Short communication

Pressurised fluid extraction of bupirimate and ethirimol from aged soils

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Abstract

This paper assesses the effect of pressurised fluid extraction (PFE) on the recovery of bupirimate and its degradation product, ethirimol from a range of soil types. The analytes were extracted under standard conditions (pressure, 2000 p.s.i.; temperature, 100°C; and, three static flush cycles of 5 min static extraction time each) using a variety of individual and combined solvents. It was found that the recovery of bupirimate was dependent upon the organic matter content of soil whereas the recovery of ethirimol was dependent upon both the organic matter and pH of soil. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pressurised fluid extraction; Bupirimate; Ethirimol

1. Introduction

Comparison of pressurised fluid extraction (PFE) with other extraction techniques is prolific in the literature [1–7]. A recent review [8] compares the merits of a range of instrumental and non-instrumental techniques for the extraction of organic pollutants from solid environmental matrices. A further review highlights the theory, instrumentation and method development required for the extraction of environmental samples using PFE [9]. The review illustrates the potential benefits of PFE using a range of examples including the extraction of phenols, PAHs,

VOCs, PCBs, dioxins and dibenzofurans, and pesticides [9]. Few studies however, have investigated the influence of soil parameters and the efficiency of different extraction solvents [1,6,10,11]. We have recently shown that organic matter and clay content can influence the recovery of polycyclic aromatic hydrocarbons from aged soils [10].

Bupirimate and ethirimol are manufactured by Zeneca AgroChemicals and are marketed under the trade names Nimrod and Milgo, respectively. Bupirimate is degraded to ethirimol in soil both microbially and photochemically [12]. Adsorption of ethirimol has been studied on various soil components, in particular peat and various types of montmorillonite clay [13]. Scant literature exists studying the extraction of bupirimate and other pyrimidine pesticides [14–16]. This paper investigates the influence

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of soil type and extraction solvent on the recovery of bupirimate and ethirimol using PFE.

2. Experimental

The solvents used in this study were certified analytical reagents (Fisher Scientific, Loughborough, Leicestershire). Hydromatrix (Varian Ltd., Surrey, UK) was used to fill the head space of the PFE (ASE™ 200 Accelerated Solvent Extractor, Dionex (UK) Ltd., Camberley, Surrey) extraction cells. Bupirimate and ethirimol standards were supplied by Zeneca AgroChemicals. *N, O*-Bis(trimethyl silyl)acetamide (BSA) and tetradecane were purchased from Sigma–Aldrich Chemical Co. (Gillingham, Dorset, UK). Various standard soils were provided by Zeneca AgroChemicals, (Jealott's Hill, Bracknell, Berkshire) (Table 1). Soil analysis was undertaken by an independent laboratory (National Resource Management Ltd., Bracknell, Berks). The soil (9×200 g), was subjected to UV light for 24 h as a sterilisation process [17].

2.1. GC–MSD Analysis

The GC–MSD (HP G1800A GCD system, Hewlett-Packard, Palo Alto, USA) was operated in selected ion monitoring mode with a splitless injection volume of 1.0 μl. The column used was a DB-5ms (J&W Scientific, Folsom, CA, USA), with dimen-sions of length 30 m$\times$0.25 mm I.D.$\times$0.25 μm film thickness. The temperature program used for the analysis was 120°C, held for 2 min to 290°C at a rate of 5°C/min, with a final hold time of 2.5 min. The injection port and detector temperatures were set at 250°C and 280°C, respectively

