SUPPLEMENTARY MATERIAL

Effects of Single-walled Carbon Nanotubes on the Bioavailability of PCBs in Field-contaminated Sediments

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The supplementary material includes further details on sediment characterization, passive sampler preparation, analysis of passive sampler data to calculate freely dissolved PCB concentration, and the following tables and figures:

Table S1. Sediment characterization including measured SWNT concentration (mg/g dry), total organic carbon (TOC %), black carbon (BC %), and total PCB concentration (µg/g dry sediment and µg/g TOC).

Table S2. Average freely dissolved interstitial water (ITW) polychlorinated biphenyl (PCB) concentrations (ng/L) measured by polyethylene (PE) passive samplers in each New Bedford

Harbor (NBH) sediment treatment with and without single-walled carbon nanotube (SWNT) amendment.

Figure S1. Biota-sediment accumulation factors (BSAFs) for representative polychlorinated biphenyls (PCBs) with increasing chlorination from A-F in the 25% New Bedford Harbor (NBH) sediment exposure.

Figure S2. Statistically significant ($p < 0.05$) biota-sediment accumulation factors (BSAFs) for congener CB-28 in the 25% NBH sediment treatment not yet illustrated.

MATERIALS AND METHODS

Sediment characterization

Briefly, sediment samples were dried at 60 °C, ground, and stored in muffled glass vials. Subsamples for total organic carbon analysis were acidified with 1 M hydrochloric acid and dried at room temperature. For black carbon analysis, dried sediment was pressed through a 425 μm sieve, weighed into crucibles, and combusted at 375 °C for 24 hours. Subsamples of combusted sediment were weighed, acidified with 1 M hydrochloric acid, and allowed to dry at room temperature (Accardi-Dey and Gschwend, 2002). All TOC and BC samples were analyzed using a CHNS-O analyzer (Thermo Finnigan Flash EA 1112 Series).

Passive sampler preparation

The PE sheeting was cut into one cm by one cm squares and the average mass determined. PE sampler thickness was 25 μm . Samplers were pre-extracted for 24 hours in hexane followed by 24 hours in methylene chloride. Samplers were soaked in Milli-Q water for 6-7 hours prior to transfer into new jars containing a performance reference compound (PRC)

mixture. The PRC mixture contained the following deuterated polycyclic aromatic hydrocarbons: d₁₀-phenanthrene, d₁₂-benzo[a]pyrene, and d₁₄-dibenz[a,h,]anthracene. Passive samplers were equilibrated with the PRC mixture in 80:20 methanol:Milli-Q water for 13 days on an orbital shaker. Following loading, PE were removed from the PRC solution, rinsed with nanopure water, dried with laboratory tissue, placed in a clean glass jar, and stored at 4°C in the dark until deployment in the bioaccumulation study approximately 48 hours later.

Analysis of passive sampler data to calculate freely dissolved PCB concentration

Exchange rate coefficients (k_e , day⁻¹) were determined for each PAH PRC in each treatment with the following equation:

$$k_e = \ln \frac{C_{PE,i}}{C_{PE,t}} \times t^{-1} \quad [1]$$

where $C_{PE,i}$ is the concentration of the PRC in the initial passive samplers (ng/g passive sampler), t is the duration of the exposure in days (28), and $C_{PE,t}$ is the concentration of the PRC in the passive samplers collected from the sediment at the conclusion of the experiment, after 28 days of equilibration (ng/g passive sampler). $C_{PE,i}$ and $C_{PE,t}$ were corrected by subtraction for concentrations of each PRC in the passive samplers collected as blanks. Exchange rate coefficients were plotted against log K_{ow} (octanol-water partition coefficient; L/kg) (Hawker and Connell, 1988, U.S.EPA, 2003) for the three PRCs within a given treatment. Exponential trend line equations were then calculated for each treatment. The corresponding exchange rate coefficients for each target PCB congener within the treatment were calculated using the known log K_{ow} for that PCB congener. Using k_e for each PCB congener in each treatment, equilibrium concentrations ($C_{PS,\infty}$, ng/g passive sampler) in all PE replicates were calculated with the following equation:

$$C_{PE,\infty} = \frac{C_{PE,t}}{1 - e^{-k_e t}} \quad [2]$$

where $C_{PE,t}$ is the PCB congener concentration in the passive sampler at day t ($t=28$) (ng/g passive sampler), corrected for initial concentrations. Equilibrium concentrations in PE were used to calculate estimated freely dissolved interstitial water concentrations ($C_{free,PE}$; ng/L) in each replicate chamber with the following equation:

$$C_{free,PE} = \frac{C_{PE,\infty}}{K_{PE-w}} \quad [3]$$

with passive sampler-water partition coefficient values (K_{PE-w}) for PE for each PCB congener from Perron et al. (2013).

