

**AMC 2011 White Mountain National Forest
Class I Wilderness Areas
Air Quality Related Values Report**

Georgia Murray, AMC Staff Scientist
Cormac Griffin, Base Research Intern

Challenge Cost-Share Agreement 09-CS-11092200-010

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Table of Contents

1.0	Introduction	1
2.0	Parameters of Study	2
2.1	Ozone	2
2.2	High Elevation Cloud and Rain Water Chemistry	3
2.3	Class I Area Stream Chemistry	10
2.3.1	Background	10
2.3.2	Wilderness Transect Study (1995-1997)	12
2.3.3	Wilderness High-Elevation Stream Monitoring (2001-Present).....	13
2.3.4	Results.....	14
	Literature Cited	26
	APPENDIX 2-A.....	29

Tables and Figures

Table 2.2-1	USDA FS Region 9 Listed Nitrogen and Sulfur Deposition Analysis Thresholds	3
Table 2.2-2	Chemical analysis methods and laboratory information.....	5
Table 2.2-3	Summary statistics in micro-equivalents per liter for field hydrogen ion only for cloud and rain water samples collected at Lakes of the Clouds site from 1984-2010. 2011 median values are provided separately for comparison.....	6
Figure 2.2-1	Box and whisker plots of ions in micro-equivalents per liter for cloud water at Lakes of the Clouds for 1984-2011.	7
Figure 2.2-2	Box and whisker plots of ions in micro-equivalents per liter for rain water at Lakes of the Clouds for 1984-2011.....	7
Table 2.2-4	Summary statistics in micro-equivalents per liter for major ions measured in cloud and rain water samples collected at Lakes of the Clouds site from 1984-2010. 2011 median values are reported separately for comparison.....	8
Figure 2.2-3	Average ion concentrations in micro-equivalents per liter by year for cloud water .	9
Table 2.3.1-1	USDA FS Region 9 AQRVs for Water-Resource Concern Thresholds.....	11
Figure 2.3.2-1	1995-1997 Stream Transect	12
Table 2.3.2-1	1995-1997 stream sample site descriptions and elevations. Bolded locations are the focus of later monitoring conducted from 2001 to the present.	13
Table 2.3.4-1	Median pH, calculated ANC, Inorganic monomeric Aluminum (I-Al+3), sum of the base cations, and nitrate concentrations grouped by location(s) and year(s). See Table 2.3.2-1 for location descriptions.....	16
Figure 2.3.4-1	Stream grab samples from two high-elevation sites in WMNF Class I Areas. Data from summertime 1995-1997 and 2001-2011 (a) silica verses calcium (b) nitrate vs calcium (c) sulfate vs. calcium.....	18
Figure 2.3.4-2	Stream grab samples from two high-elevation sites in WMNF Class I Areas. Data from summertime 1995-1997 and 2001-2011 (a) Sulfate plus nitrate and (b) inorganic monomeric aluminum verses calculated ANC in microequivalents per liter.	19

Figure 2.3.4-3 Inorganic monomeric aluminum versus calculated ANC in microequivalents per liter from ALL elevations in WMNF Class I Areas and Lakes of the Clouds sites. Data from summertime 1995-1997 and 2001-2011.	20
Figure 2.3.4-4 Inorganic monomeric aluminium in microequivalents per liter by month-year at PDR-7 and PDR-14 from 1995-1997, 2001, and 2009-2011. Note the scale shifts between the two graphs.	21
Figure 2.3.4-5 Nitrate in microequivalents per liter by month-year at GGW-1 and GGW-1 from 1995-1997 and 2009-2011. Note the scale shifts between the two graphs.	21
Figure 2.3.4-6 Nitrate in microequivalents per liter versus TOC in milligrams per liter from ALL elevations in WMNF Class I Areas and Lakes of the Clouds sites. Data from summertime 1995-1997 and 2001-2011.	22
Figure 2.3.4-7 Stream grab samples from AMC sites in WMNF Class I Areas compared to chemistry from the WMNF Stream Database (2001).	24

1.0 Introduction

Per AMC's Challenge Cost-Share Agreement 09-CS-11092200-010 with the WMNF, we are providing this report on cooperatively monitored and analyzed air quality related values (AQRVs) in and near the Great Gulf Wilderness and Presidential Range-Dry River Wilderness Class I Areas. Monitoring AQRVs has been identified in the WMNF Management Plan as baseline tracking necessary, in part, to fulfill the management objective of assessing the effects of major new or modified emission sources of air pollution on Class I Airsheds. Under the Clean Air Act PSD program, the Forest Service has the affirmative responsibility to protect Air Quality Related Values, including visibility, vegetation, and water quality, within Class I Areas.

The objective of the work described here is to conduct monitoring and analysis of ozone concentrations, rain and cloud water chemistry, and surface water quality to assess the effects of air quality on resources within the Class I Areas. Sites for monitoring locations include the summit of Mount Washington, Camp Dodge near the base of Mount Washington, Lakes of the Clouds, and various stream sampling locations throughout, and adjacent to, the Class I Areas. Also included in this report is a summary of AMC's fine particulate data as it relates to the IMPROVE monitoring collected at Camp Dodge.

AMC is an organization which promotes the protection, enjoyment, and wise use of the mountains, rivers, and trails of the Northeast, believing the mountains have an intrinsic worth and also provide recreational opportunity, spiritual renewal, and ecological and economic health for the region. Many of these values are influenced by impacts from air quality, especially those values called air quality related values such as water quality and healthy vegetation. AMC has been conducting monitoring of air pollution and its impacts on AQRVs in the White Mountains since 1981 to help the Forest Service meet its management responsibilities under the Clean Air Act. It is mutually beneficial for both AMC and the Forest Service to cooperatively conduct monitoring related to air quality related values in the Class I Areas of the White Mountain National Forest.

2.0 Parameters of Study

2.1 Ozone

Ozone in high concentrations during the growing season is known to cause visible injury to foliage, reduced photosynthesis, and growth, and premature leaf senescence to sensitive plants. Ozone sensitive plants occur in the Class I Areas on the White Mountain National Forest. Furthermore, higher-elevation areas experience relatively higher ozone exposure than lower elevations in the forest and currently exceed the 2008 primary (human health) and secondary (plant health) National Ambient Air Quality Standard (NAAQS) design value of 75 ppb. Ozone monitoring data is needed in order to track effects of ozone on the vegetation in the Class I Areas and to work with the State and Federal regulators to reduce future ozone concentration by limiting future emissions of ozone precursors.

Ozone results are given in a full report provided separately. This report includes data for 2011 and long-term trends from Mount Washington and Camp Dodge. In summary the 2011 ozone levels on Mount Washington and Camp Dodge had a lower 4th highest daily 8-hr average than in 2010, resulting in the 3-year rolling average being lower and below the 2008 standard of 75 ppb for the past two consecutive years.

The current secondary NAAQS, which mirrors the primary, is not designed to protect vegetation. The report provides a summary on the W126 cumulative metric that had been proposed by EPA as part of the re-consideration of the 2008 ozone standards. The 2010 Federal Land Managers' Air Quality Related Values Work Group (FLAG) guidance points to the need to focus on protecting native vegetation from ozone injury. AMC calculates and reports on W126 values, which for 2011 (April through September) was 26.8 ppm-hrs at the Mount Washington site. We also include information on a past study that documented some ozone injury in plants within and around the Great Gulf Wilderness Area. However, there remains a significant research need to relate current ozone conditions to presences or absences of vegetation impacts in the high and mid-elevation areas where ozone exposure is highest, yet little monitoring has been done. FLAG (2010) recommends, as part of the PSD permit review process, that FLMs should consider (1) whether or not actual ozone damage has occurred in the area, and (2) whether or not ozone exposure levels occurring in the area are high enough to cause damage to vegetation (i.e., phytotoxic O₃ exposures). This type of evaluation will be difficult without direct evaluation of known ozone sensitive plants.

2.2 High Elevation Cloud and Rain Water Chemistry

Atmospheric deposition of sulfate and nitrate cause vegetation and soil leaching of cations, changes to water quality, and potentially damage ecosystem health across the White Mountain National Forest. For example, these pollutants can alter the chemical balance often causing accelerated leaching of aluminum and other cations in the soil. Monitoring of precipitation chemistry and water quality is used to understand how the input of sulfate and nitrate from air emission sources are affecting the AQRV of water quality.

FLAG (2010) lists indicators for monitoring and evaluating effects from deposition of S and N. Freshwater chemical changes include ANC depression and changes in phytoplankton and benthic community composition, species diversity, and biomass. Terrestrial leaching of soil cations, soil acidification, and mobilization of aluminum ions are also listed, as is changes in nitrogen cycling for N specific deposition. The FLAG (2010) discusses the use of Deposition Analysis Thresholds (DATs) as a metric to evaluate the impacts of new emission sources of sulfur and nitrogen on AQRVs in Class I Wilderness Areas. The USDA FS lists DATs for N and S of 0.010 kilograms per hectare per year, shown in Table 2.2-1, based on an estimate of 0.25 kg/ha/yr natural deposition for both S and N in the eastern US and scaling and cumulative factors. New emissions sources that contribute less 0.010 kg/ha/yr would not be expect to impact AQRVs in the Class I Area. A recent update to the DAT guidance was issued in Nov. of 2011 in which clarifying steps for evaluating a new source were added as well as introduction of the use of critical loads as a tool to determine impacts of S and N deposition to natural ecosystems. Miller (2005) reported that NH state-wide modeled S and N deposition for 1999-2003 ranged from 3-19 and 3-25 kg/ha/yr respectively stating that the highest deposition occurs at the higher-elevations areas. Improved estimates of high-elevation deposition rates are needed to properly evaluate and protect AQRVs in NH Class I Wilderness Areas.

