Supercritical CO_2 Fluid Extraction of Fluometuron Herbicide from Soil

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Soil was treated with ^{14}C-ring-labeled fluometuron [*N*,*N*-dimethyl-*N'*-[3-(trifluoromethyl)phenyl]urea] (0.516 and 5.16 μmol g^{-1}), air-dried, and stored for 6 months at 5 °C. The ^{14}C was then extracted from soil with methanol by conventional extraction (twice with MeOH/H_2O 80:20 v/v; 2:1 extract/soil v/w) and with CO_2 using a supercritical fluid extractor. Supercritical fluid extraction (SFE) method development included adding modifiers and varying CO_2 fluid density, extraction temperature, sample mass, and extraction time. Adding H_2O to modify the sample was the single most effective variable which improved recovery. Extraction temperatures above 50 °C lowered recovery, presumably because of thermal instability of fluometuron. The optimum CO_2 density at 50 °C was 0.80 g mL^{-1}. Static extraction times greater than 6 min and dynamic extraction times greater than 18 min did not significantly improve recovery. Recovery using optimum SFE conditions was comparable to that obtained using conventional methods. Extraction of aged field samples indicated that this technology can also be used to extract some common fluometuron metabolites.

INTRODUCTION

Conventionally, herbicide extraction from soil is time-consuming and generates large quantities of solvent waste. Extraction with supercritical CO_2 fluid is an attractive alternative because CO_2 can be vented harmlessly into the atmosphere.

Limited supercritical fluid extraction (SFE) work has been done with herbicides, and few of these studies have dealt with extraction from soil matrices. Shah et al. (1990) studied chromatographic elution patterns of solutions of triazine and triazole herbicides using on-line supercritical fluid chromatography (SFC), and Wigfield and Lanouette (1993) described supercritical fluid extraction of fluazifop from plant material. Some herbicides extracted from soil using supercritical CO_2 include diuron and linuron (McNally and Wheeler, 1988b; Wheeler and McNally, 1989), sulfometuron (McNally and Wheeler, 1988a), 2,4-D and metribuzin (Rochette et al., 1991), and cyanazine and atrazine (Knipe et al., 1991). Others have extracted triazine, phenoxy, and urea herbicides from soils using supercritical methanol (Capriel et al., 1986).

Since many herbicides are thermally labile, properties of supercritical CO_2 fluid that support its use as an extractant for herbicides in soil include relatively low critical temperature, low critical pressure, and low reactivity (Hawthorne, 1990). Supercritical CO_2 tends to be less efficient than some other supercritical fluids in the extraction of polar to moderately polar compounds, including many herbicides. However, extraction efficiency of supercritical CO_2 can be increased by manipulating some of the extraction conditions (McNally and Wheeler, 1988). The objective of this study was to evaluate conditions favorable for extracting fluometuron herbicide from soil using supercritical CO_2 and compare this with a conventional methanol extraction method based on procedures described by Cotterill (1980).

EXPERIMENTAL PROCEDURES

Reagents and Solutions. Technical grade fluometuron (Chem Service, West Chester, PA; 99.5% purity) and ^{14}C-labeled fluometuron (Ciba-Geigy Corp., Greensboro, NC; 99% purity; specific activity 35.6 kBq μmol^{-1}) were used to prepare 1.72 and 17.2 μmol L^{-1} fluometuron solutions in deionized water. Fluometuron metabolites 3-(trifluoromethyl)phenylurea (TFMPU), demethylfluometuron (DMFM), and 3-(trifluoromethyl)aniline (TFMA) were obtained from Ciba-Geigy Corp.

Soil Preparation. Dundee silty clay loam soil (fine-silty, mixed, thermic, Aeric Ochraqualf) was collected from an area with no history of fluometuron application. Some characteristics of the Dundee soil include soil pH 5.47 (1:1 w/v, 0.01 M $CaCl_2$), organic carbon 5.92 g kg^{-1}, clay 35.2%, silt 54.5%, and sand 10.3%. The soil was air-dried and sieved to a uniform 2-mm size. Fifty-gram soil subsamples were weighed into 250-mL Nalgene flasks, and 15.0 mL of either 1.72 or 17.2 μmol L^{-1} ^{14}C-labeled fluometuron was added to individual flasks to achieve soil concentrations of 0.516 and 5.16 μmol g^{-1}, respectively. An additional 3 mL of deionized water was added to each flask, and the samples were mixed thoroughly with a glass stir rod and then allowed to air-dry. Air-dried samples were ground with mortar and pestle and stored at 5 °C for 6 months.

