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RESEARCH ARTICLE

Spatial variation of PAHs and PCBs in coastal air, seawater, and sediments in a heavily industrialized region

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Abstract Concurrent coastal seawater ($n = 22$), sediment ($n = 22$), and atmospheric samples ($n = 10$) were collected in the Aliaga industrial region, Turkey, to explore the spatial variation, sources, and air-seawater exchange of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Seawater Σ_{16}PAH concentrations (particle + dissolved) ranged between 5107 and 294,624 pg L^{-1}, while Σ_{41}PCB concentrations were in the range of 880–50,829 pg L^{-1}. Levels in sediments were highly variable ranging between 35.5–49,682 and 2.7–2450 μg kg^{-1} in dry weight for Σ_{16}PAHs and Σ_{41}PCBs, respectively. Atmospheric concentrations varied between 1791–274,974 and 104–20,083 pg m^{-3} for Σ_{16}PAHs and Σ_{41}PCBs, respectively. Sediment organic matter (OM) content and levels of Σ_{16}PAHs and Σ_{41}PCBs correlated weakly ($r^2 = 0.19$–0.23, $p < 0.05$) suggesting that the spatial variations of PAHs and PCBs were mainly affected by local sources rather than their sorption to OM. The geographical distribution of PAH and PCB concentrations in air, seawater, and sediment and factor analysis on the sediment levels pointed out that the major sources in the region are steel plants, petroleum refinery, petrochemical complex, ship breaking, loading/unloading activities at the ports, vehicular emissions, and fossil fuel combustion emissions. The direction of the air-seawater exchange was also explored by estimating seawater fugacity fractions of PAHs and PCBs. For PAHs, the number of cases implying deposition (43.0%) and volatilization (39.5%) was similar, while for PCBs, the number of cases implying volatilization (60.4%) was much higher compared to deposition (21.6%). Fugacity fractions were generally <0.36 (deposition) at the sites close to industrial and ship breaking activities where the highest seawater and sediment levels were measured, implying that atmospheric deposition is an important mechanism affecting seawater and sediment PAH and PCB levels.

Keywords PAHs · PCBs · Sediment · Seawater · Air-water exchange

Introduction

Persistent organic pollutants (POPs) enter to the surface waters by dry deposition (particle phase), air-water exchange (gas phase), and wet deposition from the atmosphere, and by wastewater discharges (Odabasi et al. 2008; Cetin et al. 2016). In the water column, hydrophobic compounds are adsorbed to the particulate matter, and they are eventually deposited to bottom sediments (Bigus et al. 2014; Kwan et al. 2014). Along with the physicochemical properties of the pollutants, accumulation in the sediment mainly depends on physical properties and adsorptive capacity of the sediment and the partitioning coefficient between the water and sediment (Bigus et al. 2014). Therefore, sediments are an important reservoir for POPs providing information on their sources, geographical and historical variations.

Recently conducted studies based on soil, ambient air, and plant (pine barks and needles) sampling have shown that there are several important local sources of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in Aliaga industrial region, Izmir, Turkey, and the region is heavily polluted (Aydin et al. 2014; Odabasi et al. 2015).

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Although atmospheric and soil levels and their exchange between these compartments have been studied well in the region, seawater and sediments that play important roles in environmental dynamics and fate of the pollutants have not been investigated. The objectives of the present study were (1) to determine the spatial variations and sources of PAHs and PCBs in coastal atmosphere, seawater, and sediments and (2) to investigate their air-sea exchange in the Aliaga industrial region, Turkey.

Materials and methods

Study area and sample collection

The study region (Aliaga, 38° 42′–38° 55′ N and 26° 50′–27° 04′ E) situated on the Aegean Sea coast (western Turkey) has a number of pollutant sources, i.e., scrap processing iron-steel plants (*n* = 5), steel rolling mills, a large petroleum refinery, a petrochemical complex, a natural gas-fired power plant, a fertilizer plant, several scrap and slag storage piles, heavy traffic of scrap iron trucks, ship breaking yards, and active ports importing/exporting products and raw materials. Aliaga town (population of ~60,000), a number of villages, and agricultural areas are also included within the study region.

Concurrent samples were collected from coastal sediment and seawater between July 13 and 20, 2009 from 22 sites along the seashore (~60 km) in the Aliaga industrial region (Fig. 1). Surface sediment samples were collected manually with a Van Veen grab sampler (2 L) from 22 different sites. Water depth at sediment sampling sites varied between 3 and 19 m. At each point, approximately 350 g of the homogenized sediment sample was transferred into a glass jar capped with Teflon-lined lid and stored in the laboratory at 4 °C as until sample preparation. Seawater samples (~10 L) were collected from 30 cm under the surface using precleaned polyethylene containers without allowing a headspace. Ambient air samples were also collected during mid-July–mid-August 2009 at ten coastal sites close to the 15 seawater sampling sites (distance <1 km) using polyurethane foam (PUF) disk passive air samplers (PAS). Average sampling time was 30 days, and the average air temperature was 27.1 °C. Before sampling, depuration compounds (^{13}C-PCB 3, ^{13}C-PCB 9, ^{13}C-PCB 15, PCB 30, PCB 107, and PCB 198), 17.5–20 ng per sample were spiked onto PUF disks to determine the compound-specific sampling rates.

The temperatures of seawater and sediment samples were measured onsite using a thermometer. For seawater and sediment samples, the average observed temperatures were 26.5 ± 0.5 °C and 25.8 ± 0.8 °C, respectively. pH of seawater was measured using a pH meter (WTW pH 720), while salinity was determined with a conductivity meter (WTW Cond 720). The average salinity and pH of the seawater were 0.65 M and ~8.0, respectively.

