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EVALUATION OF A LARGE-VOLUME EXTRACTOR FOR DETERMINING TRACE ORGANIC CONTAMINANT LEVELS IN THE GREAT LAKES

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ABSTRACT

The design, shipboard operation and performance of a large-volume extractor is described. A total of 224 water samples were extracted at up to 1 $L.min^{-1}$ with dichloromethane during monitoring cruises on lakes Ontario, Erie, Huron and Superior in the spring of 1986. To evaluate the performance of the extractor, a spiking solution containing surrogate standards was added during the course of the extraction. Five surrogate spikes were added in the field: endrin-ketone, 1,3-dibromobenzene, 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene and 2,3,5,6-tetrachlorobiphenyl. Extractor performance was evaluated for both ambient and centrifuged water samples using recovery and reproducibility as criteria. Analytical results could then be excluded on the basis of surrogate recoveries exceeding two standard deviations from the mean. Recoveries ranged from 89-130% and coefficients of variation were generally $\leq$25%.

INTRODUCTION

With increasing concern over the widespread presence of trace organic contaminants throughout the Great Lakes ecosystem, attempts have been made to quantify their levels in the water column. Because of the large scale dilution of these contaminants in the lakes, however, concentrations of these compounds have generally been below the level of detection routinely available using standard analytical and sampling methodologies (Glooschenko et al. 1976; Strachan and Glass 1978).

Various methods have been described in the literature with which aqueous solutions containing trace amounts of organic constituents can be concentrated for analysis (cf. review by Jolley 1981). Few, however, have been applied to the Great Lakes. Eisenreich et al. (1982), and Capel and Eisenreich (1985), have used XAD-2 macroreticular resins to determine concentrations of PCB isomers in Lake Superior at the parts per trillion level. McCrea and Fischer (1985) developed a batch liquid-liquid extractor capable of extracting 200 L water samples into 5 L dichloromethane (DCM). This latter study determined that a broad range of organic contaminants (organochlorine pesticides, chlorobenzenes, polychlorinated biphenyls) could be isolated at concentrations that would permit quantitation using standard analytical techniques. In addition, it was demonstrated that essentially complete extraction from water could be obtained with a single-stage process. Difficulties and time associated with the reduction of 5 L DCM to 1.5 ml for GC analysis however, suggested that a more efficient method of extraction be developed.

A continuous-flow extractor has recently been developed (Goulden and Anthony 1985) which offers a more convenient route to the isolation of organic contaminants from large volume water samples in the field. The developmental criteria considered in the design of the Goulden large sample extractor (GLSE) were to: (1) isolate organic contaminants from Great Lakes water in preparation for analysis at the parts per trillion ($ng.L^{-1}$) level, (2) provide sufficient extract to permit quantitation by gas chromatography with electron capture detection (GC/ECD) and mass spectrometric

determination (GC/MSD) at the parts per trillion level, (3) operate onboard large vessels under adverse weather conditions, and (4) to provide unattended operation.

This study describes the operation and performance of the extractor as evaluated by surrogate standards introduced during the course of the extraction. Results of trace contaminant levels throughout the Great Lakes are presented elsewhere (Stevens and Neilson in press).

METHODS

i) Field Sampling

Two extractors were installed onboard the CSS Limnos and sampling was conducted during the 1986 annual spring surveillance cruises on lakes Ontario (April 14-18), Huron (May 5-12) and Superior (May 12-19) and as part of a research cruise on Lake Erie (April 28 - May 2) at a total of 96 stations. A March submersible pump was employed with teflon-lined, stainless steel braided tubing to collect samples into 22 L glass carboys. All sampling was conducted from the windward side of the ship at a depth of 1 m. Duplicate centrifuged water samples were obtained in a similar manner at nine stations in each lake, with the water being passed through a Westfalia centrifuge at 6 $L.min^{-1}$. Duplicate whole water samples were collected at these same sites (two stations on each lake, as well as at one station on Georgian Bay) to allow for determination of reproducibility.

