

Atmospheric Deposition to Oak Forests along an Urban–Rural Gradient

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To determine the patterns of atmospheric deposition and throughfall in the vicinity of a large city, bulk deposition, oak forest throughfall, and particulate dust deposition were measured at sites along a transect within and to the north of New York City. Concentrations and fluxes of NO_3^- , NH_4^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , and Cl^- in throughfall all declined significantly with distance from the city, while hydrogen ion concentration and flux increased with distance from the city. Most of the change in concentrations and fluxes occurred within 45 km of the city. Throughfall deposition of inorganic N was twice as high in the urban sites as compared to the suburban and rural sites. Bulk deposition patterns were similar to those of throughfall, but changes along the transect were much less pronounced. The water-extractable component of dust deposition to Petri plates also was substantially higher in the urban sites for Ca^{2+} , Mg^{2+} , SO_4^{2-} , NO_3^- , and Cl^- . The dust particles had little alkalinity, suggesting that alkaline aerosols were neutralized by acidic gases in the atmosphere. We propose that dust emissions from New York City act like an “urban scrubber”, removing acidic gases from the atmosphere and depositing them on the city as coarse particle dry deposition. Despite the urban scrubber effect, most of the dry deposition of nitrate was from gaseous nitrogen oxides, which were in much higher concentration in the city than in rural sites. Excess deposition of nutrients and pollutants could be important for the nutrient budgets of forests in and near urban areas.

Introduction

Atmospheric deposition is an important source of nutrients and pollutants to ecosystems, and it is frequently measured

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as a part of ecosystem studies and regional pollutant monitoring networks (1). In the United States, air pollution monitoring is a fragmented enterprise. On one hand, national-scale networks have been established to measure atmospheric deposition of major nutrients in pollutants both in wet deposition (National Atmospheric Deposition Program/National Trends Network; 2) and in dry deposition (Clean Air Status and Trends Network; 3). These networks avoid sampling in urban areas because they seek to quantify major regional and national patterns rather than local influences. On the other hand, the U.S. government requires monitoring concentrations of health-related “criteria pollutants” to ascertain compliance with air quality standards. This monitoring is carried out by the states and occurs primarily in urban areas. The two monitoring efforts are not only spatially disjunct (urban vs rural locations), but there is only a partial overlap between them in the substances monitored and the methods used.

One of the consequences of this fragmentation is a poor knowledge of atmospheric deposition rates in and near cities. Ecologists have recently refocused efforts on the study of urban ecosystems and are currently investigating cities as complex interactive systems including both human and nonhuman biota (4–6). Despite the large body of knowledge on concentrations and chemical reactions of air pollutants in cities, there has been little work on the rates of atmospheric deposition to urban ecosystems. However, these ecosystems are likely to be subjected to large rates of deposition of anthropogenic pollutants. Some of these air pollutants are also major plant nutrients (e.g., nitrogen) and may be affecting nutrient cycles in plant-dominated areas in and around cities (7). Furthermore, studying atmospheric deposition rates in urban areas provides a quantitative estimate of the amounts of gaseous and particulate air pollutants that are removed by urban vegetation.

Decades of research on urban air quality indicate that cities are often large sources of nitrogen oxides, sulfur oxides, and dust, among many other pollutants (e.g., refs 8–12). The chemistry of urban air is exceedingly complex, and the emitted pollutants can undergo physical and chemical transformation in the atmosphere, such as oxidation reactions (e.g., NO to NO_2 to HNO_3) and gas to particle conversions (9). The gases and particles in urban air can increase rates of atmospheric deposition within and downwind of the city (12, 13).

This study was designed to measure the patterns of atmospheric deposition and forest throughfall of S, N, Ca^{2+} , Mg^{2+} , H^+ , and Cl^- to wooded sites along a transect from the New York City (NYC) to the suburban and rural areas to the north. A similar transect has previously been used for research on the effects of urbanization on forest ecosystems (e.g., ref 14). Atmospheric deposition consists of both wet deposition, which is the deposition of dissolved substances in precipitation, and dry deposition, which is the direct deposition of particles and gases from the atmosphere. Wet deposition can be measured directly with precipitation samplers, but dry deposition is much more difficult to measure (1). We used throughfall data as one indicator of processes occurring in the forest canopy. Throughfall deposition includes wet deposition and the portion of dry deposition that is washed from the canopy plus the net result of interactions between the canopy surfaces and the water passing over them (15). This latter process, which we call canopy exchange, includes both canopy retention of some elements, such as H^+ and N, and canopy release (leaching) of others, such as Ca^{2+} and Mg^{2+} (16). Sulfate and Cl^- are often considered to be relatively

