

## Are Lakes in the Cascade Mountains Receiving High Ammonium Deposition?

### Abstract

Elevated deposition of nitrogen in the western United States is of concern because of the potential to cause either acidification or eutrophication in mountainous areas containing oligotrophic lakes and streams. A survey of snow chemistry by the U.S. Geological Survey reported  $\text{NH}_4^+$  concentrations for the Oregon Cascade Mountains up to  $10 \mu\text{eq/L}$ , approximately 5 to 10 fold greater than concentrations reported in several previous investigations and with results of snow cores collected for this study. Inconsistencies in the snow chemistry data collected by the USGS suggest possible errors in the reported  $\text{NH}_4^+$  concentrations. USGS reported  $\text{NH}_4^+$  concentrations also are inconsistent with information on regional sources of  $\text{NH}_4^+$  and transport and transformation of air pollutants. Actual concentrations of  $\text{NH}_4^+$  in snow along the Oregon Cascades appear to be near background levels ( $\sim 1 \mu\text{eq/L}$ ) expected for remote areas in northern temperate climates. The highest concentrations of  $\text{NH}_4^+$  in the western mountains are found in the Sierra Nevada of California located downwind of major agricultural sources.

### Introduction

Most information regarding deposition chemistry in the western United States (NADP/NTN 1984-1990; Young *et al.* 1988) indicates low rates of acidic deposition, and results from paleolimnological (Charles *et al.* 1989) and lake chemistry studies (Landers *et al.* 1987; Charles 1991; Baker *et al.* 1990) suggests that little, if any, chronic acidification has occurred in the West. Nevertheless, the low base cation concentrations in many of these lakes may cause them to be more susceptible to acidic inputs than acidified lakes in the eastern United States, such as in Adirondack Park, New York (Eilers *et al.* 1989). Because of the dilute nature of lakes in the West, moderate concentrations of atmospheric contaminants, which would not be cause for concern for lakes in the eastern United States, could potentially cause water quality problems in dilute alpine and subalpine lakes in the West.

Laird *et al.* (1986a,b) reported concentrations of major ions and selected metals for alpine/subalpine snowpacks extending from the U.S./Canadian border to the southern Sierra Nevada. Generally, they found that anthropogenic sources were relatively insignificant in affecting the concentrations of  $\text{H}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  and other chemical constituents in the snow. One of the most striking patterns observed was the one for  $\text{NH}_4^+$ ; concentrations were low in the northern Washington Cascades, but increased abruptly in southern Washington, remained high through the Oregon Cascades, and then decreased again in the Sierra Nevada (Figure 1a). Laird *et al.* (1986a) attributed this pattern to removal of  $\text{NH}_4^+$  from

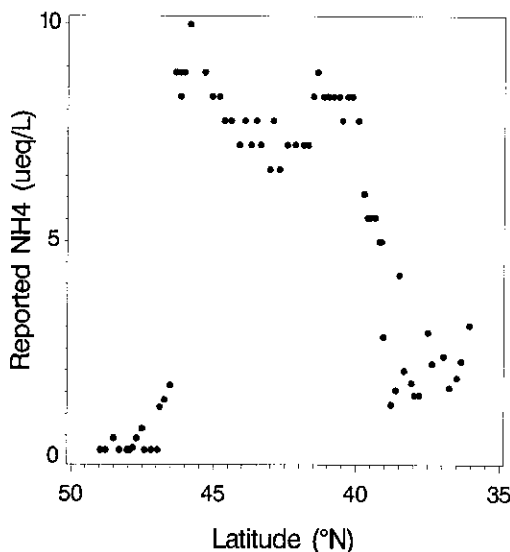


Figure 1a.  $\text{NH}_4^+$  concentrations in snow along a transect located on the crest of the Cascade-Sierra Nevada Mountains (derived from Laird *et al.* [1986b]).

snowfall in Washington and California caused by reaction with  $\text{SO}_2$  aerosols and consequent formation of ammonium bisulfate and ammonium sulfate. The  $\text{SO}_2$  presumably was derived from emissions near Puget Sound in Washington and urban areas in California. They assumed that the higher  $\text{NH}_4^+$  concentrations ( $[\text{NH}_4^+]$ ) reported for the Oregon and California Cascades (including the southern Washington Cascades) were natural. This manuscript explores alternative explanations to the high  $[\text{NH}_4^+]$  concentrations reported by Laird *et al.* (1986a,b) in the snowpack of the Cascade Mountains.

One alternate interpretation is that  $[\text{NH}_4^+]$  are at natural levels for the northern Washington Cascades, implying that  $[\text{NH}_4^+]$  in the southern Washington, Oregon and California Cascades either are elevated above background levels or are incorrect. Elevated nitrogen deposition has important implications for lakes in the Cascades because transient or long-term nitrogen limitation is increasingly recognized as an important feature of oligotrophic lakes in the West (Morris and Lewis 1988). Other examples of nitrogen-limited lakes reported in the West include Crater Lake (Larson 1988), Lake Tahoe (Goldman 1981), and Castle Lake (Axler *et al.* 1981).

