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Contamination of rivers in Tianjin, China by polycyclic aromatic hydrocarbons

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Coal combustion is suggested as a recent local source of PAHs in this area.

Abstract

Tianjin urban/industrial complex is highly polluted by some persistent organic pollutants. In this study, the levels of 16 priority polycyclic aromatic hydrocarbons (PAHs) were tested in sediment, water, and suspended particulate matter (SPM) samples in 10 rivers in Tianjin. The total concentration of 16 PAHs varied from 0.787 to 1943 μg/g dry weight in sediment, from 45.81 to 1272 ng/L in water, and from 0.938 to 64.2 μg/g dry weight in SPM. The levels of PAHs in these media are high in comparison with values reported from other river and marine systems. Variability of total concentrations of PAHs in sediment, water, and SPM from nine different rivers is consistent with each other. No obvious trends of total PAHs concentration variations were found between upstream and downstream sediment, water, and SPM samples for most rivers, which indicate local inputs and disturbances along these rivers. The spatial distributions of three-phase PAHs are very similar to each other, and they are also similar to those found in topsoil. However, their chemical profiles are significantly different from that of topsoil. The change of profiles is consistent with the different aqueous transport capability of 16 PAHs. Low molecular weight PAHs predomination suggests a relatively recent local source and coal combustion source of PAHs in the study area.

Keywords: PAHs; Tianjin; Sediment; Water; SPM

1. Introduction

As typical persistent organic pollutants and semi-volatile organic contaminants, polycyclic aromatic hydrocarbons (PAHs) are widely distributed in various environmental media (Blumer, 1976; Hites et al., 1977; Laflamme and Hites, 1978; Neff, 1979; Means et al., 1980; Gschwend and Hites, 1981). PAHs are of environmental concern due to their toxic, mutagenic, and carcinogenic potentials (IARC, 1987). Four- to seven-ring PAHs are highly mutagenic and carcinogenic, two- or three-ring PAHs are less mutagenic but can be highly toxic (Fernandes et al., 1997). For these reasons, understanding PAH's behavior, transport, fate and environmental risk to ecological systems, especially for aquatic environment, is very important.

The primary environmental sources of PAHs include both anthropogenic inputs and biological conversion of biogenic precursors (Means et al., 1980). Fossil fuel combustion, waste incineration, coal gasification and liquification processes, petroleum cracking, and the

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production of coke, carbon black, coal tar pitch, and asphalt have been identified as important anthropogenic sources of PAHs (Countway et al., 2003). Industrial wastewater, sewage, road runoff/street dust and petroleum related activities are other important sources of PAHs. A minor portion of PAHs also originates from discharges of non-combusted fossil fuel products (Bouloubassi et al., 1991; Näf et al., 1992).

Organic contaminants in aquatic systems may exist in several forms, including free dissolved phase, the phase bounded to dissolved organic matter (DOM), adsorbed to suspended particulate matter (SPM), and associated with surface sediments (Readman et al., 1984; Zhou et al., 1998; van Brummelen, et al., 1998). The distribution of PAHs among these phases is mainly controlled by the intrinsic physical–chemical properties of the individual compounds, such as solubility, vapor pressure, and adsorption coefficient (Readman et al., 1984; Zhou et al., 1998). A three-phase partitioning model has been used to describe the behavior of PAHs in particles, DOM, and freely dissolved phase (Mitra and Dickhut, 1999). Due to the particle character, a fraction of the total sediment PAH concentration is sequestered in a physical–chemical form that is unequilibrium partitioning on the time scale of 30–50 years (McGroddy and Farrington, 1995). Besides partitioning, to determine the fate of PAHs in aquatic environment, several transport and transformation processes can also be considered at the sediment–water interface (Mackay, 2001).

In China, intense industrial and commercial activities in the coastal area caused adverse effects on the aquatic system. Tianjin, China's third largest industrial center, is located in northern China near Beijing and adjacent to the Bohai Sea. The Tianjin urban/industrial complex, containing about 11 200 km^2 of land, and having a population of 10 million, is highly polluted with the development of industry and rapid urbanization. Industry and automobiles are two major sources of pollution. On average, the industrial corporation burned 15 million tons of coal per year and discharged 180 million tons of wastewater. Rivers in the Tianjin area are severely polluted with high loads of persistent organic pollutants (Tao et al., 2003). A majority of the rivers in the area are filled with wastewater from Tianjin and Beijing urban areas (Tianjin Environmental Protection Bureau, 2001).

Confronted with water shortage in agriculture, both wastewater irrigation and sludge application have been common practices in this area for more than 40 years. Tianjin's suburban area, covering approximately 3500 km^2, is dominated by farmlands irrigated with wastewater (Tianjin Environmental Protection Bureau, 1996, 2001; Wang et al., 2002).

The purpose of the present work is to quantify the distribution, composition, and assess the spatial variability of the 16 U.S. EPA priority PAHs (Keith and Telliard, 1979) in rivers in Tianjin area, to provide data for comparison with other areas, and to assess the potential harm to public health.

2. Materials and methods

2.1. Sample collection, storage, and preparation

Tianjin (39 °N, 117 °E) is located downstream of Hai River, China. Hai River, at one time, was one of the important drinking water resources of the Tianjin area. However, it is now polluted by urban and agriculture runoff. Many natural rivers are located in the northeastern and southwestern area of Tianjin city and these rivers are mainly polluted by agriculture or industry. To protect Hai River, two canals are used to collect 530-million m^3 civil wastewater per year. Because of the lack of rainfall, wastewater is stored in the river for a long period of time, which aggravates the pollution, especially the pollution of the sediments. In addition, an influx of polluted water from upstream further exacerbates the problem. Contaminants released from the sediment could also enhance the river pollution.

To try to understand the contamination and behavior of PAHs in the river system in this area, 54 sediment samples and 30 water and SPM samples were collected from 10 major rivers in the study area. The sampling locations are indicated in Fig. 1. Surface sediment samples were collected by using grab sampler, and water and SPM samples were collected by using cylinder samplers. All the samples were frozen immediately and transported to the laboratory and kept in the refrigerators at −18 °C before analysis. To eliminate randomicity, sediment samples were collected from three to five adjacent points for each site.

After centrifuging (>3000 rpm, Centrifuge TDL-5, China) and freeze drying (EYELA-FDU-830, Japan), every sediment sample was rubbed to granular powder to pass through a 70-mesh sieve and homogenized. Water samples were filtrated with water through glass fiber filters (~0.5 μm, Sartorius, ∅ = 47 mm, ashed at 450 °C before using) to separate SPM. The SPM samples were also freeze dried and stored in aluminum foil in desiccators until extraction.

2.2. Extraction

The procedures used for the analysis of PAHs in sediment and SPM samples were based on the modified procedure of U.S. EPA Method 3545 (pressurized fluid extraction), 3630C (silica gel cleanup), 3660B (sulfur cleanup), and 8270C (GC/MS quantitation) (U.S. EPA, 1986). To summarize, samples were exacted from