Journal of Chromatography, 643 (1993) 341–350
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2714

Efficient screening method for determining base/neutral and acidic semi-volatile organic priority pollutants in sediments

William M. Davis, John A. Coates, K. Lizanne Garcia, Lisa L. Signorella and Joseph J. Delfino*

Department of Environmental Engineering Sciences, A.P. Black Hall, University of Florida, Gainesville, FL 32611 (USA)

ABSTRACT

An efficient screening method capable of recovering base/neutral and acidic organic priority pollutants from sediment samples has been developed and applied to field samples. The procedure involves solvent extraction with sonication, solid-phase extract clean-up, and quantitative analysis by gas chromatography–ion-trap mass spectrometry. The method was applied to over 300 samples of both freshwater and marine sediments. Quality control data indicate that the accuracy and precision of the method are comparable to those of other techniques reported in the literature, including US Environmental Protection Agency methods for waste samples. The spatial variation of organic pollutants in adjacently collected sediments was found to be greater than anticipated and does not appear to be a result of analytical imprecision.

INTRODUCTION

Sediments are an important component of aquatic ecosystems, serving both as sources and sinks for nutrients, carbon and toxicants [1]. There is an increasing awareness of the need to assess the quality of sediments with respect to the potentially toxic pollutants which they may contain. One class of these pollutants, hydrophobic organic compounds, is frequently among the most reported contaminants in sediments [2]. The concentrations of hydrophobic organic pollutants in sediments have important implications for benthic organisms and other biota in the aquatic systems [3–7].

Despite the increasing interest in sediment contamination, techniques used to assess contaminant concentrations in sediments are neither standardized nor simple to perform and they remain the subject of much ongoing research [8–28]. The complex nature of the sample matrix is one of many factors contributing to the difficulty of these efforts. Co-extracted natural products are another difficulty that often require tedious extract clean-up for their removal. An additional complicating factor is the large number of target analytes with widely ranging chemical properties that are likely to be found in the aquatic environment [29,30].

Reported recovery values and other method performance criteria typically originate from studies conducted under research conditions optimized for specific compound classes [23,28]. Such studies generally produce small data sets over relatively short time spans [8,9,18–21]. These idealized recovery efficiencies may be difficult to obtain under normal laboratory operating conditions with methods that are designed to recover a wide range of chemicals.

The organic priority pollutants (OPPs) are a group of analytes which contain a variety of chemical classes and are often the target analytes in contaminant investigations. The priority pollutants are the result of a 1976 consent decree between the US

* Corresponding author.

0021-9673/93/$06.00

EPA and several environmental groups and include metals, volatile and semi-volatile organic compounds [31]. The semi-volatile OPPs are the subject of many investigations of contamination in sediments and soil.

This study presents an efficient and expedient screening method capable of reliably recovering different classes of OPPs from sediments. Sediments are solvent extracted with sonication, the extracts are concentrated, and natural product interferences are removed using solid-phase extraction columns. Quantification is accomplished with capillary gas chromatograph–ion-trap mass spectrometry (GC–ITMS). The method has been successfully used to screen freshwater and marine sediment samples for a wide variety of organic pollutants. The performance of this method has been evaluated for a period of over two years and involved several different analysts.

EXPERIMENTAL

Sediment samples from various surface waters throughout the state of Florida were sampled using a petite ponar dredge (Wildlife Supply, Saginaw, MI, USA). The dredge contents were placed in a flat enameled pan, mixed with a chrome-plated trowel, and obvious artifacts were removed. The sediment samples were placed in solvent rinsed one-quart glass jars with aluminum foil lined lids and placed on ice for transport to the laboratory.

The extraction procedure combines elements of EPA Method 3550 [32] and a method reported by Marble and Delfino [8]. Initially, 30 g of wet sediment are weighed into a 250-ml glass centrifuge tube and manually mixed with 60 g anhydrous sodium sulfate using a stainless-steel spatula. Sediment samples designated as matrix spikes are mixed with 0.10–0.50 ml of a solution containing OPPs in acetone prior to solvent addition. Following the sodium sulfate addition, 75 ml of acetonitrile (Optima grade, Fisher Scientific, Orlando, FL, USA) is added to the mixture. The mixed sample is then sonicated (Model W-375 Sonicator Ultrasonic Liquid Processor, Heat Systems, Farmingdale, NY, USA) for 3 min at 100% power output and 50% duty cycle. The sonicated sample is centrifuged for 30 min at 160 *g* (1000 rpm) before the solvent is decanted into a 250-ml erlenmeyer flask. This procedure is repeated twice for each sample. The extracts are combined, dried over anhydrous sodium sulfate and placed in a 250-ml round bottom boiling flask. This solution is then concentrated on a rotary flash evaporator (Rotavapor RE-111, Buchi Laboratoriums-Technik,; Fisher Scientific) to a volume of 8–10 ml and quantitatively transferred to a graduated centrifuge tube for concentration to a final volume of 6 ml under a stream of nitrogen gas (N-Evap Model 111, Organomation Assoc., Berlin, MA, USA). This extract is designated as the crude sample extract. Typically this crude extract is centrifuged to remove any suspended particulates prior to further sample clean-up.

