

## ADSORPTION OF DIMETHYL PHTHALATE ON MARINE SEDIMENTS

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**Abstract.** Experiments were performed to investigate the sorption behaviors of dimethyl phthalate on marine sediments. The sorption of dimethyl phthalate on marine sediments reached equilibrium within 10 h. The sorption behavior of dimethyl phthalate on HCl-treated and untreated sediments accorded well with the linear sorption isotherm. The sorption occurred primarily via partition function of organic carbon of marine sediments. The sorption behavior of dimethyl phthalate on H<sub>2</sub>O<sub>2</sub>-treated sediment was nonlinear and conformed to Freundlich isotherm. Sorption of dimethyl phthalate on H<sub>2</sub>O<sub>2</sub>-treated sediment was chiefly through surface function of clay in marine sediments. Salinity of seawater had an important effect on the sorption of dimethyl phthalate. As the salinity of seawater increased, both the partitioning coefficients  $K_d$  and empirical constant  $K$  would increase.

**Keywords:** dimethyl phthalate, marine sediment, sorption, partition, linear isotherm, Freundlich isotherm

### 1. Introduction

With the arrival of new century, the world is facing the threat from various problems such as the rapid growth of population, serious shortage of resources, and continuous deterioration of the environment. As far as marine is concerned, a great threat comes from the pollution by the discharge and dumping of waste containing high levels of anthropogenic organic contaminates, some of which are highly toxic, difficult to degrade and have a strong tendency to concentrate in marine food webs. As pollutant fate and ecological effects are closely associated, it is critical to understand the mechanism of transport and transformation of toxic chemicals (Zhou and Liu, 2000).

Phthalate acid esters (PAEs) are a class of chemical compounds most widely used in the industrial production. Their major applications are as plasticizers for polyvinyl chloride (PVC) resins, adhesives, and cellulose film coating (about 85% of the production) (Vitali *et al.*, 1997). Minor applications are in cosmetics, insect repellent, insecticide, and propellants (Peakall, 1975). The current world-wide yield of phthalate acid esters has reached 2.7 million metric tonnes per year



(Bauer and Hermann, 1997). The large production and utilization caused a significant environmental diffusion of these compounds. In 1984, it was estimated that at least 23,000 Mg of PAEs was yearly released into the environment (Cadogan *et al.*, 1984), and therefore, the United States Environmental Protection Agency (USEPA) and several other countries had classified the most commonly occurring PAEs as 'priority pollutants' (Keith and Telliard, 1979).

Dimethyl phthalate is among the most frequently identified PAEs in diverse environmental samples that include surface marine waters (Tan, 1995; Fatoki and Vernon, 1990; Mayer *et al.*, 1972; Giam *et al.*, 1978; Gledhill *et al.*, 1980), freshwaters (Vitali *et al.*, 1997; Gledhill *et al.*, 1980; Staples *et al.*, 2000; Schwartz *et al.*, 1979) and sediments (Tan, 1995; Gledhill *et al.*, 1980; Thuren, 1986). Due to the hydrophobic nature of dimethyl phthalate, it is expected to interact strongly with particles, once discharged into the marine environment. The distribution and fate of chemical compounds in the oceans is largely controlled by transport mechanism within phases and across phase boundaries (Sullivan *et al.*, 1982). Sorption of compounds from solution is one mechanism, which can significantly affect the transport and distribution in the ocean environment. The sorption behaviors of organic pollutants are affected by many factors such as the sediment composition, aqueous salinity, pH, DO and DOC. To our knowledge, however, no studies have been reported on the sorption of the ubiquitous dimethyl phthalate on marine sediments. The objectives of this study were to investigate the sorption kinetics and the sorption isotherms of dimethyl phthalate on marine sediments, different sorption properties of various types of sediments treated by different procedures, and effects of sediment ingredients (e.g. organic carbon and clay) and environmental factor (e.g. salinity) on the sorption of dimethyl phthalate.

## 2. Materials and Methods

### 2.1. REAGENTS AND STANDARD SOLUTION

The pure compounds used in the experiments were purchased from Shanghai Chemical Reagent Co., China, and dimethyl phthalate was further purified by distillation before the use.

Aqueous solubility of dimethyl phthalate was  $4.2 \text{ g L}^{-1}$  at  $25 \text{ }^{\circ}\text{C}$  (Staples *et al.*, 1997). 1 g of dimethyl phthalate was first dissolved into 1000 mL water, and then 20.00 mL of the solution was diluted by 980 mL water to prepare a final standard solution of  $20 \text{ mg L}^{-1}$ .

