

5.0 DRY DEPOSITION OF BASE CATIONS TO FOREST CANOPIES AT THREE PLOTS BASED ON FOLIAGE RINSING DETERMINATIONS AND ESTIMATES OF DEPOSITION TO GROUND.

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5.1 Introduction

Similarly as for nitrogen and sulfur, atmospheric dry deposition is an important source of physiologically important base cations to forest ecosystems. Lindberg et al. (1986) determined that dry deposition represented more than 50% of the annual input of Ca^{2+} and K^{+} in an oak forest in Tennessee. Dry deposition to plant communities in the forest of the California mountains is of special importance because of the small amount of wet deposition during the growing season and scarcity of nutrients in predominantly granitic soils (Rundell and Parsons, 1977). However, very little is known about deposition of base cations to forests in the western United States, with the exception of a few studies in the subalpine ecosystem of the Sierra Nevada (Bytnerowicz et al., 1991; 1992; Brown and Lund, 1994). No similar studies have been performed in the San Bernardino Mountains.

Potassium, calcium, magnesium are essential elements for most higher plants (Salisbury and Ross, 1978). Sodium is taken up by plants from the soil solution. Although a role of sodium in plant physiology is not well established (Czerwinski, 1978), it is believed that it may replace potassium in controlling cell turgor (Mengel and Kirkby, 1982). It has been established that with increased acidity of soil (which could be caused by elevated deposition of nitrogen) availability of potassium, calcium and magnesium may be impaired (Falkengren-Grerup, 1989; Duffy and Schreiber, 1990; Huettl, 1992). Acidic precipitation can also cause increased leaching of these cations from the foliage (Barker and Ashenden, 1992; Cape, 1993). Therefore it may be expected that forests which are under effects of the above-normal levels of acidic precipitation may be experiencing deficiencies of potassium, calcium and magnesium. This potential for deficiency may be compensated to some extent by dry deposition of these elements to forest trees and soils.

At the Barton Flats forest study site deposition of potassium, calcium, magnesium, and sodium to the forest were measured by a throughfall analysis and a foliage rinsing technique. In this section of the report the results obtained by the foliage rinsing technique are presented.

5.2 Methods

The foliage rinsing technique is described in Section 4.2 and in detail in the Standard Operation Procedures. Concentrations of base cations in the foliage rinses were determined with atomic absorption spectrophotometry (Perkin Elmer 5000). The branches were harvested at the end of each season and their surface area calculated according to empirically developed formulas. Results of base cation deposition are presented as fluxes ($\text{micrograms m}^{-2} \text{ h}^{-1}$).

5.2.1 Measurements of Deposition Fluxes of Base Cations on a Vertical Gradient

Deposition of base cations was determined in four levels of the mature forest canopy. Four ponderosa pine seedlings were placed at each level (top of the canopy - 29 m above the forest floor; third level - 24 m above the forest floor; second level - 16 m above the forest floor; and bottom of the canopy - 12 m above the forest floor). Measurements were performed during the 1992 and 1993 seasons.

5.2.2 Measurements of Deposition Fluxes of Base Cations to Ponderosa Pine, White Fir and California Black Oak at Three Plots

During two periods (July 19-23 and July 23-30) of the 1993 intensive study, deposition of base cations to the foliage of four seedlings and four mature trees of ponderosa pine, California black oak and white fir was measured at Plots 1, 2, and 3. Results of these measurements for Plot 2 were used for estimates of deposition of base cations at the forest stand level. Results from Plots 1 and 3 may be used for future estimates of cation inputs into these plots.

5.2.3 Estimates of Deposition of Base Cations to Forest Stand

Estimates of deposition of basic cations to the mixed coniferous forest stand (Plot 2) were made for the polluted season of 1993 (April 15 - October 15). Because no foliage rinsing was done during the rest of the year no estimates of base cation inputs to the forest for the entire year are provided.

Most of the assumptions needed for the estimating base cations inputs to Plot 2 are presented in Section 4.2.4 and Appendix A.4.1. In addition:

- a. Deposition fluxes of base cations to the branches of ponderosa pine seedlings and branches of mature trees were compared for the entire 1993 season. The correction factors (deposition flux to mature trees/deposition flux to seedlings) were derived by dividing average deposition flux to foliage of mature trees by the average deposition flux to seedlings at the forest floor level of Plots 1, 2 and 3 during the intensive study. The following correction factors were derived: K - 1.554; Na - 1.352; Ca - 0.699; and Mg - 1.318.
- b. Correction factors needed for extrapolation of the deposition from mature ponderosa pines to mature California black oak and white fir were calculated. They were derived by dividing the average deposition fluxes to branches of mature fir or oak trees by the average flux to branches of mature pines in all three plots during the intensive study (Tables 5-9 through 5-12).
- c. Surface areas of canopies (foliage + branches) used for the calculations were based on the litterfall method of LAI estimates (see section 4.2.4, Table 4-1, and Appendix A.4.1). The following estimates of surface areas at Plot 2 were used for the calculations: pine - 1909.2 m²; oak - 3118 m²; and fir - 4623 m².
- d. For calculations of deposition to ground surface the average deposition to mature tree branches of three species at Plot 2 during the two periods of the intensive study were used. These values are as follows: K - 15.01 $\mu\text{g m}^{-2} \text{ h}^{-1}$; Na - 1.52 $\mu\text{g m}^{-2} \text{ h}^{-1}$; Ca - 3.66 $\mu\text{g m}^{-2} \text{ h}^{-1}$; and Mg - 1.43 $\mu\text{g m}^{-2} \text{ h}^{-1}$ (see Table 5-11).

5.3 Results

5.3.1 Surface Deposition of Base Cations to Ponderosa Pine Seedlings and Mature Trees in a Vertical Gradient

1992 season

Deposition of potassium to ponderosa pine branches was significantly affected by the position of branches in the canopy. The highest deposition was at the canopy top and was followed by deposition at the second level (16 m). Deposition of potassium was the lowest at the third level (24 m) and at the canopy bottom. A significant effect of exposure time was seen for potassium deposition -- much higher deposition occurred during the July 16 - 23 period than during the two other exposure periods (Figure 5-1 and Table 5-1). A strong effect of position within the crown was seen for sodium -- the highest deposition occurred at the canopy top. Also a significant effect of exposure time occurred -- deposition during the September 18 - 28 period was significantly lower than during the two preceding periods (Figure 5-2 and Table 5-2). Similar effects of a position of branches within the canopy and time were determined for calcium (Figure 5-3 and Table 5-3) and magnesium (Figure 5-4 and Table 5-4).

1993 season

No significant effect of branch position in the canopy were determined for potassium, however, significant differences in deposition were seen between the individual exposure periods (Figure 5-5 and Table 5-5). Similar effects of position in the canopy and time were determined for sodium (Figure 5-6 and Table 5-6). For depositions of calcium and magnesium, significant effects of a position within the canopy and exposure time occurred (Figures 5-7 and 5-8 and Tables 5-7 and 5-8).

Deposition of potassium to branches of mature trees and seedlings at three different levels of the canopy is presented in Figures A5-1 through A5-3. Differences between the mature trees and seedlings were inconsistent. Figures A5-4 through A5-6 present deposition of sodium to branches to mature trees and seedlings. Similarly as for potassium no consistent differences between deposition to the seedlings and mature trees were seen. A trend towards higher deposition of calcium to the branches of the seedlings (Figures A5-7 through A5-9) and an opposite trend for magnesium (deposition to mature trees) (Figures A5-10 through A5-12) occurred. Based on the results of deposition to branches of mature trees and seedlings the correction factors needed for estimates of deposition to forest stand were calculated (see Section 5.2.4).

5.3.2 Surface Deposition of Base Cations to Ponderosa Pine, White Fir and California Black Oak at Three Plots

Deposition of potassium to the branches of mature trees and seedlings of pine, oak and fir at Plots 1, 2, and 3 during the July 19 - 23, 1993 period is presented in Figures A5-13 through A5-15 and for the July 23-30, 1993 period in Figures A5-16 through A5-18. Both periods were characterized by high variability of the deposition fluxes and a trend towards highest deposition occurring to California black oak.

Similarly as for potassium, deposition of sodium to the branches of mature trees and seedlings of pine, oak and fir at Plots 1, 2, and 3 during the July 19-23, 1993 period (Figures A5-19 through A5-21) was also highly variable. For Plots 1 and 3 during the July 23-30, 1993 no data were available, and for Plot 2 (Figure A5-22) the highest deposition was determined for the California black oak seedlings (Figure A5-24).

Deposition of calcium to branches of mature trees and seedlings of pine, oak and fir was also estimated to have very high variability. No consistent differences between deposition to seedlings vs. mature trees were seen and deposition to oak tended to be the highest during the July 19-23, 1993 (Figures A5-23 through A5-25) and July 23-30, 1993 periods (Figures A5-26 through A5-28).

Deposition of magnesium to the branches of mature trees and seedlings of pine, oak and fir was less variable than for other base cations. A tendency toward higher deposition to the seedlings and highest deposition to California black oak were seen during the July 19-23, 1993 period (Figures A5-29 through A5-31) and the July 23-30, 1993 period (Figures A5-32 through A5-34).

Summary of deposition of four base cations to branches of mature trees is presented in Tables 5-9 through 5-12. Results of these comparisons were used for calculation of correction factors needed for estimates of deposition of base cations to forest stand (see Section 5.2.3).

5.3.3 Estimation of Base Cation Deposition to Forest Stand

Estimates of deposition of base cations to a forest stand were made for Plot 2 during the polluted season of 1993 (i.e., April 15 to October 15). Calculations were made for the three tree species as well as for the ground surface. A sum of all of the above mentioned deposition represents a total dry deposition of each of the studied base cations to the forest stand.

5.3.3.1 Deposition of Base Cations to Tree Surfaces

Estimates of base cation deposition (g ha^{-1}) to tree surfaces of ponderosa pine, white fir and California black oak were made with an assumption that depositions to foliage and branches were similar. Separate calculations were made for each tree species using the following equation:

$$\text{Base Cation Deposition (g ha}^{-1}\text{)} = 2.08 \times F_{bc} \times X_{s/mt} \times X_t \times SA \times T \times X_m$$

Where:

- 2.08 - "hectar/Plot 2" correction factor ($10,000 \text{ m}^2 / 4,800\text{m}^2$)
- F_{bc} - deposition flux of a basic cation measured by foliage rinsing (e.g. $6.48 \mu\text{g m}^{-2} \text{ h}^{-1}$)
- $X_{s/mt}$ - seedling-to-mature tree correction factor (see Table 5-13)
- X_t - tree species correction factor (see Tables 5-9 through 5-12)
- SA - total leaf area of tree species in Plot 2 (m^2 ; see section 5.2.3)
- T - total time of exposure in the polluted season ($182.5 \text{ days} \times 24 \text{ h} = 4,380 \text{ h}$)
- X_m - mass correction factor ($10^{-6} \mu\text{g g}^{-1}$)

Example: K^+ deposition to ponderosa pine = $2.08 \times 6.48 \mu\text{g m}^{-2} \text{ h}^{-1} \times 1 \times 1,909.2 \text{ m}^2 \times 4,380 \text{ h} \times 10^{-6}$

$$= 175 \text{ g K}^+ \text{ ha}^{-1} \text{ polluted season}^{-1}$$

5.3.3.2. Deposition of Base Cations to Ground Surface

In addition, deposition to the ground surface at Plot 2 was also calculated by modifying the above equation as follows:

$$\text{Deposition to ground surface (g ha}^{-1}\text{)} = F_{gs} \times SA \times T \times X_m$$

Where: F_{gs} - deposition to ground surface (K^+ - 15.01; Na^+ - 1.52; Ca^{2+} - 3.66; Mg^{2+} - 1.43 $\mu\text{g m}^{-2} \text{ h}^{-1}$) - (see section 5.2.3 for explanation)
 SA - total surface area (1 ha = 10,000 m^2)
 T - total hours in the polluted season (4,380 h; compare 5.3.3.1)
 X_m - mass correction factor ($10^{-6} \mu\text{g g}^{-1}$)

Example: K^+ deposition to ground surface = $15.01 \mu\text{g m}^{-2} \text{ h}^{-1} \times 10,000 \text{ m}^2 \times 4,380 \text{ h} \times 10^{-6} = 657 \text{ g ha}^{-1} \text{ polluted season}^{-1}$

5.3.3.3 Total Deposition of Base Cations to the Mixed Coniferous Forest Stand

Total deposition of base cations estimated for the 1993 polluted season at Plot 2 is summarized in Table 5-14. The highest deposition expressed as $\text{g ha}^{-1} \text{ polluted season}^{-1}$ was determined for calcium (3697.4), followed by sodium (2778.3), potassium (2217.6) and magnesium (658.9).

5.4 Discussion

Position within the canopy had a significant effect on potassium deposition to ponderosa pine branches during the 1992 season, however, this effect was not significant in 1993. During both seasons significant effects of exposure time on potassium deposition occurred. Sodium deposition was the highest at the canopy top in both seasons. During both seasons a significant effect of time of collection was determined for sodium. Clear effects of canopy position and exposure time were determined in 1992 and 1993 for calcium and magnesium. Patterns of changes in these two base cations were similar to the trends observed for nitrate, ammonium and sulfate deposition in this study (see Section 4).

No clear trends were seen when depositions of potassium and sodium to branches on mature trees and seedlings at different levels of the canopy were compared during the 1993 season. Also variability of the data was very high. This could probably be attributed to large amounts of these two metals which could be leached out from the foliage during the rinsing procedures -- it has been shown that large portions of these two base cations in throughfall originate from foliar leaching (Parker, 1983). Deposition of calcium to the branches of mature ponderosa pines was higher than the deposition to the seedlings. For magnesium a tendency towards higher deposition to seedlings was observed.

Average values of potassium, sodium and magnesium deposition to ponderosa pines at Barton Flats were similar to the values determined for western white pine and lodgepole pine in the western Sierra Nevada (Bytnerowicz et al., 1991; Brown and Lund, 1994) and several times higher than the deposition to lodgepole and whitebark pines at the eastern Sierra Nevada site (Bytnerowicz et al., 1992). However, values of calcium deposition to pines at Barton Flats were about two times higher than values determined to native pines at the western Sierra Nevada site (Bytnerowicz et al., 1991; Brown and Lund, 1994) and many times higher than in the eastern Sierra Nevada (Bytnerowicz et al., 1992). This may be related to the proximity of the Mojave Desert and a long range transport of desert dust containing high concentrations of calcium into the forests of the San Bernardino Mountains. These relative differences between the Barton Flats site and other California locations indicate that dry deposition may be an important source of these cations in the mixed coniferous forests of the San Bernardino Mountains. Since the increased deposition of acidifying N compounds is known to diminish pools of potassium, calcium and magnesium this may be a special importance if elevated deposition of N compounds to these forests continue.

5.5. Summary

Deposition of potassium, calcium, magnesium and sodium to branches of mature trees and seedlings of ponderosa pine was determined on a vertical gradient in Plot 2 during the 1992 and 1993 summer seasons. In addition, during an intensive study in summer 1993, deposition of these base cations to branches of mature trees and seedlings of California black oak and white fir at forest floor of Plots 1, 2, and 3 was determined.

Similarly as for other ions, the higher the position within a canopy the higher was the deposition of the studied base cations. In general, the highest deposition fluxes of potassium, calcium, magnesium and sodium were determined for California black oak. Based on the results of various comparisons dry deposition of these cations during the polluted season (April 15 through October 15) for a forest stand was calculated. For that period the highest deposition was determined for calcium (about 3.7 kg/ha), followed by sodium (2.8 kg/ha), potassium (2.2 kg/ha) and magnesium (0.7 kg/ha). Dry deposition of potassium, calcium, magnesium were elevated and may be an important mechanism compensating for some of the negative effects (reduced amounts of available sources of these base cations) of the elevated deposition of nitrogen compounds.

5.6. References

- Barker, M. G., and T. W. Ashenden. 1992. Effects of Acid Fog on Cuticular Permeability and Cation Leaching in Holly (*Ilex aquifolium*). *Agric. Ecos. Environ.*, 42, 291-306.
- Brown, A. D., and L. J. Lund. 1994. Factors Controlling Throughfall Characteristics at a High Elevation Sierra Nevada Site, California. *J. Environ. Qual.*, 23, 844-850.
- Bytnerowicz, A., P. J. Dawson, C. L. Morrison, and M. P. Poe. 1991. Deposition of Atmospheric Ions to Pine Branches and Surrogate Surfaces in the Vicinity of Emerald Lake Watershed, Sequoia National Park. *Atmos. Environ.*, 25A, 2203-2210.
- Bytnerowicz, A., P. J. Dawson, C. L. Morrison, and M. P. Poe. 1992. Atmospheric Dry Deposition on Pines in the Eastern Brook Lake Watershed, Sierra Nevada, California. *Atmos. Environ.*, 26A, 3195-3201.
- Cape, J. N. 1993. Direct Damage to Vegetation Caused by Acid Rain and Polluted Cloud: Definition of Critical Levels for Forest Trees. *Environ. Pollut.*, 82, 167-180.
- Czerwinski, W. 1978. *Fizjologia Roslin*. PWN, Warszawa, 603 pp.
- Duffy, P. D., and J. D. Schreiber. 1990. Nutrient Leaching of a Loblolly Pine Forest Floor by Simulated Rainfall. II. Environmental factors. *Forest Science*, 36, 777-789.
- Falkengren-Grerup, U. 1989. Soil Acidification and its Impact on Ground Vegetation. *Ambio*, 18, 179-183.
- Huettl, R. F. 1993. Forest Soil Acidification. *Angew. Bot.*, 67, 66-75.
- Lindberg, S. E., G. M. Lovett, D. D. Richter, and D. W. Johnson. 1986. Atmospheric Deposition and Canopy Interactions of Major Ions in Forest. *Science*, 231, 141-145.
- Mengel, K., and E. A. Kirkby. 1982. *Principles of Plant Nutrition*. International Potash Institute, Bern, Switzerland, 655 pp.
- Parker, G. G. 1983. Throughfall and Stemflow in the Forest Nutrient Cycle. In: *Advances of Ecological Research* (A. Macfadyen and E. D. Ford, eds.), vol. 13, pp.57-133, Academic Press, London.
- Rundell, P. W., and D. J. Parsons. 1977. Montane and Subalpine Vegetation in the Sierra Nevada and Cascade Ranges. In: *Terrestrial Vegetation of California* (edited by M. J. Barbour and J. Major), pp. 559-599, Wiley, New York.
- Salisbury, F. B., and C. W. Ross. 1978. *Plant Physiology*, Wadsworth Publishing Company, Belmont, CA, 422 pp.

Table 5-1 Summary of the ANOVA for the Results of Potassium Deposition ($\mu\text{g m}^{-2} \text{h}^{-1}$) to Branches of Ponderosa Pine Seedlings at Four Levels of the Canopy During Three Periods in the 1992 Season.

	Effect of position	Effect of time	
p value	<0.0001	<0.0001	
Mean			
top	3.94 a	July 16-	3.92 a
third	2.53 b	Aug. 21-	2.29 b
second	2.92 ab	Sep. 18-	2.45 b
bottom	2.16 b		

Table 5-2 Summary of the ANOVA for the Results of Sodium Deposition ($\mu\text{g m}^{-2} \text{h}^{-1}$) to Branches of Ponderosa Pine Seedlings at Four Levels of the Canopy During Three Periods in the 1992 Season.

	Effect of position	Effect of time	
p value	<0.0001	0.0002	
Mean			
top	13.15 a	July 16-	7.73 a
third	6.17 b	Aug. 21-	6.72 a
second	3.47 c	Sep. 18-	4.81 b
bottom	2.89 c		

Table 5-3 Summary of the ANOVA for the Results of Calcium Deposition ($\mu\text{g m}^{-2} \text{h}^{-1}$) to Branches of Ponderosa Pine Seedlings at Four Levels of the Canopy During Three Periods in the 1992 Season.

	Effect of position	Effect of time	
p value	<0.0001	0.0002	
Mean			
top	27.64 a	July 16-	18.80 a
third	15.85 b	Aug. 21-	15.60 b
second	11.19 c	Sep. 18-	13.30 b
bottom	8.81 c		

Table 5-4 Summary of the ANOVA for the Results of Magnesium Deposition ($\mu\text{g m}^{-2} \text{h}^{-1}$) to Branches of Ponderosa Pine Seedlings at Four Levels of the Canopy During Three Periods in the 1992 Season.

	Effect of position	Effect of time	
p value	<0.0001	<0.0001	
Mean			
top	4.06 a	July 16-	2.65 a
third	2.13 b	Aug. 21-	2.11 b
second	1.27 c	Sep. 18-	1.69 b
bottom	1.12 c		

Table 5-5 Summary of the ANOVA for the Results of Potassium Deposition ($\mu\text{g m}^{-2} \text{h}^{-1}$) to Branches of Ponderosa Pine Seedlings at Four Levels of the Canopy During Six Periods in the 1993 Season.

	Effect of position	Effect of time	
p value	0.4773	<0.0001	
Mean			
top	6.89	May 27-	3.84 b
third	6.06	June 23-	6.20 b
second	8.77	July 19-	9.36 a
bottom	10.74	July 23-	9.70 a
		Aug. 30-	6.10 b
		Sep. 24-	4.76 b

Table 5-6 Summary of the ANOVA for the Results of Sodium Deposition ($\mu\text{g m}^{-1} \text{h}^{-1}$) to Branches of Ponderosa Pine Seedlings at Four Levels of the Canopy During Six Periods in the 1993 Season.

	Effect of position	Effect of time	
p value	0.0002	<0.0001	
Mean			
top	10.58a	May 27-	16.35 a
third	7.61b	June 23-	6.45 bc
second	5.53b	July 19-	10.54 b
bottom	10.72b	July 23-	6.31 bc
		Aug. 30-	2.87 c
		Sep. 24-	3.00 c

Table 5-7 Summary of the ANOVA for the Results of Calcium Deposition ($\mu\text{g m}^{-2} \text{h}^{-1}$) to Branches of Ponderosa Pine Seedlings at Four Levels of the Canopy During Six Periods in the 1993 Season.

	Effect of position	Effect of time	
p value	<0.0001	<0.0001	
Mean			
top	25.3 a	May 27-	21.9 ab
third	19.6 b	June 23-	18.2 bc
second	13.1 c	July 19-	16.2 bc
bottom	13.6 c	July 23-	11.1 c
		Aug. 30-	27.0 a
		Sep. 24-	12.9 c

Table 5-8 Summary of the ANOVA for the Results of Magnesium Deposition ($\mu\text{g m}^{-2} \text{h}^{-1}$) to Branches of Ponderosa Pine Seedlings at Four Levels of the Canopy During Six Periods in the 1993 Season.

	Effect of position	Effect of time	
p value	<0.0001	<0.0001	
Mean			
top	3.69 a	May 27-	4.29 a
third	2.88 b	June 23-	2.45 b
second	2.02 c	July 19-	2.09 b
bottom	2.49 bc	July 23-	1.75 b
		Aug. 30-	4.08 a
		Sep. 24-	1.97 b

Table 5-9 Deposition of Potassium ($\mu\text{g m}^{-2} \text{h}^{-1}$) and Tree Species Correction Factors (X_t) for Mature Ponderosa Pine, California Black Oak and White Fir at the Forest Floor During the Intensive Study.

Plot number	Pine	Oak	Fir
July 19-23, 1993			
1	8.65 (4.12)	15.82 (5.08)	20.04 (15.19)
2	8.54 (3.26)	20.50 (7.42)	23.56 (18.03)
3	9.29 (0.98)	19.11 (11.88)	6.94 (3.47)
July 23-30, 1993			
1	2.77 (0.70)	5.13 (1.62)	4.44 (1.94)
2	6.08 (0.73)	21.85 (1.97)	9.55 (4.05)
3	10.16 (0.14)	32.80 (18.59)	4.75 (1.56)
Correction Factor (X_t)	1.00	2.494	1.578

Table 5-10 Deposition of Sodium ($\mu\text{g m}^{-2} \text{h}^{-1}$) and Tree Species Correction Factors (X_t) for Mature Ponderosa Pine, California Black Oak and White Fir at the Forest Floor During the Intensive Study.

Plot number	Pine	Oak	Fir
July 19-23, 1993			
1	0.13 (0.06)	2.33 (2.23)	0.22 (0.01)
2	1.14 (0.78)	3.63 (2.89)	1.83 (0.78)
3	0.49 (0.23)	2.47 (3.27)	0.33 (0.120)
July 23-30, 1993			
1	-	-	-
2	1.06 (0.51)	1.15 (0.74)	0.31 (0.03)
3	-	-	-
Correction Factor (X_t)	1.00	6.707	1.054

Table 5-11. Deposition of Calcium ($\mu\text{g m}^{-2} \text{h}^{-1}$) and Tree Species Correction Factors (X_t) for Mature Ponderosa Pine, California Black Oak and White Fir at the Forest Floor During the Intensive Study.

Plot number	Pine	Oak	Fir
July 19-23, 1993			
1	1.78 (1.18)	9.05 (4.44)	3.39 (1.83)
2	0.36 (0.08)	8.06 (2.20)	4.17 (5.82)
3	1.56 (2.30)	14.71 (11.65)	0.41 (0.09)
July 23-30, 1993			
1	2.31 (0.92)	7.33 (1.93)	6.15 (3.06)
2	1.75 (0.41)	5.36 (2.93)	2.24 (0.54)
3	1.56 (0.45)	6.85 (1.95)	3.01 (1.63)
Correction Factor (X_t)	1.00	7.973	3.386

Table 5-12 Deposition of Magnesium ($\mu\text{g m}^{-2} \text{h}^{-1}$) and Tree Species Correction Factors (X_t) for Mature Ponderosa Pine, California Black Oak and White Fir at the Forest Floor During the Intensive Study.

Plot number	Pine	Oak	Fir
July 19-23, 1993			
1	0.60 (0.10)	2.54 (1.12)	0.53 (0.02)
2	0.85 (0.26)	3.48 (0.80)	1.62 (1.17)
3	0.87 (0.35)	3.22 (1.14)	0.34 (0.33)
July 23-30, 1993			
1	0.82 (0.29)	1.72 (0.47)	0.84 (0.16)
2	0.51 (0.19)	1.52 (0.22)	0.62 (0.14)
3	0.52 (0.13)	2.61 (1.28)	0.53 (0.25)
Correction Factor (X_t)	1.00	3.682	1.075

Table 5-13. Seedling-to-Mature Tree Correction factors ($X_{s/mt}$) used to calculate the base cation deposition fluxes (see Appendix A for details)

Base Cation	$X_{s/mt}$	X_t		
	All Trees	Pine	Oak	Fir
K^+	1.554	1	2.494	1.578
Na^+	1.352	1	6.707	1.054
Ca^{2+}	0.699	1	7.973	3.386
Mg^{2+}	1.318	1	3.682	1.075

Table 5-14 Total Deposition of Metals to the Mixed Coniferous Stand (Plot 2) During the 1993 "Polluted" Season (g/ha/182.5 days).

Deposition surface	K	Na	Ca	Mg
Pine	175.4	186.9	212.1	62.0
Oak	714.5	2047.7	1585.7	372.8
Fir	670.3	477.1	1739.3	161.8
Ground	657.4	66.6	160.3	62.3
Total	2217.6	2778.3	3697.4	658.9

Figure 5-1 Potassium Flux to Branches of Ponderosa Pine Seedlings in a Vertical Gradient During the 1992 Season.

Potassium flux to ponderosa pine branches on a vertical gradient, 1992 season

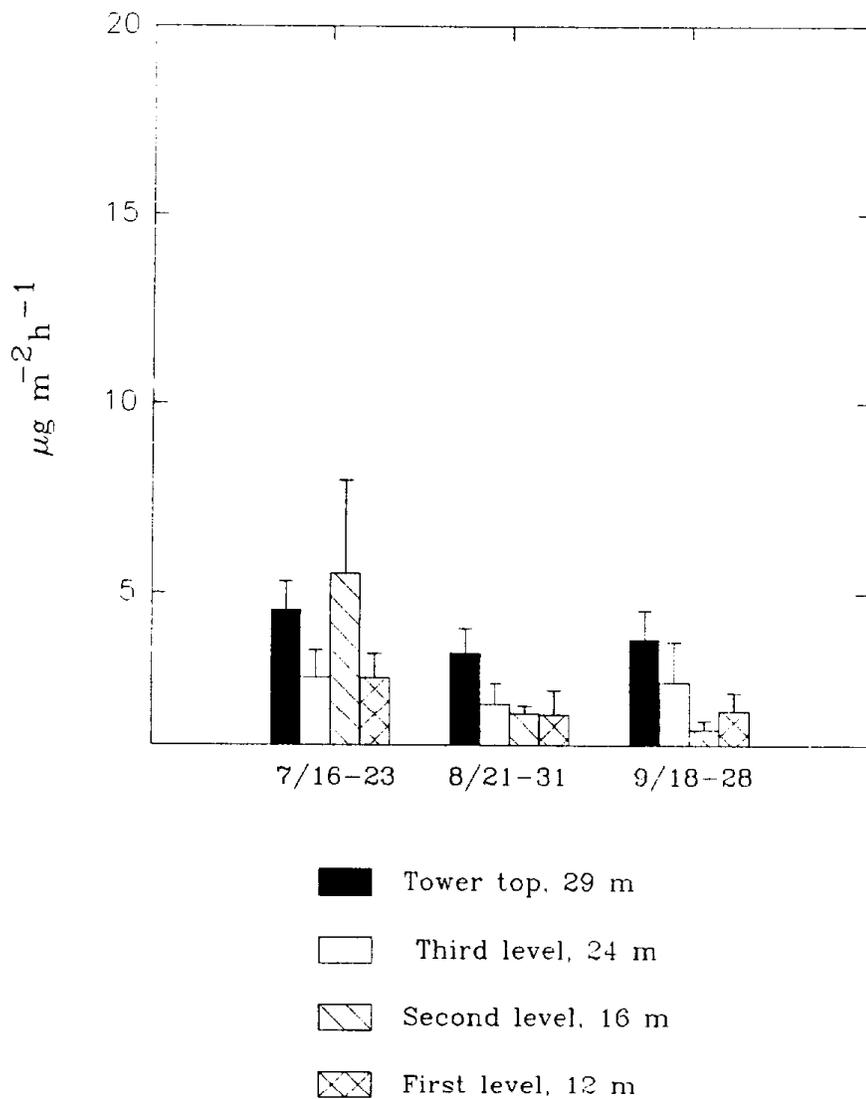


Figure 5-2 Sodium Flux to Branches of Ponderosa Pine Seedlings in a Vertical Gradient During the 1992 Season.

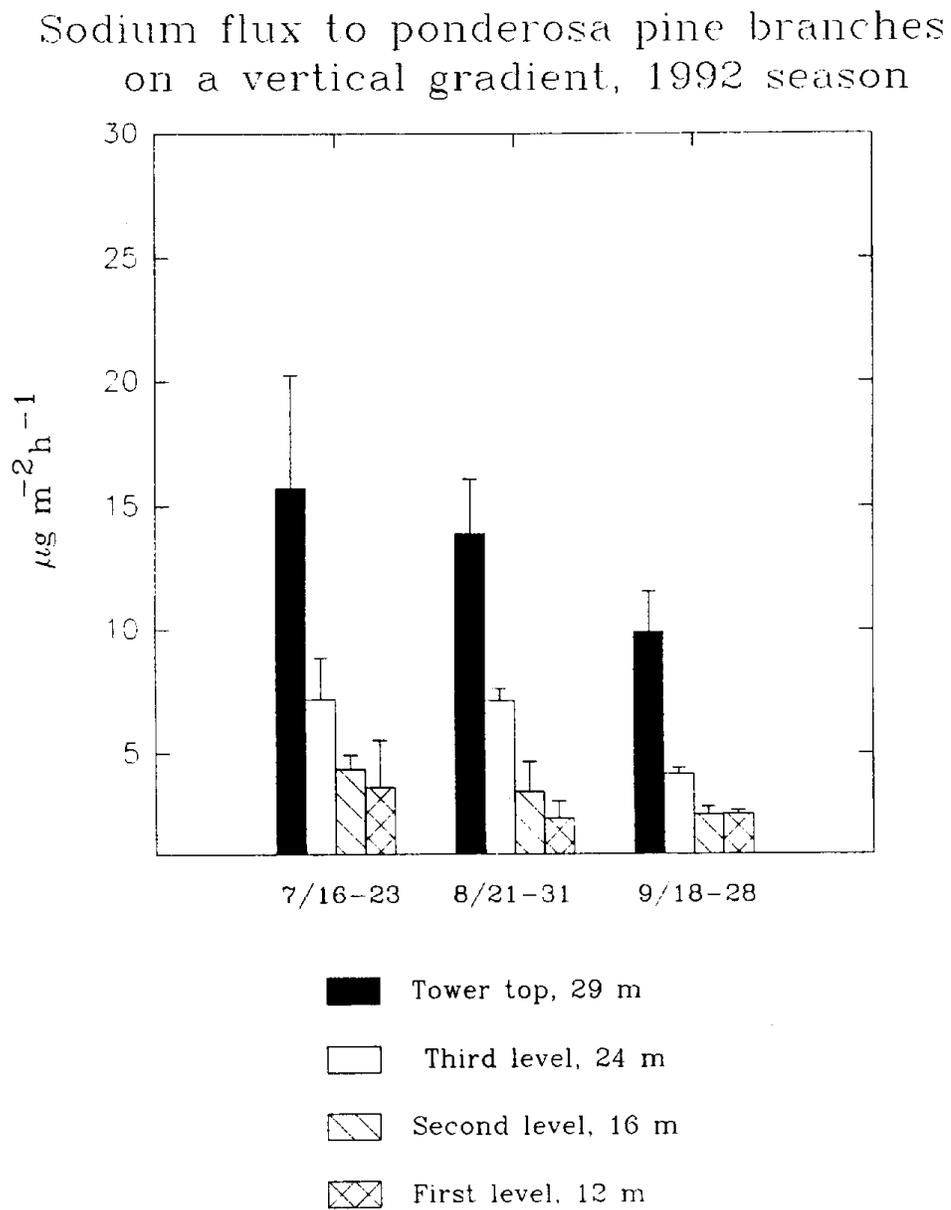


Figure 5-3 Calcium Flux to Branches of Ponderosa Pine Seedlings in a Vertical Gradient During the 1992 Season.

Calcium flux to ponderosa pine branches on a vertical gradient, 1992 season

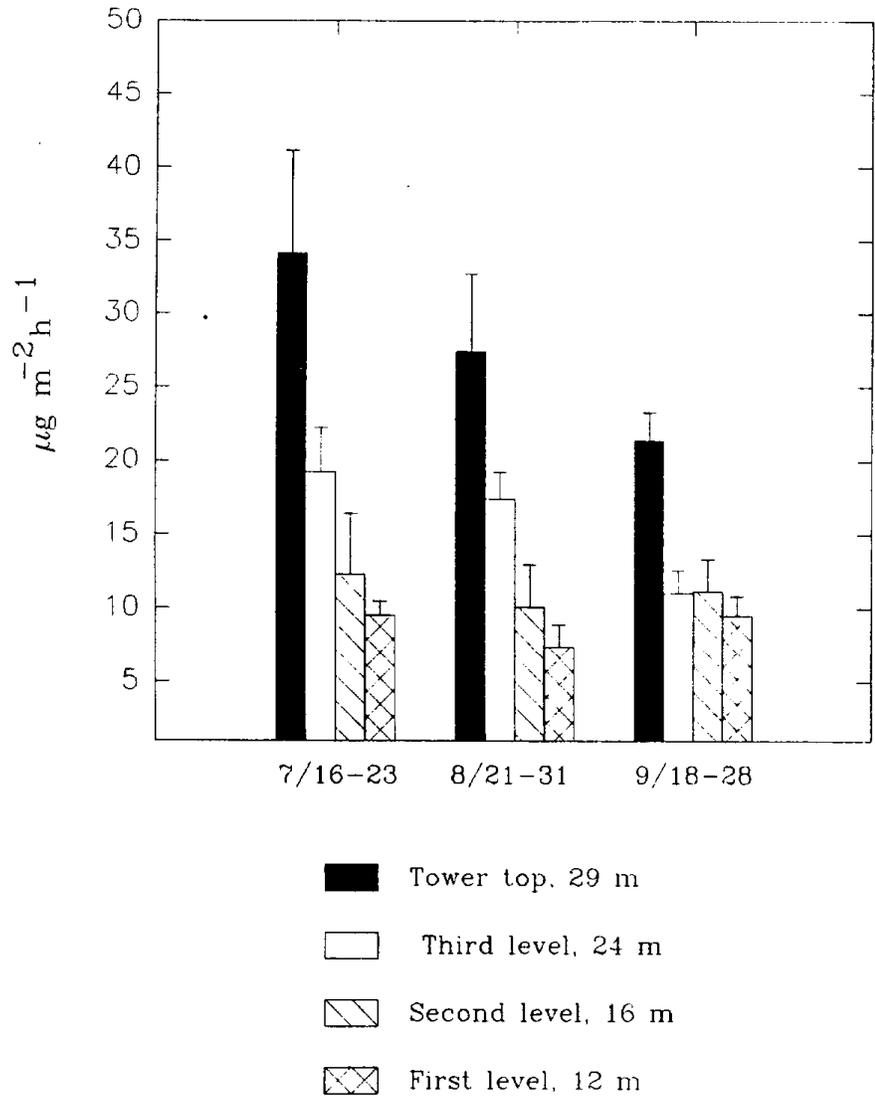


Figure 5-4 Magnesium Flux to Branches of Ponderosa Pine Seedlings in a Vertical Gradient During the 1992 Season.

Magnesium flux to ponderosa pine branches on a vertical gradient, 1992 season

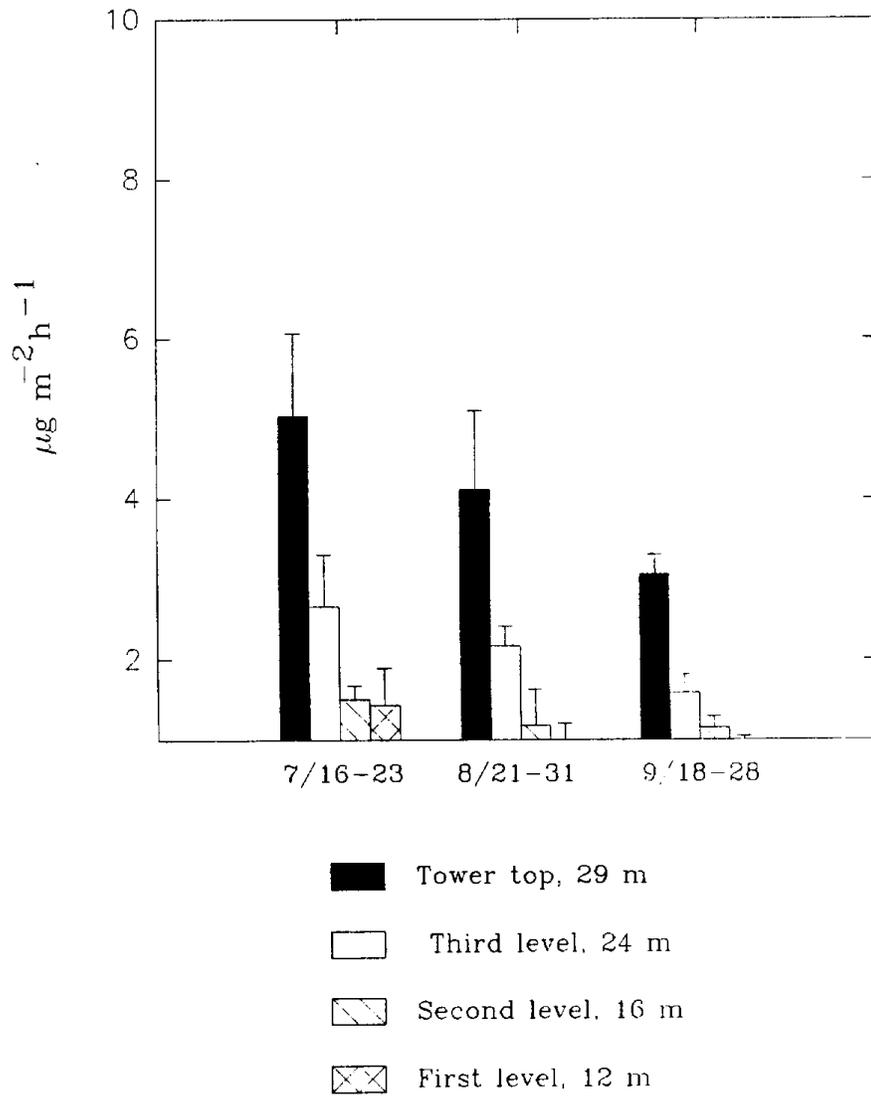


Figure 5-5 Potassium Flux to Branches of Ponderosa Pine Seedlings in a Vertical Gradient During the 1993 Season.

Potassium flux to ponderosa pine branches
on a vertical gradient

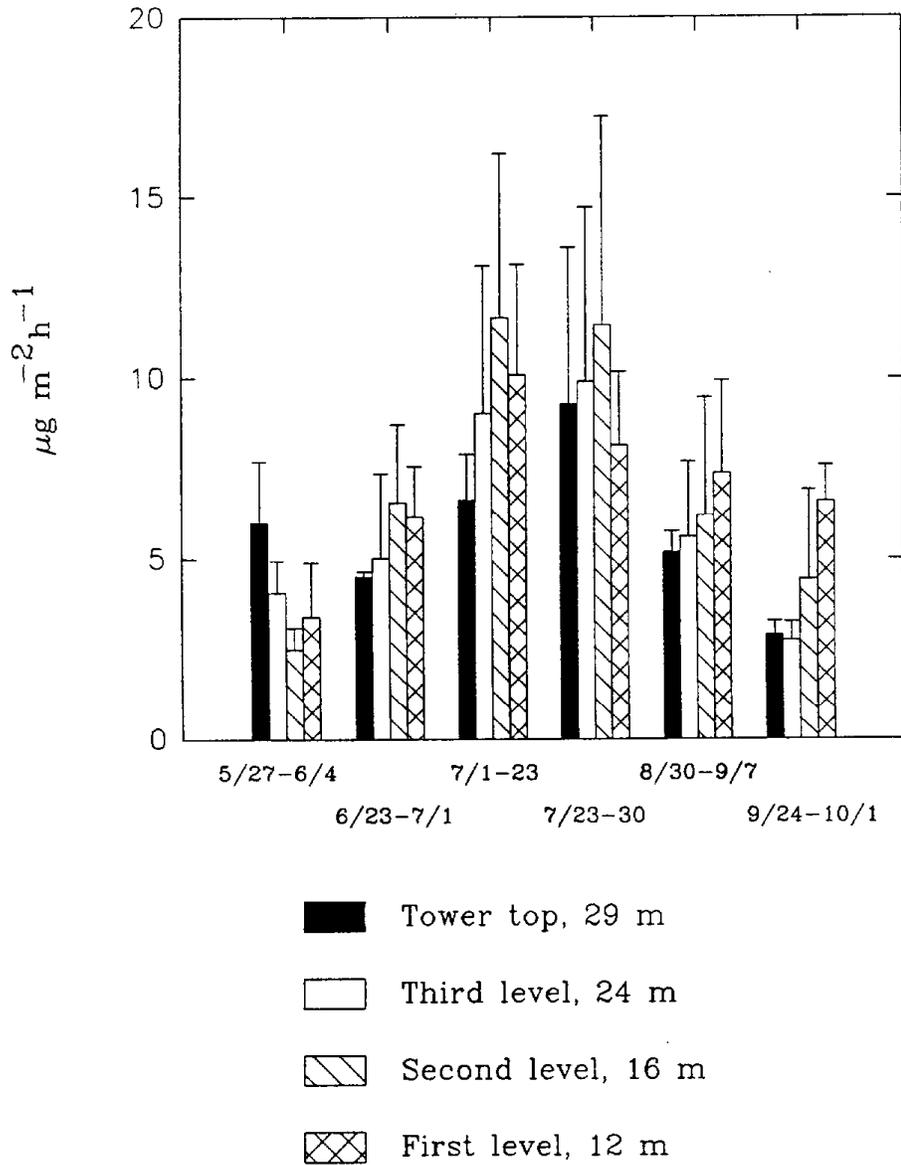


Figure 5-6 Sodium Flux to Branches of Ponderosa Pine Seedlings in a Vertical Gradient During the 1993 Season.

