

Determination of pesticides in compost by pressurized liquid extraction and gas chromatography–mass spectrometry

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Abstract

A gas chromatographic–mass spectrometric method was developed for the determination of pesticides in compost. The investigated pesticides included two fungicides, two herbicides and 10 insecticides. The pesticides were extracted from the compost by pressurized liquid extraction. The extract was cleaned up by a partition between hexane and acetonitrile followed by a dispersive solid-phase extraction using a porous carbon made from Moso bamboo (*Phyllostachys pubescens*). The overall recoveries were 81–104% and the relative standard deviations (RSDs) ranged from 2.4 to 12%. The minimum detectable concentrations were 0.02–0.04 $\mu\text{g g}^{-1}$. This method was successfully applied to a compost sample from food waste as well as commercial compost.

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1. Introduction

Composting is a method of recycling waste as well as reducing waste amounts. Livestock waste, food waste, wood waste, straw and husk, sewage sludge, etc., are used as a matrix for composting [1]. However, some waste can contain toxic chemicals [2–4]; the contamination of compost with toxic chemicals such as polycyclic aromatic hydrocarbons [2] and PCBs [5] has been reported. Pesticides are potentially present in composting feedstocks including yard trimmings, municipal solid wastes and agricultural residues [3]. For example, in USA, compost products from feedstocks containing the herbicide clopyralid have damaged non-target crops [6]. Wågman et al. [5] detected organochlorine pesticides (pentachlorobenzene, hexachlorobenzene, DDTs, dieldrin, c-heptachloroepoxide, chlordanes and nonachlors) in compost samples generated from vegetable leftovers from the staff's lunches, peat, potato peel, vegetables, fruits, newspapers, bananas and other waste from vegetables, fruits and newspaper. Moreover, several current herbicides (2,4-D,

alachlor, atrazine, etc.) and insecticides (chlorpyrifos, diazinon, malathion, carbaryl, etc.) have also been detected in compost [3]. There is no legislated or recommended reference value for the pesticides in compost. However, it is important to verify the complete absence of pesticides in the final compost because the use of contaminated compost can cause soil contamination. Moreover, the contaminated compost applied to the soil could cause the environmental contamination. Therefore, the development of determination method for pesticides in compost is also important in order to monitor pesticides in the environment.

Pesticides in compost are determined by GC–MS [2,5], GC [7] or HPLC [8] after extraction. Several extraction procedures have been developed: Soxhlet extraction [5], microwave-assisted extraction [7], solvent extraction [8] and static subcritical water extraction [2].

Pressurized liquid extraction (or accelerated solvent extraction) has been developed for the extraction of pesticides in soil [9] and food [10]. However, there are few papers describing the applicability of the method for the extraction of pesticides in compost.

This paper describes the determination of pesticides in compost using a pressurized liquid extraction for

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GC–MS determination. The investigated pesticides were two fungicides (imazalil and isoprothiolane), two herbicides (mefenacet and thiobencarb) and 10 insecticides (carbaryl, chlorpyrifos, chlorpyrifos methyl, cypermethrin, diazinon, *O*-ethyl *O*-4-nitrophenylphenyl phosphonothioate (EPN), fenitrothion, fenvalerates, malathion and pirimiphos methyl). They are commonly used for cultivation in Asian countries including Japan.

Fogg and Boxallj [8] determined the pesticides, isoproturon and chlorothalonil, in compost by HPLC without any cleanup procedure. However, Florisil column chromatography [5,7], gel permeation chromatography [5] and solid-phase extraction (SPE) using octadecyl silane [2] were reported as cleanup procedures for GC–MS or GC determination. Regarding pressurized liquid extraction, interfering components can be co-extracted from samples together with the target pesticides. Therefore, a partition between hexane and acetonitrile and a dispersive solid-phase extraction were evaluated as cleanup procedures. Anastassiades et al. [11] reported that the dispersive solid-phase extraction with a primary secondary amine sorbent could remove many polar matrix components, such as organic acids, certain polar pigments, and sugars, from the food extracts to some extent. We evaluated porous carbons [12–14] as the solid-phase.