Polar interferences are removed from the crude extracts using 1 g C_{18} solid-phase extraction columns (SPE, Part No. P469R, Fisher Scientific). An amount of 0.5 g of copper powder (purified grade, Fisher Scientific) is added on top of the C_{18} packing to remove any elemental sulfur present in the sediment sample extracts [9]. The C_{18} columns are conditioned with 6 ml of methanol (optima grade, Fisher Scientific) followed by 6 ml of deionized water [8]. After the column is conditioned, 2 ml of the crude extract are combined and mixed with 4 ml of deionized water in the column reservoir. The extract mixture is pulled through the C_{18} SPE column, which is then dried for 30 min under vacuum. The OPP analytes are eluted from the SPE column using 6 ml of a solvent mixture containing dichloromethane–hexane–acetonitrile (50:47:3, v/v) [8]. This final extract is concentrated under a stream of nitrogen to a final volume of 1 ml.

The components in the sediment extracts are separated, identified and quantified using a GC–ITMS system (GC Model 8500, and ITMS model 6210, Perkin Elmer, Norwalk, CT, USA). The mass spectrometer was tuned using perfluorotributylamine, the calibration compound specified by the manufacturer. The GC–ITMS system was calibrated for quantification of the semi-volatile OPPs using solutions prepared in our laboratory from pure primary standards (>96% purity, Supelco, Bellefonte, PA, USA) using an external calibration procedure. Injection standards were analyzed to verify that operating conditions were within acceptable QC limits each day that the system was used for analysis.

Samples were quantified by injecting a 2-μl aliquot of the final extract onto a capillary GC column

(30 m × 0.32 μm I.D., 1 μm film thickness, RX-5, part No. 10254, Restek, Bellefonte, PA, USA) using the splitless injection mode. The GC oven was temperature programmed to separate the desired analytes as follows: 50°C for 1.5 min; increased at 20°C/min to 130°C; held at 130°C for 3 min; increased at 12°C/min to 180°C; then, increased at 7°C/min to 300°C; and finally held at 300°C for 32 min. The analytes eluting from the GC column were identified and quantified using 70 eV electron ionization ITMS.

All samples analyzed using this sediment extraction procedure were spiked with a mixture of surrogate semi-volatile compounds. The surrogate spike was added to each sample before the solvent and anhydrous sodium sulfate were added. A variety of compound classes were represented in the surrogate spike mixture which included: [$^2H_4$]1,4-dichlorobenzene, [$^2H_8$]naphthalene, [$^2H_{10}$]anthracene, 4-bromophenol and 2,6-dibromophenol. These surrogate compounds were used to assess the effect of different sample matrices on OPP recovery.

RESULTS

Analyte recoveries

An initial validation experiment was performed to investigate the capability of the method to recover a wide range of OPP compound classes. For this validation experiment, 25 compounds representing each of the extractable compound classes listed in EPA Method 625 [33] were chosen. The recovery of these compounds from the C_{18} clean-up procedure was determined by directly spiking mixtures of water–acetonitrile (2:1) with OPPs and loading these samples onto C_{18} columns. The results of this experiment, presented in Table I, show excellent clean sample recovery for all analytes except 2,4-dinitrophenol.