In addition to serving as a nutrient,  $\text{NH}_4^+$  can act as an acidifying agent through biological assimilation of  $\text{NH}_3$  leaving up to one or two moles of  $\text{H}^+$  for each mole of  $\text{NH}_4^+$  (Schindler *et al.* 1985; Asman and Diederer 1987; Schuurkes and Mosello 1988). Lakes in the Cascades are considered highly susceptible to acidic deposition because they have extremely low base cation concentrations (some lakes have base cation concentrations  $< 20 \mu\text{eq/L}$ ) and alkalinity values that are as low as  $10 \mu\text{eq/L}$  in the fall (Landers *et al.* 1987) and even lower in the spring (Eilers *et al.* 1990). Thus, the potential for acidification of these lakes by  $\text{NH}_4^+$  is particularly high. The average  $[\text{NH}_4^+]$  reported by Laird *et al.* (1986b) for the Oregon Cascades is about  $8 \mu\text{eq/L}$ , equaling the combined concentrations of all other measured cations in the snow.

Here I re-examine information on deposition for the Cascade-Sierra Nevada ranges, with particular emphasis on  $\text{NH}_4^+$  deposition data for the Cascades as reported by Laird *et al.* (1986a,b). This analysis is accomplished by: 1) examining the internal consistency in the Laird *et al.* data; 2) comparing their data with results from other studies; and 3) evaluating potential sources of  $\text{NH}_4^+$ .

## Methods

The snow chemistry data reported in Laird *et al.* (1986a) were obtained from Laird *et al.* (1986b) and scanned directly into a computer file to avoid data entry errors. Concentrations of the various analytes were converted into equivalent units. The equivalent concentrations for individual ions and sums of anions and cations were plotted against one another and against latitude. The literature was reviewed for other relevant studies regarding deposition chemistry in the Cascade Mountains.

A further check on snow chemistry was made by collecting multiple snow cores at two sites in the Oregon Cascades. In April, 1989, I collected snow cores at Mt. Hood (elevation 1770 m) in the northern Oregon Cascades and near Willamette Pass (elevation 1680 m) in the central Oregon Cascades during the period of near-maximum snow accumulation. The cores were collected using a standard Soil Conservation Service stainless-steel corer identical to that used by the U.S. Geological Survey (USGS). The cores were kept frozen, and then melted and screened to remove particulates before shipment, and maintained near 4 to 9°C during transit to the laboratory. The samples were analyzed well within the holding times specified for the methods by Environmental Science and Engineering (ESE) chemists; anions were analyzed using ion chromatography (EPA Method 300.6); cations were analyzed using ICAP (EPA Method 200.7). Ammonium was measured with the automated phenate method (EPA Method 350.1) and pH and conductivity were measured using protocols specified for precipitation samples by the Illinois State Water Survey (Methods 150.6 and 120.6 respectively). ESE was selected to analyze the samples, in part, because they have considerable experience with analysis of precipitation samples for the Florida Acid Deposition Network and as contract laboratory for the National Dry Deposition Network. USGS chemists also analyzed several replicate samples from these recent snow cores.

## Results and Discussion

This re-examination of snow chemistry in the Cascade Mountains is divided into (1) an analysis of the internal consistency of the Laird *et al.* data, (2) a comparison of the Laird *et al.* data with other measurements of deposition chemistry in the region, (3) an assessment of natural and anthropogenic sources of nitrogen emissions, and (4) a brief examination of processes affecting atmospheric transport and transformation of ammonium in the atmosphere.

### Internal Consistency of Laird *et al.* Data

The quality of data can be evaluated in terms of precision (using replicate [i.e., split] samples), bias (using audit samples or comparison with standards), and detection limit (using blanks or a series of samples with incrementally lower concentrations). Laird *et al.* (1986a) reported a precision

of 0.008 mg/L (0.44  $\mu\text{eq/L}$ ) for  $\text{NH}_4^+$  (as  $\text{NH}_4^+$ ) for split samples and 0.003 mg/L (0.17  $\mu\text{eq/L}$ ) for duplicate snow cores. The detection limit for the  $\text{NH}_4^+$  analytical method was 0.003 mg/L. Both the analytical and field precision are indicative of high quality data. Samples from the USGS snow study were analyzed in random order with respect to their position in the transect, which should have minimized problems associated with spatially-related bias. No audit samples or standard reference material results were reported for  $\text{NH}_4^+$  and no information was presented regarding analytical bias.

