

Report to the

MASSACHUSETTS BAYS PROGRAM

**ATMOSPHERIC DEPOSITION OF TOXIC METALS,
POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) AND
NITROGEN ONTO MASSACHUSETTS BAYS**

(Parts One and Two)

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Polynuclear Aromatic Hydrocarbons (PAH) and
Nitrogen onto Massachusetts Bays**

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FOREWORD

The roots of the Massachusetts Bays Program extend back to 1982, when the City of Quincy filed suit against the Metropolitan District Commission and the Boston Water and Sewer Commission over the chronic pollution of Boston Harbor, Quincy Bay, and adjacent waters. Outdated and poorly maintained sewage treatment plants on Deer Island and Nut Island were being overwhelmed daily by sewage from the forty-three communities in the Metropolitan Boston area. Untreated and partially treated sewage were spilling into Boston Harbor.

Litigation over the pollution of Boston Harbor culminated in 1985 when the United States Attorney filed suit on behalf of the Environmental Protection Agency against the Commonwealth of Massachusetts for violations of the Federal Clean Water Act. The settlement of this suit resulted, in 1988, in the creation of the Massachusetts Water Resources Authority, the agency currently overseeing a multi-billion dollar project to repair and upgrade Metropolitan Boston's sewage treatment system. In addition, the settlement resulted in the establishment of the Massachusetts Environmental Trust - an environmental philanthropy dedicated to improving the Commonwealth's coastal and marine resources. \$2 million in settlement proceeds were administered by the Trust to support projects dedicated to the restoration and protection of Boston Harbor and Massachusetts Bay.

The Trust provided \$1.6 million to establish the Massachusetts Bays Program, a collaborative effort of public officials, civic organizations, business leaders, and environmental groups to work towards improved coastal water quality. The funding was used to support both a program of public education and a scientific research program focusing on the sources, fate, transport and effects of contaminants in the Massachusetts and Cape Cod Bays ecosystem. To maximize the efficiency of limited research funding, the sponsored research program was developed in coordination with research funded by the MWRA, the United States Geological Survey, and the Massachusetts Institute of Technology Sea Grant Program.

In April, 1990, following a formal process of nomination, the Massachusetts Bays Program became part of the National Estuary Program. The additional funding provided as part of this joint program of the Environmental Protection Agency and the Commonwealth of Massachusetts is being used to continue a coordinated program of research in the Massachusetts Bays ecosystem, as well as supporting the development of a comprehensive conservation and management plan for the coastal and marine resources of Massachusetts and Cape Cod Bays. This report is the first study to determine the atmospheric deposition of selected metals, polynuclear aromatic hydrocarbons and nitrogen to the surface waters of Massachusetts and Cape Cod Bays. While collection methodologies for wet and dry deposition are continuously evolving and improving, the data in this report represents a first attempt to quantify deposition of contaminants to the Bays ecosystem, using methods available at the time of the study. As methodologies are improved in the future, the accuracy of the deposition values will also improve. In the meantime, the information in this report will serve as baseline information and provide scientists and managers a sense of the magnitude and range of atmospheric deposition onto Massachusetts and Cape Cod Bays. This information is helping to meet the Massachusetts Bays Program goal of producing an area-wide management plan for water quality enhancement and protection.

The information in this document has been subject to Massachusetts Bays Program peer and administrative review and has been accepted for publication as a Massachusetts Bays Program document. The contents of this document do not necessarily reflect the views and policies of the Management Conference.

PART ONE

**ATMOSPHERIC DEPOSITION OF TOXIC METALS:
POLYNUCLEAR AROMATIC HYDROCARBONS ONTO
MASSACHUSETTS AND CAPE COD BAYS.**

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EXECUTIVE SUMMARY

Wet and dry atmospheric deposition of toxic metals and PolyAromatic Hydrocarbons (PAHs) was measured continuously over one year, from 15 September 1992 to 16 September 1993 at two coastal sites on Massachusetts and Cape Cod Bays (MCCB). One site was located in Nahant, at the tip of a peninsula jutting out 5 km into Massachusetts Bay, about 16 km NE from downtown Boston and 12 km NE from Logan International Airport. This site was chosen to be representative of atmospheric deposition received by the northern reaches of MCCB. The second site was located in Truro, 15 km from the tip of Cape Cod. This site was chosen to be representative of the southern reaches of MCCB. Wet deposition was measured by analyzing the species in precipitation collected in the wet bucket of an Aerochem-Metrics wet/dry collector. Dry deposition was measured by two methods: (1) analyzing the species in a volume of ultrapure water kept in the "dry" bucket, and (2) analyzing the species on the filters of a dichotomous particle collector ("dichot"), and multiplying the concentrations by literature values of dry deposition velocities. Two wet/dry collectors were used at each site, one made of plastics for metals; the other made of aluminum for organics. Only one dichotomous particle collector was deployed in Nahant. This site had also a complete meteorological station, measuring surface winds, temperature, pressure, humidity and precipitation. For Truro, meteorological data was obtained from the National Park Service weather station in Wellfleet, Cape Cod, 5 km away from the monitoring site. Upper air data was obtained from the National Weather Service stations in Chatham, Cape Cod, Portland, ME and Albany, NY.

The sampling period was two weeks. Thus, 26 samples were obtained each from the wet, dry and particle collectors. Alternate biweekly dichot samples were analyzed for metals and organics, respectively. The sampling periods nearly coincided, except for some commuting delays. Only two samples were lost during the year, one due to a severe winter storm, one due to a hurricane that overturned the wet/dry collector. The wet and "dry" samples were filtered, and the buckets rinsed with acid. This yielded three analyzable fractions: soluble (filtrate), insoluble (filtered) and wall desorbed fraction. The dichot yielded two size fractions, particles in the 0-2.5 μm size range (fine), and 2.5-10 μm size range (coarse). The insoluble (filtered) fraction and the particles collected on the dichot filters were analyzed by Instrumental Neutron Activation Analysis (INAA). The soluble and acid desorbed fractions were analyzed by Inducted Coupled Plasma-Mass Spectrometry (ICPMS). The samples from the "organics" wet/dry collector and the dichot were shipped to Texas A&M University for analysis of PAHs and PCBs by Gas Chromatography-Mass Spectrometry (GC-MS).

Atmospheric Deposition of Metals. For most metals, dry deposition was greater at Nahant than at Truro. This is probably due to the proximity of Nahant to the metropolitan Boston area and Logan Airport. Emission sources are fugitive dust, power plants, industrial, incinerator, residential and commercial boilers and furnaces, automobiles, trucks, aircraft and ships. On the other hand, wet deposition for most metals was greater at Truro than at Nahant. Wet deposition is the result of washout and rainout. Washout is the process of scavenging ("scrubbing") of gases and particles by falling hydrometeors. Rainout is the result of incorporating into cloud droplets of gases and particles, or indeed, cloud droplets forming on particle condensation nuclei. Clouds reaching the two sites may have traversed different geographic regions. At Nahant, westerly air masses prevailed, that is clouds which may have traveled over rural areas of Massachusetts, southern New Hampshire and Vermont, upstate New York and beyond. At Truro, southwesterly air masses had a stronger component.

Clouds reaching Truro may have traveled over the heavily industrialized and urban corridor stretching over Rhode Island, Connecticut, New York City, New Jersey and beyond. These clouds may have carried a heavier load of pollutants than those reaching Nahant.

Taking the arithmetic average of Nahant and Truro depositions as representative of average deposition rates for MCCB, and multiplying by the MCCB area of 3700 km², the following total (wet + dry) deposition rates were obtained for selected toxic metals in units of metric tonnes per year per MCCB area: Al, 377; As, 0.5, Cd 1.5; Cr, 10; Mn, 16.3; Ni, 22.2; Pb, 10; Se, 1; and Zn, 29.

For most metals the measured deposition rates fall within the range estimated by Menzie-Cura (1991). For Pb the measured rates are lower, and for Cr higher than estimated by Menzie-Cura. In the case of Pb this is certainly due to the fact that leaded gasoline was phased out since the data was taken that Menzie-Cura used for their estimates.

Atmospheric Deposition of PAHs. With a few exceptions deposition of individual PAH species was much greater at Nahant than at Truro, both in the dry and wet form. The exceptions are naphthalenes and biphenyl, for which wet depositions at Truro were greater than those at Nahant. Nahant dry deposition of all PAHs was greater than wet deposition. These observations are consistent with the properties of PAHs. They are hydrophobic, hence they are relatively insoluble in precipitation, and most of the deposition occurs in the dry mode. PAHs are relatively short-lived in the atmosphere (less than 24 hours). Thus, PAHs are expected to be deposited closer to the emission sources. PAHs are the products of incomplete combustion in boilers, furnaces, biomass (e.g. wood) burning, internal combustion engines (gasoline and diesel) and aircraft jet engines. The proximity of the metropolitan Boston urban-industrial sprawl apparently results in higher deposition of PAHs at Nahant than at Truro. Furthermore, Logan International Airport is only about 12 km from Nahant along the prevailing wind direction. Most likely the emissions from jet aircraft takeoffs and landings contribute to dry deposition of PAH gases and particles at Nahant. At Nahant the major contributors to dry deposition were fluoranthene (13%), phenanthrene (9.3%) and pyrene (9.3%); and to wet deposition fluoranthene (9%), phenanthrene (8.5%) and pyrene (5.9%). At Truro, the major contributors to dry deposition were phenanthrene (8.3%), fluoranthene (8.1%) and pyrene (5.6%); and to wet deposition phenanthrene (5%), benzo(ghi)perylene (4.1%), and C2-fluorenes (3.1%). This listing does not include naphthalene and its substitutes. Naphthalene and its substitutes contributed as much as 58.2% of the wet deposition at Truro and 25.7% at Nahant. This is probably due to the relatively high solubility in water of naphthalene.

Taking the arithmetic average of the two sites and multiplying by the area of MCCB, the total (wet + dry) deposition of PAHs onto the Bays area was 2400 kg yr⁻¹. This is twice as much as the "high" estimate of Menzie-Cura (1991), 1260 kg yr⁻¹. (The "low" estimate was 953 kg yr⁻¹.) Menzie-Cura also estimated the loading of MCCB from non-atmospheric sources, i.e. point discharges, run-off, combined sewer overflow, groundwater and riverine discharges. The range was 1390 - 10700 kg yr⁻¹. Accordingly, atmospheric deposition may contribute from 22% to 172% of the total loading of PAHs.

Dry deposition of PAHs was highest at Nahant and Truro in winter. This could be due to the greater use in winter of fossil fuel (oil and gas) for residential and commercial space heating and wood burning in stoves and fireplaces.

Several samples were analyzed for PolyChlorinated Biphenyls (PCBs). None were found above the detection limit of the analytical procedure.

1.0 INTRODUCTION

Coastal waters, especially semiconfined bays, sounds and estuaries, receive their loadings of toxic pollutants from four sources: point discharges from sewers (treated and untreated), rivers and streams, precipitation and irrigation runoff, and atmospheric deposition. Research has shown the atmospheric pathway to be an important, and in some cases, the dominant means of transport and deposition of toxic pollutants to these waters (Steinnes, 1990; Nguyen *et al.*, 1990; Duce *et al.*, 1991; Ondov *et al.*, 1992; Rojas and VanGrieken, 1993; Struyf and VanGrieken, 1993; Harrison *et al.*, 1993; U.S. EPA, 1993; Sweet and Basu, 1994; Hoff and Brice, 1994; Pirrone and Keeler, 1994; Lim *et al.*, 1994; Scudlark *et al.*, 1994; Leister and Baker, 1994; Dickhut and Gustafson, 1995). Subsequent bioaccumulation of some of these contaminants in fish and shellfish can lead to their morbidity and mortality, as well as being hazardous to human health (Massachusetts Bays Program, 1995).

Atmospheric deposition of aerosols and gases occurs in two phases: wet and dry. In the wet phase, aerosols and gases are deposited by precipitation: rain, snow, hail, fog and mist. Dry deposition occurs by direct impingement of aerosols and gaseous molecules on land or water. To obtain total atmospheric loading, it is necessary to measure both phases. While the measurement of wet deposition is relatively straightforward, the measurement of dry deposition is more problematic. In direct measurement of dry deposition usually an artificial surface is used that simulates as closely as possible the natural surface onto which dry deposition is occurring. The dry deposited material is extracted from the artificial surface for chemical analysis. In indirect methods air concentrations of the pollutants are measured, and the concentrations are multiplied by measured or literature values of deposition velocities (NAPAP, 1990).

In this work, both methods were utilized. For direct measurement a layer of ultrapure water in a bucket served as a surrogate water surface. From the layer of water dry deposited material was extracted and analyzed for contaminants. A similar method of dry deposition measurement onto a surrogate water surface was used by Crecelius *et al.* (1991), and Gardner and Hewitt (1993). For the indirect measurement aerosols were collected on a filter by a particle collector. The air concentrations of contaminants were multiplied by literature values of deposition velocities to derive dry deposition rates. Wet and dry deposition measurements were rendered for a full year in 1992/93 at two sites around Massachusetts Bay.

2.0 EXPERIMENTAL

2.1 Site Description

Massachusetts and Cape Cod Bays (MCCB) are shown in Figure 1. The waters of MCCB occupy the area between Cape Ann, 42°40'N, 70°35'W and the tip of Cape Cod, 42°05'N, 70°15'W. The area is approximately 3700 km². The western shore of MCCB encompasses the urban-industrial sprawl from Gloucester through metropolitan Boston to Plymouth, with an estimated population of 3 million. The southern and southeastern parts of the Bays are encircled by Cape Cod. Cape Cod has

a year round population of approximately 200,000. During the summer season this population swells four to five-fold, with considerable vehicular traffic. Cape Cod has no heavy industry, one oil-fired power plant (584 MW) and an Air Force base. In terms of atmospheric deposition, the Bays could also be affected by distant emission sources in the northeastern USA and southeastern Canada. These sources could be hundreds to thousands of kilometers away. Their contribution to MCCB deposition depends on the atmospheric lifetime of the contaminants, and the wind and cloud trajectories that bring them to MCCB.

To monitor atmospheric deposition two sites were selected on the shores of MCCB: Nahant and Truro. Nahant is located at the tip of a narrow peninsula jutting out about 5 km into MCCB, approximately 16 km NE from downtown Boston, and 12 km NE from Logan International Airport. The monitoring station is located at Northeastern University's Marine Science Center on a rocky, thinly overgrown promontory, about 100 m from the nearest beach and about 30 m above sea level. Other than the small settlement of Nahant, about 1 km away, and a heating plant for the Marine Science Center, there are no local point sources of pollutant emissions. The site was chosen to be representative of atmospheric deposition received by the northern reaches of MCCB. The Truro site is located about 1 km from the Nantucket Sound (outer) shore of Cape Cod, about 5 km from MCCB's (inner) shore, 15 km SE from the tip of the Cape and a few meters above sea level in a clearing of oak and pine woods. The equipment is co-located with the National Acid Deposition Program (NADP) monitoring station at Truro. There are no immediate local sources of pollution. Because of the forested area between the site and the coasts, the site is not directly exposed to sea spray. The Truro site was chosen to be representative of atmospheric deposition received by the southern reaches of MCCB.

2.2 Equipment Description

Aerochem-Metrics, Inc., Model 301 wet/dry collectors were used to collect wet and dry deposition samples (Figure 2). Two collectors were operated at each site, one for "metals," the other for "organics." This type of collector has two buckets with a shuttling lid. Normally the dry bucket is open. During precipitation (rain or snow) an electrical conductivity sensor detects precipitation and activates a motor that shuttles a lid from the wet bucket to the dry bucket. When precipitation ceases, the lid shuttles from the dry to the wet bucket, i.e. the dry bucket is open. The buckets of one collector are made of high density polyethylene for the collection of metals; the buckets of the second collector are made of aluminum for the collection of organics. The shuttling lid for the metal collector is covered with a sheet of polyethylene; the lid for the organics with aluminum foil. The "dry" bucket is filled with two to four liters of deionized water to simulate the dry deposition onto a water surface. To prevent excessive evaporation during the summer, and freezing during the winter, the dry bucket is surrounded with a bath of thermostated "antifreeze" (VWR Scientific Model 1150 constant temperature circulator) set to keep the water temperature in the bucket within 2°C of the surface temperature of the adjacent water body. The bucket's open area is 0.064 m². The collectors are powered by 110 V AC, with a 12 Volt automotive battery providing power in the event of power loss. A trickle charger ensures a fully charged battery. After each biweekly sampling period, the buckets are sealed with a plastic lid (for metals) or aluminum foil (for organics) and shipped to the laboratory for analysis.

At Nahant, an Anderson-Sierra, Inc Model 245 automatic PM-10 dichotomous particle collector ("dichot") was deployed. The dichot segregates particles into two size ranges: 0-2.5 μm and 2.5-10 μm . Each size fraction is collected on a separate filter. Teflon membrane filters (37 mm diameter, 2 μm pore size) reinforced with a polyolefin ring were used for organics. A similar Teflon filter with a polypropylene backing was used for metals. The filter membranes are inserted into polypropylene filter holders to hold the filters in place within the sampler. All filters, filter holders, and storage petri dishes were thoroughly acid cleaned in 10% nitric acid solution. A sensor built into the sampler adjusts the pressure drop across the filters to maintain a constant air flow of approximately 15 L min^{-1} over the fine and 1.7 L min^{-1} over the coarse filter. If the filters become clogged with particles, and the sampler cannot maintain a constant air flow through the filters, the sampler automatically advances to a clean set of filters and then continues sampling. A study by John and Wang (1991) documented performance anomalies for the Anderson-Sierra dichot. These anomalies resulted from non-uniform airflow within the sampler. The initial particle deposits on the filters are uniform, but as the filters become more soiled, the flow geometry changes, thus affecting the sampler's efficiency. By changing filters well before they became clogged this problem was minimized. At Nahant, a Solus Corporation Model Weathernet meteorological data collection system was deployed. The system consists of a rain gauge, temperature, humidity and pressure sensors, and an anemometer. A central computer control mechanism and data logger completes the system. For the Truro site, meteorological data collected by the Cape Cod National Seashore headquarters in Wellfleet, Massachusetts, about 5 km from the monitoring site was used. This database contains several large periods of missing data. Data collected at the Chatham, Cape Cod, National Weather Service meteorological station (about 37 km away) was substituted for the missing data. Upper air meteorological data were obtained from the National Weather Service. The nearest upper air monitoring stations are in Chatham (Cape Cod), Portland (Maine) and Albany (New York) where measurements are rendered twice daily, at 00:00 and 12:00 GMT. Upper air data was retrieved from the National Weather Service Computer Network in raw condition and required manual decoding and data entry. The decoded data was broken down into periods corresponding to sample collection periods and summarized by a computer program. Because of their proximity, upper air winds for Truro were assumed to be the same as for Chatham. For Nahant, an interpolation scheme was used based on observations at Chatham, Portland and Albany.

2.3 Sampling Protocol

Monitoring started on 15 September 1992 and terminated on 16 September 1993. Wet, dry and particle samples were collected in two week intervals. The sampling periods at the two sites did not coincide exactly because of the commuting time from the university campus to the two distant sites. With the exception of two samples, all samples were collected successfully. Sampling materials for metals (buckets, flasks, filters, etc.) which came into contact with the sample medium were thoroughly acid leached (10% HNO_3) for 24 hours prior to use. The content of the buckets were vacuum-filtered under a clean hood through a polycarbonate filter membrane, 0.4 μm pore size, into a polysulfone receiving vessel. After drying, the filtered particles ("insoluble fraction") were analyzed by INAA. The filtrate was acidified with 1 μL of ultrapure nitric acid per mL of sample, transferred into HDPE bottles and stored at 4°C until analyzed by ICP-MS for dissolved metals ("soluble fraction"). Since a portion of the suspended particles may adsorb to the bucket walls, the

bucket was rinsed with 1% nitric acid, and this solution was separately analyzed by ICP-MS for desorbed elements ("wall-desorbed fraction"). The organics buckets were thoroughly washed with pesticide grade methanol followed by pesticide grade methylene chloride. Aluminum foil baked at 500°C for two hours was used to seal the buckets before and after sampling. After sample collection, the contents of the buckets were quantitatively transferred into solvent cleaned amber glass bottles (for storage and protection from light) using pesticide grade methanol and methylene chloride. A rigorous protocol for quality control was performed throughout all the analytical procedures. Blanks were analyzed with the same analytical methods as the samples themselves. This established a background level. Analytical results were checked by replicate analyses and spiking of the samples. If the results of an analysis were outside the acceptable limits a re-analysis of the sample was performed. Particle filters from the dichot were placed into petri dishes in a desiccator prior to final weighing and laboratory analysis. Weighing of the dichot filters was performed on a Cahn Model 30 microbalance. Because of the sensitive nature of microbalance measurements, temperature and relative humidity in the microbalance room were maintained constant (22°C, 50% RH). Alternate biweekly particle samples were analyzed for metals and organics, respectively.

