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DEPOSITION OF AIR POLLUTANTS TO CASCO BAY

**FINAL REPORT
STI-902150-2209-FR2**

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July 3, 2003

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ACKNOWLEDGMENTS

The authors are grateful for the support and assistance of the following people:

- Paul Roberts, Sonoma Technology, Inc., for his suggestions and comments
- Beverly Bayley Smith, Casco Bay Estuary Project (Assistant to the Director)
- Catherine Clayton-Richardson, Ellen Doering, Andy Johnson, John Chandler, and Don Prince of the Maine Department of Environmental Protection
- Diane Gould, Alan Van Arsdale, and Jeri Weiss of the U.S. Environmental Protection Agency, Region I.
- Anonymous peer reviewer.

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EXECUTIVE SUMMARY

ES-1. INTRODUCTION

In 1990, Casco Bay was designated an “estuary of national significance” and included in the U.S. Environmental Protection Agency’s (EPA) National Estuary Program. In response to this designation, the Casco Bay Estuary Project was formed to develop a plan for managing the Casco Bay watershed. Atmospheric deposition is a natural process by which pollutants are transferred from air to soil, surface water, sediment, and groundwater and potentially to living organisms. Wet and dry deposition processes (e.g., rain out, wash out, impaction, adsorption, and absorption) remove particulate and gaseous pollutants from the atmosphere and deposit them on the surface of water bodies, vegetation, buildings and structures, and soil. Transfer of these pollutants from water bodies to sediment occurs through adsorption and sedimentation. Polluted water and sediment lead to undesirable health and environmental impacts, such as mercury-contaminated fish, harmful algal blooms, beach closures, etc.

The current role of atmospheric deposition, as it relates to nitrogen, mercury, and fine particulate matter (PM_{2.5}) pollution in Casco Bay, needed to be better understood and quantified. In response to this need, four types of instruments were deployed at the Casco Bay (Freeport) site to collect samples to investigate the concentrations and deposition of these pollutants: (1) Mercury Deposition Network (MDN) and (2) National Trends Network (NTN) samplers collected weekly samples of wet deposition (total precipitation and pollutant concentrations in the precipitation) of mercury and of inorganic nitrogen from nitrate and ammonium, respectively. Three other sites in Maine also collected mercury and inorganic nitrogen wet deposition data, including the Bridgton site which is located in the Casco Bay headwaters. (3) PM_{2.5} IMPROVE-protocol samplers collected data useful in assessing pollutant sources. These data were compared to those collected at the Acadia IMPROVE site. (4) A prototype sampler also collected polycyclic aromatic hydrocarbons (PAHs); results from these measurements are summarized by Golomb et al. (2001).

Sonoma Technology, Inc. (STI) was contracted by the University of Southern Maine to validate and analyze the data collected at the Casco Bay monitoring site from 1998 through 2001. Analyses included comparing the data from this special study monitoring site to data collected from the National Atmospheric Deposition Program (NADP) samplers at other locations in Maine. The data analysis objectives for this project were to determine

- if atmospheric deposition (both wet and dry) provides significant sources of nitrogen and mercury pollution in Casco Bay;
- how coastal Maine fits into the larger regional pattern of atmospheric deposition; and
- the relative potential contribution of atmospheric deposition to the total pollution measured in the sediments.

The data analyses were also used to determine

- the need to continue measurements of inorganic nitrogen, mercury, and PM_{2.5} data collection at Casco Bay; and

- the significance of short-term (1998-2000) seasonal and annual wet deposition patterns in inorganic nitrogen and mercury within Maine.

In this study, wet deposition is determined by multiplying the weekly amount of precipitation collected at a site by the corresponding weekly average wet concentrations of specific pollutants: ammonium, nitrate, and mercury. Annual deposition was calculated by summing the calculated weekly wet deposition amounts for that year. Dry deposition is not measured in the NADP. Dry deposition is inferred from pollutant concentrations in the ambient air or a ratio of dry deposition to wet deposition is assumed. For this report, 229 square miles was used for the surface area of Casco Bay and 985 square miles for the entire watershed surface area.

Estimating wet and dry deposition to the Casco Bay watershed, based on the measurements available, can be highly uncertain. Contributing to the uncertainty in wet and dry deposition estimates are a number of issues, including the following:

- The loss of volatile species from various sampling media during and after sampling, but before laboratory analysis.
- Uncertainty in the estimate of the surface area of the Casco Bay watershed.
- Uncertainty in the fraction of the material deposited in the Casco Bay watershed that reaches the Bay.
- Variations in the type of precipitation that produces deposition, and thus in the amount of material deposited at the surface.
- Year-to-year meteorological variability, which contributes to variability in annual deposition.

ES-2. KEY FINDINGS

- Atmospheric deposition (estimated dry and wet deposition) of inorganic nitrogen is a significant source of pollution to Casco Bay (see **Figure ES-1**).
 - Wet deposition to the Bay¹ surface area accounts for 200 to 246 tonnes/yr. Dry deposition is estimated to be 146 to 182 tonnes/yr. Total (dry + wet) deposition is 30 to 40% of overall total annual inorganic nitrogen loading to the Bay.
 - If all (wet + dry) deposition to the Casco Bay watershed reached the Bay, then inorganic nitrogen deposition totals roughly 70% of overall loading to the Bay.
- Atmospheric deposition of mercury is the dominant source of mercury to the Casco Bay (see **Figure ES-2**).
 - Wet deposition of Mercury to the Bay surface area accounts for 10 to 16 lbs/yr. Estimates of dry deposition of mercury totaled 4 to 16 lbs/yr. Total deposition may be 84 to 92% of overall mercury loading to the Bay.

¹ Ignoring 2001 data which were anomalously low (less than half the precipitation of the previous three years).

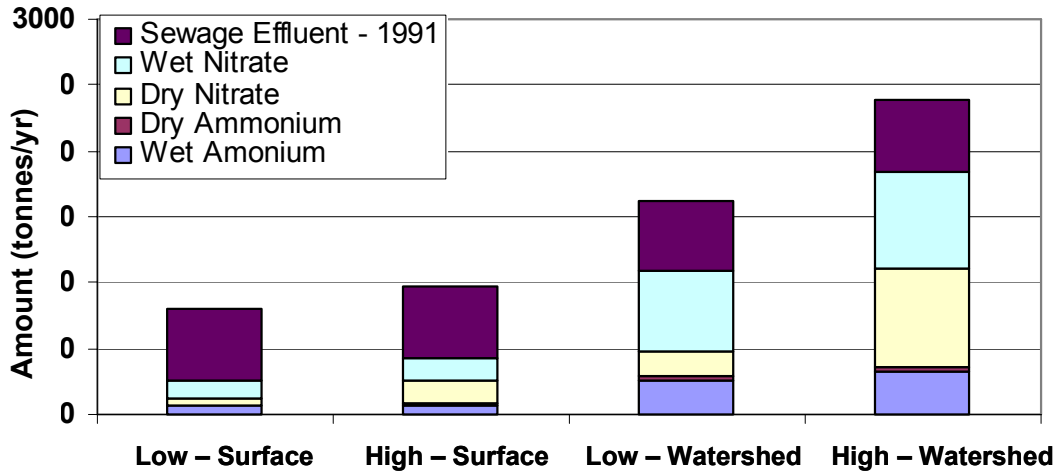


Figure ES-1. Summary of sewage effluent discharges, estimates of dry deposition, and wet deposition of inorganic nitrogen to Casco Bay from 1998 to 2000. “Low” and “high” signify deposition estimate ranges. “Surface” refers to the surface of Casco Bay while “watershed” refers to the entire watershed surface area.

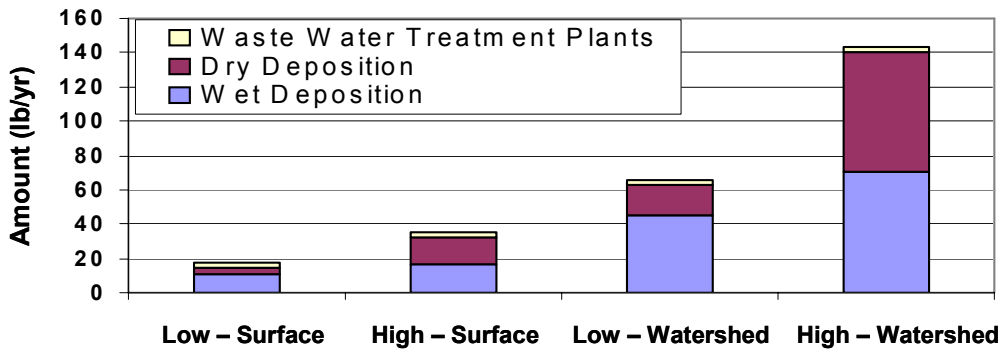


Figure ES-2. Summary of waste water treatment plant direct mercury discharges and dry (estimated) and wet deposition of mercury to Casco Bay. “Low” and “high” signify ranges in dry deposition estimates. “Surface” refers to the surface of Casco Bay and “watershed” refers to the entire watershed surface area.

- Total deposition of Mercury into Casco Bay equals 65 to 143 lbs/yr if all deposition to the Casco Bay watershed reaches the Bay.
- From 1998 to 2001, there was a trend of declining annual mercury, ammonia, and nitrate wet deposition totals at Casco Bay (see **Figures ES-3, ES-4, and ES-5**). This trend was entirely (mercury) or predominantly (ammonia) the result of a corresponding decline in annual precipitation from 1998 to 2001. For nitrate, our analysis suggests that 20% of the decline in deposition over this time period is from a potential corresponding decline in precursor emissions.

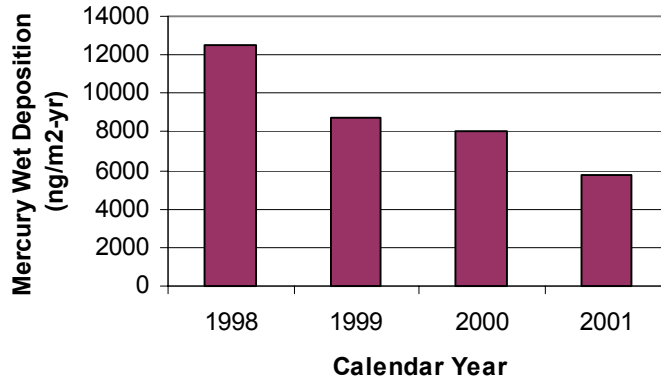


Figure ES-3. Annual wet deposition amounts for mercury from 1998 to 2001 at Casco Bay, which take into account annual changes in precipitation.

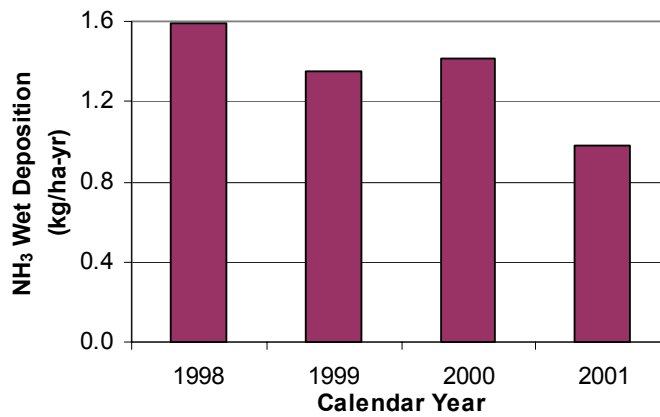


Figure ES-4. Annual wet deposition amounts for ammonia from 1998 to 2001 at Casco Bay, which take into account annual changes in precipitation.

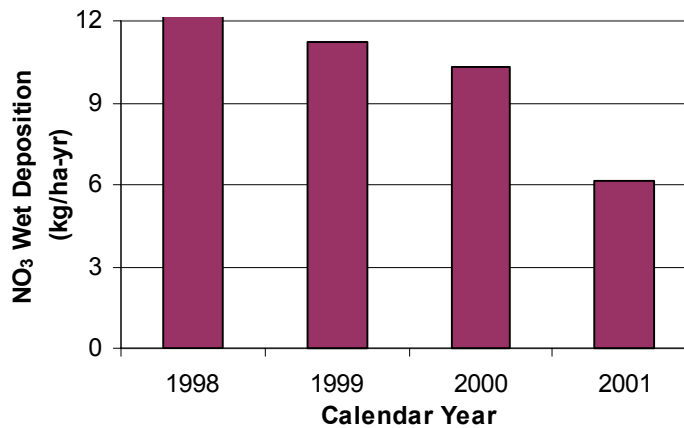


Figure ES-5. Annual wet deposition amounts for nitrate from 1998 to 2001 for Casco Bay, which take into account annual changes in precipitation.

- Understanding regional patterns of air pollution is important for Casco Bay.
 - Long-range transport of pollution in the Bay appears to be important. Trajectory analyses and source apportionment indicate polluted air masses influence the air quality of the Casco Bay area. (Note that local sources also likely contribute to pollution loading in the Bay.)
 - Data from Casco Bay monitors differ from data collected at other Maine monitoring sites, including the headwaters site of Bridgton.
- The seasonal dependence of precipitation (e.g., rain, snow) differed among the sites. Precipitation type is important because snow and rain remove different fractions of air pollutants from the atmosphere. These differences contributed to differences in wet deposition of inorganic nitrogen and mercury among the sites in Maine. For example, more of the precipitation was in the form of rain at Casco Bay than at the other Maine monitoring sites.
- Annual wet deposition rates of inorganic nitrogen are lower in Maine relative to nearby states. Since lower amounts of wet deposition indicate lower levels of air concentrations (or less precipitation) and, thus, emissions, Maine acts as a sink in terms of absorbing inorganic nitrogen emissions from other states. This is consistent with the crude mass balance analysis finding that ammonium and nitrate atmospheric deposition totals are, respectively, one-and-a-half and two to three times greater than the Maine air emission inventory for ammonium and oxides of nitrogen.
- Within Maine, annual wet deposition rates of mercury were similar to or slightly higher than those reported in nearby states. If precipitation is uniform, then similar levels of wet deposition indicate similar levels of air emissions (lb/acre) in each state, implying that Maine is neither a source nor a sink. On the other hand, the crude mass balance approach shows that atmospheric deposition to Maine is about twice the current mercury air emission inventory for Maine. Thus, the crude mass balance approach indicates that Maine is a sink. The wet deposition approach which identifies Maine as neither a source nor a sink is more likely to be correct. The data indicate a low-biased mercury inventory for Maine and/or a high-biased dry deposition rate for mercury.

ES-3. RECOMMENDATIONS

We recommend the consideration of the following studies and analyses to improve the future understanding of the role of nitrogen, mercury, and particles in the air to pollution in Casco Bay. These recommendations involve additional monitoring studies, emission inventory studies, data analyses, and modeling studies. Note that some of these recommendations could be performed using existing data, other recommendations need new resources for new measurements, while other recommendations will not occur for several years after more data is collected and/or new model components are developed.

Monitoring

- Retain speciated PM, wet deposition of nitrogen species, and wet deposition of mercury measurements at the Casco Bay monitoring site near Freeport. Differences between data collected at this site and data collected at other sites in the state are significant.
- Add a CASTNet-type monitoring site at Casco Bay to measure inorganic nitrogen (ammonium, nitrate, and nitric acid) concentrations in the ambient air. These data can be used to better estimate dry deposition rates. In addition, the weekly ambient air data typically provided by a CASTNet monitor can be combined with back trajectory analyses to identify the origin of air parcels with high and low concentrations of ammonium and oxides of nitrogen; these analyses would also help to determine the cause of higher inorganic nitrogen wet deposition concentrations in the summer.
- Assuming that ground-level mercury has some role in mercury wet deposition, monitor ambient air measurements of mercury at Casco Bay to help identify the cause of higher mercury concentrations in precipitation in summer, moderate levels in spring and fall, and lower levels in winter. If these measurements are made on a 24-hr or less sampling frequency, the data could be combined with trajectory analyses to help identify the origin of air parcels with high and low mercury concentrations.
- Consider event sampling of precipitation instead of weekly sampling. One of the observations derived from this study is that a single weekly sample could account for more than 20% of the annual mercury deposition at Casco Bay. During such a week, several storms could arrive at the site from different directions and/or sources, making an assessment of the origin of the mercury extremely difficult, if not impossible.
- Encourage the addition of comparable mercury monitoring sites in nearby states (i.e., Massachusetts, New Hampshire, and Vermont) that currently do not have mercury monitoring. Such information can improve the general understanding of mercury in Maine by classifying other states as sources and sinks. This will also allow a determination of which states are likely over- or understating mercury emissions in the region.

Emission Inventory Analyses and Development

- Update the inventory of direct inorganic nitrogen loading into rivers that empty into Casco Bay. In addition, estimate nitrogen and mercury sources that directly discharge into Casco Bay.
- Update and assess the uncertainty in the mercury air emission inventory for Maine.
- Perform mass balance analyses on data from other states and Canadian provinces. Comparison of air inventories to the corresponding atmospheric deposition rates in those states/provinces will help improve the understanding of sources and sinks of mercury in the Northeast. It will also help identify whether the regional emission inventory for mercury is complete and makes sense when compared to ambient data.
- Identify organic nitrogen air and water emission sources and emission rates (to the extent organic nitrogen is also contributing significantly to water quality issues affected by inorganic nitrogen). Measurements are needed of organic nitrogen atmospheric

deposition; and the “toxicity” of organic nitrogen relative to inorganic nitrogen needs to be established (e.g., what is the relative impact of organic nitrogen relative to inorganic nitrogen on algal blooms?).

Data Analyses

- Perform additional emissions trends analyses for other sites in Maine involving the normalization of wet deposition data by year to reflect longer-term averages.
- Conduct an analysis of seasonal source fingerprints of particles using at least another year or two of IMPROVE protocol data at Casco Bay to provide sufficient samples.
- Perform more comprehensive scatter plot, ratio, factor, and trajectory analyses (using additional years of collected data) in a manner similar to the analysis reported by Polissar et al. (2001) for Underhill, Vermont. This comprehensive analysis could identify source types that impact Casco Bay more precisely.
- Support further research on the causes of seasonal variations in inorganic nitrogen and mercury concentrations in precipitation and the potential differences in the forms of precipitation (e.g., rain versus snow) impacting atmospheric removal rates of nitrogen and mercury. For example, the variation in inorganic nitrogen and mercury concentrations in rain by season may be the result of coincidental changes in ambient temperature.
- Support further research to determine whether a substantial increase in ammonium wet deposition seen in spring, relative to winter, affects plant and marine life in Casco Bay.

Modeling

- Run the Community Multiscale Air Quality modeling system (CMAQ) to determine the contribution of local and out-of-state mercury sources on wet deposition at Casco Bay. As part of this modeling study, update the mercury inventory and dry deposition and/or wet deposition (rain vs. snow) modules. Recent study results by Dvonch et al. (1999) and others should be used to improve the CMAQ chemistry and deposition modules. Consider analysis of CMAQ predictions of wet deposition concentrations (snow vs. rain) in Maine; an EPA report (U.S. Environmental Protection Agency, 1997b) indicates the predecessor model² was calibrated to produce a factor of 2 lower wet concentration in Maine than is being measured at Casco Bay (and Acadia).
- Re-run or analyze the existing output of the EPA acid rain model to determine whether the model is correctly predicting the strong temporal correlation found between wet ammonium and wet nitrate ($r^2 = 0.69$) and between ammonium and nitric acid air concentrations ($r^2 = 0.71$) in coastal Maine and the poorer correlations found in nearby states. This is critical to our understanding and comprehension of the reliability of the chemistry module in the EPA acid rain model. This information would be helpful to further our comprehension of the reliability of the EPA acid rain model for making near- and far-field source contribution estimates within Maine.

² Regional Lagrangian Model of Air Pollution - RELMAP

- Perform a modeling analysis that estimates the range and likely percentage of mercury and inorganic nitrogen (ammonium, oxides of nitrogen) atmospheric deposition to the watershed that reaches Casco Bay. This will enable better estimations of the amount of wet deposition to the watershed that reaches Casco Bay. Timing as to when atmospheric deposition to the watershed reaches Casco Bay is also important because even though some wet deposition as snow occurs inland in the winter, it is important to understand whether most of this deposition reaches the Bay in another season (e.g., spring) after snowmelt has begun and/or has been completed. A sudden input of a large quantity of nitrogen into the Bay can result in poor water conditions.
- Perform a multimedia Casco Bay surface water and sediment modeling analysis that incorporates the findings of the watershed modeling, dry and wet deposition data, and an updated inventory of surface water sources. Such a study could be used to assess the ability to predict current levels of pollution in Casco Bay. Results could also be used to determine how future changes in air emissions would likely relate to pollution levels within the Bay.

1. INTRODUCTION

1.1 BACKGROUND

In 1990, Casco Bay (see **Figures 1-1 through 1-3**) was designated an “estuary of national significance” and included in the U.S. Environmental Protection Agency’s (EPA) National Estuary Program.³ In response to this designation, the Casco Bay Estuary Project was formed to develop a plan for managing the Casco Bay watershed. A plan for the Bay was adopted in 1996. Environmental issues identified in the Casco Bay Plan (University of Southern Maine, 1996) included the presence of the following:

- Nuisance algal blooms from excess nitrogen. The blooms cause mortality in shell fish and other marine animals.
- Elevated levels of mercury, cadmium, and polycyclic aromatic hydrocarbons.
- Fish advisories due to elevated levels of methyl mercury in watershed fish.

The current role of atmospheric deposition as it relates to nitrogen and mercury pollution in Casco Bay needed to be better understood and quantified. Three types of samplers were deployed in the Casco Bay area (Freeport) to collect data to investigate the concentrations and deposition of these pollutants. A fourth type of sampler collected polycyclic aromatic hydrocarbons (PAHs); results from these measurements are summarized by Golomb et al. (2001).

Nitrogen Sampling at Casco Bay

Atmospheric deposition is often a major source of nitrogen loading in bodies of water, such as bays. For example, EPA reports deposition has been identified as a primary source of nitrogen loading in Chesapeake Bay (U.S. Environmental Protection Agency, 2000a). Eutrophication⁴ of coastal bays due to enhanced nitrogen (nitrates and ammonia) deposition continues to be a concern of water quality planners. The National Atmospheric Deposition Program (NADP)-type collector at the Casco Bay Wolfe’s Neck Farm near Freeport, Maine, measures nitrogen and ammonia in precipitation (as well as other chemicals). This measurement of nitrogen wet deposition at Casco Bay helps analysts quantify total (wet and dry deposition) nitrogen loading.

³ The National Estuary Program was established in 1987 to protect nationally significant estuaries threatened by pollution, development, or overuse.

⁴ Gradual increase in the concentration of phosphorus, nitrogen, and other plant nutrients in an aging aquatic ecosystem such as a lake. The productivity or fertility of such an ecosystem increases as the amount of organic material that can be broken down into nutrients increases. This material enters the ecosystem mainly through runoff that carries debris. Water blooms often develop on the surface, preventing the light penetration and oxygen absorption necessary for underwater life.

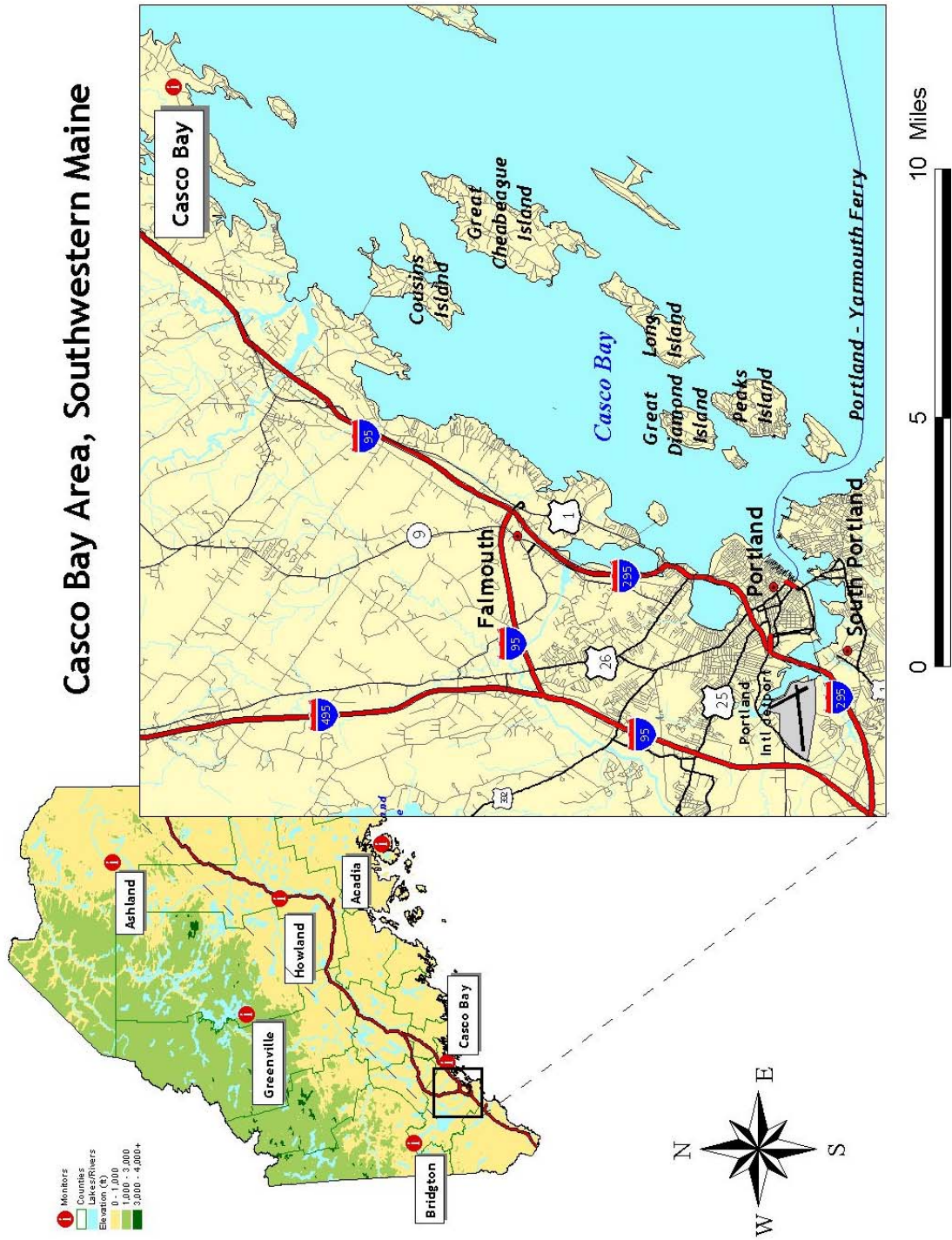


Figure 1-1. Map of the Casco Bay area.

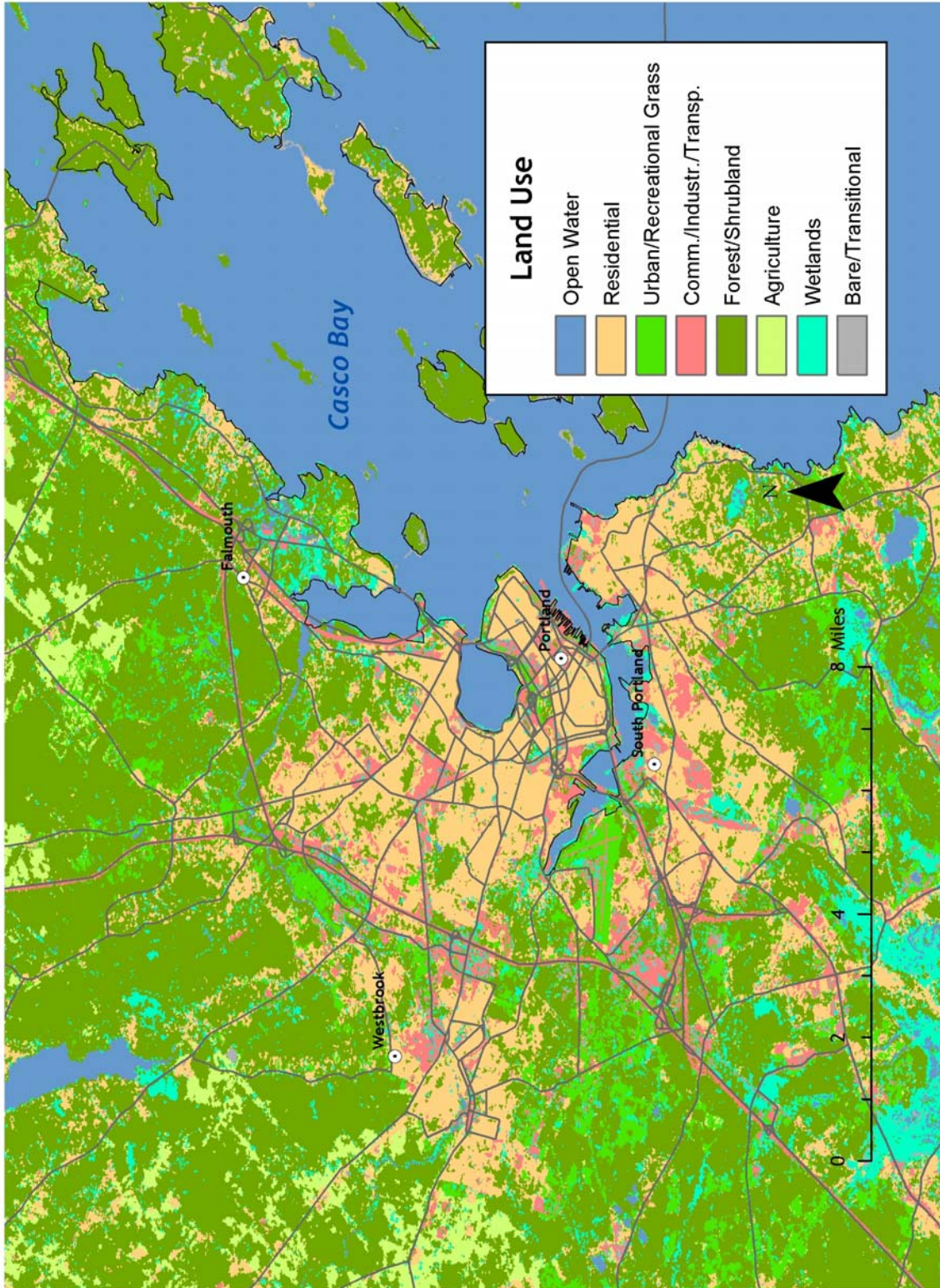


Figure 1-2. Casco Bay area land use.

The Casco Bay Watershed

The 985 square miles of land and water that drain into Casco Bay form its watershed. Water in this area flows down streams and rivers or through the ground and eventually reaches Casco Bay. The health of Casco Bay depends on protecting all water in the watershed.



Figure 1-3. Casco Bay Watershed (University of Southern Maine, 2002).

Mercury Sampling at Casco Bay

Mercury contamination has been documented for several mammals, birds, and reptiles (U.S. Environmental Protection Agency, 1997a). These species are at high risk of mercury exposure and effects because they either eat mercury-contaminated fish or consume other animals that eat these fish. EPA modeling analyses suggest it is probable that individuals of some highly exposed wildlife subpopulations are adversely affected due to bioaccumulation of mercury that originated as airborne mercury emissions (U.S. Environmental Protection Agency, 1997a). With respect to humans, women of childbearing age and infants are regarded as the population of greatest interest (U.S. Environmental Protection Agency, 2000a). Women in the Casco Bay area have been advised by the Food and Drug Administration and by state agencies to limit their consumption of potentially contaminated fish. Coastal mercury advisories are in place along the coast of Maine and from the coast of North Carolina to Texas (see **Figure 1-4**). Specifically, advisories in the United States have been issued by more than 39 states and several Native American tribes, warning against consumption of certain species of fish contaminated with methyl mercury. The Casco Bay Wolfe's Neck Farm monitoring site provides a key location within a large regional network of mercury deposition monitoring stations in New England and Eastern Canada. The Casco Bay Mercury Deposition Network (MDN)-type wet deposition data is being used to monitor deposition of mercury in Casco Bay.

PM_{2.5} Sampling at Casco Bay

The fine particulate matter (PM_{2.5}) sampler at the Casco Bay Wolfe's Neck Farm station is important because it provides estimates of the concentration of toxic trace elements. These data are useful in assessing likely source types of toxic emissions and, with the use of trajectory analyses, in assessing likely transport pathways, and therefore, source areas, of the air parcels. These data also provide a wider range of pollutants with which to compare to other sites. Measurements are made using a sampler similar to those used in the Interagency Monitoring of Protected Visual Environments (IMPROVE) program (i.e., IMPROVE-protocol samples).

Sampling at Other Maine Sites

Nitrogen and mercury wet deposition and PM_{2.5} data from other sites in Maine were also investigated as a part of this project; these data are discussed in detail in Section 2. Note that one of the sites at which measurements are made is Bridgton, situated in the headwaters of the Casco Bay watershed. Characterizing the differences and similarities in pollutant concentrations between Bridgton and Casco Bay is important to understanding deposition in the watershed. The nitrogen and mercury wet deposition measurements made at Bridgton are part of the NADP. PM_{2.5} data collection from Bridgton began in March of 2001 as part of the IMPROVE program.

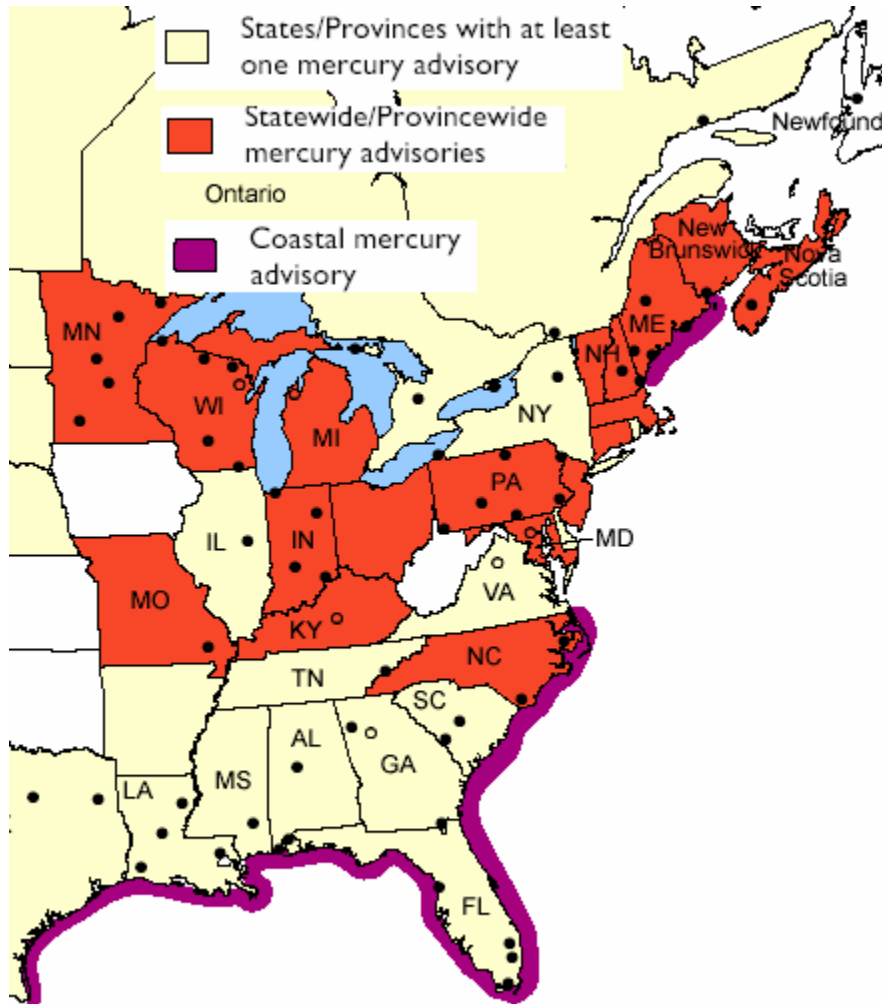


Figure 1-4. Mercury Deposition Network (MDN) sites in the eastern United States and mercury fish advisories (from <<http://nadp.sws.uiuc.edu/mdn/>, last accessed July 9, 2002>).

