

NWRI CONTRIBUTION 89-82

**A MULTI-RESIDUE METHOD FOR THE  
DETERMINATION OF CHLOROBENZENES, PCB  
ORGANOCHLORINATED INSECTICIDES, PAH  
AND CHLOROPHENOLS IN SUSPENDED SEDIMENTS**

by

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## **MANAGEMENT PERSPECTIVE**

Since 1979, suspended sediment samples have been collected by Water Quality Branch, Ontario Region, on a weekly basis from the Niagara River for the purpose of water quality monitoring. These samples were analyzed for a wide variety of organics including chlorinated insecticides, PCBs, chlorobenzenes, PAHs, and phenols. Because of the lack of a comprehensive and validated analytical method, these samples were analysed by contract laboratories in the past. By 1986, a multi-residue method for the determination of the above toxic organics with a strong emphasis on in-house quality assurance was developed by National Water Quality Laboratory and approved by members of the Analytical Protocol Group, B Committee, Niagara River Long Term Monitoring Program. This report documents the official methodology currently in use for the Niagara River sediment samples.

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## PERSPECTIVE-GESTION

Depuis 1979, la Direction de la qualité des eaux, région de l'Ontario, a prélevé toutes les semaines des échantillons de sédiments en suspension dans la rivière Niagara, à des fins de contrôle de la qualité des eaux. On a dosé dans ces échantillons des composés organiques très divers, notamment des insecticides chlorés, des BPC, des chlorobenzènes, des HAP et des phénols. Vu l'absence de méthode analytique complète et validée, on a donné antérieurement un contrat à des laboratoires pour ces dosages. Vers 1986, le Laboratoire national d'analyses de la qualité des eaux a mis au point une méthode utilisant plusieurs résidus pour doser les toxiques organiques ci-dessus en insistant sur le contrôle interne de la qualité. Cette méthode a reçu l'approbation des membres de l'Analytical Protocol Group, Comité B, Programme de contrôle à long terme de la rivière Niagara. Le présent rapport la méthodologie officielle utilisée actuellement pour les échantillons de sédiments de la rivière Niagara.

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## ABSTRACT

A multi-residue procedure was developed for the simultaneous determination of neutral and acidic environmental contaminants including polychlorinated biphenyls, organochlorinated insecticides, chlorobenzenes, polynuclear aromatic hydrocarbons, and chlorophenols in suspended sediments, at ng/g levels. This method involved an ultrasonic extraction of the sample sequentially at pH 7 and 2, silica gel column cleanup and fractionation, and final analysis by gas chromatography using electron-capture and mass spectrometric detectors. Six surrogates and one internal standard were added to the sample or the sample extract at various stages to monitor the recoveries of the analytes. Performance indicators such as method precision, accuracy and detection limits are presented. The procedure has been applied to the analysis of sediment samples in the Niagara River Water Quality Monitoring Program.

## RÉSUMÉ

On a mis au point une méthode utilisant plusieurs résidus pour doser simultanément des contaminants neutres et acides de l'environnement, notamment des biphényles polychlorés, des insecticides organochlorés, des chlorobenzènes, des hydrocarbures aromatiques polynucléaires et des chlorophénols, présents dans des sédiments en suspension à des concentrations de l'ordre du ng/g. Cette méthode consiste en une extraction aux ultrasons de l'échantillon, effectuée de façon séquentielle aux pH 7 et 2, en une purification et un fractionnement sur colonne de gel de silice et finalement en un dosage par chromatographie en phase gazeuse couplée à des détecteurs à capture d'électrons et à spectrométrie de masse. À diverses étapes, on a ajouté six substituts et un étalon interne à l'échantillon ou à l'extrait d'échantillon pour surveiller la récupération des substances à analyser. On présente les indicateurs de la performance comme la précision de la méthode, la justesse et les limites de détection. La méthode a été appliquée au dosage d'échantillons de sédiments dans le cadre du Programme de contrôle de la qualité des eaux de la rivière Niagara.

## 1.0 INTRODUCTION

In the monitoring of water quality parameters for organics, sediments are one of the most frequently analyzed matrices. Because of their adsorptive properties and constant interaction with water, the top layer of lake sediments and the suspended sediments often accumulate a vast amount of organics, especially those which are not very soluble in water. Thus, sediments are considered as enriched, composite samples, exhibiting levels of organics a few orders of magnitude higher than those found in water at the same location. Analysis of sediment core samples also provides useful historical information of an area.

