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

Prepared by the Casco Bay Air Deposition Study Team*

Abstract

This paper provides a simple method for estimating the annual rate of direct atmospheric deposition of pollutants to an estuary when little or no local monitoring data is available. The approach we describe uses relevant regional data as well as literature values. The Casco Bay Estuary, located in the southwestern Maine, is used as a case study. The paper also includes the results of a field air deposition monitoring program conducted in Casco Bay (1998 - 2000) and favorably compares the estimates developed for rate of deposition of nitrogen, mercury and PAHs to the field monitoring results. The estimation approach is a useful starting point for understanding the sources of pollutants entering water bodies that cannot be accounted for through run-off or point source discharges.

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INTRODUCTION

Background

For many communities, economic and technical constraints preclude development of an atmospheric monitoring network to quantify air deposition of pollutants directly. Further, because deposition rates vary both seasonally and interannually, a field monitoring program may require several years of data collection. One of the goals of the Casco Bay air deposition project is to develop a simple, quick, and low-cost estimation approach which is applicable in other estuaries and parts of the country as well as in Casco Bay, Maine. In this paper, we propose a broadly applicable approach that uses existing information to reasonably predict the true annual rates of deposition from the atmosphere (ideally within a factor of two or three). While the focus in this paper is on selected contaminants that were of concern in the Casco Bay Estuary (cadmium, nitrogen, PAHs, and mercury) the approach can be applied to other coastal estuaries for different contaminants of concern. The chemical characteristics of the air pollutant plus the amount of available information about wet deposition rates for that pollutant will determine the appropriate steps to take for estimating wet deposition rates of each pollutant.

Casco Bay is used as a case study. The Casco Bay Estuary Project (CBEP) and other National Estuary Programs have sought to identify and quantify sources of contamination to water bodies. In 1991 CBEP conducted a study of the pollutant concentrations in the sediments of Casco Bay. Based on this study, several pollutants were found at elevated levels including cadmium, polycyclic aromatic hydrocarbons (PAHs), and mercury. The widespread distribution of pollutants throughout the sediments of the bay suggests that atmospheric deposition may play a significant role as a pollution source. In order to place atmospheric deposition in context with municipal and industrial sources of pollution, as well as runoff from nonpoint sources (such as roads, lawns, farms, golf courses, etc.), we estimated loading using available data and simple modeling techniques described in this paper. In addition, in 1998, CBEP established an atmospheric deposition monitoring station on the coast at Wolfe's Neck Farm, Freeport, Maine. We now have three years of monitoring data and can compare the direct measurements to our estimated deposition rates/loadings.

FIRST STEP: CHARACTERIZING YOUR ESTUARY

Determine Pollutants of Concern for the Estuary

Initially, it is important to determine which pollutants are of concern in an estuary. What pollutants are being contributed by point and nonpoint waterborne sources? What are the impairments/receptors of concern? Is there information about sediment or biotic contamination? Are algal blooms common? Information from other estuaries that have similar characteristics may be helpful.

Determine if Atmospheric Deposition Is a Problem

Is atmospheric deposition a significant source of pollutant loading to the estuary, or were the pollutants present delivered primarily through another mechanism (such as point source pollution)? Understanding the loading of pollutants from other sources is necessary in order to put the atmospheric contribution in perspective. The following questions provide a useful guide to see if deposition merits further investigation.

- Is there evidence of widespread contamination in either the biota or sediments, which may suggest atmospheric input?
- Is there an indication that contaminants are present at levels that are of environmental or human health concern?
- Are other inputs known, but insufficient to explain observations?
- Are point or nonpoint water-borne sources contributing only a small portion of the pollution problem?
- Is the compound in question persistent and does it bioaccumulate?
- Does the literature indicate that other estuaries or bays with similar characteristics have atmospheric deposition issues?
- Does pollutant loading seem to be affected by weather conditions such as wind direction or presence and/or frequency of precipitation?
- Are there upwind sources which might contribute to deposition, and is there an increase in certain pollutants when the wind is coming from the direction of those sources?

How Atmospheric Pollutants Enter Estuaries

Pollutants may be deposited with rain fall or fog (wet deposition) or attached to particles during dry deposition or via vapor exchange. Depending on the type of compound under consideration wet or dry deposition will predominate. According to the World Meteorological Organization (1989), flux calculations for trace metals indicate that on the whole wet deposition from the atmosphere is more important than dry deposition (i.e., 80% from wet). This generalization may not hold true everywhere (e.g., arid areas). Dry deposition in coastal areas is not studied or well understood. According to the International Joint Commission (Atmospheric Deposition to the Gulf of Maine,1994), atmospheric contributions of synthetic organic compounds via vapor exchange to oceans are large [e.g. 80% for PCBs (polychlorinated biphenyls), and 99% for certain pesticides], During vapor exchange, gaseous chemicals enter the water and soluble chemicals volatilize into the air. For nonvolatile compounds such as dioxin, the vapor exchange at the air-water surface interface is minimal.

Understand the Contributions from the Estuary and the Watershed

For any estuary, the entire watershed of the estuary is receiving a contaminant load from the air, not just the surface of the estuary itself. Pollutants deposited from the atmosphere onto the land surface within the watershed can be washed into the estuary with storm water runoff (indirect deposition). In addition, pollutants can deposit directly to water surfaces. The ratio of watershed

land surface area to estuary water surface area provides an indication of the relative importance of indirect versus direct atmospheric deposition. Land use will also affect the delivery and type of pollutants that are contributed from the watershed. For the purposes of this estimation paper, we will address estimation of "direct" deposition to the estuary.

ESTIMATING ATMOSPHERIC DEPOSITION IN YOUR LOCALE

How Much Information is Available for Your Locale?

The approach used to estimate direct atmospheric deposition to an estuary will depend upon the quantity and applicability of information available. Broadly, the types of information generally fall into one of the following categories:

1) local deposition data (e.g., collected in a nearby watershed) are available;
2) state, regional or national deposition monitoring data from which one can extrapolate/ interpolate results for an estuary are available; or
3) no relevant deposition data are unavailable and current literature values can be used to develop appropriate estimates.

These sources of regional information can be used for a variety of chemicals and should fit most situations where deposition is possibly a significant contributor to the pollution in an estuary.

One of the first steps is to assemble all relevant monitoring data (see Table 1 for possible sources). For example, look for data from CASTNET (Clean Air Status and Trends Network, NADP (National Atmospheric Deposition Network), AIRMoN (Atmospheric Integrated Monitoring Network) , IMPROVE (Interagency Monitoring of Protected Visual Environments) and other air monitoring sites from your immediate area. The NADP has more than 200 wet deposition monitoring sites throughout the country reporting data to a central system. The NADP produces color-coded maps to show ranges of data concentrations across the contiguous United States. These can be used to interpolate rough wet deposition estimates or loads for a specific location.

