

Supercritical Fluid Extraction of Naled, Methyl Eugenol, and Cuelure in Soil

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Abstract

Supercritical fluid extraction procedures are developed for the analysis of naled, methyl eugenol, and cuelure in soil samples. Recoveries of analytes from soil spiked at 0.25–45 $\mu\text{g/g}$ levels are high using modified or unmodified carbon dioxide (CO_2) at 60°C. For methyl eugenol, recoveries of 91–101% are obtained using CO_2 , a pressure of 27.6 MPa, and 5–30% soil moisture. For naled, recoveries of 65–90% are obtained using ethyl acetate modified CO_2 , a pressure of 48.3 MPa, and 10–30% soil moisture. For cuelure, total recoveries of 76–95% are obtained with acetone-modified CO_2 using a pressure of 41.4 MPa and 10–30% soil moisture. Recoveries are also high for dichlorvos (85%) and raspberry ketone (81%), which are degradation products of naled and cuelure, respectively, in soil spiked at 45 $\mu\text{g/g}$ under optimized conditions. Cuelure was derivatized to raspberry ketone and quantitatively recovered by supercritical fluid extraction. Recoveries of naled, methyl eugenol, and cuelure from soil by supercritical fluid extraction were comparable with those of conventional solvent extraction procedures using methylene chloride or ethyl acetate modified acetonitrile. Application of optimized SFE conditions for the soil dissipation study of naled, methyl eugenol, and cuelure under laboratory conditions showed that supercritical fluid extraction is convenient, fast, and uses much less solvent relative to conventional solvent extractions.

Introduction

Pest fruit fly eradication involving the male annihilation technique commonly uses a formulation containing naled and methyl eugenol (ME) or cuelure (Figure 1) (1–4). Naled, an effective organophosphorus insecticide, can be readily degraded to dichlorvos. Dichlorvos is more toxic than naled and is a suspected carcinogen (5). Cuelure and ME, which are used as male fruit fly attractants, are also possible environmental contaminants. Naled, ME, and cuelure were effective in controlling pest fruit flies (1,4). Additional information on the fate of the compounds in the environment and their degradation products

are required to register these chemicals for fruit fly eradication in Hawaii. To our knowledge, no analytical procedure is available for cuelure in soil. The current extraction methods (6,7) for ME and naled use methylene chloride (CH_2Cl_2). Methylene chloride is expensive, and there is a concern regarding its effects on the environment and human health (8).

Supercritical fluid extraction (SFE) has been recognized as a potential alternative to conventional extraction methods for environmental chemical analyses. Supercritical fluids have liquid-like solvating powers and gas-like diffusivities and therefore are ideal for extracting contaminants from soil. SFE with carbon dioxide (CO_2) offers significant advantages over conventional solvent extraction: It is a fast and simple procedure that provides good recoveries, is suitable for thermally labile analytes, and reduces solvent consumption. SFE parameters such as type of supercritical fluid, pressure, temperature, and addition of a modifier can be varied to obtain an extraction efficiency comparable to that of solvents (9,10).

SFE of various organophosphorus pesticides from soil and sediment has been described (11–15). Approximately 30% of naled-spiked sand was recovered (11,12). SFE methods for cuelure and ME in soil were not found, although ME and related allylbenzenes were isolated from teas (16).

In this study, optimization of SFE parameters, including

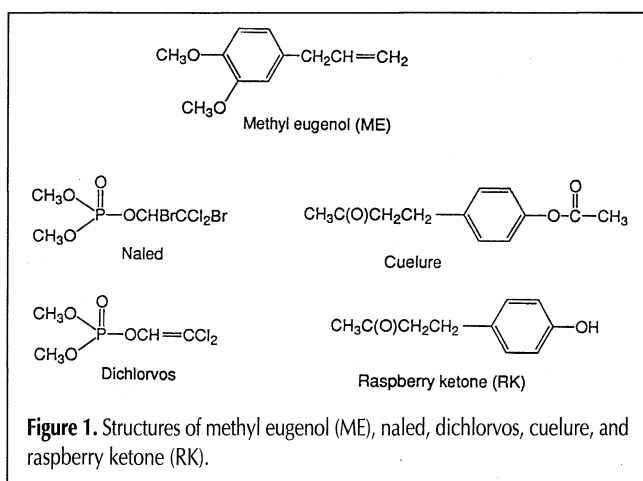


Figure 1. Structures of methyl eugenol (ME), naled, dichlorvos, cuelure, and raspberry ketone (RK).

