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Atmospheric deposition of polycyclic aromatic hydrocarbons near New England coastal waters

D. Golomb*, E. Barry, G. Fisher, P. Varanusupakul, M. Koleda, T. Rooney

University of Massachusetts Lowell, Lowell, MA 01854, USA

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Abstract

Wet and dry deposition of polycyclic aromatic hydrocarbons (PAHs) was measured at Nahant, Massachusetts, a peninsula jutting into Massachusetts Bay and Wolf Neck, a peninsula jutting into Casco Bay, Maine. Wet deposition (rain and snow) was collected in a funnel which drains into a shielded, temperature controlled receiving bottle. Dry deposition of gaseous and particulate PAHs was collected onto an exposed water surface. PAHs were analyzed by solid phase extraction and gas chromatography-mass spectrometry. Sixteen PAH species were analyzed, ranging from acenaphthylene to coronene. The mean wet deposition rate of the sum of the 16 species is $720 \text{ ng m}^{-2} \text{ cm}^{-1}$ precipitation at Nahant, and $831 \text{ ng m}^{-2} \text{ cm}^{-1}$ precipitation at Wolf Neck. Wet deposition is attributed to regional PAH emitting sources. Storm patterns appear to bring somewhat higher wet deposition of PAHs to Wolf Neck than to Nahant. The mean dry deposition rate is $95 \text{ ng m}^{-2} \text{ h}^{-1}$ at Nahant and $9.3 \text{ ng m}^{-2} \text{ h}^{-1}$ at Wolf Neck. The large difference is attributed to the fact that Nahant is close to the urban-industrial metropolitan Boston area and Logan International Airport, whereas Wolf Neck has no major PAH-emitting sources nearby. Individual measurements have an error bracket of $\pm 30\%$. The Chemical Mass Balance model was used to apportion the dry deposition to source categories. At Nahant, nine samples gave valid statistical attributes with a mean apportionment: jet exhaust 35%, gasoline fueled vehicles 32%, diesel fueled vehicles 17%, wood combustion 13%, others 3%. At Wolf Neck, six samples yielded a mean apportionment: jet exhaust 30%, gasoline vehicles 28%, diesel vehicles 18%, wood combustion 16%, others 8%. There is a considerable variation between the samples. The apportionment is greatly dependent on the quality and selection of the model inputs, i.e. source signatures, which for PAHs are questionable. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Atmospheric deposition; Wet deposition; Dry deposition; Polycyclic aromatic hydrocarbons; Massachusetts Bay; Casco Bay

1. Introduction

Sediments in Massachusetts Bay and Casco Bay, Maine, show high concentrations of polycyclic aromatic hydrocarbons (PAHs) and other toxic pollutants (Menzie and Associates, 1991; Kennicutt et al., 1993). The sources of these pollutants are unknown, but it is suspected that atmospheric deposition is a major source (US EPA, 1997). Most PAHs are of pyrogenic origin, that is, they are products of incomplete combustion of

fossil fuel (coal, oil and natural gas) and biomass burning (wood, forest and brush). Fossil fuels and their products are combusted in boilers, kilns, furnaces, open fires and internal combustion engines, such as automobiles, buses, trucks, tractors, lawn mowers, off-road vehicles, ships, boats, locomotives and aircraft. Other sources of PAHs in the sediments at these locations could be oil spills and accidental or deliberate dumping into the sea of coal tar, asphalt, crank case oil, and creosote leaching from wood piles. Some of the PAHs are known or suspected carcinogens to humans and animals. In addition, bottom feeding fish and crustaceans are likely to ingest PAHs, causing tumors and

*Corresponding author.

E-mail address: dan_golomb@uml.edu (D. Golomb).

lesions to the animals, and possibly passing them on to humans in the food chain (Moore, 1995).

PAHs are found in airborne particles (aerosols) and in the gaseous phase, as well as dissolved or suspended in precipitation. To assess the total atmospheric deposition of PAHs, it is necessary to measure both dry and wet deposition. Dry deposition results from the direct impaction on land and water of airborne gaseous and particulate PAHs. Airborne PAHs are relatively short-lived, in the order of a few to tens of hours (Mackay et al., 1992). Thus, in dry air PAHs may not travel very far from the emission sources, to a distance of a few to tens of kilometers. Wet deposition is brought to the surface by precipitating hydrometeors (raindrops and snow flakes). The lifetime of PAHs in the aqueous phase is in the order of tens to hundreds of hours (Mackay et al., 1992). Cloud droplets accumulate gaseous and particulate PAHs as they travel over long distances. Wet deposition of PAHs may originate from regional urban/industrial sources hundreds to thousand kilometers away. In the vicinity of urban/industrial areas, dry deposition predominates; in more remote areas, wet deposition predominates (Golomb et al., 1997).

Measurement of wet deposition of PAHs is relatively straightforward. Precipitation is collected in a vessel (a bucket or a funnel connected to a receiving bottle), and the PAHs are extracted from the aqueous phase by conventional methods, such a liquid–liquid extraction (LLE) or solid phase extraction (SPE), then analyzed by gas chromatography–mass spectrometry (GCMS). Measurement of dry deposition is more problematic. Basically, there are two methods: indirect and direct. In the indirect method, *airborne* concentrations of gaseous and particulate phase PAH concentrations C are measured. The concentration is multiplied by a deposition velocity v_d to obtain the dry deposition rate $D_d = C \times v_d$. The greatest uncertainty arises from selecting a proper deposition velocity. This velocity is dependent on the chemical characteristics of the measured species, the size of the gas molecule or particle, the nature of the surface upon which the deposition occurs, and the prevailing atmospheric conditions, such as winds, turbulence, temperature and humidity (Seinfeld and Pandis, 1998). Dry deposition velocities may vary by orders of magnitude depending on the above factors, thus introducing large uncertainties in estimating dry deposition rates from airborne concentrations.

In the direct method, an artificial surface is employed on which gaseous and particulate PAHs deposit. Holsen and Noll (1992) and Sheu et al. (1996) employed a silicon grease coated polyvinyl chloride plate. Gardner and Hewitt (1993), Yi et al. (1997) and Golomb et al. (1997) employed a water surface. These methods are not devoid of uncertainties, as gaseous and particulate PAHs may not deposit in equal measure, revolatilization

of gaseous PAHs may occur, especially from a water surface, degradation of the deposited PAHs may occur during the sampling period, aerodynamic obstacles of the collection device may hinder the deposition of particles (e.g. the walls of a bucket or the rim of a funnel). In spite of the potential uncertainties, an artificial water surface collection device may best simulate the uptake of gaseous and particulate PAHs on a natural water surface, such as a river, lake or ocean.

We monitored previously dry and wet deposition of PAHs at two sites on the coast of Massachusetts Bay continuously for a whole year (Golomb et al., 1997). For dry deposition, a bucket was employed, in the bottom of which a layer of water resided. Since the collection period was quite long (two weeks), some degradation of the deposited PAHs may have occurred. Also, the bucket walls protruding over the layer of water may have presented an aerodynamic obstacle to the wind blown stream of air containing the gaseous and particulate PAHs. In this paper, we present measurements using (a) shorter collection periods, and (b) a funnel filled almost to the rim with water. The water is continuously pumped into the funnel, and the overflow is collected in a shielded receiving bottle. These factors should prevent to some extent the deterioration of the deposited PAHs and the aerodynamic obstacles to deposition. The present measurements extend to another coastal site in New England, Wolf Neck at Casco Bay, Maine. Only intermittent measurements were rendered with the major goal of determining relative deposition rates as a function of climatic effects and proximity to emission sources. Attempts are made to identify the source areas and categories that contribute to atmospheric deposition of PAHs to New England coastal waters.

