

SCOPE 51 - Biogeochemistry of Small Catchments

3 Atmospheric Chemical Input to Small Catchments

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3.1 INTRODUCTION

For understanding the biogeochemical cycling of trace substances inside a small catchment it is of fundamental importance that the atmospheric input be determined. The term *wet deposition* is used to denote the input of chemicals to the ecosystem by precipitation, while *cloud deposition* is used to denote the input by riming and the impaction of clouds upon the surface. Gases and atmospheric particles can also be deposited to the biosphere in the absence of precipitation. This process is referred to as *dry deposition*. *Bulk deposition* is the operational term for a mixture of wet and dry deposition as measured by means of continuously exposed sampling devices, e.g. those exposed both to precipitation and dry deposition (only deposition of coarse particles by gravitational settling is effective-gases and fine particles are heavily underestimated by bulk sampling).

The input of chemical constituents will depend on the physiography of the catchment (elevation, slope and aspect), the nature of vegetation cover and the location of the catchment relative to natural and anthropogenic sources. The importance of each of these factors will vary from catchment to catchment. For example, high elevation catchments generally have a larger portion of chemical inputs via cloud deposition than from wet deposition (Lovett and Kinsman, 1991). Dry deposition of gaseous SO_2 tends to dominate sulphur inputs of forested catchments in regions of heavy pollution loadings, in more pristine environments wet deposition of SO_4^{2-} is the dominant source of sulphur (Lindberg, 1992).

The purpose of this chapter is to give a brief overview of the factors which influence the input of chemical substances to small catchments. [Section 3.2](#) will emphasize the physical processes of deposition which transport chemical substances to the catchment and their interaction with biota. The remainder of the chapter will review surface analysis methods for estimating atmospheric inputs.

3.2 FACTORS INFLUENCING CHEMICAL INPUTS

Catchment physiography (elevation, slope and aspect), the nature of the vegetation cover and the location of the receiving watershed relative to point and regional sources of airborne materials all exert strong influences over the forms and fluxes of airborne constituents (see review by Hosker and Lindberg, 1982). In turn, the net contribution of a particular atmospheric constituent such as acids or base cations to the system is determined by the level of interaction of precipitation, dissolved ions (e.g. H^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , K^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , and HCO_3^-) and ions associated with particles or dissolved gases with the catchment surfaces. The controls on atmospheric inputs to areas on the scale of small catchments are complex and not well understood; actual inputs to individual watersheds are extremely difficult to quantify (Hicks *et al.*, 1986). Some aspects of uncertainty in deposition estimates on these spatial scales are discussed in Hicks *et al.* (1990) and in Sisterson *et al.* (1990).

For this discussion, we will consider the physical and biological aspects of the catchment that influence deposition and will consider primarily vegetated catchments. Very little work exists on factors controlling direct deposition to bare soils and surface waters. The biological surfaces of the plant canopy and litter layer influence the chemistry of wet deposition reaching underlying soils by release of organic acids and by ion exchange reactions. However, this is largely an internal cycling process that does not result in the addition of outside material such as that originating from anthropogenic sources deposited to these surfaces. The most important role of these surfaces lies in their ability to intercept airborne gases, droplets and suspended particles. For example, increased input at forest edges, in forested vs. cleared catchments, and even in coniferous compared to adjacent deciduous catchments is due to a combination of the increased turbulence caused by the plant canopy, and to the surface area of the canopy itself (Hasselroth and Grennfelt, 1987; Bredemeier, 1988).

3.2.1 WET DEPOSITION

Due to public concern about acid deposition and the subsequent acidification of lakes and forests, regional-scale precipitation chemistry networks have existed in Europe and North America for a long time. Results from these networks indicate that spatial variations in soluble ion concentrations are smaller than the variations in the precipitation field. This is due to the fact that local topography (spatial scales greater than 1 km) can greatly influence the type, amount and duration of precipitation (Bergeron, 1960, 1961). Therefore to determine the wet deposition of a soluble ion, one can, in principle, first determine the concentration field using a somewhat sparse precipitation chemistry network and then multiply the concentration field by the detailed precipitation field generated by the national weather service. However, it is important to note that errors of around $\pm 20\%$ on precipitation estimates can be

obtained if the effects of the windfield are not taken into account (Sevruk, 1981, 1982). For catchment studies, experience has shown that measurements of precipitation amount and wind speed should be carried out at several locations inside the catchment, even at the expense of having a large number ($n > 3$) of precipitation samplers for the determination of soluble ions.

In the formation of precipitation, particles and gases are scavenged into the falling hydrometer both in and out of cloud. Precipitation formed by large-scale synoptic systems (i.e. the passage of a warm front) is associated with the lifting of warm moist air over colder surface air. The falling hydrometer will then scavenge particles and gases from the lower air masses (termed *below cloud scavenging*) with the net effect of cleansing the surface air. In convective storm cells, warm surface air rises and penetrates into the free troposphere. Due to the continued lifting of warm air, convective storms are "fed" particles, gases and vapours.

During a precipitation event the concentration of soluble ions will vary considerably (de Pena *et al.*, 1984; Ames *et al.*, 1987). The concentration of pollutants in the precipitation will depend on a large number of factors including scavenging efficiencies (both in and out of cloud), the origin of the air mass, the type of hydrometer and precipitation intensity. The latter is exemplified in [Figure 3.1](#) which shows the concentration of soluble ions in precipitation during the passage of a warm front in central Pennsylvania during March 1980 (de Pena *et al.*, 1984).

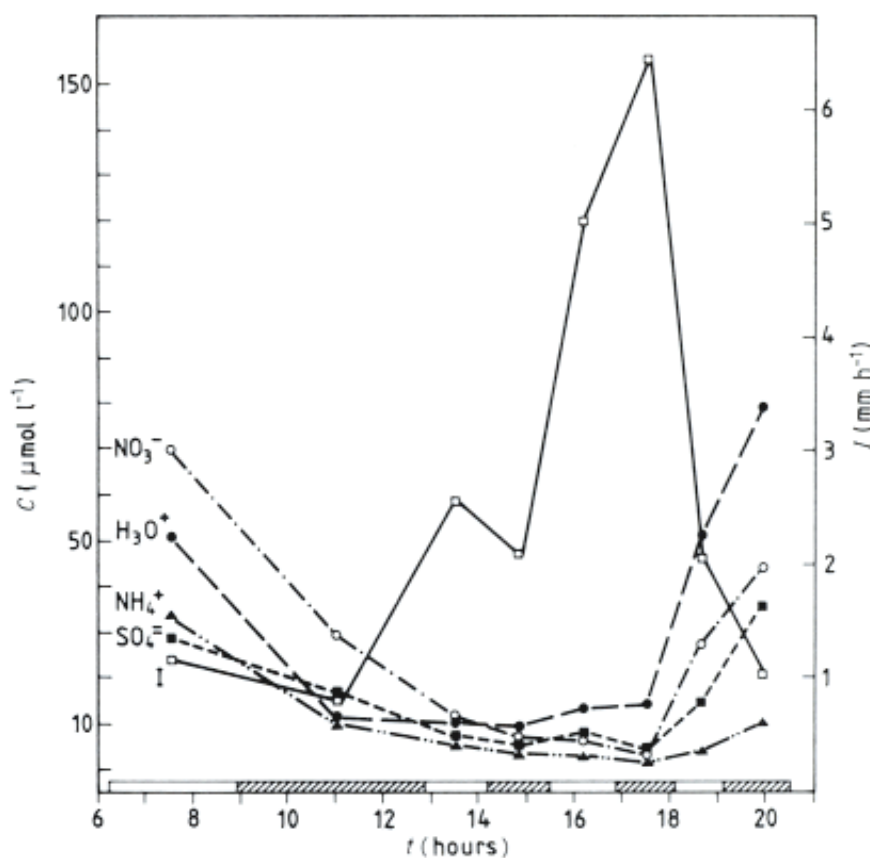


Figure 3.1 Time series of rain intensity (I) and concentrations of H^+ , SO_4^{2-} , NO_3^- , and NH_4^+ ($\mu\text{mol l}^{-1}$) in a single precipitation event collected in central Pennsylvania, on 3 March, 1980 (from de Pena *et al.*, 1984; reproduced by permission of Pergamon Press).

