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Contamination, source identification, and risk assessment of polycyclic aromatic hydrocarbons in the soils of vegetable greenhouses in Shandong, China

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A B S T R A C T

The concentrations of 16 polycyclic aromatic hydrocarbons (PAHs) were analyzed in soil (n = 196) and vegetable (n = 30) collected from greenhouses, and also in the soil (n = 27) collected from agriculture fields close to the greenhouses in Shandong Province, China. The total PAH concentration (Σ_{16}PAH) ranged from 152.2 µg/kg to 1317.7 µg/kg, within the moderate range in agricultural soils of China. Three-ring PAHs were the dominant species, with Phe (16.3%), Ace (13.1%), and Fl (10.5%) as the major compounds. The concentrations of low molecular weight (LMW ≤ 3 rings) PAHs were high in the east and north of Shandong, while the concentrations of high molecular weight (HMW ≥ 4 rings) PAHs were high in the south and west of the study area. The PAH level in soils in industrial areas (IN) was higher than those in transport areas (TR) and rural areas (RR). No significant difference in concentration of Σ_{16}PAH and composition was observed in soils of vegetable greenhouses and field soils. PAH concentration exhibited a weakly positive correlation with alkaline nitrogen, available phosphorus in soil, but a weakly negative correlation with soil pH. However, no obvious correlation was observed between PAH concentration and organic matter of soil, or ages of vegetable greenhouses. Σ_{16}PAH in vegetables ranged from 89.9 µg/kg to 489.4 µg/kg, and LMW PAHs in vegetables positively correlated with those in soils. The sources of PAHs were identified and quantitatively assessed through positive matrix factorization. The main source of PAHs in RR was coal combustion, while the source was traffic in TR and IN. Moreover, petroleum source, coke source, biomass combustion, or mixed sources also contributed to PAH pollution. According to Canadian soil quality guidelines, exposure to greenhouse soils in Shandong posed no risk to human health.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds that contain at least two condensed aromatic rings and do not contain heteroatoms or substituents (Fetzer, 2007). PAHs have elicited much concern because they exhibit strong toxic, carcinogenic, and mutagenic properties (Canadian Council of Ministers of the Environment, 2010), and 16 PAHs have been identified as priority pollutants by the United States Environmental Protection Agency (USEPA).

Being a vital resource, agricultural soil performs a key function in food and biomass production. As a primary sink for environmental pollutants, soil is increasingly subjected to different pressures. Agricultural soil is at risk of PAH contamination mainly caused by anthropogenic activities, such as incomplete combustion of wood, chemical manufacturing, oil spills, coal tars, vehicle emissions, power generation, and petroleum refining (Gan et al., 2009). Moreover, extensive application of wastewater irrigation, sewage sludge, organic substances and biowaste used as fertilizers appear to be important reasons for the accumulation of PAHs in the agricultural soil (Khan et al., 2008; Waqas et al., 2014b). Khan et al. (2008) found that soil-to-plant transfer is one of the major pathways of PAHs transport into plants, and vegetables grown in PAHs contaminated soils may take up PAHs in sufficient quantities to cause health problems for the consumers (Waqas et al., 2014a). Several studies focusing on PAHs in field soils have been conducted and have identified prevalent PAH contamination in China (Wang et al., 2007, 2015; Lu et al., 2012; Tang et al., 2010). However, few studies on PAHs in soils of vegetable greenhouses

have been conducted. On one hand, greenhouses can possibly prevent atmospheric PAHs during the plant cultivation. Moreover, the temperature in greenhouses is generally higher than that in the field, which may contribute to volatilization of PAHs. On the other hand, the amount of organic fertilizers applied in greenhouse plant cultivation is high, and the value even reaches 19.88 kg/m² in several areas in China (Mo et al., 2005). Previous studies reported that organic fertilizers contain several persistent organic pollutants, including PAHs and organochlorine (Huang et al., 2006). Therefore, PAHs in soils of vegetable greenhouses should be of concern, and determining the levels of PAHs in the soils of greenhouses is crucial.

Shandong (34.61–37.91°N and 115.08–122.41°E) is a coastal province in East China. It has a temperate climate, with average temperatures of −5 °C to 1 °C in January and 24 °C to 28 °C in July. The annual precipitation rate in the study area is ranged from 550 mm to 950 mm. Shandong is the largest industrial producer and one of the top manufacturing provinces in China. This province is dominated by petroleum, chemical, electronic, fertilizer, tire, and rubber industries. Shengli Oil Field, the second largest oil production base in China, is located in the northeast part of Shandong. Moreover, the population density of Shandong is as high as 623 people per square kilometer. With the rapid growth of its industrial production, traffic, and population density, Shandong faces serious environmental problems. Agriculture is well developed in Shandong. In particular, greenhouse vegetable cultivation accounts for 50% of the cultivation area in China (8.67×10⁵ hm² in 2010) (Liu et al., 2008). Many recent studies have indicated that organic pollutants, such as antibiotics and phthalate acid esters, are present in the soils of vegetable greenhouses in Shandong (Yin et al., 2012). However, the characteristics of PAHs in the soils of greenhouses in Shandong are unknown.

The present study has four objectives. The first is to investigate the concentration, composition, and spatial distribution of PAHs in the soils of vegetable greenhouses, and to compare the concentration and composition of PAHs in soils of vegetable greenhouses and adjacent field soils. The second objective is to analyze the correlations between PAHs and the physicochemical properties of soil and age of greenhouses, and the correlations between PAHs in vegetables and those in soils. The third objective is to identify the potential sources of PAHs and their respective contributions. The last objective is to evaluate PAH risk assessment in the soils of the study area.