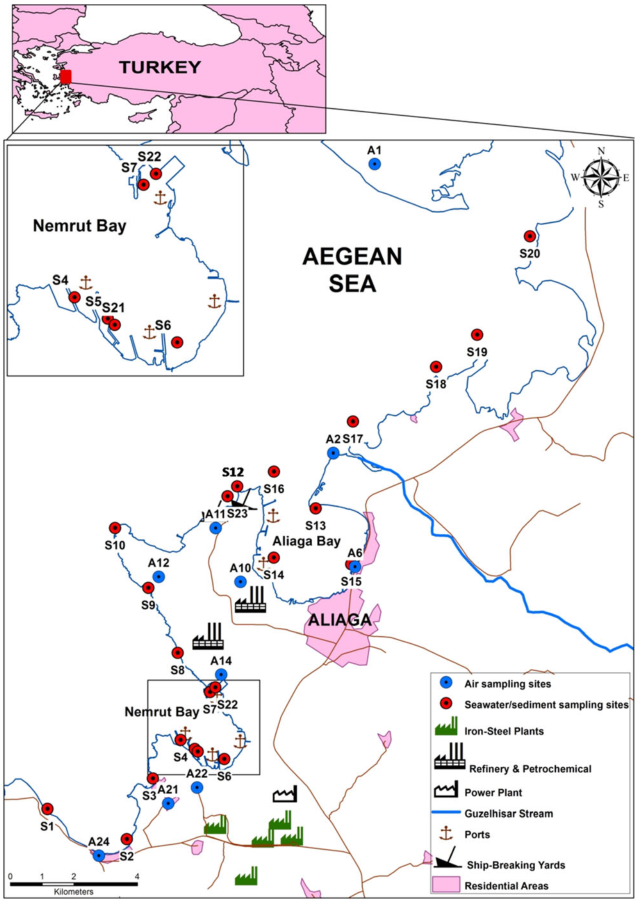

Fig. 1 General view of the study area

Sample preparation and analysis

Before extraction, PCB and PAH surrogate standards were added to all samples. Ambient air PUFs were Soxhlet extracted for 12 h with 1:1 acetone/hexane (ACE/HEX). Approximately 3–5 g of sodium sulfate was added to the 5 g of sediment sample, and the mixture was homogenized with a glass bar. Samples were soaked in 50 mL of a 1:1 ACE/HEX overnight. Then, they were ultrasonically extracted for 1 h. Water samples were filtered through a glass fiber filter (0.7 μm pore size, 47 mm diameter) to retain particle phase compounds followed by a resin column (~10 g XAD-2) to sorb dissolved phase. Dissolved and particle phase samples were ultrasonically extracted for 1 h with 1:1 ACE/HEX. Water in extracts was removed by addition of 2 g sodium sulfate. Sediment samples were treated with 1.5 g of activated copper powder to remove elemental sulfur. Volumes of all extracts were reduced to 2 mL, and they were switched into HEX utilizing a rotary evaporator and a stream of high purity N_2. Samples were cleaned up and separated into two fractions

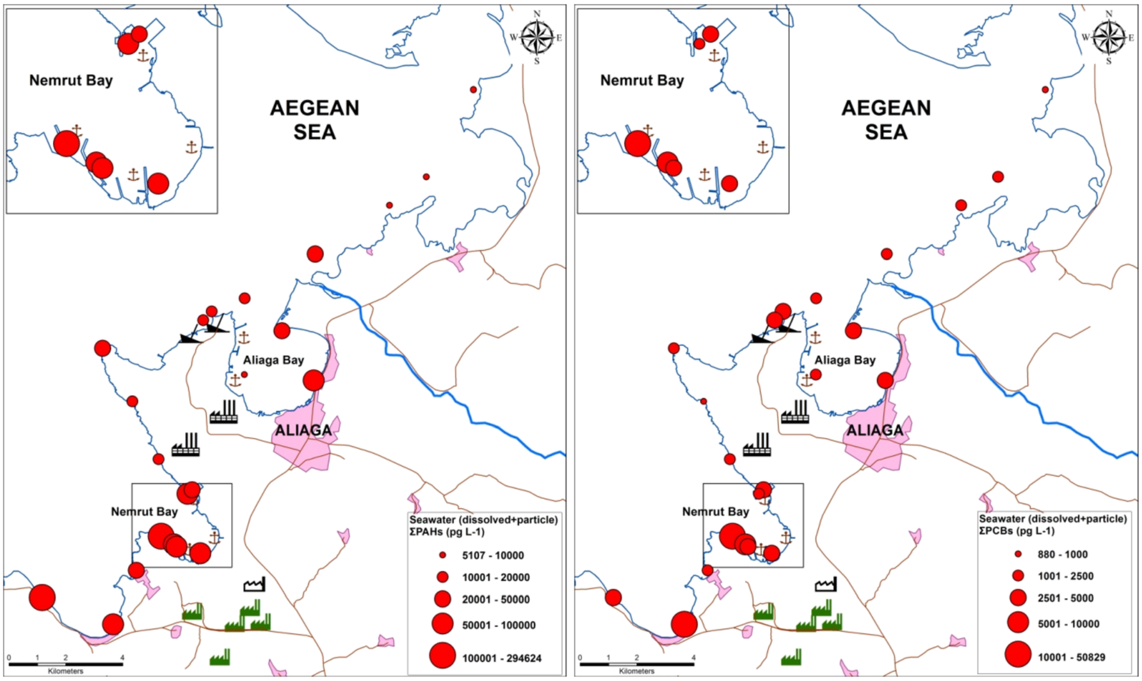

Fig. 2 Spatial distribution of seawater Σ_{16}PAH and Σ_{41}PCB concentrations in the study area

using an alumina-silicic acid column packed with 3 g silicic acid (4.5% water) and 2 g alumina (6% water). PCBs were eluted with 35 mL petroleum ether (fraction 1), while PAHs were eluted with 20 mL dichloromethane (fraction 2). The solvent of the extracts was switched into HEX, and their volume was reduced to 1 mL under a stream of N_2.

