NITROGEN AND SULFUR DEPOSITION AND FOREST NUTRIENT STATUS IN THE VALLEY OF MEXICO

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Abstract. Mexico City experiences some of the most severe air pollution in the world. Ozone injury has been documented in sensitive tree species in urban and forested areas in the Valley of Mexico. However, little is known of the levels of other atmospheric pollutants and their ecological effects on forests in the Valley of Mexico. In this study bulk throughfall deposition of inorganic nitrogen (N) and sulfur (S) was measured for one year at a forested site upwind (east) and downwind (southwest) of Mexico City. Edaphic and plant (*Pinus hartwegii* Lindl.) indicators of N and S nutrient status were also measured. Streamwater NO_3^- and SO_4^{2-} concentrations were also determined as an indicator of watershed-level N and S loss. Annual bulk throughfall deposition of inorganic N and S at the high-pollution forested site 23 km southwest of Mexico City (Desierto de los Leones National Park; DL) was 18.5 and 20.4 kg ha^{-1}. Values for N and S deposition at Zoquiapan (ZOQ), a relatively low-pollution site 53 km east of Mexico City, were 5.5 and 8.8 kg ha^{-1} yr^{-1}. Foliar concentrations of N, foliar N:P and C:N ratios, extractable soil NO_3^-, and streamwater NO_3^- concentrations indicate that the forest at DL is N enriched, possibly as a result of chronic N deposition. Sulfur concentrations in current-year foliage were also slightly greater at DL than at ZOQ, but S concentrations in one-year-old foliage were not statistically different between the two sites. Streamwater concentrations of NO_3^- ranged from 0.8 to 44.6 μEq L^{-1} at DL compared to 0.0 to 11.3 μEq L−1 at ZOQ. In summary, these findings support the hypothesis that elevated N deposition at DL has increased the level of available N, increased the N status of *P. hartwegii*, and resulted in export of excess N as NO_3^- in streamwater.

Keywords: nitrogen enrichment, nutrient ratios, streamwater nitrate, throughfall, volcanic emissions

1. Introduction

Mexico City suffers from severe photochemical smog, especially during the dry winter season (Miller *et al*., 1994). Ozone injury has been documented on a number of plants in urban, rural and montane areas in the Valley of Mexico (de Bauer and Hernández-Tejeda, 1986). Severe forest decline has been described in some areas of the Desierto de los Leones National Park (DL) located 23 km southwest of Mexico City. Air pollution has been implicated as a possible factor in the decline (Alvarado *et al*., 1993; de Bauer *et al*., 1985; de Bauer and Krupa, 1990). Air pollution concentrations are elevated in DL because of proximity to the large ur-

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ban pollution source and the prevailing northeasterly winds from Mexico City (de Bauer, 1991).

Based on published emission inventories for metropolitan Mexico City (Bravo, 1987), elevated deposition of nitrogen (N) and sulfur (S) pollutants is also expected to occur in forests downwind of Mexico City. Fossil fuel consumption, mainly for transportation, is the primary source of atmospheric N pollutants in Mexico City. Sulfurous air pollutants come primarily from burning of fossil fuels with high S content (Velasco, 1983). However, little data is available on N and S deposition and the potential effects of these pollutants on forests within the Valley of Mexico (Baez *et al*., 1997b).

Many studies have demonstrated a close relationship between levels of N deposition and effects on chemical processes in soil such as soil acidification, stimulation of nitrification and nitrate leaching, leaching of counterbalancing cations, and alleviation of N deficiency (Fenn *et al*., 1998). The objectives of this study were to compare N and S deposition and indicators of nutrient status in a forest located downwind (23 km southwest) of Mexico City and another forest upwind (53 km east) of Mexico City. We hypothesized that elevated N and S deposition occurs in forests downwind of Mexico City and that signals of chronic N and S deposition to these forests would be observable as higher N and S concentrations in soil and vegetation, and as increased losses of nitrate in streamwater. A secondary objective of this study was to compare N and S deposition and nutrient status in forests within the Valley of Mexico with published data from forests in the Los Angeles, California Air Basin where photochemical smog also predominates. A similar comparative study was recently published in regards to ozone exposure in the Valley of Mexico and the San Bernardino Mountains 90 km east of Los Angeles, California, U.S.A. (Miller *et al*., 1994),

2. Methods

2.1. Research sites

Zoquiapan Experimental Forest (low deposition) and the Desierto de los Leones National Park and Recreation Area (high deposition) are the two forested sites selected for this study. The study site in the southwestern portion of the Desierto de los Leones National Park (DL) is located in the direction of the prevailing winds from Mexico City. This area is known to be highly polluted as a result of transport of polluted air from Mexico City. The Zoquiapan Experimental Forest (ZOQ) is located in the southeast corner of Zoquiapan National Park (Figure 1). Descriptive characteristics of DL and ZOQ are given in Table I. Precipitation in the Valley of Mexico occurs predominantly from May through September. Precipitation at the study sites occurs as rainfall or hail. Snowfall rarely occurs except at sites above 4000 m in elevation. The dominant tree species at both sites are *Pinus hartwegii*

TABLE I
Characteristics of the two study sites

Characteristic	Desierto de los Leones	Zoquiapan
Altitude	3,325 m	3,350 m
Latitude[a]	19° 11′ 18″ – 19° 19′ 42″	19° 12′ 30″ – 19^{circ} 20′ 00″
Longitude[a]	99° 15′ 00″ – 99° 23′ 00″	98° 42′ 30″ – 98^{circ} 30′ 00″
Overstory vegetation	Pine and fir mix	Pine and fir mic
Understory vegetation	Predominantly pasture grasses: *Festuca, Muhlembergia, Stipa and Calamagrostis*	Predominantly pasture grasses: *Festuca, Mulembergia, Stipa and Calamagrostis*
Stand age	20 – 40 yr	40 – 60 yr
Soil type	Humic Andosol, ochric	Mollic Andosol, humic
Forest fire history	Fires are suppressed in the park	Both controlled and unregulated fires occur
Annual precipitation[b]	1455	778 mm
Climate	Temoperate subhumid with summer rain season and winter dry season	Temperate subhumid with summer rain season and winter dry season

[a] Latitude and longitude are for the entire Desierto de los Leones National Park, and for the Zoquiapan Experimental Forest (Blanco-Zavala *et al*., 1981).
[b] Values given are throughfall volumes from this study for March 1996 to March 1997.

Lindl. and *Abies religiosa* Schl. (Rzedowski, 1978). There are frequent local fires in the forest in the Zoquiapan area.

