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Polycyclic aromatic hydrocarbons in dustfall in Tianjin, China

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Abstract

Atmospheric dustfall samples from 23 locations in Tianjin, China, were collected and analyzed for 16 polycyclic aromatic hydrocarbons (PAHs) classified by the Environmental Protection Agency as priority pollutants from March 2002 to March 2003. ΣPAH16 (sum of 16 PAH compounds) concentrations in the dustfall collected during heating season ranged from 2.5 to 85.5 μg/g, while that during the nonheating season varied from 1.0 to 48.2 μg/g dry weight. The dominant components in the heating season included naphthalene, phenanthrene, fluoranthene, and chrysene, while naphthalene, fluorene, phenanthrene, and fluoranthene were dominant during the nonheating season. Compared with the nonheating season, the heating season was characterized by a higher fraction of high-molecular-weight PAHs with four to six rings with exception of the samples from the east industrial area. The east industrial area had more significant correlations between individual PAH compounds, and more discrete triangular components of three-, four-, five- and six-ring PAHs. No significant correlations were observed between the PAHs concentrations and total organic carbon (TOC) in the dustfall samples. The deposition fluxes of ΣPAH15 (sum of 15 PAHs except naphthalene), ΣPAH6 (sum of 6 carcinogenic PAHs recommended by IARC) and benzo[a]pyrene (BaP) from atmospheric deposition to the whole area were estimated as 1911, 196, and 53 μg/m^2/year, respectively. The deposition rates for PAH compounds in the east industrial area were higher than those in the urban and rural areas. Furthermore, the deposition contribution of PAHs during domestic heating season in winter was not significant relative to the annual inputs.

Keywords: PAHs; Bulk deposition; Dustfall; Seasonal variation; Tianjin

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of environmental contaminants composed of two or more fused aromatic rings, some of which are known to be mutagenic or carcinogenic (IARC, 1991; US EPA, 1991). PAHs are generally produced by the incomplete combustion of fossil fuel (coal, oil, and natural gas) or biomass (waste incineration, wood, and stubble; Venkataraman and Friedlander, 1994; Khalili et al., 1995; Harrison et al., 1996).

Once they enter the atmosphere, PAHs are distributed between gas and particle phases and subject to removal mechanisms, such as oxidative and

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photolytic reactions and wet and dry deposition (Garban et al., 2002). Low-molecular-weight PAHs (two- to three-ring PAHs) are found mostly in the gas phase, whereas high-molecular-weight PAHs (four- to six-ring PAHs) are typically associated with airborne particles (Gundel et al., 1995; Lighty et al., 2000). The pollution pathways of airborne PAHs include direct breathing or indirect intake of vegetables and grains contaminated from deposition (Smith et al., 1995). Moreover, because PAHs are lipophilic, their deposition on soil and surface waters may also lead to bioaccumulations within the food chain.

The PAH concentration in the air surrounding large cities remains high due to increasing vehicular traffic and inadequate dispersion of atmospheric pollutants (Miguel et al., 1998). Concentrations in urban soils, as well as in the sediments of lakes and bays, are also high due to the deposition of atmospheric particulates containing PAHs from urban areas (Kennicutt et al., 1993; Wild and Jones, 1995; Wang et al., 2003). Precipitation accelerates the deposition of fine particles from the atmosphere (Dickhut and Gustafson, 1995a; Wild and Jones, 1995). The atmosphere, therefore, serves as one of the major pathways for the transport and deposition of PAHs (US EPA, 1997). Research by Jones et al. (1989) found that atmospheric deposition of particulate-bound PAHs was the principle source of PAHs in Welsh soils.

There is a growing concern about atmospheric deposition of PAHs to lakes (Baker and Eisenreich, 1990; Gevao et al., 1998), coastal waters (Golomb et al., 2001), bays (Dickhut and Gustafson, 1995b; Golomb et al., 1997; Park et al., 2002), and urban and rural sites (Ollivon et al., 2002; Garban et al., 2002; Bae et al., 2002). Airborne particles may be delivered to surfaces by wet and dry deposition. Several transport mechanisms, such as turbulent diffusion, precipitation, sedimentation, Brownian diffusion, interception, and inertial migration, influence the dry deposition process of airborne particles (Seinfeld and Pandis, 1998). Large particles (d>10μm) are transported mainly by sedimentation; hence, the large particulate PAHs tend to be deposited nearer the urban setting. Small particles (d<1μm), which behave like gases, are often transported and deposited far away from the urban setting where they originated (Baek et al., 1991). Dry depositional estimates may be obtained by analyzing PAHs that have been deposited on the surface, but measurements at one location may not accurately reflect those at another nearby location depending on the specific conditions of the atmosphere, surface, and particulate PAHs (Halsall et al., 1997; Golomb et al., 2001).

Tianjin is a large industrial city in Northern China (approximately 11,919 km^2 and 120 km SE from Beijing), situated in the lower portion of the Haihe River watershed and west of Bohai Bay. Municipal wastewater from Beijing and Tianjin are used in large quantities for agricultural irrigation in the region, as well as other applications due to the severe shortage of water resources in the Tianjin area. As such, large quantities of PAHs contaminants from the wastewater have found their way into Tianjin soils. Interestingly, the investigation of PAH contents in Tianjin soils did not reflect a significant spreading of PAHs from wastewater, despite the high PAHs concentrations observed in urban or near urban soils (Wang et al., 2003). This suggests that atmospheric deposition may be the major source of PAH input into Tianjin soils. Typically, most PAHs are found in airborne hydrophobic fine particulates (Gundel et al., 1995; Lighty et al., 2000) that are not readily washed out by precipitation. Because precipitation in Tianjin is limited, the dry deposition of airborne PAHs has a high likelihood of being the predominant mode of atmospheric loading to underlying surfaces.

This paper reports the results of an investigation into the PAH content of bulk depositions (dry and wet depositions together) in the Tianjin area with estimated PAH depositional fluxes to land and water surfaces between 2002 and 2003.

2. Experimental design

2.1. Sampling and pretreatment

Sets of ceramic buckets (i.d. 26±0.5 cm, height 30 cm, flat-bottom) for collecting bulk deposition (dry and wet depositions mixed together) were placed at 26 sites in 16 districts of Tianjin, China (Fig. 1). Locations for each of the buckets were coordinated for consistency with the Tianjin Environmental Monitoring Center's monitoring plan. The nonheating sampling season started in March 2002 and extended until November, covering an average span of 157–260