Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Soils of Liaohe Estuarine Wetland

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Abstract: Present study was undertaken to determine the level of PAHs contamination in soils of Liaohe estuarine wetland. Identification and quantification of 16 priority PAHs collected from 31 surface soil samples (0~20 cm) in October 2008 were determined by gas chromatography (GC). The sum of 16 PAHs ranged from 704.7 μg/kg to 1804.5 μg/kg with an average value of 1001.9 μg/kg. The toxic equivalency factors (TEFs) were used to estimate benzo[a]pyrene equivalent concentration (BaP_{eq}). The values in all sites surpassed the Dutch target value. Therewith, quite a part of soils in the wetland were subjected to potential ecological risks.

Keywords: PAHs; Soil; Liaohe estuarine wetland; Benzo[a]pyrene equivalent; Risk assessment

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs), as priority pollutants of the US Environmental Protection Agency (US EPA), are a class of semivolatile persistent organic pollutants with strong toxic, carcinogenic, and mutagenic characteristics even at low concentrations. PAHs are made up of carbon and hydrogen with at least two fused benzene rings arranged in linear, cluster, or angular arrangements [1]. PAHs have grasped much attention due to their carcinogenic potential and ubiquitous presence in the environment [2]. Most of their emissions have been estimated to be anthropogenic, mainly including pyrolitic processes, such as the incomplete combustion processes involving carbon fuels and materials. Due to their ubiquity and persistence, soil ecosystem is a major reservoir.

Wetland is one of the most valuable and productive ecosystem. Nowadays, the function of wetland is continuously in the degradation status. PAHs present in soil not only create a risk to humans, but they may also exhibit a toxic activity towards different biological elements of the soil environment such as plants and microorganisms [3]. Analyzing ecological risk of polluted wetland is crucial for protecting of human health and environment security. The development and the establishment of a toxicity equivalency factor (TEF) are used in the assessment of mixtures containing PAHs [4]. Since BaP is well characterised toxicologically, where as comparatively less information is available for most of the other PAHs[5], the risks of PAHs have often been calculated on the basis of BaP concentration.

In this study, we conducted a detailed study of surface soils of PAHs in Liaohe estuarine wetland. 16 priority PAHs were measured and their risk was evaluated by considering the appropriate TEF. The purpose of this study is to evaluate the contamination status of PAHs, and to make risk assessment of PAHs in the examined area. The database obtained from this study will be important in offering scientific evidences for the bioremediation and management of Liaohe estuarine wetland.

2 Materials and methods

2.1 Sample collection

Surface soil samples from 31 sampling sites, distributed in 5 different districts were carried out in October 2008. The location of sampling sites is given in Figure 1. Among the 31 soil samples, 5 samples were from salina wetland area, 7 samples from Suaeda heteroptera degraded area（LH1、LH4～LH6、LH29～LH31）, 13 samples from reed field area（LH10～LH13、LH17～LH25）, 3 samples from reed degraded area（LH14～LH16）and 3 samples from reed field oil well area（LH26～LH28）. For each sampling site, 3 subsamples were taken from the same area, and mixed thoroughly to form one composite sample. Samples were taken with the help of a stainless steel auger after removal of the uppermost soil layer up to a depth of 20 cm. All the samples were sealed in polythene bags, transported to the laboratory and preserved at 4℃ until

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the moment of their analysis. In the laboratory, the samples were air dried. Soil samples were sieved through a 100 mesh stainless steel screen after removing stones and residual roots. Representative samples were obtained after coning and quartering and kept in the precombusted amber glass jar.

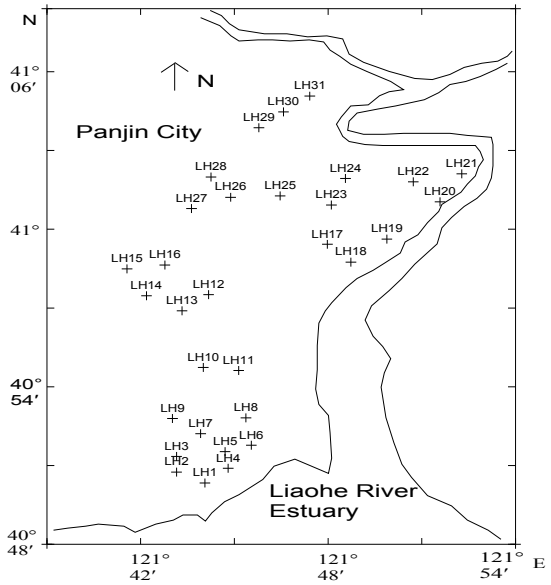

Figure 1. Sampling sites of soils in Liaohe estuarine wetland

2.2 Chemicals

Standard mixture containing 16 PAHs (16 compounds specified in USEPA method 610) and deuterated PAHs internal standard (IS) mixture (naphthalene-d8; acenaphthene-d10; phenanthrene-d10 and chrysene-d12) were procured from Supelco (Bellefonte, PA, USA). All solvents (dichloromethane, n-hexane, etc.) used for sample processing and analysis, were of GC grade.

