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EXTRACTION OF SEDIMENT-BOUND CHLORINATED ORGANIC COMPOUNDS: IMPLICATIONS ON FATE AND HAZARD ASSESSMENT

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ABSTRACT

Five methods were used for the extraction of hexachlorobutadiene and chlorobenzenes from a contaminated estuarine sediment. The following extraction methods were used: Soxhlet extraction, sonication and solvent extraction, sequential solvent extraction, saponification and solvent extraction, and supercritical fluid extraction. Soxhlet extraction resulted in better contaminant extraction efficiency and reproducibility. Most of the problems associated with the extraction methods were related to high water content and the inherent heterogeneity of the sediment samples. Drying and grinding of the sample greatly improved both extraction efficiency and reproducibility. Analyses of wet sieved and fractionated sediment samples indicated that the contaminants are not evenly distributed throughout the sediment organic fraction but rather predominate in the larger particle sediment fraction. The implications of quantification difficulties of sediment contaminants on the environmental fate and hazard assessment are discussed. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Chlorobenzenes, estuary, extraction procedures, desorption, fate, fractionation, hexachlorobutadiene, sediments.

INTRODUCTION

In spite of major efforts to protect natural water bodies from the effects of toxic chemicals, contamination problems in aquatic ecosystems persist. Bottom sediments, previously thought of as "natural sinks" for hydrophobic and recalcitrant contaminants in aquatic ecosystems, are now viewed as a source of contamination. Due to the persistence of sediment-bound contaminants, emphasis has recently been placed on the fate and transport of in-place pollutants (DePinto *et al.*, 1994). However, we still lack fundamental knowledge of the processes and process interactions that govern the mobility and transformation of sediment-bound toxic chemicals.

The Bayou d'Inde, a tributary of the Calcasieu River near Lake Charles, Louisiana, USA, has received unregulated industrial waste discharges from chemical manufacturing and petroleum industries for over forty

years. Many classes of contaminants including petroleum hydrocarbons, polycyclic aromatic hydrocarbons, and many polychlorinated aromatic and aliphatic organic compounds have been detected in the sediments, as well as in the overlying water column and the native biota of the tributary and downstream regions of the estuary (Cunningham *et al.*, 1990; Pereira *et al.*, 1988). Due to the toxicity and carcinogenicity of these contaminants, seafood consumption and primary contact recreation advisories have been issued (Mathison, 1987; LaDEQ, 1989).

The major chlorinated contaminants of the Bayou d'Inde sediments are hexachlorobenzene (HCB), other less chlorinated benzenes, and hexachloro-1,3-butadiene (HCBD). An investigation into various sediment extraction methods and method variations was performed as part of an ongoing study on contaminant fate processes, in particular microbial reductive dechlorination taking place in the Bayou d'Inde estuary. The impetus for such an investigation was the observed high variation of contaminant levels in replicate samples extracted by using the conventional Soxhlet method. The variation was initially attributed to the high organic carbon content of the sediment, the small sample sizes extracted (2-3 g dry sediment per sample), the inhomogeneity of the sediment samples, and perhaps the lack of intimate solvent/sediment contact due to the presence of water even after sample drying with sodium sulfate. The results of various contaminant extraction methods are reported here and the impact of contaminant extraction variability and inefficiency on the fate and hazard assessment is discussed.

MATERIALS AND METHODS

Sample Collection and Preparation

The site for the ongoing investigation is at the intersection of an industrial canal and Bayou d'Inde. The canal was used by a chemical plant manufacturing trichloroethylene and perchloroethylene for the discharge of effluents into Bayou d'Inde. Water quality parameters were measured in situ as a function of depth by using a Hydrolab Surveyor 2 equipped with a SVR2-SU multiprobe unit. Surface water samples were collected and stored in plastic carboys as well as glass bottles. Surface sediment samples were collected with a stainless steel petite ponar grab sampler and added to plastic carboys with minimum headspace. Water and sediment samples were transported to the laboratory where they were kept under refrigeration (4°C). The sediment samples were first wet sieved through a stainless steel screen (0.25 inch square openings), and then through a U.S. Standard sieve No. 14 (1.4 mm). Sub-sets of the sieved and well homogenized sediment samples were added to wide-mouth glass jars and sealed with Teflon-lined screw caps providing minimal headspace. All sediment samples were stored at 4°C in the dark. In order to investigate the distribution of organic carbon, specific surface area, and contaminants based on particle size, the sediment was divided into three fractions: 1400-106 μm (passing #14 standard sieve and retained on #140), 106-53 μm (passing #140 and retained on #270), and <53 μm (passing #270). Separation of the fractions was accomplished by wet sieving the sediment through stainless steel standard sieves. The fractions were collected and analyzed for total organic carbon, specific surface area and Soxhlet extracted to quantify the chlorinated contaminants.