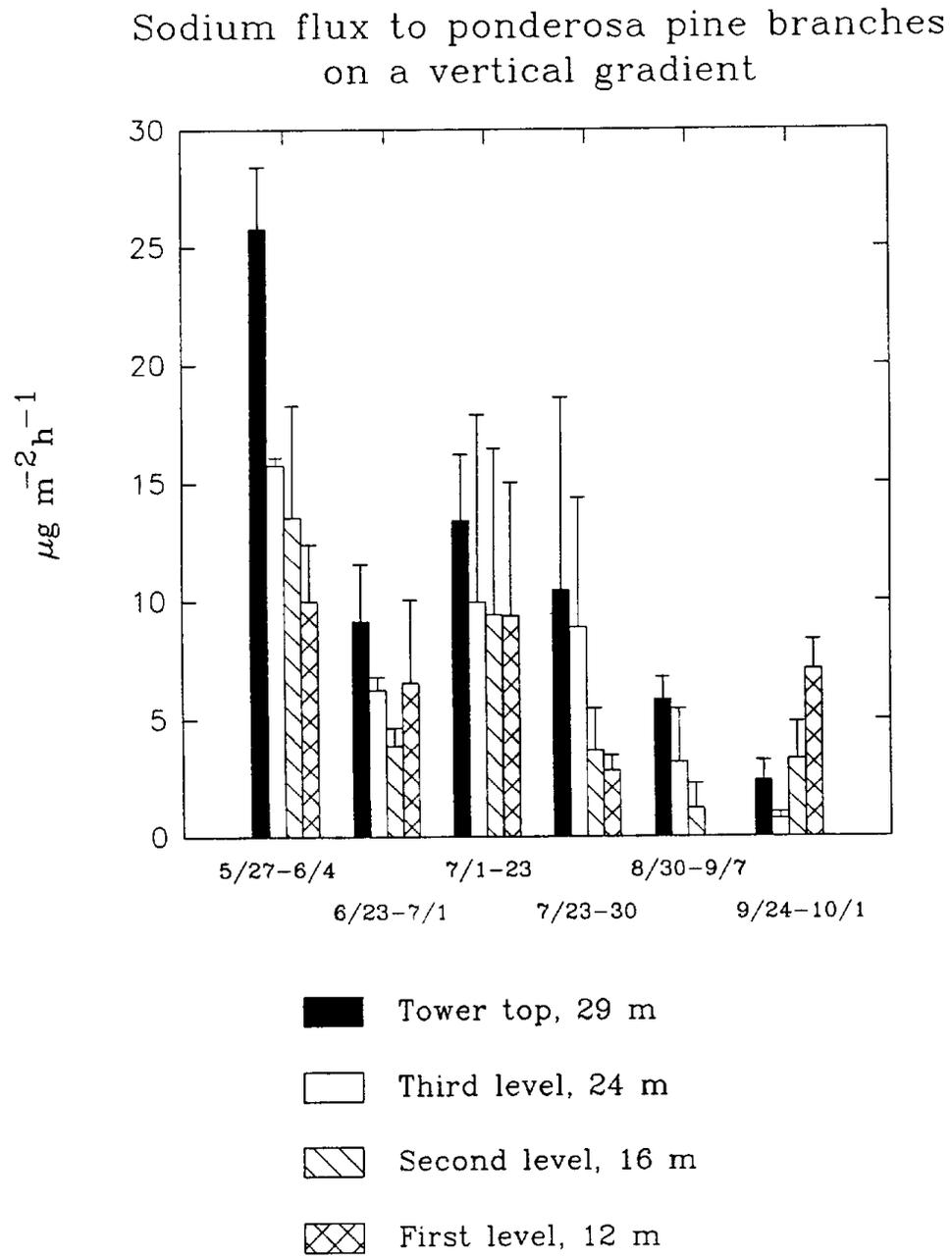


Figure 5-7 Calcium Flux to Branches of Ponderosa Pine Seedlings in a Vertical Gradient During the 1993 Season.

Calcium flux to ponderosa pine branches on a vertical gradient

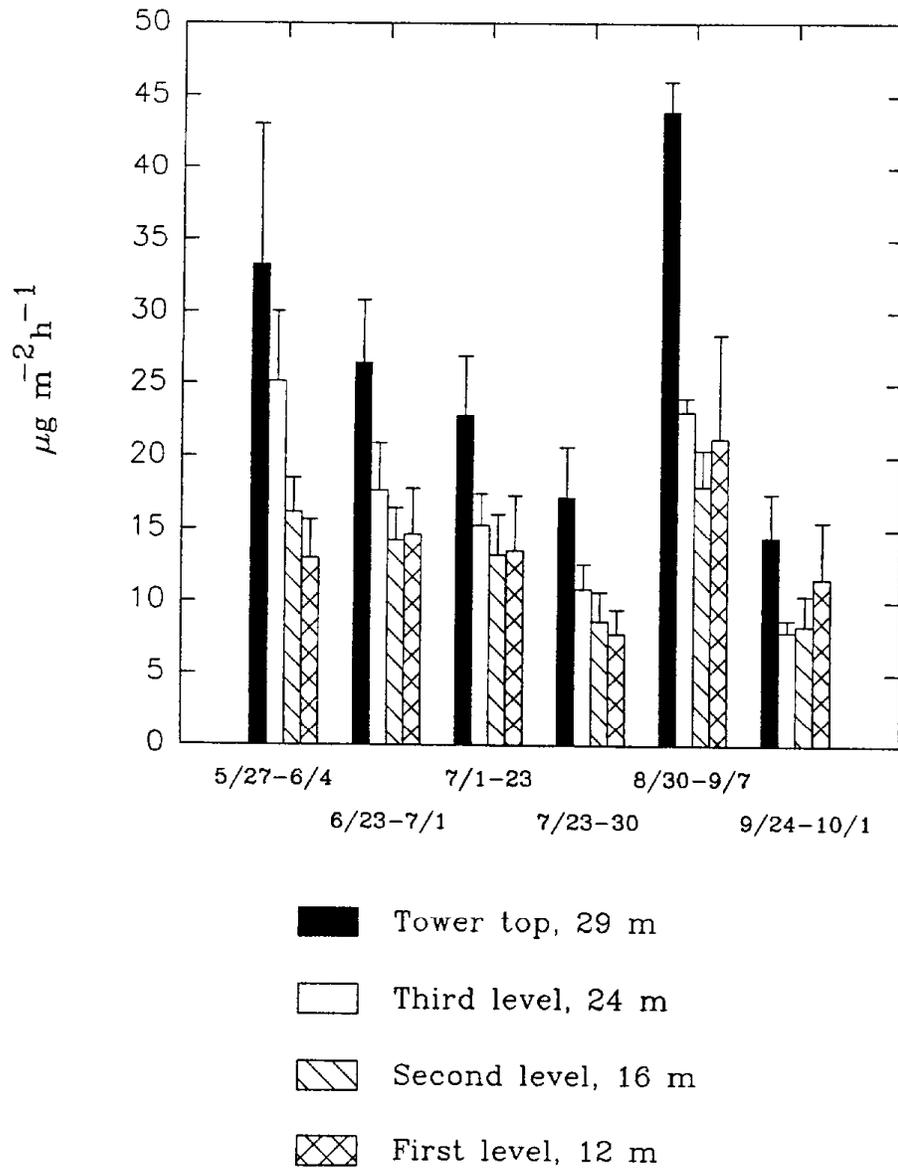
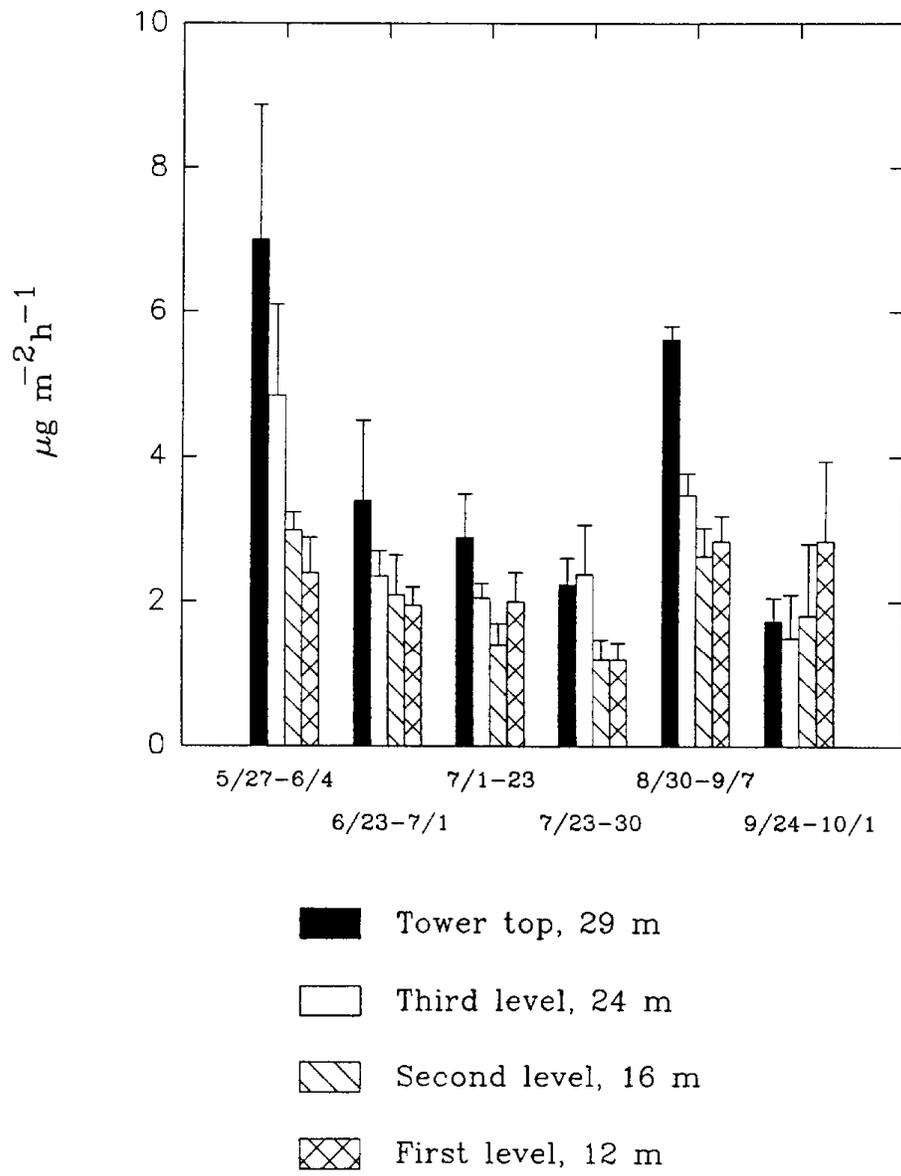


Figure 5-8 Magnesium Flux to Branches of Ponderosa Pine Seedlings in a Vertical Gradient During the 1993 Season.

Magnesium flux to ponderosa pine branches on a vertical gradient



APPENDIX A.

Figure A5-1. Comparison of Potassium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Canopy Bottom.

Deposition of potassium to branches of mature trees vs. branches of seedlings – level 1

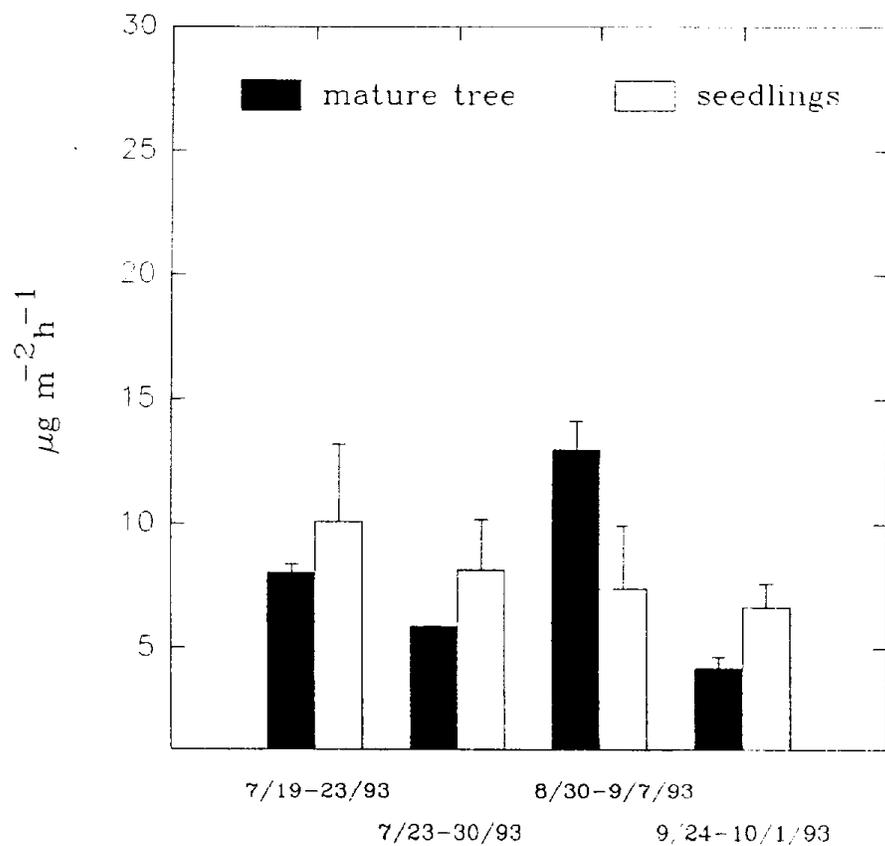


Figure A5-2. Comparison of Potassium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Second Level of the Canopy.

Deposition of potassium to branches of mature trees vs. branches of seedlings – level 2

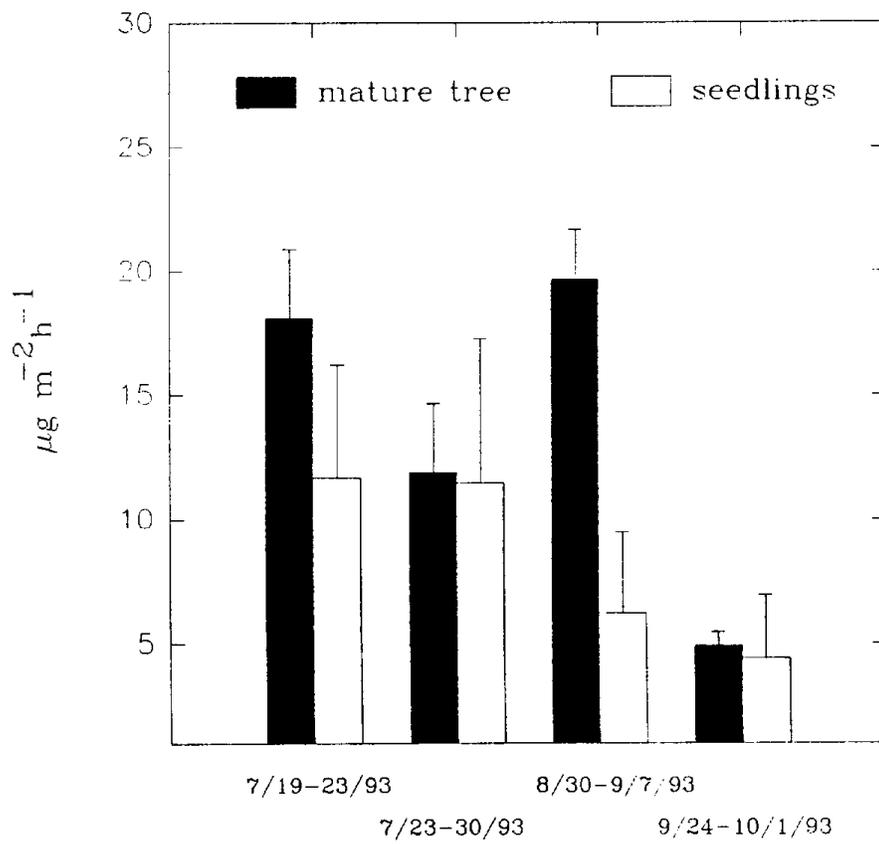


Figure A5-3. Comparison of Potassium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Third Level of the Canopy.

Deposition of potassium to branches of mature trees vs. branches of seedlings – level 3

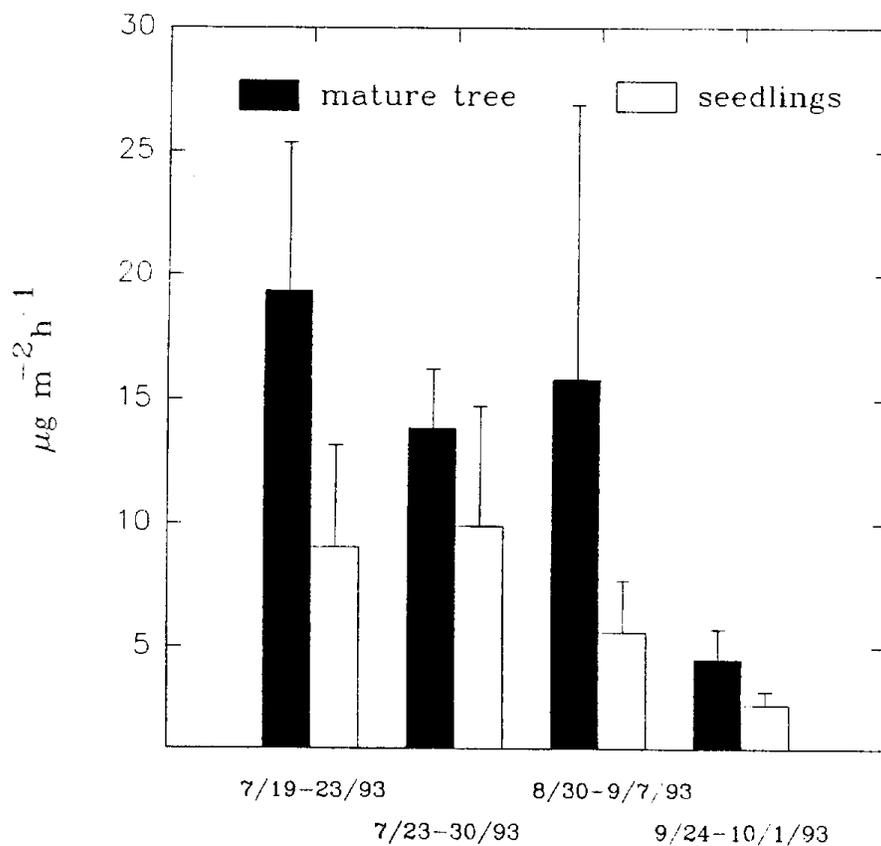


Figure A5-4. Comparison of Sodium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Canopy Bottom.

Deposition of sodium to branches of mature trees vs. branches of seedlings – level 1

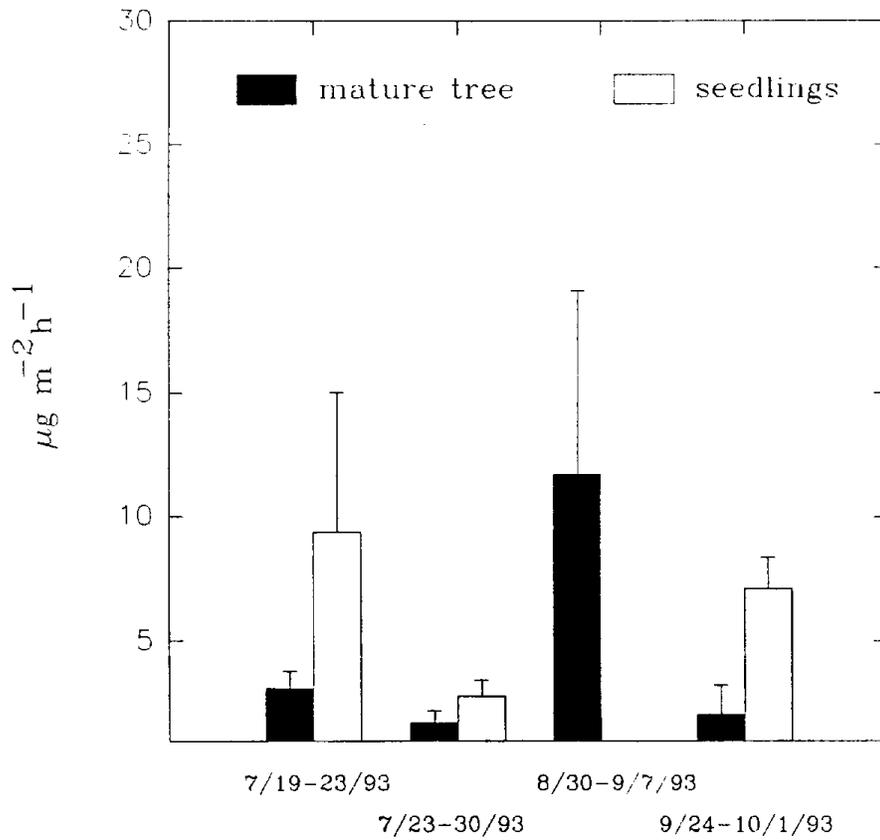


Figure A5-5. Comparison of Sodium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Second Level of the Canopy.

Deposition of sodium to branches of mature trees vs. branches of seedlings - level 2

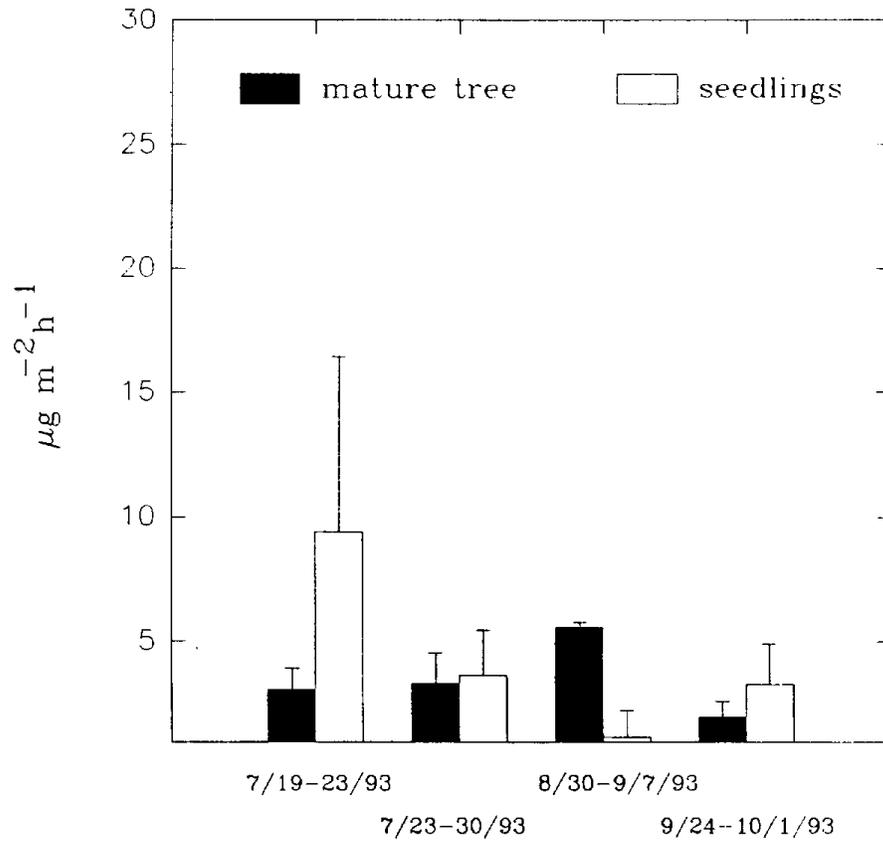


Figure A5-6. Comparison of Sodium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Third Level of the Canopy.

Deposition of sodium to branches of mature trees vs. branches of seedlings – level 3

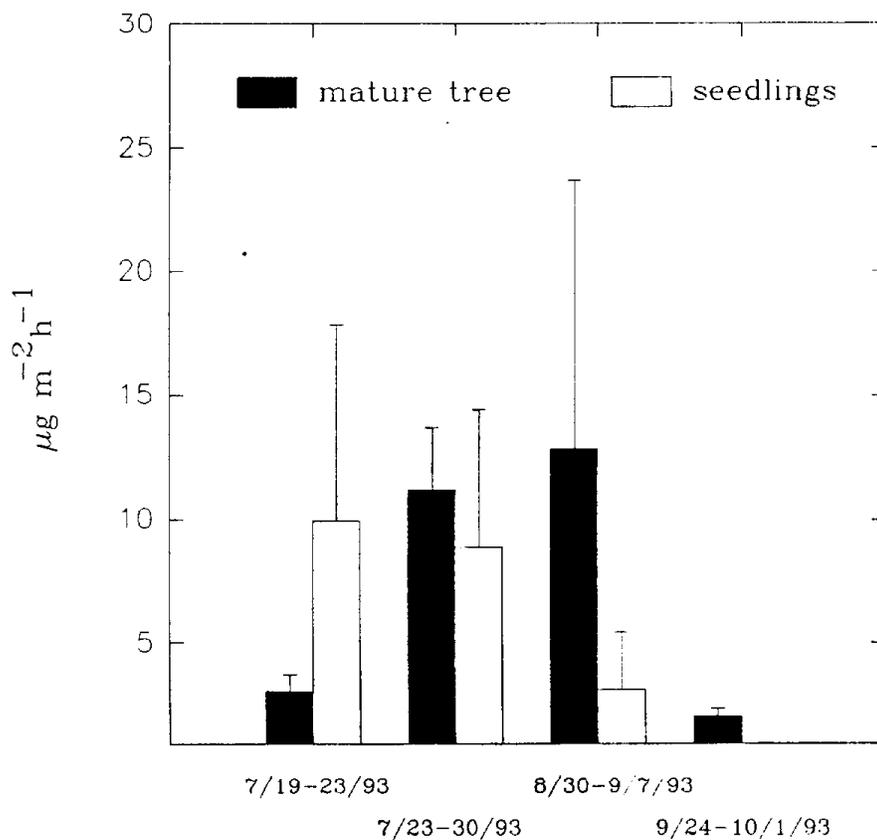


Figure A5-7. Comparison of Calcium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Canopy Bottom.

Deposition of calcium to branches of mature trees vs. branches of seedlings – level 1

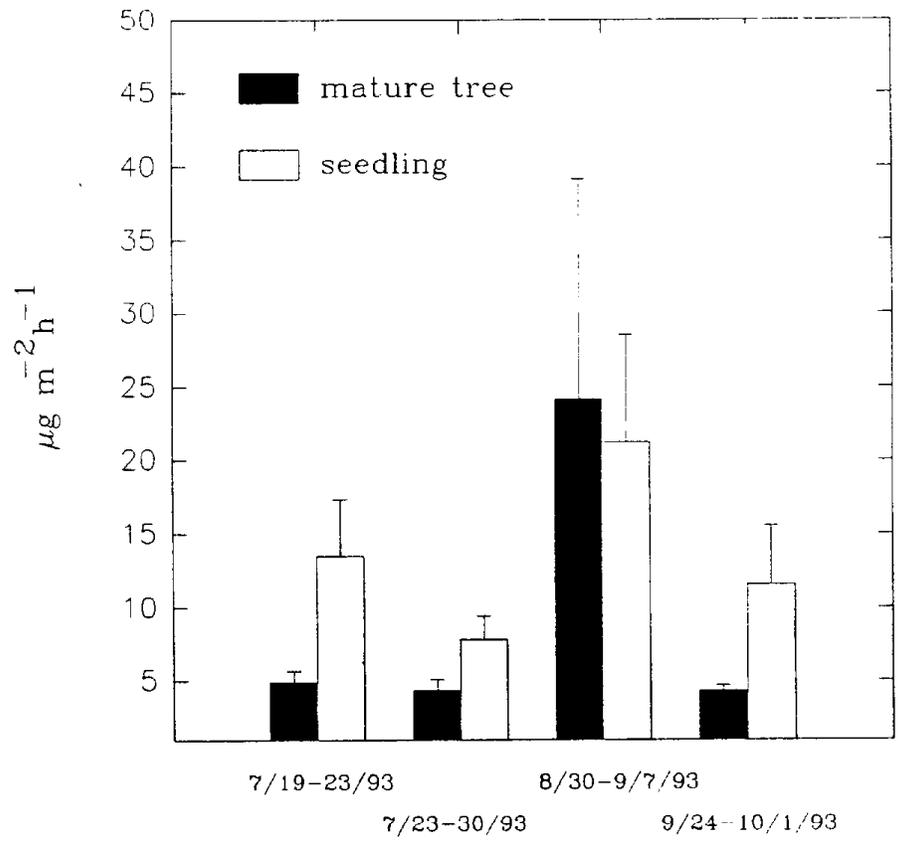


Figure A5-8. Comparison of Calcium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Second Level of the Canopy.

Deposition of calcium to branches of mature trees vs. branches of seedlings - level 2

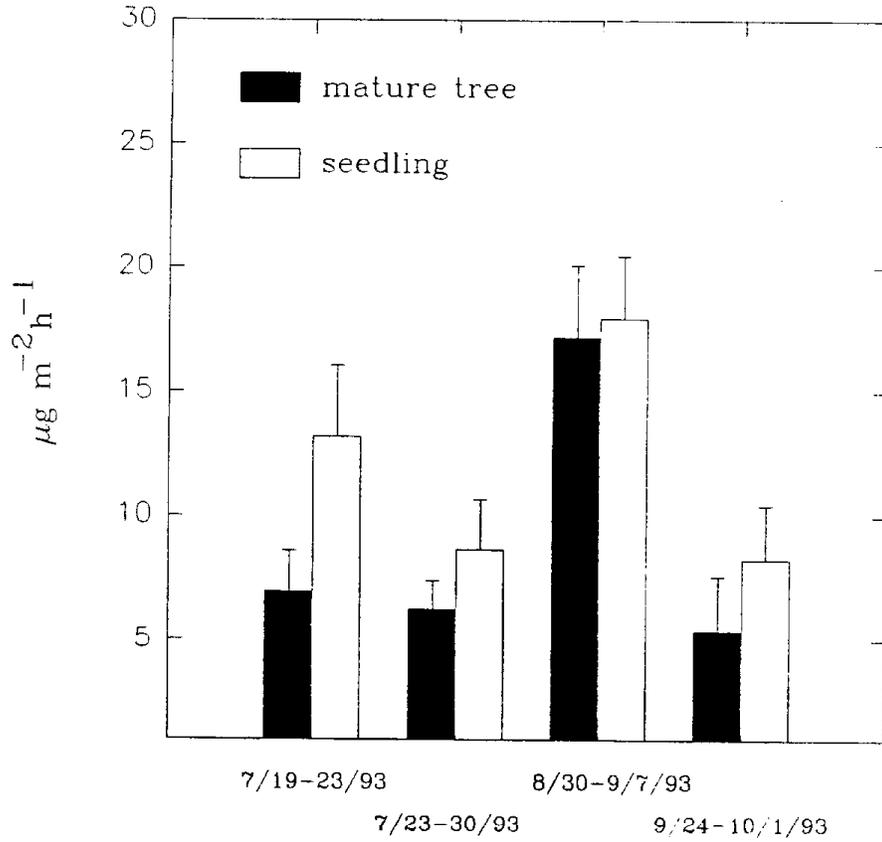


Figure A5-9. Comparison of Calcium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Third Level of the Canopy.

Deposition of calcium to branches of mature trees vs. branches of seedlings – level 3

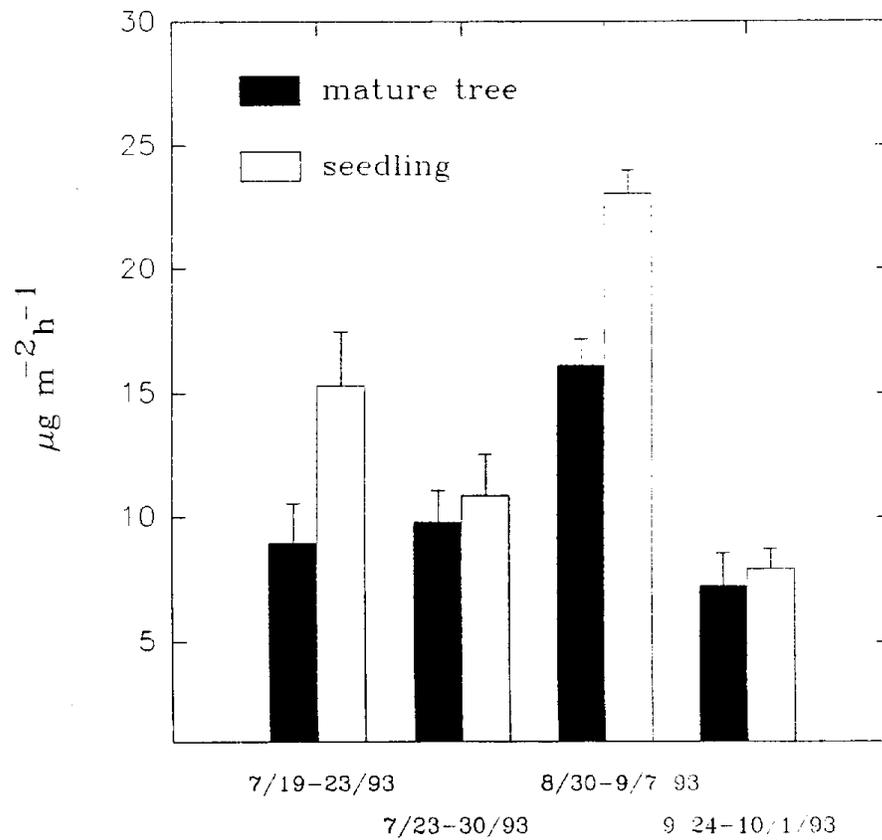


Figure A5-10. Comparison of Magnesium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Canopy Bottom.

Deposition of magnesium to branches of mature trees vs. branches of seedlings -- level 1

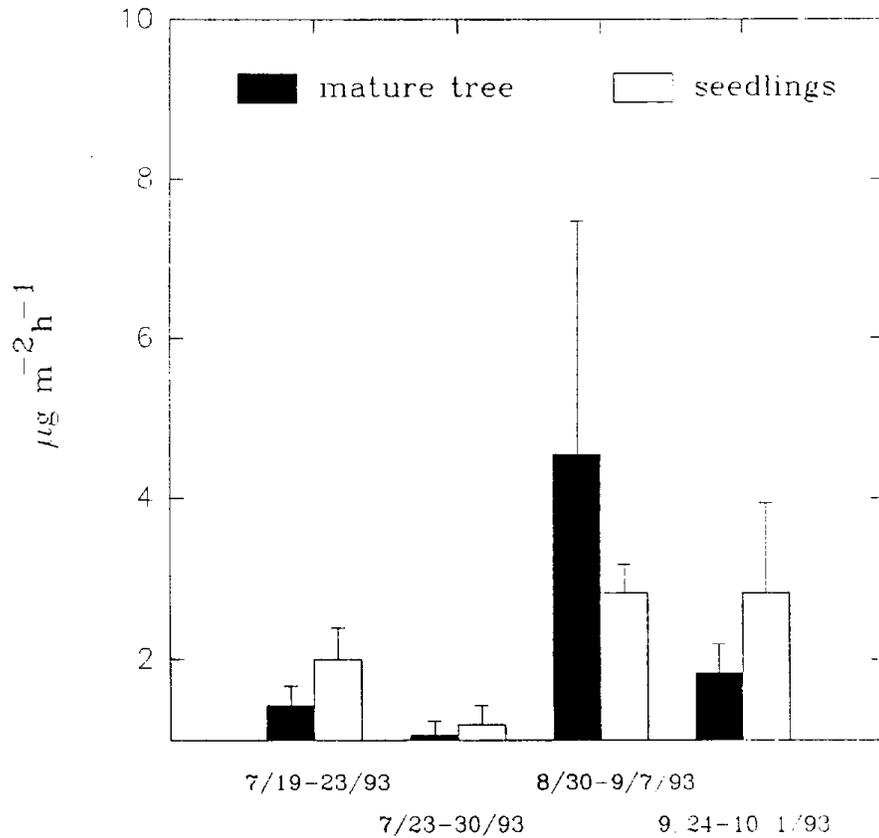


Figure A5-11. Comparison of Magnesium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Second Level of the Canopy.

Deposition of magnesium to branches of mature trees vs. branches of seedlings – level 2

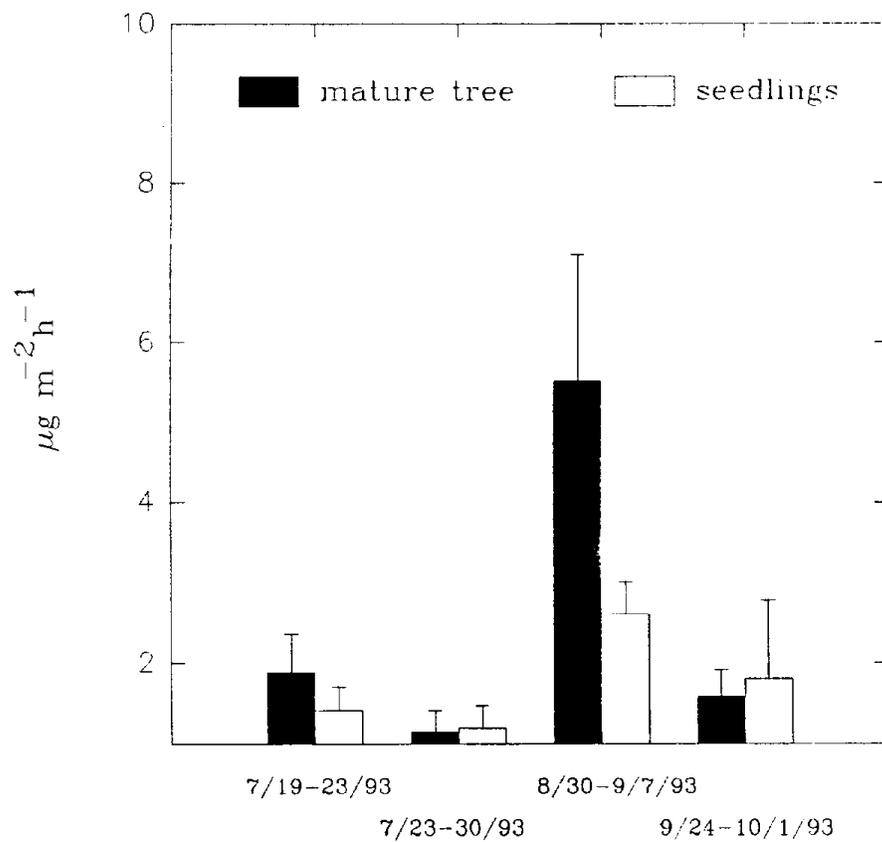


Figure A5-12. Comparison of Magnesium Deposition to Branches of Mature Ponderosa Pines vs. Seedlings at the Third Level of the Canopy.

Deposition of magnesium to branches of mature trees vs. branches of seedlings – level 3

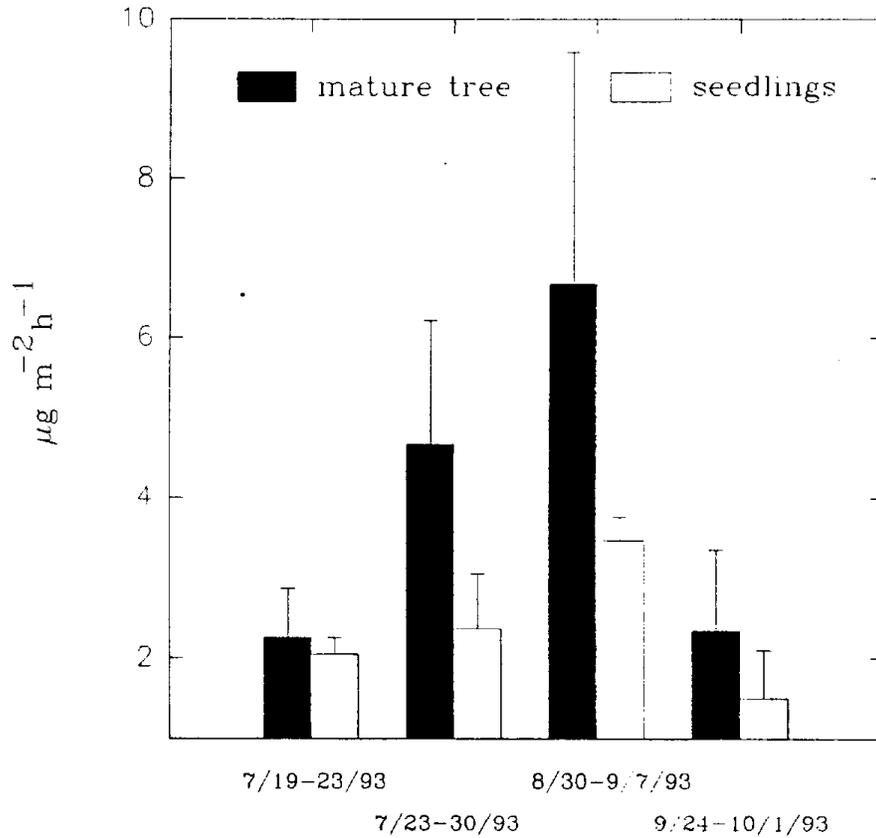


Figure A5-13. Deposition of Potassium to Branches of Mature Trees and Seedlings of Three Species at Plot 1 During the July 19-23, 1993 Period of the Intensive Study.

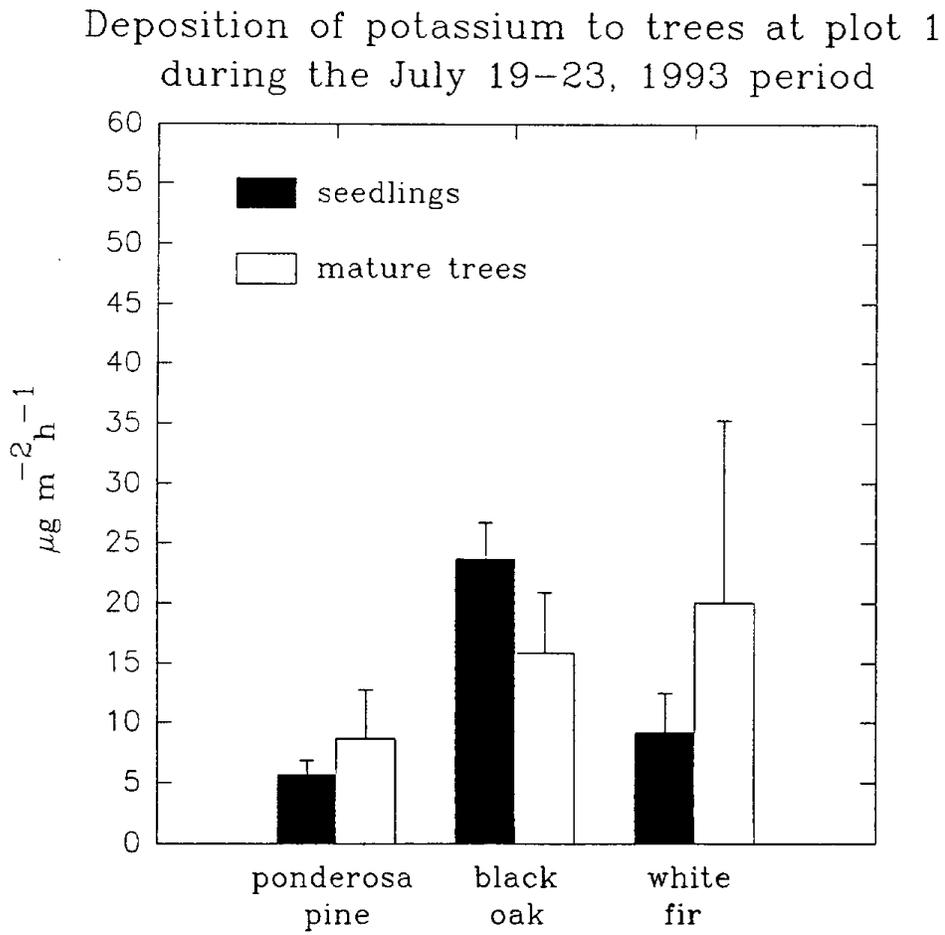


Figure A5-14. Deposition of Potassium to Branches of Mature Trees and Seedlings of Three Species at Plot 2 During the July 19-23, 1993 Period of the Intensive Study.

