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ATMOSPHERIC TRANSPORT AND DEPOSITION OF WATER-SOLUBLE NITROGEN TO THE GULF OF MAINE

BY

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DISSERTATION

Submitted to the University of New Hampshire

in Partial Fulfillment of

the Requirements for the Degree of

Doctor of Philosophy

in

Earth Sciences

December, 1999

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ACKNOWLEDGEMENTS

There is only one name on this work, but the reality is that without the efforts of many other people, you would not have anything to hold in your hands at this moment. First and foremost, I extend my deepest gratitude and hearfelt thanks to Dr. Robert W. Talbot, my thesis advisor and principal investigator on this project. He, along with Byard Mosher, got the proposal funded and let me run with it when I turned up on his doorstep. I could not have asked for, nor received, a better advisor. I will also be eternally grateful to Eric Scheuer, Garry Seid, and Kristen Olson, whose efforts in the field and in the laboratory led to the data set herein. I also truly appreciate their patience and good humor when I asked for extra effort on their parts to ensure the quality of the numbers obtained. Thanks go to Bill Keene, Judy Montag, and especially John Maben at the University of Virginia in Charlottesville for the loan of their dissolved organic nitrogen sampling equipment, and their work in the analysis of those samples. This manuscript would not be what it is without the expert help and extraordinary patience of Faith Sheridan. In addition, I appreciate the hospitality of Mr. Pendleton and his crew at the Portsmouth Harbor Station of the U. S. Coast Guard, on whose property the fieldwork was conducted. This work also would not have been completed without funding from the Gulf of Maine Regional Marine Research Program (grant number UM-S238) and the NASA Earth System Science Fellowship Program (grant number NGT5-30014).

I would also like to acknowledge the help of my committee members whose guidance helped shape this work; Barry Keim, Ted Loder, Janet Campbell, and Karen Von Damm. They have all been tremendously helpful throughout my graduate school career. In particular, Barry Keim, was pestered more than most, and he always responded quickly and with a smile (and some really great ideas!). I am also grateful to Byard Mosher for his contributions early in this project.

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In addition, I would like to thank several people from my past; from UMass-Amherst, David Van Blerkom, who pointed me in the right direction, without even realizing it; from the Air Force Geophysics Laboratory at Hanscom Air Force Base, Sue Gussenhoven who taught me how to do research, write about it, and present it; from Radex, Inc., Kris Bhavnani who gave me a chance and then let me see what I could do; from Ripon College, Dino Zei, who started me off in physics with the Basic Metaphysical Presuppositions and taught me so much more; from Evansville public schools, Mrs. Rattan and Mrs. Ellis, who influenced me at a young age in unexpected ways, Ted Moskonas and Teach Wilson, who gave me the courage to stand in front of a group, and Dr. Neil C. Goodspeed, my life as a scientist started with you.

To the friends who have supported me throughout the years from Evansville to Ripon to UMass to Boston to UNH, I cannot thank you enough. Most especially, I am grateful to Saskia Oosting, Paul Carroll, Mark Shipham, Barry Lefer, and Peter Czepiel. Who would have ever guessed that over brussel sprouts and spring rolls, you all would change my life? Finally I thank my family; from my grandmother who never asked me how soon I was getting married, because she wanted me to get my Ph.D. first; to my nephew (20 years my junior) who joked with me about finishing high school before I finally graduated (he didn't); to all my beloved relatives in between, I am grateful for all of your encouragement over the years. To my four brothers, Larry, Gary, Darryl , and John who managed to keep me in line and spoil me at the same time, you know how grateful I am, even when words fail me. To my parents, Dean and Annalee Jordan, well, this is for you. Words cannot express how much I love you, nor how proud I am of you. To my husband, Harry Fair, I thank you for your patience as well as your impatience. I cannot wait to share this, as all else, with you.

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ABSTRACT

ATMOSPHERIC TRANSPORT AND DEPOSITION OF WATER-SOLUBLE NITROGEN TO THE GULF OF MAINE

by

Carolyn Estelle Jordan

University of New Hampshire, December, 1999

An intensive sampling program was carried out from May 1994 through November 1997 on the shore of the Gulf of Maine in New Castle, New Hampshire. Daily (24 hour averages) samples of bulk aerosol and gas phase HNO_3, precipitation, and 20 aerosol size distributions were obtained. Particulate NH_4^+ and gas phase HNO_3 were the dominant water-soluble nitrogen species in the atmosphere. Nitrate was the dominant inorganic nitrogen ion in precipitation.

These samples were used with 1000 hPa streamlines to classify sampled air masses according to their surface level transport and chemistry. Overall, mixed conditions occurred in 42% of the samples, continental species were dominant in 37%, and marine species were dominant in 21%. Rain occurred frequently under sea salt dominant conditions; about 47% of the days classified as such had rain events. Particulate NO_3^- was associated with sea salt Na^+ in the coarse aerosol fraction peaking at approximately 4 μm in diameter. Particulate NH_4^+ was associated with non-sea-salt-SO_4^{2-}, with the bulk of the NH_4^+ present on particles in the 0.43 - 1.1 μm diameter range.

The direct atmospheric deposition of water-soluble nitrogen to the surface waters of the Gulf of Maine was assessed. Wet deposition dominated dry deposition, contributing 80 - 90% of the total flux annually. The total atmospheric direct nitrogen (ADN) deposition numbers reported here do not include the contributions of fog and dissolved organic nitrogen as they were not regularly sampled during this study. Total ADN flux ranged

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from 1 - 4262 μmol N m^{-2} d^{-1} (median 23 μmol N m^{-2} d^{-1}), depositing 52 mmol N m^{-2} yr^{-1} to the surface waters of the Gulf of Maine, 3% of the total N input to those waters annually. However, this deposition was highly episodic with events over 500 μmol N m^{-2} d^{-1} occurring in 8% of the days sampled, but contributing 56% of the total measured flux. Estimates of the episodic atmospheric nitrogen flux to the Gulf of Maine surface waters suggest large deposition events could be sufficient to support substantial chlorophyll *a* production.

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CHAPTER 1

CHEMISTRY OF WATER-SOLUBLE NITROGEN SPECIES AT THE NEW HAMPSHIRE SEA COAST: HNO_3, AEROSOLS, AND PRECIPITATION

Abstract

An intensive sampling program was carried out from May 1994 through November 1997 on the shore of the Gulf of Maine in New Castle, NH. Daily (24 hour averages) samples of bulk aerosol and gas phase HNO_3, precipitation, and 20 aerosol size distributions were obtained. This program was carried out to ascertain the chemistry and deposition of atmospheric soluble nitrogen to the surface waters of the Gulf of Maine. Particulate NH_4^+ and gas phase HNO_3 were the dominant water-soluble nitrogen species in the atmosphere. There was a summer peak in the mixing ratios of both of these species. Daily mixing ratios of HNO_3 and all aerosol species were highly variable, yet the annual averages tended to be similar from one year to the next. The concentrations of all the inorganic species measured in precipitation was generally higher than that of two National Acid Deposition Program (NADP) coastal sites. In particular, the annual volume-weighted means for NO_3^- (22 - 27 μmoles/liter) and NH_4^+ (11 - 17 μmoles/liter) were found to be 20% - 60% and 40% - 90% higher, respectively, than those reported from Cape Cod, MA. Nitrate was the dominant inorganic nitrogen ion in precipitation at New Castle. The prevalence of NO_3^- in rain was probably due to inefficient scavenging of submicron NH_4^+ aerosol coupled with effective scavenging of supermicron NO_3^- and highly soluble HNO_3. In autumn, concentrations of continentally derived species in precipitation decreased substantially while sea salts increased. There was insufficient NH_3 to fully neutralize HNO_3 and H_2SO_4 in aerosols and precipitation. Chloride was depleted on average 25% in aerosols and 13% in precipitation with respect to sea salt aerosols. Ammonium appeared to be present mostly as submicron aerosol associated with non-sea-salt-SO_4^{2-}. Nitrate had a

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bimodal size distribution with most of the NO_3^- seemingly associated with supermicron sea salt Na^+. The overall atmospheric chemistry in this region was heavily dominated by anthropogenic pollution products.

Introduction

The Regional Marine Research Program (RMRP) was funded by the National Oceanic and Atmospheric Administration (NOAA) to study the Gulf of Maine ecosystem as a whole unit. Part of this program evaluated the nutrient budget for this system. In particular, a better estimate of the atmospheric nitrogen input to this system was needed as was an examination as to whether this input had biological significance. Most of the nutrients available to photosynthetic organisms in the surface waters come from the upwelling of nutrient rich deep waters flowing into the Gulf from the Atlantic Ocean (Schlitz and Cohen, 1984). A significant amount of available nutrients are also due to internal nitrification (Townsend, 1998) and riverine input (Schlitz and Cohen, 1984; Loder and Becker, 1990). Although the atmospheric input has been previously estimated to play a minor role (Schlitz and Cohen, 1984; Townsend, 1998), it has been poorly characterized. Prior estimates relied solely on wet deposition inputs of nitrogen, with dry deposition assumed to contribute a comparable amount to the wet deposition (Fisher and Oppenheimer, 1991; Scudlark and Church, 1993).

In general, discussions of the relative importance of various nutrient sources to an ecosystem are based on total annual fluxes. However, nutrient input is event driven and seasonally variable. For example, freshwater input of nutrients to the Gulf of Maine is greatest during the spring freshet (Loder et al., 1997). This nutrient flux helps sustain the spring diatom bloom. Similarly, while the input of atmospheric nitrogen is not the dominant annual nitrogen source to the Gulf of Maine, it may well be important in summer when atmospheric species such as HNO_3 and aerosol NH_4^+ are at their peak. In addition to higher atmospheric concentrations, the influence of riverine nutrient input is much less in summer than in spring. Meanwhile, cold nutrient rich deep waters cannot reach the warmer

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surface waters due to thermal stratification. In fact, during summer, the surface waters of the Gulf of Maine have very low concentrations, < 1.0 μM of both NO_3^- and NH_4^+ (Martorano, 1997; T. Loder, personal communication, 1998).

Atmospheric deposition is event driven and in summer, it may well deliver a biologically significant amount of nitrogen to the surface waters of the Gulf of Maine. Mosher (1995) found that the direct atmospheric inputs to the Great Bay Estuary (which flows into the Gulf of Maine) constituted about 40% of the total point source input from wastewater treatment and industrial sources. When considering the indirect atmospheric deposition to Great Bay (via watershed runoff), Mosher found that the atmospheric nitrogen input was equal to or greater than the point source input to the watershed.

It was within this context of limited summer nutrient input from deep ocean waters and freshwater, that the role of atmospheric nitrogen deposition to the Gulf of Maine needed to be critically evaluated. This deposition may contribute sufficient amounts of nitrogen to the surface waters of the Gulf of Maine in the summer to enhance biological productivity. The New England coast is located downwind of some of the largest urban and agricultural source regions of nitrogen emissions in the country (Parrish et al., 1993). It has been estimated that 61 billion moles of nitrogen oxides per summer are emitted over eastern North America (Saeger et al., 1989), potentially leading to high deposition rates of nitrogen along the northeastern U.S. coast (Pszenny et al., 1990). Mobile sources in the northeast also contribute a substantial amount to the atmospheric nitrogen deposition (Dennis, 1995). These mobile sources emit NO_x ($NO + NO_2$) and possibly NH_3 from catalytic converters (Fraser and Cass, 1998).

Nitrogen tends to be the limiting nutrient in coastal waters, which makes these ecosystems sensitive to anthropogenic nitrogen sources, either via freshwater runoff or direct atmospheric deposition (Fisher and Oppenheimer, 1991; Paerl, 1993). There is increasing evidence that non-point source nitrogen deposition to coastal waters is a significant factor leading to eutrophication and both toxic and nuisance algal blooms (Fisher

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and Oppenheimer, 1991; Paerl, 1993; Scudlark and Church, 1993; Zhang, 1994; Mosher, 1995; Puckett, 1995). In fact, the incidence of toxic and nuisance algal blooms is seen to be increasing worldwide as are their intensity, duration, and geographic spread (Shumway, 1990; Zhang, 1994). Emissions of NO_x, NH_3, and SO_2 lead to the production of various other species in gas, aqueous, and solid phases, many of which would remain airborne from days to weeks. However, at the shoreline, these anthropogenic pollution species encounter sea salt aerosols along with increased humidity and wind speed. The pollution products and sea salts react, altering the chemistry of the air mass. This, coupled with the meteorological change in conditions, enhances the near-shore deposition of these pollution species.

With our site located at New Castle, New Hampshire, on the shoreline of the Gulf of Maine (Figure 1.1), a variety of air masses were sampled including those which were heavily polluted as they moved along the eastern United States, relatively pristine from Canada, and dominated by sea salts from the North Atlantic. This extensive data set is unique and allows questions to be addressed pertaining to the atmospheric chemistry at the land/sea interface, the atmospheric deposition of anthropogenic nitrogen to a coastal marine environment, and whether that deposition leads to any significant increase in primary production. In this chapter, an overview is presented of this aerosol, precipitation, and size distribution data set. In Chapter 2, the relationship between transport and chemistry observed at this site is presented. Finally, Chapter 3 addresses the atmospheric deposition and biological significance aspects of the data set.

Experimental

The sampling site was located on the shore of the Gulf of Maine at the Portsmouth Harbor U. S. Coast Guard Station in New Castle, New Hampshire (Figure 1.1). Samples were initially collected from May to November of 1994. Beginning in March of 1995, samples were collected year round until November of 1997.

Precipitation samples were collected daily in a polyethylene bucket using an

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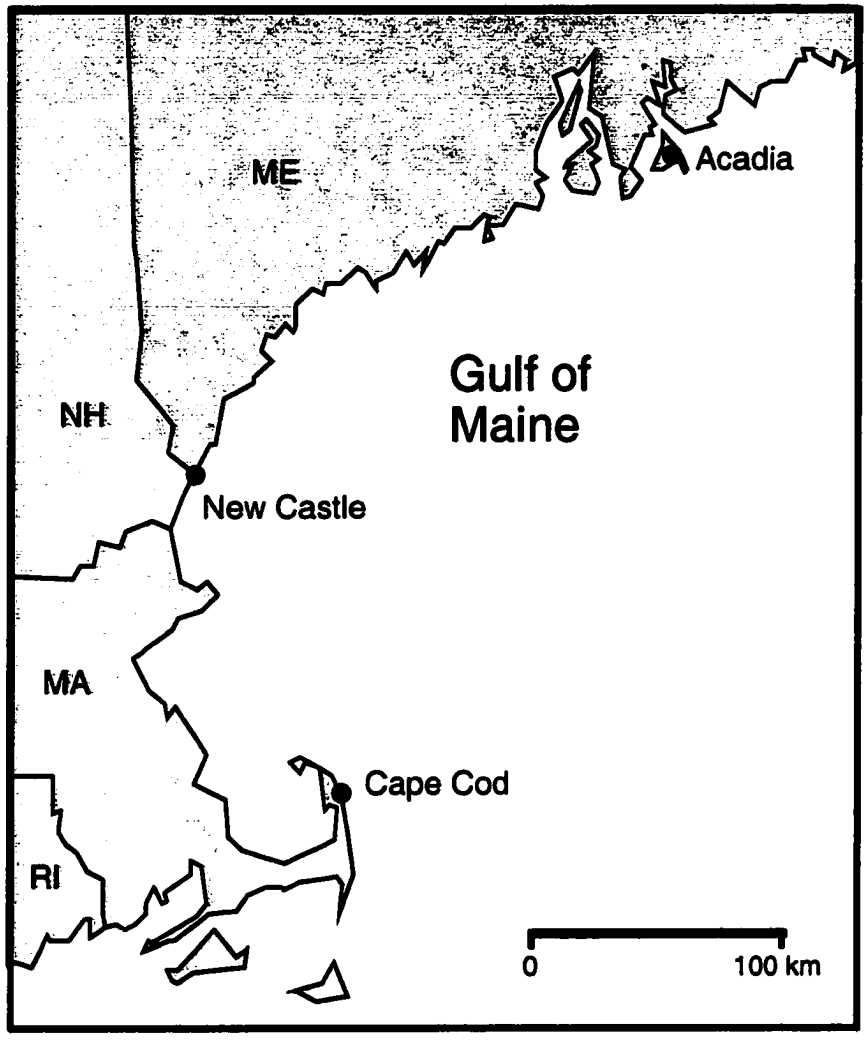

Figure 1.1. Location map of the southern part of the Gulf of Maine with the sampling site at New Castle, NH, and two NADP sites, one on Cape Cod, the other in Acadia.

Aerochem Metrics model 301 wet only sampler. The bucket was initially wiped out with a paper towel and deionized water. Then it was washed three times with deionized water and left to dry in a clean room. Blanks were run to confirm that the buckets were clean. The bucket was exchanged daily at the sampling site, whether or not there had been any precipitation.

Upon collection, precipitation samples were treated with chloroform to prevent biodegradation of the nitrogen species. The ions in the precipitation were measured using

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ion chromatography and were analyzed for the anions Cl^-, NO_3^-, and SO_4^{2-}, and cations Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} (Talbot et al., 1992).

Anions in precipitation, aerosol, and HNO_3 samples were all analyzed with an AS4 column using an eluent of 2.25 mM Na_2CO_3 and 2.8 mM $NaHCO_3$. Cations were analyzed using a CS12 column with a 20 mM CH_4O_3S eluent.

Bulk aerosol and nitric acid samples were collected daily using a filter pack system (Goldan et al., 1983) mounted within a polyethylene rain shield on a 6 m tower. Campbell Scientific Inc. (815 West 1800 North, Logan, Utah) meteorological instruments were also mounted on this tower to record hourly averages of air temperature, relative humidity, wind speed, and wind direction. The average flow rate through the filter pack system was 108 standard liters per minute. The average sampled volume was 153 m^3. Aerosols were collected on a 90 mm diameter Zefluor (Gelman) teflon filter with a 2 μm pore size. Immediately behind the teflon filter were two 90 mm diameter Nylasorb (Gelman) filters which had a 1 μm pore size. The Nylasorb filters were used to collect HNO_3.

Although several studies have recommended caution in interpreting Nylasorb-generated HNO_3 data (Spicer et al., 1982; Hering et al., 1988; Talbot et al., 1990), in the absence of other gases, these filters have been found to collect HNO_3 with 100% efficiency (Goldan et al., 1983). When sampling began in 1994, one Zefluor teflon filter was used for aerosols and one Nylasorb filter was behind it for HNO_3. Previous work (Spicer et al., 1982) had shown that all of the HNO_3 present in ambient conditions (for Claremont, California) would be collected on a single nylon filter behind a teflon filter. On eleven occasions during the first sampling season, a second Nylasorb filter was placed behind the first and in every case HNO_3 was found on the second filter. Apparently, additional ambient gases (e.g., HCl) were leading to breakthrough from the first Nylasorb to the second. This suggests that the samples collected on only one filter were a lower limit of the amount of HNO_3 present. In 1995, a second Nylasorb was used about 70% of the time. In 1996 and 1997, a second Nylasorb was used routinely (100%). When two filters were

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used, the amount of HNO_3 on each filter was added together to yield the total observed HNO_3. To ensure that the HNO_3 numbers reported for 1994 were representative of what was actually there and comparable to the numbers reported in later years, a mathematical relationship was determined between the HNO_3 found on the second filter as a function of that on the first filter. The best relationship between the HNO_3 on these filters was represented by a cubic equation with $R^2 = 0.47$. Although not perfect, it is a better approach to estimate the total HNO_3, rather than reporting lower limit values for 1994 and part of 1995.

Size distribution data for the aerosols were collected monthly using a Graseby-Anderson 10 stage cascade impactor with an 81 mm diameter Zefluor teflon filter with 2 μm pore size at each stage. A pre-separator was used as the first stage, due to the presence of large sea salt aerosols in this environment. This sampler was also mounted inside a polyethylene rain shield on the 6 m tower. Although there was a rain shield, most samples were collected under dry conditions. The average flow rate through the impactor was 30 standard liters per minute to give the desired particle size cuts on the various stages. Sampling times were typically 2 - 3 days, yielding an average sample volume of 108 m^3.

The Zefluor filters used for the bulk aerosol and impactor samples were processed in the same way. They were first wetted with 750 μL of methanol. They were then extracted twice using 10 mL of deionized water each time. Ion chromatography was then used to analyze this solution for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. Similarly, the Nylasorb filters were extracted twice using 10 mL of deionized water each time. The methanol step was unnecessary since the nylon filters are easily wetted. Again, ion chromatography was used on this solution. For the nylon filters, all of the NO_3^- in the sample was attributed to HNO_3.

To determine blank corrections for both the teflon and nylon filters, blank filters were processed in the same manner as samples. In the cases where a particular ion was below the detection limit, half the value of the lowest detectable standard solution was used

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in calculating the blank value. The following were used as below detection limit extraction solution values for each ion (μmol/L) : $Na^+ = 0.45$, $NH_4^+ = 0.3$, $K^+ = 0.27$, $Mg^{2+} = 0.36$, $Ca^{2+} = 0.26$, $Cl^- = 0.75$, $NO_3^- = 0.65$, and $SO_4^{2-} = 0.67$. The mixing ratios we observed were typically so high that the blank corrections were only a very small percentage of the sampled values. The aerosol NO_3^- and NH_4^+ blanks were only 2.8% and 0.3% respectively, of the average measured values. For HNO_3, the blank was 0.6% and 3.5% of the average on the first and second filters, respectively.

The experimental error for the precipitation data is solely a function of the analytical uncertainty. The precision for our analytical method was ±3% and comparisons to aqueous standards from the National Institute of Standards and Technology (NIST) was ±1%. The experimental error for the aerosol, HNO_3, and size distribution measurements depended on several factors. To evaluate the error for these methods, an error propagation formula (Knoll, 1979) was used. On average, errors were found for aerosol $NO_3^- = \pm 5\%$ and $NH_4^+ = \pm 4\%$, and for gas-phase $HNO_3 = \pm 5\%$. Size distribution data were collected on a series of 10 filters, so the error calculations were done for each stage of the impactor data. The results were remarkably similar, with $NO_3^- = \pm 5\%$ and $NH_4^+ = \pm 5\%$ on most stages, with the other few either ±4% or ±6%.

The units used for the aerosols and for gas phase HNO_3 are parts per trillion volume. Volume mixing ratios of aerosols are equivalent to gas phase mixing ratios. By using these units (as opposed to $\mu g/m^3$) all aerosol species and HNO_3 may be compared directly. At sea level, pptv is readily converted to $nmol/m^3$ by dividing by 22.414. From there, ng/m^3 is easily obtained for each species of interest. This data set is available from http://ekman.sr.unh.edu/Data/Talbot/index.html. For more information regarding RMRP and other Gulf of Maine data sets, go to http://oracle.er.usgs.gov/gomaine/index.htm. To get to this data set from there, click on RMRP Projects, scroll down to Talbot and Mosher Atmospheric Nitrogen, and click on the link.

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Data & Discussion

Overview of aerosol & HNO_3 data

The daily mixing ratios of HNO_3 and aerosol NH_4^+, non-sea-salt-SO_4^{2-} (nss-SO_4^{2-}), and Mg^{2+} are shown in Figure 1.2. Nss-SO_4^{2-} was calculated by assuming that all of the measured Mg^{2+} was due to sea salt (a reasonable assumption based on the observed Mg^{2+}/Na^+ ratio). Using the measured amount of Mg^{2+} and multiplying by the ratio of SO_4^{2-} : Mg^{2+} in sea water, 0.523 in equivalents units (Keene et al., 1986; Wilson, 1975), gives the amount of sea salt SO_4^{2-}. Subtracting this value from the observed total SO_4^{2-} leaves the portion of SO_4^{2-} attributable to non-sea-salt sources. The daily mixing ratios for these species were highly variable. Even the seven day moving averages showed a considerable variation in the mixing ratios (Figure 1.2). All of these species showed consistent seasonal variation with a summer peak and winter low. The seasonal variations of HNO_3, NH_4^+, and nss-SO_4^{2-}, were statistically significant as indicated by the p-values (generally < 0.01 and frequently < 0.0001) of unpaired t-tests of the means. Mg^{2+} did not display the same degree of seasonal variation, nonetheless, the summer mean was significantly different from the other seasons observed in 1994 and 1995 (p-values $\leq$ 0.097) and from winter in 1997 (p-values = 0.002). However, it was not different from the other seasons in 1996. The summer peak in HNO_3 (Figure 1.2 and Table 1.1) may be attributed to longer daylight hours and higher radiative flux which permit greater photochemical production of HNO_3 from NO_x emissions. In addition, NO_x emissions increase in the summer due to vacationers significantly increasing the automobile traffic in the northeast corridor. In particular, the tourist traffic in New Hampshire in fiscal 1996 broke down seasonally as follows: 38.4% in summer, 25.6% in fall, 20.9% in spring, and 15.1% in winter (Bill Boynton, personal communication, 1998).

The NH_4+ summer peak (Figure 1.2 and Table 1.1) can be attributed to the seasonality of NH_3 emissions coupled with altered winter transport from the midwest (Langford et al., 1992). NH_3 emissions are temperature dependent and in the United

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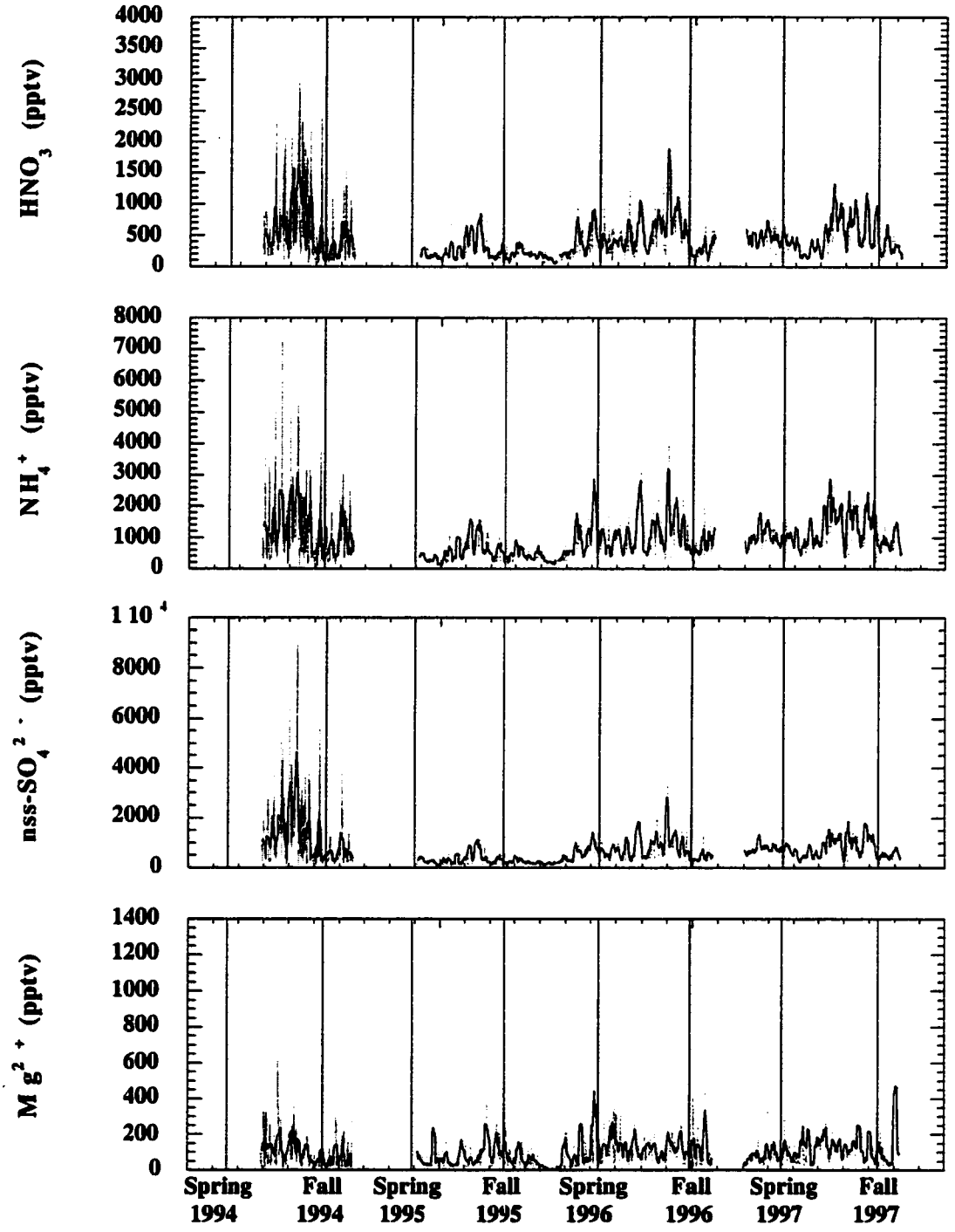

Figure 1.2. HNO_3 and aerosol NH_4^+, nss-SO_4^{2-}, and Mg^{2+} daily mixing ratios in parts per trillion volume (pptv) for 1994 - 1997 (different colors indicate different years) with 7 day moving averages (black lines). Vertical lines indicate the start of the spring/fall season. Only part of 1994 was sampled, the gap in 1996 was due to a power failure at the site.

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Table 1.1. Seasonal HNO_3, NH_4^+, and NO_3^- Averages, One Standard Deviation, Ranges, and Medians (pptv)

Species	Year	Winter	Spring	Summer	Fall
HNO_3	1994		535 ± 462 (162 – 2345) 353	792 ± 780 (43 – 3559) 451	333 ± 342 (30 – 1701) 201
	1995		207 ± 183 (29 – 881) 143	353 ± 392 (23 – 2057) 239	200 ± 162 (20 – 1043) 154
	1996	375 ± 378 (12 – 1982) 252	456 ± 375 (17 – 1892) 360	696 ± 612 (20 – 3245) 559	314 ± 261 (13 – 1127) 219
	1997	496 ± 323 (66 – 1375) 406	341 ± 272 (38 – 1499) 249	718 ± 581 (18 – 2424) 523	327 ± 284 (30 – 1414) 242
NH_4^+	1994		1238 ± 1226 (244 – 4981) 825	1505 ± 1462 (62 – 7986) 962	867 ± 704 (108 – 3147) 592
	1995		422 ± 531 (10 – 4182) 289	740 ± 781 (71 – 4278) 436	442 ± 370 (31 – 2276) 347
	1996	916 ± 953 (49 – 4663) 576	1059 ± 787 (85 – 3884) 875	1297 ± 1195 (43 – 7159) 882	847 ± 648 (77 – 2565) 586
	1997	1113 ± 693 (195 – 3597) 1020	1110 ± 982 (124 – 7289) 809	1616 ± 1367 (183 – 6271) 1188	882 ± 568 (128 – 2051) 732
NO_3^-	1994		457 ± 368 (26 – 1309) 427	290 ± 260 (10 – 1318) 226	302 ± 320 (19 – 1373) 153
	1995		185 ± 214 (10 – 1523) 121	273 ± 288 (15 – 1986) 178	161 ± 195 (12 – 1028) 88
	1996	411 ± 564 (10 – 3258) 194	367 ± 371 (10 – 1924) 269	322 ± 260 (10 – 1089) 237	346 ± 354 (10 – 1476) 210
	1997	347 ± 346 (10 – 1468) 213	371 ± 372 (11 – 1748) 258	327 ± 281 (10 – 1284) 228	329 ± 335 (10 – 1615) 228

States are dominated by agricultural practices, particularly in the midwest. Langford et al. (1992) report that there is little difference between NH_4^+ concentrations in precipitation in summer and winter in the midwest, yet there is a substantial seasonal difference in the eastern U.S. They attribute this seasonality to altered transport from the midwest to the

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east, coupled with reduced NH_3 emissions from eastern forests which can contribute up to 20% of the total emissions in this region. In addition, it was recently suggested that NH_3 is emitted by catalytic converters on cars (Fraser and Cass, 1998). Due to increased traffic in New Hampshire in summer (NHDOT, 1998), this may contribute to the observed enhancement in NH_4^+.

Aerosol NO_3^-, Ca^{2+}, Na^+, and Cl^- are species which did not exhibit any seasonality (Figure 1.3). Unpaired t-tests of the seasonal means confirmed there was no consistent seasonal variation of these species. In both Figures 1.2 and 1.3, there was considerable inter-annual variability. Note in Figure 1.2, HNO_3 and nss-SO_4^{2-} showed particularly high mixing ratios in the summer of 1994 and low mixing ratios in 1995 compared to 1996 and 1997. The species in Figure 1.3 showed less dramatic swings, although the concentrations in 1995 tended to be lower than the rest (see also Table 1.2). It is clear from these data that although one can discuss average values, there was in fact tremendous variation. This variation depends upon variable emissions of precursor gases, varying photochemical processes, and meteorological conditions which controlled transport and removal processes. Note that the spikes in the three nitrogen species were not co-located due to the different sources which produced them, and the different processes which affected them in the atmosphere (Roberts, 1995).