Extraction Methods

Five sediment extraction methods were tested. Both centrifuged (10,000 rpm or 9300 x *g*; 10 min) and wet, as well as air-dried and ground sediment samples were used for each extraction method. Air-dried samples were ground with a mortar and pestle and passed through a 500-μm sieve. The following methods were tested: Soxhlet extraction, sonication and solvent extraction, sequential solvent extraction, saponification and solvent extraction, and supercritical fluid extraction (SFE).

Soxhlet extraction. Soxhlet extractions were performed using 80 mL of 1:1 acetone/hexane in 100-mL Soxhlet flasks. Thawed sample pellets after centrifugation were mixed with anhydrous sodium sulfate, transferred to cellulose extraction thimbles and then placed into Soxhlet extractor tubes. After adding the extraction solvent,

1 mL of a tribromobenzene (TBB) standard stock solution in hexane was added to the top of each sample. Extractions were carried out for 20 h. The extracts were then passed through a sodium sulfate drying column and filtered (Whatman #1 filter paper) into a Kuderna-Danish concentrating apparatus. The extracts were concentrated to 4-6 mL then brought up to a final volume of 12 mL with hexane. Duplicate dilutions (in hexane) were prepared and analyzed by gas chromatography (GC). Surrogate TBB recoveries consistently ranged from 95 to 102%.

Sonication. Sonication extractions were performed using 1:1 acetone:hexane to resuspend centrifuged wet sample pellets and dry samples. The suspensions were sonicated with a ½ -inch probe sonicator (Misonix Inc., Model XL2020 set at level 7, 145 watts) in Teflon centrifuge tubes for a total of 2 min using a pulsed sonication program (one second on then two seconds off, for a total run time of 6 min) while kept in an ice water bath. After sonication, the samples were mixed for 1 h using a shaking table (350 rpm). After centrifugation and withdrawal of the first solvent extract, the process was repeated once more with fresh solvent. The two solvent layers were washed with hexane-rinsed deionized water (to remove acetone) and then analyzed separately by GC.

Saponification. In an attempt to facilitate the release of sediment-bound contaminants from the organic fraction of the sediment, the samples were combined with 10 mL 4N NaOH, 5 mL 3-mm glass beads, and 10 mL isooctane in 50 mL Teflon centrifuge tubes and mixed using a shaking table for 60 h. In a second series of extractions, in addition to NaOH, 2 mL of either methanol or acetone were added to enhance the solvent/sediment contact. After centrifugation, the solvent layer was removed and analyzed by GC.

Sequential solvent extraction. Dry powdered and wet (centrifuge pellet) sediment samples were combined with 5 mL acetone, 10 mL isooctane, and 10 mL 3-mm glass beads in 50 mL Teflon centrifuge tubes. The samples were placed on a shaking table and mixed for 30 h. The tubes were then centrifuged (10,000 rpm, 10 min) to separate the solvent and solid phases. The solvent layer was decanted and stored in 160 mL serum bottles with Teflon-lined septa and aluminum crimps. This process was repeated three times by adding fresh solvent (5 mL acetone and 10 mL isooctane) and mixing for 24, 48, and 48 h, respectively, before centrifuging and drawing off each new solvent layer. The combined extracts were washed with hexane-rinsed deionized water to remove acetone prior to dilution (in isooctane) and quantification by GC.

