



Distribution and sources of petroleum-hydrocarbon in soil profiles of the Hunpu wastewater-irrigated area, China's northeast

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ABSTRACT

Petroleum-contamination soil is ubiquitous. The various sources of this contamination necessitate the effective evaluation of the contamination level, contaminant transport analysis and identification of the pollution sources. In the present study, soil profiles were collected from both upland and paddy fields along the strike of the irrigation canals in the Hunpu wastewater irrigation region in northeast China. The concentrations of aliphatic hydrocarbons in the soil were analyzed. The sites near the oil wells, wastewater irrigation canal and Shenyang City were found to have high concentrations of [\sum n-alkanes (sum of n-alkanes): (0.8 to 32.2) $\mu\text{g g}^{-1}$ dry wt.; TAH (total aliphatic hydrocarbons): (5.0 to 161.2) $\mu\text{g g}^{-1}$ dry wt.]. The geochemical analysis results showed various degrees of petroleum pollution. The \sum n-alkanes varied (0.5 to 7.5) $\mu\text{g g}^{-1}$ while TAH varied (1.6 to 47.2) $\mu\text{g g}^{-1}$ at other sites where biogenic hydrocarbons were dominant. The results from the principal components and redundancy analyses showed that the samples containing hydrocarbons from wastewater irrigation, oil wells, and atmospheric deposition were partitioned into different groups. These results further represented that the soil properties had some effects on hydrocarbon distribution especially the sand content which had significantly negative correlation with oil-related hydrocarbons. The current study showed that the early input and vertical migration of hydrocarbons resulted in a high deep-soil hydrocarbon concentration.

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1. Introduction

The petroleum industry and the use of petroleum products are ubiquitous in modern society. Petroleum accidents, discharge of waste oil, reuse of wastewater or sludge containing petroleum products, and soil contamination resulting from them are frequent (Adeniyi and Afolabi, 2002; Li et al., 2005; Moreda et al., 1998; Williams et al., 2006; Xiong et al., 1997; Zhou et al., 2005). Petroleum hydrocarbons in soil pose risks to the environment and human health. They can change the physico-chemical properties of soil and affect the physioecology of flora and soil microorganisms. The toxic components migrating from soil to groundwater and crops will endanger human health. The heavy, branched-chain, and cyclic hydrocarbons which are persistent in the environment can be transformed into more toxic substances (ATSDR, 1999; CCME, 2008; Li et al., 2005; Moreda et al., 1998; Plaza et al., 2005; Rao et al., 2007; Thomas et al., 1995; Xiong et al., 1997; Ye et al., 2007).

On the basis of chemical structure and physico-chemical properties, petroleum hydrocarbons are divided into two main classes: aliphatic

and aromatic. Their compositions have been widely applied to assess the petroleum contamination level and identify the different sources. Zemo (2007) reported that the chromatogram pattern, geochemical indices (such as constitute ratios and biomarkers), age-dating releases, additives, and stable isotopes can be used to recognize various hydrocarbon sources. To identify the biogenic, petrogenic and pyrolytic hydrocarbons, previous studies analyzed the concentrations and patterns of aliphatic hydrocarbons (AHs) and/or polycyclic aromatic hydrocarbons (PAHs) and some of their common indices [range of carbon number, unresolved complex mixtures (UCM), isoprenoids, low carbon number hydrocarbons/high carbon number hydrocarbons, the n-alkane with maximum concentration (C_{max}), the ratio of the sum of all n-alkanes to hexadecane (C_{16} ratio), and carbon preference index (CPI)] (Abdullah, 1997; Commendatore and Esteves, 2004; Readman et al., 2002; Tran et al., 1997). These common indices can be combined with biomarkers, weather ratios, radiocarbon age, and/or stable carbon isotope to obtain more information about sources, maturity, and depositional environment (Harji et al., 2008; Hegazi et al., 2004; Medeiros and Bicego, 2004; Scholz-Böttcher et al., 2009; Wakeham and Carpenter, 1976; Zhu et al., 2005). Multivariate statistical analysis was efficiently used to simplify the complicated data sets on AHs and/or PAHs and determine the relationship of the different groups to different sources (Aboul-Kassim and Simoneit, 1995a,b; Aboul-Kassim and Williamson,

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2003; Kang et al., 2000; Ye et al., 2007). The relationship of hydrocarbons and samples to pollution sources are explored using R-mode and Q-mode factor analysis, respectively. The CANOCO software can simultaneously focus on both covariance relationships and inter-sample relationships and can also be used to analyze the effects of the soil properties on hydrocarbon compositions.

Hunpu region is one of the most spacious and typical wastewater irrigation areas in China and has been irrigated for more than 40 years with water from the Dahuofang Reservoir, the Hunhe River, and the Xihe River. The Xihe River is the major drainage channel of industrial effluent and municipal sewage of Shenyang City, where many petrochemical plants exist and the use of petroleum products is common (Xiao et al., 2008). The situation resulted in the excessive petroleum hydrocarbon contamination of the Xihe River and its riverbank groundwater (Song et al., 2004; Song et al., 2007), making it the most polluted river of Shenyang and a pollution source of the Hunhe River. Other than the wastewater-irrigation, there are other sources of petroleum hydrocarbons (such as oil wells and atmospheric deposition) in the region. Our objectives are to effectively evaluate petroleum contamination level of soil in the Hunpu region by analyzing the concentration, geochemical characteristics and multivariate statistical analysis of aliphatic hydrocarbons; to explain the different distributions by the possible pollution sources and the basic soil properties; and to provide the guidelines for the quantity and safety of agricultural products and soil pollution control in the Hunpu region. The sources of petroleum hydrocarbons in complex agricultural soil are rarely studied compared to sediments, and the CANOCO software is tentatively used to analyze the pollution sources in the current study.

2. Materials and methods

2.1. Soil sampling

In May 2008, soil profiles were collected at the Hunpu wastewater-irrigated area located at the southwest of Shenyang City, Liaoning Province, China. The Hunpu region has an area of 410,000 ha with a typical temperate monsoon climate. The annual mean temperature is 7.8 °C and the annual mean precipitation is 734.4 mm. Although the north wind is dominant during winter, south is the predominant direction of the wind all year. The main soil types are sandy loam and black soil. The irrigation water was delivered by the main canal and the Xihe River canal, both of which drew water from the Hunhe River. As the dominant land-use types, four paddy fields (I-1P, I-3P, I-5P, and I-7P) and four corn fields (I-2U, I-4U, I-6U, and I-8U) along the strike of the irrigation canals were chosen as sampling sites, all of which were at least 200 m away from roads (Fig. 1). The top 100 cm soil was sampled from a 1 m × 1 m hole after harvest before the next ploughing and divided into ten layers (including 0–5, 5–10, 10–15, 15–20, 20–25, 25–30, 30–40, 40–50, 50–60 and 60–100 cm). Each sample was homogeneously mixed with five randomly selected subsamples at each site, and then a portion of each sample was filled into a pre-cleaned aluminum box and transported to the laboratory at a temperature of 4 °C. The samples were freeze-dried and ground to 1 mm for petroleum hydrocarbons analysis. The other portions were air-dried and ground to 2 mm for soil particle composition, then to 1 mm for soil pH and conductivity, and finally, to 0.125 mm for organic matter (OM) analyses, respectively.