Annual mixing ratio statistics for HNO_3 and the aerosol species are given in Table 1.2. The dominant species measured at our coastal site were NH_4^+, SO_4^{2-}, Na^+, and Cl^-. HNO_3 and NO_3^- were present at levels which were a factor of 2-4 less than NH_4^+. Mg^{2+}, K^+, and Ca^{2+} were an order of magnitude lower than the dominant species. Particularly high mixing ratios were found in 1994 for several species (HNO_3, nss-SO_4^{2-}, and K^+). For HNO_3, the enhancement was seen in the average, but resulted from only a few very large events. The median value in 1994 was nearly the same as that in 1996. Not all species were enhanced during summer 1994, NH_4^+, NO_3^-, Na^+, Cl^-, Mg^{2+}, and Ca^{2+} showed no enhancement. Further, the sea salt species Na^+ and Mg^{2+} showed

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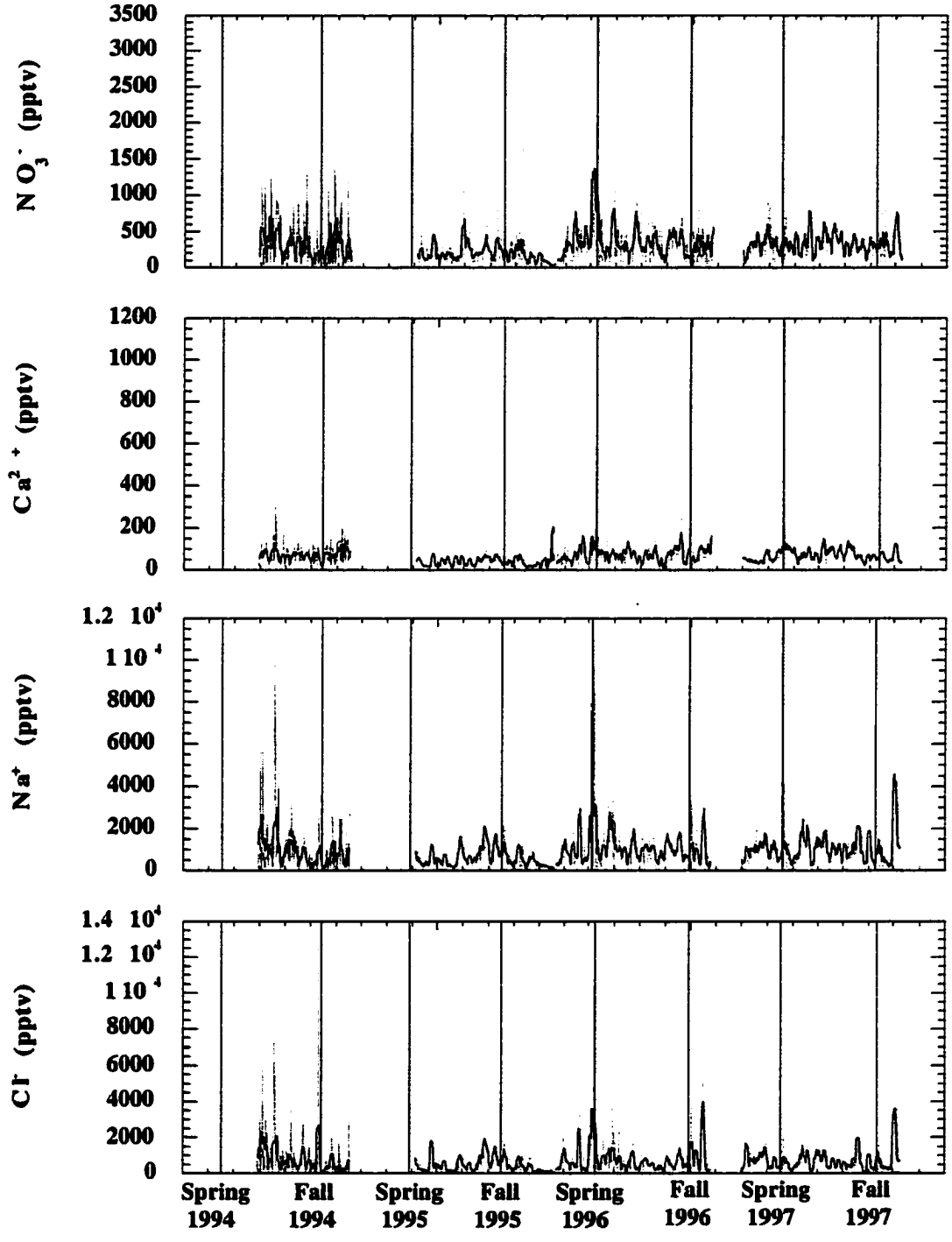

Figure 1.3. Aerosol NO_3^-, Ca^{2+}, Na^+, and Cl^- daily mixing ratios in parts per trillion volume (pptv) for 1994 - 1997 (different colors indicate different years) with 7 day moving averages (black lines). Vertical lines indicate the start of the spring/fall season. Only part of 1994 was sampled, the gap in 1996 was due to a power failure at the site.

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higher averages and medians in 1996 and 1997 (Table 1.2). This out of phase relationship was not surprising as the enhanced species were primarily due to combustion, while the species showing no enhancement had different sources: marine origin for sea salts and primarily agricultural and forest sources for NH_4^+.

Table 1.2. Annual HNO_3 and Aerosol Averages, One Standard Deviation, Ranges, and Medians (pptv)

Species	1994	1995	1996	1997	1994 – 1997
HNO_3	599 ± 649 (30 – 3559) 340	247 ± 272 (12 – 2057) 154	493 ± 464 (13 – 3245) 341	487 ± 428 (18 – 2424) 326	449 ± 469 (12 – 3559) 291
NO_3^-	322 ± 305 (10 – 1373) 226	200 ± 237 (10 – 1986) 118	377 ± 406 (10 – 3258) 241	340 ± 329 (10 – 1748) 229	313 ± 337 (10 – 3258) 200
NH_4^+	1245 ± 1243 (62 – 7986) 809	524 ±592 (10 – 4278) 338	1094 ± 963 (43 – 7159) 767	1211 ± 1028 (124 – 7289) 906	1015 ± 1003 (10 – 7986) 673
nss-SO_4^{2-}	1259 ± 1526 (75 – 9935) 654	314 ± 372 (20 – 2706) 201	747 ± 669 (62 – 5561) 517	791 ± 681 (68 – 5471) 596	740 ± 884 (20 – 9935) 459
Total SO_4^{2-}	1311 ± 1540 (115 – 10062) 708	351 ± 382 (23 – 2745) 229	813 ± 684 (64 – 5668) 587	853 ± 696 (122 – 5605) 664	796 ± 898 (23 – 10062) 512
Na^+	928 ± 1192 (10 – 10052) 624	620 ± 712 (10 – 4915) 337	1077 ± 1273 (10 – 10897) 671	1054 ± 1237 (10 – 9511) 651	934 ± 1149 (10 – 10897) 591
Cl^-	788 ± 1430 (10 – 13952) 330	486 ± 756 (10 – 6907) 199	807 ± 1370 (10 – 10344) 348	734 ± 1130 (10 – 8146) 350	704 ± 1192 (10 – 13952) 292
Mg^{2+}	98 ± 89 (10 – 611) 76	75 ± 95 (10 – 760) 38	125 ± 145 (10 – 1232) 80	117 ± 135 (10 – 1016) 72	106 ± 125 (10 – 1232) 66
K^+	60 ± 40 (11 – 398) 54	32 ± 28 (10 – 189) 25	38 ± 29 (10 – 205) 31	47 ± 40 (10 – 329) 34	43 ± 35 (10 – 398) 34
Ca^{2+}	73 ± 44 (10 – 307) 67	44 ± 73 (10 – 1012) 27	75 ± 59 (10 – 374) 64	72 ± 51 (10 – 267) 61	66 ± 60 (10 – 1012) 54

Although daily mixing ratios of the various species were seen to vary by two orders of magnitude, the annual averages and medians for 1994, 1996, and 1997 were quite

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similar. Only 1995 displayed unusually low mixing ratios in terms of the medians and averages (seasonal, Table 1.1, and annual, Table 1.2) and daily values (Figures 1.2 and 1.3). This was the case for all species, suggesting that there was something unusual about 1995. There is no reason to conclude that there were substantially lower combustion emissions in 1995 or that the photochemical conditions were different (e.g., lower daytime temperatures, more cloud cover). An analysis of various meteorological parameters (air temperature, relative humidity, wind speed and direction, and barometric pressure) did not show any substantial differences between the four years of observations. Increased rainfall cannot account for the lower mixing ratios, as the rainfall was not enhanced in 1995 (Table 1.3). In the three seasons for which measurements were made that year, the rainfall amounts were lower than those observed in 1996. In addition, summer rainfall in 1994 was comparable to that of 1995. Furthermore, comparison to the average rainfall seen in Portsmouth over the past 40 years (Table 1.3; Barry Keim, personal communication, 1998) shows the rainfall amounts during the sampling period were not particularly unusual.

Table 1.3. Rainfall Amount (cm)

Year	Winter	Spring	Summer	Fall
1994		*3.41	20.52	*14.29
1995		16.78	20.19	31.02
1996	9.34	28.82	30.46	*39.90
1997	15.38	26.78	19.43	*10.84
Average†	26.94	26.77	24.97	33.49

*short sampling season
†based on data collected from 1956-1996 at Pease International Airport, Portsmouth, NH. Barry Keim, personal communication.

Thus, washout of aerosols due to excessive precipitation cannot account for the lower aerosol mixing ratios observed in 1995. All of this suggests that transport may have been different during 1995, altering the typical aerosol levels in this area. Observations made at Summit Greenland also found unusual aerosol chemistry in 1995, which was attributed to atypical transport (Slater, 1999). Analysis of the transport during the years 1994, 1995,

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and 1996 based on streamline flow patterns, showed that although there is some variation in transport, concentrations from any given direction were lower in 1995, when compared to the other two years (Chapter 2). This difference could not be attributed to the meteorological parameters listed above. At this time, we are unable to explain the difference in the mixing ratios between 1995 and the other years of this study.

Finally, nss-SO_4^{2-} was the dominant component of the total SO_4^{2-} observed, even though the site is located right on the shoreline (Table 1.2). Over the total sampling period, nss-SO_4^{2-} comprised 89.8% ± 0.12% of the total SO_4^{2-} on average. The minimum contribution of nss-SO_4^{2-} to the total observed was 13.9%, the maximum was 100%, and the median was 94.3%. These aerosol observations are comparable to those reported by various participants in the North Atlantic Regional Experiment (Banic et al., 1996; Daum et al., 1996; Li et al., 1996; Liu et al., 1996). That body of work and this one reinforce the fact that the Gulf of Maine is downwind of major anthropogenic pollution sources. They corroborate the conclusion of Parrish et al. (1993) who found that during summer, transport of anthropogenic emissions from North America, and the subsequent photochemical production of O_3, dominated the O_3 budget in the lower troposphere over the temperate North Atlantic. These anthropogenic emissions also dominated the air chemistry we observed in this region.

Size distributions

Aerosol size distributions are a critical parameter for determining the deposition velocity of these aerosols. These size distributions vary depending upon the source region of the air mass being sampled. The size distribution data is presented in greater detail in Chapter 2, however, the main features of NO_3^- and NH_4^+ aerosol size distributions observed at New Castle, New Hampshire are illustrated here. NH_4^+, nss-SO_4^{2-}, NO_3^-, and Na^+ size distributions collected in August 1996 (Figure 1.4) show the typical features observed in the cascade impactor samples. There is a submicron peak at about 0.7 μm diameter for NH_4^+ and nss-SO_4^{2-} which were seen to have the same distribution. This

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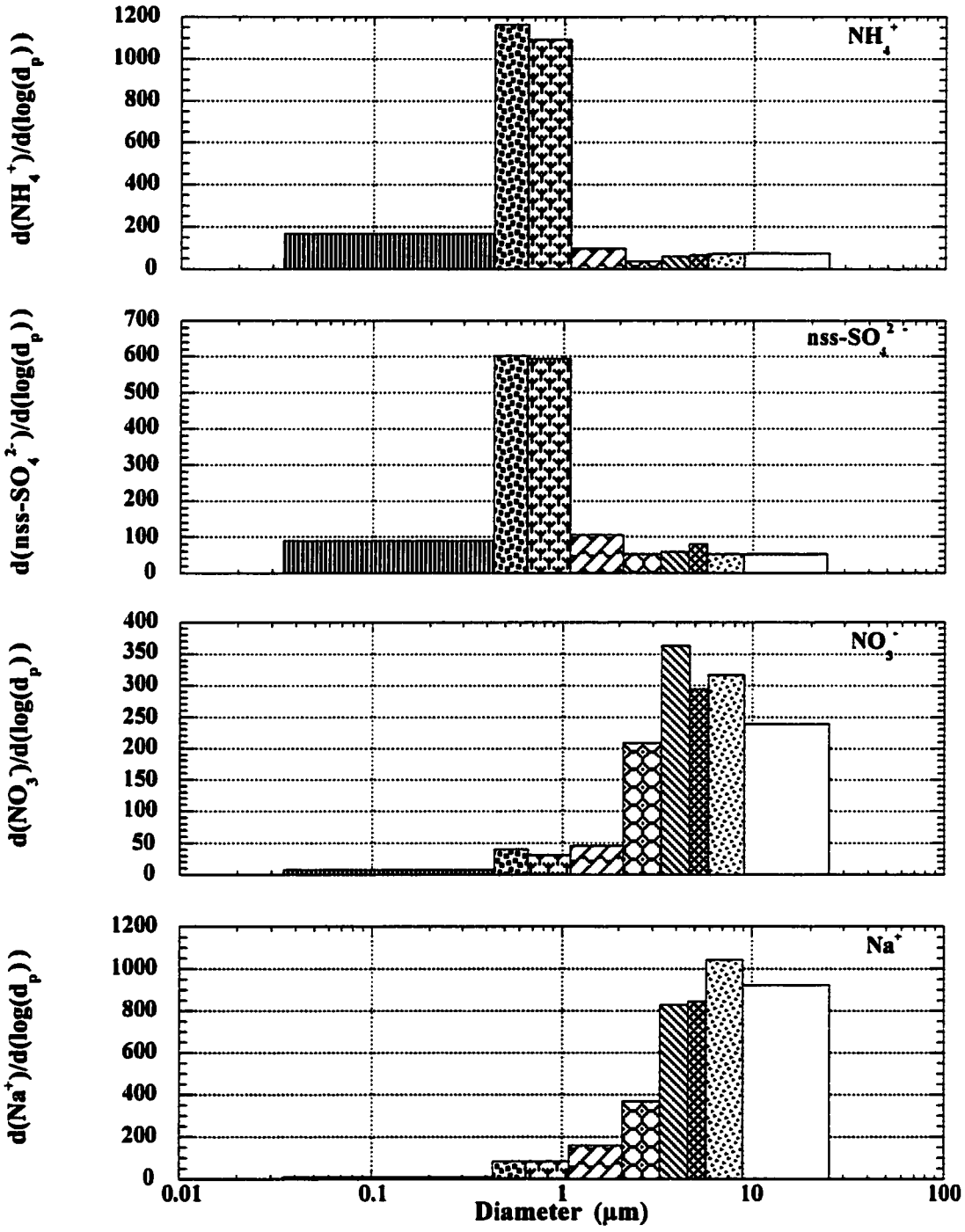

Figure 1.4. Aerosol size distribution sample collected from 18 - 21 August 1996. The units on the y-axis are the amount of the total ion collected for each size (pptv) divided by the log of the diameter range (μm) of each size fraction. These units are used to yield a log-normal distribution.

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suggests that most aerosol NH_4^+ was associated with SO_4^{2-}. Meanwhile, NO_3^- was found on supermicron particles (≈ 6 μm) and followed the size distribution of Na^+, as has been reported by Savoie and Prospero (1982). This suggests that most of the aerosol NO_3^- was in the form of $NaNO_3$. The presence of nitrogen on supermicron particles facilitates the deposition of nitrogen via both dry and wet processes. This association is produced by the reaction of HNO_3 and other gases with aerosol NaCl to yield gas phase HCl and aerosol $NaNO_3$ (see Section 4). Although not shown, there was typically no substantial difference in the size distribution of nss-SO_4^{2-} and total SO_4^{2-}, suggesting that the total SO_4^{2-} originated primarily from gas-to-particle conversion of anthropogenic SO_2.

Precipitation chemistry

Precipitation concentrations of four ions, NO_3^-, NH_4^+, nss-SO_4^{2-}, and Na^+, are shown in Figure 1.5. The measured ion concentrations in rain were highly variable, just as was shown for the aerosols. There was no particular seasonality, except for sea salts such as Na^+ which had a few very highly concentrated events mostly in the late fall and winter months. These high concentrations were associated with low amounts of rainfall, < 1 cm. Unlike in aerosols, NO_3^- appeared on average in greater quantities than NH_4^+. Submicron nss-SO_4^{2-} and NH_4^+, although abundant in the aerosol phase, were probably not as readily scavenged by rain as were supermicron NO_3^- and highly soluble HNO_3. Larger particles are much more readily scavenged than smaller pollution aerosols in the 0.1 to 1.0 μm diameter range (Slinn, 1983). Supermicron sea salts such as Na^+ were sometimes highly concentrated in rain.

The annual volume-weighted means for the chemical species in precipitation are given in Table 1.4. Sea salt ions (Na^+ and Cl^-) were by far the dominant species in the rainwater at the coast. NO_3^- and SO_4^{2-} followed in importance, with NH_4^+ and Mg^{2+} intermediate between those two and the K^+ and Ca^{2+} concentrations. This is a

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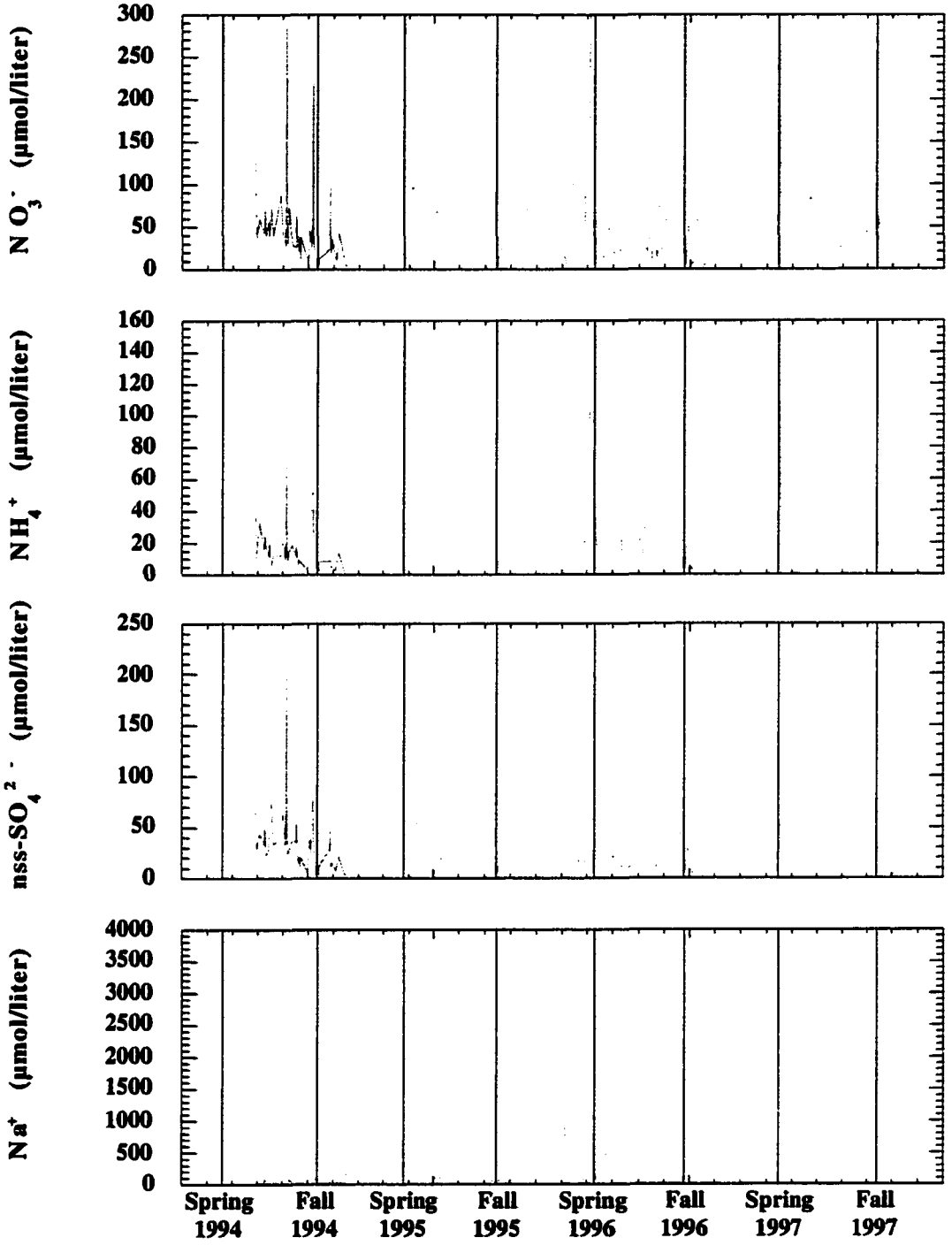

Figure 1.5. Precipitation concentrations for NO_3^-, NH_4^+, nss-SO_4^{2-}, and Na^+ observed from 1994 - 1997. Different colors denote different years. The data gap in 1996 was due to a power failure at the site.

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substantially different scenario than with the aerosol data. The precipitation concentrations were not depleted in 1995 like the aerosol mixing ratios. In fact the only notable variation seen from one year to the next was Na^+ and Cl^- in 1994, when the average concentrations were particularly low, less than half of that seen in the other years. This may have been due to the meteorology. Analysis of the meteorology associated with sampled rain events shows that in 1994 only 17% of these events were of marine origin as opposed to 36% and 46%, respectively, in 1995 and 1996.

Table 1.4. Annual Precipitation Volume-Weighted Means (μmol/liter)

Species	1994	1995	1996	1997
NO_3^-	23	24	22	27
NH_4^+	11	13	12	17
nss-SO_4^{2-}	21	18	15	21
Total SO_4^{2-}	24	23	21	27
Na^+	35	93	96	102
Cl^-	42	76	107	110
Mg^{2+}	4	9	11	11
K^+	2	3	2	2
Ca^{2+}	3	3	4	3

Precipitation concentrations of NO_3^-, NH_4^+, nss-SO_4^{2-}, total SO_4^{2-}, Na^+, and Cl^- are shown for the four seasons of the year (Table 1.5). Note, there were no samples in the winters of 1994 and 1995 and there were too few in spring of 1994 to be considered here. In all four years the concentrations of the pollution species NO_3^-, NH_4^+, and nss-SO_4^{2-} dropped substantially in the fall compared to the other three seasons. The concentration of NO_3^- and NH_4^+ in fall precipitation was only 43% and 28% respectively, of that seen during the other three seasons. Meanwhile, Na^+ and Cl^- increased in fall and winter. The Na^+ and Cl^- concentrations in fall and winter were 299% and 243%

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respectively, of that seen during the spring and summer. This behavior of lower anthropogenic species and higher sea salts in autumn suggests that the storm systems which brought precipitation to our sampling site may have been dominated in fall by coastal low pressure systems and onshore rains. Whereas during the remainder of the year, storm systems of continental origin may be delivering rain dominated by anthropogenic chemical

Table 1.5. Seasonal Precipitation Volume-Weighted Means (μmol/liter)

Species	Year	Winter	Spring	Summer	Fall
NO_3^-	1994			28	7
	1995		35	35	11
	1996	33	27	23	15
	1997	37	31	21	17
NH_4^+	1994			13	4
	1995		20	21	6
	1996	20	16	13	6
	1997	19	21	17	6
nss-SO_4^{2-}	1994			28	5
	1995		23	29	8
	1996	17	19	20	8
	1997	23	23	23	10
Total SO_4^{2-}	1994			30	9
	1995		26	31	16
	1996	30	25	22	15
	1997	30	26	27	22
Na^+	1994			20	62
	1995		30	21	176
	1996	266	98	34	104
	1997	139	55	69	214
Cl^-	1994			25	66
	1995		41	25	130
	1996	253	113	41	120
	1997	143	61	80	225

species. While in spring and summer, nss-SO_4^{2-} constituted approximately 80% - 90% of the total SO_4^{2-}, in fall, it was only about 50% of the total. This pattern was not seen in the aerosols (Table 1.1), which indicates the difference was probably a function of the storm tracks in fall rather than a mechanism influencing the overall atmospheric chemistry. This

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is consistent with analyses which show cyclonic storms, known as nor'easters, are most likely to occur from October through April (Davis and Dolan, 1993; Davis et al., 1993).

Precipitation data was compared with that of two coastal stations that participate in the National Atmospheric Deposition Program (NADP). The two NADP stations are the North Atlantic Coastal Lab (MA01) in Barnstable County, Massachusetts (referred to as Cape Cod) and the Acadia National Park - McFarland Hill site (ME98) in Hancock County, Maine (referred to as Acadia). The Cape Cod site is located at 41° 58' 33'' N latitude and 70° 01' 29'' W longitude with an elevation of 41 m. The Acadia site is located at 44° 22' 26'' N latitude and 68° 15' 38'' W longitude with an elevation of 129 m. New Castle, NH lies between these (43° 04' N 70° 42' W, elevation approximately 10 m). NO_3^-, NH_4^+, Na^+, and Cl^- in precipitation are compared on both an annual and seasonal basis between our site and the two NADP sites (Table 1.6). Again the continental species decreased, while the sea salt species increased, at all three coastal sites in fall, indicating a strong marine influence on precipitation chemistry at this time of year.

The volume-weighted means from New Castle tend to be higher, in general, than those from Cape Cod and Acadia on both a seasonal and annual basis (Table 1.6). Although only four species are listed, this was the case for all species measured. This is shown more clearly in the ratios of the means from New Castle to those of Cape Cod and Acadia (Table 1.7). Compared to Cape Cod, the New Castle annual volume weighted means tend to be higher by 20% - 60% for NO_3^-, 40% - 90% for NH_4^+, 30% - 50% for Na^+, and 20% - 40% for Cl^-. A notable exception occurs in 1994 when Na^+ and Cl^- means were only 60% of those reported from Cape Cod. Compared to Acadia, the annual means from New Castle are higher by 70% - 130% for NO_3^-, 80% - 130% for NH_4^+, 40% - 290% for Na^+, and 50% - 290% for Cl^-. Here, the large disparity between the sea salt volume weighted mean concentrations was likely due to the proximity of our site to the shoreline (within 15 m), whereas the Acadia site is 3.3 km inland on Mt. Dessert Island. Note the seasonal ratios for both Cape Cod and Acadia show a wider range of variability

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Table 1.6. NADP Comparison Volume-Weighted Means (μmol/liter)

Location	Year	Annual	Winter	Spring	Summer	Fall
				NO_3^-		
Cape Cod	1994	15			16	9
	1995	20		32	22	9
	1996	14	18	21	19	8
	1997	21	13	30	32	
New Castle	1994	23			28	7
	1995	24		35	35	11
	1996	22	33	27	23	15
	1997	27	37	31	21	17
Acadia	1994	10			18	7
	1995	12		14	13	10
	1996	11	11	11	14	8
	1997	16	13	14	24	
				NH_4^+		
Cape Cod	1994	6			8	3
	1995	9		18	10	4
	1996	7	9	10	9	3
	1997	9	4	18	8	
New Castle	1994	11			13	4
	1995	13		20	21	6
	1996	12	20	16	13	6
	1997	17	19	21	17	6
Acadia	1994	6			11	2
	1995	6		11	6	4
	1996	6	5	7	6	6
	1997	8	4	9	11	
				Na^+		
Cape Cod	1994	59			31	76
	1995	63		53	12	72
	1996	75	129	78	37	83
	1997	72	79	28	22	
New Castle	1994	35			20	62
	1995	93		30	21	176
	1996	96	266	98	34	104
	1997	102	139	55	69	214
Acadia	1994	25			8	26
	1995	42		18	3	50
	1996	25	96	31	10	26
	1997	28	35	23	19	
				Cl^-		
Cape Cod	1994	67			37	83
	1995	66		62	13	74
	1996	80	128	79	44	87
	1997	80	80	30	27	
New Castle	1994	42			25	66
	1995	76		41	25	130
	1996	107	253	113	41	120
	1997	110	143	61	80	225
Acadia	1994	27			9	31
	1995	47		19	2	58
	1996	27	104	33	12	31
	1997	32	40	26	22	

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Table 1.7. Ratio of New Castle Volume-Weighted Means to NADP Sites

Species	Year	Annual	Winter	Spring	Summer	Fall
			New Castle/Cape Cod			
NO_3^-	1994	1.5			1.7	0.8
	1995	1.2		1.1	1.6	1.2
	1996	1.6	1.9	1.3	1.2	1.8
	1997	1.3	2.8	1.1	0.7	
NH_4^+	1994	1.8			1.7	1.5
	1995	1.4		1.1	2.0	1.3
	1996	1.8	2.2	1.6	1.4	2.0
	1997	1.9	4.3	1.2	2.0	
Na^+	1994	0.6			0.6	0.8
	1995	1.5		0.6	1.7	2.5
	1996	1.3	2.1	1.3	0.9	1.3
	1997	1.4	1.8	2.0	3.2	
Cl^-	1994	0.6			0.7	0.8
	1995	1.2		0.7	2.0	1.8
	1996	1.3	2.0	1.4	0.9	1.4
	1997	1.4	1.8	2.1	3.0	
			New Castle/Acadia			
NO_3^-	1994	2.3			1.5	1.1
	1995	2.1		2.5	2.6	1.2
	1996	2.0	3.0	2.5	1.6	1.8
	1997	1.7	2.9	2.2	0.9	
NH_4^+	1994	1.8			1.2	2.0
	1995	2.1		1.8	3.3	1.4
	1996	2.0	4.3	2.5	2.0	1.1
	1997	2.3	4.7	2.3	1.6	
Na^+	1994	1.4			2.5	2.3
	1995	2.2		1.7	7.6	3.5
	1996	3.9	2.8	3.1	3.2	4.0
	1997	3.6	4.0	2.4	3.7	
Cl^-	1994	1.5			2.9	2.1
	1995	1.6		2.2	10.2	2.2
	1996	3.9	2.4	3.4	3.5	3.8
	1997	3.4	3.6	2.4	3.6	

between the sites. Caution in the interpretation of the relationship between these data sets is needed given the distance and difference in settings between the three sites. However, it is important to note that the difference between the nitrogen species reported here and those reported by NADP suggest that the total wet deposition of inorganic nitrogen to some areas along the Gulf of Maine coast may well exceed that expected, given the data from these two NADP coastal sites alone. At New Castle, the annual wet deposition of total inorganic nitrogen is 30% - 60% greater than that recorded at Cape Cod and 55% - 115% greater than Acadia.

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Chemical relationships

NH_4^+ versus the sum of nss-SO_4^{2-} and NO_3^- shows that there is insufficient base to neutralize the acids for both aerosol phase (Figure 1.6a) and precipitation (Figure 1.6b). If the acidic species were fully neutralized, the observations should fall along the 1:1 line. However, in both cases, the best fit line lies well below this with slopes of 0.48 for the aerosol and 0.19 for precipitation. As mentioned previously, NO_3^- is the dominant nitrogen ion in precipitation due to the preferential scavenging of supermicron particles versus submicron particles. Plus, nitric and sulfuric acids readily dissolve in rain drops. Thus, the precipitation was even more acidic than the aerosols would suggest. Nonetheless, even in the aerosols, twice as much NH_4^+, on average, would be required to fully neutralize the available SO_4^{2-} and NO_3^-. This is similar to results found by Lefer (1999) from measurements at Harvard Forest in Petersham, Massachusetts. He found that high mixing ratios of SO_42- in the air over the forest kept NH_3 mixing ratios well below the compensation point. Hence the forest was releasing NH_3 into the atmosphere, despite it being nitrogen limited (Lefer, 1999). In polluted air masses, Lefer found that there was insufficient NH_4^+ to neutralize the SO_4^{2-} when mixing ratios exceeded ≈ 2200 pptv. Although not shown, there was seasonal variation in this relationship. For the aerosols, summer was most acidic (slope of 0.45) and winter was least acidic (slope of 0.67). Fall and spring had slopes of 0.53 and 0.55, respectively. In precipitation, the summer was again the most acidic (slope of 0.13), while the remaining three seasons were all fairly similar with slopes ranging from 0.21 to 0.23. Thus, throughout the year, there was insufficient base to neutralize the acids.

