Supercritical Fluid Extraction of Bound Pesticide Residues from Soil and Food Commodities†

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The use of supercritical carbon dioxide with and without methanol as a modifier to extract bound ^{14}C pesticide residues from soil, plants, and wheat samples is described. These residues cannot be extracted and detected by methods devised for routine analysis of pesticides and/or metabolites in biological and environmental samples. The ^{14}C material extracted was trapped in methanol, radioassayed, and then analyzed by various chromatographic techniques. Optimal supercritical fluid extraction conditions for extraction were obtained for each pesticide by varying the temperature, pressure, and amount of modifier. Supercritical carbon dioxide modified with methanol improved the recovery of bound ^{14}C residues from soil and plant samples. Supercritical methanol was found to be less efficient than supercritical carbon dioxide or methanol-modified supercritical carbon dioxide for the extraction of bound pesticide residues. Analysis of the extracts indicated that the ^{14}C bound residues in soil, plants, and wheat samples were present in the form of parent compounds and/or metabolites.

Keywords: *Supercritical fluid extraction; bound residues; supercritical carbon dioxide; modifier; pesticide residues*

INTRODUCTION

Recently, interest in the use of supercritical fluid extraction (SFE) as an analytical technique in the field of pesticide residue analysis has increased considerably. The technique has been applied to the extraction of pesticides and/or metabolites from soil (Brady et al., 1987; Engelhardt and Gross, 1988; McNally and Wheeler, 1988; Wheeler and McNally, 1989; Snyder et al., 1992; Locke, 1993; Lopez-Avila et al., 1990, 1993) and from food products (Campbell et al., 1989; France and King, 1991; Hooper and King, 1991; Thomson and Chesney, 1992; Wigfield and Lanouette, 1993). SFE yields superior extraction efficiencies and offers a number of potential advantages compared to conventional solvent extraction methods for isolating pesticide residues from biological and environmental sample matrices. This is based on the enhanced solvating power of supercritical fluids above their critical points and their lower viscosities and higher diffusivities relative to liquid solvents (Hawthorne, 1990).

Traditional solvent-based methods of extraction have been used for quantitative recoveries of many pesticides from biological and environmental samples. However, by using radiotracer techniques, it has been demonstrated that these classical or conventional methods of extraction for certain pesticides and/or metabolites often do not always remove all of the residues from soil, plants, and food products (Huber and Otto, 1983; Khan and Dupont, 1987). Therefore, it is likely that in routine pesticide residue monitoring programs the total pesticide residues in various matrices have been underestimated. Hence, SFE may prove useful in the extraction of these nonextractable residues often referred to as "bound residues".

Capriel et al. (1986) have previously used supercritical methanol for the extraction of bound pesticide residues from soil and plant samples. However, it was observed in some instances that the high temperature and pressure used to form supercritical methanol resulted in chemical alteration of the extracted bound residues. An alternative approach is to use SFE with carbon dioxide in place of methanol or other organic solvents. Carbon dioxide is preferred as a supercritical fluid because of its relatively low critical temperature (32 °C) and pressure (73 bar), low toxicity, and reactivity. Modifiers such as methanol can be added to supercritical carbon dioxide to enhance the solubilizing power of the primary supercritical fluid. At low temperature and pressure, the smaller quantity of modifiers may not react with the pesticide and/or its metabolites.

The purpose of this study was to demonstrate that supercritical carbon dioxide, with and without methanol as a modifier, can be used to extract bound pesticide residues from soil, plant, and grain samples treated with radiolabeled pesticides. The subsequent ^{14}C-labeled material extracted by the SFE system was then characterized by chromatographic techniques.

MATERIALS AND METHODS

Chemicals. All solvents used were of pesticide grade and were used as received. The SFE-grade CO_2 was purchased from Scott Speciality Gases (Plumsteadville, PA).

Samples. The samples used in this study were generated during the course of our investigations on bound pesticide residues in soil, plants, and wheat grains (Table 1). At the end of the treatment time the samples were repeatedly extracted with appropriate solvents until no more ^{14}C was extractable, and the material containing nonextractable (bound) ^{14}C residues was air-dried and then finely ground prior to extraction by SFE. Control soil, plant, and wheat samples were processed in a similar manner except for the ^{14}C-labeled pesticide treatment. Portions of the control samples were then fortified with a standard solution of the ^{14}C-labeled pesticide in methanol and allowed to stand overnight at room temperature to evaporate the solvent. All samples were extracted and analyzed in triplicate, and average values are reported.

