Distribution patterns of polycyclic aromatic hydrocarbons among different organic carbon fractions of polluted agricultural soils

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ABSTRACT

Differences in the distribution patterns of polycyclic aromatic hydrocarbons (PAHs) among soil organic matter pools may influence PAH mobility and bioavailability in the soil. Here, we studied the distribution of 15 USEPA priority PAHs in soil light fractions (LF), heavy fractions (HF) and three additional organic matter fractions (loosely combined humus (H_1), stably combined humus (H_2) and tightly combined humus (H_3)) further separated from HF by fractionating the soil organo-mineral complexes. The contents of total PAHs in LF ranged from 51 676 to 618 651 µg kg^{-1}, far greater than in HF in which the range of values was 657 to 3869 µg kg^{-1}. Although the LF accounted for only 0.1 to 1.4% of the soil, they were associated with 17.9 to 64.1% of the PAHs present. The PAHs in HF were mainly associated with H_3, ranging from 80.8 to 92.7% of the total amount of PAHs. The degree of enrichment of the different organic matter fractions decreased in the order of LF>H_3>H_2>H_1. The environmental risks of PAHs associated with different organic matter fractions are also discussed.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants and are products of the combustion of carbon-based materials. This class of organic contaminants is important environmentally because some of them have been demonstrated to cause mutations and certain types of cancer (Enzminger, 1987; Harvey, 1991). The contents of PAHs derived from the combustion of fossil fuels in agricultural soils have increased in the last century because of continued development of urbanization and industrialization (Jones et al., 1989).

The fate and behavior of organic pollutants in soils are controlled mainly by their interactions with soil components. Both soil organic matter (SOM) and clay minerals can contribute greatly to the sorption of PAHs in soils (Hwang and Cutright, 2003) and the SOM is often the principal sorbent under hydrated conditions (Chiou, 1989; Hassett and Banwart, 1989).

Soil organic matter is present in either a mineral-free form which includes partly decomposed plant material and microbial biomass, or as an organo-mineral complex in which the organic material may be adsorbed onto mineral surfaces or sequestered within micro-aggregates (Sollins et al., 1983). The mineral-free material is less dense than the organo-mineral fractions and can be separated by flotation in organic and inorganic solutions of varying density (Turchenek and Oades, 1974; Spycher and Young, 1977).

Greenland and Ford (1964) termed the light fraction (LF) 'mineral-free materials', with a specific density <2.0 g cm^{-3}, and the organo-mineral complexes comprised the heavy fraction (HF). The mineral-free materials (or LF) are enriched in carbohydrates but the origins of the carbohydrates are not distinct (Dalal and Henry, 1988). The LF is generally thought to have a rapid turnover whereas the HF remains as a more recalcitrant fraction (Janzen et al., 1992; Ellert and Gregorich, 1995). Kanazawa and Filip (1986) concluded that more than 50% of microbial populations and enzyme activities occur in the LF. On the basis of studies using substrate induced respiration (SIR), Hassink (1995) suggested that the microbial biomass in the LF represents the active (i.e. not physically protected) microbial biomass. Studies with isotopic tracers indicate that LF organic matter has a faster turnover rate than HF (Gregorich et al., 1995), although the LF may be partitioned into pools with different turnover rates (Bonde et al., 1992). Fu (1985) suggested that the organic matter in soil HF might be further divided into three fractions, namely the loosely combined humus (H_1) firstly extracted with 0.1 mol L^{-1} NaOH, the stably combined humus (H_2) sequentially extracted with a 0.1 mol L^{-1} NaOH + 0.1 mol L^{-1} Na$_4$P$_2$O$_7$ mixture from soil, and the tightly combined humus (H_3) remaining in the soil residue. Xu and Yuan (1995) reported that the loosely combined humus was mainly associated with Fe and Al cations and the stably combined humus mainly with Ca^{2+} cations. The structural characteristics of different combined humus materials are different. For example, Schnitzer and Schuppli (1988) reported that the soil humic acids (HAs) extracted by 0.1 mol L^{-1}

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$Na_4P_2O_7$ solution tended to be more aromatic than HAs extracted by 0.5 mol L^{-1} NaOH solution as determined using ^{13}C CP/MAS NMR.

