Occurrence of Aliphatic Hydrocarbons in Water, Suspended Particulate Matter and Sediments of Daliao River System, China

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Abstract In August of 2005 a study was carried out to evaluate contamination of aliphatic hydrocarbons(AHc) in water, suspended particulate matter (SPM) and sediments from Daliao River system composed of the Hun River, Taizi River, and Daliao River in a heavy industrial area of northeast of China. The content of AHc ranged from 13.39 to 283.62 $\mu g \ L^{-1}$ in surface water, from 22.68 to 5,725.36 $\mu g \ g^{-1}$ in dry SPM, and from 61.37 to 229.42 $\mu g \ g^{-1}$ in dry sediments. High hydrocarbon levels were generally found in the areas associated with high anthropogenic impact and port activities. The calculated hydrocarbon indexes suggest that the stations with petrogenic sources and biogenic origin predominance would constitute aliphatic hydrocarbons for the river system. Hierarchical cluster analysis (HCA) of aliphatic hydrocarbons is correspondence with hydrocarbons indexes results.

Keywords Aliphatic hydrocarbons · Water · Sediments · Daliao river system

Aliphatic hydrocarbons (AHc) are complex mixtures in both composition and molecular structure, mostly originated from crude oil. AHc contain a wide range of chemical products such as gasoline, kerosene, fuel oil, jet oil, heavy oil and lubrication oil. AHc can be environmental polluting agents of risk for ecosystems and human pollution health. Pollution of the river by petroleum hydrocarbons occurs mainly through man's activities and sources such as oil operation, petroleum transport, harbor activities, wastewater discharge, atmospheric fallout, natural seepage, biogenic origin, etc. (Commendatore and Esteves 2004). Out of these, about 65.2% is discharged through municipal and industrial wastes, urban and river runoffs, oceanic dumping and atmospheric fallout; 26.2% derives from discharges during transportation, dry docking, tanker accidents, de-blasting, etc.; and remaining 8.5% comes from fixed installations like coastal refineries, offshore production facilities, marine terminals, etc. (GESAMP 1993). Though a considerable fraction of petroleum hydrocarbons entering the water environment is removed by evaporation, a portion gets distributed in water, accumulated in sediment and transferred to biota (Chouksey et al. 2004).

The area of Daliao river system is prone to oil pollution due to voluminous releases of effluents from a variety of industries including refineries and petrochemical complexes, and indiscriminate release of untreated or partially treated sewage. Previous researches indicated that the parts of Hun River at Fushun and Shenyang, the parts of Taizi River at Benxi and Liaoyang, and the part of Daliao River at Yingkou were subjected to severe pollution by organics, such as COD, petroleum and volatile hydroxybenzene (Chen 2001; Wang et al. 2003; Xing et al. 2004). In the past, investigation on water quality of Daliao River system was concentrated mostly on petroleum pollution gross control (Jia and Ju 1999). Although the significance of the Daliao River system as a water source in the Liaoning province, no studies have yet evaluated hydrocarbons concentrations throughout the area from water, SPM and sediment. The goals of this paper were to assess the extent of modified AHc contamination of water, SPM and surface sediments of the Daliao River area and to determine their possible sources using n-alkane distribution indices.

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Materials and Methods

The sampling sites are shown in Fig. 1. 16 water and SPM samples and 12 sediment samples were collected from the Hun River, Taizi River and Daliao River in flood season on August 2005. Subsurface water samples at 0.5 m depth were collected using 6 L pre-cleaned dark glass bottles. All water samples were transported to the laboratory immediately, and stored in the refrigerator at 4°C before analysis. Water samples were filtrated through partial four fluorin ethylene (PFFE) filters (0.45 μm, $d = 50$ mm, Millipore, USA) to separate SPM. SPM samples were placed directly into pre-cleaned aluminum pot and transported to the laboratory. Surface sediment (0–20 cm) samples were collected by using grab sampler (Van Veen bodemhappe 2 L) and put in aluminium containers. The SPM and sediments samples were kept in the refrigerator at −20°C before analysis.