2. Experimental

2.1. Apparatus

An ASE100 System (Dionex, Sunnyvale, CA, USA) with 11-ml stainless steel ASE vessels was used for the pressurized liquid extraction. A Finnigan POLARIS Q gas chromatograph–ion trap mass spectrometer (Thermo Electron, Waltham, MA, USA) equipped with a Combi Pal auto injection system (CTC Analytics, Zwingen, Switzerland) was used for the quantitative analysis. A 30 m × 0.25 mm i.d. (0.25 μm film thickness) fused-silica J&W DB-5MS column (Agilent, Palo Alto, CA, USA) was used for the GC separation.

2.2. Materials

The standard chemicals were purchased from Kanto (Tokyo, Japan) and Wako (Osaka, Japan). The purities of the standard chemicals were 96.0% for sypermethrins, 98.0% for EPN, fenitrothion, imazalil, malathion and pirimiphos methyl, and 99.0% for the other pesticides. Solvents of pesticide analytical grade were purchased from Kanto. Each standard pesticide was dissolved in acetone to make up a 1 mg ml⁻¹ stock standard solution. A standard solution of a mixture of target pesticides (40 μg ml⁻¹) was prepared in acetone. An internal standard solution (40 μg ml⁻¹) of 9-bromoanthracene (Aldrich, Milwaukee, WI, USA) and 1,4-diiodobenzene (Tokyo Kasei, Tokyo, Japan) were prepared

in acetone. The purified water was from a Milli-Q system (Millipore, Bedford, MA, USA).

Bark compost, cow dung compost and food waste compost were obtained from Honen Agri (Niigata, Japan), Yoshida Agri Factory (Fukushima, Japan) and A&M Shimota Farm (Ibaraki, Japan), respectively. Bamboo porous carbons (BPCs) were prepared using the same method as previously described [12–14]. In brief, Moso bamboo (*Phyllostachys pubescens*) was carbonized using an electric charcoal kiln. Three BPCs, BPC₄₀₀, BPC₇₀₀ and BPC₁₀₀₀, were obtained by carbonization at final temperatures of 400, 700 and 1000 °C, respectively. The temperature for BPC₄₀₀ was programmed from room temperature to 100 °C at 1.3 °C min⁻¹, then from 100 °C (held for 1 h) to 400 °C (held for 1 h) at 5 °C min⁻¹. The temperature for BPC₇₀₀ was programmed from room temperature to 100 °C at 1.3 °C min⁻¹, from 100 °C (held for 1 h) to 500 °C at 6.7 °C min⁻¹ and from 500 °C (held for 1 h) to 700 °C (held for 1 h) at 3.3 °C min⁻¹. The temperature for BPC₁₀₀₀ was programmed from room temperature to 100 °C at 1.3 °C min⁻¹, from 100 °C (held for 1 h) to 500 °C at 6.7 °C min⁻¹ and from 500 °C (held for 1 h) to 1000 °C (held for 1 h) at 2 °C min⁻¹. The resulting porous carbons were crushed and sieved to a particle diameter of 25–125 μm. The BET-surface area and the total pour volume of BPC₄₀₀, BPC₇₀₀ and BPC₁₀₀₀ were 2.50 m² g⁻¹ and <0.01 ml g⁻¹, 251 m² g⁻¹ and 0.143 ml g⁻¹, and 300 m² g⁻¹ and 0.153 ml g⁻¹, respectively [14].

2.3. Determination procedure

A 2-g sample was packed in the ASE vessel. The vessel was then closed and placed in the ASE system. The sample was extracted twice with acetonitrile. The extraction conditions were as follows: extraction temperature, 120 °C; extraction pressure, 11 MPa; static extraction time, 5 min; solvent flush volume, 6.6 ml; nitrogen purge time, 5 s. The extract was evaporated to 5 ml using a rotary evaporator at 30 °C, and purified with 2 ml of hexane by shaking for 1 min. After the hexane layer was discarded, the acetonitrile layer was concentrated to 1 ml under a purified nitrogen gas stream. A 100-mg sample of BPC₄₀₀ was added to the acetonitrile solution. The solution was shaken for 1 min and filtered. Two milliliters of hexane and 3 ml of purified water were added to the filtrate. After shaking for 2 min, the water layer was discarded. The hexane layer was washed with 3 ml of purified water by shaking for 1 min. After the hexane solution was dried over anhydrous sodium sulfate, the solution was concentrated to 1 ml under a purified nitrogen gas stream.