TABLE I

RESULTS OF RECOVERY EXPERIMENT FOR ANALYTES FROM SPIKED C_{18} SPE COLUMNS

Analyte	Amount spiked on C_{18} column (μg)	Mean recovery[a] (μg)	Mean recovery (%)	R.S.D. (%)
Phenol	18.4	17.3	94	8.6
[$^2H_4$]1,4-dichlorobenzene	29.3	27.2	93	8.2
Nitrobenzene	13.7	12.7	93	6.8
2,4-Dimethylphenol	15.8	18.0	114	6.0
1,2,4-Trichlorobenzene	22.9	31.3	137	3.2
Naphthalene	18.2	18.9	103	6.8
Hexachlorobutadiene	21.8	22.5	103	12.8
p-Chloro-*m*-cresol	18.7	19.6	105	8.5
Dimethyl phthalate	23.0	25.1	109	3.3
4-Nitrophenol	16.0	13.4	84	45.4
2,4-Dinitrotoluene	14.3	13.8	97	3.6
Fluorene	15.2	15.8	104	0.1
4-Bromophenyl phenyl ether	22.2	20.8	94	28.8
Pentachlorophenol	18.8	23.5	125	5.0
γ-BHC (lindane)	16.6	20.8	125	4.8
Phenanthrene	16.6	17.7	107	1.1
Anthracene	15.2	15.8	104	0.4
Aldrin	15.6	16.0	103	0.6
Heptachlor epoxide	13.2	14.7	112	7.6
Fluoranthene	14.2	15.6	109	1.1
Pyrene	16.9	18.2	108	1.3
4,4'-DDE	18.9	19.0	100	13.2
Endrin	17.8	15.5	87	35.6
Chrysene	15.8	18.7	119	29.9
2,4-Dinitrophenol	15.4	4.0	26	16.7

[a] Mean of 3 replicate experiments.

Once recovery of the analytes through the C_{18} columns had been verified, the mixture of 25 OPPs was spiked onto a sediment which had been previously screened by GC–ITMS and been determined to be free of OPPs. The spiked samples were extracted and quantified by the procedure described above. The results summarized in Table II indicate that this screening method can recover, with varying but generally satisfactory efficiency, many different types of the OPP chemicals spiked into sediment. Only two analytes (endrin and 2,4-dinitrophenol) and one surrogate ([$^2H_4$]1,4-dichlorobenzene) showed very low recoveries. Further method validation was carried out by extracting National Institute of Standards and Technology (NIST) Standard Reference Material 1941. The data collected for duplicate analyses of this sediment sample are presented in Table III, indicating quite satisfactory recoveries of target analytes. Values for anthracene were high for undetermined reasons.

Given these more than adequate recovery results, the method was applied to freshwater and marine sediment samples collected and analyzed over a period of two years. Quality assurance procedures were instituted wherein a standardized sediment, spiked with an analyte mixture, was analyzed with every set of field samples. In addition, every field sample was spiked with a mixture of surrogate compounds to assess sample matrix effects on analyte recovery. The data collected from both types of spiked samples are summarized in Table IV. It should be noted that the data presented in Table IV were collected over an extended period of time and include technique variation contributed by several different analysts. Recoveries of all analytes, except hexachloroethane, met or exceeded EPA Method 8270 acceptance criteria.

TABLE II

RESULTS OF RECOVERY EXPERIMENT FOR ANALYTES FROM SPIKED SEDIMENTS

Analyte	Spike level (mg/kg dry wt.)	Mean recovery[a] (%)	R.S.D. (%)
Phenol	3.07	34	18.5
[$^2H_4$]1,4-dichlorobenzene	4.88	8	61.8
Nitrobenzene	2.28	49	57.4
2,4-Dimethylphenol	2.63	77	17.4
1,2,4-Trichlorobenzene	3.81	45	41.2
Naphthalene	3.04	49	56.4
Hexachlorobutadiene	3.63	31	35.5
p-Chloro-*m*-cresol	3.12	105	41.4
Dimethyl phthalate	3.84	94	32.1
4-Nitrophenol	2.67	70	36.1
2,4-Dinitrotoluene	2.39	87	28.4
Fluorene	2.53	67	22.6
4-Bromophenyl phenyl ether	3.71	99	26.7
Pentachlorophenol	3.13	81	37.2
γ-BHC (lindane)	2.77	76	14.8
Phenanthrene	2.76	77	28.3
Anthracene	2.53	82	25.7
Aldrin	2.60	61	66.2
Heptachlor epoxide	2.20	70	41.9
Fluoranthene	2.37	84	32.0
Pyrene	2.81	88	32.0
4,4'-DDE	3.15	125	29.5
Endrin	2.96	9	129.
Chrysene	2.63	131	18.0
2,4-Dinitrophenol	2.56	24	13.8

[a] Mean of 8 replicate experiments.

TABLE III

RESULTS OF ANALYSES OF STANDARD REFERENCE MATERIAL 1941 (in mg/kg dry wt.)

