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Spatial distribution, emission source and health risk of parent PAHs and derivatives in surface soils from the Yangtze River Delta, eastern China

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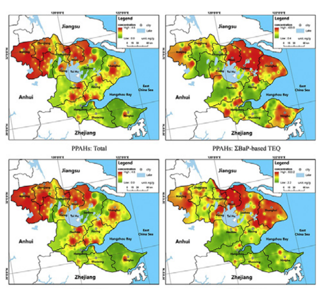
HIGHLIGHTS

- High levels of PPAHs and derivatives in topsoil occurred in northern part of YRD.
- Significant correlations of soil TOC fractions with concentrations of PPAHs.
- Source diagnostics of PPAHs by isomeric ratios, PCA, MLR and emission inventory.
- Close associations of NPAHs and OPAHs with corresponding PPAHs in topsoil.
- Cumulated probability of cancer risk showed dermal contact > ingestion > inhalation.

GRAPHICAL ABSTRACT



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ABSTRACT

243 surface soil samples were collected from the Yangtze River Delta (YRD) region, and the concentration distributions and compositional profiles of 27 parent PAHs (PPAHs), nitro- and oxy-derivatives (NPAHs and OPAHs), respectively, and health risk of 16 PPAHs were determined. Atmospheric samples were collected at two sites with high topsoil concentrations of PAHs to assist in identifying the emission sources of PPAHs. The total concentrations of PPAHs, NPAHs and OPAHs fell in the ranges of 21.0–3563.2 ng/g, 0.4–4.6 ng/g and 2.1–834.1 ng/g, respectively. PPAHs in topsoil were dominated by low and medium molecular weight species. The main components of OPAHs were 9FO and ANQ. For NPAHs, only 1N-NAP was frequently detected. Overall, the northern parts of the YRD region were more heavily contaminated by PPAHs and their corresponding derivatives. The soil TOC fraction and GDP per capita were significantly correlated with the spatial distribution of PPAHs. Specific ratios of isomeric species and principal component analysis (PCA) designated combustion of industrial coal and biomass, and traffic exhaust as the main mixed emission sources of PPAHs in surface soils in this region. The detected NPAHs and OPAHs were significantly associated with the corresponding PPAHs. The estimated incremental lifetime cancer risk attributed to 16 PPAHs in surface soil was greater than 10^{-6}, indicating a potential risk of contracting cancer by exposure to topsoil from the YRD region. The cumulative probability of

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cancer risk for both adults and children via three exposure pathways followed the sequence of dermal contact > ingestion > inhalation.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a typical group of persistent organic pollutants (POPs) prevalent in the environment and some of the individuals have been identified as a kind of carcinogenic substance (IARC, 2010). Many studies have shown that in recent years, increasing incidences of lung cancer, bronchitis, asthma and heart diseases are associated with exposure to PAHs (Haritash and Kaushik, 2009; Fu et al., 2012). Nitro-PAHs (NPAHs) and oxy-PAHs (OPAHs) are important derivatives of parent PAHs (PPAHs). Some NPAHs and OPAHs have been confirmed to show comparable or greater toxicity and carcinogenicity than their parent components, thus their corresponding concentrations and distributions are of great concern to the government and the public (Bandowe and Wilcke, 2010).

PPAHs mainly originate from anthropogenic sources, *i.e*., incomplete combustion or pyrolysis of fossil fuels and biomass, as well as the leakage of petroleum (Wang et al., 2011). In addition to the primary emission sources, including vehicle exhaust and the burning of biomass (Bamford and Baker, 2003), NPAHs and OPAHs may generate from the secondary transformation of PPAHs by photochemical oxidation and (bio)degradation (Walgraeve et al., 2010; Keyte et al., 2013). PPAHs emitted into the atmosphere can enter surface soil by wet and dry deposition (Kaya et al., 2012), and are readily adsorbed by soil solid particles and soil organic matter. As environmental conditions change, soil may become a re-emission source with release of various organic pollutants into the air (Tao et al., 2008). PPAHs in soil can be bio-accumulated in crops via the food chain (Li et al., 2008) and ultimately affect human health. Therefore, deep insight into concentration and distribution of PPAHs in soil may facilitate pollution control, decrease in crop damage, and reduction of human exposure. Numerous studies have involved almost all the aspects of PPAHs mentioned above. However, considering that a variety of NPAH and OPAH components have similar or stronger cellular and immune toxicity and carcinogenicity compared to their parental precursors (IARC, 2013), a corresponding study on derivatives is insufficient, especially distribution characteristics and relationships with their parental precursors.

