Supporting information to

Capping efficiency of various carbonaceous and mineral materials for *in situ* remediation of marine PCDD/F-contaminated sediments: sediment-to-water fluxes and bioaccumulation in boxcosm tests

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Pages: 15
Figures: 9
Tables: 5

Figure S1. The set-up of the experimental boxes. The experimental boxes (L 0.32 × W 0.28 × H 0.40 m) were placed in large tanks (L 2 × W 0.8 × H 0.6 m), with each tank fitting up to 12 boxes. The water level in the tanks was maintained about 1 cm below the rim of the experimental boxes, allowing the sea-water delivered directly to the boxes to exit between the lid and the box walls. In each box, a semi-permeable membrane device (SPMD) was completely immersed in the water to sample persistent organic pollutants. An airstone diffuser aerated and stirred the water.

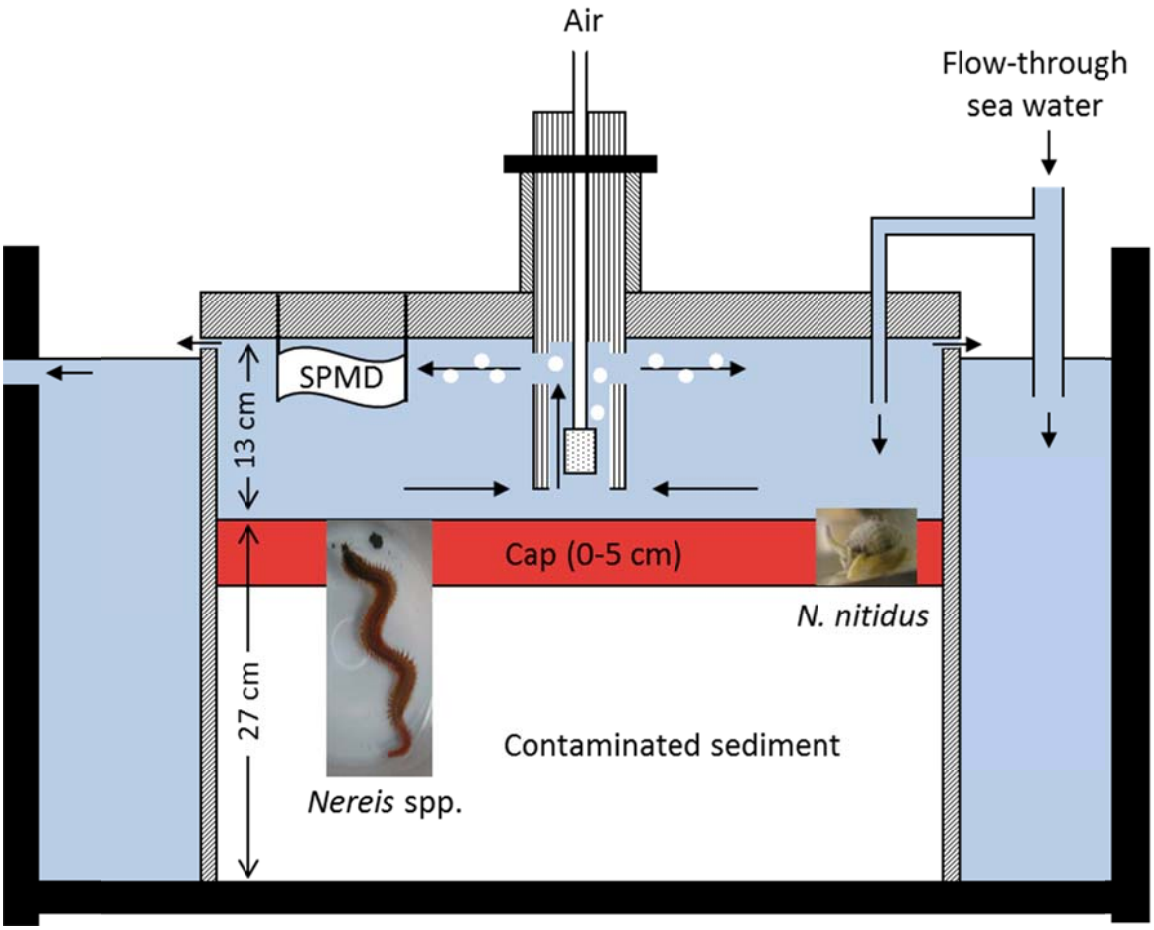


Table S1. Abundance and biomass (average ± 1 standard deviation (SD), *n*=26) of the four biota taxa in each box at the start and the end of the experiment, and the survival and lipid content measured at the end of the experiment.

	Abundance		**Biomass (g)**		**Survival**	**Lipid content**
	Start[a]	***End***	***Start***	***End***	**(%)**	**(%)**[b]
Abra nitida	7	0.077 ± 0.27	0.93 ± 0.058	*na*[c]	1.1 ± 3.9	*na*[c]
Amphiura spp.	50	0.19 ± 0.69	9.2 ± 0.90	*na*[c]	0.4 ± 1.4	*na*[c]
Nassarius nitidus	23	13 ± 4.3	*na*	3.3 ± 1.0	63 ± 16	0.80 ± 0.38
Nereis spp.	14	6.6 ± 2.7	3.5 ± 0.50	5.5 ± 1.6	47 ± 19	1.4 ± 0.28

[a] The same number was added to all boxes; SD=0.

