CONF-800560--1

AIR POLLUTANT INTERACTIONS WITH VEGETATION: RESEARCH NEEDS IN DATA ACQUISITION AND INTERPRETATION

MASTER

Steven E. Lindberg
and
S. B. McLaughlin

Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

---

[1] Research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation.

[2] Publication No. 1525, Environmental Sciences Division, ORNL.

DISCLAIMER

TABLE OF CONTENTS

1 INTRODUCTION

Collection of the data necessary to adequately address the issue of air pollutant/vegetation interactions is not a straightforward task. A formidable challenge is acquisition of data unbiased by the experimental design, uncomplicated by the wide degree of variability associated with natural systems, and uncontaminated by the sampling apparatus. Those who advocate strictly controlled experiments in which variables are manipulated are faced with noncomparability with the "real world." On the other hand, those who advocate field studies of pollutant/ecosystem interactions are often accused of being unable to clearly interpret their data in light of the known variability of several uncontrolled, interrelated parameters. The ultimate solution will likely involve an integration of these two approaches.

Another difficult problem is one of scale. The most apparent effects of air pollutants on terrestrial biota, including man, occur on a localized scale in urban and industrial areas where pollutant concentrations are high due to local activity. However, ecosystem-level effects result from pollutant exposures integrated over both time and space. Such effects are often due to chronic exposure to larger portions of the atmosphere where pollutant concentrations are much smaller because of dilution and removal mechanisms. The situation is further complicated by effects related to exposure to pollutant mixtures and to transient pulses of high pollutant concentrations. The distinction between local and regional pollutant concentrations is critical in the design of sampling programs. Because of the considerable decrease in atmospheric concentrations of gases and particles from local to regional and global scales, the necessary sample collection and analytical methodologies are quite different in many cases.

Methods useful in monitoring local pollution levels may be inappropriate for the monitoring of regional "background" levels. The problem is further compounded by the fact that most constituents of anthropogenic emissions also occur naturally in the atmosphere. This suggests the need for increased sensitivity, precision, accuracy, and time resolution in future monitoring techniques.

The objective of this discussion is to consider these and other problems involved in the acquisition, interpretation, and application of data collected in studies of air pollutant interactions with the terrestrial environment. Emphasis will be placed on a critical evaluation of current deficiencies and future research needs by addressing the following questions: (1) which pollutants are either sufficiently toxic, pervasive, or persistent to warrant the expense of monitoring and effects research; (2) what are the interactions of multiple pollutants during deposition and how do these influence toxicity; (3) how do we collect, report, and interpret deposition and air quality data to ensure its maximum utility in assessment of potential regional environmental effects; (4) what processes do we study, and how are they measured to most efficiently describe the relationship between air quality dose and ultimate impacts on terrestrial ecosystems; and (5) how do we integrate site-specific studies into regional estimates of present and potential environmental degradation (or benefit)?

2 CHARACTERIZING AND MONITORING ATMOSPHERIC CONSTITUENTS

2.1 What Pollutants Are of Interest?

Monitoring implies field measurements which can sense changes in environmental quality so that corrective measures may be taken before serious deterioration results. Physical measurements of certain atmospheric parameters (temperature, wind speed and direction) can be made with speed and simplicity, such that interpretations of changes in physical parameters can be made nearly simultaneously with the measurements. Some chemical measurements, such as pH and trace gas concentrations (SO_2, NO, O_3, CO), can also be continuously monitored using reliable field instrumentation. However, for other critical chemical parameters (toxic metals and organic compounds in either gaseous form, particle-associated, or dissolved in meteoric waters), substantial time delays between sampling in the field and measurement in the laboratory are required.

The decision of which constituents to monitor on local and regional scales is not as straightforward as it may seem. There is, of course, the general physical categorization of gas phase vs particle-associated, and beyond that, organic vs inorganic. Since in many cases scientists have specialized in either particle or gaseous pollutant interactions, this seems a logical division.

2.1.1. Particles

The sources of many of the long-lived particles in the atmosphere are various combustion processes, both natural and associated with man's activities. It follows that those elements which exhibit, or whose compounds exhibit, high volatilities might be expected to occur in relatively high atmospheric concentrations. In addition, volatile elements are generally discharged from combustion sources as either gases or associated with submicron particles, both phases being relatively poorly contained by conventional emission control technology and exhibiting relatively long atmospheric residence times (Van Hook and Shultz, 1977; Keyser et al., 1978). Gas-phase reactions with particles result in preferential concentration of volatile elements on particle surfaces (Natusch et al., 1974; Natusch and Wallace, 1974; Keyser et al., 1978) which may increase their effective bioavailability through solubilization reactions (Eisenbud and Kneip, 1975; Lindberg et al., 1979a).

A list of the elements having the above characteristics and suspected or known to cause adverse environmental effects indicates that there is some justification for the monitoring of approximately 25% of the elements in the periodic table. Although it is difficult to develop rigid priorities from such a cursory examination, it is helpful to select a more tractable list of priority constituents of atmospheric particulate matter. We have selected those elements which have been repeatedly identified elsewhere in lists of toxic elements/compounds, elements readily mobilized by man's activities, and elements highly enriched in both urban and regional aerosols (Schroeder, 1971; Duce et al., 1975; Zoller et al., 1974; Andren and Lindberg, 1977; Heindryckx, 1976; Lawson and Winchester, 1978; Gordon, 1975; Van Hook and Shultz, 1977; Morgan, 1975; Vaughan et al., 1975; Lim, 1979). This list includes the following: Hg, Cd, Pb, Sb, Se, S (as acid sulfates), and C (as hydrocarbons). Because of the existence of Hg primarily as a vapor in combustion and other industrial processes and in the ambient air (Lindberg and Turner, 1977; Lindberg, 1980), it will be considered in the discussion of gaseous pollutants.

Carbon is included in this list to represent the general class of airborne microcontaminants which are becoming increasingly important because of their ubiquity and toxicity (including carcinogenic and mutagenic activity)(Chrisp et al., 1977; Fisher et al., 1979). Of these compounds simple, polyaromatic, substituted, and halogenated hydrocarbons may be of most concern (Weisburger, 1979; Bjorseth et al., 1979; Griest and Guerin, 1979). Because of the limited knowledge concerning their behavior, considerable research is required in the areas of sampling and analytical methodology, atmospheric transport and transformation, and the effects of organic micropollutants on the terrestrial environment.

2.1.2. Gases

The gaseous pollutants which currently occur at phytotoxic levels over broad areas of industrialized countries are SO_2, O_3, and NO_2. The U.S. Environmental Protection Agency (EPA) annually publishes a National Air Quality and Emissions Trend Report (most recently for 1977) to report temporal and spatial variability in levels of these pollutants. Concern over their occurrence and distribution is based primarily on their potential interactions (see Reinert et al., 1975) at the relatively low levels ($\leq$ 0.10 ppm) at which they occur on a regional basis. Problems of a local scale may also occur around industrial point sources of HF, SiF_4, Cl_2, HCl, NH_4, and H_2S; however, none of these pollutants currently warrant the expense of a national monitoring network.

Future trends in industrial development, transportation patterns, and fossil fuel combustion may alter our air quality monitoring needs. Secondary pollutants such as peroxyacetyl nitrates (PAN and other homologs) may become more significant. Complex organic and sulfur-containing compounds may become important as effluents from the developing coal conversion industry (Gehrs et al., 1980). Their significance will depend heavily on technological choices (sulfur recovery and off-gas flaring) currently being considered.

Increased reliance on coal may make monitoring of volatile trace inorganics an important consideration in evaluating potential long-term impacts on terrestrial ecosystems. Mercury is a potentially phytotoxic pollutant which is emitted primarily in gaseous form during the combustion of coal, remains as a vapor in ambient air, and can be directly absorbed by some crop plants (Lindberg et al., 1979b; Lindberg, 1980). The potential for interactions between subacute levels of mercury and other regional-scale gaseous pollutants is not known.

2.2 What Levels of Concentration Are of Interest at the Source and at the Receptor?

The variability of trace element concentrations in ambient air and in precipitation collected above and below the forest canopy has recently been reported to be over several orders of magnitude (McMullen and Faoro, 1977; Lindberg et al., 1979a). It is apparent from these reports that some knowledge of expected concentration ranges is necessary to ensure accurate selection of both sampling and analytical techniques prior to the initiation of monitoring. Only then can one be assured of optimium precision and accuracy in reported data without complicating future data analyses with the reporting of "less than" or "below detection" values or data resulting from detector overload or nonlinear response problems.

Although there exists considerable data on time-averaged concentrations in various media, there is a need for determination of short-term concentrations at the exposure microsite itself. In the context of this symposium this includes the concentration in the air at the leaf boundary layer, the concentration of dry deposited material on the foliar surface, and the concentration of material in solution on the foliar surface as a result of wet deposition and subsequent interaction with previously dry deposited material. These data are strongly related to vegetation effects and should prove essential for predictive purposes. An additional need is for analysis of fine-scale temporal variations in concentration both at the source and at the receptor. Studies of temporal variability have proved very useful in the identification of pollutant sources and mechanisms of surface transfer and in the prediction of vegetation effects (Raynor, 1976; Lawson and Winchester, 1978; McLaughlin et al., 1979).

2.3 Sampling and Analytical Methodology

It is widely recognized by those familiar with highly sensitive, multielement analytical techniques employed in air pollution studies that problems associated with sample collection are often the "limiting step" in achieving the levels of precision and accuracy necessary for unbiased data analysis. The general problem of representative sample collection (as influenced by contamination from collection surfaces or reagents, irreversible loss of some component of the pollutant to the sample container, and post-depositional reactions between several pollutants) often controls detection limits, rather than sensitivity of the analytical instrumentation (Altshuller, 1972, Lindberg et al., 1977).

It is not the intent of this review to describe in detail the wide range of sampling and analytical techniques used in this field (see the discussion by Newman and Gordon, this symposium). Rather, we will review the problems associated with the collection, analysis, and interpretation of particulate pollutants in the atmosphere. The problems associated with sampling and analysis of gases are primarily those of achieving micro-scale response times of the associated analytical instrumentation and unequivocal separation of gas and particulate species of the same element (e.g., S, N). The former problem is largely limited to the field of micrometeorology where subsecond response times are often necessary for eddy correlation calculations of pollutant fluxes (Hicks and Wesely, 1980). In general, the available technologies afford sufficient response times (seconds to minutes) for the needs of the plant physiologist interested in major gaseous pollutant effects (O_3, SO_2, NO_2). Work is needed, however, on development of subminute response samplers/detectors for trace-level gases (e.g., CS_2, Hg°). The problem of separation of gas and particulate forms applies equally to particulate characterization and will be discussed below.

In our opinion the problems associated with particle collection are more complex and the solutions more urgently needed. While aerosol concentration monitoring is accepted as a necessity in human health effects studies, its relationship to terrestrial effects studies may not be as apparent (National Research Council, 1979). At a recent EPA-sponsored workshop on dry deposition methodologies (Hicks et al., in preparation), several experts in the field advocated the use of monitoring data on suspended-particle concentrations to calculate dry deposition fluxes. This suggestion reflected the recognition of the inadequacies of dry deposition "collectors" (discussed further in Section 4.1.2).

Particle sampling procedures are subject to errors related to gravitational, inertial, diffusional, thermal, and electrical forces and chemical interactions. In addition, the problem of spatial heterogeneity of the dispersed aerosol may, in itself, overwhelm the others. While these problems directly confront the researcher actively involved in sample collection, we are all subject to the problem of improper interpretation and application of data collected without careful attention to potential sampling and analytical errors. This discussion is aimed primarily toward those individuals, who may not be experts in the field of particle physics, with a need to interpret existing aerosol data in the context of air pollutant deposition and effects studies or to acquire their own data while constrained with limited resources. A recent, more detailed review of aerosol measurement is presented in Lundgren et al. (1979).

Suspended particles are collected primarily by three techniques: filtration, impaction, and impingement or some combination of these, with filtration and impaction used in more than 75% of the applications. With some exceptions, filtration yields only the "total" aerosol while impaction also provides the particle size distribution. In their simplest form aerosol filters consist of an inert filter holder through which air is drawn at flow rates ranging from ~ 1 liter/min to ~1800 liter/min. The most often used impactor, the cascade impactor, consists of a series of orifices of decreasing diameter behind which are mounted the impaction surfaces intended for chemical analysis, and onto which particles in a selected size range are deposited as air is drawn through the device. Impactors also often utilize filters as impaction surfaces or in a "backup" mode to collect the finest particles not impacted on the upper stages.

Care must be taken in the use of these methods and subsequent analysis and interpretation of the data, particularly when applied in the context of this symposium. Table 1 lists several specific problems inherent in these methods. In general, the specific problems all relate to the collection of a sample representative of material suspended in the atmosphere or the performance of an analysis truely representative of the collected material.

In the case of filtration methods, the analytical problems are often related to the filter itself or to post-depositional changes in particle chemistry following collection. Of the many filters now available, the most often used are glass fiber and cellulose in high volume (~ 1800 liter/min) samplers (Hi-vols), and various membrane filters (cellulose acetate, polycarbonate, teflon) in addition to glass fiber and cellulose in low volume (~ 1 to 30 liter/min) and impactor samplers. While glass fiber filters have been the standard in Hi-vol sampling and are known to exhibit high efficiencies for retention of submicron aerosols (Lockhart et al., 1963), they are often unacceptable for trace-level inorganic analysis because of their high and variable trace element content (Neustadter et al., 1975; Sievering et al., 1978). On the other hand, because of their inert nature with respect to organic solvents and their relatively low ability to adsorb many hydrocarbons, particularly polyaromatic hydrocarbons (Brown et al., in preparation), glass fiber filters may be the only choice for trace organic analysis of aerosols (see Pierce and Katz, 1975). While cellulose filters are consistently lower in trace-element content than glass fiber, they may exhibit lower particle collection efficiencies (Lindekin et al., 1963; Sievering et al., 1978), although there is some question as to the statistical significance of these differences (Neustadter et al., 1975).

Table 1. Typical problems encountered in the characterization of airborne particles by filtration and impaction methods

Filters	Impactors
1. High blanks (contamination)(+)[a]	1. High blanks (+)
2. Non-isokinetic sampling (-)[b]	2. Non-isokinetic sampling (-)
3. Small particle loss (-)	3. Particle bounce (ΔS)[c]
4. Pressure drop-decreasing flow (-)	4. Wall loss (ΔS, -)
5. Clogging (-)	5. Small particle loss (-, ΔS)
6. Gas/particle reactions on filter surface (±)	6. Pressure drop-variable flow rate (ΔS)
7. Incompatibility of filter with extraction or analytical methods (±)	7. Clogging (of backup filter) (-, ΔS)
	8. Gas/particle reactions on impaction surfaces (±, ΔS)
	9. Incompatibility of sticky-coated surfaces with extraction or analytical methods (±)
	10. Detailed aerosol behavior obscured by long sampling times (ΔS)
	11. Uncertainty in interpretation of particle sizes on backdrop filters ("less-than values")

---

[a] (+) - generally results in overestimate of concentration.

[b] (-) - underestimate.

[c] (ΔS) - results in a shift in the apparent particle size distribution.

!TABLE 1

The question of filtration efficiency also applies to low-flow samplers employing membrane filters. Large particle collection efficiencies ($> 3\ \mu m$) decrease under conditions of high filter loading, while efficiencies for smaller particles ($< 0.5\ \mu m$) may decrease under conditions of very low filter loading (Fan and Gentry, 1978; Skogerboe et al., 1977). Laboratory studies of membrane filter efficiencies have indicated that particle collection efficiency decreases rapidly, from ~ 90 to $\sim 20\%$, as particle size decreases below 1 μm for Nuclepore filters of pore size ranging from 1 to 8 μm and is dependent on pressure drop (Liu and Lee, 1976; Spurny et al., 1969, 1974). For 0.6-μm Nuclepore and 5-μm Teflon membranes, efficiencies ranged between 80 and 100% for particles 0.03 to 1.0 μm (Liu and Lee, 1976). Further research is needed to develop theory applicable under the conditions of high pressure drop and compressible gas flow occurring in routine use. Particle retention is also strongly influenced by the design of the sampler intake, its orientation with wind direction, and the use of external rain shields (Pattendon and Wiffen, 1977). A typical filter sampler collected large particles ($> 10\ \mu m$) with an efficiency of $< 15\%$. Since particles in this size range are readily removed from the atmosphere by deposition processes, the underestimate of this fraction has important implications to pollutant effects studies.

The choice and application of filter and sampler types in the field must be based on considerations of anticipated loading, particle size distribution, and analytical methodology. Such restrictions may preclude the development of a universally applicable "total" aerosol sampler. Until this becomes available it is our responsibility to present and interpret particle concentration data with consideration of the limitations of the techniques and to apply these data in effects studies with considerable care.