Prior to use, the carboys were washed with Chromerge (Fischer Scientific), followed by soap and water, 3 rinses with double-distilled water and baked at 100°C for 24 hours. The extractors were washed with soap and water followed by 3 rinses with double distilled water. A "blank" extraction of 44 L of reagent-grade water was run before using the extractors. Reagent-grade water was prepared by passing double distilled water through a Milli Q-2 cartridge system (Millipore Corp.).

ii) Extractor Design and Procedure

A schematic design of the continuous extraction equipment is given in Figure 1. Specific design features of the equipment are given in Goulden and Anthony (1985). The GLSE was designed to achieve, for compounds with octanol-water partition coefficients $\geq 10^4$ single stage extraction efficiencies approaching 100%, using 200 ml DCM and sample volumes of approximately 50 L. Other considerations, such as the prevention of emulsions, the kinetics of the extraction and extraction of colloidal and particulate material required, however, that a higher solvent to water ratio be employed at the extraction stage.

The GLSE is basically a mixer-settler in which the water sample, warmed to 20°C in the heating chamber, is continuously passed through a vessel containing dichloromethane. The water and solvent are circulated around an extraction loop by a three-bladed propellor. Separation is enhanced by passing the sample through a packed column containing "Teflon" Raschig rings which serve to coalesce any small drops of solvent and break any emulsion formed. Clean DCM is added at the top of the packed column at a rate equal to that lost by solution in the effluent water (1.5% by volume). Thus, the water leaving the settler portion of the extractor is scrubbed with a low flow of clean solvent.

When conducting an extraction, the system is initially charged with 200 ml of glass-distilled DCM in the mixing chamber, the stirrer started and the solvent pump rate set to maintain the

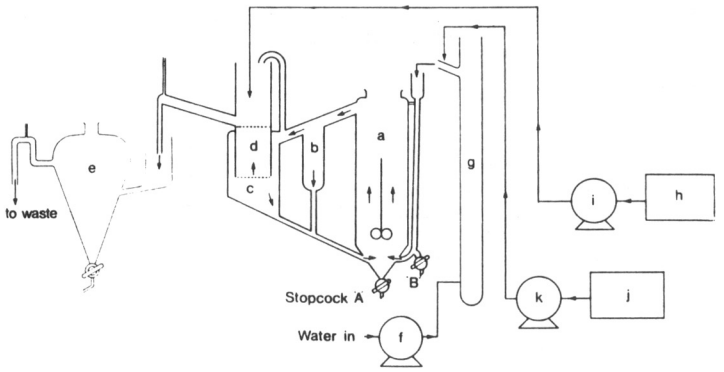

FIGURE 1. Flow diagram of the Goulden Large Sample Extractor. a) mixing chamber; b) primary settling chamber; c) secondary settling chamber; d) packed column; e) separator; f) metering pump; g) heater chamber; h) solvent supply; i) solvent make-up; j) surrogate standards supply and k) spiking pump

solvent level. The heater is turned on and the water feed pump started and operated at a rate of 600 to 1000 ml.min^{-1}, the actual flow rate being that necessary to achieve a sample temperature of 20°C. After the sample has passed through the extractor, the water and solvent feed pumps and the stirrer are stopped. Solvent in the bottom of the mixing chamber is drainedinto a teflon separatory funnel, in order to facilitate breakup of emulsion. Any solvent remaining in the packed column is brought down into the mixing chamber (and thereafter drained) by draining water out of stopcock B (see Figure 1). The solvent extract is emptied into 500 ml pre-cleaned round amber glass bottles and capped. The remaining water in the extractor is drained into the separatory funnel and reused to wash the packed column. Any solvent still in the system is then collected and added to the amber bottle. All extracts were stored in the dark at 4°C.

iii) Extractor Performance: Surrogate Standard Recoveries

To assess extractor performance with respect to recovery of contaminants from water, surrogate standards were added to the sample between the heating tube and the mixing chamber. The surrogate standards, in pesticide-grade methanol, were added at a fixed rate (1.4 ml.min^{-1}) during the course of the extraction and the run time recorded to later determine the quantity of surrogate standard added. With this procedure, the efficiency of the extraction and analytical procedure could be determined for each sample.

The surrogate standards employed, listed in Table 1 along with their respective log octanol-water partition coefficients (log Kow), were selected such that the entire chlorobenzene-organochlorine spectrum was covered. In fraction A, di- and tribromobenzene eluted within the range of di- to pentachloro-benzenes (Figure 2); the tetrabromobenzene peak was close to that of hexachlorobenzene, and tetrachlorobiphenyl had a retention time similar to that of aldrin. In fraction B, the endrin ketone peak appeared between the DDT metabolites and methoxychlor. In future studies, an additional standard, δ-BHC, that elutes in fraction B with the lighter organochlorines α- and γ-BHC (lindane), will be included.

