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Comparison of Pressurized Liquid Extraction and Matrix Solid Phase Dispersion for the Measurement of Semi-Volatile Organic Compound Accumulation in Tadpoles

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Abstract

Analytical methods capable of trace measurement of semi-volatile organic compounds (SOCs) are necessary to assess the exposure of tadpoles to contaminants as a result of long-range and regional atmospheric transport and deposition. The following study compares the results of two analytical methods, one using pressurized liquid extraction (PLE) and the other using matrix solid phase dispersion (MSPD), for the trace measurement of over 70 SOCs, including current-use pesticides, in tadpole tissue. The MSPD method resulted in improved SOC recoveries and precision compared to the PLE method. The MSPD method also required less time, consumed less solvent, and resulted in the measurement of a greater number of SOCs than the PLE method.

Keywords: tadpoles, semi-volatile organic compounds, pesticides, pressurized liquid extraction, matrix phase solid dispersion

Introduction

Declines in amphibian species have been reported worldwide [1-4]. Several factors have been suggested to be responsible for these declines, including climate change, ultraviolet radiation, habitat destruction, introduced species, disease, and contaminants [5-9]. While multiple factors are likely responsible for the declines, among contaminants, pesticide exposure has been suggested to be important [5, 10-20].

Many pesticides are semi-volatile organic compounds (SOCs), and undergo both long-range and regional atmospheric transport and deposition to remote ecosystems [21-26]. Recently, Hageman et al. and Usenko et al. have shown that regional agricultural sources are responsible for a significant portion of the pesticide deposition in remote U.S. mountain ecosystems [22, 25]. Previous studies have linked atmospheric transport and deposition of pesticides in remote areas of the Sierra Nevada Mountains to their proximity to the intensely agricultural Central Valley of California [19, 20, 22, 26-29].

Exposure of amphibians to pesticides and other SOCs occurs in low elevation ecosystems near sources, in high elevation ecosystems, and in other remote ecosystems. Previous studies on amphibian SOC body burdens have focused on measuring a fairly limited number of pesticides in tadpole or frog tissue [17, 19, 20, 27-34]. However, amphibians are likely exposed to a far greater array of pesticides. For example, over 500 different pesticides were applied in 2006 in California alone [35] (http://www.cdpr.ca.gov/docs/pur/pur06rep/06_pur.htm).

In the present study, two analytical methods were compared for the trace measurement of over 70 SOCs, including current-use pesticides and their degradation products, in tadpole tissue. One method used pressurized liquid extraction (PLE)

(referred to as the "PLE Method") and was similar to a PLE method developed for measuring SOCs in fish with a moderate to high lipid content (0.71 – 18 %) [36]. The second method used matrix solid phase dispersion (MSPD) (referred to as the "MSPD Method"). MSPD has been used for the measurement of SOCs in food products, as well as animal samples, including tadpoles and frogs, and is a relatively simple method for the extraction of SOCs from samples with a low to moderate fat content [32, 37, 38]. Because tadpoles have a relatively low lipid content (0.01 – 3.3 %) (unpublished data), MSPD was evaluated as a potential extraction method. In order to assess the current state of tadpole exposure to pesticides at low concentration, the objectives of this research were to develop and validate an analytical method to identify and quantify low concentrations of current-use and historic-use pesticides in tadpole tissue.

Materials and Methods

Chemicals and materials

In the summer of 1999, Pacific chorus frog (*Pseudacris regilla*) and Cascades frog (*Rana cascadae*) tadpoles were collected from lakes, ponds, and creeks in the Cascade Mountain Range in Northern California. In the summer of 2003, *P. regilla* tadpoles were collected from several lakes in Sequoia and Kings Canyon National Park. Tadpoles from both regions were pooled and used for analytical method development and validation.