The Internet is a useful repository of air pollution and air deposition data. Web-sites publish air pollution data sets and are supported by federal and state agencies, universities or independent projects. Some of the sites provide access to data sets that are available for immediate downloading while other sites provide a request form and will provide data at a later date via the mail. Most of the web-sites provide some information (city, state, latitude and longitude or UTM (Universal Transverse Mercator coordinates) or maps of where the data was collected. Some web-sites, such as AIRS*Data*, also provide information about specific sources of air pollution within a geographic region. Using basic search procedures for your selected web-site, combine keywords, such as air and pollution or air + pollution, acid and (+) deposition, etc. The web-sites below provide air pollution or deposition data:

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

Approach 1. Deposition data from nearby locations are available

There may be a moderate amount of deposition data available from nearby locations to estimate deposition rates to your estuary. By contacting your state environmental agency, your regional UNITED STATES ENVIRONMENTAL PROTECTION AGENCY or the National Park Service you may find that there are nearby monitoring sites established as part of NADP (National Atmospheric Deposition Program), MDN (Mercury Deposition Network) or IMPROVE (Interagency Monitoring of Protected Visual Environments) national networks. (See internet table above for web addresses.) .

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

If your assessment of available data indicates that there are no monitoring data collected nearby, but there is state, regional or national information available from which you can extrapolate and/or interpolate, this approach can be used. For example, if mercury is your pollutant of concern, apply EPA's Mercury Study to obtain estimates for mercury deposition. The Mercury Study Report to Congress (December 1997) provides estimates of wet deposition for the country. Although these estimates are for areas typically of a larger scale, they can provide an initial estimate of mercury wet deposition to a water body. The Northeast states refined the Mercury Study Report to Congress, in the "Northeast States and Eastern Canadian Provinces Mercury Study: A Framework for Action" (February 1998). The report modeled a mercury wet deposition rate based on current emissions inventory and actual emission levels where they were available. The wet deposition estimates from this study were used to calculate local deposition rates within 40 km^2 parcels.

The national mercury wet deposition network (known as MDN) is being expanded. This network, begun in 1996, is now collecting mercury wet deposition data around the country. This network will provide information on a similar scale to the NADP. Once this network is established and a baseline of data is collected, there may be monitoring data available from nearby locations and Approach 1 (described above) may be used to estimate wet deposition by interpolating between the areas of similar wet deposition levels and using a hi-split model to estimate the levels of wet deposition. Dry deposition is not part of this deposition network, but it is potentially a significant portion of the overall deposition to an estuary. Since regional monitoring data are not available, the literature search approach described below is advisable to estimate dry deposition.

Other examples of applying this extrapolation approach could include the use of existing monitoring data (e.g. CASTNET, NADP, IMPROVE, etc) that was collected in a nearby state, but not in an area representative of your estuary.

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

It may be possible to quantify potential ranges of atmospheric deposition for pollutants of interest by reviewing the current literature and applying data from other areas. While environmental managers often require more certainty than these estimates can provide, this approach can indicate what type of additional data is needed to refine the estimate. If deposition rates (wet and dry) cannot be found in the literature, concentration data may be available.

The equations given below have been used to estimate atmospheric deposition rates (metric units are usually used to calculate deposition rates). They should be used along with literature values that are specific for the contaminants of interest.

Estimating Atmospheric Deposition Rate Using Literature Values

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)

Annual Loading

For all of the approaches described above, once annual deposition rate has been estimated, simply multiply the annual deposition rate by the surface area of your estuary to determine annual loading

APPLIED CASE STUDY USING CASCO BAY

Characterizing the Estuary

Overview
The Casco Bay Watershed encompasses a 2550 square kilometer drainage area located in southwestern Maine. It includes 44 towns and is drained by 12 river and lake systems. The estuarine area itself covers 518 square kilometers (see Figure 1).