1.2 DATA ANALYSIS OBJECTIVES AND APPROACH

Sonoma Technology, Inc. (STI) was contracted by the University of Southern Maine to validate and analyze the data collected at the Casco Bay monitoring site. Data from the other Maine monitoring sites were also used in our analyses. The data analysis objectives for this project were to determine

- if atmospheric deposition (both wet and dry) provides significant sources of nitrogen and mercury pollution in Casco Bay;
- how Coastal Maine fits into the larger regional pattern of atmospheric deposition; and
- the relative potential contribution of atmospheric deposition to the total pollution measured in the sediments.

A four-step approach was used to address the objectives:

1. Acquire, format, and validate the Casco Bay data.
2. Analyze nitrogen, mercury, and fine particle data including assessing seasonal trends, and compare Casco Bay data to other Maine sites for which wet deposition measurements have been taken.
3. Estimate dry deposition for nitrogen (nitrate and ammonia) and mercury, combine estimates with wet deposition data, and compare total (wet plus dry) deposition estimates to other sources of mercury and nitrogen loading to the Bay.
4. Prepare reports and presentations and attend meetings.

The data analyses were also used to determine

- the need to continue measurements of inorganic nitrogen, mercury, and PM_{2.5} data collection at Casco Bay; and
- the significance of short-term (1998-2000) seasonal or annual patterns in inorganic nitrogen and mercury wet deposition within Maine.

1.3 DISCUSSION OF DEPOSITION

A variety of air pollutants have harmful effects on human health and the environment. Air pollutants have both natural (e.g., sea salt, volcanoes) and anthropogenic sources. Five categories of air pollutants with the greatest potential to harm water quality are nitrogen, mercury, other metals (such as cadmium), combustion emissions, and pesticides. Polluted water and sediment lead to undesirable health and environmental impacts, such as mercury-contaminated fish, harmful algal blooms, beach closures, etc.

Atmospheric deposition is one path in which pollutants are transferred from air to soil, surface water, sediment, and groundwater and potentially to living organisms (Ryan, 1993). Wet and dry deposition processes (e.g., rain out, wash out, impaction, adsorption, and absorption) remove particulate and gaseous pollutants from the atmosphere (Chinkin et al., 1994) and deposit these pollutants on the surface of water bodies (Cohen and Ryan, 1985a), soil (Cohen and Ryan, 1990), and vegetation. Transfer of these pollutants from water bodies to sediment through adsorption and sedimentation. **Figures 1-5 and 1-6** provide an illustration of the potential pathways for nitrogen and mercury to enter a system such as Casco Bay.

Additional information regarding wet and dry deposition processes is available on the Internet via educational support material (e.g., Guttorp, 1986), monitoring programs (e.g., U.S Environmental Protection Agency, 2002a, <<http://www.epa.gov/castnet/deposition.html>>), and ongoing research (e.g., National Oceanic and Atmospheric Administration, 1998). Excellent discussions of deposition processes are also provided by Seinfeld and Pandis (1998).

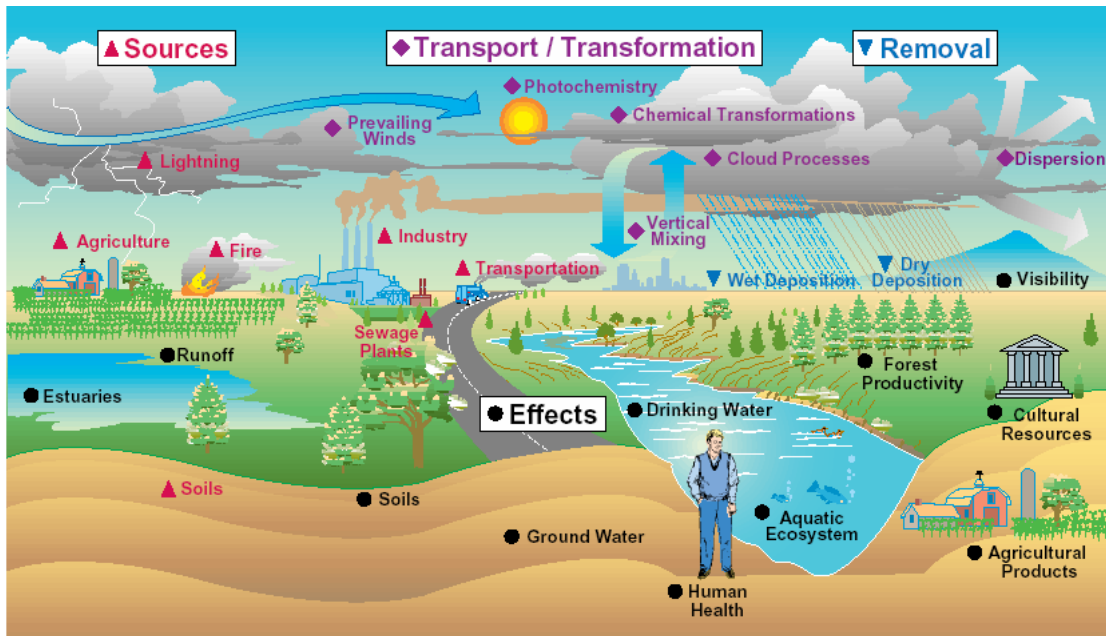


Figure 1-5. Illustration of potential pathways for nitrogen to enter estuaries and bays. (Adapted from National Science and Technology Council Committee on Environment and Natural Resources, Air Quality Research Subcommittee, 1999.)

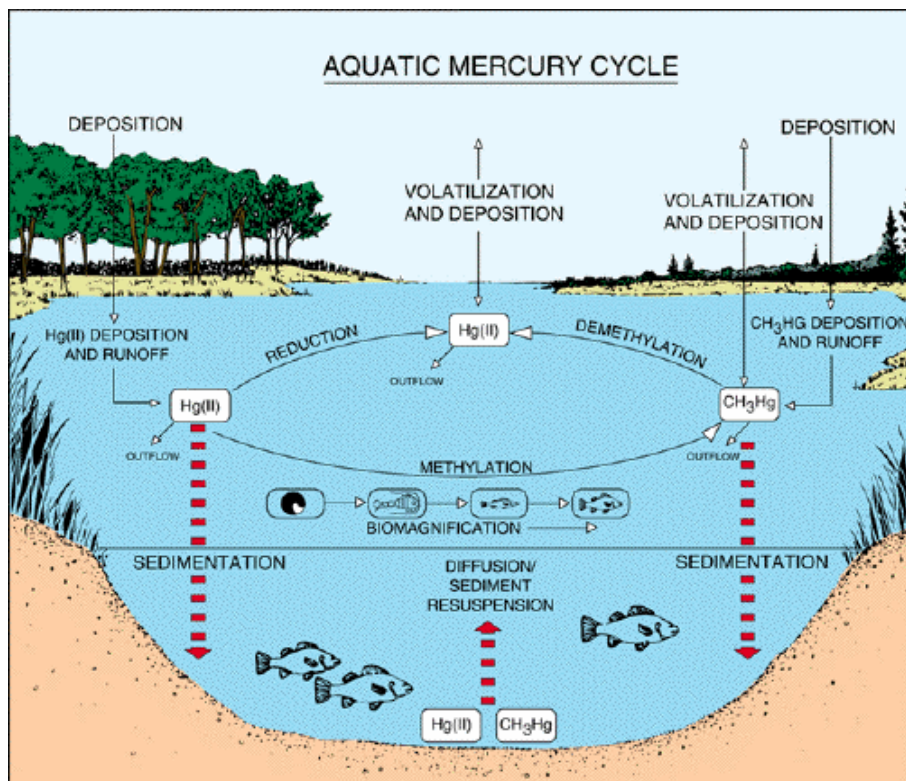


Figure 1-6. Aquatic mercury cycle (from Krabbenhoft and Rickert, 2002).

The NADP operates a Mercury Deposition Network (MDN) and a National Trends Network (NTN) that measure the wet deposition of inorganic nitrogen from nitrate and ammonium. Both networks measure weekly wet deposition (total precipitation and pollutant concentrations in the precipitation). Casco Bay is one of the sites at which mercury and inorganic nitrogen (ammonium and nitrate) wet deposition data are collected. Three other sites in Maine also collect mercury and inorganic nitrogen wet deposition data including Bridgton in the Casco Bay headwaters.

In this study, wet deposition is determined by multiplying the weekly amount of precipitation collected at a site by the corresponding weekly average wet concentrations of specific pollutants: ammonium, nitrate, and mercury. Missing data were substituted with estimates of wet deposition⁵. Annual deposition was calculated by summing the calculated weekly wet deposition amounts for that year. Because of differences in the amount of mercury and inorganic nitrogen present in the atmosphere, wet deposition amounts for these pollutants are reported differently. For mercury, wet deposition in this report is presented

- in micrograms per square meter per week ($\mu\text{g}/\text{m}^2 \text{ wk}^{-1}$);
- annually, in units of nanograms per square meter per year ($\text{ng}/\text{m}^2 \text{ yr}^{-1}$); and
- in pounds per year (lb/yr) for the surface area of Maine.

Inorganic nitrogen (ammonium, nitrate, and nitric acid)⁶ wet deposition is reported

- in units of kilograms per hectare per week ($\text{kg}/\text{ha} \text{ wk}^{-1}$);
- annually, in kilograms per hectare per year ($\text{kg}/\text{ha} \text{ yr}^{-1}$); and
- in metric tons per year (tonnes/yr) for the surface area of Maine.

Dry deposition is not directly measured in the NADP. A ratio of dry deposition to wet deposition is assumed, or dry deposition is inferred, from pollutant concentrations in the ambient air.

Atmospheric deposition is important to the watershed that serves a particular river, lake, estuary, or bay. For example, over 90% of the mercury entering the Chesapeake Bay watershed (U.S. Environmental Protection Agency, 2000a) is believed to be retained in the watershed and not reach the Bay. The Chesapeake Bay watershed is estimated as 900,000 square kilometers, which is about 350 times the size of the Casco Bay watershed of about 2,550 square kilometers. For this report, we have used 229 square miles for the surface of Casco Bay and 985 square miles for the entire watershed surface area.

⁵ When precipitation data were available but no chemistry data were reported (only a few samples), the nitrogen or mercury wet deposition was estimated by multiplying the measured precipitation amount by the ratio of the annual average wet deposition of mercury or nitrogen to the annual average precipitation. This approach is generally accepted, but not without controversy. For example, seasonal average concentrations could be applied rather than annual.

⁶ Total nitrate is measured; there is no distinction between nitrate that entered the sampler as a particle versus nitrate as gaseous nitric acid.

1.4 OVERVIEW OF THE REPORT

This report builds on previous work by Mosher (2000) and a presentation by Clayton-Richardson (2001) at the 2001 Maine Water Conference. Section 2 discusses data availability and validation. Section 3 describes the analyses of nitrogen, mercury and fine particle concentrations, and wet deposition data. Section 4 discusses wet deposition trends. Section 5 describes how STI estimated total deposition of nitrogen (nitrate and ammonia) and mercury. Section 6 provides conclusions and recommendations and Section 7 contains references cited in the report.

Several appendices contain the following information:

- Appendix A lists chemical species abbreviations.
- Appendix B contains time series plots for Casco Bay IMPROVE (1999 and 2000), NTN (1998-2001), and MDN (1998-2001) measurements.
- Appendix C contains summary statistics of IMPROVE, NTN, and MDN data from other Maine sites.
- Appendix D shows selected scatter plot matrices and box plots of pollutant data collected at Casco Bay, Acadia, Bridgton, and Greenville, Maine from 1998 to 2001.
- Appendix E contains a Pearson correlation table for Casco Bay IMPROVE data for 1999-2000.

2. DATA AVAILABILITY AND VALIDATION

2.1 OVERVIEW OF MEASUREMENTS

Data for this project were obtained from several sources. A summary of available IMPROVE, NTN, MDN, Photochemical Assessment Monitoring Station (PAMS), and Clean Air Status and Trends Network (CASTNet) data is provided in **Table 2-1**. Data were obtained from a number of sources including the network web sites, the IMPROVE contractor (Air Resource Specialists, ARS), and the EPA’s aerometric information retrieval system (AIRS). Figure 1-1 shows the locations of the Casco Bay (Freeport), Bridgton, Acadia, and Greenville sites.

Table 2-1. IMPROVE, NTN, MDN, and CASTNet data collected in Maine and used in this analysis.

Site	Network	Elevation (m)	Date Range	Data Source
Casco Bay (aka Wolf’s Neck; Freeport site)	IMPROVE	15	8/9/98-3/14/01	ARS
	NTN		1/6/98-12/4/01	NADP
	MDN		1/6/98-6/26/01	NADP
	Meteorological		1/1/98-12/31/01	NADP
Bridgton	NTN	222	1/6/98-12/4/01	NADP
	MDN		1/6/98-6/26/01	NADP
Acadia	IMPROVE	129	8/9/98-2/26/00	IMPROVE
	NTN		1/6/98-11/27/01	NADP
	MDN	152	1/6/98-6/26/01	NADP
	CASTNet		1/5/99-12/26/00	CASTNet
Greenville	NTN	322	1/6/98-12/4/01	NADP
	MDN		1/6/98-6/26/01	NADP
Ashland	CASTNet	235	1/6/98-12/26/00	CASTNet
Howland	CASTNet	69	1/6/98-12/26/00	CASTNet

IMPROVE-protocol (henceforth, IMPROVE) data have been collected at the Casco Bay site since January 1998. However, serious problems were noted in the data collected in the first part of 1998. After discussion with analytical laboratory staff, the Casco Bay Project scientists concluded that changes in the collection technique and analytical laboratory that occurred in July 1998 led to a change resulting in incomparability of data collected before and after the changes. Therefore, IMPROVE data collected at Casco Bay prior to August 8, 1998, were not included in the analyses described in this report.

All data reported below the minimum detection limit (MDL) were replaced with MDL/2 in the project database. Data reported with invalid codes by the laboratory were not used in the analyses.

Data were processed and stored in several formats including MS Excel, SYSTAT, and MS Access. The MS Access files were provided to the Casco Bay Estuary project team for future use.

2.1.1 IMPROVE Data

The IMPROVE sampler (**Figure 2-1**) at Casco Bay collects 24-hr average samples every sixth day following the State Implementation Plan (SIP) calendar. This differs from the IMPROVE program that sampled on Wednesdays and Saturdays (IMPROVE, 2002) before 2000, and every third day starting in 2000. The sampler has three modules. One module collects PM_{2.5} on Teflon filters which are analyzed by five methods:

- Gravimetric mass for PM_{2.5} mass
- Hybrid integrating plate/sphere (HIPS) method for optical absorption
- Proton elastic scattering analysis (PESA) for elemental hydrogen
- Proton induced x-ray emission (PIXE) for the elements sodium through manganese
- X-ray fluorescence (XRF) for the elements iron through lead



Figure 2-1. IMPROVE sampler similar to that used at Casco Bay (Clayton-Richardson, 2001).

A second module collects PM_{2.5} samples on nylon filters. A denuder is used before the nylon filter to remove nitric acid vapors. The denuder and filter are analyzed by ion chromatography (IC) for nitrate, chloride, sulfate, and nitrite ions. A third module collects PM_{2.5} samples on quartz filters. These samples are analyzed for eight different organic carbon (OC) and elemental carbon (EC) fractions using the thermal optical reflectance (TOR) method at Desert Research Institute.

Data were obtained for the Casco Bay site from the IMPROVE contractor (ARS). All data were reported in ng/m³. Analysis for sodium through magnesium and aluminum, bromine, calcium, chromium, iron, potassium, and manganese, switched from PIXE to XRF starting

May 30, 2000. We also noted that phosphorus concentrations were often reported as zero (below detection) until May 30, 2000, after which phosphorus concentrations were consistently reported greater than 0, indicating an improvement in the detection limit for this element.

Several species were not reported in every sample including silver, gold, cadmium, barium, and ammonium; these data were always reported as -9999 (missing) or below detection (0). The data below detection were eventually replaced with MDL/2. Cobalt, gallium, and mercury⁷ concentrations were above detection only in a few samples and were not further assessed. There were many negative OC1 and EC3 values (see Appendix A for species names). In order to prepare the total OC and EC sums, we replaced the negative values at Casco Bay with the average MDL/2. MDL values are provided in **Table 2-2** for Acadia and Casco Bay.

Seasons were assigned as follows:

Season = 1: winter = December, January, February

Season = 2: spring = March, April, May

Season = 3: summer = June, July, August

Season = 4: fall = September, October, November

Definitions of all species and units are provided in Appendix A. **Table 2-3** provides a list of sums computed using the data following the IMPROVE methods (e.g., IMPROVE, 1995; 2002).

2.1.2 NTN Data

Precipitation chemistry data collected as a part of the NADP at Casco Bay (**Figure 2-2**) reflects weekly integrated samples. The sampling bucket is set up each Tuesday and removed the following Tuesday. Samples are sent to a central analytical laboratory where they are analyzed for hydrogen ion (acidity as pH), sulfate, nitrate, ammonium, chloride, and base cations (Ca^{+2} , Mg^{+2} , K^+ , and Na^+). A rain gauge provides precipitation information.

Data below detection were replaced with MDL/2; the original data designated the concentrations below detection with a “<” sign next to the data point. Dry samples (originally designated as -9) were not used, nor were samples with a laboratory validation code of 0 (indicating an invalid sample). All species concentrations were reported in mg/L except for hydrogen ion (in pH units), with precipitation in mm as rain. In the files, dates were reported as end date. For subsequent analyses and plots, begin dates were used unless otherwise noted.

Precipitation type was found in the daily precipitation reports (obtained from the NADP web site, <<http://nadp.sws.uiuc.edu/>>, last accessed July 2002). Mixed precipitation indicates that both rain and frozen precipitation fell during the week of sampling.

⁷ Hg volatilization from the filter is also a problem.

Table 2-2. Minimum detectable limits of elements in ng/m³ for Acadia and Casco Bay IMPROVE data. MDLs were sample-specific in 1998-2000 data. Species abbreviations are provided in Appendix A.

Dates	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr
6/1988-5/1992 ^a	8.7	2.9	1.8	1.4	1.3	1.2	1.3	0.83	0.64	0.57	0.50	0.41
6/1992-5/1994 ^a	13.0	4.8	3.0	2.2	1.9	1.9	2.0	1.2	0.90	0.81	0.69	0.57
1998-2000 ^b	8.0-59.	4.5-28.	2.9-14.	2.3-11.	2.1-10.	2.0-9.5	0-150	1.3-6.3	1.0-4.7	0.96-4.3	0.82-3.5	0.68-2.8
	Fe	Ni	Cu	Zn	Ga	Se	Br	Rb	Sr	Zr	Pb	Mn
6/1988-5/1992	0.34	0.24	0.24	0.21	0.20	0.22	0.25	0.37	0.42	0.65	0.57	0.39
6/1992-5/1994	0.11	0.05	0.05	0.05	0.03	0.03	0.03	0.06	0.07	0.11	0.06	0.52
1998-2000	0.16-0.38	0.09-0.21	0.08-0.2	0.08-0.19	No data	0.05-0.11	0.06-0.11	0.1-0.18	0.11-0.22	0.17-0.34	0.1-0.2	0.56-2.8
	As	PM _{2.5}	NO ₂	NO ₃	SO ₄	OC1	OC2	OC3	OC4	OP	EC1	EC2
1998-2000	0.05-0.09	306-346	7.6-105	6.5-24	8-45	82-199	80-148	66-189	28-60	18-53	20-45	23-59
	EC3											
1998-2000	9-26											

^a From University of California Davis (1995).

^b From the data set provided.

Table 2-3. Sums computed following the IMPROVE methods (IMPROVE, 1995; 2002).

Sum	Description	Assumptions/comments
Anions	$Cl^-/35.453 + NO_3^-/62.005 + SO_4^{2-}/48.03$	
Sulfate	$4.125[S]$	Total ammonium sulfate; assumes all elemental sulfur is derived from sulfate. S from Teflon filters is a better measure than sulfate from Nylon filters.
Nitrate	$1.29[NO_3^-]$	Total ammonium nitrate; assumes that the denuder efficiency is close to 100%.
Soil	$2.2[Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti]$	This is the sum of elements predominantly associated with soil, plus oxygen for the normal oxides (Al_2O_3 , SiO_2 , CaO , K_2O , FeO , Fe_2O_3 , TiO_2), plus a correction (a factor of 1.16) for other compounds including MgO , Na_2O , water, and carbonate
Nonsoil K (KNON)	$[K] - 0.6[Fe]$	
LAC (light absorbing carbon)	$[E1] + [E2] + [E3] - [OP]$	E1 was frequently below detection; MDL/2 was substituted.
OC	$[OC1] + [OC2] + [OC3] + [OC4] + [OP]$	
OC mass (OCM)	$1.4[OC]$	Assumes the average organic molecule is 70% carbon
TC	OC + LAC	
RCFM (reconstructed fine mass)	sulfate + nitrate + OC mass + LAC + soil	
Marine	$2.5[Na^+]$	
RCFM + Marine	RCFM + Marine	



Figure 2-2. Photo of NADP sampler at the Casco Bay site (National Atmospheric Deposition Program, 2002a).

2.1.3 MDN Data

Mercury deposition data are collected weekly at Casco Bay similar to the NADP program (see Figure 2-2). Precipitation samples are collected and mailed to the Hg Analytical Lab (HAL) at Frontier Geosciences in Seattle, Washington, for analysis by cold vapor atomic fluorescence. Total mercury data are reported for Casco Bay.

MDN data with a quality control (QC) code of C (invalid data assigned by the laboratory) and “no precipitation” samples (precipitation values reported as 0 and Hg as -9 [missing]) were not used in our analyses. There were many instances of missing data (with neither 0 nor -9 reported) as listed in **Table 2-4** (the table shows both MDN and NTN data). **Table 2-5** lists the MDN samples that were not reported (but according to rain gauge information should have sampled precipitation). There were four samples missing from Casco Bay, three missing from Bridgton, and one each missing from Acadia and Greenville.

2.1.4 Meteorological Data

Precipitation data were obtained from the MDN and NTN program rain gauges. Surface meteorological data for Freeport were obtained from the Maine Department of Environmental Protection (DEP) in a series of spreadsheets.

2.1.5 CASTNet Data

We also obtained data from CASTNet for use in computing dry deposition. This network provides atmospheric data on the dry deposition component of total acid deposition, ground-level ozone, and other forms of atmospheric pollution (U.S. Environmental Protection Agency, 2002a). Ambient air concentrations of nitric acid, nitrate, and ammonium are collected hourly and used with meteorological data, land use, vegetation, and surface conditions to estimate weekly average nitric acid, nitrate, and ammonium dry deposition rates. Note these data were not available for the Casco Bay watershed.

Table 2-4. Weekly samples with no precipitation (“dry”), samples that were missing, or samples that did not meet laboratory QC screening criteria in the MDN and NTN networks (designated by “x”).

Page 1 of 2

Begin Date	Acadia MDN	Acadia NTN	Bridgton MDN	Bridgton NTN	Freeport MDN	Freeport NTN	Greenville MDN	Greenville NTN
1/27/1998							x	x
2/3/1998	x	x	x	x	x	x	x	x
3/24/1998			x	x	x	x		
4/7/1998	x	x	x	x	x	x	x	x
5/12/1998			x	x	x	x	x	x
8/4/1998	x	x						
9/15/1998	x	x						
9/29/1998			x	x	x	x		
10/20/1998	x	x	x	x	x	x		
11/3/1998	x	x	x	x	x	x		
12/15/1998	x	x						
12/22/1998	x	x			x	x	x	
1/26/1999	x	x			x	x	x	x
4/13/1999	x	x					x	x
4/20/1999			x					
4/27/1999	x	x	x	x	x	x	x	x
5/11/1999	x	x	x	x	x	x	x	
5/25/1999	x	x						
6/15/1999	x	x			x	x		
7/6/1999					x	x		
7/13/1999							x	x
7/27/1999	x	x	x	x	x	x		
8/31/1999	x	x					x	x
10/26/1999	x	x	x	x	x	x		
12/21/1999	x	x	x	x	x	x	x	x
1/18/2000			x	x	x	x		

Table 2-4. Weekly samples with no precipitation (“dry”), samples that were missing, or samples that did not meet laboratory QC screening criteria in the MDN and NTN networks (designated by “x”).

Page 2 of 2

Begin Date	Acadia MDN	Acadia NTN	Bridgton MDN	Bridgton NTN	Freeport MDN	Freeport NTN	Greenville MDN	Greenville NTN
2/1/2000	x	x	x	x	x	x	x	x
2/15/2000	x	x						
2/22/2000	x	x						
5/31/2000	x	x					x	x
7/25/2000								
9/5/2000	x	x	x	x	x	x	x	x
9/26/2000	x	x	x	x				
10/10/2000	x	x						
11/28/2000					x	x	x	x
1/23/2001			x	x	x	x	x	x
2/27/2001							x	x
4/3/2001							x	
4/17/2001							x	x
4/24/2001			x	x				
7/31/2001	x	x						x
8/21/2001	x	x	x	x				
9/11/2001	x	x					x	x
11/13/2001	x	x						

Table 2-5. MDN samples not reported in the database obtained from the MDN web site. Reasons for data gaps are not documented on the web site.

Date	Acadia	Bridgton	Freeport	Greenville
1/13/98-1/20/98		✓		
4/14/98-4/21/98		✓		✓
4/21/98-4/28/98	✓		✓	
10/20/98-10/27/98		✓		
5/15/01-5/22/01			✓	
5/22/01-5/29/01			✓	
5/29/01-6/5/01			✓	

2.2 DATA VALIDATION

2.2.1 Approach

Data validation is critical because serious errors in data analysis and modeling results can be caused by erroneous individual data values. Example guidelines that we employ for PM data validation are documented in the EPA PM_{2.5} Data Analysis Workbook (Main and Roberts, 2001). Internal consistency checks of the IMPROVE-like data include

- Inspecting time series of all species, selected species ratios, and calculated sums.
- Comparing species concentrations using scatter plots. These investigations are also useful in data analysis.
- Checking the sum of chemical species (i.e., the sum of elements, ions, and carbon with no double-counting of species such as chloride and potassium) versus PM_{2.5} mass.
- Checking physical and chemical consistency including sulfate by ion chromatography (IC) versus total sulfur by XRF (the expected ratio of water-soluble sulfate to total sulfur is about 3); soluble potassium by atomic absorption versus total potassium by XRF (the expected ratio of water-soluble potassium to total potassium should be < 1); and soluble chloride by IC versus chlorine (the expected ratio of chloride to total chlorine should be < 1).
- Preparing material balances (i.e., geological aluminum, silicon, calcium, and iron oxides; OC, EC, ammonium nitrate and sulfate, other trace elements, and unidentified mass).

For the MDN data, time series plots of mercury concentration and deposition were prepared and inspected. For the NTN data, time series and scatter plots of all ions were prepared and inspected. A scatter plot of the field versus laboratory pH was also prepared.

2.2.2 Results

We focused validation efforts on the Casco Bay data and performed only a cursory review of the data from other sites. Time series plots are provided in Appendix B.

No Casco Bay IMPROVE data were flagged. A few samples appeared odd compared to others (i.e., stood out on scatter plots as outliers)⁸; however, three of these samples appeared to be from dust events identified by high concentrations of calcium (March 1, 2000), silicon (January 29, 1998), aluminum and iron (May 24, 2000) and one from increased marine (sodium and chloride) influence (March 1, 1999). We noted two troubling items:

- Comparison of the XRF sulfur and sulfate ion concentrations at Acadia shows excellent agreement while the same comparison at Casco Bay shows much more scatter (**Figure 2-3**). In addition, the relationship between the two measurements appears to change from year to year at Casco Bay. Researchers at the University of California, Davis, recommend using the Teflon PIXE-derived sulfur values as the measure of sulfate because of possible adsorption of sulfur dioxide (SO₂) on the nylon filter (from which sulfate values are derived). This possible SO₂ adsorption would be indicated by sulfate values from the nylon filters being greater than sulfate values from the Teflon filters. A large number of the data values show the opposite of this trend in Figure 2-3 (especially all of 2000). We are not sure of the cause of this difference.
- The reconstructed fine mass and measured PM_{2.5} correlate reasonably well at both Acadia and Casco Bay (**Figure 2-4**). However, the Casco Bay data show more scatter than Acadia, and the 1998 Casco Bay data have the most outliers. We used RCFM+marine to compute fractions of key PM_{2.5} components.

Since we are not using these data to estimate deposition, but rather to investigate potential pollutant source types and regional transport, these validation items are not critical to the conclusions of this report.

For the NTN data, we flagged the potassium concentration as suspect in the weekly sample collected ending on June 14, 1999, at Casco Bay. The potassium concentration was nearly an order of magnitude higher than in any other sample (**Figure 2-5**). This sample was not used in subsequent analyses. The sample collected ending on March 30, 1999, exhibited high concentrations of several species, but the relationships were similar to other samples; therefore, the sample was not flagged. Field and lab pH values matched reasonably well (**Figure 2-6**).

We did not apply any additional flags to the MDN data. For the CASTNet data, we used annual average data only and did not perform a quality assurance/quality control (QA/QC) review of the individual data. We recommend that a QA/QC review of this data be made in the future.

⁸ Also termed “extreme values”.

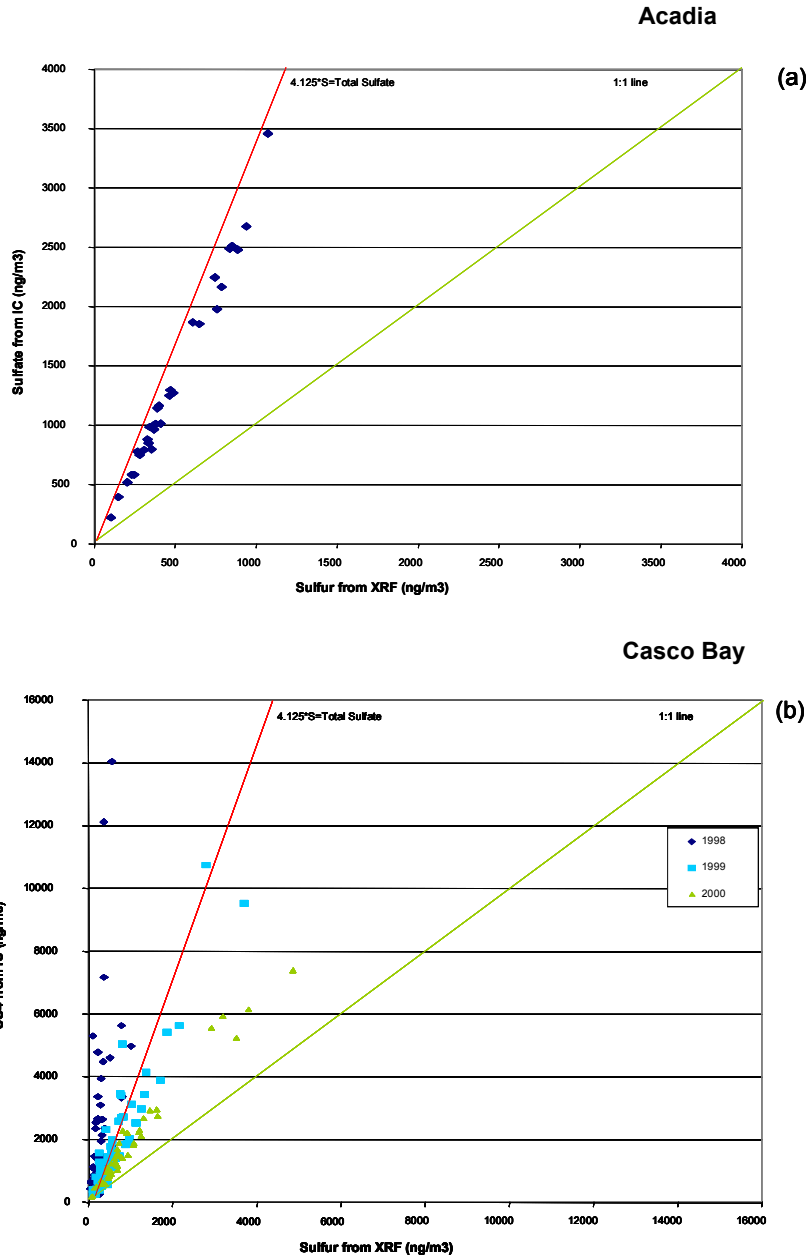


Figure 2-3. Comparison of XRF sulfur-derived sulfate (SO₄) and ion chromatography (IC) sulfate concentrations in (a) Acadia (January 1998-December 2000) and (b) Casco Bay (August 1998-December 2000). Scales differ between the two plots.

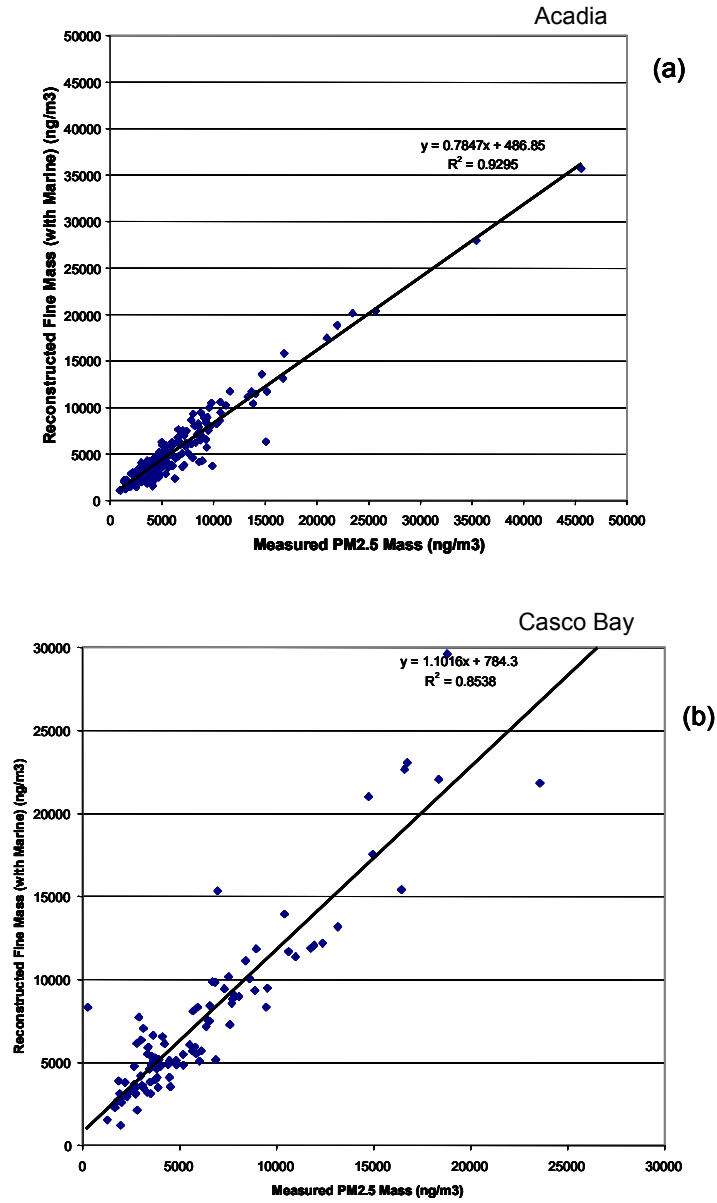


Figure 2-4. Comparison of reconstructed fine mass (with marine) and measured PM_{2.5} in (a) Acadia (January 1998-December 2000) and (b) Casco Bay (August 1998-February 2001). Scales differ between the two plots.