Analyte	This study		NIST reported values	
	Sample 1	Sample 2	SRM 1941 certified concentration[a]	SRM 1941 GC–MS concentration[b]
Phenanthrene	0.49	0.51	0.58 ± 0.06	0.60 ± 0.01
Anthracene	0.43	0.43	0.20 ± 0.04	0.23 ± 0.01
Pyrene	1.47	1.29	1.08 ± 0.20	1.24 ± 0.02
Fluoranthene	0.97	0.87	1.22 ± 0.24	1.40 ± 0.04
Benz[*a*]anthracene	0.49	0.49	0.55 ± 0.08	0.60 ± 0.01
Benzo[b + *k*]fluoranthene	0.65	0.91	1.22 ± 0.24	nr[c]
Benzo[*a*]pyrene	0.91	0.81	0.67 ± 0.13	0.75 ± 0.05
Benzo[*ghi*]perylene	0.71	0.71	0.52 ± 0.08	0.57 ± 0.06
Indeno[1,2,3-*cd*]pyrene	0.63	0.69	0.57 ± 0.04	0.56 ± 0.02
Chrysene	0.66	0.65	nr[c]	0.70 ± 0.02
			SRM 1941 non-certified conc.[b]	
Acenaphthylene	0.13	0.03	0.12 ± 0.01	
Naphthalene	0.56	0.56	1.32 ± 0.01	

[a] Values are weighted means of two or more analytical techniques ±95% prediction interval with an allowance for systematic error among the methods used.
[b] Values are determined by GC–MS ± one standard deviation of a single measurement.
[c] No concentration reported for this compound and this method by NIST.

Field duplicates

Additional quality assurance samples included field duplicate sampling at the rate of 10% of all field sampling locations. Field duplicate samples were obtained by lowering the petite ponar dredge a second time and collecting another sample as close as possible to the location of the first sample. Data for these field duplicate samples are presented in Table V.

Variation observed in the field duplicate data led to an experiment designed to identify a possible reason for this variation. Two sediment samples from a contaminated site were each homogenized by placing the wet sediment into a 1-l glass beaker. The sediments were manually stirred with a steel spatula for 45 min. Five 30-g subsamples of each homogenized sample were extracted and quantified. The data obtained from this replicate extraction experiment are presented in Table VI.

DISCUSSION

Analyte recoveries

The results of the initial method validation experiment (Tables I and II) indicated that the method recovered a wide variety of compounds from different chemical classes. The initial experiments included acidic (phenolic) as well as neutral and basic organic priority pollutants. Octadecyl bonded phase columns have been demonstrated to be the optimum non-polar phase for recovery of a wide variety of compounds from water, including phenolics, neutral and basic compounds [34]. Acidic organic compounds have a polar and non-polar fraction depending on their pK_a values and the solution pH. The addition of water to the crude acetonitrile extract increases the polarity of the mobile phase relative to the C_{18} column. Thus, the non-polar fraction of the acidic compounds is more strongly retained on the SPE column, increasing the overall