2.2. Analytical methods

For the extraction of petroleum hydrocarbons, a soil sample (ca. 10 g) was pressurized-liquid extracted with acetone/dichloromethane (1/1, v/v) using an ASE-300 (Dionex, Beijing, China). During the extraction, the cells were pressurized to 1500 psi/1.0 × 10⁷ Pa, and heated to 175 °C for 8 min. The static extraction was held for 5 min followed by flushing (75% of the cell volume) and purging for 60 s at 150 psi/1.0 × 10⁶ Pa (Dionex,

2007; EPA, 2007; Richter, 2000). The aliphatic hydrocarbons were obtained through eluting with approximately 20 mL n-hexane after purification with an alumina and silica gel chromatography column (Guo et al., 2007; Richter, 2000; Van De Weghe et al., 2006) and concentrated to 1 mL for qualitative and quantitative analysis.

The aliphatic hydrocarbon fraction was analyzed by Agilent 7890A gas chromatograph with a HP-5 fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 mm film thickness). A 2 mL volume was injected in the pulsed splitless mode. The initial oven temperature was 60 °C (held for 2 min), was increased to 320 °C at 8 °C min⁻¹ and held for 10 min. The flame ionization detector was at 330 °C. The carrier gas was N₂. The n-alkanes (nC₁₀ to nC₄₀), phytane and pristane were quantified using the external standard (Accustandard, US) method. The UCM was quantified by assuming a response factor of 1.0 based on nonadecane. The \sum n-alkanes value was the sum of all n-alkanes from nC₁₀ to nC₄₀. The total aliphatic hydrocarbons (TAH) value was the sum of the \sum n-alkanes and UCM.

The analytical procedure was strictly evaluated. Calibration graphs were constructed by plotting the peak area against the reference material concentration every two days. A linear relationship with $r^2 > 0.99$ was always obtained. The recovery test was performed with a reference material-spiked soil. A control soil sample (ca. 10 g) was spiked with three kinds of reference material solutions (the concentrations of each reference material were 2, 6, and 10 µg mL⁻¹, respectively), and the spiked sample was analyzed after being left for 30 min at room temperature. The procedure was repeated twice. The recoveries for nC₁₀ to nC₄₀, phytane and pristane were 60–120% with 3.4–17.0% RSD (except for nC₁₀ to nC₁₂ due to their volatility), as shown in Table 1.

Soil pH was measured using a pH meter (PSH-3 C, Leici, China) and the ratio of water to soil was 2.5:1. Potassium dichromate volumetric method was used to determine OM (Lu, 2000). Particle composition was determined by a micro-pipettes method (Miller and Miller, 1987). Soil conductivity was measured using a conductivity meter (DDS-12A, LIDA, China) and the ratio of water to soil was 5:1.

2.3. Statistical methods

Simple statistical analysis was done using STATISTICA 7. To describe the similarity and dissimilarity of aliphatic hydrocarbons in the eighty samples and to provide an explanation of their soil properties, the CANOCO 4.5 software bundled with CanoDraw for Windows was used for statistical analysis.

The gradient lengths of the four axes calculated from detrended correspondence analysis (DCA) were all below 3, therefore the linear model analysis methods principal components analysis (PCA), and redundancy analysis (RDA), were applied (Lepš and Šmilauer, 2003). PCA was used to investigate the hydrocarbon compositions in all samples, whereas the relationships between the hydrocarbon compositions and the measured soil properties were analyzed by RDA. The values of aliphatic hydrocarbons or soil properties were evaluated by projecting the sample points onto the arrows of aliphatic hydrocarbons or soil properties. The dissimilarities of the samples were represented by the distances between the sample points. The (linear) correlation coefficients among the aliphatic hydrocarbons or the aliphatic hydrocarbons and soil properties were indicated by the cosine values of angles between the arrows of aliphatic hydrocarbons or arrows of aliphatic hydrocarbons and soil properties. The effects of the soil properties on hydrocarbon composition were indicated by the lengths of soil properties arrows.

3. Results and discussion

3.1. The concentrations of \sum n-alkanes and total aliphatic hydrocarbons of soil samples

Kruskal–Wallis ANOVA results indicated that the \sum n-alkanes and TAH of the eight sampling sites were significantly different ($P < 0.01$).