TABLE 1. Makeup of the surrogate standard solution, in methanol

	Concentration ug.L^{-1}	log Kow[1]
1,3 - dibromobenzene (DBB)	1.028	3.75
1,3,5 - tribromobenzene (TBB)	0.408	4.5
1,2,4,5 - tetrabromobenzene (TeBB)	0.442	5.1
2,3,5,6 - tetrachlorobiphenyl (TCBP)	0.446	5.6-6.7
Endrin ketone (End-Keto)	0.100	>4

1. from Anthony and Goulden (1986)

iv) Analytical Procedures

Validation of the extraction and analytical procedures, including instrument repeatability; organochlorine and chlorobenzene spike recoveries from solvent, millipore-cleaned water and river water; and surrogate spike recoveries, can be found in Afghan et al. (1987).

The field extracts, upon submission to the National Water Quality Laboratory (Burlington, Ontario), were dried with anhydrous Na_2SO_4, then concentrated to 1.5 ml in isooctane. One ml of the concentrated extract was cleaned on a 3% deactivated silica gel column by elution with 25 ml hexane (fraction A) and then 30 ml benzene (fraction B). Concentrated fractions A and B (1.0 ml each, in isooctane) were then analyzed on GLC-ECD. Calculated values were multiplied by a factor of 1.5 to obtain total ng in the sample. GLC-MSD was used for further confirmation when necessary.

RESULTS and DISCUSSION

i) Extractor performance

Operation of the extractor was essentially problem free and required minimal attention. Run times ranged from 100 minutes on the upper Great Lakes, where 66 L of water were collected, to 40 minutes at nearshore stations in Lake Erie, where water temperatures as high as 12°C necessitated little sample prewarming. Table 2 summarizes, by lake, the recovery data for the five surrogate standards as introduced into non-centrifuged samples.

Extractor performance, based on average % recovery of spiked surrogates, was excellent. In general, minimum recoveries were noted for DBB (82.2% in Lake Erie - 98.3% in Lake Huron) and maximum recoveries were reported for TeBB (108.1% in Lake Erie - 141.2% in Lake Huron). Sampler performance was not always satisfactory on an individual sample basis, particularly in Lake Erie where recoveries of less than 40% were observed and in Lake Huron/Georgian Bay where maximum recoveries were in excess of 250%. For this reason, coefficients of variation within these lakes were higher than desired (>30%). Attempts were made to determine whether these poor recoveries were related to ambient conditions or operating environment on the ship. No relationship was observed, for example, between surrogate recoveries and *in situ* temperature, turbidity or dissolved organic carbon concentration. Neither could poor recoveries be attributed to which of the two extractors were used or to differences in flow rate. Nevertheless, recoveries were generally low in Lake Erie and high in Georgian Bay.