2. Experimental

The base of the wet/dry collector, called the UML collector, is an Aerochem-Metrics Corp., Bushnell, FL, acid deposition collector. The original collector uses plastic buckets, one for wet, the other for dry deposition sampling. A precipitation sensor activates a shuttling lid. When precipitation falls, the wet bucket is open; during dry periods, the dry bucket is open. In the UML collector, the buckets are replaced with funnels. Separate bases are used for the wet and dry collector, respectively. A schematic of the UML wet/dry collector is presented in Fig. 1.

Wet collector. The square shaped wet funnel is made of steel, the inside is coated with Teflon[®] top area 0.078 m², about 8 l volume. It has a slanted bottom with a drain hole. All precipitation (rain or snow) falling during a collection period is collected in the wet funnel and flows immediately through the drain hole via a

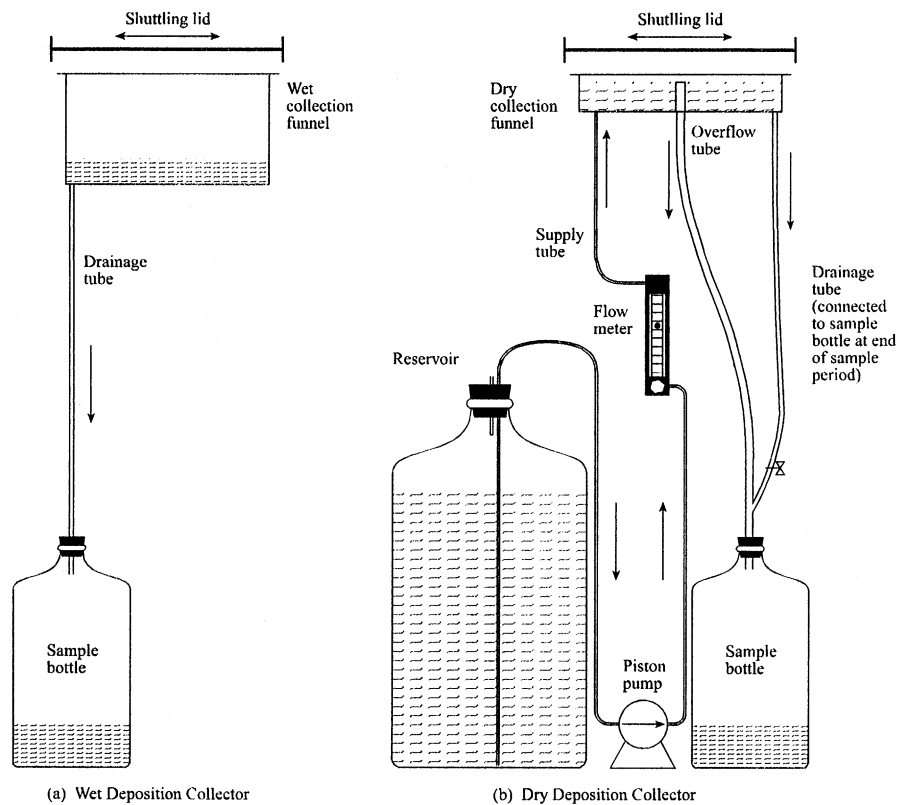


Fig. 1. Schematic of the UML atmospheric deposition collector: (a) wet deposition collector and (b) dry deposition collector.

1.25 cm ID Teflon[®] tube into a 201 glass receiving bottle, located in the insulated bottom cabinet. A thermostated blower keeps the receiving bottle above freezing temperature, as well as directing warm air toward the bottom of the funnel, so that falling snow melts immediately.

Dry collector. The dry collector exposes an artificial water surface to dry deposition of gaseous and particulate atmospheric pollutants. In this way, the dry collector simulates the uptake of pollutants onto a natural surface water; in this case, the dry deposition of PAHs onto the ocean surface. The dry funnel is also square shaped, Teflon[®] coated steel, 0.078 m² top area, 2.51 volume. Purified water is continuously circulated through the funnel. Water is supplied from a 201 glass bottle by a diaphragm pump via a flow meter at a rate of 1–1.5 ml min⁻¹. A Teflon[®] overflow tube with a 1 cm bore is inserted into the funnel drain hole, reaching to within 0.5 cm of the rim of the funnel. When the water level exceeds the top of the overflow tube, it drains through the overflow tube and a 0.5 cm ID Teflon[®] tube into a receiving 201 glass bottle. During hot summer days some evaporative losses of water may occur, such that the water level reaches only 0.5–1 cm below the

overflow tube. The water level reaches its proper height during cooler periods and at night. During gusty wind conditions, some spillage may occur over the rim of the funnel. Due to the square shape of the funnel, the surface area of the water is not affected significantly by the change of height of the water level. In a 7-day sampling period, 10–15 l water flows through the funnel into the receiving bottle. At the end of the sampling period, the residual water in the funnel is drained via a drain hole into the receiving bottle.

The wet and dry collectors receive the deposition of both gaseous and particulate pollutants. We cannot distinguish the contribution to deposition between the two phases, nor can we tell the efficiency of their collection.

PAH analysis. After a sampling period, the receiving bottles are brought to the laboratory for PAH analysis. First, 50 µl of a 1 ng l⁻¹ standard solution of surrogate PAHs is added to both the wet and dry samples. The surrogates consist of four deuterated PAHs: acenaphthene-d10, anthracene-d10, chrysene-d12 and perylene-d12 (SUPELCO, Bellefonte, PA). The concentration of the surrogates can vary between 5 and 50 ng l⁻¹ in the samples, depending on the sample

volume. From the recovery rates of the surrogates we estimate the recovery rates of the corresponding ambient PAHs during the analytical process, including extraction, elution, concentration and GCMS. Fig. 2 shows the 16 PAH species, their abbreviations, chemical structure, and the corresponding deuterated surrogates. The content of the receiving bottles with the ambient suspended particulate and dissolved PAHs, and the surrogate PAHs, is transferred by a syphon method to a SPE cartridge. After complete syphoning, the receiving bottles are rinsed with purified water, and the water rinse is also transferred to the SPE cartridge. The SPE cartridge is made of polyethylene, 20 ml volume, packed with 5 g ENVI-18, a C-18 type sorbent, supplied by

SUPELCO. The packing is held in place by top and bottom frits (20 µm pore size) made of polypropylene. The ENVI-18 is conditioned with a 10:1 mixture of water-methanol. Two aliquots of 10 ml each of methylene chloride are used to elute the PAHs from the ENVI-18 sorbent. An internal standard, benzo(a)anthracene-d₁₂, is added to the eluted solution. The internal standard serves as a volumetric marker. The eluted extract is stored at 4°C till analysis. The extract is concentrated to approximately 0.5 ml in a Kuderna-Danish concentrator. The remaining solution is further concentrated by cold nitrogen evaporation to about 50 µl. Two microliters of solution (i.e. about 4% of the original sample) are injected into a GCMS. The



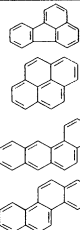
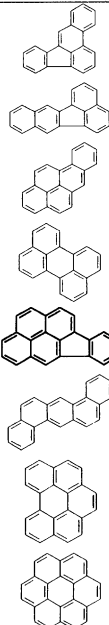
PAH	Structure	Surrogate
Acenaphthylene (ACN) Fluorene (FLU)		Acenaphthene-d ₁₀
Phenanthrene (PHN) Anthracene (ANT)		Anthracene-d ₁₀
Fluoranthene (FLA) Pyrene (PYR) Benzo(a)anthracene (BaA) Chrysene (CHR)		Chrysene-d ₁₂
Benzo(b)fluoranthene (BbF) Benzo(k)fluoranthene (BkF) Benzo(a)pyrene (BaP) Perylene (PER) Indeno(1,2,3-c,d)pyrene (I1P) Dibenz(a,h)anthracene (DaA) Benzo(g,h,i)perylene (BgP) Coronene (COR)		Perylene-d ₁₂

Fig. 2. The 16 PAH species analyzed, their abbreviations, chemical structure, and the corresponding deuterated surrogates used to quantify their recovery rates.

precise level of concentration is determined by measuring the amount of retrieved internal standard, not by volumetry.

