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Selective removal of organic contaminants from sediments: a methodology for toxicity identification evaluations (TIEs)

J.A. Lebo[a,*], J.N. Huckins[a], J.D. Petty[a], K.T. Ho[b], E.A. Stern[c]

[a] *US Geological Survey, Columbia Environmental Research Center (CERC), 4200 New Haven Road, Columbia, MO, USA*
[b] *Atlantic Ecology Division, US Environmental Protection Agency, National Health and Environmental Effects Research Laboratory (NHEERL), 27 Tarzwell Drive, Narragansett, RI, USA*
[c] *Region 2, US Environmental Protection Agency, 26 Federal Plaza, New York, USA*

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Abstract

Aqueous slurries of a test sediment spiked with dibenz[a,h]anthracene, 2,4,5,2′,4′,5′-hexachlorobiphenyl, p,p′-DDE, or phenanthrene were subjected to decontamination experimentation. The spiked sediments were agitated at elevated temperatures for at least 96 h in the presence of either of the two contaminant-absorbing media: clusters of polyethylene membrane or lipid-containing semipermeable membrane devices (SPMDs). The effects of treatment temperature and surface area of media on the removal of contaminants were explored. This work is part of a larger methodology for whole-sediment toxicity identification evaluation (TIE). A method is being sought that is capable of detoxifying sediments with respect to organic contaminants while leaving toxicity attributable to inorganic contaminants unaffected. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Whole-sediment toxity identification evaluation (TIE) research is underway in which methods are being sought that are capable of removing from sediments those toxicities attributable to entire classes of contaminants. The methods will be applied as the first tier of whole-sediment TIE (US Environmental Protection Agency, 1991a, b, 1996; Ankley and Schubauer-Berigan, 1995). Successful methods will selectively reduce the concentrations or the bioavailabilities of a targeted class without changing the toxicities of other classes of toxicants. For example, toxicities due to organic contaminants should remain unaffected by a whole-sediment TIE method designed to obstruct the toxicities of metals (Burgess et al., 1997). Also, the treatment methods should cause only minimal physical changes to the sediments.

A portion of this large body of TIE methodological research is being conducted at the Columbia Environmental Research Center (CERC) in collaboration with the EPA's National Health and Environmental Effects Research Laboratory (NHEERL). We are seeking a method that (subject to the described restrictions) is capable of removing from sediment that toxicity due to organic contaminants (Lebo et al., 1999) by reducing the concentrations or by obstructing the bioavailabilities of these contaminants. The present work explores reduction of organic contaminant concentrations by agitating aqueous slurries of the sediments at elevated temperatures in the presence of media capable of absorbing the contaminants. Low-density polyethylene (LDPE) is the medium that has shown the most promise in this role.

* Corresponding author. Tel.: +1-573-876-1837; fax: +1-573-876-1896.
E-mail address: jon_lebo@usgs.gov (J.A. Lebo).

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Presented here are the results of experiments to determine the influences of temperature and surface area of media on the degree of decontamination attained in the treatment of spiked sediments. The degree of decontamination as determined through chemical analysis can be regarded as a surrogate criterion positively correlated with the degree of detoxification – the ideal criterion of success for such a procedure. Of the experiments related here, only one used the degree of detoxification attained by a treatment as the measure of success.

2. Experimental

2.1. Reagents, apparatus and materials

(1) Test sediment-obtained in January 1997 from a pond at CERC. The sediment was air-dried to equilibrium, pulverized with a pestle, then a small portion at a time was blended with an electric blender. The portions were recombined and the entire blending operation was repeated. Finally, the sediment was sieved through 5 mm mesh into a portable cement mixer, which was used to tumble the sediment for 4 h. These steps yielded 48 kg of homogeneous, powdery sediment that contains 5.7% organic material and 3.8% organic carbon. Particle size distribution is 20% sand, 68% clay and 12% silt/loam.

(2) Triolein (1,2,3-tri[cis-9-octadecenoyl]glycerol) – Sigma Chemical, St. Louis, MO.

(3) LDPE layflat tubing – Brentwood Plastics, St. Louis, MO. The LDPE tubing used in this work was 5.1 cm wide and of two different wall thicknesses. Tubing of 150 μm wall thickness was used to make semipermeable membrane devices (SPMDs) (see below), and tubing of 38 μm wall thickness was used to make white detox spiders (see below). The LDPE used in this work contained no additives.

