DISTRIBUTION AND ECOLOGICAL RISK ASSESSMENT OF PLASTICIZERS IN THE CHAO PHRAYA DELTA, GULF OF THAILAND

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Abstract

Preceding monitoring reports indicated that di (2-ethylhexyl) phthalate (DEHP), a common plasticizer, was found in the samples of suspended sediment and water collected from the lower part of Chao Phraya River. In this continuing study, the suspended sediment and water samples from the Chao Phraya Delta were collected twice a year in January and July during January 2011 – July 2013. The analyses were performed for both DEHP and Diethyl Phthalate (DEP). Overall results showed that concentrations of both DEHP and DEP in the water samples were relatively higher than those in the suspended sediment samples. The concentrations of DEHP and DEP from all sampling periods in the water samples ranged from 1.58 – 27.55 µg/L and from 0.64 – 2.59 µg/L, respectively, whereas the concentrations of DEHP and DEP from all sampling periods in the suspended sediment samples ranged from 0.01 – 26.82 mg/g and from 0.01 – 1.93 mg/g, respectively. The concentrations of both DEHP and DEP in both suspended sediment and water samples were relatively higher in the samples collected during lower discharge period of the Chao Phraya River in July. The results indicated that sediment transport system could play an important role in the dispersion of both DEHP and DEP. The ecological risk assessment indicated that for the current level of contaminations the risk did not exceed the acceptable level.

Keywords: Endocrine disrupter, Organic carbon, Phthalate ester, Suspended sediment

Introduction

The plasticizers, especially the phthalate esters, are widely used in various plastic products to make them pliable. These compounds are found ubiquitously in both fresh and marine aquatic environments because they are readily leaked from those products (e.g. [1, 2]). Several phthalate esters, especially di (2-ethylhexyl) phthalate (DEHP), are classified as an endocrine disrupter compound (EDC) that could interfere with the endocrine system activities in aquatic organisms and even mammals at very low level of concentration [3]. The data shows that over 2,000 tons of phthalate esters were annually imported into Thailand as ingredient of instant plasticizer for plastic production and related industries during October 2009 – October 2011 [4].

In the past decades, the water qualities in the major rivers as well as the Chao Phraya River and in the Chao Phraya Delta have been continuously monitored by the Pollution Control Department (PCD). The results indicate that the general water qualities in the lower Chao Phraya River have been worsened and the levels of certain water quality parameters, such as phosphate and nitrate, have been lower than the Surface Water Quality Standard [5]. That is because there are many sources of water pollution located in this area, especially the municipal and industrial sources.

Although there are general and specific water quality parameters that are listed and required to be monitored routinely, the phthalate esters are not in such lists. For the lower

Chao Phraya River, Sirivithayapakorn and Thuyviang [6] reported that during 2007 – 2009, DEHP were found in sediment and water samples collected from the canals that received treated effluent from the factories in the Bangpoo Industrial estate, which is located nearby the Chao Phraya Delta area. Since sorption is assumed to be the primary fate of DEHP in the environment according to their log K_{ow}, the sorption on to suspended sediment could cause further dispersion of this pollutant in the aquatic environment [7].

Therefore, in this study, we collected suspended sediment and water samples from 25 sampling locations within the Chao Phraya Delta area during 2011 – 2013. The samples were analyzed for DEHP and other phthalate esters that were common plasticizers or related intermediate products from degradation, which were Di-n-butyl phthalate (DnBP), Benzyl butyl phthalate (BBP), Diethyl phthalate (DEP), and Dimethyl phthalate (DMP) [3, 8-9]. The purposes of this study were to evaluate the level of concentrations of these compounds in the Chao Phraya Delta area and to assess whether the suspended sediment could play a role in the transport of these compounds.

Materials and Methods

Suspended sediment and water samples were taken from 25 sampling stations located in the delta of Chao Phraya River (Figure 1). Both suspended sediment and water samples were collected twice each year during the high discharge period of the Chao Phraya River in January and the low discharge period in July, from January 2011 – July 2013.