A Hewlett-Packard model 5890 Series II/5971A GCMS is used with an associated library for identifying the analytes. The MS is used in the selected ion monitoring mode (SIM), which quantifies only the preselected PAH ions. The SIM mode allows quick identification and quantitation of the preselected ion peaks. On the other hand, non-preselected peaks, e.g. substituted PAHs and other pollutants are not quantified. The column is a 30 m × 0.25 mm ID PTE-5 (5% diphenyl-95% dimethylpolysiloxane) capillary with a film thickness of 0.25 μm (SUPELCO). A 3–5 m uncoated deactivated silica capillary column (Restek Corp., Bellefonte, PA) is used as a guard column. Ultrapure (99.999%) helium is used as a carrier gas. A 4 mm ID goose neck glass liner packed with glass wool is inserted into the injection port. The glass wool is deactivated with 5% dimethylpolysiloxane in toluene prior to use. The 2 μl concentrates are injected into the splitless mode at 1 min split delay. The gas chromatographic conditions are: injection temperature 300°C; temperature program starts at 35°C, held for 20 min, increases to 100°C at 20°C min⁻¹, increases to 200°C at 8°C min⁻¹, finally increases to 300°C at 5°C min⁻¹, held for 20 min.

The identity of each PAH is confirmed by the use of a standard PAH mix (EPA mix 525). Calibration of the ion peaks is performed by a five point linear regression analysis. The calibration is performed once every week. The minimum quantitation limit for most PAHs is 1–3 ng, although sub-nanogram peaks are discernible. Ultrapure water obtained with reverse osmosis and organic free filter (Barnstead/Thermolyne, Dubuque, IA) is used for preparing solutions, rinsing the bottles and funnels. Solvents are HPLC grade. NIST certified standards and surrogates are used. Laboratory glassware is rinsed with water and methanol, then baked at 300°C. When peak shapes deteriorate, the GC capillary column is regenerated by solvent rinsing or replaced. Two injections per sample are GCMS analyzed. The standard deviation of the two injections is within 20%.

In spite of the ultrapure water and HPLC grade solvents used, interfering peaks show up in the gas chromatogram at the preselected PAH ion peaks when the sample does not contain added PAHs. These interferences may be due to residual PAHs leaching from the glassware or ENVI-18. The interferences are called blanks. They are particularly noticeable for the more volatile PAHs, such as naphthalene, fluorene and phenanthrene. The amount of blank is dependent on the volume of water that passes through the ENVI-18 cartridge. A calibration curve is produced of blank amounts having the same retention time vs. water volume. Blank amounts are subtracted from the appro-

priate PAH peaks depending on the volume of water used in each sample. Since excessive amounts of the naphthalene peak are found in the blanks, ambient naphthalene deposition was difficult to quantify. Therefore, no naphthalene data are reported.

Recovery rates. For the EPA Mix 525 PAH solution in water, the SPE method yields recovery rates from 60% to 110% (S.D. ±15%). For the four deuterated surrogate PAHs, which are added to the retrieved samples, the corresponding recovery rates are lower, in the range of 46–74% (S.D. ±12%). The relatively low recovery rates of the surrogates are attributed to several factors: (a) volatilization during the drying step, (b) adsorption on glass and tubing surfaces, (c) degradation during storage time, and most importantly, (d) breakthrough occurring in the SPE cartridge. The latter is dependent on the volume of water of the samples. The more water passes the SPE cartridge the more breakthrough may occur. Note that up to 20 l of water passes through the SPE cartridge. The recovery rates of the surrogates are applied to estimate the recovery rates of the corresponding ambient PAHs.

Uncertainty range. The error bracket on individual measurements is ±30%. This is based on the deviation of two injections, and the uncertainty of recovery rates of the surrogates. The error bracket does not include possible uncertainties of the performance of the wet/dry collector.

Monitoring sites and schedule. One site is located in Nahant, Massachusetts, a peninsula jutting about 8 km into Massachusetts Bay, 16 km northeast of downtown Boston and 12 km northeast from Logan International Airport, 42: 25°N, 70:55°W (Fig. 3(a)). The mainland coast, called the North Shore, contains a string of residential-industrial towns and cities: Chelsea, Revere, Saugus, Lynn, Salem, Beverly and others further inland. There is a small residential community on the peninsula, but no other significant immediate sources of PAH emissions. The other site is located in Wolf Neck, Maine, a peninsula jutting about 4 km into Casco Bay, 26 km northeast of Portland, 28 km from Portland International Airport, and 7 km southeast of Freeport, 43:50°N, 70:04°W (Fig. 3(b)). There is a small farming community on the peninsula and a camping ground with occasional camp fires, but otherwise no major immediate sources of PAHs. Intermittent sampling at Nahant started in November 1998 and ended in May 2000. Sampling periods ranged from 34 to 165 h. We tried to minimize the sampling periods (a) to prevent deterioration of the PAHs, and (b) to allow directional identification of PAH source areas. For wet deposition, a single precipitation episode allows a singular trajectory identification that may have brought the precipitating clouds. For dry deposition, shorter sampling periods have a greater probability that winds do not fluctuate all around the compass. Sampling at Wolf Neck started in

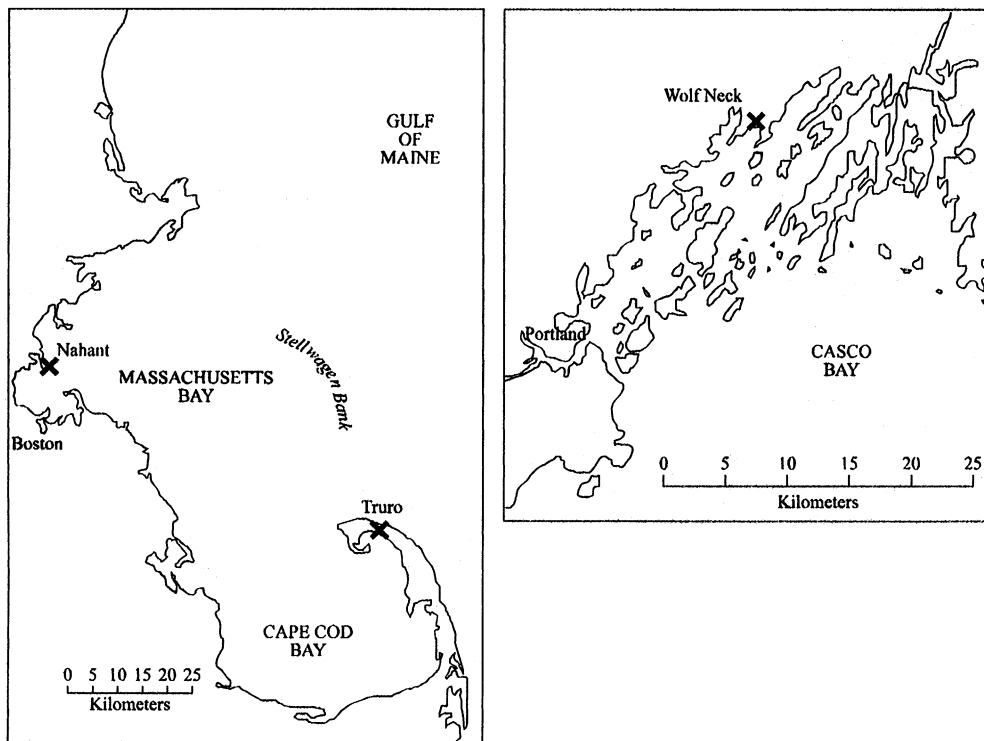


Fig. 3. Massachusetts Bay and Casco Bay, Maine, with monitoring sites indicated.