TABLE IV

RECOVERY OF ANALYTES FROM SPIKED SEDIMENTS

Analyte	n^a	Average sediment spiked conc. (mg/kg dry wt.)	Mean recovery (%)	Standard deviation	EPA Method 8270 recovery criteria (%)
Base/neutral compounds					
1,2,4-Trichlorobenzene	40	3.49	50	19.3	44-142
1,2-Dichlorobenzene	20	3.73	22	18.3	32-129
1,2-Diphenylhydrazine	20	3.13	94	29.9	–[b]
1,3-Dichlorobenzene	20	5.32	9	7.5	D–172[c]
2,4-Dinitrotoluene	40	2.18	83	34.4	39–139
2,6-Dinitrotoluene	20	3.68	82	23.0	50–158
2-Chloronaphthalene	20	3.38	88	23.2	60–118
3,3-Dichlorobenzidine	20	2.84	23	15.9	D–262
4,4′-DDD	20	3.71	98	23.8	D–145
4,4′-DDE	40	2.88	101	37.0	4–136
4-Bromophenyl phenyl ether	40	3.39	92	24.7	53–127
4-Chlorophenyl phenyl ether	20	2.65	83	18.3	25–158
Aldrin	40	2.38	84	29.5	D–166
α-BHC	20	3.48	96	36.6	–
Anthracene	40	2.32	97	33.9	27–133
β-BHC	20	2.06	78	21.3	24–149
Bis(2-chloroethoxy)methane	20	3.26	75	21.8	33–184
Bis(2-chloroisopropyl)ether	20	3.97	71	26.1	36–166
Benzyl butyl phthalate	20	3.81	92	35.6	D–152
Chrysene	40	2.40	84	36.3	17–168
4,4′-DDT	20	2.94	59	31.0	D–203
Dieldrin	20	3.99	94	27.8	29–136
Diethyl phthalate	20	4.88	83	38.4	D–114
Dimethyl phthalate	40	3.51	97	24.0	D–112
Di-*n*-butyl phthalate	20	4.05	95	30.4	1–118
Di-*n*-octyl phthalate	20	5.29	83	14.7	4–146
Endosulfan sulfate	20	3.60	90	32.3	D–107
Endrin	40	2.71	27	17.5	–
Fluoranthene	40	2.17	91	30.7	26–137
Fluorene	40	2.32	83	41.1	59–121
γ-BHC (lindane)	40	2.54	95	25.9	–
Heptachlor	20	3.40	78	31.0	D–192
Heptachlor epoxide	40	2.01	81	34.5	26–155
Hexachlorobenzene	20	3.09	95	17.8	D–152
Hexachlorobutadiene	40	3.32	29	13.3	24–116
Hexachloroethane	20	4.35	9	7.2	40–113
Isophorone	20	4.47	86	32.1	21–196
Naphthalene	40	2.78	53	21.4	21–133
Nitrobenzene	40	2.09	62	23.4	35–180
n-Nitrosodi-*n*-propylamine	20	4.19	72	26.6	D–230
Phenanthrene	40	2.52	80	20.2	54–120
Pyrene	40	2.57	76	25.8	52–115
2,2′,4,4′,5,5′-Hexachlorobiphenyl	6	3.33	58	17.3	–
2,2′,4,5,5′-Pentachlorobiphenyl	6	3.33	74	10.0	–
2,3′,4,4′,5-Pentachlorobiphenyl	6	3.33	78	10.4	–
3,3′,4,4′,5-Pentachlorobiphenyl	6	3.33	64	11.3	–
3,3′,4,4′-Tetrachlorobiphenyl	6	7.33	103	8.2	–

TABLE IV *(continued)*

Analyte	n^a	Average sediment spiked conc. (mg/kg dry wt.)	Mean recovery (%)	Standard deviation	EPA Method 8270 recovery criteria (%)
Acidic compounds					
2,4,6-Trichlorophenol	20	3.95	81	41.8	37–144
2,4-Dichlorophenol	20	3.29	88	22.9	39–135
2,4-Dimethylphenol	40	2.40	69	24.1	32–119
2,4-Dinitrophenol	8	2.34	75	32.5	D–191
2-Chlorophenol	20	5.12	62	23.7	23–134
2-Methyl-4,6-dinitrophenol	11	4.63	16	9.3	D–181
2-Nitrophenol	20	3.13	60	20.1	29–182
4-Chloro-3-methylphenol	40	2.85	119	37.2	22–147
4-Nitrophenol	40	2.44	46	24.8	D–132
Pentachlorophenol	40	2.87	51	29.3	14–176
Phenol	40	2.80	32	13.0	5–112
Surrogate compounds					
[$^2H_4$]1,4-Dichlorobenzene	306	9.95	15	14.8	–
[$^2H_8$]Naphthalene	306	11.50	69	31.3	–
[$^2H_{10}$]Anthracene	306	9.40	98	28.1	–
4-Bromophenol	306	9.05	76	12.1	–
2,6-Dibromophenol	306	10.00	93	23.8	–

[a] n = Number of replicate spikes during a 24-month period.
[b] –, No QC acceptance criteria given in EPA Method 8270.
[c] D = Detected; result must be greater than zero.

recovery efficiency of the method. This phenomenon, combined with the selection of an intermediate polarity extraction solvent, assists in the simultaneous recovery of acidic compounds along with the basic and neutral compounds without the pH adjustment and re-extraction required in other procedures [21,25]. The recovery of polar analytes by this method agrees with the results of a predecessor method that recovered (at about 50% efficiency) the multifunctional polar pesticide chlorpyrifos from sediments [8].

Non-polar solvents (*e.g.* dichloromethane, hexane and benzene) are often used for the extraction of anthropogenic chemicals from sediments [23,28]. Since these solvents are relatively immiscible with water, such methods often require drying the sediments to insure that the extraction solvent can adequately interact with the sample. Drying sediments, at even the relatively low temperatures of 50–60°C, can result in significant loss of semi-volatile analytes [20,35]. If sediments are not dried prior to extraction, it is questionable whether water immiscible solvents can effectively extract the target analytes. The use of water miscible solvents for sediment extraction allows more intimate mixing of sample and solvent without drying the sample [20].