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temperature, pressure, solvent modifiers, and soil moisture, were investigated for extracting naled, ME, and cuelure from soil. Because hydrolysis of cuelure to raspberry ketone (RK) during extraction was observed, procedures to quantitatively hydrolyze cuelure to RK (as a single analyte) prior to SFE were examined. The optimized SFE procedures were compared with conventional solvent extraction techniques, and the application of SFE procedures was demonstrated in a soil dissipation study.

Experimental

Reagents and standards

Naled and dichlorvos (both 99% pure) were obtained from Crescent Chemical (Hauppauge, NY). ME, cuelure, and RK were obtained from Aldrich Chemical (Milwaukee, WI). Sodium sulfate (Na_2SO_4) was obtained from Mallinckrodt (Chesterfield, MO) and heated at 450°C for 8 h prior to use. Optima-grade CH_2Cl_2 , ethyl acetate (EtOAc), acetonitrile (ACN), hexane, and pesticide-grade acetone were obtained from Fisher Scientific (Santa Clara, CA), and CO_2 (99.5% purity) was obtained from Gaspro (Honolulu, HI).

Stock solutions (1 mg/mL) of naled or dichlorvos were prepared in toluene, ME and cuelure were prepared in hexane, and RK was prepared in acetone. Six levels of working standards of naled or dichlorvos were diluted in EtOAc, and a mixture of ME, cuelure, and RK was diluted in hexane.

Soil and soil spikes

Three Lihue silty clay (17) soil samples (Table I) were collected from a papaya field (A), a nearby sugarcane field (B), and a nearby ironwood windbreak (C) in the Moloaa area of Kauai, Hawaii. Soil samples were air-dried for 3 days, ground, sieved through a 20-mesh filter, and stored in sealed mason jars at room temperature. Soil moisture contents were adjusted by mixing air-dried soil with appropriate amounts of distilled water at least 1 h prior to use. Oven-dried soil (120°C for 15 h) was considered to have 0% moisture. Soil C was used for the optimization study. An appropriate amount of analyte solution was added on top of the soil in the extraction cell ("spot spiked") or mixed with soil ("mixed spiked"). The solvent was evaporated (5 min in a hood) prior to extraction.

Liquid-solid extraction

Naled, ME, and cuelure were extracted from soil by two methods. The Chevron method (6) involved extraction of 50 g soil with CH_2Cl_2 (3×200 mL). After filtration and percolation through anhydrous Na_2SO_4 , the extract was concentrated in vacuo and diluted to the appropriate volume. In the second method, 50 g soil was placed in a quart-sized mason jar, acidified with 2.5 mL of concentrated HCl, and mixed with anhy-

drous Na_2SO_4 (25 g). The mixture was dispersed in 300 mL EtOAc-ACN (1:1) and homogenized by a Sorvall Omni-mixer (DuPont; Wilmington, DE) at low speed (2.5 on a scale of 10) for 10 min. After centrifugation of the slurry (2500 rpm, 0°C, 10 min), the supernatant was filtered through Na_2SO_4 , and a 100-mL aliquot was transferred to a flask containing 50 mL distilled water. Organic solvents were removed by a rotary evaporator at 40°C. The resulting solution was filtered through a Büchner funnel and extracted with hexane (3×50 mL). After the combined extracts were dried over Na_2SO_4 , 5 mL of 1% hexadecane in hexane was added. Solvents were evaporated to near dryness in vacuo at 40°C and adjusted to volume with hexane before analysis.

Table I. Characteristics of Soil Samples

	Soil A	Soil B	Soil C
pH*	7.0	6.3	5.9
Moisture† (%)	5.1	8.5	9.0
Organic C (%)	3.10	3.25	3.32

* Soil-water ratio = 1:2.5.