All samples were analyzed for 16 PAHs and 41 PCBs with an Agilent 6890 N gas chromatograph (GC)-mass spectrometer (Agilent 5973 inert MSD) using electron impact ionization and selected ion monitoring mode (SIM). An HP5-MS capillary column (30 m, 0.25 mm, and 0.25 μm) was used for the analysis, and helium was the carrier gas. Fraction 1 was

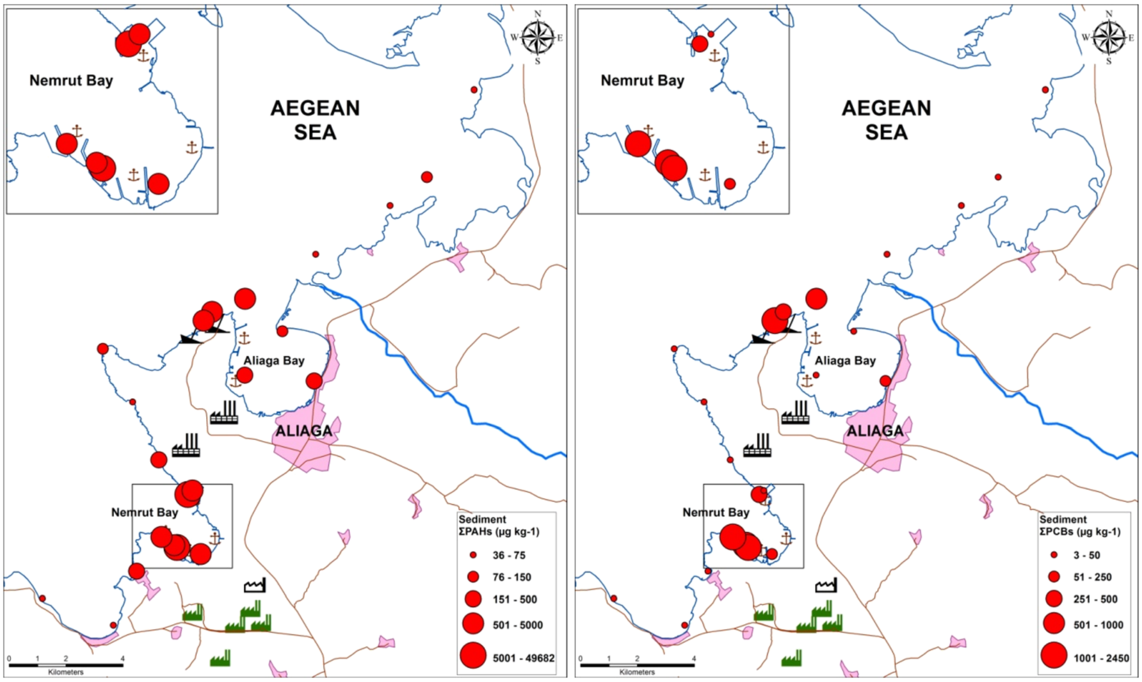

Fig. 3 Spatial distribution of sediment Σ_{16}PAH and Σ_{41}PCB concentrations in the study area

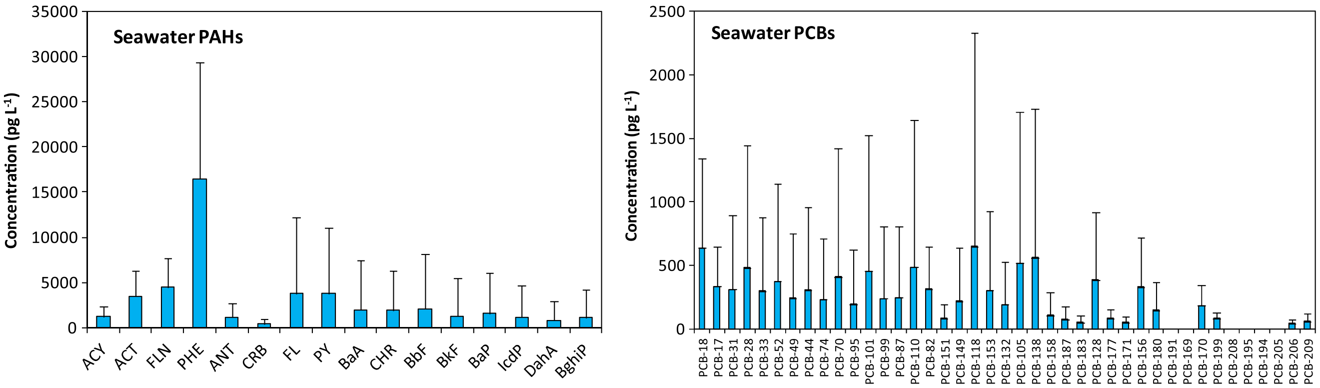

Fig. 4 Average concentrations of individual PAHs and PCBs in seawater. *Error bars* are 1 SD

analyzed for PCBs. Then, for PAH analysis, equal volumes of fractions 1 and 2 were mixed and analyzed as lighter PAHs are eluted in part with fraction 1. The identification of PAH compounds and PCB congeners was based on their retention times, target, and qualifier ions, and their quantification was performed using the internal standard calibration procedure.

Sediment water content was determined gravimetrically using sub-samples after drying at 103 °C in an oven for 24 h. The organic matter (OM) content was also determined gravimetrically by baking in a furnace at 600 °C for 4 h (Wang et al. 2011).

