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Automotive Sources of Carcinogenic Polycyclic Aromatic Hydrocarbons Associated with Particulate Matter in the Chesapeake Bay Region

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We analyzed >400 particulate samples collected from throughout the Chesapeake Bay region between 1991 and 1998 for polycyclic aromatic hydrocarbons (PAHs). Isomer ratios of PAHs associated with aerosol and surface water particles demonstrate that motor vehicles are a major source of carcinogenic combustion-derived PAHs to Chesapeake Bay. Most of the benz[*a*]anthracene, benzo-[*a*]pyrene, benzo[*b*]fluoranthene and their isomers in air, rain, and surface waters of Chesapeake Bay appear to be derived from automotive sources. Lesser, but still significant amounts (53(±5)%) of these PAHs in the sea surface microlayer near urban areas are motor vehicle-derived, with 47(±5)% being coal-derived. In contrast, PAHs in surface sediments of Chesapeake Bay are predominantly coal-derived (86(±8)%) and at most 14(±8)% motor vehicle-derived. Thus, carcinogenic PAHs input to the bay from motor vehicles are either degraded prior to deposition to the sediments or are diluted by previously deposited coal-derived PAHs in the seabed. Like anthropogenic nitrogen (NO_x), which leads to coastal eutrophication, managing the impact of carcinogenic PAHs on coastal regions will need to focus on motor vehicle use, which continues to outpace population growth in areas such as Chesapeake Bay.

Introduction

Various polycyclic aromatic hydrocarbons (PAHs) are potent mutagens and carcinogens to both aquatic and terrestrial animals including humans (*1, 2*). PAHs enter the environment predominantly through human activities such as the combustion of fossil fuels for transportation and electricity, various industrial processes, biomass burning, waste incineration, and oil spills (*3, 4*). Since more than 50% of the world population lives within 100 miles of a coast (*5*), much of the pollutant release resulting from human activities is focused in coastal regions where ~70% of commercial and recreational fish and a large fraction of waterfowl and migratory birds spend at least a portion of their life cycle (*6*). Thus, it is imperative to understand the relative importance of

pollutant emission sources to coastal air and watersheds, such that strategies to control pollutant emissions in these heavily populated and ecologically important regions may be developed.

At ambient temperatures, many PAHs released by combustion processes associate with aerosol particles in the atmosphere (*7*) including benz[*a*]anthracene (BaA) and benzo[*a*]pyrene (BaP), which are established carcinogens (*1, 2*), and benzo[*b*]fluoranthene (BbF), which has been shown to have tumor-initiating activity in mouse skin (*2*). Much of this carcinogenic particulate matter emanates in urban and heavily populated coastal areas where it can be inhaled by humans and deposited in the nasal regions or lungs as well as transported to nearby aquatic systems where it may be taken up by resident organisms. In this paper, we use detailed geochemical characterizations of PAH emission sources (*8−20*) to distinguish specific sources of carcinogenic PAHs in the Chesapeake Bay region. This region is one of the most populated areas of the U.S. Moreover, Chesapeake Bay is an economically important estuary, with an annual seafood harvest valued at $1 billion as well as an ecologically important area serving as a major stop that provides food for migratory birds traveling along the Atlantic flyway (*21*).

Methods

Sample Collection and Analysis. To identify the primary source(s) of carcinogenic PAHs to the mid-Atlantic coastal region of the U.S., we examined over 200 air, 78 water, 65 rain, 32 surface microlayer (upper $10-100$ μm of the water surface), and 28 sediment samples collected from throughout the Chesapeake Bay region between 1991 and 1998 (Figure 1). Air samples ($200-1000$ m³) were collected over $4-24$ h using high volume samplers (*22, 23*). Two week integrated rain samples (5 to >100 L) were collected using a specially designed precipitation sampler (*22*). Surface and bottom water samples ($20-40$ L) were collected by pumping water from depth using a submersible or peristaltic pump (*24*). Surface microlayer samples ($30-40$ L) were collected using a rotating drum sampler (*25*). Surface sediments ($10-20$ g) were collected using a spade box coring device (*26*). Briefly, the various particulate matter samples were collected on glass fiber filters (Gelman Type A/E precombusted for 4 h @ 450 °C), except for surface sediments, which were sampled directly. PAHs associated with these samples were removed by repeated extraction of the samples with organic solvents as described elsewhere (*22−26*), and PAHs were isolated from the extracts using silica column chromatography (*22*). Concentrations of various PAHs were then determined relative to perdeuterated surrogate standards using gas chromatography−mass spectrometry with selective ion monitoring (*22*).