† Values indicate percent of air drying, which was calculated by dividing the grams of water by the grams of oven-dried soil and then multiplying by 100.

Table II. SFE Recoveries of Naled, ME, and Cuelure from Spiked Na_2SO_4

Compound	Pressure (MPa)	Temperature (°C)	Recovery* (%)
Naled	13.8	35	92 ± 2
	13.8	45	107 ± 7
ME	13.8	40	70 ± 0.2
	27.6	40	76 ± 3
	27.6	60	92 ± 0.2
Cuelure	27.6	40	98 ± 0.2
	27.6	60	108 ± 23

* Values shown are mean plus or minus standard deviation ($n = 3-6$).

Table III. Effect of Modifiers on Recoveries of Naled, ME, and Cuelure from Spiked Soil

Compound*	Pressure† (MPa)	Recovery‡ (%)				
		Unmod. CO_2	EtOAc	ACN	MeOH	Acetone
Naled	48.3	39 ± 6	85 ± 2	66 ± 5	35 ± 17	70 ± 2
ME	27.6	89 ± 4				
	41.4	89 ± 7				
Cuelure	27.6	27 ± 1				
	41.4	67 ± 2	97 ± 1	44 ± 2	122 ± 13	105 ± 3

* Spike level was 45 µg/g in soil C, which contained 9% moisture.

† The extraction temperature was 60°C.

‡ Recovery values indicate mean plus or minus standard deviation ($n = 3-4$). 100 µL MeOH or 500 µL of other modifiers was used.

Supercritical fluid extractions

Spiked soil or Na_2SO_4 (2 or 5 g) was placed in a stainless steel extraction cell (2.5 or 10 mL) and extracted using an Isco Model SFX 2-10 extractor (Lincoln, NE). The system consisted of a microprocessor to control pressure and temperature, a restrictor heater set at 60–80°C, and a Model 260D syringe pump maintained at 10°C to deliver CO_2 . Analytes were extracted with modified CO_2 or with unmodified CO_2 at various combinations of pressure (13.8–51.7 MPa) and temperatures (35–85°C). (For modified CO_2 , the modifier was added on top of the sample in the extraction cell at a concentration of 50–250 $\mu\text{L/g}$ soil.) The CO_2 extract flow was controlled to approximately 4 mL/min using a deactivated fused-silica tubing restrictor (30 cm \times 50- μm i.d.) or a preassembled high-pressure resistant stainless steel capillary restrictor. Analytes in the extract were trapped by immersing the restrictor tip in 20 mL solvent (EtOAc for naled and ME; acetone for cuelure) in a test tube capped with a Teflon-faced septum. During collection, the capillary restrictor was prevented from freezing by occasionally immersing the bottom of the test tube in lukewarm water. Extracts were sonicated for 0.5 min to remove dissolved CO_2 and subsequently adjusted to the desired volume for analysis. Data reported in this study were averages of 3–6 replicates.

Hydrolysis of cuelure to RK

Soil C (2 g) with 20% moisture was spiked with cuelure at 45 $\mu\text{g/g}$ and mixed with aqueous NaOH (100 μL , 1 or 10N), Na_2CO_3 , or NaHCO_3 (100 mg). After a 25-min incubation period, concentrated acetic acid (100 μL) or aqueous HCl (100 μL of 1N or 150 μL of 6N) was added to the sample. The sample was subsequently mixed and allowed to rest for 5 min before SFE.

