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Sediment record of polycyclic aromatic hydrocarbons in the Liaohe River Delta wetland, Northeast China: Implications for regional population migration and economic development☆

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ABSTRACT

The polycyclic aromatic hydrocarbons (PAHs) of a ^{210}Pb-dated sediment core extracted from the Liaohe River Delta wetland were measured to reconstruct the sediment record of PAHs and its response to human activity for the past 300 years in Northeast China. The concentrations of the 16 U.S. Environmental Protection Agency priority PAHs ($\sum$16PAHs) ranged from 46 to 1167 ng g^{-1} in this sediment core. The concentrations of the 16 PAHs (especially 4- and 5+6-ring PAHs) after the 1980s (surface sediments 0−6 cm) were one or two orders of magnitudes higher than those of the down-core samples. The exponential growth of 4-ring and 5+6-ring PAH concentrations after the 1980s responded well to the increased energy consumption and number of civil vehicles resulting from the rapid economic development in China. Prior to 1950, relatively low levels of the 16 PAHs and a high proportion of 2+3-ring PAHs was indicative of biomass burning as the main source of the PAHs. A significant increase in the 2 + 3 ring PAH concentration from the 1860s−1920s was observed and could be attributed to a constant influx of population migration into Northeast China. It was suggested that the link between historical trend of PAHs and population or energy use involves two different economic stages. Typically, in an agricultural economy, the greater the population size, the greater the emission of PAHs from biomass burning, while in an industrial economy, the increase in sedimentary PAH concentrations is closely related to increasing energy consumption of fossil fuels.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants that have been the focus of many studies due to their carcinogenic and mutagenic properties. PAHs can be of anthropogenic or natural origin, and atmospheric PAHs are mainly derived from incomplete combustion of fossil fuels and biomass, as well as by coking and metal production in modern society (Yunker et al., 1996; Mai et al., 2003; Pereira et al., 1999; Xu et al., 2006). Energy consumption and emission levels could be reflected in PAH records in the sedimentary deposits, and thus can provide a picture of the economic development in a region (Pereira et al., 1999; Lima et al., 2003; Hartmann et al., 2005; Kannan et al., 2005; Liu et al., 2005; Guo et al., 2006; Itoh et al., 2010; Lin et al., 2012).

Delta environments are one of the ultimate sinks for PAHs from riverine discharge, wastewater and petroleum inputs, urban runoff, and atmospheric deposition (Mai et al., 2003; Lima et al., 2003; Xiao et al., 2014; Yang et al., 2015). The Liaohe River is the largest river in Northeast China and the 25th largest river (coursing 1345 km long) in the world (Milliman and Meade, 1983). Its drainage area covers ~30% of Northeast China, approximately 300,000 km^2, and the annual runoff is approximately 13 billion m^3. From 2001 to 2005, the Liaohe River carried an annual average of approximately 20 million tons of sediments into the Bohai Sea.

Northeast China, consists specifically of the three provinces of Liaoning, Jilin and Heilongjiang, and was the first important heavy-industry base in China (after 1949) because of its bountiful natural resources, in particular there has been considerable exploration and exploitation of petroleum in the region since the 1960s. However, before the 1860s, Northeast China was backward

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economy compared to the rest of China. The industrial development and population migration into Northeast China was forbidden by the Qing government. That prohibition broke down as the Qing began losing power in the mid 1800's (Mi and Jiang, 1996). Since then, a large population influx to Northeast China has been sustaining and the early industrial activities have been growing. Northeast China has its own unique history of energy usage and population movements, which differs completely from that of other areas of China.

In this study, a sediment core was collected from the center of Liaohe River Delta (LRD) wetland situated in the lower reaches of the Liaohe River, (Fig. 1). LRD has a relatively intact wetland environment, where water level is shallow and relatively stable. It is thus the ideal place to extract sediment core for the reconstruction of historical record of anthropogenic contaminants transported mainly from the drainage basin of the Liaohe River. This work aimed to establish the first 300-year sediment record of PAHs in the delta wetland to determine if there is a correlation between the PAH sediment record and socio-economic development (population and energy usage) in Northeast China and to infer the possible factors influencing the temporal PAH variations in the region.

2. Materials and methods

2.1. Sampling

The LRD is a flat topography made up of soft sediment soil, with several meandrous waterways that had a rich history of rerouting. LRD wetland area (121° 25′–122° 31′ E, 40° 40′–41° 25′ N) of nearly 6000 km^2, spanning the Panjin and Yingkou city of Liaoning province, is a deposition plain situated in the lower reaches of the Liao River (Fig. 1). LRD wetland is one of the largest reed coastal wetland area in China, and is also the world's second largest reed origin. Sample core GGLW was located at 41° 09′ 33.75″ N, 121° 47′ 42.71″ E, at the center of LRD wetland reed field area which is nature reserve (Fig. 1). This core was collected using a manual coring equipment in January 2012, and its length was 72 cm. The core was cut into 1-cm samples from 6 to 72 cm using a stainless steel cutter in the laboratory, while the top layer samples (0–6 cm) were sectioned every 2 cm. The samples were wrapped in aluminum foil and stored at −20 °C until analysis of organic compounds.

