



# A review of the current status of knowledge on dry deposition

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## Abstract

Dry deposition can account for a large portion of the removal of trace chemicals from the troposphere. Resistance schemes used in modeling often perform quite well in daytime conditions over flat terrain. Model results for hilly or mountainous areas, however, are considerably less reliable than those for flat terrain. Even for homogeneous atmospheric and surface conditions and flat terrain, an inadequate model description of surface properties such as vegetative species and soil moisture stress can lead to large differences between modeled and measured fluxes. Third-generation models of mesoscale meteorology and atmospheric chemistry have the potential to achieve several advances, but scaling up of local to regional flux information remains a subject of research. Also, the integrated modeling of gaseous emissions and deposition, which need to be tied together at a low level of model structure, has not yet been accomplished. Many of the processes affecting dry deposition of O<sub>3</sub> over individual types of surfaces are fairly well understood. The role of rapid in-air chemical reactions involving NO, NO<sub>2</sub>, and O<sub>3</sub> are difficult to quantify comprehensively, and the effects of water from rain or dew on uptake of gases can be highly variable. The influence of lipid solubility on the uptake of organic substances is not well understood. For large bodies of water, the dry deposition rate of most gases appears to be determined largely by water solubility. Parameterizations for the deposition of fine particles tend to be empirical or based on theories untested in natural settings outdoors. Direct measurements of fluxes are required for improved parameterizations for gases and particles and have been made successfully in many past experiments. Micrometeorological approaches have been used extensively, but they are sometimes limited by chemical instrumentation. Long-term flux measurements for diverse terrain and relatively large areas remain difficult. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Dry deposition is the process by which atmospheric trace chemicals are transferred by air motions to the surface of the Earth. Gravitational settling affects deposition of particles, especially those larger than a few micrometers in diameter. Emission of gases and particles from the surface can be the major factor in the dry air–surface exchange of some gases and particles. Deposition in precipitation is another major means of deliver-

ing substances from the atmosphere and cleansing the atmosphere, but such wet deposition processes are not considered here. Deposition by fog droplets is briefly considered.

This paper focuses on the effectiveness of methods to estimate dry deposition and on the associated uncertainties that can affect the reliability of atmospheric chemical budgets constructed with numerical models. The most detailed attention is given to oxidants and their precursors, but many other substances are considered. In general, the ability to parameterize the processes affecting dry deposition and emissions is hampered by the complexity and variability of the physical, biological, and chemical properties of the surfaces and by the diversity of

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the chemical and physical properties of the substances. In some cases, continuous measurements can be used to estimate the rates in scattered areas within regions of interest. The primary means, however, of constructing atmospheric budgets is the use of numerical models of meteorology and atmospheric chemistry that include dry deposition models or modules. Measurements at ground stations and from aircraft can provide a means of evaluating the modeled dry deposition rates. A brief review of methods of measurement is provided in Appendix A.

Estimates of the air–surface exchange rates of  $O_3$ ,  $NO$ ,  $NO_2$ ,  $HNO_3$ , peroxyacetyl nitrate (PAN),  $H_2O_2$ , other peroxides,  $NH_3$ , and  $NH_4^+$  are essential in modeling oxidant behavior in the lower atmosphere. At a secondary level of importance are formaldehyde, other aldehydes,  $N_2O_5$ ,  $SO_2$ , particulate sulfate, and particulate nitrate. Other substances, such as various organic compounds, CO, HONO, and the nitrate radical, can be important in some conditions.

The parameter commonly used to model or estimate deposition rate is the deposition velocity  $V_d$ , whose product with concentration at a specified height is the mass flux density. The deposition velocity itself is an engineering factor that must be parameterized in terms of more fundamental physical, chemical, and vegetative factors. As a rule of thumb, a deposition velocity of  $1 \text{ cm s}^{-1}$  is moderately large and is a typical value for  $O_3$  within a few meters of some vegetative surfaces. Inert substances have a mean value of zero for  $V_d$ ; highly reactive substances such as  $HNO_3$  have deposition velocities of  $2 \text{ cm s}^{-1}$  or larger. For substances whose emission rates from the surface are significant, the concept of a deposition velocity is not applicable.

Evaluation of the ambient concentrations of substances in the lower atmosphere and thus of the exposure of aboveground entities to chemicals requires construction of a budget in the atmosphere. Emissions, chemical transformations, horizontal and vertical transport, and deposition must all be considered. For example, about 30% of emissions of sulfur in the United States and Canada is removed there by dry deposition, as is about 40% of  $NO_x$ -N emissions (e.g., Shannon and Sisterson, 1992). If dry deposition were the only removal mechanism for a substance not affected significantly by chemical transformation and confined within a thoroughly mixed planetary boundary layer of height  $h$ , an exponential decay or “residence” time in the lower troposphere could be estimated as  $hV_d^{-1}$  (e.g., Slinn et al., 1978). For a typical value of 1 km for  $h$  and a moderately large  $V_d$  of  $1 \text{ cm s}^{-1}$ , a residence time of slightly more than one day would result. This rather short residence time suggests that surface removal of  $O_3$  is a major factor to consider in estimating  $O_3$  concentrations in the lower troposphere. In nature, photoproduction of  $O_3$  (e.g., Johansson and Janson, 1993) and vertical density stratification of the planetary boundary layer at night (e.g., Fast and

Berkowitz, 1996) prevent the occurrence of such a short residence time. Nevertheless, the assertion is valid that large uncertainties in deposition velocity can yield large uncertainties in modeled ambient concentrations in the planetary boundary layer. A series of sensitivity tests involving a multiday simulation with the Regional Oxidant Model for summertime conditions above the eastern half of the United States and southeastern Canada showed that daytime concentrations of  $O_3$  averaged over the modeling domain increased by up to 20% when the value of  $V_d$  was set to zero; more importantly, the number of locations where modeled maximum concentrations exceeded 120 ppb increased greatly (Olerud et al., 1995).

## 2. Overview

### 2.1. General approaches

Several recent articles have reviewed the state of the science in evaluating dry deposition, and most of the details will not be repeated here (Baldocchi, 1993; Erisman et al., 1994; Lovett, 1994; Erisman and Draaijers, 1995; Foken et al., 1995; Ruijgrok et al., 1995). Computation of the dry deposition rate of chemical species  $i$  requires that the concentration  $C_a^i$  of the substance of interest is known through model computations or measurement. In most modeling schemes, the mass flux density  $F_c^i$  is found as

$$F_c^i = -V_d^i C_a^i. \quad (1)$$

Estimates of deposition velocities  $V_d^i$  constitute the primary output of dry deposition models, both for large-scale models and site-specific methods of inferring dry deposition from local observations of concentrations, meteorological conditions, and surface conditions (e.g., Carmichael and Peters, 1984; Chang et al., 1987; Venkatram et al., 1988; Carmichael et al., 1991; Meyers et al., 1991; Harley et al., 1993; Benkovitz et al., 1994; Binkowski and Shankar, 1995; Ganzeveld and Lelieveld, 1995; Padro, 1996; Pratt et al., 1996; SAI, 1996).

For gases, the deposition velocity in existing dry deposition models is computed from a formula analogous to Ohm’s law in electrical circuits:

$$V_d^i = (R_a + R_b + R_c^i)^{-1}. \quad (2)$$

All three of the resistance terms on the right-hand side of Eq. (2) represent bulk properties of the lower atmosphere or surface and themselves must be described by parameterizations. Although this approach is practical, it can lead to oversimplification of the physical, chemical, and biological properties of the atmosphere or surface that affect deposition. The term  $R_a$  represents the aerodynamic resistance above the surface and has the same value for

all substances. The term  $R_b^i$  represents the quasi-laminar resistance to transport through the thin layer of air in contact with surface elements and varies with the diffusivity of the substance. Because fairly standard methods of computing  $R_a$  and  $R_b^i$  are widely used for flat, uniform surfaces, these terms will not be explained further here (e.g., Hicks and Liss, 1976; Wesely and Hicks, 1977). For surfaces with bluff roughness elements, values of  $R_b^i$  are considerably larger than for relatively permeable, uniform vegetative cover, and the appropriate formulations should be used (e.g., Tuovinen et al., 1998). Considerable variation from model to model is associated with the methods used to evaluate the term  $R_b^i$  for the resistance to uptake by the surface elements. Some of the possible pathways embedded in  $R_b^i$  for deposition to surface elements are represented as bulk resistances in Fig. 1. To describe particle dry deposition, the terms  $(R_b^i + R_c^i)^{-1}$  on the right-hand side of Eq. (2) must be replaced with

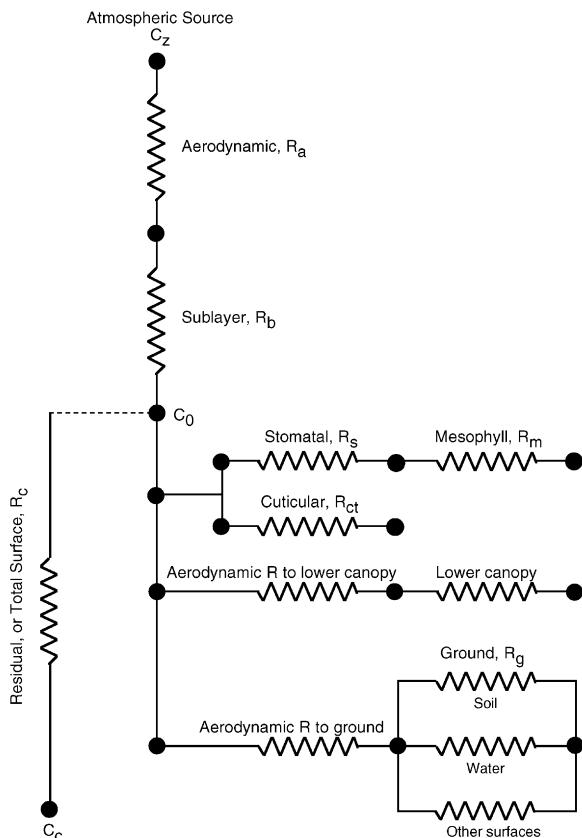


Fig. 1. Schematic representation of resistances for some of the pathways for dry deposition, where  $R$  represents resistances,  $C_z$  is the ambient concentration of the substance of interest,  $C_0$  is the concentration near the surface, and  $C_c$  represents a bulk substrate concentration, usually assumed to be zero in deposition velocity parameterizations.

a surface deposition velocity or conductance, and gravitational settling must be handled properly.