The analytical accuracy of the results was evaluated by computing ion balances for the individual snow samples; the sum of anions was computed using  $\text{Cl}^-$  values corrected for transcription errors in the reported data (H. Taylor, U.S. Geological Survey, Denver, 1988, personal communication). The results show most samples with high cation excess (Figure 1b); however, cation-anion imbalance can also result from unmeasured ions not included in the summations. In surface waters, it is common to observe an anion deficit caused by lack of a direct measure of organic anions (e.g., Linthurst *et al.* 1986). In the Laird *et al.* data, neither organic anions or bicarbonate are included in the anion sum. Bicarbonate is an

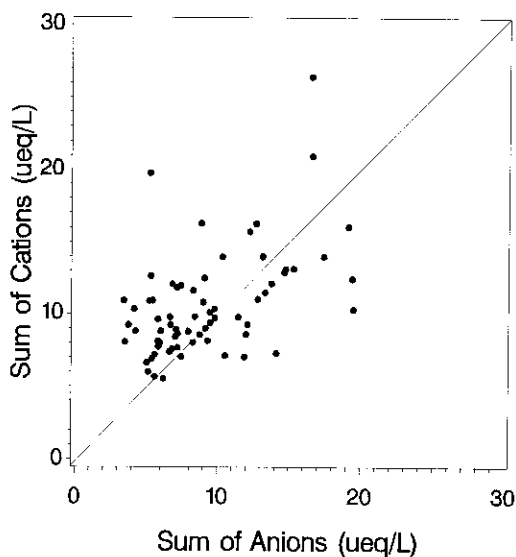


Figure 1b. Sum of measured cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{H}^+$ ,  $\text{NH}_4^+$ ) versus the sum of measured anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ) for the original data reported by Laird *et al.* (1986b) using observations with  $\text{Cl}^-$  values corrected for transcription errors. One observation  $>30 \mu\text{eq/L}$  omitted.

important anion in precipitation occurring in arid regions in the western United States where entrained soil particles can raise the pH to 6.0 or greater (NADP/NTN 1984-1990). In the Pacific Northwest, however, pH values are generally much lower; all pH values reported by Laird *et al.* were between 5.11 and 5.88 (median = 5.54). Bicarbonate concentrations, estimated using simplifying assumptions of Henry's Law (Butler 1982) could potentially equal about 3  $\mu\text{eq/L}$  for samples with high pH values (median  $[\text{HCO}_3^-] \sim 1.7 \mu\text{eq/L}$ ). There appears to be little association, however, between estimated  $\text{HCO}_3^-$  and reported  $\text{NH}_4^+$  ( $r = +0.15$ ) as might be expected if  $\text{HCO}_3^-$  was the principal unmeasured anion. Estimated  $[\text{HCO}_3^-]$  show a pattern of increased values in the middle of the transect, but the concentrations are far lower than required to balance the  $[\text{NH}_4^+]$  (Figure 1c).

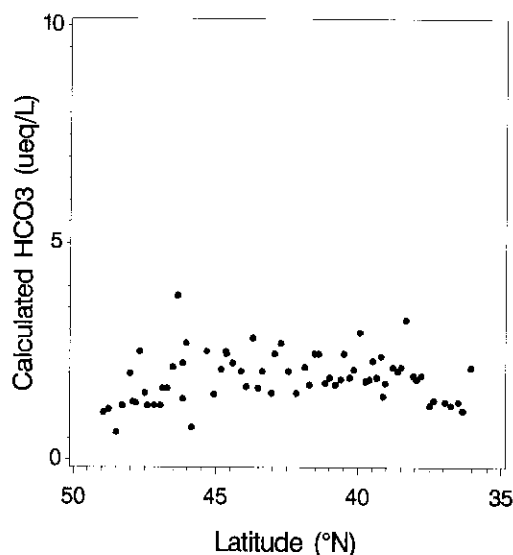


Figure 1c. Bicarbonate, estimated from pH reported by Laird *et al.* (1986b), plotted against latitude.

Organic anions can also be important constituents in precipitation samples. Keene and Galloway (1984) reported that concentrations of acetic and formic acids accounted for 16%, by volume, of free acidity in precipitation samples from Virginia; they estimated that organic acids in NADP/NTN samples, presently unmeasured, may represent 18-35% of the free acidity. Sickman and Melack (1989) reported concentrations of low-molecular weight organic anions (formate, acetate) ranging from 2.8 to 5.3  $\mu\text{eq/L}$  for snow pit samples in

the southern Sierra Nevada; acetate concentrations exceeded the concentrations of other measured anions. The cation-anion difference plotted against reported dissolved organic carbon (DOC) for the Laird *et al.* data show a significant positive relationship ( $r = +0.33$ ,  $P < 0.001$ ), but the relationship accounts for only 11% of the variance in the ion imbalance. An examination of organic anion concentrations computed from pH and DOC (Oliver *et al.* 1983) in Figure 1e shows little correspondence to the distribution of  $[\text{NH}_4^+]$  along the study transect shown in Figure 1a. Combining organic anions (estimated from DOC and pH) with the estimated  $\text{HCO}_3^-$ , however, the ion imbalance observed in Figure 1b is reduced (Figure 1d). A similar effect can be achieved by scoring all observations with reported  $\text{NH}_4^+$  exceeding  $1 \mu\text{eq/L}$  from sites north of latitude  $39^\circ$  to  $1 \mu\text{eq/L}$ , a concentration consistent with other measurements of  $\text{NH}_4^+$  for the region (Figure 1f). The ion imbalance in the Laird *et al.* data is not conclusive evidence of an analytical problem. Unmeasured anions, particularly organic acids, could account for much of the ion imbalance. However, the organic anions, as estimated from DOC, show little association with  $\text{NH}_4^+$  or with latitude.

