

Evaluation of Automated Extraction of Organochlorine Contaminants from Freshwater

Jeffrey J. Ridal,^{*,†,‡} Michael E. Fox,[§] Cheryl A. Sullivan,[§] R. James Maguire,[§] Asit Mazumder,[†] and David R. S. Lean^{†,§}

Station de Biologie des Laurentides, Université de Montreal, 440, Ch. du Lac Croche, St-Hippolyte, QC J0R 1B0, Canada, and National Water Research Institute, 867 Lakeshore Road, Burlington, ON L7R 4A6, Canada

A semiautomated solid phase extraction (SPE) system fitted with reverse phase disks was evaluated for the extraction and concentration of trace contaminants in water. Organochlorine compounds of environmental interest and covering a wide range of log K_{ow} values were dissolved in laboratory water of low dissolved organic carbon (DOC) concentration and extracted using a variety of solvents and conditions based on a survey of the literature. The most successful eluent was 15% diethyl ether in *n*-pentane which recovered 64–91% of the analytes. We tested the influence of DOC from a Canadian Shield humic lake on the recovery of organochlorine compounds by this SPE technique. Recoveries of analytes from high DOC lake water were lower by SPE (42–69%) than by a shake-flask liquid–liquid extraction method (59–98%). An additional 2–11% of analytes were recovered by solvent rinses of containers. Breakthrough, assessed by liquid–liquid extraction of water of SPE sample effluent, ranged from 6 to 38% for lake water samples. These results indicate that the DOC is a principle factor affecting SPE recoveries of organic contaminants in freshwater. Application of the optimized SPE method for analysis of organochlorine contaminants in lake enclosure experiments, however, yielded higher concentrations and better recoveries of surrogates than a large volume liquid–liquid extraction system.

The extraction of trace organic contaminants from environmental water samples has long been accomplished by partitioning into smaller volumes of immiscible solvent(s) with a high affinity for the analyte (liquid–liquid extraction, LLE). Early techniques, still in use today, involved shaking or mixing small samples of up to 2 L with appropriate solvents in separatory funnels or capped bottles. The need to extract much larger volumes of water to analyze low levels of analytes in relatively unpolluted water bodies led to the design of rugged mechanical large-volume batch extractors^{1,2} and a large-volume continuous-flow extractor.³ All

of these related techniques suffer from the drawbacks of excessive use of solvents, much of which is not easily recovered.

A parallel development in which the analytes are partitioned onto a particulate adsorbent (solid phase extraction, SPE) has been pursued since at least the mid 1970s but has only recently received any significant degree of acceptance.^{4–6} The renewed interest in SPE has been largely driven by more stringent regulations governing the use and disposal of solvents, as well as improvements in SPE technologies. For example, a thin film of relatively high capacity sorbent such as C₁₈ which, in recent developments,⁷ can be exposed to the sample in the form of a filterlike disk, has allowed the elution of many adsorbed analytes with less than 10 mL of solvent. This volume represents a 100–1000 reduction compared to that used in a typical LLE extraction.

A considerable body of information is available which evaluates disk and cartridge SPE methods for the extraction of organic contaminants from water using various eluting solvents and extraction conditions (e.g., refs 4–15). Elution solvents such as ethyl acetate, diethyl ether, and acetonitrile, sometimes used in combination with solvents such as methylene chloride and pentane, have been found to give optimum extraction efficiencies in the cited work. There is consensus that recoveries of organic contaminants dissolved in distilled water are comparable with either SPE disk or cartridge extraction compared with LLE^{5,9} or XAD resin.^{5,10} However, there is less agreement on the recoveries of contaminants with SPE methods from environmental samples containing dissolved organic carbon (DOC), with some studies showing little change^{7,10} while others report decreased recoveries of analytes.^{9,12,13}

A very recent development in SPE extraction methods has been the advent of semiautomated instruments capable of simultaneous extraction of several samples. Automation of each step in the extraction of samples, combined with precise microproces-

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[†] Université de Montreal.

[‡] Current address: St. Lawrence River Institute of Environmental Sciences, 1111 Montreal Rd., Cornwall, ON K6H 1E1, Canada.

[§] National Water Research Institute.

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sor controlled flow rates, holds the promise of substantial time savings and better reproducibility than manual methods. Such a system has been studied for automated SPE cartridge extraction of polycyclic aromatic hydrocarbons.¹⁶ To address specifically the performance of automated extraction of organochlorine contaminants using SPE disks, including the possible effects of DOC, and preliminary to using the automated SPE method in humic lake enclosure experiments, we performed recovery studies for these analytes in both distilled and well-characterized lake water.

EXPERIMENTAL SECTION

Reagents and Materials. Pesticide grade solvents were purchased from a number of suppliers and tested for purity at the approximate concentration factors that would be used in the experiments. Organochlorine compounds were obtained from Aldrich Chemical Co. Inc., Milwaukee, WI; Chem Service, West Chester, PA.; Pestanal-Caledon Laboratories Ltd., Georgetown, ON; Supelco Canada, Oakville, ON; and U.S. EPA, Research Triangle Park, NC, with a minimum purity of 98%. The organochlorine analytes were representative of a range of log K_{ow} values, were of environmental analytical interest, and were amenable to separation and sensitive analysis by electron capture gas chromatography.

