# Sorption of Phthalate Esters and PCBs in a Marine Ecosystem

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Dialkyl phthalate esters (DPEs) are widely used industrial chemicals with octanol-seawater partition coefficients ranging between 10<sup>1.80</sup> for dimethyl phthalate to 10<sup>10.0</sup> for diiso-decyl phthalate, indicating a propensity to sorb strongly to particulate matter in aquatic environments. Sorption plays a key role in controlling the long-term fate of DPEs in aquatic systems and exposure to organisms in aquatic food-webs. However, field observations of the sorption of many commercial DPEs do not exist. To characterize the sorptive nature of DPEs in a real-world aquatic ecosystem, we measured concentrations of DPEs congeners, commercial DPE mixtures, and 10 polychlorinated biphenyls (PCBs) in water, suspended sediments, and bottom sediments of a marine inlet. Sorption coefficients of spiked and native DPEs and PCBs between suspended sediments and water indicate that the apparent sorptive nature of DPEs and PCBs is substantially greater than expected from  $K_{\rm OW}$ -based sorption models. Particulate and dissolved organic matter showed similar (i.e., not statistically different) sorption affinities for native analytes. The apparent fraction of the total aqueous concentration of DPEs that is freely dissolved and absorbable via the respiratory tract of aquatic organisms varied from virtually 100% for DMP to 0.0003% for C10. The observed decline in concentration of most DPEs between suspended and bottom sediments, compared to an increase in the concentration of high  $K_{\rm OW}$ PCBs, suggests that the rate of desorption and degradation of DPEs exceeds that of organic carbon mineralization and contributes to the previously observed lack of biomagnification of DPEs in the aquatic food-web of this system.

# Introduction

Di-alkyl phthalate esters (DPEs), with current annual global production volumes of approximately 5.2 million tonnes, are widely used in consumer products. Due to their hydrophobicity and octanol—seawater partition coefficients ranging between 10<sup>1.80</sup> for dimethyl phthalate to 10<sup>10.0</sup> for diiso-decyl phthalate (Table S1, Supporting Information) (1), they have an inherent potential to sorb to particulate matter

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and bioaccumulate in aquatic organisms (2). DPEs have been subject to evaluation in response to the UNEP protocol on Long-Range Transport of Atmospheric Pollutants and other initiatives in several jurisdictions. However, reliable field data for several DPEs are scarce or absent, making such evaluations difficult.

This paper is the third in a series of the distribution of native DPEs in a marine environment. Previous studies focused on analytical methodology (3), and the distribution of individual congeners and commercial mixtures of DPEs in an aquatic food-web (4). This study focuses on the distribution of 13 individual DPE congeners, five industrial mixtures of DPEs and, for comparative reasons, 10 PCB congeners between seawater, suspended particulate matter, and bottom sediments. The distribution of native DPEs between water, suspended particulates, and bottom sediments has important implications for the global dispersal of DPEs and the exposure of organisms such as fish, filter feeders, and sediment dwelling organisms. The aim of this study is to determine sorption coefficients and elucidate the distribution of DPEs between water, suspended dissolved and particulate organic matter, and bottom sediments in a marine ecosystem, in relation to PCBs.

#### Theory

As discussed in the Supporting Information, currently available methods for measuring water concentrations of hydrophobic substances distinguish three fractions of chemical in the water:

(i) the fraction of chemical associated with large diameter (LD) or heavier particles in the water ( $f_{LD}$ , unitless):

$$f_{\rm LD} = M_{\rm LD}/M_{\rm T} = [K_{\rm LD} \times c_{\rm LD}]/[1 + (K_{\rm SD} \times c_{\rm SD}) + (K_{\rm LD} \times c_{\rm LD})]$$
(1)

(ii) the fraction of "operationally defined" freely dissolved chemical in the water, which includes chemical that is freely dissolved and chemical associated with small diameter (SD) or lighter particles ( $f_{OD}$ , unitless):

$$f_{\rm OD} = M_{\rm OD}/M_{\rm T} = [1 + (K_{\rm SD} \times c_{\rm SD})]/[1 + (K_{\rm SD} \times c_{\rm SD}) + (K_{\rm LD} \times c_{\rm LD})]$$
(2)

(iii) the freely dissolved chemical fraction in the water ( $f_{\rm FD}$  unitless), which is not easily measurable, but can be estimated as

$$f_{\rm FD} = M_{\rm FD}/M_{\rm T} = 1/[1 + (K_{\rm SD} \times c_{\rm SD}) + (K_{\rm LD} \times c_{\rm LD})]$$
 (3)

where  $M_T$ ,  $M_{LD}$ ,  $M_{OD}$ ,  $M_{FD}$ , are the masses (kg) of total, large diameter, operationally dissolved, and freely dissolved chemical in the water, respectively;  $K_{LD}$ , and  $K_{SD}$  are the solids—water partition coefficients (L/kg) of the chemical in, respectively, large and small diameter suspended matter; and  $c_{LD}$  and  $c_{SD}$  are the concentrations (kg/L) of, respectively, large and small diameter in water.