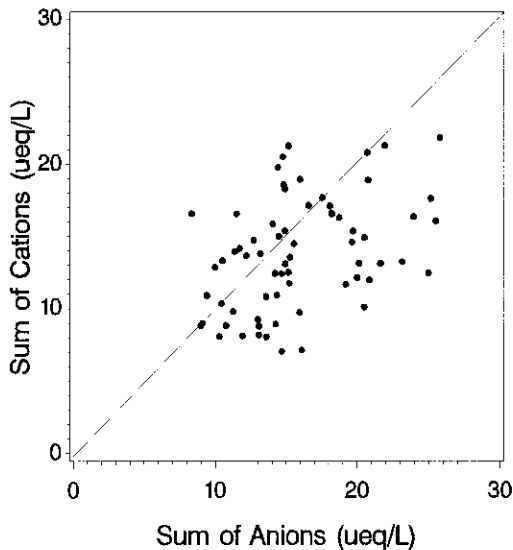


Figure 1d. Sum of measured cations versus the sum of measured anions from the original data reported by Laird *et al.* (1986b). The anion sum has been adjusted by using  $\text{Cl}^-$  values corrected for transcription errors and by adding estimates for bicarbonate and organic anions. Two observations  $> 30 \mu\text{eq/L}$  omitted.

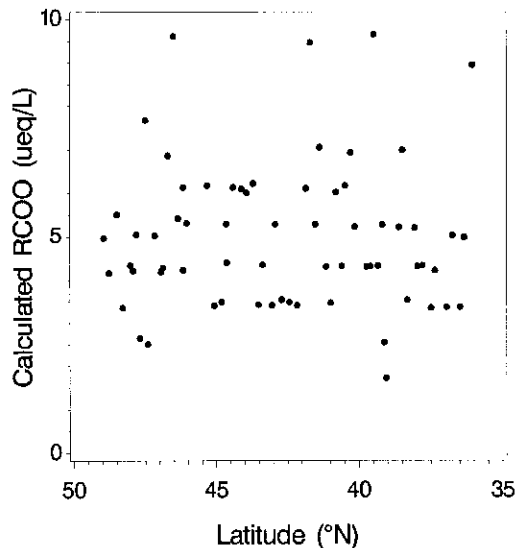


Figure 1e. An estimate of organic anions ( $\text{RCOO}^-$ ; Oliver *et al.* 1983) computed from the measurements of DOC and pH by Laird *et al.* (1986b) plotted against latitude. Three observations  $> 10 \mu\text{eq/L}$  omitted.

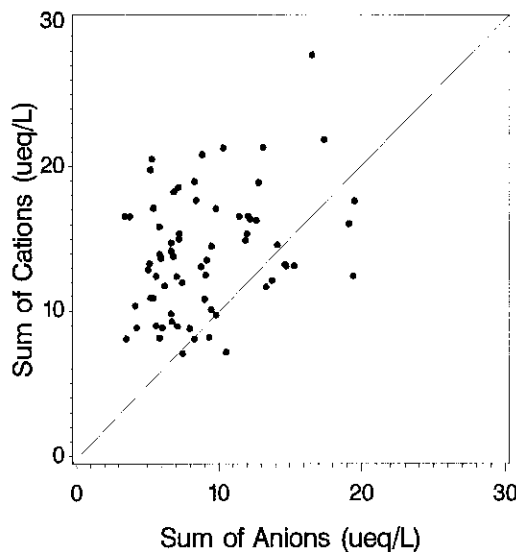


Figure 1f. Sum of measured cations versus the sum of measured anions in the snow data of Laird *et al.* (1986b).  $\text{Cl}^-$  transcription errors have been corrected and all  $\text{NH}_4^+$  concentrations greater than  $1 \mu\text{eq/L}$  for sites north of latitude  $39^\circ$  have been scored to 1.

Also of concern is the internal consistency of the summary statistics for  $\text{NH}_4^+$ , as presented by Laird *et al.* (1986a, Table VI). They reported median and mean concentrations of  $0.01 \text{ mg/L}$

(0.55  $\mu\text{eq/L}$ ) and 0.08 mg/L (4.4  $\mu\text{eq/L}$ ;  $n = 70$ ), respectively. I computed a mean  $[\text{NH}_4^+]$  equal to their reported value, but I computed a median concentration of 0.05 mg/L (2.5  $\mu\text{eq/L}$ ), five times the value reported by Laird *et al.* (1986a). The differences are not resolved by treating values reported at detection limit differently (e.g., scoring to zero, one-half of detection limit value, etc.) or by variations in treatment of duplicate samples. This inconsistency could be caused by a transcription error in either the final reported median value or a series of transcription errors in the individual  $\text{NH}_4^+$  observations.

