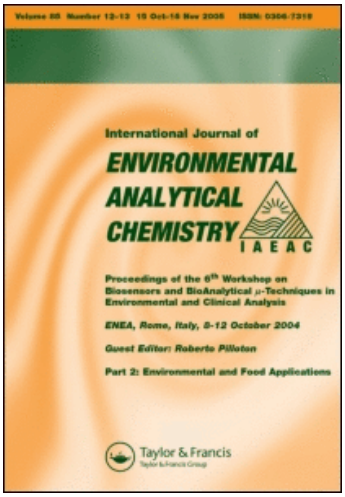

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Use of Field-Applied Quality Control Samples to Monitor Performance of a Goulden Large-Sample Extractor/GC-MS Method for Pesticides in Water

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USE OF FIELD-APPLIED QUALITY CONTROL SAMPLES TO MONITOR PERFORMANCE OF A GOULDEN LARGE-SAMPLE EXTRACTOR/GC-MS METHOD FOR PESTICIDES IN WATER

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Since 1985, the Goulden large-sample extractor (GLSE) has been used to isolate a broad array of trace-organic contaminants from large volumes of water. In this study, field-applied quality control measures, including matrix and surrogate spikes and blanks, were used to monitor method performance from GLSE extraction through GC-MS analysis. The method was applied to the determination of multiple classes of pesticides isolated from 4- to 112-L filtered surface-water samples. Average recoveries of six surrogate compounds ranged from 84 ± 18% for [$^2H_{10}$]diazinon to 15 ± 13% for 4,4'-[$^2H_8$]DDT, the low recoveries for which were largely a result of unmonitored breakdown of this surrogate by the GC injection system. Field-matrix-spike samples were prepared by fortifying 10-L, 35-L, and 110-L filtered surface-water samples with 68 pesticides to amended concentrations of 11- to 50-ng/L each. Recoveries ranged from not detected to greater than 100%. Variability in pesticide recoveries from triplicate 10-L water samples collected at one site averaged 5.7% relative standard deviation and did not exceed 19%.

Keywords: Large-volume extraction; pesticides; Goulden large-sample extractor; surface water

INTRODUCTION

A continuing need exists for analytical techniques that, when coupled with gas chromatography and electron-impact mass spectrometry (GC-EIMS), can deter-

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mine a broad spectrum of organic pesticides in water samples at nanogram-per-liter concentrations, or lower. The extraction of large volumes of water (10 to 100 L or more) can provide orders-of-magnitude greater enrichment factors, and, therefore, substantially lower analyte quantitation levels, than conventional methods that process ≤1-L sample volumes. Continuous-flow liquid-liquid extraction represents one of many large-volume preconcentration strategies available for lowering quantitation levels which benefits from having a well-developed theoretical basis[1–3] and a method compatibility with most standard GC-EIMS instrument configurations.

In 1985, Goulden and Anthony[4] reported a continuous-flow liquid-liquid extractor for the preconcentration of trace organic compounds from large volumes of water. The Goulden large-sample extractor (GLSE) functions as a single stage mixer-settler in which a continuously flowing water sample is passed through a stationary phase of dichloromethane (DCM). The theory of extraction of organic compounds from water in the GLSE is most often treated as a one-theoretical-plate-equivalent liquid-liquid distribution. Initial GLSE design criteria included, among other features, the ability to (a) handle sample volumes ranging from 4 to 50 L or more, (b) efficiently extract from water organic compounds with octanol/water partition coefficients, K_{ow}, of 10^4 or greater, (c) use rapid sample flow rates of 300 to 500 mL/min, and (d) do sequential acid-base extractions[4]. Several different versions of the GLSE have been used to extract trace organic contaminants from large-volume water samples, the GLSE-95 being the most commonly applied extractor because of high flow-rate capability (to 1000 mL/min)[5,6].

Applications of the GLSE to contaminant determinations in ambient water samples have been primarily by Canadian and U.S. scientists in studies conducted mostly in the Great Lakes region, the Pacific Northwest, the Canadian prairie, the Arctic, and the Chesapeake Bay watershed[4,6–36] (Table I). Most applications of the GLSE have involved extraction of contaminants with nonpolar to moderately polar properties, including organochlorine and organophosphorous pesticides, PCBs, polycyclic aromatic hydrocarbons, triazine, acetamide, and dithiocarbamate herbicides, and polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Using sample pH adjustment, the GLSE also has been used to isolate chlorinated phenoxyacid herbicides[28,29]. A surrogate recovery performance study further suggests successful application of the GLSE to acid herbicides, as well as to chlorophenols, resin acids, and fatty acids from pulp and paper mill effluents[37]. Extraction of tire leachate for use in fish toxicity studies is another reported application of the GLSE[38].

TABLE I Some applications of the Goulden large-sample extractor (GLSE) to contaminant determinations in environmental samples

Study basin or region[a]	*Sample types*[b]	*Compound or compound classes measured*[c]	*Quality-control data provided*[d]	*ref.*
Niagara River	WW	OC	V	[4]
Niagara River	CW	AH, CB, OC, PAH, PCB, PHT, TH	GB, RS, SS, V	[6]
Niagara River	CW	CB, OC, PCB	DL, MS, RS, SS, V	[7]
St. Lawrence River	CW	CB, OC, PCB	DL	[8]
St. Lawrence River	FW	AH, OP, TH	DL, MS, RS, SS, V	[9]
St. Lawrence River	FW	AH, OP, TH	DL, GB, MS, RS, SS, V	[10]
Green Bay, WI	FW, CW	PCB	--	[11]
Lake Michigan	FW	PCB	SS	[12]
Great Lakes	WW	CB, OC, PCB	SS, V	[13]
Great Lakes	CW, WW	AH, AP, BT, TH	--	[14]
Great Lakes	FW	chlordanes, PCBs	SS	[15]
Rainy River, ON	CW	CB, OC, PAH, PCB	DL	[16,17]
Ottawa River, ON	CW	OC	--	[18]
Grimsby, ON	R	AH, CB, OC, PAH, PCB, PHT	GB, SS	[19]
Canadian Arctic	S	OC, PCB	DL, SS	[20]
Canadian Arctic	S	PCB	GB, SS	[21]
Canadian Arctic	I, S	PAH	GB	[22]
Canadian Arctic	S, WW	α-hexachlorocyclohexane	GB, SS, V	[23]
Canadian Arctic	S	PCB	GB	[24]
Bering/Chukchi Seas	CW	AH, OP, MISC, TCH, TH	DL, SS, V	[25]
Columbia River, BC	CW	dioxins/furans	--	[26]
Fraser River, BC	CW	dioxins/furans	GB, SS	[27]
Prairie aquifers, SK	GW	AH, MISC, PXA, TCH, TH	DL, GB, MS, RS, SS, V	[28,29]
Canadian mountains in AB and BC	S	OC, PCB	--	[30]
Yakima River, WA	FW	AH, MISC, OC, OP, TCH, TH	DL, MS, SS, V	[31]
Yakima River, WA	FW	AH, MISC, OC, OP, TCH, TH	SS, V	[32]

