



## Characterization of polycyclic aromatic hydrocarbons in concurrently monitored surface seawater and sediment along Dalian coast after oil spill

Xianjie Liu<sup>a</sup>, Hongliang Jia<sup>a</sup>, Luo Wang<sup>a</sup>, Hong Qi<sup>b</sup>, Wanli Ma<sup>b</sup>, Wenjun Hong<sup>a</sup>, Jianguo Guo<sup>c</sup>, Meng Yang<sup>a</sup>, Yeqing Sun<sup>c</sup>, Yi-Fan Li<sup>\*a,b,d</sup>

<sup>a</sup> International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), Dalian Maritime University, Dalian, PR China

<sup>b</sup> IJRC-PTS, State Key Laboratory of Urban seawater Resource and Environment, Harbin Institute of Technology, Harbin, PR China

<sup>c</sup> Institute of Environmental Systems Biology, Dalian Maritime University, Dalian, PR China

<sup>d</sup> IJRC-PTS, Ryerson University, Toronto, ON, Canada M5B 2K3

### ARTICLE INFO

#### Article history:

Received 4 September 2012

Received in revised form

21 December 2012

Accepted 22 December 2012

Available online 23 January 2013

#### Keywords:

Polycyclic aromatic hydrocarbons (PAHs)

Oil spill

Sea water

Sediment

China

### ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) were measured in concurrently sampled surface seawater and sediment collected at 20 sites around Dalian, China 50 days after an oil spill accident. The concentrations of total PAHs ranged from 15 to 160 ng L<sup>-1</sup> in seawater, and from 64 to 2100 ng g<sup>-1</sup> dry weight in surface sediment. The spatial trends of PAHs in seawater, but not in sediment, showed a significant negative correlation with the distance from the oil spill site, indicating a strong source of PAHs from oil spill place to the surrounding seawater. The similar profiles for PAH composition in both crude oil and seawater could indicate that oil spill caused PAHs concentration in seawater, but not in sediment. Analysis of water–sediment exchange of PAHs showed that the direction of the net flux of PAHs was from sediment to seawater for most priority PAHs, and from water to sediment for a few HWM-PAHs.

© 2012 Elsevier Inc. All rights reserved.

## 1. Introduction

On July 16, 2010, a fuel pipeline exploded and caught fire in the southwest of Dayao Bay in Dalian, China. About 1500 t of crude oil were spilled from the pipeline. The leakage of crude oil contaminated the surrounding area and the Yellow Sea of China. A large extent of the shoreline in Dalian was significantly polluted. The spilled oil had dramatic negative ecological and economic impacts to the Dalian coastal ecosystem. The physicochemical properties of the oil, with high density and viscosity, as well as a high content of resins and asphaltenes, prompted the formation of stable emulsions with seawater (Franco et al., 2006). Evidences from oil spills have shown that oil can persist in coastal sediments for several decades (Short et al., 2004; Reddy et al., 2002). Polycyclic aromatic hydrocarbons (PAHs), defined as a group of aromatic hydrocarbons with two or more fused benzene rings, are substantially present in crude oil (Ke et al., 2002). The oil spill accident can directly lead to the contamination of PAHs. PAHs have been proved to be the main components responsible for effects on animals, due to their carcinogenic, mutagenic and toxic effects (Lotufo and Fleeger, 1997).

Moreover, PAHs are a class of organic compounds with varying mutagenic properties (Sower and Anderson, 2008). PAHs are mainly from pyrogenic and petrogenic sources (Yunker and Macdonald, 2003). Inputs of PAHs from human activities such as oil spill, offshore production, transportation and combustion are very significant and pose serious threats to coastal habitats (Corredor et al., 1990), so the assessment of the presence and corresponding sources of PAHs after the oil spill was necessary to estimate the impact of accident on the environment.

In order to estimate the extent of the impact caused by the oil spill in the coastal area of Dalian city, a concurrent monitoring of PAHs in seawater and surface sediment was carried out from Lingshui Bay to Xiaoyao Bay (see Fig. SI-1, Supplementary Information, (SI)) in September, 2010, 50 days after the accident. The samples of seawater and sediments were analyzed for PAHs to determine the spatial distribution following the accident, to identify the sources, and further more, to determine the flux of PAHs at early spills.

## 2. Materials and methods

### 2.1. Sampling

Surface seawater (0–20 cm) and sediment (0–10 cm) samples taken 50 days after the oil spill were collected along the Dalian coast adjacent to the spill on

\* Correspondence to: author at: Dalian Maritime University, International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), NO. 1, Linghai Road, Dalian, Liaoning 116026, China. Fax: +86 411 8472 8489.