Supercritical fluid extraction. Supercritical fluid extractions were performed with a Hewlett Packard 7680T SFE system using CO_2 as the extraction solvent. Wet samples were dried by mixing with ground Celite®. Extractions were carried out at two CO_2 densities, 0.5 and 0.7 g/mL, each with a 5-min static extraction followed by a 20-min dynamic extraction (7.9 and 7.5 thimble volumes swept, respectively, for each density) at a chamber temperature of 65°C. Contaminants were collected on an octadecylsilane (ODS) trap cooled to 5°C which was then rinsed twice with 1.5 mL of isooctane.

Analytical Methods

Sediment total organic carbon was measured using a modified Mebius dichromate reflux procedure described by Nelson and Sommers (1992). Specific surface area was measured by a triple-point Brunauer-Emmett-Teller (BET) method with a Quantachrome Corp. Nova-1000 Gas Sorption Analyzer, using N_2. Sediment samples were prepared for BET by oxidizing organic carbon with 10% H_2O_2 (sequentially washed with fresh peroxide solution until gas evolution ceased, then washed three times with deionized water), drying at 50°C, and then gently breaking up clumps in a small mortar. Alkalinity, total and volatile solids, water total organic carbon, chemical oxygen demand (COD), pH, and oxidation-reduction potential (ORP) were measured by following procedures outlined in *Standard Methods* (APHA, 1989). ORP measurements were made using a platinum electrode with Ag/AgCl reference in a 3.5 M KCl gel (Sensorex, Stranton, CA). Chloride and sulfate were determined by ion chromatography. Quantification of contaminant concentrations was performed using an HP 5890 series II gas chromatograph with an electron capture detector (ECD). Analytes were separated using a 60-m DB-624 megabore column (J&W Scientific) operated under the following temperature program: 100°C (4 min), 2°C/min

to 210°C (6 min). Calibrations were prepared using pure chemicals (Aldrich Chem. Co.) dissolved in isooctane. TBB was used as an internal standard.

RESULTS AND DISCUSSION

Water Analyses

The results of in situ measurement of several water quality parameters are shown in Table 1. The water column was well aerated (i.e., DO above 7.1 mg/L) and mixed as indicated by the relatively low variability of the six water quality parameters measured. The water conductivity and salinity were much lower than previously reported values of 9,000-14,000 μmho/cm and 5-9.6‰, respectively, for the Bayou d'Inde tributary (Demcheck *et al.*, 1990; Pereira *et al.*, 1988). The lower salinity values reported here are due to the fact that these measurements were conducted a few days after a heavy rainy season. Water samples collected at the intersection of the industrial canal and Bayou d'Inde when analyzed in the laboratory yielded the following results (mean ± standard deviation): pH, 6.5; alkalinity, 15.4±0.6 mg/L as $CaCO_3$; total solids, 1453±16 mg/L; volatile solids, 175±16 mg/L; chloride, 995±5 mg/L; sulfate, 144±6 mg/L; COD, 82±4 mg/L; organic carbon, 11.9±0.8 mg/L.

Table 1. In Situ Measurements of Water Column at the Intersection of the Industrial Canal and Bayou d'Inde (March 1994)

Parameter	Water Depth, m						
	0	1	2	3	3.5	4	4.5[a]
Temperature, °C	19.5	19.3	19.3	19.2	19.2	19.2	19.2
pH	6.8	6.8	6.8	6.8	6.8	6.8	6.8
ORP, mV	230	225	226	228	225	225	225
DO, mg/L	7.5	7.3	7.2	7.2	7.2	7.2	7.1
Conductivity, μmho/cm	2310	2300	2330	2350	2350	2350	2350
Salinity, ‰	0.7	0.7	0.7	0.8	0.8	0.8	0.8

