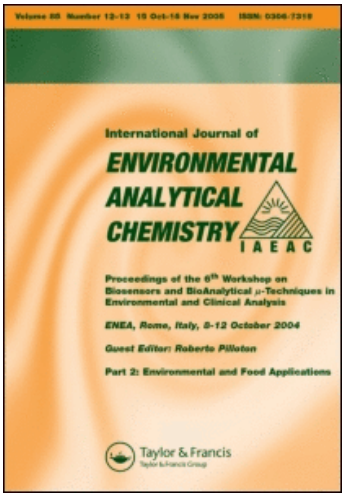

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W. C. Koskinen[a]; H. H. Cheng[b]; L. J. Jarvis[b]; B. A. Sorenson[c]
[a] Soil and Water Management Research Unit, U.S. Department Agriculture, St. Paul, MN, USA [b] Soil Science Department, Univ. Minnesota, St. Paul, MN, USA [c] Department Agronomy and Plant Genetics, Univ. Minnesota, St. Paul, MN, USA

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CHARACTERIZATION OF MECHANISMS OF PESTICIDE RETENTION IN SOILS USING THE SUPERCRITICAL FLUID EXTRACTION TECHNIQUE

W. C. KOSKINEN[1], H. H. CHENG[2], L. J. JARVIS[3] and B. A. SORENSON[4]

[1]Soil and Water Management Research Unit, U.S. Department Agriculture, Agric. Res. Ser., 1991 Upper Buford Circle, St. Paul, MN 55108, USA. [2,3]Soil Science Department, Univ. Minnesota, St. Paul, MN 55108, USA. [4]Department Agronomy and Plant Genetics, Univ. Minnesota, St. Paul, MN 55108, USA

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This research determined the relative effectiveness of supercritical fluid extraction (SFE) in extracting atrazine and its metabolites from soils which had been treated with atrazine for varying periods of time in order to characterize binding mechanisms. Aqueous methanol extraction was more effective than SFE in removing ^{14}C-atrazine residues from "aged" soils. The more polar the solvent system, the more ^{14}C-atrazine residues were extracted. The order of polarity and extractability was aqueous methanol > SF-CO_2/5% methanol > SF-CO_2. Atrazine extraction efficiency using SF-CO_2 and SF-CO_2/5% methanol decreased as samples "aged" in the field. The less than complete recovery of atrazine residues using the SFE technique could be seen as an indication that different binding mechanisms were involved in the retention of atrazine as well as its metabolites and that the binding mechanisms changed with time.

KEY WORDS: SFE, atrazine.

INTRODUCTION

One of the major processes governing the fate of pesticides in the environment is the retention of pesticides by soils. A variety of mechanisms can be involved in the binding of pesticides to soils, including: London-van der Waals forces, hydrogen bonding, protonation, cation and water bridging, cation and anion exchanges, ligand exchange, covalent bonding, and physical trapping. However, few experimental methods are available for characterizing specific mechanisms involved in pesticide retention in soils[1].

Cheng[2] has suggested that retention mechanisms could be characterized by using solvent extraction techniques. Since extraction is essentially the breaking of bonds between a chemical and the soil surface thereby releasing the chemical into the solvent solution, differences in the effectiveness of specific solvents in extracting pesticides from soils can serve as indicators of specific retention mechanisms involved.

The supercritical fluid extraction (SFE) technique is a tool which is gaining increasing use in extraction of trace organics from soils and sediments for environmental analysis. Many solvents under supercritical conditions have better mass transfer characteristics than those under ambient conditions, as they are more diffusible and less viscous[3]. The

supercritical fluid (SF) solvent strength can be adjusted by varying the temperature and pressure used for extraction, and the versatility of the solvents can be enhanced by addition of modifiers.

Oostdyk *et al*[4] postulated that the retention mechanism of 3,3'-dichlorobenzidine and benzidine on soil involved silanol groups on the soil with retention increasing with increasing base strength of the chemical. Modifying SF-CO_2 and SF-N_2O with a more basic amine, 1,6-hexanediamine, increased extractability of the two chemicals. The 1,6-hexanediamine was postulated to occupy active sorption sites resulting in less retention of the analyte. Similarly, it was postulated that the small permanent dipole of N_2O made SF-N_2O more effective than SF-CO_2 at displacing 2,3,7,8-TCDD from sorptive sites, resulting in greater extractability of 2,3,7,8-TCDD by SF-N_2O[5].