Although the manufacture of polychlorinated biphenyls (PCBs) ceased and their use was restricted in the early seventies, these toxic and carcinogenic compounds are still found almost everywhere in the Great Lakes Basin due to illegal dumping, leaching from storage tanks and accidental spillage of these persistent chemicals. Sediment PCBs concentrations ranging from high ng/g levels in some heavily polluted areas to baseline level of low ng/g have been reported [ 1-4 ]. Chlorobenzenes, albeit less commonly found than the PCBs, are another class of persistent and priority pollutants. Elevated levels of chlorobenzenes and hexachlorobutadiene have been reported in Lake Ontario and Lake Erie, particularly in areas near the Niagara River [ 5-7 ] and the St. Clair River [ 8 ]. Except for a few cases, polynuclear aromatic hydrocarbons (PAHs) are not produced for any industrial application. Their ubiquitous occurrence is closely linked to the incomplete combustion of coal and hydrocarbon fuels in

industrial and domestic situations. A wide variety of PAHs ranging from naphthalene to coronene at high  $\mu\text{g/g}$  to low  $\text{ng/g}$  levels have been reported in sediment samples from the Great Lakes [ 9,10 ]. Organochlorinated insecticides (OCs) were heavily used to control pests in crops until their toxic and persistent properties were finally realized. Unfortunately, residues of OCs such as the BHC isomers, chlordanes, the DDT group, mirex, etc., from previous applications are still detectable in many environmental samples [ 1-4 ]. Although chlorophenols are mostly occurring in pulp and paper industry effluents, these residues could be found in industrial wastes and agricultural runoffs since some of them are starting materials and potential metabolites of many common herbicides.

In the late 1970s, increasing public concern had developed over the recurring detection of persistent and toxic organics such as PCBs and mirex in the biota and sediments of Lake Ontario. Since the Niagara River is the only outflow for Lake Erie and it accounts for 50% of all incoming sediments to Lake Ontario [ 11 ], it was considered as the single largest source of these organic contaminants [ 12 ]. In 1984, the environmental protection agencies from both Canada and the United States set up a joint program to monitor the water quality of the Niagara River. In this program, the National Water Quality Laboratory (NWQL) of Environment Canada is responsible for the determination of organic parameters including PCBs, chlorobenzenes, OCs, PAHs, and chlorophenols in water and sediment samples collected at Niagara-on-the-Lake and Fort Erie on an on-going basis. An analytical protocol with strong emphasis on in-house quality assurance was developed by the NWQL and reviewed by an ad hoc committee for

analytical protocols involving scientists from Environment Canada, the Ontario Ministry of the Environment, USEPA Region II, and New York State Department of Environmental Conservation. This report documents the official methodology recommended for use in the monitoring program for the determination of the above-mentioned chlorinated organics and PAHs in sediment samples. The results given below were partially abstracted from an in-house unpublished report prepared earlier [ 13 ].

## 2.0 METHOD

### 2.1 Apparatus

- (a) Gas chromatograph.--Hewlett-Packard (Avondale, PA 19311) Model 5890A or 5700A, equipped with a split/splitless or a packed column injector, Model 7673A or 7671A autosampler, an electron-capture detector, and a HP 1000 data system.
- (b) Gas chromatography-mass spectrometry.--Finnigan (Sunnyvale, CA 94086) Model 4500 with a quadruple mass analyzer and an electron-impact ion source.
- (c) Capillary columns.--30 m x 0.25 mm id SPB-1, SPB-5 and SPB-608 fused silica capillary columns from Supelco Co. (Oakville, Ontario, Canada) or DB-5 column from J&W Scientific Co. (Chromatographic Specialties, Brockville, Ontario, Canada).
- (d) Sonicator.--Heat Systems-Ultrasonics Model W375 with a 3/4 inch High Gain Horn (East Mall, Plainview, N.Y. 11803).



## 2.2 Reagent and Chemicals

- (a) Solvents.--Acetone, hexane, dichloromethane, petroleum ether (b.p. 30 to 60°C), iso-octane and acetonitrile were distilled-in-glass grade from Burdick and Jackson (Muskegon, MI 49442).
- (b) Silica gel.--ICN 100-200 mesh, Terrochem (Mississauga, Ontario, Canada). Activate adsorbent at 130°C for 18 hr. Prepare the 3% deactivated silica gel by adding 6 mL of reagent water to 194 g of the silica gel. Shake well, equilibrate at room temperature in a sealed container and keep in a desiccator overnight before use.
- (c) Sodium sulfate.--Anhydrous, BDH Chemicals (Mississauga, Ontario, Canada). Heat at 600°C for 18 hr in a muffle furnace and store in a desiccator.
- (d) Analytical standards.--Aldrich Chemical Company (Milwaukee, WI 53233) or USEPA Pesticides Repository. Purity of standards must be >95%. Prepare stock solutions of individual compounds in iso-octane at 1000 µg/mL and store at -4°C in the dark. Prepare intermediate solutions, calibration standards and surrogate spiking solutions according to Table 1.

