1975 (cited in Davidson, 1977).

^cDavidson, 1977.

^dHuntzicker and Davidson, 1975.

^eCawse, 1974, 1975.

^fDroppo, 1976.

^hKrey and Toonkel, 1977.

ⁱGatz, 1977.

^gThis study. Dry deposition velocities determined as the ratio between the deposition rate and the air concentration for the available element fraction.

The deposition velocities of $\text{SO}_4^=$ reported by Hicks and Wesely (1978) are among the first measured on a real time basis for a forest canopy. The authors presented this preliminary data to make the point that the often used deposition velocity of 0.1 cm/sec may not be valid for a forest canopy, but that a value closer to 0.5 cm/sec should be applied for predictive purposes. If the values calculated for WBW are multiplied by 6 to reflect the $\sim 6/1$ ratio of canopy element surface area to ground surface area, the values range from 0.42 to 1.4 cm/sec, very similar to those measured by Hicks and Wesely. Indeed nearly all of the values measured in WBW indicate an estimate of V_d for a deciduous forest to be higher than the commonly used 0.1 cm/sec.

Tables 47 and 48 also summarize the precipitation scavenging ratios for 5 experimental periods in WBW and for some data recently reported in the literature. As indicated in the recent ERDA Symposium (Semonin and Beadle, 1977) there has been a revived interest in the use of washout ratios, or in the nomenclature suggested by Slinn (1977), precipitation scavenging ratios. It has been suggested that the relationship between the elemental concentration in air and in rain provides some insight into the processes within and below the cloud layer (Engelmann, 1971). Because of the obviously growing interest in the wet deposition of both acids and trace constituents (e.g., see the symposium cited above; also the symposium volume edited by Dochinger and Seliga, 1975) there is a need for developing predictive relationships for rain chemistry, many of which may interface with the concept of scavenging ratios (Gatz, 1977). The precipitation scavenging ratios calculated for the WBW data are highly variable, but

generally comparable with those observed by others (Table 48). Such large ranges are expected for values calculated from individual storms, especially for storms of small rain volume for which the variability in concentration is greatest (Chapter V). In several studies of scavenging ratios various authors (as reviewed in Krey and Toonkel, 1977) have found that such ratios are relatively independent of rainfall amount, as well as relative humidity, dew point, wind speed, direction, and air mass trajectories. However, there are some reports of inverse logarithmic relationships between precipitation volumes and scavenging ratios (Krey and Toonkel, 1977). Correlation coefficients calculated for the WBW data between rainfall amount and scavenging ratios were all negative but generally small ($|r| \leq 0.66$) with the exception of Pb (+ 0.19). Interestingly, recent data presented by Gatz (1977) exhibited the same relationships (negative but small correlation coefficients for Mg, K, Ca, Mn, Fe, and Zn, but positive for Pb). Thus, it appears that precipitation volume has a relatively minor effect on the scavenging ratio. These ratios were also apparently independent of temporal variations in the MMD of any individual element, air stagnation frequency, and relative humidity. However, the mean scavenging ratios for each element were weakly correlated with the mean MMD of each element ($r = 0.70$) as was also seen for the deposition velocity. This relationship was also reported by Gatz (1977) for the elements cited above. The author speculated this to be an indication of the relative importance of below cloud or impaction scavenging for each element, since the collection efficiency for particles by raindrops increases rapidly with particle size for particles $> \sim 0.5 \mu\text{m}$

diameter (Chapter V). The relative order of mean scavenging ratios from Table 47 is indeed similar to the relative importance of below cloud scavenging as determined by the empirical approach described in Chapter V. Because of the apparent particle size effect on the scavenging ratio and the operational dependence on air concentration, both of which are subject to large short term variations, the predictive utility of wet scavenging ratios is perhaps best when applied on a seasonal or longer term basis (Gatz, 1977).

Summary

Scanning electron and light microscopy of biological and inert deposition surfaces indicated the presence of considerable numbers of relatively large ($> 10 \mu\text{m}$) fly ash particles as well as dispersed soil fragments, primarily on upward facing surfaces, confirming the earlier indications that sedimentation was an important dry deposition mechanism to these surfaces. Possible sources of large-particle fly ash were determined by calculating upper level air mass backward trajectories for time intervals comparable to large-particle tropospheric residence times. These trajectories were found to traverse two major regional urban centers and five major regional coal-fired power plants with sufficiently rapid travel times to account for the large-particle transport. An interesting observation in several scanning electron photomicrographs was the association of submicrometer fly ash with considerably larger (5 to $20 \mu\text{m}$) fly ash and scoriaceous particles and the agglomeration of several submicron fly ash particles into large aggregates. The removal

of these large particles from the atmosphere is primarily controlled by sedimentation, which may account for the often high concentrations of small-particle-associated elements (Pb, SO_4^-) in dry deposited material.

Trace element enrichment factors, using aluminum as the reference element, indicated Pb and Zn in aerosols to occur in concentrations too high to suggest crustal derivation. This was also true for Cd in aerosols collected on the lower impactor stages (smaller particles). However, large particle Cd, and Mn in all size ranges could have been crustally derived. Elemental ratios to Mn, which is soil derived in ambient aerosols and behaves as a matrix element during coal combustion, indicated the following: (a) ratios of each element to Mn increased substantially from precipitator ash to stack ash to plume ash collected at a large, modern coal fired power plant, (b) the highest ratios occurred in the smallest particles, (c) mixing of the plume with the background air mass resulted in the decrease of the ratios of Cd, Zn and SO_4^- to Mn, but in an increase in the Pb/Mn ratio, and (d) ratios for material deposited on flat, inert surfaces in the upper canopy indicated further dilution of the original aerosol with crustally derived material with lower trace element and higher Mn concentrations, resulting in element/Mn ratios on the same order as those of soils.

The concentrations of Cd, Pb, Zn, and SO_4^- in incident precipitation were correlated with air concentrations of particles in several size classes. Inter-element correlations in incident precipitation implicated a possible common source of SO_4^- and H^+ ,

such as scavenging of acid sulfate aerosols. A large correlation coefficient between Mn and $\text{SO}_4^=$ concentrations in rain may be related to the ability of Mn to catalyze the oxidation of SO_2 in rainwater. Expressing deposition rates relative to air concentrations results in deposition velocities (V_d) for the available element fraction to individual upper canopy elements. The mean V_d values reflected the general particle size distribution of each element and indicated the generally used value of $V_d = 0.1$ cm/sec may be an underestimate ($\text{Cd} = 0.4$, cs^{-1} , $\text{Mn} = 6$, $\text{Pb} = 0.1$, $\text{Zn} = 0.4$, $\text{SO}_4^= = 0.1$).

CHAPTER VII

SUMMARY: PROCESSES AND RATES OF MASS TRANSFER
FROM THE ATMOSPHERE TO THE GROUND

Total Atmospheric Input to Walker Branch Watershed

Methods for Calculating Deposition to the Landscape

Integrating the results of the experiments, observations, and calculations presented in the previous chapters allows estimation of the total atmospheric flux to the upper canopy and to the watershed as a whole for several time periods. The most accurate estimates can be made for four of the intensive, short term experimental periods during the 1977 growing season. These values can then be applied to the full 1977 growing season and finally used to estimate the annual atmospheric deposition for a typical year.

Calculation of the total wetfall input to the watershed during the short term, intensive, sampling periods is a straightforward task since all storms which occurred were sampled:

$$\text{input} = \sum_{i=1}^N (C \cdot V) ,$$

where N = number of events per sampling interval, C = concentration in incident precipitation, and V = volume of rainfall recorded. However, for longer time periods during which all events could not be sampled it

is necessary to utilize weighted mean concentrations to estimate the total input in rain. Precipitation volume weighted means are calculated as the total mass of an element deposited in rain (or throughfall) divided by the total volume of precipitation comprising the samples:

$$\text{volume weighted mean} = \frac{\left[\sum_{i=1}^N (C \cdot V) \right]}{\sum_{i=1}^N (V)} .$$

An arithmetic mean of concentrations for individual rain events would be expected to be higher than a rainfall weighted mean of the same concentrations because the arithmetic mean gives equal weight to all samples, and the events of lower volume are characterized by generally higher concentrations. However, the volume weighted mean is a better representation of the mean concentration in rain accumulated over a period of time and is thus the best estimate to use for prediction of seasonal or annual wetfall input (Likens et al., 1967). Total input is the product of the weighted mean concentration for all events sampled during any given period and the total precipitation volume recorded during the period. This method assumes that the precipitation events which were sampled were representative of those which occurred during the period of interest. This point was considered in detail in Chapter V. Weighted mean concentrations were calculated for incident precipitation and throughfall for the 1977 growing season (4/1/77-10/24/77), 1977 as a whole, and combined 1976-1977, and are summarized in Table 49. Comparing these values with the arithmetic means in Tables 26 and 27 in Chapter V illustrates the effects of rain

Table 49. Rain volume weighted mean concentrations of trace constituents, sulfate, and hydrogen ion in incident precipitation and throughfall

Time period	Weighted mean concentration					
	Cd	Mn	Pb	Zn	SO ₄ ⁼	H ⁺
	(μg/ℓ)				(mg/ℓ)	(μeq/ℓ)
INCIDENT PRECIPITATION						
1976-1977 ^a	0.28	1.95	5.23	5.19	2.9	66
1977 ^b	0.30	2.79	5.15	5.35	2.8	54
1977 growing season ^c	0.22	2.87	5.53	5.77	3.1	67
THROUGHFALL						
1976-1977	0.83	96.6	7.39	11.2	6.6	53
1977	0.83	108	7.43	11.1	6.8	40
1977 growing season	0.82	122	8.27	11.5	8.0	59

^aTotal precipitation volume = 263.2 cm

^bTotal precipitation volume = 142.4 cm

^cTotal precipitation volume = 90.8 cm (4/1-10/25/77)

volume weighting. The mean concentrations in both rain and throughfall are decreased by as much as 50% when weighted by volume. These differences are primarily a reflection of the inverse relationship between the concentration of an element in precipitation and the rainfall volume as discussed in Chapter V.

The calculation of dry deposition to individual elements in the upper canopy for relatively short time periods was discussed in Chapter IV. The extrapolation of this data in both space and time is a difficult task involving several assumptions concerning the scavenging efficiency of leaves throughout the canopy relative to upper canopy elements and the variability of this efficiency during the seasonal cycles of canopy growth and defoliation in addition to periods of maximum and minimum canopy density. Many of the problems in measuring dry deposition were discussed in Chapter IV and have been recently reviewed by Galloway and Parker (1978). However, the specific problem at hand has apparently not previously been considered in detail. This conclusion results from a reading of several recent reviews on atmospheric deposition (Engelmann and Sehmel, 1976; Chamberlain, 1975; Hosker and Lindberg, 1978) as well as from personal communications with several individuals who have published in this field (e.g., Hicks, 1976; Hosker, 1973; Murphy, 1976).

The process of dry deposition to a forest canopy is generally considered to encompass several regimes: (1) the atmosphere above the canopy, (2) the canopy-atmosphere interface, and (3) the individual leaf-air interfaces (Droppo and Hales, 1976). Interactions between an air parcel and the receptor can be considered in the context of the

common resistance model analog (Thom, 1975). The resistances of each regime represent focal points of the dynamic interaction between suspended particles and various surfaces. The total resistance of the atmosphere and canopy is, then, the sum of the resistances of the individual regimes. The deposition velocity, discussed earlier, is equal to the reciprocal of the total canopy mass transfer resistance of the electrical analog. The effect of the canopy on the profile of windspeed and turbulence in turn effects processes in the first two regimes. The resistance to mass transfer above the canopy is necessarily the upper limit to the total mass transfer since particles cannot be scavenged within the canopy faster than they can be delivered to the top of the canopy. However, once transported to this point, within-canopy processes dominate.

The point in the canopy at which the mean wind speed approaches zero or the wind speed profile approaches a vertical line is termed the zero plane displacement height. The displacement height is used to define the boundary between the first two regimes of resistance. This height can be approximated by the point of canopy closure ($\sim 75\%$ of the total canopy height). Most of the foliage above this layer is assumed to experience little resistance of regime 2 and the deposition is controlled by regime 1 and 3 processes. The resistance of regime 2 is expected to increase progressively from the top to the bottom of the canopy. This resistance is particularly large (and hence deposition velocity is low) in the lower canopy of a forest during maximum canopy development. The available plant surface area effects the deposition rate in regime 3. For many canopies, the deposition rate (and hence

total deposition) increases as the leaf surface area per unit horizontal area (termed the leaf area index = LAI) increases. However, there is a point where this effect reaches an upper limit and increases in leaf area do not significantly increase deposition rate, presumably due to poor particle dispersion in very dense canopies. Apparently low, dense canopies such as grass experience deeper penetration than higher, less dense covers such as forests. Thus, on higher canopies most of the deposition occurs in the upper layers. Total flux to these higher canopies is considerably greater than on low, dense canopies, however, because of higher above ground to ground surface area ratios.

The relationship between deposition rates to individual surfaces in the upper canopy and deposition rates to the full canopy are obviously complex. The deposition rate to individual upper canopy elements on a surface area basis may be higher or lower relative to the deposition rate to bare ground. Despite high resistances per unit surface area of a leaf, the total deposition in a plant canopy is generally greater than on other surfaces because of the high above-ground surface area to ground surface area ratio (LAI). The relationship between deposition rate to individual leaves of the tulip poplar (Liriodendron tulipifera) and groups or assemblages of leaves was studied under controlled conditions in a wind tunnel by Wedding et al. (1975). The results indicated that the deposition rate per unit leaf area for the assemblages was essentially identical to that of the single trailing leaves. Hence, deposition rate was linearly related to the total leaf area. The authors concluded that increasing the leaf density did not result in the expected decrease in deposition rates due

to decreases in the effective flow area between leaves. These results simplify the task at hand considerably. If these observations can be taken to approximate conditions in the field, the dry deposition rate to the full canopy can be assumed to be linearly related to the LAI. The effect of increasing the surface area can be considered in terms of the resistance analog as the adding of resistive elements in parallel resulting in the total surface resistance per unit area of ground. This approach was recently utilized by Murphy (1976) in the application of the resistance analog to the estimation of dry deposition rates of SO_2 to forested landscapes. The author assumed the decrease in resistance due to the presence of a fully developed canopy could be approximated as the addition of more elements in parallel. The reduction factor was taken to be the LAI. However, as discussed earlier, and as acknowledged by the author, leaf surfaces deep within the canopy may not be as efficient in the deposition process. Thus, the simple reduction of surface resistance in inverse proportion to the LAI (and hence the increase in the deposition velocity in direct proportion to the LAI) must be considered as an upper limit estimate in the conversion of single surface deposition rates to canopy wide deposition rates. Discussions with the individuals working in this field cited above indicated a general concurrence with this assumption.

The method chosen for estimation of landscape deposition from measurements of upper-canopy-surface deposition rates relies on these assumptions but, also, is designed to improve the estimation through consideration of the temporal changes in canopy density. In addition, based on the statements presented in Droppo (1976), the linear increase

in deposition with leaf area will be assumed to apply only to the vegetation above the zero displacement plane, which will be approximated by the point of canopy closure of the deciduous forest. Thus, the developed canopy will be considered in two layers, above and below canopy closure, which include $\sim 75\%$ and $\sim 25\%$ respectively of the vegetative surfaces (S. McLaughlin, personal communication). The effectiveness of the lower layer will be related to that of the upper layer in the same proportion as the dry deposition rate of Pb measured to upper and lower canopy deposition plates during experimental period W1. This data, previously presented in Table 16 (Chapter IV), was chosen for two reasons: (1) the element Pb apparently experiences the least influence of internally recycled material relative to atmospherically derived material, and (2) the period W1 was characterized by no measurable precipitation during the experiment. This lower canopy to upper canopy layer efficiency ratio is 0.89. These efficiencies are then integrated over the time scale of interest using the temporal variation in LAI given in Huff et al. (1977) for the development of the canopy in a tulip poplar stand in eastern Tennessee. This data indicated a maximum LAI of ~ 6 from 6/1-9/20 with a nearly linear increase from 4/1 (budbreak) to 6/1 and a nearly linear decrease from 9/20-10/25 (leaf fall). The leafless canopy will be assumed to increase the deposition flux to the ground by an additional 80% relative to the unit surface deposition flux. This value is taken from the branch area index given in Yoda et al. (1965).

The Relative Contribution of Wet and Dry Deposition
Over Long and Short Time Intervals

The application of these methods to the estimation of long term dry deposition to WBW, as well as the measured short term dry deposition during several experimental periods are summarized in Table 50. The dry deposition rates used to estimate long term deposition were the mean values measured to flat, inert surfaces during periods W0, W1, W2, W3, and W6 as previously summarized in Table 19, Chapter IV. Also included in Table 50 are the calculations of total wet deposition for each of the periods of interest, and the total atmospheric deposition (wet plus dry). As expected from the earlier discussions of temporal variations in precipitation concentrations and dry deposition rates, the atmospheric input is quite variable from week to week. None of the short term experimental periods stand out as contributing an unusually large fraction of the total deposition to the watershed relative to the full growing season, however.

The relative proportion of the total deposition attributed to dry processes, which have been largely ignored in field studies until quite recently, also varied considerably during the shorter experimental periods. The fraction of the total atmospheric input due to dry deposition processes, is presented in Table 51. The atmospheric input during the dry periods W1-W3 and W6 was dominated by dry deposition in most cases. Only during period W3 was the wetfall process of greater relative importance, and only for Cd and SO_4^- -S. However, over longer time scales wet deposition dominates the total atmospheric input of Cd, Zn, and SO_4^- -S. Still, during the growing season and on an

Table 50. Total wet and dry deposition of the available fraction of several elements to Walker Branch Watershed measured during short-term experimental periods and estimated for seasonal and annual periods^a

Deposition process	Atmospheric deposition					
	Cd	Mn	Pb	Zn	SO ₄ ⁼ -S	H+
	(g/ha)				(kg/ha)	(eq/ha)
PERIOD W1 (5/9-5/16/77) (6.9 DAYS)						
Wet	0	0	0	0	0	0
Dry	0.008	3.1	0.81	0.44	0.063	--
Total	0.008	3.1	0.81	0.44	0.063	--
PERIOD W2 (5/16-5/20/77) (4.2 DAYS)						
Wet	0.005	0.31	0.040	0.040	0.070	2.3
Dry	0.023	3.7	2.0	0.29	0.16	--
Total	0.028	4.0	2.0	0.33	0.23	--
PERIOD W3 (5/30-6/6/77) (7.0 DAYS)						
Wet	0.014	0.36	0.23	0.057	0.09	3.8
Dry	0.003	19	1.2	0.31	0.08	--
Total	0.017	19.4	1.4	0.37	0.17	--
PERIOD W6 (7/12-7/18/77) (6.0 DAYS)						
Wet	0.003	0.076	0.042	0.062	0.04	2.2
Dry	0.006	7.0	2.0	0.28	0.16	--
Total	0.009	7.1	2.0	0.34	0.20	--
PERIOD = GROWING SEASON (4/1-10/25/77) (207 DAYS)						
Wet	2.0	26	50	52	9.4	610
Dry	0.69	240	62	13	4.7	--
Total	2.7	270	110	65	14	--
PERIOD = 1977 (CALENDAR YEAR)						
Wet	4.3	40	73	76	13	770
Dry	0.89	310	80	17	6.3	--
Total	5.2	350	150	93	19	--

^aDeposition is expressed as total input on an areal basis during a given time period. These values are calculated as: (measured dry deposition rate) · (time interval). As such, these values are not normalized to a unit time interval.

Table 51. Relative contribution of input by dry processes to the total atmospheric deposition in Walker Branch Watershed

Period	Dry to total deposition ratio (X100 = %)				
	Cd	Mn	Pb	Zn	SO ₄ ⁼ -S
W1(5/9-5/16/77)	100	100	100	100	100
W2(5/16-5/20/77)	82	93	~100	88	70
W3(5/30-6/6/77)	18	98	86	84	47
W6(7/12-7/18/77)	67	99	~100	82	80
1977 growing season	26	89	56	20	34
1977 annual	17	89	53	18	33

annual scale, the dry deposition process constitutes a significant fraction of the total atmospheric input of Cd and Zn ($\sim 20\%$), increasing in relative importance for $\text{SO}_4^{=}$ ($\sim 35\%$), Pb ($\sim 55\%$), and Mn ($\sim 90\%$).

Annual atmospheric deposition rates of the available element fraction to WBW are compared with values reported in the literature for several locations in Table 52. In comparing these values, one should keep in mind possible biases due to differences in sampling strategies (bulk precipitation collection, use of wet/dry collectors to measure each component separately, use of various types of dryfall samplers, and calculation of one input term from theoretical considerations, and consideration of various element fractions). Despite these limitations the data are still useful for comparison in a relative sense. As was the case for similar comparisons of aerosol concentrations and dry deposition rates, these data indicate that the values estimated for WBW are comparable to those reported for remote and rural locations.

The Role of Atmospheric Deposition in Air Pollution Effects on Plants and on Element Cycling

It is apparent that atmospheric input to the forested landscape resulting from the various mechanisms involved in the dry deposition process cannot be neglected in studies of the role of the atmosphere in geochemical cycling or in research on the effects of atmospheric constituents on plants. This process is particularly important in element cycling if the constituent of interest is delivered to the canopy in a relatively mobile form. The results discussed in Chapters III and IV indicate this to be the case for a significant

Table 52. Total atmospheric deposition measured at diverse locations

Location	Airshed Type	Total deposition (g/ha-yr)				
		Cd	Mn	Pb	Zn	SO ₄ ⁼ -S
Ensenada, Mex. ^a	remote coastal	1	600	170	150	--
U. K. ^b	remote coastal	<30	<60	160	520	--
Costa Rica ^c	remote coastal	-	--	--	--	12.5 X10 ³
Cascade Mtns, Wa ^c	remote continental	-	--	--	--	4.1 X10 ³
U. K. ^b	remote continental	<60	76	250	360	--
Hubbard Brook, NH ^d	remote continental	-	--	--	--	18.8 X10 ³
Coweeta, NC ^e	remote continental	-	--	--	--	11.9 X10 ³
Central Alberta, Canada ^f	remote continental	-	--	--	--	18.6 X10 ³
Mt. Moosilauke, NH ^g	remote continental	9	--	20	--	--
Skinface pond, GA ^h	rural	7.2	--	88	--	--
U. K. ^b	rural	<20	97	260	510	--
Shidler pond, IN ⁱ	rural	3	--	150	--	--
WBW(1973-1976) ^j	rural-suburban	-	--	--	--	18.1 X10 ³
WBW ^k	rural-suburban	5.2	350	150	93	19 X10 ³
LaJolla, CA ^a	suburban coastal	1.4	100	500	250	--
U. K. ^b	industrial	<40	<100	270	1200	--
Gary, IN ⁱ	industrial	15	--	1400	--	--

^aHodge et al, 1978 (dry measured, wet calculated).

^bCawse, 1974 (wet/dry collectors used).

^cJohnson et al, 1978 (bulk precipitation).

^dLikens, 1977 (bulk precipitation).

^eSwank and Douglas, 1977 (bulk precipitation).

^fCaiazza et al, 1978 (wet/dry collectors used).

^gSchlesinger et al, 1974 (bulk precipitation).

^hWeiner, 1978 (bulk precipitation).

ⁱPeyton et al, 1976 (bulk precipitation).

^jShriner and Henderson, 1978 (wet/dry collectors used)

^kThis study.

fraction of the particle associated Cd, Pb, Mn, and SO_4^- . The occurrence of these elements in an available form also enhances the potential for plant effects.

Dry deposition of particles is not generally considered to be an episodic event, such as the sudden inundation of the leaf surface by precipitation, but rather to represent a process characterized by the chronic, cumulative exposure of the vegetation to atmospheric constituents. However, certain conditions can combine to create an unusually harsh exposure of the vegetation to potentially toxic material. The elemental deposition rates during precipitation events of short duration, low rainfall volume, and hence generally high concentrations are considerably higher than any of the measured dry deposition rates when expressed on a comparable unit time basis. The possible importance of such events is illustrated by the comparison of the wet and dry deposition rates for several experimental periods in Table 53. The episodic wet deposition rates were calculated as the total areal wetfall input divided by the duration of the precipitation event. Although the duration of the single events which occurred during periods W2, W3 and W6 were relatively short (0.2 to 0.5 hr) the wet deposition rate during the events were ~ 2 to 3 orders of magnitude greater than the dry deposition rates (when expressed on a unit time basis).

From the standpoint of the initial bioreceptor, the upper canopy foliage, this intense, episodic flux of potentially toxic material can play an important role in physiological effects. Two interesting calculations can be presented to further illustrate this point.

Table 53. Comparison of wet and dry deposition rates on a unit time basis. Wet deposition rates are normalized to the duration of each storm event.

Period	Deposition type	Deposition rate ($\mu\text{g}/\text{m}^2 \text{ hr}$)				
		Cd	Mn	Pb	Zn	$\text{SO}_4^{2-}\text{-S}$
W2	Wet	2.7	190	24	23	42,000
	Dry	0.01	1.2	0.62	0.10	50
W3	Wet	2.7	72	45	11	17,000
	Dry	0.0003	1.9	0.12	0.03	10
W6	Wet	3.1	46	25	37	23,000
	Dry	0.001	0.9	0.24	0.03	17
Mean	Wet/dry ratio	4100	80	170	610	1300

Precipitation events of short duration, low volume, and high elemental concentrations are common during the growing season. In many cases these events follow relatively long (5 to 10 days) dry periods characterized by frequent air stagnation conditions and, hence, high air concentrations and dry deposition rates (see Chapters III and IV). When the subsequent precipitation event is very small in volume (on the order of 0.5 to 1.5 mm, not uncommon during the summer) much of the initial precipitation remains on the leaf surface, not being washed off or diluted by subsequent rainfall. The potential for physiological effects is enhanced when this solution of initially high concentration comes into contact with relatively high surface concentrations of dry deposited material. The high concentrations which develop under these conditions are further enhanced during the evaporation of droplets on the leaf surface. The event which occurred during period W2 provides an example of this phenomenon. Using the dry deposition rate of the water soluble fraction of elements to the flat, inert surface it is possible to calculate the approximate surface area concentration of dry deposited material on the leaf prior to the precipitation event, and given a typical leaf of 50 cm^2 , the total water soluble quantity of an element on the leaf surface. These values are summarized in Table 54 along with calculations of the total quantity of wet deposited material, dissolved concentrations in water droplets on the leaf surface, and total deposition to the leaf expressed relative to the leaf internal content.

A precipitation volume of 1.3 mm falling on a 50 cm^2 leaf would deposit $\sim 6 \text{ ml}$ of water. Assuming this volume to be initially retained

Table 54. Potential concentrations of several elements in solution on a typical upper canopy chestnut oak leaf surface (50 cm²) following a brief summer shower. The event of 5/18/78 (0.13 cm) is used as an example.

Parameter	Units	Water Soluble Constituents					
		Cd	Mn	Pb	Zn	SO ₄ ⁻	H ⁺
Surface area concentration of dry deposited, water soluble material	ng/cm ²	0.1	14	2.6	1.2	3600	NM ^a
Mass of dry deposited, water soluble material	ng	5	700	100	60	200X10 ³	NM
Concentration of soluble fraction dissolved by precipitation	μg/l	1	100	20	9	30X10 ³	NM
Concentration of elements in incident precipitation	μg/l	0.35	24	3.1	2.9	16X10 ³	180
Estimated total concentration in solution on the leaf surface	μg/l	1.3	130	23	12	46X10 ³	~180
Potential concentration following evaporation	mg/l	0.1	10	2	1	5X10 ³	~ 20
Total mass of elements in solution on the leaf surface	μg	0.007	0.8	0.15	0.08	300	--- ^a
Total quantity of elements bound within the leaf	μg	0.065	130	0.22	7.0	6000	---
Total quantity of available fraction of elements delivered to the leaf surface during the growing season	μg	1.1	35	30	30	5000	---
Ratio of soluble element deposition during W2 to total leaf content	-	0.11	0.01	0.68	0.01	0.05	---
Ratio of available element deposition during the growing season to total leaf content	-	17	0.3	140	4.3	0.8	---

^aNM = not measured, --- = not estimated.

on the leaf surface will result in a concentration of water soluble material which can be easily calculated. The resulting concentration will add to the already high concentration of elements in the incident precipitation. As this solution begins to evaporate the leaf is exposed, although briefly, to extremely high concentrations of soluble material (brief summer showers often occur in mid to late afternoon and are followed by clearing skies, resulting in several hours of solar radiation to enhance evaporation). Evaporation of the surface moisture to 0.6 ml results in concentrations of dissolved constituents several hundreds to several thousands times higher than typical rain concentrations (Table 54, compare with Table 26, Chapter V).