2.2. THROUGHFALL COLLECTION AND DRY DEPOSITION FLUXES

Atmospheric inputs of N and S at both study sites were evaluated by two methods: bulk throughfall and dry deposition to surrogate surfaces. Bulk throughfall was collected at both sites from March 1996 to March 1997. Throughfall was collected in standard collectors consisting of a funnel (13 cm diameter) connected to opaque collection bottles. The collection surface area was 132.7 cm^2. Throughfall was collected on a weekly basis during the wet season (March through October), and on an event basis thereafter. Throughfall collectors were placed in four parallel transects at each site with eight collectors per transect, for a total of 32 collectors per site. Throughfall volumes were recorded in the field and a subsample was collected and maintained under refrigeration (approx. 4°). Phenyl mercury acetate was added to the subsamples (10 mg mercury L^{-1} as a preservative and the samples were shipped to the Forest Fire Laboratory in Riverside, California, U.S.A. for chemical analysis. Ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}) concentrations were deter-

mined in the throughfall samples using liquid ion chromatography (Dionex* series 4000i, Sunnyvale, CA).

Dry deposition fluxes of NO_3^-, NH_4^+ and SO_4^{2-} to surrogate surfaces were also determined during the winter dry season in 1994 at DL and ZOQ. At ZOQ, dry deposition collectors were located near the hill named El Papayo, which is in the northwest corner of the Zoquiapan Experimental Forest, approximately 4 km northwest of the throughfall study site (Figure 1). Paper filter disks (Whatman No. 41, 47 mm diameter) were used as collection surfaces for comparing dry deposition fluxes at DL and ZOQ as described previously (Fenn and Bytnerowicz, 1993). Filter disks were exposed for two weeks after which the disks were collected and new disks installed. The five exposure periods began on Feb. 4, 1994 and ended on April 15, 1994. The exposed filter disks were extracted with deionized and distilled water and concentrations of NO_3^-, NH_4^+ and SO_4^{2-} determined with ion chromatography.

2.3. PLANT AND SOIL NUTRIENT ANALYSES

Various soil, plant, and hydrologic nutrient analyses were carried out for samples from both sites in order to determine whether elevated atmospheric deposition of N and S was reflected in nutrient concentrations of plants, soil and streamwater. Seven soil samples were collected at both sites in March and December 1996 from the top 15 cm and from the 15–30 cm depth in seven pits located along the same transects where throughfall was collected. Concentrations of NO_3^-, NH_4^+, and SO_4^{2-} in water extracts of soil were determined by adding 15 mL of deionized-distilled water to 7.5 g of soil and extracting on a wrist action shaker for 1 hr. After centrifuging for 15 min, ionic concentrations were determined in the supernatant. Total C, N and S were also determined in the soil from both depths with a combustion analyzer (Carlo Erba Instruments, Milan, Italy; Model NA 1500, Series 2). Soil pH was determined on a 1:2 mixture of soil and 0.01 *M* $CaCl_2$ (Fenn *et al.*, 1996).

Current-year and one-year old foliage were collected from twelve trees at DL and ZOQ in December 1996. Four branches were collected from each tree and the four annual whorls of each age class were combined to obtain one sample per age class from each tree. Foliage was analyzed for total C, N, and S by combustion analysis as described above. Total P in foliage was determined from nitric-perchloric digestion and analysis with a Technicon TRAACS 800 autoanalyzer (Glaubig and Poth, 1993).

A preliminary streamwater chemistry survey was performed in order to see if the general pattern of streamwater NO_3^- and SO_4^{2-} export paralleled atmospheric deposition inputs at DL and ZOQ. Several streams were sampled within the watershed at DL and ZOQ from December 1996 until March 1997. Three samples were taken from each stream by rinsing the collection bottle three times with streamwater before filling it. The samples were then transported to the labora-

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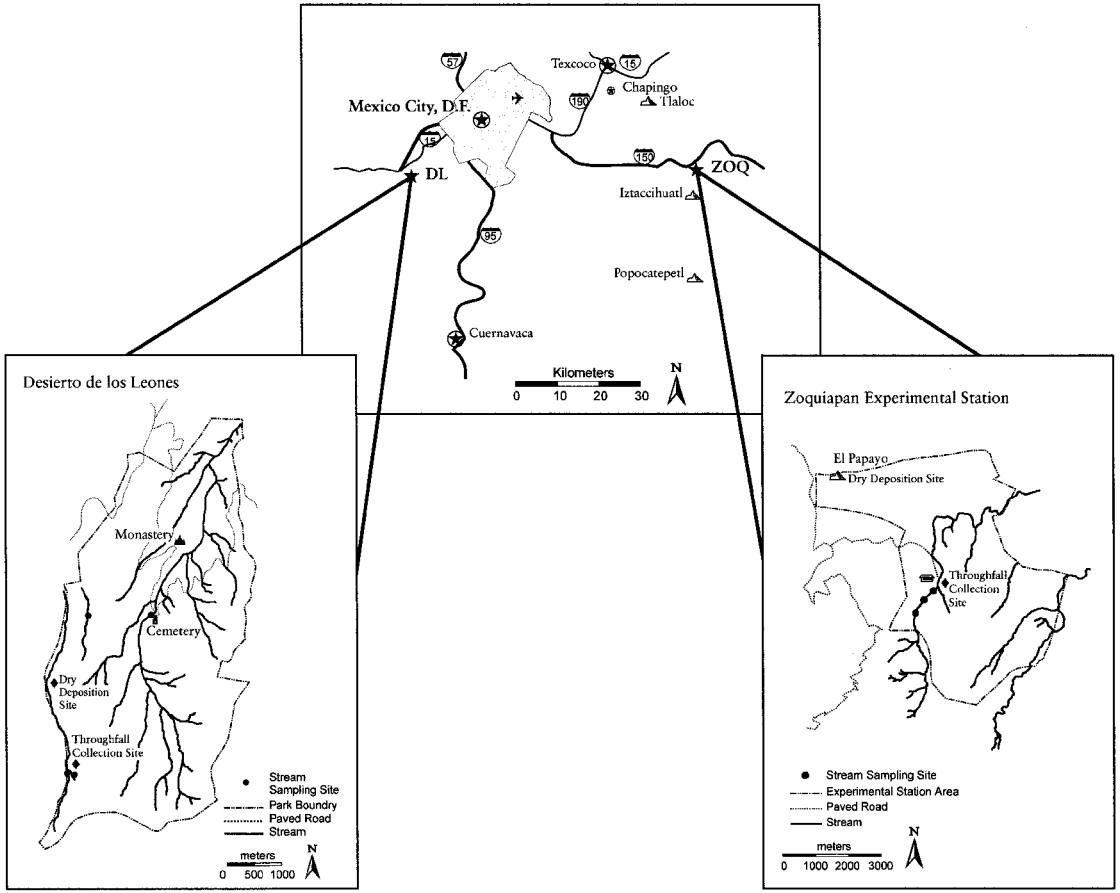

Figure 1. Map showing the location of the two study areas.

tory in the Colegio de Postgraduados and frozen. Within a few days the samples were shipped to the Riverside Forest Fire Laboratory and stored in a freezer until analyzed for NO_3^-, NH_4^+, and SO_4^{2-} via liquid ion chromatography as described previously (Fenn *et al.*, 1996). Since NH_4^+ was not detected in any of the early streamwater samples, later collections were not analyzed for NH_4^+.