PAH Isomer Ratios. Relative abundances or isomer ratios are useful indicators of PAH sources because isomer pairs are diluted to a similar extent upon mixing with natural particulate matter and distribute similarly to other phases due to comparable thermodynamic partitioning and kinetic mass transfer coefficients. Moreover, distinct source signatures for various particle-associated PAHs are observed based on isomer ratios (Table 1), rendering them useful as environmental tracers of PAH emission sources. Since previous studies have estimated that vehicular traffic, coke manufacturing, aluminum production, and forest fires/wood burning are the major PAH emission sources in the United States (*4*), isomer ratios for these sources were derived as described below, for use in evaluating the sources of PAHs associated with environmental particulate samples.

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source	BaA/chrysene	BbF/BkF	BaP/BeP	IP/BghiP
automobiles	0.53 ± 0.06	1.26 ± 0.19	0.88 ± 0.13	0.33 ± 0.06
coal/coke	1.11 ± 0.06	3.70 ± 0.17	1.48 ± 0.03	1.09 ± 0.03
wood	0.79 ± 0.13	0.92 ± 0.16	1.52 ± 0.19	0.28 ± 0.05
smelters	0.60 ± 0.06	2.69 ± 0.20	0.81 ± 0.04	1.03 ± 0.15

[a] At ambient temperatures, these PAHs remain >50% associated with aerosol particles in the atmosphere ([7]); benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), indeno(123cd)pyrene (IP), benzo(ghi)perylene (BghiP).
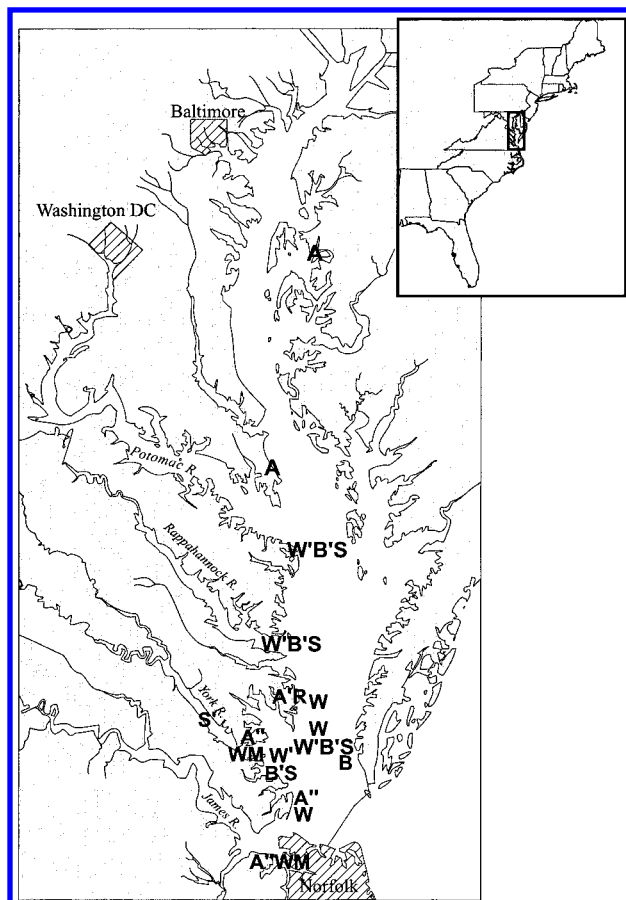

FIGURE 1. Chesapeake Bay region sampling locations. *A* — air samples collected biweekly, 1992−93, *n* = 63; *A′* — air samples collected biweekly, 1991−1995, *n* = 138; *A″* — air samples collected bimonthly, 1994−1995, *n* = 20. *R* — rain samples collected throughout 1991 and 1993−1995, *n* = 65. *M* — surface microlayer samples collected bimonthly, 1994−1995, *n* = 32. *W* — surface (≤1 m depth) water collected bimonthly 1994−1995, *n* = 31; *B* — bottom (≤1 m off bottom) water collected over two tidal cycles Aug, 1996, *n* = 11; *W′*, *B′* — surface (*n* = 9) and bottom (*n* = 15) water collected seasonally during 1996−1997. *S* — surface (0−1 cm) sediment collected seasonally during 1996−1997, *n* = 19; *S′* — surface sediment collected on an along channel transect of the York River estuary, April 1998, *n* = 9.

