2 Is atmospheric deposition a major contributor of PAHs and mercury to the Bay?

Background

The atmosphere serves as a source of toxic chemicals when particulate and gaseous pollutants released into the air are transferred to land and water surfaces through wet processes (such as precipitation and fog), and dry processes (via vapor or particles). Deposition to water bodies can be indirect (via runoff from the land) or directly to the water surface. Studies undertaken by the CBEP in 1991 and 1994 indicate that levels of heavy metals and organic pollutants are elevated above the normal background level throughout the Bay, including areas distant from point sources (see Chapter 4). In addition, elevated levels of methyl mercury have been detected in freshwater fish from water bodies throughout the state (see Chapters 6 and 8). This widespread distribution of toxic chemicals suggests that atmospheric deposition plays a major role in the delivery of toxic chemicals to the watershed and directly to the Bay. CBEP began a field monitoring program in 1998 to assess the magnitude of the atmospheric contribution of two important toxics: mercury and PAHs.

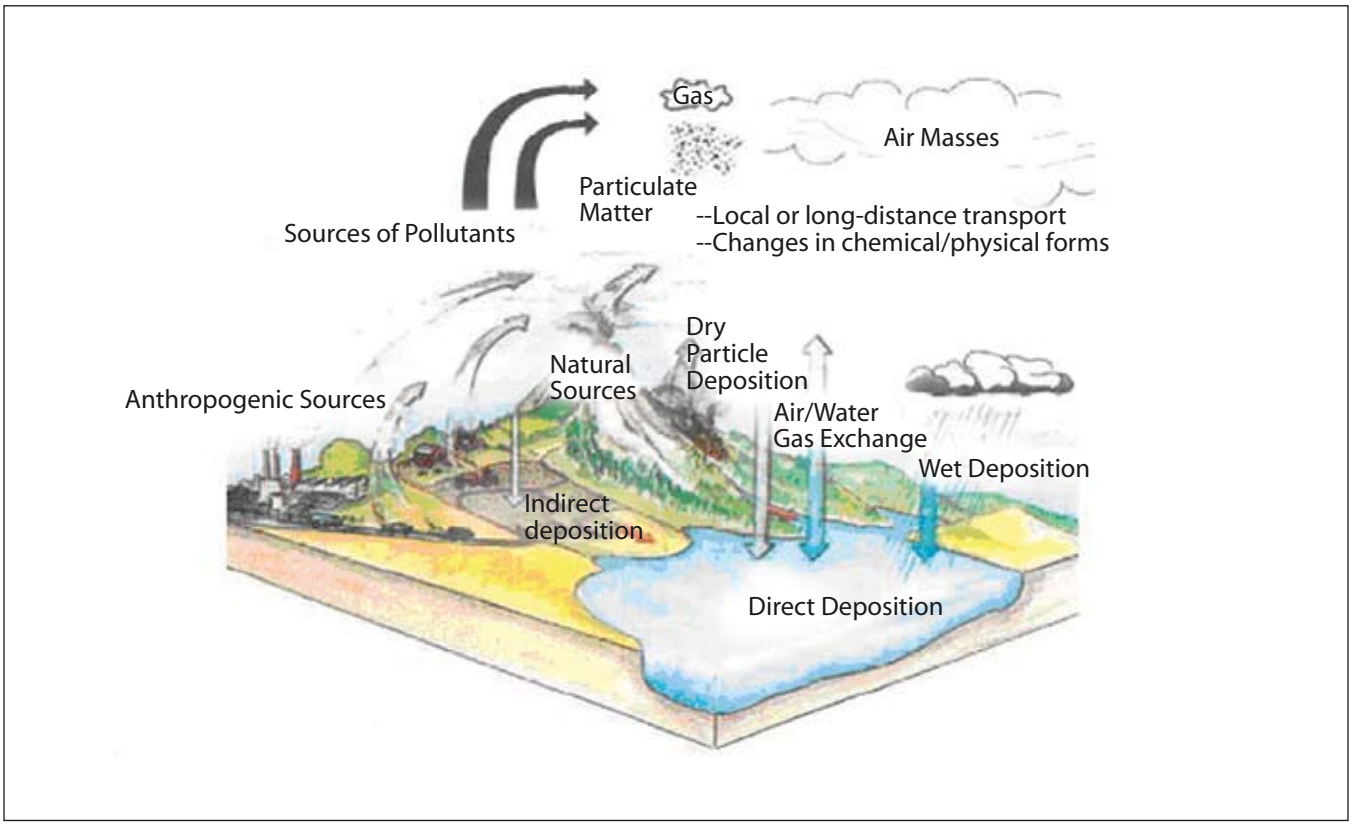

Figure 2-1. *Diagram of the sources, transport, and deposition of pollutants via the atmosphere (US EPA 2002).*

