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Cleanup of Sediment Extracts Prior to PCB Analysis

James M. Brannon and Richard Karn

US Army Engineer Waterways Experiment Station, 3909 Halls Ferry Road,
Vicksburg, Mississippi 39180, USA

Data for PCB in sediment are often difficult to evaluate because different laboratories use different sediment extraction, extract cleanup, and analytical techniques to obtain the information. Comparisons between multiple sediment data sets from the same geographic area that used different sediment extraction and extract cleanup procedures are especially difficult. Even the use of standardized procedures can produce large differences in PCB results. For example, three PCB contaminated sediment samples from New Bedford, MA were analyzed by 10 different laboratories using uniform calibration standards, standardized procedures for sample extraction, extract preparation, and chromatography (Alford-Stevens et al. 1985). Despite written standardized procedures, large differences in PCB results were reported by participating laboratories. Most laboratories in this study reported some analytical interference by coextracted sample components that were not removed during cleanup procedures.

The presence of interfering substances in sediment extracts is a major potential source of error in PCB analysis of sediment. Prior to quantification of PCBs in sediment samples by gas chromatography (GC), sediment extracts must be processed to remove interfering sample components such as oil and grease, sulfur, and organochlorine insecticides (McIntyre and Lester 1983) possessing retention times similar to those of PCB congeners. Failure to adequately remove such interfering substances prior to analysis can result in erroneous values for sediment PCB concentration. However, use of appropriate capillary columns and correct operating conditions may reduce the need for some of the more stringent separation of PCBs from other residues (McIntyre and Lester 1983, Tressl and Wessely 1977).

We report here comparative effects of four commonly used sediment extract cleanup procedures on oil and grease and sulfur concentrations determined in Chicago River sediment extracts. Concentrations of PCB were also determined in the extract to determine what

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Send reprint requests to James M. Brannon at the above address.

effect if any, interfering substances remaining in extracts following cleanup would have on capillary column GC determinations.

MATERIALS AND METHODS

A 1 kg subsample of each of two Chicago River composite sediment samples were air dried for three days, and then ground in a Brinkmann ZM-1 (TM) automatic centrifugal grinder with an internal 0.5 mm screen. The mechanically ground sediment was then sieved through a No. 10 sieve to ensure that no large particles remained, reground, and remixed.

Four different procedures (florisil and mercury, silica gel and mercury, sulfuric acid and mercury, and sulfuric acid and tetrabutylammonium-sulfite reagent (TAS) were used for cleanup of the composite sediment samples from the Chicago River. Each of the two composite sediment samples tested was replicated five times for each cleanup treatment tested.

Every sediment sample tested was soxhlet extracted using method number 3540 (EPA 1986) prior to cleanup and analysis of total PCB. Ten g of sediment was extracted with 200 mL of 1:1 hexane:acetone for 16 hr. Each extract was concentrated to approximately 50 mL to evaporate acetone, dried with 10 g of anhydrous sodium sulfate, and further concentrated to 10 mL. Two 1-mL aliquots of extract were then removed for analysis of oil and grease (1 mL) and sulfur (1 mL) in the extract prior to cleanup. The remaining 8 mL of sediment extract was put through the cleanup method assigned.

Florisil (Baker pesticide quality, 60-100 mesh) cleanup involved passing the soxhlet extract through a chromatographic column containing 20 g of florisil activated at 130°C, followed by elution with 200 mL of 20/80 methylene chloride/hexane (Mills et al. 1972). This cleaned extract fraction was concentrated to 8 mL, then reacted with elemental mercury (Hg) to remove sulfur using method 3660 (EPA 1986). The extract was analyzed for oil and grease, sulfur, and total PCB.

Method 3630, SW846 (EPA 1986) modified with the substitution of hexane for pentane as the elutant was used for silica gel cleanup. The soxhlet extract was placed into a chromatographic column containing 15 g of silica gel (Davison 923, 100-200 mesh) that had been activated overnight at 150 C. The silica gel column was eluted with 40 mL of hexane to remove interfering compounds followed by 86 mL of 20/80 methylene chloride/hexane to eluate the PCBs. The cleaned PCB fraction was then concentrated to 8 mL. The extract was then reacted with elemental Hg according to method 3660 (EPA 1986) to remove sulfur prior to analysis for oil and grease, sulfur and total PCB.

Sulfuric acid cleanup procedure 1.2.7.1 (EPA 1984) was also tested. The 8 mL of soxhlet extract was reacted with 5 mL of concentrated sulfuric acid by mechanically shaking the mixture for 1 min in a 50-mL glass test tube with a Teflon cap. The mixture was allowed to stand for 15 min to permit phase separation. The hexane phase (upper layer) was then removed; and reacted with elemental Hg according to method 3660 (EPA 1986) to remove sulfur. The extract was then analyzed for oil and grease, sulfur, and total PCB.

