

SENSITIVITY TO ACIDIFICATION OF FOUR ALPINE BASINS ON DIFFERENT BEDROCK



MT. WASHINGTON, NEW HAMPSHIRE

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Abstract

Previously, the acidification of fresh water alpine environments had not yet been studied in the northeastern U.S., despite the high rates of continued acidic deposition in the region. Consequently, the objectives of this study were, first, to determine the present sensitivity to acidification of four alpine basins on Mt. Washington, New Hampshire (Great Gulf, Oakes Gulf, Huntington Ravine, and Tuckerman Ravine); and, second, to assess the relative proportions of dissolved solutes observed in alpine stream water attributable to wet deposition or bedrock weathering. Two of the four basins included in this study lie within Class I Wilderness areas, which are to be protected, under federal legislation, from environmental degradation resulting from contaminated atmospheric deposition.

Stream water in the four alpine basins was sampled on a weekly basis over the summer of 2001 and analyzed for major cations and anions. Measures of sensitivity to acidification included $\text{pH} < 6$, acid neutralizing capacity $< 25 \text{ eq/L}$, low base cation:H ion ratio, and base cation:strong acid ion ($\text{SO}_4 + \text{NO}_3$) ratio < 1 . A correlation analysis was used to identify trends in dissolved solute concentrations and possible causal relationships. In order to quantify net losses of each solute from the basins, mean concentrations of dissolved solutes in stream water were compared to mean concentrations in wet deposition (input). Molar ratios of cations and Si in the resulting net output for each basin were compared to molar ratios of elements typical of the underlying bedrock in order to determine the contribution of weathering byproducts to observed stream chemistry.

Stream water analyses indicated that Mt. Washington's alpine zone is sensitive to acidification. The Great Gulf showed signs of nitrogen saturation, while Oakes Gulf, Huntington Ravine, and Tuckerman Ravine exhibited symptoms of sulfur saturation and possible Al-leaching. These conditions inhibit the capacity of a system to buffer strong acid ions, rendering these basins more sensitive to pH fluctuations under continued acidic deposition.

Results from this study indicate that weathering of the underlying bedrock was a stronger control on the observed stream water chemistry than input of dissolved solutes from wet deposition. Chemical weathering was the most likely source of base cations to stream water and was a likely source of strong acid ions in Oakes Gulf and Tuckerman Ravine. Basins whose bedrock contained sulfidic minerals less efficiently neutralized incoming acidifying compounds and were characterized by SO_4 -leaching and low base saturation of soils. Furthermore, the structural geology of the alpine basins played an important role in governing their sensitivity to acidification by controlling the hydrologic residence time and thus influencing the rate of geochemical interactions.



Introduction

Acidic deposition and its effects on terrestrial and aquatic environments in the northeastern United States has become a major focus of scientific research over the last few decades. Since acidic precipitation was first reported in North America by researchers at the Hubbard Brook Experimental Forest, its detrimental effects on natural systems have been widely noted (Driscoll et al. 2001). The long-term ecological consequences of acidic deposition on forested ecosystems are thought to include increased nitrate (NO_3) and aluminum (Al) mobility, leaching of exchangeable base cations, soil and stream acidification, and decreased forest growth rates, which may eventually lead to increased forest mortality (Aber et al. 1998). The recent decline of the northeastern red spruce is a prime example of the deleterious effects of acidic deposition (Driscoll 2001).

The deposition of both NO_3 and sulfate (SO_4) is primarily responsible for the acidification of freshwater environments (e.g. Galloway et al. 1983; Murdoch and Stoddard 1992). Studies in the Catskill Mountains of New York have determined that nitric acid is pivotal in controlling headwater stream acidification (e.g. Murdoch and

Stoddard 1992). Murdoch and Stoddard (1992) found that because high NO_3 concentrations tend to coincide with low pH during spring snowmelt, nitric acid may contribute significantly to the creation of toxic conditions for aquatic biota. Their study also reported that the release of NO_3 during snowmelt is believed to have increased since 1970. Furthermore, the continual addition of NO_3 to natural systems may cause nitrogen saturation, which results in the lack of nitrogen retention, even during the growing season. The ensuing mobilization of NO_3 s often results in the acidification of soils and streams (Wigington et al. 1996; Aber et al. 1998).

Similarly, sulfur saturation has been linked to reductions in stream water alkalinity, which results in long-term acidification of natural systems (Galloway et al. 1983). As available sources of base cations are depleted through cation exchange, or if weathering rates cannot produce a sufficient release of these solutes, neutralization of H^+ ions becomes inefficient and mobilization of Al results (Cronan and Schofield 1990). Consequently, base cation leaching is associated with early stages of sulfur-saturation; however, as stream acidification progresses, the ratio of base cations: H^+ decreases while SO_4 output remains high (Galloway et al. 1983). This rapid removal of base cations will eventually reduce the ecosystem's acid neutralizing capacity (ANC), further sensitizing the system to continued acidic deposition (Wigington et al. 1996).

Acidification of stream water is compounded by the fact that acidic waters facilitate chemical weathering of rock material, which can be an additional source of strong acid ions to an ecosystem. The weathering of sulfur-containing minerals in bedrock, for example, can contribute SO_4 to stream water, exacerbating the effects of atmospheric deposition (Alewell et al. 1999).

Alpine watersheds are particularly sensitive to acidification since high elevation sites tend to receive greater doses of nutrients and contaminants than comparison low elevation sites. Harsh environmental conditions and a short growing season at high-elevation make alpine vegetation extremely sensitive to chemical inputs (Weathers et al. 2000); and studies in the Rocky Mountains have shown that the alpine zone is more sensitive to moderate rates of acidic deposition than forested areas (Campbell et al. 2000). Furthermore, as snow-dominated environments, alpine watersheds are susceptible to a seasonal ionic pulse from snow melt, during which high concentrations of dissolved solutes, especially the strong acid ion NO_3 , are released into stream runoff (Melack and Sickman 1995; Baron and Campbell 1997). Limited contact time between water and soil or bedrock and a short plant growing season, impede the consumption or neutralization of NO_3 , making alpine areas prone to nitrogen saturation and NO_3 -leaching (Fenn et al. 1998).

Limited soil accumulation and sparse vegetation require the release of base cations through chemical weathering to act as the dominant process by which acidic input is neutralized (Galloway et al. 1983). Various studies of high-elevation catchments in the Sierra Nevada have reported the importance of geochemical processes in regulating the chemistry of alpine stream water despite steep slopes and short hydrologic residence time (e.g. Williams et al. 1993; Meixner et al. 1998; Meixner et al. 2000). Bricker and Rice (1989) and Hyman et al. (1998) determined that the underlying bedrock plays a substantial role in controlling stream water chemistry in the eastern U.S. as well. Yet Driscoll et al. (2001) noted that the rates of base cation release through chemical

weathering may not sufficiently keep pace with leaching rates in areas where acid-loading is occurring, increasing the sensitivity of these areas to acidification.

The present study focuses on the sensitivity to acidification of four alpine basins on Mt. Washington, New Hampshire. This area is of particular interest because of the high rates of acidic deposition in the northeastern U.S. (Appalachian Mountain Club, *personal communication*) and because Mt. Washington's height makes it one of the few mountains in New England with discrete watersheds that lie above tree line in the alpine zone. Furthermore, the Class I Wilderness status (Federal Clean Air Act) of Mt. Washington's north- and south-facing slopes, the Great Gulf Wilderness and Presidential Dry Wilderness Areas respectively, requires that these areas be protected from environmental degradation resulting from contaminated atmospheric deposition. Yet unpublished results from a stream sampling survey conducted by Hill and Eagar (1995-1997) showed that alpine streams on Mt. Washington had significantly lower pH and lower Ca concentrations than comparison small streams in the region; and high-elevation sites in Mt. Washington's Great Gulf had some of the highest reported NO₃ concentrations in 1997, with only 5% of streams in the region at higher levels.

This study addresses two principle questions. First, are the headwall streams of Mt. Washington's alpine cirques sensitive to acidification? Second, to what extent do wet deposition and bedrock weathering contribute to the stream water chemistry? In order to answer these questions the following steps were taken: (1) a correlation analysis of major cations and anions in stream water collected over the summer of 2001 from four alpine watersheds; (2) a comparison of predicted wet deposition input and observed output of

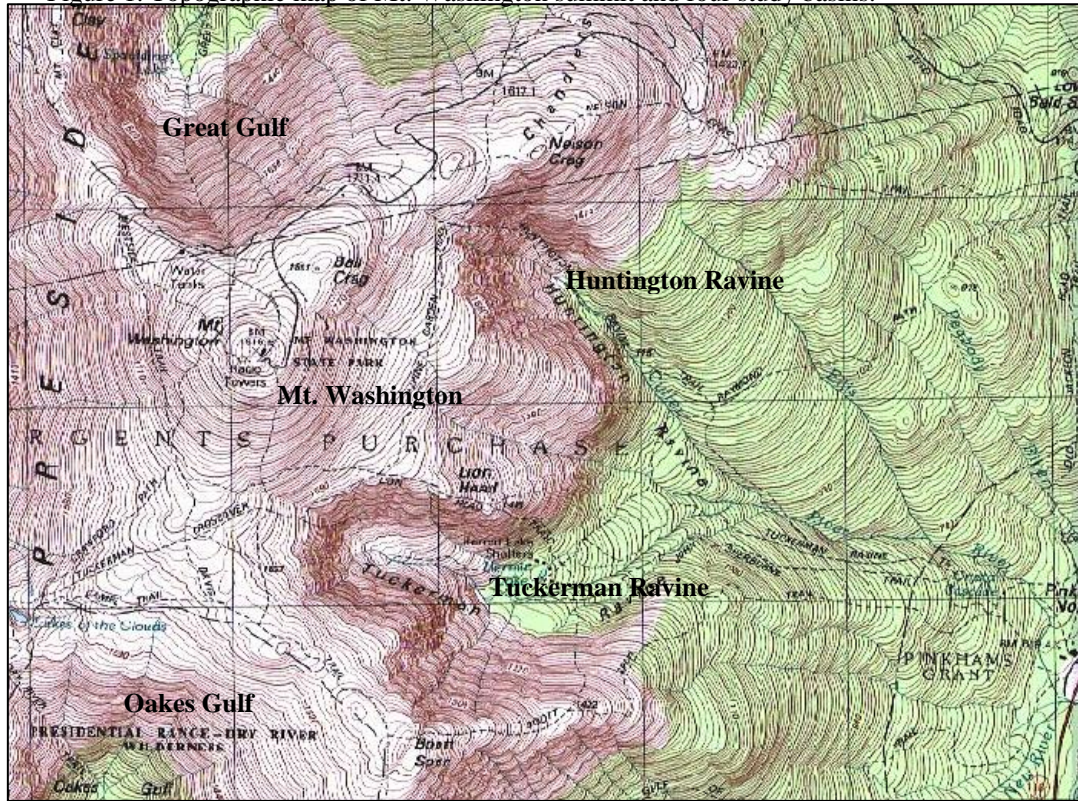
dissolved solutes in alpine stream water; and (3) a comparison of molar ratios of dissolved solutes found in Mt. Washington bedrock to ratios found in alpine streams.

Site Description

The four alpine basins included in this study are glacier cut cirques on Mt. Washington, New Hampshire (Figure 1). Mt. Washington, which forms part of the Presidential Range in the White Mountain National Forest, is the northeastern United States' tallest mountain, peaking at 1917 m, and is one of the area's most popular destinations for outdoor recreation. The summit is reached by various foot trails, an auto road, and a cog railway and is the permanent site of a visitor center, museum, weather observatory, and television station. The mean yearly temperature on the summit is -3.1° C and the mean wind speed is 56.8 kph, blowing predominantly from the west. The mean total yearly precipitation is 251.4 cm for melted deposition and 645.2 cm for snow, ice pellets, and hail (Mount Washington Observatory).

The Great Gulf, the mountain's north-facing cirque, and Oakes Gulf, one of the south-facing cirques, lie within two class I wilderness areas, which are known as the Great Gulf Wilderness and the Presidential Dry River Wilderness respectively. The Federal Clean Air Act mandates that wilderness areas be protected from terrestrial and aquatic environmental degradation resulting from contaminated atmospheric deposition. Consequently, in order to gain an understanding of the sensitivity of these alpine areas to acidic deposition, and assist in the direction of future policy decisions regarding regional

Figure 1. Topographic map of Mt. Washington summit and four study basins.



air quality, concentrations of dissolved solutes were measured in the streams that course through the Great Gulf, Oakes Gulf, and two other alpine watersheds. The sampling sites in the Great Gulf and Oakes Gulf are at 1228 m and 1374 m elevation, respectively (elevation measured with hand-held GPS unit). Basin areas are 6.51 km² and 3.67 km², respectively.

The other cirques included in this study, Huntington and Tuckerman Ravine, lie along Mt. Washington's eastern slopes and fall under the jurisdiction of the Mt. Washington State Park. Sampling sites in these ravines are at 1198 m and 1247 m elevation, respectively (elevation measured using hand-held GPS unit). The basin areas of the ravines are 11.21km² and 12.8km², respectively. All four streams included in this study are first order. The four cirques are ascended by hiking trails that tend to follow the

course of the basin headwalls' streams. Huntington and Tuckerman Ravine are especially popular recreational destinations for hikers, climbers, and backcountry skiers.

