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Dispersion and Ecological Risk Assessment of Di (2-Ethylhexyl) Phthalate (DEHP) in the Surface Waters of Thailand

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Abstract Previous environmental monitoring indicated that di (2-ethylhexyl) phthalate (DEHP) was released into the environment. This study collected both water and sediment samples from the source area, deltas of major rivers discharging into the Gulf of Thailand, and 2 tourist beaches from February 2007–August 2009. The analyses showed that the highest DEHP concentrations were 8.64 μg l^{-1} and 14.51 μg g^{-1} for water and suspended sediment samples, respectively. Nevertheless, the monitoring results indicated that the dispersion of DEHP was limited to the source area. The ecological risk assessment indicated that the ecological risk did not exceed the acceptable level for the current degree of contaminations.

Keywords Suspended sediment · Bed sediment · Ecological risk · DEHP

The phthalate esters are used as plastic softeners in various plastic products and are used in a large variety of materials, such as dispersants, lubricants, and suspending agents. These compounds are ubiquitously found in both fresh and marine environments due to the leakage from waste products and discharge of industrial wastewater (e.g. Adeniyi et al. 2008; Liu et al. 2009). There was evidence indicating that phthalate esters, such as DEHP, could interrupt endocrine system activities in human and wildlife at very low concentration (Staples et al. 1997; Saal et al. 2008).

In Thailand, about 2,000 tons of di (2-ethylhexyl) phthalate (DEHP) was imported into the country each year as part of formulated plasticizer during October 2006–October 2009 (Thai Customs Department 2009). Nevertheless, there is no current continuous environmental monitoring program set up for this particular compound. Brigden et al. (2003) reported that DEHP concentrations in several bed sediment samples collected from effluent receiving canals of Bangpoo Industrial Estate ranged from below detection limit to 1 mg kg^{-1}. According to the physicochemical properties, DEHP is highly hydrophobic (Staples et al. 1997). Then, the principal fate of DEHP in the environment is sorption to sediment. The sorption onto sediment could lead to further dispersion of these pollutants in the environment (Fromme et al. 2002). The purposes of this study were to assess the distribution of DEHP in both river and marine waters, to assess the role of suspended sediment in DEHP transport, as well as to assess the ecological risk of DEHP contaminated water.

Materials and Methods

Water and suspended sediment samples were collected from deltas of 4 major rivers that discharge into the Gulf of Thailand (GOT), namely the Bang Pa-kong River, the Chao Phraya River, the Tha-chin River, and the Mae-klong River. In addition, samplings were taken from 2 selected tourist beaches located at the western side of the upper GOT, which are Cha-am beach, Petchaburi province and Ao-manao bay, Prachuap-kiri-khan province (Fig. 1). Samples from the tourist beaches were taken 100 m offshore during the lowest tide of the day.

The samples of both water and suspended sediment were taken twice each year during the dry season (in February) and wet season (in August) from February 2007–August 2009. Water and bed sediment samples were also collected

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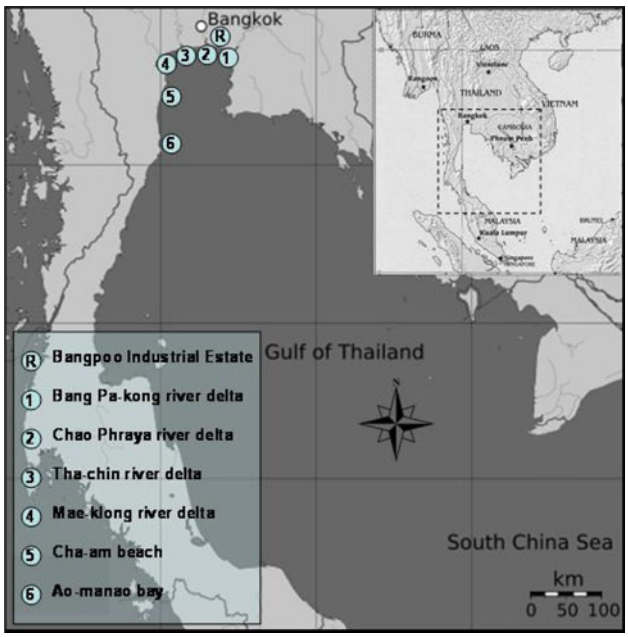

Fig. 1 Sampling stations

from effluent receiving canals of Bangpoo Industrial Estate (BIE), Samutprakarn as reference samples from source area (Fig. 1), according to the previous report by Brigden et al. (2003). The reference samples were taken in February only due to limitation to access to the site.