Filtered water samples (5 L) were extracted using a solid-phase extraction (SPE) system. The water was spiked with 5 mL 5α-cholestane as a surrogate standard prior to extraction. The Supelco SPE cartridges were first washed with 5 mL of dichloromethane, then conditioned with 5 mL of methanol followed by 5 mL of deionised water. 5 L water sample was passed through the cartridges at a flow rate of 5 mL/min under vacuum. The extracts were eluted with 10 mL (2, 3, 5) dichloromethane (DCM) at a rate of 2 mL/min. Fifteen grams of freeze-dried sediment (FD-1A, China) was spiked with 1 mL 5α-cholestane as a surrogate standard, and Soxhlet extracted with 250 mL dichloromethane/hexane (1:1, v/v) for 24 h in a water bath maintained at 60°C (Tolosa et al. 2004). 2 g of activated copper powder was added to eliminate elemental sulphur. The extract was concentrated in a rotary evaporator, and further reduced to ∼1 mL under gentle nitrogen flow and then transferred to a 2 mL amber vial before cleanup. SPM also has the same extraction procedure as sediments. According to sampling condition of SPM, analytical weight ranged from 0.1 to 3 g.

The extract of water, SPM and sediment samples passed to a 1:2 alumina/silica gel glass column with 1 g anhydrous sodium sulfate overlaying the silica gel for clean-up and fractionation. The aliphatic hydrocarbons were eluted with 15 mL of hexane and were concentrated to 0.5 mL Known quantities of $n-C_{24}D_{50}$ as internal standard (10 μL) were added to the sample prior to instrumental (GC/FID) analysis. AHc were analyzed using a Varian 3800 GC/FID with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 column (J&W Co., USA). The temperature was programmed from 50 (hold for 2 min) to 290°C at 6°C min^{-1} and was then maintained at 290°C for 15 min. Hydrogen was used as the carrier gas at a flow of 1.2 mL/mim. All data were subject to strict quality control procedures. The mean recovery of 5α-cholestane for water sample was 86.66% ± 7.25% (n = 6), and for sediment sample was 83.34% ± 9.49% (n = 6), respectively. The detection limit of method (MDL) ranged from 1.3 to 3.1 ng L^{-1} for water samples, and ranged from 0.79 to 4.82 ng g^{-1} for sediment and SPM samples. Spiked samples in each set of 15–20 samples were analyzed with mean recoveries ranging from 69.42% to 114.40%.

Sub-samples were used to determine physicochemical properties including total organic carbon (TOC) and SPM contents for water (Gustafson and Dickhut 1997), and TOC and silt–clay for sediment (Shi et al. 2005). The results are shown in Table 1. Statistical product and service solutions software (SPSS 11.0) was used to understand the distribution of AHc compounds in water and sediment. Hierarchical cluster analysis (HCA) was used to better understand the AHc composition and sources.
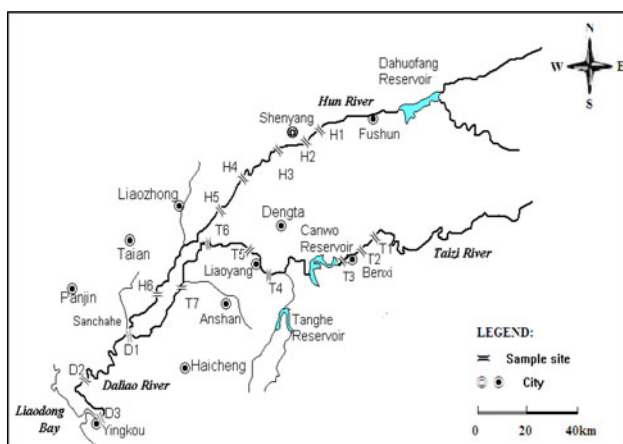
Results and Discussion