The quality of air concentration data may be limited by the accuracy of the measurement of total air flow through the sampler. An uncertainty in air flow rates of $\sim$ 25%, for example, results in an equal uncertainty in element concentrations in the atmosphere. Continuous flow monitoring is not always feasible; yet, flow rates may vary substantially during the course of a single collection period. The researcher is faced with the task of choosing a sampling interval sufficiently long to be compatible with his analytical sensitivity and yet short enough to prevent significant variations in flow rate.

Post-depositional chemical changes on the aerosol collection surface may result in losses or gains of some constituents during sampling. Berg (1976) reported that sampler design played a significant role in the conversion of particulate chlorine to gaseous form. Such reactions lead to an underestimate of particle concentrations and are enhanced by high filter loading and flow rates and may occur for other halides, some compounds of S and C, and Hg. In addition, in ambient air sampling for particulate sulfates, overestimates may result from absorption of SO_2 and subsequent oxidation to sulfate on the collection surface (Coutant, 1977; Cheney and Homolya, 1979). The effects of gas/particle interactions at sample collection surfaces must be considered in more detail (and for other elements) with the intent of developing techniques which minimize this problem.

Pollutant concentration data reported on a particle size basis may be more useful in effects research because of the influence of particle size on wet and dry deposition processes. In addition to the problems common to filters and impactors, Table 1 presents additional problems related to sampler design and aerosol chemistry which influence impactor operation. Non-isokinetic sampling, which results when sampling without compensation for wind speed and direction effects, leads to low collection efficiencies for the large particle fraction (> 5 μm). Wind tunnel tests of the widely used 8-stage Andersen impactor (28.3 liter/min flow rate) indicated collection efficiencies for 5 μm particles of ~ 70% and for 15 μm particles of 2% (Wedding et al., 1977b). Subsequent modifications to this impactor (now available from the manufacturer) have increased collection efficiencies to near 100% for 5 μm and 50% for 15 μm particles (Wedding et al., 1977b; McFarland et al., 1977). In comparing the size distributions of Pb, Cd, and Zn in aerosols collected in California, Davidson (1977) found a significantly larger mass of these elements in particles of > 10 μm during isokinetic experiments compared to non-isokinetic experiments performed earlier in the same area. Because of high deposition velocities associated with large particles (Sehmel and Hodgson, 1976), every effort must be made to sample this fraction efficiently.

Wall losses and particle bounce also involve primarily the large particle fraction. Particle rebound and impaction on surfaces other than those intended for analysis generally results in an underestimate of the large particle concentration (Cheng and Yeh, 1979). An equally serious consequence is distortion of the entire particle size spectrum with large particles being inadvertently deposited on stages designed to collect smaller particles (Dzubay et al., 1976). This phenomenon is relatively simple to detect by inspection of impaction stages by scanning electron microscopy and has been reported for some standard impactors (Dzubay et al., 1976; Lindberg et al., 1979a). These problems can be minimized by isokinetic sampling (Wedding et al., 1977), selection of samplers designed to be less subject to particle bounce (Gordon et al., 1973), or by coating the impaction surfaces with a sticky substance such as grease (Dzubay et al., 1976). However, the use of sticky substrates may not amenable to many extraction and analytical techniques and is inefficient under high temperature conditions (Cheng and Yeh, 1979; Casey, 1975). We have studied the water solubility of size-fractionated aerosols for several trace elements and have found grease-coated impaction surfaces to be incompatible with our extraction methods (Lindberg and Harriss, 1980). In addition, organic substrates are likely to cause serious matrix problems for the extraction and analysis of organic micropollutant aerosols.

Problems related to aerosol characteristics involve gas/particle interactions and the effect of relative humidity on aerosol impaction efficiency. Dingle and Joshi (1974) observed $\sim 25\ \mu m$ crystals of $(NH_4)_2SO_4$ on the stage of an Andersen impactor designed to collect $0.5\ \mu m$ particles. Crystal formation, enhanced under high relative humidities, could result in gross overestimates of fine-particle atmospheric sulfate concentrations. Relative humidity has also been found to influence particle adhesion to impactor surfaces, such that at humidities $> 75\%$ no sticky coating on the impaction surfaces was needed to reduce particle bounce (Winkler, 1974). With decreasing relative humidity the relative composition of the sampled aerosol may change due to preferential deposition of water-soluble material leading to an erroneous size distribution. Aerosol solubility is extremely important in vegetation effects (see discussion in Section 5.2.1); therefore, it is critical to accurately sample this material.

The collection, interpretation, and application of particulate, and to some extent gaseous, air pollutant concentration data are obviously complex tasks. The preceding review was intended to raise several questions in the mind of the air pollution effects researcher; we would like to raise a few more of our own. The importance of a constant and accurately known flow rate during filter sampling is even more critical in impactor sampling because of the additional dependence of particle size-separation efficiency on flow rate. When used without a backup filter, the designated constant flow rate for any given impactor can be readily maintained. However, in this mode, considerable fine particle material is not collected. When used with a backup filter, clogging and pressure drop can result in a variable and decreasing flow rate such that the specified particle retention characteristics of the impactor are no longer directly applicable. How is one to interpret the resulting size spectrum?

Another source of ambiguity in impactory data arises because a significant fraction (> 50%) of the total air concentration of many important major (S) and minor (Pb) pollutant elements are captured on the backup filter. The "aerodynamic cutoff diameter" for the backup filter in the standard 8-stage Andersen impactor, for example, is expressed as a "less-than" value ($< 0.5\ \mu$m). In the application of deposition models to these data, should this "particle size" be interpreted as equal to 0.5 μm, equal to 0.25 μm (midpoint between 0.5 μm and 0 μm) or in some other manner? This is critical in the estimation of dry deposition fluxes because of the strong dependence of deposition velocity on particle size for particles $< 0.5\ \mu$m (Sehmel and Hodgson, 1976).

Commonly used samplers require collection periods of ~ 12 h to several days. Winchester and co-workers have studied temporal variations in total particulate air concentrations of several elements using a "streaker" sampler of their own design and proton-induced x-ray emission analysis, yielding a 2-h resolution time (e.g., see Lawson and Winchester, 1978). If we hope to understand the mechanisms of deposition and its effect on vegetation, we need to develop instrumentation with the ability to provide data on short-term variations in pollutant concentrations and particle size distributions.

Although considerable research is still needed to address these issues, there have been important developments in the last five years, some of which are now in general use. The dichotomous sampler has been used in several monitoring networks [EPA, Multi-State Atmospheric Power Production Pollution Study (MAP3S), National Atmospheric Deposition Program (NADP)-selected sites] and is a virtual impactor designed to eliminate several typical impactor problems. Because this sampler was originally intended for use in inhalation studies to separate particles into respirable and nonrespirable sizes (Conner, 1966; Dzubay and Stevens, 1975), it is of limited value in studies of deposition to environmental surfaces because of the limited particle size fractionation (stage $1 \leq \sim 2$ μm, stage $2 > \sim 2$ μm). These same arguments apply to two-stage respirable aerosol samplers which use Nuclepore filters in series (Parker et al., 1977), although there are other multiple-filter -series samplers which have been used under controlled conditions to fractionate aerosols between 0.1 and 1 μm (Melo and Phillips, 1975).

A promising development is a recently designed low-pressure impactor compatible with ambient air sampling and available analytical techniques (Hering et al., 1978, 1979). The sampler provides highly accurate and efficient separation of aerosols into eight size classes ranging from

0.05 to 4.0 μm and minimizes size distribution distortion caused by particle bounce, reentrainment, wall loss, and evaporation. This device, combined with a sampler providing efficient large particle (> 4-μm) size classification, would provide the necessary data for application of theory and laboratory studies to the calculation of dry deposition fluxes.

In general, sampling problems outweigh those of analytical sensitivity, precision, and accuracy. For detailed discussions of analytical problems the reader is referred to recent papers on the analysis of pollutants in air (Altshuler, 1972) in precipitation (Turner and Lindberg, 1976; Lindberg et al., 1977; Peden et al., 1979), and in environmental samples in general (Tolg, 1975; Morgan, 1975). The application of x-ray and activation analysis to studies in the atmospheric environment was recently reviewed by Winchester and Desaedeleer (1975), while Harris (1976) has reviewed chemical and physical characteristics of atmospheric particles, describing suitable analytical techniques for most of the elements in the periodic table.

A crucial research need with respect to evaluating the exposure of terrestrial biota to air pollutants is chemical and physical speciation analysis. It may no longer be sufficient to know only the concentration of an element in suspended or deposited particles but also (1) the chemical form (for example, trivalent arsenic is considerably more toxic than the pentavalent form in solution; U.S. Atomic Energy Commission, 1973; National Academy of Sciences, 1977), (2) the physical distribution within the particle (trace elements in the atmosphere do not generally occur as discrete particles of Se, for example, but as heterogeneous mixtures of compounds distributed on the surface, and/or throughout the interior, of particles; e.g., see Keyser et al., 1978), and (3) the solubility of the various forms of the element associated with the particle (known to influence bioavailability; Lindberg and Harriss, 1980).

3 PREDICTING MESOSCALE TRANSPORT

Transport of a pollutant from source to receptor is controlled by mesoscale meteorological properties. Wind and temperature fields, precipitation patterns, terrain, vegetation cover, and turbulence encountered during transport influence the quantity of a pollutant ultimately delivered to the vicinity of the receptor. Several papers, reviews, and workshops (Gifford, 1975, 1976; Hanna, 1976; Hosker, 1974; Nappo, 1976; Haugen, 1975) have considered some of the common techniques and inherent problems in modeling the effluent delivery process. It was the consensus of the most recent workshop that there are severe limitations in the present modeling capability for regional transport, dispersion, and deposition of atmospheric pollutants. A detailed consideration of data requirements, interpretation, modeling and application to estimates of dispersion, and removal in the context of this symposium is presented in the companion paper (Hosker, this symposium).

4 MEASURING MASS TRANSFER TO THE CANOPY

Material is removed from the atmosphere by two general processes, dry deposition (convective diffusion, impaction and turbulent inertial deposition, and sedimentation) and wet deposition (precipitation scavenging occurring both within and below the cloud layer). The importance of dry deposition to the terrestrial environment is now well recognized; dry deposition of "pollutant" materials to a forest from ground-based sources appears to be comparable to wet deposition (Slinn, 1976). Wet deposition is of particular importance, due both to its episodic nature and the fact that pollutants are partly (or wholly) in solution, thereby enhancing the possibility of absorption by vegetation-surfaces and generally increasing the mobility of the element in the landscape. The consensus at two recent workshops on atmospheric deposition was that the wet segment of input is much more addressable with current methodologies than the dry component (Hicks et al., in preparation; Shriner et al., 1980); consequently, we will emphasize the acquisition, interpretation, and application of dry deposition data.

4.1 Dry Deposition

As the crucial link between transport of atmospheric pollutants and their ultimate uptake and effects on vegetation, the processes influencing dry deposition have been examined at levels of resolution ranging from cellular to regional in scale. Deposition rates of gaseous pollutants are controlled by a variety of physical, chemical, and biological factors (Bennett and Hill, 1975; Heck and Brandt, 1977). These include micrometeorological conditions above and within the plant canopy, leaf surface characteristics (shape, degree of pubescence, and surface chemistry), and the chemical and biological properties of individual pollutants (diffusivity, water solubility, and biological reactivity within cell systems). Evaluating the rates and direction of transport of pollutants in terrestrial ecosystems obviously requires generalization of the complex biological and environmental variables inherent in the structural complexity of these systems. Determining the level of generalization acceptable to addressing relevant questions in the framework of this complexity is a continuing challenge.

Transport of pollutants to the leaf surfaces within a plant canopy is controlled by the rate of air movement and its turbulent properties. With a simple, somewhat homogeneous, crop canopy, three distinct air layers can be distinguished (See review by Bennett and Hill, 1975): (1) a logarithmic wind profile layer (boundary) above the canopy surface, (2) an exponential canopy-eddy layer, and (3) the lowest plant-air layer where direct physical influence of the vegetation and ground surface influence the wind profile. Ultimate movement of pollutants into plant leaves occurs as a result of interactions between micrometeorological and plant physiological processes. The pathway of entry includes the leaf boundary layer, the stomata, and the aqueous layer on substomatal mesophyll cell walls (Bennett and Hill, 1973).

4.1.1 Gases

Studies to determine rates of pollutant flux into plant canopies have been conducted both in the field using principals of momentum, mass, and heat exchange (see review by Thom, 1975) and under controlled laboratory conditions where environmental variation is minimized (Bennett and Hill, 1973). Valuable insights have been provided by both approaches. In the field, generalizations are required both with respect to the geometry of the plant canopy, the turbulence it induces, and the "average" physiological status of foliage, which occurs in multiple layers. Wesely and Hicks (1977) and Hicks and Wesely (1980) have reviewed the processes influencing turbulent transfer and deposition of gases to vegetation. They note the importance of both diurnal and spatial variations on the series of within-canopy resistances determining deposition velocity. A major limitation of most approaches is the assumption of a uniform deposition velocity of 1 cm/s. Eddy flux measurements over a loblolly pine canopy (Hicks and Wesely 1980) indicate that resistances as high as 10 s/cm for O_3 and 15 s/cm for SO_2 can occur at night as stomatal closure occurs. Compounding this temporal variability for a monospecific forest canopy is the spatial heterogeneity of a typical mixed deciduous forest. Here, quantification of deposition rates to understory shrubs and tree seedlings represents an important consideration if we are to relate pollutant dose (typically measured as an above-canopy value) to uptake and effects of pollutants on the total forest system.

Chamber studies offer intriguing possibilities for examining not only deposition rates but also the associated effects on plant physiological properties. Major contributions in this area have been made by Hill (1971) and Bennett et al. (1973) (see also Bennett and Hill, 1975). Using a standardized plant canopy, Hill (1971) was able to compare uptake rates of HF, SO_2, Cl_2, NO_2, O_3, PAN, NO, and CO. A direct correlation between uptake rate and solubility of these pollutants in water (see Table 2) was shown. This relationship emphasizes the importance of ultimate pollutant uptake by moistened substomatal cell walls. Uptake rate was also inversely related to molecular weight, a factor directly influencing molecular diffusivity. These data suggest a potentially useful approach to screening phytotoxicity of the variety of complex organic gases (i.e. phenols) which may be released in coal conversion processes and about which very little is known.

Table 2. Solubility in water and uptake rate of pollutants (after Hill and Chamberlain, 1976)

Pollutant	Uptake rate alfalfa at 1 pphm[a] ($1\ min^{-1}\ m^{-2}$)	Equivalent deposition velocity ($cm\ s^{-1}$)	Solubility at 20°C (cm^3 gas cm^{-3} H_2O)
CO	0.0	0.00	0.02
NO	0.6	0.10	0.05
CO_2	2.0	0.33	0.88
PAN	3.8	0.63	-
O_3	10.0	1.67	0.26
NO_2	11.4	1.90	Disproportionate
Cl_2	12.4	2.07	2.30
SO_2	17.0	2.83	39.40
HF	22.6	3.77	446

[a] pphm = parts per hundred million.

!TABLE 2

A number of potentially critical questions remain that appear particularly well suited to controlled chamber studies. These include the influence of dosage kinetics, frequency, and distribution on rate of uptake; the influence of leaf surface chemistry on absorption and transformation (and possibly detoxification, i.e. $O_3 \rightarrow O_2$ or $SO_2 \rightarrow SO_4^=$) of pollutants; and the influence of pollutant mixtures on uptake of component species. Absorption of a pollutant such as SO_2 into a surface moisture layer may be very rapid but may permit subsequent volatilization and internal reabsorption as the moisture layer evaporates.

The integration of chamber-derived data into mathematical models of pollutant uptake (Bennett et al., 1973; Steinhardt et al., 1977) offers promise of a tool for calculating uptakes rates over larger temporal and spatial scales. Steinhardt et al. (1977) used a single-leaf model to calculate SO_2 uptake on a statewide basis for the Northern Great Plains. Estimates based on projected increases on a more simplistic basis may also be made over larger regions based on assumed uniform cover of a single test crop. Hill (1971), for instance, used uptake data for alfalfa to estimate that total canopy removal of SO_2 would be 562 t d^{-1} in a 3520-km^2 area near Sudbury, Ontario. Potential deposition of NO_2 in the Los Angeles basin was similarly calculated to be on the order of 100 kg km^{-2} d^{-1}. Such calculations may prove valuable for other regions in the future, as both beneficial and detrimental effects of S and N amendments are considered.

