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Sorption behaviour of benzyl butyl phthalate on marine sediments: Equilibrium assessments, effects of organic carbon content, temperature and salinity

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ABSTRACT

Benzyl butyl phthalate (BBP) is an endocrine-disrupting chemical, and its sorption behaviour on marine sediments was investigated. BBP sorption on the sediments was a rapid process, which could reach equilibrium in 6 h. The sorption equilibrium results could be well described by a linear isotherm. The BBP partition coefficient, K_d, varied from 7.16 to 12.54 L/g in approximately proportion to the organic content of the sediments. After H_2O_2 oxidation for removing the organic material from the sediments, the K_d values were reduced by more than 70%, but the organic normalised partition coefficient averaged 2165 L/g for the H_2O_2-treated sediments, which was more than three times of 598 L/g for the raw sediments. The sorption of BBP on the sediments increased with a decrease in temperature and an increase in salinity. A salting constant of 1.14 L/mol was obtained for BBP in artificial seawater. These research findings are of importance to an assessment of the fate and transport of BBP and other similar endocrine-disrupting chemicals (EDCs) in seawater–sediment systems.

1. Introduction

Phthalate esters (PEs) have been widely used as plasticisers to improve the mechanical properties, particularly flexibility, of plastic products (Staples et al., 1997; Xu et al., 2005, 2007a,b). Since PEs are not chemically bound to polymers, they may leach out from the plastic products during use and/or after disposal (Staples et al., 1997). PEs have become so widespread in the environment that they have been found in seawater (Fatoki and Ogunfowokan, 1993), river water (Sha et al., 2007), soil (Hunter and Uchrin, 2000) and sediments (Yuan et al., 2002). PEs are suspected of causing disruption of the endocrine system and hence of interfering with the reproduction and behaviour of humans and wildlife (Colon et al., 2000; Tetsuji et al., 2000). Several regulatory bodies, including the US Environmental Protection Agency and the European Union, have classified PEs as endocrine-disrupting chemicals (EDCs) and as "priority pollutants" in the water environment. Among the PEs, butyl benzyl phthalate (BBP) is one of the most significant and omnipresent environmental contaminants, and it has high bioaccumulation potential for different organisms (Staples et al., 1997).

The sorption of organic pollutants onto sediments affects their fate and transport in the aquatic systems. In recent years, much attention has been paid to the sorption of organic pollutants on marine sediments (Williams et al., 1995; Turner and Rawling, 2000; Zhao et al., 2004; Cornelissen et al., 2006; Droge and Hermens, 2007; Xu and Li, 2008; Xu et al., 2008). However, the sorption behaviour of BBP on marine sediments has not yet been reported in the literature, and the impact of such environmental factors as sediment organic content, temperature and salinity, on BBP sorption in a seawater–sediment system remains unknown.

The study reported herein focused on the sorption of BBP on marine sediments collected from different sites in Victoria Harbour, Hong Kong. Particular emphasis was placed on investigating (1) the sorption isotherm of BBP on the marine sediments, and (2) the impacts of sediment organic matter, temperature and salinity on the BBP sorption. The results obtained are important to an assessment of the fate and risks of BBP in marine waters.

2. Materials and methods

2.1. Chemicals

The pure BBP was of analytical grade and purchased from ACROS Organics (Geel, Belgium). Its molecular formula, molecular weight (g/mol) and Chemical Abstracts Registry Number (CAS#) are $C_{19}H_{20}O_4$, 312.4 and 85-68-7, respectively. BBP is slightly hydrophobic, with a water solubility less than 3 mg/L, and logarithmic values of octanol–water partition coefficient (log K_{ow}) ranged from 3.57 to 4.91 (Staples et al., 1997). The other reagents and solvents were of analytical reagent grade or better. The stock BBP solution was prepared by adding 1 g of BBP into 500 mL of methanol. One millilitre of this BBP–methanol solution was then added to artificial seawater to make 1 L of working solution with a BBP concentration of 2.0 mg/L. The artificial

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Table 1
Physicochemical characteristics of the marine sediments and partition coefficients for BBP sorption on the sediments before and after H_2O_2-treatment.

Site	Particle size distribution			Raw sediment			H_2O_2-treated sediment			f_{BC}/f_{OC}
	Sand	Clay	Silt	f_{OC} (%)	K_d (L/g)	K_{OC} (L/g)	f_{BC} (%)	K'_d (L/g)	K_{BC} (L/g)	
B1	44.2	55.7	0.1	1.38	7.98	578	0.11	2.52	2291	0.08
B2	29.4	70.4	0.2	1.96	12.54	640	0.12	3.41	2842	0.06
B3	0.2	98.1	1.7	1.81	10.87	601	0.17	2.81	1653	0.09
B4	22.5	77.3	0.2	1.29	7.16	555	0.13	2.25	1731	0.10
B5	0.3	93.5	6.2	1.87	11.52	616	0.14	3.23	2307	0.07
Mean ± SD					10.01 ± 2.33	598 ± 33		2.84 ± 0.48	2165 ± 486	

seawater was made according to the literature (Zhao et al., 2004), and had a salinity of 35. Its ionic composition was representative of real sea water, and no organic matter was included (Zhao et al., 2004).

