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Review

# Effect of soil–pesticide interactions on the efficiency of supercritical fluid extraction

J.R. Dean

*Department of Chemical and Life Sciences, University of Northumbria at Newcastle, Ellison Building, Newcastle upon Tyne NE1 8ST, UK*

## Abstract

In selecting the appropriate extraction conditions for a range of pesticides from soil, the nature of the soil–pesticide interaction is of fundamental importance. This paper reviews the work that has been undertaken with a view to understanding the role that soil–pesticide interactions have played in affecting the extraction process. Supercritical fluid extraction has been of particular interest to this work. It is noted that the majority of papers cited refer to the use of spiked soil samples. The experimental conditions required for extraction from native samples may well be different. In this situation, the use of mathematical models, both for soil–pesticide interactions and the extraction process may well be useful. The important factors affecting the recovery of analytes from soils are summarised.

*Keywords:* Reviews; Soil; Soil–pesticide interactions; Extraction methods; Environmental analysis; Pesticides

## Contents

1. Introduction .....	222
2. Studies on soil–pesticide interaction .....	222
2.1. Modelling soil–pesticide interactions .....	222
2.2. Modelling the extraction process .....	223
2.3. Practical issues .....	224
3. Pesticides .....	225
3.1. Organochlorine pesticides .....	225
3.2. Organophosphorus pesticides .....	226
4. Herbicides .....	227
4.1. Triazines .....	227
4.2. Urea herbicides .....	229
4.3. Sulfonylurea herbicides .....	230
4.4. Phenoxyacetic acid herbicides .....	230
5. Insecticides .....	231
5.1. Carbamates .....	231
References .....	232

## 1. Introduction

The extraction of an analyte from a sample consists of several steps, including solvation of the analyte by the extraction solvent, desorption from the matrix surface and, finally, transportation of the analyte into the bulk extraction fluid. Each of these steps is of importance when the analyst is seeking to design an experimental protocol for the extraction of pesticides from soil using supercritical fluid extraction (SFE). This paper utilises information from a previous review on the SFE of analytes from environmental samples [1] to consider further the nature of soil–pesticide interactions and to what extent the interactions limit the extraction efficiency achieved.

It is obvious from the above brief introduction that the solubility of the pesticide in the supercritical fluid is an important starting point in the design of any experiment. However, this is not the only consideration. Having a soluble analyte in supercritical CO<sub>2</sub> does not guarantee its extraction. In designing an experiment it is also necessary to consider the pesticide–soil interaction and how it may be overcome. Many papers have been published which seek to characterise the role of the matrix in controlling the extraction process. In environmental solid matrices, e.g. soil, attention has been primarily focused on the effect of moisture, pH, and, organic, clay, silt and sand contents. Various attempts have been made to study soil–pesticide interactions and include theoretical modelling and experimental approaches. This review will consider both approaches.

## 2. Studies on soil–pesticide interaction

### 2.1. Modelling soil–pesticide interactions

In order to determine the influence of the soil matrix on the retention of pesticides, it is necessary to obtain data relating to their sorption. The sorption of pesticides by soil is governed by various intermolecular interactions including Van der Waals, hydrogen bonding, charge transfer, ligand exchange, direct and induced ion-dipole and dipole–dipole interactions and chemisorption [2]. The soil sorption can be quantified in terms of a soil organic matter–water partition coefficient,  $K_{om}$ , where soil organic matter consists of humic and non-humic substances. The non-humic substances consist of carbohydrates, proteins, fats, waxes, resins, pigments, and low-molecular-mass compounds associated with humic acids [3]. Humic acids are amorphous, three-dimensional, polymeric, acidic substances of high molecular mass and aromatic structure. Their precise structure is not known but it is possible to characterise humic acids [4]. Various relationships have been identified between soil sorption of different classes of compounds including pesticides and their octanol–water partition coefficient,  $K_{ow}$  [5]. The derived relationships are of the form:

$$\log K_{om} = a \log K_{ow} + b$$

where the constants  $a$  and  $b$  are dependent on the specific chemicals and soils involved. The values for the constants and their applicability is shown in Table 1.

The difficulty in applying such relationships however, lies in the uncertainty of  $\log K_{ow}$  values.

Table 1  
Relationship between  $\log K_{om}$  and  $\log K_{ow}$  for a range of organic compounds (OECD, 1993)

Compounds	$a$	$b$	Correlation coefficient	Number of determinations	$\log K_{ow}$ range	Ref.
Pesticides	0.53	1.12 <sup>a</sup>	0.95	105	–0.57 to 7.4	[6]
Pesticides	0.54	1.38	0.86	45	2 to 6	[3]
Aromatic, PAHs	0.83	0.29	0.95	20	1 to 6	[7]
Aromatic herbicides	0.94	–0.01	0.97	19	NA	[8]
Aromatic	0.99	–0.35	1.00	5	2 to 5.2	[9]

NA = not available.

<sup>a</sup> This number is incorrectly cited in the OECD report [5], the actual value from [6] is 0.64.