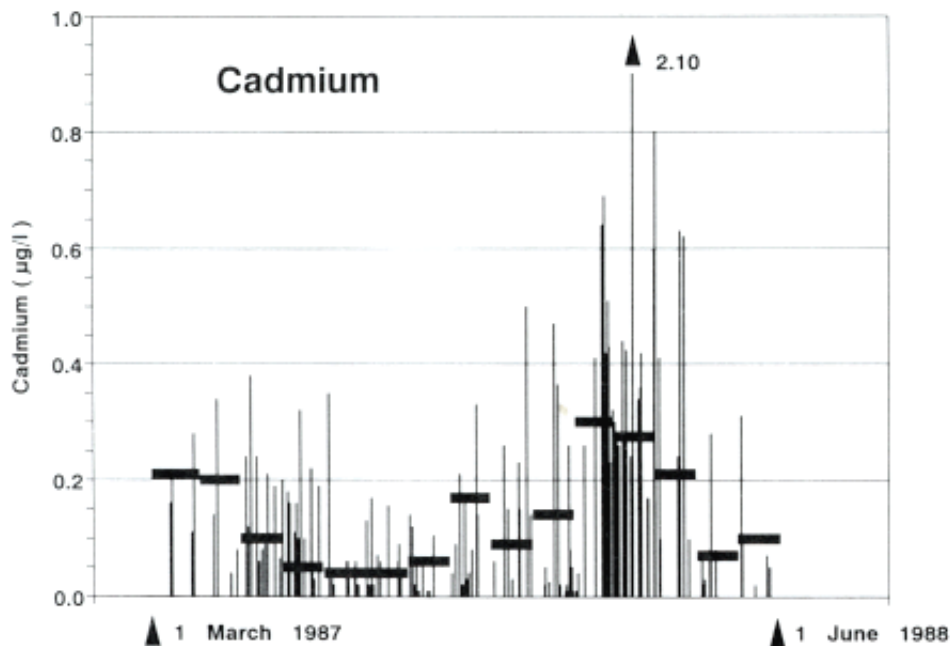


Figure 3.2 Concentration of Cd (ppb) in precipitation collected on a daily basis at a site in southern Sweden. The solid horizontal lines represent monthly volume weighted mean concentrations (from Ross, 1990a; reproduced by permission of Pergamon Press).

Concentrations of H^+ , SO_4^{2-} , NO_3^- , and NH_4^+ , first decrease through the course of the storm. Towards the end, when rain intensity is lower, concentrations generally begin to increase since the falling rain drops evaporate at a greater rate.

In mid-latitude locations in Europe and North America one generally observes seasonal variations of solutes in precipitation (Lindberg and Turner, 1988). This is exemplified in [Figure 3.2](#), which presents the concentration of Cd in precipitation at a site in southern Sweden (Ross, 1990a). The atmospheric Cd cycle in Europe is dominated by anthropogenic sources (Pacyna *et al.*, 1984) which are fairly constant ($\pm 20\%$) during the year. Hence the differences in concentrations during winter and summer are primarily due to meteorological factors. These include differences in scavenging efficiencies of snow and rain and in the height of the boundary layer. During the winter the thickness of the atmospheric layer where air is uniformly mixed is approximately half the height during the summer.

For oxides of sulphur and nitrogen the seasonal variations are more difficult to ascertain since many other factors determine their concentrations in precipitation. Firstly emissions of gaseous NO_x and SO_2 have distinct seasonal variations and reflect the increasing use of fossil fuels for heating. On the other hand, biogenic emissions during the summer may partly offset the increase in anthropogenic emissions during winter (Leck, 1989). Oxidation rates also vary significantly during the year, because atmospheric photochemical activity is lower in the winter.

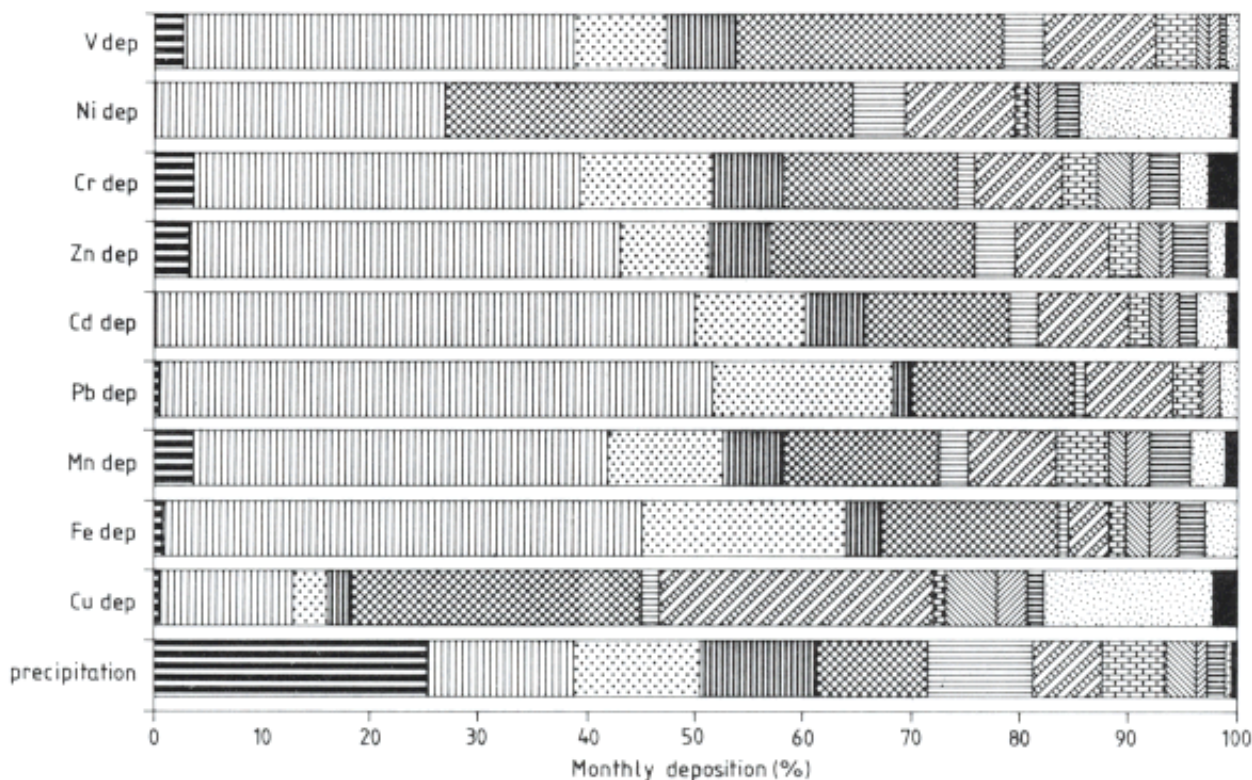


Figure 3.3 The relative contribution of individual storms (in order of decreasing precipitation amount) to the monthly deposition of several trace metals during August 1987, at a site in northcentral Sweden. The storm with the largest amount of precipitation contributed small amounts of metals; the second storm contributed approximately 10% of the monthly precipitation but over 50% of the Cd and Pb deposited in the month in question (from Ross, 1990a; reproduced by permission of Pergamon Press).

For northern Europe the net effect is that sulphur concentrations in precipitation are generally highest during the spring (Rodhe and Granat, 1983; Leck and Rodhe, 1989), while in the United States extensive data from 200 sites in the National Atmospheric Deposition Program (NADP) suggest that SO_4^{2-} concentrations generally peak during the summer (NADP, 1989).

One also observes from the Cd data in [Figure 3.2](#) that large differences in concentrations can be observed between individual precipitation events. During the 15 month sampling period, storm-to-storm variations of Cd concentrations were three orders of magnitude. These variations primarily reflect the history of the air mass: air which has passed over industrial regions has higher loadings of pollutants than air from the pristine Arctic. In [Figure 3.3](#) the per cent of deposition during August 1987, associated with individual rain events at a site in north-central Sweden is presented (Ross, 1990a). The storm with the most intense precipitation deposited approximately 25% of the water but negligible amounts of trace metals. The second storm deposited around 10% of the monthly precipitation but accounted for almost 40-50% of the metal deposition. Essentially 20-30% of the precipitation deposited contained approximately 70-80% of the metals deposited. The important point is that large variations in deposition can be expected from storm to storm and this variation is primarily due to the history and origin of the air mass rather than variations in precipitation.

3.2.2 CLOUD DEPOSITION

Fogs can be considered as clouds that are in contact with the surface. In low-altitude catchments, fog droplet capture is rarely an important hydrologic input to catchments, but can be a measurable source of

chemical input. The importance of cloudwater interception to the hydrologic and chemical budgets of high elevation ecosystems is now well recognized. Cloud droplets are efficient in accumulating various airborne materials, both soluble and insoluble, into micron-sized droplets which exhibit high deposition velocities. The location of forested catchments in mountainous terrain is conducive to elevated atmospheric inputs from orographic precipitation, increased dry deposition at high wind speeds, and cloud immersion. However, the most significant effect of elevation is on cloudwater interception (Lovett *et al.*, 1982). This interception occurs as a result of higher wind speeds at mountain sites and the relatively high needle surface area of typical conifer forests, coupled with significant periods of time during which forests in mountain areas are immersed in clouds (Unsworth and Fowler, 1988). A larger canopy cover also increases cloudwater interception by raising the rate of cloud droplet capture.