The relationship between Cl^- and Na^+ is shown for both the aerosols (Figure 1.7a) and precipitation (Figure 1.7b). The mean equivalents based ratio of Cl^-:Na^+ in sea water is 1.16 (Keene et al., 1986; Wilson, 1975). However, in aerosols at our site, this ratio was only 0.87 on average. This varied somewhat seasonally with the greatest Cl^- depletion

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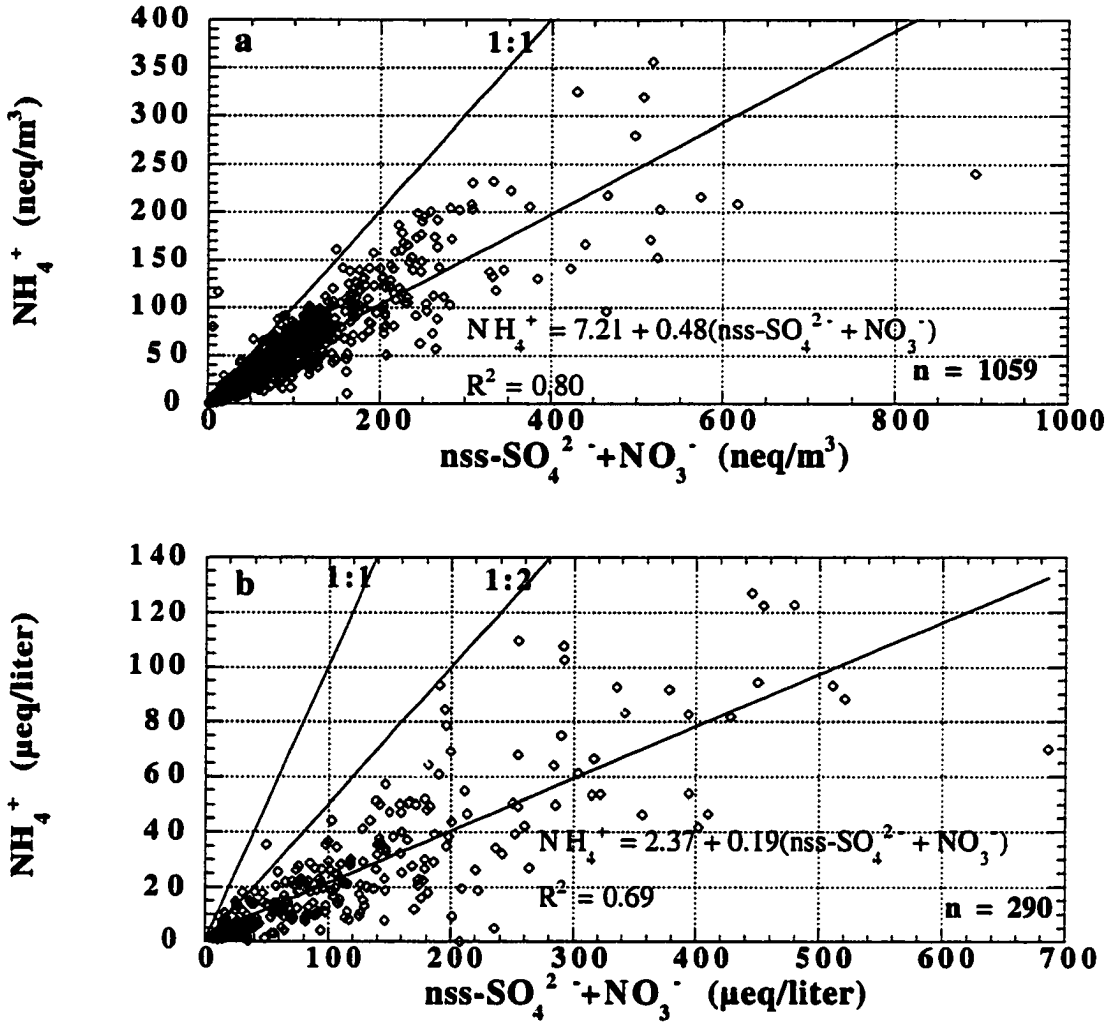

Figure 1.6. Relationship between NH_4^+ and the sum of nss-SO_4^{2-} and NO_3^- in both aerosols (a) and precipitation (b). The best fit line, along with the equation, is shown with the 1:1 line in both panels. The 1:2 line is also shown in (b).

occuring in summer (Cl^-:Na^+ = 0.73) and the least in fall (Cl^-:Na^+ = 0.99). Several mechanisms have been proposed to explain the loss of Cl^- from sea salt aerosols. First, acidic gases, HNO_3 and H_2SO_4 can dissolve onto these aerosols, reduce their pH, and drive off HCl as follows (Robbins et al., 1959; Eriksson, 1960; Martens et al., 1973; Keene et al., 1990)

$$HNO_3\ (g) + NaCl\ (p) \rightarrow HCl\ (g) + NaNO_3\ (p) \qquad (1)$$

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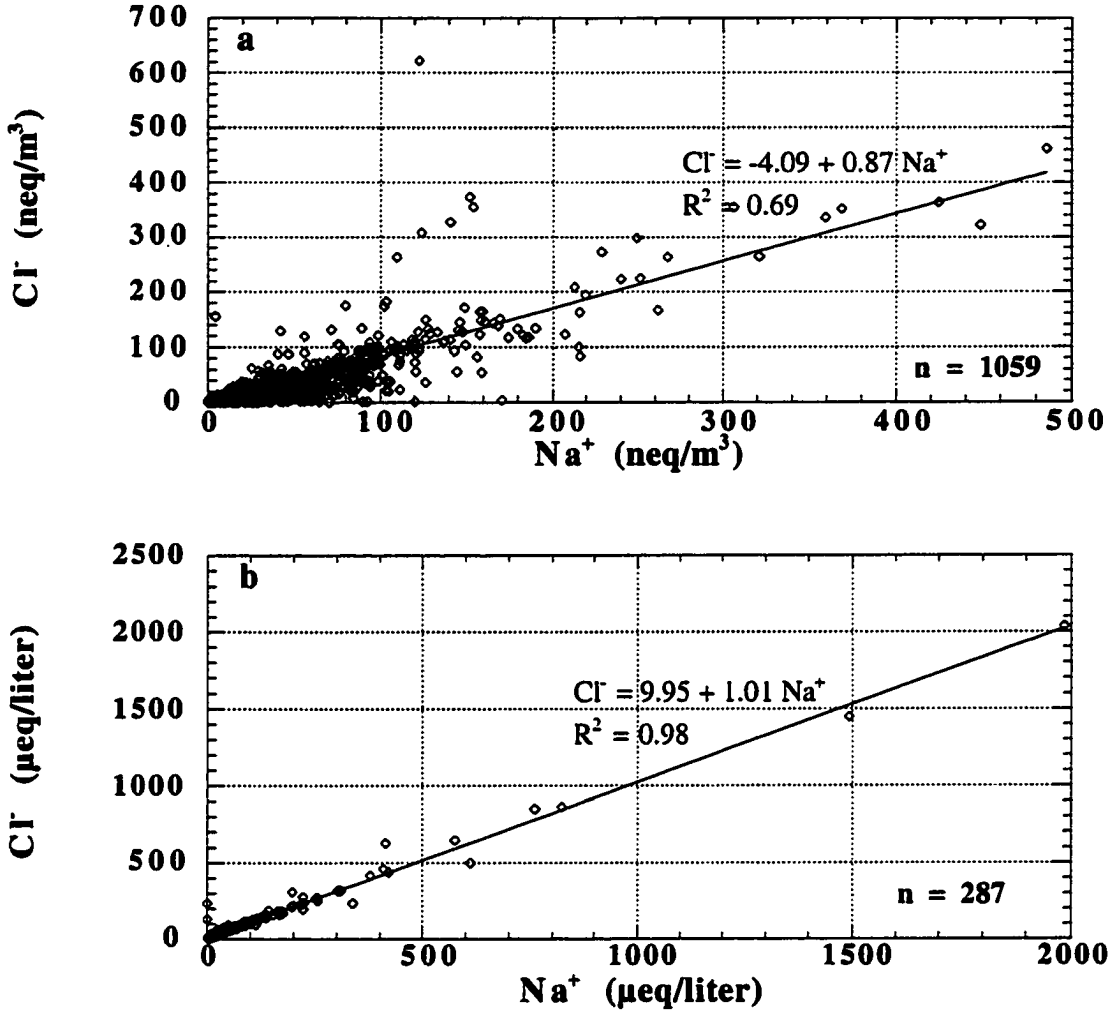

Figure 1.7. Relationship between Cl^- and Na^+ in both aerosols (a) and precipitation (b). Cl^- was depleted relative to Na^+ in both aerosol and precipitation, given a sea salt ratio of $Cl^-:Na^+ = 1.16$ (Keene et al., 1986; Wilson, 1975).

$$H_2SO_4\ (g) + 2NaCl\ (p) \rightarrow 2HCl\ (g) + Na_2SO_4\ (p) \qquad (2)$$

Second, non-acidic gases have been proposed to react with sea salt particles (Altshuller, 1958; Schroeder and Urone, 1974; Finlayson-Pitts, 1983; Finlayson-Pitts et al., 1989; Keene et al., 1990), e.g.,

$$2NO_2\ (g) + NaCl\ (p) \rightarrow NOCl\ (g) + NaNO_3\ (p) \qquad (3)$$

$$ClNO_3\ (g) + NaCl\ (p) \rightarrow Cl_2\ (g) + NaNO_3\ (p) \qquad (4)$$

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$$N_2O_5\ (g) + NaCl\ (p) \rightarrow ClNO_2\ (g) + NaNO_3\ (p) \qquad (5)$$

In equations 3-5, the product gases all undergo rapid photolysis and hydrolysis processes which in the end result in HCl and $NaNO_3$ as final products (Keene et al., 1990). These latter three reactions are only important in polluted areas (Singh and Kasting, 1988; Keene et al., 1990). Third, a proposed process in which O_3 drives off gas phase Cl_2 from sea salt aerosols in the presence of H_2O has the following stoichiometry (Behnke and Zetzsch, 1989; Keene et al., 1990)

$$2Cl^- + O_3\ (p) \rightarrow Cl_2\ (g) + 2OH^- + O_2\ (g) \qquad (6)$$

Photolysis of Cl_2 results in the production of Cl atoms which lead to the production of HCl and $ClNO_3$ (Keene et al., 1990). Which mechanisms are important here cannot be determined, although it is anticipated some combination of them occurs in this polluted coastal environment.

In precipitation, Cl^-:Na^+ was 1.01 (Figure 1.7b), higher than in aerosols, but still less than that expected from sea water. This suggests that some of the Cl^- driven off as HCl is scavenged by precipitation. The fact that precipitation was still depleted compared to sea water may be due to several factors. First, not all of the available HCl may have been scavenged by the rain. Second, some of the HCl driven off from the aerosols may have dry deposited, especially to the water surface, prior to the rain event. HCl is highly soluble, so it will readily deposit to wet surfaces. Jacob et al. (1985) report results which suggest HCl may dry deposit more quickly to the ocean than aerosol Cl^- particles, thereby enhancing the observed Cl^- loss in fogs when the gas phase HCl should be readily scavenged by the water droplets. Third, if other gas phase products have been produced, e.g., Cl_2, they are less soluble and less easily scavenged by precipitation (Graedel and Keene, 1995).

The Cl^- deficit versus NO_3^- is shown in Figure 1.8. This deficit is calculated by multiplying the measured Na^+ by 1.16 to get the amount of Cl^- expected in sea salt aerosol. The calculated Cl^- is subtracted from the measured Cl^-, with the negative result

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referred to as the Cl^- deficit. If all of the particulate NO_3^- was produced via reactions 1, 3, 4, and 5 and none of the HCl was lost, then these two species would have a 1:1 relationship. Note, SO_4^{2-} is not considered here because this figure uses bulk aerosol data and most of the SO_4^{2-} present is in fine particles (Figure 1.4) with non-sea-salt origins. Nonetheless, a simple regression with a slope of 0.92 is found, although there is a substantial amount of scatter yielding $R^2 = 0.32$. Both the slope and the scatter suggest

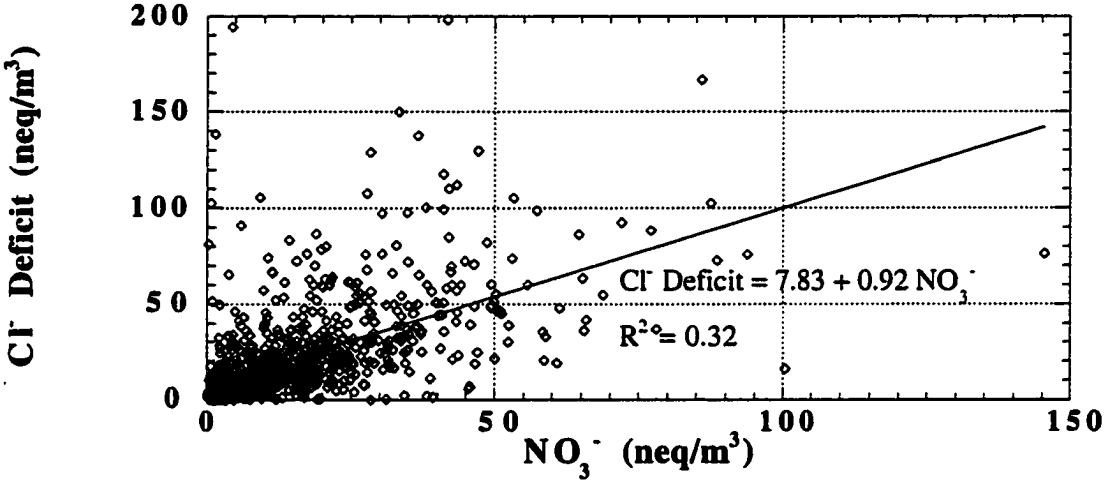

Figure 1.8. Aerosol Cl^- deficit versus NO_3^-. If all of the particulate NO_3^- was produced as HCl was driven off, then this plot should yield a 1:1 relationship.

that other processes, which do not produce $NaNO_3$ are also important (e.g., equations 2 and 6).

Nss-SO_4^{2-} versus total SO_4^{2-} is plotted for both aerosols (Figure 1.9a) and precipitation (Figure 1.9b). In aerosols, the relationship was essentially 1:1, i.e. nearly all of the SO_4^{2-} observed at this site was of non-sea-salt origin. This was true despite the fact that the site was located on the shore of the Gulf of Maine. These results illustrate the importance of continental sources on the air chemistry in the coastal zone. Note, in precipitation, the non-sea-salt portion of the total was slightly less than it was for aerosols (although it still contributed 92% on average). This was likely due to the types of storm

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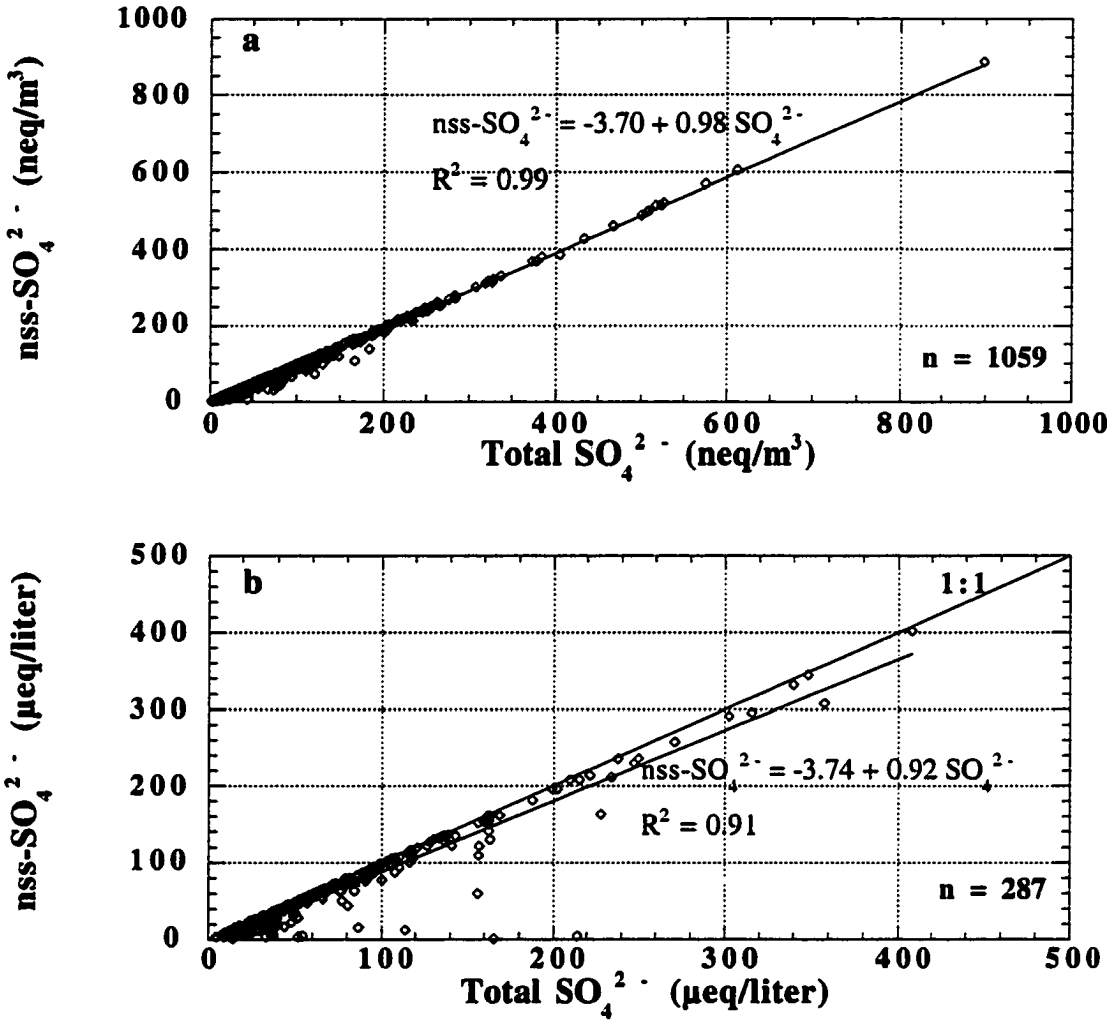

Figure 1.9. Relationship between nss-SO_4^{2-} and total SO_4^{2-} in both aerosols (a) and precipitation (b). Despite the proximity to the coast, the SO_4^{2-} contributed by sea salt was only a tiny fraction of the total SO_4^{2-}observed.

systems which brought rain to this area. There are systems which come across the continent from the west, e.g., Colorado Lows and Alberta Clippers. These systems bring rain in which the SO_4^{2-} is nearly all of non-sea-salt origin. Other systems bring rain from a low pressure system sitting offshore, e.g. a Nor'easter. This type of rain contains a much higher percentage of sea salt SO_4^{2-} than rain systems of continental origin.

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Summary

The importance of looking at atmospheric chemistry relevant to nitrogen deposition in the coastal marine environment, particularly along the east coast of the United States, has been presented in this chapter. Being downwind of major anthropogenic emissions can lead to enhanced nutrient loading of the coastal ecosystem. With this in mind, an overview of the HNO_3, aerosol, and precipitation chemistry observed over a three and a half year period has been presented.

This overview may be summarized as follows. Daily HNO_3 and aerosol mixing ratios were highly variable, with mixing ratios ranging over an order of magnitude. HNO_3 and NH_4^+ were seen to have summer peaks. The HNO_3 peak was due to enhanced NO emissions coupled with longer days which enhanced its photochemical production. The NH_4^+ peak was attributed to its biogenic sources being stronger in summer, coupled with transport that apparently brings greater amounts of NH_4^+ to the eastern United States from the midwest during this season. In addition, this peak may be enhanced due to increased traffic in New England releasing NH_3 from catalytic converters in cars. NO_3^- did not exhibit any summer peak. Average annual aerosol mixing ratios tended to be similar, although 1995 was anomalous and led to annual variations of about a factor of two. Gas phase HNO_3 and particulate NH_4^+ were the dominant water soluble nitrogen species in the atmosphere, while NO_3^- was the dominant nitrogen ion in precipitation. This change in dominance was due to more effective scavenging of gas phase HNO_3 and supermicron NO_3^- than of submicron NH_4^+. This submicron NH_4^+ was closely correlated with nss-SO_4^{2-}. Most of the SO_4^{2-} observed, 80% - 95% was of non-sea-salt origin. Meanwhile the supermicron NO_3^- was associated with Na^+ and was presumed to be in the form $NaNO_3$. NO_3^- ends up on supermicron sea salt particles via reaction with HNO_3 and other gases. This process also leads to the depletion of Cl^- as particulate $NaNO_3$ is formed and gas phase HCl is driven off of the particles. There was insufficient ammonia available to fully neutralize the nitric and sulfuric acids present. In precipitation, the concentrations

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of continentally derived species were seen to drop significantly, while sea salt species increased in autumn precipitation. This was attributed to storm systems in the fall being predominantly of marine origin. There was significantly more NO_3^- and NH_4^+ in precipitation at New Castle, NH than reported by two NADP coastal sites.

These observations have the following implications for the deposition of nitrogen to the Gulf of Maine. First, more nitrogen is being deposited at some locations along the coast of the Gulf of Maine than currently indicated by the NADP network. Second, large particles dry deposit much more readily than small particles. Thus, the processes which lead to the presence of NO_3^- on supermicron aerosols can enhance dry deposition of NO_3^- to coastal waters. Third, there is an abundance of HNO_3 in this region. Dry deposition of HNO_3 is enhanced by the higher humidity and wind speeds over the water. These three factors combined suggest that nitrogen deposition to the Gulf of Maine has been previously underestimated. In addition, atmospheric mixing ratios of HNO_3 and NH_4^+ peak in summer. This is when NO_3^- and NH_4^+ are most depleted in the surface waters of the gulf. Hence, the time when the highest atmospheric deposition of nitrogen is anticipated coincides with the time at which this deposition may be most influential.

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CHAPTER 2

ATMOSPHERIC TRANSPORT AND RELATED CHEMICAL SIGNATURES OF HNO_3, AEROSOLS, PRECIPITATION AND FOG

Abstract

Gas phase HNO_3, aerosol, precipitation, and fog water samples collected from 1994 - 1997 at a coastal site in New Hampshire, were used in conjunction with 1000 hPa streamlines to classify sampled air masses according to their surface level transport and chemistry. Eight characteristic groups were defined, of these the three primary groups were polluted continental, "clean" continental, and marine. Highly variable mixing ratios of HNO_3 and aerosol species were observed within each group from day-to-day, yet each group had a unique average chemical signature. On average, the HNO_3 and aerosol mixing ratios observed in 1995 were roughly a factor of two lower than seen for the groups in other years. Overall, mixed conditions occurred in 42% of the samples, continental species were dominant in 37%, and marine species were dominant in 21%. Rain occurred frequently under sea salt dominant conditions; about 47% of the days classified as such had rain events. Fog chemistry and average aerosol chemical size distributions were evaluated based on which species dominated their chemical signatures, marine, continental, or a relatively even mixture of the two. Particulate NO_3^- was associated with sea salt Na^+ in the course aerosol fraction peaking at approximately 4 μm in diameter. There was also a distinct secondary peak in the submicron fraction observed in air dominated by continental aerosols. Particulate NH_4^+ was associated with non-sea-salt-SO_4^{2-} (nss-SO_4^{2-}), with the bulk of the NH_4^+ present on particles in the 0.43 - 1.1 μm diameter range. Although nss-SO_4^{2-} was primarily found in the submicron size range, a substantial fraction (≥ 25%) was found in the supermicron range for all three cases. A deficit of Cl^- was observed in the sea

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salt aerosols, with the deficit greatest for particles in the 1.1 - 3.3 μm and 9.0 - 25 μm diameter ranges.

Introduction

A multi-year sampling program was carried out at the southern coast of the Gulf of Maine in New Castle, New Hampshire in which daily gas-phase HNO_3 and bulk aerosol samples (24 hour averages) were collected along with event based precipitation samples, fog water samples, and aerosol size distribution samples. Synoptic weather patterns frequently bring air masses of different origins and different physico-chemical properties to this sampling site. This variability is particularly noticeable at the land/ocean interface in the vicinity of substantial anthropogenic input to the atmosphere. Not only does the chemical speciation change between air masses exposed to anthropogenic versus natural sources, but properties such as aerosol size distribution vary as well.

SO_4^{2-} is found predominantly in the fine fraction of aerosols due to various oxidation processes of SO_2. In marine air masses, there is also a substantial supermicron mode for both non-sea-salt-SO_4^{2-} (nss-SO_4^{2-}) and sea-salt-SO_4^{2-} (Savoie and Prospero, 1982; Milford and Davidson, 1987). Savoie and Prospero (1982) attributed the coarse nss-SO_4^{2-} to surface processes including the heterogeneous reaction of SO_2 on sea salt particles and the agglomeration of small SO_4^{2-} aerosols with coarse sea salt particles. They suggest the latter process is more important and they suggest that this mechanism also accounts for the presence of NH_4^+ in the coarse mode as well. Sievering et al. (1991) evaluated several mechanisms to explain coarse mode nss-SO_4^{2-}. Cloud conversion, coagulation, and collision-coalescence could not account for the amount of coarse fraction nss-SO_4^{2-} observed at Bermuda. Most cloud processes result in the production of fine mode nss-SO_4^{2-}. Their results suggest diffusion of SO_2 to the surface of sea salt particles and its subsequent oxidation via O_3 in the surface water layer of the particle can explain the coarse nss-SO_4^{2-}.

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NO_3^- also exhibits a bimodal distribution with the fine mode due to gas to particle conversion of NH_3 and HNO_3 leading to NH_4NO_3, and the coarse fraction attributed to adsorption of HNO_3 onto soil and sea salt particles (Milford and Davidson, 1987). In marine locations, the coarse mode is dominant and has been seen to be associated with and shifted to slightly smaller sizes than the Na^+ peak, suggesting surface processes at work (Savoie and Prospero, 1982). Observations in Tokyo, showed a bimodal size distribution of NO_3^- due to NH_4NO_3 in the fine fraction and $NaNO_3$ in the coarse mode (Yoshizumi and Hoshi, 1985). Fine mode NO_3^- was dominant in winter and coarse NO_3^- was dominant in summer, due to increased volatility of NH_4NO_3 with increasing temperature leading to less fine NO_3^- in summer. There were similar amounts of $NaNO_3$ in both winter and summer, so the seasonal variation observed in the size distribution was truly due to the presence or absence of NH_4NO_3. At New Castle, little NH_4NO_3 is anticipated as there are sufficient amounts of SO_2 to neutralize all of the ambient NH_3 (Chapter 1). As NH_3 reacts with SO_2 more readily than HNO_3 and NH_4HSO_4 and $(NH_4)_2SO_4$ are more stable than NH_4NO_3 (Stelson et al., 1979; Stelson and Seinfeld, 1982), it is anticipated that NH_4NO_3 will not be a dominant feature here. Aerosol size distributions made at Harvard Forest in Petersham, Massachusetts corroborate this expectation. The fine mode is dominated by NH_4^+ and SO_4^{2-}, while most of the NO_3^- is associated with coarse soil (Ca^{2+}) particles and only a small fraction of the NO_3^- in the fine mode (Lefer, 1997).

Several mechanisms involving acidic and non-acidic gases as well as O_3 have been proposed to explain the loss of Cl^- from sea salt particles (Altshuller, 1958; Robbins et al., 1959; Eriksson, 1960; Martens et al., 1973; Schroeder and Urone, 1974; Finlayson-Pitts, 1983; Behnke and Zetzsch, 1989; Finlayson-Pitts et al., 1989; Keene et al., 1990). NO_3^- size distributions in Finland indicated coarse NO_3^- formed via reactions of HNO_3 with soil and sea salt particles Pakkanen (1996). The sea salt reactions drive off HCl resulting in Cl^- depletion from the sea salt particles. Coarse nss-SO_4^{2-} also suggests H_2SO_4 or SO_2 reacted with sea salt, further driving off HCl. The percentage of Cl^- loss was found to

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decrease with increasing particle size, suggesting a surface mechanism for the loss. There was nearly complete depletion of Cl^- in the 1 - 2 μm range.

In this work, the properties of different types of air masses which pass by the site at New Castle, New Hampshire, were investigated. In particular, did surface flow from different areas bring in air with different chemical signatures? Did the size distribution of chemical species change depending on the type of air being sampled? Other authors have reported findings of different physico-chemical properties depending on the source region of the sampled air mass. Results have been reported from various locations including: western Pacific islands (Mukai and Suzuki, 1996; Nagao et al., 1999), the Portuguese coast (Pio et al., 1996a and 1996b), southern Norway (Pakkanen et al., 1996), central Ontario (Isaac et al., 1998), and North Carolina (Ulman and Saxena, 1997; Bahrmann and Saxena, 1998).

In a study at South Uist, about 100 km off the northwest coast of Scotland on one of the Outer Hebrides, Lowe et al. (1996) found continental air masses from Europe were dominated by $(NH_4)_2SO_4$ aerosols. In maritime air masses, these aerosols dominated the fine fraction, while sea salts dominated the coarse mode. They also observed a few air masses of Arctic origin which had very little pollution. Finally, they reported mixed air masses where either continental air had been modified by its passage over water or marine air was subjected to continental influences prior to reaching the site. These results are very similar to those reported here, on the other side of the Atlantic, with the continental air masses originating over North America.

Locally, several similar studies have been carried out. At Harvard Forest in Petersham, Massachusetts, Shipham et al. (1998) looked at regional transport to account for observed variations in CH_4 mixing ratios. They found that transport from the southwest quadrant was most polluted and the northeast was the cleanest. This was attributed to the distribution of local landfills and wetlands which are strong sources of CH_4. Aerosol, NH_3 and HNO_3 observations divided into three sectors, showed the

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greatest pollution arrived from the southwest sector (180° - 270°) at Harvard Forest (Lefer, 1997). Cluster analysis of back trajectories where three trajectories per day were coupled with three hour averages of trace gas measurements (Moody et al., 1998) showed background conditions, with lower pollutant mixing ratios and lower variance, under north and northwest-fast flow at Harvard Forest. Anthropogenic pollutants were highest under southwest flow conditions which were also generally warm, moist, and relatively cloudy (warm sector transport).

Another project carried out nearby was the North Atlantic Regional Experiment (NARE) off the coast of New England and the Canadian Maritime provinces. This work was primarily concerned with O_3 transport from North America over the North Atlantic. Transport from three sectors was described (Banic et al., 1996; Li et al., 1996): source (polluted), north (low pollution), and maritime . These sectors are very similar to those independently defined here as groups 1, 2, and 3, respectively.

In fact, observations from Harvard Forest, NARE, and now New Castle, New Hampshire, all indicate that most pollution arrives in this region from the southwest. The cleanest continental sector is from the north and the marine air from the east is important in regional air chemistry. It is interesting to note, that Ulman and Saxena (1997) also report a 3 sector system centered at Mt. Mitchell, North Carolina, with marine, polluted, and clean continental sectors. However, their pollution arrives from the north/northeast while their clean sector is to the southwest. This, in conjunction with the results from the northeastern United States and southeastern Canada, suggests the strongest pollution sources in the eastern United States lie between North Carolina and New England.

In this paper, data from New Castle, New Hampshire are presented in the context of chemical signatures associated with air mass source regions. Three basic chemical signatures were identified: (1) marine air dominated by the sea salt species Na^+ and Cl^-, (2) polluted air dominated by HNO_3, NH_4^+, and SO_4^{2-}, and (3) "clean" continental air also dominated by these three species, but with much lower ambient mixing ratios. These

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data were classified into eight groups which consisted of these three basic groups along with five combinations of the three. Twenty aerosol size distribution samples were analyzed to see if there were distinct size distributions characteristic of these categories. These data could not be sorted according to the eight groups, but they could be separated into the three basic classifications.

Methods

Measurements were made on the shore of the Gulf of Maine at the Portsmouth Harbor Coast Guard Station in New Castle, NH. These measurements included daily (24 hour averages) bulk aerosol and HNO_3 samples, event based precipitation samples, 20 aerosol size distribution samples, and 36 fog water samples. Various meteorological parameters were also measured and saved as hourly averages. Samples were initially collected from May through November of 1994, then starting in March of 1995 sampling continued through November of 1997. An overview of our data set and a complete discussion of our methods are in Chapter 1.

On average, errors for the bulk aerosol were $NO_3^- = \pm 5\%$ and $NH_4^+ = \pm 4\%$, and for the gas phase $HNO_3 = \pm 5\%$ (Chapter 1). The size distribution data were collected on a series of 10 filters, so the error analysis was carried out for each filter. The results were remarkably similar, with $NO_3^- = \pm 5\%$ and $NH_4^+ = \pm 5\%$ on most stages, with the other few either ±4% or ±6%. The experimental error for our precipitation and fog concentration data is solely a function of the analytical uncertainty. The precision of our analytical method was ±3% and our comparisons to the National Institute of Standards and Technology (NIST) standards was ±1%.

The fog sampling protocol was not described previously, so it will be presented here. Fog samples were collected at three locations: at New Castle, New Hampshire, within 10 m of the shore at the same location as the aerosol and precipitation samplers; at Plum Island, Massachusetts, within 10 m of the Gulf of Maine, and on the west side of Plum Island within 5 m of the water. An active sampler based on a design by Global

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Geochemistry Corporation (Hering et al., 1987) was used. A fan is used to pull the fog through a thick mesh of polypropylene strands. The fog water condenses on the strands and runs down a teflon lined PVC pipe to a sample bottle at the bottom of a V-shaped configuration. Fog droplets larger than 5 μm are sampled with at least 98% collection efficiency (Hering et al., 1987). Samples are collected over a period ranging from 30 to 90 minutes, depending on the liquid water content of the fog, with denser fogs requiring less sampling time. The sample bottles are kept on ice until they can be frozen. Prior to analysis, they are thawed and treated with chloroform to prevent biodegradation of the nitrogen species. The samples are diluted and analyzed by ion chromatography to determine the concentrations of the following ions: Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}.

Initially, to establish whether air masses of a particular origin had a characteristic chemistry, hourly wind direction data corresponding to each sample were averaged with that average used as an indication of origin. However, those averages did not necessarily indicate air mass origin, due to micro- and meso-scale weather features imbedded within the synoptic-scale transport mechanisms, yielding misleading averages. Given that the bulk samples were collected over approximately 24 hour periods, using back trajectories seemed inappropriate as there would not be a well defined air parcel to extrapolate backward in time to its point of origin (Kahl, 1993). Thus, streamline maps produced by NASA for their Global Troposphere Experiment program (e.g., Figure 2.1) were acquired. Figure 2.1a is an example of a flow pattern which brings marine air onshore. Figure 2.1b is an example of a pattern which flows along the eastern seaboard of the United States advecting polluted air to New Castle, NH. These streamlines are available on their website (http://asd-www.larc.nasa.gov/David/gteplotpage.html) for 0 and 12 hrs UT. On average, there were two streamlines per daily sample. Unfortunately, due to a file format change to the raw data file used by NASA, their data set ends at the end of 1996. Thus, for this part of the analysis, only data collected from 1994 through 1996 were evaluated.

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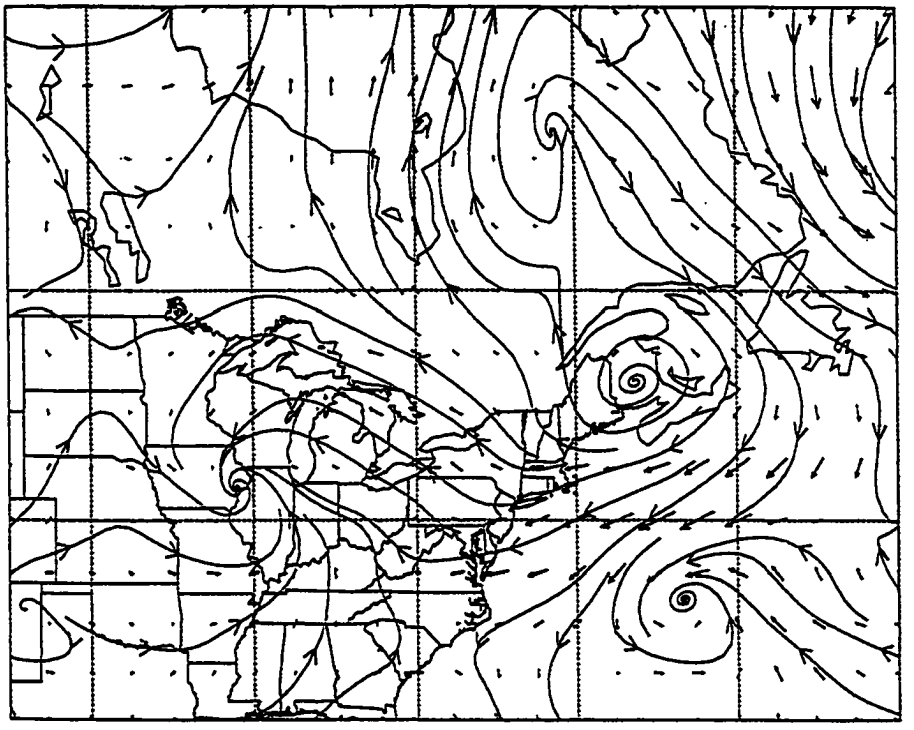
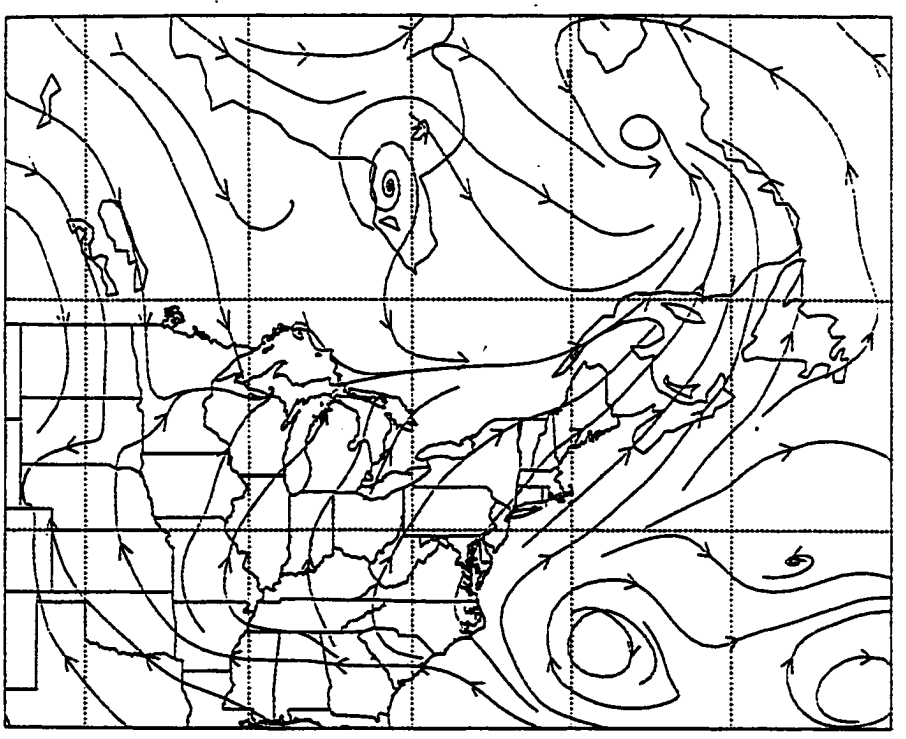


a.



b.

