

Partitioning and source diagnostics of polycyclic aromatic hydrocarbons in rivers in Tianjin, China

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Distribution of PAHs among water, suspended solids and sediment was under strong influence of naturally occurring organic carbon.

Abstract

Water, suspended particulate matter (SPM), and sediment samples were collected from ten rivers in Tianjin and analyzed for 16 polycyclic aromatic hydrocarbons (PAHs), dissolved organic carbon (DOC), particulate organic carbon (POC) in SPM and total organic carbon (TOC) in sediment. The behavior and fate of PAHs influenced by these parameters were examined. Generally, organic carbon was the primary factor controlling the behavior of the 16 PAH species. Partitioning of PAHs between SPM and water phase was studied, and K_{OC} for some PAH species were found to be significantly higher than the predicted values. The source of PAHs contamination was diagnosed by using PAH isomer ratios. Coal combustion was identified to be a long-term and prevailing contamination source for sediment, while sewage/wastewater source could reasonably explain a short-term PAHs contamination of SPM.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic priority pollutants, ubiquitous in various environmental systems, and have resulted in much concern due to their toxicity, carcinogenicity and mutagenicity (US EPA, 1993). PAHs are formed and emitted primarily during incomplete combustion (pyrogenic source) of organic matter from different sources, such as combustion engines, home heating, power generation from fossil fuels, industrial activities, and biomass burning (Broman et al., 1991; Heemken et al., 2000). The productions of coke, black carbon, coal tar pitch, and asphalt have been identified as important anthropogenic sources of PAHs (Countway et al., 2003). Noncombustion-

derived petrogenic PAHs are also sources for contamination (Naes and Oug, 1997).

The aquatic ecosystem is one of the major sinks of PAH contamination (Tao et al., 2003), which has received most attention because of their lipophilic characteristic and bioconcentration effect (Haitzer et al., 1998). PAHs enter the aquatic environment through atmospheric deposition, industrial and residential wastewater discharge, oil pollution by ships, or urban and surface runoff (Heemken et al., 2000). Aquatic systems are not only important sinks in the global cycling of PAHs, but are also secondary sources of contamination (Sanders et al., 1996). Fresh water systems have received more attention for PAH contamination, although most studies focused on sediment or water phase (Christensen and Bzdusek, 2005). Thus, a comprehensive study of PAH behavior including water, suspended particulate matter, sediment, and sediment pore water phases would be most informative (Mitra and Dickhut, 1999).

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In aquatic systems, PAHs exist in freely dissolved, dissolved organic matter (DOM) associated, suspended particulate matter (SPM) associated, and sediment-associated phases. The distribution of PAHs among these phases is primarily controlled by physical/chemical properties of the individual species, such as solubility, vapor pressure, and sorption coefficient, as well as the characteristics of each phase (Readman et al., 1984; Zhou et al., 1999). Suspended organic and inorganic particles are ubiquitous in surface waters and are important vectors for the transport and distribution of contaminants in aquatic ecosystems.

The characteristics of different sorbents are also a critical factor. Particulate sorption dynamics of PAHs are of great importance for their distribution, revolatilization, sedimentation, and resuspension (Broman et al., 1991; Leppard et al., 1998). Dissolved organic matter has generally linear and reversible partitioning behavior (Xing and Pignatello, 1997; Xia and Pignatello, 2001) and fast equilibrium. In contrast, soot particles have high organic carbon to oxygen ratio and are viewed as being comprised of “glassy” organic matter responsible for strong PAH sorption, nonlinear adsorption behavior, and slow mass transfer rates (Xia and Pignatello, 2001; Rockne et al., 2002). In an organic matter rich system, the physical/chemical interaction of PAHs with organic matter is the dominant mechanism to determine the behavior and fate of PAHs. This interaction affects dispersal patterns, bioavailability and ultimate impact on aquatic organism, and may also reflect sources of PAHs.