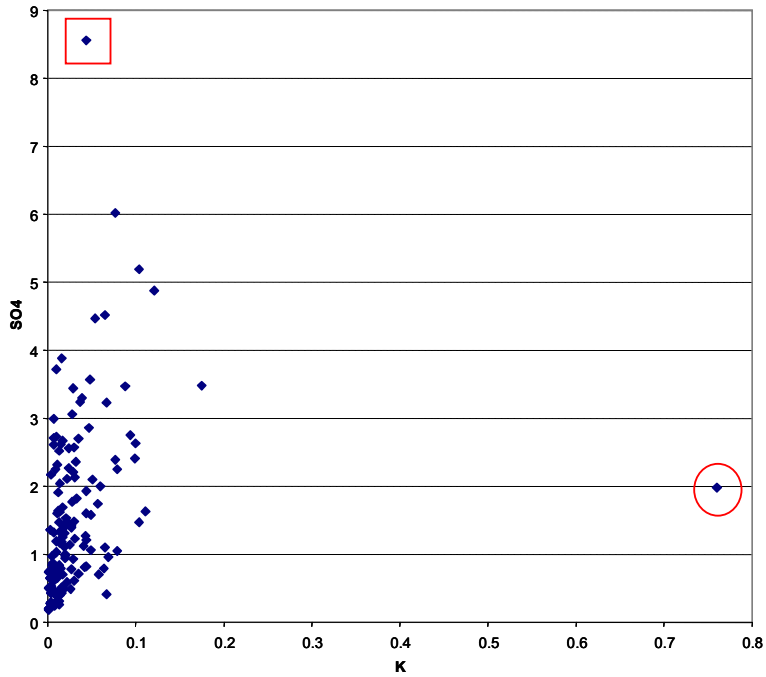


Figure 2-5. Scatter plot of sulfate (SO₄) versus potassium (K) concentrations (mg/L) in the Casco Bay NTN data, 1998-2000. The circled data point (June 8-June 15, 1999) was a sample with high pollen content (per NTN notes). The data point with a box around it was a sample collected on March 23-March 30, 1999.

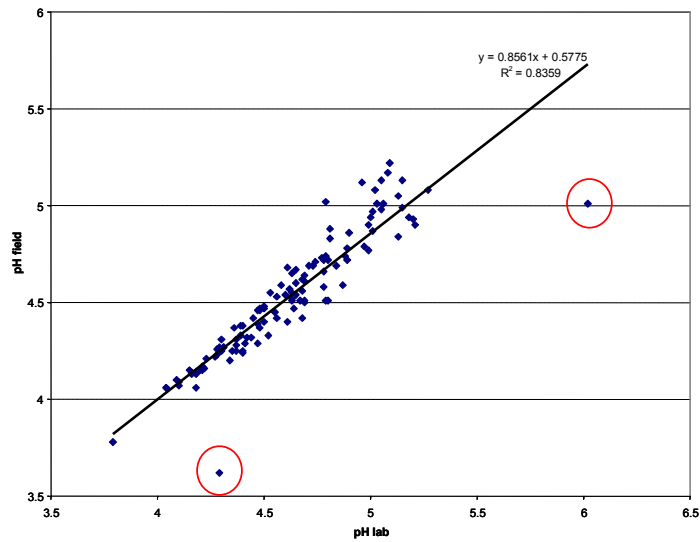


Figure 2-6. Comparison of the field and laboratory pH values at Casco Bay (1998-2000). Low field pH values (circled) did not affect other analyses.

3. DESCRIPTIVE ANALYSES OF NITROGEN, MERCURY AND FINE PARTICLE CONCENTRATIONS, AND WET DEPOSITION DATA

3.1 GENERAL CHARACTERISTICS

This section describes the general characteristics of annual precipitation, pollutant concentrations, and pollutant wet depositions by site in Maine.

3.1.1 Precipitation

Annual precipitation at Casco Bay (discussed in more detail in Section 4) varied from a maximum of about 1500 mm in 1998 to a minimum of about 600 mm in 2001. For comparison purposes, annual precipitation at Acadia declined from 1500 mm in 1998 to about 500 mm in 2001. Both Bridgton and Greenville showed a maximum in annual precipitation in 1999 with minimums in 2001. Spatial maps of annual precipitation (e.g., **Figure 3-1**) show that annual precipitation tends to be higher at coastal than inland sites.

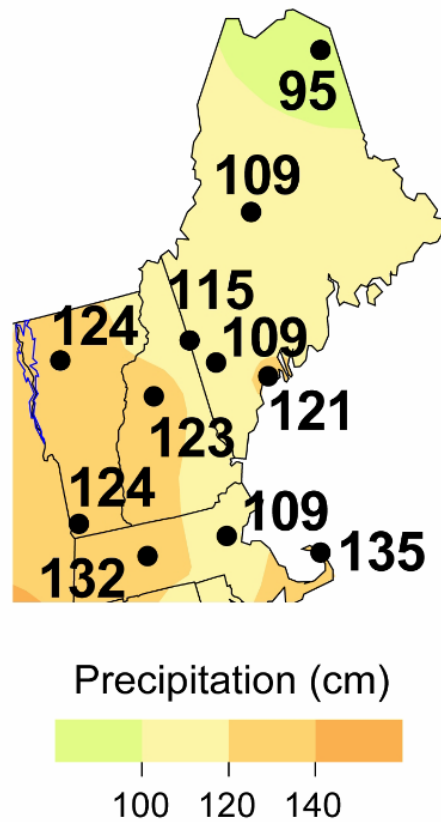


Figure 3-1. Annual precipitation measured in cm at NTN sites in the Northeast in 2000 (National Atmospheric Deposition Program, 2002b; Claybrooke, 2002).

3.1.2 IMPROVE PM_{2.5} Concentrations

Summary statistics of IMPROVE PM_{2.5} data concentrations (ng/m³) in 2000 at Casco Bay are shown in **Table 3-1**. Differences in the number of cases among species are due to missing data (MDL/2 was used to replace concentrations below detection). Summary statistics for 1998 and 1999 for Casco Bay and Acadia are provided in Appendix C.

Table 3-1. Summary statistics of IMPROVE PM_{2.5} data concentrations (ng/m³) during 2000 at Casco Bay. Note concentrations < MDL are indicated. Parameter and species abbreviations are provided in Appendix A.

Page 1 of 2

Parameter/Species	Number of Cases	Minimum	Maximum	Median	Mean	Standard Deviation	Coefficient of Variance
PM _{2.5}	58	543	18900	5740	6390	4140	0.67
RCFM	48	1190	29100	5720	7310	5610	0.77
RCFM + MARINE	48	1190	29600	5970	7570	5920	0.78
AL	58	<MDL	419	<MDL	23	63	2.68
AS	58	<MDL	2.76	0.41	0.53	0.64	1.21
BR	58	<MDL	5.89	1.36	1.62	1.31	0.81
CA	58	<MDL	148	10	16	22	1.43
CR	58	<MDL	4.03	<MDL	0.64	1.11	1.74
CU	58	<MDL	4.98	0.69	0.77	0.88	1.13
FE	58	3	107	17	21	18	0.89
H	58	55	891	239	283	190	0.67
K	58	10	140	42	47	28	0.59
MG	58	<MDL	182	<MDL	9	34	4.01
MN	58	<MDL	8.69	0.70	1.49	2.07	1.39
NA	58	<MDL	1377	68	121	215	1.77
NI	58	<MDL	6.74	0.86	1.36	1.49	1.09
P	58	<MDL	210	7	22	40	1.83
PB	25	0.21	7.87	1.90	2.35	1.92	0.82
RB	25	<MDL	0.55	0.24	0.23	0.16	0.72
S	58	68	4863	645	919	941	1.02
SE	25	<MDL	1.10	0.15	0.27	0.29	1.08
SI	58	8	1310	39	102	206	2.02
TI	58	<MDL	23.7	3.1	4.5	5.2	1.15
V	58	<MDL	16.5	2.7	3.9	3.8	0.97
ZN	58	0.95	25.6	5.3	6.8	5.3	0.78
ZR	25	<MDL	0.20	<MDL	0.04	0.07	1.72
CLI	50	5	896	218	219	150	0.68
NO ₂	38	<MDL	163	13.5	20.5	32.9	1.60
NO ₃	56	21	1401	243	371	332	0.90
SO ₄	56	172	7396	1350	1801	1552	0.86

Table 3-1. Summary statistics of IMPROVE PM_{2.5} data concentrations (ng/m³) during 2000 at Casco Bay. Note concentrations < MDL are indicated. Parameter abbreviations are provided in Appendix A.

Parameter/Species	Number of Cases	Minimum	Maximum	Median	Mean	Standard Deviation	Coefficient of Variance
E1	57	75	2197	487	601	412	0.69
E2	51	3	165	56	66	44	0.67
E3	51	1.3	26.6	8.3	9.5	5.2	0.54
O1	56	2	934	62.5	156	205	1.32
O2	56	2	1063	247	303	246	0.81
O3	56	40	2099	487	578	431	0.74
O4	57	98	1985	309	485	399	0.82
OP	56	<MDL	735	154	184	164	0.89
OC	56	327	6040	1550	1710	1130	0.66
EC	50	37	2207	363	486	416	0.85
Ammonium	56	4	174	35	44	36	0.82
Total Sulfate	58	282	20060	2660	3790	3880	1.02
Total Nitrate	56	27	1810	313	478	429	0.90
SOIL	58	40	3510	168	360	600	1.67
MARINE	58	<MDL	3440	169	3040	536	1.77
Non-Soil K	58	7	114	34	35	21	0.60
OCM	56	457	8450	2180	2400	1580	0.66
TC	50	442	8250	1800	2170	1520	0.70
RCFM/PM _{2.5}	47	0.62	2.25	1.17	1.20	0.30	0.25
OC/TC	50	0.65	0.92	0.78	0.78	0.062	0.08
EC/TC	50	0.08	0.35	0.22	0.22	0.062	0.28

Figures 3-2 and 3-3 summarize the mean composition of PM_{2.5} reconstructed fine mass (RCFM) (including marine) for Casco Bay and Acadia, respectively. Natural soil and marine components account for only 9% of the mass at Casco Bay and 16% at Acadia. These two components are usually more important in coarse (> 2.5 μm) aerosol. The remainder of the mass is largely derived from anthropogenic sources. Overall, the OC and sulfate fractions account for 77% of the RCFM at Casco Bay and 73% at Acadia. The sulfate fraction at Casco Bay is only slightly higher than the OC fraction while the sulfate dominates at Acadia. The marine component is higher at Acadia than at Casco Bay.

Figures 3-4 and 3-5 summarize the mean PM_{2.5} concentrations of selected species and species groups at Casco Bay and Acadia. The plots are limited to complete years of data (1999-2000 for Casco Bay and 1998-1999 for Acadia). Median concentrations for the RCFM components (Figure 3-5) were similar in 1999 and 2000 at Casco Bay and generally higher than Acadia (except for marine). Aluminum concentrations at Casco Bay were low in 2000 compared to 1999. RCFM was lower than measured PM_{2.5} mass at Acadia in 1999, which is consistent with other years, and may indicate an artifact from VOC adsorption or nitrate volatilization. Phosphorus concentrations were quite variable, though this is due to a few events impacting the mean; median values show less variation.

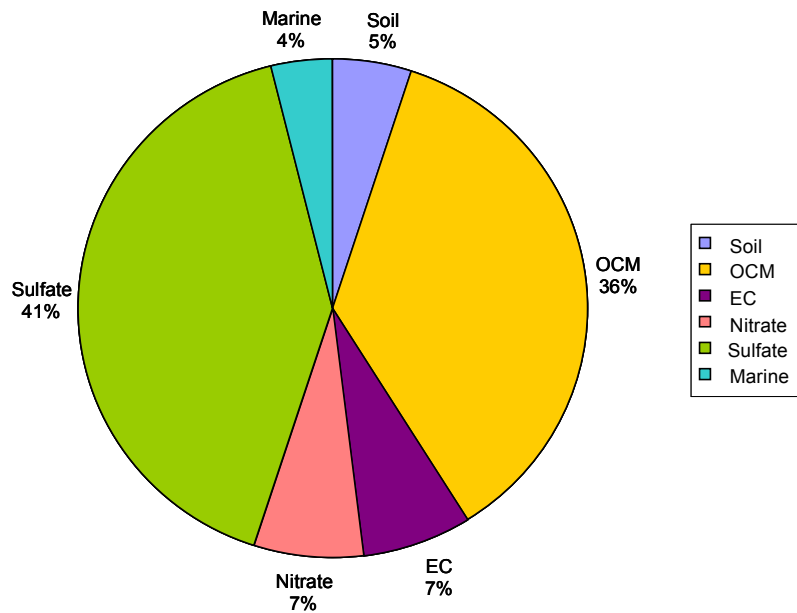


Figure 3-2. Mean composition of PM_{2.5} aerosol by RCFM with marine (7.02 µg/m³) at Casco Bay in 1999-2000.

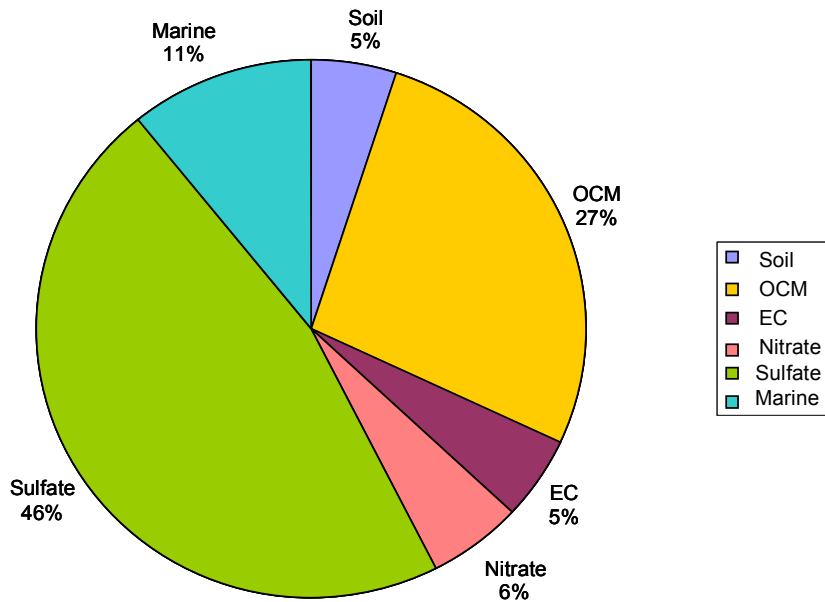


Figure 3-3. Mean composition of PM_{2.5} aerosol RCFM with marine (5.28 µg/m³) at Acadia in 1999. Data for 2000 were incomplete.

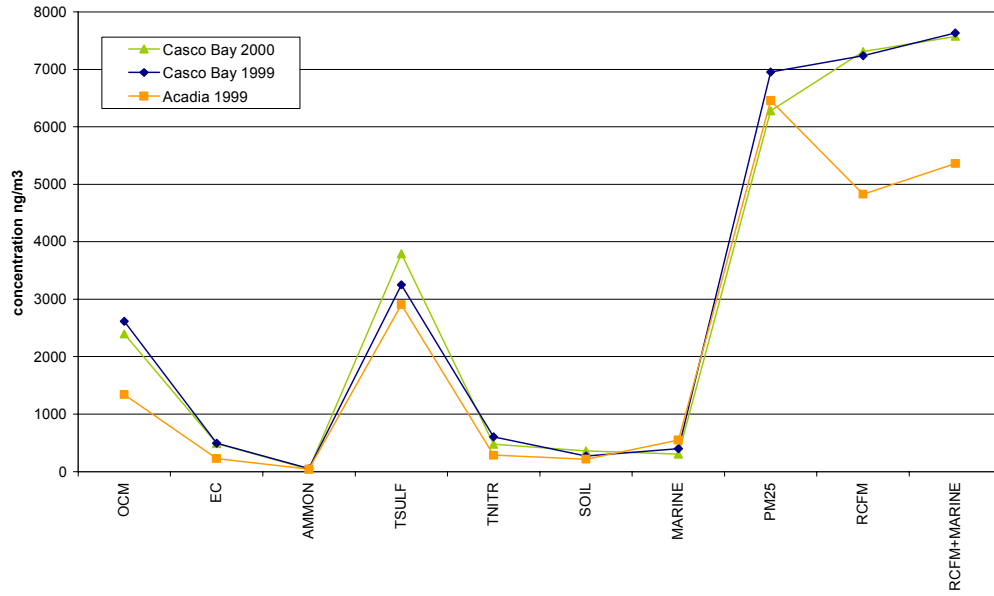


Figure 3-4. Mean PM_{2.5} concentrations of major species at Casco Bay, 1999-2000, and Acadia, 1999. Species abbreviations are provided in Appendix A.

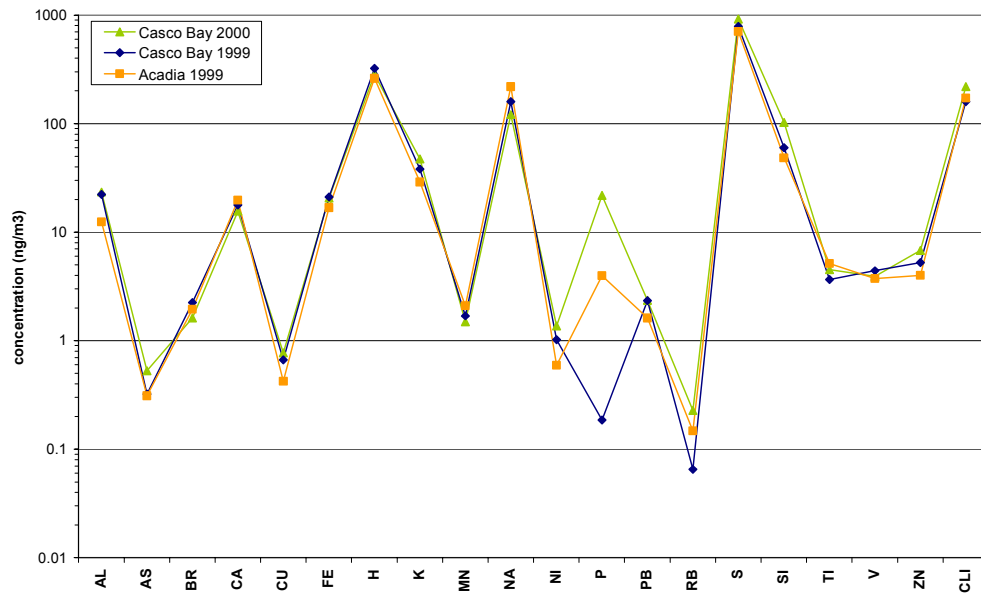


Figure 3-5. Mean PM_{2.5} concentrations of elements and ions at Casco Bay, 1999-2000, and Acadia, 1999. Species abbreviations are provided in Appendix A.

3.1.3 MDN Concentration and Deposition

Table 3-2 provides summary statistics of MDN mercury concentrations and depositions at Casco Bay in 1998-2001. A time series of MDN data shows that the samples with high concentrations of mercury did not always result in a larger deposition of mercury (Appendix B). **Figures 3-6 and 3-7** illustrate the distribution of concentrations and depositions by year and season at Casco Bay for the same time period.⁹ The samples with high concentrations of mercury did not always result in a larger deposition of mercury. A few large events contributed more than 10% of annual mercury wet deposition as shown in **Table 3-3**. Note that all the events occurred in spring or summer except one December event.

Table 3-2. Summary statistics of weekly mercury concentration (ng/L) and deposition (ng/m²) at Casco Bay by year.

	Statistic	1998	1999	2000	2001
Mercury concentration (ng/L)	Number	40	44	48	45
	Maximum	25.9	30.3	23.0	162.2
	Mean	9.9	10.7	7.9	13.6
	Median	8.1	8.7	7.0	7.5
	Minimum	2.7	2.0	1.2	1.6
	Standard Deviation	6.0	7.1	5.4	24.4
	Coefficient of Variance	0.60	0.67	0.68	1.80
Mercury deposition (ng/m ² wk ⁻¹)	Number	40	44	48	45
	Maximum	2210	993	848	617.5
	Mean	264	189	164	107
	Median	155	142	115	54
	Minimum	4	3	1	4.2
	Standard Deviation	369	195	164	126
	Coefficient of Variance	1.40	1.03	1.00	1.18

Time series for the Casco Bay site are shown in Appendix B. In 2000, at least one event occurred in different weeks at each site that accounted for more than 10% of the annual mercury deposition. In 1998 and 1999, there was only one week—from June 9 to 16, 1998 (rain)—in which more than 10% of the annual mercury deposition occurred at any site; this one major event accounted for 21% of total deposition for the year.

⁹ Figure 3-10 provides a definition of the statistics shown in Figures 3-6 and 3-7.

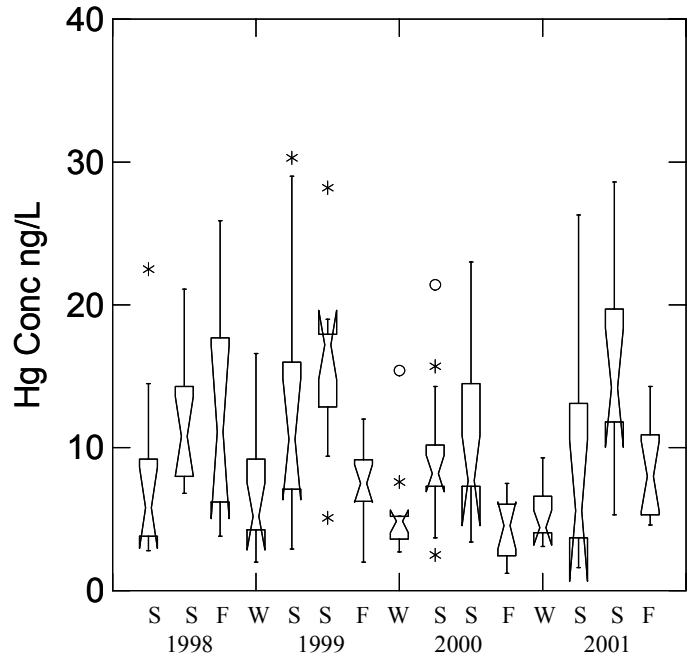


Figure 3-6. Notched box whisker plots of weekly mercury concentrations (ng/L) by season and year at Casco Bay from 1998 through 2001. Spring = March-May, summer = June-August, fall = September-November, winter = December-February.

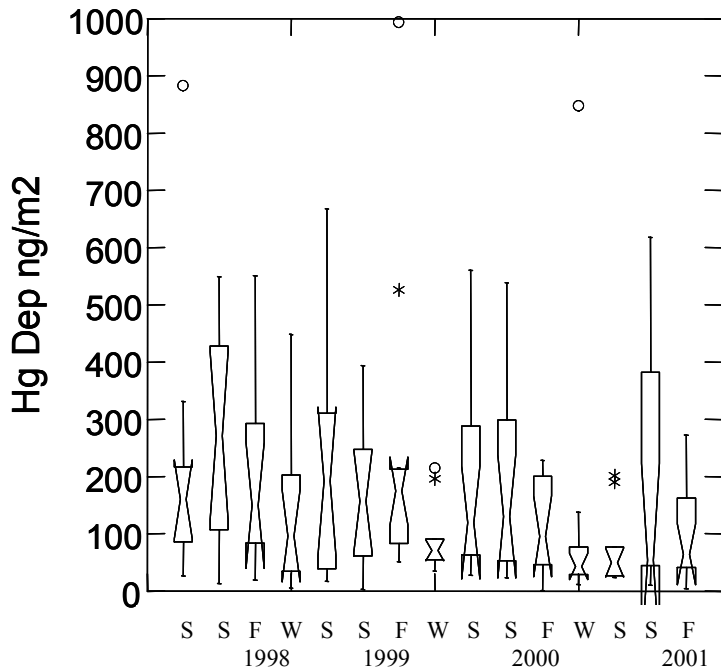


Figure 3-7. Notched box whisker plots of weekly mercury deposition (ng/m²) by season and year at Casco Bay from 1998 through 2001. Spring = March-May, summer = June-August, fall = September-November, winter = December-February.

Table 3-3. Mercury deposition events accounting for more than 10% of annual deposition (1998-2000).

End Date	Percent of Annual Deposition (Precipitation in mm)			
	Casco Bay	Bridgton	Greenville	Acadia
6/16/98	21% (188)	14% (189)	17% (98)	
9/21/99	12% (121)			16% (103)
4/25/00				11% (178)
5/16/00			11% (57)	
8/15/00		11% (35)		
12/19/00	11% (91; snow)		13% (84)	
5/29/01		11% (493)		11% (529)
6/12/01	13% (618)			

3.1.4 NTN Concentrations and Deposition

Summary statistics of NTN species concentrations are provided for Casco Bay in **Table 3-4**. Statistics for the other sites are provided in Appendix C. **Figure 3-8** shows mean concentrations of NTN data for each site in 2000. Sodium and chloride ion concentrations were highest at Acadia (consistent with the IMPROVE data) and higher at the coastal sites (Acadia and Casco Bay) than at the inland sites (Bridgton and Greenville), consistent with proximity to the ocean. Nitrate and sulfate concentrations were similar among the Casco Bay, Acadia, and Bridgton sites (i.e., within 10%). **Figure 3-9** shows a spatial map of average laboratory pH values from the NADP web site.

3.2 TEMPORAL (SEASONAL) TRENDS

Trends by season and by year were investigated. Seasonal and annual changes in pollutant concentrations and deposition totals are a function of transport patterns and synoptic meteorology, temperature, available sunlight, precipitation, emission sources, and emission controls.

One way to compare sites and obtain an overall understanding of the data is to inspect various stratifications of the data using graphical depictions of the central tendencies of the data. A useful plot is a box whisker plot (an example is shown in **Figure 3-10**) that shows the 25th, 50th (median), and 75th percentiles. Using SYSTAT software, the whiskers always end on a data point, so when the plots show no data points beyond the end of a whisker, the whisker shows the value of the highest or lowest data point. The whiskers have a maximum length equal to 1.5 times the length of the box (the interquartile range). If there are data outside this range, the points are shown on the plot and the whisker ends on the highest or lowest data point within the range of the whisker. The “outliers” (or extreme values) are also further identified with asterisks representing the points that fall within three times the interquartile range from the end of the box and circles representing points beyond this. These plots are also useful for data validation.

Table 3-4. Summary statistics of NTN data at Casco Bay, 1998-2001. Species abbreviations are provided in Appendix A.

Year	Statistic	CA	MG	K	NA	NH ₄	NO ₃	CL	SO ₄
1998	Number of weekly samples	28	28	28	28	28	28	28	28
	Minimum mg/L	0.01	0.00	0.00	0.02	0.01	0.16	0.05	0.24
	Maximum mg/L	0.29	0.31	0.10	3.12	1.02	7.03	4.83	6.02
	Median mg/L	0.06	0.03	0.01	0.19	0.09	0.89	0.35	0.98
	Mean mg/L	0.07	0.07	0.03	0.61	0.17	1.55	0.99	1.61
	Standard deviation mg/L	0.06	0.09	0.03	0.88	0.21	1.67	1.34	1.49
	Coefficient of variance	0.84	1.26	1.12	1.44	1.29	1.08	1.35	0.92
1999	Number of weekly samples	31	31	31	31	31	31	31	31
	Minimum mg/L	0.02	0.00	0.00	0.03	0.01	0.18	0.05	0.28
	Maximum mg/L	0.68	0.52	0.18	4.22	1.59	5.95	6.97	8.56
	Median mg/L	0.07	0.05	0.03	0.43	0.12	1.11	0.78	1.23
	Mean mg/L	0.11	0.08	0.03	0.69	0.19	1.54	1.16	1.72
	Standard deviation mg/L	0.14	0.10	0.03	0.92	0.29	1.36	1.46	1.60
	Coefficient of variance	1.26	1.24	1.03	1.33	1.48	0.88	1.26	0.93
2000	Number of weekly samples	41	41	41	41	41	41	41	41
	Minimum mg/L	0.01	0.00	0.00	0.01	0.01	0.12	0.04	0.2
	Maximum mg/L	0.26	0.35	0.11	2.95	0.49	5.02	5.14	3.57
	Median mg/L	0.06	0.03	0.02	0.22	0.14	0.95	0.35	1.32
	Mean mg/L	0.08	0.06	0.03	0.50	0.16	1.40	0.86	1.43
	Standard deviation mg/L	0.06	0.07	0.03	0.67	0.14	1.26	1.14	0.95
	Coefficient of variance	0.75	1.23	0.88	1.33	0.83	0.90	1.32	0.66
2001	Number of weekly samples	42	42	42	42	42	42	42	42
	Minimum mg/L	0.01	0.00	0.00	0.00	0.01	0.09	0.03	0.18
	Maximum mg/L	0.57	0.19	0.12	1.72	0.73	8.68	3.03	4.88
	Median mg/L	0.07	0.03	0.01	0.17	0.19	0.99	0.32	1.29
	Mean mg/L	0.10	0.04	0.02	0.26	0.21	1.60	0.49	1.60
	Standard deviation mg/L	0.11	0.04	0.03	0.30	0.17	1.60	0.52	1.18
	Coefficient of variance	1.13	0.96	1.04	1.14	0.83	1.00	1.07	0.74

Because we were also interested in how similar or dissimilar the data are among time periods, we used an option called a notched box whisker plot to analyze data in this study (also shown in Figure 3-10). These plots include notches that mark confidence intervals. The boxes are notched (narrowed) at the median and return to full width at the 95% lower and upper confidence interval values. If the 95% confidence interval is beyond the 25th or 75th percentile, then the notches extend beyond the box (hence the "folded" appearance). The confidence interval is a function of the number of samples – fewer samples lead to a larger confidence interval. When comparing data among different stratifications, if the confidence intervals between two median values do not overlap, then the data are likely statistically significantly different. Statistical tests such as a t-test can be used to confirm and quantify the difference.

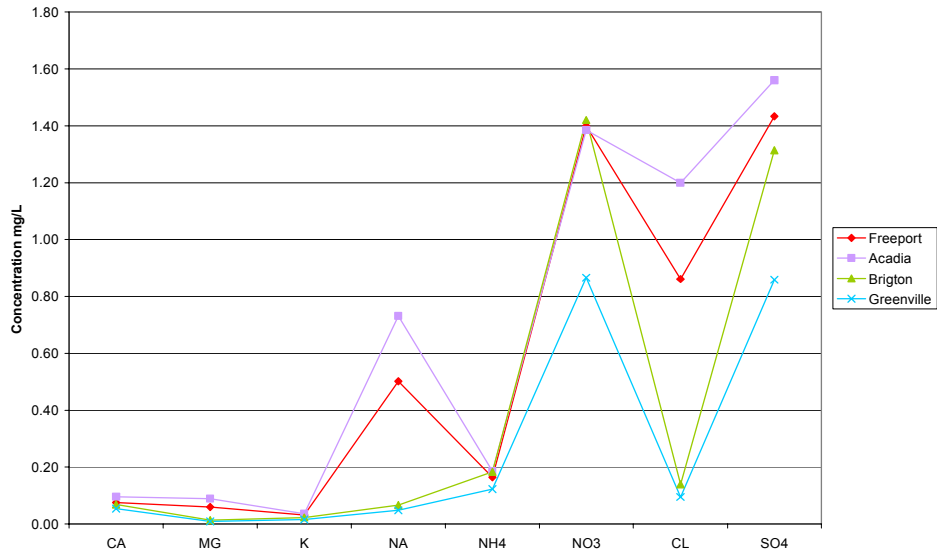


Figure 3-8. Mean concentrations (mg/L) of ions at Casco Bay, Acadia, Bridgton, and Greenville in 2000.

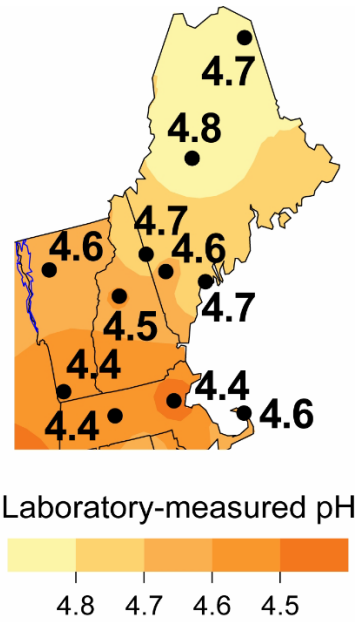


Figure 3-9. Spatial variation in annual average laboratory-measured pH in the Northeast in 2000 (National Atmospheric Deposition Program, 2000; Claybrooke, 2002).

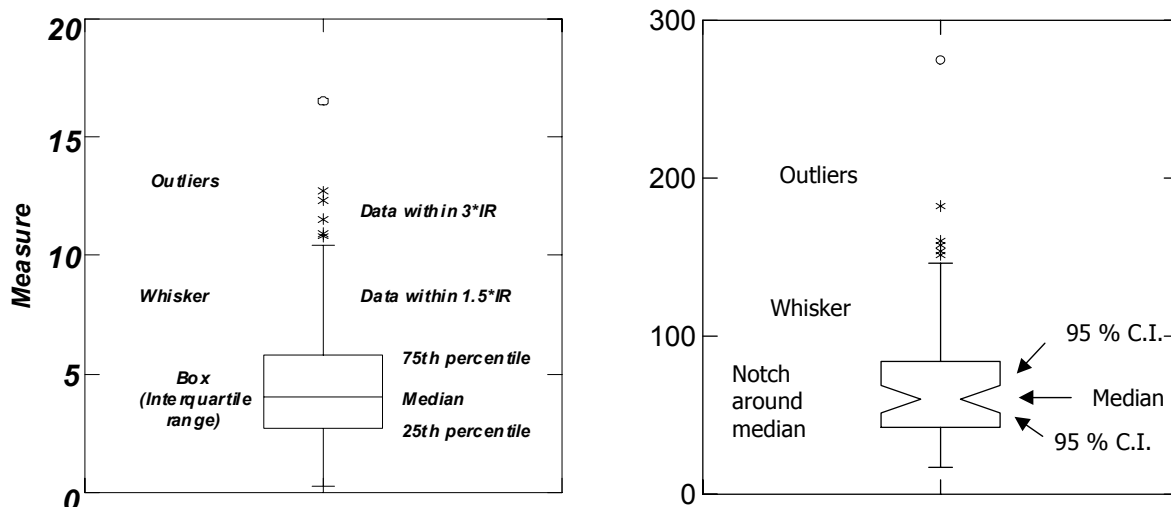


Figure 3-10. Illustration of box whisker plots and notched box whisker plots as defined by SYSTAT statistical software.

3.2.1 IMPROVE Concentrations

Table 3-5 provides summary statistics for IMPROVE species concentrations by season including 1998-2000 data for Casco Bay. The tables of summary statistics for Acadia are provided in Appendix C. Box whisker plots for sulfate, nitrate, RCFM, soil, and marine component concentrations at Casco Bay by season are provided in Figure 3-11.