Supercritical Fluid Extraction (SFE). Samples ranging from 0.5 to 1 g were used. The SFE system (Suprex Model

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Table 1. Bound ^{14}C Residue Levels of Pesticides in Soil, Plant, and Wheat Samples

sample	pesticide	treatment ^{14}C (μCi/g)	treatment ppm	treatment time	bound ^{14}C (%)
organic soil	prometryn	0.047	12	1 year	57.4
	deltamethrin	0.017	10	6 months	19.2
	atrazine	0.006	25	1 year	54.0
mineral soil	atrazine[a]	0.012	10	9 years	50.0
	diuron	0.322	10	6 months	20.0
	2,4-D	0.226	10	3 months	14.0
wheat	deltamethrin	0.050	5	168 days	11.5
	pirimiphos-methyl	0.100	5	28 weeks	9.9
beans	pirimiphos-methyl	0.140	10	6 months	4.2
onion	fonofos[b]	0.067	10	130 days	21.8
radishes	dieldrin[c]	0.005	10	21 days	24.0
canola	atrazine[d]	0.006	4	10 days	44.0

[a] Soil samples were obtained from field plots treated with [^{14}C]atrazine. [b] Onion samples were obtained from field plots treated with [^{14}C]dyfonate. [c] Radishes were grown in sand pots containing 0.005 μCi/mL [^{14}C]dieldrin in Hoagland nutrient solution. [d] Canola was grown in Hoagland nutrient solution containing 0.006 μCi/mL [^{14}C]atrazine.

SFE-50, Suprex Corp., Pittsburgh, PA) consisted of a 250 mL syringe pump with the necessary valves and connecting lines to the extraction vessel, a control module for the SFE system, an extraction oven, a 5 mL extraction vessel for containing the sample, and a four-port valve connected to an outlet restrictor. The restrictor was vented into the first of the four glass tubes containing trapping solvents. Each of the first three tubes contained 50 mL of methanol to collect ^{14}C material that was released by SFE. The fourth tube contained a solution (Carbosorb) to trap $^{14}CO_2$ and was initially changed after every 5 min and then less frequently during the extraction. Preliminary experiments indicated that the loss of ^{14}C residues in the form of $^{14}CO_2$ during SFE was negligible. These solvents in the glass tubes were used to ensure complete trapping of the released ^{14}C material as about 8–10% ^{14}C was often found to be carried over in the second tube. SFE-grade carbon dioxide was delivered as liquid CO_2 at a flow rate at 1.0 mL/min. Methanol delivery was controlled by an HPLC pump (Varian 2510) when carbon dioxide premixed with methanol was used as the extraction fluid. The flow rate for carbon dioxide and methanol was adjusted to obtain the desired proportion (vol %) of the modifier. The extracted ^{14}C materials in the trapping solvents of the first three tubes were combined, evaporated to a small volume, radioassayed, and finally subjected to chromatographic analysis. The material collected in the fourth tube was also radioassayed.

Preliminary experiments were carried out to determine the optimum SFE conditions and the minimum extraction time to obtain maximum recovery from the spiked samples. The