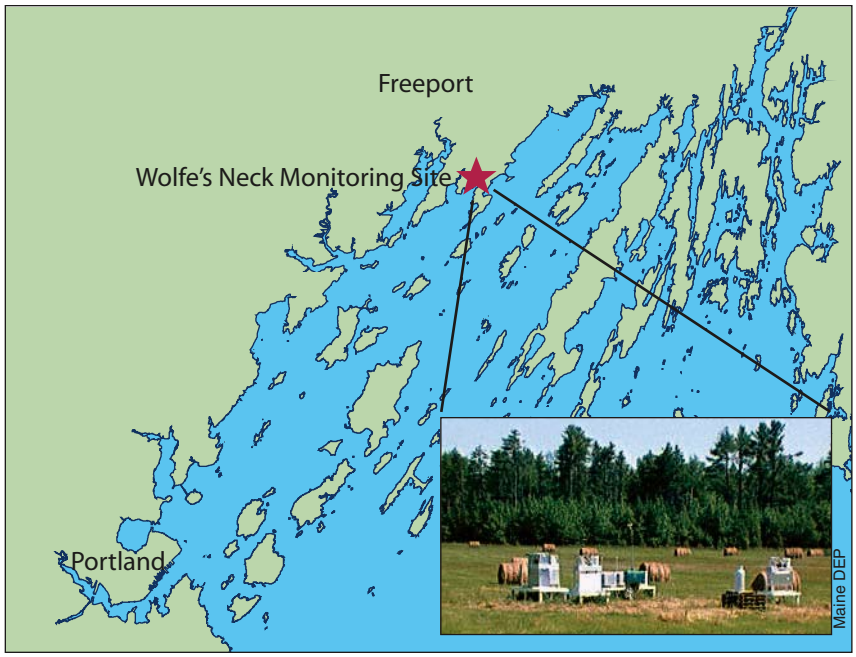

Figure 2-2. *Casco Bay Monitoring Site at Freeport*

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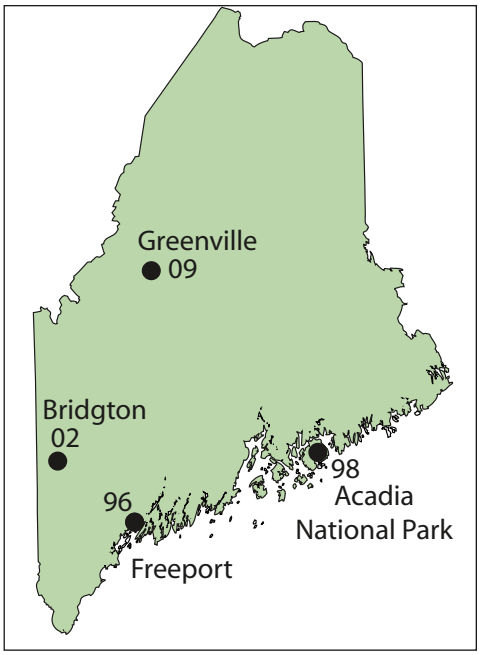

Figure 2-3. *There are four Mercury Deposition Network Sampling sites in Maine. ME96 is the Wolfe's Neck site in Freeport. ME02, also located in the Casco Bay watershed, is an inland site in Bridgton. ME 98 is another coastal site, located in Acadia National Park. ME09 is in Greenville.*

Mercury Deposition

Sources of mercury to the atmosphere include combustion of coal, oil, wood or natural gas, incineration of mercury-containing garbage, and industrial processes. Funded by a grant from US EPA, an atmospheric deposition monitoring station was established at Wolfe Neck Farm on the coast in Freeport, Maine (see Figure 2-2). A Mercury Deposition Network (MDN) sampler collected weekly samples of wet deposition (total precipitation and pollutant concentrations in the precipitation) of mercury from 1998-2001. Following the conclusion of the CBEP-funded study, DEP has continued data collection at the Freeport site. Data from other MDN sampling sites in Maine including Bridgton, which is an inland site located at the headwaters of the Casco Bay watershed, Greenville, and another coastal site in Acadia National Park is available for comparison to the Freeport data (see Figure 2-3).