### 2.2. WATER AND SEDIMENT SAMPLES

Natural seawater (NSW), collected from open ocean, was first filtered through  $0.45 \text{ }\mu\text{m}$  filter membrane, and then irradiated with strong ultraviolet light to

TABLE I

Sampling stations of sediments and their organic carbon and clay contents (%)

No.	Location	Water depth (m)	Organic carbon (%)	Clay (%)
1	11 °N, 110 °E	665	2.02	23
2	10 °N, 112.5 °E	2560	2.53	16
3	6 °N, 113 °E	1883	2.68	23

eliminate the effects of natural dissolved organic matter as far as possible. The salinity and pH value of the seawater were 33.4‰ and 8.03, respectively. In this study, deionized water (DW) (salinity 0‰) and diluted seawater (DSW) with a final salinity of 16.7‰ were also chosen as media to investigate the effect of salinity on the sorption behavior of dimethyl phthalate.

The experimental sediment samples were collected from the South China Sea and treated using the following three methods:

- No-treatment.* The collected sediment samples were only washed with distilled water, air-dried, and then ground. The part which could pass 60–80 mesh sieves was chosen as experimental sorbent.
- HCl-treatment.* Sediment samples from A were treated according to the method as described in Zhao *et al.* (2001, 2002, 2003). The aim of this treatment was to partly remove the carbonate of sediment and increase the percentage of sediment organic carbon content on dried weight basis.
- H<sub>2</sub>O<sub>2</sub>-treatment.* The sediment from A was treated by the method as described in the literature (Yang and Zhang, 1997). After this treatment, most of the sediment organic carbon was removed by the oxidation of H<sub>2</sub>O<sub>2</sub>.

In this investigation, the organic carbon and clay contents of No-treatment sediments were analyzed using a Leco Total Carbon Analyzer and a Model D/max-rb X-ray diffraction instrument (Rigaku, Japan), respectively. The analytical results and sampling stations of sediments are shown in Table I.

### 2.3. SORPTION KINETICS OF DIMETHYL PHTHALATE

In the sorption kinetics experiment, 100 mg of sediment, approximately 100 mL of natural seawater, and a fixed volume of dimethyl phthalate standard solution were first added to a series of 250 mL ground glass stoppered flasks to make up a whole suspension volume of 100 mL. Afterwards, the solution pH was adjusted to  $8.00 \pm 0.03$ . Then samples were shaken at  $25 \pm 0.5$  °C in a temperature-controlled water bath at different time intervals as indicated in Figure 1. The agitation speed of the suspension was controlled at the constant speed in order to assure that the mass transport characteristics could hold the same in sorption

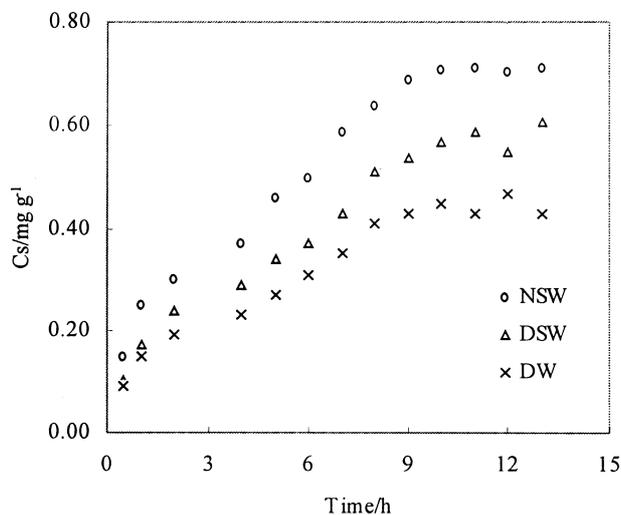


Figure 1. The kinetics of dimethyl phthalate by marine sediment at initial concentration of  $2.00 \text{ mg L}^{-1}$ .

kinetics experiment. Solid and aqueous phases were separated at the speed of  $8\,000 \text{ r min}^{-1}$  for five minutes by a model LG-2.4 centrifuger (Beijing Physical Utilization Centrifuger Factory, China). The supernatant solution was finally analyzed by UV absorption at  $230 \text{ nm}$  in seawater and  $199 \text{ nm}$  in freshwater using a Model UV 1100 spectrophotometer (Beijing Ruili Analysis Instrument Co., China). The sorbed amount of dimethyl phthalate in sediment could be obtained by the difference between the initial concentration and the final equilibrium concentration in aqueous phase. The analysis and the dimethyl phthalate uptake values were reproducible with a relative standard deviation of the method smaller than 5%.