A principal utility of measurements of dry deposition rates of gases lies in their potential for relating effects on the physiology, growth, and productivity of the exposed vegetation to the actual dose received (Winner and Mooney, 1980a,b). Unfortunately, very little concurrent data exist on the relationship between external dose, internal dose, and plant effects. The recent development of advanced-design exposure and uptake chambers by Rogers et al. (1977) should make these data more easily available in the future. While these data may be obtained now in the controlled laboratory situation (see Section 5.1), documentation of responses under field conditions must await development of suitable fast-response instrumentation. In this regard, eddy correlation techniques utilizing concurrent measurements of CO_2, H_2O, SO_2, and O_3 may provide a powerful tool for assessing impacts on primary production processes of natural systems.

4.1.2 Particles

Problems encountered in measuring particle deposition to vegetation include aerodynamic effects, small-particle diffusion, large-particle sedimentation, and particle bounce from the receptor surface. Physical entrapment by structural components of the surface is also a factor. Particularly important aspects requiring attention are the behavior of particles during impaction on foliage and the efficiency of retention. Particle deflection, bounce, rebound, and resuspension from surfaces all contribute to the local air concentration at the same time that deposition is occurring. Thus, particle fluxes may actually occur against a measured gradient. Because of these uncertainties, measured and calculated fluxes are often in poor agreement.

Several experts recently gathered at a USEPA-sponsored workshop to critically examine the field and laboratory methods used to determine the dry deposition of pollutants to environmental surfaces (Hicks et al., in preparation). The participants compiled a list of methods currently or previously in use for estimating dry deposition and discussed in detail their applicability to monitoring and vegetation effects studies, emphasizing their shortcomings, advantages, and developmental needs.

The methods fell into three basic groups: (1) Physical measurements performed in the field, (2) field and wind tunnel meteorological techniques, and (3) indirect methods of calculation. These are summarized in Table 3 with an indication of their applicability to gaseous or particulate pollutants, suitability for use in routine monitoring, and utility in recent studies (if available). This discussion will be concerned primarily with methods of Groups I and III since these are generally more applicable to routine or wide-scale use and include methods with which the authors are experienced. The techniques in Group II are more applicable in a research mode and are briefly considered in the companion paper in this session (Hosker, this symposium).

Group III methods are dependent on accurate airborne concentrations and, additionally, on accurate particle-size determinations in some cases. The method of concentration sampling involves use of an assumed relationship between atmospheric concentration and deposition rate. The ratio between the vertical flux of an element (F) and its mean concentration in the air (c) at some reference height is termed the deposition velocity: $V_d = F/c$ (Chamberlain, 1955). Deposition flux can thus be estimated, given the air concentration and published values of V_d. An advantage of this method is the existence of several networks which currently monitor air particulate concentrations. As we continue to improve our understanding of the relationship between deposition flux and air concentration, we can apply this information to existing data bases. The disadvantages of this

Table 3. Methods used to estimate dry deposition

Method	Pollutant measured	Suitability	Reference to recent application
I. Physical measurement in the field			
1. Surface snow "contamination"	Particles (and gases?)	Monitoring/research	Barrie and Walmsley, 1978
2. Background atmospheric radioactivity	Particles	Monitoring	Hodge et al., 1978; Graustein and Armstrong, 1978
3. Applied tracers	Particles or gases	Research	Garland, 1976
4. Open pots or buckets	Particles (and gases?)	Monitoring	Gibson and Baker, 1979
5. Discs, plates, dishes	Particles (and gases?)	Monitoring/research	Lindberg et al., 1979a; Davidson, 1977
6. Sticky surfaces	Particles	Monitoring/research	
7. Filter paper	Particles (and gases?)	Monitoring	Cawse, 1974
8. Foliage washing	Particles (and gases?)	Monitoring/research	Lindberg et al., 1979a; Parker et al., 1980
II. Wind tunnel and field meteorological techniques			
9. Box budget	Particles or gases	Research	See discussions in Kellogg et al., 1972; Whelpdale, 1978
10. Gradient	Particles or gases	Research/monitoring?	Droppo, 1980
11. Eddy correlation	Particles or gases	Research	Hicks and Wesely, 1980
12. Eddy accumulation	Particles or gases	Research	(See discussion in Hicks & Wesely, 1978a
13. Variance method	Particles or gases	Research	(see discussion in Hicks & Wesely, 1978a
14. Bowen ratio	Particles or gases	Research	(See discussion in Hicks & Wesely, 1978a
15. Wind tunnel studies	Particles	Research	Wedding et al., 1975; Klepper & Craig, 1975
16. Chamber mass balance studies	Gases	Research	Hill, 1971
III. Indirect methods of calculation			
17. Air concentration	Particles or gases	Monitoring/research	Andren & Lindberg, 1977
18. Calculations based on physical fundamentals	Particles	Research, monitoring?	Davidson, 1977

!TABLE 3

technique include those associated with accurate determination of air concentrations and size distributions (Section 2.3). The calculated deposition flux is also limited by the accuracy of the deposition velocity used. Considerable research is needed in this entire field.

We need a more thorough understanding of the influence of particle size on V_d because many published values are given for specific elements without regard to size distribution (e.g., see Cawse, 1974); we need to define a standard reference height above the deposition surface for all field and laboratory determinations of V_d; and we need to define the relationships between field and laboratory determinations of deposition velocities. Sehmel (1980) recently reviewed deposition velocities for particulate and gaseous pollutants, commenting that, even for specific elements, literature values of V_d ranged over several orders of magnitude. This has hindered the generalization of this type of data. Because of the wide-ranging values and lack of control of several variables under field conditions, predicted deposition velocity models based on field data are scarce (Sehmel, 1980). Another knowledge gap is in the reliable application of deposition velocity data in complex terrain situations. While this problem has been considered on a regional basis for SO_2 (Murphy, 1976) it has not been approached for particulate pollutants.

The calculation method based on physical fundamentals also relies on accurate measurements of atmospheric concentrations, but combines them with existing laboratory data on particle fluxes to well-defined, geometrically simple surfaces. Because of the complexity of natural surfaces, several simplifying assumptions are necessary in this application (Davidson, 1977).

Considerable research is needed on deposition to complex-geometry surfaces before this method can be applied to general vegetated canopies.

Several Group I methods are particularly appealing for use in monitoring networks or in field effects studies. These include the use of living vegetation or surrogate surfaces such as open pots, buckets, sticky surfaces, shallow pans, flat plates, etc. These methods are readily adaptable to most environments, are relatively inexpensive, can be deployed by personnel with a minimum of training, are adaptable to extraction and analytical techniques, are applicable to uniform use in monitoring networks, and yet, can be used in a research mode (for purposes of calibration with vegetation, for example). The remaining methods are somewhat more involved technically or analytically (background atmospheric radioactivity and applied tracer methods) or are applicable only under certain conditions (surface snow contamination), making them useful for monitoring only in a limited number of situations, although they are very useful in a research mode.

Consider first this latter subset of methods. Recent analytical and sampling advances have made it possible to accurately quantify trace contaminants in snow. In practice, (1) surface snow is sampled immediately following a snowfall and again several days later, the net increase in chemical content being ascribed to dry deposition; or (2) snow cores are analyzed in vertical sections to yield a measure of temporal variations in "bulk" deposition over time scales of years (Boutron and Lorius, 1978; Boutron, 1979; Dovland and Eliassen, 1976; Barrie and Walmsley, 1978; Jernelov and Wallin, 1973; Applequist et al., 1978). While this method is relatively straightforward and can provide historical deposition information, the results may be confounded by spatial inhomogeneity in snow chemistry, ease of sample contamination, element migration in snow layers, sublimation of surface snow, and wind redistribution of surface snow layers. Further research is needed to quantify the influence of these complicating factors.

The use of background atmospheric radioactivity to estimate deposition may be applied to "closed" systems, such as lakes or instrumented watersheds, as well as in smaller-scale studies of particle flux, taking advantage of radioactive fallout as a tracer (e.g., see the symposia proceedings edited by White and Dunaway, 1977; Klement, 1965; Fowler, 1965; also Shinn, 1977; Hodge et al., 1978; Graustein and Armstrong, 1978). The technique may require the use of sophisticated counting equipment, but it does result in accurate estimates of radioactive small-particle fluxes. Details of deposition mechanisms or short-term deposition rates are not generally possible, however, because of the often necessarily long averaging times. In investigations of radionuclide accumulation in water bodies, plants, or sediments, it is difficult to differentiate between wet and dry deposition. Research is needed to more thoroughly define the atmospheric particle-size distribution of background radioactivity to enhance our understanding of the responsible deposition mechanisms. This point also applies to the use of tracers in laboratory and field studies. While most often used as gases such as $^{35}SO_2$ (Noggle, 1980; Garland, 1976; Owens and Powell, 1974), particulate tracers (^{131}I, ^{198}Au, for example) have been used in wind tunnels to measure deposition processes and rates to foliar or inert surfaces (Clough, 1973; Klepper and Craig, 1975; Carlson et al., 1976) and in field studies of deposition and particle retention by vegetation (see review by Chamberlain, 1970). In many applications, the labelled particles are monodisperse or, if polydisperse, are not representative of the size distribution encountered in the atmosphere. Further research is needed using labelled aerosols with realistic size distributions applied on larger spatial scales to facilitate interpretation of data for extrapolation to the field. This method may be very useful in the "calibration" of artificial surfaces with vegetation, a point considered in the following discussion. Research on this question must be encouraged.

The methods in Table 3 which are most readily adaptable to regional monitoring networks involve surrogate surfaces. Although this was the consensus of opinion at the EPA Workshop, it was the only statement regarding inert surfaces which had such support; no other topic generated as much controversy. From a practical standpoint, it must be accepted that such methods hold the only hope, at present, for the monitoring of pollutant dry deposition (if indeed it can be monitored). This sentiment was also expressed at the Expert Meeting on Dry Deposition in Sweden (Brosset et al., 1977).

The problems of field measurement of dry deposition by inert surfaces have been considered in detail (Galloway and Parker, 1980; Lindberg et al., 1979a). Since measurement of dry deposition on natural surfaces is particularly difficult, it is not straightforward to relate deposition on an artificial surface to that on living vegetation. With few exceptions most large collection devices for deposited particles currently in use detect primarily the fall of relatively large, sedimenting particles. Efficient collection of small particles and gases transferred via turbulence and deposited by impaction processes likely will require modified samplers and techniques. Conventional methods suffer not only from artificiality of the surfaces but also from their common use at ground level. For evaluation of the overall mass transfer to the forest canopy, there seems little alternative to the task of direct in-canopy sampling.

The various surrogate surfaces in use include the so-called HASL (Health and Safety Laboratory) bucket, which has been adapted by the MAP3S and NADP networks as a standard collection device, perhaps as much for convenience as any other reason because wetfall is collected by the same device (Volchock et al., 1974; Gibson and Baker, 1979; Dana, 1979); discs and cylinders coated with a sticky substance, non-coated discs (White and Turner, 1970), flat teflon plates or discs (Elias et al., 1976; Davidson, 1977), polyethylene petri dishes (Lindberg et al., 1979a), filter paper (Cawse, 1974), artificial foliage (Schlesinger et al., 1974), stacks of plastic sheeting (Nihlgard, 1970), and polyethylene screen (Hart and Parent, 1974). These devices have been situated at ground level in the open, 1 m above bare ground, and beneath, within, or above forest canopies. Several methods devised to deal with the complications of unwanted "deposition" (i.e., bird droppings, rain) include permanent covers, wetfall-activated covers, manual collection prior to rainfall, and "anti-bird spikes." It should be understood here that we are considering the use of these devices to measure dry deposition only and not bulk deposition (wet plus dry) which is discussed in Section 4.2.

Since several mechanisms comprise the dry deposition process, no one surface may suffice to collect a representative sample of "total dry deposition," each process requiring a different technique with its own inherent problems. To accurately measure the flux of particulate pollutants to the terrestrial system, it is necessary to essentially duplicate the vegetation surface (Galloway and Parker, 1980). Because of its biological and chemical reactivity, its complex microstructure, and its diverse variety of occurrence, the foliar surface is currently non-duplicable. Thus, measurement of dry deposition by any surrogate surface yields only an estimate of deposition flux, obviously limiting our understanding of the deposition process and its effects. Research in the fields of plant surface morphology and pollutant/foliage interactions should be encouraged to develop an inert, reproducible surface more representative of vegetation than those currently in use.

With these qualifying statements firmly in mind, it is useful to consider the advantages, disadvantages, and further needs associated with the surface collection methods currently available. The open plastic bucket, although perhaps the most widely used "surface," was also the most assailed at the EPA workshop. Its major advantage is wide-spread use under standard conditions (e.g., in an upright position, 1 m above bare ground, as in the HASL wet/dry sampler), thus facilitating intercomparative studies. Its ability to collect relatively large quantities of material facilitates analysis for both chemical speciation and concentration. The major disadvantages lie in the geometry of the bucket with its large side/bottom surface area ratio. Material is deposited to all surfaces, both inside and outside of the vertical walls, such that the amount of material ultimately analyzed is strongly dependent on leaching procedures, not all of which are standard. The relationships between the exposed bottom surface area and the true collection surface area are poorly understood and probably not consistent under field conditions. As the bucket shape is known to result in unusual turbulence over the sampler (Munn and Bolin, 1971), these data should not be used to estimate absolute mass transfer rates. The effect of such turbulence on deposition should be quantified under controlled conditions. The bucket is also subject to higher levels of contamination because of the need to leach the large surface area. Plastic buckets may not be compatible with extraction and analysis of collected particles for trace organics because of adsorption problems.

These problems are minimized by the use of inert discs, plates, or shallow dishes which are smaller in size with much lower side/bottom surface area ratios than the bucket, which can be readily employed at various orientations in the canopy, and which are more amenable to ultra-clean laboratory procedures (if Teflon) or extraction for trace organics (if glass). In addition, chemical speciation and elemental solubility can be determined for samples collected over relatively short time intervals (4-7 d; Davidson, 1977; Lindberg et al., 1979a). Work is currently underway in our laboratory (and perhaps others) to develop a "standard" inert surface with a precipitation-activated mechanical cover for use in the forest canopy; more such research is needed.

Coating these surfaces with a sticky substance will increase the aerosol capture efficiency, but it has several disadvantages. A standard coating which is easy to apply and is trace contaminant "free" does not exist. The problems of (1) efficient recovery of the captured particles for analysis and (2) analytical matrix effects must be solved. Samples collected on sticky surfaces are not amenable to elemental solubility or speciation studies. Finally, we are not aware of any compelling experimental evidence to indicate that a sticky surface is any better analog of foliage than a nonsticky surface.

Filter paper, a widely used collection surface in the United Kingdom, is reproducible, relatively inert and "contaminant-free" (if carefully selected), and amenable to standard collection methods (in practice, placed 1-5 m above the ground beneath a fixed 1-m^2 plastic rain cover; see Cawse, 1974). This surface may be incompatible with chemical speciation or solubility studies, and in practice, requires relatively long collection periods (~ 30 d).

The other surface methods in Table 3 (plastic foliage, sheets, or screens) have generally been applied only in small-scale, highly specialized studies of the chemistry of rain above and below the forest canopy. Because of the size of some of these surfaces, they may be subject to contamination problems, difficulties in efficient deposited-particle recovery and analysis, and incompatibility with typical monitoring studies.

There are several general dry deposition research needs which must be addressed in future studies. The most urgent is for both field-scale and environmental-chamber or wind-tunnel studies to establish the relationship between material collected by surrogate surfaces and foliage. There was considerable discussion at the EPA workshop that surrogate surfaces must be calibrated with vegetation for a thorough understanding of inert-surface, dry deposition data. A combination of the inert-surface methods in Group I (Table 3) with foliar-washing experiments holds some promise, though there are many problems regarding foliar washing which must be considered. Such an experiment has been attempted on a very small scale by a comparison of deposition rates of four trace elements and sulfate determined by leaching (washing) inert surfaces and foliage situated in the upper canopy during a 7-d dry period (Lindberg et al., 1979a). Dry deposition rates measured to each surface type agreed within a factor of ~ 2 for Cd, Mn, Zn, and sulfate, while the apparent deposition rate of Pb to the inert surface exceeded that measured to the leaf surface by an order of magnitude. Leaf surface absorption of soluble Pb may have been a factor and is a phenomenon worthy of further investigation for its potential effects.