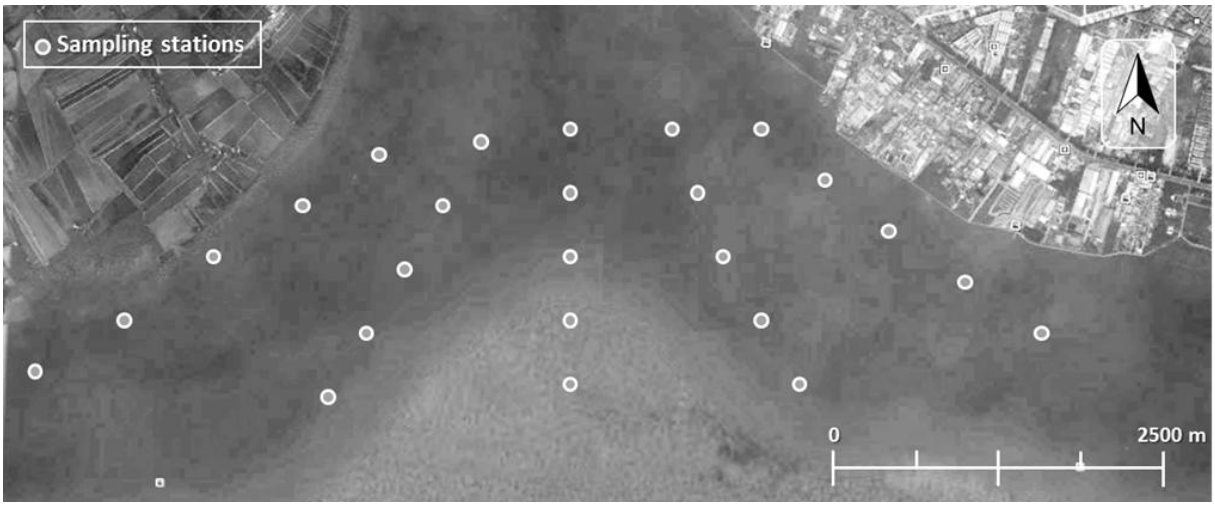

Figure 1. Sampling locations in the Chao Phraya Delta

Surface water samples from each station were kept still in 10 liter glass containers for 60 minutes to separate the settleable solid particles. The suspended solid particles were subsequently separated by centrifugation for 120 seconds at 4,000 rpm. The removed suspended solid particles were dried in the oven for 10 hours at 85^{o}C, and then stored in a desiccator until cool down to room temperature and separated into two portions. The first portion, 1 gram, was analyzed for the Total Organic Cabon (TOC) content according to procedures explained by Ingalls et al. [10]. The second portion, at least 10 grams, was subjected to the extraction process using n-hexane according to the procedure described by Sirivithayapakorn and Thuyviang [6].

The analyses of water and hexane extracted sediment samples were carried out in the GC/MS in triplicate. The method detection limits were calculated for both water and hexane extracted sediment samples to be 0.10 µg/L and 0.01 mg/g, respectively [11]. The

necessary quality control procedures were applied according to the procedures suggested by U.S. EPA [12].

The ecological risk assessment was carried out according to the U.S. EPA guideline by choosing a group of sensitive organism or representative organism from the ecosystems of interest [13]. The maximum concentration of the contaminants in the water was used as the environmental contaminant concentration (EEC). Then, value of Hazard Quotients (HQ) was obtained by comparing the value of EEC with the reported value of screening benchmark (SCB) derived from toxicology test of the selected group of organisms or the selected organism as shown in Equation (1).

$$HQ = \frac{EEC}{SCB} \tag{1}$$

In general, the acceptable level of HQ is below 1.0.

In this work, the ecosystems of the sampling stations can be classified as river delta ecosystem. The selected groups of environmentally sensitive organisms were identified according to the previous study of the Pollution Control Department of Thailand (PCD) [14].

Results and Discussions

The results indicated that the average concentrations of suspended solids in the water samples were 609.4 mg/L (ranged from 270.0 – 3,086 mg/L) and 143.0 mg/L (ranged from 86.5 – 318.0 mg/L) for the water samples taken in January and July, respectively. The average amount of organic content in the suspended sediment samples taken in January and July were 9.08 mg/g (ranged from 0.07 – 30.16 mg/g) and 4.13 mg/g (ranged from 0.90 – 19.15 mg/g), respectively. The results showed that the average values of both suspended solids in the samples of water and the organic content in the samples of suspended sediment were relatively higher in the samples taken in January, which is the higher discharge period, in comparison to those taken in July, which is the lower discharge period.

