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Air Deposition of Pollutants to Casco Bay: Field Monitoring and Estimation Protocols

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Air Deposition of Pollutants to Casco Bay: Field Monitoring and Estimation Protocols

Casco Bay Estuary Project

DEPARTMENT OF ENVIRONMENTAL PROTECTION · STATE OF MAINE ·

EPA

STi
Sonoma Technology, Inc.

Acknowledgments

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- **Sonoma Technology**
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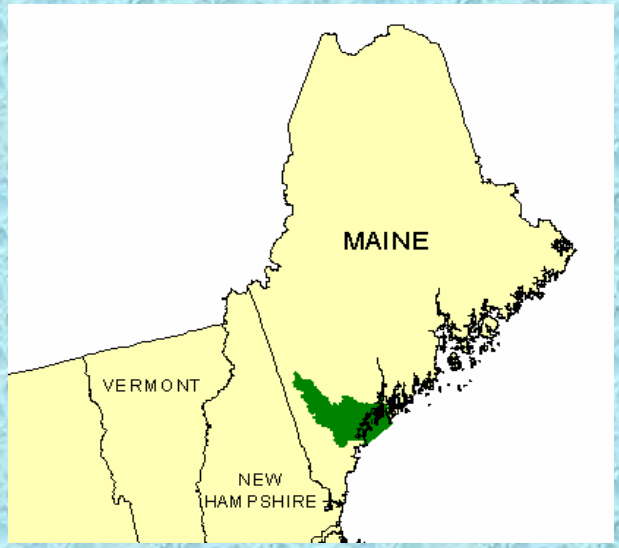
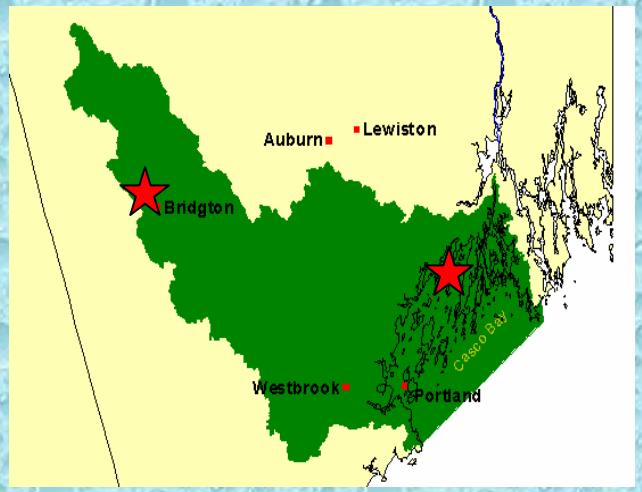
Casco Bay: A Perspective

- Casco Bay surface area: 229 sq. miles
- Casco Bay watershed surface area: 985 sq. miles
- Not all deposition that falls reaches the bay



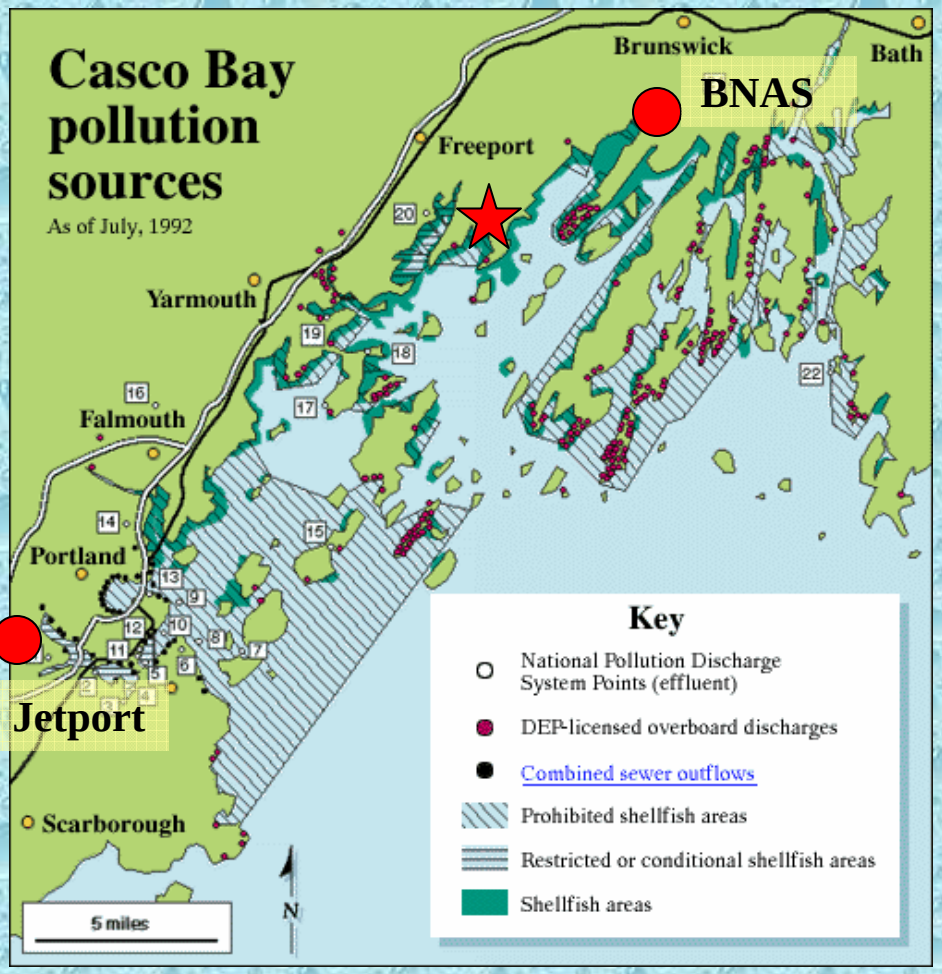


Casco Bay: Estuary of National Significance

- In 1990, Casco Bay was included in the U.S. EPA's National Estuary Program to protect nationally significant estuaries threatened by pollution, development, or overuse.
- The Casco Bay Estuary Project (CBEP) mission: preserve the ecological integrity of Casco Bay and ensure compatible human uses of the Bay's resources through public stewardship and effective management.

Issues Identified by the Casco Bay Plan

- Nuisance algal blooms from excess nitrogen
- Elevated levels of mercury, cadmium, and PAH
- Fish advisories due to elevated levels of methyl mercury in watershed fish



Overview of Air Deposition Study

- Is air deposition a current source of pollution to the Bay?
- What is the contribution of deposition to total pollution loading?
- What is the relationship of the estuary to regional patterns of air pollution?

A long-term deposition monitoring site was established near Casco Bay to collect nitrogen, mercury, acid deposition, PAH, and fine particle data.

Freeport/Casco Bay Site

Objectives of Air Deposition Study

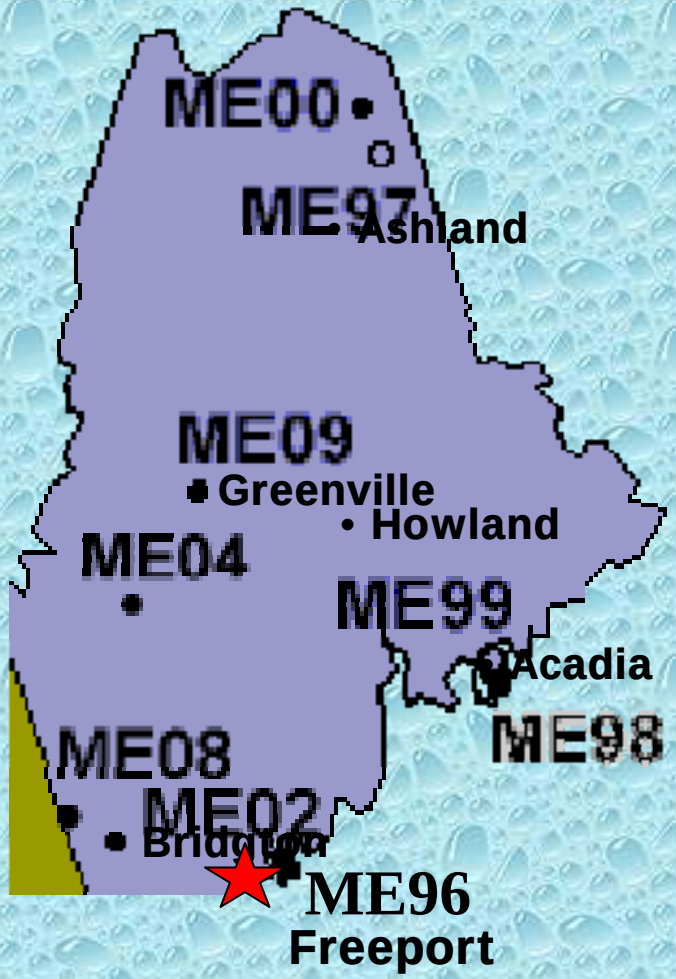
- Determine relationships among pollutants
  - Scatter plots, factor analysis
- Define trends in wet deposition
  - Annual, seasonal
- Estimate dry deposition
  - Assume a ratio of dry deposition to wet deposition or
  - Compute dry deposition from ambient concentrations
- Assess role of air (dry+wet) deposition
  - Compare to direct emissions into the water (% contribution)
  - Compare to Maine air emissions inventory
  - Review source apportionment and back trajectories