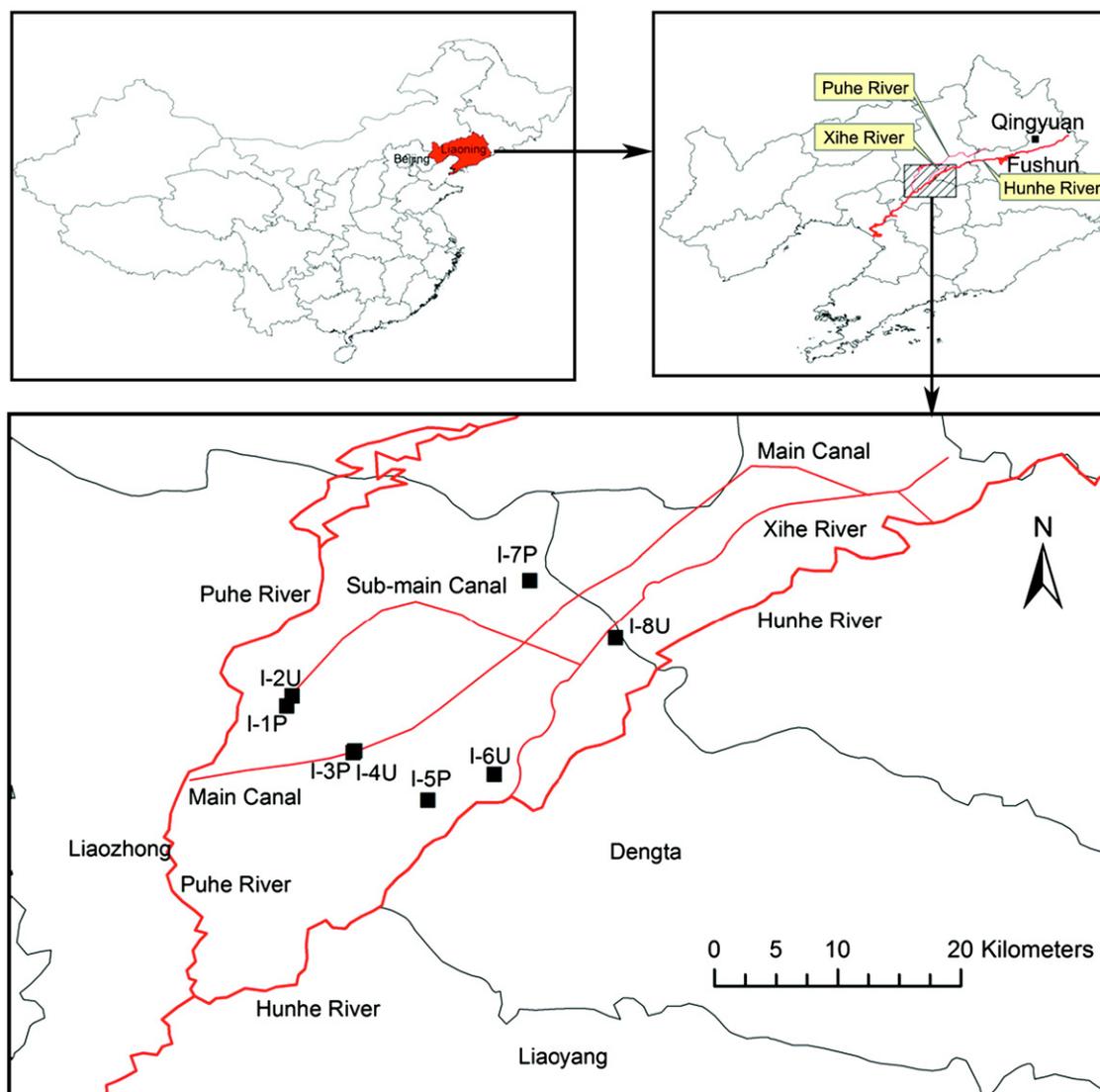


Fig. 1. Location of sampling sites in the Hunpu wastewater irrigation region. Four soil profiles from paddy fields: I-1P, I-3P, I-5P, and I-7P; four soil profiles from upland fields: I-2U, I-4U, I-6U, and I-8U.

The hydrocarbon concentrations were relatively higher at I-2U, I-6U, and I-5P, which were near the oil wells or the downstream of the wastewater irrigation canal. The \sum n-alkanes ranged from 1.1 to 32.2 $\mu\text{g g}^{-1}$, and the TAH ranged from 10.9 to 161.2 $\mu\text{g g}^{-1}$. The highest concentration was at I-6U. The concentrations of \sum n-alkanes and TAH were medial at I-7P and I-8U at the suburb of Shenyang and the middle-upper stream of the Xihe River, where the \sum n-alkanes and TAH were

0.8 to 13.1 $\mu\text{g g}^{-1}$ and 5.0 to 65.6 $\mu\text{g g}^{-1}$, respectively. The hydrocarbon concentrations at I-1P, I-3P and I-4U were low, where the \sum n-alkanes value was 0.5 to 7.5 $\mu\text{g g}^{-1}$ and the TAH was 1.6 to 47.2 $\mu\text{g g}^{-1}$. I-4U was the lowest concentration site. The Kruskal–Wallis test showed that there were no significant differences among the ten layers for \sum n-alkanes and TAH. However, the Mann–Whitney test showed that the \sum n-alkanes at 0–10 cm (1.7–32.2 $\mu\text{g g}^{-1}$) were significantly higher than those at the other layers (0.5–15.5 $\mu\text{g g}^{-1}$), due to biogenic hydrocarbons and fresh oil entering the topsoil. For TAH, the concentrations at 0–10 cm were highest (4.1–141.4 $\mu\text{g g}^{-1}$), the values at 20–25 cm and 50–100 cm were medial (1.8–161.2 $\mu\text{g g}^{-1}$), and those at the other layers were lower (1.6–109.1 $\mu\text{g g}^{-1}$). The higher TAH values in the deep soil were caused by both input and downward migration of difficultly-degraded petroleum hydrocarbons in the previous years.

The total aliphatic hydrocarbon concentrations were over 10 $\mu\text{g g}^{-1}$ in all layers at I-2U, I-5P, I-6U, and I-7P (except 0–5 cm) and some layers at I-1P (0–5, 30–50, and 60–100 cm); I-3P (0–15 and 60–100 cm); I-4U (5–10, 30–40, and 50–100 cm); and I-8U (0–15, 20–30, 40–50, and 60–100 cm). Therefore, the cleanup was required according to the most rigorous level (10 $\mu\text{g g}^{-1}$ for total petroleum hydrocarbon in soil) suggested by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) (Gustafson et al., 1997). Furthermore, the TAH values

Table 1
The average recoveries with RSD of n-alkanes, pristane, and phytane.

	Mean recovery ± RSD (%)	Mean recovery ± RSD (%)	Mean recovery ± RSD (%)
nC ₁₀	43 ± 8.2	nC ₁₉ 108 ± 14.0	nC ₃₀ 83 ± 13.9
nC ₁₁	45 ± 8.1	nC ₂₀ 100 ± 12.6	nC ₃₁ 87 ± 11.0
nC ₁₂	50 ± 5.7	nC ₂₁ 96 ± 6.7	nC ₃₂ 71 ± 8.1
nC ₁₃	105 ± 3.4	nC ₂₂ 79 ± 3.1	nC ₃₃ 90 ± 10.1
nC ₁₄	115 ± 13.0	nC ₂₃ 68 ± 5.8	nC ₃₄ 92 ± 9.3
nC ₁₅	93 ± 13.1	nC ₂₄ 60 ± 7.3	nC ₃₅ 56 ± 11.4
nC ₁₆	74 ± 7.8	nC ₂₅ 71 ± 10.7	nC ₃₆ 113 ± 9.5
nC ₁₇	98 ± 7.2	nC ₂₆ 60 ± 6.5	nC ₃₇ 108 ± 12.5
Pristane	73 ± 8.1	nC ₂₇ 66 ± 9.6	nC ₃₈ 101 ± 7.5
nC ₁₈	85 ± 6.9	nC ₂₈ 69 ± 5.8	nC ₃₉ 125 ± 17.0
Phytane	83 ± 11.0	nC ₂₉ 95 ± 12.6	nC ₄₀ 96 ± 4.3

in some soil layers of I-2U (10–15, 20–25, and 50–100 cm), I-5P (0–10 and 40–100 cm), I-6U (all layers except 60–100 cm), I-7P (25–30 cm), and I-8U (0–5 cm) were over $50 \mu\text{g g}^{-1}$, which was the generic and top 2 ft soil total petroleum hydrocarbon cleanup level provided by the Oklahoma Department of Environmental Quality (DEQ) (DEQ, 2004). All soil samples were below the level for petroleum hydrocarbons (boiling point ranges from $n\text{C}_{10}$ to $n\text{C}_{16}$: $150 \mu\text{g g}^{-1}$, $n\text{C}_{16}$ to $n\text{C}_{34}$: $300 \mu\text{g g}^{-1}$ and $n\text{C}_{34+}$: $2800 \mu\text{g g}^{-1}$) established by the Canadian Council of Ministers of the Environment (CCME) (CCME, 2008).

3.2. Vertical distribution of Σn -alkanes, UCM, and TAH of different soil profiles

The patterns of vertical distribution of the aliphatic hydrocarbons in the eight profiles were not uniform (Fig. 2). The complicated distribution was a result of various input quantities at different periods and the many influential factors of migration rate. The hydrocarbon concentrations were low in the topsoil and high in the soil layers below 30 cm at I-1P and I-4U. In summary, the concentrations at the two sites were quite lower compared with those of the other sites and close to the natural distribution without obvious pollution sources.