Overall contributions from organic mass (OCM), EC, total sulfate, total nitrate, soil, and marine influences in the RCFM by season for Casco Bay are detailed in Figures 3-12 through 3-15, and for Acadia in Figures 3-16 through 3-19. Scatter plots of selected species at Casco Bay are shown in Figure 3-20. Observations of seasonal trends follow:

- At both Casco Bay and Acadia, organic mass and sulfate were the dominant aerosol components during all seasons. Sulfates comprised the greatest fraction of $PM_{2.5}$ at Casco Bay (except in spring), while sulfates contributed the most at Acadia in all seasons.
- Elemental carbon contributed slightly more to $PM_{2.5}$ composition at Casco Bay than at Acadia. The marine component was up to three times greater overall at Acadia than at Casco Bay.
- Elemental carbon did not show a seasonal trend at Casco Bay as illustrated in the scatter plot of EC and sulfur (Figure 3-20) similar to results at Underhill, Vermont (Polissar et al., 2001). A minimum of EC concentrations can be seen at Casco Bay during spring. At Acadia, the maximum concentrations occurred in the summer.
- Vanadium and nickel correlate reasonably well at Casco Bay indicating a common source, most likely oil combustion (see Polissar et al., 2001).

Table 3-5. Summary statistics of IMPROVE data concentrations (ng/m³) by season 1998-2000 at Casco Bay. Species abbreviations are provided in Appendix A. Numbers are rounded to two or three significant digits, depending on the magnitude.

Page 1 of 2

Species	Dec-Feb			Mar-May			Jun-Aug			Sep-Nov		
	Median	Mean	Standard Deviation	Median	Mean	Standard Deviation	Median	Mean	Standard Deviation	Median	Mean	Standard Deviation
PM _{2.5}	6380	6230	3780	3570	422	2870	5210	8020	7840	3840	5470	4270
RCFM	686	8250	4600	4030	5080	3420	6050	7620	4260	5080	7250	6860
RCFM with MARINE	7500	8640	4900	4280	5510	4010	6150	7770	4400	5080	7490	7500
AL	7.36	20.7	24.8	0.00	37.3	77.7	0.00	9.85	31.3	0.00	7.9	15.2
AS	0.29	0.41	0.50	0.00	0.14	0.23	0.14	0.48	0.78	0.33	0.46	0.56
BR	1.65	1.83	1.41	1.72	1.74	1.11	1.19	1.53	1.19	1.33	1.69	1.50
CA	9.19	11.2	10.6	17.4	20.1	26.6	10.4	16.0	18.0	12.2	15.3	13.7
CU	0.49	0.62	0.57	0.52	0.68	1.00	0.62	0.61	0.68	0.72	0.97	1.18
FE	11.6	16.3	12.7	15.7	19.2	19.4	12.8	23.8	26.0	15.0	20.5	20.2
H	254	279	163	191	207	119	246	394	398	177	251	205
K	46.5	49.2	25.8	32.3	40.4	25.7	26.5	34.9	32.6	27.9	30.9	17.3
MG	0.00	11.8	36.4	0.00	14.1	38.8	0.00	1.45	4.91	0.00	13.1	40.7
MN	1.56	1.92	2.31	0.22	1.66	2.62	0.40	0.86	1.52	1.56	1.84	1.73
NA	91.1	123	135	81.0	171	290	0.00	63.9	129	45.6	120	199
NI	1.06	1.31	1.17	0.34	0.48	0.48	0.66	1.12	0.94	0.91	1.35	1.63
PB	2.50	2.55	1.49	1.28	1.65	1.38	2.13	2.37	1.83	1.46	2.01	1.74
RB	0.22	0.22	0.20	0.00	0.08	0.12	0.00	0.04	0.08	0.00	0.07	0.14
S	549	623	481	451	572	525	578	976	1110	501	809	1050
SE	0.21	0.39	0.39	0.09	0.15	0.16	0.24	0.36	0.43	0.27	0.38	0.41
SI	35.7	45.9	34.5	53.3	136	258	34.9	62.7	81.3	29.4	40.2	38.9
SR	0.11	0.13	0.14	0.00	0.17	0.29	0.17	0.29	0.57	0.00	0.11	0.18
TI	3.25	3.63	2.98	3.94	5.66	5.86	1.26	2.87	4.31	2.34	3.19	3.55
V	3.91	4.70	3.61	2.68	2.81	2.10	3.49	4.14	3.64	3.78	5.35	4.39
Y	0.00	0.05	0.10	0.00	0.04	0.08	0.00	0.07	0.13	0.00	0.02	0.06
ZN	5.15	6.42	5.01	3.53	4.54	4.40	3.93	4.69	3.11	5.16	5.99	4.36
Chloride	76.5	134	128	166	237	332	163	170	145	137	147	130
NO ₂	7.00	25.0	48.3	17.3	35.9	44.7	5.72	13.8	17.4	4.95	9.49	13.6

Table 3-5. Summary statistics of IMPROVE data concentrations (ng/m³) by season 1998-2000 at Casco Bay. Species abbreviations are provided in Appendix A. Numbers are rounded to two or three significant digits, depending on the magnitude.

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Species	Dec-Feb			Mar-May			Jun-Aug			Sep-Nov		
	Median	Mean	Standard Deviation	Median	Mean	Standard Deviation	Median	Mean	Standard Deviation	Median	Mean	Standard Deviation
	NO ₃	618	780	592	236	353	355	219	344	436	228	312
SO ₄	1520	1840	1190	1240	1500	1200	1710	2340	2180	1180	1960	2050
E1	533	620	375	345	424	312	698	688	295	596	659	395
E2	102	116	92.4	51.9	62.2	41.5	60.2	73.3	52.6	81.1	86.0	48.4
E3	9.96	14.4	12.5	8.25	9.77	6.23	8.25	13.3	12.8	9.14	11.7	8.10
O1	209	320	331	62.5	102	112	62.5	241	325	62.5	158	187
O2	373	433	275	127	189	194	455	514	291	298	338	215
O3	780	825	566	264	325	235	710	728	364	399	489	295
O4	591	700	499	203	291	199	412	529	299	403	453	272
OP	85.0	127	154	186	212	187	209	262	189	245	271	160
OC	2200	2340	1400	807	1040	613	2080	2330	1120	1570	1640	719
EC	558	655	471	268	292	180	451	500	274	430	527	337
Ammonium	48.6	51.3	31.7	30.0	37.4	29.3	39.8	54.9	52.0	30.1	46.3	46.9
Total Sulfate	2260	2570	1980	1860	2360	2160	2380	4020	4590	2070	3340	4350
Total Nitrate	797	1010	764	304	456	458	282	444	563	294	403	394
SOIL	172	211	150	256	470	740	138	248	332	146	188	150
MARINE	228	308	336	202	427	724	0.00 ¹⁰	160	322	114	301	497
OCM	3080	3280	1960	1130	1450	859	2910	3260	1570	2200	2290	1010
TC	2820	3130	1870	1093	1340	780	2470	2770	1360	2010	2220	1040
RCFM/PM _{2.5} MASS	1.17	1.22	0.26	1.27	1.23	0.31	1.02	2.18	5.44	1.32	1.31	1.17
OC/TC	0.78	0.78	0.05	0.78	0.77	0.06	0.83	0.82	0.05	0.78	0.77	0.78
EC/TC	0.22	0.22	0.05	0.22	0.23	0.06	0.17	0.18	0.05	0.22	0.23	0.22
NO ₃ /SO ₄	0.46	0.46	0.25	0.22	0.25	0.16	0.15	0.15	0.09	0.16	0.21	0.46

¹⁰ Both Na and Cl concentrations were often reported as zero, resulting in a median value of zero. The mean value is more representative in this case.

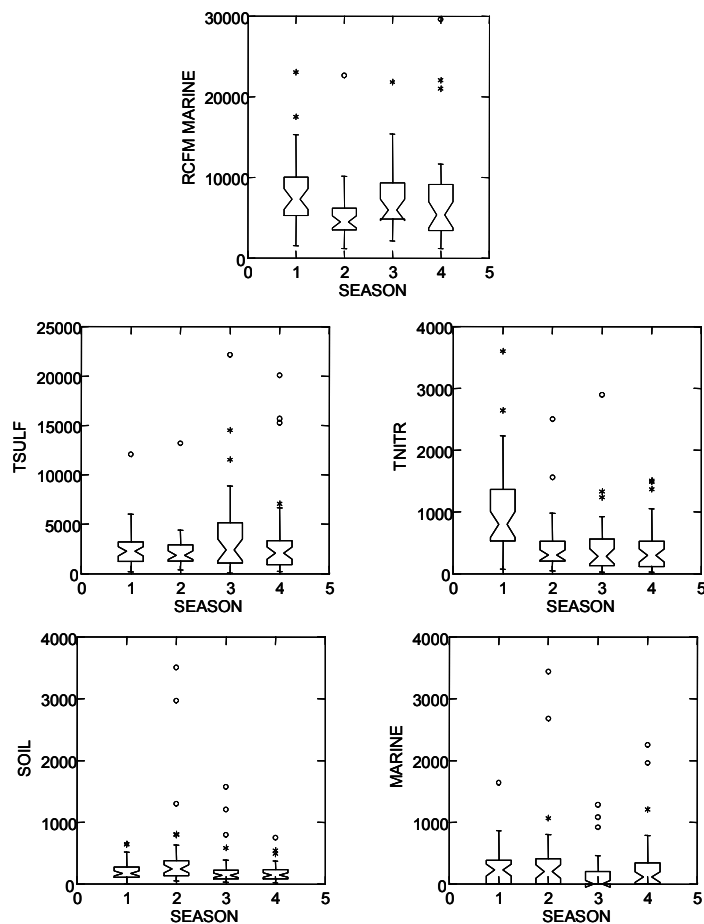


Figure 3-11. Seasonal variation in RCFM plus marine (RCFM MARINE), total sulfate (TSULF), total nitrate (TNITR), soil, and marine component concentrations (in ng/m^3) in IMPROVE data collected at Casco Bay from 1998 to 2000; 1 = winter, 2 = spring, 3 = summer, and 4 = fall.

- Selenium concentrations were higher in winter; this is consistent with the use of winter coal. Selenium is a tracer for coal combustion (see Polissar et al., 2001).
- Concentrations of soil components (e.g., aluminum, calcium, silicon) were greater in the spring at Casco Bay and were at a minimum in winter at Acadia.
- Nitrate concentrations were highest in the winter at both sites, consistent with nitrate formation mechanisms which favor cold, wet conditions.
- Potassium concentrations were highest in winter at Casco Bay, possibly indicating increased wood burning. Also, note that the slope of the relationship between EC and sulfur is higher in the winter which generally represents wood burning (see Polissar et al., 2001).

Table 3-6 summarizes selected maxima and minima in species concentrations at Casco Bay and Acadia.

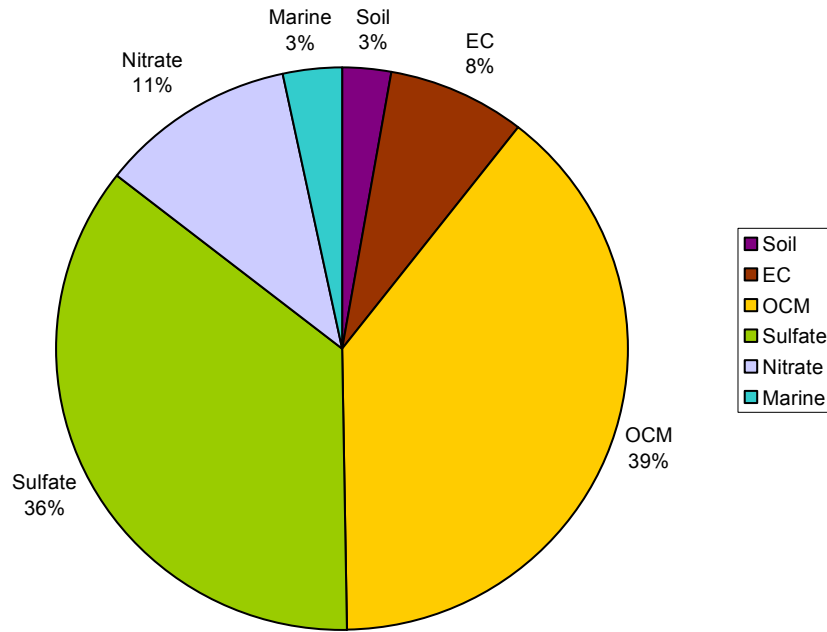


Figure 3-12. Mean composition of PM_{2.5} aerosol by RCFM with marine (4.28 µg/m³) at Casco Bay, March-May 1999-2001.

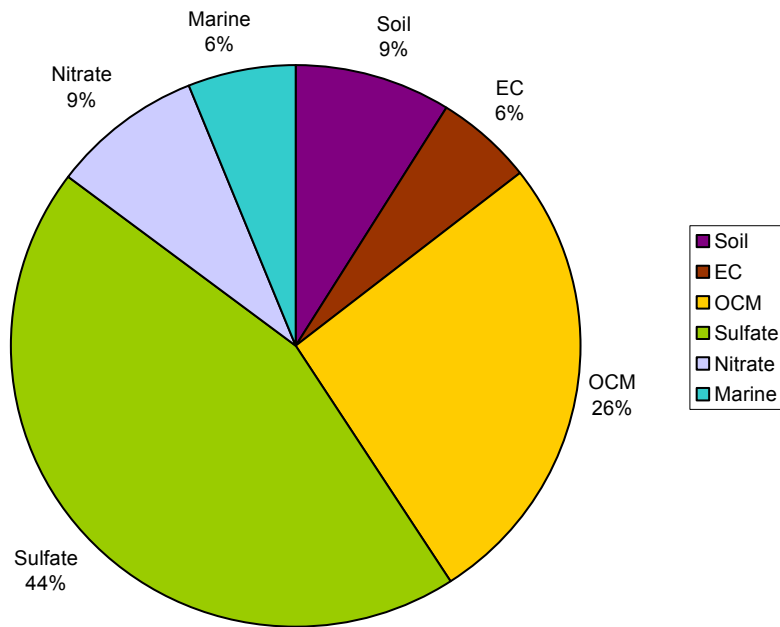


Figure 3-13. Mean composition of PM_{2.5} aerosol by RCFM with marine (8.30 µg/m³) at Casco Bay, June-August 1999-2001.

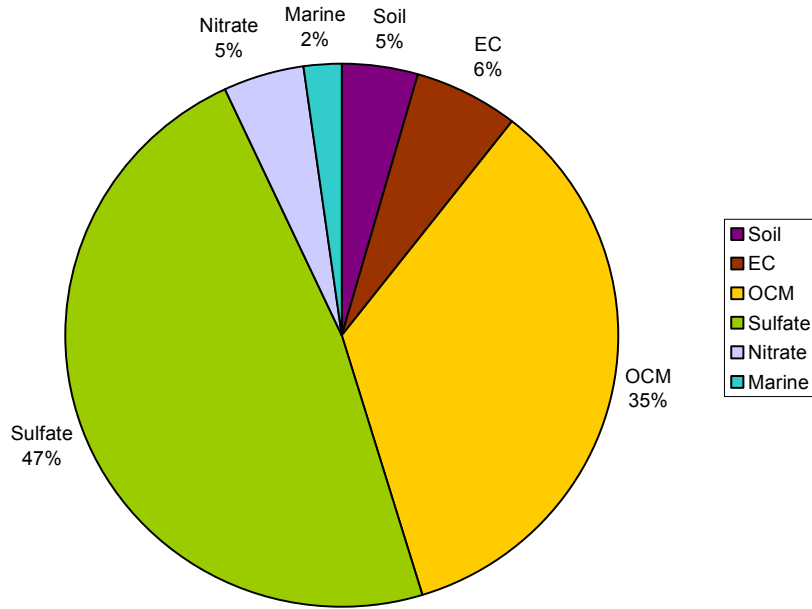


Figure 3-14. Mean composition of PM_{2.5} aerosol by RCFM with marine (7.78 µg/m³) at Casco Bay, September-November 1999-2001.

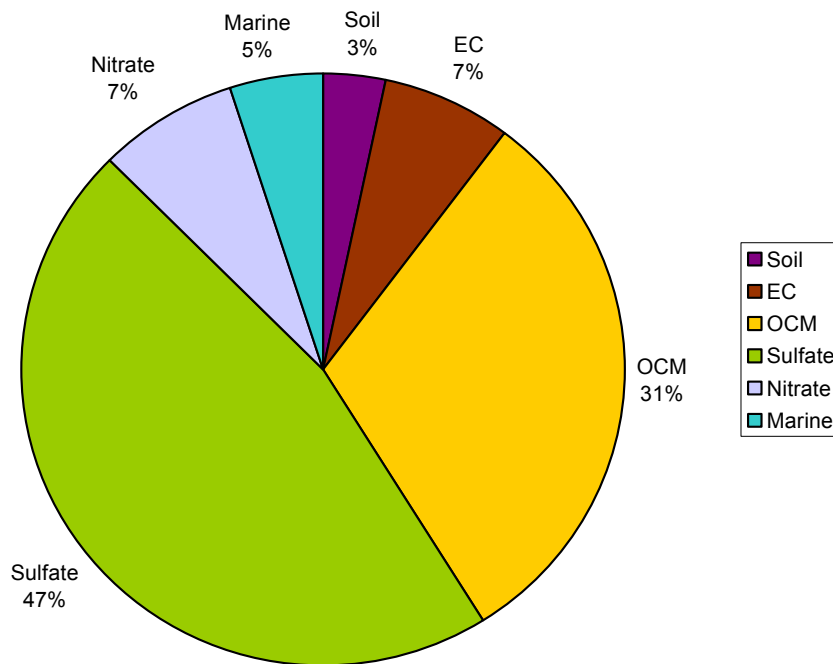


Figure 3-15. Mean composition of PM_{2.5} aerosol by RCFM with marine (6.83 µg/m³) at Casco Bay, December-February 1999-2001.

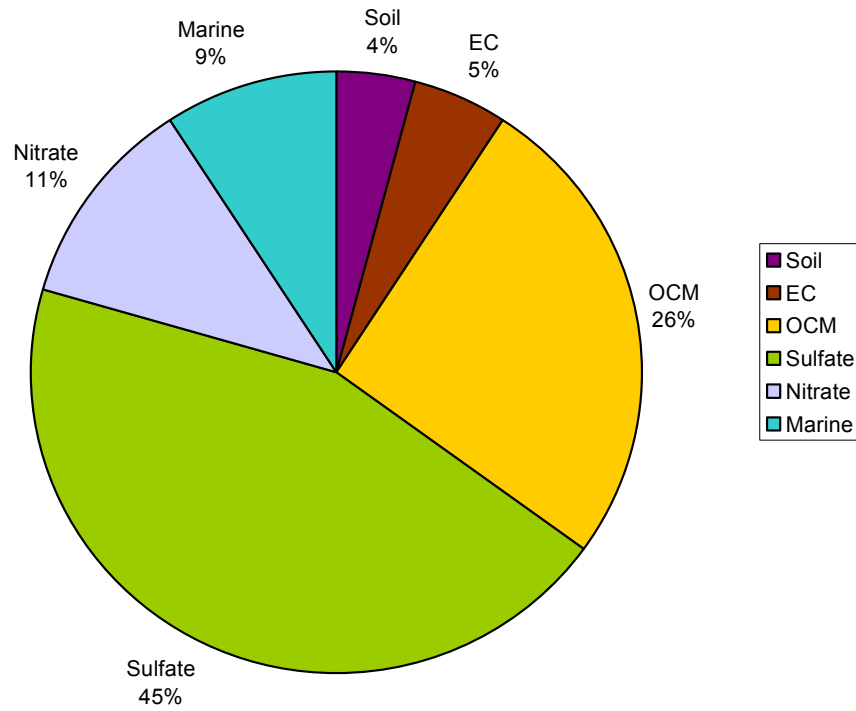


Figure 3-16. Mean composition of PM_{2.5} aerosol by RCFM with marine (3.91 $\mu\text{g}/\text{m}^3$) at Acadia, March-May 1999-2001.

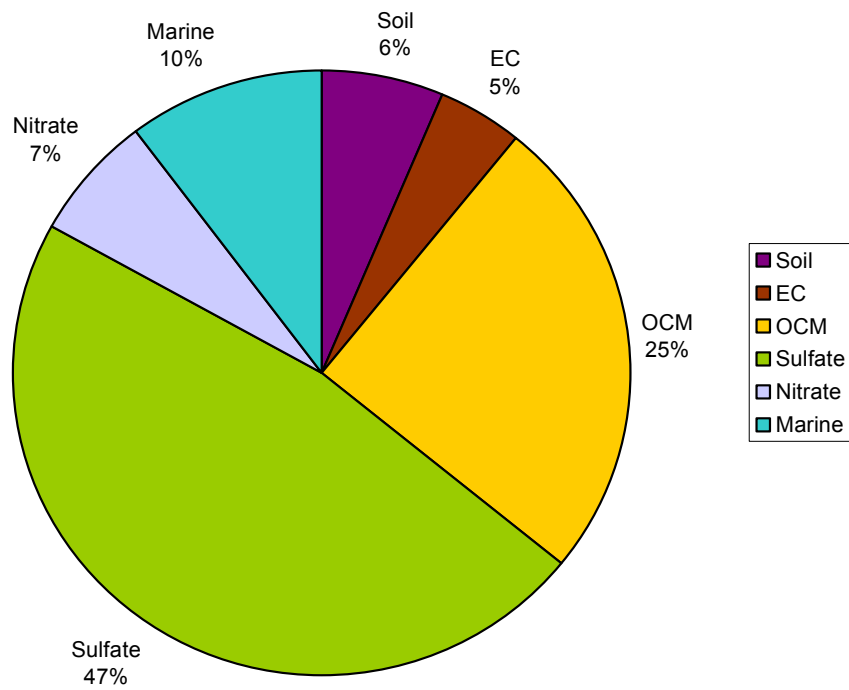


Figure 3-17. Mean composition of PM_{2.5} aerosol by RCFM with marine (8.36 $\mu\text{g}/\text{m}^3$) at Acadia, June-August 1999-2001.

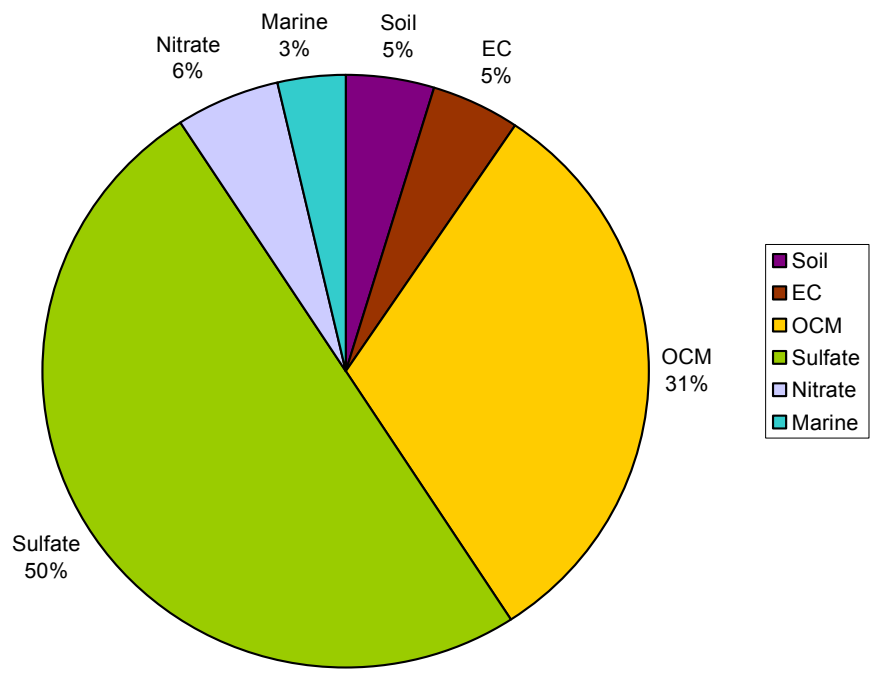


Figure 3-18. Mean composition of PM_{2.5} aerosol by RCFM with marine (4.61 µg/m³) at Acadia, September-November 1999-2001.

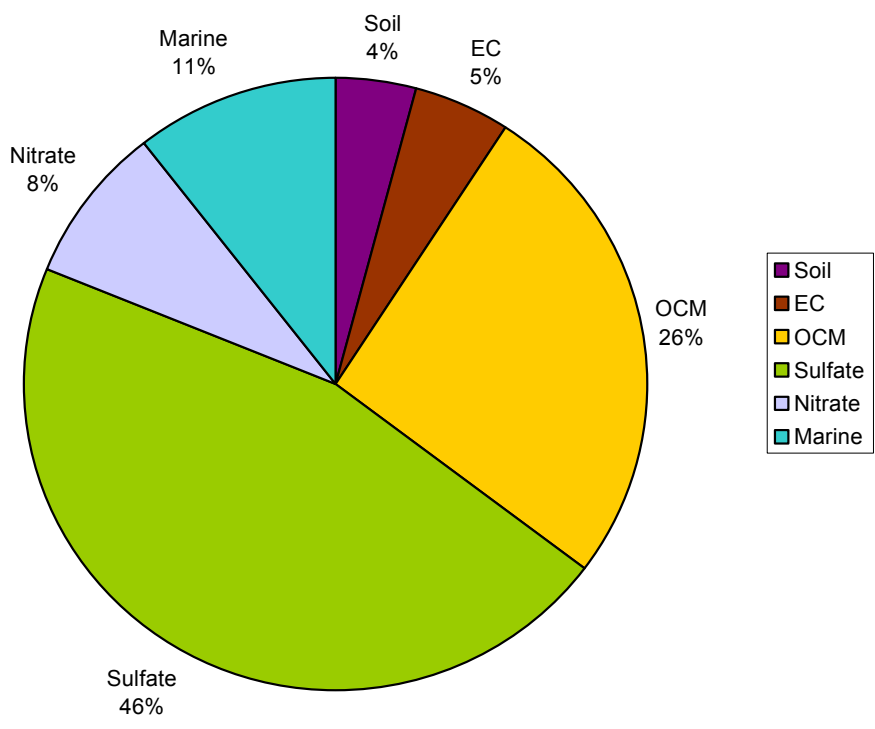


Figure 3-19. Mean composition of PM_{2.5} aerosol by RCFM with marine (4.45 µg/m³) at Acadia, December-February 1999-2001.

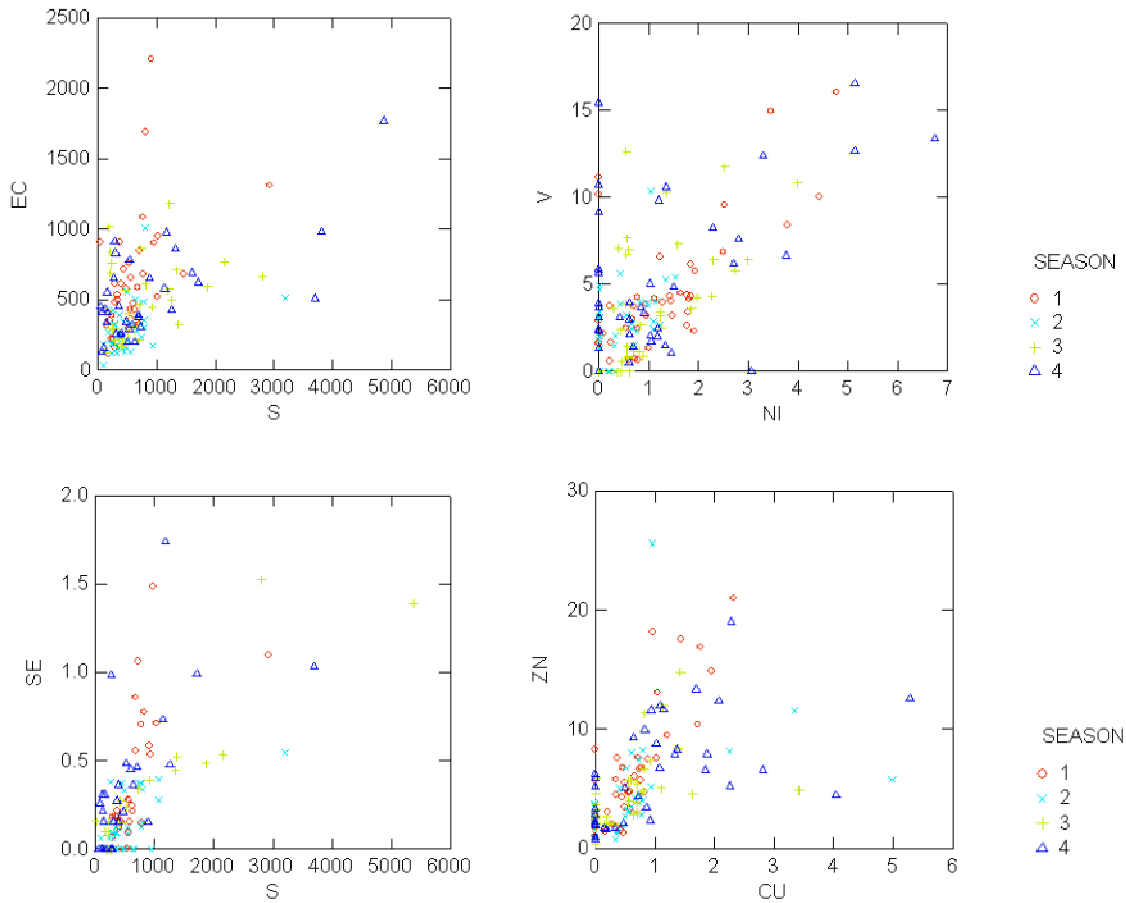


Figure 3-20. Scatter plots of selected IMPROVE species concentrations (in $\mu\text{g}/\text{m}^3$) at Casco Bay in 1998-2000; \circ = winter; \times = spring; $+$ = summer; Δ = fall.

Table 3-6. Selected maxima and minima in median IMPROVE $\text{PM}_{2.5}$ component concentrations at Casco Bay and Acadia in 1998-2000.

Species	Casco Bay				Acadia			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Fine mass	Max		Max				Max	
Sulfate			Max				Max	
Nitrate	Max				Max			
Soil		Max			Min			
Elemental carbon		Min					Max	
Organic carbon	Max		Max				Max	
Potassium	Max							

3.2.2 MDN Concentrations and Deposition

Table 3-7 provides summary statistics for mercury concentrations and deposition by season, including 1998-2001 data at Casco Bay. The summary statistics for other sites are provided in Appendix C. **Figures 3-21 through 3-24** show box whisker plots of mercury concentrations and deposition by season and site. All sites except Casco Bay¹¹ show statistically significant higher concentrations in summer than in other seasons based on a comparison of 95% confidence intervals around the seasonal medians. Annual trends are discussed in Section 4.

Table 3-7. Summary statistics for Casco Bay MDN mercury data by season (1998-2001).

Measurement	Number of Cases	Minimum	Maximum	Median	Mean	Standard Deviation	Coefficient of Variation
Winter							
Precipitation (mm)	34	0.5	91.2	16.2	25.2	24.0	
Mercury concentrations (ng/L)	37	2.0	16.7	4.8	6.1	3.8	0.6
Mercury deposition (ng/m ²)	37	4.1	848	64.0	123	160	1.3
Spring							
Precipitation (mm)	39	0.8	112	19.3	29.2	28.9	
Mercury concentrations (ng/L)	43	1.6	54.1	8.2	11.1	10.0	0.9
Mercury deposition (ng/m ²)	43	17.1	883	91.3	178	187	1.1
Summer							
Precipitation (mm)	31	0.8	188	17.2	26.4	33.3	
Mercury concentrations (ng/L)	40	3.4	28.6	12	13.2	6.2	0.5
Mercury deposition (ng/m ²)	40	2.8	2210	163	266.	360	1.4
Fall							
Precipitation (mm)	33	1.0	121	23.6	27.5	24.8	
Mercury concentrations (ng/L)	33	1.2	25.9	6.5	7.6	5.3	0.7
Mercury deposition (ng/m ²)	33	1.3	993	126	185	197	1.1

3.2.3 NTN Concentrations and Deposition

Table 3-8 provides summary statistics for NTN concentrations and deposition by season for Casco Bay from 1998 through 2001. Summary statistics for other sites are provided in Appendix C.

¹¹ The median concentrations of mercury are higher in the summer at Casco Bay; however, the overlap in confidence intervals indicates the difference between summer and spring is not statistically significant (likely a function of the relatively small number of samples).

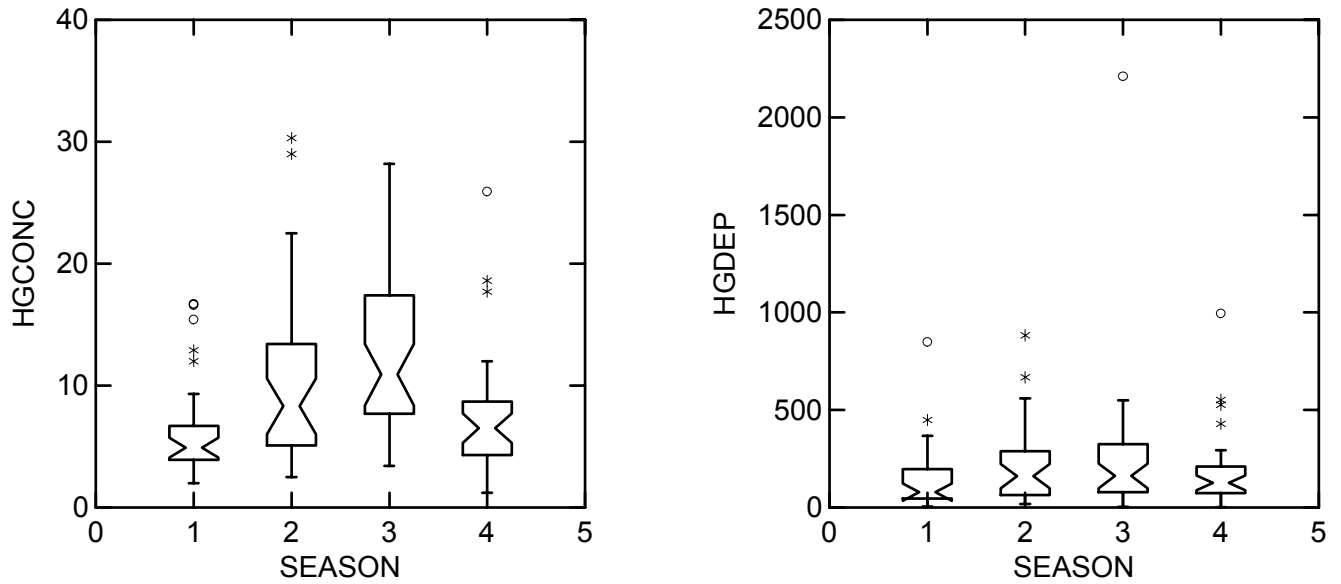


Figure 3-21. Notched box whisker plot of mercury concentration (HGCONC) in ng/L and deposition (HGDEP) in ng/m² at Casco Bay in 1998-2001; season 1 = winter, 2 = spring, 3 = summer, and 4 = fall.