Tadpoles were placed in cryovials and in liquid nitrogen or on dry ice after collection and during shipment and were stored at -20ºC to -80ºC until analysis. A liquid nitrogen – cooled mortar, CoorsTek 99.5% alumina pestles (100 mm) and sodium sulfate

(Na_2SO_4) was purchased from VWR (West Chester, PA, USA). Octadecylsilyl (C_{18}) (bulk sorbent), empty 60 ml solid phase extraction (SPE) columns, and silica SPE columns (Mega Bond-elut 20 g) were purchased from Varian, Inc. (Palo Alto, CA, USA). Non-labeled SOC standards (**Table 1**) were purchased from Chemical Services (West Chester, PA, USA), Restek (Bellefonte, PA, USA), Sigma-Aldrich (St. Louis, MO, USA), and AccuStandard (New Haven, CT, USA), or obtained from the U.S. Environmental Protection Agency repository [39]. Isotopically labeled chemical standards, including 24 surrogate standards, were purchased from CDN Isotopes (Pointe-Claire, QC, Canada) and Cambridge Isotope Laboratories (Andover, MA, USA) and used for quantificaiton [39]. All chemical standards were stored at 4°C until use. Optima grade solvents (acetonitrile, dichloromethane, hexane, and ethyl acetate) were purchased from Fisher Scientific (Fairlawn, NJ, USA).

Pressurized Liquid Extraction (PLE) Method

The PLE method was used to extract SOCs from tadpole tissue as described in Ackerman et al. 2008 for extracting SOCs from fish tissue [36]. Briefly, 2 grams of frozen, ground tadpole tissue was further ground with 65 g Na_2SO_4 (enough to fill the PLE cell) and the mixture was packed into a 66 ml PLE cell (Dionex, Salt Lake City, UT, USA). In the case of SOC spike and recovery experiments, non-labeled SOC standards (Table 1) were added to the ground sample at the top of the PLE cell prior to extraction to assess SOC recoveries over the entire analytical method. In order to measure and subtract the background SOC concentration in the tadpole tissue (tissue blanks) used in the spike and recovery experiments, the isotopically labeled surrogates were added to the ground sample at the top of the PLE cell prior to extraction. Lab blank experiments

consisted of 65 g Na_2SO_4 without tadpole tissue packed into the PLE cell and spiked with the isotopically labeled surrogates at the top of the PLE cell prior to extraction. The standards, both non-labeled and labeled, were spiked at approximately 150 ng and the PLE conditions used dichloromethane (DCM) at 100ºC, 1500 psi, 2 cycles of 5 min, and 150% flush volume [36] (see **Table 2** for PLE method details). Additional Na_2SO_4 was added to the extracts to remove any remaining water. The extracts were reduced in volume (TurboVap II, Caliper Life Sciences, Hopkinton, MA, USA; 12 psi N_2, 30 ˚ C), solvent exchanged to hexane, purified with silica gel, solvent exchanged to DCM and further purified using gel permeation chromatography (Waters, Milford, MA, USA) [36].

Matrix Solid Phase Dispersion (MSPD) Method

The ground tadpole tissue (2 g) was further ground with C_{18} and Na_2SO_4 in proportions of 1:5:17.5 by weight, respectively. The tadpole to C_{18} ratio was similar to a previously published MSPD method [38] and the Na_2SO_4 ratio was adjusted so that the mixture filled the solid phase extraction column within approximately 2 cm of the top of the column. This tadpole mixture was packed into a 60 ml solid phase extraction column containing 30 g Na_2SO_4. In the case of SOC spike and recovery experiments, non-labeled SOC standards (Table 1) were added to the tadpole mixture on the top of the MSPD column to assess SOC recoveries over the entire analytical method. Tissue blanks and lab blanks were analyzed as described in the PLE method, by spiking the isotopically labeled surrogates on the top of the MSPD column prior to extraction. The standards, both non-labeled and labeled, were spiked at approximately 150 ng. The MSPD column containing the ground tadpole sample, was placed on a vacuum manifold (Supelco, Bellefonte, PA, USA), a vacuum was applied, and the sample was eluted with 300 ml