(4) SPMDs made from LDPE layflat tubing of 150 μm wall thickness and triolein by the following procedure. Tubing was cut into 10 cm long segments, one end of each segment was heat-sealed, 1.0 or 2.0 ml of triolein was loaded into the segments, then the other ends were heat-sealed. Each SPMD had 102 cm^2 of external surface area. To keep the SPMDs submerged in the sediment slurries during treatment, two split shot (lead fishing sinkers) were attached to one end of each.

(5) Coconut charcoal-impregnated LDPE layflat tubing-made at Brentwood Plastics using Calgon coconut charcoal (powdered). The black tubing is 7.6 cm wide, of 51 μm wall thickness, and consists of 2% coconut charcoal by weight. This custom-made, charcoal-impregnated tubing was used, according to the following procedure, to make contaminant-sorbing clusters for immersion in sediment slurries. Segments of the black tubing 132 cm long (weighing 10.0 g and containing 200 mg of charcoal) were cut from the roll. Each segment was split along the folds that ran along each side, resulting in two overlying segments of black plastic, 132 cm × 7.6 cm. The overlying plies were folded in half, crosswise three times, then the folded plastic was stapled twice near the middle. The folds on either end were sliced through, and the stapled plastic was split lengthwise from both ends toward the two staples so that the finished clusters had multiple tendrils. Each cluster had 4000 cm^2 of surface area. These clusters will hereafter be referred to as black detox spiders.

(6) White detox spiders – made from 134 cm long segments of 38 μm wall thickness 'white' LDPE layflat tubing using a procedure similar to that described above for black detox spiders. Before use, the white detox spiders were cleaned en masse by soaking in hexane for 24 h. The white spiders weighed 5.0 g and had 2700 cm^2 of surface area.

(7) Mason jars – 1.9 l, polypropylene, Cole-Parmer Instrument Company, Vernon Hills, IL.

(8) Incubator shaker – Series 25, New Brunswick Scientific, Edison, NJ. This instrument shakes with an orbital motion (2.5 cm orbit diameter) and was operated at 175 rpm. The operating temperature was set at 30°C, 40°C or 50°C, depending on the experiment. As configured, the incubator shaker is capable of shaking 15 of the 1.9 l Mason jars simultaneously.

(9) Liquid scintillation counting (LSC) cocktails-Ecolume cocktail, ICN Pharmaceuticals, Costa Mesa, CA; and Ready Organic Cocktail, Beckman Instruments, Fullerton, CA.

2.2. Spiking and aging of sediment

The spiking and aging techniques described below were used in all experiments. Sediments were spiked with radiolabeled (^{14}C) contaminants to radiometric concentrations of about 0.0015 μCi/g and to gravimetric concentrations of 20 μg/g. Spiking solutions were made as follows: 10.0 mg of 'cold' contaminant was combined with about 0.75 μCi of a ^{14}C-labeled version of the same contaminant in 50 ml of hexane and dichloromethane. These solutions were applied over large areas of the surfaces of the dry test sediment (500 g portions spread out in shallow layers in casserole dishes), then the sediments were stirred with spatulas. The solvent was allowed 3d to evaporate, then the sediments were homogenized with a blender.

Next, the spiked and homogenized sediments were transferred to 1.9 l polypropylene Mason jars, and 750 ml of deionized (DI) water was added to each jar. The jars were capped and were swirled vigorously until the sediments were completely wetted. The sediments were allowed to age quiescently for 7d at ambient temperature.

2.3. Decontamination experiments using SPMDs

Twelve decontamination experiments, designated A–L, were performed in which SPMDs were used as the contaminant-absorbing medium. The general design of these experiments (i.e., conditions common to all 12) is described immediately below, then conditions specific to individual experiments are listed. (To facilitate understanding of experiments A–L, summaries of their experimental conditions are also given in Table 1.) In these decontamination experiments, Mason jars containing the slurries of spiked, aged sediment were mechanically shaken at elevated temperatures while multiple SPMDs were submerged in the sediments. Afterward, the SPMDs were analyzed. The durations of treatments in all 12 experiments were $\geqslant 96$ h. At all times during decontamination treatments, the sediments had either 5 or 10 (depending on the experiment) SPMDs submerged in them. Treatments were always begun at 8:00 am. Exposed SPMDs were replaced with fresh ones at 4:00 pm and 8:00 am each day of the treatments (i.e., after alternating 8 and 16 h treatment intervals). Thus, in experiments of 96 h duration, sediments were treated with totals of either 40 or 80 SPMDs.