Empore C₈ and C₁₈ extraction disks were purchased from Chromatographic Specialties, Inc., Brockville, ON, and SPEC-47-C₁₈ AR disks were purchased from the SPEC Division of ANSYS, Inc. (Los Angeles, CA). Anhydrous sodium sulfate powder (analytical grade) was purchased from BDH Inc., Toronto, ON. Sodium sulfate and glassware used to contain samples for DOC were heated at 500 °C for 24 h. All other glassware was cleaned rigorously and solvent-rinsed prior to use.

Instrumentation and Methods. The Zymark AutoTrace (Hopkinton, MA) used in these experiments is a semiautomated device which pumps up to six aqueous samples simultaneously through SPE disks or cartridges at preselected constant flow rates of up to 60 mL/min. The disk pretreatment, sample loading, and various rinse, pause, dry, and elute conditions are chosen by the analyst and loaded into the instrument microprocessor from a method diskette created on a nondedicated PC. Another advantage of this system is the use of positive pressure for disk loading and elution processes. Many other disk or cartridge SPE systems use suction to draw fluids through the adsorbent. Suction systems are prone to air voids, dry surfaces, and variable flow rates, all of which can lead to variable recoveries of analytes.

We chose not to investigate sample loading rates, disk elution rates, or the effects of pH, all of which had relatively minor impacts on analyte recoveries.^{6,15} Although some differences in analyte recoveries using different wetting agents and different concentrations were reported,¹⁵ we selected methanol at 0.5% (v/v), based on that study and our selection of analytes. Test solutions were prepared by adding 2.5 mL of an organochlorine (OC) mixture dissolved in methanol to 500 mL of Milli-Q (Millepore-Waters, Mississauga, ON) or lake water. Table 1 lists the concentrations of contaminants used for both Milli-Q and lake water experiments.

Drying Experiment. An experiment was conducted to ensure disks were dry prior to elution with solvent. Two of each type of extraction disk (Empore C₁₈, Empore C₈, and SPEC C₁₈) were weighed, placed in the disk holders of the AutoTrace instrument, conditioned with 10 mL of methanol, rinsed with 10 mL of Milli-Q

Table 1. List of Analytes, log Octanol-Water Partition Coefficients, and the Concentrations in Water Samples after Spikes Were Added

analyte ^a	log K_{ow}	target concn ^b (ng/L)
α -hexachlorocyclohexane (HCH)	3.8	87.6
1,2,4-trichlorobenzene (TriCB)	4.0	212
methoxychlor (Methoxy)	4.3	100
tetrachlorobenzene (TeCB)	4.5	85.2
pentachlorobenzene (PeCB)	4.9	81.6
hexachlorobenzene (HCB)	5.4	80.7
heptachlor	5.4	96.2
<i>trans</i> -chlordane (<i>t</i> -Chl)	6.0	103 (221)
<i>cis</i> -chlordane (<i>c</i> -Chl)	6.0	78.4
<i>trans</i> -nonachlor (<i>t</i> -Nona)	6.1	41.8
<i>cis</i> -nonachlor (<i>c</i> -Nona)	6.4	44.0
DDT	6.4	80.4
mirex	6.9	80.7 (117)

^aItalic type, analytes used in the study with Milli-Q water. ^bValues in parentheses are concentrations in the lake water solution.

water, and then loaded with 1000 mL of Milli-Q water. After excess water was removed with nitrogen gas, the instrument was paused, and the disks were removed, weighed, and placed into a desiccator. The disks were reweighed every 15 min for 2 h to remove all residual water. A constant weight was found for all disks after ~50 min, but a conservative time of 2 h was chosen for routine use.¹⁷

It was also found that some water drops were retained on the sides of the Teflon disk holders. Once disks had been removed to dry in the desiccator, water from the disk holders and lines was removed by incorporating a methanol rinse step into the AutoTrace command sequence to remove the water, followed by a rinse with the first extraction solvent. If the extraction solvent was not miscible with methanol, an intermediate rinse step with a comiscible solvent was added. Dried disks were then replaced to the disk holders and extracted. The general AutoTrace disk preparation and extraction procedure is shown in Table 2.

Evaluation of Available Proprietary SPE Disks. In preliminary work, three types of SPE disks (Empore C₁₈, Empore C₈, SPEC C₁₈) were tested for ease of use and extraction efficiencies. A blank and three spiked Milli-Q solutions were loaded onto each of SPE disks and eluted with a sequence of three solvents: 5 mL of ethyl acetate, 3 mL of dichloromethane (DCM), and finally 5 mL of 1:1 ethyl acetate-DCM. The combined extracts were dried by passing through microcolumns containing sodium sulfate. Isooctane (2 mL) was added, and the extract was concentrated to a final volume of 1 mL under a stream of dry nitrogen.

