Reports

Atmospheric Deposition of Metals to Forest Vegetation

Abstract. *Atmospheric deposition during the growing season contributes one-third or more of the estimated total flux of lead, zinc, and cadium from the forest canopy to soils beneath an oak stand in the Tennessee Valley but less than 10 percent of the flux of manganese. The ratio of the wet to dry deposition flux to the vegetation during this period ranges from 0.1 for manganese to 0.8 for lead to ~ 3 to 4 for cadmium and zinc. Interactions between metal particles deposited on dry leaf surfaces and subsequent acid precipitation can result in metal concentrations on leaves that are considerably higher than those in rain alone.*

Forest vegetation is the initial point of contact between the atmosphere and the ground for much of the eastern United States, and yet the atmospheric deposition of trace elements to forested ecosystems has not been studied in detail. With the recent emphasis on understanding acid precipitation, extensive monitoring programs for atmospheric deposition in general are being considered (*1*); however, the information on the temporal and spatial character of deposition is insufficient to permit one to design a widely applicable sampling strategy. We describe here an investigation of the rates and processes of Cd, Mn, Pb, and Zn deposition to a forest canopy at Walker Branch Watershed, a catchment in the Tennessee Valley known to receive acid precipitation [2-year mean *p*H ~ 4.1 (*2*)]. Our data illustrate the variability in atmospheric deposition, its particular importance in the biogeochemical cycle of Pb, and the need to consider the interaction between acid precipitation and deposited particles.

These measurements provide a data base useful in the design of deposition monitoring networks. Our data on dry deposition are limited but are presented to explore the potential importance of a process for which there are no generally accepted sampling methods. We used flat-plate and foliage collection techniques to estimate dry deposition to the oak canopy during the 1977 growing season (*3*) and wetfall-only collectors to sample rainfall above and below the canopy on an event basis. Details of the sampling and analytical methodology and precision are available (*2*).

The forest canopy is exposed to a wide range of conditions resulting from variable deposition rates and mechanisms. The atmospheric deposition to upper canopy surfaces in this deciduous forest during wet-dry cycles lasting several days (Table 1) may consist of comparable contributions by wet and dry processes or may be dominated by either. The ratio of wet to dry deposition input during these periods (not including 9 to 16 May) ranges from 0.07 to 26 (mean = 5.0, standard deviation = 7.7). For short-duration, small-amount rain events (storms of < 0.5 cm occur with a frequency of ~ 40 percent), wet deposition gives rise to a more intense inundation of the vegetation surface with trace metals than dry deposition. Single-event wet deposition rates exceed dry deposition rates during the intervening periods by factors ranging from 40 to 11,000 (Table 1). However, the residence time of dry-deposited material is generally longer than that of precipitation-delivered material. The mean duration of dry periods at this site is ~ 5 days (range, 0.2 to 16 days), whereas that for rain events is 0.7 day (0.04 to 2.4 days); this finding suggests that the leaf contact time for dry deposition is considerably longer than for wet deposition. The pronounced differences in the temporal character of wet and dry deposition may have important implications for ecological assessment. Exposure dynamics have a strong influence on the effects that gaseous air pollutants may have on plants (*4*); however, data necessary to assess such effects of wet- and dry-deposited metals are not yet available.

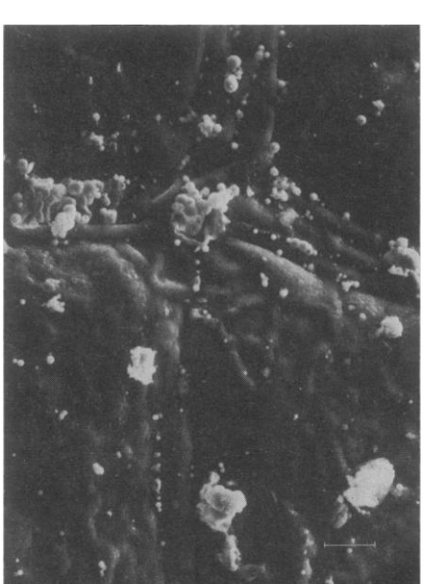

Fig. 1. Adaxial surface of a chestnut oak leaf (*Quercus prinus*) collected in the upper canopy (scale bar, 30 μm). Deposited particles (resolution, ~ 0.5 μm) are heterogeneously distributed on the leaf, often occurring as aggregates in surface irregularities of the leaf.

