

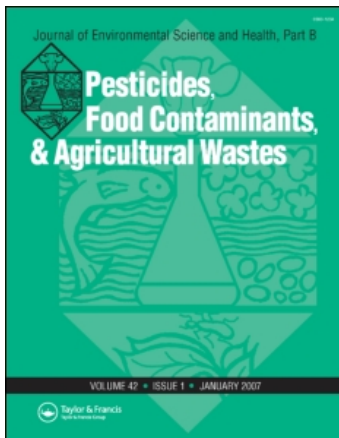
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### OPTIMIZING MICROWAVE-ASSISTED SOLVENT EXTRACTION (MASE) OF PESTICIDES FROM SOIL

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## OPTIMIZING MICROWAVE-ASSISTED SOLVENT EXTRACTION (MASE) OF PESTICIDES FROM SOIL

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### ABSTRACT

Microwave-assisted solvent extraction (MASE) was investigated as an alternative for extraction of parathion (*O,O*-diethyl *O*-4-nitrophenyl phosphorothioate), methyl parathion (*O,O*-dimethyl *O*-4-nitrophenyl phosphorothioate), *p,p'*-DDE [1,1'-dichloro-2,2-bis(4-chlorophenyl)ethane], hexachlorobenzene (HCB), simazine (6-chloro-*N*<sup>2</sup>,*N*<sup>4</sup>-diethyl-1,3,5-triazine-2,4-diamine) and paraquat dichloride (1,1'-dimethyl-4,4'-bipyridinium) from two different soils and from an earthworm-growing substrate. The matrices were fortified with <sup>14</sup>C-radiolabeled pesticides and extracted with various solvent systems under different microwave conditions. Recoveries of more than 80% could be obtained depending on the used microwave conditions and solvent, except for paraquat whose recovery was generally less efficient. Thus, MASE can be successfully used to extract pesticides from environmental and biological samples and could be a viable alternative to conventional extraction methods. The technique uses smaller amounts of organic solvents, thereby minimizing the costs of the analysis and the disposal of waste solvent.

*Key Words:* Pesticides; Soils; Extraction; Solvents; Microwave conditions

### INTRODUCTION

Conventional Soxhlet techniques to extract pesticides from different matrices usually require large amounts of solvents and long extraction times (1–3). More

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efficient extraction methodologies would give rise to less waste solvent (4–6). Microwave-assisted solvent extraction (MASE) has been investigated since 1986 (7) because smaller amounts of matrix and solvents are required, and extraction is rapid (8,9).

The use of  $^{14}\text{C}$ -radiolabeled pesticides aids quantitative assessment of the extraction methods because it facilitates the determinations of small amounts of pesticides and their distribution in the system (10).

Because the organic matter content of soil and the chemical class of the pesticides are determining factors of adsorption, degradability, and bound residues formation (11,12), this work investigated MASE of pesticides of different chemical classes from two different soils and one substrate used for growing earthworms, which is very rich in organic matter. The MASE conditions were investigated for the following pesticides: parathion, methyl parathion, *p,p'*-DDE, hexachlorobenzene (HCB), simazine, and paraquat dichloride.

## MATERIALS AND METHODS

### Matrices

A substrate for growing earthworms and two different soils (respectively, S.1, S.2, and S.3 in Tab. 1) never exposed to pesticides were used for comparison of the methodology.

The two soils (S.2 and S.3) were collected at 0–15 cm of soil profile and sieved to 2 mm. S.2 is a clay soil from an experimental farm of Campinas (SP, Brazil) and S.3 is a sandy soil collected at Praia Grande (SP, Brazil). The moisture content of the matrices was determined in a Moisture Analyzer (Mettler LJ16). Because the water content helps absorbance of microwave energy (3), it was adjusted to 50% of the maximum water-holding capacity before the addition of pesticide.