Figure 2.1. Examples of NASA GTE 1000 hPa streamline maps showing surface flow patterns which brought a) marine air, and b) anthropogenically polluted air up along the eastern seaboard of the United States to New Castle, NH.

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Streamlines were used primarily qualitatively, to indicate the flow direction at the surface (1000 hPa). The direction from which an air mass was advected to New Castle was obtained by assigning a point on a circle surrounding New Castle (Figure 2.2). A circle of approximately 1100 km radius centered on New Castle, NH was drawn on a plastic sleeve slid over each map. This was done to ensure consistency from one paper

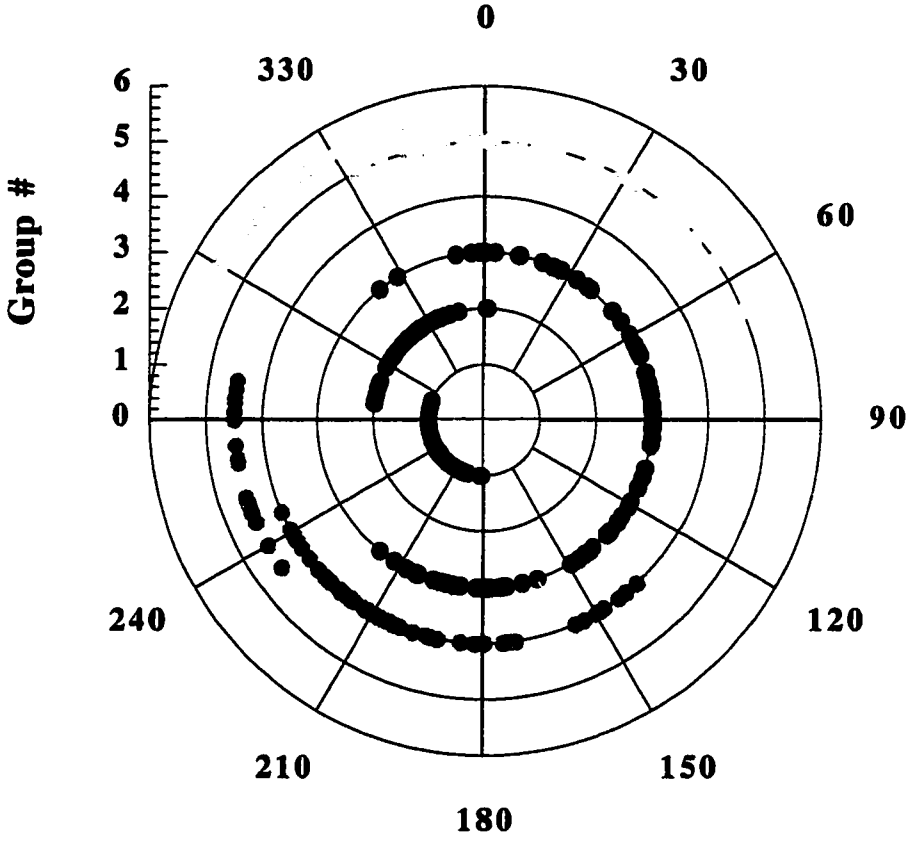

Figure 2.2. Polar plot showing the direction from which air masses arrived at the site at New Castle, NH. Samples were grouped according to air mass direction and chemistry.

map to the next. Then the one or two nearest streamlines to New Castle were followed back to the circumference of the circle. The degrees from north were measured and that direction was assigned to that particular streamline. However, this is not an entirely straightforward procedure as the streamlines are not truly radial. In the cases where the streamline turned 90° between New Castle and the circumference, the streamline was

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followed back to the 90° turn and then the angle was determined from that point. The choice of 1100 km as the radius was arbitrary and no conclusions have been drawn regarding the distance of source regions to our site. This analysis was solely used to determine a general direction from which the air mass was transported to the site.

Typically, a given sample had two streamlines associated with it (although, a few cases had a duration which led to more or less streamlines). The samples were initially sorted according to whether the two streamlines for a given sample came from a relatively consistent location or completely different locations (e.g., easterly flow in one, westerly flow in the other). If the streamlines were from completely different directions or were inconclusive due to the presence of a high or low pressure system directly over the area, these samples were classified as mixed streamlines. In this case, no attempt was made to assign a direction to the air mass origin as there were different air masses being sampled over the duration of the sample. For the cases where the streamlines originated from a similar direction, the azimuth angle of the streamline was determined. The directions for the streamlines associated with a given sample were then averaged and that average was used as the direction from which the sampled air mass came.

The point of this exercise was to determine if air masses of different origins had different chemical signatures. Thus, to establish final groupings for the streamlines, the chemistry was considered and essentially three different chemical groups were found: marine, polluted continental, and clean continental. Here, "clean" is used in its relative sense, i.e., compared to the "polluted" sector. "Clean" refers to an aged air mass without recent emission inputs where various mechanisms (e.g., dilution, oxidation, and deposition) have reduced the mixing ratios of the observed species. However, it is in no way "clean" compared to air parcels in remote locations. At this site, air originating from approximately 180° to 290° azimuth (Figure 2.2) was typically polluted continental air (group 1). Weather conditions that drive this pattern consist of return flow from a high

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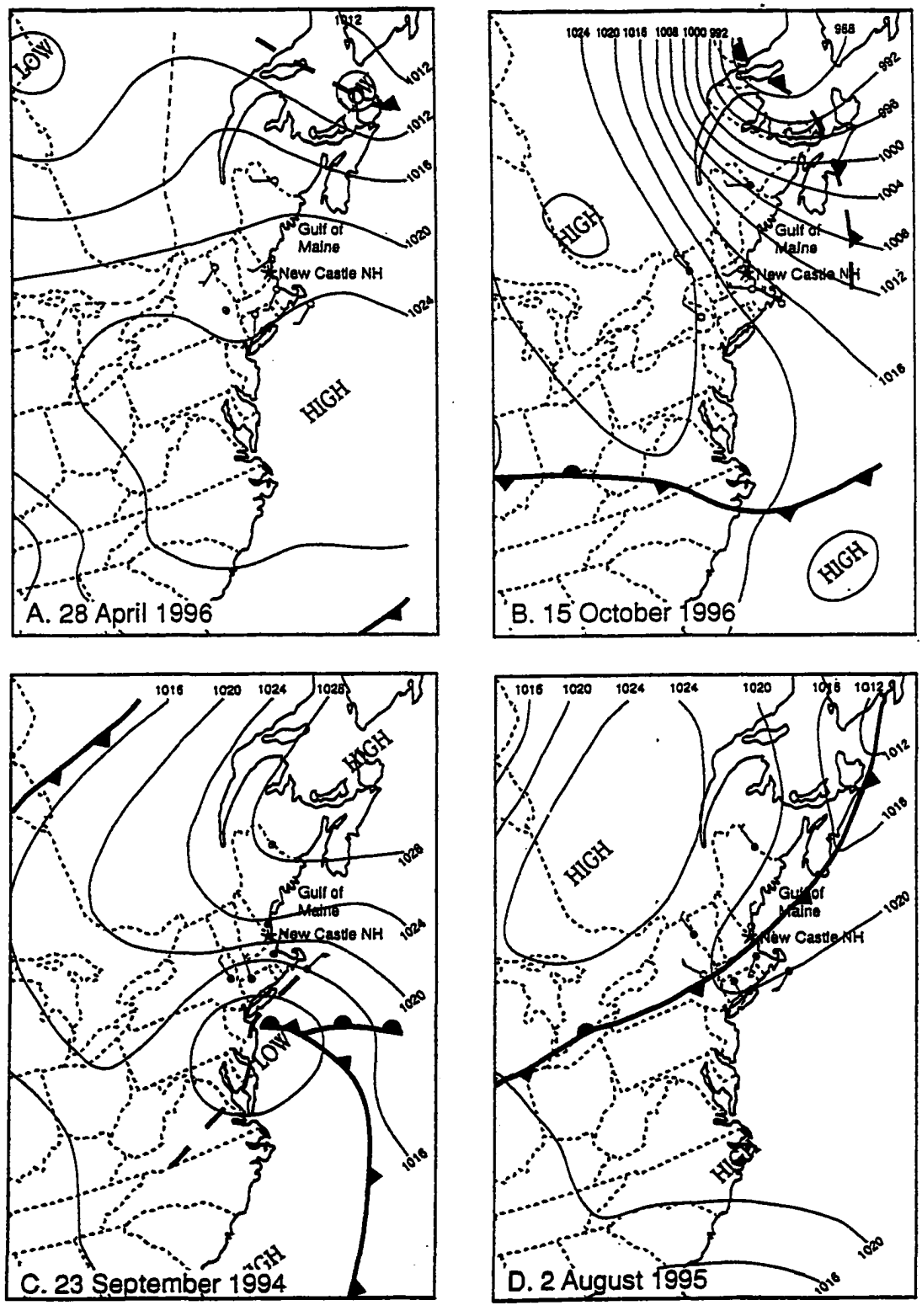

Figure 2.3. Four examples of synoptic weather patterns which lead to surface flow to New Castle, NH from different directions.

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pressure system located in the mid-Atlantic states or just off the East Coast (Figure 2.3a). Clean continental air (group 2) emanates from 290° to 360° which is typically due to high pressure positioned over the Great Lakes or eastern Canada (Figure 2.3b). Marine flow (group 3) from 0° to 180° is usually caused by coastal northeaster conditions along the East Coast (Figure 2.3c). Note, that there is some overlap, though generally marginal, between these groups as seen in Figure 2.2. An unpaired t-test between the means of these groups showed that they are significantly different with p-values <0.0001.

In addition, there were two groups of mixed species. These were typically seen when the streamlines were from two sources, including marine (group 3) and continental (groups 1 or 2). Group 4 is the mixture of groups 1 and 3 and is essentially southerly flow with higher mixing ratios observed than for group 5. Group 5 is a mixture of groups 2 and 3 (northerly flow). Note, in Figure 2.2 groups 4 and 5 were subdivided. Groups 4.5 and 5.5 are mixed cases when the streamlines indicated group 1 or 2, respectively, where local onshore flow probably enhanced sea salt mixing ratios. An unpaired t-test of the mean azimuth angles of these groups showed that these groups are significantly different than the others with p-values <0.0001, with the exception of groups 2 and 5 which had a p-value of 0.1390. Although groups 4 and 4.5 (and 5 and 5.5) were defined differently according to their streamlines, they were analyzed as one group in terms of chemistry since they exhibit the same chemical qualities. Mixed cases are defined as those in which mixing ratios of the sea salt species (Na^+ and Cl^-) and continental species (gas phase HNO_3 and aerosol SO_4^{2-} and NH_4^+) are within a factor of 2 of each other. Otherwise, the sample is considered to be either sea salt or continental dominant.

Finally, the mixed streamline cases were subdivided into three groups depending on the chemical signature: marine dominant (group 6), continental dominant (group 7), or mixed species (group 8). In each of these mixed group cases, either mixed scale interactions are taking place, or a front has passed through the region on the day in question

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(e.g., Figure 2.3d). Hence, the region was exposed to two or more different air masses during the sample period.

Data & Discussion

HNO_3 and Aerosol Average Chemistry for each Group

Using all of the data from 1994 through 1996, HNO_3 and aerosol chemical data were separated according to the streamline classes. The average chemistry for each group was then calculated. Table 2.1 shows the average of each species for each group, the standard deviation, along with the minimum, maximum, and median mixing ratios observed for that species within each group. As reported for the overall data (Chapter 1), there was wide variation in the mixing ratios observed for a species within a given group.

The average chemistry of groups 1 through 8 is shown in Figure 2.4. In groups 1 and 2, polluted and clean continental, respectively, gas-phase HNO_3 and aerosol SO_4^{2-} and NH_4^+ were the dominant species observed. Note the mixing ratios of these dominant species were approximately a factor of 4 lower in group 2 than group 1 (e.g., $NH_4^+ \approx$ 2000 pptv for group 1 versus $\approx$ 500 pptv for group 2). Group 3 (marine flow) was dominated by the sea salts Na^+ and Cl^-. On average, the magnitude of the mixing ratios of the dominant species in group 3 and 1 were about the same ($\approx$2000 pptv for Na^+ and Cl^- in group 3 and NH_4^+ in group 1). Groups 4 and 5 (mixed southerly and northerly flow, respectively) had sea salts and continental species appearing at similar strengths (e.g., Na^+ and $NH_4^+ \approx$ 1200 pptv in group 4 and $\approx$ 340 pptv in group 5). As with groups 2 and 1, mixing ratios of group 5 were approximately a factor of 4 lower than group 4. Groups 6, 7, and 8 were the mixed streamline groups, where no attempt was made to define a direction of origin. These three groups were separated according to their chemical signature, with the sea salts dominant in group 6, the continental species dominant in group 7, and group 8 showing a comparable mixture of sea salts and continental species. This subdivision of the mixed streamline samples was done to evaluate the relative dominance of a particular chemistry over another during the course of the field study.

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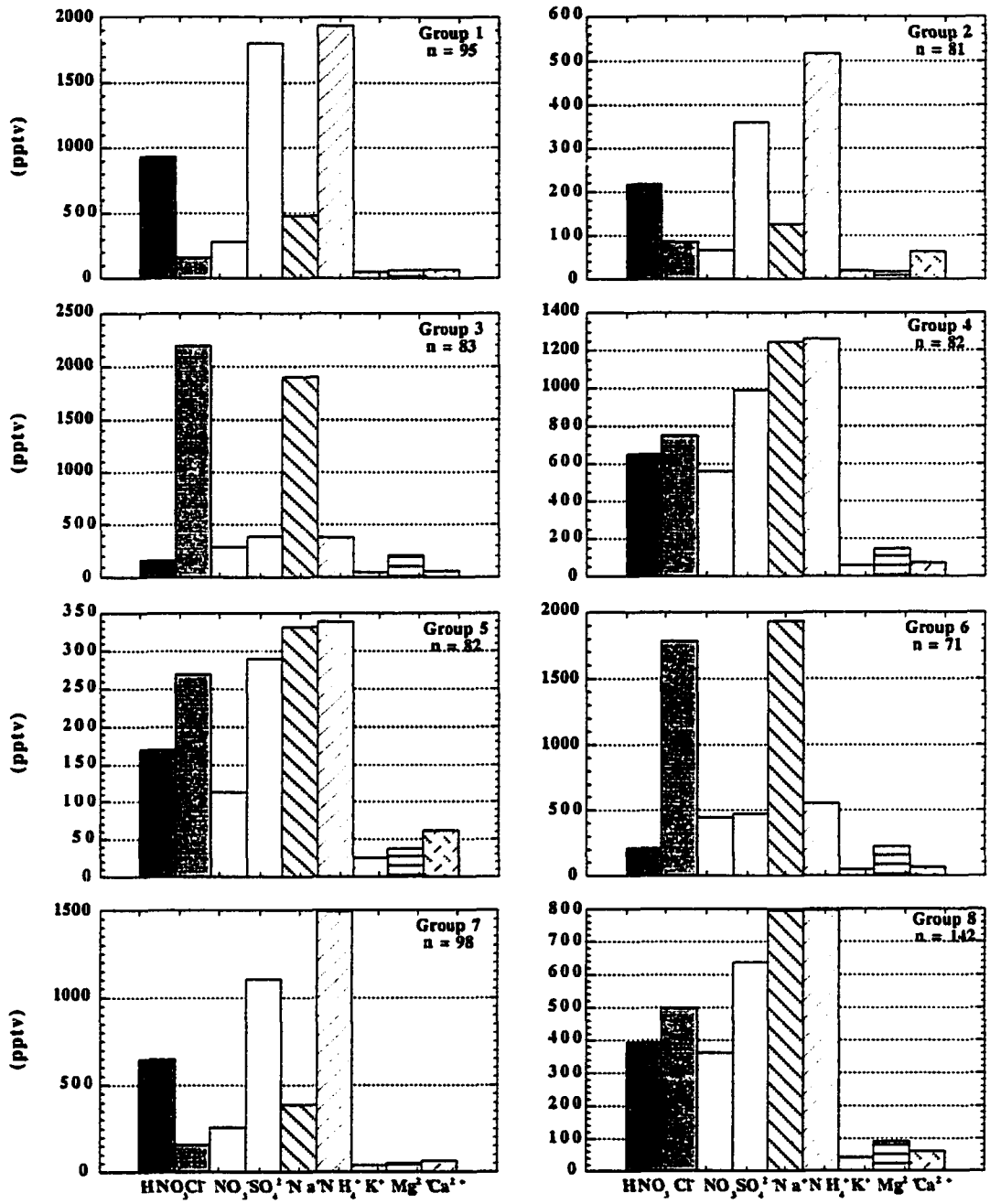

Figure 2.4. Average mixing ratios for HNO3 and eight aerosol species for all samples collected from 1994 - 1996, sorted according to air mass origin and chemistry. Each group has a characteristic chemical signature.

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Table 2.1. 1994-1996 HNO_3 and Aerosol Averages, One Standard Deviation, Ranges, and Medians Sorted According to Group Classification

Grp. #	HNO_3	Cl^-	NO_3^-	SO_4^{2-}	nss-SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
1	931 ± 765	160 ± 167	282 ± 273	1803 ± 1848	1770 ± 1828	484 ± 412	1935 ± 1367	50 ± 34	63 ± 50	69 ± 42
	(95-3559)	(2-889)	(8-1313)	(116-10062)	(113-9935)	(2-1891)	(218-7159)	(6-179)	(0-238)	(6-175)
	667	99	204	1118	1106	434	1584	45	52	64
2	217 ± 154	86 ± 68	67 ± 64	361 ± 211	352 ± 208	127 ± 110	516 ± 314	19 ± 14	17 ± 11	64 ± 61
	(41-765)	(4-337)	(1-345)	(49-860)	(46-841)	(2-506)	(35-1473)	(0-66)	(0-47)	(2-360)
	163	74	43	291	289	98	458	15	15	42
3	158 ± 142	2197 ± 2181	288 ± 281	386 ± 336	275 ± 283	1904 ± 1635	383 ± 299	44 ± 27	208 ± 152	56 ± 44
	(13-774)	(172-13952)	(21-1373)	(34-1943)	(25-1766)	(187-10052)	(59-1252)	(4-154)	(16-775)	(2-307)
	108	1398	179	286	190	1491	272	41	184	49
4	649 ± 457	751 ± 551	558 ± 385	990 ± 698	914 ± 668	1245 ± 854	1264 ± 770	59 ± 50	144 ± 88	72 ± 44
	(96-2057)	(18-2743)	(5-1986)	(74-2986)	(74-2862)	(174-4853)	(134-4000)	(7-398)	(10-368)	(9-214)
	515	602	494	757	697	1065	1095	52	133	68
5	170 ± 124	270 ± 203	114 ± 109	290 ± 211	271 ± 196	332 ± 268	339 ± 228	25 ± 21	37 ± 35	62 ± 119
	(12-765)	(35-946)	(8-583)	(23-1075)	(20-957)	(3-1992)	(0-1180)	(2-140)	(0-222)	(1-1012)
	130	204	86	246	231	263	288	19	29	35
6	209 ± 184	1787 ± 1854	441 ± 506	471 ± 408	352 ± 326	1931 ± 1766	552 ± 564	48 ± 35	223 ± 211	67 ± 61
	(22-1100)	(84-10344)	(33-3258)	(65-2054)	(47-1551)	(293-10897)	(74-3854)	(4-205)	(19-1232)	(6-374)
	153	1032	320	367	271	1527	428	38	164	51
7	648 ± 539	158 ± 172	258 ± 319	1104 ± 964	1078 ± 947	385 ± 366	1494 ± 1312	42 ± 29	51 ± 44	66 ± 67
	(34-2589)	(3-1059)	(1-2249)	(66-5708)	(62-5607)	(8-1768)	(132-7986)	(1-186)	(0-242)	(1-355)
	556	116	140	883	845	276	1139	36	41	50
8	394 ± 332	498 ± 489	362 ± 327	637 ± 558	589 ± 530	796 ± 648	798 ± 670	42 ± 29	91 ± 70	61 ± 45
	(38-2317)	(9-3472)	(19-2102)	(43-3651)	(39-3518)	(70-4029)	(27-4663)	(3-208)	(8-428)	(0-195)
	302	370	253	465	422	651	629	34	76	55

Units in parts per trillion by volume.

Annual Variations in the Chemistry and Occurrence of Groups

As reported previously, widely varying chemistry was observed, not only from day to day, but also from year to year. Tables 2.2, 2.3, and 2.4 are similar to Table 2.1; they show the average, the standard deviation, minimum, maximum, and median mixing ratios for each species for each group for the years 1994, 1995, and 1996, respectively. In 1995, mixing ratios were about a factor of 2 lower than in 1994 or 1996. It was first suspected that the "cleaner" chemistry was due to markedly different transport in 1995 than the other years which brought aged air (i.e., northerly flow) to our site. Although the transport was somewhat different in 1995, a comparison of the mixing ratios for a particular group between the three years still shows 1995 mixing ratios which on average were approximately a factor of 2 lower than those seen in the other years. Precipitation,

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Table 2.2. 1994 HNO_3 and Aerosol Averages, One Standard Deviation, Ranges, and Medians Sorted According to Group Classification

Grp. #	HNO_3	Cl^-	NO_3^-	SO_4^{2-}	nss-SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
1	1215 ± 922	200 ± 212	276 ± 263	2979 ± 2395	2933 ± 2370	649 ± 484	2340 ± 1461	65 ± 26	86 ± 58	80 ± 33
	(107-3559)	(2-889)	(24-1045)	(270-10062)	(263-9935)	(2-1891)	(326-5398)	(28-161)	(8-238)	(21-143)
	934	145	226	2492	2432	624	2208	61	83	79
2	268 ± 207	117 ± 70	71 ± 49	452 ± 206	443 ± 205	142 ± 148	633 ± 389	32 ± 14	18 ± 6	83 ± 38
	(77-765)	(37-286)	(25-192)	(214-796)	(207-782)	(8-506)	(237-1473)	(14-66)	(12-32)	(21-167)
	225	92	43	352	344	84	428	28	15	76
3	223 ± 191	3358 ± 3380	458 ± 415	560 ± 563	449 ± 502	2467 ± 2605	454 ± 424	59 ± 34	207 ± 146	74 ± 70
	(30-774)	(582-13952)	(23-1373)	(115-1943)	(75-1766)	(521-10052)	(62-1252)	(14-154)	(55-611)	(12-307)
	180	2206	263	299	201	1479	230	56	176	54
4	854 ± 551	956 ± 623	534 ± 302	1385 ± 774	1311 ± 749	1297 ± 916	1625 ± 913	88 ± 77	139 ± 69	73 ± 44
	(173-1992)	(64-2743)	(139-1318)	(371-2986)	(330-2862)	(347-4640)	(305-4000)	(23-398)	(21-283)	(17-211)
	725	774	452	1120	1031	1090	1725	76	133	70
5	206 ± 104	411 ± 244	137 ± 117	356 ± 171	334 ± 162	319 ± 178	354 ± 166	39 ± 16	41 ± 23	79 ± 49
	(77-435)	(133-841)	(37-478)	(141-886)	(133-842)	(107-624)	(95-792)	(11-65)	(12-88)	(18-168)
	181	319	97	320	307	314	324	43	37	66
6	187 ± 138	1721 ± 1011	493 ± 320	624 ± 496	524 ± 455	1991 ± 1233	582 ± 364	65 ± 24	188 ± 98	56 ± 26
	(62-527)	(494-3837)	(89-1130)	(243-1636)	(215-1489)	(511-4831)	(222-1429)	(33-112)	(54-393)	(6-87)
	148	1555	380	408	323	1612	513	58	193	58
7	647 ± 551	202 ± 153	229 ± 210	1612 ± 1332	1583 ± 1312	422 ± 402	1800 ± 1762	61 ± 35	54 ± 44	66 ± 46
	(119-2345)	(3-657)	(1-708)	(247-5708)	(234-5607)	(15-1576)	(231-7986)	(25-186)	(8-190)	(3-171)
	520	151	129	1196	1175	321	1218	55	44	57
8	474 ± 481	681 ± 669	396 ± 318	891 ± 737	840 ± 711	850 ± 616	892 ± 642	58 ± 33	96 ± 63	68 ± 44
	(49-2317)	(28-3472)	(19-1309)	(167-3651)	(155-3518)	(94-2694)	(281-2641)	(19-208)	(16-251)	(5-182)
	331	520	265	627	582	710	699	50	79	66

Units in parts per trillion by volume.

temperature, relative humidity, barometric pressure, and wind speed were analyzed to try to find a reason for this behavior, but these have not appeared to explain the variation.

The entire year was not sampled during 1994 and 1995; data extends from May - November, 1994 and from March - December, 1995. Although sampling could have been conducted for all of 1996, a failure of the power line to our site prevented sample collection from November 7 - December 18, 1996. So care must be taken in comparing data too closely from one year to the next. For the entire data set, 1994 -1996, the relative occurrence of each group is shown in Figure 2.5a. Polluted continental air (group 1) occurred slightly more frequently than either the clean continental or marine air (groups 2 and 3), 95 versus 82 and 84 days, respectively. The number of days each group occurred during each year is given in Table 2.5. Polluted continental flow occurred as frequently

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Table 2.3. 1995 HNO_3 and Aerosol Averages, One Standard Deviation, Ranges, and Medians Sorted According to Group Classification

Grp. #	HNO_3	Cl^-	NO_3^-	SO_4^{2-}	nss-SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
1	622 ± 504	101 ± 81	224 ± 213	906 ± 859	886 ± 850	264 ± 247	1481 ± 1294	55 ± 50	37 ± 31	59 ± 55
	(95-1912)	(6-310)	(20-955)	(116-2745)	(113-2706)	(9-904)	(218-4278)	(6-179)	(0-131)	(6-174)
	416	88	174	464	444	171	871	41	34	44
2	136 ± 68	61 ± 51	47 ± 44	200 ± 99	195 ± 97	96 ± 75	305 ± 188	18 ± 12	10 ± 7	25 ± 27
	(41-324)	(4-191)	(1-156)	(49-518)	(46-504)	(3-295)	(35-908)	(4-46)	(0-26)	(4-147)
	121	58	34	176	172	89	243	14	9	21
3	146 ± 127	1197 ± 712	177 ± 119	214 ± 147	144 ± 120	1200 ± 684	277 ± 179	30 ± 16	132 ± 80	34 ± 19
	(20-498)	(172-3355)	(50-551)	(34-646)	(25-485)	(187-2835)	(59-710)	(4-78)	(16-329)	(2-76)
	106	1085	121	158	95	984	218	26	109	26
4	480 ± 419	452 ± 328	468 ± 403	505 ± 345	455 ± 322	822 ± 500	781 ± 453	55 ± 42	98 ± 61	54 ± 39
	(96-2057)	(68-1583)	(39-1986)	(74-1580)	(74-1495)	(185-1944)	(134-2139)	(7-189)	(10-229)	(9-164)
	363	356	437	499	418	721	812	41	111	42
5	103 ± 67	175 ± 134	67 ± 66	181 ± 142	171 ± 134	224 ± 166	227 ± 153	17 ± 12	22 ± 23	60 ± 171
	(12-283)	(35-614)	(8-338)	(23-648)	(20-586)	(3-904)	(0-697)	(2-52)	(0-117)	(1-1012)
	94	125	53	152	138	202	186	14	16	18
6	169 ± 111	1396 ± 1399	343 ± 329	328 ± 235	226 ± 164	1478 ± 1064	439 ± 339	37 ± 26	191 ± 166	55 ± 49
	(22-488)	(84-6907)	(33-1523)	(65-1062)	(47-736)	(293-4915)	(74-1554)	(4-131)	(35-760)	(8-241)
	140	899	304	262	169	1229	372	33	152	40
7	304 ± 245	94 ± 64	127 ± 123	437 ± 340	425 ± 332	183 ± 196	661 ± 499	31 ± 19	26 ± 20	42 ± 43
	(40-1130)	(26-236)	(2-611)	(66-1142)	(62-1126)	(8-706)	(132-1724)	(6-68)	(1-76)	(3-142)
	211	69	107	308	305	122	487	27	20	27
8	239 ± 139	286 ± 270	213 ± 178	311 ± 261	281 ± 240	469 ± 409	468 ± 422	28 ± 21	55 ± 52	35 ± 31
	(53-541)	(9-1387)	(21-638)	(43-1506)	(39-1366)	(72-2033)	(27-2030)	(7-95)	(8-263)	(5-114)
	220	215	132	224	202	309	326	22	36	24

Units in parts per trillion by volume.

(34 d) as clean continental and marine flow combined (33 d) in 1994. While in 1995, both marine (35 d) and clean continental flow (27 d) occurred more frequently than polluted flow (21 d). In 1996, polluted (40 d) and clean continental flow (38 d) occurred a bit more frequently than marine flow (33 d). Considering the mixed flow cases, clean continental (group 2 and group 5) and marine air (group 3) dominated the samples in 1995, while polluted air (group 1 and group 4) dominated in 1994. Clean continental and marine air were also more frequent in 1996, but to a lesser extent than 1995. Thus, there was somewhat different prevailing transport in 1995. However, as noted earlier, this does not account for the lower mixing ratios observed that year as even within a given group, the mixing ratios observed in 1995 were lower (Tables 2.2, 2.3, and 2.4).

The relative occurrence of continental, marine, and mixed chemistry was as

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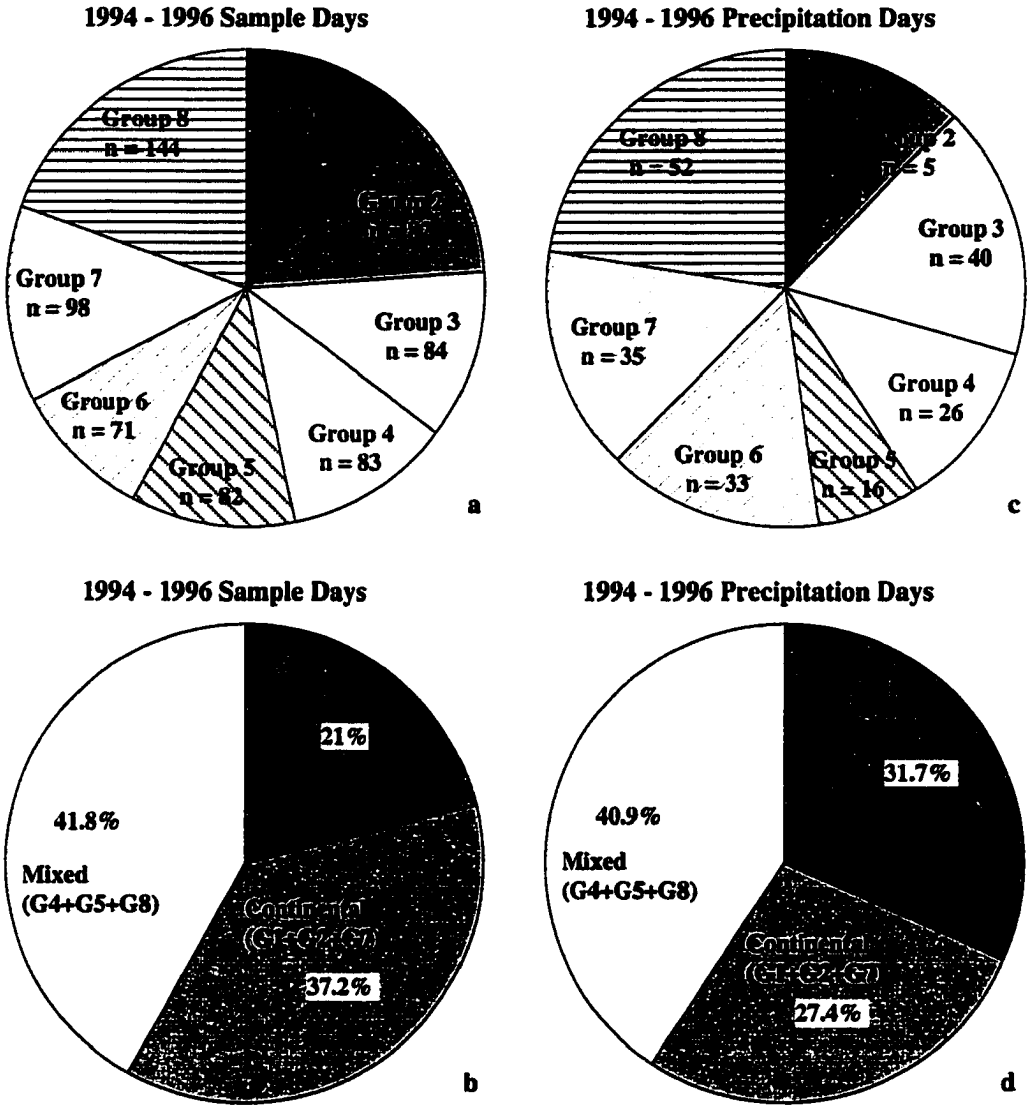

Figure 2.5. Pie charts showing the relative occurrence of the eight chemical groups for all the samples collected and for sample days with precipitation. The overall breakdown of the occurrence of samples dominated by marine species, continental species, or a mixture of both are also shown.

follows: mixed chemistry occurred 42% of the time, followed by continental at 37%, and marine the least frequent at 21%, (Figure 2.5b). In all years, mixed chemistry was observed nearly equally, about 42% of the time (Table 2.5). In addition, all years show that air dominated by continental species occurred more frequently than marine dominated air (Table 2.5). This is to be expected as west is the prevailing wind direction in New

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Table 2.4. 1996 HNO_3 and Aerosol Averages, One Standard Deviation, Ranges, and Medians Sorted According to Group Classification

Grp. #	HNO_3	Cl^-	NO_3^-	SO_4^{2-}	nss-SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
1	860 ± 666	155 ± 148	319 ± 309	1275 ± 1038	1245 ± 1022	454 ± 357	1829 ± 1255	34 ± 24	58 ± 43	64 ± 40
	(216-3245)	(5-561)	(8-1313)	(291-5668)	(268-5561)	(4-1451)	(559-7159)	(6-111)	(6-201)	(6-175)
	586	119	221	939	901	345	1570	28	46	57
2	253 ± 152	90 ± 72	85 ± 83	437 ± 209	426 ± 206	138 ± 105	617 ± 277	15 ± 12	21 ± 14	84 ± 73
	(61-642)	(6-337)	(6-345)	(118-860)	(116-841)	(2-494)	(226-1413)	(0-62)	(1-47)	(2-360)
	198	73	64	370	363	117	546	13	19	77
3	140 ± 124	2709 ± 2098	326 ± 282	487 ± 248	331 ± 190	2394 ± 1518	460 ± 303	52 ± 26	292 ± 173	70 ± 39
	(13-463)	(687-8364)	(21-1174)	(111-1232)	(62-900)	(753-7190)	(77-1240)	(14-131)	(84-775)	(12-168)
	99	2075	253	464	318	2105	388	46	249	65
4	643 ± 381	829 ± 555	631 ± 410	1080 ± 657	986 ± 622	1489 ± 913	1382 ± 712	46 ± 24	177 ± 99	83 ± 43
	(162-1892)	(18-2047)	(5-1924)	(263-2970)	(249-2844)	(174-4853)	(279-2949)	(8-95)	(25-368)	(17-214)
	593	628	614	951	878	1465	1187	48	196	70
5	235 ± 148	312 ± 197	160 ± 126	392 ± 240	365 ± 223	477 ± 345	474 ± 265	27 ± 27	52 ± 45	55 ± 55
	(70-765)	(65-946)	(8-583)	(105-1075)	(97-957)	(88-1992)	(149-1180)	(7-140)	(6-222)	(5-224)
	186	293	123	332	298	391	418	19	38	39
6	259 ± 245	2230 ± 2400	527 ± 685	564 ± 478	421 ± 359	2393 ± 2365	661 ± 773	52 ± 44	270 ± 272	84 ± 78
	(37-1100)	(531-10344)	(64-3258)	(137-2054)	(67-1551)	(561-10897)	(85-3854)	(8-205)	(19-1232)	(9-374)
	218	1147	332	393	299	1581	473	38	188	56
7	888 ± 559	182 ± 219	363 ± 415	1282 ± 763	1248 ± 747	512 ± 382	1895 ± 1163	39 ± 27	64 ± 48	82 ± 84
	(34-2589)	(8-1059)	(8-2249)	(378-3610)	(377-3575)	(72-1768)	(173-5205)	(1-134)	(0-242)	(1-355)
	732	138	190	1153	1109	382	1621	36	52	63
8	468 ± 289	556 ± 438	460 ± 380	743 ± 486	682 ± 455	1024 ± 719	1003 ± 752	41 ± 28	116 ± 76	76 ± 46
	(38-1443)	(64-2975)	(26-2102)	(87-2621)	(82-2393)	(70-4029)	(130-4663)	(3-131)	(8-428)	(0-195)
	386	490	392	620	543	793	819	34	98	73

Units in parts per trillion by volume.