Vegetation

Vegetation is sparse in Mt. Washington's alpine zone, which begins at approximately 1250-1350 m. Plant communities include sedge meadow, dwarf shrub and heath, snowbank, spruce and alder, and krummholtz (Slack and Bell 1995; Appalachian Mountain Club, *unpublished data*). Spruce and alder and krummholtz are the largest plants in the alpine zone but are still small in comparison to subalpine vegetation. Much of the study basins' headwalls is exposed bedrock or talus and lacks vegetation (*personal observation*).

Geology

The bedrock geology characteristic of the Great Gulf's alpine zone is a substratigraphy of the Rangeley formation known as the Mt. Clay member. Of Silurian origin, the rock was later metamorphosed and is best characterized as a gray migmatitic orthogneiss with abundant calc-silicate lenses. The mineral composition includes quartz, plagioclase, feldspar, biotite, muscovite, chlorite, sericite, sillimanite, garnet, and ilmenite. The Mt. Clay member is distinguished from other substratigraphies by its interspersed layers of quartz + feldspar and black biotite-rich schist (Eusden et al. 1996).

The upper parts of the headwall are underlain by two members of the Devonian Littleton formation: the Great Gulf member and the Cow Pasture member. The former is a well-bedded schist and quartzite, and the latter is almost entirely schist with only 10%

quartzite. The mineral assemblage of the schist includes quartz, muscovite, biotite, plagioclase, chlorite, sericite, sillimanite, ilmenite, tourmaline, staurolite, and garnet (Eusden et al. 1996).

The Oakes Gulf headwall is composed of the Bigelow Lawn member of the Littleton formation, the Silurian Madrid formation, and the Silurian Smalls Falls formation. As in the Great Gulf, the Littleton rock in Oakes Gulf is mostly schist with a small proportion of quartzite and rare calc-silicate lenses. Actinolite, quartz, biotite, plagioclase, sphene, and garnet make up the fine-grained granofels of the Madrid formation (Eusden et al. 1996). Pyrite has been detected in the layers of schistose granofels (Billings et al. 1946), which alternate with calc-silicate granofels typical of this formation. The Smalls Falls formation is an easily weathered, well-foliated schist composed of less than 5% quartzite. The mineral composition includes quartz, plagioclase, biotite, muscovite, chlorite, and sericite. The small area of Oakes Gulf's subalpine zone that was included in the sampling site's upstream catchment area lies atop the Rangeley formation (Eusden et al. 1996).

The Tuckerman Ravine and Huntington Ravine members of the Littleton formation constitute most of Huntington Ravine's bedrock. Both members are well-bedded schists and quartzites (Eusden et al. 1996).

Tuckerman Ravine bisects a variety of Littleton formation members, as well as the Madrid, Smalls Falls, and Rangeley formations. The ravine also encompasses a thin strip of the Perry Mountain formation, which is a dark gray schist interbedded by nearly 40% quartzite. This formation includes quartz, plagioclase, biotite, muscovite, chlorite, and sericite (Eusden et al. 1996).

Methods

Precipitation was collected, beginning in June and continuing through August, in Nalgene FLPE bottles. The collection site is near the Appalachian Mountain Club's (AMC) Lakes of the Clouds hut, located atop the Presidential Range, between the summits of Mt. Washington and Mt. Monroe. Samples were refrigerated before transport and analysis.

Stream sampling sites were chosen such that the upstream catchment area would fall predominantly within the alpine zone. However, in order to ensure that stream flow was detectable where sampling was performed, most sites were located just below tree line, resulting in the inclusion of some subalpine vegetation in the upstream catchment area. All sites were within twenty meters of the trail. Site elevations were determined using a hand-held GPS unit.

The four headwall streams were sampled on a weekly basis beginning in June or July and lasting through the end of August. Samples were collected in 250mL Nalgene LDPE bottles that were rinsed three times with stream water immediately prior to sampling. All bottles had previously been acid washed using a 10% HCl solution and subsequently rinsed six times with DI water.

pH analysis of both rain and stream water was performed at the AMC's Lakes of the Clouds hut and at the Pinkham Notch research station at the base of Mt. Washington. Lakes of the Clouds used a Portable Orion Model 230A. The pH analyzer used at Pinkham Notch was a Fisher ACCUMET Model 830. A small aliquot of each sample was

allowed to warm to room temperature before pH was measured. The remainder of the sample was refrigerated until it was transported to the USDA-Forest Service, Northeastern Research Station, Louis C. Wyman Forest Sciences Laboratory in Durham, NH. There, concentrations of Ca, Mg, Na, K, and M-Al were measured using Inductively Coupled Plasma Atomic Emission Spectrometry. SO_4 was analyzed with a methylthymol blue reaction; NO_3 was analyzed using a copper cadmium reductor column, Marshall Reagent; Cl was analyzed using a ferricyanide, ferric thiocyanate reaction; and SiO_2 was analyzed with a molybdenum blue reaction.

Because alkalinity was not directly measured in the field, the acid neutralizing capacity (ANC) was estimated by subtracting the sum of SO_4 , NO_3 , and Cl concentrations from the sum of the base cations (Ca, Mg, Na, and K) (Martins et al. 2000). Correlation analysis was used to detect associations and trends among the dissolved solutes measured in Mt. Washington stream water. A 99% significance level was used for all statistical analysis. An α of 0.1000 was used to distinguish partial significance.

In order to predict the relative contribution of wet deposition to the observed stream chemistry, Cl was considered conservative (Likens and Bormann 1995). An evapoconcentration factor was calculated for each study basin by dividing the concentration of Cl for each stream by the Cl concentration of precipitation and then taking the mean. These mean evapoconcentration factors were then multiplied by observed concentrations of cations and anions in precipitation in order to predict the dissolved solute concentrations in stream water that are attributable to input by wet deposition.

Results

Wet Deposition Analysis

The mean pH of rainwater for the summer of 2001 was 4.31. Mean concentrations of major cations and anions measured in precipitation collected at Lakes of the Clouds during the summer of 2001 are listed in Table 1. H is the dominant ion, constituting 34.5% of the total dissolved solute concentration, followed by NH₄, which constitutes 12.2% of the total concentration. SO₄ represents 23.4% of the total dissolved solute concentration and NO₃ 11.6%. None of the base cations exceeds 4% of the total concentration. Consequently, the mean base cation:H volume-weighted ratio is 0.66, and the mean base cation:SO₄+NO₃ volume-weighted ratio is 0.51. The mean concentration of Al is less than 1 ueq/L, and the SiO₂ concentration in rainwater is negligible. Mean volume-weighted ratios of Ca:Na and Ca:Al in wet deposition are 1.80 and 11.93 respectively.

Table 1. Mean, min, and max dissolved solute concentrations in wet deposition and alpine headwall streams for the summer of 2001, reported in ueq/L. SiO₂ measured in mg/L.

Solute	Wet Deposition (n=25; *n=20; **n=24)			Great Gulf (n=12; *n=11)			Oakes Gulf (n=14; *n=12)			Huntington Ravine (n=10; *n=9)			Tuckerman Ravine (n=9; *n=8)		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
H ⁺	*49.46	10.00	158.49	*1.47	0.62	2.30	*3.21	0.69	7.94	*2.00	0.52	4.68	*2.73	0.78	5.62
Ca ²⁺	5.70	0.21	46.80	63.95	55.03	74.24	37.78	27.25	47.19	36.02	31.01	48.26	31.68	28.32	36.27
Mg ²⁺	1.82	0.07	11.00	44.17	40.14	49.29	17.70	12.17	22.26	27.83	24.70	38.93	23.12	19.70	26.46
Na ⁺	5.53	0.52	62.03	20.39	17.48	22.72	15.21	10.57	21.80	16.22	13.51	22.04	13.57	11.22	16.33
K ⁺	4.59	3.43	7.73	7.55	6.64	8.43	4.97	2.62	10.03	7.44	6.26	9.67	6.01	5.09	6.95
Al ³⁺	0.74	0.00	5.59	0.38	0.13	1.23	5.10	3.40	10.62	2.26	1.39	3.89	1.70	0.27	4.29
NH ₄ ⁺	17.48	1.76	61.66	0.25	0.00	0.59	0.59	0.00	2.94	0.59	0.00	1.76	0.59	0.00	5.28
SO ₄ ²⁻	**33.46	1.67	125.19	53.10	46.03	58.32	62.28	54.37	78.74	45.22	42.91	47.49	39.97	33.12	46.45
NO ₃ ⁻	16.62	1.43	64.25	47.12	39.27	55.69	10.96	9.28	14.99	23.49	20.70	28.56	21.89	19.99	23.56
Cl ⁻	**7.77	1.13	104.38	18.06	13.26	24.26	5.56	2.26	11.00	3.44	2.26	4.23	7.68	5.64	9.59
SiO ₂	0.07	0.00	0.25	2.40	2.18	2.57	2.81	1.92	3.30	2.86	1.47	3.19	2.14	0.24	2.58

Stream Water Analysis

Great Gulf: The mean pH and mean estimated ANC of the Great Gulf headwall stream are 5.88 and 17.79 ueq/L respectively. These are the highest values of any of the alpine basins included in this study (Table 2). The corresponding mean H ion concentration is only 1.47 ueq/L. The lack of correlation between the H ion concentration and the ANC suggests that the ANC is not pH dependent in this watershed.

The headwall stream of the Great Gulf is characterized by concentrations of Ca, Mg, Na, K, NO₃, and Cl that are much higher than those typical of the other three basins studied (Table 1). The mean concentrations of these solutes are 63.95 ueq/L, 44.17 ueq/L, 20.39 ueq/L, 7.55 ueq/L, 47.12 ueq/L, and 18.06 ueq/L respectively. Ca, representing 24.9% of the stream's dissolved solute concentration, is the headwall stream's dominant cation. Mg and Na, in comparison, constitute only 17.2% and 7.95% respectively of the total concentration.

NO₃, although it represents less of the dissolved solute concentration than SO₄, is more strongly correlated with the base cation concentration of the Great Gulf headwall stream. NO₃ constitutes 18.4% of the stream's dissolved solute concentration while SO₄ constitutes 20.7%. Very high positive correlations were observed between NO₃ and Ca, Mg, or SiO₂. SiO₂ also exhibits strong positive correlations with Ca and Mg (Figure 2). SO₄, on the other hand, exhibits much weaker correlations with the individual base cations and with SiO₂, but is more strongly and negatively correlated with the stream's ANC than NO₃ (Figure 3).

Additional measures of sensitivity to acidification include the base cation:H and base cation:SO₄+NO₃ volume-weighted ratios, which are 112.10 and 1.36 respectively for the Great Gulf. The headwall stream's Ca:Na volume-weighted ratio, which is a measure of preferential chemical weathering, is 3.14 and is higher than the Ca:Na ratios of wet deposition and of the other three basins (Table 2). The Ca:Al volume-weighted ratio, which is a measure of preferential cation exchange and/or weathering, is 252.65.

Oakes Gulf: Oakes Gulf has the lowest mean pH (5.58) and the only negative mean ANC (-3.15 ueq/L) of the four study basins (Table 2). The stream's ANC also exhibits the largest variance of the four watersheds.

As in the other basins, Ca is the dominant cation, constituting 23.1% of the total dissolved solute concentration in stream water. Mg and Na, whose mean concentrations are not significantly different from each other (P=0.0399), are the next most abundant. Together they constitute just over 20% of the dissolved solute concentration. The base cations, especially Ca and Mg, exhibit positive correlations with the ANC and SiO₂ and negative correlations with H (Figures 4 & 5). The SiO₂ concentration is also positively correlated with the ANC (Figure 4).

Al is much more abundant in the Oakes Gulf headwall stream than in any of Mt. Washington's other alpine watersheds (P<0.0001; [1.344, 2.286]) and contributes more to the dissolved solute concentration of the stream than K. The mean concentration of Al in Oakes Gulf is 5.10 ueq/L and is positively correlated with H and inversely related to the ANC (Figure 6).

Figure 2a. Great Gulf.

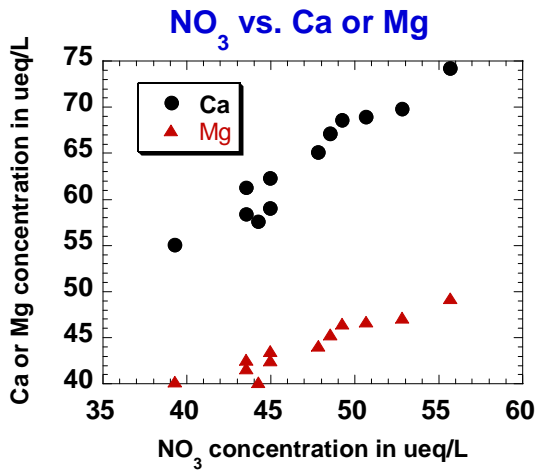


Figure 2b. Great Gulf.

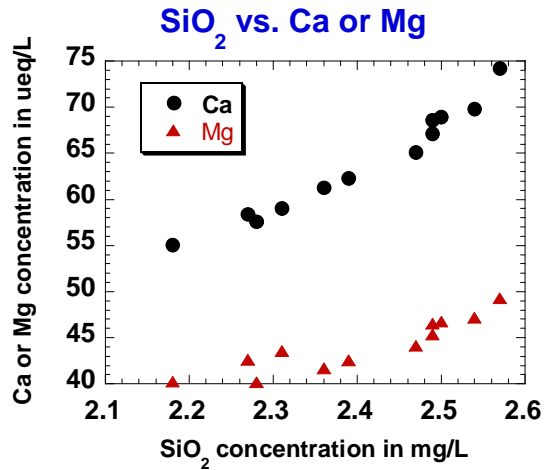


Figure 2c. Great Gulf.