Quality control

Average recoveries for the surrogate standards ranged between 60 and 74% (acenaphthene-d10), 75–78% (phenanthrene-d10), 67–79% (chrysene-d12), 63–76% (perylene-d12), 71–86% (PCB-14), 70–88% (PCB-65), and 71–89% (PCB-166), and sample amounts were corrected for surrogate recoveries. For 1 μL injection, instrumental detection limits (IDL) were 0.15 and 0.10 pg for PAHs and PCBs, respectively. PAH and PCB levels in blank samples (n = 4 for each sample type) were also determined. Definition of the method detection limit (MDL) was MDL = mean blank value + 3SD. For the compounds that could not be detected in blank samples, IDLs were substituted. Mean analyte quantities in blanks were generally <5% of the sample quantities. Sample amounts above the MDL were quantified, and they were blank-corrected by subtracting the average blank levels from those in samples.

Sampling rates (R, m^3/day) for atmospheric samples were determined based on the loss of spiked depuration compound amounts, and they averaged as 2.14 ± 0.46 m^3/day. The effective air sampling volumes (V_{air}, m^3) for individual compounds/congeners during the sampling period were estimated using the methodology developed by Shoeib and Harner (2002). Sampling rate and effective sampling volume calculations were detailed by Kaya et al. (2012). For the calculation of V_{air}, it was assumed that both gas phase and particle phase compounds have similar sampling rates (Harner et al. 2014; Harner et al. 2013).

Estimation of gas phase concentrations

PUF disk passive air samplers mainly target gas phase compounds. However, recent studies have implied that PUF disk

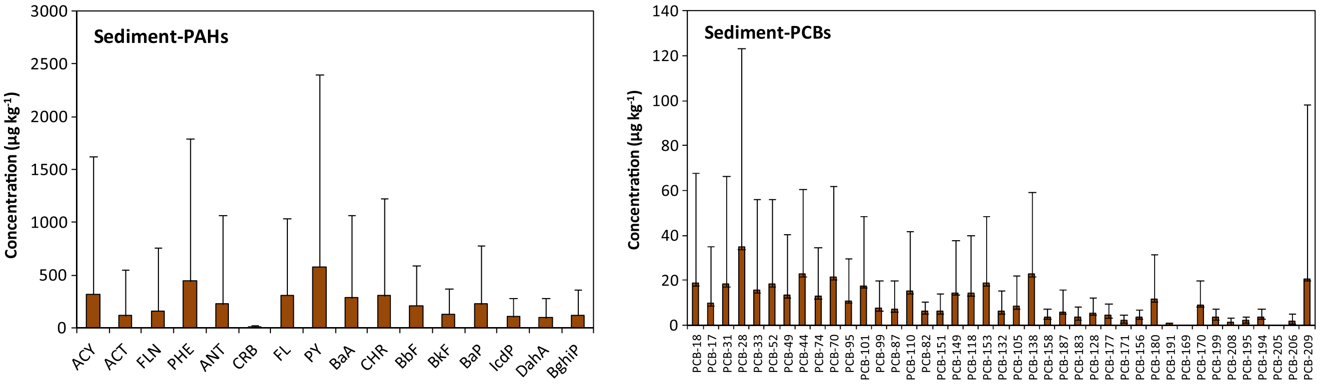

Fig. 5 Average concentrations of individual PAHs and PCBs in sediment. *Error bars* are 1 SD

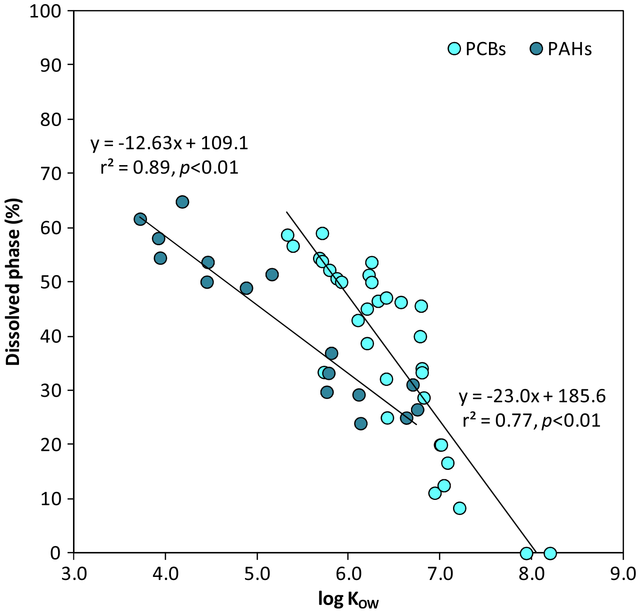

Fig. 6 Relationships between dissolved phase PAH and PCB percentages and K_{OW}

passive air samplers also collect particles, and the sampling rates are typically in the range 4 ± 2 m^3 day^{-1} for both gas and particle phase compounds (Markovic et al. 2015; Harner et al. 2014; Harner et al. 2013). Since gas phase concentrations are needed to assess air-seawater gas exchange of pollutants, atmospheric total (gas + particle phase) PAH and PCB levels measured with passive samplers were used to estimate the gas phase concentrations in the present study.

Distribution of atmospheric semivolatile organic compounds between the gas and particle phases is explained using the gas-particle partition coefficient, K_p (m^3 μg^{-1}) (Harner and Bidleman 1998):

$$K_p = \left(C_p / C_{TSP}\right) / C_g \tag{1}$$

where C_p *and* C_g are the concentrations in the particle and gas phases, respectively (ng m^{-3}), and C_{TSP} is the atmospheric total suspended particulate concentration (μg m^{-3}).

The octanol-air partition coefficient (K_{OA}) and organic matter fraction of particles (f_{OM}) were used to estimate K_p assuming that the major distribution process is absorption (Harner and Bidleman 1998):

$$\log K_p = \log K_{OA} + \log f_{OM} - 11.91 \tag{2}$$

Gas phase concentrations were estimated as:

$$C_g = C_t \left\{1 - \left[\left(K_p\, C_{TSP}\right) / \left(1 + K_p\, C_{TSP}\right)\right]\right\} \tag{3}$$

where C_t is the total (gas + particle phase) concentration measured with the PUF disk passive air sampler.

