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Application of a self-organizing map and positive matrix factorization to investigate the spatial distributions and sources of polycyclic aromatic hydrocarbons in soils from Xiangfen County, northern China

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ABSTRACT

The concentrations of 16 priority polycyclic aromatic hydrocarbons (PAHs) were measured in 128 surface soil samples from Xiangfen County, northern China. The total mass concentration of these PAHs ranged from 52 to 10,524 ng/g, with a mean of 723 ng/g. Four-ring PAHs contributed almost 50% of the total PAH burden. A self-organizing map and positive matrix factorization were applied to investigate the spatial distribution and source apportionment of PAHs. Three emission sources of PAHs were identified, namely, coking ovens (21.9%), coal/biomass combustion (60.1%), and anthracene oil (18.0%). High concentrations of low-molecular-weight PAHs were particularly apparent in the coking plant zone in the region around Gucheng Town. High-molecular-weight PAHs mainly originated from coal/biomass combustion around Gucheng Town, Xincheng Town, and Taosi Town. PAHs in the soil of Xiangfen County are unlikely to pose a significant cancer risk for the population.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a class of persistent organic pollutants, are ubiquitous in the environment (Hoffman et al., 1984). Owing to their potential ecological and health risks, 16 PAHs were listed as priority pollutants by the US Environmental Protection Agency (OFR, 1982) and seven of them are considered probably to be carcinogenic (IARC, 2010). PAHs are mainly generated from the incomplete combustion or pyrolysis of organic material, such as vehicle emissions, coal- and fossil fuel-powered generation, petroleum refining, straw and firewood burning, industrial processing, chemical manufacturing, oil spills, coal tars, and domestic heating (Peng et al., 2011).

China is well known for PAH pollution. It was estimated that the total PAH emission in China was 25 300 t in 2003 (Xu et al., 2006). Straw burning (34.6%) and coke production (27.2%) are the main sources of PAHs in China (Lang et al., 2008). Linfen City (Shanxi Province, northern China), is located at the heart of China's enormous coal industrial belt, which supplies about two-thirds of the nation's energy (Cao et al., 2015). Unfortunately, since China carried out reform and open policy (1978), the operation of numerous illegal and uncontrolled coal mines, steel factories, and tar refineries has made Linfen City one of the most polluted cities in the world (Blacksmith Institute, 2006). During the last decade, the local government has implemented a series of measures to improve environmental quality. As a result, the environmental conditions have improved significantly (Report on the State of the Environment in Shanxi Province, 2000–2013). To investigate the status of environmental quality in Linfen, we conducted this research in a representative region (Xiangfen County) of it. Xiangfen County, located in southern Linfen, is rich in mineral resources, with coal and iron being particularly abundant. Based on these resources, several coal-based pillar industries have become established in Xiangfen County, including coking, metallurgy, and power generation, and have dominated the county's socio-economic development. Unfortunately, these industries have also severely polluted the local environment.

Soil is the primary reservoir and sink for environmental pollutants, including PAHs (Wang et al., 2010). Because of their persistence and hydrophobicity, PAHs can strongly adsorb to soil organic matter and are then retained in the soil for a long time. Therefore, soil has been proved to be a perfect material for investigating PAH pollution and its

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environmental behavior (Wild and Jones, 1995). In this study, a self-organizing map (SOM) and positive matrix factorization (PMF) were used to identify the PAH sources and their contribution to overall soil pollution in Xiangfen County. The SOM can serve as a useful tool for classification and pattern recognition, meanwhile PMF can further help apportion the contributions of different sources. To the best of our knowledge, this is the first study to investigate PAH sources using SOM and PMF simultaneously. This work will not only help to understand the quantitative PAH sources and its environmental influence in Linfen, but should also provide some useful guidance for other polluted regions.

2. Materials and methods

2.1. Study area and soil sampling

Xiangfen County is located in southern Linfen City, with China clay the main representative soil type. The area has a temperate semi-wet monsoon climate, with average annual temperature and rainfall of 12.4 °C and 508.6 mm, respectively. The sampling method has been introduced by Ma et al. (2016). Briefly, 128 surface (0–20 cm) soil samples were collected from across Xiangfen County using a gridded sampling design with a grid spacing of approximately 3 km in May, 2012 (Fig. 1). At each sampling site, five subsamples were taken from a rectangular zone (~100 m^2), then pooled and homogenized to form one composite sample.