England (U. S. Department of Commerce, 1995). However, the partitioning between these two differ from year to year. For example, continentally dominated air was observed 43% of the time in 1994, compared with 15% for the marine air. In 1995, marine air was dominant 26% of the time compared to 31% for the continental air. In 1996, the continental air was dominant 39% of the time compared with 20% for the marine cases.

Precipitation Average Chemistry for Each Group

Using the same classification scheme developed for the HNO_3 and aerosol data, the precipitation data were sorted according to the group number assigned to the day the sample was collected. The volume-weighted means of the precipitation chemistry were then calculated for each group. These means (Figure 2.6) resembled those of the aerosols. Groups 3 (marine flow) and 6 (mixed streamlines - sea salt) are dominated by the sea salts,

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Table 2.5. Number of Total Days Sampled and Precipitation Days for Each Group and the Percent of Days Classified as Marine, Continental, and Mixed

		1994	1995	1996	1994	1995	1996
		Sample Days (# of days)			*Precipitation Days (# of days)*		
Group 1		34	21	40	11	4	8
Group 2		17	27	38	0	2	3
Group 3		16	35	33	6	12	22
Group 4		21	25	37	6	5	15
Group 5		16	37	29	3	9	4
Group 6		11	31	29	5	13	15
Group 7		24	30	44	10	11	14
Group 8		36	47	61	10	20	22
		Sample Days (%)			*Precipitation Days (%)*		
Marine	(G3+G6)	15	26	20	22	33	36
Continental	(G1+G2+G7)	43	31	39	41	22	24
Mixed	(G4+G5+G8)	42	43	41	37	45	40

Na^+ and Cl^-. These groups had the most rainfall of all eight groups, 72.4 and 39.3 cm, respectively. Groups 4 (mixed southerly flow) and 8 (mixed streamlines - mixed) are mixed, as expected, with sea salts and continental species appearing at similar strengths. Groups 1 (polluted continental) and 7 (mixed streamlines - continental) both were dominated by continental species, but not by as large a margin as were the aerosols. Groups 2 (clean continental) and 5 (mixed northerly flow) however, did not exhibit the same behavior as the aerosols. Both of these groups had the fewest events and least amount of rainfall contributing to them, 4 events for a total of 1.6 cm of rain for Group 2 and 13 events for a total of 4.6 cm of rain for Group 5. Group 2 showed fairly evenly mixed continental species and sea salts, with the exception of NO_3^-. This is due to unusually high NO_3^- from one of the 4 events, and is likely an artifact of averaging over so few events. Group 5 was dominated by continental species rather than being mixed as in the aerosol case. Note, NO_3^- is more prevalent in precipitation than aerosols, frequently exceeding both NH_4^+ and SO_4^{2-}. This is probably due to efficient scavenging of gas phase HNO_3 and coarse fraction particulate NO_3^-.

In general, precipitation occurs under frontal conditions, where opposing air masses meet, with denser colder air forcing warmer lighter air aloft. One such example

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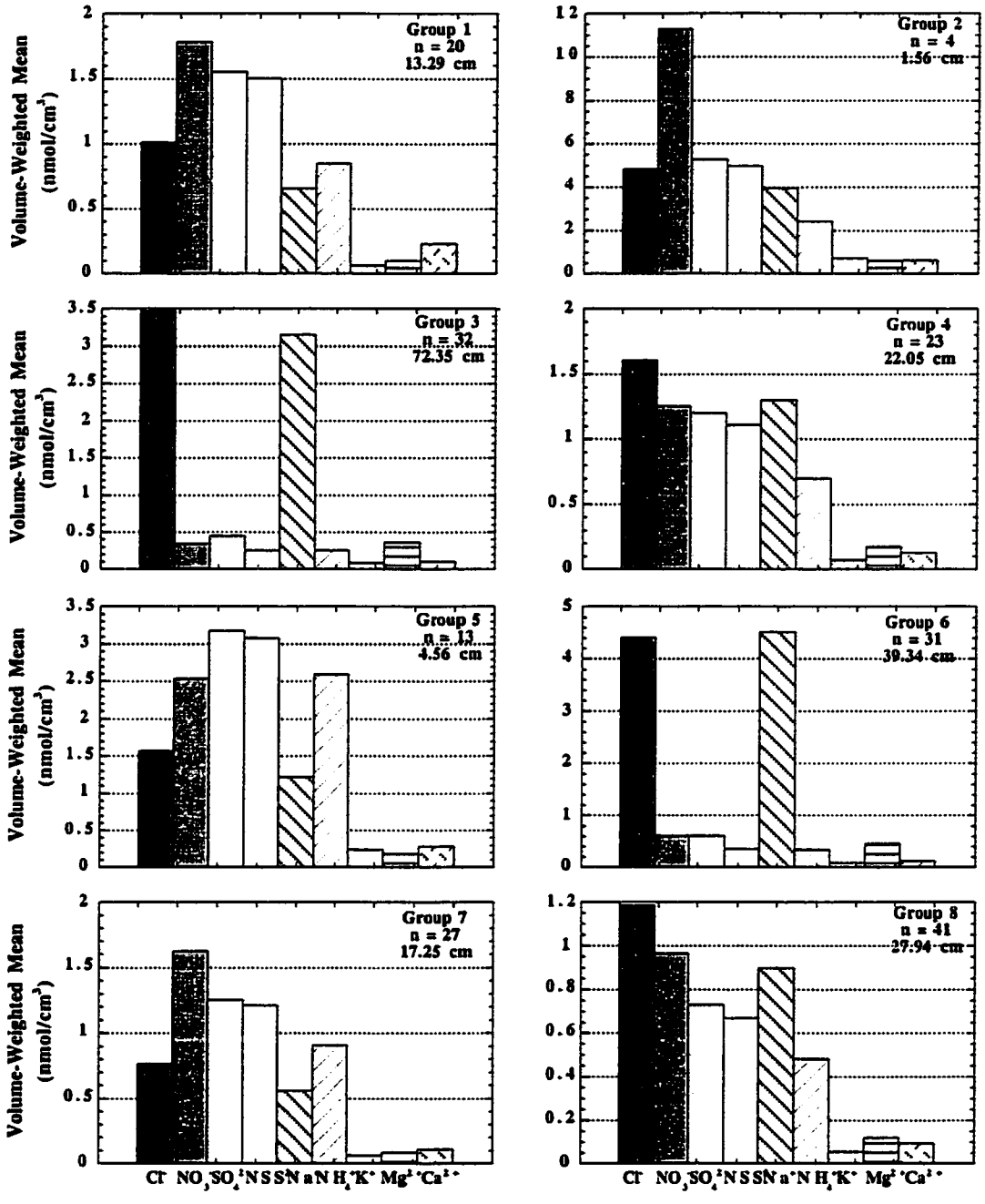

Figure 2.6. Volume-weighted means of precipitation samples collected from 1994 - 1996, sorted according to the group classification of their sample days.

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includes a cold continental air mass at the surface being lifted and overrun by warm marine air along a cold frontal boundary. Another example would include a northeaster, where a cold marine air mass is present at the surface which is overrun by warm marine air along a warm frontal boundary. In the former case, the balance between continental and marine species scavenged and deposited in precipitation is determined by the distance of the sampling site from the front and by the relative depth of the warm and cold layers over the site through which the precipitation passes. This leads to the difference observed between the average precipitation chemistry versus the average aerosol chemistry for a given group, i.e., the continental species are not as dominant in precipitation as they are in aerosols for any of the groups. The latter case of two marine air masses leads to the strong dominance of the sea salts Na^+ and Cl^- seen for groups 3 and 6. Here, an offshore low pressure system brings rain onshore, with minimal influence from continental air.

Occurrence of Each Precipitation Group

The occurrence of precipitation during these types of patterns was also investigated. On average, over the entire data set, precipitation was most likely to occur during marine flow, group 3, and least likely to occur during clean continental flow, group 2, (Figure 2.7). This makes sense in view of the synoptic meteorology of the Gulf of Maine area. Rain brought in on northeasterly winds is typically due to an offshore northeaster (Figure 2.3c). Whereas, rain coming from a low pressure system to the west of the site will include a stronger component of south or southeasterly winds, and typically do not include northerly or northwesterly winds. Rain occurred on nearly 50% of the days classified as group 3, while for group 2, rain only occurred on about 5% of those days. Precipitation was unlikely for groups 2 and 5 due to weather conditions in which a high pressure system builds into New England from Canada or from over the Great Lakes, bringing static stability to the site. Northerly flow experienced the fewest rain days (groups 2 and 5), southerly flow produced rain on about 24% (group 1) and 30% (group 4) of those days, and about 47% of the marine dominant (group 3) days had rain (Figure 2.7). A pie chart of

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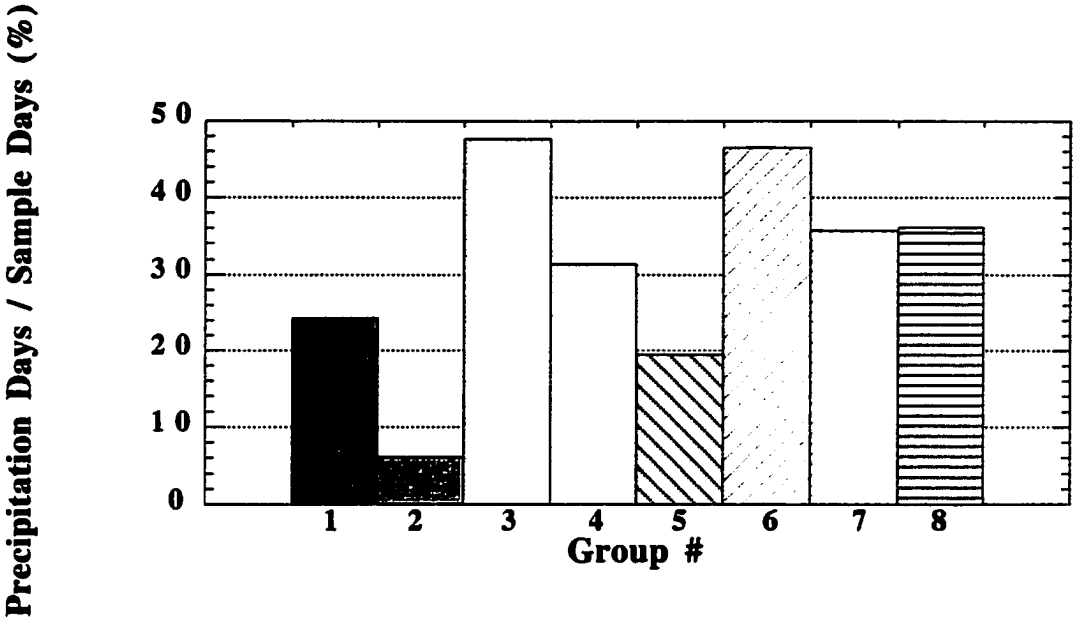

Figure 2.7. The likelihood that a given flow pattern produces rain. Here, nearly 50% of the days classified as groups 3 and 6 had precipitation, while only about 5% of the group 2 days produced rain.

how much each group contributed to the total days of rain (Figure 2.5c), shows a very different distribution than for the sample days (Figure 2.5a). Here, marine flow (group 3) dominated continental flow (groups 1 and 2), with very few occurrences of rain from the clean continental sector (group 2). This was also true in both 1995 and 1996 (Table 2.5), but not in 1994. Group 2 produced no rain in the 1994 samples, however, group 1 produced more rain days than any of the other groups that year. Mixed northerly flow (group 5) produced less rain than mixed southerly flow (group 4) in both 1994 and 1996, but not in 1995. In 1994 and 1996, the mixed streamline days (groups 6, 7, and 8) yielded about 50% of the rain days, but in 1995, they accounted for slightly more of the rain days, about 58%.

In general, including mixed streamline cases, more rain was produced in marine than continental air, except for 1994, and mixed air produced the most rain in 1995 and 1996 (Table 2.5). Over the whole data set (Figure 2.5d), mixed air produced 41% of the rain days, marine air 32%, and continental 27%. The year 1994 was anomalous with continental air yielding 41% of rain days, mixed air 37%, and marine air 22%. The years

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1995 and 1996 had 45% and 40%, respectively, of their rain occurring on mixed days, 33% and 35% on marine days, and 22% and 24% on continental days (Table 2.5).

Fog Chemistry

Fog sampling was conducted only at the end of the field program. Commencing in July 1996 and ending in May 1998, 36 samples were collected during 8 fog events. Unfortunately, unlike other years where fog was frequent, during this period of time, fog was particularly infrequent. Only two of the events sampled occurred in 1996, for the remaining 6, there are no streamlines available. However, the chemistry observed fits in well with the trends in aerosols and precipitation. Three fog events were dominated by sea salt Na^+ and Cl^-, 1 June 1997, 29 August 1997, and 14 September 1997. Four events were dominated by continental species, 25 July 1996, 8 August 1996, 16 April 1998 and 4 May 1998. One event was mixed, 2 September 1997. The chemical signature of a marine fog event is shown in Figure 2.8a. The concentrations of Na^+ and Cl^- are nearly an order of magnitude greater (≈ 1500 μmol/L) than the third most concentrated species, SO_4^{2-} (≈ 150 μmol/L). Two different chemical signatures are shown for continentally dominated fogs in Figure 2.8b and 2.8c. In one type of continental fog (Figure 2.8b), NO_3^- was the dominant species (≈ 1600 μmol/L), more than twice that of NH_4^+ (≈ 700 μmol/L) and nearly eight times greater than Na^+ and Cl^- (≈ 200 and 250 μmol/L, respectively). In the other (Figure 2.8c), NH_4^+ and SO_4^{2-} are the most concentrated species (≈ 750 and 500 μmol/L, respectively). The difference between these two is likely due to the presence of HNO_3 in the precursor air mass. If there is a substantial amount of HNO_3, NO_3^- will likely be the dominant species due to the high solubility of this gas phase species. If there is relatively little HNO_3, then NH_4^+ and SO_4^{2-} will dominate the continental signature given their prevalence in aerosol form. Finally, a fog event with a mixed signature is shown in Figure 2.8d. Here, NH_4^+, Na^+, NO_3^-, and Cl^- all appear at comparable concentrations.

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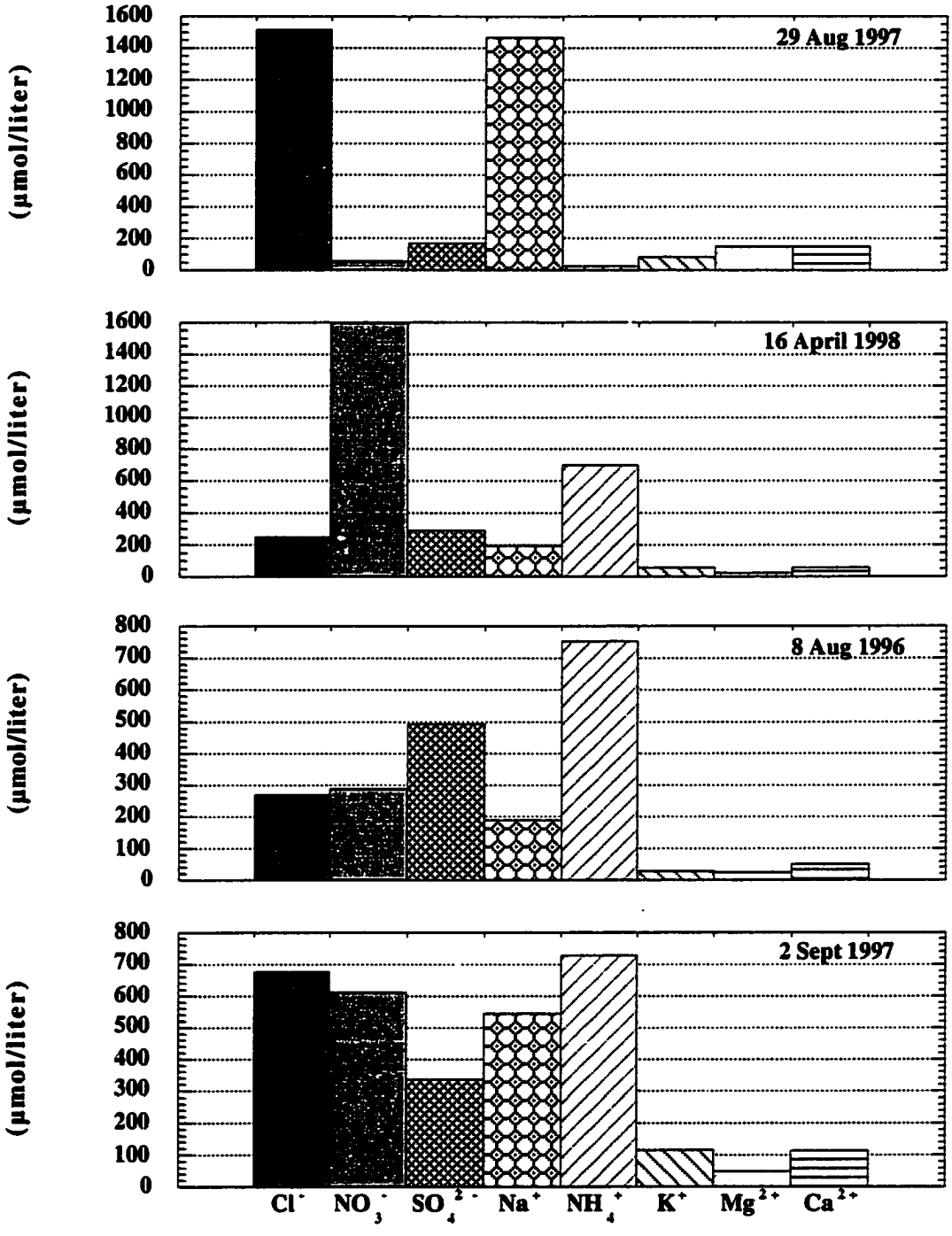

Figure 2.8. Four examples of fog water chemistry. Sea salt dominant (a), continental dominant (b and c), and mixed (d) cases are shown.

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Seasonal Comparisons

There was nearly a complete year of data in 1996 for the aerosols, HNO_3, and precipitation. Note, winter of 1996 also includes a few days at the end of 1995 (from 22 December onward). Unfortunately, due to a power failure, about a month of fall 1996 data was missed. Therefore, care must be taken in evaluating Table 2.6 which shows the percentage of the occurrence of each group during the four seasons of that year.

Table 2.6. Percent of Days Each Group Occurred During the Four Seasons of 1996

	Winter	Spring	Summer	Fall
Group 1	3	36	33	28
Group 2	28	39	10	23
Group 3	21	33	24	21
Group 4	23	34	34	9
Group 5	63	14	17	6
Group 6	24	24	35	17
Group 7	25	23	39	14
Group 8	28	28	34	10

Nonetheless, 1996 may be used to illustrate seasonal variability. Polluted continental flow (group 1) rarely occurred in winter, only 3% of all group 1 days occurred in winter. Clean continental flow (group 2) occurred least frequently (10%) in summer. Marine flow (group 3) occurred nearly evenly throughout 1996. Both the mixed northerly flow (group 5) and mixed southerly flow (group 4) were least likely to occur in the fall, 6% and 9%, respectively. Mixed northerly flow (group 5) appeared most often in winter, 63% of the group 5 days. While this pattern may not hold every year, given annual variations, it does give a sense of the extent of seasonal variation possible between groups.

Aerosol Size Distributions

The nature of the impactor samples precluded the determination of the aerosol size distribution for each group. The impactor was typically operated over three days to ensure measurable quantities were collected on the middle stages. Over this period of time, several weather patterns would typically bring varying air masses to the site. Two short samples (33 and 30 hrs) were collected which fortuitously were a classic marine and polluted

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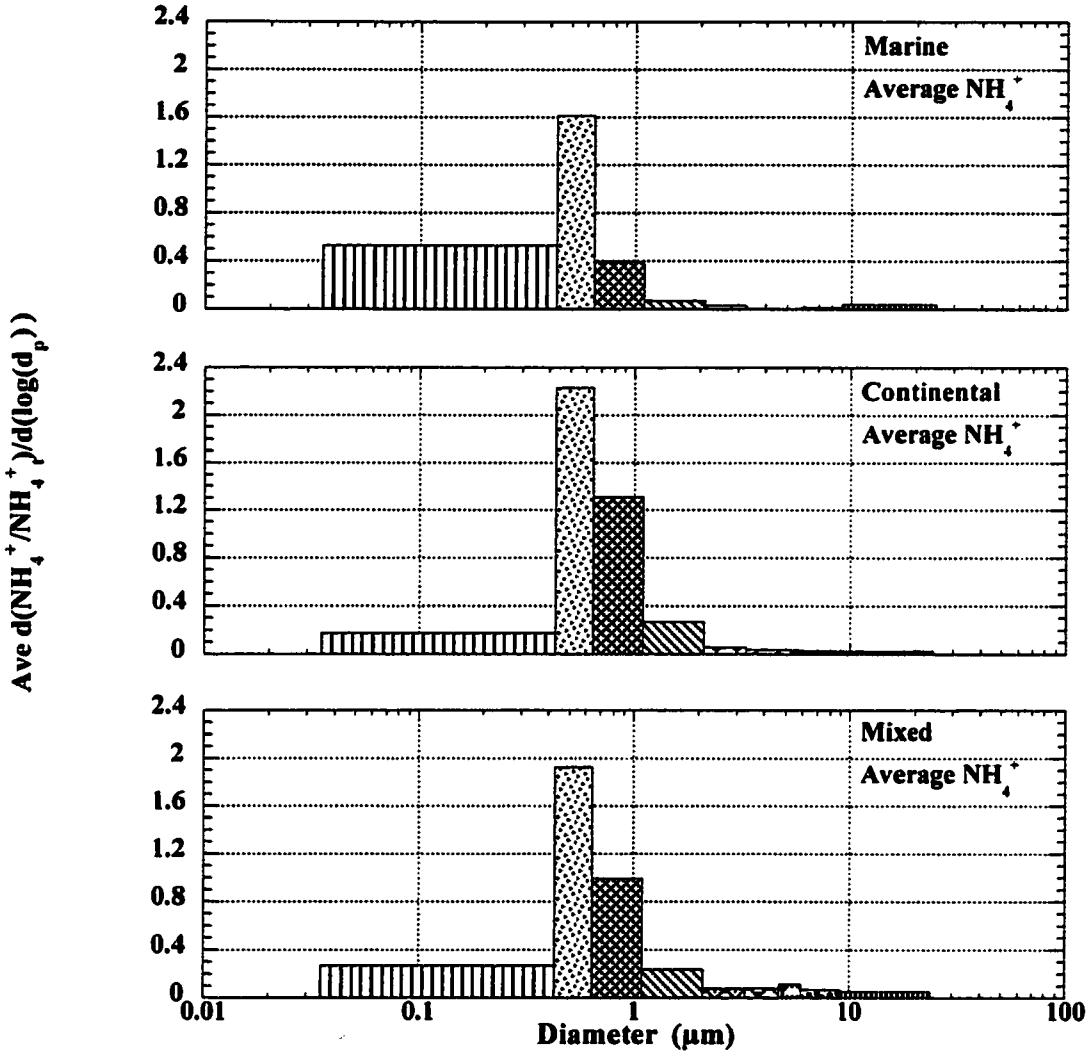

Figure 2.9. Average NH_4^+ size distributions for three types of air masses, marine dominant, continental dominant, and mixed. These distributions are normalized both for the total amount of the sample collected and for the width of the size fraction.

continental air mass, respectively. The ambient mixing ratios were high enough during these two events, that all of the impactor stages had measurable quantities of all species sampled. The remaining impactor samples had mixed streamlines, with the bulk of the samples being mixed species (13). However, there were 4 cases of sea salt dominant air masses and 3 cases of continental dominant air masses sampled. The samples collected for each of these three groups were averaged to yield a typical size distribution for that group.

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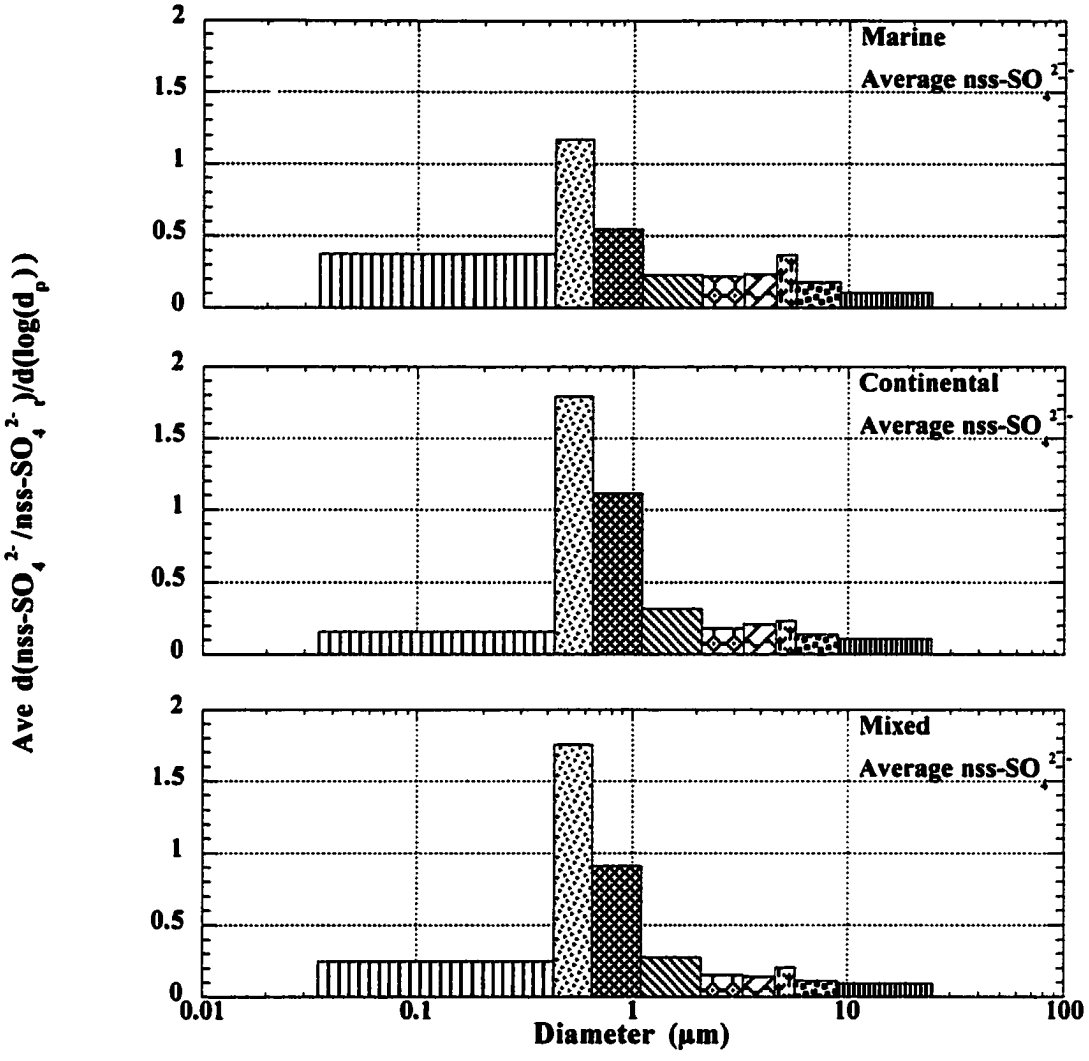

Figure 2.10. Average nss-SO_4^{2-} size distributions for three types of air masses, marine dominant, continental dominant, and mixed. These distributions are normalized both for the total amount of the sample collected and for the width of the size fraction.

There was variation between all of the chemical species size distributions collected. However, there were certain properties typical of the marine, continental, and mixed groups. Figures 2.9-2.14 show the size distributions of selected chemical species for each of these three types. Note, the mixing ratio of a given species for each size cut of a sample was normalized to the total collected for that sample to minimize bias towards highly concentrated samples. Further, the width of each size bin was normalized.

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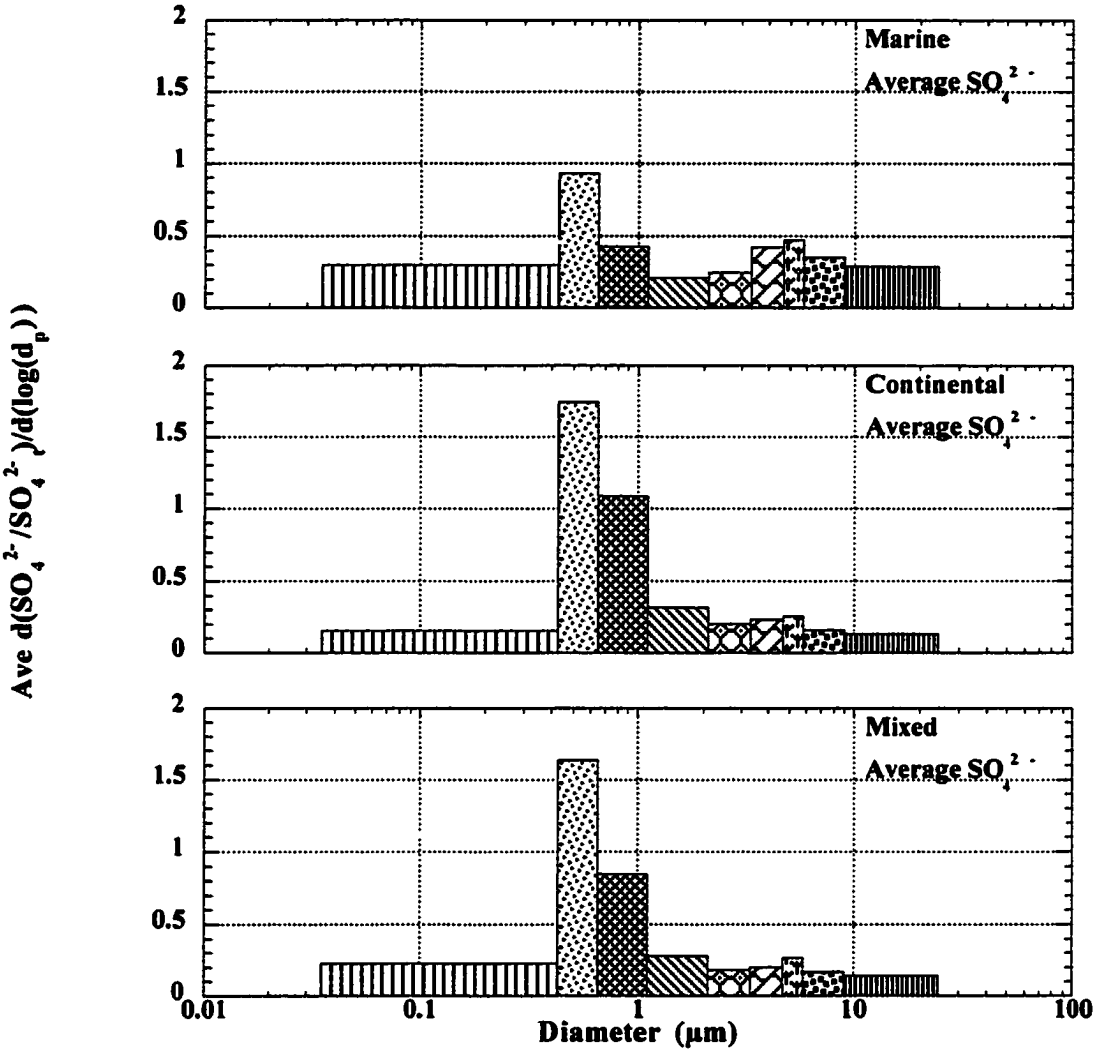

Figure 2.11. Average total SO_4^{2-} size distributions for three types of air masses, marine dominant, continental dominant, and mixed. These distributions are normalized both for the total amount of the sample collected and for the width of the size fraction.

The nitrogen species, NO_3^- and NH_4^+ are of particular interest due to their nutrient input potential for the Gulf of Maine. Beginning with the NH_4^+ (Figure 2.9), for all three cases, most of the NH_4^+ (84% - 94%) present was in the submicron (<1 μm diameter) fraction. Very little NH_4^+ (6% - 16%) appeared in the supermicron (>1 μm diameter) stages. The average marine size distribution, shows that the NH_4^+ was enhanced in the smallest size fraction (< 0.43 μm diameter) relative to the average continental and mixed

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cases (20% vs. 4% and 7%, respectively). The average continental NH_4^+ size distribution shows the greatest amount (85%) in the 0.43 - 1.1 μm range. In this size range, NH_4^+ seems to be associated with non-sea-salt SO_4^{2-} (Figure 2.10). For the non-sea-salt fraction of SO_4^{2-}, there was an appreciable amount in the supermicron size range. This was true for all three averages, with the supermicon fraction constituting 39% of the total for the marine case, 28% for the continental case, and 25% for the mixed case. However, most of the non-sea-salt SO_4^{2-} was in the submicron fraction, with a peak from 0.43 - 1.1 μm, just as in NH_4^+. This is not surprising, as there was an excess of acidic species observed at our site (Chapter 1). As $(NH_4)_2SO_4$ is formed via gas to particle conversion and is quite stable in the atmosphere (Bassett and Seinfeld, 1984), it was anticipated these two ions would have similar size distributions. Total SO_4^{2-} (Figure 2.11) had a similar size distribution to that of nss-SO_4^{2-}, but with the course fraction enhanced. This was especially true of the marine case, where there was a distinct bimodal distribution of the SO_4^{2-} with both a submicron and supermicron peak. The supermicron peak diminishes substantially in comparison to the submicron peak for continental and mixed cases.

