Environmental Pollution 156 (2008) 769–774

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Characterization of extractable and non-extractable polycyclic aromatic hydrocarbons in soils and sediments from the Pearl River Delta, China

Lulu He[a,b], Jianzhong Song[a], Ping'an Peng[a,*]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, P.O. Box 1131, Guangzhou 510640, China
[b] Graduate School of Chinese Academy of Sciences, Shijingshan, Beijing 100039, China

Non-extractable PAHs took large proportions of total PAHs in field soils and sediments.

ARTICLE INFO

Article history:
Received 25 January 2008
Received in revised form 27 May 2008
Accepted 2 June 2008

Keywords:
Polycyclic aromatic hydrocarbons
Extractable PAHs
Non-extractable PAHs
Humic acids
Humin

ABSTRACT

Formation of bound residues of pollutants in soils and sediments is an important process to control the fate of pollutants in the environment. The most of bound residue is not solvent extractable. In this paper, we measured both extractable and non-extractable polycyclic aromatic hydrocarbons (PAHs) in different organic matter fractions of samples from the Pearl River Delta, China. Non-extractable PAHs concentration was 234.45–1424.57 μg/kg and accounted for 33.78–57.44% of total PAHs. 2–3 Ring PAHs were the dominant species and differed in concentration substantially between the samples. The atomic ratio of PAHs over organic-C in the fractions ordered as solvent soluble organic matter > humin > humic acids, matching the content of aliphatic moieties in the fractions of organic matter. The ratio of extractable and non-extractable PAHs may relate to the aging process of PAHs in soil and sediment.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are mainly produced during incomplete combustion, pyrolysis of organic materials by industry, agriculture and traffic, or in diagenetic alteration processes of natural organic matter (Luo et al., 2004; Conte et al., 2001). They are ubiquitous in ambient air, water, sediment and soil, and some such as pyrene, benzo[*a*]pyrene and benzo[*b*]-fluoranthene are recognized as mutagens and carcinogens. Owing to their toxicity and widespread presence in the environment, PAHs have received much attention by environmental chemists, toxicologists and regulatory agencies for over three decades (Chen et al., 2005).

Most studies have focused on organic solvent-extractable PAHs in samples because they can be readily conducted in laboratories (Chen et al., 2005; Mai et al., 2001). However, non-extractable, namely, bound PAHs in literature are now thought to be as important as extractable PAHs because they may be a significant proportion of total PAHs and play an important role in PAHs' behavior in natural systems. This may include diminishing bioavailability, toxicity and mobility, or retarding of degradation (Chung and Alexander, 1998; Nam and Kim, 2002). The definition of bound residues of pollutants varies with researchers and their extraction methods (Kaufman and Blake, 1973). Fuhr et al. (1998) stated that it "represent compounds in soil, plant or animal, which persisted in the matrix form of the parent substance or its metabolite(s) after extraction, and the extraction method must not substantially change the compounds themselves or the nature of the matrix". In this paper, we use "non-extractable" instead of bound residue to describe the pollutant fraction which is not extractable by solvent. It is similar to bound residue in scientific meaning but more laboratory operative. Bound residues are thought to be formed from chemical binding, entrapment of pollutants in micropores of an inorganic–organic matrix, and other mixture sequestration processes of pollutants in a matrix. Generally, the non-extractable fraction of pollutants increases with residence time in soils and sediments (Gevao et al., 2000; Northcott and Jones, 2001).

The non-extractable hydrophobic pollutants in soils and sediments are mostly present in recalcitrant organic matter such as humic acids, kerogens and black carbon etc. (Cornelissen et al., 2005). These organic materials can be characterized or further

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* Corresponding author. Tel.: +86 20 85290126/13318839751; fax: +86 20 85290117.
E-mail addresses: helulu122@126.com (L. He), songjzh@gig.ac.cn (J. Song), pinganp@gig.ac.cn (Ping'an Peng).

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doi:10.1016/j.envpol.2008.06.003

classified by van Krevelen diagram (Kim et al., 2003). The atomic ratio H/C is an indicator for content of aliphatic moieties in structures of these organic materials. The detailed presentation of pollutants in those organics is not well known.