Deposition of potassium to trees at plot 2 during the July 19-23, 1993 period

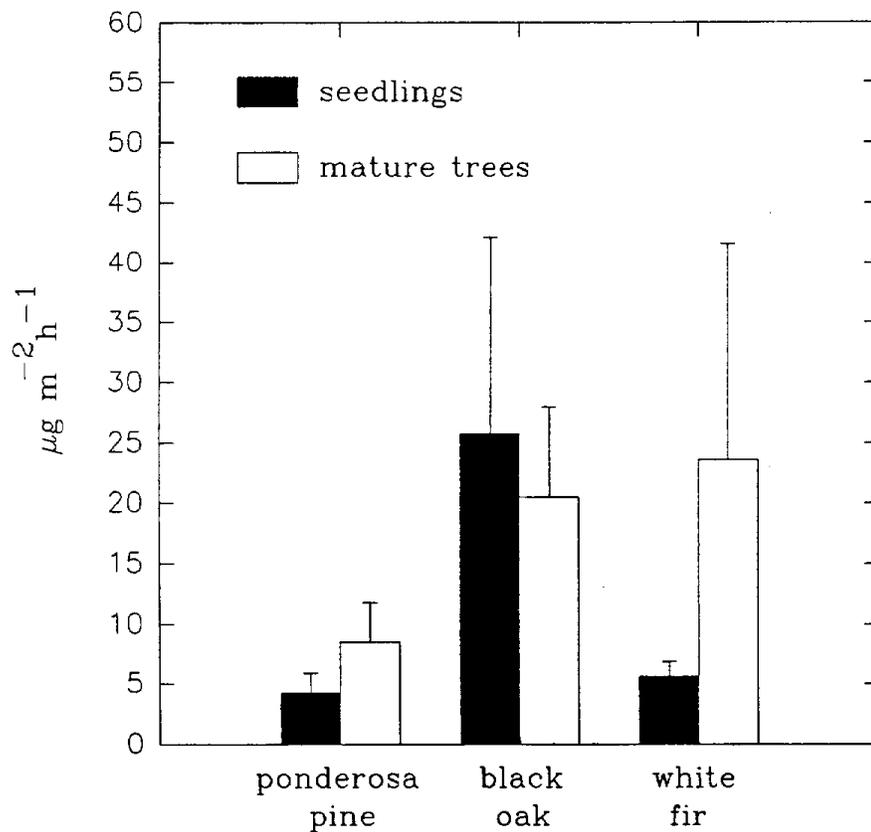


Figure A5-15. Deposition of Potassium to Branches of Mature Trees and Seedlings of Three Species at Plot 3 During the July 19-23, 1993 Period of the Intensive Study.

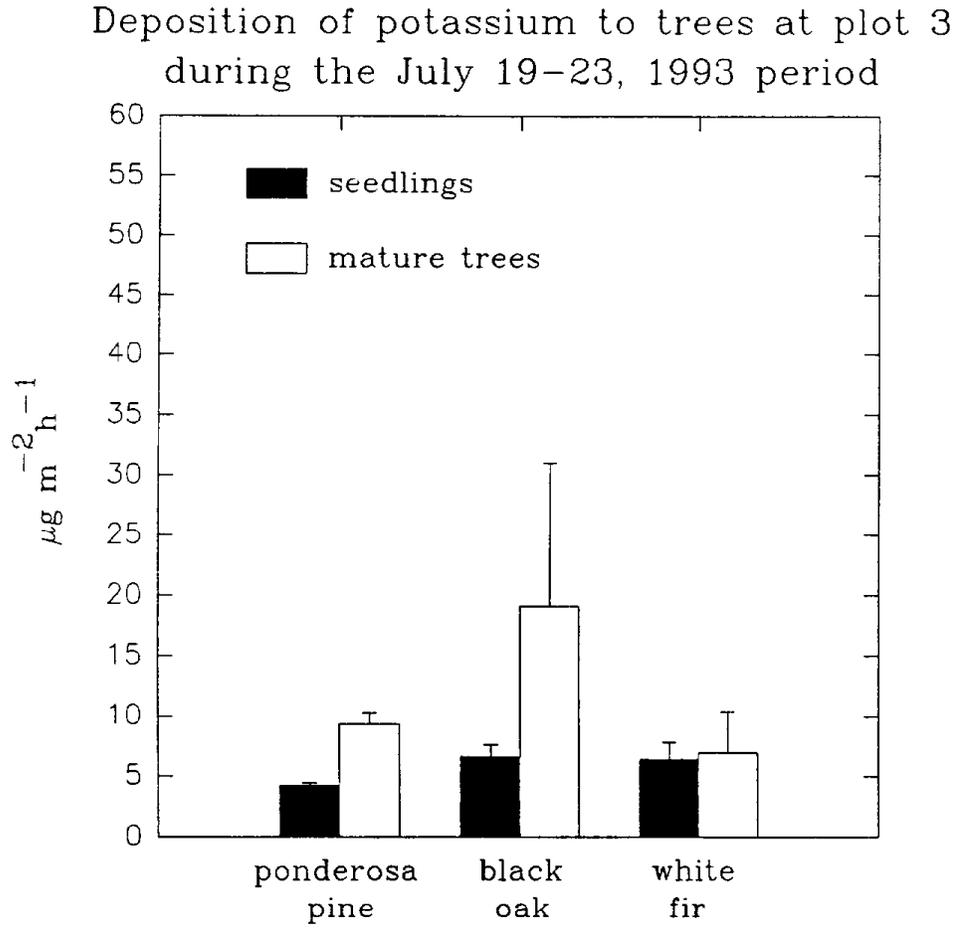


Figure A5-16. Deposition of Potassium to Branches of Mature Trees and Seedlings of Three Species at Plot 1 During the July 23-30, 1993 Period of the Intensive Study.

Deposition of potassium to trees at plot 1 during the July 23-30, 1993 period

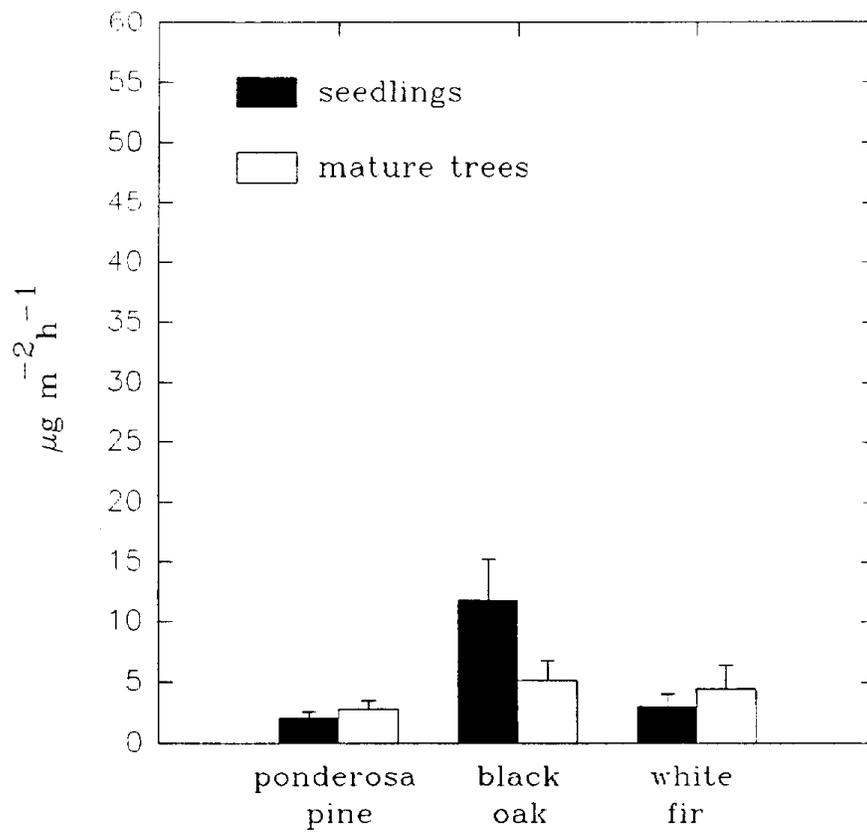


Figure A5-17. Deposition of Potassium to Branches of Mature Trees and Seedlings of Three Species at Plot 2 During the July 23-30, 1993 Period of the Intensive Study.

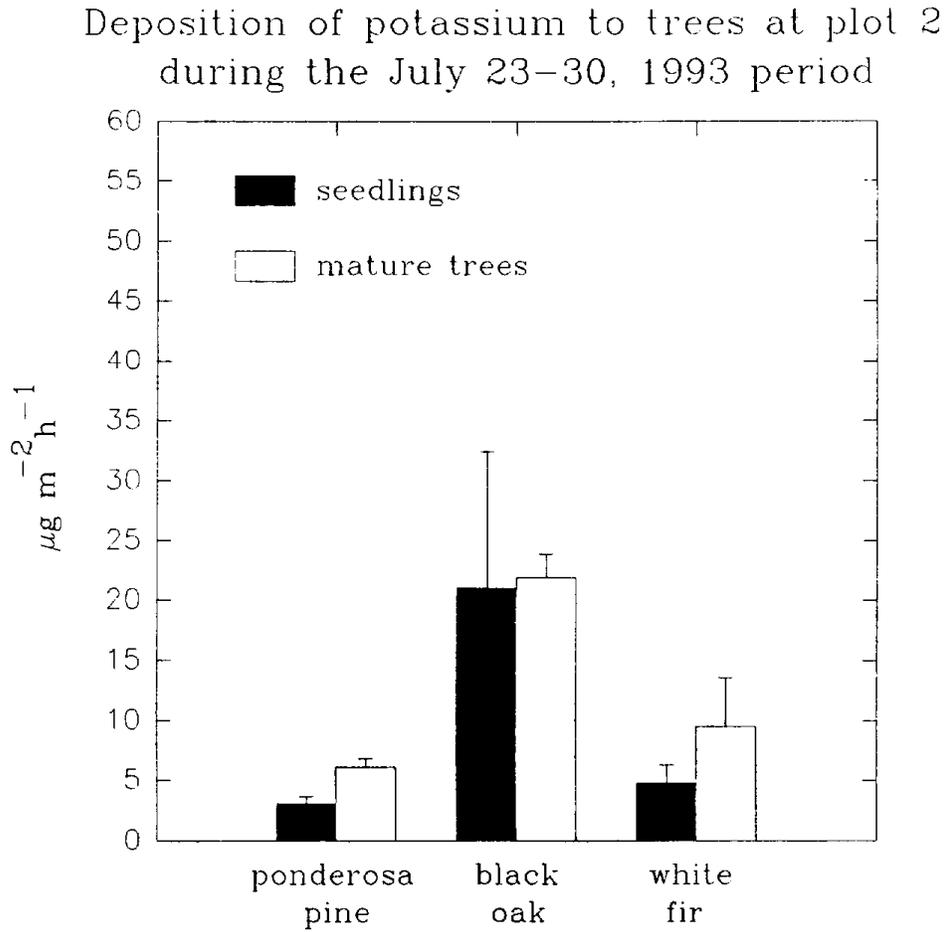


Figure A5-18. Deposition of Potassium to Branches of Mature Trees and Seedlings of Three Species at Plot 3 During the July 23-30, 1993 Period of the Intensive Study.

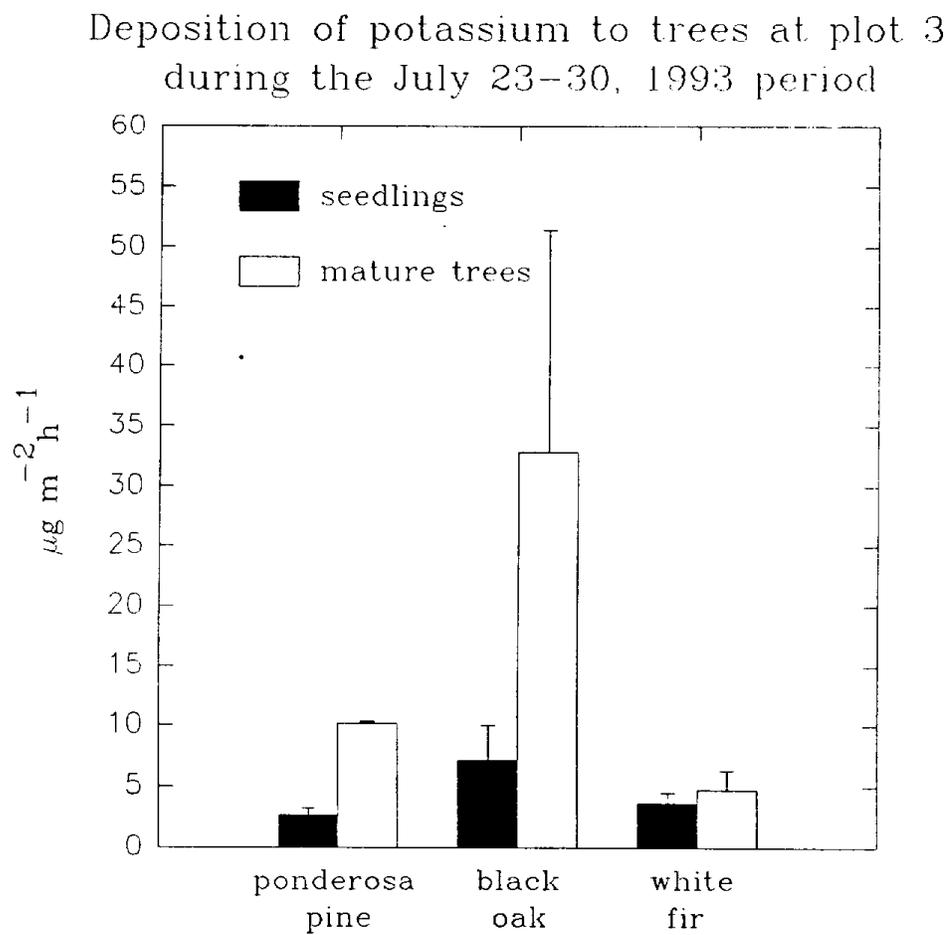


Figure A5-19. Deposition of Sodium to Branches of Mature Trees and Seedlings of Three Species at Plot 1 During the July 19-23, 1993 Period of the Intensive Study.

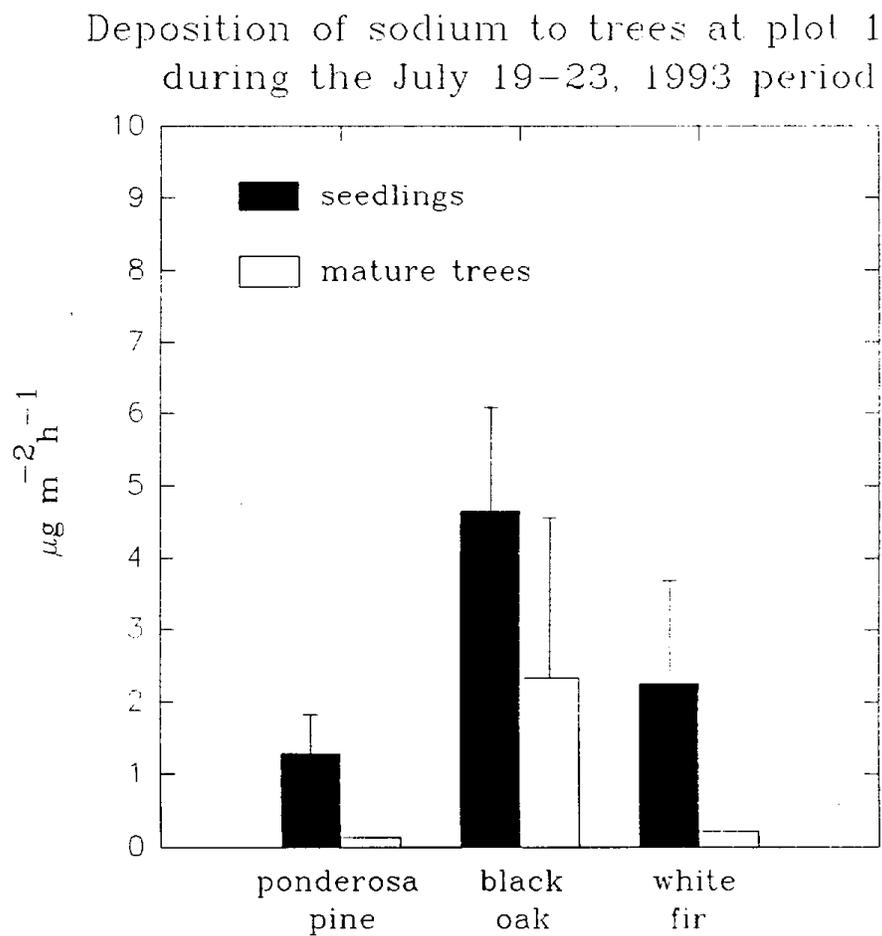


Figure A5-20. Deposition of Sodium to Branches of Mature Trees and Seedlings of Three Species at Plot 2 During the July 19-23, 1993 Period of the Intensive Study.

Deposition of sodium to trees at plot 2 during the July 19-23, 1993 period

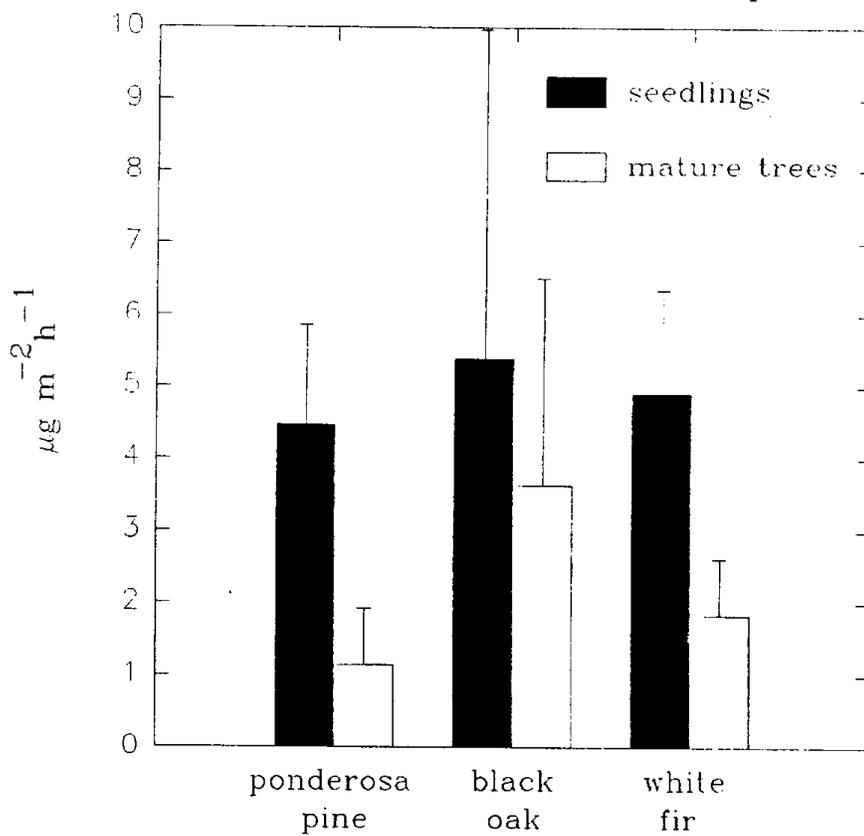


Figure A5-21. Deposition of Sodium to Branches of Mature Trees and Seedlings of Three Species at Plot 3 During the July 19-23, 1993 Period of the Intensive Study.

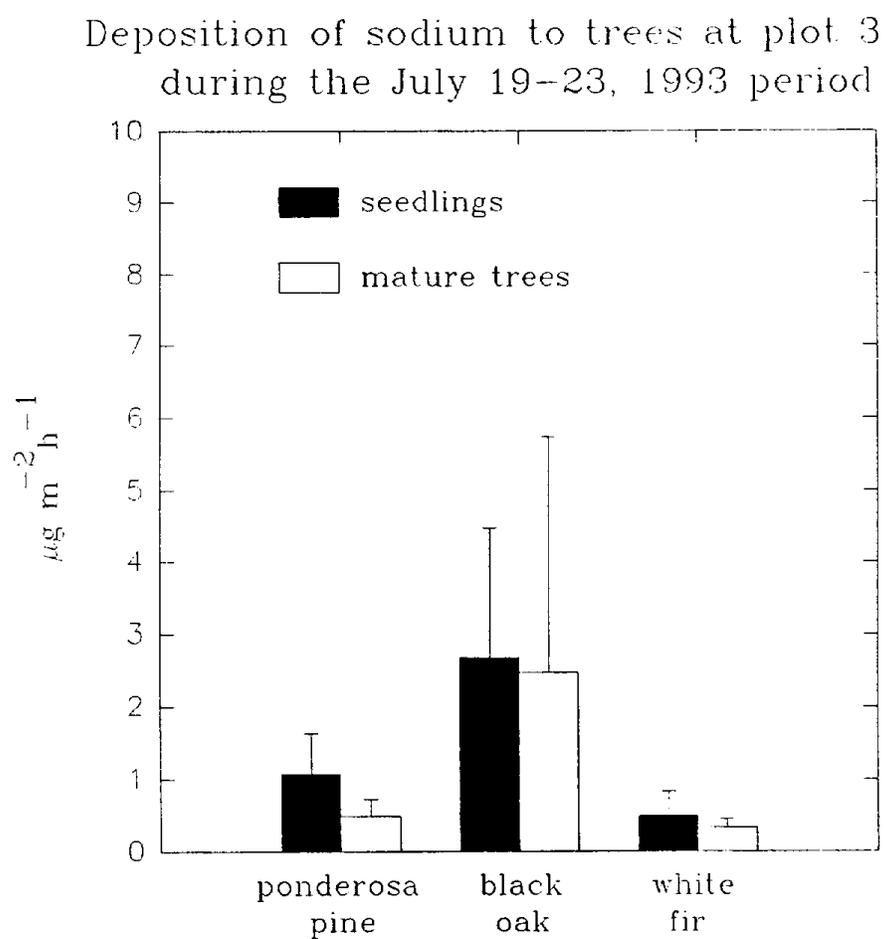


Figure A5-22. Deposition of Sodium to Branches of Mature Trees and Seedlings of Three Species at Plot 2 During the July 23-30, 1993 Period of the Intensive Study.

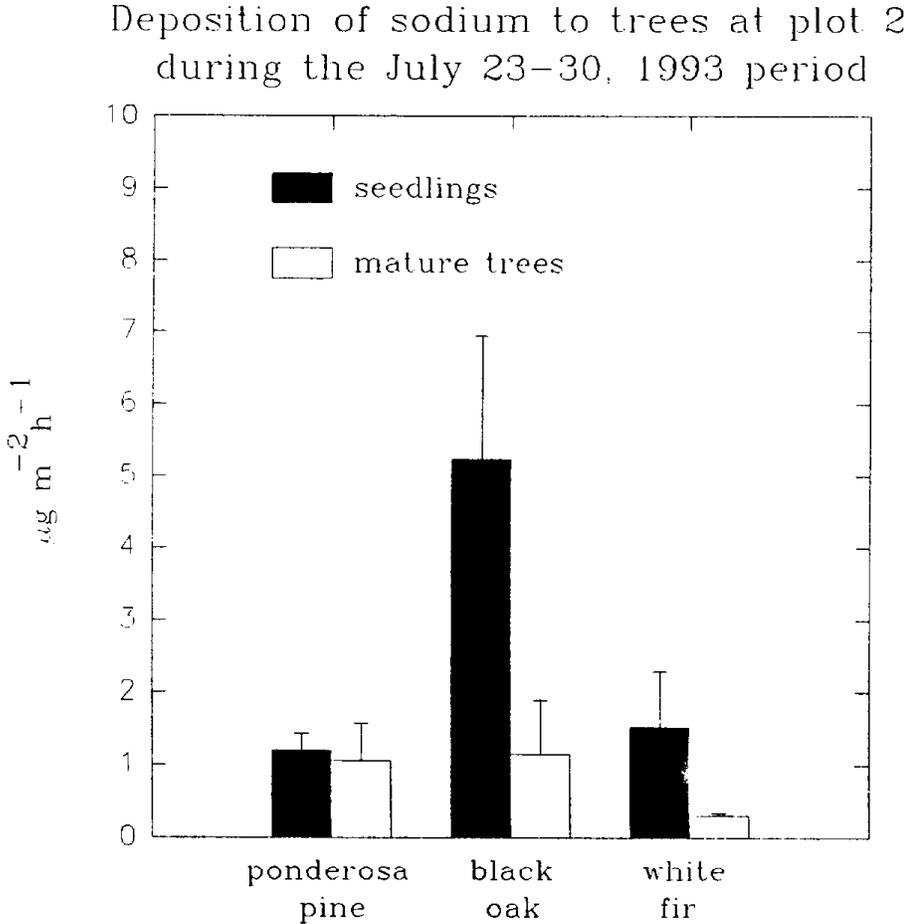


Figure A5-23. Deposition of Calcium to Branches of Mature Trees and Seedlings of Three Species at Plot 1 During the July 19-23, 1993 Period of the Intensive Study.

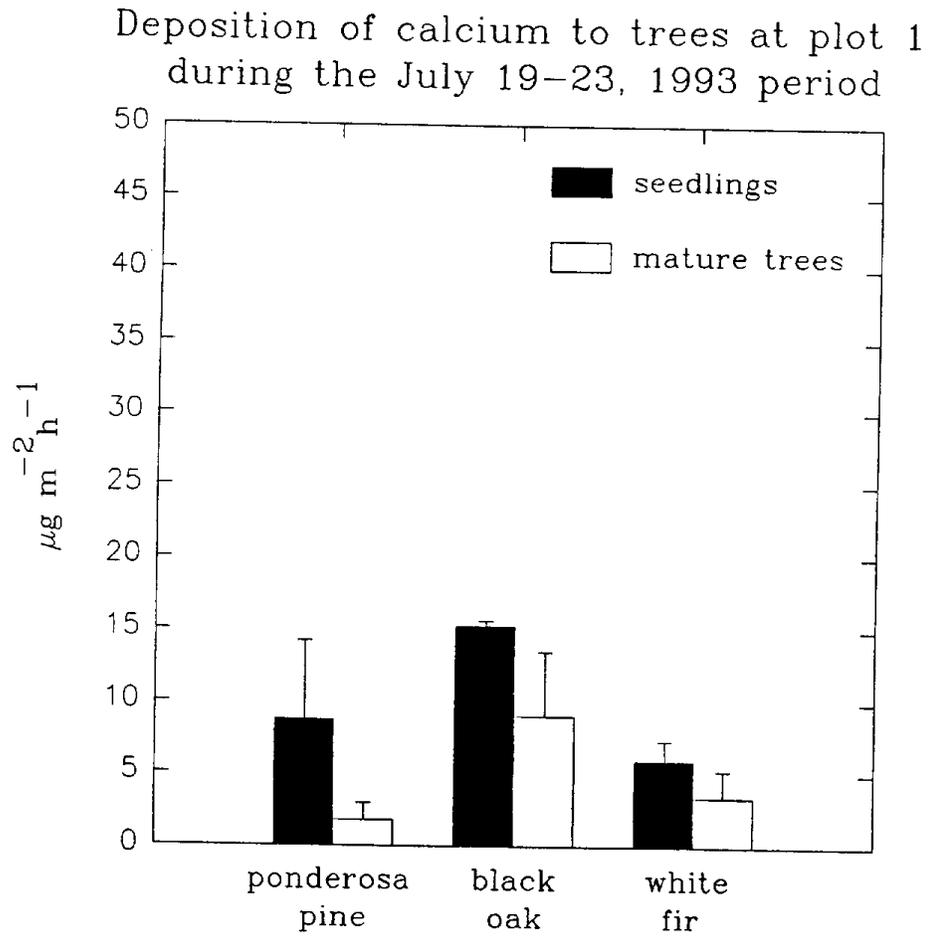


Figure A5-24. Deposition of Calcium to Branches of Mature Trees and Seedlings of Three Species at Plot 2 During the July 19-23, 1993 Period of the Intensive Study.

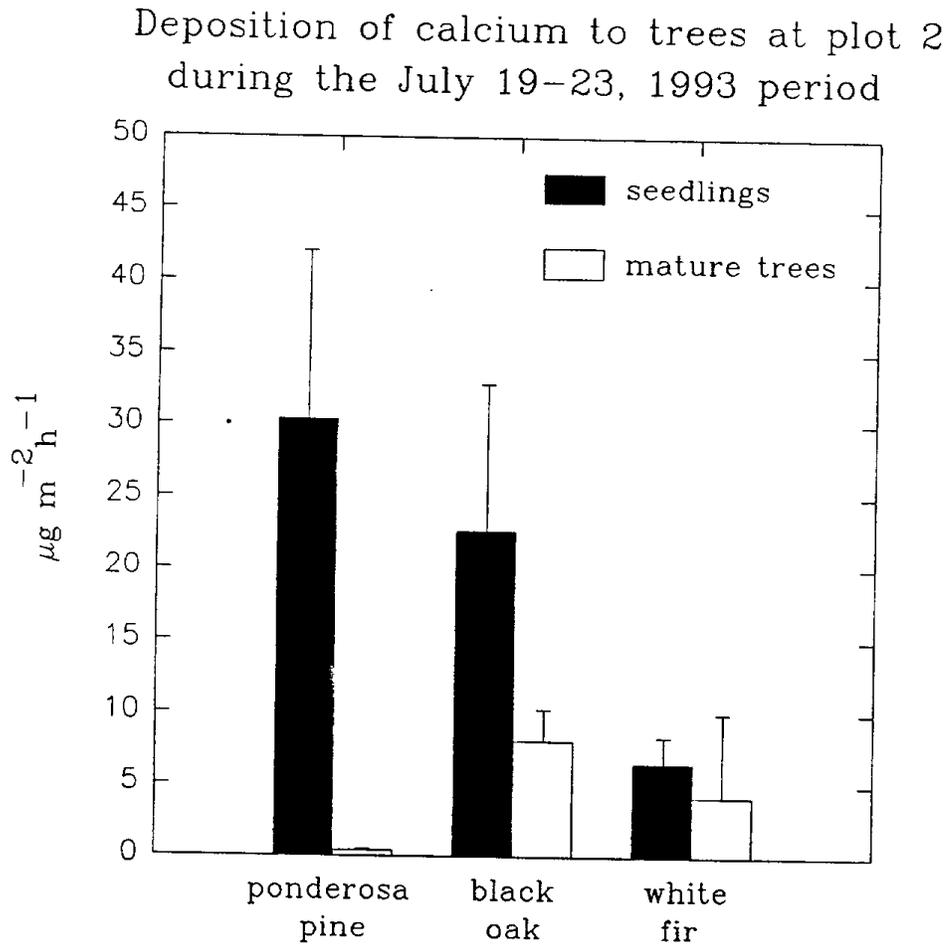


Figure A5-25. Deposition of Calcium to Branches of Mature Trees and Seedlings of Three Species at Plot 3 During the July 19-23, 1993 Period of the Intensive Study.

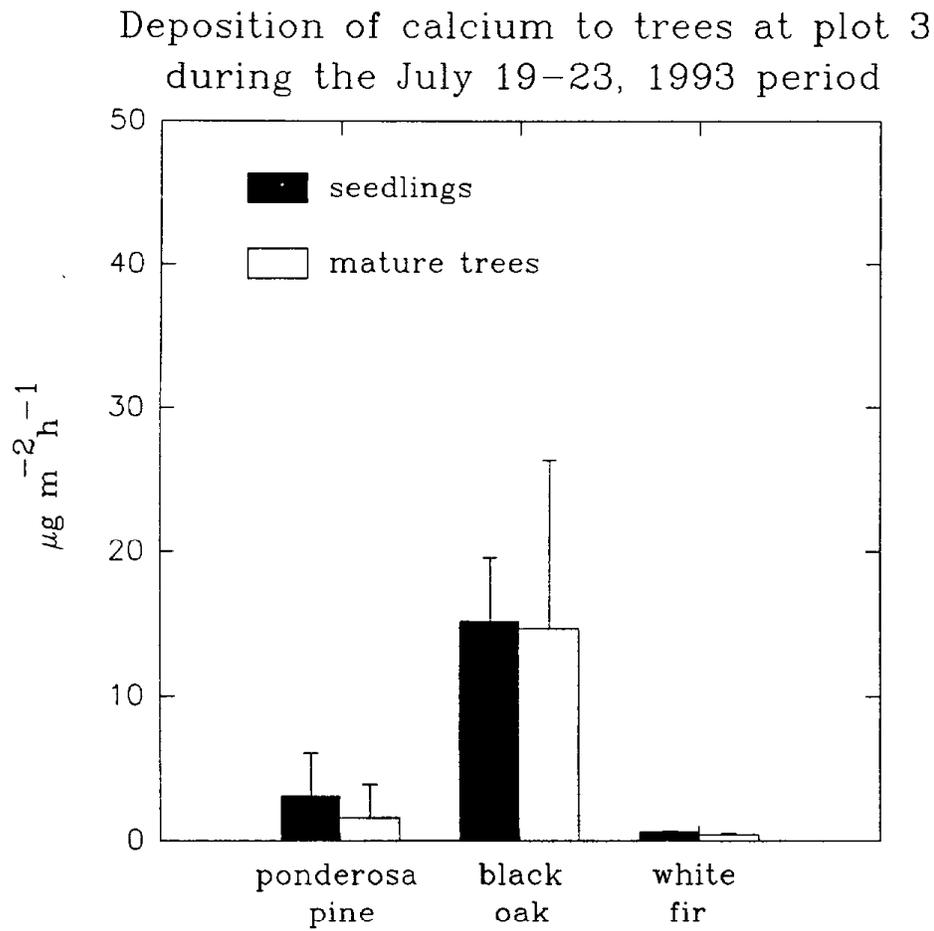


Figure A5-26. Deposition of Calcium to Branches of Mature Trees and Seedlings of Three Species at Plot 1 During the July 23-30, 1993 Period of the Intensive Study.

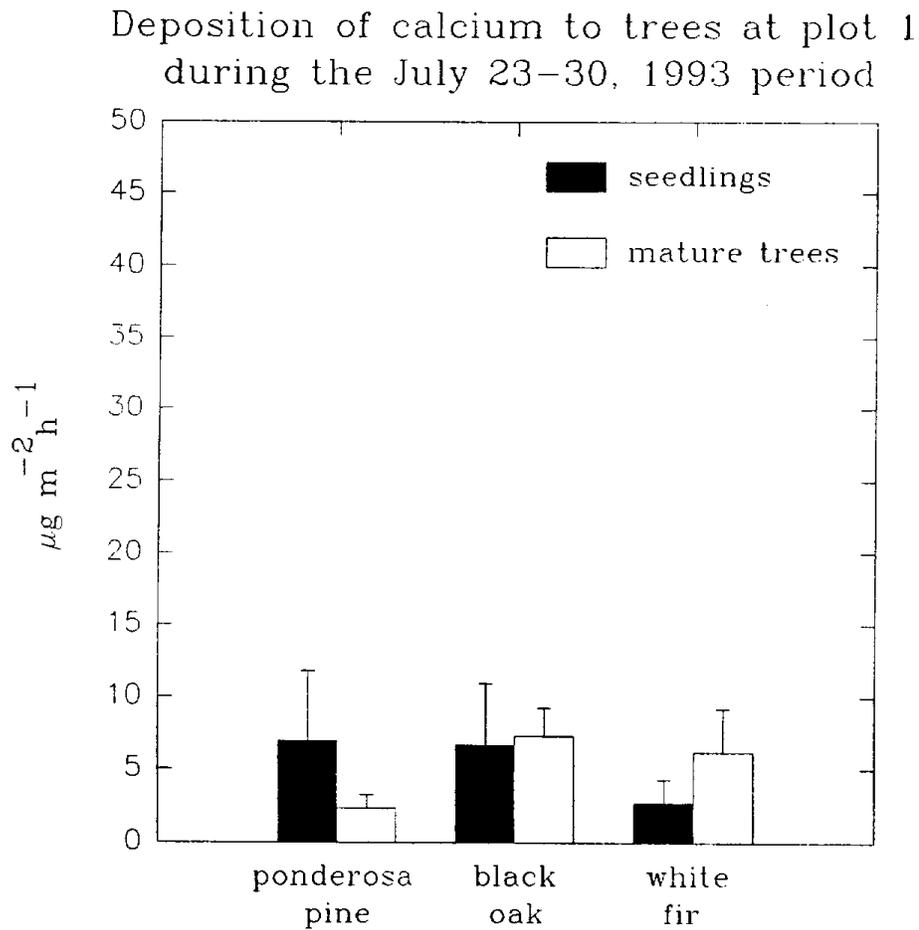


Figure A5-27. Deposition of Calcium to Branches of Mature Trees and Seedlings of Three Species at Plot 2 During the July 23-30, 1993 Period of the Intensive Study.

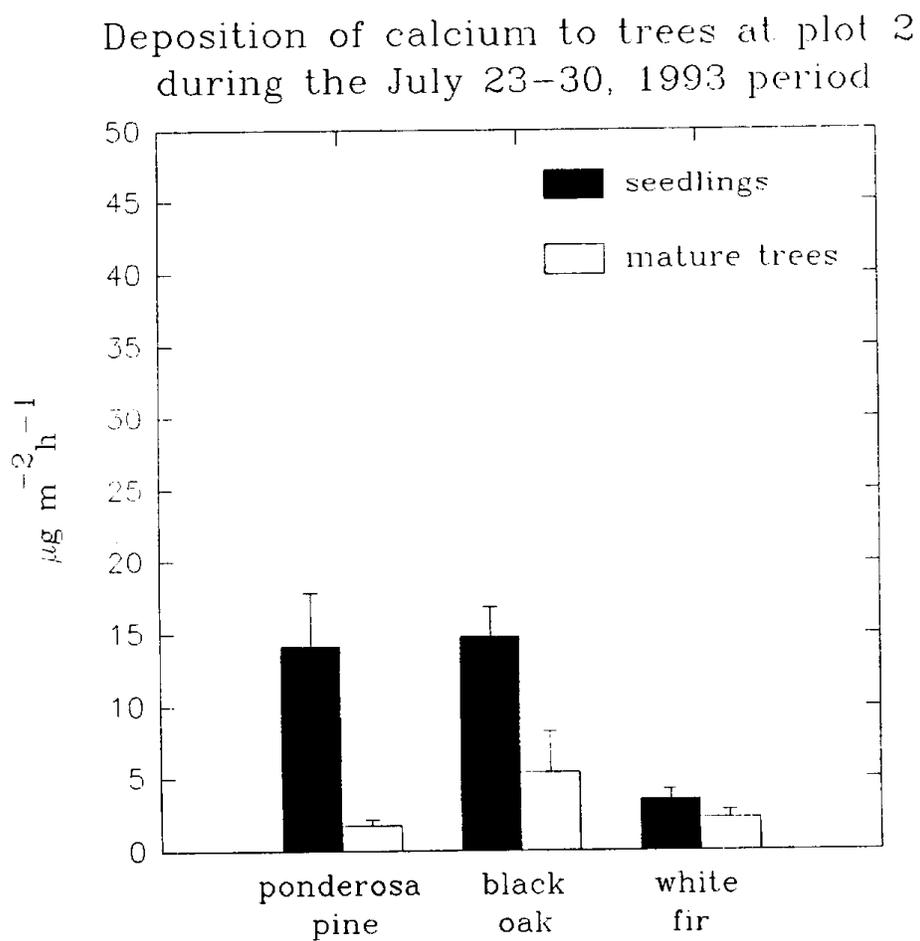


Figure A5-28. Deposition of Calcium to Branches of Mature Trees and Seedlings of Three Species at Plot 3 During the July 23-30, 1993 Period of the Intensive Study.

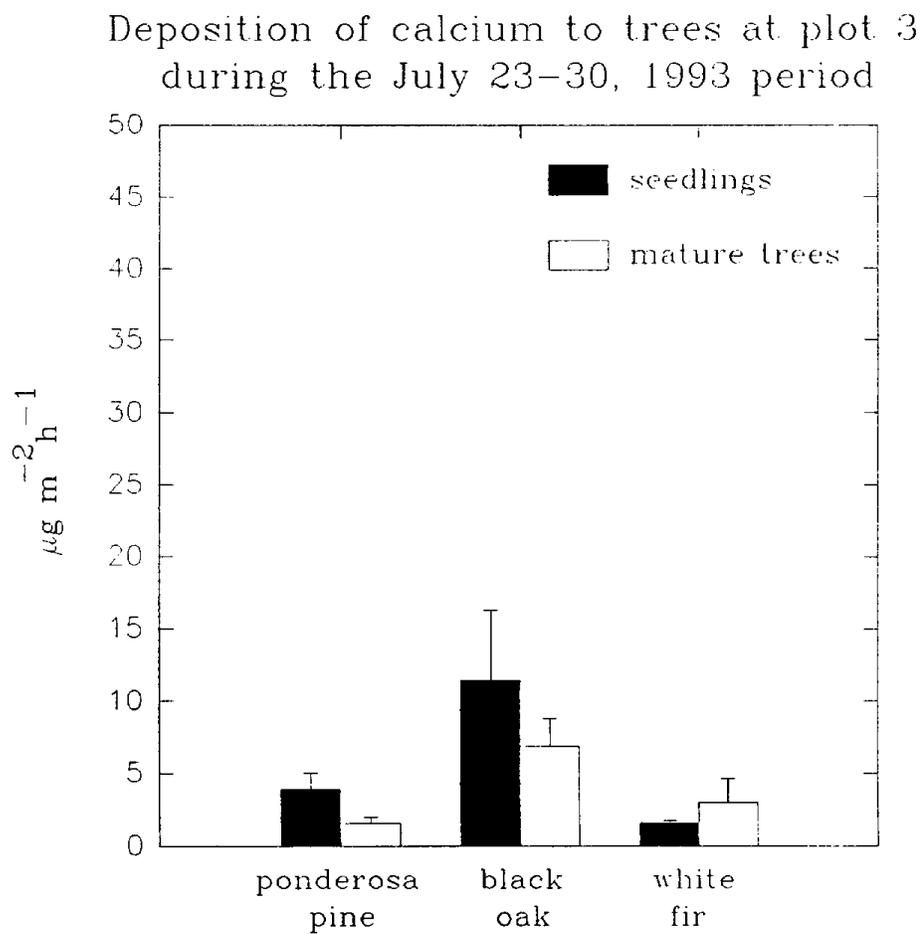


Figure A5-29. Deposition of Magnesium to Branches of Mature Trees and Seedlings of Three Species at Plot 1 During the July 19-23, 1993 Period of the Intensive Study.