March 1998 and ended in April 2000. At Wolf Neck, all sampling periods, wet and dry, lasted one week (approximately 168 hours), one or more samples per month. Thus, some PAH deterioration, multiple precipitation episodes, and fluctuating winds may have occurred in each sampling period.

3. Results and discussion

3.1. Wet and dry deposition rates

Nahant. Of all the collected samples, 23 wet and 14 dry samples were selected for detailed analysis, distinguished by relatively clean chromatograms and unique features, such as a single precipitation episode for wet deposition and dominant surface winds for dry deposition. For Nahant, Fig. 4(a) presents the bar chart of wet deposition of the sum of 16 PAH species in units of $\text{ng m}^{-2} \text{cm}^{-1}$ precipitation. The mean of all samples is $720 \text{ ng m}^{-2} \text{cm}^{-1}$, with a range of $55\text{--}4773 \text{ ng m}^{-2} \text{cm}^{-1}$ (Table 1). The bars on the left of the dashed line are for samples collected in the heating season, defined as 15 October–15 April, the ones on the right are for samples collected in the non-heating season, defined as 15 April–15 October. The mean for the heating season is $1099 \text{ ng m}^{-2} \text{cm}^{-1}$, for the non-heating season is

$342 \text{ ng m}^{-2} \text{cm}^{-1}$, indicating that for unit rate of precipitation wet deposition is higher in winter than in summer, due to the greater use of fossil fuels and wood for space heating in the winter months.

On the bar chart, the samples indicated with NC were collected during non-convective, stratiform precipitation events, and those indicated with C were collected during convective, shower-type precipitation events. The non-convective events give a higher mean deposition amount, $1054 \text{ ng m}^{-2} \text{cm}^{-1}$, than the convective events, $300 \text{ ng m}^{-2} \text{cm}^{-1}$. We interpret this finding on account of non-convective events bringing wet deposition from wide-spread regional sources, whereas convective events incorporate into precipitating cloud droplets PAHs only from local sources. Among the non-convective samples we selected a pair with similar precipitation depth, one with large deposition (10 January 1999, 1.9 cm precipitation, $2280 \text{ ng m}^{-2} \text{cm}^{-1}$ wet deposition), one with low deposition (31 December 1998, 1.9 cm precipitation, $1147 \text{ ng m}^{-2} \text{cm}^{-1}$ wet deposition). We performed a back trajectory analysis, using the HYSPLIT4 model (Draxler and Hess, 1997). The chosen altitude is 1000 m, which is within the average mixing layer of the eastern US (Holzworth, 1972), and a height at which nimbostratus precipitating clouds may form. The trajectories for the two samples are presented in Fig. 5 superposed on a map of population density. The trajectories go back 48 h

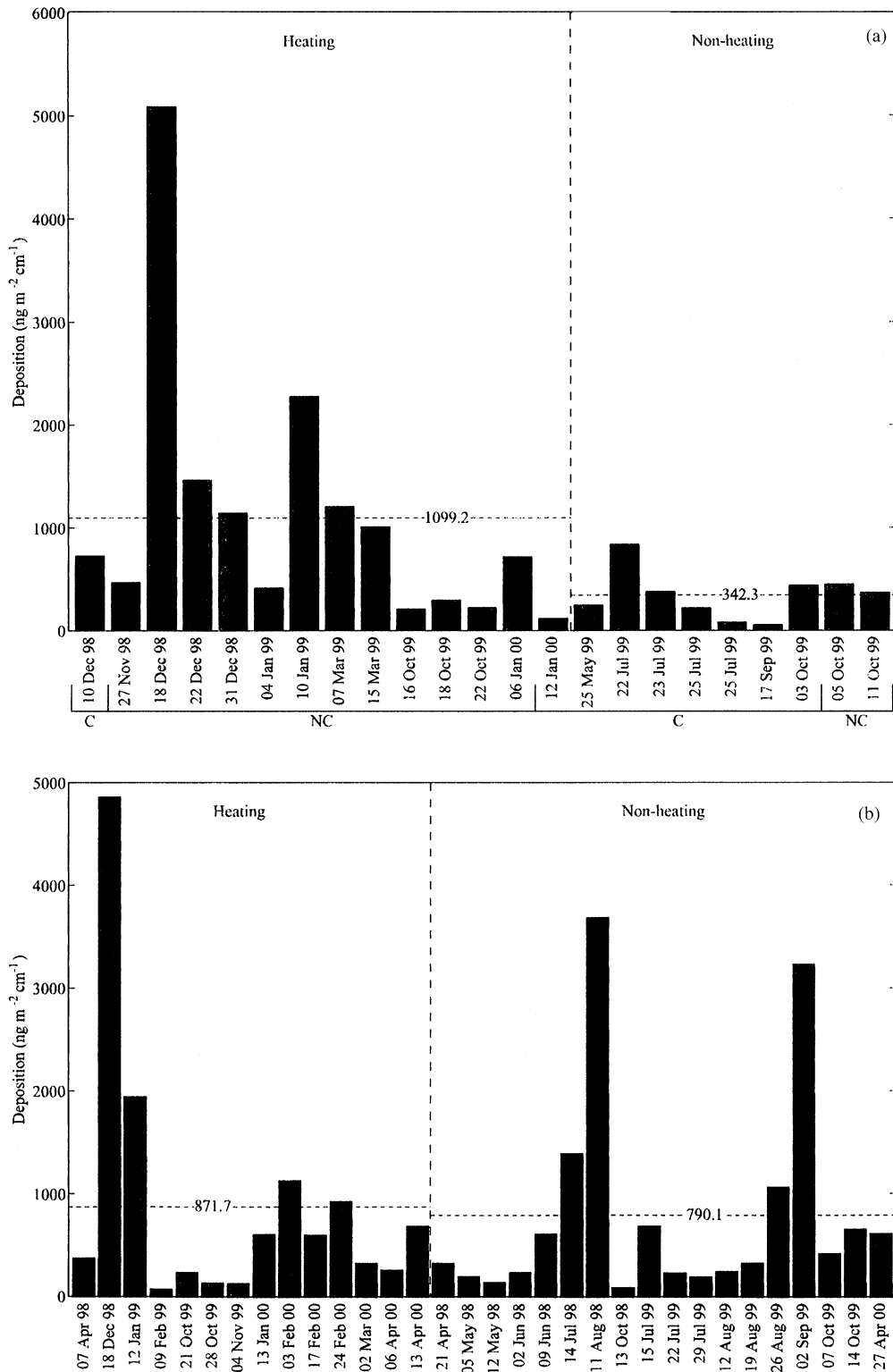


Fig. 4. Wet deposition rates of the sum of 16 PAH species. (a) Nahant, MA, (b) Wolf Neck, ME. Dates indicate end of collection period. Segregated by heating and non-heating seasons. Dashed lines are averages. C = convective precipitation events, NC = non-convective events. Units: $\text{ng m}^{-2} \text{cm}^{-1}$ precipitation.

with 6 h intervals indicated. The air masses that brought the higher wet deposition to Nahant (trajectory **a**) originated in the Great Lakes region, then passed over Pennsylvania, New Jersey, New York, then swung up the southern New England coast. The air masses that brought the lower deposition (trajectory **b**) also originated in the Great Lakes region, but took a northerly pass over southern Canada and Maine, then swung over the Gulf of Maine toward Nahant.