#### 2.4. SORPTION ISOTHERMS OF DIMETHYL PHTHALATE

Sorption isotherm experiments were performed according to similar method to the above, but the volumes of standard solution added were variable. After equilibration, the suspended solution was separated, and then analyzed by UV absorption. According to the difference between the initial concentration and the final equilibrium concentration in aqueous phase, the sorbed amount of dimethyl phthalate in solid phase was calculated. To determine the degree of the compound sorption on the glassware, a blank sorption experiment with no added sediment was carried out at the same time. The result showed that the amount of dimethyl phthalate adsorbed to the glass wall was extremely small as compared with that adsorbed by sediment. Therefore, the amount adsorbed by glassware could be neglected.

### 3. Results and Discussion

#### 3.1. KINETICS OF DIMETHYL PHTHALATE SORPTION

The results from the kinetics experiments showed that sorption of dimethyl phthalate onto the marine sediment reached maximum values within 10 h, no matter what media (natural seawater, diluted seawater and deionized water) were utilized (Figure 1). After 10 h, the dissolved and sorbed concentrations remained relatively constant. In order to assure the sufficient sorption of dimethyl phthalate onto marine sediments, 12 h was adopted in the sorption isotherm experiment. In addition, from Figure 1 it can be seen that the maximum saturate sorption amount of dimethyl phthalate on marine sediments varied with the media in the sequence: NSW > DSW > DW. This point demonstrated that the sorption behavior of dimethyl phthalate was influenced by the medium. The relevant reasons were discussed in detail below.

#### 3.2. SORPTION ISOTHERMS OF DIMETHYL PHTHALATE

The experimental results obtained from the study were regressively analyzed using linear model and Freundlich model.

##### 3.2.1. Linear Isotherm

The sorption of low molecular weight organic compounds on sediments (and soils) depended largely on the aqueous solubility of the organic compounds and on the organic carbon contents of the sediment (Karickhoff *et al.*, 1979; Chiou *et al.*, 1979). In general, sorption of these solutes increases with a decrease in solubility and is directly proportional to the organic carbon content of the sediment. Sorption of nonionic organic compounds by sediments is generally referred to partitioning. Sorption isotherms for hydrophobic solutes are typically linear, and the sorption behavior can be described by the following equation:

$$C_s = K_d C_e, \quad (1)$$

where  $C_s$  denotes the concentration of sorbate on the sediments, relative to dry weight (for the compound, conveniently expressed as  $\text{mg g}^{-1}$ );  $C_e$  is the equilibrium solution sorbate concentration ( $\text{mg L}^{-1}$ ) and  $K_d$  is the partition coefficient.

The sorption results of dimethyl phthalate on HCl- and No-treatment marine sediments were regressively analyzed by the linear isotherm. The sorption isotherms are illustrated in Figure 2, and the sorption equations and correlation coefficients ( $R^2$ ) are shown in Table II. From Figure 2 and Table II, it can be seen that the sorption behavior of dimethyl phthalate on HCl- and No-treatment marine sediment was highly linear in the concentration range investigated. The results therefore indicated that dimethyl phthalate distribution between water and sediments at low concentrations was mainly through a partition process.

TABLE II

Linear sorption isotherms of dimethyl phthalate on HCl- and No-treatment marine sediments in NSW

Treatment mean	Station 1	$R^2$	Station 2	$R^2$	Station 3	$R^2$
HCl	$C_s = 0.527 C_e$	0.9896	$C_s = 0.656 C_e$	0.9869	$C_s = 0.752 C_e$	0.9936
No	$C_s = 0.469 C_e$	0.9738	$C_s = 0.513 C_e$	0.9665	$C_s = 0.587 C_e$	0.9801
$K_{oc}$ (No-treatment)	32.2		20.3		21.9	