Temperature (T) dependent K_{OA} values of the PAHs and PCBs (log $K_{OA} = A + B/T$) were calculated using the constants (A and B) reported by Odabasi et al. (2006a), Odabasi et al. (2006b), Harner and Bidleman (1996), Chen et al. (2002), Zhang et al. (1999). Recently measured average TSP concentration in Aliaga region (95 μg m^{-3}) and its OM content (50%)

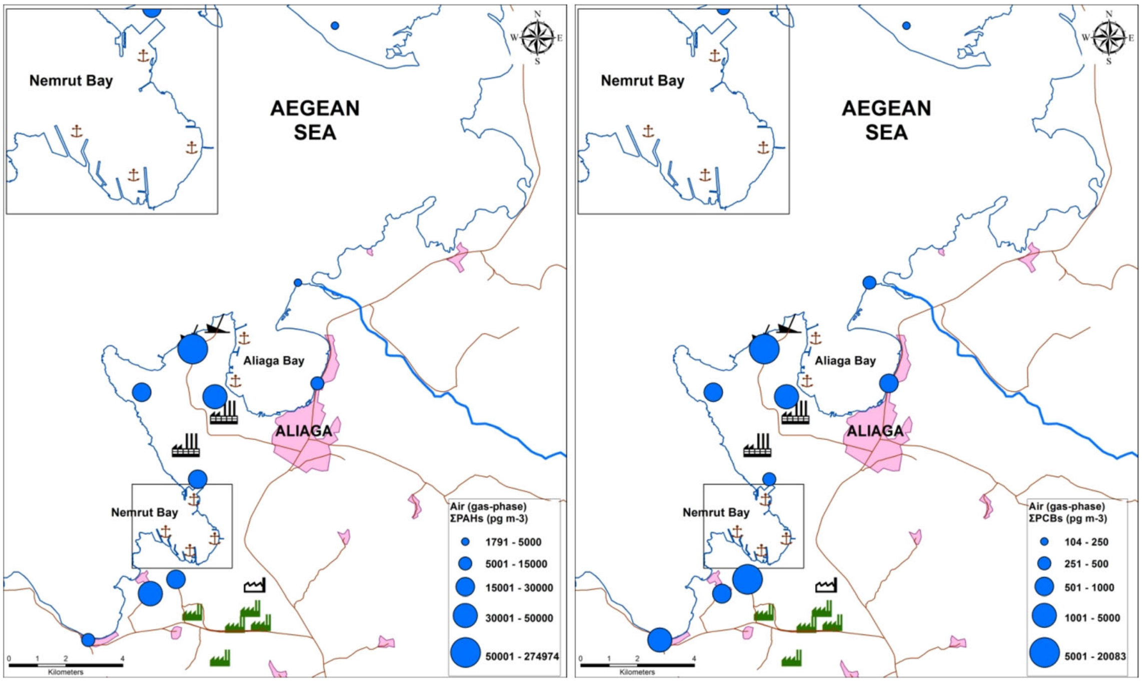

Fig. 7 Spatial distribution of atmospheric Σ_{16}PAH and Σ_{41}PCB concentrations in the study area

Table 1 Factor analysis results for PAHs in coastal sediments

	Factor 1	Factor 2
Acenaphthylene	0.906	
Acenaphthene	0.898	
Fluorene	0.898	
Phenanthrene	0.857	0.514
Anthracene	0.887	
Carbazole		0.919
Fluoranthene	0.746	0.663
Pyrene	0.851	0.524
Benz(a)anthracene	0.813	0.582
Chrysene	0.840	0.542
Benzo(b)fluoranthene	0.580	0.814
Benzo(k)fluoranthene	0.625	0.777
Benzo(a)pyrene	0.765	0.643
Indeno(1,2,3-cd)pyrene		0.894
Dibenz(a,h)anthracene	0.605	0.787
Benzo(g,h,i)perylene	0.647	0.757
% of variance	56.3	43.2

were used for the calculation of K_p and gas phase fractions (Bozlaker et al. 2008a; Cetin and Odabasi 2008).

Results and discussions

PAH and PCB concentrations in seawater, sediment, and air

Total (particle + dissolved) Σ_{16}PAH concentrations in the seawater samples ranged between 5107 and 294,624 pg L^{-1}, while Σ_{41}PCB concentrations were in the range of 880–50,829 pg L^{-1} (Fig. 2). Seawater PAH and PCB levels observed in this study were within the ranges reported previously (Totten et al. 2001; Nizzetto et al. 2008; Valavanidis et al. 2008). It was reported that the average aqueous Σ_{14}PAH concentration in Izmir Bay, Turkey, was 12,700 pg L^{-1}, while Σ_{41}PCB concentrations were 250–390 pg L^{-1} (Demircioglu et al. 2008; Odabasi et al. 2008). Izmir Bay is not influenced by any industrial PAH/PCB source. Most of the PAH and PCB levels observed in the present study were substantially higher than those reported for Izmir Bay, further indicating that surface waters in Aliaga region are polluted by the industrial sources.