Organic pollutants in soils, and hydrophobic organic pollutants (HOCs) especially, are always associated with organic matter. PAHs and their metabolites have also been found covalently linked to ma-cromolecular soil organic matter (Richnow et al., 1997; Käcker et al., 2002) and only the turnover of the soil organic matter will lead to the mineralization of the PAHs. Hence, the bioavailability of PAHs bound with different soil organic matter fractions may be different. The degradability of PAHs is generally high when they bond with the biologically active organic matter fractions and their environmental risk is also very high. So far, numerous studies have focused on highly condensed organic matter such as black carbon (BC), kerogen carbon (KC) and aged organic matter (e.g. humin) which represent a pool of hard organic matter showing high K_{OC} values for PAHs (Xiao et al., 2004; Ran et al., 2007a,b; Pan et al., 2006). The results have shown that these highly condensed organic materials play a dominant role in the overall sorption for PAHs in bulk soil and sediment samples and are expected to be the most important soil components affecting the bioavailability and ultimate fate of HOCs.

Dissolved organic matter (DOM) represents the most active or-ganic carbon fraction in soils. Totsche et al. (1997) reported that DOM can enhance the retention of PAHs in soils. However, Gao et al. (2007) found that the presence of inherent DOM in soils impeded phe-nanthrene sorption. On the other hand, the influence of exotic DOM on phenanthrene sorption was related to DOM concentrations. Low exo-tic DOM concentrations (≤28 mg DOC/L) promoted phenanthrene sorption. In contrast, higher concentrations (≥52 mg DOC/L) of added exotic DOM clearly impeded phenanthrene sorption.

Several studies have focused on the distribution of PAHs in soil fractions according to physical and chemical fractionation methods. The concentrations of 20 PAHs and 12 PCBs in soil density fractions decreased in the order light (<2.0 g cm^{-3}) > medium (2.0–2.4 g cm^{-3}) > heavy fraction (>2.4 g cm^{-3}) (Krauss and Wilcke, 2005). The average sum of the concentrations of 20 PAHs in particle-size separates of 10 urban surface soils decreased in the order silt > clay > fine sand > coarse sand (Müller et al., 2000). Nam and Kim (2002) reported that about 90–93% of added phenanthrene was recovered from the humin-mineral fraction of Lima loam whereas less than 12% was found in humic and fulvic acids of the same soil after aging of phenanthrene for 1, 7 and 100 days. However, there has been little investigation on the distribution of PAHs in soil LF, HF and three additional organic mat-ter fractions (H_1, H_2 and H_3) associated with minerals through different bridge cations in HF. The objectives of the present study were therefore (i) to examine the distribution patterns of PAHs in different soil organic matter fractions of polluted agricultural soils and (ii) to assess the bioavailability and environmental risks of PAHs according to the turnover rates of the different organic matter frac-tions in the soils.

2. Materials and methods

2.1. Soil samples

Nine soil samples (0–20 cm depth) were collected from arable land in Wuxi district, Jiangsu province, east China. The soils are classified as Albic Fe-leachi-Stagnic Anthrosols. The climate is subtropical monsoon with four distinct seasons. Annual average temperatures range from 16 °C to 18 °C and annual average rainfall ranges from 800 to 1600 mm. Paddy fields represent the predominant land use in this region to-gether with cultivated dry land, woods and scrub and wasteland. Many town and village enterprises such as smelting plants, paper mills, gas stations and wiring disassembly factories are located in the rural areas. Energy used in many of these plants is generated from coal, leading to substantial environmental degradation if the gases and wastes are discharged without appropriate treatment. In fact, most plants are