The physiological effects of surface deposited metals on vegetation either in particulate or dissolved form are very poorly understood, with several conflicting reports on toxicity in the literature (as reviewed by Krause and Kaiser, 1977; and Zimdahl, 1976). However, the estimated pH of this leaf-surface solution (< 2) has been shown to result in adverse effects in several plant species exposed to simulated acid rain (Shriner, 1976).

There are, of course, many assumptions involved in these calculations; however, they result in both over- and underestimates of concentrations. For example, the rainfall volume of 1.3 mm may rapidly run off the leaf removing a considerable quantity of dissolved material. However, personal observations in the field indicated that a considerable quantity of rain can be retained by leaves situated in nearly horizontal positions and under calm conditions. The calculations also assume a uniform surface concentration of dry

deposited material which is a poor assumption as indicated in Chapter VI. Thus, at isolated points on the leaf surface where deposited material accumulates, episodic concentrations could be considerably higher than those estimated here. The calculations also assume no neutralizing capacity of the surface deposited particles or the leaf itself for H^+ . As discussed in Chapter V such a situation apparently can (and did, during W2) occur under some circumstances as indicated by comparable or even lower pH levels in throughfall beneath the developed canopy.

Table 54 also summarizes estimates of the magnitude of the deposition inputs during one event and over the growing season relative to the total leaf internal burden of each element. Elemental content was analyzed for several prewashed chestnut oak leaves following wet digestion as described in Chapter IV. These values thus approximate the total internal metal content of typical leaves. The quantity of Pb estimated to be in solution on the leaf surface following the rain event of 5/18/77 was within a factor of 0.7 of the total Pb content of the leaf. Lesser, but still significant quantities of soluble Cd and $SO_4^{=}$ relative to the internal leaf content were deposited during this event. During the full growing season the leaf surface was exposed to 1 to 2 orders of magnitude more available Cd and Pb and nearly equal amounts of available Zn and $SO_4^{=}$ relative to the total contained within the leaf. The importance of atmospheric deposition in the cycling of these elements in the landscape is apparent.

Integrating the above calculations of annual wet and dry deposition to the watershed with, (1) the earlier discussions of

seasonal variations in precipitation chemistry above and below the canopy, (2) the estimated contribution of in- and below-cloud scavenging to wetfall inputs, and (3) published information on seasonal variations in leaf and branch area indices and leaffall, provides the necessary data with which to calculate the relative contribution of several mechanisms to the total element flux from the atmosphere to the forest canopy and to the forest floor. The distribution and transfer rates between several element cycling components were determined for a typical year using the precipitation chemistry and hydrologic data for 1977 (Chapter V; J. Jones and D. Huff, unpublished data), personal observations of the dates of budbreak (4/1) and leaffall (10/25) for the chestnut oak, and the leaffall biomass data for oak-hickory stands in WBW (Grizzard et al., 1976). Since the below canopy precipitation data (throughfall) was collected primarily beneath chestnut oaks, the leaf internal concentrations measured for chestnut oaks, and the leaffall biomass data determined beneath oak-hickory stands, the resulting input values should be operationally defined as representative of a chestnut oak stand during a typical year.

These calculations are presented in Table 55 in terms of mass transfer rates between compartments and attributed to various mechanisms. The dry deposition component has been separated into three components (flux to the leafy canopy, to branches, and to the litter-soil surface) based on the assumptions discussed earlier regarding the temporal variations in leaf area index and the influence of branches on the dry deposition flux to the full canopy relative to the ground. The breakdown largely reflects the duration of the fully

Table 55. Annual atmospheric and internal fluxes of the available fraction of trace elements and sulfate-sulfur in a chestnut oak stand.

Mechanism or Pathway	Mass transfer				
	Cd	Mn	Pb	Zn	SO ₄ ^s -S
	(g/ha-yr)				(kg/ha-yr)
Total wet deposition above canopy	4.3	40	73	76	13
In-cloud scavenging component	2.5	28	65	-	12
Below-cloud scavenging component	1.8	12	8	-	0.91
Total dry deposition	0.89	310	80	17	6.3
Dry deposition to leafy canopy	0.68	240	62	13	4.8
Dry deposition to branches ^a	0.09	31	8	1.7	0.63
Dry deposition to forest floor ^a	0.12	39	10	2.3	0.87
Throughfall deposition to forest floor ^b	12	1540	110	160	32
Net removal from canopy ^c	7.7	1500	37	84	19
Canopy Leaching ^d	6.9	1230	(-33)	69	14
Leaffall ^e	0.4	910	1.6	50	15
Total flux to forest floor ^f	13	2490	120	210	48
Internal flux to forest floor ^g	7.3	2140	(-31)	120	29
Atmospheric flux ultimately reaching the forest floor ^h	5.2	350	150	93	19

^aCalculated as deposition occurring during the dormant season.

^bTotal wet flux beneath the canopy, excluding stem flow.

^c(Throughfall deposition) - (total wetfall deposition).

^d(Net removal) - (dry deposition to canopy and branches).

^eFlux of the total element fraction bound internally.

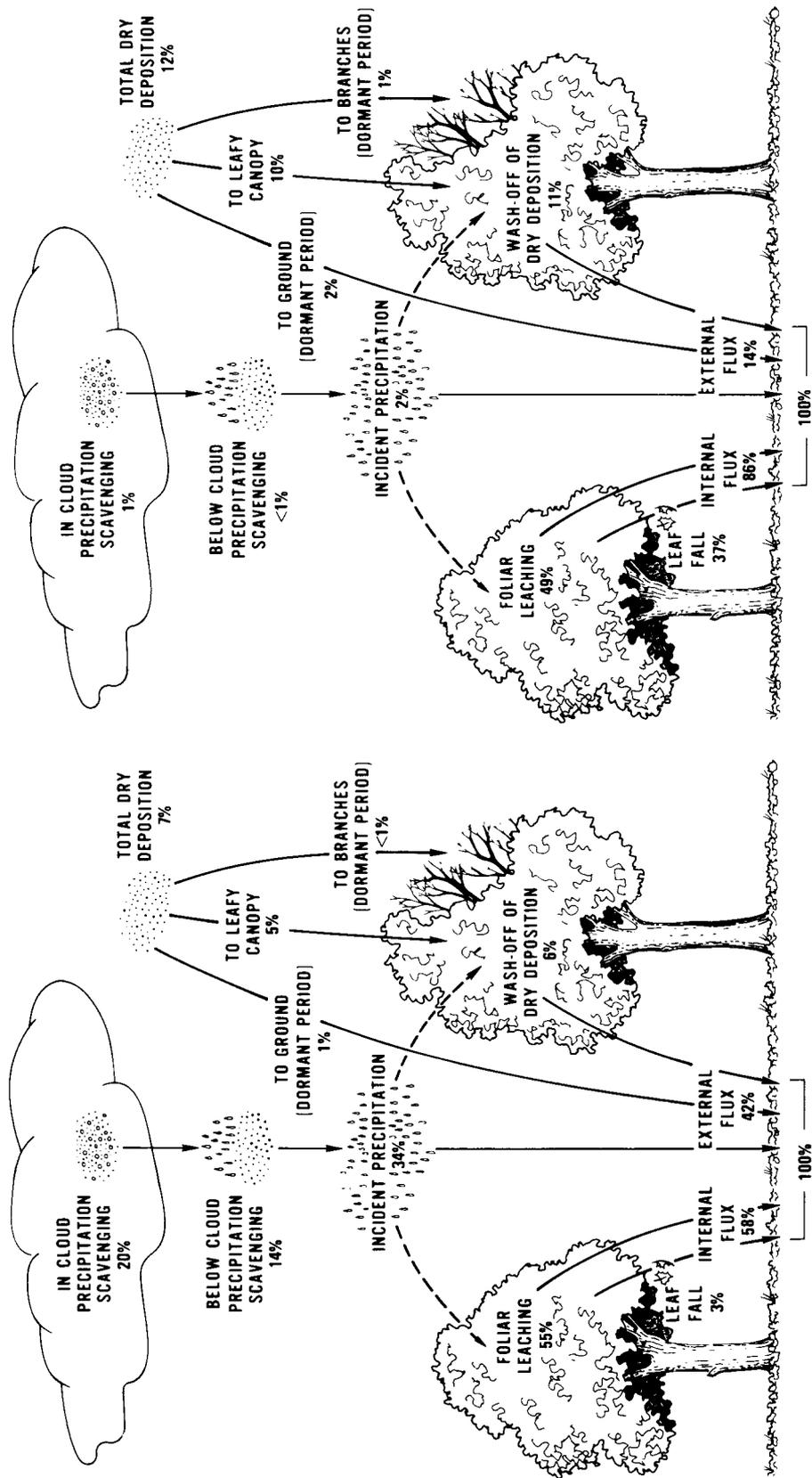
^f(Throughfall flux) + (leaffall) + (dry deposition to forest floor).

^g(Leaffall) + (canopy leaching).

^h(Total wet deposition) + (total dry deposition).

developed canopy, with deposition to the ground and bare soil assumed to be of primary importance only during the dormant season. Throughfall deposition was calculated from the weighted mean concentration of precipitation collected beneath the chestnut oak canopy and thus represents the total wetfall flux to the forest floor including incident precipitation, leaf surface wash off, and foliar leaching. Net removal is the difference between the wet deposition flux above and beneath the canopy, representing the canopy contribution. This term has been used in previous studies as an estimate of the dry deposition component (McColl and Bush, 1977; Mayer and Ulrich, 1974), the foliar leaching component (Raybould et al., 1977), and as an estimate of both (Nihlgard, 1970; Eaton et al., 1973), depending on the element of interest. Foliar (canopy) leaching is the difference between the annual net removal from the canopy and the dry deposition to the surface of the leaves and branches. This net difference is thus taken as an indication of the flux of an element to the forest floor due to internal leaching processes. The total flux to the forest floor includes two components, internally cycled material and atmospheric deposition. The internally cycled material is comprised of the foliar leaching plus leaf fall components (litterfall other than leaves was ignored since it has been reported to contribute a relatively minor amount to the total litterfall on an annual basis; Grizzard et al., 1976).

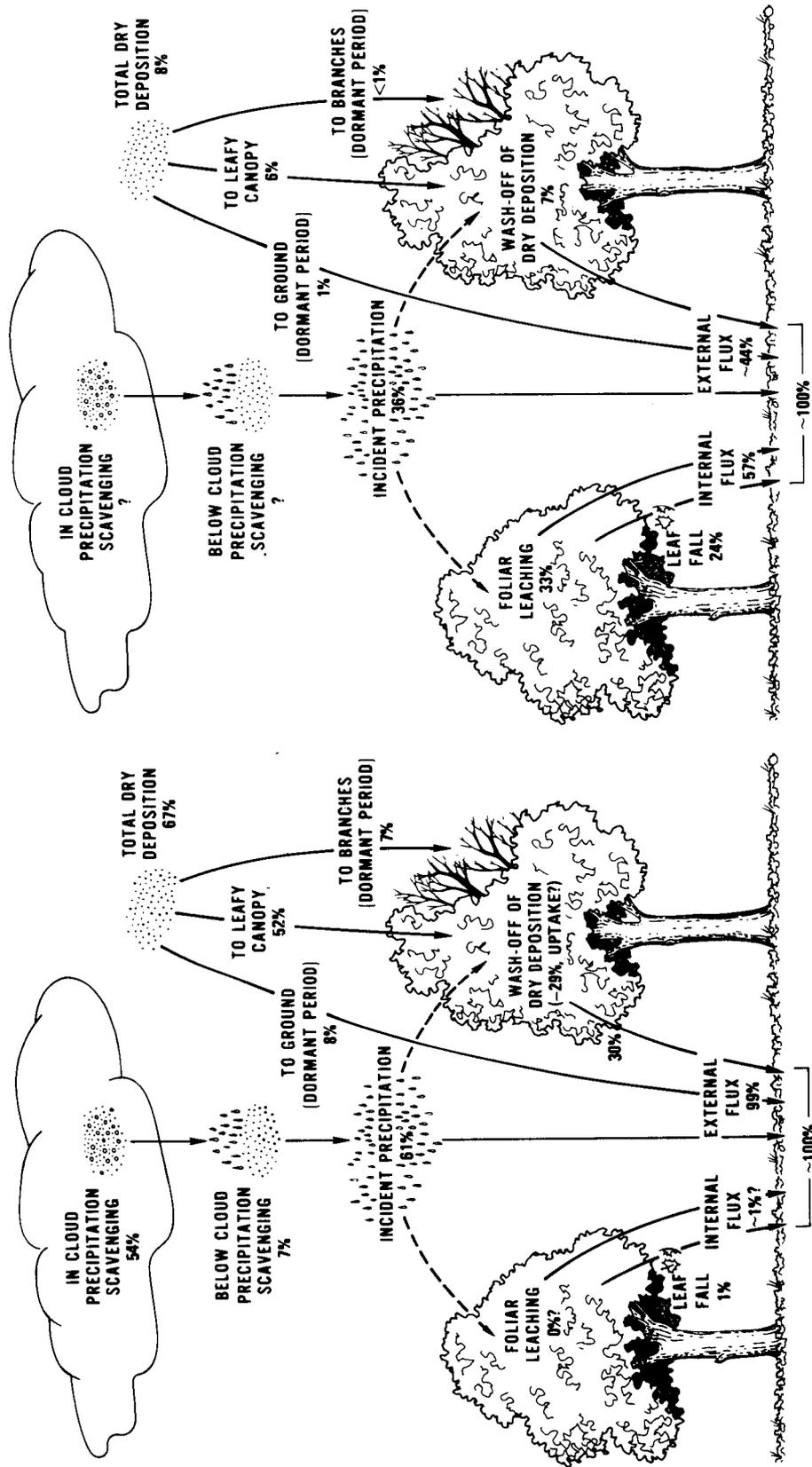
The relative mass transfer rates calculated from Table 55 are summarized in Figures 56 to 58. In each case the elemental flux attributed to a given deposition mechanism or internal cycling pathway



RELATIVE ANNUAL MASS TRANSFER RATES OF Cd TO THE FOREST FLOOR

RELATIVE ANNUAL MASS TRANSFER RATES OF Mn TO THE FOREST FLOOR

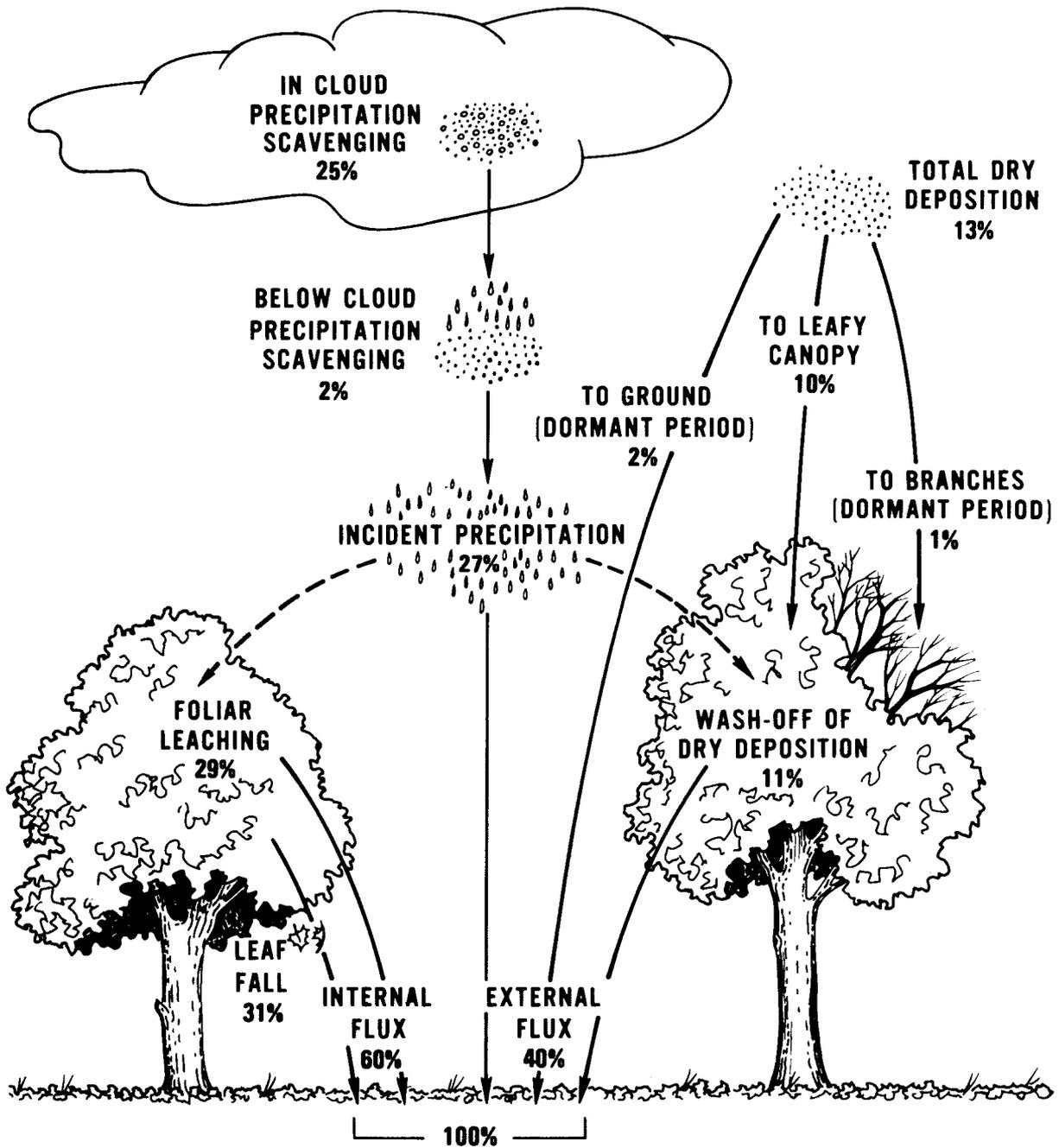
Fig. 56. Annual mass transfer rates of Cd (left) and Mn (right) expressed as a percentage of the estimated total annual flux of the element to the forest floor beneath a representative chestnut oak stand.



RELATIVE ANNUAL MASS TRANSFER RATES OF Zn TO THE FOREST FLOOR

RELATIVE ANNUAL MASS TRANSFER RATES OF Pb TO THE FOREST FLOOR

Fig. 57. Annual mass transfer rates of Pb (left) and Zn (right) expressed as a percentage of the estimated total annual flux of the element to the forest floor beneath a representative chestnut oak stand.



**RELATIVE ANNUAL MASS TRANSFER RATES
OF SO_4^{2-} -S TO THE FOREST FLOOR**

Fig. 58. Annual mass transfer rates of sulfate expressed as a percentage of the estimated total annual flux of the element to the forest floor beneath a representative chestnut oak stand.

has been expressed as the percentage of the total flux to the forest floor. The largest fraction of the total flux to the forest floor is attributable to several different mechanisms depending on the element of interest. The mechanism/pathway of greatest relative importance to the total mass transfer of Cd and Mn is foliar leaching. This was expected for Mn as previously discussed in Chapters IV and V. In fact, of the total Mn flux, 86% is estimated to be due to internal element cycling processes, not surprising for a micronutrient with a relatively high mobility in the soil/plant system (Chapter V). Although Cd exhibited the second highest throughfall to incident precipitation concentration ratio (Chapter V), there was little indication from the leaf washing experiments that Cd was a significant internal, leachable component. The leaf bagging experiments did, however, suggest that foliar Cd leaching could occur. The indication that the Cd flux to the forest floor is largely related to internal processes (58% internal, 42% external) is surprising given the absence of a physiological requirement for Cd by plants. Underestimation of the dry deposition rate of Cd to the canopy would result in overestimation of the leaching component. However, the dry deposition rate of Cd to flat, inert surfaces and living leaves were in good agreement for the period of comparison (W1). Clearly, more extensive investigations of the dry deposition rates of Cd over longer time periods will be required to test foliar leaching hypothesis. Relative to the total Cd flux to the forest floor, the internal and external sources are of nearly equal importance, with the internal flux contributing $\sim 16\%$ more. Since the internal flux is composed largely of canopy leachate this implies that

Cd must cycle very rapidly through the foliage in a readily leachable form, very little being bound within the leaf. Since Cd is characterized by a relatively high solubility in surface water/soil systems (Turner et al., 1977) it may cycle passively through the plant in the translocated water. This rapid plant cycling could represent a mechanism whereby Cd toxicity is avoided.

The situation for Pb is somewhat difficult to interpret. Recall from Table 55 that net removal from the canopy was actually less than the predicted dry deposition to the canopy. This resulted in a negative canopy leaching term, suggesting absorption of the dry deposited Pb. The relative amount of Pb absorbed was 29% of the estimated total Pb flux to the forest floor and represented $\sim 20\%$ of the atmospheric deposition of Pb. As discussed in Chapter IV, there are several lines of evidence each of which point to foliar absorption of dry deposited Pb in the canopy. The relatively small contribution of leaf fall to the Pb flux may indicate translocation of Pb from leaves to roots. This has been previously reported by Krause and Kaiser (1977) for plants treated with foliar applications of Pb salts, including PbO. Regardless of the fate of dry deposited Pb, it is apparent that the flux of this element through the chestnut oak stand is the most sensitive to external sources, which comprise $\sim 99\%$ of the total Pb flux to the forest floor. The element with the next most important external source is Zn (44% of the mass transfer to the forest floor is related to atmospheric deposition processes). However, the total downward flux of this element is nearly equally divided between

wet deposition (36%), canopy leaching (33%), and leaffall (24%), the dry deposition process contributing $\sim 10\%$.

The mass transfer of S, in the form of soluble sulfate, is also nearly equally divided between leaffall (31%), canopy leaching (29%), and wet deposition (27%), with the input due to dry deposition of aerosol sulfate contributing an additional 13%. The relative contribution of internal and external pathways to the total flux to the forest floor is also similar to Zn, with the internal processes comprising 60% of the total. This mass transfer budget for S is, of course, missing a very important component, the dry deposition and foliar absorption of SO_2 . The dry deposition experiments were not specifically designed to include the collection of dry deposited SO_2 . However, as discussed in Chapter IV, much of the dry deposition of SO_2 may occur to wet leaf or inert surfaces, followed by oxidation to SO_4^- . Hence it is possible that a large fraction of the SO_4^- collected in the deposition plates or washed from leaf surfaces was due to SO_2 deposition. The relationship between surface wetness and the deposition rate of SO_4^- discussed in Chapter IV supports this contention. However, direct absorption of SO_2 gas through leaf stomates obviously could not have been measured by the inert surfaces. The annual input due to gaseous uptake has been previously estimated for WBW on an areal basis, using a yearly average predicted ground level SO_2 concentration for this area, and assuming leaf uptake for 8 hours/day over a 7 month growing season (Shiner and Henderson, 1977). The resulting value of 25 kg/ha (as S) was assumed to represent an upper limit. If this value is roughly applicable it

further emphasizes the importance of external sulfur sources to the mass transfer to the forest floor.

Conclusions

Aerosol Chemistry, Particle Size, and Atmospheric Transport

1. Elemental size distribution and concentrations of the available fraction (water soluble plus dilute acid leachable) of aerosol associated elements and the manner in which they are influenced by various atmospheric parameters suggest a soil dust source for Mn, secondary atmospheric particle and combustion sources for Pb and SO_4^- , and both small particle combustion and large particle dispersion sources for Cd and Zn.
2. Trace element enrichment factors, using aluminum as the reference element, indicated Pb and Zn in aerosols to occur in concentrations too high to suggest crustal derivation. This was also true for Cd in aerosols collected on the lower impactor stages (smaller particles). However, large particle Cd, and Mn in all size ranges could have been crustally derived.
3. Elemental ratios to Mn, which is soil derived in ambient aerosols and behaves as a matrix element during coal combustion, indicated the following: (a) ratios of each element to Mn increased substantially from precipitator ash to stack ash to plume ash collected at a large, modern coal-fired power plant, (b) the highest ratios occurred in

the smallest particles, and (c) mixing of the plume with the background air mass resulted in the decrease of the ratios of Cd, Zn, and $\text{SO}_4^{=}$ to Mn, but in an increase in the Pb/Mn ratio.

4. Experimental sampling periods characterized by increased precipitation volume and duration are also characterized by increased mass median diameters (MMD) of aerosol-associated Cd, Pb, Zn, and $\text{SO}_4^{=}$ but decreased MMD of aerosol-associated Mn.
5. As regional air stagnation increases, the air concentrations of the available fraction of particulate Cd, Pb, Zn, and $\text{SO}_4^{=}$ increase, while the air concentration of the available fraction of particulate Mn decreases.
6. Substantial amounts ($> \sim 75\%$) of the available fraction of Mn, Zn, Cd, and Pb in aerosols were soluble in distilled water. In addition, significant fractions ($> \sim 65\%$) of the total Mn and Cd were water soluble. However, smaller fractions ($< \sim 30\%$) of the total Pb and Zn in aerosols were water soluble.
7. The solubility and the water soluble to available element ratio (termed relative solubility) both increased with decreasing particle size and with the duration of atmospheric water vapor saturation during the sampling period.
8. Ambient aerosols exhibited considerably higher relative solubilities than aerosols collected in the stack of a coal-fired power plant. However, relative solubilities

increased during plume aging (measured by plume travel from 0.25 to 7 km) to levels similar to those measured for ambient aerosols. The two preceding observations suggest the importance of aerosol hydration in elemental solubility.

9. Wind direction exhibited no apparent effects on the MMD of aerosol-associated trace metals or sulfate. However, slight increases in air concentrations accompanied an increased frequency of winds from "other than local source" directions. This suggests that atmospheric chemistry over WBW is generally reflective of regional air transport phenomena rather than a direct reflection of local source emissions. As an apparent result of the utilization of tall stacks at the two major local coal fired power plants, the elemental air concentrations at WBW do not reflect a significant influence of local coal combustion, being more similar to concentrations measured at remote and rural locations than at urban or industrialized areas.

Particle Deposition by Dry Processes

1. Two methods for the empirical determination of dry deposition rates, flat, inert surfaces situated in the upper canopy, and washing of upper canopy leaves, proved amenable to field and laboratory studies.
2. The circumstances of sampling provided one period (7 days) for which the dry deposition rate to inert, flat surfaces could be compared with that estimated from sequential leaf

washing. The agreement in deposition rates was very good for Cd, $\text{SO}_4^{=}$, Zn (within $\sim 30\%$), and Mn (within a factor of 2) but poor for Pb (an order of magnitude higher rate measured to the inert surface). Leaf surface absorption of dry deposited Pb could be a factor.

3. Sample to sample variability in the surface area concentrations of trace metals and sulfate on leaves was similar for samples collected across the watershed (on a scale of 100's of m) and from the same tree (on a scale of cm).
4. The leaf leaching experiments revealed several lines of evidence that internal foliar leaching was a significant source for Mn (particularly during late growing season) and $\text{SO}_4^{=}$ (during early growing season), a lesser source for Cd and Zn (late growing season), but an insignificant source of Pb.
5. The water soluble to available element ratios (relative solubilities, RS) of trace elements associated with dry deposited particles were lower than similar ratios exhibited by suspended particles collected on a total air filter. The inverse relationship between aerosol RS and particle size suggest the deposited particles to exhibit a larger particle size than the parent suspended particle population.
6. Scanning electron and light microscopy of biological and inert deposition surfaces indicated the presence of considerable numbers of relatively large ($> 10 \mu\text{m}$) fly ash

particles as well as dispersed soil fragments, primarily on upward facing surfaces, suggesting particle sedimentation to be a major mechanism of dry deposition to these upper canopy elements.