Conventional Methanol Extraction. Sufficient extracting solution consisting of methanol/H_2O (80:20) was added to soil to obtain a ratio of 2:1 solution/soil (v/w). The samples were shaken for 24 h and then centrifuged (1900*g*). The supernatant was decanted into another container, and the entire extraction process was repeated with a 3-h shaking. Supernatant from the second extraction was combined with the first, and methanol from the combined extracts was removed by rotary evaporation at 40 °C. Evaporated extracts were filtered through C_{18} solid-phase extraction columns (J. T. Baker Inc., Phillipsburg, NJ), and analyte was eluted from the columns with 2.0 mL of acetonitrile. Aliquots of the eluted extracts were then analyzed using HPLC methods (see below) and liquid scintillation counting (Packard Tri-Carb 4000 liquid scintillation counter, Packard Instruments, Downers Grove, IL).

HPLC Conditions. The HPLC system consisted of a Waters Maxima controller, a Waters UV detector Model 490 (202 and 254 nm), a Waters fluorescence detector Model 470 (exc 292 nm, em 345 nm), and a Waters WISP automatic sampler (Waters Corp., Milford, MA). The initial mobile phase composition was 70% acetonitrile and 30% water at a flow rate of 1 mL min^{-1}, with a linear gradient to 40% acetonitrile and 60% water over 14.0 min. A 50-μL aliquot of sample was injected. An Econosil (Alltech Associates, Deerfield, IL) reversed-phase C_{18} analytical column was used. Analyte retention times were 8.6 min for TFMPU, 10.8 min for DMFM, 12.9 min for fluometuron, and 14.6 min for TFMA. Standard curves for the four analytes were linear in the range considered (r^2 = 0.99 for all regression curves).

Total Sample Oxidation. Herbicide-treated soil (0.3 g, oven-dried) was mixed with 0.5 g of cellulose and then oxidized with a Packard Instruments Tri-Carb B306 oxidizer. The $^{14}CO_2$

evolved from sample oxidation was trapped in Carbo-sorb and mixed with Permafluor scintillation cocktail for counting.

Supercritical Fluid Extraction. A Hewlett-Packard Model 7680A supercritical fluid extractor (Hewlett-Packard Co., Avondale, PA) was used for all extractions. Preliminary investigations provided information for establishing general baseline conditions. These conditions were used for all samples unless one of the individual parameters was being evaluated. General SFE conditions included 4.0-g air-dry soil subsamples, with 0.80 mL of deionized water added as a modifier (5:1 w/v), 3 mL min^{-1} CO_2 flow rate, 50 °C extraction chamber temperature, 50 °C nozzle temperature, 50 °C trap temperature, acetonitrile as a rinse solvent, SFC grade CO_2 (Scott Specialty Gases, Plumsteadville, PA) at a density of 0.80 g mL^{-1}, ODS (octadecyl) analyte trap material, and static and dynamic extraction times of 6 and 25 min, respectively. Unless otherwise specified, all extracts were analyzed by scintillation counting.

Parameters evaluated included modifier addition to sample, CO_2 density, extraction temperature, sample mass, and static and dynamic extraction times. Experimental conditions for each parameter are outlined below. Analysis of variance was used for mean comparison with Fisher's LSD as a test statistic (SAS Institute, 1990).

Modifier. Soil treated with the 1.72 μmol L^{-1} solution was used. Modifier conditions included none, 0.80 mL of H_2O, 0.10 mL of methanol, 0.80 mL of 90:10 H_2O/methanol, or 0.80 mL of 0.01 M $CaCl_2$, with each modifier run in triplicate.