Sampling Schedule

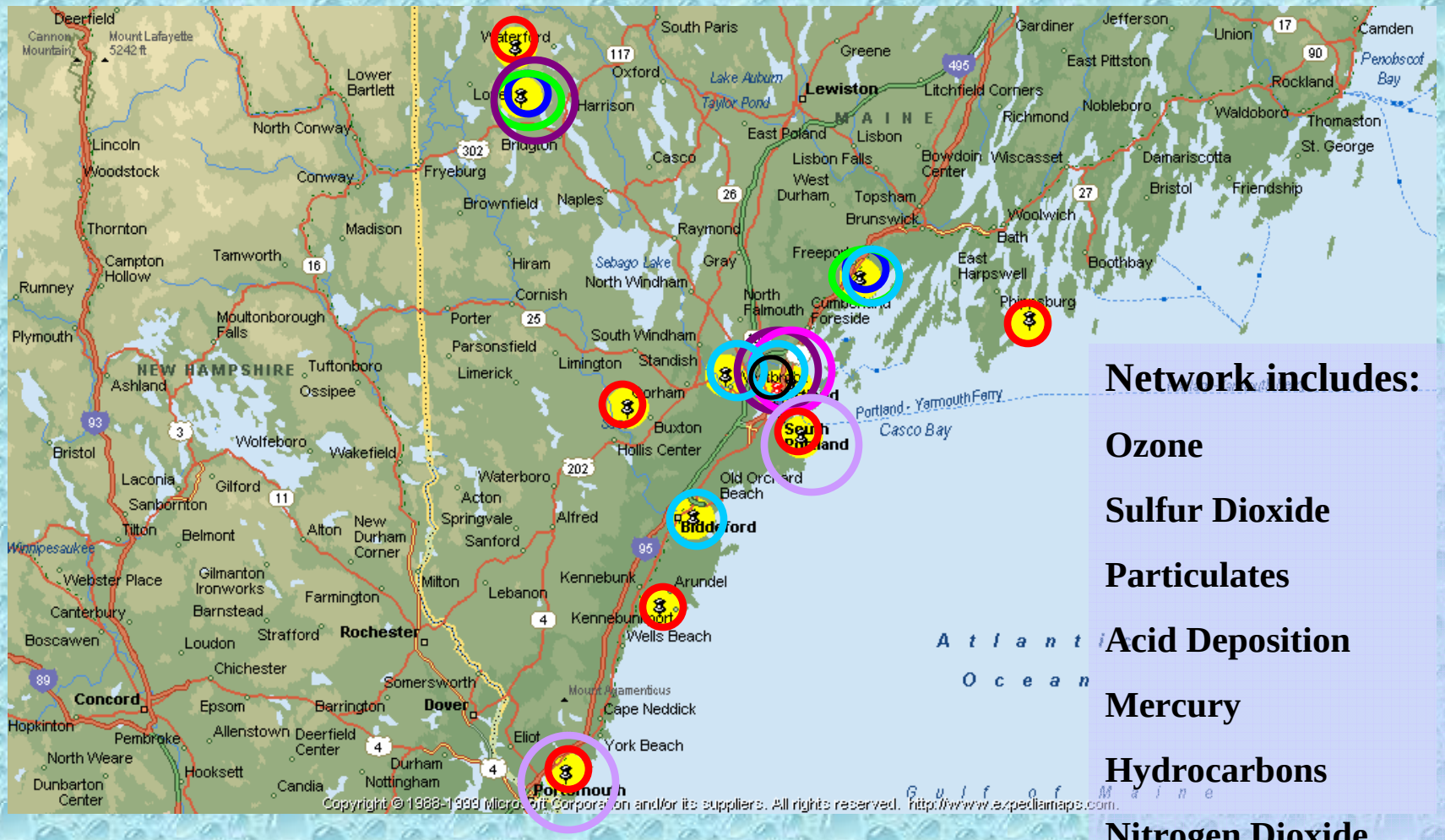
- Fine aerosol (IMPROVE)—24-hr average sample collected every 6th day and analyzed for mass; elements; hydrogen; nitrate, chloride, sulfate, and nitrite ions; and 8 different organic and elemental carbon (OC and EC) fractions
- Precipitation chemistry (NADP)—weekly integrated sampling (sampling bucket Tuesday to Tuesday) analyzed for pH, sulfate, nitrate, ammonium, chloride, calcium, magnesium, potassium, and sodium
- Mercury deposition (MDN)—weekly integrated sampling (same as NADP) analyzed for total mercury
- PAH—48 dry deposition and 38 wet deposition samples were collected between March 1998 and February 2000

Other Monitoring Sites

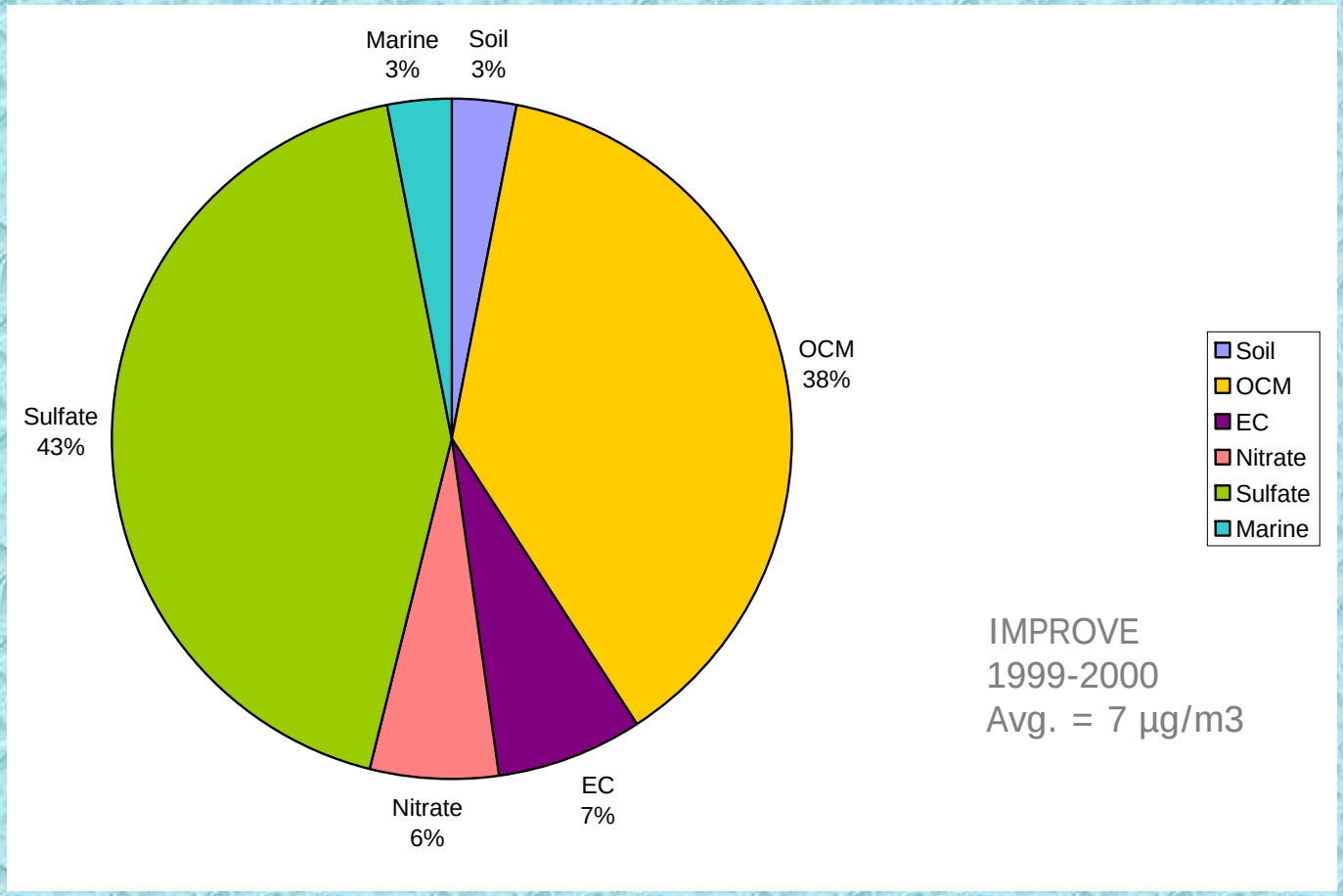
- IMPROVE – Acadia, Bridgton, Casco Bay
- NADP and MDN – Acadia, Bridgton, Casco Bay, and Greenville
- CASTNet – Ashland, Howland



The Casco Bay deposition site is part of the MEDEP's Southern Maine Air Monitoring Network

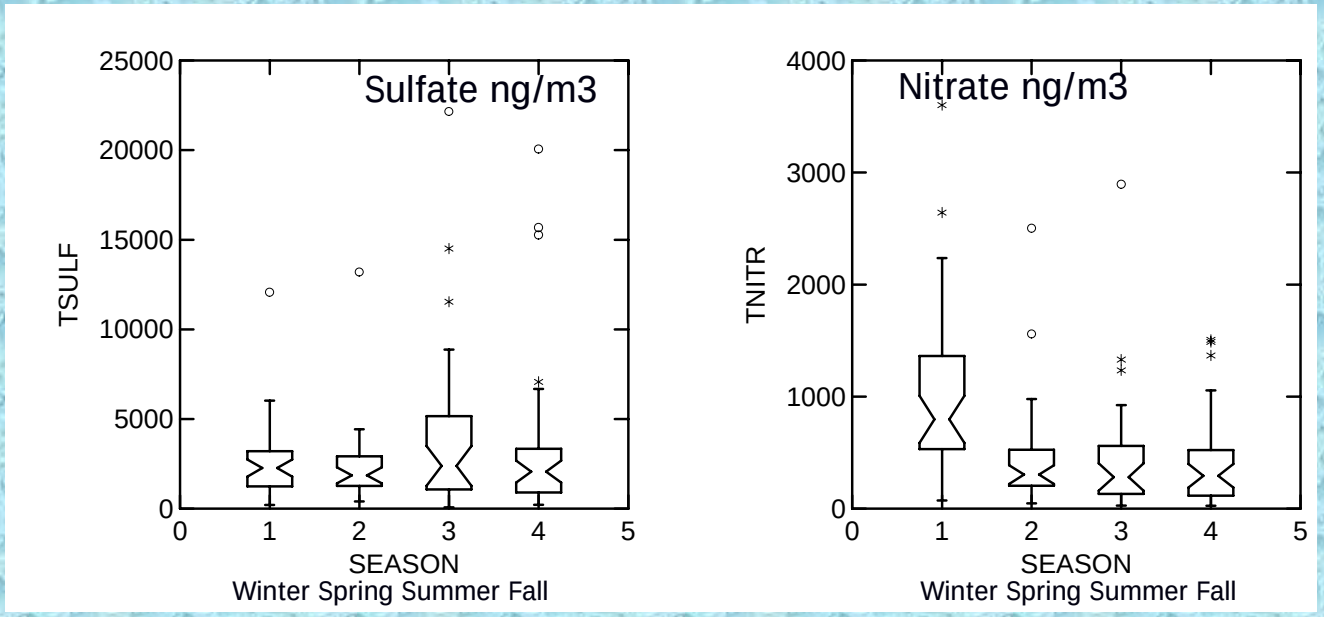


Characterizing $PM_{2.5}$ at Casco Bay



Fine particulate matter is dominated by man-made pollutants, primarily sulfate and OC.