Various methods are available to estimate and measure  $\log K_{ow}$  values and these have recently been summarised for pesticides [10].

Alternatively, the soil–water distribution ratio,  $K_d$ , or sorption coefficient can be determined. Experimentally determined sorption isotherms generally have the form:

$$C = K_d C_w^{1/n}$$

where  $C$  is the concentration of analyte adsorbed to the soil in equilibrium with the concentration,  $C_w$ , in solution, and  $n$  is a measure of the non-linearity involved. This equation is sometimes referred to as the Freundlich isotherm. The values of  $n$  commonly range from 0.7 to 1.2 [11]. The soil–water partition coefficient,  $K_d$ , is related to the organic matter (OM) content of the soil. This provides the organic matter partition coefficient,  $K_{om}$ .

$$K_{om} = (100 \cdot K_d) / \%OM$$

Recently, Binstein and Devillers [12] have developed a structure–activity relationship model for estimating the  $K_d$  values of both ionised and non-ionised compounds. The proposed model was elaborated from 229  $K_d$  values obtained for 53 chemicals and then tested on 500 other  $K_d$  values obtained for 87 chemicals. The following relationship was obtained:

$$\log K_d = 0.93 \log K_{ow} + \log f_{oc} + 0.32 CFa - 0.55 CFb' + 0.25$$

where  $CFa$  and  $CFb'$  are the anionic species concentration and the corrected cationic species concentration, respectively, and  $f_{oc}$  is the fraction of organic carbon associated with the sorbent. This model was based on 229 determinations, giving a standard deviation of 0.433, a correlation coefficient of 0.966 and a probability level of  $p < 0.01\%$ .

## 2.2. Modelling the extraction process

The key factors in the extraction process relate to pesticide solubility in the supercritical fluid, desorption of the pesticide from the matrix surface and, finally, diffusion of the desorbed pesticide into the

bulk solvent. The solubility of analytes in supercritical fluids is one topic that has been extensively investigated for selected analytes. Methods of solubility determination include equations of state e.g. Peng-Robinson [13,14], chromatographic retention [15–19], gravimetric assay, and molecular structure and solubility parameter [20–23]. In contrast, the desorption stage has not been as well studied. The group at the University of Leeds, UK have developed models based on the diffusion of the analyte from a homogenous spherical particle into a medium in which the extracted analyte is infinitely dilute [24–26]. Ashraf et al. [26] used this so-called ‘hot-ball’ model to predict conditions for the extraction of atrazine from spiked sandy loam soils (1.1% organic content). Solubilities determined using the Peng–Robinson equation of state (EOS) were in agreement with those experimentally determined. The authors discussed the relative solubilities of simazine and atrazine as predicted using the EOS. It was found that at 50°C simazine is much less soluble in supercritical  $CO_2$  than atrazine. This correlated well with results reported by Janda et al. [27] who observed that the recoveries of simazine from sediment were lower than those obtained for atrazine at 42°C.

A kinetic model, based on a packed-tube extractor, has been described for SFE [28]. The model is based on established principles of mass transfer kinetics, chromatographic elution and the convolution theorem. It was suggested that only two void volumes of the supercritical fluid are required for quantitative removal of desorbed analytes if no retention of the analyte occurs on the matrix. In order to complete this process, it is necessary that (a) the analyte is soluble in the supercritical fluid and (b) rapid mass transfer of the analytes can occur between the matrix and the supercritical fluid. In both situations, optimisation of operating conditions will be required. The author concluded that “when more is known about matrix–native analyte interactions, then a more educated guess about the optimisation procedure can be made”! It is difficult to see the value of this model, particularly as everything requires optimisation. Experience, in this authors laboratory suggests that the key issue in extraction (SFE or otherwise) is the matrix–analyte interaction.

### 2.3. Practical issues

The matters that arise when considering practical issues related to the SFE of pesticides from soils can vary. Firstly, the nature and composition of the soil will be considered. This will be followed by the effect the soil properties may have on the extraction process.

As we have seen previously, the use of soil-organic matter to predict soil–pesticide interaction is important. The actual composition of soil organic matter is usually dismissed in terms of its characterisation into humic and fulvic acids. Qiang et al. [4] were able to characterise two commercially obtained and eight soil-derived humic acids. They noted that there were significant differences between humic acids derived from soil and those obtained from commercial suppliers, in particular, the ash content, major and micro-element constituents, *E4/E6* ratio, total acidity and  $^{13}\text{C}$  NMR spectroscopy, although data from stability constant and IR spectroscopy indicated similarity. The differences are primarily due to the different geographic sources and the extraction/purification procedures used to obtain the pure humic acids. These differences in the nature of the humic acids will have serious consequences when researchers compare the effects of soil organic matter and pesticide retention.