E-mail addresses: [ijrc\\_pts\\_paper@yahoo.com](mailto:ijrc_pts_paper@yahoo.com), [dr\\_li\\_yifan@yahoo.com](mailto:dr_li_yifan@yahoo.com) (Y.-F. Li).

September 5, 2010. A map with locations of sampling sites can be found in Fig. SI-1, SI, and detailed information is given in Table SI-1. The twenty sampling sites can be divided into three groups, residential areas (Sites R01–R05), industrial areas (Sites I01–I04), and oil spill areas (Sites OS01–OS11). The sites in the oil spill areas were further divided into two subgroups: OS-1 (OS01–04) containing sites closer to the oil spill site and OS-2 (OS05–11) including sites farther away from the oil spill site. In addition, three crude oil samples were collected near the oil spill site on July 20, 2010. All seawater, sediment and crude oil samples were gathered in a clean acetone rinsed glass bottle with Teflon-lined cap, and sent to the laboratory of the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), Dalian Maritime University, Dalian, China and stored at  $-20\text{ }^{\circ}\text{C}$  (sediment and crude oil) and  $4\text{ }^{\circ}\text{C}$  (water) until the time for extraction.

## 2.2. Extraction and analysis

Samples were treated, extracted, and analyzed according to the methods established at the National Laboratory for Environmental Testing (NLET), Environment Canada. All solvents used were of pesticide grade purity (J.T. Baker, USA). PAHs standards (24 PAHs compounds) were purchased from the Supelco, Inc. (Supelco, USA), including 5 two-ring PAHs, 7 three-ring PAHs, 4 four-ring PAHs, 6 five-ring PAHs, and 2 six-ring PAHs (See Table 1 for details).

After spiking with surrogate standard (Naphthalene-D10, Fluorene-D10, Pyrene-D10, and Perylene-D12) (Ma et al., 2010), 1 L of seawater samples were extracted with 100 mL Dichloromethane (DCM) in a separatory funnel with agitation followed by an hour settling time. Extraction was repeated three times, followed by DCM collection and rotary-evaporation to 1 mL. Ten grams of wet sediment and 10 g anhydrous sodium sulfate were measured into a pre-cleaned extraction thimble and spiked with surrogate standard (Naphthalene-D10, Fluorene-D10, Pyrene-D10, and Perylene-D12). After mixing, samples were Soxhlet extracted for 24 h with 200 mL mixed solvent (hexane/acetone, 1:1 v/v). Extracts were then rotary evaporated to 1 mL. The 1 mL extracts were passed through a 5.5 g silica gel column (Silica 60, Merck, Germany) after a 25 mL hexane pre-rinse and eluted with 40 mL of hexane/DCM mixture (1:1, v/v). The extract was rotary-evaporated to 2 mL, then solvent-exchanged into isooctane and reduced to 1 mL under nitrogen evaporation prior to gas chromatography–mass spectrometry (GC–MS) analysis.

For crude oil, 0.2 g of samples were measured into a centrifuge tube and were shaken for 1 h with 5 mL hexane, 2 g anhydrous sodium sulfate were added and then centrifuged for 15 min at a centrifugal force of 1000 g. Take 1 mL extract from top to a vial prior to GC–MS analysis. Further details can be found elsewhere (Wang et al., 2008a).

All PAHs were identified and quantified with GC–MS (Finnigan PolarisQ), DB-5 MS of 0.25 mm ID and 30 m length was used. The column oven temperature was

programmed at a rate of  $25\text{ }^{\circ}\text{C min}^{-1}$  from an initial temperature of  $60\text{ }^{\circ}\text{C}$  to a temperature of  $180\text{ }^{\circ}\text{C}$  (1-min hold),  $3\text{ }^{\circ}\text{C min}^{-1}$  to  $280\text{ }^{\circ}\text{C}$  (30-min hold). Injector, transfer line, and ion source temperatures were 280, 250 and  $250\text{ }^{\circ}\text{C}$ , respectively.

## 2.3. Quality assurance/quality control

All compounds were identified within  $\pm 0.05$  min of the calibration standard and selected mass ions. All samples were spiked with a labeled recovery standard (Naphthalene-D10, Fluorene-D10, Pyrene-D10, and Perylene-D12) prior to extraction. The surrogate standard recoveries ranged from 72 to 113 percent ( $91 \pm 19$  percent) in all samples. Spike and blank samples were included at a rate of one for every ten soils extracted and treated as the same processes with the real samples, the recoveries of all 24 PAHs were 78–110 percent. The instrument detection limits (IDLs) were determined by assessing the injection amount that corresponded to a signal-to-noise value of 3:1, and then transfer this amount in the unit of concentration in the corresponding medium. The IDLs of 24 PAHs ranges from 0.02 to  $5.0\text{ ng g}^{-1}$  dw (dry weight) for sediment samples, and from 0.02 to  $4.2\text{ ng L}^{-1}$  for water samples. Only Nap and Phe were detected in blanks with the mean value of 4.5 and  $0.4\text{ ng L}^{-1}$  in water, 3.7 and  $1.5\text{ ng g}^{-1}$  dw in sediment. The data reported in this study were all blank corrected.