[b] Lipid content (%) was calculated as g lipid/g wet weight

[c] *Abra nitida* and *Amphiura* spp. were only found in two boxes after the experiment. Their biomass and lipid content was therefore not analyzed (*na*), but based on the weight per individual at the start of the experiment the average biomass per box was estimated to be <0.02 g for *Abra nitida* and <0.04 g for *Amphiura* spp.

Chemical analyses and QA/QC

POP analyses

Before extraction, isotope-labeled (^{13}C) congeners corresponding to each analyte were added to the samples as internal standards. SPMDs were extracted with 2×150 mL *n*-hexane for 2×24 hours while vertically shaken. ***N. nitidus*** samples were extracted by mixing with 20 g of Na_2SO_4, and eluted with 40 mL acetone/*n*-hexane (5/2 v/v) followed by 40 mL *n*-hexane/diethylether (9/1 v/v). For *Nereis* spp., 50 g of Na_2SO_4 and 100 + 100 mL of elution solvents were used. The lipid content was determined gravimetrically after the solvent had been removed by rotary evaporation. Sediment and cap materials were dried at room temperature before Soxhlet-Dean-Stark extraction with 250 mL of toluene for 24 hours.

For clean-up and instrumental analysis, the procedure in Josefsson et al. [1] was followed. In short, samples were purified on multilayer (acid and basic) silica columns and fractionated on a carbon column. Sulfur was removed from sediment extracts by reaction with activated copper granules (-10 +40 mesh, Sigma-Aldrich, St Louis, USA). For the instrumental analysis, an Agilent 6890N GC coupled to a Waters Micromass Autospec Ultima HRMS in EI mode was used. The GC was equipped with a DB5-ms column (60 m × 0.25 mm × 0.25 μm; J&W Scientific, Folsom, CA, USA) and the oven temperature program started at 190ºC (held for 2 min), then increased with 3ºC min^{-1} to 278ºC, followed by an increase with 10ºC min^{-1} to 310ºC (held for 1.5 min). Sample extract (2 μL) was injected in splitless mode at 280ºC. Two ions in the molecular cluster for each compound were monitored, and the ratio between the monitored ions had to be within 20% of the theoretical isotope ratio for a positive identification.

Hg analyses

Total-Hg was analyzed using a RA-915+ Mercury Analyzer coupled to a PYRO-915+ pyrolyzer (Lumex Ltd., St. Petersburg, Russia). The pyrolyzer temperature was 520-580°C. For instrument calibration, certified reference material IAEA- 405 was used (IAEA, Vienna, Austria), and MESS-3 (NRC, Canada) was used to verify the calibrations. Samples were analyzed wet and the water content was determined gravimetrically after heating to 105°C for 24 h.

QA/QC

The recovery of the internal standards was on average 87% for SPMD samples, 89% for biota samples, and 86% for sediment and cap material samples. The chromatographic peak had to have a signal-to-noise ratio ≥3 to be considered detected, and this limit of detection (LOD) was also used as the limit of quantification (LOQ). Non-detected congeners for SPMD and biota samples were set to 0.5×LOD to replace missing values in subsequent calculations (51 of 1292 values, i.e. 3.9% of the data). Blanks were run continuously during the analyses, and samples were blank-corrected by subtracting amounts found in the corresponding blank. The average relative standard deviation (RSD) for flux and bioaccumulation by ***N. nitidus*** and *Nereis* spp. in the triplicate treatments (No cap, 0.5 cm CL/LG and 0.5 cm CL/AC; Table 1) was 32% for HCB, 35% for OCS and 37% for PCDD/F-TEQs. The RSD for biota survival was 32%, and 23% for biota biomass.

Flux calculations

The sediment-to-water flux (N; pg m^{-2} day^{-1}) was calculated from the mass of contaminants found in the SPMD:

$$N = \frac{M \times f}{A \times t} \quad \text{(Eq. 1)}$$

where M is the mass of the contaminant in the SPMD, A is the sediment surface area (0.09 m^2), and t is the exposure time of the SPMD (99 days). The factor f is calculated as the water flow for the specific box divided by the average flow for all boxes, and it thus corrects for the variations in water flow between the boxes. The water flow varied between 0.86 and 1.05 mL/min (average ± 1 standard deviation = 0.94 ± 0.05 mL/min, n = 26), and the factor f thus varied between 0.92 and 1.12 (average ± 1 standard deviation = 1.00 ± 0.06). The amount of POPs in the influent water was assumed to be very low in comparison to the amount remobilized from the sediment, since the sediment in the experimental boxes was heavily contaminated with POPs.