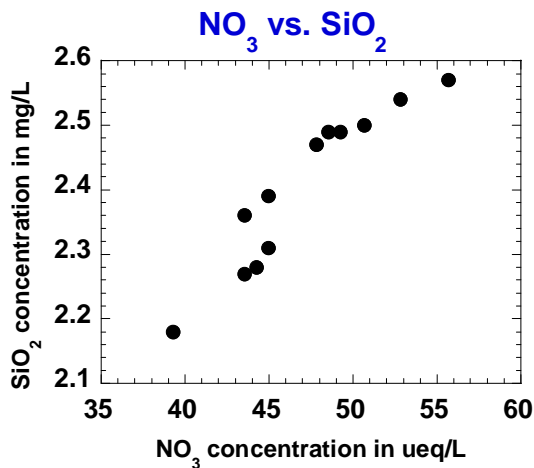


Figure 3. Great Gulf.

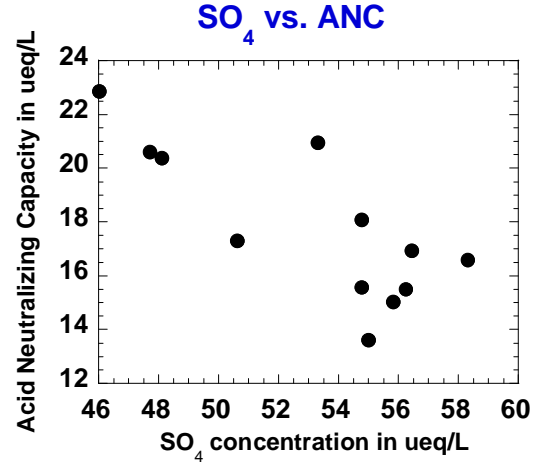


Table 2. Measurements of sensitivity to acidification in the alpine basins.

Measurement	Great Gulf			Oakes Gulf			Huntington Ravine			Tuckerman Ravine		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
BC:20 ⁺ +NO ₃	1.30	1.1	1.40	1.02	0.72	1.41	1.38	1.01	1.81	1.31	1.01	1.31
BC:H	115.10	20.70	531.12	30.7	20.7	115.11	14.50	1.33	111.31	11.14	20.28	100.31
ANC	11.71	10.14	78.55	-3.12	-12.52	40.05	10.21	1.38	20.05	18.4	10.10	10.10
pH	8.82	10.2	12.0	8.22	0.2	11.0	7.2	2.33	8.50	20.2	22.2	11.1

Figure 4a. Oakes Gulf.

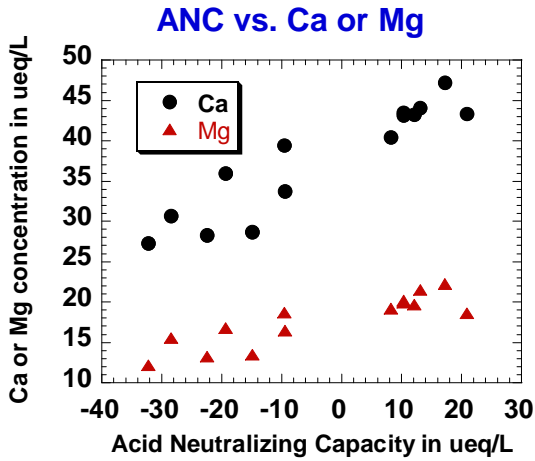


Figure 4b. Oakes Gulf.

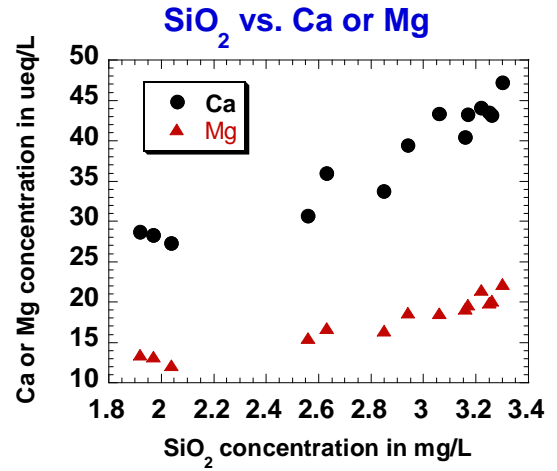


Figure 4c. Oakes Gulf.

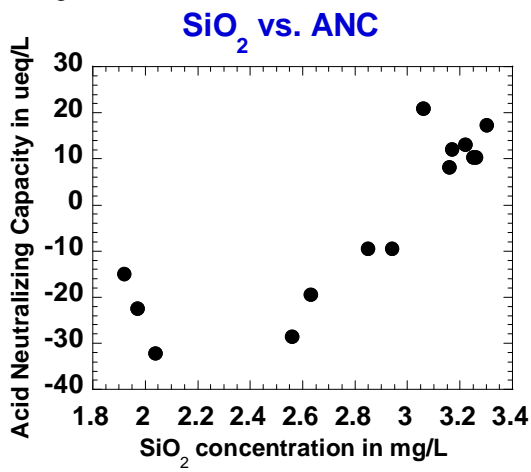


Figure 5. Oakes Gulf.

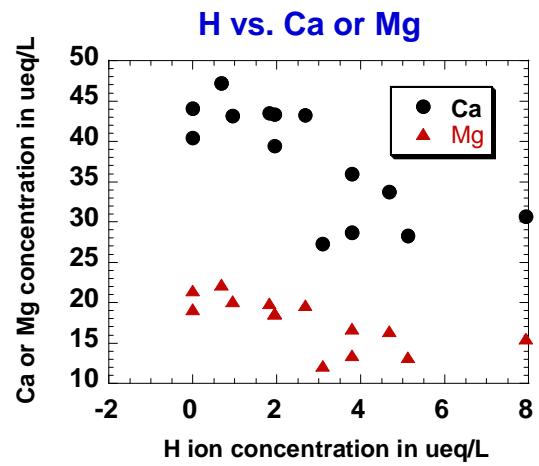


Figure 6a. Oakes Gulf.

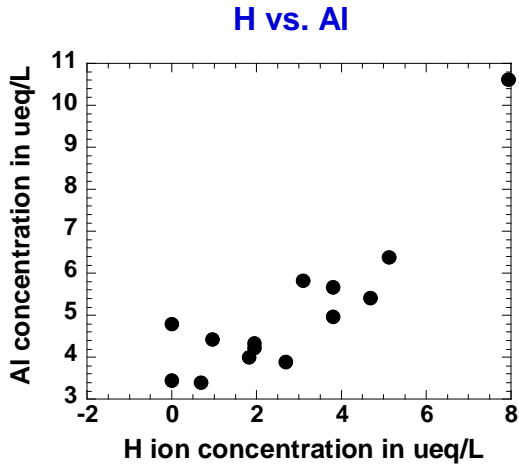


Figure 6b. Oakes Gulf.

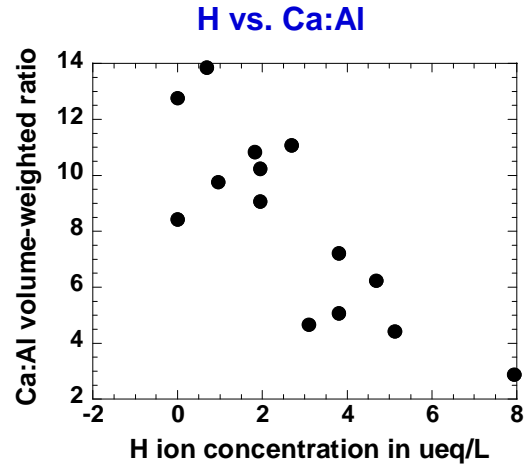


Figure 6c. Oakes Gulf.

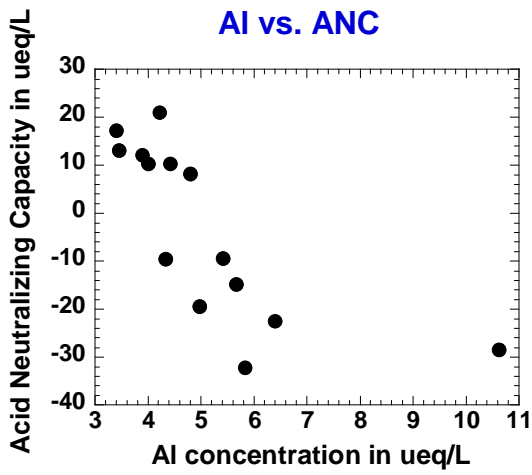
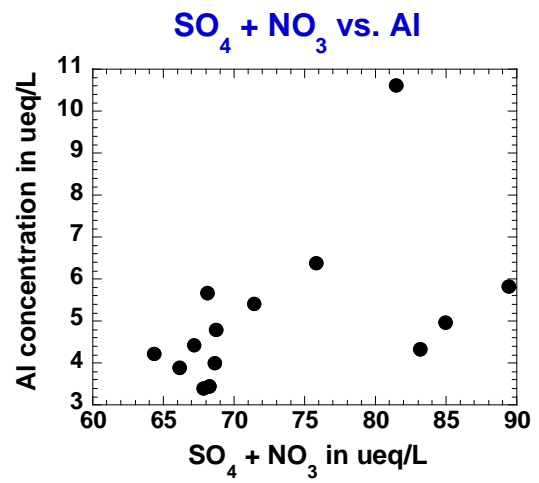
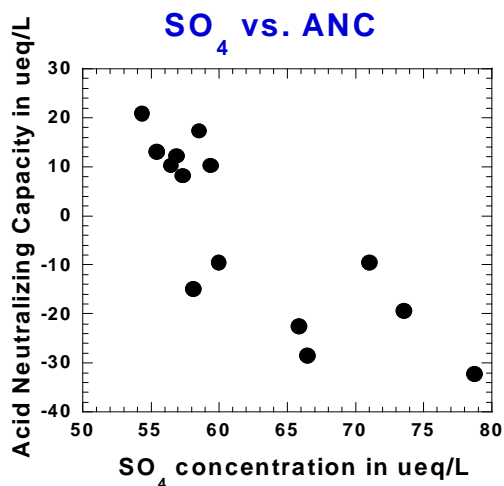


Figure 6d. Oakes Gulf.



Nevertheless, the sensitivity to acidification of the headwall stream of Oakes Gulf seems most affected by the concentration of SO_4 . SO_4 represents 38.1% of the stream's total dissolved solute concentration, while NO_3 makes up only 6.71% of the total.

Figure 7. Oakes Gulf.



Furthermore, the mean concentration of SO_4 is significantly higher than concentrations observed in the other three headwall streams (Table 1; $P < 0.0001$, [47.62, 55.54]) while the NO_3 concentration is significantly lower (Table 1; $P < 0.0001$, [19.81, 31.34]). A very strong negative correlation was

observed between SO_4 and the ANC (Figure 7), whereas NO_3 appears to have little effect on the buffering capacity of the stream.

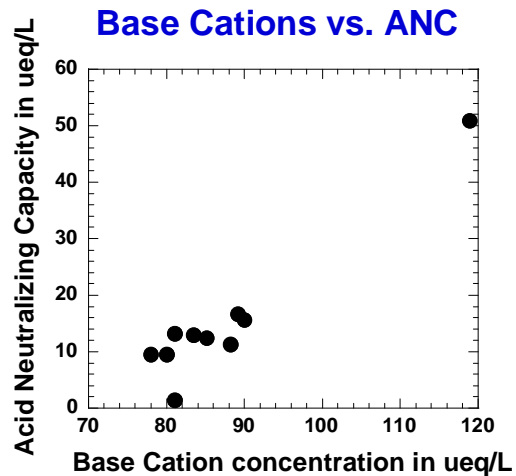
Oakes Gulf has the lowest base cation:H ion volume-weighted ratio and base cation: $\text{SO}_4 + \text{NO}_3$ volume-weighted ratio of the four alpine basins (Table 2). These ratios are 39.07 and 1.05 respectively. The Ca:Na and Ca:Al volume-weighted ratios are 2.53 and 8.33 respectively.

Huntington Ravine: The mean pH (5.77) and ANC (15.4 ueq/L) of Huntington Ravine are higher than both Oakes Gulf and Tuckerman Ravine. However, like Oakes Gulf, the ANC of Huntington Ravine's stream exhibits a large variance (Table 2).

Ca is the most abundant of the basin's cations, although the charge contributions of Mg and Na to total dissolved solute concentration are also substantial. Ca, Mg, and Na constitute 21.9%, 16.9%, and 9.86% of the total dissolved solute concentration respectively. The total base cation concentration is strongly and positively correlated with the ANC (Figures 8).

The mean concentration of Al in Huntington Ravine stream water is 2.26 ueq/L, and strong positive correlations were observed between H and Al. Also, a negative linear relationship was observed between Al and the ANC, although this association is only slightly significant (Figure 9).

Figure 8. Huntington Ravine



Like Oakes Gulf, although to a lesser degree, the Huntington Ravine headwall stream is dominated by SO_4 , which represents 27.5% of the total dissolved solute concentration. NO_3 , however, is also important, representing 14.3% of the total dissolved solute concentration. No clear trends were observed between either SO_4 or NO_3 and the following: base cation concentration, SiO_2 , ANC, or H.

The relationship of SiO_2 to the ANC and total base cation concentration is also difficult to interpret. At first, SiO_2 appears negatively correlated with both. However, upon removal of the first stream sample from the data set, these trends reverse, and SiO_2 correlates positively with the ANC and the base cations (Figure 10). Whether or not the first stream sample is an outlier is impossible determine, since removing the data point

Figure 9a. Huntington Ravine.