The rate of pesticide extraction from the soil matrix will be partially controlled by the inability of the supercritical fluid to diffuse through the matrix. One way to improve this diffusion is to control the particle size of the soil matrix. This physical property of the soil matrix was considered by Andersen et al. [29]. They suggested, on the basis of Fick's second law, that by having an average particle size of  $500\ \mu\text{m}$  should result in 99% recovery in 5 min! The same group also considered the effect of incomplete extraction in cells that are too large for the amount of sample to be extracted. As the flow through a typical cell is likely to be laminar (most extraction cells are long, narrow tubes), no mixing will occur perpendicular to the general flow. Also, in laminar flow the velocity near the cell wall is slower than in the centre of the cell. As a consequence a small amount of sample placed in a sample cell will not experience sufficient mixing to encourage quantitative recovery. Ideally therefore, the volume of the

sample cell should approximate the volume of the sample. If smaller samples are to be used, it is imperative to use an inert support thoroughly mixed with the sample, to occupy the space available. A suitable support material for SFE is diatomaceous earth [30]. As well as allowing the sample to be dispersed, the use of diatomaceous earth also allows wet samples to be successfully extracted.

A particularly real problem with natural samples is the prospect of blockages when using fixed restrictors in SFE. Burford et al. [31] suggested heating all but the last 3 cm of the fixed restrictor and to depressurise directly into the collection solvent. A range of temperatures were evaluated for heating (50 to  $200^\circ\text{C}$ ), the final temperature depending upon the sample matrix. Pyle and Setty [32] reported blockages when extracting soils with a high sulphur content. The researchers reported that the addition of a copper scavenger column placed in-line after the sample cell could effectively eliminate the sulphur from the extracts, without loss of analyte, and thereby eliminate potential blockages.

The SFE of polar analytes with supercritical  $\text{CO}_2$  requires the addition of a polar modifier. Fahmy et al. [33] have studied the effects of modifier addition on the swelling of soil and clay matrices under supercritical conditions. In this work the effect of matrix swelling was investigated on soils and two clays, montmorillonite and kaolinite. The former clay is known to undergo swelling in a suitable solvent while the latter does not. In the presence of supercritical  $\text{CO}_2$  only, neither clay underwent any noticeable swelling. However, in the presence of supercritical  $\text{CO}_2$  and water (as a modifier, 20–25 ml) the montmorillonite clay underwent swelling. Similar but reduced swelling was observed when using a Tama soil; a matrix with organic and inorganic components and 14% uncharacterised clay. It was experimentally observed that the percentage swelling was analogous to the extraction efficiency of diuron ("spot" spiked onto 1–2 g of clay and the methylene chloride solvent evaporated under a stream of nitrogen, prior to SFE). However, it should be noted that maximum swelling did not occur at the maximum pressure (3500 p.s.i.; 1 p.s.i. = 6894.76 Pa) investigated. It was postulated that the expansion of the clay provided access for the modified supercritical fluid to solvate diuron trapped within the clay

structure. It was suggested that systems could be selected that contain agents for matrix swelling and also for solubilising the analyte, i.e. mixtures of modifiers. In this manner, it may be possible to design systems in which water acts as the matrix swelling agent while the addition of a second modifier e.g. methanol, acts to solubilise the analyte of interest.

Quantitative SFE is an obvious area of concern. However, while attention has often focused on the extraction system itself, quite often little attention has been given to the method of collection after extraction. Two main possibilities exist. The first is that a suitable solvent is selected that allows quantitative retention of analytes after SFE or, without relying solely on the choice of collection solvent, an additional trap is used. This will typically take the form of a solid-phase extraction cartridge with suitable packing material e.g. C<sub>18</sub>. This latter situation has been ably demonstrated recently by the work of Stearman et al. [34]. In this work, a C<sub>18</sub> solid-phase trap was compared with liquid acetone, as the collection solvent for the SFE of herbicides from soils. Perhaps not surprisingly the solid-phase trap allowed quantitative recovery to be achieved (90%) while only 65% recovery was achieved using acetone. A more detailed study has been undertaken by Langenfeld et al. [35]. In this study, 47 compounds (semi-volatile pollutants) of varying polarity and volatility were investigated with respect to collection-efficiency using methylene chloride, chloroform, acetone, methanol and hexane. The poorest collection solvents were identified as methanol and hexane. Further work was carried out using 60 semi-volatile pollutants with methylene chloride as the collection solvent, maintained at 5°C. The average recoveries for all pollutants ranged from 92–104%, with the R.S.D. (relative standard deviation) for all the test compounds being <6%. The same group [35] also investigated the effects of cell geometry on the recovery of PAHs (polycyclic aromatic hydrocarbons) from railroad bed soil. By comparing extraction cells of constant internal volume, but differing in their overall dimensions, i.e. long narrow cells versus short broad cells, the recoveries were found to be negligible.

This paper now reviews the literature with a view to establishing the role that soil–pesticide interac-

tions have played in affecting SFE. The reader should not consider this to be a comprehensive review of SFE and environmental samples (for such information other sources should be used [1,36,37]). This section will focus on soil–pesticide interactions using SFE. The context taken with respect to pesticides is based on its loose association that allows incorporation of herbicides and other related analytes. The paper is sectionalised into two general areas: pesticides and herbicides, with further subdivisions as required.