In systems without flow-through of water, the SPMDs function as infinite sinks for hydrophobic compounds, i.e. negligible amounts are found in the water phase compared to in the SPMD, and the amount found in the SPMD can thus be considered equal to the amount that has been remobilized from the sediment [2]. In flow-through systems, however, analytes released from the sediment are lost from the system via the effluent water. In the present experiment, a low water flow was maintained to improve conditions for the benthic organisms. Thus, the absolute sediment-to-water fluxes estimated by Eq. 1 from the amounts in the SPMDs, using an infinite-sink approach, underestimated the real flux.

An alternative approach would be to calculate the water concentration from the amount of POPs sampled by the SPMDs, and use the general flux equation for a flow-through system to estimate the sediment-to-water flux. However, this requires knowledge of sampling rates (R_S), which are commonly obtained by measuring the dissipation rate of performance reference compounds (PRCs) added to the SPMD before the deployment [3]. This was not possible in the present experiment since the water flow was too low to flush the dissipated PRCs from the boxcosms, and therefore, a re-uptake of the dissipated PRCs from the water to the SPMDs occurred. Instead, the infinite-sink approach was used, with a correction for the variations in water flow between the treatments (f).

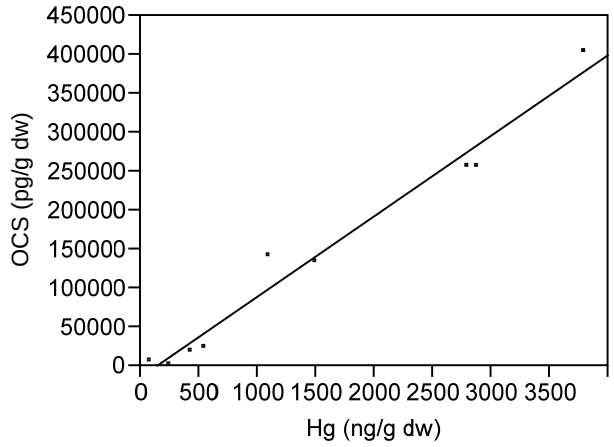
To what extent the absolute sediment-to-water fluxes of the analytes are underestimated depends on how fast the analytes are taken up by the SPMDs in comparison to how fast they are lost via the effluent water, which depends on uptake kinetics (sampling rates) and water flow. Since the sampling rates are lower for highly chlorinated compounds (uptake rates for PCDD/Fs decreasing with log K_{OW} [4]), it is likely that the loss is larger for highly chlorinated compounds. However, even though the absolute fluxes in the experiment are underestimations of the real fluxes, the flow-rate (f) corrected relative fluxes (comparisons between capped treatments and uncapped reference treatments) can reliably be used for evaluations. This is true because the sampling rates for a specific congener can be considered equivalent between boxes, since temperature and water stirring conditions were similar, and since no biofouling of the SPMDs was apparent in any of the treatments.

Table S2. Concentrations of Hg (ng/g dw) and analyzed POPs (pg/g dw) in cap material (activated carbon (AC), lignin (LG), coarse (CO) and fine (FI) limestone material, clay (CL)) and in contaminated Frierfjord sediment, and a comparison between concentrations in CL and Frierfjord sediment. Non-detected values denoted by ND (detection limit in parenthesis). Values for samples analyzed in replicates are given as average ± 1 standard deviation (*n*=3; analytical replicates for raw materials; field replicates for Frierfjord sediment).

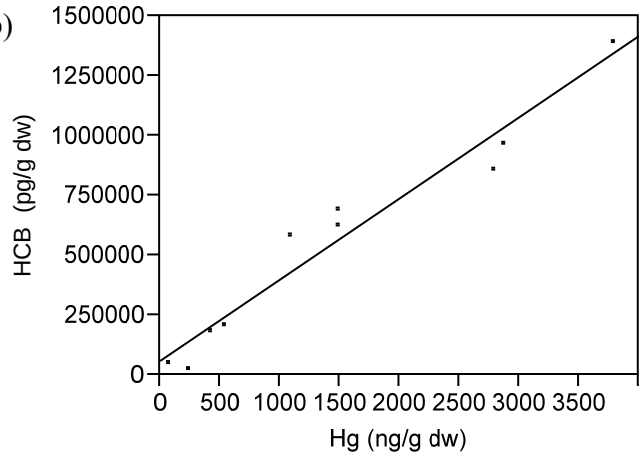
	Active material		Passive material			Frierfjord sediment	% CL of Frierfjord sediment
	AC	LG	CO	FI	CL		
Hg	ND (10)	65 ± 4.5	12 ± 5.7	4.2 ± 0.57	370 ± 42	3100 ± 550	11.8%
OCS	0.20	ND (31)	0.17	0.091	310	310000 ± 85000	0.10%
HCB	23	65	21	5.8	3700	1100000 ± 280000	0.34%
2378-TCDF	0.046	0.069	0.054	0.016	75	18000 ± 4400	0.43%
12378-PeCDF	ND (0.06)	ND (0.2)	0.089	0.015	120	18000 ± 3700	0.64%
23478-PeCDF	ND (0.05)	0.12	0.13	ND (0.02)	71	13000 ± 3300	0.53%
123478-HxCDF	ND (0.04)	0.15	0.14	ND (0.02)	290	55000 ± 11000	0.52%
123678-HxCDF	ND (0.03)	0.084	0.15	ND (0.02)	170	33000 ± 5900	0.53%
234678-HxCDF	0.061	0.076	0.21	0.033	84	15000 ± 3000	0.54%
123789-HxCDF	0.13	0.11	0.10	0.047	81	15000 ± 2100	0.54%
1234678-HpCDF	0.11	0.23	0.56	0.033	740	120000 ± 22000	0.62%
1234789-HpCDF	ND (0.07)	0.073	0.13	ND (0.018)	290	47000 ± 8100	0.61%
OCDF	0.090	0.34	0.55	0.017	2800	390000 ± 66000	0.71%
2378-TCDD	ND (0.03)	ND (0.02)	ND (0.01)	ND (0.01)	2.0	480 ± 100	0.41%
12378-PeCDD	0.039	0.093	0.076	0.021	12	2100 ± 420	0.60%
123478-HxCDD	ND (0.2)	ND (0.3)	0.040	ND (0.1)	11	1600 ± 320	0.69%
123678-HxCDD	0.14	0.14	0.13	0.052	18	3300 ± 630	0.56%
123789-HxCDD	ND (0.06)	ND (0.06)	0.075	ND (0.03)	16	2300 ± 480	0.68%
1234678-HpCDD	0.11	0.30	0.88	0.024	99	12000 ± 2300	0.84%
OCDD	0.72	1.5	2.4	0.55	220	16000 ± 2300	1.41%
PCDD/Fs	1.7	3.6	5.7	0.93	5100	760000 ± 130000	0.67%
TEQ-PCDD/F	0.12	0.23	0.23	0.056	130	23000 ± 4700	0.54%