Wet and dry deposition interacting with the canopy over a period of several weeks results in a considerable variability in the water-soluble metal concentrations on leaves collected over a range of spatial scales from millimeters (disks cut from same leaf) to kilometers (leaves collected across the watershed). Mean surface concentrations (in nanograms per square centimeter) generally vary over an order of magnitude: 0.035 to 0.30 for Cd, 0.60 to 18 for Pb, 1.9 to 37 for Zn, and 91 to 120 for Mn, with no consistent trend in concentrations between spatial scales. The degrees of variability within each spatial scale are considerable, on the order of 30 percent (coefficient of variation of the mean, that is, the standard deviation divided by the mean) for Mn, 75 percent for Pb, and 120 percent for Zn and Cd, and are relatively independent of spatial scales ranging from 10^{-3} to 10^{3} m. Examination of leaves by scanning electron microscopy reveals a heterogeneous distribution of particles on adjacent leaves as well as on the same leaf (Fig. 1), reflecting the variability in metal concentrations.

Interactions between moisture on vegetation and previously dry-deposited material can result in dissolved metal concentrations at the leaf surface that are ~ 50 to 500 times higher than those we measured in rain alone (*5*). Leaf moisture arising from light showers or intercepted fog is common, has high initial metal concentrations and acidity, wets the leaf but does not necessarily flush it, and is often evaporated before runoff (*2*). For example, the events occurring during 16 to 20 May (Table 1) result in the following estimated metal concentrations (in micrograms per liter) in solution on the leaf surface due to particle dissolution in rain and partial moisture evaporation (*6*): Cd ~ 13, Zn ~ 120, Pb ~ 230, and Mn ~ 1300. Surface-deposited metals can be absorbed by vegetation, but their physiological effects are not clearly defined (*7, 8*).

We determined particle deposition ve-

0036-8075/82/0326-1609$01.00/0

locities (V_d, in centimeters per second) (*9*) to individual surfaces in the upper canopy from the ratio of the dry deposition flux (Table 1) to the concentration in air (*10*). Particle-associated metals characterized by larger mass median diameters (MMD, in micrometers) exhibited higher deposition velocities [for Mn, MMD = 3.4 ± 0.7, V_d = 6.4 ± 3.6; for Cd, MMD = 1.5 ± 0.7, V_d = 0.37 ± 0.18; for Zn, MMD = 0.9 ± 0.2, V_d = 0.38 ± 0.10; for Pb, MMD ≤ 0.5, V_d = 0.06 ± 0.01 (means and standard errors of four experiments for each metal)]. These data indicate that the use of the often-cited V_d value of 0.1 cm sec^{-1} (*11*) may lead to large errors in estimates of dry deposition fluxes to forests, particularly when one is considering the fully foliated canopy (*12*).

The degree of spatial and temporal variability in metal deposition rates and limitations in the extent of our dry deposition sampling permit only rough approximations of deposition fluxes during the 208-day forest growing season (*13*). Such estimates are useful in assessing the potential importance of deposition to forest ecosystems. Deposition appears to be of particular importance in the biogeochemical cycle of Pb; nearly 100 percent of the estimated total growing-season flux to the forest floor (~ 8 mg m^{-2}, which includes wet and dry deposition to the canopy, foliar leaching, leaf fall, and dry deposition directly to the forest floor) can be accounted for in terms of the atmospheric deposition to the canopy alone. This external flux exceeds the internal flux (leaf fall plus foliar leaching) by a factor of ~ 90. The estimated ratio of wet to dry deposition of Pb to the canopy during the growing season (0.8) suggests a comparable contribution by each process.