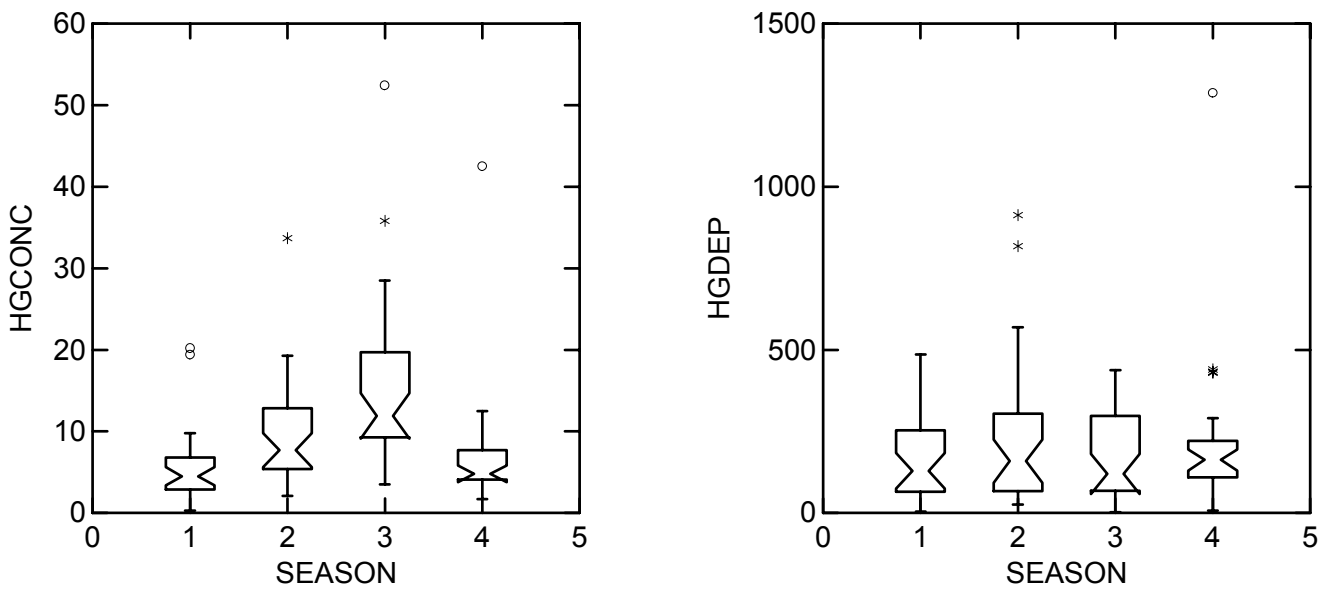


Figure 3-22. Notched box whisker plot of mercury concentration (HGCONC) in ng/L and deposition (HGDEP) in ng/m² at Acadia in 1998-2001; season 1 = winter, 2 = spring, 3 = summer, and 4 = fall.

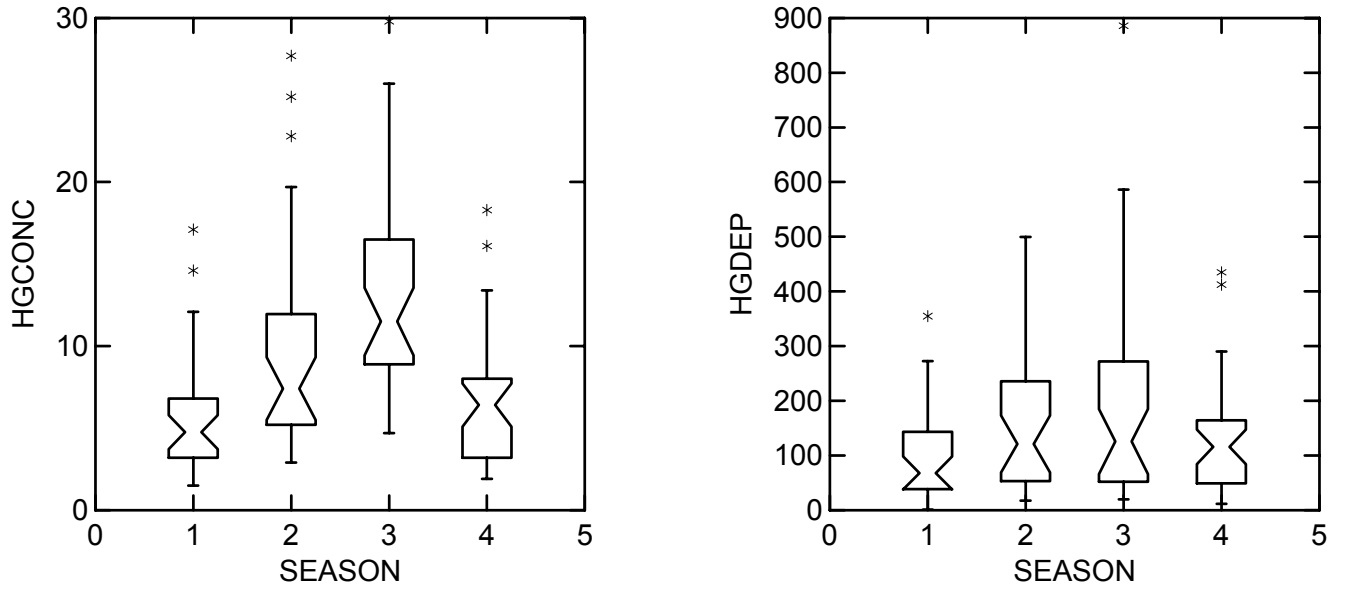


Figure 3-23. Notched box whisker plot of mercury concentration (HGCONC) in ng/L and deposition (HGDEP) in ng/m² at Bridgton in 1998-2001; season 1 = winter, 2 = spring, 3 = summer, and 4 = fall.

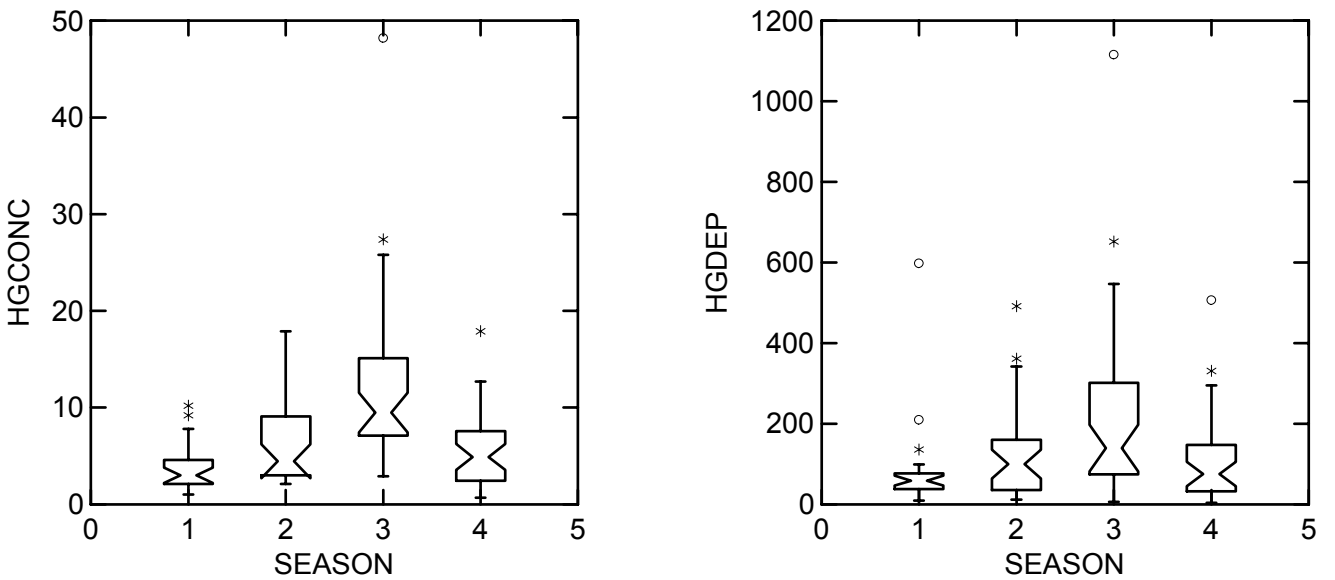


Figure 3-24. Notched box whisker plot of mercury concentration (HGCONC) in ng/L and deposition (HGDEP) in ng/m² at Greenville in 1998-2001; season 1 = winter, 2 = spring, 3 = summer, and 4 = fall.

Table 3-8. Summary statistics of NTN data by season at Casco Bay, 1998-2001. Species abbreviations are provided in Appendix A.

	Statistic	CA	MG	K	NA	NH ₄	NO ₃	CL	SO ₄
Winter (Dec-Feb)	Number of cases	24	24	24	24	24	24	24	24
	Minimum mg/L	0.03	0.01	0.00	0.06	0.01	0.55	0.11	0.27
	Maximum mg/L	0.09	0.08	0.03	0.80	0.22	3.03	1.30	2.56
	Median mg/L	0.04	0.03	0.01	0.18	0.11	1.78	0.30	1.02
	Mean mg/L	0.05	0.03	0.01	0.28	0.11	1.73	0.50	1.23
	Standard deviation mg/L	0.02	0.02	0.01	0.24	0.09	0.84	0.39	0.84
	Coefficient of variance	0.44	0.74	0.68	0.84	0.82	0.49	0.79	0.68
Spring (Mar-May)	Number of cases	39	39	39	39	39	39	39	39
	Minimum mg/L	0.01	0.01	0.00	0.02	0.01	0.09	0.06	0.18
	Maximum mg/L	0.57	0.11	0.12	0.42	0.73	6.05	0.74	4.88
	Median mg/L	0.07	0.03	0.02	0.19	0.18	0.87	0.31	1.31
	Mean mg/L	0.15	0.04	0.03	0.20	0.21	1.37	0.36	1.63
	Standard deviation mg/L	0.17	0.03	0.03	0.13	0.20	1.57	0.23	1.45
	Coefficient of variance	1.12	0.75	1.11	0.65	0.95	1.14	0.64	0.89
Summer (Jun-Aug)	Number of cases	27	27	27	27	27	27	27	27
	Minimum mg/L	0.04	0.01	0.00	0.00	0.11	0.41	0.03	0.43
	Maximum mg/L	0.20	0.05	0.10	0.31	0.52	3.39	0.58	3.06
	Median mg/L	0.10	0.02	0.03	0.12	0.31	1.21	0.24	2.41
	Mean mg/L	0.09	0.02	0.03	0.13	0.29	1.64	0.27	1.91
	Standard deviation mg/L	0.04	0.01	0.03	0.10	0.12	1.00	0.18	0.92
	Coefficient of variance	0.47	0.60	0.91	0.82	0.43	0.61	0.66	0.48
Fall (Sep-Nov)	Number of cases	53	53	53	53	53	53	53	53
	Minimum mg/L	0.02	0.01	0.00	0.01	0.01	0.18	0.11	0.4
	Maximum mg/L	0.33	0.19	0.07	1.72	0.71	8.68	3.03	4.47
	Median mg/L	0.05	0.04	0.01	0.34	0.20	0.84	0.60	1.18
	Mean mg/L	0.08	0.05	0.02	0.44	0.21	1.80	0.81	1.60
	Standard deviation mg/L	0.08	0.05	0.02	0.48	0.19	2.35	0.82	1.21
	Coefficient of variance	1.06	1.02	0.88	1.08	0.88	1.30	1.02	0.76

Time series plots of ion concentrations from the NTN network for Casco Bay (1998-2001) are provided in Appendix B. Typically, sulfate and nitrate were the highest contributors among the ions. **Figure 3-25** shows a line graph of median concentrations of precipitation ions by year in Casco Bay. Seasonally, the ammonium and sulfate ion concentrations in precipitation were higher in the summer at Casco Bay (**Figure 3-26**).

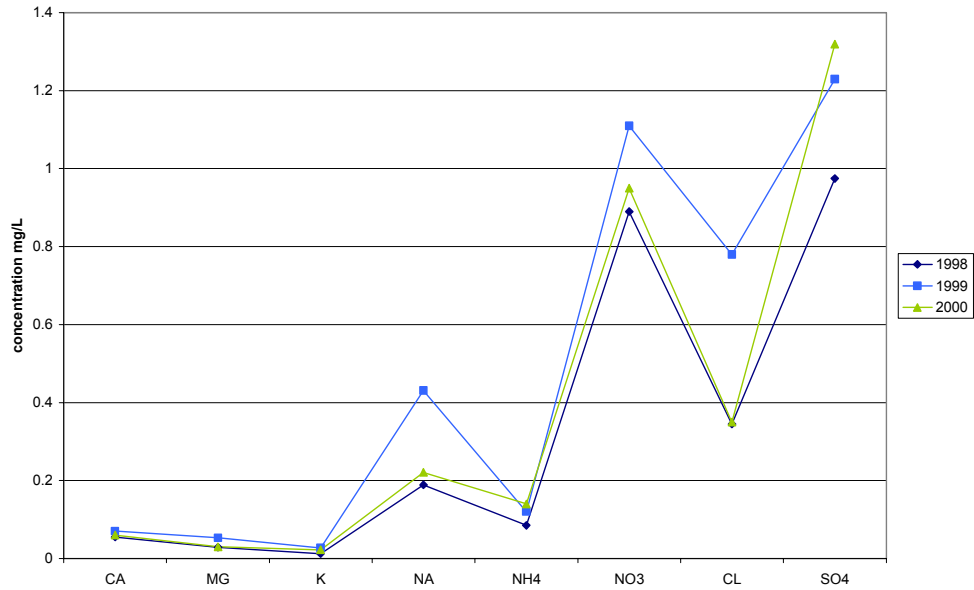


Figure 3-25. Annual median concentrations (mg/L) of ions at Casco Bay, 1998-2001.

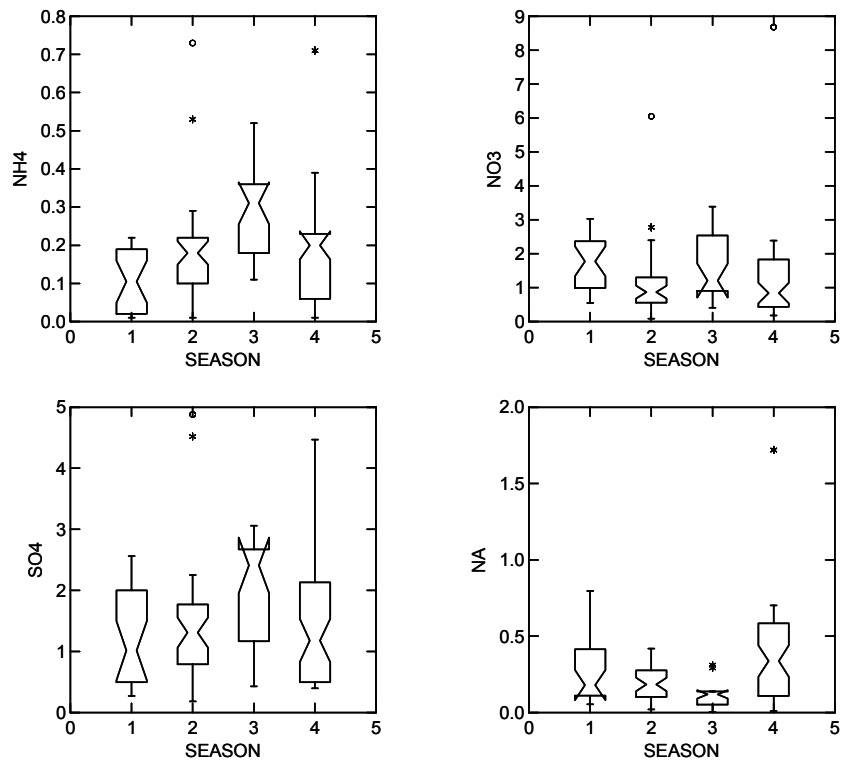


Figure 3-26. Casco Bay precipitation concentrations (ng/l) of ammonium (NH₄), nitrate (NO₃), sulfate (SO₄), and sodium (NA) ions from 1998 through 2001; 1 = winter, 2 = spring, 3 = summer, and 4 = fall.

3.3 INTERSITE COMPARISONS

We investigated the relationships of concentrations among sites to assess how well two sites track each other. If good correlations exist, it may not be necessary to maintain monitors at all the sites.

3.3.1 IMPROVE

We prepared scatter plots (and linear regression) of matching IMPROVE samples at Acadia and Casco Bay. **Figures 3-27 and 3-28** summarize the constructed parameter comparisons. The figures illustrate the following:

- EC concentrations were higher at Casco Bay and the correlation is modest ($r^2 = 0.55$).
- OCM concentrations were also higher at Casco Bay; and the data do not show a linear correlation between the two sites.
- The sulfate data show two different relationships. In 1998, the total sulfate concentrations were higher in all samples at Acadia than at Casco Bay. After 1998, the sulfate concentrations were either similar or the Casco Bay concentrations were higher than at Acadia. This comparison, coupled with the findings presented in Section 2 regarding Casco Bay sulfur measurements, leads us to question the 1998 sulfur measurements at Casco Bay. Note that the correlation between the two sites for total sulfur is very good for the 1999 and 2000 data (slope = 1.3, $r^2 = 0.97$). This relationship indicates similar sources (or regional air mass) of sulfate.
- Total nitrate concentrations also correlated reasonably well ($r^2 = 0.76$) when one Acadia outlier is removed.
- Soil and marine components of $PM_{2.5}$ did not correlate well between the two sites. This makes sense because these components would tend to be of more local origin. There are also significant topographical and climatological differences between the two sites.
- The RCFM plus marine concentrations, largely driven by OCM and sulfate, show significant scatter. This also makes sense because OCM does not correlate between the two sites while sulfate does.

3.3.2 Nitrogen

Weekly Casco Bay inorganic nitrogen wet deposition, concentrations, and precipitation data from 1998 to 2000 were compared to those reported at Acadia, Bridgton, and Greenville (see **Table 3-9**). Casco Bay ammonium and nitrate data correlate best with corresponding measurements reported at Bridgton, which is located in the same watershed but inland. Although precipitation ammonium ion concentrations at Acadia correlate modestly with Casco Bay ($r^2 = 0.53$), the wet deposition data do not correlate well. Measurements at Greenville, located inland and well north were in relatively poor temporal agreement with those found at Casco Bay.

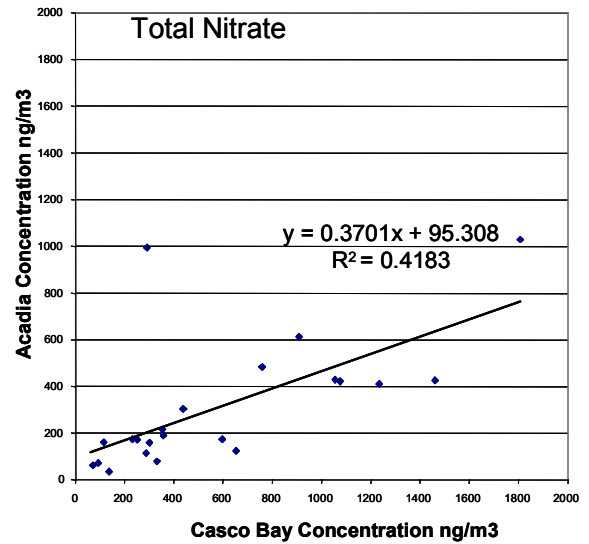
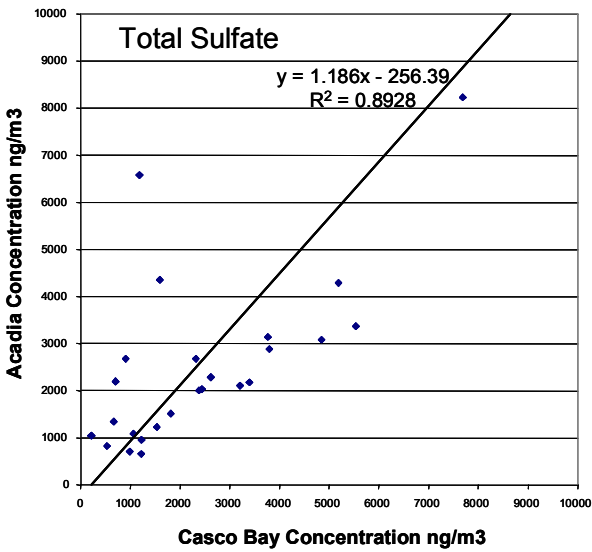
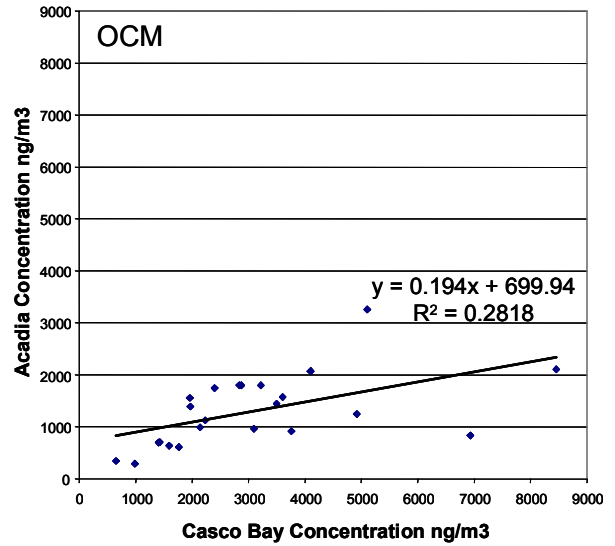
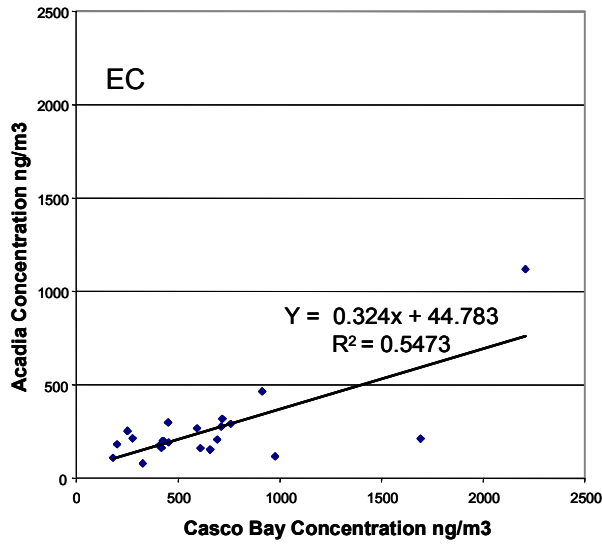


Figure 3-27. Scatter plots of EC, OCM, total sulfate, and total nitrate concentrations (ng/m³) at Acadia versus Casco Bay using IMPROVE data from August 1998 through 2000 for matching days.

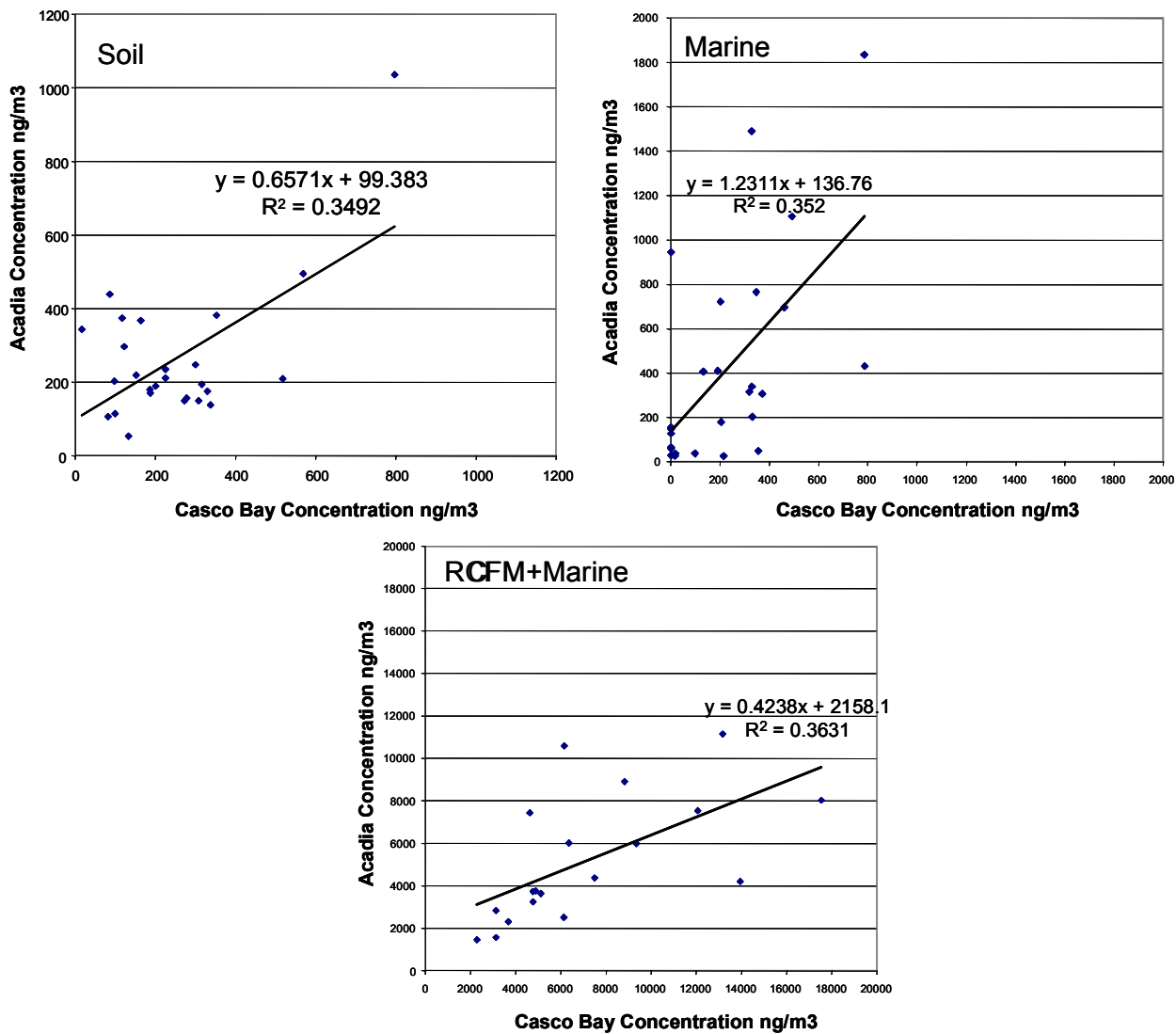


Figure 3-28. Scatter plots of soil, marine, and RCFM+marine component concentrations (ng/m³) at Acadia versus Casco Bay using IMPROVE data from August 1998 through 2000 for matching days.

Table 3-9. Statistical relationships found between pollutant concentrations at Casco Bay and each of the other Maine sites.

Statistic	Acadia	Bridgton	Greenville
Ammonium			
Correlation coefficient (r^2)			
Wet deposition	0.10	0.40	0.08
Concentration	0.53	0.49	0.32
Precipitation	0.38	0.79	0.46
Nitrate			
Correlation coefficient (r^2)			
Wet deposition	0.18	0.59	0.18
Concentration	0.35	0.67	0.14
Precipitation	0.38	0.79	0.46
Annual wet deposition			
Ammonium	-7%	+27%	-6%
Nitrate	-9%	+3%	-20%

Despite the differences in concentrations, annual average ammonium and nitrate wet deposition (1998-2000) at Acadia were only 7% and 9% lower than ammonium and nitrate depositions, respectively, estimated for Casco Bay. In contrast, Bridgton annual average wet deposition totals for ammonium and nitrate were 27% and 3% higher than those reported for Casco Bay.

3.3.3 Mercury

Weekly Casco Bay mercury wet deposition, concentrations, and precipitation data from 1998 to 2000 were compared to those reported at Acadia, Bridgton, and Greenville (see **Table 3-10**). Casco Bay mercury data correlate best with corresponding measurements reported at Bridgton, which is located in the same watershed. Although mercury wet deposition data at Greenville correlate modestly with Casco Bay data ($r^2 = 0.49$), the mercury concentrations do not correlate well. Mercury concentrations at Acadia were in relatively poor temporal agreement with those found at Casco Bay.

Despite the differences between Acadia and Casco Bay mercury concentrations, annual average mercury wet deposition (1998-2000) at Acadia was only 6% higher than that estimated for Casco Bay. Bridgton wet deposition was 16% lower than that reported for Casco Bay, making it the least accurate annual estimator of Casco Bay wet deposition totals for the period of record.

Table 3-10. Statistical relationships found between precipitation and mercury wet deposition and concentration measures at Casco Bay and other Maine sites.

Statistic	Acadia	Bridgton	Greenville
Correlation coefficient (r^2)			
Wet deposition	0.28	0.58	0.49
Concentration	0.28	0.48	0.07
Precipitation	0.37	0.77	0.48
Annual wet deposition	+6%	-16%	-10%

3.4 INTER-POLLUTANT COMPARISONS AT CASCO BAY

We investigated the relationship among the chemical species measured in the IMPROVE samples to learn more about possible sources of the pollutants; we used scatter plots, correlation matrices, and factor analysis to carry out this investigation. Scatter plots and correlation matrices can identify strong relationships among the chemical species. Factor analysis groups data by similarity among variables (i.e., variables that are highly correlated are grouped). Possible sources can be inferred by comparing the resulting “profiles” with measured source profiles, likely sources and their location. Results for Casco Bay were compared to published results at Acadia, Maine, and Underhill, Vermont.

A comprehensive analysis using more sophisticated multivariate tools (e.g., positive matrix factorization [PMF]) combined with trajectory analyses, such as the analyses discussed by Polissar et al. (2001), was beyond the budget of this project. We have included recommendations for this type of analysis in Section 6.

3.4.1 Scatter Plots

Scatter plot analyses can range from straightforward x-y plots of data to extensive ratio analysis by season such as the analyses performed by Polissar et al. (2001). For this project, scatter plots using different symbols for seasons and scatter plot matrices were prepared for Casco Bay and Acadia IMPROVE data. A scatter plot matrix is shown in **Figure 3-29**. To interpret a scatter plot matrix, locate the row variable (e.g., PM₂₅ in Figure 3-29 near the top left) and the column variable (TSULF) on the bottom. The intersection is the scatter plot of the row variable on the vertical axis against the column variable on the horizontal axis. Each column and row is scaled so that data points fill each frame. Scale information is omitted and these plots are useful in a qualitative way. The diagonal plots contain histograms of the data for each column variable.

Because the PM_{2.5} mostly consists of OCM and total sulfate components, we would expect a relatively strong relationship between these components and the total mass. Similarly, the soil component mostly consists of Al, Ca, Si, and Fe and we would expect these species to correlate well with the soil component (with a few outliers). The data show a significant amount of scatter which is one indicator that source emissions are not individually very distinct, perhaps due to distance and mixing of sources. Other scatter plot matrices are shown in Appendix D.

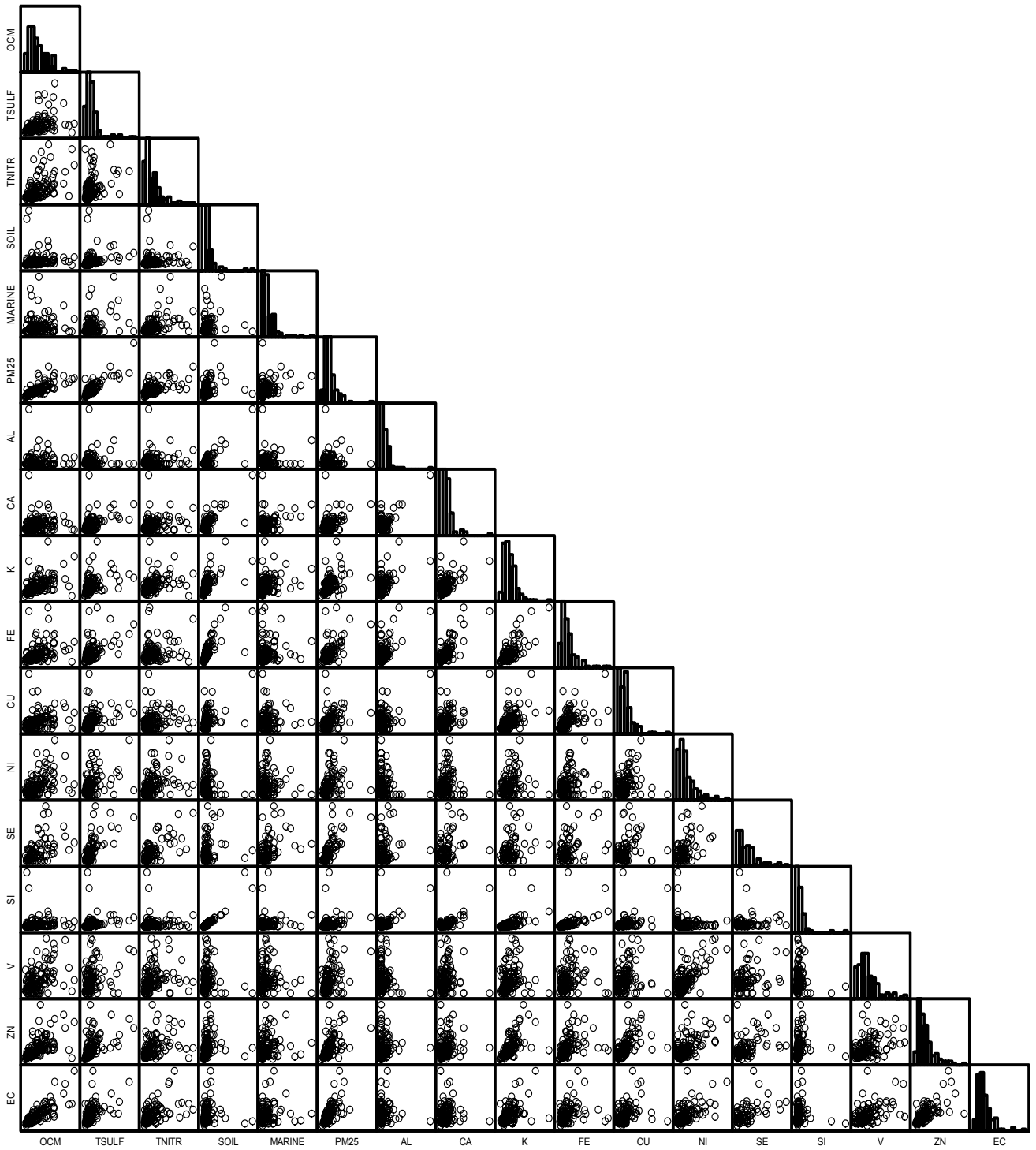


Figure 3-29. Scatter plot matrix for Casco Bay 1999-2000 data. Species abbreviations are provided in Appendix A.

We also prepared scatter plots of Casco Bay MDN and NTN wet data. These scatter plots are shown in **Figure 3-30**. A poor temporal correlation ($r^2 = 0.44$; $r^2 = 0.29$ with one data point removed) exists between nitrate and mercury wet deposition data. On the other hand a relatively strong temporal correlation ($r^2 = 0.69$) is observed between weekly ammonium and nitrate wet deposition amounts. With this correlation, we would normally conclude that the majority of ammonium and nitrate emissions impacting Casco Bay come from the same set of sources. However, this goes against current wisdom—EPA reports nationally 95% of NO_x emissions derive from on-road and off-road engines (53%) and fuel combustion (42%); (U.S. Environmental Protection Agency, 2002b). For comparison purposes, 86% of ammonium emissions nationally come from miscellaneous sources (including livestock and fertilizer).

