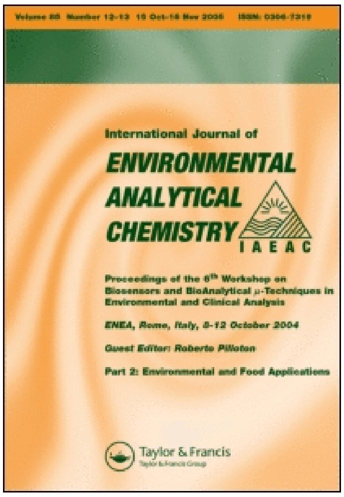

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Enhanced Preconcentration of Pesticides from Water Using the Goulden Large-Sample Extractor

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ENHANCED PRECONCENTRATION OF PESTICIDES FROM WATER USING THE GOULDEN LARGE-SAMPLE EXTRACTOR

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Recoveries of nine model pesticides measured in water samples ranging from 4 to 120 liters using the Goulden large-sample extractor and were similar to recoveries predicted by a continuous liquid–liquid extraction model. Recoveries from the largest volumes were affected by emulsion formation at high sample flow rates. Limits of detection using the Goulden extractor under optimized conditions were lower than those obtained from 1 liter serial batch extractions by factors inversely proportional to sample volumes for pesticides with logarithm of solvent/water partition coefficients greater than 2. Average limits of detection for the pesticides were 9 ng/l for 10 liter samples and 1 ng/l for 120 liter samples. Extraction of large water samples with methylene chloride using the Goulden large-sample extractor is an alternative technique to extraction of water by using solid-phase sorbents.

KEY WORDS: Preconcentration, Goulden large-sample extractor, continuous-flow liquid–liquid extraction, detection limits.

INTRODUCTION

Tracking pesticide runoff and transport through a river basin is hampered by the lack of adequate detection limits in GC/MS analytical techniques. Concentrations of pesticides and their associated breakdown products in stream waters are normally very low, typically below 100 nanograms per liter. Conventional liquid–liquid or solid-phase extraction of 1–2-liter samples can provide only a 1000 to 5000-fold concentration of the analyte prior to GC/MS analysis when a 50 000-fold or greater concentration is needed.

Enhanced preconcentration can lower detection limits and may be accomplished by using continuous-flow liquid–liquid extraction (CFLLE). CFLLE has advantages relative to resin or bonded-phase silica sorbents for the extraction of large batch samples, especially in preliminary chemical surveys and screening procedures

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from which target pesticides are identified for further study; the thermodynamics of liquid–liquid partitioning is well-understood;[1–3] sample flow rates can be quite rapid in CFLLE devices (up to 1 liter per minute); and low recoveries of some trace organic contaminants associated with dissolved organic matter using XAD resins[4] and C-18 bonded-phase sorbents[5] have been demonstrated. Devices, theory, and examples of successful applications of CFLLE to the analysis of trace organic contaminants in large water samples have been previously reported.[6–10]

The recently introduced Goulden large-sample extractor[11,*] is ideally suited for the analysis of pesticides in streams because of the requirement for depth and cross-sectionally integrated sampling regimes; the entire sample must be collected, filtered, and composited before extraction, making rapid extraction techniques highly desirable in basin-wide synoptic surveys of water quality. The Goulden large-sample extractor functions as a single stage mixer-settler, in which a continuously flowing sample is extracted by a fixed-volume of stationary methylene chloride. The objective of the present study was to model the extraction behavior of selected pesticides in the Goulden large-sample extractor to facilitate recovery estimations for pesticides with known physicochemical properties, and to determine conditions under which decreases in detection limits can be kept inversely proportional to increases in sample volumes up to a 120 liter limit.