Table 1

Mean (and range) of wet and dry deposition at Nahant, MA and Wolf Neck, ME

Wet deposition ($\text{ng m}^{-2} \text{cm}^{-1}$)		Dry deposition ($\text{ng m}^{-2} \text{h}^{-1}$)	
Nahant, MA	Wolf Neck, ME	Nahant, MA	Wolf Neck, ME
$n = 23$	$n = 32$	$n = 14$	$n = 41$
720(55–4773)	831(69–4846)	95(22–206)	9.3(1–35)

There is no correlation between amount of precipitation and amount of PAH wet deposition. In fact, a relatively low precipitation event that follows a high pollution episode may bring more PAH wet deposition than a sustained precipitation event following clear days. For example, a sample (31 December 1998) with 1.9 cm precipitation resulted in 2179 ng m^{-2} deposition, whereas Hurricane Floyd (17 September 1999) with 9.3 cm precipitation resulted in 516 ng m^{-2} deposition.

Fig. 6(a) presents the results of 14 dry deposition samples at Nahant in the form of a bar chart. Units are $\text{ng m}^{-2} \text{h}^{-1}$. The mean of all samples is $95 \text{ ng m}^{-2} \text{h}^{-1}$, with a range of $22\text{--}206 \text{ ng m}^{-2} \text{h}^{-1}$ (Table 1). The bars on the left of the dashed line are for the heating season, those on the right for the non-heating season. The mean for the heating season is $92 \text{ ng m}^{-2} \text{h}^{-1}$, that for non-heating is $97 \text{ ng m}^{-2} \text{h}^{-1}$ if one includes the event of 13 May 2000, and $75 \text{ ng m}^{-2} \text{h}^{-1}$ excluding this event. The seasonal difference is not as large as we found in the 1992/93 campaign, when the dry deposition was much higher in winter than in summer, but this could be due to

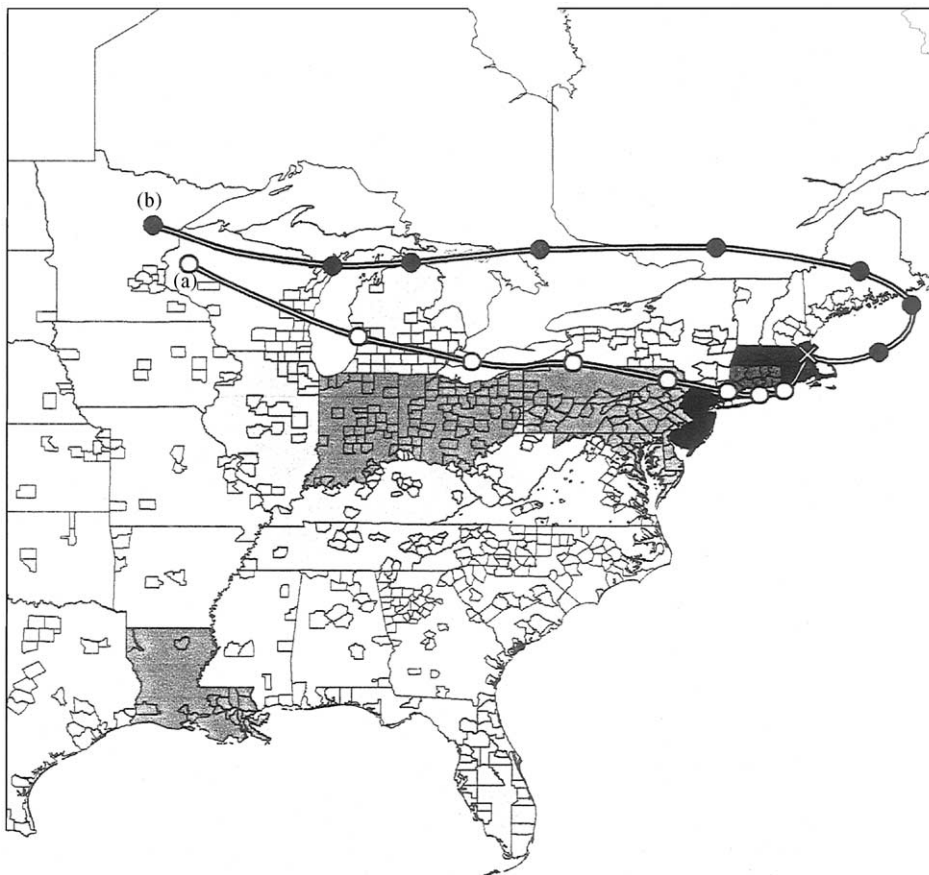


Fig. 5. Two types of upper air (1000 m) trajectories bringing similar (1.9 cm) precipitation to Nahant, MA. (a) High deposition event ($2280 \text{ ng m}^{-2} \text{cm}^{-1}$), (b) low deposition event ($1147 \text{ ng m}^{-2} \text{cm}^{-1}$). Shading indicates population density in the United States.