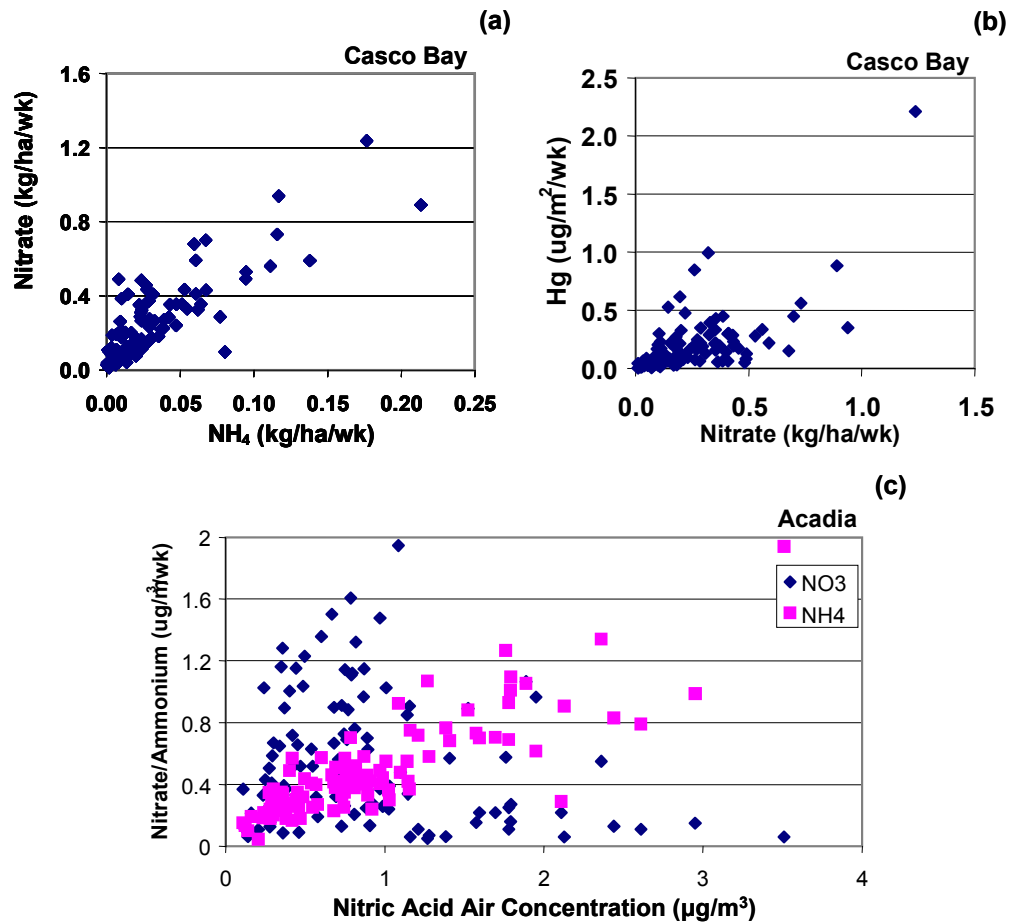


Figure 3-30. Scatter plots of weekly (1998 to 2000) (a) nitrate and ammonium wet deposition at Casco Bay ($r^2 = 0.69$); (b) nitrate and mercury wet deposition at Casco Bay ($r^2 = 0.44$; 0.29 with one data point excluded); and (c) nitric acid air concentrations compared to nitrate ($r^2 = 0.03$) and ammonium ($r^2 = 0.71$) at Acadia. Units are provided in the plots.

Because Casco Bay is not a site where ambient air concentrations of ammonium and nitrate are collected, we are unable to directly determine whether the temporal correlation seen in Casco Bay wet deposition data is also seen in ambient air observations. The nearest coastal Maine CASTNet site is in Acadia, Maine. Based on our analysis of 1998 to 2000 Acadia data, our finding is that no correlation ($r^2 = 0$) exists between nitrate and ammonium air concentrations, yet a strong temporal correlation ($r^2 = 0.71$) was found between nitric acid and ammonium air concentrations as well as nitric acid and wet ammonium at Acadia.

Based on this finding, we investigated whether other nearby CASTNet sites showed similar strong correlations between ammonium and nitric acid air concentrations from 1998 to 2000. Our finding is that two Northeastern sites showed somewhat more modest correlations—Abington, Connecticut ($r^2 = 0.50$) and Claryville, New York ($r^2 = 0.45$); the nearest out-of-state site showed a very small positive correlation—Woodstock, New Hampshire ($r^2 = 0.23$). Evidently, Maine is regionally unique in that nitric acid and ammonium concentrations in air are strongly correlated. Further research into this issue would prove helpful in understanding whether this effect plays an important role in wet deposition in Maine and, if so, whether it can be used to advantage in reducing wet deposition.

Because of the strong temporal correlation found between wet ammonium and wet nitrate ($r^2 = 0.69$) and between wet ammonium and nitric acid air concentrations ($r^2 = 0.71$) in coastal Maine, the data suggest that in Maine almost all nitrate observed in wet deposition at Casco Bay came from nitric acid (and not nitrate) in the atmosphere¹². Further research that compares the ratio of wet ammonium to wet nitrate to the ratio of ammonium and nitric acid air concentrations would reveal whether these two species were being scavenged from the atmosphere proportionately or not within Maine. Such research information can also be applied to validate and/or update how models handle nitric acid versus nitrate.

3.4.2 Pearson Correlation Analysis

We prepared a Pearson correlation analysis of the Casco Bay and Acadia IMPROVE data collected in 1998-2000. Results for both sites are shown in Appendix E. Few species relationships in this data set had correlation coefficients (r^2) greater than 0.7 (accounting for more than 50% of the variability in the data). Of the correlated species, the relationships are consistent with those shown in the scatter plot analyses and previous discussions (e.g., soil components, sulfur and hydrogen, and marine components).

3.4.3 Factor Analysis

Factor analysis was performed using SYSTAT software to investigate the Casco Bay data. Factor analysis is a useful first look at data before other, more sophisticated analytical tools are employed, including UNMIX or PMF. We selected a varimax rotation (the results are easier to interpret) and used the data collected from August 1998 through 2000. Data below detection were replaced by zeroes in the analysis because of the lack of MDL information. We obtained seven factors, listed in **Table 3-11**. These factors are similar to the sources identified for Acadia

¹² Another possibility is that the data are potentially biased by ammonium nitrate aerosol decomposing from the front Teflon filter and being collected as nitrate on the back Nylon filter.

(Coutant et al., 2001) and for Underhill, Vermont (Polissar et al., 2001). At Acadia, sources included secondary OC and secondary sulfate (both with peaks in the summer); incinerator; marine; wood smoke (with a peak in the winter); and small crustal, oil/diesel factors. At Underhill, sources included midwest coal (both a summer and a winter factor); wood smoke, zinc-lead; east coast oil; smelting; soil; and a manganese factor. Transport is clearly an important source of PM_{2.5} species at Underhill and Casco Bay.

Table 3-11. Summary of results of factor analysis using Casco Bay IMPROVE data.

Factor	% of Variance	Key Species
Soil	16	Aluminum, calcium, silicon, iron, potassium, strontium
Oil combustion	12	Nickel, vanadium, zinc, arsenic
Marine	8	Chlorine, sodium, magnesium
Municipal waste incineration	8	Lead, rubidium, selenium
Secondary/transport	10	OC, EC, nitrate, sulfate
Coal-fired power plant	11	Selenium, sulfur, hydrogen
Smelting	6	Manganese, copper

We attempted to perform factor analysis on the data segregated by season but results were difficult to interpret because of the relatively low number of seasonal samples. Different approaches to data below detection and the use of more sophisticated factor analysis tools might improve these results, along with the addition of more years of data.

3.5 CASE STUDIES

3.5.1 Transport Regimes in the Northeastern United States

Blumenthal et al. (1997) and Blumenthal et al. (1997) observed that during the 1995 multi-day summer ozone episodes in the northeastern states corridor, pollutant transport was affected by three transport regimes that differ with altitude (see **Figure 3-31**):

- A boundary layer synoptic-scale transport regime that extends from about 800 meters above ground level (m agl) to about 1500 m agl (i.e., regional transport that could cross the Appalachians).
- A regional-scale channeled flow regime that extends from about 200 to about 800 m agl (i.e., nocturnal low-level jets and channeled flows along the Appalachians and major river valleys).
- A near-surface flow regime that extends from the surface to about 200 m agl (i.e., nighttime stagnation, sea breeze and land breeze, and offshore flows).

Although conditions during ozone episodes in the region often include light and variable winds at the surface and enhanced photochemistry, Figure 3-31 shows that winds typically transport

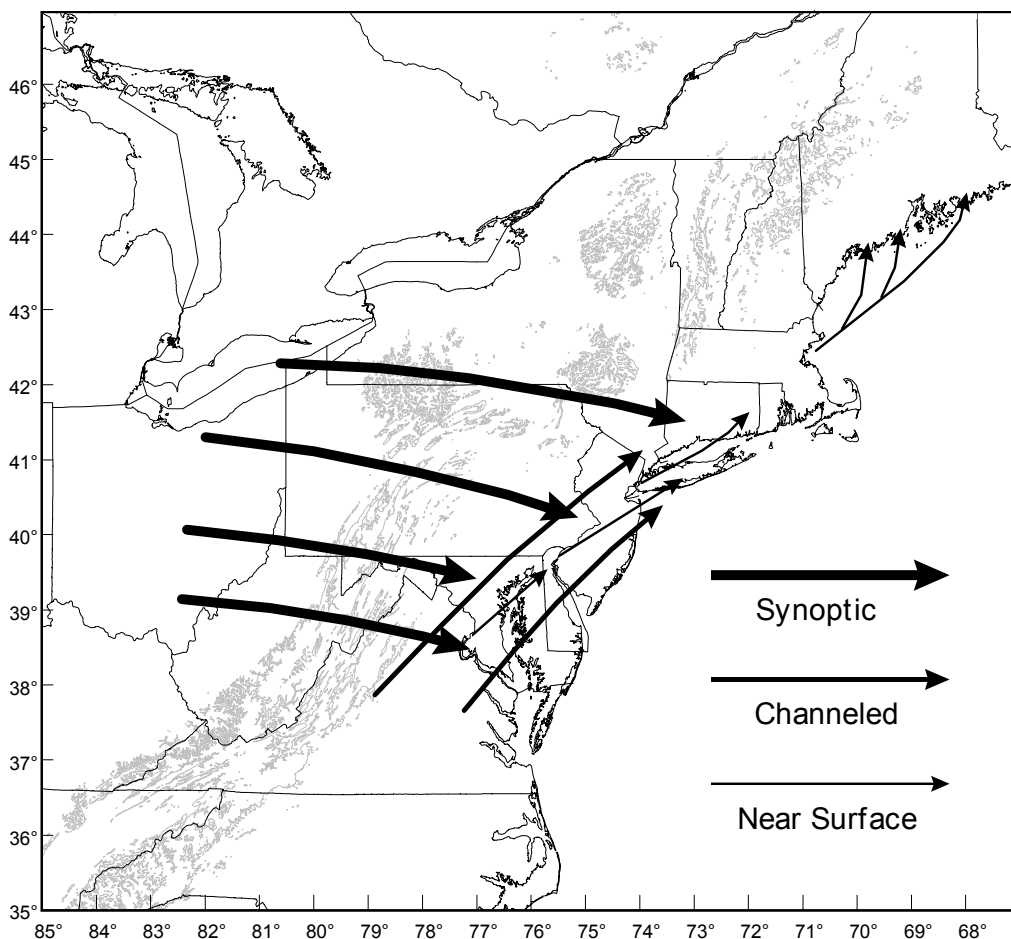


Figure 3-31. Transport regimes observed during the 1995 ozone episodes in the Northeast corridor (from Blumenthal et al., 1997).

ozone, ozone precursors, and particles along a westerly or southwesterly flow path. Trajectory analyses show similar transport directions (see Blumenthal et al., 1997). While these analyses were performed for ozone and its precursors in the summer, the observations are also relevant to PM_{2.5} during the summer and other photochemically sensitive constituents of atmospheric pollution.

3.5.2 Trajectory Analysis Using Casco Bay Data

The NOAA HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model (Draxler, 1996) is a three-dimensional air mass trajectory model based on weather model data. This model, obtained from the NOAA web site at <<http://www.arl.noaa.gov/ready/hysplit4.html>> (last accessed July 2002), was used to compute daily backward trajectories for air masses arriving at Casco Bay. Backward trajectories were run at noon local time for each day with an ending height of 1500, 1000, and 500 m, in order to capture potentially changing boundary heights. The weather data, a product of the Global Data Assimilation System (GDAS) that uses the Global Spectral Medium Range Forecast model (MRF), was used. This data set uses a 129-km x 129-km

polar stereograph grid at approximately 190 km resolution with 12 vertical layers and is run at 6-hr increments. It utilizes three-dimensional wind components, temperature, relative humidity, and radioactive and momentum fluxes. Additional information can be found at <http://www.arl.noaa.gov/ready-bin/fnl.pl> (last accessed July 2002).

These trajectories are only an approximation of from where the air parcel has traveled. The exact latitude and longitude calculated by the back trajectory model does not mean that only those points affected the composition of the air parcels. The farther away in distance and time from the origin, the more error is involved at each point along the trajectory path. The area around each point plotted affects the air parcels, and with error increasing with time and distance, the potential area of effect also increases. Absolute trajectory error generally ranges from 20% to 30% of the travel distance (Draxler, 1991). This is not to discount the trajectories' utility, but to highlight that only general areas of influence can be established.

We ran backward trajectories for selected days of interest using the IMPROVE data; a list is provided in **Table 3-12**. **Figure 3-32** shows a trajectory path carrying air parcels through the northeastern United States urban corridor to Maine; other trajectories are provided in Appendix F. Air parcels of interest typically arrived from three general directions: (1) from the north, (2) from the southwest along the northeastern United States urban corridor, and (3) from the west. Trajectories from the southwest and west correspond to the flow regimes identified in ozone transport work (Figure 3-31). Trajectories for 1998 were reported by Mosher (2000) and are summarized in **Table 3-13**. The results are consistent with other analyses and research. However, to obtain more robust and detailed results, it would be best to apply an approach similar to that of Polissar et al. (2001) in which PMF was used to obtain source profiles and then prepare a large number of air parcel trajectories to obtain probable geographical source locations as a function of these profiles.

Table 3-12. Days for which backward trajectories originating in Casco Bay were performed.

Date	Interesting Feature	Trajectory Result
6/29/99	High nitrate, soil, and sulfur	From the northeastern United States urban corridor
7/5/99	Potassium and soil (Fourth of July fireworks!)	From the west, appears to be relatively high wind speeds
7/17/99	High sulfur	From the west
9/9/99	High sulfur and ammonium	From the northeastern United States urban corridor
11/2/99	High magnesium	From the south, southwest along the coast
11/26/99	High chromium	From the south; 500 m winds show stagnation for the 0800 back trajectory
2/24/00	High sulfur and OC	From the west and northwest
3/1/00	High aluminum, potassium, silicon (likely local soil source)	Generally from the north, mostly remaining in Maine
5/18/00	Abundant nitrates, sodium, and sulfur, high PM _{2.5}	From the northeastern United States. urban corridor
9/9/00	High sulfur	From the northwest, primarily Canada
10/27/00	High PM _{2.5} (high Na, P, SO ₄ , NO ₃ , OC)	From the south, southwest along the coast

NATIONAL OCEANIC ATMOSPHERIC ADMINISTRATION
 Backward trajectories ending at 18 UTC 09 Sep 99
 FNL Meteorological Data

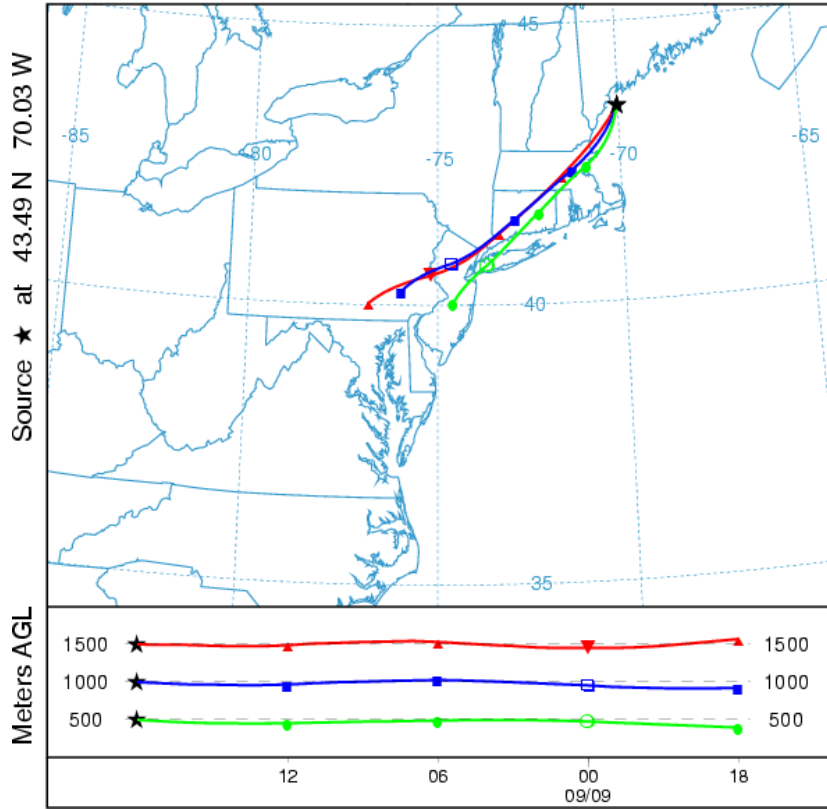


Figure 3-32. Back trajectory from Casco Bay at 1200 EST on September 9, 1999, at three altitudes.

Table 3-13. Summary of previous results for back trajectories reported by Mosher (2000).

Date	Interesting Feature	Trajectory Result
12/7/98	High nitrate, marine	From the west
12/31/98	High potassium, arsenic	From the west and northwest

We investigated a few trajectories for the MDN and NTN data; however, these trajectories are much less meaningful for data collected on a weekly basis. **Figure 3-33** shows a series of 72-hr trajectories for the week ending June 16, 1998 (corresponding to high mercury deposition). The trajectories differed from day to day, even on days with precipitation. The differences make it nearly impossible to ascertain the source of the mercury because we are not even sure which day of rain had the highest concentrations.

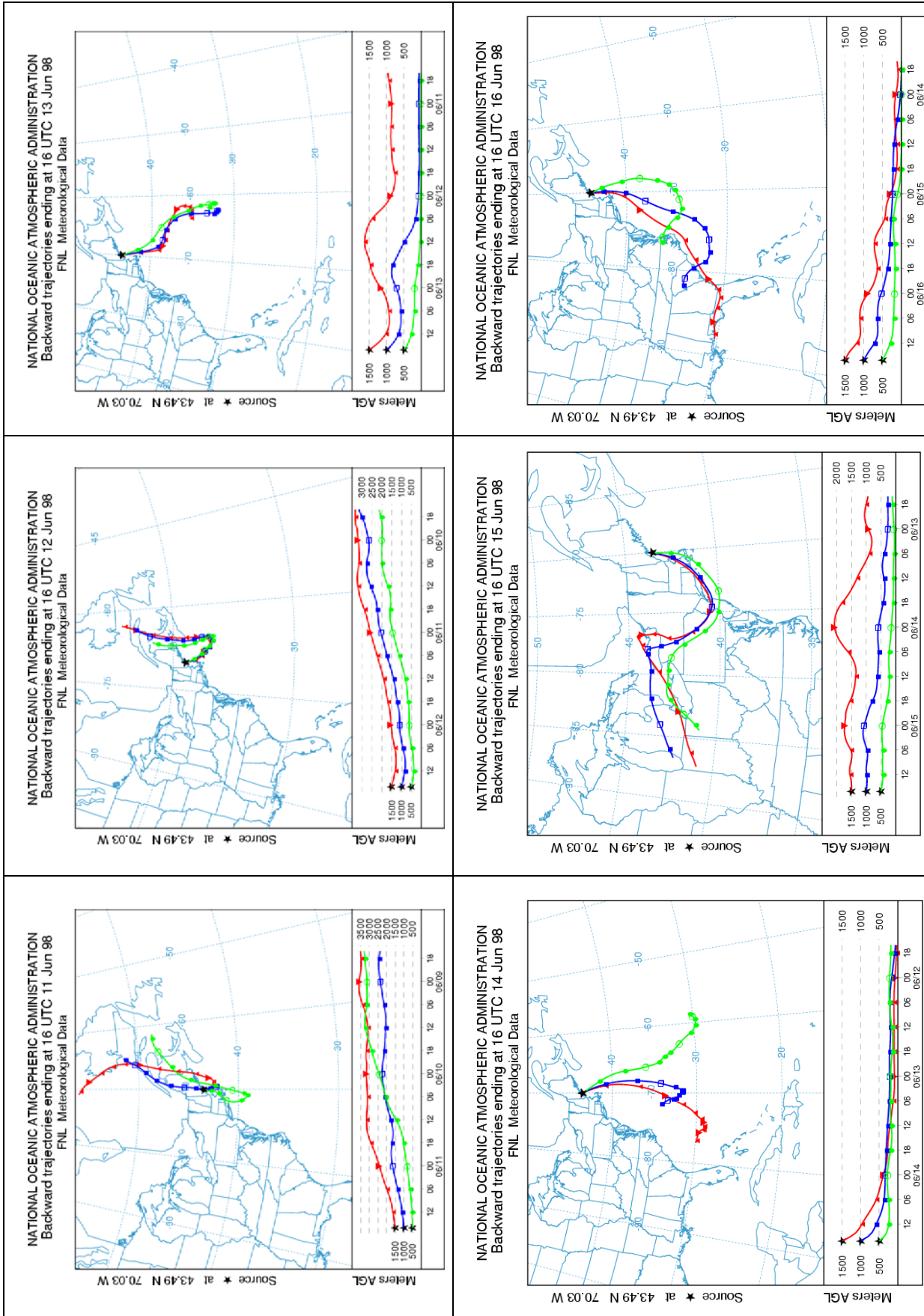


Figure 3-33. Seventy-two-hour HYSPLIT trajectory runs from Casco Bay for June 11 through June 16, 1998.

4. WET DEPOSITION TRENDS RELATED TO EMISSION CHANGES

A variety of assessment methodologies were used to investigate trends in mercury, ammonia, and nitrate wet deposition at Casco Bay and three other sites in Maine: Acadia National Park, Bridgton, and Greenville during 1998-2001. The assessment methodologies consisted of (1) presenting the short-term precipitation trends that occurred at these sites, (2) comparing actual annual wet deposition amounts and trends at Casco Bay to the other three sites; this is the traditional approach, (3) presenting the wet deposition concentration trends, and (4) creating “adjusted” annual wet deposition totals that better illustrate trends related to emission changes.

4.1 ACTUAL WET DEPOSITION TRENDS

The annual wet deposition by year was investigated and observations were noted. No conclusions about the efficacy of current control strategies (for example) should be drawn from the 1998-2001 time span of results available for analysis.

4.1.1 Precipitation

It is important to understand the precipitation patterns and forms of precipitation that take place in Maine because short-term trends in annual wet deposition can be the result of short-term precipitation trends as opposed to emission trends. Alternatively, because snow and rain remove different fractions of ambient air pollutants, a short-term annual trend of decreasing or increasing percentages of precipitation as rain versus snow can create a corresponding annual wet deposition trend in the absence of other effects.

Precipitation samples were collected weekly at each of the Maine sites from 1998 to 2001. The precipitation samples were classified as rain, snow, a mixture of the two, or unknown, depending on local knowledge of what occurred during the week. Based on this information as illustrated in **Figure 4-1**, rain represented 50% to 70% of total precipitation at Acadia and Casco Bay from 1998 to 2001. At Bridgton, rain constituted 40% to 60% of total precipitation. At Greenville, rain represented 30% to 70% of total precipitation, making it the site with the greatest year-to-year variation in rain representation.

At most, 6% of total precipitation in any one year was classified as snow at the coastal sites (Acadia and Casco Bay). A much larger 25% of precipitation collected was classified as a mixture (rain and snow). The fact that four times as much precipitation was a mixture (25%) relative to snow (6%) at coastal sites means that uncertainty exists as to how much and what percentage of rain and snow was actually received at Casco Bay in any year. In general, this level of uncertainty about the actual percentage of rain and snow by year limits our ability to make conclusions about wet deposition trends because snow and rain scavenge air pollutants at different rates (this is illustrated Section 4.1.6).

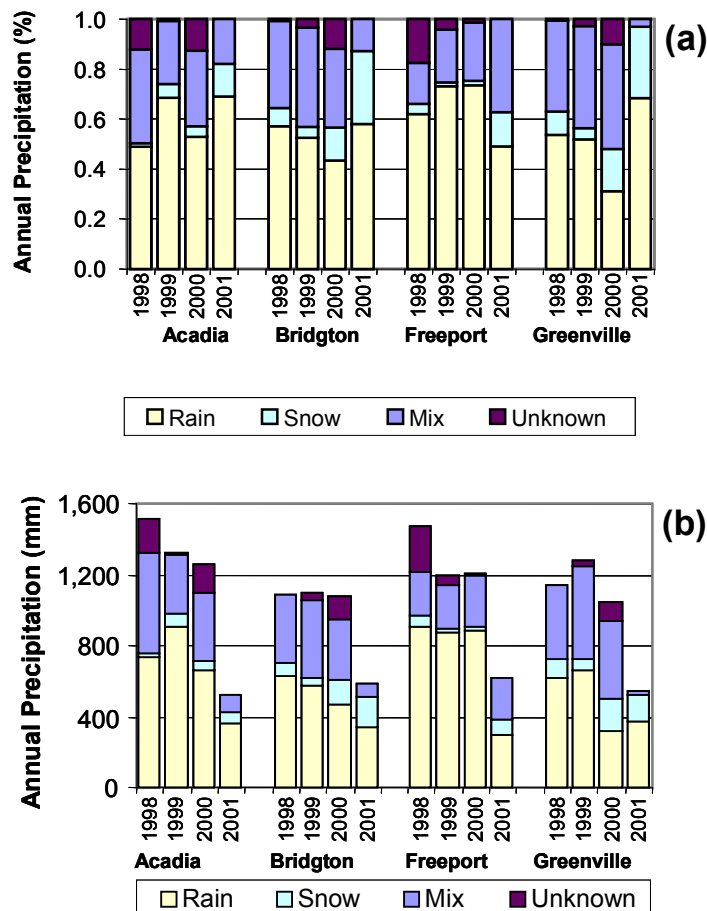


Figure 4-1. The 1998 to 2001 annual precipitation amounts at four Maine sites classified as rain, snow, a mixture, and unknown in (a) percents (%) and (b) millimeters (mm).

Annual precipitation at Casco Bay (see Figure 4-1) declined by roughly 60% from a maximum of 1470 mm to a minimum of 616 mm from 1998 to 2001. Annual precipitation at Acadia, the other coastal site, declined by roughly 66% from 1510 mm to 520 mm from 1998 to 2001. In contrast, Bridgton and Greenville recorded similar levels of annual precipitation from 1998 to 2000 followed by a sharp 50% decline in 2001. As illustrated in Figure 4-1, annual precipitation is greater at the coastal sites (i.e., Casco Bay and Acadia) compared to the inland sites (i.e., Bridgton and Greenville). In summary, all four sites had declining precipitation totals from 1998 to 2001.

4.1.2 Mercury

Annual mercury wet deposition at Casco Bay (see **Figure 4-2**) declined from a maximum of 12,500 ng/m² to a minimum of 5700 ng/m² from 1998 to 2001. Likewise, annual mercury wet deposition at Acadia declined from 9250 ng/m² to 5240 ng/m² from 1998 to 2001. Bridgton and

Greenville recorded similar declines in annual mercury wet deposition from 1998 to 2001. As illustrated in Figure 4-2, annual mercury wet deposition is generally greater at the coastal sites (i.e., Casco Bay and Acadia) compared to the inland sites (i.e., Bridgton and Greenville). These declining short-term trends in annual wet deposition are consistent with corresponding declining annual precipitation totals.

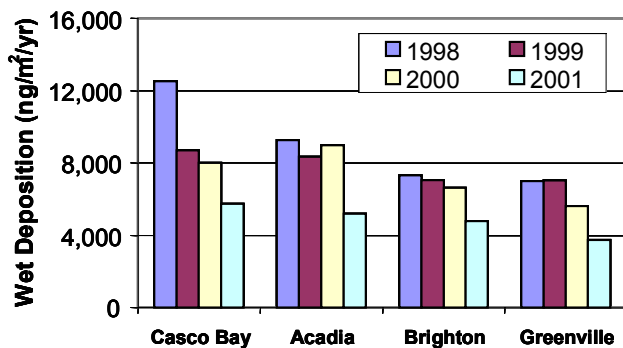


Figure 4-2. Annual 1998-2001 mercury wet deposition amounts ($\text{ng}/\text{m}^2 \text{ yr}^{-1}$) for sites in Maine.

4.1.3 Ammonia

The short-term trend in observed annual wet deposition for ammonia at Acadia, Bridgton, and Greenville, was different from Casco Bay in that the maximum annual wet deposition amount was recorded in either 1999 or 2000 (as opposed to 1998) before reaching a minimum amount in 2001. The maximum annual ammonia (reported as nitrogen) wet deposition amount recorded at the four sites was 1.3 kg/ha at Bridgton in 2000. The minimum annual ammonia wet deposition total of 0.5 kg/ha was recorded in 2001 at Acadia. Annual ammonia wet deposition at Casco Bay (see **Figure 4-3**) declined by 40% from a maximum of 1.23 kg/ha to a minimum of 0.76 kg/ha from 1998 to 2001. As illustrated in Figure 4-3, annual ammonia wet deposition amounts are similar at the coastal sites (i.e., Casco Bay and Acadia) and at the inland sites (i.e., Bridgton and Greenville). These declining short-term trends in wet deposition are consistent with corresponding declining precipitation totals during the same period.

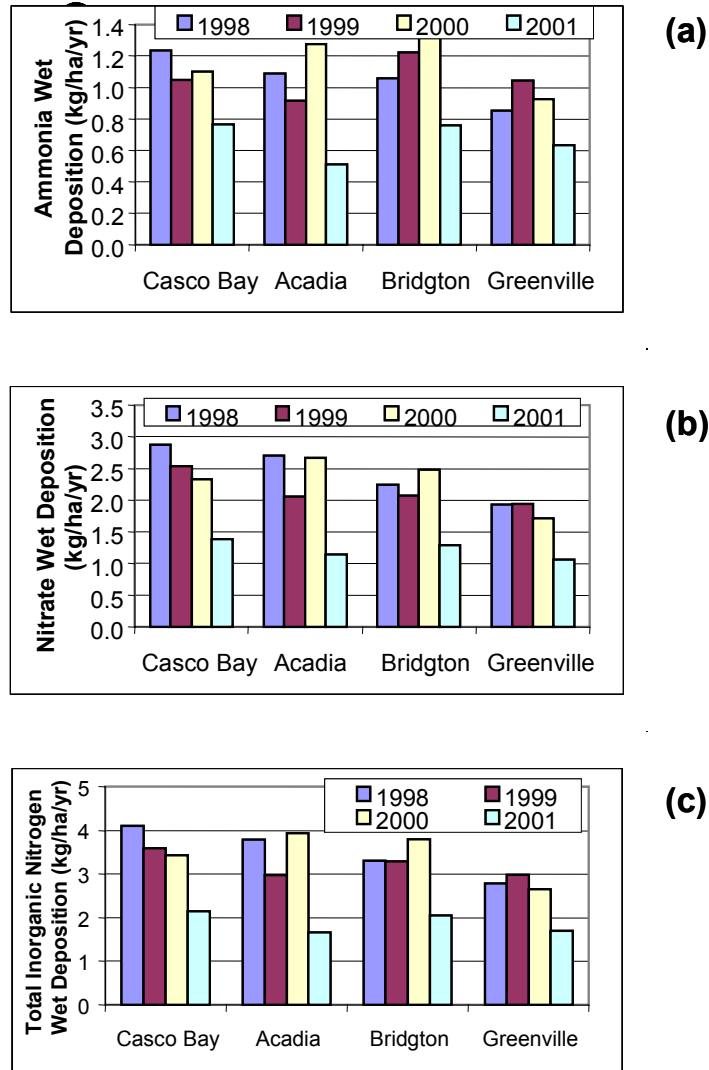


Figure 4-3. Annual 1998-2001 (a) ammonia (reported as nitrogen), (b) nitrate (reported as nitrogen), and (c) total inorganic nitrogen wet deposition amounts for four sites in Maine.

4.1.4 Nitrate

Annual nitrate wet deposition at Acadia, Bridgton, and Greenville exhibited a wet deposition trend, different from Casco Bay, in which the annual wet deposition total for nitrate peaked in either 1999 or 2000 (as opposed to 1998) before reaching a minimum value in 2001. These trends are consistent with those observed for ammonium. The maximum annual nitrate (reported as nitrogen) wet deposition amount recorded at the four sites was 2.8 kg/ha at Bridgton in 2000. The minimum was 1.0 kg/ha recorded in 2001 at Greenville. Annual nitrate wet deposition at Casco Bay (see Figure 4-3) declined by 50% from a maximum of 2.86 kg/ha to a minimum of 1.38 kg/ha from 1998 to 2001. As illustrated in Figure 4-3, annual nitrate wet

deposition may be slightly higher at the coastal sites (i.e., Casco Bay and Acadia) relative to the Bridgton inland site. All three of these sites recorded higher annual nitrate wet deposition amounts relative to Greenville.

4.1.5 Inorganic Nitrogen

Inorganic nitrogen wet deposition equals the sum of ammonia wet deposition and nitrate wet deposition. Annual inorganic nitrogen wet deposition at Acadia, Bridgton, and Greenville exhibited a trend, different from Casco Bay, in which the maximum annual wet deposition amount of inorganic nitrogen occurred in either 1999 or 2000 (as opposed to 1998 for Casco Bay) but the minimum amount occurred in 2001, similar to Casco Bay. The maximum annual inorganic nitrogen wet deposition amount was 4.1 kg/ha in 1998 at Casco Bay. The minimum annual inorganic nitrogen wet deposition total was 1.6 kg/ha in 2001 at Acadia. Annual inorganic nitrogen wet deposition at Casco Bay (see Figure 4-3) declined by 50% from a maximum of 4.1 kg/ha to a minimum of 2.1 kg/ha from 1998 to 2001. As illustrated in Figure 4-3, annual inorganic nitrogen wet deposition totals appear to be similar at the coastal sites (i.e., Casco Bay and Acadia) and the Bridgton inland site. All three of these sites recorded higher annual inorganic nitrogen wet deposition amounts relative to Greenville.

4.1.6 Wet Deposition Concentrations

As illustrated in Figures 4-2 and 4-3, the amount of mercury and inorganic nitrogen wet deposition recorded at Casco Bay declined from 1998 to 2001. A similar trend was also observed in annual precipitation at Casco Bay. To determine if annual variations in precipitation are the sole cause of the trend of lower annual mercury and inorganic nitrogen wet deposition from 1998 to 2001 at Casco Bay, the annual pollutant wet deposition rates shown in Figure 4-2 or Figure 4-3 for these pollutants were divided by the corresponding annual precipitation rates shown in Figure 4-1. This gives annual average pollutant concentrations in precipitation.

As illustrated in **Figure 4-4**, the maximum annual average mercury concentration computed in this manner was 12 ng/L in 2001 at Casco Bay. The minimum annual average mercury concentration was 6.1 ng/L in 2001 at Greenville. No trend in annual average mercury concentrations in wet deposition was observed at the four Maine sites, except at Casco Bay where the mercury concentration in 2001 (12 ng/L) was roughly 50% greater than the 1998-2000 average (8 ng/L).