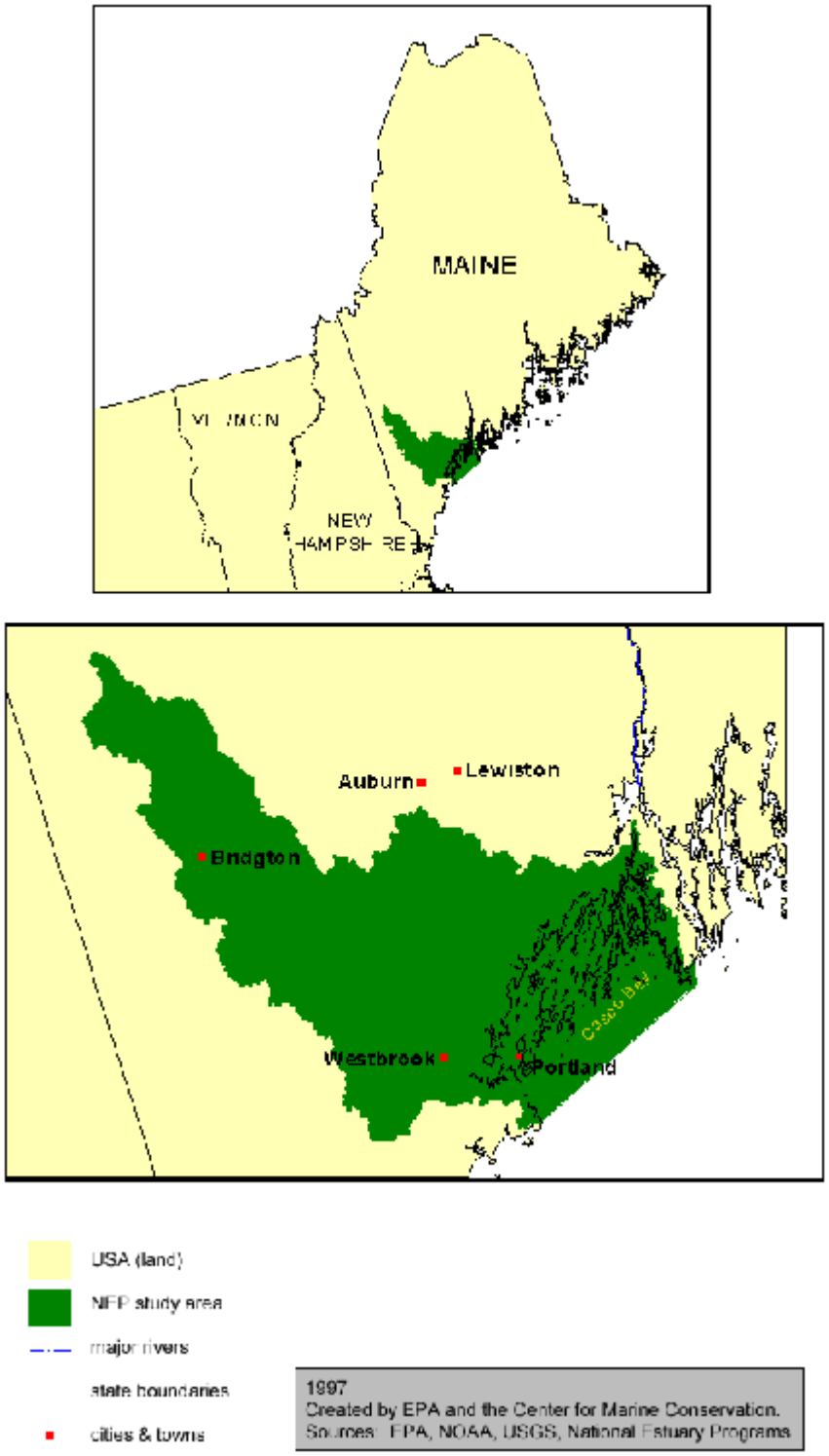


Figure 1. Casco Bay Watershed

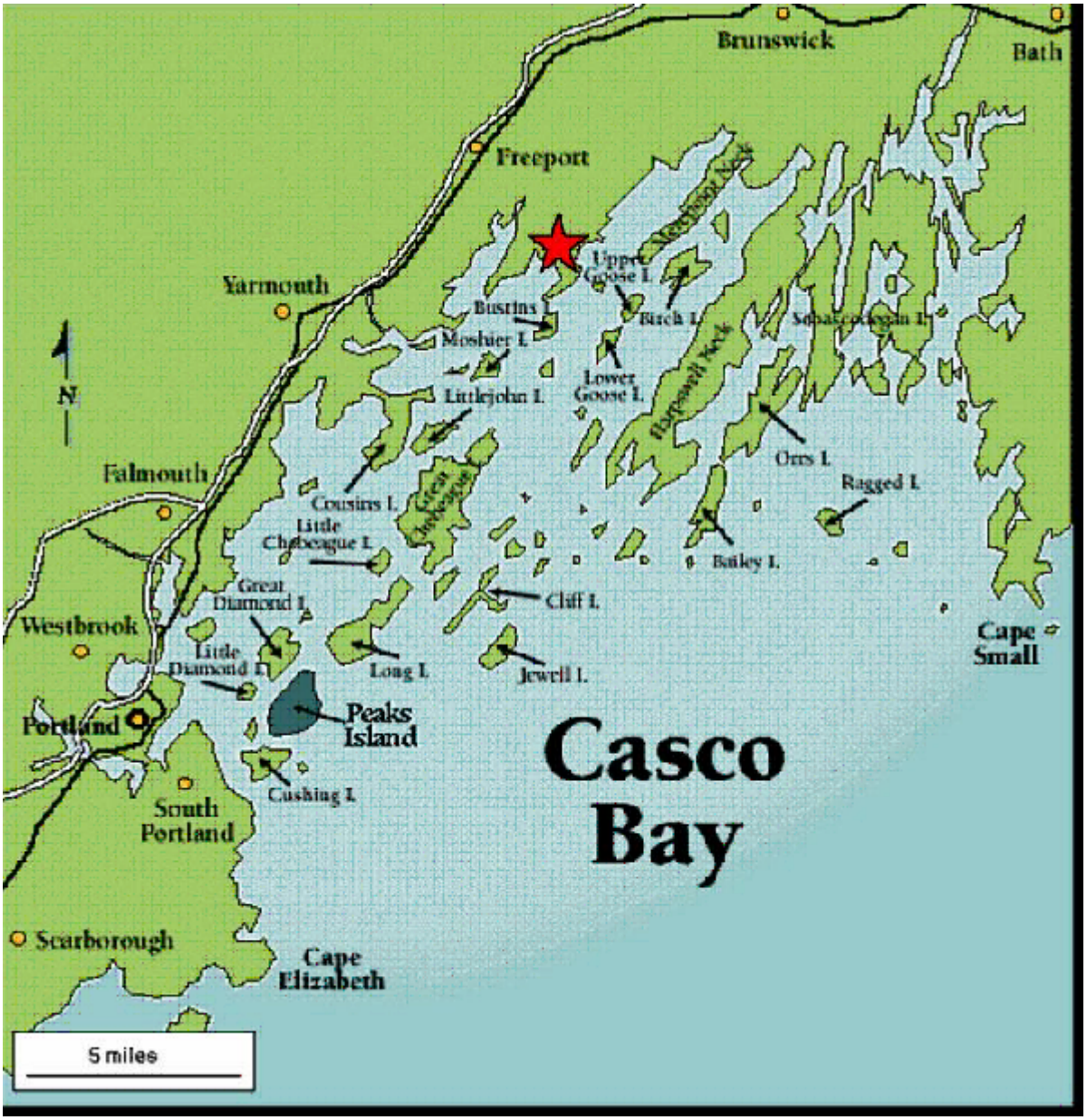


Figure 2. Project air monitoring station at Wolfe's Neck Farm in Freeport, Maine.

Wolfe's Neck, Freeport, Maine, which the CBEP has selected as a representative coastal site for the collection of monitoring data, is a peninsula separated from the mainland by the estuary of the Harraseeket River. See Figure 2. The Harraseeket watershed (part of the coastal sub watershed of the bay) has been identified by the Maine Department of Environmental Protection as a priority area for protection from nonpoint source pollution. Upstream, (e.g., Frost Gully Stream) urban runoff has been noted as a source of low dissolved oxygen levels and degraded aquatic habitat (Maine DEP, 2000).

The Freeport area has experienced rapid growth. For example, between 1970 and 1990 the lower Casco Bay watershed, which includes the Freeport area, increased by 50,000 people and 70,000 cars. An additional 9% population increase was projected for the year 2000 (CBEP, 1996).

Contaminants of Concern

Research done in the early 1980's on the sediments of Casco Bay indicated that high levels of toxic contaminants were accumulating, the result of historic and contemporary sources of point and nonpoint source pollution, including petroleum products, agriculture, and industrial sources that dated to mid-1800. An analysis of the historic sources of contamination to the Bay documented that the Portland area waterfront of the past was even more heavily industrialized than it is today. PAHs from coal gas works and later PAHs and PCBs from electrical power production were released to the water directly and through runoff, and to the air via smokestacks (Hawes, 1993).

Today there are 17 major and 24 minor licensed wastewater point source discharges in the Casco Bay watershed, including the Freeport Publically Owned Treatment Works. These licensed discharges contribute a variety of pollutants, including PAHs, heavy metals, chlorine, bacteria, nitrogen and phosphorous. Air emissions in Maine are also licensed and are likely contributors of PAHs, dioxins, pesticides, heavy metals and nitrogen oxides (Nox). (See Figures 3 and 4). The City of Portland (26 km southwest of Wolfe's Neck) and the Portland International Airport (35 km from Wolfe's Neck) are local emission sources, with prevailing winds generally W/NW in winter, S/SE in summer. Note that measuring local emissions doesn't provide the whole picture (it doesn't tell us anything about toxicity) but it is an important component. It also doesn't provide information about transport of chemicals from outside of the region. The East Coast of the United States and industrial sources in western Pennsylvania and Ohio are also sources of deposition (e.g., nitrogen and mercury) onto the waters of Casco Bay (CBEP, 1996).