### 3. Pesticides

#### 3.1. Organochlorine pesticides

A study on the effects of pesticide adsorption on soils and the subsequent removal by SFE was reported by Brady et al. [38]. In this study, DDT could not be quantitatively recovered from a high organic content (12.6%) top soil; residual DDT (~30%) was strongly adsorbed on the soil. The presence of water was found to slow the extraction process.

Lopez-Avila et al. [39] extracted organochlorine pesticides (OCPs) from spiked sands (8 g) using either only CO<sub>2</sub> or CO<sub>2</sub> + 10% MeOH. It was found that the presence of 10% methanol-modified CO<sub>2</sub> resulted in excellent recoveries of 38 out of the 41 OCPs studied, the exceptions being hexachlorocyclopentadiene, chlorobenzilate and DBCP. Similarly, excellent results were obtained using 5% methanol-modified CO<sub>2</sub> for OCPs from spiked soils samples using on-line SFE-SFC-GC. [40]. Lindane and *p,p'*-DDT were quantitatively extracted from spiked soils (700–900 mg) using supercritical CO<sub>2</sub> only [41]. SFE was compared with solvent extraction and Soxhlet extraction for the recovery of OCPs from spiked soils [42]. In all cases, high recoveries (85–105%) were obtained using supercritical CO<sub>2</sub> at 20 MPa and 50°C.

A more detailed study was undertaken by Liu et al. [43] who investigated the role of various modifiers for the extraction of OCPs from three characterised spiked soils. It was noted that the highest extraction efficiencies were obtained when using polar modifiers, e.g. methanol and DMSO (dimethyl

sulphoxide) than with non-polar toluene. It was suggested that the interactions of the soil matrix and OCPs are dependent on the pesticides polarity. This polarity can be identified by considering the octanol-water partition coefficient. It was observed that analytes with higher  $K_{ow}$ , i.e. non-polar, partition more readily into the soil. This general statement was emphasised by considering the extraction recovery in supercritical  $CO_2$ . By considering three OCPs, aldrin, dieldrin and endrin with log  $K_{ow}$  of 5.66, 5.15 and 4.56 respectively, the extraction recoveries were found to be 51.7, 30.3 and 20.8% respectively, in  $CO_2$  only. Obviously, this is only a guide as the highest recovery obtainable was only approx. 50%. The nature of the soil matrix, i.e. organic matter content, is also an important factor to consider.

Excellent recoveries of six OCPs from a range of spiked soils (sand, clay, top soil and river sediment) were obtained by Snyder et al. [44]. In this work methanol modified (5%) supercritical  $CO_2$  at 350 atm (1 atm = 101 325 Pa) and 50°C was able to quantitatively extract the OCPs. Perhaps more importantly from this work was the significantly poorer recoveries obtained from a spiked top soil that was aged by storage at 4°C for 8 months. In this situation, the overall average recoveries (6 OPPS and 6 OCPs) dropped from 91.6 to 63.5%. A comparison between sonication and SFE on three native soils contaminated with OCPs found no significant difference in recovery. In a subsequent paper from the same group [45], the effect of the soil matrix was investigated. As before, four soils were evaluated plus a furnace treated (400°C) soil in which as much organic matter as possible is removed. Spiking involved the addition of a 20  $\mu$ l spike to the soil (2 g) directly in the extraction cell followed by a time period to allow the solvent (acetone) to evaporate. This method of spiking seems to be totally inappropriate to the author of this paper. So it is not surprising to observe that with 3% methanol-modified  $CO_2$  at 350 atm and 50°C, excellent recoveries are achieved. The role of modifiers in SFE was also postulated. Three possibilities were suggested: firstly, that the addition of a modifier allows a more polar solvent system to be formed; secondly, that the modifier may displace polar analytes from the adsorption sites on the soil; finally, that the modifier can swell the soil matrix,

thereby exposing the internal structure of the matrix to the supercritical fluid. It is probable that the extraction mechanism is a combination of all three.

### 3.2. Organophosphorus pesticides

Lopez-Avila et al. [39] extracted organophosphorus pesticides (OPPs) from spiked sands (8 g), using  $CO_2$  only and  $CO_2$  + 10% MeOH. Under supercritical conditions, diazinon was not recovered, with or without modifier addition whereas it was observed that a modifier was required for the extraction of mevinphos, dimethoate, fensulfothion, azinphos methyl and coumaphos. Perhaps more surprisingly, phorate, dimeton-S and dimeton-o, while being recovered using  $CO_2$  only, were not recovered at all when modified  $CO_2$  was used. It was postulated that these three compounds hydrolyse under the conditions used. Further work was reported in the paper for an additional 22 OPPs, quantitative recoveries were obtained for methanol-modified  $CO_2$ , except for TEPP which is known to decompose under gas chromatography (GC) conditions.