2.3 Sample extraction and clean-up

Soil samples were extracted by ultrasonication, a method developed and recommended by various authors [6-8]. Soil sample (2.0 g) was mixed with 2.0 g anhydrous sodium sulfate, extracted twice with 20 mL n-hexane/ dichloromethane (1:1 v/v) and 0.5 g activated Cu for 20 min by ultrasonic, and then kept standing for 0.5 h. Both the extracts were subsequently mixed and concentrated to 1.0 mL by rotary vacuum evaporation. The concentrated extracts were cleaned up by a silica gel column. Before use, some of n-hexane was added to for degassing. The 20 cm silica gel column was packed from the bottom with glass wool, 1 cm anhydrous sodium sulfate, 12 cm activated silica, 6 cm neutral alumina, followed by 1 cm anhydrous sodium sulfate. Concentrated sample extract was poured over the packed column. After transferred the sample extract, the column was eluted with little of n-hexane and 30 mL dichloromethane / n-hexane (3:7 v/v). The first fraction containing n-alkanes was discarded, and the second fraction containing PAHs was collected. The extract was transferred to a rotary evaporator and preconcentrated to a volume of 1 mL; it was then eluted with n-hexane three times and concentrated to 1 mL under a gentle N_2 stream before GC analysis.

2.4 GC analysis

Quantitative analysis of the soil extracts was carried out by GC. All the samples were analyzed on a Shimadzu 2010 series GC equipped with FID and SPB-5 capillary column (30 m × 0.32 mm i.d. with 0.25 μm film thicknesses). The GC conditions for analysis were as follows: the injection port was set at 250 °C; splitless injection of 1 μL of sample was conducted using autosampler. Column initial temperature started at 80 °C and held for 1 min, followed by an increase to 255 °C at 15 °C /min with a holding time of 1 min,increased at a rate of 1 °C /min to 265 °C, held for 1 min and raised to 295 °C at 2.5 °C /min and held for 5 min. Helium/air was used as the carrier gas at a flow of 1.1 mL/min.

3 Results and discussion

3.1 Total PAHs content

US EPA has identified 16 unsubstituted PAHs as priority pollutants, inculding naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3,cd)pyrene (Ind), dibenzo(a,h)anthracene (DBA), and benzo(g,h,i)perylene (Bpe). The 16 target PAHs were detected in all soil samples. All the concentrations were calculated on the base of dry weight unless special mention. To simplify the overview results from this paper, the total concentrations of 16 PAHs in soil samples at different sampling sites were briefly summarized, as shown in Figure 2. Total PAHs concentrations in the examined area varied from 704.7 μg/kg (at site LH1) to 1804.5 μg/kg (at site LH26) with a mean value of 1001.9 μg/kg. Moreover, BaP, one of the most potent carcinogenic PAHs, varied from 28.3 μg/kg to 52.4 μg/kg with an average of 37.7 μg/kg. Concentration of Bap observed in the present study was found to be higher as compared to the Dutch target value (25 μg/kg). The higher concentrations of the total PAHs (>1400 μg/kg) were detected in soil samples at site LH26, LH27, and LH28. These sites were located in reed field oil well area, which might be heavily polluted by oil. The lower concentrations (<800 μg/kg) were observed in soil samples at site LH1, LH2, LH4 and LH7. At all the sites,

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Nap was the predominant compounds. Table 1 compares the results of the present study with PAHs concentrations

Table 1. Concentrations of PAHs (μg/kg) compiled from literature

Study area	Number of PAHs	Total PAHs Concentration	Average Concentration	Reference
Elizabeth River Wetlands	16	1200～22200	—	[9]
Arable Soil in Poland	16	80～7264	395	[10]
New Orlenans	16	647～40692	3731	[11]
Baiyangdian Area	16	146～645.9	417.4	[12]
The Yellow River Delta	16	27.45～128.97	71.1	[13]
Surface soil of Shanghai	16	203.8～6753.9	1172.7	[14]
Liaohe Estuarine Wetland	16	704.7～1804.5	1001.9	Present study

measured in other locations worldwide. PAHs average concentration observed in the present study was found to be higher than arable soil in Poland [10], soil of Baiyangdian area [12], the northern wetland of the yellow river delta [13], but lower than New Orleans soils and sediments [11], surface soil of north suburban Shanghai [14].

The concentration of PAHs in soils is not yet regulated in China, and only a few recommendations or guidelines exist worldwide. The concentration of about 100 μg/kg is typical in the areas where no anthropogenic pollution sources occur [6]. Also it has been suggested [15] that the typical endogenous PAHs in soil, resulting from plant synthesis and natural fires is in the range of 1～10 μg/kg. It can be concluded that soils from Liaohe estuarine wetland are contaminated above the natural level. PAHs concentrations were compared with Dutch (20～50 μg/kg) and Polish standards (200～10,000 μg/kg) [16]. Comparison suggested that total PAHs concentration in soils exceeds the Dutch standard by two orders in magnitude. According to Polish standards, site LH14, LH18, LH19, LH22～LH31 can be classified under pollution class III, i.e. polluted (1000–5000, pollution class III).

