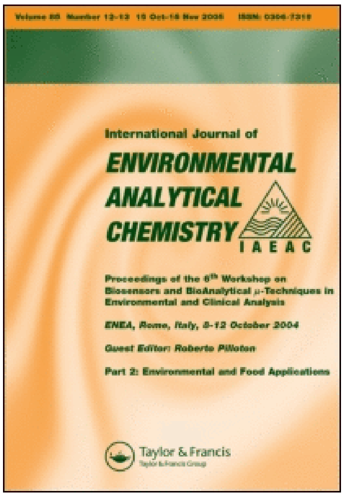

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MICROWAVE-ASSISTED EXTRACTION METHOD FOR ORGANOCHLORINATED PESTICIDES AND POLYCHLORINATED BIPHENYLS FROM COMPOST

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A laboratory study was conducted to determine the recoveries for selected organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) by a new microwave assisted extraction (MAE) method developed for compost. The organic matter content of the compost samples is very high and partly soluble in the extraction solvent. Florisil was used as the adsorbent in the cleaning procedure for the extract, and found to clean very well and to give good recoveries from a solution containing a high concentration of humic substances. The compost was spiked 24 h prior to the extraction. Pollutant recoveries were higher when the extraction solvent was hexane-acetone (1:1) (91 to 105 % with a standard deviation of 4 to 8 %) on air-dried compost.

Keywords: Organochlorinated pesticides; polychlorinated biphenyls; PCBs; microwave assisted extraction; compost; soil

INTRODUCTION

Composting is a method used to reduce the amount of waste that is buried in landfills. About 30 % of the urban waste can be used for composting. The reduction of urban waste will increase the life span of landfills and assure better environmental management which will be beneficial for the community. Adding compost to soil will improve its abilities to absorb water and to resist erosion. Since public interest in composting is increasing rapidly, it is necessary to develop an adequate analytical method to control the quality of the compost produced. Standard environmental organic extraction methods such as Soxhlet and

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ultrasonic are typically labor intensive and time consuming, and require large amounts of undesirable solvents that eventually need disposal. MAE is an innovative method which uses microwave energy to facilitate the extraction of organic compounds from solid materials such as soils[1–3]. It was observed that the presence of even a low percentage organic matter in soils can cause major interferences[4]and have a dramatic effect on the extraction recoveries[5]. However compost is a very complex matrix because its components vary and have different molecular weight and different physico-chemical properties. In addition, a compost contains 40 to 60%, or more, of organic matter compared to about 5% in a soil.

One of the difficulties in extracting OCPs and PCBs from compost is that humic substances are soluble in the extraction solvent which is usually hexane-acetone (1:1). Some authors have studied the MAE of organic pollutants from soil[1,2] and sediment[5,6]. Since they contain weak humic substances, these matrices do not create additional problems for the analysis as compost does. As a result, cleaning of the extract is not necessary with such samples. Lopez-Avila *et al.*[7] tried to analyze several organic pollutants in compost. Several pesticides were extracted with either very low or very high (up to 200%) recovery rates. The authors attribute the high recoveries to matrix interference. It is possible that the major problem is the large amount of humic substances in the compost in the published method. In our study, we have evaluated the MAE of some OCPs and PCBs in compost. Our method included a cleanup of extracts of composts and soil.

EXPERIMENTAL

Chemicals

All organic solvents used were pesticide grade and purchased from Matheson Coleman & Bell and J.T. Baker. The polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were purchased as neat material from Ultra Scientific. The purity of all compounds was stated to be higher than 97%. The spiking solution and the working calibration standards were prepared by serial dilution of the composite stock solution containing all the compounds studied in isooctane or toluene.

Samples analyzed and preparation

The following types of garbage compost were considered. The percentages of material are expressed in volume/volume of raw material.

Windrow 8

a compost produced from 55% of pulp and paper sludge, 18% of wood bark and 27% of pig manure. This compost was used for development of MAE and cleanup procedure.

Windrow 6

a compost produced from 60% of pulp and paper sludge, 20% of wood bark and 20% of chicken manure.

Municipal compost

a compost produced from domestic and industrial wastes by TIRU Company (Traitement Industriel des Résidus Urbains), city of Moncton, New Brunswick, Canada.

Shrimp compost

a compost sold commercially. It is produced from shrimp waste, bovine and chicken manures and peat moss unknown proportions.

Baie-du-Vin-Galloway soil

a soil found in St-Thomas, New Brunswick, Canada. It was composed of 65–90% sand, 5–20% mud and 2–10% clay.