Study basin or region[a]	*Sample types*[b]	*Compound or compound classes measured*[c]	*Quality-control data provided*[d]	*ref.*
Chesapeake Ray	FW	AH, OC, PAH, PCB, TH	DL, GB, MS, SS, V	[33]
Chesapeake Bay	FW	AH, OP, TH	--	[34]
Anacostia River, DC	FW	OC, PAH, PCB	GB, RS, SS	[35]
Susquehanna R., MD	FW	OC, PAH, PCB	GB, MS, SS	[36]

a. River basin, lake basin, sea, or locality from which samples were processed using the GLSE. Canadian provinces: AB, Alberta; BC, British Columbia, ON, Ontario; SK, Saskatchewan; United States: DC, District of Columbia; MD, Maryland; WA, Washington; WI, Wisconsin.
b. CW, centrifuged water; FW, filtered water; GW, ground water; WW, whole water; I, melted ice water; R, rain; S, melted snow water.
c. AH, acetamide herbicides; AP, alkylphosphates; BT, benzothiazoles; CB, chlorobenzenes; dioxins/furans, chlorinated dibenzo-p-dioxins and dibenzofurans; MISC, miscellaneous pesticides; PAH, polycyclic aromatic hydrocarbons; PCB, polychlorinated biphenyls; PHT, phthalate esters; PXA, chlorinated phenoxyacid herbicides; OC, various organochlorine pesticides; OP, organophosphorus insecticides; TCH, thiocarbamate herbicides; TH, triazine herbicides.
d. Ancillary GLSE method quality control or performance data provided. DL, detection or quantitation level estimates; GB, GLSE blanks; MS, matrix spike recoveries; RS, reagent water spike recoveries; SS, surrogate spike recoveries; V, GLSE method variability information.

A number of studies reporting environmental sample measurements using the GLSE also provide some supporting GLSE method operational details and/or performance information. The latter include recoveries of surrogate or selected contaminant compounds, or both, that were spiked into ambient or reagent water samples, estimated detection or reporting limits, method precision determinations, and field GLSE method blank data (Table I). Other reports focus largely or exclusively on design and/or quality control performance-related information for the GLSE. Supporting reports include detailed descriptions of the extractor and/or operational considerations[4,5,39–41], GLSE performance in relation to extraction theory[3,4,42], and other performance evaluations[37,41,43]. The majority of reported GLSE extraction information has been for hydrophobic organic contaminants (e.g., those with K_{ow}s > 10^4), while there also exists a need to determine parts-per-trillion levels of moderate polarity pesticides (e.g., organophosphate insecticides and triazine and chloroacetamide herbicides) in natural waters. The performance of the GLSE coupled with GC-MS in the determination of moderately polar pesticides from natural water samples ranging from 10 to ~100 L is not well understood.

In previous studies[3,32,43], the U.S. Geological Survey (USGS) evaluated the GLSE for the isolation of up to 43 pesticides from large-volume water samples followed by analysis using GC-EIMS. In this study, the GLSE was used to concentrate a broader suite of 68 pesticides from 4-to 112-L filtered surface-water samples collected as part of a synoptic survey of the Yakima River basin, Wash-

ington, a pilot basin of the USGS's National Water-Quality Assessment Program. Some field-applied quality-control features were included in the study to monitor overall performance of the GLSE GC-EIMS method, including (a) the addition of surrogate compounds to all sample types, (b) sample replication at one site, (c) matrix spike samples, and (d) GLSE blank samples. This paper provides additional information on overall method performance under field application conditions for 53 pesticides previously tested by the USGS or others, and provides a preliminary assessment of performance for 15 other pesticides of primarily moderate polarity not previously tested using the GLSE. Some conditions that limited GLSE performance and GC-MS analysis of the pesticides are highlighted.

MATERIALS AND METHODS

Reagents

All solvents were pesticide-residue grade. Pesticide standards were obtained in neat form from the U.S. Environmental Protection Agency's Pesticide Repository (Research Triangle Park, NC, USA). Mixed standard solutions were serially diluted to yield GC-EIMS calibration mixtures in ethyl acetate and a 68-component spike solution at 4 ng/μL of each chemical in methanol.

[$^2H_5$]Atrazine (note: abbreviated atrazine-d5 in Figure 2), gamma-[$^2H_6$]hexachlorocyclohexane (gamma-HCH-d6 in Figure 2), 4,4′-[$^2H_8$]DDT (DDT-d8 in Figure 2), and [$^2H_{10}$]diazinon (diazinon-d10 in Figure 2) (all obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, USA), isodrin, and terbuthylazine were made up in methanol and used as surrogate spiking standards. Water used for blanks was distilled and stored in heat-treated glass carboys.

Sample collection and preparation

The Yakima River Basin study area has been described by McKenzie and Rinella[44]. Surface-water samples were collected using an equal-width-increment sampling procedure. Synoptic sampling relied on extraction of ≤10-L water volumes for lower stems of the Yakima River, as well as those creeks and drains historically exhibiting the greatest concentrations of pesticides. Water volumes of ~35 L were used for mid-river and major tributary locations and volumes of ~110 L were used for up-river and background sites expected to have minimal concentrations. Specific sampling locations and corresponding determined pesticide concentrations are described by Rinella and others[31]. Locations of surface-water samples discussed in this paper are listed in Table II.