Before larger-scale comparative studies are attempted, several questions raised in earlier work (Tukey et al., 1965; Mecklenberg et al., 1966; Tukey, 1970; Lindberg et al., 1979a) must be addressed. What fraction of the material washed from excised foliage is internally derived (i.e., by cellular leaching)? Is there an optimum leaching medium (such as distilled water, dilute acid, detergent) which is amenable to trace-level analytical techniques and is efficient at dislodging or solubilizing surface-deposited particles, but does not promote internal foliar leaching? What is the optimum leaching duration; does surface-associated material dissolve before internal material? Is there any physiological reason to analyze for the non-water-soluble fraction of an element in deposited particles? If vegetation samples are collected and washed on a daily basis for determination of the net increase in "surface deposition," can one assume that the internal leaching pool of any element is constant over that time interval? We have measured order of magnitude variations in the surface area concentrations of some elements on adjacent chestnut oak leaves (<u>Quercus prinus</u>) on the same tree and similar variations in leaves collected from trees several kilometers apart (Lindberg et al., 1979a). This has serious implications if foliar washing data are to be used to estimate canopy-wide dry deposition rates (see further discussion on these points in Parker et al., 1980). Work is also needed to determine the means by which deposition rates measured to individual inert or foliar surfaces can be extrapolated to whole canopies. Multiplication of the single surface deposition rate by the applicable leaf area index should provide an upper limit, but research is needed to more completely quantify this relationship.

Another question involves several recent reports of measured net upward fluxes over forested canopies (determined by eddy correlation methods) and over bare ground (determined by gradient methods) for several pollutant and nonpollutant elements (Hicks and Wesely, 1980; Droppo, 1980; Davidson and Elias, 1979). These observations indicate that a serious problem may exist in our interpretation of deposition data based on surface-accumulation measurements. The upward fluxes measured over bare ground were attributed to local, ground-level dust resuspension (Droppo, 1980; Davidson and Elias, 1979), while upward fluxes of S, measured over a pine forest, were tentatively attributed to foliar emissions (Hicks and Wesely, 1978). Some grasses, several herbaceous plants, some crop plants, and pine trees are also known to release particulate forms of several trace metals (Beauford et al., 1975, 1977). These "internal cycles" of particles resuspended from soils or vegetation or released from within foliage can result in gross overestimates of true atmospheric deposition based on surface accumulation measurements.

We are obviously faced with a major challenge in this field to develop a standard dry deposition collection technique that meets the above requirements. This is best approached as a multidisciplinary task: the effects researcher needs to define the optimum sampling period - or define a dry deposition "event"; the meteorologist should provide guidance on the physical shape, orientation, and placement of the samplers in the field; the plant physiologist needs to define the microstructure of a typical foliar surface; the particle physicist should describe the mechanisms by which particles interact with various surfaces including the relative importance of particle removal by sedimentation, impaction, and diffusion; the atmospheric chemist needs to describe the gas/particle interactions which occur both in the air and on the surface of deposition which may influence the mobility or toxicity of a deposited element; the analytical chemist needs to develop an inert, contaminant "free" surface which can be readily analyzed; the geochemist must define the relative importance of "internal" element cycles to the captured particle pool; the monitoring agency should prepare standard procedures for using the samplers; the engineer must design the sampler with a precipitation-activated cover for reliable operation under field conditions; and we all need to consider a means of calibrating the instrument with living foliage.

4.2 Wet Deposition

The wet component of atmospheric deposition is much more addressable with current methodologies than the dry component, as indicated by recent workshops and symposia (Semonin and Beadle, 1977; Dochinger and Seliga, 1976; Hicks et al., in preparation). As a result of the interest in precipitation chemistry generated by the acid rain phenomenon, there have been several recent studies concerned with development of precipitation sampling and analytical methodology for major and trace components (described in detail in Table 4).

It is our opinion that the most important research needs in this area concern the design of field experiments for collection of data appropriate

Table 4. Recent developments in the collection, analysis, and interpretation of precipitation chemistry data

Problem or question	Reference to discussion and analysis of the problem
1. Need for collection of wetfall-only samples	Galloway and Likens, 1978
2. Need for event sampling and event definition	Galloway and Likens, 1978; Lindberg et al., 1979a
3. Design of wetfall-only automatic sampler	Volchok et al., 1974; Dana, 1977
4. Comparability of collectors	Galloway and Likens, 1976; Dana, 1979
5. Collection of representative samples	Galloway and Likens, 1976, 1978; Lindberg et al., 1977, 1979a
6. Preservation of samples in the field	Galloway and Likens, 1978; Lindberg et al., 1977
7. Laboratory storage of samples for chemical analysis	Peden and Skowron, 1978
8. Development of standard handling, analysis, and storage methods	Peden et al., 1979
9. Determination of precipitation and throughfall acidity by standard methods	Galloway et al., 1979; Hoffman et al., 1980
10. Collection procedures for trace inorganic analysis	Lindberg et al., 1977
11. Collection procedures for trace organic analysis	Lunde et al., 1977; Galloway, 1980
12. Filtration of rain samples	Kennedy et al., 1979; Lindberg et al., 1977
13. Treatment of suspended solids in rain	Kennedy et al., 1979; Lindberg et al., 1977
14. Stabilization of dissolved gases in collected rain	Dana, 1977
15. Analytical variability among several laboratories and techniques	Turner and Lindberg, 1976; Bogen et al., 1978
16. Procedural variability compared with natural field variations	Lindberg et al., 1977, 1979a
17. Temporal and spatial variability of precipitation chemistry	Semonin, 1976; Lindberg et al., 1977, 1979a; Slanina et al., 1979; Gatz, 1978
18. Frequency distributrion of element concentrations in precipitation and and rain volume for statistical analysis	Essenwanger, 1960; Lindberg et al., 1979a
19. Interpretation of rain volume/concentration relationships	Lindberg et al., 1979a; Kennedy et al., 1979; Parker et al., 1980
20. Determination of relative importance of precipitation-scavenging mechanisms	Semonin and Beadle, 1977; Raynor, 1976; Lindberg et al., 1979a
21. Extrapolation of single-point precipitation volume measurements	Rogers and Zawadski, 1979
22. Urban influence on rain volume	Chagnon, 1979
23. Optimum location of samplers in urban areas	Gatz, 1980
24. Use of wind trajectory analysis with precipitation data	Miller et al., 1976
25. Need for and utility of within-event sampling or sequential sampling	Raynor, 1976; Raynor and Haynes, 1977; Parker et al., 1980
26. Design of an automatic sequential sampler	Gascoyne, 1977; Ronneau et al., 1978; Raynor and McNeil, 1979
27. Development of standard methods for regional and national monitoring networks	Dana, 1977; Galloway and Cowling, 1978

!TABLE 4

for improving our understanding of plant/pollutant interactions. This topic is discussed in Section 5.2. However, there are several aspects of the physical collection of wet deposition which need to be addressed in future studies (some of these recommendations were drawn from Galloway et al., 1978): (1) methods for contamination-free collection of precipitation for trace organic/inorganic analyses should be further refined; (2) regional-scale multi-site studies are needed to determine applicability of single-site measurements; (3) input from meteorologists is needed on the ancillary observations or measurements which should be made during precipitation collection; (4) methods should be developed for routine collection of intercepted fog; (5) elemental solubility studies in rain are needed to assess the relative importance of particulate components in precipitation; (6) input from plant physiologists is needed on the most appropriate time scale for collection of precipitation data (subevent, event, weekly? - discussed further in Section 5.2); (7) a wetfall-only sampler suitable for use below plant canopies (throughfall) needs to be developed; (8) further work is needed to assess the effects of gas exchange on rain chemistry while samples are in the field prior to their return to the laboratory; (9) the "wetness" sensor head currently in use (Wong or HASL design) on wet/dry samplers needs to be redeveloped to provide more reliable operation and to assure collection of the entire precipitation event while minimizing exposure time of the sampler to dry deposition; (10) a sampler should be designed to reliably filter precipitation as it is collected; (11) studies on the chemical stability of throughfall samples are needed; and (12) coordinated collection of cloud water and precipitation at several levels between the cloud base and ground is needed to increase our understanding of scavenging mechanisms and gas/particle interactions with precipitation.

5 UNDERSTANDING PLANT-POLLUTANT INTERACTIONS

All investigations of the effects of air pollutants on vegetation should be concerned with careful characterization and correlation of both pollutant dose and plant response. A fundamental problem confronting plant researchers in this regard is determining (1) how to measure pollutant dose so that principal phytotoxic components (both chemical species and exposure kinetics) are identified, and (2) how to characterize plant response in ways which can lead directly to quantifying actual or potential economic or ecological loss.

As the product of concentration x time, pollutant dose may be characterized in a wide variety of ways. The choice of an appropriate averaging time and the potential influence of peak concentrations during the exposure history will vary with both the biochemical reactivity and the mode of occurrence of the pollutant species. From measurements of SO_2 concentrations near smelters at Biersdorf, Germany, Stratmann (1963) identified several exposures which were considered important as indicators of pollutant stress. These included: (1) the mean concentration (assumed to describe a single-exposure event), (2) the total dose (concentration-time integral), (3) the variability of concentrations, (4) the frequency of recovery periods between exposures, and (5) the frequency of concentration peaks. In our eastern regional environment with a high density of urban and industrial sources, we must add a sixth factor - the concentration ratios and sequence of occurrence of additional pollutants such as ozone, nitrogen oxides, and PAN (peroxyacetyl nitrate).

In general rather minimal effort has been directed toward identifying the critical features of pollutant dose, particularly with respect to combinations of pollutants. With single pollutants such as SO_2 or HF which are released from point sources, localized effects may be envisioned to occur primarily as a result of well-defined exposure episodes determined by local meteorology or topography. Here, typical exposure kinetics are characterized by high peak-to-mean ratios and a high variability of exposure concentrations over time. This regime may be superimposed on regional-scale levels of "background" pollutants. Especially with pollutants such as SO_2 which may be metabolized and detoxified at low levels, these episodes achieve particular significance in influencing plant response to the total exposure dose.

With studies designed to evaluate chronic effects of regional-scale pollutants such as O_3, SO_2, and NO_x (see review by Reinert et al., 1975), conditions must be designed to approximate the multiday exposures involving multiple pollutants under generally less-variable pollutant concentrations. With any exposure regime, the permutations of exposure episodes and relatively pollutant-free intervals can be considered to influence heavily plant physiological recovery from pollutant stress.

5.1 Controlled Exposure Studies

Important early conceptual contributions to the characterization of SO_2 dose were made by Zahn (1961, 1970) in a series of controlled laboratory studies. These studies emphasized the importance of the distribution of dose during the exposure interval, the duration of intervening recovery periods, and the role of low concentrations in amplifying visible injury following subsequent higher concentrations. With two species, wheat and larch, daytime pretreatment with subacute levels of SO_2 (0.4 ppm for 33-77 h) provided protection against visible injury by subsequent high doses (1-2 ppm for 2-3 h). More recently, McLaughlin et al. (1979) examined the influence of SO_2 dosage kinetics on photosynthesis, transpiration, and growth of kidney beans. Working at concentrations below the threshold for visible injury (3-h avg $\leq$ 0.5 ppm), they found that SO_2-induced photosynthetic depression could be strongly influenced by varying the ratio of the peak to the mean concentration during exposure without changing the total SO_2 dose. No strong evidence was obtained to indicate that plants were sensitized to SO_2-induced suppression of photosynthesis by previous exposure. Plant growth appeared to be responding to a combination of exposure kinetics and exposure history in these experiments.

Exposure history has also been demonstrated to be important in plant responses to ozone (Johnston and Heagle, in prep.). Here chronic exposure at levels below the visible injury threshold (4 pphm, 6 h/d for 10 d) predisposed plants to greater sensitivity to a subsequent acute O_3 dose (10 pphm for 3 h). Intervening periods without O_3 partially alleviated the sensitization as did chronic exposure to levels $\geq$ 6 pphm which produced visible injury.

The importance of exposure kinetics on plant uptake of pollutants has also been demonstrated for fluoride, a task made easier by the fact that fluoride is accumulated by foliage. Compared to continuous exposure, fluoride from the same total dose of HF was accumulated more readily with intermittent exposure at a higher peak:mean ratio (MacLean et al., 1969) and less readily by intermittent exposure at the same peak:mean ratio as in the continuous exposure case (MacLean and Schneider, 1969). These authors suggest that fluoride content of foliage be used as a basis for regulatory action, a possibility which is not feasible for most other pollutants which are more readily metabolized in plant systems.

Attempts to generalize dose-response data into vegetation-response equations have been made since the time of O'Gara (1922). Heck and Brandt (1977) have recently reviewed these equations for the major phytoxic pollutants. One of the most intensive examinations of air quality data and the utility of dose-response relationships in air quality regulation was provided by Larsen and Heck (1976). In general, currently available dose-response equations are derived from acute exposures at continuous pollutant levels and use visible leaf injury as the dependent variable. The major need, at present, appears to be development of relationships which define plant response under chronic exposure regimes which include more than one pollutant and reflect the importance of the distribution of typical episodic stress sequences occurring under field conditions.

The definition of plant response represents the second critical feature of dose-response studies. Our obvious interest is in losses in productivity, stability, or quality of the plant system. The essential need is for suitable indices of these effects. For years, visible injury has been a primary measuring stick for assessing plant damage. This concept was based, in part, on experiments by Hill and Thomas (1933) indicating growth losses in alfalfa were directly proportional to visible injury of foliage. Evidence has accumulated rapidly in recent years from laboratory and field experiments to indicate that growth may be reduced in the absence of visible injury. Interest in subtle responses has led to a variety of mechanistic studies aimed at detecting cytological, enzymatic, or general physiological responses of plants to pollutants (see reviews by Ziegler, 1973; Mudd and Kozlowski, 1975). While both leaf injury and measures of physiological change offer a convenient short-term basis for defining plant response, neither is adequate alone. Plant physiological resilience, both in space and time, makes plant growth and yield the most reliable ultimate indicators of the effects of pollutant stress on plant systems and emphasizes the importance of measuring whole-plant responses. Recognition of the importance of whole-plant patterns of allocation of carbon (photosynthate), water, and nutrient resources in response to stress (McLaughlin and Shriner, 1980) implies that additional responses such as altered allocation between roots and shoots may be meaningful indicators of plant/environment (including pollutant and other stresses) interactions.

Ultimate development of dose-response relations in a way that can be meaningfully used in air quality regulation is obviously a tremendously complex task. At present, we have only a few of the pieces required to complete the task. To adequately address it will require generalization of the multiple interactions of plant species, growing environment, pollutant dose (kinetics, composition, and history), and measured plant processes. Deciding on the acceptable level of generalization is an important challenge to us all.

5.2 Field Research

Carefully designed field-level research on the effects of atmospheric deposition on vegetation is the logical extension of controlled exposure studies. These methods may provide the only means of validation of laboratory results as well as providing realistic mixtures of wet and dry deposition and gas/particle interactions.

5.2.1 Quantifying wet/dry/deposition and gas/particle interactions

A key need regarding field-level deposition research is the integration of mechanistic deposition studies with vegetation effect studies in the forest canopy. Dry deposition can no longer 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 is particularly important if a constituent of dry deposition is delivered to the canopy in a relatively mobile (e.g., soluble) form, as recently demonstrated for Cd, Pb, Mn, Zn, and S in both suspended and deposited particles (Lindberg et al., 1979a).

The relative proportion of total atmospheric deposition attributed to dry processes has been largely ignored in field studies until quite recently. Table 5 (right-hand section) indicates the relative contribution of dry deposition to total deposition measured at the Walker Branch Experimental Watershed in eastern Tennessee over several time scales (from Lindberg et al., 1979a). The atmospheric input during the short-term experiments (periods W2, W3, and W6) was generally dominated by dry deposition; only during period W3 was the wetfall process of greater relative importance for Cd and $SO_4^{=}$-S. Even over the longer time scales dry deposition constituted a significant fraction of the total atmospheric input of Cd (~ 20%), $SO_4^{=}$ (~ 35%), and Pb (~ 55%).

Table 5. Comparison of wet, dry, and total deposition measured at Walker Branch Watershed. Wet and dry deposition rates to individual upper canopy surfaces are compared when normalized to a unit time basis in the center section of the table. The right-hand portion of the table indicates the relative contribution of dry deposition to the total deposited quantity of an element to the entire canopy over several time periods.

Period	Normalized deposition rates ($\mu g\ m^{-2}\ h^{-1}$)			Relative contribution of dry to total deposition (dry/total) · 100		
	Cd	Pb	$SO_4^{=}$-S	Cd	Pb	$SO_4^{=}$-S
W2[a]				82%	100%	70%
Wet	2.7	24	42,000			
Dry	0.01	0.62	50			
W3[b]				18	86	47
Wet	2.7	45	17,000			
Dry	0.0003	0.12	10			
W6[c]				67	100	80
Wet	3.1	25	23,000			
Dry	0.0001	0.24	17			
W2,3,6						
Mean wet/dry ratio	4100	170	1300			
Growing season[d]	-	-	-	26	56	34
Annual[e]	-	-	-	17	53	33

[a] 5/16 - 5/20/77; wet event duration = 0.007 d, total period duration = 4.2 d.