Preparation

Moist compost

was the raw material (as receiving). There were no drying or milling treatments of these samples.

Air-dried compost and soil

The samples were air-dried until we obtained a constant mass (24–48 hours). The water content of the air-dried samples is given as residual humidity in Table I.

After air-drying, the compost was milled in a Brook Crompton mill (Series 2000); the maximum particles diameter was 1 mm. The soil was air-dried and sieved (<20 mesh) with USA Standard Testing Sieve ro-tap (VWR Scientific, Leeson).

TABLE I Characteristics of matrices studied

Sample (Compost or Soil)	*Organic Matter (%)*	*pH*	*Humidity (%)*	*Residual Humidity[a] (%)*
Windrow 8	67.6	6.16	61.1	3.7
Windrow 6	19.9	7.25	59.8	23.2
Municipal	46.1	7.75	16.8	3.5
Shrimp	62.3	6.89	71.4	16.9
Soil	4.9	5.42	14.9	–

a. After air-drying.

Oven-dried compost

The samples were dried at 105 °C until we obtained a constant mass (24–48 hours) and milled to a maximum particle diameter of 1 mm.

Spiked samples

A 5-g portion of each dried matrix was weighed in a Teflon extraction vessel (100 mL) and 0.5 mL of composite solution was added and left for 24 hours before extraction. The size of the moist samples was 12 g to compensate for 60% of water content. Concentrations of pollutants in spiked samples (per gram of dried-matter) were: 0.4 μg/g of PCB 21, 0.6 μg/g of PCB 24, 0.6 μg/g of PCB 26, 0.6 μg/g of PCB 49, 0.3 μg/g of PCB 153, 0.4 μg/g of p,p′-DDD, 0.3 μg/g of p,p′-DDE, 0.3 μg/g of p,p′-DDT, 0.3 μg/g of Endrin and 0.4 μg/g of Mirex.

Characterization of samples

pH measurements

The pH measurements were made with AOAC Method (no 973.04).

Total water content

ASTM method (D 2974–87) was used to measure the water content of the raw material.

Residual water content

ASTM method (D-2974–87) was used on the air-dried samples. The residual humidity was calculated as

$$\left(\frac{\text{(Mass of air-dried compost)} - \text{(Mass of oven-dried compost)}}{\text{(Mass of air-dried compost)}}\right) \times 100$$

Organic matter contents

The organic matter content was measured by ASTM method (D 2974–87)

Microwave-Assisted Extraction procedure

All MAEs were performed with the Milestone Microwave Laboratory System (MLS 1200, 1200 watts), equipped with an exhaust module (EM 5) and an automatic capping module (ACM 100). The eight Teflon vessels MV 100 (100 mL) were equipped with SV.10 super valve (pressure release 227–284 psi). The system was able to extract eight samples simultaneously: one solvent blank, one compost blank and the six compost samples. The eight Teflon vessels were used in rotation for the controls: the solvent blank and the compost blank. We observed no cross contamination, and no pollutants were detected in the controls (solvent blank and compost blank).

Thirty milliliters of hexane-acetone (1:1) was added to the spiked samples and the controls in the extraction vessel. The vessels were hermetically closed with the automatic capping module (ACM 100). Extraction was performed at 600W for one minute and 0W for two minutes (waiting time). The two steps were performed five times for a total of 15 minutes. The extraction vessels were cooled in an ice bath for 15 minutes before opening. The extracts were centrifuged for 10 min at 3000 g and 0°C. Precisely 10 mL of supernatant was taken, concentrated with a rotary evaporator to 1 to 2 mL and then cleaned.

Cleanup procedure

The Florisil (60–100 mesh, PR grade, Fisher Scientific) was activated at 677 °C for 3 hours and left at 130 °C for five days before use, as well as for storage[8]. Then 3.5 g of Florisil was mixed with hexane and the slurry mixture was inserted in the cleanup column (16 cmX8 mm). One cm of anhydrous Na_2SO_4 was added at the top to retain water. A mixture 85:15 (V:V) of petroleum ether: diethyl ether was used to condition the column (25 mL) and to elute the analytes by gravity. When the extract was added to the column, elution was done until a 10-mL volumetric flask containing the internal standard was filled. The solvent was evaporated and replaced with toluene. The sample was then ready for the analysis. Blank experiments were conducted in order to check for the absence of PCBs or OCPs contamination in the Florisil column.

The load of humic substances was evaluated from the absorbance of the solution at 465 nm and 665 nm; this is just an evaluation of sample cleanness.