The frequency of cloud immersion at a site is a function of elevation ([Figure 3.4](#)), aspect and local climate. These factors may combine to create important diurnal and seasonal trends. For example, Lindberg and Johnson (1989) reported significantly higher cloud immersion at the Integrated Forest Study (IFS) site in the Smoky Mountains in North Carolina (1740 m) during the forest dormant season (November-March) compared to that during the growing season. For sites in the Mountain Cloud Chemistry Program (MCCP) in the Appalachian Mountains, annual cloud immersion frequencies ranged from 10-20% for sites at 1000 m a.s.l. to 30-40% for sites at 1500-2000 m a.s.l. (Mohnen, 1988). However, cloud immersion can be extremely variable even at one mountain location, and it is difficult to generalize from these data without actual on-site measurements (Lovett and Kinsman, 1991).

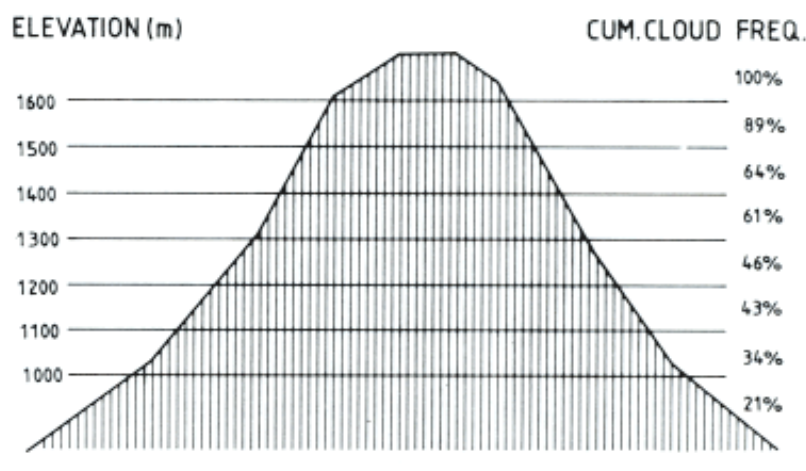


Figure 3.4 Cumulative per cent of cloud hours with cloud base heights less than the given elevation at Whitetop Mountain, VA (in the southern Appalachians) for the forest growing season (April-October). The data are from reflectometer and video camera measurements and represent the three-year means for 1986-88. The total cloud impaction frequency at the summit was 28% of all hours (from Vong, 1990; reproduced by permission of NAPAP).

Several methods have been employed to ascertain the amount of water being deposited by clouds to alpine systems. These include the direct collection of cloudwater (Falconer and Falconer, 1980), the measurement of throughfall and stemflow during fog episodes (Lovett *et al.*, 1982), and the modelling of cloud droplet impaction to vegetation (Lovett, 1984). The modelling of water inputs to a stand of Balsam Fir at a height of 1220 m using a micrometeorological approach (Lovett, 1984) indicated that mean wind speed, cloud immersion time, liquid water content (LWC) and drop size are key parameters in the estimation of cloudwater deposition. The model calculations indicate that small changes ($\pm 25\%$ of the initial values) were sufficient to change water input estimates by a factor of 5 ([Table 3.1](#)).

Table 3.1 The estimated input of water to a balsam fir stand at 1220 m a.s.l. for the months of July-October (from Lovett, 1984)

Wind speed (ms ⁻¹) 1)	Drop diameter (μm)	Cloud immersion time (%)	Liquid water content (g m ⁻³)	Water flux (cm)
3	10	30	0.3	27
4	10	40	0.4	64
5	10	50	0.5	125

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a.s.l., above sea level.

Many studies have illustrated that cloud droplets are characterized by significantly higher chemical concentrations than found in their associated rain drops because of their lower liquid water content (Dollard *et al.*, 1983; Weathers *et al.*, 1988). Lovett and Kinsman (1991) have summarized the results of several recent cloudwater deposition studies and concluded that cloudwater significantly increased the input of chemicals at all high elevation sites studied. At eight different sites, cloudwater contributed from 15-86% of the total wet plus dry deposition of SO_4^{2-} (the median contribution to total deposition was 50%) and NO_3^- (median 60%), generally increasing in importance with elevation. Lindberg *et al.* (1988b) used the model of Lovett (1984) to estimate H^+ cloud deposition to forests under a range of conditions characteristic of sites between 300 and 1800 m elevation in the southern Appalachian Mountains. In general, an increase in H^+ was predicted with an increase in height. The most important parameters in determining H^+ deposition were H^+ concentration in cloud, cloud liquid water content, cloud immersion time and wind speed.

Forests in low elevation catchments below cloud base may also be influenced by deposition of fog water droplets. Fog droplet deposition is controlled by the same processes described above, and these droplets have also been reported to contain elevated pollutant levels (Waldman *et al.*, 1982; Weathers *et al.*, 1988). However, annual deposition rates of ions in fog droplets to trees at valley sites are generally lower than those of ions in cloud droplets to trees at mountain sites because of lower wind speeds and immersion frequencies.

3.2.3 DRY DEPOSITION

The purpose of this section is to provide a very brief overview of the processes which govern dry deposition of gases and particles to small catchments. For a more detailed discussion of this complex subject the reader is referred to a number of excellent reviews on the subject (Sehmel, 1980; Slinn, 1982, 1983; Davidson and Wu, 1989; Wiman *et al.*, 1990). The estimation of dry deposition through direct measurements is difficult and a wide variety of techniques have been developed. These include micrometeorological approaches where the fluxes of gases and particles are related to heat and momentum transfer (Droppo, 1985; Neumann and den Hartog, 1985), gradient methods where the concentration of a substance is measured at different heights (Davis and Wright, 1985), high frequency eddy correlation methods, models coupled to ambient air data (Hicks and Matt, 1988) and the use of surrogate surfaces (Davidson *et al.*, 1985). Hicks *et al.* (1986) provide a review of the advantages and limitations of these various methods. The use of mass balance data from small catchments to study dry

deposition processes will be discussed separately in the next section.

How quickly a gas or a particle is deposited to the surface is reflected in the substance's *dry deposition velocity* (V_d). The larger V_d , the faster a substance is removed at the surface. Fluxes of a substance are then:

$$D = V_d \times C \quad (3.1)$$

where C is the atmospheric concentration of the substance. It should be emphasized that V_d is a gross parameter and is dependent on a wide variety of factors ([Table 3.2](#)). The deposition process may also be conceptually viewed as a series of resistances where:

$$V_d = R_d^{-1} = (R_a + R_b + R_c)^{-1} \quad (3.2)$$

Here R_a is the aerodynamic resistance and accounts for the turbulent transfer of the gas or particle from the free atmosphere to the regime of laminar flow near the surface, R_b is related to molecular diffusion in the laminar flow regime (boundary layer resistance) and R_c can be viewed as the ability of the surface or canopy to absorb the gas or particle.

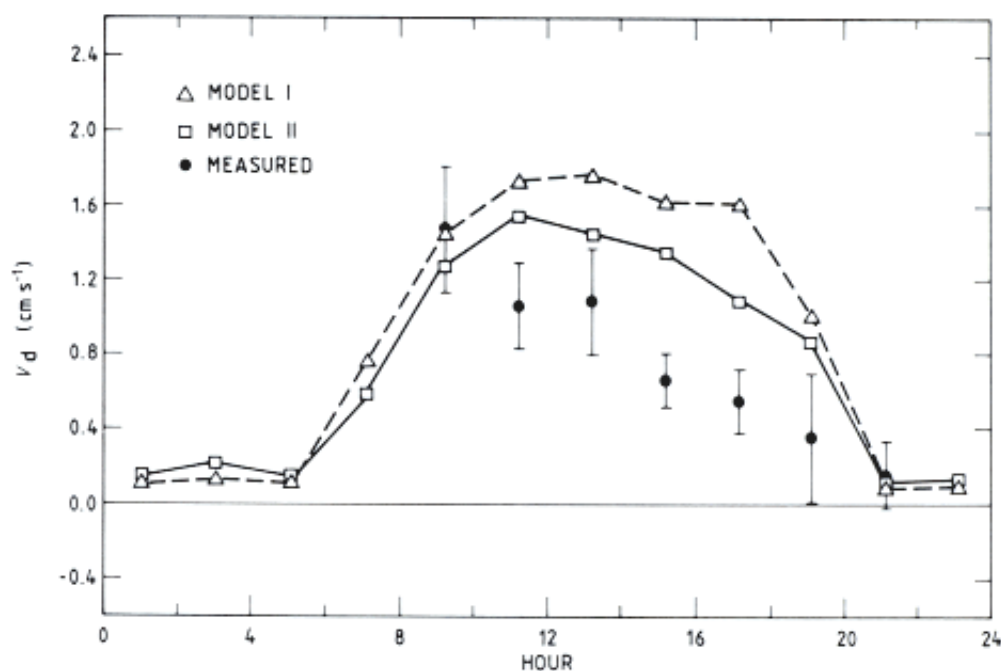


Figure 3.5 Diurnal variation of SO_2 dry deposition velocity in a mixed deciduous forest (Oak Ridge, TN, USA) during July 1985. "Model I" and "Model II" are resistance analogue models as described by Hicks *et al.* (1987); the differences in the models pertain to the treatment of SO_2 surface resistance and how changes in stomatal resistance are calculated (from Matt *et al.* 1987; reproduced by permission of Kluwer Academic Publishers).