### Comparison with Other Deposition Data

Another check on the accuracy of data can be made by comparing the Laird *et al.* snow data with information from other sources. Ammonium data, derived from snow sampling conducted at selected sites in the northern Washington Cascades and the southern Sierra Nevada (Sickman and Melack 1989), show close agreement with the data reported by Laird *et al.* (1986b). Sickman and Melack (1989) reported  $[\text{NH}_4^+]$  in snow (collected during maximum accumulation) ranging from 0.9 to 2.5  $\mu\text{eq/L}$  in 1987 and from 1.8 to 5.2  $\mu\text{eq/L}$  in 1988, at four watersheds in the Sierra Nevada. In comparison, Laird *et al.* (1986b) reported  $[\text{NH}_4^+]$  ranging from 1.1 to 2.8  $\mu\text{eq/L}$  for the 10 southernmost sites. Similarly, Loranger and Brakke (1988) reported  $[\text{NH}_4^+] < 1 \mu\text{eq/L}$ , in agreement with those of the 10 northernmost sites from Laird *et al.* Duncan *et al.* (1989) reported volume-weighted mean  $[\text{NH}_4^+]$  in bulk snow samples collected at two locations in the central Washington Cascades ranging from 0.3 to 1.1  $\mu\text{eq/L}$  at Stevens Pass (elevation 1525 m) and 1.5 to 3.5  $\mu\text{eq/L}$  at Snoqualmie Pass (elevation 1220 m) for 1983-1988, with annual median values of 0.75 and 1.64  $\mu\text{eq/L}$ , respectively. Laird *et al.* (1986b) measured  $[\text{NH}_4^+]$  ranging from detection limit to 0.66  $\mu\text{eq/L}$  at sites in the vicinity of these two Washington locations.

Some of the earliest snow chemistry measurements in the Oregon Cascades consisted of two snow samples collected adjacent to Waldo Lake (elevation = 1650 m, latitude = 43° 40') by Malueg *et al.* (1972). They reported  $[\text{NH}_4^+]$  of 1.4 and 0.8  $\mu\text{eq/L}$  for samples collected 1 m below the snow surface in February 1969 and 1970, respectively. Recent snow chemistry data in the Oregon Cascades are also available from bulk

deposition data collected at Crater Lake and from two snow cores collected north of Crater Lake. The weekly bulk deposition data collected at Crater Lake (site located near the park headquarters on the southwest rim of the caldera, elevation 2150 m), for the period November through March 1988 show  $[\text{NH}_4^+]$  in filtered samples of about 1.2  $\mu\text{eq/L}$  on a volume-weighted basis (Reilly 1989). In contrast, Laird *et al.* (1986b) reported  $[\text{NH}_4^+]$  at site 37 near Crater Lake of 7.8  $\mu\text{eq/L}$ .

I also collected snow core samples at two sites adjacent to sites sampled by Laird *et al.* (1986b). Laird *et al.* (1986b) reported  $[\text{NH}_4^+]$  concentrations of 8.3  $\mu\text{eq/L}$  and 7.8  $\mu\text{eq/L}$ , for sites near Mt. Hood (site 23) and Willamette Pass (site 33), respectively, whereas I found average concentrations of 1.7  $\mu\text{eq/L}$  and  $< 0.7 \mu\text{eq/L}$  for snow cores from the same locales (Table 1). The split samples of these recent cores showed close agreement between  $\text{NH}_4^+$  measured at a private laboratory (ESE) and USGS. Examination of other ions in the snow samples shows that most of these recent samples also exhibit an apparent anion deficit (Table 1). Hydrogen and bicarbonate ions account for about 1 to 5  $\mu\text{eq/L}$  in these samples, but do little to alter the anion deficit. It is likely that the majority of the anion deficit in these recent snow core samples is attributed to unmeasured organic anions.

Data from NADP/NTN (1984-1990) have been used extensively to characterize deposition chemistry in the United States. NADP/NTN maintains several sites adjacent to or on the western slopes of the Cascade-Sierra Nevada ranges (the number of operating sites varies among years). NADP/NTN reports moderately high  $[\text{NH}_4^+]$  for some of the sites in the central and southern Sierra Nevada (Table 2), which is consistent with the high proportion of agricultural land use west of the Sierra Nevada. The NADP/NTN data also show low  $[\text{NH}_4^+]$  for sites in western Oregon and Washington. Annual variability of  $\text{NH}_4^+$  at the sites receiving low ammonium deposition was about 1  $\mu\text{eq/L}$ . Variability of  $\text{NH}_4^+$  for sites in the West were among the lowest reported in the United States (Knapp *et al.* 1988), suggesting that annual variation cannot explain the deviations between  $\text{NH}_4^+$  data reported by Laird *et al.* (1986b) and other investigations.

