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Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: A case study in Dalian, China

Zhen Wang, Jingwen Chen *, Xianliang Qiao, Ping Yang, Fulin Tian, Liping Huang

Department of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

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Abstract

To estimate the distribution and sources of soil polycyclic aromatic hydrocarbons (PAHs) in metropolitan and adjacent areas, soil samples were collected from urban, suburban and rural locations of Dalian, China, and concentrations of 14 PAHs were determined. The spatial PAH profiles were site-specific and determined by the sources close to the sampling sites. PAH concentrations decreased significantly along the urban–suburban–rural transect. The gradient implied that the fractionation effect influenced PAH distribution. Bivariate plots of selected diagnostic ratios showed general trends of co-variation and allowed to distinguish samples taken from different areas. An improved method, factor analysis (FA) with nonnegative constrains, was used to determine the primary sources and contributions of PAHs in soils. The FA model showed traffic average (74%) and coal related residential emission (26%) were two primary sources to Dalian soils. In addition, the FA model provided reasonable explanations for PAH contributions in soils from different sites. The results suggest that FA with nonnegative constraints is a promising tool for source apportionment of PAHs in soils.

Keywords: Composition profile; Diagnostic ratio; Factor analysis; PAHs; Soil

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous and persistent organic pollutants (POPs) in the environment, and produced mainly from incomplete combustion of fossil fuels, biomass and pyrosynthesis of organic materials. It is believed that combustion processes, including thermal combustion conditions, fuel/stove types and even burning stages, are responsible for the abundance and profiles of PAHs that enter the environment (Chen et al., 2005). Of combustion-derived PAHs, low molecular weight (LMW) (three rings) species are abundantly produced at low to moderate temperatures, such as wood and coal combustion. On the contrary, high molecular weight (HMW) (four and more rings) PAHs are generated at high temperatures, such as vehicle emission (Mastral and Callén, 2000). Once PAHs are released into the atmosphere, they are subject to sink in soil via dry and wet deposition. Because of their persistence, low vapor pressures (P_L) and high octanol/air partition coefficients (K_{OA}), PAHs can strongly adsorb to soil organic matter (SOM), and are likely to be retained for a long time (Wilcke, 2000). Consequently, soil is one of the main reservoirs for PAHs in the environment. Previous studies implied that POPs measured in soils correlate with those in the atmosphere, and therefore, soil PAH concentrations are usually considered as good indicators of the surrounding pollution (Wild and Jones, 1995).

In general, it is necessary to identify the primary sources of pollutants through the use of various technique. So far, there have been several methods applying to apportion the origins of PAHs presented in different environmental media. Diagnostic ratio is one of widely used technique (Yunker et al., 2002; Bucheli et al., 2004). The ratios of different PAHs are expected to vary with sources most likely due to the various routes of PAH formation under different

* Corresponding author. Tel./fax: +86 411 8470 6269.
E-mail address: jwchen@dlut.edu.cn (J. Chen).

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combustion conditions. The method is probably more pronounced at extreme locations such as urban areas close to the point sources. Factor analysis (FA) is another tool for distinguishing the sources of pollutants. The main applications of FA are to reduce the number of variables and to detect the structure in the relationships between variables, that is, to classify variables. FA can be used to apportion the sources with minimal knowledge about source characteristics, metrological conditions, transport and incorporation mechanisms of pollutants into the environment, etc., which usually are not available (Christensen and Bzdusek, 2005). However, from the viewpoint of matrix factorization, conventional FA method will inevitably get negative values, which usually lose the physical meaning in practice. An improved technique, FA with nonnegative constraints provides a new way for matrix factorization. The technique ensures factor axes to become less orthogonal and makes factor scores and loadings more interpretable due to fewer negative values (Rachdawong and Christensen, 1997).

The objectives of this study are to investigate the spatial distributions of PAHs from urban to rural soils of Dalian, and to determine the primary sources of PAHs by applying diagnostic ratios and FA with nonnegative constraints. FA with nonnegative constraints is also employed to estimate the source contributions. To our knowledge, scarce application of FA with nonnegative constraints has been engaged to apportion the sources of PAHs in soils.

2. Materials and methods

2.1. Study area

Dalian (38°43′–40°10′N and 120°58′–123°31′E) is on the east coast of Eurasia and the southern tip of Liaodong peninsular in northeast China (Fig. 1). The city lies in the warm temperate zone, with maritime feature of warm temperate continental monsoon climate. The average temperature of the year is 10.5 °C. The urban population is about 2.7 million, and the urban area is 2415 km^2.

2.2. Sampling and preparation

The sampling sites are shown in Fig. 1. Soils were collected from 24 sampling sites, of which 11 sites (1–11#) along the different roads and six sites (12–17#) in park or residential areas in urban Dalian were selected to present urban signal, five sites were located to present suburban areas (18–22#) and two sites remote from the immediate impact of potential sources to represent rural areas (23–24#).

Surface soils were collected in April 2005 and the sampling depth was 0–5 cm after removal of the litter layer. About 10 cores, taken over an area of several hundred square meters, were bulked together to form one sample. The samples were air-dried at room temperature, and were ground and sieved with a 60-mesh sieving screen. The remaining water content in soil was determined gravimetrically after heating in an oven at 110 °C for 8 h. All results reported here are dry weight basis. Content of SOM was determined by loss in weight on ignition at 450 °C for 8 h (Konen et al., 2002; Hassanin et al., 2005).

2.3. Sample extraction, cleanup and analysis

Soil samples (about 5 g) were mixed with anhydrous sodium sulfate (2 g) and activated copper powder (1 g). The samples were extracted in a mixture of 30 mL acetone/dichloromethane (DCM) (1:1, v:v) for 30 min in an ultrasonic shaking apparatus. The samples were recovered by vacuum filtration. The same extraction was repeated

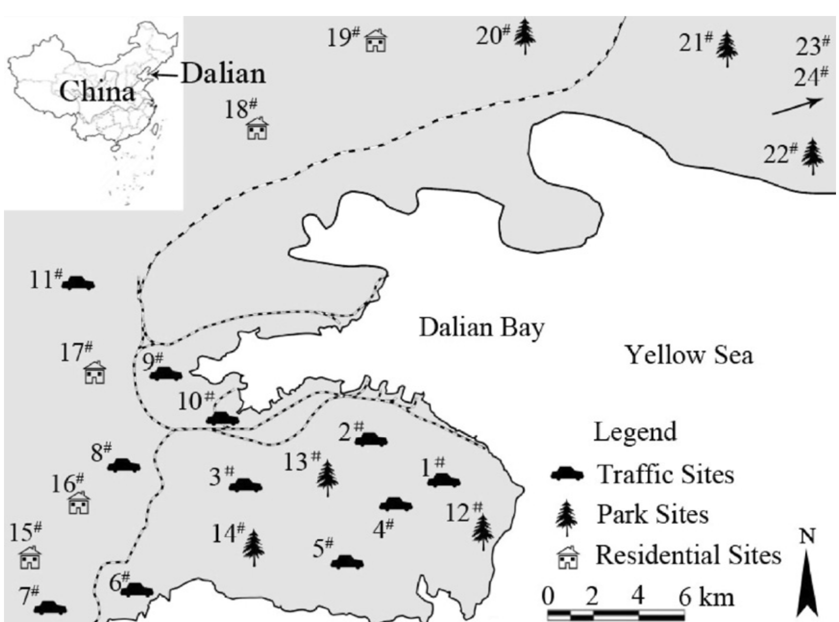

Fig. 1. Map of soil sampling sites in Dalian, China.