Figure S2. The correlation between the concentrations of the different POPs and the concentration of Hg in sediment samples, for a) OCS, b) HCB, and c) PCDD/F-TEQ.

a)



b)



c)

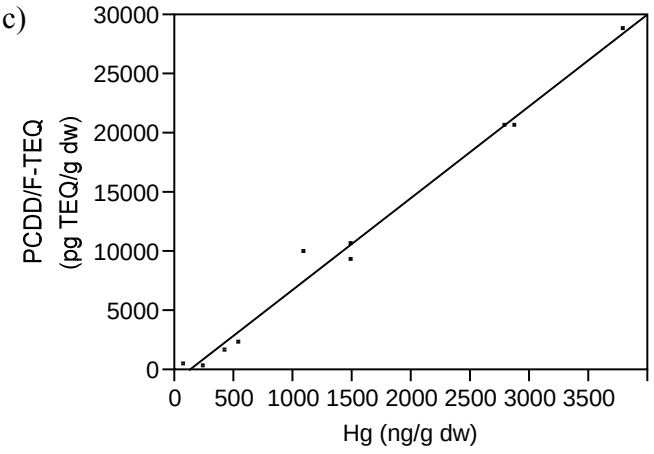


Table S3. Parameters for the correlations between POPs and Hg in sediment: $C_{POP} = a + b \times C_{Hg}$, where C_{POP} is the concentration of the POP (pg/g dw) and C_{Hg} is the concentration of Hg (ng/g dw), with the r^2 of respective correlation.

POP	***a***	***b***	r^2
OCS	-14100	104	0.97
HCB	59600	338	0.95
2378-TCDF	-457	5.91	0.98
12378-PeCDF	-354	6.03	0.99
23478-PeCDF	-475	4.48	0.99
123478-HxCDF	-2630	18.4	0.99
123678-HxCDF	-1630	10.8	0.98
234678-HxCDF	-711	5.13	0.99
123789-HxCDF	-530	4.90	0.98
1234678-HpCDF	-5320	39.4	0.99
1234789-HpCDF	-1730	15.5	0.99
OCDF	-14200	129	0.99
2378-TCDD	-11.4	0.158	0.98
12378-PeCDD	-77.9	0.687	0.98
123478-HxCDD	-55.2	0.537	0.99
123678-HxCDD	-184	1.09	0.99
123789-HxCDD	-93.9	0.777	0.99
1234678-HpCDD	-491	3.91	0.99
OCDD	-472	5.19	0.99
PCDD/Fs	-29400	252	0.99
TEQ-PCDD/Fs	-952	7.75	0.99

Figure S3. Sediment contamination profiles (visualized as Hg concentration) in treatments with different cap thicknesses. For 0.5 and 3 cm caps the average value of all treatments was used (n=11 for 0.5 cm, n=9 for 3 cm). For 1, 2, and 5 cm caps, the only treatment was CL with no active material (n=1), and for No cap, n=3. Error bars displayed are ± 1 SD. Sediment was sliced in 1 cm-layers from 0 to 4 cm depth, and in 2 cm-layers from 4 to 8 cm depth.