2.4 Analytical Methods

2.4.1 INAA

Particles collected on the dichot filters and the insoluble (suspended) particles filtered from the aqueous samples were analyzed by Instrumental Neutron Activation Analysis (INAA) at the UMass Lowell Radiation Laboratory. The samples were spiked with gold and irradiated for 6 hours at a flux of $4 \times 10^{12} \text{ n cm}^{-2}$. Samples were counted twice using an automated dual detector gamma ray analysis system. The first count was done 3-5 days after irradiation to determine the gamma ray intensities for short half-life radioisotopes. The second count was done 3-6 weeks after irradiation for long half-life isotopes. Peak areas were determined using Canberra Spectra-AT computer code, and after decay, interference, and flux corrections, final values were determined by reference to an irradiation standard (US Geological Survey standard reference material SCO-1). A National Institute of Standards and Technology reference material (S.M. 1646) was included in each sample batch as a quality assurance standard. Replicate analyses of the standard indicate a precision (1σ) and accuracy of better than 5% for Fe, 10% for Cr, 8% for Co, 10% for As and 19% for Zn. The minimum detection limit for elements varies from a few nanograms for Se to 100-200 nanograms for Cd and Zn. INAA gives the mass of each analyte in nanograms. After subtraction of the mass found in a blank sample, the residual mass was divided by the bucket open area and the time of the collection period. This gives the deposition rate of the insoluble metal in units of $\text{ng m}^{-2} \text{ t}^{-1}$. The mass of metals found on the dichot filters was divided by the volume of air drawn through the filters. This gives the airborne concentration in units of ng m^{-3} . Multiplying by a deposition velocity, the deposition rate is obtained in $\text{ng m}^{-2} \text{ t}^{-1}$.

2.4.2 ICP-MS

The soluble and wall-desorbed metals were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). These analyses were performed on a Perkin-Elmer Sciex Elan Model 5000

instrument at the Harvard University School of Public Health. The instrument was operated according to the manufacturer's recommended specifications for instrumental parameters and sample matrix modification. Samples were analyzed for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. ICP-MS gives concentrations of the analytes in units of ng L^{-1} . After subtracting the concentration in a blank sample, the residual concentration was multiplied by the volume (L) of the filtrate, divided by the bucket open area, and the time of the collection period. This gives deposition rates of the analyte in units of $\text{ng m}^{-2} \text{t}^{-1}$.

2.4.3 *Mercury Analysis*

During the fall 1993, the wet/dry collector at Nahant was used to measure mercury concentration in rain. Six weekly samples were collected. Because of the relatively high volatility of mercury, special precautions were taken. A collection bottle and funnel were placed into the "wet" bucket and surrounded by bags of water for support and thermal insulation. Airflow around the sample was restricted. The bottle and funnel were only open for sampling during precipitation episodes. A preservative was added prior to the collection of precipitation, consisting of a 26 mL solution of 2.5% potassium chromate and 25% nitric acid in deionized water. After collection, samples were immediately shipped for mercury analysis to the University of Minnesota-Duluth. Mercury concentrations were determined by Cold Vapor Atomic Absorption Spectrometry (CVAA) (Glass *et al.*, 1990; and Sorensen *et al.*, 1990). The minimum detection limit for this procedure was 2 ng L^{-1} of Hg for an average sample size of 150 mL.

2.4.4 *PAH and PCB Analysis*

The contents of the "organics" buckets were transferred to amber glass flasks and shipped to Texas A&M University for analysis of PAHs and PCBs by Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography- Electron Capture Detection (GC-ECD), respectively. The detailed procedure for extracting organics from a water sample is described in GERG (1989a). Briefly, concentrated hydrochloric acid was added to yield a pH of 2 or less. Internal standards were added. The organics were extracted with methylene chloride, separated from the water in a separatory funnel, dried with anhydrous sodium sulfate, and concentrated in a hot water bath to a volume of 1 mL. The GC-MS analytical procedure is described in detail in GERG (1989b). Briefly, a Hewlett Packard 5890A temperature programmable gas chromatograph was used in conjunction with a Hewlett Packard MSD mass spectrometer. The capillary column was 30 m, 0.32 mm ID, fused silica with DB-5 bonded phase. An autosampler injected 1-4 μL samples in the splitless mode. The mass spectrometer electron energy was 70 eV. Identification of PAHs and PCBs is based on relative gas chromatography retention times coupled with standards. Detection limits were approximately 1 ng for individual PAH and PCB compounds. Referring to the total volume from which the analyte was extracted, and dividing by the bucket open area and time of collection gives deposition rates in units of $\text{ng m}^{-2} \text{t}^{-1}$. The particles collected on the dichot filters were also analyzed for PAH and PCB content. Every alternate biweekly sample of particles collected on the dichot filters (Teflon membrane) was shipped in solvent rinsed 40 mL vials to Texas A&M University, where the organics were extracted and analyzed as described above.

2.5 Uncertainty Analysis

The concentration measurement uncertainty varies from method to method (i.e. INAA, ICP, GC), and also from compound to compound. Generally, the concentration measurements of standard samples were within 10-20% of the nominal values. However, in atmospheric deposition measurements the major source of uncertainty is not in the concentration measurement, but in the method of collecting deposition samples (Lovett, 1994). For wet deposition, there may be some loss of fine rain drops or light snow flakes, especially under windy conditions. Furthermore, mist or light snow may not activate the precipitation sensor, and hence the shuttling lid may stay open over the dry bucket. During the two weeks sampling period, some revolatilization or deterioration of deposited material could occur, especially organics. For dry deposition, the aerodynamic effects are even more pronounced. Particles, especially in the submicron to micron size range, are subject to Brownian and turbulent motion, and may be blown over the bucket rather than deposited into it. It is difficult to quantify the uncertainty range of atmospheric deposition measurements. There is no standard or "ground-truth" to compare the results with. In the following, the measurements are presented "as is," without correction for possible sampling errors, adjustment for possible aerodynamic effects or for the fact that the deposition into the buckets may not be the same as that onto an open water surface.

3.0 RESULTS AND DISCUSSION

3.1 Meteorological Data

Detailed meteorological data for the biweekly sampling periods are given in the Appendix. Here we summarize the general findings. At Nahant westerly surface winds predominated, i.e. winds from the continent. At Truro southwesterly surface winds predominated, but winds also blew from the south, north and east, i.e. from the ocean. Upper air (850 mb) winds were quite similar at both sites, which is not surprising because for Truro entirely, and for Nahant partially, a common data set was used, that of Chatham, Cape Cod. Generally, upper air winds blew from the NW, W and SW sectors. However, Truro upper air winds occasionally had strong S and N components. At Nahant the biweekly precipitation depths ranged from 0.2 to 20.3 cm; at Truro from 0.1 to 11.9 cm. The total annual precipitation was at Nahant 95.3 cm and Truro 103.3 cm.

3.2 Deposition of Trace Metals

Table I lists the annual deposition rates at Nahant and Truro for several trace metals. Some metals were analyzed in one, two or all three fractions (insoluble, soluble and wall-desorbed). Only Co, Cr, Fe and Zn were analyzed in all three fractions. In estimating the average deposition rate over the Bay area, the arithmetic average of the two sites was taken. The averaging is justified because the differences between the two sites are generally within a factor of two. The dry deposition rates listed in Table I are based on the analysis of the content of the "dry" bucket, not on the concentration of elements found on the dichot filters. A comparison of the two methods will be given later.

Figure 3 presents the deposition data in the form of bar charts. From the bar charts the following pattern emerges. For most metals, dry deposition was greater at Nahant than at Truro. This is probably due to the proximity of Nahant to the metropolitan Boston area and Logan Airport. Emission sources are fugitive dust, power plants, industrial, incinerator, residential and commercial boilers and furnaces, automobiles, trucks, aircraft and ships. On the other hand, wet deposition for most metals was greater at Truro than at Nahant. Wet deposition is the result of washout and rainout. Washout is the process of scavenging ("scrubbing") of gases and particles by falling hydrometeors. Rainout is the result of incorporating into cloud droplets of gases and particles, or indeed, cloud droplets forming on particle condensation nuclei (NAPAP, 1990). Clouds reaching the two sites may have traversed different geographic regions. At Nahant, westerly air masses prevailed, that is clouds which may have traveled over rural areas of Massachusetts, southern New Hampshire and Vermont, upstate New York and beyond. At Truro, southwesterly air masses had a stronger component. Clouds reaching Truro may have traveled over the heavily industrialized and urban corridor stretching over Rhode Island, Connecticut, New York City, New Jersey and beyond. These clouds may have carried a heavier load of pollutants than those reaching Nahant.

Figure 4 shows bar charts of seasonal deposition rates of several metals. There is no clear seasonal trend to the metal depositions. Of note is the high dry deposition rate in summer at Nahant of Fe, Cu, Mn and Ni. However, Pb dry deposition at Nahant was highest in winter. At Truro, dry deposition of Cd and Ni was highest in the summer, whereas Fe, Cu and Pb dry deposition was highest in the winter.

Table II lists the dates of the biweekly sampling periods at Nahant and Truro, respectively, and the depth (cm) of precipitation. Also listed are the concentrations in precipitation of four metals: Co, Cr, Fe and Zn (ng L^{-1}). These metals were analyzed in all three fractions: soluble, insoluble and wall-desorbed. Generally, the concentrations varied inversely with precipitation depth, that is, the less precipitation the higher the concentration. In the bottom of Table II are listed the annual volume weighted mean concentrations and standard deviations. The large standard deviations indicate the variability of concentrations over the sampling periods. The weighted volume mean concentrations of all four metals were lower at Nahant than at Truro. However, since dry deposition rates were generally higher at Nahant than at Truro, the total deposition rates of these metals were higher at Nahant than Truro. A detailed analysis of concentrations and deposition rates for the biweekly sampling periods as a function of meteorological conditions will be a subject of a separate study.

3.3 Mercury Deposition

Wet deposition of mercury was measured at Nahant during six weekly periods in the fall of 1993. The range of concentrations in 5 weekly samples was 4 - 20 ng L^{-1} . The sixth sample gave 97 ng L^{-1} , but in that sample there was only a trace of precipitation. The volume weighted average concentration in 5 samples was 10.1 ng L^{-1} . Vermette *et al.* (1995) at Sturgeon Point, New York, in the fall of 1993, measured weekly concentrations ranging from 4.3 to 17.9 ng L^{-1} , with an average concentration of 10 ng L^{-1} . The range and average concentrations were similar at Nahant and Sturgeon Point, NY.

3.4 Total Deposition

To obtain total deposition rates for those metals for which only the soluble or insoluble fraction was analyzed, solubility partitioning coefficients were used. Several studies have been published on the partitioning of elements between the soluble and insoluble (suspended) phase in precipitation (Flament *et al.*, 1984; Lim and Jickells, 1990; Heaton *et al.*, 1990; Lim *et al.*, 1994). The solubilities found in these studies vary widely from area to area, and also between precipitation episodes, due to pH variations and possible complexation of the metals or ions. Table III lists the solubilities reported in these studies, including the four metals for which we have data. (We have not included in the soluble fraction the wall-desorbed fraction. Since a 1% nitric acid solution was used for desorption, it is not clear whether the wall adsorbed metals were in solution or in suspended particle form. However, the wall-desorbed fraction contained only 10-20% of the total amount of these metals.) By averaging the solubilities, multiplying factors can be derived for converting percent soluble or insoluble, respectively, to total concentration. The multiplying factors for metals that were analyzed only in the soluble or insoluble fraction, respectively, are listed in Table III.

Total deposition rates in all three fractions in units of $\mu\text{g m}^{-2} \text{yr}^{-1}$ are listed in Table IV. The arithmetic average of Nahant and Truro depositions was used to estimate the average for MCCB. For Co, Cr, Fe and Zn no multiplying factors were applied as these metals were analyzed in all three fractions. Al, Cd, Cu, Mn, Ni and Pb were analyzed only in the soluble fraction, whereas As, Sb and Se were analyzed only in the insoluble fraction. For these metals appropriate multiplying factors from Table III were used. Table IV includes results from other studies in N. America and Europe. In comparison with Scudlark *et al.* (1994) similar *wet* deposition rates were found for MCCB and Chesapeake Bay for Mn, Pb and Zn. For As and Se higher deposition rates were found for Chesapeake Bay. This may be due to the fact that Chesapeake Bay is closer and more directly downwind of major coal burning areas in Virginia, West Virginia, Pennsylvania and Ohio. Emissions of As and Se are usually associated with coal burning (NAPAP, 1990). The other metals had higher deposition rates for MCCB than Chesapeake Bay: Al(2.2x), Fe(3.5x), Cd(4.4x), Cr(17x), Cu(2.7x) and Ni(9.6x). Al and Fe are crustal elements (e.g. fugitive dust), the other metals probably originate from non-ferrous metal smelting, metal plating, tanneries (Cr) and other industries. Apparently, emissions of these metals are greater along the air trajectories reaching MCCB compared to Chesapeake Bay.

In comparison to European data the striking differences are that depositions of Pb and Zn are far lower both for MCCB and Chesapeake Bay than for the North Sea (Cambray *et al.*, 1979; Flament *et al.*, 1984; Otten, 1991), the Severn Estuary (Harrison *et al.*, 1993) and the Dutch Delta (Nguyen *et al.*, 1990). For Pb, this is most likely due to the phase-out of leaded gasoline in the USA in the late 1970's. For Zn, European emissions must be considerably higher.

Table V gives a comparison of metal depositions measured in this work to previous estimates by Menzie-Cura (1991). Table V lists total deposition rates (wet + dry) in metric tonnes per year per total area of MCCB, estimated by Menzie-Cura as 3700 km^2 . For this comparison we used the arithmetic average of depositions at Nahant and Truro. Since Menzie-Cura used data from different sources and times, their estimates span a wide range. For most metals the measured deposition rates

fall within the range estimated by Menzie-Cura. For Co and Pb the measured rates are lower, and for Cr higher than estimated by Menzie-Cura. In the case of Pb this is certainly due to the fact that leaded gasoline was phased out since the data was taken that Menzie-Cura used for their estimates. For Hg we measured only the concentration in wet precipitation in 6 weekly samples at Nahant. The volume weighted mean concentration was 10.1 ng L^{-1} . Extrapolating for the annual precipitation depth and the total area of MCCB, one derives a *wet* deposition rate of 37 kg per year per MCCB area, which is in the range of *total* deposition rate for mercury estimated by Menzie-Cura: $24 - 73 \text{ kg yr}^{-1} \text{ MCCB}^{-1}$.

3.5 Particles and Dry Deposition from Airborne Concentrations

Particles were collected in a dichot collector at Nahant. Alternate biweekly samples were analyzed for metals by INAA. Thus, 13 samples were analyzed for the fine ($< 2.5 \mu\text{m}$) and coarse ($2.5 - 10 \mu\text{m}$) size range in the course of the year. The concentrations (mass divided by the volume of air that passed the filters) averaged over the 13 samples are listed in Table VI. The average concentration is taken as the annual average airborne PM-10 concentration of metals at Nahant. Table VI also lists the fraction of metal concentrations in the fine and coarse size ranges, respectively. It is seen that for most metals the majority was contained in the fine size range. The metals Co and Zn were found in equal concentrations in both size ranges.

Dry deposition rates were obtained from $D_d = Cv_d$, where C is concentration and v_d is deposition velocity. Since particles were found in two size ranges for which different deposition velocities are appropriate, total deposition rates were obtained from the summation $D_d = v_{d,f}\alpha C + v_{d,c}(1 - \alpha)C$, where $v_{d,f}$ is the dry deposition velocity for the fine and $v_{d,c}$ for the coarse size range, α is the fraction of concentration in the fine and $1 - \alpha$ in the coarse size range. In addition to the particle size, the deposition velocity depends on particle composition, deliquescence, surface conditions (e.g. land, water or vegetation) and atmospheric conditions (e.g. wind speed, turbulence, temperature). For the fine size range, $v_{d,f} = 0.25 \text{ cm s}^{-1}$ was selected; for the coarse size range, $v_{d,c} = 1 \text{ cm s}^{-1}$. These are midrange values from the literature (McMahon and Denison, 1979; Slinn and Slinn, 1980; Hicks and Williams, 1980; Dasch and Cadle, 1984; Walcek *et al.*, 1986; Lin *et al.*, 1994). The derived dry deposition rates are listed in Table VI, fifth column. The sixth column lists the dry deposition rates at Nahant obtained from the dry bucket method. In the dry bucket Co, Cr, Fe and Zn were analyzed in all three fractions (insoluble, soluble and wall-desorbed). As, Sb and Se were analyzed only in the insoluble fraction. For the latter, multiplying factors were applied taken from Table II. The agreement between the dichot and bucket method is very good for As, but for all other metals higher deposition rates by factors of 2 to 5 were obtained from the dichot method. This could be due in part to the dry bucket undercollecting particles, especially the smaller ones. However, the greater part of the discrepancy is probably due to the selected deposition velocities. Since the dominant contribution to deposition rate is from coarse particles, it is likely that $v_{d,c} = 1 \text{ cm s}^{-1}$ is too large. We may assume that the dry deposition rates obtained from the bucket method represent lower values, that from the dichot method upper values. The last column in Table VI lists the deposition rates obtained at Chesapeake Bay by Wu *et al.* (1994). These authors also used a dichotomous sampler to collect particles. They applied a range of deposition velocities, thus a range of deposition rates for each metal was obtained. For As and Se, the derived dry deposition rates were

similar at Massachusetts and Chesapeake Bays; for Cr, Fe and Zn the deposition rates were higher at Massachusetts than at Chesapeake Bay. This is in accordance of the findings for wet deposition rates.

3.6 Deposition of PAHs

Table VII lists the annual deposition rates for individual PAH species. Bar charts of deposition for grouped substituted PAHs are given in Figure 5. It is seen that with a few exceptions deposition of PAHs at Nahant was much greater than at Truro, both in the dry and wet form. The exceptions are naphthalenes and biphenyl, for which wet deposition at Truro was greater than that at Nahant. Nahant dry deposition of all PAHs was greater than wet deposition. These observations are consistent with the properties of PAHs. They are hydrophobic, hence they are relatively insoluble in precipitation, and most of the deposition occurs in the dry mode. PAHs are relatively short-lived. Kao (1994) estimates the atmospheric life-time of naphthalene as 16 hours, and "polycyclic organic matter" in general less than one day. Hence PAHs are expected to be deposited closer to the emission sources. PAHs are the products of incomplete combustion in boilers, furnaces, biomass (e.g. wood) burning, internal combustion engines (gasoline and diesel) and aircraft jet engines (Daisey *et al.*, 1986). The proximity of the metropolitan Boston urban-industrial sprawl certainly results in higher deposition of PAHs at Nahant than at Truro. Furthermore, Logan International Airport is only about 12 km from Nahant along the prevailing wind direction. Most likely the emissions from jet aircraft takeoffs and landings contribute to dry deposition of PAH gases and particles at Nahant.

A bar chart of total annual deposition of all PAHs is given in Figure 6. The annual deposition rates are as follows:

Nahant, dry	700 $\mu\text{g m}^{-2} \text{yr}^{-1}$
Nahant, wet	270
Truro, dry	130
Truro, wet	200

Taking the arithmetic average of the two sites and multiplying by the area of MCCB, 3700 km^2 , the total (wet + dry) deposition onto the Bays area was 2400 kg yr^{-1} . This is twice as much as the "high" estimate of Menzie-Cura (1991), 1260 kg yr^{-1} . (The "low" estimate was 953 kg yr^{-1} .) Menzie-Cura also estimated the loading of MCCB from non-atmospheric sources, i.e. point discharges, run-off, combined sewer overflow, groundwater and riverine discharges. The range was 1390 - 10700 kg yr^{-1} . Accordingly, atmospheric deposition may contribute from 22% to 172% of the total loading of PAHs.

Figure 7 shows the seasonal deposition rates for PAHs. Dry deposition was highest at Nahant and Truro in winter. This could be due to the greater use in winter of fossil fuel (oil and gas) for residential and commercial space heating and wood burning in stoves and fireplaces. Another reason could be the lower mixing heights prevailing in the winter over much of N. America (Holzworth, 1972). Lower mixing heights cause pollutant particles and gases to be more concentrated, and

consequently their deposition rates will be higher. Figure 8 shows pie charts of the composition of PAHs in dry and wet deposition at Nahant and Truro. At Nahant the major contributors to dry deposition were fluoranthene (13%), phenanthrene (9.3%) and pyrene (9.3%), and to wet deposition fluoranthene (9%), phenanthrene (8.5%) and pyrene (5.9%). At Truro, the major contributors to dry deposition were phenanthrene (8.3%), fluoranthene (8.1%) and pyrene (5.6%); and to wet deposition phenanthrene (5%), benzo(ghi)perylene (4.1%), and C2-fluorenes (3.1%). The pie charts also include naphthalene and its substitutes. In a strict sense, naphthalene is not a polycyclic aromatic hydrocarbon, it is bicyclic. Naphthalene and its substitutes contributed as much as 58.2% of the wet deposition at Truro and 25.7% at Nahant. This is probably due to the relatively high solubility in water of naphthalene, 31 mg L^{-1} vs. phenanthrene 1.1 mg L^{-1} , pyrene 0.13 mg L^{-1} and benzo(ghi)perylene $0.00026 \text{ mg L}^{-1}$ (Mackay et al., 1992). Clouds arriving at Truro and Nahant may contain naphthalene from distant as well as from local sources.

The samples from the wet/dry collectors were analyzed for PCB's. However, none were found above the detection limit of the analytical method. Every alternate sample from the dichotomous particle collector was also analyzed for PAHs and PCBs. No PCBs were found, and very small amounts of PAHs. This is most likely due to evaporation of the organic compounds during the long collection period (two weeks) under a constant air flow over the filters of the particle collector, and the fact that some of the PAHs are found in the vapor phase in the atmosphere.

Long term sampling of PAHs was conducted at a central location on Chesapeake Bay by Leister and Baker (1994) and at a southern location by Dickhut and Gustafson (1995). These authors measured wet deposition of PAHs (and PCBs) directly in a wet-only collector, and dry deposition indirectly via airborne concentrations. Their results are compared with Massachusetts Bay results in Table VIII. Due to the different methodologies of dry deposition measurements, the comparison of wet deposition is more meaningful. Also, because of the similar distances to major pollution sources, Truro wet depositions are to be compared with the central and southern Chesapeake Bay data. Generally, PAH depositions were similar at Truro and the sites on Chesapeake Bay. However, Nahant received more wet deposition of most PAH species than either Truro or the sites on Chesapeake Bay.