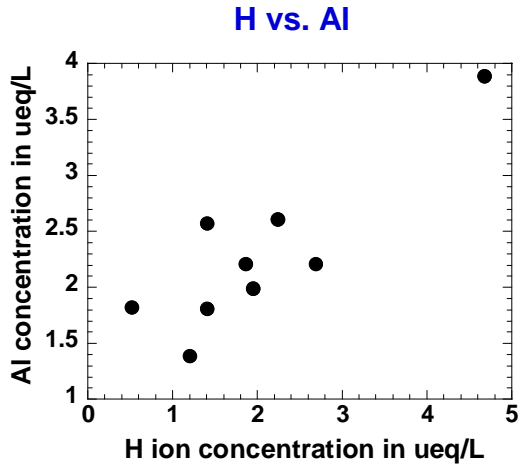


Figure 9b. Huntington Ravine.

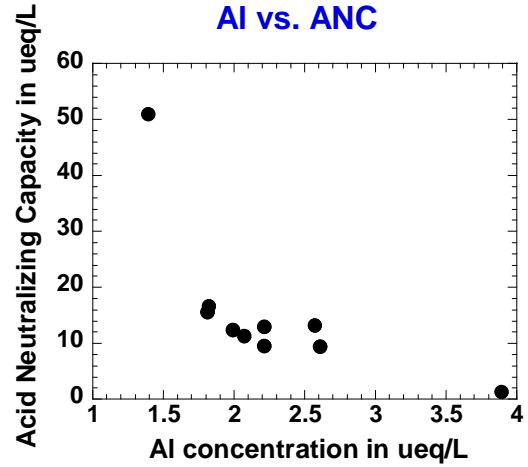


Figure 10a. Huntington Ravine (first data point excluded).

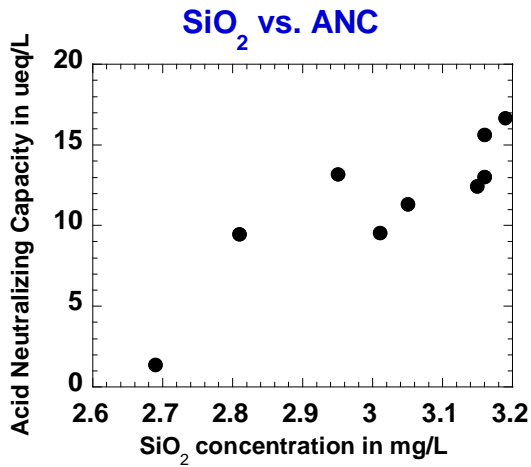
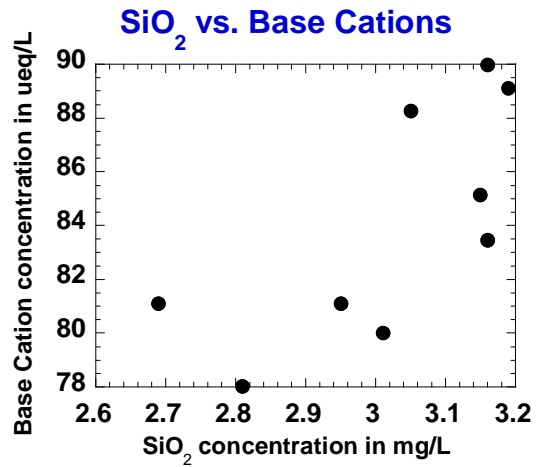


Figure 10b. Huntington Ravine (first data point excluded).

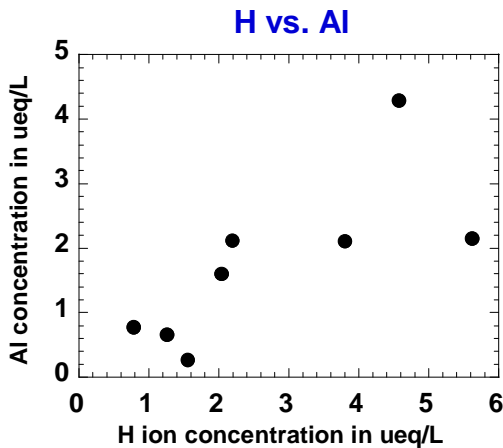


does not substantially change either the magnitude or direction of trends involving the other parameters. Therefore the point was conserved in all other analyses.

The mean base cation:H volume-weighted ratio and mean base cation:SO₄+NO₃ volume-weighted ratios for Huntington Ravine are 62.50 and 1.28 respectively. The mean Ca:Na and Ca:Al volume-weighted ratios are 2.23 and 17.54 respectively. Both the H ion and NO₃ concentrations are positively correlated with the Ca:Na ratio.

Tuckerman Ravine: The mean pH of Tuckerman Ravine’s stream water is 5.65, which is the second lowest mean pH of the four study basins (Table 2). Interestingly, the H ion concentration does not correlate well with any of the measured parameters, except for a partially significant and positive correlation with Al (Figure 11). The stream’s mean ANC is only 4.83 ueq/L and at times drops below zero.

Figure 11. Tuckerman Ravine.



Tuckerman Ravine is unique in that the observed concentrations of the base cations and anions are lower than those of the other three alpine basins. This difference is significant for concentrations of Ca, Mg, Na, and SO₄ (P<0.0001; P=0.0053; P<0.0001; P<0.0001). Ca constitutes 21.3% of the total dissolved

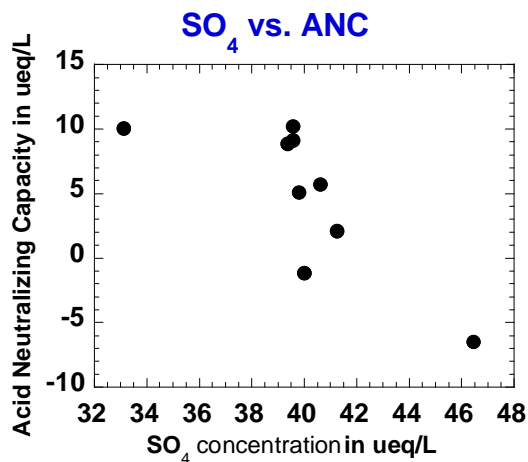
solute concentration. Mg constitutes 15.5% and Na 9.11%. SO₄ is the dominant anion, constituting 26.8% of the total dissolved solute concentration, and is followed by NO₃, which represents 14.7% of the total concentration. The SO₄ concentration is strongly and

negatively correlated with the stream's ANC (Figure 12). The positive correlation between the base cation concentration and the ANC is only partially significant, while NO_3 and the ANC do not exhibit a clear relationship.

In general, correlations between the various ion concentrations are weak and inconclusive. Even where higher correlation coefficients were generated, the graphic representations do not show clear trends.

The base cations, for example, do not correlate well either independently or as a group with either H or SO_4 . NO_3 appears better associated with the base cations, although none of the correlations between NO_3 and the individual base cations are significant.

Figure 12. Tuckerman Ravine.



Tuckerman Ravine's mean base cation:H ion volume-weighted ratio is only 41.24. The mean base cation: SO_4+NO_3 volume-weighted ratio is 1.21, and is at times close to 1.00. The mean Ca:Na and Ca:Al volume-weighted ratios are 2.34 and 33.39 respectively.

Contribution of Wet Deposition

The evapoconcentration factors for the Great Gulf, Oakes Gulf, Huntington Ravine, and Tuckerman Ravine are 2.32, 0.72, 0.44, and 0.99 respectively (see *Methods*).

The results from comparing the predicted concentration values generated using these

evapoconcentration factors to the observed concentration values are graphed in Figures 13-16 and discussed below.

Great Gulf: Observed concentrations of Ca and Mg are significantly higher than those predicted based on 2001 precipitation chemistry ($P < 0.0001$; $P < 0.0001$), while observed concentrations of K and NH_4 are significantly lower than their predicted values ($P < 0.0001$; $P = 0.0001$). Stream water concentrations of Na, Al, SO_4 , and NO_3 reasonably match those expected from precipitation input if there are no additional sources or sinks of solutes in the system. The differences between observed and predicted values for these solutes are not significant ($P = 0.1967$; $P = 0.0482$; $P = 0.1721$; $P = 0.2810$). The net output, or observed stream water concentration minus the corrected input from wet deposition, of base cations is 93.78 ueq/L, which is contrasted with a net gain, or negative net output, of 113.53 ueq/L of H ions.

Oakes Gulf: Observed concentrations of Ca, Mg, Na, and Al are all significantly higher than the predicted values ($P < 0.0001$ for all), suggesting some other source for these elements besides wet deposition. SO_4 concentrations in stream water also far exceed expected concentrations ($P < 0.0001$). The deficit of NH_4 with respect to its predicted concentration ($P = 0.0001$) suggests that there is a net sink within the system. NO_3 and K concentrations differ negligibly from their predicted values and appear to reflect input from precipitation.

Figure 13. Great Gulf.

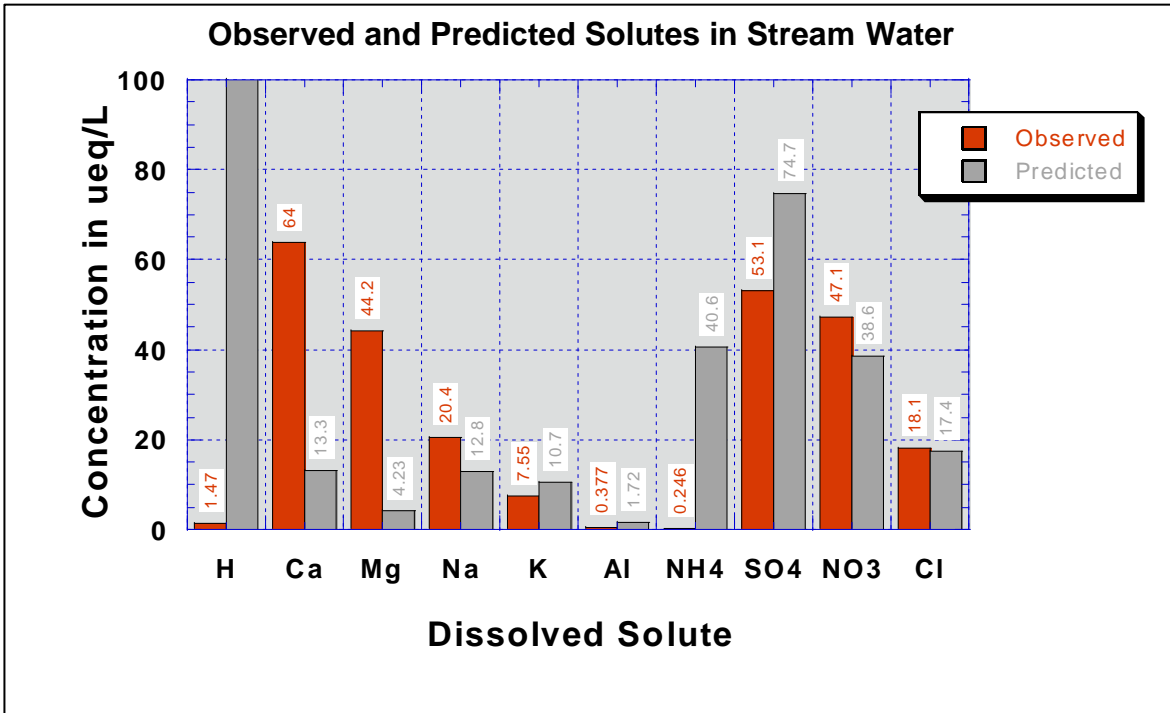


Figure 14. Oakes Gulf.

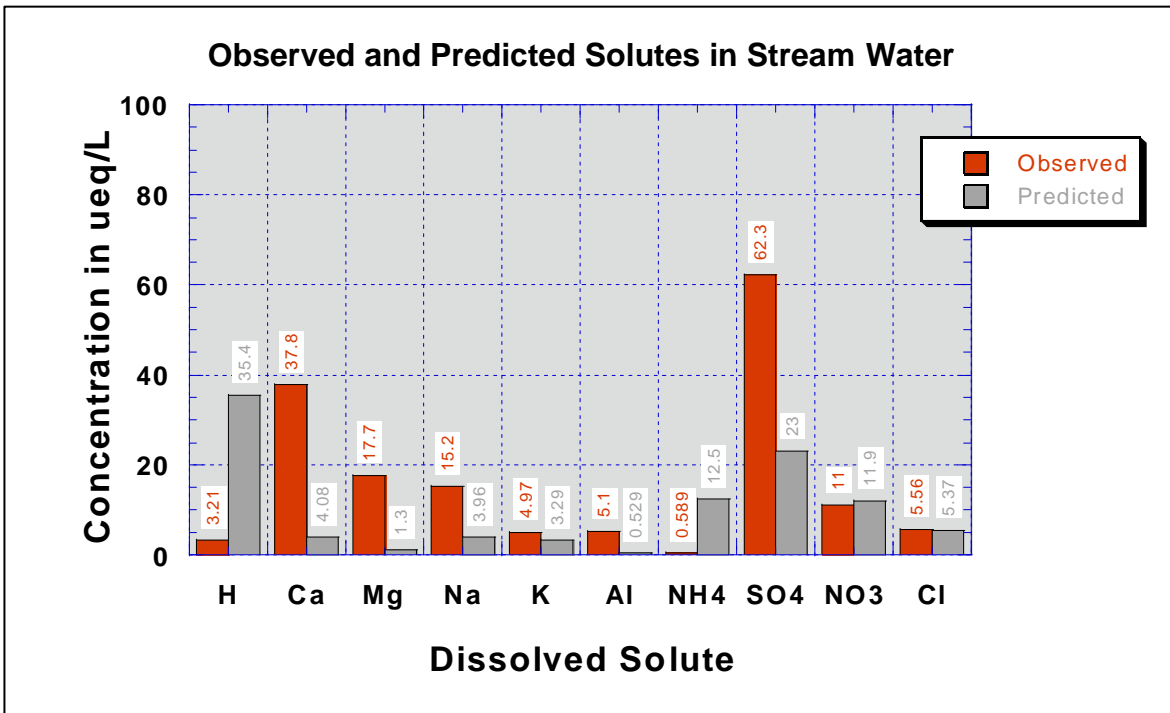


Figure 15. Huntington Ravine.

