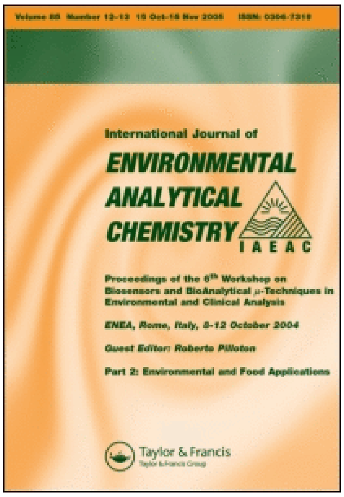

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SUPERCRITICAL FLUID EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM SOIL

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A supercritical fluid extraction (SFE) method was developed for the extraction of 21 organochlorine (OC) pesticides from soil using dichloromethane as cosolvent and magnesium sulfate as drying agent. Average recoveries of spiked OCs from six different soils generally ranged from 70 to 95 %, with an average replicate precision of ± 13%. For the extraction of two soils containing "native" OCs, the SFE method gave generally similar or higher concentrations compared to Soxhlet extraction. The precision of replicate analyses of native OCs using SFE and Soxhlet extraction was ± 0.009 and ± 0.007 ug/g, with 24 and 13 degrees of freedom respectively.

KEY WORDS: Soils, SFE, organochlorine pesticides.

INTRODUCTION

Organochlorine pesticides may be analyzed by US EPA Method 8080, which specifies either Soxhlet or sonication extraction (Methods 3540 and 3550 respectively). The Soxhlet method involves overnight extraction using 300 mL of dichloromethane per sample, followed by concentration and column cleanup of the extract. Supercritical fluid extractions take typically less than 1 hour, use CO_2 rather than toxic chlorinated organic solvent, and the extracts may be analyzed directly by gas chromatography (GC) without cleanup.

Reported recoveries of OCs from spiked soil using pure supercritical CO_2 were variable depending on the soil type[1]. In another study, also using pure S-CO_2, poor recoveries from spiked soil were observed for several OCs including endosulfan sulfate (57%), endrin (10%), and methoxychlor (47%)[2]. In the case of endrin, its recovery from spiked soil was improved from 21% to 100% using DMSO as cosolvent[3]. Methanol cosolvent also gave significantly improved recoveries[4]. Essentially identical results were obtained when three soils containing "native" (naturally weathered) OCs were extracted by SFE and Soxhlet methods[5].

This work provides new information related to 1) cosolvent comparison, 2) methodology for drying agent use, 3) recovery of spiked OCs from different soil types, and 4) accuracy of SFE relative to Soxhlet extraction for native OCs. The analytes included 21 OC pesticides, all of which, except one (toxaphene) are listed in Method 8080.

EXPERIMENTAL

Equipment

SF extractions were performed using a Hewlett Packard (HP) 7680T instrument. The GC was a HP5890 with 7673 Autosampler-Injector, split/splitless injector, DB-5 and DB-1701 columns (both 30 m × 0.25 mm and 0.25 µm film; J & W Scientific, Folsom, CA, USA), and electron capture detector (ECD).

Standards and reagents

A 1-ug/mL spiking standard was prepared by combining the following solutions: Supelpreme-HC Pesticide Mix (2000 ug/mL, Supelco Inc., Oakville ON, Canada), HCB solution in toluene (1000 ug/mL, Nanogen, Watsonville, CA, USA), mirex solution (1000 ug/mL, Nanogen), α- and γ-chlordane solution in acetonitrile (1000 ug/mL, NSI Environmental Solutions, Research Triangle Pk, NC, USA). The solvents were evaporated to dryness at room temp., and the solution made up in dichloromethane. A calibration standard was prepared by diluting 100 uL of the spiking standard to 1.0 mL with dichloromethane. Pesticide grade organic solvents were obtained from BDH (Toronto, Canada). SFC grade CO_2 (Air Products, Allentown, PA, USA) was used for extractions.