[a] Sediment/water interface

Whole-Sediment Characterization

The results of analyses of whole-sediment samples are reported in Table 2. Based on the reported particle size distribution, more than 78% of the sediment mass was of a particle size of 75 μm or less. Therefore, more than 78% of this sediment is composed of silt and clay. HCB was the predominant chlorinated organic compound. The following isomers of the partially chlorinated benzenes were detected: 1,3- and 1,4-dichlorobenzene (DCB); 1,3,5- and 1,2,4-trichlorobenzene (TrCB); 1,2,4,5- and 1,2,3,5-tetrachlorobenzene (TeCB); and pentachlorobenzene (PeCB). Significant HCBD concentrations were also detected. A summary of the sediment chlorinated organic compounds obtained based on the various extraction methods is provided in Table 3. These results indicate that extraction reproducibility is greatly enhanced by the drying and grinding of the sediment. This effect is most likely due to the increased uniformity and smaller particle size resulting from grinding. However, because of the extensive sample manipulation in preparing dried and ground samples, some loss of contaminant occurred. The Soxhlet extraction method resulted in a relatively high extraction efficiency, although for the wet samples a large data variation was observed. Wet sediment extraction via sequential solvent extraction yielded the best overall results (both high extraction efficiency and low variability), but this method took over a week to perform, and would be inappropriate for frequent sample analysis. Although the use of NaOH in combination with either methanol or acetone (in addition to the acetone/hexane solvent mixture) resulted in high contaminant extraction efficiency, it exhibited a poor reproducibility (i.e., very high data variability). SFE of the wet sample yielded the lowest contaminant levels, indicating contaminant mass transfer

problems between the solvent (i.e., CO_2) and the wet sediment sample. The same method when used with the dry samples resulted in concentrations of both HCB and PeCB similar to those obtained by Soxhlet extraction. However, the SFE method, especially for the wet samples, resulted in very low concentrations of the more volatile, less hydrophobic compounds (such as TrCB, DCB, and HCBD). Further method development is required for the successful application of the SFE method for contaminant mixtures containing both extractable and volatile compounds.

Table 2. Results of Whole-Sediment Characterization

Parameter	Value[a]	Parameter	Value[a]
Particle Size Distribution, %		Total Organic Carbon, %	5.74 ± 0.02 [b]
850-1400 μm	1.9	Specific Surface Area[c], m^2/g	31.3 ± 0.5
250-850 μm	3.1	Chlorinated Organics[d], mg/kg	
150-250 μm	2.2	Hexachlorobutadiene	13.7 ± 2.3
106-150 μm	3.7	Hexachlorobenzene	89.5 ± 31.1
75-106 μm	10.7	Pentachlorobenzene	12.2 ± 2.1
53-75 μm	8.0	Tetrachlorobenzenes	2.6 ± 0.3
< 53 μm	70.4	Trichlorobenzenes	11.6 ± 1.2
pH	6.6	Dichlorobenzenes	49.0 ± 3.2
ORP, mV	-410		

[a] On a dry weight basis; [b] Mean ± standard deviation; [c] Three-point BET; [d] Soxhlet extraction

Table 3. Results of Various Methods for the Extraction of Chlorinated Organic Compounds from Bayou d'Inde Sediment (mg/kg, dry weight basis; mean ± standard deviation)

Method/Conditions	HCB	PeCB	TeCB	TrCB	DCB	HCBD
1. Soxhlet						
a. Wet (2.7/12)[a]	89.5±31.1	12.5±2.7	2.6±0.3	10.8±1.5	44.2±4.7	13.7±2.3
b. Dry (2.7/6)	84.7±3.1	12.8±0.4	2.7±0.2	8.9±0.5	41.2±3.1	11.0±0.6
2. Sonication						
a. Wet (2.1/3)	56.8±11.0	8.7±1.0	1.8±0.3	10.6±1.3	19.7±0.3	10.9±6.1
b. Dry (2.1/3)	71.7±2.2	9.6±0.6	1.8±0.1	7.5±0.4	ND[b]	9.4±0.6
3. Sequential Extraction						
a. Wet (2.5/3)	97.1±3.2	11.4±0.7	2.2±0.5	13.5±1.4	21.1±1.7	13.0±6.9
b. Dry (2.5/3)	75.6±5.0	10.7±0.5	2.5±0.2	7.5±0.4	13.0±2.2	10.2±0.9
4. NaOH + Isooctane						
a. Wet (2.1/3)	60.5±11.2	9.5±1.3	1.6±0.3	9.3±1.2	14.3±0.5	9.5±2.0
b. Dry (2.1/3)	69.9±5.5	10.6±0.5	1.6± 0.1	5.7±0.5	7.3±0.6	9.1±0.3
c. +MeOH, wet (2.1/3)	89.0±33.6	12.6±2.8	1.3±0.1	6.4±0.9	11.9±1.1	12.0±1.2
d. +Acetone, wet (2.1/2)	52.8±3.9	9.1±1.4	1.6±0.1	7.4±1.5	14.8±0.8	12.5±3.5
5. SFE						
a. Wet (0.5/2)	5.2±1.5	1.4±0.2	ND	1.6±0.2	ND	1.1±0.3
b. Dry (1.0/2)	82.3±3.4	10.4±0.6	ND	2.3±0.1	ND	9.0±0.1