Characterizing $PM_{2.5}$ at Casco Bay



- Sulfate and OC concentrations were highest in the summer, in part due to enhanced formation in the atmosphere.
- Nitrate concentrations have a maxima in the winter.

Source Investigation

- Factor analysis was used to investigate IMPROVE data to help identify sources.
- Factor analysis is a statistical process to group data by similarity among variables (i.e., variables that are highly correlated are grouped).

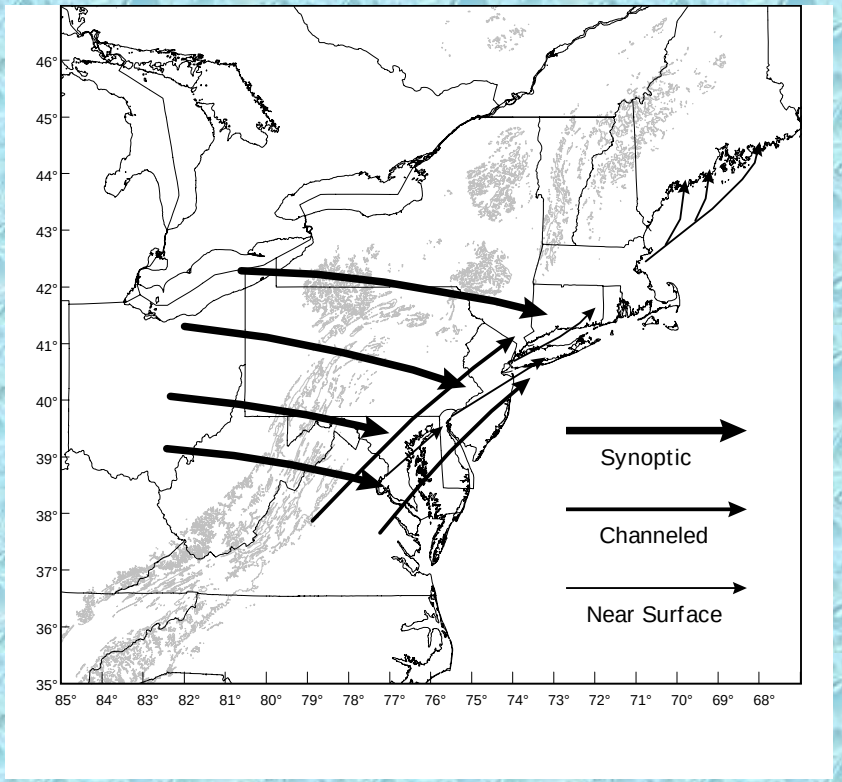
Source Investigation Results

Factor	% of Variance	Key Species
Soil	16	Al, Ca, Si, Fe, K, Sr
Oil combustion	12	Ni, V, Zn, As
Marine	8	Cl, Na, Mg
Municipal waste incineration?	8	Pb, Rb, Se
Secondary/transport	10	OC, EC, nitrate, sulfate
Coal-fired power plant	11	Se, S, H
Smelting	6	Mn, Cu

- There were too few data points to pursue separate seasonal factors.
- Other source apportionment tools, combined with trajectory analyses, could provide further information.

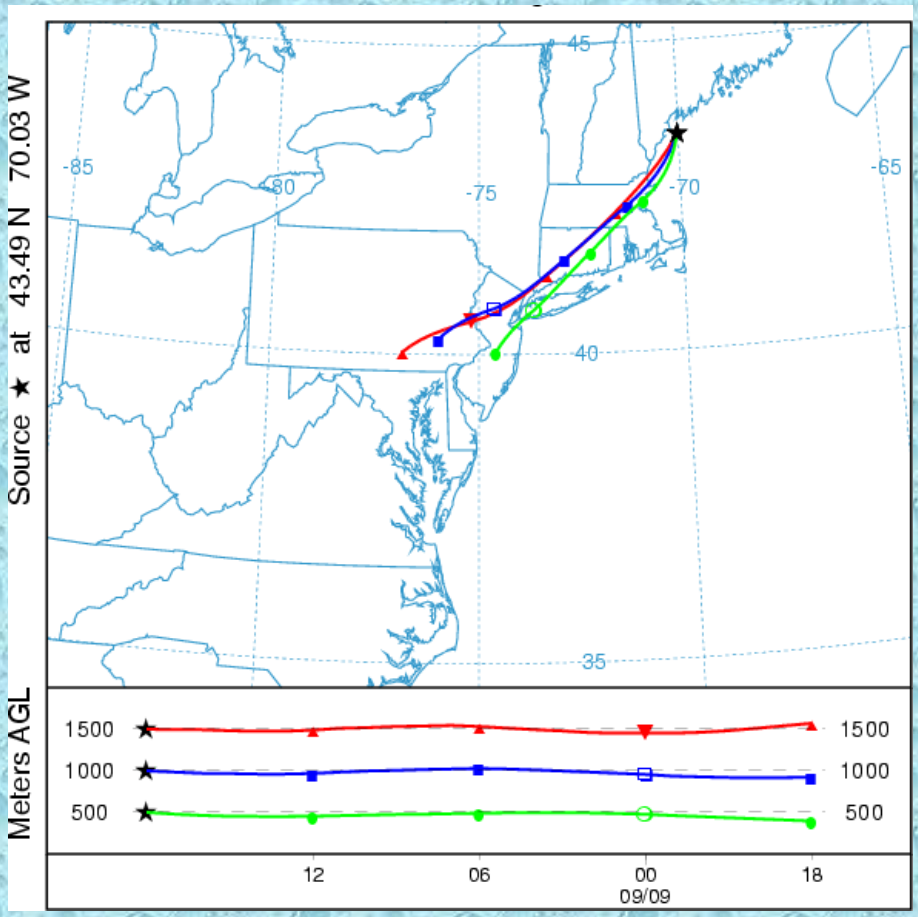
Typical Transport Pathways

- Pollutant transport in the summer in the Northeast corridor shows:
  - Regional transport that could cross the Appalachians).
  - Regional-scale channeled flow (i.e., nighttime low-level jets and channeled flows along the Appalachians and major river valleys).
  - Near-surface flow (i.e., nighttime stagnation, sea breeze and land breeze, and offshore flows).



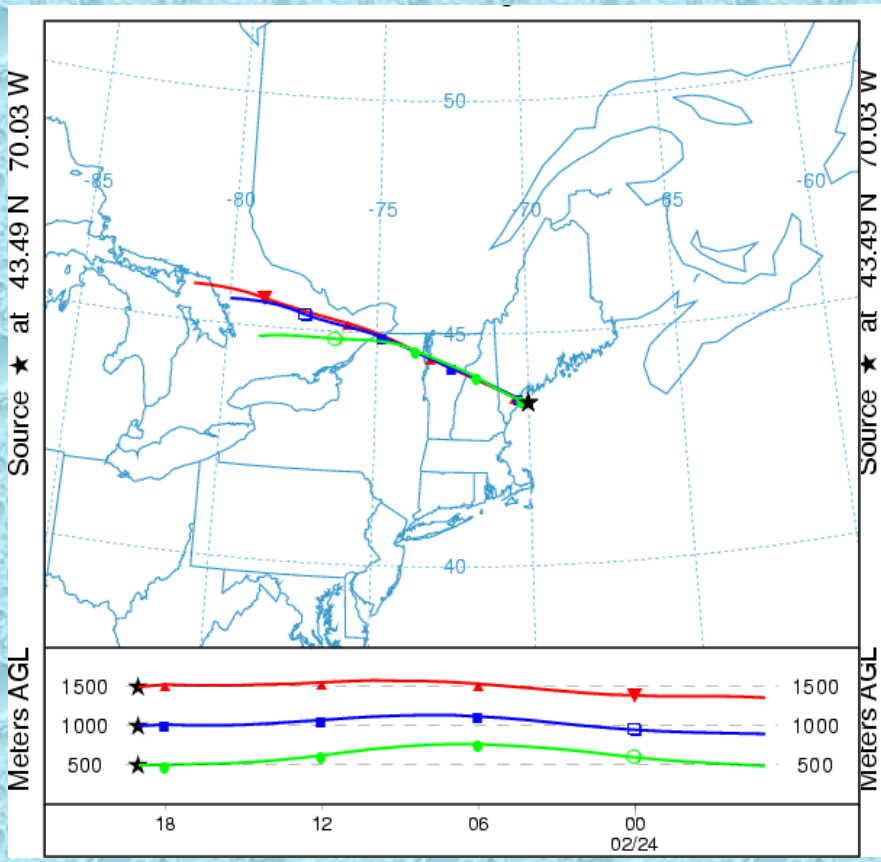
Trajectory Analyses (1 of 2)

- HYSPLIT used to investigate selected IMPROVE samples
- Three backwards trajectories per day used (0800, 1200, 1600 EST)
- Three altitudes used (500, 1000, and 1500 m)

