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Seasonal variation in diffusive exchange of polycyclic aromatic hydrocarbons across the air–seawater interface in coastal urban area

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ABSTRACT

Concentrations of 15 polycyclic aromatic hydrocarbons (PAHs) in air–seawater interface were measured over 1 year in the coastal region of Incheon, South Korea. Most individual PAHs and total PAHs in air displayed statistically significant negative correlations with temperature, but not significant in seawater. Less hydrophobic compounds with three rings were at or near equilibrium in summer, while PAHs with four to six rings were in disequilibrium in all seasons, with higher fugacity gradients in colder seasons and for more hydrophobic compounds. Differently from fugacity gradients, the highest net fluxes occurred for some three- and four-ring PAHs showing the highest atmospheric concentrations. Net gaseous exchange, which was higher in winter, occurred from air to seawater with an annual cumulative flux of 2075 μg/m^2/year (for Σ15PAHs), indicating that atmospheric PAHs in this region, originating from coal/biomass combustion, can deteriorate the quality of seawater and sediment.

1. Introduction

Deterioration of the environment in coastal regions is a major problem in the 21st century because of the release of various pollutants accompanying industrialization and urbanization. Among these hazardous substances, polycyclic aromatic hydrocarbons (PAHs) are significant due to not only their ubiquity in various media in coastal environments, but also their toxic effects on marine organisms, including carcinogenicity, mutagenicity, and teratogenicity (IARC, 2013).

Large amounts of PAHs are emitted into the air by the combustion of fossil fuels and biomass, and global emissions of PAHs were estimated to exceed 500 Gg in 2007 (Shen et al., 2013). PAHs were listed as long-range transboundary air pollutants in 1998 by the United Nations Economic Commission for Europe (UNECE, 1998). Atmospheric PAHs can enter seawater via gaseous diffusion and dry/wet deposition. By contrast, coastal seawater receives PAHs via direct inputs from the leakage/spillage of fossil fuels or illegal discharge from potential sources in coastal regions. Because of these multiple sources and pathways, PAHs have attracted considerable attention in terms of controlling or managing pollution in aquatic systems in coastal regions.

Incheon coastal region, located in the middle of the western coast of the Korean Peninsula facing the Yellow Sea, has experienced land reclamation activities and construction of new cities. The extensive wetland in this region due to high tidal range is a source of various fish/shellfish products and a site for the breeding of endangered migratory birds. Therefore, for the management of this region, wetland conservation and coastal development are the two important goals to be achieved.

Marine aquatic quality of this region is influenced by various PAHs inputs present, including atmospheric release by combustion activities as well as discharge to water by unintentional oil spill from urban/industrial areas, municipal waste incinerator, international airport, harbors, river, and so on. Given the rapid increase in energy consumption in China (Tie et al., 2006) and prevailing Westerlies, anthropogenic pollutants from China could affect air quality in South Korea and Japan (Bey et al., 2001; Kim et al., 2012). According to source apportionment and air mass trajectory analysis, atmospheric PAHs measured in winter at a mega city in South Korea had been transported from China and/or North Korea (Lee and Kim, 2007; Kim et al., 2013). Therefore, in addition to potential local sources, long-range transboundary transport is considered as another source of atmospheric PAHs in this region that is the closest coast to northeast China.

During the recent several years, a main concern to PAH contamination in Korean coastal environment has been related with the Hebei Spirit oil spill event, which occurred at the southern area of Incheon/Gyeonggi coast in 2007 and spilled approximately 10,800 tons of oil (Hong et al., 2012; Lee et al., 2013; Hong et al., 2016). That is, many

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studies have focused on assessing the adverse effect and ecological recovery from that oil spill event. However, it should be noted that petroleum contamination by oil spill events happens transiently while atmospheric input does routinely. PAHs in sediments along the entire coast of the Korean Peninsula exhibited the diagnostic indices of both pyrogenic and petrogenic sources (Yim et al., 2007). This supports the significance of atmospheric input of PAHs to coastal seawater/sediment. Thus, it is required to evaluate the relative importance of atmospheric input and petroleum contamination for effective control of PAHs in the coastal aquatic ecosystem. The estimation of air–water net diffusive flux has been applied as a useful approach to determine the relative burden of semi-volatile pollutants to air and water, and the direction of their transport between these two media (Baker and Eisenreich, 1990; Nelson et al., 1998; Fang et al., 2012; Tsapakis et al., 2006; Galbán-Malagón et al., 2013). This can be an important key in managing water quality. In this study, seasonal variation of the diffusive exchange flux of PAHs across the air–seawater interface was measured from paired samples of air and seawater collected over 1 year and then annual fluxes were estimated for 15 PAH compounds in the coastal region of Incheon.

2. Materials and methods

2.1. Sampling area

Songdo coastal region (population ~ 100,000) is a new city under construction on reclaimed land, located in the southern coastal region of Incheon (population ~ 3 million) (Fig. 1). The wide mudflat surrounding this city is a site for the breeding of endangered migratory birds and is managed as a local wetland conservation area. This coastal region is prone to environmental pollutants from various sources, including the Incheon Harbor (10 km to the northwest), which serves 17,514 vessels and ships annually; the estuary of the Han River, which flows through Seoul; Shihwa Lake (9 km to the east), which is surrounded by industrial zones, discharging its water into the sea; Incheon International Airport (15 km to the northwest); and wastewater treatment plants.