Soils spiked with parathion and a degradation product, 4-nitrophenol, were extracted using methanol-modified  $CO_2$  [46]. In this work, quantitative recovery from spiked, fine, sandy loam soil (3 g) was achieved in 20 min and 15 min for parathion and 4-nitrophenol, respectively at 2000 p.s.i. and 5% methanol addition. The method was evaluated using GC and enzyme-linked immunosorbent assay (ELISA) detection.

Excellent recoveries of six OPPS from a range of spiked soils (sand, clay, top soil and river sediment) were obtained by Snyder et al. [44] using 3% methanol-modified supercritical  $CO_2$  at a pressure of 350 atm and 50°C. However, significantly poorer recoveries were obtained from a spiked top soil that was aged by storage at 4°C for 8 months using the same SFE conditions as described previously. In this situation, the overall average recoveries (6 OPPS and 6 OCPs) dropped from 91.6 to 63.5%. Also, the volatile dichlorvos was not recovered after the ageing process. In a subsequent paper from the same group [45], the effect of the soil matrix was investigated. An interesting aspect of the work was the effect that moisture, acting as a modifier, had on recovery using  $CO_2$  only. This was exemplified by

the dramatic increase in recovery for the polar OPPs studied (diazinon, methidathion, tetrachlorvinphos and dichlorvos), all of which showed an increase in recovery in the presence of 5% moisture. At moisture levels greater than 10% however, an equally dramatic loss in recovery was noted. This was probably due to the limited solubility of water in supercritical CO<sub>2</sub> and the subsequent formation of a two-phase system within the extraction vessel.

More recently Wuchner et al. [47] have studied the recovery of OPPs from spiked soils. In this case, the nature of the spiking process was investigated: spot-spiking versus slurry spiking. Using methanol-modified CO<sub>2</sub> >90%, recoveries were obtainable in <15 min. Using CO<sub>2</sub> only however, the nature of the spiking approach was evaluated. Spot-spiked soils, glass-wool and sand all gave quantitative recoveries using CO<sub>2</sub> only, at 250 bar and 50°C, except dimethoate. However, with the slurry-spiked approach, extracted 11 days after spiking, the recoveries decreased (ranging from 37% for dimethoate to 75% recovery for carbofenthion). It was suggested that solute–matrix interactions prevent desorption of all the OPPs and that analyte solubility in supercritical CO<sub>2</sub> does not guarantee efficient recovery from environmental matrices.

## 4. Herbicides

### 4.1. Triazines

One of the first references to consider the extraction of *s*-triazine herbicides from sediment was reported in 1989 [27]. In this study five triazines were considered (atrazine, cyanazine, propazine, simazine and terbutylazine). A lyophilised (dried) sediment (0.5 g) was spiked with a methanolic solution of the triazines (over the range of 28.0 to 81.2 ppm) and left overnight to allow evaporation of the solvent. Analysis was by GC with flame ionization detection (FID). Acceptable recoveries using CO<sub>2</sub> only (82.4 to 96.4%) were obtained for four of the triazines, the exception being simazine (42.5%). This poor recovery for simazine was investigated further by adding a 20 μl spike of methanol directly to the sample in situ. All recoveries were improved: reported recoveries ranged from 90.2 to 96.4% for all

five triazines. The increase in the simazine recovery was suggested to be due to the fact that it has low solubility in low-polarity solvents, including benzene. By increasing the polarity of the supercritical fluid, recovery of simazine improved to 92%. It is also interesting to note that the extraction of co-extractives from the sediment prevented analysis at lower concentrations, using GC with FID. Lower spiked concentrations (4 ppm to 28 ppb) were extracted and analysed using high-performance liquid chromatography (HPLC) with UV detection.

The recovery of atrazine, 2-hydroxyatrazine and deisopropyl-desethyl-2-hydroxyatrazine (MET) from spiked C<sub>18</sub> silica and soil was investigated by Papillound and Haerdi [48]. Initial studies investigated the role of extraction time, pressure, temperature and flow-rate on extraction recovery. It was noted that an organic modifier was necessary to improve the recovery of atrazine. The preferred method of methanol addition was using a second pump dynamically. High pressure (250 bar) at 50°C, a flow-rate of 0.5 ml min<sup>-1</sup> and a 45 min extraction time was required to achieve quantitative recovery of atrazine and 2-hydroxyatrazine. MET was only poorly recovered, however, under these conditions (20%). The additional use of water (2%) in the methanol was found to increase the recovery of MET to 52%. Subsequent extractions used the 2% water–methanol modifier for all triazines studied. No deleterious effect was noted on the recoveries of atrazine and 2-hydroxyatrazine. Soil, containing 4% natural organic matter, collected from a riverbank (Arve River) were pounded and then dried for 24 h at 120°C. The soil was then spiked at the 20 ppm level using the same procedure as the silica spiked samples (method given in text). It was found necessary to (a) increase the pressure to 300 bar, (b) increase the extraction time to 60 min, (c) increase the flow-rate to 1.0 ml min<sup>-1</sup>, and (d) raise the temperature to 65°C, to improve extraction recoveries. The reported recoveries were all still lower than those obtained from the silica matrix (5, 55 and 88% recovery for MET, 2-hydroxyatrazine and atrazine, respectively). The lower recoveries were suggested to be due to the more complex nature of the natural matrix (soil). Some improvements in recovery were possible by the inclusion of a washing step. Two washing step positions were considered: prior to extraction and