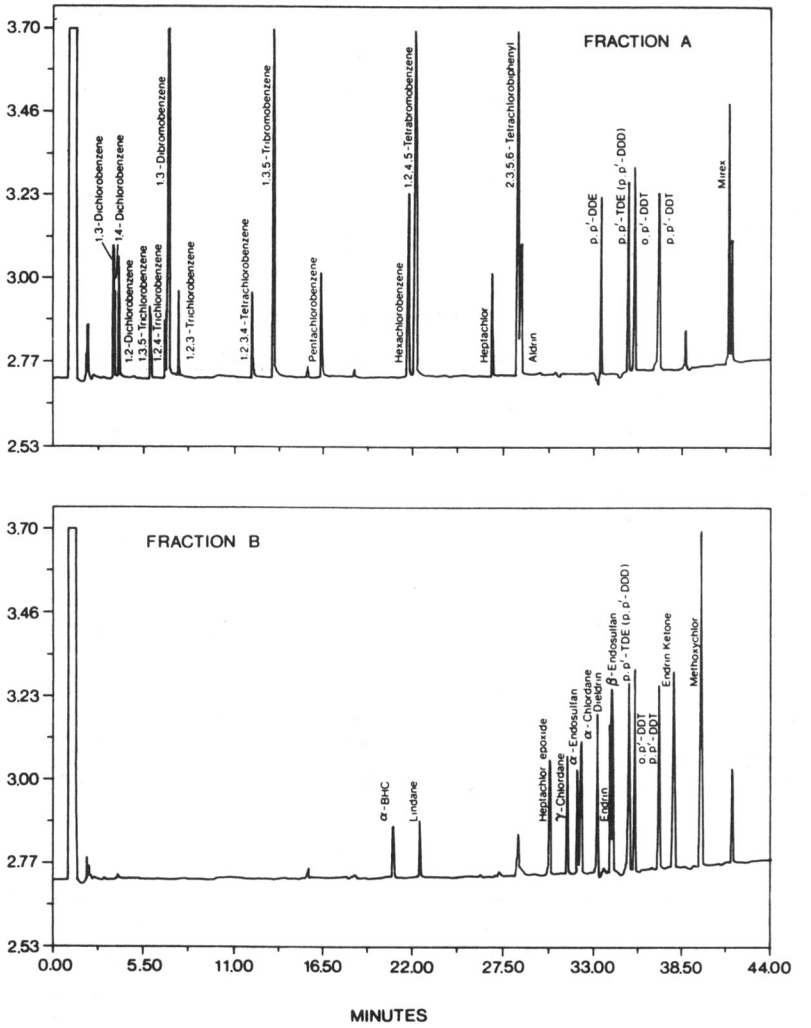

FIGURE 2. Capillary column GC/ECD trace of fraction A and B standards

One of the principal advantages of obtaining recovery data on individual samples is that, if desired, it can be used as a basis for determining outliers. For the purposes of data interpretation, analytical results were excluded if surrogate recoveries were in excess of ± 2 standard deviations of the mean recovery of all samples. For those surrogates eluting in fraction A (DBB, TBB, TeBB, TCBP), all results for that fraction were excluded if any surrogate exceeded the rejection criteria. On this basis, 14 of 104 results from fraction A, and 13 from fraction B, were rejected.

Summary statistics for the revised data are provided in Table 3. As expected, results of surrogate recoveries for Lake Erie exhibited the greatest difference, with coefficients of variation

TABLE 2. Recovery of surrogate standards

Lake Superior

	End-Keto	DBB	TBB	TeBB	TCBP
n	21	21	21	21	21
$\bar{x}$	99.7	90.9	112.4	114.2	97.7
s.d.	15.4	14.9	28.8	21.5	14.1
minimum	75.3	67.9	81.3	85.7	74.1
maximum	122.1	126.7	203.3	170.9	129.8
C.V.(%)	15.5	16.4	25.6	18.8	14.4

Lake Huron/Georgian Bay

	End-Keto	DBB	TBB	TeBB	TCBP
n	28	28	28	28	28
$\bar{x}$	119.4	98.3	134.0	141.2	104.6
s.d.	25.2	19.5	45.3	42.2	26.5
minimum	86.0	69.8	81.5	83.5	64.4
maximum	173.5	148.3	253.8	243.8	151.9
C.V.(%)	21.1	19.8	33.8	29.9	25.4

Lake Erie

	End-Keto	DBB	TBB	TeBB	TCBP
n	23	23	23	23	23
$\bar{x}$	95.5	82.2	91.9	108.1	103.6
s.d.	30.4	27.9	31.0	38.7	32.0
minimum	46.8	34.8	37.6	39.4	44.3
maximum	170.6	118.7	135.7	167.3	147.7
C.V.(%)	31.8	33.9	33.7	35.8	30.9

Lake Ontario

	End-Keto	DBB	TBB	TeBB	TCBP
n	32	32	32	32	32
$\bar{x}$	90.9	89.4	98.9	109.2	111.1
s.d.	17.9	18.6	22.2	23.9	24.1
minimum	50.5	28.1	28.9	31.9	35.8
maximum	143.0	123.8	138.1	142.9	156.0
C.V.(%)	19.7	20.8	22.4	21.9	21.7

being approximately half that before removal of outliers. These values lie well within those given for recovery of analytes from spiked solvent, as reported by the National Water Quality Laboratory (Afghan et al. 1987), indicating that the extraction procedure contributes little additional variability to the final results.