2.2. Fortification and extraction procedures

Sterilised soil (30 g) was slurry spiked with bupirimate and ethirimol (at 20 μg/g level) in DCM (25.00 ml). The solvent was allowed to evaporate and the soil was left to age in the dark, at room temperature, for a period of 1 month. The aged soil was then sub-sampled by placing 1 g, accurately weighed, into a stainless steel PFE extraction cell (11 ml capacity) on top of a filter to prevent cell frit blockage. Hydromatrix was used to fill the head space to reduce solvent consumption. The cell was placed in the carousel and extracted used the following conditions: pressure; 2000 p.s.i. (1 p.s.i.= 6894.76 Pa), temperature, 100°C, with a static extraction time of 5 min. Three static/flush cycles were used. The total extraction time was 35 min per sample. An aliquot (1.00 ml) was removed and placed in a tapered tube (10 ml). BSA derivatising agent (100 μl) was added and the mixture was mixed (10 s) using a vortex mixer. Internal standard, tetradecane, (50 μl) was added and the derivatised extract was analysed on the GC–MSD. Six replicates

Table 1
Soil composition

Soil	% Silt	% Clay	% Sand	pH	CEC	% OM
Hyde farm	23	19	58	6.7	17.4	3.2
Chamberlain	4	9	87	7.3	11.0	4.5
18 Acres	24	20	56	6.3	14.0	4.7
Chalgrove Farm	29	37	34	7.4	29.7	5.8
Garden[a]	18	11	71	7.2	16.5	9.8
Mix 2[b]	3	11	86	5.9	12.7	17.5
Mix 1[b]	22	25	53	5.3	32.1	31.3
Mix 3[b]	21	30	49	5.2	41.7	59.4
Compost[c]	22	48	30	5 0	17.6	82.7

[a] Soil collected from a local garden.

[b] Mix 1=0.5 kg Compost+0.5 kg Hyde Farm; Mix 2=0.25 kg Compost+0.75 kg Hyde Farm; Mix 3=0.75 kg Compost+0.25 kg Hyde Farm.

[c] John Innes Compost No. 2.

were performed on each soil type with each solvent system evaluated.

3. Results and discussion

Calibrations were produced for the quantitation of bupirimate and ethirimol. It was found that correlation coefficients for both analytes were excellent $R^2=0.9924$ and $R^2=0.9961$, for bupirimate and ethirimol respectively, indicating linear behaviour over the chosen calibration range (0–4 μg ml^{-1}). Nine data points were used to construct the calibration graphs.

To investigate the influence of the soil matrix and effect of the extraction solvent on the recovery of the analytes nine soils of various compositions (Table 1) were slurry spiked with bupirimate and ethirimol and aged for 1 month. The soils were extracted with six different solvents covering a range of polarities and classes, to determine the influence of solvent type. Table 2 shows that a mixture of acetonitrile:dichloromethane 1:1 v/v gives the highest extraction results for bupirimate, with 79% recovery for Hyde Farm soil, and 69% recovery for compost soil. The results also show that three other solvents, acetonitrile:dichloromethane 1:4 v/v and iso-hexane:(acetonitrile:dichloromethane 1:1, v/v) 2:1 v/v, and dichloromethane also gave relatively high extraction recovery. Iso-hexane and acetonitrile gave the lowest extraction recoveries, ~38% on compost, and 55% on Hyde Farm soil. This implies that both

extraction solvent and soil type influence the recovery of bupirimate. With regard to ethirimol extraction, Table 3 shows that a mixture of acetonitrile:dichloromethane 1:1 v/v is the optimum extraction solvent, and iso-hexane and acetonitrile gave the poorest extraction recoveries, extracting between 40 and 55% recovery, depending on soil type. To determine which soil parameters have a direct influence on the extraction, multiple linear regression was performed on the data. Multiple linear regression is a technique that assesses the significance of the individual soil constituents to the overall extraction recovery. Eq. (1) shows the general multiple linear regression equation:

$$y = \beta_0 + \beta_1\chi_1 + \beta_2\chi_2 + \beta_3\chi_3 \ldots + \beta_{1.2}\chi_{1.2} + \beta_{1.3} \ldots \beta i\chi_I \tag{1}$$

Where β_0 is the value of the intercept, χ_i are the individual soil parameters, and β_i are the regression coefficients for the parameters.