prior to spiking. The washing step involves clean-up of the soil of residual non-polar material using toluene and *n*-hexane. Dramatic increases in recoveries were noted for all three triazines studied. The best improvements were noted when the spiked soil was washed prior to extraction (41, 96 and 75% for MET, 2-hydroxyatrazine and atrazine, respectively). The loss of atrazine in the non-polar wash was evident however. An action of the non-polar washing was suggested. Washing with a non-polar mixture allows natural organic acids, especially fulvic and humic acids, to be preferentially removed, thus reducing interactions with the soil which led to improved recovery from the soil. The major disadvantage of the non-polar washing was the loss of atrazine [a lower recovery (75%) was noted after the washing step than had been experienced prior to washing (88%)]. The use of non-polar washing has been reported previously [49] as a procedure for clean-up after solid-liquid extraction.

Robertson and Lester [50] have also investigated the recovery of spiked *s*-triazines from sediments. In this case however, they chose to investigate some of the important operating parameters most likely to effect the recovery of the triazines, i.e. extraction temperature, time of extraction and supercritical fluid density. These variables were investigated initially using CO<sub>2</sub> only. Using a spike level of 20 μg g<sup>-1</sup> for the four triazines investigated (atrazine, simazine, deethylatrazine and deethylsimazine), it was noted that at a fixed density of 0.71 g ml<sup>-1</sup>, an increasing temperature caused an increase in the recoveries reported. However, even when using a 40 min extraction time, quantitative recovery was only obtained for atrazine at the maximum temperature considered of 140°C. It was suggested that elevated temperature (>200°C) may be necessary to achieve quantitative recoveries. Density effects were also considered at a fixed temperature of 100°C. Once again similar effects were noted: approaching quantitative recovery was obtained for atrazine at high density (0.8 g ml<sup>-1</sup>) with poorer recoveries obtained for the other three triazines. It was suggested that the degree of recovery was dependent upon the polarity of the analyte and hence its solubility in supercritical CO<sub>2</sub> to be extracted. So, the most polar triazine considered, i.e. deethylsimazine, had the lowest recovery. The time of extraction was also evaluated

and found to be sufficient to allow exhaustive extraction, provided extraction conditions were maintained above 100°C and a density of >0.67 g ml<sup>-1</sup>.

The effects of organic modifier were also evaluated [50]. They identified acetone as a more suitable modifier than methanol for the SFE of triazines. Previous, unreported work had identified that acetone was more suitable as a modifier when matrix effects were important, viz. the extraction of triazines from granular activated carbons. The dynamic addition of 20% acetone provided quantitative recoveries for all four triazines studied. The most dramatic effect was noted for the most polar triazine studied, i.e. deethylsimazine, which showed an increase from 39% (without modifier) to 100% (with 20% acetone, as modifier). The authors concluded that this indicated a "significant role for analyte solubility in the SFE process" [50]. When the results, using optimised SFE conditions, were compared with the results obtained using Soxhlet extraction at a spike level of 100 ng g<sup>-1</sup>, it was found that higher recoveries were obtained in a shorter time scale using acetone-modified supercritical CO<sub>2</sub>. It is interesting to note that this one-at-a-time variable approach could be more effectively done using an experimental design approach [51].

Steinheimer et al. [52] have compared the recovery of atrazine, cyanazine, desethylatrazine and deisopropylatrazine from soils of different composition using principal component analysis. The four soils investigated had a range of properties which included the organic carbon percentage, cation exchange, pH and the percentages of sand, silt and clay. Details of the soil spiking procedure were given. It is interesting to note that the same group of workers have compared modified supercritical fluid CO<sub>2</sub> extraction with microwave extraction. Microwave extraction was done using dilute mineral acid/soil slurry. A comparison of the HPLC traces (figure included) clearly identifies a major benefit of SFE, a simpler chromatogram. The PCA results on the spiked soils for the four triazines studied provided valuable information. The higher the polarity of the triazine, the greater the effect of the soil carbon content on extraction recovery. Thus the most polar triazine studied, as estimated by water solubility studies, deisopropylatrazine, was shown to be the



most affected. This effect was exemplified by the high recoveries (mean recovery of 93%) obtained for the triazines when extracted from sand (<0.05% organic content). Extraction temperature was also noted to be significant for the triazines studied. Over the temperature range studied (40 to 120°C), it was noted that higher temperatures gave lower recoveries. The optimal temperature was found to be approximately 40°C. Not surprisingly then, the reverse trend was observed for pressure: a high pressure correlating to a high recovery, with the exception of cyanazine. This anomaly for cyanazine was suggested to be due to its chemical reactivity. Under high temperature and/or pressure conditions in the presence of methanol or aqueous methanol modified supercritical CO<sub>2</sub>, it was postulated that cyanazine could undergo hydration, hydrolysis or methanolysis reactions. If these suggestions do occur, they all lead to the formation of more polar products than cyanazine and, consequently, to stronger binding to the matrix (hence lower recovery). The role of modifier was also included (static addition of 20% water or dynamic addition of 20% methanol in water) and, not surprisingly, it was noted that the recovery of the triazines is greatly influenced by the use of modifiers. It was concluded that optimum extraction conditions for atrazine, desethylatrazine and deisopropylatrazine from soils required high extraction pressure coupled with low temperature in the presence of 4–5% water. For cyanazine, lower extraction pressure is required, while the organic content of the soil was an important consideration in triazine recovery.