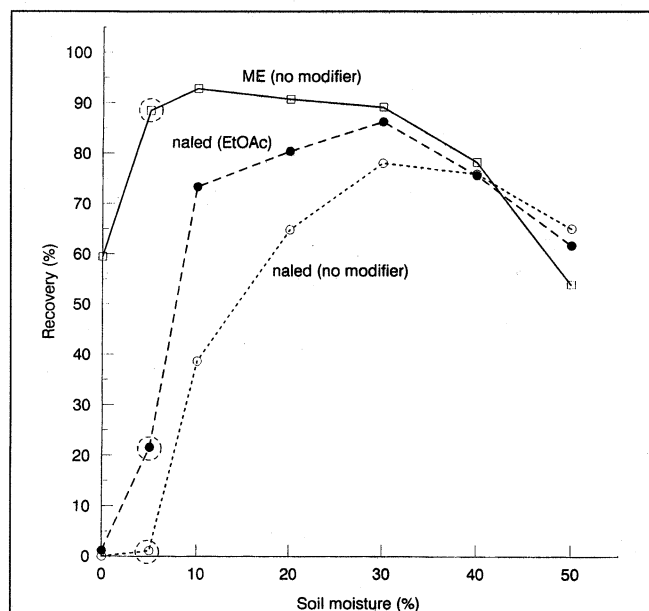


Figure 2. Effect of soil moisture on naled and ME recoveries by SFE. Soil spiked with 45 $\mu\text{g/g}$ naled or ME. Recoveries were from soil C except for the dotted circles, which were from soil A. SFE conditions: temperature, 60°C; pressure, 48.3 MPa; and EtOAc, 500 μL ; extraction cell, 2.5 mL.

Dissipation study of naled, ME, and cuelure in soil under laboratory conditions

Soil C was adjusted to 20% moisture (30% for naled), and each 2 g sample was spiked with naled, ME, or cuelure at 45 $\mu\text{g/g}$. After evaporation of solvent in a hood for 5 min, each sample was thoroughly mixed. Spiked, mixed samples were extracted using the SFE procedure at the appropriate time intervals. Half-lives were calculated by fitting a first-order rate equation to the data.

GC analysis of naled and dichlorvos

Naled and dichlorvos were analyzed with a Hewlett-Packard 5890 gas chromatograph (GC) equipped with flame-photometric detector, HP 7673A autosampler, and DB-17 column (15 m \times 0.53-mm i.d., 1.0- μm film) (J&W Scientific; Folsom, CA). The oven temperature was programmed from 110–210°C at 25°C/min and held at 210°C for 12 min. Injector and detector temperatures were set at 150 and 250°C, respectively. The flow rate of helium (carrier gas) was 32 mL/min at 69 kPa column head pressure. The thermal breakdown of the naled standard to dichlorvos ($\leq 5\%$) was observed as previously reported (6). This problem can be minimized by periodically changing the injection liner and washing the column with 20 mL CH_2Cl_2 -acetone (7:3) in a capillary column washer using nitrogen gas at 138 kPa. Analyses were completed within

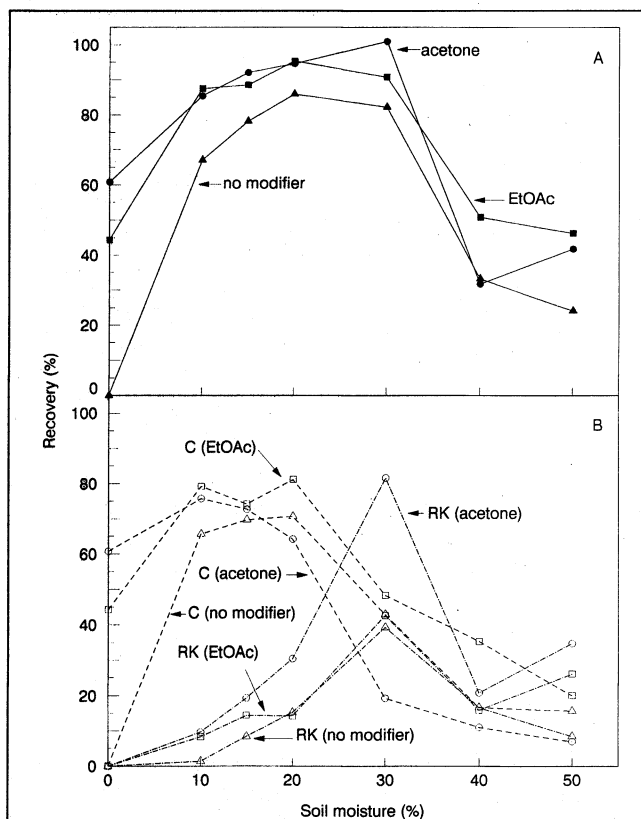


Figure 3. Effect of soil moisture on cuelure (C) and RK recoveries by SFE (soil C). SFE conditions: temperature, 60°C; pressure, 41.4 MPa; EtOAc or acetone, 500 μL ; extraction cell, 2.5 mL. Soil was spiked with 45 $\mu\text{g/g}$ cuelure only. In A, the total cuelure (C+RK) recovery is shown. In B, the recoveries of parent cuelure and the breakdown of RK are shown.