TABLE II Number of detections in field blanks, and selected water-quality parameters and ambient concentrations (in nanograms per liter) of some example pesticides for replicate filtered surface-water samples used to prepare Goulden large-sample extractor matrix-spike samples*

	Detections in 13 blanks	*Granger Drain*	*Moxee Drain*	*South Drain*	*Sulfur Creek*	*Satus Creek*	*Pacific Power Wasteway*	*Yakima River at Umtanum*	*Yakima River at Kiona*		
									35-L	*~9-L triplicates*	
collection date, 6/day/89		27	28	27	26	26	25	28		26	
stream discharge, m^3/s		1.0	1.8	2.3	7.5	0.34	14.2	102.8		42.5	
TSP (>0.45 µm), mg/L		643	436	145	245	2	4	25		30	
DOC (≤0.45 µm), mg/L		3.3	2.9	2.7	2.3	1.2	1.2	2.4		2.1	
pH		8.2	6.2	8.3	8.1	7.8	7.8	8.1		8.6	
sample volume, L		12.1	10.9	10.8	4.4	109	111	34.5	34.5	8.8, 9.5, and 9.8-L	
Pesticide										triplicates	
Total detected/quantifiable		28/12	20/9	18/8	26/10	3/0	6/5	33/8	24/15	24/15	
organochlorines										*Mean*	*(%RSD)*
4,4′-DDD	3	D <2.8	D <3.3	D <3.3	D <22	<0.3	<1.6	D <1.6	D <1.6	D <3.3	
4,4′-DDE	6	1.0	3.8	2.4	12	<0.1	0.2	D <0.4	2.5	0.8/0.9	m=2
4,4′-DDT	1	D <8.9	<1 1	<1 1	nq	<1.0	nq	nq	nq	<4.1	
4,4′-[$^2H_8$]DDT (*surrogate*)	--	<5%#	<5%	nd	nq	5%	nq	nq	nq	22%	(53)
dieldrin	2	D <3.1	D <3.4	D <3.4	35	<0.3	<0.2	0.9	3.6	2.5/2.7	m=2
endrin		<6 1	<6. 8	<6.8	<3 5	<0.7	<0.2	1.5	<0.6	na	
γ-[$^2H_6$]HCH (*surrogate*)	--	106%	101%	58%	<7%	54%	47%	101%	55%	48%	(18)

	Detections in 13 blanks	*Granger Drain*	*Moxee Drain*	*South Drain*	*Sulfur Creek*	*Satus Creek*	*Pacific Power Wasteway*	*Yakima River at Umtanum*	*Yakima River at Kiona*		
									35-L	*~9-L triplicates*	
										Mean	*(% RSD)*
isodrin (*surrogate*)	--	nd	51%	28%	<4%	37%	nd	64%	77%	18%	(10)
mirex		<1.9	<2.1	<2.1	<18	<0.2	<0.4	D <1.4	<1.4	<0.3	
organophosphates											
diazinon	2	11	410	150	66	<0.6	<0.6	D < 2.0	39	40	(0.2)
[$^2H_{10}$]diazinon (*surrogate*)	--	92%	86%	91%	139%	69%	81%	91%	99%	92%	(2.1)
dimethoate	1	D <12	<13	<13	330	<1.3	<1.1	<3.7	<3.7	<8.6	
malathion	6	D <9.9	D <11	D <11	D <44	<1.1	5.6	D <3.9	70	12	(6.9)
methyl parathion	3	<13	<14	<14	<11	<1.4	<1.3	D <4.1	<4. 1	<10	
phosphamidon	3	56	43	<11	D <37	<1.0	<2.0	D <6.5	5.3	6.4/5.9	m=2
triazines											
atrazine	9	48	8.5	130	49	D <0.6	<0.2	10	32	36	(1.9)
[$^2H_5$]atrazine (*surrogate*)	--	115%	97%	110%	135%	48%	56%	75%	79%	81%	(2.4)
cyanazine		8.6	<3.7	<3.7	D <31	<0.4	<0.5	<1.7	<1.7	3.3	(24)
metribuzin	1	<3.8	<4.5	<4.5	D <27	<0.4	<1.0	<2.9	<2.9	D <6.7	
prometon	1	32	3.8	D <2.7	26	<0.3	<0.3	1.1	3.0	3.0	(27)
simazine	8	130	<3.6	<3.6	81	<0.4	<0.2	2.2	18	21	(3.3)

	Detections in 13 blanks	*Granger Drain*	*Moxee Drain*	*South Drain*	*Sulfur Creek*	*Satus Creek*	*Pacific Power Wasteway*	*Yakima River at Umtanum*	*Yakima River at Kiona*		
									35-L	*~9-L triplicates*	
										Mean	*(% RSD)*
terbuthylazine (*surrogate*)	--	115%	104%	111%	133%	70%	61%	89%	85%	77%	(0.4)
chloroacetamides											
alachlor		33	<4.0	17	33	<0.4	<0.5	<1.6	12	9.4	(0.2)
metolachlor		D <2.8	<3.1	6.0	D <15	<0.3	<0.4	D <1.3	1.9	1.6	(6.3)
thiocarbamate											
EPTC	1	3.1	D <2.7	3.4	D <5.0	<0.3	<0.3	1.6	3.3	4.9	(10)
miscellaneous											
propargite I and II	1	40	210	160	260	<0.6	<0.7	D <2.1	7.2	11	(3.6)

*Complete Table II information for all pesticides available in supplement[41]. TSP, total suspended particles; DOC, dissolved organic carbon; D, detected less than (<) the quantitation level; m, number of quantifiable measurements if less than three with individual concentrations shown; nq, not quantifiable; nd, not detected and no quantitation level determined; na, not analyzed.

#Percent recovery of the spiked surrogate compound.

At each collection site, sampled water was placed in one or more 37.5-L stainless steel milk cans that were cleaned between use with nonphosphate detergent and rinsed with tap water, methanol, and acetone. Aliquots of collected water samples were separately measured in the field for pH and total suspended particles (TSP, >0.45 μm), and at the USGS National Water Quality Laboratory (NWQL) for dissolved organic carbon (DOC, <0.45 μm)[31].

GLSE samples were filtered using 293-mm diameter type A/E glass-fiber filters, having a 1-μm nominal pore size (Gelman, Inc.). The filtered water was dispensed into one clean, empty can for each 10- or 35-L sample, or into three cans for each 110-L sample to provide a composite for the extraction of unspiked and corresponding matrix-spiked samples.

The surrogate spiking solution was added to the filtrate during filtration to facilitate surrogate-water mixing and to aid in evaluating overall GLSE method performance for each sample. The amounts of surrogate solution added to the samples varied in proportion to the sample volume. Resultant surrogate concentrations were 25 ng/L for 10-L samples, 28 ng/L for 35-L samples, and 11 ng/L for 110-L samples. The terbuthylazine surrogate concentrations were ~5 times greater. Matrix-spike samples were similarly prepared using aliquots of the composited, filtered water for the sample locations listed in Table II. These aliquots were fortified with the spike solution to a final concentration of 50 ng/L (10-L samples), 28 ng/L (35-L samples), or 11 ng/L (110-L samples) for each of the 68 selected pesticides. The concentrations used were designed to simulate expected concentrations at the various sites. All fortified samples were manually mixed at least once during an otherwise static equilibration time of at least 30 min prior to extraction.