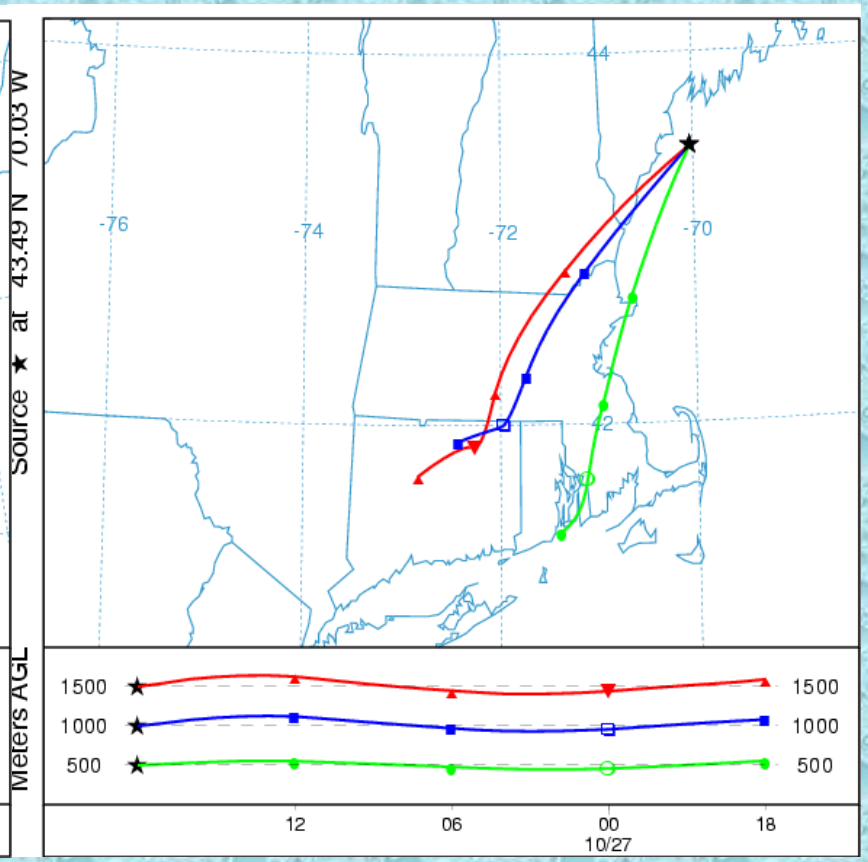


High ammonium and sulfur sample
Sept. 9, 1999 midday

Trajectory Analyses (2 of 2)

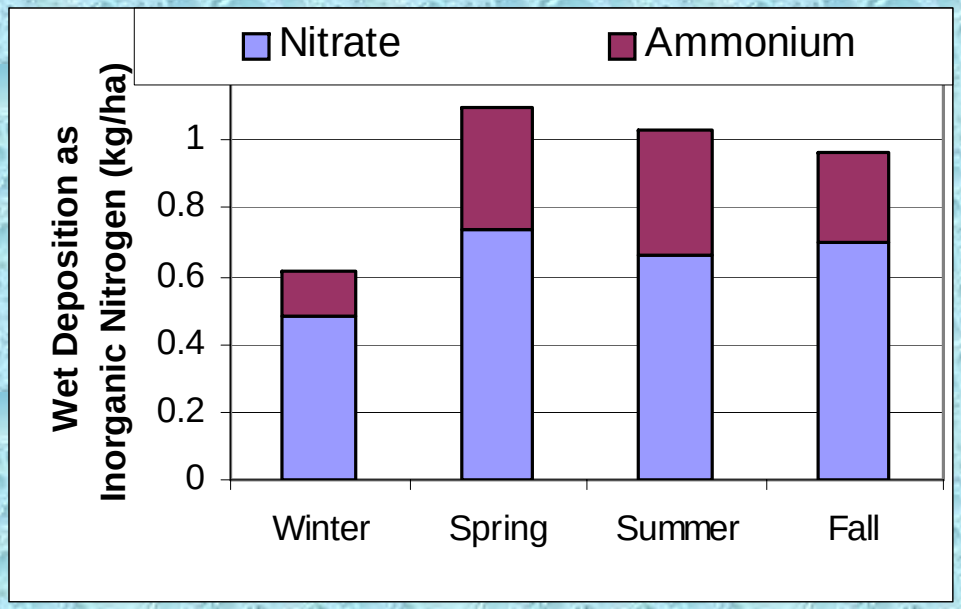


High sulfur, OC sample
February 24, 2000 midday



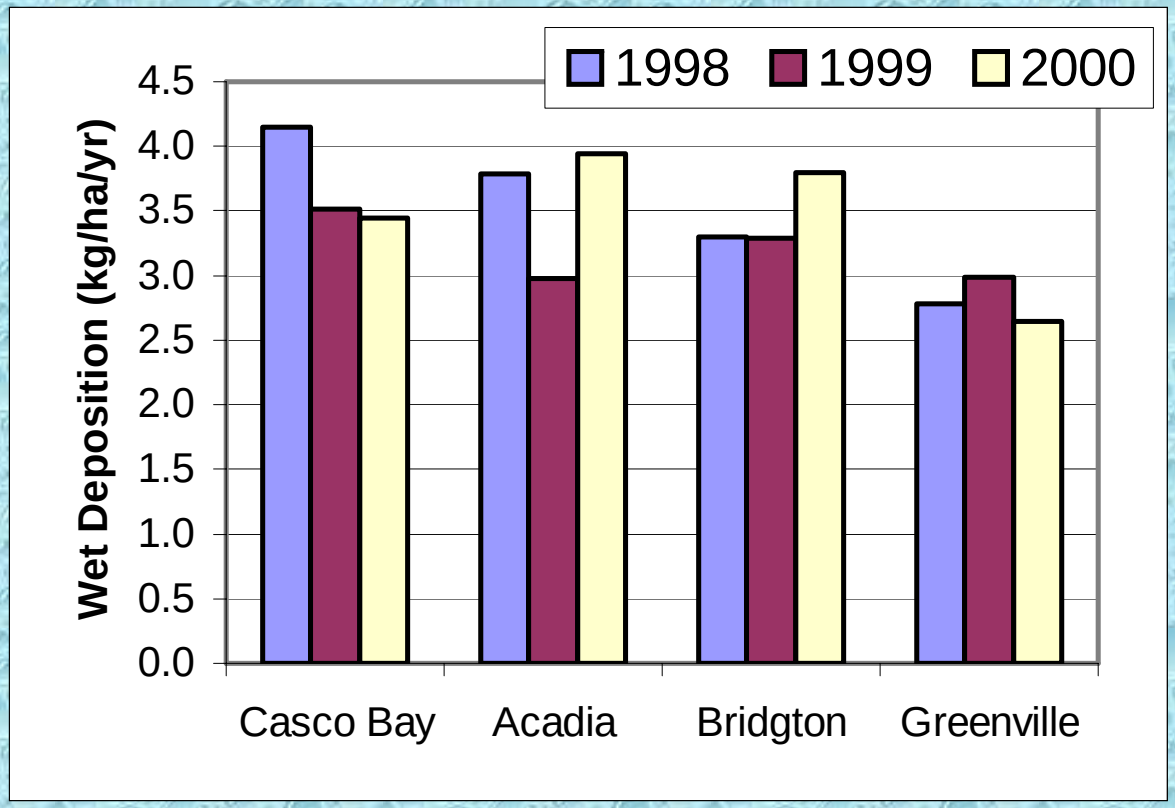
High $PM_{2.5}$ mass sample
Oct. 27, 2000 midday

Nitrogen Deposition (1 of 3)



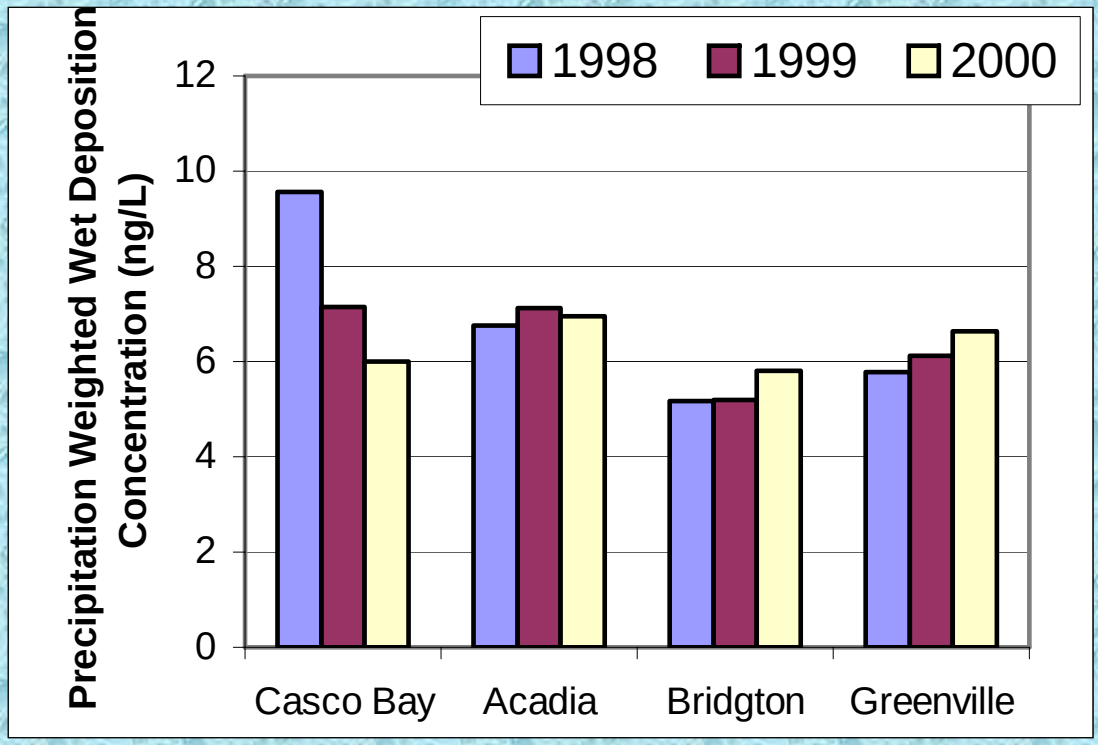
- Wet deposition of inorganic nitrogen is primarily in the form of nitrate (70%) with a significant amount from ammonium (30%).
- Ammonium wet deposition is almost 3 times higher in the spring and summer and 2 times higher in the fall than in the winter.
- These seasonal variations in ammonium deposition are likely the result, in part, of variations in seasonal application rates of fertilizer.