The aliphatic hydrocarbon (AHc) fraction of the surface water showed a variable distribution (Fig. 2a). The concentrations of total Alk ranged from 6.95 to 33.74 μg/L, UCM ranged from 3.63 to 276.03 μg/L, and AHc ranged from 13.39 to 283.62 μg/L in surface water. In the Hun River, the higher value of AHc were 227.42 μg/L at site H2 and 283.62 μg/L at site H3, which may be influenced by the water quality due to receiving some sewage from Shenyang city. The concentration gradually decreased to 85.92 ng L^{-1} at H6, due to the dilution of river water. In the Taizi river, the higher value of AHc were 95.86 μg/L at site T1, 88.23 μg/L at site T2 and 117.72 μg/L at site T3 located in the upstream of Taizi River near Benxi Steel Company. In the Daliao River, the pollution was mainly

Fig. 1 The study areas and sampling locations in the Daliao River watersystem, China

Table 1 Physicochemical properties and evaluation indices of AHc in water SPM and surface sediment of Daliao River watershed, China

Station	TOC[a] mg/L	TOC[b] %	Clay %	LMW/HMW			Pri/Phy			UCM/Alk		
				Water	SPM	Sediment	Water	SPM	Sediment	Water	SPM	Sediment
H1	18.33	0.88	30.25	0.68	0.23	0.16	0.73	0.72	0.53	0.73	0.06	3.38
H2	15.43	0.68	32.05	0.56	0.68	0.06	0.89	0.54	0.67	7.67	4.04	4.92
H3	15.84	NC	NC	1.06	0.12	NC	0.40	0.73	NC	36.36	1.73	NC
H4	18.51	1.16	33.41	0.19	0.13	0.05	0.34	2.44	2.44	5.67	2.42	6.18
H5	66.20	0.15	48.67	0.19	0.94	0.09	0.48	0.55	0.67	3.63	5.00	4.64
H6	36.09	0.69	39.43	1.17	0.11	0.06	0.76	0.55	0.72	1.72	3.64	6.69
T1	22.48	2.60	24.97	0.29	0.82	0.06	0.83	0.59	0.77	2.30	0.90	4.14
T2	14.82	0.41	27.88	0.42	0.61	0.03	0.96	0.49	0.80	3.91	3.55	3.76
T3	27.31	NC	NC	1.16	0.33	NC	0.78	0.60	NC	5.00	4.39	NC
T4	14.55	0.88	30.96	0.34	0.52	0.03	0.64	0.80	0.85	1.14	4.66	3.51
T5	48.17	0.70	29.53	0.07	0.56	0.06	0.61	0.54	0.70	0.20	4.24	4.71
T6	62.74	NC	NC	1.45	0.48	NC	ND	0.79	NC	0.37	4.39	NC
T7	17.55	NC	NC	1.29	0.77	NC	1.03	0.55	NC	0.13	4.62	NC
D1	36.29	2.56	34.87	0.28	0.71	0.05	1.04	0.54	0.57	1.77	4.36	4.11
D2	39.84	0.41	42.22	0.25	0.18	0.03	1.49	0.07	0.66	0.46	1.28	4.32
D3	17.77	0.86	82.01	0.11	0.10	0.04	0.65	0.76	0.57	0.77	3.30	4.46