CONCLUSIONS

Trace metal and polycyclic aromatic hydrocarbon (PAH) deposition rates were measured for one year (1992/93) at two sites on the shoreline of Massachusetts Bay, one near Boston (Nahant), the other at the tip of Cape Cod (Truro). Nahant received more atmospheric depositions of trace metals and PAHs than Truro, especially in the dry form, indicating the influence of the nearby metropolitan Boston and Logan Airport emission sources. The uncertainty in the wet deposition estimates is due to limitations in analytical procedures, and to the possibility that fine rain droplets, mist or snow flakes are not finding their way into the wet bucket. The dry deposition estimates are hampered by the lack of knowledge of what fraction of gas molecules and particles settle in the dry bucket, and whether the layer of water in the "dry" bucket closely simulates an open water surface.

in terms of atmosphere-ocean surface transfer. Also, during the biweekly sampling period, some revolatilization and deterioration of species, especially PAHs, may have occurred.

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Element	Fractions Analyzed	Nahant			Truro			Bays Average #		
		Dry	Wet	Total	Dry	Wet	Total	Dry	Wet	Total
Co	(1)	6.7E+01	9.0E+00	7.6E+01	2.6E+01	1.4E+01	4.0E+01	4.7E+01	1.2E+01	5.8E+01
Cr	(1)	1.3E+03	1.6E+03	2.9E+03	1.2E+03	1.4E+03	2.5E+03	1.2E+03	1.5E+03	2.7E+03
Fe	(1)	1.3E+05	2.2E+04	1.6E+05	8.3E+04	5.0E+04	1.3E+05	1.1E+05	3.6E+04	1.4E+05
Zn	(1)	5.4E+03	2.1E+03	7.6E+03	4.8E+03	3.2E+03	8.0E+03	5.1E+03	2.7E+03	7.8E+03
As	(2)	2.6E+01	0.0E+00	2.6E+01	1.2E+01	6.9E+00	1.9E+01	1.9E+01	3.5E+00	2.2E+01
Sb	(2)	3.1E+01	1.1E+01	4.2E+01	1.7E+01	2.1E+01	3.8E+01	2.4E+01	1.6E+01	4.0E+01
Se	(2)	8.0E+00	1.0E+01	1.8E+01	1.1E+01	1.8E+01	2.9E+01	9.5E+00	1.4E+01	2.4E+01
Al	(3)	1.7E+04	4.7E+03	2.2E+04	7.8E+03	5.1E+03	1.3E+04	1.2E+04	4.9E+03	1.7E+04
Cd	(3)	1.2E+02	1.4E+02	2.6E+02	1.4E+02	1.5E+02	2.8E+02	1.3E+02	1.4E+02	2.7E+02
Cu	(3)	1.9E+03	4.5E+02	2.4E+03	2.1E+03	5.4E+02	2.6E+03	2.0E+03	5.0E+02	2.5E+03
Mn	(3)	3.0E+03	6.5E+02	3.7E+03	2.3E+03	8.5E+02	3.1E+03	2.7E+03	7.5E+02	3.4E+03
Ni	(3)	1.0E+03	6.6E+02	1.7E+03	8.1E+02	5.7E+02	1.4E+03	9.3E+02	6.2E+02	1.5E+03
Pb	(3)	1.8E+03	5.2E+02	2.3E+03	7.7E+02	6.1E+02	1.4E+03	1.3E+03	5.7E+02	1.8E+03

- (#) Massachusetts Bay average based on (Nahant + Truro)/2
(1) Insoluble (INAA), soluble and wall desorbed (ICP-MS)
(2) Insoluble fraction only (INAA)
(3) Soluble and wall desorbed fractions only (ICP-MS)

Table I. Atmospheric deposition of metals onto MCCB ($\mu\text{g m}^{-2} \text{yr}^{-1}$).

Nahant Wet Deposition

Sample Period Start	Sample Period End	Precip (cm)	Co (ng/L)	Cr (ng/L)	Fe (ng/L)	Zn (ng/L)
92-Sep-16	92-Sep-30	4.7	1.5E+01	7.9E+02	2.1E+04	1.1E+03
92-Sep-30	92-Oct-14	3.0	1.5E+01	1.3E+02	1.8E+04	7.4E+03
92-Oct-14	92-Oct-27	1.4	1.9E+01	4.4E+02	3.6E+04	7.8E+03
92-Oct-27	92-Nov-10	2.5	2.0E+01	7.4E+02	3.0E+04	4.9E+03
92-Nov-10	92-Nov-23	7.0	2.9E+01	3.5E+02	4.9E+04	7.7E+03
92-Nov-23	92-Dec-07	3.4	ND	4.6E+02	1.8E+04	8.4E+03
92-Dec-07	92-Dec-21	20.3	no sample	no sample	no sample	no sample
92-Dec-21	93-Jan-06	3.9	5.6E+01	5.4E+03	9.2E+04	7.8E+03
93-Jan-06	93-Jan-20	1.3	2.0E+01	9.9E+02	5.2E+04	7.5E+03
93-Jan-20	93-Feb-02	1.2	1.5E+01	8.8E+03	5.9E+04	4.7E+03
93-Feb-02	93-Feb-15	6.1	2.2E+01	4.1E+02	5.1E+04	1.9E+03
93-Feb-15	93-Mar-02	3.9	1.1E+01	2.1E+03	4.3E+04	8.0E+03
93-Mar-02	93-Mar-16	2.0	3.6E+01	1.8E+03	1.1E+05	7.7E+03
93-Mar-16	93-Mar-30	8.6	1.5E+02	2.2E+04	9.1E+04	1.4E+04
93-Mar-30	93-Apr-14	4.6	3.7E+01	2.0E+03	7.6E+04	8.7E+03
93-Apr-14	93-Apr-27	5.4	1.5E+01	4.3E+03	6.9E+04	9.7E+03
93-Apr-27	93-May-13	0.3	4.5E+01	7.9E+03	1.8E+05	9.0E+03
93-May-13	93-May-26	1.4	5.1E+01	3.3E+03	1.2E+05	7.2E+03
93-May-26	93-Jun-09	3.0	9.7E+01	2.2E+04	1.0E+05	1.3E+04
93-Jun-09	93-Jun-23	1.4	7.3E+01	2.2E+03	1.5E+05	9.1E+03
93-Jun-23	93-Jul-07	0.2	no sample	no sample	no sample	no sample
93-Jul-07	93-Jul-22	0.8	1.4E+01	1.6E+03	4.7E+04	4.6E+03
93-Jul-22	93-Aug-04	2.6	7.0E+01	2.0E+04	8.0E+04	9.7E+03
93-Aug-04	93-Aug-18	1.5	6.9E+01	1.0E+04	1.0E+05	6.8E+03
93-Aug-18	93-Sep-01	0.9	7.0E+01	6.1E+03	5.3E+04	7.4E+03
93-Sep-01	93-Sep-14	3.9	2.2E+02	2.1E+04	1.5E+05	1.2E+04
Total		95.3				
Weighted Volume Mean			1.2E+01	1.5E+03	1.9E+04	2.1E+03
Weighted Volume St. Dev.			1.0E+00	7.5E+01	4.8E+02	4.2E+01

Truro Wet Deposition

Sample Period Start	Sample Period End	Precip (cm)	Co (ng/L)	Cr (ng/L)	Fe (ng/L)	Zn (ng/L)
92-Sep-15	92-Sep-29	5.6	3.8E+00	3.6E+02	3.9E+04	1.6E+03
92-Sep-29	92-Oct-13	3.7	3.6E+00	2.3E+02	2.3E+04	2.5E+03
92-Oct-13	92-Oct-27	2.1	5.9E+00	2.3E+02	3.2E+04	4.2E+03
92-Oct-27	92-Nov-10	2.6	2.7E+00	1.3E+02	2.0E+04	2.4E+03
92-Nov-10	92-Nov-24	7.3	1.3E+01	3.1E+02	2.5E+05	3.6E+03
92-Nov-24	92-Dec-08	3.9	7.6E+00	3.5E+02	4.1E+04	3.3E+03
92-Dec-08	92-Dec-24	6.2	8.5E+01	1.5E+03	2.8E+06	1.6E+04
92-Dec-24	93-Jan-07	5.3	4.1E+00	3.3E+02	6.1E+04	2.0E+03
93-Jan-07	93-Jan-21	3.1	7.6E+00	2.9E+02	7.7E+04	2.1E+03
93-Jan-21	93-Feb-04	2.4	1.1E+02	6.4E+03	4.6E+05	1.1E+04
93-Feb-04	93-Feb-20	6.8	8.3E+00	1.1E+02	2.0E+05	2.6E+03
93-Feb-20	93-Mar-03	1.6	1.0E+01	4.0E+02	4.7E+04	4.8E+03
93-Mar-03	93-Mar-20	9.3	1.0E+02	7.3E+02	2.8E+06	4.7E+03
93-Mar-20	93-Apr-08	11.9	2.4E+00	1.8E+03	9.1E+04	1.8E+03
93-Apr-08	93-Apr-29	9.7	2.5E+00	6.9E+01	1.1E+05	1.4E+03
93-Apr-29	93-May-25	5.2	8.2E+00	1.4E+02	1.8E+05	2.6E+03
93-May-25	93-Jun-09	3.1	1.2E+01	3.7E+02	1.4E+05	4.2E+03
93-Jun-09	93-Jul-01	1.2	2.1E+01	9.1E+03	4.3E+04	3.9E+03
93-Jul-01	93-Jul-15	2.7	5.5E+00	5.2E+03	4.2E+04	1.1E+03
93-Jul-15	93-Jul-28	2.7	7.0E+00	6.1E+03	1.0E+05	3.3E+03
93-Jul-28	93-Aug-08	0.8	ND	1.3E+03	1.4E+04	5.2E+03
93-Aug-08	93-Aug-21	0.4	3.6E+01	7.2E+02	3.3E+04	2.1E+04
93-Aug-21	93-Sep-01	0.1	1.6E+01	9.3E+03	1.1E+04	2.1E+04
93-Sep-01	93-Sep-17	5.6	4.9E+00	5.6E+03	1.2E+05	3.2E+03
Total		103.3				
Weighted Volume Mean			1.8E+01	1.4E+03	5.1E+04	3.1E+03
Weighted Volume St. Dev.			2.0E+00	6.4E+01	5.6E+03	9.8E+01

Table II. Dates of sampling periods, precipitation depth, and concentrations of Co, Cr, Fe, and Zn in wet precipitation.

metal	ave(SD)	Heaton et al. 1992	Lim et al. 1994	mean	Lim & Jickells 1990	mean	Flament et al. 1984	Gatz & Chu 1986	Ave Sol (%)	sol.-tot.	insol.-tot.	Multiplying Factor
Al		4-25	15	13					14	6	6	
As		65-98							81.5			6
Cd						53-78			65.5	1.5		
Co	14(27)								14			
Cr	30(32)								30			
Cu			63			63-94			73	1.4		
Fe	8(12)								8			
Mn		54-98							76	1.3		
Ni							21-31		26	4.8		
Pb			69	45				83	66	1.5		
Sb		60-90							75			4
Se		86-100	86						91			11
Zn	71(26)					68-87			75			

Table III. Solubility of metals in precipitation and multiplying factors to convert from soluble and insoluble to total concentration.

metal	This work Mass Bay	This work Mass Bay ⁽¹⁾	Scudlark et al. 1994 Chesap Bay ⁽¹⁾	Flament et al. 1984 North Sea	Harrison et al. 1993 Severn, UK ⁽²⁾	Otten 1991 North Sea	Cambrey et al. 1979 North Sea ⁽¹⁾	Nguyen et al. 1990 Dutch Delta ⁽¹⁾
Al	102000	29400	13600					
As	132	21	49					
Cd	405	210	48	300-1400	100	350		146
Co	58	12						73
Cr	2700	1500	88		236		1400	
Cu	3500	700	260	6100-16200	1050	2680	10500	2274
Fe	140000	36000	10400					
Mn	4420	975	1190					
Ni	6000	2480	257		335			880
Pb	2700	855	556	5600-13500	6960	6500	11000	4234
Sb	160	64						
Se	264	154	214					
Zn	7800	1500	1335	20600-55600	11800	19700	31000	12665

(1) Wet deposition only

(2) "Bulk" deposition (kg yr⁻¹) divided by 3×10^9 m², the estimated area of Severn Estuary

Table IV. Atmospheric deposition of metals onto coastal waters in North America and Europe ($\mu\text{g m}^{-2} \text{yr}^{-1}$).

Metal	Total ⁽¹⁾ deposition (T yr ⁻¹ MCCB ⁻¹)	
	This work	Menzie-Cura (1991)
Ag	—	13
Al	377	—
As	0.5	0.14-0.93
Cd	1.5	2.5
Co	0.2	7.3-7.8
Cr	10	0.14-5.1
Cu	13	18.4
Fe	518	122-529
Hg	—	0.02-0.07
Mn	16.3	3.9-5.8
Ni	22.2	11.3
Pb	10	213
Sb	0.6	0.05-0.3
Se	1	0.02-0.3
V	—	3.2-88
Zn	29	5.3-88

⁽¹⁾Total = wet + dry

Table V. Atmospheric deposition of metals onto MCCB. Comparison of this work with previous estimates by Menzie-Cura (1991). Units metric tonnes per year per MCCB area (3700 km²).

metal	Annual ave. conc. (ng m ⁻³)	Fine fraction		Dry deposition ($\mu\text{g m}^{-2} \text{yr}^{-1}$)		
		α	1- α	Nahant dichot	bucket	Chesapeake ⁽¹⁾ dichot
As	1.2	0.75	0.25	165	156*	54-150
Co	1.7	0.5	0.5	332	67	
Cr	16	0.7	0.3	2376	1300	110-300
Fe	1210	0.6	0.4	208120	130000	34000-97000
Sb	3	0.6	0.4	516	124*	
Se	3	0.7	0.3	446	88*	130-360
Zn	79	0.5	0.5	15443	5400	1000-2900

(1) Wu et al., 1994

* Multiplying factor applied

Table VI. Airborne concentrations (ng m⁻³) and dry deposition rates ($\mu\text{g m}^{-2} \text{yr}^{-1}$).

Compound	Nahant			Truro		
	Dry	Wet	Total	Dry	Wet	Total
NAPHTHALENE	2.2E+04	2.4E+04	4.6E+04	2.2E+04	6.5E+04	8.7E+04
C1-NAPHTHALENES	1.8E+04	1.6E+04	3.4E+04	1.5E+04	3.0E+04	4.5E+04
C2-NAPHTHALENES	1.3E+04	1.5E+04	2.8E+04	7.5E+03	2.0E+04	2.7E+04
C3-NAPHTHALENES	2.0E+04	2.1E+04	4.1E+04	9.4E+03	1.6E+04	2.5E+04
C4-NAPHTHALENES	4.5E+03	3.1E+03	7.6E+03	1.9E+03	5.1E+03	7.0E+03
BIPHENYL	3.1E+03	1.2E+03	4.3E+03	2.6E+03	5.1E+03	7.7E+03
ACENAPHTHYLENE	3.3E+03	1.9E+03	5.2E+03	2.8E+03	5.0E+02	3.3E+03
ACENAPHTHENE	3.4E+03	1.6E+03	5.0E+03	8.1E+02	9.6E+02	1.8E+03
FLUORENE	5.0E+03	2.6E+03	7.6E+03	1.9E+03	5.5E+02	2.4E+03
C1-FLUORENES	2.8E+03	3.4E+03	6.2E+03	1.9E+03	8.8E+02	2.8E+03
C2-FLUORENES	4.8E+03	9.7E+03	1.4E+04	5.4E+03	3.1E+03	8.5E+03
C3-FLUORENES	9.3E+03	1.2E+04	2.2E+04	6.2E+03	3.1E+03	9.4E+03
PHENANTHRENE	7.8E+04	2.7E+04	1.1E+05	1.6E+04	7.1E+03	2.3E+04
ANTHRACENE	7.9E+03	1.6E+03	9.5E+03	1.5E+03	2.2E+03	3.7E+03
C1-PHENANTHRENE	3.2E+04	1.3E+04	4.5E+04	7.7E+03	3.7E+03	1.1E+04
C2-PHENANTHRENE	2.2E+04	1.2E+04	3.4E+04	6.1E+03	3.7E+03	9.8E+03
C3-PHENANTHRENE	1.3E+04	8.5E+03	2.2E+04	4.6E+03	4.6E+03	9.2E+03
C4-PHENANTHRENE	4.6E+03	2.7E+03	7.3E+03	2.6E+03	1.8E+03	4.4E+03
DIBENZOTHIOPHENE	4.7E+03	1.4E+03	6.1E+03	1.9E+03	3.6E+02	2.3E+03
C1-DIBENZOTHIOPHENE	4.4E+03	3.6E+03	8.0E+03	1.2E+03	8.1E+02	2.0E+03
C2-DIBENZOTHIOPHENE	7.2E+03	5.6E+03	1.3E+04	3.0E+03	2.8E+03	5.9E+03
C3-DIBENZOTHIOPHENE	4.3E+03	3.7E+03	8.0E+03	1.6E+03	1.7E+03	3.3E+03
FLUORANTHRENE	1.0E+05	2.7E+04	1.3E+05	1.5E+04	9.1E+03	2.4E+04
PYRENE	7.8E+04	1.9E+04	9.8E+04	1.1E+04	5.8E+03	1.7E+04
C1-FLUORANTHRENE/PYRENE	3.1E+04	8.8E+03	3.9E+04	4.8E+03	2.7E+03	7.5E+03
BENZ(A)ANTHRACENE	2.6E+04	5.2E+03	3.2E+04	2.5E+03	1.2E+03	3.6E+03
CHRYSENE	4.3E+04	9.6E+03	5.3E+04	4.6E+03	3.7E+03	8.3E+03
C1-CHRYSENES	1.5E+04	4.2E+03	1.9E+04	7.4E+02	2.8E+02	1.0E+03
C2-CHRYSENES	1.6E+04	2.6E+03	1.8E+04	3.2E+02	2.9E+02	6.2E+02
C3-CHRYSENES	1.8E+03	3.3E+02	2.1E+03	1.1E+02	3.4E+01	1.4E+02
C4-CHRYSENES	5.8E+03	8.2E+02	6.6E+03	2.7E+02	1.1E+02	3.8E+02
BENZO(B)FLUORANTHRENE	3.8E+04	8.8E+03	4.4E+04	4.0E+03	2.8E+03	6.8E+03
BENZO(K)FLUORANTHRENE	3.7E+04	8.3E+03	4.6E+04	3.9E+03	2.9E+03	6.8E+03
BENZO(E)PYRENE	2.8E+04	5.2E+03	3.3E+04	2.7E+03	1.1E+03	3.8E+03
BENZO(A)PYRENE	2.6E+04	4.8E+03	3.0E+04	2.3E+03	2.1E+03	4.4E+03
PERYLENE	1.1E+04	6.4E+02	1.2E+04	2.4E+03	7.9E+02	3.2E+03
INDENO[1,2,3-CD]PYRENE	2.8E+04	4.8E+03	3.3E+04	2.7E+03	2.1E+03	4.8E+03
DIBENZ(AH)ANTHRACENE	5.3E+03	4.6E+02	5.8E+03	5.9E+02	2.0E+02	7.9E+02
BENZO(GHI)PERYLENE	2.5E+04	4.4E+03	2.9E+04	2.5E+03	1.6E+03	4.1E+03
2-METHYLNAPH	9.6E+03	9.2E+03	1.9E+04	7.9E+03	1.4E+04	2.2E+04
1-METHYLNAPH	6.0E+03	6.0E+03	1.2E+04	6.0E+03	1.3E+04	1.9E+04
2,6-DIMETHNAPH	3.6E+03	1.6E+03	5.2E+03	1.5E+03	5.2E+03	6.7E+03
2,3,5-TRIMETHNAPH	3.3E+03	5.7E+02	3.8E+03	8.2E+02	1.6E+02	9.9E+02
1-METHYLPHEN	8.5E+03	1.5E+03	1.0E+04	3.3E+03	6.3E+02	3.9E+03

Table VII. Atmospheric deposition of individual PAHs onto MCCB ($\text{ng m}^{-2} \text{yr}^{-1}$).

Compound	This work Nahant		This work Truro		Leister & Baker 1994 C. Chesapeake Bay		Dickhut & Gustafson 1995 S. Chesapeake Bay	
	wet	dry	wet	dry	wet	dry	wet	dry
Acenaphthene	1.6	3.4	1.0	0.8				
Acenaphthylene	1.9	3.3	0.5	2.8				
Anthracene	1.6	7.9	2.2	1.5	1	1	0.4	1
Benzo(ghi) perylene	4.4	24.8	1.6	2.5	2	11	2	9
Biphenyl	1.2	3.1	5.1	2.6				
Chrysenes	17.5	81.3	4.3	5.6	5	12	2	10
Dibenzothiophenes	14.3	20.5	5.6	7.6				
Fluoranthene	27.0	102.0	9.1	14.8	15	16	5	19
Fluorenes	28.1	21.9	7.6	15.4	2	2	2	ND
Napthalene	107.0	99.6	168.0	72.0				
Perylene	0.6	10.9	0.8	2.4				
Phenanthrenes	65.4	149.7	20.9	21.0	9	12	8	11
Pyrenes	19.4	78.4	5.8	11.1	20	15	4	16

Table VIII. Atmospheric deposition of grouped PAHs onto MCCCCB and Chesapeake Bay ($\mu\text{g m}^{-2} \text{yr}^{-1}$).