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Table S1. Sediment characterization including measured SWNT concentration (mg/g dry), total organic carbon (TOC %), black carbon (BC %), and total PCB concentration (μg/g dry sediment and μg/g TOC).

Sediment	Treatment	mg SWNT / g dry ^a	TOC % ^a	BC % ^a	Total PCB ^b (μg/g dry)	Total PCB ^b (μg/g TOC)
25% NBH	Unamended	NA	2.67 (±0.12)	0.51 (±0.04)	60.1 (±17.5)	2250 (±658)
	1 mg/g SWNT	0.54 (±0.04)	3.22 (±0.40)	0.62 (±0.08)	70.8 (±5.2)	2200 (±161)
	10 mg/g SWNT	4.89 (±0.62)	3.36 (±1.49)	0.73 (±0.03)	58.6 (±23.3)	1740 (±692)
50% NBH	Unamended	NA	4.75 (±0.23)	0.92 (±0.11)	105 (±3)	2210 (±71)
	1 mg/g SWNT	0.47 (±0.04)	5.74 (±0.25)	0.88 (±0.10)	171 (±91)	2970 (±1580)
75% NBH	Unamended	NA	7.35 (±0.13)	1.33 (±0.11)	219 (±68)	2980 (±931)
	1 mg/g SWNT	0.83 (±0.02)	7.19 (±0.56)	1.23 (±0.14)	164 ^c	2280 ^c
100% NBH	Unamended	NA	9.28 (±0.78)	1.62 (±0.28)	285 (±21)	3070 (±221)
	1 mg/g SWNT	0.52 (±0.04)	9.42 (±0.25)	1.58 (±0.12)	316 (±101)	3350 (±1070)

Sample size: ^an=3, ^bn=2, and ^cn=1; NA=not applicable

Table S2. Average freely dissolved interstitial water (ITW) polychlorinated biphenyl (PCB) concentrations (ng/L) measured by polyethylene (PE) passive samplers in each New Bedford Harbor (NBH) sediment treatment with and without single-walled carbon nanotube (SWNT) amendment. n = 1-4, *p<0.05 compared to unamended control from the same treatment.

PCB congener	Average PCB concentration (ng/L) per treatment									
		25% NBH			50% NBH		75% NBH		100% NBH	
	LIS + Gum Arabic	Un-amended control	+ 1 mg/g SWNT	+ 10 mg/g SWNT	Un-amended control	+ 1 mg/g SWNT	Un-amended control	+ 1 mg/g SWNT	Un-amended control	+ 1 mg/g SWNT
8	55.2 (±44.9)	2960 (±391)	1670 (±546)*	114 (±6)*	2640 (±1130)	2990 (±468)	4340 (±365)	4130 (±909)	5500	2650 (±259)
18	61.4 (±35.2)	3390 (±627)	1940 (±685)	339 (±21)*	4960 (±479)	2750 (±153)*	4210 (±1020)	5580 (±408)	5260	2940 (±815)
28	16.3 (±17.7)	1950 (±321)	1400 (±145)	169 (±19)*	2980 (±622)	2030 (±19)	2630 (±83)	2960 (±148)*	3610	1790 (±149)
52	4.71 (±4.65)	512 (±103)	380 (±42)	81.0 (±8.0)*	810 (±205)	570 (±28)	741 (±22)	807 (±22)*	1030	485 (±33)
44	1.80 (±2.02)	152 (±16)	110 (±13)*	27.0 (±3.5)*	230 (±29)	153 (±10)*	214 (±25)	253 (±7)	265	162 (±10)
70	0.56 (±0.23)	47.1 (±9.2)	27.6 (±7.6)*	5.10 (±1.03)*	67.9 (±15.6)	47.7 (±4.3)	59.9 (±8.1)	69.9 (±3.8)	116	45.9 (±5.0)
66	0.15 (±0.21)	50.5 (±9.6)	41.9 (±6.9)	6.09 (±0.80)*	81.5 (±29.5)	51.9 (±3.2)	64.4 (±2.5)	78.4 (±4.0)*	108	47.2 (±2.2)
101	0.48 (±0.42)	31.5 (±0.7)	22.4 (±3.6)*	4.55 (±1.87)*	40.9 (±14.4)	32.4 (±3.0)	56.9 (±3.9)	63.7 (±13.5)	86.4	41.6 (±3.1)
99	0.39 (±0.36)	34.6 (±9.1)	23.9 (±1.8)	6.23 (±0.54)*	52.6 (±14.4)	38.1 (±4.4)	49.1 (±3.1)	62.8 (±7.1)*	74.8	36.2 (±2.6)
81	--	--	--	--	--	--	--	--	--	--
77	--	1.80 (±0.31)	2.29 (±0.56)	0.49 (±0.11)*	3.25 (±1.86)	2.48 (±0.57)	2.63 (±0.12)	3.14 (±1.37)	5.37	2.39 (±0.51)
110	0.62 (±0.45)	52.5 (±11.3)	45.3 (±4.8)	11.1 (±0.89)*	83.9 (±28.8)	61.4 (±4.9)	75.8 (±2.64)	98.0 (±7.6)*	107	52.7 (±2.1)