Concentrations in sediments varied highly and ranged between 35.5–49,682 and 2.7–2450 μg kg^{-1} in dry weight for Σ_{16}PAHs and Σ_{41}PCBs, respectively (Fig. 3). Observed sediment PAH concentrations were generally within the ranges reported previously. ΣPAH concentrations reported for Hong Kong sediment ranged between 22.4 and 4420 μg kg^{-1} dry weight (Zheng and Richardson 1999), and for coastal sediments in the Pearl River Delta in China, they were 94–4300 μg kg^{-1} dry weight (Fung et al. 2005). Feo et al. (2011) have reported a wider interval for Naples harbor sediments (12–21,740 μg kg^{-1} dry weight). Observed sediment PCB concentrations were comparable to Σ_{28}PCB concentrations reported for the Pearl River Delta sediments (6.0–290 μg kg^{-1} dry weight) (Fung et al. 2005) and for the Venice Lagoon, Italy (89–717 μg kg^{-1} dry weight) (Frignani et al. 2005), and they were substantially higher than those measured for Singapore's coastal sediments where Σ_{28}PCBs

Table 2 Factor analysis results for PCBs in coastal sediments

	Factor 1	Factor 2	Factor 3	Factor 4
PCB-18	0.976			
PCB-17	0.966			
PCB-31	0.974			
PCB-28	0.988			
PCB-33	0.983			
PCB-52	0.931			
PCB-49	0.939			
PCB-44	0.923			
PCB-74	0.909			
PCB-70	0.907			
PCB-95	0.778		0.543	
PCB-101	0.825		0.512	
PCB-99	0.825			
PCB-87	0.830			
PCB-110	0.848			
PCB-151		0.670	0.669	
PCB-149	0.500		0.817	
PCB-118	0.886			
PCB-153	0.526		0.814	
PCB-132	0.630	0.523	0.567	
PCB-105	0.849			
PCB-138	0.663		0.714	
PCB-158		0.898		
PCB-187		0.543	0.799	
PCB-183		0.834	0.513	
PCB-128	0.698	0.644		
PCB-177		0.802	0.557	
PCB-171		0.980		
PCB-156		0.917		
PCB-180			0.886	
PCB-170		0.546	0.752	
PCB-199		0.895		
PCB-194		0.916		
PCB-206		0.796		0.596
PCB-209				0.997
% of variance	47.2	26.2	21.4	4.0

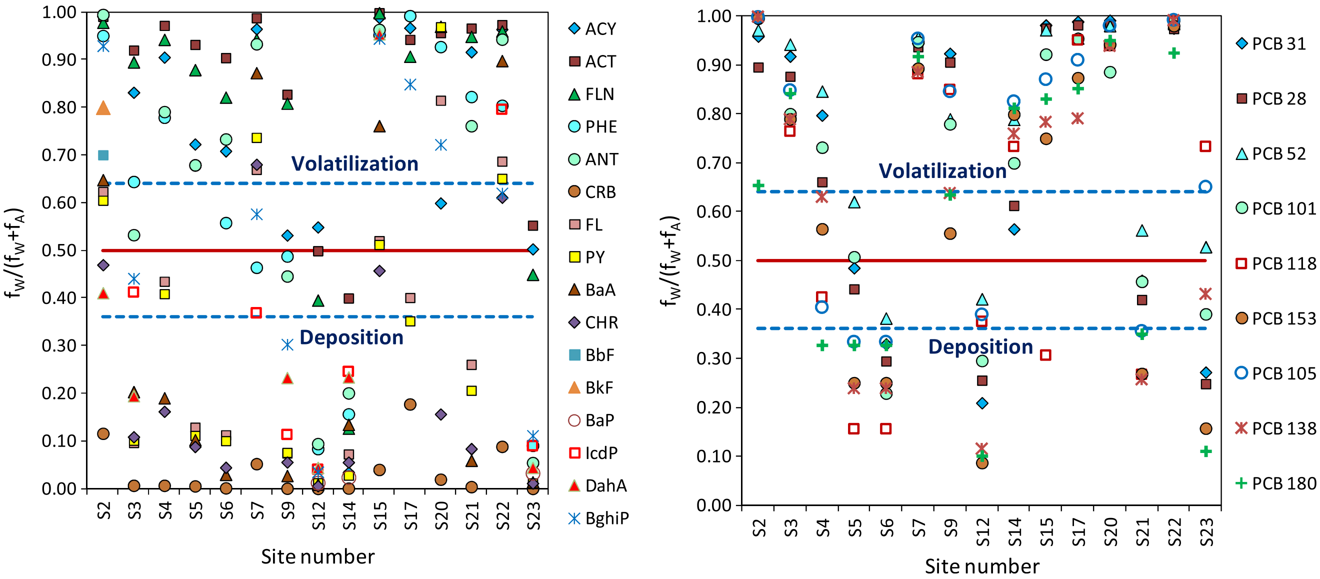

Fig. 8 Seawater fugacity fractions of PAHs and PCBs at different sampling sites. The *solid horizontal line* represents equilibrium, and *dashed lines* indicate the uncertainty range

ranged between 0.339 and 1.356 μg kg^{-1} dry weight (Wurl and Obbard 2006).

Seawater PAH and PCB compound/congener profiles were dominated by low to medium molecular weight (MW) compounds for PAHs (phenanthrene, fluorene, acenaphthene, fluoranthene, and pyrene) and PCBs (PCB-118, 18, 138, 105, 110, 28, 101, and 70). Pyrene, phenanthrene, fluoranthene, benz(a)anthracene, and chrysene were dominant PAHs for sediment samples, and PCB-18, 138, 44, 70, 209, 18, 153, and 52 were the congeners having the highest levels. In general, seawater and sediment profiles were similar. However, the contributions of high molecular weight compounds were higher to total PAHs and PCBs in sediment relative to seawater (Figs. 4 and 5). The difference in seawater and sediment PAH and PCB profiles may be ascribed to differential partitioning of the individual compounds (i.e., high MW compounds have relatively higher octanol-water partition coefficients (K_{OW}); thus, their sorption to organic matter is relatively higher).

Distribution of PAHs and PCBs between particle and dissolved phases in the seawater is mainly decided by their physicochemical properties (i.e., solubility, octanol-water partition coefficient-K_{OW}, and organic carbon partition coefficient (K_{OC}) (Bigus et al. 2014). PAHs and PCBs were distributed between particle and dissolved phases in the present study. Dissolved phase fraction ranged between 24–65% and 0–59% for PAHs and PCBs, respectively, and decreased with K_{OW}. Dissolved phase fraction and K_{OW} correlated well ($p < 0.01$) and K_{OW} explained the 77 and 89% of variability in dissolved phase fractions for PAHs and PCBs, respectively (Fig. 6).