acetonitrile, followed by 100 ml DCM at a flow rate of approximately 25 ml/min (see Table 2 for MSPD method details). The DCM fraction was reduced and stored as an archive fraction. To determine if additional SOCs were eluted from the MSPD column with the DCM, this fraction was analyzed and contained no spiked SOCs. Acetonitrile was chosen as the MSPD column elution solvent because of its ability to simultaneously elute SOCs with a wide range of polarities. The acetonitrile fraction was reduced to 0.5 ml using a TurboVap II (12 psi N_2, 30 ˚ C), approximately 1.0 ml hexane was added, and silica cleanup was performed. The 20 g silica solid phase extraction column was preconditioned as described in [36] and the SOCs were eluted from the column using 100 ml ethyl acetate. Different silica column elution solvents were tested and it was determined that ethyl acetate successfully eluted the target SOCs with minimal co-elution of matrix interferences.

Instrumental Analysis

Just prior to instrumental analysis, the triplicate recovery extracts were reduced and spiked with the isotopically labeled surrogates and internal standards to assess spiked SOC recoveries over the entire method. In the case of the tissue and lab blanks, the internal standards were spiked into the extract just prior to instrumental analysis.

Semi-volatile organic compounds were identified and quantified using an Agilent 6890 gas chromatograph (Santa Clara, USA) coupled to an Agilent 5973N mass selective detector. Briefly, 1 µl of the extract was injected using an HP 7683 autosampler, a pulsed splitless injection was performed, and 30 m x 0.25 mm inner diameter x 0.25 um film thickness DB-5 column (J&W Scientific, Palo Alto, CA, USA) was used for separation of the SOCs [39]. Standard calibration curves were prepared prior to instrumental analysis

of samples. Selective ion monitoring mode was used to identify and quantify the SOCs. Either electron impact ionization or electron capture negative ionization was used based on the mode of ionization with the lowest instrumental detection limit for a given SOC [39].

For quality assurance and quality control, one lab blank was included with each batch of samples. Calibration curves were monitored throughout using check standards run for every 3 to 4 samples. Ion abundances were considered a match if they were within ± 20% of the standard or National Institute of Standards and Technology mass spectra library. A signal to noise ratio of 3:1 was used in identification of target analytes and retention times were monitored such that identified target analytes matched check standards within ± 0.05 minutes. Sample specific estimated detection limits were calculated using Environmental Protection Agency method 8280A [40] (**Table 3**). The instrumental limits of detection, ions monitored, and gas chromatograph oven parameters for electron impact mode and negative chemical ionization mode have previously been published [39].

Statistical Analysis

Average analyte recoveries were compared using a two-sided, two-sample t-test in SPLUS (version 8.0). A p value < 0.01 was considered significant. Individual SOC average recoveries greater than 180 % or less than 20 % were excluded from statistical analysis, including average and standard deviation calculations, as these recoveries were outside the acceptable range.

Results and Discussion

Comparison of PLE Method for Fish and Tadpoles

The PLE method resulted in higher average SOC recoveries from fish tissue (54.8 ± 15.5 % [standard deviation]) than from tadpole tissue (46.8 ± 15.3 %) (ref. [36] and Table 1). This was especially true for the DDXs (DDTs, DDDs, and DDEs), and PCBs ($p < 0.01$) (Table 1). The additional SOC losses from tadpole tissue in the PLE method may have been due to higher SOC losses during extract evaporation and solvent exchanges.

The precision for the PLE method, as indicated by the percent relative standard deviations of the SOC recoveries, was higher for the fish tissue (ranged from 0.46% to 21.6%, with an average of 5.88%) than for the tadpole tissue (ranged from 17.4% to 96.9%, with an average of 34.1%) (ref. [36] and Table 1). This may also be due to additional SOC losses during tadpole extract evaporation and solvent exchange.