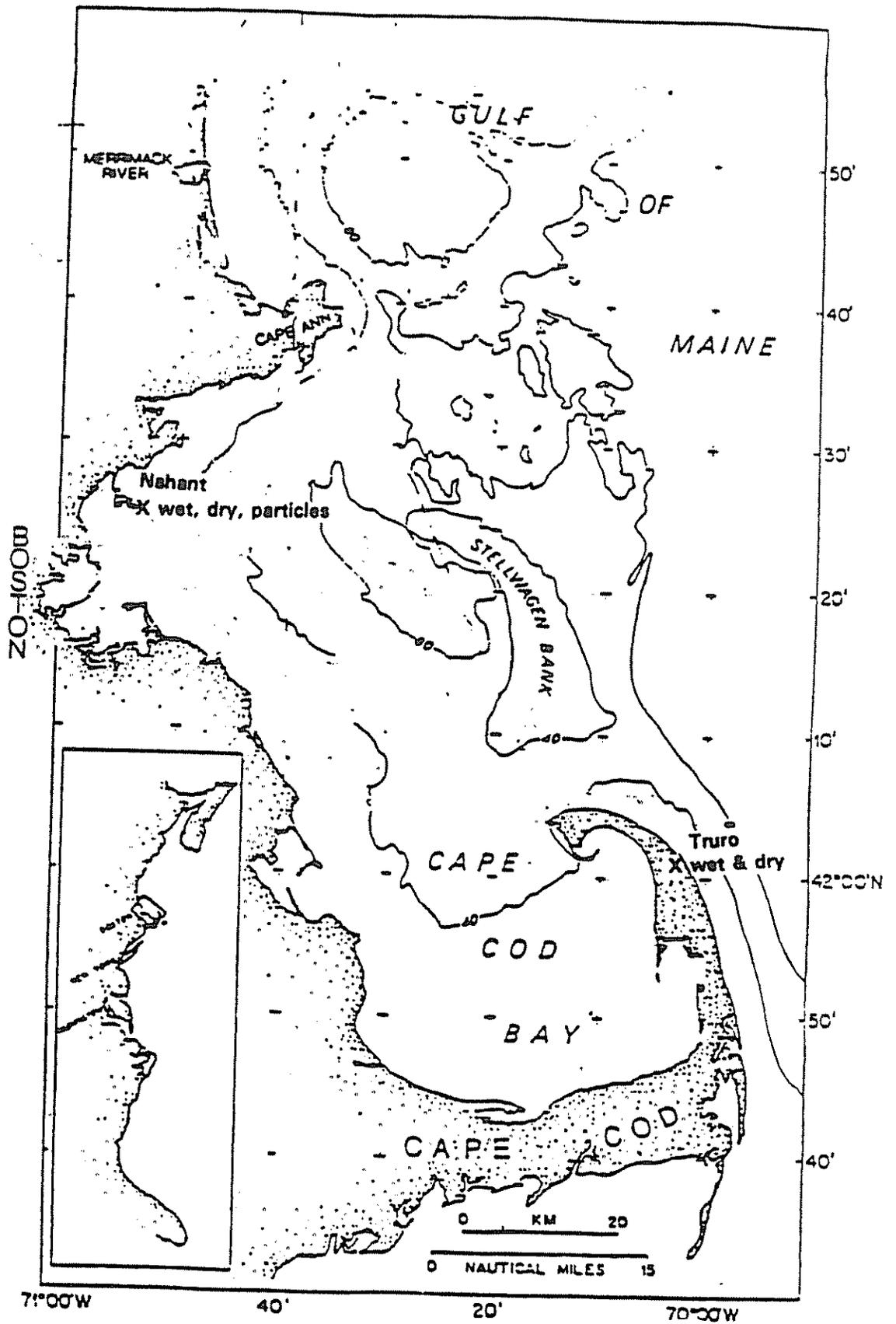


Fig. 1. Map of Massachusetts Bay. Nahant and Truro field sites marked X.

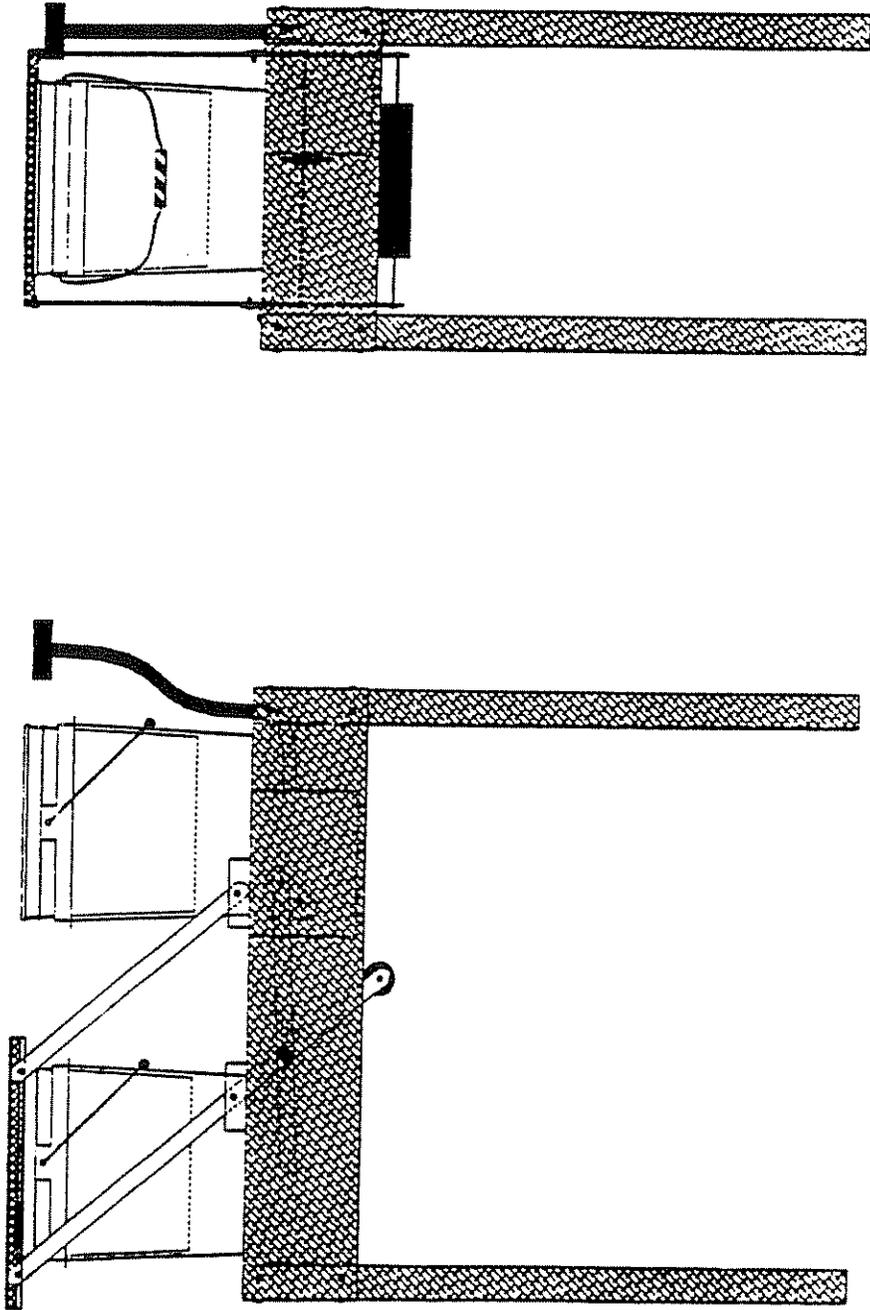


Figure 2. Wet/dry collector

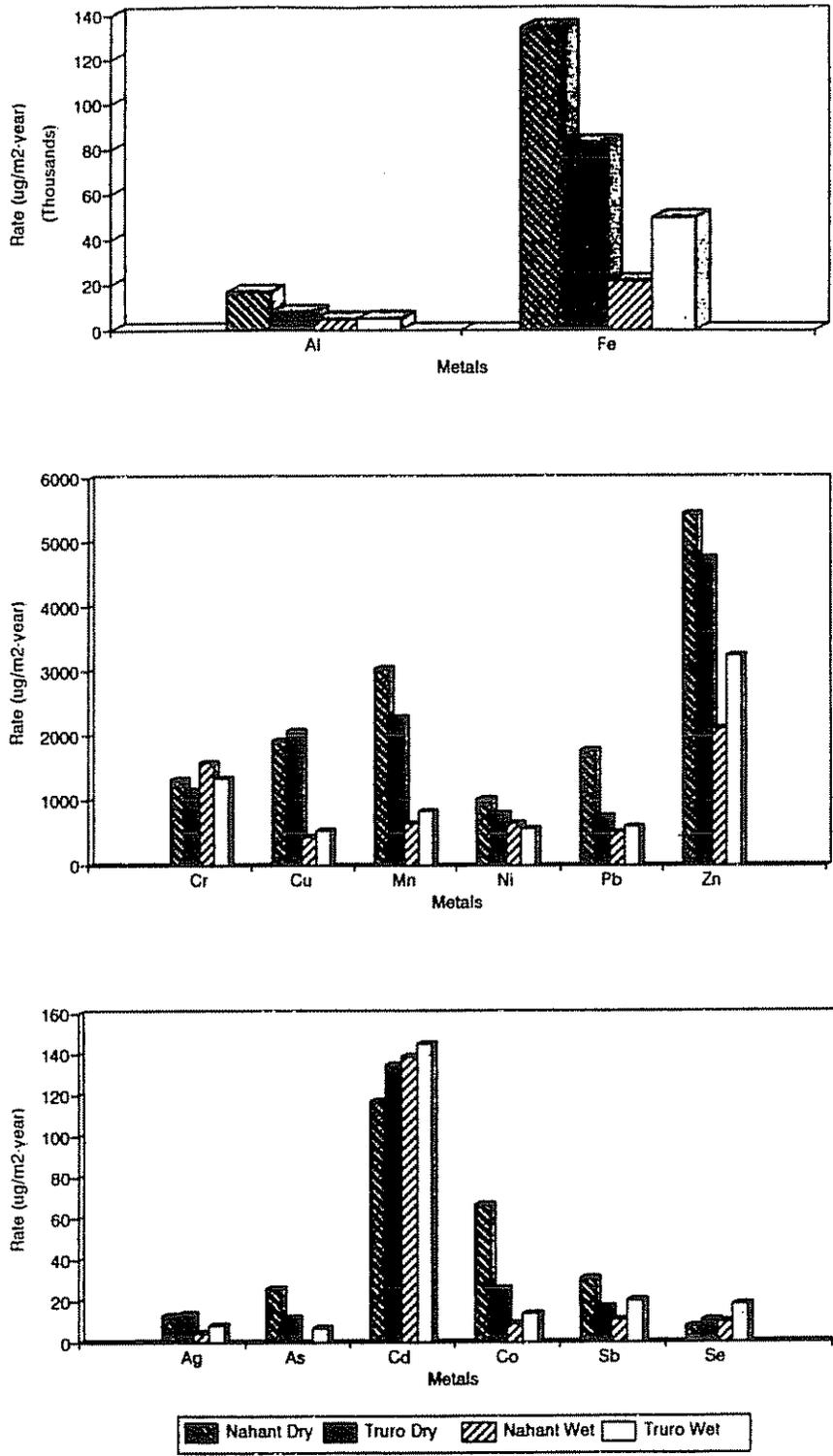


Figure 3 Bar chart of annual deposition rates of metals

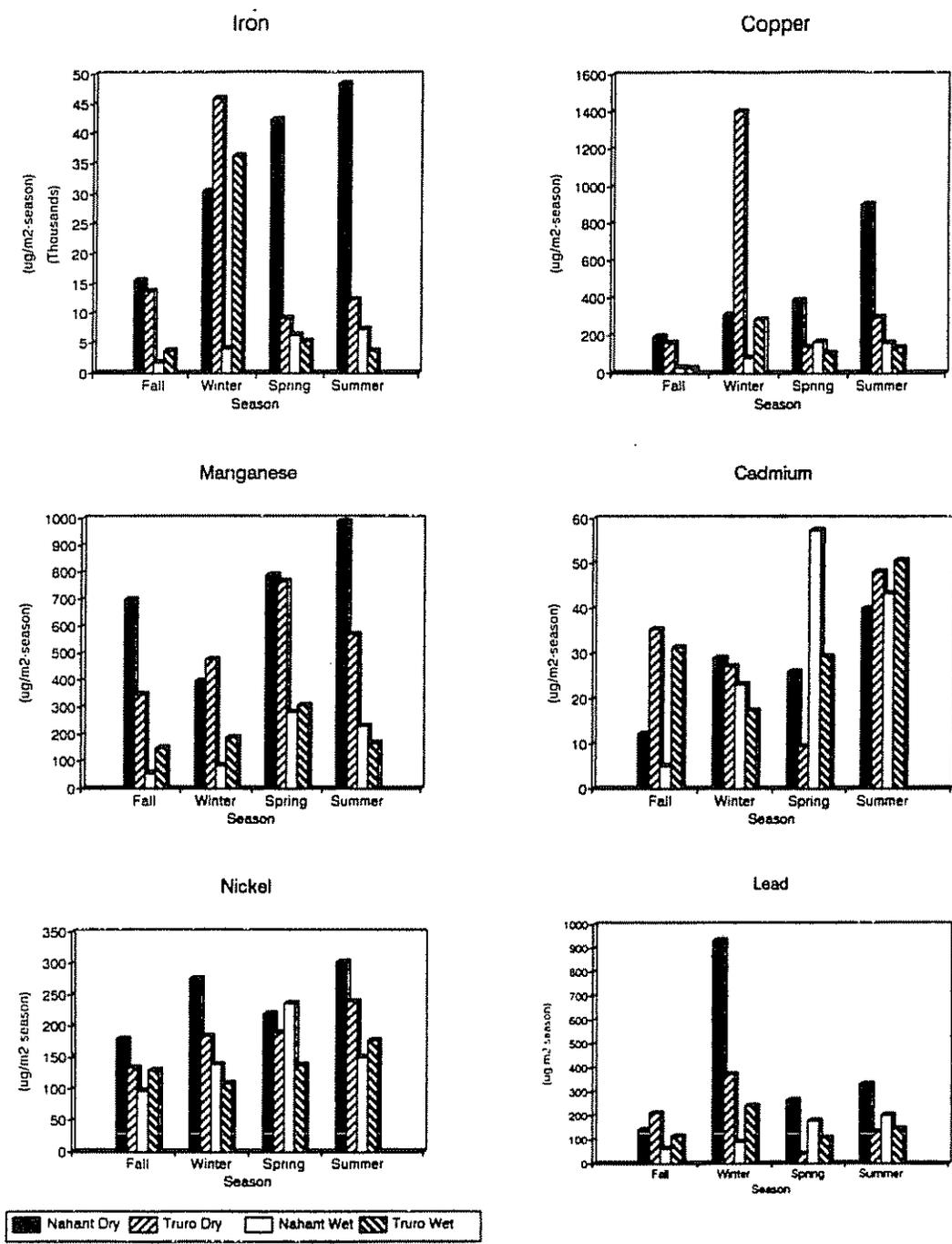


Figure 4. Bar chart of seasonal deposition rates of metals

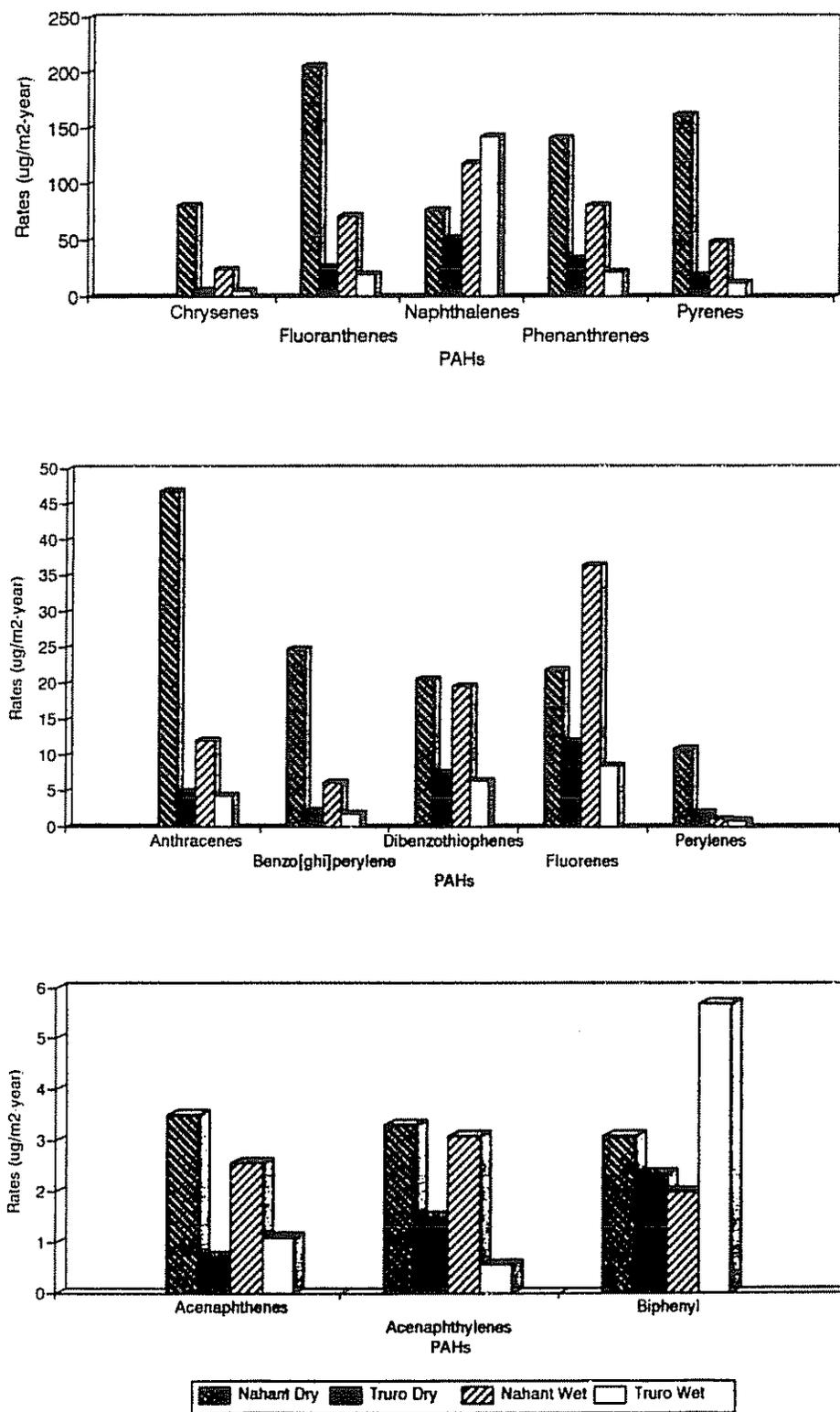


Figure 5. Bar chart of annual deposition rates of grouped PAHs.

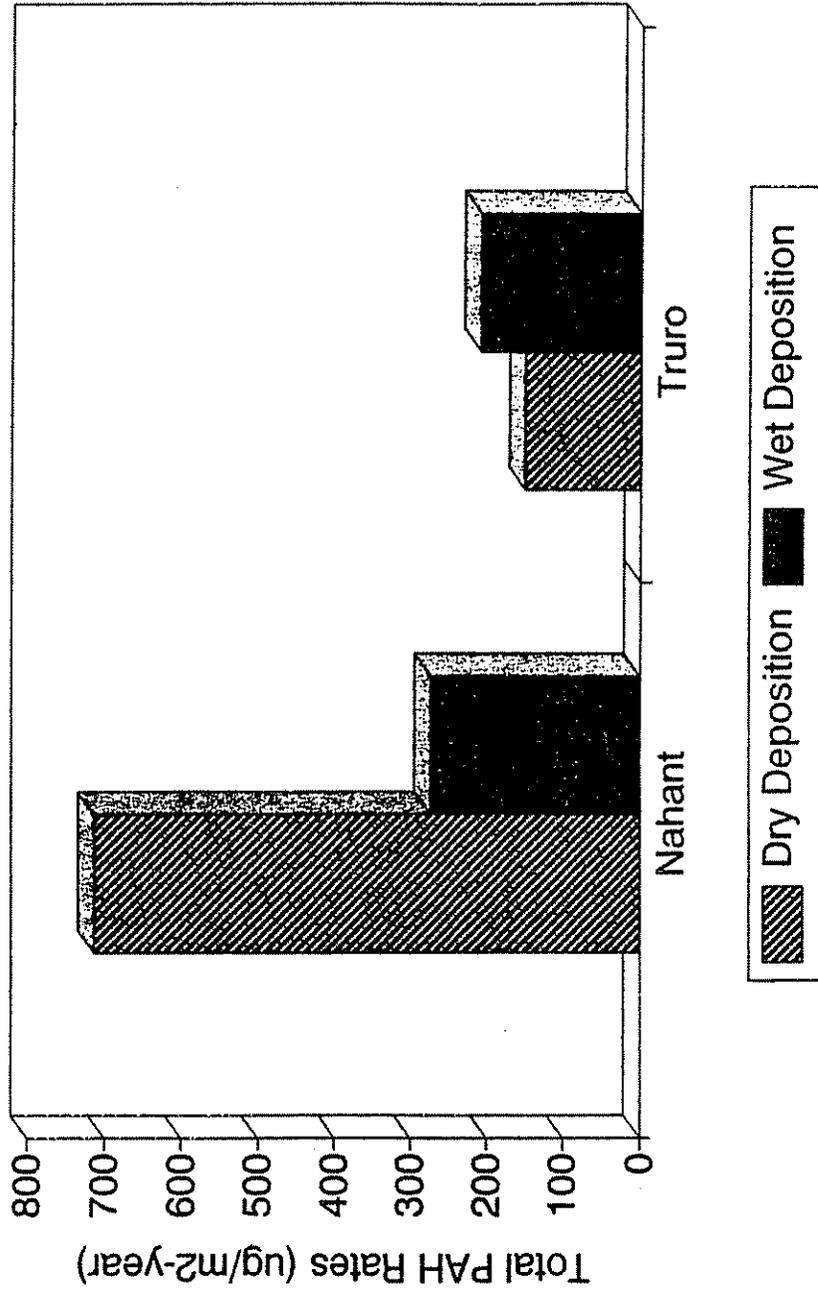


Figure 6. Bar chart of total PAH deposition onto MCCB.

