Source apportionment of polycyclic aromatic hydrocarbons in soils of wetlands in the Liao River Delta, Northeast China

Chuanliang Ma [a], Siyuan Ye [b,*], Tian Lin [c], Xigui Ding [b], Hongming Yuan [b], Zhigang Guo [a,*]

[a] Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China
[b] Key Laboratory of Coastal Wetland Biogeosciences, China Geologic Survey, Qingdao Institute of Marine Geology, Qingdao 266071, China
[c] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

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ABSTRACT

The polycyclic aromatic hydrocarbons (PAHs) of 55 surface soil samples from the wetlands in the Liao River Delta, Northeast China were measured in order to apportion their sources. The total concentrations of 16 US EPA priority PAHs and alkyl-PAHs in this region ranged 106–3148 ng g^{-1} (dry weight) (average: 550 ± 565 ng g^{-1}) and 54–5564 ng g^{-1} (average: 517 ± 838 ng g^{-1}), respectively. Based on the positive matrix factorization analysis of alkylated and parent PAHs, six sources of PAHs were identified including petroleum (23%), biomass burning (23%), air–soil exchange (18%), coal combustion (17%), traffic emission (14%) and biogenic origin (6%). The positive correlation between low molecular weight (LMW) PAHs and TOC contents could demonstrate a potential positive influence of TOC on the accumulations of LMW PAHs in soils by the air–soil exchange. The petrogenic PAHs may pose a limited harmful effect on aquatic organisms although they were abundant in the area.

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1. Introduction

A group of chemical compounds known as polycyclic aromatic hydrocarbons (PAHs) that consist of two or more fused aromatic rings have been received a great concern due to their carcinogenic and mutagenic properties. Generally, PAHs are derived mainly from anthropogenic inputs, e.g., the fossil oil discharges and incomplete combustion of organic matter such as fossil fuels, biomass and municipal wastes (Yunker et al., 2002; Mai et al., 2003). Soils are usually regarded as one of the ultimate sinks of PAHs emitted from the point sources and non-point sources, either by atmospheric deposition or direct discharges from ambient environment.

The wetlands have been known as one of the most biologically important and productive ecosystems on the earth. With the fast industrialization and urbanization of China, the fossil fuel usage and spill may have caused a severe pollution problem in the coastal wetlands in China. The wetland in the Liao River Delta (LRD) is such a case. This wetland, (121°25′–122°31′E longitude, 40°40′–41°25′N latitude), one of the biggest and well preserved wetland ecological block in the world (about 223,000 ha), is a deposition plain situated in the lower reaches of Liao River (Fig. 1). It is a low-lying basin district with extensive freshwater marsh, salt marsh, and inter-tidal zone areas. The LRD has the largest reed stands in Asia, and it is the second largest one in the world. It has been shown that the Liao River Oilfield, once the third largest oilfield in China, has an ecological risk on the delta ecosystem due to oil leaks and spills from underground tanks, pipelines and illegal disposal. Thus, the unique environmental conditions of LRD have been of a great concern due to its environmental significance, ecological sensitivity and development potentials.

There were several studies on the ecological issues (Ji et al., 2009), sewage (mainly from Liao River Oilfield) treatment (Ji et al., 2007), and the PAH contamination level of limited samples in LRD (Wang et al., 2011b). However, the quantitative source apportionment of PAHs in soils in entire LRD based on the combining data sets of alkylated and parent PAHs has been untouched. This work aims to quantitatively apportion the sources of PAHs using principal component analysis (PCA) and positive matrix factorization (PMF), and assess the level of PMF-based PAH contamination and their ecological risks in the region.