2.4. GC–MS analysis

A 5-μl aliquot of the internal standard solution was added to the concentrated solution and 1 μl of the resulting mixture was injected into the GC–MS instrument. The target pesticides in a sample were simultaneously determined in

Table 1
Retention times and selection ions for determination of pesticides

Compound	Use ^a	Mw ^b	TR (min) ^c	m/z	
				Q ^d	I ₁ ^e
Carbaryl	I	201.2	13.46	144	116
Chlorpyrifos	I	350.6	13.93	197	199
Chlorpyrifos methyl	I	322.5	13.29	286	288
Cypermethrins	I	416.3	19.84	163	181
			20.00	163	181
			20.07	163	181
			20.16	163	181
Diazinon	I	304.3	12.59	152	199
EPN	I	323.3	16.99	157	169
Fenitrothion	I	277.2	13.72	125	109
Fenvalerates	I	419.9	21.47	181	152
			20.90	181	152
			15.14	215	217
Imazalil	F	297.2	15.14	215	217
Isoprothiolane	F	290.4	15.19	118	162
Malathion	I	330.3	13.80	127	125
Mefenacet	H	298.4	17.76	192	136
Pirimiphos methyl	I	305.3	13.65	180	233
Thiobencarb	H	257.8	13.97	125	72
9-Bromoanthracene	IS	329.9	15.04	256	258
1,4-Diiodobenzene	IS	257.1	9.96	330	203

^a F, fungicide; H, herbicide; I, insecticide; IS, internal standard.

^b Molecular weight.

^c Retention index.

^d Quantitation ion.

^e Confirmation ion.

one injection. The monitored ions for quantification of the compounds are listed in Table 1 together with their retention times. The ratios of the peak areas of the quantitative ions to those of the internal standards were used for quantification of the pesticides.

The GC–MS conditions were as follows: column temperature, programmed from 50 °C (held for 1 min) to 280 °C (held for 10 min) at a rate of 15 °C min⁻¹; injector temperature, 200 °C; injection mode, splitless; helium carrier gas flow rate, 1.0 ml min⁻¹; MS transfer temperature, 290 °C; ion source

temperature, 250 °C; ionization mode, electron impact; ionization energy, 70 eV; mass scan range, *m/z* 50–450.

3. Results and discussion

3.1. Evaluation of the pressurized liquid extraction conditions

Extraction conditions, namely, extraction solvent, extraction temperature and extraction cycle times, were evaluated in order to achieve the most efficient extractions for the target pesticides. These conditions are important parameters for achieving a quantitative extraction [15]. Experiments for the evaluation were performed on fortified compost samples for optimization of the pressurized liquid extraction conditions. The 11 pesticides listed in Table 2 were used for the evaluations.

First, the extraction solvent was evaluated. Desorption efficiencies from the compost after one extraction cycle were studied for the 11 pesticides. Hexane, dichloromethane, acetone, methanol and acetonitrile were investigated as extraction solvents. The results are shown in Table 2. When hexane was used, the recoveries of the target pesticides did not exceed 30%. Dichloromethane, acetone and methanol produced recoveries of 44–84%, 47–95% and 45–96%, respectively. Among the solvents investigated, acetonitrile produced the best recoveries of 58–108%. Moreover, the partition between hexane and acetonitrile was successfully performed (86–95%) for the target pesticides as will be described later. Therefore, when acetonitrile was used as the extraction solvent, the extract was simply cleaned up by the partition between hexane and acetonitrile. Consequently, acetonitrile was recommended for the extraction of the target pesticides.

Second, the effect of the extraction temperature on the recoveries of the 11 pesticides was evaluated for one

Table 2
Influence of solvent extraction on pesticide recoveries

	Analytical recovery (%) ^a									
	Hexane		DCM ^b		Acetone		Methanol		Acetonitrile	
	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)
Carbaryl	7	7.9	57	19	60	21	60	12	73	3.7
Chlorpyrifos	7	9.4	44	18	48	9.2	43	13	58	3.3
Chlorpyrifos methyl	16	14	56	16	47	8.6	49	9.4	62	3.3
Diazinon	23	13	64	15	55	7.3	52	6.2	77	2.4
Fenitrothion	19	19	64	19	56	20	60	12	73	6.1
Imazalil	22	26	84	20	95	9.0	96	7.6	108	5.7
Isoprothiolane	6	16	47	26	61	18	66	17	98	4.6
Malathion	14	20	65	16	67	15	74	12	90	2.8
Mefenacet	13	27	51	17	73	12	71	15	78	3.4
Pirimiphos methyl	15	18	50	18	61	16	51	12	67	2.4
Thiobencarb	15	16	68	16	64	11	65	12	87	2.6

Pesticides (2 µg each) were spiked to 2 g of compost (*n* = 3).