The SFE technique has the potential to extract pesticides from soils. However, the focus of research has been to maximize pesticide extraction efficiency from soils and sediments. For instance, SF-CO_2 has been shown to quantitatively extract (> 90%) triazine herbicides, including atrazine (6-chloro-*N*-ethyl-*N*'-(1-methylethyl)-1,3,5-triazine-2,4-diamine), from freshly spiked soil samples[6]. In contrast, no significant quantities of substituted-urea herbicides (diuron, *N*'-(3,4-dichlorophenyl)-*N*,*N*-dimethylurea; linuron, *N*'-(3,4-dichlorophenyl)-*N*-methoxy-*N*-methylurea; and fluometuron, *N*,*N*-dimethyl-*N*'-[3-(trifluoromethyl)phenyl]urea) were extracted from soil using SF-CO_2[7,8]. However, if SF-CO_2 is modified with 10% methanol or ethanol, diuron and linuron extraction efficiency is 80 – 90%[7]. Extraction efficiency of fluometuron using SF-CO_2 is 80% if the soil is moistened prior to extraction[8].

Whether the SFE technique has the potential to break more recalcitrant bonds between a pesticide chemical and soil surface after the pesticide has "aged" in the soil and whether SFE can be used to elucidate binding mechanisms has not been explored extensively. The objective of this study was to compare the relative effectiveness of the SFE technique and the organic solvent extraction technique under ambient conditions in extracting atrazine and its metabolites from soil at varying periods of time after atrazine application in the field. The differences in extraction efficiency could be used to elucidate the mechanisms of pesticide retention.

MATERIALS AND METHODS

Chemicals and solvents

Atrazine (98.7% purity), deethylatrazine, 6-chloro-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine (DEA) (99% purity), deethyldeisopropylatrazine, 6-chloro-1,3,5-triazine-2,4-diamine (DEDIA) (90%, purity), deisopropylatrazine, 6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine (DIA) (98% purity), hydroxyatrazine, 6-hydroxy-*N*-ethyl-*N*'-(1-methylethyl)-1,3,5-triazine-2,4-diamine (HA) (97% purity), deethylhydroxyatrazine, 6-hydroxy-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine (DEHA) (97% purity), deisopropylhydroxyatrazine, 6-hydroxy-*N*-ethyl-1,3,5-triazine-2,4-diamine (DIHA) (95% purity) were obtained from Ciba-Geigy Corporation* (Greensboro, NC 27419). ^{14}C-uniformly ring-labeled atrazine (0.38 GBq $mmol^{-1}$) was purchased from Pathfinder Laboratories (St. Louis, MO 63178). Technical grade methanol, chloroform, ethyl

* Mention of a trade name is for information only and does not imply a recommendation or endorsement by USDA-ARS or the University of Minnesota.

acetate, dichloromethane, and scintillation grade toluene were used as received. SFE grade CO_2 (Air Products, Allentown, PA 18195) and SFE grade CO_2 modified with 5% methanol (Scott Specialty Gases, Plumsteadville, PA 18949) were used for supercritical fluid extraction.

Field samples

A Webster clay loam from Waseca, MN, pH 6.2, 4.3% O.C., 33% clay, was used in the research. ^{14}C-atrazine (0.85 MBq) in 5 ml methanol was applied to a 10 cm diam circle of soil, 2.5 cm below the soil surface, at multiple locations in a field. Following application, 2.2 kg ha^{-1} atrazine was applied to the entire plot area. Triplicate treated areas were removed 35 and 138 days after treatment and stored at -15°C until processing.

Organic solvent extraction

^{14}C-residues were extracted from field-moist (13 – 15% water w:w) soil by shaking the soil 1 hr with 3M LiCl (1:1 soil : solution w:v) followed by refluxing the soil 3 times with 4:1 methanol : water (5:1 solvent : soil). After refluxing, the slurry was filtered and the methanol removed by evaporation at 40°C under reduced pressure. The ^{14}C-chemicals were partitioned from the aqueous solution into dichloromethane (3 times) and chloroform (3 times) using 5:1 water : solvent (v:v). The residues were evaporated just to dryness at 40°C under reduced pressure and redissolved in ethyl acetate.

