

Vertical distribution of polycyclic aromatic hydrocarbons (PAHs) in Hunpu wastewater-irrigated area in northeast China under different land use patterns

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Abstract The concentrations of polycyclic aromatic hydrocarbons (PAHs) were determined in ground-water and soil profiles from upland field and paddy field in the Hunpu wastewater-irrigated area of northeast China. In the study area, the peak concentrations of total PAHs were within or just below the topsoil, and the contents decline with depth at various trend verified by the Spearman's rank correlation test. The total PAH concentrations in upland soil layers ranged from 46.8 to 2,373.0 $\mu\text{g}/\text{kg}$ (dry wt.), while

the concentrations in paddy soil layers ranged from 23.1 to 1,179.1 $\mu\text{g}/\text{kg}$ (dry wt.). The 16 priority PAHs were all detected in the analyzed soil samples, and naphthalene (Nap), phenanthrene (Phe), fluoranthene (Fla), chrysene (Chr), and benzo[a]pyrene (Bap) were selected for further study in terms of their vertical distributions. The concentrations of both total and individual PAHs in upland soil were generally higher than those in the corresponding layers of paddy soil. The concentrations of total and individual PAH were notably different between the corresponding horizons in upland and paddy soil were probably attribute to the different sources and properties of the PAHs and soil; different methods of soil tillage and plant growing. Special PAH compound ratios, such as phenanthrene/anthracene, fluoranthene/pyrene, LMW/HMW, and parent PAH ratios (Ant/178, Fla/202, BaA/228, and IIP/276) were used to identify the source of soil PAHs. The data suggests that the possible sources of PAHs in the Hunpu wastewater-irrigation area are the incomplete combustion of coal, petroleum and crude oil, automobile exhausts. These sources lead to pollution of the soil and groundwater by wet/dry deposition and vertical downward migration.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are Persistent Organic Pollutants (POPs) that exist in nature and in human habitats. The United States Environmental Protection Agency (US EPA) has identified 16 PAHs as priority pollutants because they are acutely toxic, genotoxic, and carcinogenic (Baumann 1998; White et al. 1998). PAHs are formed as by-products of the incomplete combustion of organic materials and have been identified in many emission sources such as vehicle exhausts; power plants; chemical, coke, and oil-shale industries; and urban sewage. Soils are an important reservoir for PAHs (Ockenden et al. 2003). Both gaseous and particulate PAHs input to soil by wet/dry atmospheric deposition at over short and long distances (Tremolada et al. 1996; Park et al. 2000); there they accumulate mainly in the humus layer. The dissipation of PAHs is mostly attributed to biodegradation, while other pathways like volatilization, irreversible sorption, leaching and uptake by plants coexist in soil edatope (Reilley et al. 1996). PAHs are likely to be retained in soil for many years and may even enter the aquatic environment, inducing further hydrosphere pollution due to their hydrophobicity (Readman et al. 1984; Cousins et al. 1999).

Since the 1960s, wastewater has been used for agricultural irrigation in the Liaoning province of China as a solution to water shortages and disposal of urban sewage; this practice continued until 2002. The irrigated area had expanded to 8,900 folds over approximately 30 years of irrigation. Hunpu region is one of most spacious and typical wastewater irrigation area in Liaoning. Irrigation water supplied to the Hunpu farm was obtained from the mixing of water from Dahuofang Reservoir, the Hun River, and Xi River, which is badly contaminated by petroleum effluent and sanitary waste from city and heavy industry factories upstream. As a result of the application of contaminated water, the accumulation of multiple-source PAHs in the soil may lead to the contamination of vegetables and the food chains (Kipopoulou et al. 1999), thereby posing a great health risk to humans. The contamination of wastewater-irrigation by PAHs has been reported in several cities within China (Song et al. 1997; Tao et al. 2004; Wang et al. 2004); however, most of these studies focused on surface soil pollution (Aislabie et al. 1999), with little attention paid to the vertical dis-

tribution of PAHs (Cousins et al. 1999; Krauss et al. 2000). Furthermore, it has been demonstrated that various land-uses influence the distribution of PAHs in soil (Nam et al. 2003). Consequently, it is important to identify variations in the vertical distribution of PAHs associated with different land uses.

In this study, we compared the vertical distribution of PAHs in soil samples from upland and paddy fields contaminated by long-term irrigation with wastewater. In addition, groundwater samples collected close to the soil-sampling sites were analyzed to further explain the distribution of PAHs in the soil profiles (for this purpose, we optimized the extraction and quantification of representative PAHs from the soil). Possible sources of the PAHs were identified on the basis of specific PAH compound ratios.

