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SPATIAL VARIATION OF PAHS AND PCBs IN COASTAL AIR, SEAWATER, AND SEDIMENTS IN A HEAVILY INDUSTRIALIZED REGION

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Introduction

Recent 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^{1,2}. Although atmospheric and soil levels and their interaction have been studied well in the region, seawater and sediments that play important roles in environmental dynamics and fate have not been investigated. The objective of the present study was to determine the spatial variations of PAHs and PCBs in coastal atmosphere, seawater and sediments and to investigate their air-sea exchange in the Aliaga industrial region, Turkey.

Materials and methods

Aliaga (Turkey) region located on the coast of the Aegean Sea contains several pollutant sources (i.e., scrap processing steel plants, a petroleum refinery, a petrochemical complex, ship-breaking yards, and busy ports for product and raw material transportation). Seawater and sediment samples were collected between July 13 and 20, 2009 from 22 sites. Surface sediment samples were collected with a Van Veen grab sampler from 22 sites. Seawater samples (~10 L) were collected from 30 cm depth. Air samples were collected from mid July to mid August 2009 at 10 coastal sites close to the seawater sampling sites (< 1 km) using polyurethane foam (PUF) disk passive samplers deployed for 30 d.

Extraction solvent for all samples was 1:1 acetone:hexane. PUFs were Soxhlet extracted for 12 hours. Sediment samples (5 g) + 5 g of sodium sulfate were soaked in 50 mL solvent overnight and they were ultrasonically extracted for 1 h. Water samples were filtered through a glass fiber filter (0.7 µm) (particle-phase) and a resin column (~10 g XAD-2) (dissolved-phase). They were ultrasonically extracted for 1 h. Extract volumes were reduced and transferred into hexane. Samples were cleaned up and fractionated on an alumina-silicic acid column. PCBs were eluted with 35 mL petroleum ether while PAHs were eluted with 20 mL dichloromethane. The final solvent exchanged into hexane and the volume was reduced to 1 mL.

Samples were analyzed for 16 PAHs and 41 PCBs with a gas chromatograph (Agilent 6890N)-mass spectrometer (Agilent 5973 inert MSD) (electron impact ionization, selected ion monitoring). The capillary column was HP5-MS (30 m, 0.25 mm, 0.25 µm). Compounds were identified based on their retention times, target and qualifier ions, and were quantified using internal standard calibration.

Average surrogate recoveries ranged between 60-74% (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). The limit of detection of the method (MDL, ng) was defined as the mean blank+3SD. Average analyte amounts in blanks were generally <5% of sample amounts.

Results and discussions

Total (particle+dissolved) Σ 16PAH concentrations in the seawater samples ranged between 5107 and 294624 pg L⁻¹ while Σ 41PCB concentrations were in the range of 880-50829 pg L⁻¹ (Fig. 1). Seawater concentrations measured in this study were within the ranges reported previously^{3,4,5}. Concentrations in sediments were highly variable and ranged between 35.5-49682 and 2.7 and 2450 µg kg⁻¹ dry wt for Σ 16PAHs and Σ 41PCBs, respectively (Fig. 2). Observed sediment PAH concentrations were generally within the ranges reported previously^{6,7}. Sediment PCB concentrations were comparable to those reported for the Pearl River Delta sediments⁷ while they were substantially higher than those measured for Singapore's coastal sediments⁸. Atmospheric concentrations were also highly variable and ranged between 1791-274974 and 104-20083 pg m⁻³ for Σ 16PAHs and Σ 41PCBs, respectively.

For all sample types (air, seawater and sediment), the lowest PAH and PCB concentrations were measured at sites away from industrial sources. However, the highest levels were detected at sampling points located at Nemrut Bay where the ports for product and raw material (imported ferrous scrap used in steel plants) transportation or near the ship breaking activities. The spatial distribution of PAH and PCB concentrations are in agreement with the recent studies reporting that the major local sources are steel plants, petroleum refinery, petrochemical complex, and ship breaking activities^{1,2}. The present study further indicates that these sources substantially affect the coastal seawater and sediments in the region.