Combustion of different fossil fuels produces PAH emissions with different signature. Thus, it is possible to identify the sources based on their PAHs emission “fingerprints” (Yunker et al., 1996). Furthermore, these source signatures can be altered by environmental processes such as photodegradation, volatilization, and solubilization, which act selectively or differentially on individual PAH species (Simpson et al., 1996; Zhang et al., 2005). As a result, by using the differences in reactivity and solubility of two PAH isomers, such as phenanthrene/anthracene, fluoranthene/pyrene, benz[a]anthracene/chrysene, benzo[b]fluoranthene/benzo[k]fluoranthene, indeno[1,2,3-*cd*]-pyrene/benzo(*g,h,i*)perylene, or benzo[*a*]pyrene/benzo[*g,h,i*]perylene, both the source and delivery routes for the PAHs can be examined (Gschwend and Hites, 1981).

Tianjin, China's third largest industrial center with an area of 12,000 km² and a population over 9.5 million, is located in the lower reaches of Hai River near Beijing and adjacent to the Bohai Sea. The Tianjin urban/industrial complex is highly impacted with rapid industrialization and urbanization. Industry and automobiles are two major sources of pollution. On average, the industries burn 15 million tons of coal a year and discharge 180 million tons of wastewater. Ten major rivers/canals in the study area collect the majority of natural runoff and industrial and domestic effluents in Tianjin. Most of these rivers carry a significant amount of wastewater from Tianjin and Beijing urban areas (Tianjin Environmental Protection Bureau, 2001). A large portion of the discharged water is used in agricultural irrigation (within an area of 3500 km²) due to the severe shortage of water resources in the Tianjin area. PAHs are among the most ubiquitous hydrophobic organic pollutants in

Tianjin. PAH sources include the coking industry, domestic and industrial coal combustion, automobile emissions, and open-air biomass burning.

To provide an overall picture of PAH contamination in Tianjin's rivers, an extensive survey was conducted with concurrent sampling of water, SPM, and sediment. Our previous paper quantitatively provided the levels and spatial variations of PAH contamination (Shi et al., 2005). This study particularly focused on the partitioning among the three phases and PAH source identification. A better understanding of the geochemical processes, transport, and fate of PAH contamination at a mechanistic level is essential for public safety management.

2. Materials and methods

2.1. Sample preparation and PAH analysis

Fifty-four sediment and 30 water (containing suspended particular matter) samples were collected from ten rivers in Tianjin. At each location, sediment samples were collected from three to five adjacent points, and well mixed. All samples were frozen immediately and kept at -18 °C before analysis. Sample preparation, PAH analysis, and analytical quality controls were reported in detail in our previous paper (Shi et al., 2005), and will only be described briefly here. After centrifuging or filtering and freeze drying, sediment and SPM samples were extracted by accelerated solvent extraction (ASE300, Dionex), cleaned via silica gel (US EPA Method 3630C, 3600B), and analyzed by GC/MS (Agilent 6890 GC, 5973 MSD) in both total ion scan and selected ion monitoring (SIM) modes. Water samples were first filtered (Sartorius glass fiber filter, ~0.5 μm, ashed at 450 °C) and extracted by solid phase micro-extraction (SPME, 100 μm film thickness coatings of poly(dimethylsiloxane), Supelco), then analyzed by GC/MS with external PAH standards. SPME was performed by filling a 3.4 ml Supelco vial with filtrate, and were agitated with a stir bar for 1 h at 1000 rpm. The 16 PAHs detected in sequence were: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), dibenz[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP). The 16 PAHs standard mixture was purchased from ChemService (PPH-10JM, ChemService Inc.). Organic carbon and grain size analytical methods are available in the supplementary information.

2.2. Analytical quality controls

For individual PAH analysis, the method detection limits were on average 50–250 ng/g (dry wt.) for 2–10 g of sediment with GC/MS total scan mode, 1 ng/ml for 4 ml water sample, and 1 ng/g (dry wt.) for 0.1 g SPM with GC/MS SIM mode. The recoveries ranged from 76% to 127% at spiking levels of 10 ng/g and 50 ng/g for 16 spiked individual PAH species. PAH concentrations of each sample were corrected by corresponding recoveries. Procedure blanks were run simultaneously with every set of samples (10–16 samples per set) and were subtracted from the analytical results. No less than 20% replicate samples were examined in sediment PAH analysis to further monitor the precision of analytical results. DOC and TOC were determined in triplicates with a relative standard deviation less than 1%. Sediment granularity was measured for 6 times for each sample to obtain better replication.

3. Results and discussion

3.1. Relationship between TOC, DOC, and SPM content

Levels of PAH contamination in Tianjin's rivers were described in our previous paper (Shi et al., 2005). The

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