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Structural equation modeling of PAHs in ambient air, dust fall, soil, and cabbage in vegetable bases of Northern China☆

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ABSTRACT

A series of field samples including ambient air (gaseous and particulate phases), dust fall, surface soil, rhizosphere soil and cabbage tissues (leaf, root and core), were collected in vegetable bases near a large coking manufacturer in Shanxi Province, Northern China, during a harvest season. A factor analysis was employed to apportion the emission sources of polycyclic aromatic hydrocarbons (PAHs), and the statistical results indicated coal combustion was the dominant emission source that accounted for different environmental media and cabbage tissues, while road traffic, biomass burning and the coking industry contributed to a lesser extent. A structural equation model was first developed to quantitatively explore the transport pathways of PAHs from surrounding media to cabbage tissues. The modeling results showed that PAHs in ambient air were positively associated with those in dust fall, and a close relationship was also true for PAHs in dust fall and in surface soil due to air-soil exchange process. Furthermore, PAHs in surface soil were correlated with those in rhizosphere soil and in the cabbage leaf with the path coefficients of 0.83 and 0.39, respectively. PAHs in the cabbage leaf may dominantly contribute to the accumulation of PAHs in the edible part of cabbages.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) may pose environmental contamination and health risks due to their carcinogenicity, persistence, bioaccumulation and long-range transport potential (Hou et al., 2017; Hou and Li, 2017). China is estimated to be one of the largest emission sources of PAHs in the world (Shen et al., 2013a,b); in particular, Shanxi Province is a top coal-producing region, and the coking industry accounted for 69% of the total PAHs emissions in 2003 (Xu et al., 2006). To date, PAHs have extensively occurred in multimedia, such as air, soil, and various plants via root uptake and leaf absorption (Jiao et al., 2007; Kang et al., 2017). Considering diet as a primary pathway of human exposure to PAHs (Phillips, 1999), the presence of PAHs in vegetables may directly threaten dietary quality and safety. Consequently, insight into the sources, transport and distribution of PAHs in surrounding media and vegetables is of great concern, and essential for human health (Li et al., 2016), pollution control (Hou, 2011; Hou et al., 2012, and remediation planning (Hou and Al-Tabbaa, 2014; Qi et al., 2017; Zhang et al., 2017).

Some specific approaches have been developed to investigate the source and fate of PAHs, such as diagnostic ratios of paired isomers (Wang et al., 2010; Chen et al., 2016; Dudhagara et al., 2016; Cai et al., 2017), statistical analysis (Xiong et al., 2017), chemical mass balance (CMB) model (Li et al., 2003), and fugacity model (Wang et al., 2013). However, some shortages, such as deviations in isomeric ratios due to differences in (bio)degradation during transfer process (Zhang et al., 2005) and a lack of abundant source profile data, have been indicated. In this sense, introducing structural equation modeling (SEM) may benefit the understanding of emission sources and transport pathways of PAHs. To date, SEM has been widely applied in different fields (Anderson and Gerbing, 1988; Johnson, 1999; Hou et al., 2014), while to our best knowledge,

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there is no report on the behaviour characteristics of PAHs in the environmental multimedia.

In the current study, based on multimedia samplings in some cabbage bases (including ambient air, dust fall, surface soil, rhizosphere soil and cabbage tissues) and statistical analyses (mainly as factor analysis) of the corresponding measured data, a SEM was first developed to systematically and quantitatively investigate the source, transport and fate of PAHs in different surrounding media and cabbage tissues and to further explore the possible PAHs transport pathways from the source to the receptor. Since cabbage is one of the most commonly consumed vegetables in the diet of local populations (Zhong and Wang, 2002), the obtained results are of particular significance to food safety and human health in Northern China.

2. Materials and methods

2.1. Data acquisition

Multimedia samplings were conducted in eight vegetable plots near a large-scale coking manufacturer located in Shanxi Province, as shown in Fig. S1. Ambient air (gaseous phase plus particulate phase), dust fall (comprising dry and wet deposition), surface soil, rhizosphere soil (*i.e.*, root soil) and cabbage (*Brassica oleracea Linnaeus var. capitata Linnaeus*, a popular vegetable with large yields in Northern China) tissues (including outer leaf, root, and edible core) were collected during the local harvest time. Since the local cabbages were usually irrigated by well water without sewage irrigation, and PAH species strongly tended to stay in soil particles (Sverdrup et al., 2002) instead of water due to their lipophilicity or hydrophobicity (Xu and Zhou, 2017), the water samples were not included in the samplings. Ambient air and dust fall samplings lasted for 30 days and covered the whole sampling period of soil and cabbage samples. A total of 24 ambient air samples (passive sampling, $n = 24$, and calibrated by active sampling, $n = 12$), 21 dust fall samples (using stainless-steel cylinder), 100 surface soil samples, 101 rhizosphere soil samples, 103 outer-wrapping leaf samples, 101 core samples and 101 root samples were obtained.