2. Materials and methods

2.1. Sampling and preparation

A total of 196 surface soil samples (0–20 cm) were collected from vegetable greenhouses in 15 counties in Shandong in July 2015 (Fig. 1). Besides, 27 surface soil samples from the field, which were close to vegetable greenhouses, were collected to compare the concentration and composition of PAHs in soils of vegetable greenhouses and soils of field. Among the 196 samples from vegetable greenhouses, 36 were close to industrial pollution sources (IN), which included power plants, petrochemical plants, coal mines, and coke production plants. A total of 59 samples were collected from busy traffic areas (TR), and 100 rural samples (RR) were obtained far from pollution sources (> 4 km) or roads (> 100 m).

A total of 30 vegetable samples were collected from vegetable greenhouses. These samples were collected from shoots of leafy vegetables, including spinach (n=8), crown daisy chrysanthemum (n=6), leek (n=4), lettuce (n=3), rapeseed (n=3), celery (n=3), and chrysanthemum (n=3).

Five subsamples (four corners and center) at each sampling point were obtained and combined to acquire a composite sample. The collected soil and vegetable samples were freeze dried at −50 °C and 123 ± 2 Pa (Khan and Cao, 2012), homogenized, made to pass through a 20-mesh sieve, and stored in amber glass bottles at −4 °C until
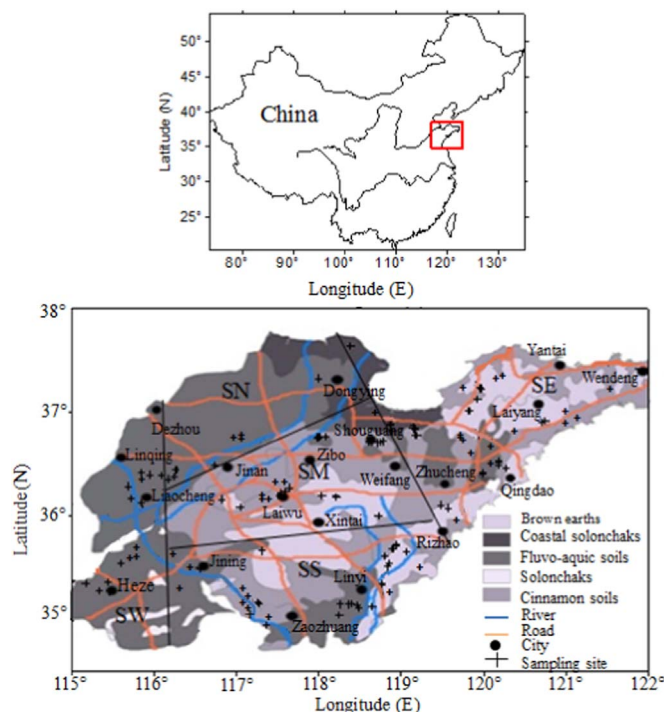

Fig. 1. Schematic map showing the soil sampling sites of vegetable greenhouses in five regions in Shandong (SE: east of Shandong, SS: south of Shandong, SW: west of Shandong, SN: north of Shandong, SM: middle of Shandong).

analysis.

The pH value of the soil samples was measured with a pH meter, and organic matter (OM) was determined through wet oxidation with chromate (Schwartz, 1995). Alkaline nitrogen, available phosphorus, and available potassium were determined according to Bao (2000).

2.2. Sample extraction, cleanup, and analysis

Two grams of soil or vegetables samples were placed in a glass centrifugal tube and sonicated for 1 h with 10 ml dichloromethane (DCM). The mixture was then centrifuged for 10 min at 4000 r/min, and the extract was collected. The same extraction process was repeated by adding 10 ml DCM to the filter residue. The two extract solutions were combined and concentrated to approximately 1 ml through rotary evaporation.

The concentrated extracts were purified with a 20 cm×10 mm i.d. glass column packed with 4 g activated silica gel and 4 g anhydrous Na₂SO₄ from the bottom to the top (Wang et al., 2015; Maliszewska-Kordybach et al., 2009). Silica gel (200 mesh to 300 mesh) was activated for roughly 5 h at 180 °C, and granular Na₂SO₄ was baked at 450 °C for 5 h before use. Elution was performed with 11 ml DCM and n-hexane (v: v, 1:1). The eluent was further concentrated nearly to dryness under a gentle stream of nitrogen gas and re-dissolved in 2.0 ml methanol for analysis.

PAH concentration was measured through high-performance liquid chromatography; the instrument was equipped with an ultraviolet and fluorescent detector (HPLC–UV–FLD, Shimadzu). The 16 PAHs were separated with an Inertsil ODS-P column (250 mm×4.6 mm, 3.5 μm particle size, 1000 nm pore size) with the mobile phase of methanol--water (80:20, by volume) through gradient elution with a flow rate of 1.0 ml/min. Detection was carried out with the FLD wavelength switching program at an excitation wavelength of 265, 260, 290 and 250 nm, and emission wavelength of 420, 430, and 500 nm. The UV detection was carried out with double wavelength pattern at wavelength channel 1 of 254 nm and wavelength channel 2 of 220, 280 and 210 nm. The column temperature was set to 40 °C, and the injection