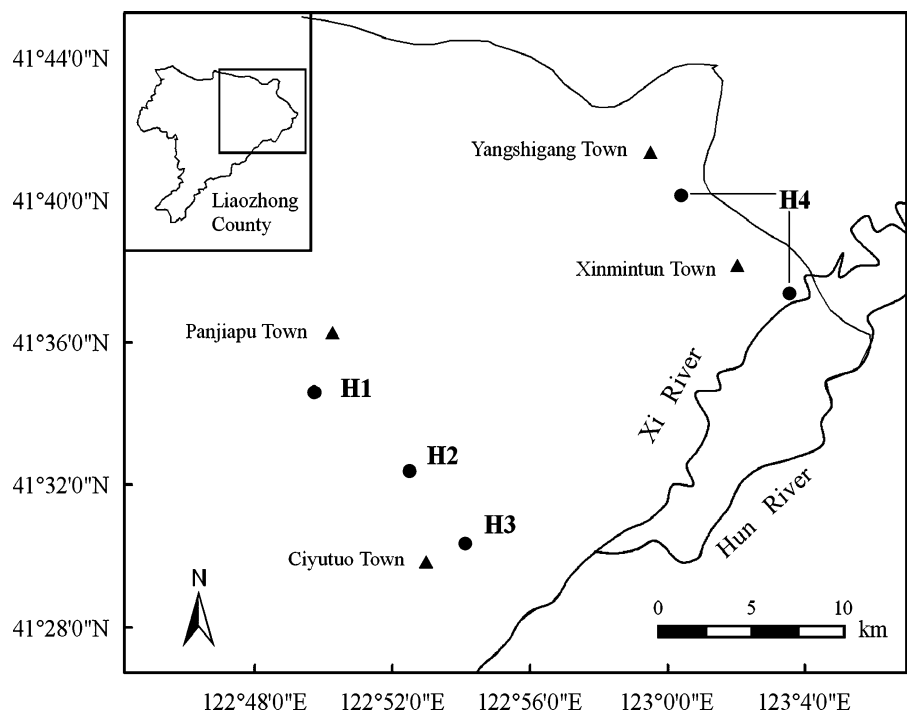
Materials and methods

Sample collection

Soil and groundwater samples were collected from the Hunpu wastewater-irrigation area of Liaozhong County, Liaoning Province, China (Fig. 1). Liaoning Province has a temperate continental monsoon climate with four distinct seasons, an average annual rainfall of 695 mm, and an annual mean temperature of 8.1°C. In summer, and wind direction was dominated in south, and lead in northwest in winter. The main soil types are black soil, according to the traditional soil genesis classification in China. Paddy fields and upland fields are the predominant land use in this region, although areas of tidal flat and marsh also exist. The study area was located at the southwest of the heavy industry city Liaoning, which including several paper mill, chemical plants and oil refineries, and at the north of the Liaoyang City which distributed some petroleum refineries.

In October 2005, after the harvesting of crops, soil samples were collected from profiles at eight sites (HP1, HU1, HP2, HU2, HP3, HU3, HP4, and HU4) that were located at least 100 m from the roadside (Fig. 1). All sites were selected according to the strike of the main channel which against to the Hun River, and every representative profile sample was mixed with five subsamples, which collected in 100×100 m² area at random. Ten horizon layers were identified for collection of the soil profile: 0–2, 2–5, 5–10, 10–15,

Fig. 1 Location of sampling sites in Hunpu wastewater-irrigation area. *H1* Location of the upland field site (HU1), paddy field site (HP1), and groundwater sampling station (G1); *H2* location of HU2, HP2, and G2; *H3* location of HU3, HP3, and G3; *H4* location of HU4 (in the south), HP4 (in the north), G4 (close to HU4), and G5 (close to HP4)



15–20, 20–25, 25–30, 30–40, 40–60, and 60–100 cm. Firstly, we flattened tops for accurate measurement with stainless steel spoon, and then cored a 100 cm depth column with a corer (30 cm i.d. × 100 cm). After it removed from the ground, the soil core was sliced into 10 layers (Cousins et al. 1999). All soil samples collected using a stainless steel scoop. Five groundwater samples (G1, G2, G3, G4, and G5) were collected from water supply well in the fields close to the soil sites (Zhang et al. 2007). Soil and groundwater were collected into pre-cleaned clean brown glass jars and stored in a cool box (4°C). On return to the laboratory, the soil sample were capped and kept in the dark at –20°C and water samples stored at 4°C prior to analysis for PAHs.

The pH_{H_2O} of the soil horizon samples varied from 3.72 to 6.87 among different layers, with a mean value of 5. Concentrations of soil organic carbon ranged from 0.2 to 2.8 g/kg in different soil horizons, with an average of 1.4 g/kg.

Chemicals and materials

The standard PAHs mix from Supelco consisted of a solution in methanol-dichloromethane (50:50, v/v) of

naphthalene (Nap) 1,000 (µg/ml), acenaphthylene (Any) 1,000 µg/ml, acenaphthene (Ane) 2,000 µg/ml, fluorene (Fle) 200 µg/ml, phenanthrene (Phe) 100 µg/ml, anthracene (Ant) 100 µg/ml, fluoranthene (Fla) 200 µg/ml, pyrene (Pyr) 100 µg/ml, benzo[a]anthracene (Baa) 100 µg/ml, chrysene (Chr) 100 µg/ml, benzo[b]fluoranthene (Bbf) 200 µg/ml, benzo[k]fluoranthene (Bkf) 100 µg/ml, benzo[a]pyrene (Bap) 100 µg/ml, dibenzo[a,h]anthracene (Daa) 200 µg/ml, benzo[g,h,i]perylene (Bgp) 100 µg/ml, and indeno[1,2,3-c,d] (Ild) 100 µg/ml. HPLC-grade pentane, dichloromethane, cyclohexane, acetone, acetonitrile, and methanol were supplied by J.T.Baker (Phillipsburg, NJ, USA). The calibration solutions were prepared by diluting the PAHs mixture with acetonitrile to make concentrations in the range of 10–2,000 µg/l.