Non-extractable residues of hydrophobic pollutants in soils and sediments have been studied in laboratories (Macleod and Semple, 2003; Mordaunt et al., 2005). Mordaunt et al. (2005) investigated the mineralization, volatilization and organic solvent-extractable residues of pesticides in purpose-built microcosms to evaluate the significance of non-extractable residues. Beyond all doubt, laboratory studies are necessary to understand pollutant behavior in soils, but many questions remain due to laboratory limitations. For example, the conditions differ between laboratory experiments and nature, so results may not reflect field conditions (ten Hulscher et al., 1999). Generally, laboratory results need validation in the field.

In this study, we chose four soil/sediment field samples that have been polluted by PAHs for many years. PAHs in organic matter fractions, such as solvent soluble organic matter, humic acids, crude humin and organic-C enriched humin were determined, and contribution of organic matter fractions to bound residues of PAHs were discussed.

2. Experimental

2.1. Sample collection

Four soil/sediment samples from the Pearl River Delta, China were used. These samples were collected in 2000 and represented different polluted surface aquatic environments in this region that has experienced rapid economic development for the past three decades. They included: (1) a brownish/yellowish sandy soil (SS) from a paddy field; (2) a pond sediment (PS) collected at 0–10 cm depth from Baishigang; (3) a river sediment (RS) collected at 0–15 cm depth from the Pearl River; and (4) a marine sediment (MS) collected at 0–15 cm depth from the Wushan Archipelago (22°22′05″N, 113°49′20″E) of Zhuhai. The samples were freeze-dried and passed through a 1.0-mm sieve after collection. Then they were stored in well-sealed glass bottles under N_2 atmosphere and kept in the dark until use. For characterization of these samples see Song et al. (2002).

2.2. Materials

Sixteen PAHs (16 compounds specified on EPA Method 610) in samples were carried out. They include naphthalene (N*a*P), acenaphthylene (Acy), acenaphthene (Ace), fluorene (F*l*), phenanthrene (P*he*), anthracene (A*nt*), fluoranthene (F*lu*), pyrene (P*yr*), benz[*a*]anthracene (B*a*A), chrysene (C*hr*), benzo[*a*]pyrene (B*a*P), benzo[*b*]fluoranthene (B*b*F), Benzo[*k*]fluoranthene (B*k*F), dibenz[*a*,*h*]anthracene (D*ah*A), indeno[1,2,3-*cd*]pyrene (I*cd*P) and benzo[*g*,*h*,*i*]perylene (B*ghi*P). Five deuterated PAHs including naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} were used as surrogate standards (Ultra Scientific Inc, North Kingston, RI, USA). PAH standard reference material (SRM 1491) was used (National Institute of Standards and Technology, Gaithersburg, MD, USA). Hexamethylbenzene used as injection standard was acquired initially as a solid of 99% purity (Aldrich Chemicals, Gillinghan and Dorset, USA). The organic solvents, dichloromethane (DCM), hexane and methanol (MeOH) (Dikma Co, Beijing, China) were re-distilled with a glass system. Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) (Wushi Chemicals Inc, Shanghai, China) were extracted for 72 h with a mixture of DCM and MeOH at the volume ratio of 93:7 by Soxhlet extractors. Upon drying under room temperature conditions, silica gel and alumina were baked at 130 and 250 °C for 12 h, respectively. Anhydrous sodium sulfate (Guangzhou Chemicals Inc, Guangzhou, China) was baked at 450 °C for 4 h and stored in sealed containers before use.

2.3. Sample extraction and fractionation

The PAHs in each sample were isolated and separated into four fractions: (F1) extractable PAHs in solvent soluble organic matter; (F2) PAHs in humic acids; (F3) PAHs in crude humin; and (F4) PAHs in organic-C enriched humin.

Fig. 1 shows the detailed experiment procedure. The first step was Soxhlet extraction: 15.00 g of samples were Soxhlet extracted with DCM for 72 h. Activated Cu was added for desulfurization. The extract was concentrated and solvent-exchanged to hexane, and then reduced to about 1 mL under gentle nitrogen flow. Then the extract was spiked with surrogate standards and separated on a 1:2 alumina/silica gel glass column. The first fraction containing aliphatic hydrocarbons was eluted with 15 mL of hexane. The second fraction containing PAHs was eluted with 5 mL hexane and 70 mL mixture of DCM:hexane (3:7 by volume). The second fraction was collected and concentrated under gentle N_2 flow. A known quantity of injection standard was added to the sample before instrumental analysis.