The analytical results showed that only DEHP and DEP in both water and suspended sediment samples could be found at the concentrations above detection limit. The concentration contours of both DEHP and DEP in the samples of water and sediment are created by the inverse distance to a power gridding method [15] and are presented in Figure 2 – 5. In general, the DEHP concentrations in both water and suspended samples were higher than the concentrations of DEP in all sampling periods, even though DEP is much more soluble in water than DEHP (Table 1). Although we do not have data about the rate of release of both compounds from their sources, one of the reasons that we found higher concentrations of DEHP in water samples could be due to the fact that DEP is subjected to more degradation with reported half-life of 10 days [16], while DEHP is less subjected to degradation with reported half-life of 50 days [17].

Moreover, the concentrations of both DEHP and DEP in water samples were relatively higher in July in comparison to January (Figure 2 – 3). If we assumed that the discharge rate of these compounds from their sources were relatively constant all year round, this could indicate that the concentrations of both phthalate esters in water were diluted by large volumes of water discharged into the Gulf of Thailand during high discharge period.

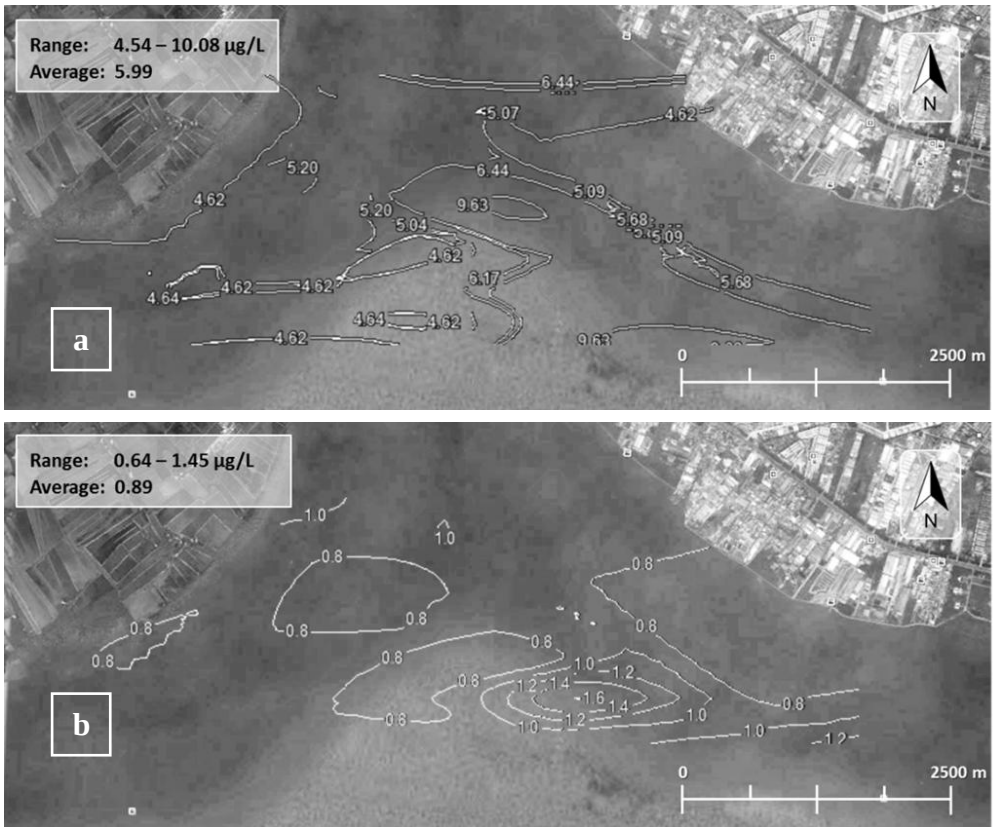

Figure 2. Distribution of a) DEHP and b) DEP in water in January

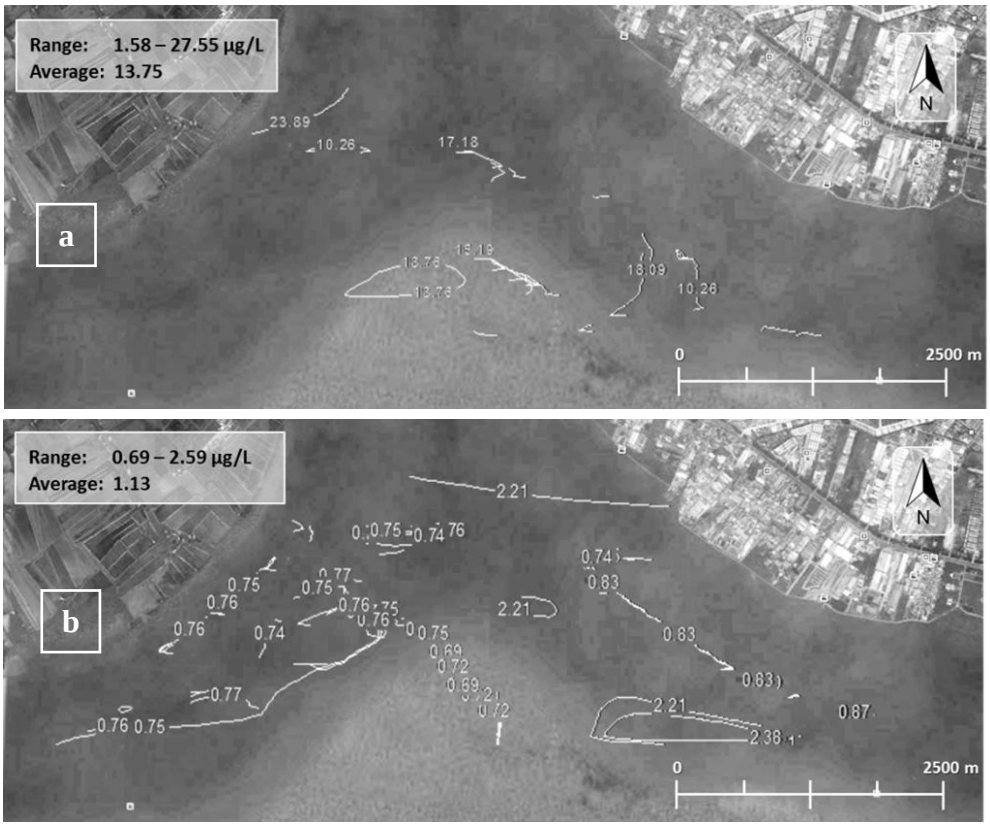

Figure 3. Distribution of a) DEHP and b) DEP in water in July

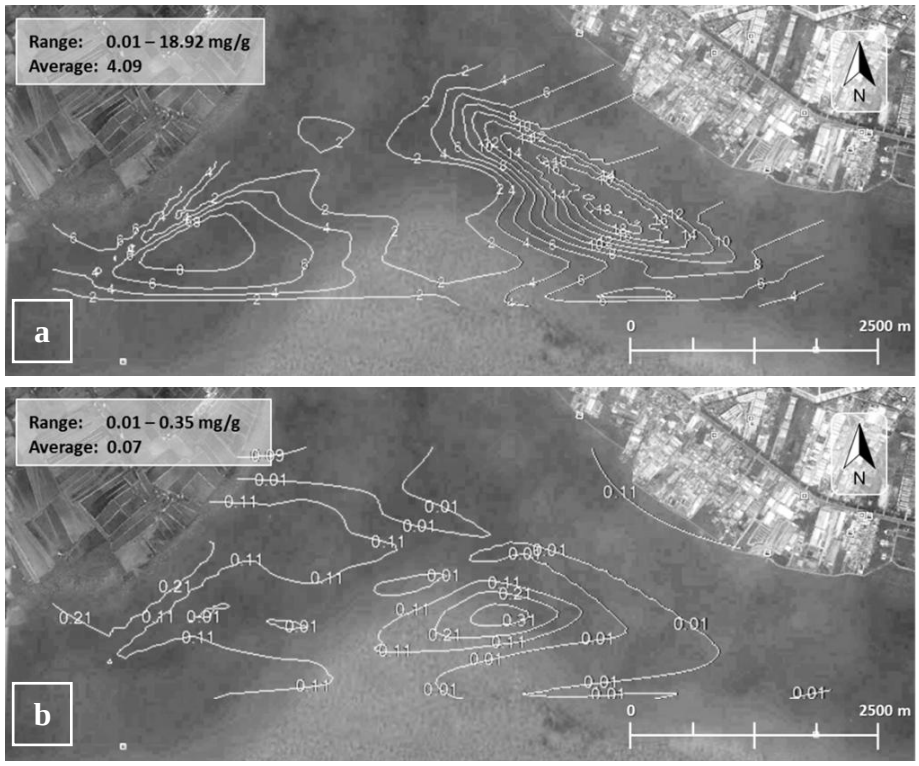

Figure 4. Distribution of a) DEHP and b) DEP in suspended sediment in January

Figure 5. Distribution of a) DEHP and b) DEP in suspended sediment in July