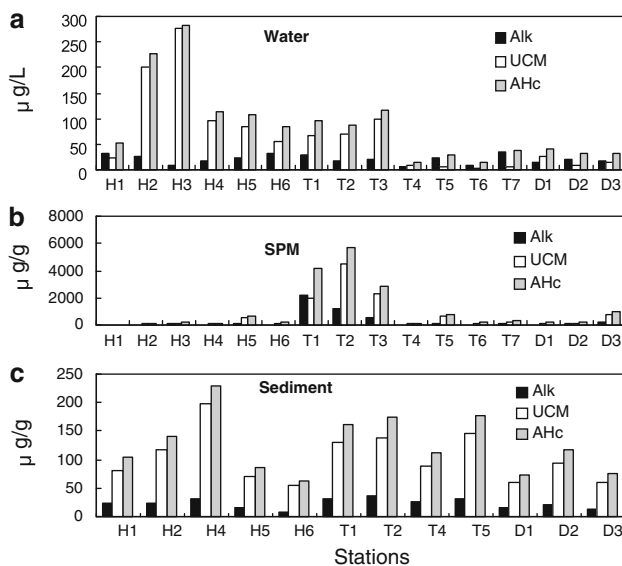*NC* not collected, *ND* not detected

[a] Water

[b] Sediment

Fig. 2 Aliphatic hydrocarbon concentrations in water, SPM and sediment from Daliao River system

from the upper Hun River and Taizi River, and some city wastewater from Anshan city. The higher value of AHc were 40.41 μg/L at site D1.

AHc fraction of the SPM also showed a variable distribution (Fig. 2b). The concentrations of total Alk ranged from 18.91 to 2,179.34 μg/g dry weight, UCM ranged from 1.35 to 4,467.74 μg/g dry weight, and AHc ranged from 22.68 to 5,725.36 μg/g dry weight in SPM. In the Hun River, the highest value of AHc were 621.80 μg/g at site H5, In the Taizi river, the higher value of AHc were 4,143.87 μg/g at site T1, 5,725.36 μg/g at site T2 and 2,889.13 μg/g at site T3 located in the upstream of Taizi River near Benxi Steel Company. Similar trend was found in the Taizi River in comparison with the distribution of AHc in surface water. In the Daliao River, the higher value of AHc were 1,015.22 μg/g at site D3. Port activities are the main source of hydrocarbon contamination (Commendatore et al. 2000).

AHc fraction of the sediment showed different distribution of resolved components Alk and UCM in comparison with water and SPM samples (Fig. 2c). Hydrocarbon values were high in all sites. According to UNEP (1992), hydrocarbon concentrations in heavy polluted sediments are greater than 10 μg/g dry weight, which can be caused by industrial and harbor activities. The concentrations of total Alk ranged from 7.98 to 36.47 μg/g dry weight, UCM ranged from 53.39 to 197.46 μg/g dry weight, and AHc ranged from 61.37 to 229.42 μg/g dry weight in sediment. In the Hun River, the highest value of AHc was 229.42 μg/g at site H4. In the Taizi river, the high value of AHc (>162.0 μg/g) were at sites T1 and T2 located in the upstream of Taizi River near Benxi Steel Company and site T5 located in the midstream of Taizi River near Liaoyang Petroleum chemistry & Engineering Company. Similar trend was found in the Taizi River in comparison with the

distribution of AHc in surface water and SPM. In the Da-liao River, the higher value of AHc were 116.64 μg/g at site D2. It was reported that site D2 was used as a port in the past. The distribution of AHc, UCM and Alk were different from water and SPM samples, due to river water receiving direct petroleum pollutants inputs from various sources, and sediment indicating contamination in the past.