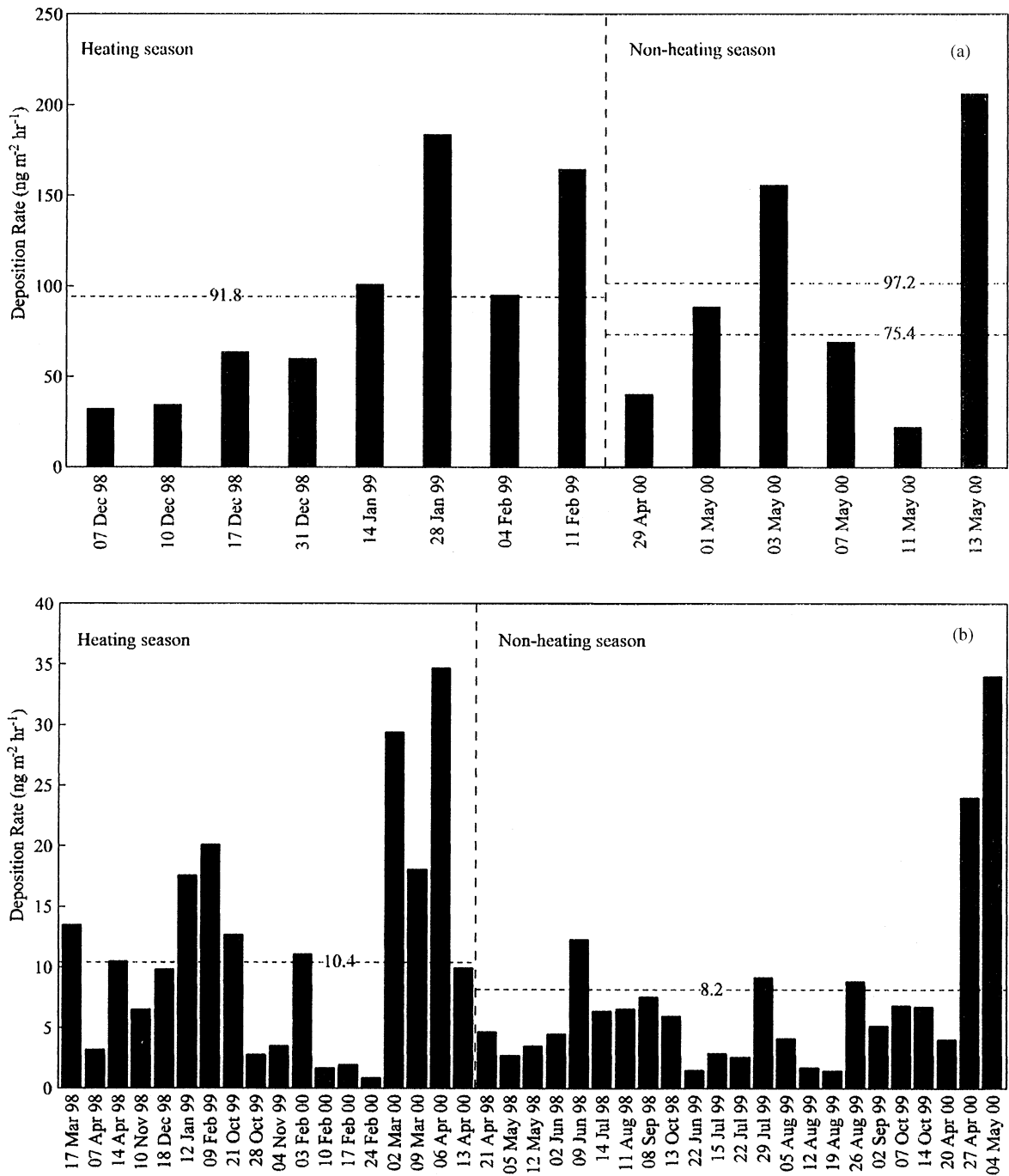


Fig. 6. Dry deposition rates of the sum of 16 PAH species. (a) Nahant, MA, (b) Wolf Neck, ME. Dates indicate end of collection period. Segregated by heating and non-heating seasons. Dashed lines are averages. Units: $\text{ng m}^{-2} \text{h}^{-1}$.

the limited number of samples (eight in the heating season and six in the non-heating season). Gardner and Hewitt (1993) sampled a similar aggregation of PAHs in dry deposition with a similar water surface collector as ours at two sites in the UK. For Esthwaite

Water, Cumbria, the average of four winter samples was $155 \text{ ng m}^{-2} \text{ h}^{-1}$, for three summer samples $26 \text{ ng m}^{-2} \text{ h}^{-1}$; for Castleshaw, Lancashire, the average of three winter samples was $67 \text{ ng m}^{-2} \text{ h}^{-1}$, for five summer samples $89 \text{ ng m}^{-2} \text{ h}^{-1}$. While there are

individual differences attributable to different locations and climatic conditions, the similar results indicate that the Lancaster University and UML collectors are performing similarly.

Table 2 presents the wind statistics of the dry samples. The table lists the percentages of the sampling period when winds blew from the indicated sectors. Wind data were taken from Logan International Airport, which is on the coast of Massachusetts Bay, about 12 km SW from the monitoring site. For most high deposition samples, SW, W, NW and N winds had the highest percentages. The SW sector includes downtown Boston, the exhaust fans from the Callahan Tunnel, and Logan International Airport. The W sector contains the industrial suburbs Revere and Saugus; the NW sector Lynn; the N sector Salem and Beverly. All sectors are traversed with major traffic arteries. An exception is the event of 13 May 2000, when the predominant winds were from SE and E, which is over Massachusetts Bay. Perhaps, exhaust from aircraft taking off and landing over that corridor caused the high deposition of PAHs in that sample.

Wolf Neck. At Wolf Neck, 32 wet and 41 dry weekly samples were obtained. The bar chart of Fig. 4(b) presents the wet deposition in units of $\text{ng m}^{-2} \text{cm}^{-1}$ precipitation. The mean of all samples is $831 \text{ ng m}^{-2} \text{cm}^{-1}$, with a range of $69\text{--}4846 \text{ ng m}^{-2} \text{cm}^{-1}$ (Table 1). The mean is somewhat larger than at Nahant, $720 \text{ ng m}^{-2} \text{cm}^{-1}$. We found previously that Truro, at the tip of Cape Cod, receives more wet deposition of PAHs than Nahant (Golomb et al., 1997). Apparently, Wolf Neck (175 km northeast of Nahant) and Truro (86 km southeast of Nahant) lie closer to the storm patterns that bring precipitating clouds with a higher

PAH content than do clouds that precipitate over Nahant. The mean during the heating season is $872 \text{ ng m}^{-2} \text{cm}^{-1}$, during the non-heating season $790 \text{ ng m}^{-2} \text{cm}^{-1}$.

Fig. 6(b) presents a bar chart of dry deposition at Wolf Neck in units of $\text{ng m}^{-2} \text{h}^{-1}$. The mean of all samples is $9.3 \text{ ng m}^{-2} \text{h}^{-1}$, with a range of $1\text{--}35 \text{ ng m}^{-2} \text{h}^{-1}$. The mean dry deposition at Wolf Neck is about 10 times lower than that at Nahant. The mean of the heating season is $10.4 \text{ ng m}^{-2} \text{h}^{-1}$, of the non-heating season $8.2 \text{ ng m}^{-2} \text{h}^{-1}$. Clearly, Wolf Neck is not exposed to as much dry deposition of PAHs than Nahant, as there are no major PAH emitting sources nearby. Kennicutt et al. (1993) measured very low concentrations of PAHs in the sediments of Casco Bay close to Wolf Neck. In the southern reaches of Casco Bay, near Portland, Maine, sediments contained tens to hundreds times more PAHs than those near Wolf Neck.

3.2. Composition

The distribution of the 16 PAH species in wet and dry deposition is given in the pie charts of Fig. 7. At Nahant, the major contributors to wet deposition are phenanthrene (24.3%), fluoranthene (13.8%) and pyrene (11.1%). The composition of wet deposition at Wolf Neck is quite similar, indicating that wet depositions at the two sites have a similar origin. At Nahant, the major contributors to dry deposition are benzo(*b* and *k*)fluoranthene (14.1%), fluoranthene (13.8%), phenanthrene (12.7%), anthracene (11.5%) and pyrene (10.4%). At Wolf Neck, the major contributors are fluoranthene (22%), pyrene (17.9), benzo(*b* and *k*) fluoranthene (11.5%) and acenaphthylene (11.5%). The different

Table 2

Wind statistics for the 14 dry deposition collection periods for Nahant, MA. Data taken from Logan International Airport^a

Date	Rate	Calm	N	NE	E	SE	S	SW	W	NW
07 Dec 98	32.3	5.6	4.3	0.6	7.4	8.7	3.7	40.7	24.1	5.0
10 Dec 98	34.3	0.0	18.5	0.0	6.1	1.5	0.0	1.5	27.8	44.6
17 Dec 98	63.5	1.2	10.8	0.0	0.0	0.6	2.4	33.8	26.5	24.6
31 Dec 98	60.0	0.7	6.7	1.4	4.7	2.0	18.1	20.1	39.6	6.7
14 Jan 99	100.8	0.0	19.0	2.3	0.0	0.0	15.6	22.0	22.6	19.6
28 Jan 99	183.4	0.0	5.9	9.8	11.8	9.8	2.9	7.8	31.4	20.5
04 Feb 99	95.3	10.9	17.0	4.7	8.5	0.8	3.9	16.3	21.7	16.3
11 Feb 99	164.7	0.6	9.1	1.3	0.6	3.9	5.1	11.7	24.5	43.3
29 Apr 00	40.6	10.2	10.2	2.0	12.2	6.1	12.2	26.6	10.2	10.2
01 May 00	88.8	18.0	8.0	0.0	2.0	8.0	6.0	12.0	16.0	30.0
03 May 00	155.9	9.8	24.3	2.4	12.2	4.9	14.6	12.2	4.9	14.6
07 May 00	69.4	4.2	2.1	8.4	39.6	10.5	2.1	2.1	25.0	6.3
11 May 00	22.1	0.0	15.4	28.2	23.1	0.0	0.0	0.0	10.3	23.1
13 May 00	206.4	0.0	10.4	2.1	35.4	18.8	12.5	2.1	12.5	6.3

^aDates indicate end of collection period. Numbers are percent of collection period that winds blew from a given sector. Dry deposition rate in units $\text{ng m}^{-2} \text{h}^{-1}$.