Nitrogen Deposition (1 of 2)



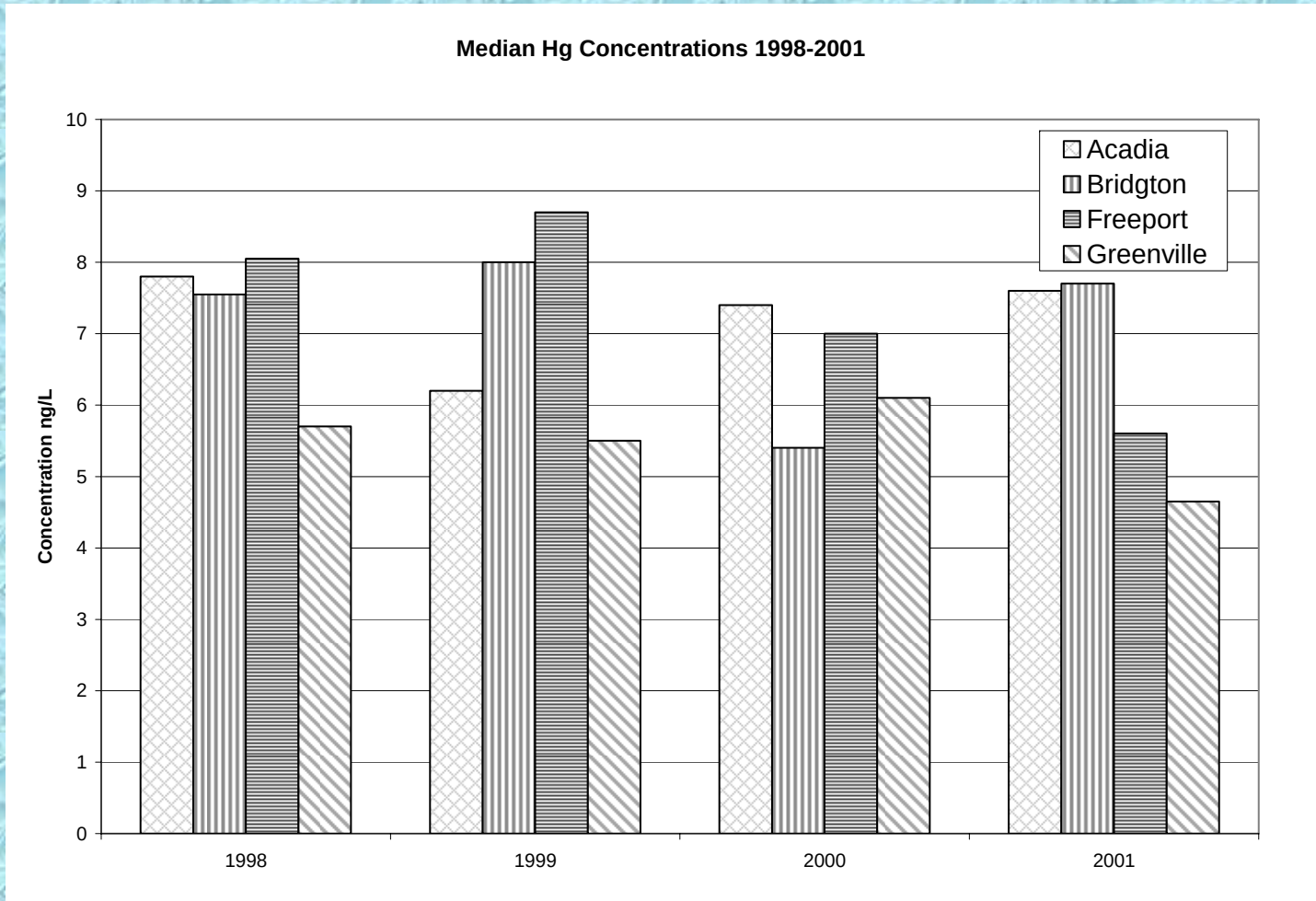
Wet deposition amounts depend on precipitation amounts.

Nitrogen Deposition (2 of 2)



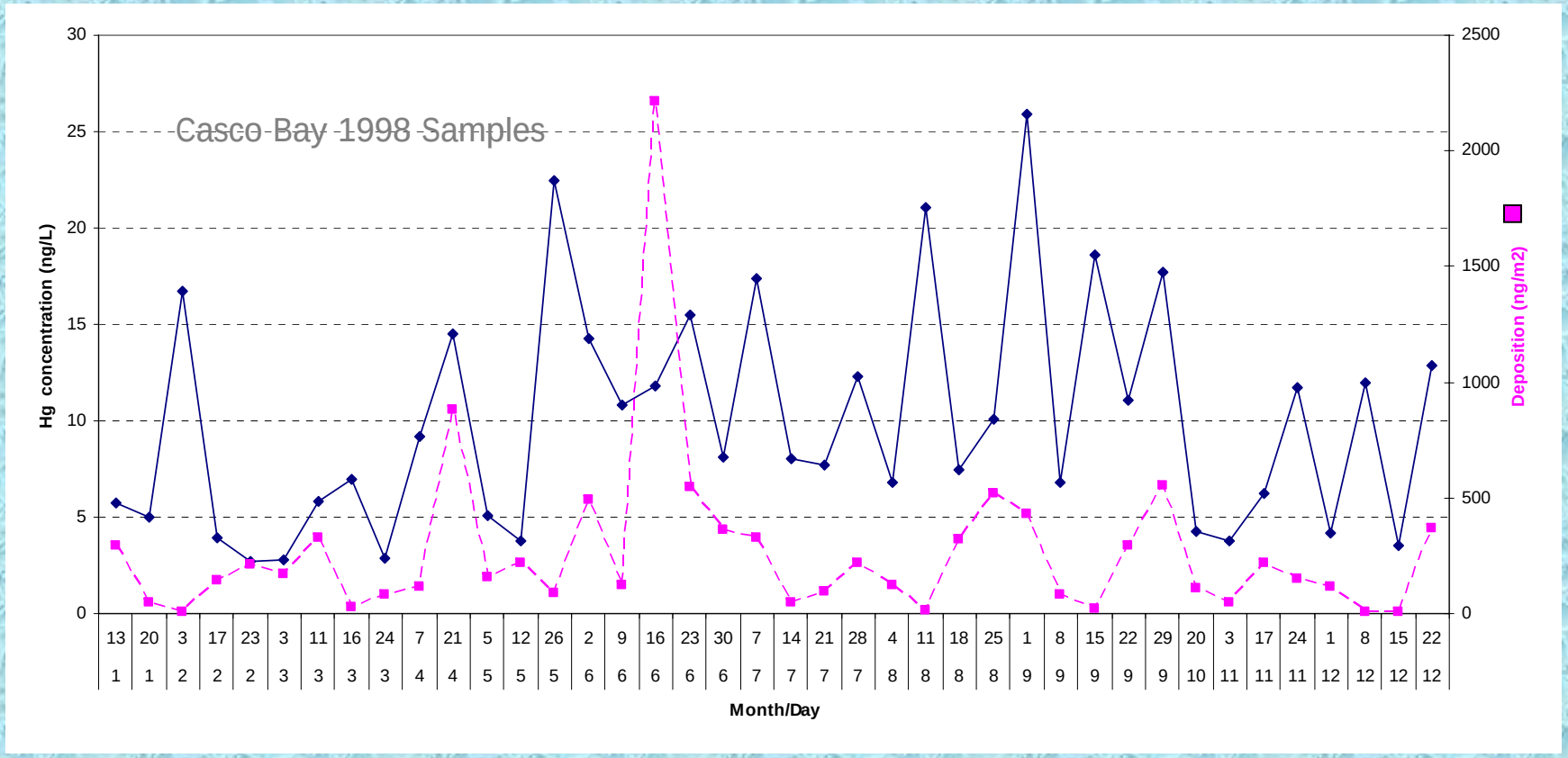
- Removal of annual precipitation variations results in a trend of decreasing inorganic nitrogen concentrations in wet deposition at Casco Bay and an opposite trend of increasing concentrations at Bridgton and Greenville.
- Possible reasons include a shift in annual average wind direction distribution.

Characterizing Mercury (1 of 4)



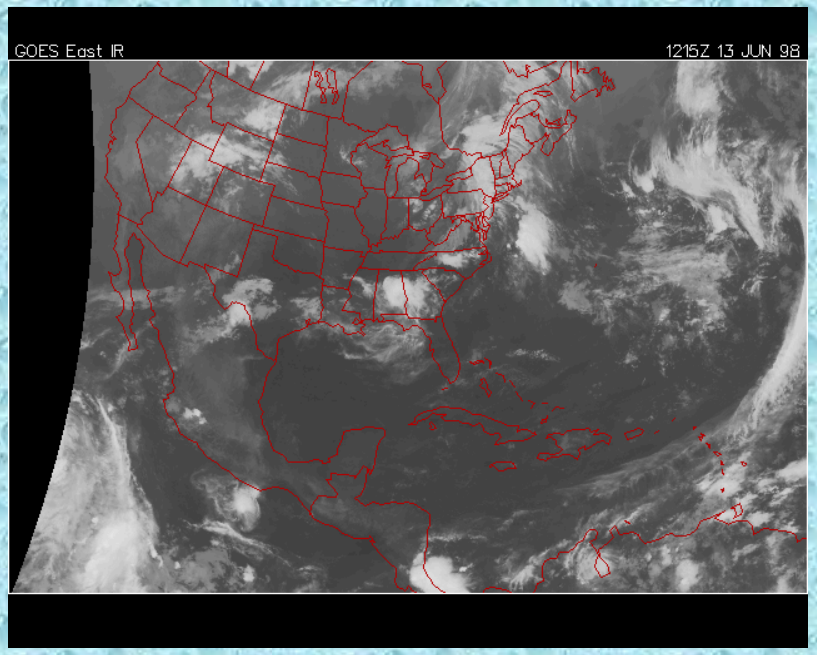
The spatial pattern in mercury concentrations among the selected four sites varied from year to year.

Characterizing Mercury (2 of 4)



- Samples with high concentrations did not always result in more deposition.
- A few large events contributed more than 10% of annual mercury wet deposition.
- The highest weekly mercury deposition event occurred from June 9 to 16, 1998; this one major event accounted for 21% of total deposition for the year.