Comparison of Elution Solvent Mixtures. Experiments were also conducted using mixtures of diethyl ether in pentane. Mixtures of 0, 10, 15, 20, and 25% of diethyl ether in *n*-pentane were tested for efficiency of extraction of OCs from SPEC C₁₈ disks. The AutoTrace procedure was the same as the ethyl acetate-DCM elution studies except that two successive 5-mL extractions were used instead of the three-step extraction procedure. Additionally, in two experiments (100% *n*-pentane and 10% diethyl ether in pentane), the water from the blank and

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Table 2. Generalized AutoTrace Disk Preparation, Sample Loading, and Extraction Scheme Used To Test Extraction Efficiencies of Disks for Milli-Q and Lake Water Experiments

step	method procedure
1	process 6 samples using the following procedure
2	wash syringe with 10 ml of methanol
3	wash syringe with 10 ml of elution solvent 1
4	rinse disks with 10 ml of elution solvent into solvent waste
5	dry disk with gas for 0.5 min
6	wash syringe with 10 ml of methanol
7	condition disks with 10 ml of methanol into solvent waste
8	wash syringe with 10 mL of Milli-Q water
9	condition disks with 10 mL of Milli-Q water into aqueous waste
10	load 500 mL of sample onto disks (40 mL/min)
11	rinse disks with 10 mL of Milli-Q water
12	dry disk with gas for 0.5 min
13	pause and alert operator (remove disks and place in desiccator for 2 h)
14	wash syringe with 10 mL of methanol
15	rinse disks with 10 mL of methanol ^a
16	wash syringe with 10 mL of elution solvent 1
17	rinse disks with 10 mL of elution solvent 1 ^a
18	dry disks with gas for 1 min
19	pause and alert operator (replace dried disks into holders)
20	collect 5-mL fraction into sample tube using elution solvent 1 ^b
21	wash syringe with 5 mL of elution solvent 2 (if necessary)
22	collect 3-mL fraction into sample tube using elution solvent 2 ^b
23	wash syringe with 5 mL of elution solvent 3 (if necessary)
24	collect 5-mL fraction into sample tube with elution solvent 3 ^b
25	concentrate sample with gas for 0.5 min
26	end

^a These steps added to remove water adhering to disk holders, with disks removed. ^b Soak and elute command used with Empore disks.

spiked solutions was collected directly from the discharge pipe into 1-L separatory funnels after passing through the SPE disks in order to test for analyte breakthrough. The discharge samples were extracted with 3 × 30 mL of DCM (the first two 30-mL fractions were used to rinse the sample container and then added to separatory funnel for extraction). The extracts were dried and concentrated to 1 mL in isoctane as described earlier. Also, the eluted extraction disks from the 100% pentane and 10% diethyl ether in pentane studies were placed in a 100-mL beaker containing 50 mL of DCM and allowed to soak for 18 h. The DCM was then transferred to 250-mL round-bottomed flasks and 3 × 10 mL of DCM was rinsed through the disks and added to the flasks. Extracts were then concentrated to 1 mL in isoctane as described earlier. The SPE disk extracts were treated as described earlier.

Recovery Experiments with Lake Water. Lake water from Lac Cromwell (a 10-ha humic lake located 100 km north of Montreal; DOC 12.1 mg of C/L, pH 6.7, calcium 3.7 mg/L, total P 9 μg/L) was sampled by submersible pump into solvent-rinsed 20-L stainless steel cans and pressure-filtered using 1-μm pore-sized glass fiber filters (147 mm, combusted; Gelman). Samples of filtered Lac Cromwell water were taken from the cans into 100-mL glass vials, acidified to pH 3 with reagent grade phosphoric acid, and stored together with distilled water blanks at 4 °C. Analyzes of samples for dissolved organic carbon content were performed with a high-temperature combustion instrument (Shimadzu) using glucose standard solutions and standard protocols.¹⁸

OC-fortified environmental samples were prepared by mixing the spiking solution into the 18 L of filtered lake water to give a

0.5% methanol final concentration. A slightly different composition of OC pesticides was used in these experiments with lake water than those with Milli-Q water (Table 1). The lake water solution was mixed slowly with an electric mixer for 1 h prior to subsampling for extraction experiments.

Duplicate 500-mL subsamples of the lake water solution were liquid-liquid extracted with DCM and the extracts prepared for analysis using the methods described earlier. Solid phase extraction analysis was performed on four additional subsamples using optimized protocols resulting from the recovery study with Milli-Q water. Disks were twice extracted with 5 mL of 15% diethyl ether in pentane. To check for completeness of these extractions, the disks were additionally extracted with two 5-mL aliquots of 100% dichloromethane. SPE extracts were passed through a minicolumn of anhydrous sodium sulfate, evaporated under nitrogen, solvent switched to 1 mL final volume of isoctane, and analyzed without further cleanup. In this experiment, aldrin was added as an internal standard to the final 1 mL for both LLE and SPE samples. Upon completion of the experiments, the container holding OC-spiked lake water was emptied, allowed to air-dry, and then twice rinsed with 100 mL of DCM to assess loss to container walls.