## 2.3 Sampling Protocol

Use a continuous flow separator, Model KA-02-06-075 Westfalia centrifuge to collect suspended sediment samples by centrifuging river water at a flow rate of 6 L/min [ 14 ]. When this process is done, scrape suspended sediments from the centrifuge bowl with a Teflon scraper into a precleaned amber sample bottle. Record the weight, and

keep at  $-20^{\circ}\text{C}$  in the dark until extraction.

#### 2.4 Sample Extraction

Homogenize the wet sediment thoroughly either by stirring or blending the sample. Accurately weigh  $10.00 \pm 0.02$  g of the sample into a 250 mL stainless steel beaker. In the validation experiments, spike 100  $\mu\text{L}$  of each spiking solution (Table 1) evenly to the sediment sample, mix well and equilibrate at  $4^{\circ}\text{C}$  overnight before extraction. Add 100 mL of a 1:1 mixture of acetone and hexane and 100  $\mu\text{L}$  of SM1 (Table 1) to the sample. Place the beaker in an ice bath, extract the sample for three min by setting the sonicator to full power and 40% duty cycle. Dry a replicate sample at  $105^{\circ}\text{C}$  to constant weight for moisture determination. After sonication, allow sediment particulates to settle for 2 min. Transfer the supernatant to a 5 cm, pre-washed Celite column in a glass Allihn filter funnel and collect the filtrate in a 1 L round bottom flask. Repeat the extraction once more with another 100 mL of the solvent. This fraction contains all of the neutral organics and some phenolics. Acidify the above sediment sample to pH2 by adding 6 drops of 50%  $\text{H}_2\text{SO}_4$  and repeat the extraction twice more with 100 mL aliquots of 1:1 acetone and hexane. After each extraction, filter the extract which contains the remaining phenols through the same Celite bed into the 1 L flask as used for the neutrals. Add 100  $\mu\text{L}$  of SM2 (Table 1), reduce the volume of the combined extract to ca. 200 mL on a rotary evaporator. Transfer the remaining extract which is now mainly in hexane to a 1 L separatory funnel. Add 100 mL reagent water to the funnel and shake for two min.

If an emulsion forms, add 25 mL of a saturated sodium sulfate solution and gently shake the mixture again. After phase separation, drain the aqueous (bottom) layer into a 500 mL separatory funnel and extract, for two min each, with 100, 50 and 50 mL of dichloromethane (DCM). Pass the DCM and hexane extract in the above 1 L funnel through 60 g of anhydrous sodium sulfate contained in an Allihn funnel to remove residual water left in the extract. Add 10 mL iso-octane as a keeper and evaporate the solvents with a rotary evaporator and a 40°C water bath. Quantitatively transfer the concentrated extract to a 15 mL graduated tube, add 100 µL of SM3 (Table 1) and make up to 10.0 mL with iso-octane.

## 2.5 Silica Gel Column Cleanup

Plug a 350 x 12 mm id glass column with a piece of silanized glass wool. Fill the column with 3.4 g of the 3% deactivated silica gel and top with 2.5 cm of anhydrous sodium sulfate. Wash column with 40 mL of hexane and discard the washing. Transfer 5.0 mL of the above concentrated extract to the column, elute with 40 mL of hexane and collect (Fraction A). Continue the elution with 60 mL of 1:1 mixture of DCM and hexane and collect (Fraction B). To each fraction, add 5 mL of iso-octane, evaporate to ca. 2 mL, add 50 µL of the octachloronaphthalene (OCN) solution (Table 1) and make up to 5.0 mL. Treat Fraction A with purified mercury to remove sulfur and sulfur compounds until the metal is shiny.

## 2.6 Instrumental Analysis

Analyze Fraction A for CBs and OCs and Fraction B for OCs by GC-ECD using the following conditions: injector 250°C, detector 300°C, column initial temperature 80°C (hold for 2 min), programming rate 4°C/min from 80 to 280°C, hold final temperature for 16 min. Carrier gas, hydrogen. Column head pressure, 13 psi. Makeup gas, argon/methane 5+95 at 30 mL/min. Inject 2 µL of the sample extract in splitless mode with a valve time of 0.5 min. Using an inlet splitter, split the sample onto either one of the following two capillary column pairs: SPB-1 and SPB-5 or SPB-1 and SPB-608. The analyte is identified if its retention times on both columns match with those of an authentic standard. Quantify each peak by external standard method and analyze a calibration standard for every five samples.

Identify PCBs in Fraction A by comparison of retention times of sample with a 1:1:1 mixture of Aroclors 1242, 1254, and 1260. Determine the amount of total PCBs using a 1.8 m x 2 mm id 3% OV-1 packed column operating at 190°C and a flow rate of 30 mL/min. Sum the total peak areas (or heights) of the identified PCB peaks and compare with the total responses of the same peaks in a calibration standard to determine the concentrations.