7. Possible sources of large-particle fly ash were determined by calculating upper level air mass backward trajectories for time intervals comparable to large-particle tropospheric residence times. These trajectories were found to traverse two major regional urban centers and five major regional coal-fired power plants with sufficiently rapid travel times to account for the large-particle transport.
8. An interesting observation in several scanning electron photomicrographs was the association of submicrometer sized fly ash with considerably larger (5 to 20 μm) fly ash and scoriaceous particles and the agglomeration of several submicron fly ash particles into large aggregates. The removal of these large particles from the atmosphere is primarily controlled by sedimentation, which may account for the often high concentrations of small-particle-associated elements (Pb, $\text{SO}_4^{=}$) in dry deposited material.
9. The dry deposition rates of Cd, Pb, Zn, and $\text{SO}_4^{=}$ to the upper canopy were correlated with air stagnation frequency, total air concentrations of each element, and the frequency of winds from directions other than those influenced by local sources. Thus, dry deposition, as well as air concentrations, is not detectably enhanced by local emissions.

10. The relative order of the mean dry deposition rates calculated for 5 experimental periods was comparable to the order of atmospheric concentrations, as follows (in $\mu\text{g}/\text{m}^2$ day): $\text{SO}_4^=$ (1500 ± 600) > Mn (25 ± 6) > Pb (6.5 ± 2.2) > Zn (1.4 ± 0.3) > Cd (0.072 ± 0.034).
11. Expressing deposition rates relative to air concentrations results in deposition velocities (V_d) for the available element fraction to individual upper canopy elements. The mean V_d values reflected the general particle size distribution of each element and indicated the generally used value of $V_d = 0.1 \text{ cs}^{-1}$ may be an underestimate (Cd = 0.4, cs^{-1} , Mn = 6, Pb = 0.1, Zn = 0.4, $\text{SO}_4^= = 0.1$).

Chemistry of Precipitation Collected Above and Beneath the Forest Canopy

1. The distribution of Cd, Mn, Pb, Zn, and $\text{SO}_4^=$ concentrations in incident precipitation and Cd, Pb, Zn, and $\text{SO}_4^=$ in throughfall do not depart significantly from log normality. The distributions of H^+ concentrations in rain and throughfall do not depart significantly from normality.
2. Nonparametric statistical analysis of the multisite precipitation/throughfall data indicated that only one element, Mn, exhibited significant inter-site differences in concentration in both incident precipitation and throughfall. The significant internal foliage source of Mn undoubtedly accounted for the difference between throughfall

sites, with concentrations at one site beneath a single mature chestnut oak consistently higher than at all other sites.

3. Analysis of variance and covariance procedures were applied to the data to reveal seasonal effects on chemistry of rain above and below the canopy. For elements exhibiting significant seasonal effects, the maximum concentrations of Pb, SO_4^- , and H^+ in rain occurred during the summer while the peak for Zn occurred in the fall. In throughfall the highest concentrations of Pb and SO_4^- occurred during summer, Zn during fall, and H^+ during winter when foliar interception of rain is at a minimum. Although Cd and Mn did not exhibit significant seasonal effects, concentrations in rain also tended to increase in summer. The summer maxima may be in response to synoptic meteorologic conditions which result in elevated aerosol concentrations due to air stagnation, and in generally lower rain volumes per event and hence less dilution of scavenged material.
4. The concentrations of Cd, Pb, Zn, and SO_4^- in incident precipitation were correlated with air concentrations of particles in several size classes.
5. Inter-element correlations in incident precipitation suggested a possible common source of SO_4^- and H^+ , such as scavenging of acid sulfate aerosols. A large correlation coefficient between Mn and SO_4^-

concentrations in rain may be related to the ability of Mn to catalyze the oxidation of SO_2 in rainwater.

6. Dilution phenomena in incident precipitation were indicated by significant negative correlation coefficients between element concentrations and rainfall amount, storm duration, and intensity.
7. The expected positive correlations between rain concentrations and time since previous rainfall were not apparent, suggesting the local atmospheric reequilibration with the regional air mass to be relatively rapid.
8. A simple model was applied to the empirical relationship between rain concentration and rainfall volume in an attempt to estimate the relative importance of in-cloud vs below-cloud scavenging to the wet deposition of each element. The calculations indicated that, on an annual basis, $\sim 90\%$ of the wet deposition of the primarily small-particle atmospheric constituents Pb and SO_4^- was attributable to scavenging by in-cloud processes, while for the large particle-associated elements, Cd and Mn, removal by below-cloud scavenging was somewhat more important, accounting for 30 to 40% of the deposition. Theoretical calculations of scavenging efficiencies confirmed the greater importance of the in-cloud processes in Pb deposition relative to Mn deposition.
9. The interception of incoming rain by the forest canopy resulted in a net increase in the concentrations of Cd, Mn,

Pb, Zn, and $\text{SO}_4^{=}$, but a net decrease in the concentration of H^+ . The elemental enrichments on an annual basis were as follows: Mn (factor of 160), Cd(4), Zn and $\text{SO}_4^{=}$ (3), Pb (2.7), H^+ (0.9). Simple linear regression models were applicable in the prediction of throughfall concentrations of Mn, Pb, Zn, $\text{SO}_4^{=}$, and H^+ during the growing season based on concentrations in incoming rain. The variances of concentrations in incoming rain accounted for the following fractions of the variances in throughfall: $\text{SO}_4^{=}$ and Zn ($\sim 80\%$), Pb and Mn ($\sim 55\%$), H^+ (27%).

10. The uptake of H^+ and concomitant loss of several elements by the canopy suggests a cation exchange process, with the net exchange seen to increase with increasing free acidity of the incoming rain and with increasing residence time of the rain on the leaf surface. On an equivalent basis, the hydrogen exchange can easily account for the trace cation leaching from the canopy, but for $< 10\%$ of the estimated total cation leaching from the canopy during the growing season, indicating the importance of other processes as well.
11. In throughfall collected beneath the chestnut oak canopy during the growing season, weak acids were responsible for approximately twice as much of the total acidity ($57 \pm 4\%$ as weak acids) than was the case for incoming rain ($33 \pm 3\%$; mean \pm standard error), although the contribution of weak acids to free acidity (H^+) was generally negligible. The

leaching of weak acids from the canopy may be related to the uptake of H^+ and consequent cation displacement suggesting some degree of physiological alteration of the leaf surface.

Mass Transfer to the Landscape

1. The estimated total annual atmospheric deposition to WBW of the elements of interest was similar to values reported in the literature for remote and rural locations. These rates were as follows (in g/ha yr): $SO_4^{2-}-S = 19 \times 10^3$, Mn = 350, Pb = 150, Zn = 93, Cd = 5.2.
2. On an annual scale the dry deposition process constitutes a significant fraction of the total atmospheric input of Cd and Zn ($\sim 20\%$), increasing in relative importance for SO_4^{2-} ($\sim 35\%$), Pb ($\sim 55\%$), and Mn ($\sim 90\%$). However, when measured during short term periods (days), the ratio of dry/total deposition for any element may range over an order of magnitude.
3. The importance of wet deposition to the bioreceptor as an episodic inundation of the leaf surface is seen from a comparison of wet and dry deposition rates on a comparable unit time basis (i.e., wet deposition rate calculated for the duration of an individual storm). Wet deposition rates expressed in this manner are 2 to 3 orders of magnitude greater than measured short-term dry deposition rates.

4. The potential for plant effects can be further illustrated by calculating the deposition to an individual leaf during one event and over the growing season relative to the total leaf internal pool of the element. A single dry/wet event was seen to deposit a quantity of Pb to the leaf surface equal to $\sim 70\%$ of the internal pool. Deposited quantities of Cd and $\text{SO}_4^{=}$ were equal to 11 and 5%, respectively, while quantities of Mn and Zn were $\sim 1\%$ of the internal pool. During the growing season, the leaf surface was exposed to 1 to 2 orders of magnitude more Cd and Pb, and nearly equal amounts of Zn and $\text{SO}_4^{=}$, relative to that contained within the leaf.
5. The total annual flux to the forest floor beneath a representative stand of chestnut oaks was attributable, to a significant extent, to external sources (atmospheric deposition by wet and dry processes) for Pb (99%), Zn (44%), Cd (42%), $\text{SO}_4^{=}$ (39%), and Mn (14%), the remainder attributable to internal element cycling mechanisms (leaffall plus foliar leaching). The pathways of highest relative importance to the total flux to the forest floor of each element were varied: foliar leaching for Cd (55% of the total) and Mn (49%), dry deposition for Pb (67%), wet deposition for Zn (36%), and leaffall for $\text{SO}_4^{=}$ (31%).

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APPENDIX A

WALKER BRANCH WATERSHED ELEMENT CYCLING STUDIES:
COLLECTION AND ANALYSIS OF WETFALL FOR TRACE ELEMENTS AND SULFATE

WALKER BRANCH WATERSHED ELEMENT CYCLING STUDIES:
COLLECTION AND ANALYSIS OF WETFALL FOR TRACE ELEMENTS AND SULFATE

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ABSTRACT--A precipitation sampling network designed specifically to optimize sample collection and handling for trace analysis has been established at Walker Branch Watershed, Tennessee, to accurately quantify the atmospheric input of trace elements. The network consists of 6 rain activated wetfall collectors of the AEC-HASL design which have been modified with respect to construction materials and arrangement of components in order to minimize trace element contamination. Wetfall has been collected through a combination of event and continuous sampling at 4 throughfall, 1 ground level incident, and 1 above canopy incident precipitation sites. Trace metal analyses were performed by graphite furnace atomic absorption spectroscopy without preconcentration to reduce the chance of contamination. Sulfate-S was determined by a modified methylthymol blue technique. Both methods underwent quality control and interlaboratory comparison studies and were judged to be sufficiently sensitive and accurate to be applicable to trace level rainwater analysis. The overall procedural variability was determined to be low enough to distinguish natural variations in precipitation chemistry from those variations imposed by the analyst.

Preliminary data for water year 1975-76 yielded weighted mean concentrations (and coefficients of variation) for Cd, Mn, Pb, Zn, and $\text{SO}_4\text{-S}$ in incident precipitation as 0.89 (108%), 1.5 (97%), 5.5 (54%), 7.1 (111%), and 840 (48%) $\mu\text{g/l}$, respectively. For storm events spatial effects on incident and throughfall rain chemistry were significant. Temporal effects on chemistry were also significant at some incident and throughfall sites. In comparison with published trace element concentrations in rain, the levels at WBW were closer to those measured at rural and remote forested locations than those observed near industrial or urban centers.

Reprinted from Watershed Research in Eastern North America: A Workshop to Compare Results, Vol. 1. 2/28-3/3/77. Edited by David L. Correll. Chesapeake Bay Center for Environmental Studies, Smithsonian Institution, Edgewater, MD 21037.

INTRODUCTION

It is generally accepted that various human activities, especially combustion of fossil fuels, introduce certain trace elements into the atmosphere and subsequently into the aquatic and terrestrial environment at rates comparable to those of natural processes. Existing data has illustrated this point for S, Pb, Se, and Hg (Kellog et al. 1972; Hitchcock and Wechsler 1972; Tatsumoto and Patterson 1963; Klein et al. 1975). Although the literature contains information on the anthropogenic emission rates and atmospheric concentrations of many elements, data for their removal, such as deposition rates to the terrestrial landscape, have not been readily available until quite recently (Schlesinger et al. 1974; Cawse 1974; Gatz 1975). Of the two major removal mechanisms, wet deposition is of particular importance due to both its episodic nature and the fact that particle and gaseous-associated elements are delivered to the forest canopy partly in solution, thereby enhancing the possibility of absorption by vegetation surfaces. In addition, wetfall may simultaneously remove previously deposited or impacted material from the canopy increasing the mobility of particle-associated trace elements.

The importance of precipitation in nutrient and major element cycling on a watershed scale has been well documented (Fisher et al. 1968; Johnson and Swank 1973; Likens et al. 1967; Swank and Henderson 1976). However, few studies have combined the unique sample collection design and possessed the analytical sensitivity required for trace analysis of wetfall with the facilities of a well-calibrated, easily monitored, terrestrial ecosystem. These considerations have prompted us to investigate the atmospheric input of selected trace elements into Walker Branch Watershed (WBW) as part of a more comprehensive program dealing with the geochemical cycling and transport mechanisms of elements through the terrestrial-aquatic ecosystem. The specific objective of the precipitation research project is to characterize deposition of Cd, Mn, Pb, Zn, and $\text{SO}_4\text{-S}$ onto the watershed by wet and dryfall on time scales commensurate with the identification of meteorologic and other factors regulating the magnitude of episodic trace element inputs. The purpose of this paper is to present a detailed discussion of analytical and sample collection methods developed, modified, or tested specifically for use in trace analysis of precipitation. Further

discussions of initial results of this program have been reported elsewhere (Andren and Lindberg 1977; Turner and Lindberg 1977).

The research facilities associated with Walker Branch Watershed, an intensively monitored forest catchment on the Oak Ridge National Laboratory (ORNL) reservation, provides an ideal field laboratory in which to examine deposition and accumulation of airborne trace contaminants derived from coal combustion processes. This catchment is situated within 20 km of two large and one small coal-fired power plants with combined coal consumption of over 7×10^6 metric tons/year. Earlier and continuing studies on the watershed provide correlative information on meteorology, hydrology, chemistry, and biology which are essential to our interpretation of the deposition measurements (e.g. as described in related papers on Walker Branch site description, Harris, this symposium; hydrology, Henderson et al., this symposium; stream chemistry, Henderson et al., Turner et al., this symposium; and organic matter cycling, Comisky et al., this symposium).

Materials and Methods

Many problems have been associated with the collection of rainfall for major element and nutrient chemistry and have been reviewed by Galloway and Likens (1976). These difficulties are, in general, compounded when trace analysis is intended due to both the high probability of sample contamination and possibility of element loss to container surfaces (e.g. see the recent review paper by Morgan, 1975). All of these problems were considered during the development of the precipitation sampling network on Walker Branch Watershed.

Precipitation collector design - The utility of using wet/dry or wet only samplers (automatic devices designed to expose the collector surfaces only during precipitation) for collection of rain for chemical analysis has been well established (Galloway and Likens, 1976; Bennett et al., 1977). Accordingly we chose the USAEC (now USERDA) - HASL design, a reportedly reliable (Galloway and Likens, 1976) wet/dry sampler which we felt could be relatively easily modified to minimize contamination from metal components of the sampler itself or from spurious dry deposition into the wetfall samples. The HASL collector is a 110 V AC powered, rain activated unit, the

basic plans for which are available from the Health and Safety Laboratory (Energy Research and Development Administration, New York, New York 10014) catalogued as wet/dry fallout collector. The major advantages of the basic design are: (1) its ability to minimize the "splash off" of dry deposition and other contaminants on the lid into the collector area during precipitation (by the use of a sharply sloped lid which pivots 12 cm away from the collection bottles during rain), (2) its ability to minimize the chance of dry deposition entering the wetfall collector during dry periods (by the use of a pivoting lid fitted with a plastic covered foam insert which results in a positive seal over the wetfall collector), (3) its portability (the entire sampling unit can be handled by two people and weighs ~25 kg), (4) its ability to separately sample dryfall and wet deposition such as rain, sleet, or snow, and (5) its ability to collect a number of individual samples in separate bottles in each sampler simultaneously due to the relatively large ($\sim 0.07 \text{ m}^2$) surface available for collection of wetfall.

The unit as modified for our purposes is illustrated in Figure 1. Major modifications to the basic design are as follows: (1) substitution of a molded sheet-nylon lid attached with stainless steel and nylon rivets to stainless steel supporting pivot arms (thus all components above the level of the sample bottles are composed of relatively inert, acid washable materials), (2) enclosure of the foam lid sealing surface in a polyethylene bag to allow thorough cleaning or replacement prior to each use, and (3) substitution of a Wong type two dimensional sensor for the HASL three dimensional sensor grid and relocation of this metal coated wet sensor grid from the lid of the sampler to a separate post mounted 2 m away from and below the level of the collector. In addition the electronics for the sensor unit which relays the signal to the motor drive of the collector lid is relocated in a separate waterproof case. A simple 3-position switch mounted on the electronics case allows for overriding the wet sensor so as to either open the sampler during dry periods or close the sampler during wet periods as field maintenance requires.

Site location and sampling procedures - The placement of the individual samplers is illustrated in Figure 2 along with the relative location of WBW in the eastern United States. The sampling network consists of four

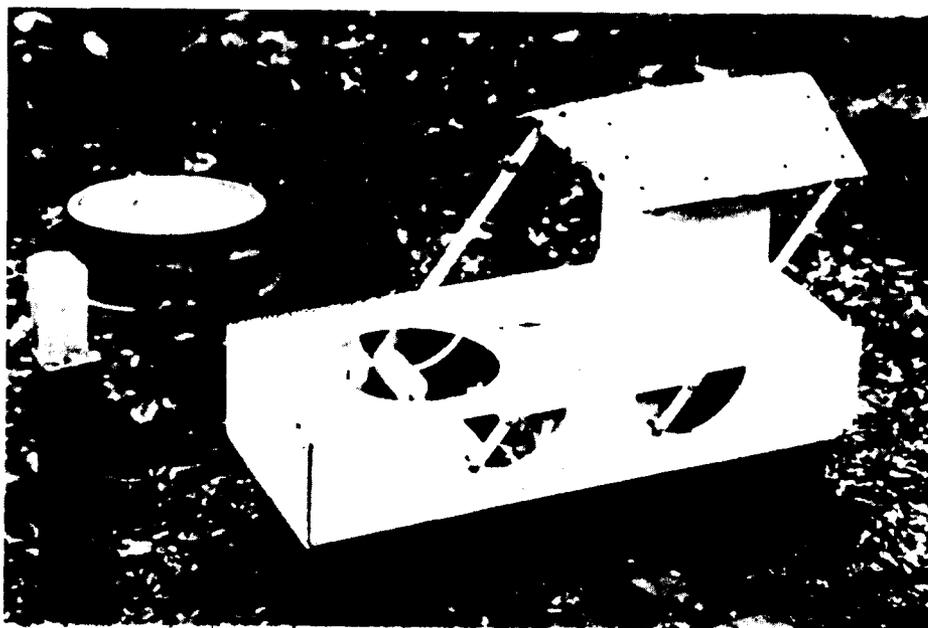


Fig. 1. Modified HASL wetfall/dryfall collector used at Walker Branch Watershed. The sampler is shown as used for wetfall collection only.

throughfall (T), one ground level incident (GI), and one above canopy incident (CI) collection sites.

At two sites, throughfall and incident precipitation samples are paired to facilitate event comparisons between rain chemistry above and below the canopy or at ground level both below the canopy influence and in the open. The most unique sample location is the canopy incident site located 10 m above the deciduous canopy atop a 33 m walkup meteorological tower on the western ridge of the watershed. This collector is situated above all manmade metal structures in the watershed (except for two adjacent 2 m aluminum lightning rods) and is believed to yield the "cleanest" possible samples from a contamination standpoint. This is extremely useful when comparing the metal concentrations in rain at various sites from the same event for the purpose of identifying contaminated samples. In addition this site yields the only measure of precipitation chemistry before it enters the

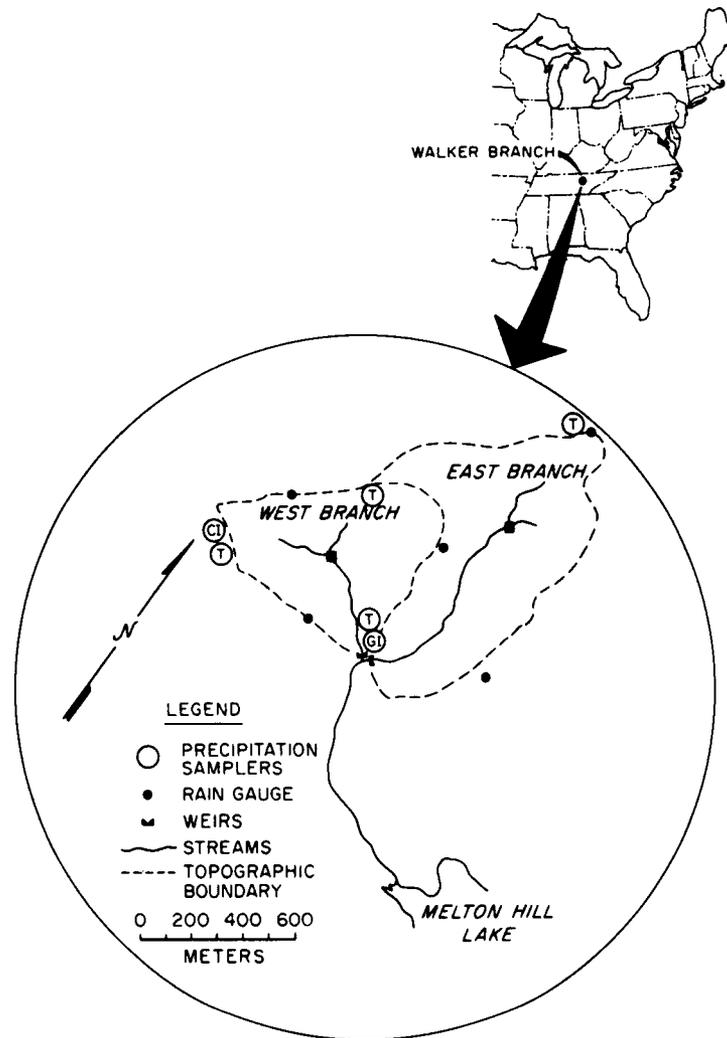


Fig. 2. Walker Branch Watershed study area, indicating trace element wetfall collection sites and rain gauge locations.

sphere of watershed influence. The paired throughfall sampler is located approximately 40 m south of the base of the tower. The ground level incident (GI) site is located adjacent to the streambed in the valley below the ridge where the tower stands, approximately 110 m in height below the CI sampler. The composition of rain collected at this site (compared to the CI site) thus exhibits the additional effect on precipitation chemistry of particle and gas washout from the air mass within the watershed. The remaining two throughfall sites are located on the central and northern ridges of the watershed. All throughfall collectors are situated beneath mixed hardwood stands (predominantly oak, hickory; beech, poplar in one case).

Rainfall volume is monitored continuously at 5 ground level rain gauge sites (see Figure 2) by Fisher-Porter automatic recorders which allow calculation of the weighted average daily rainfall input to the watershed (Henderson et al., this symposium). In addition, at each HASL sampler site a portable wedge type rain gauge is located which is read on an event basis thus giving an indication of intersite variability in rainfall.

Two different methodologies were employed in the timing of sample collection depending on the intended use of the data. Samples used to construct trace element budgets for the watershed were collected on a continuous 14 day basis at the paired CI and throughfall site. Samples were never retrieved during periods of rain but rather between events. Event samples, as described below, were also used in the calculation of weighted mean trace element concentrations in rain for application to the watershed mass balance studies.

For the purpose of characterizing trace element deposition by wetfall and throughfall on time scales commensurate with identification of meteorological factors regulating the magnitude of trace element inputs, samples were collected occasionally on an event basis at all six sites. Although the importance of event collection has been stressed (Galloway and Likens, 1976; Bennett et al., 1977; Andren and Lindberg, 1977) the problem of event definition continues to plague precipitation researchers. In our studies the samplers were serviced and activated just prior to initiation of rainfall (generally < 24 hours) and all samples were retrieved soon after precipitation had ceased and weather conditions indicative of a general clearing had appeared (normally within 36 hours of the last recorded

rainfall). This was considered as an event. Using this procedure we have infrequently (during winter months) sampled a series of closely spaced periods of rain, each of short duration, as if they were one event. In general, however, this method led to sampling of well defined precipitation events for which correlative meteorological parameters could be measured or obtained. For example, from 9/75 to 8/76 we sampled 14 such events, the characteristics of which are summarized in Table 1. By using this definition we were able to sample 34% of the precipitation input by volume during this period as individual events while minimizing the length of time sample bottles were in the field both before and after the rainfall occurred.

In practice the collection procedure is designed (1) to minimize the chance of contamination of the sample container in the field prior to the occurrence of rainfall and to the sample itself during precipitation and prior to retrieval from the field; (2) to reduce the chance of chemical alteration of the original sample by evaporation, degassing, biological action, and sorption phenomena. Although in the original design the large polypropylene bucket in the HASL sampler was intended to act as the rainfall collector, we used individual prewashed 500-1000ml polyethylene bottles fitted with 12 cm prewashed polypropylene funnels for the collection of all samples (using separate bottles for trace metal samples and pH and sulfate

Table 1. Characteristics of Individual Precipitation Events Sampled During 9/75-8/76

Period	Number of Events Sampled	Fraction of Total Rainfall Sampled (%)	Statistic	Time Period ¹ (days)	Precipitation Amount (cm)	Duration ² (days)	Individual Periods of Rain ³
September-October	3	88	mean	4	4.4	0.9	1.3
			range	1-6	3.1-5.5	0.5-1.4	1-2
November-February	6	25	mean	2.4	2.0	0.6	1.2
			range	0.2-5	0.6-4.1	0.2-1.0	1-2
March-April	2	25	mean	3.7	3.7	2.2	1
			range	3.7-3.8	1.8-5.6	0.6-3.7	1
May-August	3	31	mean	3.2	3.8	0.6	1
			range	1-5	2.2-6.9	0.5-0.8	1
Annual	14	34	mean	3.1	3.1	0.9	~1
			range	0.2-6	0.6-6.9	0.2-3.7	1-2

¹Total length of time samples were deployed (i.e. bottle set-up to retrieval).

²Total length of time of continuous measurable precipitation (where measurable is taken as 0.03 cm in an hour, as measured at a nearby NOAA meteorological station).

³Where each period must be preceded by at least 6 continuous hours of no measurable precipitation.

samples). The use of the funnel-bottle arrangement, though decreasing the surface area for wetfall collection somewhat, has a number of advantages: (1) each component is more easily subjected to rigorous acid/distilled water washing procedures than is the large bucket, (2) the funnels can be easily fitted with 200 μ mesh nylon screen, to exclude coarse organic debris from entering the sample bottles, for use at throughfall sites, (3) individual bottles can be subjected to different washing and sample preservation techniques (e.g. acidification for trace metal samples) for stabilization of various chemical parameters and still be used in the same sampler, (4) samples can be collected, stored, and analyzed from the same bottles thus minimizing transfers and chance of contamination, and (5) replacement of the funnels and bottles is far less expensive than the large buckets.

In preparation for event sampling polyethylene bottles for trace element samples were cleaned in the laboratory by rinsing with distilled, deionized, filtered water (produced in a glass still and drawn from a Millipore Milli-Q clean water system with a 0.5 μ after-filter), leaching with 2N reagent grade HNO_3 for 16 hours on a reciprocating shaker, rinsing profusely with Milli-Q water, and finally leaching for at least 8 hours with Milli-Q water. Repeated analyses of the Milli-Q water used in our laboratory over the last year has indicated reproducible, acceptably low levels of various metal contaminants (see Table 2 and compare with wetfall concentrations in Tables 8 and 9.

Polyethylene bottles for collection of samples for pH, conductance, or sulfate determinations were washed as above but eliminating the acid leaching step. Polypropylene funnels were washed as above for use with either trace analysis collection bottles or pH bottles, the acid or water leaching step being replaced by a soaking step using polyethylene vats of 2N

Table 2. Trace Element Concentrations in Distilled, Deionized, Filtered Water (Milli-Q Water) Used in Trace Analysis Work (in $\mu\text{g/l}$)

Statistic	Cd	Cu	Cr	Fe	Mn	Pb	$\text{SO}_4\text{-S}$	Zn
Mean	0.01	0.10	0.21	0.17	0.04	0.07	70	0.39
r	0.003	0.16	0.22	0.06	0.05	0.06	7	0.26
range	<0.005-0.014	<0.01-0.43	<0.01-0.43	<0.05-0.24	<0.05-0.16	<0.01-0.16	67-83	0.2-0.78
n	9	6	8	5	8	7	5	4

HNO₃ or Milli-Q water. In addition, the polyethylene covered foam lid insert and polypropylene bucket used in the sampler itself (which have been removed from the sampler, rinsed, and stored in the laboratory since the previous sample collection) were rinsed with 2N HNO₃, and profusely rinsed with distilled water immediately prior to use.