I-2U was near an abandoned oil well, which stopped production ten years ago. The hydrocarbon concentration was therefore low and had a slightly increasing trend in the top soil. Due to the high

input quantities ages ago and the subsequent downward migration, high hydrocarbon concentration accumulated at 20–25 cm was discovered. The concentration in the bottom soil was also high because of the petroleum input at an earlier time. Moreover, the soil particles were finer at 20–25 cm and 50–100 cm, which was the reason of the hydrocarbons accumulation at the depths.

I-5P was irrigated by wastewater from the lower Xihe River canal. The hydrocarbons concentration in the top soil (0–20 cm) decreased dramatically with depth, which was related to the input of petroleum from the irrigation wastewater in near term. The concentration at 20–25 cm began to increase and that in bottom soil was especially high. Acher et al. (1989) and Muszkat et al. (1993) suggested that sewage and moisture would promote the downward mobility of organic pollutants, which could explain that the higher hydrocarbon concentration in deep soil compared with that in shallow soil and the different distributions between the upland fields and wastewater-irrigated paddy fields.

I-3P was also affected by the wastewater from the Xihe River resulting in some similarities between I-3P and I-5P because the main canal was connected to the Xihe River canal.

The hydrocarbon concentration was high and had a descending trend as depth increases at I-6U, which was caused by the continuous input of petroleum hydrocarbons from a nearby petroleum exploration. For I-8U at the suburb of Shenyang City, the concentration was medial

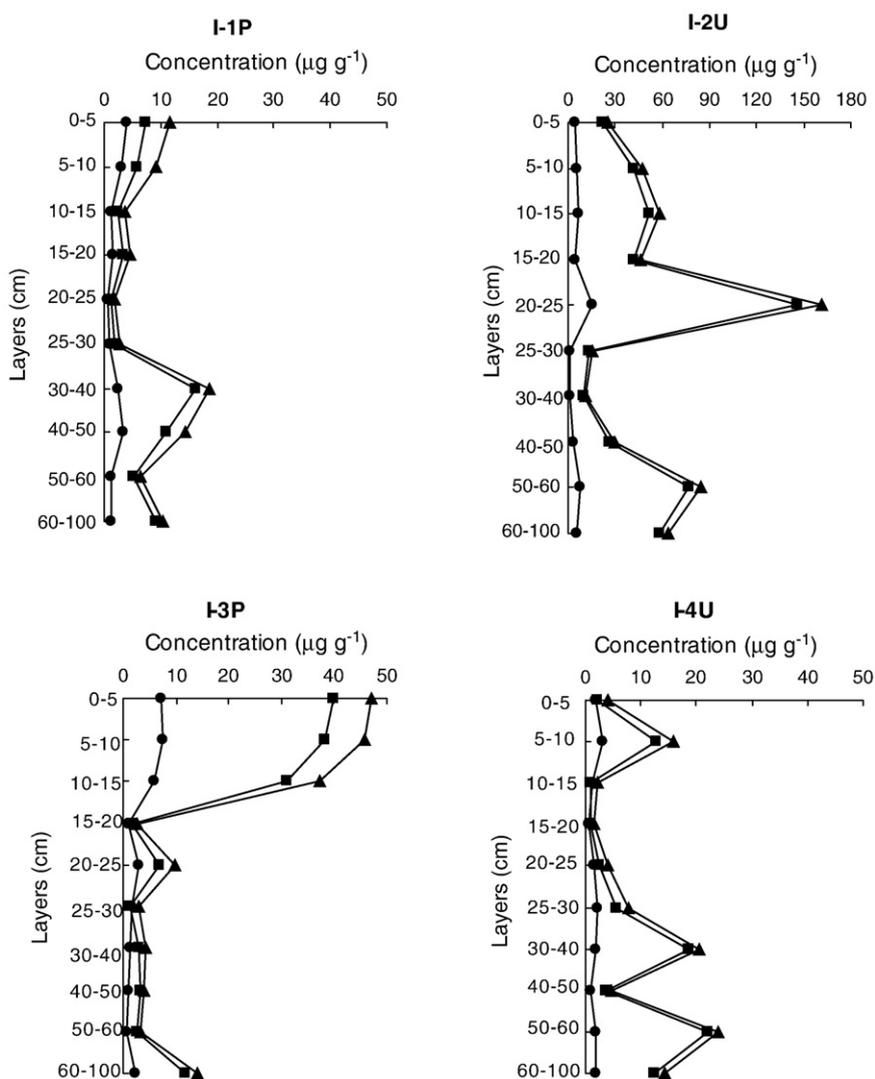


Fig. 2. The concentrations of Σn -alkanes, unresolved complex mixtures (UCM), and total aliphatic hydrocarbons (TAH) at different depths of eight profiles (I-1P, I-2U, I-3P, I-4U, I-5P, I-6U, I-7P, and I-8U).

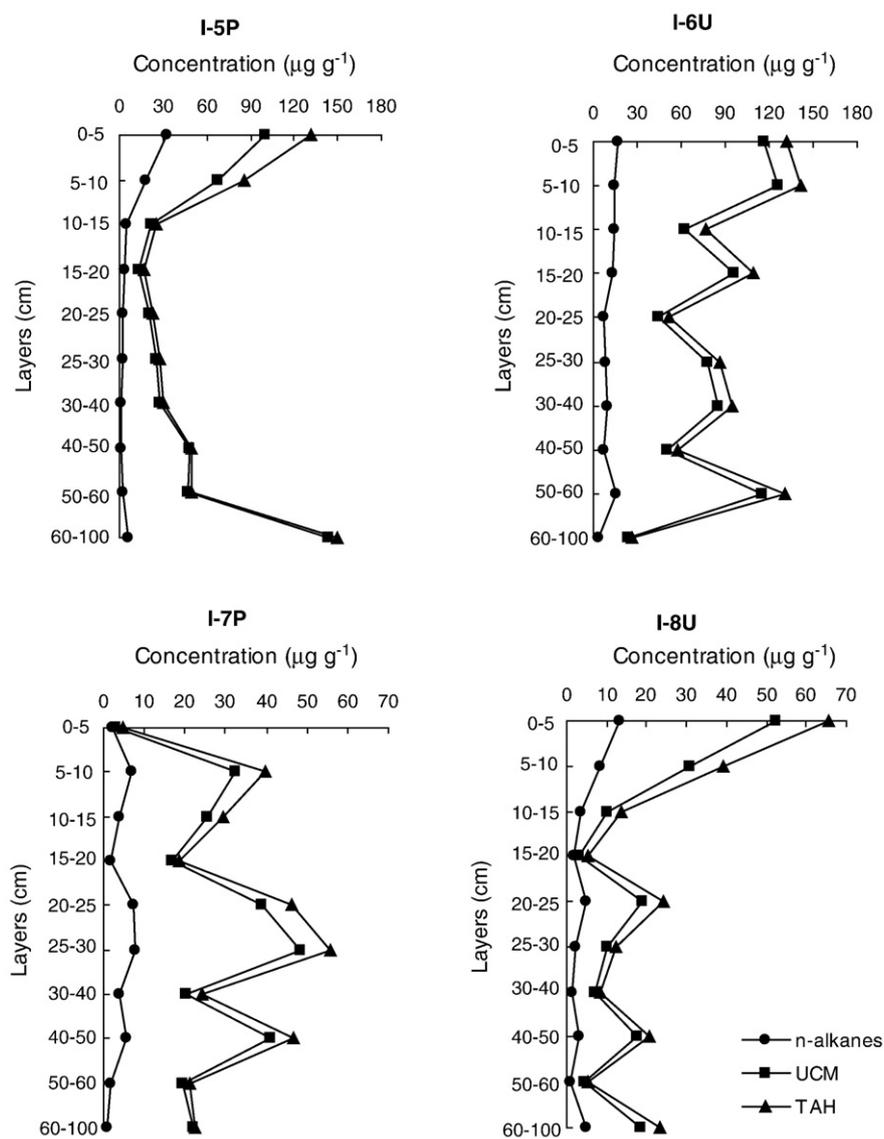


Fig. 2 (continued).