Dry deposition models or modules require several types of inputs from observations or from simulations of atmospheric chemistry, meteorology, and surface conditions. To compute fluxes, the concentrations of the substances must be known. Inputs required from meteorological models are values of friction velocity  $u_*$ , atmospheric stability via the Monin–Obukhov length scale  $L$ , aerodynamic surface roughness  $z_0$ , and aerodynamic displacement height  $d$ . Most dry deposition models also need solar radiation or, preferably, photosynthetically active radiation; ambient air temperature at a specified height; surface temperature; humidity at a specified height; and measures of surface wetness caused by rain and dewfall. All models require a description of surface conditions, but the level of detail depends on the model chosen. Descriptions could include broad land use categories, plant species, leaf area index, greenness as indicated by the normalized difference vegetation index, various measures of plant structure, amount of bare soil exposed, and soil pH.

## 2.2. Models

Many dry deposition models have been developed during the past 10 years, and efforts continue to improve their capabilities. The dry deposition module in the Acid Deposition and Oxidant Model (ADOM) was initially developed in the early 1980s (Pleim et al., 1984) and has undergone testing and revisions (e.g., Padro and Edwards, 1991; Padro, 1996). The Regional Acid Deposition Model (RADM) has a dry deposition module (Chang et al., 1987; Walcek et al., 1986), the latest completed version of which was described by Wesely (1989) and Walmsley and Wesely (1996). The ADOM and RADM dry deposition modules have appeared in several applications. For example, the RADM module has been adapted for the California Institute of Technology photochemistry airshed model (Harley et al., 1993), the Urban Airshed Model (SAI, 1996), studies involving the California Ozone Deposition Experiment (CODE) (Massman et al., 1994; Pederson et al., 1995), the global chemistry model (GChM) (Leucken et al., 1991; Benkovitz et al., 1994), and EURAD in western Europe (Hass et al., 1995). The ADOM module has, for example, been used in the “CALGRID” photochemical oxidant model (Yamartino et al., 1992).

Several models have been developed in Europe. For example, the Estimation of Deposition of Acidifying Components in Europe (EDACS) and the Dutch Empirical Acid Deposition Model (DEADM) have been used with long-range modules to map modeled deposition amounts for sulfur and nitrogen compounds (e.g., Erisman and Draaijers, 1995). Concern over the accuracy of estimates of particulate deposition have led to several

experimental efforts (see Erisman et al., 1997, and companion articles in the same journal issue). In addition, dry deposition routines for general circulation models coupled with chemistry modules have been carried out for the European Centre Hamburg Model (ECHAM) (Ganzeveld and Lelieveld, 1995).

Continuous estimates of dry deposition velocity at specific sites of the US Environmental Protection Agency's (EPA's) Clean Air Status and Trends Network (CASTNet, originally known as the National Dry Deposition Network) have focused on an inferential approach that requires local measurements of ambient concentrations, observations of surface conditions, and standard surface meteorological observations (Clarke et al., 1997). This inferential approach initially relied on the "big-leaf" method, which estimated the three major resistances in Eq. (2) with limited consideration of additional components or plant canopy layers (Hicks et al., 1987; Meyers et al., 1991). Inferential approaches coupled with modeling that extends site-specific estimates to wider areas have been applied in the Canadian Air and Precipitation Monitoring Network (Sirois and Barrie, 1988) and the European Monitoring and Evaluation Programme (Erisman and Draaijers, 1995). A relatively sophisticated, multilayer model (MLM) has been developed and applied (e.g., Pratt et al., 1996) for CASTNet. Refinements of the MLM have continued, in part on the basis of comparisons of model estimates to direct flux measurements at individual sites (Meyers et al., 1998). Another approach to continuous deposition estimates is being developed by J.R. Brook at the Atmospheric Environment Service of Canada and colleagues, who use an operational mesoscale meteorological model to provide inputs to a multilayer model to compute seasonal dry deposition estimates (J. Padro, private communication).

Advection over a patchwork of surfaces with differing uptake characteristics is one of several problems associated with scaling up from small scales to landscapes. In areas that contain sharp contrasts in surface characteristics, edge effects, and hilly terrain, the assumptions inherent in the micrometeorological formulations that are commonly used extensively in large-scale and site-specific models are questionable. These subjects have been addressed by a large number of publications, a small sample of which are the works by Byun (1990), Claussen and Klaassen (1992), Mahrt and Ek (1993), Moore et al. (1993), Mahrt et al. (1995), and Parlange and Katul (1995). In mountainous terrain or where patchy forest conditions exist, the approach of measuring the amounts and chemical composition of throughfall and stemflow in forests at specific sites is considered more reliable for some substances, especially sulfur, than are conventional micrometeorological methods (e.g., Draaijers et al., 1994; Lovett, 1994; Veltkamp and Wyers, 1997).

### 3. Analysis

#### 3.1. Model performance

Eqs. (1) and (2) have several shortcomings. A common criticism is that use of a transfer velocity instead of a deposition velocity would be much sounder micro-meteorologically;  $C_a^i$  would be replaced by  $(C_a^i - C_0^i)$  to utilize the concentration  $C_0^i$  of the substance somewhere within the surface. Although the approach of using a deposition velocity is practical for modeling because the subsurface concentration is rarely known, it greatly increases the difficulty of adequately parameterizing  $R_c^i$ . For estimating substances that are emitted from the surface or whose deposition is affected significantly by variations of concentrations inside surface elements, the deposition velocity concept is of little value.

The separation of quasi-laminar resistances and surface resistances to gas uptake into two separate terms,  $R_b^i$  and  $R_c^i$ , is an oversimplification in many cases, especially for tall plant canopies. That is, to account properly for sources and sinks of many substances in tall canopies, a multilayer model that distributes these two resistances vertically in the canopy according to the vertical distribution of leaves and other plant components is desired and sometimes necessary. Development of multilayer models for air-surface exchange of water vapor and  $\text{CO}_2$  has continued for many years, but adaptation of such models for pollutant dry deposition is relatively rare. Meyers and Baldocchi (1988) described the successful application of two multilayer models to estimate  $\text{O}_3$  and  $\text{SO}_2$  deposition to a forest. Zhang et al. (1996) found that the multilayer model of Baldocchi (1988) could be adapted to several types of plant canopies. A general finding is that selection of input parameters such as stomatal, cuticle, and soil resistances are as crucial to good results for multilayer models as they are for simpler models. Another important reason to consider multilayer models for tall vegetation is adequate simulation of fast in-air chemical reactions in the canopy (Gao et al., 1993).

The spatial variability of the air-surface exchange of trace chemicals over a landscape with various types of surface vegetation, soil characteristics, water surfaces, and man-made structures can be quite large (e.g., Guo et al., 1995). Methods of scaling up or integrating estimates of surface removal rates from small, relatively uniform areas to large areas present several challenges and remain a subject of research (e.g., Foken et al., 1995). To reduce uncertainties to acceptable levels, say to less than  $\pm 50\%$ , for specific regions with diverse surface or terrain conditions, a very careful application of dry deposition models, some model development, and support by experimental observations appear to be necessary. Several difficult problems exist in developing accurate methods of summing deposition amounts computed for differing types of surfaces in a landscape: the effects of (i)

variations in surface uptake properties within each type of surface or land use category, (ii) advection of chemicals above one type of surface to another with a different uptake rate, (iii) horizontal transport to receptors on sloping terrain, and (iv) advection along the edges of fields with variations in vegetation height. Widely accepted methods of addressing these problems for pollutant deposition have not been established, and definitive, comprehensive assessments of the uncertainties associated various approaches do not exist.

The CODE was one of the few (if not the only) large efforts in recent years that investigated  $O_3$  removal over a set of diverse landscapes (Pederson et al., 1995). Studies on tropospheric chemistry such as the North Atlantic Regional Experiment (Fehsenfeld et al., 1996) have often included components that require estimates of the air–surface exchange of ozone and other chemicals. Major studies addressing air–surface exchange of energy, water vapor, and carbon dioxide over large areas have produced parameterizations that can be used in evaluating the air–surface exchange of the chemicals of interest in tropospheric chemistry. These studies include the Hydrologic Atmospheric Pilot Experiment and Modélisation du Bilan Hydrique (Pinty et al., 1989), the First International Satellite Land Surface Climatology Project Field Experiment (Sellers et al., 1992), the Boreal Ecosystem-Atmosphere Study (Sellers et al., 1995), and numerous related programs of the Biospheric Aspects of the Hydrological Cycle (see the World Wide Web at <http://www.pik-potsdam.de/~bahc/>) of the International Geosphere Biosphere Programme. Modeling efforts have been well organized and have advanced the state of the science to third-generation models (e.g., Henderson-Sellers et al., 1995; Sellers et al., 1997). The results of such research should be exploited toward the goal of developing general approaches that simulate all of the processes having a significant effect on chemical dry deposition and emission rates and are sufficiently efficient for incorporation into atmospheric chemistry models.