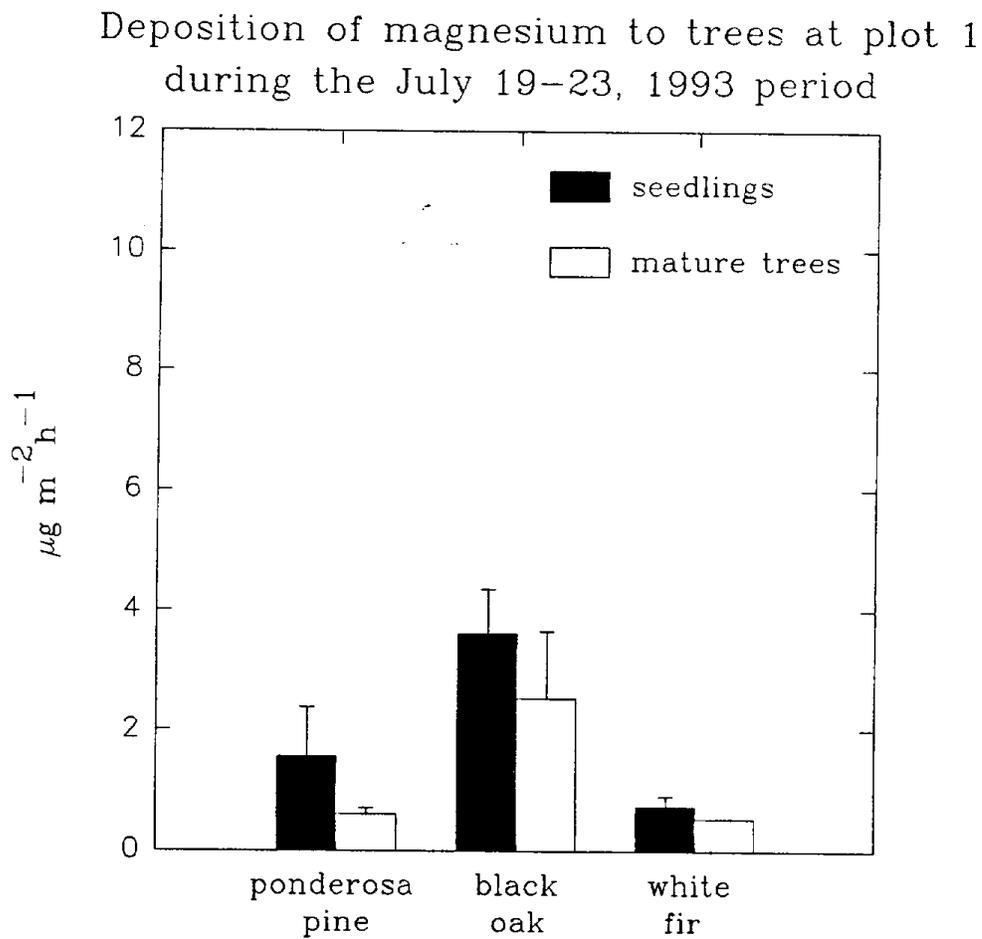


Figure A5-30. Deposition of Magnesium to Branches of Mature Trees and Seedlings of Three Species at Plot 2 During the July 19-23, 1993 Period of the Intensive Study.

Deposition of magnesium to trees at plot 2 during the July 19-23, 1993 period

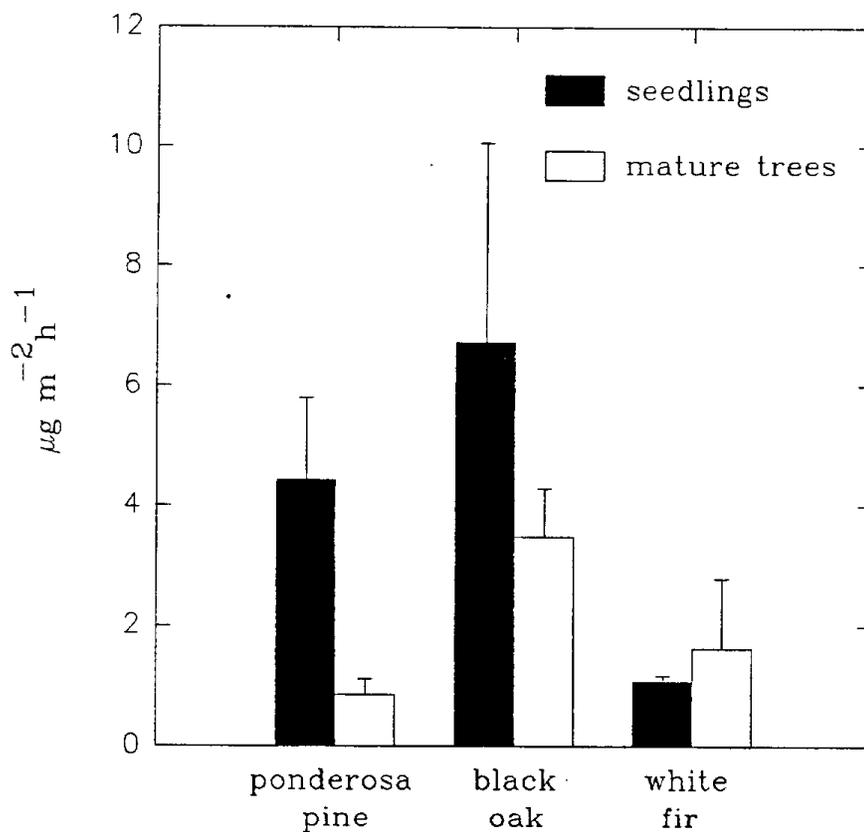


Figure A5-31. Deposition of Magnesium to Branches of Mature Trees and Seedlings of Three Species at Plot 3 During the July 19-23, 1993 Period of the Intensive Study.

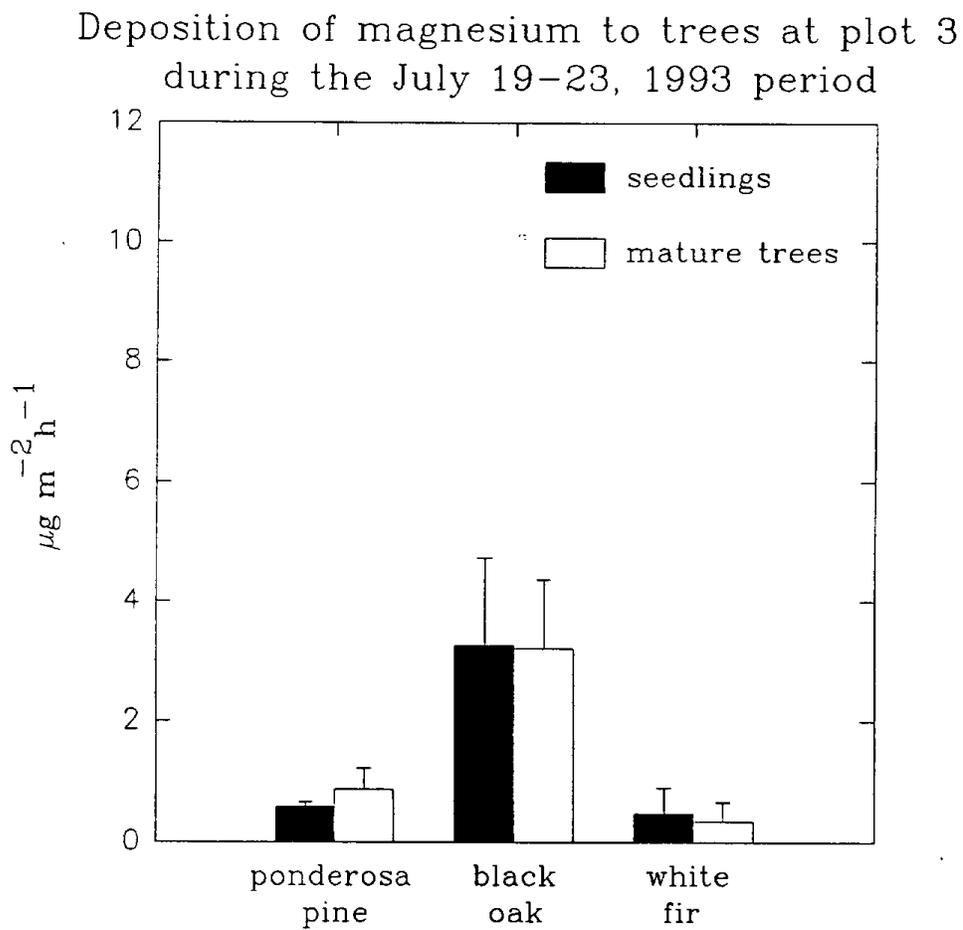


Figure A5-32. Deposition of Magnesium to Branches of Mature Trees and Seedlings of Three Species at Plot 1 During the July 23-30, 1993 Period of the Intensive Study.

Deposition of magnesium to trees at plot 1 during the July 23-30, 1993 period

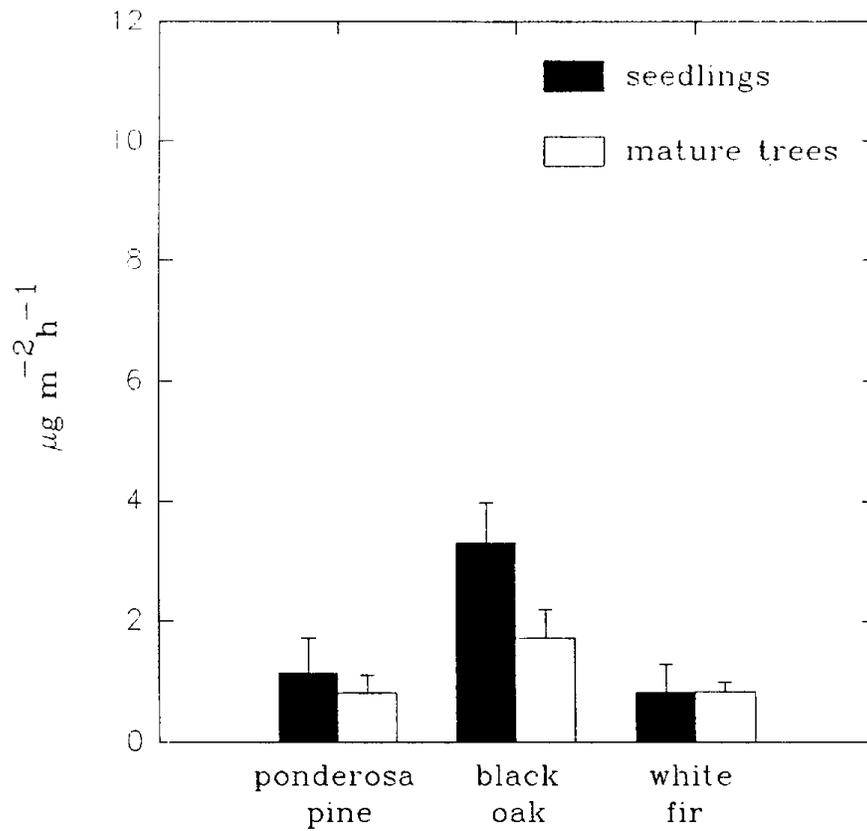


Figure A5-33. Deposition of Magnesium to Branches of Mature Trees and Seedlings of Three Species at Plot 2 During the July 23-30, 1993 Period of the Intensive Study.

Deposition of magnesium to trees at plot 2 during the July 23-30, 1993 period

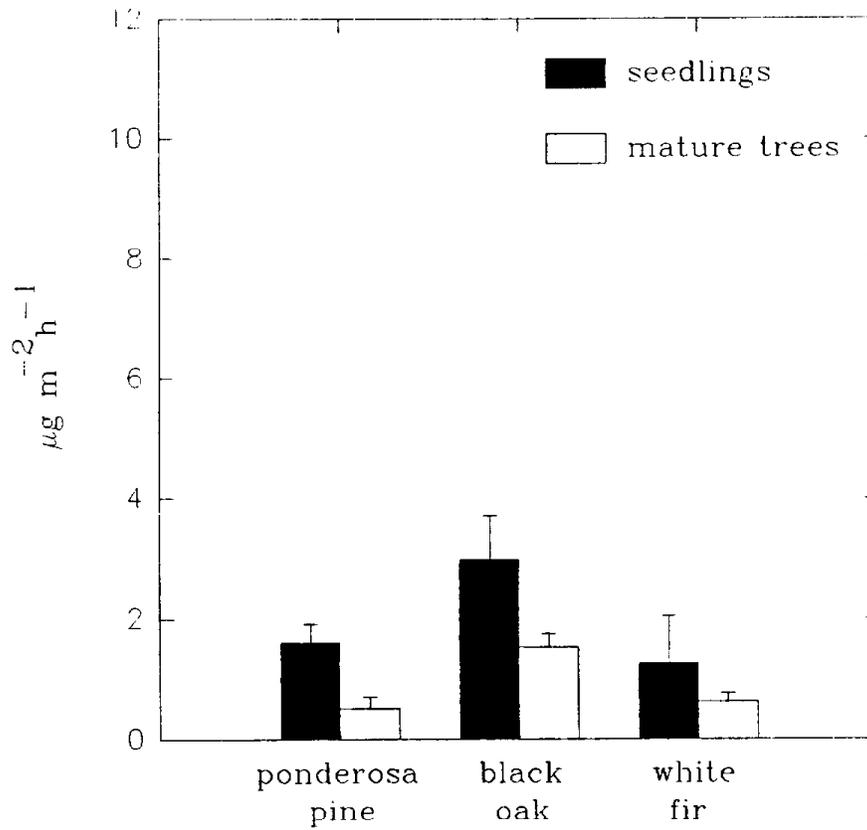
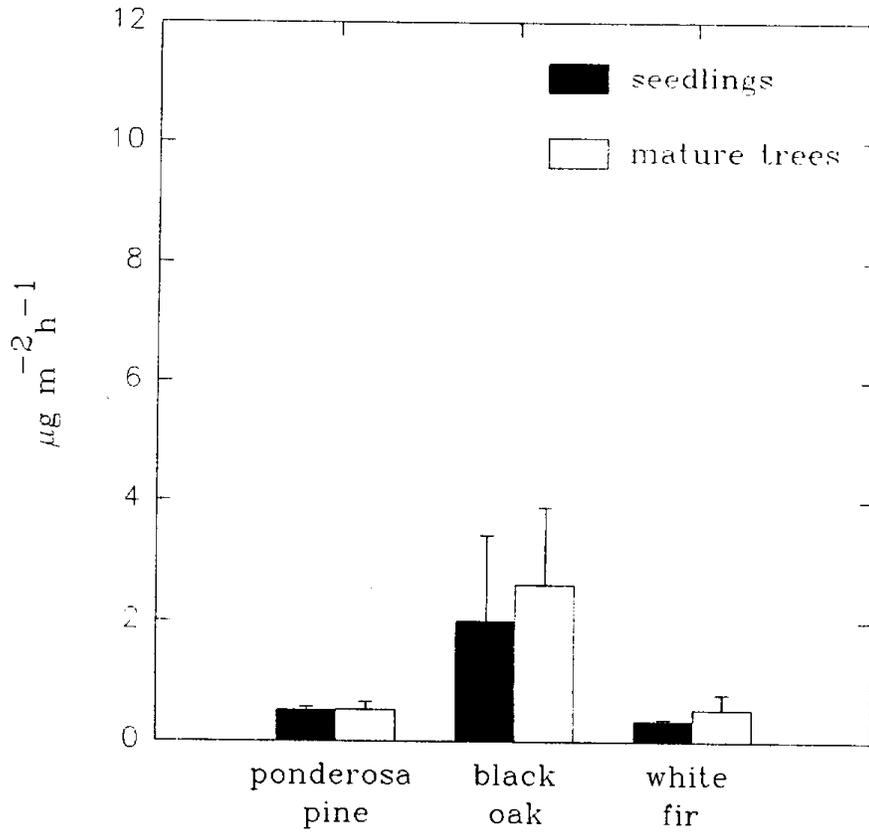


Figure A5-34. Deposition of Magnesium to Branches of Mature Trees and Seedlings of Three Species at Plot 3 During the July 23-30, 1993 Period of the Intensive Study.

Deposition of magnesium to trees at plot 3 during the July 23-30, 1993 period



6.0 ALL-YEAR WET DEPOSITION MEASUREMENTS IN THE SAN BERNARDINO MOUNTAINS AND SAN DIMAS EXPERIMENTAL FOREST

M. Fenn, A. Bytnerowicz, R. Glaubig, D. Jones, and S. Schilling

6.1 Introduction

Recent data clearly demonstrates high dry deposition fluxes of N pollutants in the more highly-exposed areas of the San Gabriel and San Bernardino Mountains (Bytnerowicz et al., 1987; Fenn and Bytnerowicz, 1993), and to a lesser degree in the southern and western portions of the Sierra Nevada Mountains (Bytnerowicz et al., 1990). Except for National Atmospheric Deposition Program (NADP) precipitation data from Tanbark Flat and limited data on snow and rime ice at Strawberry Peak in the SBM (Berg et al., 1991), very little data on winter deposition of pollutants in the mountains of southern California are available. It has previously been assumed that winter deposition was insignificant even in forested sites with high dry deposition of N and ozone exposures in the summer (Fenn and Bytnerowicz, 1993). In this section we present data on winter and early springtime wet and dry deposition of N and S at three sites across an air pollution gradient in the SBM, including the Barton Flats monitoring station (Figure 6-1). Another objective of this portion of the study was to compare wet deposition of N and S and precipitation acidity at the highly-polluted Tanbark Flat site in the San Gabriel Mountains and the Barton Flats (BF) monitoring station (Figure 6-1b). We were also able to compare the performance of the flip-top rain collectors designed for this study with the NADP Aerochem Metrics precipitation collectors (wet bucket) employed at Tanbark Flat and BF (Section 2.2.1.2).

6.2 Methods

6.2.1 Twin Bucket Sampler at Barton Flats vs Tanbark Flat NADP Site

General procedures for the twin bucket samplers are according to the National Atmospheric Deposition Program, National Trend Network guidelines. Procedures are also outlined in the Standard Operating Procedures manual (SOP) accompanying this report (see SOP 4, Vol. 2 for bucket operation and how samples were collected, SOP 15 to SOP 17, Vol. 2 for Desert Research Institute laboratory procedures, and Appendix I to SOP volume 1 for chemical analysis procedures at the Riverside Fire Laboratory). Buckets were changed weekly on Tuesday. The Tanbark bucket was sealed and mailed express to the laboratory for analysis. Ion concentration data and precipitation volume data were used to calculate wet deposition on a land area basis (kg ha^{-1}). Precipitation and deposition data from the weekly collections were combined to obtain quarterly (three month summaries) values. The four quarters were defined as:

- Quarter 1: December of the previous year through February of the current year
- Quarter 2: March through May
- Quarter 3: June through August
- Quarter 4: September through November

6.2.2 Rain, Fog, and Snow, With and Without Dry Deposition Exclusion at Camp Paivika, Barton Flats and Heart Bar

Winter and early springtime deposition of air pollutants in the form of rain, snow, and dry deposition was monitored at three sites across a west to east atmospheric deposition gradient in the SBM (Figure 6-1b; Fenn and Bytnerowicz, 1993). The flip-top throughfall and rainfall collectors (Glaubig and Gomez, 1994) described in Section 7 were modified for collecting winter/spring wet deposition. Modifications included replacing the butyrate plastic inner and outer collection cylinders with a polyvinylchloride (PVC) capped tube; this tube was approximately 75 cm deep to allow for heavy snowfalls. In addition, the triggering papers for the winter/spring deposition collectors were lightly sprinkled with NaCl which hastened the melting of snow necessary for triggering the collectors. Three replicate wet-only collectors at each site remained closed with a flip-top lid until a precipitation event. Three wet-plus-dry collectors without lids were also located adjacent to the wet-only collectors at each site. These open collectors were thus exposed to dry deposition between precipitation events, and samples from these collectors included both wet and dry deposition components. Wet-only and wet-plus-dry samples were collected shortly after each storm event. Wet deposition samples were collected at Camp Paivika (CP), BF and Heart Bar (HB) on eleven dates from December 13, 1993 through April 11, 1994. Samples were collected on four additional dates at CP only, with the last collection on June 1, 1994. Samples were analyzed for concentrations of SO_4^{2-} , NH_4^+ , and NO_3^- according to the procedures described for the analysis of throughfall and rainfall (SOP 9, Vol. 1).

The construction and placement of the fog/dry deposition collectors is described in detail in SOP 35, Vol. 1. Nylon lines arranged in parallel constituted the collection surface for dry deposition and fog condensation. The collectors in the field were covered with a 1.2 m x 1.2 m roof of polyethylene sheeting to exclude rain and snow from contacting the collectors. The fog condensate collected by the nylon lines runs down the lines through a funnel and into a polypropylene bottle. The nylon lines were also rinsed with purified distilled water at the time of sample collection. Fog condensate and line rinse samples were collected approximately every 14 days (SOP 36, Vol. 1). Both the condensate and rinse water were saved for chemical analysis (SOP 37, Vol. 1). Sample collection at CP, BF and HB occurred from December 3, 1993 until April 6, 1994. Sample collection continued at CP until June 1, 1994.

6.2.3 Statistical Analyses

Data analysis for comparing results between sites were performed using SigmaStat™ statistical software from Jandel Scientific Software (San Rafael, CA). Unless otherwise stated, differences between plots were considered statistically significant at $P \leq 0.05$. Differences in deposition of ions between sites in rain and throughfall were tested by one-way ANOVA and pairwise multiple comparison procedures (Fox et al., 1994). Differences between wet deposition chemistry at Tanbark Flat and BF were determined with ANOVA and a paired t-test. All statistical tests with data on the pH of rainfall and throughfall were performed with the data expressed as hydrogen ion concentrations (H^+). Likewise, average pH values were determined from average H^+ concentrations.

6.3 Results

6.3.1 Three Month Summaries of Rain Volume and Chemistry at Barton Flats and Tanbark Flats from Fall 1991 to Fall 1993

The wet deposition data weakly reflect the higher air pollution exposure at Tanbark Flat compared to BF (Figures 6-2 and 6-3). However, the low power of the paired t-tests may have precluded the detection of significant differences between sites with some variables. The pH of wet deposition was more acidic ($p=0.03$) at Tanbark Flat than at BF, and precipitation levels were also significantly greater at Tanbark Flat ($p<0.10$). In three of four quarters NO_3^- and SO_4^{2-} deposition at Tanbark appears to be greater than at BF, although overall, significant differences were not detected (p values for the paired t-test were 0.3 for NO_3^- and 0.19 for SO_4^{2-}). In the third quarter (June through August) of 1992 however, it seems clear that rain pH was lower, while precipitation amount and deposition of SO_4^{2-} , NH_4^+ , and NO_3^- were greater at BF than at Tanbark (Figures 6-2 and 6-3). Precipitation was relatively high at BF at this time due to five relatively large rain events from July 7 to August 18, 1992 compared to only one similar magnitude rain event during the same period at Tanbark Flat (Figure 6-2).

Precipitation amount and ionic deposition in the wet bucket and throughfall collectors were also compared during the winter of 1993/1994 and during the summers of 1993 and 1994 at the monitoring station near plot 1 at BF. Precipitation volume in the winter was 2.9% higher in the flip-top collector than in the wet bucket. This small difference is probably not statistically significant based on the variation between sample volumes in the replicate rain collectors (Figure 6-4). Only one wet bucket was employed at BF. In the third quarter of 1993 (June through August) precipitation volume was 6.4% greater in the flip-top collector than in the wet bucket. However, in the third quarter of 1994 precipitation volume was 11.6% greater in the wet bucket compared to the flip-top rain collector (Figure 6-5). Only one collector of each type was employed at the BF monitoring station, precluding statistical comparisons of the two collector types for the summer period. Deposition of NO_3^- , NH_4^+ , and SO_4^{2-} in the winter collections appear to be greater in the flip-top rain collector compared to the wet bucket collector (Figure 6-4). Sulfate deposition in summertime precipitation samples were highly similar with both collector types, while NH_4^+ deposition appeared to be much greater in the wet bucket (Figure 6-5). Summertime NO_3^- deposition was more variable, with deposition nearly twice as high in the flip-top collector in 1993, but similar between the two collector types in 1994 (Figure 6-5).

6.3.2 Chemistry of Rain, Fog and Snow With or Without Dry Deposition Exclusion at Camp Paivika, Barton Flats, and Heart Bar

Winter and early spring deposition of N and S is clearly minimal at HB and BF compared to the more western site at CP (Figures 6-6 and 6-7). The molar ratio of $\text{NO}_3^-:\text{NH}_4^+:\text{SO}_4^{2-}$ in the wet-plus-dry deposition samples at CP was 6:5:1 (Figure 6-6). Dry deposition of NO_3^- appears to be greater than NH_4^+ . Dry deposition in winter/spring caused a noticeable increase in N deposition and to a lesser degree of S deposition at CP (Figure 6-6). The cumulative total of wet plus dry deposition of $\text{NH}_4\text{-N}$ at CP from 11 precipitation events was 3.37 kg ha^{-1} , but only 0.19 and 0.38 kg ha^{-1} at HB and BF, respectively. Analogous values for $\text{NO}_3\text{-N}$ at CP were 4.32 kg ha^{-1} compared to 0.35 and 0.49 kg ha^{-1} at HB and BF (Figure 6-6). After 11 collection dates cumulative $\text{SO}_4\text{-S}$ deposition at CP totaled 1.73 kg ha^{-1} compared to 0.19 and 0.32 kg ha^{-1} at HB and BF. Total N ($\text{NH}_4^+ + \text{NO}_3^-$) and S deposition to the modified throughfall collectors at CP from

December 13, 1993 to June 1, 1994 were 11.9 and 2.7 kg ha⁻¹, respectively (Figure 6-6).

Fog and dry deposition to nylon line collectors also demonstrate the greater magnitude of N deposition compared to S deposition (Figure 6-7). The molar ratio of NO₃⁻:NH₄⁺:SO₄²⁻ in the fog plus dry deposition samples at CP was 98:50:1 (Figure 6-7). By the end of the eighth collection on April 6, 1994 the cumulative deposition of NO₃⁻, NH₄⁺ and SO₄²⁻ to the fog and dry deposition collectors was 15, 18 and 6 fold greater at CP than at BF (Figure 6-7).

6.4 Discussion

The results of this study suggest that winter and early spring deposition of N and S in the SBM is greater than previously thought. A recent study reported that NO₃⁻ and SO₄²⁻ concentrations in rime ice and snow at Strawberry Peak in the SBM were higher than at montane sites in central and northern California (Berg et al., 1991). However, only ion concentration data were presented, and no attempts were made to determine landscape level nutrient loadings in rime ice and snow. In our wet plus dry winter and early spring (5.5 months) deposition collections we measured total N and S deposition at CP to be 11.9 and 2.7 kg ha⁻¹ in the open areas. Presumably, deposition to the forest canopy during the winter and early spring would be considerably higher due to the high surface area of conifer foliage for scavenging of dry gases and particles and collection of snow and rime ice. Somewhat surprisingly, wet deposition of NH₄⁺ (4.29 kg ha⁻¹) was nearly equal to wet deposition of NO₃⁻ (4.74 kg ha⁻¹) at CP, possibly largely due to precipitation scavenging of ammonium nitrate. Ammonia emissions from the dairy farms concentrated in the Chino area may also be a source of the high inputs of NH₄⁺.

The increase in total deposition of NO₃⁻ in the wet plus dry collection compared to the wet-only collection (open collectors versus those opened only during a storm) was greater than for NH₄⁺. This result suggests that dry deposition of NO₃⁻ in winter and early spring is greater than dry deposition of NH₄⁺—an observation that has been well established for summertime measurements in montane areas of the Los Angeles Air Basin (Bytnerowicz et al., 1987; Fenn and Bytnerowicz, 1993). Nitric acid vapor is probably a major source of the greater dry deposition of NO₃⁻ compared to NH₄⁺ (Bytnerowicz et al., 1987; Solomon et al., 1992). It should be noted that the open-cylinder collectors were not designed for efficient collection of dry particles and gases. The primary purpose of the collectors was for site comparison and as a surrogate measure of the relative magnitude of winter and early spring dry and wet deposition inputs at three sites traversing the atmospheric deposition gradient in the SBM. Nevertheless, the data clearly indicate that in high-deposition areas such as near Crestline in the western SBM, winter and spring inputs of N are an important component of the annual N budget, and that dry deposition contributes to the overall winter and spring deposition loading.

High winter and springtime N and S inputs may have important effects on nutrient cycling since snowmelt releases nutrient pulses into the soil. Plant nutrient uptake may be high in the spring due to concomitant high soil water availability and nutrient release from snowmelt. A variety of nutritional indicators from Camp Paivika suggest that this site is N saturated, presumably as a result of at least four decades of N deposition on the order of 25 to 45 kg ha⁻¹ yr⁻¹ (Fenn and Bytnerowicz, 1993 and winter/spring deposition data in this

study). Available N at CP seems to be in excess of biotic demand based on lack of response in ponderosa pine (*Pinus ponderosa* Laws.) to N fertilization, high NO_3^- concentrations in the soil solution, high fluxes of nitric oxide (NO) gas from soil, accumulation of NO_3^- in foliage, high foliar N:P ratios, low soil C:N ratios, and soil acidification. Temporal changes in soil pH and C:N ratios over the last 20 years also suggest that the soil at CP has become more acidic and N enriched (Fenn et al., 1995). The available evidence suggests that the primary pathway for short-term plant uptake and utilization of atmospherically-deposited N is via throughfall transport of N into the rooting zone of the forest floor and soil (Fenn and Leininger, 1995), although canopy uptake of N undoubtedly occurs as well.

This study confirms that wet and dry deposition of N and S vary greatly across the air pollution gradient in the SBM in the winter and spring as well as during the summer smog season (Fenn and Bytnerowicz, 1993). It should be pointed out that the samples collected at CP, BF and HB from the fog/dry deposition collectors, and from the open-top throughfall collectors, include ionic deposition in both wet and dry forms. The dry deposition component in the wet-plus-dry throughfall collectors can be estimated by subtracting deposition from the wet-only collectors (those that opened only when precipitation occurred). While this experiment clearly demonstrated the occurrence of a deposition gradient during the winter, actual dry deposition of N and S to the forest cannot be determined from dry deposition to rainfall collectors. Similarly, the nylon line fog/dry deposition collectors confirmed the deposition gradient in the SBM, but the deposition fluxes cannot be quantitatively related to deposition fluxes to the forest. Because a roof was constructed over the fog/dry deposition collectors, precipitation was excluded. We presume that what was collected by the nylon lines was a combination of fog and dry gases and particles. However, the relative importance of each component cannot be determined and was not the purpose of this study.

Overall differences in wet deposition amounts between BF and Tanbark may have been confounded by an unusually wet third quarter in 1992 at BF compared to Tanbark Flat. Five relatively large rain events occurred at BF in the third quarter of 1992, compared to only one at Tanbark Flat. Rainfall amount was over three times greater at BF than at Tanbark during the third quarter of 1992. Ionic concentrations were consistently higher at Tanbark throughout the study, but the greater rain volume resulted in greater ionic deposition at BF during the third quarter in 1992.

Wet deposition data only weakly reflected the higher air pollution exposure at Tanbark. However, published dry deposition data from Tanbark, and at sites across an atmospheric deposition gradient in the SBM (including BF), clearly demonstrate the much greater air pollution exposure at Tanbark Flat than at BF (Bytnerowicz et al., 1987; Fenn and Bytnerowicz, 1993). Wet deposition chemistry probably does not strongly reflect the relative atmospheric deposition loadings of BF and Tanbark because of the temporal separation between the high-pollution or smog season and the rainy season in this Mediterranean climate. The major precipitation inputs occur during the winter when air pollution concentrations are much lower and inversion layers infrequent compared to the dry summer months. Another factor may be the inefficiency with which rainfall scavenges dry pollutants from the atmosphere.

Discrepancies were found in ionic deposition between the flip-top rainfall collectors and the wet bucket at the BF monitoring station. It is not known why summertime NH_4^+ deposition was higher in the wet bucket than

in the flip-top rain collector. The most likely cause of higher NH_4^+ , NO_3^- and SO_4^{2-} deposition in the flip-top collectors in winter and spring, and higher deposition of NO_3^- in the flip-top collector in summer (in 1993 but not in 1994) is transport of ions from the forest canopy to the collectors after opening. The flip-top collectors used to collect rainfall were placed at ground level in open areas of the stands. The wet bucket on the other hand, was placed approximately 2.5 m aboveground on the roof of the monitoring station, and would appear to be positioned more remotely from contaminating influences of dust or the forest canopy. There was approximately three times more rain in the third quarter (June-August) of 1993 compared to 1994, which may explain why differences in NO_3^- deposition between the two sampler types wasn't found in the summer of 1994. There may not have been enough summer rain in 1994 to transport ions from nearby canopies to the rain collector. Likewise, winter and springtime precipitation was much greater than during the June-August quarter---thus underscoring the greater potential in winter and early spring for transport of ions to the collectors after opening. Windy conditions during and after storms would be a major factor in transporting ions from canopies to nearby rain collectors.

6.5 Summary

Winter and early springtime deposition in both wet and dry forms in the SBM was greater than previously estimated. Total N and S inputs during five and one-half months during the winter/spring period at CP were 11.9 and 2.7 kg ha^{-1} , which is a substantial input of N to a forest ecosystem. Winter and springtime deposition of N may be especially important in the nutrient cycle if snow melt releases and transports N into the soil for microbial and plant uptake as has been shown for California montane systems (Williams et al., 1995). Winter and springtime deposition of N probably contributes significantly to the developing N saturation at CP. Atmospheric deposition during the winter/spring at BF and Heart Bar was very low compared to CP and levels there were not considered to have noticeable impacts on nutrient cycling or forest health in the short term. The higher pollution exposures that occur at Tanbark Flat compared to BF were weakly reflected in the wet deposition data. Summertime dry deposition data much more clearly differentiates these two sites. Comparisons of the performance of the flip-top collector and the wet bucket collector raise some concerns regarding differences in ionic deposition sampled in the two types of collectors.

6.6 References

- Berg, N.; Dunn, P.; Fenn, M. 1991. Spatial and temporal variability of rime ice and snow chemistry at five sites in California. *Atmospheric Environment* 25A:915-926.
- Bytnerowicz, A.; Dawson, P.J.; Morrison, C.L.; Poe, M.P. 1990. Deposition of atmospheric ions to pine branches and surrogate surfaces in the vicinity of Emerald Lake Watershed in Sequoia National Park. *Atmospheric Environment* 25A:2203-2210.
- Bytnerowicz, A.; Miller, P.R.; Olszyk, D.M. 1987. Dry deposition of nitrate, ammonium and sulfate to a *Ceanothus crassifolius* canopy and surrogate surfaces. *Atmospheric Environment* 21:1749-1757.
- Fenn, M.E.; Poth, M.A.; Johnson, D.W. 1995. Evidence for nitrogen saturation in the San Bernardino Mountains in southern California. *Forest Ecology and Management* (In Press).
- Fenn, M.E.; Leininger, T.D. 1995. Uptake and distribution of nitrogen from acidic fog within a ponderosa pine (*Pinus ponderosa* Laws./litter/soil system. *Forest Science* 41:In press.
- Fenn, M.E.; Bytnerowicz, A. 1993. Dry deposition of nitrogen and sulfur to ponderosa and Jeffrey pine in the San Bernardino National Forest in southern California. *Environmental Pollution* 81:277-285.
- Fox, E.; Kuo, J.; Tilling, L.; Ulrich, C. 1994. SigmaStat™ for Windows User's Manual, Revision SSW 1.0. Jandel Scientific, San Rafael, California.
- Glaubig, R.; Gomez, A. 1994. A simple, inexpensive rain and canopy throughfall collector. *Journal of Environmental Quality* 23:1103-1107.
- Solomon P.A.; Salmon, L.G.; Fall, T; Cass, G.R. 1992. Spatial and temporal distribution of atmospheric nitric acid and particulate nitrate concentrations in the Los Angeles area. *Environmental Science and Technology* 26:1594-1601.
- Williams, M.W.; Bales, R.C.; Brown, A.D.; Melack, J.M. 1995. Fluxes and transformations of nitrogen in a high-elevation catchment, Sierra Nevada. *Biogeochemistry* 28:1-31.

Figure 6-1. (a) Map showing the location of plots 1-3 and the monitoring station at Barton Flats. (b) Map showing sites in the Angeles National Forest and San Bernardino National Forest where precipitation and winter deposition samples were collected.

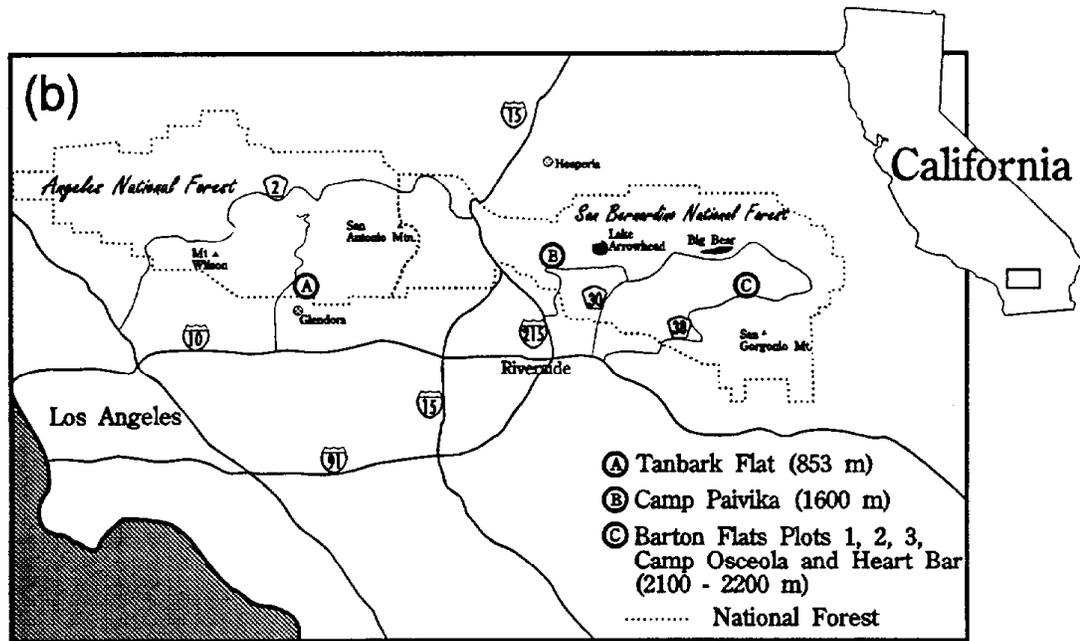
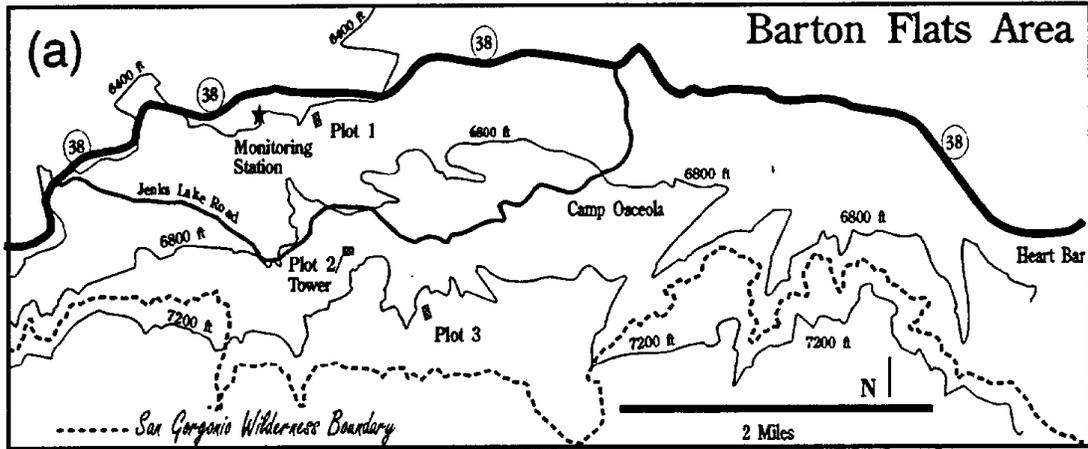


Figure 6-2. Comparison of precipitation pH and amount of precipitation at the Barton Flats monitoring station and Tanbark Flat. Data are for a two-year period during 1993 and 1994.

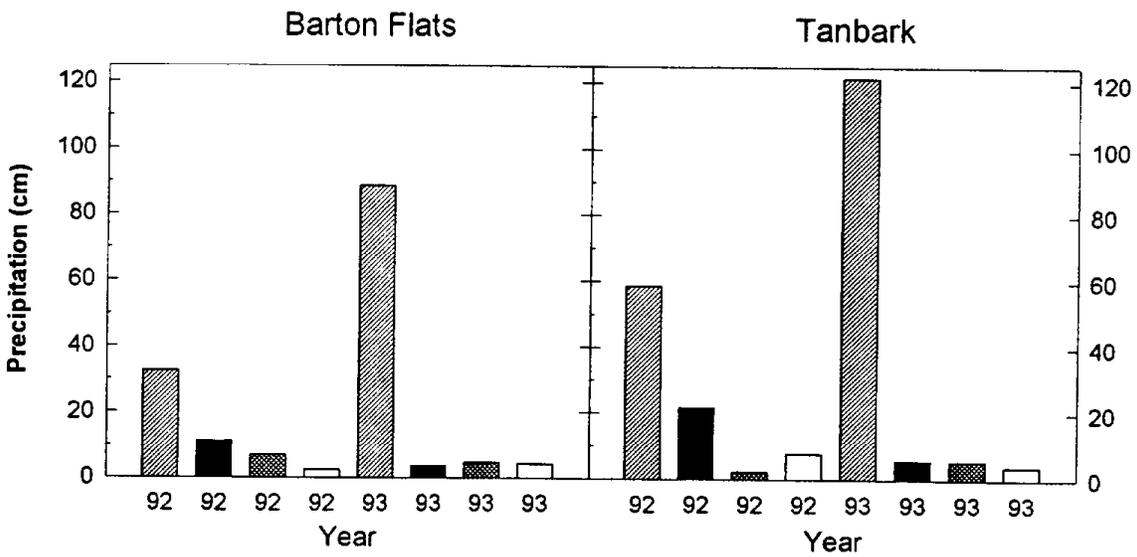
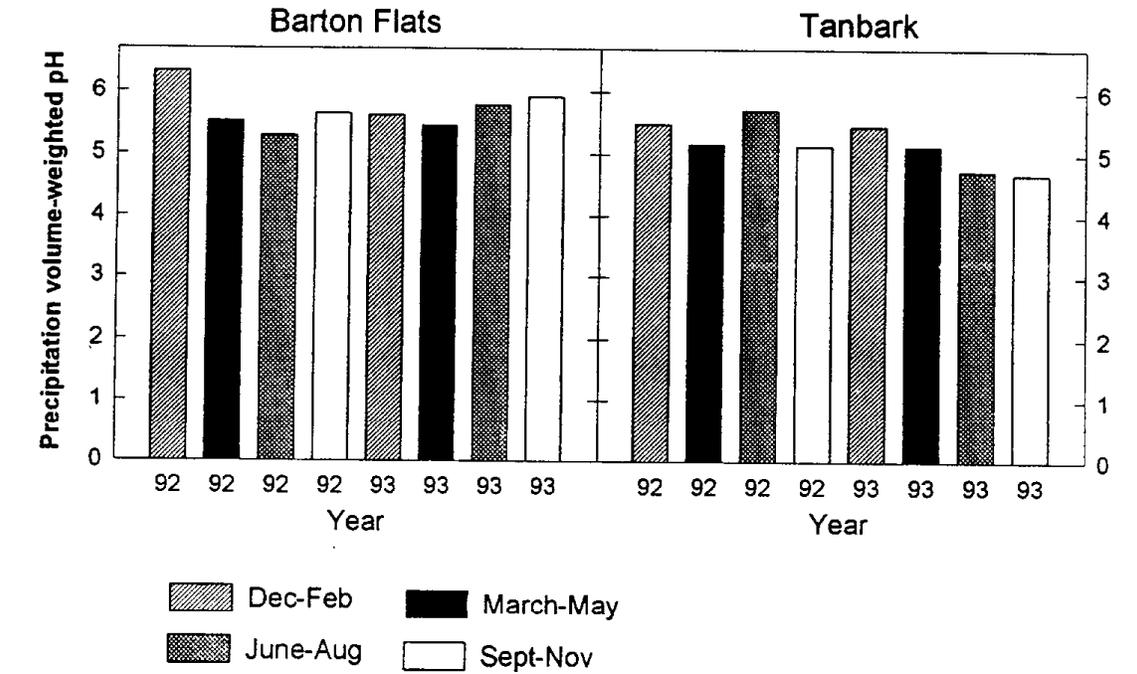


Figure 6-3. Deposition of SO_4^{2-} , NH_4^+ and NO_3^- in precipitation at the Barton Flats monitoring station and Tanbark Flat.