and decreased with the increase of depth, because the petroleum hydrocarbons continuously entered the soil through the atmospheric deposition.

The distribution in the layers below 5 cm at I-7P was similar to that at I-8U, both of which were due to long-term effect of its location relative to the Shenyang City. The quite low concentration in the layer 0–5 cm at I-7P was possibly due to washing by the treated water from the upper reach of the Xihe River approaching the 2008 Olympic Games. The differences of the water quality in the Xihe River resulted in the different concentrations and distributions between I-5P and I-7P.

The concentration of saturated hydrocarbons in Beijing was 1.5 to 54.1 $\mu\text{g g}^{-1}$, which decreased with depth within the top 30 cm and kept constant in the lower layers (He et al., 2008). In Tianjin, the hydrocarbon content in most samples was within 20 $\mu\text{g g}^{-1}$, and the maximum occurrence at the suburb area was 80 $\mu\text{g g}^{-1}$. The contents decreased with depth, which was identical to the distribution of PAHs in Hunpu (Bu et al., 2007; Xiao et al., 2008). The diesel range organics in soil varied from 0.2 to 4200 $\mu\text{g g}^{-1}$ at the three oil release sites at Big South Fork National River and Recreation Area, Tennessee and Kentucky, where the concentration of deep layer was higher compared with that of the shallow layer at some points (Williams et al., 2006).

3.3. Geochemical characteristics and source analysis of aliphatic hydrocarbons in the soil samples

The features of the determined geochemical indices were not consistent among the samples at different depths of the eight profiles (Table 2). The geochemical characteristics of I-1P and I-4U were similar. The C_{max} of soil above 30 cm at I-1P and above 25 cm at I-4U showed high carbon number, which suggested a low maturity (Scholz-Böttcher et al., 2009; Zhang et al., 2004). Low carbon number C_{max} elucidates that major hydrocarbons are from petroleum, while C_{max} higher than C_{27} means higher plants input (Aboul-Kassim and Williamson, 2003; Ye et al., 2007). Hexadecane and isoprenoid hydrocarbons were small in those samples, but they were mostly detected in petroleum hydrocarbons (Aboul-Kassim and Simoneit, 1995b; Medeiros and Bicego, 2004; Readman et al., 2002; Ye et al., 2007; Zhu et al., 2005). The ratio of UCM to the sum of n-alkanes (U/N) was also low. A U/N higher than 2 reflects a significant petroleum product contamination (Aboul-Kassim and Simoneit, 1995a; Harji et al., 2008). A separately revised CPI was selected to evaluate the contribution of biogenic hydrocarbons (Harji et al., 2008; Marzi et al., 1993; Zhu et al., 2005). High CPI was obtained and all characteristics confirmed that biogenic hydrocarbons were predominant.

Table 2
Distribution of geochemical indices of soil samples collected in Hunpu region.

Sites	Layers (cm)	U/ N	Isoprenoid $\mu\text{g g}^{-1}$ dry wt.		CPI			C_{max}	C_{16} ratio
			Pr	Ph	CPI _{13–35}	CPI _{13–22}	CPI _{23–35}		
I-1P	0–5	2	0	0	1.7	0.7	1.8	nC ₂₉	801
	5–10	2	0.01	0.02	1.5	0.8	1.7	nC ₃₁	977
	10–15	2	0.02	0	2.1	NA	2.1	nC ₃₁	NA
	15–20	2	0	0	1.7	NA	1.7	nC ₃₁	NA
	20–25	2	0	0	5.0	NA	4.5	nC ₂₇	NA
	25–30	2	0.002	0	3.0	3.3	2.9	nC ₁₂ , nC ₃₁	189
	30–40	7	0.20	0.15	1.2	1.2	1.2	nC ₁₆	7
	40–50	3	0.15	0.16	1.1	1.1	1.2	nC ₁₆	7
	50–60	5	0.003	0.008	2.0	2.3	1.7	nC ₁₁	196
	60–100	7	0.07	0.05	2.1	2.2	1.9	nC ₁₂	69
I-2U	0–5	5	0.09	0.08	1.8	1.5	2.1	nC ₁₃ , nC ₂₉	58
	5–10	8	0.25	0.28	1.8	1.3	2.8	nC ₁₃ , nC ₃₁	36
	10–15	8	0.42	0.21	2.2	1.5	5.0	nC ₁₂	25
	15–20	8	0.32	0.18	1.8	1.5	15.4	nC ₁₃	18
	20–25	10	1.66	1.17	1.4	1.3	5.2	nC ₁₃	13
	25–30	10	0.08	0.05	1.8	1.5	6.9	nC ₁₁	19
	30–40	9	0.09	0.08	1.4	1.1	27.5	nC ₁₁	16
	40–50	9	0.14	0.07	1.7	1.7	6.0	nC ₁₂	27
	50–60	10	1.79	1.19	1.2	1.1	1.8	nC ₁₅	7
	60–100	11	0.72	0.47	1.5	1.4	27.2	nC ₁₃	12
I-3P	0–5	5	0.08	0.05	1.8	1.5	2.0	nC ₃₁	78
	5–10	5	0.09	0.05	2.0	1.1	2.5	nC ₃₃	157
	10–15	5	0.15	0.10	2.3	1.6	3.0	nC ₁₉ , nC ₃₁	62
	15–20	2	0	0	6.2	NA	4.3	nC ₁₅ , nC ₃₆	NA
	20–25	2	0.01	0.07	1.4	1.0	1.8	nC ₃₁	801
	25–30	1	0	0	0.7	13.9	0.6	nC ₂₄	295
	30–40	2	0.03	0.12	3.0	2.4	3.7	nC ₁₉ , C ₃₁	NA
	40–50	4	0	0	3.1	3.2	3.0	nC ₁₁	NA
	50–60	4	0	0	0.9	0.3	6.9	nC ₂₀	NA
	60–100	5	0.08	0.07	1.0	0.9	1.5	nC ₁₆	7
I-4U	0–5	1	0.03	0.03	2.3	0.8	2.7	nC ₃₁	154
	5–10	4	0.08	0.09	1.6	1.1	2.1	nC ₁₉ , nC ₃₁	65
	10–15	1	0.07	0.004	2.4	3.5	2.3	nC ₃₁	NA
	15–20	2	0	0	3.2	NA	3.2	nC ₃₅	NA
	20–25	2	0.007	0.003	1.7	1.2	1.8	nC ₃₁	NA
	25–30	3	0.05	0.06	1.9	1.4	2.2	nC ₁₉ , nC ₃₁	71
	30–40	10	0.07	0.05	2.7	1.4	6.2	nC ₁₅ , nC ₃₁	17
	40–50	5	0.03	0.11	2.1	1.5	6.6	nC ₁₃ , nC ₃₆	31
	50–60	12	0.07	0.04	2.3	1.5	3.7	nC ₁₃ , nC ₃₁	93
	60–100	7	0.04	0.12	1.4	1.2	3.2	nC ₁₃	48
I-5P	0–5	3	0.13	0.18	1.3	0.9	1.4	nC ₃₁	233
	5–10	4	0.10	0.07	1.7	0.7	2.0	nC ₃₁	434
	10–15	5	0.06	0.03	2.5	1.7	2.9	nC ₃₁	203
	15–20	4	0.07	0	2.2	3.4	2.0	nC ₃₉	163
	20–25	7	0.09	0.05	2.3	1.6	2.9	nC ₁₂ , nC ₃₅	27
	25–30	11	0.13	0.04	2.4	2.0	2.7	nC ₁₅ , nC ₃₃	34
	30–40	16	0.18	0.12	2.4	2.3	2.8	nC ₂₁	291
	40–50	31	0.33	0.17	3.2	2.9	4.2	nC ₁₅	NA
	50–60	17	0.30	0.28	1.8	1.5	2.2	nC ₁₅	NA
	60–100	23	0.67	0.29	1.8	1.7	2.4	nC ₁₃	55
I-6U	0–5	7	1.06	0.76	1.6	1.4	2.6	nC ₁₃	12
	5–10	9	1.71	1.14	1.7	1.4	3.5	nC ₁₅	15
	10–15	4	0.81	0.78	1.3	1.1	1.8	nC ₁₆	9
	15–20	7	1.22	0.88	1.5	1.3	3.5	nC ₁₃	11
	20–25	6	0.71	0.67	1.4	1.2	2.5	nC ₁₅	10
	25–30	9	1.21	0.87	1.4	1.3	4.3	nC ₁₃	14
	30–40	8	0.89	0.67	1.6	1.5	2.3	nC ₁₃	19
	40–50	8	0.47	0.35	1.5	1.3	6.2	nC ₁₂	15
	50–60	7	1.64	1.82	1.2	1.0	2.6	nC ₁₃	16
	60–100	8	0.51	0.43	1.3	1.1	31.8	nC ₁₂	12