Soxhlet extraction

Ten grams of sample were Soxhlet-extracted for 16 hr using 300 mL dichloromethane, based on US EPA Method 8080/3540. Briefly, the extracts were dried over sodium sulfate and concentrated by rotary evaporation. Cleanup was performed by florisil column chromatography, and final extracts were concentrated to 1 mL in isooctane.

SFE

One gram of sample was placed in a 7-mL extraction thimble on top of a glass wool plug and a layer of $MgSO_4$ (0.5 g, dried at 140°C for 12 hours). Dichloromethane cosolvent (400 uL) was added. The sample was immediately covered with another layer of $MgSO_4$ (0.5 g) followed by glass wool and extracted with CO_2 at 30 MPa (300 bar), and 50°, in static mode for 10 min., and in dynamic mode (1 mL/min supercritical-CO_2) for 20 min. The S-CO_2 passed through a variable restrictor (50°) and was depressurized into a trap containing 40 µm C_{18}-silica maintained at 20°. After extraction, the trap was rinsed with dichloromethane (1.5 mL) which was collected in a vial and exchanged to isooctane. This extract was analyzed directly by GC-ECD.

Soil samples were spiked (at 0.1 – 0.6 ug/g) by adding 100 uL of spiking solution on top of the soil in the extraction thimble, followed by an additional 300 uL of dichloromethane for a total of 400 uL of dichloromethane cosolvent. The samples were then immediately extracted.

GC-ECD

1.5 uL of extract was injected into the injection port (splitless mode) maintained at 220°C. The oven, containing dual capillary columns (DB-5 and DB-1701) was programmed as follows: 80° (hold 2 min.) to 185° at 40°/min, 185° to 228° (hold 1 min.) at 2°/min, 228° to 285° (hold 6 min.) at 10°/min. The ECD detector was maintained at 320°.

RESULTS AND DISCUSSION

Method development

The extraction of spiked OCs from sand was initially examined using reported SFE parameters. The recoveries of most OCs were greater than 70% using pure supercritical-CO_2 (spiking solvent evaporated). This method was then used to extract three different soils designated SS–1, SS–2, and SS–3. The moisture and organic matter contents of these soils were 17, 80, and 6% and 0.18, 30, and 0.03% respectively. Recoveries of spiked OCs were generally greater than 80% for two of the three soils, whereas low recoveries of approx. 50% were observed for SS-2, which contained the highest moisture and organic matter contents. Recoveries of spiked OCs from this soil were improved by 1) using dichloromethane as cosolvent, and 2) "sandwiching" the 1-gram sample between 0.5-gram layers of magnesium sulfate drying agent. Acetone and methanol were also investigated as cosolvents, but gave poorer recoveries of spiked OCs compared to dichloromethane.

Although the function of magnesium sulfate drying agent was unclear, it may have influenced the efficiency of analyte collection on the C_{18} trap, rather than analyte extraction from soil. It was found that mixing the magnesium sulfate with the sample gave generally poorer recoveries of native OCs compared to "sandwiching" the sample between layers of magnesium sulfate (Table 1). This implied that the presence of sample moisture aided the extraction of OCs using S-CO_2 with dichloromethane cosolvent.

Table 1 Average (n = 2) observed concentrations and deviations[a] (ug/g) of native OCs in soil sample 2J-1, comparing mixed (1-g) and layered (2 × 0.5 g) magnesium sulfate drying agent.