Add 500 ng of anthracene-d<sub>10</sub> in 5 µL to 5 mL of the raw extract and analyze this fraction for the PAHs and chlorophenols. Set up GC-MS to acquire multiple ion monitoring (MIM) data for the parameters according to Table 2. Inject 2 µL of this fraction in splitless mode onto a 30 m x 0.25 mm id DB-5 column interfaced to a Finnigan 4500 mass spectrometer using the following conditions: ion

source temperature 150°C, oven initial temperature 70°C (hold 3 min), programming rate 10°C/min to 300°C, hold final temperature for 10 min, carrier gas, helium at a head pressure of 10 psi. In GC-MS analyses, identification of a compound is based on the agreement of its retention time as well as the ratio of its characteristic ions with an authentic standard (see Results and Discussion). If a positive identification is made, quantify the analyte by an internal standard method according to the following equation:

$$W_{an} = (W_i/A_i) \times (A_{an}/RF)$$

where:  $W$  = weight ( $\mu\text{g}$ )

$an$  = analyte

$i$  = internal standard (anthracene- $d_{10}$ )

$A$  = area under the peak

$$RF = (W_i/A_i) \times (A_{an}/W_{an})$$

Analyze a calibration standard for every five samples.

### 3.0 RESULTS AND DISCUSSION

Before this multi-residue method was developed, National Water Quality Laboratory had been using basically the same procedure for the determination of PCBs and OCs in sediments since 1978. Later on, the same procedure was extended to determine chlorobenzenes and PAHs in sediments with satisfactory results. With the advent of inert and high resolution fused silica capillary columns, complex sample extracts containing different classes of pollutants can be analyzed in a single run without further fractionation. It is thus feasible to develop a consolidated multi-residue method for the simultaneous

determination of the above neutral and acidic compounds. A few years ago, a method for the determination of 51 priority organic compounds in sediments was reported [ 15 ]. That method involved sequential extraction of the sediment at  $\text{pH} > 11$  and  $\text{pH} < 2$  with a Tekmar Tissuemizer blending probe, cleanup by silica gel column or gel permeation chromatography (GPC) and GC-MS analysis. Validation data were obtained at 400 and 4000 ng/g fortification levels. Our method described here covers similar types of compounds but uses a combination of GC-ECD and GC-MS-MIM techniques and was validated at lower levels, i.e. 5 to 50 ng/g for OCs and chlorobenzenes, 200 ng/g for total PCBs, 200 to 400 ng/g for PAHs, and 400 to 800 ng/g for the phenols. In addition, an elaborated in-house QA/QC procedure is also presented to assure the data quality.

### 3.1 Extraction

Traditionally, soxhlet extraction is often used for sediment samples because of its high efficiency of recovering organics. With the development of ultrasonic devices, there have been many successful examples of the extraction of organics from solid and liquid samples using the sonication technique [ 15,16 ]. In comparison to the soxhlet apparatus, ultrasonic extraction has the advantages of achieving similar recoveries in a much shorter time (minutes versus hours) as well as eliminating the need for special glasswares. Thus, it is particularly suitable for the extraction of a large number of sediment samples on a routine basis. However, a potential drawback of ultrasonic extraction is the loss of the more volatile components such

as chlorobenzenes and the BHC isomers because of the heat and vibration generated during extraction. The use of an ice bath to maintain the sample at low temperatures improved the recoveries of these compounds to better than 75% except for the di- and tri- chlorobenzenes (Table 3). Since some of the OCs are unstable under strongly acidic or basic conditions, these labile organics were isolated from the sediment by first performing extractions at neutral pH. However, the chlorophenols were only partially recovered at this pH and thus further extractions at pH 2 must be carried out and the extracts combined.

### 3.2 Cleanup

A 3% deactivated silica gel column was used for the cleanup of the sediment extracts. With judicious choice of the eluting solvents, this column provided complete separation of chlorobenzenes and PCBs from the PAHs. However, OCs were split into both fractions and thus analysis was done on those fractions to determine OCs. Although more than two fractions were collected by some workers in the silica gel cleanup step [ 15 ], only two were collected in this study to minimize work and splitting of the analytes. Since chlorophenols were not quantitatively recovered on this column, analyses of these parameters were performed on the raw extracts.

Sulfur and sulfur compounds in sediment extracts were most conveniently removed by shaking with prepurified metallic mercury. Although activated copper powder was also effective, this reagent could not be kept for more than a few hours and thus had to be generated each time before use. After the removal of sulfur, both fractions would be

suitable for analyses by GC-ECD or GC-MS-MIM. However, if full scan GC-MS analyses were required, additional cleanup by gel permeation chromatography using either a Sephadex LH-20 [ 17 ], a Bio-Beads S-Xn [ 18 ], or a  $\mu$ Styragel [ 19 ] column to remove the aliphatic hydrocarbons in some sediment samples would be necessary.