The results of the mercury sampling were analyzed to determine whether atmospheric deposition is a significant source of mercury entering Casco Bay. Also, the study looked at how coastal Maine fits into the larger pattern of regional atmospheric deposition of mercury and whether there are annual or seasonal trends in wet deposition.

Wet deposition was determined by multiplying the weekly amount of precipitation collected at a site by the corresponding weekly average wet concentration of mercury. Annual deposition was calculated by summing the calculated weekly wet deposition amounts for that year. Dry deposition was inferred from pollutant concentrations in the ambient air or by assuming a ratio of dry deposition to wet deposition. For this study, 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:

- Uncertainty in the fraction of the toxic material deposited on water bodies and land surfaces in the Casco Bay watershed that ultimately reaches the Bay; and
- Year-to-year meteorological variability, which contributes to variability in annual deposition of metals and PAHs.

Results of the Mercury Monitoring

- Atmospheric deposition of mercury is the dominant source of mercury to Casco Bay when compared to loading from major point sources (see Figure 2-4).
- Mercury concentrations and deposition were generally higher in the spring and summer at Casco Bay. Snow and rain remove different fractions of air pollutants from the atmosphere and rain typically has higher concentrations of mercury.
- Large storm events can be a significant source of mercury deposition. One major storm during the period June 9-16, 1998 accounted for 21% of the total wet deposition for the year.
- Long-term monitoring data is critical in the assessment of trends in mercury deposition due to interannual variations in precipitation (see Figure 2-5).
- Wet deposition of mercury directly to the Bay surface area accounts for 10.5 to 16.4 lbs/yr. Estimates of dry deposition of mercury totaled 4.2 to 16.4 lbs/yr. (see Table 2-1). Total deposition from the atmosphere may be 85 to 92% of overall mercury loading directly to the Bay (Ryan *et al.* 2003). This estimate does not include the nonpoint source contribution of mercury to the Bay from runoff into rivers and streams that enter the Bay.