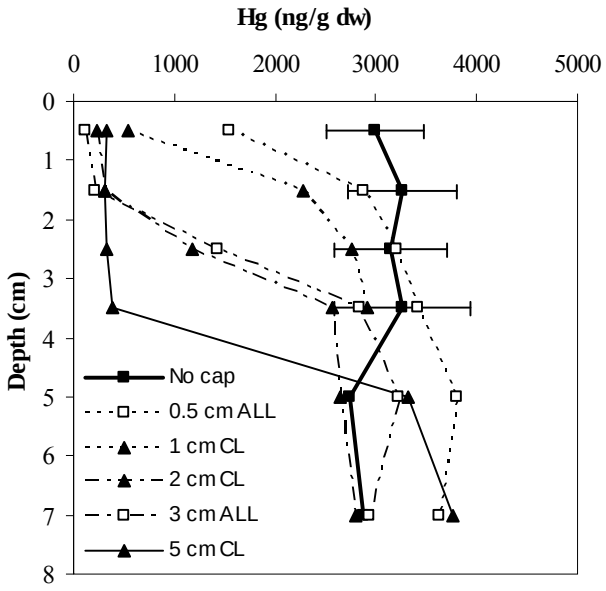


Table S4. Analysis of variance (using the Fit Model-platform in JMP) to test the effect of cap thickness, passive and active material on POP sediment-to-water fluxes and concentrations in *N. nitidus* and *Nereis* spp., and on survival, biomass and lipid content of *N. nitidus* and *Nereis* spp. at the end of the experiment. The 0, 1, 2 and 5 cm cap thickness treatments were excluded to achieve a more balanced analysis, and three-way interactions were assumed absent. Statistically significant ($p<0.05$) factors marked in bold. POP concentrations and lipid content in *Nereis* spp. were not analyzed in 0.5 cm cap treatments with two of the passive materials (CO, FI), thus, only the factors *Active* and *Thickness* could be tested. DF = degrees of freedom.

Parameter	**Source**	**Flux**			*N. nitidus*			***Nereis* spp.**		
		DF	**F ratio**	***p***	**DF**	**F ratio**	***p***	**DF**	**F ratio**	***p***
ln (OCS)	Passive	2	0.338	0.7261	2	0.989	0.4347			
	Active	2	8.03	**0.0201**	2	10.4	**0.0167**	2	21.6	**0.0002**
	Thickness	1	24.5	**0.0026**	1	86.2	**0.0002**	1	59.4	**<0.0001**
	Passive×Active	4	0.837	0.5486	4	0.712	0.6182			
	Passive×Thickness	2	2.63	0.1513	2	2.78	0.1545			
	Active×Thickness	2	1.63	0.2718	2	3.75	0.1013	2	7.81	**0.0091**
	Error	6			6			10		
ln (HCB)	Passive	2	0.663	0.5495	2	0.481	0.6439			
	Active	2	35.0	**0.0005**	2	21.5	**0.0035**	2	17.3	**0.0006**
	Thickness	1	45.3	**0.0005**	1	71.1	**0.0004**	1	25.9	**0.0005**
	Passive×Active	4	1.27	0.3774	4	1.25	0.3973			
	Passive×Thickness	2	4.34	0.0682	2	2.35	0.1909			
	Active×Thickness	2	2.59	0.1548	2	1.74	0.2663	2	2.23	0.1579
	Error	6			6			10		
ln (PCDD/F-TEQ)	Passive	2	1.17	0.3735	2	0.885	0.4688			
	Active	2	3.03	0.1231	2	4.60	0.0737	2	2.30	0.1502
	Thickness	1	12.5	**0.0123**	1	86.1	**0.0002**	1	13.9	**0.0039**
	Passive×Active	4	0.727	0.6049	4	1.26	0.3936			
	Passive×Thickness	2	3.04	0.1225	2	4.63	0.0729			
	Active×Thickness	2	3.78	0.0866	2	1.27	0.3580	2	0.784	0.4828
	Error	6			6			10		
Survival (%)	Passive				2	0.925	0.4466	2	0.383	0.6971
	Active				2	0.145	0.8682	2	1.86	0.2346
	Thickness				1	0.229	0.6492	1	4.20	0.0862
	Passive×Active				4	0.145	0.9589	4	0.696	0.6219
	Passive×Thickness				2	0.413	0.6791	2	3.97	0.0798
	Active×Thickness				2	0.147	0.8662	2	13.2	**0.0064**
	Error				6			4		
Biomass (w.w.)	Passive				2	1.18	0.3704	2	0.329	0.7317
	Active				2	0.197	0.8260	2	2.36	0.1753
	Thickness				1	0.0570	0.8192	1	8.49	**0.0269**
	Passive×Active				4	0.289	0.8753	4	1.52	0.3070
	Passive×Thickness				2	1.30	0.3397	2	4.23	0.0716
	Active×Thickness				2	0.0365	0.9644	2	3.18	0.1146
	Error				6			4		
Lipid content (%)	Passive				2	2.15	0.2124			
	Active				2	1.47	0.3138	2	2.29	0.1517
	Thickness				1	0.975	0.3688	1	2.26	0.1640
	Passive×Active				4	1.01	0.4799			
	Passive×Thickness				2	0.262	0.7796			
	Active×Thickness				2	0.587	0.5901	2	0.22	0.8072
	Error				6			4		

Figure S4. PCDF homologue patterns in *Nereis* spp. and *N. nitidus* from treatments where both species were analyzed for POP contents. PCDDs were not included since their concentrations constituted on average only 6.3 % of total PCDD/F concentrations.