The annual average Acadia mercury concentrations from 1998-2001 in wet deposition of 8 to 9 ng/L are at least double the concentration of 3.62 ng/L reported for Acadia during 1994 to 1995 by the EPA in validating the use of RELMAP for estimating mercury transport and deposition in the United States (U.S. Environmental Protection Agency, 1997b). This means previous studies of mercury transport and deposition over Maine appear to have substantially underestimated the concentration, and therefore, wet deposition of mercury in Maine. This likely brings into question any conclusions previously drawn from these studies with regard to the likely contributions to coastal Maine of long-range (other states) and short-range (inland and coastal Maine) sources. A review of the previous RELMAP modeling results predicted for Maine is therefore needed to verify what we suspect that mercury impacts in Maine were

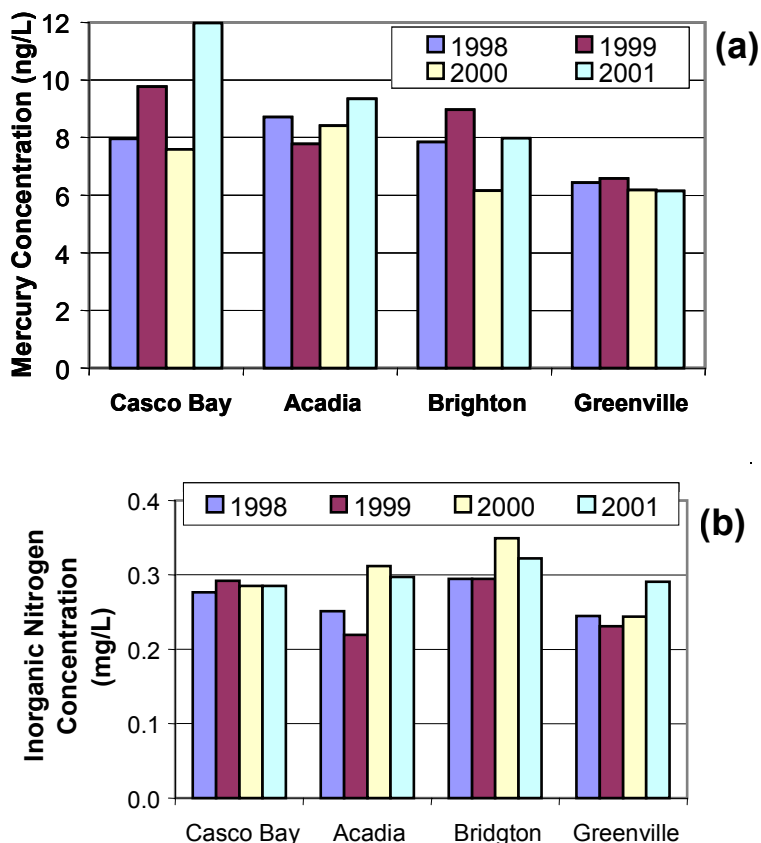


Figure 4-4. Annual 1998-2001 (a) mercury concentrations and (b) inorganic nitrogen concentrations in wet deposition for four sites in Maine.

understated. If this review verifies what we suspect, an updated RELMAP (or now CMAQ; <<http://www.epa.gov/asmdnerl/mercury.html>>) modeling analysis is recommended, incorporating the most recent information to provide a better understanding of the expected contribution of long-range and short-range sources on mercury transport, transformation, and deposition in coastal Maine.

For the four sites, the maximum annual inorganic nitrogen concentration in wet deposition was 0.35 mg/L in 2000 at Bridgton. The minimum annual inorganic nitrogen concentration was 0.22 mg/L in 1999 at Acadia. As shown in Figure 4-4, if a trend exists, it is of increasing annual inorganic nitrogen concentrations in wet deposition from 1998 to 2001 at the four Maine sites.

The difficulty with this simplified approach is that concentrations of mercury and inorganic nitrogen components (ammonia and nitrate) vary significantly as a function of season and precipitation type (see **Figure 4-5**). The 4-yr average concentration of mercury in snow was 4.8 ng/L. At the same time, the 4-yr average concentration of mercury in rain varied from a minimum of 5.0 ng/L in the winter, to 6.9 to 7.7 ng/L in the fall and spring, to a maximum of 11.7 ng/L in the summer. Similarly, the average concentration of inorganic nitrogen in snow was 0.12 mg/L. The average concentration of inorganic nitrogen in rain varied from a minimum of

0.24 mg/L in the winter, to 0.24 to 0.26 mg/L in the fall and spring, to a maximum of 0.29 mg/L in the summer.

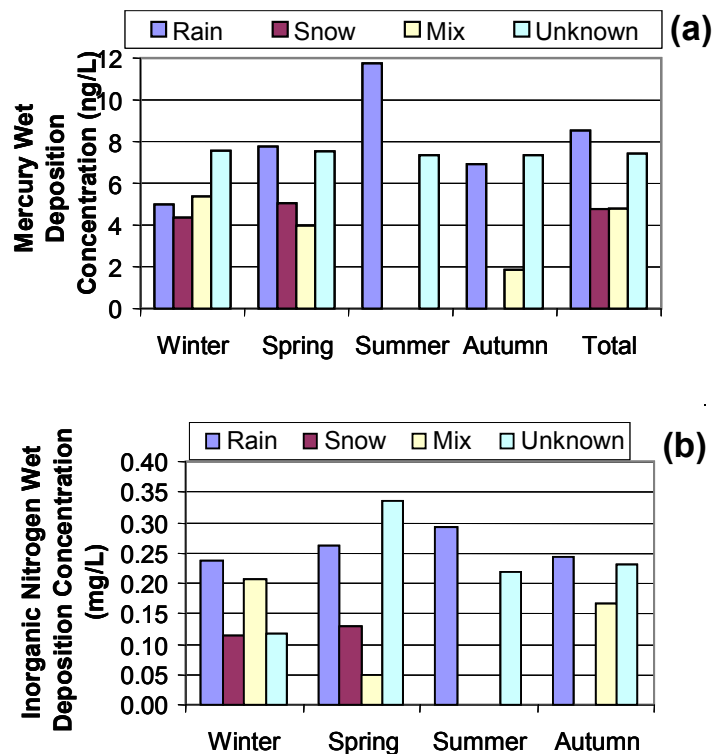


Figure 4-5. Seasonal 1998-2001 (a) mercury concentrations and (b) inorganic nitrogen concentrations in wet deposition by precipitation type for four sites in Maine.

These differences in mercury and inorganic nitrogen concentrations in snow and rain and the seasonal variations in mercury and inorganic nitrogen concentrations in rain are significant. These findings illustrate that annual average concentrations as calculated in this section by dividing annual wet deposition by total precipitation ignores underlying seasonal and precipitation type issues, making this approach a poor tool to use as a refined trend analysis.

4.2 “ADJUSTED” WET DEPOSITION TRENDS

Trends in wet deposition are traditionally assessed, as described in Section 4.1, by the measurement of deposition over a wide geographic area over a long period of time (i.e., 10 years of data or more). A long time period is needed because it is difficult to statistically quantify trends in actual deposition totals or annual wet deposition concentrations for shorter periods of time.

Traditionally, no attempt has been made to remove/reduce the effect of inter-annual precipitation variations as a function of season and precipitation type, even though Figure 4-5

illustrates the importance of these variables. The net effect is that a decade or more of data is relied upon to make a qualitative assessment of trends in deposition. Unfortunately, this means more than a decade must pass before an emission control strategy designed to reduce pollutants present in wet deposition can be assessed for its qualitative effect. Also, a quantitative effect for the control strategy must be estimated which is difficult using actual wet deposition data, given annual precipitation variations.

To shorten the amount of time required to assess the effect of a control strategy on wet deposition, and to allow for quantitative rather than qualitative assessments, an improvement in the existing data analysis approach is needed. An improved methodology developed and evaluated by STI is as follows. For the years of data being analyzed, multi-year average precipitation totals by season and by precipitation type are determined. The actual wet deposition totals recorded by season, precipitation type, and year are then multiplied by the ratio of the multi-year average to the corresponding actual precipitation total. Annual wet deposition totals are obtained by summing these seasonal specific and precipitation type adjusted wet deposition totals. This methodology is mathematically described in Equation 4-1 as follows:

$$\text{“adjusted” wet deposition} = \sum_j \sum_k WD_{ijk} (P_{jk} / P_{ijk}) \quad (4-1)$$

where WD_{ijk} is the measured wet deposition rate in year i within season j (i.e., winter, spring, summer, or fall) for precipitation type k (e.g., rain or snow). P_{ijk} is the actual precipitation amount measured in year i within season j of precipitation type k . P_{jk} denotes the corresponding multi-year average precipitation amount measured in season j of precipitation type k .

Adjusted annual wet deposition totals calculated using Equation 4-1 should allow better assessment of trends in deposition that are related to trends in emissions.

To illustrate this point, application of this methodology results in no trend in the wet deposition of mercury at Casco Bay from 1998 to 2001 (see **Figure 4-6**). This finding indicates that declines in precipitation and changes in the type of precipitation can explain the mercury wet deposition decline observed from 1998 to 2001 at Casco Bay (see Figure 4-2). Therefore, when precipitation totals return to the 1998 level, it is plausible that mercury wet deposition amounts will also return to the 1998 observed level.

This approach results in a modest decline in “adjusted” ammonia annual wet deposition amounts at Casco Bay from 1998 to 2001. The decline equates to 3.4% over the four-year period of interest (**Figure 4-7**) and is equivalent to an annual average decline in the wet deposition of ammonia of roughly 0.8%. Thus, if annual precipitation amounts return to the 1998 level, annual ammonia wet deposition may decline relative to that observed in 1998.

Figure 4-8 shows that even with the removal of inter-annual seasonal precipitation variations, a 20% decline is predicted to have occurred in the wet deposition of nitrate at Casco Bay from 1998 to 2001.

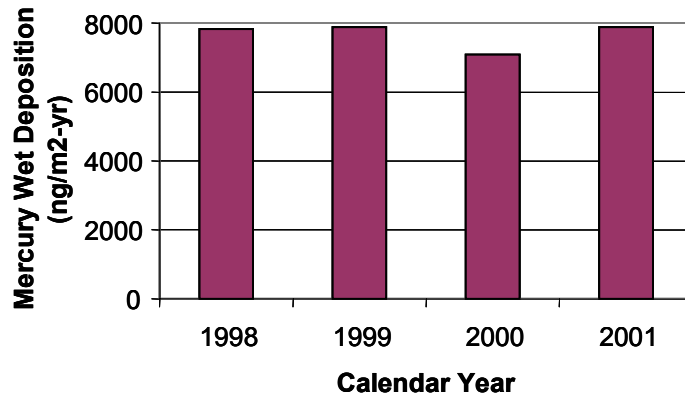


Figure 4-6. “Adjusted” annual wet deposition amounts for mercury from 1998 to 2001 at Casco Bay.

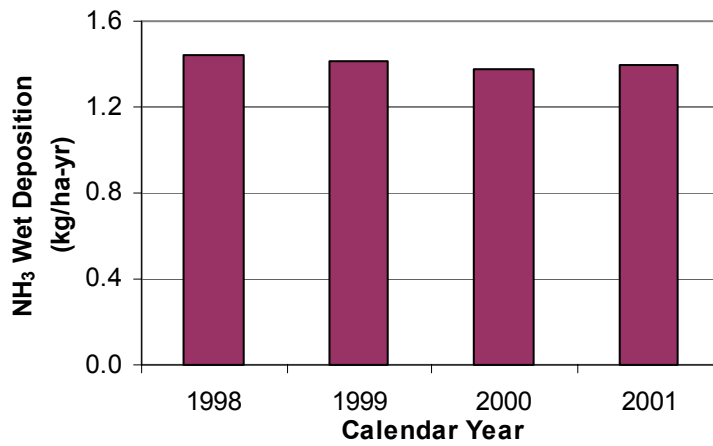


Figure 4-7. “Adjusted” annual wet deposition amounts for ammonia from 1998 to 2001 at Casco Bay.

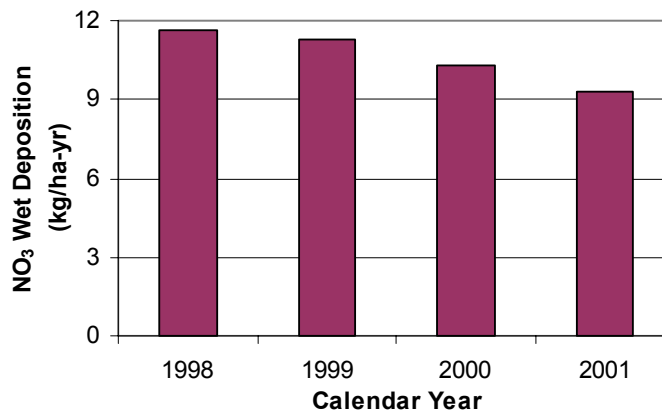


Figure 4-8. “Adjusted” annual wet deposition amounts for nitrate from 1998 to 2001 for Casco Bay.

Beside precipitation, atmospheric processes and emission reductions can contribute to inter-annual variations in wet deposition. Distinguishing between contributions from atmospheric processes and emission reductions is a difficult process. However, if atmospheric processes (e.g., mixing height, reactivity, temperature) varied significantly enough between years to contribute to a short-term trend in wet deposition for a pollutant, it seems likely that such a contribution would be of the same order of magnitude for all pollutants examined (mercury, ammonia, and nitrate). The fact that annual “adjusted” mercury and ammonia wet deposition totals remain unchanged or show a very small decline (3.4%) while annual “adjusted” nitrate wet deposition amounts show a significant (20%) declining trend over the 1998-2001 time period suggests atmospheric processes did not contribute to the “adjusted” annual wet deposition trends calculated.

While not definitive evidence, these findings imply that the roughly 20% reduction of “adjusted” nitrate totals in wet deposition from 1998 to 2001 may be due to a corresponding reduction in precursor emissions. Because oxides of nitrogen are the predominant precursors of nitrate, the implication of this analysis is that local and regional reductions in NO_x emissions from 1998 to 2001 are the most likely cause of the roughly 5% reduction per year in “adjusted” nitrate wet deposition determined from 1998 to 2001 at Casco Bay. Future work involving the use of this methodology for more sites and over more years is recommended. Additional sites are needed to better characterize and assess the accuracy of this approach as well as identify any pitfalls.

5. ESTIMATING TOTAL DEPOSITION OF MERCURY AND NITROGEN (NITRATE AND AMMONIA)

Total deposition is the sum of dry and wet deposition. Section 5.1 presents a review of literature describing existing dry deposition approaches for mercury and nitrogen. Annual wet deposition totals at Casco Bay and other Maine sites from 1998 through 2000 are described in Section 4. STI's estimate(s) of total atmospheric deposition into Casco Bay (Section 5.2) is based on the dry deposition approach described in Section 5.1 combined with 1998 through 2000 annual wet deposition totals (Section 4). Wet deposition totals for 2001 are ignored, due to an anomalously low amount of precipitation for this year. Total (dry plus wet) deposition is compared to other indirect and direct emissions into the Bay in order to develop a preliminary assessment of the importance of atmospheric deposition relative to other sources of emissions into Casco Bay. An assessment of nitrogen and mercury atmospheric deposition in Maine within the larger regional scale is presented in Section 5.3.

5.1 ESTIMATING DRY DEPOSITION RATES

Dry deposition is extremely difficult and expensive to monitor directly. No routine dry deposition measurements for nitrogen or mercury exist. The lack of a reliable approach¹³ for quantifying dry deposition remains a significant gap in the understanding of the deposition process and its effects. In the absence of measured dry deposition rates, investigators have relied on two approaches to estimate dry deposition:

- assume a ratio of dry deposition to wet deposition; and
- infer dry deposition based on ambient concentrations (use CASTNet - measured ambient concentrations multiplied by model dry deposition velocities to estimate dry deposition amounts).

These approaches are examined with the recognition that both approaches introduce significant uncertainty. The examination of both approaches will improve our understanding of the uncertainty.

5.1.1 Mercury

Mercury in the atmosphere is present primarily in five forms:

- Gaseous elemental mercury vapor (Hg^0 or zero valent mercury)
- Gaseous divalent mercury (Hg^{+2}) also called reactive gaseous mercury (RGM)
- Particulate mercury (both Hg^0 and Hg^{+2} , relative proportion not known)
- Organic mercury (mostly mono-methyl mercury) that can be measured in rainfall, but in amounts much lower than the other forms.
- In precipitation or cloud water.

¹³ Eddy correlation and eddy accumulation methods to estimate dry deposition are generally accepted but very expensive and data-intensive. Also, eddy correlation measurements require homogeneous terrain and other data requirements that are difficult to meet, especially in areas of diverse landscapes.

Recent tests suggest that RGM represents most of the mercury deposited by dry deposition (Dvonch et al., 1999).

Reports prepared by EPA on a mercury study for Congress and for the Savannah Watershed estimate that mercury dry deposition can be estimated as 100% (U.S. Environmental Protection Agency, 1997a) and 40% (U.S. Environmental Protection Agency, 2001a) of wet deposition. The range of 40% to 100% is used in this report as a simple metric to derive a range of annual dry deposition totals for mercury in Maine.

5.1.2 Nitrogen

Nitrogen in the atmosphere is present primarily in three forms:

- Oxidized inorganic nitrogen
- Ammonium compounds
- Organic nitrogen compounds

In this study, the role and effect of organic nitrogen compounds is ignored. This is not to say that organic nitrogen is not important; rather, that we have insufficient information upon which to base conclusions about organic nitrogen compounds. For example, measurements of dry organic nitrogen deposition are unreliable. While measurements of wet organic nitrogen over the mid-Atlantic coast indicated that organic nitrogen averages at least 20% of total dissolved nitrogen in precipitation, we do not know whether this is also true for Maine and whether its “toxicity” is equal to or different than inorganic nitrogen in its contribution to and/or affect on water quality. Future studies to resolve these issues are needed.

In the absence of measured inorganic nitrogen dry deposition rates, many investigators have attempted to estimate nitrogen dry deposition based on assuming a ratio of dry deposition to wet deposition. A 1:1 ratio is most commonly derived (Hinga et al., 1991; Valiela et al., 1997) and is applied in this study. This approach introduces considerable uncertainty, and the 1:1 ratio is applicable only for oxidized inorganic nitrogen, not ammonium compounds (Dennis, 1999; Chimka et al., 1997).

In order to estimate ammonium dry deposition, as well as to provide a different assessment of oxidized inorganic nitrogen dry deposition, CASTNet dry deposition estimates reported for 1998 to 2000 for Acadia, Ashland, and Howland, Maine, were obtained. Acadia is the only coastal site (~300 m msl). Ashland and Howland are located north of Acadia, and well inland. The annual estimated inorganic nitrogen dry deposition totals for Acadia¹⁴ are 1.37 and 0.92 kg/ha in 1999 and 2000, respectively. These deposition totals are about 50% higher than those reported at Ashland and Howland (see **Table 5-1**).

¹⁴ The CASTNet Acadia site data did not include dry deposition estimates. However, nitric acid, nitrate, and ammonium ambient air concentrations were provided. This made it possible to develop nitric acid, nitrate, and ammonium dry deposition estimates as follows: the Acadia ambient concentrations were multiplied by the annual dry deposition to concentration ratio reported by CASTNet for Howland, Maine. While this approach contains uncertainty, it seems to provide an estimate of Acadia and, therefore, coastal Maine deposition for oxidized nitrogen, ammonium, and total inorganic nitrogen.

Table 5-1. CASTNet 1998-2000 annual nitrate, ammonium, and total inorganic dry deposition estimates (kg/ha).

Site	Nitrate (as N)	Ammonium (as N)	Total Nitrogen ^a
Acadia			
1998	—	—	—
1999	1.15	0.17	1.37
2000	0.76	0.11	0.92
Ashland			
1998	0.31	0.11	0.43
1999	0.42	0.13	0.57
2000	0.37	0.12	0.50
Howland			
1998	0.48	0.16	0.67
1999	0.70	0.17	0.90
2000	0.51	0.11	0.65

^a Includes nitrate

According to the Acadia CASTNet observations, dry deposition of inorganic nitrogen is predominately in the form of nitric acid plus nitrate (87%) with a small ammonium component (13%). These Acadia dry deposition estimates are used for Casco Bay.

5.2 WHAT IS THE ROLE OF ATMOSPHERIC DEPOSITION TO POLLUTION IN CASCO BAY?

The Casco Bay water surface covers 229 square miles and its watershed surface covers 985 square miles (U.S. Environmental Protection Agency, 2001b; see Figure 1-3). This section describes the estimation of lower and upper limits of the amount of total deposition to Casco Bay. The lower limit is estimated by mercury and nitrogen deposition to the Casco Bay water surface. The upper limit is estimated based on the entire watershed area.

To put atmospheric deposition in perspective with other Casco Bay pollutants, all sources of pollutant emissions into Casco Bay must be estimated. We performed a literature review to estimate emissions into Casco Bay as a result of indirect and direct emission discharges into Casco Bay. Due to a lack of data, this analysis did not consider emissions associated with pollutant exchange with the sediment and the Atlantic Ocean.

5.2.1 Mercury

At Casco Bay, wet deposition of mercury declined from 12,500 to 8,000 ng/m² yr⁻¹ from 1998 to 2000. Multiplying these annual wet deposition totals by the Casco Bay water surface

area of 229 square miles yields 16.4¹⁵ to 10.5 lb/yr of mercury wet deposition into Casco Bay from 1998 to 2000. Multiplying these annual wet deposition totals by the Casco Bay watershed area of 985 square miles yields 45 to 70 lb/yr of mercury wet deposition to the Casco Bay watershed from 1998 to 2000. Because not all wet deposition that falls within the watershed area reaches the Bay, the 45 to 70 lb/yr wet deposition range to the watershed represents an upper limit of the amount of wet deposition that reached the Bay.

Assuming that mercury dry deposition ranged from 40% to 100% of wet deposition from 1998 to 2000 (see Section 5.1), the contribution of dry deposition is believed to have ranged from 4.2 to 16.4 lb/yr as input directly into Casco Bay and from 18 to 70 lb/yr assuming all dry deposition to the watershed surface area reached Casco Bay¹⁶.

Therefore, direct atmospheric (dry plus wet) deposition of mercury into Casco Bay is estimated to have ranged from 14.7 to 32.8 lb/yr from 1998 to 2000. Mercury atmospheric deposition to the entire watershed area is estimated to have ranged from 65.5 to 143 lb/yr from 1998 to 2000. This means mercury atmospheric deposition to Casco Bay is estimated to have ranged from 14.7 to 143 lb/yr from 1998 to 2000. The order of magnitude range that exists is primarily due to the uncertainty regarding the fraction/amount of atmospheric deposition to the watershed that reaches the Bay. Future work should be performed on refining this range.

In a report issued by the Maine Department of Environmental Quality (2002), Maine wastewater treatment plants were estimated to directly discharge 10.2 lb/yr of mercury into Casco Bay. STI estimates wastewater treatment plants in the Casco Bay area account for nearly 25% of all mercury emissions in Maine, since the Casco Bay watershed area contains nearly 25% of the state's population. Multiplying 10.2 lb/yr of wastewater discharges for Maine by 25% gives 2.55 lb/yr of mercury as the estimated discharge into Casco Bay.

As summarized in **Table 5-2** and illustrated in **Figure 5-1**, based on this wastewater emission estimate and the total deposition estimates, total atmospheric deposition (dry plus wet deposition) directly into Casco Bay accounts for 85% to 92% of total mercury emissions into the Casco Bay water surface. Assuming that deposition over the entire watershed eventually reaches Casco Bay, then atmospheric deposition (dry plus wet deposition) accounts for a much higher 96% to 98% of total mercury emissions into Casco Bay. In either case, deposition is estimated to be the most significant route for mercury pollution into the Bay. This is a preliminary finding because other unaccounted for sources of mercury emissions may exist.

¹⁵ It is noted that the 16.4 lb/yr estimate of mercury wet deposition for 1998 is 55% greater than the 10.4 lb/yr previously reported for 1998 in the Casco Bay Air Deposition Study (Mosher, 2000). After further review, this difference is attributed to a multiplication error made in the previous study.

¹⁶ This is a scientifically more credible estimate of dry deposition compared to the assumption that mercury dry deposition is zero, which is what the previously funded Casco Bay study (Mosher, 2000) purported.

Table 5-2. Estimated mercury discharges in the Casco Bay area.

Transport Process	Water Surface		Watershed Surface	
	Discharges lb/yr	% of Total	Discharges lb/yr	% of Total
Wet deposition	10.5-16.4	61-46	45.0-70.4	69-49
Dry deposition	4.2-16.4	24-46	18.0-70.4	27-49
Wastewater plants	2.55	15-8	2.55	4-2
Total	17.2-35.4	100	65.5-143	100

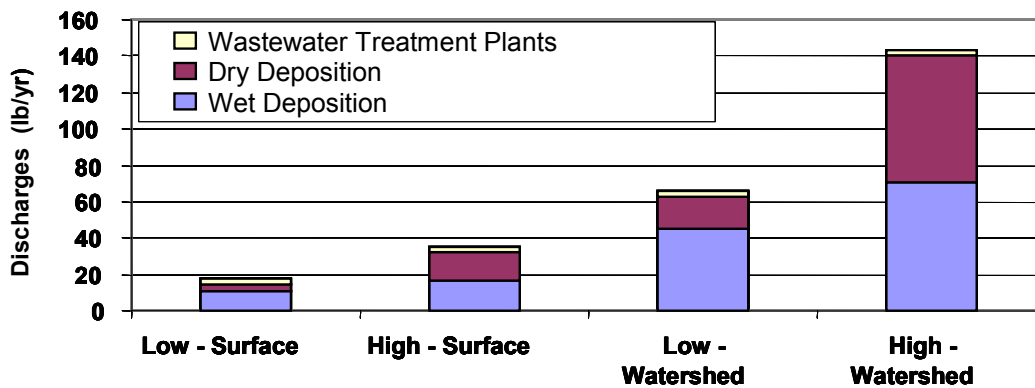


Figure 5-1. Summary of wastewater treatment plant direct mercury discharges and dry and wet deposition of mercury to Casco Bay (in lb/yr). “Low” and “high” signify ranges in dry deposition estimates. “Surface” refers to the surface of Casco Bay while “watershed” refers to the entire watershed surface area.

5.2.2 Nitrogen

In the Casco Bay area, wet deposition of inorganic nitrogen declined from 4.15 to 3.38 kg/ha yr⁻¹ from 1998 to 2000 (**Table 5-3**). Multiplication of these wet deposition amounts by the Casco Bay water surface area of 229 square miles means inorganic nitrogen deposition into Casco Bay ranged from 246¹⁷ to 200 tonnes/yr from 1998 to 2000. Multiplication of these wet deposition amounts by the Casco Bay watershed area gives a range of inorganic nitrogen wet deposition from 862 to 1059 tonnes/yr.

Annual ammonium dry deposition according to CASTNet data is 10% of the NADP wet deposition total¹⁸. Annual dry deposition of nitric acid, a component of inorganic nitrogen, is estimated to have ranged from 35% to 100% of nitrate wet deposition. The lower 35% estimate equals the ratio of CASTNet dry deposition to NADP wet deposition for the coast of Maine

¹⁷ The 246-tonnes/yr inorganic nitrogen wet deposition for 1998 is about 35% higher than the 180 tonnes/yr of inorganic nitrogen wet deposition estimated by Mosher (2000). The difference arises from a lower (and seemingly erroneous) wet deposition estimate of 3.49 kg/ha yr⁻¹ relied upon by Mosher (2000).

¹⁸ The estimate that ammonia dry deposition is 10% of wet deposition is scientifically more credible than the assumption made by Mosher (2000) that dry ammonium deposition equals wet ammonium deposition.

Table 5-3. Inorganic nitrogen discharges in the Casco Bay area from 1998 to 2000 using CASTNet dry deposition data (1998-2000).

Transport Process	Emission Factors (kg/ha yr ⁻¹)	Water Surface		Watershed Surface	
		Discharges (tonnes/yr)	% of Total	Discharges (tonnes/yr)	% of Total
Wet deposition	3.38-4.15	200-246	25%-28%	862-1,059	53%-54%
Nitric acid (as N)	—	—		—	
Ammonium (as N)	1.03-1.25	61-74		263-319	
Nitrate (as N)	2.35-2.90	139-172		600-740	
Dry deposition	0.92-1.37	55-81	7%-15%	235-350	14%-18%
Nitric acid (as N)	0.76-1.15	45-68		194-293	
Ammonium (as N)	0.11-0.17	7-10		28-43	
Nitrate (as N)	0.05	3		13	
Sewage effluent ^a	-	540	68%-62%	540	33%-28%
Total	-	795-867	100%	1,637-1,949	100%

^a Mosher (2000); 1991 point-source discharges

(see **Table 5-4**). The upper 100% estimate assumes annual dry nitric acid deposition equals wet nitrate deposition. Note that, with either the nitric acid dry deposition approach (CASTNet) or the dry-equals-wet deposition approach, dry deposition of inorganic nitrogen is almost exclusively in the form of nitric acid plus nitrate (87%-95%) with a minor percentage as ammonium (5%-13%).

Table 5-4. Inorganic nitrogen discharges in the Casco Bay area assuming dry deposition equals wet deposition for nitric acid plus nitrate (1998-2000).

Transport Process	Emission Factors (kg/ha yr ⁻¹)	Water Surface		Watershed Surface	
		Discharges (tonnes/yr)	% of Total	Discharges (tonnes/yr)	% of Total
Wet deposition	3.38-4.15	200-246	23%-25%	862-1,059	42%-44%
Nitric acid (as N)	—	—		—	
Ammonium (as N)	1.03-1.25	61-74		263-319	
Nitrate (as N)	2.35-2.90	139-172		600-740	
Dry deposition	2.46-3.07	146-182	16%-19%	628-783	31%-33%
Nitric acid (as N) ^a	2.35-2.90	139-172		600-740	
Ammonium (as N)	0.11-0.17	7-10		28-43	
Sewage effluent ^b	-	540	61%-56%	540	27%-23%
Total	-	886-968	100%	2,030-2,382	100%

^a Includes nitrate

^b Mosher, 2000; 1991 point-source discharges

As a result, total (dry plus wet) inorganic nitrogen deposition to the Casco Bay surface ranged from 255 to 428 tonnes/yr. Over the 985 square mile watershed surface area total (dry plus wet) inorganic nitrogen deposition ranged from 1097 to 1842 tonnes/yr. This means atmospheric (dry plus wet) deposition of inorganic nitrogen into Casco Bay is estimated to have ranged from 225 to 1842 tonnes/yr from 1998 to 2000 (see **Figure 5-2**). The factor of 8 range in the inorganic nitrogen atmospheric deposition total is primarily the result of uncertainty about the fraction/amount of atmospheric deposition to the watershed that reaches the Bay. Future work should be performed to refine this range by investigating and estimating the role and/or percentage of atmospheric deposition to the watershed that reaches the Bay.

Total (dry plus wet) inorganic nitrogen deposition is predominately in the form of nitric acid plus nitrate (70%-80%) with the remainder in the form of ammonium (20%-30%). This information is summarized in Tables 5-3 and 5-4.

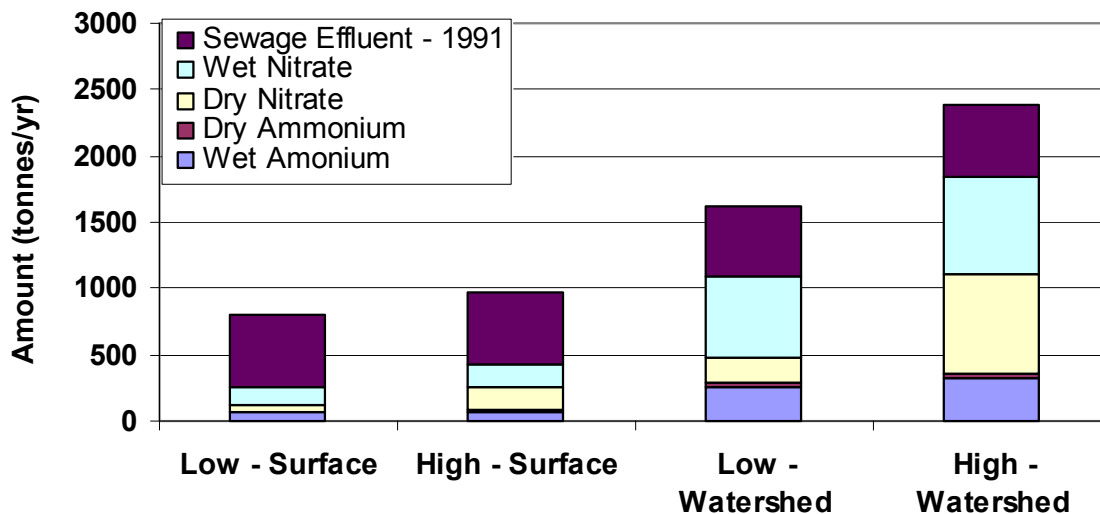


Figure 5-2. Summary of sewage effluent discharges, dry deposition, and wet deposition of inorganic nitrogen to Casco Bay from 1998 to 2000. “Low” and “high” signify deposition estimate ranges. “Surface” refers to the surface of Casco Bay while “watershed” refers to the entire watershed surface area.

Mosher (2000) reported that point-source discharges in 1991 from sewage treatment effluent introduced roughly 540 tonnes of nitrogen per year into Casco Bay. These 1991 data were used because more recent data are lacking. Based on this information and our atmospheric deposition estimates, we find that a range of 30% to 70% of the total amount of inorganic nitrogen pollution entering Casco Bay comes from atmospheric deposition. For comparison, 21% of the nitrogen pollution entering Chesapeake Bay comes from the air (e.g., U.S. Environmental Protection Agency, 2000a). Thus, atmospheric deposition is estimated to be a greater source of inorganic nitrogen input to Casco Bay (30% to 70%) than it is to Chesapeake Bay (21%).

Given that Chesapeake Bay suffers from excess¹⁹ inorganic nitrogen inputs, there is reason to believe that Casco Bay may also suffer from excess inorganic nitrogen inputs. Further comparisons of Chesapeake Bay and Casco Bay are needed to confirm this conjecture. Even so, it follows that atmospheric deposition is a significant component of the pollutant loading into Casco Bay. The extent to which atmospheric deposition is important depends upon dry deposition. Thus, additional research is needed to determine which approach (dry equals wet or dry equals about 35%-40% of wet) should be used to estimate nitrate dry deposition.

5.3 HOW DOES COASTAL MAINE FIT INTO THE REGIONAL PATTERN OF DEPOSITION?

Regional maps of mercury wet deposition, inorganic nitrogen wet deposition, and precipitation were analyzed to determine how Maine fits into the regional pattern of wet deposition for these pollutants. In order to provide a quantitative picture of the likely importance that local and remote emissions have on wet deposition in Maine, a comparison was made of total estimated pollutant (mercury and inorganic nitrogen) deposition within Maine to air emissions from Maine.

Regional wet deposition rates at coastal Maine sites were compared to rates at other locations to determine whether coastal Maine receives either higher or lower levels of wet deposition relative to inland Maine and to other states. One hypothesis is that higher levels of wet deposition (mercury or inorganic nitrogen) imply higher ambient air concentrations (mercury or inorganic nitrogen) at a site relative to other sites. Higher ambient air concentrations suggest that the site is located near sources of emissions. For this situation, the strategy to reduce wet deposition would be to focus on controlling local sources. On the other hand, if lower levels of wet deposition (ambient air concentrations) are found at coastal Maine sites relative to the region, the importance of controlling or investigating local sources of emissions is reduced because long-range transport of emissions from other states may be the predominant source of pollutant deposition.