Isomer ratios for automotive sources were determined by averaging values for catalyst equipped automobile and heavy-duty diesel truck emissions (*8*), and air concentration ratios from a bus terminal, traffic roundabout, automobile parking garage, and tunnel (*11*). Since isomer ratios were similar for automobile and heavy-duty diesel truck emissions (*8*), we did not attempt to distinguish PAHs from these two mobile sources in the present work. For coal sources the PAH isomer ratios were determined by averaging values for emissions from coke oven doors as well as ratios in tars and pitches produced under different coking conditions (*12, 13*).

We could find little information on PAH isomer ratios emitted from coal combustion sources, but the values for coal/coke sources presented here are consistent with those measured for BaA/chrysene (1.44) and BaP/BeP (1.32) associated with particulate matter collected from the stacks of coal-fired power plants (*27*). Isomer ratios for wood combustion were determined by averaging values for emissions from residential fireplaces (*14*) and wind tunnel simulations of open burning of agricultural and forest woods (*15*). Finally, isomer ratios for smelter emissions were calculated by averaging air, sediment, and effluent concentration ratios in the vicinity of aluminum smelters as well as isomer ratios from industrial smokes and blast furnace emissions (*16−20*).

Isomer ratios were also determined for PAHs associated with various types of particulate matter from the Chesapeake Bay region, by plotting the isomer concentrations relative to each other and fitting for the slope of the line with an intercept of zero (Figure 2). While there is no a priori reason to force these regressions though a zero intercept, normal linear regression analysis yielded intercept values that were not significantly different from zero (p > 0.05) as well as slopes that were not significantly different (p = 0.92, paired t-test) from those derived via zero intercept regression analysis. Consequently, only slopes (isomer ratios) for the zero intercept regression analysis were used here. The isomer ratios for the particle-associated PAHs in air, rain, and the surface microlayer were then corrected for photodegradation, which occurs during atmospheric transport of combustion particles, using the following equation

$$\textit{isomer ratio}_{initial} = \textit{isomer ratio}_{observed} \exp((\lambda_1 - \lambda_2)*60) \tag{1}$$

where λ_1 and λ_2 are the average photodegradation rate constants (h^{-1}) on gray particles (*28*) for the PAHs in the numerator and denominator of the isomer ratio, respectively. The time over which photodegradation occurs (60 h) was estimated based on an aerosol residence time of 5 days (*29*) and assuming 12 daylight hours per day. This calculation further assumes that particle-associated PAHs in the surface microlayer are primarily derived from atmospheric deposition. Using eq 1 the BaA/chrysene and BaP/BeP isomer ratios for air, rain, and surface microlayer particles derived from regression analysis were increased by 23(±0.5)%, whereas those for BbF/BkF remained unchanged. Adjustments to the observed isomer ratios due to other atmospheric reactions were not considered.