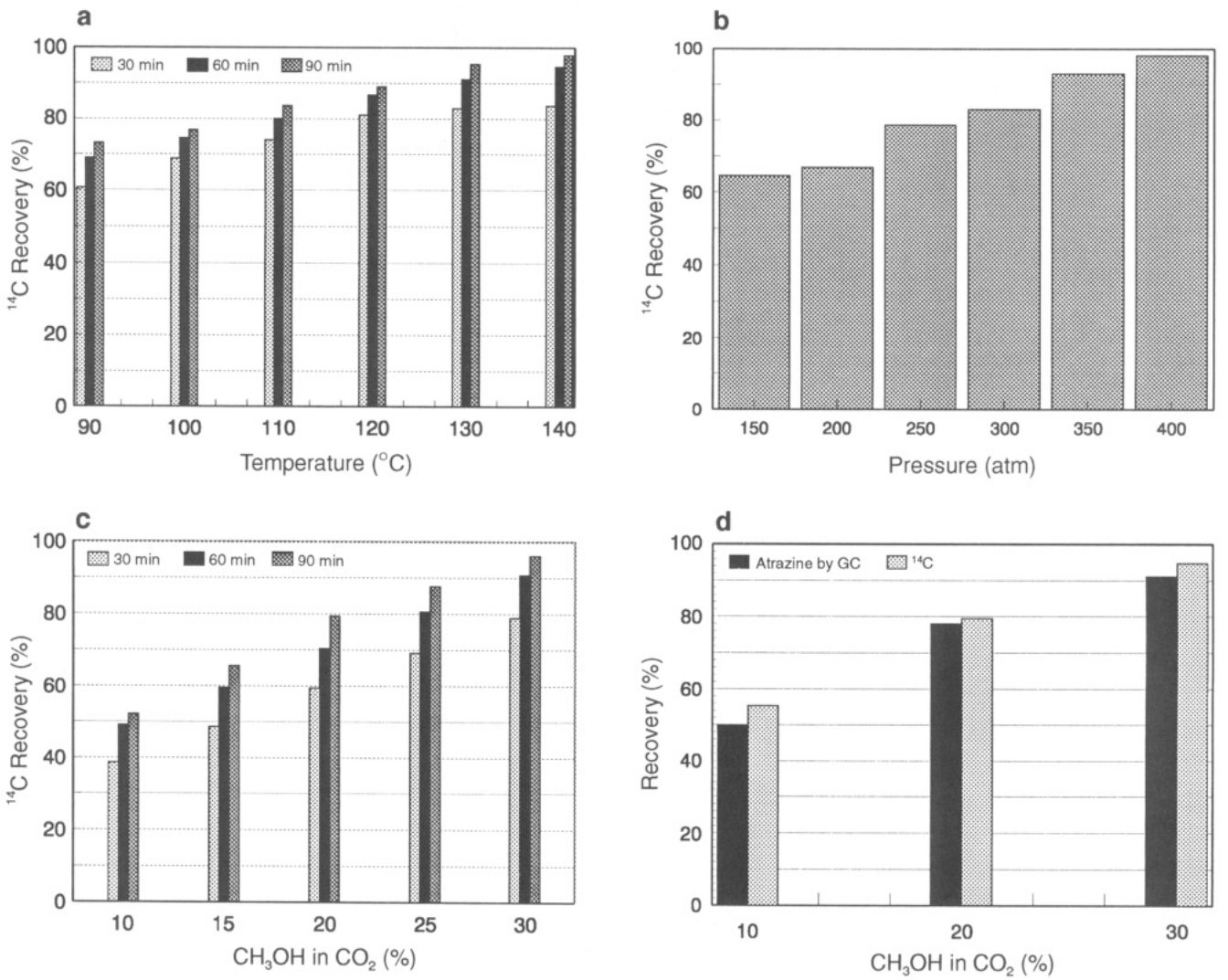

Figure 1. Recovery of ^{14}C from mineral soil spiked with [^{14}C]atrazine using supercritical carbon dioxide: (a) influence of extraction temperature on the recovery of ^{14}C at 350 atm and with 30% methanol modifier; (b) influence of extraction pressure on the recovery of ^{14}C at 125 °C and with 30% methanol modifier using a 90 min extraction; (c) influence of methanol modifier on the recovery of ^{14}C at 350 atm and 125 °C; and (d) influence of methanol modifier on the recovery of ^{14}C and atrazine at 350 atm and 125 °C using a 90 min extraction.