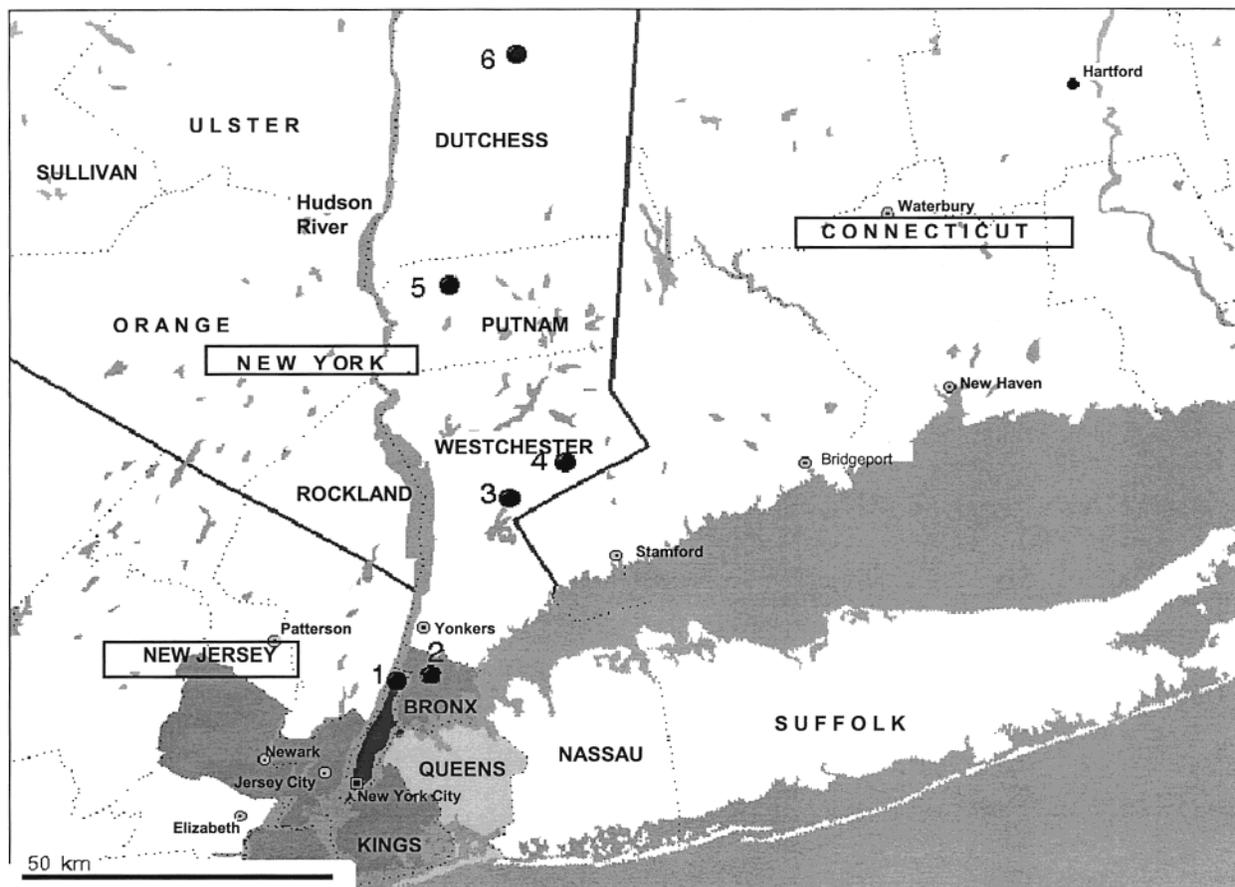


FIGURE 1. Locations of sampling sites. Urban sites are (1) Inwood Hill Park (IHP) and (2) New York Botanical Garden (NYB). Suburban sites are (3) Louis Calder Center (LCC) and (4) Mianus River Gorge (MRG). Rural sites are (5) Fahnestock State Park (FSP) and (6) Institute of Ecosystem Studies (IES).

unreactive in the canopy, although minor amounts of canopy leaching are sometimes observed (16, 17). Thus, for sulfur (S) and Cl^- , total deposition to the forest floor in throughfall is often considered a good estimate of total atmospheric deposition because canopy uptake and leaching are minimal (18, 19). Throughfall flux is likely to be an underestimate of atmospheric deposition of nitrogen (N) because N is usually taken up by forest canopies (20). Nonetheless, throughfall is sometimes used as an estimate of total N deposition in areas of high N pollution (21–23), where canopy uptake may be minor as compared to deposition.

Experimental Section

Field and Laboratory Methods. Our measurements were made at six sites in a north–south transect ranging from 11 to 128 km from Central Park in NYC (Figure 1). Because NYC is large, we chose Central Park in midtown Manhattan as a reference point from which to measure distances along the transect. Each site contained an oak-dominated forest. At each site, 10–12 mature, dominant red oak (*Quercus rubra* L.) trees were chosen, and a throughfall collector was placed beneath each tree at a point halfway along the crown radius. By standardizing the placement of throughfall collectors this way, we focus the study on patterns of deposition caused by differences in air and precipitation chemistry along the transect rather than differences in canopy structure or species composition. Each collector consisted of a 20 cm diameter polyethylene funnel supported about 1 m off the ground on a stake and connected by inert, flexible tubing to a 4-L polyethylene collection jug. The jug was partially buried in the ground and was covered with an opaque, reflective hood to keep the contents as cool and dark as possible. A polyester

fiber plug was placed in the stem of the funnel to filter out large debris. Two to four identical collectors were placed in an open area near the throughfall site to collect bulk deposition.

At the time of each collection, the collection jugs and polyester filters were replaced, and the funnel and tubing were rinsed with deionized water. Samples were returned to the laboratory, where volume was recorded by weighing, and an aliquot was taken for later chemical analysis. The aliquot was treated with 100 μL of chloroform/100 mL of sample and stored at 4 °C until chemical analyses could be performed. A separate aliquot was used to measure pH (using a pH meter) as soon as the sample was at room temperature.

Collections were made approximately weekly at all six sites from June 25 to September 10, 1996, and at three of the sites (Inwood Hill Park, Louis Calder Center, and Institute of Ecosystem Studies) from June 10 through September 6, 1997. There were 11 collection periods in each year.