Table 2.2-1 USDA FS Region 9 Listed Nitrogen and Sulfur Deposition Analysis Thresholds

Region	Pollutant Exposures	Level Name	Thresholds
R9	Nitrogen	EXCEEDANCE	The Deposition Analysis Threshold for nitrogen deposition below which estimated impacts from a source are considered negligible is 0.010 kilograms/hectare/year.
R9	Sulfur	EXCEEDANCE	The Deposition Analysis Threshold for sulfur deposition below which estimated impacts from a source are considered negligible is 0.010 kilograms/hectare/year.

Rain and cloud samples were collected at Appalachian Mountain Club (AMC) Lakes of the Clouds Hut (1534 m) during the summer months of 1984 to 2011. The site is situated above tree line approximately 1.7 km southwest of the summit of Mount Washington (1917 m) in north central New Hampshire, USA. While summertime only sampling does not provide sufficient data to calculate annual deposition of sulfur and nitrogen it does allow comparison to lower elevation sites and documents the importance of cloud contribution to total inputs in Class I Areas.

Methodology

A passive cloud collector, designed by Appalachian Mountain Club and Worcester Polytechnic Institute, was used to collect cloud water. The passive cloud collector is constructed of acrylic plastic, requires no power, excludes heavier rain droplets, and uses the wind to deliver cloud droplets on a bank of Teflon strands (Daube et al., 1987; Weathers et al., 1986; 1988). A full description of the collector can be found in Daube et al., (1987). Cloud events were sampled in the summer time, generally early June through August, from 1984 to 2011. The sampling regime does not represent 100% seasonal coverage due to staffing capabilities. Collections of clouds were preceded by a 5 to 15 minute purge and then typically divided into 6 hour samples or a 10 to 12 hour overnight sample. Consequently, we also collected both sequential samples within continuous cloud events and sample from non-contiguous cloud events. Water is collected into a polyethylene sample bottle through Tygon tubing.

Rainwater was also collected during rain events in a polyethylene funnel and Tygon tubing that led to a polyethylene sample bottle. All materials were rinsed with DI water between events. All instruments were covered during fair weather to prevent input from dry deposition.

Samples were transported to a field laboratory on site, measured for pH using an Orion Model 339 A/F pH meter (1984- 1994), Thermo Orion Model 230A with a Ross 8102 electrode (1995 – 2004, Thermo Scientific Orion 3 Star (2005-2011), and field techniques used by the Global Precipitation Chemistry Project (Galloway et al., 1982). From 1984-2000 volume of water collected was determined using the pre-marked increments on the collection bottle. Therefore they are not exact (plus or minus ~25 ml). In 2001 samples were weighted tarring out the weight of the empty bottle. Samples were shipped to the Institute of Ecosystem Studies analytical laboratory for cation-anion analysis from 1984-1990 and to the USFS lab from 1994 to 2011. A table of laboratory methods and instruments is shown below.

Table 2.2-2 Chemical analysis methods and laboratory information.

Chemical Parameter	IES Lab 1984-1990	USFS Lab	USFS Lab Changes
Lab pH	Fisher Accumet 610A pH meter	NA	NA
Sulfate Nitrate	Ion Exchange Dionex 21 I and Dionex 14	Continuous Flow Analysis (CFA) Technicon and Scientific Instruments Sulfate: Methylthymol blue reaction Nitrate: Copper-cadmium reductor column, Marshall Reagent (conc. * 4.43=NO3)	July 2002 Ion Chromatography, Anions with chemical suppression, with electrochemical detection (ELCD) and conductivity detection
Chloride Ammonium	Technicon autoanalyser Chloride: Mercuric thiocyanate method Ammonium: Indophenol method	Continuous Flow Analysis (CFA) Technicon and Scientific Instruments Chloride: Ferricyanide, ferric thiocyanate reaction Ammonium: Phenate, indophenol blue Bethelot Reaction	July 2006 Flow Injection, Lachat QuickChem QC8500 Automated Ion Analyzer
Potassium Sodium	Flame Atomic Absorption Perkin Elmer 2380	Inductively Coupled Plasma atomic emission spectroscopy with charge-coupled detector	No change
Calcium Magnesium	Inductively coupled plasma emission spectroscopy, Perkin Elmer 6000		

Other parameters recorded at the time of sampling include start and end temperature, wind speed, and direction. Odometer readings that recorded total wind run were also taken over the duration of the sample event; however some years are missing this information. Because sample volumes were only estimated for a significant portion of the dataset, from 1984 to 2000, we do not attempt to volume weight concentrations. Samples that were collected overnight, without record of whether the rain or cloud event was continuous or not, may include some dry deposition as well as wet deposition. Rationale for retaining these samples in analysis summaries is discussed below.

The data set includes a large number of samples where pH alone was measured; therefore we did not exclude samples if the ion balance could not be calculated. When all ions were available ion balance was calculated and samples excluded if the following criteria were met: when (anion + cation) >=101 and IPD >21, or when (anion + cation) >=51 and IPD >31, or when (anion + cation) <51 and IPD >61.

$$IPD = (\text{anion} - \text{cations}) * 100 / (\text{anion} + \text{cations}) \quad (1)$$

The ion balance criteria was applied to the data reported on here. It should be noted that in reports previous to 2010, no criteria was applied. In the data analysis if lab hydrogen was missing, field hydrogen as used as a substituted, and vice-versa. For testing significant differences between datasets non-parametric Kruskal-Wallis One-way Analysis of variance was applied, with a Mann-Whitney U Test statistic, using Systat 12.

Results

Basic Statistics

Median field hydrogen ion concentrations, calculated from pH, are reported in Table 2.2-3 for cloud and rain samples. Field pH was measured without significant breaks throughout the entire record. The 2011 field hydrogen median values are considerably lower than in previous years, in fact they are at or below the 10th percentile values for the 1984-2010 record.

Table 2.2-3 Summary statistics in micro-equivalents per liter for field hydrogen ion only for cloud and rain water samples collected at Lakes of the Clouds site from 1984-2010. 2011 median values are provided separately for comparison.

Field Hydrogen Ion	Cloud	Rain
1984-2010		
n	1216	785
median	74	32
90 th Percentile	331	112
10 th Percentile	11	8
2011 median	10.8	7.2
2011 n	35	29

Figure 2.2-1 and Figure 2.2.-2 are box and whisker plots for all chemistry measured in cloud and rain water samples. The hydrogen ion median value in this graph is the *lab* hydrogen ion, which was measured separately from field pH. Median concentrations are greater for all chemical parameters in cloud water than in rain, with the sum of sulfate, nitrate, ammonium, and hydrogen ion concentrations 3x higher.

Figure 2.2-1 Box and whisker plots of ions in micro-equivalents per liter for cloud water at Lakes of the Clouds for 1984-2011. (a) Includes Calcium (CA), Chloride (CL), Sodium (NA), Magnesium (MG), and Potassium (K) and (b) includes Lab Hydrogen (H), Sulfate (SO4), Ammonium (NH4), and Nitrate (NO3).

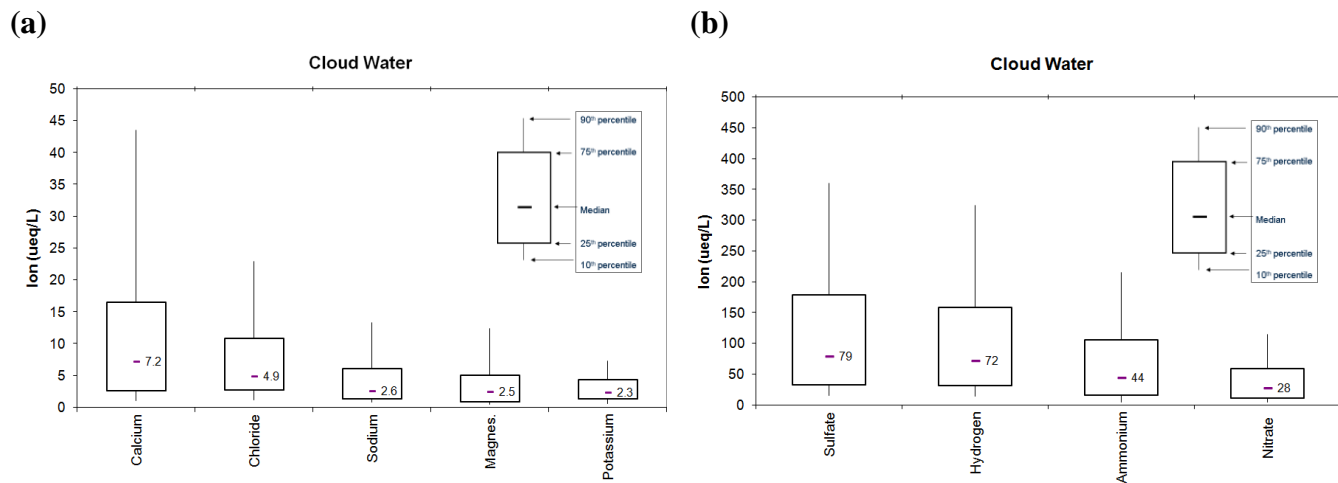


Figure 2.2-2 Box and whisker plots of ions in micro-equivalents per liter for rain water at Lakes of the Clouds for 1984-2011. (a) Includes Calcium (CA), Chloride (CL), Sodium (NA), Magnesium (MG), and Potassium (K) and (b) includes Lab Hydrogen (H), Sulfate (SO4), Ammonium (NH4), and Nitrate (NO3).