Comparison of PLE and MSPD Methods for Tadpoles

The MSPD method had significantly higher average SOC recoveries for tadpole tissue (80.6 ± 25.9 %) than the PLE method (46.8 ± 15.3 %) (Table 1) ($p < 0.01$). In addition, the average MSPD recoveries of organochlorine pesticides, organophosphorous pesticides, PCBs, and PAHs were significantly higher than the average PLE recoveries of these same SOCs ($p < 0.01$). However, the MSPD average recoveries for dieldrin and endrin were above the acceptable range (Table 1) and may be the result of these target analytes not behaving in the same manner as the labeled surrogate standards they were quantified against (d_4-endosulfan I and d_4-endosulfan II, respectively). The average tadpole PLE recoveries of acenaphthylene, acenaphthene, parathion, and endrin aldehyde were below the acceptable range (Table 1) and may be a result of losses during solvent evaporation.

The MSPD method also had higher precision, as indicated by the percent relative standard deviation of the SOC recoveries, (ranging from 0.86 % to 40.7 %, with an average of 11.3 %) than the PLE method (ranging from 17.4 % to 96.9 %, with an average of 34.1 %) for tadpole tissue (Table 1). Instrumental precision was assessed using replicate injections of extracts and standards on an intra- and inter-day basis for both MS ionization modes. Intra-day instrumental precision ranged from 0 % to 20.6 % relative standard deviation for extracts (all SOCs detected; n = 20) and 0.025 % to 13.1 % for standards (all SOCs; n = 10). Inter-day instrumental precision ranged from 0 % to 38.6 % relative standard deviation for extracts (n = 20) and 0.63 % to 15.9 % for standards (n = 13).

The PLE and MSPD estimated detection limits were not significantly different and ranged from 0.19 to 2900 pg/g wet weight (Table 3). Both the PLE and the MSPD methods were capable of detecting, but not quantifying, carbaryl and carbofuran. However, the MSPD method was capable of detecting 15 additional current-use pesticides and their degradation products, including the triazine herbicides, over the PLE method (Table 1). The ability to measure current-use pesticides in tadpole tissue is particularly important because some have been reported to cause sublethal effects in amphibians at low concentrations and are among the pesticides implicated in population declines [16, 18, 20, 41].

In addition to significantly higher recoveries for several SOC classes, better precision, and detection of a larger number of SOCs, the MSPD method resulted in shorter extract preparation time and less solvent consumption (Table 2). The MSPD

method also resulted in reduced use of dichloromethane, a chlorinated solvent and probable human carcinogen (Table 2) [42] (http://www.epa.gov/iris/subst/0070.htm).

Analytical Variability vs. Tadpole SOC Concentration Variability

The MSPD method was used to measure SOC concentrations in tadpole samples collected from several site in the Cascades Mountains, California, USA. Comparisons of the relative standard deviation of intra-day injections of the same tadpole extract (injection replicates), subsamples of the same tadpole sample processed using the MSPD method (analytical replicates), and different tadpole samples collected from the same site and processed using the MSPD method (site replicates) are shown in **Figure 1**. For most SOCs measured in these samples, the site variability (25 to 100% average relative standard deviation) was greater than the analytical (5 to 45%) and instrumental (1 to 5%) variability. This indicates that the MSPD method is precise enough to study intra- and inter-site variability in tadpole SOC concentrations. This method will be used in future studies to understand the accumulation of SOC in tadpoles collected throughout the California Cascade and Sierra Nevada Mountains.

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views and policies of the SWRCB, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. This publication was made possible in part by the U.S. National Institute of Environmental Health Sciences (grant P30ES00210). The authors would like to thank Luke Ackerman and Glenn Wilson for helpful discussions and assistance.

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423 Figure 1. SOC concentration variability among tadpole samples collected from the
424 Cascade Mountains, California, USA using the MSPD method. "Injection
425 replicates" are intra-day injections of the same tadpole extract (n = 9); "analytical
426 replicates" are subsamples of a tadpole sample processed using the MSPD method
427 (n = 8); "site replicates" are different tadpole samples, collected from the same
428 site, processed using the MSPD method (n = 8). "< detection limit" indicates

concentrations were below the estimated detection limit in greater than 50 % of replicates. Only replicate sets with at least 50% detections are shown and values below the estimated detection limit (EDL) were substituted with ½ EDL.