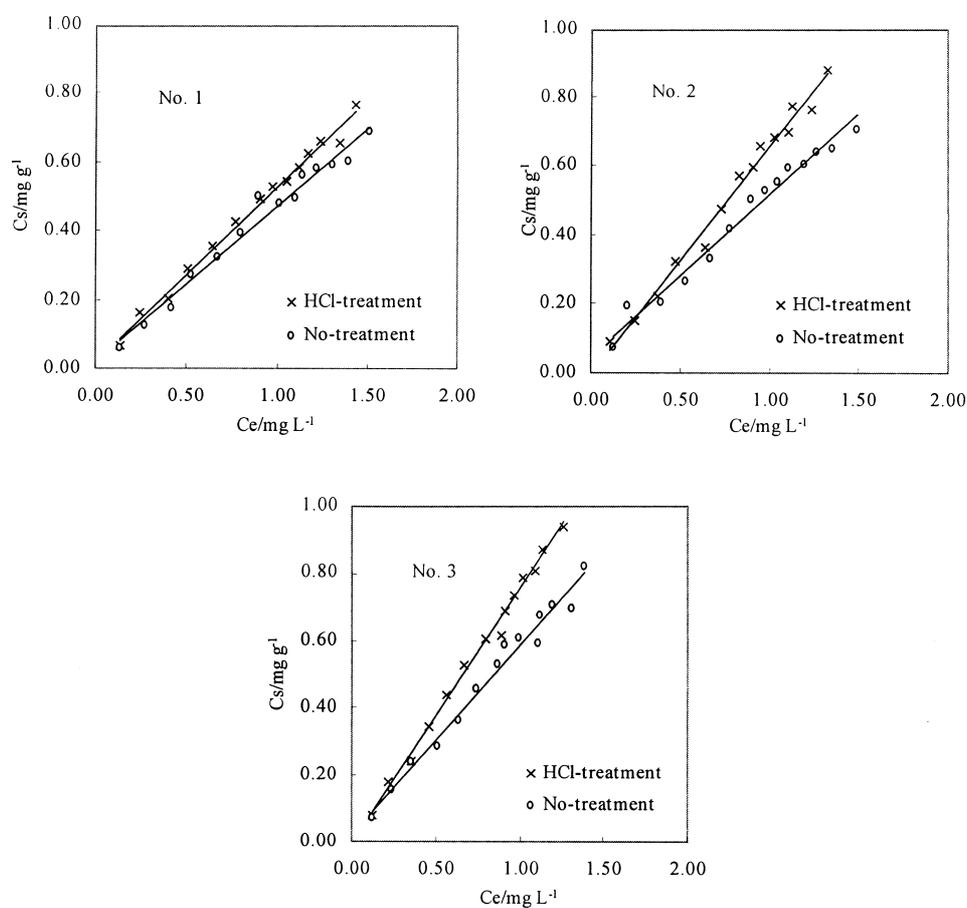


Figure 2. Linear sorption isotherms for dimethyl phthalate on HCl- and No-treatment marine sediments in NSW.

Chiou (1981, 1977) found a significant relationship between partition coefficient  $K_d$  and solubility or octanol-water partitioning coefficient. As for the organic pollutants such as dimethyl phthalate,  $K_d$  of linear sorption isotherms is comparatively small if solubility of pollutants in water is high and octanol-water partitioning coefficient is low. Aqueous solubility and octanol-water partitioning coefficient of

dimethyl phthalate is  $4.2 \text{ g L}^{-1}$  and  $40.7$ , respectively (Staples *et al.*, 1997), so relatively small  $K_d$  values of dimethyl phthalate were reasonably expected in this study, as shown in Tables II and V. From Table II, it can be also found that the  $K_d$  of dimethyl phthalate sorption isotherms varied with the sampling stations and treatment means of sediments. At different stations,  $K_d$  varied in the sequence:  $K_d$  (3) >  $K_d$  (2) >  $K_d$  (Equation 1). The sequence was consistent with the order of organic carbon contents of sediments. In addition, the carbonate of sediment was removed after HCl-treatment. This accordingly increased the organic carbon contents of sediments and enhanced the partitioning effect of sediments. As a consequence,  $K_d$  value on HCl-treatment sediment exceeded  $K_d$  value on No-treatment sediment at each station. The above observation clearly demonstrated that the partitioning of sediment organic carbon played a major role on the sorption of dimethyl phthalate, and  $K_d$  values of linear isotherms were proportional to the organic carbon contents of sediments.

Because partition process is dominated by the organic carbon content of sediment, typically the partition coefficient  $K_d$  is transformed by normalization to organic carbon content:

$$K_{oc} = K_d/f_{oc}, \tag{2}$$

where  $K_{oc}$  is organic carbon-normalized partition coefficients, and  $f_{oc}$  is the fraction organic carbon content of sediment.  $K_{oc}$  values (No-treatment) obtained from Equation (2)) are listed in Table II. Many attempts to correlate sorbate properties with sorption showed that the sorbate solubility in water ( $S_w$ ) and octanol-water partitioning coefficient ( $K_{ow}$ ) appeared to be the primary factors affecting the sediment organic matter-water partitioning coefficient ( $K_{oc}$ ). Some  $K_{oc}$  values predicted from empirical equations in the literature are shown in Table III. In the present study, the  $K_{oc}$  values of dimethyl phthalate varied from 20.3 to 32.2, in good agreement with the predicted results of literatures which ranged from 13.0 to 69.9 (Table III).