2.2. Extraction and PAH analysis

Analytical procedures and quality assurance/quality control essentially followed the methods reported by Mai et al. (2003) and Lin et al. (2011). The approximately 8 g of the sample were freeze-dried, ground, and spiked with a mixture of recovery standards of four deuterated PAHs (acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}). The samples were extracted in a Soxhlet extractor for 72 h with dichloromethane, and then activated copper was added to remove the sulfur in the samples. The extract was fractionated in a silica-alumina (1:1) column using hexane/dichloromethane (1:1) as eluent. The PAH fraction was concentrated to approximately 0.5 ml under a gentle nitrogen stream, and hexamethylbenzene was added to the mixture as an internal standard. The samples were analyzed by the Agilent 5975C

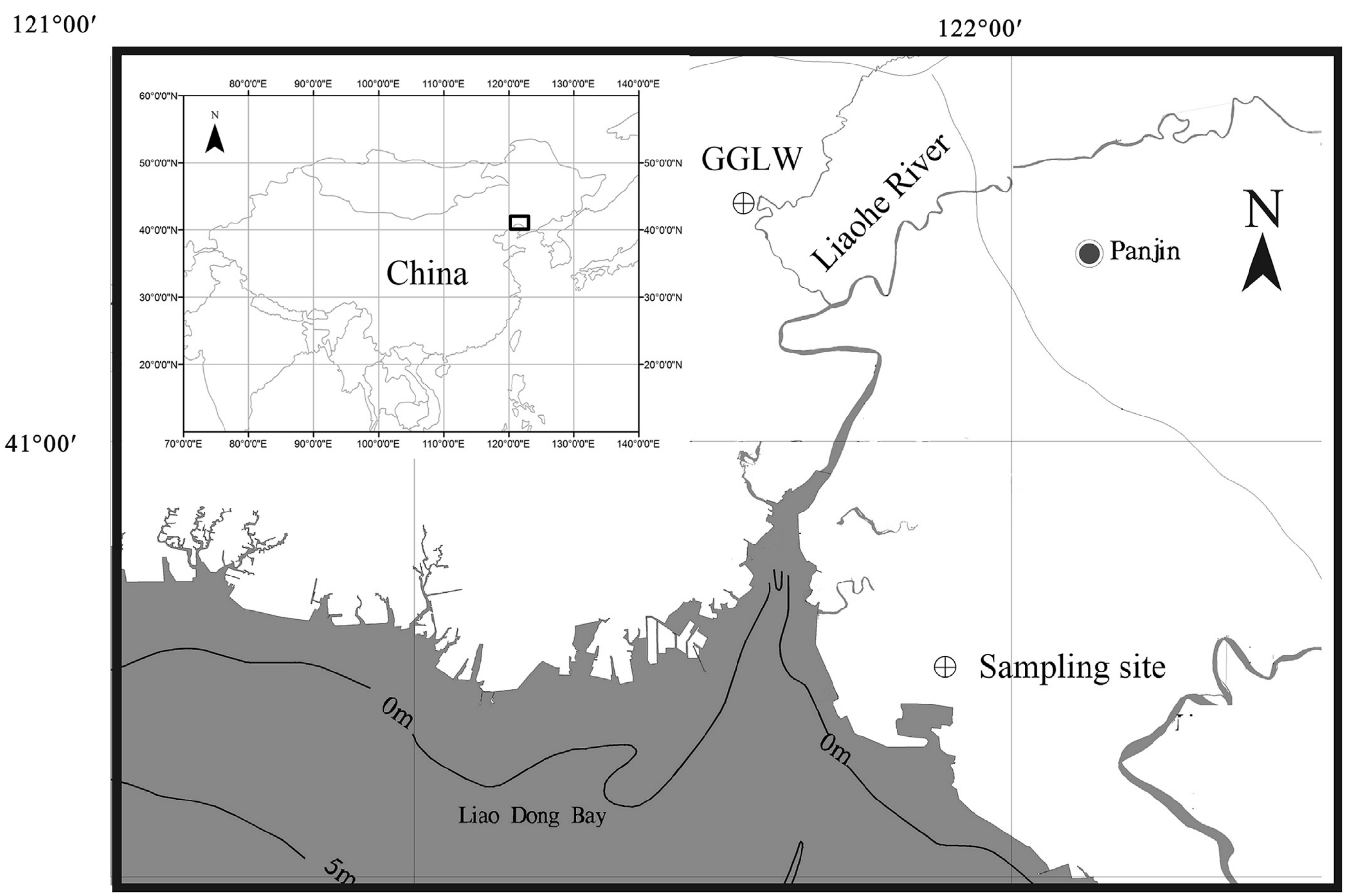

Fig. 1. Study area and location of the sampling site [revised from Ma et al., 2014].