In 1997, we also measured the water-extractable component of dry particle deposition at the same three sites from August 6 to September 6. Following the methods described in earlier papers (24, 25), dry deposition was collected on polycarbonate Petri plates exposed to the atmosphere during rain-free periods. The mass of material collected on these plates is dominated by particles large enough to deposit by gravitational sedimentation (24); henceforth, we will refer to the collected material as dust. Four replicate dust collection plates (8.5 cm diameter, 1 cm rim height) were held horizontally 2–4 m above the ground on an arm extending laterally from a vertical mast. At the urban site, the mast was located on the roof of a small building to discourage vandalism. The plates were exposed for four dry periods of

TABLE 1. Precipitation Amount (cm), Volume-Weighted Mean Concentrations ($\mu\text{mol L}^{-1}$), and Mean Fluxes and Net Fluxes (mmol m^{-2}) of Solutes in Bulk Deposition and Throughfall at the Six Sites for the Period June 25–September 10, 1996^a

| site no. | site code | precip amt | H ⁺ | Ca ²⁺ | Mg ²⁺ | NO ₃ ⁻ | NH ₄ ⁺ | inorg N | SO ₄ ²⁻ | Cl ⁻ |
|-----------------|-----------|------------|----------------|------------------|------------------|------------------------------|------------------------------|---------|-------------------------------|-----------------|
| Concentration | | | | | | | | | | |
| bulk deposition | | | | | | | | | | |
| 1 | IHP | 18.7 | 37.1 | 18.8 | 7.9 | 42.0 | 27.3 | 69.3 | 40.5 | 30.2 |
| 2 | NYB | 17.0 | 28.1 | 21.3 | 8.5 | 38.1 | 24.9 | 62.9 | 38.5 | 25.9 |
| 3 | LCC | 25.9 | 38.6 | 5.6 | 3.0 | 24.8 | 19.0 | 43.9 | 27.1 | 17.5 |
| 4 | MRG | 27.4 | 40.7 | 4.8 | 2.8 | 24.7 | 16.4 | 41.1 | 25.3 | 17.0 |
| 5 | FSP | 33.8 | 53.8 | 7.6 | 2.5 | 35.5 | 18.1 | 53.6 | 30.0 | 7.5 |
| 6 | IES | 28.8 | 52.1 | 5.7 | 2.1 | 34.0 | 15.5 | 49.3 | 25.6 | 5.4 |
| throughfall | | | | | | | | | | |
| 1 | IHP | 14.3 | 11.5 | 59.5 | 25.0 | 126.5 | 56.6 | 182.9 | 76.0 | 50.8 |
| 2 | NYB | 13.8 | 5.7 | 58.2 | 29.3 | 137.8 | 75.6 | 213.5 | 89.8 | 57.5 |
| 3 | LCC | 21.1 | 27.5 | 19.6 | 9.8 | 47.0 | 15.7 | 62.4 | 40.4 | 23.5 |
| 4 | MRG | 22.0 | 18.5 | 16.0 | 9.4 | 32.7 | 12.3 | 44.9 | 40.8 | 22.6 |
| 5 | FSP | 30.3 | 43.9 | 22.1 | 6.8 | 47.6 | 19.4 | 66.9 | 47.4 | 16.3 |
| 6 | IES | 21.9 | 23.9 | 19.9 | 7.9 | 48.8 | 15.0 | 63.8 | 37.2 | 9.7 |
| Flux | | | | | | | | | | |
| bulk deposition | | | | | | | | | | |
| 1 | IHP | | 6.94 | 3.52 | 1.49 | 7.86 | 5.10 | 12.96 | 7.58 | 5.66 |
| 2 | NYB | | 4.77 | 3.61 | 1.44 | 6.45 | 4.21 | 10.66 | 6.52 | 4.38 |
| 3 | LCC | | 9.99 | 1.45 | 0.79 | 6.41 | 4.91 | 11.35 | 7.00 | 4.51 |
| 4 | MRG | | 11.15 | 1.32 | 0.77 | 6.76 | 4.50 | 11.26 | 6.94 | 4.65 |
| 5 | FSP | | 18.20 | 2.57 | 0.85 | 12.01 | 6.13 | 18.14 | 10.14 | 2.53 |
| 6 | IES | | 15.00 | 1.63 | 0.61 | 9.78 | 4.45 | 14.20 | 7.37 | 1.55 |
| throughfall | | | | | | | | | | |
| 1 | IHP | | 1.64 | 8.52 | 3.57 | 18.11 | 8.10 | 26.18 | 10.88 | 7.27 |
| 2 | NYB | | 0.78 | 8.04 | 4.05 | 19.03 | 10.44 | 29.47 | 12.40 | 7.94 |
| 3 | LCC | | 5.80 | 4.13 | 2.06 | 9.91 | 3.31 | 13.17 | 8.52 | 4.95 |
| 4 | MRG | | 4.07 | 3.51 | 2.07 | 7.18 | 2.69 | 9.87 | 8.95 | 4.97 |
| 5 | FSP | | 13.29 | 6.68 | 2.06 | 14.39 | 5.86 | 20.25 | 14.35 | 4.92 |
| 6 | IES | | 5.25 | 4.36 | 1.74 | 10.70 | 3.28 | 13.98 | 8.16 | 2.13 |
| net throughfall | | | | | | | | | | |
| 1 | IHP | | -5.30 | 5.00 | 2.09 | 10.25 | 2.99 | 13.21 | 3.30 | 1.61 |
| 2 | NYB | | -3.99 | 4.43 | 2.61 | 12.58 | 6.23 | 18.80 | 5.87 | 3.55 |
| 3 | LCC | | -4.19 | 2.67 | 1.28 | 3.50 | -1.60 | 1.82 | 1.51 | 0.43 |
| 4 | MRG | | -7.08 | 2.19 | 1.30 | 0.42 | -1.81 | -1.39 | 2.01 | 0.32 |
| 5 | FSP | | -4.91 | 4.12 | 1.21 | 2.39 | -0.27 | 2.11 | 4.21 | 2.39 |
| 6 | IES | | -9.75 | 2.73 | 1.13 | 0.92 | -1.17 | -0.22 | 0.79 | 0.58 |

^a Site numbers and codes are as in Figure 1.

