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Polycyclic aromatic hydrocarbons in soils from urban to rural areas in Nanjing: Concentration, source, spatial distribution, and potential human health risk

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HIGHLIGHTS

- Vehicle emissions were the primary source of soil PAHs based on the PMF model.
- Concentrations of heavier PAHs decreased from urban to rural soils.
- The commercial center and old urban district are high health risk sites based on BaP_{eq}.

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) have become a major type of pollutant in urban areas and their degree of pollution and characteristics of spatial distribution differ between various regions. We conducted a comprehensive study about the concentration, source, spatial distribution, and health risk of 16 PAHs from urban to rural soils in Nanjing. The mean total concentrations of 16 PAHs ($\sum_{16}$PAHs) were 3330 ng g^{-1} for urban soils, 1680 ng g^{-1} for suburban soils, and 1060 ng g^{-1} for rural soils. Five sources in urban, suburban, and rural areas of Nanjing were identified by positive matrix factorization. Their relative contributions of sources to the total soil PAH burden in descending order was coal combustion, vehicle emissions, biomass burning, coke tar, and oil in urban areas; in suburban areas the main sources of soil PAHs were gasoline engine and diesel engine, whereas in rural areas the main sources were creosote and biomass burning. The spatial distribution of soil PAH concentrations shows that old urban districts and commercial centers were the most contaminated of all areas in Nanjing. The distribution pattern of heavier PAHs was in accordance with $\sum_{16}$PAHs, whereas lighter PAHs show some special characteristics. Health risk assessment based on toxic equivalency factors of benzo[a]pyrene indicated a low concentration of PAHs in most areas in Nanjing, but some sensitive sites should draw considerable attention. We conclude that urbanization has accelerated the accumulation of soil PAHs and increased the environmental risk for urban residents.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants that are human carcinogens, mutagens, and toxic to all living organisms (Tobiszewski and Namieśnik, 2012). The United States Environmental Protection Agency (USEPA) has identified 16 PAHs as priority pollutants. PAHs originate from natural processes such as forest fires, volcanic eruptions, and diagenesis (Wang et al., 2007b), and also from anthropogenic sources such as vehicle emissions, coal and fossil fuel power generation, petroleum refining, industrial processing, chemical manufacturing, oil spills, and coal tars (Peng et al., 2011). Generally, anthropogenic factors have the most impact on PAH distribution in urban areas, whereas natural factors affect their distribution in remote areas. PAHs have become a major pollutant in urban areas (Jiang et al., 2009).

Soil is the most important sink for PAHs in the environment (Yin et al., 2008). This is because PAHs are sparingly soluble, readily adsorbed by soil particles, and resist degradation (Tang et al., 2005). It has been estimated that approximately 90% of total residues remain in the soil (Hu et al., 2013). Urban areas are very populated and are accompanied by an increased production of industrial waste, traffic pollution, and household garbage, which produce many PAHs and other pollutants that migrate into urban soils through dry and wet atmospheric deposition. Generally, the concentration of PAHs in urban areas is significantly higher than in suburban or rural areas (Zhang et al., 2006; Wang et al.,

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2007a,b). Consequently, the soil system is a major reservoir and a good indicator of environmental pollution and environment risk for human exposure (Jiang et al., 2009). However, the health risk of exposure to PAHs from urban soils is not well understood.

Nanjing, located in eastern China, has a total area of 6597 km^2. It has a subtropical monsoon climate, with an annual average temperature of 15.4 °C, and an annual rainfall of 1200 mm. The population of Nanjing has exceeded 8 million and more than 6 million occupy the urban area. The city is an ancient capital of six dynasties with a history of more than 2500 years and a profound cultural background. As a main port along the Yangtze River, Nanjing is a complex industrial base dominated by electronics, automobiles, and chemicals. Due to the rapid growth of industrial production, traffic, and population density, it is faced with serious environmental problems. In recent years, many studies have indicated that persistent organic pollutants such as organochlorine pesticides, polychlorinated biphenyls, polybrominated diphenyl ethers, and PAHs are present in various environmental media (Gao et al., 2005; Yin et al., 2008; Su et al., 2012). However, the concentrations and distributions of PAHs in urban soils of Nanjing are unknown.

