



Association of 16 priority polycyclic aromatic hydrocarbons with humic acid and humin fractions in a peat soil and implications for their long-term retention[☆]



Weixiao Chen^a, Hui Wang^{a, b}, Qian Gao^a, Yin Chen^a, Senlin Li^a, Yu Yang^c, David Werner^d, Shu Tao^a, Xilong Wang^{a, *}

^a Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

^b China Institute of Water Resources and Hydropower Research, Beijing 100038, China

^c Department of Civil and Environmental Engineering, University of Nevada, Reno, NV 89557, USA

^d School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne, UK

ARTICLE INFO

Article history:

Received 11 May 2017

Received in revised form

12 July 2017

Accepted 13 July 2017

Available online 20 July 2017

Keywords:

PAHs

Humic acid

Humin

Soil

Retention

ABSTRACT

To elucidate the environmental fate of polycyclic aromatic hydrocarbons (PAHs) once released into soil, sixteen humic acids (HAs) and one humin (HM) fractions were sequentially extracted from a peat soil, and sixteen priority PAHs in these humic substances (HSs) were analyzed. It was found that the total concentration of 16 PAHs ($\sum 16\text{PAHs}$) increased evidently from HA1 to HA16, and then dramatically reached the highest value in HM. The trend of $\sum 16\text{PAHs}$ in HAs relates to surface carbon and C-H/C-C contents, the bulk aliphatic carbon content and aliphaticity, as well as the condensation enhancement of carbon domains, which were derived from elemental composition, XPS, ¹³C NMR, as well as thermal analyses. HM was identified to be the dominant sink of 16 PAHs retention in soil, due to its aliphatic carbon-rich chemical composition and the highly condensed physical makeup of its carbon domains. This study highlights the joint roles of the physical and chemical properties of HSs in retention of PAHs in soil and the associated mechanisms; the results are of significance for PAH-polluted soil risk assessment and remediation.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic contaminants containing two or more fused benzene rings; they are ubiquitous in the environment. Due to the recalcitrant properties of PAHs, some of which are potentially mutagenic/carcinogenic, sixteen members in this group have been listed as priority pollutants by the United States Environmental Protection Agency (US EPA). The PAH pollution in soil (Wang et al., 2015), sediments (Luo et al., 2006), sludge (Shen et al., 2007), airborne particles (Wei et al., 2015), and water (Hong et al., 2016) has been investigated worldwide. Among all these environmental compartments, soil was viewed as a remarkable sink for PAHs from diverse sources such as direct emissions, aerosol dust deposition and wastewater

irrigation (Chen et al., 2005; Demircioglu et al., 2011). As reported, very high concentrations of PAHs in soils in China were detected in the areas with rapid economic development, e.g., Yangtze River Delta, Pearl River Estuary region and Beijing (Ma et al., 2008; Peng et al., 2011; Wang et al., 2015). In particular, the average surface soil PAH concentrations from Shanghai and Nanjing reached as high as 3780 and 1680 ng/g dry soil; they were classified into the heavy contamination group according to the criteria proposed by Maliszewska-Kordybach (1996), and they apparently exceeded the soil target value for PAHs presented in the “New Dutch List (2000)”; it is the most commonly used soil quality standard issued by the Ministry of Housing, Department of Soil Protection of Netherlands. In the “New Dutch List”, the target values are set up to fully restore the functional properties of the soil for humans, plants and animals. A total concentration of 1 μg/g for 10 PAHs is set as the target value for this group of chemicals in soils. Unfortunately, up to date, such a criterion for 16 priority PAHs in soil is not available in China. Such a high level of PAHs in soils may pose severe health risks to exposed human beings via food consumption, as crops grown on PAH-

[☆] This paper has been recommended for acceptance by B. Nowack.

* Corresponding author.

E-mail address: xilong@pku.edu.cn (X. Wang).

contaminated soils have been demonstrated to accumulate a certain amount of these contaminants (Khan and Cao, 2011). Jiang et al. (2011) revealed that the total BaPeq (toxic equivalent data based on benzo[*a*]pyrene) values of ten Dutch target PAHs in 72% agricultural soil samples from Shanghai were higher than their reference total carcinogenic potency. It is thus of great significance and indispensable to examine the mechanisms on how these compounds are retained in soil and which soil compartment/fraction/constituent is their predominant sink.