Comparison of SPE and a Large-Volume Extraction Method for Analysis of Lake Enclosure Samples. Environmental analyzes of surface water typically requires extraction of volumes of water larger than the 500-mL samples used in the previously described side-by-side recovery experiments. Accordingly, the SPE method was tested against a commonly used large-volume LLE method² for the analysis of OC-enriched water taken from large (500 m³) lake enclosures. The general experimental details of these lake enclosures, situated in lac Croche (a small humic lake; DOC typically 5–8 mg/L), are described in detail elsewhere.^{19,20}

Briefly, organochlorine contaminants were added to lake enclosures by subsurface injection at nominal concentrations ranging from 10 to 20 ng/L. Approximately two days after OC additions, replicate samples of 18 L from one of these enclosures was sampled by submersible pump into four 20-L stainless steel cans and pressure-filtered as described previously. For each of the four 18-L samples, a 2-L subsample for SPE analysis was drawn into a brown solvent bottle. Surrogate standards (4–7 ng/L δ-HCH, dieldrin, and octachloronaphthalene) dissolved in acetone were added by micropipet to both the 2-L SPE and 16-L LLE samples. Methanol (10 mL) was immediately added to the SPE samples. All samples were mixed for 5 min by gentle shaking or stirring and immediately processed.

The large-volume LLE method employs triplicate solvent extraction using 400-, 200-, and 200-mL aliquots of DCM and moderate stirring (10 min each extraction) with a long-shafted electric mixer. LLE sample cleanup followed the methods described previously. In the SPE method, SPEC disks were extracted using successive 5-mL aliquots of 15% diethyl ether in pentane extractions followed by 3 mL of DCM. SPE extracts were reduced to 1 mL, treated to Florisil cleanup, and reduced to a final volume of 1 mL in isoctane.

Gas Chromatographic Analysis. All samples were analyzed on a Hewlett Packard 5890 Series II gas chromatograph with dual

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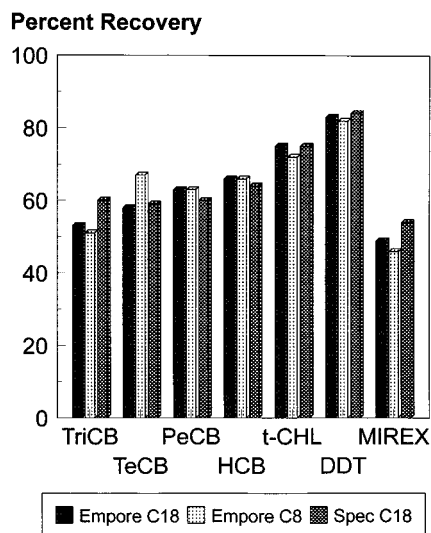


Figure 1. Comparison of recoveries of organic contaminants from Milli-Q water by solid phase extraction for three types of bonded phase disks. Results are means of triplicate extractions. Refer to Table 1 for list of abbreviations.

electron capture detectors (300 °C), single splitless injector (250 °C), and dual columns. The front column was a Hewlett-Packard HP-50, and the rear column a J&W Scientific DB 5-MS. Both columns were 30 m × 0.25 mm i.d. with a film thickness of 0.25 μm. The initial column temperature was 90 °C for 1 min, followed by heating to 280 °C at a rate of 20 °C/min with a final hold at 280 °C for 5 min. Hydrogen carrier gas flowed at rates of 1.10 and 1.15 mL/min for front and rear columns, respectively, and nitrogen auxiliary gas flowed at 38.5 and 36.2 mL/min for front and rear columns, respectively. Flows were held constant at all temperatures by electronic flow control.

Quality Control. Gas chromatographic results were determined by the method of external standards, and corrections for recoveries of the internal standard (aldrin) were made where appropriate. Reference standards were run initially and then every 10 samples thereafter. Analytical blanks were assessed by analyzing disks extracted after solvent prerinses, and also after treating the disks with 500-mL aliquots of unfortified Milli-Q or lake water. In all cases, blanks values were <1% spiked water concentrations.

RESULTS AND DISCUSSION

Comparison of SPE Disks. Three types of SPE disks, Empore C₁₈, Empore C₈, and SPEC C₁₈, were tested in separate experiments using loading and elution procedures suited to the differing physical properties of the disk substrates. The results of analyzes with each disk type are given in Figure 1. Recoveries were very similar for each disk type (differences generally less than 5%) and ranged from 48 to 82% with relative standard deviations (RSDs) between 2 and 12% (*n* = 3). Therefore, we selected the SPEC C₁₈ disks for further use since the cost was significantly lower than the PTFE-based disks. In addition, the glass fiber composition of the SPEC disks allowed for greater flow rates than the PTFE-based disks and were found easier to handle. A further significant consideration was that we found SPEC disks gave cleaner blank chromatograms in our experiments.