Principal Components Analysis. PCA is a procedure that determines a few linear combinations of original variables that can be used to summarize a data set (*30*). Here, PCA was used to examine variability in the rain, surface microlayer, surface water, and sediment data in order to identify groups of PAH isomers indicative of compounds with similar sources and modes of transport in the data sets. For the PCA, fractional (PAH/ΣPAH, where ΣPAH = Σfluorene, phenanthrene, anthracene, fluoranthene, pyrene, BaA, chrysene, BbF, BkF, BeP, BaP, IP, dibenz[ah]anthracene, BghiP) data were used in order to minimize differences in sample concentrations
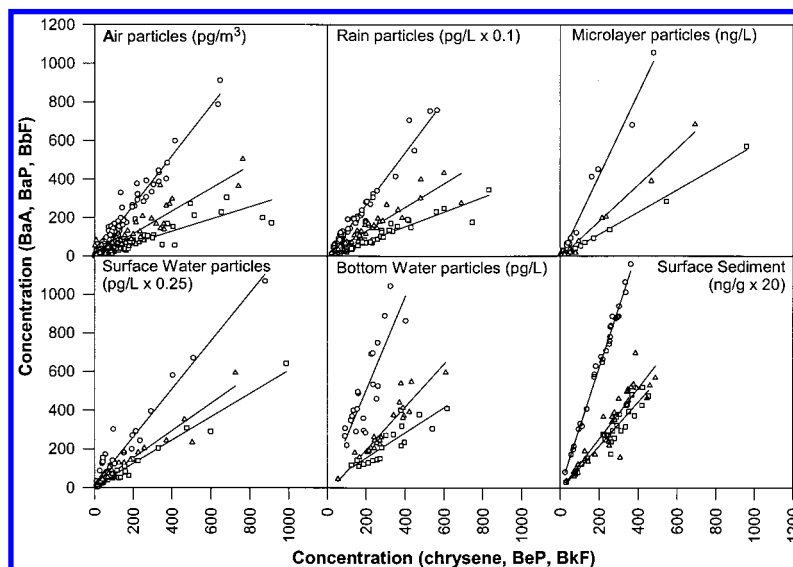
FIGURE 2. Relative concentrations of carcinogenic PAHs and their isomers in particle samples from the Chesapeake Bay region collected from 1991 to 1998. Isomer ratios for each sample type were determined using the equation: concentration (BaA, BbF, or BaP) = isomer ratio × concentration (chrysene, BkF, or BeP) and fitting for the slope of the line (isomer ratio). BaA/chrysene (□), BbF/BkF (○), and BaP/BeP (△).

in the data set and examine differences in the relative concentrations of the various PAHs. All of the PAHs except fluorene and dibenz[ah]anthracene were included in the PCA so that the sum of compounds included in the analysis was <1 and PAH concentrations remained independent of one another. Note that methyl-PAHs indicative of direct petroleum emissions were also not included in these analyses, since these compounds were not measured in all of the studies. However, several methyl-PAHs were determined in analysis of the sediment samples, and these data indicate that methyl-PAHs comprise only a small fraction of PAHs in Chesapeake Bay sediments (*26*). PCA was performed using Minitab 12.1 with a correlation matrix. Only principal components with eigenvalues > 1.0 are reported (*30*).

Results and Discussion

We found remarkably consistent isomer ratios (relative standard error = 1−5%) for PAHs associated with Chesapeake Bay particulate matter (Figure 2), indicating that the sources of the isomer pairs to the different sampling locations around the Bay were similar throughout the 2−5 years over which the data were collected (Figure 1). However, to distinguish the multiple sources of these PAHs requires examination of several isomer ratios. Consequently, if different groups of isomers can be shown to have similar associations with particulate matter in the study region, then combinations of these isomer ratios can be used to apportion sources.

As noted above, PCA was used to examine variability in the rain, surface microlayer, surface water, and sediment data in order to identify groups of PAH isomers indicative of compounds with similar sources and modes of transport in the data sets. Derived principal components (PCs) that define the data structure explained 73−88% of the variance in each of these data sets (Figure 3). Since these PCs are linear combinations of the original variables (i.e. the fractional PAH concentrations), by examining the contribution each original variable makes to the linear combination (i.e. loadings), the mechanisms, which may include PAH source, mode of delivery, and physical-chemical behavior, that define the data structure can be explored (*30*). The PCA distinguished three to four groups of PAHs associated with particulate matter in each medium in the lower Chesapeake Bay region based on the magnitude and direction of the PC loadings (Figure 3). These groups include the volatile (phenanthrene,

anthracene, fluoranthene, pyrene), heavy molecular weight (IP, BghiP), and carcinogenic (BaA, BaP, BbF, and their isomers) PAHs on particulate matter. In some cases, phenanthrene and anthracene exhibited distributions that were distinct from the other relatively volatile PAHs, fluoranthene, and pyrene (e.g. rain and surface water particles). Note however, that the various PAH isomers tended to group together indicating that the isomers likely have similar sources and modes of transport in the region, in addition to similar physical-chemical properties.