2.4. Statistical analyses

Data analysis was performed using SigmaStat™ statistical software from Jandel Scientific Software (Fox *et al.*, 1994). Differences in ion concentrations in throughfall and nutrient concentrations in foliage and soil between DL and ZOQ were determined by t-tests. Comparisons of dry deposition fluxes to surrogate surfaces were tested using one-way repeated measures ANOVA on ranks, followed by Dunnett's tests for mean comparison. Differences were considered statistically significant at $p \leq 0.10$ (Fox *et al.*, 1994).

3. Results

Dry deposition measurements were made to indicate the level of exposure to atmospheric N and S in the forest at DL and ZOQ. Throughfall measurements provided an estimate of annual atmospheric inputs of N and S to the forest floor and soil. Foliar nutrient concentrations indicated the amount of N and S taken up by the trees from soil and the atmosphere. Streamwater NO_3^- concentrations were measured as an indicator of excess N within the watersheds, or in other words, N that was not retained via soil abiotic mechanisms, or taken up by soil microorganisms and vegetation (Fenn *et al.*, 1998).

3.1. Throughfall and dry deposition

Annual inorganic N (NH_4-N + NO_3-N) and S deposition at DL were 18.5 and 20.4 kg ha^{-1}. Analogous values at ZOQ were 5.5 and 8.8 kg ha^{-1} yr^{-1} (Figure 2). Annual throughfall was 1455 mm at DL and 778 mm at ZOQ. Patterns of cumulative deposition inputs of NO_3^- and NH_4^+ paralleled cumulative precipitation volume at DL, but at ZOQ deposition of NO_3^- and NH_4^+ was less responsive, lagging behind the trend of cumulative precipitation. Cumulative SO_4^{2-} deposition trends generally tracked cumulative precipitation at both sites (Figure 2). Volume-weighted annual mean concentrations of NH_4^+ and NO_3^- in throughfall were 1.6 and 1.8 times higher at DL than at ZOQ, while SO_4^{2-} concentrations in throughfall were only 1.2 times higher at DL (Figure 3).

Dry deposition fluxes of NO_3^- and SO_4^{2-} to surrogate surfaces were significantly greater at DL compared to the Papayo site in ZOQ (Figure 4) according to repeated measures ANOVA. However, SO_4^{2-} fluxes were similar at both sites on the last two

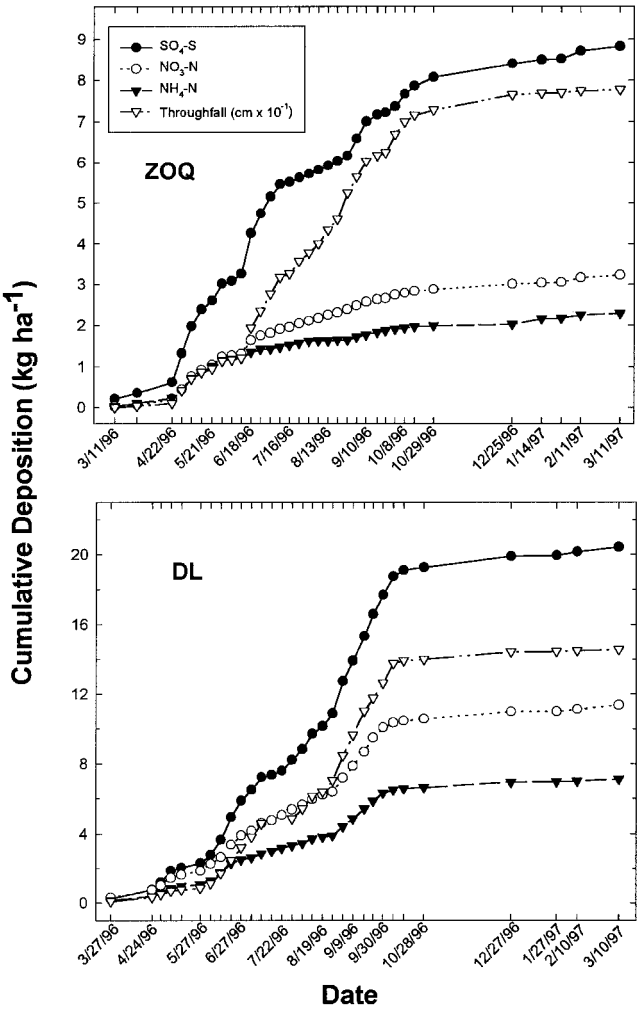

Figure 2. Cumulative bulk throughfall deposition of SO_4^{2-}, NO_3^-, and NH_4^+ and throughfall volumes at DL and ZOQ.

collection dates. Fluxes of NH_4^+ to the paper filter disks were not significantly different between the two sites.