### 3.3 GC-ECD and GC-MS-MIM Analyses

Analyses of chlorobenzenes in fraction A and the OCs in fraction B are straightforward since the capillary columns used provided adequate resolution of all analytes and other coextractives in the same retention time window. Some OCs such as aldrin, heptachlor, p,p'-DDE, mirex, and small amounts of the DDT group compounds coeluted with the PCBs in fraction A. Since these OCs might partially overlap with the PCB peaks in the chromatogram using the primary analytical column, a second or even a third capillary column was used to eliminate the potential interference. Since a validated quantitation method for PCBs using capillary columns was not in place, total PCBs were quantitated by packed column chromatography. In these cases, abnormally large PCB peaks in the aldrin, p,p'-DDE and mirex regions were excluded in the calculation if the capillary column analysis of this fraction also indicated the presence of such OCs in large quantities. The GC-MS-MIM technique was chosen for the quantitation of PAHs since this method is more selective and is also ca. 100 times more sensitive than flame ionization detection.



### 3.4 Method Performance

Before the onset of the monitoring program, a bulk sediment was collected at Niagara on the Lake. This sample was subsequently homogenized and subsampled into 10.0 g aliquots. Ten of these aliquots were fortified with the PCBs, OCs, chlorobenzenes, PAHs and chlorophenols to concentrations ranging from 5 to 800 ng/g as shown in Table 3. These samples along with blanks were processed and analyzed and the mean spike recoveries and coefficients of variation are tabulated in Table 3. Of these recovery data, 33 out of the 42 parameters were between 70 and 115% recovered and only four compounds registered recoveries below 50%. Lower recoveries of some of the chlorobenzenes and hexachlorobutadiene were largely due to evaporative losses. The proficiency of the present multi-residue procedure was further exemplified in a couple of interlaboratory QA/QC studies involving the determination of naturally contaminated organics in certified sediment reference materials [ 20,21 ]. Although not all of the parameters in this method were included in the above studies, the results obtained by this procedure were generally close to either the certified values or the interlaboratory medians (Table 4), indicating accuracy and comparability of the data.

Based on a 10.0 g sample of wet sediment with a moisture content of 63 %, the method detection limits (MDL) for each parameter calculated by the following equation, are given in Table 3.

$$MDL = t_{(n-1)} \times s$$

where:  $t_{(n-1)}$  = the two-sided Student's t-value for n-1 degrees of freedom at 95% confidence level

s = standard deviation of replicate ( $n \geq 7$ ) analyses of spiked samples

### 3.5 Quality Assurance

During the monitoring program, a rigorous in-house quality control program was designed and implemented to assure the performance of this procedure in the daily analysis of naturally contaminated samples. In addition to following all the steps of Good Laboratory Practices [ 22 ], the quality of sediment data was scrutinized on the basis of the recovery of various surrogates added to the samples at the following stages. (1) For each sample collected in the field, solution SM1 containing 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene, and  $\delta$ -BHC was added directly to the sediment prior to extraction. The recovery of these surrogates acted as a monitor of the entire extraction, solvent evaporation and fractionation steps of the procedure. (2) Solution SM2 containing 1,3-dibromobenzene was added to every sediment extract prior to the solvent displacement step to monitor evaporative losses of the more volatile components. (3) Solution SM3 containing 2,3,5,6-tetrachlorobiphenyl and endrin ketone was added to the concentrated extract just before the silica gel column cleanup to monitor whether or not the fractionation pattern is proper. (4) A solution of octachloronaphthalene was spiked into both fractions A and B for ECD analyses to monitor the reproducibility of GC retention times. (5) An anthracene- $d_{10}$  solution was added to fraction B and the raw extract of each sample and used as an internal standard to calibrate GC-MS response factors.

In addition to the above, one sediment sample fortified with all the analytes and SM1 was analyzed with every 20 samples to determine recoveries and possible interferences. The daily percent recoveries of each surrogate from every sample were plotted in a quality control chart, consisting of the target concentration as well as the upper and lower control limits which were defined as  $\pm$  two standard deviations. If a value fell outside of these control limits, a problem was indicated and the corresponding analytical sub-process was thoroughly examined until the exact problem was found and solved. A typical quality control chart for the surrogate 1,3,5-tribromobenzene is depicted in Figure 1.