[b] 5/30 - 6/6/77; wet event duration = 0.02 d, total period duration = 7.0 d.

[c] 7/12 - 7/18/77; wet event duration = 0.007 d, total period duration = 6.0 d.

[d] 4/1 - 10/25/77; total period duration = 207 d.

[e] calendar year 1977 (data from Lindberg et al. 1979).

!TABLE 5

Particle deposition is not generally considered to be an episodic event, such as the sudden inundation of the leaf surface by precipitation, but rather a 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. Wet deposition rates of Cd, Pb, and sulfate measured during events of short duration and low rainfall volume, and hence generally high concentrations, were considerably higher than any of the measured dry deposition rates when expressed on a comparative unit-time basis (center column of Table 5). The episodic wet deposition rates were calculated as the areal wetfall input divided by the duration of the precipitation event. Although the duration of the rain events during W2, W3, and W6 was short (10 to 30 min), the wet deposition rates during the events were ~ 2 to 3 orders of magnitude greater than the dry deposition rates measured for each period (when expressed on a per hour basis).

For the initial bioreceptor, this intense episodic flux of potentially toxic material can play an important role in physiological effects. Precipitation events of short duration, low volume, and high elemental concentrations were common during the growing season at Walker Branch Watershed. In many cases, these events followed relatively long (5 to 10 d) dry periods characterized by high air concentrations and dry deposition rates. When the subsequent precipitation event was very small in volume (~ 0.5 to 1.5 mm), much of the initial precipitation remained on the leaf surface, not being washed off or diluted by subsequent rainfall. The potential for physiological effects is enhanced when this solution contacts previously dry deposited material on the leaf surface. 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 measured to surfaces in the upper canopy, it is possible to estimate the approximate surface area concentrations of dry deposited material on a leaf prior to the precipitation event. These values are summarized in Table 6 including 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.

Precipitation of 1.3 mm falling on a 50-cm^2 leaf would deposit ~ 6 ml of water. As this solution begins to evaporate, the leaf is exposed, although briefly, to extremely high concentrations resulting from the interaction between surface moisture and dry deposition. Hundred-fold evaporation of the surface moisture would result in concentrations of dissolved constituents several hundred to several thousand times higher than typical rain concentrations (compare the concentrations in Table 6 with average rain concentrations at Walker Branch Watershed of Cd = 0.44 μg/liter, Pb = 6.8 μg/liter, and $SO_4^=$-S = 1200 μg/liter). Knowledge of this situation is particularly important in relating precipitation chemistry to vegetation effects observed in the field; the need for both event sampling and wet/dry segregation is obvious. If wetfall had been sampled on a weekly basis during this same period, the occurrence of a larger storm following the 1.3-mm event would have further diluted the apparent concentrations to which the vegetation was exposed because of the inverse relationship between precipitation concentrations and rain volume (Lindberg et al., 1979a). The

Table 6. Potential concentrations of several elements in solution on a typical upper-canopy chestnut oak leaf surface (50 cm^2) following a brief summer shower which was preceded by a 10-d dry period

	Water-soluble constituents			
Parameter	Units	Cd	Pb	$SO_4^=$-S
Surface area concentration of previously dry deposited, water-soluble material[a]	ng/cm^2	0.1	2.6	1200
Mass of dry deposited, water-soluble material	ng	5	100	70×10^3
Concentration of soluble fraction dissolved by precipitation	μg/liter	1	20	10×10^3
Concentration of elements in incident precipitation	μg/liter	0.35	3.1	5×10^3
Estimated total concentration in solution on the leaf surface	μg/liter	1.3	23	15×10^3
Potential concentration following evaporation	μg/liter	130	2300	1.5×10^6
Total mass of elements in solution on the leaf surface	μg	0.007	0.15	100
Total quantity of elements bound within the leaf	μg	0.065	0.22	2000
Total quantity of available fraction of elements delivered to the leaf surface during the growing season	μg	1.1	30	1700
Ratio of soluble element deposition during W2 to total leaf content[a]	-	0.11	0.68	0.05
Ratio of available element deposition during the growing season to total leaf content	-	17	140	0.8

---

[a] Wet and dry deposition were separately sampled at Walker Branch Watershed from 5/16 to 5/20/77 (period W2). Although the rain event, which occurred on 5/18, was preceded by a 10-d dry period, dry deposited element concentrations were determined only for the ∿2.4-d sampling period preceding the rain. Dry deposited element concentrations are thus conservative estimates of total dry material on the leaf surfaces prior to the rain (data from Lindberg et al., 1979a).

!TABLE 6

effect of weekly wetfall sampling in this situation would be to obliterate the details of the series of events which may or may not have resulted in an observed effect on the vegetation. Considerable effort should be directed toward understanding the combined effects of wet and dry deposition on vegetation.

The assumptions in the above calculations result in both over- and underestimates of concentrations. For example, rainfall 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 if situated horizontally and under calm conditions (the interception storage of the forest in Walker Branch has been estimated at ~0.6 mm of precipitation, based on simulation studies, R. J. Luxmoore, personal communication). The calculations also assume a uniform surface concentration of dry deposited material, which is a poor assumption as indicated in Fig. 1 (from Lindberg et al., 1979a). At isolated points on the leaf surface where deposited material accumulates, episodic concentrations in solution could be considerably higher than those estimated here. More work is needed on surface distribution of dry deposition on vegetation.

The physiological effects of surface-deposited metals on vegetation, either in particulate or dissolved form, requires considerable study, as they are very poorly understood. There are several conflicting reports on toxicity in the literature (as reviewed by Krause and Kaiser, 1977; Zimdahl, 1976). However, the estimated pH of the resulting solution on the leaf surface ($\simeq 2$, not indicated in table) can cause adverse effects in several plant species (Shriner, 1976). Our calculation of acidity assumes no

Figure 1. Scanning electron photomicrograph of a typical chestnut oak leaf collected in Walker Branch Watershed. Note the heterogeneous distribution of dry deposited particles, including combustion ash (spherical particles) (from Lindberg et al., 1979a).

neutralizing capacity of the surface-deposited particles or of the leaf itself, a situation which is unusual but which has been documented (Lindberg et al., 1979a; Hoffman et al., 1980).

Table 6 also summarizes estimates of the magnitude of the deposition inputs during one event and over the growing season relative to the total leaf internal content of each element. The quantity of Pb estimated to be in solution on the leaf surface following the single event was nearly comparable to the total Pb content of the leaf. Lesser but still significant quantities of soluble Cd and $SO_4^=$ were deposited during this event. During the full growing season, the leaf surface was exposed to one to two orders of magnitude more dissolved Cd and Pb and nearly equal amounts of $SO_4^=$ relative to the leaf content. While the effects of such exposures are unknown, the importance of atmospheric deposition in the cycling of these elements in the landscape is obvious and warrants continued research.

Another poorly understood and infrequently considered aspect of pollutant interactions in the field is the role of gas/particle reactions on the foliar surface. The role of trace metals, particularly Mn, in the catalytic oxidation of SO_2 in rain has been demonstrated in the laboratory; however, the application of these laboratory studies to the atmosphere is exceedingly complex (Barrie and Georgii, 1976; Barrie et al., 1977; Penkett et al., 1979). This phenomenon may play a significant role only under certain atmospheric conditions, such as in long-lived cloud droplets or urban fogs. A possibly more important situation is the absorption and oxidation of SO_2 by wetted foliar surfaces. The leaves of certain forest trees rapidly leach Mn into solution upon wetting, with concentrations in leaf moisture as high as 500 μg/liter resulting from internally leached Mn and Mn solubilized from deposited particles (Lindberg et al., 1979a). Since the residence time of wetness (dew, rain) on leaf surfaces can easily approach several hours, this may represent a significant mechanism of increasing the deposition rate of SO_2 to vegetation. The ability of dew-covered surfaces to rapidly accumulate $SO_4^=$ was recently reported by Brimblecomb (1978). Deposition was controlled by the capacity of the solution to absorb SO_2; thus, presence of sufficient Mn to catalyze the oxidation should result in an increased rate of deposition. The relative importance of such interactions to deposition rates and to vegetation effects is largely unknown. The oxidation of SO_2 to $SO_4^=$ releases free H^+ to solution which, if not neutralized by reaction with alkaline particle components, may result in damaging pH levels. Future studies should be directed at quantifying the role of gas/particle reactions in vegetation effects.

Continuing examination of the chemistry resulting from the rain-leaf interaction is both prudent and necessary to achieve a fuller understanding of internal and external mechanisms affecting leaf processes. The phenomenon of strong acid scavenging from rain by the forest canopy is a well-known but poorly understood phenomenon resulting in the release of plant-related weak acids and nutrients (Hoffman et al., 1980). The resulting pH of throughfall is often in the 5 to 6 range, not characteristic of "acid rain." Future research in forests where this occurs (e.g., eastern deciduous forest) should concentrate on canopy effects rather than on soil effects, particularly on the role of hydrogen uptake and subsequent organic carbon and nutrient loss from foliage.

Additional refinements in experimental design necessary for understanding plant-pollutant interactions should include studies of the following: (1) the influence of leaf surface microstructure and leaf exudates on particle capture, retention, and gas absorption; (2) dose-response relationships for particle deposition; (3) possible effects of shifting to a dominant direct atmospheric source of plant nutrients and toxins rather than a dominant soil-uptake route; (4) episodic exposure of the canopy to high deposition rates of both wet and dry components; (5) wet and dry deposited material distribution on individual leaves and within the canopy; (6) deposited particle solubility under various moisture and chemical regimes; and (7) interaction of dew and intercepted fog or mist with deposited particles on vegetation and subsequent effects of the resulting solution.

5.2.2 Assessing pollutant effects on plant growth and development

Quantifying pollutant impacts on plant growth and development under field conditions is a complex task for two primary reasons. First, variations in site quality between control and test sites can make differentiation of pollutant effects from experimental "noise" difficult. Secondly, particularly with perennial species, competition between plants within terrestrial ecosystem is a potentially important modifier of individual and community-level responses. The task is somewhat easier when high levels of emissions from point sources are involved. Gordon and Gorham (1963), for example, were able to measure community-level changes along a 63-km gradient from an iron-sintering plant at Wawa, Ontario. Alteration of community composition under high pollutant burdens may be ascribed to differences in sensitivity between species which can result either in direct effects on those species or indirect effects due to altered competitive relationships within the plant community. In most present situations, however, such well-defined concentration gradients do not exist and regionally elevated levels of pollutants from multiple sources are involved (Shriner et al., 1977). Here, quantifying pollutant impacts require evaluation of growth under comparable control conditions. Major progress in creating a basis of comparison has come with the development of the field chamber approach (Heagle et al., 1973; Mandl et al., 1973). With charcoal filtration providing the "control" condition and compared with growth of plants in unfiltered ambient plots, assessment of impacts of ambient air regimes on productivity of annual crops (see review by Heck and Brandt, 1977) has been greatly facilitated. Two main research needs can still be identified with this approach: (1) determining whether pollutant uptake, plant physiological condition, and growth are comparable between unfiltered chambers and field grown plants; and (2) providing adequate description of pollutant dose characteristics so that critical features can be identified. Primary concerns in the first regard are that gas exchange characteristics including CO_2, water, and pollutants are comparable inside and outside the chambers. The increased likelihood of developing water deficits in the continuously stirred atmosphere of the chambers must be recognized and supplemental irrigation must be provided when significant differences between chambers and field plots occur. With respect to pollutant monitoring, it is essential that the exposure history over the plant growth cycle be characterized both with respect to occurrence of primary pollutants and the sequence of principal stress episodes. Here, a variety of physiological processes (photosynthetic capacity, nutrient and water relations, carbon allocation, etc.) may serve as useful indicators of the sequence of events producing growth responses. Information of this type will be important in identifying what principal features of air quality data may be useful in estimating potential yield losses at other sites. Another recently developed field chamber technique which shows promise for assessing pollutant impacts under field conditions is the linear gradient system of Shinn et al. (1980). This approach allows a predictable concentration gradient to be produced by linear dilution of a pollutant introduced into the incoming air stream. Dose-response data obtained by subsampling along the gradient at levels both below and above ambient concentrations may be a very cost effective way to provide the response functions necessary to accurately predict potential impacts of future increases in concentrations of air pollutants on field-grown crops. Questions of physiological comparability with unchambered plants and dose distribution patterns should also be answered before this approach is put into wide-scale field use.

Field research on growth impacts on natural communities under chronic stress regimes is sorely needed. Here, both temporal and spatial characteristics of community structure greatly increase the complexity of the task. A good example of the challenges inherent in addressing ecosystem-level effects on a grassland ecosystem is the Colstrip Project (EPA, 1979). In this study, multitrophic-level studies are being conducted around an artificial source of SO_2 to assess potential effects of siting coal-fired power plants in the area. The fact that sensitivity to pollutant stress varies both within and between plant populations must be recognized. Recent work with natural populations of Geranium carolinianum L., a weedy species sensitive to SO_2, has demonstrated that genetic selection for resistance to air pollution stress may occur rather rapidly ($\leq$ 30 years) (Taylor, 1978). Studies in England with perennial ryegrass have also indicated that populations growing in areas with high SO_2 concentrations (100-700 $\mu g\ m^{-2}$) evolved resistance to growth reduction by SO_2. The degree of evolution of tolerance was also shown to be directly related to the level of SO_2 under which they had grown. Additional work on the plasticity of genetic pools in response to SO_2 and other pollutants is necessary if we expect to predict responses of plant communities to chronic stress.

Because of their ubiquity, ecological, and economic importance, forest trees constitute a major focus of concern with respect to chronic air pollution stress on natural systems. Unfortunately, few data exist to permit adequate assessment of these effects. A number of approaches are being used to address this task. An intensive multidisciplinary approach to oxidant effects on the Coniferous San Bernadino National Forest near Los Angeles has been described by Miller and McBride (1973). It includes both field sampling of responses at several trophic levels and mathematical simulations in an effort to assess alterations in system components. Another multidisciplinary effort (Legge et al., 1978) conducted in a coniferous forest ecosystem near a gas processing plant in Northern Alberta Canada has demonstrated the utility of considering pollution impacts on the total plant/soil system. In this case, reduced growth of overstory lodgepole pine and larkpine growing within 1.5 km of the SO_2 source was attributed to reduced photosynthesis of foliage, an apparent consequence of reduced foliar retention of potassium and phosphorus, reduced pigment content, and lower levels of adenosine triphosphate. Growth losses appeared to be due more to sulfur-mediated changes in availability of soil nutrients than to chronic levels of sulfur uptake by foliage. A unique advantage available to these researchers was the distinctly different and constant $^{34}S:^{32}S$ ratios of SO_2 being introduced into the soil-plant system. Thus, impacts and fate of sulfur could be identified within system components. More attention to research opportunities with radioisotopes, both stable and nonstable, may greatly assist future efforts to evaluate chronic pollutant impacts on ecosystem processes. In the eastern environment, McClenahen (1978) has used ecological indices of community diversity and structure to assess responses of deciduous forests along a 50-km gradient of air pollution levels along the heavily industrialized Ohio River Valley. Rosenberg et al. (1979) also found increases in species diversity and importance in a mixed oak forest in Pennsylvania as distance from a coal-burning power plant increased. They found that compositional changes were generally more sensitive indicators of pollution damage to overstory species than were growth assessments.

Two newly emerging tools, dendroecology and simulation modeling, offer promise for quantifying individual tree and community-level responses. Dendroecology is a discipline of dendrochronology, the science of dating growth rings of woody plants (Fritts, 1971). As a tool for studying air pollution effects, dendroecology relies on multivariate statistical techniques to separate effects of tree age and local climate from those induced by air pollution (Nash et al., 1975). These data may be particularly useful when coupled with forest simulation models (see Shugart et al., 1980, and Section 6) to examine long-term community-level changes. Of basic concern to this task are the mechanisms by which species' responses are integrated into system responses and the effects of these stresses over time. Additional data on growth responses at levels ranging from seedlings to mature trees are badly needed.

6 APPLYING POLLUTANT/VEGETATION INTERACTION DATA TO INTEGRATED ASSESSMENT MODELS

There is increasing emphasis on evaluating "ecosystem-level" effects of developing energy technologies. With terrestrial systems under our present air quality regimes, such studies imply assessment of changes within and between components of both soil and plant systems over multi-year time scales. In reality, almost all evaluations of air pollution effects under these conditions focus on only a few components, with inferences being made to unmeasured ecosystem-level changes at a larger scale. Nevertheless, emphasis on ecosystem changes and total impacts of developing technologies has defined the need as never before to integrate and focus our necessarily smaller-scale experiments toward larger-scale objectives. The essential challenge may be posed as a question -- How do we evaluate present air pollution impacts to terrestrial systems in such a way that both present and projected future impacts may be quantified? This task may be approached in several ways.