## 2.4. Organic matter fraction determination

Ten grams of sediment samples were isolated for percent moisture determination and total organic matter ( $\phi_{OM}$ ) measurement. Sediment samples were first oven-dried at  $105\text{ }^{\circ}\text{C}$  for eight hours to a constant weight. After moisture elimination, the samples were placed in a muffle furnace and  $\phi_{OM}$  determined by measuring their loss after baked at  $550\text{ }^{\circ}\text{C}$  for five hours. The data of  $\phi_{OM}$  are listed in Table SI-1, SI, ranged from 2.96 to 9.92 percent. Organic carbon fraction ( $\phi_{OC}$ ) for each sediment sample can be calculated by assuming  $\phi_{OC} = \phi_{OM} 1.8^{-1}$  (Li et al., 2010).

## 3. Results and discussions

### 3.1. PAHs in sediment and seawater

Detailed PAHs concentrations in seawater and sediment at twenty sites are listed in Table SI-2 and SI-3, SI, respectively, and corresponding data are presented in Table 1. In seawater, the concentration of  $\Sigma_{24}$ PAHs (total 24 PAH compounds) ranged

**Table 1**  
PAHs concentrations in seawater and sediment in Dalian Bay.

PAHs	Full name	Ring no.	logK <sub>OC</sub> (L kg <sup>-1</sup> )	Seawater (ng L <sup>-1</sup> )			Sediment (ng g <sup>-1</sup> dw)		
				Mean	Min.	Max.	Mean	Min.	Max.
ThN	Tetrahydronaphthalene	2		0.26	BDL <sup>a</sup>	1.1	0.11	BDL	0.25
Nap	Naphthalene	2	3.11	19	5.4	54	21	5.1	88
2-MN	2-Methy-Naphthalene	2		9.9	2.3	32	13	2.7	37
1-MN	1-Methy-Naphthalene	2		12	3.8	30	9.0	3.3	21
BcN	Beta-chloronaphthalene	2		BDL	BDL	BDL	0.063	BDL	0.15
Acy	Acenaphthylene	3	3.75	BDL	BDL	BDL	3.2	0.60	12
Ace	Acenaphthene	3	3.59	0.23	BDL	1.3	4.9	0.19	19
Flo	Fluorene	3	4.15	3.7	0.82	11	10	3.9	28
Dib	Dibenzothiopene	3		BDL	BDL	BDL	2.1	0.62	3.9
Phe	Phenanthrene	3	4.42	1.5	0.43	5.1	50	11	190
Ant	Anthracene	3	4.41	4.1	1.3	8.7	14	6.0	47
Ret	Retene	3		BDL	BDL	BDL	BDL	BDL	BDL
Flu	Fluoranthene	4	5.22	0.77	0.22	4.4	52	7.8	210
Pyr	Pyrene	4	4.64	1.5	0.23	4.5	42	5.9	170
BaA	Benz[a]anthracene	4	5.65	0.15	BDL	0.59	40	1.2	220
Chr	Chrysene	4	5.45	0.33	BDL	1.4	23	3.5	83
BbF	Benzo[b]fluoranthene	5	5.90	0.093	BDL	0.39	92	2.0	400
BkF	Benzo[k]fluoranthene	5	6.30	0.054	BDL	0.24	9.0	2.5	23
BeP	Benzo[e]pyrene	5	7.20	0.032	BDL	0.24	21	1.7	80
BaP	Benzo[a]pyrene	5	5.93	0.10	BDL	0.41	32	1.7	130
Per	Perylene	5		0.11	BDL	0.33	11	3.0	33
DahA	Dibenz[a,h]anthracene	5	6.31	BDL	BDL	BDL	11	BDL	59
IcdP	Indeno[1,2,3-cd]pyrene	6	6.50	0.19	BDL	3.8	29	0.65	120
BghiP	Benzo[g,h,i]perylene	6	6.80	0.18	BDL	3.6	22	BDL	112
Total PAHs				54	16	140	510	73	1900

<sup>a</sup> BDL: below detection limit.

Download English Version:

<https://daneshyari.com/en/article/6312445>

Download Persian Version:

<https://daneshyari.com/article/6312445>

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