2–5 d duration. At the end of the exposure period, the plates were collected, sealed, and transported to the laboratory while being kept in a horizontal position. The plates were extracted by adding 20 mL of deionized water and a clean Teflon stirring bar to the plate and stirring for 30 min. The extractant was then decanted and refrigerated until analysis.

Ammonium and NO₃⁻ concentrations in throughfall were measured on an Alpkem autoanalyzer (Alpkem Total Flow Solutions III) using the indophenol blue and cadmium reduction methods, respectively. Calcium and Mg²⁺ were measured with a Perkin-Elmer P400 inductively coupled plasma emission spectrometer (ICP). Sulfate and Cl⁻ concentrations were measured with a Dionex DX-500 ion chromatograph. Dust plate extract concentrations were measured in the same way, except that NO₃⁻ was measured on the ion chromatograph rather than the autoanalyzer and H⁺ and NH₄⁺ were not measured because of insufficient sample volume. All analyses were performed in the IES analytical laboratory.

Data Analysis. Deposition fluxes for throughfall and bulk deposition were calculated as the product of concentration and precipitation volume for each collection period and sampler. Net throughfall fluxes were calculated by subtracting bulk deposition fluxes from throughfall fluxes. Site means were calculated for each collection period. For the 1996 data (6 sites), we used regression analysis (SAS GLM procedure; 26) to determine relationships between throughfall and bulk deposition fluxes (site means for each collection period) and distance from Central Park. Because previous experience

indicated that precipitation amount was a major controlling factor for throughfall fluxes and net throughfall fluxes (27), we included precipitation amount as an additional independent variable in the regressions.

The data were aggregated across the summer sampling period by calculating mean chemical concentrations weighted by precipitation volume for each site. The volume-weighted mean concentrations for each site were multiplied by the total summer precipitation volume for the site to calculate total fluxes. Fluxes in bulk deposition were subtracted from throughfall fluxes to calculate net throughfall fluxes for each site for the entire summer.

Results and Discussion

Throughfall and Bulk Deposition. Precipitation amount during the summer of 1996 at the urban sites was only 62% of that received at the suburban and rural sites (Table 1) and that pattern was repeated in 1997 (data not shown). However, longer-term mean data show very similar precipitation amounts along this transect. The 1990–1998 annual mean precipitation amounts were 103 cm for Staten Island in NYC, 112 cm for Mt. Ninham in Putnam County, and 110 cm for the IES site in Millbrook (28, 29). Volume-weighted mean concentrations of Ca²⁺, Mg²⁺, NO₃⁻, NH₄⁺, SO₄²⁻, and Cl⁻ decreased with distance from NYC in both throughfall and bulk deposition, while the concentration of H⁺ increased with distance in both throughfall and bulk deposition (Table 1). The urban throughfall had a higher NO₃⁻:SO₄²⁻ ratio than

TABLE 2. Results of Linear Regression Analysis for 1996 Data^a

| solute | | ln(distance) | precip amt | n | R ² |
|-------------------------------|------|--------------|-------------|----|----------------|
| H ⁺ | TF | 0.2340* | 0.0856* | 56 | 0.16** |
| | bulk | 0.3237* | 0.1829*** | 54 | 0.32**** |
| | net | -0.1010 ns | -0.1039 *** | 54 | 0.30**** |
| Ca ²⁺ | TF | -0.2040**** | 0.0525*** | 56 | 0.47**** |
| | bulk | -0.1029**** | 0.0197*** | 55 | 0.50**** |
| | net | -0.1051*** | 0.0322** | 55 | 0.30**** |
| Mg ²⁺ | TF | -0.1128**** | 0.0302**** | 56 | 0.62**** |
| | bulk | -0.0495**** | 0.0191**** | 55 | 0.56**** |
| | net | -0.0634**** | 0.0111** | 55 | 0.42**** |
| NO ₃ ⁻ | TF | -0.4163*** | 0.0701 ns | 56 | 0.21** |
| | bulk | 0.0415 ns | 0.1048**** | 55 | 0.21** |
| | net | -0.4650**** | -0.0357 ns | 55 | 0.46**** |
| NH ₄ ⁺ | TF | -0.2861**** | 0.0375 ns | 56 | 0.32**** |
| | bulk | -0.0322 ns | 0.0576* | 55 | 0.09 ns |
| | net | -0.2590**** | -0.0208 ns | 55 | 0.37**** |
| inorg N | TF | -0.7021**** | 0.1076 ns | 56 | 0.27*** |
| | bulk | 0.0085 ns | 0.1625** | 55 | 0.17** |
| | net | -0.7229**** | -0.0566 ns | 55 | 0.47**** |
| SO ₄ ²⁻ | TF | -0.1643* | 0.1219**** | 56 | 0.28*** |
| | bulk | -0.0374 ns | 0.1156**** | 55 | 0.33**** |
| | net | -0.1455*** | 0.0036 ns | 55 | 0.23** |
| Cl ⁻ | TF | -0.2899**** | 0.1585**** | 56 | 0.47**** |
| | bulk | -0.2149** | 0.1566**** | 55 | 0.47**** |
| | net | -0.0731* | 0.0021 ns | 55 | 0.11* |