3.2. N AND S CONCENTRATIONS IN SOIL

Ionic concentrations in soil tended to be higher in March before the rainy season began compared to samples collected in December, three months after the wet season. Sulfate concentrations in soil extracts were low (4.5 to 8.6 mg kg^{-1}) and varied little between sites, sampling depths, and dates, although SO_4^{2-} concentrations were significantly higher at DL in two of the four data/soil depth combinations (Figure 5). Ammonium concentrations in soil extracts ranged from 0.0 to 1.2 mg kg^{-1},

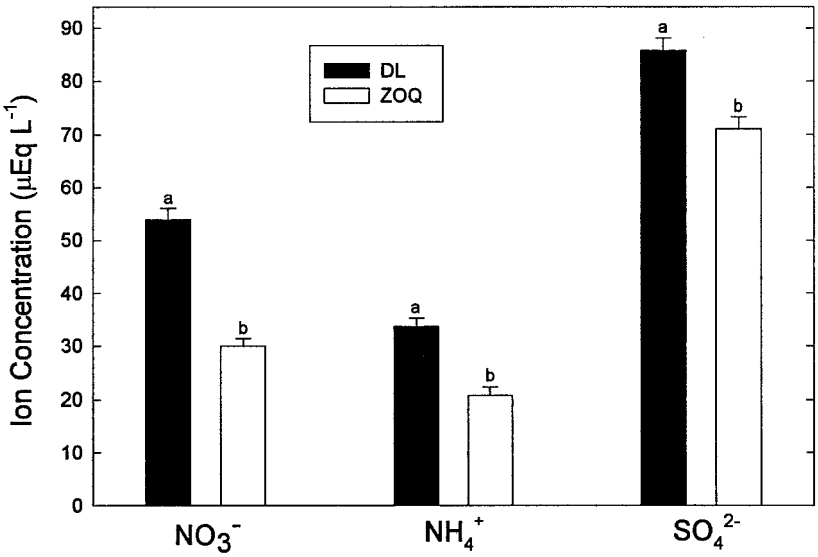

Figure 3. Volume-weighted annual mean ion concentrations at DL and ZOQ. Error bars represent standard errors of the plot means. Letters above the bars indicate significant differences between site means.

and were significantly greater at DL in March but not in December. No NH_4^+ was detected in aqueous soil extracts of the December 15–30 cm depth samples. The nitrate:sulfate concentration ratio in water extracts was typically 2–3 times higher in March than in December. Nitrate concentrations were consistently higher at DL than at ZOQ (Figure 5).

Total soil C and N were significantly higher at DL in all cases. Total soil S tended to be higher at DL as well, but differences in S content were significant only in the December samples from the 0–15 cm depth ($p = 0.15$ for the 15–20 cm depth in December). C:N ratios were low at both sites (15.2–16.7), but were not significantly different (Table II). Average values for soil pH showed a tendency towards greater soil acidity at DL, but differences bwteeen DL and ZOQ were not statistically significant. However, the p value was 0.13 for comparison of soil pH at the 15–30 cm depth at the two sites in March 1996 (Table II).

3.3. N AND S CONCENTRATIONS IN FOLIAGE

Total N concentrations and N:P ratios in 1995 and 1996 foliage were higher at DL than at ZOQ, but total P concentrations did not differ among the two sites. Total S concentrations in 1995 foliage were similar at DL and ZOQ, but S in 1996 foliage was slightly higher at DL (Figure 6). Foliar N:S ratios were higher at DL in 1995 needles, but N:S ratios for 1996 needles didn't differ between the two sites. Foliar C:N was lower at DL for both years (Figure 6).

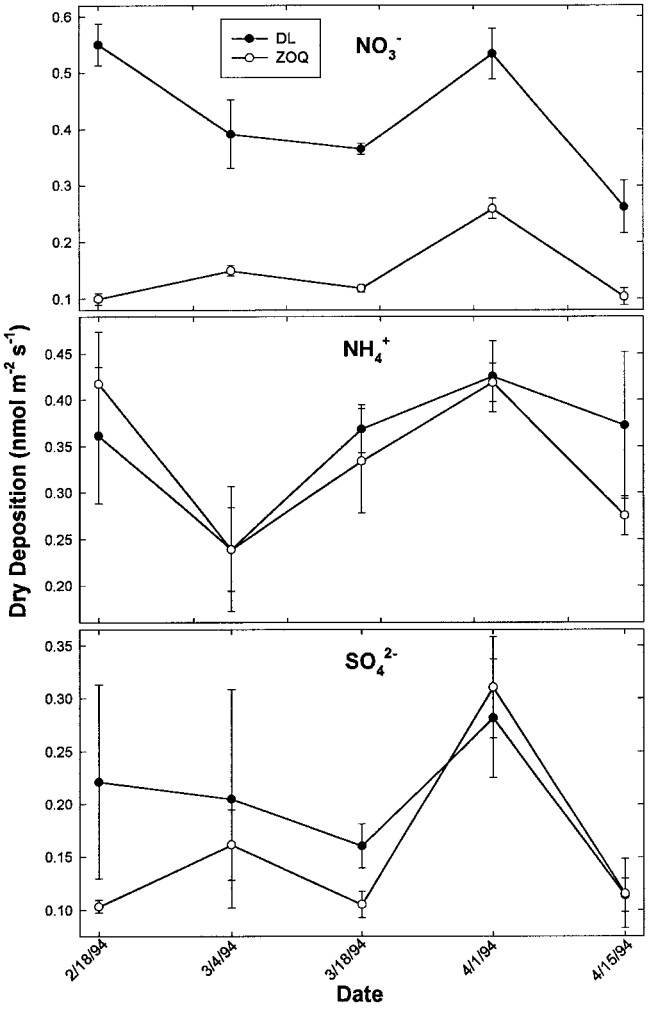

Figure 4. Average dry deposition fluxes to paper filter disks at forested sites southeast (Papayo) and southwest (Desierto) of Mexico City. Error bars are standard errors of the site means.

3.4. STREAMWATER CHEMISTRY

Except for two data points, SO_4^{2-} concentrations in streamwater were clearly higher at ZOQ than at DL. Ignoring the two possible outlier points, SO_4^{2-} concentrations in streamwater at ZOQ ranged from 130 to 226 μEq L^{-1}, compared to 28 to 92 μEq L^{-1} at DL (Figure 7). Differences in NO_3^- concentrations in streamwater between the two sites were less dramatic than for SO_4^{2-}. Nonetheless, NO_3^- concentrations were often much higher at DL, where values ranged from (1–45 μEq L^{-1}) compared to 0–11 μEq L^{-1} at ZOQ (Figure 7). Nitrate concentrations in 50% of the