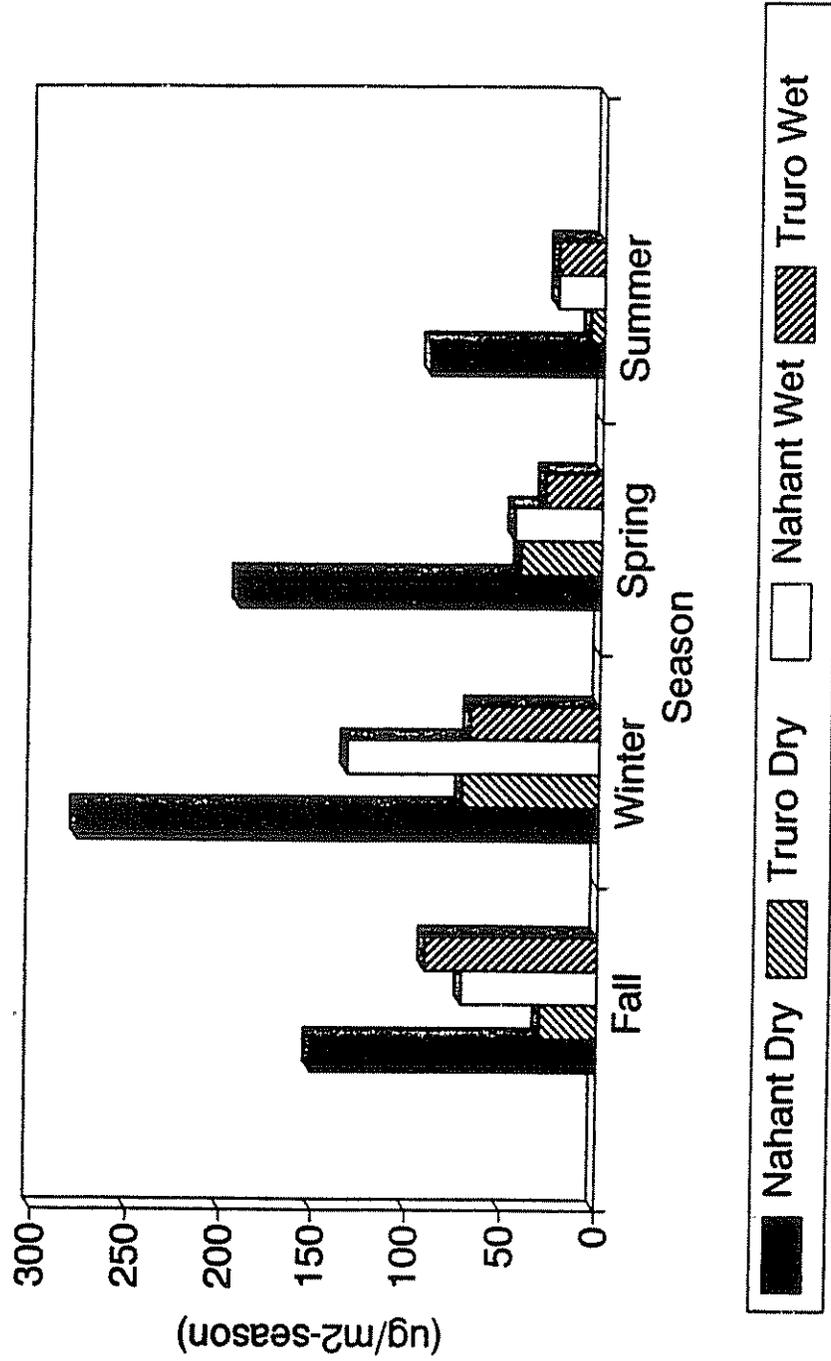


Figure 7. Bar chart of seasonal deposition rates of PAHs.

PART TWO:

**ATMOSPHERIC DEPOSITION OF NITROGEN COMPOUNDS TO THE
MASSACHUSETTS BAYS**

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Atmospheric Deposition of Nitrogen Compounds to the Massachusetts Bays

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1 Introduction and summary

Previous investigators (Menzie-Cura & Associates, 1991) estimated that atmospheric deposition may contribute 5–16% of the total loading of nitrogen to the Massachusetts Bays. This range was derived from a review of the literature relevant to the deposition of nitrogen-containing compounds in coastal environments. As part of further research on this topic, the "Atmospheric Deposition of Contaminants onto Massachusetts and Cape Cod Bays" study proposed a refined analysis of nitrogen deposition through a more extensive analysis of the information available in the scientific literature. This report describes the results of this research.

In summary, this analysis finds that the best estimate of the rate of nitrogen deposition from the atmosphere is closer to the lower-end estimate derived by Menzie-Cura & Associates (1991) (Section 5.5). This revised estimate results from a lower estimate for the dry deposition of nitrogen-containing species (Sections 5.2 and 5.1).

Compared to other estimates of nitrogen loadings to the Bays, direct atmospheric deposition is a small component of total loading. Menzie-Cura & Associates (1991) estimated that discharges (rivers, sewers, and industrial sources) and storm runoff contribute 23–31 Gg N/year¹ to the Bays. This research estimates that 2 Gg N/year of nitrogen are deposited directly from the atmosphere (Section 5.3), which constitutes 6–8% of total direct loadings (discharge, runoff, and deposition).

The ramifications of atmospheric deposition, however, are more complex. First, since deposition occurs over the entire surface area of the Bays, it differs in nature from other sources of direct loading, which may impact local areas near points of discharge. Second, within the Bays, direct loadings play only a partial role in the overall nitrogen budget, which is also influenced by the import of water-borne nitrogen from the Gulf of Maine.

Finally, atmospheric deposition is of immediate importance to the seasonal nutrient uptake of the biologically-active surface-layer. Viewed from this perspective, direct atmospheric deposition is judged to be responsible for 2% of the surface-layer nitrogen budget (Section 5.5). This value

¹ 1 Gg N = 10⁹ g nitrogen

may understate the role of atmospheric deposition somewhat since it is derived for the winter season when nitrogen concentrations (and hence throughput) are largest in the Bays. Table 10 indicates swings of 10–40 in seasonal nitrate and nitrite concentrations in the Bays, and during the summer months, atmospheric deposition may serve as an important source of nutrients.² Consideration of only direct deposition to water also underestimates the total role of atmospheric deposition since some portion of the nitrogen deposited to lands within the Bays' watershed will subsequently be transported to the Bays.

2 Role of atmospheric deposition of nitrogen species

Menzie-Cura & Associates' (1991) estimate that 5–16% of nitrogen loading to the Massachusetts Bays is derived from atmospheric deposition must be interpreted carefully. In addition to atmospheric deposition, Menzie-Cura & Associates (1991) evaluated discharges from rivers, groundwater, coastal point sources (including publicly-owned treatment works), and coastal runoff. For two reasons, however, these loadings do not reflect the relative contribution of atmospheric deposition to the total amount of nitrogen present in the surface layer of the Bays. First, the estimates do not include nitrogen compounds convected within the water column from the Gulf of Maine. Second, the loading estimates do not account for the vertical distribution of nitrogen within the Bays. For much of the year, surface-layer concentrations of species such as nitrate are lower than concentrations deeper within the water column. This gradient is primarily a consequence of nutrient-consuming biosynthesis that is most significant in the surface-layer. Consequently, atmospheric deposition contributes nitrogen-containing compounds directly into region where they are in greatest demand (the surface-layer).

Thus, a more meaningful estimate of the importance of atmospheric deposition can be derived by comparing the flux of atmospheric deposition to the total nitrogen budget within the surface layer. The latter component has been investigated by Becker (1992), who has estimated the total amounts of nitrogen species present in the Bays. A rough estimate of the rate at which nitrogen moves through the surface layer can be estimated by dividing the total amount of nitrogen in the surface layer by a characteristic residence time for water within the Bays. Geyer *et al.* (as referenced in Becker, 1992) determined an average residence time of 20–50 days for the Bays.

Residence times reflect the rates at which water masses move through the Bays. Nitrogen, however, is removed from the surface layer both by physical transport and by biogeochemical processes. In order to make a relevant comparison of sources of nitrogen to the Bays,

² The average concentration of nitrogen in precipitation is 20 μM , which is considerably greater than most of the concentrations listed in Table 10. This difference is diluted, however, by the fact that precipitation is intermittent, and not continuous, to the surface layer.

biogeochemical losses must be taken into account so that the physical residence time of the water also reflects the residence time of nitrogen species. For this purpose, the most relevant measurements of the nitrogen content within the surface layer are those taken when (1) the nitrogen content is the greatest (indicative of minimal biologic activity) and (2) nitrogen concentrations in the surface layer are similar to those in deeper layers (indicative of limited vertical stratification) (Kelly, 1993). Within the available data, such conditions were found in the late winter/early spring, when a maximum of 770×10^6 moles of nitrogen was estimated (from measurements) to be contained within the top 20 meters of the Bays (Becker, 1992). Assuming a characteristic residence time of 35 days, the maximum rate of nitrogen throughput in the upper 20 m of the Bays is 0.31 Gg N/day. The Menzie-Cura & Associates estimates of atmospheric deposition, adjusted to reflect the surface area considered by Becker (1992),³ range from 0.0041 to 0.011 Gg N/day. With these values, atmospheric deposition would account for 1–4% of the total nitrogen budget within the surface-layer of the Bays. Percentages would be much greater, however, in summer months when the nitrogen content of surface waters is at a minimum level.

Estimates of the relative contribution of atmospheric deposition to the nitrogen budget are subject to uncertainties in both the nitrogen flux within the surface layer and the rate of nitrogen deposition. As stated above, the purpose of this work is to investigate the latter component in greater detail. The findings of this investigation are presented below.

3 Atmospheric deposition of nitrogen: Modes and species evaluated

Direct deposition of nitrogen from the atmosphere to the Massachusetts Bays occurs *via* two modes. Wet deposition accounts for nitrogen compounds that are delivered to the Bays in precipitation, while dry deposition includes nitrogen compounds that are contributed by (1) particles that settle onto and are retained within the surface layer of the water and (2) gases that dissolve into the water layer.

Numerous nitrogen-containing chemical species may be deposited *via* each of the two modes. Based upon many years of measurements at numerous locations within the United States (NAPAP, 1990), the principal inorganic species of importance in wet deposition are nitrate NO_3^- and ammonium (NH_4^+) ions (although significant levels of organic nitrates may also be deposited in precipitation). Dry deposition, however, can encompass a greater number of species, which can deposit as gases or aerosols (particle-bound). A recent review (Duce *et al.*, 1991) identifies the species of greatest importance. Gases include ammonia (NH_3); oxides of nitrogen (NO and NO_2); and nitric acid (HNO_3) and volatile organic nitrates. Aerosol forms are dominated by NO_3^-

³ Menzie-Cura & Associates (1992) used a surface area of 3700 km² for the Bays, while Becker (1992) used a surface area of 3428 km².

and NH_4^+ . All of these species are considered for dry deposition. Duce et al. (1991) also discuss the potential importance of organic species that contain nitrogen such as amines and amino acids. The paucity and uncertainty of relevant data, however, preclude the assessment of these species. Table 1 summarizes the species that are considered.

Table 1 Species evaluated for deposition of nitrogen to the Massachusetts Bays

Wet deposition	Dry deposition	
	Gases	Aerosols
NO ₃ ⁻ NH ₄ ⁺	NO NO ₂ HNO ₃ volatile organic nitrates NH ₃	NO ₃ ⁻ NH ₄ ⁺

4 Wet deposition

Menzie-Cura & Associates (1991) estimated the annual rate of wet deposition of nitrogen to the Massachusetts Bays as the product of the nitrogen concentration in precipitation and the annual average depth of precipitation. A range of 200–479 µg/l was considered for the nitrogen concentration in precipitation, and a value of 1.1 m was used for the average depth of precipitation. Multiplied together and scaled to units of kg/ha,⁴ these parameters correspond to a range of 2.2–4.8 kg N/ha-year.

In this section, more detailed estimates of wet nitrogen deposition are presented that consider (1) multiple years of data, (2) deposition measurements obtained on a weekly basis, and (3) nitrate and ammonium ions independently. These elaborations provide better estimates of year-to-year variability in wet deposition and differentiate the relative importance of NO₃⁻ and NH₄⁺.

The National Acid Deposition Program (NADP) measures the wet deposition of the major ionic constituents in precipitation (including NO₃⁻ and NH₄⁺) at a network of monitors across the United States. Monitors in Massachusetts are located at Truro (on Cape Cod),⁵ in the central portion of the state near the Quabbin Reservoir, and in the eastern portion of the state near the city of Waltham.

⁴ 1 ha = 1 hectare = 100 m × 100 m = 10⁴ m².

⁵ One of the two deposition monitors in the University of Massachusetts study was located near the NADP collector at Truro.

Wet deposition measurements of NO_3^- and NH_4^+ were obtained from the NADP for the three Massachusetts sites plus an additional site in Maine (NADP, 1992), which, because of its coastal location, was considered of possible relevance to the Massachusetts Bays.

The names of the monitoring stations and periods of data collection are listed in Table 2. Note that two site identifiers are included for the Maine monitor because it was moved a short distance in 1981. The locations of ME98 and ME99 are very close to each other, and they cover complementary sampling periods (ME98 is a continuation of ME99). Consequently, data collected at the two sites are simply combined and treated as continuous.

NADP collects wet deposition samples on a weekly basis. Computer programs were written to read and stratify the NADP into monthly and annual summaries. Further analysis and plotting of the results has been performed in Quattro Pro spreadsheets. The data files were used essentially as received from NADP, excepting several cases where sampling was initiated or discontinued in the middle of a month. In these cases, dummy records (containing no data) were added to the NADP data file to complete the length of the period (*i.e.*, the remainder of the month) so that the data analysis programs would function correctly.

Table 2 Locations of wet deposition monitors

Monitor Identifier	Location	Sampling Period
MA01	Truro, MA	12/81-3/92
MA08	Quabbin Reservoir, MA	3/82-3/92
MA13	East (Waltham), MA	2/82-3/92
ME98/ME99	Acadia National Park, ME	11/80-3/92

Weekly sampling periods often fall within two months, and for late December samples, can overlap the change of the year. NADP has assigned each sample to the specific month which includes the majority of the sampling period. These classifications are used to aggregate monthly data. The consequences of this approach typically produce months of 28 and 35 days duration. There is, however, no practical method to segregate the data on a precise monthly basis.

Annual summaries of the raw NADP data are presented in Table 3. Within each annual summary, two totals of days are included to assess data coverage. First, the total number of days in the annual summary is listed (N_{period}). Due to equipment malfunctions or the fact that the monitor may have been brought on-line in the middle of a year, sample collection may not have covered all days in the period. Also, occasional difficulties in sample collection, handling, and

laboratory analysis lead to the loss of some samples or the invalidation of results. The second sum (N_{data}) is the number of days for which laboratory-validated sample analyses have been obtained. The numbers of valid sampling days (N_{data}) are determined from validation codes provided by NADP. Specifically, valid, trace, and dry samples are all included in calculating N_{data} , while invalidated samples (*e.g.*, samples that collected both wet and dry deposition due to a failure of the wet/dry collector to close properly) are excluded.

By their definitions, $N_{\text{period}} \geq N_{\text{data}}$. These measures of data completeness have two implications with regard to the estimation of annual deposition values. First, in cases where N_{data} is smaller than N_{period} , the uncertainty over whether the data available are representative of wet deposition during the entire period generally increases as the difference between N_{data} and N_{period} becomes greater. Second, in cases of incomplete data records, for which N_{data} is less than N_{period} , the raw measured deposition amounts underestimate total wet deposition if any precipitation occurs during the portion of the period for which valid data are unavailable.

The total measured wet deposition values of NO_3^- and NH_4^+ that represent sums over the N_{data} days of validated data are presented in Table 3. Starting with these sums, two measures were implemented to derive the best reliable estimates of annual wet deposition. First, as suggested by NADP (1992), annual sums were considered only if validated data were available for more than 75% of the period (*i.e.*, $N_{\text{data}}/N_{\text{period}} > 0.75$).⁶ Second, in cases where N_{data} is sufficient to meet the first criterion but still smaller than N_{period} , the annual estimate of wet deposition is extrapolated from the sum of deposition measured in N_{data} days by multiplying by the precipitation depth that occurred in the entire period (N_{period} days) and dividing by the precipitation depth that fell in the days covered by valid measurements (N_{data} days). These precipitation depths, as derived from the NADP data, are presented in the final two columns of Table 3.⁷

Applying these criteria, the best estimates of wet NO_3^- and NH_4^+ deposition are graphed in Figure 1 and Figure 2, respectively. Within these figures, the four curves correspond to the four monitoring stations. On each curve, symbols indicate the yearly estimates of deposition.

⁶ A second criterion — that N_{data} cover 75% of a calendar year — was also applied in cases where the sampling period N_{sampling} did not cover an entire calendar year (*i.e.*, sampling was initiated mid-year, or samples were not collected over a significant portion of the year).

⁷ Within the NADP data, precipitation depths are available from rain gauge measurements (in addition to estimates derived from sample volume collection). Hence, rain amounts are typically available over periods in which valid samples were not collected. Extrapolation based on the ratio of precipitation depths implicitly assumes that equal volume-weighted concentrations of NO_3^- and NH_4^+ are present in sampled and unsampled precipitation.

Adjacent yearly estimates are connected by line segments, and breaks occur if a yearly estimate has been omitted due to the failure to meet the coverage criterion.

The year-to-year patterns in Figure 1 and Figure 2 suggest that wet deposition is similar at the two coastal sites (Truro and Acadia) and the site in eastern Massachusetts (near Waltham). Deposition fluxes are markedly higher, however, at the inland site in central Massachusetts (near the Quabbin Reservoir). Perhaps this persistent trend simply reflects a difference between inland and coastal regimes that is induced by meteorological factors. However, the goal of estimating deposition to the Bays is unaffected by this difference, since the deposition patterns at the three easternmost locations (those closest to the Bays) are quite similar.

Table 3 Annual measurements of wet deposition of nitrate (NO₃⁻) and ammonium (NH₄⁺)^a

Year (19xx)	Number of days:		Does year meet minimum coverage criteria?	Measured deposition (kg/ha) (total mass)		Precipitation depth (mm) summed over the days:	
	in the period (N _{period})	in the period with valid data (N _{data})		ammonium (NH ₄ ⁺)	nitrate (NO ₃ ⁻)	in the period (N _{period})	with valid data (N _{data})
Data collected at Truro, Massachusetts (NADP station MA01)							
81	28	14	No	0.044	0.708	76	76
82	371	355	Yes	1.780	13.830	1343	1292
83	364	239	No	0.949	8.319	1605	1170
84	365	330	Yes	1.336	8.870	1344	1216
85	363	272	No	1.472	9.715	1210	918
86	364	280	Yes	0.994	9.698	1190	831
87	183	112	No	0.228	2.823	580	249
88	370	299	Yes	0.513	7.469	964	635
89	364	343	Yes	1.341	10.797	1078	1011
90	364	350	Yes	1.148	8.784	1003	945
91	364	274	Yes	0.817	7.750	1027	599
Data collected near the Quabbin Reservoir, Massachusetts (NADP station MA08)							
82	309	252	No	1.628	12.136	1028	884
83	364	196	No	1.022	9.847	1509	606
84	365	250	No	1.467	12.369	1318	711
85	363	307	Yes	2.096	18.410	1092	960
86	364	315	Yes	1.507	14.193	1132	979
87	364	322	Yes	1.400	11.579	982	968
88	372	302	Yes	0.812	8.642	959	716
89	363	336	Yes	2.915	17.066	1347	1269
90	363	301	Yes	2.003	12.960	1423	1168
91	365	294	Yes	1.441	12.984	1402	1236

Table 3 Annual measurements of wet deposition of nitrate (NO₃⁻) and ammonium (NH₄⁺)^a

Year (19xx)	Number of days:		Does year meet minimum coverage criteria?	Measured deposition (kg/ha) (total mass)		Precipitation depth (mm) summed over the days:	
	in the period (N _{period})	in the period with valid data (N _{data})		ammonium (NH ₄ ⁺)	nitrate (NO ₃ ⁻)	in the period (N _{period})	with valid data (N _{data})
Data collected near Waltham, Massachusetts (NADP station MA13)							
82	336	330	Yes	1.294	11.226	962	959
83	364	350	Yes	1.292	10.753	1336	1297
84	365	344	Yes	1.311	10.496	1226	1185
85	363	321	Yes	1.326	13.625	920	875
86	364	350	Yes	1.671	11.863	1075	1039
87	364	336	Yes	1.075	10.361	1028	984
88	371	350	Yes	1.071	10.283	929	900
89	364	350	Yes	1.673	13.636	1097	1084
90	365	330	Yes	1.477	11.954	1316	1197
91	363	314	Yes	1.183	9.846	1046	935
Data collected at Acadia National Park, Maine (NADP station ME98/ME99)							
80	59	42	No	0.138	2.128	199	199
81	364	308	Yes	1.719	12.621	1264	1153
82	371	181	No	0.645	5.213	1225	575
83	364	266	No	1.195	7.505	1936	1393
84	365	323	Yes	1.540	9.520	1429	1236
85	363	300	Yes	1.278	9.439	1112	911
86	364	308	Yes	1.402	10.840	1397	1240
87	364	280	Yes	0.799	5.748	1286	851
88	371	336	Yes	0.743	8.604	1334	1150
89	364	330	Yes	1.687	11.420	1424	1303
90	364	344	Yes	1.906	13.336	1533	1404
91	364	343	Yes	1.036	8.840	1423	1311

^a Deposition estimates are presented to a greater degree of precision than are justified by the uncertainty in the data. Estimates are probably accurate to two significant figures. Greater precision is provided for readers who wish to reproduce calculations.