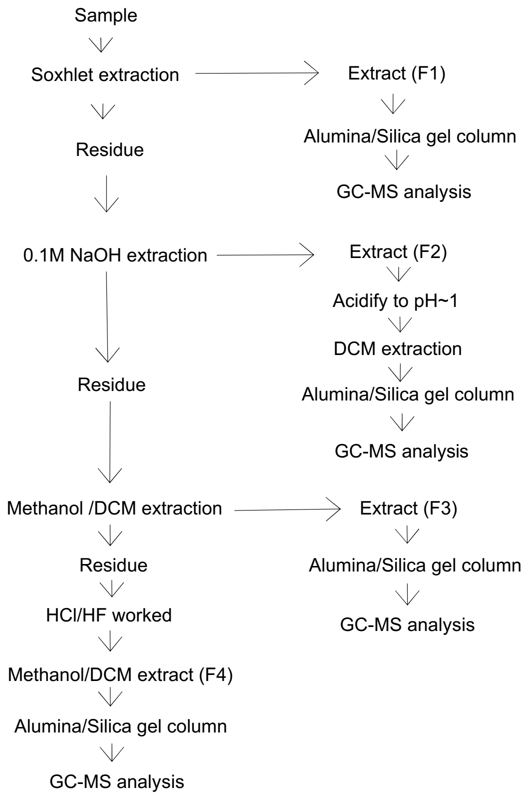

Fig. 1. Experimental protocol in this study. Respectively, F1, F2, F3 and F4 are PAHs in solvent soluble organic matter, PAHs in humic acids, PAHs in crude humin and PAHs in organic-C enriched humin.

After Soxhlet extraction, 100 mL of 0.1 M NaOH was added to the soil and sediment samples. The mixture was shaken vigorously on a shaking bed for 12 h and then centrifuged at 1870 g for 20 min, and the supernatant collected. This procedure was repeated 3–4 times until the supernatant was colorless. The combined supernatant was acidified to pH ∼ 1 using the solution of 6 M HCl. To extract PAHs in humic acid (HA), 100 mL of DCM and surrogate standards were added to the suspension. The whole mixture was shaken vigorously for 30 min and then left to stand for 1 h, and DCM collected. The suspension was extracted for 3–4 times until it was colorless in DCM. The combined extract was separated into two fractions by column chromatography using the same method as the first step and then PAHs in HA were obtained.

The residue soil and sediment samples were defined as crude humin (Wang and Xing, 2005). Methanol (100 mL) was added, and was shaken for 30 min. The mixture was loaded in an ultrasonic bath for 1 h and then centrifuged at 1870 g for 20 min, and the methanol collected. Then the successional extractions were carried out with 100 mL methanol:DCM (1:1 by volume), 100 mL DCM and 100 mL DCM step by step. Each time the mixture was centrifuged, the extract was collected and combined into a flask. Total extract was spiked with surrogate standards and 250 mL distilled water was added. The mixture was shaken and settled. The DCM was collected. This process was repeated three times and extract was fractioned into aliphatics and aromatics using the same method as above and PAHs in crude humin were obtained.

The residues were treated with HCl and HF to remove the dominant mineral matrix of the crude humin. The crude humin was first treated with 6 M HCl for 12 h. After centrifuged (1870 g) for 30 min, the supernatant was collected and the sample was treated with HF:HCl (1:1) for 12 h. Then the sample was centrifuged (1870 g) and the supernatant was collected. The residue was rinsed with 2 M HCl three times. HCl solution was collected. After treatment by HCl and HF, the sample was defined as organic-C enriched humin (Wang and Xing, 2005) or kerogen (Song et al., 2002). The organic-C enriched humin was added to 100 mL methanol and shaken for 30 min. The mixture was loaded in an ultrasonic bath for 1 h and then centrifuged at 1870 g for 20 min, and the methanol collected. Then the mixtures were introduced in an ultrasonic bath and processed in the same way as described for the previous extraction step. Acid and organic solvent extract solution were combined and separated by separation funnel. The extract collected after three-time extraction with DCM was dried and fractioned into aliphatics and aromatics using the same method as above and PAHs in organic-C enriched humin were obtained.