THEORY

Continuous extraction of an analyte from water into methylene chloride after a single pass through the Goulden large-sample extractor can be predicted upon integration of the mass-balance relation shown below, assuming the analyte is not lost from either of the two phases through chemical transformations, sorption, or volatilization:

$$dC_2 = [(C_1 - C_2/K_p)/V_2] \times dV_1 \qquad (1)$$

C_2 is the concentration of the analyte in methylene chloride; C_1 is the concentration of the analyte in the water sample prior to extraction; V_2 is the volume of methylene chloride; K_p is the methylene chloride/water partition coefficient; and V_1 is the sample volume. Integration of Eq. (1), and rearranging terms to solve for extraction efficiency (E) produces the extraction model:

$$E = K_p(0.2)/V_1\{1 - \exp[-V_1/K_p(0.2)]\}. \qquad (2)$$

During operation, the solvent volume (V_2) is maintained at 200 ml. Predictions of analyte recovery from a known sample volume can be made using Eq. (2) if the concentration of analyte in the sample remains constant (an assumption met by

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[*] Use of brand and trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

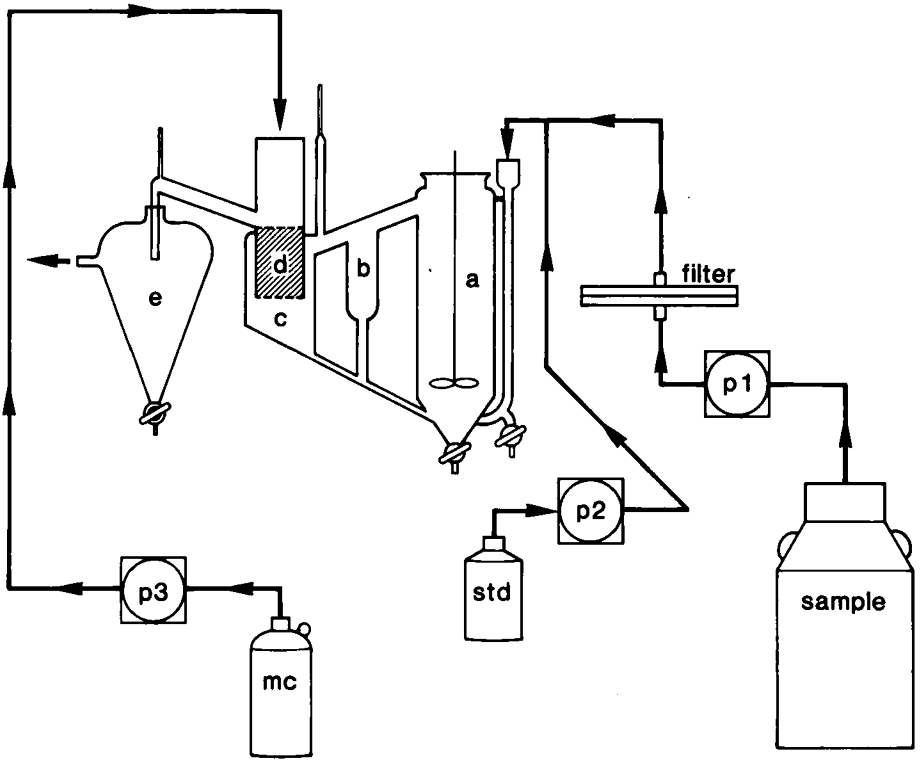

Figure 1 Schematic representation of the Goulden large-sample extractor: (a) mixing chamber, (b) first and (c) second stage settling chambers, (d) packed column, and (e) third stage settling chamber; fluid metering systems including (p1) sample, (p2) standard (std), and (p3) methylene chloride (mc) make-up pumps.

compositing the sample), and equal chemical potential of the analyte is reached in each phase after a single pass through the extractor.