The sets of widely used micrometeorological formulations employed to evaluate  $R_a$  should be considered inaccurate for nonuniform terrain where a significant horizontal component exists in flow to receptor surfaces. For substances whose uptake is regulated much more strongly by surface resistance than by aerodynamic resistance, relatively simple approximations for the value of  $R_a$  suffice (e.g., Hicks and Meyers, 1988). For substances such as  $HNO_3$  that have very small values of surface resistance, however, the  $R_a$ -induced uncertainties in deposition velocity are large (e.g., Brook et al., 1997). Significant progress on this problem has not been made in recent years. Throughfall techniques can be used to infer dry deposition amounts in tall canopies in such circumstances, although extrapolation to large areas surrounding local measurement sites is difficult, and the approach

does not work for substances such as  $O_3$  that do not accumulate conservatively on surfaces (e.g., Lovett, 1994). In addition, the role of horizontal flow or advection near edges of vegetation stands of varying heights might cause significant inaccuracies in estimates of  $R_a$  if such edge effects are ignored (e.g., Draaijers et al., 1994). Detailed modeling of such interactions between fields of varying types might be needed (e.g., Baldocchi and Rao, 1995). A comprehensive evaluation of the net impact of ignoring edge effects over a landscape with a mixture of vegetation heights is needed; estimation of deposition rates downwind of a change from tall to short vegetation should be included.

Even for flat terrain with uniform surface conditions, estimates of eddy diffusivity and thus  $R_a$  cannot be made easily with conventional micrometeorological approaches in very stable near-surface atmospheric conditions that can occur at night (e.g., Mahrt et al., 1998). Direct simulation of these conditions is not achieved with the types of numerical models typically used with dry deposition modules (e.g., Mahrt, 1998). If this situation can be identified, the deposition velocity can be set to nearly zero by setting  $R_a$  to a large value. The effects of hilly terrain, gravity waves, and mesoscale motions, however, can make identification of this case unreliable because of the limited vertical and horizontal resolution of the numerical models.

A fairly common approach to estimating model uncertainties is comparison of deposition velocities produced by various models for relatively small areas where deposition measurements have been made (e.g., ENSR, 1993; Massman et al., 1994; Chinkin et al., 1994; Brook et al., 1996; Padro, 1996; Zhang et al., 1996). The studies show that uncertainties at least as large as  $\pm 30\%$  in deposition velocity are common. The validity of such model comparisons is limited when the models were developed on the basis of experiments conducted in areas where characteristics such as the soil moisture content or the height, maturity, or structure of the vegetation were significantly different than at the site addressed in the comparison. In such circumstances, caution should be used in arriving at judgements on model performance and in adjusting model parameterizations. An important result of these comparisons, nevertheless, is that the current level of sophistication of most dry deposition models is relatively low and relies heavily on empirical data.

### 3.2. Modeling progress

Models such as ADOM, RADM, EDACS, DEADM, GChM, and ECHAM are mostly “second-generation” models that make extensive use of the resistance analogy (2) in one form or another for deposition calculations. “Third-generation” models are expected to have improved capabilities that can reduce the dependency on empirically derived resistance values and provide a

means of coupling deposition and emission more closely (Peters et al., 1995). Third-generation models are likely to incorporate better simulations of the structure of the planetary boundary layer (Pleim and Chang, 1992; Pleim and Xiu, 1995) and to provide estimates of soil moisture content and evapotranspiration, which can be a valuable input to dry deposition modules (Pleim et al., 1997). Techniques of incorporating data on surface spectral reflectances sensed remotely by satellites are being developed to provide a better description of surface conditions (Gao, 1995; Gao and Wesely, 1995). Another important facet is the effects of rapid in-air reactions, which can invalidate the resistance analogy because of a rapid change of flux with height. An example is the conversion of NO emitted from soils to NO<sub>2</sub> within a few meters of the surface (e.g., Gao and Wesely, 1994; Vilà-Guerau de Arellano and Duynkerke, 1995; Galmarini et al., 1997). Although fairly sophisticated numerical models that couple chemistry with turbulence have been used to evaluate the effects of such rapid in-air reactions, simplified approaches are more suitable for large-scale models (Padro et al., 1998).

The methods by which estimates of dry deposition rates are made for categories of surface conditions or individual sites have an influence on the techniques used to obtain areal averages of deposition. One of the simplest and most commonly used methods is computation of deposition velocities according to land use type, to which values are assigned for variables such as  $z_0$ ,  $d$ , and resistances that make up  $R_c^i$ . The resistance values are usually modified extensively with use of data on local meteorological conditions from models or observations. Then the deposition velocities are areally weighted to obtain average  $V_d^i$  for the grid square of the larger model or for the area chosen. This approach is a considerable improvement over using constant deposition velocities for long periods of time and large areas (e.g., Ganzeveld and Lelieveld, 1995; Ganzeveld et al., 1998). For third-generation models, the possible availability of data on plant physiological and soil moisture parameters suggests that alternative approaches might be used for vegetated surfaces, e.g., spatial averaging of the parameters contributing to the resistances prior to computation of the deposition velocity (e.g., Foken et al., 1995). In addition, the advection of mass from one type of surface to another might be computed more rigorously with third-generation models, which would result in more realistic simulations of air-surface exchange and its role in atmospheric budgets. Although momentum fluxes are distributed according to surface type in many second-generation models, advection of quantities other than momentum is largely ignored in their boundary layer models.

The great variability in rates of uptake by various parts of plants and the soil surface presents challenges in development of dry deposition models for vegetated surfaces. For substances such as O<sub>3</sub> and SO<sub>2</sub> for which the

value of  $R_c^i$  is strongly affected by leaf stomatal resistances, however, the accuracy of deposition velocity estimates is usually limited by inadequate simulation of plant physiological processes. Factors such as plant species, leaf area, canopy structure, and response to solar radiation, water stress, and other environmental variables need to be considered more thoroughly. The work cited previously (Pinty et al., 1989; Sellers et al., 1992, 1995, 1997; Henderson-Sellers, 1995) that evaluates the role of plant physiological processes in controlling air-surface exchange has not yet been significantly incorporated into dry deposition modules used in atmospheric chemistry simulations. As reviewed by Niyogi and Raman (1997), for example, parameterizations that incorporate the effects of photosynthesis and CO<sub>2</sub> on vegetative stomatal resistance appear to provide more accurate description than the Jarvis-style approach that has been used widely in mesoscale meteorological and dry deposition models.

### 3.3. Parameterizations

#### 3.3.1. Ozone and sulfur dioxide

A large number of experiments have been conducted on O<sub>3</sub> dry deposition, and parameterizations have been developed and tested extensively. Experiments in recent years suggest that approaches to parameterizing deposition to many surfaces are fairly sound, e.g., to dry forests canopies and green grasslands in the summertime (Meyers and Baldocchi, 1988; Matt and Womack, 1989; Padro et al., 1991; Rondón et al., 1993; Stocker et al., 1993). With an adequate modeling of removal by leaves, the bulk or integrated removal by such canopies can usually be computed with some confidence.

The contrasting chemical properties of O<sub>3</sub> and SO<sub>2</sub> provide a means of estimating the surface resistances of other substances by scaling according to measures of solubility and oxidizing capacity (e.g., Wesely, 1989). Early studies provided considerable information on the parameterization of O<sub>3</sub> removal by freshwater, seawater, snow, bare soil, grass, soybeans, maize, and some types of forests in the eastern United States (e.g., Wesely, 1983). Many other types of surfaces have been studied subsequently. For the broad category of agricultural crops, parameterizations derived by Wesely (1989) mostly for soybeans and maize work fairly well for cotton but are inadequate for vineyards; the senescent grass found in the San Joaquin Valley of California appears to behave more like barren land than rangeland in Wesely's parameterizations (Massman et al., 1994; Padro, 1996). Over deciduous forest in the winter, uptake of both O<sub>3</sub> and SO<sub>2</sub> was considerably underestimated, possibly because of the effects of surface wetness (Padro et al., 1992, 1993). Such results show that generalization of surface conditions into broad categories can lead to large discrepancies in modeled versus measured fluxes at specific sites.

In a scheme that uses surface resistances of O<sub>3</sub> and SO<sub>2</sub> as reference points to estimate resistances for other substances, the information on O<sub>3</sub> and SO<sub>2</sub> resistances must be as accurate as possible. Aside from the work cited in the previous paragraph, however, field observations of SO<sub>2</sub> deposition velocities have been limited in recent years. One exception is the work by Meyers et al. (1998), who conducted a series of field experiments in the 1990s for the EPA with modern equipment and found values of V<sub>d</sub> for SO<sub>2</sub> that were slightly larger than estimated in current models for fields of maize, soybeans, and mixed grasses. The deposition velocities for SO<sub>2</sub> were usually larger than those for O<sub>3</sub>, which is the reverse of the situation often modeled (e.g., Wesely, 1989). The primary improvement needed in the parameterization for SO<sub>2</sub> appears to be a decrease in soil resistance for moist, nonacidic soils, which is largely accomplished in the model described by Meyers et al. (1998).