Analysis of extracts

The analysis of the OCPs and PCBs was performed on a 5890 series II gas chromatograph (Hewlett Packard) equipped with an 7673 autoinjector and two electron capture detectors (ECD). The samples were injected in a split mode (1/10) and introduced via a 30 m length × 0.25 mm i.d. × 0.25 µm film thickness PTE-5 (Supelco, Inc.) fused-silica open tubular column and a 30 m length × 0.25 mm i.d. × 0.25 µm film thickness SPB-608 (Supelco, Inc.). The flow rate of helium carrier gas was 1 mL/min. The column's initial temperature was set at 90°C. The temperature was increased to 160 °C at 5 °C/min, then increased to 290 °C at 4°C/min. The final temperature was maintained for 16 minutes. The injection volume was 1 µL, and the injector temperature was 240 °C. The detector temperature was 300 °C and the make-up gas was argon/methane (95:5) at a flow rate of 110 mL/min for each detector.

RESULTS AND DISCUSSION

Characteristics of the matrix studied

The amounts of organic matter and humidity as well as the pH of the five samples are studied presented in Table I. As expected, the composts were much richer in organic matter (19.9 to 67.3%) than is soil (4.9%). The residual humidity (after air-drying) is low for two of the four composts. The organic content and the residual humidity are two important determinants of the recoveries of the pollutants by microwave assisted extraction. For the development of the MAE method, only the compost "windrow 8" is used in order to eliminate variability in sample composition.

Methods of preparation of the compost sample

The compost samples (windrow 8) were prepared in three different ways: (1) oven-dried at 105 °C for 24 h, (2) air-dried, and (3) as received. All samples were spiked, extracted by MAE and subjected to the cleanup procedures. The absorbances were measured at 465 and 665 nm to evaluate the cleanness of the samples (Table II). The uncleaned extracts showed high absorbances at 465 and 665 nm; after the cleanup procedure, the absorbances were very low. Cleanup of the extracts is necessary because humic substances interfere with the analyses. These interferences are chromatographic column contamination, decrease in detector sensitivity, etc.

TABLE II Determination of the absorbances of the extracts

Cleaned extract	*Absorbance*^{a} *465 nm*	*Absorbance*^{a} *665 nm*
MAE, oven dried compost and hexane-acetone (1:1)	0.020 (0.003)	0.001 (0.001)
MAE, moist compost and hexane	0.003 (0.003)	0.002 (0.001)
MAE, air-dried compost and hexane-acetone (1:1)	0.002 (0.002)	0.002 (0.001)
MAE, air-dried compost and hexane	0.002 (0.002)	0.000 (0.000)
MAE, air-dried compost hexane-acetone (1:1) plus 0.5 mL of water	0.016 (0.010)	0.003 (0.003)
Uncleaned extract (for comparison with cleaned extract)		
MAE, air-dried compost and hexane-acetone (1:1)	0.314	0.079

a. Mean (standard deviation) for n = 6.

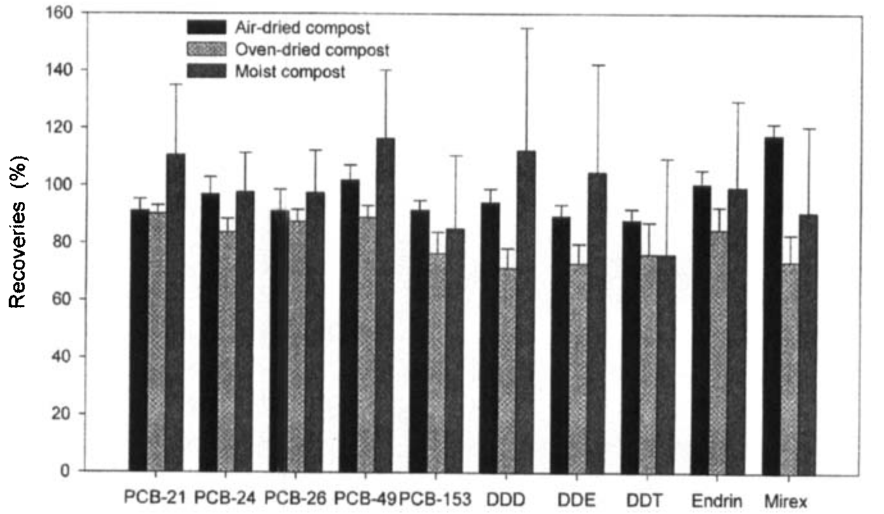

FIGURE 1 Evaluation of compost preparation for MAE method (n=6)