Table 2-1. 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

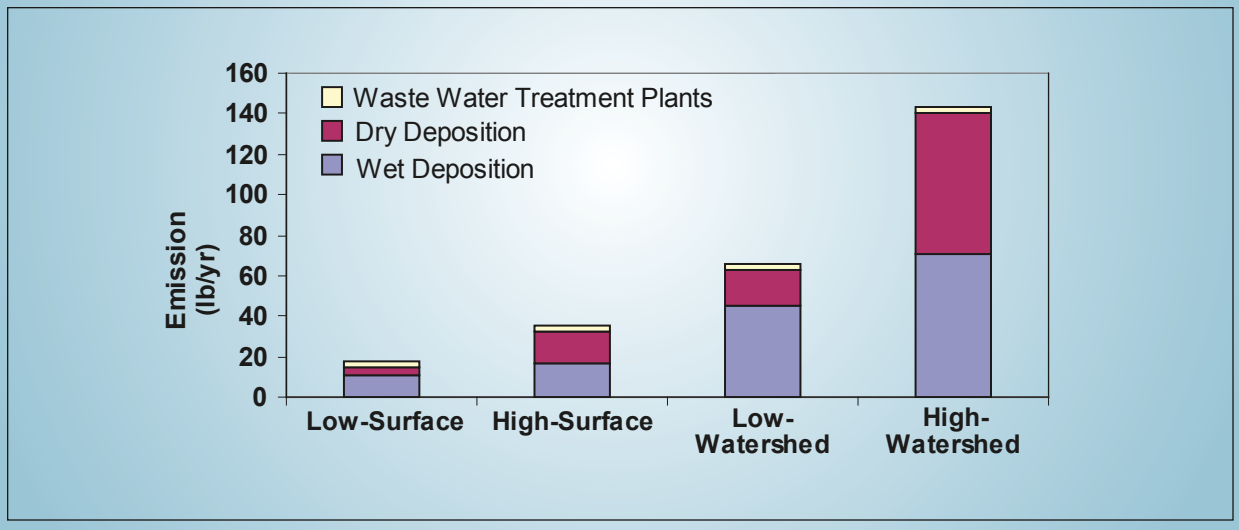

Figure 2-4. *Summary of wastewater treatment plant direct mercury discharges and dry and wet deposition of mercury to Casco Bay (in lb/yr). "Low" and "high" signify ranges in dry deposition estimates. "Surface" refers to the surface of Casco Bay while "watershed" refers to the entire watershed surface area (Ryan* et al. *2003). Low refers to the lowest estimated value, high to the highest estimated value.*

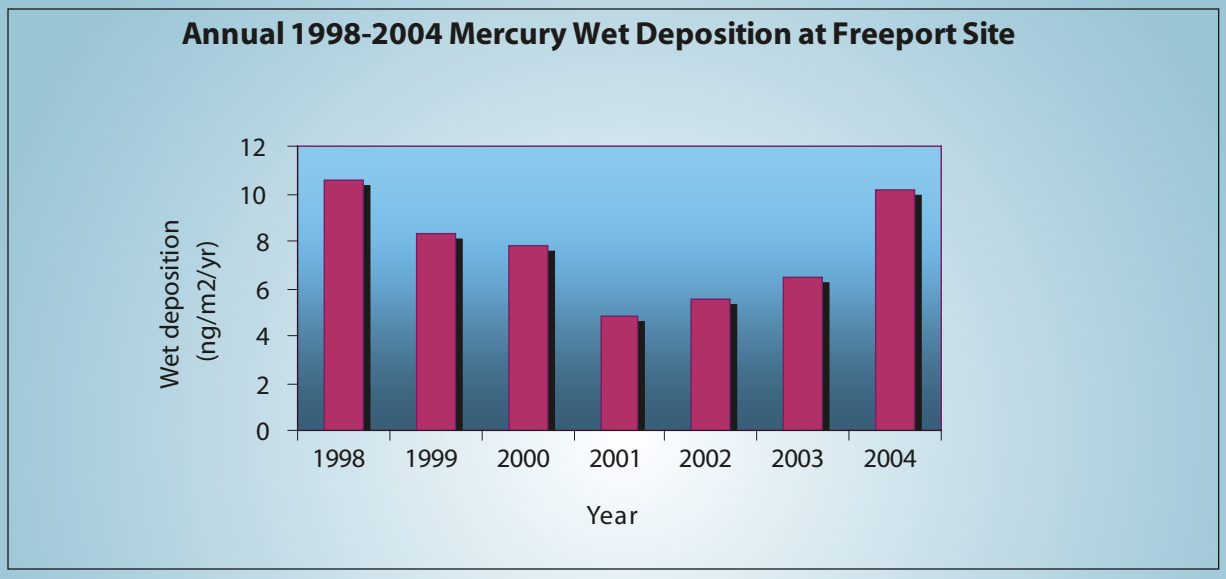

Figure 2-5. Assessing trends over time. *From 1998 to 2001, there appears to be a general trend of decreasing concentration of mercury deposited at the Freeport site. This apparent trend is the direct result of decreasing amounts of rainfall over the sampling period. In fact, the results of subsequent mercury monitoring conducted by Maine DEP in Freeport in 2002-2004 show an increasing amount of mercury deposition over that three-year period (Ryan* et al. *2003, Vanarsdale 2005). Clearly, long-term monitoring data is critical in the assessment of trends due to interannual variations in precipitation.*

Regional Mercury Air Pollution Patterns

Studying regional patterns of air pollution helps us to understand what is happening in Casco Bay. For example:

- Long-range transport of pollution in the Bay appears to be an important source of mercury. Wind trajectory analyses (studies of the movement of air masses) and source apportionment (studies that quantitatively identify the relative contributions of different source types to ambient air pollutant concentrations) indicate that polluted air masses from other regions (*e.g.,* coal-fired power plants) influence the air quality of the Casco Bay area. Local sources, such as vehicle emissions and industrial smokestacks, also likely contribute to pollution loading in the Bay.