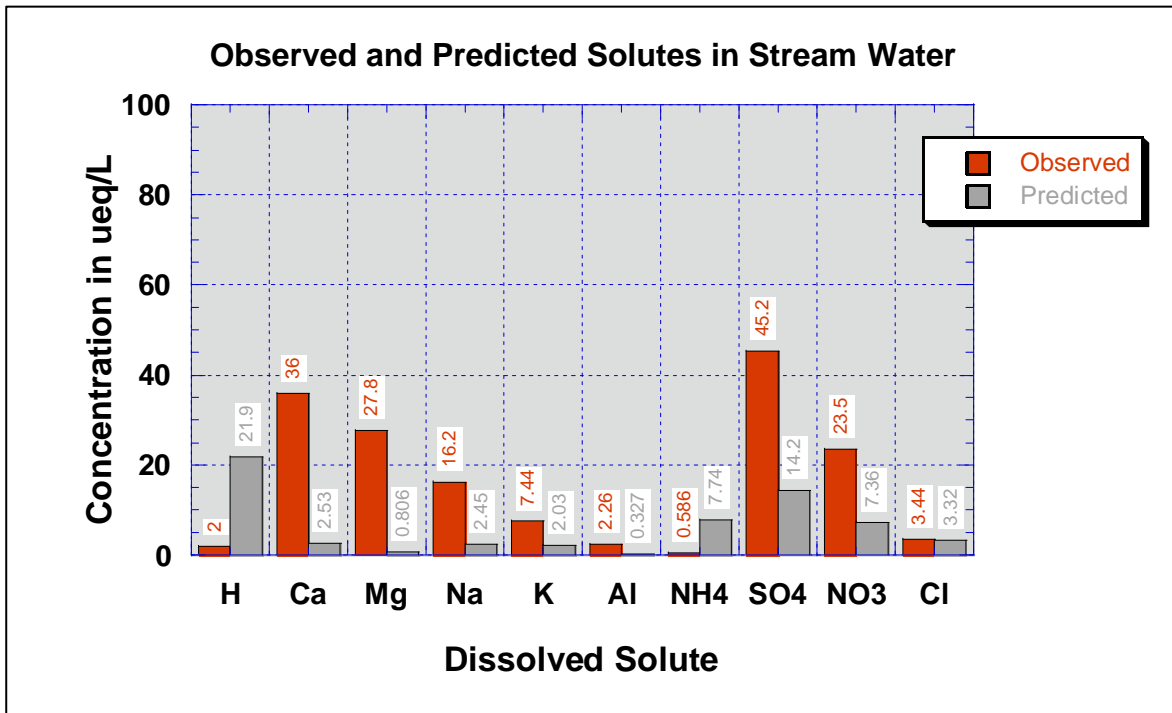
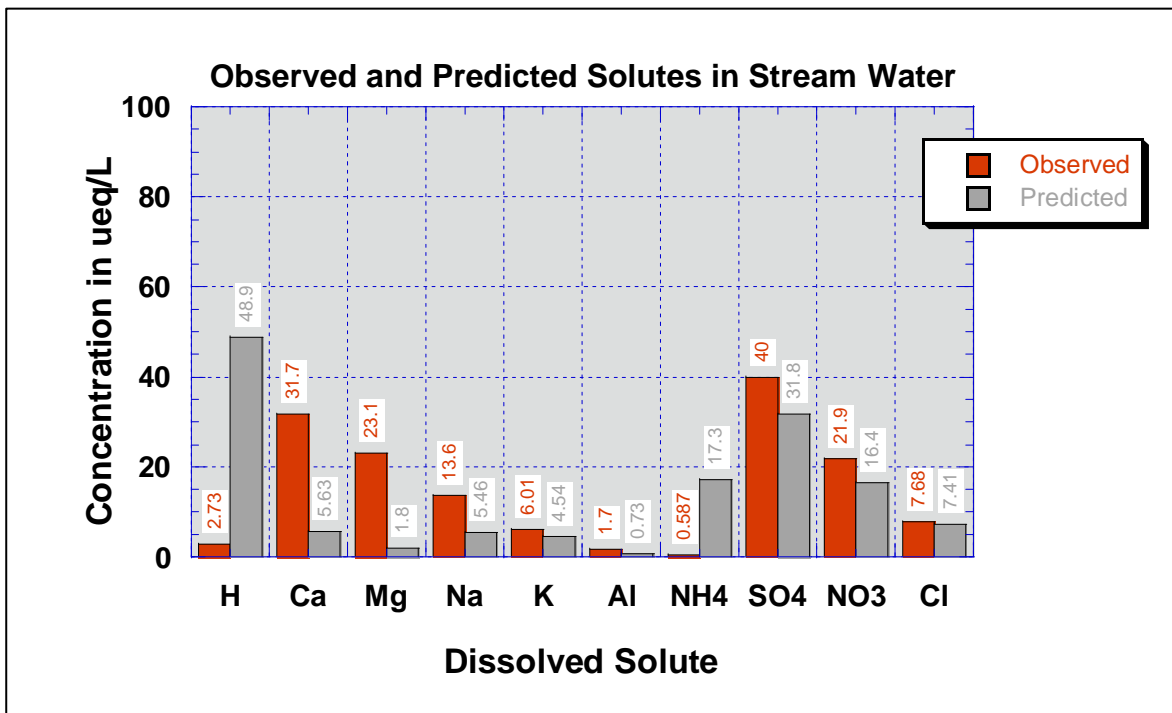


Figure 16. Tuckerman Ravine.



The net output of base cations, after the effect of evapotranspiration is considered, is 63.04 ueq/L. Adding the net output of Al to this number gives 67.61 ueq/L, which is more than twice the net gain in H ions. Comparatively, the net loss of SO₄ is 39.30 ueq/L.

Huntington Ravine: The observed base cation concentrations, Al, SO₄, and NO₃ are all significantly higher than the predicted solute concentrations (P< or=0.0001 for all). The net gain in NH₄ is also significant (P<0.0001).

Tuckerman Ravine: The differences between the observed and predicted solute concentrations are not significant for Al, SO₄, or NO₃ (P=0.0622; P=0.2268; P=0.1054). There is, however, a significant net loss of base cations equal to 56.98 ueq/L and a significant gain in H ions equal to 46.17 ueq/L. The NH₄ deficit is also significantly different from zero (P=0.0001).

Contribution of Bedrock Weathering

Molar ratios of the individual cations and Si are listed for each basin in Table 3. These ratios are based on the net output of dissolved solutes found in stream water after

Table 3. Molar ratios in alpine stream water and Littleton bedrock.

Molar Ratio	Great Gulf Streamwater	Oakes Gulf Streamwater	Huntington Ravine Streamwater	Tuckerman Ravine Streamwater	Littleton Gneiss*	Littleton Schist**
Ca ²⁺ :Mg ²⁺	1.268	2.055	1.240	1.224	0.156	1.443
Ca ²⁺ :Na ⁺	3.336	1.500	1.217	1.602	0.231	1.129
Ca ²⁺ :K ⁺		10.036	3.093	8.871	0.121	0.528
Ca ²⁺ :Si ⁴⁺	0.297	0.121	0.164	0.171	0.010	0.049
Mg ²⁺ :Na ⁺	2.630	0.730	0.982	1.308	1.280	0.782
Mg ²⁺ :K ⁺		4.883	2.495	7.245	0.776	0.366

*Billings and Fowler-Billings 1975

**Anderson and Hawkes 1958

the input from wet deposition times the evapoconcentration factor was subtracted from the observed ion concentrations in stream water.

Discussion

Problematic Assumptions

Certain key assumptions were made in order to assess the stream chemistry of the four alpine basins on Mt. Washington. First, the input from wet deposition for all four alpine basins was estimated using precipitation collected near Lakes of the Clouds, at an Appalachian Mountain Club research station located atop the ridge of the Presidential Range, just over 2 km south of the Mt. Washington summit. All study basins are within a 5 km radius of this collection site and of each other, thus orthographic effects on deposition were assumed negligible and all sites were believed to receive the same type and amount of rainfall. Vitousek (1977) reported that comparison of stream sampling sites from different locations on Mt. Washington was not problematic so long as all sites were roughly situated at the same elevation. The sites in this study lie within a 180 m vertical range of each other. However, Vitousek primarily sampled along the ridge and along the summit cols, whereas the four sites of this study are located at the base of cirque headwalls and are separated by 300+ m ridges. Thus, while the horizontal distance between sites may be negligible, it may not have been appropriate to ignore the influence of orthography on local rain patterns. Incorrect assumptions regarding wet deposition

input would affect the assessment of the contribution of wet deposition to the observed stream water chemistry by altering the predicted concentration values.

A second assumption of this study is that wet deposition is the principle form of atmospheric deposition. The influence of dry and occult deposition on stream water was ignored. Because vegetation in the alpine zone is sparse and necessarily below 2 m in height, there is little canopy upon which dry or occult matter can be deposited. Nevertheless, studies in the Rocky Mountains have suggested that dry deposition may be significant in a talus environment at high elevation and influence substantially the dissolved solute concentrations in stream water (e.g. Clow and Mast 1995; Clow and Sueker 2000). Cloud deposition collected at Lakes of the Clouds over the summer of 2001 suggests that occult deposition on Mt. Washington has much higher ion concentrations than rainwater, especially for H, Ca, NH₄, SO₄, and NO₃ (*data not shown*). The fact that neither dry nor occult deposition were included in the stream chemistry analysis presented in this study could be a potential source of error and would result in an overestimation of the net outputs of dissolved solutes in stream water.

Third, in adjusting the precipitation input by an evapoconcentration factor for each basin, Cl was assumed to be biologically inactive. Previously, no studies had reported finding Cl in the bedrock (Billings and Fowler-Billings 1975; Peters 1992; Eusden et al. 1996); and studies conducted at Hubbard Brook, which is also underlain by Littleton Formation bedrock, treat Cl as a conservative ion (Likens and Bormann 1995). If Cl were present in the bedrock or altered by biological processes, then this would affect the estimated contribution of wet deposition to observed stream chemistry.

Furthermore, in order to assess the contributions of wet deposition and bedrock weathering to the stream chemistry of the four study basins, it was assumed (1) that groundwater residence time is short, such that input from wet deposition is almost immediately transformed into surficial flow, and (2) that vegetation does not play a significant role in altering chemical input from the atmosphere before it is assimilated into the aquatic environment. Vegetation at high elevation is generally sparse and biomass is low; and steep slopes and high ion mobility impede the assimilation of dissolved solutes by vegetation. However, the influence of vegetation on stream chemistry could be significant.

Lastly, it should be noted that characterization of Mt. Washington's alpine stream water is limited to a sampling season that spans only the summer months. Yet the charge contributions of ions change substantially over the course of a water year and may cause the buffering capacity of a system to vary seasonally (Likens and Bormann 1995). For instance, when NO_3 concentrations pulse during snowmelt, streams may undergo significant pH drops, resulting in episodic acidification (Murdoch and Stoddard 1992). This study, which was based on data whose collection was limited to the summer of 2001, may fail to produce a robust characterization of the alpine zone's sensitivity to acidification since it does not capture seasonal changes in dissolved solute concentrations in stream water.

Present Stream Sensitivity to Acidification

All of the alpine study basins exhibit mean $\text{pHs} < 6$ and $\text{ANCs} < 20 \text{ ueq/L}$. This is below the threshold value of 25 ueq/L , used by MacAvoy and Bulger (1995) to define

streams that are “most sensitive to acidification.” They observed significant declines in the survivorship of aquatic biota in waters with an ANC less than this value. Driscoll et al. (2001) described lakes in the northeastern U.S. as chronically acidic if they have an $ANC < 0$ ueq/L and as sensitive to acidification if they have an $50 > ANC > 0$ ueq/L. A low ANC is associated with low base saturation in soils and insufficient rates of base cation release through chemical weathering of bedrock, which indicate a limited ability to neutralize strong acid anions. Furthermore, low base cation:H ion ratios have been observed in streams that have become chronically acidified as a result of sulfur saturation (Galloway et al. 1983). Sulfur saturation occurs when a system, after receiving continued acidic deposition, exhausts its capacity to consume additional incoming SO_4 and becomes a net source of SO_4 into local waters. The individual basins are discussed below in further detail.

Great Gulf: Particularly noteworthy in Great Gulf stream water is the alarmingly high concentration of NO_3 . High NO_3 concentrations in stream water output, especially during the summer when nitrogen is expected to be a limiting nutrient for plant growth, are indicative of nitrogen-saturated environments (Martin et al. 1999). Moreover, studies in the Catskills have demonstrated a causal relationship between nitrogen saturation and the creation of toxic conditions for stream biota through the acidification of fresh water environments (Murdoch and Stoddard 1992). An abundance of NO_3 in stream water may render the Great Gulf watershed more sensitive to additional inputs of strong acid ions and, consequently, to acidification.