No.[b]	*Analyte*	*Layers*		*Mixed*	
		Concentration	*Deviation*[a]	*Concentration*	*Deviation*[a]
2	HCB	0.014	0.014	0.024	0.005
3	β-BHC	0.022	0.010	0.019	0.004
4	Lindane	0.004	0.004	0.005	0.002
5	δ-BHC	0.002	0.002	0.006	0.001
6	Heptachlor	0.003	0.001	nd	
7	Aldrin	0.005	0.005	nd	
10	α-Endosulfan	0.575	0.004	0.336	0.036
12	pp'-DDE	0.035	0.005	0.016	0.010
15	β-Endosulfan	0.579	0.064	0.355	0.032
18	Endosulfan sulfate	0.068	0.003	0.035	0.011

[a] Deviation = range/2

[b] GC elution order

nd = not detected

Increasing the extraction pressure (from 30 to 37 MPa (300 to 370 bar)), temperature (from 50° to 100°), or extraction times (dynamic: 20 min. to 40 min., or static: 10 min. to 40 min.) did not improve recoveries of spiked OCs from soil SS-2 in the absence of cosolvent (data not shown).

Method validation

Spiked OCs Recoveries of spiked OCs from 6 soils were determined (Table 2). Endrin aldehyde showed the poorest recoveries; the average for the 6 soils was 53%. The average recoveries of the remaining OCs from the 6 soils were 70% or greater. The overall average replicate precision of OC recovery was ± 13% (standard deviation).

"Native" OCs: SFE vs Soxhlet extraction Two soil samples were obtained which contained several naturally weathered OCs. Both samples were similar in terms of moisture content (26%), organic matter content (17%), and texture (loamy). In both samples, generally similar or higher OC concentrations were observed using SFE compared to Soxhlet extraction (Tables 3 and 4). In sample 2J-2 (Table 4), native DDE and DDD were observed at levels approximately 2 orders of magnitude higher than the detection limits in the Soxhlet extract, but were not observed in the SFE extracts. This may have been due to an interference in the Soxhlet extract. Note that the concentrations of native DDE and DDD in sample 2J-1 were in close agreement (Table 3).

Table 2 Average (n = 2) SFE recoveries (%) of spiked OCs from 6 soils in order of overall average recovery.

No.[a]	*Compound*	*Soil*						*Average*	*SD*[b]
		SS-1	*SS-2*	*SS-3*	*2J-1S*	*5J-13*	*5J-10*		
14	Endrin	76	79	78	152	117	116	103	15
20	Methoxychlor	58	92	92	131	144	76	99	25
21	Mirex	84	74	133	84	108	104	98	18
5	δ-BHC	69	69	78	97	119	121	92	18
6	Heptachlor	80	80	81	110	99	98	91	9
16	pp′-DDD	69	73	78	116	108	101	91	12
15	β-Endosulfan	77	73	78	101	93	97	86	15
18	Endosulfan sulfate	73	76	59	115	91	96	85	14
7	Aldrin	81	75	78	84	88	105	85	10
13	Dieldrin	76	67	75	110	90	90	85	14
8	Heptachlor epoxide	75	68	66	97	95	95	83	8
9	γ-Chlordane	73	67	84	97	82	87	82	12
3	β-BHC	65	70	66	91	85	104	80	12
10	α-Endosulfan	71	62	69	96	96	78	79	12
4	Lindane	62	69	60	92	107	79	78	12
2	HCB	72	67	97	74	67	82	77	18
12	pp′-DDE	69	74	81	43	86	104	76	11
19	pp′-DDT	69	76	71	75	81	82	76	15
11	α-Chlordane	69	60	71	67	86	69	70	12
1	α-BHC	56	60	57	84	78	85	70	9
17	Endrin aldehyde	55	35	51	82	37	59	53	5
								Average	13

[a] GC elution order

[b] Estimated from the ranges of duplicate recoveries from 5 soils[6]

Table 3 Observed concentrations (ug/g) of native OCs in soil sample 2J-1 using SFE and Soxhlet extraction.