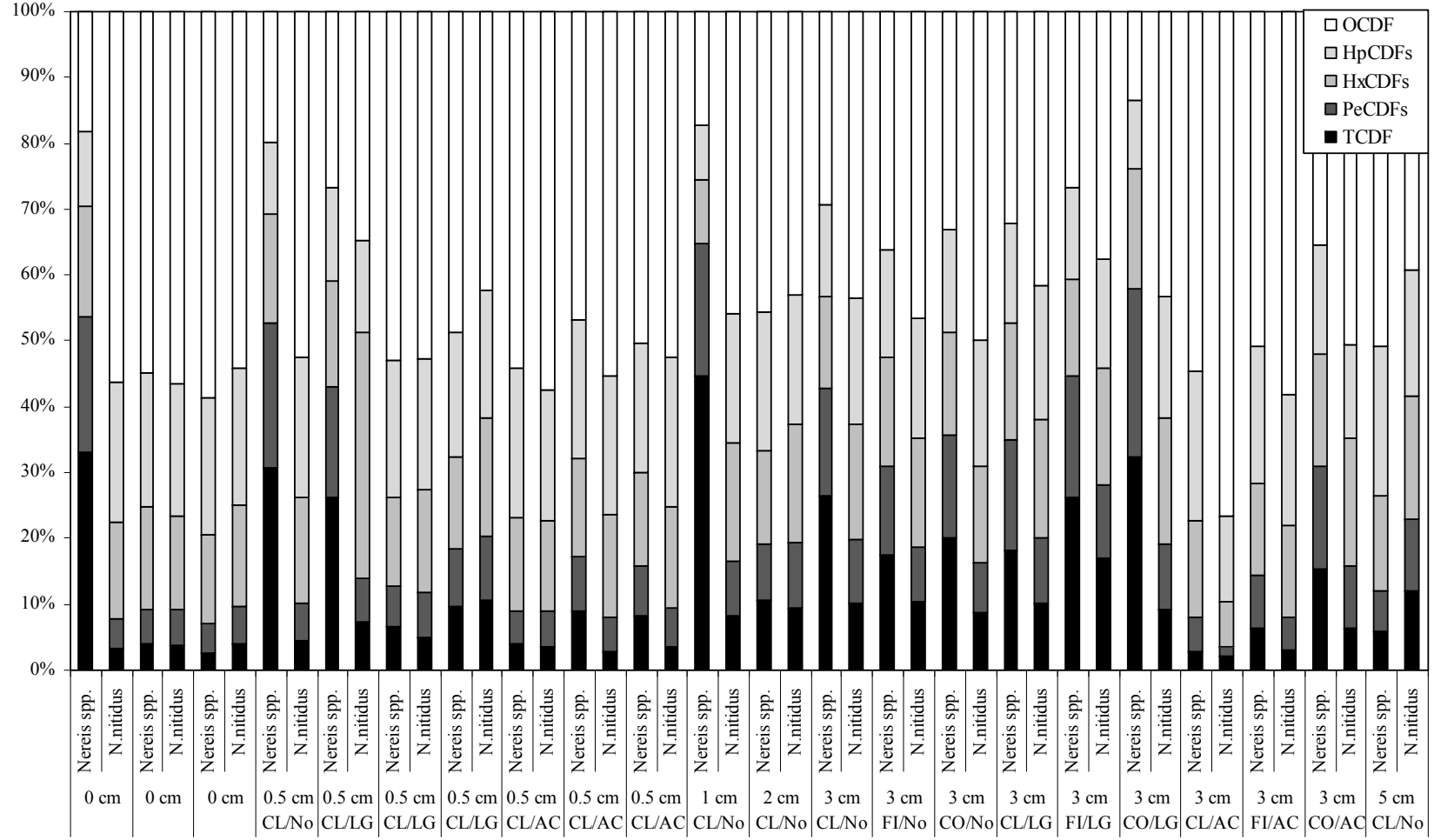


Figure S5. Redox potentials along the sediment profile in boxes with different cap thicknesses, with error bars (± 1 SD) displayed for No cap treatments (*n*=3 for No cap, *n*=11 for 0.5 cm cap, and *n*=9 for 3 cm).

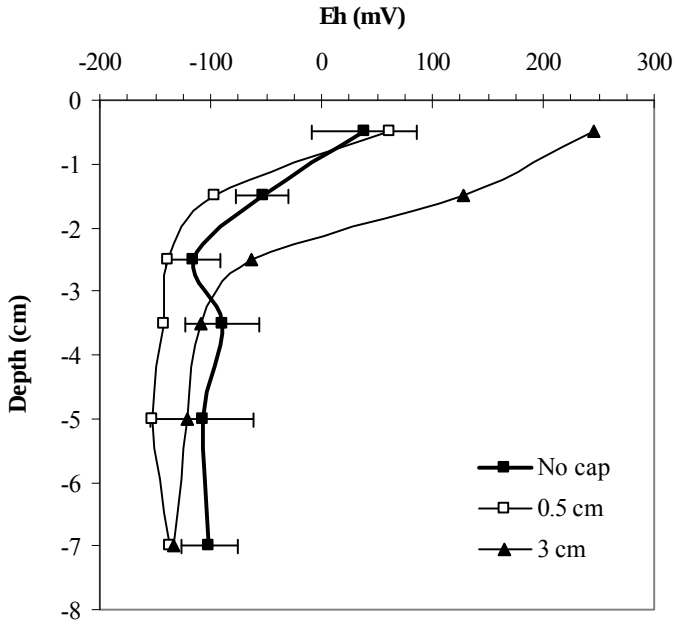


Figure S6. Redox potentials along the sediment profile in boxes without caps and with 3 caps with different active materials (No active material, AC or LG; *n*=3 for all treatments).