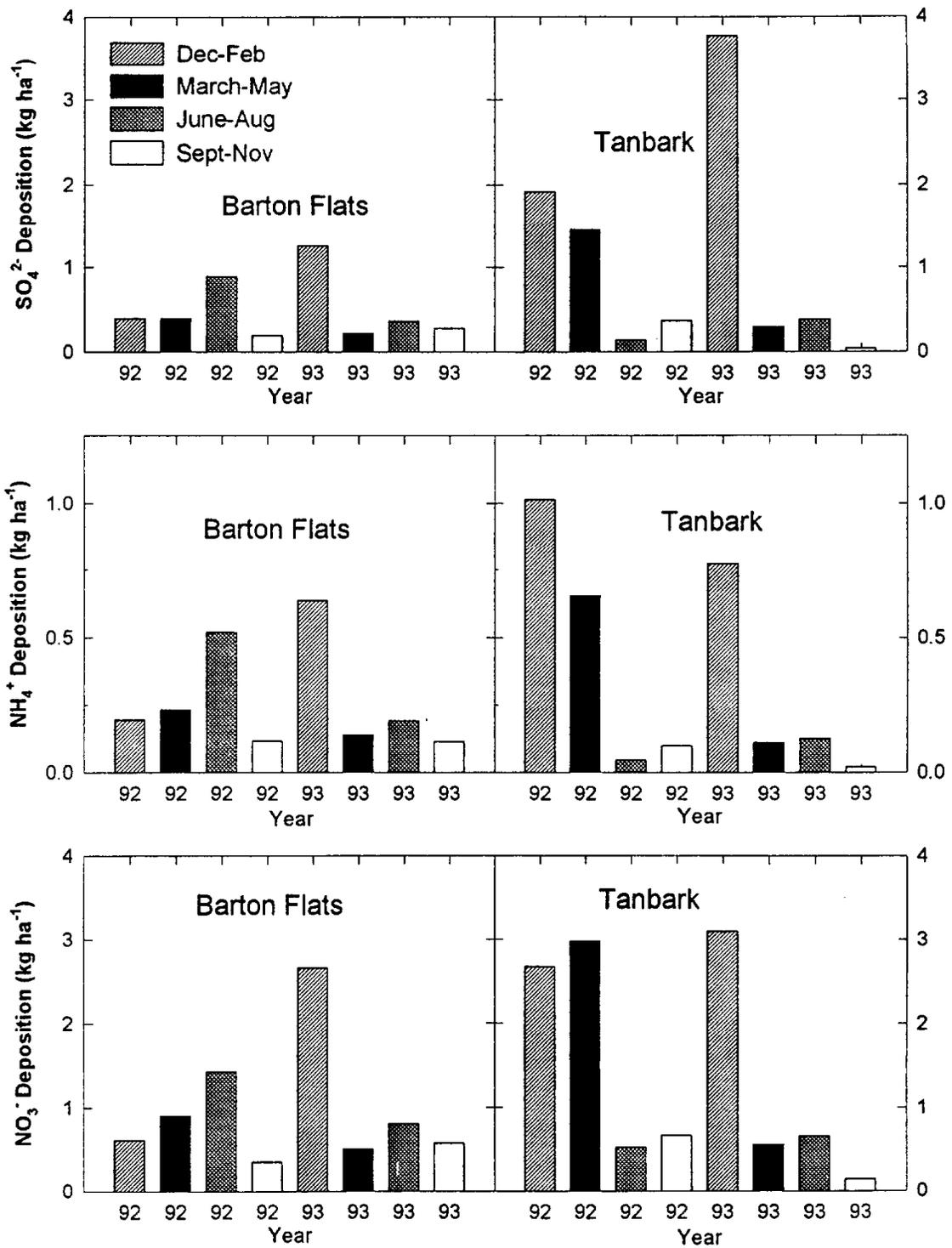


Figure 6-4. Comparison of winter precipitation volume and ionic deposition collected at the Barton Flats monitoring station in the wet bucket, flip-top rain collector without a lid (wet/dry), and flip-top collector with a lid (wet collector). Error bars are standard errors of the mean (not available for the wet bucket due to lack of replication).

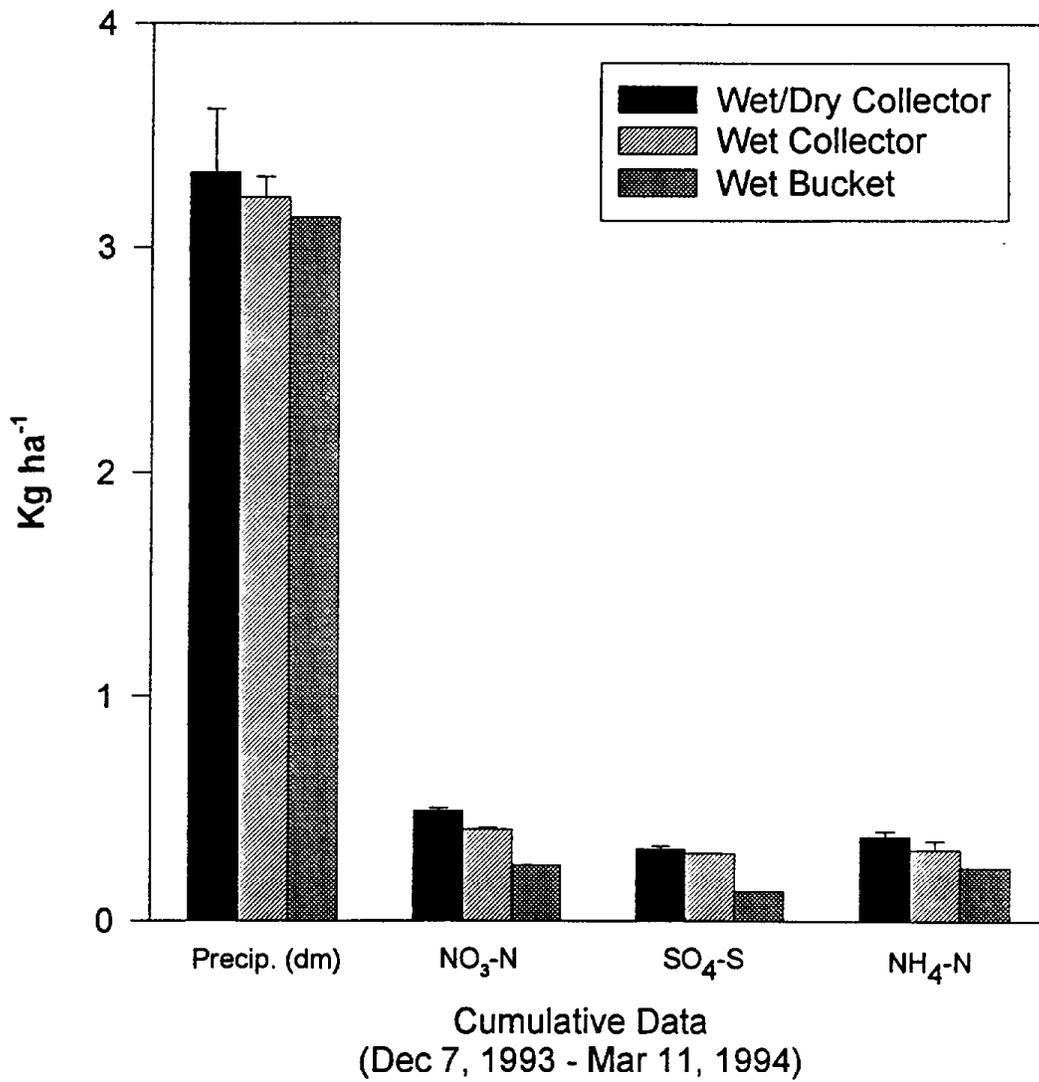


Figure 6-5. Comparison of summer precipitation volume and ionic deposition collected at the Barton Flats monitoring station in the wet bucket and flip-top rain collector. Data is for the third quarter of 1993 and 1994 (June through August).

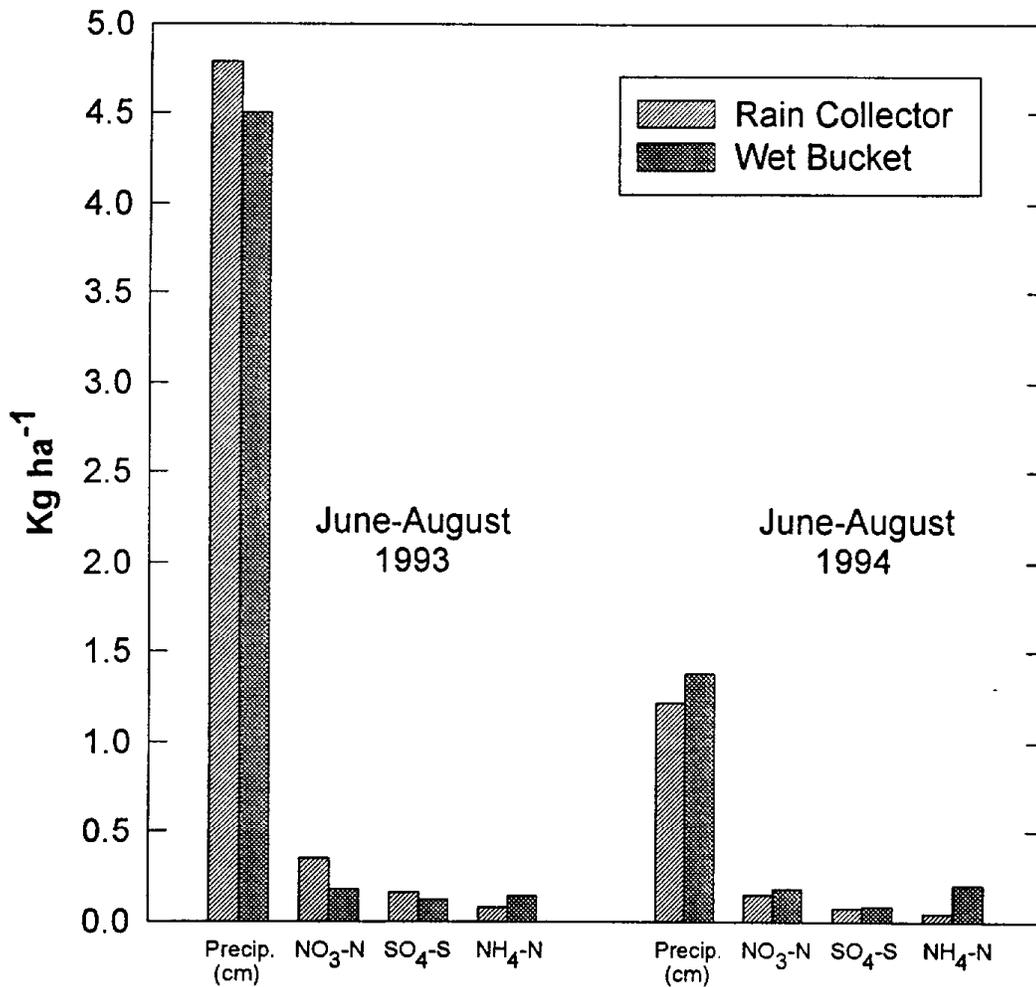


Figure 6-6. Winter 1993/1994 wet deposition (w) and wet plus dry (w/d) deposition at Heart Bar (HB), Barton Flats (BF), and Camp Paivika (CP).

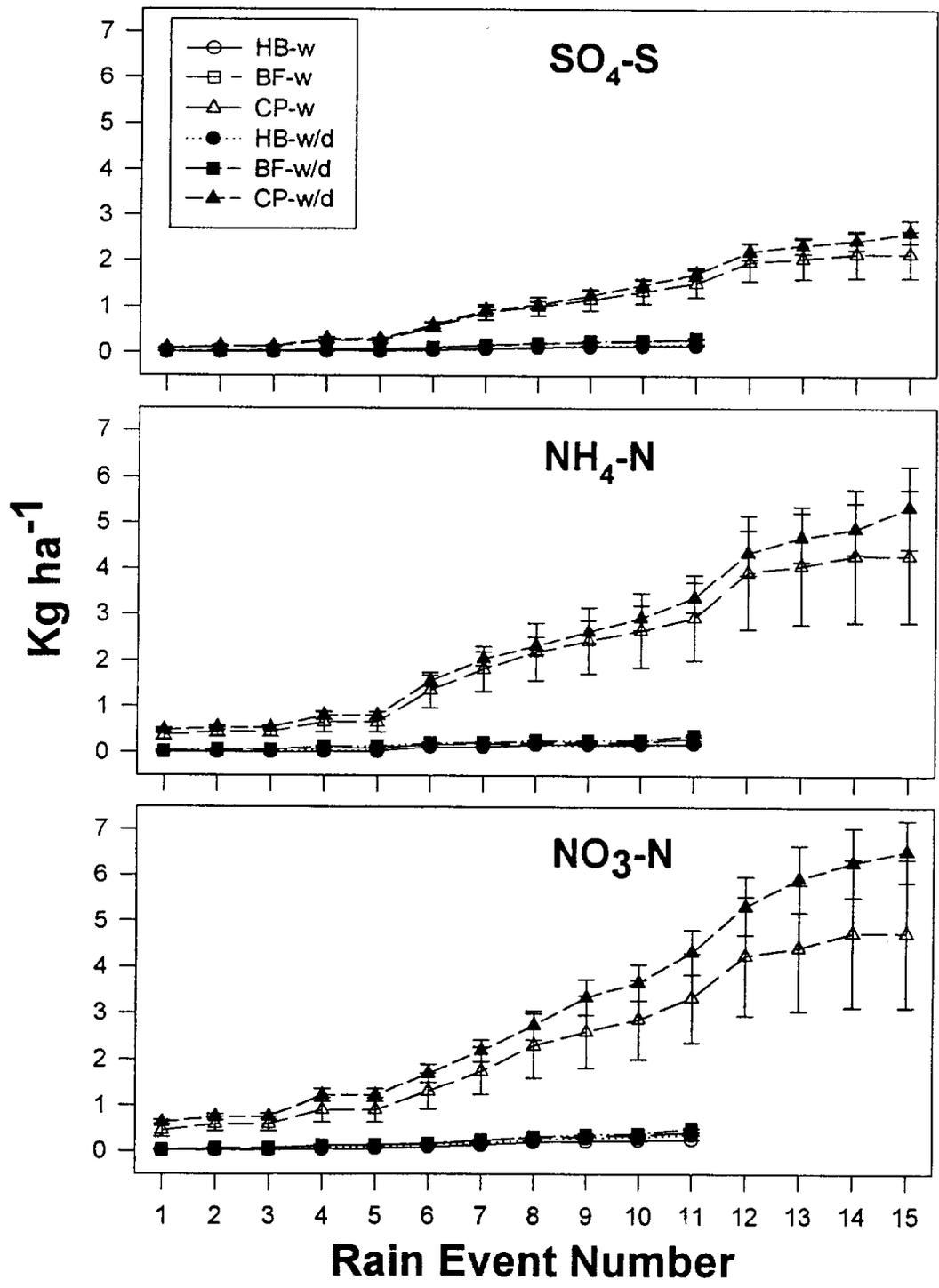
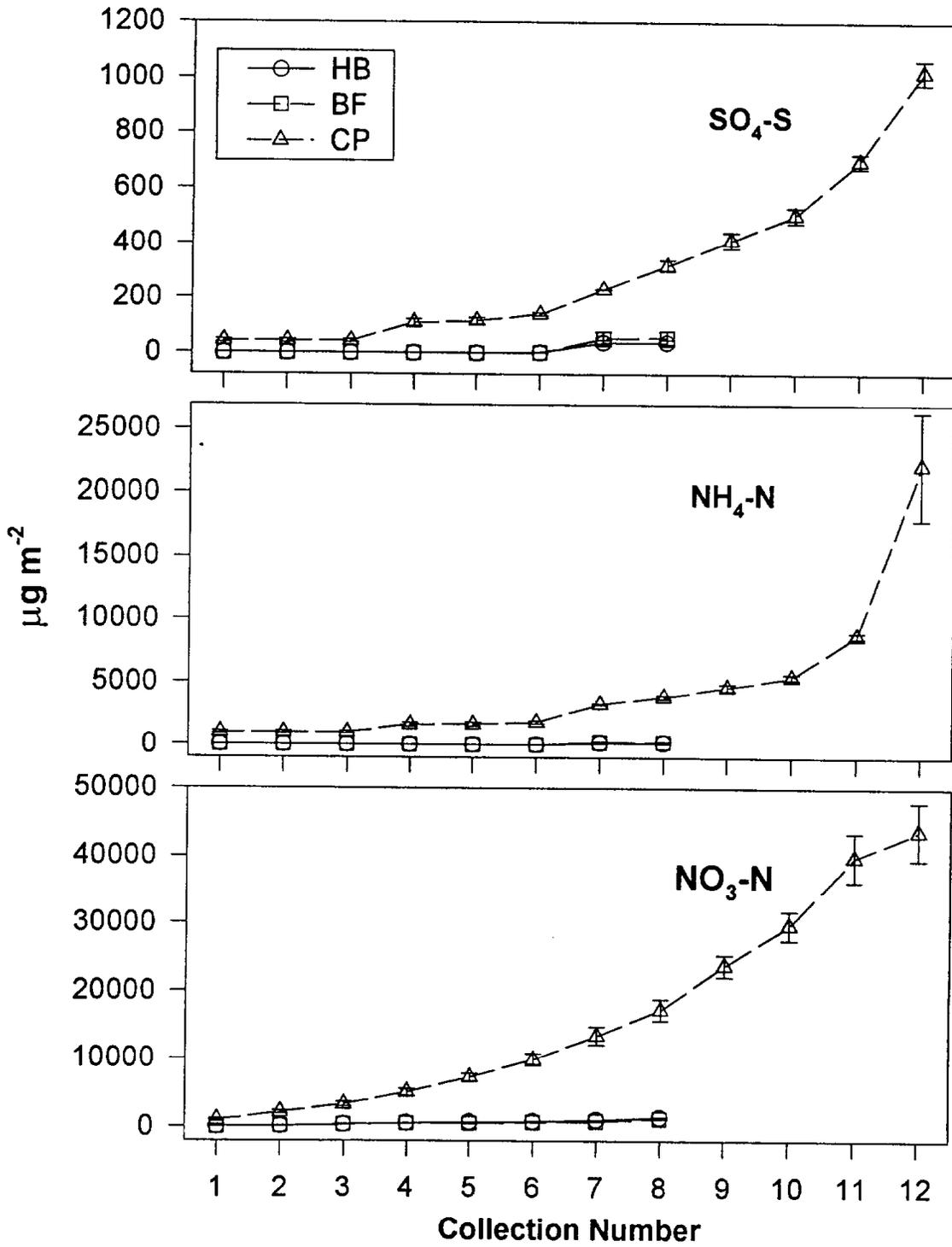


Figure 6-7. Winter 1993/1994 fog plus dry deposition fluxes to nylon line collectors at Heart Bar, Barton Flats and Camp Paivika.



7.0 WET DEPOSITION AND THROUGHFALL MEASUREMENTS IN RELATION TO THE FOREST CANOPY AT 3 PLOTS

M. Fenn, R. Glaubig, D. Jones, and S. Schilling

7.1 Introduction

Throughfall is the solution formed as precipitation is intercepted by and interacts with the forest canopy. Precipitation chemistry is modified considerably as it passes through the canopy, especially in areas of high atmospheric dry deposition inputs. The determination of throughfall inputs to the forest floor provide a useful integrative measure of total wet and dry atmospheric inputs to forest stands. However, pollutants interact in different ways with forest canopies. In many instances throughfall S fluxes have been shown to effectively estimate total atmospheric deposition to forests as most of the deposited S is removed by precipitation and little S is leached from the canopy (Joslin and Wolfe, 1992; Lindberg and Lovett, 1992). For N deposition however, it is common for 20-35% of the deposited N to be retained by the canopy (Cadle et al. 1991; Friedland et al. 1991; Hanson and Garten 1992; Johnson and Lindberg 1989; Lovett 1992; Lovett and Lindberg, 1993; Marshall and Cadle 1989). Estimates of atmospheric deposition of N from throughfall are thus believed to underestimate atmospheric deposition to forests. Leaching from internal plant tissue of the more leachable ions (notably K^+) can also complicate the estimation of atmospheric deposition from throughfall data (Parker, 1983).

7.2 Methods

7.2.1 Aerial Photo Representation of Canopies at 3 Plots

On May 15, 1993 aerial photographs of the three Barton Flats (BF) plots were obtained by Don Kaneko of I.K. Curtis. To mark the plots, a "T" 40 ft. wide by 20 ft. tall of white paper was fastened down at the center beginning and center end of the plots. A 40 ft. by 40 ft. "+" was also placed in an open area inside each plot. Three photos of each plot (scale = 1:1440) were taken. The photo with the plot most nearly centered was chosen for scanning and further computer analysis. The photograph was scanned on a flatbed scanner at 300 dpi in 24 bit color connected to a UNIX workstation. The image was imported into Photoshop (Adobe Systems Inc., Mountain View, California) for initial processing. The image was cropped to include only the plot area, and imported into MultiSpec (Purdue Research Foundation, West Lafayette, Indiana), an image analysis program. Training areas were set up to recognize area classes such as "ground" for open areas, "tree" and "tree shadow". After a few iterations, the program was ready to properly "read" the plot image. Results are reported as the number of pixels in each class. From these counts the percent of the plot covered by canopy and the percent "open" was calculated. The percent of the plot which was open was used to determine deposition levels in rain to the open areas of the plot (Section 7.2.2). A computer-generated graphic of the image for plot 2 is shown in Figure 7-1.

7.2.2 Calculations of Rainfall and Throughfall Deposition and Concentrations

Construction and placement of the flip-top throughfall collectors are described in SOP 6 and 7, Vol. 1. The throughfall collectors were designed to remain closed until the slightest precipitation collected in a small funnel directed a small amount of moisture to wet a narrow strip of dissolvable "magic" paper. This paper held the lid closed against a counter weight. When the paper dissolved, the counter weight caused the lid to flip open. Construction and operation of the collectors are also described in Glaubig and Gomez (1994). Major advantages of these collectors include their ease of operation, ability to effectively exclude dry deposition, no power source is needed for operation of the collectors, and the low cost of construction and maintenance. The same collectors were used for collecting rain and throughfall. Rain was collected in stand openings free of canopy influences, but adjacent to throughfall collector trees. Chemical analysis procedures for rain and throughfall samples are described in SOP 9, Vol. 1. In each year of the study throughfall and rain were collected during the spring, summer and early fall period (SOP 8, Vol. 1). Wet deposition samples were collected only at the monitoring station during the winter season (Section 2.2.1.2 and 6.3.1). Thus throughfall data for BF cover the spring through fall period, and exclude winter wet deposition in the form of snow and snowmelt from canopies. Although annual throughfall input data is not available, annual deposition inputs at BF were estimated from branch rinse data and other known deposition parameters as described in Section 4.3.5 and from computer simulation modelling (Section 8.3.4). Throughfall inputs to all the major overstory species were determined in plots 1 and 2 in 1993 and in 1994. In 1992 throughfall was collected only under Jeffrey/ponderosa pine in plots 1, 2 and 3.

Calculating total throughfall input was determined by extrapolating from deposition to the land area covered by the collector openings (using the average of all the replicate trees) to the land area covered by the drip areas of all the trees of that species. Throughfall solutions in the collectors were assumed to be representative of throughfall occurring under all the trees of that same species in the plot. Data from each rain event in a given season were totaled to obtain seasonal totals for throughfall inputs.

Rainfall inputs were calculated in a similar manner to throughfall: The content (concentration x volume) of each ion in the open collectors was determined and averaged. Rain deposition per land area was determined by extrapolation from deposition to the land area covered by the collector openings to the open area of the plot. The percent of the plot which was open or uncovered by canopy was determined by summing the total drip areas of all the trees in the plot and also from image analysis of aerial photographs as described in 7.2.1 above. Combining the value for rainfall deposition in the open with gross throughfall deposition under the canopy areas provides an estimate of total atmospheric deposition in the plot during the sampling period.

Volume-weighted ionic concentrations ($\mu\text{Eq L}^{-1}$) for a given season were calculated using standard weighted-average calculations. The basic formula was:

$$(V_1 \times C_1) + (V_2 \times C_2) + (V_3 \times C_3) / (V_1 + V_2 + V_3)$$

where V=rain or throughfall volume and C=ionic concentration in rain or throughfall. This was done for each of the rain events within the season for each collector to obtain a volume-weighted seasonal average ion

concentration for each collector. Average volume-weighted means were then determined for rain or for each tree species (throughfall) by averaging the values for the replicate rain collectors or throughfall collectors under pine, oak, or fir trees.

7.2.3 Statistical Analyses

Data analysis for comparing results between plots, species, and between rain and throughfall were performed using SigmaStat™ statistical software from Jandel Scientific Software (San Rafael, CA). Unless otherwise stated, differences between plots were considered statistically significant at $P \leq 0.05$. Differences in concentrations of ions in rain and throughfall were tested by one-way ANOVA and Bonferroni's all pairwise multiple comparison procedures. When the data failed the normality test, the Kruskal-Wallis one way analysis of variance on ranks test was used, followed by Dunn's all pairwise multiple comparison procedures (Fox et al., 1994). When only two plots or years were compared t-tests were used to determine significant differences. Differences between wet deposition chemistry at Tanbark Flat and BF were determined with ANOVA and a paired t-test. All statistical tests on pH of rainfall and throughfall were performed with the data expressed as hydrogen ion concentrations (H^+). Likewise, average pH values were determined from average H^+ concentrations.

7.3 Results

7.3.1 Volume-Weighted Throughfall and Rainfall Ionic Concentrations in 3 Plots

7.3.1.1 Rain and Throughfall Volume

Rainfall volumes were usually greater than throughfall volumes except under occasional conditions of persistent fog. Throughfall volumes were generally greatest under oak and pine canopies, and lowest under fir (Table 7-1). Average rainfall in the three plots during the summer throughfall collection periods was 9.37 cm in 1992, 5.94 cm in 1993 and 1.82 cm in 1994 (data for only plots 1 and 2 in 1994). In 1992, the year with the highest volume of summer rainfall, throughfall volumes under pine were significantly lower than rainfall volumes in all three plots (Table 7-1). In 1993, rain and throughfall volumes under pine and oak were not significantly different in plots 1 and 2, although in plot 3 pine throughfall volume was lower than for rainfall. In 1993 fir throughfall volumes were lower than for rain, oak or pine (Table 7-1). In 1994, the year with the lowest volume of summer rainfall, rainfall volumes were higher than fir, pine or oak throughfall volumes.

7.3.1.2 Comparisons of Rain and Throughfall Ionic Concentrations

In 1992 the concentration of all ions in rain were significantly lower than in pine throughfall (Figures 7-2 and 7-3). Similarly, in 1993 ionic concentrations in rainfall were lower than in pine throughfall, except in the case of Na^+ in plot 1, SO_4^{2-} in plot 2, and K^+ in all three plots (Figures 7-4 and 7-5). Concentrations in fir throughfall were always greater than in rainfall in plots 1 and 2 in 1993. Ionic concentrations in fir throughfall tended to be greater than in pine throughfall as well, although in about half the cases differences were not statistically significant (Figures 7-4 and 7-5). Throughfall concentrations for oak were less than for

fir in every case. Throughfall concentrations for oak were generally less than for pine although differences were not always statistically significant. Ion concentrations in rainfall and oak throughfall in 1993 were similar (Figures 7-4 and 7-5).

In 1994 ion concentrations in pine and fir throughfall were nearly always greater than in rainfall. Fir throughfall concentrations were not significantly greater than pine throughfall, although there was a pattern of higher absolute mean values for fir throughfall (Figure 7-6). Fir throughfall concentrations were greater than in oak, while only NH_4^+ concentrations in pine throughfall were greater than in oak throughfall. In oak throughfall, NH_4^+ and SO_4^{2-} concentrations were slightly greater than in rainfall (Figure 7-6).

Passage through pine canopies generally resulted in throughfall that was more acidic than precipitation (Table 7-2). Interaction with the oak canopy had no significant effect on throughfall pH (Table 7-1), and overall had less effect on throughfall chemistry than did contact with fir and pine canopies. The pH of fir throughfall was not significantly different than the pH of precipitation in plot 2, but fir throughfall was less acidic than precipitation in plot 1 (Table 7-2).

7.3.1.3 Plot Comparisons of Ionic Concentrations

Ionic concentrations in rain and pine throughfall in 1992 were nearly always higher in plot 1 compared to plots 2 and 3 (Table 7-3). However, in a few cases differences between plots were not statistically significant in rainfall because of variability between replicate samples and because only three replicate rain collectors were employed in each plot in 1992. Concentrations of most ions in pine and fir throughfall and in rain were at least two-fold higher in plot 1 than in plots 2 and 3 in 1993 (Table 7-4). However, in throughfall under oak in 1993, only NH_4^+ , Ca^+ , Mg^+ , and Na^+ concentrations were higher in plot 1 compared to plot 2. Concentration differences for rain between plot 1 and the other plots in 1993 were particularly pronounced for NO_3^- and NH_4^+ . Concentrations of NO_3^- , NH_4^+ , and SO_4^{2-} were also consistently higher in rain and throughfall in plot 1 than in plot 2 in 1994, although due to variability between replicate samples, differences were not statistically significant in 5 of 12 cases (Table 7-5).

The pH of rain and pine throughfall in 1992 were significantly more acidic in plot 1 than in plots 2 and 3. Rainfall acidity in 1993 was greater in plots 1 and 2 than in plot 3 (Table 7-2). In 1993, pine throughfall acidity was greatest in plot 1 and lowest in plot 3. Fir throughfall was more acidic in plot 2 than in plot 1, but oak throughfall pH was not significantly different in plots 1 and 2.

7.3.1.4 Year to Year Comparisons of Ionic Concentrations

The pH of rainfall and pine throughfall were significantly lower in 1992 than in 1993, except for throughfall in plot 2 and rainfall in plot 1 (Table 7-2). However, rainfall acidity in plot 1 in 1992 was nearly significantly higher ($p=0.15$), and differences between the two years may have been detected with greater replication (Only 3 replicate collectors for rain in the open areas were used per plot in 1992). Ion concentrations in rainfall differed little from year to year (Tables 7-6 and 7-7). Concentrations of NO_3^- in pine throughfall were higher in 1994 than in 1992 and 1993. Absolute values for NH_4^+ and SO_4^{2-} in pine

throughfall were higher in 1994 than in the previous years, but differences were not always significantly different (Table 7-6). Concentrations of NO_3^- , NH_4^+ , and SO_4^{2-} in fir and oak throughfall were consistently higher in 1994 than in 1993 in plots 1 and 2 (Table 7-6).

Chloride and major cations in rain and throughfall were only measured in 1992 and 1993. Potassium, calcium, and magnesium concentrations in pine throughfall were lower in 1993 than in 1992 in all three plots (Table 7-7). Sodium in pine throughfall was higher in 1993 than in 1992 in all three plots, while chloride concentrations did not differ between the two years.

7.3.2 Stand-Level Throughfall and Rainfall Deposition in 2 Plots

Summertime deposition of NO_3^- in 1993 was more than twice as high in plot 1 compared to plot 2. Ammonium deposition in summer 1993 was also approximately twice as great in plot 1 as in plot 2. Sulfate deposition was only slightly greater in plot 1 than plot 2 (Figure 7-7). Statistical analyses for determining differences between plots or years in total inputs (kg ha^{-1}) to each plot was not possible because of the manner in which inputs are calculated from throughfall data. Seasonal throughfall inputs in the plots are sums of inputs under pine, fir and oak and in rainfall. Statistical analyses comparing deposition to replicate collectors under each tree species and in the open areas (rain) are summarized below. Total N (NH_4^+ plus NO_3^-) deposition from rain and throughfall in plot 1 in summer 1993 was 5.7 kg ha^{-1} compared to 2.2 kg ha^{-1} in plot 2. Total S deposition in summer 1993 was 0.48 and 0.36 kg ha^{-1} in plots 1 and 2 respectively (Figure 7-7). Deposition of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- and PO_4^{3-} were also much greater in plot 1 than in plot 2 in 1993 (Figure 7-8). Good agreement was found between estimates of total N deposition to plot 2 from branch rinse data (Section 4.3.5) and throughfall data, although individual estimates for deposition to fir and oak varied considerably (Table 7-8).

In 1993 total throughfall deposition of NO_3^- (mg ion/collector) was greater in plot 1 than plot 2 for pine, oak and fir, while NH_4^+ and SO_4^{2-} deposition were only greater in plot 1 for pine and oak. In 1994 total throughfall deposition (mg ion/collector) of NO_3^- , NH_4^+ and SO_4^{2-} was not significantly different between plots 1 and 2 (Figure 7-7). Rainfall deposition also differed very little between plots 1 and 2 in either 1993 or 1994. Potassium, sodium, calcium, magnesium, chloride and phosphate deposition were only measured in 1993. Throughfall deposition of all of these ions under pine, oak and fir were significantly higher in plot 1 than in plot 2, while only deposition of K^+ in rainfall was significantly greater in plot 1 (Figure 7-8).

7.4 Discussion

The atmospheric deposition levels of N and S, and presumably of other nutrients at BF, are not expected to cause serious perturbations in nutrient cycling, according to our current understanding of N deposition effects on forest nutrient cycling (Dise and Wright, 1995; Fenn et al., 1995). However, cumulative long term effects cannot be ruled out. Recent studies in the San Bernardino and San Gabriel Mountains suggest that the threshold N deposition level at which N saturation effects are evident in these mixed conifer forests is approximately $25\text{-}35 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Fenn et al., 1995). A survey of 65 forested plots throughout Europe also indicated that above a N deposition threshold of $25 \text{ kg ha}^{-1} \text{ yr}^{-1}$ significant N saturation occurs as evidenced

by N leaching (Dise and Wright, 1995). The estimated summertime deposition levels at BF for 1993 and 1994 in plots 1 and 2 of 1.4-5.7 kg ha⁻¹ for N (NH₄⁺ + NO₃⁻) and 0.2-0.5 for S are within expected deposition levels at this site. Fenn and Bytnerowicz (1993) calculated annual wet and dry deposition inputs of 6.0 and 0.9 kg ha⁻¹ yr⁻¹ at Camp Osceola located approximately four km east of BF. Throughfall deposition of N has been widely reported to underestimate total deposition of N to forests due to canopy retention of approximately 20-35% of wet and dry deposited N (Cadle et al. 1991; Friedland et al. 1991; Hanson and Garten 1992; Johnson and Lindberg 1989; Lovett 1992; Marshall and Cadle 1989). Thus, summertime deposition of N at BF may be as much as 25% greater than the throughfall inputs shown in Figures 7-7 and 7-8. Throughfall S deposition on the other hand is much more representative measure of total atmospheric S deposition to forests (Joslin and Wolfe, 1992; Lindberg and Lovett, 1992).

Branch rinse estimates of N deposition to branch and foliar surfaces (Section 4.3.5) probably also underestimate N deposition. Branch rinse and throughfall deposition data for the summer polluted season agreed very well (Table 7-2). Total N deposition to plot 2 using the higher and probably more reliable leaf area index of 3.82 for the stand yielded an estimated annual N deposition of 7.6 kg ha⁻¹ yr⁻¹ (Table 4-11). Simulation modeling of N deposition at BF estimated an annual N deposition of 14.5 kg ha⁻¹ at BF (Section 8.3.4). Considering that throughfall deposition of N in plot 1 was ca. twice as high as plot 2, it seems that there is reasonable agreement between the simulation and branch rinse calculations, although the simulation results probably overestimate current N deposition at BF. There was also good agreement between the proportion of N to S deposition in rain and throughfall at BF and known deposition and atmospheric concentration levels of these pollutants in the South Coast Air Basin (Bytnerowicz et al., 1987; Fenn and Bytnerowicz, 1993).

Ionic concentrations in rain were generally within the range of values reported for highly polluted forest sites, except for NO₃⁻ which was several-fold higher in rain at BF in 1993 than the highest concentration reported for rain in a number of studies in Europe and eastern North America (Lindberg et al., 1990; Mitchell et al., 1992; Probst et al., 1990; Stevens et al., 1990). Ionic concentrations in throughfall at BF were many-fold greater than in polluted forests elsewhere (Lindberg et al., 1990; Mitchell et al., 1992; Probst et al., 1990; Stevens et al., 1990). Such high concentrations in rainfall, and more especially in throughfall, was an unexpected finding in this study, considering the low atmospheric inputs at BF compared to more western sites in the San Bernardino Mountains (SBM; Fenn and Bytnerowicz, 1993) and in other forests with chronic atmospheric deposition (Johnson and Lindberg, 1992). The high throughfall concentrations are apparently due to the washoff of accumulated dry pollutants from the forest canopy with low summer rain volumes (2.0-10.7 cm in the three plots in 1992-1994). The yearly distribution of rainfall at the BF monitoring station from November 1991 through December 1994 is shown in Figure 7-9. The high plant surface areas of the mature overstory trees above the throughfall collectors at BF also contributed to the high throughfall concentrations as a result of the accumulation of pollutants in the dry periods preceding summer rain events. That the amount of surface area above the collectors had a major influence on throughfall concentrations is further evidenced by the observation that ionic concentrations were highest under white fir, the species with the largest foliar surface area (Section 4.3).

In contrast to BF, annual N deposition in throughfall to forests in south-central Ontario Canada was over

twice as high as at BF, yet maximum NO_3^- and NH_4^+ concentrations in throughfall over a three year period were $< 90 \mu\text{Eq L}^{-1}$ (Neary and Gizyn, 1994) compared to several thousand $\mu\text{Eq L}^{-1}$ of NO_3^- and NH_4^+ at BF in 1994 when summer precipitation was lowest. In the Canadian forests annual precipitation varied little from year to year, was greater than 100 cm each year, and was evenly distributed between the dormant season and the growing season (Neary and Gizyn, 1994). Throughfall deposition under these eastern conditions consists of greater overall deposition than at BF, but solutes are transported to the forest floor in large volumes as more dilute solutions compared to throughfall fluxes in the SBM. However, annual throughfall N deposition in the more western sites in the San Bernardino Mountains is likely as great as in many polluted forests in the northern hemisphere. Annual throughfall N deposition and precipitation in a white spruce forest in southwest Alberta, Canada were similar to BF, although summer precipitation was probably much greater at the Canadian site (Blew et al., 1993). Maximum NO_3^- and NH_4^+ concentrations in throughfall in the spruce forest were 24 and 101 $\mu\text{Eq L}^{-1}$. Throughfall concentrations were presumably lower than at BF due to greater summer rainfall volumes in the Canadian spruce forest, although annual precipitation distribution data is not given in Blew et al. (1993).

Because of the high ionic concentrations in throughfall and infrequent summer rains at BF, throughfall inputs to the forest floor during the growing season are typically characterized by infrequent pulses of highly concentrated nutrient solutions. The importance of these pulses in providing nutrients to vegetation in the current growing season will depend on the volume of rain and the extent to which the solution is able to penetrate through the canopy into the forest floor and into the rooting zone. The thickness of litter layers and microbial immobilization of throughfall nutrients will also have a major effect on how readily available the wet-deposited nutrients are for plant utilization. Except for the few larger-volume summer rain events which occur only in some years, throughfall in summer is not likely to provide a major nutrient source via root uptake for overstory tree species. However, a minor fraction of the nutrients retained by the canopy are likely taken up directly (Fenn and Leininger, 1995) and shallow roots probably also periodically utilize wet-deposited nutrients following summer rain events of sufficient magnitude to infiltrate the upper rooting zone.

Presumably, throughfall volumes were lowest and throughfall concentrations highest under fir due to the high leaf surface area above the collectors placed under fir canopies (see section 4.3.1). Higher foliage surface area results in higher canopy interception and retention of water from rain and of dry-deposited gases and particles. The oak collectors have the lowest leaf surface area above the collectors due to the relatively low leaf area of oak compared to fir, and because oak foliage is distributed over a wider area due to the canopy architecture of California black oak. The much lower ionic concentrations and higher volumes of oak throughfall reflect the reduced contact precipitation had with the oak canopy compared to the fir canopy.

It is not readily apparent why ionic concentrations in rain and throughfall were generally much higher in plot 1 compared to plots 2 and 3. The greater concentrations in throughfall and rain may be in part due to the closer location of plot 1 to the main highway (highway 38) and proximity to private cabins, and because of a more open exposure to incoming air masses from urban centers to the west (Figure 6-1a). Plot 1 (1976 m) is also located at a lower elevation than plot 2 (2164 m) and plot 3 (2200 m; Figure 6-1a). The lower elevation may have also resulted in exposure to higher pollutant concentrations. In 1992, the summer with the greatest precipitation, rainfall in plot 1 was only 75-85% as great as in plots 2 and 3, suggesting that lower rainfall

may have had an additional effect on the higher throughfall concentrations, due to lower dilution effects. However, in 1993 and 1994 rainfall volume in plot 1 was 96-97% as great as in plots 2 and 3. Local dust is another possible source of greater ionic concentrations in plot 1, although this would not seem to be a major source since even rainfall concentrations were greatest in plot 1. Dust would be expected to affect throughfall concentrations to a much greater extent than rainfall due to dust accumulation on canopy surfaces.

Additional evidence as to the most likely sources of higher deposition in plot 1 can be obtained by comparing the various ions between the plots. For example K^+ concentrations in rain and throughfall of fir were roughly three times greater in plot 1 than in plots 2 and 3. Chorover et al., (1994) also reported that canopy leaching in throughfall of Ca^{2+} and more especially of K^+ was much greater than for other ions in white-fir dominated forests in Sequoia National Park. The concentration of K^+ in pine throughfall was nearly 17 times greater in plot 1 compared to plot 2. Potassium is known to be highly leachable from foliage (Parker, 1983; Tukey, 1970), and internal pine tissue seems the likely source of the greater K^+ in plot 1. Although speculative, these results suggest that pine foliage, and possibly fir foliage, in plot 1 were more severely predisposed to leaching than foliage in plots 2 and 3. Leachability of foliage could have been affected by exposure to oxidant air pollution and acidic deposition, although the foliar injury may not necessarily have been visible. However, throughfall and branch rinse K^+ data from plots 1-3 were highly variable (Section 5.4), probably due to erratic leaching rates as a result of heterogenous canopy structures and foliar injury and senescence.

The all-sided leaf area index (LAI) in plot 1, based on indirect optical estimates of LAI, was 6% higher than plot 3 and 55% higher than plot 2. Greater foliage area for accumulation of pollutants and greater ion leaching may have also contributed to the greater throughfall deposition in plot 1, but doesn't appear to be the major factor since ionic concentrations in rainfall were also greater in plot 1. In summary, it is uncertain why ionic concentrations and deposition in rain and especially in throughfall were greater in plot 1 compared to plots 2 and 3, but possible sources include: lower elevation and greater exposure to incoming polluted air masses, closer location to the main highway, dirt roads and cabins, dust from human activities and wind, greater foliar leaching (possibly related to foliar stresses and injury), lower precipitation volumes, and greater foliar surface area in plot 1.

7.5 Summary

Throughfall inputs of plant nutrients (especially N) are enriched due to the accumulation of dry pollutants on plant canopy surfaces. Summertime throughfall inputs likely provide a pulse of nutrients for limited direct canopy uptake and for root uptake when rain volumes are sufficient to transport nutrients into the rooting zone in the forest floor and soil. However, atmospheric deposition of N, S and other nutrients at BF are below the levels believed to cause serious short-term perturbations in plant nutrient relations or of nutrient cycling processes in temperate forests. Ionic concentrations in throughfall at BF were higher than typically reported for even highly-polluted forests in Europe and eastern North America because of the accumulation of dry deposition on the extensive canopies of large trees followed by washoff in low-volume rain events. Throughfall concentrations were generally highest under white fir, the species with the greatest foliar surface area and lowest under black oak. Washoff of NO_3^- and NH_4^+ from the canopy led to very high

concentrations of these ions, while foliar leaching appears to have been important in causing high concentrations of K^+ and Ca^{2+} in throughfall. Concentrations of other cations and of Cl^- in throughfall were also high relative to rainfall concentrations. The acidity of rainfall ranged from 4.21-4.79 while throughfall acidity ranged from 4.01-4.66. Throughfall acidity was apparently buffered by high cation concentrations. Oak throughfall was not acidified compared to rainfall, and was less modified chemically than was throughfall of pine and fir.