The model contaminant used for experiments A–D was dibenz[a,h]anthracene (DBA); for experiments E–I, it was p,p′-DDE (DDE); and for experiments J, K and L, it was 2,4,5,2′,4′,5′-hexachlorobiphenyl (HCBP). The decontamination treatments for experiments A, B, E, F and J were performed at 50°C; for experiments C, G and K they were performed at 40°C; and for experiments D, H, I and L the treatments were performed at 30°C. For all experiments except A and E, the sediments were treated with 10 SPMDs (each containing 1.0 ml of triolein) at once. Sediments A and E were treated with only 5 SPMDs (each containing 2.0 ml of triolein) at once. All decontamination treatments were of 96 h duration with the following exceptions. The treatments of sediments C, G and K were of 120 h duration and the treatment of sediment F was of 144 h duration. Also, experiment I differed from all others in that sediment I was begun shaking at elevated temperature 48 h before the first 10 SPMDs were placed in the Mason jar. In all other respects, the conditions for experiment I were identical to those of H.

Exposed SPMDs were analyzed as follows: Each SPMD was cut open with scissors, and its triolein was rinsed with hexane into a scintillation vial. The membrane from the SPMD was cut into small pieces, which were placed in another vial. 10 ml of Ecolume cocktail was added to vials containing triolein solutions, and 10 ml of Ready Organic cocktail was added to vials containing membrane fragments. (At least 18 h was allowed for the LDPE fragments to interact with Ready Organic cocktail before the radiometric evaluation began.) Radiometric analyses were performed with a Beckman LS 6500 liquid scintillation counter.

2.4. Decontamination experiments using white or black detox spiders

Several decontamination or detoxification experiments (designated M–S) were performed in which white or black detox spiders were the contaminant-absorbing media. As in experiments A–L, jars containing the sediments and contaminant-absorbing media were mechanically shaken at elevated temperatures. Experiments M–S are described in detail in the following paragraphs. The conditions under which these experiments were performed are also summarized in Table 2.

DBA was the model contaminant in experiments M and N. Eight white spiders and four black spiders were submerged in sediments M and N, respectively, at all times during their 96 h (50°C) treatments. The white and black detox spiders were replaced with fresh media only once-after 8 h. Thus, there were two treatment intervals for experiments M and N: the 0–8 h interval and the 8–96 h interval. The two groups of eight white detox spiders from experiment M's two treatment intervals were separately analyzed. (The method used for the extraction and analysis of white spiders is given later.) Due to the nearly irreversible adsorption of DBA on the coconut charcoal (Huckins et al., US Patent), the two groups of black detox spiders exposed to sediment N were discarded. Both sediments M and N were analyzed after their 96 h treatments.

Experiments O and P were performed similarly to experiment M but differed from M in the following ways. The duration of treatment for sediments O and P was 120 h rather than 96 h, and the treatment temperature was 40°C rather than 50°C. The model compound used for experiment O was HCBP (for experiment P, it was DBA). Also, the eight white detox spiders used to treat sediments O and P remained in the Mason jars throughout the 120 h treatments. No spider changes were made. After the 120 h decontamination efforts had been completed, the treated sediments were discarded, and the exposed white detox spiders were analyzed.

DBA was the model contaminant used in experiments Q and R. Immediately after the 7d aging period, eight white detox spiders were placed in sediment Q (none were placed in R). The Mason jars containing the two sediments were begun shaking at 40°C. After 8 h, sediment Q's jar was removed from the incubator shaker, and its spiders were analyzed. After 48 h of shaking at 40°C, eight white spiders were placed in sediment R, it was shaken for another 8 h, then sediment R's spiders were analyzed. Neither sediment Q nor R was analyzed after the treatments.