Two potential problems arise when comparing NADP/NTN data with the Laird *et al.* data. As noted earlier, NADP/NTN deposition collectors in

TABLE 1. Analytical results of snow core, surface snow, and blank samples collected in the Oregon Cascades, April 1989. All analyses were completed by ESE<sup>a</sup> with the exception of the split samples analyzed for NH<sub>4</sub><sup>+</sup> by USGS<sup>b</sup>. Units for all ions are in  $\mu\text{eq/L}$ .

Site	Sample Type	pH	Conductivity ( $\mu\text{S}$ )	NH <sub>4</sub> <sup>+</sup>		Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
				ESE <sup>a</sup>	USGS <sup>b</sup>						
Mt. Hood <sup>c</sup>	Core	5.89	3.4	1.9	—	6.7	1.2	3.5	0.3	8.9	4.0
	Core	5.69	3.6	1.5	—	5.6	2.2	7.2	0.3	8.1	4.0
	Surface	5.33	3.4	2.3	2.2	3.0	1.6	3.3	0.5	3.9	5.3
	Blank	5.54	1.5	<0.7	0.2	0.2	0.6	<0.5	<0.1	<0.6	<0.8
Willamette Pass <sup>d</sup>	Core	5.51	2.7	<0.7	—	4.9	1.2	1.7	0.2	1.8	1.2
	Core	5.55	2.6	<0.7	—	4.5	1.3	1.9	0.2	2.6	1.2
	Core	—	—	—	0.9	—	—	—	—	—	—
	Blank	5.54	1.7	<0.7	—	0.3	0.7	<0.5	<0.1	<0.6	<0.8

<sup>a</sup>Environmental Science and Engineering, Inc., Gainesville, FL.

<sup>b</sup>U.S. Geological Survey, Arvada, Colorado. Results represent the mean of five replicate analyses.

<sup>c</sup>Samples collected on April 4 west of Timberline Lodge, latitude 45° 19' 50", longitude 121° 43' 01". Snow depth was approximately 5 m, but the corer only penetrated to about 2.5 m. ESE laboratory codes are ARLP\* 15 through 18; field codes are T-1 through T-4.

<sup>d</sup>Samples collected on April 2 west of Willamette Pass Ski Area, latitude 43° 35' 50", longitude 122° 02' 23". Snow depth was about 3 m. All cores penetrated to the soil layer. ESE laboratory codes are ARLP\* 11, 12, and 14; field codes are W-1, 2, 3, and 5.

TABLE 2. Mean annual (and winter quarter [Dec-Feb]) volume-weighted [NH<sub>4</sub><sup>+</sup>] for NADP/NTN sites located west of and adjacent to the Cascade-Sierra Nevada ranges (Source: NADP/NTN 1984-1990).

Site	Latitude	Elevation (m)	NH <sub>4</sub> <sup>+</sup> ( $\mu\text{eq/L}$ )					
			1983	1985	1986	1987	1988	1989
<i>Washington</i>								
Cascades National Park	48° 32'	120	—	—	1.1	1.1	0.6(0.6)	2.2(0.6)
La Grande	46° 50'	607	—	—	1.7	2.8(1.7)	1.1	3.3(0.6)
<i>Oregon</i>								
Bull Run	45° 27'	267	—	2.2(2.2)	1.7	3.3	2.2(1.1)	6.1(1.7)
H. J. Andrews Experimental Forest	44° 12'	436	—	0.6	1.1	1.1(0.6)	0.6(0.6)	1.1(1.1)
<i>California</i>								
Montague	41° 45'	805	—	—	5.0	5.0(3.9)	3.9(2.2)	6.1(6.1)
Yosemite National Park	37° 47'	1408	5.0	—	—	—	—	18.8
Sequoia National Park	36° 34'	1856	7.2	8.3(2.8)	14.4	—(5.5)	—(1.7)	15.5(4.4)

the West are typically located 1000 to 2000 m lower than the alpine and subalpine lakes. Deposition chemistry is expected to change with elevation as a consequence of a variety of processes including differences in dry and occult deposition, increasing distance from emission sources, and changing proportions of rain and snow. However, it is unlikely that sites at lower elevation would exhibit lower [NH<sub>4</sub><sup>+</sup>] than high elevation sites in the same vicinity. Blanchard *et al.* (1989), for example, found the [NH<sub>4</sub><sup>+</sup>] in deposition increased with

decreasing elevation along a transect in southern California (elevation ranged from 140 m to 2800 m). Another possible limitation of the NADP/NTN data for this comparison is the delay in collection and analysis of the precipitation samples from the buckets resulting in possible loss of nitrogen from the samples. It seems reasonable to assume, however, that delays would affect samples from all sites, not just those from selected sites in the transect. Thus, the presence of appreciable concentrations of NH<sub>4</sub><sup>+</sup> from the California NADP/NTN sites