***n*-Pentane–Diethyl Ether Recovery Study.** Figure 2 summarizes the efficiency of extraction using different pentane–ether mixtures. Increasing recoveries were observed as the amount of

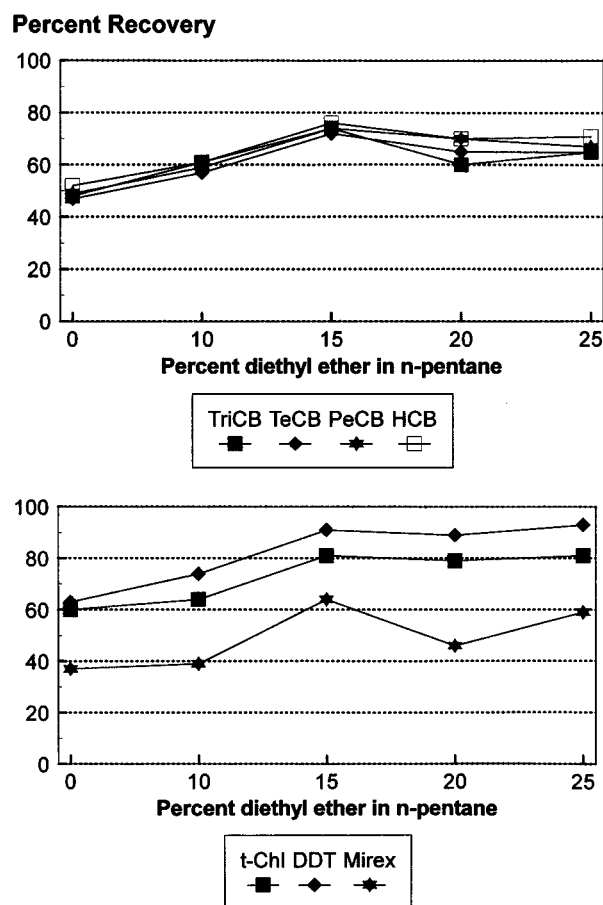


Figure 2. Summary of recoveries of organic contaminants from Milli-Q water by SPE (SPEC disk) for different mixtures of diethyl ether and pentane as the extraction solvent. Results are means of triplicate extractions and organochlorine abbreviations are listed in Table 1.

diethyl ether in pentane was enriched from 0 to 15%, after which recoveries stabilized. Average recoveries increased from 51 ± 6% when 100% pentane was used as the eluting solvent to 77 ± 8% for the mixture of 15% diethyl ether in pentane. Recoveries with the diethyl ether in pentane mixture ranged from 74% recovery for 1,2,3, 4-tetrachlorobenzene to 91% recovery for DDT with relative standard deviations for each analyte ranging from 1 to 13% (*n* = 3).

Figure 3 compares the recoveries using 15% diethyl ether in pentane extraction with the recoveries obtained earlier using ethyl acetate–dichloromethane. A Student's *t*-test analysis indicated a significant difference between the two methods at the 95% probability level. Consequently, the extraction method using 15% diethyl ether in pentane was selected for further experiments. McDonnell et al.¹⁴ demonstrated, using water from Hamilton Harbour, ON, that although a 25% ether in pentane solution would give a better overall recovery than a 10% solution, it would also elute a large quantity of pigment and/or nonspecific interference which may compromise chromatographic analysis and give rise to large relative standard deviations. Since we have shown that a 15% ether in pentane solution gives recoveries similar to a 25% ether in pentane solution, this mixture was chosen as the best compromise between extraction efficiency and the elution of interfering compounds.

In their study using Empore C₈ and C₁₈ disks, McDonnell et al.¹⁴ defined three levels of recoveries: high yield (70% or better), low yield due to breakthrough, and those in low yield for unknown

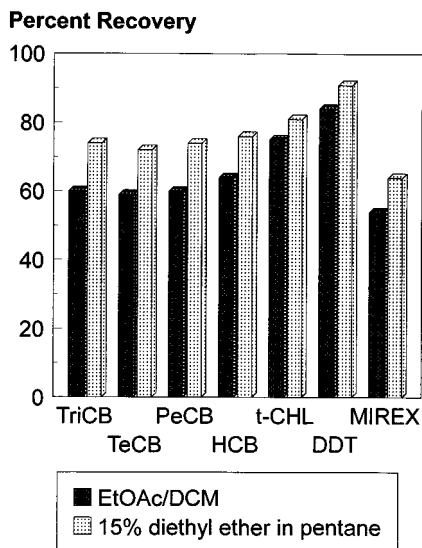


Figure 3. Comparison of recoveries of organic contaminants from Milli-Q water using 15% diethyl ether in pentane and ethyl acetate–dichloromethane (EtOAc/DCM) extraction solutions. Results are means of triplicate extractions and organochlorine abbreviations are listed in Table 1.

causes. To examine the reasons for analyte loss in more detail, we collected and re-extracted the SPE-extracted water and saved the eluted disks for examination for retained analytes from the first two experiments of this study as described in the Experimental Section. Recoveries of analytes by LLE from the SPE-extracted water were generally low (<2%), but up to ~12% of the mirex appeared to have broken through the disks or remained adsorbed to the walls of the vessel containing the test solution. Since we combined the solvent rinses of this vessel with the discharge water extraction, we were unable to distinguish between the two loss routes. Amounts of analytes recovered by leaching eluted disks were insignificant ($\leq 1\%$); therefore, combined losses of mirex due to breakthrough and retention on the disks represent a maximum of 13% of added analyte. Since the recovery of mirex from the eluent did not exceed 64%, we could not account for at least 20% of this analyte.