SFE

Triplicate 6.0-g field-moist (13 – 15% water w:w) soil samples were extracted using a Hewlett Packard 7680A SFE module (Hewlett Packard Corp., Wilmington, DE 19808) using SF-CO_2 and SF-CO_2/5% methanol. The SFE conditions are listed in Table 1. The conditions were optimized for maximum recovery. There was no increase in recovery with increases in temperature, pressure, or extraction time. For instance, increasing the

Table 1 Supercritical fluid extraction conditions

	Conditions	
Parameters	*Step 1*	*Step 2*
Fluid Delivery		
density, g mL^{-1}	0.15	0.90
pressure, bar	76	281
flow, mL min^{-1}	1.0	3.0
Extraction chamber		
temperature, °C	80	40
equilibration time, min	2.0	2.0
extraction time, min	11.3	20.4
Analyte trap		
temperature, °C	67	80
packing	C_{18}– ODS Tenax	C_{18}– ODS Tenax

extraction time from 20 to 120 min with SF-CO_2 or SF-CO_2/5% methanol did not increase the extraction efficiency or change the product distribution. Also, increasing the water content of the soil from the "field moist" state to the saturated state did not increase the SFE extraction efficiency using SF-CO_2 or SF-CO_2/5% methanol as the solvent. Although the soil was extracted with a two-step procedure, the first step was not necessary. The first step was to decrease the water content of the soil to the same amount for all samples, however it removed < 1% of the water. The extracted ^{14}C chemicals were trapped on Tenax sorbent or C_{18}-ODS and then eluted with 1.8 mL methanol or recovered in methanol through which the waste CO_2 passed.

Analyses

To determine total radioactivity in soil, three subsamples (0.3 to 0.5 g) from each soil sample, were combined with an equivalent volume of microcrystalline cellulose and oxidized using a Packard 306 sample oxidizer (Packard Instruments Co., Downers Grove, IL 60515). Radioactivity was determined by liquid scintillation spectroscopy (LSS) using a Packard 1500 Tri-carb scintillation analyzer (Packard Instruments Co., Downers Grove, IL 60515). $^{14}CO_2$ was trapped with 6 ml Carbosorb II and combined with 16 ml Permablend III scintillation cocktail. Oxidation efficiency was 0.90 ± 0.03.

^{14}C-compounds from the organic solvent extraction were separated and quantified using thin layer chromatography (TLC) with 20 x 20 cm 0.25 mm silica TLC plates. R_f values of analytical standards following two elutions in 110:2:2 chloroform : methanol : formic acid (v:v:v) were 0.88, 0.66, 0.59, 0.23 and 0.03 for atrazine, DEA, DIA, DEDIA and hydroxylated derivatives, respectively. To quantify the chlorinated products and total hydroxylated residues, plates were scanned for 10 min on a Berthold linear plate analyzer (Berthold Scientific Instruments Company, Pittsburg, PA 15233). Peaks were integrated, backgrounds subtracted, and retention times compared to analytical standards. To isolate hydroxylated derivatives the plates were developed in a second solvent system (75:20:4:2, chloroform : methanol : water : formic acid v:v:v), R_f values of analytical standards were 0.98, 0.93, 0.90, 0.71, 0.62, 0.38, 0.32 for atrazine, DEA, DIA, DEDIA, HA, DEHA, DIHA, respectively. Plates were rescanned, peaks integrated and retention times compared with those of analytical standards.

SFE extracts were analyzed using TLC as previously described and using a HP 1090 HPLC with diode array detector and an Adsorbosphere C_{18} column (5 μ, 250 mm by 4.6 mm). HPLC conditions were : flow, 1.0 mL min^{-1}; mobile phase, 40% methanol/60% 1% acetic acid (0 – 7 min), 90% methanol/10% 1% acetic acid (7 – 10 min), 40% methanol/60% 1% acetic acid (10 – 16 min); wavelength, 240 – 250 nm. Fractions of mobile phase corresponding to the retention times of atrazine and its metabolites were collected and ^{14}C counted by liquid scintillation counting techniques, correcting for quenching and background.

RESULTS

Of the applied ^{14}C, 95% and 70% remained 35 and 138 days after application, respectively. The decrease in ^{14}C over time is attributed to mineralization of the ring-labelled ^{14}C to $^{14}CO_2$[11].

Exhaustive aqueous methanol extraction was effective in removing ^{14}C-atrazine residues from "aged" soils. However, the longer the atrazine-treated soil was "aged", the

Table 2 Exhaustive aqueous methanol extraction of ^{14}C-atrazine residues 35 and 138 days after treatment

Time	*atrazine*	*DEA*	*DIA*	*DEDIA*	*HA*	*PM*[a]	*NR*[b]
days	----------% of ^{14}C in sample[c]----------						
35	62	4	2	1	9	4	18
138	36	3	2	1	24	8	26

[a]PM = hydroxylated polar metabolites
[b]NR = nonextractable residues
[c]coefficient of variation < 5%

Table 3 Supercritical fluid extraction of ^{14}C-atrazine residues 35 and 138 days after treatment

Time	*SF*	*AT*	*DEA*	*DIA*	*PM*[a]	*NR*[b]
days	---------- % of ^{14}C in sample[c] ----------					
35	CO_2	30	1	T[d]	T	69
	CO_2/MeOH	41	2	1	T	56
138	CO_2	11	2	T	0	87
	CO_2/MeOH	19	5	2	1	73