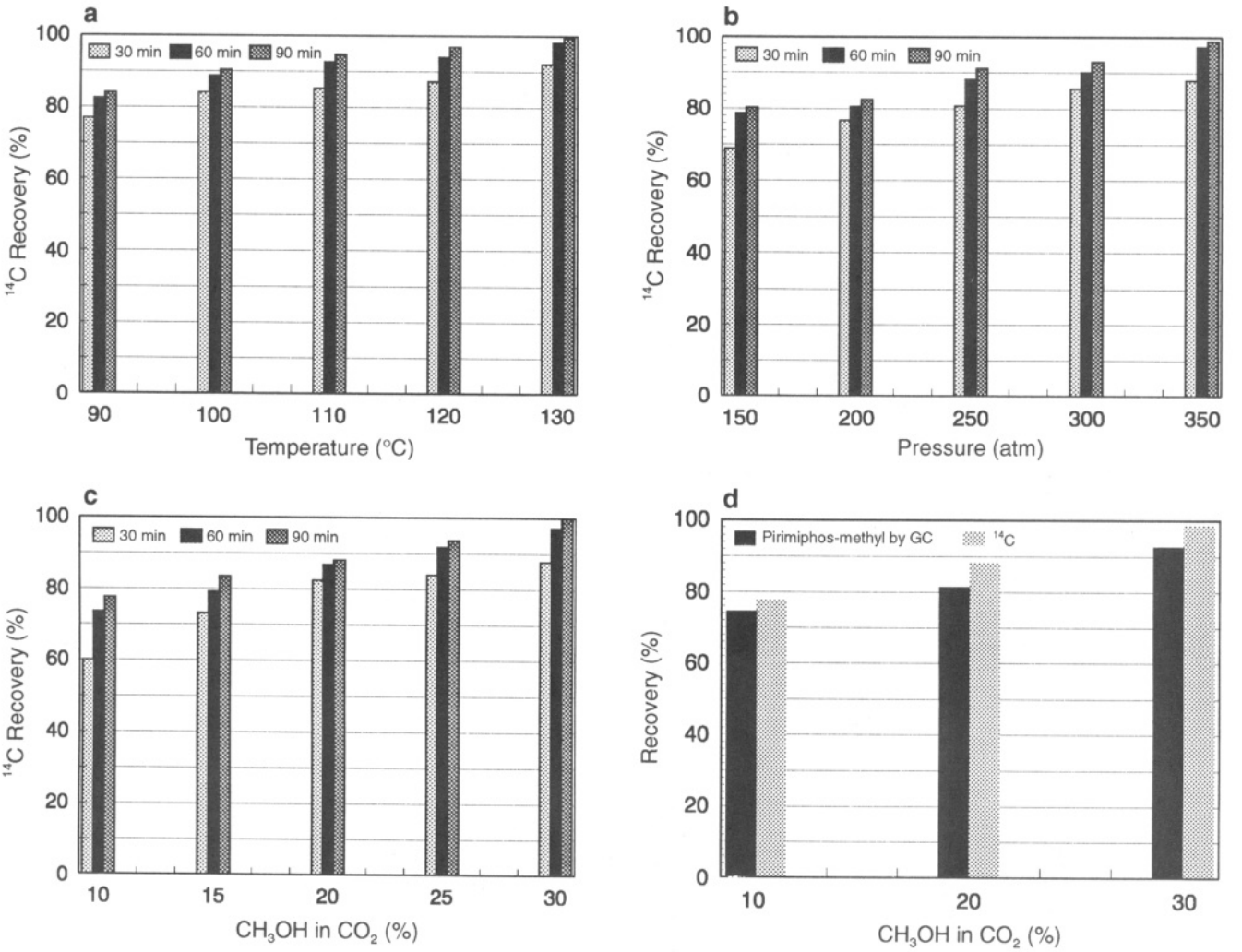

Figure 2. Recovery of ^{14}C from wheat spiked with [^{14}C]pirimiphos-methyl using supercritical carbon dioxide: (a) influence of extraction temperature on the recovery of ^{14}C at 350 atm and with 30% methanol modifier; (b) influence of extraction pressure on the recovery of ^{14}C at 125 °C and with 30% methanol modifier; (c) influence of methanol modifier on the recovery of ^{14}C at 350 atm and 125 °C; and (d) influence of methanol modifier on the recovery of ^{14}C and pirimiphos-methyl at 350 atm and 125 °C using a 90 min extraction.

SFE conditions thus obtained for each pesticide in soil, plants, and wheat samples were then used for the extraction of bound residues by supercritical carbon dioxide (SC-CO_2). Although the optimal extraction SFE conditions varied individually, the SFE system for all samples was first equilibrated statistically at 120 °C and 150 atm for 5 min, during which time there was no net flow of CO_2 through the system. This was followed by a dynamic extraction at 300–360 atm extraction pressure and temperature ranging from 120 to 130 °C for 3.0 h. In the presence of the modifier, the extraction efficiency for the spiked samples was assessed by studying the following variables: (i) modifier to carbon dioxide ratio at constant temperature and pressure; (ii) extraction temperature at constant pressure and modifier; and (iii) extraction pressure at constant temperature and modifier. These preliminary experiments provided optimized conditions to gain maximum extraction efficiency. Figures 1 and 2 demonstrate one of these preliminary experiments for atrazine in a mineral soil and for pirimiphos-methyl in wheat grains. Thus, as indicated, the extraction of bound residues by modified carbon dioxide (SC-CO_2/MeOH) was carried out at 125 °C and 350 atm for 1.5 h after initial equilibrium of the SFE system for 5 min at 120 °C and 150 atm. Methanol alone was also used as supercritical fluid (SC-MeOH) for the extraction of bound residues by first equilibrating the SFE system at 235 °C and 100 atm followed by dynamic extraction at 235 °C and 150 atm for 3 h.