This similarity is also demonstrated by the statistical summaries of annual deposition that are contained in Table 4. NO_3^- and NH_4^+ deposition fluxes, when averaged over multiple years, are very similar for the Truro and Waltham sites, which are the closest monitoring locations to the Massachusetts Bays. At the Acadia site, the NO_3^- deposition rate is very similar to the values measured at Truro and Waltham, but the NH_4^+ deposition rate is slightly higher, perhaps reflecting a greater influence of local emissions of ammonia.⁸ As apparent by eye in Figure 1 and Figure 2, however, deposition of both species at the Quabbin site are greater than at the other locations.

Figure 1 and Figure 2 illustrate year-to-year variability in wet deposition fluxes. Consequently, the annual deposition of each ion may be expected to be higher in some years and lower in others, and thus will be of varying importance to the total nitrogen budget within the surface water of the Massachusetts Bays. The degree of interannual variability is smaller for nitrate deposition than for ammonium deposition. As a percentage of the annual mean value, one standard deviation represents 11–20% of NO_3^- deposition and 15–33% of NH_4^+ deposition (Table 4). Also, there is general trend for nitrate and ammonium depositions to vary with each other, as shown in the scatter plot of Figure 3. Expressed on a molar basis, ammonium contributes roughly 30% as much nitrogen as nitrate *via* wet deposition on average for the four monitoring sites.

The rough correlation between NO_3^- and NH_4^+ depositions suggests that the two ions originate from common, but perhaps broad, geographic areas. The tendency for all four sites to follow a similar pattern, combined with the well-established importance of long-range transport (100 km and greater) in NO_3^- and NH_4^+ deposition (NAPAP, 1990), suggests that regional sources (New England and perhaps beyond) play an important role. Interannual differences most likely result from variability in synoptic meteorology, since similar time trends are observed at the four sites. In some cases, trends differ between sites (*e.g.*, 1985 deposition at the Quabbin site). Differences in trends may reflect the influence of local sources, or might also be due to missing or non-representative data.

To estimate wet deposition rates to the Massachusetts Bays, deposition measurements at the Truro site are used because (1) the site is located directly on Massachusetts Bay and (2) the deposition pattern is similar to those of the other nearby sites (Waltham and Acadia). Total deposition rates are calculated as the sum of the nitrogen contributed by both NO_3^- and NH_4^+ deposition in a single year.⁹ For the seven valid years of data at the Truro site, the average

⁸ Reviewers' comments indicate that the Acadia monitor is situated over a leaching field, which may provide a local source of ammonia emissions.

⁹ The statistical values in Table 4, which separately describe NO_3^- and NH_4^+ depositions, cannot be weighted and summed to provide the total nitrogen deposition estimates in Table 5,

nitrogen annual deposition from these two species is 3.8 kg N/ha, with a maximum value of 4.7 kg N/ha and a minimum value of 3.1 kg N/ha. These estimates are summarized in Table 5, where they are presented alongside the estimates derived by Menzie-Cura & Associates (1991). Although the magnitude of the estimates remains similar, the range of annual depositions derived in this analysis is smaller than that estimated by Menzie-Cura and Associates. This difference results from the detailed accounting of weekly *deposition* measurements that was pursued herein, as contrasted with previous calculations derived from a range of concentrations in precipitation multiplied by annual precipitation amounts. The latter method neglects the tendency for concentration to vary inversely with rainfall amount, and hence overestimates the importance of high and low concentration measurements in estimating annual deposition.

As a final note on wet deposition, it must be emphasized that wet deposition does exhibit seasonal differences (as previously noted by Menzie-Cura & Associates, 1991). Figure 4 illustrates the seasonal nature of NO_3^- and NH_4^+ deposition. In this plot, which is constructed from data at the Truro site alone, monthly deposition rates are depicted. A straight line is drawn at the value of the annual-average deposition rate. Monthly values above the horizontal line indicate a deposition rate greater than the annual-average rate, and *vice-versa*. For both the NO_3^- and NH_4^+ ions, the highest monthly depositions occur in the spring months. A greater degree of variability is shown by the NH_4^+ ion, which distinctly peaks in May. This peak reflects both higher-than-average precipitation and enhanced emissions (possibly from agricultural activities such as the application/spreading of fertilizer).

because these are derived from year-to-year sums of the two ions and minima and maxima may occur in different years.

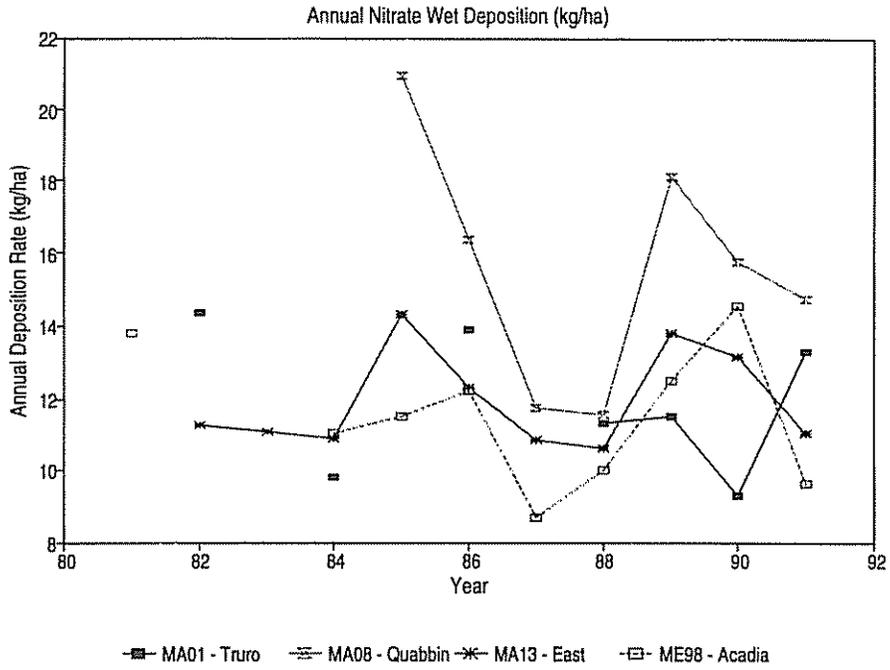


Figure 1 Annual estimates of wet deposition of nitrate (NO_3^-) (kg/ha)

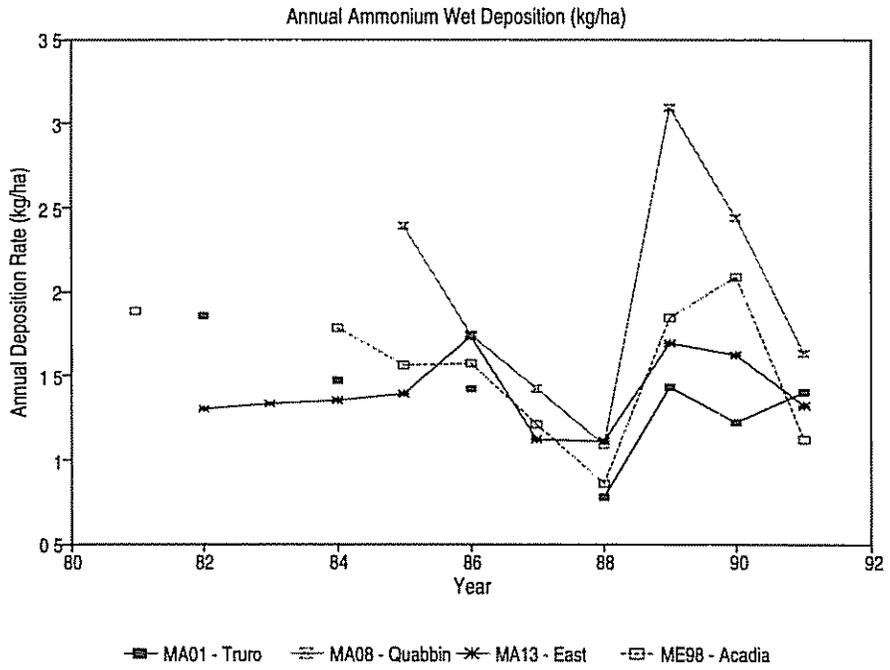


Figure 2 Annual estimates of wet deposition of ammonium (NH_4^+) (kg/ha)

Table 4 Statistical summary of annual estimates of wet deposition^a

Monitoring Station (NADP Identifier)	Number of years that satisfy the coverage criterion	Nitrate deposition (kg NO ₃ ⁻ /ha)			Ammonium deposition (kg NH ₄ ⁺ /ha)			NO ₃ ⁻ /NH ₄ ⁺ deposition ratio (molar basis)	
		Mean	Standard deviation	Maximum	Mean	Standard deviation	Maximum		
Truro (MA01)	7	11.93	1.83	14.38	1.37	0.30	0.78	1.85	2.5
Quabbin (MA08)	7	15.61	3.10	20.93	1.97	0.64	1.09	3.09	2.3
Waltham (MA13)	10	11.92	1.30	14.32	1.40	0.21	1.10	1.73	2.5
Acadia (ME98/ME99)	9	11.54	1.84	14.56	1.55	0.38	0.86	2.08	2.2

^a Deposition estimates are given to 3–4 digits of precision so that calculations may be reproduced. Deposition estimates are not accurate to this degree, but rather to 1–2 significant figures

Table 5 Estimates of annual wet nitrogen deposition (kg N/ha)

	Estimates from seven years of data collected at Truro, Massachusetts	Estimates from Menzie-Cura & Associates (1991)
Minimum	3.1	2.2
Best estimate	3.8	—
Maximum	4.7	4.8

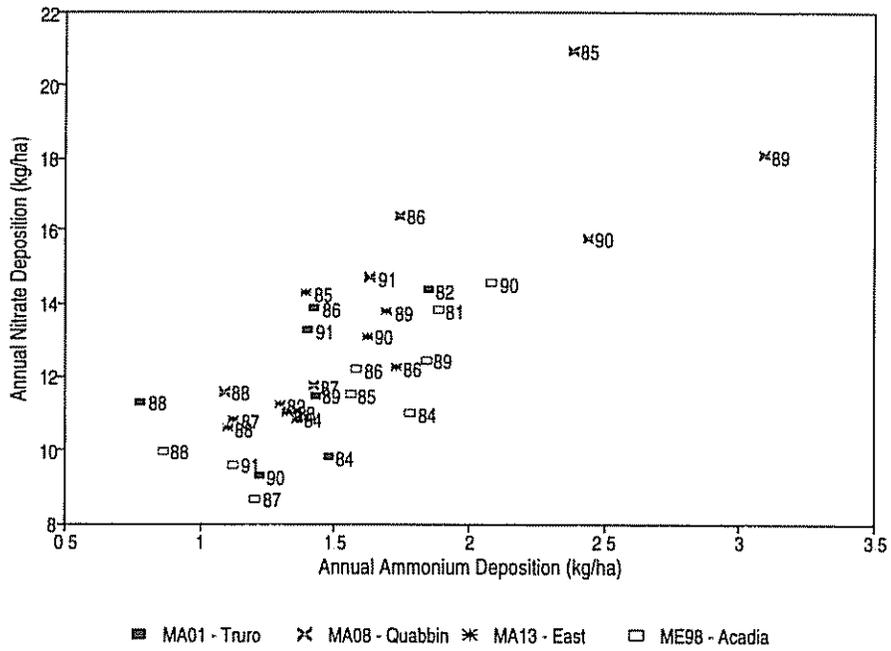


Figure 3 NH_4^+ and NO_3^- scatter plot. Annual deposition rates indicated by year for each species.

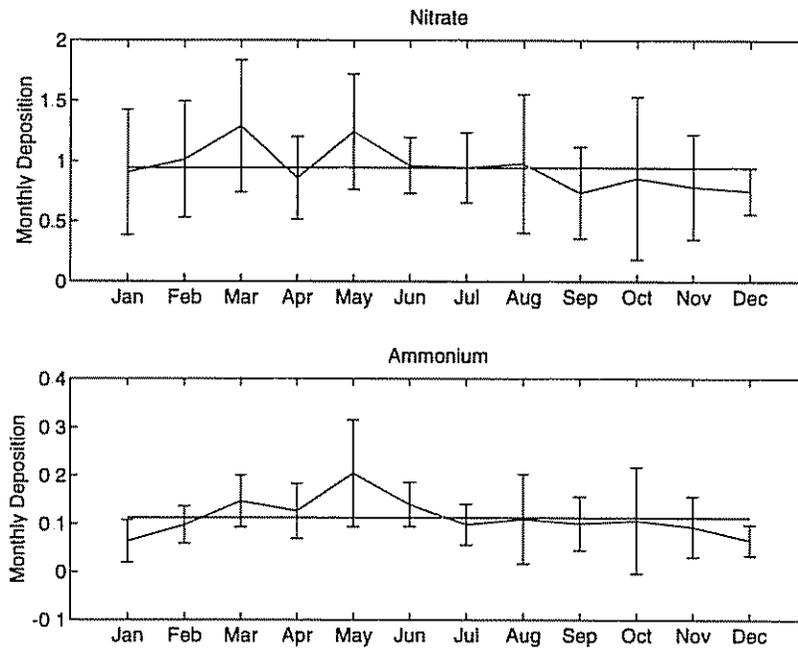


Figure 4 Seasonal patterns of wet deposition of NO_3^- and NH_4^+ . Vertical bars indicate standard errors of the mean monthly ratios.

5 Dry deposition

Compared with wet deposition, estimates of dry deposition are much more uncertain, largely because experimental techniques to measure dry deposition are fraught with uncertainty (NAPAP, 1990). In short, it is difficult to design a practical device to measure dry deposition that (1) does not introduce aerodynamic interference and/or (2) simulates the surface-layer resistance critical to the deposition of particles and gases.¹⁰

In the absence of direct measurements, dry deposition flux is traditionally estimated as the product of an airborne concentration and a deposition velocity:

$$D_d = c v_d s \quad (1)$$

where

- D_d is the rate of dry deposition (kg/ha/yr),
- c is the mass concentration of the species in air ($\mu\text{g}/\text{m}^3$),
- v_d is the deposition velocity (cm/s), and
- s is a units conversion factor of $3.16 \text{ kg}\cdot\text{m}^3\cdot\text{s}/\mu\text{g}\cdot\text{ha}\cdot\text{cm}\cdot\text{yr}$.¹¹

Menzie-Cura & Associates (1991) estimated that annual dry deposition ranged from 2.1 to 6.9 kg/ha, based upon atmospheric concentrations of 1.7–5.5 $\mu\text{g}/\text{m}^3$ (Galloway *et al.*, 1984; and Galloway and Whelpdale, 1987) and a deposition velocity of 0.4 cm/s (Galloway and Whelpdale, 1987). Particle-borne (aerosol) and gaseous nitrogen-containing species were not distinguished.

As discussed in Section 3, however, the characteristics of dry deposition of nitrogen differ among species. Consequently, a comprehensive literature search was conducted to identify the nitrogen-containing species of interest. For this purpose, the best source of information identified was the review article by Duce *et al.* (1991), from which the list of species in Table 1 is principally derived. The dry deposition of aerosol and gaseous species are considered separately.

¹⁰ These considerations are of prime importance to the dry deposition measurements of trace metals species (see the main portion of this study).

¹¹ The value of 3.16 (kg N)-s/ppb-ha-cm-yr for s is derived as:

$$s = \frac{365.25 \text{ dy}}{\text{yr}} \times \frac{24 \text{ hr}}{\text{dy}} \times \frac{3600 \text{ s}}{\text{hr}} \times \frac{\text{kg}}{10^9 \mu\text{g}} \times \frac{10^4 \text{ m}^2}{\text{ha}} \times \frac{\text{m}}{100 \text{ cm}}$$

5.1 Dry deposition of aerosol species

Dry deposition of aerosol species is calculated by Equation (1), which requires estimates of the mass concentration in air and the deposition velocity. Data to estimate NO_3^- deposition have been summarized by Galloway *et al.* (1984), Galloway and Whelpdale (1987), and Duce *et al.* (1991). Inland concentrations of $0.14 \mu\text{g N/m}^3$ and $0.05 \mu\text{g N/m}^3$ were measured by the Inhalable Particle network and the SURE experiment, respectively (Galloway *et al.*, 1984). Off-shore measurements are somewhat larger. An NO_3^- concentration of $0.41 \mu\text{g N/m}^3$ was measured at 43 W, 60 N, but closer to shore, $0.21 \mu\text{g N/m}^3 \text{NO}_3^-$ was observed (Galloway and Whelpdale, 1987). Based upon a review of the available data, Duce *et al.* (1991) assigned an average concentration of $0.29 \mu\text{g N/m}^3$ to coastal locations along the eastern seaboard.

In consideration of these values, a NO_3^- concentration of $0.3 \mu\text{g N/m}^3$ is selected to estimate dry NO_3^- deposition to the Bays. This value is consistent with offshore measurements, rather than the lower values measured inland, to capture the influence of the urban Boston NO_x plume, which serves as a potential source of NO_3^- formation over the Bays.

Since nitrate aerosol is formed in the atmosphere, it is mostly found on small particles (NAPAP, 1990). Duce *et al.* (1991) suggest a deposition velocity of 0.3 cm/s that is appropriate for particles of the order of one micron in diameter. In the marine environment, nitrate tends to deposit on seasalt particles that are characteristically several microns in size. Consequently, a somewhat higher deposition velocity is possible, especially given the interaction of seasalt with the urban Boston NO_x plume. Duce *et al.* (1991) consider a range of deposition velocities from 0.2 to 1.0 cm/s . For conditions across the Bays, the high-end value of this range is likely to be more appropriate. Consequently, a deposition velocity of 0.8 cm/s is adopted as a best estimate.

Measurements of ammonium aerosol are sparse. In their review, Duce *et al.* (1991) fail to identify any measurements appropriate to coastal locations in eastern North America. Recent measurements of NH_4^+ have been taken by the Northeast States for Coordinated Air Use Management at a site in central Massachusetts. These data, which are described in Schichtel and Husar (1991), yield an annual-average NH_4^+ concentration of $0.7 \mu\text{g N/m}^3$. Duce *et al.* (1991) suggest a deposition velocity of 0.1 cm/s based upon the observation that NH_4^+ is found in very small (accumulation mode) particle sizes.

A summary of nitrogen deposition from aerosols is presented in Table 6. The estimated deposition flux of NO_3^- is roughly $3\frac{1}{2}$ times that of NH_4^+ , largely due to the significantly higher value used for deposition velocity.

Table 6 Estimates of dry nitrogen deposition due to aerosols

Species	Concentration c ($\mu\text{g N/m}^3$)	Deposition velocity v_d (cm/s)	Deposition flux predicted by Equation (1) (kg N/ha-yr)
Nitrate (NO_3^-)	0.3	0.8	0.76
Ammonium (NH_4^+)	0.7	0.1	0.22
Total dry nitrogen deposition of aerosols			0.98

5.2 Dry deposition of gases

In estimating the dry deposition of gases, it is more convenient to rewrite Equation (1) in terms of the molar (e.g., parts per billion, or ppb) concentration in air. For nitrogen-containing species, the dry deposition flux of gases can be estimated as:

$$D_d = c_a v_d f \quad (2)$$

where

- D_d is the rate of dry deposition of nitrogen (kg N/ha/yr),
- c_a is the concentration of the nitrogen-containing species in air (ppb),
- v_d is the deposition velocity (cm/s), and
- f is a units conversion factor of 1.81 (kg N)-s/ppb-ha-cm-yr.¹²

Duce *et al.* (1991) also emphasize that the dry deposition of gases to water is a mass transfer process that in some circumstances is inadequately described by Equation (2). In these cases, dry deposition is better expressed as:

$$D_d = K [c_a - c_{af}] f \quad (3)$$

¹² The value of 1.81 (kg N)-s/ppb-ha-cm-yr for f is derived as:

$$f = \frac{365.25 \text{ dy}}{\text{yr}} \times \frac{24 \text{ hr}}{\text{dy}} \times \frac{3600 \text{ s}}{\text{hr}} \times \frac{\text{kg}}{10^9 \mu\text{g}} \times \frac{10^4 \text{ m}^2}{\text{ha}} \times \frac{\text{m}}{100 \text{ cm}} \times \frac{0.573 \mu\text{g N/m}^3}{\text{ppb}}$$

where

- K is a mass transfer velocity (cm/s), which depends upon aerodynamic factors and chemical properties,
 c_{af} is the pollutant concentration in the air-film layer (ppb) just above the surface of the water, which is influenced by the volatility of the chemical and its dynamic behavior in the water layer, and

D_d , c_{af} , and f are defined as in Equation (2). Although the functional dependencies of K and c_{af} can become quite complex, the simple form of Equation (3) differs from Equation (2) in a fundamental manner. Applied to the Massachusetts Bays, Equation (2) describes a one-way transfer of material to the water. Equation (3), however, allows for pollutant transfer in either direction because D_d is modeled as proportional to a difference in concentrations. Thus, both the direction and the rate of mass transfer depend upon the relative abundance of the chemical in the air and the water. For completeness, Equation (3) is used in preference to Equation (2) to estimate the deposition of gases. For most species, however, the inclusion of the film-layer resistance is inconsequential to overall deposition estimates, as discussed in 5.4.