The composition and distribution patterns of the individual Alk in the water were plotted for the three sites (H2, H6, T7) that had the highest concentrations of total Alk (Fig. 3a). It appears for sites H6 and T7, the concentrations of C9 to C11 hydrocarbons were higher concentration. In comparison, the water Alk observed at sites H2 were more concentration in Alk with a chain length C29. The patterns in SPM were plotted for the three sites (T1, T2, T3) that had the highest concentrations of total Alk (Fig. 3b). It appears for three sites, the concentrations of C15 to C29 hydrocarbons were higher concentration. The most dominant compound found in both SPM was C27 (Fig. 3b). The patterns in sediments were plotted for the three sites (H4, T1, T2) that had the highest concentrations of total Alk (Fig. 3c). It appears for three sites, the concentrations of C23 to C33 hydrocarbons were higher concentration. The dominant compound found in both sediments was C25, C27, C29, C30 (Fig. 3c). A abroad carbon numbers distribution was observed in water and SPM samples, but high molecular weight hydrocarbons distribution was found in sediment samples relatively. For all water and sediments, a clear odd to even carbon predominated distribution pattern
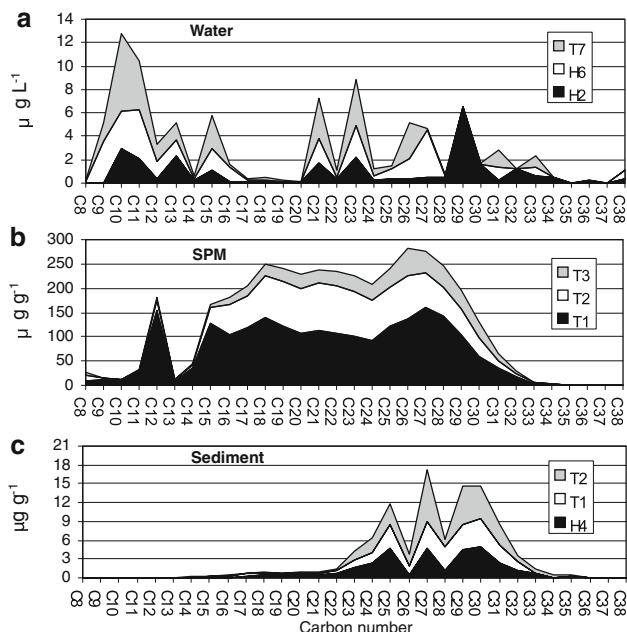
was seen, the same as what has been observed in many coastal sediments where the main inputs come from terrestrial plant organic matter (Volkman et al. 1992).

In this study, the relationship between the concentrations of AHc and Alk with TOC has been analyzed. No correlation between total AHc and Alk concentration and TOC in water characteristic ($r_{TOC} = -0.322$ and $r_{TOC} = -0.022$, $p > 0.05$, n = 16). In sediment samples, no correlations were found between AHc and Alk with TOC ($r_{TOC} = 0.036$ and $r_{TOC} = 0.053$, $p > 0.05$, n = 12), and negative correlation was found between AHc and Alk with clay-silt% ($r_{clay-silt\%t} = -0.501$, $p > 0.05$; $r_{clay\%t} = -0.589$, $p > 0.05$, n = 12). Our study suggested that the distribution and concentrations of AHc and Alk in water and sediment would be determined more by direct input and the lack of association between hydrocarbon concentrations with TOC and clay-silt% in samples. Similar result has been studied (Commendatore and Esteves 2004).

LMW/HMW indices ranged from 0.07 to 1.45 for water samples, from 0.1 to 0.94 for SPM samples and from NC to 0.16 for sediments (Table 1). The ratios presented values (<1) indicating petroleum and terrigenous inputs in most stations (Zakaria et al. 2000), other than sites H6, T3, T6, T7 (LWM/HWM > 1) water samples including algae and plankton hydrocarbon inputs. In addition, the values of LWM/HWM for water and SPM was higher than those of sediments, which suggested low molecular weight hydrocarbons of petroleum contaminations entering the water environment were reduced by degradation and weathering, and high molecular weight hydrocarbons were reserved and mineralized in sediment for being degraded difficultly relatively. The UCM/Alk ratio ranged from 0.06 to 36.36 (Table 1). According to the ratios in water and SPM, the widespread presence of important petroleum related residues and inputs from petroleum and chemistry industrial area along the river. For sediments, the high value of UCM/Alk (>4) in many stations would indicates important biodegradation of petroleum related inputs (Simoneit 1982). Alternatively, a relatively low value at stations H1, T2 and T4 near the Fushun and Liaoyang petroleum company can be indicative of recent inputs.