8 h after extraction, and quantitation of naled and dichlorvos was based on the average of 2–3 injections.

Gas chromatographic–mass spectrometric analysis of ME, cuelure, and RK

An HP 5890 GC/5970A mass selective detector equipped with an HP 7673A autosampler and a DB-5 column (30 m × 0.25-mm, 0.25- μ m film) was used. The oven temperature was held at 100°C for 1 min then programmed at 15°C/min to 250°C and held for 5 min. The injector and ion source temperatures were set at 250°C, and the helium (carrier gas) head pressure was 34.5 kPa. Electron impact (EI, 70 eV) ionization mass spectra were recorded. Parent compounds and degradation products were identified by comparison of retention times and mass spectra with those of corresponding standards. Quantitation was based on calibrating integrated peak areas of the selected molecular ion of each analyte: ME, m/z 178; cuelure, m/z 206; and RK, m/z 164.

Results and Discussion

SFE of naled, ME, and cuelure from Na₂SO₄

High recoveries of naled (92–107%), ME (92%), and cuelure (98–108%) from spiked Na₂SO₄ (45 μ g/g) using unmodified CO₂ were obtained by optimizing supercritical temperature and pressure (Table II). High recoveries confirm good extraction efficiency in this matrix and little loss of analytes in succeeding steps.

SFE of naled, ME, and cuelure from soil

In the optimization experiments, good recovery (89%) of ME was obtained at 60°C and 27.6 or 41.4 MPa using unmodified CO₂. However, recoveries of only 39 and 67% for naled and cuelure, respectively, were achieved with unmodified CO₂. Therefore, various modifiers were tested to increase recoveries of naled and cuelure.

Organic solvents such as MeOH, EtOAc, and acetone are often used as modifiers to adjust the solvating power of CO₂, to facilitate analyte desorption, and to improve supercritical fluid penetration through soil particles (18). The effect of modifiers on the recoveries of naled, ME, and cuelure from soil are shown in Table III. For the SFE of naled from soil, EtOAc was the most effective modifier (85% recovery) followed by acetone (70%), ACN (66%), and MeOH (35%). MeOH-modified CO₂ generated more dichlorvos from naled than other modifiers (data not shown).

Recoveries of cuelure from spiked soil using unmodified CO₂ at 27.6 and 41.4 MPa were 27 and 67%, respectively. High recoveries (97–122%) were obtained using

EtOAc, MeOH, or acetone as modifiers when the detected RK was combined with cuelure. Approximately 6% or less of the parent cuelure was converted to RK in soil C with 9% moisture. ACN-modified CO₂ recovered only 44% of the spiked cuelure. MeOH was not a preferred modifier because of chromatographic peak tailing possibly caused by coextractives.

Table IV. Derivatization of Cuelure in Soil to RK and Recoveries by SFE

Reagent	Hydrolysis time (min)	Acidifier	Recovery* (%)	
			Cuelure	RK
NaOH, 1N	25		2	66
	25	HCl, 1N	4	50
	55	HCl, 1N	1	52
NaOH, 10N	25		2(ND ^{††})	88(81 [†])
	25	HCl, 6N	ND	65
	55	HCl, 6N	0.4	62
	25	CH ₃ CO ₂ H	6	98
Na ₂ CO ₃	25		45	29
NaHCO ₃	25		16	62

* Extraction conditions: temperature, 60°C; pressure, 41.4 MPa; amount of acetone modifier, 500 μ L.
[†] Values in parentheses are recoveries obtained with 100 μ L MeOH as a modifier.
^{††} ND = not detected.