In the field the HASL samplers were hand washed with distilled water and Kimwipes to remove any dry deposition, especially from components above the level of the sample bottles. Samplers were then assembled, each containing 1-2 each of trace element and pH bottles with funnels depending on whether replicate samples from each site were desired. Trace metal sample bottles were on some occasions preacidified prior to placement in the field to stabilize the low level metal concentrations in rain during the period of sample collection and storage prior to retrieval. In other cases samples were acidified upon return to the laboratory (see discussion).

Analytical methods - The parameters pH and specific conductance were measured immediately upon return to the laboratory on samples allowed to reach room temperature. Hydrogen ion concentration (pH) was determined by standard methods on samples equilibrated with atmospheric CO₂ using a combination reference-pH electrode (Galloway et al., 1976). Conductance was measured on a separate aliquot using a conductance bridge/probe arrangement and corrected to 25°C. Another 25 ml aliquot for sulfate was transferred into a 25 ml prewashed polyethylene bottle and stored at 4°C in the dark until analysis (<7 days). The importance of storing samples in a full bottle became apparent after discovery of evaporation problems when small aliquots (25 ml) were stored in large bottles (200 ml) prior to analysis. For standards of 3-5 mg/l sulfate (1000-1700 µg/l SO₄-S), concentration was observed to increase over a 10 day storage period (4°C in the dark) by up to 30%, presumably due to solution evaporation. This effect was not apparent for samples stored in full bottles (D. Bostick, personal communication).

Sulfate was determined using an improved methylthymol blue colorimetric procedure with a Technicon Auto Analyzer II system. The method has been described in detail by McSwain et al. (1974) and involves the following: (1) pH is determined to assure that highly acid samples are not analyzed without neutralization (samples of pH < 3 are evaporated to dryness and diluted to volume with distilled water), (2) samples of suspected high

sulfate-S levels ($>3300 \mu\text{g/l}$) are diluted into the $300\text{--}2100 \mu\text{g/l}$ range, (3) replicate samples, spiked samples, and standards in 4 ml aliquots are loaded into the autosampler tray, and (4) analysis is initiated. To check for interference problems caused by solution matrix effects selected samples from a given set were spiked with 2 mg/l sulfate as Na_2SO_4 ($670 \mu\text{g/l SO}_4\text{-S}$). If a matrix problem occurred as evidenced by reduced recoveries, all samples in the set were spiked to determine recovery efficiencies and the concentrations corrected accordingly. Alternately, if very low recoveries ($<80\%$) occurred the sample was reduced in volume on a steam bath and returned to volume with distilled water in an attempt to minimize matrix effects. In this case spiked samples were carried throughout the entire procedure. Reported concentrations were determined by the standard curve method with the limit of detection for natural water samples, as determined by experience, being $66 \mu\text{g/l}$ as $\text{SO}_4\text{-S}$.

Table 3 contains information on analytical precision (based on replicate analyses of the same sample), accuracy (based on analysis of gravimetrically prepared Na_2SO_4 standards), and spike recoveries ($\%R$) for rainfall samples. For all three parameters the statistics apply to a number of replicate analyses, check standards, or spikes for different samples analyzed during the past year. For the concentration range of $\text{SO}_4\text{-S}$

Table 3. Analytical Precision, Accuracy, and Spike Recoveries for Sulfate-S in Precipitation Samples Analyzed by the Technicon Methylthymol Blue Procedure

Concentration Range ($\mu\text{g/l}$)	Precision			Accuracy			Spike Recovery		
	\bar{x}	σ	n	\bar{x}	range	n	\bar{x}	σ	n
300-1700	4%	3	22	1%	-5 to 7.5	28	96%	8	22
1700-3300	3	1	7	—	—	—	98	6	7
>3300	2	1	10	—	—	—	99	4	10
300-6700 (organic rich samples ¹)	10	10	8	—	—	—	93	11	15

¹Dissolved organic carbon in the $10\text{--}50 \text{ mg/l}$ range, and samples highly colored. These samples represented rainwater after it had leached through the 01 organic litter layer.

normally encountered in precipitation samples (300-1700 $\mu\text{g}/\text{l}$) the average precision and accuracy were $\pm 4\%$ and 1% respectively. The calculated mean accuracy is somewhat misleading in that signed (\pm) relative deviations from expected values were averaged. When the absolute values are used the mean accuracy for samples in this range is 3% . Matrix effects were generally nonexistent ($\%R > 90\%$) except for the samples designated as organic rich. These samples represented rainwater which had percolated through the O1 soil horizon and were highly colored solutions with dissolved organic carbon (DOC) concentrations of 10-50 mg/l. Efforts to determine the nature of the matrix effects included sample oxidation with H_2O_2 to reduce the DOC, sample evaporation and re-dissolution in distilled water, and analysis by an alternate sulfate method (spectrokinetic zirconium-methylthmol blue procedure performed on a centrifugal fast analyzer; see Bostick, 1976, for procedure details). The spectrokinetic method yielded the only results which did not indicate a matrix interference. As this method was based on the measured rate of color formation and not final color density it was felt that the source of the interference was the actual color of the original sample (D. Bostick, personal communication). However, since rain and throughfall samples never exhibited this color problem, further research was not pursued. The important point is that, although the exact nature of the matrix interference was not discovered, sulfate recoveries on environmental samples should be checked to determine if matrix effects are influencing the analytical results of the standard methylthmol blue technique.

Samples for trace metal analyses, previously stabilized by the addition of concentrated Ultrex HNO_3 to $\text{pH} < 1.5$ (see discussion), were stored at 4°C in the dark until analysis (generally < 30 days, never > 6 months). All metal analyses were performed using a Perkin Elmer (PE) Model 503 atomic absorption spectrometer with deuterium background correction in conjunction with a P.E. HGA 2100 graphite furnace (GFAAS). Standard conditions as specified by the manufacturer were employed in all analyses. Because of reported matrix effects for some natural aqueous samples analyzed by GFAAS (Cruz and Van Loon, 1974; Edmunds et al., 1973; Barnard and Fishman, 1973) all solutions were analyzed by the method of standard additions. This routinely involved duplicate injections of 25-100 μl of sample into the graphite furnace using meticulously cleaned Eppendorf pipets (Sommerfield et al., 1975) followed by injection of another aliquot of the same sample

spiked with a Fisher trace metal standard (as the nitrate salt). Although previously reported matrix problems generally involved complex solutions (seawater, digests, leachates) such effects, manifested as both depressed and enhanced signals for spiked solutions, occurred during the analysis of some precipitation samples. The use of deuterium background correction did not result in any significant alleviation of matrix effects. Thus because of potential interferences with varying sample composition the method of standard additions is recommended for routine analysis of precipitation samples by GFAAS.

The published instrumental sensitivity of this method (Kerber, 1974), if achievable in practice, can eliminate the need for sample preconcentration by chelation, cation exchange, evaporation, or ashing prior to analysis for many natural freshwater samples. Such pretreatment methods expose the sample to numerous sources of trace contamination by reagent addition, sample transfers, or simply by exposure to the atmosphere for an extended period of time (Tolg, 1972; Morgan, 1975). In addition, problems of trace element losses during various preconcentration steps have been documented (Bruland, 1974; Begnoche and Risby, 1975). Thus if the actual sensitivity is sufficient to detect trace concentrations of metals in precipitation without preconcentration, many of the above problems can be circumvented.

Lisk (1974) stated that for GFAAS it may be background contamination from reagents and impurities rather than instrument sensitivity which controls the limits of detection (L.D.). The operational detection limits as determined from experience during the past year are compared with Ultrex HNO_3 (the only "reagent" added to the rain samples prior to analysis) and the lowest measured rainwater values in Table 4 for the four elements routinely studied and three additional which were analyzed in selected samples. The minimum values recorded for rain approached the operational L.D. for Cd and exceeded that for Mn. Extreme instrument stability occurred infrequently but resulted in transient L.D. lower than those reported for normal operating conditions. However by comparing these values with those in Tables 8 and 9 (see discussion) which include statistics for precipitation analyzed over a 12 month period, it is apparent that this technique affords sufficient sensitivity for direct trace analysis of rain samples. Only in the case of Cr and possibly Cd was the acid blank within a factor of 5 of the minimum value. The acid blank for Mn was within a factor

Table 4. Comparison of Operational Detection Limits, Blank Concentrations, and Minimum Measured Precipitation Concentrations for Selected Trace Metals Analyzed by Graphite Furnace Atomic Absorption Spectrometry

Element	Detection Limit from Experience ($\mu\text{g/l}$)	Acid Blank Concentration ¹ ($\mu\text{g/l}$)	Lowest Precipitation Values Measured ($\mu\text{g/l}$)
Cd	0.005	<0.005	0.01
Mn	0.05	0.004	0.03
Pb	0.05	0.005	0.34
Zn	0.05	0.005	1.30
Cr	0.01	0.2	0.09
Cu	0.01	0.003	0.27
Fe	0.05	0.05	5.00

¹Ultrex HNO₃ added to a sample at the rate of 5 ml/l. Values represent final diluted reagent blank additions as calculated from the manufacturers certificate of analysis of stock acid.

of 8 of the minimum while for the other elements the minimum concentrations exceeded the blank values by factors of 70-260. However, compared to the majority of the values recorded for precipitation (Tables 8 and 9), the reagent blanks are insignificant.

Analytical precision and accuracy were determined soon after installation of the GFAAS system in July 1975 as part of an interlaboratory comparison of trace analyses (Turner and Lindberg, 1976). This experiment involved comparison of 4 laboratories (ORNL, 2 independent analytical chemistry labs, and one university analytical group) using similar P.E. GFAAS units to analyze replicate natural water samples and diluted EPA quality control trace element standards. Some results relevant to this discussion are illustrated in Table 5. The reported precisions actually involve more than simple analytical reproducibility as samples and standards were divided into 12 equal aliquots in separate prewashed polyethylene bottles 30 days prior to analysis. The labs received 3 bottles of each sample type. Although ORNL performed as well or considerably better than the other laboratories in both precision and accuracy, certain problems became apparent. These were primarily the precision of Zn and accuracies of

Table 5. Summary of Pertinent Analytical Quality Control Results Obtained from an Interlaboratory Comparison of Trace Analysis by GFAAS. Modified from Turner and Lindberg (1976).

	Accuracy ¹ (expected and reported values in µg/l)									Precision ² , as Coefficient of Variation (%)			
	Expected	ORNL		Lab 2		Lab 3		Lab 4		ORNL	Lab 2	Lab 3	Lab 4
		R ³	A ⁴	R	A	R	A	R	A				
Cd	0.18	0.22	20%	0.1	44%	0.17	-6%	0.2	11%	+2%	+38%	+22%	+16%
Mn	1.3	1.2	-8	0.8	-38	0	130	2.0	54	1	1	17	10
Pb	2.8	3.6	29	4.5	61	2.1	-25	4.1	46	2	25	8	7
Zn	1.0	0.9	10	0	100	0	100	5	400	44	14	8	36

¹Accuracy as relative deviation from expected value of EPA control sample.

²Precision as coefficient of variation of analyses of replicate precipitation samples.

³R = reported concentration (as mean of 3 replicates).

⁴A = accuracy as defined above, in %.

Pb and Cd analyses. Completing this interlaboratory test 60 days prior to initiation of full-scale precipitation sampling for trace metals on WBW allowed us to evaluate and modify procedures then in use. As operator experience with the GFAAS equipment increased through continued analysis of natural water samples, both precision and accuracy improved considerably. Table 6 reports quality control results for another series of EPA control samples prepared and analyzed from 1/76 to 2/77. Although this series of "standards" as supplied by EPA contained metals in higher concentrations than analyzed in the first set, we feel the results reflect an overall improvement in quality control. The precisions are all $\leq 10\%$ and the accuracies indicate results generally within 5% of expected values (ranging from 19% low to 14% high). When compared with the measured natural variation of trace element concentrations in precipitation it is apparent that both accuracy and precision are sufficient to quantitatively detect such natural variability (see discussion, Table 8).

Table 6. Analytical Precision and Accuracy for EPA Quality Control Trace Element Samples Analyzed by GFAAS

Element	Expected Concentration ($\mu\text{g/l}$)	Measured Concentration ($\mu\text{g/l}$)			Precision ¹ (%)	Accuracy ² (%)	
		\bar{x}	σ	n		\bar{x}	range
Cd	5.2	5.1	0.4	16	8	-3	-19 to 8
Mn	26	25.2	1.3	13	5	-3	-11 to 6
Pb	22	21.9	0.9	19	4	-0.5	-5 to 7
Zn	11	10.8	1.1	10	10	-2	-17 to 14

¹Expressed as the coefficient of variation (σ/\bar{x}).

²Expressed as the relative deviation of the measured value from the true value.

Results and Discussion

The major problems inherent in the study of the chemical composition of rain have been well stated by Galloway and Likens (1976). Briefly these involve efficiency of the sampler to collect a representative sample, postdepositional chemical alterations of the sample, storage effects on sample chemistry, sample contamination, and the definition of what constitutes a precipitation event. Some aspects of these problems have been addressed in the methods section, the remainder will be considered here.

The problem of representative precipitation sampling with automated devices largely relates to the ability of the sensor head to detect wetfall as it occurs and to open the device immediately. The collection efficiency of the HASL samplers was tested by two methods over different time scales. On an event basis the expected volume catch of a sample was calculated given the exposed funnel surface area and quantity of rain measured at that site. This yielded efficiencies ranging from 1% low to 3% high, averaging 1% low. Monthly checks were made by comparing volume catches in bottles placed inside and outside the automatic sampler. These resulted in efficiencies ranging from 16% low to 18% high but, as above, averaged 1% low. This indicates that from the standpoint of representative precipitation collection, event sampling is also preferred. It is suggested that similar

checks be continued throughout a sampling program to assure that collection efficiencies do not decrease with time as has been noted for some collectors (Galloway and Likens, 1976).

Given the limited quantity of rain often collected and the problems inherent in obtaining representative uncontaminated samples of "dissolved" trace constituents from "total" samples by the method of membrane filtration (Marvin et al., 1970; Robertson, 1968; Spencer and Manheim, 1969; Morgan, 1975) we decided to analyze routinely for only total trace element concentrations in rain (operationally defined as that material in solution at $\text{pH} = 1.5$). In general acid leachable trace metal concentrations would be greater than simple water soluble metal concentrations for any given sample. However, some samples were fractionated by filtration (0.5μ membrane) in the lab or by a method of "in situ" membrane filtration as the precipitation is collected. To date contamination problems have precluded the use of much of this data with the exception of "dissolved" Mn and Pb and "particulate" Zn (analyzed by digestion of the particles retained on the membrane filter). This preliminary data was useful in that it indicated Mn to be 88-95% in the dissolved phase, Pb 75% dissolved, and Zn 8% particulate (hence 92% dissolved) which suggests that total sample concentrations may represent from 75-92% of the true soluble levels of these metals.

The recognized problem of trace metal stabilization against container wall losses from aqueous samples (Morgan, 1975) was addressed by two methods. Trace element sample bottles were preacidified with concentrated Ultrex HNO_3 before placement in the field or precipitation samples were acidified to $\text{pH} < 1.5$ immediately upon return to the laboratory by the addition of concentrated Ultrex HNO_3 at the rate of 5 ml/1000 ml of sample. The latter method assumes reversibility of any adsorption reactions between container walls and trace elements (Patterson et al., 1973; Tolg, 1972). While the former method has the advantage of allowing the sample to be acidified as it is collected and while it remains in the field, it has the disadvantages of (1) exposing the initial rainfall to a concentrated acid medium resulting in unknown chemical alterations of the sample as well as exposing other samples in the HASL collector to strong acid vapors, (2) uncontrollable final acid concentration in the sample to be analyzed leading to both matrix problems and variable acid blanks, and (3) greater chance of

contaminants leaching from the sample bottle while exposed to the concentrated acid prior to rainfall.

Thus if it could be demonstrated that trace element-polyethylene sorption reactions are reversible or simply not significant for the time period involved, the latter procedure of acidification after collection would be desirable. Duplicate bottles, one preacidified and one not, were placed in the HASL samplers prior to a storm event. On return to the laboratory, following sample retrieval, the second bottle was acidified as described above and both samples analyzed for Cd, Mn, Pb, and Zn. This procedure was performed on 5 separate storms. The mean deviations of the nonpreacidified (NPA) sample concentrations from the preacidified (PA) sample concentrations, expressed as $(NPA-PA)/PA$, were as follows: Cd -20%, Pb -3%, Mn +1%, and Zn +8%. Thus only Cd exhibited significant losses in samples acidified after collection. The low losses (gains) for Pb and Mn agree with observations of other workers (Ter Haar et al., 1967; Struempfer, 1976). The apparent increase in Zn levels may relate to higher blank concentrations as the preacidified samples had higher acid to sample ratios than those acidified in the lab. Thus the procedure chosen was acidification of all trace metal samples immediately following collection; the discrepancy for Cd was judged to be on the same order as previously described limits of analytical precision and accuracy for low level Cd determinations.

A further test of the reliability and utility of the precipitation network was to determine the precision of replicate samples from a single HASL collector for individual rain events. Four events were sampled wherein duplicate bottles were used in one collector for trace metal, sulfate, and pH determinations. The results are summarized in Table 7. The precision of replicate samples ranged from <1 to 26% with Cd and Zn exhibiting the largest variability. This agrees with the instrumental precisions reported earlier. The importance of this type of precision determination, which represents a combination of sample collection, handling, preservation, and analytical reproducibility, is for comparison with observed "natural" variations. The goal of identifying mechanistic relationships between precipitation trace element chemistry and meteorologic, locational, seasonal, and air quality parameters cannot be reached unless natural variations can be resolved from procedural variations.

Table 7. Results of Replicate Sampling of Storm Events for Determination of Overall Procedural Precision

Event	Statistic	Cd	Mn	Pb	Zn	SO ₄ ²⁻ -S	pH
1	replicates ¹ precision ²	0.18,0.17 3	1.1,0.79 16	3.5,3.4 1	6.2,8.4 15	550,580 2	4.02,4.29 3
2	replicates precision	1.2,2.0 25	1.3,1.5 7	5.8,4.8 9	— —	530,490 3	3.77,3.94 2
3	replicates precision	0.31,0.26 9	1.9,1.7 6	5.3,5.7 4	1.7,1.4 10	1180,1170 <1	3.81,3.83 <1
4	replicates precision	0.17,0.10 26	0.4,0.3 14	6.1,5.4 6	0.42,0.28 20	543,540 <1	4.59,4.31 3
	mean precision σ	16% 12	11% 5	5% 3	15% 5	2% 1	2% 1

¹Concentrations in $\mu\text{g/l}$.

²Precision as coefficient of variation of the mean.

The results of the initial year's effort with the network are summarized in Table 8 which presents measured concentration ranges and coefficients of variation (relative standard deviations of the arithmetic means) for incident precipitation (I) and throughfall (T) for all sites during 9/75-8/76. Also included are mean coefficients of variation between different I sites or T sites for all storms sampled (thus representing location effects for given events) and coefficients of variation for any given site over the year (thus representing temporal effects at individual sites). In studying precipitation chemistry of trace elements, it must be accepted that large concentration variations do occur. Table 8 illustrates this point for various combinations of the rain data. In any one storm or at one location and time during the year an isolated measurement of a trace element concentration can give a value which varies by up to 100% or more from the mean. This emphasizes the importance of employing a multisite network over an annual cycle to determine wetfall inputs.

Comparing the observed variabilities with the estimated overall procedural precisions presented in Table 7 gives an indication of the possible significance of spatial and temporal effects on precipitation chemistry. For most data combinations the observed variabilities exceed the

Table 8. Observed Variability in Precipitation (Incident = I, Throughfall = T) Chemistry for the Period 9/75-8/76

Sample Description	Cd	Mn	Pb	Zn	SO ₄ -S
All I, range (ug/l)	0.01-3.9	0.03-8.40	0.34-12.0	1.3-36	360-1920
All I, C.V. (%)	108	97	54	111	48
All T, range (ug/l)	0.11-3.7	19.5-110	3.9-8.2	4.1-18.0	730-6600
All T, C.V. (%)	130	73	26	38	76
Storm I, C.V. (%) ¹	86	48	45	79	4
Storm T, C.V. (%)	96	67	19	39	25
<u>Individual Stations C.V. (%)²</u>					
I, ground level (GI)	82	82	57	77	42
I, above canopy (CI)	188	138	42	96	45
T#1, paired with GI	46	76	18	42	92
T#2, paired with CI	95	26	42	35	12
T#3	25	20	73	108	26
T#4 ³	—	—	—	—	—

¹Storm values are presented as the averages of the coefficients of variation calculated for each storm sampled for either all I sites or all T sites.

²Individual station coefficients of variation are calculated for any one station based on 12 months data.

³Throughfall site #4 was not operational for a sufficient length of time to be included.

procedural precisions by >2 to 46 times. Thus significant site effects during storm events occur for all elements in both incident precipitation and throughfall. Temporal effects on rain chemistry are significant both above and below the influence of the forest canopy for Pb, Zn, and SO₄-S at all sites and Cd and Mn at all but one site. However, for certain elements the smallest observed coefficients of variation are within a factor of 2 of the procedural precisions (e.g., measured variability of Cd at T#3). For these values the significance of the measured variations may be questionable. Research is presently underway to determine the factors controlling each type of observed variability. Speculation on the factors controlling rain chemistry and the geochemical significance of precipitation and dryfall inputs to mineral cycling in Walker Branch Watershed is discussed elsewhere (Turner and Lindberg, 1977; Lindberg et al., 1977).

A comparison of trace element concentrations in incident precipitation at WBW with other research locations is presented in Table 9. The values

Table 9. Trace Element Concentrations in Precipitation at Diverse Locations

Location	Station Type	Concentrations in Rain ($\mu\text{g/l}$)				
		Cd	Mn	Pb	Zn	$\text{SO}_4^{2-}\text{-S}$
32 U.S. Stations ¹	mixed	—	12	34	107	—
8 Delaware Watersheds ²	agricultural	7.9	—	7.1	—	—
Mt. Moosilauke, New Hampshire ³	forested	0.6	—	13.4	—	—
Coweeta Experimental Watershed, North Carolina ⁴	forested	—	—	—	—	670
Hubbard Brook Experimental Watershed, New Hampshire ⁵	forested	—	—	—	—	1100
Chadron, Nebraska ⁶	rural	0.26	5.4	4.3	10	—
7 Stations in the United Kingdom ⁷	urban	18	—	173	—	—
1 Station in the United Kingdom ⁷	rural	32	—	25	—	—
Walker Branch Watershed, Tennessee ⁸	forested	0.89	1.5	5.5	7.1	840

¹Lazrus et al., 1970.²Biggs et al., 1973.³Schlesinger et al., 1974.⁴W. Swank, personal communication.⁵G. Likens, personal communication.⁶Streumpler, 1976.⁷Harrison et al., 1975.⁸This work.

for WBW, Mt. Moosilauke, Chadron, Coweeta, and Hubbard Brook are weighted mean concentrations (total mass of an element deposited divided by total rainfall volume sampled; Likens et al., 1967) while others are given as arithmetic means. Although different methodologies were employed in each of these studies it is interesting to note the very large variations in reported mean trace element concentrations in rain. Manganese ranges over a factor of 8, Zn over a factor of 16, Pb over a factor of 31, and Cd over a factor of 123. This obviously relates to differences in site characteristics with respect to proximity to major urban or industrial centers. Although literature data are sparse, the lowest concentrations consistently occur in the rural Nebraska location or in one of the

relatively remote forested areas. Comparing our preliminary data with that of other workers, it appears that precipitation trace element concentrations in WBW are not significantly elevated above those reported in more remote areas.

Acknowledgements

The authors wish to acknowledge the following individuals: J. Alford and E. Culver for construction of the modified HASL samplers, K. Talbot, D. Bostick, and C. Clark for analytical assistance, and D. Shriner and G. Henderson for comments on the manuscript.

This research has been sponsored by the Energy Research and Development Administration under contract with Union Carbide Corporation. Publication No. 1024, Environmental Sciences Division, ORNL.

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APPENDIX B

WALKER BRANCH WATERSHED PRECIPITATION AND THROUGHFALL DATA, 1976-1977

ABBREVIATIONS FOR TABLE B1

PERIOD	Calendar dates during which sample bottles were in place in the watershed.
STATION	Station codes conform to those give in Figure 20, Chapter V.
MEASPT	Rainfall volume in cm (see Table 32, Chapter V; figures are valid to three significant figures).
COND	Conductance in $\mu\text{mhos}/\text{cm}^2$.
CD, MN, PB, ZN	Concentrations in $\mu\text{g}/\text{l}$.
SULFATE	Concentrations in mg/l .
COL_YEAR, MONTH, DAY	Date of sample retrieval.
OR_PPT	Published precipitation for the National Weather Service Oak Ridge site (inches).
ANTECEDT	Time since previous precipitation, in days.
DURATN	Time interval of events sampled, in days.
NO_EVENT	Number of events sampled per period.
SMPLTYPE	I = incident precipitation, T = throughfall.
INTENSTY	Rainfall intensity, in mm/hr .
HYDROGN	H^+ concentration, in $\mu\text{eq}/\text{l}$.
SEASON	Expressed relative to the forest canopy condition.
LEAFSTAT	Status of the deciduous canopy with respect to leaf growth.

Table B1. Walker Branch Watershed Precipitation and Throughfall Data, 1976-1977

OBS	PERIOD	STATION	HEASPTT	PH	COND	SULFATE	CD	HW	PB	ZN	COL_YEAR
1	3/26-3/30/76	T1	4.9530	3.92	53.2	3.68	0.090	5.80	6.9	9.1	1976
2	4/20-4/22/76	T1	0.4572	4.65	106.0	19.80	1976
3	4/29-5/3/76	CI	1.7272	4.79	12.3	1.39	1976
4	4/29-5/3/76	T1	1.8288	5.90	32.5	3.69	1976
5	4/29-5/3/76	T2	1.7780	5.38	15.7	4.77	1976
6	5/6-5/11/76	CI	2.2352	4.21	24.6	2.37	0.630	0.80	4.2	14.8	1976
7	5/6-5/11/76	T2	2.2606	4.72	20.6	5.12	0.510	110.00	4.5	18.0	1976
8	5/6-5/11/76	T1	2.2606	4.61	19.1	6.90	0.240	30.00	6.6	6.4	1976
9	5/27-5/28/76	CI	2.3368	4.59	12.4	1.63	0.170	0.40	1.1	1.7	1976
10	5/27-5/28/76	T3	2.2860	5.32	26.9	4.60	2.600	26.00	5.6	10.2	1976
11	5/27-5/28/76	T1	2.2098	5.18	111.0	2.18	0.300	62.00	8.5	11.8	1976
12	5/27-5/28/76	T2	2.7940	4.78	23.8	3.84	1.300	87.00	3.9	11.1	1976
13	5/27-5/29/76	CI	6.2992	4.31	18.2	1.62	0.100	0.30	2.6	1.4	1976
14	5/29-6/11/76	CI	2.2860	3.91	46.8	4.03	2.200	0.90	4.8	4.2	1976
15	6/15-6/20/76	CI	6.6548	4.08	36.5	2.80	0.34	0.34	5.8	4.2	1976
16	6/15-6/20/76	GI	6.8580	4.17	26.3	2.43	0.090	1.70	10.4	5.2	1976
17	6/15-6/20/76	T1	6.6040	4.32	30.1	6.06	0.160	25.20	6.5	4.1	1976
18	6/15-6/20/76	T2	8.1788	4.73	29.1	4.42	0.110	65.00	8.2	9.4	1976
19	6/15-6/20/76	T3	3.9878	4.52	41.5	6.70	3.700	19.50	8.1	10.3	1976
20	6/11-6/28/76	CI	6.7056	4.11	30.3	.	0.050	0.38	6.0	1.3	1976
21	6/28-7/5/76	CI	6.0198	4.07	35.2	3.49	0.003	0.03	6.0	1.9	1976
22	7/5-7/19/76	CI	4.3180	4.14	31.4	3.49	0.210	4.90	7.0	4.5	1976
23	7/22-8/13/76	CI	3.5814	3.87	57.7	5.80	0.100	1.80	5.8	10.4	1976
24	8/13-8/31/76	CI	4.9530	4.11	28.7	2.86	0.029	0.57	2.6	2.2	1976
25	8/31-9/11/76	CI	1.5240	4.00	43.5	4.12	0.660	0.87	8.8	12.9	1976

OBS	MONTH	DAY	OR_PPT	ANTECEDT	DURATM	NO_EVENT	SHP1TYPE	INTENSITY	HYDROG	SEASON	LEAFSTAT
1	3	30	2.56	0.58	3.71	1	T	0.69003	120.226	BUDBREAK	NOLEAVES
2	4	22	0.25	0.58	0.67	1	T	0.37313	22.387	BUDBREAK	LEAVES
3	5	3	0.73	5.83	0.63	1	I	1.15873	16.218	MAYGROTH	LEAVES
4	5	3	0.73	5.83	0.63	1	T	1.15873	1.259	MAYGROTH	LEAVES
5	5	3	0.73	5.83	0.63	1	T	1.15873	4.169	MAYGROTH	LEAVES
6	5	11	0.62	3.75	0.50	1	I	1.24000	61.660	MAYGROTH	LEAVES
7	5	11	0.62	3.75	0.50	1	T	1.24000	19.055	MAYGROTH	LEAVES
8	5	11	0.62	3.75	0.50	1	T	1.24000	24.547	MAYGROTH	LEAVES
9	5	28	1.48	9.79	0.48	1	I	3.08333	25.704	MAYGROTH	LEAVES
10	5	28	1.48	9.79	0.48	1	T	3.08333	4.786	MAYGROTH	LEAVES
11	5	28	1.48	9.79	0.48	1	T	3.08333	6.607	MAYGROTH	LEAVES
12	5	28	1.48	9.79	0.48	1	T	3.08333	16.596	MAYGROTH	LEAVES
13	5	29	2.52	9.79	1.38	2	I	1.82609	48.978	MAYGROTH	LEAVES
14	6	11	2.67	0.29	0.79	4	I	3.37975	123.027	MAYGROTH	LEAVES
15	6	20	1.84	13.13	0.83	1	I	2.21687	83.176	MAYGROTH	LEAVES
16	6	20	1.84	13.13	0.83	1	I	2.21687	67.608	MAYGROTH	LEAVES
17	6	20	1.84	13.13	0.83	1	T	2.21687	18.621	MAYGROTH	LEAVES
18	6	20	1.84	13.13	0.83	1	T	2.21687	47.863	MAYGROTH	LEAVES
19	6	20	1.84	13.13	0.83	1	T	2.21687	30.200	MAYGROTH	LEAVES
20	6	28	1.88	7.69	0.67	1	I	2.80597	77.625	MAYGROTH	LEAVES
21	7	5	2.64	7.92	1.13	5	I	2.33628	85.114	MAYGROTH	LEAVES
22	7	19	1.78	0.75	0.63	3	I	2.82540	72.444	MAYGROTH	LEAVES
23	8	13	1.87	6.74	0.42	3	I	4.45238	134.896	MAYGROTH	LEAVES
24	8	31	3.62	6.33	0.58	3	I	6.24138	77.625	MAYGROTH	LEAVES
25	9	17	1.16	4.13	0.75	5	I	1.54667	100.000	SENESCWT	LEAVES

Table B1 (Cont.)