In GC-MS-MIM analysis, quality of data was determined by the "FIT" parameter according to the following equations:

$$FIT_{gc} = 1 - (RT_{std} - RT_{an})/RT_{std}$$

$$FIT_{ms} = 1 - \Sigma(I_{std} - I_{an})/n-1$$

where: RT = relative retention time

std = standard

an = analyte

n = number of ions in the spectrum

I = intensity of ions normalized to anthracene-d<sub>10</sub>

and:  $FIT_{total} = FIT_{gc} \times FIT_{ms}$

A FIT value greater than 0.9 was regarded as a positive identification. If a FIT value lied between 0.75 and 0.9, further confirmation must be carried out. A FIT value lower than 0.75 was considered a mismatch and no identification was made.

### 3.6 Application

This method has been used for the determination of OCs, PCBs, chlorobenzenes and PAHs in suspended sediments samples collected from the Niagara River since 1986. Over 350 samples have since been processed and the results were reported elsewhere [ 13 ].

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Figure 1. Quality control chart for the recoveries of surrogate 1,3,5-tribromobenzene. The upper and lower control limits are  $\pm 2$  standard deviations.

**TABLE 1**  
**Spiking Solution for Chlorobenzenes, Organochlorines Pesticides,**  
**PCBs, Halogenated Surrogates, PAH's and Phenols**

Parameter	Volume Stock Req'd (μL)*	Spiking** Solution	Conc (ng/μL)
1,3-Dichlorobenzene	500	SS1	5.0
1,4-Dichlorobenzene	500	SS1	5.0
1,2-Dichlorobenzene	500	SS1	5.0
1,3,5-Trichlorobenzene	50	SS1	0.5
1,2,4-Trichlorobenzene	50	SS1	0.5
1,2,3-Trichlorobenzene	50	SS1	0.5
1,2,3,4-Tetrachlorobenzene	50	SS1	0.5
Pentachlorobenzene	50	SS1	0.5
Hexachlorobenzene	50	SS1	0.5
α-BHC	50	SS1	0.5
Lindane	50	SS1	0.5
Heptachlor	50	SS1	0.5
Aldrin	50	SS1	0.5
Heptachlor epoxide	50	SS1	0.5
γ-Chlordane	50	SS1	0.5
α-Chlordane	50	SS1	0.5
α-Endosulfan	50	SS1	0.5
p,p'-DDE	100	SS1	1.0
Dieldrin	100	SS1	1.0
Endrin	100	SS1	1.0
o,p'-DDT	150	SS1	1.5
p,p'-TDE (p,p'-DDD)	150	SS1	1.5
1,5'-DDT	150	SS1	1.5
1,5ndosulfan	100	SS1	1.0
Mirex	100	SS1	1.0
Methoxychlor	500	SS1	5.0
Hexachlorobutadiene	50	SS1	0.5
PCB (Aroclor 1242;1254;1260)	2000	SS3	20.0
1,3,5-Tribromobenzene	200	SM1	2.0
1,2,4,5-Tetrabromobenzene	200	SM1	2.0
δ-BHC	100	SM1	1.0
1,3-Dibromobenzene	500	SM2	5.0
2,3,5,6-Tetrachlorobiphenyl	200	SM3***	2.0
Endrin Ketone	100	SM3***	1.0
Octachloroanaphthalene	240	OCN***	2.4
Fluoranthene	2000	SS2	20
Pyrene	2000	SS2	20
Benzo(a)anthracene	2000	SS2	20
Chrysene	4000	SS2	40
Benzo(b)fluoranthene	4000	SS2	40
Benzo(k)fluoranthene	4000	SS2	40
Benzo(a)pyrene	4000	SS2	40
2,4,6-Trichlorophenol	4000	SS2	40
2,4,5-Trichlorophenol	4000	SS2	40
Pentachlorophenol	8000	SS2	80
Phenol	8000	SS2	80

\* Volume of stock solution req'd for dilution to 100 mL with MeOH to provide 100 mL of spiking solution. All stock solutions are at 1000 ng/μL; (for PCBs the concentration of each Aroclor in the stock solution is 333 ng/μL.

\*\* SS = Spiking Solution

\*\*\* SM = Surrogate Mix



TABLE 2

Detection Characteristics of the Aromatic Hydrocarbons

Parameter	Quantitation Mass	Confirmation Mass			Retention Times relative to Anthracene d10	Relative Response Factor
Anthracene-d10	188.0	203.0	200.0	101.0	1.00000	1.000
Fluoranthene	202.0	203.0	200.0	101.0	1.17624	0.964
Pyrene	202.0	203.0	200.0	101.0	1.20935	1.084
Benzo(a)anthracene	228.0	229.0	226.0	114.0	1.39435	1.211
Chrysene	228.0	229.0	226.0	114.0	1.40214	1.093
Benzo(b)fluoranthene	252.1	253.1	250.1	126.0	1.56573	0.992
Benzo(k)fluoranthene	252.1	253.1	250.1	126.0	1.57254	1.083
Benzo(a)pyrene	252.1	253.1	250.1	126.0	1.61733	0.722
Phenol	94.0	95.0	66.0		0.30867	1.029
2,4,6-Trichlorophenol	196.0	198.0	200.0	132.0	0.66602	0.194
2,4,5-Trichlorophenol	196.0	198.0	200.0	132.0	0.67478	0.131
Pentachlorophenol	265.9	263.9	267.9	269.9	0.97955	0.099