The corresponding details on the procedures of different sample collection, storage, pretreatment, quantitative measurement of PAHs, as well as quality assurance (QA) and quality control (QC) can be found in our previous study (Xiong et al., 2017), and a brief summary is described as follows. The particulate phase (by glass fibre filter, GFF) and gaseous phase (by polyurethane foam, PUF, Teflon holder) PAHs in ambient air were sampled by passive air samplers in triplicate (Tao et al., 2009) and calibrated by the active air samplings (QCD-3000, Tianyue Instrument Ltd. Company, China). Each surface soil (including 5 sub-samples, 0–5 cm depth), rhizosphere soil (0–5 mm away from the root surface, careful stripping with a stainless-steel knife), dust fall and particulate phase air sample was pre-treated by microwave extraction (MARS2Xpress, CEM, USA) with a mixture of *n*-hexane and acetone (V:V = 1:1) and purified through an alumina-silica gel column. Each freeze-dried cabbage tissue sample was similarly microwave-extracted with acetonitrile, and purified by a florisil-silica gel column. The gaseous phase air samples were pre-treated by Soxhlet extraction using the mixture of *n*-hexane and acetone and purified by the aforementioned alumina-silica gel column. The qualitative and quantitative analysis of PAHs was performed by a gas chromatography equipped with a mass spectrometer detector (GC/MS, Agilent GC6890/5973 MSD, Agilent Technology, USA). All the samples were measured in triplicate. Half of all the studied samples were randomly selected and spiked with 2-fluoro-1,1′-biphenyl and *p*-terphenyl-D14 (AccuStandard, USA) as the recovery rate indicators, and the corresponding recoveries were 50%–98% and 89%–150%, respectively. The method recoveries of the 16 PAHs in different sampling media ranged from 70% to 130%. The detection limits of the different components were from 0.01 to 0.64 ng/mL. The procedural blanks were examined for all types of samples to eliminate the possible external contamination during the whole pretreatment procedures. In this study, sixteen parent PAHs were determined as naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo [b]fluoranthene (BbF), benzo [k]fluoranthene (BkF), benzo [a]pyrene (BaP), indeno [1,2,3-cd]pyrene (IcdP), dibenz [a,h]anthracene (DahA), and benzo [g,h,i]perylene (BghiP). Due to the relatively high blank concentration and low recovery rate, NAP was excluded from the final results of total PAHs. It should be noted that the measured results of PAHs in environmental media and cabbage tissues were summarized in a previous paper (Xiong et al., 2017). The current study focuses on a combination of factor analysis and SEM simulation to quantitatively describe the source, transport and fate of PAHs.

2.2. Model framework

Currently, inconsistences remain surrounding the relative contribution of the two possible pathways (foliage absorption and root uptake) of PAHs (including total amount and individual species) from surrounding media to plant tissues (Fismes et al., 2002; Zhong and Wang, 2002; Wang et al., 2015; Xiong et al., 2017). Therefore, a systematic and comprehensive study by SEM is required to quantify the relative contributions of various transport pathways of PAHs, in combination with the corresponding multivariate statistical analysis.

Since the edible cabbage cores were usually wrapped by the outer leaves, PAHs in atmospheric particles and dust fall had no access to the cores (Xiong et al., 2017). Consequently, exogenetic PAHs generally entered cabbage tissues by root uptake and leaf deposition and absorption, and then PAHs in edible cores came from the inner translocation of PAHs in roots and leaves. PAHs in leaves mainly originated from ambient air, dust fall, and flying dust due to re-suspension of surface soil particles by blowing winds. Therefore, a hypothetical model was established, as shown in Fig. 1.

2.3. Statistical analysis

The analytical data on PAHs in different surrounding media and cabbage tissues were employed to extract indicator variables by factor analysis (FA) and were implemented using the principle component method with varimax rotation (Hou et al., 2014) to identify the interrelated variables and reduce the number of

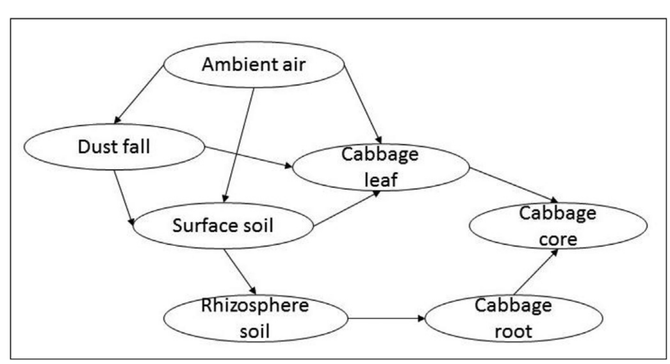

Fig. 1. A hypothetical model for PAHs in environmental multimedia and in cabbage tissues.