No.[a]	*Compound*	*SFE (Avg. n = 2)*	*Deviation*	*Soxhlet (n = 1)*
2	HCB	0.022	0.002	0.043
3	β-BHC	0.069	0.004	0.054
5	δ-BHC	0.010	0.001	0.012
6	Heptachlor	0.002	0.002	nd
7	Aldrin	0.022	0.007	nd
9	γ-Chlordane	0.020	0.006	nd
10	α-Endosulfan	0.855	0.050	0.890
12	pp'-DDE	0.007	0.001	0.007
15	β-Endosulfan	0.758	0.125	0.530
16	pp'-DDD	0.008	0.002	0.008
17	Endrin aldehyde	0.002	0.002	nd
18	Endosulfan sulfate	0.077	0.010	0.041
19	pp'-DDT	0.006	0.000	0.031
21	Mirex	0.001	0.001	nd

[a] GC elution order

nd = not detected

Table 4 Observed concentrations (ug/g) of native OCs in sample 2J-2 using SFE and Soxhlet extraction.

No.[a]	*Compound*	*SFE*			*Soxhlet*
		Avg (n = 4)	*SD*	*%RSD*	
1	α-BHC	0.021	0.002	8%	nd
2	HCB	0.069	0.008	11%	0.041
3	β-BHC	0.442[b]	0.066	15%	0.370
4	Lindane	0.033	0.005	15%	0.019
5	δ-BHC	nd			0.012
8	Heptachlor epoxide	0.103[b]	0.010	10%	0.014
10	α-Endosulfan	35.000	5.672	16%	28.400
12	pp'-DDE	nd			0.320
15	β-Endosulfan	17.500	2.712	15%	0.860
16	pp'-DDD	nd			0.230
17	Endrin aldehyde	0.042	0.007	16%	nd
19	pp'-DDT	0.710	0.073	10%	1.100
21	Mirex	0.036	0.021	59%	nd
			Average	13%[c]	

[a] GC elution order

[b] not confirmed on the second GC capillary column

[c] excluding the outlier; 59%

nd = not detected

The precisions of replicate analyses of native OCs using SFE and Soxhlet extraction were ± 0.009 and ± 0.007 ug/g, with 24 and 13 degrees of freedom respectively. The Soxhlet standard deviation was calculated[6] from duplicate results of two soils (Table 5). The SFE value was calculated from results in Tables 3 and 4. The ranges of observed OC concentrations were similar for both calculations. Therefore, the precisions of the two extraction methods were similar.

Table 5 Average (n = 2) concentrations (ug/g) of native OCs observed in two soils using Soxhlet extraction.

No.[a]	*Analyte*	*Soil lj-2*		*Soil lj-4*	
		Conc.	*Deviation*	*Conc.*	*Deviation*
2	HCB	nd	nd	0.0085	0.0015
8	Heptachlor epoxide	0.008	0.0005	0.004	0.0007
9	γ-Chlordane	0.017	0.0010	0.011	0.0025
10	α-Endosulfan	0.017	0.0110	nd	nd
11	α-Chlordane	0.020	0.0005	0.016	0.0030
12	pp′-DDE	0.019	0.0015	0.033	0.0021
13	Dieldrin	0.046	0.0040	nd	nd
15	β-Endosulfan	0.023	0.0166	nd	nd
18	Endosulfan sulfate	0.068	0.0215	nd	nd
19	pp′-DDT	0.031	0.0020	0.014	0.0009

[a] GC elution order
nd = not detected

CONCLUSIONS

Spiked OCs were acceptably extracted with pure CO_2 from sand and two soils. However, a third soil, containing relatively high organic matter and moisture contents, required dichloromethane cosolvent and magnesium sulfate drying agent for acceptable recoveries. This SFE method gave average recoveries of spiked OCs of 70% or greater for 6 different soil types (excluding endrin aldehyde; 53%). For the extraction of native OCs from 2 similar soils, the observed concentrations of the SFE method were generally similar or greater than those observed using Soxhlet extraction. The precision of replicate analyses of native OCs was similar for the two extraction methods. To thoroughly validate this SFE method for use in a commercial laboratory, additional SFE/Soxhlet comparisons are desirable for the extraction of native OCs from different soil types. Approximately 8 GC-ready extracts could be produced in one working day using this (serial extraction) SFE method, compared to 2 to 3 days using the Soxhlet method.

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