Estimates of ozone V<sub>d</sub> and R<sub>c</sub> derived from an existing dry deposition module (Wesely, 1989) are shown in Table 1. Some measurements taken by Argonne National Laboratory above flat terrain in eastern North Carolina in 1995 (Fig. 2) and 1996 (Fig. 3) illustrate the point that the deposition velocities for soybeans and a field of short maize differ considerably, and neither set of velocities matches well with the values in Table 1 for agricultural

land in summer. Another example is that cotton fields remove O<sub>3</sub> almost as rapidly as do soybeans, but grape vineyards have maximum deposition velocities similar to those for maize (e.g., Massman et al., 1994; Grantz et al., 1997). When a single, broad categorization of agricultural land is used, differences in the plant physiology are ignored, and the role of uptake at the soil surface is inferred with inadequate consideration of the

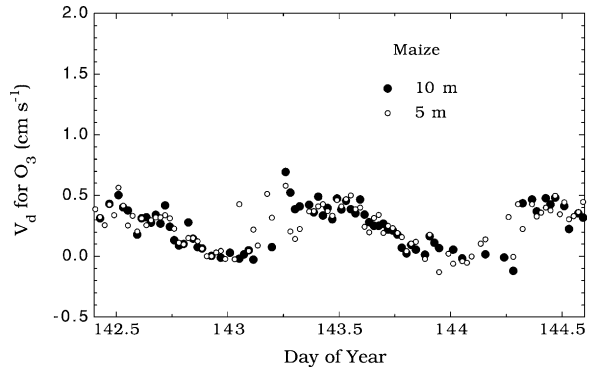


Fig. 2. Ozone deposition velocities measured by eddy correlation at two heights above a field of immature maize less than 1 m tall. A considerable amount of the soil surface was exposed between the rows of plants.

Table 1

Typical ozone deposition velocities V<sub>d</sub> (cm s<sup>-1</sup>) at a height of 10 m and bulk surface resistances R<sub>c</sub> (s cm<sup>-1</sup>) for selected conditions. Cases 1–5 correspond to solar irradiances of 800, 500, 300, 100, and 0 W m<sup>-2</sup>, respectively. Dry surfaces and moderate wind speeds are assumed

Case	Agricultural land					Rangeland					Deciduous forest				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
<i>Midsummer with lush vegetation</i>															
V <sub>d</sub>	1.0	0.9	0.7	0.4	0.2	0.7	0.6	0.5	0.3	0.2	0.8	0.7	0.6	0.3	0.1
R <sub>c</sub>	0.8	0.8	0.9	1.7	2.9	1.1	1.1	1.3	1.9	2.5	1.0	1.1	1.3	3.2	9.6
<i>Autumn with unharvested cropland</i>															
V <sub>d</sub>	0.4	0.4	0.4	0.3	0.2	0.4	0.4	0.4	0.3	0.2	0.2	0.2	0.2	0.1	0.1
R <sub>c</sub>	2.0	2.0	2.2	2.4	2.8	2.0	2.0	2.2	2.4	2.8	4.3	4.7	5.2	7.1	13
<i>Late autumn after frost, no snow</i>															
V <sub>d</sub>	0.5	0.5	0.4	0.3	0.2	0.4	0.4	0.4	0.3	0.2	0.2	0.2	0.2	0.2	0.1
R <sub>c</sub>	1.4	1.4	1.5	1.5	1.6	2.0	2.1	2.2	2.4	2.8	3.9	4.2	4.6	6.1	9.6
<i>Winter, snow on ground and near freezing</i>															
V <sub>d</sub>	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.0	0.2	0.2	0.1	0.1	0.0
R <sub>c</sub>	9.2	9.6	10	13	27	9.2	9.6	11	13	27	5.6	6.2	7.1	11	32
<i>Transitional spring with partially green short annuals</i>															
V <sub>d</sub>	0.7	0.6	0.5	0.4	0.2	0.5	0.5	0.4	0.3	0.2	0.5	0.4	0.4	0.2	0.1
R <sub>c</sub>	1.0	1.1	1.2	1.5	1.9	1.4	1.5	1.6	2.0	2.5	1.8	2.0	2.3	4.3	9.4

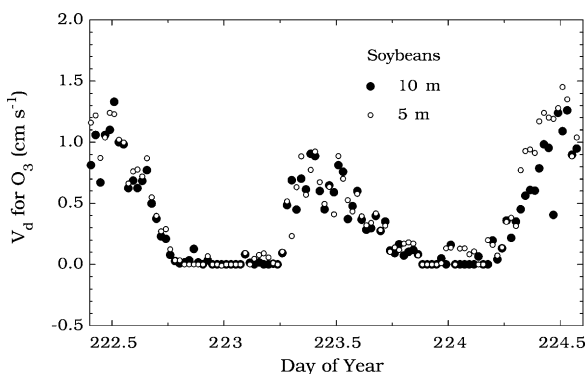


Fig. 3. Ozone deposition velocities above a soybean field with a closed canopy.

height of the canopy and the amount of soil surface not covered by the canopy.

The effect of vegetative surface wetness on removal of  $O_3$  ranges from mild inhibition to a significant enhancement; for  $SO_2$ , surface wetness usually increases uptake substantially (Enders et al., 1992; Baldocchi, 1993; Erisman, 1994; Padro, 1994; Grantz et al., 1995; Van Hove and Adema, 1996). Variations are expected as a result of the source of the wetness (i.e., rain, dew, or surface hygroscopicity) and the contributions from the substrate to the chemical composition of the water. The diversity of the situations that arise prevents much generalization; site-specific measurements of deposition might be necessary to reduce uncertainties of deposition velocities for wetted surfaces to acceptable levels.

Portions of vegetative canopies other than green leaves can be fairly efficient in removal of  $O_3$ , especially when senescent leaves exist and, for deciduous forests, even when leaves are absent (Wesely et al., 1978, 1983; Hicks et al., 1989; Padro et al., 1992). Daytime deposition velocities can be near  $0.5 \text{ cm s}^{-1}$  for well mixed conditions; nighttime values are usually dependent on the extent of mixing, e.g., as indicated by values of  $u_{*c}$ . For  $SO_2$ , a study by Padro et al. (1993) indicated that deposition velocities were substantial over a deciduous forest in winter. Overall, experiments that have evaluated deposition velocities of  $O_3$  and  $SO_2$  over fall, winter, and spring landscapes have been rare compared to experiments during summer.

Studies of the removal of  $O_3$  by snow show that deposition velocities to fresh snow are typically about  $0.1 \text{ cm s}^{-1}$  but decrease fairly rapidly as the snow ages (e.g., Padro et al., 1992; Stocker et al., 1995). Ideally, deposition velocity models would incorporate such a change of deposition velocity with time. Deep snowpack appears to store ozone and slowly release it in some circumstances (Zeller and Hehn, 1996).

Ozone removal rates by soil surfaces are highly variable (e.g., Massman, 1993; Meyers and Baldocchi, 1993;

Güsten et al., 1996; Sánchez et al., 1997). Removal rates tend to be largest for soils whose exposed surface has high levels of organic matter and a low to moderate moisture content. Soil surface deposition velocities can be as large as  $1 \text{ cm s}^{-1}$ . Very wet soils and soils with very little organic matter have surface deposition values on the order of  $0.1 \text{ cm s}^{-1}$ . For  $SO_2$ , uptake by soils increases with soil pH and moisture content; in optimal conditions, surface deposition velocities can be significantly larger than  $1 \text{ cm s}^{-1}$  (e.g., Baldocchi, 1993). In general, estimates of the resistance of soil surfaces to uptake should be modified according to surface organic matter content, soil moisture content, and, for  $SO_2$ , pH; soil resistances for broad land use categories in dry deposition models should be used with caution for soil conditions that are considerably different than those assumed in the model.

The resistance to removal of  $O_3$  by vegetation such as mosses, lichen, sedges, and shrubs typical of tundra and subarctic environments tends to be fairly large,  $2.5\text{--}5 \text{ s cm}^{-1}$ , and to have a weak diurnal variation (Jacob et al., 1992; Tuovinen et al., 1998). The average deposition velocity for such areas when not covered with snow appears to be about  $0.15 \text{ cm s}^{-1}$ .

Strong reductions in  $O_3$  concentrations frequently occur near the surface at night as a result of surface removal and chemical reactions, especially when the mixing from aloft is limited by strong vertical density gradients (e.g., Colbeck, 1989; Johansson and Janson, 1993). As is illustrated in Fig. 3, deposition velocities near zero are easily found in flat terrain at night, when  $R_a$  becomes very large. In high-elevation or mountainous areas, such reductions are rare because of enhanced exposure to  $O_3$  in the troposphere (Taylor et al., 1992). It is not clear that mesoscale or large-scale meteorological models describe mixing in the lower 50 m or so of the atmosphere with detail sufficient to achieve an accurate depiction of such nighttime  $O_3$  conditions.

Work in the 1980s showed that  $O_3$  deposition velocities over ocean are typically measured to be  $0.01$  to  $0.05 \text{ cm s}^{-1}$ , larger than expected on the basis of water solubility alone. Deposition velocities over freshwater lakes have been found to be about  $0.01 \text{ cm s}^{-1}$  or smaller. Surface films might increase the deposition of oxidants and of some organic substances.