Table 1: Average semi-volatile organic compound recoveries over the entire pressurized liquid extraction (PLE) and matrix solid phase dispersion (MSPD) methods for tadpoles (RSD = relative standard deviation, NR = not recovered)

	Log Kow	PLE Average Recovery (% RSD)	MSPD Average Recovery (%RSD)
Amide Pesticides			
Alachlor	2.6	NR	76.3 (8.6)
Acetochlor	3.0	NR	60.7 (9.7)
Metolachlor	3.1	NR	120 (9.2)
Propachlor	2.4	NR	174 (12.3)
Organochlorines Pesticides and Metabolites			
HCH, gamma	3.8	35.0 (49.3)	76.8 (8.2)
HCH, alpha	3.8	28.0 (64.4)	71.0 (8.6)
HCH, beta	4.0	48.4 (25.8)	87.0 (10.1)
HCH, delta	4.1	47.8 (25.6)	84.6 (8.4)
Methoxychlor	4.5	55.9 (27.3)	92.8 (14.6)
Heptachlor	5.2	44.0 (47.4)	106 (6.5)
Heptachlor epoxide	4.6	27.0 (32.9)	48.7 (10.1)
Hexachlorobenzene	5.5	26.2 (70.8)	64.5 (9.6)
Endrin	5.2	75.3 (24.2)	224 (8.0)
Endrin aldehyde	4.8	13.9 (35.9)	84.6 (14.2)
Chlordane, trans	6.1	26.4 (30.1)	33.1 (12.5)
Chlordane, cis	5.9	27.7 (29.1)	35.8 (13.1)
Nonachlor, trans	6.1	26.5 (29.8)	33.1 (12.7)
Nonachlor, cis	6.1	41.5 (26.9)	50.3 (14.6)
Chlordane, oxy	5.5	27.3 (32.3)	43.4 (11.2)
Dieldrin	5.5	114 (25.4)	236 (8.4)
Aldrin	6.4	37.5 (43.3)	76.6 (8.7)
o,p'-DDT	6.5	40.6 (21.4)	56.4 (11.7)
o,p'-DDD	6.1	49.4 (25.5)	98.6 (18.1)
o,p'-DDE	5.5	45.4 (23.7)	83.7 (9.3)
p,p'-DDT	6.9	43.6 (26.4)	69.6 (11.8)
p,p'-DDD	5.9	54.2 (19.5)	116 (9.2)
p,p'-DDE	6.8	46.4 (23.8)	67.2 (10.5)
Mirex	6.9	51.1 (26.0)	89.5 (14.2)
Organochlorine Sulfide Pesticides and Metabolites			
Endosulfan I	4.7	32.7 (30.2)	46.0 (12.7)
Endosulfan II	4.8	49.7 (26.3)	73.2 (13.3)
Endosulfan sulfate	3.7	53.1 (27.4)	58.5 (9.1)
Phosphorothioate Pesticides			
Methyl parathion	2.7	36.2 (40.6)	63.5 (7.9)
Malathion	2.9	NR	59.9 (18.7)
Diazinon	3.7	NR	70.1 (6.0)
Parathion	3.8	19.4 (75.2)	81.6 (12.0)
Ethion	5.1	38.3 (41.4)	46.6 (17.8)
Chlorpyrifos	5.1	55.0 (36.2)	87.6 (9.5)