Because the surrogates were added at the beginning of the extraction process, it was not possible to differentiate between variability attributable to the extraction process and that due to the laboratory procedure. Since a number of surrogates were used, however, it was possible to obtain some information on the source of the variability by comparing their ratios before and after extraction and analysis. Normalizing to DBB, the inital ratio of surrogates in the standard solution was 1: 0.40: 0.44: 0.43: 0.10

TABLE 3. Recovery of surrogate standards after exclusion of outliers

Lake Superior

	End-Keto	DBB	TBB	TeBB	TCBP
n	21	20	20	20	20
$\bar{x}$	99.7	89.3	107.8	111.4	96.7
s.d.	15.4	13.3	20.4	17.6	13.7
minimum	75.3	67.9	81.3	85.7	74.1
maximum	122.1	126.7	168.6	153.1	129.8
C.V.(%)	15.5	14.9	18.9	16.8	14.2

Lake Huron/Georgian Bay

	End-Keto	DBB	TBB	TeBB	TCBP
n	23	24	24	24	24
$\bar{x}$	113.3	93.0	120.4	130.6	100.8
s.d.	18.9	14.9	31.2	34.2	25.1
minimum	86.0	69.8	81.5	83.5	64.4
maximum	151.4	124.7	195.5	185.1	149.4
C.V.(%)	16.7	16.0	25.9	26.2	24.9

Lake Erie

	End-Keto	DBB	TBB	TeBB	TCBP
n	20	17	17	17	17
$\bar{x}$	91.3	96.6	107.9	127.5	119.8
s.d.	21.3	14.6	16.3	22.6	17.8
minimum	55.6	66.7	74.7	77.4	76.4
maximum	133.0	118.7	135.7	167.3	147.7
C.V.(%)	23.3	15.1	15.1	17.8	14.9

Lake Ontario

	End-Keto	DBB	TBB	TeBB	TCBP
n	27	29	29	29	29
$\bar{x}$	92.2	93.3	102.9	113.0	114.6
s.d.	16.6	11.5	14.7	14.5	14.5
minimum	64.8	68.3	80.1	87.4	83.7
maximum	143.0	123.8	138.1	142.9	142.8
C.V.(%)	18.0	12.3	14.3	12.9	12.7

(DBB:TBB:TeBB:TCBP:End-Keto). If recoveries were high or low but the proportions of surrogates recovered were similar to those added, then it is suggested that the variability is attributable to the extraction procedure. Where the ratios varied markedly from the standard solution, it is suggested that losses are due to the analytical procedure.

Maintenance of surrogate ratios can be evaluated by computing the correlation coefficients between the various pairs of surrogates as well as examining X-Y scattergrams of these pairs. Pearson product moment correlation coefficients (r) are given in Table 4. It is apparent that there is little relationship between recoveries in fraction B (End-Keto) and those in fraction A (DBB, TBB, TEBB, TCBP) as r values were all less than 0.3. The octanol-water partition coefficient for End-Ket is similar to that of DBB and TBB (approx. 4, Anthony and Goulden 1986) and, consequently,

TABLE 4. Pearson product moment correlation coefficients (r) of surrogate standards in Great Lakes ambient samples

	DBB	TBB	TeBB	TCBP	End-Keto
DBB	---	0.85	0.81	0.65	0.18
TBB	---	---	0.92	0.60	0.27
TeBB	---	---	---	0.72	0.20
TCBP	---	---	---	---	0.07

they should exhibit similar recoveries during the extraction procedure. Hence, differences in their respective recoveries are thought to be due to the analytical procedure.

Maintenance of surrogate ratios was considerably improved within fraction A with all r values significant at the 1% level. In general, the more comparable the octanol-water partition coefficients of the surrogates, the more similar were their extraction recoveries. Examination of the scattergrams for surrogates in fraction A revealed that, of the 14 samples that were rejected as described above, 5 were a result of disproportionate recoveries that likely were attributable to laboratory procedure. An additional 7 samples exhibited disproportionate recoveries but were not severe enough to have been excluded as outliers. Disproportionate recoveries were arbitrarily defined as those samples that fell outside the 80% confidence interval of the regression line between each of the surrogate pairs.

ii) Centrifuged vs. ambient samples

Differing requirements of monitoring programs within the Great Lakes necessitate determination of trace organic contaminants in both whole (i.e., ambient) and "dissolved" water samples. Consequently, we wanted to ensure that recoveries of surrogates from the GLSE would not be influenced by particulate matter in the water column. The effects of centrifugation on surrogate recoveries was assessed with analysis of variance (ANOVA) on a 2 X 9 factorial design, the two factors being centrifugation (or not) and station (ANOVA in SPSS, Nie et al. 1975). Station was included as an additional factor as differences related to centrifugation may have appeared only at those stations where particulate load was higher. For example, % transmission, which provides an indication of particulate matter concentration, ranged from 100% at stations in Lake Superior to <10% in the western basin of Lake Erie.