2.2. Sampling and measurement of meteorological conditions

Ambient air samples were collected using passive air samplers (PAS) for measuring PAH concentrations in the gas phase at three stations (A1–A3) in Incheon coastal region, South Korea (Fig. 1). Sampling was performed every 2 months for seven consecutive periods from October 2013 to December 2014 (Table 1). Polyurethane foam (PUF) disk (diameter and thickness of 14 and 1.35 cm, respectively; Ziemer Chromatographie, Germany) was used as a sorbent for PAS after being precleaned by Soxhlet extraction in a mixture of dichloromethane (DCM) and *n*-hexane (3:1, v/v). Air temperature and wind speed were also measured concurrently at station A3 using a 110WX Ultrasonic WeatherStation (Airmar®, Fondriest Environmental Inc., OH, USA). Rainfall data were obtained from data measured at Songdo Meteorological Observatory (www.kma.go.kr). The average air temperature in each period ranged from −0.2 °C in period 2 to 23.5 °C in period 5, with a positive correlation with rainfall (Spearman's rho = 0.96; $p < 0.01$) and no significant correlation with wind speed (Spearman's rho = −0.68; $p = 0.94$). The average wind speed was 2.9 m/s, with no seasonal trend.

A total of 20 L of seawater was collected 10 cm below the sea surface at three stations (W1–W3) using a precleaned amber bottle at the beginning of each air sampling period from October 2013 to September 2014 (each $n = 3$ for 28 Oct. 2013; 2 Dec. 2013; 24 Jan. 2014; 27 Mar. 2014; 30 May 2014; 1 Aug. 2014; and 30 Sep. 2014). Buoy stations were operated to measure the salinity and water temperature around station W2 during the entire sampling period. There were significant correlations between air and seawater temperatures ($r^2 = 0.89$; $p < 0.01$) and between salinity and water temperature ($r^2 = 0.48$; $p < 0.01$). Although salinity was significantly lower in summer, its seasonal variation was narrow in the range of 24.8–30.7 (29.2 ± 1.1) psu over the entire sampling period.

2.3. Chemical analysis and QA/QC

The retrieved PUF disks, stored in precleaned amber bottle below −18 °C before analysis, were Soxhlet-extracted for 18 h using 300 mL of DCM:*n*-hexane mixture (3:1, v/v). Deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) were spiked into PUF disk as surrogate standards before extraction. After cleanup by 5% deactivated silica gel column (5 g) using 50 mL of *n*-hexane:DCM mixture (9:1), the extracts were concentrated to 0.5 mL by rotary evaporator and nitrogen blowdown.

Seawater (20 L) was filtered by a glass fiber filter (Whatman®; 47-mm i.d., 0.7-μm apparent pore size) to obtain the dissolved water phase. After the surrogate standards were spiked, the filtered water was passed through precleaned PUF (Ziemer Chromatographie,

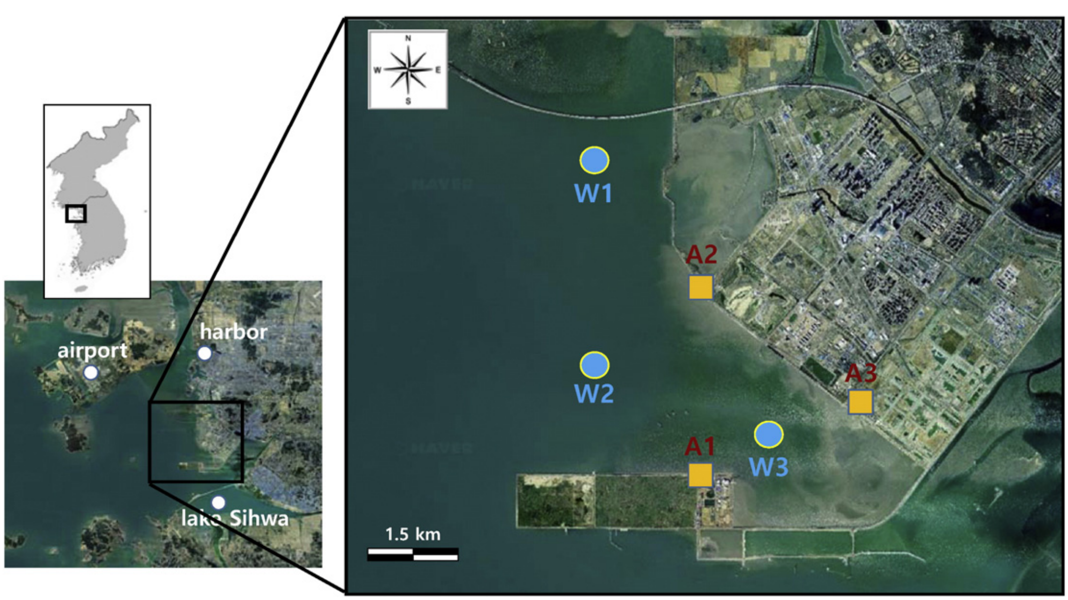

Fig. 1. Sampling stations: three monitoring stations for air (squares; A1–A3) and seawater (circles; W1–W3).