TABLE III

A collection of dimethyl phthalate  $K_{oc}$  values predicted from empirical equations in the literature

Predicted $K_{oc}$ value	Equation	References
42.3	$\log K_{oc} = 4.04 - 0.557 \log S_w (\mu\text{mol L}^{-1})$	Chiou (1981)
33.8	$\log K_{oc} = 0.53 - 0.6 \log S_w (\text{mol L}^{-1})$	Jin (1992)
21.8	$\log K_{oc} = 0.44 - 0.54 \log S_w (\text{mol L}^{-1})$	Karickhoff <i>et al.</i> (1979)
69.9	$\log K_{oc} = 4.33 - 0.686 \log S_w (\mu\text{g mL}^{-1})$	Means (1995)
13.0	$\log K_{oc} = 0.944 \log K_{ow} - 0.485$	Jin (1992)
25.1	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	Karickhoff <i>et al.</i> (1979)
19.6	$\log K_{oc} = 1.00 \log K_{ow} - 0.317$	Means (1995)

### 3.2.2. Nonlinear Isotherm

As shown in Figure 3, the sorption isotherms of dimethyl phthalate on  $H_2O_2$ -treatment sediments did not accord with linear isotherm in the concentration ranges studied, differing greatly from those observed on both HCl- and No-treatment sediments. This finding meant that a different sorption mechanism for dimethyl phthalate on the  $H_2O_2$ -treatment sediment probably appeared.

In general, the composition of organic material in marine sediments was extremely complex. The previous studies (Yang and Zhang, 1997; Yang, 1999; Yang *et al.*, 1998) showed that marine sediments in the South China Sea were composed chiefly of four fractions including organic material, carbonate, quartz and clays (illite, kaolinite, chlorite and montmorillonite). In comparison with sediment organic carbon, the inorganic material constituted the majority of the marine sediments. After the  $H_2O_2$ -treatment, the major part of organic carbon on the surface of sediment inorganic material was removed by peroxide. As a result, the percentage of

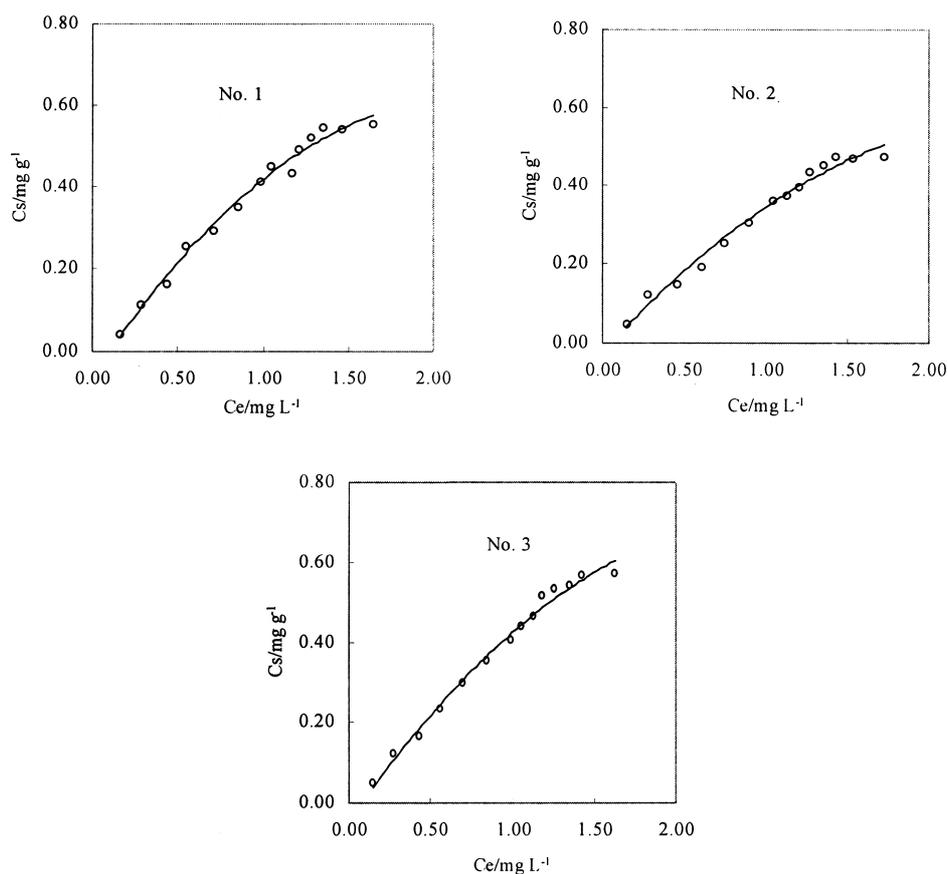


Figure 3. Freundlich sorption isotherms for dimethyl phthalate on  $H_2O_2$ -treatment marine sediments in NSW.

inorganic material such as clays on a dried weight basis became higher after the H<sub>2</sub>O<sub>2</sub>-treatment. Especially, after the organic carbon was obviated, the surface area of sediment inorganic material, such as clays, which was among the main components of the marine sediment used in the experiments (Yang and Zhang, 1997; Yang, 1999; Yang *et al.*, 1998), would increase. Therefore, more surface sorption sites would expose to the organic chemicals in the system of seawater-sediment. Accordingly, the sorption capacity of sediment inorganic material would increase.