Pretreatment and chromatographic analysis

For preclude the pore water and interfering compounds, the 10 g weigh PAH-spiked soil was added with anhydrous sodium sulfate (heated at 400°C for 4 h) and copper powder (activated with dilute hydrochloric acid, distilled water, methanol, and n-hexane). In order to obtaining high recovery of PAHs

compounds. the mixture was sonicated for 30 min with 40, 30, and 30 ml of dichloromethane: acetone (1:1, v/v) respectively. The concentrated extracts changed solvent into cyclohexane before centrifuged for 3–5 min at 3,000 rpm. The silica gel (heated at 130°C for more than 16 h) column (10 mm i.d.) was precluded with pentane for eliminate satisfied and naphthenic hydrocarbon. Supernate was placed into the column and the PAHs were obtained by eluted with 50 ml of a mixture of dichloromethane–pentane (2:3, v/v). The eluate was concentrated at 35°C with nitrogen stream under reduced pressure to near-dryness and then dissolved in 1 ml of acetonitrile pending analysis.

The water samples were purified and concentrated by solid phase extraction (SPE) on Supelco (Bellefonte, PA, USA) using a Supelco solid phase extraction vacuum for simultaneous processing of up to 12 SPE cartridges. The adsorbent was activated by eluting with dichloromethane and distilled water. The SPE extractions were performed with 250 ml water samples and extracting for around 50 min and controlling the flow rate to 5 ml/min. The extracts were collected by eluting the carrier with 5, 4, and 3 ml of dichloromethane; and then concentrated and changed the solvent before determination by HPLC (Zhang et al. 2007).

We used a Shimadzu (Tokyo, Japan) 2010 HPLC system equipped with a fluorescence detector (RF-10A_{XL}) and an ultraviolet detector (SPD-10A_{VP}) to analyze for the 16 PAHs. Separation was carried out on a Supelcosil LC-PAH column (Supelco, 4.6×250 cm i.d., particle size 5 μm). The chromatographic data were collected and processed using LC solution Version 1.11 SP1 software. The optimized parameters for the chromatographic analysis of PAHs were as follows: elution conditions, begin with 5 min from 60:40 isocratic elution and then 25 min linear gradient elution to 100:0 acetonitrile/water followed by 15 min isocratic elution and 100% acetonitrile for 10 min; flow rate, 1 ml/min throughout; elution temperature 30°C (constant temperature was necessary for reproducible PAH retention times, which are essential for optimal sensitivity and specificity); fluorescence detection, with the excitation and emission wavelengths (optimized for the best compromise between fluorescence response and selectivity) listed in Table 1; and wavelengths of ultraviolet detector, 254 nm.

Table 1 Fluorescence detector wavelength program

Time (min)	λ_{ex} (nm)	λ_{em} (nm)	PAHs detected
0.0	275	330	Nap, Ane, Fle
15.0	250	366	Phe
17.0	250	400	Ant
19.0	270	460	Fla
21.0	270	390	Pyr, Baa, Chr
30.0	255	410	Bbf, Bkf, Bap
37.2	290	410	Daa, Bgp
41.3	290	500	Ilp

Data quality control

All data were subjected to strict quality control procedures. The calibration solutions were found to be stable for at least 2 months (the maximum period for which they were kept). Calibration graphs were constructed by plotting the peak-area against the PAH concentration. A linear relationship with $r^2 > 0.9987$ was always obtained. Because extraction with an organic agent followed by purification with a silica cartridge fully recovered all PAHs in the soil samples, method characterization was performed with PAH-spiked soil. The spiked soil (10 g) was then fortified with PAHs stock solution (1 mg/ml), and the spiked sample was analyzed after being left for 30 min at room temperature. The results were summarized in Table 2 and percent RSDs were lower than 13%. Limits of detection (LOD) and quantitation (LOQ) calculated in accordance with ACS norms (ACS 1980) were defined as the concentration of the analyte that produced a signal-to-noise ratio of 3 and 10; these were then tested experimentally by spiking blank samples at this level. The total recovery percentages of PAHs and detection limits obtained for individual PAHs are shown in Table 2. Results of blanks extracted under the same conditions were below detection limits and sample results without blank correction are presented.

Results and discussion

Vertical distribution of the total PAHs content in different profiles

Table 3 presents a summary of the mean values and range of values measured for the concentrations of

Table 2 Limits of detection (LODs) of and limits of quantitation (LOQs) of PAHs with the extraction and quantification methods used in this study ($n=7$) and their recoveries from spiked soils ($n=6$)

PAH	Mean recovery \pm RSD (%)	LOD ($\mu\text{g}/\text{kg}$)	LOQ ($\mu\text{g}/\text{kg}$)	PAH	Mean recovery \pm RSD (%)	LOD ($\mu\text{g}/\text{kg}$)	LOQ ($\mu\text{g}/\text{kg}$)
Nap	50 \pm 6	3.5	10	Baa	105 \pm 4	1	2
Any	60 \pm 1	1.2	4	Chr	101 \pm 2	1	2
Ane	61 \pm 0	1	3	Bbf	98 \pm 1	2	6
Fle	68 \pm 0	0.8	3	Bkf	93 \pm 2	1	2
Phe	79 \pm 2	0.5	3	Bap	99 \pm 11	1	4
Ant	85 \pm 3	0.5	1.5	Daa	75 \pm 0	2	6
Fla	91 \pm 2	1	3	Bgp	79 \pm 0	4	12
Pyr	68 \pm 0	1	3	Ilp	83 \pm 2	7	22

PAH in upland and paddy soils. The total PAH concentration ranged over about two orders of magnitude from 46.8 to 2,373.0 $\mu\text{g}/\text{kg}$ (dry wt.) in upland field layers and from 23.1 to 1,179.1 $\mu\text{g}/\text{kg}$ (dry wt.) in horizons within paddy field. The mean concentrations of total PAH for all samples collected from upland layers ranged from 125.6 to 843.8 $\mu\text{g}/\text{kg}$ (dry wt.), while that ranged from 76.5 to 468.2 $\mu\text{g}/\text{kg}$ (dry wt.) in paddy soil horizons.