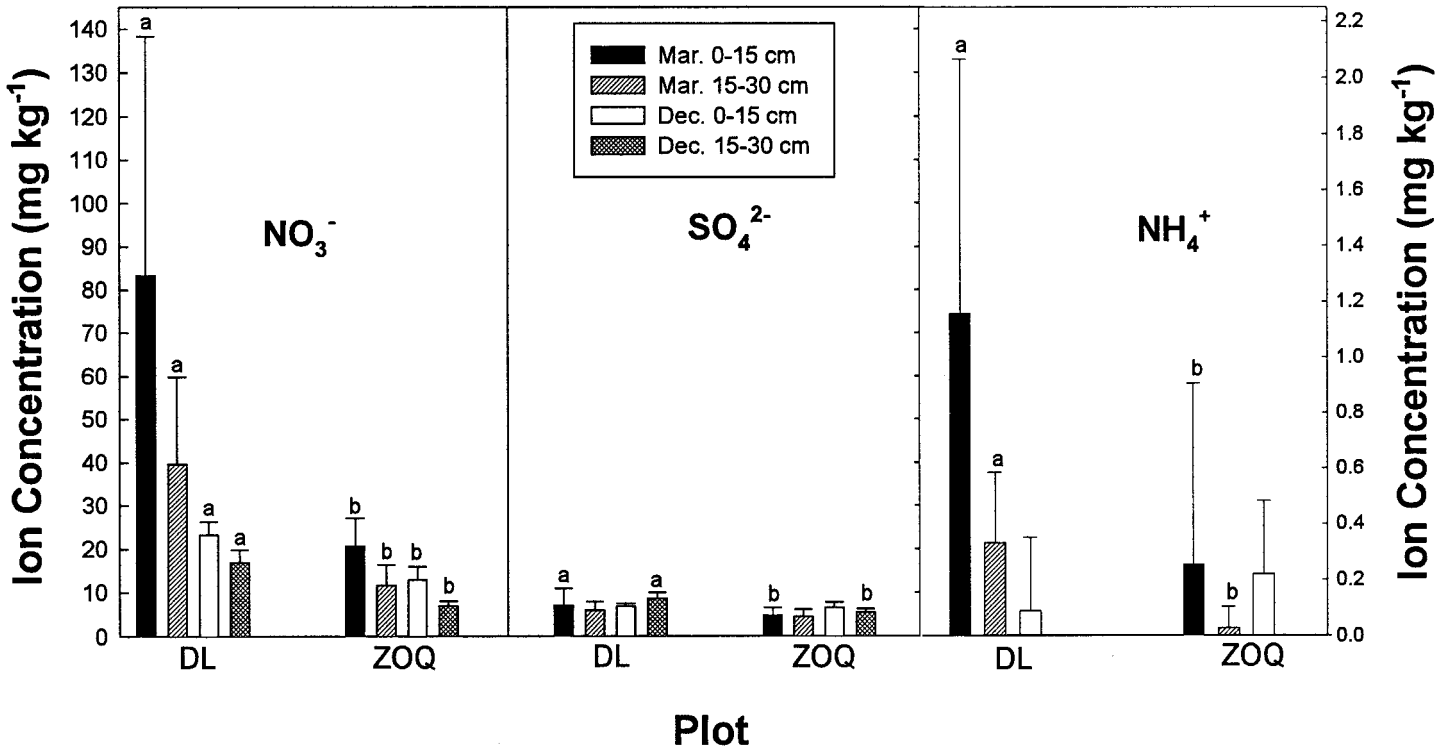

Figure 5. Ionic concentrations in aqueous extracts of soil sampled at two depths in March and December 1996. To NH_4^+ was detected in soil at either site in December, 1996. Error bars represent standard errors of the plot means. Letters above the bars indicate when ion concentrations were significantly different between DL and ZOQ for the corresponding sample date and soil depth.

TABLE II
Nutrient concentrations[a] and pH of soil from DL and ZOQ

Site	Nutrient Concentration (g kg^{-1})			C:N Ratio	pH
	Sulfur	Carbon	Nitrogen		
March 1996, 0–15 cm Depth					
DL	0.44	91.9 a	6.1 a	15.2	4.51
ZOQ	0.37	66.1 b	4.4 b	15.2	4.54
March 1996, 15–30 cm Depth					
DL	0.42	74.7 a	4.9 a	15.3	4.53
ZOQ	0.37	48.6 b	3.2 b	15.4	4.57
December 1996, 0–15 cm Depth					
DL	0.58 a	78.7 a	4.9 a	16.0	–
ZOQ	0.50 b	60.9 b	3.7 b	16.5	–
December 1996, 15–30 cm Depth					
DL	0.53	64.4 a	4.0 a	16.1	–
ZOQ	0.47	47.3 b	2.9 b	16.7	–

[a] Letters following nutrient concentrations indicate significant differences ($p \leq 0.10$) between DL and ZOQ.

streamwater samples from DL were $\geq 15 \mu$Eq L^{-1}, while at ZOQ, 75% of the streamwater samples contained $< 10\ \mu$Eq L^{-1} NO_3^-.

4. Discussion

4.1. Nitrogen and sulfur deposition

Bulk throughfall deposition of N and S at DL was relatively high compared to many forests throughout the world. This findings was not unexpected considering the high emissions of N and S oxides from Mexico City (Bravo, 1987; Velasco, 1983). Sulfur deposition in the Valley of Mexico is relatively high due to industrial sources and burning of fuels with a high S content (Valesco, 1983). Ionic concentrations in throughfall decreased as follows: $SO_4^{2-} > NH_3^- > NH_4^+$. In contrast, two recent studies of wet deposition in the Valley of Mexico (on the northern flank of the volcano Popocatépetl 70 km SE of Mexico City, an Rancho Viejo, a forested site 80 km of Mexico City) ion concentrations decreased in the following order: $SO_4^{2-} > NH_4^+ > NO_3^-$ (Baez *et al.*, 1997a; Baez *et al.*, 1997b). These sites are further from Mexico City than DL (23 km SW of Mexico City) and ZOQ (53 km E of Mexico City) and are less affected by air pollution from Mexico City.