Recoveries from Lake Water. In Figure 4, we compare recoveries for the entire suite of organochlorine contaminants listed in Table 1 from lake water by both SPE and LLE techniques. LLE recoveries ranged from 58 to 98% (mean 75%) with RSDs between 1 and 10% ($n = 2$). Lower recoveries were generally obtained by SPE for the lake water samples and ranged from 42 to 67% (mean 55%) with RSDs between 2 and 15% ($n = 4$). The larger range of standard deviations for SPE results was in part due to a poorer baseline early in the chromatogram, likely the result of coextracted humic material. Interfering peaks prevented accurate analysis of trichlorobenzene. Normal phase sample cleanup for high-DOC samples analyzed by SPE would likely have increased the accuracy and precision of the results for the early-eluting tetra- and pentachlorobenzenes; accordingly, these results have been rounded off to the nearest 5%. The baseline for other analytes was acceptable ($S/N > 30:1$) and comparable to LLE analyzes that had been treated to Florisil sample cleanup. Sample cleanup following Empore disk SPE was necessary for acceptable analysis of municipal wastewater effluent with $[DOC] \approx 40$ mg of C/L.⁹

To check for completeness of extraction with the standard 15% ethyl ether in pentane solution for lake water samples, eluted disks

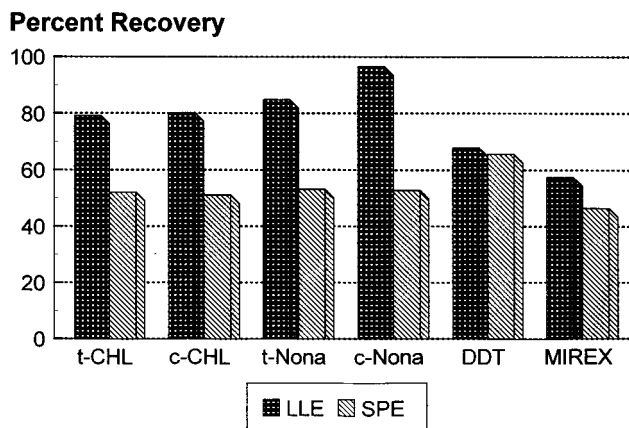
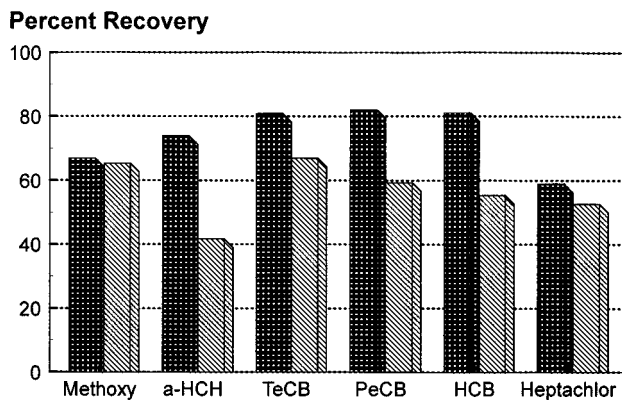


Figure 4. Comparison of recoveries of organochlorine contaminants (abbreviations and concentrations listed in Table 1) from lake water by LLE and SPE methods. Results for trichlorobenzene are not reported due to interfering peaks in the chromatograms. Results are means of duplicate extractions for LLE and four replicates for SPE.

Table 3. Recoveries of Target Analytes from Lake Water by Solid Phase Extraction Using Standard 15% Diethyl Ether–Pentane Elution Steps Followed by Additional Extractions with Dichloromethane^a

analyte	% recovery		total % extracted
	diethyl ether/pentane	DCM	
HCH	42	nd ^b	42
methoxychlor	65	2	67
TeCB	70	2	72
PeCB	60	2	62
HCB	55	3	58
heptachlor	53	2	55
trans-chlordane	52	nd ^b	52
cis-chlordane	51	3	54
trans-nonachlor	53	5	58
cis-nonachlor	52	2	54
DDT	67	2	69
mirex	46	3	49

^a Values shown are means of four samples. ^b nd, not detected. Interferences early in the diethyl ether–pentane chromatograms precluded analysis of trichlorobenzene; values for TeCB and PeCB have been rounded off to nearest 5%.

were subjected to additional extractions with DCM. Surprisingly, up to 5% more of the analytes were recovered as indicated in Table 3 (<1% were recovered in similar tests for Milli-Q solutions). Overall recoveries from extracting disks with both solvents ranged from 42 to 72% (mean 58%). In work reported in detail elsewhere,²¹ we found that the amounts recovered from eluted disks by