TABLE 3

Recovery of Organics from Spiked Suspended Sediments  
(Blank Corrected) (No. of Replicates = 10)

Parameter	Spiked Amount (ng/g)	Recovery (%)	Coeff. of Var. (%)	Detection Limit (ng/g)
1,3-Dichlorobenzene	50.0	23	19	4.1
1,4-Dichlorobenzene	50.0	42	11	4.2
1,2-Dichlorobenzene	50.0	35	16	5.3
1,3,5-Trichlorobenzene	5.0	48	15	0.7
1,2,4-Trichlorobenzene	5.0	58	24	1.3
1,2,3-Trichlorobenzene	5.0	56	14	0.7
1,2,3,4-Tetrachlorobenzene	5.0	88	12	1.0
Pentachlorobenzene	5.0	120	12	1.4
Hexachlorobenzene	5.0	96	24	2.3
$\alpha$ -BHC	5.0	104	9	0.9
Lindane	5.0	118	9	1.0
Heptachlor	5.0	82	7	0.5
Aldrin	5.0	92	7	0.6
Heptachlor epoxide	5.0	114	6	0.7
$\gamma$ -Chlordane	5.0	90	7	0.6
$\alpha$ -Chlordane	5.0	92	10	0.8
$\alpha$ -Endosulfan	5.0	82	6	0.5
p,p'-DDE	10.0	104	11	2.0
Dieldrin	10.0	92	7	1.2
Endrin	10.0	102	6	1.0
o,p'-DDT	15.0	94	10	2.5
p,p'-TDE (p,p'-DDD)	15.0	107	7	2.2
p,p'-DDT	15.0	111	9	2.7
$\beta$ -Endosulfan	10.0	84	7	1.0
Mirex	10.0	88	10	1.6
Methoxychlor	50.0	109	7	6.5
PCB (Aroclor 1242;1254;1260)	200	99	8	2.8
Hexachlorobutadiene	5.0	50	33	1.5
1,3,5-Tribromobenzene	50.0	94	7	-
1,2,4,5-Tetrabromobenzene	20.0	79	6	-
$\delta$ -BHC	20.0	112	4	-
1,3-Dibromobenzene	20.0	108	4	-
2,3,5,6-Tetrachlorobiphenyl	10.0	107	16	-
Endrin Ketone	10.0	104	10	-
Octachloroanaphthalene	24.0	104	8	-
Fluoranthene	200	80	24	77
Pyrene	200	95	19	66
Benzo(a)anthracene	200	85	31	97
Chrysene	400	92	26	178
Benzo(b)fluoranthene	400	105	20	156
Benzo(k)fluoranthene	400	105	20	154
Benzo(a)pyrene	400	95	18	126
2,4,6-Trichlorophenol	400	73	17	260
2,4,5-Trichlorophenol	400	50	23	106
Pentachlorophenol	800	75	9	220
Phenol	800	95	15	310