Table 3.2

Factors which influence the dry deposition of trace gases and particles to vegetation (adapted from Sehmel, 1980)

Meteorological variables	Depositing material		Surface variables
	Particles	Gases	
Aerodynamic roughness	Agglomeration	Chemical reactivity	Biotic surface
Atmospheric stability	Diameter	Diffusivity	Canopy growth and structure
Diffusion	Density	Equilibrium with the surface	Senescent
Flow separation	Diffusion	Solubility	Electrostatic properties
Friction velocity	Diffusiophoresis		Leaf characteristics
Inversion layer	Electrostatic effects		Prior deposition loadings
Pollutant concentrations	Gravitational settling		
Relative humidity	Hygroscopicity		
Season	Impaction		
Solar radiation	Interception		
Surface heating	Momentum		
Temperature	Resuspension		
Terrain	Shape		
Turbulence	Size		
Wind velocity	Thermophoresis		
Zero-plane displacement			

For trace gases the most important parameters are the rate of turbulent transfer to the boundary layer and the ability of the surface to absorb the gas. For vegetative surfaces, highly reactive gases such as HNO_3 and H_2O_2 react directly with the foliage. Less reactive gases such as SO_2 and NO_2 are absorbed by the plant stomata. Hence, to estimate accurately the dry deposition of gases, detailed information on forest (topography, tree species) and plant structure (e.g. leaf area index and stomatal conductance) is needed.

Deposition velocities should not be considered constant but will vary considerably both during the day and season. The results of Matt *et al.* (1987) for SO_2 dry deposition to a mixed deciduous forest illustrate the substantial diurnal variations in V_d which can be observed. During the day, canopy resistance to SO_2 uptake is much larger than R_a and R_b (i.e. there are large amounts of turbulent transfer), at night, if conditions are more stable (i.e. low wind speeds and increasing temperature with height), R_a will dominate. The net effect of diurnal variations of R_a , R_b and R_c on the V_d of SO_2 is illustrated in [Figure 3.5](#). Highest V_d is observed during midday when vertical mixing is largest ($V_d > 1 \text{ cm S}^{-1}$); at night V_d decreases to $< 0.2 \text{ cm S}^{-1}$.

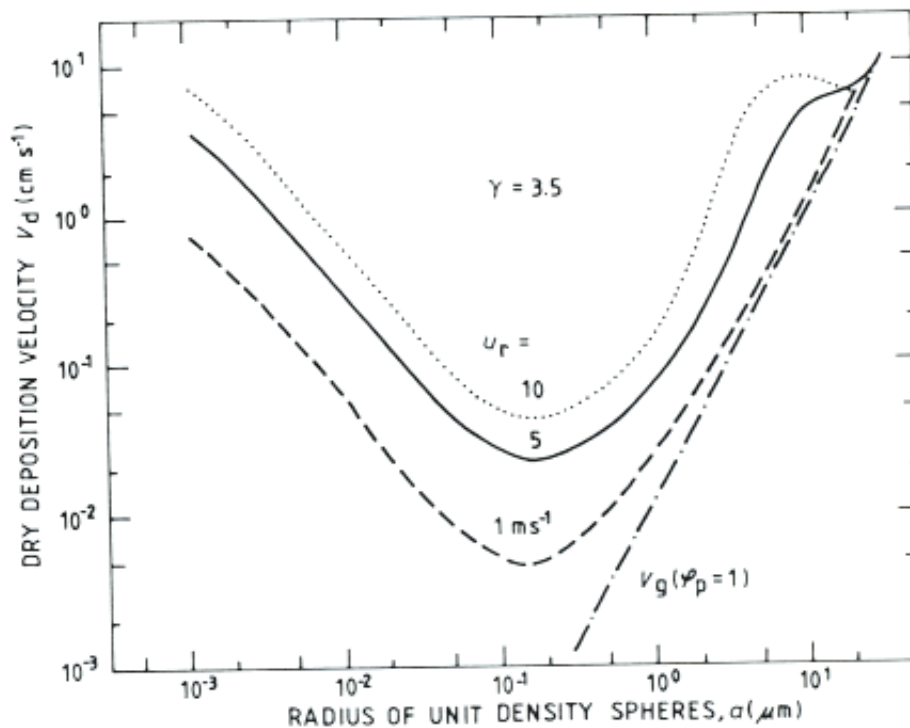


Figure 3.6 Model estimates of the dry deposition velocities (V_d) with respect to particle size and wind speed (u_r) using data for Eucalyptus forest. Also shown is the gravitational settling velocity of a particle with a specific density ($\phi_p=1$) (from Slinn, 1982; reproduced by permission of Pergamon Press).

As indicated by [Table 3.2](#) the dry deposition of particles is more complex than that of trace gases since more factors are important in determining particle deposition rates. For example, the gravitational settling velocity of the particle needs to be taken into account. Studies in forest ecosystems have indicated that topography and forest structure are also important factors. As with precipitation, particle deposition is enhanced on exposed hilltops and even at edges of forest stands (Hasselroth and Grennfelt, 1987). Model calculations reveal that the latter is primarily due to abrupt changes in the wind and turbulent eddy fields (Wiman, 1985, 1988). Dry deposition of airborne particles will be dependent on the tree species; coniferous forests, due to their perennial leaf cover and high leaf area index, receive larger loadings of particles than do adjacent deciduous forest stands (Höfken, 1983; Wiman and Ågren, 1985; Wiman, 1988).

[Figure 3.6](#) shows model results for the dry deposition of particles to a Eucalyptus forest (Slinn, 1982). The deposition velocities of the particles are highly dependent on particle diameter; largest deposition velocities are for particles having diameters $< 0.01 \mu\text{m}$ or particles having a diameter $< 10 \mu\text{m}$. For the large particles gravitational settling is the dominant factor controlling V_d . For the small particles V_d is dominated by Brownian diffusion. The dependence on wind speed is due to the fact that particles must be in motion to be captured by the vegetation.

3.3 METHODS FOR THE QUANTIFICATION OF INPUTS TO SMALL CATCHMENTS

Different techniques have been developed for the measurement of atmospheric deposition of airborne compounds to underlying surfaces, but few have been applied on the scale of even small catchments. Considerable progress has been made in the past 10 years in regional-scale measurements of wet deposition (e.g. NADP, 1989), in "monitoring" and modelling of dry deposition (e.g. Hicks *et al.*, 1987), and experimental measurement of cloudwater deposition (see [Section 3.2.2](#)). Some of these methods

could be combined to produce estimates for catchments, but this has not yet been widely tested, due largely to the high costs, intensive equipment management, and stringent siting criteria of the dry and cloud deposition methods. Catchment-scale wet deposition methods are well in hand, and recent developments in regional-scale modelling for dry deposition may prove quite useful for catchment studies (e.g. Wesely, 1989). However, for now, developments such as analysis of biomonitors such as bryophytes (carpet-forming mosses) for the determination of trace metals and organic contaminants (Rühling and Tyler 1968, 1973; Rühling *et al.*, 1987), foliage for natural radionuclides (Bondietti *et al.*, 1984), throughfall measurements (Lovett and Lindberg, 1984), and watershed mass balances (Hultberg *et al.*, 1983) are promising for both routine monitoring and process-level studies of wet, dry, and total deposition in small catchments. Methods such as these, which rely on the measurement of material which has accumulated on surfaces or which has been transported over one surface and accumulated on another, are referred to as surface analysis methods.

At this point, some discussion is necessary on the widespread use of bulk deposition collectors in forest plot, small catchment and watershed-scale studies. Bulk collectors include any continuously open containers which are usually placed at ground level and sampled over event to relatively long averaging times. These are attractive due to low cost and maintenance, and have been used for decades in a wide variety of studies. While bulk deposition has long been recognized as limited in its utility (NRC, 1983), quantitative comparisons with more accurate deposition data have been lacking. However, recent studies establish the inadequacy of bulk deposition collectors in biogeochemical and nutrient cycling studies. The problems are related due to two primary issues: (1) chemical changes in solutions during long-term field storage which result in losses of "reactive" species, especially nitrogen (Richter and Lindberg, 1988); and (2) the inability of buckets, funnels and other inert open collectors to collect representative samples of dry and cloudwater deposition.