Assuming that the organic carbon fraction of particulate matter contains the majority of hydrophobic organic chemicals found in particles, the sorption coefficients  $K_{\text{LD}}$  and  $K_{\text{SD}}$  can be rewritten as

$$K_{\rm LD} = \phi_{\rm OC,LD} \times K_{\rm OC,LD}$$

and

$$K_{\rm SD} = \phi_{\rm OC,SD} \times K_{\rm OC,SD} \tag{4}$$

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where  $\phi_{OC,LD}$  and  $\phi_{OC,SD}$  (kg/kg), respectively, represent the organic carbon contents of large and small diameter particulate matter in the water and  $K_{OC,LD}$  and  $K_{OC,SD}$  are the organic carbon–water sorption coefficients (L/kg) for ,-respectively, large and small diameter particulate matter.

There is considerable ongoing research on the sorptive nature of various types of organic carbon and the extent to which  $K_{\text{OC}}$  can be represented by  $K_{\text{OW}}$  (5–7). Seth et al. (5) proposed that  $K_{\rm OC}$  ranges between  $0.14 \cdot K_{\rm OW}$  to  $0.87 \cdot K_{\rm OW}$ . Based on a review of literature data, Burkhard (6) concluded that  $K_{\rm OC}$  of dissolved organic matter is approximately 0.08.  $K_{\rm OW}$  with 95% confidence limits equivalent to a factor of 20. A sorptive capacity 10-100 times greater than that of octanol has been apportioned to carbonaceous organic materials such as black carbon (7). It has also been proposed that, under field conditions, K<sub>OC</sub> can be naturally elevated over its thermodynamic quantity for hydrophobic substances, such as PCBs, that are desorbing and degrading at rates slower than the natural degradation rate of the organic carbon in particles (8). In addition, it is possible that water-to-air transport produces chemical concentrations in the water that are below thermodynamically controlled sorption coefficients. Despite the lack of a clear understanding of the mechanism underlying the relationship between  $K_{OC}$  and  $K_{\rm OW}$ , a simple linear relationship has often been used or assumed as an appropriate first approximation:

and

$$K_{\rm OC,SD} = \alpha_{\rm OC,SD} \times K_{\rm OW}$$
(5)

where  $\alpha_{OC,LD}$  and  $\alpha_{OC,SD}$  (L/kg OC) are proportionality constants relating the organic carbon sorption affinity of the chemicals to that of octanol.

 $K_{\rm OC,LD} = \alpha_{\rm OC,LD} \times K_{\rm OW}$ 

Substitution of eqs 4 and 5 into eqs 2–3, and using a parameter  $\beta$  (unitless) to represent the product of  $c \cdot \phi \cdot \alpha$ , the operationally dissolved and freely dissolved fraction of chemical in the water can be related to  $K_{\text{OW}}$  following eq 6 and 7, respectively:

$$f_{\rm OD} = [1 + (K_{\rm OW} \times \beta_{\rm SD})]/$$
$$[1 + (K_{\rm OW} \times \beta_{\rm SD}) + (K_{\rm OW} \times \beta_{\rm LD})] (6)$$

$$f_{\rm FD} = 1/[1 + (K_{\rm OW} \times \beta_{\rm SD}) + (K_{\rm OW} \times \beta_{\rm LD})]$$
(7)

where,

$$\beta_{\rm SD} = c_{\rm SD} \times \phi_{\rm OC,SD} \times \alpha_{\rm OC,SD}$$

and

$$\beta_{\rm LD} = c_{\rm LD} \times \phi_{\rm OC,LD} \times \alpha_{\rm OC,LD} \tag{8}$$

Nonlinear regression between  $f_{\text{OD}}$  and  $K_{\text{OW}}$  can be performed to determine the coefficients  $\beta_{\text{LD}}$  and  $\beta_{\text{SD}}$  (in eq 6) and to estimate the fraction of freely dissolved chemical in the water using eq 7. Measurement of  $c_{\text{SD}}$ ,  $\phi_{\text{SD}}$ ,  $c_{\text{LD}}$ , and  $\phi_{\text{LD}}$  then provides an opportunity to explore the sorptive capacities  $\alpha_{\text{SD}}$  and  $\alpha_{\text{LD}}$ of DPEs to organic carbon in different size fractions of suspended sediments using eq 8.

#### Methods

**Materials and Preparation.** Materials, methods and quality control/quality assurance (QA/QC) protocols used for the analysis of DPEs and PCBs in this study are described in detail in respectively (*3*, *4*) and (9). HPLC grade solvents were used. Hexane was doubly distilled. Glassware was detergent washed, rinsed with distilled water, acetone, hexane, dichlo-

romethane, and isooctane, baked at 350 °C for at least 10 h, stored in solvent-rinsed aluminum foil, and re-rinsed prior to use. The final glassware rinsate was analyzed by GC–MS to ensure that the glassware was not contaminated with DPEs.

**Sampling Site.** False Creek Harbor is a shallow marine inlet in Vancouver (*3*, *4*). Historically, it was an industrial site, but since 1968, the inlet has become urbanized and hosts a public market, several marinas and docks, and public entertainment venues. Three bridges span the inlet, and pollution from nearby roadways, CSOs, and boat traffic enters the inlet. Four locations were sampled in False Creek to assess potential variability in concentrations in the inlet. Average temperature and salinity were 11 °C and 30 ‰, respectively.

**Water Sample Collection.** 4-L water samples were collected in pre-cleaned amber glass bottles from approximately mid-depth (i.e., 4-5 m) at 4 locations in the shallow inlet. Each location was sampled in triplicate, for a total of 12 samples. The bottles were capped with solvent-rinsed aluminum foil, placed in a cooler with ice in the field, and transferred to a 4 °C refrigerator prior to filtration. Extraction of water was conducted within 12 h after sample collection. Spring water, used for procedural blanks, was collected from Lynn Headwater Regional Park.