Sorption studies (Yang and Zhang, 1994, 1997) have demonstrated that hydrophobic solutes are also sorbed by inorganic surfaces of pure minerals such as kaolinite, illite, and montmorillonite. The removal of organic carbon by the H<sub>2</sub>O<sub>2</sub> treatment brings about the differences in the sorption isotherm shapes (Figures 3 and 5) observed in our study. This may be attributed to obvious differences in the sorption site energies between organic carbon and inorganic material of sediment, as the sediment surfaces become heterogeneous after peroxide treatment. Therefore nonlinear sorption isotherms could be observed on this type of sediment surface.

Nonlinear isotherms are frequently described by the Freundlich equation, which encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies,

$$C_s = K C_e^{1/n}, \tag{3}$$

where  $C_s$  represents the amount of the solute sorbed by unit weight of sediment (mg g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of the solute in aqueous solution (mg L<sup>-1</sup>), and  $K$  and  $1/n$  are empirical constants.  $K$  is a measure of the degree of strength of sorption, while  $1/n$  is used as an indication of whether sorption remains constant ( $1/n = 1$ ) or decreases with increasing solute concentration ( $1/n \neq 1$ ).

The experimental results of dimethyl phthalate on H<sub>2</sub>O<sub>2</sub>-treatment sediments were analyzed regressively by Freundlich isotherm and the isotherm equations and correlation coefficients ( $K_d$ ) are shown in Table IV. From Table IV it can be seen that the sorption behavior of dimethyl phthalate on H<sub>2</sub>O<sub>2</sub>-treatment can be described by Freundlich isotherm very well. Furthermore it can also be found that the empirical constant  $K$  value of the isotherms varied in the sequence:  $K(1) \cong K(3) > K(2)$ . The sequence was constant with the sequence of clay contents of marine sediment

TABLE IV  
Freundlich sorption isotherms of dimethyl phthalate on H<sub>2</sub>O<sub>2</sub>-treatment marine sediments in NSW

Station	Isotherms	R <sup>2</sup>
1	$C_s = 0.395 C_e^{1.100}$	0.9705
2	$C_s = 0.329 C_e^{0.933}$	0.9825
3	$C_s = 0.407 C_e^{1.016}$	0.9895

(Table I). Considering that large part of the original organic carbon was removed from the surface of sediment after the oxidation by  $H_2O_2$ , the sorption of dimethyl phthalate on  $H_2O_2$ -treated sediment would take place mainly through the surface adsorption, other than the partition of the organic carbon. The previous studies (Yang and Zhang, 1994) have shown that, clays of sediment inorganic materials contributed significantly to the adsorption of organic chemicals. Because the sorption capacity of sediment and the empirical constant  $K$  of Freundlich isotherm had direct relation with the clay content in marine sediment, our study provided further evidence for the above conclusion.

### 3.3. EFFECT OF SALINITY ON THE SORPTION OF DIMETHYL PHTHALATE

As far as seawater is concerned, salinity is an important environmental factor which may affect sorption behavior of organic contaminants on marine sediments. No. 3 sediment was chosen as the sorbent to study how the salinity affected the sorption behavior of dimethyl phthalate. The sorption isotherms and sorption equations are shown in Figures 4 and 5, and Tables V and VI, respectively.

From Figure 4, it is apparent that the sorption behavior of dimethyl phthalate on HCl- and No-treatment sediments fitted well with linear sorption isotherm in different media. In addition, Table V illustrate that the  $K_d$  values of isotherms on the same treated sediment increased with the increase of salinity. A three-fold increase in  $K_d$  values on HCl- or No-treatment sediments was observed when salinity varied from 0‰ to 33.4‰. The increase of sorption with salinity may be clearly interpreted by the following two reasons. On the one hand, for neutral organic compounds such as dimethyl phthalate, the sorption behavior was generally determined by their aqueous solubility (Zhou and Liu, 2000; Tan, 1995; Chiou, 1979; Karickhoff, 1979). In natural seawater, there are various inorganic ions such as  $Na^+$ ,  $K^+$ ,  $Cl^-$  and  $SO_4^{2-}$  which can affect the aqueous activity of the solutes such as dimethyl phthalate (Means, 1995; Jurner and Rawling, 2001; Whitehouse, 1984). The solutes are gradually salted out from seawater with increasing salinity. This will correspondingly decrease the aqueous solubility of dimethyl phthalate. As a result, the amount of dimethyl phthalate into marine sediment via partition action of sediment organic carbon will increase. On the other hand, the release of sediment organic matter into aqueous solution is depressed by the 'salting out' effect of the electrolytes in seawater (Jurner and Rawling, 2001). This accordingly leads to both the enhancement of the partition effect of marine sediment and the increase of the sorption capacity of the sediment. Consequently, the salinity indirectly influenced the sorption behavior of dimethyl phthalate through directly influencing the property of aqueous solubility of dimethyl phthalate and sediment sorption capacity.