123	--	--	--	--	--	--	--	13.6 (±23.5)	--	--
118	0.16 (±0.23)	25.8 (±5.1)	26.7 (±2.5)	4.94 (±0.40)*	43.8 (±24.2)	27.6 (±2.9)	34.9 (±2.5)	45.8 (±5.5)*	53.7	23.9 (±1.1)
114	--	--	--	--	--	--	--	--	--	--
153	0.14 (±0.19)	17.3 (±5.6)	11.9 (±1.2)	2.98 (±0.76)*	22.8 (±8.1)	19.3 (±3.3)	24.7 (±4.2)	33.3 (±7.7)	35.4	15.5 (±1.2)
105	--	1.08 (±0.23)	0.83 (±0.02)	0.21 (±0.07)*	1.44 (±0.63)	1.06 (±0.09)	1.27 (±0.16)	1.78 (±0.47)	2.19	0.93 (±0.14)
138	--	11.1 (±4.0)	8.07 (±0.92)	1.94 (±0.18)*	15.6 (±4.7)	13.2 (±1.9)	15.7 (±2.4)	20.0 (±4.7)	22.6	9.44 (±0.44)
126	--	--	--	--	--	--	--	--	--	--
156	--	1.16 (±0.10)	0.91 (±0.19)	0.31 (±0.06)*	1.42 (±0.46)	1.15 (±0.11)	1.89 (±0.26)	2.00 (±0.41)	2.17	1.04 (±0.15)
157	--	1.02 (±0.88)	0.48 (±0.06)	--	1.26 (±0.39)	1.09 (±0.06)	1.48 (±0.17)	2.08 (±0.53)	2.15	1.04 (±0.13)
180	--	1.74 (±1.55)	1.01 (±0.89)	0.26 (±0.37)	2.58 (±1.12)	1.85 (±0.02)	2.45 (±0.44)	20.94 (±0.27)	3.39	2.32 (±0.33)
169	--	--	--	--	--	--	--	--	--	--
170	--	--	0.99 (±0.40)	--	1.24 (±0.84)	1.36 (±0.66)	2.71 (±0.92)	2.17 (±1.12)	2.20	1.45 (±0.33)
189	--	--	--	--	--	--	--	--	--	--
206	--	--	--	--	--	--	--	--	--	--
Total	1410 (±1070)	9240 (±520)	5710 (±1350)*	774 (±61)*	12000 (±1600)	8800 (±535)	12500 (±1420)	14200 (±1180)	16300	8310 (±943)

--Below detection limit

Figure S1. Biota-sediment accumulation factors (BSAFs) for representative polychlorinated biphenyls (PCBs) in the polychaete, *Nereis virens*, with increasing chlorination from A-F in the 25% New Bedford Harbor (NBH) sediment exposure.

Figure S2. Statistically significant ($p<0.05$) biota-sediment accumulation factors (BSAFs) for congener CB-28 in the 25% NBH sediment treatment not yet illustrated.

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