As discussed in [Section 3.2](#), dry and cloudwater inputs are largely controlled by aerodynamic effects and canopy surface characteristics. Bulk collectors will never simulate the complex combination of aerodynamic and canopy effects that control deposition of either gases, cloud droplets, or aerosols. While this shortcoming has been debated for some time (Cole and Rapp, 1981) it has generally been accepted as fact for systems in highly polluted environments where dry deposition is significant, or in mountain catchments where cloudwater inputs are significant (NRC, 1983). However, use of bulk collectors has been advocated for systems in less impacted environments and to estimate inputs of some base cations under all circumstances. New data from the Integrated Forest Study (IFS) clearly indicate that even these applications are subject to considerable uncertainty (Lindberg, 1992). [Figure 3.7](#) illustrates the differences in bulk deposition and total wet + dry fluxes of several ions across the IFS sites (measured with state-of-the-art methods over three years; Lindberg and Lovett, 1992). The underestimates of the actual input provided by bulk collectors are clearly shown, ranging from a 30% underestimate of SO_4^{2-} at a "background" red alder forest near Seattle, Washington to a factor of ~6 for total N at a spruce forest in the Smoky Mountains of North Carolina. It is clear that even at the "background" IFS sites, bulk methods are questionable. The implications of using incomplete and inaccurate results from bulk deposition measurements to attempt to quantify foliar leaching or uptake rates and to understand the role of the atmosphere in forest biogeochemical cycles, are now clear (Johnson *et al.*, 1991).

Environmental surfaces are difficult to simulate either mathematically or physically. However, they have the natural ability to integrate the net result of dry deposition of various airborne compounds. Surface analysis methods can be used to quantify the amount of deposited material residing on such surfaces for constituents that are not irreversibly adsorbed. From knowledge of the area of the surface and the duration of the period of deposition, the net dry deposition rate to the surface can be computed. Important problems in quantifying dry deposition to plant canopies include spatial and temporal representativeness of modelled fluxes, and scaling from point measurements (in both space and time) to the landscape. Many micrometeorological approaches are limited to simple terrain and short time

intervals and are not applicable to coarse particles. Quantifying dry deposition of coarse particles, such as Ca and Mg in soil dust, is necessary to predict the effects of deposition on catchment acidification and on forest nutrition (Driscoll *et al.*, 1989). Surface analysis methods address many of these problems. They may be particularly useful for comparison with, and for validation of, deposition models. For example, foliar extraction and inert surfaces may be the only two available methods at present to develop and test mechanistic models of aerosol deposition within a forest canopy (McCartney and Aylor, 1987).

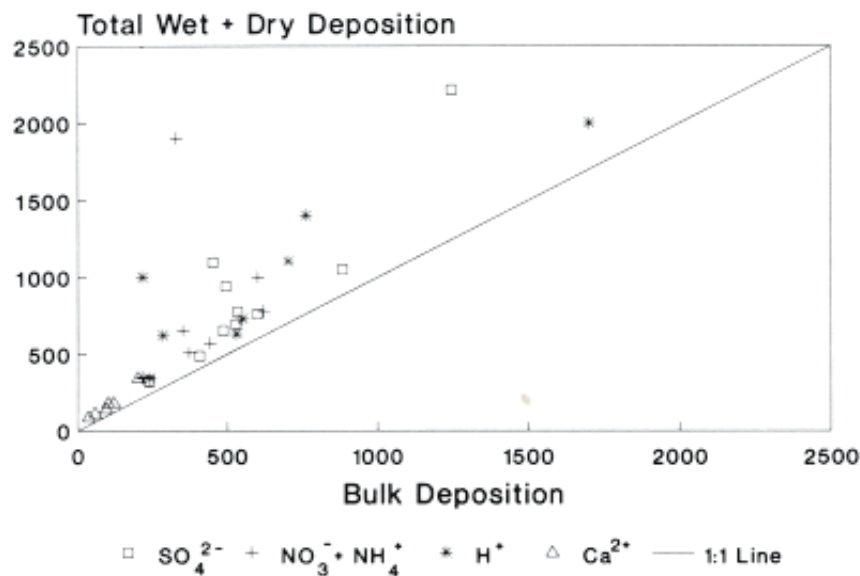


Figure 3.7 The relationship between the measured annual mean bulk deposition and total atmospheric deposition (wet plus dry) determined at each Integrated Forest Study (IFS) site for various ions. Units are $\text{eq ha}^{-1} \text{ year}^{-1}$.

Surface methods may also be the only approaches currently applicable for measurement of aerosol fluxes to forested catchments in mountain areas (Lindberg *et al.*, 1988a) and for quantifying edge effects (Hasselroth and Grennfelt, 1987; Draaijers *et al.*, 1988). Highly complex terrain prevents the application of many standard dry deposition modelling and measurement methods. Although recent developments in the application of eddy-correlation and gradient methods to complex terrain hold some promise (McMillen, 1988), such methods still require empirical methods for validation.

Many approaches have previously been used to determine dry deposition by surface methods (Mayer and Ulrich, 1974; Miller *et al.*, 1976; Bache, 1977; Eaton *et al.*, 1978). A recent critique of dry deposition methods in general concluded that the most promising natural surface analysis methods included foliar extraction, throughfall and watershed mass balance (Hicks *et al.*, 1986). These methods are complementary as they address deposition on different scales, from cm^2 to km^2 . Some of the methods are applicable to dry deposition alone, while others address total wet plus dry deposition and cloudwater interception (Lindberg and Garten, 1988; Lovett, 1988).

3.3.1 BIOMONITORS

The use of various organisms such as carpet-forming mosses and lichens to monitor atmospheric deposition is now well established for trace metals (Rühling and Tyler 1968; 1973; Folkesson, 1979; Rühling *et al.*, 1987; Glooschenko and Arafat, 1988) and for PAH, PCBs and chlorinated pesticides (Thomas *et al.*, 1984; Thomas, 1986). The basis for the technique is that certain bryophytes obtain nearly all of their nutrient supply from the atmosphere via wet deposition. Concentrations inside the moss are then related to atmospheric deposition:

$$D = C \times A \times E^{-1} \quad (3.3)$$

where D is the atmospheric deposition ($\text{mg m}^{-2} \text{ year}^{-1}$), C is the concentration in the biomonitor (mg kg^{-1} dry weight), A is a growth factor ($\text{kg m}^{-2} \text{ year}^{-1}$) and E an efficiency factor which represents the uptake by the organism. Studies in Sweden indicate that *Hylocomium splendens*, a common bryophyte in Swedish coniferous forests, grows relatively uniformly throughout the country at a rate of $0.116 \pm 0.014 \text{ kg m}^{-2} \text{ year}^{-1}$. If one considers that the new shoots cover 75% of the projected surface, a growth factor of about $0.150 \text{ kg m}^{-2} \text{ year}^{-1}$ is obtained. Studies of E for trace metals indicate that it varies according to species and metal (Folkesson, 1979; Ross, 1990b). Highest affinities are thought to be for Pb (100 %), while only 32% of the As is retained (Rühling *et al.* 1987; Steinnes, 1985).

Caution should be used when trying to determine quantitatively atmospheric input to a catchment via biomonitors. For example, interaction of precipitation with the forest canopy will alter the composition of the water; for some substances there could be substantial leaching from the canopy. This effect can be somewhat minimized by taking moss samples in forest clearings. Since the adsorption mechanism is essentially a cation effect, differences in the ionic strength of the precipitation will also influence uptake efficiencies (Steinnes, 1989). With regard to the question whether concentrations in biomonitors actually represent atmospheric deposition, Ross (1990b) has concluded that special care must be taken since interactions in the ecosystem will sometimes dominate metal concentrations inside the biomonitor.

3.3.2 FOLIAR EXTRACTION

Foliar extraction involves the selective removal and analysis of dry deposited material on the surface of foliage. Recent studies have confirmed the applicability of foliar extraction methods to quantifying aerosol dry deposition rates and deposition velocities to both leaves and needles (Lindberg and Lovett, 1985; Bytnerowicz *et al.*, 1987; Davidson and Wu, 1989). Although this method is directly applicable only on the scale of individual leaves and needles, it may be possible to develop mechanistic models of aerosol transfer within whole plant canopies using these approaches. Such studies are now under way, and significant progress is expected in the coming years. Due to its limitations, this method cannot be currently considered for application on the scale of even small catchments. However, a related method which relies on the "natural" washing of foliage by rainfall is applicable on this scale and is described in the following section.

3.3.3 THROUGHFALL METHODS

While foliar extraction methods address processes on the scale of leaves, throughfall and watershed mass balance methods are needed to address deposition to individual trees, forest stands and small catchments. To the extent that deposited material is washed from the canopy by rain, the flux of an ion below the canopy in throughfall provides some information on dry deposition. Relative differences in throughfall fluxes between sites have long been used to estimate differences in atmospheric deposition (Mayer and Ulrich, 1974, 1978). However, ions in throughfall are a sum of the incoming rain, dry deposition and foliar leaching. Hence, net throughfall (NTF), defined as the flux of an ion in throughfall minus its flux in incident precipitation, is a better indicator of the in-canopy effects. For example, Höfken *et al.* (1981) used wet-only fluxes in rain and throughfall to show that dry deposition was much greater to a spruce than to an adjacent beech stand. In addition, controlled washing of protected branches allowed for an estimate of foliar leaching and dry deposition for a variety of ions.