Moreover, Figure 5 and Table VI demonstrate that the sorption behavior of dimethyl phthalate on  $H_2O_2$ -treatment sediment (No. 3) could be described by Freundlich isotherm very well in the media (natural seawater, diluted seawater and deionized water). By comparing these sorption isotherms of dimethyl phthalate

TABLE V

Linear sorption isotherms of dimethyl phthalate on HCl- and No-treatment marine sediments (No. 3) in different media

Treatment means	NSW	$R^2$	DSW	$R^2$	DW	$R^2$
HCl	$C_s = 0.752 C_e$	0.9936	$C_s = 0.413 C_e$	0.9801	$C_s = 0.235 C_e$	0.9752
No	$C_s = 0.587 C_e$	0.9801	$C_s = 0.353 C_e$	0.9725	$C_s = 0.179 C_e$	0.9844

in different media (Table VI), it could be found that the empirical constant  $K$  of Freundlich isotherm also increased with the increase of salinity, and the  $K$  value in natural seawater was over three-fold higher than that in deionized water. As has been pointed out above, the increase in the salinity could result in the increase in

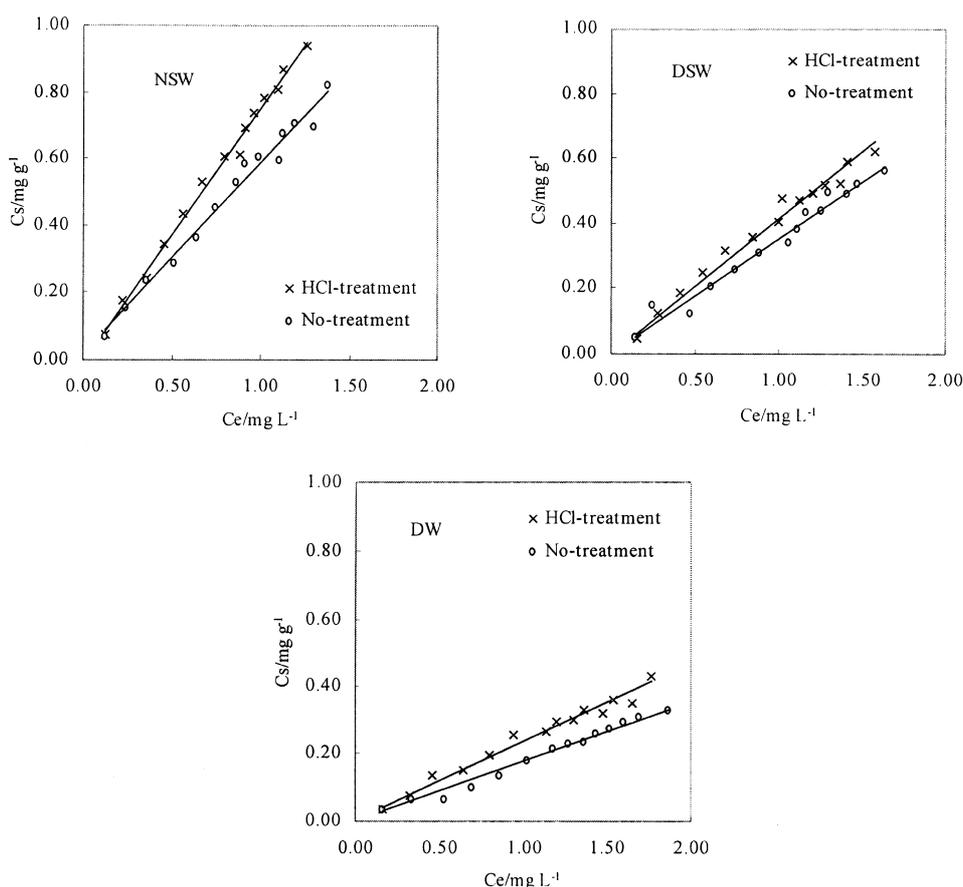


Figure 4. Linear sorption isotherms for dimethyl phthalate on HCl- and No-treatment marine sediments (No. 3) in different media.