Rapid in-air chemical reactions can cause a substantial change of  $O_3$  flux with height in the planetary boundary layer, mainly as a result of photochemical production and destruction by reaction with NO (e.g., Godowitch, 1990, and references cited therein). Although the strength of flux change with height is usually less than for NO and  $NO_2$ , the apparently rapid removal by some surfaces, as detected by eddy correlation measurements of  $O_3$  fluxes from towers and aircraft, might have been caused in part by the rapid in-air chemical reactions (e.g., Gao et al., 1996). For  $O_3$ , models should simulate deposition



velocities of  $O_3$  at heights no greater than about 10 m if the rapid in-air chemical reactions are not taken into account. Changes of  $O_3$  deposition velocities with height below 10 m can sometimes occur, however, as is noticeable in the right-hand portion of Fig. 3 where the velocities for 5 m are greater than for 10 m.

### 3.3.2. Nitric oxide

Because of its low solubility and low oxidizing capacity, NO dry deposition is usually negligible. Atmospheric chemical reactions provide the primary means of destruction of NO in the lower atmosphere. Studies of the dry air–surface exchange of NO have focused on emissions rather than deposition (e.g., Davidson et al., 1991; Slemr and Seiler, 1991; Williams et al., 1992; Valente and Thornton, 1993; Aneja, 1994; Potter et al., 1996; Aneja et al., 1997; Thornton et al., 1997). Although some schemes exist that are suitable for estimating NO emissions from soils with large-scale models, the great variability in soil properties that affect NO emissions is difficult to simulate adequately. Fertilization of agricultural fields can at least temporarily greatly increase local NO emissions. Because of the strong effects on near-surface  $NO_2$  and  $O_3$  concentrations of NO emitted from soils, reasonably good evaluation of these emissions is vital in atmospheric chemistry models. The emission models need to be tied closely to dry deposition models, so that local concentrations and thus deposition of  $NO_2$  and  $O_3$  can be estimated with some confidence.

### 3.3.3. Nitrogen dioxide

The assumption often used in modeling dry deposition of  $NO_2$  is that its limited solubility and fairly large oxidative ability result in deposition velocities similar to those for  $O_3$ . However, this assumption is rarely confirmed with observations, in part because soil emissions of NO that react rapidly with  $O_3$  to produce  $NO_2$  can greatly diminish the magnitude of the downward  $NO_2$  flux and sometimes cause it to be directed upward; furthermore, plants and soils can emit  $NO_2$  if the ambient concentrations are small (Bakwin et al., 1992; Coe and Gallagher, 1992; Rondón et al., 1993; Stocker et al., 1993, 1995; Gao et al., 1996). Deposition velocities similar to that of  $O_3$  are seen only in cases where ambient concentrations of  $NO_2$  are fairly large, soil emissions of NO are minimal, and vegetation provides a canopy of leaves with open stomata (Wesely et al., 1982; Gravenhorst and Böttger, 1983).

Modeling  $NO_x$  (NO and  $NO_2$ ) dry deposition instead of NO and  $NO_2$  separately is not practical because of the distinctly different mechanisms that control the air–surface exchange of the two substances. Thus, the processes of emission of NO from soils, rapid in-air reactions,  $NO_2$  deposition, and, in some cases,  $NO_2$  emission need to be evaluated (e.g., Delany et al., 1986). Such a task represents a significant challenge to modelers, especially if the

processes are to be described adequately in regional- and large-scale models. For the rapid in-air chemical reactions, an approach proposed by Padro et al. (1998) might suffice. Further experimentation and modeling is needed (e.g., Gao and Wesely, 1994; Vilà-Guerau de Arellano and Duynkerke, 1995; Aneja et al., 1997; Galmarini et al., 1997).

### 3.3.4. Ammonia

Recent studies have confirmed many earlier findings about  $NH_3$ . (See Sutton et al. (1998a) and the companion articles in the same issue of *Atmospheric Environment*.) Ammonia is taken up very rapidly by moist surfaces that do not have a high pH and quickly through leaf stomata when ambient concentrations are large (e.g., Duyzer et al., 1992; Schjoerring, 1995; Van Hove and Adema, 1996; Yamulki and Harrison, 1996). Parameterization of the  $NH_3$  deposition velocities in such conditions should be fairly straightforward. If ambient concentrations are small, however, uptake through leaf stomata can be limited, and emission of  $NH_3$  can occur from leaves (e.g., Dabney, 1990; Langford and Fehsenfeld, 1992). Exchange of  $NH_3$  often appears to behave as if a “compensation point” exists (i.e., an effective nonzero subsurface concentration exists), typically in the range of 0.5 to 5.0 ppb. A similar situation exists for  $NO_2$ . The closeness of such compensation points to ambient concentrations and the variability of the compensation point values among various types of vegetation and differing soil conditions make it difficult to construct surface resistance-emission schemes having wide applicability. A high level of generality with more dynamic modeling approaches, such as by treating cuticular uptake as a capacitance, is also difficult to achieve (Sutton et al., 1998b). For a particular region, experimental studies might be necessary to achieve confidence in parameterizations of air–surface exchange of  $NH_3$  and  $NO_2$ . In areas with fertilized rice fields, emissions can be a significant source of  $NH_3$  (e.g., Trevitt et al., 1988).

Where the high concentrations of ambient  $NH_3$  exist, such as downwind of domestic livestock production and sewage treatment areas, the flux is expected to be directed downward. However, codeposition of acidifying substances such as  $SO_2$  can result in a decrease of the downward  $NH_3$  flux. More importantly, the surface uptake of  $SO_2$  can be increased considerably when ambient concentrations of  $NH_3$  deposition are large. For example, Erisman and Wyers (1993) found that the value of  $R_c$  for  $SO_2$  can decrease to zero in such situations, if the humidity exceeds about 60% or the surface is wet. Cape et al. (1998) found that fumigation of a section of Scots pine (*Pinus sylvestris* L.) forest with  $NH_3$  notably increased sulfur deposition.

### 3.3.5. Nitric acid vapor

Since the observations by Huebert and Robert (1985) were reported, the assumption that the surface resistance

of natural surfaces to uptake of  $\text{HNO}_3$  is effectively zero has been used without significant challenge. Numerical models and observations have suggested that nitrate aerosol can be formed rapidly in the presence of high ammonia concentrations near the surface, with the result that the amount of  $\text{HNO}_3$  vapor removal near the surface is enhanced, which could be a concern near local  $\text{NH}_3$  sources such as livestock feedlots (Brost et al., 1988; Huebert et al., 1988). Overall, the primary concern in modeling  $\text{HNO}_3$  is adequate representation of  $R_a$ , especially for complex terrain, as has already been discussed.

### 3.3.6. Other gases

Parameterizations of surface resistances for peroxyacetyl nitrate (PAN), HONO,  $\text{H}_2\text{O}_2$ , other peroxides, various organic compounds, formaldehyde,  $\text{N}_2\text{O}_5$ , CO, and the nitrate radical are often based on theoretical considerations such as the previously mentioned scaling with  $\text{O}_3$  and  $\text{SO}_2$  resistances by use of measures of solubility and oxidation capacity. Very few experimental observations of deposition velocities and inferred surface resistances have been published in the open literature. For PAN, studies by Dollard et al. (1990) with ventilated chambers found surface resistances of approximately  $10 \text{ s cm}^{-1}$  above grass in acidic soils,  $7 \text{ s cm}^{-1}$  for grass in alkaline soils, and  $4\text{--}15 \text{ s cm}^{-1}$  for bare soil, with the wet, calcareous soils giving the smallest resistance. The dry deposition velocity for HONO appears to be only slightly smaller than the value of  $V_d$  for  $\text{HNO}_3$ , but surface production of HONO occurs when concentrations of ambient  $\text{NO}_2$  are more than a few parts per billion (Harrison et al., 1996). Hall et al. (1997) found that the value of  $R_c$  for  $\text{H}_2\text{O}_2$  was near zero in forest canopies at all times of the day, which suggests that  $\text{H}_2\text{O}_2$  behaves similarly to  $\text{HNO}_3$  because of the high solubility and reactivity of  $\text{H}_2\text{O}_2$  with surface elements. Hall et al. (1999) found that organic peroxides (ROOH) had an average  $R_c$  of  $0.1\text{--}15 \text{ s cm}^{-1}$  above coniferous forest and  $0.2\text{--}0.4 \text{ s cm}^{-1}$  above deciduous forest; the quality of data was not sufficient to evaluate the relative role of various ROOH deposition pathways in the canopies. For light organic acids, Hartmann et al. (1991) found deposition velocities of  $0.64\text{--}1.0 \text{ cm s}^{-1}$  for formic acid and  $0.5\text{--}1.0 \text{ cm s}^{-1}$  for acetic acid at a Venezuelan savanna site; Sanhezu et al. (1992) found deposition velocities of about  $1.1 \text{ cm s}^{-1}$  for formic acid and  $0.7 \text{ cm s}^{-1}$  for acetic acid, respectively, in a tropical cloud forest. The moderately large deposition velocities for these organic acids are expected because of their strong solubilities in water. For organic substances that are weakly soluble in water and are not reactive with most natural surfaces, the lipid solubility or octanol–water partition coefficient provides a theoretical means of evaluating the uptake by plant leaves and other surface components; however, the capacity for continued uptake is limited, and the possibil-

ity of revolatilization is significant (e.g., Riederer, 1990; Deinum et al., 1995).