7.6 References

- Blew, R.D.; Iredale, D.R.; Parkinson, D. 1993. Throughfall nitrogen in a white spruce forest in southwest Alberta, Canada. *Canadian Journal of Forest Research* 23:2389-2394.
- Bytnerowicz, A.; Miller, P.R.; Olszyk, D.M.; Dawson, P.J.; Fox, C.A. 1987. Gaseous and particulate air pollution in the San Gabriel Mountains of southern California. *Atmospheric Environment* 21:1805-1814.
- Cadle, S.H.; Marshall, J.D.; Mulawa, P.A. 1991. A laboratory investigation of the routes of HNO₃ dry deposition to coniferous seedlings. *Environmental Pollution* 72:287-305.
- Chorover, J.; Vitousek, P.M.; Everson, D.A.; Esperanza, A.M.; Turner, D. 1994. Soil solution chemistry profiles of mixed-conifer forests before and after fire. *Biogeochemistry* 26:115-144.
- Dise, N.B.; Wright, R.F. 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management* 71:153-161.
- Fenn, M.E.; Leininger, T.D. 1995. Uptake and distribution of nitrogen from acidic fog within a ponderosa pine (*Pinus ponderosa* Laws)/litter/soil system. *Forest Science* 41:645-663.
- Fenn, M.E.; Poth, M.A.; Johnson, D.W. 1995. Evidence for nitrogen saturation in the San Bernardino Mountains in southern California. *Forest Ecology and Management* 76:(In Press).
- Fenn, M.E.; Bytnerowicz, A. 1993. Dry deposition of nitrogen and sulfur to ponderosa and Jeffrey pine in the San Bernardino National Forest in southern California. *Environmental Pollution* 81:277-285.
- Fox, E.; Kuo, J.; Tilling, L.; Ulrich, C. 1994. SigmaStat™ for Windows User's Manual, Revision SSW 1.0. Jandel Scientific, San Rafael, California.
- Friedland, A.J.; Miller, E.K.; Battles, J.J.; Thorne, J.F. 1991. Nitrogen deposition, distribution and cycling in a subalpine spruce-fir forest in the Adirondacks, New York, USA. *Biogeochemistry* 14:31-55.
- Glaubig, R.; Gomez, A. 1994. A simple, inexpensive rain and canopy throughfall collector. *Journal of Environmental Quality* 23:1103-1107.
- Hanson, P.J.; Garten, C.T. Jr. 1992. Deposition of H¹⁵NO₃ vapour to white oak, red maple and loblolly pine foliage: experimental observations and a generalized model. *New Phytologist* 122: 329-337.
- Johnson, D.W.; Lindberg, S.E. 1992. Atmospheric Deposition and Forest Nutrient Cycling. *Ecological Studies* 91, Springer-Verlag, New York.
- Johnson, D.W.; Lindberg, S.E. 1989. Acidic deposition on Walker Branch Watershed. *In Acidic*

precipitation, vol. 1. Case Studies, (Eds.) D.C. Adriano and M. Havas, Springer-Verlag, New York. pp. 1-38.

Joslin, J.D.; Wolfe, M.H. 1992. Tests of the use of net throughfall sulfate to estimate dry and occult sulfur deposition. *Atmospheric Environment* 26:63-72.

Lindberg, S.E.; Lovett, G.M. 1992. Deposition and forest canopy interactions of airborne sulfur - Results from the Integrated Forest Study. *Atmospheric Environment* 26:1477-1492.

Lindberg, S.E.; Bredemeier, M.; Schaefer, D.A.; Qi, L. 1990. Atmospheric concentrations and deposition of nitrogen and major ions in conifer forests in the United States and Federal Republic of Germany. *Atmospheric Environment* 24A:2207-2220.

Lovett, G.M.; Lindberg, S.E. 1993. Atmospheric deposition and canopy interactions of nitrogen in forests. *Canadian Journal of Forest Research* 23:1603-1616.

Lovett, G.M. 1992. Atmospheric deposition and canopy interactions of nitrogen. *In* *Atmospheric deposition and forest nutrient cycling*. (Eds.) D.W. Johnson and S.E. Lindberg. Springer-Verlag, New York. pp. 152-166.

Marshall, J.D.; Cadle, S.H. 1989. Evidence for trans-cuticular uptake of HNO₃ vapor by foliage of eastern white pine (*Pinus strobus* L.). *Environmental Pollution* 60: 15-28.

Mitchell, M.J.; Burke, M.K.; Shepard, J.P. 1992. Seasonal and spatial patterns of S, Ca, and N dynamics of a northern hardwood forest ecosystem. *Biogeochemistry* 17:165-189.

Neary, A.J.; Gizyn, W.I. 1994. Throughfall and stemflow chemistry under deciduous and coniferous forest canopies in south-central Ontario. *Canadian Journal of Forest Research* 24:1089-1100.

Parker, G.G. 1983. Throughfall and stemflow in the forest nutrient cycle. *Advances in Ecological Research* 13:57-133.

Probst, A.; Dambrine, E.; Viville, D.; Fritz, B. 1990. Influence of acid atmospheric inputs on surface water chemistry and mineral fluxes in a declining spruce stand within a small granitic catchment (Vosges Massif, France). *Journal of Hydrology* 116:101-124.

Stevens, P.A.; Adamson, J.K.; Reynolds, B.; Hornung, M. 1990. Dissolved inorganic nitrogen concentrations and fluxes in three British sitka spruce plantations. *Plant and Soil* 128:103-108.

Tukey, H.B. Jr. 1970. The leaching of substances from plants. *Annual Review of Plant Physiology* 21:305-324.

Table 7-1. Total summertime rain and throughfall volumes (cm precipitation) in three plots at Barton Flats. Letters next to numbers indicate significant differences between rain and throughfall within a given plot/year combination (across the row). Values in parentheses are standard errors of the plot mean.

Plot	Year	Rain	Throughfall		
			Fir	Pine	Oak
1	1992	7.96 a (0.39)	---	4.15 b (0.34)	---
2	1992	9.45 a (0.35)	---	5.72 b (0.23)	---
3	1992	10.70 a (0.58)	---	5.47 b (0.28)	---
1	1993	5.66 a (0.19)	3.83 b (0.49)	5.40 a (0.26)	6.11 a (0.42)
2	1993	5.78 a (0.47)	4.09 b (0.42)	5.23 a (0.16)	5.14 a (0.23)
3	1993	6.37 a (0.25)	--	4.88 b (0.20)	--
1	1994	1.64 a (0.15)	0.13 c (0.03)	0.27 bc (0.05)	0.45 b (0.06)
2	1994	1.99 a (0.05)	0.26 c (0.04)	0.48 b (0.05)	0.58 b (0.09)

Table 7-2. Throughfall and rainfall pH in three plots in 1992 and 1993. Letters next to numbers indicate significant differences between rain and throughfall within a given plot/year combination (across the row).

Plot	Year	Rain	Throughfall		
			Fir	Pine	Oak
1	1992	4.21 a	--	4.01 b	--
2	1992	4.33 a	--	4.19 a	--
3	1992	4.32 a	--	4.15 a	--
1	1993	4.40 b	4.66 c	4.13 a	4.62 bc
2	1993	4.60 b	4.29 ab	4.24 a	4.56 b
3	1993	4.79 b	--	4.36 a	--

Table 7-3. Plot to plot comparisons of cat ion and anion concentrations ($\mu\text{Eq L}^{-1}$) in rain and throughfall in 1992. Letters

next to numbers indicate significant differences between plots for a given ion (down the column).

Plot	NO_3^-	NH_4^+	SO_4^{2-}	K^+	Ca^{2+}	Mg^{2+}	Na^+	Cl^-
RAIN								
1	96 a	88 a	30 a	24 a	64 a	24 a	18 a	20 a
2	48 a	22 b	19 b	16 a	29 b	8 b	7 b	18 a
3	37 a	12 c	14 c	15 a	28 b	6 b	7 b	14 a
PINE THROUGHFALL								
1	1090 a	688 a	58 a	231 ab	454 a	154 a	81 a	132 a
2	378 b	231 b	27 b	174 b	195 b	78 b	34 b	71 b
3	413 b	229 b	29 b	233 a	196 b	86 b	42 b	90 ab

Table 7-4. Plot to plot comparisons of cat ion and anion concentrations ($\mu\text{Eq L}^{-1}$) in rain and throughfall in 1993. Letters

next to numbers indicate significant differences between plots for a given ion (down the column).

Plot	NO_3^-	NH_4^+	SO_4^{2-}	K^+	Ca^{2+}	Mg^{2+}	Na^+	Cl^-
RAIN								
1	286 a	147 a	24 a	53 a	85 a	27 a	58 a	56 a
2	47 b	13 b	12 b	14 b	23 b	12 b	26 b	20 b
3	39 b	13 b	11 b	16 b	23 b	7 b	32 b	30 b
PINE THROUGHFALL								
1	896 a	455 a	37 a	20 a	229 a	93 a	115 a	155 a
2	362 b	187 b	21 b	9 b	114 b	42 b	65 b	73 b
3	443 b	229 b	24 b	14 b	128 b	50 b	93 a	94 b
OAK THROUGHFALL								
1	282 a	82 a	17 a	6 a	139 a	61 a	43 a	59 a
2	208 a	39 b	19 a	9 a	102 b	40 b	35 b	45 a
FIR THROUGHFALL								
1	1575 a	395 a	76 a	971 a	487 a	304 a	182 a	309 a
2	622 b	182 a	50 b	329 b	244 b	118 b	94 b	135 b

Table 7-5. Plot to plot comparisons of NO_3^- , NH_4^+ and SO_4^{2-} concentrations ($\mu\text{Eq L}^{-1}$) in rain and throughfall in 1994. Letters

next to numbers indicate significant differences between plots for a given ion (down the column).

Plot	NO_3^-	NH_4^+	SO_4^{2-}
RAIN			
1	149 a	69 a	20 a
2	84 a	20 b	17 a
PINE THROUGHFALL			
1	2733 a	1479 a	104 a
2	1061 b	579 b	42 b
OAK THROUGHFALL			
1	991 a	259 a	65 a
2	465 b	132 b	34 a
FIR THROUGHFALL			
1	6868 a	1983 a	358 a
2	2856 a	469 a	122 b

Table 7-6. Yearly comparisons (1992-1994) of NO_3^- , NH_4^+ and SO_4^{2-} and concentrations ($\mu\text{Eq L}^{-1}$) in rain and throughfall. Letters next to numbers indicate significant differences between years within a given plot/ion combination (down the column).

	Plot 1				Plot 2		
Year	NO_3^-	NH_4^+	SO_4^{2-}		NO_3^-	NH_4^+	SO_4^{2-}
RAIN							
1992	96 a	88 a	30 a		48 a	22 a	19 b
1993	286 a	147 a	24 a		47 a	13 a	12 a
1994	149 a	20 a	69 a		84 b	20 a	17 b
PINE THROUGHFALL							
1992	1090 a	688 ab	58 b		378 a	231 bc	27 b
1993	896 a	455 a	37 a		362 a	187 ac	21 a
1994	2733 b	1479 b	104 b		1061 b	579 b	42 b
OAK THROUGHFALL							
1993	282 a	82 a	17 a		208 a	39 a	19 a
1994	991 b	259 b	65 b		465 b	132 b	34 b
FIR THROUGHFALL							
1993	1575 a	395 a	76 a		622 a	182 a	50 a
1994	6868 b	1983 b	358 b		2856 b	469 b	122 b

Table 7-7. Yearly (1992-1994) comparisons of K^+ , Ca^{2+} , Mg^{2+} , Na^+ and Cl^- concentrations ($\mu Eq L^{-1}$) in rain and pine throughfall. Letters next to numbers indicate significant differences between years within a given plot/ion combination (down the column).

Plot	Year	K^+	Ca^{2+}	Mg^{2+}	Na^+	Cl^-
RAIN						
1	1992	24 a	64 a	24 a	18 a	20 a
1	1993	53 a	85 a	27 a	58 a	56 a
2	1992	16 a	29 a	8 a	7 a	18 a
2	1993	14 a	23 a	12 a	26 b	20 a
3	1992	15 a	28 a	6 a	7 a	14 a
3	1993	16 a	23 a	7 a	32 a	30 b
PINE THROUGHFALL						
1	1992	231 a	454 a	154 a	81 a	132 a
1	1993	20 b	229 b	93 b	115 b	155 a
2	1992	174 a	195 a	78 a	34 a	71 a
2	1993	9 b	114 b	42 b	65 b	73 a
3	1992	233 a	196 a	86 a	42 a	90 a
3	1993	14 b	128 b	50 b	93 b	94 a

Table 7-8. Comparison of summertime inorganic N ($\text{NO}_3^- + \text{NH}_4^+$) deposition (kg ha^{-1}) in plot 2 based on branch rinse[§] and throughfall data.

Species or Parameter	Branch Rinses	Throughfall
Fir	0.56	1.10
Oak	1.59	0.45
Pine	0.62	0.51
Rain [¶]	0.53	0.53
Total	3.30	2.59

[§]Branch rinse data is from section 4.3.5.

[¶]Rain deposition data are from flip-top rain collectors located in open areas of the plot. Rain data represents deposition to the open areas of the plot only.

Figure 7-1. Scanned image of Plot 2 obtained from an aerial photograph. The T-shaped markers at each end of the plot are 40ft X 40ft. Arrow locates the 94ft tower.

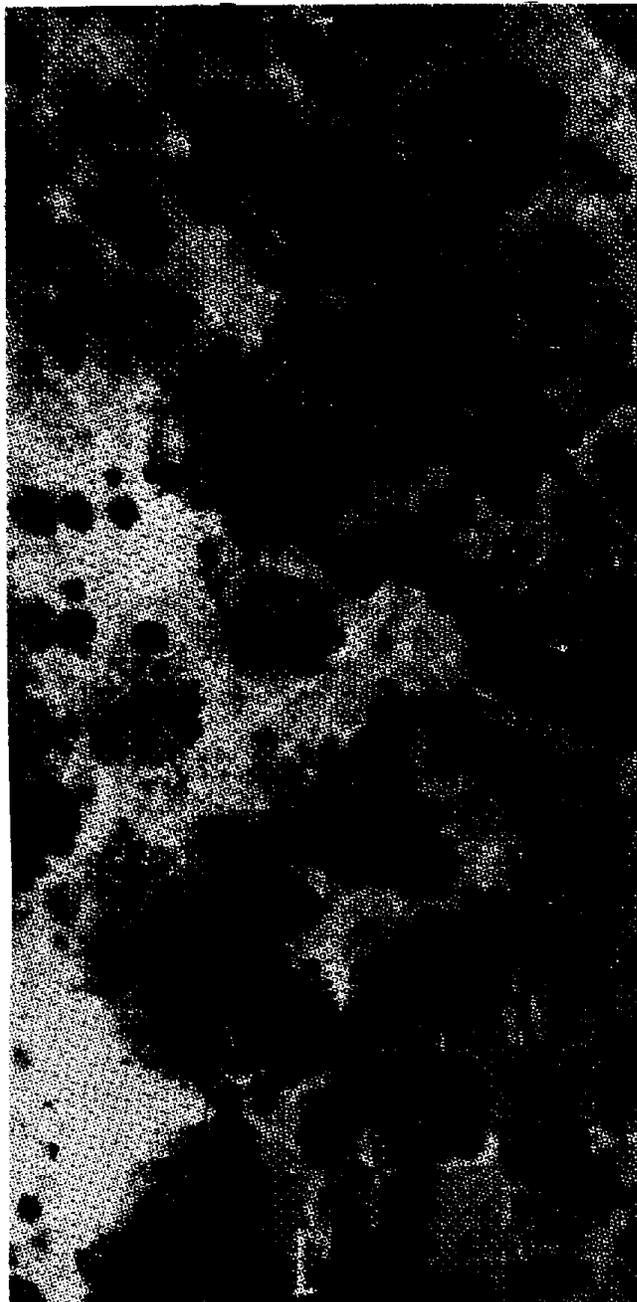


Figure 7-2. Ionic concentrations of SO_4^{2-} , NH_4^+ , and NO_3^- in rain and throughfall under pine canopies in 1992. In every case ion concentrations in throughfall were significantly greater than in rain.

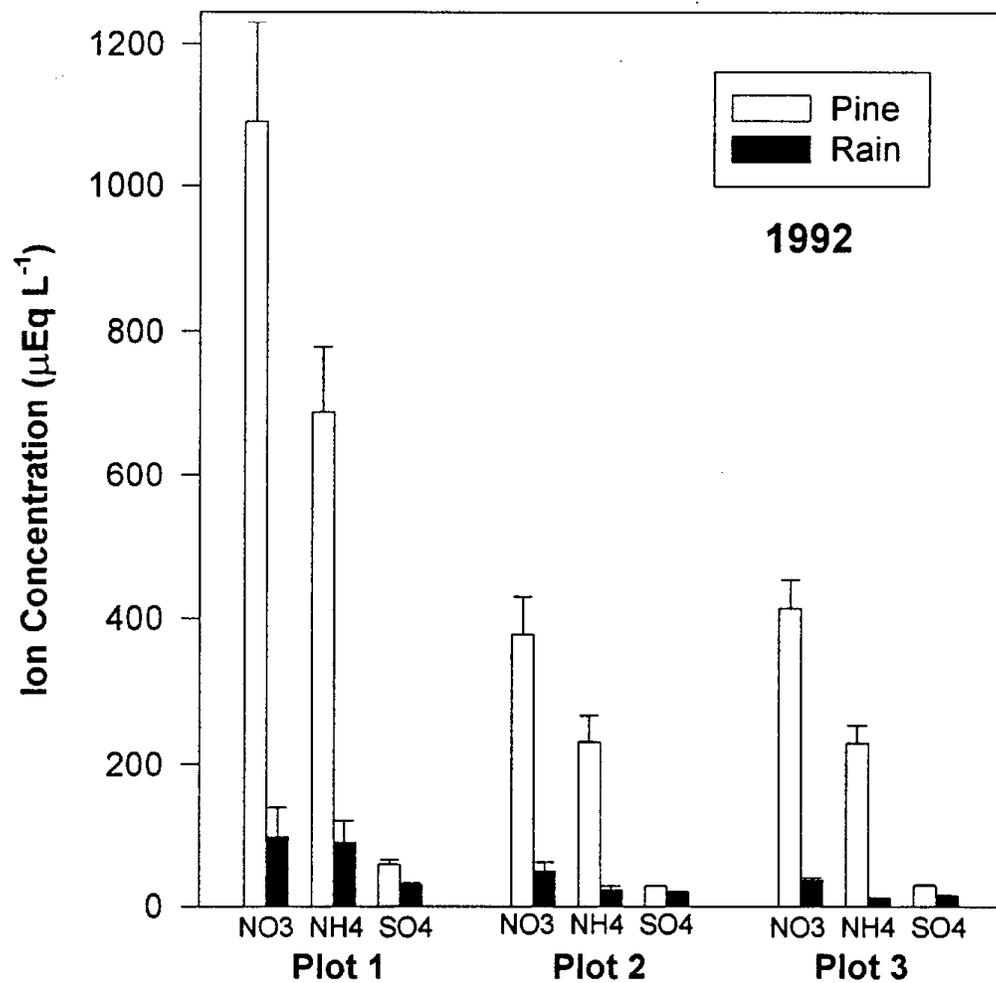


Figure 7-3. Ionic concentrations of Cl^- , Ca^{2+} , Mg^{2+} , Na^+ and K^+ in rain and throughfall under pine canopies in 1992. In every case ion concentrations in throughfall were significantly greater than in rain.

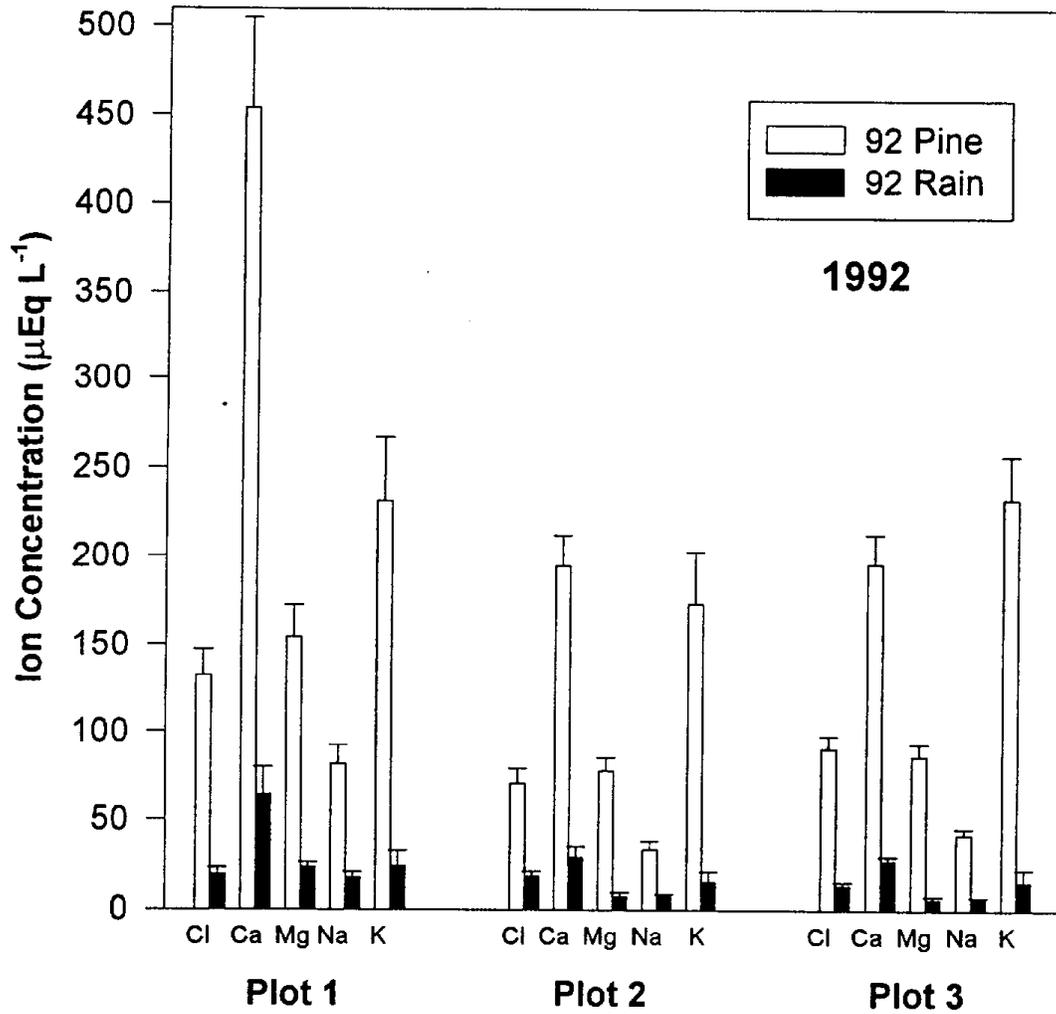


Figure 7-4. Ionic concentrations in rain and throughfall under fir, pine and oak canopies in 1993. Letters above the bars represent significant differences between rain and throughfall of the three species for a given ion.

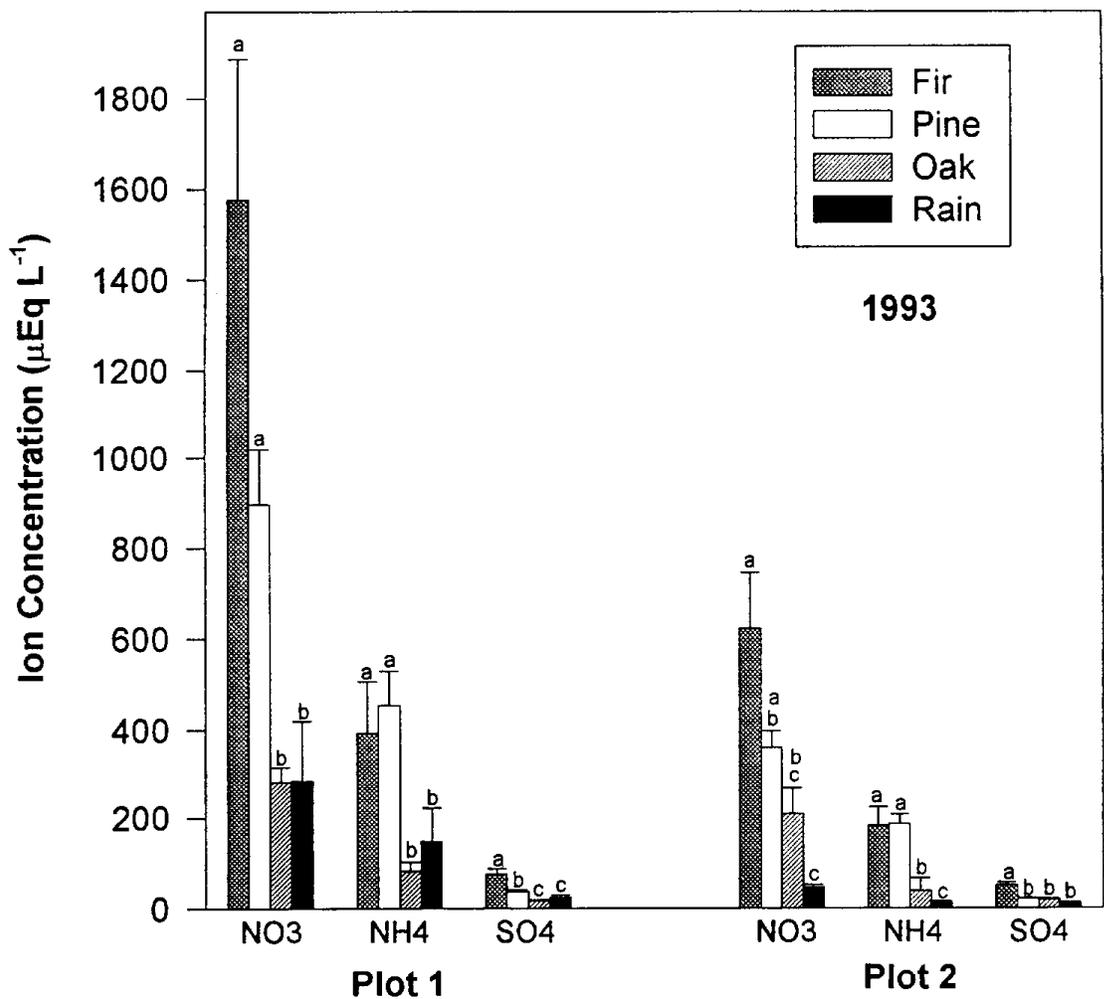


Figure 7-5. Ionic concentrations of Cl^- , Ca^{++} , Mg^{++} , Na^+ and K^+ in rain and throughfall under fir, pine and oak canopies in 1993.

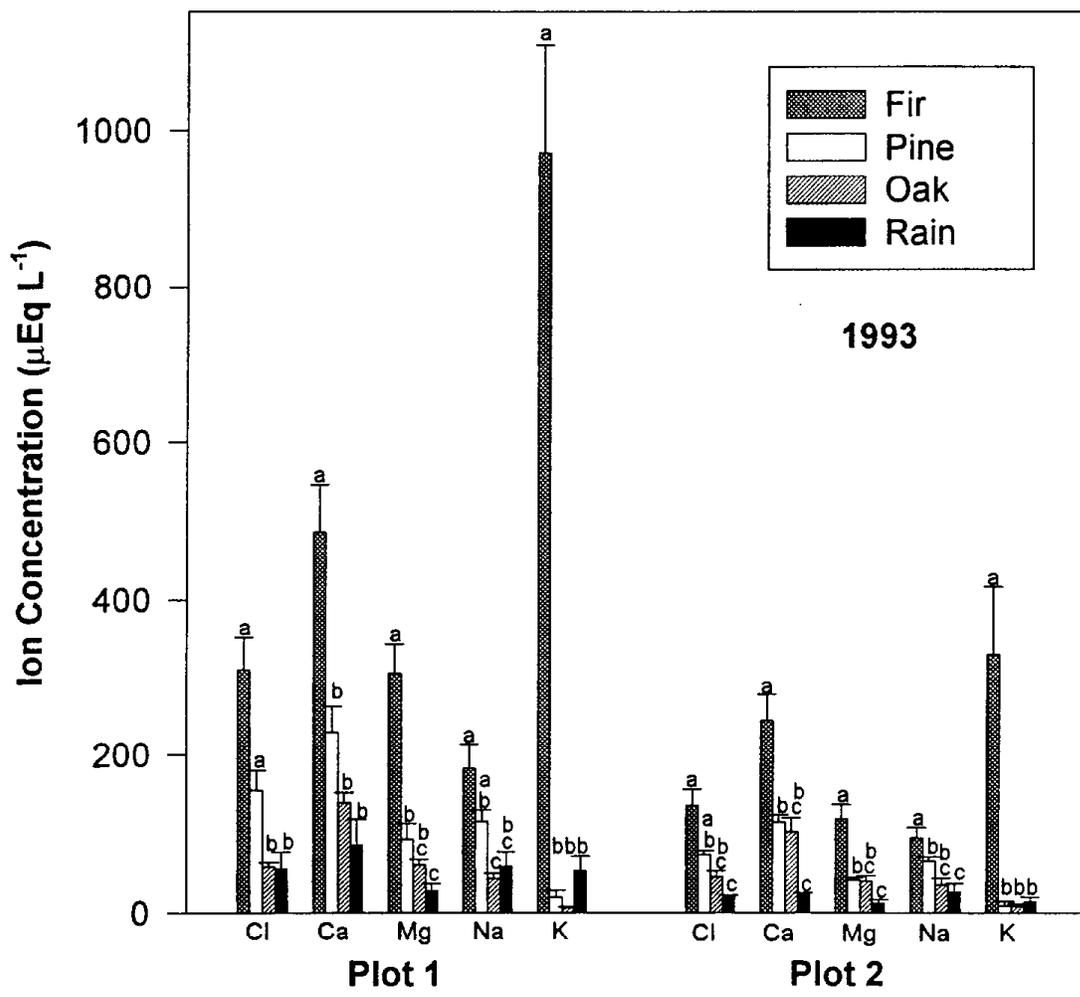


Figure 7-6. Ionic concentrations of SO_4^{2-} , NH_4^+ and NO_3^- in rain and throughfall under fir, pine and oak canopies at Plots 2 and 3 in 1994.

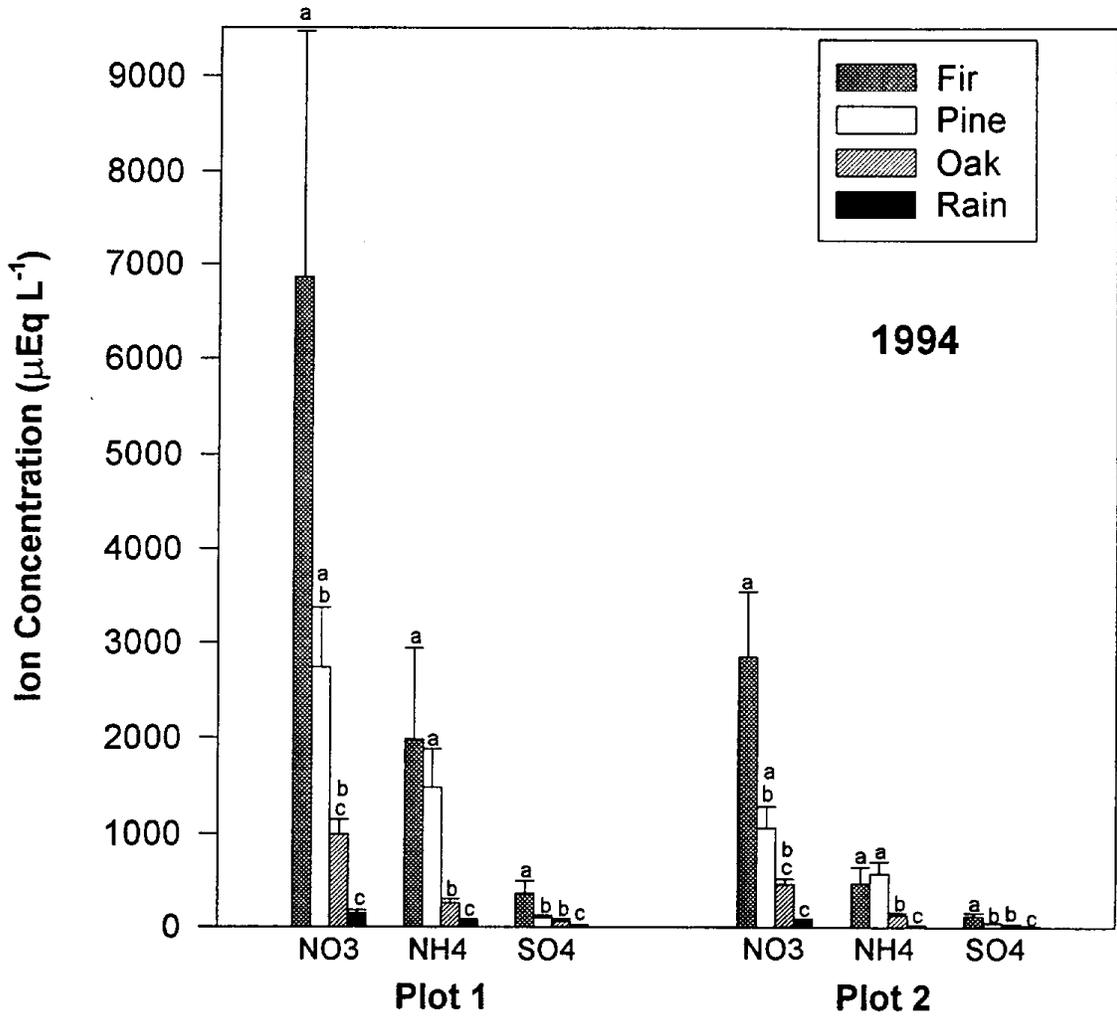


Figure 7-7. Ionic deposition of SO_4^{2-} , NH_4^+ and NO_3^- to the forest canopy at Barton Flats plots 1 and 2 during the summer of 1993 and 1994. Values represent the total of rain and throughfall deposition.

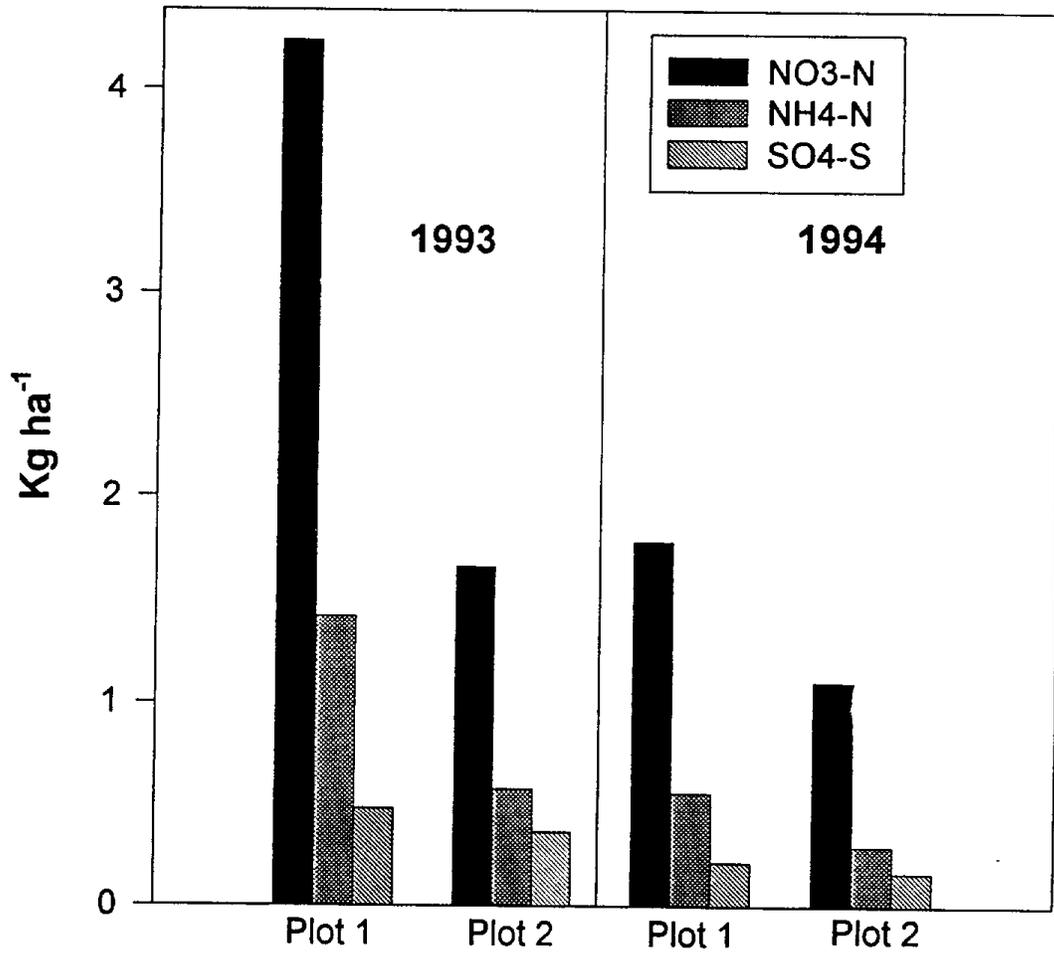


Figure 7-8. Summer 1993 ionic deposition of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- and PO_4^{3-} to the forest canopy in plots 1 and 2 at Barton Flats. Values represent the total of rain and throughfall deposition.

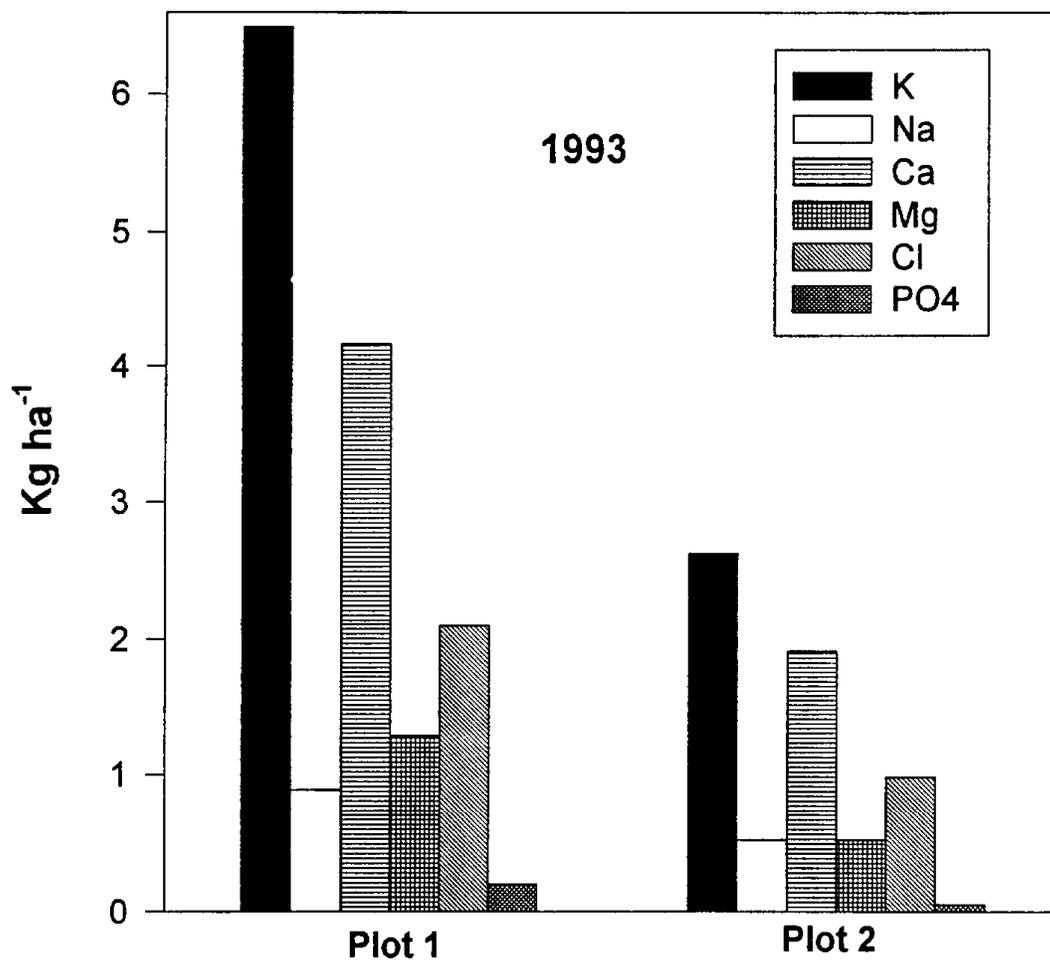
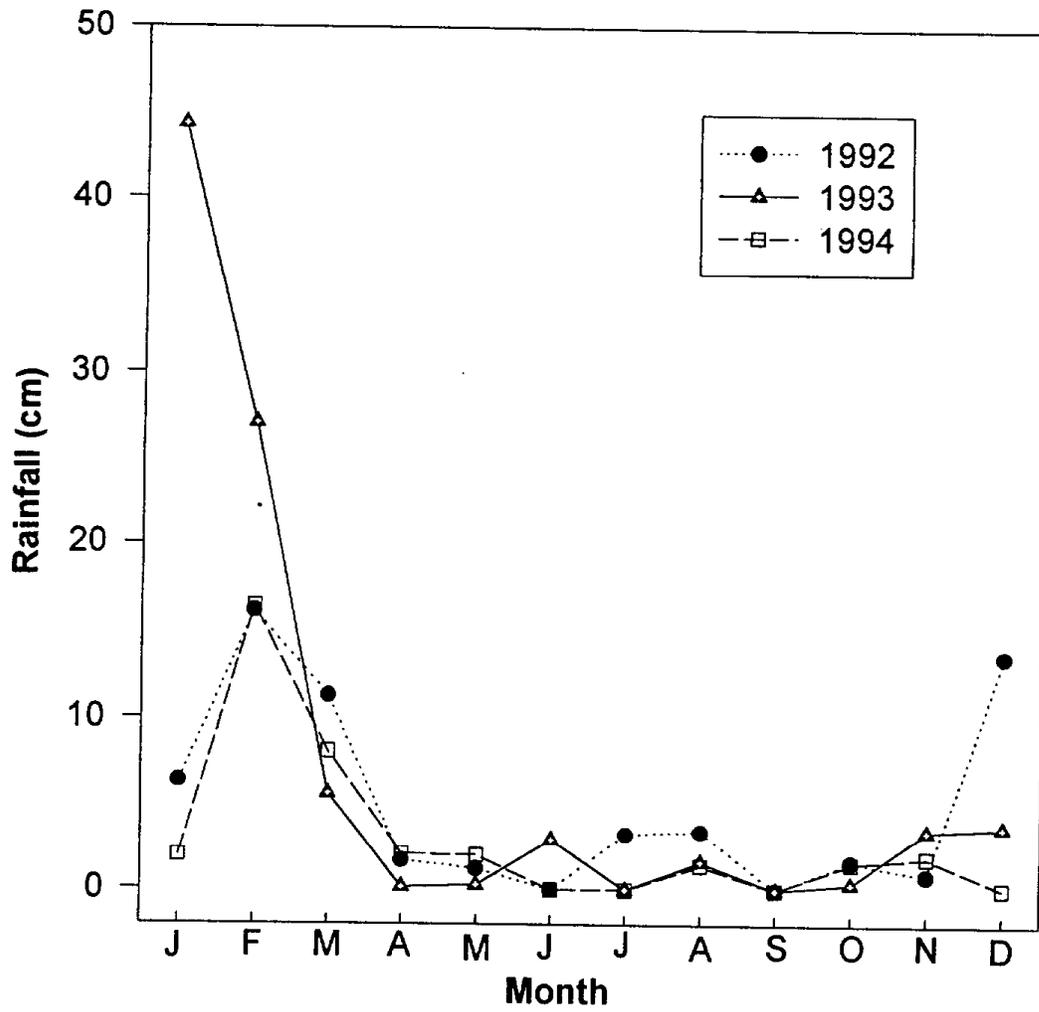


Figure 7-9. Precipitation totals by month at the Barton Flats monitoring station.