The sulfuric acid clean-up procedure 1.2.7.1 (EPA 1984) was also used in conjunction with tetrabutylammonium-sulfite (TAS) as given in EPA Method 3660 for removal of sulfur (EPA 1984). Sulfuric acid procedures were as described in the previous paragraph. The extract was shaken for 1 min with 7 mL of the TAS reagent and 14 mL of 2-propanol in a 50-mL glass centrifuge tube with a Teflon cap. Distilled water was added, and the mixture was shaken for an additional min. The mixture was then allowed to stand for 15 min to permit the phases to separate, and the hexane layer was removed by pipet. The hexane extract was analyzed for oil and grease, sulfur, and total PCB.

In each of the four treatments, three additional sediment replicates were fortified with approximately equal amounts of Aroclor 1242 and Aroclor 1254 to monitor the percent recovery of each method. A reagent blank was run to evaluate and identify any interferences or contamination in extraction and cleanup materials and solvents. In addition, an EPA PCB quality control sediment (WP978 Group 3) was extracted in duplicate and run through each cleanup procedure to verify the analytical procedure accuracy. All PCB concentrations measured were within the 95% confidence interval of the quality control sample.

Hexane aliquots removed prior to and following cleanup in each treatment replicate for sulfur analysis were evaporated to dryness. The residue was oxidized to sulfate with nitric and perchloric acid using the procedures detailed in method 28-2.2.3.1 (Tabatabai 1982). Sulfate concentrations were determined in the digests with an inductively coupled argon plasma emission spectrophotometer having a vacuum UV detector using the 182.037 nm sulfur line.

Oil and grease concentrations in the aliquots removed prior to and following cleanup in each treatment replicate were determined using Method 503D (Standard Methods 1985). Each 1-mL aliquot of extract was placed into a preweighed container, the solvent evaporated, and the residue weighed. The weight of oil and grease also includes any other compounds extractable with hexane.

Total PCB analysis was conducted on an automated Tracor Model 540 Dual Electron Capture Detector Gas Chromatograph with a Precision Scientific Auto Sampler (10 µL/injection). Two different capillary columns were used for the analysis. The primary column was a 30 m by 0.25 mm i.d. fused-silica capillary bonded with a 0.25-µm film thickness of 5% phenyl methylsilicone (Durabond 5, J & W Scientific, Inc.). The confirmatory column was 30 m by 0.25 nm i.d. fused silica capillary with 0.25-µm film thickness of 35% phenyl methylsilicone (SPB-608, Supelco, Inc.). Initial column temperature conditions preceding injection were at 90 C. This temperature was held for 0.5 min following sample injection, followed by a programmed temperature increase of 30 C/min until 160 C was reached. This temperature was held for 5 min, then a programmed temperature rate increase of 3 C/min was initiated until 260 C was reached. This temperature was held for 3 min. This sequence required a run time of 45.3 min. Inlet port temperature was 250 C, and the detector temperature was 350 C. The carrier gas was helium and the column head pressure was 20 psi.

Total PCB concentration was calculated using equal amounts of Aroclor 1242, 1254, and 1260 as standards. The calculations were based on approximately 25 identified peaks. Concentrations of Aroclor 1242 and Aroclor 1254 in the EPA Quality Control sample were determined using Aroclor 1242 or 1254 as standards.

Data from each treatment were analyzed using one-way analysis of variance (anova) to detect statistically significant differences among treatment means using the SAS ANOVA procedure (SAS 1985). Means for more than two groups were compared using the Waller-Duncan k-ratio t-test (SAS 1985) with a k-ratio of 100, to produce statistical groupings of means (indicated by small letters in the tables). Because the k-ratio does not correspond directly to a pre-set significance level (alpha), the significance of the statistical groupings may be determined by looking at the probability (P) associated with the anova F statistic. A P value of greater than 0.05 was the minimum significance reported for results of this study.

RESULTS AND DISCUSSION

Concentrations of total PCB, oil and grease, and sulfur for the sediments analyzed are presented in Tables 1 and 2. Oil and grease concentrations in the soxhlet extract prior to cleanup in composite sample 1 (Table 1) ranged from 916 to 1248 mg/kg compared to a range of from 2280 to 2740 mg/kg in composite sample 2 (Table 2), an approximate difference of two- to three-fold. Sulfur concentrations in the soxhlet extract prior to cleanup of composite sample 2 was generally 3 to 4 times higher than sulfur concentrations in the corresponding soxhlet extract of composite sample 1. Total PCB concentrations were approximately 3 times higher in composite sample 2 compared to composite sample 1.