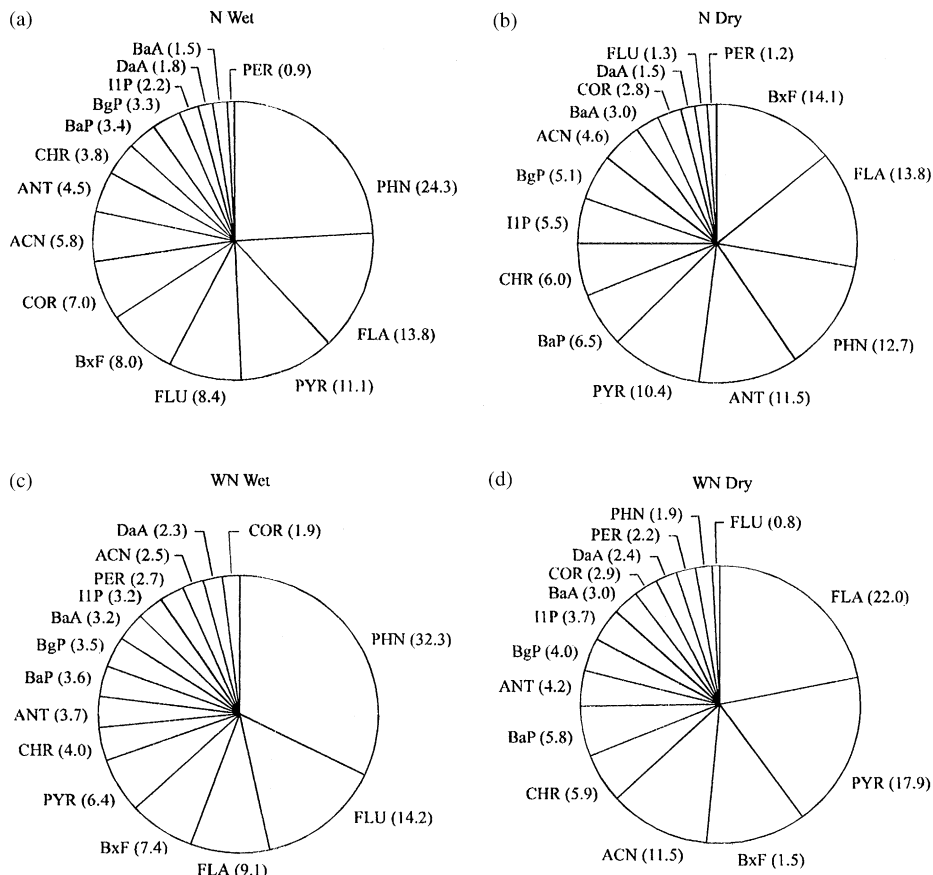


Fig. 7. The percentages by mass of the 16 PAH species. (a) Nahant wet deposition, (b) Nahant dry deposition, (c) Wolf Neck wet deposition, (d) Wolf Neck dry deposition.

compositions indicate that dry deposition at the two sites have a different origin. Several of the PAHs are suspected carcinogens (Menzie et al., 1992), so their presence in wet and dry deposition is of concern.

3.3. Source apportionment

Receptor models use chemical and physical characteristics of gases and particles measured at the sources to quantify the source apportionment at the receptor (Watson et al., 1990). We used the US EPA Chemical Mass Balance (CMB) Model 8.0. A major challenge to the application of CMB for PAH source apportionment is finding reliable “source signatures”, i.e. the distribution of PAH species in the emissions of fossil fuel and biomass combustion. After an extensive literature survey, and a consideration of the likely major emission source categories that may contribute to PAH dry deposition at the monitoring sites, as well as the abundance of PAH species found in the majority of dry deposition samples, we focused on six species: fluoranthene, pyrene, chrysene, benzo(a)anthracene,

benzo(a)pyrene and benzo(g,h,i)perylene. In CMB modeling the number of source categories cannot exceed the number of species. The statistical attributes improve when the difference between the two is greater. Thus, we focused on four major emission source categories that are likely to affect the two monitoring sites: gasoline fueled vehicles, diesel fueled vehicles, jet aircraft exhaust, and wood combustion. Table 3 lists the six species and their normalized distribution in the four emission source categories taken from Khalili et al. (1995), US EPA (1998), and Rogge et al. (1993). Normalization means that the mass of each PAH species is divided by the sum of the masses of the six species, corrected for molecular weight. In such a fashion, mole fractions are used, rather than absolute mass. In CMB modeling, conservation of mass between the source and the receptor is assumed. The total mass of a given PAH species at the receptor is the linear sum of the masses of that species contributed by all sources. If a given species is likely to decay en route to the receptor, a “decay factor” must be introduced in order to satisfy the conservation of mass. The decay factor depends on a number of variables

Table 3

Source signatures of six PAH species for four source categories. Numbers are mole fractions of the total mass of the six species

PAH species	No decay factors applied				Decay factor ^a	
	Auto (w/catalyst) ^b	Diesel ^c	Jet ^d	Wood ^{c,e}	Nahant	Wolf Neck
FLA	0.138	0.111	0.422	0.246	0.93	0.90
PYR	0.172	0.085	0.516	0.258	0.93	0.90
BaA	0.116	0.292	0.024	0.004	0.60	0.50
CHR	0.232	0.159	0.025	0.075	0.93	0.90
BaP	0.105	0.278	0.012	0.415	0.73	0.65
BgP	0.237	0.075	0.002	0.001	0.80	0.72

^aVenkataraman and Friedlander (1994). Decay factors are listed assuming that average travel time of PAHs from the sources to Nahant, MA is 3 h, to Wolf Neck, ME, 6 h.

^bRogge et al. (1993).

^cKhalili et al. (1995).

^dUS EPA (1998).

^eBgP was added to wood signature at minimal level for inclusion in CMB Model.

including atmospheric residence time, duration and intensity of sunlight, humidity and temperature. Kamens et al. (1988) attempted to quantify the decay of PAH species residing in soot particles as a function of humidity, solar irradiation and temperature. First-order rate constants were obtained for various PAH species. Humidity and solar irradiation appear to be the major factors influencing PAH decay. Ambient temperature has an indirect effect, as humidity is a function of temperature. Applying the first-order reaction rate constants measured by Kamens et al., Venkataraman and Friedlander (1994) estimated relative decay factors for 10 PAH species for the Los Angeles area. Average residence times from the sources to two receptor sites were estimated to be 2.35 and 5.28 h, respectively. Table 3 also lists the decay factors for the six PAH species. For Nahant we assigned a residence time of 3 h, for Wolf Neck 6 h.

The CMB model gave valid statistical attributes (R^2 , χ^2 and T -statistics) for nine dry deposition samples at Nahant and six samples at Wolf Neck. There is considerable variation in source apportionment for the individual samples. The results are listed in Table 4. The largest contribution at both sites appears to be due to jet aircraft exhaust. Logan International Airport, the seventh busiest airport in the US, is 12 km from Nahant, along the prevailing southwesterly winds. At Logan, there are more than 1300 daily flights, most of them jet aircraft taking off and landing. Wolf Neck is 28 km northeast from Portland International Airport with 310 daily flights (but only about one half are jet aircraft), and 15 km south from Brunswick Naval Air Station with an unspecified (but probably small) number of daily flights. While aircraft relative contribution to total dry deposition at both sites are similar, the small number of flights at Portland and Brunswick compared to Logan can explain the difference in the absolute deposition

Table 4

Source apportionment of dry deposition of PAHs using the CMB Model at Nahant, MA and Wolf Neck, ME

Source category	Source apportionment (%)	
	Nahant ($n = 9$) mean (range)	Wolf Neck ($n = 6$) mean (range)
Jet aircraft	35 (24–47)	30 (24–37)
Gasoline fueled vehicles	32 (25–42)	28 (23–42)
Diesel fueled vehicles	17 (8–26)	18 (13–22)
Wood combustion	13 (5–23)	16 (6–28)
Others	3 (1–5)	8 (6–10)

rates. Gasoline and diesel fueled vehicles are the next largest contributors to dry deposition of PAHs. The coastal conurbation and major traffic arteries, as well as the exhaust fans of traffic tunnels, are all within a few to tens of kilometers from Nahant. While Wolf Neck is also within a few kilometers from I-95 highway, and the tourist town of Freeport, Maine, the traffic density is much smaller than that affecting Nahant. Wood combustion is common throughout New England as a secondary fuel source, contributing in similar proportions to the dry deposition at the two sites. The relatively small apportionment to “other” sources is a reflection of the limited choice of PAH species and source categories used as an input to the model. If the source profiles include all of the six PAH species, the model attempts to optimize the apportionment to the inputted source profiles, rather than to “others”. For example, removing the wood profile, the model still indicates valid statistical attributes, but rather than shifting wood to “others,” it apportions a greater percentage to diesel and jet.