^a Value after one extraction at 120 °C.

^b Dichloromethane.

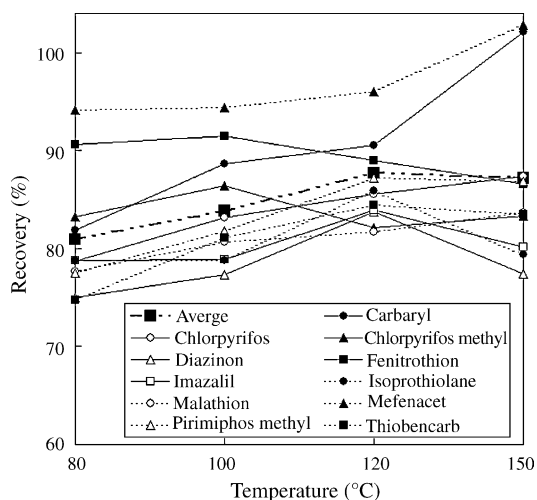


Fig. 1. Effect of extraction temperature on pesticide recoveries.

extraction cycle. These results are shown in Fig. 1. The recoveries of chlorpyrifos methyl and fenitrothion at 100 °C were higher than those at 80, 120 and 150 °C. Those of carbaryl, chlorpyrifos and mefenacet increased as the temperature increased. On the other hand, those of the other pesticides at 120 °C were the highest of the investigated extraction temperature conditions. Moreover, the mean recovery at 120 °C (88%) was higher than those at 80 °C (81%), 100 °C (84%) and 150 °C (86%). It is suggested that the increased temperature can disrupt the strong solute–matrix interactions of the solute molecules and active sites in the matrix [16]. However, Concha-Grāna et al. [9] reported that recoveries of organochlorine pesticides from soils on the pressurized liquid extraction at 150 °C were slightly lower than those at 100 °C. In this study, the mean recovery at 150 °C was rather lower than that at 120 °C, which agreed with the results of organochlorine pesticides. Therefore, we selected 120 °C as the extraction temperature.

Third, the influence of the extraction cycle times on the recoveries of the pesticides were examined at 120 °C. These results are given in Table 3. The recoveries of chlorpyrifos, fenitrothion, imazalil, isoprothiolane, malathion and thiobencarb increased as the extraction cycle times increased. Those of chlorpyrifos methyl and diazinon were the highest for two extractions under the investigated conditions. In contrast, negligible differences were found between one, two and three

Table 3
Influence of extraction cycle times on pesticide recoveries

	Recovery (%)		
	1 ^a	2 ^a	3 ^a
Carbaryl	91	91	90
Chlorpyrifos	86	88	89
Chlorpyrifos methyl	82	99	98
Diazinon	84	95	94
Fenitrothion	89	92	94
Imazalil	84	95	96
Isoprothiolane	86	94	95
Malathion	90	94	96
Mefenacet	96	95	97
Pirimiphos methyl	96	93	95
Thiobencarb	87	95	96
Mean	88	94	95

^a Number of extraction cycles.

cycle times for those of carbaryl, mefenacet and pirimiphos methyl. These pesticides were well recovered (>90%) after one extraction and hence did not affect the extraction cycle times. The mean recoveries after one, two and three extraction cycles were 88, 94 and 95%, respectively. Although three extraction cycles provided the maximum recovery, the difference between two and three extraction cycles was not significant. Moreover, it should be noted that three extraction cycles increase the extraction solvent volume and prolong the total extraction time without any remarkable effect. Consequently, we chose two extraction cycles for this study.

3.2. Evaluation of cleanup

A partition between hexane and acetonitrile [17] was evaluated as a cleanup procedure. Five milliliters of an acetonitrile extraction from the cow dung compost containing 2 µg of the target pesticides was added to 2 ml of hexane, and then shaken for 1 min. Recoveries of the pesticides from the acetonitrile layer are listed in Table 4. All the pesticides were nearly 90% recovered. This partition procedure was applied to the compost extracts. The procedure was found effective in removing fatty substances in the extracts as shown by slight yellow coloration in the hexane layer.