Table V. Comparison of SFE and Solvent Extraction of Naled, ME, and Cuelure in Soil at Different Spike Levels

Compound	Soil	Conc. (μ g/g)	Recovery (%)		
			SFE*	CH ₂ Cl ₂	EtOAc–ACN [†]
Naled	A	45	89 ± 3	93 ± 7	98 ± 6
		45	90 ± 3	94 ± 10	
		45	87 ± 1	92 ± 3	89 ± 10
	B	5.0	83 ± 2		
		2.5	81 ± 3		
		1.0	73 ± 3		
		0.25	65 ± 3	83 ± 8	75 ± 2
ME	A	45	97 ± 3	94 ± 9	86 ± 11
		45	94 ± 4		
	C	45	91 ± 7	94 ± 10	86 ± 11
		5.0	96 ± 1		
	1.0	101 ± 2			
	0.25	98 ± 9	83 ± 2	65 ± 5	
Cuelure	C	45	95 ± 8	77 ± 30	89 ± 10
		5.0	94 ± 8		
		1.0	82 ± 8		
		0.5	85 ± 18		
		0.25	76 ± 1	57 ± 5	86 ± 5

* SFE conditions: naled, 60°C, 48.3 MPa, and CO₂ modified with EtOAc; ME, 60°C, 27.6 MPa, and unmodified CO₂; and cuelure, 60°C, 41.4 MPa, CO₂ modified with EtOAc.
[†] EtOAc–ACN ratio = 1:1.

Effect of soil moisture on recovery by SFE and degradation of analytes

Good ME recoveries (89–92%) were obtained from soil with 5–30% moisture (Figure 2). ME recoveries were 59, 78, and 54% from soil with 0, 40, and 50% moisture, respectively.

Naled recoveries using unmodified CO₂ progressively increased from 0–78% as soil moisture increased from 0–30%; however, recovery slightly decreased at 40 and 50% moisture (Figure 2). Naled recoveries using EtOAc-modified CO₂ ranged from 73–86% in soil containing 10–40% moisture (optimum at 30%). In addition to thermal breakdown by GC, approximately 5% or less dichlorvos was derived from naled during SFE. Soil moisture did not affect dichlorvos formation. Recovery of dichlorvos from soil C (30% moisture) spiked at 45 µg/g was 85% following SFE (Figure 2) of naled. This recovery was comparable with the results reported for the recovery of dichlorvos from soil (13,15) at different SFE conditions.

Soil moisture and modifiers (EtOAc or acetone) significantly affected recovery of cuelure from soil (Figure 3). When unmodified or modified CO₂ was used, high total cuelure recoveries (67–98%) were obtained from soil with 10–30% moisture, and relatively low recoveries (0–61%) were obtained from soil

with 0, 40, and 50% moisture (Figure 3A). The increase of detected RK as soil moisture increases (Figure 3B) indicates that water facilitates the hydrolytic degradation of cuelure to RK (19). RK formation can be reduced by lowering soil moisture. When the soil contained 40% or more moisture, considerably smaller amounts of RK were detected, probably due to poor extraction efficiency at corresponding conditions. Higher RK levels detected in extracts using acetone-modified CO₂ compared with unmodified or EtOAc-modified CO₂ suggested that acetone enhanced the hydrolysis of cuelure and was an effective modifier for RK extraction.

Adjusting soil moisture improved recoveries of naled, ME, cuelure, and other compounds previously reported (20,21). However, the following problems may occur when soil contains 40% or more moisture: poor recoveries; difficulty in quantitatively transferring wet soil into the extraction cell; and frequent plugging of the restrictor, probably due to ice formation and deposition of extractives on the extraction cell outlet frit. The plugged restrictor can be cleared by immersing the collector in lukewarm water or sonicating the cell outlet frit in aqueous phosphoric acid (5%) and acetone.