It is concluded from the data in Tables 1 and 2 that all cleanup procedures resulted in a significant lowering of oil and grease and sulfur concentrations. Silica gel cleanup resulted in the lowest levels of oil and grease (Table 2) and the highest percent removal (82%) of this component for composite sample 2. Sample extracts for this sediment were highest in oil and grease. There was much less difference in oil and grease concentrations following cleanup between treatments for soxhlet extract initially lower in oil and grease concentration (Tables 1 and 3). The silica gel/Hg and sulfuric acid/TAS cleanup procedures resulted in the lowest concentrations of sulfur (Tables 1 and 2) and highest

Table 1. Concentrations [mean (standard error)] of Total PCB, Oil and Grease Prior to and Following Cleanup, Sulfur Prior to and Following Cleanup, and Percent Recovery of Added PCB for Composite Sample 1.

Treatment	Total PCB, mg/kg	Oil and Grease, mg/kg		Sulfur, mg/kg		% Recovery of PCBs
		Before Cleanup	After Cleanup	Before Cleanup	After Cleanup	
Florisil/Hg	8.20 (1.68)a*	926 (33)b	618 (31)a	6.58 (0.47)a	3.10 (0.20)a	75.0 (0.00)b
Sulfuric/TAS	6.98 (0.50)ab	916 (74)b	420 (31)b	4.04 (0.21)b	0.14 (0.02)c	77.7 (12.1)b
Sulfuric/Hg	3.90 (0.53)b	950 (54)b	446 (43)b	4.08 (0.37)b	1.52 (0.61)b	122.2 (10.0)a
Silica Gel/Hg	8.06 (1.34)a	1248 (21)a	584 (12)a	3.62 (0.50)b	0.22 (0.02)c	84.7 (1.39)b

* Means for a Parameter Followed by the Same Letter Within a Column are not Statistically Different

Table 2. Concentrations [mean (standard error)] of Total PCB, Oil and Grease Prior to and Following Cleanup, Sulfur Prior to and Following Cleanup, and Percent Recovery of Added PCB for Composite Sample 2.

Treatment	Total PCB, mg/kg	Oil and Grease, mg/kg		Sulfur, mg/kg		% Recovery of PCBs
		Before Cleanup	After Cleanup	Before Cleanup	After Cleanup	
Florisil/Hg	21.9 (1.7)ab*	2704 (79)a	1868 (69)a	13.4 (0.4)b	4.3 (1.3)a	90.3 (2.8)a
Sulfuric/TAS	26.6 (1.3)a	2326 (36)bc	1622 (81)b	11.5 (1.2)b	0.6 (0.07)b	95.8 (18.2)a
Sulfuric/Hg	22.0 (1.5)ab	2558 (56)ab	1514 (62)b	15.9 (0.6)a	5.4 (1.1)a	65.5 (4.0)a
Silica Gel/Hg	20.2 (2.2)b	2280 (121)c	422 (32)c	16.0 (0.6)a	0.7 (0.2)b	75.6 (0.3)a

* Means for a Parameter Followed by the Same Letter Within a Column are not Statistically Different

Table 3. Efficacy of cleanup procedures (percent reduction) for oil and grease and sulfur in sediment extracts.

Treatment	Oil and Grease Cleanup, Percent		Sulfur Cleanup, Percent	
	Sediment 1	Sediment 2	Sediment 1	Sediment 2
Florisil	33	31	53	68
Sulfuric/TAS	54	30	97	95
Sulfuric/Hg	33	41	63	66
Silica Gel	53	82	94	96

percent sulfur removal (94-96.5%) in the extracts prior to analysis.

Despite the differences noted in cleanup efficacy for oil and grease and sulfur in the soxhlet extracts following different cleanup procedures, only small differences in concentrations of total PCBs were noted between treatments (Tables 1 and 2). For composite 1, total PCB concentration was significantly lower following sulfuric acid/Hg cleanup than total PCB concentrations following florisil and silica gel cleanup. For composite sample 2, total PCB concentration was significantly lower following silica gel cleanup than PCB concentrations following sulfuric acid/TAS cleanup. However, the magnitude of these differences for both composite samples 1 and 2 were small (less than 32 percent for composite sample 2). Percent recovery of added PCB was generally similar for all treatments in both sediments.

The results in this study were obtained with state-of-the-art capillary columns and a confirmatory capillary column that eliminates a large number of false peaks caused by interferences. Under these analytical conditions, any of the cleanup procedures used provided acceptable PCB values. However, if packed columns with no confirmatory columns were used, PCB results obtained following cleanup procedures less efficient in removing oil and grease and sulfur than silica gel/Hg may not exhibit the same freedom from interference.

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