It is interesting to note that the heavy molecular weight PAHs (IP, BghiP) have different PC loadings relative to the carcinogenic compounds (Figure 3), since both groups strongly associate with particulate matter in the environment. It may be that IP and BghiP have a unique source in the Chesapeake Bay region. Several researchers have used BghiP as a tracer of automobile sources of PAHs (*31−35*). However, IP/BghiP ratios determined in this study for the various Bay region particle samples range from 0.96(±0.02) for surface water particles to 1.21(±0.04) for surface sediments, whereas the IP/BghiP ratio for motor vehicle emissions is 0.33(±0.06) (Table 1). Clearly, these compounds are not solely derived from motor vehicle emissions in the Chesapeake Bay region. Instead, measured IP/BghiP ratios are more reflective of coal or aluminum smelter emissions (Table 1). Alternatively, the measured IP/BghiP ratios may be indicative of incinerator emissions. Colmsjö et al. (*11*) measured IP/BghiP ratios of 1.0, similar to the values observed here, in the vicinity of a municipal incinerator but consistently measured IP/BghiP < 1.0 where automotive sources of PAHs dominate. Thus, sources other than motor vehicle emissions apparently influence the measured IP/BghiP ratio in the Chesapeake Bay region, but without additional information it is difficult to ascertain what these sources are.

Although initially included in the PCA, the air particle data set was excluded here. As noted by others (*36−38*), we observed that the dominant feature in the PCA for the air particle data is related to gas-particle partitioning of the PAHs. This likely indicates that volatile PAHs, which can readily partition into the gas phase during atmospheric transport of aerosols, are probably not reliable tracers of combustion-derived particulate matter and associated PAHs from source(s) to sink(s). Therefore, the subsequent examination of PAH sources in the Chesapeake Bay region is limited to the
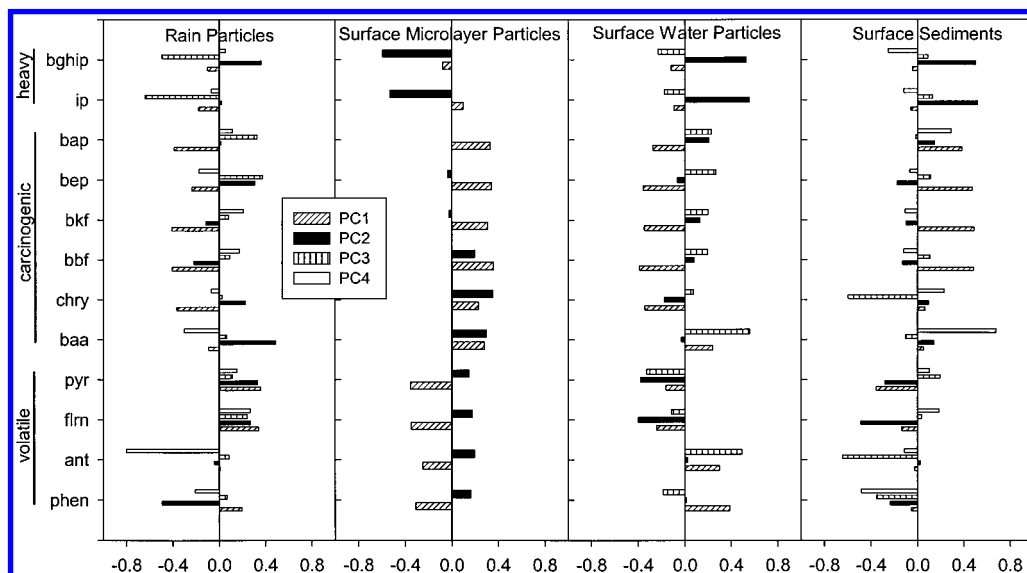
FIGURE 3. Results of principal components analysis of fractional PAH concentrations associated with particulate matter in air, rain, surface microlayer, and surface water of Chesapeake Bay; phen = phenanthrene, ant = anthracene, flrn = flouranthene, pyr = pyrene, baa = benz[*a*]anthracene, chry = chrysene, bbf = benzo[*b*]fluoranthene, bkf = benzo[*k*]fluoranthene, bep = benzo[*e*]pyrene, bap = benzo[*a*]-pyrene, ip = indeno[123cd]pyrene, bghip = benzo[ghi]perylene. Principal components 1, 2, 3, and 4 account for 36.6%, 22.1%, 15.3%, and 11.1% of the variability in the rain data, respectively, 53.5%, 19%, 0%, and 0% of the variability in the surface microlayer data, respectively, 41.4%, 19.4%, 13.7%, and 0% of the variability in the surface water data respectively, and 31%, 26%, 17.1%, and 13.7% of the variability in the surface sediment data, respectively.