A comparison of the Maine emission inventory (U.S. Environmental Protection Agency, 2002b) for mercury and inorganic nitrogen to total deposition was used to assess findings based on the regional wet deposition picture. This comparison independently suggests whether Maine is a source (i.e., emits more of a pollutant than is deposited) or a sink (i.e., deposits more of a pollutant than is emitted).

5.3.1 Mercury

As the data show in **Figure 5-3**, coastal Maine mercury wet deposition rates in 1999 and 2000 were higher than those observed at inland Maine and surrounding Canadian sites. A similar pattern (not shown) was observed in 1998. The higher mercury wet deposition rates along coastal Maine relative to inland might be the result of local coastal sources contributing significantly to coastal wet deposition. It is also possible that Coastal Maine received more precipitation as rainfall (vs. snow/sleet) relative to inland sites.

¹⁹ Excess nutrients lead to increased algal production and organic matter, a process known as eutrophication.

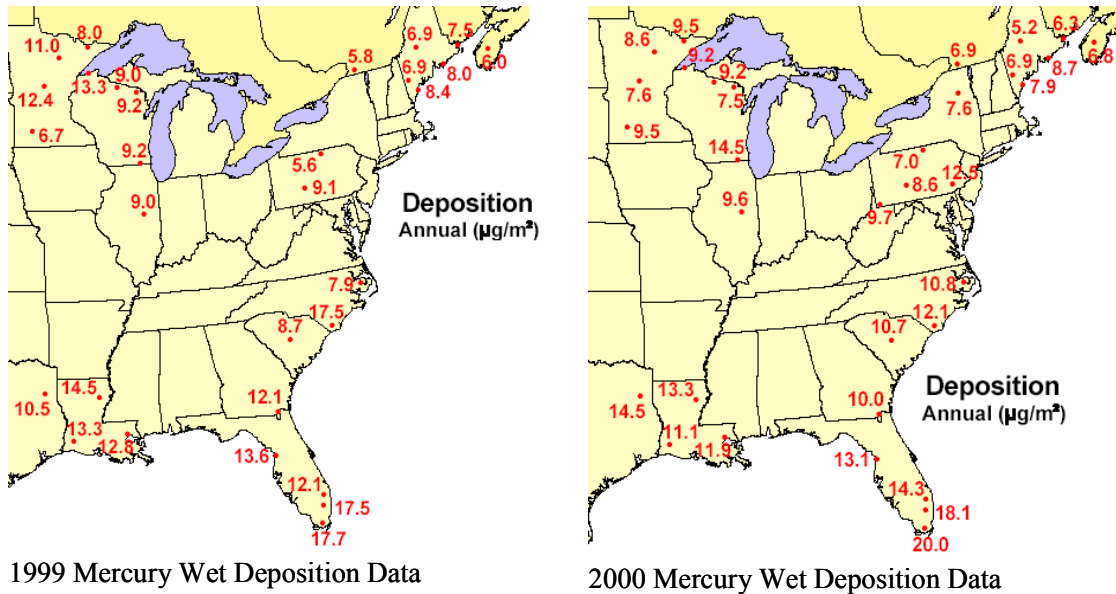


Figure 5-3. MDN 1999 and 2000 annual wet deposition data for the eastern United States (National Atmospheric Deposition Program, 2002b; Claybrooke, 2002).

The lack of data from nearby states (Connecticut, Massachusetts, Rhode Island, and Vermont) makes it difficult to put these Maine mercury wet deposition rates into context with what is occurring nearby. As shown in Figure 5-3, mercury wet deposition along the coast of Maine is comparable to that reported for Pennsylvania.

For 1998-2000, an annual mercury wet deposition rate of approximately 8000 ng/m² (as reported by the four Maine sites) is equivalent to a wet deposition total of 1614 lb/yr for an area the size of Maine. The following assumptions were made when comparing mercury deposition to the emission inventory.

- Assuming that dry deposition equals wet deposition, the total annual mercury deposition from 1998 to 2000 over the state of Maine would be about 3228 lb/yr. The State of Maine reports that the total air emission rate of mercury within the state is 1467 lb/yr (in 2001). Under this scenario, twice as much mercury is deposited in Maine than is emitted within the state (see **Figure 5-4**).
- Assuming surrounding states were major contributors to Maine’s ambient mercury concentrations, one would expect to see greater mercury wet deposition totals (due to higher emissions) in those states compared to Maine. However, Figure 5-3 does not confirm such a regional pattern²⁰; mercury wet deposition along the coast of Maine is comparable to that reported for nearby states.

²⁰ Note that other data exist for this comparison that were not available to STI at the time of this report.

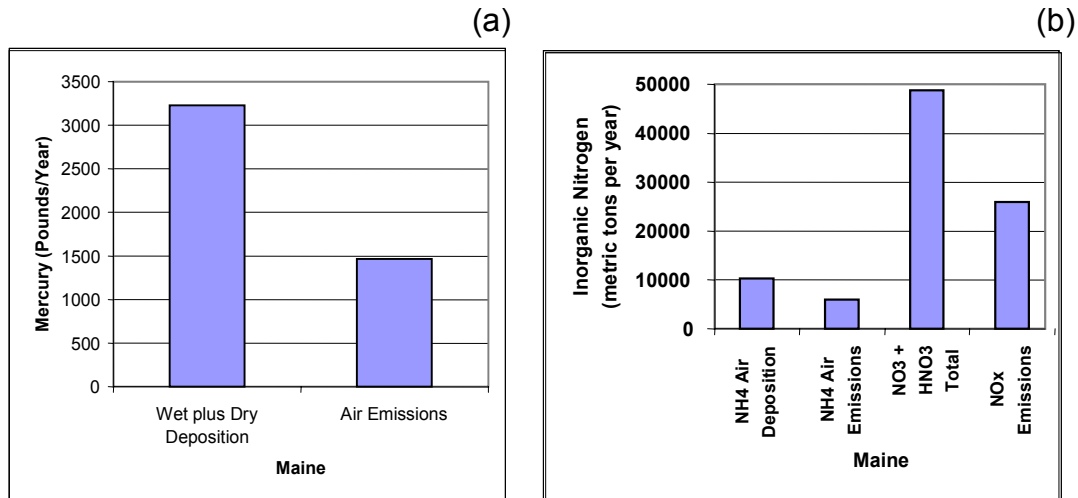


Figure 5-4. Comparison of (a) total (wet plus dry) mercury deposition to air emissions and (b) wet ammonium deposition to air emissions and total nitrate plus nitric acid deposition to oxides of nitrogen in the emission inventory.

Based on these assumptions and findings, we do not believe that total deposition of mercury in Maine is twice as high as currently estimated mercury emissions for Maine. Because wet deposition data should be relatively accurate, either the mercury emission inventory is too low or mercury dry deposition is much lower in Maine than the literature suggests.

In summary, within Maine, annual wet deposition rates of mercury were similar to or slightly higher than rates reported in nearby states. Similar or slightly higher levels of wet deposition indicate similar or slightly higher levels of air emissions (lb/acre) in Maine relative to the surrounding area, which implies that Maine is a mercury *source*. On the other hand, atmospheric deposition to Maine equals twice the current mercury air emission inventory for Maine. Thus, the crude mass balance approach identifies Maine as a *sink* for mercury. We give more credence to the wet deposition comparison because it does not depend upon inventory development and dry deposition assumptions. However, both analyses are uncertain.

An error in the crude mass balance approach could be due to the use of either a low-biased emission inventory and/or the possibility that mercury dry deposition is much lower in Maine than reported in the literature. It is noted that a low-biased emission inventory would not be out of the question. Note that in a recently released comprehensive emission inventory for mercury in New Jersey, four of the top five categories involve the use/management of mercury-added products that were not previously a part of the New Jersey mercury inventory (e.g., scrap metal processing).

5.3.2 Nitrogen

Figure 5-5 presents four maps showing annual ammonium, nitrate, and total inorganic nitrogen (ammonium plus nitrate) wet deposition and corresponding annual precipitation for 2000. These maps identify annual measurements as made at 11 sites in the New England area. These maps show that the highest wet deposition and precipitation totals are measured in the

southwest portion of the region shown (far from Maine) and the lowest totals are observed in Maine.

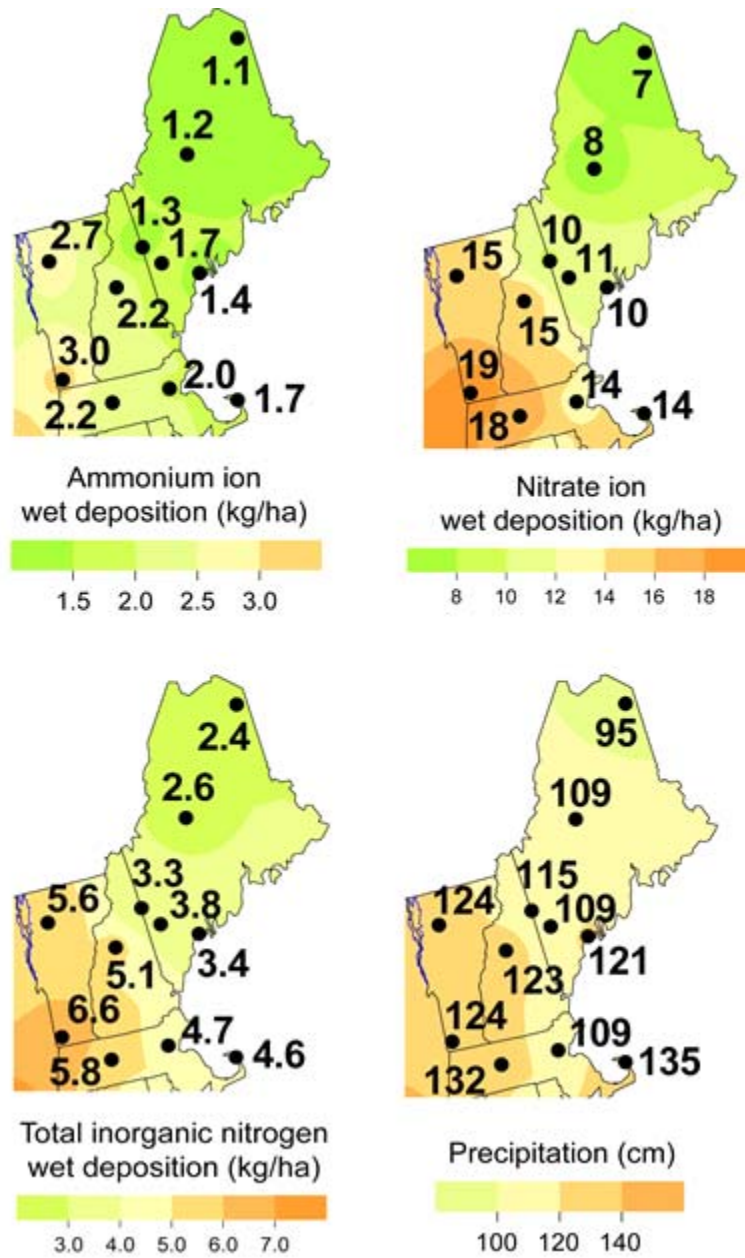


Figure 5-5. NADP 2000 annual ammonium, nitrate, and total inorganic nitrogen wet deposition and precipitation for the northeastern United States (National Atmospheric Deposition Program, 2002b; Claybrooke, 2002).

Annual ammonium, nitrate, and total inorganic nitrogen wet deposition totals in Maine are about a factor of 2 lower than those measured in the southwestern part of the region shown. Corresponding precipitation in Maine is about 30% lower than in the southwestern part of. The

most plausible explanation for these trends is that emissions are greatest closer to regional sources.

Another reason why Maine likely receives the lowest amount of wet deposition in the New England region is that atmospheric emissions from Maine are likely substantially less than total (dry plus wet) deposition. To test this hypothesis as well as obtain a quantitative estimate of the ratio of deposition to emissions in Maine, the following analyses were performed.

The EPA reports (U.S. Environmental Protection Agency, 2000b) total air emissions of ammonium (reported as nitrogen) within Maine of about 6,000 tonnes per year. As illustrated in Section 4, the annual average ammonium (reported as nitrogen) wet deposition total from 1998 to 2000 at the four Maine sites is roughly 1 kg/ha yr^{-1} , which for the area of Maine is equivalent to an annual ammonium wet deposition total of 9000 tonnes per year. Accounting for dry deposition, total ammonium deposition to Maine is estimated at 10,300 tonnes per year. The ratio of total (dry plus wet) deposition to emissions is equal to a factor of 1.7, which means 1.7 times as much ammonium is deposited in Maine as is emitted.

Air emissions of oxides of nitrogen (reported as nitrogen) within Maine are about 25,960 tonnes per year. The annual average nitrate plus nitric acid wet deposition total at the four Maine sites from 1998 to 2000 is roughly 4 kg/ha yr^{-1} , which for the area of Maine is equivalent to an annual ammonium wet deposition total of 36,000 tonnes per year. Total nitrate plus nitric acid deposition to Maine has a range from 49,000 tonnes per year (dry deposition equals 35% of wet deposition as observed from CASTNet data) to 73,000 tonnes per year (dry equals wet deposition). The ratio of total deposition to emissions has a range from 1.9 to 2.8, which means that 1.9 to 2.8 times as much oxides of nitrogen emissions are deposited in Maine than are emitted in Maine.

While these ratios of total deposition to emissions are rough approximations, they illustrate that Maine is estimated to be absorbing via deposition much more ammonium and oxides of nitrogen emissions than it emits. As a significant fraction of Maine emissions are likely deposited outside the state, the importance of remote sources on wet deposition in Maine is even greater than implied by the computed deposition-to-emissions ratios of 1.7 for ammonium and 1.9 to 2.8 for nitrate. For example, if 50% of Maine emissions are deposited outside the state, then the ratio of total deposition in Maine to emissions that remain in Maine is 3.4 for ammonia and 3.8 to 5.6 for nitrate. Ratios of 3.4 and 5.6 are equivalent to 70% and 80%, respectively, of total deposition being associated with emissions from outside Maine. Therefore, controlling local sources of air emissions may not significantly reduce wet deposition within Maine.

5.4 WHAT IS THE ROLE OF ATMOSPHERIC DEPOSITION TO SEDIMENT POLLUTION?

Sediments can act as an indicator of environmental health in marine ecosystems like Casco Bay because many toxic contaminants, which do not dissolve readily in water, become attached to sediments and organic material and settle to the bottom.

As reported in the Casco Bay Plan, mercury concentrations in sediment (see **Figure 5-6**) were determined in 1991 to be highest in the Inner Bay along the Inner Fore River and in the Back Cove area of Casco Bay. As shown in **Figure 5-7**, the Inner Fore River and Back Cove area are located in the southwest end of Casco Bay. The combination of local topography (which may disproportionately overload this area with runoff), local sources (air and water), and the flow characteristics of the Inner Fore River and Back Cove area can contribute the elevated concentrations of mercury in these sediments.

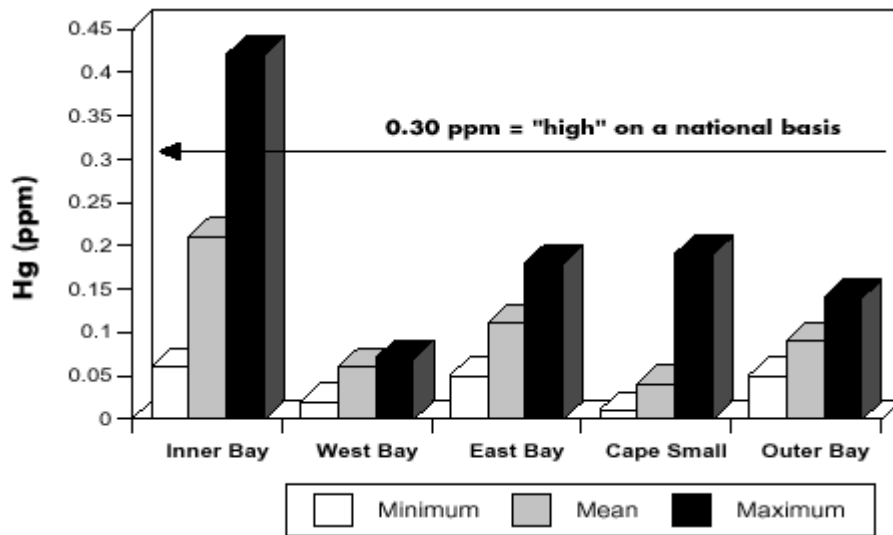


Figure 5-6. Mercury concentrations in Casco Bay sediments (Kennicutt et al., 1992 and O'Connor, 1990).

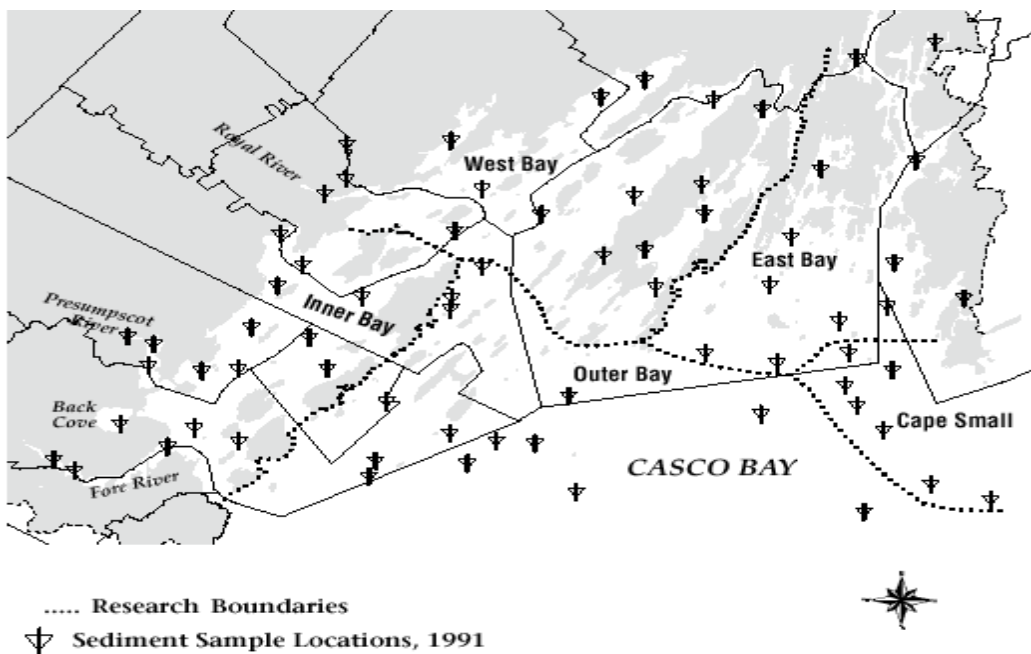


Figure 5-7. Casco Bay sediment sample locations (University of Southern Maine, 1996).

In a separate Casco Bay report, the maximum concentrations of mercury (presumably, in surface water) are reported to be in the Inner Bay. For this reason, we recommend a microscale, multimedia study for these areas that incorporates atmospheric deposition, watershed runoff, direct discharge into surface water (see **Figure 5-8**), and surface water/sediment modeling of the Inner Fore River, Back Cove, and Inner Bay. Sediment chemistry needs to be examined, since the formation of methyl mercury is a key to understanding the entry of mercury into the food chain. This type of multimedia study would likely help improve our understanding of the causes of higher mercury contamination in this area of Casco Bay.

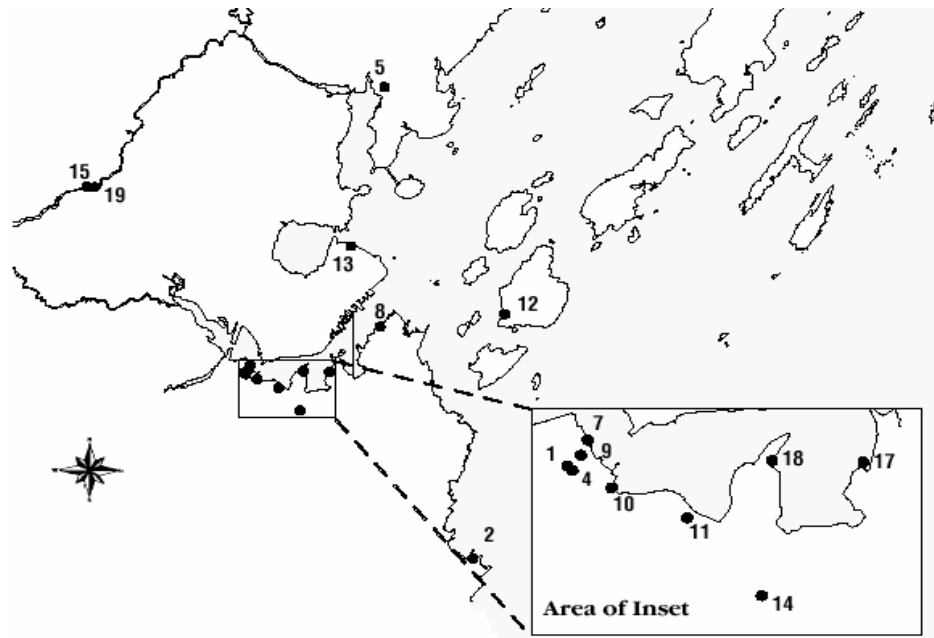


Figure 5-8. Point source discharges into Casco Bay and its watershed (University of Southern Maine, 1996). The numbers in the figure identify locations of licensed facilities considered to have significant discharges of nitrogen into the Casco Bay watershed although no documentation is provided showing that these facilities have significant mercury discharges.

Maquoit Bay suffered from a harmful algal bloom in 1988. Marine algal blooms are often triggered by excess nitrogen. Maquoit Bay is small, shallow, free from point sources of pollution and extensive urban development, and subject to excess concentrations of fecal coliform bacteria. As reported in the Northeast Coastal Condition report (U.S. Environmental Protection Agency, 2001c), a model was developed to assess Maquoit Bay's potential sources of nitrogen (e.g., agricultural and residential runoff, sewage). The study found that septic systems, particularly failing ones, and manure or fertilizer were the largest sources of nitrogen and bacteria entering the Maquoit Bay.

6. CONCLUSIONS AND RECOMMENDATIONS

This section summarizes our conclusions and provides recommendations for additional monitoring and analyses.

6.1 CONCLUSIONS

Estimating wet and dry deposition to the Casco Bay watershed, based on the measurements available, can be highly uncertain. Contributing to the uncertainty in wet and dry deposition estimates are a number of issues, including the following:

- The loss of volatile species from various sampling media during and after sampling, but before laboratory analysis.
- Uncertainty in the estimate of the surface area of the Casco Bay watershed.
- Uncertainty in the fraction of the material deposited in the Casco Bay watershed that reaches the Bay.
- Variations in the type of precipitation that produces deposition, and thus in the amount of material deposited at the surface.
- Year-to-year meteorological variability, which contributes to variability in annual deposition.

Key Findings

- Atmospheric deposition (dry plus wet deposition) of inorganic nitrogen is a significant source of pollution to Casco Bay.
 - Wet deposition to the Bay²¹ surface area accounts for 200 to 246 tonnes/yr. Estimated dry deposition totals 146 to 182 tonnes/yr. Total (dry + wet) deposition is 30 to 40% of overall inorganic nitrogen loading to the Bay.
 - If all (wet + dry) deposition to the Casco Bay watershed reached the Bay, then deposition totals roughly 70% of overall loading to the Bay.
- Atmospheric deposition of mercury is the dominant source of mercury loading into Casco Bay.
 - Wet deposition to the Bay surface area accounts for 10 to 16 lbs/yr. Dry deposition totals 4 to 16 lbs/yr. Total deposition equals 84 to 92% of overall mercury loading to the Bay.
 - Total deposition into Casco Bay equals 65 to 143 lbs/yr if all deposition to the Casco Bay watershed reaches the Bay.
- From 1998 to 2001, there was a trend of declining annual wet deposition of mercury, ammonia, and nitrate totals at Casco Bay. These declining trends were determined to be

²¹ Ignoring 2001 data which were anomalously low (less than half the precipitation of the previous three years).

entirely (mercury) or predominantly (ammonia) the result of a corresponding decline in annual precipitation from 1998 to 2001. For nitrate, our analysis suggests that 20% of the decline in deposition over this time period is from a corresponding decline in precursor emissions.

- Understanding regional patterns of air pollution is important for Casco Bay.
 - Long and medium-range transport of pollution is important. Trajectory analyses and source apportionment indicate polluted air masses from outside Maine likely effect the Casco Bay area. (Note that local sources also likely contribute to pollution loading in the Bay.)
 - Data from Casco Bay monitors generally differ from data collected at other Maine monitoring sites including the headwaters site of Bridgton.

Data Validation

Very few problems were noted in the Casco Bay data, indicating that sampling and analysis protocols were being followed properly.

Characterizing PM_{2.5} at Casco Bay

At Casco Bay, PM_{2.5} (measured using an IMPROVE-protocol sampler) is dominated by manmade pollutants, primarily sulfate and OC; this finding is consistent with Acadia data although the split among pollutants differs. The IMPROVE data were useful in further investigating seasonal variations in PM_{2.5} composition and the potential sources impacting the site. Source types identified included soil, oil combustion, marine, secondary/transport, coal-fired power plant, and two metals sources that appear to be municipal waste incineration and smelting. Additional data are needed to investigate source types on a seasonal basis.

Trajectory analyses and previous studies of pollutant transport show that regional transport pathways include westerly flow across the Appalachians, flow along the Appalachians (e.g., along the urban corridor/eastern seaboard), and near-surface flow (i.e., nighttime stagnation, sea breeze, and land breeze). Combining the speciated PM_{2.5} data with trajectory analyses provided further evidence that transport of anthropogenic pollutants is important to Casco Bay.

Precipitation Characteristics

It is important to understand the precipitation patterns in Maine, as illustrated in this document, because short-term trends in annual wet deposition in Maine can be the result of precipitation variations and not emission changes. The precipitation amounts differed annually at each Maine site and among sites. At Casco Bay,

- Rain accounted for 75% of inorganic nitrogen wet deposition; 29% of annual wet deposition occurred during the spring.

- Rain accounted for 70% of mercury wet deposition (slightly less than reported for inorganic nitrogen); about one-third (35%) of annual wet deposition occurred during the summer.

Precipitation type is important because snow and rain remove different fractions of ambient air pollutants. Precipitation type appeared to be an important factor in spatial differences of mercury and inorganic nitrogen wet deposition totals in Maine.

- More of the precipitation was in the form of rain at Casco Bay than at the other Maine monitoring sites.
- The form of precipitation (e.g., rain, snow) differed among the sites. These differences likely contributed to differences in wet deposition of inorganic nitrogen and mercury among the sites.

Inorganic Nitrogen Deposition

Wet deposition of inorganic nitrogen was primarily in the form of nitrate (70%) with a significant amount from ammonium (30%). A strong temporal correlation was found between wet nitrate and ammonium concentrations at Casco Bay and between air concentrations of nitric acid and ammonium at Acadia (ambient air nitric acid or ammonium concentrations are not measured at Casco Bay). In contrast, nearby out-of-state sites showed lower correlations.

Wet deposition of ammonium was about three times higher in spring and summer and two times higher in fall than in winter. This seasonal variation in ammonium wet deposition was possibly a result of livestock operations and variation in seasonal application rates of fertilizer (including animal waste).

Removal of annual precipitation variations resulted in a trend of decreasing inorganic nitrogen concentrations in wet deposition at Casco Bay and an opposite trend of increasing concentrations at Bridgton and Greenville. This analysis further illustrates the uniqueness of the Casco Bay monitoring site.

Putting Nitrogen Deposition Estimates in Context

Annual wet deposition rates of inorganic nitrogen were lower in Maine relative to nearby states in New England. Lower levels of wet deposition indicate lower levels of ambient concentrations and thus emissions. This was consistent with the mass balance finding that ammonium and nitrate atmospheric deposition totals are 1.5 and 2-3 times greater than the air emission inventory for ammonium and oxides of nitrogen, respectively, for the state of Maine.

A range of about 30% to 70% of inorganic nitrogen entering Casco Bay comes from atmospheric deposition. In comparison, atmospheric deposition at Chesapeake Bay was estimated to account for about 21% of inorganic nitrogen entering the Bay. Differences in watershed surface area and land use likely contribute to the difference in estimates.

Mercury Deposition

Atmospheric deposition was the dominant loading source of mercury to the Casco Bay; direct atmospheric deposition (estimated dry plus wet) accounted for 84% to 92% of total mercury loading into the Casco Bay water surface.

The spatial pattern of mercury concentrations and deposition among the four sites varied from year to year. In general, higher mercury wet deposition rates along coastal Maine were likely the result of upwind sources contributing to coastal wet deposition or coastal Maine receiving more precipitation as rainfall (versus snow, etc.) relative to inland sites.

Putting Mercury Deposition Estimates in Context

Within Maine, annual wet deposition rates of mercury were similar to or slightly higher than those reported in nearby states. If precipitation is uniform, then similar levels of wet deposition indicate similar levels of air emissions (lb/acre) in each state, implying that Maine is neither a source nor a sink. On the other hand, the crude mass balance approach shows atmospheric deposition to Maine equaled twice the current mercury air emission inventory for Maine. Thus, the crude mass balance approach identifies Maine as a sink. We hypothesize that the wet deposition approach which identifies Maine as neither a source nor a sink is more likely to be correct. The data point to a low-biased mercury inventory for Maine and/or a high-biased dry deposition rate for mercury.

6.2 RECOMMENDATIONS

We recommend the consideration of the following studies and analyses to improve the future understanding of the role of nitrogen, mercury, and particles to pollution in Casco Bay. These recommendations involve additional monitoring studies, emission inventory studies, data analyses, and modeling studies. Note that some of these recommendations could be performed using existing data, other recommendations need new resources for new measurements, while other recommendations will not occur for several years after more data is collected and/or new model components are developed.

Monitoring

- Retain speciated PM, wet deposition of nitrogen species, and wet deposition of mercury measurements at the Casco Bay monitoring site near Freeport. Differences among data collected at this site and data collected at other sites in the state are significant.
- Add a CASTNet-type monitoring site at Casco Bay to measure inorganic nitrogen (ammonium, nitrate, and nitric acid) concentrations in the ambient air. These data can be used to better estimate dry deposition rates. In addition, the weekly ambient air data typically provided by a CASTNet monitor can be combined with back trajectory analyses to identify the origin of air parcels with high and low concentrations of ammonium and oxides of nitrogen; these analyses would also help to determine the cause of higher inorganic nitrogen wet deposition concentrations in the summer.

- Assuming that ground-level coastal mercury has some role in mercury wet deposition, monitor ambient air measurements of mercury at Casco Bay to help identify the cause of higher mercury concentrations in precipitation in summer, moderate levels in spring and fall, and lower levels in winter. If these measurements are made on a 24-hr or less sampling frequency, the data could be combined with trajectory analyses to help identify the origin of air parcels with high and low mercury concentrations.
- Consider event sampling of precipitation instead of weekly sampling. One of the observations derived from this study is that a single weekly sample could account for more than 20% of the annual mercury deposition at Casco Bay. During such a week, several storms could arrive at the site, making an assessment of the origin of the mercury extremely difficult, if not impossible.
- Encourage the addition of mercury monitoring sites in nearby states (i.e., Massachusetts, Connecticut, New Hampshire, and Vermont) that currently do not have mercury monitoring. Such information can improve the general understanding of mercury in Maine by classifying states as sources and sinks. This will also allow a determination of which states are likely over- or understating mercury emissions in the region.

Emission Inventory Analyses and Development

- Update the inventory of direct inorganic nitrogen loading into rivers that empty into Casco Bay. In addition, estimate nitrogen and mercury discharges to Casco Bay.
- Update and assess the uncertainty in the mercury air emission inventory for Maine and neighboring states.
- Perform mass balance analyses on data from other states and Canadian provinces. Comparison of updated air inventories to the corresponding atmospheric deposition rates in those states/provinces will help improve the understanding of sources and sinks of mercury in the Northeast. It will also help identify whether the regional emission inventory for mercury is complete and makes sense when compared to ambient data.
- Perform research to identify organic nitrogen air and water emission sources and emission rates (to the extent organic nitrogen is also contributing significantly to water quality issues affected by inorganic nitrogen). Measurements are needed of organic nitrogen atmospheric deposition; and the “toxicity” of organic nitrogen relative to inorganic nitrogen needs to be established (e.g., what is the relative impact of organic nitrogen relative to inorganic nitrogen on algal blooms?).

Data Analyses

- Perform additional emissions trends analyses for other sites in Maine involving the normalization of wet deposition data by year to reflect longer-term averages.
- Collect at least another two years of IMPROVE protocol data at Casco Bay to provide sufficient samples to conduct an analysis of seasonal source fingerprints.
- Perform more comprehensive scatter plot, ratio, factor, and trajectory analyses (using additional years of collected data) in a manner similar to the analysis reported by Polissar

et al. (2001) for Underhill, Vermont. This comprehensive analysis could more precisely identify source types that impact Casco Bay.

- Support research on the seasonal variations in inorganic nitrogen and mercury concentrations in precipitation and the potential differences in the forms of precipitation (e.g., rain versus snow) impacting atmospheric removal rates of nitrogen and mercury. For example, the variation in inorganic nitrogen and mercury concentrations in rain by season may be the result of coincidental changes in ambient temperature.
- Support research to determine whether a substantial increase in ammonium wet deposition seen in spring, relative to winter, affects plant and marine life in Casco Bay.

Modeling

- Run CMAQ to determine the contribution of local and out-of-state mercury sources on wet deposition at Casco Bay. As part of this modeling study, updates to the mercury inventory and dry deposition and/or wet deposition (rain vs. snow) modules will need to be made. Recent study results by Dvonch et al. (1999) and others should be used to improve the CMAQ chemistry and deposition modules. Consider analysis of CMAQ predictions of wet deposition concentrations (snow vs. rain) in Maine; an EPA report (U.S. Environmental Protection Agency, 1997b) indicates the predecessor model²² was calibrated to produce a factor of 2 lower wet concentration in Maine than is being measured at Casco Bay (and Acadia).
- Re-run or analyze the existing output of the EPA acid rain model to determine whether the model is correctly predicting the strong temporal correlation found between wet ammonium and wet nitrate ($r^2 = 0.69$) and between ammonium and nitric acid air concentrations ($r^2 = 0.71$) in coastal Maine and the poorer correlations found in nearby states. This is critical to our understanding and comprehension of the reliability of the chemistry module in the EPA acid rain model. This information would be helpful to further our comprehension of the reliability of the EPA acid rain model for making near- and far-field source contribution estimates within Maine.
- Model estimates for the range and likely percentage of mercury and inorganic nitrogen (ammonium, oxides of nitrogen) atmospheric deposition to the watershed that reaches Casco Bay. This will enable better estimations of the amount of wet deposition to the watershed that reaches Casco Bay. Timing as to when atmospheric deposition to the watershed reaches Casco Bay is also important because even though some wet deposition as snow occurs inland in the winter, it is important to understand whether most of this deposition reaches the Bay in another season (e.g., spring) after snowmelt has begun and/or has been completed. A sudden input or a large quantity of nitrogen into the Bay can result in poor water conditions.
- Perform a multimedia Casco Bay surface water and sediment modeling analysis that incorporates the findings of the watershed modeling, dry and wet deposition data, and an updated inventory of surface water sources. Such a study could be used to assess our ability to predict current levels of pollution in Casco Bay. Results could also be used to determine how future changes in air emissions would likely relate to pollution levels

²² Regional Lagrangian Model of Air Pollution - RELMAP

within the Bay. For example, would re-volatilization of manmade mercury now in the sediment limit the improvement in Bay concentrations for decades to come, even with a reduction in atmospheric deposition?

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