The Yangtze River Delta (YRD) is one of the most densely populated and economically prosperous regions in the world. Intensive anthropogenic activities, large ownership of vehicles and high consumption of fossil fuels lead to massive emissions and accumulation of PPAHs and their derivatives, directly threatening the local environment quality and human health (Zhang et al., 2009). Therefore, it is of critical significance to determine the concentration range and geographical distribution of PPAHs, NPAHs and OPAHs in surface soils in this region, to provide fundamental data for monitoring and controlling contamination from POPs, and to create a reliable basis for risk management and decision-making by the local government.

To date, many studies have been performed on topsoil PPAHs in the YRD region (Jiang et al., 2011; Wang et al., 2015); yet these studies mainly focused on historical occurrence and concentration range of PPAHs and only covered some small-scale areas. Few recent studies characterize, on the entire region-scale of surface soils, geographic distribution and source apportionment of PPAHs, being essential for policy-makers to take effective measures to control and abate the pollution. Similarly, only a minority of reports have addressed NPAHs and OPAHs in atmosphere, partly due to time-consuming and laborious measurements, so the filling of data gap is urgently needed. In this study, we collected surface soil (0–10 cm) samples (sample size $n = 243$) from 11 cities in the region to: (1) investigate the concentration ranges, compositional profiles and geographical distributions of 27 PPAHs, 12 OPAHs and 4 OPAHs; (2) preliminarily identify the local emission sources of PPAHs and their derivatives; (3) reveal the associations of NPAHs and OPAHs with the corresponding PPAHs in surface soils; and (4) initially assess the potential health risk of PPAHs for local adults and children exposed to surface soils via different pathways. Moreover, based on some previous results (Ping et al., 2007; Jiang et al., 2011), ambient air samples, including active and passive sampling with a total of 32 samples and a sampling period of 60 days, were gathered at 2 sites with high topsoil PPAHs concentrations to assist in diagnosing the local emission sources of PPAHs in surface soils.

2. Materials and methods

2.1. Background of the sampling region

As a highly developed agricultural and industrial region in China, the YRD region concentrated various large-scale industrial bases, and 4.6 million vehicles accounted for 16% of the national total (NBSC, 2015), leading to a large quantity of traffic exhaust. Fossil fuels, *e.g*., coal, liquefied petroleum gas (LPG) and natural gas gradually displaced traditional domestic fuels (crop straw and firewood); whereas crop straws were directly open burned after harvest.

2.2. Sample collection

2.2.1. Surface soil samples

An evenly distributed sampling network composed of 243 sites was created to cover 11 cities, including Shanghai ($n = 30$), Nanjing ($n = 12$), Zhenjiang ($n = 14$), Changzhou ($n = 24$), Wuxi ($n = 18$), Suzhou ($n = 22$), Huzhou ($n = 26$), Jiaxing ($n = 24$), Hangzhou ($n = 25$), Shaoxing ($n = 18$) and Ningbo ($n = 30$). The detailed information was shown in Fig. S1 and in the relevant statements in S-1 (Supplementary Materials).

2.2.2. Ambient air samples

Based on our preliminary investigation and related data from previous studies (Ping et al., 2007; Jiang et al., 2011), air samples, including simultaneous active sampling and passive sampling, at two sites in Kunshan City (affiliated to Suzhou) with reported high topsoil PPAHs concentrations were collected. PPAHs and their derivatives in the particulate phase and gaseous phase were gathered using a glass fiber filter (GFF) and polyurethane foams (PUFs), respectively. The full descriptions on atmospheric sampling were given in S-1. A total of 32 air samples, *i.e*., 16 paired samples (gaseous phase plus particulate phase), were obtained.