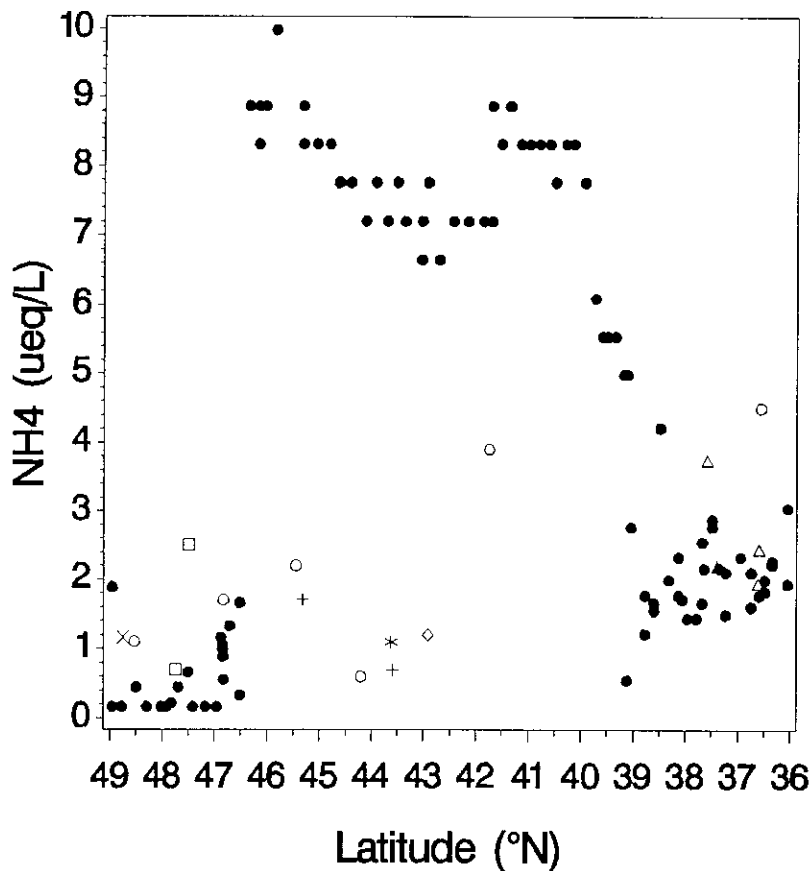


Figure 2.  $\text{NH}_4^+$  concentrations in snow reported by Laird *et al.* (1986a,b)(●), compared to precipitation and snow chemistry reported by NADP/NTN (1984-1989) (○); Duncan *et al.* (1989) (□); Loranger and Brakke (1988)(x); Malueg *et al.* (1972) (\*); Reilly (1989) (open diamond); Sickman and Melack (1989) (△); and this study (+).

suggests ammonium loss from the wet deposition samples is probably insufficient to explain the discrepancy between the USGS snow core data and the NADP/NTN precipitation data.

Other precipitation data for the West generally show  $\text{NH}_4^+$  concentrations that are comparable to concentrations reported by NADP/NTN; concentrations were generally less than  $1 \mu\text{eq/L}$  in western Oregon and slightly greater than  $2 \mu\text{eq/L}$  in western Washington (Junge 1958). Precipitation concentrations on the east side of the Cascades exceeded  $20 \mu\text{eq/L}$   $\text{NH}_4^+$  during the spring and summer, but these sites were located in agricultural areas with alkaline soils where  $\text{NH}_4^+$  emissions would be high and retention in the soils would be comparatively low. The data from these recently cited deposition studies, when plotted against the Laird *et al.* data (Figure 2), show a marked deviation

beginning near latitude  $46^\circ$  (southern Washington) and extending southward to latitude  $39^\circ$  (northern California).

#### Sources of $\text{NH}_4^+$

Ammonium is naturally emitted from soils and forest litter during denitrification. The rate of  $\text{NH}_4^+$  emission is, in part, a function of the pH of the media. Alkaline conditions favor emission of  $\text{NH}_4^+$ , whereas  $\text{NH}_4^+$  is more highly retained under acidic conditions. Thus, precipitation in areas of the Great Basin and the central United States contain greater  $[\text{NH}_4^+]$  than areas west of the Cascades (Junge 1963). The Spodosols, Inceptisols, and Ultisols in western Washington and Oregon are relatively low in base saturation and pH and these soils would not be considered major sources of  $\text{NH}_4^+$  to the Cascades.

Anthropogenic sources of  $\text{NH}_4^+$  can be significant in some areas. For example, feedlots (beef, hogs, poultry) and dairy operations are principal sources of  $\text{NH}_4^+$  affecting surface waters in the Netherlands (Schuurkes and Mosello 1988). In the Pacific Coast states, livestock densities were greatest in the Sacramento/San Joaquin Valley of California which may explain, in part, the higher  $\text{NH}_4^+$  deposition measured at NADP/NTN sites located east of the valley. Three of the four largest cattle-producing counties in California were located in the San Joaquin Valley upwind of the Sierra Nevada. Livestock densities in California exceeded those in Oregon by a factor of 2 for beef cattle, 5 for dairy cattle, and 14 for poultry; densities for hogs and sheep were comparable (Hornbeck 1983; Jackson 1975). Most livestock operations in California are also located in the central valley upwind of the Sierra Nevada, whereas there is a more uniform distribution of livestock on either side of the Oregon Cascades.