ill equipped, with no treatment systems due to shortage of funds or a deliberate avoidance of environmental protection measures. In addition, crop straw has been replaced as a domestic fuel by fossil fuels in some more economically developed regions, and most crop residues are burned in the open air after the crops are harvested. As a result, all of these are potential sources of contamination with PAHs. The total area from which soil samples were collected was about 4 km^2. Fresh soil samples were stored under ice and transported to the laboratory on the day of collection for pretreatment. Field moist soils were sieved to <2 mm and large pieces of plant residues and soil animals were removed. Then all the soil samples were freeze-dried for PAH analysis, soil fractionation and determination of physico-chemical properties. Soil land use history and some physico-chemical properties are shown in Table 1.

2.2. Soil physical and chemical analyses

Soil pH (soil:H_2O = 1:2) was measured using a pH meter with a glass electrode. Soil total organic C (TOC) and 'total' N (TN) were determined by dichromate oxidation (Nelson and Sommers, 1982) and Kjeldahl digestion (Bremner and Mulvaney, 1982), respectively.

2.3. Soil organic matter fractionation

Soil organic matter was separated by density into LF and HF following the procedure of Spycher et al. (1983). Briefly, 30 g of freeze-dried soil (<2 mm) was weighed into a 200-mL Teflon centrifuge tube and 100 mL zinc bromide ($ZnBr_2$) (density ~1.8 g cm^{-3}) liquid solution was added to the tube. The mixture was placed on a rotary shaker for 60 min. After dispersion, the suspension was centrifuged at 2500 rpm for 10 min. The suspended light fraction (LF) was decanted and transferred to a pre-weighed Whatman No. 1 filter paper pre-extracted with dichloromethane, and rinsed thoroughly with distilled, deionized water. The soil remaining in the centrifuge tube was re-suspended after adding a further 100 mL $ZnBr_2$ and the procedure was repeated to obtain a second aliquot of LF. The two aliquots of LF were combined, freeze-dried and weighed to obtain the LF dry weight. The soil remaining in the centrifuge tube (HF) was rinsed several times to remove $ZnBr_2$ by mixing with distilled, deionized water, and then freeze-dried for the separation of combined humus.

The HF obtained were further fractionated into loosely (H_1), stably (H_2) and tightly (H_3) combined humus according to the method described by Fu (1985) with some modifications. In brief, 10 g HF soils were weighed into 200-mL Teflon centrifuge tubes and 120 mL 0.1 mol L^{-1} NaOH was added to each tube. The mixtures were shaken overnight on a rotary shaker (200 rpm) at 25 °C. The supernatant was separated from the residual soil solids by centrifugation (12 000 rpm for 15 min). The supernatant was stored in a brown glass bottle. The procedure of the extraction with 120 mL 0.1 mol L^{-1} NaOH was repeated 4–5 times until the supernatant was clear. All the supernatant was combined to give H_1. Then the 100 mL 0.1 mol L^{-1} NaOH + 0.1 mol L^{-1} $Na_4P_2O_7$ mixture was

Table 1
Land use and some selected properties of the tested soils

Soil	Crop	pH (H_2O)	TOC	TN	Total PAHs (µg kg^{-1})
			(g kg^1)		
AZ-01	Wheat	5.3	16.0	1.63	2491
AZ-02	Wheat	6.2	15.9	1.60	1753
AZ-03	Vegetables	4.4	14.0	1.37	9500
AZ-04	Vegetables	6.7	18.7	1.91	3165
AZ-05	Vegetables	7.8	15.0	1.68	5441
AZ-06	Rice paddy	5.4	18.1	1.69	5579
AZ-07	Rice paddy	5.3	17.7	1.61	1338
AZ-08	Rice paddy	5.9	18.5	1.80	1058
AZ-09	Uncultivated	4.8	17.0	1.94	2436