Comparison with other methods and techniques

Sonication extraction using non-polar solvents for the recovery of polynuclear aromatic hydrocarbons (PAHs) from sediments has been reported to yield lower recoveries than either tumbling [28] or supercritical-fluid extraction [23]. Our recovery values for PAHs in Tables II and IV compare favorably with the values reported for these analytes by the tumbling and supercritical-fluid extraction methods. Satisfactory PAH recovery by our method is further confirmed by the data presented for SRM 1941 in Table III.

The recovery limits for EPA Method 8270 [36] and the recovery ranges obtained for the method we developed and reported here are compared in Table

TABLE V

FIELD DUPLICATE RESULTS FOR VARIOUS SAMPLES AND SELECTED ANALYTES (in mg/kg dry wt.)

Analyte	Sample concentration	Sample duplicate concentration
Anthracene	0.33	1.09
Anthracene	0.88	5.85
Anthracene	0.25	0.74
Benz[*a*]anthracene	0.04	<0.04[a]
Benz[*a*]anthracene	2.02	0.32
Benz[*a*]anthracene	1.15	<0.04
Benz[*a*]pyrene	0.13	0.51
Benz[*a*]pyrene	2.61	2.52
Chrysene	0.70	2.46
Chrysene	3.16	2.79
Fluoranthene	5.96	0.52
Fluoranthene	20.72	18.04
Fluoranthene	0.33	0.31
Fluoranthene	6.62	<0.03
Fluorene	<0.08	<0.08
Fluorene	0.38	7.88
Pyrene	2.14	5.67
Pyrene	2.13	0.30
Pyrene	1.17	1.18
Pyrene	4.02	<0.03
4,4′-DDE	<0.21	1.11
4,4′-DDE	0.50	<0.21
4,4′-DDE	7.23	8.80
4,4′-DDD	0.64	0.77
4,4′-DDD	0.40	<0.11

[a] <, Value indicates the limit of detection.

IV. The precision of our method is comparable with the precision required by EPA Method 8270. However, since the data for our method in Table IV were obtained using external standard calibration, the precision could be improved by using internal standard calibration procedures [37]. Current EPA methods now require analysis by the internal standard procedure [36,38]. The recovery data provided for the OPPs are the result of quality control spike samples analyzed with sets of field samples. The surrogate spike recovery data in Table IV are based on data collected for over 300 analyses of field sample extracts, including both freshwater and marine sediment samples. The recovery values for our method are comparable with data in the literature for various individual classes of compounds [19,21,23,27,28]. The data in Table IV indicate that this method can accurately and reproducibly recover these analytes from sediment matrices.

Poorly recovered compounds

The low recoveries observed for the dichlorobenzenes and some other analytes are likely due to their relatively high volatility. Lopez-Avila *et al.* [19] reported low recovery of dichlorobenzene isomers relative to other chlorinated hydrocarbons in their evaluation of EPA Method 8120. That method is similar to our method and involves the sonication extraction of sediment and soil samples with dichloromethane followed by gas chromatography–elec-

TABLE VI

REPLICATE EXTRACTION OF CONTAMINATED SEDIMENTS

Analyte	Sediment 1		Sediment 2	
	Mean[a] concentration	R.S.D. (%)	Mean[a] concentration	R.S.D. (%)
4,4′-DDD	6.06	9.6	nd[b]	nd
4,4′-DDE	0.68	7.5	nd	nd
Acenaphthalene	nd	nd	0.04	14.5
Acenaphthene	82.9	12.8	6.47	15.6
Anthracene	3.18	35.3	3.68	28.0
Benz[*a*]anthracene	3.52	18.2	0.69	14.3
Benz[*a*]pyrene	9.22	17.0	0.59	35.1
Benzo[*b*+*k*]fluoranthene	29.9	15.8	6.71	15.8
Chrysene	3.14	39.4	0.59	19.0
Fluoranthene	20.7	15.3	5.65	22.6
Fluorene	75.2	14.5	5.22	12.4
Naphthalene	29.6	10.1	0.44	30.2
Phenanthrene	76.5	31.1	11.7	25.8

[a] Mean of 5 replicate experiments expressed in mg/kg dry weight basis.
[b] nd = Analyte not found in sample.

tron-capture detection. Several of the phenolic compounds were also poorly recovered presumably due to their low pK_a values. Many of the compounds with lower recoveries are ones which would be less likely to associate with sediments due to their greater water solubility or higher volatility. The low recovery of endrin by our method is likely due to thermal degradation in the GC injection port [33].