Sediment Sample Collection. Surface sediment samples were collected in 250 mL pre-cleaned glass jars from four locations in False Creek, using a petit ponar grab sampler. Four (or five) samples from each location were collected for a total of 17 samples. The top layer (0.5-1.0 cm) of each grab sample was collected. Vials were immediately placed on ice and were stored at -20 °C in the dark prior to analysis.

Water Extraction and Cleanup. From each 4-L seawater sample or spring water blank, 1.00 L was spiked with 100 ng of each deuterated phthalate ester standard (i.e., dimethyl  $(DMP-d_4)$ , di-*n*-butyl  $(DnBP-d_4)$ , and di-*n*-octyl  $(DnOP-d_4)$ ) in acetone, 30 ng of each <sup>13</sup>C-PCB 52, <sup>13</sup>C-PCB 128, <sup>13</sup>C-PCB 209 in methanol, and 5 mL HPLC grade methanol 1 h prior to extraction. Each sample was run through a stainless steel water filtration apparatus (Figure S1), consisting of an FMI valveless pump, which pumped water at a flow rate of 8-10 mL/min; a 0.45- $\mu$ m pore size glass fiber filter (GFF) from Gelman Laboratory, Pall Corporation, Ann Arbor, Michigan; and two independent octadecyl (C<sub>18</sub>) extraction disks from 3M (St. Paul, MN) with a reported composition of 90% octadecyl bonded silica particles and 10% matrix PTFE by weight. The GFF and C<sub>18</sub> disks were each housed in 47mm stainless steel in-line filter holders from Gelman Laboratory, Pall Corporation, Ann Arbor, Michigan, and 0.5 in. stainless steel tubing was used. Extensive cleaning of the C18 disks prior to extraction by three sequential 15 min sonications, first in isooctane, then doubly distilled toluene, and finally 1:1 DCM/hexane was required to remove phthalate ester residues from the commercial membranes. The final extract was checked by GC-MS to confirm that residual phthalate levels were negligible.

After filtration of the 1.00 L seawater sample, the GFF and C<sub>18</sub> disks were removed from the system and extracted independently by three sequential 5 min sonications with 20 mL 1:1 DCM/hexane. The extracts from the three sonications were combined and concentrated to 3-5 mL under a gentle stream of high purity nitrogen, and quantitatively transferred to a neutral alumina column for cleanup. The column was packed with 15 g deactivated alumina (15% H<sub>2</sub>O, w/w), topped with 2 cm anhydrous Na<sub>2</sub>SO<sub>4</sub>. 15–20 mL doubly distilled hexane was run through the column. The sample extract was then eluted with three consecutive 30 mL fractions of hexane, 1:9 DCM/hexane, and 1:1 DCM/hexane. The first fraction contained the PCBs and the third fraction contained the DPEs. The fractions were concentrated to 100  $\mu$ L and spiked with recovery standards, i.e., 2 ng of <sup>13</sup>C-PCB-111 and 50 ng each

of dueterated diethyl phthalate  $(\mbox{DEP-d}_4)$  and butylbenzyl phthalate  $(\mbox{BBP-d}_4).$ 

**Sediment Extraction and Cleanup.** Details of the chemical analysis are described in ref 3 for DPEs and ref 9 for PCBs. Briefly, 2 g of sediment was spiked with the internal standards described above for DPEs, and blended with 15 to 20 g of prebaked Na<sub>2</sub>SO<sub>4</sub>. PCB internal standards were <sup>13</sup>C labeled PCB-52, 101, 128, 180, 194, 208, 209, 28, and 118. The homogenate was extracted three times using 1:1 DCM/ hexane. Extracts were eluted in a deactivated alumina column, with hexane for PCBs, and 1:1 DCM/hexane for DPEs. The PCB fraction underwent further cleanup with silica and dry alumina columns. The DPE fraction for GC/LRMS was further cleaned on a Florisil column. All extracts were spiked with the recovery standards described above prior to analysis.

**Instrumental Analysis.** Sample extracts containing PCBs were analyzed by gas chromatography high resolution mass spectrometry (GC/HRMS) following ref 9. Although the analytical methodology provided full congener PCB data, only ten PCB congeners/coeluters (i.e., PCB-18, 16/32, 53, 73/52, 110, 149, 132/153, 187/182, 180, and 194) are reported in this study.

Sample extracts containing the DPEs were first analyzed by gas chromatography low resolution mass spectrometry (GC/LRMS) for the quantification of the individual compounds (i.e., DMP, DEP, di-iso-butyl (DiBP), DnBP, BBP, di-(2-ethylhexyl) (DEHP), DnOP, di-*n*-octyl (DnNP)), followed by liquid chromatography electrospray ionization mass spectrometry (LC/ESI–MS) for quantification of the isomeric commercial mixtures of DPEs (i.e., di-iso-hexyl (C6), di-isoheptyl (C7), di-iso-octyl (C8), di-iso-nonyl (C9), and di-isodecyl (C10)) (3). Tandem mass spectrometry (MS–MS) using the VG Quattro MS machine operated in multiple reaction monitor (MRM) mode, confirmed that there were no chromatographic and/or isobaric interferences with DPE isomeric mixtures in sediment and water samples (3).