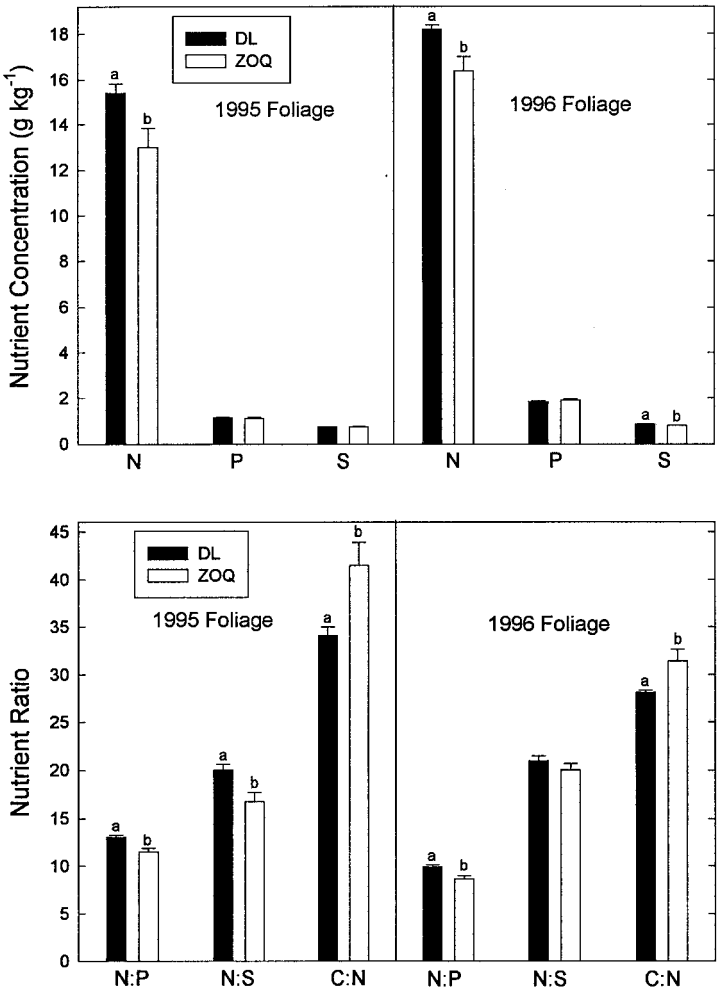

Figure 6. Nutrient concentrations and ratios in current-year and one-year old foliage. Error bars and letters are as described for Figure 3.

Ion concentration data from the studies of Baez *et al*. (1997a, b) are not directly comparable to our data because they collected precipitation or cloudwater, but did not collect throughfall. Throughfall includes a much greater dry deposition component than in wet deposition collected in open (canopy-free) areas because of the filtering capacity of the canopy for collecting dry deposition. Baez *et al*. (1997a) concluded that Mexico City air pollution did not affect cloud or rain water chemistry at Popocatépetl, but that wet deposition was affected by pollution from the sity of Puebla or from volcanic emissions – depending on wind direction during precipitation or cloud events.

Sulfur deposition in throughfall is generally considered to be a reasonable estimate of total S deposition to a forest. However, many studies demonstrate that 20 to

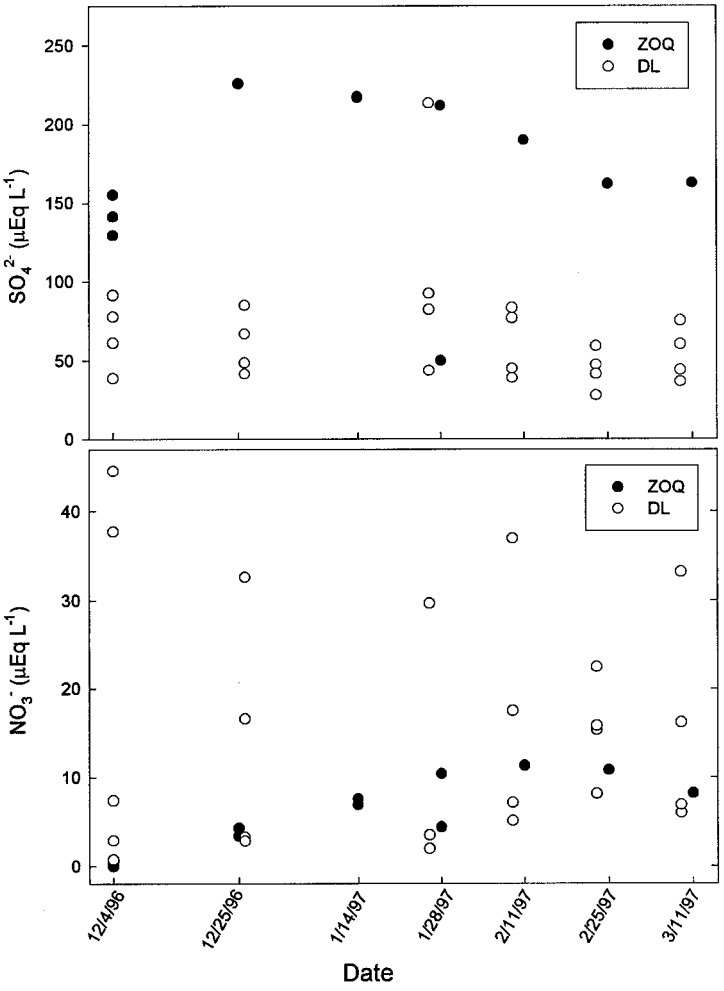

Figure 7. Scatter plot of concentrations of NO_3^- and SO_4^{2-} in streams at DL and ZOQ.

40% of atmospheric N deposited to a forest is retained within the canopy and thus not measured in throughfall analysis (Cadle *et al.*, 1991; Friedland *et al.*, 1991; Hanson and Garten, 1992; Lovett, 1992; Lovett and Lindberg, 1993; Marshall and Cadle, 1989; Schulze, 1989). Assuming that significant canopy retention of N also occurred in this study, total N deposition to the forest expressed on a mass basis (kg ha^{-1}) was slightly higher than total S deposition. For example, if the forest canopy retained from 20–40% of atmospherically-deposited N, total N deposition would be 22.2 to 25.9 kg ha^{-1} yr^{-1} at DL and 6.6 to 7.7 kg ha^{-1} yr^{-1} at ZOQ. In any case, deposition of N and S to the forest at DL is 10 to 20 times greater than levels measured in forests with minimal anthropogenic atmospheric deposition, assuming that background levels of N and S deposition in relatively pristine forests

are ca. 1–2 kg ha^{-1} yr^{-1} (Young *et al*., 1988). Deposition of N and S at ZOQ was approximately 3 to 9 times greater than background levels.