Non-homogeneity of sediments

Normal field QA procedures required that duplicate sediment samples be obtained at the rate of one field duplicate for every nine field sampling locations. The results of analyses of field duplicate samples (Table V) indicate a larger variation between some duplicate samples than can be attributed to the laboratory analytical precision alone (Tables II and IV). This variation was presumed to be related to the non-homogenous nature of the sediments rather than the variation contributed by the sediment extraction method. The results of a replicate extraction experiment, presented in Table VI, in addition to the SRM recovery data in Table III, support this hypothesis. The variation among the different replicate extractions from single homogenized samples is well within the variation of the analytical method. This indicates that the variation observed in Table V for the analyses of field duplicate samples is related to the non-homogeneous spatial distribution of organic contaminants in these field duplicate samples rather than to the sediment extraction analytical method.

The non-homogeneous spatial distribution of organic contaminants in sediments related to direct chemical analysis has received little attention. However, a few reports indicate that sediment toxicity exhibits a high degree of spatial variability [1,39,40]. Stemmer *et al.* [1] reported extreme spatial variation of toxicological bioassay response in creosote contaminated sediment samples taken from a river in Ohio. They noted that toxicological response varied by up to two orders of magnitude among subsamples taken within a given square meter area. The data presented in Table V indicate that some field duplicate sediment samples analyzed during our study appear to be reasonably homogeneous while other field duplicate samples vary in contaminant concentration by over one order of magnitude. Swartz *et al.* [40] reported strong correlations among the spacial distribution of sediment toxicity, total organic carbon and 4,4′-DDE concentration in sediment cores. These findings support a hypothesis that the wide variations we observed in the field duplicate analyses (Table V) may be due in part to a non-homogeneous distribution of natural organic carbon in sediments.

CONCLUSIONS

The method presented in this paper reliably recovers OPPs, representing a variety of chemical classes, from both freshwater and marine sediments. The procedure provides an efficient and rapid method to simultaneously screen sediment samples for both base, neutral and acidic extractable organic priority pollutants in sediments. The use of a water soluble organic solvent (acetonitrile) for sediment extraction improves the recovery of polar compounds without sample pH adjustment or drying.

The method has been used to screen for OPPs in more than 300 freshwater and estuarine sediment samples from throughout the state of Florida. The surrogate spike recovery data, with one exception, indicate the method's broad applicability. The analysis of field duplicate samples indicates that near-scale spatial variation in the distribution of organic pollutants exists in some sediments.

ACKNOWLEDGEMENT

This work was funded, in part, by Contract No. WM266 from the Florida Department of Environmental Regulation, Tallahassee, FL, USA. The project manager was Mr. Dean Jackman.

REFERENCES

1 B. L. Stemmer, G. A. Burton, Jr. and G. Sasson-Brickson, *Environ. Toxicol. Chem.*, 9 (1990) 1035.
2 *An Overview of Sediment Quality in the United States*, Office of Water Regulation and Standards, EPA, Washington, DC, 1988.
3 R. B. Spies, D. W. Rice Jr. and J. Felton, *J. Mar. Biol.*, 98 (1988) 181.
4 R. B. Spies, H. Kruger, R. Ireland and D. W. Rice Jr., *Mar. Ecol. Progr.*, 54 (1989) 157.
5 A. Yasuhara and M. Morita, *Chemosphere*, 16 (1987) 2559.
6 D. C. Malins, B. B. McCain, D. W. Brown, S. Chan, M. S. Myers, J. T. Landahl, P. G. Prohaska, A. J. Friedman, L. D.