**Quantitation.** Concentrations of identified DPE and PCB compounds were determined by the internal standard isotope-dilution method. Minimum detectable amounts (MDA), which correspond to the amount of chemical that produces a 3:1 signal-to-noise ratio, ranged from 0.03 to 0.6 pg for individual DPEs and from 8 to 213 pg for the five DPE isomeric mixtures and were approximately 1.8 pg for the 10 PCB congeners (Table S2, Supporting Information).

QA/QC. Each sample batch consisted of three procedural blanks and 3-6 matrix samples. Procedural blanks consisted of 1 L of spring water for the seawater samples and 15-20 g of sodium sulfate for the sediment samples, and samples were blank corrected. Method detection limits (MDLs) were determined as the mean MS response + 3 times the standard deviation of the mean response of each DPE and PCB in the procedural blanks. Only the seawater and sediment concentrations of DPEs and PCBs that exceeded the MDL were included in further analysis and reporting. This procedure was selected to ensure that background contaminants that were introduced during sample extraction and analysis did not contribute to the reported environmental concentrations. Background contamination was believed to be the main cause of observed chemical concentrations below the MDL. For DPEs in seawater samples, the MDL was determined on a per batch basis, based on the analyses of three spring water blanks. This per-batch method was used due to variability in background concentrations between batches, particularly for BBP, DnNP and the C6 to C9 isomers (Table S2). PCB MDLs in seawater, and both DPE and PCB MDLs in sediment were determined using the mean MS response + 3 standard deviations for n = 10 spring water blanks for seawater and n = 18 sodium sulfate blanks for sediment, since blank concentrations were consistent between batches.

**Quantification of Suspended Particulate Matter.** Suspended particulate matter was found on both the GFF and the primary  $C_{18}$  extraction disk. To quantify the amount of suspended particulate matter in the water, 3-L of the original 4-L of sample water was pumped through the filtration system containing the GFF and  $C_{18}$  disks. Suspended particulate matter was measured as the difference between pre- and post-filtration dry weights of the GFF and  $C_{18}$  disk. Particulate matter present on the GFF was greater than 0.45  $\mu$ m in diameter and is defined as large diameter (LD) suspended matter. The particulate matter measured on the  $C_{18}$  disk was fine-grain material and is defined as small diameter (SD) suspended matter.

**Organic Carbon Contents.** The total organic carbon (TOC) content of large and small diameter particulate matter were measured using a Leeman's 440 Elemental Analyzer following (*10*). The fraction of organic carbon in the bottom sediments was 2.80% ( $\pm 0.31\%$  (SD), n = 12) and TOC of large and small diameter suspended particulate matter was 40% ( $\pm 4\%$  (SD), n = 12).

**Statistics.** Standard deviations are reported along with means, unless otherwise specified. Other statistical methods are reported in each section of the results.

#### **Results and Discussion**

**Recovery**. Recovery of water extraction was determined as the mass fraction of spiked internal standards found on the GFF and both C<sub>18</sub> extraction disks. Average recoveries ( $\pm$  one standard deviation) of DMP-d<sub>4</sub>, D*n*BP-d<sub>4</sub> and D*n*OP-d<sub>4</sub> were, respectively, 70 ( $\pm$ 32), 79 ( $\pm$ 36), and 48 ( $\pm$ 22) % in spring water, and 70 ( $\pm$ 20), 86 ( $\pm$ 28), and 37 ( $\pm$ 12) % in seawater. The apparent drop in recovery from D*n*BP to D*n*OP agreed with similar observations in ref *11* and is believed to reflect the increase in the DPE adsorption affinity to the glass vessel with increasing *K*<sub>OW</sub> from log 4.58–8.20. Recoveries for <sup>13</sup>C labeled PCB congeners 52, 128, and 209 were 42 ( $\pm$ 6), 43 ( $\pm$ 2), and 28 ( $\pm$ 3) % in seawater and also indicate increased adsorption of the highest *K*<sub>OW</sub> PCBs onto glass.

The extraction recoveries of DPEs from bottom sediment samples were 82 ( $\pm$ 12), 89 ( $\pm$ 12), and 95 ( $\pm$ 19) % for DMPd<sub>4</sub>, D*n*BP-d<sub>4</sub>, and D*n*OP-d<sub>4</sub>, respectively, and they indicate an efficient extraction procedure. Recoveries for the nine PCB internal standards in sediments were between 37% ( $\pm$ 14) for PCB-28 and 58% ( $\pm$ 9) for PCB-128, and were typical for this method of analysis (9). All congener concentrations (PCBs and DPEs) were corrected for the recoveries of the internal standards.

**Method Detection Limit (MDL).** Minimum and maximum MDLs of DPEs in 4 batches of water samples varied from 3.3 ng/L for DMP to 1,060 ng/L for C8 isomers (Table S2). For DMP, DEP, DiBP, DnBP, BBP, DEHP, DnOP, and C10, differences in method detection limits between analyses were small, indicating good reproducibility of the MDL between analyses. However, for BBP, DnNP, C6, C7, C8, and C9, there were substantial differences between MDLs among batches of water samples due to background contamination during extraction. MDLs for DPEs in sediment ranged from 0.6 to 41 ng/g for C6 and C8, respectively. MDLs for PCBs were low and ranged from 20 pg/L (PCB-194) to 620 pg/L (PCB-18) for seawater, and from 3 pg/g (PCB-194) to 260 pg/g (PCB-18) for sediment (Table S2).