Concentrations of NO_3^- and NH_4^+ in throughfall at DL were 1.8 and 1.6 times greater than at ZOQ, while SO_4^{2-} concentrations were only 1.2 times greater at DL. The lower DL:ZOQ concentration ratio for S compared to N, suggests that there are sources of atmospheric S other than air pollution from Mexico City which contribute to S loading at ZOQ. Dry deposition fluxes of SO_4^{2-} to the surrogate surfaces at DL and ZOQ were highly similar on some dates, which also supports the hypothesis hat there are significant atmospheric sources of S pollution in forests at ZOQ. Possible additional sources of S include local industrial sources or volcanic S emissions. The volcano Popocatépetl, located 28 km south of ZOQ, has increased in fumarolic activity since 1991 (Del Pozzo *et al*., 1996) and is a likely source of SO_2 at ZOQ. In December 1994 Popocatépetl began erupting. Activity declined in late spring 1995, but eruptions resumed on March 5, 1996. On April 30, 1996 a large explosion occurred on the dome showering the area to the NE with ejecta (Athenosopolis *et al*., 1996; Del Pozzo *et al*., 1996). In recent years Popocatépetl has been degassing and generating SO_2 (2.6×10^6 tons in 617 days) at sustained high rates (Athenosopolis *et al*., 1996; Kress, 1997). The latest cycle of volcanic activity (March/April 1996) coincided with the beginning of throughfall sampling (March 1996) at ZOQ and DL. In late March to mid June 1996 S deposition in throughfall at ZOQ increased at a much greater rate than did throughfall volume (Figure 2), possibly because of high S inputs from volcanic emissions. At DL, which is not located downwind of Popocatépetl, S deposition and throughfall volumes increased at similar rates during the same time period. Increased wet deposition of SO_4^{2-}, NO_3^-, and other ions has been observed downwind of Popocatépetl (Baez *et al*., 1997a).

Greater total annual N and S deposition DL may have been partially due to the greater volume of throughfall collected at DL (Prado-Fiedler, 1990). However, greater volume-weighted ionic concentrations in throughfall at DL, also indicate that greater atmospheric concentrations were the main factor leading to greater total N and S deposition at DL compared to ZOQ. Greater dry deposition fluxes of NO_3^- and SO_4^{2-} to surrogate surface collectors at DL compared to ZOQ (Papayp) also support this conclusion.

4.2. Forest nutrient status

Plant, soil and hydrologic measurements indicate increased N availability in soil, N concentrations in foliage, and NO_3^- losses in streamwater at DL, possibly as a result of chronic N deposition. In the present study, the best indicator of enhanced N fertility at DL is the higher N:P ratio and lower C:N ratio at DL compared to ZOQ for current-year and previous-year foliage. Foliar nutrient ratios are more indicative of nutrient status than nutrient concentrations alone (Aber *et al*., 1995; Fenn and Poth, 1997; Fenn *et al*., 1998). This is especially true for ratios of nutrients that

are primarily involved in physiology rather than structure, such as N and P (Perry, 1994). The use of ratios rather than absolute concentrations is the basis of the Diagnosis and Recommendation Integrated System (DRIS), a diagnostic approach for determining plant nutrient status (Shumway and Chappell, 1995; Walworth and Sunner, 1987). For evaluation of site N status, the foliar N:P ratio has been found to be an effective indicator in many vegetation types (Boeye *et al*., 1997; Boxman *et al*., 1994; Ericsson *et al*., 1993; Fenn *et al*., 1996; Koerselman and Meuleman, 1996; Mohren *et al*., 1986; Williams *et al*., 1996; Zinke, 1980).

Nitrate and ammonium concentrations in soil also indicate greater N availability at DL, probably as a result of more nutrient-rich soil organic matter and higher nitrification rates. The Stoddard (1994) watershed N saturation model, and the analogous terrestrial N saturation model (Aber *et al*., 1989) describe four progressive stages of development in regards to N saturation. The data presented in this paper suggests that the forest at DL is at least at stage 1 and probably progressing toward stage 2 of the terrestrial conceptual model. Nitrogen fertilization studies would be helpful in determining whether N limitation of tree growth at DL has been reversed as a result of chronic N deposition.

At the watershed scale, streamwater NO_3^- concentration is a key indicator of N saturation (Fenn and Poth, 1997; Stoddard, 1994). Although only three months of streamwater data were collected in this study, the trends clearly indicate that NO_3^- export in streamwater is significantly greater at DL area than at ZOQ. However, seasonal trends in streamwater NO_3^- concentrations from throughout the year are needed to more fully characterize watershed N retention and loss. The primary definition of stage 2 watershed N saturation is when the terrestrial watershed and streams are incapable of retaining excess N even when biotic N demand is greatest the warmer months. Twelve of 24 stream samples contained NO_3^- concentrations ≥ 15 μEq L^-), concentrations which are typically found in watersheds at or approaching stage 2 of the Stoddard model. However, streamwater NO_3^- data for the summer growing season, when most rainfall occurs, is needed to confirm this hypothesis.

The possible effects of S deposition on S availability and plant S concentrations were not as evident as for N. In fact, SO_4^{2-} concentrations in streamwater were consistently higher at ZOQ than at DL. It isn't clear why streamwater SO_4^{2-} concentrations were nearly always higher at ZOQ compared to DL. Because S deposition at DL is more than double that at ZOQ, the much greater streamwater SO_4^{2-} concentrations at ZOQ must be a result of inherent soil SO_4^{2-} storage and release, and leaching that would occur even in the absence of elevated atmospheric deposition, although data on extractable SO_4^{2-} from soil in this study do not support this conclusion. Total S and SO_4^{2-} levels in soil extracts were similar at the two sites, although slightly higher at DL in some instances. However, the soils data in this study are inadequate for determining the source of streamwater SO_4^{2-}. The soils sampled for analysis represent a small area in DL and in ZOQ (at the same sites where throughfall samples were collected) of only one of the watersheds per site

where streamwater was sampled. Furthermore, soils were only sampled from the top 30 cm of the soil profile, while streamwater SO_4^{2-} is likely released from much deeper soil layers as well. Further study will be needed to elucidate the source and mechanisms leading to greater streamwater SO_4^{2-} concentrations at ZOQ compared to DL.

4.3. Ecosystem responses to N deposition in different climates

The Stoddard watershed N saturation model (Stoddard, 1994) and the Aber terrestrial N saturation model (Aber *et al.*, 1989) were developed using data from the northeastern United States. These models are conceptual in nature rather than quantitative, and are designed to facilitate understanding and to provide a framework for investigation of long-term ecosystem and watershed responses to chronic N additions. Recent studies in high-elevation tundra in the Colorado Front Range of the Rocky Mountains, U.S.A. (Baron *et al.*, 1994; Williams *et al.*, 1996) and in summer-dry (Mediteranean) forests (Fenn *et al.*, 1996), chaparral, and grassland (Riggan *et al.*, 1985) watersheds in southern California suggest that the primary responses of these various systems to chronic N inputs are similar to mesic forests in eastern North America. These reponses include increased – leaching of NO_3^-, leaching of cations, soil acidification, foliar N, nitrogenous trace gas emissions from soil, and increased nitrification rates. However, threshold levels of N deposition required to induce elevated NO_3^- export, the primary nitrogenous trace gas emitted from soil (Fenn *et al.*, 1996), and the timing of peak NO_3^- export from N-saturated watersheds vary in different climates/biomes (Fenn *et al.*, 1998). Chaparral and forest stands in southern California primarily emit nitric oxide (NO) from soil whereas in eastern North America nitrous oxide (N_2O) fluxes are dominant (Fenn *et al.*, 1998). In the San Gorgonio Wilderness, a moderate N deposition region in the San Bernardino Mountains in southern California, streamwater NO_3^- concentrations were usually highest in winter (period of greatest precipitation and lowest temperatures) as described in the Stoddard model. However, streamwater NO_3^- concentrations as high as 370 μeq L^{-1} occurred after a summer thundershower (M. E. Fenn and M. A. Poth, unpublished data). This contrasts with the Stoddard watershed model, which purports that NO_3^- concentration peaks occur only in the off season or during snowmelt (Stoddard, 1994).