EXPERIMENTAL

Apparatus

A schematic representation of the Goulden large-sample extractor (Allen Scientific Glassware, Boulder, CO) is shown in Figure 1. The sample was pumped from a 38-l stainless steel reservoir (Spartanburg Steel Products Inc., Spartanburg, SC) by a positive displacement pump (Model RP-D-2CSC, Fluid Metering Inc., Oyster Bay, NY) through a 142-mm Gelman 1-μm glass fiber filter (type A/E binder-free) to the extractor. A methanol solution containing the pesticides was continuously fortified and mixed into the sample at a glass T-joint to minimize volatility and sorption losses by using a low-flow metering pump (Model RHOCKC head with a Model RP-G-6 drive motor, Fluid Metering Inc.). A stirrer (Fisher Dyna-Mix) was used to mix the sample and methylene chloride. A column packed with 4 mm × 4 mm o.d. Teflon Raschig rings was placed above the third chamber, providing resistance to the loss of small solvent droplets. Droplets of methylene chloride breaking through the core unit were collected in a third stage settler, which consisted of a 1-liter Teflon separatory funnel. Methylene chloride lost from the system by dissolution was replenished at the top of the packed column from a fresh supply by using a positive displacement pump (Model RP-SY-1CSC, Fluid Metering Inc.). All liquids were allowed to contact only glass, Teflon, stainless steel or ceramic surfaces.

Optimum mixing and separation of the sample and methylene chloride was observed at a sample flow rate of 680 ml/min. The spike pump metered the standard solution into reference water at 400 μl/min. The methylene chloride make-up pump delivered fresh solvent to the extractor at a rate of 9 ml/min at 25 °C. Each pump was calibrated immediately before use, and volume deliveries were determined from the time of operation. The pesticide standard solution was weighted before and after extractions to confirm volume delivery.

Chemicals

The pesticides and breakdown products used to study extraction behavior were atrazine (6-chloro-N-ethyl-N′-(1-methylethyl)-1, 3, 5-triazine-2, 4-diamine), bromacil (5-bromo-6-methyl-3-(1-methylpropyl)-2, 4(1H, 3H)-pyrimidinedione), 4-bromoaniline, 4-chlorophenol, lindane (1a, 2a, 3e, 4a, 5a, 6e-hexachlorocyclohexane), linuron (N′-(3, 4-dichlorophenyl)-N-methoxy-N-methylurea), methyl parathion (0, 0-dimethyl-0-(4-nitrophenyl)phosphorothioate), metribuzin (4-amino-6-(1, 1-dimethylethyl)-3-(methylthio)-1, 2, 4-triazin-5(4H)-one), and permethrin ((3-phenoxyphenyl)methyl-3-(dichloroethenyl)-2, 2-dimethylcyclopropanecarboxylate—*cis* and *trans* isomers). The chemicals were obtained with a purity of 97–99% (Crescent Chemical Co., Hauppague, NY), which was verified by gas chromatographic analysis. Pesticide residue grade methylene chloride and methanol, and GC^2 grade ethyl acetate were used as purchased (Burdick and Jackson, Muskegon, MI).

Extraction Procedure

Recovery evaluations were performed by using water obtained from the tap in the laboratory. Alkalinity, hardness, pH, conductivity, total residual chlorine, and dissolved organic carbon concentrations were measured in tap water periodically throughout the recovery experiments. Recoveries of each of the model pesticides were determined at fortification levels of 1000, 100, and 10 ng/l from sample volumes of 4, 10, 40, and 120 liters. The samples were extracted with the flow rate set at 680 ml/min, and each extraction was replicated three to five times.

A single extraction was performed using 40 liters of glass distilled water as a comparison to tap water recoveries. Recoveries of the analytes also were determined in duplicate from 40 and 120 liters of tap water at a sample flow rate of 340 ml/min to evaluate the effect of sample flow rate on extraction efficiency.

Separatory funnel extractions of 1 liter of fortified tap water were used as a reference. Field water samples of 10, 40, and 120 liters were fortified with methyl parathion and δ-hexachlorocyclohexane (δ-HCH) and extracted using a flow rate of 680 ml/min in the Goulden large-sample extractor.

The methylene chloride extracts were dried using anhydrous sodium sulfate, and were reduced in volume to 0.5 ml by using rotary-film flash evaporation and a gentle stream of nitrogen. Before solvent volume reduction, 15 ml of ethyl acetate was added to the extracts to function as a keeper. Loss from solvent removal was determined by spiking 250 ml of methylene chloride with each pesticide and reducing the volume to 0.5 ml. Blanks were determined in duplicate for 4, 10, 40 and 120 liter extractions of tap water.