Sample extraction

The GLSE (Allen Scientific Glassware, Boulder, CO, USA) was similar to that described by Goulden and Anthony[4]. GLSE operational conditions are detailed elsewhere[31] and were similar to previous USGS studies[3,32,43]. Briefly, the filtered water sample was pumped at 350 mL/min through Teflon tubing into the GLSE. The sample was mixed with DCM using a stirrer in the mixing chamber. DCM/water separation then occurs in three settling chambers, the second of which contains a column designed to help break emulsions. DCM lost from the GLSE by both dissolution in sample water (1.3% v/v at 20°C in pure water) and volatilization out the open-top was replenished by pumping DCM at 9 mL/min directly into the column in the second mixing chamber.

Sample volumes processed through the GLSE ranged from 4.4 to 112 L, depending on the anticipated pesticide concentrations. After the sample was

pumped through the extractor, 500 mL of distilled water was added to the sample can and pumped into the extractor to help ensure that the entire sample had reached the GLSE. DCM and water were drained from the GLSE, and the DCM was collected in a pre-cleaned 500-mL amber glass bottle. The entire extractor was rinsed with DCM, which was combined with the previous DCM fraction. Empty cans were not rinsed with DCM to determine pesticide residues remaining on the can walls. Extracts were immediately stored, and subsequently shipped, on ice to the USGS NWQL. At the lab, the samples were stored at 4 °C until volume reduction prior to analysis.

After processing each natural, spike, or blank sample, the GLSE was cleaned by pumping sequentially 100 mL of acetone and 100 mL of methanol through the Teflon inlet tubing into the mixing chamber. The extractor was rinsed thoroughly with acetone and methanol. For the final rinse, the GLSE was filled with charcoal filtered tap water and then drained.

Blanks

Blanks consisted of 5 to 8 L of distilled water that was passed through the filtration device and then through the GLSE (FG blank) or through the GLSE only (extractor blank). Extractor or FG blanks were processed through each of the two GLSE units used in this study immediately following a matrix spike sample to assess pesticide carryover potential. Additionally, FG blanks were processed at the beginning and end of all sample extractions. Except for sample volume limitations, these blanks were treated identically to other samples.

Extract preparation and analysis

Anhydrous sodium sulfate was used to remove residual water from DCM extracts. DCM extract volumes were reduced sequentially by vacuum rotary and nitrogen gas evaporation and solvent exchanged into ~200 μL in toluene. This resulted in theoretical enrichment factors ranging from ~22,000 to 560,000 depending on the sample volume.

The extracts were fortified with an internal injection standard solution of per-deuterated polycyclic aromatic hydrocarbons and analyzed by GC-MS with a Hewlett-Packard (HP) 5890 GC, interfaced to a HP 5970A mass selective detector operated in the selected ion monitoring mode using procedures similar to those previously described[3,32,43]. Separations were carried out on a 30 m × 2.5 mm DB-1701 column (J & W Scientific, Inc., Folsom, Calif.) with a 0.25-μm film thickness. An HP 7673A autosampler was used to inject 2 μL of extract at 250°C

with a 2 min splitless time. The liner was a cup splitter type (Allen Scientific Glassware; similar to no. 20709, Restek Corp., Bellefonte, PA, USA) that was deactivated using a dichlorodimethylsiloxane solution (Sylon CT, Supelco, Inc., Bellefonte, PA) and contained a small amount of silanized glass wool. Detector interface temperature was 285 °C. The GC temperature program was 80 °C for 2 min, 20 °C/min to 120 °C, and 2.5 °C/min to 285 °C and held for 18.5 min. Additional procedures have been described previously[31].

Pesticide detection required (a) retention index agreement between sample and standards, (b) the presence of the quantification ion plus at least one other characteristic ion, and (c) the confirmation of the relative ion abundance ratio of at least one of the characteristic ions to the quantitation ion. Quantitation levels were set equivalent to the limit of detection and were estimated using the approach of Miller and Miller[45], using 0.0015 alpha and 0.025 beta error levels. Sample-specific quantitation levels (< values in Table II and in the supplement[41] for all pesticides) ranged from about 0.1 to 45 ng/L and varied based on sample volume and because of changes in instrument response over the 4-month timeframe of sample analyses.

RESULTS AND DISCUSSION

Quality-control samples represented a large percentage of the total samples processed during GLSE application in the Yakima basin, since the device was in the evaluation stage. Of the 56 total GLSE extractions performed, 32 were natural samples (including triplicate ~10-L extractions of water collected from the Yakima River at Kiona), 11 were matrix spiked samples (including triplicate ~10-L matrix spike extractions of water from the Yakima River at Kiona), and 13 were blanks (8 FG blanks and 5 extractor blanks).

Blanks

Of the 69 pesticides measured (which included 67 of the 68 pesticides added to fortified samples plus 2 triazine herbicide degradation products), 34 were not detected in any blanks. Only methyl parathion (mean concentration of 12 ± 3 ng/L in 3 blanks) and 4,4′-DDE (2.0 ng/L in 1 blank) were detected in blanks greater than quantitation levels. Methidathion and triadimefon were each detected in a blank sample at a concentration less than the quantitation level, but greater than the limit of decision, which is ~1.5 times lower[45]. All other observed pesticides

were detected at trace levels lower than the detection level (frequency of detection information for all analytes is provided in Table II supplement[41]).

Those compounds that exhibited more than two detections in all of the blanks correlated with the most frequently identified pesticides in the samples (e.g., 4,4′-DDE, malathion, atrazine, and simazine, Table II). Most detections in the blanks presumably were attributable to carryover from the preceding spike sample, and likely arose from incomplete cleaning of the cans or components of the GLSE, or both, since detections were often observed in extractor blanks. Blank volumes were close to the ~10-L field samples, but were kept low because of limitations in the amount of distilled water on hand. The majority of trace detections in blanks suggested artifacts and carryover in quantitation were not problematic. However, results from low-volume blanks may not have been completely representative of large-volume samples that required longer processing times, used substantially more DCM, and, in the case of ~110-L samples, required three cans. Additional cleaning of the cans and GLSE components beyond that undertaken in this study seems necessary to further minimize carryover.

Surrogate recoveries

Surrogate compounds were added to all GLSE extractions to monitor method performance from the GLSE step through GC-EIMS. The surrogates used had structural similarities to three of the pesticide classes under investigation. The surrogate solution was added to the filtered water sample in the can(s) prior to processing through the GLSE.