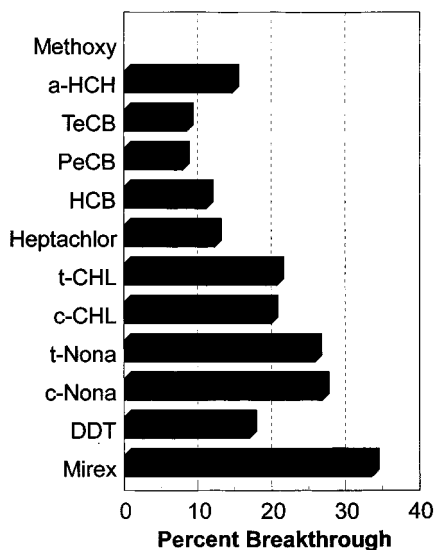


Figure 5. Percentage of analytes recovered by liquid-liquid extraction of duplicate lake water samples previously extracted by solid phase extraction.

additional DCM extractions increased when the sample volume and the total DOC load of the lake water sample was increased by 2–4-fold. These results suggest that the presence of lake water DOC on disks reduces the effectiveness of the diethyl ether–pentane extraction. It is conceivable that DOC bound to the SPE disks, particularly larger molecular weight humic acid material, may physicochemically prevent solvent penetration to C_{18} -bound analytes.

Dissolved organic matter may lower extraction efficiencies of pesticides for SPE methods by competing for available sorption sites on the solid phase material. The presence of dissolved organic matter sorbed onto disks used to analyze lake water samples was clearly visible. Additionally, SPE may not detect pesticides associated with organic macromolecules.^{9,12,18} The results reported here agree with the observations of decreased recoveries of pesticides dissolved in humic acid solutions¹² or in municipal waste effluent⁹ compared with distilled water. In the latter work, recoveries of organochlorine compounds, including chlordane, DDTs, and mirex, decreased to $77 \pm 14\%$ for spiked municipal effluent compared with recoveries averaging $98 \pm 13\%$ for distilled water.

We measured contaminants passing through the SPE disks (breakthrough) by sampling the effluent of selected samples. As shown in Figure 5, up to 38% of target compounds were found in the effluent of the lake water samples. We also measured the amounts of analytes recovered from rinsing the containers holding lake water solutions upon completion of the experiments. An additional 1–11% of analytes were recovered from solvent rinses of the lake water container; the highest levels (6–11%) of recovered compounds were those with $\log K_{ow} \geq 6.0$.

Total recoveries from all sources for the lake water experiment were lower for compounds with $\log K_{ow}$ 4–6 ($74 \pm 8\%$ by LLE and $54 \pm 11\%$ for SPE) than for higher K_{ow} compounds ($85 \pm 11\%$ by LLE and $77 \pm 11\%$ for compounds with $\log K_{ow} > 6$). Lower overall recoveries of low- $\log K_{ow}$ compounds may be the result of evaporative losses during the sample concentration step or may

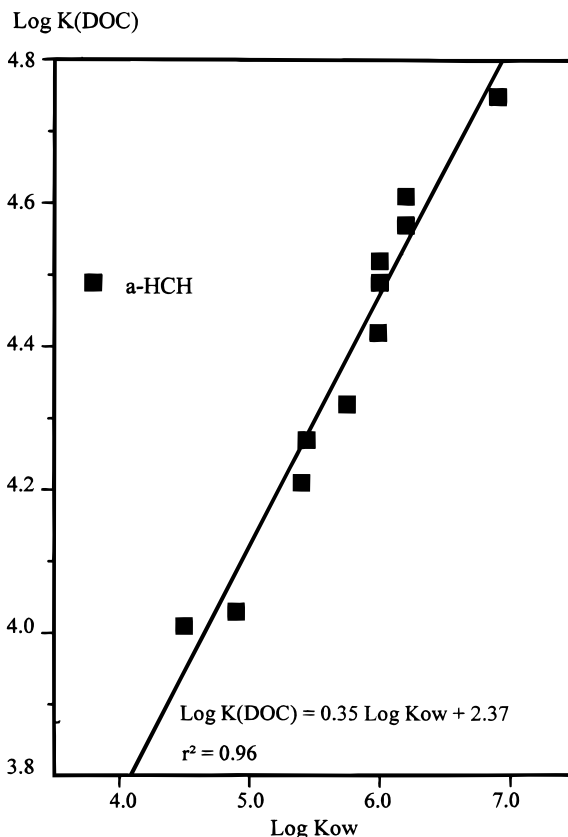


Figure 6. Plot of logarithms of octanol–water partition coefficient ($\log K_{ow}$) versus the dissolved organic carbon (DOC)–water partition coefficient ($\log K_{DOC}$) for the analytes listed in Table 3. Linear regression fitted by disregarding point for α -HCH.

reflect the generally greater difficulty of extracting these compounds from freshwater owing to their higher aqueous solubilities. Unexplained losses could occur from solvent evaporation steps, losses to glassware during sample transfers, and losses during Florisil cleanup of LLE samples. Losses to tubing, valve manifolds, and other exposed surfaces in the AutoTrace instruments may account for generally lower recoveries by SPE observed in this study compared with those using manual SPE techniques.^{9,10}