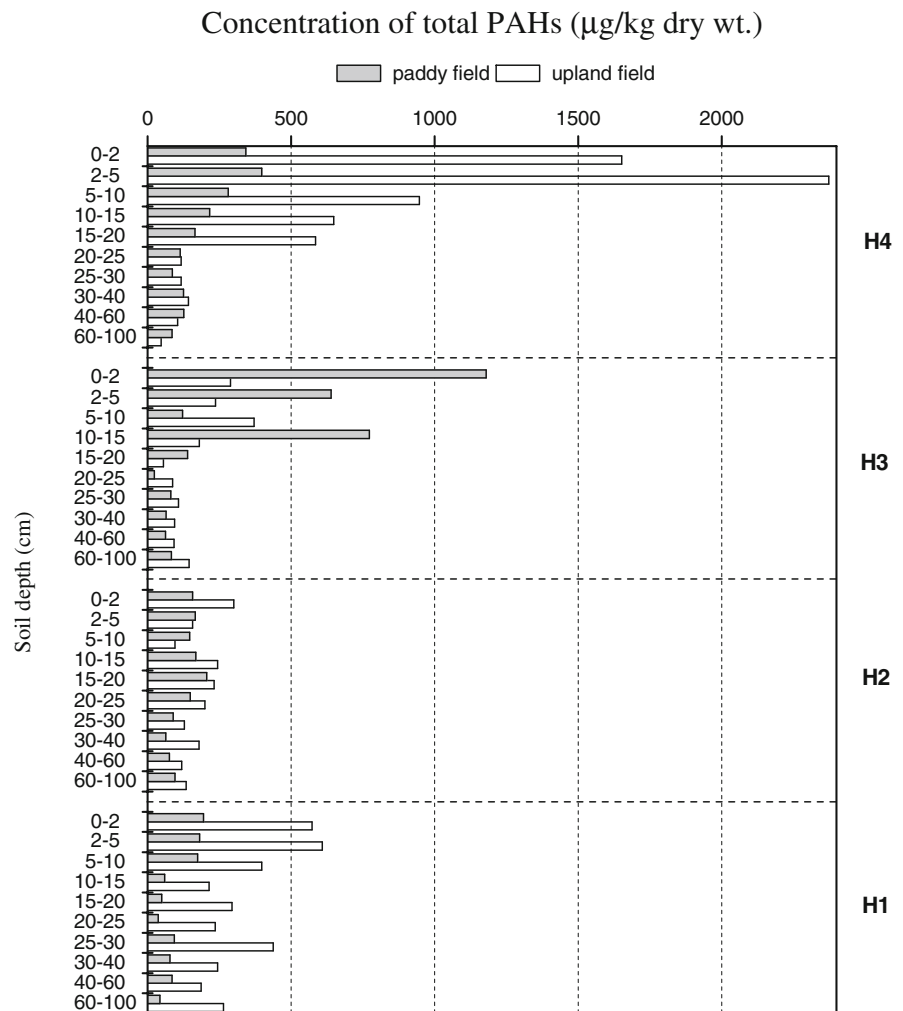
In all sites, the Σ PAHs concentrations maximum at or just below the soil surface and its content declined with depth (Fig. 2). Spearman analysis showed HU4

and HP4 profiles had significantly negative correlation between PAHs concentration and soil depth ($p < 0.05$), and correlation coefficients of the majority of the others were between -0.4 and -0.7 , which means they had moderately reverse correlation between PAHs contents and farmland deepness. This is in agreement with recent publications that have documented data on the vertical distribution of PAHs (Cousins et al. 1999; Pichler et al. 1996). The fact that higher PAH concentrations were found in the surface soil layer than in deeper soil layers suggests that the input rate of PAHs to the upper soil in the study area

Table 3 Mean and range of Σ PAHs, 2 + 3 rings, 4 rings, and >4 rings in all depth sections