Partition Coefficients

Methylene chloride/water partition coefficients were determined for atrazine, lindane, linuron, methyl parathion, metribuzin, and permethrin. One milliliter of a solution of the pesticide in methylene chloride (3–16 mg/ml) was equilibrated in a shaker for 24 h at 25 °C with 5 ml of pre-filtered (0.02-μm Anodisc filter, Alltech Associates Inc., Deerfield, IL) distilled water (Burdick and Jackson) in 10-ml Teflon-lined screw cap centrifuge tubes. Subsequently, the tubes were centrifuged for 45 min at 2500 rpm, and the concentration of the pesticide was determined in each phase.

Water (4 ml) from each tube was sequentially extracted three times with 2-ml portions of ethyl acetate. The three solvent extracts were combined and dried using anhydrous sodium sulfate prior to quantitation by gas chromatography. The volume of the methylene chloride phase was measured with a microsyringe, and an aliquot was diluted into ethyl acetate and analyzed by using gas chromatography. Partition coefficients were measured in triplicate for each pesticide.

Chromatographic Analysis

A Hewlett-Packard (HP) Model 5890A gas chromatograph equipped with an HP Model 5970A mass selective detector (MSD) was fitted with a 30 m × 0.25 mm i.d. DB-5 (0.25 μm film thickness) fused-silica capillary column (J & W Scientific Inc., Rancho Cordova, CA). Chromatographic separations were temperature programmed from an initial temperature of 50 °C (2 min hold time) to 120 °C at 20 °C/min for the first ramp, then to 285 °C at 10 °C/min for the second ramp with a final hold of 8 min at 285 °C. Helium was used as the carrier gas at a linear velocity of 32 cm/sec at 100 °C. Sample inlet and transfer lines were maintained at 250 °C and 285 °C, respectively. Samples (2 μl) were injected into a splitless injector by using an HP Model 7673A autosampler. The purge activation time was set at 0.75 min for all of the auto-injections.

The MSD source emission current corresponded to an electron impact ionization energy of 70 eV. The electron multiplier voltage ranged between 1600–2000 V. Selected ion monitoring data were acquired from the mass selective detector by an HP 59970C Chemstation data system using an HP Series 200

Table 1 Recoveries of pesticides from 250 ml to 0.5 ml solvent volume reduction

Pesticide	*% Recovery*[a,b]
4-Chlorophenol	77 (7.7)
4-Bromoaniline	78 (5.6)
Bromacil	106 (8.1)
Metribuzin	92 (8.5)
Atrazine	94 (9.4)
Linuron	98 (1.9)
Methyl parathion	93 (2.8)
Lindane	82 (6.6)
Permethrin	96 (0.9)

[a] $N=4$.

[b] Mean and std. deviation (in parentheses).

computer. Quantitation was accomplished by using external standard calibration on selected ions.

RESULTS AND DISCUSSION

Recoveries of 4-bromoaniline were determined only at the highest fortification because of a substantial matrix effect in chromatographic separations that limited interpretations at the lower levels. Recoveries of 4-chlorophenol from water were always corrected for the amount of un-ionized phenol (pKa = 9.43) extractable into methylene chloride at the experimental pH. 4-Chlorophenol and 4-bromoaniline are not actually considered to be pesticides, but they represent two classes of breakdown products of environmental concern: phenols and aromatic amines. For convenience, all of the model compounds will hereafter be referred to as pesticides.

The range of values obtained from the analyses of tap water were as follows: pH, 7.6–8.1; specific conductance, 100–290 μS/cm; alkalinity (as $CaCO_3$), 20–60 mg/l; Ca^{+2}, 10–30 mg/l; Mg^{+2}, 1.5–6.6 mg/l; dissolved organic carbon, 2.0–2.5 mg/l; and total residual chlorine, <0.1 mg/l. Since reactive chlorine is known to be capable of oxidizing trace organic compounds in water, sodium thiosulfate (5 mg/l) was added to tap water as a reducing agent prior to several continuous flow extractions. Recovery values were not affected whatsoever by the presence of sodium thiosulfate, demonstrating that any chlorine present in tap water did not react with the pesticides. Sodium thiosulfate was not added to tap water subsequent to the preliminary recovery studies.