Calculation of Partition Coefficients. Predicting the partitioning of contaminants between freely dissolved and DOC-bound phases in the aquatic environment is useful in calculating the movement of such compounds in the environment. Assuming that all breakthrough for lake water samples is due to OC–DOC binding, we calculated the OC–DOC partition coefficients (K_{DOC})^{5,11} where

$$K_{DOC} = \% \text{ breakthrough} / (\% \text{ extracted} \times [\text{DOC}, \text{g/mL}]) \quad (1)$$

The range of $\log K_{DOC}$ values falls between 3.83 and 4.64, and with the exception of HCH, values increase with increasing K_{ow} . Excluding the HCH value gives the linear relationship ($r^2 = 0.96$) shown in Figure 6, which is in good agreement with the relationship

$$\log K_{DOC} = 0.24 \log K_{ow} + 2.78 \quad (r = 0.61) \quad (2)$$

(21) Ridal, J. J.; Fox, M. E.; St-Arnaud, D.; Mazumder, A.; Lean, D. R. S. NWRI Contribution, National Water Research Institute, Department of the Environment, 867 Lakeshore Rd., Burlington, ON, Canada L7R 4A6, in press.

Table 4. Comparison of Organochlorine Contaminant Concentrations in Lake Enclosure Water Analyzed by SPE and Large-Volume LLE Method^a

analyte	measured concn (ng/L) ^a	
	SPE	LLE
α-HCH	7.6 (1.4)	3.0 (0.2)
methoxychlor	24.0 (2.4)	6.6 (0.7)
heptachlor	3.2 (0.6)	1.9 (0.4)
<i>trans</i> -chlordane	3.9 (0.7)	2.0 (0.3)
<i>cis</i> -chlordane	6.0 (1.2)	3.5 (0.5)
<i>trans</i> -nonachlor	2.7 (0.5)	1.4 (0.2)
<i>cis</i> -nonachlor	3.8 (0.4)	2.2 (0.2)
mirex	2.2 (0.4)	0.5 (0.1)
surrogate	recovery ^c (%)	
	SPE	LLE
δ-HCH	64 (14)	28 (5)
dieldran	59 (12)	19 (11)
octachloronaphthalene	71 (29)	45 (50)

^a Values shown are means of four samples. ^b Detection limits estimated at better than 2.0 ng/L for SPE method for all OCs except methoxychlor (5 ng/L) for 2-L sample (cf ref 8) and 0.3–1 ng/L for the LLE method for a 16-L sample. Values in parentheses are standard deviations ($n = 4$) in nanograms per liter. ^c Percent recoveries of surrogates with percent RSDs in parentheses.

found by Eadie et al.²² for selected radiolabeled hydrophobic organic contaminants and DOC from Great Lakes waters. The HCH outlier in Figure 6 probably indicates some breakthrough of this low- K_{ow} compound for the truly dissolved species.

Comparison of Optimized SPE with Large-Volume LLE.

To assess performance at near environmental concentrations, an optimized SPE method (see Experimental Section) was compared with a commonly used large-volume LLE method to extract OC-enriched water from large lake enclosures. The results of this comparison are shown in Table 4. The SPE method yielded higher concentrations of OCs and better surrogate recoveries than the large-volume LLE method. Although analyte concentrations were at the low-nanogram per liter level, similar relative standard deviations were found for both methods and averaged 16% for the SPE method and 18% for the LLE method. Furthermore, the automated SPE method provided a considerable savings in manual labour and solvent over the large-volume LLE method.

Fox² obtained recoveries between 70 and 90% with the large-volume LLE method for PCBs and OC pesticides dissolved in low-DOC water. However, in comparison with the SPE method as well as the previous studies with a shake-flask LLE method, the performance of the large-volume method as applied in this study

of humic lake water is less than optimal. One factor that may have contributed to low recoveries with the large-volume LLE method was the necessity to moderate the solvent–water mixing speeds to avoid emulsions, which readily form when high-DOC water is extracted. Under such conditions, longer contact times than originally specified² may be necessary to improve recoveries with the large-volume method.

CONCLUSIONS

Automated solid phase disk extraction provided satisfactory recoveries (64–91%) of seven model organic compounds with log K_{ow} 3.8–6.4 when dissolved in Milli-Q water. Lower recoveries (42–72%) were obtained for a larger suite of organochlorine compounds dissolved in high-DOC lake water. While more analytes (58–98%) were recovered from lake water samples by a shake-flask LLE method, we estimate a 4-fold time savings with the automated SPE method over LLE. The presence of DOC resulted in increased breakthrough for samples prepared with lake water samples compared with Milli-Q water. While the most successful recovery of analytes was achieved for Milli-Q water solutions using an elution mixture of 15% diethyl ether in pentane, tests with lake water indicate an additional extraction with DCM should be used for exhaustive extraction of SPE disks. Because of the possible variability of DOC in environmental samples, the careful analyst should ensure that this extraction sequence provides satisfactory performance on a case by case basis. As it was observed that recoveries from lake water varied between low- and high- K_{ow} compounds, it is recommended that surrogate or matrix spikes of compounds similar to the target analytes be used to determine possible differences in extraction efficiencies between samples from natural waters. The use of appropriate internal standards following extraction is also recommended to control for losses during sample concentration steps.

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