A detailed analysis of contaminants accumulated in marine sediments can help to determine the potential sources of contaminants entering the marine environment. In 1991, the Casco Bay Estuary Project funded a comprehensive inventory and statistical analysis of contaminants within the surficial coastal sediments of the Bay. Undisturbed sediment samples were collected and analyzed for trace metals, aliphatic and polycyclic aromatic hydrocarbons (PAHs),

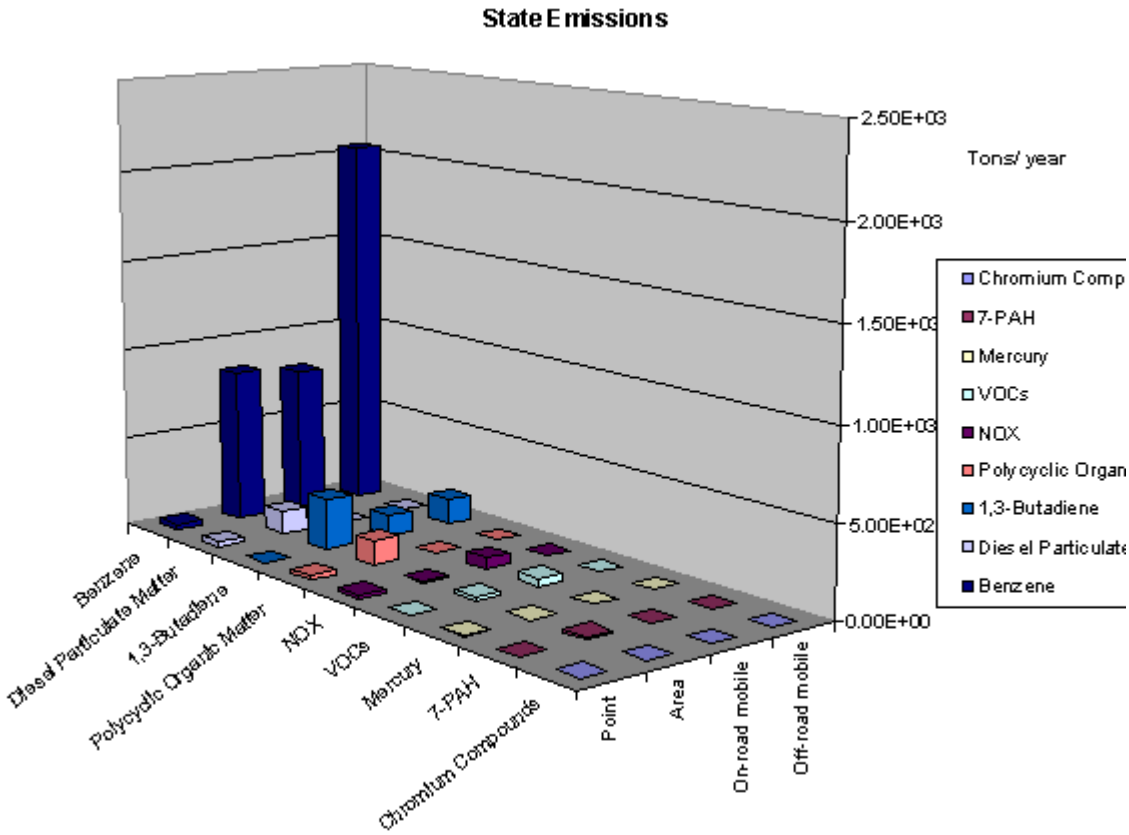


Figure 3. Air emissions contribution of toxics in tons/year by source for Maine. Data for this graph came from the 1996 National Air Toxics Assessment: **http://www.epa.gov/ttn/atw/nata/nsata1.html** and from additional data on VOCs (volatile organic compounds) and mercury collected by Maine Department of Environmental Protection in 1999. In Figures 2 and 3, Polycyclic Organic Matter (POM) refers to a set of 16 PAH compounds formed primarily from combustion and present in the atmosphere in particulate form. Of those 16, 7 are carcinogenic to humans. These 7-PAHs are Benz[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Chrysene, Dibenz[a,h]anthracene, and Indeno[1,2,3-cd]pyrene. Nox refers to nitrogen oxides. Major "point" sources are defined by the Clean Air Act as those stationary facilities that emit or have the potential to emit 10 tons of any one toxic air pollutant or 25 tons of more than one toxic air pollutant per year. "Area" sources include facilities that have air toxics emissions below this major source threshold, such as dry cleaners. On-road mobile sources include cars, trucks, buses etc. found on roads. Off-road mobile includes, for example, airplanes, trains, lawn mowers, construction vehicles and farm machinery. Other emissions sources are diverse and include forest and wildfires, agricultural burning, residential wood burning, and hazardous waste sites (personal communication, David Wright, Maine DEP).