Yet the high pH and ANC of the Great Gulf, with respect to the other study basins, suggest that it is the least acidified of the four headwall streams. Substantial net outputs of base cations may be responsible for this, as shown by the relatively high base cation:H and base cation:SO₄+NO₃ volume-weighted ratios.

The strong positive correlations between NO₃ and Ca or Mg suggest that as NO₃ input increases, so too does the release of cations into the stream water. However, the strong association between these ions does not necessarily demonstrate causality. The mineralization of organic matter will release high concentrations of both NO₃ and cations simultaneously. Therefore, correlations between NO₃ and cations not released by biological processes, such as Al, are much better predictors of leaching caused by acidification (Vitousek 1977). Unfortunately, no such conclusive trends were observed in the Great Gulf. However, the observation of strong positive correlations between the base cations and SiO₂, whose only significant sources are soils and bedrock, indicates that rock material is the primary source of base cations. In addition, the fact that NO₃ correlates strongly with both SiO₂ and the base cations in the Great Gulf suggests that NO₃ may influence geochemical transformations, thereby affecting the release of cations and the acidity of the stream water (Figure 2). This suggests that the high concentrations of NO₃ and cations in Great Gulf stream water are not merely coincidental.

In fact, the strong positive association between NO₃ and the base cations may confound the effects these dissolved solutes have on the Great Gulf's ANC. The ANC is expected to rise with increases in the base cations yet decrease with increases in strong acid ions such as NO₃. However, since NO₃ and the base cations increase concurrently in the Great Gulf, a clear understanding of the independent influence of each dissolved

solute on the ANC is not possible. This is reflected in the non-significant correlation coefficients for NO_3 and the ANC and for the total base cation concentration and the ANC.

The dissolved solute that best correlates with the Great Gulf's ANC is SO_4 , which is the strong acid ion most often implicated in the acidification of northeastern ecosystems (Driscoll et al. 2001). The negative correlation between SO_4 and the ANC indicates that strong acid-loading increases the Great Gulf's sensitivity to acidification (Figure 3). This does not mean that NO_3 is less important in regulating the stream's buffering capacity, only that as the SO_4 concentration increases while other parameters remain constant, the ANC will probably decrease in a predictable linear fashion. Weak correlations between SO_4 and the base cations or NO_3 suggest that the SO_4 concentration in stream water is controlled by separate processes from the other solutes (Table 2).

Oakes Gulf: Oakes Gulf's pH is lower than the other study basins, but a mean pH of 5.58 alone is not strongly suggestive of sensitivity to acidification. What is most alarming is the fact that strong-acid loading appears to have significantly impacted the stream's ANC. A negative ANC is symptomatic of chronic acidification (Driscoll et al. 2001), and Oakes Gulf's ANC is often below zero, dropping to -32.21 at its summer minimum for 2001. Oakes Gulf's limited ability to neutralize strong acid ions is also reflected in the variance of the stream's pH. Over the summer of 2001, the pH ranged from 5.10 to 6.16, which is the largest variance of the four study basins (Table 2). This may indicate that waters in the gulf are much more sensitive to chemical inputs that have less significant impacts on other areas of Mt. Washington's alpine zone.

Other indicators of chemical imbalance in Oakes Gulf stream water include the fact that the base cation: SO_4+NO_3 volume-weighted ratio is often below 1.00 and that the minimum base cation: SO_4+NO_3 ratio for Oakes Gulf is lower than the base cation: SO_4+NO_3 ratio found in wet deposition. Strong negative correlations between SO_4 and the ANC suggest that high SO_4 concentrations in Oakes Gulf's stream water may be responsible for this basin's limited ANC (Figure 7).

Oakes Gulf's large net output of SO_4 with respect to the other study basins demonstrates that this alpine area has become a net source of SO_4 (Figure 14). This, in addition to the fact that concentrations of SO_4 are much higher in Oakes Gulf stream water than in the other basins, is evidence of sulfur saturation (Galloway et al. 1983). A low base cation:H volume-weighted ratio, as was observed, is also characteristic of sulfur saturation, and suggests two possibilities: first, that base saturation of whatever poorly developed soils exist in Mt. Washington's alpine zone is low; and secondly, that weathering rates of base cation-containing minerals do not produce an adequate supply of base cations in order for Oakes Gulf to be able to buffer inputs of strong acid ions (Galloway et al. 1983).

Further evidence of sulfur saturation and a low buffering capacity is the observation of substantial Al leaching. Al tends to leach out of soil sites only when base cations have become depleted, presumably through interactions with acidifying compounds, since Al is generally the most difficult cation to mobilize (e.g. Anderson and Hawkes 1957; Aber and Melillo 1991). In the alpine zone, where soil accumulation is minimal, relatively large outputs of Al may indicate higher weathering rates. However, the fact that Al and H are both inversely related to SiO_2 , suggests that cation exchange,

and not bedrock weathering, is the dominant process affecting the release of Al into stream water. Furthermore, the bedrock underlying Oakes Gulf contains abundant Ca-rich minerals (Peters 1992); yet Oakes Gulf's Ca:Al volume-weighted ratio is lower than the Ca:Al ratio of precipitation, indicating that some other endogenous factor controls the relative concentrations of dissolved solutes in stream water.

If cation exchange is depleting available base cation pools, then the system may eventually become unable to balance the high concentration of strong acid ions, and stream water may become acidified. The positive correlation between Al and H and the strong negative correlation between H and the Ca:Al volume-weighted ratio suggest that as waters become more acidic, more Al is leached from soils (Figure 6). The positive trend between Al and $\text{SO}_4 + \text{NO}_3$ implicates these strong acid ions in the acidification of Oakes Gulf's stream water. Furthermore, the release of base cations into stream water actually decreases as the H concentration increases, indicating that the acidification of Oakes Gulf's headwall stream reinforces the system's inability to neutralize strong acid ions. Together, a negative ANC, high concentrations of SO_4 , and a limited supply of base cations make Oakes Gulf extremely susceptible to increases in acid-loading and suggest that even a small change in the input-output balance will significantly alter the stream's pH.

Huntington Ravine: Huntington Ravine's mean pH and mean ANC indicate that the basin is sensitive to acidification. The variance of both the pH and the ANC are nearly as large as Oakes Gulf's, which reflects high variability in Huntington Ravine's degree of sensitivity, probably as a result of a non-constant supply of dissolved solutes to

stream water (Table 2). Huntington Ravine's ANC is better correlated with the concentration of base cations (ignoring the potential outlier) and with SiO_2 than with SO_4 or NO_3 (Figures 8 & 10), which suggests that the ANC is more sensitive to the base saturation of its limited soils and/or the weathering rates of rock material than to the input of acidifying compounds from wet deposition. There is no source of SO_4 or NO_3 in the bedrock underlying the ravine (Eusden et al. 1996).

Nevertheless, SO_4 does appear to have a significant negative impact on the ravine's ecosystem. The large net output of SO_4 (Figure 15), low base cation:H ratio, and strong positive correlation between H and Al (Figure 9), suggest that Huntington Ravine, like Oakes Gulf, is sulfur-saturated and unable to buffer acid-loading due to limited availability and/or limited release of base cations through chemical weathering. At high acidity, Al is leached into the stream water, indicating either that base saturation of Huntington Ravine's limited soils is not sufficient for base cations alone to neutralize the system or that the rates of base cation release through chemical weathering cannot keep up with the input of strong acid ions from atmospheric deposition. Consequently, Al must assume the role of an acid buffer. The positive trend between Al and SO_4+NO_3 supports the idea that these strong acid ions contribute to the acidification of Huntington Ravine's stream water (Figure 9).

Interestingly, Huntington Ravine's mean base cation: SO_4+NO_3 volume-weighted ratio is the second highest of the four study basins (Table 2), and this finding seems to contradict the hypothesis that the supply of base cations is not adequate given the strong acid ion input. However, while concentrations of SO_4 and NO_3 are nearly constant in the headwall stream, the base cation: SO_4+NO_3 ratio rises and falls significantly over the

course of the summer. Al leaching probably occurs when the base cation: $\text{SO}_4 + \text{NO}_3$ ratio is closer to 1.00, according to the inverse relationship between Al and the base cations.

Tuckerman Ravine: Signs of sensitivity to acidification in Tuckerman Ravine include a low mean pH and a mean $\text{ANC} < 5.00$ ueq/L. The base cation:H volume-weighted ratio is nearly as low as the ratio observed in Oakes Gulf (Table 2), which suggests that sulfur saturation may be occurring in this basin as well (Galloway et al. 1983). Tuckerman Ravine's SO_4 concentration is lower than the SO_4 concentrations of the other three alpine basins (Table 1), but SO_4 is the ravine's most abundant dissolved solute. Furthermore, the correlation analysis indicates that although SO_4 does not affect the total base cation concentration, it plays an important role in controlling the acidification of Tuckerman Ravine's stream water, as indicated by a strong negative correlation with the ANC (Figure 12). NO_3 and H, in contrast, appear to have little influence on the stream's capacity to buffer the input of acidifying compounds.

Although evidence of Al leaching in Tuckerman Ravine is not conclusive, it does appear that more Al is released into stream water as H ion concentrations increase (Figure 11). More acidic waters may deplete available base cations in the ravine's limited soils or preferentially increase weathering of certain rock types, thus causing Al to leach into stream water. Low base cation availability or low rates of base cation release from bedrock weathering, in addition to a relatively high SO_4 concentration in stream water, indicates that this system has little ability to neutralize incoming acidifying compounds.

Contribution of Wet Deposition

Various factors could have decreased considerably the accuracy of the assessment of wet deposition contribution to observed stream water chemistry. The first is the use of precipitation collected at a single location as an estimate for the atmospheric input into four spatially diverse basins. Concentrations of dissolved solutes in stream water are usually twice the ionic strength of concentrations found in precipitation (Likens and Bormann 1995); yet evapoconcentration factors are much less than 2.00 for Oakes Gulf, Huntington Ravine, and Tuckerman Ravine. Since it is unlikely that Cl is being consumed by vegetation, it is possible that the predicted input of Cl is incorrect. Orthographic effects may have altered the deposition of salts and other particles mixed with rainwater, such that heavier particles were deposited on the western slopes of Mt. Washington, before reaching the cirques. Conversely, the precipitation sampling site would have collected these particles since it is to the southwest of Mt. Washington's summit.

Another possible factor affecting the contribution of wet deposition is that the summer of 2001 was particularly dry in the northeastern United States. Mt. Washington Observatory, located at the summit of Mt. Washington, has kept extensive records of temperature, wind, and precipitation on the mountain throughout the 20th and 21st centuries. Their measurements indicate substantial rain deficits from normal for both July and August and hotter than normal temperatures for June and August. Also, the USDA Forest Service stream gauge on the Ellis River in Jackson, NH, approximately 15 km south of Mt. Washington, showed that discharge was lower than normal for the summer of 2001.

When input from wet deposition is low, as is the case for the summer of 2001, stream water is mostly generated from groundwater and reflects baseflow conditions (Likens and Bormann 1995). Consequently, stream water chemistry may reflect more clearly than usual the contribution of geochemical processes. Still, observed stream water concentrations of major cations and anions were compared with rainwater concentrations, that were adjusted by the appropriate evapoconcentration factor for each basin, in order to assess the fraction of each ion concentration in stream water that may be explained by wet deposition (see *Methods*).

Great Gulf: The net outputs of Ca, Mg, and Na indicate that precipitation alone cannot explain the high concentrations of these cations (Figure 13). Input from wet deposition explains only 20.78% of the observed Ca concentration, 9.57% of the observed Mg concentration, and 62.75% of the Na concentration. In comparison, the observed concentrations of Al and NH₄ are significantly lower than those expected based on the contribution of wet deposition, suggesting an important sink for these dissolved solutes within the ecosystem.

NH₄ might be quickly consumed by vegetation in nitrogen-limited environments like the alpine zone; and the assumption that uptake by vegetation is negligible along Mt. Washington's headwalls could be incorrect. The net gain in K supports this possibility, since K is also quickly assimilated by vegetation during the summer season (Likens and Bormann 1995). However, another explanation for the NH₄ sink is nitrification, which would help explain the high NO₃ concentration. Studies in the alpine zone of the Rocky Mountains have shown that nearly all incoming NH₄ is consumed either through

assimilation by vegetation or nitrification (Meixner et al. 2000). Campbell et al. (2000) found that a combination of sparse vegetation, an active microbial population, and a carbon-poor substrate are conducive to nitrification, making talus environments a significant source of NO_3 .

The net gain in Al is less easily explained since Al is not usually affected by biological processes. This discrepancy may be an indication that the predicted dissolved solute concentrations in stream water, based on precipitation, are overestimated for the Great Gulf. Perhaps this also explains, assuming orthography did affect deposition patterns, why the Great Gulf is the only one of the four study basins whose evapoconcentration factor is greater than 1.00. Since the evapoconcentration factor is related to the observed Cl concentration in stream water, a large evapoconcentration factor reflects a high Cl concentration. This could be evidence that the assumption of short groundwater residence time in the Great Gulf is violated, since Cl will concentrate in pooled water (Meixner et al. 2000).