Experimental design, based on multiple linear regression, was used by van der Velde et al. [51] to study the effects of parameters on the SFE of triazines (atrazine, simazine, terbuthylazine, deisopropylatrazine and desethylatrazine) from soils. The experimental design involved the following parameters: pressure (20–50 MPa); temperature (50–100°C); extraction time (30–70 min); type of modifier (MeOH, mixed CO<sub>2</sub>-MeOH and mixed CO<sub>2</sub>-acetone); amount of modifier (100–1000 μl); cell volume (3.5 and 10 ml); amount of triazines (25–400 μl); type of soil (sand, peat and clay with organic carbon content of 0.3, 3.3 and 6.8%, respectively). All soils were dried at 40°C, passed through a 2.8 mm sieve and homogenised in a ball mill. It

was found that pressure had a significant effect on recovery, a high pressure relating to a high recovery. The addition of a modifier was also found to be important, with increasing amounts of modifier being required for triazines of increasing polarity. Extraction time and temperature of extraction were not found to be significant. Only a small effect was noted by the type of soil used.

The SFE of simazine and atrazine from a range of spiked soils (from sandy loam to silty clay) has been evaluated and compared with liquid vortex extraction [34]. In this work, the use of enzyme immunoassay analysis was compared with both GC and HPLC; no performance deterioration was noted between the detection techniques ( $r^2=0.95$ ). Using supercritical CO<sub>2</sub> only, the recoveries found for simazine and atrazine were 56 and 57%, respectively. However, the addition of 1.5 ml of triethylamine to a 100 ml acetone–water (9+1) modifier proved more successful: recoveries for simazine and atrazine improved to 79 and 90%, respectively. Clay content and type were identified to be important soil properties that seemed to influence recovery.

#### 4.2. Urea herbicides

Wheeler and McNally [53] investigated the effects of density, temperature and organic modifier on the recovery of linuron and diuron from a sandy loam soil, i.e. Sassafra soil. It was noted that >95% extraction efficiency could be achieved, provided high density and an organic modifier was added. The effect of modifier addition was noted to be compound specific, methanol for diuron and ethanol for linuron providing the highest recoveries.

Robertson and Lester [50], as well as investigating the extraction of triazines, also investigated the extraction of phenylurea herbicides, namely, monuron, chlortoluron, isoproturon, diuron and linuron. After spiking soil (100 ng g<sup>-1</sup>) with the phenylurea herbicides, the effects of organic modifier and extraction time were investigated. As the phenylurea herbicides are soluble in acetone and as a consequence of the work on triazines, acetone-modified supercritical CO<sub>2</sub> was evaluated. As with the triazines, the addition of 20% acetone-modified supercritical CO<sub>2</sub> improved extraction recoveries to acceptably high levels. It was also noted that linuron

could be extracted with a 79% efficiency using supercritical CO<sub>2</sub> only. So, even though the molecular structure and solubility of linuron in supercritical CO<sub>2</sub> is not markedly different from the other structures (e.g. diuron has an extra ether linkage), the pronounced effect on the recovery from the spiked soil is noticeable. This suggests that analyte solubility in the supercritical fluid is not the only factor that needs to be considered when seeking quantitative recovery. The effect of extraction time was also studied. It was found that for the majority of the herbicides studied, >75% recovery was achieved after a 10 min extraction period. Finally, SFE was compared with Soxhlet extraction using either dichloromethane or acetone. For Soxhlet extraction it was noted that acetone was a more efficient extraction fluid than dichloromethane and that SFE gave higher recoveries than Soxhlet extraction with acetone. It is important to note that phenylurea herbicides are thermally labile compounds which become unstable above 70°C. This may have led to poorer than expected recoveries of isoproturon during Soxhlet extraction.

#### 4.3. Sulfonylurea herbicides

An investigation into the recovery of chlorsulfuron and metsulfuron methyl from four different soils has been investigated [54]. The soils were collected from sites in Switzerland, sieved at 2 mm, dried and sterilized by heating to 120°C. The soils were characterised with respect to pH, organic carbon, exchange capacity and clay content. Operating parameters were investigated for SFE. It was concluded that a temperature of 50°C, a pressure of 370 bar, an aliquot (80 µl) of methanol to 4 g soil and a 10-min static extraction followed by an 8-min dynamic extraction was required. Acceptable recoveries were obtained for both herbicides from three of the soils, the exception being the soil with the highest organic carbon content (4.2%) and clay content (56%). In this situation only 50% of the spiked herbicides could be recovered.