OBS	PERIOD	STATION	HEASPT	PH	COND	SULFATE	CD	MN	PB	ZN	COL_YEAR
26	9/17-10/5/76	CI	5.8420	4.31	21.7	2.20	0.050	0.94	5.80	13.50	1976
27	10/5-10/18/76	CI	2.9210	4.23	27.5	0.110	0.110	0.89	9.60	9.60	1976
28	10/18-10/26/76	CI	8.0010	4.37	18.0	2.48	0.090	0.13	6.20	3.50	1976
29	10/29-11/1/76	CI	1.8288	4.37	19.5	3.56	0.190	0.22	6.10	7.50	1976
30	10/29-11/1/76	GI	1.8796	4.30	21.6	2.68	0.310	0.47	3.70	3.70	1976
31	10/29-11/1/76	T1	1.9812	4.75		11.20	1.000	59.00	7.00	70.00	1976
32	10/29-11/1/76	T2	1.6764	4.29	36.8	6.20	2.000	159.00	17.90	20.00	1976
33	10/29-11/1/76	T3	1.7272	4.32	40.6	7.52	0.180	74.00	7.80	6.20	1976
34	10/26-11/9/76	CI	1.3716	4.20	28.9	2.96	0.500	0.12	4.30	3.10	1976
35	11/9-11/24/76	CI	0.5334	3.90		4.28	0.150	3.20	11.30	8.20	1976
36	11/24-12/7/76	CI	8.4328	4.18	24.6	2.40	0.100	0.11	3.50	2.60	1976
37	12/7-12/21/76	CI	4.4450	4.00	40.4	4.02	0.020	0.42	5.70	1.90	1976
38	12/21-1/6/77	CI	2.9210	4.15	24.6	1.43	0.080	1.20	4.20	1.00	1977
39	1/6-1/12/77	CI	2.9210	4.23	18.0	1.76	0.110	0.15	2.70	1.30	1977
40	1/21-2/4/77	CI	1.0922	4.35	15.6	1.04					1977
41	1/21-2/4/77	T2	1.0922	4.27	24.8	1.44					1977
42	2/11-2/14/77	CI	0.8128	4.15	18.7	3.11	1.200	4.00	2.40	2.20	1977
43	2/11-2/14/77	GI	1.0160	4.22	22.5	3.33	2.600	4.00	2.10	3.80	1977
44	2/11-2/14/77	T1	0.9906	4.02	56.2	9.76	1.000	57.00	3.50	3.50	1977
45	2/11-2/14/77	T2	0.8128	4.08		4.17	3.500	100.00	3.40	9.10	1977
46	2/11-2/14/77	T3	0.8890	4.10	37.1	5.60	7.000	120.00	4.00	5.30	1977
47	2/4-2/22/77	CI	0.8636	4.00	44.2	3.36					1977
48	2/4-2/22/77	T2	0.8636	4.00	45.0	4.05					1977
49	2/22-2/24/77	CI	1.6256	4.60	10.1	1.32	1.900	7.90	4.60	5.50	1977
50	2/22-2/24/77	T2	1.6510	4.15	34.5		3.500	88.00	10.80	6.30	1977

OBS	MONTH	DAY	OR_PPT	ANTECEDT	DURATN	NO_EVENT	SMPLETYPE	INTEMSY	HYDROGN	SEASON	LEAFSTAT
26	10	5	3.40	1.46	1.38	4	I	2.46377	48.978	SEWESCNT	LEAVES
27	10	18	1.54	5.85	1.17	5	I	1.31624	58.884	SEWESCNT	LEAVES
28	10	26	3.62	2.48	1.92	2	I	1.88542	42.658	SEWESCNT	LEAVES
29	11	1	0.75	4.50	0.71	1	I	1.05634	42.658	DORMANT	NOLEAVES
30	11	1	0.75	4.50	0.71	1	I	1.05634	50.119	DORMANT	NOLEAVES
31	11	1	0.75	4.50	0.71	1	I	1.05634	17.783	DORMANT	NOLEAVES
32	11	1	0.75	4.50	0.71	1	T	1.05634	51.286	DORMANT	NOLEAVES
33	11	1	0.75	4.50	0.71	1	T	1.05634	47.863	DORMANT	NOLEAVES
34	11	9	0.75	4.50	0.71	1	I	1.05634	63.096	DORMANT	NOLEAVES
35	11	24	0.31	6.42	0.50	2	I	0.62000	125.893	DORMANT	NOLEAVES
36	12	7	3.64	11.67	2.38	4	I	1.52941	66.069	DORMANT	NOLEAVES
37	12	21	1.94	0.83	1.63	5	I	1.19018	100.000	DORMANT	NOLEAVES
38	1	6	1.40	1.00	1.92	6	I	0.72917	70.795	DORMANT	NOLEAVES
39	1	12	1.17	0.00	1.17	2	I	1.00000	58.884	DORMANT	NOLEAVES
40	2	4	0.48	3.79	0.50	3	I	0.96000	44.668	DORMANT	NOLEAVES
41	2	4	0.48	3.79	0.50	3	T	0.96000	53.703	DORMANT	NOLEAVES
42	2	14	0.42	16.50	0.25	1	I	1.68000	70.795	DORMANT	NOLEAVES
43	2	14	0.42	16.50	0.25	1	I	1.68000	60.256	DORMANT	NOLEAVES
44	2	14	0.42	16.50	0.25	1	T	1.68000	95.499	DORMANT	NOLEAVES
45	2	14	0.42	16.50	0.25	1	T	1.68000	83.176	DORMANT	NOLEAVES
46	2	14	0.42	16.50	0.25	1	T	1.68000	78.433	DORMANT	NOLEAVES
47	2	22	0.43	16.50	0.29	2	I	1.48276	100.000	DORMANT	NOLEAVES
48	2	22	0.43	16.50	0.29	2	T	1.48276	100.000	DORMANT	NOLEAVES
49	2	24	0.72	5.71	0.29	1	I	2.48276	25.119	DORMANT	NOLEAVES
50	2	24	0.72	5.71	0.29	1	T	2.48276	70.795	DORMANT	NOLEAVES

Table B1 (Cont.)

OBS	PERIOD	STATION	HEASPT	PH	COND	SULFATE	CD	MN	PB	ZN	COL_YEAR
51	2/25-2/28/77	CI	1.7780	4.49	14.00	1.31	0.820	4.80	4.20	2.30	1977
52	2/25-2/28/77	T2	1.7272	3.82	51.70	2.48	1.400	36.00	8.70	2.40	1977
53	3/2-3/4/77	T2	1.4224	4.05	38.50	3.36	1977
54	3/4-3/7/77	CI	0.6096	4.10	34.00	1977
55	3/4-3/7/77	T2	0.6350	4.05	35.60	1977
56	3/09-3/14/77	CI	5.2832	4.75	10.00	0.57	1.500	1.30	1.10	1.80	1977
57	3/09-3/14/77	GI	5.8928	4.95	7.90	0.68	0.390	1.60	1.30	0.84	1977
58	3/09-3/14/77	T1	5.4610	4.71	16.30	1.84	4.300	9.40	2.00	3.40	1977
59	3/09-3/14/77	T2	4.7498	4.81	9.90	0.84	0.240	13.00	1.60	3.30	1977
60	3/09-3/14/77	T3	4.8260	4.75	10.10	0.88	0.070	6.80	1.00	0.71	1977
61	3/14-3/22/77	CI	1.9304	4.48	23.70	2.92	0.065	10.00	6.40	1.10	1977
62	3/14-3/22/77	T2	1.7780	4.79	21.70	2.72	0.230	43.00	6.90	2.30	1977
63	4/1-4/4/77	T1	16.2306	4.31	23.40	3.03	0.040	7.90	2.90	1.13	1977
64	4/1-4/4/77	GI	19.1770	4.25	22.30	2.12	0.020	2.54	2.95	0.75	1977
65	4/20-4/25/77	GI	1.7272	4.51	19.20	1.25	6.70	6.70	4.70	1.30	1977
66	4/20-4/25/77	T2	1.6256	5.30	28.20	11.30	7.700	270.00	8.30	4.30	1977
67	4/20-4/25/77	T3	1.2192	6.07	44.20	13.70	0.080	190.00	11.00	2.90	1977
68	4/20-4/25/77	T1	1.4732	6.00	26.70	3.03	0.240	40.00	7.20	2.20	1977
69	5/4-5/9/77	GI	0.7620	5.20	20.90	2.74	0.180	4.00	3.30	2.60	1977
70	5/4-5/9/77	T1	0.8128	5.45	23.30	8.18	0.400	33.00	6.60	3.20	1977
71	5/16-5/18/77	GI	0.1270	3.75	112.00	16.46	0.350	24.00	3.10	2.90	1977
72	5/16-5/18/77	T4	0.1778	5.12	157.70	37.51	0.800	733.00	5.50	24.00	1977
73	5/19-5/23/77	GI	4.3180	4.00	44.30	5.68	0.260	2.80	12.00	3.40	1977
74	5/19-5/23/77	T4	3.6830	4.00	73.50	17.20	0.260	382.00	15.00	5.70	1977
75	5/30-6/6/77	CI	0.3048	3.90	100.00	8.60	0.450	12.00	7.70	1.90	1977

OBS	MONTH	DAY	OR_PPT	ANTECEDT	DURATN	NO_EVENT	SHPLTYP	INTENSTY	HYDROGN	SEASON	LEAFSTAT
51	2	28	0.74	2.88	0.29	1	I	2.55172	32.359	DORMANT	NOLEAVES
52	2	28	0.74	2.88	0.29	1	T	2.55172	151.356	DORMANT	NOLEAVES
53	3	4	0.68	3.79	0.54	3	T	1.25926	89.125	BUDBREAK	NOLEAVES
54	3	7	0.21	1.63	0.33	1	I	0.63636	79.433	BUDBREAK	NOLEAVES
55	3	7	0.21	1.63	0.33	1	T	0.63636	89.125	BUDBREAK	NOLEAVES
56	3	14	2.30	5.88	0.54	1	I	4.25926	17.783	BUDBREAK	NOLEAVES
57	3	14	2.30	5.88	0.54	1	T	4.25926	11.220	BUDBREAK	NOLEAVES
58	3	14	2.30	5.88	0.54	1	I	4.25926	19.498	BUDBREAK	NOLEAVES
59	3	14	2.30	5.88	0.54	1	T	4.25926	15.488	BUDBREAK	NOLEAVES
60	3	14	2.30	5.88	0.54	1	T	4.25926	17.783	BUDBREAK	NOLEAVES
61	3	22	0.92	5.54	0.38	3	T	2.42105	33.113	BUDBREAK	NOLEAVES
62	3	22	0.92	5.54	0.38	3	T	2.42105	16.218	BUDBREAK	NOLEAVES
63	4	4	7.50	3.08	1.37	2	T	5.47445	48.978	BUDBREAK	LEAVES
64	4	4	7.50	3.08	1.37	2	I	5.47445	56.234	BUDBREAK	LEAVES
65	4	25	0.51	2.50	0.71	2	T	0.71831	30.903	BUDBREAK	LEAVES
66	4	25	0.51	2.50	0.71	2	T	0.71831	5.012	BUDBREAK	LEAVES
67	4	25	0.51	2.50	0.71	2	T	0.71831	0.851	BUDBREAK	LEAVES
68	4	25	0.51	2.50	0.71	2	T	0.71831	1.000	BUDBREAK	LEAVES
69	5	9	0.20	3.50	0.13	1	I	1.53846	6.310	HAIGROTH	LEAVES
70	5	9	0.20	3.50	0.13	1	T	1.53846	3.548	HAIGROTH	LEAVES
71	5	18	0.05	10.21	0.08	1	I	0.62500	177.828	HAIGROTH	LEAVES
72	5	18	0.05	10.21	0.08	1	T	0.62500	7.586	HAIGROTH	LEAVES
73	5	23	0.36	3.92	0.13	1	I	2.76923	100.000	HAIGROTH	LEAVES
74	5	23	0.36	3.92	0.13	1	T	2.76923	100.000	HAIGROTH	LEAVES
75	6	6	0.10	0.00	1.80	1	I	0.05556	125.893	HAIGROTH	LEAVES

Table B1 (Cont.)

OBS	PERIOD	STATION	MEASPT	PH	COND	SULFATE	CD	MN	PB	ZN	COL_YEAR
76	5/30-6/6/77	T4	0.2286	3.82	109.20	26.99	0.95	266.00	34.00	2.70	1977
77	6/6-6/13/77	CI	1.2700	4.01	54.30	6.85	0.65	18.00	24.00	1.90	1977
78	6/6-6/13/77	T4	0.9398	4.09	102.60	22.33	2.50	552.00	43.00	9.70	1977
79	6/13-6/17/77	CI	2.5908	4.08	44.60	4.99	0.34	3.50	13.00	1.50	1977
80	6/13-6/17/77	T4	3.1750	3.99	92.40	23.56	0.34	198.00	16.00	4.50	1977
81	6/17-6/20/77	CI	1.4732	4.00	47.60	5.46	0.21	3.30	12.00	1.80	1977
82	6/17-6/20/77	GI	2.2860	4.00	38.70	4.65	0.30	6.00	12.00	2.00	1977
83	6/17-6/20/77	T4	1.4732	3.85	83.90	21.67	0.30	312.00	21.00	9.90	1977
84	6/17-6/20/77	T3	1.8288	4.10	47.30	14.80	0.15	49.00	15.00	2.70	1977
85	6/17-6/20/77	T1	1.7272	4.10	47.30	8.74	0.05	46.00	13.00	1.30	1977
86	6/20-6/27/77	T4	11.8364	4.29	47.01	6.26	0.04	190.00	5.10	4.10	1977
87	6/20-6/27/77	CI	11.4046	4.28	28.05	2.67	0.04	4.60	5.00	0.44	1977
88	6/27-7/5/77	CI	0.3556	3.93	51.60	5.92	0.03	11.00	4.40	3.50	1977
89	6/27-7/5/77	T4	0.1524	4.18	71.90	13.28	0.97	135.00	12.00	5.40	1977
90	7/11-7/13/77	CI	0.2032	3.95	48.01	5.72	0.15	3.80	2.10	3.10	1977
91	7/11-7/13/77	GI	0.2286	3.95	47.80	6.66	0.91	6.00	6.70	6.80	1977
92	7/11-7/13/77	T4	0.1778	4.91	105.60	27.23	2.10	434.00	39.00	18.00	1977
93	7/11-7/13/77	T3	0.0762	4.80	33.15	3.70	3.70	289.00	47.00	17.00	1977
94	7/11-7/13/77	T2	0.3048	4.71	62.10	14.37	11.00	232.00	36.00	45.00	1977
95	7/22/77	CI	4.8006	3.90	52.10	5.38	0.40	1.50	8.30	1.40	1977
96	7/22/77	GI	5.4610	3.90	57.01	5.90	0.05	2.50	7.90	2.20	1977
97	7/22/77	T1	4.3180	3.90	53.90	6.54	0.03	17.80	12.00	1.50	1977
98	7/22/77	T2	5.0292	4.00	51.90	6.04	0.03	16.00	2.10	47.30	1977
99	7/22/77	T3	2.1336	3.87	68.20	8.08	0.07	34.60	21.00	1.90	1977
100	7/22/77	T4	5.8420	4.00	55.40	7.18	0.88	139.00	17.00	3.40	1977

OBS	MONTH	DAY	OR_PP1	ANTECEDT	DURATN	NO_EVENT	SMLTYPE	INTENSTY	HYDROGN	SEASON	LEAFSTAT
76	6	6	0.10	0.00	1.80	1	T	0.05556	151.356	HAIGROTH	LEAVES
77	6	13	0.29	11.67	0.08	2	I	3.62500	97.724	HAIGROTH	LEAVES
78	6	13	0.29	11.67	0.08	2	I	3.62500	81.283	HAIGROTH	LEAVES
79	6	17	0.82	1.33	0.38	2	I	2.15789	83.176	HAIGROTH	LEAVES
80	6	17	0.82	1.33	0.38	2	I	2.15789	102.329	HAIGROTH	LEAVES
81	6	20	1.65	2.75	0.33	3	I	5.00000	100.000	HAIGROTH	LEAVES
82	6	20	1.65	2.75	0.33	3	I	5.00000	100.000	HAIGROTH	LEAVES
83	6	20	1.65	2.75	0.33	3	I	5.00000	141.254	HAIGROTH	LEAVES
84	6	20	1.65	2.75	0.33	3	I	5.00000	141.254	HAIGROTH	LEAVES
85	6	20	1.65	2.75	0.33	3	I	5.00000	79.433	HAIGROTH	LEAVES
86	6	27	3.85	1.38	1.04	6	T	3.70192	79.433	HAIGROTH	LEAVES
87	6	27	3.85	1.38	1.04	6	T	3.70192	51.286	HAIGROTH	LEAVES
88	7	5	1.28	3.75	0.50	2	I	3.70192	52.481	HAIGROTH	LEAVES
89	7	5	1.28	3.75	0.50	2	I	3.70192	117.490	HAIGROTH	LEAVES
90	7	13	0.01	7.67	0.04	1	I	0.25000	66.069	HAIGROTH	LEAVES
91	7	13	0.01	7.67	0.04	1	I	0.25000	112.202	HAIGROTH	LEAVES
92	7	13	0.01	7.67	0.04	1	I	0.25000	112.202	HAIGROTH	LEAVES
93	7	13	0.01	7.67	0.04	1	I	0.25000	12.303	HAIGROTH	LEAVES
94	7	13	0.01	7.67	0.04	1	I	0.25000	15.849	HAIGROTH	LEAVES
95	7	22	1.10	12.75	0.17	1	I	6.47059	125.893	HAIGROTH	LEAVES
96	7	22	1.10	12.75	0.17	1	I	6.47059	125.893	HAIGROTH	LEAVES
97	7	22	1.10	12.75	0.17	1	I	6.47059	125.893	HAIGROTH	LEAVES
98	7	22	1.10	12.75	0.17	1	I	6.47059	100.000	HAIGROTH	LEAVES
99	7	22	1.10	12.75	0.17	1	I	6.47059	134.896	HAIGROTH	LEAVES
100	7	22	1.10	12.75	0.17	1	I	6.47059	100.000	HAIGROTH	LEAVES

Table B1 (Cont.)

OBS	PERIOD	STATION	HEASPTT	PH	COND	SULFATE	CD	MM	PB	ZN	COL_YEAR
101	7/18-7/22/77	CI	0.2032	3.90	.	11.32	0.600	20.50	23.00	3.30	1977
102	7/18-7/22/77	T4	0.1270	4.50	114.00	28.92	13.000	467.00	54.00	23.00	1977
103	7/24-7/26/77	CI	2.0320	3.95	44.00	4.39	0.800	2.54	9.50	2.40	1977
104	7/24-7/26/77	T4	2.3876	4.00	58.90	10.32	0.320	160.00	12.00	3.60	1977
105	8/2-8/11/77	CI	1.3716	3.81	49.00	5.75	0.660	5.12	16.00	4.60	1977
106	8/2-8/11/77	T4	0.9906	3.92	69.80	14.49	1.900	480.00	22.00	19.00	1977
107	8/12-8/15/77	CI	1.3970	3.93	53.20	4.92	0.590	2.08	16.00	9.10	1977
108	8/12-8/15/77	GI	1.7780	3.98	43.70	4.42	0.820	3.88	13.00	8.40	1977
109	8/12-8/15/77	T1	1.3208	4.38	26.80	5.70	1.100	36.10	8.30	11.00	1977
110	8/12-8/15/77	T3	1.2192	3.95	56.30	8.86	0.990	59.40	21.00	15.00	1977
111	8/12-8/15/77	T2	1.3970	3.95	51.30	8.26	0.680	114.00	18.00	21.00	1977
112	8/12-8/15/77	T4	0.8890	3.93	69.90	11.84	1.100	184.00	17.00	21.00	1977
113	8/11-8/17/77	CI	1.5240	3.95	56.66	5.64	0.200	2.06	13.00	5.10	1977
114	8/11-8/17/77	T4	0.9652	3.93	69.90	13.22	4.300	155.00	17.00	86.00	1977
115	9/07/77	CI	3.6830	4.13	26.83	2.97	0.410	0.57	1.72	37.21	1977
116	9/07/77	GI	4.1910	4.23	20.50	1.68	0.080	1.10	1.81	22.00	1977
117	9/07/77	T1	3.6830	4.96	20.93	5.04	0.510	43.00	4.96	39.00	1977
118	9/07/77	T4	3.5560	4.20	26.94	5.89	0.460	117.48	3.85	22.52	1977
119	9/07/77	T2	3.5560	4.24	29.12	6.04	0.500	89.00	5.21	23.00	1977
120	9/07/77	T3	3.3020	4.13	36.49	5.44	0.180	49.00	3.77	12.00	1977
121	9/12-9/19/77	CI	8.4074	4.25	23.86	2.70	0.320	1.40	1.03	20.00	1977
122	9/12-9/19/77	T4	6.9342	4.23	33.35	4.82	3.300	117.00	6.41	29.00	1977
123	9/23-9/26/77	CI	3.3528	4.45	15.10	1.75	0.100	0.78	1.74	5.70	1977
124	9/23-9/26/77	GI	3.4290	4.55	13.04	1.69	0.120	1.40	2.68	6.90	1977
125	9/23-9/26/77	T4	2.7940	4.52	26.60	5.45	0.180	176.00	6.68	26.00	1977

OBS	MONTH	DAY	OR_PPT	ANTECEDT	DURATN	NO_EVENT	SMPITYPE	INTENSTY	HIDROGN	SEASON	LEAFSTAT
101	7	22	0.10	0.70	0.32	1	I	0.31250	125.893	MAIGROTH	LEAVES
102	7	22	0.10	0.70	0.32	1	I	0.31250	31.623	MAIGROTH	LEAVES
103	7	26	1.37	2.54	0.33	1	I	4.15152	112.202	MAIGROTH	LEAVES
104	7	26	1.37	2.54	0.33	1	T	4.15152	100.000	MAIGROTH	LEAVES
105	8	11	0.83	1.46	0.46	4	I	1.80435	154.882	MAIGROTH	LEAVES
106	8	11	0.83	1.46	0.46	4	T	1.80435	120.226	MAIGROTH	LEAVES
107	8	15	0.74	2.75	0.38	3	I	1.94737	117.490	MAIGROTH	LEAVES
108	8	15	0.74	2.75	0.38	3	T	1.94737	104.713	MAIGROTH	LEAVES
109	8	15	0.74	2.75	0.38	3	I	1.94737	41.687	MAIGROTH	LEAVES
110	8	15	0.74	2.75	0.38	3	T	1.94737	112.202	MAIGROTH	LEAVES
111	8	15	0.74	2.75	0.38	3	I	1.94737	112.202	MAIGROTH	LEAVES
112	8	15	0.74	2.75	0.38	3	T	1.94737	117.490	MAIGROTH	LEAVES
113	8	17	1.06	3.79	0.58	5	I	1.82759	112.202	MAIGROTH	LEAVES
114	8	17	1.06	3.79	0.58	5	T	1.82759	117.490	MAIGROTH	LEAVES
115	9	7	1.42	0.20	0.58	1	I	2.44828	74.131	SENESENT	LEAVES
116	9	7	1.42	0.20	0.58	1	I	2.44828	58.884	SENESENT	LEAVES
117	9	7	1.42	0.20	0.58	1	T	2.44828	10.965	SENESENT	LEAVES
118	9	7	1.42	0.20	0.58	1	T	2.44828	63.096	SENESENT	LEAVES
119	9	7	1.42	0.20	0.58	1	T	2.44828	57.544	SENESENT	LEAVES
120	9	7	1.42	0.20	0.58	1	T	2.44828	74.131	SENESENT	LEAVES
121	9	19	3.73	5.58	1.45	1	I	2.57241	56.234	SENESENT	LEAVES
122	9	19	3.73	5.58	1.45	2	T	2.57241	58.884	SENESENT	LEAVES
123	9	26	1.45	6.08	0.37	1	I	3.91892	35.481	SENESENT	LEAVES
124	9	26	1.45	6.08	0.37	1	I	3.91892	28.184	SENESENT	LEAVES
125	9	26	1.45	6.08	0.37	1	T	3.91892	30.200	SENESENT	LEAVES

Table B1 (Cont.)