One very fundamental approach would involve the development of empirical dose-response equations developed from both laboratory and field research with a variety of species. These data would then be used with existing air monitoring data for a region to predict the range and distribution of growth and yield alterations to be expected at those or projected future levels. Such an approach implies that experiments have identified the principal exposure characteristics limiting yield and that air quality data be reported in such a manner that these characteristics can be quantified. Neither condition is at present adequately satisfied. When these data are available, generalizations will have to be made with respect to dose-response equations and regions within which air quality data and modifying environmental variables can be considered homogeneous. This approach appears to have its greatest potential with monospecific agricultural or forest crops where interspecific competition is not a factor.

A second and very promising approach involves the use of an empirical dose-response function for a single site or selected group of sites to determine likely responses of vegetation over a range of other sites. An example of this approach was recently discussed by Heagle et al. (1979). In this study, yield reductions of corn, wheat, soybeans, and spinach measured with open-top field chambers at ambient and above-ambient levels of ozone were used to predict potential nationwide losses to these crops. In spite of the many assumptions implied in such an approach, it represents a very reasonable initiation point of large-scale estimates of crop loss. At present, EPA is planning an expanded network of these chambers to quantify regional differences in response of several crop species. Thus, nationwide damage estimates may be possible in the future, based on much-needed regionalized response functions. Potential applicability of these results to other species should be broadened by comparative controlled-fumigation or field studies involving those test species and other species of regional importance.

Another research approach which has evolved rapidly during the last decade is the use of mathematical models to integrate data from diverse sources to describe responses of complex whole systems. Modeling has been a necessary and integral part of developing an understanding of how ecosystems function and respond to stress. In air pollution studies, models have been restricted primarily to single-plant or single-species dose-response functions involving visible injury and dose or visible injury and yield (see review by Heck and Brandt, 1977). A much broader application of modeling is now gradually evolving and provides a framework within which we can address more comprehensive analyses. Such questions as the relationship of alterations in plant physiological processes to whole-plant function, and the relationship of community responses to individual species' responses can be addressed with simulation techniques.

The area in which models would appear to most effectively extend our understanding involves responses of forest ecosystems to chronic air pollution stress. Here, the complex structure and perennial growth habit of forest communities, particularly uneven-aged mixed deciduous forests, makes measurement and prediction of responses a difficult task. Botkin et al. (1972) made important early contributions to the understanding of forest community dynamics with the development of JABOWA, a 12-species model of growth and succession for a northern hardwood forest. With it, Botkin (1976) subsequently examined and emphasized the important role of species interactions in responses of forest ecosystems to environmental perturbation. More recently, Shugart and West (1977) developed and parameterized a 33-species model of southeastern forests (FORET), which was used to examine the influence of chestnut blight on growth and successional patterns of eastern forests. This model has subsequently been used by McLaughlin et al. (1978) and West et al. (1980) to examine the potential influence of chronic growth inhibition by air pollution on both species and stand-level biomass responses. In these studies, hypothetical levels of externally introduced stress on growth of each species were assumed, based on literature data on species' relative sensitivity to visible injury and growth responses. A maximum growth stress of 0 to 20% was imposed depending on a species' sensitivity ranking. A model of this type allows one to study interactions between stand age and composition at the time of stress initiation, level of stress, and time since stress was initiated on total stand biomass and its distribution between component species. In these studies, both competition and stand age were identified as important modifiers of forest responses to air pollution. Other types of forest models and their potential applicability to air pollution problems have been reviewed by Shugart et al. (1980).

At present, models of the type described above must be regarded as tools with which to address difficult tasks, integrate data, and identify needed research. Their output cannot provide final quantitative answers until we have better data on chronic stress effects on individual species. They emphasize the need for data on relative species' sensitivity to chronic stress and for better quantification of responses to stress of mature trees in mixed communities. The former may be addressed through use of field-chamber techniques now used primarily for agricultural crops. The second task is more difficult. However, the field of dendroecology has great potential for addressing this problem. To document impacts of air pollution on forest growth over the past 40 years, during which chronic regional-scale stress has increased sharply, will require techniques for assessing changes in annual pollutant levels. One potentially useful tool for obtaining histories of exposure to general air pollution stress is heavy metal analysis in the individual rings (Lepp, 1975). This approach has been used in Sweden (Symeonides, 1979) to construct histories of heavy metal pollution, though Tian and Lepp (1977) caution that factors such as radial transport and soil uptake must be fully understood to use this technique accurately. In the Swedish study, both lead and copper showed little lateral movement and were useful in constructing a decade-level history of metal pollution at the study site. Recent developments coupling x-ray emission spectroscopy (Valkovic et al., 1979) with growth-ring analysis show promise for using a variety of trace elements for historical analyses. As these techniques are further developed, they may provide useful data for constructing historical indices of regional-scale chronic stress.

Ultimately, assessment of air pollution impacts over large spatial scales must rely on development of large-scale data bases defining the nature and distribution of the resources which may be sensitive to those impacts. Such a system depends on computer analysis of multiple variables for a large number of landscape units. The size and amount of detail entered for these units may vary depending on the nature of the task addressed. An example of such a system is the Geoecology Data Base developed by Olson et al. (1980). Formatted at a county level, it includes over 1000 variables on terrain, water resources, forestry and other vegetation, wildlife, agriculture, land use, climate, air quality, population, and energy. The utility of such a system in addressing regional-scale assessment of effects of acid precipitation on soils was recently illustrated by Klopatek et al. (1980). Here computer maps of soil pH, cation exchange capacity, and base saturation were overlain with similar maps of current levels of hydrogen ion loading from acid rain. Resultant analysis identified at a county level of resolution those areas in which soil pH was most likely to be impacted. This type of system has great diversity and utility for a wide range of ecological problems. While one of its great values is its ability to use generalized ecological relationships in large-scale analyses, it calls on us to identify and perform those experiments which will make generalizations as accurate as reasonably possible.

REFERENCES

Altshuller, A. P., "Analytical Problems in Air Pollution Control," in W. W. Meinke and J. K. Taylor, Eds., Analytical Chemistry: Key to Progress on National Problems, NBS Spec. Publ. No. 351, National Bureau of Standards, Washington, D.C., 1972.

Andren, A. W., and S. E. Lindberg, Atmospheric input and origin of selected elements in Walker Branch Watershed, Oak Ridge, Tennessee, Water Air Soil Pollut., 8, 199-215 (1977).

Applequist, H., K. O. Jensen, T. Sevel, and C. Hammer, Mercury in the Greenland ice sheet, Nature, 273, 657-659 (1978).

Barrie, L. A., S. Beilke, and H. W. Georgii, "Sulfur Dioxide Removal by Cloud and Fog Drops as Affected by Ammonia and Heavy Metals," in R. G. Simonin and R. W. Beadle, Eds., Precipitation Scavenging (1974), ERDA Symposium Series No. 41, CONF-741003, National Technical Information Service, Springfield, Virginia, 1977.

Barrie, L. A., and H. W. Georgii, An experimental investigation of absorption of SO_2 by water drops containing heavy metal ions, Atmos. Environ., 10, 743-749 (1976).

Barrie, L. A., and J. L. Walmsley, A study of sulphur dioxide deposition velocities to snow in N. Canada, Atmos. Environ., 12, 2321-2332 (1978).

Barton, J. R., S. B. McLaughlin, and R. K. McConathy, The effects of SO_2 on components of leaf resistance to gas exchange, J. Environ. Pollut., in press, 1980.

Beauford, W., J. Barber, and A. R. Barringer, Heavy metal release from plants into the atmosphere, Nature, 256, 35-37 (1975).

Beauford, W., J. Barber, and A. R. Barringer, Release of particles containing metals from vegetation into the atmosphere, Science, 195, 571-573 (1977).

Bennett, J. H., and A. C. Hill, Absorption of gaseous air pollutants by a standardized plant canopy, J. Air Pollut. Control Assoc., 23, 203-206 (1973).

Bennett, J. H., and A. C. Hill, "Interactions of Air Pollutants with Canopies of Vegetation," in J. B. Mudd and T. Kozlowski, Eds., Response of Plants to Air Pollution, Academic Press, New York, 1975, 383 pp.

Bennett, J. H., A. C. Hill, and D. M. Gates, A model for gaseous pollutant uptake by air pollutants, J. Air. Pollut. Control Assoc., 23, 957-962 (1973).

Berg, W. W., Jr., Chlorine Chemistry in the Marine Atmosphere, Ph.D. Dissertation, Department of Oceanography Technical Report 2-76, Florida State University, Tallahassee, Florida, 1976.

Bjorseth, A., G. Lunde, and A. Lindskog, Long-range transport of polycyclic aromatic hydrocarbons, Atmos. Environ., 13, 45-53 (1979).

Bogen, D. C., S. J. Nagourney, and G. A. Welford, MAP3S Precipitation Chemistry Intercomparison Study, Environmental Measurements Laboratory Report No. EML-341, Department of Energy, New York, 1978.

Botkin, D. B., "The Role of Species Interactions in the Response of a Forest Ecosystem to Environmental Perturbation," in B. C. Patten, Ed., Systems Analysis and Simulation in Ecology, Vol. IV, Academic Press, New York, 1976, pp. 147-173.

Botkin, D. B., J. F. Janak, and J. R. Wallis, Some ecological consequences of a computer model of forest growth, J. Ecol., 60, 849-872 (1972).

Boutron, C., Past and present day tropospheric fallout fluxes of Pb, Cd, Cu, Zn, and Ag in Antarctica and Greenland, Geophys. Res. Lett., 6, 159-162 (1979).

Boutron, C., and C. Lorius, Historical record of trace metals in Antarctic snows since 1914, Nature, 277, 551-554 (1978).

Brimblecomb, P., Dew as a sink for SO_2, Tellus, 30, 151-157 (1978).

Brosset, C., et al., Report of the Expert Meeting on Dry Deposition, held by the World Meteorological Organization in Gothenburg, Sweden, April 18-22, 1977.

Brown, D. K., P. Lowry, S. E. Lindberg, S. E. Herbes, and J. M. Coe. Sorption of PAH from aqueous solutions filtered through membrane and glass fiber filters, Oak Ridge National Laboratory, Oak Ridge, Tennessee (in preparation).

Carlson, R. W., F. A. Bazzaz, and J. J. Stukel, Physiological effects, wind reentrainment, and rainwash of Pb aerosol particulate deposited on plant leaves, Environ. Sci. Technol., 10, 1139-1142 (1976).

Casey, A. W., Scanning Electron Microscopy Techniques for Determining Atmospheric Particle-size Distribution, UCRL-51895, Lawrence Livermore Laboratory, Livermore, California, 1975.

Cawse, P. A., Survey of Atmospheric Trace Elements in the United Kingdom (1972-1973), R-7669, Atomic Energy Research Establishment, Harwell, England, 1974.

Chamberlain, A. C., Aspects of Travel and Deposition of Aerosols and Vapor Clouds, MP/R 1261, Atomic Energy Research Establishment, Harwell, England, 1955.

Chamberlain, A. C., Interception and retention of radioactive aerosols by vegetation, Atmos. Environ., 4, 57-78 (1970).

Chamberlain, A. C., "Movement of Particles in Plant Communities," in J. L. Montieth, Ed., Vegetation and the Atmosphere, Vol. I: Principles, Academic Press, London, 1975, pp. 155-203.

Changnon, S. A., Jr., Rainfall changes in summer caused by St. Louis, Science, 205, 402-404 (1979).

Cheney, J. L., and J. B. Homolya, Sampling parameters for sulfate measurement and characterization, Environ. Sci. Technol., 13, 584-588 (1979).

Cheng, Yung-Sung, and Hsu-Chi Yeh, Particle bounce in cascade impactors, Environ. Sci. Technol., 13, 1392-1396 (1979).

Chrisp, C. E., G. L. Fisher, and J. Lammert, Mutagenicity of filtrates from respirable coal fly ash, Science, 199, 73-75 (1977).

Clough, W. S., Transport of particles to surfaces, Aerosol Sci., 4, 227-234 (1973).

Conner, W. D., An inertial-type particle separator for collection of large samples, J. Air Pollut. Control Assoc., 16, 35-38 (1966).

Coutant, R. W., Effect of environmental variables on collection of aerosol sulfate, Environ. Sci. Technol., 11, 873-878 (1977).

Dana, M. T., The MAP3S Precipitation Chemistry Network: First Periodic Summary Report, PNL-2402, Pacific Northwest Laboratory, Richland, Washington, 1977.

Dana, M. T., The MAP3S Precipitation Chemistry Network: Second Periodic Summary Report, PNL-2829, Pacific Northwest Laboratory, Richland, Washington, 1979.

Davidson, C. I., Deposition of Trace-Metal-Containing Aerosols on Smooth Flat Surface and on Wild Oatgrass, Ph.D. Dissertation, California Institute of Technology, Los Angeles, California, 1977.

Davidson, C. I., and R. W. Elias, Dry Deposition of Trace Elements at a Remote Site in the High Sierra, Preprint of a paper presented at the Meeting of the American Institute of Chemical Engineers, 1979. Department of Civil Engineering, Carnegie-Mellon Institute, Pittsburgh, Pennsylvania.

Dingle, A. N., and B. M. Joshi, Ammonium sulfate crystallization in Andersen cascade impactor samples, Atmos. Environ., 8, 1119-1130 (1974).

Dochinger, L. S., and T. Seliga (Eds.), Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, USDA Forest Service Technical Report NE-23, 1976.

Dovland, H., and A. Eliassen, Dry deposition on a snow surface, Atmos. Environ., 10, 783-785 (1976).

Droppo, J. G., "Experimental Techniques for Dry Deposition Measurements," in D. S. Shriner, C. R. Richmond, and S. E. Lindberg, Eds., Atmospheric Sulfur Deposition: Environmental Impact and Health Effects, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1980.

Duce, R. A., G. Hoffman, and W. H. Zoller, Atmospheric trace metals at remote northern and southern hemisphere sites: Pollution or natural?, Science, 187, 59-61 (1975).

Dzubay, T. G., L. E. Hines, and R. K. Stevens, Particle bounce errors in cascade impactors, Atmos. Environ., 10, 229-234 (1976).

Dzubay, T. G., and R. K. Stevens, Ambient air analysis with dichotomous sampler and x-ray fluorescence spectrometer, Environ. Sci. Technol., 9, 663-668 (1975).

Eisenbud, M., and T. Kneip, Trace Metals in Urban Aerosols, EPRI-117, Electric Power Research Institute, Palo Alto, California, 1975, 418 pp.

Elias, R. W., T. Hinkley, T. Hirao, and C. Patterson, Improved techniques for study of mass balance and fractionation among families of metals within the terrestrial ecosystem, Geochem. Cosmochem. Acta., 40, 583-587 (1976).

Environmental Protection Agency (EPA), Bioenvironmental Impact of a Coal-Fired Power Plant, Fourth Interim Report, Colstrip, Montana, E. M. Preston and T. M. Gullet, Eds., EPA-600/3-79-044, Corvallis Environmental Research Laboratory, Corvallis, Oregon, 1979.

Essenwanger, O., "Frequency Distribution of Precipitation," in Physics of Precipitation, Geophysical Monograph No. 5, American Geophysical Union, NAS-NRC No. 746, National Academy of Sciences, Washington, D.C., 1960.

Fan, Kuo-Chung, and J. W. Gentry, Clogging in Nuclepore filters, Environ. Sci. Technol., 12, 1289-1294 (1978).

Fisher, G. L., C. E. Chrisp, and O. G. Raabe, Physical factors of the mutagenicity of fly ash from a coal fired power plant, Science, 204, 879-881 (1979).

Fritts, H. C. Dendroclimatology and dendroecology, Quat. Res. N.Y., 1, 419-449 (1971).

Fowler, E. B., Ed., Radioactive Fallout, Soils, Plants, Food, Man, Elsevier Publishing Co., New York, 1965, 317 pp.

Galloway, J. N. (Ed.), Proceedings of a Workshop on Toxic Substances in Atmospheric Deposition, U.S. Environmental Protection Agency, held at Jekyl Island, Georgia, November 1979, USEPA, Washington, D.C., 1980.

Galloway, J. N., and E. B. Cowling, The effects of precipitation on aquatic and terrestrial ecosystems: A proposed precipitation chemistry network, J. Air Pollut. Control Assoc., 28, 229-235 (1978).