^a Regression model was (flux of solute) = $a + b_1(\ln(\text{distance})) + b_2(\text{precip amt})$, with solute flux in mmol m^{-2} , distance in km, and precipitation amount in cm. TF, throughfall; bulk, bulk deposition; and net, net throughfall flux. Statistical significance is given as follows: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$; ****, $p < 0.0001$; ns, not significant.

throughfall at the other sites. Changes in bulk deposition were in all cases quantitatively less than changes in throughfall along the transect. Patterns of concentration and flux vs distance from NYC were distinctly nonlinear, with the steepest decline occurring between the urban and suburban sites (Table 1, Figures 2–4). The increase in throughfall and bulk deposition fluxes at the rural end of the transect is probably due to the higher precipitation in the more rural sites (Table 1).

We found that for most solutes the logarithm of distance from NYC produced a better fit to the data than did the untransformed distance. Regression analysis on the throughfall and net throughfall fluxes for each collection period showed significant trends of decreasing flux with $\ln(\text{distance})$ from NYC for all solutes measured except H⁺ (Table 2). There was a significant increase in throughfall flux of H⁺ with $\ln(\text{distance})$, and no significant pattern in net throughfall flux of H⁺. Bulk deposition fluxes showed a significant decrease with $\ln(\text{distance})$ for Ca²⁺, Mg²⁺, and Cl⁻; a significant increase with $\ln(\text{distance})$ for H⁺; and no significant trends for NH₄⁺, NO₃⁻, or SO₄²⁻. The amount of precipitation had a variable influence on the throughfall and net throughfall fluxes. Sometimes it was a significant term in the regression model, and other times it was not (Table 2). Precipitation amount and distance from the city usually explained less than half of the total variation in flux for each collection period (Table 2). This is not surprising given that the air mass histories and pollutant loads could vary substantially among weeks and sites. Moreover, the time for accumulation of pollutants on the canopies prior to a rainfall event could also vary from week to week and site to site, because if a site received no rain in a week its canopy would have accumulated pollutants for 2 weeks before the next throughfall collection.

Concentration and flux of NO₃⁻ in throughfall in 1996 decreased by roughly a factor of 2–3 from the urban to the rural sites (Figure 2). In comparison, bulk deposition concentrations and fluxes of NO₃⁻ changed only slightly over the transect (Figure 2). Throughout the transect, throughfall fluxes of NO₃⁻ were greater than bulk deposition fluxes,

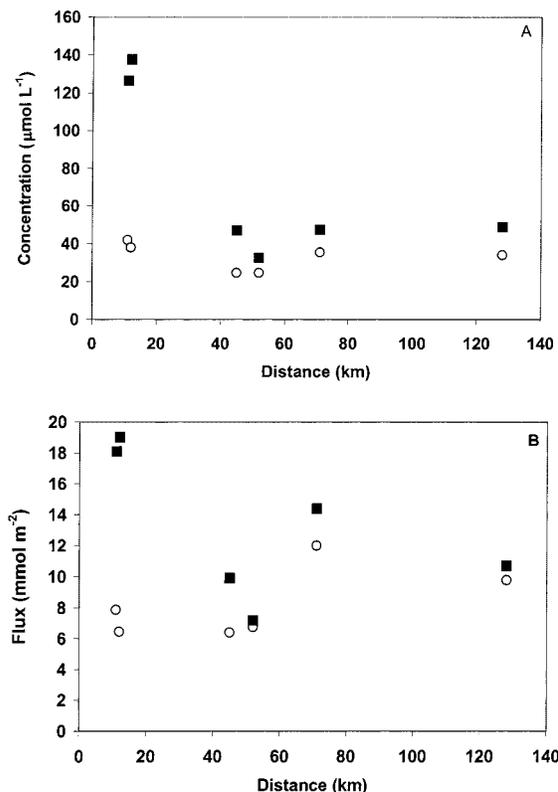


FIGURE 2. Concentration (A) and deposition (B) of NO₃⁻ in bulk deposition and throughfall vs distance from Central Park, NYC. Collection period from June 25 to September 10, 1996. Filled squares are throughfall and open circles are bulk deposition.

resulting in a positive net throughfall flux (throughfall flux minus bulk deposition flux). Because the net throughfall flux of N is the difference between dry deposition to the canopy and canopy uptake (20), we interpret the positive net throughfall flux to mean that dry deposition of NO₃⁻ exceeded canopy uptake along the entire transect. Concentrations and fluxes of NH₄⁺ followed similar patterns to those of NO₃⁻ except that the deposition amounts were somewhat lower, and the bulk deposition fluxes exceeded throughfall fluxes (i.e., net throughfall fluxes were negative) at all except the two urban sites (Figure 3). Negative net throughfall fluxes indicate that canopy uptake exceeds dry deposition.

Total throughfall deposition of inorganic N (NO₃⁻ + NH₄⁺) was almost twice as high at the two urban sites as compared to the average of the four nonurban sites (Table 1). Net throughfall flux of inorganic N decreased from a mean of 16.0 mmol m^{-2} at the urban sites to a mean near 0 at the suburban and rural sites. This indicates that N dry deposition approximately equaled canopy N uptake in the suburban and rural sites, but dry deposition greatly exceeded canopy uptake at the urban sites.