OBS	PERIOD	STATION	HEASPT	PH	COND	SULFATE	CD	MN	PB	ZN	COL_YEAR
126	9/23-9/26/77	T2	3.4290	4.54	18.00	3.44	0.680	63.00	5.07	15.0	1977
127	9/23-9/26/77	T3	2.4384	4.85	23.20	5.13	0.270	53.00	7.39	11.0	1977
128	9/23-9/26/77	T1	3.4290	6.15	29.20	5.15	0.640	72.00	5.70	14.0	1977
129	9/29-10/10/77	CI	6.0198	4.00	17.30	1.60	0.140	1.58	3.30	5.9	1977
130	9/29-10/10/77	T4	4.5974	4.85	29.60	3.73	0.200	135.00	4.80	12.0	1977
131	9/29-10/10/77	T3	4.9784	5.09	27.20	4.78	0.093	159.00	4.20	24.0	1977
132	9/29-10/10/77	T2	6.0960	4.67	19.60	3.52	0.100	84.80	4.10	5.9	1977
133	10/12-10/17/77	CI	0.3810	4.35	26.60	1.93	0.810	4.67	14.00	19.0	1977
134	10/12-10/17/77	T4	0.2286	4.58	56.80	9.66	2.200	198.00	16.00	46.0	1977
135	10/24-10/25/77	CI	2.1844	4.71	7.90	0.90	0.310	0.44	0.70	11.0	1977
136	10/24-10/25/77	GI	3.3020	4.80	7.17	0.45	0.120	2.15	0.62	9.6	1977
137	10/24-10/25/77	T1	3.8100	6.18	69.50	9.98	0.180	150.00	4.50	11.0	1977
138	10/24-10/25/77	T2	2.2860	4.62	80.10	15.72	0.480	184.00	9.10	19.0	1977
139	10/24-10/25/77	T4	2.7940	4.45	37.80	6.22	0.700	190.00	7.80	25.0	1977
140	10/24-10/25/77	T3	3.1750	4.37	70.40	12.88	0.560	187.00	10.00	38.0	1977
141	10/31-11/7/77	CI	3.8354	4.31	18.80	1.89	0.190	0.25	2.73	10.0	1977
142	10/31-11/7/77	T4	3.1242	4.20	36.20	6.82	0.320	146.00	2.97	28.0	1977
143	12/29-1/3/78	CI	0.8128	4.05	38.80	3.42	0.200	1.90	20.00	14.0	1978
144	12/29-1/3/78	GI	1.0160	4.08	36.00	3.00	0.960	2.10	16.00	12.0	1978
145	12/29-1/3/78	T1	0.8890	3.95	56.40	6.93	0.310	30.00	18.00	15.0	1978
146	12/29-1/3/78	T3	0.8636	4.09	41.30	4.17	0.800	58.00	13.00	33.0	1978
147	12/29-1/3/78	T4	0.9144	4.89	64.30	7.91	0.340	125.00	16.00	16.0	1978
148	12/29-1/3/78	T2	0.9398	4.03	41.60	3.92	0.630	45.00	14.00	19.0	1978

OBS	MONTH	DAY	OR_PPT	ANTECEDT	DURATN	NO_EVENT	SMLTYPE	INTENSTY	HYDROGN	SEASON	LEAFSTAT
126	9	26	1.45	6.08	0.37	1	T	3.91892	28.840	SENESCNT	LEAVES
127	9	26	1.45	6.08	0.37	1	T	3.91892	14.125	SENESCNT	LEAVES
128	9	26	1.45	6.08	0.37	1	T	3.91892	0.708	SENESCNT	LEAVES
129	10	10	2.71	2.12	1.29	3	I	2.10078	39.811	SENESCNT	LEAVES
130	10	10	2.71	2.12	1.29	3	T	2.10078	14.125	SENESCNT	LEAVES
131	10	10	2.71	2.12	1.29	3	T	2.10078	8.128	SENESCNT	LEAVES
132	10	10	2.71	2.12	1.29	3	T	2.10078	21.380	SENESCNT	LEAVES
133	10	17	0.15	3.12	0.04	1	I	3.75000	44.668	SENESCNT	LEAVES
134	10	17	0.15	3.12	0.04	1	T	3.75000	26.303	SENESCNT	LEAVES
135	10	25	0.86	0.00	0.50	1	I	1.72000	19.498	SENESCNT	LEAVES
136	10	25	1.18	9.20	0.41	1	I	2.87805	15.849	SENESCNT	LEAVES
137	10	25	1.18	9.20	0.41	1	T	2.87805	23.988	SENESCNT	LEAVES
138	10	25	1.18	9.20	0.41	1	T	2.87805	35.481	SENESCNT	LEAVES
139	10	25	1.18	9.20	0.41	1	T	2.87805	42.658	SENESCNT	LEAVES
140	10	25	1.18	9.20	0.41	1	T	2.87805	48.978	DORMANT	NOLEAVES
141	11	7	1.87	8.20	1.50	4	I	1.24667	63.096	DORMANT	NOLEAVES
142	11	7	1.87	8.20	1.50	4	T	1.24667	89.125	DORMANT	NOLEAVES
143	1	3	0.40	5.13	0.75	2	I	0.53333	83.176	DORMANT	NOLEAVES
144	1	3	0.40	5.13	0.75	2	I	0.53333	112.202	DORMANT	NOLEAVES
145	1	3	0.40	5.13	0.75	2	T	0.53333	81.283	DORMANT	NOLEAVES
146	1	3	0.40	5.13	0.75	2	T	0.53333	12.882	DORMANT	NOLEAVES
147	1	3	0.40	5.13	0.75	2	T	0.53333	93.325	DORMANT	NOLEAVES
148	1	3	0.40	5.13	0.75	2	T	0.53333			

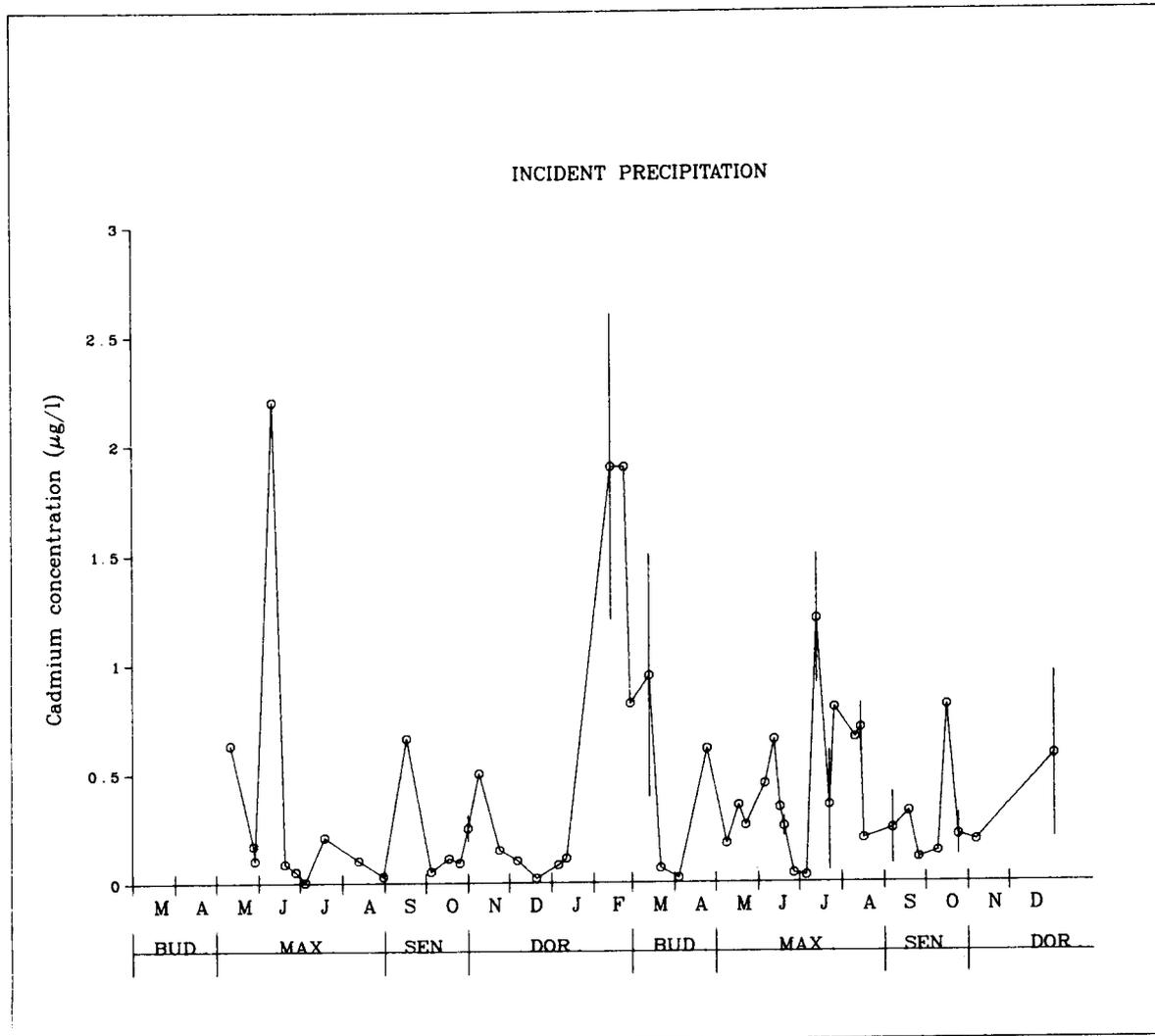


Fig. B1. Temporal variations in the concentration of Cd in incident precipitation from May 1976 to December 1977. Events sampled at one station are represented by individual circles. Events sampled at more than one station are represented by circles (mean concentration) intersected by vertical lines (range in concentrations).

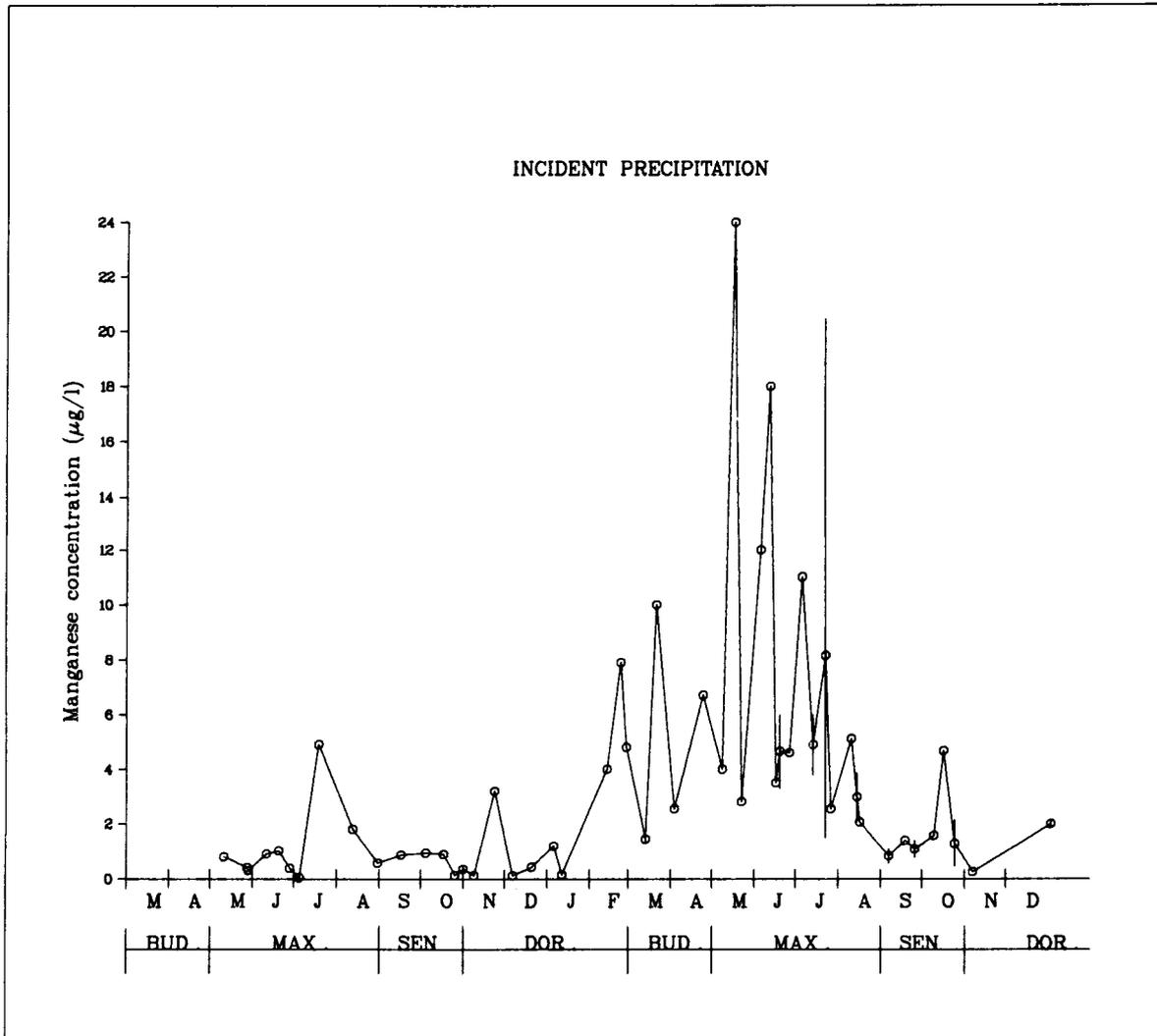


Fig. B2. Temporal variations in the concentration of Mn in incident precipitation from May 1976 to December 1977. Events sampled at one station are represented by individual circles. Events sampled at more than one station are represented by circles (mean concentration) intersected by vertical lines (range in concentrations).

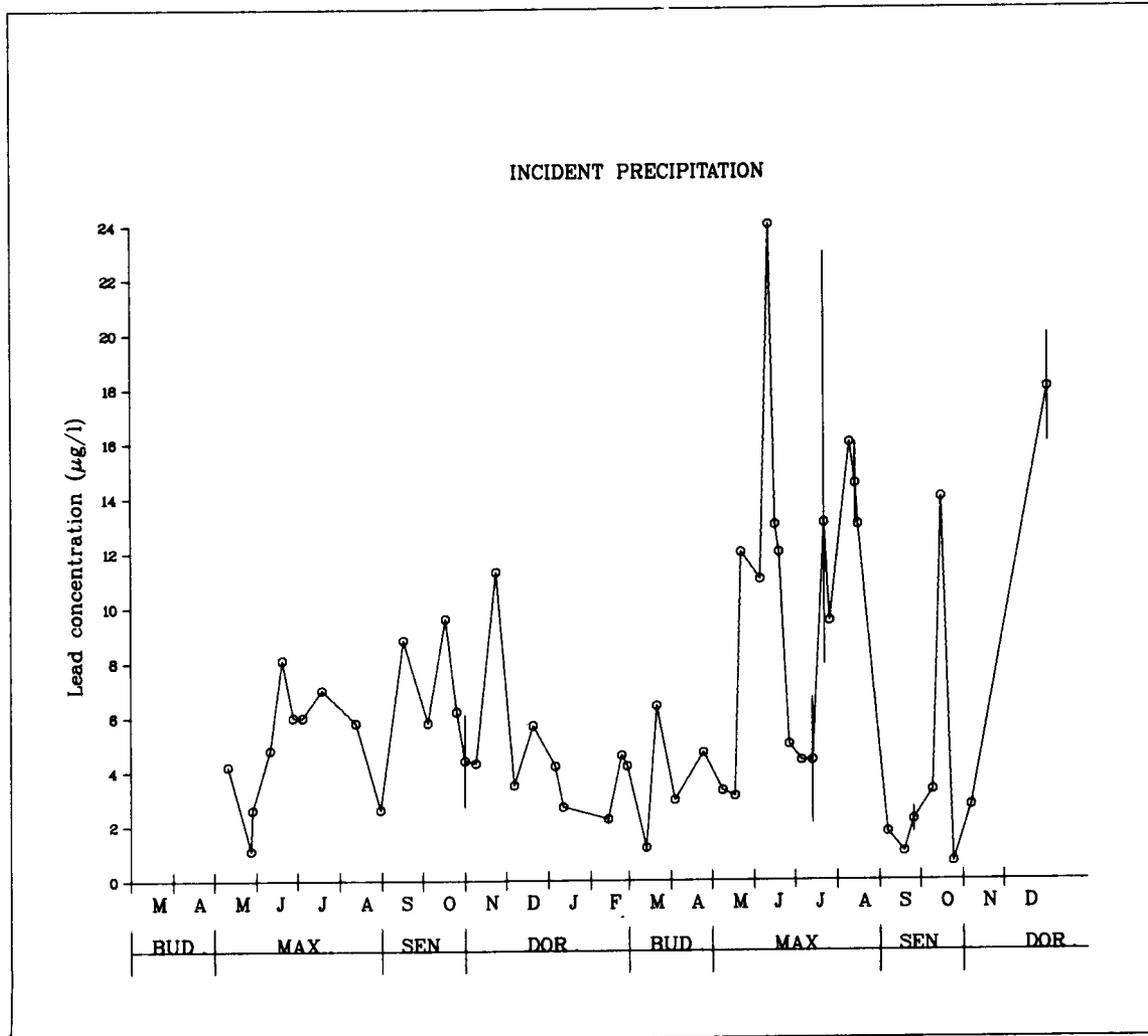


Fig. B3. Temporal variations in the concentration of Pb in incident precipitation from May 1976 to December 1977. Events sampled at one station are represented by individual circles. Events sampled at more than one station are represented by circles (mean concentration) intersected by vertical lines (range in concentrations).

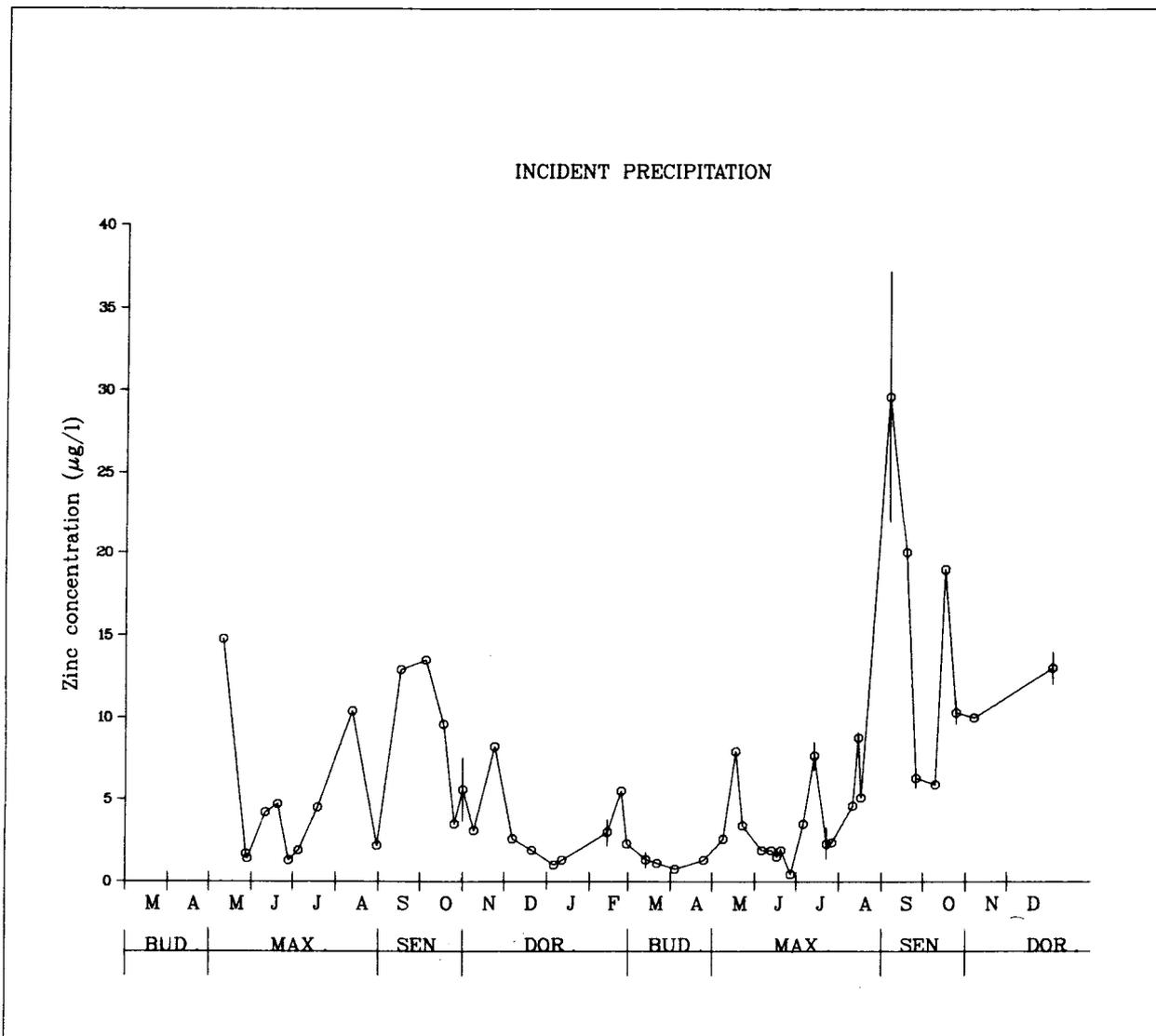


Fig. B4. Temporal variations in the concentration of Zn in incident precipitation from May 1976 to December 1977. Events sampled at one station are represented by individual circles. Events sampled at more than one station are represented by circles (mean concentration) intersected by vertical lines (range in concentrations).

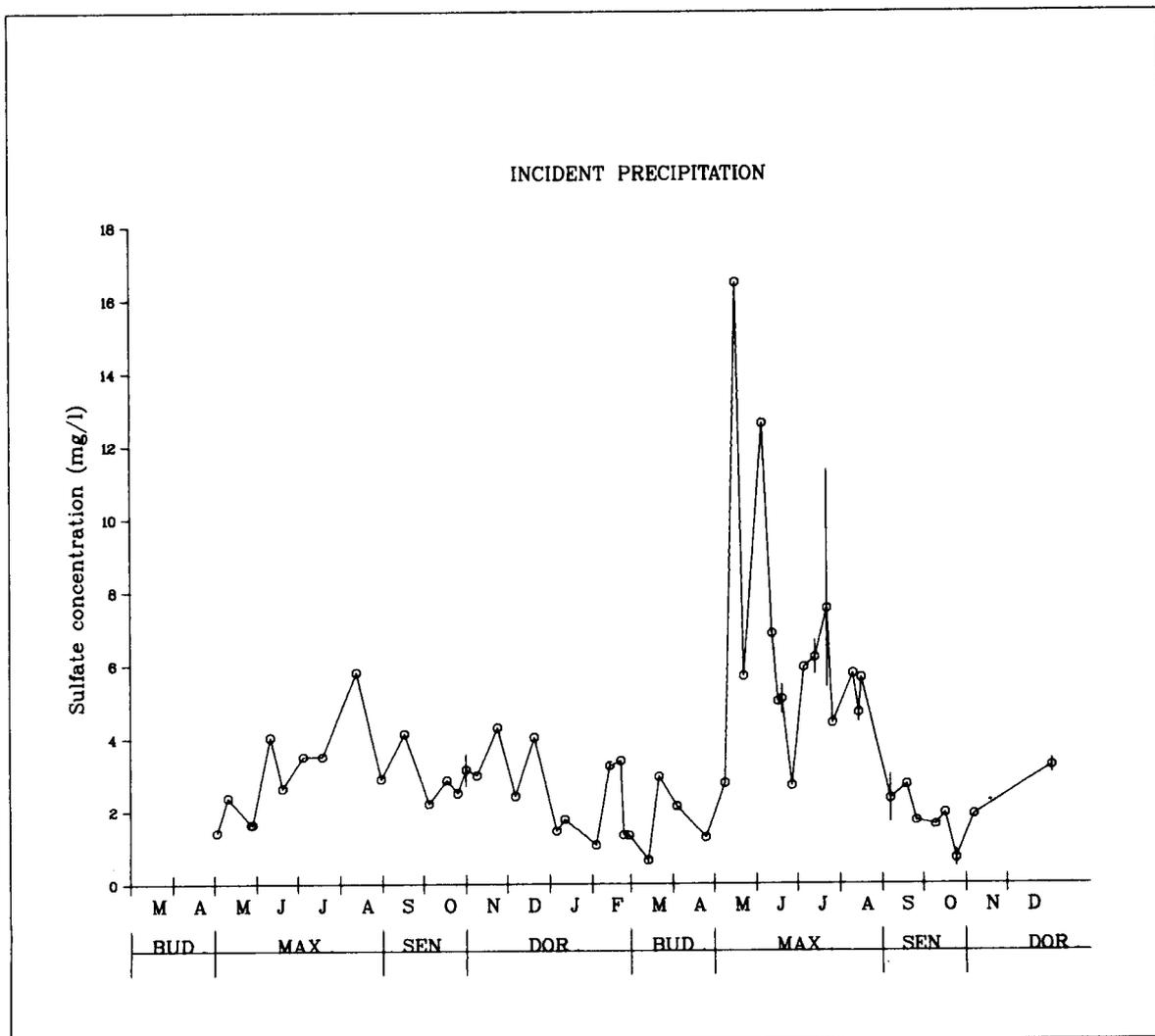


Fig. B5. Temporal variations in the concentration of sulfate in incident precipitation from May 1976 to December 1977. Events sampled at one station are represented by individual circles. Events sampled at more than one station are represented by circles (mean concentration) intersected by vertical lines (range in concentrations).

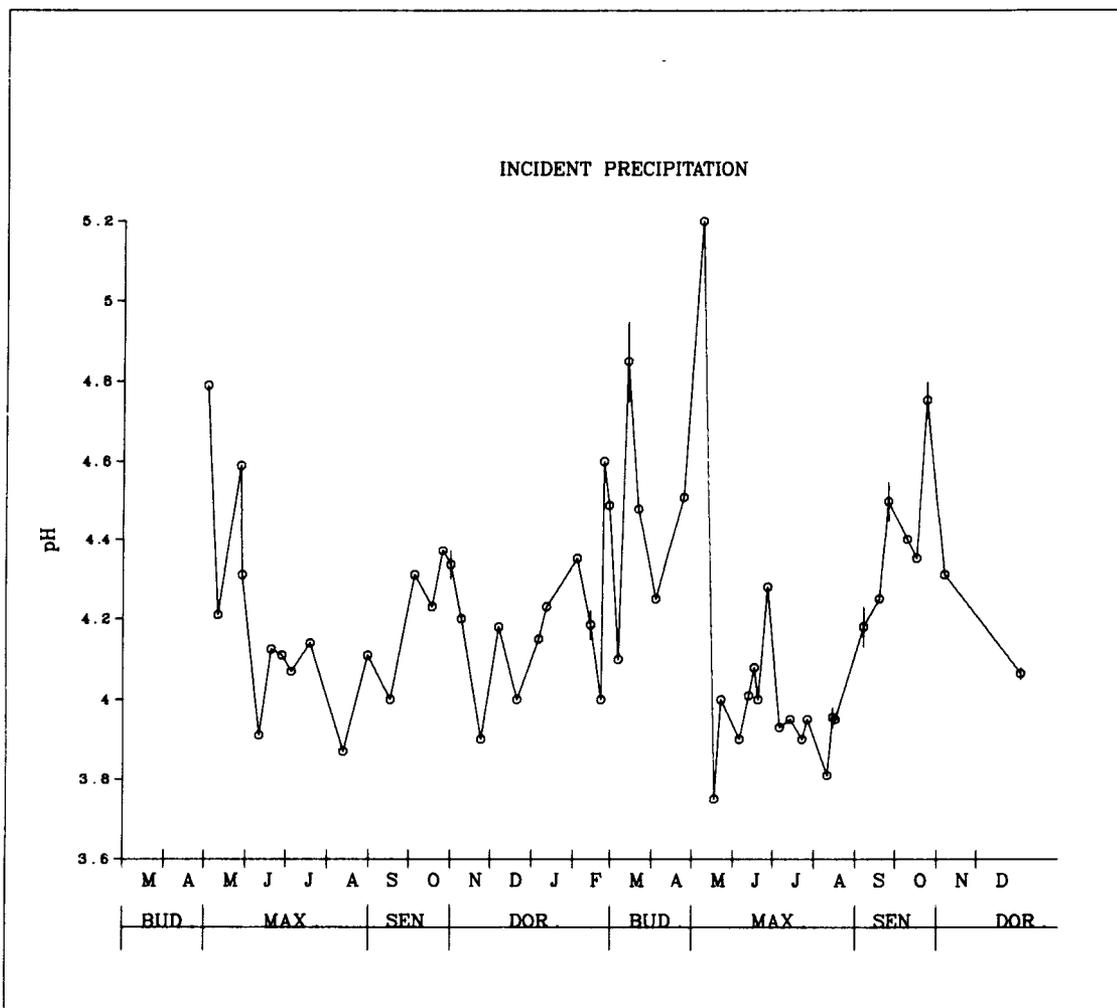


Fig. B6. Temporal variations in the concentration of pH in incident precipitation from May 1976 to December 1977. Events sampled at one station are represented by individual circles. Events sampled at more than one station are represented by circles (mean concentration) intersected by vertical lines (range in concentrations).