A statistical approach has also been developed to separate ion fluxes in NTF into their component parts

of dry deposition washoff and foliar leaching by Lovett and Lindberg (1984). The approach involves a multiple linear regression of measured NTF fluxes of ions on the duration of the antecedent dry period for each event and on the duration of each event, and requires well defined single event samples of both rain and throughfall. The resulting regression coefficients represent event average dry deposition and foliar leaching rates. Recent measurements of sequential throughfall fluxes on a sub-event basis support the model assumptions that dry deposition washoff is proportional to the antecedent dry period, and that foliar leaching and uptake are strongly influenced by the event duration (Schaefer and Reiners, 1990). Since throughfall includes only material which is washed from the canopy by rainfall, dry deposition that is irreversibly sorbed by the canopy is not measured by this method. Hence, the model results are most reliable for water-soluble components of aerosols, and possibly for soluble gases deposited to leaf exteriors.

The NTF regression model has been applied to several forested sites in both the eastern and western USA and in Europe (Lovett and Lindberg, 1984; Potter, 1987; Lindberg *et al.*, 1990; Sievering *et al.*, 1989; Ragsdale *et al.*, 1991). In these studies the regression model accounted for generally >50% and as much as 90% of the variance in mean NTF fluxes of several ions and yielded statistically significant ($P < 0.05$) dry deposition rates (from the model regression coefficients) for most major ions. Although Sievering *et al.* (1989) have successfully used this model and tested some of its assumptions in a western conifer forest in Colorado, other studies in a conifer forest in Wyoming resulted in no significant regressions (Fahey *et al.*, 1988). It is thought that this is probably due to local climate or to the sampling approach used. Hence, the success of the method is strongly dependent on accurate measurements of antecedent dry period and event duration, and the use of only well-defined single events.

The throughfall model has also been used to address an important limitation of some dry deposition methods, that of scaling from point measurements of deposition to a forest canopy. The mean dry deposition fluxes of Ca^{2+} to several forests in the Integrated Forest Study (IFS) were determined from the regression model. These fluxes were compared to the mean dry deposition rates measured to inert deposition plates which had been exposed above the canopies to determine plateau-canopy scaling factors (SF), where:

$$\text{SF} = (\text{flux to canopy [from model]}) / (\text{flux to plates [measured directly]})^{-1} \quad (3.4)$$

SFs ranged from 1.3 to 5, were proportional to canopy surface area, and were nearly constant from year to year (Lindberg *et al.*, 1988a). The increase in the coarse particle dry deposition (30% to a factor of 5) is due to the larger surface area of the canopy relative to the plates and to increased turbulent flow. If one then assumes that Ca^{2+} is a tracer of the general behaviour of coarse aerosols, SFs can then be used to scale inert surface data for other ions associated with coarse aerosols. [Figure 3.8](#) summarizes total base cation ($\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$) dry deposition inputs for 12 IFS forest stands (Ragsdale *et al.*, 1991). Dry deposition contributed from 17 to 63% (median 49%) of the total base cation input to these forests, was highest in magnitude at the drier Southeastern sites (LP, DL, CP) and lowest at the wetter sites in the Pacific Northwest (RA, DF).

Surface methods such as throughfall could be much simplified if it could be shown that the only source of an ion to NTF was washoff of dry and/or cloudwater deposition. The idea that foliar leaching is insignificant has been suggested for Cl^- , Na^+ , and SO_4^{2-} , but field data conflict as to the accuracy of this assumption (Richter *et al.*, 1983; Cape *et al.*, 1987; Mayer and Ulrich, 1978; and as reviewed by Lovett, 1988). However, recent studies support the hypothesis that foliage leaching is a small component of

SO_4^{2-} NTF. Bredemeier (1988) summarized nutrient cycling data from forests in northern Germany and concluded that throughfall fluxes of SO_4^{2-} are dominated by wet and dry deposition. At the IFS sites in North America and Europe, comparisons of estimated total annual atmospheric deposition of SO_4^{2-} with measured fluxes in throughfall plus stemflow (Lindberg, 1992) indicate that the variance in throughfall plus stemflow fluxes account for 95% of the variance in estimated deposition (Figure 3.9), and suggests minor canopy exchange for SO_4^{2-} . Total deposition was estimated using state-of-the-art methods (Lindberg *et al.*, 1989) and models (Hicks *et al.*, 1987) with chemical, surface structure and meteorological data collected at each site for up to three years.

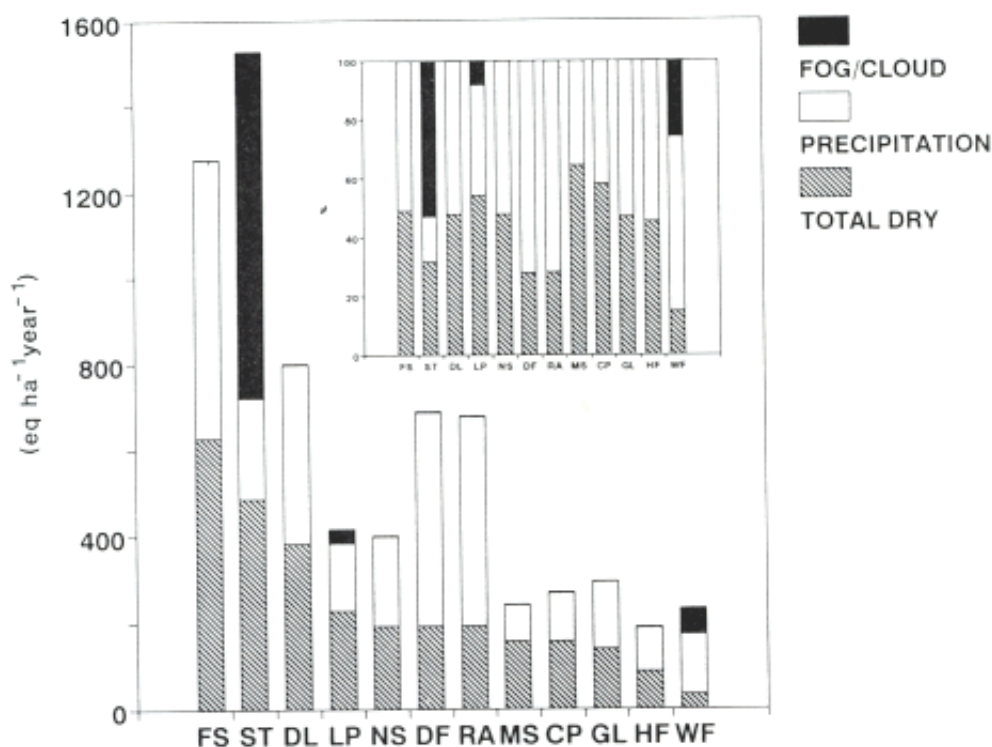


Figure 3.8 Estimated total dry and wet deposition of the sum of base cations ($\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$) to sites in the Integrated Forest Study (adapted from Ragsdale *et al.*, 1991). Site codes and elevations as follows: FS = Gainesville, FL (pine, 38 m a.s.l.); ST = Smoky Mountains, NC (spruce, 1740 m a.s.l.); DL = Duke Forest, NC (pine, 215 m a.s.l.); LP = Oak Ridge, TN (pine, 300 m a.s.l.); NS = Nordmoen, Norway (spruce, 200 m a.s.l.); DF = Thompson Forest, WA (fir, 220 m a.s.l.); RA = Thompson Forest, WA (alder, 220 m a.s.l.); MS = Howland, ME (spruce, 65 m a.s.l.); CP = Coweeta Hydrologic Laboratory, NC (pine, 800 m a.s.l.); GL = Grant Forest, GA (pine, 175 m a.s.l.); HF = Huntington Forest, NY (mixed deciduous, 530 m a.s.l.); WF = Whiteface Mountain, NY (spruce/fir, 1000 m a.s.l.).

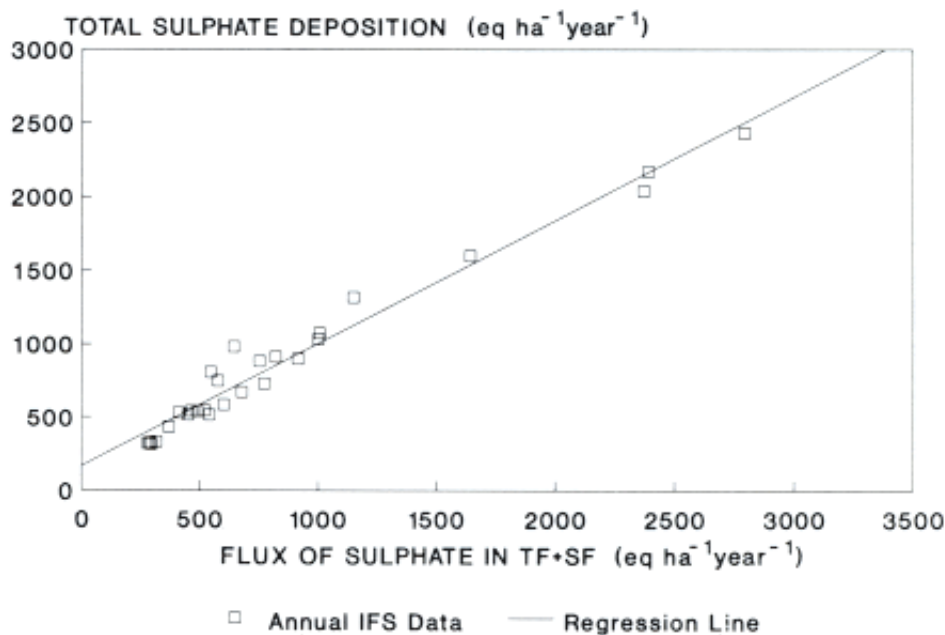


Figure 3.9 Relationship between the estimated total atmospheric deposition of SO_4^{2-} and the measured flux of SO_4^{2-} in throughfall (TF) plus stemflow (SF) for sites in the Integrated Forest Study (source: Lindberg and Garten, 1988; Lindberg 1992). Shown is the 1:1 line for comparison (the regression line has a slope of 0.85, an intercept of 140, and $r^2=0.97$).