Galloway, J. N., E. B. Cowling, E. Gorham, and W. W. McFee, A National Program for Assessing the Problem of Atmospheric Deposition, Report to the Council on Environmental Quality, National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado, 1978.

Galloway, J. N., B. J. Crosby, Jr., and G. E. Likens, Acid precipitation: Measurement of pH and acidity, Limnol. Oceanogr., 24, 1161-1165 (1979).

Galloway, J. N., and G. E. Likens, "Calibration of Collection Procedures for the Determination of Precipitation Chemistry," in Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, USDA Forest Service Tech. Report NE23, 1976, pp. 137-156.

Galloway, J. N., and G. E. Likens, The collection of precipitation for chemical analysis, Tellus, 30, 71-82 (1978).

Galloway, J. N., and G. Parker, "Difficulties in Measuring Wet and Dry Deposition on Forest Canopies and Soil Surfaces," in T. C. Hutchinson and M. Havas, Eds., Effects of Air Pollutants on the Terrestrial Ecosystem, Proceedings of NATO Advanced Research Institute on the Effects of Acid Rain on Terrestrial Ecosystems, NATO Conf. Series 1: Ecology, Vol. 4, Plenum Publ. Co., New York, 1980, pp. 57-68.

Garland, J. A., "Dry Deposition of SO_2 and Other Gases," in R. J. Engelmann and G. A. Sehmel, Eds., Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants (1974), ERDA CONF-740921, Technical Information Center, Oak Ridge, Tennessee, 1976.

Gascoyne, M., Design and operation of a simple sequential precipitation sampler with some preliminary results, Atmos. Environ., 11, 397-400 (1977).

Gatz, D. F., "An Urban Influence on Deposition of Sulfate and Soluble Metals in Summer Rains," in D. S. Shriner, C.R. Richmond, and S. E. Lindberg, Eds., Atmospheric Sulfur Deposition: Environmental Impacts and Health Effects, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1980.

Gatz, D. F., "Spatial Variability of Atmospheric Deposition," in R. G. Semonin, D. F. Gatz, M. E. Peden, G. J. Stensland, Eds., Study of Atmospheric Pollution Scavenging, COO-1199-59, Illinois State Water Survey, University of Illinois, Urbana, Illinois, 1978.

Gehrs, C. W., D. S. Shriner, S. E. Herbes, E. Salmon, and H. Perry, "Environmental Safety and Health Implications of Increased Coal Utilization," in M. Elliott, Ed., Chemistry of Coal Utilization, Chapter 31, National Academy of Sciences, 1980.

Gibson, J. H., and C. V. Baker, First Data Report - July 1978 to February 1979, National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado, 1979.

Gifford, F. A., Atmospheric Dispersion Models for Environmental Pollution Application, Lectures on Air Pollution and Environmental Impact Analysis, Boston, Massachusetts, American Meteorological Society, 1975, pp. 35-38.

Gifford, F. A., Turbulent diffusion typing schemes: A review. Nucl. Saf. 17, 68-86 (1976).

Gordon, A. G., and E. Gorham, Ecological aspects of air pollution from an iron sintering plant at Wawa, Ontario, Canada, J. Bot., 41, 1063-1078 (1963).

Gordon, G., Study of the Emissions from Major Air Pollution Sources and their Atmospheric Interactions, Progress Report-75, University of Maryland, College Park, Maryland, 1975.

Gordon, G. E., E. S. Gladney, J. M. Ondov, T. Conry, and W. H. Zoller, "Problems with the use of cascade impactors," in W. Fulkerson, W. D. Shultz, and R. I. Van Hook, Eds., First Annual NSF Trace Contaminants Conference, CONF-730802, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1973, pp. 138-145.

Graustein, W. C., and R. L. Armstrong, Measurement of dust input to a forested watershed using $^{87}Sr/^{86}Sr$ ratios, Geol. Soc. Am. Abstr., 10, 411 (1978).

Greist, W. H., and M. R. Guerrin, Identification and Quantification of Polynuclear Organic Matter (POM) on Particulates from a Coal-Fired Power Plant, EA-1092, Electric Power Research Institute, Palo Alto, California, 1979.

Hanna, S. R., Local and global transport and dispersion of airborne effluents, in Proceedings of American Nuclear Society and American Institute of Chemical Engineers Symposium on Controlling Airborne Effluents from Fuel Cycle Plants, Sun Valley, Idaho, July 1-14, 1976.

Harris, F. S., Atmospheric Aerosols: A Literature Summary of Their Physical Characteristics and Chemical Composition, NASA Report CR2626, National Aeronautics and Space Administration, Washington, DC, 1976.

Hart, G. E., and D. R. Parent, Chemistry of throughfall under Douglas-fir and Rocky Mountain juniper, Am. Midl. Nat., 92, 191-201 (1974).

Haugen, D. A. (workshop coordinator), Lectures on Air Pollution and Environmental Impact Analyses, American Meteorological Society, Boston, Massachusetts, 1975, 296 pp.

Heagle, A. S., A. J. Riordan, and W. W. Heck, "Field Methods to Assess the Impact of Air Pollutants on Crop Yields," Paper 79-46.6, in Proceedings 72nd Annual Meeting Air Pollution Control Association, Cincinnati, Ohio, 1979.

Heagle, A. S., D. E. Body, and W. W. Heck, An open-top field chamber to assess the impact of air pollution on plants, J. Environ. Qual., 2, 365-368 (1973).

Heck, W. W., and C. S. Brandt, "Air Pollution Effects on Vegetation: Native Crops and Forests," in A. Stern, Ed., Air Pollution, 3rd ed., Academic Press, New York, pp. 157-229.

Heindryckx, R., Comparison of the mass size functions of the elements in the aerosols fo the Ghent industrial district with data from other areas: Some physico-chemical implications, Atmos. Environ., 10, 65-71 (1976).

Hering, S. V., S. C. Hagan, and S. K. Friedlander, Design and evaluation of new low-pressure impactor, 1, Environ. Sci. Technol., 12, 667-673 (1978).

Hering, S. V., S. K. Friedlander, J. J. Collins, and L. W. Richards, Design and evaluation of a new low-pressure impactor, 2, Environ. Sci. Technol., 13, 184-188 (1979).

Hicks, B. B., and M. L. Wesely, An Examination of Some Micrometeorological Methods for Measuring Dry Deposition," EPA-600/7-78-116, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978a, 18 pp.

Hicks, B. B., and M. L. Wesely, Recent Results for Particle Deposition Obtained by Eddy Correlation Methods, ERC-78-12, Argonne National Laboratory, Argonne, Illinois, 1978b, 17 pp.

Hicks, B. B., and M. L. Wesely, "Turbulent Transfer Processes in the Canopy and at Vegetation Surfaces," in D. S. Shriner, C. R. Richmond, and S. E. Lindberg, Eds., Atmospheric Sulfur Deposition: Environmental Impacts and Health Effects, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1980.

Hicks, B. B., et al., Workshop Report on Dry Deposition Methodology, held at Argonne National Laboratory, December, 1980, Sponsored by U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (in preparation).

Hill, A. C., Vegetation: A sink for atmospheric pollutants, J. Air Pollut. Control Assoc., 21, 341 (1971).

Hill, A. C., and E. M. Chamberlain, "The Removal of Water Soluble Gases from the Atmosphere by Vegetation," in R. Engelmann and G. Sehemel, Eds., Atmosphere - Surface Exchange of Particulate and Gaseous Pollutants, ERDA Symposium Series-38, CONF-740921, National Technical Information Service, Springfield, Virginia, 1976, pp. 153-171.

Hill, G. R., and M. D. Thomas, Influence of leaf destruction by sulphur dioxide and by clipping on yield of alfalfa, Plant Physiol., 8, 223-245 (1933).

Hodge, V., S. R. Johnson, and E. Goldberg, Influence of atmospherically transported aerosols on surface ocean water composition, Geochem. J. 12, 7-20 (1978).

Hoffman, W. A., Jr., S. E. Lindberg, and R. R. Turner, Precipitation acidity: The role of forest canopy in acid exchange, J. Environ. Qual. 9, 95-100 (1980).

Horsman, D. C., T. M. Roberts, and A. D. Bradshaw, Studies on the effect of sulphur dioxide on perennial ryegrass (Solium perenne L.), II. Evolution of tolerance, J. Exp. Bot., 30, 495-501 (1979).

Hosker, R. P., Jr., Practical application of air pollution deposition models: Current status, data requirements and research needs, (this symposium).

Hosker, R. P., Jr., "Estimates of Dry Deposition and Plume Depletion over Forests and Grassland," in The Physical Behavior of Radioactive Contaminants in the Atmosphere, IAEA Symposium SM-181, Vienna, Austria, 1974, pp. 291-310.

Jernelov, A., and T. Wallin. Airborne mercury fallout on snow and around five Swedish chlor-alkali plants, Atmos. Environ., 7, 209-214 (1973).

Johnston, J. W., and A. S. Heagle, The response of soybeans to an acute exposure following chronic ozone exposures (submitted to Phytopathology).

Kellogg, W. W., R. D. Cadle, E. R. Allen, A. L. Lazrus, E. A. Martell, The sulfur cycle, Science, 175, 587-596 (1972).

Kennedy, V. C., G. W. Zellwenger, and R. J. Avanzino, Variation of rain chemistry during storms at two sites in northern California, Water Resour. Res., 15, 687-702 (1979).

Keyser, T. R., D. F. S. Natusch, C. A. Evans, Jr., and R. W. Linton, Characterizing the surfaces of environmental particles, Environ. Sci. Technol., 12, 768-773 (1978).

Klement, A. W., Jr., Radioactive Fallout from Nuclear Weapon Tests, AEC Symposium No. 5, CONF-765, National Bureau of Standards, U.S. Dept. of Commerce, Springfield, Virginia, 1965.

Klepper, B., and D. K. Craig, Deposition of airborne particulates onto plant leaves, J. Environ. Qual., 4, 495-499 (1975).

Klopatek, J. M., W. F. Harris, and R. J. Olson, "A Regional Ecological Assessment Approach to Atmospheric Deposition," in D. S. Shriner, C. R. Richmond, and S. E. Lindberg, Eds., Atmospheric Sulfur Deposition: Environmental Impacts and Health Effects, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1980.

Krause, G. H. M., and H. Kaiser, Plant response to heavy metals and SO_2, Environ. Pollut., 12, 63-71 (1977).

Larsen, R. I., and W. W. Heck, An air quality data analysis system for interrelating effects, standards, and needed source reductions: Part 3, Vegetation injury, J. Air Pollut. Control Assoc., 26, 325-333 (1976).

Lawson, D. R., and J. W. Winchester, Sulfur and crystal reference elements in nonurban aerosols from Squaw Mountain, Colorado, Environ. Sci. Technol., 12, 716-721 (1978).

Legge, A. H., D. R. Soques, G. W. Harvey, H. R., Krouse, H. M. Brown, E. C. Rhodes, M. Nosal, H. V. Schellhase, J. Mayo, A. P. Hurtgerink, P. F. Lester, R. G. Amundson, and R. B. Walker, Sulfur Gas Emissions in the Boreal Forest: The West Whitecourt Case Study, Final Report to the Whitecourt Environmental Study Group, Kananaskis Center for Environmental Research, the University of Calgary, Alberta, Canada, 1978.

Lepp, N. W., The potential of tree-ring analysis for monitoring heavy metal pollution patterns, Environ. Pollut., 9, 49-61 (1975).

Lim, M. Y., Trace Elements from Coal Combustion-Atmospheric Emissions, Report No. ICTIS/TR05, International Energy Agency of Coal Research, London, 1979, 58 pp.

Lindberg, S. E., Mercury partitioning in a power plant plume and its influence on atmospheric removal mechanisms, Atmos. Environ., 14, 227-231 (1980).

Lindberg, S. E., and R. C. Harriss, "Emissions from Coal Combustion: Use of Aerosol Solubility in Hazard Assessment," in J. Singh and A. Deepak, Eds., Environmental and Climatic Impact of Coal Utilization, Academic Press, New York, 1980.

Lindberg, S. E., R. C. Harriss, R. R. Turner, D. S. Shriner, and D. D. Huff, Mechanisms and Rates of Atmospheric Deposition of Selected Trace Elements and Sufate to a Deciduous Forest Watershed, ORNL/TM-6674, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1979a, 514 pp.

Lindberg, S. E., D. R. Jackson, J. W. Huckabee, S. A. Janzen, M. J. Levin, and J. R. Lund, Atmospheric emission and plant uptake of mercury from agricultural soils near the Almaden Mercury Mine, J. Environ. Qual., 8, 572-578 (1979b).

Lindberg, S. E., and R. R. Turner, Mercury emissions from chlorine production solid waste deposits, Nature, 268, 133-136 (1977).

Lindberg, S. E., R. R. Turner, N. M. Ferguson, and D. Matt, "Walker Branch Watershed Element Cycling Studies: Collection and Analysis of Wetfall for Trace Elements and Sulfate," in D. L. Correll, Ed., Watershed Research in Eastern North America, Smithsonian Institute Press, Edgewater, Maryland, 1977, pp. 125-150.

Lindeken, D. D., R. L. Morgin, K. F. Petrock, Collection efficiency of Whatman-41 filter paper for submicron aerosols, Health Phys., 9, 305-308 (1963).

Liu, B. Y. H., and K. W. Lee, Efficiency of membrane and Nuclepore filters for submicrometer aerosols, Environ. Sci. Technol., 10, 345-350 (1976).

Lockhart, L. B., Jr., R. L. Patterson, and W. L. Anderson, Characteristics of Air Filter Media Used for Monitoring Airborne Radioactivity, Naval Research Laboratory Report 6054, Washington, D.C., 1963.

Lunde, G., J. Gether, N. Gjos, and M. B. S. Lande, Organic micropollutants in precipitation in Norway, Atmos. Environ., 11, 1007-1014 (1977).

Lundgren, D. A., F. S. Harris, W. H. Marlow, M. Lippmann, W. E. Clark, M. D. Durham, Aerosol Measurement, University Presses of Florida, Gainesville, Florida, 1979, 720 pp.

MacLean, D. C., R. E. Schneider, and L. H. Weinstein, Accumulation of fluoride by forage crops, Contrib. Boyce Thompson Inst., 24, 165-166 (1969).

MacLean, D. C., and R. E. Schneider, Fluoride accumulation by foliage: Continuous vs. intermittent exposures to hydrogen fluoride, J. Environ. Qual., 2, 501-503 (1973).

Mandle, R. H., L. H. Weinstein, D. C. McCune, and M. Keveny, A cylindrical, open-top chamber for exposure of plants to air pollutants in the field, J. Environ. Qual., 2, 371-376 (1973).

McClenahen, J. R., Community changes in a deciduous forest exposed to air pollution, Can. J. For. Res., 8, 432-438 (1978).

McFarland, A. R., J. B. Wedding, and J. E. Cermak, Wind tunnel evaluation of a modified Anderson impactor an an all weather sampler inlet, Atmos. Environ., 11, 535-539 (1977).

McLaughlin, S. B., and D. S. Shriner, "Allocation of Resources to Defense and Repair," in J. G. Horsfall and E. B. Cowling, Eds., Plant Disease: An Advanced Treatise, Academic Press, New York, 1980, Chapter 20.

McLaughlin, S. B., R. K. McConathy, and L. K. Mann, The effects of SO_2 dosage kinetics and exposure frequency on photosynthesis and transpiration of kidney beans (Phaseolus vulgaris L.), Environ. Exp. Bot., 19, 179-191 (1979).

McLaughlin, S. B., D. C. West, H. H. Shugart, and D. S. Shriner, "Air Pollution Effects on Forest Growth and Succession: Applications of a Mathematical Model," in 71st Meeting Air Pollution Control Association, Houston, Texas, 1978, Paper 78-24.5, 17 pp.

McMullen, T. B., and R. B. Faoro, Occurrence of eleven metals in airborne particulates and in surficial materials, J. Air Pollut. Control Assoc., 27, 1198-1202 (1977).

Mecklenberg, R. A., H. B. Tukey, and J. V. Morgan, A mechanism for the leaching of Ca from foliage, Plant Physiol., 41, 610-613 (1966).

Melo, O. T., and C. R. Phillips, Aerosol-size spectra by means of Nuclepore filters, Environ. Sci. Technol., 9, 560-564 (1975).

Meszaros, A., On the size distribution of atmospheric aerosol particles of different composition, Atmos. Environ., 11, 1075-1081 (1977).