[a] Sediment dry mass extracted (g)/number of replicates; [b] ND, not detected

Characterization of Sediment Fractions

The results of the sediment organic carbon, specific surface area and contaminant distribution in the three sediment fractions are shown in Tables 4 and 5. About 59% of the total moles of contaminant recovered was found in the largest sediment fraction (i.e., 106-1400 μm size range), which represented only about 10% of the whole sediment mass. Although this fraction had the highest organic carbon content (14.5% dry mass basis), it only represents 27% of the total organic carbon and about 4% of the total specific surface area in the whole sediment. These data indicate that the contaminants are not evenly distributed throughout the organic fraction of the sediment, but rather predominate in the larger particle sediment fraction. The non-uniform distribution of the sediment properties and contaminant levels may be explained by the presence of different adsorbents (e.g., algal cells, plant detritus, microbial cells, clay minerals), each presenting a different sorption affinity for the contaminants as has been discussed by Koelmans *et al.* (1993). Such diverse adsorbents are more characteristic of surface sediments, as was the case in the present study.

Table 4. Results of Sediment Analysis after Fractionation (dry weight basis; mean ± standard deviation)

Parameter	Fraction I 106-1400 μm	Fraction II 53-106 μm	Fraction III < 53 μm
Mass Fraction, %	10.8	18.7	70.5
Total Organic Carbon, %	14.5±0.9	2.1±0.1	5.4±0.1
Specific Surface Area[a], m^2/g	11.7±0.6	6.7±1.1	36.9±0.2
Chlorinated Organics[b], mg/kg			
Hexachlorobutadiene	95.1±14.6	2.8±0.02	1.9± 0.06
Hexachlorobenzene	517±111	31.2±2.7	7.6± 0.5
Pentachlorobenzene	77.9±10.0	4.2±0.2	2.3±0.01
Tetrachlorobenzenes	18.2±2.1	1.2±0.02	0.6±0.04
Trichlorobenzenes	61.1±7.0	3.3±0.1	2.8±0.4
Dichlorobenzenes	164±40	20.4±0.2	43±20

[a] Three-point BET; [b] Soxhlet extraction

Table 5. Distribution of Sediment Properties

Fraction	Sediment Mass, %	TOC, %	Specific Surface Area, %	Contaminant Moles, %
I (106-1400 μm)	10.8	27.5	4.4	58.7
II (53-106 μm)	18.7	6.8	4.3	7.6
III (< 53 μm)	70.5	65.7	91.3	33.7

Implications on Fate and Hazard Assessment

The observed high contaminant extraction variability also indicates inefficient extraction. Both extraction efficiency and variability will affect fate and hazard assessments. In addition to the need for an accurate quantification of the total chemical mass in contaminated sediments, the mobility of the contaminants within the sediments and at the sediment-water interface is also extremely important in assessing the fate and hazards associated with the contaminants. During this research, it was hoped that by employing different extraction methods with variable contaminant extraction potential, the total amount of contaminant mass could be divided into several classes according to their extractive facility (or binding strength). Our results indicate that the less severe extraction methods resulted in the highest extraction variability, therefore increasing the uncertainty of contaminant quantification.