Direct measurements of foliar leaching have recently been reported for mature conifer and deciduous trees internally labelled with $^{35}\text{SO}_4^{2-}$ (Garten *et al.*, 1988; Lindberg and Garten, 1988; Garten, 1990). The minor contribution of foliar leaching of SO_4^{2-} was confirmed in these studies; internal sulphur contributed an average of 6% of SO_4^{2-} in NTF and »3% of the total flux of SO_4^{2-} in throughfall. These experiments also indicated that a significant portion of dry-deposited SO_2 appears as SO_4^{2-} in throughfall. The authors concluded that, given the uncertainty in all deposition estimates, measurements of fluxes of SO_4^{2-} in through fall beneath forests can provide useful estimates of spatial and temporal trends in the atmospheric deposition of sulphur in industrialized areas. The results of these studies contradict earlier data from a Scots pine stand in Great Britain where foliar leaching was concluded to be the primary source of SO_4^{2-} in throughfall (Cape *et al.*, 1987). More recent experiments with $^{35}\text{SO}_4^{2-}$ applied to soils at this site tend to support the conclusions of minor foliar leaching at this site as well (Cape *et al.*, 1990). However, both studies noted the potential for non-steady state behaviour of the applied $^{35}\text{SO}_4^{2-}$ tracer, suggesting that further testing of these approaches on various forest types under different conditions, and comparison of the data with results of micrometeorological methods, are clearly needed.

If the results of these studies are representative, the measurement of SO_4^{2-} fluxes in throughfall will be an important tool for characterizing input to forested catchments on scales where long-range transport model results may be inappropriate or inaccurate. For example, Ivens *et al.* (1990) compared modelled sulphur deposition rates to European forests using regional scale long-range transport models with extensive throughfall data. He concluded that the models significantly underestimated sulphur deposition to conifer forests where throughfall data were available. Interestingly, the throughfall and model results were comparable for deciduous forests. However, this agreement may be fortuitous if the long-range

models do not account for lower dry deposition to leafless, deciduous forests in winter. Thus, it is possible that they underestimate fluxes to the leafy canopy, and overestimate them to the barren canopy. The need for on-site data is clear. Although these comparisons were made for sulphur fluxes in forests, recent data indicate that throughfall methods may also be applied to deposition of some nitrogen compounds in forests (Ivens, 1990; Wyers *et al.*, 1990; Lovett, 1992) and to deposition of sulphur and nitrogen in non-forested catchments (Bobbink *et al.*, 1990).

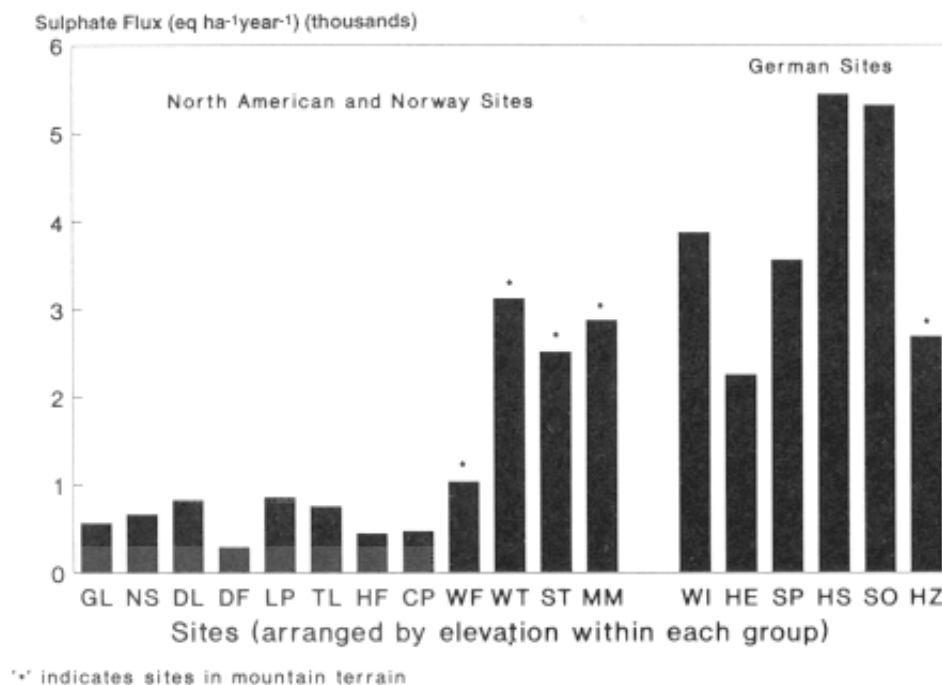


Figure 3.10 Measured annual throughfall fluxes of SO_4^{2-} to high and low elevation forests (source: Bredemeier, 1988; Mohnen, 1988; Wolfe, 1988; Lindberg and Lovett, 1992; Lindberg, 1992; Shepard *et al.* 1989). The site codes and elevations are as follows: GL = Grant Forest, GA (pine, 175 m a.s.l.); NS = Nordmoen, Norway (spruce, 200 m a.s.l.); DL = Duke Forest, NC (pine, 215 m a.s.l.); DF = Thompson Forest, WA (fir, 220 m a.s.l.); LP = Oak Ridge, Tennessee (pine, 300 m a.s.l.); TL = Turkey Lakes, Ontario, Canada (mixed deciduous, 350 m a.s.l.); HF = Huntington Forest, New York (mixed deciduous, 530 m a.s.l.); CP = Coweeta Hydrologic Laboratory, North Carolina (pine, 800 m a.s.l.); WF = Whiteface Mountain, New York (spruce/fir, 1000 m a.s.l.); WT = White Top Mountain, VA (spruce, 1690 m a.s.l.); ST = Smoky Mountains, NC (spruce, 1740 m a.s.l.); MM = Mount Mitchell, NC (spruce, 1950 m a.s.l.); WI = Wingst, FRG (spruce, 40 m a.s.l.); HE = Heide, FRG (pine, 80 m a.s.l.); SP = Spanbeck, FRG (spruce, 250 m a.s.l.); HS = Hils Mountains, FRG (spruce, 460 m a.s.l.); SO = Solling, FRG (spruce, 500 m a.s.l.); HZ = Harz Mountains, FRG (spruce, 700 m a.s.l.),

Figure 3.10 illustrates the range in annual average SO_4^{2-} throughfall fluxes to the forest floor of several North American and European forests. If our understanding of canopy processing mechanisms is correct for SO_4^{2-} , then these trends strongly reflect differences in total atmospheric deposition to these forests. In North America, the trend of higher fluxes at mountain sites is apparent. However, this trend is less apparent at the German sites, possibly due to the stronger influence of local sources near some of these sites. The fluxes to the low-elevation sites in Germany far exceed those to the low elevation sites in Norway and North America. The fluxes to the high-elevation sites in North America, where deposition is significantly enhanced by the interception of cloudwater (Lovett *et al.*, 1982) approach those at the German sites. This suggests that SO_4^{2-} fluxes to forests in Central Europe are generally much higher

than in North American forests, but that some forests in mountainous terrain of the USA may experience the levels of SO_4^{2-} loading typical of forests in Germany.

The deposition of nitrogen is commonly less of an issue in forest catchments than sulphur, because nitrogen is generally utilized by the forest and therefore does not significantly interact with soil water and streamflow. In low-elevation forests not directly influenced by local emissions of NH_3 , the input of inorganic nitrogen is comparable to or less than that of sulphur (see [Figure 3.11](#) comparing the IFS sites). In forests where nitrogen deposition exceeds the forest requirement, "nitrogen saturation" may occur (this volume, [Chapter 11](#)). This in turn may lead to significant nitrogen leaching and elevated levels of Al and H^+ in streamflow. Such is the case at the high elevation Smoky Mountains sites in the IFS (Johnson *et al.*, 1991), where deposition is enhanced by cloud interception to approximately $30 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (e.g. site ST in [Figure 3.11](#)).