Table 2 (continued)

Sites	Layers (cm)	U/ N	Isoprenoid $\mu\text{g g}^{-1}$ dry wt.		CPI			C_{max}	C_{16} ratio
			Pr	Ph	CPI _{13–35}	CPI _{13–22}	CPI _{23–35}		
I-7P	0–5	2	0.04	0	2.2	2.9	2.1	nC ₃₁	971
	5–10	5	0.04	0.03	2.5	2.0	2.8	nC ₃₃	138
	10–15	7	0.07	0.05	1.5	1.3	1.7	nC ₁₉ , nC ₂₉	85
	15–20	10	0.02	0	4.0	1.7	6.1	nC ₃₁	19
	20–25	5	0.26	0.35	1.6	1.1	1.8	nC ₃₁	24
	25–30	6	0.36	0.37	1.4	1.1	1.6	nC ₃₁	21
	30–40	5	0.14	0.12	1.7	1.2	2.0	nC ₃₁	20
	40–50	7	0.76	0.52	1.3	1.2	1.5	nC ₁₅	13
	50–60	10	0.21	0.20	1.8	1.4	3.7	nC ₁₇ , nC ₃₁	11
	60–100	28	0.08	0.01	5.6	3.3	NA	nC ₁₅	75
I-8U	0–5	4	0.26	0.19	1.5	1.4	1.6	nC ₃₁	40
	5–10	4	0.08	0.04	1.2	1.5	1.1	nC ₃₉	172
	10–15	3	0.02	0.02	1.4	3.0	1.3	nC ₃₃	137
	15–20	2	0.01	0	1.8	10.6	1.7	nC ₃₁	433
	20–25	4	0.02	0	1.7	2.1	1.7	nC ₃₁	490
	25–30	5	0.07	0.05	2.3	1.3	2.9	nC ₃₃	20
	30–40	5	0.04	0.004	4.4	4.6	4.3	nC ₃₁	350
	40–50	5	0.12	0.10	1.9	1.2	2.5	nC ₃₁	17
	50–60	4	0	0	3.7	1.7	4.6	nC ₃₁	NA
	60–100	4	0.16	0.08	2.3	1.2	2.9	nC ₃₁	18

Indices included: U/N, the ratio of unresolved complex mixture to the sum of n-alkanes; Pr, pristane; Ph, phytane; CPI_{13–35}, odd to even carbon preference index from C₁₃ to C₃₅; CPI_{13–22}, odd to even carbon preference index from C₁₃ to C₂₂; CPI_{23–35}, odd to even carbon preference index from C₂₃ to C₃₅; C_{max} , the n-alkane with maximum concentration; C_{16} ratio, the ratio of the sum of all n-alkanes to hexadecane.

NA: not analyzed

$$CPI = \frac{\left(\sum_{i=n}^m C_{2i+1} \right) + \left(\sum_{i=n+1}^{m+1} C_{2i+1} \right)}{2 \times \left(\sum_{i=n+1}^{m+1} C_{2i} \right)}$$

However, the soil below had a low carbon number C_{max} and U/N was 3–12. Higher concentrations of isoprenoid hydrocarbons and lower C_{16} ratio were also detected. CPI_{13–22} and CPI_{23–35} were 1.1–2.3 and 1.2–6.6, respectively. These suggested that different degrees of petroleum pollution existed. The layers 30–40 and 40–50 cm of I-1P were similar with the petroleum-polluted sediments from the Chubut River (Commendatore and Esteves, 2004).

According to the geochemical indices of I-3P, the aliphatic hydrocarbons in the top 15 cm soil showed some degree of petroleum pollution. The composition of hydrocarbons in the bottom layer was similar to petroleum, but not with the other soil layers.

I-2U and I-6U were typical petroleum-contaminated sites. They were rich in low carbon number hydrocarbons and poor in high carbon number hydrocarbons except the top two soil layers of I-2U, which was also displayed by C_{max} . Both the low carbon number C_{max} and high carbon number C_{max} existed in the top 10 cm soil of I-2U, whereas C_{max} showed low carbon number in other samples. The concentrations of UCM and isoprenoid hydrocarbons were high, and all the U/N was over 4. The C_{16} ratio was generally around 15, which indicated hydrocarbons from petroleum source; relatively, the value was up to 50 for biogenic hydrocarbons (Colombo et al., 1989; Harji et al., 2008; Tran et al., 1997). CPI_{13–22} ranged from 1.0 to 1.7, while CPI_{23–35} ranged from 1.8 to 31.8. The results indicated that the low carbon number hydrocarbons were mainly from petroleum, whereas the high carbon number hydrocarbons received more hydrocarbons from the higher plant wax.