Figure 1 shows the best recoveries (88–102% except 118% for Mirex) and the smaller SD (3.5–7.5%) for air-dried compost. For oven-dried compost samples, the recoveries of all analytes were lower (72–90% with RSD 3–11%) probably caused by changes in the configuration of the humic molecules by the lost of hydration water. The humic substances must gain in hydrophobic character so that they are more soluble in the extraction solvent. In addition, the amount of humic substances in the cleaned sample solutions is greater than those from air-dried compost, (Table II). This demonstrates the increase in solubility of the humic substances obtained from oven-dried compost. For extraction with moist compost, the solvent is, hexane, which is not miscible with water. The recoveries (76 to 116 %) from the moist compost (as receiving) are more variable than those from air-dried compost. In addition, the precision of the extraction is very poor (standard deviation 14 to 44 %). The variation must be caused by the heterogeneity of the sample (raw material) and the variable moisture in each extraction vessel. Since the spiking procedure took 24 h, the humidity in the compost had partially evaporated and it varies from vessel to vessel. Despite this variation, the recoveries are better for some analytes, especially the PCBs. This is probably caused by a decrease in the interaction of the analyte with the compost when the humic substances are not dried. The air-dried method is the best for sample preparation with good recoveries for the majority of the analytes (88 to 102%, except 118% for Mirex) and the smaller standard deviation (3.5 to 7.5%).

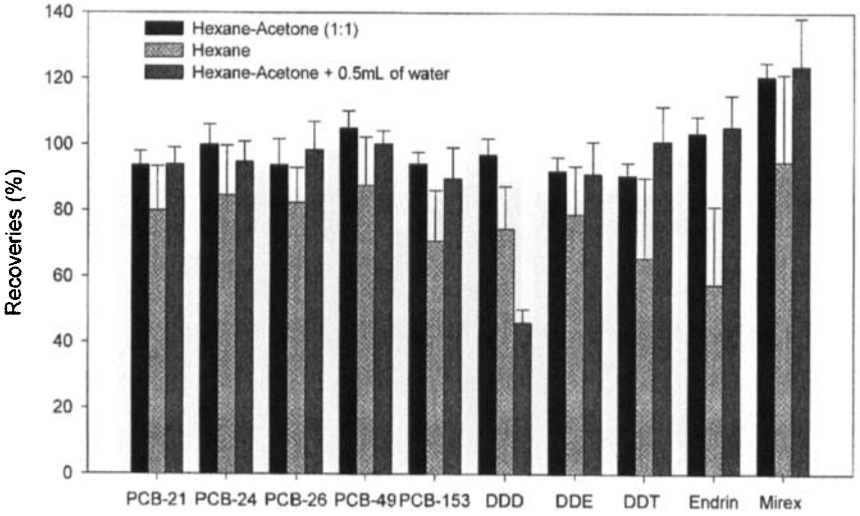

FIGURE 2 Effect of different solvents on recoveries of pollutants by MAE method (n=6)

Extraction solvent

The extraction was performed on air-dried compost (windrow 8) for the two series: hexane-acetone (1:1) and hexane. Hexane-acetone(1:1) is the best solvent for the extraction of OCPs and PCBs from compost. The recoveries range from 91 to 105 % (except for mirex, 121%) with standard deviations of 4–8 %,

Figure 2. In comparison, the recoveries with hexane alone as solvent were lower (58–95% with SD 11–26%) and there is a significant difference (t-test) between the means of the series at a 95% confidence levels. These lower values might be due poor solvation of the matrix by hexane. Even though the compost has lost its hydration water and has some hydrophobic character, it still has many polar groups. Thus, the extracts obtained with hexane are much cleaner which shows that the degree of solvation of organic matter is lower. Therefore hexane as extraction solvent, interacts with the air-dried compost less well than acetone. It appears that acetone helps solvate the matrix slightly and favors the recoveries. In addition, the extraction with hexane-acetone (1:1) occurs at a higher effective temperature than hexane alone because acetone absorbs microwave energy. Acetone is heated rapidly because it has a dipole moment which rotates when microwave energy is applied. So the system using hexane-acetone (1:1) generates heat which probably helps the extraction.