CO_2 Density. Only soils treated with the 1.72 μmol L^{-1} solution were used. Five CO_2 densities were considered (0.40, 0.50, 0.60, 0.70, or 0.80 g mL^{-1}) in quadruplicate.

Extraction Temperature. The 17.2 μmol L^{-1} treated soil was used. Five extraction temperatures were evaluated (six replications): 40, 50, 60, 70, or 80 °C. The extraction temperature experiment was repeated, and aliquots of the sample extracts were analyzed with HPLC. Effects of temperature on the stability of fluometuron were further investigated by adding 2 mL of 8.60 μmol L^{-1} ^{14}C-labeled fluometuron solution to Kimwipe (Kimberley-Clark, Roswell, GA) tissue and extracting at 40, 50, 60, 70, or 80 °C, with four replications for each extraction temperature. Extracts were analyzed with HPLC.

Sample Mass. Soil treated with the 17.2 μmol L^{-1} solution was used. Three sample masses were considered in quadruplicate: 1.0, 4.0, or 8.0 g of soil.

Static Extraction Time (Equilibration). The 1.72 μmol L^{-1} treated soil was used. Three static extraction times (3.0, 6.0, or 10.0 min) were run in triplicate.

Dynamic Extraction Time. Soil treated with 1.72 μmol L^{-1} was used. Three dynamic extraction times (10.0, 18.0, or 25.0 min) were run in triplicate.

Aged Field Sample. A Dundee soil sample was collected from an area that had been treated with fluometuron (0.90 kg ha^{-1}) 5 months earlier. Forty grams of soil was weighed moist into a 250-mL Nalgene flask and extracted and processed using the conventional methanol extraction protocol. Extractions were run in quadruplicate. A separate subsample was used for moisture determination. Triplicate 4.0-g subsamples of the field soil were weighed moist into extraction thimbles, sufficient water was added to achieve a 5:1 w/v moisture content, and the soil was extracted with supercritical CO_2. Extracts from both the conventional solvent extraction and SFE were analyzed with HPLC.

RESULTS AND DISCUSSION

Conventional Extraction and Oxidation. Recovery of ^{14}C by conventional methanol extraction, total oxidation, and supercritical fluid extraction (optimum conditions) is shown in Table I. Recoveries were similar (84–88%) for all three methods. From HPLC analysis it was determined that fluometuron was the only analyte of interest in the methanol extracts (data not shown).

Modifier. Polar solvents are often added to the sample matrix for extraction with supercritical CO_2 fluid to improve analyte recovery. They can be added directly to the sample, as in the present study, or with the extraction fluid. Although mechanisms are not completely understood, it is believed that some modifiers improve the solubility of polar analytes in nonpolar CO_2. Absence of modifier resulted in poor analyte recovery (Table II). Adding methanol alone was an improvement, likely because fluometuron is very soluble in methanol. In preliminary experiments, it was determined that the addition of more than 0.1 mL of methanol as a modifier decreased extraction efficiency. Excess methanol may have caused premature elution of analyte from the trap with subsequent analyte loss in waste or to the atmosphere. Water, alone or in combination with methanol or $CaCl_2$, provided the best recovery (Table II). No advantage was observed in adding either methanol or $CaCl_2$ with the water. The benefits of using water as a component of conventional extracting solutions are well-known (Cotterill, 1980). However, since water is immiscible with supercritical CO_2, the results obtained in this study were not anticipated. Knipe et al. (1992) obtained similar results when water was added to samples spiked with atrazine and cyanazine. One explanation for the results in the present study is that the water aided the initial dissolution of fluometuron. Probably more importantly, water altered the soil matrix structure by expanding clay mineral lattices and swelling organic soil colloids. Expansion of clay and organic colloids would expose a greater surface area, thus enabling the supercritical fluid to more completely penetrate the sample.