Rhodes, D. G. Burrows, W. D. Gronlund and H. O. Hodgins, *Environ. Sci. Technol.*, 18 (1984) 705.
7 B. D. Melzian, C. Zoffman and R. B. Spies, *Mar. Pollut. Bull.*, 18 (1987) 388.
8 L. K. Marble and J. J. Delfino, *Am. Lab*, 20 (1988) 23.
9 R. J. Ozertich and W. P. Schroeder, *Anal. Chem.*, 58 (1986) 2041.
10 J. N. Sieber, D. E. Glotfelty, A. D. Lucas, M. M. McChesney, J. C. Sagebiel and T. A. Wehner, *Environ. Contam. Toxicol.*, 19 (1990) 583.
11 C. Nerin, I. Echarri and J. Cacho, *Fresenius' J. Anal. Chem.*, 339 (1991) 684.
12 W. Dedek, W. D. Wenzel, H. Oberlander, B. Mothes and J. Mannig, *Fresenius' J. Anal. Chem.*, 339 (1991) 201.
13 J. Sherma, *Anal. Chem.*, 59 (1987) 18R-31R.
14 J. W. Carr and J. M. Harris, *Anal. Chem.*, 60 (1988) 698.
15 M. M. Krahn, L. K. Moore, R. G. Bogar, C. A. Wigren, S. Chan and D.W. Brown, *J. Chromatogr.*, 437 (1988) 161.
16 H. Steinwandter, *Fresenius' Z. Anal. Chem.*, 327 (1987) 309.
17 K. G. Furton and J. Rein, *Anal. Chim. Acta.*, 236 (1990) 99.
18 I. Holoubek, J. Paasivirta, P. Maatela, M. Lahtipera, I. Holoubkova, P. Korinek, Z. Bohacek and J. Caslavsky, *Toxicol. Environ. Chem.*, 25 (1990) 137.
19 V. Lopez-Avila, N. S. Dodhinala, J. Milanes and W. F. Beckert, *J. Assoc. Off. Anal. Chem.*, 72 (1989) 593.
20 W. Auer and H. Malissa, Jr., *Anal. Chim. Acta*, 237 (1990) 451.
21 V. Lopez-Avila, R. Northcutt, J. Onstot, M. Wichham and S. Billets, *Anal. Chem.*, 55 (1983) 881.
22 T. G. Greco and R. L. Grob, *J. Environ. Sci. Health*, A25 (1990) 185.
23 S. B. Hawthorne and D. J. Miller, *Anal. Chem.*, 59 (1987) 1705.
24 P. Capriel, A. Haisch and S. V. Khan, *J. Agric. Food Chem.*, 34 (1986) 70.
25 J. A. McFall, S. R. Antoine and I. R. Deleon, *Chemosphere*, 14 (1985) 1561.
26 V. Lopez-Avila, J. Milanes and N. S. Dodhiwala, *J. Chromatogr. Sci.*, (1989) 209.
27 A. L. Alford-Stevens, J. W. Eichelberger and W. L. Budde, *Environ. Sci. Technol.*, 22 (1988) 304.
28 M. M. Krahn, G. M. Ylitalo, J. Joss and S. Chan, *Mar. Environ. Res.*, 31 (1991) 175.
29 P. Peterman and J. J. Delfino, *Biomed. Environ. Mass Spec.*, 19 (1990) 755.
30 O. Hutzinger and A. A. M. Roof, in B. K. Afghan and D. Mackay (Editors), *Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment*, Plenum Press, New York, 1980, p. 9.
31 L. H. Keith and W. A. Telliard, *Environ. Sci. Technol.*, 13 (1979) 416.
32 EPA Method 3350, in *Test Methods For Evaluating Solid Waste, SW-846*, Office of Solid Waste and Emergency Response, Washington, DC, 1986.
33 EPA Method 625, in *Federal Register*, Vol. 49, No. 209, October 26, 1984.
34 C. E. Rostad, W. E. Pereira and S. M. Ratcliff, *Anal. Chem.*, 56 (1984) 2856.
35 N. Vogt, F. Brakstad, K. Thane, S. Norderson, J. Krane, E. Aamot, K. Kolset, K. Esbensen and E. Steinnes, *Environ. Sci. Technol.*, 21 (1987) 35.
36 EPA Method 8270, in *Test Methods For Evaluating Solid Waste, SW-846*, Office of Solid Waste and Emergency Response, Washington, DC, 1986.
37 M. A. Kaiser and F. J. Dobbrecht, in R. L. Grob (Editor), *Modern Practice of Gas Chromatography*, Wiley, New York, 1977, Ch. 4, p. 151.
38 EPA Method 625, *Fed. Reg.*, 40, Appendix A (1990) 474–501, July 1, 1990.
39 B. J. Dutka, K. K. Kwan, S. S. Rao, A. Jurhovic, R. McInnis, G. A. Palmteer and B. Hawkins, *Environ. Toxicol. Water Qual.*, 6 (1991) 309.
40 R. C. Swartz, D. W. Schultz, J. O. Laberson and R. J. Ozretich, *Mar. Environ. Res.*, 31 (1991) 215.