Pistikopoulos et al. (1990) estimated large contributions by gasoline and diesel vehicles to airborne PAH concentrations in Paris, France. Venkataraman and

Friedlander (1994) attributed the majority contribution to fine particulate PAHs in the Los Angeles area to automobile traffic (without distinction between gasoline and diesel fueled vehicles). On the other hand, Simcik et al. (1999), attributed the majority of airborne PAHs in the Chicago area to coal combustion (48%), natural gas combustion (26%), coke combustion (14%), and relatively little to vehicular combustion (9%). The source apportionment for dry deposition and airborne concentrations of PAHs using CMB and other receptor models is greatly dependent on the quality of the source signatures, and the selection of the source categories to be modeled, which may be subjective.

4. Conclusions

Wet and dry atmospheric deposition of PAHs has been measured intermittently at two sites near coastal waters of New England: Nahant, on Massachusetts Bay and Wolf Neck, on Casco Bay, Maine. The most significant feature of the collector is that dry gaseous and particulate PAHs are deposited directly onto a water surface, thus simulating the uptake of these pollutants onto a natural water surface, in this case, the ocean. The water in the collector is constantly being replenished, so as to diminish deterioration and revitalization of the PAHs. The PAHs are extracted from the aqueous solution/suspension by solid phase extraction and analyzed by gas chromatography–mass spectrometry. Nahant, being closer to the metropolitan Boston area and Logan International Airport, experiences much more dry deposition than Wolf Neck, which is farther from likely emission sources. On the other hand, Wolf Neck experiences greater wet deposition, as upper air masses carrying PAHs from regional sources and incorporating them into precipitating clouds arrive preferentially at this site. In general, during the heating season there is more dry and wet deposition at both sites. Non-convective precipitation events bring more wet deposition than convective events. There is no correlation between the amount of precipitation and the wet deposition of PAHs. Using a selected mix of six PAHs species and four source categories, the CMB model apportions dry deposition at these sites to jet exhaust 32–35%, gasoline fueled vehicles 28–32%, diesel fueled vehicles 17–18%, wood combustion 13–16%, and “others” 3–8%. These apportionments are dependent on the quality of source signatures and model input choices, which are somewhat subjective.

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References

- Draxler, R. R., Hess G. D., 1997. Description of the HYSPLIT-4 modeling system. US Environmental Protection Agency Technical Memorandum ERL ARL-224, National Oceanic and Atmospheric Administration, Silver Springs, MD.
- Gardner, B., Hewitt, C.N., 1993. The design and application of a novel automated sampler for wet and dry deposition to water surfaces. *Science of the Total Environment* 135, 55–66.
- Golomb, D., Ryan, D., Underhill, J., Wade, T., Zemba, S., 1997. Atmospheric deposition of toxics onto Massachusetts Bay-II. Polycyclic aromatic hydrocarbons. *Atmospheric Environment* 31, 1361–1368.
- Holsen, T.M., Noll, K.E., 1992. Dry deposition of atmospheric particles: application of current models to ambient data. *Environmental Science and Technology* 26, 1807–1815.
- Holzworth, G. C., 1972. Mixing heights, wind speeds, and potential for urban air pollution throughout the contiguous United States. Report AP-101, US Environmental Protection Agency, Research Triangle Park, NC.
- Kamens, R.M., Guo, Z., Fulcher, J.N., Bell, D.A., 1988. Influence of humidity, sunlight and temperature on the daytime decay of polyaromatic hydrocarbons on atmospheric soot particles. *Environmental Science and Technology* 22, 103–108.
- Kennicutt, M.C., Wade, T.L., Presley, B.J., Requejo, J.M., Denoux, G.J., 1993. Sediment contaminants in Casco Bay: inventories, sources and potential for biological impact. *Environmental Science and Technology* 28, 1–15.
- Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels and wood combustion emissions. *Atmospheric Environment* 29, 533–542.
- Mackay, D., Shiu, W.Y., Ma, K.C., 1992. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate of Organic Chemicals*. Lewis Publishers, Boca Raton, FL.
- Menzie, C. A., et al., 1991. Sources and loadings of pollutants to Massachusetts Bay. Final report to Massachusetts Bay Program, US Environmental Protection Agency, Boston, MA.
- Menzie, C.A., Potocki, B.B., Santodonato, J., 1992. Exposure to carcinogenic PAHs in the environment. *Environmental Science and Technology* 26, 1278–1284.

- Moore, M., 1995. Mutagenesis and carcinogenesis of PAHs in the marine environment. In: Sources, Fate and Effects of PAHs in Massachusetts Bay. Massachusetts Bay Program, US Environmental Protection Agency, Boston, MA.
- Pistikopoulos, P., Masclet, P., Mouvier, G., 1990. A receptor model adapted to reactive species: PAHs; evaluation of source contributions in an open urban site-I. Particle compounds. *Atmospheric Environment* 24A, 1189–1197.
- Rogge, W.F., Hillman, L.M., Mazurek, M.A., Cass, G.R., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental Science and Technology* 27, 636–651.
- Seinfeld, J. H., Pandis, S. N., 1998. *Atmospheric Chemistry and Physics*. Wiley, New York, pp. 958–996.
- Sheu, H.-L., Lee, W.-J., Su, C.-C., Chao, H.-R., Fan, Y.-C., 1996. *Journal of Environmental Engineering* 122, 1101–1109.
- Simcik, M.F., Eisenreich, S.J., Liroy, P.J., 1999. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmospheric Environment* 33, 5071–5079.
- Venkataraman, C., Friedlander, S.K., 1994. Source resolution of fine particulate PAHs using a receptor model modified for reactivity. *Journal of Air and Waste Management Association* 44, 1103–1108.
- US EPA, 1997. Deposition of toxic air pollutants to the Great Waters. Second Report to Congress, EPA-749/R-97/001B, US Environmental Protection Agency, Research Triangle Park, NC.
- US EPA, 1998. Locating and estimating air emissions from sources of polycyclic organic matter. Report 454/R-98-014, US Environmental Protection Agency, Research Triangle Park, NC.
- Watson, J. G., Robinson, N. F., Chow, J. C., Henry, R. C., Kim, B., Nguyen, Q. T., Meyer, E. L., Pace, T. G., 1990. Receptor Model Technical Series, Vol. III (1989 Revision), CMB User's Manual. Report No. 450/4-90-004, US Environmental Protection Agency, Research Triangle Park, NC.
- Yi, S.-M., Holsen, T.M., Noll, K.E., 1997. Comparison of dry deposition predicted from models and measured with a water surface sampler. *Environmental Science and Technology* 31, 272–278.