Water samples were collected in 30 L bottles and kept undisturbed for 60 min to settle out heavy particles. The particles that stayed suspended in the water samples after 60 min were separated from water by centrifugation at 4,000 rpm for 120 s. The separated particles were dried at 85°C and stored in a desiccator.

Both suspended sediment and bed sediment samples were analyzed for organic carbon content. Three aliquot sediment samples (1 g each) were taken to measure the content of organic carbon. The samples were acidified by adding sulfurous acid to the sediment before performing total organic carbon analyses according to methods described by Ingalls et al. (2004).

All the analyses in this study were done by GC/MS equipped with capillary column (coated with 5% phenyl 95% dimethylsiloxane, 0.25 μm) with the following conditions: the injection port temperature was held at 300°C; the column temperature was initially held at 200°C for 1 min and then increased at 30°C min^{-1} to 300°C. Ions monitored for DEHP were 149, 167, and 279.1. Nitrogen was used as a carrier gas. The solid phase micro-extraction technique (SPME) was used to extract DEHP from the solution. The selected type of fiber was polyacrylate coating (Supelco).

The analyses of DEHP concentration in sediment samples were done by placing 1 g of dried sediment in a 10 ml vial. The vial then was filled with *n*-hexane and placed on a shaker for 30 min. After that, the whole vial was centrifuged. The supernatant *n*-hexane was analyzed by GC/MS. All samples were analyzed in triplicate. The detection limit was calculated according to method described by Miller and Miller (1993). The detection limit for water and sediment samples were 1.10 and 8.34 μg g^{-1}, respectively. The quality control practices including calibration, initial quality control, and batch quality control were applied according to the US EPA (1995).

Ecological risk assessment was done according to the guideline of US EPA (1998) by selecting a proper organism or group of organisms from the ecosystems of interest. The assessment was based on estimated maximum environmental contaminant concentration (*EEC*) in water samples. The value of *EEC* was compared with screening benchmark (*SCB*), which was obtained from toxicity testing in plants and animals, to calculate Hazard Quotients (*HQ*) as follows:

$$HQ = \frac{EEC}{SCB} \quad (1)$$

The acceptable target of the *HQ* is less than 1.0.

This study used the data of ecological sensitive group of organisms that were representative of the ecosystems of the sampling stations. The ecosystems of the sampling stations can be classified into 2 groups, that were river mouth and sand beach ecosystems. The representative groups of environmentally sensitive organisms were selected according to the study of Pollution Control Department of Thailand (PCD) (2006).

Results and Discussion

The analyses indicated that the average organic carbon contents in the suspended sediment and bed sediment samples were 0.04%–1.10% and 1.46%–1.52%-C by weight, respectively (Table 1). The samples from Bang Pa-kong and Chao Phraya rivers contained higher average suspended sediment concentrations and organic carbon contents than the samples from other sampling stations. The possible reasons contributing to higher suspended sediment concentrations and organic carbon contents in water samples from Bang Pa-kong and Chao Phraya rivers include topography and land use. All water samples contained DEHP below detection limits, except the samples taken from effluent receiving canal of the BIE (Table 1). The highest concentration found in the water samples was 8.64 μg l^{-1}.

The DEHP concentrations in all suspended sediment samples were below detection limits, i.e. 8.34 μg g^{-1}. Nonetheless, the bed sediment samples taken from effluent

Table 1 DEHP concentrations in water and suspended/bed sediment samples and average organic carbon content in suspended/bed sediment samples