Mean surrogate recoveries, along with percent relative standard deviation (%RSD) of the mean, are shown in Table III for the blanks, for three surface-water sample volume ranges, and for all sample types. Mean recoveries for [$^2H_{10}$]diazinon, [$^2H_5$]atrazine, and terbuthylazine were >75% for all but the largest sample volumes. The lower recoveries for these surrogates at larger sample volumes were expected on the basis of extraction theory[3]. Mean recoveries for γ-[$^2H_6$]HCH were similar at all volumes, were lower than predicted based on recoveries of γ-HCH observed in our previous studies[3,43], and were likely lower, in part, because of volatilization losses during DCM volume reduction of the extracts to 200 μL. In several cases (e.g., Sulfur Creek, Table II), γ-[$^2H_6$]HCH recoveries were extremely poor even though recoveries for [$^2H_{10}$]diazinon, [$^2H_5$]atrazine, and terbuthylazine were good. Nevertheless, mean recoveries of γ-[$^2H_6$]HCH for 35-L samples were ~20 to 40% greater than those obtained for the surrogate δ-HCH previously tested in GLSE samples from the Yakima River basin[32]. Isodrin and 4,4′-[$^2H_8$]DDT recoveries were unusually low, especially considering that extraction theory predicts a near 100%

recovery for these hydrophobic chemicals (if truly in the dissolved phase) at volumes up to 120 L[43]. For [$^2H_8$]DDT, a mean percent recovery is shown only under the all-sample-types category and does not include the 40 nondetections. A 10 to 12% loss of [$^2H_8$]DDT via sorption to a single can wall is predicted based on the amount of DDT observed in can rinses from previous spike recovery studies[43,46]. However, much of the apparent loss (or nonrecovery) of [$^2H_8$]DDT was due to unmonitored conversion of this compound to 4,4′-[$^2H_8$]DDD in the GC injection port. A follow-up investigation of this GC degradation problem was undertaken for a subset of the Yakima samples[47], which revealed sample matrix-enhanced GC degradation of [$^2H_8$]DDT in excess of 60% for some Yakima samples. These degradation amounts were well above the levels of degradation indicated by bracketing injections of a performance-evaluation standard containing [$^2H_8$]DDT. Reasons for low recoveries of isodrin are less obvious, but may be caused by unrecognized GC degradation or by instability of this pesticide in water. Schradan, another candidate surrogate, appeared unstable, was not recovered, and was omitted. This organophosphorus compound also may have been susceptible to GC degradation.

Batch spiking of the surrogate solution to the filtered sample while in the milk can, as was performed in this study, was logistically simpler than continuously metering in the spiking solution to the sample influent stream, as was done in our previous Yakima River field study[32], even though the latter on-line technique[39] has been a popular procedure in GLSE applications[6,9,10,13,18,21,28,37]. The batch spiking approach allows the surrogate an opportunity to undergo sorption to the can wall and to sample DOC and colloids, and to possibly undergo degradation reactions in the water, providing a mechanism for further gaging matrix effects that might go unrecognized with the on-line metering approach. On-line metering of the surrogates into the GLSE would minimize these potential loss processes[28], as would direct addition of the entire surrogate solution into the GLSE prior to beginning the extraction, another reported fortification approach[20,21,23].

Matrix spike recoveries

Matrix spike samples were prepared using filtered water collected from select locations in the Yakima basin (Table II) and were used as a mimic of the natural water samples to assess recovery of the 68 amended pesticides from water volumes of ~10, 35, and 110 L. Mean recoveries were determined for organochlorine (Figure 2a) and organophosphorus (Figure 2b) insecticides, triazine and chloroacetamide herbicides (Figure 2c), and several carbamate, thiocarbamate, and miscellaneous pesticides (Figure 2d). Mean recoveries are shown for spikes

of triplicate 10-L aliquots of water from the Yakima River at Kiona (labeled Kiona 10 L in Figure 2), ~12-L samples from Sulfur Creek and Granger, Moxee, and South Drains (Four 12-L sites), ~36-L samples from the Yakima River at Umtanum and Kiona (Two 36-L sites), and ~110-L samples from Satus Creek and Pacific Power Wasteway (Two 112-L sites). Error bars in Figure 2 represent either one standard deviation of the mean or, for the 36- and 110-L spikes, the high recovery.

All spike recoveries were corrected for the amount of native pesticides detected in the corresponding unspiked sample (Table II) that was processed through the GLSE immediately prior to the matrix spike. For the Kiona 10-L spikes, recovery corrections were calculated using the mean of triplicate ~10-L unspiked sample extractions at this site (Table II[41]). The spike amounts were nominally 50, 28, and 11 ng/L at 10-, 35-, and 110-L volumes, respectively. These fortification levels were too low for many analytes because comparable or higher concentrations of the pesticides were measured in the corresponding unspiked samples, especially in the three drains and Sulfur Creek that receive the heaviest pesticide inputs from runoff[31]. For example, relatively high ambient concentrations were observed at one or more sample location for diazinon, atrazine, simazine, and propargite (Table II; see[41] for all pesticides). In some cases, recovery corrections produced abnormally low recoveries, and even negative recoveries for six pesticides, and resulted in negative mean recoveries for simazine and propargite for the four 12-L sites. For example, concentrations of propargite in the corresponding unspiked 10-L samples ranged from 40 to 260 ng/L (Table II), the latter being 5 times higher than the spike concentration (assuming no native propargite in the sample). In other instances, recoveries well in excess of 100% were obtained and the correction appeared insufficient or was not applied because the pesticide was detected below the quantitation level in the unspiked sample. Examples of apparent substantial positive bias occurred for the chlordanes, endrin, and several of the organophosphorus insecticides, including methyl parathion and phosphamidon. The combined low fortification levels in the spikes coupled with natural occurrence in the unspiked samples strongly influenced both the resultant mean recoveries and variability for a number of pesticides over the volume ranges tested. Consequently, the best indication of GLSE method performance, especially for ~10-L extractions, should be the triplicate Kiona 10-L mean recovery information, since recovery corrections were based on the mean of triplicate unspiked concentrations, the precision for which ranged up to 27% RSD for prometon (Table II). In general, recoveries for the Kiona 10-L spike samples were either comparable to or 10 to 20% less than previously determined using amended quadruplicate 10-L samples from two Colorado creeks[43]. Although a common practice, matrix spiking at levels near ambient pesticide concentrations poses additional variability to method perform-

ance assessments. However, this approach remains the most efficient way to obtain recovery information in natural waters for each analyte in broad-spectrum pesticide analyses.