[a]PM = hydroxylated polar metabolites and HA DEDIA
[b]NR = nonextractable residues
[c]coefficient of variation < 5%
[d]T = trace

less ^{14}C-atrazine residues were extracted. Aqueous methanol extraction could extract 82 and 74% of the ^{14}C remaining in the soil 35 and 138 days after application, respectively (Table 2), of which 62 and 36% was atrazine at 35 and 138 days after application, respectively. During the 138-days field incubation, atrazine degraded to a number of extractable nonpolar (i.e. DEA, DIA, DEDIA) and polar (i.e. HA) metabolites, similar to those reported elsewhere[12,13], without loss of the ^{14}C (Table 2).

SFE was less effective in removing ^{14}C-atrazine residues than the aqueous methanol extraction. SF-CO_2/5% methanol and SF-CO_2 extracted 37 and 20% (averaged over the two sampling times) of the ^{14}C-atrazine residues, respectively (Table 3). While exhaustive aqueous methanol extraction extracted a significant amount of hydroxylated polar metabolites of atrazine (Table 2), little or no hydroxylated polar metabolites were extracted by SFE using either SF-CO_2/5% methanol or SF-CO_2 as solvents (Table 3).

Atrazine extraction efficiency using SF-CO_2 and SF-CO_2/5% methanol decreased as samples "aged" in the field. Based on the amount of atrazine present in the soil determined using exhaustive aqueous methanol extraction as 100%, SF-CO_2 extracted 48% of the atrazine present after 35 days in the field and the extraction efficiency decreased to 31% at 138 days. Atrazine extraction efficiency using SF-CO_2/5% methanol was 66% for samples "aged" 35 days and decreased to 50% at 138 days.

DISCUSSION

These studies indicate that aqueous methanol solvent extraction is nonselective; both atrazine and its polar and nonpolar metabolites are readily extractable and that unreacted

atrazine would be quantitatively extractable even from "aged" soils. This procedure, however, only determines the total amount of atrazine in the soil; it does not provide information as to binding mechanisms.

The decrease in extractability by SFE compared to aqueous methanol was not the result of solvent diffusion limitations or kinetic effects. For instance, increasing the extraction time from 20 to 120 min with SF-CO_2 or SF-CO_2/5% methanol did not increase the extraction efficiency or change the product distribution. Therefore, the less than complete recovery of atrazine residues using the SFE technique, compared to aqueous methanol extraction, could be seen as an indication that different binding mechanisms were involved in the retention of atrazine as well as its metabolites as suggested by Cheng[2].

The SFE extraction data also suggest that the binding mechanisms changed with time, becoming stronger with incubation. Extraction of atrazine with both SF-CO_2 and SF-CO_2/methanol decreased with time after application. Again due to nature of supercritical fluids, the decrease in extractability as a function of time was not the result of solvent diffusion limitations or kinetic effects. Multiple binding mechanisms of atrazine to humic acid has also been suggested by the data of Piccolo *et al*[14] who found that SF-methanol desorbed atrazine bound to all humic acids studied except the humic acid that had the highest aromatic character, whereas methanol could only desorb atrazine bound to the humic acid with the lowest aromatic character.

While at present we do not know the specific binding mechanisms of atrazine to soil, we have been able to show that different binding mechanisms occur and that the mechanisms or binding strengths appear to change with time. It does appear that polarity of the solvents is a key in atrazine extractability provided a minimum amount of water is present in the soil. The order of both extractability and solvent polarity was aqueous methanol > SF-CO_2/5% methanol > SF-CO_2. This is in agreement with Locke[8] who found that a small amount of water (20% by weight) was necessary for maximum extraction of fluometuron from soil using SF-CO_2. However, we found that increasing the water content above "field moist" did not improve extractability.

The increased extractability by adding a polar modifier, such as methanol, could in part be due to competition for sorption sites between the added polar chemicals and the atrazine residues or increased solubility of the atrazine in the SF or both. The solubility of a chemical in a nonpolar SF has been shown to increase by the addition of a polar component. The 620% increase in solubility of 2-aminobenzoic acid in SF-CO_2 by the addition of 3.5 mol% methanol, was attributed to strong hydrogen bonding between methanol and the solute[15]. Since the polarity and the solvating power of the solvent mix used in the SFE system can be readily manipulated, it appears possible that SFE can be used to delineate the relationship between the extractability of pesticides and the polarity or other solvent characteristics, such as solvating power, which in turn can be used to characterize binding mechanisms. This possibility should be further explored.

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