Extraction Efficiencies

There were no trends in magnitudes of accuracy or precision values that may have indicated a dependency of recoveries on the fortification level within the same sample volume. Recoveries varied randomly throughout the 10 to 1000 ng/l spike range. Therefore, replicate values were combined and corrected for volume reduction losses (Table 1) to provide overall extraction efficiencies for each of the sample volumes (Figures 2a and b).

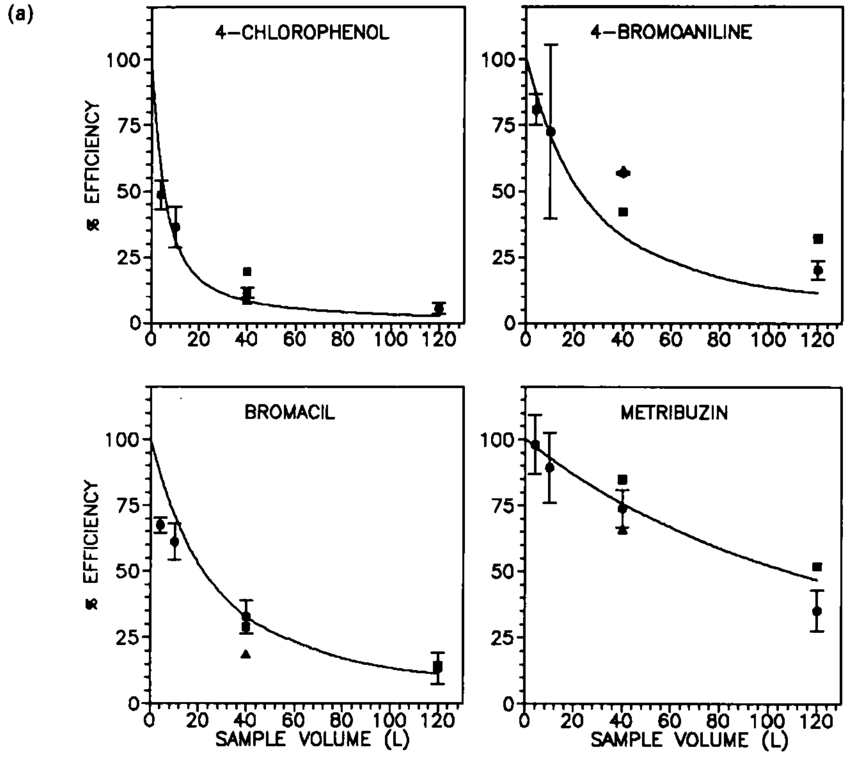

Figure 2 Comparisons of measured and predicted extraction efficiencies for the model pesticides. Predicted extraction efficiencies determined from Eq. (3) (solid lines) are shown for the entire range of sample volumes. Measured extraction efficiencies for tap water (● ± 1 std. deviation) and distilled water (▲) were determined with a sample flow rate of 680 ml/min, and at 340 ml/min for tap water (■). Pesticides that have logarithm of methylene chloride partition coefficients < 3 are shown in (a), and those with logarithm of partition coefficients > 3 are shown in (b).

Pesticides with logarithm of partition coefficients less than 3 (Table 2) had observed extraction efficiencies that were close to predicted efficiencies for all of the sample volumes tested (Figure 2a). Significantly lower than expected efficiencies were noted for 4-chlorophenol at 4 liters, bromacil at 4 liters and 10 liters, and metribuzin at 120 liters (Table 3). Extraction efficiencies for 4-chlorophenol and 4-bromoaniline at 40 liters and 120 liters were significantly different from predicted values, but were greater than expected (Table 3). It has been noted that methylene chloride/water partition coefficients in some cases can be larger than *n*-octanol/water partition coefficients, suggesting that predicted efficiencies for 4-chlorophenol, 4-bromoaniline, and bromacil could be underestimated.

None of the pesticides with logarithm of partition coefficients greater than 3 had lower than expected efficiencies from 4 liter samples, but one was noted from 10 liters, three from 40 liters, and all of them were significantly lower than expected from 120 liters (Table 3). The more hydrophobic pesticides showed a downward trend in extraction efficiencies as the sample volume was increased, and was markedly evident for 120 liter samples.