	Log Kow	PLE Average Recovery (% RSD)	MSPD Average Recovery (%RSD)
Thiocarbamate Pesticides			
EPTC	3.2	NR	56.5 (8.1)
Pebulate	3.8	NR	65.3 (4.9)
Triallate	4.6	61.3 (40.9)	142 (12.2)
Triazine Herbicides and Metabolites			
Atrazine desisopropyl	1.4	NR	91.2 (0.9)
Atrazine desethyl	1.8	NR	58.8 (40.7)
Atrazine	2.3	NR	84.4 (9.6)
Simazine	2.2	NR	103 (3.2)
Metribuzin	1.7	NR	103 (13.7)
Miscellaneous Pesticides			
Etridiazole	2.6	NR	71.7 (5.9)
Dacthal	4.3	70.5 (34.7)	152 (3.5)
Trifluralin	5.3	38.0 (58.3)	75.9 (9.0)
Polycyclic Aromatic Hydrocarbons			
Acenaphthylene	3.9	14.6 (102)	64.8 (4.9)
Acenaphthene	4.0	21.0 (93.6)	65.1 (6.9)
Fluorene	4.2	19.6 (91.8)	60.0 (8.5)
Anthracene	4.5	33.2 (49.0)	76.4 (8.2)
Phenanthrene	4.5	23.9 (96.9)	50.4 (15.8)
Pyrene	5.1	48.7 (20.4)	79.3 (10.5)
Fluoranthene	5.2	48.4 (21.6)	79.4 (12.0)
Chrysene + Triphenylene	5.7	51.4 (24.5)	106 (17.6)
Benzo(a)anthracene	5.9	61.3 (22.8)	100 (13.4)
Retene	6.4	63.3 (20.4)	94.0 (11.6)
Benzo(k)fluoranthene	6.5	54.5 (24.6)	104 (16.5)
Benzo(a)pyrene	6.5	46.1 (17.4)	73.1 (11.0)
Benzo(b)fluoranthene	6.6	58.5 (24.6)	113 (17.6)
Benzo(e)pyrene	6.9	57.6 (24.4)	108 (17.5)
Indeno(1,2,3-cd)pyrene	6.7	57.2 (24.2)	83.5 (10.6)
Dibenz(a,h)anthracene	6.8	55.2 (25.5)	91.0 (9.7)
Benzo(ghi)perylene	7.0	51.9 (24.2)	77.5 (9.6)
Polychlorinated Biphenyls			
PCB 74	6.3	45.8 (32.5)	101 (10.5)
PCB 101	6.4	47.4 (33.9)	87.3 (12.3)
PCB 118	7.0	47.7 (35.6)	75.0 (15.3)
PCB 153	6.9	50.1 (34.2)	96.4 (9.4)
PCB 138	6.7	51.8 (34.1)	99.1 (10.2)
PCB 187	7.2	49.7 (36.1)	86.3 (10.4)
PCB 183	8.3	49.8 (35.8)	86.2 (10.8)
Ave, Min, and Max Recoveries, % RSD			
ave		46.8 (34.1)	80.6 (11.3)
max		114	236
min		14.6	33.1