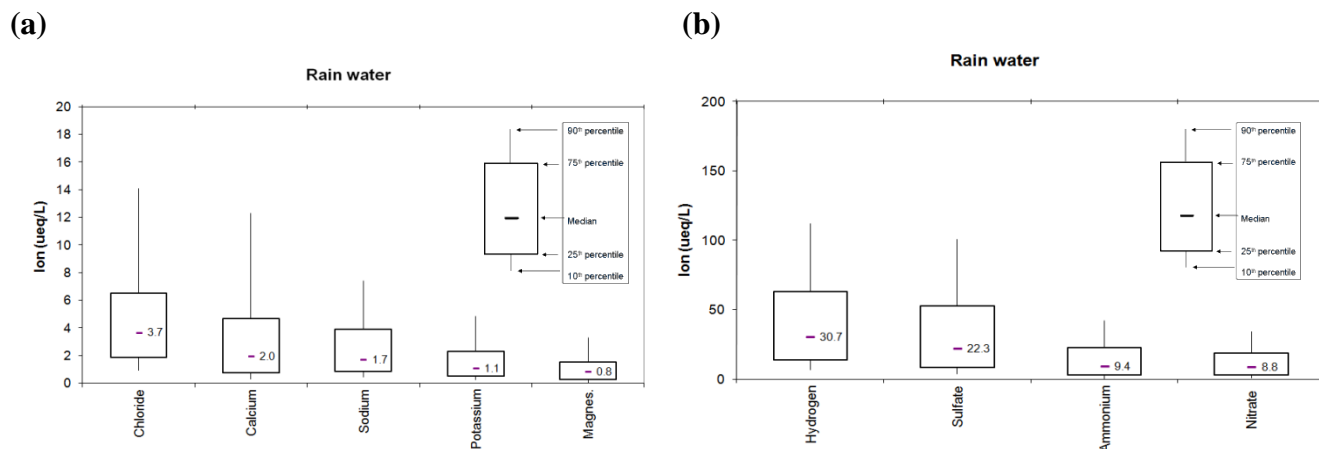


Table 2.2-4 shows statistics for the major ions measured including *lab* hydrogen ion, which was measured separately from field pH. Overnight samples are included. An analysis of potential differences in concentrations at nighttime is being conducted by the AMC. It is expected that the overnight boundary layer setting up below the Lakes of the Clouds sampling site causing increases in wind speeds and transport times from pollution source regions to this elevation.

Table 2.2-4 Summary statistics in micro-equivalents per liter for major ions measured in cloud and rain water samples collected at Lakes of the Clouds site from 1984-2010. 2011 median values are reported separately for comparison.

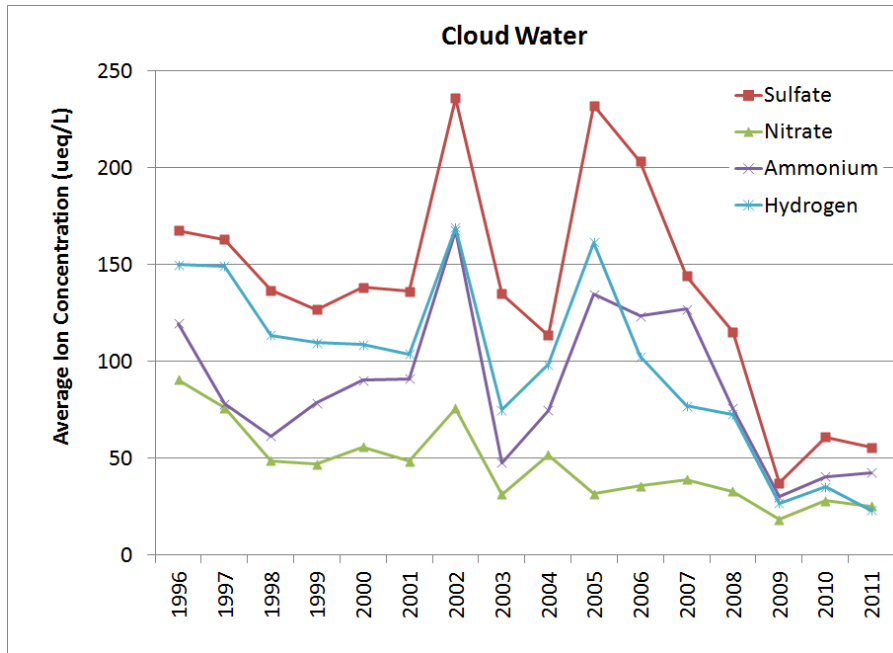
CLOUD WATER	CA	MG	K	NA	NH4	NO3	SO4	CL	LAB_H
n	667	667	668	668	664	666	667	668	1216
Median	7.2	2.5	2.3	2.8	47	29	87	5.1	74
10 th percentile	1.0	0.4	0.6	0.8	5	4	17	1.1	15
90 th percentile	44	13	8	14	222	117	377	24	331
2011 Median (n=33)	8.2	1.7	3.5	1.8	24.6	15.3	28.1	2.7	10.7

RAIN WATER	CA	MG	K	NA	NH4	NO3	SO4	CL	LAB_H
n	440	441	440	438	436	440	441	440	785
Median	2.0	0.8	1.0	1.7	10	9	23	3.7	32
10 th percentile	0.3	0.0	0.3	0.4	1	1	4	0.9	8
90 th percentile	13	3	5	8	42	36	102	16	112
2011 Median (n=23)	1.5	0.6	1.5	3.5	5.1	4.5	6.3	2.5	5.4

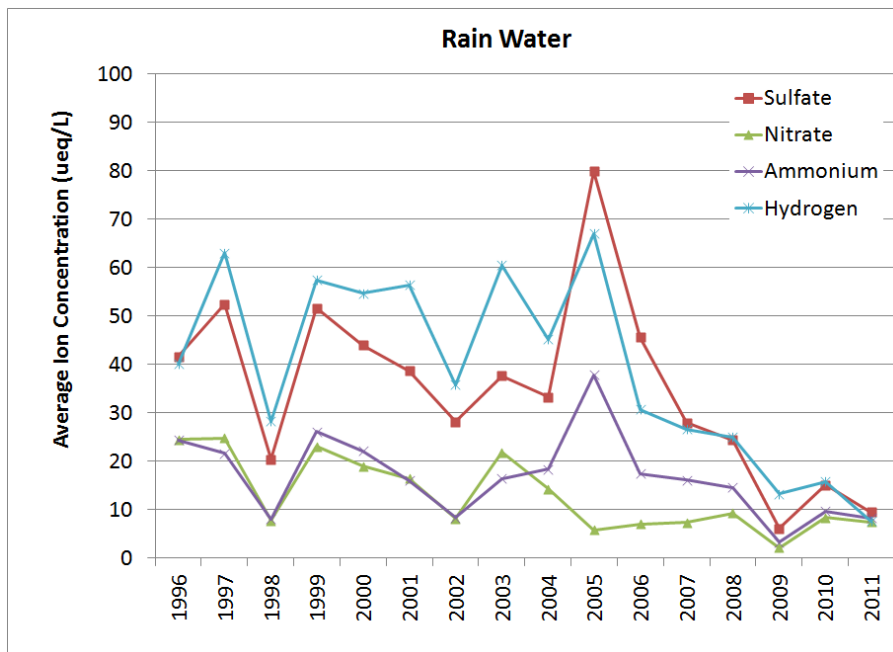
In 2011 the median values for sulfate, nitrate, ammonium, and hydrogen ions were considerably lower than the median levels from 1984-2010 for both cloud and rain water. Median ammonium as a percentage in cloud water is nearly equal to that of hydrogen in the most recent monitoring years. That maybe due to this site being in a rural location, further from fresh acidic aerosol formation, and due to the declines in sulfate which allows for a larger percent of the total sulfate to be more neutralized. The last 3 years of the record have some of the lowest *average* concentration for the major pollutants; sulfate, nitrate, ammonium and hydrogen ions, Figure 2.2-3. The average values do not account for differences in total deposition due to not being volume weighted. The AMC is conducting an update of an analysis of the long-term cloud and rain chemistry including a more in-depth look at day versus night samples and in the context of pre and post Clean Air Act Amendments.

Figure 2.2-3 Average ion concentrations in micro-equivalents per liter by year for cloud water (a) and rain water (b) at Lakes of the Clouds.