Atmospheric deposition does not dominate the estimated total growing-season flux to the forest floor of Cd, Zn, or Mn; the atmosphere contributes 30 to 40 percent of the Cd and Zn and ~ 10 percent of the Mn flux (total fluxes ~ 0.8, 20, and 200 mg m^{-2}, respectively). Atmospheric deposition is dominated by precipitation for Cd and Zn (estimated wet to dry flux ratio ~ 3 to 4) but by dry deposition for Mn (ratio ~ 0.1). Foliar leaching appears to be the major internal pathway for the transfer of Cd from the forest canopy to soils, exceeding leaf fall by a factor of 10, whereas leaf fall is comparable to foliar leaching as transfer pathways for Mn and Zn.

The atmospheric deposition of soluble metals results in both long-term and episodic exposure of forest canopy surfaces. Light rain, fog, and dew solubilize particulate trace metals on leaves, enhancing the potential for interaction with internal tissue (*8*) and possibly increasing the deposition of SO_2 and its associated acidity through the catalytic action of Mn^{2+} (*14*). Rainfall removes some fraction of both soluble and particulate metals from the canopy and produces an episodic flux to forest soils. The concentrations and speciation of metals in rain will be modified by interactions in the canopy among rain, particles, and dissolved organic material leached from plant tissue (*2, 5, 15*).

The quantification of the interactions between wet and dry deposition and the resulting conditions to which vegetation is exposed requires monitoring networks to sample wet and dry deposition separately, and on an event basis. Our estimates of the ratio of wet to dry deposition and of atmospheric deposition to the total flux to the forest floor suggest that atmospheric deposition of metals should not be neglected and that dry deposition must be included in future sampling strategies. If the primary sources of atmospheric Pb, Cd, and Zn are anthropogenic (*16*), man may be exerting a significant influence on the cycle of these elements in the forest environment. More attention should be focused on the combined effects of trace metal and acid deposition in studies of atmosphere-biosphere interactions.

Table 1. Atmospheric deposition rates and fluxes to upper-canopy surfaces in Walker Branch Watershed (*3*). These data represent one dry period for which deposition rates measured by leaf washing and surrogate surface collection are compared (9 to 16 May) and four other periods including both wet and dry deposition, all of which occurred during the forest growing season.

Period	Rainfall amount (cm)	Deposition surface	Deposition rate (pg cm^{-2} $hour^{-1}$)*								Deposition flux (μg cm^{-2})					
			Dry				Wet				Dry				Wet			
			Mn	Zn	Cd	Pb	Mn	Zn	Cd	Pb	Mn	Zn	Cd	Pb	Mn	Zn	Cd	Pb
2–13 April†	16.2	Inert	58	4.2	0.50	22	3,900	540	20	1,400	13	0.95	0.11	5.0	130	18	0.66	46
9–16 May‡	0	Inert	62	8.3	0.14	15	0	0	0	0	10	1.4	0.02	2.5	0	0	0	0
9–16 May‡	0	Leaves	28	5.8	0.10	1.7	0	0	0	0	4.7	0.97	0.02	0.28	0	0	0	0
16–20 May§	0.13	Inert	120	9.6	0.75	62	19,000	2,300	270	2,400	12.1	0.97	0.08	6.2	3.2	0.39	0.05	0.41
30 May–6 June‖	0.30	Inert	190	3.2	0.03	12	7,100	1,100	270	4,600	32	0.54	0.005	2.0	3.4	0.53	0.13	2.2
12–18 July¶	0.20	Inert	88	3.2	0.08	24	4,600	3,700	310	2,500	13	0.46	0.01	3.4	0.78	0.63	0.05	0.42

*Rates are normalized to the duration of either the wet or the dry event. †Wet event duration, 33 hours; total duration, 259 hours. ‡Total duration of dry period, 167 hours. §Wet event duration, 0.17 hour; total duration, 101 hours. ‖Wet event duration, 0.48 hour; total duration; 168 hours. ¶Wet event duration, 0.17 hour; total duration, 144 hours.