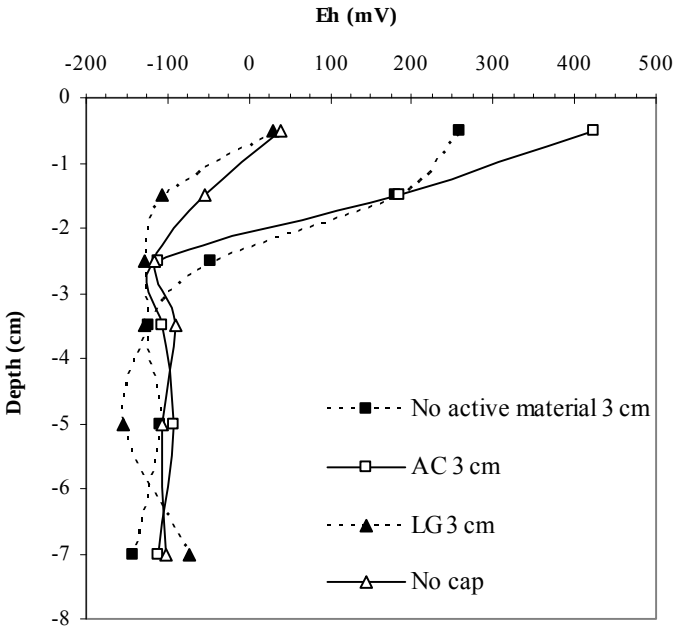


Figure S7. Saturation of free oxygen (O_2, %) along the sediment profile in boxes with different cap thicknesses, with error bars (± 1 SD) displayed for 3 cm cap treatments (*n*=3 for No cap, *n*=11 for 0.5 cm cap, and *n*=9 for 3 cm).

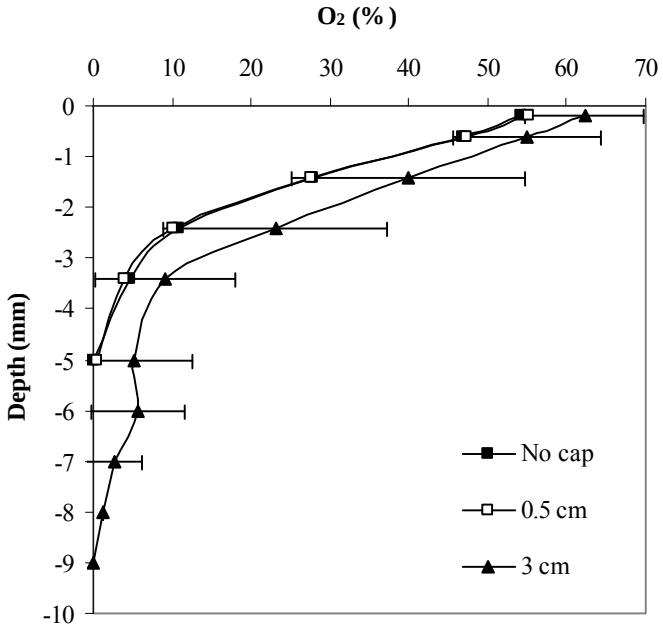


Figure S8. Survival of *Nereis* spp. and *N. nitidus* in uncapped treatments and 3 cm cap treatments with AC, LG, or without active material, compared to redox potentials in the 0-1 cm sediment layer. Error bars denote ±1 SD (*n*=3).