(a)



(b)



2.3 Class I Area Stream Chemistry

2.3.1 Background

Acidic deposition in the northeastern United States has caused significant changes in chemical cycling within discrete catchment areas (Driscoll et al. 2001). Output from small watersheds via the stream network is often used to detect changes in the chemical signal of the ecosystem due to increased acidic deposition (Clow & Mast 1999; Flum & Nodvin 1995; Goodale 1998; Lawrence et al. 1999; Vitousek 1977). The long-term ecological consequences of acidic deposition are thought to include increased nitrate and aluminum mobility, leaching of exchangeable base cations, declines in acid neutralizing capacity (ANC), 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 from both rain and clouds (Driscoll et al. 2001). Additionally, the leaching of base cations reduces an ecosystem's ANC, further sensitizing the system to continued acidic deposition (Wigington et al. 1996). High streamflow following storm events may exacerbate the effects of chemical imbalances by diluting base flow, which often has higher buffering capacity, and bring a pulse of acidic pollutants and organic acids further decreasing the ANC. This is frequently observed during spring run-off from snow melt when headwater streams tend to be more acidic (Wigington et al. 1996).

Alpine watersheds, with their fragile vegetation communities and heightened exposure to acidic deposition, are potentially some of the most at-risk ecosystems. High-elevation sites tend to receive greater doses of nutrients and contaminants than comparable low-elevation sites; and the harsh environmental conditions and short growing season of the alpine zone makes the vegetation susceptible to stress from chemical inputs (Weathers et al. 2000). Atmospheric deposition rates increase with elevation, and cloud deposition becomes significant above 1000 meters (Weathers et al. 2000). A study of stream chemistry in the Catskill Mountains over an elevation range of 817-1234 meters has shown a strong positive correlation between elevation and concentrations of nitrates and sulfates while concurrently showing a strong negative correlation between elevation and concentrations of exchangeable base cations (Lawrence et al. 1999).

Within the White Mountain National Forest (WMNF), two previous investigations studied nutrient cycling and streamwater chemistry at higher elevations (Goodale 1998; Vitousek 1977), yet only

Vitousek (1977) focused on the alpine zone. Between 1973 and 1974 Vitousek (1977) sampled concentrations of elements in 40 streams on Mount Moosilauke, in the southwestern corner of the WMNF, and 17 streams on Mount Washington. Eleven of these were in alpine tundra, above 1400 meters. Vitousek (1977) found that nitrate concentrations did not vary with elevation, but rather with the successional status of the watershed. Old-aged ecosystems had higher concentrations of nitrate in stream water than young, rapidly-growing systems due to their lower nutrient saturation point. Sulfate concentrations in streams were best explained by precipitation input and did not seem affected by interactions with terrestrial components. Vitousek (1977) also observed higher pH in alpine streams and suggested that the local geology might control for this.

The USDA Forest Service (FS) lists chronic and episodic ANC as a sensitive indicator for water AQRV with a threshold of greater than 25 ueq/L to maintain healthy biological function in perennial streams of the two Class I Wilderness Areas in the WMNF, see Table 2.3.1-1.

Table 2.3.1-1 USDA FS Region 9 AQRVs for Water-Resource Concern Thresholds

AQRV Type: WATER			
Region	Sensitive Receptor	Sensitive Receptor Indicator	Thresholds
R9	Perennial Streams	Chronic Acid Neutralizing Capacity	To maintain healthy biological functioning in perennial streams, the chronic acid neutralizing capacity must be ≥ 25 ueq/l.
R9	Perennial Streams	Episodic Acid Neutralizing Capacity	To maintain healthy biological functioning in perennial streams, the episodic acid neutralizing capacity must be ≥ 25 ueq/l.

The recent 2010 USFS Watershed Condition Framework class assessment¹ scored water quality in the Peabody River as 3 (poor condition) and the Headwaters of the Saco as 2 (functioning at risk) for physical water quality class. The overall watershed class was scored better, accounting for other watershed health factors, at 2 (functioning at risk) and 1 (functioning properly) for the two watersheds, respectively. This assessment provides the USFS with:

“a new consistent, comparable, and credible process for improving the health of watersheds on national forests and grasslands. This framework will help focus our efforts in a consistent and accountable manner and make new investments in watershed restoration that will provide economic and environmental benefits to local communities.”

¹ <http://www.fs.fed.us/publications/watershed/>

2.3.2 Wilderness Transect Study (1995-1997)

Stream water chemistry was monitored in Great Gulf Wilderness (GGW) and Presidential Range-Dry River Wilderness (PDR) during the summers of 1995-1997 as part of a cooperative project with Dr. Christopher Eagar of the Northeastern Research Station, Durham, NH. The objectives of this monitoring effort were 1) to develop baseline data on water quality in these unique, high-elevation ecosystems and 2) to use this data to determine if there is a need for additional investigations into the sensitivity of these ecosystems to acid deposition. Water samples were collected from the West Branch

of the Peabody River that drains Great Gulf Wilderness and the Dry River and Rocky Branch in Presidential Dry River Wilderness. Samples

were collected at several sites along the length of the main stream as well as from two tributaries to each stream, see Figure 2.3.2-1. In 1995 and 1996, samples were collected biweekly during the period May to September. In 1997, samples were collected monthly during the summer months and the number of sample sites was reduced in Dry River and Rocky Branch, since data from the previous two years indicated little spatial variability in stream water chemistry. Water samples were analyzed at the Northeastern Forestry Sciences Laboratory in Durham, NH.

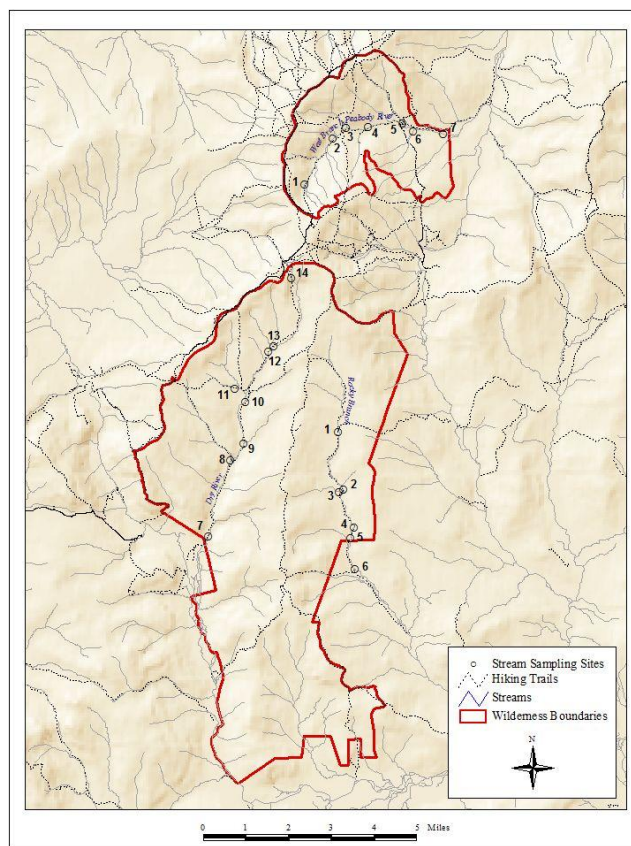


Figure 2.3.2-1 1995-1997 Stream Transect sampling sites in GG and PDR Wilderness Areas

Table 2.3.2-1 1995-1997 stream sample site descriptions and elevations. Bolded locations are the focus of later monitoring conducted from 2001 to the present.

<i>Wilderness/Sites</i>	<i>Location ID</i>	<i>Site Description</i>	<i>Elevation(m)</i>
Great Gulf Wilderness	GGW-1	Tributary above Spaulding Lake	1311
	GGW-2	Trunk of Peabody	1097
	GGW-3	Tributary Jefferson Brook	927
	GGW-4	Trunk of Peabody below Chandler Brook	838
	GGW-5	Tributary Parapet Brook (Madison Gulf)	689
	GGW-6	Trunk of Peabody before Boulder Falls	530
	SL	Spaulding Lake Outlet	1289
Presidential Range Dry River Wilderness	PDR-1	Trunk of Rocky Branch at shelter 2	853
	PDR-2	Trunk of Rocky Branch	625
	PDR-3	Tributary: Stairs Brook	625
	PDR-4	Trunk of Rocky Branch	564
	PDR-5	Trunk of Rocky Branch	503
	PDR-6	Trunk of Rocky Branch at Shelter 1	436
	PDR-7	Trunk of Dry River Wild Boundary	396
	PDR-8	Tributary Clinton Brook	610
	PDR-9	Trunk of Dry River	671
	PDR-10	Trunk of Dry River	792
	PDR-11	Tributary at Isolation Trail	853
	PDR-12	Trunk Dry River- Shelter 3	917
	PDR-13	Trunk of Dry River	945
	PDR-14	Tributary at Treeline- Oakes Gulf	1524
Lakes of the Clouds Lake sites	UL	Upper Lake	1539
	LL-S	Lower Lake Spring (sampled in 2001)	1528
	LL-Bog	Lower Lake Bog outlet (sampled in 2001)	1528
	LL	Lower Lake	1528

2.3.3 Wilderness High-Elevation Stream Monitoring (2001-Present)

Based on the findings of the 1995-1997 stream transect study AMC initiated a summertime stream monitoring effort in 2001 at high-elevation sites in the two Class I Wilderness Areas, sites GGW-1, SL, PDR-14, and UL, described in Table 2.3.2-1. Sampling sites were selected based on the previous studies locations but also factored in the best representative confluence near the edge of the alpine zone to capture chemical output dominated by the alpine vegetation community type. Samples were taken in Huntington and Tuckerman ravines from 2001-2006 but are not reported here.