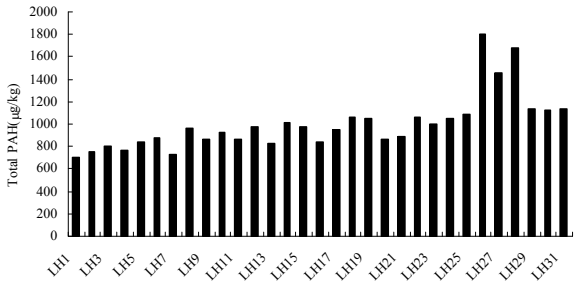

Figure 2. The total concentrations of PAHs in the sampling sites

3.2 Risk assessment

The development and the establishment of a TEF are used in the assessment of different classes of toxic PAHs mixtures. BaP is the only PAHs for which toxicological data are sufficient for derivation of carcinogenic PAHs [17]. In the present study, TEFs were used to quantify the risk of other PAHs relative to BaP and to estimate BaP_{eq}. In order to compare the risk associated with the total PAHs concentrations at examined sites, the sum of each individual Bap_{eq} (i.e., total Bap_{eq}) was used as a surrogate indicator. To date, several proposals for TEFs are available[18-21]. The list of TEFs compiled by Tsai et al. was adopted in this study[21].The calculated TEF_s for Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, Bap, Ind, DBA , Bpe are 0.001, 0.001, 0.001, 0.001, 0.001, 0.01, 0.001, 0.001, 0.1, 0.01,0.1,0.1,1,0.1,1 and 0.01 respectively. The total BaP_{eq} was calculated as:

$$\text{Total } BaP_{eq} = \sum C_i \times \ TEF_i$$

where C_i is the concentration of individual PAHs and TEF_i is the corresponding toxic equivalency factor.

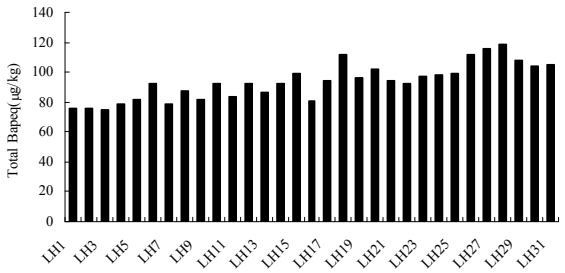

Figure 3. The value of Bap_{eq} of PAHs in the sampling sites

In this study, the total PAHs BaP_{eq} in different functional groups showed in Figure 3. BaP_{eq} values calculated for soil samples in this study varied from 74.8 μg/kg to 118.3 μg/kg, with an average of 93.6 μg/kg. The total Bap_{eq} was found to be maximum value at site LH28,

followed by the 116.0 μg/kg and 112.0 μg/kg at site LH27 and LH26. This is due to the higher concentration of PAHs species having a higher carcinogenic potency at these sites. Site LH3, LH2 and LH1 had the lowest average concentrations of 74.8, 75.4 and 75.7 μg/kg, respectively. The mean value (93.6 μg/kg) in soils of Liaohe estuarine wetland was lower than those in surface soils of Agra, India (650 μg/kg–BaP_{eq})[22], soil around airport in India (1021 μg/kg–BaP_{eq}) [8], soil from Tarragona County of Spain (124 μg/kg-BaP_{eq}) [23], roadside soil of Shanghai, China (892 μg/kg-BaP_{eq}) [24]. BaP is one of the most important PAHs in the carcinogenic group. In the soil samples BaP accounted for 40% of the total BaP_{eq} with only 3.8% of the total concentration. The reference total carcinogenic potency was calculated as a sum of multiplied Dutch target concentrations for unpolluted soil with appropriate Bap_{eq}. The toxicity and carcinogenetic of the investigated sites was estimated by comparing the total carcinogenic potency with reference once. The value were 2～4 times higher than the Dutch target value (32.96 μg/kg) , indicating the increased carcinogenic burden of soils from these sites. The result suggests that the carcinogenic potency of PAHs should be given more attention due to potential environmental risk in the study area. Therefore, PAHs contamination in Liaohe estuarine wetland should be further investigated because of strong potential carcinogenicity of high molecular weight PAHs, such as DBA and BaP.

4 Conclusions

PAHs concentrations in the study area varied from 704.7 μg/kg to 1804.5 μg/kg, remarkably higher than some found in a number of investigations from different regions and countries. The PAHs levels for all sites were higher than the target value set by Dutch government for unpolluted soil. It can be concluded that soils in Liaohe estuarine wetland are contaminated above the natural level. The risk assessment of the soils has been performed, taking as references the Dutch guidelines. 2～4 times higher carcinogenic potency of PAHs in soils is an indication of high degree of risk. Thus, appropriate remedial measures were required to minimize the adverse effects.

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