The mean net throughfall flux of inorganic N for the two urban sites (16.0 mmol m^{-2}) was 35% greater than the mean bulk deposition at these sites (Table 1). Because most canopies take up some deposited N, net throughfall underestimates dry deposition of inorganic N (20). Bulk deposition includes some particulate dry deposition and thus represents an overestimate of wet deposition (20). If we use net throughfall flux as a minimum estimate of dry deposition of N and bulk deposition as a maximum estimate of wet deposition, we conclude that dry N deposition exceeded wet N deposition in the urban sites, but the opposite was likely true at the rural sites.

Strong acid (H⁺) deposition fluxes in both in bulk deposition and throughfall were higher in the suburban and

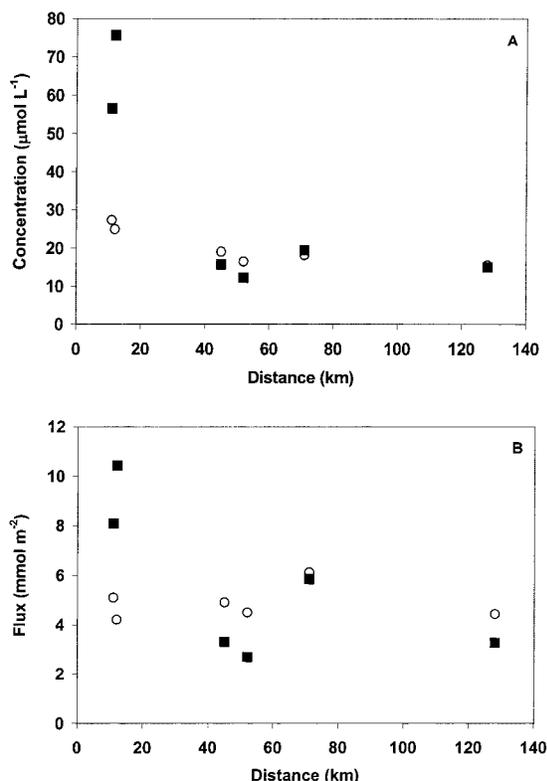


FIGURE 3. Concentration (A) and deposition (B) of NH_4^+ in bulk deposition and throughfall vs distance from Central Park, NYC. Collection period from June 25 to September 10, 1996. Filled squares are throughfall and open circles are bulk deposition.

rural than in the urban sites. The highest H^+ deposition occurred at site 5, 71 km from NYC (Table 1). Compared to the urban sites, acid fluxes to the forest floor averaged over 4-fold higher at sites 3, 4, and 6 and over 10 times higher at site 5. Hydrogen ion was consumed in all the canopies, with the amount of net consumption (= negative net throughfall flux) largest at IES, the most rural site (Table 1).

Sulfate fluxes in throughfall were more variable but also showed a peak at site 5 (FSP). Site 5 received the most precipitation and also had relatively high concentrations of H^+ and Ca^{2+} in throughfall as compared to sites 4 and 6. Site 5 lies approximately 15 km east (downwind) from an electric power plant located on the Hudson River. We suspect that emissions from this plant contributed to the total deposition of SO_4^{2-} , H^+ , and possibly NO_3^- at site 5 and that this additional acid deposition caused more leaching of Ca^{2+} from the canopy (17, 30). Alternatively, this site could be receiving Ca in dust generated by the power plant.

Concentrations and fluxes of Ca^{2+} (Figure 4), Mg^{2+} , and Cl^- showed decreases of a similar relative magnitude (Table 1) to those of the N species. Net throughfall fluxes of Ca^{2+} and Mg^{2+} also declined with distance (Table 1), and Ca^{2+} showed the strong peak at site 5 (FSP) that we attribute above to canopy leaching. The high deposition of Ca^{2+} at the urban sites is consistent with the findings of Pouyat et al. (14), who found higher exchangeable Ca^{2+} and Mg^{2+} concentrations in soil at sites in NYC than in suburban and rural sites to the north and suggested that urban dust deposition might be the cause.

The urban sites had higher bulk deposition of all measured ions except H^+ , but it is not clear from these data how much of the bulk deposition was due to wet deposition as opposed to particle deposition into the open funnels. However, wet-only deposition in Chicago shows a similar neutralization

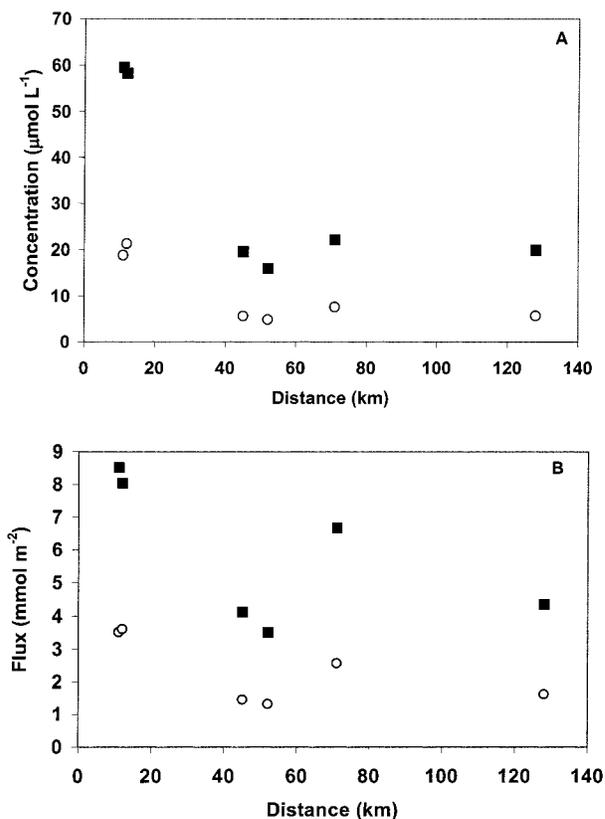


FIGURE 4. Concentration (A) and deposition (B) of Ca^{2+} in bulk deposition and throughfall vs distance from Central Park, NYC. Collection period from June 25 to September 10, 1996. Filled squares are throughfall and open circles are bulk deposition.