In a trend comparable to the surrogate recoveries, the organophosphorus insecticides (OPs) and especially the triazine and chloroacetamide herbicides had overall higher recoveries than did the organochlorine insecticides (OCs). The results of this study show that the GLSE can efficiently preconcentrate pesticides which have K_{ow}'s less than $10^4$and indicate that broad spectrum analysis with the GLSE is feasible, as also recently reported by Sabik et al[9] for 16 moderately polar pesticides from 35-L water samples.

Reduced recoveries observed for most of the triazine, chloroacetamide, organophosphorus, and miscellaneous pesticides in 110-L spike samples (Figure 2) clearly show the thermodynamic limitations in GLSE extraction efficiencies expected for larger volume samples[3,4,42]. For example, metribuzin (K_{ow} of $10^{1.7}$[48]) and dimethote (K_{ow} of $10^{0.8}$[48]) show a trend of decreasing recoveries with increasing sample volumes reflective of pesticides with K_{ow}s < 10^3 and sample volumes from 10 to 110 L[3]. For most of the pesticides sampled in the Yakima basin, however, GLSE extraction theory predicts efficient isolation up to the optimal 50-L volume for which the device was designed, and this prediction was verified from the matrix spike results. With low to moderate K_{ow}'s, most of these pesticides exhibited minimal or no sorption to colloids, DOC, or the can walls. A number of the organophosphorus compounds should have behaved similarly, but may have been confounded by GC degradation problems. Pesticide degradation in the water sample also can bias the results. For example, Sabik et al.[9] observed low recoveries of spiked chloropyrifos in filtered water samples isolated by the GLSE and speculated that hydrolysis substantially reduced recoveries. In our study, chloropyrifos was well recovered (>80%) as predicted from its K_{ow} of $10^{5.0}$[48]. However, although methamidophos produced good GC-EIMS calibration curves, it was not recovered in any spikes and appeared to be unstable in the water samples.

As observed for the [$^2H_8$]DDT surrogate (see above), a portion of 4,4′-DDT's apparent poor recovery (Figure 2a) was attributable to substantial matrix-enhanced degradation of this pesticide in the GC injection system[47]. Other method pesticides are recognized (see citations in[47]) as thermolabile (e.g., endrin, 2,4′- and 4,4′-methoxychlor, azinphos-methyl, dimethoate, methamidophos, malathion, terbufos, carbaryl, and carbofuran) and also may have undergone variable amounts of GC-derived degradation leading to poorer and more variable recoveries that may not be attributable to GLSE performance. However, GC-derived degradation is not believed responsible for the low recoveries of other presumably thermostable compounds, e.g., mirex and the permethrins.

TABLE III Mean percent recoveries of pesticide surrogate compounds from Goulden large-sample extractor samples

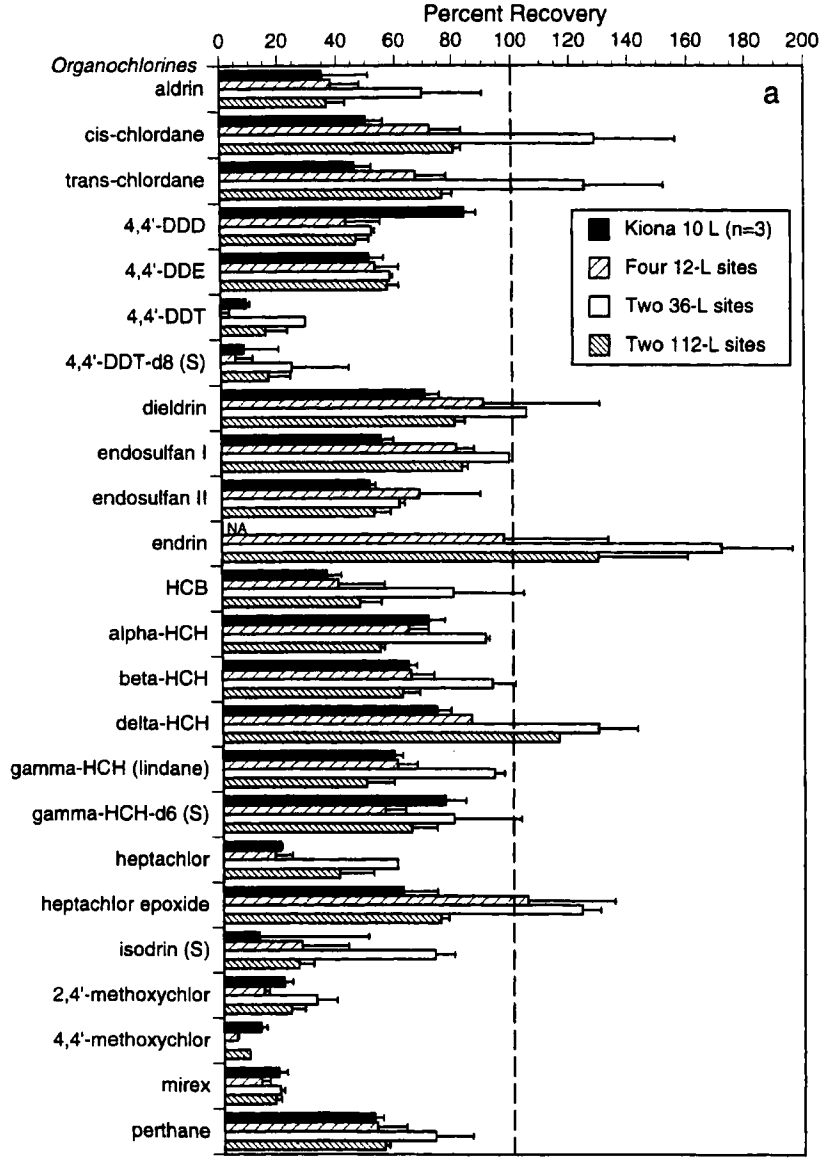
Sample vol., L	*Total no. of samples*	*Mean % recovery (% relative standard deviation)*					
		[$^2H_{10}$]Diazinon	*γ-[$^2H_6$]Hexachlorocyclohexane*	*Isodrin*	*[$^2H_5$]Atrazine*	*Terbuthylazine*	*4,4'-[$^2H_8$]DDT*
5.0 – 7.7 blanks[a]	13	81 (20)	59 (73)	18 (106)	84 (17)	84 (18)	
4.4 – 12	14	93 (15)	61 (43)	18 (89)	91 (20)	88 (26)	
34 – 37	17	87 (12)	62 (34)	45 (31)	76 (14)	80 (11)	
72 – 113	11	69 (38)	65 (31)	27 (63)	47 (40)	63 (32)	
All samples/blanks	55	84 (21)	62 (45)	28 (71)	76 (29)	79 (24)	15 (87), n=16[b]