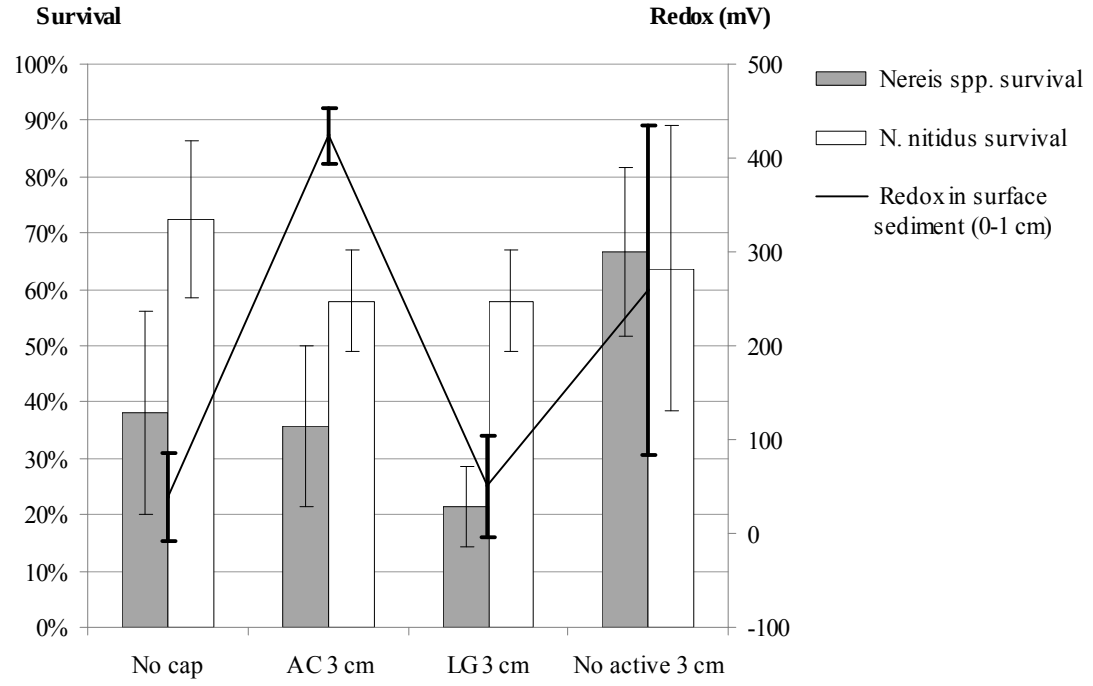
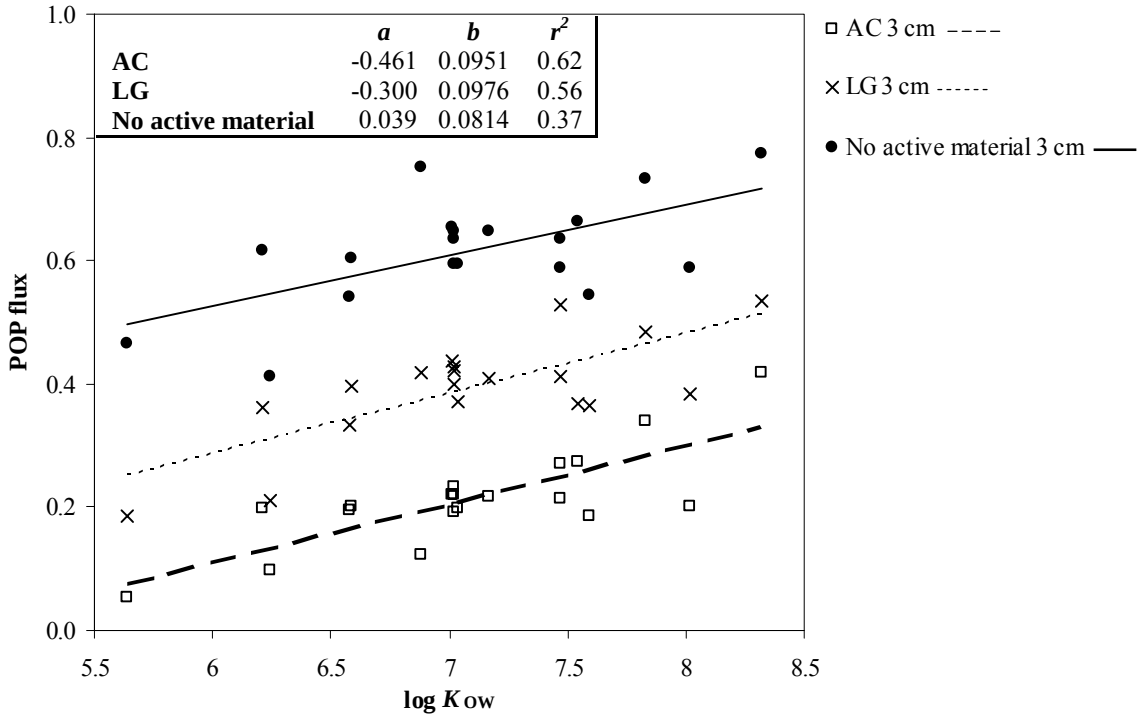


Table S5. The concentration of Hg (ng/g dw) in the surface (0-1 cm) layer of sediment in 3 cm cap treatments and uncapped treatments (n=3). Concentrations in raw materials (passive materials and sediment) are available in Table S2.

3 cm caps		Active material		
		No	LG	AC
Passive material	CL	290	290	260
	FI	70	60	54
	CO	14	22	11
Uncapped		2990 ± 480		

Figure S9. Reduction in POP sediment-to-water fluxes from 3 cm cap treatments as a function of POP congener hydrophobicity. Fluxes are relative to the average fluxes in uncapped treatments, which were defined as 1. Slopes (b) of all regressions (POP flux = a + b ×log K_{OW}) significantly different from zero (p<0.05, n=19). K_{OW} values were from Åberg et al. [5] for PCDD/Fs, from Shen and Wania [6] for HCB, and from Mackay et al. [7] for OCS.



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