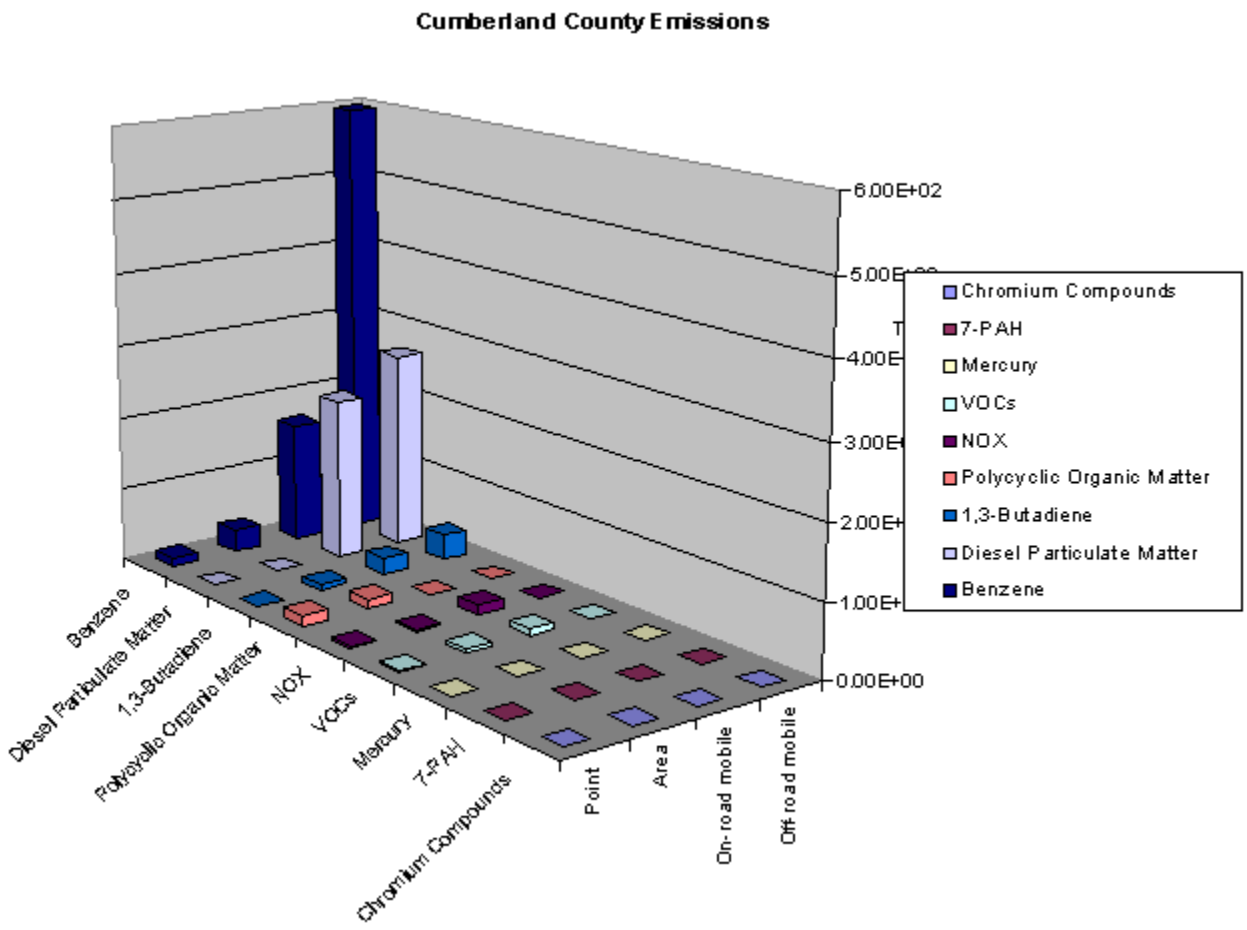


Figure 4. Air emissions contribution of toxics in tons/year by source for Cumberland County. Cumberland County includes most of the Casco Bay watershed. Data for this graph came from the 1996 National Air Toxics Assessment: **http://www.epa.gov/ttn/atw/nata/nsata1.html** and from additional data on VOCs (volatile organic compounds) and mercury collected by Maine Department of Environmental Protection in 1999. (See Figure 3 legend for further explanation of this graph).

pesticides and PCBs (polychlorinated biphenyls). The location of the sampling stations was intended to include representative benthic (sediment-dwelling) communities, provide good areal coverage, and include sediments of varying ages and textures (Kennicutt, et. al., 1994). For the purpose of the study, the Bay was divided into five zones: Inner Bay (which includes the densely populated Portland area), the West Bay, which includes the Wolfe's Neck area of Freeport, the East Bay, Cape Small and the Outer Bay. (See Figure 5).

Aliphatic hydrocarbons and PAHs were detected at all sampling stations. The PAHs were predominantly highly condensed ring structures with few alkylations, indicating a pyrogenic or combustion source. Total concentrations of PAHs ranged from 16 to 20,778 ppb. Contaminants tended to decrease in concentration with distance from densely populated areas in the Inner Bay. Levels in the Inner Bay, which includes the Portland and Fore River area, were considered high on a national basis and comparable to other contaminated estuaries. They were above the PAH concentrations considered toxic to marine benthic organisms ($\geq$ 35,000 ppb). There were also regionally elevated sites in East Bay and Cape Small. PCBs and pesticides were also present in highest concentrations in the Inner Bay, although, even in the Inner Bay, they were not considered high on a national basis (Kennicutt et. al., 1992, 1994) .

While the trace metal data demonstrated some geographic variability, generally the highest average values were in the Inner Bay, with elevated levels of Cd, Pb, Ag, Zn, and Hg attributable to human activities. The average concentrations of metals, however, were not considered high on a national basis (Kennicutt et.al., 1994).

Contaminants were detected at all of the sampling locations. The results indicated that the sediment sites in the Outer and East Bay exhibited a predominantly biogenic (natural) contaminant influence from detrital and autochthonous sources. Sites in the lower East Bay contained a greater contaminant component originating from combustion of fossil fuels. The inner Bay and shallow water sites near the City of Portland were characterized by inputs of weathered petroleum, probably resulting from chronic inputs from runoff and point sources. The weathering process results from physical and biological processes such as evaporation and microbial breakdown. In general, the more exposed to the elements petroleum is, the more rapidly it weathers. The contaminant composition of sediments from Cape Small, far from urbanized sources, was similar to that of the Inner Bay. Sites in the West Bay (the portion of the Bay directly west of the Freeport air deposition sampling site) show a relative enrichment of C_{10}-C_{22} *n*-alkanes suggesting a localized source of contamination, perhaps fresh diesel fuel (Kennicutt, et al., 1994).

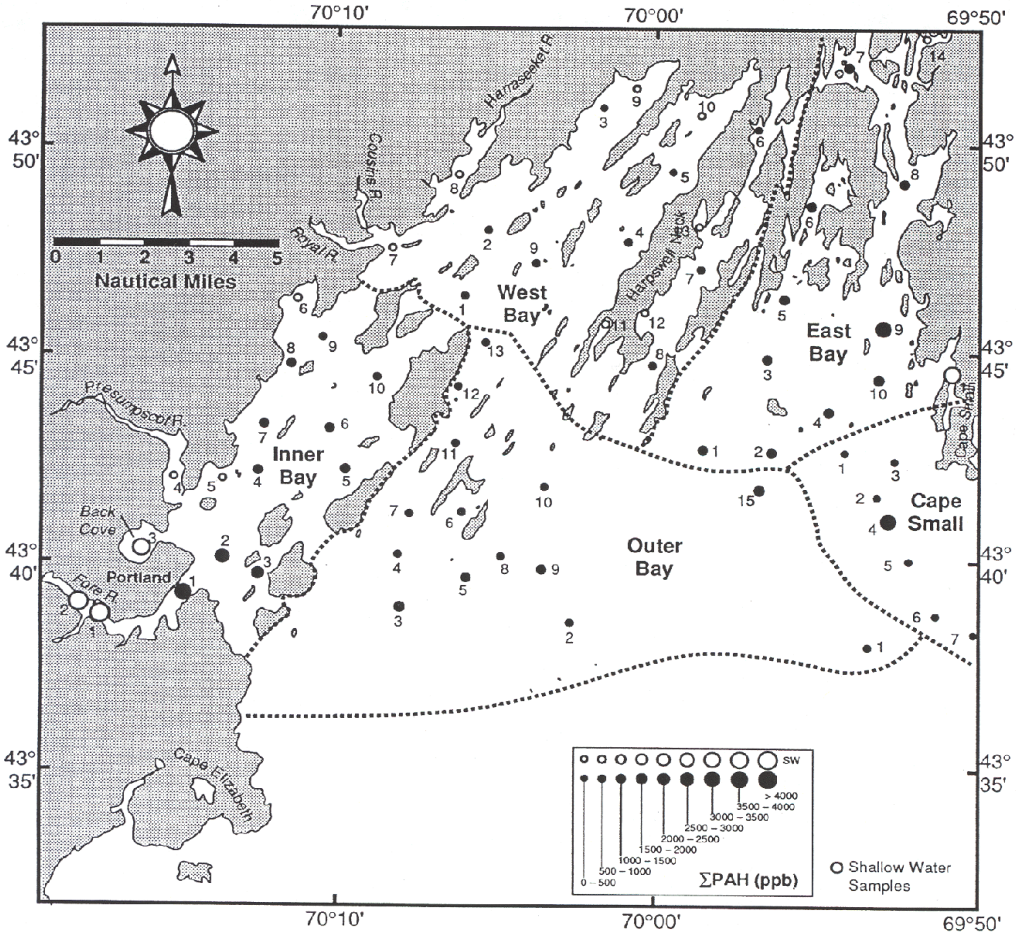


Figure 5. Regional distribution of PAH concentrations (ppb dry weight, surrogate corrected) in sediments from Casco Bay (Kennicutt et al., 1992)

The widespread distribution of contaminants at elevated concentrations in the Bay, including in areas that are not located near any historical sources of waterborne point or nonpoint source pollution, suggests that atmospheric deposition has played a significant role in the accumulation of metals and PAHs in the sediments. Point and non-point waterborne sources appear to control the characteristic regional contaminant profiles displayed by the sediments in the five sampling regions (Kennicutt, et al., 1994).