Intensive sampling of alpine drainage streams was conducted in 2001 by Adriana Raudzens working as an AMC intern and as part of a senior project at Brown University (Raudzens, 2002). Raudzens (2002) analysis of 2001 summertime samples found that all stream had mean pH values <6.0 and calculated mean ANC values of < than 20 ueq/L indicating that they are acidic and poorly buffered. Further,

Raudzens found that monomeric aluminum was being mobilized with a strong correlation with hydrogen ion in PDR and Huntington Ravine alpine watersheds. The GGW site had relatively more calcium, magnesium, and nitrate than the other three sites sampled.

Since 2001, sampling has focused on GGW-1 and PDR-14 high-elevation sites and is conducted approximately every two weeks in summertime from June – August. Some samples have been collected in May and September but not consistently. Samples have also been collected in the Lakes of the Clouds lower lake (LL) periodically. In 2011, early spring-time samples were collected at lower elevations in each Wilderness Area, GGW-5 and PDR-7, to capture spring run-off at, or near the base of each Wilderness watershed as part of a WMNF wide sampling program. Timing of these spring samples relative to nearby river discharge volumes and the Mount Washington snow depth are shown in Appendix 2-A.

All samples are analyzed for pH by AMC within a few days of collection and at the end of the field season are sent to the USFS Durham lab for chemical analysis. Below detection values were included as zeros. Acid neutralizing capacity is calculated by summing major cations (calcium, magnesium, potassium, and sodium) and subtracting the sum of sulfate, nitrate, and chloride, the major anions. Inorganic monomeric aluminium (I-Al) is calculated by subtracting organic aluminium (O-Al) from monomeric aluminium (M-Al). Samples are not volume weighted as stream flow and discharge is not monitored. Therefore, the reader should recognize that concentrations differ by season, year, and elevation may be related to differences in stream flow.

2.3.4 Results

Table 2.3.4-1 shows median values of stream pH, calculated ANC, I-Al, the sum of base cation, and nitrate concentrations. Data are grouped by sample location(s) and year(s) collected. For 2011 GGW-1 and PDR-14 samples both median pH (5.9 and 5.5 respectively) and ANC values (15.3 and 4.8 respectively) varied little when compared to all years with summertime ANC remaining below the AQRV threshold of 25 ueq/L . PDR-14 continues to have lower pH and ANC values when compare to GGW-1. The early-season samples at GGW-6 and PDR-7 had ANC values of 17.4 (n=2) and 19.4 (n=1), respectively. Median values for these same locations from all years that they were sampled are provided in Table 2.3.4-1 for context. However, it is difficult to make a direct comparison because most

of the previous samples were taken from 1995-1997 between late May and early September and there are likely differences in seasonal discharge volumes.

All the sites have fairly low I-Al concentrations. There was a slight increase in I-Al at both GGW-1 and PDR-14 with the latter showing relatively higher concentrations. It is instructive to observe that the lower-elevation sites (GGW-6 and PDR-7) have similar to elevated ANC values compared to higher-elevation sites yet I-Al mobilization is slightly higher. Elevational difference in chemistry will be discussed further below.

Median nitrate concentrations are lower for both sites in 2011 compared to previous years with GGW-1 (21.9 ueq/L) continuing to have significantly higher levels than PDR-14 (5.5 ueq/L). Decreases in nitrate concentrations in surface waters over 20+ years has been observed in other WMNF streams (Martin et al. 2000, Goodale et al. 2003). In the study by Goodale et al. (2003) White Mountain mid-elevation streams had a mean nitrate level of 5 ueq/L in the summers of 1996 and 1997 at sites that ranged from about 880 to 1080 m. There is evidence that microbial communities and hydrologic flow paths both play a large role in nitrogen cycling in alpine watersheds in the Rocky Mountains (Campbell et al. 2000) and in the Northeast (Pardo et al. 2004). Pardo et al. (2004) discusses how watersheds with steep slopes and deep groundwater reservoirs can contribute to high nitrate stream concentrations. This may be why the Great Gulf alpine sites have high nitrate concentrations throughout the summer. Dominant vegetation communities along the flow path in the Great Gulf, which has a significant amount of nitrogen fixing alder, may also play a role. In comparison, the PDR Wilderness sample site drainage area, while largely composed of alpine vegetation, does include considerable krummholtz communities and more organic soils that could be retaining more nitrogen.

Table 2.3.4-1 Median pH, calculated ANC, Inorganic monomeric Aluminum (I-Al³⁺), sum of the base cations, and nitrate concentrations grouped by location(s) and year(s). See Table 2.3.2-1 for location descriptions.

Great Gulf Wilderness											
Location	Years Sampled	pH	n	Calc. ANC	n	∑ Base Cations	n	I-Al³⁺	n	NO₃	n
GGW-1	2011	5.9	8	15.3	8	98	8	0.7	8	21.9	8
GGW-1	1995-1997, 2001-2011	5.9	85	15.6	85	121	85	0	85	32.8	85
SL	1995-1997, 2006, 2009	5.7	25	9.8	25	115	25	1.1	24	31.4	25
GGW-6	2011 (April)	5.6	2	17.4	2	64	2	2.8	2	8.8	2
GGW-6	1995-1997, 2006, 2011	5.6	24	18.5	24	88	24	2.2	24	5.4	24
All GGW sites	1995-1997, 2001-2011	5.7	214	13.7	217	98	217	1.1	214	17.1	217
Presidential Range-Dry River Wilderness											
Location	Years Sampled	pH	n	Calc. ANC	n	∑ Base Cations	n	I-Al³⁺	n	NO₃	n
PDR-14	2011	5.5	7	4.8	7	50	7	1.6	7	5.5	7
PDR-14	1995-1997, 2001-2011	5.5	80	5.2	82	65	82	1.1	81	6.2	82
PDR-7	2011 (April)	5.5	1	19.4	1	65	1	3.8	1	2.0	1
PDR-7	1995-1997, 2001-2011	5.7	20	20.3	20	103	20	2.2	20	1.7	20
All PDR sites	1995-1997, 2001-2011	5.6	161	11.4	163	79	163	1.2	163	3.6	163
All Rocky Branch sites	1995-1997	6.2	63	40.0	63	79	63	0	63	2.1	63
Lakes of the Clouds sites in Ammonoosuc Watershed											
Location	Years Sampled	pH	n	Calc. ANC	n	∑ Base Cations	n	I-Al³⁺	n	NO₃	n
All Lakes of the Clouds sites: UL, LL, LL-S, LL-Bog	1995-1997, 2001-2011	5.3	39	-1.9	45	53	45	1.4	44	10.0	45

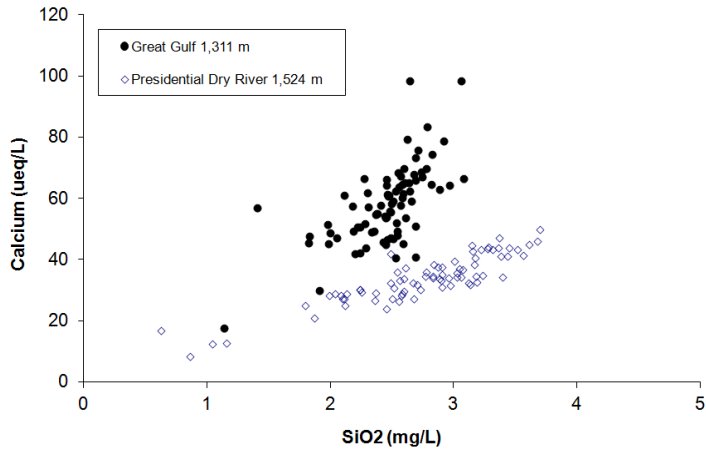
Lake and spring sites, which includes SL, LL (including lake, spring, and outlet samples), and UL, are grouped in Table 2.3.4-1 and have median pH and ANC lower than the high elevation stream sites. Median nitrate concentrations are similar between SL and GGW-1, while nitrate is somewhat elevated at UL and LL compared to nearby PDR-14. Baron et al. (2011) reports that high-elevation lakes in New England have been found to have an average nitrate concentration of 14 ueq/L, however that encompasses lakes from New York to Maine. While the GGW-1 and SL have some of the highest nitrate concentrations of this dataset, similar concentrations have been detected in the lower lake spring (LL-S), ranging from 26-32 ueq/L, that was sampled in 2001 as part of a larger survey conducted by A. Raudzens. Relatively high nitrate concentrations in springs and intermittent streams was consistent during that 2001 survey on Mount Washington and Mount Moosilauke (unpublished data). Similar to the GGW-1 site these seeps could be providing water from large groundwater reservoirs that accumulate nitrate.

Figures 2.3.4-1 and 2.3.4-2 show relationships between different chemical parameters within grab samples from the two high-elevation sites in each Wilderness Area (GGW-1 and PDR-14, Table 2.3.2-1) for all years sampled. Calcium concentrations show a general linear relationship with silica in both GGW-1 and PDR-14 sites indicating that it is mobilized through weathering of soils (Figure 2.3.4-1 a). However, GGW-1 stream calcium and nitrate levels are also positively correlated indicating either a causal or co-variance factor at this site. The calcium levels also increase with sulfate in GGW-1 samples but there is more scatter (Figure 2.3.4-1 b and c). PDR-14 shows relatively lower nitrate and calcium levels and only a weak calcium-to-sulfate correlation (Figure 2.3.4-1 c). Lovett et al. (2000) suggests that in Catskill mountain watershed streams with low nitrate output, sulfate drives calcium leaching, while in high-nitrate watersheds, the control switches to nitrate controlling calcium loss.