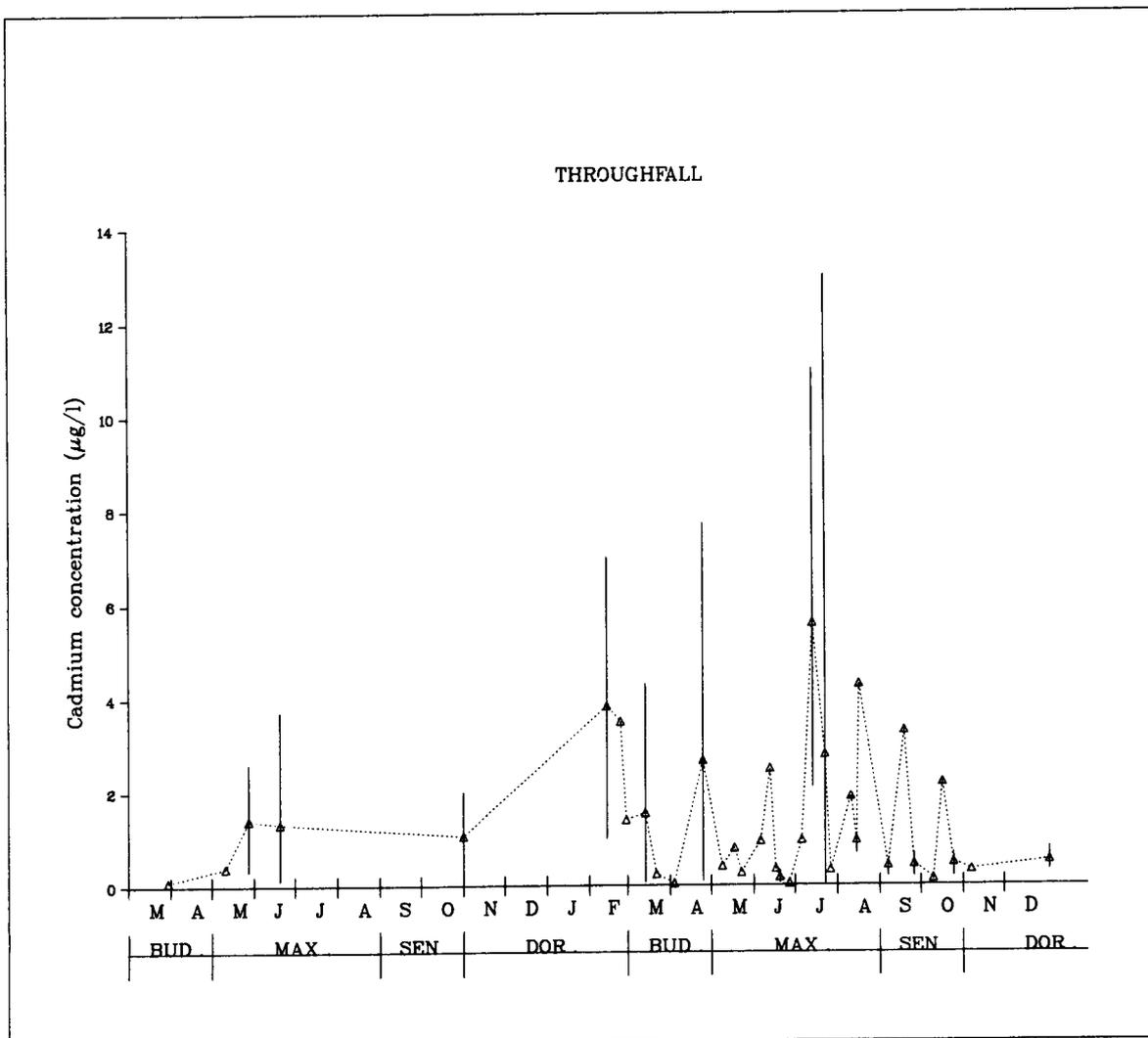


Fig. B7. Temporal variations in the concentration of Cd in incident precipitation from March 1976 to December 1977. Events sampled at one station are represented by individual triangles. Events sampled at more than one station are represented by triangles (mean concentration) intersected by vertical lines (range in concentrations).

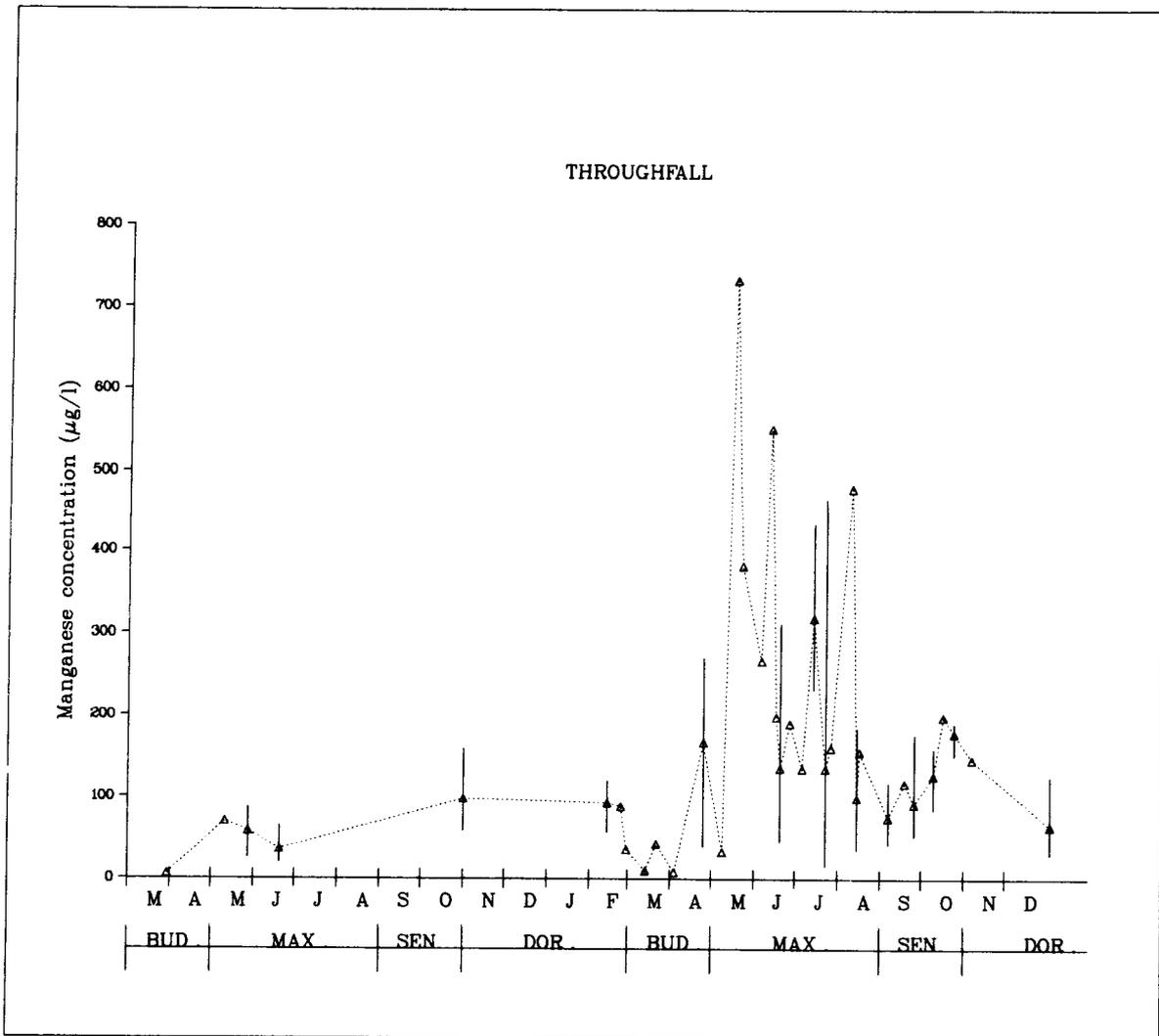


Fig. B8. Temporal variations in the concentration of Mn in incident precipitation from March 1976 to December 1977. Events sampled at one station are represented by individual triangles. Events sampled at more than one station are represented by triangles (mean concentration) intersected by vertical lines (range in concentrations).

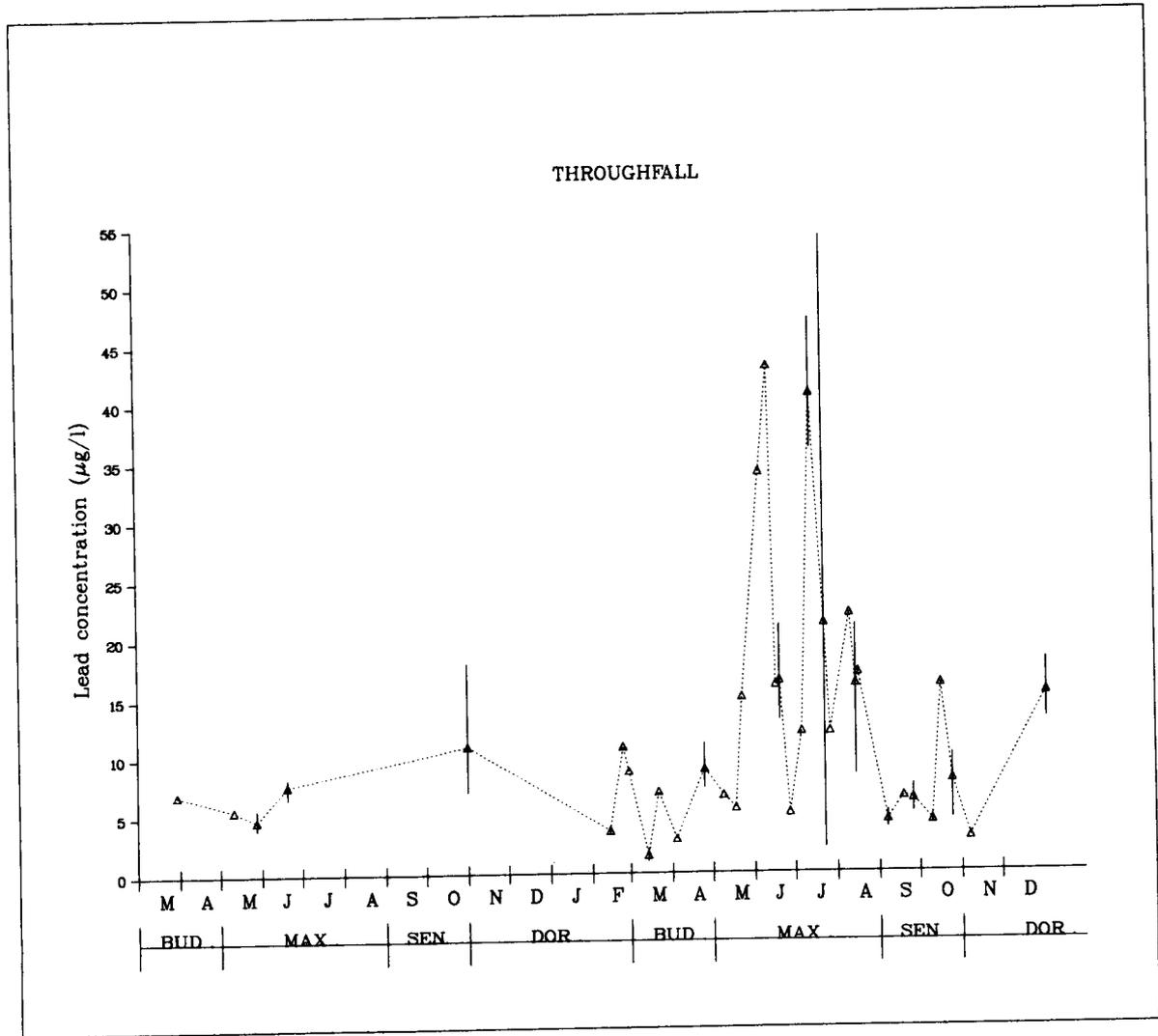


Fig. B9. Temporal variations in the concentration of Pb in incident precipitation from March 1976 to December 1977. Events sampled at one station are represented by individual triangles. Events sampled at more than one station are represented by triangles (mean concentration) intersected by vertical lines (range in concentrations).

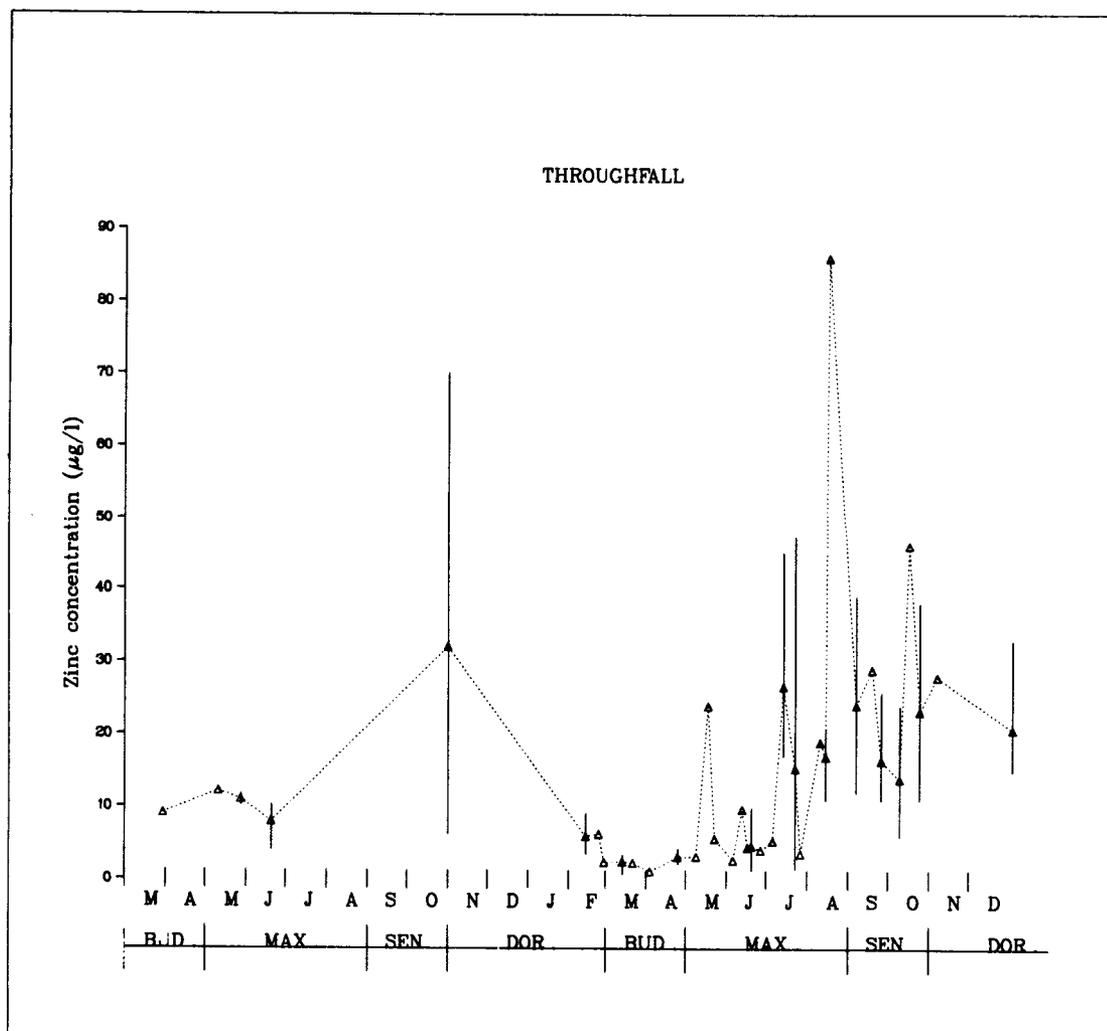


Fig. B10. Temporal variations in the concentration of Zn in incident precipitation from March 1976 to December 1977. Events sampled at one station are represented by individual triangles. Events sampled at more than one station are represented by triangles (mean concentration) intersected by vertical lines (range in concentrations).

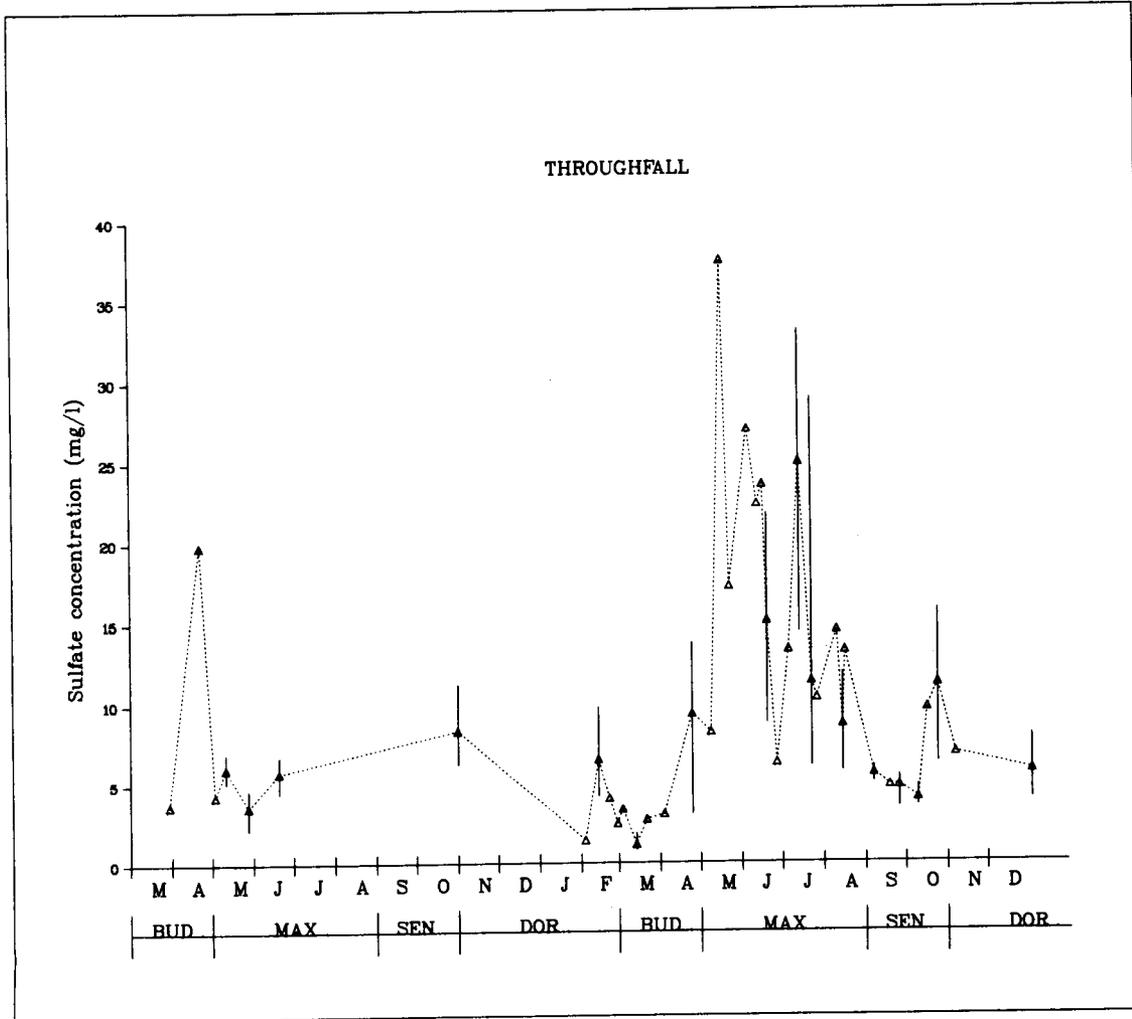


Fig. B11. Temporal variations in the concentration of sulfate in incident precipitation from March 1976 to December 1977. Events sampled at one station are represented by individual triangles. Events sampled at more than one station are represented by triangles (mean concentration) intersected by vertical lines (range in concentrations).

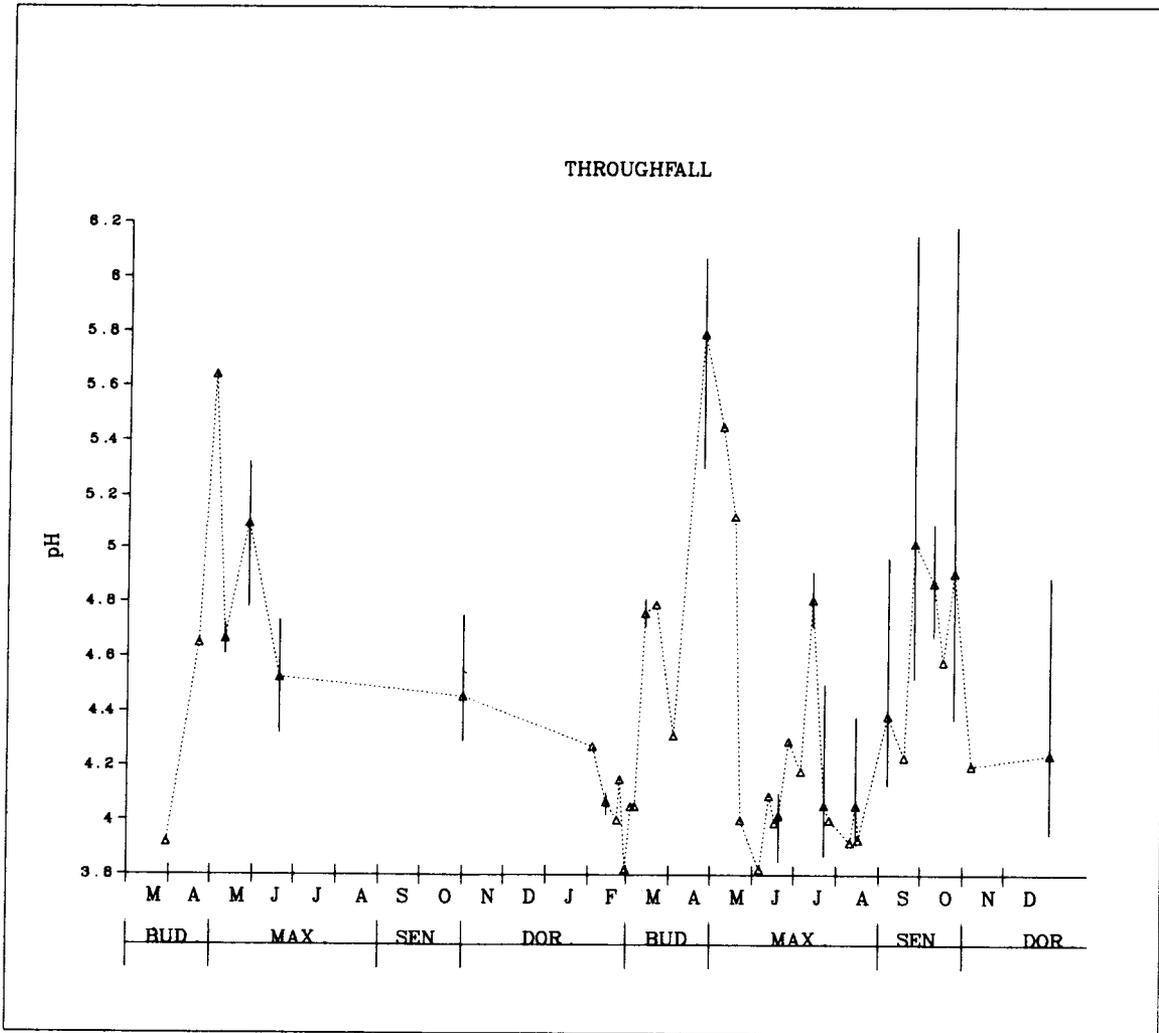


Fig. B12. Temporal variations in the concentration of pH in incident precipitation from March 1976 to December 1977. Events sampled at one station are represented by individual triangles. Events sampled at more than one station are represented by triangles (mean concentration) intersected by vertical lines (range in concentrations).

APPENDIX C
STATISTICAL CONSIDERATION OF TEMPORAL AND SPATIAL EFFECTS
ON CONCENTRATIONS IN RAIN AND THROUGHFALL

STATISTICAL CONSIDERATION OF TEMPORAL AND SPATIAL EFFECTS
ON CONCENTRATIONS IN RAIN AND THROUGHFALL

Spatial Variability

Because of the large variability in rain and throughfall chemistry during the 2-year study and because of the nature of the distributions of the data previously described, it is useful to initially compare plots of percentiles data sets at each sample location. These sites were illustrated and described in detail in Chapter V. Figures C1 and C2 contain such plots for all elements in rain and throughfall by sample site. Each plot illustrates the frequency distribution of an element in rain or throughfall showing overall range, interquartile range (25th to 75th percentiles), median, selected upper level percentiles, and number of observations. The utility of these plots is for preliminary, visual, comparisons of diverse data sets, since they provide a simple summary of the data in any given set.

The plots of incident precipitation in Figure C1 reveal some interesting trends. Median values of Cd and Zn concentrations in rain are higher at the GI (ground level) site than the CI (above canopy) site, although the interquartile ranges are somewhat smaller and show considerable overlap between sites. For Pb and $\text{SO}_4^{=}$ the opposite is true with the GI site showing lower median values but somewhat greater interquartile ranges, still with considerable overlap, however. For Mn the interquartile range and median concentration at

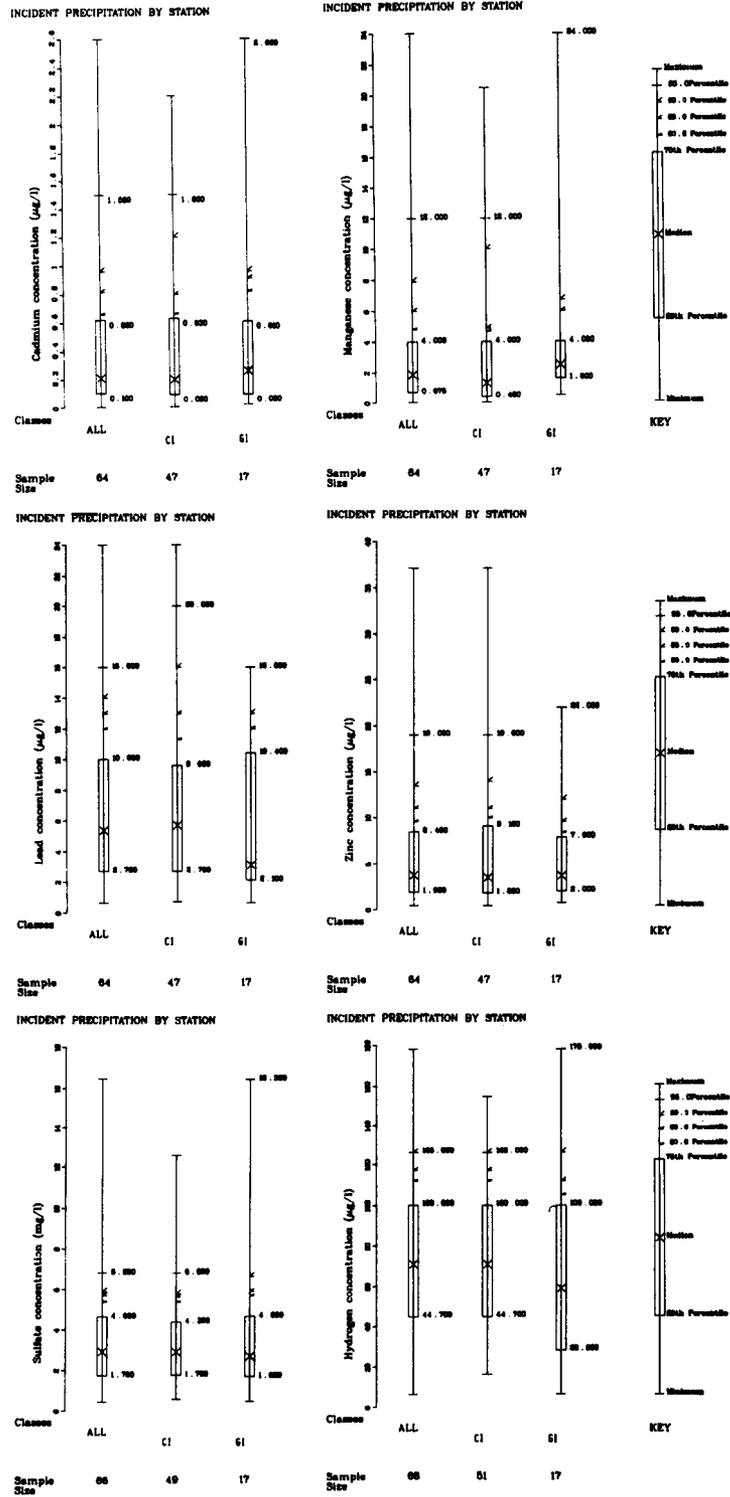


Fig. C1. Plots of percentiles of concentrations in incident precipitation at two rain sampling sites during 1976-1977.