It has been widely accepted that a remarkable proportion of hydrophobic organic compounds (HOCs) including PAHs that entered into soil would tightly associate with the soil aggregates and persist in soil, also referred to as the aging or sequestration phenomenon (Luo et al., 2012). The two most widely accepted mechanisms accounting for this include strong association with soil organic matter (SOM), especially with a portion of its constituents: the carbonaceous components such as combustion-derived black carbon (BC) including soot, tar, chars, and penetration into tiny pores in soil matrix created by SOMs and minerals (Cornelissen et al., 2005; Koelmans et al., 2006). It was found that SOMs were the predominant sorption domains for HOCs in soils and the sequestration levels of persistent organic pollutants in soils were usually positively correlated with their SOM contents (Nam et al., 1998; Yang et al., 2010). Humic substances (HSs) including humic acid (HA) and humin (HM) were major carbon-containing components in SOMs; they were demonstrated to have considerable high sorption capacity for HOCs due to their abundant hydrophobic carbon domains including macromolecular aliphatic chains and aromatic carbon components as well as significant amount of small pores, which facilitated retention of HOCs in soils (Zhang et al., 2009; Nam and Kim, 2002). Based upon these, sorption mechanisms of PAHs to SOMs and HSs have been widely investigated (Chefetz et al., 2000; Salloum et al., 2002). Limited by water solubility of the organic chemicals, most of the previous studies on sorption generally worked with the PAHs with relatively low molecular weights (LMW-PAHs), such as naphthalene (Gunasekara and Xing, 2003), phenanthrene (Kang and Xing, 2005; Wang et al., 2011; Zhang et al., 2010), and pyrene (Pan et al., 2006). Few high molecular weight PAHs (HMW-PAHs) were examined, aside from benzo[*a*]pyrene investigated by Zhang et al. (2009), while HMW-PAHs are more toxic and persistent than those with lower molecular weights (Kanaly and Harayama, 2000). However, the sorption process illustrated in these studies is totally different from the retention behavior we discuss in the current work. Because sorption experiments mainly focus on the process that the sorbate goes to the sorbent from the aqueous phase in a relatively short term (so called equilibrium time), while the released pollutants retained in soil may undergo complex environmental processes in a long term (such as biodegradation, evaporation, and leaching, etc.), which in turn would affect their binding with various soil components. A specific compound with high sorption capacity or affinity to soil or its HSs observed in the sorption experiments does not mean it will have strong association with the sorbent in the natural conditions. Hence, sorption experiments with PAHs added as spiked chemicals to HSs isolated from soil may not fully elucidate how PAHs are retained and sequestered in soil.

Aside from sorption experiments using LMW-PAHs as sorbates and soils/HSs as sorbents, endeavor had also been made to further study how PAHs were retained in the soil matrix; field-contaminated soils with historic PAHs were investigated. Industrially impacted soils were reported to be separated into different grain size and density fractions and PAHs concentrations in each fraction were measured (Ahn et al., 2005; Yang et al., 2008); scientists tried to figure out PAHs in soil would tend to associate with which types of carbonaceous particles. However, to the best of our

knowledge, no study was performed to fractionate a field-contaminated soil sample into many different natural organic matter fractions (particularly, humic acid and humin) to identify the predominant retention domain of historic PAHs in the intact soil matrix without undergoing any artificial interference. All prior work with fractions of natural organic matter was done earlier by spiking PAHs on soil aggregate to investigate their aging procedures (Doick et al., 2005; Nam and Kim, 2002). However, when the studied soil is spiked with the organic compounds of interest, its physicochemical properties (e.g., aggregate structure) and the soil matrix association of the organic compounds are very different from soils which have sorbed the organic compounds in the natural environment. Hence, it is necessary to analyze the retention behavior of PAHs in different HS fractions in naturally contaminated soils, which would provide more realistic information on their environmental fate.

As a first attempt to address this knowledge gap, the objectives of this study are to find out which soil HS fraction is the major sequestration sink for PAHs after they are naturally introduced to soil, and to unveil the underlying mechanisms. To achieve our research aim, sixteen HAs and one HM fractions were sequentially isolated from a peat soil, then concentrations of 16 priority PAHs in these HS fractions and the bulk soil were measured. Different from the abovementioned studies using HSs as sorbents in sorption experiments (Kang and Xing, 2005; Wang et al., 2011) and studies in which HSs were extracted from the PAH-spiked soil samples (Guthrie et al., 1999; Nam and Kim, 2002), or studies in which the soil samples naturally contaminated by PAHs were separated into different grain size and density fractions (Ahn et al., 2005; Yang et al., 2008), 16 priority PAHs including HMW-PAHs (4–6 rings) studied in the present study were naturally introduced, distributed and sequestered in soil and they were determined in different SOM fractions derived from the soil. Based on these innovations, the results of this study would improve understanding of the environmental fate of PAHs in soil, and provide theoretical and practical information for PAH-polluted soil risk assessment and remediation on a global scale.

2. Materials and methods

2.1. Sequentially extracted soil humic substance fractions

A peat soil was collected from a wetland in Sanjiang Plain, Jilin Province, Northeast China (Guo et al., 2017). This plain is one of the key grain production bases in China. A high SOM content of this soil made it suitable for extensive HS extraction and the moderate PAH contamination level may help generalize the scientific findings to severer or lighter pollution situation. It was air-dried and ground to pass through a 20-mesh sieve. A total of 2 kg soil was used to extract HA and HM at a solid-to-liquid ratio of 1 g/10 mL. Sixteen HA fractions (named HA1-HA16) were progressively extracted ten times first with 0.1 M Na₄P₂O₇ + 0.1 M NaOH and then six times with 0.2 M NaOH; the residue remaining after HA extraction was collected as HM. A high resolution fractionation procedure was applied to acquire more thoroughly-differentiated HA fractions and a HM residue. Details for purification of HSs are described elsewhere (Gunasekara and Xing, 2003). The HAs, HM, and the bulk soil were air-dried, ground to pass through a 70-mesh sieve and stored in a freezer (4 °C) for further experiments.

2.2. Pretreatment and instrumental analysis for determination of PAHs

The priority 16 PAHs were extracted and their concentrations were measured (The names and abbreviations of 16 PAHs are listed

Download English Version:

<https://daneshyari.com/en/article/5748732>

Download Persian Version:

<https://daneshyari.com/article/5748732>

[Daneshyari.com](https://daneshyari.com)