In this study, we investigated the PAH concentrations in urban soils of Nanjing. The specific objectives were as follows: (1) to measure the concentrations of PAHs from urban to rural soils in Nanjing, (2) to identify the possible sources of PAHs by positive matrix factorization (PMF), (3) to analyze the spatial distribution of PAHs by using Kriging interpolation, and (4) to evaluate the human health risk of PAHs in Nanjing soils.

2. Material and methods

2.1. Soil sampling and preparation

The study region is the city of Nanjing, Jiangsu province, Eastern China. We collected 139 surface soil (0–5 cm) samples from urban to rural areas in June 2014 (Fig. 1). The study region was classified into three areas: urban, suburban, and rural. At each 10 m × 10 m sampling site, 5 subsamples (four corners and center) were taken and bulked together to form one composite sample. All the samples were air-dried at room temperature for one week, sieved to 100-mesh size particles after removing stones, residual roots and other materials, and stored in amber glass containers at −4 °C until analysis.

2.2. Chemicals and materials

A composite standard solution of 16 PAHs was purchased from Supelco (Bellefonte, PA, USA) and included naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), 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 (InP), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BP). Each component had a concentration of 2000 μg ml^{-1}. Silica gel (100–200 mesh) was purchased from Qingdao Haiyang Chemical Co. (Shandong, China) and was dried under ventilation after it was extracted using acetone, dichloromethane, and n-hexane, then activated for approximately 16 h at 130 °C, and then kept in n-hexane before use. Granular anhydrous sodium sulfate was baked at 450 °C for 5 h, and then stored in a sealed desiccator before use. All solvents and chemicals (n-hexane, dichloromethane, acetone, and methanol) were HPLC grade and redistilled before use.

2.3. Sample preparation

A 5 g soil sample was mixed with 5 g anhydrous sodium sulfate, and then Soxhlet extracted for 24 h with 100 ml hexane/dichloromethane (v/v = 1:1). The extracts were concentrated to 2 ml by rotary vacuum evaporation and then solvent-exchanged to hexane. The concentrated extracts were cleaned up using silica gel column chromatography (25 cm × 1 cm internal diameter). The glass chromatography column

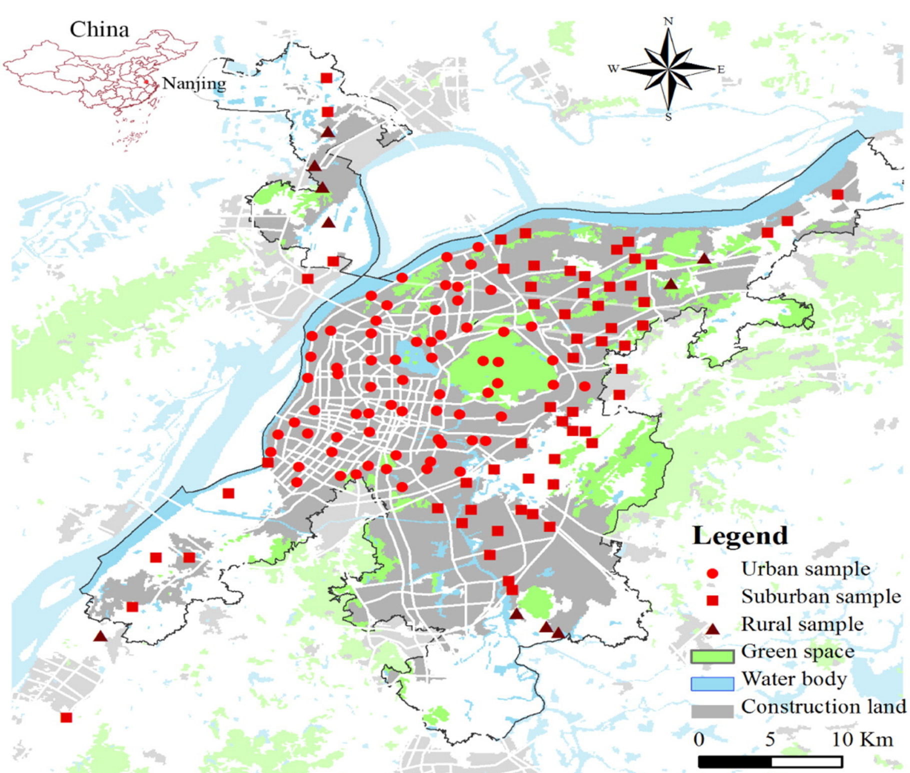

Fig. 1. The distribution of sampling sites in Nanjing.