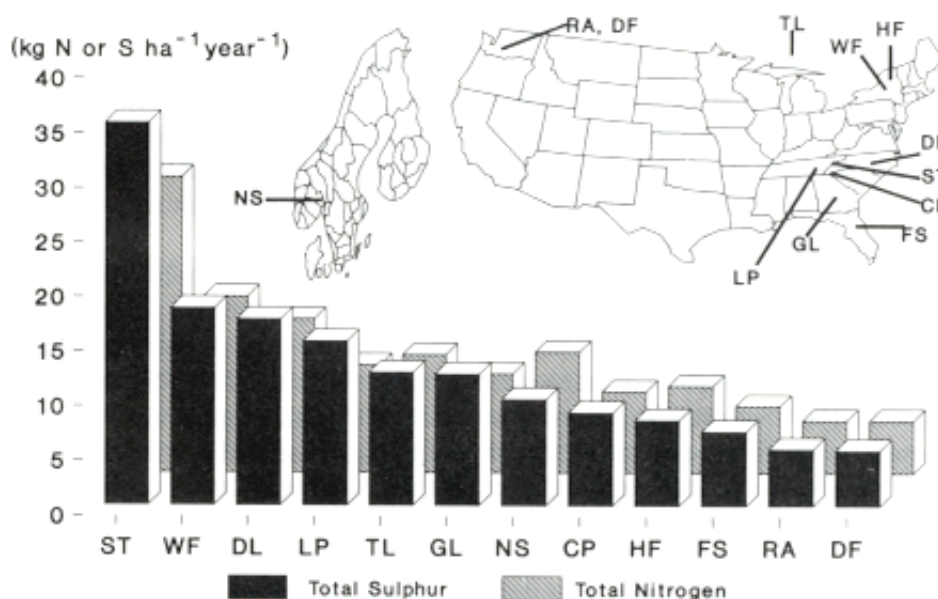


Figure 3.11. Deposition fluxes of sulphur and total nitrogen ($\text{NO}_3^- + \text{NH}_4^+$) delivered to the canopies of forests in the Integrated Forest Study (IFS) by wet, dry and cloudwater processes.

The use of throughfall to estimate nitrogen deposition to forests and catchments is open to debate. There appears to be significantly more canopy interaction of both wet- and dry-deposited nitrogen compounds than occurs for sulphur, with most canopies absorbing deposited nitrogen (Lindberg *et al.*, 1987). However, under some conditions, such as the high loading of NH_3 that occurs in some European forests, throughfall may approximate deposition when the canopy capacity for uptake is greatly exceeded (Ivens, 1990). In areas of less extreme loading, it may also be possible to establish a relationship between fluxes of nitrogen in throughfall and fluxes in total deposition. This has recently been reported for the IFS forests discussed earlier. Lovett (1992) found that the annual fluxes of total inorganic N ($\text{NO}_3^- + \text{NH}_4^+$) in deposition were strongly related to their annual fluxes in throughfall ($r^2 = 0.80$). The slope of the relationship indicated that the IFS forests on an average absorbed about 40% of the deposited nitrogen. Although this relationship is not as robust as that for sulphur discussed above, it does suggest that the method may be useful given sufficient data to establish a regression.

3.3.4 MASS BALANCE STUDIES OF SULPHUR

Throughfall methods are generally limited in space to forest plots or small catchments ($\gg 100$ s of m^2). If locations exist where deposited SO_4^{2-} is a conservative ion within an entire watershed, hydrologic mass balance methods may be used to derive mean deposition rates over larger spatial and possibly longer time scales. These calculations require that the hydrologic cycle of the system be well characterized and that significant sources and sinks of SO_4^{2-} do not exist within the system, or are well quantified.

Three recent studies have successfully applied mass balances in the northeastern USA and in Sweden where the SO_4^{2-} adsorption capacity of soils is low and therefore insignificant year-to-year or long-term accumulation may be assumed. Norton *et al.* (1988) used SO_4^{2-} concentrations in surface waters of six lakes in Maine along with SO_4^{2-} wet deposition data, estimates of sulphur storage and hydrologic budgets to estimate dry deposition. Their results suggested that dry deposition was highly variable in space, and contributed from 0 to $>50\%$ of the total SO_4^{2-} deposited. The contribution increased with watershed size, relief and vegetation area. However, only relative and not absolute dry deposition rates were determined with these data.

At forested catchments near Lake Gårdsjön in Sweden, Hultberg and Grennfelt (1990) have monitored the fluxes of sulphur for ten years. They report that the long-term mean fluxes of SO_4^{2-} in throughfall and streamflow within a given catchment are similar to each other, and that this relationship holds across a range of catchments. The SO_4^{2-} fluxes in stream runoff increased linearly with the proportion of the catchment that was forested, indicating that runoff was strongly linked to dry and cloudwater deposition which increase similarly. In a related study, a close relationship between the dry deposition of sulphur estimated from mass balance calculations and from air concentration data was observed (Grennfelt *et al.*, 1985; Hultberg, 1985). In an attempt to determine the plant mobility of internal sulphur on a catchment scale, these authors amended soils of one catchment with Na_2SO_4 , and soils of another with elemental sulphur. These forms of sulphur were used to simulate both highly mobile (Na_2SO_4) and slowly released (elemental sulphur which is slowly oxidized to SO_4^{2-}) forms of SO_4^{2-} . Results of both studies, carried out over several years, indicated no increase of SO_4^{2-} in throughfall, only in streamflow, confirming the conclusions from the sulphur isotope throughfall studies discussed above.

Likens *et al.* (1990) used 23 years of data on hydrologic fluxes of SO_4^{2-} in bulk deposition and streamflow with estimates of weathering and gaseous losses and changes in biological pools to estimate dry deposition rates for the Hubbard Brook watershed. For this system the authors maintained that the most significant variables in the SO_4^{2-} budget are wet and dry deposition and streamflow since cloudwater interception is insignificant in this forest; hence:

$$\text{Dry deposition} = \text{Stream export} - \text{wet deposition input} \quad (3.5)$$

A regression analysis was used to estimate a long-term mean dry deposition rate of between 400 and 500 $\text{eq SO}_4^{2-}\text{-S ha}^{-1} \text{ year}^{-1}$ which was approximately 40% of the estimated mean total sulphur input (Figure 3.9). Shorter term estimates were subject to large uncertainty due to changing hydrologic conditions, but indicated no significant long-term trend in dry deposition at this site.

3.4 CONCLUSIONS

This chapter has summarized processes which transfer water and chemical compounds from the atmosphere to small catchments. It has emphasized that large spatial variations in deposition can occur, which are primarily due to the interaction of the atmosphere and the catchments, physiography and biota. For estimating atmospheric inputs accurate estimates of wet and dry deposition are required. For high elevation sites, information on cloudwater deposition is also crucial.

It is now quite clear that estimates of catchment inputs based solely on bulk deposition measurements or data are subject to serious error. The implications of using highly unreliable results from bulk deposition measurements to quantify biogeochemical processes in catchments or to understand the role of atmospheric deposition in catchment studies, are now clear. However, the intensive methods needed to measure accurately total deposition are not yet available for widespread use in typical catchment studies.

Over the past ten years important progress has been made in the development and application of various surface analysis methods for quantifying atmospheric inputs to small catchments where micrometeorological methods are not applicable. While some of these methods are most applicable to SO_4^{2-} , detailed data on the spatial and temporal trends in sulphur deposition can be used to develop landscape-scale deposition models which will be useful for quantifying inputs of other airborne constituents to small catchments. For example, spatial maps of SO_4^{2-} fluxes in throughfall and net throughfall in catchments in complex terrain provide data on the terrain and vegetation features that influence atmospheric wet and dry deposition in general. Thus, throughfall studies will be useful for analysis of spatial patterns in deposition to catchments over event-to-seasonal time scales. Small catchment mass balance studies of SO_4^{2-} and Cl^- are most applicable over annual- to-longer time scales, provide areal averaged deposition rates, and can be used to estimate temporal trends in mean annual fluxes. Their applicability is limited to areas where release of sulphur from weathering of bedrock is known to be negligible. In addition, these methods may provide data for: (1) testing of regional deposition models; (2) development and testing of process-level models of in-canopy and whole-canopy dry deposition; and (3) comparison with results of the initial applications of micrometeorological methods to deposition in complex terrain. However, some assumptions of these methods have not been rigorously tested and require further evaluation in field and controlled studies.

3.5 SUGGESTED READING

There have been several useful discussions of aspects of deposition measurement in the recent literature pertinent to this chapter. These include a critique of dry deposition methods (Hicks *et al.*, 1986); a review of atmospheric deposition in mountainous forests (Lovett and Kinsman, 1991); a summary of the US National Acidic Precipitation Assessment Program Deposition data (Hicks *et al.*, 1990; Sisterson *et al.*, 1990); and two books on atmospheric deposition and forest biogeochemistry, one on whole catchment studies (Johnson and Van Hook, 1989), and one on forest plot studies (Johnson and Lindberg, 1992).

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