NO_3^- had a very different distribution (Figure 2.12) than NH_4^+. This species was predominantly on the course fraction of the aerosol in all three cases, peaking at about 4 μm. In all three cases, there was also an enhancement in submicron NO_3^- in the 0.43 - 0.65 size fraction. In the continental case, the submicron enhancement was a substantial secondary peak, where the three smallest size bins contributed 20% of the total NO_3^-, compared to 9% for both the marine and mixed averages.

NO_3^- in the supermicron mode appears to be associated with Na^+ (Figure 2.13). The average marine size distribution of Na^+ showed the strongest peak in the 5.8 - 9.0 μm size range, while the other two cases have a peak shifted to slightly smaller sizes. In all three cases, the peak tapered off slowly with decreasing diameter. The continental case showed the slowest decrease through these sizes. Similarly Cl^-, another sea salt, was predominantly distributed among the supermicron size fractions (Figure 2.14). Here,

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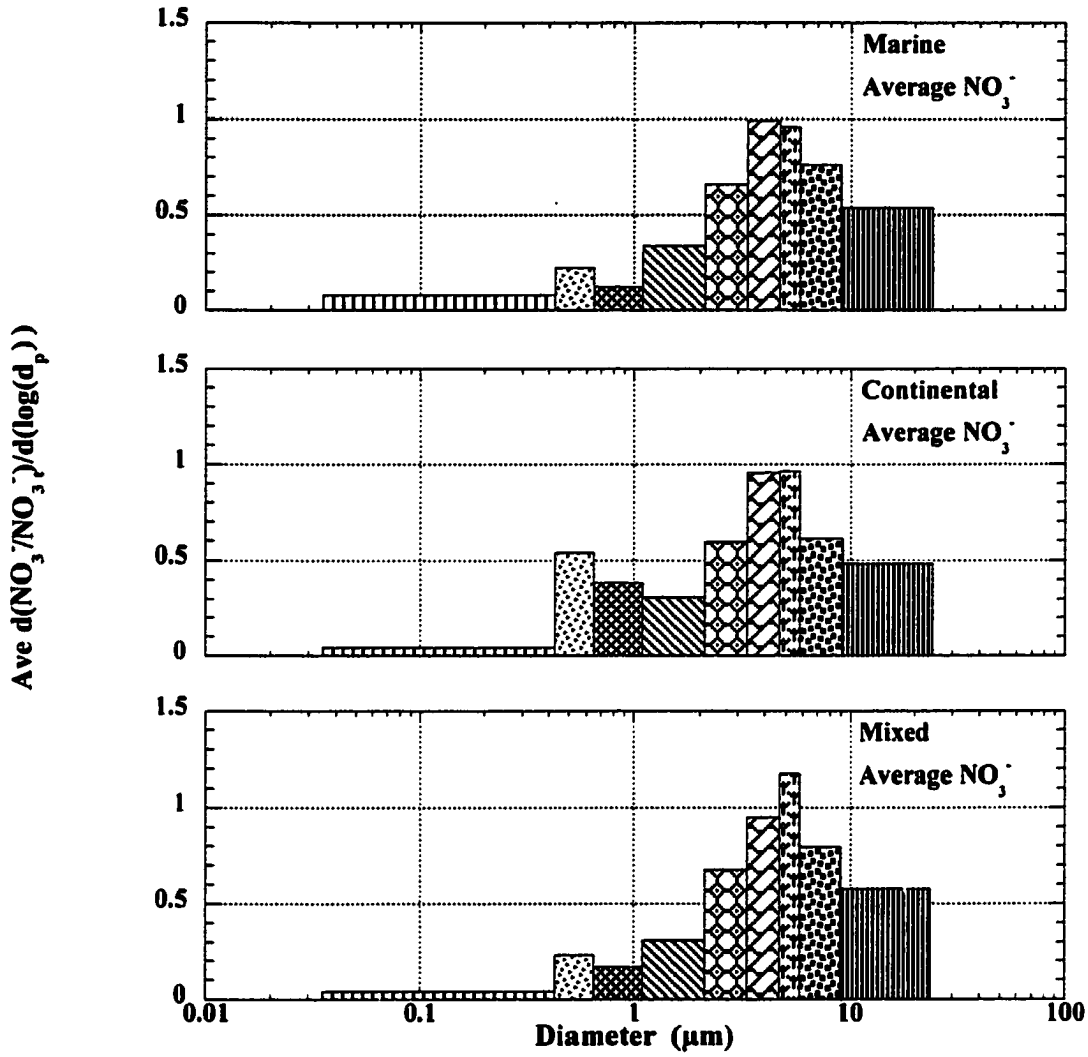

Figure 2.12. Average NO_3^- size distributions for three types of air masses, marine dominant, continental dominant, and mixed. These distributions are normalized both for the total amount of the sample collected and for the width of the size fraction.

however, there was a small but distinct secondary peak in the submicron fraction 0.43 - 0.65 μm for the continental case. This secondary peak did not exist in the marine case, and may reflect NH_4Cl formed over continental areas from NH_3 and anthropogenic HCl emissions.

As mentioned previously, various mechanisms have been proposed to explain the loss of Cl^- from sea salt particles. Some of these mechanisms result in particulate $NaNO_3$,

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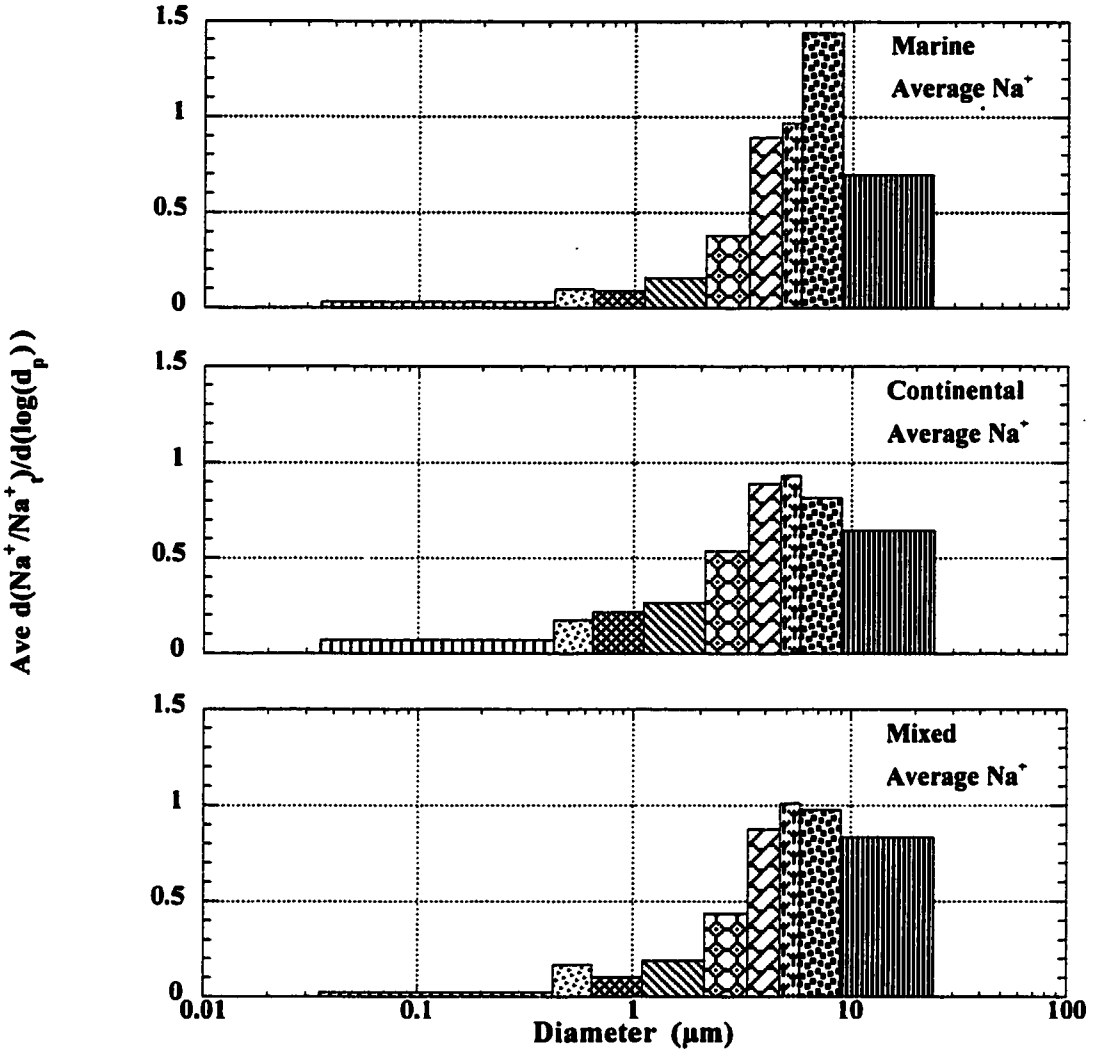

Figure 2.13. Average Na^+ size distributions for three types of air masses, marine dominant, continental dominant, and mixed. These distributions are normalized both for the total amount of the sample collected and for the width of the size fraction.

which explains why NO_3^- is found on the larger particles in the impactor samples. Looking at the Cl^- depletion relative to Na^+ given the expected sea salt ratio of Cl^- to Na^+ of 1.16 (Keene et al., 1986; Wilson, 1975) the greatest depletion was from the 1.1 - 3.3 μm and the 9.0 - 25 μm particles (Figure 2.15). This is similar to the results of Pakkanen (1996) where nearly all of the Cl^- in the 1 - 2 μm range had been driven off. Note, the amount of Cl^- depletion was a function of the air mass origin as well as particle size.

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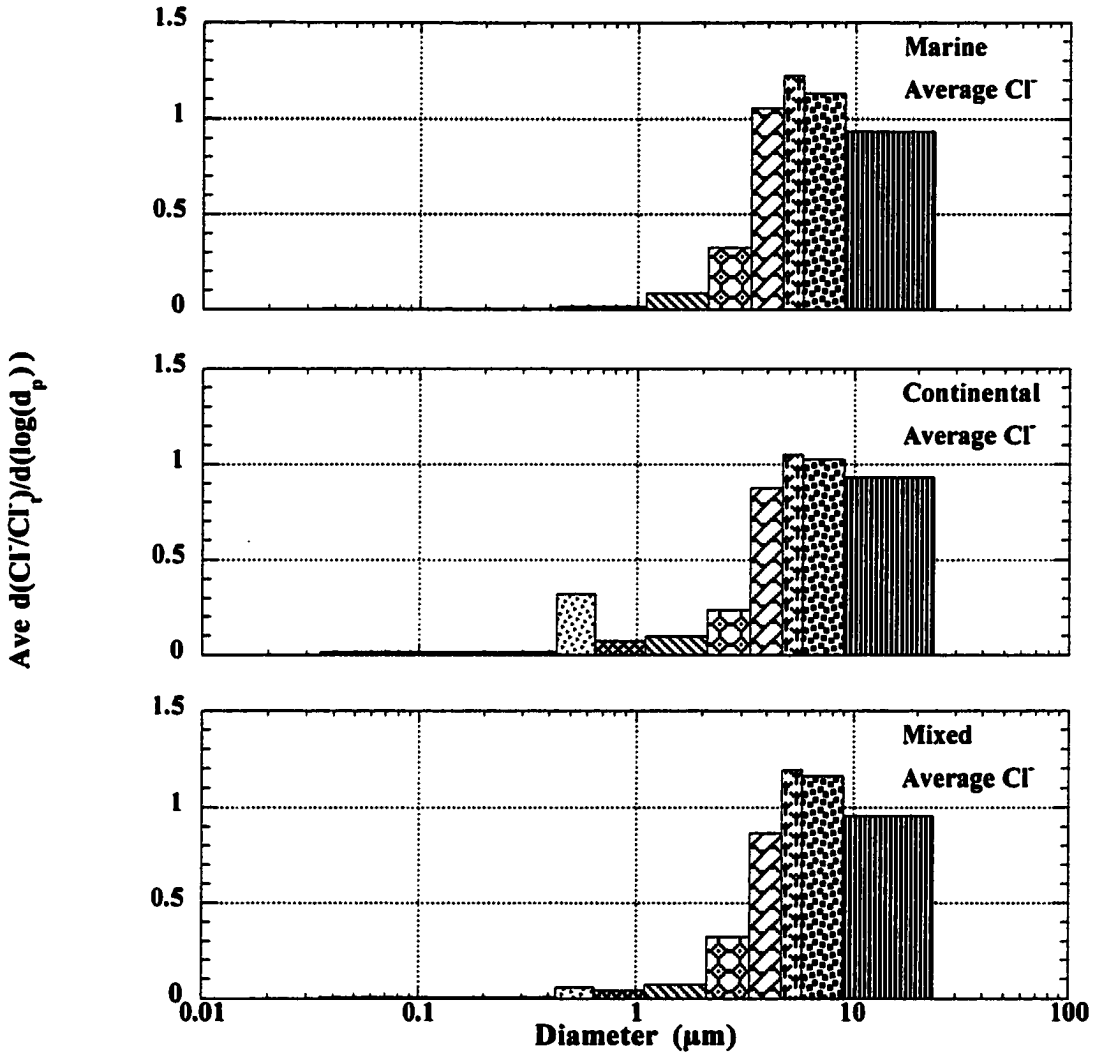

Figure 2.14. Average Cl^- size distributions for three types of air masses, marine dominant, continental dominant, and mixed. These distributions are normalized both for the total amount of the sample collected and for the width of the size fraction.

Group 3 (marine aerosols) showed very little depletion, with a linear regression of Cl^- (neq/m^3) = 3.256 + 1.157 * Na^+ (neq/m^3) with $R^2 = 0.471$. Whereas, group 1 aerosols showed the greatest depletion with a linear regression of Cl^- (neq/m^3) = 4.047 + 0.143 * Na^+ (neq/m^3) with $R^2 = 0.15$. As indicated by the R^2 values there is a lot of scatter in the data. Nonetheless, except for the two marine groups (3 and 6), all of the other groups showed Cl^- to Na^+ ratios which were less than half that of sea water. Thus the processes

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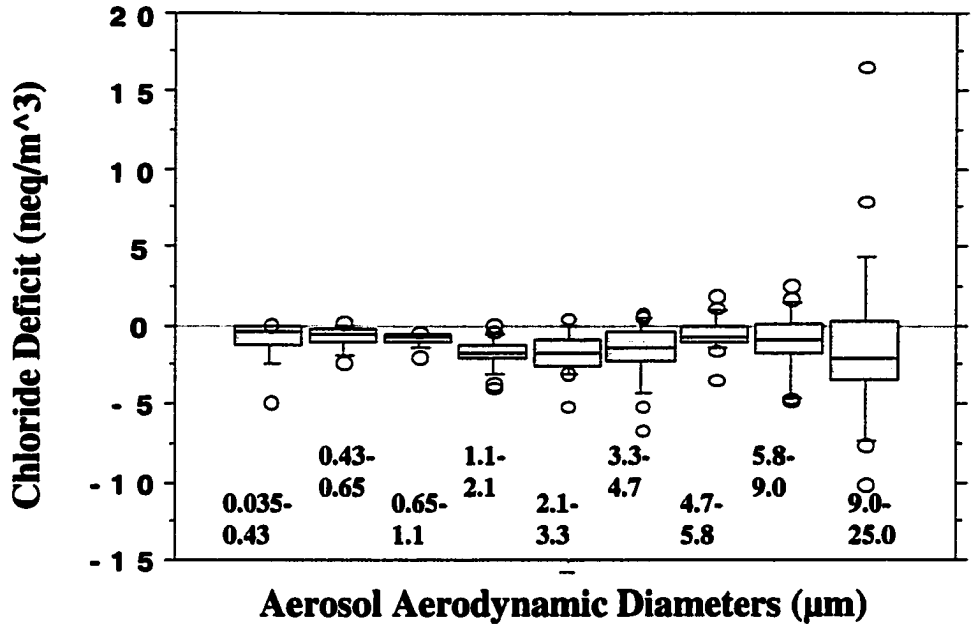

Figure 2.15. Box plot of the observed Cl^- deficit for all size distribution samples (n=20). The deficit is generally greatest for particles with an aerodynamic diameter of 1.1 - 3.3 µm and 9.0 - 25.0 µm.

which lead to the Cl^-deficit are clearly important here.

Summary

In this paper the chemical signature of various air masses sampled at New Castle, New Hampshire has been described. Using air parcel streamlines applied to each sample, it was possible to assign an origin to the air masses sampled. The combined streamline and chemical data were sorted into 8 characteristic groups: 1 - polluted continental air masses originating from approximately 180° - 290° azimuth; 2 - clean continental air from 290° - 360°; 3 - marine air from 0° - 180°; 4 - mixed species, southerly flow; 5 - mixed species, northerly flow; 6 - mixed streamlines, sea salt dominant chemistry; 7 - mixed streamlines, continental dominant chemistry; and 8 - mixed streamlines, mixed chemistry.

Highly variable mixing ratios were observed from day to day as well as from year to year. The lower mixing ratios observed in 1995 could not be attributed to annual

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differences in the general transport outlined here, as even within a given group, the average values were roughly a factor of two lower in 1995. Over the entire sampling period, polluted conditions occurred slightly more frequently than either clean or marine conditions. Including the mixed streamlines, mixed conditions occurred 42% of the time, while continental and marine dominant days occurred 37% and 21% of the time, respectively, over the entire study. Note, these percentages may be slightly biased as all four seasons were not sampled equally over the three years reported here. Given the observations from 1996, where polluted flow was least likely in winter and clean continental flow was least likely in summer, these overall percentages may have been somewhat different had all four seasons been equally represented.

Precipitation chemical signatures for the eight groups were similar to those of the aerosols. Although, in general, NO_3^- was enhanced relative to the other continental species, since precipitation NO_3^- is a combination of scavenged gas-phase HNO_3 and particulate NO_3^-. Rain was most likely to occur under sea salt dominant conditions (about 47% of days for both groups 3 and 6 had precipitation) and least likely to occur during clean continental flow (about 5% of group 2 days had precipitation). Overall 41% of the rain days occurred when mixed species were prevalent (indicative of a frontal passage), 32% and 27% for marine and continental dominant conditions, respectively.

Fog chemistry was a reflection of the chemistry of its precursor air mass. While there were too few samples and insufficient streamline information to classify the fog data into the eight groups, the chemical signatures observed all fit in with the three general categorizations of marine, continental, and mixed. As seen in the precipitation data, in continental and mixed fogs NO_3^- is enhanced relative to the other continental species observed in the aerosol signatures, since it is a combination of both gas-phase HNO_3 and particulate NO_3^-.

Finally, the size distribution data were averaged according to whether marine or continental species were dominant or whether there was a relatively even mixture of both.

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NH_4^+ was observed to be associated with nss-SO_4^{2-} and was primarily found on submicron particles. Total SO_4^{2-} showed a bimodal distribution in the marine case, with the submicron fraction the primary peak and the supermicron fraction the secondary peak. This secondary peak nearly disappeared in comparison to the submicron peak under continental and mixed conditions, when nss-SO_4^{2-} constitutes the bulk of the total SO_4^{2-}. Even nss-SO_4^{2-} was seen to have a substantial coarse mode fraction in all three cases, ranging from 25% - 39% of the total. NO_3^- was primarily found in the supermicron fraction, associated with Na^+. Although, there was also submicron NO_3^- for all three cases, with a distinct secondary peak for the continental case (20% of the total compared to 9% for the other two cases). Cl^- was mostly on supermicron particles in all three cases, but the continental case showed a small submicron peak. The Cl^- deficit, was found to be greatest for particles 1.1 - 3.3 μm and 9.0 - 25 μm in diameter.

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CHAPTER 3

DIRECT ATMOSPHERIC DEPOSITION OF WATER-SOLUBLE NITROGEN TO THE GULF OF MAINE

Abstract

Measurements were made at New Castle, New Hampshire, on the shore of the Gulf of Maine from 1994 - 1997 to assess direct atmospheric deposition of water-soluble nitrogen to the surface waters of the Gulf. Daily dry deposition was highly variable and ranged from about 1 - 144 μmol N m^{-2} d^{-1} (median 16 μmol N m^{-2} d^{-1}). Wet deposition dominated dry deposition, contributing 80 - 90% of the total flux annually. Wet deposition was also highly variable and ranged from 3 - 4264 μmol N m^{-2} d^{-1} (median 214 μmol N m^{-2} d^{-1}). Fog water nitrogen deposition could contribute as much as large precipitation nitrogen deposition events, in excess of 500 μmol N m^{-2} d^{-1}. Dissolved organic nitrogen (DON) in precipitation constituted only a small fraction (3%) of the total precipitation nitrogen flux most of the year, except in spring where it comprised 14%, on average, of the total. The total atmospheric direct nitrogen (ADN) deposition numbers reported here do not include the contributions of fog and DON as they were not sampled regularly over the course of this study. The total ADN flux ranged from 1 - 4262 μmol N m^{-2} d^{-1} (median 23 μmol N m^{-2} d^{-1}), depositing 52 mmol N m^{-2} yr^{-1} to the surface waters of the Gulf of Maine, 3% of the total N input to those waters annually. However, this deposition was highly episodic with events over 500 μmol N m^{-2} d^{-1} occurring in 8% of the days sampled, but contributing 56% of the total measured flux and events in excess of 1000 μmol N m^{-2} d^{-1} occurring in 2% of the samples and contributing 22% of the total measured flux. It is these large events which may influence biological productivity of the Gulf of Maine. The annual wet deposition of inorganic N measured at New Castle exceeded that reported by two NADP sites by 43% on average of that reported from Cape

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Cod, Massachusetts, and by 70% of that at Mt. Dessert Island, Maine. Estimates of the episodic atmospheric nitrogen flux to the surface waters of the Gulf of Maine suggest large deposition events could be sufficient to support substantial chlorophyll *a* production, especially under calm conditions.

Introduction

Atmospheric nitrogen deposition has been suggested to play a role in the eutrophication of coastal ecosystems, the primary productivity in oligotrophic surface waters of oceans, and the increasing occurrence of toxic and non-toxic algal blooms. This nitrogen can be deposited to aquatic ecosystems either directly or indirectly (via deposition to a watershed and subsequent downstream transport). Indirect atmospheric nitrogen deposition to watersheds has been suggested to contribute to eutrophication of coastal waters by several authors (e.g., Peierls et al., 1991; Jaworski et al., 1997; and Howarth et al., 1996). Ten watersheds in the northeastern United States have been reported to have nitrate fluxes which increased 3 - 8 fold since 1900 as nitrogen oxide emissions increased 5 fold over this period (Jaworski et al., 1997). An analysis of the watersheds which flow into the North Atlantic found that although the Amazon contributed the largest fraction of nitrogen per year (3.3 Tg/yr of 13.1 Tg/yr), the largest nitrogen fluxes on a per area basis came from the most disturbed watersheds around the North Sea, northwestern Europe, and northeastern United States (Howarth et al., 1996). Howarth et al. (1996) also report that atmospheric deposition of nitrogen, primarily of industrial origin, is the major control over nitrogen export in some areas, such as the northeastern United States.

Direct atmospheric nitrogen deposition to various coastal and oceanic areas has been reported by some authors to have negligible importance on biological productivity (e.g., Knap et al., 1986; Michaels et al., 1993) and by others to have a significant role (e.g., Paerl, 1985, 1993, 1995; Glover et al., 1988; and Owens et al., 1992; Zhang and Liu, 1994). Comparison of atmospheric deposition with riverine flux of nitrogen to the Yellow Sea showed that atmospheric deposition may have an equal or greater influence on the

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productivity of this region than the riverine flux (Zhang and Liu, 1994). Paerl (1995) reported that contributions of atmospheric nitrogen deposition to total external nitrogen loading ranged from 10% to over 50%. Nanomolar changes in nitrate concentration led to high productivity in the surface waters of the Sargasso Sea (Glover et al., 1988). A nine year record of atmospheric nitrogen deposition to the Sargasso Sea found that episodic events could contribute an important proportion of new production (Owens et al., 1992). Atmospheric nitrogen deposition has also been suggested to play a role in toxic and non-toxic algal blooms worldwide (Paerl, 1993, 1995; Zhang, 1994; Zhang and Liu, 1994). These blooms have been increasing worldwide in frequency, size, geographic extent, and species complexity (Shumway, 1990; Smayda, 1990; and Pelley, 1998).

This study estimates the direct atmospheric nitrogen deposition to the Gulf of Maine, a coastal marine ecosystem downwind of substantial anthropogenic nitrogen sources to the atmosphere (Saeger et al., 1989; Parrish et al., 1993; Chapter 1, this work). The Gulf of Maine is essentially an inland sea with the exchange of water between it and the Atlantic far more restricted than its shoreline would suggest (Figure 3.1). This is due to Browns Bank, Georges Bank, and Nantucket Shoals effectively isolating the Gulf from the Atlantic below 100 m (Brooks and Townsend, 1989; Townsend, 1991; 1998). Between Browns and Georges Bank lies the Northeast Channel, through which nutrient rich slope water can enter the Gulf from the Atlantic. This slope water is one of the main sources of nitrogen to the surface waters of the Gulf of Maine (Schlitz and Cohen, 1984; Townsend, 1998). The Gulf is subject to strong tidal mixing, particularly in the eastern portion and in the Bay of Fundy. This tidal forcing is primarily responsible for mixing the nutrient rich deep water into the surface waters thereby elevating the concentrations of nitrogen. It is also partly responsible for driving the coastal current, which then transports the nitrogen down along the coast to the western and central Gulf (Brooks and Townsend, 1989; Townsend, 1991; 1998). Following the spring bloom, the nitrogen supply is severely depleted in the surface waters of the western Gulf due to vertical stratification of the water

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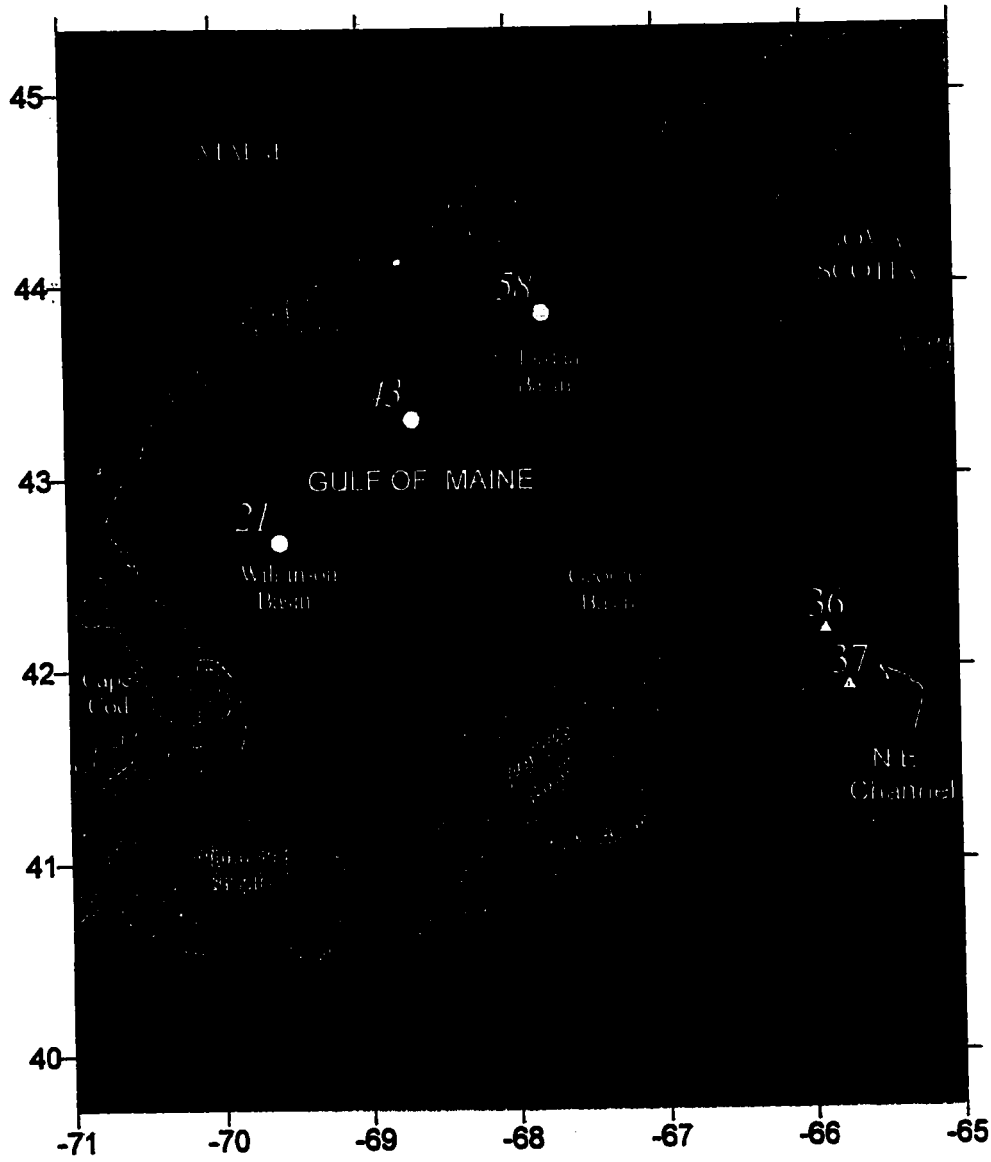

Figure 3.1. Map of the Gulf of Maine showing the banks which isolate the Gulf from the Atlantic and the three basins (from Townsend, 1998).

column. During the warm months of the year, both NO_3^- and NH_4^+ concentrations are < 1.0 μM in these surface waters (Martorano, 1997; T. Loder, personal communication, 1998).

The daily direct atmospheric nitrogen deposition from mid-1994 through 1997 has been estimated to assess the atmospheric contribution to the nitrogen budget in the Gulf of Maine. Annually, the atmospheric component is minor compared to upwelling of nutrient

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rich deep ocean water, contributing only a small fraction of the total new nitrogen flux to the Gulf each year (about 3%, this work and Townsend, 1998). However, atmospheric deposition is highly variable with daily deposition values ranging over 3 orders of magnitude. Deposition events of 500 μmol m^{-2} or more occurred only 8% of the time, but deposited 56% of the total nitrogen over the span of our measurements. Deposition events of 1000 μmol m^{-2} occurred only 2% of the time, yet contributed 22% of the total nitrogen deposited. There is no seasonal pattern in these deposition events. However, the events which occur during the period when the surface waters of the Gulf are stratified and isolated from the nutrient rich deeper waters (May through September, Bub, 1997) may be an important mechanism for delivering nitrogen to the surface waters. This direct atmospheric N deposition may be important on an event basis and sufficient to support substantial chlorophyll *a* production.

Methods

Data

Measurements were made on the shore of the Gulf of Maine at the Portsmouth Harbor Coast Guard Station in New Castle, NH. These measurements included daily (24 hour averages) bulk aerosol and HNO_3 samples, event based precipitation samples, 20 aerosol size distribution (cascade impactor) samples, and 36 fog water samples. Various meteorological parameters were also measured and saved as hourly averages. Samples were initially collected from May through November of 1994, then starting in March of 1995 sampling continued through November 1997. An overview of this data set and a complete discussion of the methods used are presented in Chapters 1 and 2.

On average, errors for the bulk aerosol were $NO_3^- = \pm 5\%$ and $NH_4^+ = \pm 4\%$, and for the gas phase $HNO_3 = \pm 5\%$ (Chapter 1). The size distribution data were collected on a series of 10 filters, so the error analysis was carried out for each filter. Results were remarkably similar, with $NO_3^- = \pm 5\%$ and $NH_4^+ = \pm 5\%$ on most stages, with the other few either ±4% or ±6%. The experimental error for the precipitation and fog concentration

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data is solely a function of the analytical uncertainty. The precision of the analytical method was ±3% and our comparisons to the National Institute of Standards and Technology (NIST) standards are ±1%.

The organic nitrogen sampling protocol has not been described in the previous chapters, so it will be presented here. Dissolved organic nitrogen (DON) in precipitation samples is unstable, with losses approaching 100% within a few hours of collection (Scudlark et al., 1998). These losses are minimized by freezing the sample during collection and keeping it stored at dry ice temperatures until the sample may be analyzed (Scudlark et al., 1998). Using samplers designed at the University of Virginia - Charlottesville (UVA), and following the sampling protocol described by Southwell (1997), 22 precipitation samples were collected from 17 events from July 1997 through June 1998. Two liter polyethylene bottles and funnels were prepared for use in the field by washing with Liqui-Nox soap, followed by an HCl rinse, then repeated rinsing with DI water. Washed funnels and bottles were stored in a clean room until their use. Sample bottles were placed in modified styrofoam coolers packed with dry ice, such that the top of the bottle extended about 5 cm through a hole cut in the lid of the cooler. A funnel was attached to the top of the bottle at the sampling site. Samplers were put out within an hour of the start of a rain event and retrieved within a few hours of the end of the event such that there was still plenty of dry ice in the cooler to keep the sample frozen. Samples were stored on dry ice until they were shipped overnight to UVA for analysis. Samples were analyzed for total N, NO_3^-, NO_2^-, and NH_4^+. The difference between the measured total N and the three inorganic species is defined as DON. DON ranged from < 1 μM N to 16 μM N.

Dry Deposition

Two models were used to estimate dry deposition velocities, one for gas phase HNO_3 and the other for aerosol particles. HNO_3 deposition velocities were calculated using Valigura's bulk exchange model (1995). This model assumes the HNO_3 flux is

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unidirectional, i.e., it deposits to the surface and is not re-emitted from it. Further, given the high solubility of HNO_3, dry deposition to a water surface can be simplified as the quasi-boundary layer resistance is negligible compared to the aerodynamic resistance (R_a) even in very light wind conditions. Thus, the HNO_3 flux may be approximated as follows:

$$F = ([HNO_3]_o - [HNO_3]_z)/R_a$$

where $[HNO_3]_o$ = HNO_3 concentration at the surface

$[HNO_3]_z$ = HNO_3 concentration at height z

Assuming the concentration of HNO_3 at the surface is zero (it all deposits), the flux may be written:

$$F = V_d[HNO_3]_z$$

where the deposition velocity (V_d in m/s) is the inverse of the aerodynamic resistance. The air/water exchange of sensible heat is also controlled by the aerodynamic resistance ($R_{a,H}$). Assuming $R_a = R_{a,H}$, the deposition velocity can be written in terms of the heat transfer coefficient, which in turn is determined from bulk exchange equations.

$$V_d = 1/R_{a,H} = D_H u_z$$

where D_H = dimensionless heat transfer coefficient

u_z = wind speed at height z

For a thorough discussion of bulk transfer equations see Valigura (1995), Hicks (1975), and Liu and Schwab (1987). The advantage of this approach is that the deposition velocity may be estimated from four readily measured parameters: wind speed, relative humidity, and air and sea surface temperatures. Valigura (1995) anticipates that this method underestimates the deposition velocity somewhat since the assumption of equivalent transfer rates for heat and HNO_3 does not account for scavenging of $HNO_3$by aerosol particles or water droplets, which would enhance the deposition rates. He also notes that the conditions required by the assumptions of the bulk transfer equations may be violated under very low wind speeds (e.g., < 2 m/s).