Experiments A–R dealt with degrees of decontamination (i.e., degrees of detoxification as predicted by instrumental measurements). No toxicity tests were performed with sediments A–R before or after their treatments. Experiment S comprised both instrumental

Table 1
Cumulative percentages of contaminants removed from spiked sediments shaken with SPMDs. Each sediment jar contained either 5 or 10 SPMDs at once. Exposed SPMDs were replaced with fresh ones after alternating 8 and 16 h treatment intervals. The individual decontamination experiments are denoted by same upper case letters as are used in the text

Experiment (compound; temp.)	Treatment interval (h)											
	0–8	8–24	24–32	32–48	48–56	56–72	72–80	80–96	96–104	104–120	120–128	128–144
A[a] (DBA; 50°C)	2.2	7.2	10.3	14.1	16.4	21.0	23.9	26.8	–	–	–	–
B (DBA; 50°C)	7.3	21.0	26.5	34.8	38.0	44.5	47.5	52.0	–	–	–	–
C (DBA; 40°C)	4.6	11.4	14.4	20.2	22.5	27.4	29.8	33.6	35.3	39.0	–	–
D (DBA; 30°C)	1.8	5.4	7.0	9.6	11.0	13.5	14.6	16.9	–	–	–	–
E[a] (DDE; 50°C)	8.1	24.8	31.1	40.1	44.2	49.9	52.6	56.2	–	–	–	–
F (DDE; 50°C)	19.3	39.1	47.5	57.5	61.5	66.6	68.7	71.9	73.3	75.4	76.4	77.9
G (DDE; 40°C)	9.2	20.9	25.8	33.7	36.8	42.6	45.0	49.4	50.9	54.1	–	–
H (DDE; 30°C)	6.1	16.1	20.8	28.8	32.3	38.1	41.1	45.8	–	–	–	–
I[b] (DDE; 30°C)	7.0	17.8	22.5	29.4	33.4	39.2	41.9	46.3	–	–	–	–
J (HCBP; 50°C)	10.5	23.9	29.7	38.0	41.6	46.9	49.0	52.9	–	–	–	–
K (HCBP; 40°C)	6.4	15.9	19.6	25.9	28.5	33.8	36.2	40.1	41.4	43.3	–	–
L (HCBP; 30°C)	3.2	9.0	11.6	15.9	17.8	21.3	22.6	25.7	–	–	–	

[a] Sediments A and E were treated with 5 SPMDs (each containing 2 mL of triolein) at once. All other sediments were treated with 10 SPMDs (each containing only 1 ml of triolein) at once.

[b] Sediment I was shaken at 30°C for 48 h before it was exposed to SPMDs. Otherwise, experiment I was conducted identically to experiment H.

Table 2
Percentages of contaminants removed from sediments M–S and a summary of the treatment conditions used

Experiment or sediment	Radiolabeled contaminant	Treatment temperature	Treatment duration (h)	Type of spider	No. of spiders used simultaneously	When spiders were changed or removed (h)[a]	Percentage of contaminant removed[b]
M	DBA	50°C	96	White	8	8 and 96	90[c] 95[d]
N	DBA	50°C	96	Black	4	8 and 96	97[c]
O	HCBP	40°C	120	White	8	120	73
P	DBA	40°C	120	White	8	120	77
Q	DBA	40°C	8	White	8	8	38
R[e]	DBA	40°C	8	White	8	8	29
S1	Phenanthrene	30°C	96	White	10	96	64
S2	Phenanthrene[f]	30°C	96	White	10	96	64 (inferred)
S3	Unspiked	30°C	96	White	10	96	–
S4	Phenanthrene[f]	Ambient	None	None	None	–	–

[a] Included in this column are listings of spider removal times at the ends of treatments as well as times of spider changes during treatments.
[b] Unless otherwise noted, all of the numbers reported in this column were obtained by analyses of exposed detox spiders.
[c] This value was obtained by analysis of the treated sediment.
[d] This value, as shown, has been upwardly revised to adjust for loss of sediment during the treatment.
[e] Sediment R was shaken at 40°C for 48 h before it was exposed to white detox spiders but was otherwise treated identically to sediment Q.
[f] Spiked with 'cold' phenanthrene only.