Furthermore, if the predicted dissolved solute concentrations are too high, then the interpretation of the anion budgets changes substantially. Instead of there being a net gain of SO_4 , the difference between this anion's input and output narrows, which is what is expected since there is no obvious SO_4 sink in the Great Gulf. On the other hand, the net loss of NO_3 becomes more significant, indicating that wet deposition alone cannot explain the NO_3 concentration in stream water. Some of this NO_3 could be the product of nitrification, which was already mentioned as a potential sink for NH_4 . Another possibility is that the presence of nitrogen-fixing species increases concentrations of NO_3 in adjacent stream water. A casual inspection of the vegetation in the alpine zone of the

Great Gulf revealed populations of nitrogen-fixing alder growing in the riparian zone of the headwall. Vitousek (1977) also noted that *Alnus crispa*, which is known to fix nitrogen with the aid of microrrhizal symbionts, grows in the White Mountains. However, if the hydrologic residence time is indeed longer than expected, as suggested by the relatively high Cl concentration, then NO₃ may also be preferentially concentrating in groundwater pools, since the concentration of this dissolved solute increases with water volume (Likens and Bormann 1995). Moreover, if the assumption of a short groundwater residence time is violated, then the assessment of wet deposition contribution to Great Gulf stream water chemistry is likely inaccurate.

Oakes Gulf: Wet deposition could only explain 10.79% of the observed Ca concentration, 7.34% of the observed Mg concentration, 26.05% of the observed Na concentration, and 10.37% of the observed Al concentration (Figure 14). Since the difference between observed and predicted values of K is not statistically significant, either wet deposition fully explains the K concentration of stream water, or additional sources and sinks, including bedrock weathering and vegetation uptake, balance the K input and output. The net gain in NH₄ may support either the possibility that assimilation by vegetation is significant or that nitrification plays an important role in altering Oakes Gulf's stream chemistry.

The observed concentration of NO₃, however, reflects almost exactly the predicted concentration based on wet deposition input, suggesting no major sources or sinks of NO₃ in the system. Oakes Gulf is the closest of the alpine basins to Lakes of the Clouds, the collection site of the precipitation used in this study, and therefore stream

water chemistry in this basin is expected to reflect most closely the estimated atmospheric input of acidifying compounds. Furthermore, there is no source of nitrogen in Oakes Gulf bedrock (Peters 1992) and an absence of nitrogen-fixing vegetation in the basin (Appalachian Mountain Club, *unpublished data*). On the other hand, the loss of SO₄ from the system is far in excess of the SO₄ input, which indicates an additional source of SO₄ from either soil or bedrock. Wet deposition explains only 36.92% of the observed SO₄ concentration.

Huntington Ravine: Input from wet deposition explains only 7.03% of the observed Ca concentration, 2.90% of the observed Mg concentration, 15.12% of the observed Na concentration, 27.28% of the observed K concentration, and 14.47% of the observed Al concentration (Figure 15). Predicted concentration values for SO₄ and NO₃ are barely 30% of the observed concentration values, despite there being no source of either anion in the bedrock and an absence of nitrogen-fixing vegetation (Eusden et al. 1996; *personal observation*). The net output of NO₃ is, however, coupled by a net gain in NH₄, which might reflect the conversion of NH₄ to NO₃ through nitrification. Nevertheless, given the significant differences between all of the observed and predicted dissolved solute concentrations, precipitation from Lakes of the Clouds is probably not a good estimate of atmospheric input into Huntington Ravine. Moreover, additional sources of dissolved solutes, such as dry or occult deposition, may be significant and perhaps should not have been ignored in assessing input-output budgets.

Tuckerman Ravine: Only a small percentage of the individual base cation concentrations in Tuckerman Ravine's headwall stream can be explained by input from wet deposition (Figure 16). Only 17.76% of the observed Ca concentration, 7.79% of the observed Mg concentration, and 40.15% of the observed Na concentration can be attributed to wet deposition. Presumably, an additional source of solutes must account for the net losses of these base cations in Tuckerman Ravine.

The fact that wet deposition appears to explain considerably more of the observed K concentration in stream water (75.54%) may be confounded by vegetation uptake. Assimilation of K by vegetation would mask additional releases of this dissolved solute from the system; and the significant net gain in NH_4 may be further evidence that vegetation is a significant sink for certain dissolved solutes. Nevertheless, the NH_4 deficit could also be attributed to the process of nitrification. The results from this study, unfortunately, are not sufficient to determine which of these two biological processes is more influential with respect to its influence on Tuckerman Ravine's stream chemistry.

The net gains in SO_4 and NO_3 are both statistically insignificant; thus it would be reasonable to assume that wet deposition is the source of these strong acid ions and, consequently, that the acidifying compounds in atmospheric deposition control Tuckerman Ravine's sensitivity to acidification. However, although wet deposition may be the predominant source of these dissolved solutes, wet deposition fails to explain 21.50% of the observed SO_4 concentration and 25.11% of the observed NO_3 concentration in stream water. While soils and bedrock are both potential sources of SO_4 (Alewell et al. 1999), NO_3 is more probably affected by biological processes, since there

is no source of nitrogen in the bedrock underlying Tuckerman Ravine (Eusden et al. 1996). One possible source of NO_3 within the system is nitrification, which was previously mentioned as a potential sink for NH_4 . Another possible source is nitrogen-fixing vegetation. Like the Great Gulf, Tuckerman Ravine hosts populations of nitrogen-fixing *Alnus* in the riparian zone along the headwall (*personal observation*). These dwarf trees could be releasing NO_3 into the nearby stream channel, thus elevating concentrations of this strong acid ion in stream water and rendering Tuckerman Ravine more sensitive to inputs of NO_3 from atmospheric deposition.

Contribution of Bedrock Weathering

Chemical weathering of bedrock is an important source of dissolved solutes that influences the sensitivity to acidification of stream water, especially in areas where vegetation and soil accumulation are minimal (Galloway et al. 1983). Despite the steep slopes and high anion mobility characteristic of catchment headwalls in the alpine zone, various studies have shown that water contact time is long enough for geochemical transformations to occur (e.g. Meixner et al. 2000). Where water contacts areas of exposed rock, ion exchange, cation release, and H buffering are all possible. In fact, in a Rocky Mountain study that compared the stream chemistry of two alpine watersheds, the basin with more exposed bedrock and less soil exhibited higher pH and a higher ANC than the basin with more extensive soil accumulation (Meixner et al. 1998).

The results from this study indicate that chemical weathering of bedrock accounts for a significant proportion of the dissolved solutes observed in the stream water of four of Mt. Washington's alpine basins. Furthermore, since the poorly developed soils at high-

elevation are likely to reflect closely the mineral composition of bedrock, the byproducts of water-soil interactions will be highly controlled by primary mineral weathering rates. As a significant source of base cations, the bedrock underlying the headwalls plays an important role in regulating the acidity and the ANC of the headwall streams.

Great Gulf: Despite the fact that both a minimal soil substrate and bare rock surface in the Great Gulf may be capable of cation exchange, the lack of correlation between H and the other cations suggests that this mechanism is not the principal means by which H ions are consumed. Instead, the strong correlations between NO_3 and both SiO_2 and the base cations lend evidence toward weathering as the source of acid buffering and cation release into stream water.

In addition to the strong positive correlations between NO_3 and both Ca and Mg, the NO_3 concentration in stream water exhibits a direct linear relationship with the Ca:Al volume-weighted ratio. This suggests that strong acid ions in the Great Gulf preferentially weather Ca-containing minerals in the bedrock, which is what is expected given the relative mobilities of cations in Littleton Formation bedrock. Anderson and Hawkes (1958) showed that in the White Mountains, Ca and Mg are the most mobile of the base cations and the first to be leached, while Al is the most immobile and the last to be leached. The correlation analysis does not indicate that SO_4 plays as significant a role in weathering and cation leaching.

In order to determine if the bedrock in the Great Gulf could produce the relative concentrations of base cations in stream water, molar ratios of the base cations and Si observed in the stream's net output were compared to molar ratios of these elements

found in the bedrock underlying the gulf (Table 3). Estimates for the molar ratios characteristic of the gneiss in the Rangeley Formation are given for a sample taken by Billings and Fowler-Billings (1975) at Green's Grant along the Peabody River, just north of the Great Gulf. Billings and Fowler-Billings referred to the gneiss as part of the Littleton Formation, although since their study it has been reassigned to the Rangeley Formation (Peters 1992). Because plagioclase is the principle source of Ca and Na in both Littleton gneiss and Littleton schist (Billings and Fowler-Billings 1975), the Ca:Na molar ratios from the gneiss are used as an estimate for the Ca:Na ratio produced by plagioclase weathering in the Littleton schist as well. Garnet may be another source of Ca in these metamorphic rocks, although because it constitutes only 3% of Littleton gneiss (Billings and Fowler-Billings 1975), its contribution to stream water chemistry was ignored.

The Ca:Na molar ratio of the Great Gulf's headwall stream far exceeds that expected from the bedrock estimates, as do the Ca:Si and Mg:Na molar ratios. Therefore, it appears that Ca and Mg are leached far in excess of what would be produced by the weathering of gneiss and schist. Furthermore, the weathering of garnet cannot explain the excess Ca without producing a lower Ca:Si ratio. Instead, it is probable that the source of the relatively high Ca concentration in Great Gulf stream water is the preferential weathering of calc-silicate lenses interspersed throughout the gneiss.

Although no estimates were found of the Ca:Si ratio characteristic of the calc-silicate lenses described by Eusden et al. (1996), it is known that these rocks compose approximately 3% of the entire Littleton Formation (Billings and Fowler-Billings 1975), including what is now known as the Rangeley gneiss. Yet studies of alpine catchments

have determined that up to 40% of the Ca observed in stream water is the byproduct of the weathering of trace minerals in the bedrock (e.g. Drever and Hurcomb 1986; Mast et al. 1990). Furthermore, the intense rate of physical weathering at high elevation causes the continual exposure of trace minerals in fresh bedrock, such that the relatively high rates of chemical weathering of these less abundant materials is plausible (Mast et al. 1990; Sueker et al. 2000). Vitousek (1977) concluded that high concentrations of dissolved solutes in the streams in Mt. Washington's alpine zone were probably the result of high rates of physical weathering. Thus the Ca concentration in the Great Gulf stream water could reflect preferential weathering of the calc-silicate lenses interspersed throughout the gneiss and schist. The high Ca:Al volume-weighted ratio could be additional evidence that calc-silicates are preferentially weathered over Al-containing minerals such as plagioclase.

Another possible source for the relatively high Ca concentration in Great Gulf stream water is the dissolution of calcite from eolian dust (Mast et al. 1990). Talus is believed to trap eolian dust and contribute to high Ca concentrations in stream runoff (Meixner et al. 2000). Also, debris lodged in bedrock cracks and crevices may be Ca-rich and influence stream chemistry since runoff is likely to course through these fissures as it moves down gradient (Meixner et al 1998). The Ca:Na volume-weighted ratio of Great Gulf stream water is typical of water that courses through a talus environment, where the contribution of litter and debris to stream chemistry is significant (Clow and Sueker 2000). However, Clow et al. (1997) contended that despite the dissolution of particles from dust, the talus zone is still dominated by bedrock weathering. The strong positive correlation between Ca and SiO₂ in the Great Gulf supports the idea that cations are

predominantly derived from the weathering of silicate material (Figure 2). Furthermore, neither the dissolution of calcite nor the break down of debris can explain the Great Gulf's relatively high concentrations of other dissolved solutes, such as the conservative anion Cl.

The most likely explanation for the high concentrations of Cl in the headwall stream is the preferential concentration of elements in pools of groundwater formed deep within the bedrock. Meixner et al. (2000) believed that such pools of melt water produced a wintertime source of Cl to high-elevation streams in the Rocky Mountains. Moreover, the strong positive correlation between Cl and NO₃ indicates that NO₃, which may be an important weathering agent in the Great Gulf, may also be preferentially concentrating in groundwater. The longer the hydrologic residence time is, the longer the contact time is between water and rock, and the more opportunity for geochemical transformations to occur. Sueker et al. (2000) found higher concentrations of weathering byproducts where hydrologic residence time was greater. Thus, it is no surprise that Ca and Mg concentrations increase simultaneously with concentrations of Cl and NO₃. As the NO₃ concentration increases in pools of groundwater, weathering of rock material should be facilitated and large amounts of base cations released. If it is primarily the calc-silicate lenses that are being weathered, this would explain the high Ca:Na and Ca:Al volume-weighted and molar ratios in stream water. Given the correlation analysis, the concentration of NO₃ in pools of groundwater seems a more significant source of NO₃ to stream water than the production of NO₃ by nitrogen-fixing alder in the gulf's riparian zone.

The hypothesis that a long residence time of water is contributing to the high concentrations of dissolved solutes in Great Gulf stream water was supported by a casual inspection of the structural geology of the Great Gulf headwall. Extensive, decompression-related fracturing was observed throughout the gulf's bedrock. Fractures are aligned parallel to the gulf, approximately 2-8m apart and would allow for the penetration of wet deposition and the pooling of groundwater (Erikson, *personal communication*). Additionally, Eusden et al. (1996) believed they found evidence of a thrust fault along the edges of the gulf, which separates this basin structurally from other sections of the Littleton Formation. The unique geologic structure of the Great Gulf appears to be influential in determining its stream water chemistry, since it explains both the high concentrations of dissolved solutes in general and the preferential weathering of Ca-rich materials.