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3. During five experiments over 35 days of the 207-day growing season (Table 1), prewashed polyethylene petri dishes were exposed in the forest canopy and then leached to determine particulate metal retention. For comparison, we washed oak (*Quercus prinus*) leaves collected in the upper canopy over short time periods to determine the net accumulation of deposited metals. Leaf surface areas were determined by a light attenuation method (Lambda area meter). Results of the methods are compared in Table 1. A critique of surrogate surface methods for dry deposition, our response to these comments, and justifications of such methods have been published [R. A. Kerr, *Science* **211**, 692 (1981); B. B. Hicks, M. Wesely, J. L. Durham, *Critque of Methods to Measure Dry Deposition* (Report EPA-600/9-80-050, Environmental Protection Agency, Washington, D.C., 1980)]. We sampled 80 percent of the growing-season rainfall (91 cm) by using automated samplers. Suspended parti-

cles were collected above the canopy by filtration and with cascade impactors. We extracted and analyzed for the water- and dilute acid–soluble (0.1*N* Ultrex HNO_3) fraction of each metal by using flameless atomic absorption spectroscopy; insoluble material is not readily available for uptake by plants (*7*).
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6. These values were estimated from the measured concentrations of distilled water–soluble metals that had accumulated on upper-canopy surfaces during the 2.4-day dry period preceding the rain event on 18 May. The metal concentrations result from the dissolution of this material in the rain, the initial composition of which was measured; the solution was then concentrated to 1/10 of its earlier volume by evaporation. Factors influencing these calculations are as follows: (i) rainfall *p*H; as *p*H decreases, dry deposition solubility increases; (ii) moisture contact time with the leaf; although heavier rains result in runoff, brief drizzle and captured fog droplets may remain on the leaf surface for 2 to 5 hours prior to evaporation; (iii) degree of concentration by evaporation; any value could be used because ultimately the solution volume reaches zero; and (iv) deposited-particle distribution on the leaf surface; as suggested in Fig. 1, considerably higher (or lower) concentrations than the surface average value determined here can occur on smaller areas of the leaf.
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10. We sampled suspended particles above the forest canopy (*3*) during four periods simultaneously with the exposure of flat plates in the canopy (Table 1). The wind speeds during each period were as follows (given as the frequency of occurrence of speeds in each of three classes, ≤ 0.8, 0.8 to 2.5, and > 2.5 m sec^{-1}); for 9 to 16 May, 49, 32, and 19; for 16 to 20 May, 56, 40, and 4; for 30 May to 6 June, 47, 40, and 13; and for 12 to 18 July, 58, 33, and 9. Mass median diameters were calculated from particle size distributions determined from cascade impactor samples collected during each period. Further details of air quality and meteorological conditions are available (*2*).
11. *Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Ecological Consequence of Fossil Fuel Combustion* (National Academy of Sciences, Washington, D.C., 1981).
12. An upper-limit approximation of the effect of the canopy is the product of the single-surface deposition rate and the leaf area index (~ 6 m^2, foliar surface area per square meter of ground surface area).
13. Wet deposition above and below the canopy is the product of the growing season (1 April to 25 October 1977) precipitation or throughfall amount and the volume-weighted mean concentration in each. The sampling plus analytical reproducibility for wetfall is ± 5 to 15 percent, whereas rainfall amounts are accurate to ± 5 percent (*2*). We calculated the dry-deposition flux by using a simplified two-layer canopy (above and below canopy closure) for which deposition rates were measured separately (*2*), the temporal variation in the leaf area index, and the mean dry-deposition rates measured to inert surfaces (Table 1, relative standard errors of the means range from 0.23 for Mn, 0.24 for Zn, 0.33 for Pb, to 0.47 for Cd). Foliar leaching is calculated as the difference between the wet-deposition flux below the canopy (throughfall flux) minus the sum of the wet- plus dry-deposition fluxes to the canopy itself.
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Global Sea Level Trend in the Past Century