**Bottom Sediment Concentrations.** Concentrations of DPEs between stations were not statistically significantly different (ANOVA, p < 0.05), and appeared to be log-normally distributed as tested by Kolmogorov–Smirnov and Shapiro–Wilk normality tests. Geometric mean concentrations were calculated for the combined False Creek data set (n = 12-17, Table S3, Supporting Information). Concentrations of individual DPEs and isomeric mixtures were between 4.0 (DiBP) and 2100 (DEHP, C8) ng/g dry weight. Other DPEs



FIGURE 1. Concentrations of phthalate esters and polychlorinated biphenyls in (A) seawater (total water concentration) (ng/L), and (B) bottom sediments (ng/g dw) from False Creek.

found in relatively high concentrations in the sediments (Table S3, Figure 1B) were DnBP (114 ng/g dw), C9 (483 ng/g dw), and C10 (385 ng/g dw).

PCB concentrations in the sediments were approximately 10–1000-fold lower than DPEs, ranging between 0.30 for PCB-53 and 4.9 ng/g-dw for PCB-110, determined for the 10 test chemicals (Table S3, Figure 1B).

**Suspended Particulate Matter in Water.** The suspended matter concentration in the seawater at our test site, as determined by the mass of suspended matter measured on the GFF after filtration, was 1.47 ( $\pm$ 1.05) mg/L (n = 12). The first C<sub>18</sub> extraction disk after the GFF contained small diameter particulate matter at a mean concentration of 0.66 ( $\pm$ 0.28) mg/L (n = 7).

Total Water Concentrations. Total water concentrations were determined as the combined amounts of the test chemicals measured on the glass fiber and C<sub>18</sub> extraction disks. The total number of observed concentrations exceeding the MDL ranged between 100% for DMP to 17% for C8 (Table S2). For PCBs, the number of detectable water concentrations above the MDL ranged from 8% for PCB-194 to 50% for PCB-149 (Table S2). DPE and PCB congener concentrations above the MDL did not show statistically significant differences (ANOVA, p < 0.05) among the four sampling stations in the inlet. The total water concentrations of DPEs and PCBs in seawater were, therefore, determined as the geometric mean of all observations exceeding the MDL. This method was used because the majority of sample concentrations found to be in excess of the MDL were in batches with a high degree of background contamination in the blanks. A minimum of 4 observations above the MDL was considered to constitute a large enough sample size to determine the average water concentration. Hence, the water concentrations of C8, C9, and PCB-53, 110, 132/153, 180, and 194, were only considered estimates.

Total water concentrations of DPEs ranged from 3.5 ng/L for DMP and BBP to 275 ng/L for DEHP (Table S3, Figure



FIGURE 2. Ratio of the total seawater concentration ( $C_W$ , ng/L) to the aqueous solubility ( $S_W$ , ng/L) for phthalate esters ( $\oplus$ ) and polychlorinated biphenyls (gray  $\blacklozenge$ ), as a function of the octanol—seawater partition coefficient (log  $K_{OW}$ ). The solid horizontal line represents a  $C_W/S_W$  ratio of one.

1A). Significant losses of DPEs due to biodegradation, previously reported to occur within a period of 3-17 days [12-14] at 20 °C but which were negligible at 4 °C (*15*), were not expected to be a factor in this study because of the short pre-extraction (i.e., less than 12 h) period at 4 °C. The concentration of DEHP (275 ng/L) was comparable to concentrations measured in Lake Yssel, Netherlands (100–300 ng/L) (*15*) and the Tama river, Japan (13–3600 ng/L) (*16*), but lower than those in the Ebro River and Tarragon Sea, Spain (700–3200 ng/L) (*17*), Lake Baikal (600–1400 ng/L) (*15*), and the North and Irish Seas, UK (70–8400 ng/L) (*18*) and below the U.S. Environmental Protection Agency's adopted Maximum Acceptable Concentration of 6000 ng/L (*19*).

Concentrations of PCBs in seawater were approximately 1000-fold lower than those of DPEs and ranged between 12 and 277 pg/L, for PCB-110 and 16/32, respectively (Table S3, Figure 1A).

Seawater Concentration vs Aqueous Solubility. A comparison of the observed total water concentrations to the aqueous solubilities of DPEs (1) indicates that, while DMP concentrations in seawater were only a minute fraction of DMP's solubility in water (i.e.,  $6.7 \times 10^{-8}$ %), the ratio of the water concentration ( $C_W$ ) to the aqueous solubility ( $S_W$ ), i.e.,  $C_W/S_W$ , appears to increase with increasing log  $K_{OW}$  to a maximum value of 59% for C10 (Figure 2). This suggests that the higher molecular weight DPEs are approaching a "saturation level". This is highly unlikely but indicates that small amounts of suspended matter in the water column play a dominant role in controlling the apparent or total water concentration. The difference in  $C_W/S_W$  between DPEs and PCBs is likely due to the much larger inputs and resulting concentrations of DPEs in the system compared to PCBs.