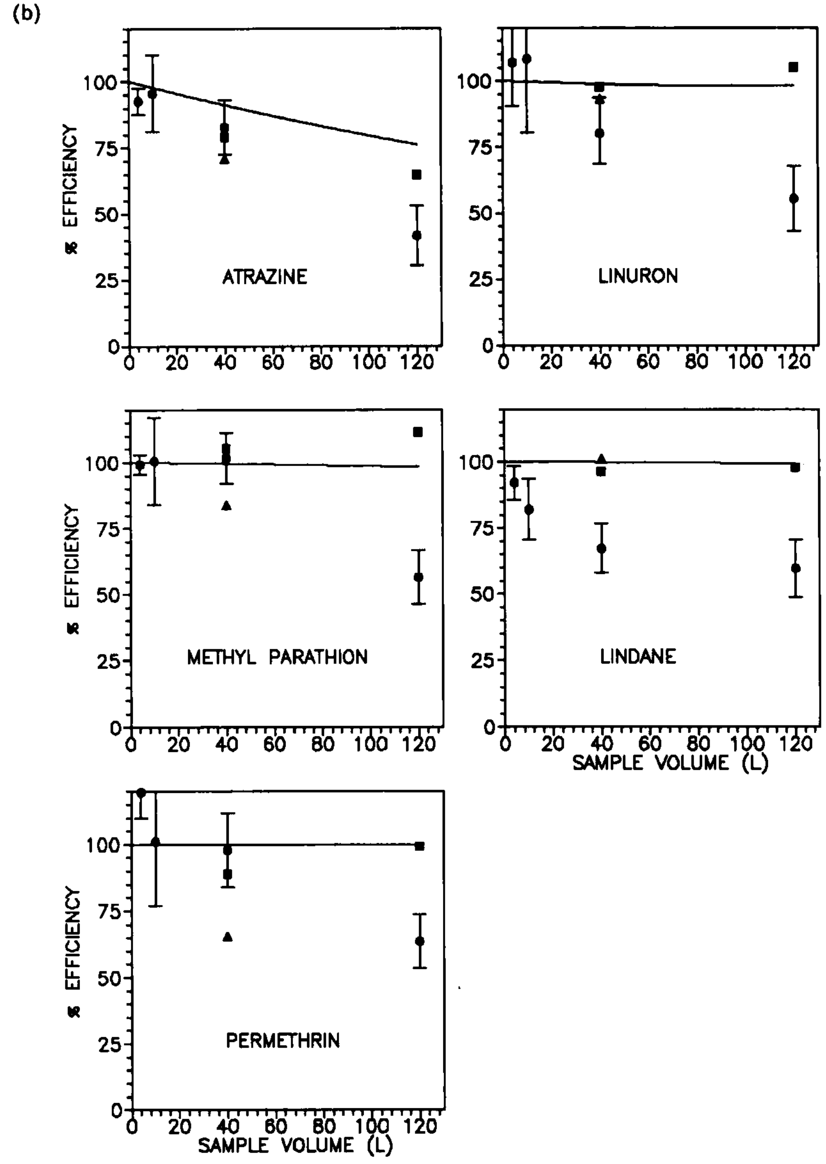

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Table 2 Logarithms of methylene chloride/water partition coefficients (Log K_p) and octanol/water partition coefficients (Log K_{ow}) of the pesticides

Pesticide	Log K_p[a]	Log K_{ow}[b]
4-Chlorophenol	ND[c]	1.22
4-Bromoaniline	ND	1.75
Bromacil	ND	1.84
Metribuzin	2.53	
Atrazine	3.02	
Linuron	4.18	
Methyl parathion	4.23	
Lindane	4.59	
Permethrin	5.53	

[a] Log K_p values from three measurements were averaged.
[b] Log K_{ow} values were obtained from Hanch and Leo.[12]
[c] ND = not determined.