### Pesticides

Technical-grade parathion (*O,O*-diethyl *O*-4-nitrophenyl phosphorothioate); methyl parathion (*O,O*-dimethyl *O*-4-nitrophenyl phosphorothioate) and *p,p'*-DDE [1,1'-dichloro-2,2-bis(4-chlorophenyl)ethane] from Greyhound Chromatography and Allied Chemicals (United Kingdom); HCB from Rhodia (Brazil); simazine (6-chloro-*N*<sup>2</sup>,*N*<sup>4</sup>-diethyl-1,3,5-triazine-2,4-diamine) from Sipcan (Italy), and

**Table 1.** Physicochemical Characteristics of the Matrices

Matrix	pH	Organic Matter (g dm <sup>-3</sup> )	Sand	Silt (%)	Clay
Earthworm substrate, S.1	6.0	172	50.0	17.0	33.0
Clay soil, S.2	4.5	33	49.0	25.0	26.0
Sandy soil, S.3	5.0	2	99.8	<0.1	0.1



**Table 2.** Concentrations of [ $^{14}\text{C}$ ]-Pesticides Applied to the Different Matrices

[ $^{14}\text{C}$ ]-Pesticide	Concentration in Matrix ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Radiocarbon in Matrix ( $\text{kBq} \cdot \text{g}^{-1}$ )	Application Solvent
Parathion	2.000	0.240	Hexane
Methyl parathion	2.400	0.550	Hexane
DDE	2.000	0.161	Hexane
HCB	2.000	0.160	Hexane
Simazine	1.200	0.962	Methanol
Paraquat	0.015	1.036	Water

paraquat-dichloride (1,1'-dimethyl-4,4'-bipyridinium) from ICI (Brazil) were used in solution with the corresponding [ $^{14}\text{C}$ ]-pesticides. The [ $^{14}\text{C}$ ]-parathion and [ $^{14}\text{C}$ ]-*p,p'*-DDE (specific activities 0.55 and 1.14 GBq mmol $^{-1}$ , respectively) were obtained from the Hungarian Academy of Sciences (Hungary), [ $^{14}\text{C}$ ]-methyl parathion and [ $^{14}\text{C}$ ]-HCB (specific activities 1.07 and 0.11 GBq mmol $^{-1}$ , respectively) from Internationale Isotope München (Germany) and [ $^{14}\text{C}$ ]-simazine and [ $^{14}\text{C}$ ]-paraquat (specific activities 1.04 and 0.44 MBq mmol $^{-1}$ , respectively) from Sigma-Aldrich Chemical Company (United States).

### Fortification Procedure

The [ $^{14}\text{C}$ ]-pesticide solutions were applied to the different matrices according to Table 2. The mixtures were homogenized for 20 min and triplicates of 0.5 and 3.0 g (dry weight equivalent) subsamples of each treatment were analyzed to verify, respectively, the amounts applied and recovered by the different extraction procedures.

### Apparatus

The initial amounts of [ $^{14}\text{C}$ ]-pesticide applied were verified by combustion of each treated matrix (0.5 g in triplicate) in a Biological Oxidizer (OX 600, Harvey Instrument), according to Andréa et al. (13).

A commercial microwave (Panasonic, 1600 W) with variable power output (from 10 to 50%), time of exposure to microwave energy (from 10 to 240 s) and number of microwave cycles (from 2 to 15) was used for extraction of the 3.0-g subsamples of each treated matrix.

### Conditions of MASE

The solvents tested were methanol, dichloromethane, hexane, acetone, toluene, ethyl acetate, cyclohexane, and sulfuric acid (the latter at 9, 10, or 11 mol  $\cdot$  L $^{-1}$