**Sorption of Spiked DPE Internal Standards.** The objective of the water filtration method was to separate particulatebound analytes (captured on the 0.45- $\mu$ m GFF) from the apparent freely dissolved chemical in the water column. However, small diameter particulate matter was observed on the C<sub>18</sub> extraction disks. This indicates that the chemical concentration measured on the C<sub>18</sub> extraction disks should be referred to as the operationally defined freely dissolved chemical concentration. The operationally defined freely dissolved chemical concentration. The operationally defined freely dissolved chemical concentration of the spiked DPEs in seawater was *K*<sub>OW</sub>-dependent and dropped from >99% for DMP-d4 to 6% for D*n*OP-d4 (Figure 3A). This observed relationship of chemical partitioning between the GFF and C<sub>18</sub> extraction disks is in



FIGURE 3. Operationally dissolved chemical fractions measured on the C<sub>18</sub> disks (%,  $\pm$  one standard deviation) for (A) spiked phthalate ester internal standards ( $\bullet$ ) and (B) seawater-borne native phthalate esters ( $\bullet$ ), and PCBs (gray  $\bullet$ ) in False Creek seawater samples and nonlinear regressions representing the operationally dissolved fraction (solid line) and freely dissolved fraction (dashed line) derived from eqs 6 and 7 are plotted against the salinity corrected log octanol-water partition coefficient (log  $K_{0W}$ ).

general agreement with eq 2. In Figure 3A, the solid line represents the results of a nonlinear regression (using the least sum of squared errors between the measured and modeled mean operationally defined freely dissolved fractions) based on eq 6 between the operationally defined freely dissolved fraction and  $K_{\text{OW}}$ , where  $\beta_{\text{LD}}$  was determined to be 4.85 (±0.01) × 10<sup>-6</sup> and  $\beta_{\rm SD}$  was 3.07 (±0.01) × 10<sup>-7</sup> (n = 3,  $\pm$  one standard error). This indicates that 94% of the DPEs bound to particulate matter in the water were found on the large diameter particles and only 6% on small diameter particulate. Since as reported above,  $c_{\rm SD} = 0.66~(\pm 0.28)~\times$  $10^{-6}$  kg/L,  $c_{\rm LD} = 1.47 (\pm 1.05) \times 10^{-6}$  kg/L,  $\phi_{\rm OC,SD} = 0.40 (\pm 0.04)$ kg OC/kg, and  $\phi_{OC,LD} = 0.40 \ (\pm 0.04)$  kg OC/kg, eq 7 shows that  $\alpha_{SD}$  and  $\alpha_{LD}$  are, respectively, 1.16 (±0.49) L/kg OC and 8.24 ( $\pm$ 5.89) L/kg OC. The latter indicates that  $K_{OC}$  (L/kg OC) of the large particulate matter exceeds  $K_{OW}$  (L/L) and that the small diameter particulates appear to contain 1.16/8.24 or 14% of the sorptive capacity of the large diameter particles. The apparent sorptive capacities of the spiked DPEs in both the large and small diameter suspended particulates are substantially greater than those found previously for hydrophobic organic substances of comparable  $K_{OW}$ , i.e.,  $\alpha =$ 0.35 (5), 0.08 (for dissolved organic carbon) (6) or 0.41 (20).

Sorption of Native DPEs. Partitioning of seawater-borne native DPEs between the GFF and  $C_{18}$  disks also shows a relationship with  $K_{OW}$  (Figure 3B). The operationally dissolved  $C_{18}$  fraction of native DPEs drops from  $89 \pm 4.4\%$  (n = 12) for DMP and  $89 \pm 9.9\%$  (*n* = 12) for DEP to approximately 40% ( $\pm$  17) for D*n*NP and the other high *K*<sub>OW</sub> DPEs (Figure 3B). Operationally defined freely dissolved fractions for PCBs were between 45  $\pm$  11% for PCB-16/32 and 53  $\pm$  11% for PCB-73/52 and corresponded with measurements for DPEs of comparable  $K_{OW}$  (Figure 3B). Figure 3B further presents the results of the nonlinear regression (solid line) of the operationally dissolved fraction and  $K_{OW}$ . It shows the general agreement of the data with the model (i.e., eq 6) where  $\beta_{LD}$ is 2.07 (± 0.64) × 10<sup>-5</sup> and a  $\beta_{\rm SD}$  is 1.63 (±0.56) × 10<sup>-5</sup> (n =13,  $R^2 = 0.93$ ,  $\pm$  one standard error). This illustrates that, of suspended-matter-bound DPEs, 56% was associated with large particles (>0.45  $\mu$ m), and 44% with small diameter suspended matter. These fractions are in approximate agreement with the 69:31 ratio of the concentrations of large, i.e., 1.47 (±1.05) mg/L (n = 12), and small, i.e., 0.66 (±0.28) mg/L (n = 7) diameter suspended matter in the seawater.  $\alpha_{SD}$  and  $\alpha_{LD}$  were, respectively, 61 (±47) L/kg OC and 35  $(\pm 19)$  L/kg OC. The latter indicates that  $K_{OC}$  (L/kg OC) of DPEs in large and small suspended particulate matter exceed  $K_{\rm OW}$  (L/L) and that the apparent sorptive capacities of organic carbon in the small and large particulate fractions are not significantly different. The distribution of the higher molecular weight (and more hydrophobic) DPEs between the particulate fractions in natural waters differs substantially

from that measured in the spiking experiment where small diameter suspended matter exhibited only 14% of the sorptive capacity of large diameter suspended matter. This suggests that spiking is not an accurate method to determine the distribution of DPEs between water and suspended particulate matter in the field. This may be caused by the difference in chemical sorption time, i.e., 1 h for the internal standards and much longer periods for seawater-borne native DPEs.