Sampling stations	Water samples		Suspended sediment/bed sediment samples	
	DEHP (μg l^{-1})	Suspended sediment concentrations (mg l^{-1})	DEHP (μg g^{-1})	Organic carbon content (%-C by weight)
February 2007–2009 (average ± SD)				
1 Bang Pa-kong river	<1.10	100.11 ± 8.22	<8.34	1.10 ± 0.18
2. Chao Phraya river	<1.10	123.30 ± 6.05	<8.34	0.92 ± 0.22
3. Tha-chin river	<1.10	50.64 ± 4.17	<8.34	0.48 ± 0.18
4. Mae-klong river	<1.10	48.75 ± 5.24	<8.34	0.61 ± 0.28
5. Cha-am beach	<1.10	32.41 ± 3.74	<8.34	0.06 ± 0.01
6. Ao-manao bay	<1.10	35.54 ± 4.18	<8.34	0.05 ± 0.02
7. Effluent receiving canal of BIE, East[b]	<1.10–8.64[a]	–	91.1 ± 9.12	1.52 ± 0.17
8. Effluent receiving canal of BIE, West[b]	<1.10–1.28[a]	–	<8.34–14.51[a]	1.46 ± 0.32
August 2007–2009 (average ± SD)				
1. Bang Pa-kong river	<1.10	167.51 ± 10.2	<8.34	0.95 ± 0.45
2. Chao Phraya river	<1.10	178.84 ± 12.6	<8.34	0.79 ± 0.63
3. Tha-chin river	<1.10	75.57 ± 9.75	<8.34	0.56 ± 0.46
4. Mae-klong river	<1.10	64.75 ± 11.85	<8.34	0.55 ± 0.71
5. Cha-am beach	<1.10	47.77 ± 5.79	<8.34	0.05 ± 0.01
6. Ao-manao bay	<1.10	33.50 ± 4.84	<8.34	0.04 ± 0.01

[a] Range of concentration (not average ± SD)

[b] Bed sediment samples

Table 2 The values of *SCB* for selected representative groups of organisms

Representative groups of organisms	Example	*SCB* (mg l^{-1})
Sandy Beach		
Invertebrates	Mole crab (*Hippa* spp.), Wedge shell (*Donax faba*), Sand worm (*Neris* sp.), Sand dollar (*Arachnoides* sp.)	0.37
River Delta		
Omnivorous fish	Mullet (*Liza vaigiensis* and *Valangugil siheli*)	0.18
Invertebrates	Polychaete worm (*Capitella* sp.), Tube worm (*Ditrupa* sp.), Green mussel (*Perna viridis*)	0.37
Phytoplankton	Ceratium (*Ceratium furca*)	0.32

receiving canal of BIE contained DEHP. The detectable concentration found in both water and bed sediment samples taken from the effluent receiving canal of BIE confirmed the existence of DEHP source. Since DEHP could strongly partition to sediment due to its hydrophobicity, we found high concentration close to the source areas in the bed sediment samples, which contained high organic content. It is possible that these sediment act as a sink for the discharged DEHP in the effluent. This is similar to what has been found recently by Björklund et al. (2009) that DEHP has a high tendency to be adsorbed to solids in water and sediment is an important sink for this substance. In this study, there was no evidence that suspended sediment plays a role in dispersion of DEHP into the surface water environment; instead the sediment could act as a sink and limit the distribution of this compound.

The selected group of ecological sensitive species and their values of *SCB* for DEHP are shown in Table 2 (Naito et al. 2002; PCD 2006). In case of compound capable of bioaccumulation, the maximum *EEC* would be calculated based on the accumulation in the trophic levels, not the concentration in water. Since, Gobas et al. (2003) reported that DEHP did not bioaccumulate; the *EEC* used for our assessment was 8.64×10^{-3} mg l^{-1} (the highest concentration found). The assessment results indicated that the ecological risks for representative group of organisms were

Table 3 The values of *HQ* for selected representative groups of organisms

Representative groups of organisms	*EEC* (mg l^{-1})	*SCB* (mg l^{-1})	*HQ*
Phytoplankton	8.64×10^{-3}	0.32	2.70×10^{-2}
Invertebrate	8.64×10^{-3}	0.37	2.34×10^{-2}
Omnivorous fish	8.64×10^{-3}	0.18	4.80×10^{-2}

not above unacceptable level, i.e. $HQ < 1$ (Table 3). At the current level of DEHP release, the distribution of DEHP in the environment is limited to the area close to the source. Nevertheless, it was possible that certain conditions such as fast runoff could lead to more dispersion contaminated water and bed sediment from source zone. The risk assessment results from this study could be used to support regulatory decision-making. For instance, the decision whether additional measures, such as removal, treatment, or containment of the contaminated sediment, are needed.

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