A dispersive solid-phase extraction was evaluated as an additional cleanup procedure. Activated carbons are typical adsorbents for the cleanup procedure. Generally, amounts

Table 4
Partition between hexane and acetonitrile

	Recovery (%)	RSD (%)		Recovery (%)	RSD (%)
Carbaryl	93	2.6	Fenvalerate	94	9.1
Chlorpyrifos	86	1.9	Imazalil	94	7.6
Chlorpyrifos methyl	91	3.9	Isoprothiolane	92	5.6
Cypermethrin	93	6.7	Malathion	95	6.4
Diazinon	87	2.0	Mefenacet	95	1.3
EPN	94	1.8	Pirimiphos methyl	92	4.1
Fenitrothion	91	2.5	Thiobencarb	88	2.7

Pesticides (2 µg each) were spiked to extract of compost ($n = 3$).

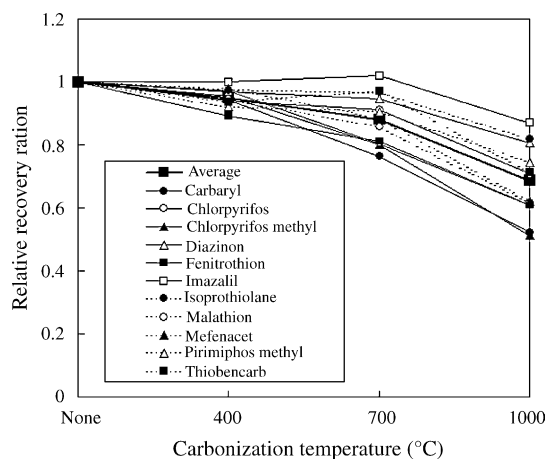


Fig. 2. Pesticide recoveries with the dispersible solid-phase extraction using porous carbons.

of compounds adsorbed to the activated carbon increase as the surface area and the total pore volume of the activated carbon increase. A typical commercial porous carbon (the BET-surface area, $1350 \text{ m}^2 \text{ g}^{-1}$; the total pore volume, 0.611 ml g^{-1}) made from coconut-shell adsorbed the pesticide bensulfonmethyl strongly [14]. Therefore, the dispersible solid-phase extraction using the activated carbon should give poor recoveries of the pesticides. On the other hand, the bamboo porous carbons had the BET-surface areas of $2.5\text{--}300 \text{ m}^2 \text{ g}^{-1}$ and the total pore volumes of <0.01 to 0.153 ml g^{-1} , and adsorbed less amounts of bensulfonmethyl than the activated carbon [14].

Therefore, three porous carbons, BPC₄₀₀, BPC₇₀₀ and BPC₁₀₀₀, were examined as the solid phase to remove the matrix compounds. These results are shown in Fig. 2. The mean of the recovery ratios with the procedure to those without the procedure were 0.95 for BPC₄₀₀, 0.88 for BPC₇₀₀ and 0.69 for BPC₁₀₀₀. This tendency agreed with the result that BPC₄₀₀ adsorbed bisphenol A and estradiol less than

BPC₇₀₀ which adsorbed them less than BPC₁₀₀₀ [13]. Therefore, BPC₄₀₀ was used for the cleanup procedure.

These cleanup procedures were applied to extracts from compost samples using the pressurized liquid extraction. The extract was of dark yellow color. On the other hand, a pale yellow solution was obtained after the proposed cleanup procedures.

3.3. Evaluation of method performance

To evaluate the performance of the method, the overall recoveries of the target pesticides from the compost samples were investigated. A compost sample (2 g) was fortified with standard pesticides ($0.1 \mu\text{g}$ each) and left for 30 min at room temperature for solvent evaporation. The sample was treated by the method described in Section 2.3 and analyzed by GC-MS as described in Section 2.4.

Three compost samples, bark compost, cow dung compost and food waste compost, were used for the evaluation. Two grams of each compost sample was treated using the method described above, and the obtained solution was used as the blank sample. No target pesticides were detected from the blank samples.