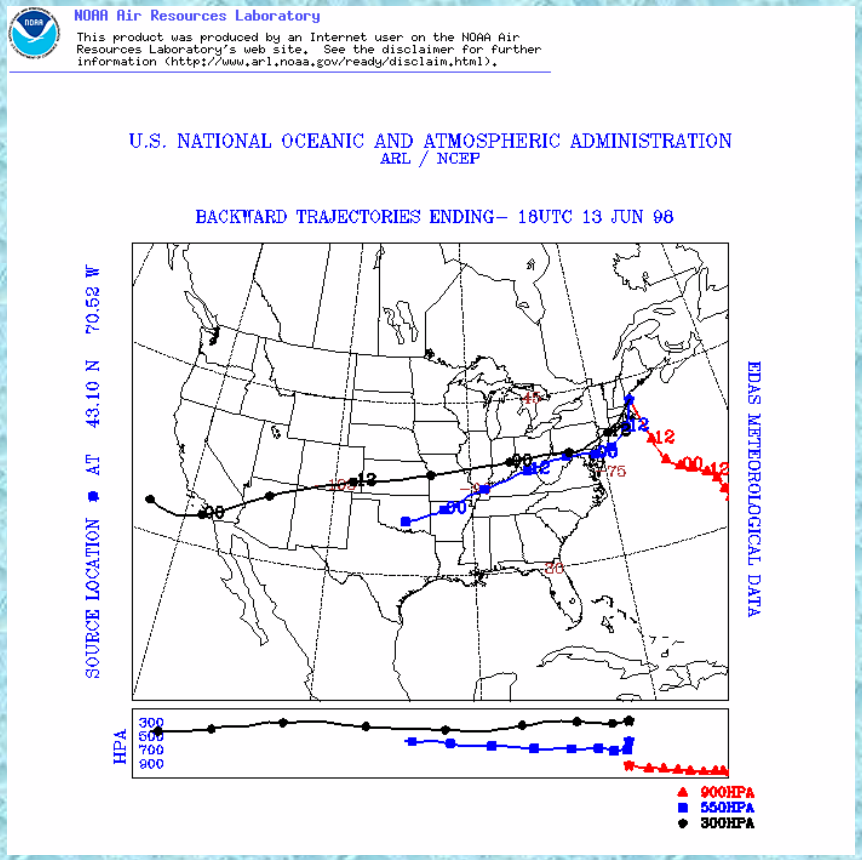
Characterizing Mercury (3 of 4)



Red = 1000 m

Blue = 5000 m

Black = 10000 m

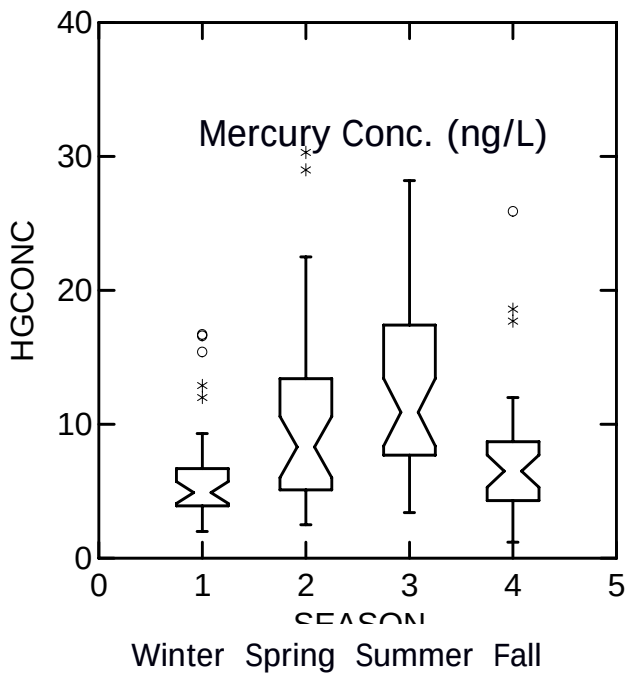


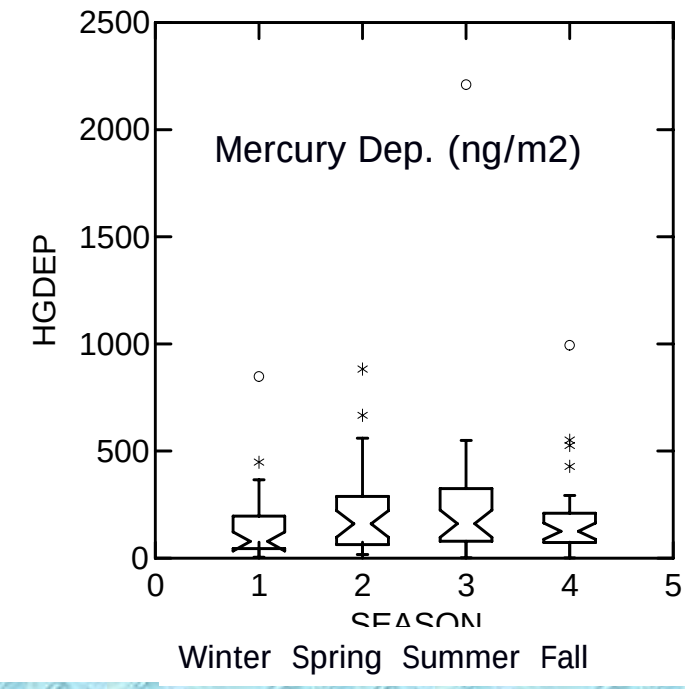
- ✓ June was 3rd wettest on record - 9.01 inches; 7 inches fell from 6/12 through 6/17

- ✓ On June 13th Freeport received 3.58 inches of rain

www.arl.noaa.gov/ready/hysplit4.html

Characterizing Mercury (4 of 4)

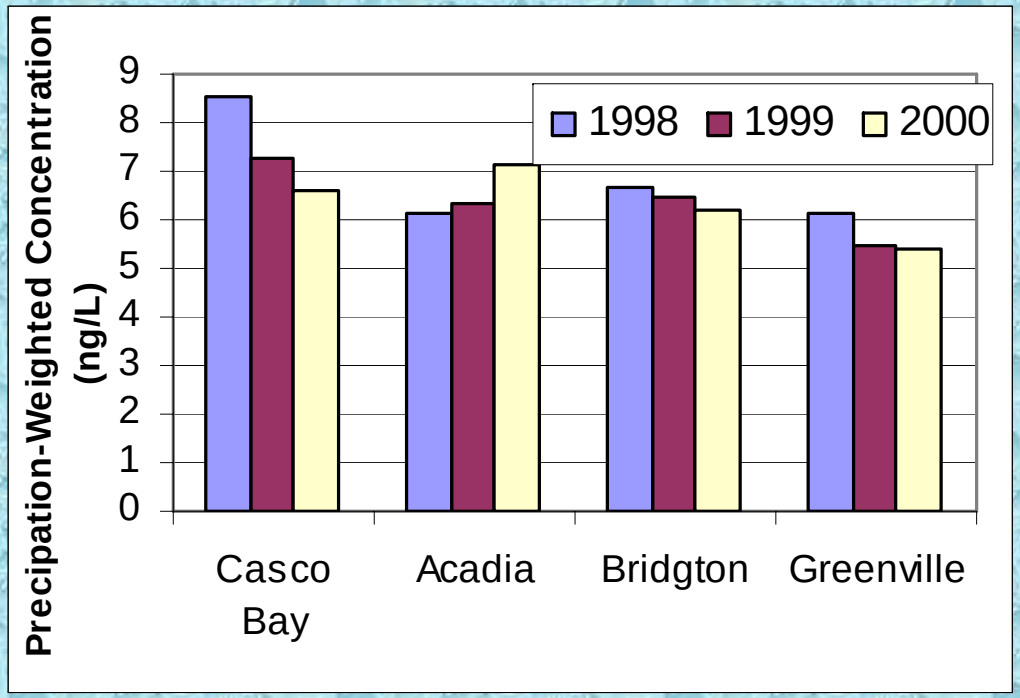




Mercury concentrations and deposition were generally higher in the spring and summer at Casco Bay.

Mercury Deposition

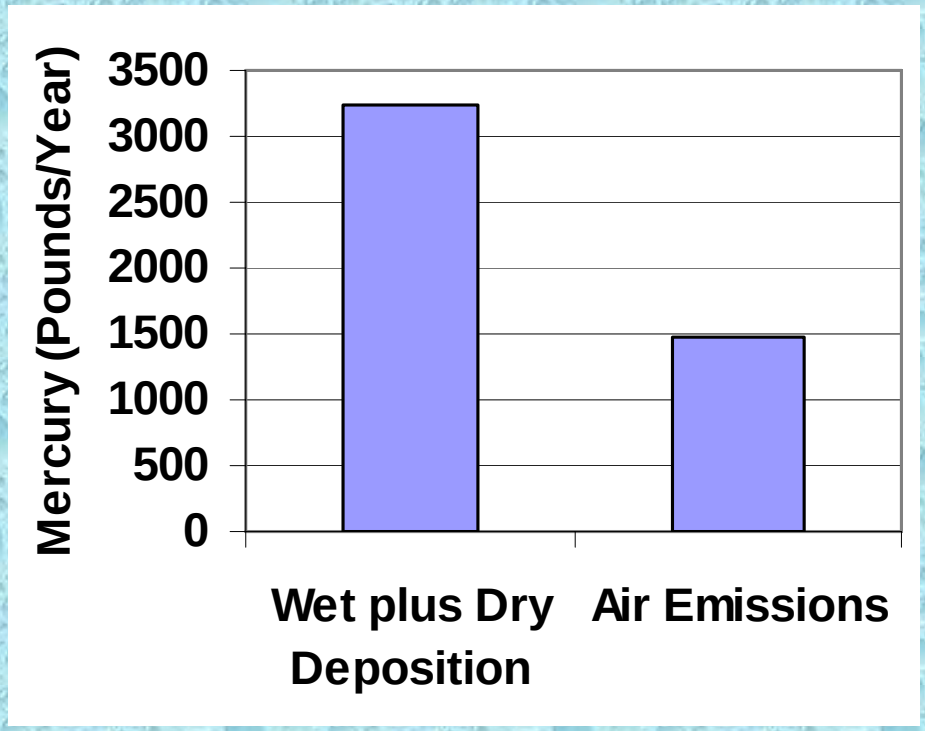
- Removal of annual precipitation changes from wet deposition data results in a trend of decreasing annual concentrations at Casco Bay, Bridgton, and Greenville.
- In contrast, there is a trend of increasing concentrations at Acadia from 1998 to 2000.