Based on the ANOVA, no significant effects ($p<0.05$) from either centrifugation or station were noted for End-Ket, DBB or TCBP. For TBB and TeBB, no significant effects due to centrifugation were noted, indicating that the GLSE performs equally well on both ambient and centrifuged samples. Significant effects due to station were found for these two compounds, as shown in Table 5. It should be noted that this aspect of the study did not address the effectiveness of the GLSE for removal of contaminants from particulate matter.

The significant effect of station on extraction was not surprising in light of the previous discussion on increased variation in extractor performance due to outliers. This was evident for TBB at the 9 select stations, as illustrated in Figure 3. Stations S031 (Superior) and GB033 (Georgian Bay), exhibited extremely high recoveries of TBB in both the centrifuged

TABLE 5. Results of analysis of variance for extractions of centrifuged and ambient water samples

Surrogate: 1,3,5-tribromobenzene

Source of Variation	Degrees of Freedom	Mean Square	F	Signif of F
Main Effects	9	4137.92	8.83	0.001
Centrifugation	1	1349.34	2.88	0.107
Station	8	4486.49	9.58	0.001
Interactions	8	234.50	0.50	0.840
Explained	17	2301.01	4.91	0.001
Residual	18	468.41		
Total	35	1358.53		

Surrogate: 1,2,4,5-tetrabromobenzene

Source of Variation	Degrees of Freedom	Mean Square	F	Signif of F
Main Effects	9	2425.57	3.34	0.014
Centrifugation	1	2835.56	3.90	0.064
Station	8	2374.32	3.26	0.018
Interactions	8	458.02	0.63	0.743
Explained	17	1499.66	2.06	0.069
Residual	18	727.36		
Total	35	1102.48		

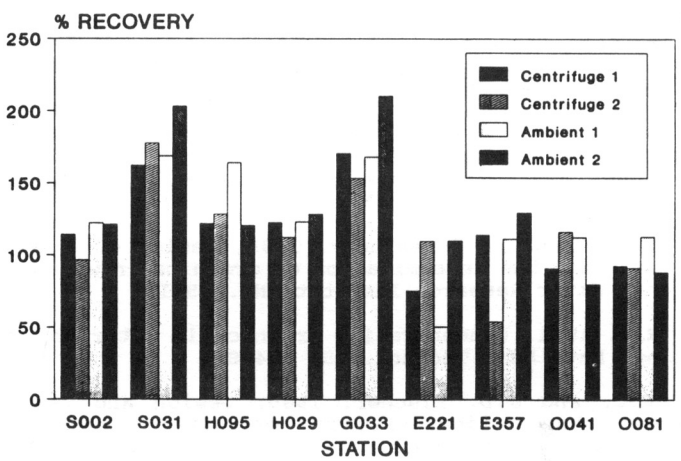

FIGURE 3. Recovery of 1,3,5-tribromobenzene at nine Great Lakes stations. S=Superior, H=Huron, G=Georgian Bay, E=Erie, O=Ontario

and ambient extractions whereas station E221 (Lake Erie) exhibited low recoveries of TBB in one of the duplicates in each of the centrifuged and ambient extractions. Similar patterns were noted for TeBB.

This study has demonstrated that the GLSE is a reliable apparatus for the quantitative recovery of trace organic compounds with log K_{ow}'s > 3.5 from both ambient and centrifuged water. Variability of recovery of surrogates from the GLSE in a field application is not markedly different from that achieved in the laboratory by spiking directly into DCM. To aid in isolating the source(s) of variability in future studies, an additional surrogate standard, δ-BHC, will be added that will elute in fraction B to coincide with the lighter organochlorines (e.g. α- and γ-BHC). Further, a two-stage spiking procedure will be used,with one set of surrogates being introduced in the field, the other added to the DCM extracts immediately before being submitted for analysis. This procedure will allow us to clearly differentiate between losses due to the extraction procedure and those due to laboratory analysis.

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