For I-5P, the aliphatic hydrocarbons were composed of rich heavy hydrocarbons and small light hydrocarbons in the top 10 cm soil. Gas chromatogram showed a big hump in heavy hydrocarbons, a feature of heavy oil pollutants (Colombo et al., 1989; Hegazi et al., 2004;

Scholz-Böttcher et al., 2009) or weathered oil (Cripps, 1989). UCM from nC₂₂ to nC₃₃ and C_{max} between nC₂₂ and nC₃₃ were also found in sediments affected by industrial effluents in Kuwait and Daliao River watershed, China, respectively (Beg et al., 2003; Guo et al., 2007).

Thus, we deduced that I-5P was impressed by irrigation water from Xihe River which contained industrial effluents. The measured geochemical indices also showed an oil input. The concentration decreased dramatically from 10 to 20 cm and the characteristics of oil became less evident. The indices at the layers 20-30 cm revealed petroleum input. U/N of 30-60 cm was quite high, although CPI and the C₁₆ ratio did not present obvious characteristics of petroleum. U/N over 5 showed significant input of degraded petroleum products (Damas et al., 2009). Therefore, contamination could have been a period of time ago. Reversely, the layer 60-100 cm contained rich light hydrocarbons and a big hump located at low carbon number part, and geochemical analysis indicated a contamination of light oil, which resembled the pattern of I-2U and I-6U.

Geochemical indices showed that the layer 0-5 cm of I-7P was dominated by biogenic hydrocarbons; however, petrogenic hydrocarbons gradually became predominant as the depth increased. Soil at 15-60 cm was obviously contaminated by petroleum, and the bottom soil was affected by degraded petroleum products. Compared to I-7P, layer 0-5 cm of I-8U was contaminated by petroleum. From 0 to 20 cm, the features of petroleum gradually disappeared with the increase of depth, but some characteristics of petroleum appeared in the soil below.

3.4. PCA and RDA analysis of n-alkanes, UCM, and isoprenoid hydrocarbons of soil samples

For PCA, the percentage variances of the aliphatic hydrocarbons explained by the first and second axes were 69.9 and 18.8, respectively (the cumulative percentage variance explained by the two axes was 88.7). The hydrocarbons from different sources were differentiated by PCA (Fig. 3). Low carbon number n-alkanes, Pr, Ph and UCM collectively defined the first axis which represented hydrocarbons mainly from

petroleum pollution, while high carbon number n-alkanes assembled and defined the second axis which represented hydrocarbons dominated by higher plants or heavy oil.

The compositions of aliphatic hydrocarbons of different paddy fields as well as those of the different upland fields were not consistent (Fig. 4). The eighty samples had three main composition patterns: first, the high carbon number n-alkanes and UCM concentrations of the samples were quite high, while the low carbon number n-alkanes concentration was low (grouped in the first quadrant of Fig. 4); second, for the samples in the second or third quadrant, the concentrations of all aliphatic hydrocarbon components were low showing the pattern of I-1P and I-4U (samples presented by up-triangle symbols in Fig. 4) with minor or no contamination; third, in the fourth quadrant, the low carbon number n-alkanes, Pr, Ph, and UCM of the samples were all rich, and most samples of I-2U and I-6U (samples presented by star symbols) had this pattern because both were affected by nearby oil wells. I-3P and I-8U (samples presented by right-triangle symbols) contained two patterns: the top soil had the first pattern, while 15-100 cm of I-3P and 10-100 cm of I-8U had the second one. The samples at I-5P and I-7P (samples presented by circle symbols) were affected by wastewater-irrigation and basically belonged to the first pattern group.

The cumulative percentage variance of the aliphatic hydrocarbons explained by the measured soil basic properties in the RDA was 23.5 (four axes). The percentage variances explained by the first and second axes were 17.4 and 5.7, respectively. Unrestricted permutation under a reduced model result showed that the aliphatic hydrocarbon composition had highly significant correlation with sand content (P = 0.002) and pH value (P = 0.006), while the correlations between the aliphatic hydrocarbons and the other soil properties were not significant. The variances explained by sand content and pH value were 14% and 6%, respectively. In Fig. 5, it was found that the low carbon number n-alkanes, Pr, Ph, and UCM had a negative correlation with sand while having a positive correlation with fine materials (silt and clay). This meant that the soil composed of high silt and clay could potentially contain more oil or hydrocarbon than sandy soil, which was consistent with the findings of Colombo et al. (1989) and Abdullah (1997). Commendatore and Esteves (2004) did not find any correlation between fine fraction and OM or TAH. Early research also reported that n-alkanes, especially terrestrial hydrocarbons were related with coarse fraction, but UCM was related with finer

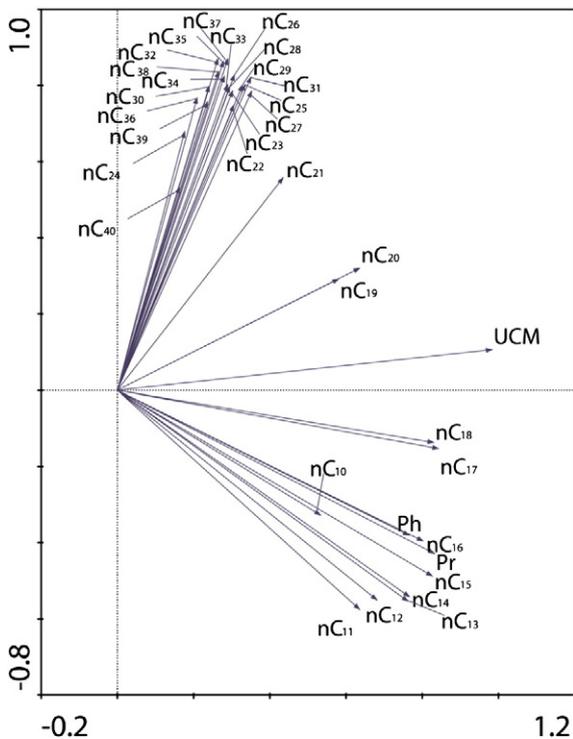


Fig. 3. Scatter plot of aliphatic hydrocarbons (AHs, included: n-alkanes (nC₁₀ to nC₄₀), phytane (Ph), pristane (Pr), and UCM) from PCA analysis.