Based on the reported values of octanol-water partitioning coefficient (log K_{ow}) (Table 1), both compounds have high tendency to adsorb onto the sediment. Therefore, it is very likely that the sediment transport could play an important role on the dispersion of these

compounds, especially for DEHP. The results in Figure 4 – 5 showed that the concentrations of DEHP in the suspended sediment samples were higher than those of DEP. This could be due to several factors, including the higher ambient water concentrations and the higher value of log K_{ow} of DEHP.

Table 1. Solubility and Log K_{ow} of DEHP and DEP

Phthalate Esters	Water Solubility at 25°C (mg/L)	Log K_{ow}	Source
DEHP	0.285	4.89	[16]
DEP	1,080	2.47	[17]

For the river delta ecosystem of Thailand, the representative ecological sensitive species and their corresponding SCB values for phthalate esters are described in Table 2 [9, 14]. Since both DEHP and DEP are not the bioaccumulated compounds [16-18], the highest concentrations in water were taken as the value of EEC. Therefore, the values of EEC used in this study are 0.028 mg/l and 0.003 mg/L for DEHP and DEP, respectively.

The assessment showed that the value of HQ calculated for the selected group of sensitive organisms is lesser than 1 or the risk level is still acceptable (Table 3) at the current level of DEHP and DEP found in the water. Since both DEHP and DEP are relatively stable when absorbed to the sediment [16, 17], we may be able to treat them as conservative tracers and use the long term monitoring data for the modeling of sediment transport. The risk assessment results also crucial for the policy making, such as the evaluation whether additional treatment or regular monitoring are required, or even for the setup of standards of these compounds in the future.