8.0 MODELLING DRY DEPOSITION OF NITROGEN, SULFUR AND OZONE TO THE FOREST STAND AT BARTON FLATS

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8.1 Introduction

Atmospheric deposition is the process by which chemicals in the atmosphere are transferred to the earth's surface. In the context of the study at Barton Flats, deposition is restricted to wet and dry deposition to the forested landscape (with landscape defined as the sum of all deposition to all components of the forest including foliage, bark, and litter surfaces). The wet deposition component is solely that which is deposited via rain and snow. Dry deposition includes the transfer of gases and particles to the forest canopy (Lovett, 1994).

The methodologies for estimating atmospheric inputs via dry deposition in mountainous, forested landscapes are limited and differ from those that have been developed in more agricultural settings. The first methodology is one of throughfall or leaf washing analysis, which measures the residue of elements and chemicals that are deposited to forest foliage and is subsequently washed off, either through natural rainfall or via artificial leaf washings (Bytnerowicz *et al.*, 1987; Fenn and Bytnerowicz, 1993; Sections 4.0 and 5.0). The second involves the parameterization of a model to estimate dry deposition of gases and particles and the subsequent "running" of the model to estimate deposition at multiple spatial and temporal scales.

The study at Barton Flats was designed to estimate dry deposition of particles and gases using the Big Leaf model (Baldocchi *et al.*, 1987). The design required the integration of site-specific data from the atmospheric science's studies (Section 2.0) with physiological and ecological data from the plant science's community (Sections 1.0 and 11.0). The emphasis was on estimating the deposition of the chemicals and compounds of greatest concern from an ecological and physiological perspective. Accordingly, the data are summarized with respect to the chemicals that contribute to the dry deposition of nitrogen (nitrogen dioxide, NO₂; ammonia, NH₃; nitric acid vapor, HNO₃), sulfur (sulfur dioxide, SO₂), and ozone (O₃). Particle deposition was not included since it contributed $\leq 10\%$ for either S or N.

The objectives of the study were the following:

- parameterize the Big Leaf Model to simulate the exchange of gases for the Barton Flats forest site;
- simulate the dry deposition of gases to the forest canopy at Barton Flats on multiple time scales;
- summarize the dry deposition data for total nitrogen (N), sulfur (S) and ozone (O₃) deposited from multiple chemical forms;
- compare the importance of deposition via wet and dry processes for N and S inputs to the forested landscape at Barton Flats; and
- address the uncertainties in the estimate of dry deposition.

8.2 Methods

The methodology for estimating dry deposition using the Big Leaf Model has been documented in a general sense in a variety of forums (Baldochi *et al.*, 1987; Johnson and Lindberg, 1992). The specific application to the Barton Flats' site is presented in Taylor *et al.* (1994). Figure 8-1 is a schematic of the model, showing the pathways and series of resistance that govern the flux of materials from the atmosphere to sites of deposition on or within the plant canopy.

The essential features of the simulation procedure are straight forward and require two sets of data. The first is the hourly chemistry data on the composition of the air mass at the Barton Flat's site (Section 2.0). These data are in either volumetric (ppbv) or gravimetric ($\mu\text{g}/\text{m}^3$) units. The second data set are model simulations of the deposition velocity (V_g ; cm/s) of specific chemicals in the atmosphere on an hourly time step. These data are products of the Big Leaf model. The estimate of deposition is the product of concentration ($\mu\text{g}/\text{m}^3$) and V_g (cm/s), normalized to gravimetric ($\mu\text{g}/\text{m}^2/\text{h}$) or molar ($\mu\text{mol}/\text{m}^2/\text{h}$) units. The data are summed by canopy type (*Pinus ponderosa*, Ponderosa Pine; *Abies concolor*, White Fir; and *Quercus kelloggii*, Black Oak) over the diurnal period, and aggregated across the three canopies for increasing temporal scales (days, months and year) at the landscape level. The summary analysis for N and S focuses on the units of kg N or S/ha/y.

The only distinction in this analysis procedure is that for O_3 . The interest in O_3 is physiologically based, so that the key features are O_3 uptake per unit of projected leaf area per hour. Accordingly, the units of O_3 deposition are $\mu\text{moles}/\text{m}^2/\text{h}$, and the area component is solely for the respective forest species that comprise the canopy.

8.3 Results

The results are presented in series for O_3 (8.3.1), the major N-containing pollutants (8.3.2), including NO_2 (8.3.2.1), HNO_3 (8.3.2.2) and NH_3 (8.3.2.3), and the sole S-containing (8.3.3) pollutant SO_2 (8.3.3.1). Within each series, the data demonstrate the periodicity of the deposition processes over time (time steps of 24 h during the growing season and month).

A summary of the concentration data for each of the major S- and N-containing gases is shown in Figure 8-2. The figure highlights the patterns in concentration as a function of the season (growing versus dormant season) and time of day (day versus night). These distinctions are important with respect to the receptor, which is the foliage within the canopies. The data clearly show very marked differences between the growing and dormant season for all four pollutants, with the higher concentrations occurring during the growing season. The greatest differences are for the N-containing gases, and the most striking is the 3-7 fold higher concentrations in the growing season for HNO_3 and NH_3 . The diurnal pattern is also consistent, with concentrations during the daylight hours being higher than those at night. As noted above, the most striking differences are for HNO_3 and NH_3 .

The appendices contains all of the summary data for each species (Appendix A - *Pinus ponderosa* or

Ponderosa Pine; Appendix B - *Abies concolor* or White Fir; Appendix C - *Quercus kelloggii* or Black Oak) by month. The data for each chemical species include means by hour for (i) concentration, (ii) V_g , (iii) total deposition and (iv) average deposition.

8.3.1 Ozone

Ozone deposition to the forest canopy varied markedly on a diurnal and seasonal time step, reflecting the periodicity of the leaf's physiological activity that controls the canopy's sink potential. As an example, O_3 deposition is shown for the growing season averaged by hour of the diurnal cycle for Ponderosa Pine (Figure 8-3). The results demonstrate a two-fold range in deposition, from a low of $\sim 150 \mu\text{g}/\text{m}^2/\text{h}$ in the late evening and early morning hours to a maximum of $\sim 400 \mu\text{g}/\text{m}^2/\text{h}$ in the late afternoon and early evening hours (1600 - 1900 h). The time period for maximum deposition was in the late afternoon, reflecting the trend for maximum O_3 concentrations in areas down wind from urban centers to be delayed relative to that in urban landscapes (Lovett, 1994). Conversely, maximum V_g values for O_3 , indicative of the leaf's porosity, extend from 1000 h until 1600 h. The intervening periods of rapid increase (morning and midday) and precipitous decline (late evening) in O_3 deposition demonstrate the periodicity in the processes governing the flux of O_3 and reflect both receptor sink capacity and O_3 concentrations in the atmosphere.

The seasonal pattern of O_3 deposition is equally striking and the pattern is shown for all three species from November 1991 - September 1993 (Figure 8-4); the deposition units are at the level of the landscape rather than leaf area. Thus, deposition to the landscape sums the deposition to all species. As expected, deposition during the dormant season (range from 1400 to 2000 $\mu\text{moles}/\text{m}^2/\text{month}$) was $\leq 50\%$ of that during the growing season (range of 3000 - 4500 $\mu\text{moles}/\text{m}^2/\text{month}$) for each of the three species. The pattern of O_3 deposition showed the following species-specific behavior during the growing season:

White Fir > Black Oak > Ponderosa Pine.

During the dormant season, the pattern was as follows:

White Fir > Ponderosa Pine \geq Black Oak.

The mean O_3 deposition ($\mu\text{mol}/\text{m}^2/\text{h}$; area unit is the leaf surface) during the growing season for Ponderosa Pine, White Fir and Black Oak indicate nearly a two-fold difference in deposition among the three species. Mean deposition in Ponderosa Pine, White Fir and Black Oak approached 8, 4 and 7 $\mu\text{moles}/\text{m}^2/\text{h}$, respectively (Figure 8-5). Accordingly, even though the species "experienced" the same O_3 exposure, the deposition rate was species-specific and largely accountable to the species' physiological and ecological properties controlling the porosity of the leaf (i.e., stomatal resistance).

8.3.2 Nitrogen-Containing Gases

The N-containing gases were investigated separately, and a summary of each is provided.

8.3.2.1 Nitrogen Dioxide

Unlike that observed for O_3 , there was little diurnal periodicity to NO_2 deposition (Figure 8-6). The underlying porosity of the leaf surface for NO_2 (V_g for NO_2) did vary in a diurnal pattern, with porosity being greater during the daylight hours (Appendices A - C). However, this pattern of V_g was counterbalanced by a inverse pattern in NO_2 concentration in the atmosphere (Appendices A - C).

NO_2 deposition by month over the duration of the study for all three species (Figure 8-7) showed a pattern similar to that of O_3 . Deposition during the dormant season was typically $\leq 10,000 \mu g NO_2/m^2/month$, and deposition was nearly equivalent for all three species. With the onset of the growing season, NO_2 deposition increased to a maximum in 1992 of between 15,000 and 20,000 $\mu g/m^2/month$. Thus, NO_2 deposition during the growing season exceeded that of the dormant season by a factor of 3-6. Deposition during the growing season was higher in all three species during 1992 versus 1993, and the difference was approximately 30%. At the landscape level, NO_2 deposition during the growing season was greatest for White Fir, followed by Black Oak and Ponderosa Pine.

Over the course of a full growing season, the deposition of N- NO_2 was nearly equivalent for all three species, ranging from, ~ 0.3 (Black Oak) to 0.35 (White Fir) kg N/ha/y (Figure 8-8). Cumulative N deposition in the form of NO_2 was 0.979 kg N/ha/y.

8.3.2.2 Nitric Acid Vapor

The deposition of HNO_3 showed a very marked periodicity over the diurnal time step during the growing season (Figure 8-9). Nighttime deposition was characteristically $\leq 500 \mu g/m^2/h$. With the onset of daylight, HNO_3 deposition rose abruptly at 0600 h and continued to increase to $\sim 15,000 \mu g/m^2/h$ from 1400 - 1500 h. Thereafter, deposition dropped precipitously between 1700 and 1800 h. This precipitous drop is largely an artifact of the sampling methodology, which split the diurnal samples at this time interval.

Over the course of the two years, HNO_3 deposition differed between the dormant and growing season (Figure 8-10). Dormant season deposition was commonly $\leq 50,000 \mu g/m^2/month$ (landscape level) for all species, whereas the growing season deposition increased by a factor of 3 - 5. HNO_3 deposition was higher on average in 1993 than in 1992. Unlike the other pollutants, HNO_3 deposition showed little variation among tree species, which reflects the fact that the forest canopy (leaf surface) is a perfect sink for HNO_3 (Hanson and Lindberg, 1991). Because the site of deposition is principally the exterior leaf surface, physiological features controlling porosity are not important.

The deposition of N- HNO_3 at the landscape level in units of kg N/ha/y ranged from a high of 3.5 for Ponderosa Pine to 2.5 for White Fir (Figure 8-11). Cumulatively, N- HNO_3 deposition at the landscape level was 9.63 kg N/ha/y.

8.3.2.3 Ammonia

As with the other pollutants, the patterns of NH_3 deposition varied as a function of month, time of day, and tree species. Over the diurnal cycle during the growing season, NH_3 deposition showed a pronounced periodicity, with nighttime values approaching 7.5 - 10 $\mu\text{g}/\text{m}^2/\text{h}$ (Figure 8-12). Deposition during the day ranged from 15 to 17 $\mu\text{g}/\text{m}^2/\text{h}$. Thus, there was a 2-fold variation in NH_3 deposition between night and day.

Over the course of the sampling period, NH_3 deposition ranged from a low of $\sim 1000 \mu\text{g}/\text{m}^2/\text{month}$ in the December - February and a maximum of 15,000 - 25,000 $\mu\text{g}/\text{m}^2/\text{month}$ in May - July (1992) and July - August in 1993 (Figure 8-13). Thus, the monthly deposition of NH_3 varied by a factor of 15. Whereas this pattern was consistent for all three species, deposition during the growing season was highest for White Fir followed in order by Black Oak and Ponderosa Pine. This pattern reflects the differences among the three species in stomatal resistance.

The deposition of N in the form of NH_3 at the landscape level was intermediate between that for NO_2 and HNO_3 . Cumulative N deposition was 2.29 kg N/ha/y, and the species contribution was nearly equivalent, ranging from 0.7 to 0.8 kg N/ha/y (Figure 8-14).

8.3.3 Sulfur-Containing Gases

8.3.3.1 Sulfur Dioxide

The pattern of SO_2 deposition over the diurnal cycle during the growing season was similar to that observed for NH_3 in that there was a pronounced difference in SO_2 deposition between day and night (Figure 8-15). Nighttime deposition of SO_2 ranged between 1.5 and 1.75 $\mu\text{g}/\text{m}^2/\text{h}$, and daytime values were ~ 2 times higher (2.5 - 2.75 $\mu\text{g}/\text{m}^2/\text{h}$).

Over the 23 month period of the study, the deposition of SO_2 showed patterns similar to that of the N-containing gases, although the periodicity was not as distinct (Figure 8-16). Dormant season rates were $\leq 1500 \mu\text{g}/\text{m}^2/\text{month}$. Conversely, growing season SO_2 deposition was more variable, ranging from values approaching 2000 $\mu\text{g}/\text{m}^2/\text{month}$ up to 6500 $\mu\text{g}/\text{m}^2/\text{month}$. Deposition of SO_2 was higher in all three species in 1992 versus 1993.

At the landscape level, S deposition *via* SO_2 in units of kg S/ha/y ranged from 0.125 (Ponderosa Pine) to 0.175 (White Fir) (Figure 8-17). In a cumulative fashion, total dry deposition of S in the form of SO_2 was 0.44 kg S/ha/y.

8.4 Discussion

Total N deposition is the summation of inputs *via* wet and dry deposition (Figure 8-18). At the landscape level, total N deposition was 14.5 kg N/ha/y. Of this total, wet deposition accounted for $\sim 15\%$. The

majority (62%) of the N deposition occurred as dry deposition of N-HNO₃. The ratio of wet to dry N deposition was 6.25. Clearly, the input of atmospheric N is largely dictated by the dry deposition of gases to the canopy, and the principal species of concern are HNO₃ > NH₃ > NO₂. Wet deposition played a very minor role in contributing to the input of N to the forest at Barton Flats.

The input of S contrasts significantly with that of N deposition. Total S deposition was ~ 2 kg S/ha/y from a combination of wet and dry inputs (Figure 8-19). Of this total, dry deposition of S-SO₂ accounted for ~ 25%, and the remainder (75%) was due to wet deposition.

The O₃ deposition to each of the tree species during the growing season was greater than that in many other regions of North America in which O₃ is reported to be influencing the physiology and growth of sensitive forest species (Taylor *et al.*, 1994). It is proposed that the deposition to ponderosa pine is well in excess of the threshold for effects on processes controlling carbon dioxide assimilation, photosynthate partitioning, and stomatal physiology. There are insufficient data to evaluate whether the O₃ deposition during the growing season in White Fir and Black Oak are sufficient to adversely affect leaf physiology. Part of the uncertainty in this evaluation lies in the consequences for the co-deposition of N and how this excess N may enhance or diminish the toxicity of O₃ (Fenn and Bytnerowicz, 1993; Taylor *et al.*, 1994)

Any modelling activity has inherent uncertainties associated with the methodology and these uncertainties are unrelated to the error in the collection of experimental data. Thus, any uncertainty in the aerometric (e.g., concentration of HNO₃) or stand level (e.g., leaf area index) data would be proportionally applicable to the model computations.

The more meaningful uncertainty analysis for the Big Leaf Model rests with the assumptions in the model. Given the model's application in a variety of landscapes in North America and Western Europe, most of these uncertainties have been analyzed and tend to approach an uncertainty level of ± 30% (Johnson and Lindberg, 1992). Thus, the dry deposition of S could be higher or lower by 30%, although the existing deposition of S is well below any rate that would be considered of concern with respect to ecological or physiological issues.

Conversely, the estimate of N deposition is already at a level of concern with respect to long-term effects on stand-level biogeochemistry and physiological behavior of at-risk tree species (Taylor *et al.*, 1994). If the N load was further increased by 30%, the concern would be even greater. A parallel reduction in N loading by 30% would somewhat diminish the concern, although even that level of N deposition is high enough to be a concern for at-risk landscapes.

The only unresolved uncertainty surrounds the analysis of N deposition via HNO₃ and NH₃. The majority of data in the literature clearly demonstrates that the leaf is a perfect sink for HNO₃ (Hanson and Lindberg, 1991), and these data arise in varied disciplinary studies including micrometeorology, plant physiology, and plant N metabolism. In the model, this "perfect sink" feature is part of code and is specified by a near perfect sink for the cuticle, not the leaf interior. In order for a change in the code (cuticular resistance to HNO₃) to have a demonstrate effect on the N deposition, the perfect sink capacity needs to be dropped by

nearly a factor of 10. Thus, it is unlikely that a reduction of this magnitude is in order in light of the wealth of data that exists.

The uncertainty with NH_3 is far greater. Unlike the knowledge base for HNO_3 and NO_2 , there are few data available to help parameterize the Big Leaf Model for NH_3 . There are physiological observations that suggest the canopy resistance could be lower by 30-40% or far higher, by as much as 60-70%. Unfortunately, all of these data are for agricultural crops and thus are not transparently applicable to forest trees.

This uncertainty for NH_3 is even more critical given the site of HNO_3 deposition. For HNO_3 , deposition is largely to the leaf cuticle, after which the HNO_3 is either partially absorbed through the cuticle or washed off during rainfall events. This N simply increments the soil N pool by a very small percentage. Conversely, the site of NH_3 deposition is the leaf interior, after which the N is largely unavailable for washoff. The deposition of a reduced N species at physiologically-sensitive sites within the leaf interior clearly has long-term implications for plant physiology and biogeochemistry. As a consequence, the uncertainty surrounding NH_3 deposition is far greater than that for HNO_3 .

8.5 Summary

The results from the Big Leaf Model simulations at the Barton Flats site in Southern California indicate that total N deposition *via* wet and dry processes was 14.5 kg N/ha/y. Dry deposition accounted for 85% of this total, and HNO_3 and NH_3 were the principal chemical species contributing to the N input. Most of the N deposition *via* dry processes occurred during the growing season. In the case of S deposition, total inputs were 2 kg S/ha/y, and dry deposition accounted for 25% of the total. The deposition of O_3 was highly variable among species and over time (seasonal and diurnal time steps). The O_3 deposition to ponderosa pine was well above the threshold for physiological effects in at-risk species. It is hypothesized that the deposition of N and O_3 over extended periods of time (years to decades) are sufficient to adversely impact at-risk species, possibly ecosystem-level biogeochemistry, and the competitive interactions between species.

8.6 References

- Baldocchi, D.D., Hicks, B.B., Camara, P. 1987. A Canopy Stomatal Resistance Model for Gaseous Deposition to Vegetated Surfaces. *Atmospheric Environment* 21:91-101.
- Bytnerowicz, A., Miller, P.R., Olszyk, D.M. 1987. Dry Deposition of Nitrate, Ammonium and Sulfate to a *Ceanothus Crassifolius* Canopy and Surrogate Surface. *Atmospheric Environment* 21: 1749-1757.
- Fenn, M.E., Bytnerowicz, A. 1993. Dry Deposition of Nitrogen and Sulfur to Ponderosa Pine and Jeffrey Pine in the San Bernardino National Forest in Southern California. *Environmental Pollution* 81: 277-285.
- Hanson, P.J. and Lindberg, S.E. 1991. Dry Deposition of Reactive Nitrogen Compounds: a Review of Leaf, Canopy, and Non-foliar Measurements. *Atmospheric Environment* 25: 1615-1634.
- Johnson, D.W. and Lindberg, S.E. (editors). 1992. *Atmospheric Deposition and Forest Nutrient Cycling: a Synthesis of the Integrated Forest Study*. Ecological Series 91. Springer-Verlag, New York, USA.
- Lovett, G.M. 1994. Atmospheric Deposition of Nutrients and Pollutants in North America: an Ecological Perspective. *Ecological Applications* 4: 629-650.
- Taylor, G.E., Jr., Johnson, D.J., Andersen, C.P. 1994. Air Pollution and Forest Ecosystems: a Regional to Global Perspective. *Ecological Applications* 4: 662-689.

Figure 8-1. Schematic diagram of the Big Leaf Model, showing the pathways for transport and the resistances governing the rate of flux.

Big Leaf Model

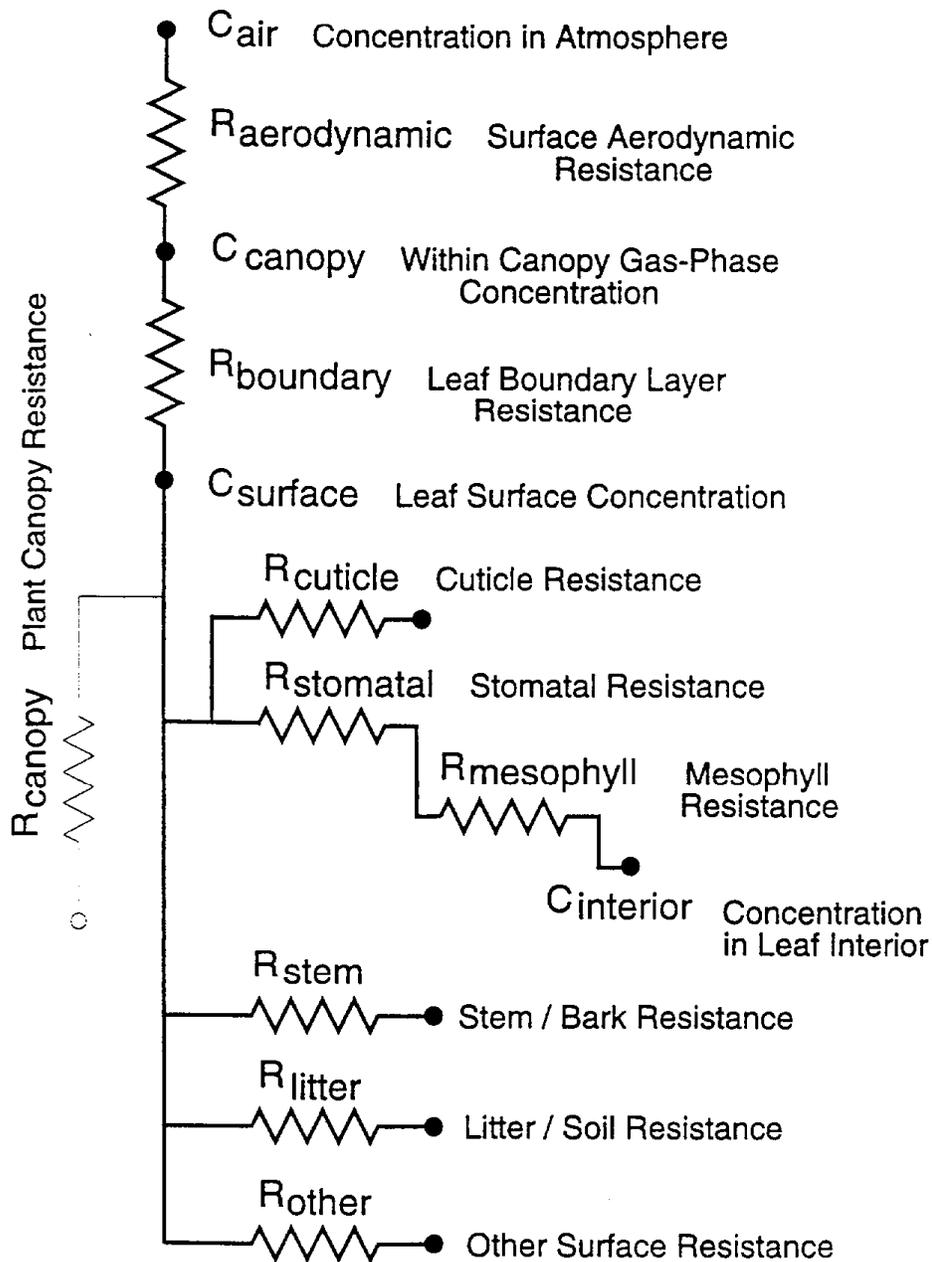


Figure 8-2. Diurnal concentration of the principal gas-phase species as a function of season (growing versus dormant) and time of day (day versus night).

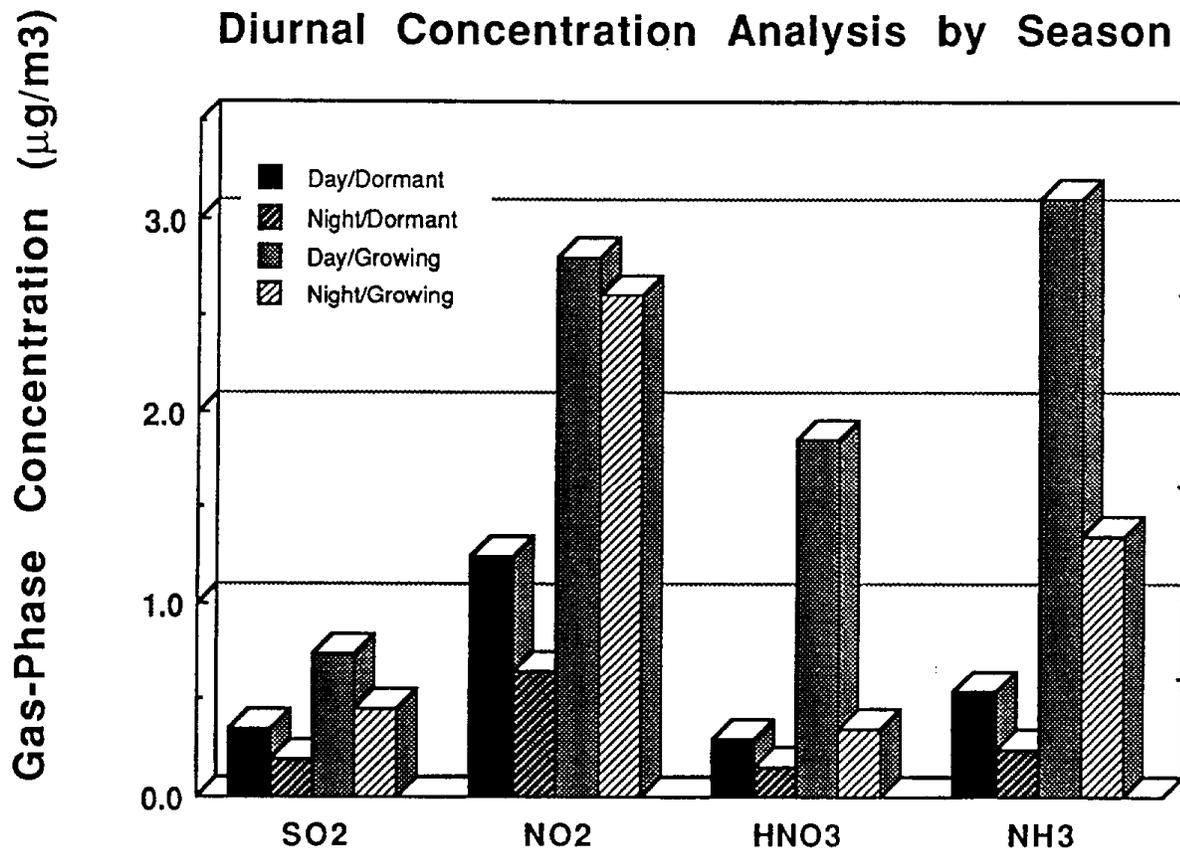


Figure 8-3. Deposition of O₃ in Ponderosa Pine over the diurnal cycle during the growing season.

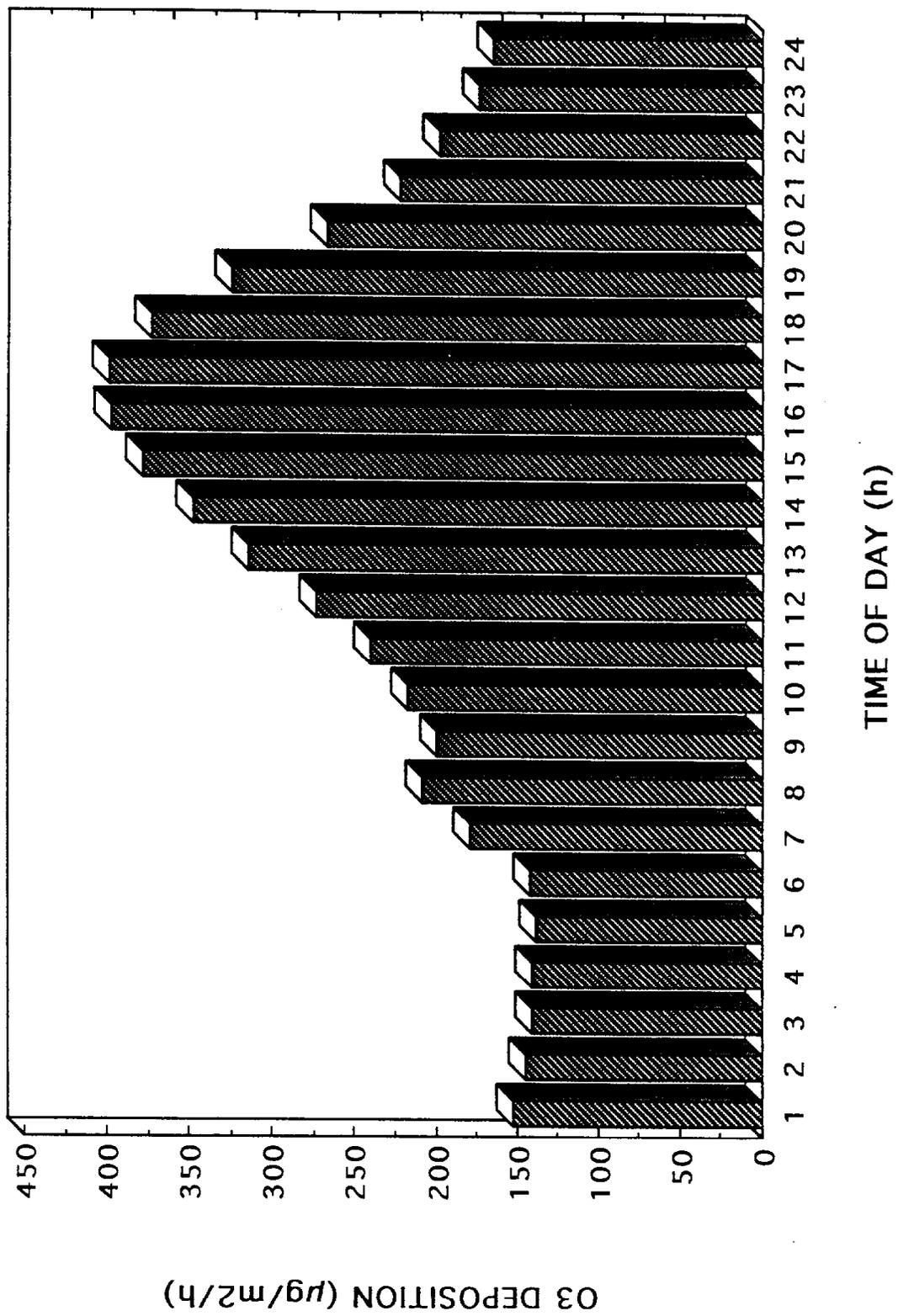


Figure 8-4. Deposition of O₃ by month to each of the three species over the 23 month period of study.

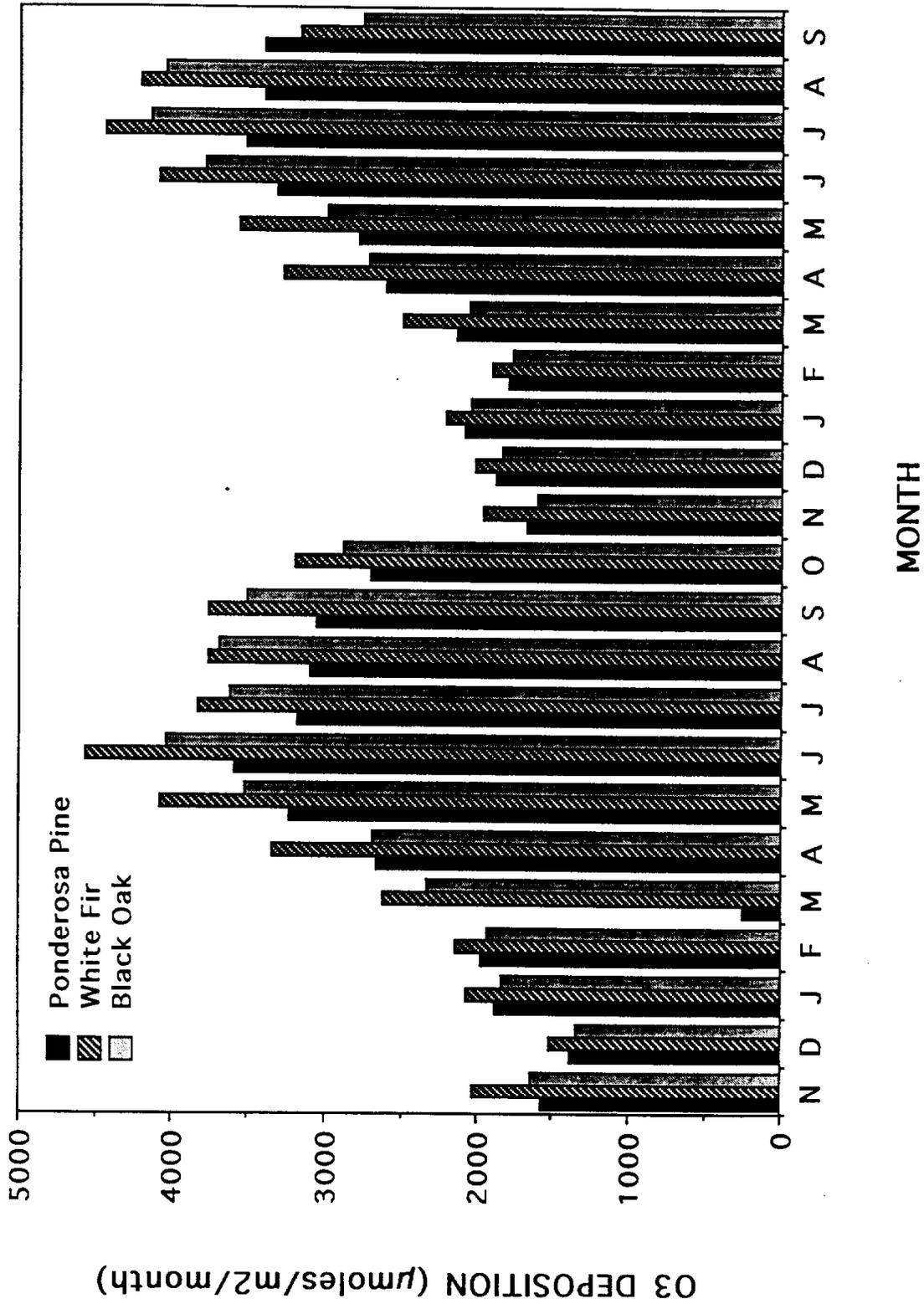


Figure 8-5. Mean O₃ deposition for each species during the growing season.

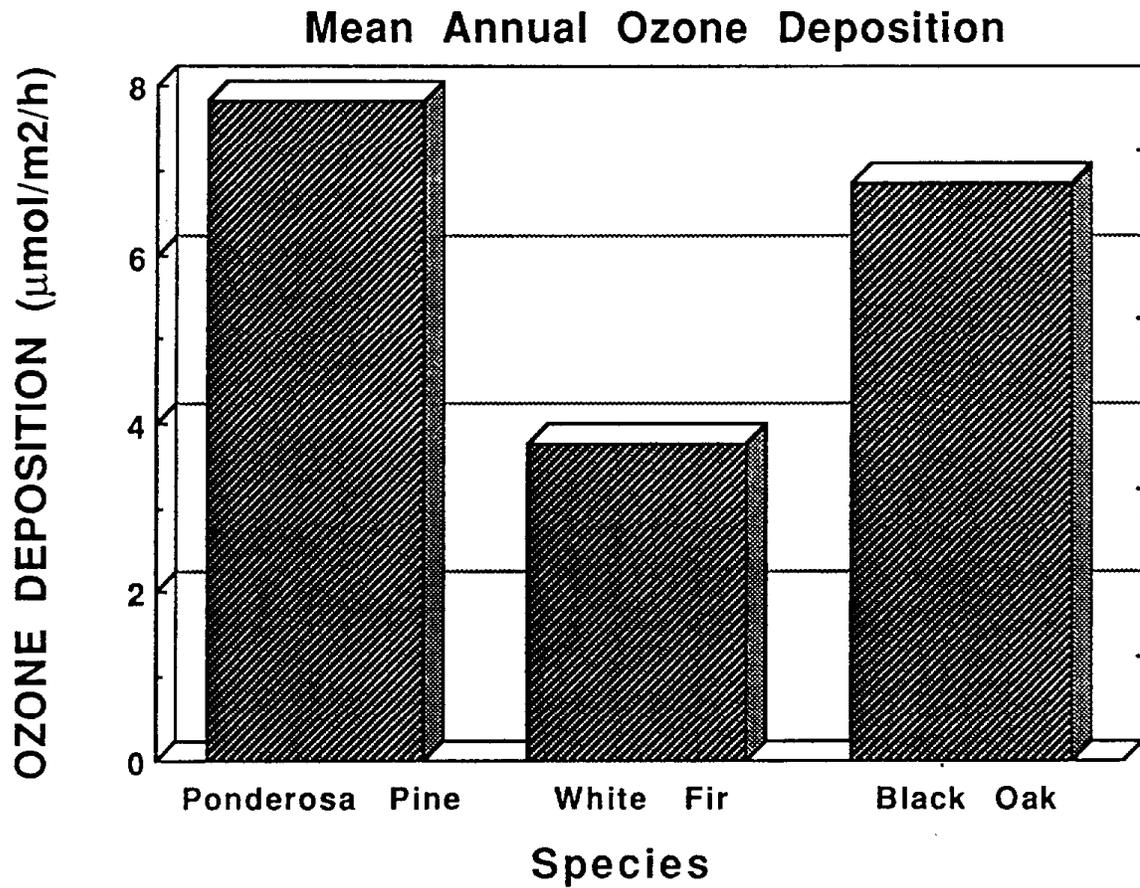


Figure 8-6. Deposition of NO₂ over the diurnal cycle during the growing season in Ponderosa Pine.

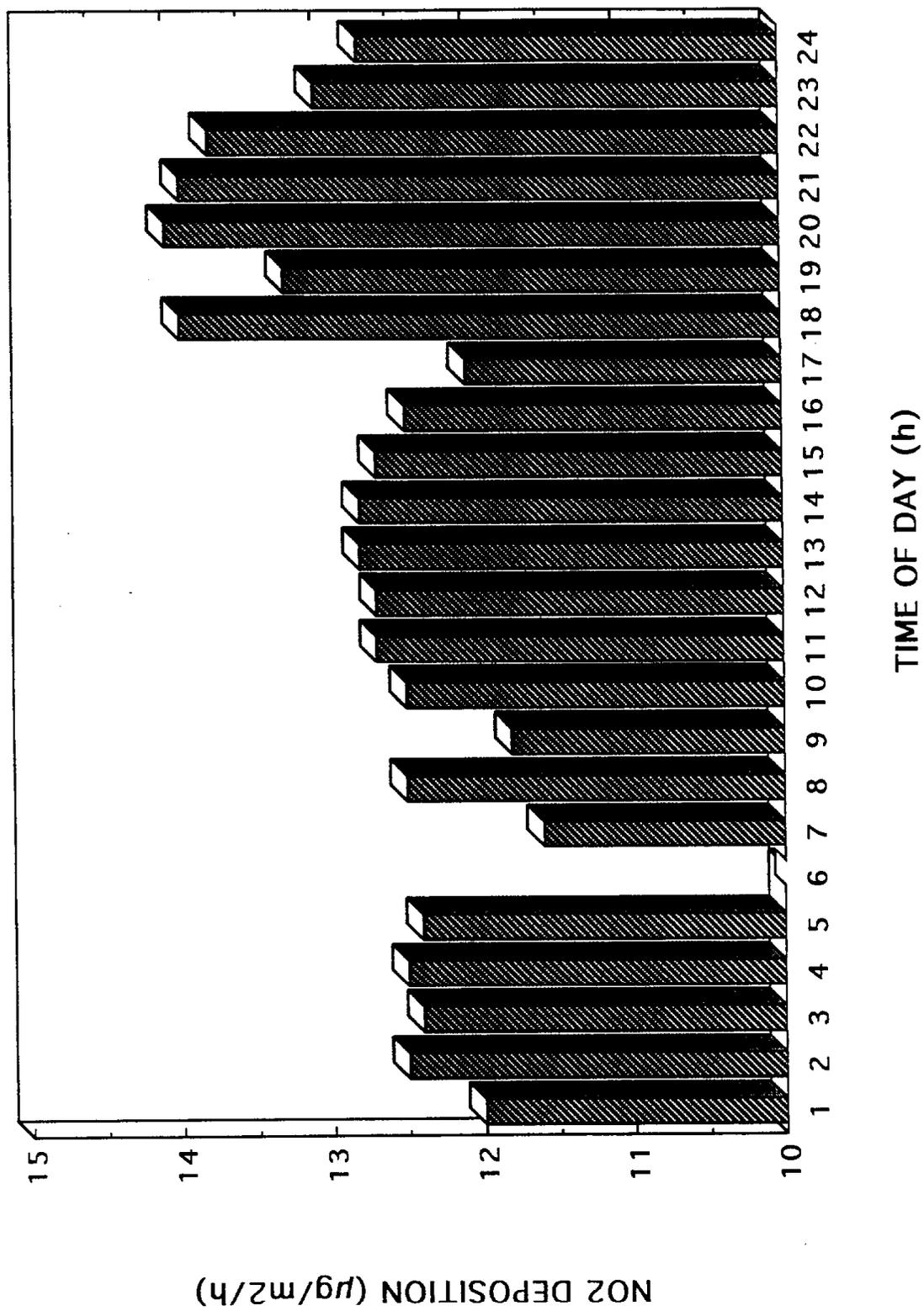


Figure 8-7. Total deposition of NO₂ by month over the duration of the 23 month study.

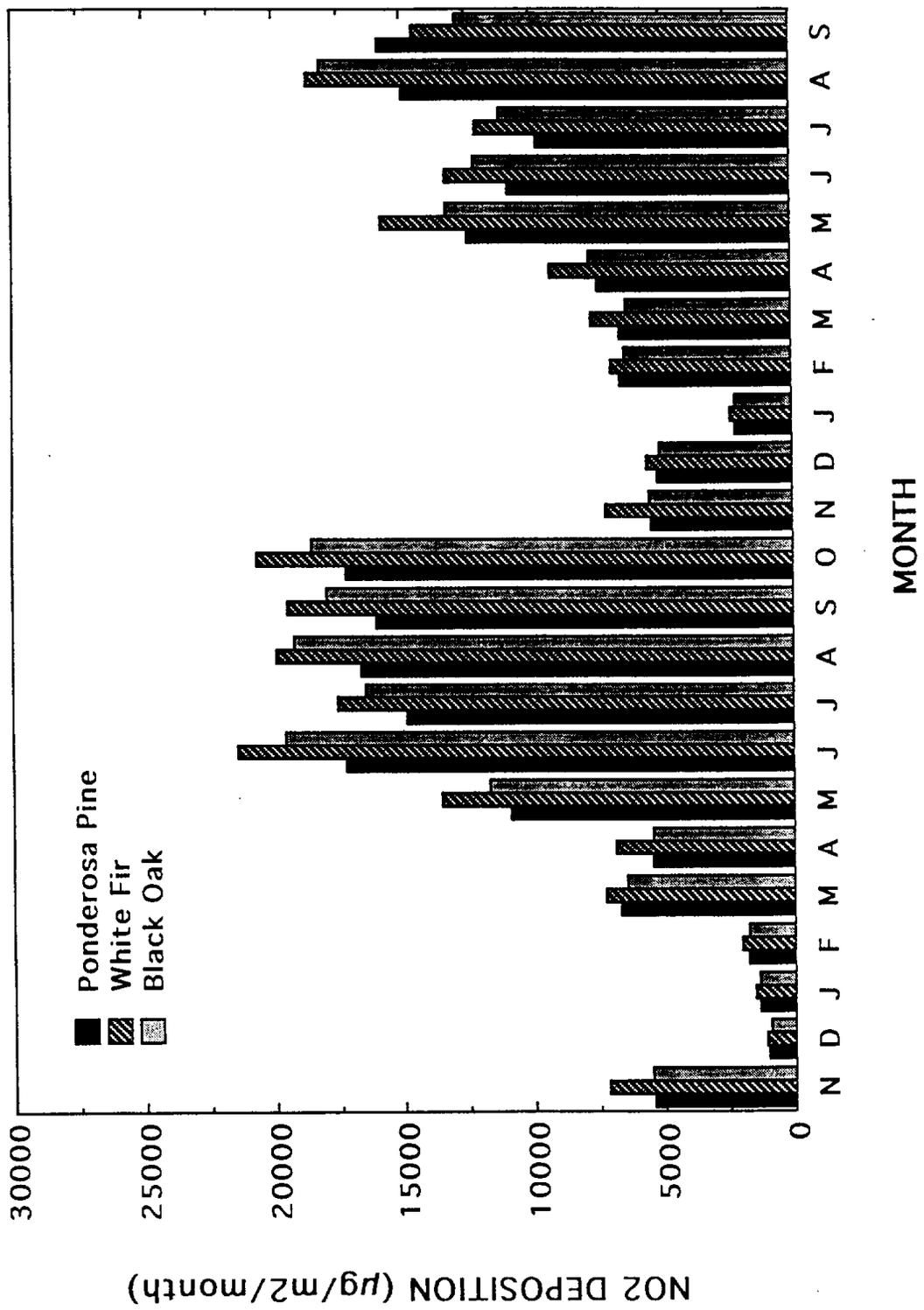


Figure 8-8. Deposition of N in the form of NO₂ by tree species on an annual time step and summed by landscape units.