- In many of the years sampled, the Freeport site in Casco Bay had the highest rate of mercury deposition of the four sites in Maine. Coastal sites tend to receive more rainfall, contributing to the higher rates of wet deposition of mercury at the Freeport and Acadia sites, which are on the coast (see Figure 2-6). There may also be local coastal sources of mercury contributing significantly to coastal wet deposition.

- Within Maine, annual wet deposition rates of mercury were similar to or slightly higher than those reported in nearby states (see Figure 2-7). 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 for mercury (Ryan *et al.* 2003).

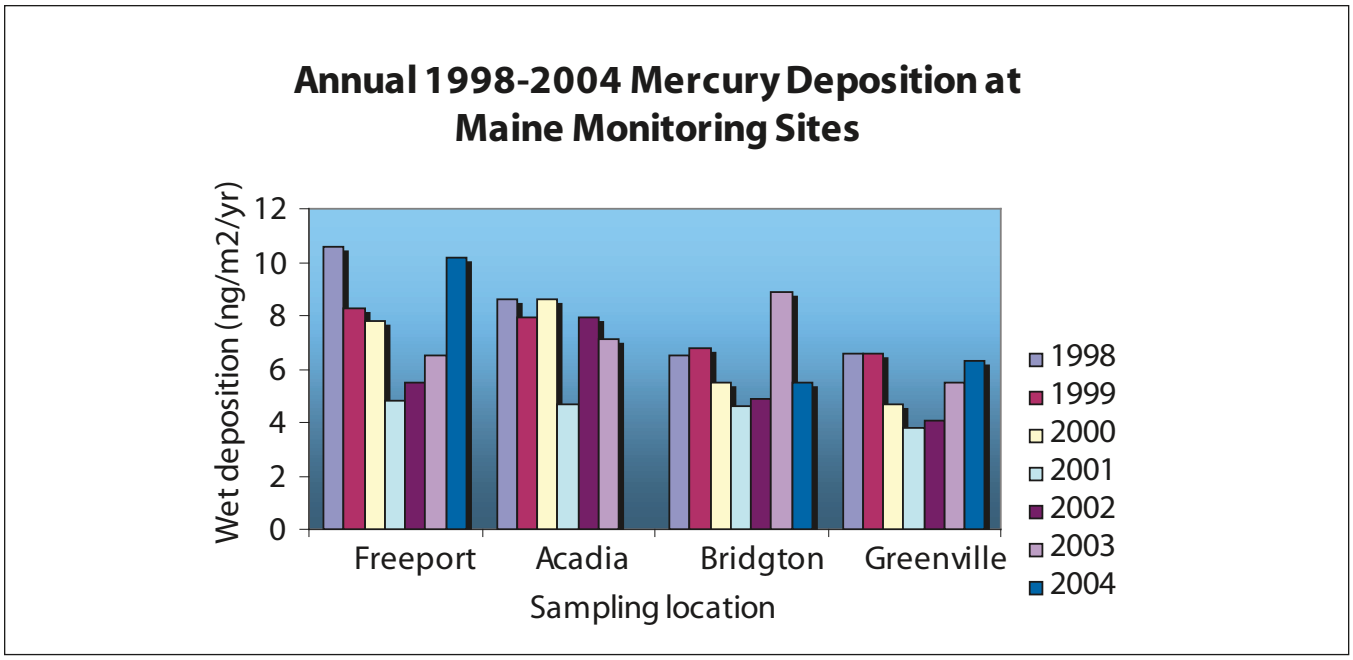

Figure 2-6. *Coastal sites tend to receive more rainfall, contributing to the higher rates of wet deposition of mercury seen at the Freeport and Acadia sites in many of the years during the sampling period.*