Due to the high degree of correlation between the soil parameters (Table 4), only three soil parameters can be investigated at any one time. These combinations are: % silt, % OM and CEC; % clay, pH and CEC; % OM, % sand and CEC; and, % sand, pH and CEC. Each of these combinations were regressed for both compounds against each solvent. Components with a P-value of <0.05, are considered to have a significant effect on the recovery of bupirimate at the 95% confidence level. The results of the multiple linear regression determined that the organic matter

Table 2
Soil/solvent study results for bupirimate extraction (as % recovery)[a]

Soil	DCM	Iso-hexane	ACN	ACN:DCM 1:1 v/v	ACN:DCM 1:4 v/v	Iso-hexane: (ACN:DCM 1:1 v/v) 2:1 v/v
Hyde farm	67	55	55	79	75	61
Chamberlain	66	52	53	78	74	60
18 Acres	65	53	53	76	72	59
Chalgrove Farm	64	51	51	74	70	59
Garden	64	46	50	70	68	54
Mix 2	63	49	47	70	67	51
Mix 1	63	49	45	70	66	49
Mix 3	62	39	43	69	66	48
Compost	62	37	39	69	65	45

[a] RSD 3–5% in all instances ($n=6$).

Table 3
Soil/solvent study results for ethirimol extraction (% recovery)[a]

Soil	DCM	Iso-hexane	ACN	ACN:DCM 1:1 v/v	ACN:DCM 1:4 v/v	Iso-hexane: (ACN:DCM 1:1 (v/v) 2:1 v/v
Hyde farm	64	49	52	77	67	59
Chamberlain	64	51	55	77	71	58
18 Acres	63	47	50	77	68	58
Chalgrove Farm	62	49	52	76	65	62
Garden	61	46	48	76	64	56
Mix 2	60	45	47	76	62	45
Mix 1	60	44	45	76	61	44
Mix 3	59	41	42	76	59	41
Compost	59	40	41	75	59	48

[a] RSD 3–5% in all instances ($n=6$).

Table 4
Correlation data

	Sand	Silt	Clay	pH	% OM	CEC
Sand	1.00					
Silt	−0.87	1.00				
Clay	−0.94	0.66	1.00			
pH	0.35	−0.09	−0.48	1.00		
% OM	−0.53	0.16	0.71	−0.83	1.00	
CEC	−0.54	0.52	0.48	−0.40	0.41	1.00

content of the soil had a direct influence on bupirimate extraction when using either acetonitrile ($P=0.02$), iso-hexane ($P=0.01$) or iso-hexane:(acetonitrile:dichloromethane 1:1, v/v) 2:1 v/v ($P=0.02$). The influence of organic matter decreased for solvents that gave good extraction recoveries, i.e., acetonitrile:dichloromethane 1:1 v/v, ($P=0.07$), acetonitrile:dichloromethane 1:4 v/v ($P=0.05$), and di-

chloromethane ($P=0.09$). Organic matter content and pH of the soil influenced ethirimol extraction when acetonitrile, iso-hexane, or iso-hexane:(acetonitrile:dichloromethane 1:1, v/v) 2:1 v/v were used for the extraction. The influence of these soil parameters decreased when acetonitrile:dichloromethane 1:1 v/v, dichloromethane and acetonitrile:dichloromethane 1:4 v/v were used as the extraction solvent (Table 5).

Table 5
Comparison of % OM P-values for various extraction solvents used for ethirimol extraction

Solvent	P-value for % OM	P-value for pH
DCM	0.05	0.06
Iso-hexane	0.02	0.03
ACN	0.01	0.03
ACN:DCM 1:1 v/v	0.07	0.09
ACN:DCM 1:4 v/v	0.05	0.06
Iso-hexane: (ACN:DCM 1:1 v/v) 2:1 v/v	0.03	0.04

4. Conclusions

It is concluded that soil properties can influence the recovery of bupirimate and ethirimol from aged samples. However by careful choice of solvent any influence from soil properties can be negated. It is therefore important to include solvent as a variable when undertaking any extraction optimization.

Acknowledgements

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