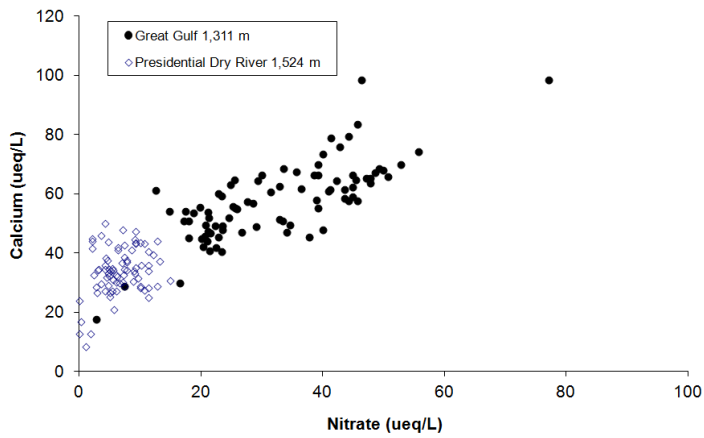
Differences in stream calcium concentrations between the two WMNF Wilderness Areas may be explained by the underlying bedrock content (Eusden et al. 1996) and/or different geological structure. The Great Gulf headwall is comprised of significant fractured rock which may allow for more weatherable surface area, relative to PDR, providing more calcium. Raudzens (2002) discusses the role of geo-physical and geo-chemical characteristics in influencing stream chemistry in the Wilderness Areas extensively.

Figure 2.3.4-1 Stream grab samples from two high-elevation sites in WMNF Class I Areas. Data from summertime 1995-1997 and 2001-2011 (a) silica versus calcium (b) nitrate vs calcium (c) sulfate vs. calcium.

(a)



(b)



(c)

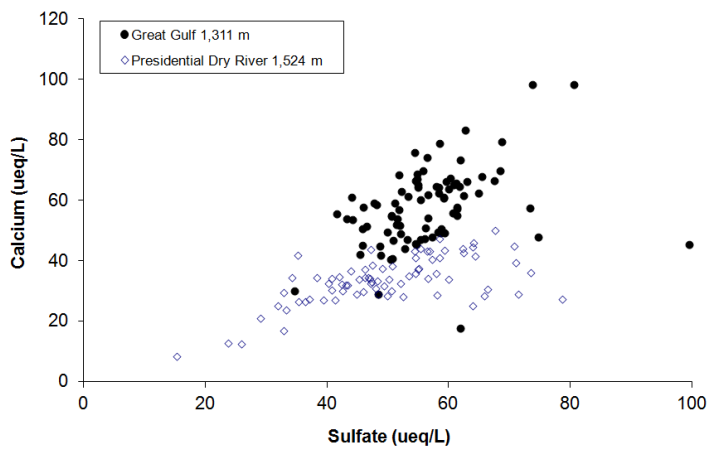
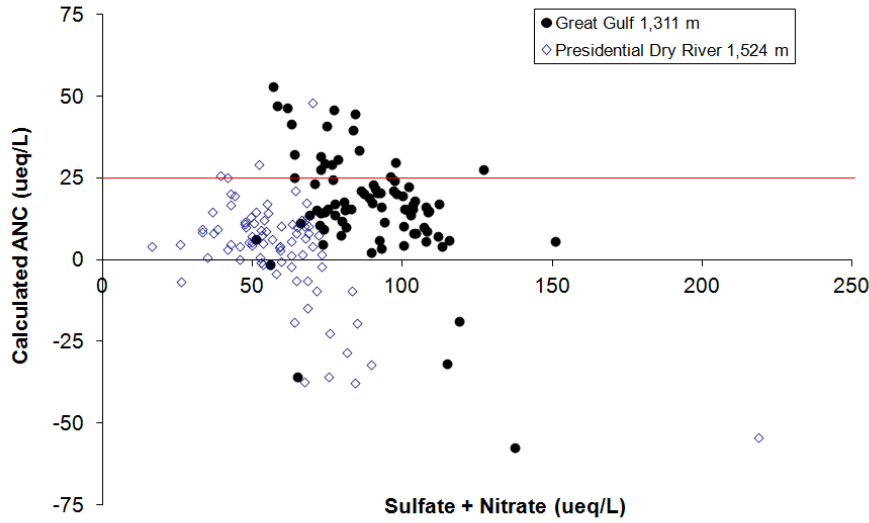


Figure 2.3.4-2 Stream grab samples from two high-elevation sites in WMNF Class I Areas. Data from summertime 1995-1997 and 2001-2011 (a) Sulfate plus nitrate and (b) inorganic monomeric aluminum verses calculated ANC in microequivalents per liter.

(a)



(b)

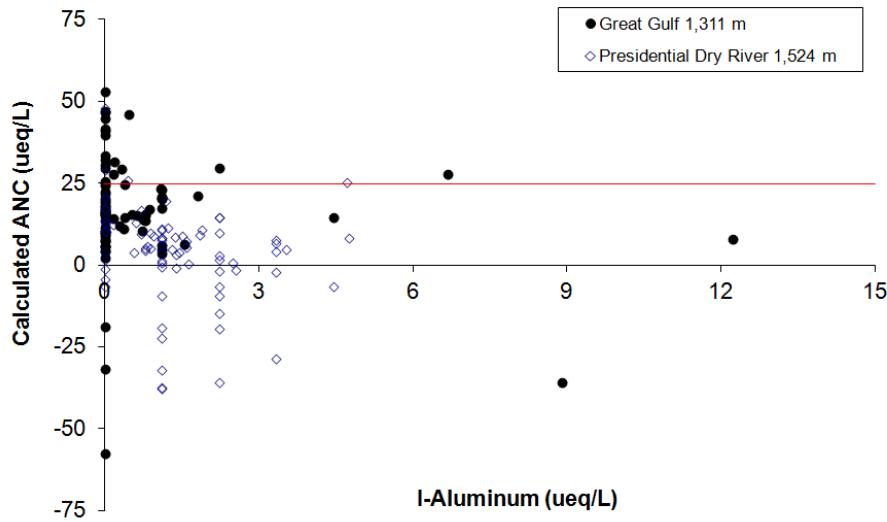
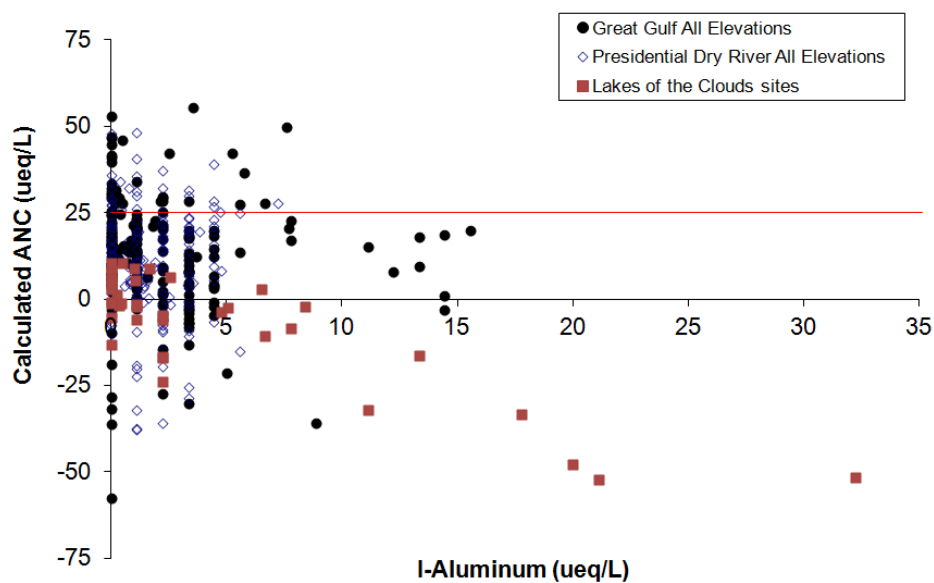


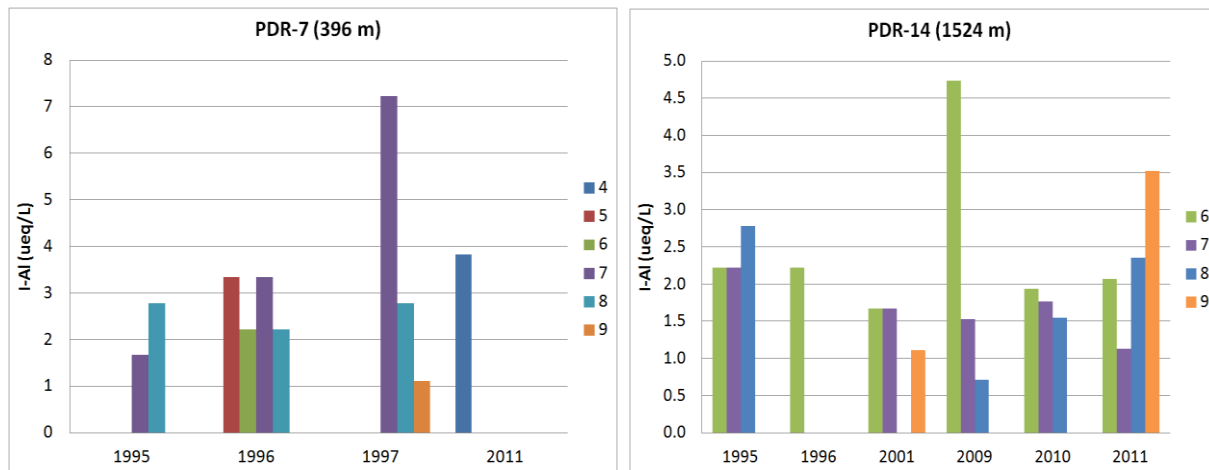
Figure 2.3.4-2 (a) shows that calculated ANC is below 25 ueq/L in the majority of samples collected in summertime from the two Wilderness Area high-elevation stream sites (GGW-1 and PDR-14) and a general pattern of decreasing ANC as sulfate and nitrate increase. Figure 2.3.4-2 (b) show that I-Al concentrations are often greater at PDR-14 and concentrations are not tightly coupled with ANC values at either locations. The relationship between ANC and aluminum remains weak when all sites within each Class I Wilderness Area (Figure 2.3.4-3). The highest I-Al concentrations and lowest ANC values were observed at the Lakes of the Clouds lakes and spring sites.