Putting Mercury Deposition Estimates in Context

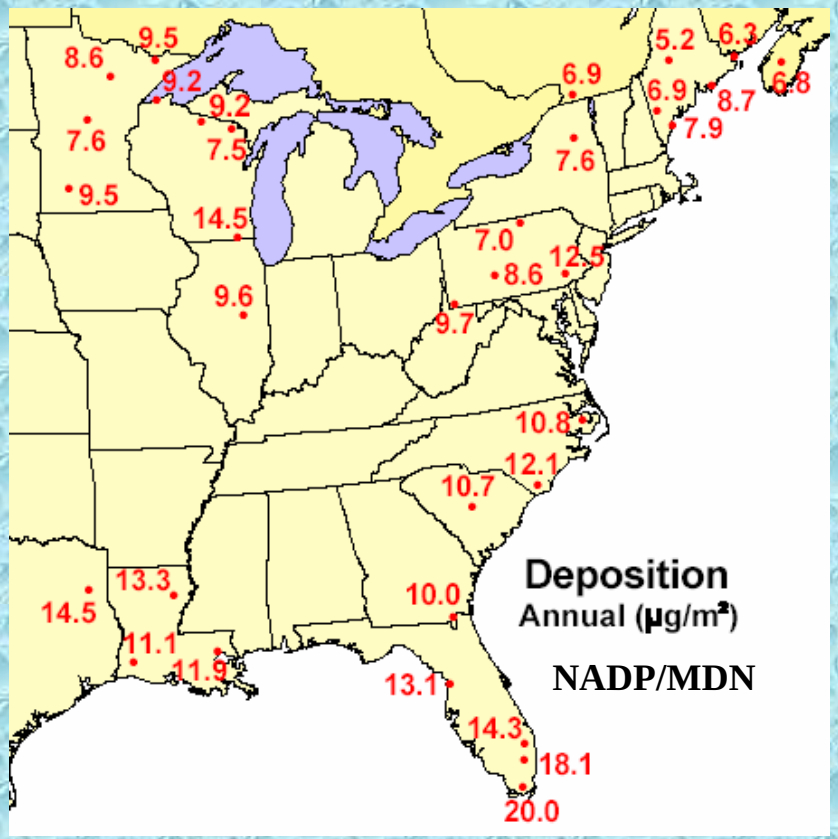
1998-2000 average annual total deposition comparisons in Maine show

- Hg deposition in Maine is similar to surrounding states.
- Hg emissions estimates are too low, or
- Dry deposition estimates are too high.



How Does Coastal Maine Fit into the Regional Pattern of Deposition? (1 of 2)

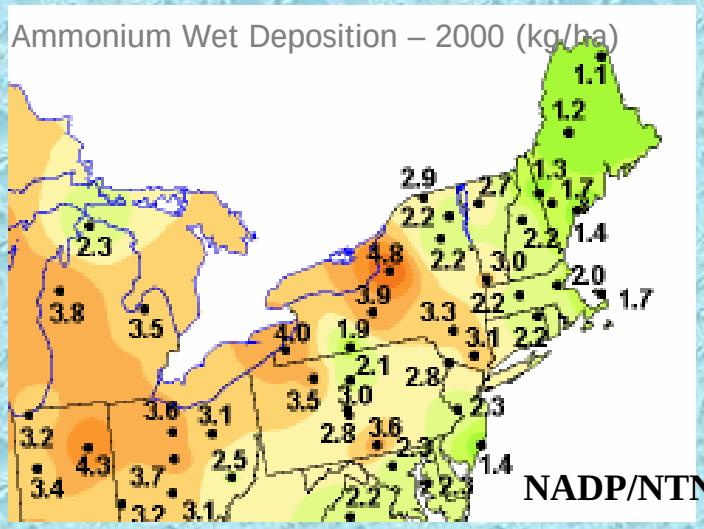
- The higher mercury wet deposition rates along coastal Maine relative to inland might be:
  - Result of local coastal sources contributing significantly to coastal wet deposition.
  - Coastal Maine received more precipitation as rainfall (vs. snow/sleet) relative to inland sites; this would explain the higher wet deposition totals observed along the coast.

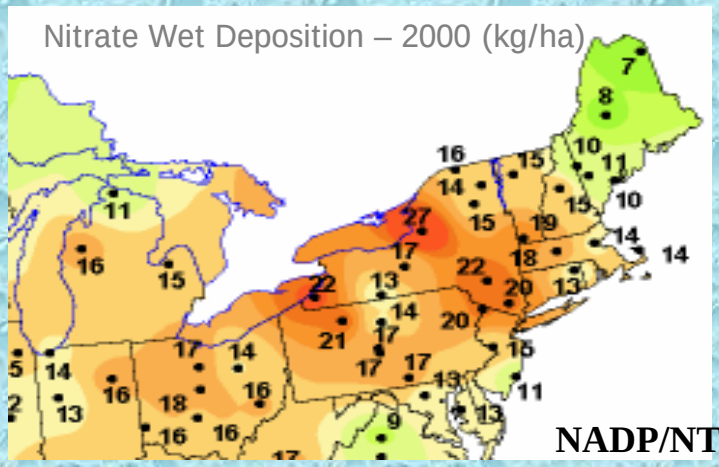


Wet deposition of Hg, 2000

How Does Coastal Maine Fit into the Regional Pattern of Deposition? (2 of 2)

- Lower ammonium and nitrate wet deposition rates along coastal Maine relative to other northeast states is likely the result of lower local emissions.
- Higher wet deposition totals observed along the coast compared to inland Maine could be from more ammonium and nitrate emissions along the coast relative to inland sites.





PAH Monitoring (1 of 5)

1998 - 2000

Dan S. Golomb and Eugene F. Barry
- Principal Investigators

University of Massachusetts - Lowell

Figure 1. The UML wet/dry collector

Figure 2. The interior of the dry collector

PAH Monitoring (2 of 5)

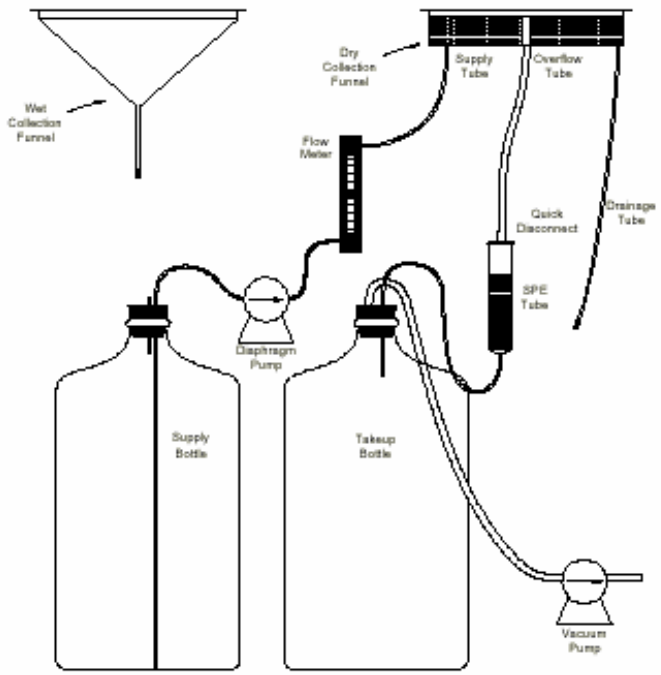


Figure 1. Schematic of UML wet/dry collecto

Wet deposition runs into a funnel that drains into a temperature controlled, shielded collection flask. Dry deposition onto the surface of a funnel continually filled with purified water. The overflow (collection surface) is caught by the receiving flask. (Simulating the ocean surface)

PAH Monitoring (3 of 5)

Dry deposition collection surface

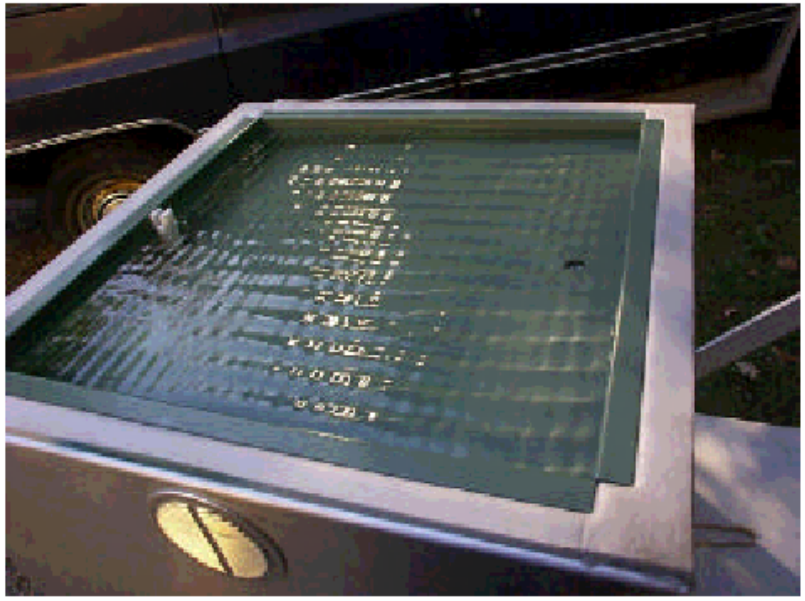


Figure 3. Top view of the dry collector

Inside the collector

Figure 2. Photo of UML wet/dry collector

PAH Monitoring Summary:

- ✓A modified precipitation collector designed by Dr. Dan Golomb (UMass-Lowell) was deployed at the Freeport site for two years
- ✓48 dry deposition and 38 wet deposition samples were collected between March 1998 and February 2000
- ✓Dry PAH deposition at Freeport was lowest during the summer and highest during the winter months
- ✓Dry deposition rates at more urban locations (Boston area) are much higher than those found at Freeport, suggesting that local emissions are a major source for PAHs in dry deposition
- ✓There was no clear seasonal variation in wet deposition of PAHs at Freeport
- ✓Precipitation amount does not appear to influence PAH concentrations in precipitation
- ✓No definitive source(s) for the PAHs found in wet and dry deposition at Freeport could be identified
- ✓General increase of PAHs during heating season due to fossil fuel use

PAH Monitoring (5 of 5)

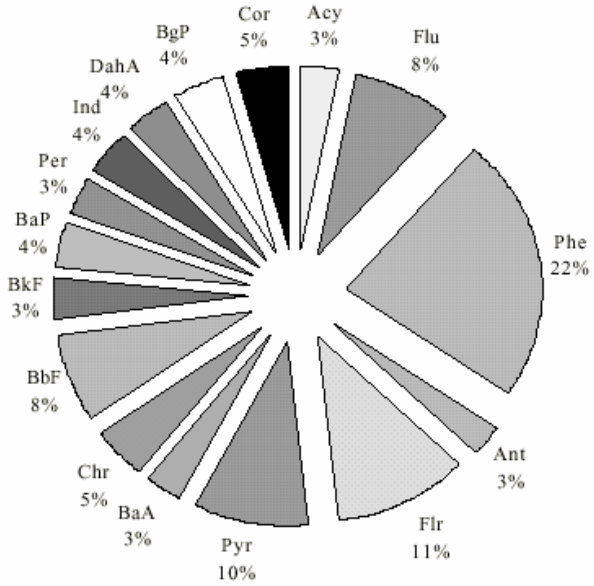


Figure 4. Average annual composition of PAH species in wet deposition

There was very little difference between the average annual composition of PAH species in the wet and dry deposition.

Chemical Mass Balance Model:

(6 PAH species / 4 source categories)

- ✓ **Jet Exhaust: 32-35%**
- ✓ **Gas Fueled Vehicles: 28-32%**
- ✓ **Diesel Fueled Vehicles: 17-18%**
- ✓ **Wood Combustion: 13-16%**
- ✓ **"others": 3- 8%**

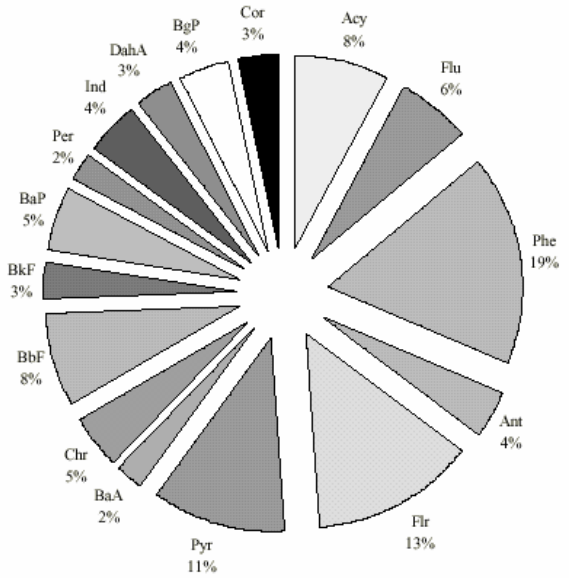


Figure 5. Average annual composition of PAH species in dry deposition

Estimating Estuarine Pollutant Loading From Atmospheric Deposition Using Casco Bay, Maine as a Case Study

Simple - “back of the envelope” - 1st cut

Applicable to other estuaries

Applicable to other pollutants

Low cost - use of Internet resources

ESTIMATING ATMOSPHERIC DEPOSITION IN YOUR LOCALE

How Much Information is Available for Your Locale?

Approach 1. Deposition data from nearby locations are available

Approach 2. Adequate state, regional or national deposition monitoring data are available to extrapolate/interpolate results for your estuary

Approach 3. Local deposition data are not available and current literature values are used to develop appropriate estimates

Table 1 - Data Sources			
	Pollutant Types		
Web Sites	Air Concentrations	Deposition	Other
AIRS Data: www.epa.gov/airsweb	x		
Air Web: //www2.nature.nps.gov/ard/vis/vishp.html (or use IMPROVE site)	x	x	x
CAPITA: //capita.wustl.edu/CAPITA	x	x	x
NADP: //nadp.sws.uiuc.edu		x	
NEARDAT: //capita.wustl.edu/NEARDAT	x		x
NOAA READY: //www.arl.noaa.gov/ready/hysplit4			x
NPS: (Particulate Data) www2.nature.nsp.gov/ard/vis	x		
CASTNET: //www.epa.gov/castnet/	x	x	x

Annual Wet Deposition (mass/m^2 year) = PCp x PR

PCp = volume weighted average concentration of pollutant in precipitation (mass/m^3)(find in the literature)

PR = precipitation depth (m/year) (use local meteorological data)

Annual Dry Deposition (mass/m^2 square area per year) = PCa x PF x Vd*

PCa = total (gas and particle) ambient concentration (mass/m^3)

PF = fraction of ambient concentration in particle phase

Vd = dry deposition velocity of particles (m/year) (Vd is usually reported as cm/sec) .**

*This formula applies only to the particulate fraction of the deposition (dominated by particles greater than 2.5 um).

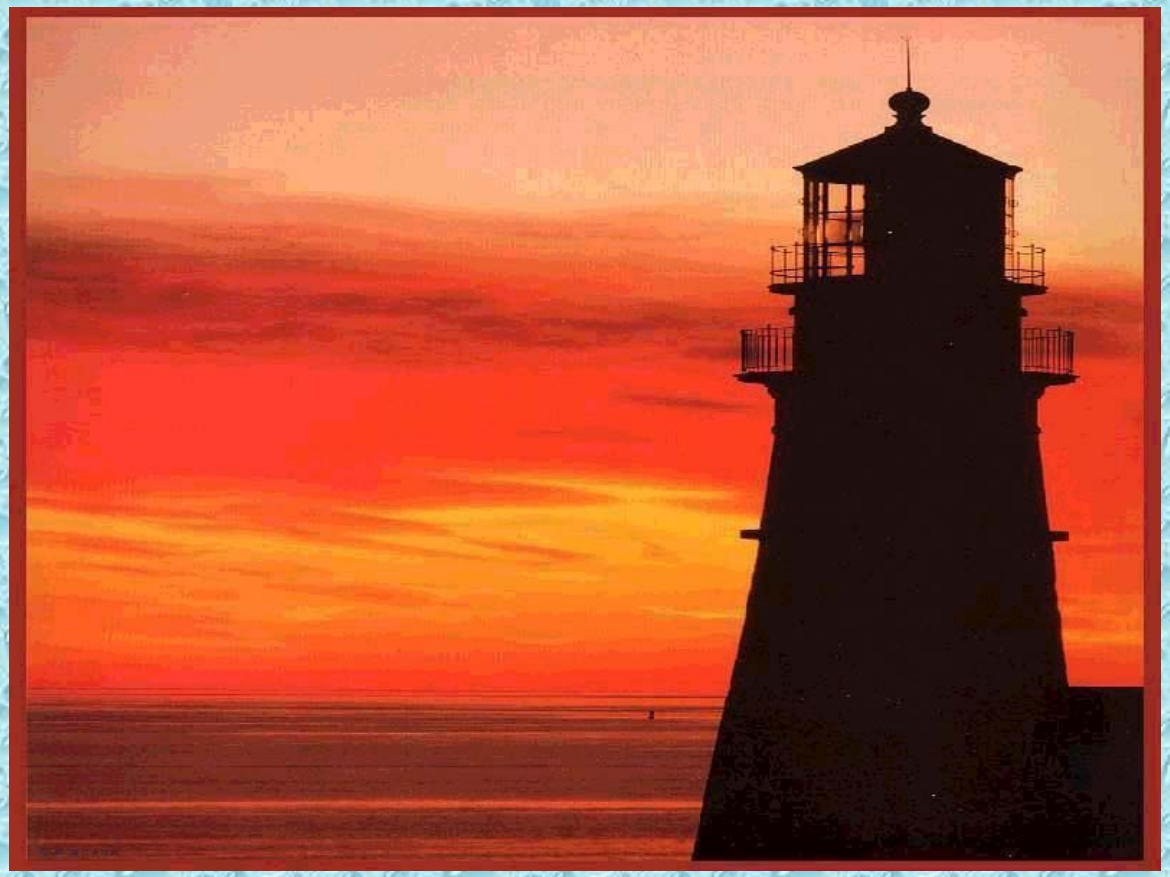
**Example of literature value: 1 - 5 cm/sec (Holsen et al., 1997); 0.2 cm/sec (Eisenreich, 1998); .5 - 4 cm/sec for PCBs and PAHs where the larger value is for large articulate matter, i.e. urban , close to the source (Franz, et al., 1998)

Casco Bay Case Study Estimates Compared to Field Monitoring Data

	Pollutant	**Estimated Atmospheric Input/Year**	**Casco Bay Monitoring Data 1998 - 2000 Average Direct Input/Year**
1	Nitrate (wet)	13 kg/hectare (1997) = 1.3 g/m^2	10.8 kg/hectare = 1.08 g/m^2*
	Ammonium (wet)	1.6 kg/hectare (1997) = .16 g/m^2	1.3 kg/hectare = .13 g/m^2*
	Total Inorganic Nitrogen (as N)	.41 g/m^2	.37 g/m^2*
2	Mercury (wet)	10 - 30 ug/m^2	10 ug/m^2*
3	PAH		
	Total (wet)	20 - 635 ug/m^2	91 ug/m^2**
	(dry)	20 - 5035 ug/m^2	81.5 ug/m^2**
	Species (e.g..)		
	Phenanthrene (wet)	3 - 150 ug/m^2	25 ug/m^2**
	(dry)	3 - 400 ug/m^2	1.5 ug/m^2**

*(Ryan, P. A., H.H. Main and S. G. Brown, 2002)

**Based on the 16 PAH species monitored by Golomb, D., E. F. Barry, Jr., et al. (2001b)



http://www.cascobay.usm.maine.edu/index.html

http://www.state.me.us/dep/index.shtml