analysis to assess the degree of decontamination and toxicity testing to assess the degree of detoxification attained by the sediment treatment. For experiment S, the test sediments were spiked and aged as described for experiments A–R, with the following exceptions. Phenanthrene was the test chemical, the spike concentration was 30 μg/g, and the spiked sediments were wetted, aged, and treated in salt water (30 parts-per-thousand as NaCl; made by reconstituting brine with DI water) rather than in DI water. White detox spiders were used for the 96 h decontamination/detoxification treatment in experiment S. Experiment S was like experiments O–R in that the spiders were never changed, but differed from them in that each sediment (S1, S2 and S3) was treated with ten 5 g white spiders instead of 8. After homogenization and aging, sediments S1 (spiked with radiolabeled phenanthrene), S2 (spiked with cold phenanthrene), and S3 (unspiked) were subjected to the described decontamination/detoxification treatment. Sediment S4 (spiked with cold phenanthrene) was stored quiescently, at ambient temperature, and without spiders during the 96 h treatment. After the treatment was completed, the white spiders exposed to S1 were extracted and analyzed to determine the extent of decontamination. Sediment S1 itself was not analyzed after treatment. Sediment S4 and the treated sediments S2 and S3 were evaluated by 96 h toxicity tests with amphipods (*Ampelisca abdita*).

Analyses of exposed white detox spiders were performed as follows: Staples were removed from the spiders, and running tap water was used to rinse adhering sediment from the pieces of LDPE. The LDPE was blotted dry with paper towels. Then the LDPE pieces from all of the exposed spiders from each experiment (or from each exposure interval of experiment M) were extracted en masse by the following procedure. The pieces of LDPE were dipped briefly in a jar containing 1 l of methanol then placed in a jar containing 1 l of hexane. The hexane was allowed 48 h at ambient temperature to desorb the contaminants from the LDPE then was decanted off and replaced with 1 l of fresh hexane. After another 48 h had elapsed, the two hexane portions were combined and the extracted LDPE was discarded. (The hexane extracts from experiment M's 0–8 h spiders were analyzed separately from those of the 8–96 h spiders.) The methanol into which the LDPE had been dipped was transferred to a 2 l separatory funnel, 400 ml of DI water was added, and the methanol-water phase was partitioned with two 200 ml portions of hexane. The hexane extract of the methanol was combined with the hexane extract of the LDPE. (The hexane extract of experiment M's methanol was analyzed separately.) The solutions were concentrated by rotary evaporation, transferred to culture tubes, and diluted to 10.0 ml volumes. Because the LDPE extracts were strongly translucent yellow, only small aliquots (i.e., 0.5 ml) of each 10 ml solution were radiometrically evaluated in order to reduce color-quenching. Ecolume LSC cocktail was used in these analyses.

3. Results

3.1. Results from decontamination experiments with SPMDs

Table 1 shows the cumulative (running total) percentages of the contaminants removed from sediments A–L throughout the 96, 120 or 144 h treatments of these sediments. Figs. 1 and 2 are graphic presentations of some of the data given in Table 1. Fig. 1 is a bar graph of the partial decontamination of an HCBP-spiked sediment J over 96 h. Because a 16 h treatment interval followed every 8 h interval, the front row of data points (the percentages of the total HCBP removed per treatment interval) has a sinuous aspect. Predictably, more HCBP was removed during 16 h treatment intervals than during the preceding 8 h intervals. The cumulative percentages of HCBP removed from sediment J throughout the 96 h treatment are represented by the rear row of data points in Fig. 1. Fig. 2 shows the cumulative percentages of DBA removed from sediments B, C and D (at 50°C, 40°C and 30°C, respectively) throughout their treatments. Note that only the first 96 h of experiment C's 120 h treatment is represented in Fig. 2.

3.2. Results from decontamination experiments with white or black detox spiders

Analyses of quadriplicate portions of treated sediments M and N indicated that 90 ± 0.4% and 97 ± 0.1%,

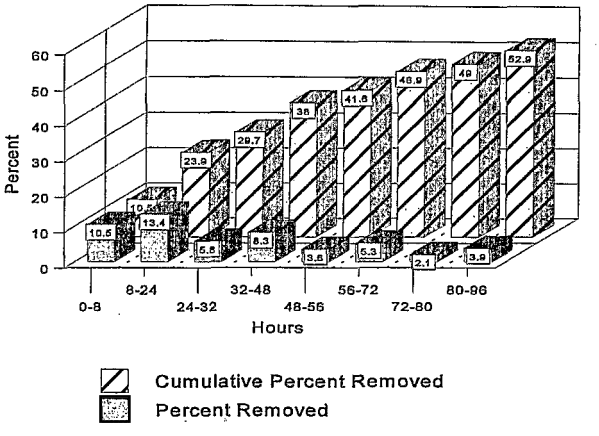

Fig. 1. Percentage and cumulative percentage removal of 2,4,5,2′,4′,5′-hexachlorobiphenyl from spiked (20 ppm) test sediment shaken for 96 h at 50°C in the presence of SPMDs.