The mass transfer velocity K models the effective resistance to deposition across the air-water interface. Duce et al. (1991) present an empirical relationship for estimating K that combines resistance terms from both the air and water phases:

$$K = \frac{100}{\frac{770 + 45 M_w^{1/3}}{u} + \frac{H}{R T \alpha \beta k_w}} \quad (4)$$

where

- M_w is the molecular weight of the pollutant (g/g-mole),
 u is the wind speed (m/s),
 H is the chemical-specific Henry's Law Constant (atm-m³/g-mole),
 R is the universal gas constant, equal to 8.205×10^{-5} atm-m³/g-mole-K,
 T is temperature (K),
 k_w is a water resistance parameter (cm/hr),
 β is a conversion factor of 1 m-hr per 360,000 cm-s, and
 α is a deposition enhancement factor due to chemical reactivity.

The water resistance parameter is expressed as an empirical function of wind speed (Duce et al., 1991, based on Liss and Merlivat, 1986):

$$\begin{aligned}
 k_w &= 0.17 u && \text{for } u \leq 3.6 \text{ m/s} \\
 k_w &= 2.85 u - 9.65 && \text{for } 3.6 \leq u \leq 13 \text{ m/s} \\
 k_w &= 5.9 u - 49.3 && \text{for } u > 13 \text{ m/s.}
 \end{aligned}
 \tag{5}$$

5.2.1 Chemical-specific mass transfer velocities

Equation (4) is used to estimate chemical-specific mass transfer velocities. For simplicity, volatile organic nitrates are not distinguished from HNO₃ (consistent with Duce *et al.*, 1991).¹³ Due to a lack of data, the value of α is assumed to be unity for the gases of interest, as recommended by Duce *et al.* (1991). Table 7 lists values of K that are estimated using (1) the average wind speed u of 12.5 mph (5.6 m/s) for Boston (U.S. Bureau of the Census, 1991), (2) chemical-specific property values of H and M_w (as listed in Table 7), and (3) a temperature T of 298 K (which is consistent with the values of H). The predicted values of K vary for the four gases. Aerodynamic resistance is the principal factor that controls the dry deposition velocity for HNO₃ and NH₃, whereas low solubility, as reflected in the Henry's Law constants, controls and greatly limits the deposition velocities of NO and NO₂.

Table 7 Estimates of mass transfer velocities (K) for gases of interest

Chemical Species	Molecular weight M_w (g/g-mole)	Henry's Law Constant H (atm-m ³ /g-mole) [at 298 K, from Seinfeld (1986)]	Predicted mass transfer velocity K (cm/s)
NO	30	0.53	0.00008
NO ₂	46	0.11	0.0004
HNO ₃ /volatile organic nitrates (modeled as HNO ₃)	63	4.8×10^{-9}	0.59
NH ₃	17	1.6×10^{-5}	0.51

¹³ This assumption probably introduces little uncertainty, since atmospheric concentrations of organic nitrates appear to be smaller than those of HNO₃ (see section 5.2.2).

5.2.2 Concentrations of nitrogen-containing species

The second goal of the literature review of dry deposition was to identify appropriate atmospheric concentrations for each of the species listed in Table 1. Gases of interest include NO_x ($\text{NO} + \text{NO}_2$), HNO_3 (nitric acid), volatile NO_3^- , organic nitrate compounds (which include compounds such as peroxyacetyl nitrate [PAN]), and ammonia.

Separate consideration of each of the gases of interest is difficult for two reasons. First, the data to assess some of the species are sparse in general, and in some cases, not available for locations near the Massachusetts Bays. Second, the analytical measurement techniques often are not specific to individual species. As examples, most analytical techniques cannot distinguish between HNO_3 and volatile organic nitrates (Duce *et al.*, 1991). Reported concentrations of NO_2 (as measured by chemiluminescence) typically reflect total NO_x ($\text{NO}_2 + \text{NO}$) due to regulatory requirements. NO_x measurements may also be sensitive to interferences from HNO_3 and volatile organic nitrates such as peroxyacetyl nitrate (PAN) (Misanchuk *et al.*, 1987). Many early measurements of NH_3 are thought to be biased high because of off-gassing of NH_4^+ from front-end filters (Duce *et al.*, 1991). Consequently, available measurements of nitrogen-containing species must be considered with caution.

Identification of representative NO_x concentrations for assessing deposition to the Massachusetts Bays is not trivial for two reasons. First, comprehensive measurements over the Bays are unavailable. Second, there are at least three source/meteorological regimes that may be of importance to average NO_x concentrations: (1) the urban Boston area, in which NO_x concentrations are elevated due to concentrated anthropogenic emissions, (2) regional transport that accounts for NO_x sources distributed throughout eastern North America, and (3) sea breezes that convey air masses from over the ocean (which are presumably influenced by terrestrial emissions, but diluted because of mixing and chemical depletion).

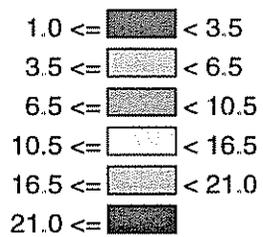
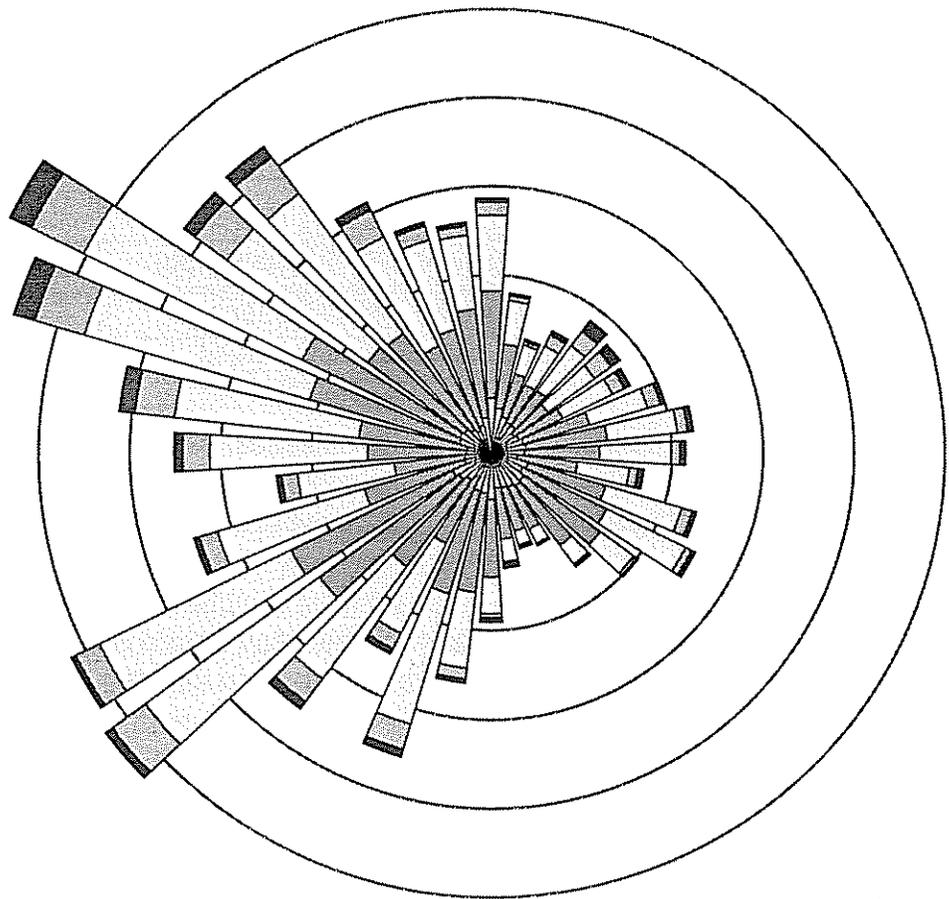
To account for these influences, an average NO_x concentration is constructed by weighting data appropriate to each of the three regimes. Urban NO_x is routinely measured at a number of locations in the Boston area. Annual average NO_x concentrations of 24.7 ppb¹⁴ (8 sites), 25.2 ppb (7 sites), and 24.9 ppb (7 sites) were measured at monitoring stations in Suffolk and Norfolk counties in 1990, 1991, and 1992, respectively (U.S. EPA, 1991; U.S. EPA, 1992; and U.S. EPA, 1993). These concentrations are elevated relative to NO_x concentrations measured elsewhere in Massachusetts. For comparison, annual-average concentrations of 9, 9, and 8 ppb have been measured at a monitoring site near the Quabbin Reservoir during 1990, 1991, and 1992, respectively (U.S. EPA, 1991; U.S. EPA, 1992; and U.S. EPA, 1993). Based on these data, a NO_x concentration of 25 ppb is assumed to characterize the urban Boston area.

¹⁴ For NO_x , 1 ppb (part-per-billion) is equal to $1.9 \mu\text{g}/\text{m}^3$ at standard atmospheric conditions.

The literature reports some historical measurements of NO_x that are relevant to the estimation of regional NO_x concentrations. A concentration of 9 ppb was measured in western Massachusetts in the 1977 EPRI-SURE experiment (as referenced in NAPAP, 1989). This value is consistent with recent NO_x measurements taken near the Quabbin Reservoir (as cited above). Galloway *et al.* (1984), in estimating the seaward flux of nitrogen from North America, assigned a ground-level NO_x concentration of 8 ppb for their region 5, which covered the eastern seaboard from New Hampshire through Delaware. In a review of this work, Galloway and Whelpdale (1987) assigned a surface-layer NO_x concentration of 11.6 ppb over coastal latitudes from 33 N to 43 N (approximately New Hampshire through South Carolina). Based upon these data, a NO_x concentration of 9 ppb is considered representative of regional concentrations in eastern North America.

Data to assess sea breeze contributions were collected by Misanchuk *et al.* (1987), who measured NO_x concentrations 50 km offshore of Cape Cod. These researchers found an average NO_x concentration of 2.9 ppb in the marine boundary layer, which is significantly lower than the land-based observations discussed above. The lower values probably reflect both the dilution of air masses that originated over land, the conversion of NO_x to aerosol nitrate, and the contribution of cleaner air masses from other regions.

In summary, concentrations of 25, 9, and 2.9 ppb are judged to be representative of total NO_x concentrations from urban, regional, and sea breeze influences, respectively. In weighting these values, it is assumed that their influence will scale roughly with the frequencies that winds originate from relevant areas. Figure 5 is a wind rose, which depicts the relative frequencies of hourly measurements of wind direction and wind speed at Logan International Airport. The length of each of the 36 petals indicates the total frequency of time that winds blow from the indicated direction, and divisions within each petal categorize the distribution of wind speeds. Qualitatively, Figure 5 demonstrates that the predominant winds in coastal Boston originate from the northwest and southwest. By convention, wind angles are measured from a northward azimuth in a clockwise direction such that angles of 0, 90, 180, 270, and 360 degrees indicate winds blowing from the north, east, south, west, and north, respectively. Using these conventions and considering the orientation of the Bays with respect to the three sources, ranges of wind directions are assigned to each source. These ranges are presented in Table 8 along with the frequency of winds that originate from these directions (derived from Figure 5). Using these data, a representative NO_x concentration of 9.8 ppb is estimated as a weighted-average of the contributions of the three sources.



Boston, MA (Logan Airport)

1984 - 1992 data

Wind speeds in knots

Calms: 0.7%

Isopleths at 2, 3, 4, and 5%

Figure 5 Wind rose of meteorological observations at Logan Airport, Boston, MA

Table 8 Estimation of average NO_x concentration in air over the Massachusetts Bays

Source of influence	Range of wind directions (degrees)	Frequency of winds from the assigned directions (see Figure 5)	Average NO _x concentration assigned to source (ppb)	NO _x concentration due to source (ppb)
Urban Boston	260–300	0.17	25	4.4
Regional	180–260, 300–360	0.50	9	4.5
Sea breeze	0–180	0.33	2.9	0.9
Total weighted-average NO _x concentration in air over the Bays (ppb)				9.8
Concentration of NO ₂ assumed for deposition estimates (ppb)				7.4
Concentration of NO ₂ assumed for deposition estimates (ppb)				2.4

To separately assess NO and NO₂, the NO fraction of NO_x is needed. Misanchuk *et al.* (1987) measured both NO and NO_x, which they measured at an average concentrations of 0.56 and 2.9 ppb, respectively, in the marine boundary layer. Based on these values, NO appears to constitute at least 20% of total NO_x in the offshore boundary layer. In urban locale, NO and NO₂ concentrations are about equal (Seinfeld, 1986). Since (1) most combustion-related NO_x is emitted in the form of NO and (2) the Bays are adjacent to the urban Boston area, the NO fraction of total NO_x in the air over the Bays is likely to be greater than the 20% value observed offshore. In view of the frequency that the Boston area is judged to influence NO_x concentrations in air over the Bays, a NO to total NO_x ratio of 0.25 is assumed as the best estimate for calculating deposition. The concentrations of 7.4 and 2.4 ppb for NO₂ and NO, respectively, that correspond to this distribution are listed in Table 8.

Information on nitric acid (HNO₃) and volatile organic nitrate concentrations in the atmosphere are scant. Duce *et al.* (1991) in a comprehensive review of available data, assume that HNO₃ (including volatile NO₃) constitutes 15% of total (aerosol) NO₃⁻. An HNO₃ concentration of 0.08 ppb can be estimated based on (1) this percentage and (2) the concentration of 0.3 μg N/m³ assumed for NO₃⁻ (section 5.1). Other volatile nitrates (such as PAN) may increase this total somewhat. Based on the few measurements discussed in Duce *et al.* (1991), organic nitrate concentrations are expected to be less significant than HNO₃. Based on these marine data, a total HNO₃/volatile organic nitrate concentration of 0.1 ppb appears appropriate.

HNO₃ measurements inland, however, suggest significantly higher concentrations may be appropriate for calculating the deposition flux to the Bays. Measurements taken as part of the National Dry Deposition Network (NDDN) suggest that HNO₃ concentrations are several times larger than NO₃⁻ concentrations, with measured HNO₃ concentrations of the order of 1 ppb (NAPAP, 1990). Such a concentration would be about ten times smaller than NO_x concentration of 9.8 ppb judged to be appropriate for the Bays. NO_x/HNO₃ ratios of the order of ten are

consistent with observations taken in urban regions (Seinfeld, 1986). Most of these data, however, were collected in filter packs that are known to overestimate HNO_3 due to the volatilization from filtered NO_3^- (Duce et al., 1991; NAPAP, 1990).

Total concentrations of HNO_3 and NO_3^- measured $0.7 \mu\text{g N/m}^3$ at a NDDN site in West Point, New York (NAPAP, 1990). Concentrations near urban Boston may be higher or lower than this value, depending upon the effect of local and regional sources of NO_x emissions and representative air masses affecting the Bays. As a first approximation, a similar value is assumed for the total concentration of both species. To be consistent with the NO_3^- concentration of $0.3 \mu\text{g N/m}^3$ estimated in section 5.1, an HNO_3 concentration of $0.4 \mu\text{g N/m}^3$, or 0.7 ppb, is implied. This value, which lies between the marine-based (0.1 ppb) and NDDN-based (~1 ppb) concentrations, is selected to assess HNO_3 deposition to the Bays. Due to the uncertainty of these estimates, no adjustment is made to include volatile organic nitrate species.

As further justification, an HNO_3 concentration of the order of 1 ppb is consistent with tropospheric NO_x chemistry. Reaction of NO_2 with hydroxyl ($\text{OH}\cdot$) radicals to form HNO_3 proceeds at a rate of $1.1 \times 10^{-11} \text{ cm}^3\text{-molecule/sec}$, and a typical $\text{OH}\cdot$ concentration is $10^6 \text{ molecules/cm}^3$ (Seinfeld, 1986). Coupled with an NO_2 concentration of 7.4 ppb (Table 8), an HNO_3 formation rate of $8 \times 10^{-5} \text{ ppb/s}$ can be calculated. A transport (residence) time of 12,000 s can be estimated as the average distance across the Bays (60 km)¹⁵ and a typical wind velocity of 5 m/s. Multiplied together, the product of the formation rate and the travel time is 0.96 ppb.

A typical atmospheric concentration of NH_3 is 1 ppb in the clean troposphere, but concentrations can be as high as 10–25 ppb in polluted regions (Seinfeld, 1986). A range of 1–5 ppb is typical of measurements taken in the eastern United States, with the closest measurements to Boston obtained at Whiteface Mountain in New York (0.3–5.5 ppb, with a median of 2.2 ppb) and Long Island, New York (1.9–4.8 ppb) (ATSDR, 1990). These measurements, however, are thought to overestimate actual NH_3 concentrations due to sampling difficulties (as discussed above). Duce et al. (1991) list significantly lower concentrations as typical for the marine atmosphere; high-end values of the order of 0.1 ppb appear appropriate for the open ocean. Given land-based emissions of ammonia, somewhat higher levels can be expected over the Bays. Based on these considerations, a representative value of 0.5 ppb is selected to estimate deposition.

Representative concentrations of the gases c_a considered are summarized in Table 9, along with air film-layer concentrations $c_{a,f}$, which are described in the following section.

¹⁵ Calculated as the square root of the approximate area of the Bays ($3,600 \text{ km}^2$).

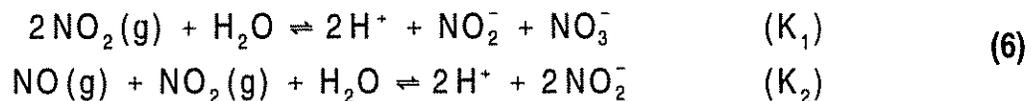
Table 9 Representative concentrations of gases of interest

Chemical Species	Ambient concentration c_a (ppb)	Air film-layer concentration c_{af} (ppb)	Notes
NO	2.4	0.16	See Table 8
NO ₂	7.4	3.1×10^{-7}	See Table 8
HNO ₃ /volatile organic nitrates (modeled as HNO ₃)	0.7	0	
NH ₃	0.5	0.33	

5.2.3 Estimates of film-layer concentrations

The application of Equation (3) requires the determination of film-layer concentrations, which involves the consideration of aqueous-phase chemistry. Equilibrium methods to estimate film-layer concentrations of NO, NO₂, and NH₃ are described in Seinfeld (1986).

For a system in which gaseous NO_x is present over water, nitrate and nitrite ions are the dominant nitrogen-containing species in the aqueous phase. Seinfeld (1986) summarizes the system with two overall reactions and equilibrium constants:



where

- NO(g) and NO₂(g) are the respective concentrations of NO and NO₂ in the thin film of air above the water (atm), which are the values of c_{af} for use in Equation (3),
- NO₂⁻ and NO₃⁻ are the dissolved concentrations of nitrite and nitrate ions in the water column (M = mole/l),
- H⁺ and H₂O are the concentrations of dissociated hydrogen ions and water (M), respectively, in the aqueous phase, and
- K₁ and K₂ are the equilibrium constants for the two reactions, equal to 244 and $3.28 \times 10^{-5} \text{ M}^4/\text{atm}^2$, respectively, at 298 K.

Assuming equilibrium conditions, expressions can be written for the film-layer concentrations in terms of the aqueous concentrations and the equilibrium constants:

$$[\text{NO}_2(\text{g})] = \sqrt{\frac{[\text{H}^+]^2 [\text{NO}_2^-] [\text{NO}_3^-]}{K_1}} \quad (7)$$

$$[\text{NO}(\text{g})] = \frac{[\text{H}^+]^2 [\text{NO}_2^-]^2}{K_2 [\text{NO}_2(\text{g})]}$$

where brackets have been added to denote species concentrations.

Data collected by Loder (1993) and Becker (1992) in a study sponsored by the Massachusetts Bays Program (Scott, 1993) are used to estimate the aqueous concentrations of nitrite and nitrate in the Bays. Within the surface layer, these ions exhibit a strong seasonal trend due to the nutrient cycle, and concentrations are markedly depleted in the summer months. Consequently, the use of annual averages is inappropriate. Based upon gross similarities in the surface-layer data, three time periods are considered: spring/fall, summer, and winter. The sample collection dates that correspond to these categories are listed in Table 10. Only samples from depths of 1 m or shallower were considered to capture surface conditions. The number of surface samples that meet this surface-water constraint are listed in the third column of Table 10.

The remaining columns of Table 10 present means and standard deviations of three variables that are constructed over the surface samples for each season: the sum of nitrite and nitrate ion concentrations, the ratio of nitrite to the sum of nitrite and nitrate, and the ammonium ion concentration. The data in Table 10 clearly demonstrate a seasonal trend. The mean concentration of nitrite+nitrate is more than 40 times higher in the winter season than it is in the summer, during which time the supply is depleted by biologic activity. Also, the relative abundance of nitrite is inversely proportional to the total nitrite+nitrate concentration, with the fraction increasing from a mean value of 0.04 in the winter season to a mean value of 0.15 in the summer season. Ammonium ion concentrations also exhibit a seasonal profile, but the disparity between the summer and winter seasons is much less severe than that of nitrite+nitrate.

For many of the parameters in Table 10, standard deviations exceed mean values. This degree of scatter is due to the influence of high concentrations (relative to the mean value) that are found in the distribution of samples within each season.