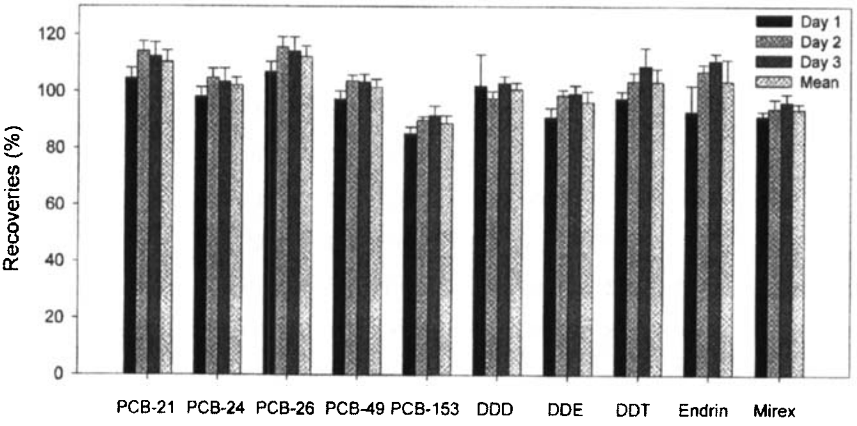

FIGURE 3 Repeatability and reproducibility of MAE method (n=6)

Addition of water to the extraction solvent

A volume of 0.5 mL of deionized and distilled water was added to the extraction vessel prior to extraction. This addition was made to obtain a higher extraction temperature and to determine the effect on the recoveries. The extraction was made on air-dried spiked compost with hexane-acetone (1:1). The addition of water did not increase the recoveries of the analytes, and there is not a significant difference between the means of the two series: hexane-acetone (1:1) without or with addition of 0.5 mL of water, (Figure 2). There is one exception: DDD was less after addition of water, although the coefficient of variation was good at

4.1 %. But the cleanup of the extracts with water left the clean extracts with more humic substances. Table I shows the absorbance at 465 nm of the clean sample solution. The absorbance of the samples extracted after addition of water are higher. For DDD, the loss of analyte must have been due to some interaction with the humic substances. For Mirex there must have been some interference causing a higher recovery.

TABLE III Comparison of composts and soil extracted by MAE method

	Recoveries (%)									
	Windrow 8		*Windrow 6*		*TIRU*		*Shrimp*		*Soil*	
	Mean[a]	*SD*[b]	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
PCB-21	114	4	113	2	118	2	104	5	104	1
PCB-24	105	3	102	1	104	2	98	4	101	1
PCB-26	116	4	113	2	118	2	104	5	104	1
PCB-49	104	2	105	2	111	1	101	4	105	1
PCB-153	90	1	88	1	106	1	101	4	108	1
p,p'-DDD	98	2	95	2	120	2	119	4	103	2
p,p'-DDE	99	2	99	4	113	2	110	5	106	1
p,p'-DDT	103	3	103	3	107	1	98	7	109	1
Endrin	107	2	111	3	118	3	116	5	66	43
Mirex	94	3	98	3	99	7	100	3	98	3
	Absorbance (SD)									
465 nm	0.009[a]		0.006		0.009		0.002		0.001	
	(0.004)[b]		(0.002)		(0.003)		(0.001)		(0.001)	
665 nm	0.000		0.001		0.000		0.000		0.000	
	(0.000)		(0.001)		(0.002)		(0.001)		(0.000)	

a. Mean (n = 6, except for TIRU compost n = 5).
b. Standard deviation.

Analytical performances

The repeatability of the method developed has been determined for 6 samples per day. Figure 3 shows good recoveries each day with acceptable standard deviations (2 to 11 %). The reproducibility was evaluated on 3 days. The means were from 94 to 112% with small standard deviations (2 to 8%).

Analysis of different samples

The MAE method was developed with a compost produced from pulp and paper sludge, wood bark and pig manure (windrow 8, described in previous section).

The MAE method has been applied to other composts and to a soil, with characteristics as in Table I. The organic content varied from 20 to 67% for composts, and was 5% for the soil. The residual humidity after air-drying varied somewhat. Table III summarizes results from five different samples. Average recoveries were >80% for all compounds except for Endrin (66% with SD 43%) in soil. The low recovery and precision for Endrin could indicate a weak solvation of the analyte present in the soil.

CONCLUSION

The MAE method is a very effective method for the extraction of OCPs and PCBs from compost and soil. The samples should be air-dried and extracted with hexane-acetone (1:1). The recoveries and the SD were good for soil and composts which have different organic matter content. In addition, the MAE method including cleanup procedure is completed in less then two hours for eight samples with considerable cost savings and solvent savings over conventional Soxhlet extraction technique.

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