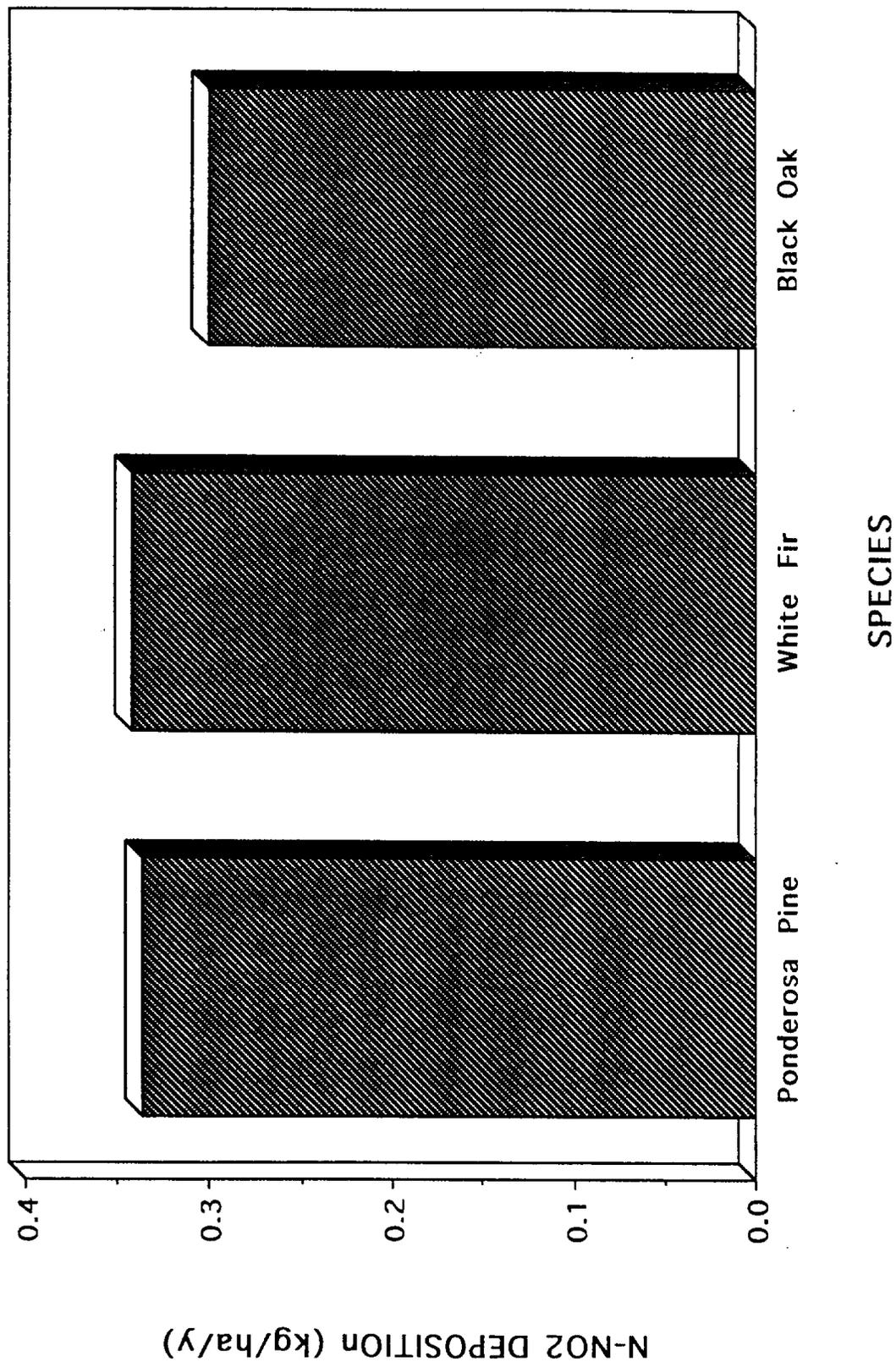


Figure 8-9. Deposition of HNO₃ over the diurnal cycle of the growing season in Ponderosa Pine.

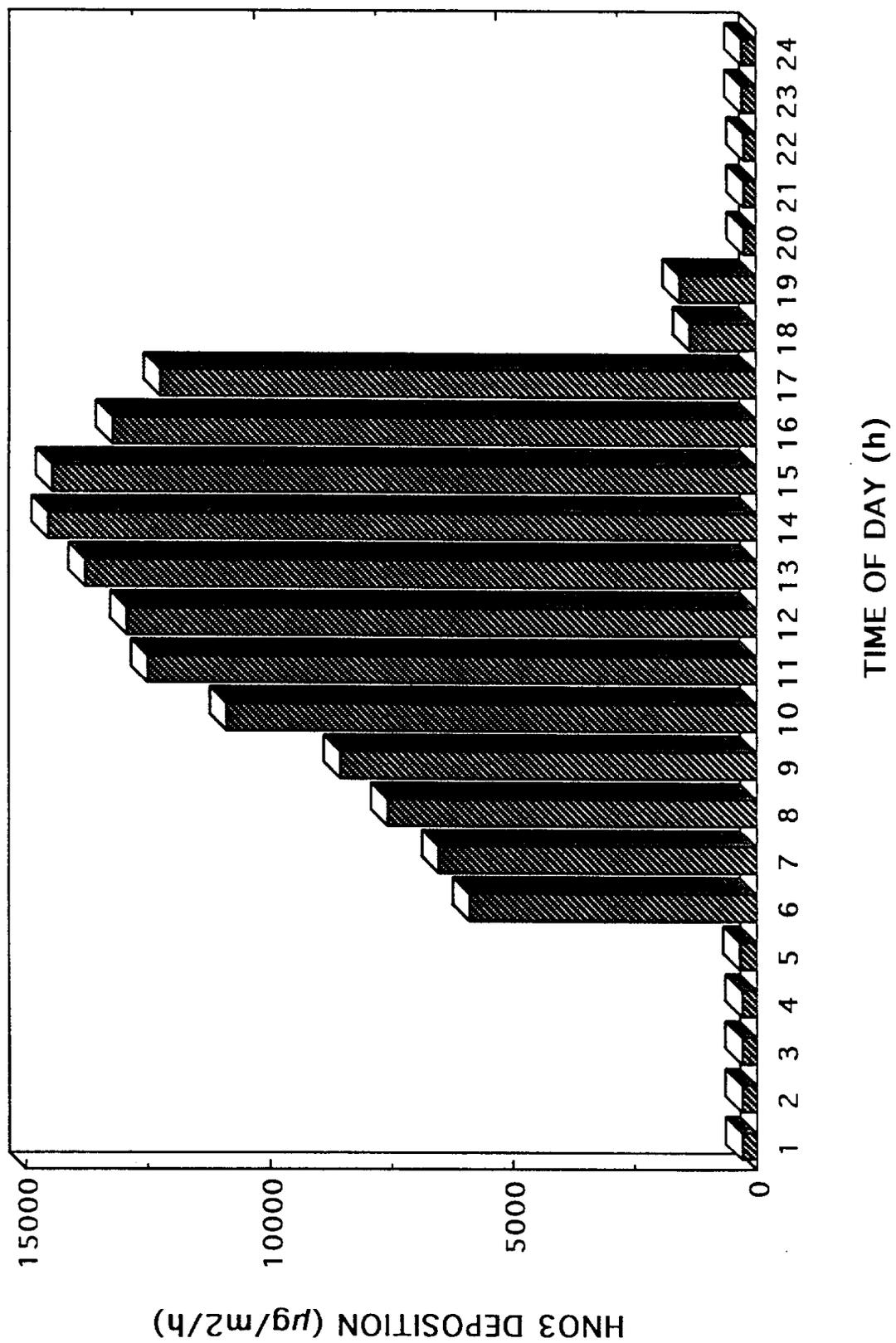


Figure 8-10. Deposition of HNO₃ by month for each of the three species over the duration of the 23 month study.

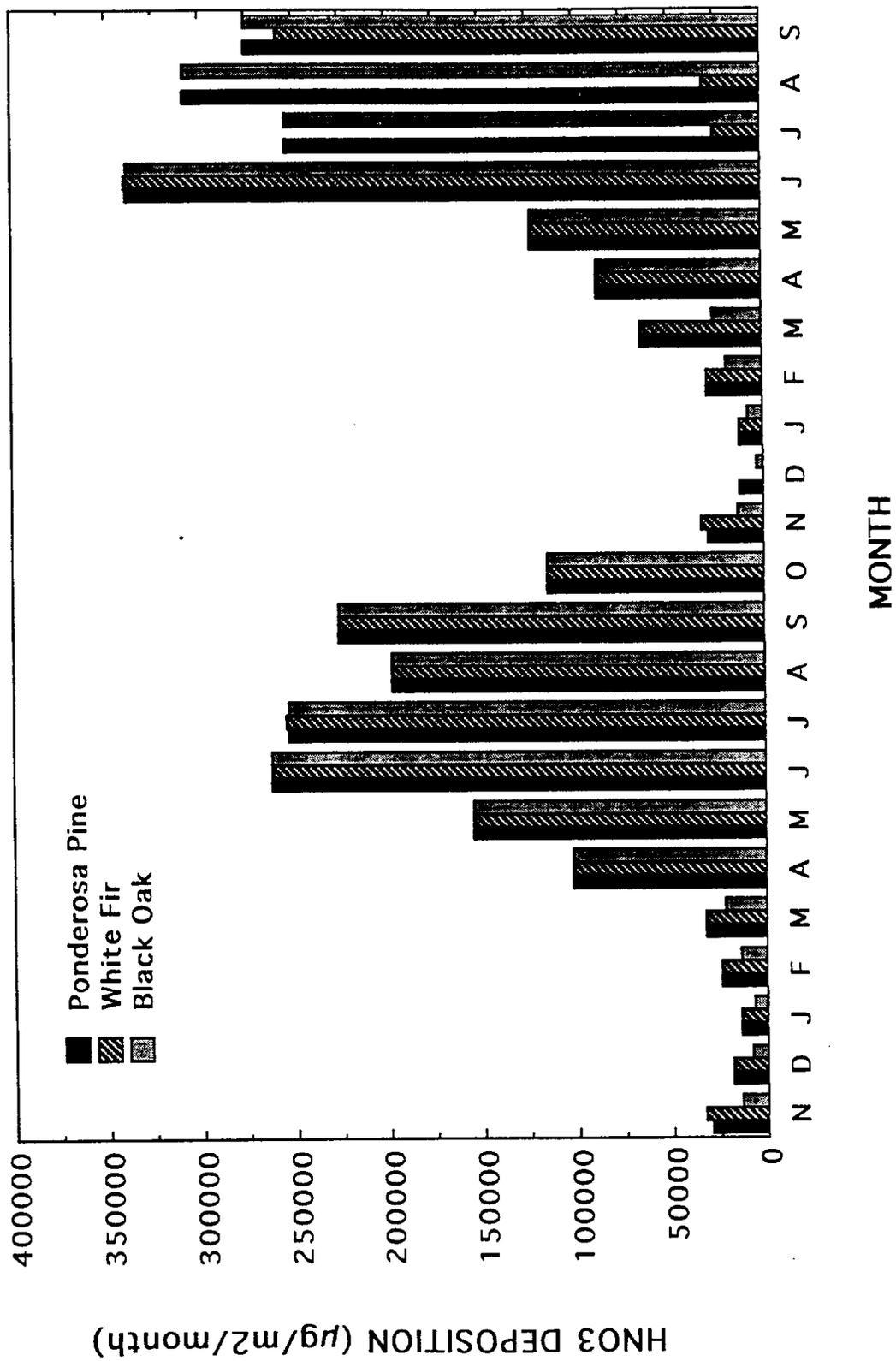


Figure 8-11. Deposition of N in the form of HNO₃ for each of the three species and summed by landscape units.

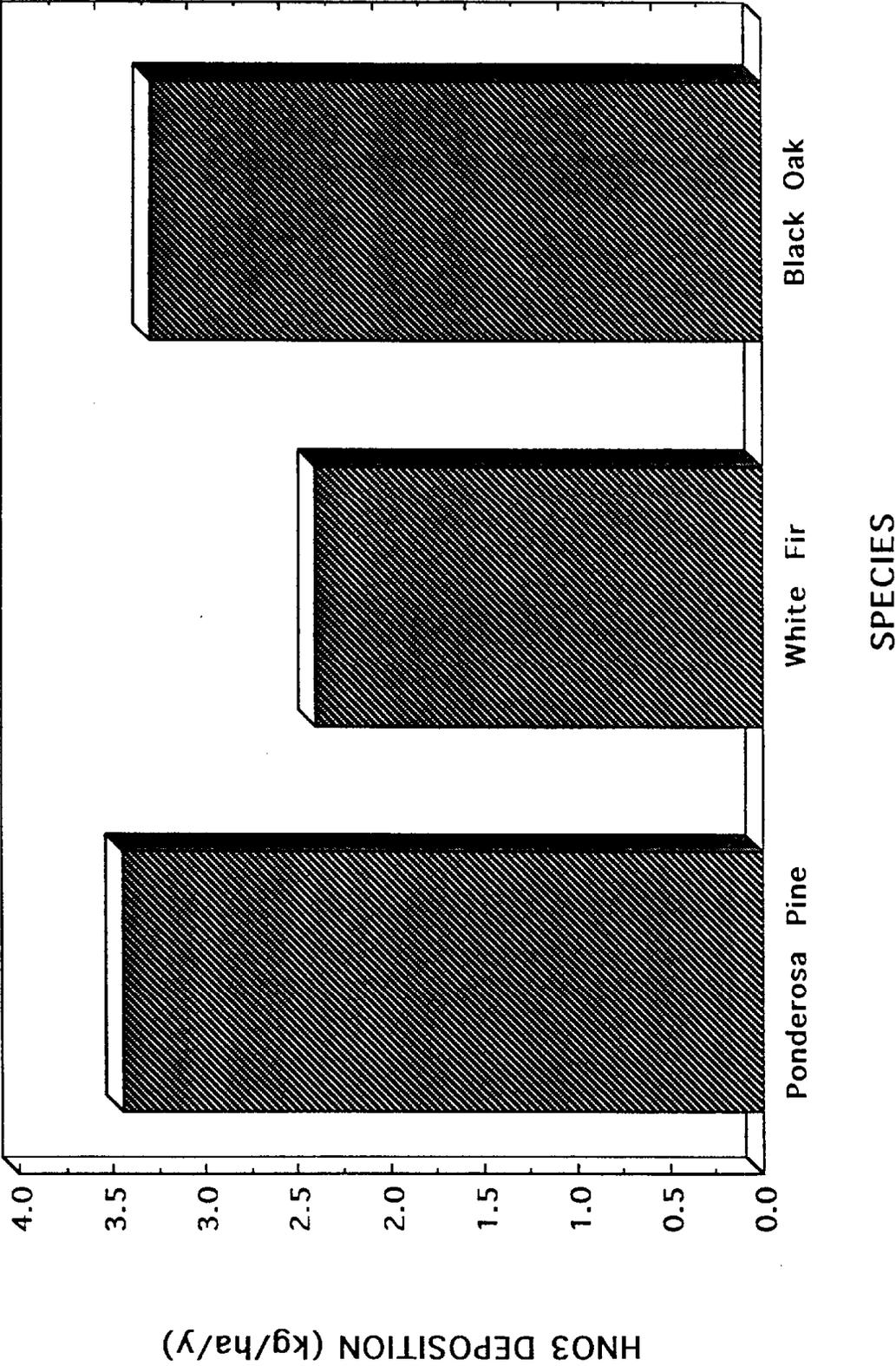


Figure 8-12. NH₃ deposition over the diurnal cycle during the growing season in Ponderosa Pine.

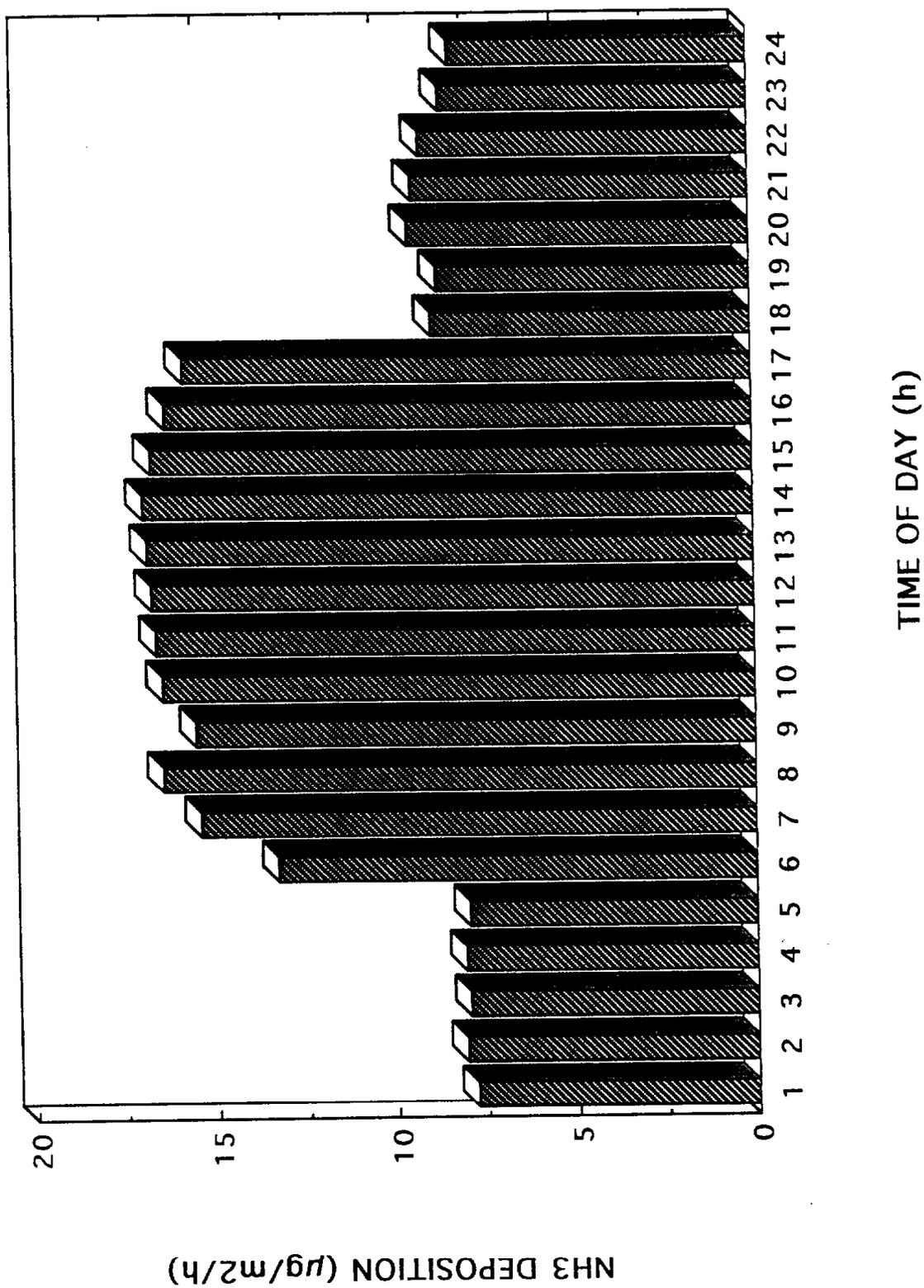


Figure 8-13. NH₃ deposition by month for each of the three species over the 23 month period of the study.

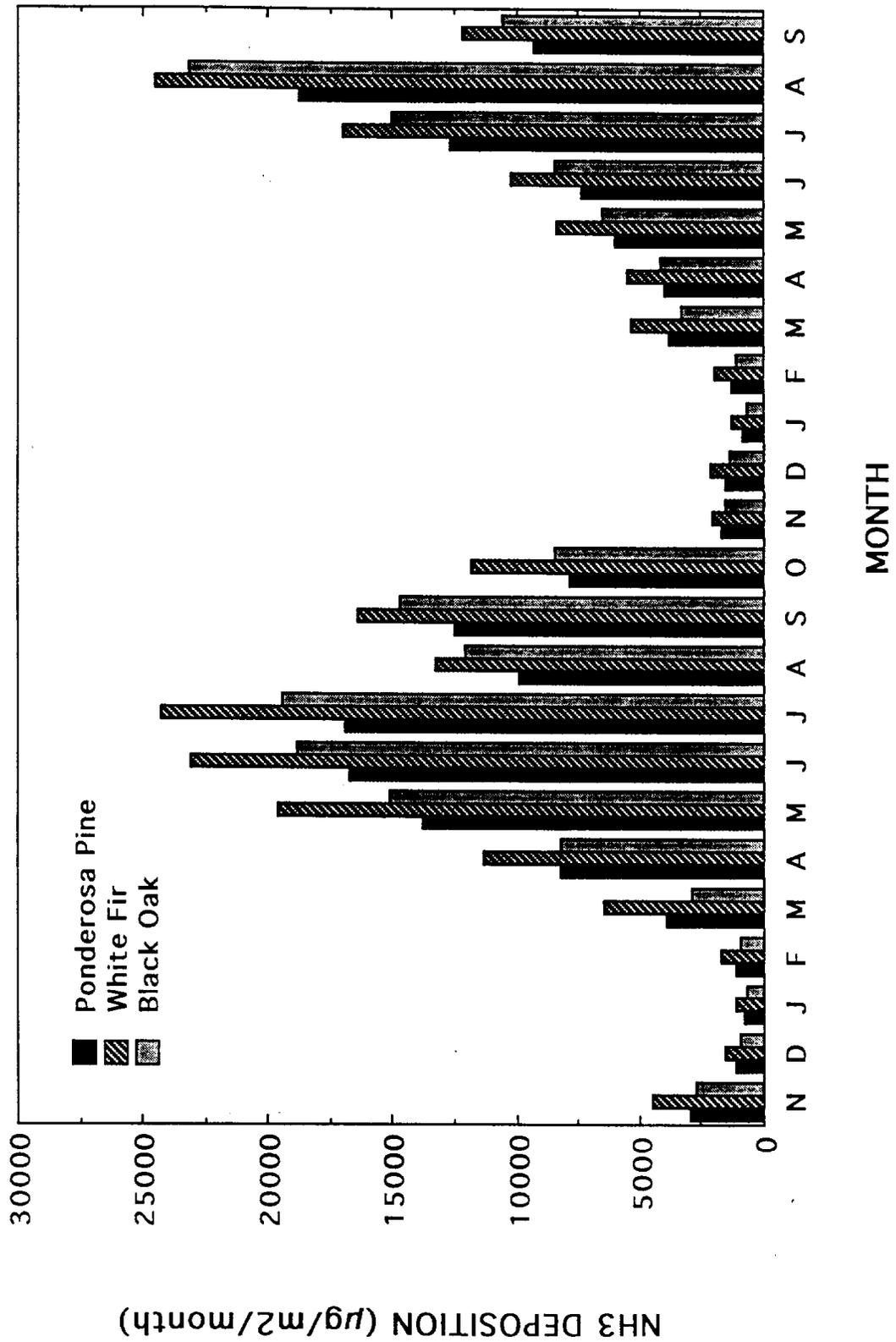


Figure 8-14. Deposition of N in the form of NH_3 by species and summed by landscape unit.

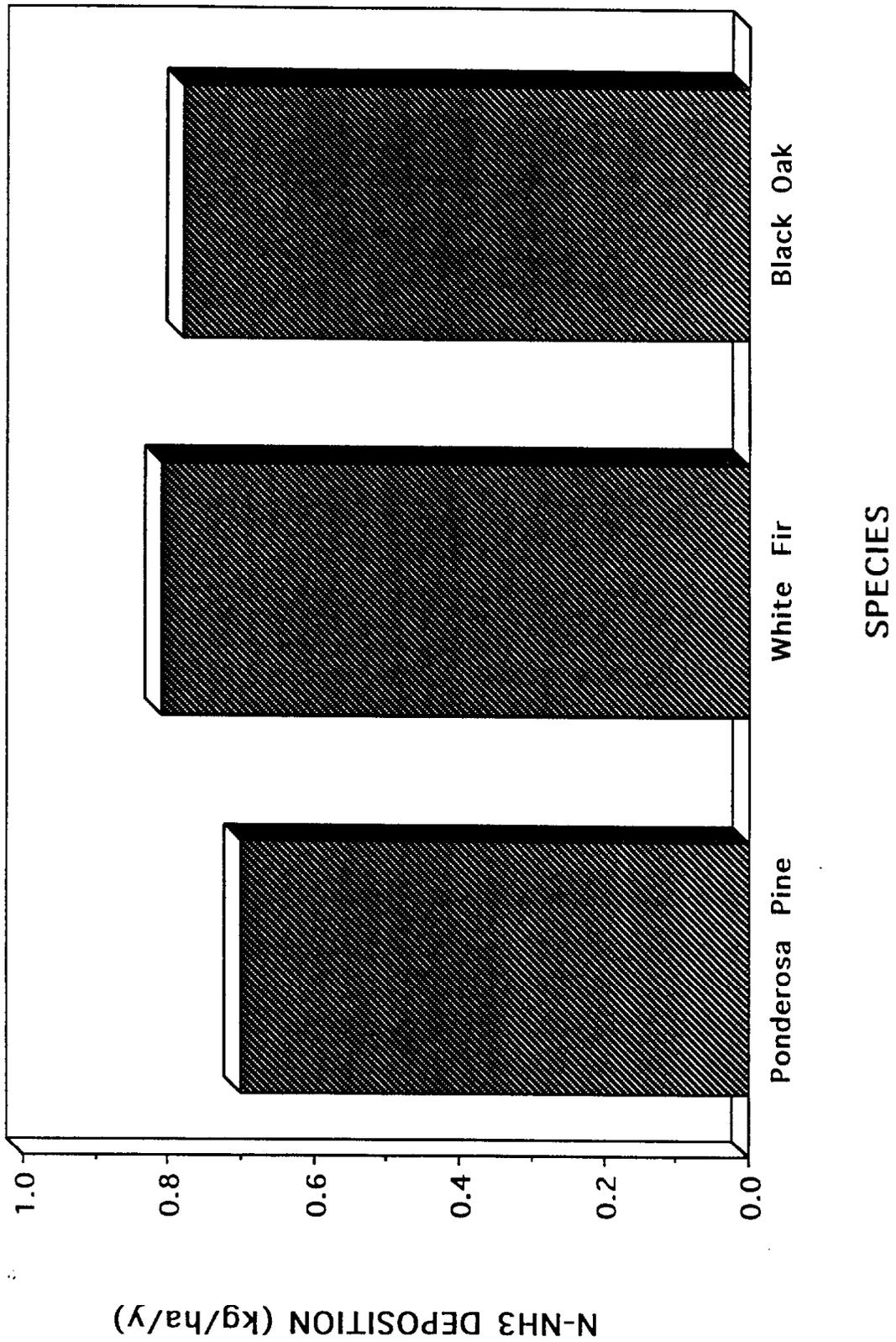


Figure 8-15. Deposition of SO₂ over the diurnal cycle of the growing season for Ponderosa Pine.

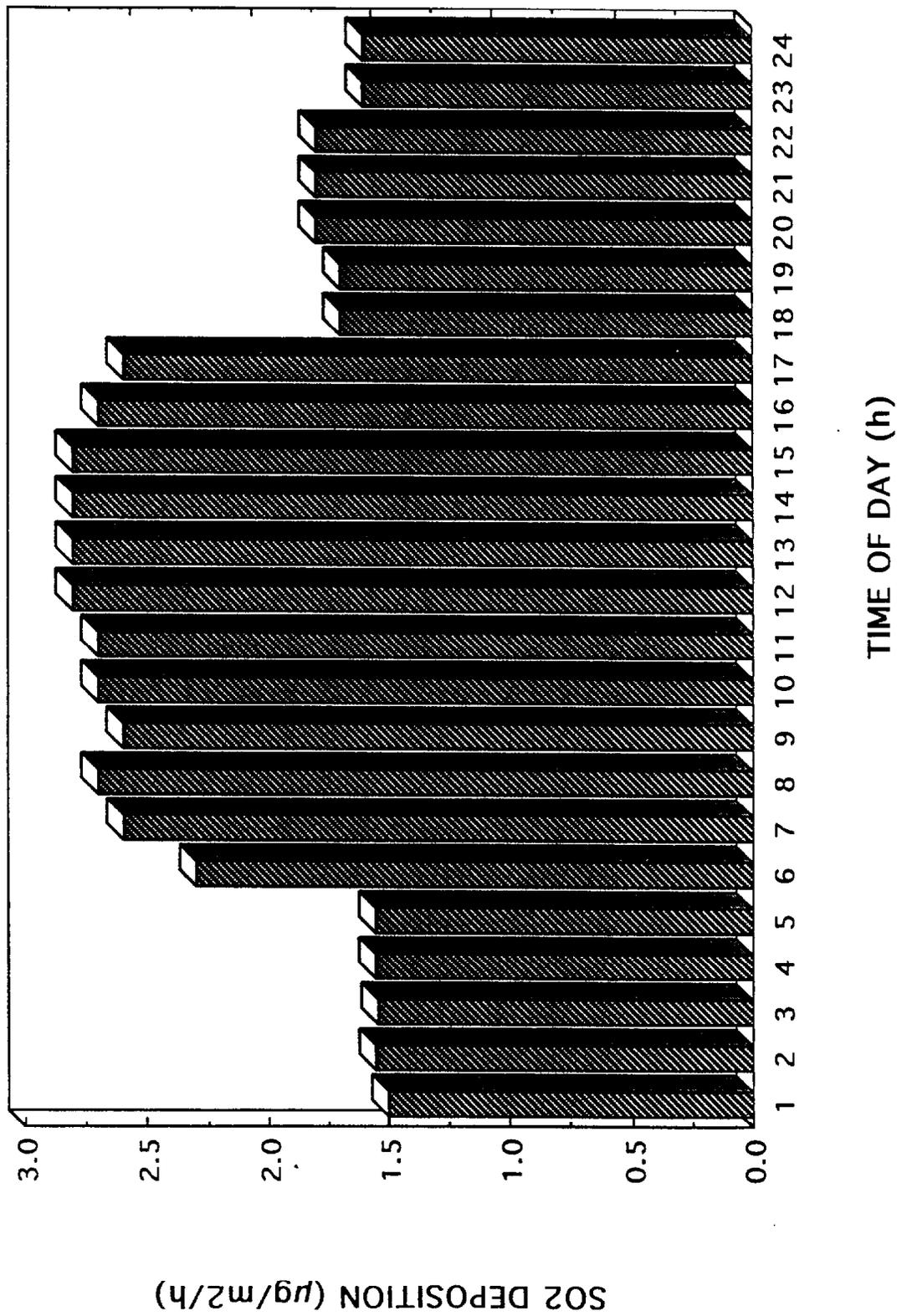


Figure 8-16. Deposition of SO₂ summed by month for each of the three species over the 23 month period of study.

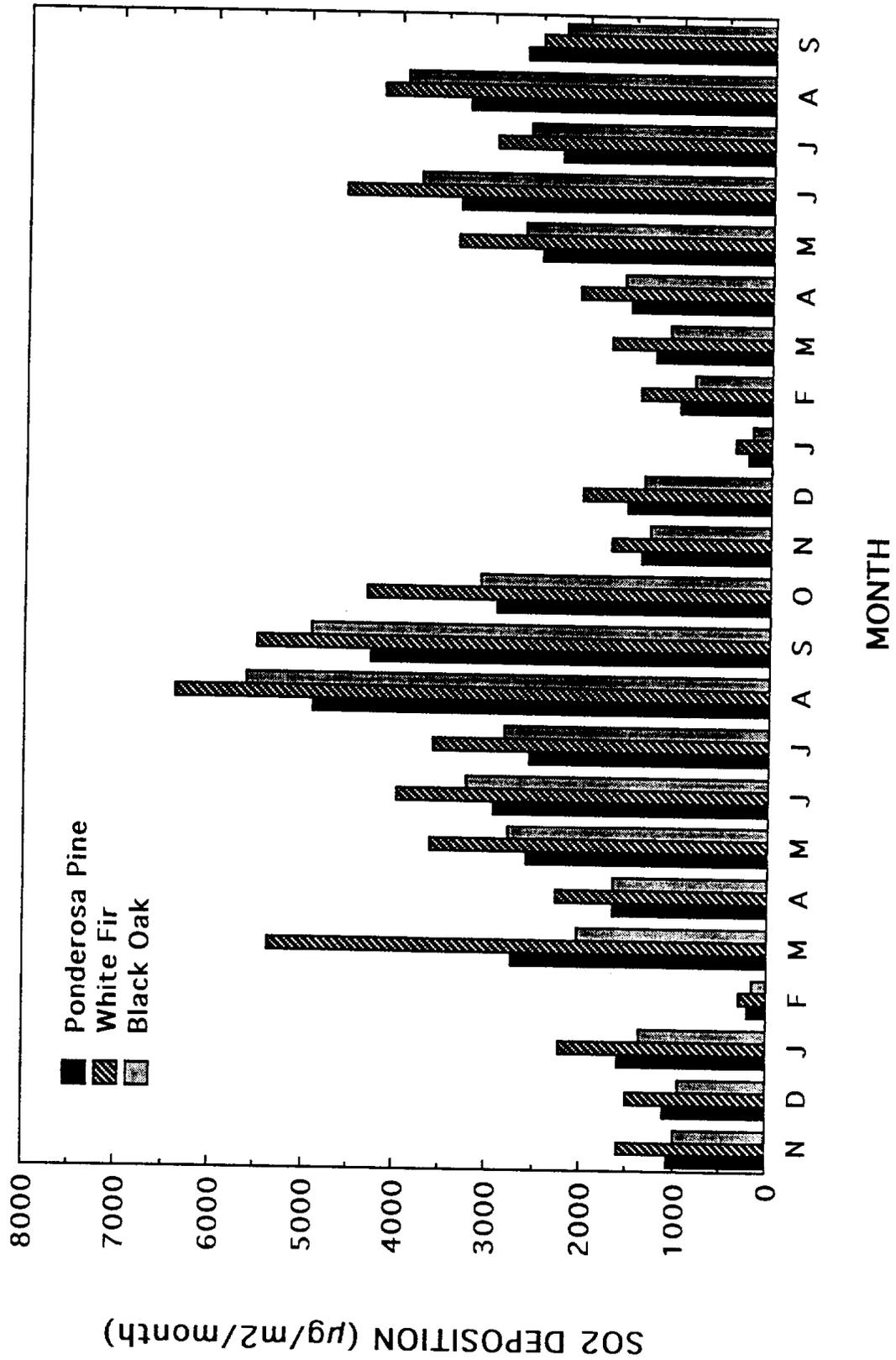


Figure 8-17. Annual deposition of S in the form of SO₂ by species and summed by landscape unit.

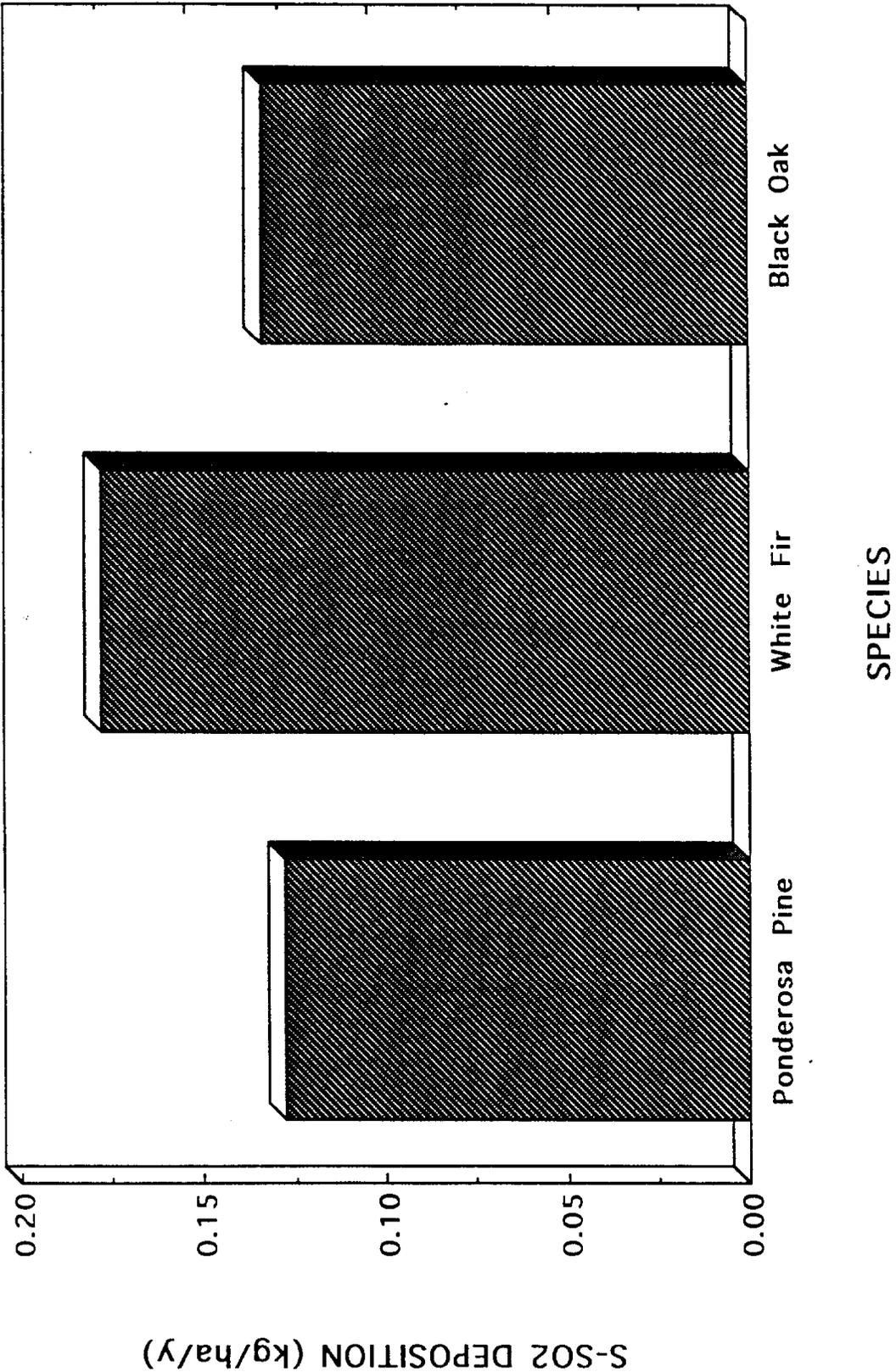


Figure 8-18. Annual deposition of N to the landscape in various chemical and physical forms for the entire forest at Barton Flats

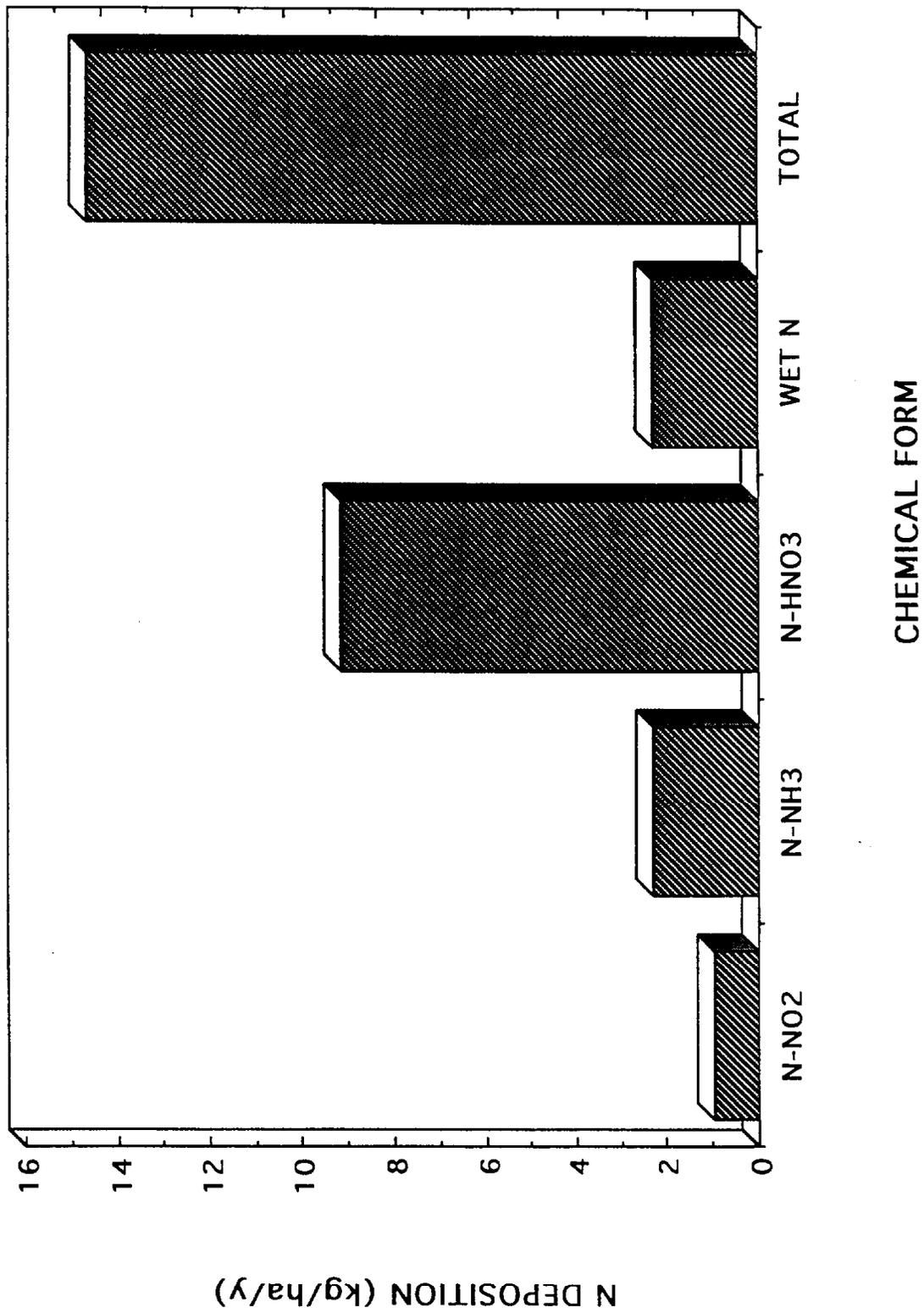


Figure 8-19. Annual deposition of S to the landscape in various chemical and physical forms for the entire forest at Barton Flats.