Oakes Gulf: Despite evidence of Al-leaching indicating some degree of cation exchange in Oakes Gulf's poorly developed soils (Figure 6), bedrock weathering appears to be the primary source of the base cations observed in Oakes Gulf stream water. This hypothesis is supported by the strong positive correlations between the base cations and SiO₂, whose only source, as aforementioned, is bedrock weathering (Figure 4). Plagioclase should be the only source of additional Na in Oakes Gulf (Peters 1992). Consequently, and since plagioclase is the only major source of both Ca and Na in the Littleton gneiss (Billings and Fowler-Billings 1975), the Ca:Na molar ratio from the gneiss was used as an estimate for the molar ratio expected from bedrock weathering in Oakes Gulf to determine if the stream's Ca net output could be explained by plagioclase

alone. However, the high Ca:Na molar ratio in Oakes Gulf's stream water indicates that plagioclase weathering cannot explain the Ca concentration (Table 3).

Instead, the minerals tremolite and diopside are more probable sources of Ca in this basin's bedrock. Peters (1992) showed that the Madrid Formation contains abundant tremolite and diopside, which are both Ca-containing silicates. Both of these minerals preferentially release Ca through geochemical interactions (Brantley and Chen 1995); and their break down through chemical weathering would be consistent with both the strong correlations observed between Ca, Mg, and SiO₂ and the lack of correlations between these solutes and Na or K.

While Oakes Gulf's Mg concentration may be attributable to the weathering of tremolite and diopside, it can also potentially be explained by chemical weathering of biotite, orthoclase, and muscovite, which are all present in the Littleton schist and in the Smalls Falls Formation. Mg:K molar ratios in the bedrock underlying the alpine basin's headwall range from 0.06 for the Small Falls Formation to 106.87 for subunits of the Madrid Formation (Peters 1992). In comparison, the Mg:K molar ratio of stream water is 4.88. However, it is also possible that both the high Mg:K and Ca:K molar ratios are better explained by the uptake of K by vegetation. K is one of the first cations to be assimilated by vegetation, and net consumption of K is typical during the summer months (Likens and Bormann 1995). The net gain in NH₄ lends support to the idea that biological interactions may significantly alter stream water chemistry.

Nevertheless, bedrock weathering appears to be pivotal in regulating the sensitivity of Oakes Gulf's stream water to acidification. The ANC is higher when Ca, Mg, and SiO₂ are released, presumably from the weathering of tremolite and diopside

(Figure 4). The pH of the headwall stream is also higher when Ca and Mg concentrations are greater. Furthermore, Oakes Gulf's ANC is very sensitive to the SO_4 concentration in stream water (Figure 7); and bedrock weathering is likely the source for Oakes Gulf's relatively large SO_4 output.

The Madrid Formation and, in particular, the Smalls Falls formation contain pyrite as part of their mineral assemblage, and the Smalls Falls formation is thought to be easily weathered (Billings et al. 1946; Peters 1992). Consequently, weathering of this bedrock material is a potential source of SO_4 that would explain why correlations between SO_4 and SiO_2 and SO_4 and the base cations are weak. Pyrite dissolution from Smalls Falls rock would produce the additional SO_4 observed in Oakes Gulf stream water without affecting the amounts of base cations or SiO_2 released. This additional source of SO_4 within the system makes Oakes Gulf especially sensitive to atmospheric inputs of acidifying compounds.

Huntington Ravine: In order to determine whether the large net losses of base cations in Huntington Ravine can be attributed to the release of these solutes through the process of bedrock weathering, molar ratios of base cations and Si observed in Huntington Ravine stream water were compared to molar ratios determined using weight percentages of elements measured by Anderson and Hawkes for Littleton schist (1958) (Table 3). The Ca:Mg, Ca:Na, and Mg:Na molar ratios observed in stream water are very similar to those calculated using Anderson and Hawkes' results, suggesting that the bedrock is a significant determinant of the ravine's stream water chemistry.

The observed Ca:K and Mg:K molar ratios from this study are much higher than what would be expected to leach from the bedrock; however, this may be explained by the rapid assimilation of K by vegetation at the base of the headwall, just above the sampling site. The Ca:Si molar ratio from this study is also slightly higher than the ratio reported in Anderson and Hawkes' study (1958). Yet because the Mg:Si and Na:Si molar ratios observed in Huntington Ravine stream water are also higher than those expected, it is likely that either base cations are preferentially released over SiO₂ in chemical weathering reactions or that some degree of cation exchange is producing additional base cations. The inverse relationship, despite being statistically weak, between the H ion concentration and the base cation concentration and evidence of Al-leaching suggest that cation exchange may be occurring in the ravine's thin soil substrate or even in the bedrock (Meixner et al. 1998). Additionally, it can be inferred, from the net gain in H and net loss in base cations (Figure 15), that H is consumed either through exchange with Ca, Mg, Na, K, and possibly Al or through geochemical interactions.

Because neither SO₄ nor NO₃ showed strong correlations with either the base cations or SiO₂, it is difficult to determine whether either of these strong acid ions might be contributing to the release of cations through bedrock weathering along the headwall of Huntington Ravine. NO₃ is, however, strongly and positively correlated with the volume-weighted Ca:Na ratio, which is an indicator of the preferential weathering of Ca-containing minerals. Moreover, the Ca:Na ratio increases with the H ion concentration, suggesting that the acidity of water may affect relative weathering rates. Nevertheless, what is interesting about Huntington Ravine is that the ANC seems more sensitive to the release of base cations and SiO₂ from soils and rock material than to the atmospheric

deposition of SO_4 and NO_3 . Except for one outlier, the base cation concentration and SiO_2 concentration exhibit a direct linear relationship, which would suggest that bedrock is the predominant source of the stream's cations (Figure 10). If Huntington Ravine's ANC is base cation dependent, then it is clear that the system's sensitivity to acidification is governed by rock weathering rates.

Huntington Ravine's basin walls are the steepest of the four study basins; and the slope of the headwall may reduce water contact time with soils and bedrock such that geochemical interactions are limited. The large variance in the ANC suggests that weathering rates are also highly variable in the ravine and may depend on hydrologic pathways. At times when water courses quickly through the environment and is mostly in the form of surficial run-off, hydrologic residence time will be short, and the release of base cations may not be adequate to buffer sufficiently a continual deposition of strong acid ions.

Tuckerman Ravine: As was observed in the other alpine basins, much of Tuckerman Ravine's stream chemistry can be attributed to bedrock weathering. Tuckerman Ravine is underlain by many of the same bedrock types as Oakes Gulf, plus a small amount of the orthogneiss of which the Rangeley Formation is composed. Thus, the only geologic source of Na should be plagioclase. As was done for the Great Gulf and Oakes Gulf, the Ca:Na molar ratio of the Littleton gneiss was used as a reference for the Ca:Na molar ratio calculated for the net losses of Ca and Na in Tuckerman Ravine stream water (Figure 16).

The Ca:Na molar ratio calculated for Tuckerman Ravine stream water is higher than what would be expected if plagioclase were the only source of both Ca and Na. Clearly, the weathering of other minerals contributes significantly to the relatively high Ca concentration in stream water. Like Oakes Gulf, Tuckerman Ravine is underlain by the Madrid formation, which contains abundant tremolite and diopside, and may be leaching large proportions of Ca and Mg (Peters 1992).

In comparing Tuckerman Ravine's net output to Oakes Gulf's net output, the similarities between the molar ratios of Ca:Na and Ca:Si for each basin are noticeable. This suggests that weathering rates of plagioclase and calc-silicates, such as tremolite and diopside, are comparable between the two basins. However, Tuckerman Ravine's Ca:Mg and Ca:K ratios are lower than Oakes Gulf's, while Tuckerman Ravine's Mg:Na and Mg:K rates are much higher. It is possible that the relative release of Ca and Mg from tremolite and diopside is different for the two basins. Tuckerman Ravine's bedrock, for instance may contain lower proportions of Ca:Mg than Oakes Gulf's bedrock. This would explain both the relatively low Ca:Mg and high Mg:Na and Mg:K in the ravine's stream water.

Another possible explanation for discrepancies in molar ratios between the two basins is the weathering of biotite, which may release Mg and K in a ratio ranging anywhere from 0.06 to 106.87 for the bedrock types in Mt. Washington's alpine zone (Peters 1992). Depending on the chemical composition of the biotite specific to Tuckerman Ravine, the weathering of this mineral could feasibly produce the concentrations of Mg and K observed in the ravine's stream water, in addition to

explaining both the low Ca:Mg and Ca:K molar ratios relative to those observed in Oakes Gulf.

The weathering of bedrock is also a possible source for Tuckerman Ravine's SO_4 concentration. Despite the fact that the difference between the predicted SO_4 input and the observed output is not statistically significant, this net loss could nevertheless be real, suggesting an endogenous source of SO_4 (Figure 16). The dissolution of pyrite in the Smalls Falls formation, which underlies the ravine, could contribute additional SO_4 to stream runoff. This would explain the poor correlations between SO_4 and the base cations, since the cations are presumably released from different minerals. If SO_4 is primarily from a source other than wet deposition, this would also explain the very poor correlations between SO_4 and NO_3 .

Conclusion

Low pHs, ANCs, and base cation:H ratios indicate that the four alpine basins on Mt. Washington that were included in this study are highly sensitive to acidification. A net loss of NO_3 was observed in the Great Gulf, and net losses of SO_4 were observed in Oakes Gulf, Huntington Ravine, and Tuckerman Ravine. The combination of these findings are consistent with tell-tale indications of a system's inability to consume acidic input sufficiently (Galloway et al. 1983; Campbell et al. 2000). Furthermore, such findings are especially alarming considering the Class I Wilderness or State Park status of the four basins included in this study.

The Clean Air Act mandates that Class I Wilderness areas, including the Great Gulf and Oakes Gulf, be protected from terrestrial and aquatic degradation resulting from contaminated atmospheric deposition. Yet this study indicates that strong acid weathering, likely influenced by high acidic loading from deposition, is severely compromising the buffering capacity of Mt. Washington's alpine streams. The Great Gulf, in particular, demonstrates signs of nitrogen saturation while Oakes Gulf's observed stream chemistry indicates possible sulfur saturation. Both of these conditions can accelerate the acidification of stream water (Galloway et al. 1983; Murdoch and Stoddard 1992), producing extreme episodic acidification events, and perhaps eventually creating long term toxic conditions for aquatic biota.

Huntington Ravine and Tuckerman Ravine are not protected under federal jurisdiction. Nevertheless, the health of these ecosystems is an important issue. Since both ravines are popular recreational destinations, their natural aesthetic is valuable; and the proper management of these fragile areas is essential. Environmental stress from the input of acidifying compounds, either through wet deposition or rock weathering, is compounded by the harsh weather conditions of high elevation, delicate vegetation, and high recreational use, making these ravines especially weak in their resilience to and recovery from acidification. Possible evidence of Al leaching in Huntington Ravine and Tuckerman Ravine suggests that the availability of base cations is limited in these basins and is a clear indication of their sensitivity to acidic deposition.

Despite the relative proximity of the four study basins and the similarity in environmental conditions to which they are exposed, stream water chemistry varies greatly among the four study basins, indicating heterogeneous responses to acidic deposition on a very local

scale. While orthographic effects cannot be ruled out, it is still highly likely that different stream outputs are the result of unique basin responses to acid input and do not simply reflect different atmospheric inputs.

Although all four headwall streams are dominated by Ca and SO_4 , distinct charge contributions of cations and anions for each basin's stream suggest that the specific processes controlling water chemistry may have different strengths in, or even be unique to each catchment area. High concentrations of dissolved solutes in the Great Gulf are best explained by the pooling of groundwater. As a result, the long hydrologic residence time facilitates the weathering of calc-silicate lenses. Biological processes may also influence the level of nitrogen saturation of Great Gulf stream water. In comparison, the sensitivity of Oakes Gulf and Tuckerman Ravine to acidification seems to be controlled by the output of SO_4 from the weathering of pyrite found in the underlying bedrock. On the contrary, the sensitivity of Huntington Ravine is neither SO_4 - nor NO_3 -driven, but seems to be determined by the availability of base cations, which is in turn controlled by the contact time of water on soil and bedrock as it courses down the steep basin walls.

In general, the geologic characteristics of Mt. Washington's basins, including the structure of the basin and the mineral assemblage of the bedrock, appear to be very influential on stream water chemistry. Wet deposition, on the other hand, seemed much less influential during the sampling regime of this study, despite the fact that acid rain is a significant source of SO_4 and NO_3 . This study suggests that alpine basins whose underlying bedrock includes sulfur-containing minerals are especially sensitive to deposition of strong acid ions. The deposition of acidifying compounds can facilitate bedrock weathering, thus releasing additional strong acid ions, such as SO_4 , from the

bedrock while concurrently reducing the ANC by leaching base cations and Al from the system.

This study also suggests that the residence time of water as it contacts soil and bedrock may be another important determinant of sensitivity to acidification. Where the headwall is steep and water contact time is especially low in Huntington Ravine, the availability of base cations is limited; and this appears to be highly influential on the stream's buffering capacity and ability to respond to acidic deposition. In comparison, where water residence time is longer in the Great Gulf, the pH and the ANC are both much higher. Hydrologic residence time clearly impacts the chemistry of stream water by influencing rates of geochemical interactions.

Although much of the observed stream water chemistry could be attributed to the weathering of rock material, discrepancies between observed and predicted concentrations of N and K were often noted. These results indicate that nitrification and/or assimilation by vegetation may be important processes even in the alpine zone where both biomass and ground cover are minimal. This is consistent with findings by Baron and Campbell (1997), who reported that biological activity in talus-dominated alpine areas significantly affected local stream water chemistry. The contribution of biological processes to stream water chemistry was ignored in this study, and yet such processes may play an important part in regulating the sensitivity to acidification of Mt. Washington's alpine zone.

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Appendix
Correlation Analysis