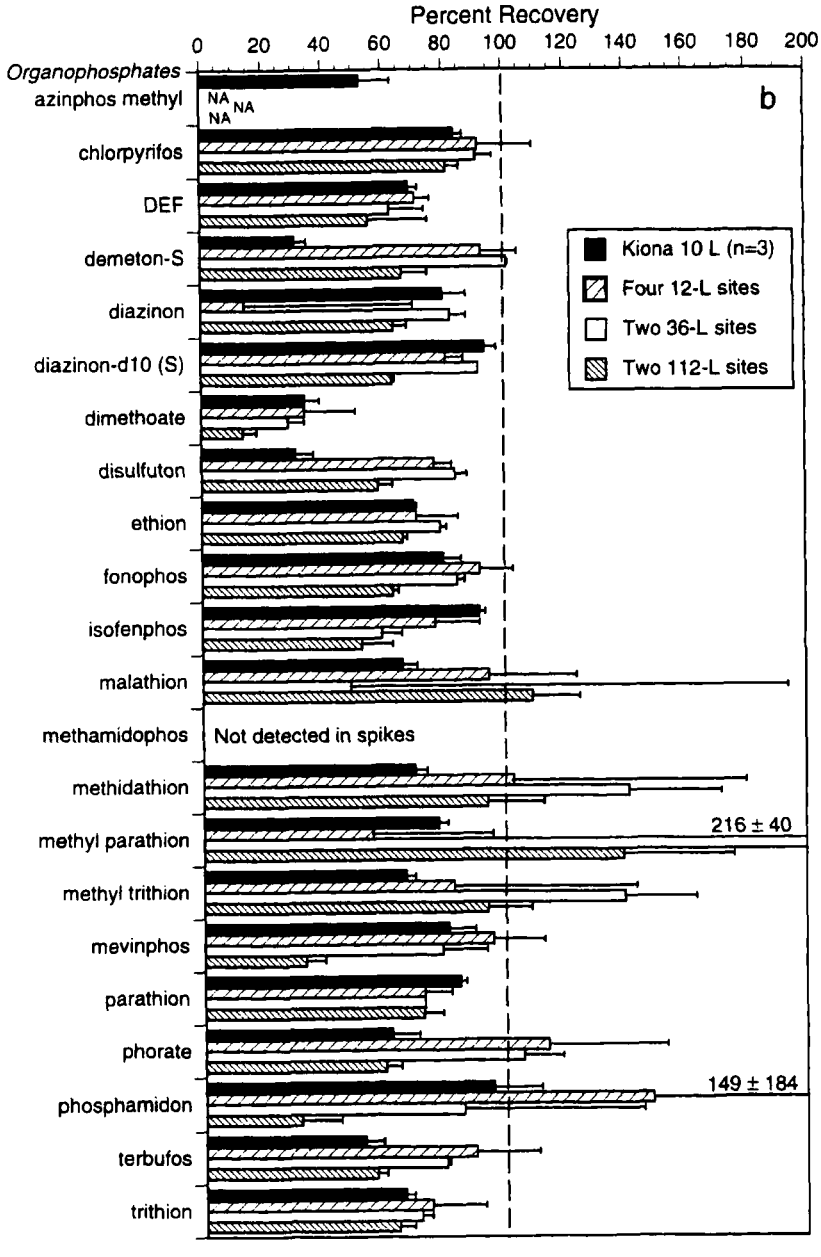
a. Distilled water FG or extractor blanks.
b. n, number of quantifiable observations used to compute mean recovery.

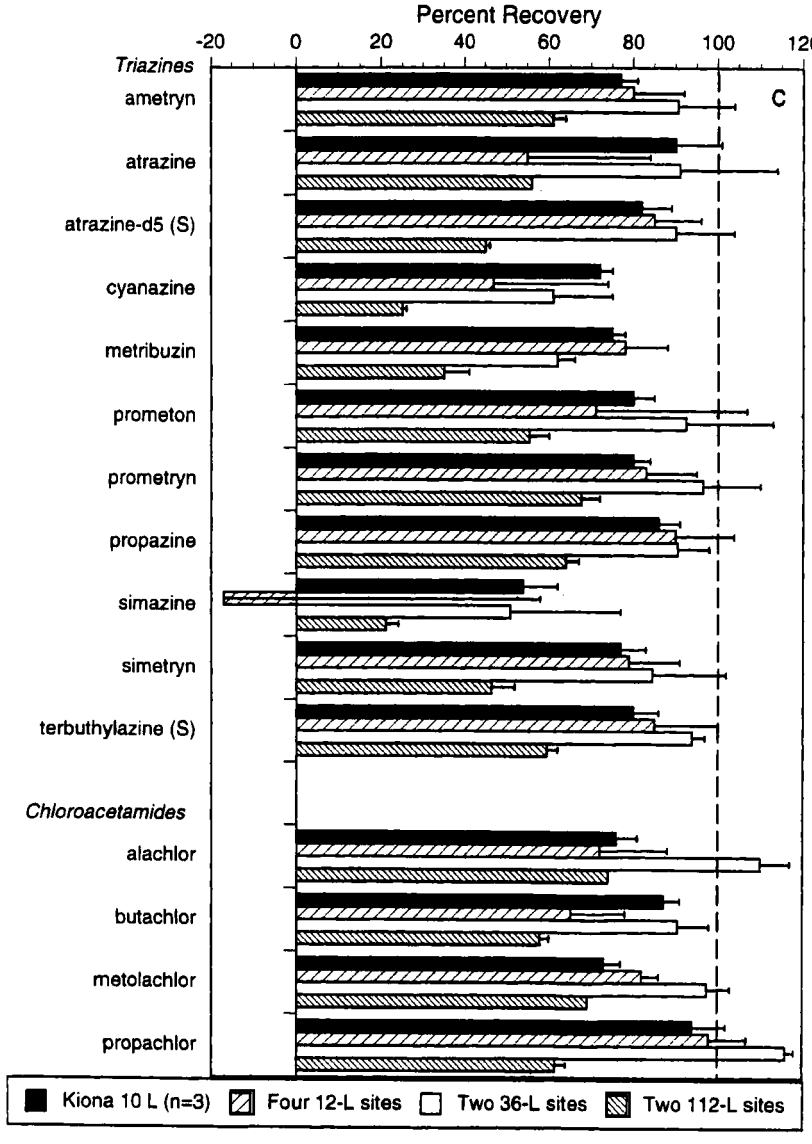
Most of the OCs have relatively large K_{ow}'s (i.e., > $10^{3.5}$)[49] and, hence, are predicted to have high DCM/water partition coefficients and expected recoveries of nearly 100% at volumes up to 110 L. However, predicted high recoveries are dependent on the compound being in the truly dissolved phase. Because many of the OCs also have relatively high sediment/water (K_d) and DOC/water (K_{doc}) partition coefficients, they were likely to have partitioned to some extent into colloidal materials in the filtered water samples during the > 0.5 h equilibration period preceding GLSE isolation. Anthony[40] noted that the GLSE was capable of providing estimates of contaminant "dissolved-phase" concentrations, but the device was not designed to extract pollutants associated with small particles, colloids, and DOC in filtered water. The rapid sample flow rates do not allow much time for contact of the sample with DCM for exhaustive particle phase extraction. Foster[42] attempted to model the effect that contaminant uptake by DOC and colloids has on limiting GLSE extraction efficiency, and he noted that this effect can be substantial for very hydrophobic contaminants like cis- and trans-permethrin. In addition, studies by Driscoll et al[50] and Maguire et al[51] show that for many OCs, efficient solvent extraction into hexane is achieved only after treatment of surface water samples with chromic acid to digest humic substances. Moreover, the OC mirex showed the greatest reduction in extraction efficiency without the chromic acid treatment[50,51], suggesting that mirex may be partitioned into colloidal materials present in the filtered water samples, thereby affecting GLSE recoveries in our study.