Climatology of Casco Bay

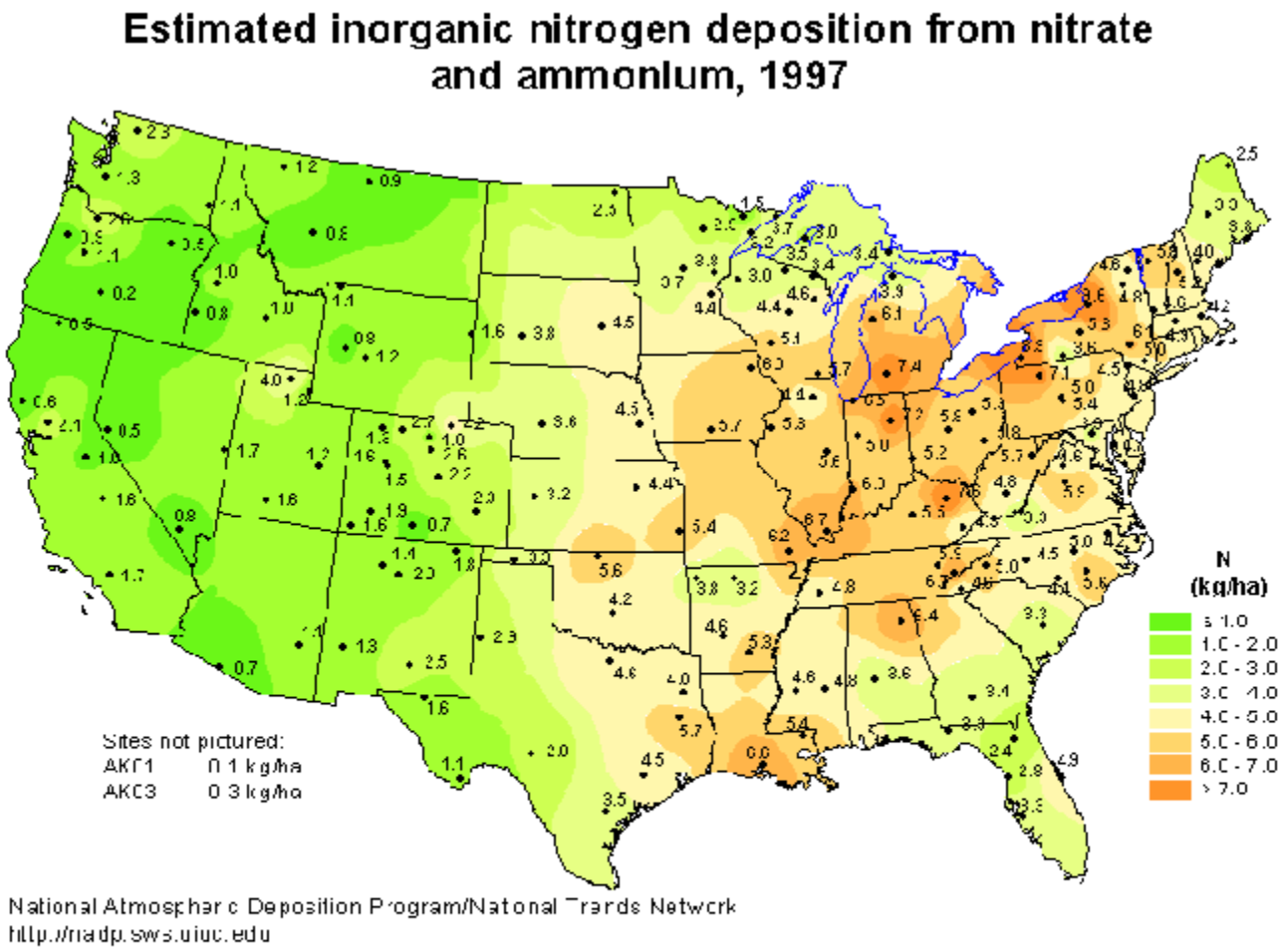
The Casco Bay area is located in a temperate zone. The yearly maximum daily temperature average is 12.8°C . The yearly minimum daily average is 2.2°C. July has the hottest maximum daily average of 26.1°C and January has the lowest daily minimum average of -11.4°C. In any given year one may expect five days where the temperature rises above 32.2°C and twenty- three days when the temperature drops below -15°C. The average yearly precipitation in water equivalent is about 111.8 centimeters. There are about 129 days with some form of precipitation in any given year and 101 clear ones. The region experiences fog and a range of precipitation extremes. Fog events have lasted up to 14 consecutive days (June 1998) and ice storms (January 1998) have caused considerable damage. Precipitation events can drop significant amounts of rain/snow in a short period of time. In March of 2001, 41.9 cm of snow fell in one 24 hour period and over 102.87 cm of snow fell in 4 separate storms during the month. In October of 1996 over cm of rain fell in one 24-hour period with a total of 36.88 cm of rain for the entire 2-day event.

Climate and meteorological information available from the National Weather Service (NWS) is helping us to identify sources that would have impacts on Casco Bay. The NWS provides seasonal wind speed and direction data along with seasonal precipitation data. This information, used with mathematical meteorological models like READY (National Oceanic and Atmospheric Administration) provides some sense of where the pollution originated. The READY model uses meteorological data to "back track" air or calculate where it traveled and potentially picked up more pollution.

Applying Local Deposition Data to Estimate Nitrogen Deposition to Casco Bay

To estimate nitrogen deposition to Casco Bay, we applied Approach 1, using data available from the NADP program on their web site at: http://nadp.sws.uiuc.edu/<http://nadp.sws.uiuc.edu/ . Data from across the country, including several sites in Maine, is summarized in yearly isopleth maps. The 1997 maps were used to estimate wet nitrate and ammonium deposition for Casco Bay as: nitrate (NO3) deposition - 13 kg/hectare and ammonium (NH4) deposition - 1.6 kg/hectare. Converted to elemental nitrogen, the combined total N deposition from nitrate and ammonium is 4.1 kg/ha. (See Figure 6). Converted to annual loading rate, direct wet deposition is estimated to introduce 212,380 kg of N to Casco Bay.

Figure 6.



Dry deposition of inorganic

nitrogen species is not well defined. Also, dissolved and particulate organic nitrogen are also not well understood, and some researchers believe that dissolved organic nitrogen deposition contributions may be significant.