Abstract. *Data derived from tide-gauge stations throughout the world indicate that the mean sea level rose by about 12 centimeters in the past century. The sea level change has a high correlation with the trend of global surface air temperature. A large part of the sea level rise can be accounted for in terms of the thermal expansion of the upper layers of the ocean. The results also represent weak indirect evidence for a net melting of the continental ice sheets.*

Sea level change is of current interest because of its possible sensitivity to climate change. It has been suggested, for example, that global warming due to increasing atmospheric CO_2 could melt the marine West Antarctic ice sheet, raising the global sea level 5 to 6 m (*1*). A sea level rise of as little as 15 cm may double the probability of damaging storm surges on the coast of Britain (*2*). Such a rise would also cause substantial beach erosion and the intrusion of seawater into low-lying areas that are now freshwater regions.

Many processes affect the sea level position measured on shorelines. Among the most important are eustatic sea level changes due to changes in the ocean water volume, caused mainly by the melting or growth of ice sheets, and isostatic adjustments of the earth's crust, caused mainly by ice sheet growth or decay and the associated change in the ocean water mass (*3, 4*). Tectonic movement and river sedimentation can generate local sea level trends comparable to eustatic and isostatic changes, as can changes in ocean currents and prevailing winds, although such trends are of limited duration.

We used tide-gauge measurements to estimate global sea level change in the past century. Data from more than 700 stations were obtained from the Institute for Oceanographic Science, Birkenhead, England. We excluded stations with records shorter that 20 years (a majority of the stations) and stations in seismically active areas such as the Pacific coast of Japan and in rapidly subsiding localities such as Galveston, Texas, and the Mississippi delta. The remaining 193 stations were divided into 14 regions on the basis of geographic proximity and the expected similarity of isostatic or tectonic behavior.

We reduced the individual station records to a common reference point by fitting a least-squares regression line to sea level as a function of time and by defining the zero point to be the value of the regression curve for 1940. The annual mean sea level curves for stations within a geographical region were then averaged to yield a mean sea level curve for each region. We obtained the global mean sea level curve by averaging the regional mean sea level curves, weighting each region equally (excluding the isostatically uplifting region of Scandinavia). Sea level trends, obtained by fitting a regression line through the mean sea level curves, are summarized in Table 1.

We also attempted to remove the long-term (usually 6000-year) sea level trends from the station data in order to obtain short-term sea level fluctuations, which are perhaps more appropriate for correlation with global climate variations in the past century. The cause of the long-term trend is uncertain. It has been argued that as much as 90 percent of it is residual isostatic uplift of continents due to the removal of the Wisconsin ice sheets (*4*). However, the long-term trend may contain a eustatic component, for example, due to a change in volume of the Antarctic or Greenland ice sheets.

The estimates for long-term sea level change are based on ^{14}C dating of measured positions of shoreline indicators in the geologic records, for example, mollusks, corals, and brackish-water peats (*5*). The 6000-year time interval was chosen to be as large as possible without approaching the period of the North American and European ice sheets, thus minimizing the effect of errors in the estimated sea level trend. However, for Scandinavia, where there has been a high rate of isostatic uplift since the last deglaciation, we used as a time interval the last 2500 years to improve the likelihood of obtaining a linear trend applicable to the past century. We corrected the dating of sea level positions to use the recent 5730-year estimate for ^{14}C half-life (*6*), rather than the 5570-year standard that had been used for most of the records (*5*), and to account for past atmospheric ^{14}C fluctuations (*7*).

The raw global sea level trend that we obtain for the past century is a rise of about 12 cm per century. After subtraction of the long-term trend, the result is a rise of 10 cm per century or 1 mm/year. The inferred long-term trend of 2 cm per century is very small as compared to the long-term trends of 1 m per century or more that are common at times of continental ice sheet growth or decay (*3*). Evidently the past few millennia have remained too warm to permit ice sheet formation on the North American or

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