Adsorption of POPs onto sediments strongly depends on the properties of both the pollutants (adsorbate) and sediments (adsorbent), the contaminant concentration, and sediment OM content (Bigus et al. 2014). OM contents of the sediment samples collected in the present study varied highly and ranged from 2.6 to 17.6% (dry weight, 9.4 ± 4.8%, average ± SD). Sediment OM content and concentrations of Σ_{16}PAHs and Σ_{41}PCBs correlated significantly ($p < 0.05$). However, OM content explained only the 19 and 23% of variability in PAH and PCB concentrations, respectively. This suggested that the spatial variations of Σ_{16}PAHs and Σ_{41}PCBs in sediments were mainly affected by local sources rather than their sorption to organic matter.

Atmospheric concentrations were also highly variable and ranged between 1791–274,974 and 104–20,083 pg m^{-3} for Σ_{16}PAHs and Σ_{41}PCBs, respectively (Fig. 7). Low molecular weight compounds, i.e., phenanthrene, fluorene, fluoranthene, and pyrene, dominated the observed Σ_{16}PAH levels. Low molecular weight congeners (PCB-18, 28, 31, 33, 52, and 49) also dominated the atmospheric Σ_{41}PCB levels.

Sources of PAHs and PCBs

For all sample types (air, seawater, and sediment), the lowest PAH and PCB concentrations were measured at sites far from industrial sources. However, the highest levels were detected at sampling points located at Nemrut Bay where there are active ports for product and raw material import/export for steel plants, refinery/petrochemical plant, and near the ship breaking yards. In a recent study in the study area, using Positive Matrix Factorization, five sources for atmospheric PAHs were identified as biomass and coal combustion, iron-steel production, unburned crude oil and petroleum products, and diesel and gasoline exhaust emissions with contributions of 40, 27, 27, 3, and 3%, respectively (Aydin et al. 2014). Identified sources of atmospheric PCBs were iron-steel production and ship breaking activities, coal and wood combustion, and evaporative emissions from technical PCB mixtures with contributions of 57, 31, and 12%, respectively (Aydin et al. 2014). The spatial distribution of PAH and PCB levels observed in the present study are in agreement with the previous studies reporting that steel plants, petroleum refinery, petrochemical complex, and ship breaking activities are the primary sources of atmospheric PAHs and PCBs in the region (Aydin et al. 2014; Odabasi et al. 2015). These findings further suggest that these sources may substantially affect the PAH and PCB levels in coastal seawater and sediments in the region.

Possible sources of PAHs and PCBs measured in sediments were further investigated by factor analysis. Principal component analysis was used for extraction, and the raw calculated factor loading coefficients were rotated by Varimax with Kaiser Normalization (SPSS software version 20.0 for Windows by SPSS Inc.). Only major principal components (PCs) having eigenvalues >1.0 were extracted and significant clusters having factor loadings >0.5.

The number of factors extracted for PAHs were two. These factors accounted for the 99.5% of the total variance (Table 1). The first factor (56.3% of the variance) had high loadings on acenaphthylene, acenaphthene fluorene, phenanthrene, anthracene, fluoranthene, pyrene, banz[*a*]anthracene, and chrysene. Low molecular weight PAHs, especially acenaphthylene, were reported as markers for scrap processing iron-steel plants by Odabasi et al. (2009). Therefore, factor 1 could be attributed to iron-steel production. The second factor (43.2% of the variance) was dominated by non-volatile PAHs like benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*g,h,i*]perylene. These compounds were indicated as source fingerprints for vehicular exhaust emissions (Motelay-Massei et al. 2003; Callen et al. 2012; Tian et al. 2013). Carbazole had also a high loading in factor 2. Carbazole is found in fossil fuels (i.e., crude oil, coal), and it is primarily emitted from coal combustion (Odabasi et al. 2006b). These results indicate that factor 2 is not a fully resolved factor, and therefore, it could be attributed to vehicular exhaust and other fossil fuel combustion emissions (i.e., crude oil and coal).

Four factors were extracted for PCBs accounting for the 98.8% of the total variance (Table 2). The first factor (47.2% of the variance) was highly loaded on PCB-17, PCB-18, PCB-28, PCB-31, and PCB-33. It was reported that these low molecular weight congeners dominate the iron-steel plant emissions (Odabasi et al. 2009). This factor had also high loadings on PCB-52, PCB-49, PCB-44, PCB-74, PCB-70, PCB-95, PCB-101, PCB-99, PCB-87, PCB-110, PCB-118, and PCB-105. Lee et al. (2005) have reported that coal and hardwood combustion emissions are dominated by PCB-49, PCB-52, PCB-28, PCB-44, PCB-101, PCB-110, and PCB-118. These indicate that factor 1 is not a fully resolved factor, and therefore, it could be attributed to iron-steel plant and combustion (i.e., coal and wood) emissions. Highly chlorinated congeners (PCB-158, PCB-183, PCB-177, PCB-171, PCB-156, PCB-199, PCB-194, and PCB-206) showed high correlations for factor 2 (26.2% of the variance). Highly chlorinated congeners (PCB-149, PCB-153, PCB-138, PCB-187, PCB-180, and PCB-170) were also associated with factor 3 (21.4% of the variance). Most of these congeners are major components of technical PCB mixtures like Aroclor 1254, Arochlor 1260, and Kanechlor 600 (Takasuga et al. 2005; Takasuga et al. 2006; Jin et al. 2012). Therefore, factors 2 and 3 could be attributed to technical PCB mixtures. The last factor (4.0% of the variance) was highly loaded on PCB-209. PCB209 is not a technical mixture component, but it is present in phthalocyanine green and titanium dioxide white pigments that are used for various applications (Hu et al. 2011). These pigments are likely to be contained in ferrous scrap that is used as the raw material in iron-steel production in the region. Scrap is produced by ship breaking, and it is also imported through the ports in the area. The highest sediment PCB-209 levels were measured at sites close to ports (sites 4, 5, 6, 7, and 21) and ship breaking yards (sites 12, 16, and 23). Thus, factor 4 could be attributed to ship breaking and scrap loading/unloading activities at the ports.