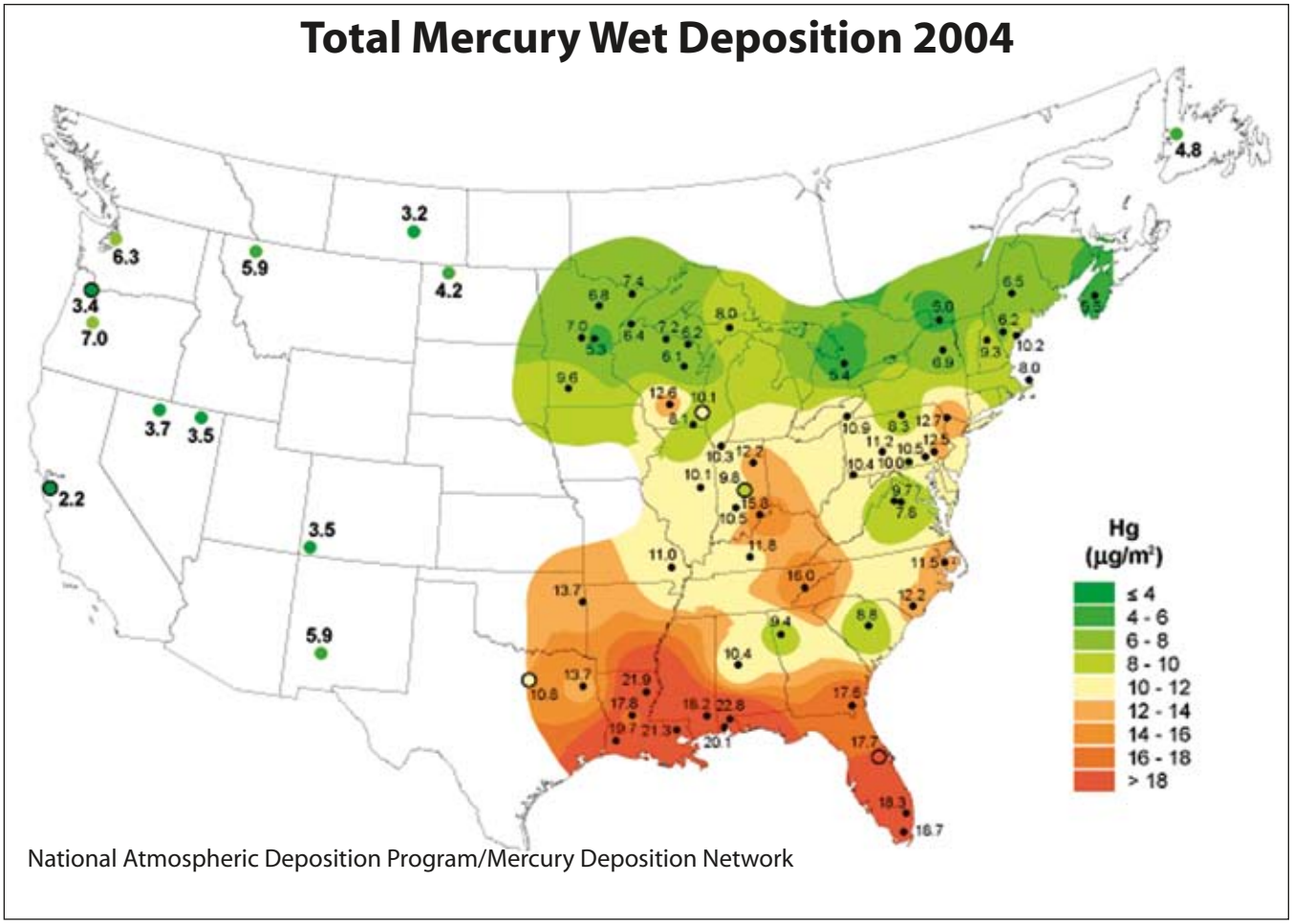

Figure 2-7. *Total Mercury Wet Deposition 2004 for Eastern USA (NADP/MDN 2006)*

Trace Metal Analysis

In 2002 a trace metal sampling train was added to the mercury (MDN) sampler at the Freeport site. With assistance from DEP and a grant from US EPA, weekly integrated wet deposition samples were collected for the trace metals selenium, arsenic, cadmium, chromium, copper, manganese, magnesium, nickel, lead and zinc. Trace metals found in wet deposition samples are useful as markers for different emission sources and can be used to verify changes in pollutant loading. For example:

- Antimony is found in flame retardants and indicates waste incineration as a source.
- Selenium/arsenic/zinc are indicators of coal combustion as a source.
- Vanadium/nickel are indicators of oil combustion as a source.
- Beryllium is an indicator of coal combustion as a source.
- Cadmium is an indicator of incineration as a source.
- Manganese is an indicator of cement/steel production as a source.