The results of the overall recovery tests for 14 pesticides are shown in Table 5. Recoveries of the pesticides from the three compost products ranged from 81 to 104% for the bark compost, 86–99% for the cow dung compost and 87–102% for the food waste compost. These results indicate that the recoveries of the pesticides were good. The relative standard deviations (RSDs) ranged from 4.2 to 12% for the bark compost, 2.4–11% for the cow dung compost and 3.6–12% for the food waste compost. These results indicate that the accuracy of the method was good. Consequently, the pesticides were satisfactorily determined by this method.

The minimum detection limits (MDLs) were calculated by considering the values three times the standard deviation of the replicate analyses in $\mu\text{g g}^{-1}$ obtained from the results

Table 5
Recoveries from compost samples and minimum detection limits of pesticides

	Bark compost		Cow dung compost		Food waste compost		MDL ($\mu\text{g g}^{-1}$) ^a
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Carbaryl	96	6.6	88	6.5	88	7.5	0.02
Chlorpyrifos	90	9.9	93	9.0	97	4.5	0.03
Chlorpyrifos methyl	89	11	93	9.0	87	3.6	0.03
Cypermethrins	91	10	95	6.5	95	5.7	0.03
Diazinon	85	6.7	92	7.6	96	6.0	0.02
EPN	101	11	99	2.4	97	3.8	0.03
Fenitrothion	91	6.5	86	10	88	9.7	0.03
Fenvalerates	91	5.9	91	6.9	95	8.4	0.03
Imazalil	81	11	98	8.5	100	6.8	0.03
Isoprothiolane	86	4.2	99	7.4	100	10	0.03
Malathion	85	5.9	92	11	93	12	0.04
Mefenacet	104	12	96	6.1	96	7.5	0.04
Pirimiphos methyl	89	6.4	95	9.0	99	7.0	0.03
Thiobencarb	87	5.3	96	8.8	102	7.9	0.03

Pesticides ($0.1 \mu\text{g}$ each) were spiked to compost ($n = 5$).

^a Minimum detection limit.

of the recovery tests ($n=5$) using the three compost products (Table 5). Since the MDLs could be affected by the matrix of the samples used, the largest value derived from the three recovery tests of each pesticide was determined as the MDL [18]. The calculated MDLs of the target pesticides were $0.02 \mu\text{g g}^{-1}$ (carbaryl and diazinon) to $0.04 \mu\text{g g}^{-1}$ (malathion and mefenacet) as shown in Table 5.

3.4. Application to compost samples

This method was used for the determination of the pesticides in four commercially available compost samples. The samples were rice husk compost, leaf compost, cow dung compost and fowl droppings compost. No target pesticides were detected from the blank samples.

This method was also used for the determination of pesticides in a compost sample prepared by adding chlorpyrifos and fenitrothion to food waste from a restaurant. The concentrations of chlorpyrifos and fenitrothion in the waste were 1.5 and $210 \mu\text{g g}^{-1}$ on dry weight, respectively. The waste was composted for 100 days with mixing every 20 days. The concentrations of chlorpyrifos and fenitrothion in the compost were 0.38 and $<0.02 \mu\text{g g}^{-1}$ on dry weight, respectively. The water content of the waste (76%) was reduced to 12% during the composting. The other investigated pesticides were not detected from the samples. Fenitrothion was completely degraded by the composting because the increased microbial activity of the compost can increase the degradation rates of fenitrothion. On the other hand, 25% of chlorpyrifos remained in the compost during the composting conditions. Vischetti et al. [19] reported that chlorpyrifos was decomposed in a biological reactor system, while chlorpyrifos was the best retained compared to the fungicide metalaxyl and herbicide imazamox due to its physico-chemical characteristics. Moreover, the half-life of pesticides were affected by composting conditions. Therefore, the lower degradation rate of chlorpyrifos in the present study resulted from the characteristics as well as the investigated composting conditions.

4. Conclusions

A pressurized liquid extraction method was developed for the gas chromatographic–mass spectrometric determination of 14 pesticides in compost. The optimum conditions for

the extraction process, two extractions with acetonitrile at 120°C , were established. A partition between hexane and acetonitrile and a dispersive solid-phase extraction using a porous carbon made from Moso bamboo (*P. pubescens*) were successfully adopted as cleanup procedures. This method was validated using three compost samples fortified with standard pesticides, and was successfully applied to a compost sample from food waste as well as commercially available compost in Japan.

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