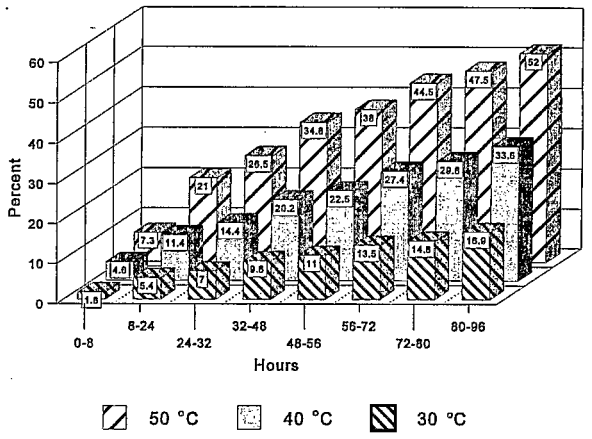

Fig. 2. Cumulative percentages of dibenz[a,h]anthracene removed from spiked (20 ppm) test sediments shaken for 96 h at 30°C, 40°C and 50°C, in the presence of SPMDs.

respectively, of the DBA had been removed by the 96 h (50°C) treatments with white and black spiders (Table 2). Because the adsorption of DBA to coconut charcoal is essentially irreversible, the black spiders that had been exposed to sediment N were discarded. However, experiment M's white detox spiders were analyzed with the following results. The eight white spiders from sediment M's 0–8 h treatment interval contained 61.2% of M's DBA. The spiders removed after the 8–96 h treatment interval contained another 23.0%. The methanol into which the 0–8 h and the 8–96 h detox spiders had been dipped contained another 1.0% of M's DBA. Thus, 85.2% of sediment M's DBA was recovered from these two groups of spiders. Note that when exposed detox spiders were removed from sediment slurries, large quantities of adhering sediment were inadvertently removed with them. Unfortunately, the constraints of TIE prohibited us from washing this adhering sediment back into the Mason jars (i.e., adding significant volumes of water to the sediment slurries). Experiment M began with 500 g of sediment, and after we removed the second group of white detox spiders, only 199 g remained in the jar. We assumed that one half of the 301 g of sediment lost during experiment M was lost during the removal of the first eight spiders after the 0–8 h treatment interval. In other words, we assumed that the 8–96 h spiders were exposed to only 350 g of sediment. Therefore, we revised upward the estimated percentage of DBA removed during the 8–96 h treatment interval (23%) as follows.

$$23.0\% \ (500 \ \text{g}/350 \ \text{g}) = 23.0\% \ (1.43) = 33.0\%.$$

Thus, $61\% + 33\% + 1\% = 95\%$.

This crudely revised estimate (95% DBA-removal) obtained via analysis of the exposed detox spiders should be compared to the previous estimate (90% DBA-removal) obtained via analysis of the treated sediment M (Table 2).

Sediments O and P (spiked with HCBP and DBA, respectively) were treated for 120 h at 40°C with eight white detox spiders each. The spiders were never changed. The exposed spiders contained 73.3% of sediment O's HCBP and 76.8% of P's DBA (Table 2).

Sediments Q and R (spiked with DBA) were treated for 8 h at 40°C with eight white spiders each, but the jar containing sediment R was shaken for 48 h at 40°C before spiders were placed in it. Analyses of the exposed spiders indicated that they contained 38.4% and 29.1%, respectively, of the DBA from sediments Q and R (Table 2).

The treatment of sediment S1 (30 μg/g of ^{14}C-phenanthrene) with 10 (instead of eight) white spiders for 96 h at 30°C removed 64.4% of the phenanthrene. This degree of decontamination was inferred for sediment S2 (30 μg/g of cold phenanthrene), which had been subjected to an identical treatment. The results from toxicity tests performed with sediments S2, S3 (unspiked, but subjected to a spider treatment identical to that of sediments S1 and S2), and S4 (30 μg/g of 'cold' phenanthrene; stored quiescently at ambient temperature during the treatments of the others) are given in Table 3.