carcinogenic PAHs: BaA, BaP, BkF and their isomers, which have similar distributions on particulate matter in the region as demonstrated by the PCA, and which tend to remain largely associated with particles in the environment. These PAHs should be efficient tracers of particulate matter from combustion sources.

As noted above, previous studies have estimated that vehicular traffic, coke manufacturing, aluminum production, and forest fires/wood burning are the major PAH emission sources in the United States (*4*). Consequently, we derived isomer ratios for PAHs from these sources (Table 1) for use in evaluating the sources of PAHs to Chesapeake Bay. Comparison of the isomer ratios for the carcinogenic PAHs to those for the proposed major PAH emission sources (*4*) reveals that the isomer ratios for the different Bay region samples lie predominantly between the values for automotive and coal sources (Figure 4). Based on this limited source analysis, it would appear that most if not all of the BaA, BaP, BbF and their isomers in air, rain, and surface waters of lower Chesapeake Bay are currently derived from motor vehicle combustion of fossil fuel (Figure 4). In contrast, in the surface microlayer, bottom water, and surface sediments of the Bay these same PAHs are apparently derived from more than one source. If atmospheric deposition influences the levels of PAHs in the surface microlayer, bottom water, and surface sediments of the Bay as expected, then sources of PAHs in these media should reflect those of aerosol particles. Since the isomer ratios for carcinogenic PAHs in the surface microlayer, bottom water, and surface sediments of the Bay tend to lie within the range of the mixing curves for automotive and coal-derived material (Figure 4), we interpret this to mean that these are the dominant sources of these contaminants. However, it must be recognized that this is a simplified interpretation and that varying combinations of the PAH sources considered as well as other sources not considered in this assessment may contribute to the observed isomer ratios.

Our interpretation of the predominance of motor vehicle combustion of fossil fuel as the primary source of carcinogenic PAHs is supported by previous investigations. For example, Harrison et al. (*38*) determined that 88% of the BaP in air

samples collected in Birmingham, U.K. was derived from road traffic emissions. In addition, several investigations have recently characterized emission rates for PAHs associated with particulate matter from various combustion sources (*8−10*), and these data coupled with current energy consumption information (*39, 40*) support the idea that motor vehicles are the major source of fossil fuel combustion-derived PAHs in the U.S. (Table 2). Moreover, coal is a major resource for electrical power generation in the Chesapeake Bay region constituting 40% and 58% of energy sources for power plants in Virginia and Maryland, respectively (*41, 42*). Also, coal and steel industries prevail in a large fraction of the Chesapeake Bay watershed drained by the Susquehanna River (*43*). Thus, the expected predominance of motor vehicle and coal-derived PAHs compared with wood combustion or smelter emissions in the region is plausible.

Based on this assessment, we calculate that the relative importance of motor vehicle-derived PAHs decreases progressively from the atmosphere and surface waters of Chesapeake Bay, to the bottom waters and sediments of the Bay (Figure 4). Using a two-component mixing model (*44*)

$$fraction_{auto} = \frac{(isomer\ ratio_{sample} - isomer\ ratio_{coal})(isomer\ ratio_{auto} + 1)}{(isomer\ ratio_{auto} - isomer\ ratio_{coal})(isomer\ ratio_{sample} + 1)} \quad (2)$$