TABLE VI  
 Freundlich sorption isotherms of dimethyl phthalate on HCl- and No-treatment marine sediments (No. 3) in different media

Media	Isotherms	$R^2$
NSW	$C_s = 0.407 C_e^{1.016}$	0.9895
DSW	$C_s = 0.356 C_e^{0.692}$	0.9791
DW	$C_s = 0.215 C_e^{0.920}$	0.9695

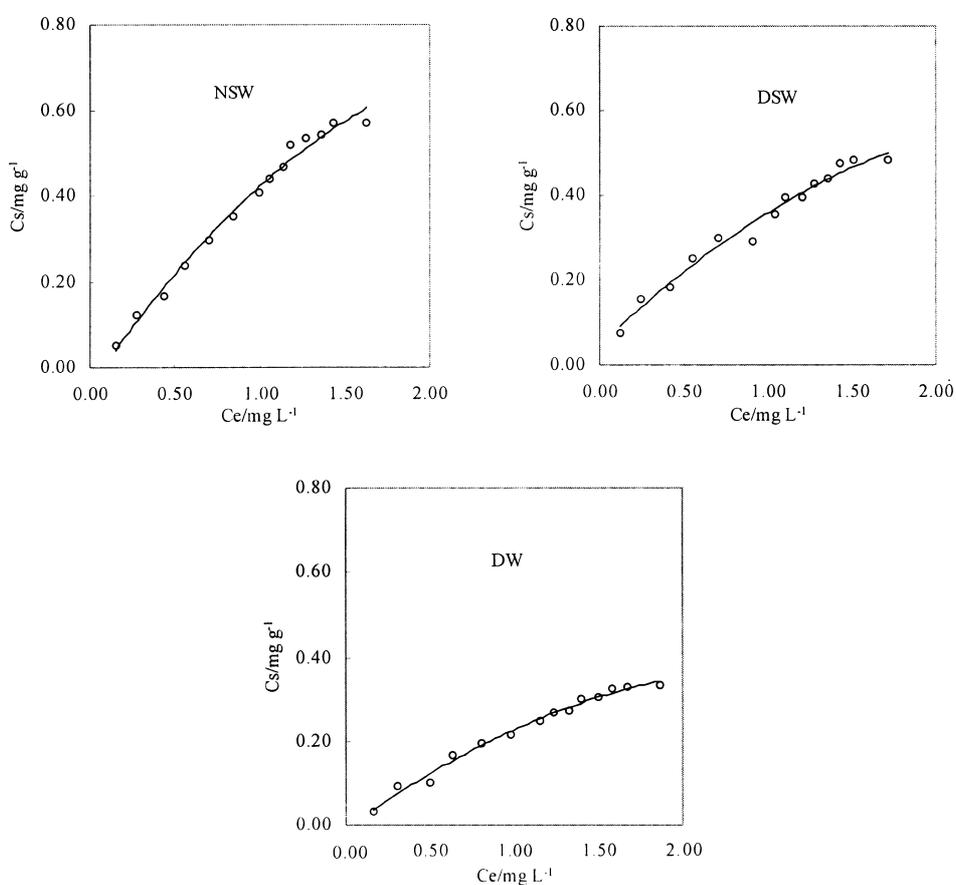


Figure 5. Freundlich sorption isotherms for dimethyl phthalate on  $H_2O_2$ -treatment marine sediments (No. 3) in different media.

'salting out' effect of electrolyte and the according decrease in aqueous solubility of dimethyl phthalate. As a result, the amount of dimethyl phthalate that came into the sediment through surface adsorption would correspondingly increase. Therefore, higher  $K$  value was reasonably observed in natural seawater.

#### 4. Conclusion

In the present study, some important insights have been gained into the sorption behaviors of dimethyl phthalate on marine sediments treated by different methods:

- a) About 10 hours was needed for equilibration of dimethyl phthalate sorption on marine sediment in three different media (i.e. natural seawater diluted seawater and deionized water).
- b) The sorption behaviors of dimethyl phthalate on HCl- and No-treatment sediment accorded well with the linear sorption isotherm. The sorption occurred principally via partition function of organic carbon of sediments.
- c) The sorption behavior of dimethyl phthalate on H<sub>2</sub>O<sub>2</sub>-treatment sediments was nonlinear and conformed to Freundlich isotherm. Sorption mechanism for dimethyl phthalate on H<sub>2</sub>O<sub>2</sub>-treatment sediments was thought to be through surface function of clay in the sediments.
- d) As aqueous salinity increased, solubility of dimethyl phthalate would decrease and simultaneously the release of sediment organic matter into solution would reduce by the effect of 'salting out'. Consequently, partition coefficients  $K_d$  and empirical constant  $K$  increased with increasing salinity of seawater.

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