No mass balance studies have been done in the Casco Bay region which would help us determine what percentage contribution of the total nitrogen is from the atmosphere. However, studies in the Chesapeake Bay area indicate that 25% of the nitrogen to the Bay is from nitrate deposition, which comes primarily from nitrogen oxide emissions from high temperature combustion (e.g., utilities, manufacturing ,and transportation). As reported by Eisenreich, et al., 1998, mass balances done by Nixon et al., 1996 and Prospero et al., 1996 indicate that atmospheric deposition is approximately 20% of the total nitrogen loading to the North Atlantic continental shelf, of which Casco Bay is a part. We also looked at estimations that had been developed for Long Island Sound, Narragansett Bay, Rhode Island and Waquoit Bay in Massachusetts. The percent loading from the atmosphere for Waquoit Bay is about 29% based on atmospheric deposition of nitrogen loads from the watershed only, excluding direct nitrogen deposition to the bay surface. Narragansett Bay, has a lower contribution from the atmosphere of about 4%, but only nitrogen that is directly deposited on to the bay was used in this estimate. The estimate for Long Island Sound is about 20% of nitrogen is from atmospheric deposition. This estimate includes deposition to the watershed and directly to the bay. ("Deposition of Air Pollutants to the Great Waters, Third Report to Congress, June 2000)

Extrapolating from Monitoring Data Collected at a Larger Scale to estimate Mercury Deposition to Casco Bay

Here, we applied Approach 2. For the northeast, there is a report available about mercury deposition in New England and Eastern Canada. This information is on a larger scale than the Casco Bay Estuary, but it does provide an estimated range of deposition. The document, "Northeast States and Eastern Canadian Provinces Mercury Study: A Framework for Action" (February 1998), provides an estimated range of wet depositional rates applicable for Casco Bay (10 ug/m^2 to 30 ug/m^2). No mass balance has been done for mercury in Casco Bay but values developed for Lake Michigan suggest that atmospheric deposition of mercury contributes 10-85% of the total loading.

Using Literature Values to Estimate Cadmium Deposition Rate to Casco Bay

In many areas the atmospheric input of trace elements exceeds those from direct water discharges (Duce, 1991, as reported by Eisenreich et al, 1998). Cadmium is released to the air from metal mining and smelting operations, pigments and pigment manufacturing, and from fuel and waste combustion. Coal-fired utilities contribute small amounts of cadmium. It is present in the atmosphere as fine particulates. According to EPA, approximately 66% of total air releases in the US are due to fuel combustion. It is typically present as cadmium oxide (some as salts) and does not undergo significant chemical transformation in the atmosphere.

Fine particulate cadmium may be transported as much as several thousand kilometers before eventual dry or wet deposition. Localized deposition of large particulate cadmium can occur

near large sources (e.g., smelters). Deposition near these sources of large particulate cadmium is approximately ten times greater than in other areas.

No Maine or even New England data is available for cadmium deposition in Casco Bay. We looked to the literature (Approach 3) to determine what estimates have been made for other parts of the country. In the Chesapeake Bay and at Lewes, Delaware, wet deposition dominates the total atmospheric flux for trace elements, including cadmium (Baker et al., 1993). However, atmospheric fluxes may be dominated by dry deposition of larger particles immediately downwind of significant sources (Eisenreich et al, 1998). Using literature values of 0.03 - 0.1 ug/liter for the cadmium concentration in precipitation, Eisenreich et al developed wet deposition estimates of 40 to 130 $ug/m^{2*-year}$ for Chesapeake Bay and Lewes, Delaware.

Since cadmium does not exist in the vapor phase in the atmosphere, dry deposition calculations do not need to account for the differences in vapor and aerosol fractions. Similarly, vapor exchange at the air/water surface is not important. Literature values for atmospheric concentrations of cadmium associated with aerosols range from 0.1 to 1.0 ng/m^3; these values were obtained from the Great Lakes, Chesapeake Bay, and the Mid-Atlantic Bight. Using these values, Eisenreich et al 1998 developed dry deposition estimates of 10 to 34 ng/m^{2-year}. He applied these estimates to the New Jersey area.

While the estimated cadmium ranges indicated above were developed for areas other than New England, they can be used as first estimates for Casco Bay Estuary and other estuaries areas where little or no local data are available.

Applying Literature Values to Calculate Rate of PAH Deposition to Casco Bay

According to EPA (EPA 1994, Keeler 1993), approximately 9400 metric tons of PAHs are emitted annually into the atmosphere in the eastern U.S., of which 31% is due to residential wood combustion, and 29% is due to industry. Stationary fuel combustion, transportation, and other sources (e.g. incineration) account for 17, 12 and 11% respectively.

To estimate PAH deposition to Casco Bay, we used literature estimates of the concentration of the pollutant in precipitation or ambient air taken from Eisenreich, et. al., 1998 (using the boxed equations in the discussion of Approach 3). The results are given in Table 2 below (adapted from a similar table developed for New Jersey in Eisenreich, et. al., 1998). The ranges reflect the differing literature values provided for rural and urban environments.

To estimate wet deposition of PAHs, a precipitation rate of 100 cm/yr was used (National Weather Service, Portland, Maine First Order Weather Station). For dry deposition, the deposition velocity for particles was assumed to be 0.2 cm/sec in rural areas, and 1 cm/sec in urban areas, although the particle dry deposition velocities have been observed to be as much as 4 or 5 cm/sec in urban areas (Eisenreich 1998). While Maine is largely rural, Casco Bay is adjacent to Maine's most heavily suburban/urbanized areas, therefore both urban and rural values were calculated.

Here is an sample calculation for wet deposition of phenanthrene:

PCp = .003 - .150 ug/1000 cm^3 (Eisenreich, et. al., 1998)
PR = 100 cm/yr
Pcp x PR = Annual Wet Deposition (mass/m^2/yr) = 3 - 150 ug/m^2/yr

The low numbers in the ranges in Table 2 reflect rural environments, high numbers reflect urban environments. PAH species highlighted in bold have been monitored as part of the Casco Bay atmospheric deposition program; other species are given because they are commonly found in the literature.

Table 2: ESTIMATED WET AND DRY ATMOSPHERIC DEPOSITION IN SOUTHERN MAINE

Polynuclear Aromatic Hydrocarbons (PAHs) Species	Wet Deposition ug/m^2 year	Dry Deposition ug/m^2 yearr
Acenaphthylene	0.5 – 10	0.03 – 10
Acenaphthene	0.5 – 10	0.1 – 15
Fluorene	1 –10	0.5 – 60
Phenanthrene	3 – 150	3 – 400
Anthracene	0.3 – 15	0.1 – 50
Fluoranthene	3 – 125	3 – 600
Pyrene	3 – 125	3 – 400
Benz(a)anthracene	0.4 – 20	2 – 500
Chrysene/Triphenylene	2 – 50	2 – 700
Benzo(b+k)fluoranthene	2.5 – 50	3 – 1000
Benzo(e)pyrene	1 – 20	1 – 400
Benzo(a)pyrene	1 – 20	1 – 400
Indeno(c,d)pyrene	1 – 20	1 – 400
Dibenz(a,h)anthracene	0.5 – 10	0.3 – 100

(**Naphthalene** and **Perylene, Biphenyl, Dibenzothiophene** were monitored as PAHs by Casco Bay. Several works do not include these chemicals as PAHs).