Air-seawater exchange of PAHs and PCBs

Measured air and seawater concentrations were used to determine the direction of PAH and PCB transfer between the air and seawater interface. The seawater fugacity fraction [$f_W/(f_W + f_A) = (H'C_w)/(H'C_w + C_g)$] > 0.5 implies net contaminant volatilization from seawater; values <0.5 indicate net gas phase deposition from air, while in the case of equilibrium, $f_W/(f_W + f_A)$ value is ~0.5. Here, C_w and C_g are the dissolved phase water and gas phase air concentrations (pg m^{-3}), and H' is the dimensionless Henry's law constant for PAHs (Ten Hulscher et al. 1992; Bamford et al. 1999) and PCBs (Schenker et al. 2005). Salting-out constants (K_s, L mol^{-1}) were estimated using the method by Ni and Yalkowsky (2003) and the K_{OW} values for PAHs (Finizio et al. 1997; Jonker and Koelmans 2002; VCCL 2016; NLM 2016) and PCBs (Han et al. 2006). H^* is the Henry's law constant in saline water. It was determined through [$\log (H^*/H) = K_s C_s$] where C_s is the molar salt concentration of seawater (measured as 0.65 M). The uncertainty of the calculated fugacity fractions was estimated using a propagated error analysis. Uncertainty in H values was estimated as <25% (Ten Hulscher et al. 1992; Bamford et al. 1999; Schenker et al. 2005). The uncertainties of C_g and C_w were taken as 10% (Cetin and Odabasi 2007; Odabasi et al. 2008). It should be noted that the estimation of gas phase concentrations introduces additional errors that could not be assessed easily. Previously collected atmospheric concentration data in Izmir region based on active sampling (Odabasi et al. 2008; Bozlaker et al. 2008a; Bozlaker et al. 2008b; Demircioglu et al. 2011) was evaluated in terms of the partitioning model used in the present study. It was found that the modeling errors are variable for different compounds having different volatilities and for sample sets collected at different locations (i.e., suburban, urban). Model performs well (errors 1.0–20%) for compounds with log K_{OA} values <9.0, while errors increase up to ~50% for those with log K_{OA} values >12.0. Variability based on site characteristics does not allow assigning certain values for modeling errors associated with C_g. If a conservative modeling error of 50% is taken into account, error propagation related to estimation of $f_W/(f_W + f_A)$ implies that the equilibrium is denoted by a fraction of 0.5 ± 0.14 (a range of 0.36–0.64). It should be noted that the seawater samples were grab samples, while air samples were 1-month integrated samples. Therefore, possible variations in seawater concentrations during the air sampling period introduce additional uncertainty to fugacity calculations. The fugacity fractions for most of the PAHs (82.5%) and PCBs (82.0%) indicated non-equilibrium conditions (Fig. 8). For PAHs, the number of the cases implying deposition (43.0%) and volatilization (39.5%) were similar. However, for PCBs, the number of cases implying volatilization (60.4%) was higher compared to deposition (21.6%). Low molecular weight PAHs (i.e., acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene) volatilized at all sites, while the remaining compounds volatilized or deposited at different sites. However, a similar pattern was not observed for PCB congeners that were volatilized at the majority of the sampling sites.

Fugacity fractions were generally <0.36 at the sites near the industrial activities and near ship breaking yards where the highest seawater and sediment concentrations were observed, indicating that gas phase deposition from the atmosphere might be an important mechanism affecting seawater and sediment PAH and PCB levels. Dry particle deposition was not determined in the present study. However, recent studies in the Aliaga region based on measurement of dry deposition fluxes and estimation of those for air-soil exchange have reported that both mechanisms are equally important for the transfer of PAHs and PCBs to the terrestrial surfaces (Bozlaker et al. 2008a; Bozlaker et al. 2008b).

Conclusions

The spatial variation, sources, and air-seawater exchange of PAHs and PCBs were explored in the Aliaga industrial region, Turkey. Σ_{16}PAHs (particle + dissolved) in the seawater ranged between 5107 and 294,624 pg L^{-1}, while Σ_{41}PCB levels were in the range of 880–50,829 pg L^{-1}. Levels in sediments were highly variable ranging between 35.5–49,682 and 2.7–2450 μg kg^{-1} in dry weight for Σ_{16}PAHs and Σ_{41}PCBs, respectively. Atmospheric concentrations varied between 1791–274,974 and 104–20,083 pg m^{-3} for Σ_{16}PAHs and Σ_{41}PCBs, respectively.

Sediment OM content and levels of Σ_{16}PAHs and Σ_{41}PCBs correlated weakly suggesting that the spatial variations of PAHs and PCBs were mainly affected by local sources rather than their sorption to OM. Previous atmospheric studies in the region, the observed geographical distribution of PAH and PCB levels in air, seawater, and sediment, and factor analysis conducted on the sediment levels in the present study pointed out that the major sources in the region are steel plants, petroleum refinery, petrochemical complex, ship breaking, loading/unloading activities at the ports, vehicular emissions, and fossil fuel combustion emissions.

The direction of the air-seawater exchange was also explored by estimating seawater fugacity fractions of PAHs and PCBs. For PAHs, the cases showing deposition and volatilization were similar, while for PCBs, the number of cases implying volatilization was higher compared to deposition. Fugacity fractions for most of the PAHs and PCBs indicated deposition at the sites close to industrial and ship breaking activities where the highest seawater and sediment levels were observed, indicating that gas phase transfer is an important mechanism affecting seawater and sediment PAH and PCB levels.

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