2.2. Adsorbents — marine sediments

Marine sediment samples (0 to 20 cm) were collected from five different sites in Victoria Harbour, Hong Kong, in April 2006. The sampling sites from the east (B1) to the west (B5) were selected to provide a good coverage of the harbour area. The latitudes/longitudes of sites B1, B2, B3, B4 and B5 are 22°14.800/114°16.000, 22°17.500/114°13.500, 22°17.470/114°11.180, 22°18.400/114°06.500 and 22°18.142/114°03.051, respectively. Site B1 is closer to the open ocean, whilst site B5 is closer to the river mouth of an estuary. The organic content was therefore expected to increase in the sediments from B1 to B5. The fresh sediment mixtures had a pH of around 7.5. After shells and gravels were removed manually, the size distributions of the sediment samples were measured by a particle size analyser (Coulter LS 13 320, Beckman, Fullerton, CA) and the sediment compositions in terms of their sand, silt and clay fractions were estimated accordingly (Table 1). The sediment samples were air-dried and then homogenised. They were ground into particles that could pass through a 60-mesh (<250 μm) sieve because the sorption onto suspended sediments was not to be replicated. The sediment samples were treated gently and simply so that the treatment processes had the least impact on the integrity of the samples.

The organic content of the sediment samples were measured with a total organic carbon (TOC) analyser (TOC-5000, Shimadzu, Japan) with a solid sample module (SSM-5000A, Shimadzu, Japan). In addition to the raw sediment samples, a portion of each sediment sample was further treated by H_2O_2 oxidation to remove the organic matter. Following the procedure described by Zhao et al. (2004), 30 mL of 30% H_2O_2 was added to 10 g of dried sediment. When the mixture had cooled down, a second 30 mL of 30% H_2O_2 was added. After this H_2O_2-treatment, the sediments were washed thoroughly with deionised (DI) water, dried and then ground. Approximately 90% of the organic carbon could be removed from the sediments by H_2O_2 oxidation, and the remaining organic carbon content on the sediments was called as black carbon (BC) (Table 1). BBP sorption experiments were conducted on both the raw and H_2O_2-treated sediments.

2.3. BBP sorption experiments

For the sorption test on a sediment sample, about 0.1 g of the dry raw sediment (or 0.3 g H_2O_2-treated sediment) was placed in each of ten 250-mL Erlenmeyer flasks, followed by the addition of 90 mL artificial seawater. Sodium azide was dosed into the seawater at 0.02% (by weight) to inhibit bacterial growth (Gao et al., 1998). In this study, different amounts of the stock BBP solutions were added into the flasks for pre-determined concentrations at 100, 150, 200, 300, 400, 600, 800, 900, 1100 and 1200 μg/L, which resulted in the concentrations of BBP in aqueous phase and sediment comparable with those in marine environment. Artificial seawater was then added to make up a suspension volume of 100 mL in each flask. The pH of the sediment suspensions was adjusted with HCl or NaOH to pH 7.5. The flasks were immediately sealed with parafilm and shaken mechanically at 25 ± 1 °C in a temperature-controlled S150 shaking incubator (Stuart, UK) at a shaking speed of 100 rpm. According to the tests on BBP sorption kinetics, the sorption of BBP on the marine sediments could reach equilibrium in less than 6 h. In this study, the flasks in the sorption test were shaken overnight. After then, the suspension in the flask was centrifuged at 4000 *g* for 10 min, and 50 mL of the supernatant was then collected for BBP measurement. A blank sorption experiment was conducted following the same test procedure except that no sediment was added. Adsorptive losses to the flask walls were found to be less than 5% of the BBP dosed.

The sorption experiment was conducted three times for each sediment sample, and each individual chemical assay was conducted in duplicate. The mean values for determination of the sorption isotherm model are presented together with error bars that indicate the standard deviations of the three experiments for each sample.

2.4. Effects of temperature and salinity on BBP sorption

The effects of environmental factors, including temperature and salinity, on BBP sorption were investigated on the sediment from site B1. For the temperature study, temperatures at 298, 303 and 308 K were tested, which was the temperature range of laboratory temperature to the highest temperature of the environment under study. For the salinity effect, the artificial seawater with a salinity of 35 was diluted to different salinities using the deionized water (Zhao et al., 2004). BBP sorption by the sediments in seawater with salinities of 35, 30, 25, 20, 15, 10 and 5, respectively, was studied. In addition, the deionized water (salinity 0) was also chosen as medium to investigate the effect of salinity (Zhao et al., 2004).

2.5. BBP measurement

The BBP concentration in a solution was determined by high performance liquid chromatography (HPLC) after solid phase extraction. For solid phase extraction, a Waters SPE C_{18} cartridge (500 mg) was first conditioned with 2 mL of methanol and then 5 mL of DI water. Fifty millilitres of a sample containing BBP were pumped through the cartridge at a flow rate of 2 mL/min. The analyte retained in the SPE cartridge was eluted with methanol (1 mL × 2), and the

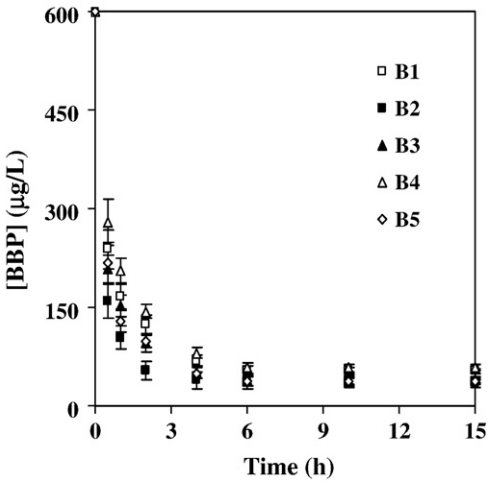

Fig. 1. Change of BBP concentration in the seawater with the time of sorption by the marine sediments at salinity 35, pH 7.5 and temperature 25 °C (initial BBP concentration = 600 μg/L).