The water-air fugacity ratio ($f_w/f_A = H'C_w/C_g$) > 1 indicates net volatilization from water, values < 1 indicate net gas-phase deposition from air while for a system in equilibrium, f_w/f_A value is ~1. C_w and C_g are the dissolved-phase water and gas-phase air concentrations (pg m^{-3}), H' is the dimensionless Henry's law constant^{9,10}. Error propagation showed that the equilibrium is represented by $f_w/f_A = 1.0 \pm 0.31$. The fugacity ratios of most of the PAHs (88.4%) and PCBs (89.6%) indicated non-equilibrium conditions (Fig. 3). For PAHs, the number of the samples indicating deposition (42.8%) and volatilization (45.7%) were similar. However, for PCBs number of samples indicating deposition was higher (63.7%) compared to volatilization (25.9%). Fugacity ratios for all compounds were < 1.0 at the sites located at Nemrut Bay and ship breaking facilities where the highest seawater and sediment concentrations were observed, indicating that atmospheric deposition is an important mechanism affecting seawater and sediment PAH and PCB levels.

References

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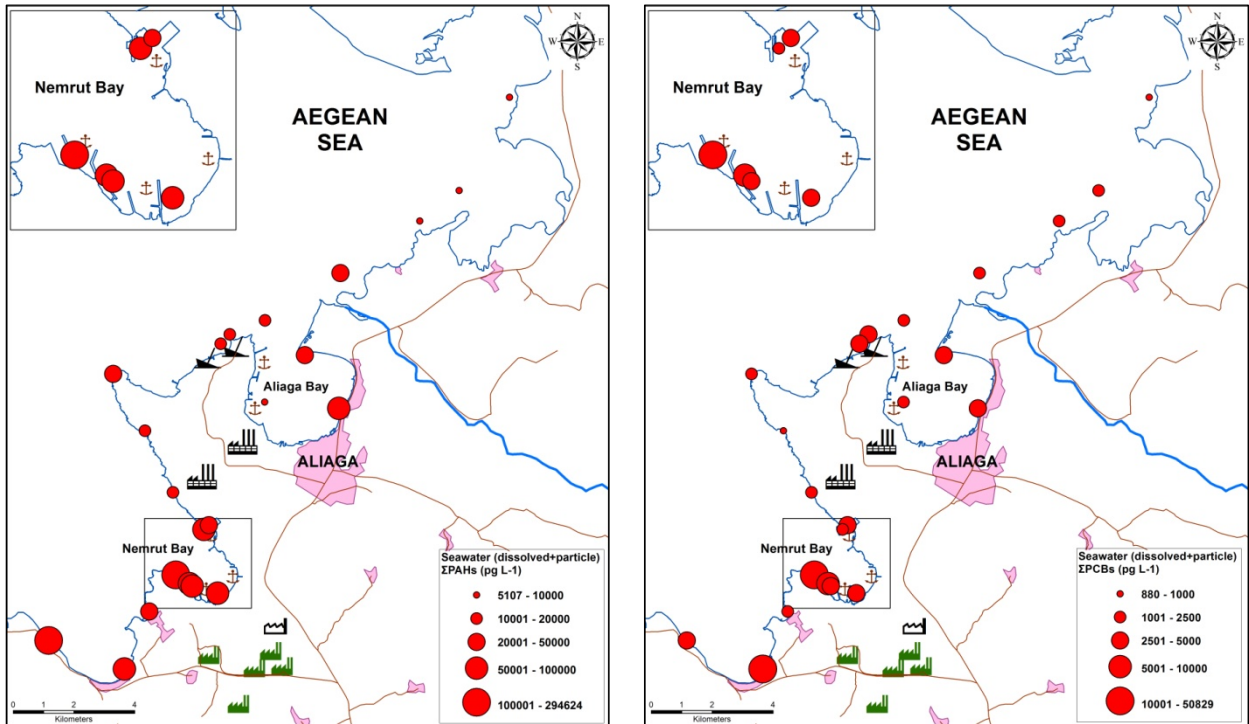


Figure 1. Spatial distribution of seawater PAH and PCB concentrations ($\mu\text{g L}^{-1}$) in the study area.