Table 2. The SCB Values for Different Representative Groups of Organisms

Groups of Representative Organisms	Example of Species	*SCB* (mg/l)
Fish (Omnivore)	Mullet (*Liza vaigiensis* and *Valangugil siheli*)	0.18
Invertebrates	Polychaete (*Capitella sp*), Tube worm (*Ditrupa sp*.), Mussel (*Perna viridis*)	0.37
Phytoplankton	Ceratium (*Ceratium furca*)	0.32

Source: Pollution Control Department of Thailand (PCD) [14]

Table 3. The Calculated HQ of the Representative Groups of Organisms

Groups of Representative Organisms	*EEC* (mg/l)	*SCB* (mg/l)	*HQ*
Assessment for DEHP			
Phytoplankton	0.028	0.32	0.088
Invertebrate	0.028	0.37	0.076
Fish (Omnivore)	0.028	0.18	0.156
Assessment for DEP			
Phytoplankton	0.003	0.32	0.009
Invertebrate	0.003	0.37	0.008
Fish (Omnivore)	0.003	0.18	0.017

Conclusions

This study showed that the plasticizers, both DEHP and DEP, could be found at µg/L level in the water samples and at mg/g level in the suspended sediment samples taken from the Chao Phraya Delta. The results showed that the concentration of both compounds were higher during the low discharge period of the Chao Phraya River. Due to the tendency to adsorb to the sediment of both compounds, relatively high concentrations were found in the suspended sediment. This indicated that the sediment transport system could be important in the dispersion and transport of these compounds in the aquatic environment. At the current degree of contaminations, the assessments showed that the ecological risks were within the acceptable level.

Acknowledgements

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