CO_2 Density. Higher CO_2 densities were achieved by increasing pressure in the sample chamber at a constant temperature of 50 °C. Increasing CO_2 density from 0.40 to 0.50 g mL^{-1} improved recovery, but no further improvement with increase in CO_2 density was observed until 0.80 g mL^{-1} (Table III). However, variation among replicates declined with each incremental increase in CO_2 density. Higher fluid densities increase the solvent strength and might, therefore, have improved extraction of the moderately polar fluometuron at 0.80 g mL^{-1}. No explanation can be given as to why recovery did not improve when CO_2 density was increased from 0.50 to 0.70 g mL^{-1}. It is possible that at 50 °C the solubility of the moderately polar fluometuron in supercritical CO_2 fluid reaches a maximum such that little additional improvement in recovery would occur until some other parameter such as temperature is changed.

Table I. Percent Recovery of ^{14}C by Methanol Extraction, Oxidation, and Supercritical Fluid Extraction

added concn, μmol g^{-1}	methanol, %		oxidation, %		supercritical fluid,[a] %	
	mean	SD[b]	mean	SD[b]	mean	SD[b]
0.516	86.8[c]	2.35	86.9[c]	3.38	84.2[e]	2.83
5.16	87.9[d]	2.24	87.0[d]	2.06	84.6[f]	2.73

[a] SFE conditions: 0.80 g mL^{-1} CO_2 density, 50 °C extraction temperature, 4.0-g subsample, 6.0 min of static extraction time, 25.0 min of dynamic extraction time. [b] Standard deviation. [c] Mean of 9 replications. [d] Mean of 6 replications. [e] Mean of 12 replications. [f] Mean of 10 replications.

Table II. Effect of Modifier on SFE Recovery of ^{14}C[a]

modifier	% recovery mean[b]	% recovery SD[c]
none	5.60c	1.74
0.80 mL of H_2O	86.3a	2.47
0.10 mL of methanol	56.5b	6.60
0.80 mL of 10:90 methanol/H_2O	87.0a	5.03
0.80 mL of 0.01 M $CaCl_2$	85.4a	4.11

[a] SFE conditions: 0.80 g mL^{-1} CO_2 density, 50 °C extraction temperature, 4.0-g subsample, 6.0 min of static extraction time, 25.0 min of dynamic extraction time. [b] Means (three replications) followed by the same letter are not significantly different ($\alpha = 0.05$). [c] Standard deviation.

Table III. Effect of CO_2 Density on SFE Recovery of ^{14}C[a]

CO_2 density, g mL^{-1}	% recovery		
	mean[b]	SD[c]	n[d]
0.40	75.6c	4.44	4
0.50	81.4b	4.07	3
0.60	79.4b	3.12	4
0.70	80.9b	2.64	4
0.80	83.4a	1.39	3

[a] SFE conditions: 0.80 mL of water as modifier, 50 °C extraction temperature, 4.0-g subsample, 6.0 min of static extraction time, 25.0 min of dynamic extraction time. [b] Means followed by the same letter are not significantly different (α = 0.05). [c] Standard deviation. [d] Number of replicates.

Table IV. Effect of Sample Mass on SFE Recovery of ^{14}C[a]

soil mass, g	% recovery	
	mean[b]	SD[c]
1.0	90.3a	8.04
4.0	83.2ab	3.34
8.0	76.4b	5.69

[a] SFE conditions: 0.80 g mL^{-1} CO_2 density, 0.80 mL of water as modifier, 50 °C extraction temperature, 6.0 min of static extraction time, 25.0 min of dynamic extraction time. [b] Means (four replications) followed by the same letter are not significantly different (α = 0.05). [c] Standard deviation.

Table V. Effect of Extraction Temperature on SFE Recovery of ^{14}C[a]

extraction temp, °C	% recovery		
	mean[b]	SD[c]	n[d]
40	81.9c	2.95	6
50	85.6abc	2.32	6
60	89.5a	2.78	5
70	87.4ab	5.07	6
80	83.7bc	4.75	6

[a] SFE conditions: 0.80 g mL^{-1} CO_2 density, 0.80 mL of water as modifier, 4.0-g subsample, 6.0 min of static extraction time, 25.0 min of dynamic extraction time. [b] Means followed by the same letter are not significantly different (α = 0.05). [c] Standard deviation. [d] Number of replicates.