Good correlations between metals indicate similar sources or source regions. Analysis of trace metal data collected from 2003 to 2004 indicated that there was a good correlation among zinc, lead, cadmium, and chromium, and among the metals zinc, lead, arsenic and selenium. Wind trajectory analysis showed that concentrations of arsenic, selenium, mercury, cadmium, chromium and magnesium were highest when the wind was from the west. Concentrations of copper and zinc were lowest when the wind was from the south or southeast, suggesting that these metals are from different sources (Wu *et al*. 2006). CBEP is undertaking a follow up study on this and conducting further analyses of the trace metals data to help identify sources of the metals.

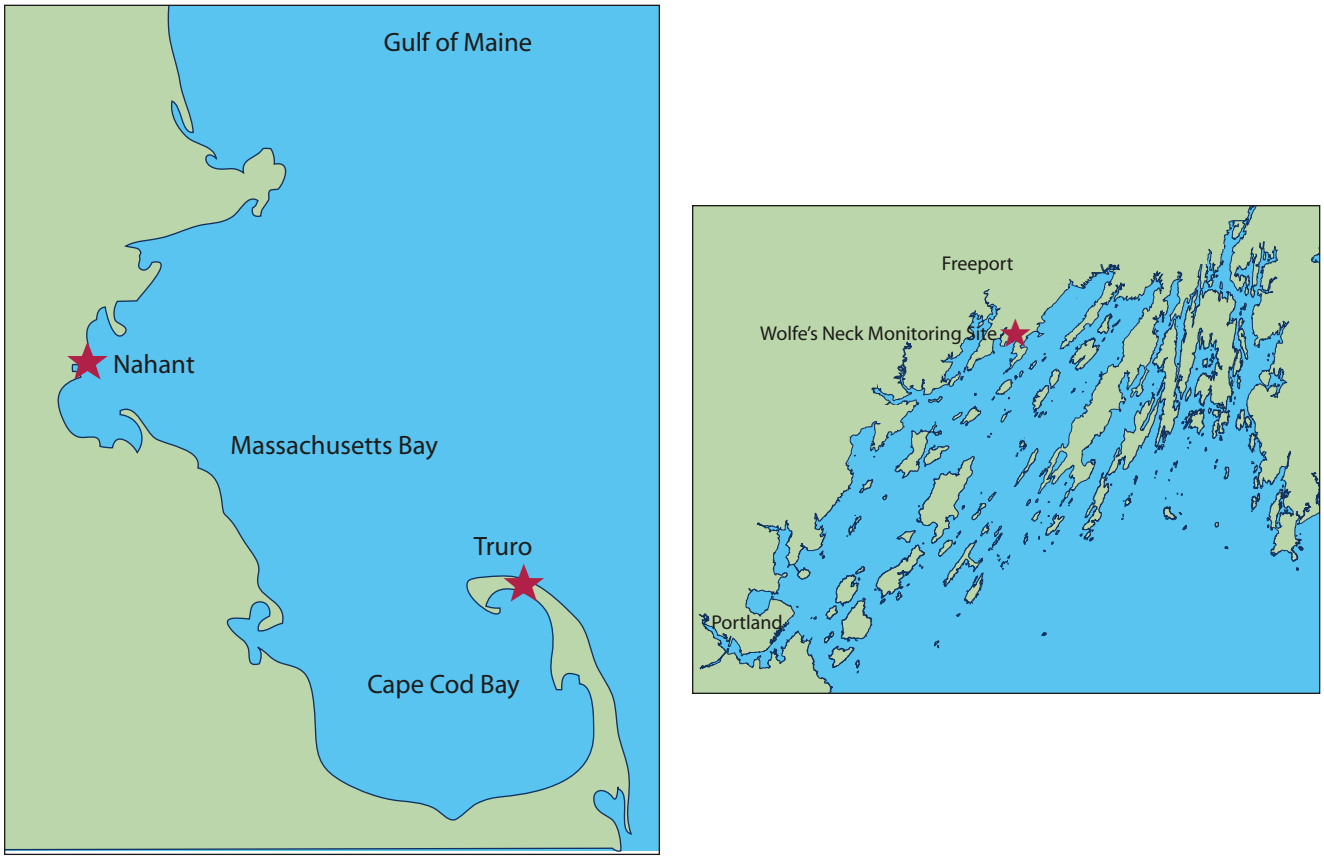

Figure 2-8. *Location of PAH monitoring sites in Massachusetts Bay and Casco Bay (Golomb 2001b).*