Figure 2.3.4-3 Inorganic monomeric aluminum versus calculated ANC in microequivalents per liter from ALL elevations in WMNF Class I Areas and Lakes of the Clouds sites. Data from summertime 1995-1997 and 2001-2011.



To provide more context as to how I-Al behaves inter and intra annually average concentrations are presented by month-year in Figure 2.3.4-4 for PDR-7 and PDR-14. There does not appear to be a consistent seasonal pattern discernable from the data available.

Figure 2.3.4-4 Inorganic monomeric aluminium in microequivalents per liter by month-year at PDR-7 and PDR-14 from 1995-1997, 2001, and 2009-2011. Note the scale shifts between the two graphs.



Seasonal difference and changes over time can also be seen in average nitrate concentrations at GGW-1 and GGW-6, Figure 2.3.4-5. Most notable is the decline in nitrate concentrations at GGW-1 between the 1995-1997 sampling and the most recent years 2009-2011. This is consistent with a trend in Northeastern forested sites where nitrate export in stream, especially those with relatively high concentrations, is declining.

Figure 2.3.4-5 Nitrate in microequivalents per liter by month-year at GGW-1 and GGW-6 from 1995-1997 and 2009-2011. Note the scale shifts between the two graphs.

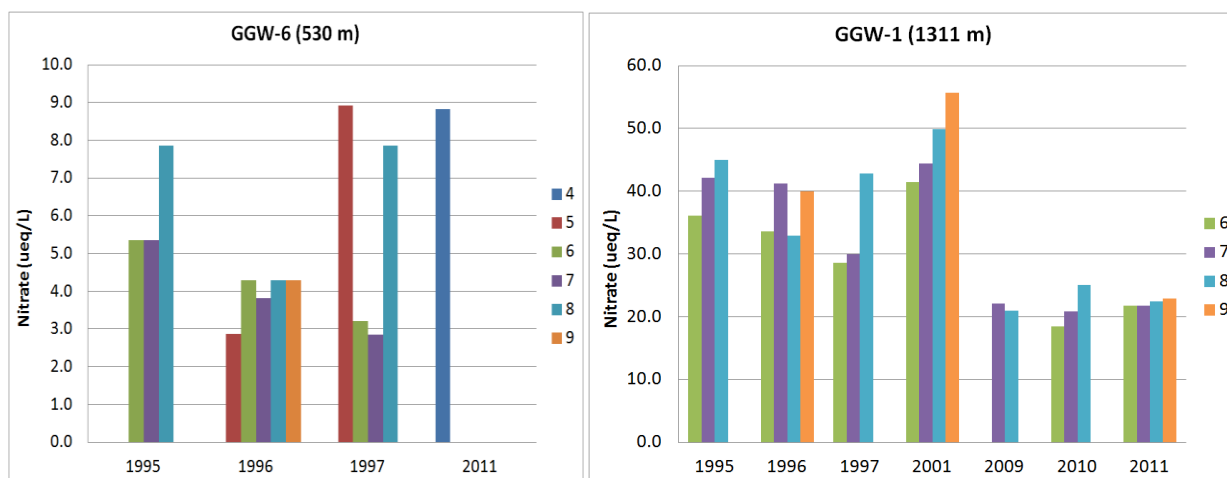
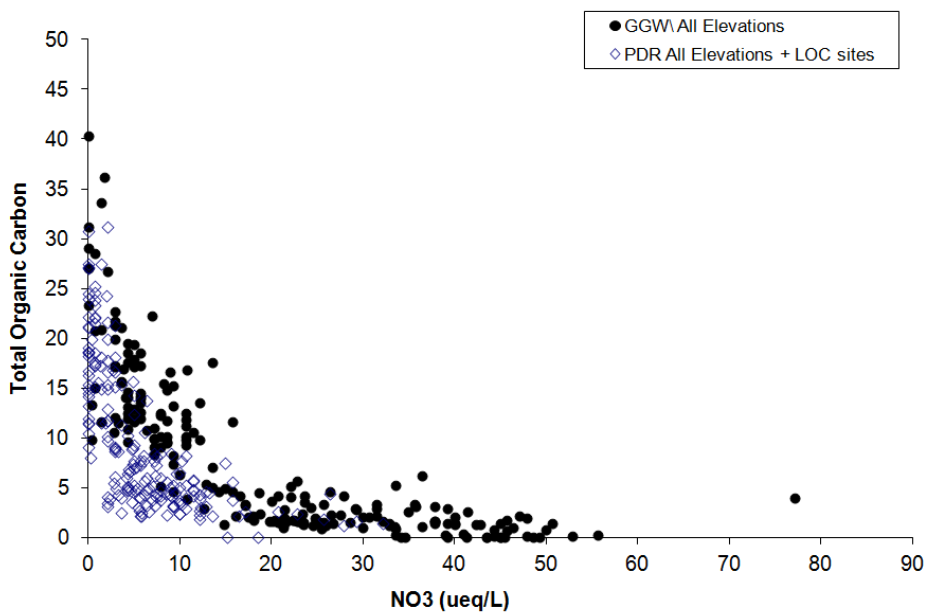


Figure 2.3.4-6 shows nitrate concentrations compared to total organic carbon measurements in all samples from the two watersheds. The hyperbolic curve in this relationship is in part due to elevation where high elevations have little organic soils providing low total organic carbon TOC to streams while the nitrate loads are high. As you move down in elevation there is an increase in organic soils and vegetation that provide more TOC but retain nitrate.

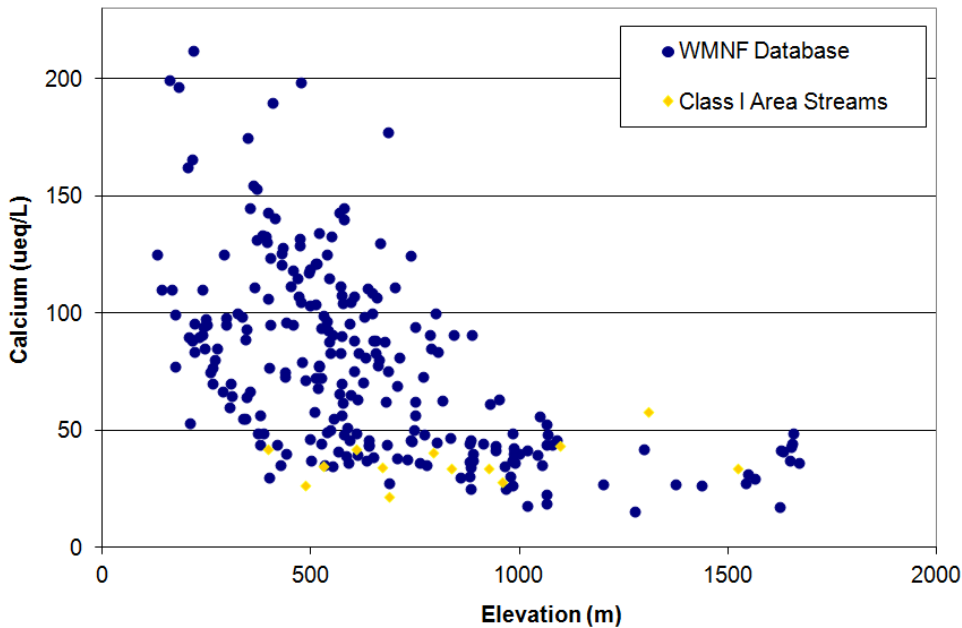
Figure 2.3.4-6 Nitrate in microequivalents per liter versus TOC in milligrams per liter from ALL elevations in WMNF Class I Areas and Lakes of the Clouds sites. Data from summertime 1995-1997 and 2001-2011.