Table 10 Summary of surface water concentrations of nitrogen-containing species in the Massachusetts Bays [analysis of data collected by Loder (1993)]

Season	Data collection times	Number of surface (≤ 1 m) samples	Sum of nitrite and nitrate concentrations (μM)		Ratio of nitrite to total		Ammonium concentration (μM)	
			($[\text{NO}_2^-] + [\text{NO}_3^-]$)		$\frac{[\text{NO}_2^-]}{[\text{NO}_3^-] + [\text{NO}_2^-]}$			
			Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Spring/ Fall	Late April, 1990 Late September, 1990 Mid October, 1990 Late April, 1991	109	0.70	1.0	0.10	0.16	0.75	1.2
Summer	Late June, 1990 Late July, 1990 Mid June, 1991	42	0.15	0.17	0.15	0.27	0.42	1.0
Winter	Mid April, 1990 Early February, 1991 Late March, 1991	88	6.9	3.2	0.043	0.042	0.91	1.7

The final piece of information needed to estimate film-layer concentrations of NO and NO₂ gases is the hydrogen ion concentration, which is related to the standard water quality parameter pH by:

$$\text{pH} = -\log_{10}([\text{H}^+]) \quad (8)$$

The pH of ocean water typically ranges from 7 to 8 (Weast, 1978), with the upper-end of the range (pH = 8) representative of open waters. pH values measured in Boston Harbor range from a maximum of 8.4 in the early spring to a minimum of 7.5 in the summer (Robinson *et al.*, 1990). The Massachusetts Bays as a whole, however, are influenced by other waters and may not mimic conditions in the Harbor. Measurements of pH throughout the Bays are not available. Given this consideration, the temporal pH profiles measured in the Harbor (Robinson *et al.*, 1990) are moderated somewhat to reflect the typical range of values in seawater, and time-averaged pH values of 8, 7.6, and 8 are assumed for the spring/fall, summer, and winter seasons, respectively.

Using these values of pH along with the mean concentrations of NO_2^- and NO_3^- listed in Table 10, Equation (7) can be used to estimate film-layer gaseous concentrations. These concentrations are presented in Table 11.¹⁶ The predicted concentrations of NO are orders of magnitude greater than the predictions of NO_2 . The concentration estimates for both gases are highest for the winter season when aqueous-phase NO_3^- concentrations are also highest. In absolute magnitude, the predicted film-layer concentration of NO is about an order of magnitude smaller than the atmospheric NO_x concentrations discussed above, while the predicted film-layer concentration of NO_2 is negligible compared to typical atmospheric values. The implications for mass-transfer are two-fold. First, because the estimates of film-layer concentrations are smaller than atmospheric concentrations, the direction of NO_x flux will be from the air into the water. Second, the predicted film-layer concentrations suggest that there will be limited gradient resistance to NO deposition, but essentially no resistance to NO_2 deposition. Thus, the separate consideration of NO and NO_2 is merited because NO has a small but significant film-layer concentration.

Table 11 Estimated film-layer concentrations of NO_2 and NO gases [for use as c_{af} in Equation (3)]

Season	Season weighting factor	Assumed average pH	Film-layer gaseous concentrations (ppb) predicted by:		
			Equation (7)		(9)
			NO_2	NO	NH_3
Spring/fall	0.5	8.0	1.3×10^{-7}	0.11	0.38
Summer	0.25	7.6	9.8×10^{-8}	0.13	0.08
Winter	0.25	8.0	9.0×10^{-7}	0.30	0.46
Average weighted values			3.1×10^{-7}	0.16	0.33

¹⁶ In applying Equation (7), the aqueous-phase concentrations listed in Table 10 must be converted from μM to M by dividing by 10^6 and the concentration of $[\text{H}^+]$ is calculated from pH using Equation (8). The predicted gaseous concentrations are converted from atm to ppb by multiplying by 10^9 .

A film-layer concentration of NH_3 can also be estimated using air-water equilibrium chemistry. The equilibrium equation that describes the partitioning is (Seinfeld, 1986):

$$[\text{NH}_3(\text{g})] = \frac{[\text{NH}_4^+]}{[\text{H}^+]K_{\text{am}}} \quad (9)$$

where

$[\text{NH}_3(\text{g})]$ is the air-phase concentration of ammonia (atm), which serves as the measure of the film-layer concentration c_{af} ,
 $[\text{NH}_4^+]$ is the dissolved concentration of ammonium ion in the aqueous-phase (M),
 $[\text{H}^+]$ is the aqueous-phase concentration of dissociated hydrogen ion (M), and
 K_{am} is the equilibrium constant of 2×10^{11} /atm at 298 K.

Table 10 presents measured concentrations of NH_4^+ that are derived from data collected by Loder (1993), as described previously. Using seasonal estimates of pH for the Bays (Table 11) to estimate H^+ concentrations [via Equation (8)], seasonal estimates of c_{af} for use in Equation (3) are 0.38, 0.08, and 0.46 ppb for the spring/fall, summer, and winter seasons, respectively, which correspond to a weighted average of 0.33 ppb.¹⁷

HNO_3 is very soluble, and as evidenced by the extremely low value of its Henry's Law Constant (Table 7), exhibits a strong preference for the dissolved state. Consequently, HNO_3 can be expected to have a negligible film-layer concentration. Consequently, the film-layer concentration of HNO_3 is assumed to be zero.

5.2.4 Dry deposition estimates for gases

The estimates of dry deposition of nitrogen-containing trace gases are presented in Table 12. Total annual deposition estimate of 0.92 kg N/ha results from the application of Equation (3). The total deposition estimate is dominated by the HNO_3 /volatile organic nitrate species. Deposition rates of NO_x compounds are negligible by comparison due to their low solubility (and correspondingly low mass transfer velocities). The total deposition rate of gases is estimated to be about the same magnitude as the dry deposition of aerosol species (Table 6).

¹⁷ Equation (9) is applied in a manner similar to Equation (7). See footnote 16.

Table 12 Estimates of dry deposition rates of nitrogen-containing trace gases

Species	Concentration in air c_a (ppb) (Table 9)	Film-layer concentration c_{af} (ppb) (Table 9)	Mass transfer velocity K (cm/s) (Table 7)	Dry deposition estimate (kg N/ha) predicted by Equation (3)
NO	2.4	0.16	0.00008	0.0003
NO ₂	7.4	3.1×10^{-7}	0.0004	0.005
HNO ₃ /volatile organic nitrates	0.7	0	0.59	0.75
NH ₃	0.5	0.33	0.51	0.16
Total dry deposition of gases (kg N/ha)				0.92

5.3 Summary of nitrogen deposition estimates to Massachusetts Bays

The best estimates of annual wet and dry deposition fluxes of nitrogen from the atmosphere to the Massachusetts Bays are summarized in Table 13. Dry deposition is found to be smaller than wet deposition, constituting about one-third of the total deposition estimate.

Table 13 Estimates of total nitrogen deposition to the Massachusetts Bays (fluxes in kg N/ha)

	Source	Best estimate	Total estimate
Wet deposition	Table 5	3.8	3.8
Dry deposition	Gases — Table 12	0.9	1.9
	Aerosols — Table 6	1.0	
Total annual nitrogen deposition			5.7

5.4 Variability, uncertainty, and sensitivity of deposition estimates

The values of deposition flux presented in Table 13 are considered best estimates, but in actuality may over- or underestimate the rate nitrogen deposition from the atmosphere. As a general rule, wet deposition estimates are more robust than dry deposition estimates since they are derived from direct measurements over a multi-year period. These measurements illustrate the interannual variability of wet deposition, which range from 3.1–4.7 kg N/ha-yr over six years of measurements (Table 5).

Wet nitrogen deposition, which constitutes the majority of total deposition, is probably underestimated for two reasons. First, ion concentrations in precipitation are known to change with time. In particular, the weekly sampling protocol of the NADP network has been shown to underestimate the deposition of ammonium, which is thought decrease in concentration due to microbial immobilization (Ramundo and Seastedt, 1990). Sisterson *et al.* (1985) found 30% less NH_4^+ in weekly samples than was contained in rain event samples, and Ramundo and Seastedt (1990) found a slightly larger decrease. Other data suggest a more modest (of the order of 10%) loss of NH_4^+ (NAPAP, 1991).

A second factor that likely underestimates wet deposition of nitrogen is the failure to account for dissolved organic nitrogen (DON) species that have been measured in precipitation. The NADP network measures only the principal inorganic species (NO_3^- and NH_4^+). Deposition of DON has been measured to be 50% as large as the deposition of inorganic nitrogen, although values vary considerably among locations (Timperley *et al.*, 1985), and data are scant.¹⁸

To estimate a range of annual nitrogen fluxes, the smallest rate observed over the seven-year period at the Truro monitor (3.1 kg/ha-yr, Table 5) is adopted as a low-end estimate. A high-end estimate is derived by starting with the highest observed inorganic deposition rate (4.7 kg/ha-yr, Table 5) and adding increments of 1.8 kg/ha-yr to account for the presence of DON, and 0.4 kg/ha-yr to compensate for the potential loss of NH_4^+ .¹⁹ Thus, a total high-end deposition estimate of 6.9 kg/ha-yr is estimated.

Dry deposition estimates are inherently uncertain since they are estimated indirectly from (1) measurements of airborne concentrations and (2) estimates of deposition velocities. Dry

¹⁸ Due to uncertainty over these values, organic nitrate deposition has not been incorporated in the best estimate of nitrogen deposition.

¹⁹ DON deposition of 1.8 kg N/ha-yr is estimated as 50% of the best estimate value of inorganic nitrogen deposition (3.7 kg/ha-yr, Table 5). The NH_4^+ correction term of 0.4 kg N/ha-yr is estimated assuming that the best estimate value of 1.37 kg NH_4^+ /ha-yr (Table 4) reflects a 30% loss rate.

deposition estimates are dominated by the deposition of HNO_3 and NO_3^- . The species present at the highest concentrations — NO and NO_2 — are predicted not to deposit to the Bays at appreciable rates compared to other species. These species are relatively insoluble, a property reflected by very small modeled deposition velocities (Table 7). Other researchers (*e.g.*, Galloway and Whelpdale, 1987) have used significantly larger deposition velocities for NO_x (0.4 ± 0.3 cm/s), but such values are not supported by recent experimental studies designed to measure airborne NO_x removal by water. In particular, Cape *et al.* (1993) measured NO_2 reaction rates with water that corroborate the NO_2 mass transfer velocity used herein (Table 7).

It is very difficult to estimate the uncertainty of the dry deposition estimates due to the fact that no direct measurements exist. The estimate that dry deposition accounts for one-third of total nitrogen deposition is consistent with the findings of the National Acid Precitation Program, which concluded that dry deposition is responsible for 30–50% of the nitrogen that deposits in eastern North America. The finding that the deposition estimate to the Bays is nearer the low end of the range suggests that dry deposition of NO_x is of greater significance at inland sites than to open waters (in which NO and NO_2 are relatively insoluble).

Deposition velocities for the various species considered vary by a factor of two or more in the literature. Similarly, it is difficult to identify representative concentrations for many species. As an example, consider NO_x , for which a fair number of measurements have been taken. Three different source regions are weighted to derive estimates of representative NO_x over the Bays. Measurements of NO_x at inland locations, which are used to characterize urban Boston and regional sources, are fairly robust as they reflect annual-average concentrations and are available for several years. Measurements of airborne NO_x off the coast, which are used to characterize sea breeze influences, may not be representative of annual-average concentrations because they were collected over a two-month period (Misanchuk *et al.*, 1987). Representative concentrations for these three regions vary over about a factor of ten, and it is not certain exactly how they should be weighted. In addition to the uncertainty associated with identifying concentrations appropriate for the Bays, all measurements are subject to analytical uncertainties, which for nitrogen species is compounded by the inability to differentiate some species and avoid interferences.

The uncertainty level of dry deposition estimates may be considerable. As a practical matter, the estimates could be inaccurate by a factor of three (or possibly more). An uncertainty factor of three is assumed in order to derive low and high-end estimates.

Table 14 Uncertainty estimates for annual nitrogen deposition fluxes (kg/ha-yr)

	Deposition estimates derived in this study			Deposition estimates developed by Menzie-Cura & Associates (1991)	
	Best estimate	Low-end	High-end	Low-end	High-end
Wet deposition	3.8	3.1	6.9	2.2	5.1
Dry deposition	1.9	0.6	5.7	2.1	7.0
Total deposition	5.7	3.7	12.6	4.3	12.1

5.5 Comparison with previous nitrogen deposition estimates and discussion

Table 14 compares the range of deposition estimates with the values previously developed by Menzie-Cura & Associates (1991). Graphical comparisons are provided in Figure 6 and Figure 7. The total (wet plus dry) estimate of deposition falls within the range estimated by Menzie-Cura & Associates (1991), although it is closer to the low-end estimate (Figure 6). For wet deposition (Figure 7), Menzie-Cura & Associates' low-end estimate lies below the range estimated in this study. The present high-end estimate of wet deposition is somewhat larger than that derived by Menzie-Cura because it accounts for organic nitrogen deposition and the loss of ammonium demonstrated in NADP samples. The present best estimate of dry deposition is slightly smaller than the low-end estimate previously derived by Menzie-Cura & Associates (1991) (Figure 7), and the present high-end dry deposition estimate is also lower than the high-end estimate developed by Menzie-Cura & Associates (1991).

Direct atmospheric deposition is small, but not insignificant, to other estimates of nitrogen loadings to the Bays. For example, Menzie-Cura & Associates (1991) estimated that discharges (rivers, sewers, and industrial sources) and storm runoff contribute 23–31 Gg N/year to the Bays. Integrating the total deposition estimate of 5.7 kg/ha-yr (Table 14) over a surface area of 3700 km² (Becker, 1992; Menzie-Cura & Associates, 1991), this research estimates the Bays receive 2 Gg/year of nitrogen from direct atmospheric deposition. Thus, atmospheric deposition contributes an estimated 6–8% of total direct loadings (discharge, runoff, and deposition).

The biogeochemical ramifications of atmospheric deposition, however, are more complex. First, since deposition occurs over the entire surface area of the Bays, it differs in nature from other sources of direct loading, which may impact local areas near points of discharge. Second, within the Bays, direct loadings play only a partial role in the overall nitrogen budget, which is also

Total Annual Nitrogen Deposition to Massachusetts Bays

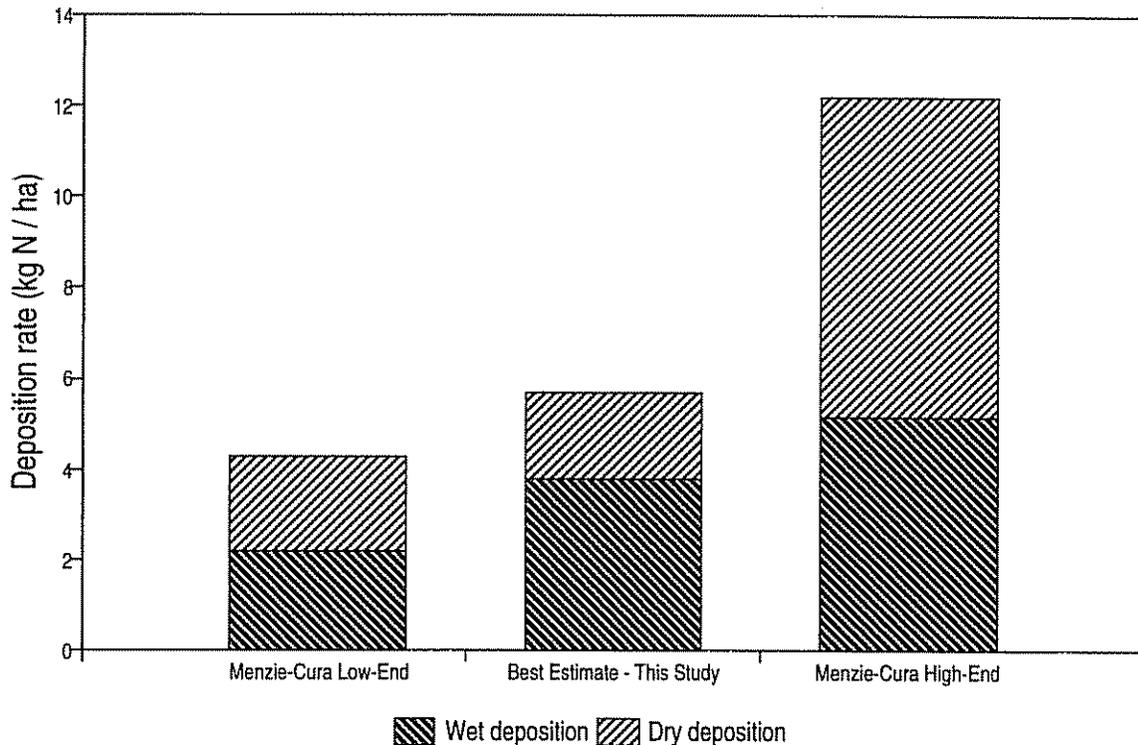


Figure 6 Comparison of nitrogen deposition estimates with previous estimates by Menzie-Cura & Associates (1992)

influenced by the import of water-borne nitrogen from the Gulf of Maine. Third, atmospheric deposition of nitrogen is of immediate importance to the seasonal nutrient cycle that characterizes the surface-layer. As discussed in Section 2, nitrogen cycles through the surface layer (top 20 m) at a rate of 0.31 Gg N/day. Over an area of 3428 km² (Becker, 1992), direct atmospheric deposition of 2 kg N/ha-yr contributes 0.007 Gg N/day, or only 2% of the total nitrogen budget. This value may understate the role of atmospheric deposition somewhat since it is derived during for the winter period when nitrogen concentrations (and hence throughput) are largest in the Bays. Table 10 indicates swings of 10–40 in seasonal nitrate and nitrite concentrations in the Bays, and during the summer months, atmospheric deposition may serve as an important source of nutrients.

Note, however, that this estimate only includes direct deposition to the Bays. Atmospheric deposition is also responsible for some of the nitrogen that (1) first falls on land and is transported to the Bays through runoff and/or river flows and (2) falls on waters that are subsequently transported into the Bays by the general circulation pattern. Thus, the estimate of

Total Annual Nitrogen Deposition to Massachusetts Bays

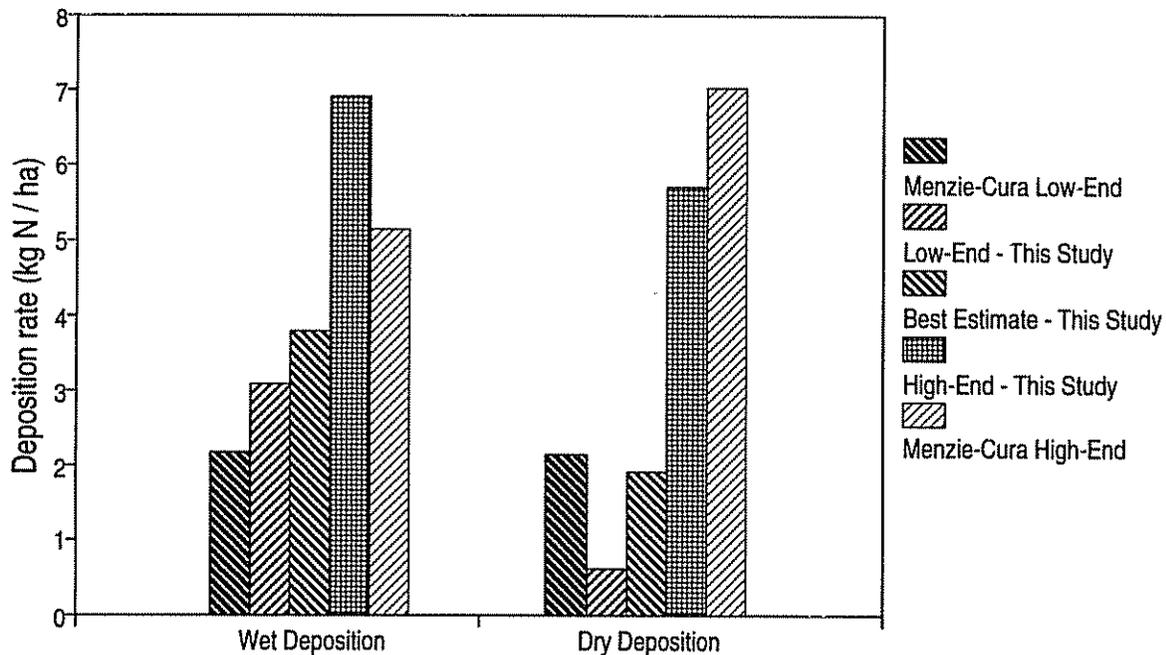


Figure 7 Comparison of nitrogen deposition estimates with previous estimates by Menzie-Cura & Associates (1991)

2% underestimates the total role of atmospheric deposition. Consideration of these phenomena, however, are beyond the scope of this research.

5.6 Recommendations

Estimates of nitrogen deposition to the Bays from the atmosphere can be improved with further research. Field study of several important parameters is recommended. First, *in-situ* measurements of the species of greatest importance to dry deposition (NO_3^- , NH_4^+ , HNO_3 , volatile organic nitrates, and NH_3) will help to refine dry deposition estimates. Second, dissolved organic nitrogen (DON) may be important species in wet deposition that has not been sufficiently studied. Measurements of DON in precipitation samples should be undertaken to quantify its role in wet deposition of nitrogen.

An effort should be made to quantify the total contribution of atmospheric deposition to nitrogen loading by estimating the amount of nitrogen deposited to land that reaches the Bays through groundwater and surface water transport. As a first approximation, it may be possible to simply assume that all nitrogen deposited within the Massachusetts Bays' watershed ultimately reaches the Bays. As demonstrated in section 4, such an analysis should consider that nitrogen deposition at inland receptors may be higher than direct deposition to the Bays.

Finally, a more careful analysis should be made of the potential role of atmospheric deposition in the summer months. Cursory throughput calculations indicate that atmospheric deposition may serve as an important source of nutrients in the summer months when surface layer concentrations of nitrate and nitrite are low.

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