High ME (45 µg/g) recoveries (90–93%) were obtained from either spot-spiked or mixed-spiked soil samples. Recoveries decreased by 9% for naled (from 87 to 78%) and cuelure (from 95 to 86%) by mixed spiking relative to spot spiking. Sixty-eight percent of the total cuelure (cuelure + RK) recovered from spot-spiked soil (20% moisture) was parent cuelure, whereas only 16% parent cuelure was recovered from the

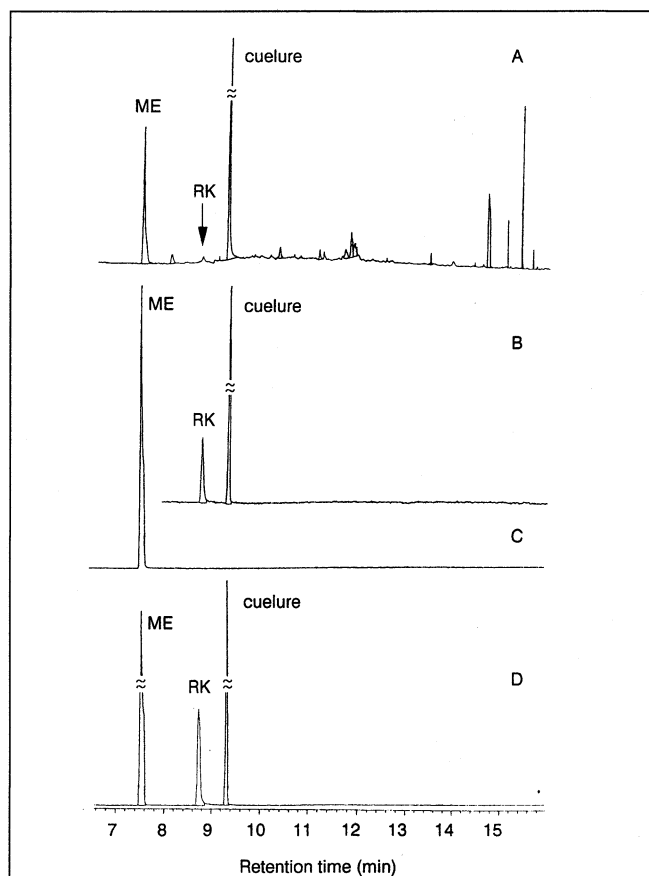


Figure 4. GC-MS total ion chromatograms of ME, cuelure, and RK: A, CH₂Cl₂ extract of soil spiked with 45 µg/g of ME and cuelure; B, acetone-modified CO₂ extract of soil spiked with 45 µg/g of cuelure; C, CO₂ extract of soil spiked with 45 µg/g of ME; and D, ME, RK, and cuelure standards with retention times of 7.52, 8.75, and 9.31 min, respectively. In A and B, RK was the hydrolysis product of cuelure.

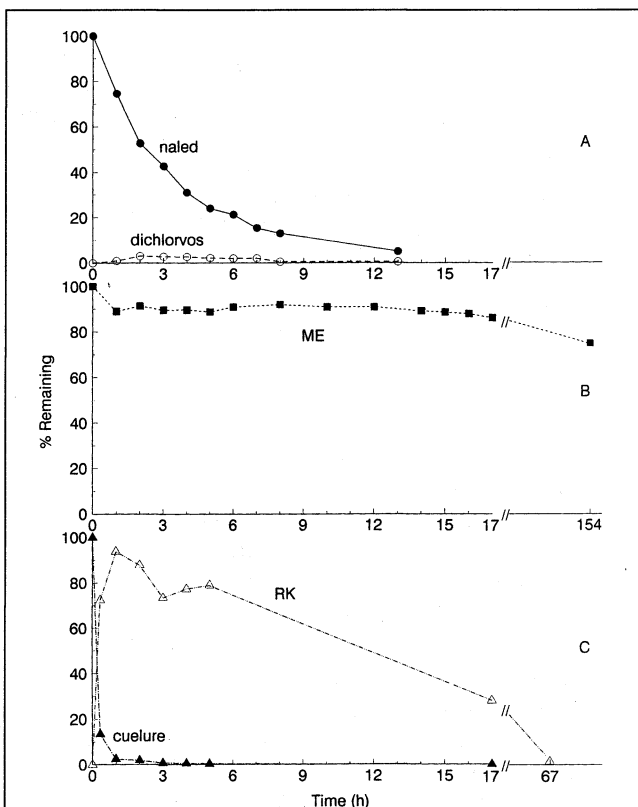


Figure 5. Dissipation of naled, ME, and cuelure in soil C under laboratory conditions using SFE.

mixed spiked samples. Apparently, mixed spiking enhanced decomposition of cuelure and naled, and therefore spot spiking was used in the optimization study to determine SFE efficiency for parent analytes.