### 3.3.7. Particles

For deposition of particles in the submicron, accumulation size mode to aerodynamically rough surfaces, a formulation derived from micrometeorological observations and dependent only on local micrometeorological conditions might suffice, e.g., for sulfate involved in long-range transport (Wesely et al., 1985; Hicks et al., 1989; Gallagher et al., 1997). The deposition velocities tend to decrease at night but increase substantially during the daytime with dynamically unstable conditions near the surface. Less empirical approaches are needed to consider the fine structures of the surface that enhance collection of particles, particle growth in areas of high relative humidity close to surface elements, aerodynamically smooth surfaces, and a wide range of particle sizes (e.g., Slinn and Slinn, 1980; Ibrahim et al., 1983; Williams, 1982; Davidson et al., 1982; Slinn, 1982; Peters and Eiden, 1992; Binkowski and Shankar, 1995; Ruijgrok et al., 1997). Very little flux measurement of fine particles has been made over natural water bodies. The case of strong winds (i.e., those greater than about  $10 \text{ m s}^{-1}$  at a height of 10 m above water) is not well understood for both particle and gas fluxes.

Experimental evaluation of particle dry deposition models in a natural outdoor setting is difficult and is rarely done with thoroughness like that described by Erisman et al. (1997), Ruijgrok et al. (1997), and companion articles in the same journal issue. These studies suggest that impaction of particles to Douglas fir in The Netherlands was larger than expected from previous micrometeorological experiments (Wesely et al., 1985; Hicks et al., 1989) and that large particles contributed substantially to deposition amounts for several chemicals. The variability in the measured deposition velocities for sulfate and nitrate, however, was large, and the role of stable atmospheric conditions in affecting the results is not entirely clear.

### 3.3.8. Fog and cloud deposition

Deposition via fog or cloud droplets in mountainous areas can be substantial, although it is not considered a major factor in low-lying areas (Unsworth and Fowler, 1988; Lovett and Kinsman, 1990; Lovett and Lindberg, 1993). Measurements have shown that (i) the process of droplet deposition is dominated by impaction and by gravitational settling that can be modeled reasonably well in some cases and (ii) drizzle can contribute substantial deposition amounts (Vermeulen et al., 1997). An experimental study by Vong and Kowalski (1995) suggested that evaporation can cause significant flux divergence of particles above the surface in variable cloud conditions at high elevations, although the soundness of this finding could have been

compromised by the effects of terrain-induced divergence of mean flow.

#### 4. Conclusions

Models developed in the United States, Canada, and Europe for deposition over regional and large scales have been improving gradually. These models rely in one way or another on multiple-path resistance schemes. The resistance schemes use highly stylized depictions of surface conditions; methods of estimating the resistances typically have empirical aspects based on field and laboratory investigations and sometimes are investigated with relatively sophisticated models.

Resistance schemes used in modeling appear to function quite well in daytime conditions over flat terrain. However, model results for hilly or mountainous areas and for very stable atmospheric conditions at night are considerably less reliable because the parameterizations of aerodynamic resistances in such complex situations are not well developed. Most of the current knowledge of the factors that make up the individual resistances is based on laboratory studies or on field experiments made in simple circumstances.

Even for homogeneous atmospheric and surface conditions and flat terrain, an inadequate model description of surface properties such as vegetative species and soil moisture stress often leads to large differences between modeled and measured fluxes. Although use of data from satellites can substantially improve description of surface properties for regional- and large-scale models, results from flux measurements at individual sites can diverge from modeled results by large amounts. A useful comparison of regional- and large-scale model results to observational data would require that the latter represent averages over tens of kilometers or more. Scaling up of local to regional flux information remains a subject of research.

Many of the processes affecting dry deposition of  $O_3$  are fairly well understood. Rapid in-air chemical reactions involving  $NO$ ,  $NO_2$ , and  $O_3$  can make difficult the interpretation of field data and prevent standard resistance approaches from achieving accurate simulation of the surface removal rates and vertical fluxes of  $NO$  and  $NO_2$ .

Modeling attempts are often confounded by the effects of surfaces wetted by rain or dew on the uptake of gases, particularly in forested areas, where the variability in liquid water amount can be large from one region to another. Measurements of fluxes are recommended to evaluate the effectiveness of parameterizations in models.

For inorganic gases that are either highly soluble in water (e.g.,  $HNO_3$ ,  $SO_2$ ,  $NH_3$ ,  $H_2O_2$ ) or are quite reactive with surface materials (e.g.,  $O_3$ ,  $NO_2$ , strong oxidants), the available parameterization schemes can

usually describe fairly well the interactions of the gases with surface elements. Nonreactive, insoluble gases typically have very small deposition rates relative to ambient concentrations. The influence of lipid solubility on the uptake of organic substances is not well understood; parameterization of the dry deposition of organic substances currently relies on inferences, with practically no direct measurement.

For large bodies of water, dry deposition rates of most gases appear to be largely determined by water solubility. This conclusion, however, has not been tested much by field experimentation. For example,  $O_3$  deposition velocities over ocean are typically measured to be  $0.01$ – $0.05\text{ cm s}^{-1}$ , larger than expected on the basis of water solubility alone. Surface films might increase the deposition of oxidants and of some organic substances. Very little flux measurement of fine particles has been done over natural water bodies. Furthermore, the case of strong winds (i.e., those greater than about  $10\text{ m s}^{-1}$  at a height of  $10\text{ m}$ ) is not well understood for both gas and particle fluxes.

The uptake of gases by bare soil surfaces has received some experimental attention. For  $O_3$ , extremely wet soils or soils with very little organic matter tend to have small deposition velocities. For  $SO_2$ , both acidity and moisture of surface soils appear to have a major role. An adequate description of soil properties for times and locations where the soil is exposed is a significant challenge in the development of parameterizations and in characterizing surface properties adequately. Models that include parameterizations of uptake by soils should be used with skepticism in areas with notably different soil properties from locations for which the models were developed.

Modeling of gaseous emissions and deposition needs to be tied together at a low level of model structure, which has not yet been accomplished. Ideally, a single comprehensive description of surface vegetative properties would serve multiple purposes and achieve self-consistency in regional- and large-scale modeling.

The use of compensation point concentrations to infer the balance of emission versus deposition of  $NO$ ,  $NO_2$ , and  $NH_3$  has been shown to be applicable to a few case studies. Generalization of the approach of using compensation points in regional large-scale models, however, has not been achieved and might not be practical because of the large variability of surface conditions.

Development of the parameterization and modeling of the deposition rates of particles has been slowly advancing. Measurements have been informative, but a comprehensive understanding of particle deposition has not been achieved. Innovative methods of measuring particle deposition need to be developed and applied to derive more universal parameterizations of deposition in natural settings outdoors.

Methods have been developed to measure the local deposition rates of many inorganic gases to flat,

homogeneous terrain. Application of micrometeorological approaches is limited by the capabilities of analyzers for many substances. Long-term flux measurement for diverse terrain or relatively large areas remains very difficult. Surrogate surface methods should be viewed with extreme caution because no artificial surface adequately includes the complexity of natural surfaces, where the controlling processes are usually located.

The findings in this paper indicate that many of the parameterizations used in models must be improved in order to achieve reliable estimates of dry deposition. The priorities of the basis research needed depend a great deal on the issue being addressed. For regional episodes of high ozone concentrations, for example, simulation or parameterization of rapid in-air chemical reactions near the surface needs to be incorporated efficiently into deposition models, and the role of uptake by soil needs to be better understood. For substances such as  $\text{SO}_2$  that are soluble but not highly reactive, direct measurements of fluxes are necessary to achieve confidence in model estimates of the effects of surface wetness in terrestrial regimes. Reliable, field-tested models of particles as a function of particle size are needed for studies of the regional transport of particles. Evaluation of model performance over hilly and nonuniform terrain is needed to achieve more confidence in model estimates of deposition velocities in general. Third-generation models of meso-scale meteorology and atmospheric chemistry have the potential to achieve several advances, foremost among which is an improved description of surface conditions.

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### Appendix A: Methods of measurement

The rate of  $\text{O}_3$  dry deposition is determined by the removal rate and depends largely on the nature of the surface itself, as is explained in the main portion of

this text, the resistances of surface elements to  $\text{O}_3$  removal vary widely according to their chemical, physical, and biological properties. Quite a different situation exists for  $\text{HNO}_3$ , which appears to be taken up with practically zero surface resistance by all natural surfaces. By contrast, CO and other relatively inert substances are deposited very slowly. For  $\text{NH}_3$ , deposition velocities can be large when ambient concentrations are high and the surface is wet; however, the flux can be dominated by emissions when soil-plant systems are rich in nitrogen. To learn how to express these complex behaviors in numerical models, one must measure the fluxes and investigate their dependence on the various controlling properties. Thus, accurate measurement of the fluxes is necessary. This Appendix emphasizes the methods that are now most popular and the demands they place on instrumentation and siting. The reader is referred to past reviews for more detailed information on methodology, achievable accuracies, and alternate approaches such as the variance technique and the use of environmental enclosures (e.g., Businger, 1986; Hicks et al., 1986; Hicks and Lenschow, 1989; Erisman and Draaijers, 1995).

#### A.1. Micrometeorological methods

Most studies of  $\text{O}_3$  deposition have relied on micrometeorological methods, as have studies of a number of other atmospheric trace species. These methods range from direct measurement of the rate of transfer from the atmosphere by eddy correlation (the eddy covariance technique) to calculation of the flux from measured concentration differences between various heights, using a diffusion coefficient derived from other measurements (gradient techniques).