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Hourly wind speed, air and water temperatures were obtained from NOAA buoy 44007 (43° 31' N 70° 8' W, near Portland, Maine). None of the Gulf of Maine buoys have dew point data, so relative humidity recorded at our tower site was used. These hourly meteorological parameters were used to calculate the HNO_3 deposition velocity. The hourly deposition velocities were then averaged over the sample interval (typically 24 hours) to get an average deposition velocity for each HNO_3 measurement. The HNO_3 flux was determined by multiplying the measured mixing ratio by the average deposition velocity as well as the period of each sample to obtain flux in $\mu mol\ m^{-2}$. Note, the wind speed averaged over the sample interval was < 2 m/s in only 2% of the samples.

Aerosol particle deposition velocities were calculated using the Williams (1982) model. This model uses a similar formalism to the Valigura (1995) model which considers dry deposition in terms of resistances and bulk transfer equations. In this model, Williams (1982) incorporates the effects of spray formation in high winds, increased gravitational settling due to particle growth in the high humidity near the air/water interface, as well as the variation of turbulent transfer with wind speed, air/water temperature difference, and surface roughness. The processes involving spray formation and particle growth near the air/water interface both enhance the dry deposition such that wind speed and particle size were found to be the most important parameters in determining the particulate deposition velocities (Williams, 1982). Thus, these are the input parameters used here. For a thorough discussion of the equations used, see Williams (1982).

The wind speed averaged over each chemical sampling interval was input to the Williams model along with 9 particle diameters, representing the mid-point of each size fraction measured by a Graseby-Anderson cascade impactor to determine the deposition velocity for each particle size. All of the chemical measurements were classified into three categories: marine, continental, and mixed (Chapter 2). Impactor samples for each of these three cases were averaged together to arrive at a "typical" size distribution for each

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classification. These size distributions were used to calculate the percent of the bulk measurement of each species present in each size fraction.

Occasionally, there were gaps in either the meteorological or buoy data when we had chemical data. To obtain the most complete deposition record possible, data from either buoy IOSN3 (42° 58' N 70° 37' W, Isle of Shoals, New Hampshire) or from the weather record at Pease International Tradeport Airport (43° 4' N 70° 43' W, Portsmouth, New Hampshire) were used to fill gaps. A linear regression was used to find a relationship between Pease RH (relative humidity, calculated from dew point, air temperature, and station pressure) and New Castle RH,

$$\text{New Castle RH} = 16.867 + 0.904*\text{Pease RH}, \qquad R^2 = 0.708$$

This relationship was used to approximate the relative humidity at New Castle when those data were absent. For times when wind speed was missing from the 44007 buoy records, IOSN3 buoy data was used to fill the gaps. Again a linear regression was applied to find a relationship between 44007 and IOSN3 wind speeds,

$$\text{44007 W. Sp.} = 0.669 + 0.646*\text{IOSN3 W. Sp.}, \qquad R^2 = 0.572$$

This is not a strong correlation, but it is preferable to having a data gap. By filling in the missing ancillary data in this way, the temporal coverage of the dry deposition calculations was improved from 30% to 48% of 1994, 60% to 70% of 1995, 72% to 86% of 1996, and 41% to 85% of 1997. Note, the large discrepancy in 1997 was due to a period extending over several months during which no wind speed was available from buoy 44007.

Wet Deposition

Inorganic N Species. Wet deposition of nitrogen is a straightforward calculation where the concentrations of NO_3^- and NH_4^+ (μmol L^{-1}) are multiplied by the rainfall amount for an event (cm) to arrive at the flux in μmol m^{-2}. The NO_3^- and NH_4^+ fluxes are summed to get the total N wet deposition for an event.

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Dissolved Organic Nitrogen. Globally, DON in precipitation has been found to range from 7 - 37 μM (Scudlark et al., 1998; Southwell, 1997). While there is no apparent geopgraphical pattern (Scudlark et al., 1998), there is a seasonal pattern with more DON observed in the warmer months (Southwell, 1997). Twenty two precipitation samples from 17 events from July 1997 to June 1998 were collected to assess the contribution of DON to the total nitrogen deposited via rain. Throughout most of the year, DON is frequently ≤ 1.0 μM N, contributing on average 3% of the total nitrogen in precipitation when it was detectable (0.9 μM volume-weighted mean). However, in the spring, there was a peak in DON with a volume weighted mean of about 3.9 μM. At this time of year, DON contributed, on average, 14% of the total nitrogen in precipitation. These results are similar to those reported in Virginia (Southwell, 1997), where DON was found to comprise <2.5 - 23% of the total N in precipitation with a mean of 9.8%. Due to this seasonal variability and the limited number of samples, DON has not been included in the total N deposition numbers. This is of little importance throughout most of the year, although in spring, this leads to a slight underestimate of the deposition. In terms of biological productivity in the Gulf of Maine, it may not matter, as it is still unclear whether DON is available for phytoplankton production.

Fog Deposition

To determine the amount of nitrogen deposited via fog, the deposition of fog water ($g\ m^{-2}\ s^{-1}$) using Arp's (1995) equation was calculated, based on the Unsworth-Crossley (1987) equation:

$$D_{fw} = W\ \{v_s + k^2\mu/\ln(z/z_0)\}$$

where, W = liquid water content (g/m^3)

v_s = sedimentation velocity(m/s)

k = von Karman's constant (= 0.41)

μ = wind speed (m/s) at z

z = reference height (m)

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z_o = roughness length (m)

Here, we used Arp's values for the following:

$v_s = 0.0213$ m/s

$\mu = 8.6$ m/s (wind speed at the top of fog banks)

$z = 224$ m (height of fog banks)

$z_o = 0.01$ m

We used our own measured W. Nitrogen deposition (μmol m^{-2} s^{-1}) via fog is then calculated by:

$$D_N = D_{fw} (C_N/r_w)$$

where, D_{fw} = fog water deposition (g m^{-2} s^{-1})

C_N = concentration of N species in fog water (μmol/m^3)

r_w = density of water (g/m^3)

Liquid water content was determined from the weight of the fog water sample (g) divided by the volume of air pulled through the Global Geochem Mesh Sampler (Hering et al., 1987), corrected for the amount of water lost in the instrument (i.e., stuck to the mesh or the sides of the sampler). The fog sampling protocol is described in detail in Chapter 2.

Results

Dry Deposition

Daily dry deposition values for all years of the sampling program are shown in Figure 3.2. Note the data gap late in 1996 was due to a power failure at the site during which time no measurements could be made. These deposition values were highly variable, ranging over two orders of magnitude from about 1 - 144 μmol N m^{-2} d^{-1} . The daily dry flux tended to be lower in 1995 than the other three years. This was due to the lower mixing ratios observed during that year (Chapters 1 and 2).

The total N dry flux is the sum of gas phase HNO_3 deposition, and bulk aerosol NO_3^- and NH_4^+ deposition (Figure 3.3). Gas phase HNO_3 contributes the most to the dry flux of all three species (Figure 3.3) due to its high atmospheric mixing ratios and

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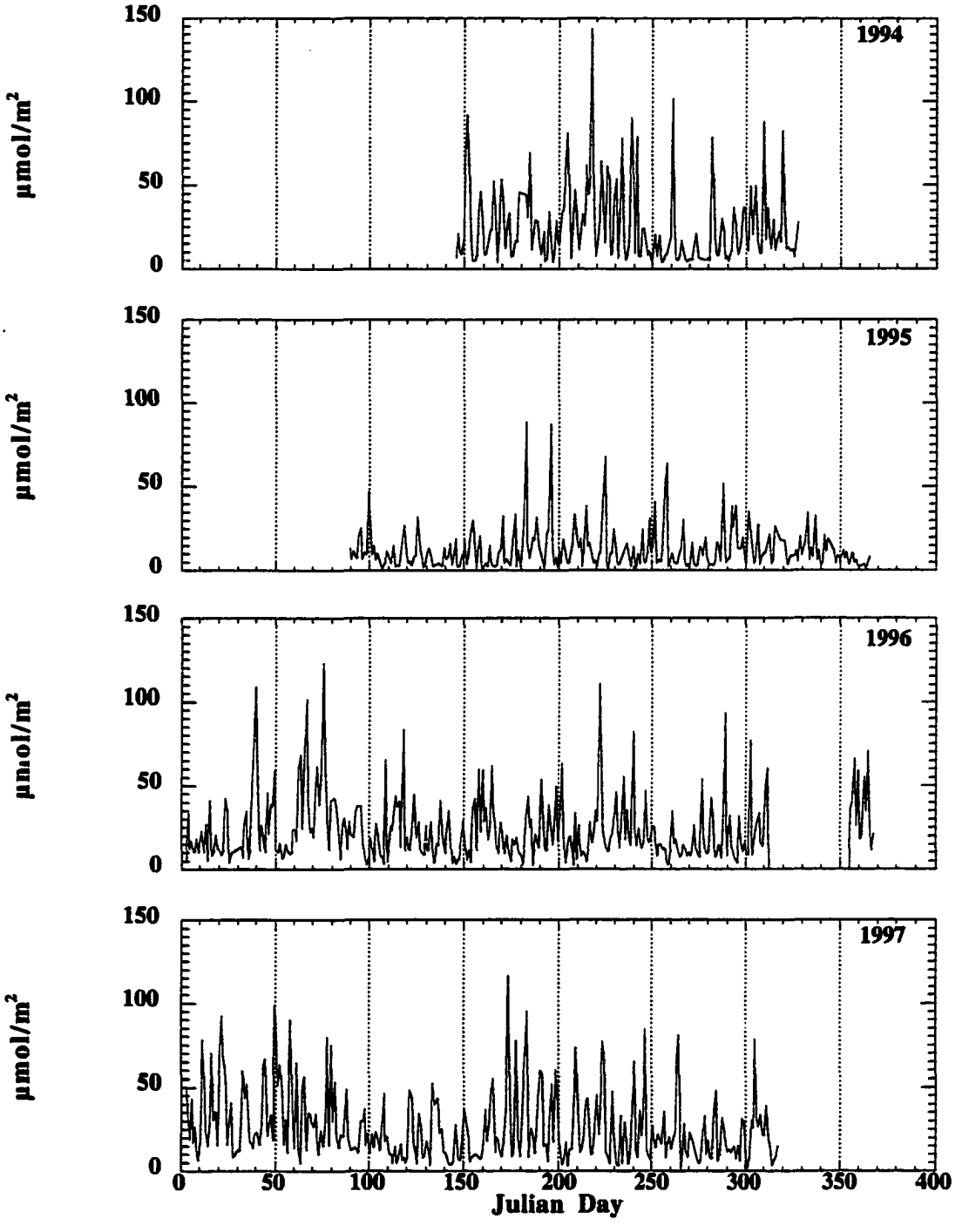

Figure 3.2. Daily total dry nitrogen (sum of gas-phase HNO_3, particulate NO_3^- and NH_4^+) deposition values over the course of the study at New Castle, New Hampshire. The data gap in 1996 was due to a power failure at the site.

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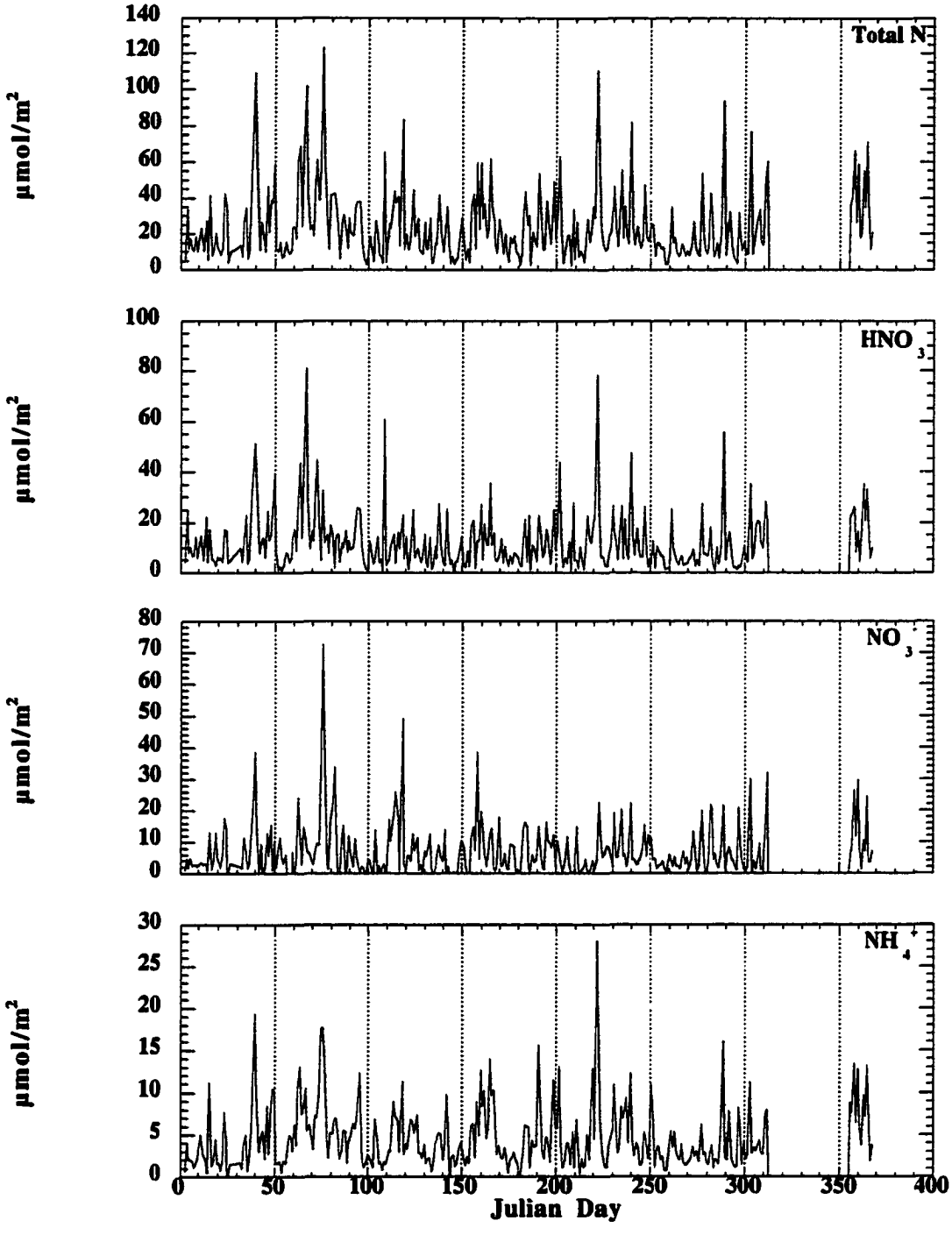

Figure 3.3. 1996 daily dry deposition values (total, HNO_3, NO_3^-, and NH_4^+). HNO_3 and NO_3^- dominate the total dry nitrogen flux. The data gap in 1996 was due to a power failure at the site.

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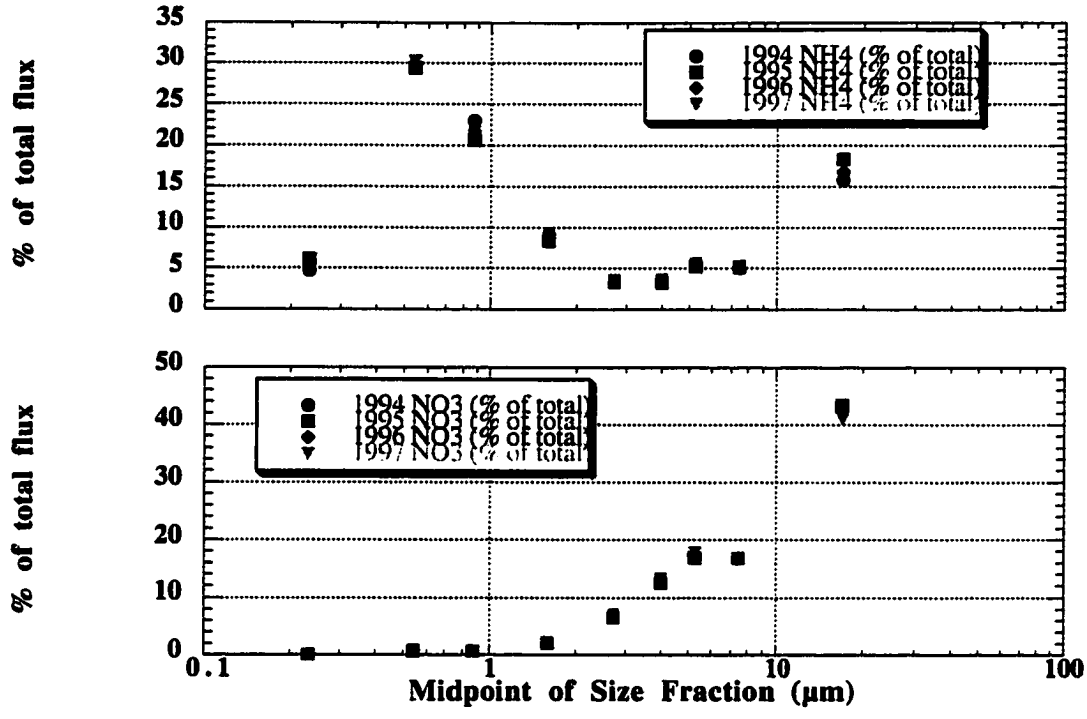

Figure 3.4. Percent of the total dry flux as a function of particle size. Most of the NH_4^+ flux is carried by submicron particles, with a substantial fraction deposited by the coarsest fraction. The largest sizes carry most of the NO_3^- flux.

solubility. Particulate NO_3^-, also comprised a substantial fraction of the dry flux. Most NO_3^- was found on large particles (Chapter 2) with the coarsest size fraction depositing over 40% of the total NO_3^- (Figure 3.4). The next two smaller sizes (4.7 - 5.8 μm and 5.8 - 9.0 μm) each contributed about 18% of the total, with the smaller size fractions contributing less.

Although NH_4^+ was present at much higher mixing ratios in the atmosphere than NO_3^- (Chapter 1), it contributed less to the dry flux (Figure 3.3). This was due to NH_4^+ being present primarily on submicron particles, which deposit less readily than supermicron particles. For NH_4^+ the 0.43 - 0.65 μm aerosol size fraction deposited more than any of the others, carrying about 30% of the total NH_4^+ (Figure 3.4). The 0.65 - 1.1 μm size fraction deposited about 22% of the total while the coarsest fraction (>9 μm)

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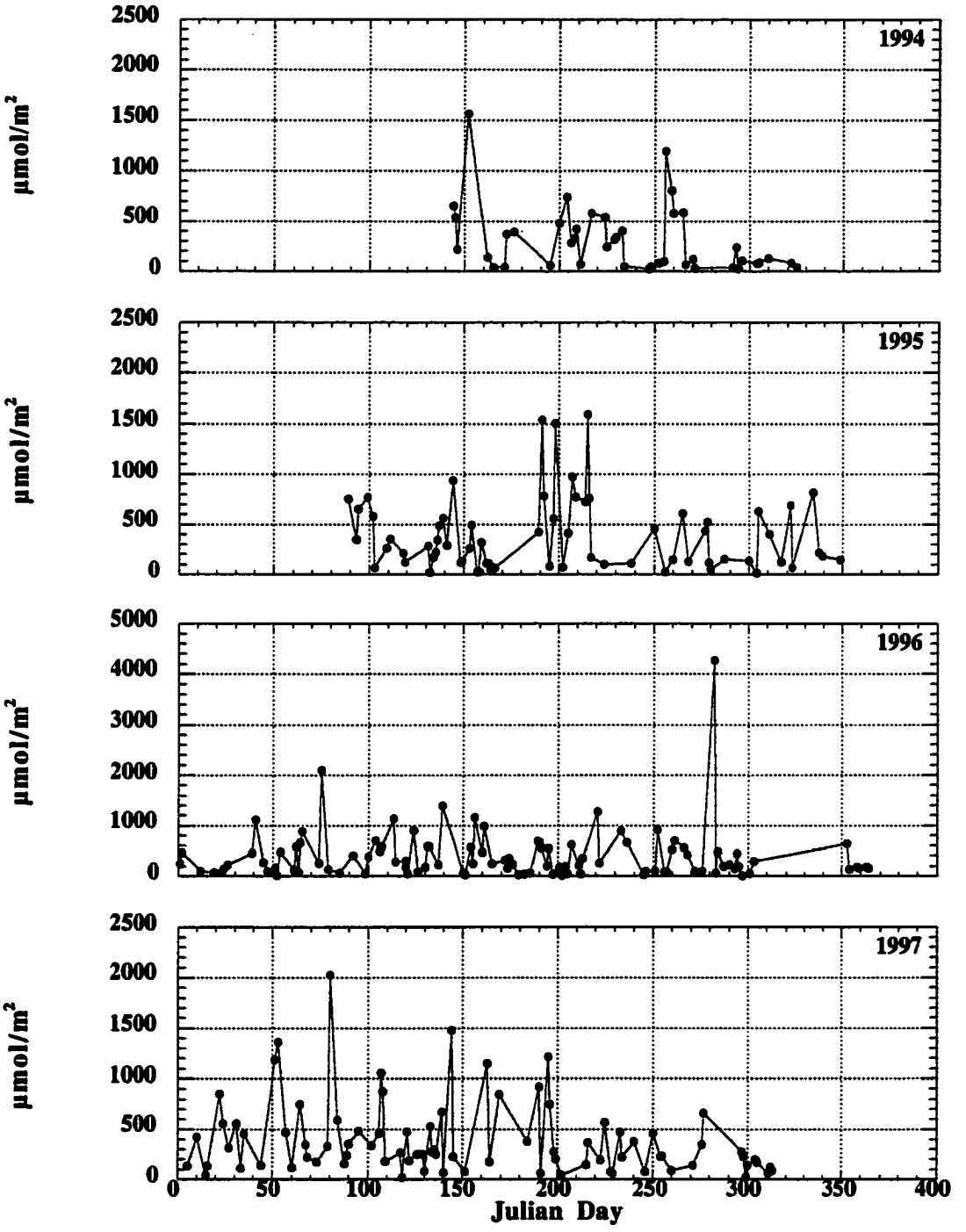

Figure 3.5. Daily total wet nitrogen (sum of NO_3^- and NH_4^+) deposition values over the course of the study at New Castle, New Hampshire. Note, 1996 is on a different scale than the other years due to a particularly large event which exceeded 4000 µmol N m^{-2}. The data gap in 1996 was due to a power failure at the site.

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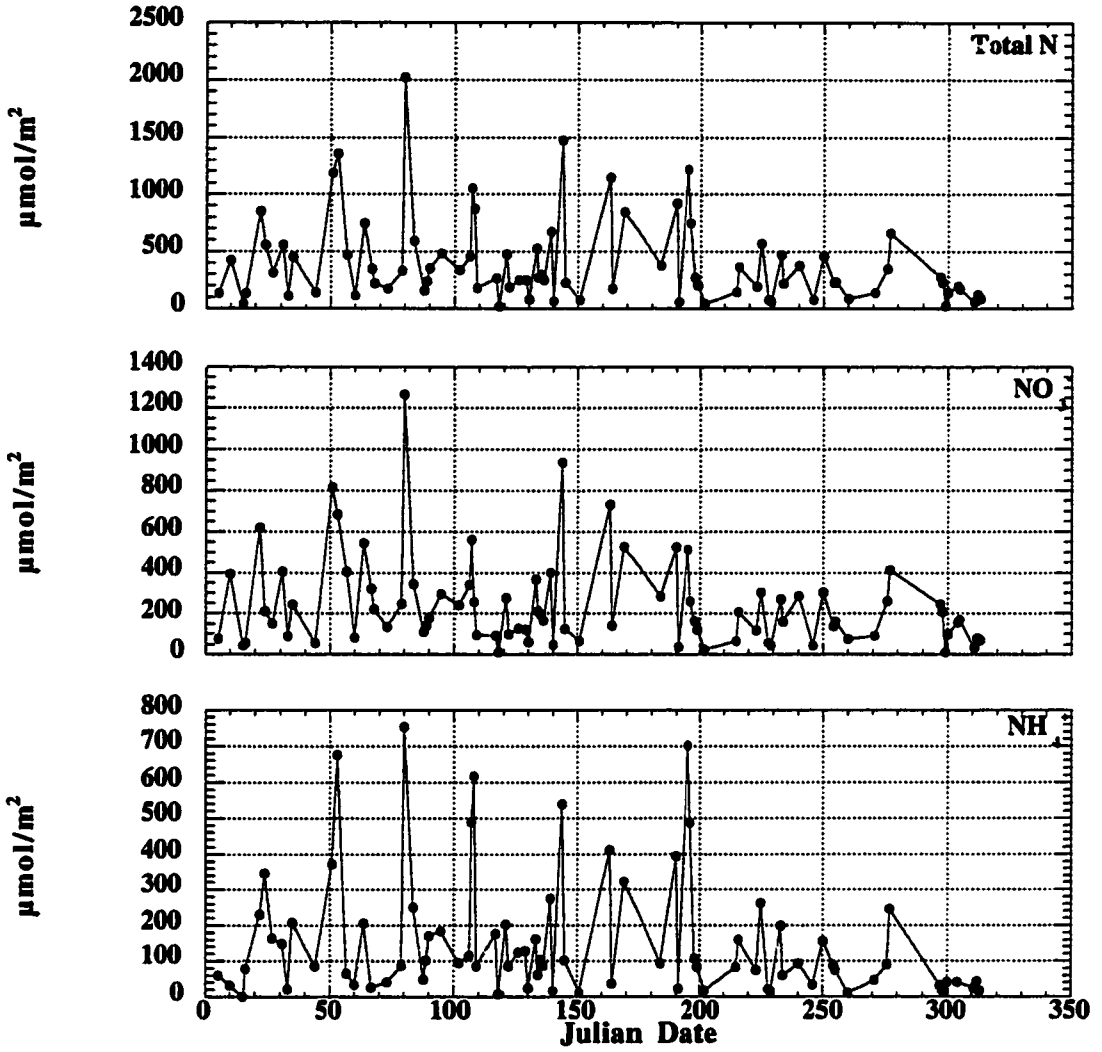

Figure 3.6. 1997 daily wet deposition values (total, NO_3^-, and NH_4^+). NO_3^- dominates the total wet nitrogen flux.

contributed about 17%. Given the average NH_4^+ size distribution for a mixed air mass at New Castle had 51% in the 0.43 - 0.65 µm fraction, 26% in the 0.65 - 1.1 µm fraction, and 1% in the coarsest fraction, this illustrates the bias of coarse particles and their associated chemical species on the deposition compared to the atmospheric mixing ratio.

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Wet Deposition

The total wet deposition is shown in Figure 3.5. Note, that 1996 is on a different scale than the other three years due to a particularly large event which exceeded 4000 μmol m^{-2}. Note the scale of the wet deposition is an order of magnitude greater than the dry deposition (Figure 3.2). Hence, most of the nitrogen deposition to the Gulf of Maine is carried by precipitation (80 - 90% of the total, Table 3.3). As with the dry deposition, wet deposition is highly variable from one event to the next depending on the concentrations of NO_3^- and NH_4^+ in the precipitation as well as the amount of precipitation. Also like dry deposition, NO_3^- tends to exceed NH_4^+ in precipitation in most, but not all, cases (Figure 3.6).

Fog Deposition

Fog can also lead to a substantial amount of nitrogen deposition. Although, fog deposits less water than precipitation, the concentrations of chemical species can be so much higher than precipitation, that more of a solute can be deposited via a fog event. Characteristic chemical signatures are shown for four fog events in Figure 3.7. Note, as reported by Klemm et al. (1994) the variation of the chemistry during an event tends to be less pronounced than the chemical variation observed from one event to another. The chemical signature of a given fog event was found to reflect the chemistry of its precursor air mass (Chapter 2). As was done for the chemical signatures of air masses (Chapter 2), the chemistry of a fog event can be viewed in terms of an overall marine, continental, or mixed signature. The terms marine fog, continental fog, and mixed fog in this context refer only to the chemistry and not to fog formation processes (e.g., advection or radiation fog). The event on August 29, 1997 was typical of a marine fog (Figure 3.7). The sea salt species Na^+ and Cl^- were dominant. The events on April 16, 1998 and August 8, 1996 represent two types of fogs formed in continental air. The former is more typical, with HNO_3 and NO_3^- in the precursor air mass combining to make NO_3^- the dominant species in solution. However, NH_4^+ can also be the dominant species in a continental fog as seen

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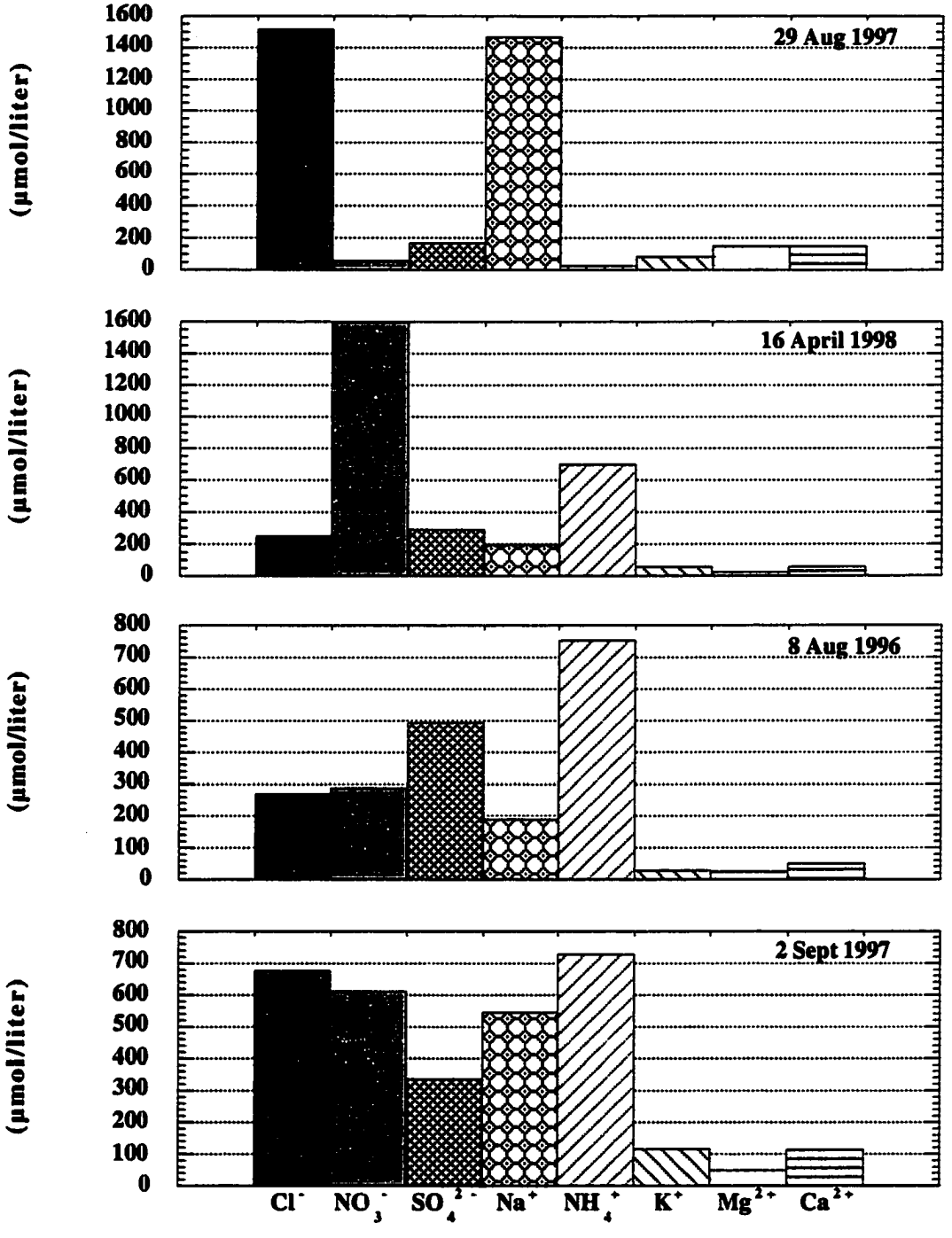

Figure 3.7. Four examples of fog water chemistry: marine (top panel), two types of continental (middle panels), and mixed chemistry (bottom panel). The chemistry of the fog water depends upon the chemistry of the precursor air mass.

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Table 3.1. Influence of Fog N Flux on Total N Flux

Start Date	Stop Date	Wet + Dry N Flux, μmol/m^2	Fog N Flux, μmol/m^2	Total N Flux, μmol/m^2
7/24/96	7/25/96	2	29	31
8/8/96	8/8/96	111	93	204
5/31/97	6/1/97	94	229	323
8/29/97	8/29/97	8	21	29
9/2/97	9/2/97	85	371	456
9/13/97	9/14/97	8	63	71
4/16/98	4/16/98		672	
5/4/98	5/4/98		274	

in the latter case. The fourth example shows the chemistry of a fog formed in a mixed air mass. Here, the sea salts and nitrogen species appear at comparable strengths.

In addition to the concentrations of the nitrogen species in fog water, the duration and the liquid water content of a fog determine whether a substantial amount of nitrogen is deposited. Table 3.1 lists the calculated fog N flux during 8 events. In all but one case, the fog contributes more than the combined wet and dry N flux on those days. For the two fog events from 1998, we have no aerosol or precipitation data, but it is clear from the April 16, 1998 case, that fog can deposit as much nitrogen as a high N depositing precipitation event.

Note, as with precipitation, it would be anticipated that DON would enhance fog N deposition in spring, but that during the remainder of the year, it would play a minor role if any. Due to insufficient data, no fog deposition has been calculated to add to the daily total N flux presented here. However, fog may play a substantial role in nitrogen deposition to the Gulf of Maine as it frequently occurs in this area. The coast along the Gulf of Maine experiences in excess of 60 days with fog a year (Stone, 1936; Court and Gerston, 1966). A day with fog is defined as a day during which fog obscures visibility to a given distance for an hour or more (Court and Gerston, 1966). Further, dense fog occurs 10-20 days a year along the southern Gulf of Maine coast and 20-40 days a year along the northern coast, with areas over the Gulf itself experiencing more the 50 days a year of dense fog

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Table 3.2. Fog and Mist Hours at Pease International Tradeport Airport

	Total	Winter (Jan-March)	Spring (April-June)	Summer (July-Sept)	Fall (Oct-Dec)
			All		
1994	753	94	207	372	80
1995	740	235	140	233	132
1996	817	123	173	352	169
1997	481	86	86	246	63
			Low visibility (<5 km)		
1994	449	50	153	207	39
1995	446	171	82	130	63
1996	525	89	107	221	108
1997	274	46	42	152	34
			Very Low Visibility (<2 km)		
1994	164	27	63	63	11
1995	269	141	53	45	30
1996	260	61	41	104	54
1997	127	32	15	56	24

(Court and Gerston, 1966). Dense fog is defined as that with visibility ≤ 0.25 miles (or ≤ 0.40 km) (Court and Gerston, 1966). Data from the Pease International Tradeport Airport weather station, shows fog observations during this study (Table 3.2). A fog "hour" is defined here as an hour in which fog was observed, it may or may not have lasted an entire hour. The greatest deposition will occur during the lowest visibility fogs, when the liquid water content is highest.