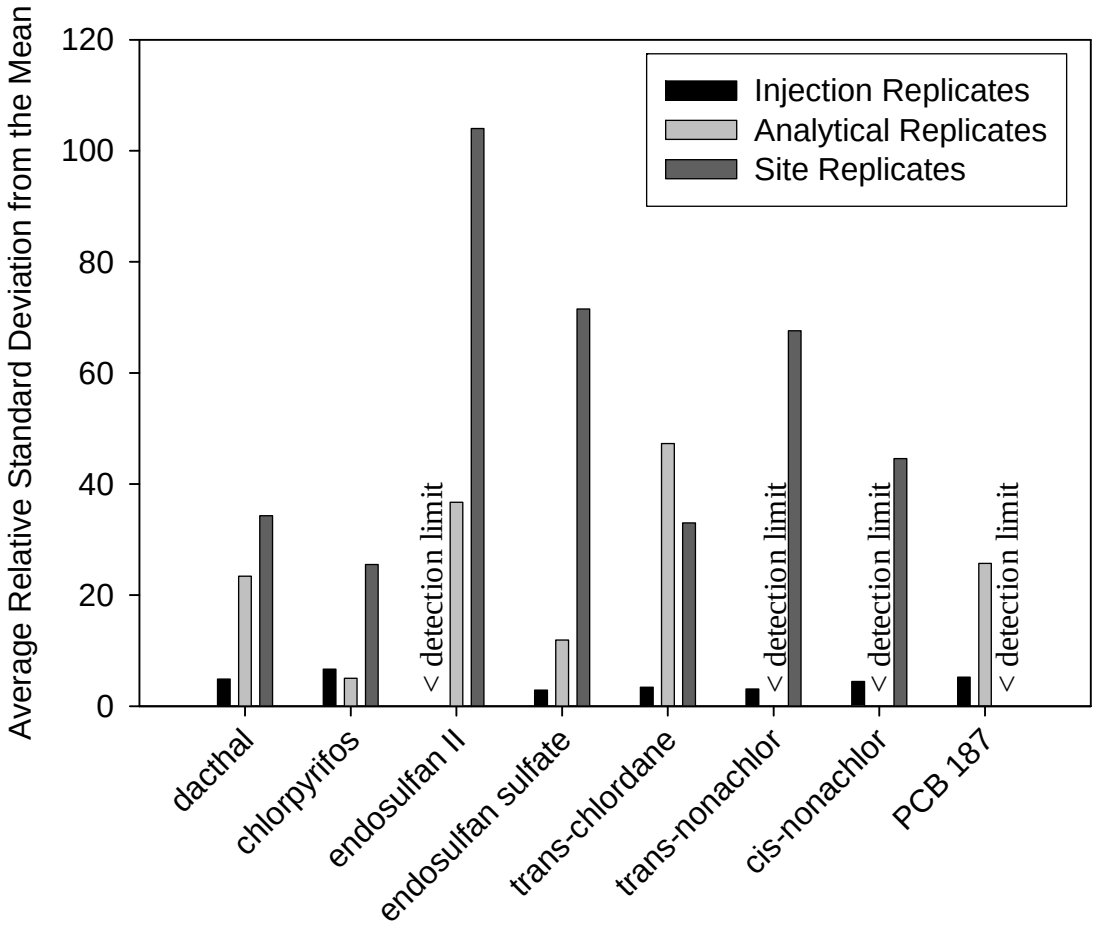
Table 2: PLE and MSPD method conditions (DCM = dichlormethane, MeCN = acetonitrile, HEX = hexane, EA = ethyl acetate, SPE = solid phase extraction)

	PLE method	**MSPD method**
Sample Mass	2 g	2 g
Grinding Agent	Na_2SO_4	Na_2SO_4, C_{18}
Mass	65 g	35 g, 10 g
Extraction		
Pressure / Flow	1500 psi	25 ml/min
Temperature	100ºC	25ºC
Solvent	DCM	MeCN, DCM
Solvent Volume	200 ml	300ml, 100 ml
Solvent Exchanges	2	0
HEX	4 X 10 ml	
DCM	4 X 10 ml	
Extract Purification	**Silica SPE**	**Silica SPE**
Conditioning Solvent	HEX, EA, DCM	HEX, EA, DCM
Solvent Volume	75 ml, 40 ml, 25 ml	75 ml, 40 ml, 25 ml
SPE Solvent	HEX, DCM	EA
Solvent Volume	62.5 ml, 62.5 ml	100 ml
	Gel Permeation Chromatography	
Elution Solvent	DCM	
Solvent Volume	200 ml	
Total Solvent Volume	745 ml	640 ml
Total DCM Volume	528 ml	125 ml
Extract Preparation Time (Set of 4 Samples)	12 hours	9.3 hours

Table 3: Tadpole semi-volatile organic compound estimated detection limits in pg/g wet weight (NR = not recovered) for the pressurized liquid extraction (PLE) and matrix solid phase dispersion (MSPD) methods.