Layer (cm)	Mean Σ PAHs	Range	Mean value for 2+3 rings	Range	Mean value for 4 rings	Range	Mean value for >4 rings	Range
Upland field ($\mu\text{g}/\text{kg}$ dry wt.)								
0–2	703.5	289.0–1,651.8	299.6	87.6–502.6	269.6	60.3–710.3	134.3	12.7–438.9
2–5	843.8	156.5–2,373.0	308.0	73.0–701.14	321.7	70.0–927.3	214.1	1.6–744.6
5–10	452.0	95.8–947.2	124.1	24.2–197.0	189.1	59.9–367.9	138.8	11.8–381.9
10–15	321.9	180.7–648.4	154.8	62.4–333.24	132.5	81.7–256.9	34.6	15.0–59.2
15–20	291.6	55.3–585.4	102.0	20.7–169.2	104.8	18.7–229.3	84.8	0–278.7
20–25	160.0	86.7–117.3	98.5	47.3–139.8	50.7	27.4–76.8	15.2	0–23.1
25–30	197.5	107.9–437.3	141.1	57.7–371.6	49.1	31.7–66.7	15.1	0–18.6
30–40	165.1	93.8–244.2	108.8	37.0–167.9	48.5	36.2–69.0	18.3	0–20.6
40–60	125.6	187.0–92.3	78.3	49.2–139.8	44.4	40.3–47.2	0.0	0
60–100	147.7	46.8–264.3	95.6	36.9–183.1	44.4	9.9–73.4	18.5	0–23.0
Paddy field ($\mu\text{g}/\text{kg}$ dry wt)								
0–2	468.2	156.6–1,179.1	176.8	41.8–429.0	177.6	77.9–441.9	113.8	32.8–308.2
2–5	338.6	135.5–639.9	99.6	37.5–169.3	147.6	74.0–310.0	91.4	24.0–209.8
5–10	180.7	121.7–281	59.1	28.3–84.5	79.1	60.6–115.1	42.5	22.4–81.4
10–15	304.1	59.0–772.6	86.0	37.7–156.9	138.4	21.1–375.4	79.6	0–240.3
15–20	139.7	49.6–205.8	55.3	11.3–120.8	59.2	28.0–105.6	25.2	10.3–46.2
20–25	80.7	23.1–148.9	42.8	2.5–87.2	29.6	7.7–75.6	17.2	0–21.3
25–30	87.4	81.2–92.9	57.3	4.0–67.6	27.2	16.3–43.8	0.0	0
30–40	82.5	63.4–124.6	58.9	31.2–106.8	21.9	8.8–31.1	0.0	0
40–60	87.6	62.8–125.8	59.6	36.2–108.5	26.1	13.3–40.1	0.0	0
60–100	76.5	42.9–95.3	49.5	33.5–6.4	26.3	9.5–45.7	0.0	0

Fig. 2 Depth variations of total PAHs with depth in Hunpu soil profiles



was higher than the rate of vertical mobilization and transport along the soil column; however, the fact that vertical variations were not apparent in most of the soil profiles may reflect the application of freshwater irrigation. The contents of PAHs frequently increased from the Oi to Oa horizons; because the PAH disappearance rate, which is governed by decomposition, volatilization, deposition from the atmosphere, and leaching to underlying soil horizons, is slower than organic matter turnover. Therefore, the maximum concentration of ΣPAHs in most profiles was at 2–5 or 5–10 cm excluding the 0–2 cm soil layer by the reason of that PAHs in the top soil are more easily depredated by photolysis and volatilization (Alcock et al. 1993; Jones 1994).

Within the study area, the HU4 section dominated the upland field and the HP3 section dominated the

paddy field. In the HU4 soil profile, the total concentration of ΣPAHs in the 0–20 cm layer was above 500 $\mu\text{g}/\text{kg}$ (dry wt.), but it was decreased rapidly to 46.8 $\mu\text{g}/\text{kg}$ (dry wt.) with soil depth. The high level of PAH at this site can be ascribed to the fact that the Xi River, which is itself badly contaminated, was used for the long-term irrigation of agricultural soils. The higher PAH concentration at the G4 and G5 groundwater-sampling sites (24 and 17 $\mu\text{g}/\text{l}$, respectively) is further testimony to this fact (Fig. 3). The concentration of ΣPAHs in the HU1 section was always above 187.0 $\mu\text{g}/\text{kg}$ (dry wt.) and showed little vertical variation. The HU2 and HU3 sections showed similar ΣPAHs distribution trends, with both containing low levels.

The averaged total concentration of detected PAHs in the paddy field is 5.8–150.1% lower than that in

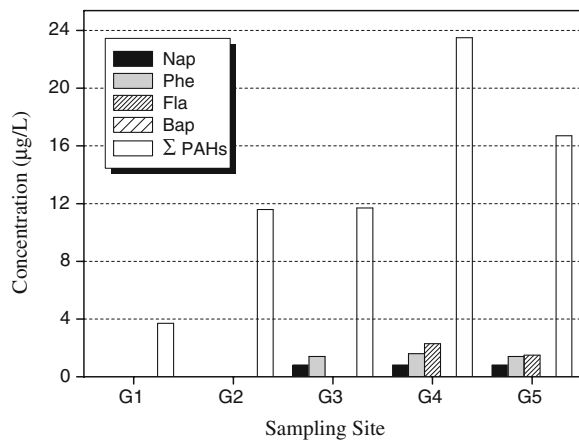


Fig. 3 Contents of Nap, Phe, Fla, Bap, and total PAHs in five groundwater stations located next to the soil-sampling sites

the upland soil for corresponding horizons (Table 4); PAHs with different benzene rings dominated in the upland field. This difference between the two areas can be explained by the fact that paddy soils are irrigated, soaked, and drained for about 6 months each year, leading to the leaching of PAH from the soils (Nam et al. 2003). Figure 2 shows that the peak value of ΣPAHs in the HP3 profile is just half that in the HU4 section, although both sections show similar variations. In an exception to the general trends, the total PAHs concentrations in the upper five layers of the HP3 section are higher than those in the corresponding layers of the HU3 profile. The concentration of ΣPAHs in HP1 was expected to be lower than that in HP2 because of longer distance from the wastewater source, yet their pollution levels were equivalent. This may reflect the fact that freshwater irrigation has been applied to HP2 for more than two decades.