Miller, J. M., J. N. Galloway, and G. E. Likens, "The Use of ARL Trajectories for the Evaluation of Precipitation Chemistry Data," in L. S. Dochinger and T. A. Seliga, Eds., Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, USDA Forest Service Tech. Report NE-23, 1976.

Miller, P. R., and J. R. McBride, Oxidant Air Pollution Effects on a Western Coniferous Forest Ecosystem, Statewide Air Pollution Research Center, University of California, Riverside, California, 1973.

Morgan, J. J., "Sampling and Analysis of Metals in Air, Water and Waste Products," in International Conference on Environmental Sensing and Assessment, Vol. I, Section 1-2, University of Nevada, Las Vegas, 1975.

Mudd, J. B., and T. T. Kozlowski, Responses of Plants to Air Pollution, Academic Press, New York, 1975, 383 pp.

Munn, R., and B. Bolin, Review: Global air pollution - meteorological aspects, Atmos. Environ., 5, 363-402 (1971).

Murphy, B. D., The Influence of Ground Cover on the Dry Deposition Rate of Gaseous Materials, UCCND/CSAD-19, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976, 28 pp.

Nappo, C. J., The Simulation of Atmospheric Transport Using Observed and Estimated Winds. Preprint of Third Symposium on Atmospheric Turbulence, Diffusion, and Air Quality, Raleigh, North Carolina. American Meteorological Society, 1976, pp. 100-106.

Nash, T. H., H. C. Fritts, and M. A. Stokes, A technique for examining non-climatic variation in widths of annual tree rings with special reference to air pollution, Tree-Ring Bull., 35, 14-24 (1975).

National Academy of Sciences (NAS), Arsenic - Medical and Biological Effects of Environmental Pollutants, ISBNO-309-02604-0, Washington, D.C., 1977.

National Research Council (NRC), Airborne Particles, Report by the Subcommittee on Airborne Particles, Committee on Medical and Biologic Effects of Environmental Pollutants, Division of Medical Sciences, University Park Press, Baltimore, Maryland, 1979, 343 pp.

Natusch, D. F. S., and J. Wallace, Urban aerosol toxicity: Influence of particle size, Science, 186, 695-699 (1974).

Natusch, D. F. S., J. Wallace, and C. Evans, Toxic trace elements: Preferential concentration in respirable particles, Science, 183, 202-204 (1974).

Neustadter, H. E., S. M. Sidik, R. B. King, J. S. Fordyce, J. C. Burr, The use of Whatman-41 filters for high volume air sampling, Atmos. Environ., 9, 101-109 (1975).

Nihlgard, B., Precipitation, its chemical composition and effect on soil water in a beech and spruce forest in southern Sweden, Oikos, 21, 208-217 (1970).

Noggle, J. C., "The Role of Gaseous Sulfur in Crop Nutrition," in D. S. Shriner, C. R. Richmond, and S. E. Lindberg, Eds., Atmospheric Sulfur Deposition: Environmental Impacts and Health Effects, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1980.

O'Gara, P. I., Sulfur dioxide fume problems and their solutions, J. Ind. Eng. Chem., 14, 744 (1922).

Olson, R. J., J. M. Klopatek, and C. J. Emerson, "Regional Environmental Studies: Application of the Geoecology Data Base," in Mapping Collection Harvard Library of Computer Graphics, Vol. V, 1980.

Owens, M. J., and A. W. Powell, Deposition velocity of SO_2 on land and water surfaces using ^{35}S tracer methods, Atmos. Eviron., 8, 63-67 (1974).

Parker, G. G., S. E. Lindberg, and J. M. Kelly, "Atmosphere/Canopy Interactions of Sulfur in the Southeastern United States, in D. S. Shriner, C. R. Richmond, and S. E. Lindberg, Eds., Atmospheric Sulfur Deposition: Environmental Impact and Health Effects, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1980.

Parker, R. D., G. H. Buzzard, T. G. Dzubay, and J. P. Bell, A two-stage respirable aerosol sampler using Nuclepore filters in series, Atmos. Environ., 11, 617-621 (1977).

Pattenden, N. J., and R. D. Wiffin, The particle size dependence of the collection efficiency of an environmental aerosol sampler, Atmos. Environ., 11, 677-681 (1977).

Peden, M. E., and L. M. Skowron, Ionic stability of precipitation samples, Atmos. Environ., 12, 2343-2349 (1978).

Peden, M. E., L. M. Skowron, and F. M. McGurk, Precipitation Sample Handling, Analysis, and Storage Procedures, Research Report 4, Illinois State Water Survey, Urbana, Illinois, 1979.

Penkett, S. A., B. M. R. Jones, and R. E. J. Eggleton, A study of SO_2 oxidation in stored rainwater samples, Atmos. Environ., 13, 139-147 (1979).

Pierce, R. C., and M. Katz, Dependency of polynuclear aromatic hydrocarbon content on size distribution of atmospheric aerosols, Environ. Sci. Technol., 9, 347-353 (1975).

Raynor, G. S., Meteorological and Chemical Relationships from Sequential Precipitation Samples, CONF-761102, Brookhaven National Laboratory, Upton, L. I., New York, 1976.

Raynor, G., and J. Haynes, Experimental Data from Analysis of Sequential Precipitation Samples at Brookhaven National Laboratory, BNL-50826, Atmospheric Sciences Division, Brookhaven National Laboratory, Upton, L. I., New York, 1977.

Raynor, G. S., and J. P. McNeil, An automatic sequential precipitation sampler, Atmos. Environ. 13, 149-155 (1979).

Reinert, R. A., A. S. Heagle, and W. W. Heck, "Plant Responses to Pollutant Combinations," in J. B. Mudd and T. T. Kozlowski, Eds., Response of Plants to Air Pollution, Academic Press, New York, 1975, 383 pp.

Rogers, H. H., H. E. Jeffries, E. P. Stahel, W. W. Heck, L. A. Ripperton, and A. M. Witherspoon, Measuring air pollutant uptake by plants: A direct kinetic technique, J. Air Pollut. Control Assoc., 27, 1192-1197 (1977).

Rogers, R. R., and I. I. Zawadski, Rainfall statistics for application to plume rainout models, Atmos. Environ., 13, 279-286 (1979).

Ronneau, C., J. Cara, J. L. Navarre, and P. Priest, An automatic sequential rain sampler, Water Air Soil Pollut., 9, 171-176 (1978).

Rosenberg, C. R., R. J. Hutnik, and D. D. Davis, Forest composition at varying distances from a coal-burning power plant, Environ. Pollut., 13, 307-317 (1979).

Schlesinger, W., W. Reiners, and D. Kropman, Deposition of water and cations on artificial foliar collectors in fir-Krummholz of New England mountains, Ecology, 55, 378-386 (1974).

Schroeder, H. A., Metals in the air, Environment, 13, 18-32 (1971).

Scurfield, G., Air pollution and tree growth, For. Abstr., 21, 339-347 (1960).

Sehmel, G. A., "A Summary of Dry Deposition Velocity Data," in D. S. Shriner, C. R. Richmond, and S. E. Lindberg, Eds., Atmospheric Sulfur Deposition: Environmental Impacts and Health Effects, Ann Arbor Science Publishers, Ann Arbor, Michigan, 1980.

Sehmel, G. A., and W. Hodgson, Particle and Gaseous Removal in the Atmosphere by Dry Deposition, BNWL-SA-4941, Battelle Pacific Northwest Laboratory, Richland, Washington, 1976.

Semonin, R. G., The variability of pH in convective storms, Water Air Soil Pollut., 6, 395-406 (1976).

Semonin, R., and R. Beadle, Eds., Precipitation Scavenging (1974), ERDA Symposium Series 41, CONF-741003, National Technical Information Service, Springfield, Virginia, 1977, 842 pp.

Shinn, J. H., "Estimation of Aerosol Plutonium Transport by the Dust-Flux Method: A Perspective on Application of Detailed Data," in M. G. White and P. B. Dunaway, Eds., Transuranics in Natural Environments, NVO-178, Nevada Applied Ecology Group, Las Vegas, Nevada, 1977.

Shinn, J. H., B. R. Clegg, and M. L. Stuart, A linear gradient chamber for exposing field plants to controlled levels of air pollutants, Environ. Pollut. (in press).

Shriner, D. S., Effects of simulated rain acidified with sulfuric acid on host-parasite interactions, Water Air Soil Pollut., 8, 9-14 (1976).

Shriner, D. S., S. B. McLaughlin, and C. F. Baes, Character and Transformation of Pollutants from Major Fossil Fuel Energy Sources, ORNL/TM-5919, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1977, 39 pp.

Shugart, H. H., and D. C. West, Development and application of an Appalachian deciduous forest succession model and its application to assessment of the impact of the chestnut blight, J. Environ. Manage., 5, 161-179 (1977).

Shugart, H. H., S. B. McLaughlin, and D. C. West, "Forest Models: Their Development and Potential Applications for Air Pollution Effects Research," in Proceedings, Symposium on Effects of Air Pollutants on Temperate and Mediterranean Forest Ecosystems, USDA Forest Service (1980).

Sievering, H., J. Dave, G. McCoy, and K. Walther, Cellulose filter high-volume cascade impactor aerosol collection efficiency, A technical note, Environ. Sci. Technol., 12, 1435-1437 (1978).

Skogerboe, R. K., D. L. Dick, and P. L. Lamothe, Evaluation of filter inefficiencies for particulate collection under low loading conditions, Atmos. Environ., 11, 243-249 (1977).

Slanina, J., J. G. Van Raaphorst, W. L. Zijp, A. J. Vermeulen, and C. A. Roet, An evaluation of the chemical composition of precipitation sampled with 21 identical collectors on a limited area, Int. J. Environ. Anal. Chem., 6, 67-81 (1979).

Slinn, W. G. N., "Some Approximations for the Wet and Dry Removal of Particles and Gases from the Atmosphere," in L. S. Dochinger and T. Seliga, Eds., Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem," USDA Forest Service Technical Report NE-23 (1976), pp. 857-894.

Spurny, K. R., J. P. Lodge, Jr., E. R. Frank, and D. C. Sheisley, Aerosol filtration by means of Nuclepore filters - aerosol sampling and measurement, Environ. Sci. Technol., 3, 453-63 (1969).

Spurny, K. R., J. Havlova, J. P. Lodge, Jr., E. R. Ackerman, D. C. Shusley, and B. Wilder, Aerosol filtration by means of Nuclepore filters, Environ. Sci. Technol., 8, 758-761 (1974).

Steinhardt, I., D. G. Fox, and W. E. Marlott, "Modeling the Uptake of SO_2 by Vegetation," in Proceedings, 4th National Conference on Fire and Forest Meteorology, St. Louis, Missouri, November 16-18, 1976, USDA For. Serv. Gen. Tech. Rep. RM-32, 1977, 239 pp.

Stratmann, H., "Field Experiments to Determine the Effects of SO_2 on Vegetation, Part II, Measurement and Evaluation of SO_2 Ground Level Concentrations, Forschungsberichte des Landes Nordrhein-Westfalen Freiland versuche zur Ermittlung von schwefeldioxyd wirkung auf die vegetation, Part II, No. 1184, 1963, 69 pp.

Symeonides, C., Tree-ring analysis for tracing the history of pollution: Application to a study in Northern Sweden, J. Environ Qual., 8, 482-486 (1979).

Taylor, G. E., Genetic analysis of ecotype differentiation within an annual plant species, Geranium carolinianum L., in response to sulfur dioxide, Bot. Gaz., 139, 362-368 (1978).

Thom, A. S., Momentum, mass, and heat exchange of plant communities, in J. L. Monteith, Ed., Vegetation and the Atmosphere, Academic Press, London, 1975, 439 pp.

Tian, T. K., and N. W. Lepp, Further studies on the development of tree ring analysis as a method for constructing heavy metal pollution histories. Proceedings, University of Missouri Annual Conference on Trace Substances, Environ. Health, 11, 440-447 (1977).

Tolg, G., "Elemental Analysis with Minute Samples," in Comprehensive Analytical Chemistry, III, Elsevier, New York, 1975.

Tukey, H. B., The leaching of substances from plants, Annu. Rev. Plant Physiol., 21, 305-324 (1970).

Tukey, H. B., R. A. Mecklenberg, and J. V. Morgan, "Mechanisms for the Leaching of Metabolites from Foliage," in Isotopes and Radiation in Soil-Plant Nutrition, IAEA Symposium Series 1965, International Atomic Energy Agency, Vienna, 1965.

Turner, R. R., and S. E. Lindberg, An Interlaboratory Comparison of Trace Analysis by Graphite Furnace AAS, ORNL/TM-5422, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976, 21 pp.

U.S. Atomic Energy Commission, Toxicity of Power Plant Chemicals to Aquatic Life, USAEC WASH-1249, Washington, D.C. (1973).

Valkovic, V., D. Rendic, E. K. Biegert, and E. Andrade, Trace element concentrations in tree rings as indicators of environmental pollution, Environ. Int., 2, 27-32 (1979).

Van Hook, R. I., and D. Shultz, Eds., Effects of Trace Contaminants from Coal Combustion, Proceedings of a Workshop, ERDA 77-64, Energy Research and Development Administration, Washington, D.C., 1977, 79 pp.

Vaughan, B. E., K. H. Abel, D. A. Cataldo, J. M. Hales, C. E. Hane, L. A. Rancitelli, R. C. Routson, R. E. Wilding, and E. G. Wolf, Review of Potential Impact on Health and Environmental Quality from Metals Entering the Environment as a Result of Coal Utilization, A Battelle Energy Program Report, Battelle Memorial Institute, Richland, Washington, 1975, 75 pp.

Volchok, H. L., L. E. Toonkel, and M. Schonberg, Trace Metals - Fallout in New York City, II, U.S. Atomic Energy Commission Report HASL-281, Health and Safety Laboratory, New York, New York, 1974.

Wedding, J. R., R. W. Carlson, J. Stukel, and F. Bazzaz, Aerosol deposition on plant leaves, Environ. Sci. Technol., 9, 151-154 (1975).

Wedding, J. B., R. W. Carlson, J. J. Stukel, and F. A. Bazzaz, Aerosol deposition on plant leaves, Water Air Soil Pollut., 7, 545-550 (1977a).

Wedding, J. B., A. R. McFarland, and J. E. Cermak, Large particle collection characteristics of ambient aerosol samplers, Environ. Sci. Technol., 11, 387-390 (1977b).

Weisburger, K., Natural carcinogenic products, Environ. Sci. Technol., 13, 278-281 (1979).

Wesely, M. L., and B. B. Hicks, Some factors that affect the deposition rates of SO_2 and similar gases on vegetation, J. Air Pollut. Control Assoc., 27, 1110-1116 (1977).

West, D. C., S. B. McLaughlin, and H. H. Shugart, Simulated forest response to chronic air pollution stress, J. Environ. Qual., 9, 43-49 (1980).

Whelpdale, D. M., Atmospheric Pathways of Sulphur Compounds: A General Report, MARC Report No. 7, Chelsea College, University of London, London, 1978.

White, E. J., and F. Turner, A method of estimating income of nutrients in a catch of airborne particles by a woodland canopy, J. Appl. Ecol., 7, 441-460 (1970).

White, M. G., and P. B. Dunaway, Transuranics in Natural Environments, NVO-178, Nevada Applied Ecology Group, Las Vegas, Nevada, 1977.

Winchester, J. W., and G. G. Desaedleer, "Applications of Trace Element Analysis to Studies of the Atmospheric Environment," in S. Amiel, Ed., Nondestructive Activation Analysis, Elsevier Scientific Publishing Co., Amsterdam, 1975.

Winkler, P., Relative humidity and the adhesion of atmospheric particles to the plates of impactors, Aerosol. Sci., 5, 235-240 (1974).

Winner, W. E., and H. A. Mooney, Ecology of SO_2 resistance: II. Photosynthetic changes of shrubs in relation to SO_2 absorption and stomatal behavior, Oecologia (in press) (1980a).

Winner, W. E., and H. A. Mooney, Ecology of SO_2 resistance: I. Effects of fumigators on gas exchange of deciduous and evergreen shrubs, Oecologia (in press) (1980b).

Zahn, R., The effect on plants of a combination of subacute and toxic sulfur dioxide doses, Staub, 30, 20-23 (1970).

Zahn, R., Effects of sulfur-dioxide on vegetation, Staub, 21, 56-60 (1961).

Ziegler, I. S., The effect of air polluting gases on plant metabolism, Environ Qual. Saf., 2, 182-208 (1973).

Zimdahl, R., Entry and movement in vegetation of lead, J. Air Pollut. Control Assoc., 26, 655-660 (1976).

Zoller, W. H., E. S. Gladney, and R. A. Duce, Atmospheric concentration and sources of trace metals at the South Pole, Science, 183, 198-200 (1974).