Sorption of hydrophobic contaminants to the container walls also lowers recoveries, as noted above for the [$^2H_8$]DDT surrogate. Previous studies[43,46] demonstrated that some pesticides were found in can rinses, with butachlor (9% maximum observed), DDT (12%), ethion (14%), cis- and trans-permethrin (26%), propargite (10%), and trifluralin (12%) exhibiting some of the highest sorbed amounts. Not all of the pesticides were tested in the earlier studies. Chemical residues remaining in the cans were not determined in these GLSE spike samples. After processing all of the water sample through the GLSE, the procedure could be modified to incorporate DCM rinsing of the pesticides from the can surfaces, followed by pumping of this DCM into the GLSE for collection with the extractor DCM.

For some compounds, combinations of the loss mechanisms outlined above produced the low recoveries and/or high variability observed. Clearly, reported concentrations[31] are underestimates of the total concentration in filtered Yakima basin water samples for a number of the OCs and some other pesticides. Nevertheless, the GLSE method provided at least 1 to 2 orders of magnitude lower quantitation levels than was available with traditional 1-L methods for pesticides in water in use at the National Water Quality Laboratory.







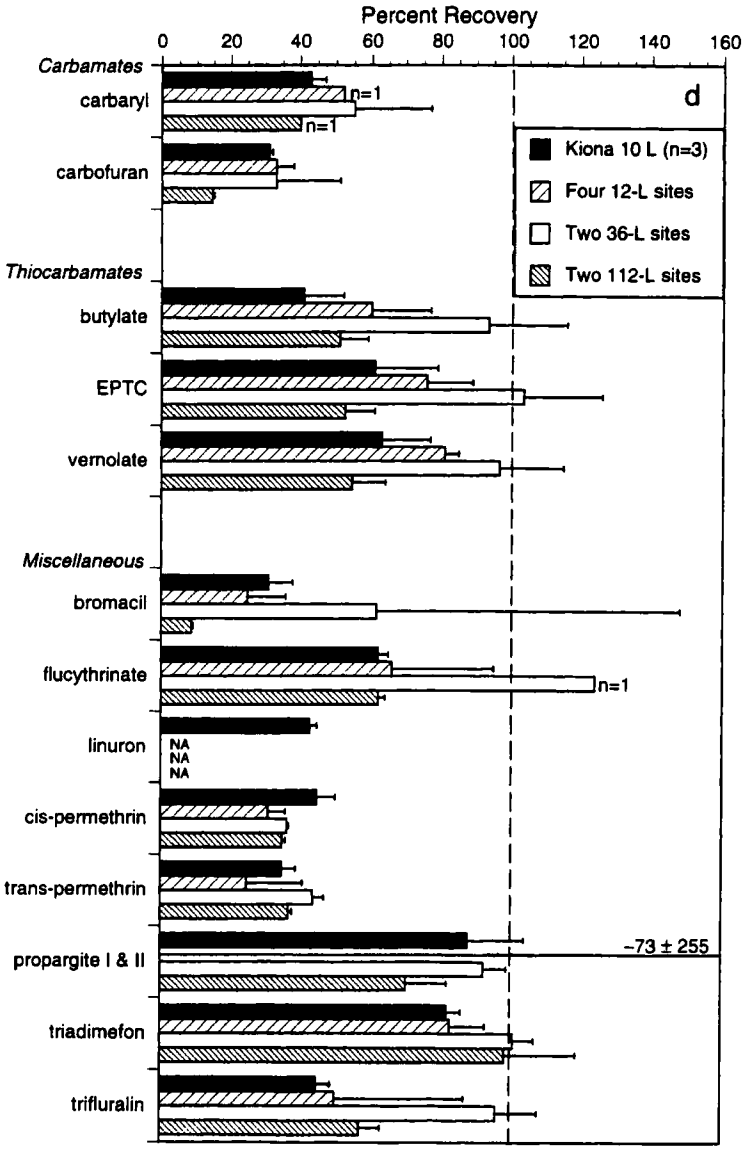


FIGURE 1 Mean recoveries of (a) organochlorine and (b) organophosphate insecticides, (c) triazine and chloroacetamide herbicides, and (d) carbamate, thiocarbamate and miscellaneous pesticides, spiked into triplicate 10-L aliquots of water from the Yakima River at Kiona (Kiona 10 L), into ~12-L water samples from four sites (Four 12-L sites), into ~36-L samples from two sites (Two 36-L sites), and into ~112-L samples from two sites (Two 112-L sites). Sites correspond to those listed in Table II. Error bars represent either one standard deviation of the mean or, for the 36- and 112-L spikes, the high recovery. (S), surrogate compound; NA, not analyzed. See text for details

Although the quality control samples collected in this study did not represent a rigorous evaluation of the GLSE GC-MS method, our observations suggest performance capabilities ranging from marginal to excellent for many of the compounds not previously tested using this method. Our findings also highlight the need to include field quality-control procedures in environmental studies even for compounds whose performance previously was well characterized.

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