Because of winter drought and heavy summer rainfall in the Valley of Mexico, temporal watershed NO_3^- export responses to chronic N deposition may differ from watershed responses in the summer-dry climate of California or from temporal responses described in the Stoddard model based on mesic forests in eastern North America. In the Valley of Mexico, cold temperatures in winter may limit N retention capacity, but low precipitation amounts are expected to limit the capacity for leaching N through the soil profile and out of the watershed. The data in this study demonstrate that significant winter export of NO_3^- occurs, but NO_3^- export in winter would undoubtedly be much greater if not for the winter drought. During

summer, high temperatures should favor biotic N retention, but heavy rainfall favors hydrologic export of NO_3^-. Further streamwater monitoring studies are needed to determine the net effect on N retention of the counteracting factors of high temperatures and high hydrologic fluxes during summer. We have recently initiated year-round streamwater chemistry studies at DL and ZOQ in order to investigate seasonal trends in streamwater NO_3^- export.

4.4. Comparison of air pollutants and effects on forests near Mexico City and Los Angeles California

Los Angeles, California (USA) and Mexico City are widely known to experience high photochemical smog exposure because of meteorological and topographical features that, in combination with elevated emissions of N oxides and hydrocarbons from fossil fuel burning, favor photochemical reactions and the buildup of high pollutant concentrations. Elevated ozone exposure occurs in both regions during the summer, but wintertime concentrations are much higher in the Valley of Mexico than in forests in southern California (Miller *et al.*, 1994). A critical factor in terms of ozone effects on vegetation in the Valley of Mexico is the co-occurrence of elevated ozone concentrations and adequate moisture for stomatal uptake of ozone during the growing season. In southern California, the summer drought limits ozone uptake even when concentrations are highly elevated (Temple and Miller, 1997). Sulfur emissions and deposition are much greater in the Valley of Mexico than in the Los Angeles area. Bulk throughfall S deposition at a high-pollution site near Crestline in the San Bernardino Mountains east of Los Angeles was 3 kg ha^{-1} yr^{-1} (M. E. Fenn, unpublished data; Fenn and Bytnerowicz, 1993) compared to 20 kg ha^{-1} yr^{-1} at DL in this study. However, forests in the Los Angeles Air Basin, which are close to the ocean (i.e., within 80 km) can experience elevated S deposition as a result of S in seasalt (Fenn and Kiefer, 1998). Heavy metal deposition is also of concern for forests near Mexico City because of elevated atmospheric concentrations of trace metals in Mexico City (Barfoot *et al.*, 1984; Bravo, 1987; Levinson and Shetty, 1992; Salazar *et al.*, 1981). High levels of lead, cadmium and zinc have recently been measured in soils and vegetation at DL (S. Watmough, personal communication).

The available evidence suggests that the N status of the forest at DL is similar to that of a high-pollution site (Camp Paivika) in the San Bernardino Mountains in the Los Angeles Air Basin (Fenn *et al.*, 1996). Foliar concentrations of N, P, and S in *P. hartwegii* at DL (this study) were higher than analogous concentrations in ponderosa pine (*P. ponderosa* Laws.) at Camp Paivika. Higher nutrient levels at DL were likely because of differences in soil characteristics, plant species effects, and climatic differences. However, similar N:P ratios in current-year foliage and similar soil C:N ratios at both sites indicate comparable N status of these forests. Streamwater NO_3^- concentrations were also high in both systems, although indufficient data is currently available from DL to make definitive comparisons.

In summary, forests downwind of Mexico City are probably more severely impacted by air pollution than forests near Los Angeles because of favorable moisture conditions for stomatal uptake of ozone during the summer growing season and because a greater number of major pollutants occur at high concentrations in the Valley of Mexico. Forests in high-pollution areas within the Los Angeles Air Basin experience elevated ozone exposure during the dry warmer months, chronic N deposition in dry forms in spring and summer, and wet and dry forms of N deposition in late fall and in winter (Fenn and Bytnerowicz, 1997). Forests downwind of Mexico City are exposed to elevated ozone levels year-round, experience elevated atmospheric deposition of N and S pollutants, and may also be impacted by chronic heavy metal inputs.

5. Conclusions

The findings of this study suggest that atmospheric deposition of N may have contributed to greater N availability, higher plant N status, and increased NO_3^- loss in streamwater at DL. However, the severity and geographic extent of N saturation symptoms in forests within the Valley of Mexico needs further study. Nitrogen deposition in bulk throughfall at DL (18.5 kg ha^{-1} yr^{-1}), a forest site downwind of metropolitan Mexico City, was significantly greater than at ZOQ (5.5 kg ha^{-1} yr^{-1}), a more distant site not directly exposed to the prevailing winds. Sulfur deposition in bulk throughfall was also greater at DL (20.4 kg ha^{-1} yr^{-1}) compared to ZOQ (8.8 kg ha^{-1} yr^{-1}). However, more local sources, including volcanic emissions, may have contributed to S deposition at ZOQ. Total S concentrations in current-year foliage were slightly higher at DL compared to ZOQ, but S concentrations were not different in year-old foliage. Watershed-level N saturation at DL was claerly evidenced by the fact that NO_3^- concentrations in 50% of the streamwater samples from DL were $\geq$ 15 μEq L^{-1}, while at ZOQ, 75% of the streamwater samples contained < 10 μEq L^{-1} NO_3^-. Forests downwind of Mexico City may be at greater risk from air pollution stress than forests in the Los Angeles, California Air Basin because high soil moisture availability and ozone exposures co-occur (favoring greater ozone uptake), and because a greater number of major pollutants occur at high concentrations (photochemical oxidants, N compounds, S pollutants, and trace metals).

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