Gas Chromatography (GC). Analyses of the SFE extracts from samples containing bound ^{14}C residues of atrazine, prometryn, fonofos, and pirimiphos-methyl were carried out on a Varian Model 6000 chromatograph fitted with a thermionic detector. A silica megabore column (15 m × 0.5 mm i.d.) coated with Carbowax 20 (0.25 μm) as a stationary phase was used. The oven temperature was programmed at 1.5 °C/min from 190 to 220 °C. The detector and injector port temperatures were 300 and 200 °C, respectively. Helium was used as carrier gas at a flow rate of 20 mL/min. Aliquots (1–5 μL) of reference standards as well as SFE extracts were injected, followed by immediate programming of the column temperature, as described above. A calibration curve for each reference standard was constructed by plotting quantity injected against its respective peak height. Under the GC conditions described, atrazine, the methoxy derivative of hydroxyatrazine, prometryn, the methoxy derivative of hydroxyprometryn, fonofos, and pirimiphos-methyl showed peaks with retention times at 11.0, 8.2, 8.0, 4.4, 8.5, and 3.3 min, respectively. The identities of the compounds were confirmed by comparing the GC retention times with those of reference standards, by cochromatography, and finally by gas chromatography–mass spectrometry (GC–MS). A high-resolution mass spectrometer, Model VG 2AB-2F, connected to a Varian GC Model 3700 was used for confirmation. All mass spectra were recorded at 70 eV. Confirmation of identity was achieved by congruence of MS spectra to those in spectral data bases.

Analysis of the SFE extracts from samples containing bound ^{14}C residues of deltamethrin, diuron, 2,4-D, and dieldrin was carried out on a Varian Model 6500 chromatograph fitted with a ^{63}Ni detector. A megabore column, 15 m × 0.524 mm (i.d.), coated with DB-17 (1.5 μm) was used except for diuron. In

Table 2. Recoveries from Soil, Plant, and Wheat Grain Samples Spiked with the Radiolabeled Pesticide and Extracted with Supercritical Carbon Dioxide (SC-CO_2)

		spiking level		$SC-CO_2$ extraction			
substrate	pesticide	dpm/g ($\times 10^3$)	ppm	recovery by radioassay (%)	RSD (%)	recovery by GC (%)	RSD (%)
organic soil	atrazine	18	3.0	89.4	3.7	88.3	6.3
	prometryn	48	3.0	91.4	5.3	89.8	4.4
mineral soil	atrazine	20	4.0	96.8	3.0	89.9	3.9
	diuron	20	5.0	91.5	7.8	72.2	5.7
	2,4-D	16	5.0	78.3	7.9	62.5	7.0
wheat	deltamethrin	22	5.0	95.2	5.0	90.6	4.2
	pirimiphos-methyl	54	10.0	90.4	4.8	90.9	3.9
beans	pirimiphos-methyl	88	10.0	87.7	6.8	88.1	5.4
onion	fonofos	30	5.0	94.3	2.6	92.6	3.2
radishes	dieldrin	22	2.0	91.7	3.7	89.3	6.8
canola	atrazine	52	4.0	24.3	8.6	17.6	8.3

the latter case the silica megabore column coated with Carbowax 20 described above was utilized. The oven temperature was programmed at 10 °C/min from 100 to 240 °C for dieldrin; at 3 °C/min from 100 to 250 °C for 2,4-D, deltamethrin, and its metabolites; and at 3 °C/min from 190 to 215 °C for diuron and its metabolite dichloroaniline. The detector and injector port temperatures were 180–200 and 300 °C, respectively. Nitrogen was used as carrier gas at a flow rate of 20 mL/min. Under the GC conditions described, deltamethrin and its two metabolites, 3-PB acid and Br_2CA, showed peaks at retention times of 14.8, 5.3, and 9.1 min, respectively. Similarly, diuron and its metabolite dichloroaniline showed peaks at retention times of 7.5 and 2.0 min, respectively. Furthermore, 2,4-D and dieldrin showed peaks at retention times of 2.6 and 11.7 min, respectively. Other details of GC analysis and peak identification were similar to those described above.