Total Deposition

Daily total N deposition for the duration of this study is shown in Figure 3.8. Note, the open circles mark dates of precipitation events for which we had no data and the open diamonds mark the dates of fog events. These are shown to indicate where the flux was probably higher, but how much higher is unknown. The open diamonds indicate fog events which persisted longer than 5 hours for continental and mixed chemistry fogs (presumed higher N concentrations), and longer than 10 hours for oceanic fogs (presumed lower N concentrations). As with the wet deposition, 1996 is shown at a different scale due to an unusually large event, over 4000 μmol m^{-2}. The deposition was highly variable from one day to the next, ranging over 4 orders of magnitude.

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Table 3.3. Total N Deposition: Sampled and Corrected to Complete Years

	Fraction of Time Sampled	Fraction of Precipitation Sampled		Sampled Total N Deposition $\mu mol/m^2$	Corrected Total N Deposition $\mu mol/m^2$
1994	0.48	0.34	dry	4433	9235
			wet	13247	38736
			total	17680	47971
1995	0.70	0.63	dry	3164	4534
			wet	25746	40783
			total	28910	45317
1996	0.86	0.80	dry	7640	8847
			wet	40976	51179
			total	48616	60026
1997	0.85	0.71	dry	8149	9617
			wet	32741	45841
			total	40890	55458

Annual nitrogen deposition estimates are shown in Table 3.3. The total deposition is shown both in terms of the total calculated from our samples and corrected for the entire year. The dry deposition is corrected using the fraction of time sampled and the wet deposition is corrected using the fraction of precipitation sampled. This approach allows for some comparison of deposition from one year to the next. Less deposition was found in 1995 than the other three years, due to lower ambient mixing ratios observed that year (Chapters 1 and 2). Nonetheless, the annual nitrogen deposition was relatively consistent from year to year, with the average annual deposition equal to 52 ± 7 mmol m^{-2}.

Given the highly variable nature of the daily deposition (Figure 3.8), the contribution of events relative to the total deposited was investigated (Table 3.4). Two thresholds were considered: first, where the daily deposited nitrogen exceeded 500 $\mu mol\ m^{-2}$, and second, where it exceeded 1000 $\mu mol\ m^{-2}$. Events of 500 $\mu mol\ m^{-2}$ or more occurred in 8% of the samples (Table 3.4a), yet they contributed 56% to all of the observed deposited nitrogen (Table 3.4b). Events exceeding 1000 $\mu mol\ m^{-2}$ occurred only in 2% of the samples (Table 3.4a), but contributed 22% to the total observed(Table 3.4b).

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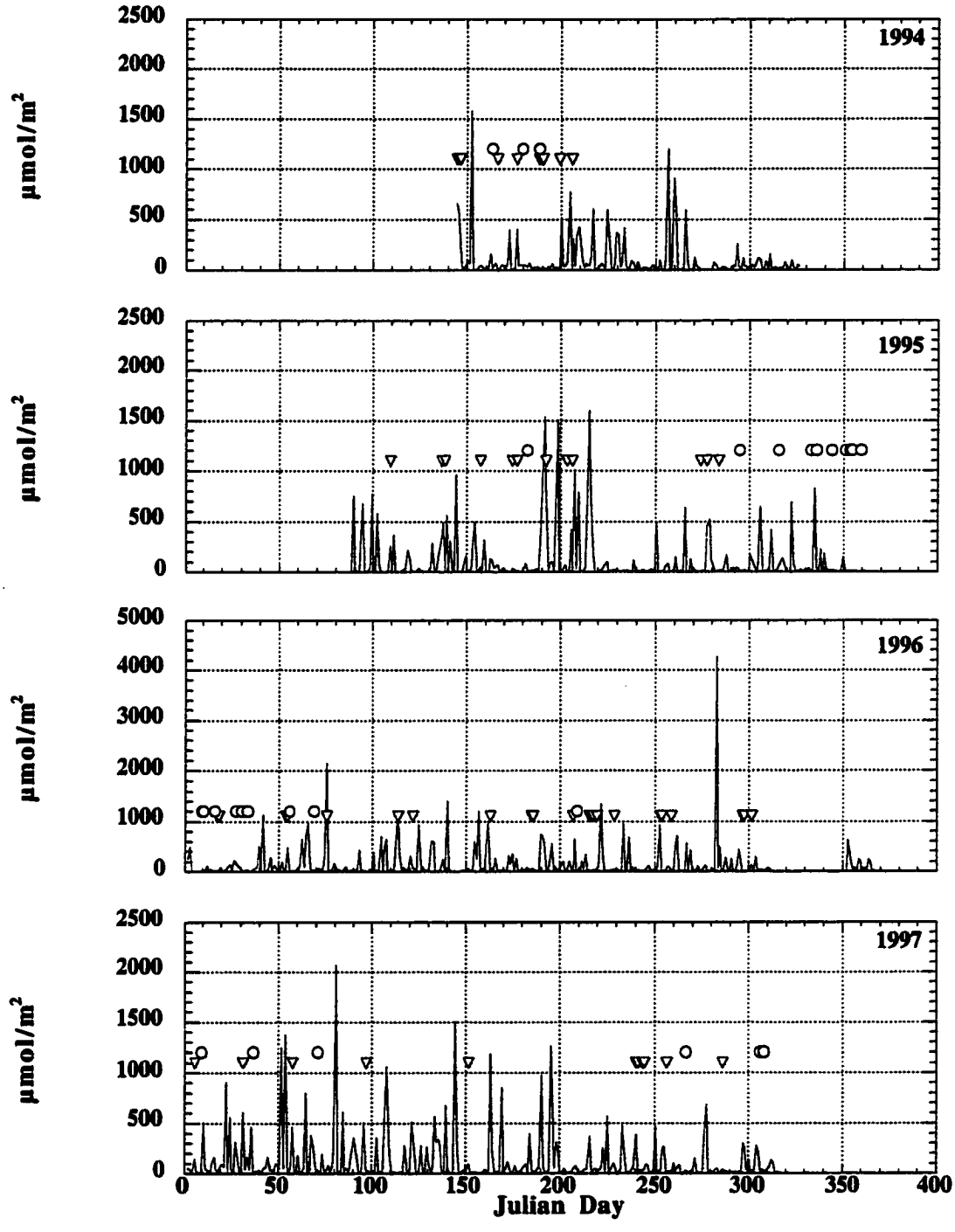

Figure 3.8. Daily total N flux (sum of wet and dry inorganic N species) over the course of the study at New Castle, NH. The open circles denote precipitation events for which we had no chemical data to calculate N deposition. The open triangles denote fog events which may have potentially deposited a substantial amount of N, but for which we had insufficient information to estimate the flux. The data gap in 1996 was due to a power failure at the site.

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It is these infrequent, yet very large pulses of nitrogen deposition that may play a role in the productivity distribution of the Gulf of Maine ecosystem.

Table 3.4a. Number of Events (n) Compared to Total Observations

	Total n	n where deposition >500 μmol/m^2	% of Total n	n where deposition >1000 μmol/m^2	% of Total n
1994	176	11	6	2	1
1995	261	20	8	3	1
1996	318	31	10	7	2
1997	313	24	8	7	2
1994-1997	1068	86	8	19	2

Table 3.4b. Contribution of Events to Total N Deposition

	Total N Deposition, μmol/m^2	Events (> 500) Total N Deposition, μmol/m^2	% Contribution to Total by Events	Events (> 1000) Total N Deposition, μmol/m^2	% Contribution to Total By Events
1994	17680	8620	49	2781	16
1995	28910	16982	59	4153	14
1996	48615	29384	60	12700	26
1997	40890	21252	52	9724	24
1994-1997	136095	76238	56	29358	22

Discussion

Comparison to Other Measurements

Wet deposition of nitrogen from this study can be compared to other measurements made in New England and in the western Atlantic. Measurements made at Bermuda from 1980 through 1989 reported by Owens et al. (1992) show atmospheric wet deposition events similar to those reported here (Table 3.5). Most of the events measured at Bermuda (90%) deposited less than 400 μmol N m^{-2}, although there were several events which exceeded 500 μmol N m^{-2} and a few above 1000 μmol N m^{-2}. The wet deposition values reported here are somewhat higher, with a median value of 242 μmol N m^{-2} compared to a median at Bermuda of 85 μmol N m^{-2}. Large events in both locations are rare. The largest ones at New Castle are over 1000 μmol N m^{-2} and are comparable to the largest events

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seen in Bermuda, although they are more frequent at New Castle. In addition, two events in New Castle exceeded 2000 μmol N m^{-2}. The higher N deposition at New Castle is likely the result of its proximity to anthropogenic sources. At Bermuda, air masses have travelled further from source regions, allowing additional removal of nitrogen by dry and wet deposition.

Table 3.5. Comparison of Wet N Deposition at New Castle, NH to Bermuda

	Number of Events		Total Wet N Flux, μmol m^{-2} $event^{-1}$
New Castle[1] (1994-1997)	300	Min	3.28
		Max	4262.24
		Median	241.50
Bermuda[2] (1980-1989)	512	Min	0.70
		Max	1470.00
		Median	85.10

[1]This study
[2]Owens et al., 1992

Annual wet deposition for various sites along the western Atlantic Ocean are given in Table 3.6 (modified from Duce et al., 1991). Considering the first group of numbers in Table 3.6 (from Duce et al., 1991), there is clearly a north-south gradient in the wet deposition flux, with the peak deposition occurring in New Jersey (41 mmol N m^{-2} yr^{-1}), Delaware (37 mmol N m^{-2} yr^{-1}), and New York (34 mmol N m^{-2} yr^{-1}). To the north and south of this area, the annual wet nitrogen flux drops off to about 14 mmol N m^{-2} yr^{-1} in Newfoundland and Florida. The average annual deposition from two National Acid Deposition Program (NADP) coastal sites (ME98, Mt. Desert Island, Maine and MA01, Cape Cod, Massachusetts) during the course of this study are comparable to the values reported a decade earlier by the same sites (31 v. 28 mmol N m^{-2} yr^{-1} in Massachusetts; 26 v. 27 mmol N m^{-2} yr^{-1} in Maine). However, the wet nitrogen deposition measured at

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Table 3.6. New Castle, NH Wet Deposition Compared to Other Western Atlantic Sites

			Inorganic N Wet Deposition mg N m^{-2} yr^{-1}	Inorganic N Wet Deposition mmol N m^{-2} yr^{-1}
Bermuda[1]	32°N 65°W	April 1980-May 1984	141	10
Florida[2]	24°N 80°W	1984-1985	203	14
Florida[2]	30°N 82°W	1984-1985	340	24
Georgia[2]	33°N 82°W	1984-1985	301	21
N. Carolina[2]	37°N 77°W	1984-1985	350	25
Delaware[3]	39°N 75°W	1979-1983	512	37
New Jersey[2]	40°N 75°W	1984-1985	570	41
New York[3]	41°N 73°W	1979-1983	471	34
Massachusetts[2]	42°N 70°W	1984-1985	387	28
Massachusetts[2]	42°N 71°W	1984-1985	392	28
Nova Scotia[4]	44°N 65°W	1985-1986	339	24
Maine[2]	44°N 68°W	1984-1985	375	27
Nova Scotia[4]	45°N 64°W	1985-1986	317	23
New Brunswick[4,5]	46°N 65°W	1985-1986	291	21
Maine[2]	47°N 68°W	1984-1985	267	19
Newfoundland[4,5]	48°N 55°W	1985-1986	202	14
Newfoundland[4,5]	49°N 55°W	1985-1986	94	7
NADP/NTN: MA01[6]		1994-1997		31
New Castle[7]		1994-1997		44
NADP/NTN: ME98[6]		1994-1997		26

[1]Galloway et al., 1989; Duce et al., 1991
[2]NADP 1986; 1987; Duce et al., 1991
[3]Dana and Easter, 1987; Duce et al., 1991
[4]Vet et al., 1986; Duce et al., 1991
[5]R. J. Vet, personal communication as cited by Galloway and Whelpdale, 1987; Duce et al., 1991
[6]NADP data from website: http://nadp.sws.uiuc.edu/
[7]This study

New Castle, NH was substantially higher than that of the neighboring NADP sites (MA01 and ME98).

The New Castle wet deposition is corrected for the year by dividing the total deposited by the fraction of precipitation sampled. Similarly, NADP, corrects for annual deposition by determining the volume-weighted mean concentrations and multiplying by the total precipitation for the year. Averaging all four years at each of these three sites, we report 43% more N deposition than reported on Cape Cod and 70% more than reported at

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Mt. Dessert Island. The higher deposition compared to that of NADP is due to the higher concentrations of NO_3^- and NH_4^+ measured at New Castle (Chapter 1). Annual precipitation amounts at these three sites are comparable averaging 125 cm (MA01), 120 cm (New Castle), and 140 cm (ME98) from 1994 through 1997. The reason for the higher concentrations observed at New Castle are unclear, but may be related to the different sampling protocols. The NADP samples are weekly bulk samples, whereas as New Castle precipitation samples were collected daily and preserved immediately to prevent biodegradation. However, without side by side comparisons, it cannot be confirmed whether there are nitrogen losses from the NADP samples or whether there is some unknown local source of nitrogen near New Castle (although, this latter possibilty is unlikely in our opinion).

In addition to the contribution of N to the Gulf of Maine via direct atmospheric deposition to its surface, indirect atmospheric deposition of N to the watershed may also contribute a significant amount of N to the Gulf. Mosher (1995) estimated that atmospheric N deposition to the Great Bay Estuary and its watershed input more nitrogen to the Bay than point sources. Further, he found that atmospheric N deposition was greater than or equal to all other non-point sources of nitrogen to the Bay. Jaworski et al. (1997) found that in watersheds saturated with nitrogen, which is common in the northeastern United States, nearly all atmospheric N deposition via wet and dry processes was exported from rivers. They found a linear relationship between both nitrogen oxide emissions and atmospheric N deposition to the watersheds, and the subsequent riverine flux. Thus, it is expected that a large precipitation N deposition event would not only input an immediate pulse of N directly into the Gulf, but that a subsequent pulse would follow as atmospheric N deposition to the watershed is washed downstream into the Gulf.

It is also expected that deposition over the Gulf of Maine may be enhanced by chemical processing which occurs over the Gulf. For example, HNO3 is produced by the reaction of NO2 with OH. Thus, as NO2 is transported off the continent, and HNO3 is

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produced, deposition will be enhanced by this additional supply of HNO3. Also, peroxyacetylnitrate (PAN), another gas phase N species produced by the oxidation of NOx, can also enhance the mixing ratios of HNO3 over the Gulf of Maine as it thermally breaks down to NO2 in summer and then produces HNO3 via the pathway mentioned above. NOy which denotes the total reactive nitrogen in the atmosphere (including NOx, HNO3, PAN, and aerosol NO3-) has been reported to have a geometric mean mixing ratio ranging from about 3100 to 3500 pptv from July to September at Harvard Forest in Petersham, Massachusetts (Munger et al., 1998). The Harvard Forest site (42.53°N 72.18° W; 340 m elevation) is 100 km inland from the Gulf of Maine. At Sable Island (43° 55' N 60° 01' W), east of the Gulf of Maine, the median NOy mixing ratio was 266 pptv (arithmetic mean, 376 pptv) during the 1993 summer intensive, July - September, (Wang et al., 1996), approximately an order of magnitude lower than observed at Harvard Forest. It has been suggested that only a small fraction of this NOy vents into the free troposphere from the boundary layer (Munger et al., 1998). Further, only a small fraction of these nitrogen oxides are transported from North America beyond 60° W longitude (Galloway and Whelpdale, 1987; Galloway, 1990). This suggests, that most of the observed nitrogen transported off the coast of New England deposits in western North Atlantic waters. Thus, continuing gas phase and heterogeneous reactions which occur as continental air masses move offshore are anticipated to enhance direct atmospheric N deposition compared to the numbers reported here.

N budget of the Gulf of Maine

The exchange of water between the Atlantic Ocean and the Gulf of Maine is more restricted than its shoreline indicates (Brooks and Townsend, 1989; Townsend, 1991; Townsend, 1998). The Gulf is separated from the Atlantic below 100 m by the Nantucket Shoals, Georges Bank and Browns Bank (Figure 3.1), except for a narrow channel through which Atlantic water enters between Georges and Browns banks called the Northeast Channel. This deep water (>150 m) then flows into the three basins of the Gulf,

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Georges, Jordan, and Wilkinson. Georges Basin is the deepest (370 m) and is an extension of the Northeast Channel. The three basins all exceed 250 m depth and are isolated from each other below 200 m (Figure 3.1). Shallower water (<75 m) enters both over the Northeast Channel and around Nova Scotia, flows generally counter-clockwise around the Gulf and exits to the south around Cape Cod and to the east above the northern edge of Georges Bank (Townsend, 1991). The counter-clockwise flow at the surface follows the coastline (the coastal current), as well as forming gyres over the three basins (Figure 3.9). Tides range from 2-3 m along the Massachusetts coastline to about 5 m along the eastern Maine coastline, and peak in the Bay of Fundy at >15 m. In the eastern Gulf, strong tidal forcing drives currents and effectively mixes the water column limiting thermal

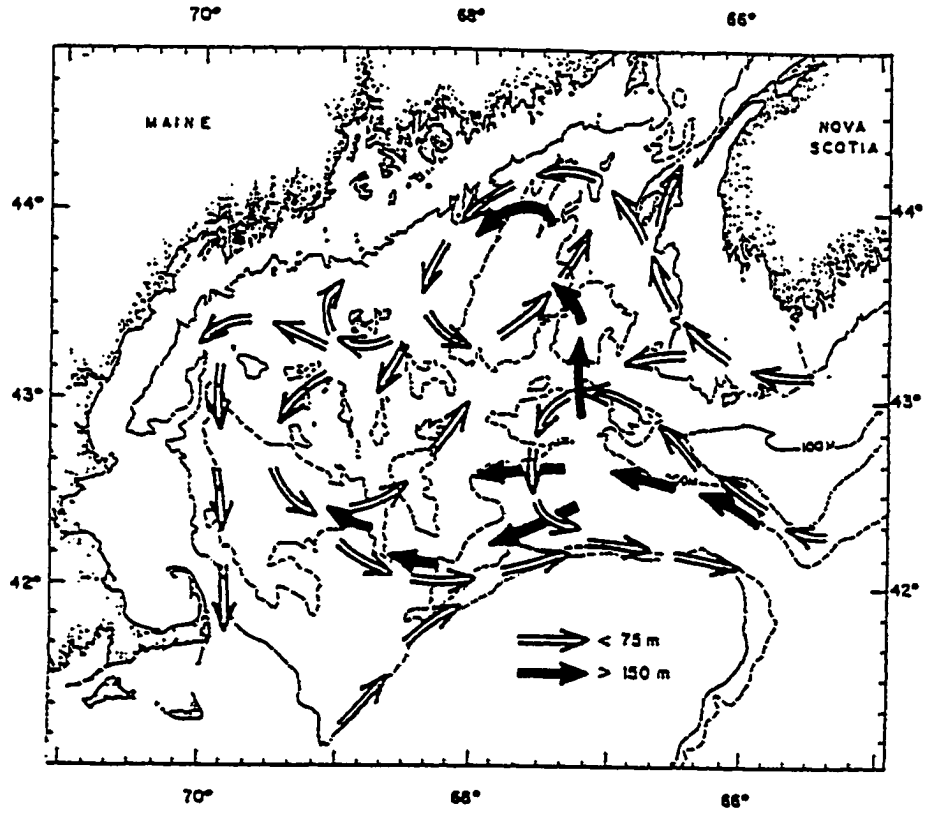

Figure 3.9. Map showing the flow of water entering the Gulf of Maine. Black arrows indicate the influx of deep water through the Northeast Channel, white arrows illustrate the surface circulation (from Townsend, 1992).

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stratification in the warmer months (Townsend, 1991). In the western part of the Gulf, however, the water column does become stratified in the warmer months with the mixed surface layer extending 10 - 20 m in depth (Bub, 1997). Riverine flux leads to a spring freshet which is important in the development of the coastal current in the spring. Most of this riverine freshwater flows along the coast into the western Gulf. Scotian Shelf water is another significant source of freshwater. It enters around the southwest of Nova Scotia and affects currents in the eastern Gulf (Townsend, 1991).

Nitrogen enters the surface waters in the Gulf of Maine primarily by: (1) vertical mixing by tides and upwelling in the eastern Gulf and on the southwest Scotian Shelf, (2) vertical fluxes across the seasonal pycnocline, and (3) winter convection (Townsend, 1991; 1998). Internal waves have also been suggested as a mechanism by which nitrogen may reach the surface waters (Townsend, 1998). On an annual basis the flux of nitrogen from atmospheric and riverine sources adds only a small fraction (about 3%) to the nitrogen supplied by the slope water and Scotian Shelf water (Schlitz and Cohen, 1984; Townsend 1998; see Table 3.7 modified from a table in Townsend, 1998). About 44% of the nitrogen which enters the Gulf via the Northeast Channel reaches the surface waters of the eastern Gulf in the Grand Manan area (Townsend et al., 1987; Brooks and Townsend, 1989; Townsend, 1991). Grand Manan Island is near the U.S.-Canadian border at the entrance to the Bay of Fundy. In winter, NO_3^- concentrations in the upper water column can reach 8μM (Townsend, 1991). This nitrogen is then transported to the western and central Gulf via the coastal current. In evaluating the primary production in the Gulf of Maine, Townsend (1998) found that the influx of nitrogen was insufficient to support all of the observed primary production, as a substantial amount of that nitrogen flows out of the Gulf before becoming available to the primary producers. He suggested that the intermediate layer of water (between the surface and deep layers) is a nitrite reservoir which mixes a sufficient amount of nitrogen into the surface waters to support the relatively high rates of primary production.

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Table 3.7. Comparison of Various N Sources to the Gulf of Maine Surface Waters

		Volume, 10^{12} m^3 yr^{-1}	[N], μmol N l^{-1}	N flux yr^{-1}, 10^9 mol N yr^{-1}
Inflows to the Gulf of Maine	Atmosphere (wet + dry)			5.38
	Rivers	0.08	10	0.8
	Scotian Shelf Water	6.31	5.0	31.5
	Slope Water (NE Channel)	8.7	17	147.9
	Total			185.58

From Townsend (1998) with revised atmospheric contribution (this study).
Other numbers modified by Townsend from Christensen et al., 1995 and McAdie, 1994.
Fluxes are for area of Gulf, assumed = 1.03×10^{11} m^2

Phytoplankton production tends to be limited either by light or nutrients. Light and nutrient availability depend on mixing of the water column. A deep well mixed layer tends to have sufficient nutrients, but light limits the extent of productivity, whereas a vertically stratified layer has sufficient light, but limited nutrients (Townsend, 1991). In the Gulf of Maine both exist. Along the Maine coast, the 100 m isobath (Figure 3.1) delineates the regions in which light limited production occurs (to the east) and nutrient limited production occurs (to the west), (Townsend, 1991). In the stratified waters, there is a pronounced spring diatom bloom which depletes the surface waters of nitrogen. The stratification restricts the resupply of nitrogen from below, such that the NO_3^- concentrations in the surface waters remain < 1.0 μM throughout the summer (Townsend, 1991; Martorano, 1997; T. Loder, personal communication, 1998). In addition to the spring bloom, there can also be a substantial fall diatom bloom as the stratified waters overturn and nutrients are again mixed into the surface from the deeper waters (Townsend, 1991). In the well-mixed eastern waters, production continues throughout the warmer months, and the spring bloom is only a small enhancement to that production (Townsend, 1991). Most of the production in the Gulf is in these well mixed waters (Yentsch and Garfield 1981; Townsend, 1991). This production is supported by a plentiful supply of nutrients from deep waters. In this region, the atmospheric contribution to the nitrogen supply is expected to be a small percentage of the total.

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Biological Significance

Experiments have shown that adding rainwater to seawater samples can lead to enhanced chlorophyll *a* levels and primary production (Paerl, 1985, 1993; Willey and Cahoon, 1991). In these experiments, sea water samples were collected, rainwater added in proportions typical of a large rain event, and bioassays performed. Willey and Cahoon (1991) found NO_3^- concentrations typical of continental storm systems increased chlorophyll *a* production after the addition of 5% by volume of a synthetic rainwater solution. After incubation for two days, the chlorophyll *a* increased 2.5 times relative to controls. Paerl (1985) collected seawater samples from various locations off the North Carolina coast, then added rainwater at 10% and 20% levels by volume. These additions were chosen based on typical rainwater dilutions of near-surface (0 - 5 m) water following large (1 -5 cm) deposition events, prior to enhanced dilution by freshwater runoff from rivers following these events. He found that the nitrogen in the rainwater led to enhanced chlorophyll *a* production for 6 - 7 days following the addition of rainwater with high nitrogen levels (continental rain) and for 2 - 3 days following the addition of rainwater with relatively low nitrogen levels (oceanic rain). Samples collected before and after storm events off North Carolina's coast supported the bioassay results, in that precipitation nitrogen input led to significant enhancement of phtoplankton production in these N limited waters. Paerl (1985) also reported that a two day lag occurred between extensive rainfall and enhancement of near-shore chlorophyll *a* levels.

Observations reported by Glover et al., (1988) from the Sargasso Sea showed that 417 μmol NO_3^- m^{-2} in the upper water column (above 25 m) supported a bloom of *Synechococcus*. They also found that grazers rapidly removed 70% of the *Synechococcus* cells produced. The source of this NO_3^- was uncertain. Although, major storms preceded these observations, the authors felt the rainfall could not account for all of the added NO_3^-. Other studies in the Sargasso Sea have yielded mixed results. Owens et al. (1992) reported that atmospheric deposition of nitrogen could lead to substantial new production, while

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Michaels et al. (1993) reported atmospheric additions of nitrogen to the mixed layer in the summer and fall would add only a negligible amount to the productivity observed.

Here, there is insufficient data to determine whether atmospheric N deposition supported any increased productivity in the Gulf of Maine over the course of these measurements. However, the production of chlorophyll *a* can be estimated from the Redfield Ratio of 6.6 mol C/mol N and the approximation that 60 μg C produce 1 μg chlorophyll *a* (Michaels et al., 1993). The results of this calculation are shown in Table 3.8 for three levels of atmospheric N deposition events, 500, 1000, and 4000 μmol N m^{-2}.

Table 3.8. Estimate of Potential Chlorophyll *a* Production from a Direct Atmospheric Deposition Event

Total N Deposition, μmol/m^2	Total N Deposition, μg N/m^2	N:Chl *a*, μg N/μg Chl *a*	Chlorophyll *a* Production, μg Chl *a*/m^2	Mixed Depth, m	Chlorophyll *a* Production, μg Chl *a*/m^3
500	7003.35	10.60	661	1	661
				5	132
				10	66
				15	44
				20	33
1000	14006.7	10.60	1321	1	1321
				5	264
				10	132
				15	88
				20	66
4000	56026.8	10.60	5285	1	5285
				5	1057
				10	528
				15	352
				20	264

The largest number reflects the largest deposition event observed here. Depending on the rate at which the precipitation nitrogen mixes into the mixed layer, different concentrations of chlorophyll *a* could be found. In the warmer months of the year, the depth of the mixed layer of the Gulf of Maine is about 10 - 20 m (Bub, 1997). If all of the nitrogen is used in chlorophyll *a* production, there would be a noticeable increase in chlorophyll *a* for all events above 500 μmol m^{-2}, even if the rainwater was quickly mixed to 20 m. Mixing of

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surface waters is primarily a function of wind stress. Michaels et al. (1993) report that for wind speeds in excess of 5 m/s, the fresh surface layer mixed to 10 m in the Sargasso Sea in 2 - 4 hours. However, for calm conditions with wind speeds ≤ 1m/s, the very shallow rain layer can persist for more than a day. The SeaWiFS (Sea-viewing Wide Field-of-view Sensor) satellite instrument is capable of detecting 0.01 mg Chl *a* m^{-3}. Thus, using data from this instrument to look for changes in chlorophyll *a* prior to and following a large deposition event may reveal whether or not direct atmospheric deposition leads to increased primary productivity.

These results suggest that if atmospheric nitrogen deposition enhances productivity in the Gulf of Maine, the best time to look for evidence of it would be following a large deposition event, especially if calm conditions exist during or following such an event. Large precipitation events occur both as a result of high volumes of water being deposited, even with relatively low N concentrations, and as a result of high nitrogen concentrations transported by smaller amounts of water. In addition to rainfall events, long duration fog events should also be considered. Fog may be particularly important as it tends to occur under calm conditions and a long duration event with sufficient NO_3^- and NH_4^+ concentrations can deposit in excess of 500 μmol N m^{-2} (Table 3.1). The observations reported here did not overlap SeaWiFS observations long enough for a thorough analysis of chlorophyll *a* concentrations compared to atmospheric N deposition. However, future studies could certainly take advantage of those satellite observations. Given the results here, fog and rain events from weather systems of continental origin (i.e., high nitrogen) or which deposit large amounts of water even with low nitrogen, under calm conditions are the most likely to result in enhanced productivity in the surface waters in the stratified part of the Gulf of Maine. If it is found that these large events do lead to discernible new production, then further investigation could reveal how much production is the result of these episodic events and what is the threshold required to induce such production. Note, there may well be other factors involved should enhanced productivity be found, trace

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metals may play a role as well as nitrogen, or the chemical properties of the rainfall may be less important than the physical forcings of a storm. Some care will be required to sort out all of these factors.

Much has been suggested about increased point and non-point source pollution leading to eutrophication of coastal waters and the increased occurrence, frequency, distribution, and species diversification of nuisance and toxic algal blooms (e.g., Smayda, 1990; Paerl, 1993, 1995; Zhang, 1994; and Zhang and Liu, 1994). Worldwide there are several different species which can have various adverse effects on ecosystems (Shumway, 1990). In the Gulf of Maine, the most common bloom problem involves the toxic dinoflagellate *Alexandrium tamarense*. This species is consumed by filter feeding shellfish, which become toxic as the dinoflagellate builds up in their system. This in turn is unhealthy for human consumption, hence the shellfish beds are closed until the episode passes and the shellfish flush the toxin. Blooms of this species date back to 1958 along the Maine coast, and have been an annual occurrence along the north shore of Massachusetts from May to October since 1972, except for 1987 (Loder and Becker, 1990; Franks and Anderson, 1992). While atmospheric deposition has been implicated in the occurrence of nuisance and toxic algal blooms elsewhere, it is unlikely that a direct link will be found between them in the Gulf of Maine due to the fact that *Alexandrium* has a very complicated life cycle and multiple factors are likely to be important in creating bloom conditions. While the atmosphere cannot be ruled out in terms of either physical or chemical forcings related to the occurrence of blooms of this toxic species in the Gulf of Maine, it would be advantageous to look first at the production of a ubiquitous phytoplankton species such as chlorophyll *a* to establish the role the atmosphere plays in the primary productivity of the Gulf of Maine.

Summary

Measurements have been made at New Castle, New Hampshire from 1994 through 1997 to assess direct atmospheric nitrogen deposition to the surface waters of the Gulf of

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Maine. Daily dry deposition ranged over two orders of magnitude from about 1 - 144 μmol N m^{-2} d^{-1} (with a median of 16 μmol N m^{-2} d^{-1}) with HNO_3 and particulate NO_3^- dominating the dry nitrogen flux. The year 1995 had lower dry nitrogen deposition than the other years observed. Wet deposition dominates dry deposition, contributing 80 - 90% of the total inorganic nitrogen flux annually. Wet deposition was highly variable from one event to the next ranging over three orders of magnitude from 3 - 4262 μmol N m^{-2} d^{-1}, with a median of 241 μmol N m^{-2} d^{-1}. Large deposition events could be attributed both to large water fluxes with moderate nitrogen concentrations and to moderate water fluxes with high nitrogen concentrations. NO_3^- wet deposition tended to exceed that of NH_4^+. Fog can also lead to substantial nitrogen deposition if the event persists long enough (several hours) with sufficient liquid water content (dense fog), particularly for those formed in continental air masses. Dissolved organic nitrogen contributes little to wet deposition, except in spring, when it contributes about 14% to the total on average. Note, the deposition reported here is underestimated somewhat as both fog deposition and organic nitrogen deposition were not included in the numbers reported here, due to insufficient sampling. Also, gas phase processes which continue to produce HNO3 from NO2, PAN, and OH, over the Gulf of Maine, which could then potentially deposit via dry, wet, and occult (fog) processes were not included in the estimated deposition here, due to insufficient data. Thus, the deposition inputs reported here should be considered a lower limit on the direct atmospheric N flux to the Gulf of Maine.

Total direct atmospheric nitrogen deposition to the Gulf of Maine was highly variable from one day to the next, ranging over three orders of magnitude (from about 1 - 4262 μmol N m^{-2} d^{-1}) with a median daily deposition rate of 23 μmol N m^{-2} d^{-1}. Annual atmospheric nitrogen deposition (on average 52 mmol N m^{-2} yr^{-1}) only contributes about 3% of the total nitrogen input to the surface waters of the Gulf of Maine (5 of 186 x 10^9 mol N yr^{-1}). However, this mechanism is highly episodic with events over 500 μmol N m^{-2} d^{-1} occurring only 8% of the time, yet depositing 56% of the annual flux and

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events over 1000 μmol N m^{-2} d^{-1} occurring only 2% of the time and depositing 22% of the annual flux. Thus, it is estimated that atmospheric nitrogen deposition may be an important source of nitrogen to the Gulf of Maine on an event basis.

The atmospheric nitrogen deposition events reported here are similar to observations from Bermuda. The annual nitrogen flux observed at New Castle was substantially higher than that reported by two nearby NADP coastal sites, exceeding the reported deposition from Cape Cod by 43% and from Mt. Dessert Island by 70% and from reports of other studies in Maine and Massachusetts by about 60%. It is not clear whether these differences are due to nitrogen losses from weekly sampling protocols (as opposed to the daily event based sampling at New Castle) or whether there is a local source of nitrogen near the New Castle sampling site.

The Gulf of Maine has limited access to nutrient rich deep Atlantic waters, although it is well mixed due to tidal forcing. In summer, in the western Gulf of Maine, the water column becomes stratified and the isolated surface waters become severely nitrogen depleted. It is during this time of year, when episodic direct atmospheric nitrogen deposition may enhance the productivity of the Gulf of Maine. It is suggested that large atmospheric nitrogen deposition episodes be used in conjunction with SeaWiFS chlorophyll *a* data to ascertain whether these events lead to discernible blooms, particularly when calm conditions prevail during or following an event. Dense fogs of long duration may be especially suitable for investigation.

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