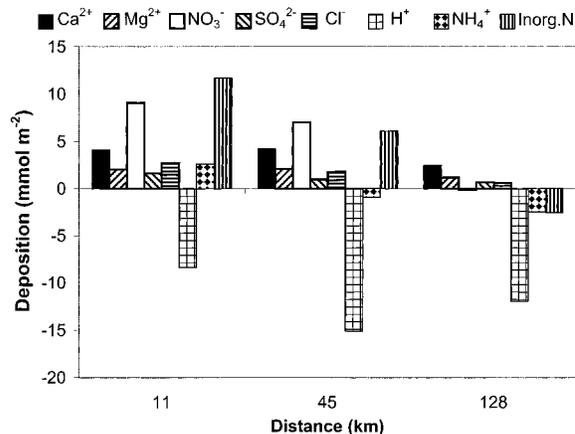


FIGURE 5. Net throughfall flux for urban, suburban, and rural sites from 1997 data (collection period June 10–September 6).

phenomenon, with an urban site having higher Ca^{2+} and lower H^+ as compared to a suburban site (31).

Throughfall fluxes and net fluxes decreased with distance from NYC in 1997 in a pattern similar to that observed in 1996 (net throughfall fluxes shown in Figure 5). We did not perform the regression analysis on the 1997 data because only three sites were used.

Dust Collections and Atmospheric Concentrations. Our measurements of the water-extractable component of dust deposition also showed that Ca^{2+} , Mg^{2+} , NO_3^- , SO_4^{2-} , and Cl^- in dust decreased strongly with distance from NYC (Figure 6). On a charge basis, Ca^{2+} and Mg^{2+} approximately balanced NO_3^- , SO_4^{2-} , and Cl^- in the dust extracts, indicating little alkalinity in the deposited dust. Ratios of SO_4^{2-} , Ca^{2+} , and

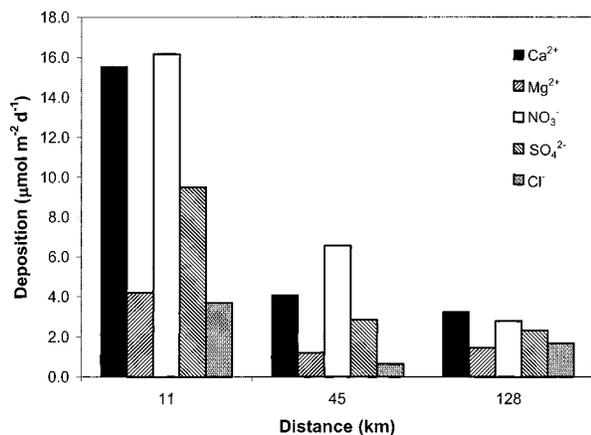


FIGURE 6. Deposition to dust collection plates for urban, suburban, and rural sites in 1997.

TABLE 3. Concentrations of Several Important Air Pollutants at Urban, Suburban, and Rural Locations within and North of New York City^a

| | gases | | | | particles | | |
|----------|---------|-----------------|------------------|-----------------|------------------|-------------------------------|------------------------------|
| | NO | NO ₂ | HNO ₃ | SO ₂ | TSP | SO ₄ ²⁻ | NO ₃ ⁻ |
| urban | 23(a) | 31(a) | | 13(b) | >117(c) 57(d) | 8.5(d) | 4.9(d) |
| suburban | | | | 2.5(e) | 37(f) | 7.8(f) | 4.1(f) |
| rural | 0.47(g) | 2.9(g) | 0.80(g) | 2.6(g) | | | |

^a NO, NO₂, and SO₂ in nL/L (ppbv); all other data in μg m⁻³, followed by location code in parentheses. TSP, total suspended particles. All data are mean of annual mean data for 1996 and 1997 if available, otherwise, one of the two years was used. Location codes: a, New York Botanical Garden, Bronx; b, Morrisania, Bronx; c, midtown, Manhattan; d, Greenpoint, Brooklyn; e, Mt. Ninham, Putnam County; f, Mt. Vernon, Westchester County; g, Institute of Ecosystem Studies (IES), Dutchess County. Urban and suburban data from New York State Department of Environmental Conservation (<http://www.dec.state.ny.us/website/dar/reports/>). See this web site for location of sites and details of methods. IES data from Kelly (28), except IES NO and NO₂ data from NYSDEC (Brian Lay, NYSDEC, personal communication). Blanks indicate that data are not available. Methods: NO and NO₂: gas-phase chemiluminescence analyzer. HNO₃: nylon filter, weekly. SO₂: at IES, sodium carbonate-impregnated filter, weekly; at other sites, pulsed fluorescence analyzer. TSP, SO₄²⁻, and NO₃⁻: high-volume filtration on glass fiber filter.