Determination of Radioactivity. Combustion of dried solid samples was done in a Packard sample oxidizer Model 306 to produce $^{14}CO_2$. The $^{14}CO_2$ was absorbed in and admixed with an appropriate volume of oxisorb and oxiprop (Packard Instrument of Canada, Ltd.). Aliquots of the SFE extracts or solutions containing ^{14}C residues were analyzed in a Packard Model 3320 liquid scintillation spectrometer, using an external standard and correcting the data for quenching.

RESULTS AND DISCUSSION

Table 2 shows the recovery by supercritical carbon dioxide (SC-CO_2) of the various radiolabeled pesticides spiked onto the soil, plant, and wheat grain samples. With the exception of atrazine and 2,4-D spiked onto canola and mineral soil, respectively, the recoveries of ^{14}C ranged from 87.7 to 96.8%. The poor recovery of ^{14}C residues from canola spiked with radiolabeled atrazine suggests that the nature of the matrix may affect the extraction efficiency of SC-CO_2. It was noted that the recovery from the two soils spiked with radiolabeled atrazine was considerably better than under similar SFE conditions used for canola (Table 2). However, the recovery of ^{14}C residues from canola was considerably improved by using methanol as a modifier. It is likely that the improved recovery may be due in part to modifier swelling the matrix, as recently demonstrated by Fahmy et al. (1993). The low recovery of ^{14}C residues from radiolabeled 2,4-D-spiked samples may be due to the fact that this pesticide is relatively more polar and may have limited solubility when SC-CO_2 is used as extracting fluid. The use of methanol as modifier helped to overcome this effect and improved recovery considerably.

The percentage recoveries of various pesticides determined by GC analyses were nearly similar to those obtained by radioassay. Thus, no decomposition or breakdown of these compounds occurred during SFE. The only exceptions were 2,4-D and diuron spiked onto the mineral soil and atrazine spiked onto canola, for which recoveries of the intact compounds determined by GC were lower than those observed for ^{14}C residues by radioassay. This indicates that, in addition to the parent compounds, SC-CO_2 also extracted some other ^{14}C-labeled products which could not be identified under the experimental conditions used. Radioassay of the solution used to trap $^{14}CO_2$ indicated that SFE did not decompose the radiolabeled pesticides used in this investigation.

Preliminary experiments (Figures 1 and 2) showed that, in general, at constant pressure and modifier concentration the recovery of ^{14}C residues from spiked samples using SC-CO_2 increased with extraction temperature. Higher temperatures were not attempted so as to avoid any thermal degradation of the pesticide and/or metabolites. Similarly, an increase in pressure at constant temperature and modifier concentration resulted in the improvement of recovery. Pressures higher than 400 atm were not tested because of the possibility of leakage of the supercritical carbon dioxide out of the extraction vessel. An extraction period of 90 min was used to obtain maximum recovery from most of the samples when using modified SC-CO_2.

The bound ^{14}C residues determined by combustion and by SC-CO_2 extraction are shown in Table 3. While combustion of samples containing ^{14}C bound residues may provide a quantitative estimate of total bound ^{14}C in the form of $^{14}CO_2$, it destroys the identities of such residues. It was observed that the recoveries of bound ^{14}C from canola and mineral soil treated with radiolabeled atrazine and 2,4-D, respectively, were rather low. GC analyses of the extracts revealed the presence of the parent and/or metabolites in the form of bound residues (Table 2). These residues will not be detected by the conventional analytical procedures using solvent extraction. Thus, SC-CO_2 extraction provides an alternate means of determining the amounts and nature of bound pesticide residues in various substrates.