4. Discussion and conclusions

Except for phenanthrene (log $K_{ow} = 4.52$), the model contaminants used in this work were very hydrophobic (log K_{ow}s $\geqslant 6.01$). Comparisons of experiments A–B and E–F dramatically emphasize the significance of the external surface area of contaminant-absorbing media

Table 3
Results of 96-h toxicity tests with *Ampelisca abdita* of treated sediment S. Sediment S had been spiked to 30 μg/g with phenanthrene, aged 7 d, then treated with white spiders for 96 h at 30°C

Description of sediment	Amphipod survival: raw data (alive/dead)[a]	Amphipod survival (%)
S2 'Cold' phenanthrene-spiked; spider-treated	10/0; 10/0; 9/1	97
S3 Unspiked test sediment; spider-treated	10/0; 9/0; 6/0	83
S4 'Cold' phenanthrene-spiked; untreated	4/3; 0/0; 0/4	13
Long Island sound control; untreated	10/0; 9/0; 10/0	97

[a] All tests were run in triplicate. A missing amphipod was regarded as a dead amphipod.

to uptake of hydrophobic contaminants. Detox spiders have much more surface area than do SPMDs of comparable weight. For example, the 10 SPMDs that were submerged in sediment C at any moment of its 120 h treatment had a total external surface area of 1020 cm^2. The eight white detox spiders used in the 120 h treatment of sediment P had a total of 21 600 cm^2 of surface area, a 21-fold advantage over C's SPMDs. However, large quantities of mud adhered to exposed spiders during removal. We decided upon completion of experiments M and N that thereafter, exposed spiders would only be removed from sediments upon cessation of decontamination treatments. Despite their relatively low surface areas, SPMDs were used in preference to spiders for much of this work because they could be cleanly removed from a sediment slurry. SPMDs could be frequently changed during a treatment with negligible losses of sediment, enabling us to gather multiple data points per experiment (Table 1).

Table 1 clearly shows the influence of temperature on the aqueous desorption of contaminants from sediment and on the concurrent scavenging of the contaminants by SPMDs. Maximum contaminant removal, a long-term goal of our research, will entail use of the highest treatment temperatures and the longest treatment durations that are permitted by the constraints of whole-sediment TIE. Table 1 also shows that the recalcitrance of the model contaminants are in general proportion to their log K_{ow}s (DDE = 6.01; DBA = 6.75; HCBP = 6.90).

In comparing the results of experiments B and M, it is striking that in the first 8 h of treatment, 10 SPMDs removed only 7.3% of B's DBA whereas eight white detox spiders removed 61% of M's DBA. This advantage for the white spiders is partly accounted for by their 21-fold greater aggregate surface area. However, this surface area difference does not explain why the uptake curves of some of the contaminants from sediments treated with SPMDs eventually reached asymptotes well short of complete decontamination. The contaminant uptakes unaccountably slowed down. We hypothesized that (1) our spiking and aging techniques inadequately simulated natural environmental incorporation and aging of similar contaminants in sediments and (2) if a contaminant molecule were not quickly absorbed by a medium (SPMD or spider), the agitation and elevated temperature were enabling it to sorb to a more recalcitrant site within a sediment particle. In other words, the treatment conditions were continuing and were effectively accelerating the sediment aging process. To test this hypothesis, the treatments of sediments I and R were begun with 48 h intervals during which the sediments were shaken at elevated temperatures without SPMDs or spiders. Experiments I and R should be compared to H and Q, respectively, in which contaminant-absorbing media were present in the sediments immediately upon commencement of treatments. The uptake curves of DDE from sediments H and I seem to be almost identical, apparently belying our hypothesis. However, the removal of DBA from sediment R was much reduced relative to its removal from sediment Q. These mutually discrepant results, interpreted in combination with other data in Table 1, prevent us from making an inference about the validity of our hypothesis. Further experimentation is needed to confirm the hypothesis.

Additional note. As was explained above, the sole reason for using SPMDs in this work was that they could be cleanly removed from sediment slurries. The superiority of white detox spiders over SPMDs for decontaminating sediments in this TIE context is convincingly demonstrated by the data presented here. However, these data do not suggest that white detox spiders (i.e., sheets of LDPE) are superior to SPMDs for sampling and quantifying contaminants in water or air. The enhanced capacity of the lipid-containing SPMD (Huckins et al., 1996) and the applicability of permeability reference compounds render the SPMD superior for such contaminant-monitoring applications, especially where less hydrophobic contaminants are targeted.

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