Table 3 Comparisons between observed and predicted extraction efficiencies of pesticides from tap water using Gouldon large-sample extractor with a flow rate of 680 ml/min.[a]

Pesticide	*Sample volume (liters)*			
	4 liters	*10 liters*	*40 liters*	*120 liters*
4-Chlorophenol	–[b]	*	+	+
4-Bromoaniline	*[c]	*	+	+
Bromacil	–	–	*	*
Metribuzin	*	*	*	–
Atrazine	*	*	–	–
Linuron	*	*	–	–
Methyl parathion	*	*	*	–
Lindane	*	–	–	–
Permethrin	+[d]	*	*	–

[a] Observed extraction efficiencies were compared to extraction efficiencies predicted by Eq. (2) using one-tailed Student *t*-tests.[14]
[b] $P < 0.05$, (–): observed values are less than predicted.
[c] $P > 0.05$, (*): observed and predicted values are equal.
[d] $P < 0.05$, (+): observed values are larger than predicted.

Because mean recoveries of the hydrophobic pesticides from 120 liter samples were <65% in all cases, it was suspected that the originally optimized sample flow rate for the Goulden extractor was too rapid for large samples. Quantitative recoveries of organochlorine pesticides from water samples larger than 100 liters using CFLLE techniques have been demonstrated at much lower extraction rates.[6, 13] An attempt was made to increase extraction efficiencies from 120 liter samples by decreasing the sample flow rate to 340 ml/min. As a result, improved recoveries were observed for linuron, methyl parathion, lindane, and permethrin (Figure 2b).

Improved recoveries of the hydrophobic and intermediate polarity pesticides were observed for 120 liter samples at the 340 ml/min extraction rate because emulsions developed in the extractor at the higher flow rate; emulsions visually intensified at sample volumes >40 liters at a flow rate of 680 ml/min. Upon emulsion formation, more of the methylene chloride is lost from the extractor as fine droplets. When the sample flow rate was lowered to 340 ml/min, loss of solvent droplets during extraction was reduced because the Goulden large-sample extractor was allowed to function more efficiently as a mixer-settler. The rate of loss of minute solvent droplets from the extractor did not appear to be a linear function of the sample volume, but increased rapidly as emulsions developed.

Extraction efficiencies of the pesticides, excluding permethrin and lindane, obtained from 40 liters of distilled water were comparable to within 15% of those obtained from reference water at either the 340 or 680 ml/min sample flow rates (Figures 2a and b).

Measured extraction efficiencies for the pesticides with logarithm of partition coefficients less than 3 changed markedly throughout the 4 to 120 liter volume range as predicted by Eq. (2) (Figure 2a). The water-to-solvent ratio changes during the course of extraction in accordance with the increase in sample volume, and efficiency (E) is limited primarily by thermodynamic partitioning. For example, the pre-exponential $(0.2/V_1)$ term in Eq. (2) acts to diminish the magnitude of E if it is not countered by a large K_p term. Thus, extraction efficiency is poor for analytes with small partition coefficients when sample volumes are relatively large.

Extraction efficiencies of the hydrophobic pesticides, such as methyl parathion and permethrin, were less affected by large sample volumes as predicted by Eq. (2) when losses due to emulsion formation were minimized. Large partition coefficients (i.e., >10000) promote nearly complete mass transfer from water into methylene chloride. High extraction efficiencies should be obtained for analytes with partition coefficients >1000 for sample volumes up to 120 l.

Thermodynamically optimal operating conditions should exist for an analyte when the ratio of the methylene chloride/water partition coefficient to the sample volume $(K_p/V_1) \geqq 8$, which predicts an extraction efficiency of $\geqq 75\%$ according to Eq. (2). Recoveries and extraction efficiencies are equal terms when analyte losses during solvent evaporation and handling are nil. Design of the appropriate extraction scheme should consider the partition coefficient to sample volume ratio for the analyte, desired limit of detection, and expected degree of emulsion formation in the Goulden large-sample extractor during the preconcentration process. Prediction of a recovery value can be made for a particular analyte if its methylene chloride/water or *n*-octanol/water partition (K_{ow} can be used if K_p is not available) coefficient of the analyte is known. Thus, extractions can be optimized easily. In cases were stream waters are being screened for the presence of non-target pesticides, more accurate quantitative measurements can be achieved by correcting for extraction efficiencies. The ability to predict extraction efficiencies is clearly advantageous.