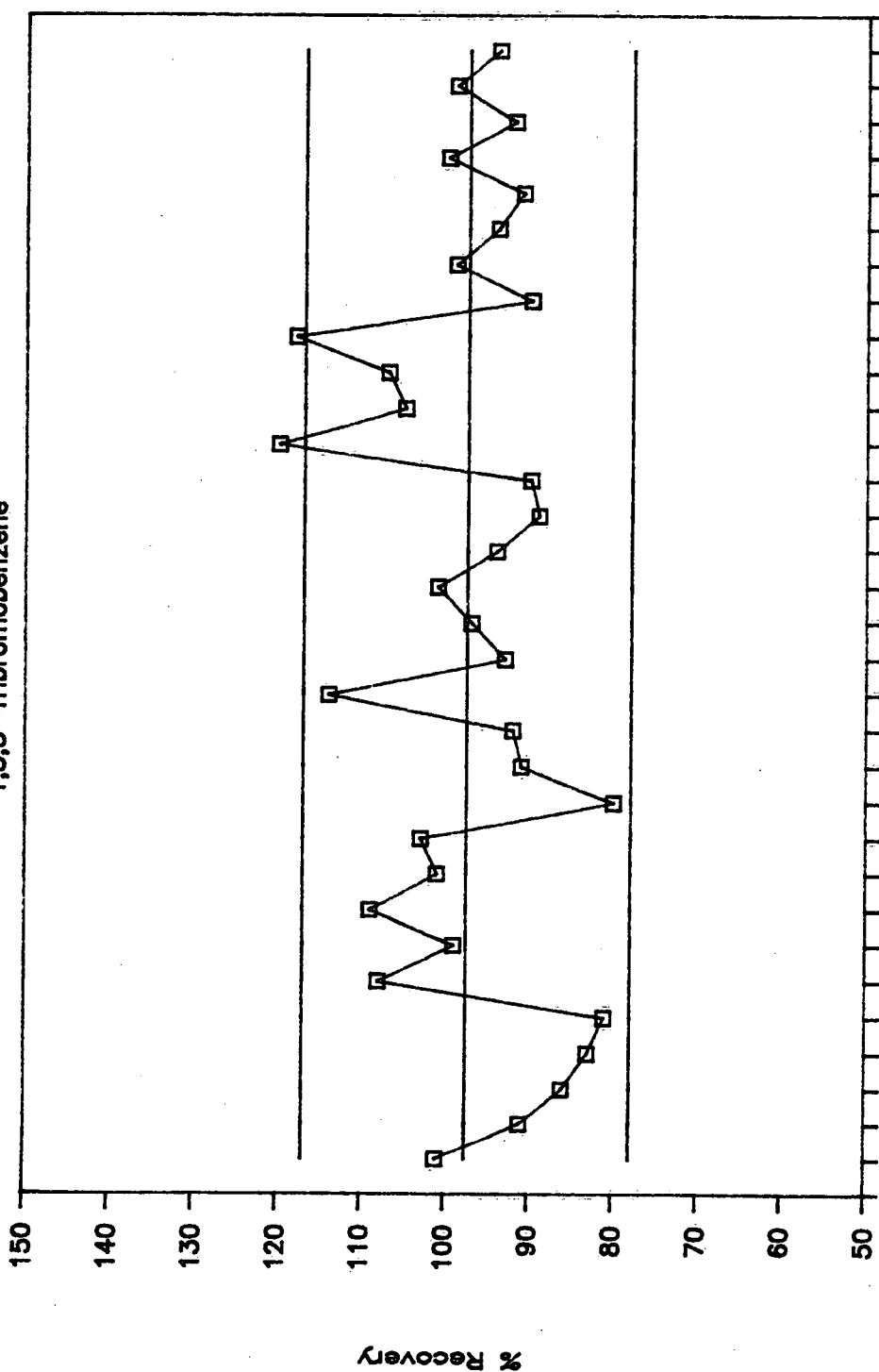
TABLE 4

Analytical Results (ng/g) of Some Chlorinated Organics and PAHs in  
Sediment Reference Materials as Obtained in Interlaboratory Studies  
(True Values of Interlab Medians are given in Parentheses)

Parameter	Sample A		Sample B	
1,3-Dichlorobenzene	27.6	(78)	54.7	(99)
1,4-Dichlorobenzene	34.2	(59)	54.5	(107)
1,2-Dichlorobenzene	9.9	(10)	16.9	(16)
1,3,5-Trichlorobenzene	17.7	(34.3)	49.8	(98)
1,2,4-Trichlorobenzene	40.7	(80.7)	71.2	(118)
1,2,3-Trichlorobenzene	3.0	(5)	3.6	(8)
1,2,3,4-Tetrachlorobenzene	31.4	(36.5)	21.0	(41)
Pentachlorobenzene	51.9	(48.6)	45.1	(61)
Hexachlorobenzene	150	(153)	184	(213)
$\alpha$ -BHC	2.5	(1.2)	3.1	(2.5)
Lindane	1.8	(1.8)	2.8	(2.3)
Heptachlor epoxide	0.4	(2.3)	0.4	(1.0)
$\gamma$ -Chlordane	0.4	(2.0)	1.5	(1.9)
$\alpha$ -Chlordane	4.6	(4.0)	2.0	(3.4)
p,p'-DDE	30.1	(19.3)	45.8	(30.2)
Dieldrin	0.4	(4.2)	2.4	(2.4)
p,p'-DDD	12.8	(7.0)	43.8	(46.0)
p,p'-DDT	22.7	(20.0)	16.8	(11.3)
Mirex	21.3	(20.7)	70.7	(70.0)
Hexachlorobutadiene	16.0	(21.3)	48.2	(59.0)
PCB (total)	800	(1100)	160	(84)
Fluoranthene	3210	(3220)	580	(590)
Pyrene	2650	(2440)	510	(520)

# QC Chart for Surrogate Recoveries

1,3,5-Tribromobenzene



From April 86 to November 86