**Table 3.** Recovery of [<sup>14</sup>C]-Parathion, [<sup>14</sup>C]-Methylparathion, and [<sup>14</sup>C]-DDE by MASE

MASE Conditions				% <sup>14</sup> C-Recovery (± Standard Deviation)			
Solvent (Proportion) [Volume]	Power (W)	Cycles (No.)	Time/Cycle (s)	Matrix	Parathion	Methylparathion	DDE
Methanol [15 mL]	160	15	20	S.1	82.5 ± 2.8	81.2 ± 4.5	74.2 ± 4.2
				S.2	89.2 ± 3.3	96.8 ± 3.9	100.6 ± 3.9
				S.3	101.00 ± 4.2	99.2 ± 3.1	102.2 ± 1.3
Dich.:met.:wat. <sup>a</sup> (6:8:1) [15 mL]	800	10	10	S.1	58.0 ± 5.6	7.2 ± 0.4	6.8 ± 0.3
				S.2	90.1 ± 2.0	92.9 ± 2.0	102.8 ± 3.1
				S.3	101.8 ± 1.2	95.2 ± 5.5	103.8 ± 5.5
Dich.:met.:wat. <sup>a</sup> (1:8:8) [17 mL]	800	15	20	S.1	22.3 ± 7.1	32.9 ± 5.9	43.00 ± 1.0
				S.2	54.7 ± 18.6	84.0 ± 1.5	31.1 ± 2.4
				S.3	105.0 ± 3.5	62.2 ± 6.9	84.3 ± 3.0
Hexane:acetone (9:1) [15 mL]	160	2	240	S.1	102.00 ± 6.4	71.5 ± 8.6	9.7 ± 1.8
				S.2	85.7 ± 2.6	88.7 ± 3.7	43.1 ± 2.6
				S.3	99.6 ± 1.2	98.0 ± 1.3	105.2 ± 2.8
Hexane:acetone (75:25) [16 mL]	160	12	60	S.1	97.8 ± 7.2	99.5 ± 4.6	35.9 ± 1.1
				S.2	87.8 ± 1.3	87.3 ± 0.5	97.2 ± 3.0
				S.3	94.2 ± 1.6	92.6 ± 3.1	100.1 ± 7.6

<sup>a</sup>Dichloromethane, methanol, water.

water) used alone or combined in different proportions (Tabs. 3–6). Each microwave cycle was followed by immersion in an ice bath to avoid overheating and volatilization. A maximum of nine samples were placed symmetrically on the microwave turntable.

**Table 4.** Recovery of [<sup>14</sup>C]-HCB by MASE

MASE Conditions				% <sup>14</sup> C-Recovery (± Standard Deviation)	
Solvent (Proportion) [Volume]	Power (W)	Cycles (No.)	Time/Cycle (s)	Matrix	(± Standard Deviation)
Hexane:acetone (9:1) [10 mL]	160	4	60	S.1	34.7 ± 2.4
				S.2	26.6 ± 3.3
				S.3	87.6 ± 1.5
Hexane:acetone (9:1) [10 mL]	160	12	60	S.1	24.6 ± 1.3
				S.2	69.8 ± 2.9
				S.3	97.0 ± 8.4
Hexane:acetone (75:25) [10 mL]	160	12	60	S.1	42.5 ± 5.1
				S.2	80.3 ± 0.2
				S.3	114.9 ± 2.0
Hexane:acetone (75:25) [10 mL]	160	12	120	S.2	69.5 ± 3.0
				S.3	99.9 ± 5.1
Hexane [10 mL]	160	2	240	S.3	48.1 ± 6.2
Toluene [10 mL]	160	2	240	S.3	47.2 ± 1.8
Ethyl acetate [10 mL]	160	2	240	S.3	83.8 ± 3.6
Cyclohexane [10 mL]	160	4	240	S.3	67.3 ± 2.6



**Table 5.** Recovery of [<sup>14</sup>C]-Simazine by MASE

MASE Conditions					
Solvent (Proportion) [Volume]	Power (W)	Cycles (No.)	Time/Cycle (s)	Matrix	% <sup>14</sup> C-Recovery (± Standard Deviation)
Hexane:acetone (75:25) [15 mL]	160	12	60	S.1	73.2 ± 1.5
				S.2	81.1 ± 1.2
				S.3	82.4 ± 0.2
Dich.:met.:wat. <sup>a</sup> (6:8:1) [15 mL]	800	10	10	S.1	89.4 ± 1.3
				S.2	58.6 ± 0.8
				S.3	76.4 ± 1.5
Methanol [15 mL]	480	20	20	S.1	17.7 ± 0.8
Methanol:dich. <sup>b</sup> (1:9) [12 mL]	800	10	20	S.1	27.3 ± 3.0

<sup>a</sup>Dichloromethane, methanol, water.<sup>b</sup>Methanol, dichloromethane.