Limits of Detection

Improved limits of detection for all of the pesticides from 10, 40 and 120 liter

Table 4 Comparisons of limits of detection for the pesticides among sample volumes. All limits of detection were corrected for analyte recoveries. Sample volumes > 1 liter were extracted using Goulden large-sample extractor

Pesticide	*Minimum detectable mass in GC/MS-MSD*	*Sample volume (liters)*				
	ng (std. deviation)	*1*	*10*	*40*	*120*[a]	*120*[b]
		Limit of detection, ng/l				
4-Chlorophenol	0.10 (0.024)	30	6.9	6.4	4.3	ND[c]
4-Bromoaniline	0.18 (0.062)	48	6.2	2.0	1.9	1.2
Bromacil	0.10 (0.030)	25	4.1	1.9	1.6	1.4
Metribuzin	0.16 (0.055)	42	4.5	1.4	1.0	1.52
Atrazine	0.10 (0.025)	26	2.6	0.79	0.52	0.32
Linuron	0.50 (0.17)	140	12	3.9	1.9	1.1
Methyl parathion	1.2 (0.40)	360	30	7.5	4.7	2.5
Lindane	0.13 (0.043)	38	4.0	1.4	0.52	0.28
Permethrin	0.16 (0.053)	40	4.0	1.0	0.52	0.37
Mean limit of detection		83	8.8	2.9	1.9	0.96

[a] Determined at a sample flow rate of 680 ml/min.
[b] Determined at a sample flow rate of 340 ml/min.
[c] ND = not determined.

samples in relation to 1 liter separatory funnel extractions were obtained (Table 4). Gains in limits of detection overall were inversely proportional to the increases in sample volumes. The magnitude of the gains in limits of detection depends on the enrichment of the analyte through the extraction and solvent volume reduction processes. For example, the procedure of extracting water with the Goulden large-sample extractor yielded limits of detection for 4-chlorophenol that ranged from 4 ng/l (120 liters) to 7 ng/l (10 liters) (Table 4). Improved limits of detection for 4-chlorophenol were not observed upon extracting more than 10 liters of sample. In contrast, one order of magnitude lower limits of detection were achieved for permethrin when 120 liters of sample was extracted at 340 ml/min relative to 10 liters (Table 4), because permethrin recoveries from the large samples were quantitative.

Field Extractions

Methyl parathion and δ-HCH were used as surrogate spikes for extractions carried out in the field in the Yakima River Basin, Washington. Recoveries of methyl parathion were lower in Naches River and Moxee Drain samples than in tap water for comparable volumes (Table 5); however, δ-HCH recoveries were consistently higher in stream water than lindane recoveries in tap water. Lower recoveries in stream water relative to tap water often can be attributed to matrix effects.

Preliminary field extractions using 340 ml/min flow rates in the Goulden large-sample indicate that comparable recoveries of pesticides between tap water and natural water are routinely achieved. In the configuration described in this study, it is recommended that the Goulden large-sample be used to extract natural water

Table 5 Recoveries of methyl parathion (MP) and δ-HCH from filtered stream water by using the Goulden large-sample extractor at a flow rate of 680 ml/min

Sample	*% Recovery*[a,b]	
	MP	*δ-HCH*
Naches River water (liters)		
10	74	84
40	61 (8)	69 (14)
120	48	52
Moxee Drain water (liters)		
10	93 (4)	84 (4)
40	80	70

Water chemistry	*Naches R.*	*Moxee Dr.*
pH	7.5	8.0
Sp. conductance, μS/cm	50	280
Hardness (as Ca^{+2} and Mg^{+2}), mg/l	18	97
Alkalinity (as $CaCO_3$), mg/l	23	120
Dissolved organic carbon, mg/l	1.8	2.6

[a] Fortification level was 100 ng/l.

[b] Mean of duplicate or triplicate (followed by std. deviation) extractions.

at flow rates of 340 ml/min to obtain the thermodynamically-optimum pesticide recoveries predicted by the extraction model.

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