	Log Kow	PLE Estimated Method Detection Limit (pg/g ww)	MSPD Estimated Method Detection Limit (pg/g ww)
Amide Pesticides			
Alachlor	2.6	NR	620
Acetochlor	3.0	NR	320
Metolachlor	3.1	NR	240
Propachlor	2.4	NR	210
Organochlorines Pesticides and Metabolites			
HCH, gamma	3.8	24	26
HCH, alpha	3.8	21	19
HCH, beta	4.0	29	71
HCH, delta	4.1	17	44
Methoxychlor	4.5	17	150
Heptachlor	5.2	108	240
Heptachlor epoxide	4.6	68	48
Hexachlorobenzene	5.5	0.19	1.4
Endrin	5.2	800	400
Endrin aldehyde	4.8	140	48
Chlordane, trans	6.1	2.7	1.1
Chlordane, cis	5.9	69	44
Nonachlor, trans	6.1	2.7	1.2
Nonachlor, cis	6.1	5.3	6.0
Chlordane, oxy	5.5	56	80
Dieldrin	5.5	260	260
Aldrin	6.4	44	160
o,p'-DDT	6.5	270	240
o,p'-DDD	6.1	190	270
o,p'-DDE	5.5	400	170
p,p'-DDT	6.9	63	310
p,p'-DDD	5.9	93	260
p,p'-DDE	6.8	110	250
Mirex	6.9	12	84
Organochlorine Sulfide Pesticides and Metabolites			
Endosulfan I	4.7	13	16
Endosulfan II	4.8	34	7.6
Endosulfan sulfate	3.7	2.7	9.7
Phosphorothioate Pesticides			
Methyl parathion	2.7	1100	310
Malathion	2.9	NR	260
Diazinon	3.7	NR	120
Parathion	3.8	1600	230
Ethion	5.1	390	210
Chlorpyrifos	5.1	6.9	22

	Log Kow	PLE Estimated Method Detection Limit (pg/g ww)	MSPD Estimated Method Detection Limit (pg/g ww)
Thiocarbamate Pesticides			
EPTC	3.2	NR	710
Pebulate	3.8	NR	150
Triallate	4.6	36	39
Triazine Herbicides and Metabolites			
Atrazine desisopropyl	1.4	NR	2900
Atrazine desethyl	1.8	NR	390
Atrazine	2.3	NR	300
Simazine	2.2	NR	830
Metribuzin	1.7	NR	44
Miscellaneous Pesticides			
Etridiazole	2.6	NR	620
Dacthal	4.3	32	7.5
Trifluralin	5.3	4.1	11
Polycyclic Aromatic Hydrocarbons			
Acenaphthylene	3.9	230	160
Acenaphthene	4.0	290	730
Fluorene	4.2	68	360
Anthracene	4.5	130	520
Phenanthrene	4.5	50	290
Pyrene	5.1	66	33
Fluoranthene	5.2	130	120
Chrysene + Triphenylene	5.7	24	41
Benzo(a)anthracene	5.9	26	68
Retene	6.4	93	160
Benzo(k)fluoranthene	6.5	320	110
Benzo(a)pyrene	6.5	180	190
Benzo(b)fluoranthene	6.6	220	74
Benzo(e)pyrene	6.9	170	130
Indeno(1,2,3-cd)pyrene	6.7	95	210
Dibenz(a,h)anthracene	6.8	120	160
Benzo(ghi)perylene	7.0	77	110
Polychlorinated Biphenyls			
PCB 74	6.3	730	250
PCB 101	6.4	180	710
PCB 118	7.0	12	23
PCB 153	6.9	11	19
PCB 138	6.7	26	98
PCB 187	7.2	5	3.2
PCB 183	8.3	4.7	2.8
Ave, Min, and Max Recoveries, % RSD			
ave		160	230
max		1600	2900
min		0.19	1.1


Average Relative Standard Deviation from the Mean
120
100
80
60
40
20
0
Injection Replicates
Analytical Replicates
Site Replicates
< detection limit
< detection limit
< detection limit
< detection limit
dacthal
chlorpyrifos
endosulfan II
endosulfan sulfate
trans-chlordane
trans-nonachlor
cis-nonachlor
PCB 187