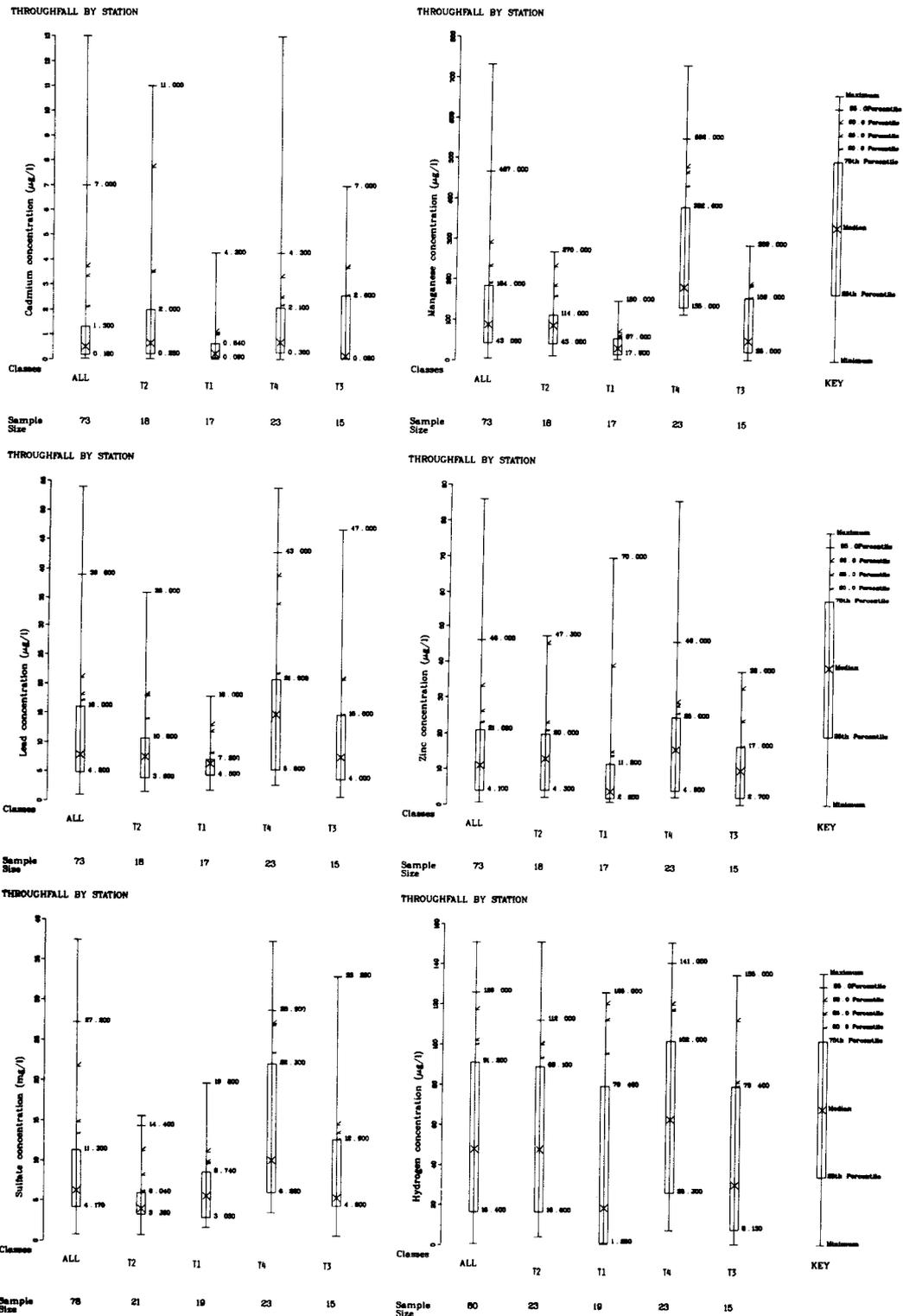


Fig. C2. Plots of percentiles of concentrations in throughfall at four below-canopy sampling sites during 1976-1977.

the GI site are both somewhat higher than at the CI site. For H^+ , both the median and interquartile range are lower at the ground level site than the above canopy site.

In the case of throughfall, site variability in chemistry is illustrated in Figure C2. The most obvious trend in these plots is the consistently higher median concentration and generally higher interquartile range at the T4 site (single chestnut oak tree) for each element. With the exception of $SO_4^{=}$, the T1 site (beech-poplar) exhibited generally lower median levels and interquartile ranges. For Cd, Pb, Zn, and H^+ however, the interquartile ranges show considerable overlap from site to site. Only in the case of Mn, and perhaps $SO_4^{=}$, are there obvious differences in both median concentrations and interquartile ranges between stations.

As indicated on the frequency plots the number of observations at each station were not equal. For various reasons including isolated power outages during storm sampling, sampler malfunction, maintenance work, and occasional visible contamination of a sample by bird feces, insects, etc., samples were not collected at all locations during every event. Thus, to more accurately determine the significance of the trends indicated by the percentile plots, separate, balanced data sets were compiled for both rain and throughfall samples consisting of several events sampled simultaneously at both incident precipitation sites or at all 4 throughfall sites over the 2-year period. To preclude seasonal or rain volume biases in this data, events were selected from each season and ranging in rainfall from 0.2 to 6.6 cm.

The data yielded 12 such events for incident precipitation and 8 for throughfall. Because of the non-normality of the data distributions and the limited number of observations in these two data sets, nonparametric tests were utilized to determine statistically significant differences between sites for either rain or throughfall chemistry. For the rain data (CI vs GI sites) the Wilcoxon signed rank test was used while in the multiple site case of throughfall Friedman's rank sum test was applied (Hollander and Wolfe, 1973).

The results of the nonparametric tests are summarized in Figure 31 (in the text, Chapter V) which presents a comparison of the mean values, standard errors of the means, and statistical significance of differences between sites. Differences were tested at both the 0.01 and 0.05 probability levels of significance and are so indicated on the figure. Although the trends noted above for the complete incident precipitation data set are still apparent (i.e., Cd and Mn somewhat higher at GI; Pb, and Zn, and $\text{SO}_4^{=}$ comparable at both sites; H^+ somewhat lower at GI site) only for Mn was there a highly significant ($P \leq 0.01$) difference in rain chemistry between the GI and CI sites (CI mean concentration = $1.7 \pm 0.4 \mu\text{g/l}$; GI = $2.6 \pm 0.5 \mu\text{g/l}$). In addition there were somewhat less significant ($P \leq 0.05$) location effects on Cd concentration (CI, $\bar{X} = 0.42 \pm 0.10 \mu\text{g/l}$; GI, $\bar{X} = 0.74 \pm 0.23 \mu\text{g/l}$) and on H^+ concentration (CI, $\bar{X} = 74 \pm 11 \mu\text{g/l}$; GI, $\bar{X} = 0.068 \pm 0.011 \mu\text{g/l}$). The tests were used with both two sided hypotheses (CI = GI) and one sided hypotheses (GI > CI or GI < CI). For the elements with significant site effects the one sided tests yielded the following:

for Mn the null hypothesis that $GI \geq CI$ could not be rejected at the 0.01 level, similarly for Cd the hypothesis that $GI \leq CI$ could not be rejected at the 0.05 level while for H^+ the hypothesis that $GI \leq CI$ could not be rejected at the 0.05 level. It is worth noting that the significance of the station differences for Mn and H^+ is difficult to discern from Figure 31 ($\bar{X} \pm SE$) in Chapter V. However, the calculation used in the nonparametric tests indicated that for both Mn and H^+ , although the differences between CI and GI were small, the arithmetic sign of the differences was consistent. In every event sampled the GI concentration of Mn exceeded the concentration at CI while in the case of H^+ every storm but one exhibited equal or lower H^+ concentrations at the GI site relative to the CI site.

The differences in Mn and H^+ concentrations between the ground level and above canopy incident precipitation sites may be related to the possible canopy interception effects described above for the GI site. Rain marginally interacting with the edges of the canopy before being collected by the GI sampler would be expected to show enrichment in the element whose concentration is most strongly influenced by canopy interception. For the suite of elements studied here, this element is Mn (as indicated by a comparison of mean values in rain and throughfall in Table 26, Chapter V). In addition; as discussed above, the effect of the canopy on H^+ chemistry is generally to decrease the H^+ levels in throughfall relative to rain. This effect is, however, less pronounced than the Mn effect, being both seasonally dependent and site specific. This may account for the fact that the location effect on H^+ in incident rain was somewhat less significant ($P \leq 0.05$).

Figure 31, Chapter V, also illustrates the differences in mean throughfall concentrations for storms sampled simultaneously at all 4 sites. As noted earlier for the complete data set (Figure C2), site T4 generally exhibited the highest elemental concentrations in throughfall while T1 exhibits the lowest. Despite this trend the nonparametric tests indicated only one series of significant site effects, those for Mn. Site T4 produced throughfall with a significantly greater Mn concentration than T1 ($P \leq 0.01$) and marginally greater than sites T2 and T3 ($P \leq 0.05$), although there were no significant differences between T1, T2, and T3 ($P > 0.05$). Thus it appears that, although there is a trend of somewhat lower throughfall concentrations for all elements beneath the beech-poplar canopy (T1) compared to the chestnut oak canopies, there are generally no significant differences between the two canopy types. Rather, the significant difference for Mn concentrations in throughfall is between the beech-poplar site and one specific chestnut oak site (single-tree site) in throughfall Mn levels. It is interesting that the element in rain whose concentration is most strongly influenced by interaction with the forest canopy, Mn, is the only element to exhibit significant location effects in throughfall. The nature of this interaction, including a discussion of the sources of various elements in throughfall, is presented in a subsequent section in more detail. It appears from this discussion and data presented in Chapters IV, V, and VII, that Mn is the only element of the group studied here whose concentration in throughfall results primarily from internal leaf leaching and only to a minor extent from surface associated dry deposition. Thus Mn would be the most likely of

the elements studied to exhibit differences in throughfall concentrations beneath different canopy types or between different age class trees of the same species.

Temporal Variability

The seasonal distribution of all chemical data collected during 1976-1977 is presented in Figures C3 and C4, in the form of percentile plots (described in the previous section). The seasons listed in the figures are related to conditions of the deciduous forest canopy and roughly correspond to the natural seasonal cycle with "dormant" comprising the months of November to February; "budbreak" includes the months of March and April and is the period during which all major deciduous forest species are forming new leaves; "maximum growth" runs from May to August and represents the period of maximum leaf growth and canopy development; and "senescence" which includes September and October and is the period during which deciduous species are in the process of losing their leaves.

From the figures it is apparent that seasonal variations are quite complex with each constituent exhibiting unique trends for incident precipitation and throughfall. For example, somewhat higher levels of Cd in both rain and throughfall occurred during the dormant and maximum growth periods (as shown by the interquartile ranges); the concentration of Mn, Pb, and SO_4^- each reached maxima in both rain and throughfall during the maximum growth period; Zn concentration peaked during the senescence period; while H^+ in rain was highest during maximum growth while in throughfall H^+ was highest during

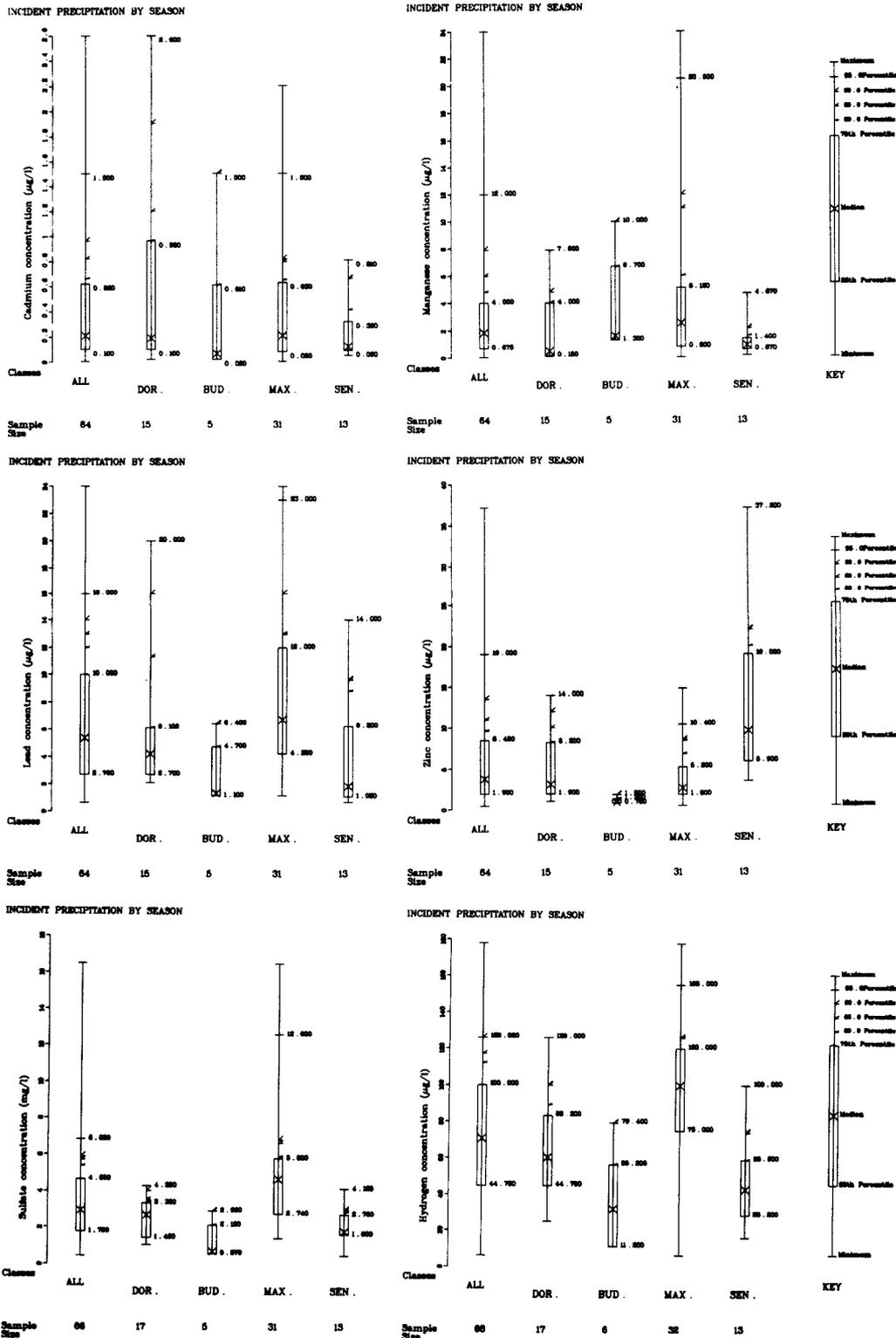


Fig. C3. Plots of percentiles of concentrations in incident precipitation within each of four periods of canopy development during 1976-1977. These periods roughly correspond to the four seasons as follows: Dormant, Nov.-Feb. (~ winter); Budbreak, Mar.-Apr. (~ spring); Maximum Growth, May-Aug. (~ summer); Senescence, Sept.-Oct. (~ fall).

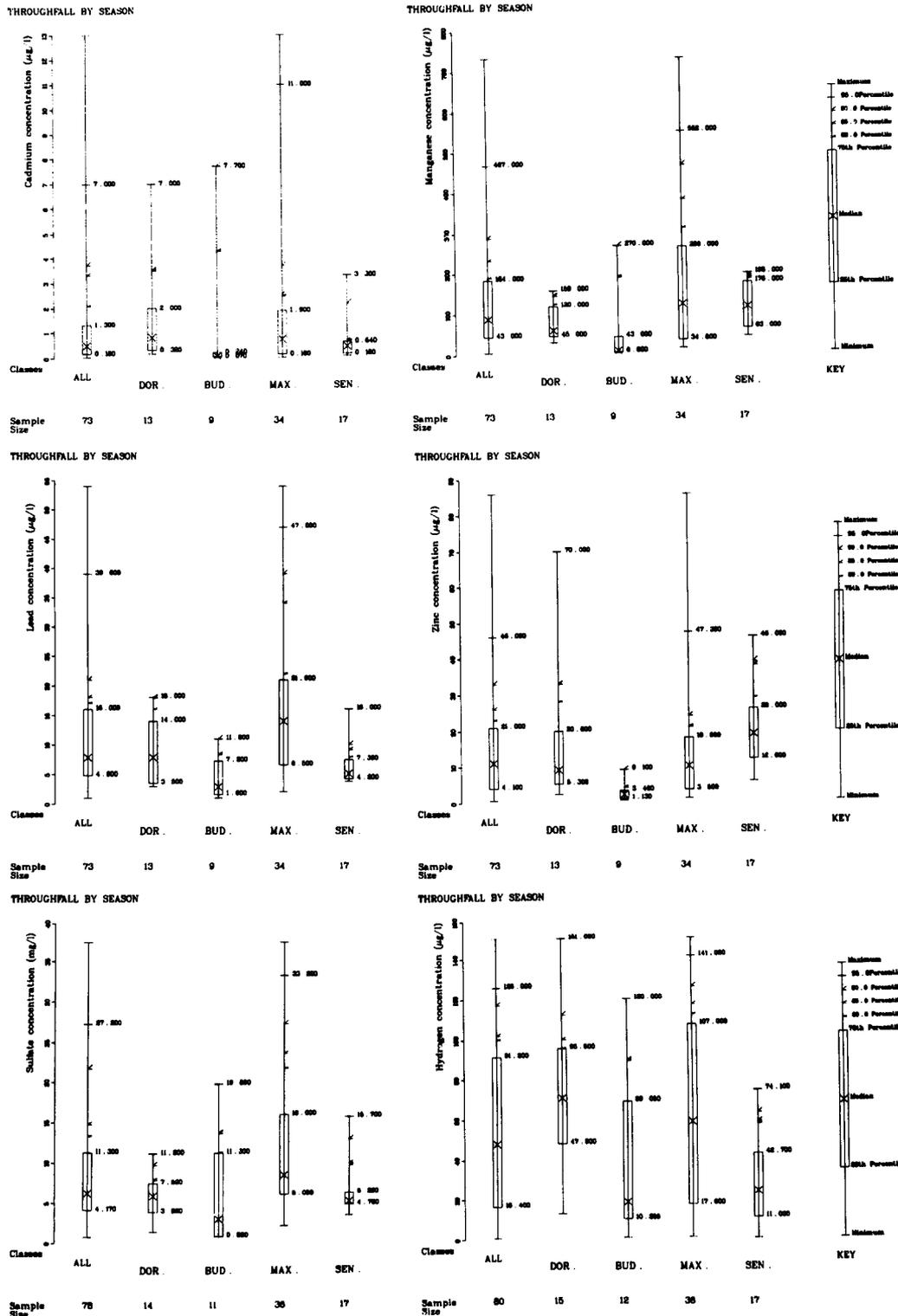


Fig. C4. Plots of percentiles of concentrations in throughfall within each of four periods of canopy development during 1976-1977. These periods roughly correspond to the four seasons as follows: Dormant, Nov.-Feb. (~ winter); Budbreak, Mar.-Apr. (~ spring); Maximum Growth, May-Aug. (~ summer); Senescence, Sept.-Oct. (~ fall).

dormant and maximum growth. However it is clear that there is considerable overlap of the seasonal data distributions for any one element, with the exception of Zn and H^+ in incident precipitation and Zn in throughfall. It is also clear from the frequency plots that in the case of Cd in rain, for example, the mean concentration for different seasons could be strongly influenced by a relatively small number of high concentrations (those above the 75th percentile) even though the median values are similar and the interquartile ranges overlap.

With this in mind analysis of variance (ANOVA) was used to determine significant seasonal effects on rain and throughfall chemistry. Because of the lognormal distribution of most of the data, the possible effect of rain volume, and the previously discussed effect of station location on some of the parameters a number of models were tested. The initial model was devised to test for seasonal and annual effects on elemental concentrations using a modified data set containing only those elements for which no highly significant station effects had been found ($P \leq 0.01$; i.e., all elements except Mn). Since significant location effects were not found for these parameters the data sets were modified by replacing every group of "replicate" observations of either incident or throughfall elemental concentrations for any given event by a single concentration equal to the mean of the "replicate" concentrations. Although this had the effect of decreasing the total number of observations in the data sets, it satisfied the requirements for the use of ANOVA concerning independence between observations. In the case of Mn which exhibited significant station

effects, the ANOVA tests were run on individual stations. In addition, to better satisfy the other ANOVA assumptions of normality in the data distributions, the tests were run using log transformed concentrations in the case of Cd, Mn, Pb, Zn, and sulfate (which exhibited lognormal distributions). Hydrogen ion concentrations were tested without transformation since they exhibited normal distributions.

This initial model ignored the effect of year and season on rainfall volume which, manifested as differences in precipitation amount per event for each season or year, could have an effect on rain chemistry. The model was defined as a two factor main effects analysis of variance with one crossed factor:

$$C_{ijk} = \mu + S_i + Y_j + (S * Y)_{ij} + f_{ijk}$$

(where C = elemental concentration in rain or throughfall, μ = constant, S = seasonal effect, Y = annual effect, S * Y = season by year interaction effect, f = error residual). Thus if ANOVA yielded highly significant effects with the above model for any given element in rain or throughfall, ($P \leq 0.01$), Duncan's new multiple range test (Duncan) was used to distinguish significant differences between seasonal or annual concentrations. The results of these comparisons are summarized in Table 27, Chapter V. The table presents annual and seasonal average concentrations and standard errors for the modified data set indicating significant differences as determined by ANOVA and Duncan. Annual or seasonal mean values followed by the same or no letter are not significantly different ($P > 0.01$).

Concentrations of each element in rain and throughfall, with the exception of Zn, exhibited the trend of higher concentrations in 1977 compared to 1976, although in no cases were the differences significant. The mean rain volume for the events sampled in 1976 was somewhat higher than that for those sampled during 1977 (3.7 cm vs 2.9 cm) which may partially account for the trend toward higher concentrations during 1977 for Cd, Pb, and $\text{SO}_4^{=}$ in both rain and throughfall. However, the higher concentration of H^+ in throughfall during 1977 relative to 1976 can not be due to a similar trend in the incident rain which actually decreased in mean H^+ concentration from 1976 to 1977. Rather the higher throughfall concentrations of H^+ relate to the influence of a 4-week period during the summer of 1977 when the throughfall H^+ concentrations approached and, on occasion, exceeded the incident rain concentrations. This suggested little if any effect of the fully developed forest canopy in scavenging H^+ from incoming rain during this period. This phenomena was discussed in detail in in detail Chapter V. Similarly for Mn, which had to be considered for each individual station (summarized in Table 28, Chapter V), there were higher concentration levels during 1977 at all stations except T2. However, only for the two incident stations were the between year differences significant. The necessity to consider Mn on a station by station basis may have precluded the discovery of more significant effects because of the more limited data sets which had to be used. This is especially true in the case of seasonal effects on Mn concentrations. As discussed above the frequency plots of the combined Mn data set indicated higher levels in rain and throughfall during the

maximum growth period. However, as Table 28 (Chapter V) indicated, this is not reflected at all stations. The above canopy site (CI) experienced somewhat higher Mn concentrations during budbreak while at the ground level incident site the highest concentrations occurred during the maximum growth period. This is related to the canopy interception effect at the station, as described above, which is expected to be more pronounced during full canopy development. In the case of the throughfall sites, the beech-poplar canopy (T1) yielded highest Mn levels during leaf senescence, the multiple tree chestnut oak sites (T2, T3) showed relatively little seasonal variations in Mn levels, while the single tree chestnut oak site (T4) exhibited considerably higher Mn concentration during the maximum growth period. It is apparent that the station differences in throughfall, Mn concentrations discussed above are further manifested in the seasonal behavior of Mn concentrations in throughfall beneath various canopies.

Significant seasonal effects ($P \leq 0.01$) were found for all elements except Cd and Pb in rain and Cd and H^+ in throughfall (Table 27, Chapter V). Although the seasonal variations for each element were different, in general the seasonal trends for any element in rain were reflected by similar trends in throughfall. This is true for Pb, Zn, and $SO_4^{=}$ where the seasonal patterns between rain and throughfall were identical, and for Cd to a lesser extent. This suggest that, although the forest canopy has an obvious influence on the chemistry of rain passing through it, the composition of throughfall is still somewhat related to the composition of the incoming rain.

Maximum concentrations of Pb and $\text{SO}_4^{=}$ in both rain and throughfall occurred during the maximum growth period, when the deciduous canopy was fully developed. The levels of $\text{SO}_4^{=}$ during maximum growth were significantly different from all other seasonal concentrations in both incident precipitation and throughfall. The seasonal differences for Pb were not significant in rain but were in throughfall ($P \leq 0.01$). Hydrogen ion in rain exhibited highest concentrations during maximum growth with the levels during the period being significantly different from budbreak and senescence but not dormant. Although the highest seasonal H^+ concentration in incoming rain occurred during the maximum growth period, the ability of the fully developed canopy to scavenge hydrogen ions was evident in the considerably decreased concentration of H^+ in throughfall during this period. However, during the dormant, leafless period the incident and throughfall H^+ levels were comparable, with the peak concentration in throughfall occurring at the time. The role of the canopy as an exchange site for H^+ is considered in detail in a subsequent section. Zinc in both rain and throughfall occurred in highest concentrations during the senescence period with the incident rain concentration being significantly different from all other seasons. In throughfall the concentration of Zn during this period was significantly different only from the budbreak concentration. Cadmium in rain and throughfall did not exhibit any significant seasonal effects although the trend was for highest concentrations in rain to occur during dormant and highest throughfall concentrations during maximum growth.

As a final test of the validity of the above seasonal effects a second ANOVA model was used which included the effect of rainfall volume per event for each sample. The analysis of variance was done using the same models described above but including the continuous variable "measured precipitation" as a covariable in each model. Two variations of each original model were used: one assuming parallel slopes of measured precipitation vs elemental concentration for a given element in each season (i.e., the effect of rain volume on the concentration of an element in rain or throughfall is the same during each season), and a second assuming separate slopes for each season (i.e., different effects of rain volume on elemental concentrations during each season).

The inclusion of the rain volume covariate did not substantially alter the conclusions of the ANOVA models discussed above. However, the analysis of covariance models did indicate a significant influence of precipitation volume on all elemental concentrations except for Zn in rain and Zn and H^+ in throughfall. Where significant rain volume effects were seen, the slopes of the predicted rain volume - elemental concentration equations were not significantly different between seasons. However, for certain season/element combinations in both rain and throughfall, the slopes were not significantly different from zero. This indicates that the effect of rain volume on elemental concentrations is similar from season to season but not necessarily significant during certain seasons.

Thus the net results of the analyses of variance and covariance of the incident precipitation and throughfall data are as follows: (1) Cd and Mn exhibited no significant seasonal effects; (2) Pb in rain showed a significant seasonal effect only during 1977, Pb in throughfall showed an effect of season for the 2 year data set; (3) Zn and $\text{SO}_4^{=}$ concentrations in rain and throughfall were significantly influenced by season; and (4) H^+ in incident precipitation exhibited a significant season effect for the 2-year data set, while H^+ in throughfall showed a significant season effect only during 1977. For elements with significant seasonal effects, the maximum concentrations of Pb, $\text{SO}_4^{=}$, and H^+ in rain occurred during the maximum growth period while the peak in Zn occurred during senescence. In throughfall the maximum concentrations of Pb and $\text{SO}_4^{=}$ occurred during maximum growth, Zn during senescence, and H^+ during the dormant period.

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