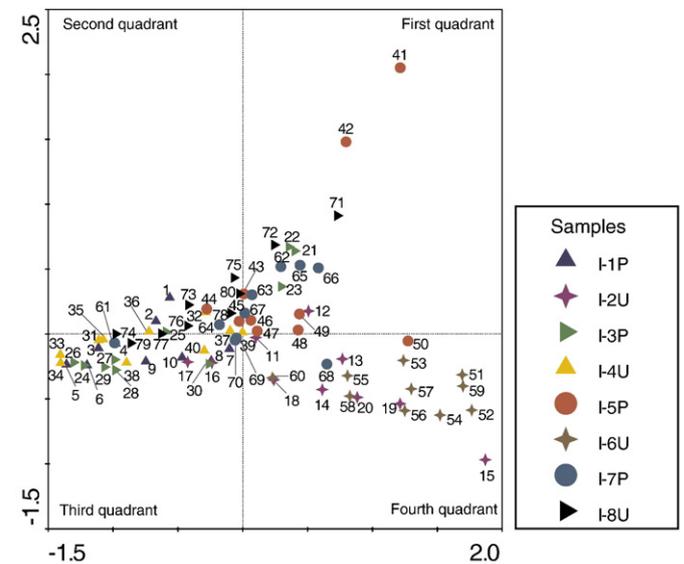


Fig. 4. Scatter plot of soil samples from PCA analysis. Samples were classified according to sampling sites (samples from top to bottom, each sites were labeled with consecutive indices).

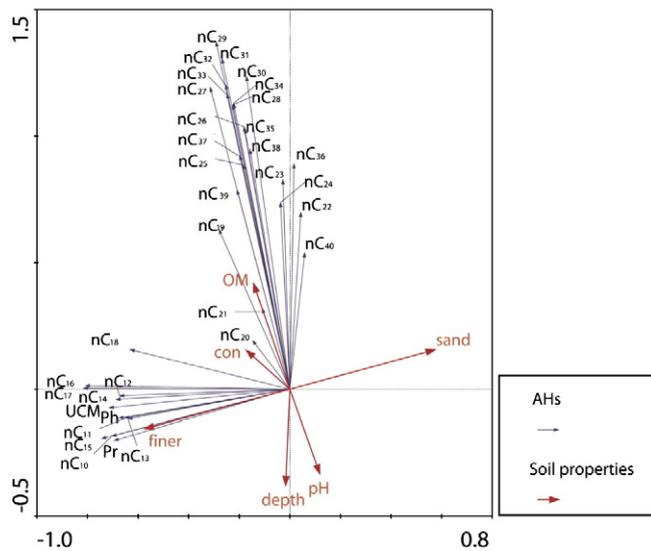


Fig. 5. Biplot of aliphatic hydrocarbons (AHs) and soil properties from RDA analysis. AHs included: n-alkanes (nC₁₀ to nC₄₀), phytane (Ph), pristane (Pr), and UCM. Soil properties included: sand content, sand; total content of silt and clay, finer; organic matters, OM; pH; conductivity, con; depth.

particles (Readman et al., 2002). High carbon number n-alkanes had a positive correlation with sand and OM. Nonpolar organic pollutants were considered to be absorb on OM when clay content of soil was low (Moreda et al., 1998).

The eight sample sites were divided into two main clusters by RDA (Fig. 6): I-5P, I-6U, I-7P, and I-8U near the Xihe River canal, deep soil at I-1P assembled on the left (the first cluster), and I-2U, I-3P, I-4U and upper layers at I-1P near the main canal clustered on the right (the second cluster). This was obviously different from the result from PCA, which meant that the pollution source rather than the soil properties determined the aliphatic hydrocarbon composition in soil. Compared to the second cluster, the soil from the Xihe River canal was finer and the differences between the upland and paddy fields were better observed. The conductivity of the upper layers of soil near the Xihe River canal was relatively higher. These differences suggested that the soil properties could be affected by pollutants. For all samples, pH increased with depth, but the content of organic matter

declined. The measured soil properties and hydrocarbon compositions determined in deep soil of the eight profiles were similar, which indicated that the upper horizon soil was easily impressed by environment and human activities.

4. Conclusions

The result from the concentration analysis agreed with that from the geochemical analysis, which was successfully visualized by PCA and RDA. The soil from I-2U and I-6U (with nearby oil wells still operating or abandoned) had rich hydrocarbons (\sum n-alkanes: 1.1–16.4 $\mu\text{g g}^{-1}$ dry wt. and TAH: 10.9–161.2 $\mu\text{g g}^{-1}$ dry wt.), obvious characteristics of petroleum hydrocarbons, and were grouped together by PCA. The hydrocarbon concentrations of the samples from I-5P was also high (\sum n-alkanes: 1.6–32.2 $\mu\text{g g}^{-1}$ and TAH: 16.7–149.7 $\mu\text{g g}^{-1}$) and displayed oil contamination led by irrigation with wastewater from the downriver of the Xihe River. The hydrocarbon concentrations of I-7P and I-8U, which were affected by the industrial city of Shenyang, were medium (\sum n-alkanes: 0.8–13.1 $\mu\text{g g}^{-1}$ and TAH: 5.0–65.6 $\mu\text{g g}^{-1}$) and had certain characteristics of petroleum contamination. I-5P and I-7P were grouped together because of wastewater irrigation. Another group contained I-1P and I-4U (\sum n-alkanes: 0.5–4.0 $\mu\text{g g}^{-1}$ and TAH: 1.6–23.8 $\mu\text{g g}^{-1}$), which had a small hydrocarbons. Biogenic hydrocarbons dominated in most samples and no obvious pollution source was detected. I-8U was affected by atmospheric deposition and I-3P had a similar pattern. The result from RDA indicated that the hydrocarbon compositions were also impacted by the soil properties. The differences between the results from PCA and those from RDA also suggested that the hydrocarbon composition was mainly determined by the pollution sources.

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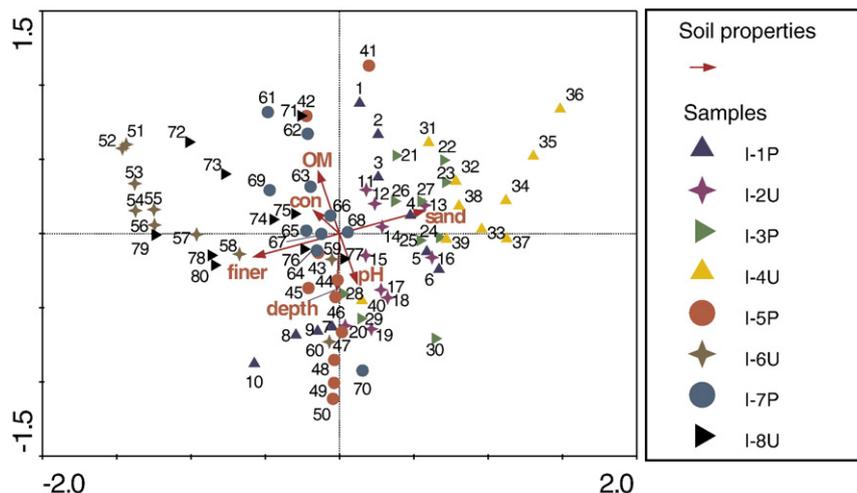


Fig. 6. Biplot of soil properties and soil samples from RDA analysis. Soil properties included: sand content, sand; total content of silt and clay, finer; organic matters, OM; pH; conductivity, con; depth. Samples were classified according to sampling sites (samples from top to bottom, each sites were labeled with consecutive indices).

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