2.2. Chemicals

A deuterated PAH mixture standard solution (Supelco, Bellefonte, PA, USA) was used in the present study, including d_{10}-Phe, d_{12}-Pyr, d_{10}-Ace, d_{12}-Chr, and d_8-Nap. Anhydrous sodium sulfate (Sigma-Aldrich, St. Louis, Missouri, USA) was baked at 450 °C for 5 h. A 100- to 200-mesh silica gel (Sigma-Aldrich, St. Louis, Missouri, USA) was activated for approximately 16 h at 130 °C. Residue-analysis grade solvents (Fisher Scientific, Fair Lawn, New Jersey, USA) were used for the extraction and cleanup procedures. Deuterated PAH and 2-difluorobiphenyl were used as surrogate and injection internal standards, respectively. The 16 USEPA priority PAHs were Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (Baa), Chrysene (Chr), Benzo(b)fluoranthene (Bbf), Benzo(k)fluoranthene (Bkf), Benzo(a)pyrene (Bap), Dibenzo(a,h)anthracene (Daa), Benzo (g,h,i)perylene (Bgp) and Indeno(1,2,3-cd)pyrene (I1p).

2.3. Sample extraction, cleanup, and analysis

The sample extraction, cleanup and instrument analysis procedures for PAHs were followed the method of Jiang et al. (2009), with slight modifications. Briefly, we used Soxhlet-extraction followed by neutral activated silica column for clean-up then used GC/MS to quantitatively analyzed 16 PAHs. The detailed methods were listed in Supplementary material.

2.4. Quality control

To ensure the correct identification and quantitation of target compounds, the following quality control criteria were applied: (a) A method blank (solvent and glassware), a matrix spike (working standards spiked into pre-extracted soil), and a duplicate sample for every seven samples were processed together with the soil samples by performing the entire extraction, cleaning, and analytical procedures. (b) The limit of detection (LOD, signal-to-noise ratio = 3) was in the range of 0.12–0.48 ng/g dry weight (dw). (c) The average recovery of the surrogate standards were in the range of 72% to 106% (Table S2). (d) The coefficient of variation of PAH concentrations in the duplicates was < 15%.

2.5. Data analysis

The SOM is an unsupervised learning neural network (Herrero et al., 2001), which provides projection of multi-dimensional data into a two-dimensional map (Corne et al., 1999). The adjacent map units called neurons in a SOM are connected by neighborhood relations. In the training process, the input vector is chosen and the weight vectors are calculated using some distance measure like Euclidean Distances (Kohonen, 2001). The neuron, whose weight vector is closest to the input vector, is called best-matching unit (BMU). The weight vectors

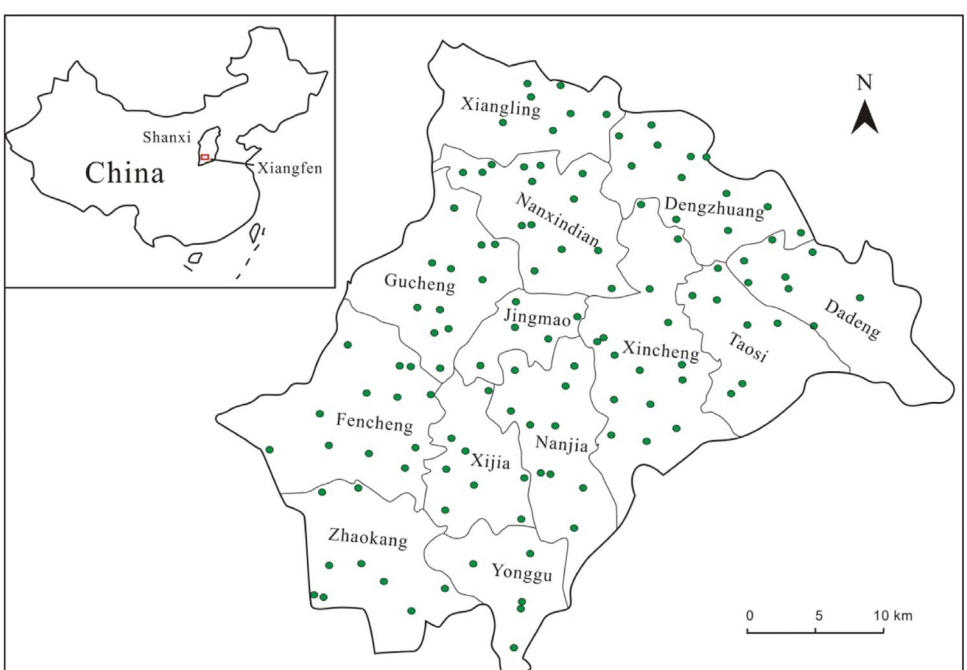

Fig. 1. Locations of the sampling sites in Xiangfen County.