Variations of individual PAHs within vertical sections

Table 3 shows that the concentrations of different rings of PAH declined with depth. In all soil profiles, the peak content was not in the 0–2 cm layer; this is consistent with the vertical distribution of ΣPAHs. Among the PAHs with different benzene rings, the average concentration of two- to three-ring PAH homologues was the highest [78.3–308.0 µg/kg (dry wt.) in upland fields; 42.8–176.8 µg/kg (dry wt.) in paddy soils] and that for more than four rings PAH was the lowest [0–214.1 µg/kg (dry wt.) in upland fields; 0–113.8 µg/kg (dry wt.) in paddy soils]. The

mean concentrations of four rings PAH compounds ranged from 44.4 to 321.7 µg/kg (dry wt.) in upland fields and 26.1–177.6 µg/kg (dry wt.) in paddy areas. The fact that two to three rings PAH dominated the wastewater-irrigation area may be due to contributions of different sources (this is discussed in “Possible sources of soil PAHs”).

The 16 PAHs were all detected in the analyzed soil profiles and the dominant compounds including naphthalene (Nap), phenanthrene (Phe), fluoranthene (Fla), and chrysene (Chr), containing two, three, four, and four rings, respectively. These compounds occurred at high concentrations in the upper layers, and acenaphthylene, acenaphthene, dibenzo [a, h] anthracene, and anthracene were mainly concentrated in the upper five horizons (<20 cm) at low levels. Nap, which is extremely toxic and easy to volatilize, has been detected in many rural areas (Nam et al. 2003; Song et al. 1997). Phe and Fla may lead to groundwater contamination because of their high aqueous solubility. Benzo[a]pyrene (Bap) is a strong carcinogen and has attracted significant public attention. Nap, Phe, Fla, and Bap were therefore selected for the profile distribution study. Nap was detected in many soil horizons and dominated in the paddy field. The water solvability of Nap is up to 31.7 g/l (25°C), while the *K_{ow}* value is the lowest of the 16 PAHs (up to 1,950), therefore, it readily migrates downward. The peak value of Nap in the 0–2 cm layer of the HP3 section (up to 239.9 µg/kg dry wt.) may reflect the proximity of the Hun River. The concentration of Phe

Table 4 Estimated PAHs sources based on the ratios of selected PAH compounds

Ratios PAHs source	LMW/HMW	Phe/An	Fla/Pyr	An/178	Fl/Fl +Py	Ba/228	IP/IP +Bghi
Pyrolytic	<1 ^a	<10 ^a	>1 ^a	>0.1 ^b	>0.5 ^b	>0.2 ^c	>0.5 ^c
Petrogenic	>1 ^a	>10 ^a	<1 ^a	<0.1 ^b	<0.5 ^b	<0.35 ^c	<0.2 ^c
Vehicular exhaust		<4 ^d			0.41–0.49 ^c		0.2–0.5 ^c
Fuel oil			0.6–0.9 ^c				

^a Socio et al. (2000)

^b Budzinske et al. (1997)

^c Yunker et al. (2002)

^d Yang et al. (1991)

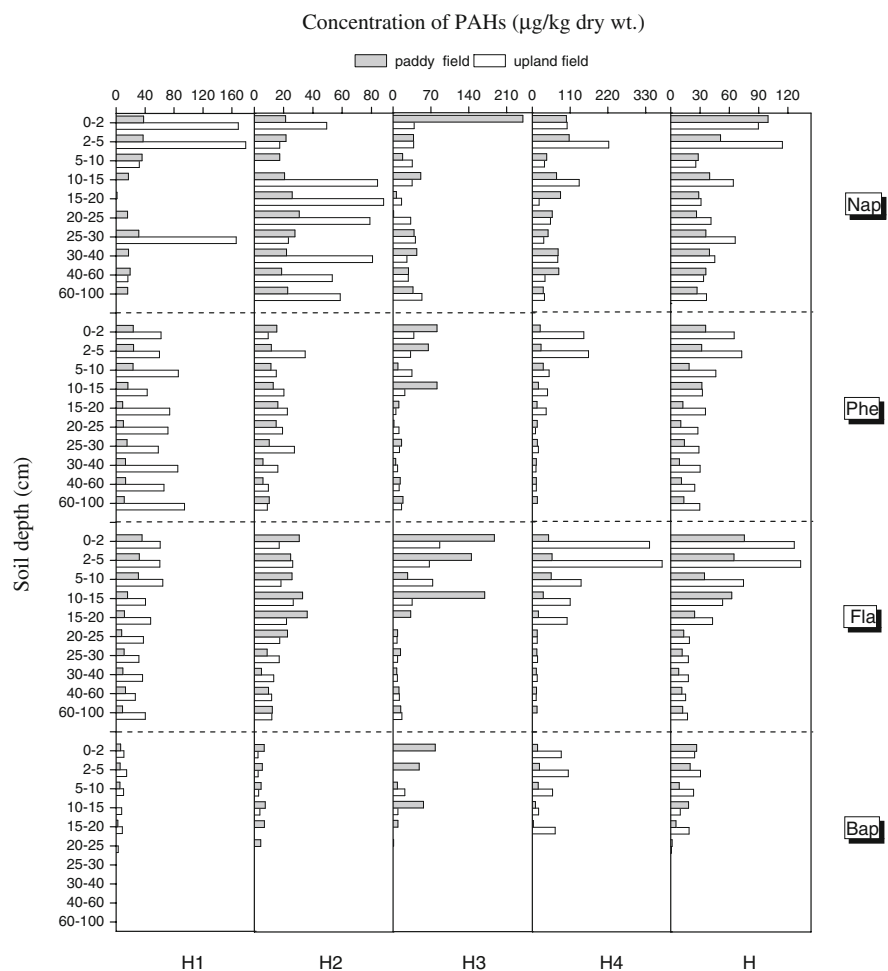
^e Gschwend and Hites (1981)