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs, the most common toxic pollutants found in the sediments of the Bay, enter the atmosphere primarily from the incomplete combustion of fossil fuels such as coal, oil and natural gas, and from wood burning. Airborne PAHs in the dry phase (aerosols or gases) are short-lived, surviving only tens of hours at most. Thus, in dry air, PAHs are deposited close to emission sources. When carried by raindrops and snow, PAHs can survive up to hundreds of hours and can travel thousands of miles from distant industrial sources (Mackay *et al*. 1992).

Table 2-2. PAHs measured in the Golomb et al. 2001b study

Acenaphthelene
Fluorene
Phenanthrene
Anthracene
Fluoroanthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoroanthene
Benzo(k)fluoroanthene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-c,d)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene
Coronene

In 1998, CBEP funded a study of the wet and dry atmospheric contribution of 16 types of PAHs (see Table 2-2). The research was conducted at Wolfe's Neck in Freeport by Dr. Dan Golomb and associates from the University of Massachusetts/Lowell. Between March 1998 and February 2000, 41 dry deposition and 32 wet deposition samples were collected at the Wolfe Neck, Freeport site. The monitoring study estimated that the annual wet deposition of the 16 measured PAHs was 91 $\mu g/m^2$/yr. The Freeport data were compared to data from monitoring stations at Nahant and Truro on Massachusetts Bay (see Figure 2-8). The lower estimated wet deposition of 78.5 $\mu g/m^2$/yr at Nahant suggests that upper air trajectories and precipitating clouds carry somewhat more wet deposition to Freeport (Golomb *et al*. 2001a). The dominant species of PAHs reaching Freeport via wet deposition were phenanthrene (32.3%), fluorene (14.2%) and fluoranthene (9.1%). The composition of species reaching the Nahant site was quite similar, suggesting that the origin of the PAHs arriving at these two sites via wet deposition is similar (Golomb *et al*. 2001b).

Major sources of dry atmospheric deposition of PAHs are jet exhaust, gasoline fueled vehicles, diesel fueled vehicles, wood combustion and others in that order (Golomb *et al*. 2001b). Dry deposition varies from week to week, with greater deposition during the heating season. The estimated dry deposition at Freeport was 81.5 $\mu g/m^2$/yr, far less than the 832 $\mu g/m^2$/yr measured in Nahant. This suggests that dry deposition is due to local emission sources, which are far fewer and more distant around Wolfe's Neck than around Nahant, which is located about 10 kilometers from Logan International Airport, close to Boston and several industrial suburbs. Wolfe's Neck is about 30 km from the metropolitan Portland area and Portland International Airport, and there are no industrial suburbs in the vicinity of the monitoring site (Golomb *et al.* 2001b). The dominant PAH species deposited via dry deposition in Freeport were fluoroanthene (22%), pyrene (17.9%), benzo (b and k) fluoroanthene (11.5%) and acenaphthylene (11.5%). The dominant species deposited in Nahant were benzo (b and k) fluoroanthene (14.1%), fluoranthene (13.8 %), phenanthrene (12.7%), anthracene (11.5%), and pyrene (10.4%). These differences further support the idea that different local sources are involved (Golomb *et al*. 2001b).

Using the results of the weekly wet and dry deposition sampling in Freeport, the total direct annual atmospheric input of PAHs to the surface of Casco Bay was calculated to be 64 kg PAHs/yr. While data is not available on the contribution of PAHs from other nonpoint sources, atmospheric PAHs have been estimated to represent 30-56% of total input of PAHs to the estuary (Richardson *et al*., 2003)

Summary/Conclusions

The Casco Bay atmospheric deposition studies indicate that the atmosphere is the major contributor of mercury and the likely source of 30% or more of the PAHs that enter the coastal ecosystem. Pollutants can be deposited from nearby sources or can travel from other regions of the country via wind and precipitation. Further studies will be necessary to assess the locations of the major sources contributing toxic pollutants to the Bay and its watershed via the atmosphere. See Chapter 9 for a discussion of efforts to reduce local sources of atmospheric loading of toxic chemicals.

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