All micrometeorological methods measure the rate of transfer above the surface. This flux will be the same as that at the bulk surface only if the flux is constant with height. Changes of fluxes with height are expected to be significant when obstructions exist in the upwind terrain, the surface has nonuniform vegetation or roughness, or sufficiently rapid chemical reactions occur in the air. Sites must be selected with care. For example, if the goal is to study the effects of the wetness of grass on  $\text{O}_3$  deposition, a large area of uniform grass in a flat area should be found. A common rule of thumb is that the upwind fetch of such surface conditions should extend to a distance of 100–200 times the height of measurement. For studies of the dry deposition of  $\text{O}_3$ , no strong point or line sources of  $\text{NO}_x$  should exist for distances upwind that are perhaps 1000 times the height of measurement, to avoid an excessive height-dependent flux variation caused by rapid in-air chemical reactions. If such constraints are met, estimates of fluxes above the surface can usually be assumed to be the same as the flux values for the bulk surface. Estimates of  $R_c$  in Eq. (1) for dry deposition rates or of a surface emission rate can then be

inferred with a reasonably high level of confidence. Such constraints on site uniformity usually do not influence the successful application of  $R_c$  or surface emission parameterizations in atmospheric chemistry models.

The height of measurement must be considered in the experimental strategy. For eddy correlation from towers, the sensors need to have responses sufficiently fast to resolve fluctuations fully at frequencies up to about  $n = 2uz^{-1}$ , where  $u$  is the mean horizontal wind speed and  $z$  is the height above the effective zero-plane displacement height, which is typically 60–75% of the height of a vegetative canopy. The corresponding exponential response times are a fraction of a second for measurements at a height of about four meters. This height, in turn, imposes the need to select a uniform area for measurements that has an upwind dimension of several hundreds of meters.

The advantages of the eddy covariance approach provide a strong incentive for the development of fast-response chemical sensors (Hicks and Lenschow, 1989). Recent developments include fast-response sensors for isoprene (Guenther and Hills, 1998) and gases such as acetone, formic acid, and ammonia (Shaw et al., 1998).

For gradient measurements, an initial consideration is to choose height intervals sufficiently large to yield concentration differences that can be measured reliably with the chemical sensors available. In practice, height differences are often chosen to be approximately equal to the geometric means of the corresponding two measurement levels. Even then, accurate measurement of the concentration difference is a demanding technical task because the differences are not likely to exceed 5% of the mean concentration. When the concentration difference is measured successfully, an eddy diffusivity must be derived to compute the vertical flux. The relationships available for this purpose are based on the assumption that the surface is spatially homogeneous. Compromises are often necessary in balancing competing requirements associated with site homogeneity, height of measurements, and chemical sensor performance characteristics. Nevertheless, the gradient approach is often used successfully (e.g., Zeller, 1994; Horváth et al., 1998).

Some recent notable extensions of the eddy correlation and gradient approaches have been developed. These variations retain a fundamentally micrometeorological character. In the eddy accumulation method, the need for a fast-response chemical sensor is replaced with the requirement for measurements of concentration differences in two samples, one for updrafts and one for downdrafts. The magnitudes of the differences are typically as small as those associated with gradient methods, but the eddy accumulation approach has the advantage of not requiring an estimate of eddy diffusivity. In initial studies, samples were collected at a rate proportional to the vertical component of the wind. For eddy accumulation with conditional sampling, or “relaxed eddy accumula-

tion,” a more easily implemented approach has been developed: samples are collected at a constant rate for the two accumulation reservoirs (Businger and Oncley, 1990). The relaxed eddy accumulation method has been tested and used for several substances (e.g., Baker et al., 1992; Pattey et al., 1993; Nie et al., 1995; Guenther et al., 1996) but has rarely, if ever, been applied to measure  $O_3$  fluxes, primarily because fast-response  $O_3$  sensors are readily available for standard eddy correlation.

The modified Bowen ratio approach is a variation of the gradient method that does not require an estimate of eddy diffusivity to be derived explicitly. The approach assumes that the diffusivity of the substance of interest is equal to the diffusivity for a reference scalar quantity, usually heat content (temperature) or water vapor content. The assumption allows the flux of the chemical to be computed as the product of the flux of the reference quantity and the ratio of the concentration difference to the difference in the reference quantity. The differences should be measured across the same heights, and the individual mean values for the substance of interest should be sampled as closely as possible to the points where the reference quantity is measured. The flux of the reference quantity can be computed by whatever means is available, e.g., by eddy correlation or the energy balance Bowen ratio method. One difficulty with the modified Bowen ratio approach is that it assumes that the sources and sinks for the quantity of interest are collocated with those for the reference quantity, which is not necessarily the case for vegetative canopies (Denmead and Bradley, 1987). The modified Bowen ratio approach has been used in a number of field studies, primarily for chemicals for which fast response sensors are not readily available (e.g., see Lee et al., 1993, regarding  $HNO_3$ ; Kim et al., 1995, for Hg; Hall and Claiborn, 1997, for  $H_2O_2$ ).

## A.2. Ozone sensors

For eddy correlation applications, a number of fast-response  $O_3$  sensing systems have been developed. A widely accepted technique involves detection of the chemiluminescence of  $O_3$  reacting in partial vacuum with excess NO; exponential time responses of less than 0.1 s can be achieved (Eastman and Stedman, 1977; Pearson and Stedman, 1980). A similar approach with excess ethylene supplied to the reaction chamber at near-ambient atmospheric pressures yields time responses of 0.2–1.0 s (Warren and Babcock, 1970; Cook and Wesely, 1977). Organic dyes on a solid substrate have also been used effectively as the reactive agent and can provide response times of less than 0.1 s (Güsten et al., 1992; Delany et al., 1997).

For gradient and eddy accumulation techniques, many types of analyzers that detect chemical reactions and optical absorption have been used to measure the mean  $O_3$  concentrations. The measured concentration

differences peak at about 5% during typical field experiments; the differences can be considerably smaller for substances whose flux is small or whose ambient concentration is high. Because the error in measuring the chemical differences usually results in a similar error in the flux estimates, extremely stable, accurate analyzers or a means of overcoming sensor deficiencies must be used. To lessen the effects of variations in analyzer offset and response, a single detector can be used by switching the air sample streams from multiple heights or different accumulation vessels. For two or more detectors, routine switching of samples to the detectors is strongly advised. Care must be taken to avoid disparities in the chemical concentrations caused by chemical uptake in tubing of different lengths, pressure drops because of flow constrictions, etc. For  $O_3$ , such concerns and the availability of reliable fast-response sensors have resulted in the majority of flux data being acquired by eddy correlation.

### A.3. Aircraft applications

Measurements of fluxes by eddy correlation are becoming more common. The velocity components relative to the aircraft are detected with various types of three-dimensional anemometers. In modern applications, high-resolution global positioning systems are sometimes used to measure aircraft motion, to allow computation of velocities relative to the surface of the Earth. Signals from fast-response air chemistry sensors carried on the aircraft are combined with the velocity data to estimate the eddy fluxes along the flight path (e.g., Godowitch, 1990; MacPherson et al., 1995; Oncley et al., 1997).

Aircraft data are often obtained in combination with tower observations, which provide a relatively continuous temporal sequence of flux estimates, while the aircraft obtains spatial averages over limited periods of time. In addition, the tower observations are frequently employed to evaluate the accuracy of the aircraft systems. The California Ozone Deposition Experiment of 1991 is a superb example of how the various flux measurement techniques can be applied synergistically. (See Pederson et al., 1995, and the companion articles in the same issue of *Atmospheric Environment*).

Fig. 4 illustrates the spatial variability of  $O_3$  deposition velocities derived from eddy correlation measurements aboard a Twin Otter research aircraft operated by the National Oceanic and Atmospheric Administration (R.T. McMillen, private communication). The spatial variability is quite large, suggesting that models should consider field-to-field variations in surface removal rates to obtain realistic spatial averages. At the 1995 Southern Oxidant Study (part c of Fig. 4), the variability of the deposition velocities could have been enhanced by in-air chemical reactions associated with pollutant emission sources located upwind of the flight path. By measuring the flux at several heights in the lower atmosphere, the