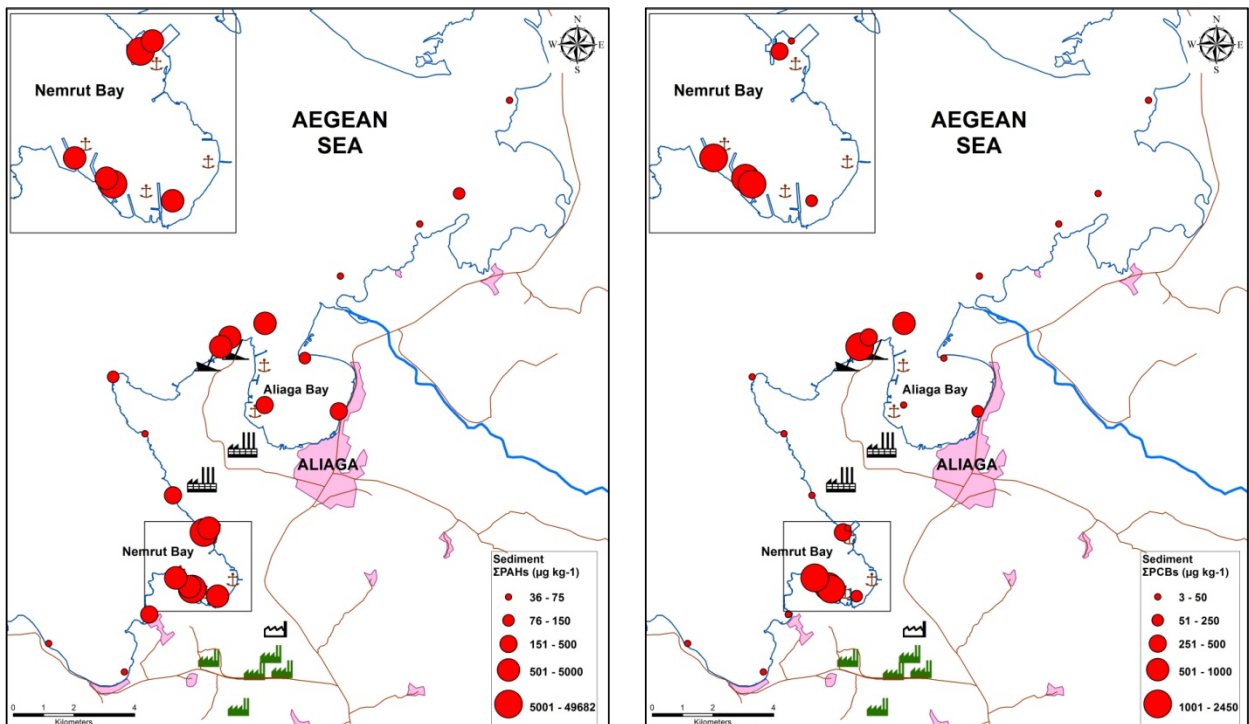


Figure 2. Spatial distribution of sediment PAH and PCB concentrations ($\mu\text{g kg}^{-1}$) in the study area.

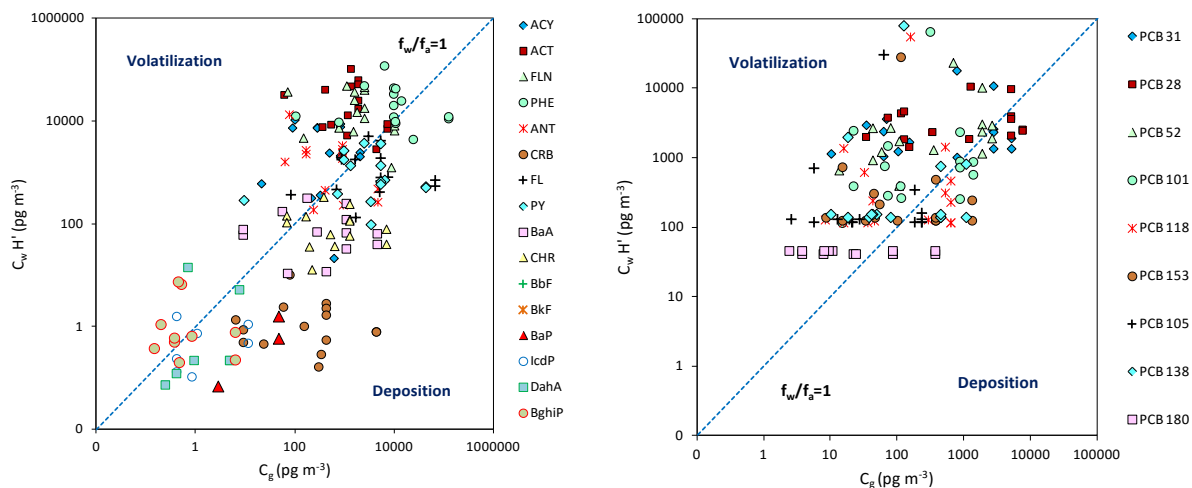


Figure 3. PAH and PCB fugacities in seawater and air.