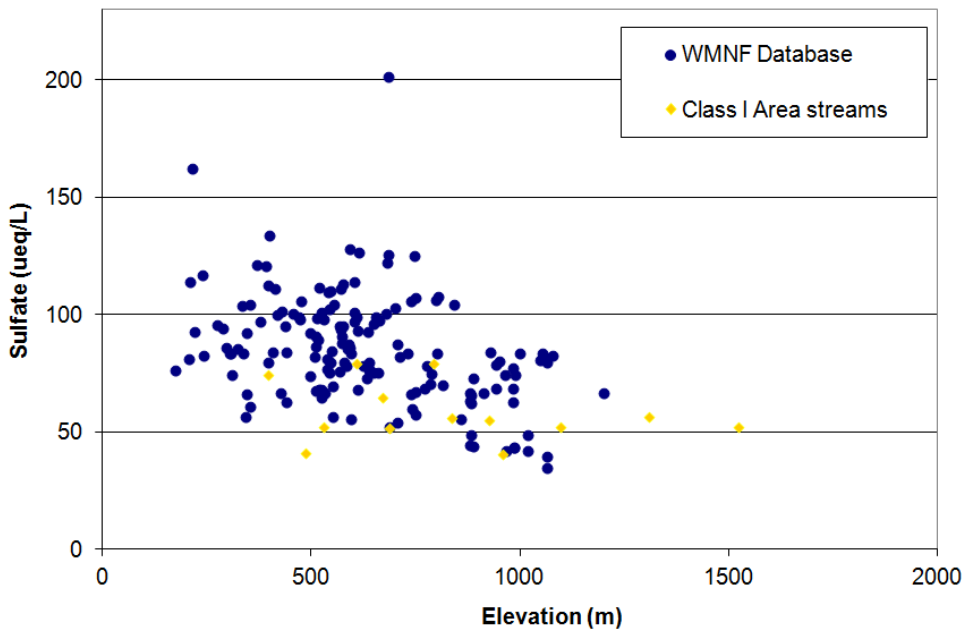
Finally, average values for some chemical parameters reported in the 2001 WMNF Stream Database are compared to averages from the two Class I Wilderness Area streams (all years) and plotted by elevations in Figure 2.3.4-7 (a-d). This comparison does not account for stream discharge differences. Generally, Class I Wilderness Area sites are in the low range for calcium, with the exception of high-elevation GGW sites, and mid-to-low range for sulfate. Average pH values are low at AMC sample sites with again the exception of high-elevation GGW sites. Included is a graph of total alkalinity by elevation from the WMNF Streams Database demonstrating the general decline as elevation increases.

In summary, Class I Wilderness Area streams have low summertime calculated ANC, often below the AQRV threshold of 25 ueq/l. The high-elevation sites vary dramatically in major anion concentrations and geological and hydrological factors may be a significant cause of buffering of incoming acids in the GGW alpine drainage. Lower-elevation sites have more dissolved organic acids which contribute to overall acidity and reduce buffering capacity, and may lead to more aluminum leaching.

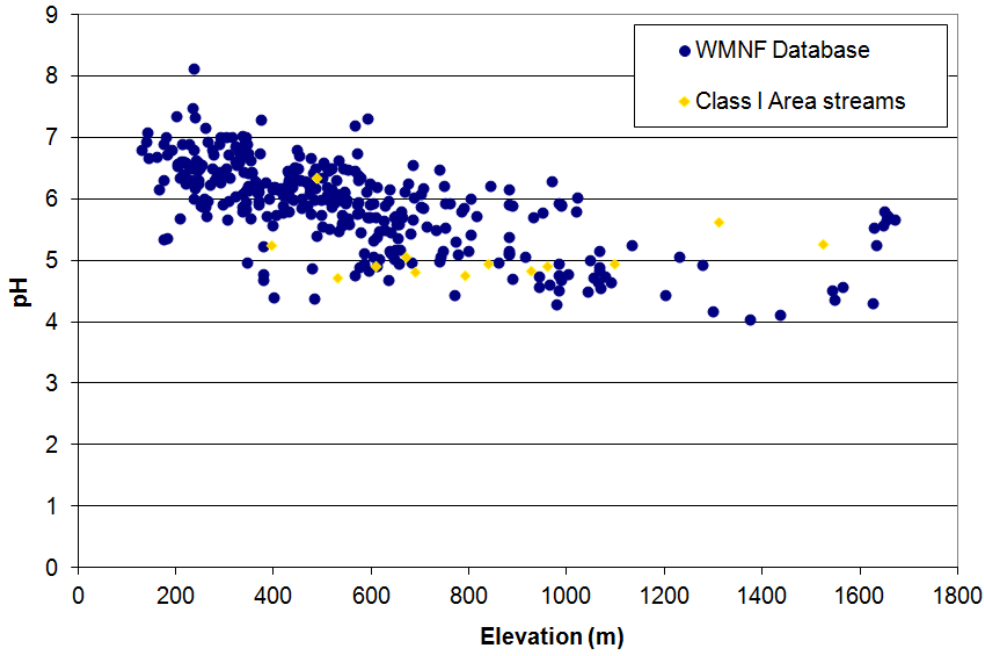
Figure 2.3.4-7 Stream grab samples from AMC sites in WMNF Class I Areas compared to chemistry from the WMNF Stream Database (2001). AMC data from summertime 1995-1997 and 2001-2011 ALL elevations included. Elevation (m) is plotted against average (a) Calcium (b) Sulfate (c) pH and (d) Total Alkalinity from WMNF Stream Database only, not measured in AMC samples (a)



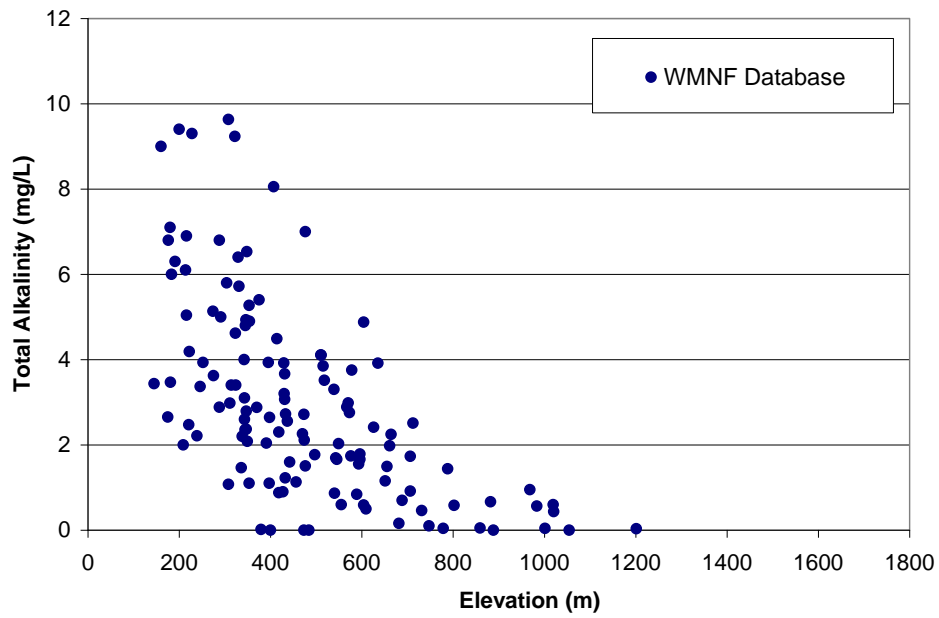
(b)



(c)



(d)



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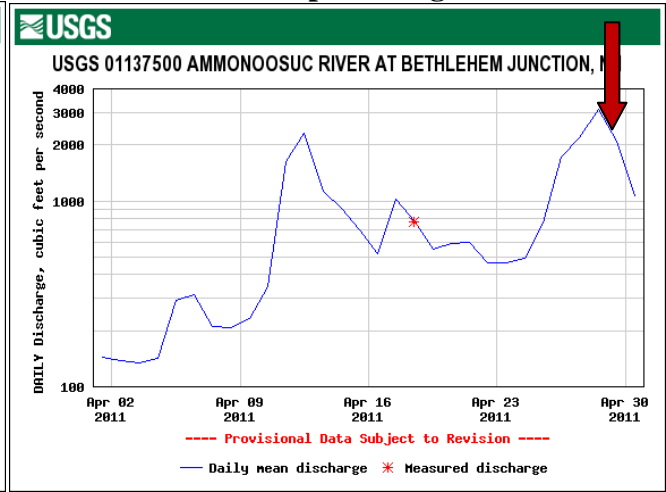
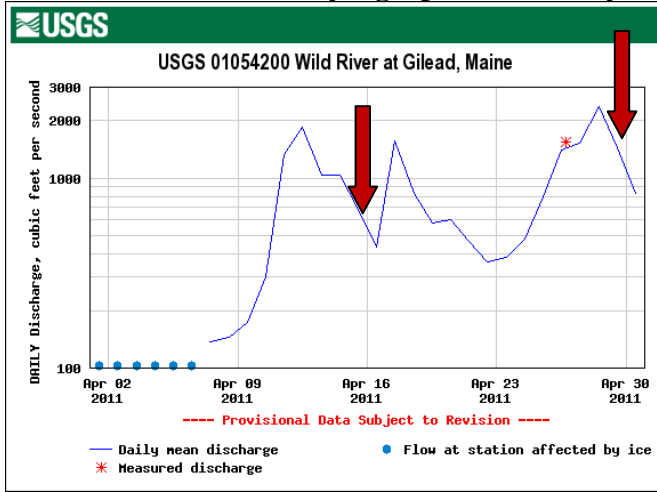
APPENDIX 2-A

Spring runoff and Wilderness streams sample timing

GGW-1 – April 15th, and April 29th, 2011

PDR-7 – April 29th, 2011

USGS Hyrographs for nearby rivers. Arrows show sample timing.



Snow depth on Mount Washington. Arrows show sample timing.