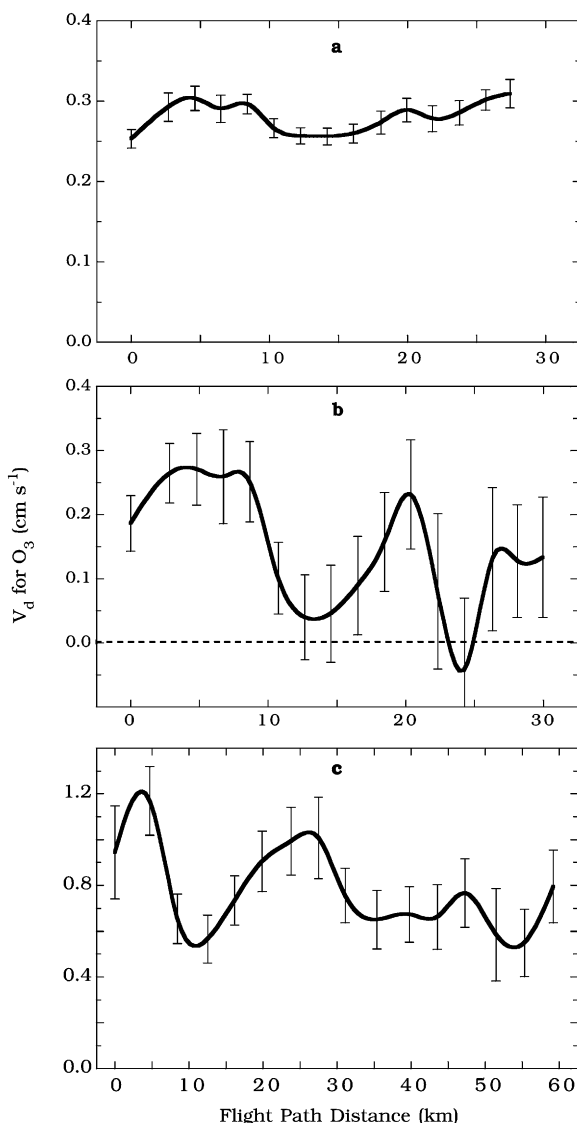


Fig. 4. Averaged ozone deposition velocities derived by eddy correlation measurements from aircraft, where the error bars indicate standard deviations of values obtained within intervals of longitude. Flights during midday, convective conditions were made repeatedly along the same paths (a) about 30 m above flat terrain with a patchwork of early-season agricultural crops during rapid green-up in central Illinois; (b) about 50 m above rolling terrain with rangeland and some agricultural crops during spring in the Walnut River Watershed located just east of Wichita, Kansas; and (c) 100–130 m above suburban and partially agricultural land during summer in and near Nashville, Tennessee.

flux divergence can be computed (e.g., Lenschow et al., 1981); some results from measurements aboard the Twin Otter during the Southern Oxidant Study are shown in Fig. 5. The position of the peak of the production

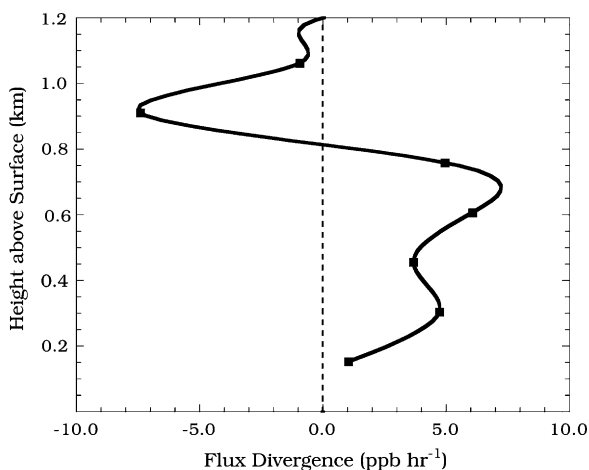


Fig. 5. Estimates of  $O_3$  flux divergence at various heights (solid squares) inferred from aircraft measurements during the daytime above urbanized land in Tennessee. Uncertainties are roughly  $\pm 2$  ppb  $hr^{-1}$ , associated mostly with advection.

rate near the middle of the planetary boundary layer conforms to expectations and previous studies, but the magnitude of the production rate is sufficiently large to suggest an enhancement of photochemical reactions involving pollutants emitted in the region. In general, the role of in-air chemical reactions must be considered when  $O_3$  flux measurements made at considerable height above the surface are extrapolated to the surface itself.

#### A.4. Other approaches

For some chemical species, throughfall-stemflow techniques can be used to infer dry deposition amounts in tall canopies, although extrapolation to large areas surrounding the specific site where the measurements are made is difficult, and the approach does not work for substances such as  $O_3$  that do not accumulate conservatively on surfaces (e.g., Lovett, 1994; Veltkamp and Wyers, 1997). One of the major advantages of throughfall-stemflow techniques is that they usually can be applied more successfully than micrometeorological approaches in mountainous terrain or in areas with nonhomogeneous surface conditions.

Future progress in understanding the effects of surface discontinuities on surface fluxes will probably require application of surface-sampling techniques, such as throughfall-stemflow methods for particulate chemicals. For the study of deposition to landscapes, detailed modeling of interactions between fields of various types might be needed (e.g., Baldocchi and Rao, 1995). Horizontal flow or advection near edges of vegetation stands of varying heights can be significant and are not addressed well in resistance models (e.g., Draaijers et al.,

1994). A comprehensive evaluation of the net impact of ignoring edge effects over a landscape with a mixture of vegetation heights is needed; estimates of deposition rates downwind of a change from tall to short vegetation should be included.

Remote-sensing methods for deriving  $O_3$  flux data are now starting to be used in field programs. Senff et al. (1996) reported the application of eddy correlation principles to measurements of  $O_3$  concentrations aloft and coincident (in time and space) velocity data, derived by using advanced lidar and radar systems. Fiorani et al. (1998) described use of a differential absorption lidar to measure both  $O_3$  concentrations and vertical wind speeds in order to compute  $O_3$  eddy flux. Whether such methodologies will be widely used, or whether their high cost will prove prohibitive, remains to be seen.

Chamber techniques have been used extensively to study air–surface exchange for bare soil and short vegetation, especially for substances whose concentrations are difficult to measure with sufficient accuracy in gradient approaches and for studies of emission rates (e.g., see Hicks and Lenschow, 1989; Dollard et al., 1990; Davidson et al., 1991; Slemr and Seiler, 1991; Valente and Thornton, 1993; Aneja, 1994; Aneja et al., 1997; Guenther et al., 1996).

Results of studies of deposition to surrogate surfaces are frequently reported. These surrogate surfaces are typically treated plastic, metal surfaces, or water surfaces in some configuration that is deemed appropriate. Because the controlling property of uptake is determined by either the surface itself or the configuration of its exposure in the environment, the surrogate surfaces can rarely provide reliable deposition data. Nevertheless, such surfaces, when exposed to polluted air, will yield a collection of chemicals. The difficulty is that the amount of deposition does not represent fluxes to the natural surroundings in a way that can yet be identified, except perhaps when the surfaces yield a reliable measure of concentration and an estimate of deposition velocity can be made independently.

For studies of damage to specific surfaces by exposure to  $O_3$ , samples of such surfaces can be deployed and the effects assessed by watching trends with time. Standardized methods have been adopted for deploying samples of materials in comparative studies to determine which material withstands exposure the best. (e.g., ASTM, 1997). Results of studies of this kind are frequently reported in materials effects literature. The surfaces tested are typically materials used in construction or in consumer products – paints, metals, plastics, rubber products, etc. Because the property controlling uptake is either determined by the surface itself or the configuration of its exposure in the environment, data from such exposure studies rarely lead to accurate estimates of areal deposition from the atmosphere, or of the actual rate of deposition to the same surface or material when it is

exposed in other surroundings. Such tests are strictly comparative.

For large particles, gravitational settling is a major component that can be sampled with some types of surrogate surfaces. Studies have shown, however, that impaction and interception of particles are important for vegetative canopies (e.g., Davidson et al., 1982; Hofschreuder et al., 1997); these processes are moderated considerably by the structure and texture of the canopy, and their effects are not reproduced in the design of any standardized artificial collection device.

Finally, methods of routinely measuring fluxes should not be confused with monitoring based on models or inferential techniques. Long-term flux measurements require considerably greater effort (e.g., Enders et al., 1992; Munger et al., 1996) at each site than does inferring deposition rates on the basis of concentration measurements, meteorological measurements, observations of surface conditions, and calculation of deposition velocities by use of parameterizations or models (e.g., Hicks et al., 1987; Meyers et al., 1991; Clarke et al., 1997). When numerical models are used to derive some of the input parameters for deposition velocity calculations, the results are further removed from direct measurements. At individual sites, the estimation of pollutant fluxes can be assisted by use of measurements of the air–surface exchange of other parameters, such as water vapor (Pleim et al., 1999); however, the resistances to air–surface exchange can be quite different along certain pathways for water vapor, as compared to ozone or other trace chemicals, so the pathways must be carefully considered and modeled when they are significant.

#### A.5. Concluding remarks

The reader is referred to past publications that include reviews of methods to measure dry deposition (Businger, 1986; Hicks et al., 1986; Hicks and Lenschow, 1989; Lovett, 1994; Erisman and Draaijers, 1995) and to many of the publications cited previously in this paper.

The range of measurement methods is limited. Studies of the processes that control dry deposition require direct measurement of the rates of air–surface exchange. For the oxidants of principal interest here, the only method of direct measurement is eddy correlation. This technique is well developed and can be applied by using both surface towers and aircraft platforms. Operation on floating platforms requires a means to correct for platform motion. To date, eddy flux measurements of atmospheric trace gases have been most successful for  $O_3$ ,  $CO_2$ ,  $SO_2$ ,  $NO$ ,  $NO_2$ ,  $NO_x$ ,  $NO_y$ , and  $H_2O$ . Micrometeorological gradients are often used for  $HNO_3$ ,  $NH_3$ ,  $H_2O_2$ , and  $Hg$ , among others. The fluxes of particulate species are measured with both eddy correlation and with gradient approaches.

New approaches are needed, especially for particles and gases for which sensors sufficiently fast for eddy correlation or sufficiently accurate for gradient approaches are not available. The micrometeorological approach of eddy accumulation and its variations have been successfully developed to overcome the need for fast-response sensors, but the requirement for accuracy in measurement of concentrations is as demanding as for gradient approaches. For nonuniform landscapes and hilly terrain, the methodology of micrometeorological approaches is not well developed. Techniques based on collection of throughfall and stemflow in tall vegetative canopies can be used successfully for substances that are not retained or leached in the plant canopy during rainfall.

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