Sample Mass. With most supercritical fluid extractors, sample size is a limitation. The sample chamber available for the instrument in the present study can accommodate approximately 9 g of soil, depending on the soil density. Increasing sample size from 1.0 to 8.0 g decreased recovery (Table IV). The larger the sample size, the greater the surface area which must be extracted, and, presumably, a longer extraction time might achieve the same recovery as with smaller sample masses. In practice, sample size may be a limitation for supercritical fluid extraction of field samples where analyte levels are at the low end of detection limits. Larger sample chambers may not be beneficial unless extraction methods that improve penetration of the sample matrix in an acceptable period of time can be developed.

Extraction Temperature. In general, both solvent strength and diffusivity can be increased by raising the extraction temperature. There was some increase in ^{14}C recovery from 40 to 60 °C, but recovery declined again above 70 °C (Table V). The decline in recovery at higher temperatures may be due to thermal instability of fluometuron. This is illustrated in Figure 1, showing overlaid HPLC chromatograms for soil extractions at three temperatures. As the temperature was raised, there was an increase in the peak coeluting with TFMA. To eliminate the possibility that the TFMA formation was a phenomenon specific to soil, another experiment was conducted in which herbicide solution was extracted from tissue paper. The results from the second experiment corroborated results from the soil extraction experiment with a

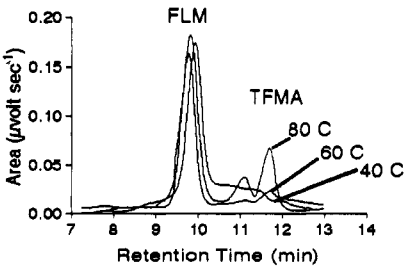

Figure 1. HPLC chromatogram showing effects of temperature on fluometuron (FLM) extracted from soil.

Table VI. Effect of Extraction Temperature on Fluometuron and TFMA Extracted from Tissue Paper[a] (Results Quantified by HPLC Analysis)

extraction temp, °C	fluometuron, μmol L^{-1}		TFMA, μmol L^{-1}		
	mean[b]	SD[c]	mean[b]	SD[c]	n[d]
40	6.96a	0.03	0.01d	0.01	3
50	6.88a	0.41	0.1d	0.10	4
60	6.63a	0.32	0.31c	0.06	4
70	6.12b	0.26	0.77b	0.10	4
80	4.86c	0.53	1.65a	0.14	4

[a] SFE conditions: 0.80 g mL^{-1} CO_2 density, 0.80 mL of water as modifier, 6.0 min of static extraction time, 25.0 min of dynamic extraction time. [b] Within a column, means followed by the same letter are not significantly different (α = 0.05). [c] Standard deviation. [d] Number of replicates.

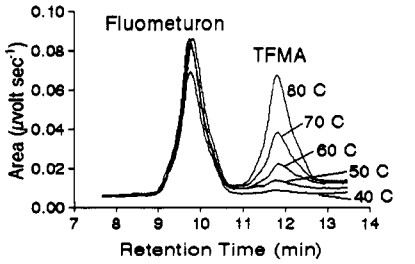

Figure 2. HPLC chromatogram showing effects of temperature on fluometuron extracted from tissue paper.

decrease in fluometuron and an increase in TFMA at higher extraction temperatures (Table VI; Figure 2). Only minor TFMA formation was observed at 40 and 50 °C, while at 80 °C a 30% decline in fluometuron was offset by a comparable increase in TFMA. Under the conditions of heat and high pressure during the extraction process, it was speculated that hydrolysis of fluometuron was occurring with CO_2, dimethylamine, and TFMA as end-products.

Static and Dynamic Extraction. One purported advantage of SFE is that the period of time required to prepare one sample for analysis is shorter (10–60 min) as compared with that for conventional solvent extractions (hours to days). Therefore, it is of interest to know the minimum extraction time necessary to obtain satisfactory recovery. The SFE system used in this study can accommodate two extraction stages. The first step is the static extraction stage in which CO_2 fluid is recycled through the sample for a period of time to allow the extraction fluid to fully penetrate the sample and dissolve the analyte. A static equilibration time longer than 6.0 min did not significantly improve recovery, but there was lower variance among replications with increased equilibration time (Table VII). Overall extraction time might be reduced by using the shortest time for static equilibration, but it is necessary to balance the economics of shorter extraction times with the advantages of lower sample variation.