2. Materials and methods

2.1. Sampling

Fifty-five surface soil samples (0–5 cm) mainly from reed wetlands and paddy fields were collected using a grab sampler in August, 2011 (Fig. 1). Subsequently, samples were wrapped in aluminum foil and stored at −20 °C until analysis. The locations
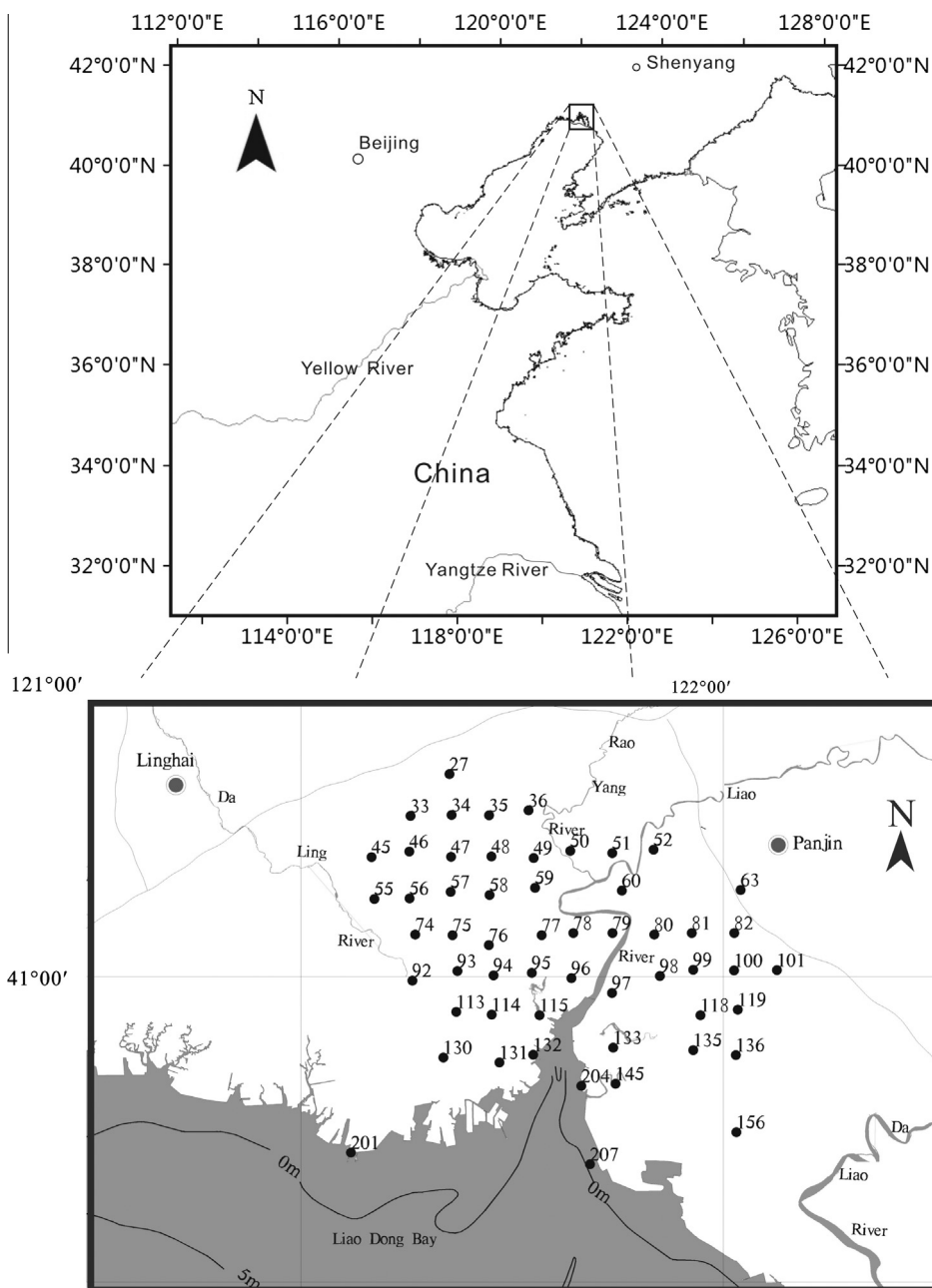
Fig. 1. Study area and the locations of the sampling sites.

of sampling sites were shown in Fig. 1. These sampling areas virtually covered the entire wetlands.

2.2. Analysis of total organic carbon (TOC)

Samples for TOC analysis were acidified with diluted HCl before analysis to remove carbonates. Contents of TOC were determined on a CHNS Vario E1 III elemental analyzer following the method described by Lin et al. (2011). Replicate analysis of one sample (n = 12) gave a precision of ±0.02 wt.% for TOC.

2.3. Extraction and PAH analysis

Analytical procedures and QA/QC essentially followed those methods reported by Guo et al. (2006). Briefly, homogenized samples were freeze-dried and ground. About 20 g of the sample was

spiked with a mixture of recovery standards of three deuterated PAHs (phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}). The samples were extracted with dichloromethane in a Soxhlet extractor for 72 h, with activated copper added to remove the sulfur in the samples. The extract was concentrated and fractionated using a silica–alumina (1:1) column. PAHs were eluted using 35 ml of hexane/dichloromethane (1:1). The PAHs fraction was concentrated to 0.5 ml, and hexamethylbenzene was added as internal standard before the mixture was subjected to GC–MS analysis. An Agilent 5975C mass spectrometer interfaced to an Agilent 7890 gas chromatography was used to analyze the samples. The GC was equipped with a DB-5MS capillary column (30 m long × 0.25 mm inside diameter × 0.25 μm film thickness), with He as carrier gas. The chromatographic conditions were as follows: injector temperature, 290 °C; detector temperature, 300 °C; temperature program: 60 °C (3 min), 60–290 °C at 3 °C/min, held at