The effect of methanol as a modifier on the extractability of supercritical carbon dioxide is shown in Table 4 (methanol in CO_2, 30% v/v). It is obvious that the addition of methanol as a modifier to SC-CO_2 improved recoveries. This effect was more pronounced for 2,4-D in mineral soil and atrazine in canola (Tables 3 and 4). Thus, the recovery of ^{14}C from radiolabeled 2,4-D and atrazine bound residues in soil and canola increased from 57 and 10% to 93 and 86%, respectively. GC analysis of these extracts revealed that most of the released ^{14}C material was present in the form of parent

Table 3. Bound Residues in the Radiolabeled Pesticide-Treated Samples Extracted with Supercritical Carbon Dioxide ($SC-CO_2$)

sample	pesticide	bound ^{14}C residues (combustion to $^{14}CO_2$) (dpm, $\times 10^3$)	recovery of ^{14}C after $SC-CO_2$ extraction (% of bound ^{14}C)	RSD (%)	GC analysis of the extract: compound identified	ppm	RSD (%)
organic soil	atrazine	100	83.2	2.7	atrazine	4.3	8.3
					hydroxyatrazine	7.8	12.6
	prometryn	40	91.4	3.8	prometryn	1.6	6.3
					hydroxypropazine	0.5	17.1
	deltamethrin	12	75.8	5.0	Br_2CA	0.4	13.9
mineral soil	atrazine	12.9	86.9	2.1	atrazine	0.3	6.7
					hydroxyatrazine	0.4	13.8
	diuron	143	88.3	6.0	diuron	0.6	6.1
					dichoraniline	1.3	14.4
	2,4-D	70.4	57.4	10.1	2,4-D	0.8	11.5
wheat	deltamethrin	16.8	86.8	4.0	Br_2CA	0.5	13.1
					PB acid	0.6	9.2
	pirimiphos-methyl	21	92.4	3.2	pirimiphos-methyl	0.4	7.5
beans	pirimiphos-methyl	13.1	89.9	4.9	pirimiphos-methyl	0.4	9.0
onion	fonofos	12.2	85.7	2.8	fonofos	1.0	10.1
radishes	dieldrin	19	90.8	4.0	dieldrin	6.7	2.0
canola	atrazine	17	10.4	14.5	atrazine	<0.1	

Table 4. Bound Residues in the Radiolabeled Pesticide-Treated Samples Extracted with Supercritical Carbon Dioxide/Methanol ($SC-CO_2$/MeOH) and Supercritical Methanol (SC-MeOH)

sample	pesticide	recovery of ^{14}C after $SC-CO_2$/MeOH extraction (% of bound ^{14}C)	RSD (%)	recovery of ^{14}C after SC-MeOH extraction (% of bound ^{14}C)	RSD (%)
organic soil	atrazine	89.2	3.6	72.4	5.8
	prometryn	93.4	1.2	78.8	8.9
	deltamethrin	72.9	3.3	52.4	11.1
mineral soil	atrazine	90.8	1.6	65.3	5.4
	diuron	91.4	3.5	33.7	18.6
	2,4-D	93.3	5.3	80.7	9.2
wheat	deltamethrin	91.9	4.2	57.4	11.4
	pirimiphos-methyl	96.6	3.4	96.1	4.7
beans	pirimiphos-methyl	95.1	5.6	86.2	5.2
onion	fonofos	95.4	5.2	73.4	10.1
radishes	dieldrin	91.8	7.0	94.9	10.3
canola	atrazine	86.6	8.4	72.3	10.9

compound. In general, modified carbon dioxide ($SC-CO_2$/MeOH) also improved ^{14}C residue recovery from samples containing bound residues. Extraction by supercritical methanol alone (SC-MeOH) resulted in lowering the ^{14}C residue recoveries for most of the samples. Therefore, it appears that supercritical carbon dioxide modified with methanol may provide a viable alternative technique to existing methodologies for determining the amounts and nature of bound pesticide residues in various substrates. The information provided in this paper adds significantly to the previously published applications of SFE to pesticide residue analysis in a variety of spiked and incurred soil and plants samples and in food products.

CONCLUSIONS

SFE can be effectively applied to the extraction of bound pesticide residues in a variety of matrices including soil, plants, and wheat grains. Extraction of the bound residues increased with extraction temperature and pressure and by addition of methanol as a modifier. The SFE method did not appear to result in thermal degradation of the residues. Extraction time could be markedly reduced and recovery could be improved by the addition of a modifier to supercritical carbon dioxide. The SFE procedures employed require smaller samples, are quicker, and are not labor- and solvent-intensive. Bound residues of each new pesticide in various matrix combinations may require slightly different SFE conditions, depending on the optimization experiments performed for the best recovery.

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