Mg²⁺ to Cl⁻ were consistently much higher in our dust and precipitation samples than would be expected if the material were primarily of marine origin. For example, the molar ratio of SO₄²⁻:Cl⁻ in the marine aerosol is 0.21 (9), while in our samples the ratio ranged from 1.2 to 5.8 in bulk deposition, from 1.0 to 4.5 in throughfall, and from 1.4 to 4.5 in deposited dust (1997 data). Similarly, the molar ratio of Ca²⁺:Cl⁻ in the marine aerosol is 0.03, while our measured ratios ranged from 0.43 to 0.71 in bulk deposition, from 0.75 to 1.7 in throughfall, and from 1.9 to 6.4 in deposited dust. Thus, neither the deposited dust nor the throughfall or bulk deposition solutions had the chemical signature of the marine aerosol.

We compiled data from several sources to compare atmospheric concentrations of sulfur and nitrogen oxides and particles in urban, suburban, and rural sites near our transect. While the data should be interpreted with caution because of different methodology at the different sites, it seems clear that urban air in NYC contains larger concentrations of suspended particles, nitrogen oxides, and SO₂ than does the air at suburban or rural sites (Table 3).

Interaction of Gaseous and Particulate Air Pollutants: The "Urban Scrubber". Cities are well-known sources of gaseous pollutants such as S and N oxides arising from fossil fuel combustion. However, cities are also large sources of

atmospheric dust, emanating mainly from roadways and from excavation, construction, and demolition activities. These two types of emissions are quite different in that the sulfur and nitrogen oxides react to form acids in the atmosphere, while the dust particles are generally alkaline in nature because of the metal oxides and carbonates they contain (32). Our results demonstrate the influence of both types of emissions in the deposition of materials to forests in and around NYC and further demonstrate the interaction of gaseous and particulate pollutants.

The strong and coincident gradients of net throughfall of N, Ca²⁺, and Mg²⁺ suggest that at least part of the N dry deposition was associated with particulate deposition of Ca²⁺ and Mg²⁺. This could occur if dust bearing calcium and magnesium oxides and carbonates was generated in the urban areas and reacted in the atmosphere with sulfur and nitrogen oxide gases such as SO₂, NO₂, and HNO₃ producing calcium and magnesium sulfates and nitrates in particulate form. Several studies have discussed the reaction of acidic gases with alkaline particulates in the air (33–35). Lee (36) suggested that reaction between CaCO₃ and SO₂, either in the air or on surfaces, was responsible for the high correlation between Ca²⁺ and SO₄²⁻ in precipitation sampled throughout Manchester, England. Our dust deposition data suggest that this same process may be occurring over NYC.

The source of the dust we measured at the urban sites was most probably in the city itself, because the dust did not have a marine chemical signature and the urban air had high measured particulate concentrations. The approximate charge balance between Ca²⁺ and Mg²⁺ cations and SO₄²⁻, NO₃⁻, and Cl⁻ anions suggests that the dust, which was probably generated as calcium and magnesium oxides and carbonates from rock, soil, and cement, was neutralized in the atmosphere by reaction with gaseous sulfur and nitrogen oxides. It is also possible that some of the neutralization occurred on the emission surfaces (e.g., buildings or roads) prior to emission. However, much more surface area would be exposed to chemical reaction after the material was pulverized and sent aloft as dust. In any event, the hypothesis that the neutralization occurred prior to deposition is also supported by the net throughfall H⁺ data. Despite the high deposition rates of Ca²⁺ and Mg²⁺ at the urban sites, the in-canopy neutralization of H⁺ in precipitation (i.e., net throughfall H⁺) is not significantly higher at these sites. This indicates little alkalinity in the material deposited to the forest canopy.

Because dust particles are relatively large (>2 μm diameter), they have a high rate of gravitational sedimentation that limits their dispersal distance in the atmosphere (37). The reaction of nitrogen and sulfur gases with dust particles could "scrub" some of the gases from the urban atmosphere deposition and cause them to be deposited locally rather than dispersing downwind. This process is similar in principle to a common type of power plant scrubber in which powdered limestone is added to the exhaust stream to remove acidic gases (38). Dust generation in New York City may therefore function as an "urban scrubber".

While dust clearly played a role in delivering dry deposition to the urban forest canopies, it was not the only source of dry deposition in these canopies. The molar ratio of NO₃⁻:Ca²⁺ in the dust collected at the urban site was 1.0, whereas the ratio in urban throughfall (1997 data) was 2.2. This implies that at least half of the NO₃⁻ in net throughfall was from a source other than dust. Since there is generally little canopy leaching of inorganic N compounds (20), the nondust portion of the net throughfall NO₃⁻ probably arose from dry deposition of nitrogen oxide gases or NH₄NO₃ particles. The ratio of NO₃⁻:Ca²⁺ was 3.1 in bulk deposition at the urban site, suggesting an even greater contribution of nondust sources to the NO₃⁻ in urban rainfall.

Our data indicate that the enhanced deposition associated with NYC along this transect was limited to sites within the city itself. Sites as little as 45 km from the city center, or just over 30 km from our urban sites at the periphery of the city, showed little enhancement of deposition relative to the most rural sites over 100 km away. The restriction of the urban effect may be a consequence of the limited travel of the coarse particles, as discussed above.

Because atmospheric deposition of nutrients and pollutants can have a significant influence on forest ecosystem processes, the urban effect should be considered in the management of forests near large cities. In particular, urban forests may be receiving more nitrogen and less acidity than would be expected based on studies from nonurban forests. Moreover, the urban effect may be important in the computation of large-scale regional budgets of emission and deposition of pollutant compounds.

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