Because of the inability of the C<sub>18</sub> extraction disks to distinguish between freely dissolved and DPEs sorbed to small diameter particulates, actual freely dissolved seawater concentrations can only be estimated by introducing the values for  $\beta_{\text{LD}}$  of 2.07 × 10<sup>-5</sup> and a  $\beta_{\text{SD}}$  of 1.63 × 10<sup>-5</sup> into eq 7. This produces estimates of the freely dissolved fraction  $(f_{FD})$ ranging from virtually 100% for DMP to very low values of  $2.8 \times 10^{-4}$ % for C10. For example, of the total DEHP aqueous concentration of 275 ng/L, only 0.02% or 0.05 ng/L may be in the freely dissolved form (Figure 3B). If only the freely dissolved chemical concentrations can be absorbed by aquatic organisms via the respiratory surface (21), then the measured total and the operationally defined freely dissolved water concentration can be expected to exceed the actual exposure concentrations (via the respiratory tract) by manyfold. These findings suggest that 0.45  $\mu$ m filtration is insufficient to distinguish between freely dissolved and particulate-bound DPEs and that it can lead to overestimation of the freely dissolved water concentration, underestimation of sorption coefficients and erroneous sorption models when such sorption coefficients are used in the derivation of sorption models.

**Sorption to Suspended Matter.** Table S3 lists and Figure 4A illustrates organic carbon normalized suspended sediment–water distribution coefficients ( $K_{SSW,OC}$ ) of DPEs and PCBs.  $K_{SSW,OC}$  was derived as the ratio of the organic carbon normalized concentration in the large diameter suspended particulate matter, collected on the GFF, ( $C_{SS,OC}$ ) and the operationally defined freely dissolved concentration in the water ( $C_{OD}$ ), i.e., as  $C_{SS,OC}/C_{OD}$ . Figure 4A shows that  $K_{SSW,OC}$  follows a weak relationship with  $K_{OW}$ , i.e., for DPEs:

$$\log K_{\text{SSW,OC}} = 0.096 \ (\pm 0.041) \cdot \log K_{\text{OW}} + 5.35 \ (\pm 0.29), \ n=13, \ R^2 = 0.33, \ p=0.041 \ (9)$$

where standard errors are reported within brackets in eq 9-12. If the distribution coefficients for DPEs are expressed based on estimated freely dissolved water concentration, i.e., as  $C_{SS,OC}/C_{FD}$ , the relationship improves to

Log 
$$K_{\text{SSW,OC}} = 0.798 \ (\pm 0.057) \cdot \log K_{\text{OW}} + 2.95 \ (\pm 0.40), \ n = 13, \ R^2 = 0.95, \ p = 2.4 \times 10^{-8} \ (10)$$



FIGURE 4. Observed distribution coefficients of phthalate esters ( $\bullet$ ,  $\bigcirc$ ) and polychlorinated biphenyls (gray  $\blacklozenge$ ,  $\blacktriangle$ ) between (A) suspended sediment and water and (B) bottom sediment and water based on the operationally dissolved (OD) water concentration ( $\bullet$ , gray  $\blacklozenge$ ), and the estimated freely dissolved (FD) water concentration ( $\bigcirc$ ,  $\blacktriangle$ ) and the predicted sediment—water equilibrium partition coefficient (-),  $K_{0C}$ , L/kg OC, based on ref 5. Linear regression between  $K_{0C}$  and  $K_{0W}$  are presented for DPEs OD (dashed line - - -); DPEs FD (thin solid line —), PCBs OD (dark gray line —), and PCBs FD (light gray line —).

Regressions statistics for PCBs equivalent to eq 9-12 are presented in the Supporting Information. Figure 4A shows that DPEs and PCBs follow similar relationships with  $K_{OW}$ . Based on measured operationally defined freely dissolved water concentrations (C<sub>OD</sub>), K<sub>SSW,OC</sub> of low K<sub>OW</sub> PCBs and DPE are greater than expected from equilibrium partitioning following (5), while  $K_{\text{SSW,OC}}$  of the higher  $K_{\text{OW}}$  DPEs and PCBs are lower than the equilibrium values. Such relationships are not uncommon for hydrophobic organic substances in natural systems (8), but are substantially different from the Karickhoff style expressions sometimes used in environmental fate models. Based on freely dissolved water concentrations (CFD), KSSW, OC of all PCBs and DPEs are substantially greater than sorption coefficients derived from Karickhoff style equilibrium partitioning relationships (5, 20). The observation that the apparent K<sub>OC</sub> of DPEs and PCBs exceed  $K_{\rm OW}$  by 1–2 orders of magnitude suggests caution in the application of conventional sorption models (e.g., refs 5, 6, 20 for modeling the fate of DPEs in marine aquatic systems, and indicates the need to develop sorption models with better predictive capabilities. The finding that the increase of  $K_{\text{SSW,OC}}$ over the corresponding Karickhoff style  $K_{OC}$  is greatest for the low Henry Law constant (H) DPEs (Table S1) and becomes smaller for DPEs with greater H (and hence a greater volatilization loss rate from water) indicates that loss of chemical from water-to-air is probably not the main cause for the apparent greater than expected sorption coefficients of DPEs.