the carcinogenic PAHs and their isomers are estimated to be 54($\pm$12)% automotive-derived and 46($\pm$12)% coal-derived in bottom waters of the Bay, but only 14($\pm$8)% automotive-derived and 86($\pm$8)% coal-derived in surface sediments of Chesapeake Bay. The fact that the bottom water ($\leq$1 m off the bottom) particles tend to contain more coal-derived PAHs compared with surface waters is likely due to resuspension of surface sediments enriched in PAHs originating from coal sources. The predominance of coal-derived PAHs in surface sediments compared with the atmosphere or surface waters implies that either motor vehicle-derived PAHs are degraded during transport through the air and water of Chesapeake Bay or that PAHs in the seabed are dominated by historically or recently deposited coal-derived PAHs.
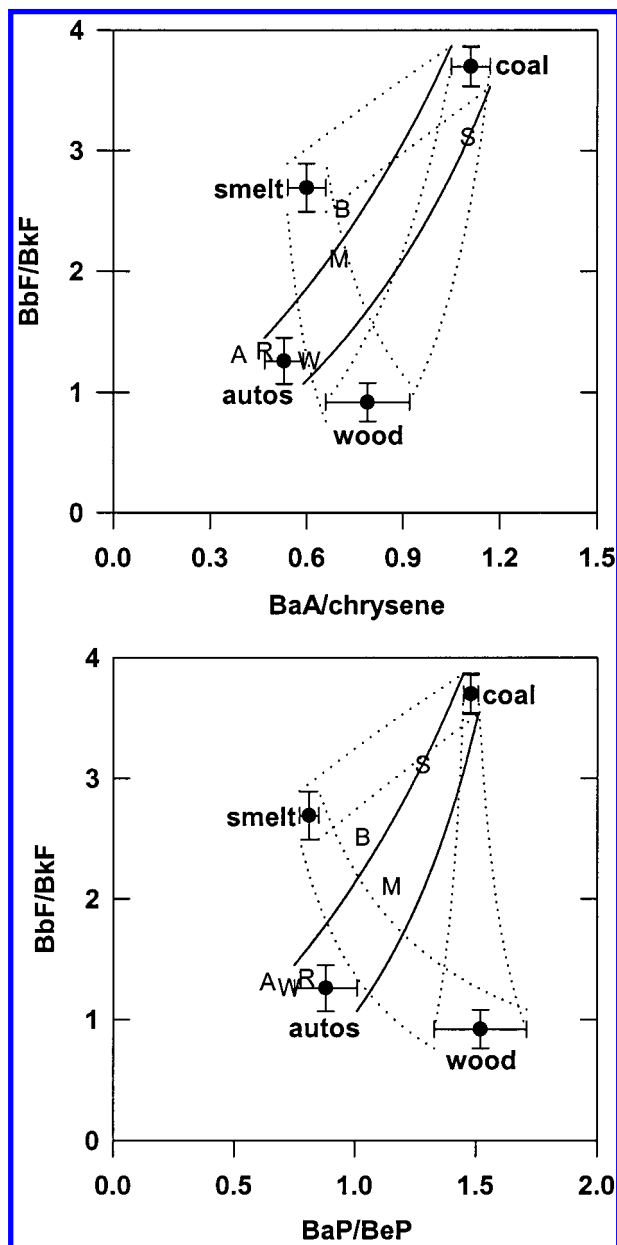
FIGURE 4. PAH isomer ratios on particulate matter collected from Chesapeake Bay air, water, and sediments between 1991 and 1998, and those for various emission sources ± standard error (Table 1). A — air particles, R — rain particles, M — surface microlayer particles, W — surface water particles, B — bottom water particles, S — surface sediments. Solid lines represent the range in mixing lines between automotive and coal sources based on the upper and lower limits of the isomer ratios for each source; dotted lines indicate the range in mixing lines between coal-wood, coal-smelter, and smelter-wood sources.