declined slightly with soil depth before increased again in the deepest horizons. In soil profiles, the coefficients of variation (CV) for Fla exceeded 100%, showing much greater variation in concentration throughout the soil horizons than Phe, especially in the HP3 and HU4 soil profiles. Lighter molecular weight PAHs such as Nap, Phe, and Fla are easily degraded, but they were present throughout the soil sections. This observation may be related to the constant input of combustion sources (Berset et al. 2001). The mean concentration of Bap was less than 30 $\mu\text{g}/\text{kg}$ (dry wt.), and it was below the detection limit for soil depths greater than 20 cm. The Bap content in groundwater was also below the detection limit for all water-sampling sites (Fig. 3).

The general profile of PAHs was similar in the two types of soil (Fig. 4). The average value of individual PAHs in *H* showed that concentrations of PAH are

generally higher in upland soil and this may be due to a number of factors included among which are that the upland soils contain a higher organic matter content than do paddy soils (PAH associates with organic soils to a greater extent than with mineral soils) and that because paddy soils are irrigated and saturated with water for a significant part of the year, leading to an increased likelihood of the leaching of PAH into groundwater. At the HG4 sampling site, the concentration of ΣPAH is 40.7%, higher than that at the HU4 station (Fig. 3); this may explain the observed monitoring results. Figure 4 reveals that the highest concentrations of PAHs in the upland field dominated in the subsoil while the peak values of PAHs in the paddy soil were observed in the topsoil. This trend can be ascribing to different methods of tillage that led to the mixing of PAHs down to the plough depth, resulted various content distributions

Fig. 4 Depth variations of Nap, Phe, Fla, and Bap in Hunpu soil profiles. *H* Mean value of PAHs concentration in all upland soil profiles and in all of the paddy field sectors



in the soil profile. The content of individual PAHs compounds in upland vertical sections decreased in the order of HU1>HU2>HU3. This may reflect the long-range atmospheric transport of PAH from point sources of pollution to remote rural sites (Halsall et al. 2001). The opposite trend was observed in paddy soil, which was more affected by water supply source on the basis of its land use pattern, probably due to the long-range irrigation of remote rural areas using polluted wastewater from the Hun River, in this sense, the concentration of PAHs declined as the distance.

It is acknowledged that soil organic matter (SOC) is a principal factor in influencing the distribution of PAHs (Chiou et al. 1998). However, the linear regression analysis indicated the fact that the Σ PAHs and SOC content demonstrated poor correlation at majority profiles, with the low correlation coefficients (<0.4) could hardly closely associate the PAHs vertical distribution variation. Simpson et al. (1996) noted that the relationship between total PAHs and organic carbon is significant only for highly contaminated sites where the total PAH concentration was in excess of 2,000 $\mu\text{g}/\text{kg}$, and the high concentration had only occurred in the 2–5 cm layer of the HU4 section in the study area. Besides the SOC, ionic strength (Lee et al. 2003), pH (Laor et al. 1998), and colloids can also influence the binding of PAHs in soils. The PAHs downward transportation may have been assisted by increased mobilization of PAHs associated with dissolvable organic matter due to an increase in soil pH (Gabcia-Falcón et al. 2006). This view is supported by the fact that pH values increase from 4 to 5 with depth. The distribution characteristics of Σ PAHs and individual PAH in soil profiles vary widely depending on the structure and physiochemical features of PAH and their source.

Furthermore, biodegradation or biotransformation could be another factor affecting the distribution and concentration of PAHs around the root of the plants cultivated in the upper soil. Walton et al. (1994) suggested that rhizosphere could stabilize pollutants by polymerization reactions such as humification and speculated that when a chemical stress is present in soil, a plant may respond by increasing or changing exudation to the rhizosphere, which modifies rhizospheric microflora composition or activity. Binet et al. (2000) showed the dissipation was higher for three-ring PAHs (phenanthrene and anthracene) than for the other high molecular weight compounds. Although

plants may contribute to the dissipation of PAHs by an increase in microbial numbers, improvement of physical and chemical soil conditions, increased humification and adsorption of pollutants in the rhizosphere, the impact of each process has not been clearly elucidated. Several researchers had reported the fact that the plant rhizosphere was able to enhance degradation of PAHs (Reilley et al. 1996; Goodin and Webber 1995). Whereas, the adaptation period and model experiment time could not give a definite and comprehensive explanation under complicated and long-term contamination situation at the situ.

The observed differences in the distribution of soil PAHs at the eight sites may be due to many factors including the different sources and properties of the PAHs, as well as the different soil properties. It should be noted that the method of soil tillage and plants growing could also probably influence the vertical distribution of PAHs. Which factors, and how these factors affect the vertical distribution of PAHs in wastewater irrigation soils will be an important issue in our future study.