Note: Ranges reflect differences between rural and urban environments; low numbers reflect rural environment, high numbers reflect urban environment. PAH species highlighted in bold have been sampled as part of the Casco Bay Deposition Program (Golomb et al. , 2001); other species are given because they are commonly found in the literature.

Adapted from: Atmospheric Deposition Assessment – New Jersey; S.J. Eisenreich, et al. Rutgers University 1998.

Table 2 indicates that wet deposition is approximately 50% of the total atmospheric deposition for the dominant PAHs measured in rural areas. In urban areas, dry deposition generally dominates atmospheric flux of PAHs. For example, Golomb (2001a), noted that in monitoring samples taken in Nahant, Massachusetts near a busy urban airport, dry deposition of PAHs (832 ug/m^2/year) was far more significant than wet deposition (78.5 ug/m^2/year).

The total loading of PAHs from all sources to Casco Bay is unknown. However, numerous studies in the Great Lakes and Chesapeake Bay show that the atmosphere is a dominant source (30-50%) of products of incomplete combustion, of which PAHs are a component. It is highly likely, then, that the atmosphere is a significant source of PAHs to the Bay and a contributor to the polluted sediments of the Bay.

Casco Bay Atmospheric Deposition Loading Rate Summary

Table 3 (below) summarizes the Casco Bay Estuary estimates developed in this case study.

Table 3: Summary of Casco Bay Case Study Estimates

Pollutant	**Estimated Atmospheric Input/Year**	**Estimation Approach (Based on amount of information available)**	**Estimated Percent of Total Pollutant Input to the Estuary (see Note below)**
Nitrate (wet) Ammonium (wet) Total Inorganic Nitrogen (as N)	13 kg/hectare (1997) = 1.3 g/m^2 1.6 kg/hectare (1997) = .16 g/m^2 .41 g/m^2	1	20%*
Mercury (wet)	10 - 30 ug/m^2	2	10-85%**
Cadmium (wet) (dry)	40 - 130 ng/m^2 10 - 34 ug/m^2	3	<5%***
PAH Total (wet) (dry) Species (e.g.) Phenanthrene (wet) (dry)	 20 - 635 ug/m^2 20 - 5035 ug/m^2 3 - 150 ug/m^2 3 - 400 ug/m^2	3	30 - 56%***

Note: Total loading of N, Hg, Cd and PAHs to Casco Bay is unknown. The figures given indicate ranges of atmospheric contribution seen in other US waters as estimated in the U.S. Environmental Protection Agency: Deposition of Air Pollutants to the Great Waters. Third Report to Congress. 2000
* Based on estimates for various Great Waters in the US (US EPA 2000)
**Based on estimates for Michigan (US EPA 2000)
*** Based on estimates for Chesapeake Bay (US EPA 2000)

Casco Bay Atmospheric Deposition Monitoring Program

In 2003, the Casco Bay Estuary Project completed an analysis of three years (1998 - 2001) of atmospheric deposition monitoring data collected at a coastal site in Freeport, Maine (and other inland sites in the Casco Bay watershed). The results of this monitoring effort has enabled us to determine how successfully our estimates compare to actual field data. The Freeport monitoring site included NADP, MDN and IMPROVE samplers, as well as a wet and dry PAH collection monitoring system. We now have field measurements of wet deposition of nitrate, ammonia and mercury, as well as wet and dry deposition of PAHs. The reports *Deposition of Air Pollutants to Casco Bay*, by P. Ryan, H. Main and S. Brown, Casco Bay Estuary Project, 2003 and *Atmospheric Deposition of Polycyclic Aromatic Hydrocarbons near New England Coastal Waters* by D. Golomb, E. Barry, et al., *Atmospheric Environment*, 35:36, 2001, are being made available on the Casco Bay website *http://www.cascobay.usm.maine.edu/*. In March, 2003 we began collection of cadmium in precipitation and hope to compare those results to our cadmium estimates in the future.

The results of our monitoring program are summarized and compared to our estimated deposition numbers in Table 4. Estimated values for mercury and nitrogen deposition closely match values derived from the field monitoring data. The values for PAHs measured at the Freeport site are also a reasonable match for the lower range of estimates for PAH deposition rate. Since the community of Freeport has no significant local sources of PAHs other than motor vehicles, it is expected that the field measurements for dry PAH deposition would reflect the largely rural character of the surrounding area. Clearly, the estimates developed from literature and regional monitoring data provide a reasonable estimation of the rates developed using the much more costly and time-consuming field monitoring approach.

Table 4

Casco Bay Case Study Estimates Compared to Field Monitoring Data

Pollutant	**Estimated Atmospheric Input/Year**	**Casco Bay Monitoring Data 1998 - 2001 Average Direct Input/Year**
Nitrate (wet)	13 kg/hectare (1997) = 1.3 g/m^2	9.9 kg/hectare = .99 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	.33 g/m^2*
Mercury (wet)	10 - 30 ug/m^2	8.7 ug/m^2*
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, 2003)
**Based on the 16 PAH species monitored by Golomb, D., E. F. Barry, Jr., et al. (2001b)

CONCLUSIONS

Resources, tools and strategies for pollution abatement must be effectively targeted at priority sources if our estuaries are to be protected. Understanding the sources and annual loading of contaminants to an estuary guides good water quality management by defining the range of controls of both air and water pollution needed to achieve a desired result. The cost of conducting monitoring to determine atmospheric loading to a water body can be prohibitively high. Also, collection of monitoring data is a long-term undertaking, since a minimum of three years of data is advisable in order to "smooth out" interannual variability. The estimation techniques described in this paper can serve as a useful and inexpensive "first-cut" at understanding the importance of the atmospheric as a pollution source, and can help to pinpoint those areas where field measurements are needed to guide future management decisions.

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ADDITIONAL WEB RESOURCES

Air Quality & Emissions Trends
http://www.epa.gov/ne/topics/air/aqemissions.html

Dioxin
http://www.epa.gov/ne/topics/pollutants/dioxin.html

Maine Department of Environmental Protection homepage
http://www.state.me.us/dep/index.htm

DEP Mercury Site
http://www.state.me.us/dep/mercury/

DEP Air Toxics and HAPs site - address may change with overhaul
http://www.state.me.us/dep/air/emissions/atidefault.htm

Mercury
http://www.epa.gov/ne/topics/pollutants/mercury.html

National Air Toxics Assessment 1996
http://www.epa.gov/ttn/atw/nata/nsata1.html

New England Estuaries: Including Casco Bay
http://www.epa.gov/ne/topics/ecosystems/estuaries.html

New England Rivers - Watersheds
http://www.epa.gov/ne/topics/water/watersheds.html

Nonpoint sources of pollution
http://www.epa.gov/ne/topics/water/npsources.html

NOx
http://www.epa.gov/ne/eco/airqual/nox.html