Combustion of vegetation and wood products also can be a significant source of nitrogen emissions. Wood burning for home heating purposes, however, appears to be insignificant relative to the magnitude of the  $[\text{NH}_4^+]$  differences along the transect. Potassium, often associated with combustion of wood products, showed no concomitant increase with  $\text{NH}_4^+$  in the Laird *et al.* data. Furthermore, emissions inventories of  $\text{NO}_x$  (Wagner *et al.* 1986) are inconsistent with the spatial patterns in  $\text{NH}_4^+$  reported by Laird *et al.* (1986a). California ranked 2nd in the United States in  $\text{NO}_x$  emissions (1.4M tons/yr), compared to only 0.29M ton/yr for Washington (rank 30th) and 0.23M tons for Oregon (rank 37th). There appears to be no major source of  $\text{NH}_4^+$  to explain the relatively high concentrations in the Cascades reported by Laird *et al.* (1986a,b).

#### Transport and Transformation of $\text{NH}_4^+$

The mechanism for supposedly lower  $[\text{NH}_4^+]$  in Washington and California offered by Laird *et al.* (1986a) is inconsistent with the behavior of  $(\text{NH}_4)_2\text{SO}_4$  particulates. They suggested that  $\text{SO}_2$  emissions at the northern and southern ends of the transect oxidized and reacted with ammonia, forming ammonium bisulfate and ammonium sulfate which subsequently deposited before reaching the mountains. However, ammonium sulfate particulates are easily transported. Data from visibility

monitoring sites show that ammonium sulfate particulates account for about 20 to 50% of the fine particulate mass in the West (Trijonis *et al.* 1990). The widespread distribution of ammonium sulfate particulates in the United States is evidence of the ease with which  $[\text{NH}_4^+]$  is transported great distances. Yet visibility along the transect is greatest at the Crater Lake visibility monitoring site with a median visual range of 176 km (Energy and Resource Consultants, Inc. 1988), suggesting that ammonium sulfate particulates and ammonium deposition rates in the Oregon Cascades are very low. Thus, although ammonium sulfate aerosols are formed as a consequence of  $\text{SO}_2$  emissions, there is no evidence that this process disproportionately affects the ammonium concentrations in the snow along the transect.

#### Summary and Conclusions

Laird *et al.* (1986a) speculated that the pattern of  $\text{NH}_4^+$  concentrations in snow along the crest of the Cascade-Sierra Nevada was caused by a loss of  $\text{NH}_4^+$  at both ends of the transect. Data from areas with low deposition of  $\text{SO}_4^{2-}$  strongly suggest that  $[\text{NH}_4^+]$  are naturally low in northern Washington. Rather than being low as a consequence of anthropogenic emissions of  $\text{SO}_2$ ,  $\text{NH}_4^+$  deposition in the southern Sierra Nevada appears to be elevated above natural levels (NADP/NTN 1984-1990; Blanchard *et al.* 1989).

Based on a re-examination of these and other data, I conclude that the relatively high  $[\text{NH}_4^+]$  reported for the Cascades by Laird *et al.* are incorrect and that the highest  $[\text{NH}_4^+]$  in deposition in this region occurs in the southern Sierra Nevada. The evidence to support this conclusion includes (1) the internal inconsistency of Laird *et al.* data; the ion imbalance is inconclusive evidence of an analytical error, but the lack of agreement in reported and calculated median  $[\text{NH}_4^+]$  is very suspicious; (2) the inconsistency between Laird *et al.* data and deposition data from several independent sources (Junge 1958; NADP/NTN 1984-1990; Maleug *et al.* 1972; Reilly 1989; this study); USGS reports an average  $[\text{NH}_4^+]$  of 8  $\mu\text{eq/L}$  for the Oregon Cascades compared to values near 1  $\mu\text{eq/L}$  for other studies; (3) the lack of appreciable sources of natural and anthropogenic emissions of nitrogen in Oregon; livestock densities and fertilizer-intensive crops are substantially lower in Oregon compared to California, which explains

the higher concentrations of  $\text{NH}_4^+$  in the Sierra Nevada; and (4) the lack of realistic mechanisms for transporting and transforming nitrogen species; ammonium sulfates are capable of being transported considerable distances, yet ammonium sulfate particulate concentrations are very low in Oregon. Available evidence indicates that  $[\text{NH}_4^+]$  in snow in the Oregon Cascades are lower than values reported by Laird *et al.* by nearly an order of magnitude and are generally about  $1 \mu\text{eq/L}$ .

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