Possible sources of soil PAHs

The ratios of pairs of individual PAH have often been employed as a method of determining the most significant sources of PAH detected in environmental samples (McCready et al. 2000; Socio et al. 2000). The abundance ratio of two and three-ring hydrocarbons to four to six-ring hydrocarbons (LMW/HMW) can be used to assist in distinguishing petrogenic and pyrolytic sources (Tam et al. 2001; Yuan et al. 2001). These results of previous studies are summarized in Table 4. On the basis of the data presented in Table 3, it is evident that the origin of PAHs in the present study is dominated by the combustion of coal; however, LMW/HMW is >1 in the 20–100 cm horizons, suggesting to some extent a contribution from irrigation with petrogenic wastewater. Socio et al. (2000) recommend the ratios such as phenanthrene/anthracene (Phe/Ant) and fluoranthene/pyrene (Fla/Pyr) to differentiate between Pyrolytic and Petrogenic sources. The soil samples collected mostly showed the fact that the Phe/Ant <10 for the dominance of pyrolytic sources, moreover, the ratios of the HU1 more layers >10 for some petrogenic inputs. The same consideration can be applied to the Fla/Pyr ratio. The Fla/Pyr values greater than 1 were

dominant in all sampling sites which classical linked to the Pyrolytic origin, namely to the coal combustion.

Parent PAH ratios have been widely used to detect combustion-derived PAHs (Socio et al. 2000; Budzinske et al. 1997). Combustion and/or anthropogenic input are often inferred from an increase in the proportion of the less stable species, “kinetic” PAH isomers relative to the more stable, “thermodynamic” isomers (Yunker and Macdonald 1995) The ratio of the molecular masses 178 and 202 is commonly used to distinguish between combustion and petroleum sources (Budzinske et al. 1997). In the present study, the an anthracene to anthracene plus phenanthrene (Ant/178) ratios are close to or above 0.1 in all horizons, which indicates that coal combustion is the main origin of PAHs; a fluoranthene to fluoranthene plus pyrene (Fla/202) ratios are largely >0.50, indicating a dominance of combustion sources. For mass 228 a benz[a]anthracene to benz[z]anthracene plus chrysene (BaA/228) and mass 276 a indeno [1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[ghi]perylene (IP/IP+Bghi) are used less frequently as parent PAH indicators and few guidelines have been established for their interpretation (Yunker et al. 1996). The results showed in Table 4 indicated the expected contribution of petroleum sources, while crude, vehicle, and coal combustion might have supplied PAHs via wet/dry deposition under the aid of wind direction in various season. As the samples were collected after harvest and the open burning of crop straw in the Hunpu area, of the burning may have made a contribution to soil PAHs. Furthermore, exhaust from industry and residents, who used coal as a major energy source without appropriate treatment, lead to the prevalence of PAHs in Liaoning province (LSB 1995).

PAHs with four and more rings (mass of 202 and higher) are not easily segregated into combustion and petroleum sources, and the interpretations of PAH ratios are most definitive for masses of 202 and 276 (the PAHs with the greatest differences in thermodynamic stability between isomers). In summary, the sources of PAHs in the Hunpu wastewater-irrigation area include the combustion of coal and petroleum, automotive exhausts, the incomplete combustion of crude oil, and the open burning of crop straw. Particle and aerosol PAH input to the soil surface by wet/dry deposition (Park et al. 2000) and eolian transportation. It then migrates downward into deeper layers,

and even into the groundwater, at different rates depending on soil type and edatope.

Conclusions

At all sites, the Σ PAHs concentrations maximum at or just below the soil surface, and the contents decline with depth at various trend, which supported by nonparametric Spearman’s rank correlation test. The total PAH concentration ranged over about two orders of magnitude from 46.8 to 2,373.0 $\mu\text{g}/\text{kg}$ (dry wt) in the upland field and from 23.1 to 1,179.1 $\mu\text{g}/\text{kg}$ (dry wt) in the paddy field. The mean concentration of total PAH for all of the sampled upland layers ranged from 125.6 to 843.8 $\mu\text{g}/\text{kg}$ (dry wt), while the range for paddy soils was 76.5 to 468.2 $\mu\text{g}/\text{kg}$ (dry wt). The HU4 section contained the highest concentrations of PAHs in the upland field, while the HP3 section contained the highest concentrations in the paddy field. PAHs of two to three rings were dominant in the wastewater-irrigation area. Individual PAHs such as Nap, Phe, Fla, and Chr accounted for a large proportion of the total PAHs. The vertical distributions of Nap, Phe, Fla, and Bap were noticeable different. Nap was detected in many soil horizons and dominated the paddy field. In soil profiles, the coefficients of variation (CV) for Fla exceeded 100%, showing much greater variation in concentration throughout the soil horizons than that recorded for Phe. The mean concentration of Bap was less than 30 $\mu\text{g}/\text{kg}$ (dry wt), and was below the detection limit at soil depths greater than 20 cm and within groundwater. In all layers, the concentrations of individual and total PAH in upland soil were significantly higher than those in paddy soil in each corresponding horizon. The observed differences in the distribution of soil PAHs at the eight sampling sites may be explained by different sources; the properties of the PAHs and soil as well as soil tillage practices, and plant growing could also possibly have influenced the vertical distribution of PAHs. Possible soil PAH sources were identified from values of Phe/Ant, Fla/Py, LMW/HMW, and parent PAH ratios (Ant/178, Fla/202, BaA/228, and Ip/276). The origin of PAHs in the Hunpu wastewater-irrigation area is ascribed to the combustion of coal and petroleum, automotive exhausts, the incomplete combustion of crude oil, and the open burning of crop

straw. Particle and aerosol PAH input to the soil surface by wet/dry deposition and transported to deeper soil horizons and groundwater by downward vertical migration.

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