Recent emissions of coal-derived PAHs in the mid-Atlantic region of the U.S. are evident due to the large contribution of PAHs (47(±5)%) from these sources to the surface microlayer of Chesapeake Bay (Figure 4). This indicates that coal continues to be a source of PAHs to the environment, particularly in the vicinity of coal storage and combustion activities where the surface microlayer samples were collected (25). Further, the lack of coal-derived PAHs in the atmosphere and surface waters of the Bay implies short atmospheric and water column residence times for coal-derived particles. Thus, the surface microlayer data indicate that current coal emissions could account for as much as half of the input of the carcinogenic group of PAHs to Chesapeake Bay, but that

TABLE 2. Fossil Fuel Combustion-Derived Particulate PAH Emissions in the United States

	% of total U.S. fossil fuel-derived energy use[a]	particle-associated PAH emission rates (ng/kJ total fossil fuel-derived energy)[b]
Transportation		
petroleum[c]	28.9	33 ± 8
natural gas	0.9	
Residential and Commercial		
petroleum	2.7	0.65
natural gas	10.2	0.68[d]
coal	0.2	8.2
Industrial		
petroleum	11.1	0.12 ± 0.04
natural gas	12.1	0.8[d]
coal	3.3	0.05[e]
Electric Utilities		
petroleum	1.4	
natural gas	4.3	
coal	25.0	0.2

[a] 100 × fraction of total energy consumption in the U.S. (1990−1996) (39, 40) × fraction of the energy demand met by fossil fuel type (39, 40)/Σ fraction of total energy consumption in the U.S. (1990−1996) × fraction of the energy demand met by fossil fuel type. [b] ng/kJ fossil fuel-derived energy (4, 8−10) × fraction of total fossil fuel-derived energy. [c] 96−97% of the domestic demand for gasoline in the U.S. is for automobile use (39). [d] Based on the PAH emission rate for natural gas home appliances (10). [e] Coal-fired industrial boiler PAH emission rate (4).

the input of these contaminants from coal sources is likely much less due to rapid settling of coal-derived material out of the atmosphere leading to enrichment of PAHs from these sources at the air/water interface. Likewise, rapid settling of coal-derived material out of the water column should lead to a similar enrichment (i.e. 47%) of PAHs from these sources in surface sediments. The greater enrichment of PAHs from coal sources observed in surface sediments of Chesapeake Bay, therefore, is likely due to the influence of historically deposited PAHs from these sources, input of coal-derived PAHs via processes other than atmospheric transport and deposition, and/or preferential degradation of automotive-derived PAHs prior to deposition in the seabed.

Ice core data indicate a significant decline in global PAH emission from coal-derived sources over the last century (45). However, since historically PAH emissions were predominantly coal-derived (45), deep seabed mixing due to both biological and physical processes in many areas of Chesapeake Bay (46), likely increases the relative proportion of coal-derived PAHs in surface sediments. Moreover, current emissions of coal-derived PAHs in the coal and steel industrial region of Pennsylvania (43) may influence the PAH composition of Chesapeake Bay sediments since the Susquehanna River which drains this region contributes 25% of the sediment load to the Bay (47). In addition, photodegradation of PAHs associated with gray aerosols, typical of automobile emissions, is expected to occur during atmospheric transport, whereas PAHs associated with black coal particles are resistant to photolysis (28). If similar preferential degradation of motor vehicle-derived PAHs occurs within surface waters, aided by the apparently greater residence time for PAHs from this source in the water column, such degradation processes may also contribute to the greater enrichment of carcinogenic PAHs from coal sources observed in surface sediments of Chesapeake Bay.

Regardless of whether PAHs emitted from motor vehicles are preferentially degraded or deposited to sediments dominated by PAHs from other sources, this study demonstrates that motor vehicles were likely a significant source of

carcinogenic PAHs to the atmosphere and surface waters of Chesapeake Bay over the past decade. Subsequently, various terrestrial and aquatic organisms of the Chesapeake Bay coastal region have been predominantly exposed to carcinogenic PAHs through motor vehicle combustion of fossil fuels. Moreover, it is likely that motor vehicles will continue to be the dominant source of carcinogenic PAHs in populated coastal regions of the United States. Total energy consumption in the U.S. has more than doubled since 1960 and is continuing to rise (*39, 40*). Projections also indicate that the proportion of the population living in coastal regions will increase to 75% over the next 30 years (*5*). In the Chesapeake Bay watershed, the number of vehicle miles traveled rose 117% from 1970 to 1997, whereas population growth in the region was only 28% over the same time period (*21*). Further, this trend of motor vehicle use outpacing population growth is expected to continue (*21*). Thus, the current and potential future impact of population growth, highway development, and motor vehicle-derived carcinogens on coastal ecosystems should be considered in the development of environmental management strategies.

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