The second extraction stage, termed dynamic extraction, refers to a period of time when fresh CO_2 is continuously

Table VII. Effect of Static Equilibration Time on SFE Recovery of ^{14}C[a]

time, min	% recovery mean[b]	% recovery SD[c]
3.0	81.7b	7.21
6.0	84.8ab	5.27
10.0	86.7a	3.17

[a] SFE conditions: 0.80 g mL^{-1} CO_2 density, 0.80 mL of water as modifier, 50 °C extraction temperature, 4.0-g subsample, 25.0 min of dynamic extraction time. [b] Means (three replications) followed by the same letter are not significantly different (α = 0.06). [c] Standard deviation.

Table VIII. Effect of Dynamic Extraction Time on SFE Recovery of ^{14}C[a]

time, min	% recovery mean[b]	% recovery SD[c]
10.0	76.1b	5.71
18.0	81.4a	2.36
25.0	82.4a	2.20

[a] SFE conditions: 0.80 g mL^{-1} CO_2 density, 0.80 mL of water as modifier, 50 °C extraction temperature, 4.0-g subsample, 6.0 min of static extraction time. [b] Means (three replications) followed by the same letter are not significantly different (α = 0.06). [c] Standard deviation.

Table IX. Quantity of Fluometuron and Metabolites Extracted from Dundee Field Samples Using Conventional Methanol Extraction and Supercritical Fluid Extraction (Results Quantified by HPLC Analysis)

chemical	conventional methanol extraction, μmol kg^{-1} mean	SD[b]	n[c]	supercritical fluid extraction,[a] μmol kg^{-1} mean	SD[b]	n[c]
DMFM	0.133	0.036	4	0.124	0.009	3
fluometuron	0.168	0.022	4	0.134	0.009	3
TFMA	0.095	0.028	4	0.119	0.019	3

[a] SFE conditions: 0.80 g mL^{-1} CO_2 density, 6.0 min of static extraction time, 25.0 min of dynamic extraction time, 50 °C extraction temperature. [b] Standard deviation. [c] Number of replicates.

pumped through the sample to both dissolve and remove the analyte from the sample chamber. Increasing dynamic extraction from 10.0 to 18.0 min improved recovery, but no significant improvement was observed for longer extractions (Table VIII). If one used 6.0 min of static equilibration time with 18.0 min of dynamic extraction time, total extraction time would be 24.0 min. Add to that the time it takes to achieve proper pressure and temperature conditions, and one extraction of a 4.0-g sample would take approximately 45–50 min.

Field Sample. The results comparing conventional extraction with supercritical fluid extraction of field soil samples are shown in Table IX. Both methods extracted compounds coeluting with fluometuron, TFMA, and DMFM standards. Neither method extracted a compound coeluting with the TFMPU standard. Both methods recovered similar quantities of compounds coeluting with TFMA and DMFM; however, slightly more fluometuron was recovered using supercritical fluid extraction (Table IX).

Summary and Conclusions. Effects of modifier addition, CO_2 fluid density, extraction temperature, sample mass, and extraction times on supercritical fluid extraction efficiency were investigated. Adding H_2O as a modifier to the sample provided significant improvement in recovery. Extraction temperatures above 50 °C resulted in lower fluometuron extraction, presumably because of thermal instability of the herbicide. A CO_2 density of 0.80 g mL^{-1} provided the best recovery at 50 °C. Static extraction times greater than 6.0 min and dynamic extraction times greater than 18.0 min did not significantly improve recovery. When optimum conditions were used, fluometuron recovery with supercritical CO_2 was approximately the same as with conventional methodology. Extraction of field samples indicated that this technology can also be used to extract some of the more common fluometuron metabolites including DMFM and TFMA. However, recovery efficiency for the metabolites was not evaluated. These results demonstrate the potential for supercritical fluid extraction of fluometuron from soil matrices, but further work needs to be done with field soil samples of varying properties.

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