Based on the interstitial, liquid-phase as well as the solid-phase HCB and DCB concentrations and assuming linear partitioning, the apparent partition coefficients for those two compounds were estimated as 24,190 and 145 mL/g, respectively (Figure 1). However, previously reported partition coefficients for HCB and DCB equal 6,150 and 98 mL/g, respectively (data taken from Gess, 1994 and U.S. EPA, 1986). Therefore, the solid-phase HCB and DCB labile fraction (*i.e.*, the contaminant fraction which desorbs and attains equilibrium in a relatively short time) is 25 and 68%, respectively. This analysis indicates that for chronic contamination, slow contaminant desorption and diffusion preclude the use of the Equilibrium Partitioning approach, especially for the more hydrophobic contaminants.

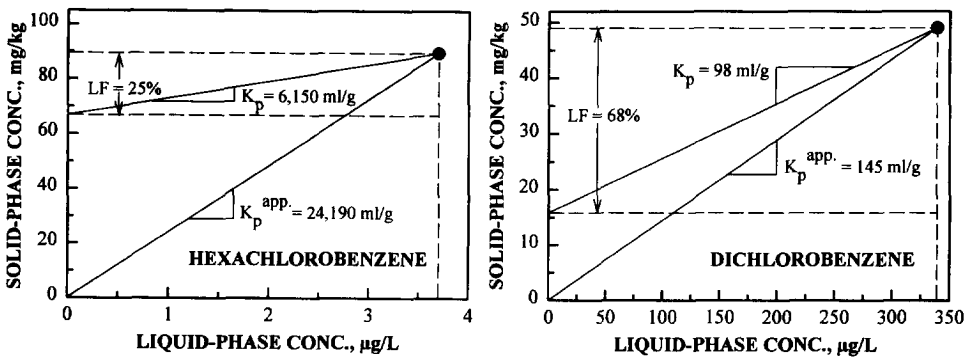

Figure 1. Linear partitioning of HCB and DCB (Data points correspond to the measured solid- and liquid-phase contaminant concentrations in the Bayou d'Inde sediment; LF, contaminant labile fraction; K_p, partition coefficient; $K_p^{app.}$, apparent partition coefficient).

Microbial reductive dechlorination of the chlorinated organic compounds proceeds very slowly in the Bayou d'Inde sediments and is mainly controlled by the availability of the sediment organic matter serving as the electron donor as well as the contaminant bioavailability (Prytula and Pavlostathis, 1995). Contaminant desorption tests have also shown that a very small fraction (less than 10%) of the sediment chlorinated compounds are released in water over an equilibration time in excess of 60 days (Gess, 1994). The long contaminant residence time in the sediments may be responsible for the slow and incomplete desorption of the chlorinated organic compounds as previously demonstrated and discussed (Pavlostathis and Mathavan, 1992; Koelmans *et al.*, 1993).

A previous study on the fate of chlorinated organic compounds in the Bayou d'Inde by the application of a steady-state mass balance model revealed that over 95% of the contaminant mass entering this estuary from the industrial canal leaves the system by advective outflow and net dispersion (Dilks *et al.*, 1993). The uncertainty associated with the quantification of the sediment contaminant levels when combined with that of other analytical measurements (e.g., organic carbon content, contaminant concentration in the interstitial water, partition coefficient) and the inherent spatial heterogeneity of the sediments result in a severely impaired interpretation of the biological impact of sediment contamination as previously discussed (Coates and Delphino, 1993). Our analysis of the existing sediment contamination indicates that due to the low contaminant desorption and biotransformation rates, these contaminants will persist for decades to come and the predominant contaminant fate mechanism will be particle resuspension and transport.

CONCLUSIONS

Quantification of old sediment contamination remains a challenge. Based on the methods used in this study, the conventional Soxhlet extraction method gave the best results (high extraction efficiency and reproducibility). Preparation of the sediment sample (*e.g.*, wet *vs.* dry) has the greatest effect on the outcome of the extraction method. Dry and ground sediment samples resulted in the lowest extraction variability (i.e., lowest standard

deviation). Although sample drying improves the extraction reproducibility, loss of the more volatile compounds remains a problem. The contaminant extraction efficiency and variability introduce uncertainties in the assessment of both the environmental fate and hazard associated with recalcitrant, hydrophobic contaminants. A significant fraction of the solid-phase contaminant concentration was found to be non-labile. Therefore, use of interstitial water contaminant concentrations and assuming equilibrium partitioning would result in an underestimation of the sediment contaminant levels.

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