Derivatization of cuelure to RK for SFE

Partial hydrolysis of cuelure to RK in the analysis of cuelure required the determination of both cuelure and RK. To avoid this complexity, a variety of procedures (Table IV) were investigated for quantitative conversion of cuelure to RK and for high recovery of RK. Sodium carbonate or sodium bicarbonate converted less cuelure to RK in comparison with NaOH. The following procedure resulted in high conversion and recovery of RK. Cuelure in soil spiked at 45 $\mu\text{g/g}$ was hydrolyzed to RK with 10N NaOH and subsequently neutralized with acetic acid. Complete extraction of RK was obtained by acetone-modified CO_2 at 60°C and 41.4 MPa. MeOH-modified CO_2 also gave high RK recovery (81%) from soil when cuelure was hydrolyzed with 10N NaOH. However, SFE using MeOH as a modifier generated turbid extracts that required removal of water before GC-MS analysis.

Comparison of SFE and solvent extraction of naled, ME, and cuelure from soil

Recoveries of naled, ME, and cuelure from soil by SFE were comparable with recoveries by solvent extraction (Table V). ME recoveries from soil spiked at 0.25, 1.0, 5.0, and 45 $\mu\text{g/g}$ were 91–101% by SFE, 83–94% by CH_2Cl_2 , and 65–86% by a mixture of EtOAc and ACN (1:1). Naled recoveries from soil samples spiked at 45 $\mu\text{g/g}$ were 87–90% by SFE, 92–94% by CH_2Cl_2 , and 89–98% by EtOAc-ACN. Naled recoveries from soil samples spiked at 0.25 $\mu\text{g/g}$ were 65, 83, and 75% by SFE, CH_2Cl_2 , and EtOAc-ACN, respectively. Additionally, recoveries of 73–83% were obtained by SFE when spiked with naled at 1.0–5.0 $\mu\text{g/g}$. SFE of total cuelure (including RK) from soil spiked at 0.25–45 $\mu\text{g/g}$ was more efficient (76–95% recovery) than CH_2Cl_2 (57–77%) and comparable with EtOAc-ACN (86–89%). The overall average relative standard deviation (RSD) of recoveries by SFE (5.4%) was slightly lower than those obtained by CH_2Cl_2 (9.3%) and EtOAc-ACN (7.5%).

Selected ion monitoring chromatograms of extracts of ME, cuelure, and RK by SFE showed much less background interference than those obtained with the solvent extraction method (Figure 4). Determining naled by solvent extraction required frequent GC column washes and replacement of the injection liner to minimize breakdown of naled to dichlorvos, which is possibly caused by coextractives.

Dissipation studies of naled, ME, and cuelure using SFE

The optimized SFE procedures were applied to study the degradation of naled, ME, and cuelure in soil C under laboratory conditions (Figure 5). Half-lives ($t_{1/2}$) of cuelure, naled, and ME were 0.4, 2.9, and more than 154 h, respectively. Cuelure was rapidly converted to the relatively more stable RK ($t_{1/2} = 9.5$ h). This study illustrates that these SFE procedures can be used to determine the environmental fate and dissipation of these chemicals.

Conclusion

Recoveries of the target analytes by SFE were comparable with those by solvent extraction. SFE is superior in terms of time and use of solvent; for naled, cuelure, and ME in soil samples, SFE was completed in 30 min. Corresponding solvent extractions required over 3 h. Supercritical fluid extracts were collected in 20 mL of solvent (EtOAc or acetone), whereas solvent extraction used more than 600 mL CH_2Cl_2 or 300 mL EtOAc-ACN. Hazardous solvent volume was greatly reduced using SFE. Also, SFE did not require tedious solvent concentration steps.

Various SFE parameters can be optimized to efficiently, quickly, and selectively extract the analytes of interest. Limitations such as partial hydrolysis of cuelure during extraction, sample size, and the influence of soil moisture on recovery were apparent. The SFE equipment used in this study can extract up to two samples simultaneously. Supercritical fluid extractors capable of handling up to six samples at a time are commercially available.

Acknowledgments

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