**Sorption to Bottom Sediment.** Organic carbon normalized bottom sediment–water distribution coefficients ( $K_{SW,OC}$ ) of the DPEs and PCBs were derived as the ratio of the organic carbon normalized concentration in the bottom sediments ( $C_{S,OC}$ ) and the operationally dissolved concentration in the overlying (i.e., not interstitial) water ( $C_{OD}$ ) (Table S3). Figure 4B illustrates the relationship between log  $K_{SW,OC}$  (i.e.,  $C_{S,OC}/C_{OD}$ ) and log  $K_{OW}$  for DPEs and PCBs. It shows a statistically insignificant correlation between  $K_{SW,OC}$  and  $K_{OW}$ , i.e., for DPEs:

Log 
$$K_{SW,OC} = 0.098 \ (\pm 0.067) \cdot \log K_{OW} + 4.52 \ (\pm 0.47)$$
,  $n = 13$ ,  $R^2 = 0.16$ ,  $p = 0.17 \ (11)$ 

While DMP and DEP exhibited relatively high bottom sediment–water distribution coefficients in relation to their  $K_{\text{OW}}$ , the high molecular weight DPEs showed lower than predicted bottom sediment–water distribution coefficients.



FIGURE 5. Relationship between DPE and PCB concentrations in bottom sediment ( $C_{BS,OC}$ ) and in suspended sediment ( $C_{SSW,OC}$ ).

If bottom sediment—water distribution coefficients are expressed based on a theoretically calculated freely dissolved water concentration, i.e., as  $C_{S,OC}/C_{FD}$ , a statistically significant relationship between log  $K_{SW,OC}$  and log  $K_{OW}$  becomes apparent, for DPEs:

Log 
$$K_{\text{SW,OC}} = 0.826 \ (\pm 0.099) \cdot \log K_{\text{OW}} + 2.04 \ (\pm 0.69) \ n = 13, R^2 = 0.86, p = 4.2 \cdot 10^{-6} \ (12)$$

This relationship, shown in Figure 4B, suggests that organic carbon normalized bottom sediment–water distribution coefficients for DPEs are substantially greater (i.e., 3-50-fold for the majority of DPEs) and 17 000-fold for DMP than the organic carbon–water partition coefficients estimated from a Karickhoff style  $K_{OC}$ - $K_{OW}$  relationship.

Figure 4B also illustrates that DPEs and PCBs do not follow similar  $K_{SW,OC}-K_{OW}$  relationships. This is in contrast to the relationships for suspended sediments, which are comparable for DPEs and PCBs (Figure 4A). Figure 5 graphically illustrates the magnitude of change in concentration of DPEs and PCBs that occurs between suspended and bottom sediments as log( $C_{BS,OC}/C_{SS,OC}$ ). It shows that for the majority of DPEs,  $C_{BS,OC}$ is substantially smaller than  $C_{SS,OC}$ , while for the higher-log  $K_{OW}$  PCBs (i.e., PCBs 73/52, 110, 149, 132/153, 187/182, and 180),  $C_{BS,OC}$  is greater than  $C_{SS,OC}$ . Apparently, when suspended matter is incorporated into the bottom sediments of False Creek, the concentrations of very hydrophobic PCBs (e.g., 73/52, 110, 149, 132/153, 187/182, 180, and 194) in organic particulate matter increase (e.g., from 34 ng/g OC for PCB 180 in the suspended matter to 136 ng/g OC in the bottom sediments). This increase in concentration (i.e., 4-fold for PCB180) corresponds with a 14-fold drop in organic carbon content (i.e., from 40% in suspended sediments to 2.8% in bottom sediments), combined with a less than a proportional loss of PCB mass from particulate matter that occurs when suspended particulate matter is incorporated into bottom sediments. This can occur if the rate of organic carbon decomposition outpaces the combined rate of desorption and degradation of the PCBs (8). The latter may not have occurred to PCB18, 16/32, and 53 because of their lower  $K_{\rm OW}$ 's and higher rates of desorption and/or degradation in comparison to the more hydrophobic PCBs. With the exception of DEHP, C8, and DMP, concentrations of DPEs in bottom sediments are significantly smaller than those in suspended sediments (e.g.,  $56 \mu g/g OC$  for D*n*BP in suspended particulate matter and 3.7  $\mu$ g/g OC in bottom sediments). The decline in concentrations from suspended to bottom sediments for the majority of DPEs suggests that desorption and transformation rates of DPEs occur at rates that match or exceed the rate of decline in the organic carbon content of particulate matter. These transformation processes are likely mediated by organisms. The lack of an observed magnification in settling sediment particles for most DPEs further supports the observation that DPEs do not magnify in aquatic food-webs (4).

The high sorption coefficients of spiked and native DPEs and PCBs to particulate matter, observed in this and previous studies (8), indicate that the application of current  $K_{OW}$ -based equilibrium models for estimating sorption coefficients can lead to substantial underestimation of the degree of chemical sorption in the field and cause subsequent errors in environmental fate calculations. A higher-than-expected affinity of the chemicals for organic carbon or certain fractions of organic carbon, as evidenced by the high sorption coefficients for spiked test DPEs and PCBs, is likely. In addition, organic carbon mineralization in real aquatic systems is expected to further raise sorption coefficients of native substances over expected Kow-based values for chemicals (e.g., PCBs) that degrade slowly while more quickly degrading substances (e.g., certain DPEs) show a smaller degree of sorption. The high sorption coefficients imply that freely dissolved chemical concentrations in the water phase can reach very low levels, hence reducing exposure of aquatic organisms via the respiratory route.

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## **Supporting Information Available**

Theory and equations expressing particulate and dissolved chemical fractions in the water, and PCB regression statistics; Physical-chemical properties of the test chemicals (Table S1), Instrumental minimum detectable amounts and method detection limits (Table S2), Measured concentrations in bottom sediment, suspended sediment and water, and sorption coefficients (Table S3), and Water filtration apparatus (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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