## RESULTS AND DISCUSSION

Because MASE is a new methodology, the combination of matrix/pesticide/solvent/time of extraction needs to be investigated in order to optimize recoveries (14). Results here reported (Tabs. 3–6) show that the process can be generally used, providing very good recoveries of pesticide, and yielding extracts that were mostly very clear, avoiding the need for further cleanup.

The highest recoveries were obtained from the sandy soil, probably because it contained very little organic matter. The poorest recoveries were from the earth-worm substrate, which is nearly all organic matter and which would strongly adsorb the pesticides.

**Table 6.** Recovery of <sup>14</sup>C-Paraquat-Dichloride by MASE

MASE Conditions					
Solvent (Proportion) [Volume]	Power (W)	Cycles (No.)	Time/Cycle (s)	Matrix	% <sup>14</sup> C-Recovery (± Standard Deviation)
Water:sulfuric acid 9 <sup>a</sup> (2:13) [15 mL]	1120	15	30	S.1	72.9 ± 0.7
				S.2	22.1 ± 0.3
				S.3	105.3 ± 3.5
Sulfuric acid 9 [15 mL]	480	7	30	S.1	37.9 ± 0.2
Sulfuric acid 10 [15 mL]	480	20	30	S.1	39.5 ± 0.6
Sulfuric acid 10 [15 mL]	800	10	50	S.1	42.6 ± 0.7
Sulfuric acid 11 [15 mL]	480	7	30	S.1	34.2 ± 1.3

<sup>a</sup>Water, sulfuric acid, 9 mol · L<sup>-1</sup>.

Best recoveries of [ $^{14}\text{C}$ ]-parathion from all matrices (Tab. 3) were obtained using either methanol (recoveries from approximately 82–101%) or hexane:acetone (86:102%). The power output of only 160 W (10%) proved to be efficient, and when hexane:acetone (75:25 vol.-%) was used, 12 cycles of 1 min each resulted in very high recoveries.

[ $^{14}\text{C}$ ]-Methyl parathion was also best recovered by the same solvents independent of the matrix. But the mixture hexane:acetone was effective only when the number of cycles was high (Tab. 3).

The persistent [ $^{14}\text{C}$ ]-DDE was only well recovered from all tested matrices when methanol was the solvent (Tab. 3). In contrast, [ $^{14}\text{C}$ ]-HCB was recovered only by the mixture hexane:acetone in different proportions; the other solvents gave poor recovery even from the sandy soil (Tab. 4). The herbicide [ $^{14}\text{C}$ ]-simazine was also best recovered from the different matrices by hexane:acetone (Tab. 5).

Even the strongly adsorbed [ $^{14}\text{C}$ ]-paraquat (11) could be extracted with sulfuric acid mixed with water (Tab. 6), though recovery from S.2 was poor.

The clearest extracts were obtained by hexane:acetone mixtures, even from S.1. These extracts might be directly analyzed by gas or liquid chromatography, minimizing the time for analysis. Methanol alone or in combination with other solvents seemed to extract some organic matter for the extracts, although completely translucent, presented a pale color. In these cases, filtration by a Millipore membrane may be useful. But sulfuric acid seemed to dissolve the organic matter, and a cleanup procedure would certainly be needed before chromatographic analysis.

## CONCLUSIONS

MASE has been evaluated for six pesticides spanning a range of physicochemical properties, added to three different soil matrices. It proved to be significantly faster, more economic, and gave rise to less waste solvent, compared to conventional Soxhlet extraction or mechanical shaking. Depending on the solvent system used, extracts seemed sufficiently clean to be directly analyzed by gas or liquid chromatography.

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