Pristane and phytane are products of geologic alteration of phytol and are often used as good indicators of petroleum contamination and depositional environment (Readman et al. 2002). In the study, most stations additionally at D2 (waters ample) and H4 (SPM and sediments), the pristine to phytane ratios were less and close to 1 reflecting petroleum contamination (Broman et al. 1987; Table 1). There were some degree biogenic hydrocarbons inputs for stations D2 and H4. In addition, phytane occurs in reducing conditions and pristine occurs in oxidizing conditions in sediments, which originate from lipids of zooplankton and bacteria (Volkman et al. 1992). The value of Pri/Phy in
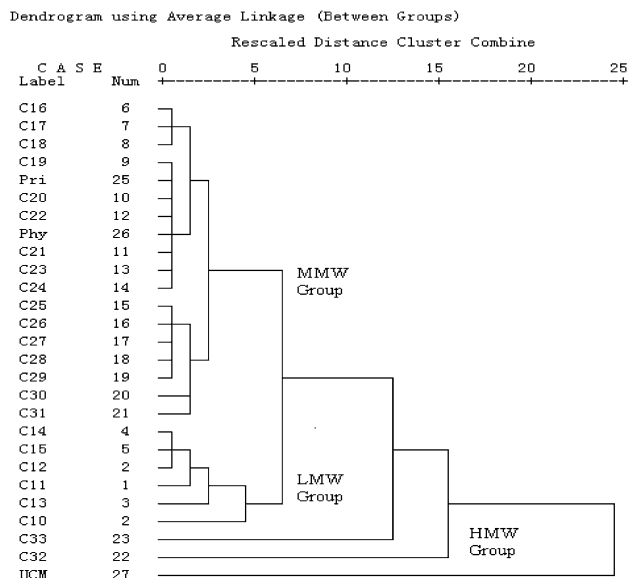

Fig. 3 Distribution of individual Alk in the water, SPM and sediments of the three sites that had the highest n-alkane concentrations

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Dendrogram using Average Linkage (Between Groups)
                    Rescaled Distance Cluster Combine
   C A S E        0         5        10        15        20        25
  Label   Num    +---------+---------+---------+---------+---------+
  C16       6
  C17       7
  C18       8
  C19       9
  Pri      25
  C20      10
  C22      12
  Phy      26
  C21      11
  C23      13                    MMW
  C24      14                    Group
  C25      15
  C26      16
  C27      17
  C28      18
  C29      19
  C30      20
  C31      21
  C14       4
  C15       5
  C12       2
  C11       1                    LMW
  C13       3                    Group
  C10       2
  C33      23
  C32      22                             HMW
  UCM      27                             Group
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Fig. 4 Dendrogram of cluster analysis for hydrocarbons composition. *MMW* medium molecular weight, *LMW* low molecular weight, *HMW* high molecular weight

sediment samples also indicated an anaerobic reducing depositional environment in Daliao river system sediment.

The relationship between the hydrocarbons composition patterns was further analysed for all samples using hierarchical cluster analysis. To remove the effect of dimension on the component in different environmental media, the data were standardized before HCA. In addition, to unify the contaminants of hydrocarbons detected in samples, the data of the lower molecular weight hydrocarbons (C_{8-9}) and the higher molecular weight hydrocarbons (C_{34-38}) were discarded. The dendogram (Fig. 4) shows the results of applying the between-groups linkage aggregation strategy for all the samples. In a dendrogram, the results of cluster analysis showed that five cluster present four source categories. The first category presenting medium molecular weight (MMW) hydrocarbons ranged from C_{16} to C_{31}, which could be explained by the contribution of terrestrial plants and riverine algaes and widespread petroleum contamination. The second category presenting low molecular weight (LMW) hydrocarbons ranged from C_{10} to C_{15}, which could be explained by the contribution of fresh oil inputs. The third category presenting high molecular weight (HMW) hydrocarbons ranged from C_{32} to C_{33}, which could be explained by the contribution of terrestrial high level plants. The fourth category presenting UCM could be explained by the contribution of petrogenic hydrocarbons and weathering of the oil residues. According to the relationship between hydrocarbon source and hydrocarbon composition, hierarchical cluster analysis (HCA) of aliphatic hydrocarbons is correspondence with hydrocarbons indexes results.

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