#### 4.4. Phenoxyacetic acid herbicides

Burk et al. [55] studied the extraction of three phenoxyacetic acid herbicides (dicamba, picloram and 2,4-D) from a soil. The soil was pre-treated by

heating to 600°C in air to remove interfering organics. It was noted that the polar phenoxyacetic acid herbicides were poorly extracted using supercritical CO<sub>2</sub> (the highest recovery was 6% for dicamba). In contrast, Soxhlet extraction with methanol provided quantitative recovery for 2,4-D only. The poor recoveries noted by SFE were not, however, due to the lack of solubility in supercritical CO<sub>2</sub> but to the strong interaction between the soil matrix and the herbicides.

This problem of extracting polar phenoxyacetic acid herbicides from soils has been investigated by two groups from an original viewpoint [56,57]. In these cases, the methodology of extraction involves the derivatization of the herbicide to a less polar analogue which will be more effectively extracted using SFE. Lopez-Avila et al. [56] used tetrabutylammonium hydroxide and methyl iodide as the derivatising agents to extract seven chlorophenoxy acid herbicides from soil. The herbicides investigated were as follows: dicamba, MCPP, MCPA, 2,4-D, 2,4,5-T, MCPB and 2,4-DB. Supercritical fluid extraction was carried out at 400 atm and 80°C with a 15-min static extraction followed by a 15-min dynamic extraction, at a flow-rate of 1.5 ml min<sup>-1</sup>. In situ methylation of the chlorophenoxy acid herbicides resulted in an average recovery from the three soils at two spike levels of 95.5% (standard deviation 18.1%), with individual recoveries ranging from 57.4 to 141%. No noticeable difference was noted between sand, a clay soil and a top soil. By comparison, extraction with supercritical CO<sub>2</sub> or methanol-modified supercritical CO<sub>2</sub> resulted in all cases in lower recoveries compared with the derivatization method.

Similarly, Rochette et al. [57] have also investigated in situ derivatization and matrix modification methods for the SFE of 2,4-D from soils. The two soils chosen had noticeably different organic carbon contents of 0.3% and 4.2%. Several methods of derivatization were considered. Silyl esterification of 2,4-D was successfully achieved under supercritical conditions in the absence of soil (91% recovery). However, when 1.2 g of spiked soil was extracted with and without the derivatization agent, recoveries ranged from 0 to 18%, respectively. Subsequent extractions with the Tri-Sil concentrate yielded further 2,4-D (the accumulated recovery from six extraction's was 31%). The presence of moisture can

also interfere with the silylation. An alternative approach was investigated using  $\text{BF}_3$ /methanol (methyl esterification). The recovery using this methyl esterification method was 90%. However, as the nature of the reagents had deleterious effects on the GC column, its further use was negated. Alternative procedures were evaluated based on ion-pairing and ionic displacement. Ion-pairing using *m*-trifluoromethylphenyl trimethylammonium hydroxide gave low recoveries of 2,4-D (14 and 19%) whereas ionic displacement using 0.2 M calcium chloride in methanol was more successful (86 and 87%). Similar work using calcium chloride and methanol has previously been reported for the extraction of atrazine from soil [58]. The use of this salt solution for SFE was compared to Soxhlet extraction [acetone–hexane (1:1) used as solvent] using the organic-rich soil. The results indicated that the extraction efficiency was better by a factor of 2 using the SFE approach, but that the average recovery was of the order of 47%. This procedure of using salt solution to increase extraction efficiencies of polar compounds has potential for investigation.

Stearman et al. [34] have evaluated the recovery of 2,4-D from a range of soil types. It was found that with supercritical  $\text{CO}_2$  the recovery of 2,4-D was poor (7%). However, quantitative recovery could be obtained by the addition of 1.5 ml of triethylamine to a 100 ml acetone–water (9:1) modifier. Soil properties were identified as a potential influence on analyte recovery.

## 5. Insecticides

### 5.1. Carbamates

Alzaga et al. [59] have evaluated a range of supercritical fluids with and without modifiers to

extract pirimicarb from topsoil. The supercritical fluids investigated were carbon dioxide, nitrous oxide and chlorodifluoromethane with and without the following modifiers: toluene, methanol, pyridine, triethylamine and pyrrolidine. The objectives of this work were (a) to investigate the effect of SFE temperature on extraction recovery, (b) to compare the results with those obtained by Soxhlet extraction and (c) to assess the type of interactions between the soil and the insecticide, based on the nature of the modified and unmodified supercritical fluid. Of particular concern in this paper is the classification of the type of interactions most likely to be occurring. Both the supercritical fluids and modifiers were assessed in terms of their polarity and potential solvent interactions (modifiers only). The main features of this are summarised in Table 2 and Table 3. The soil sample was collected 25 days after spraying of the pirimicarb at a dose of 1 kg per ha. The soil sample was then freeze-dried, crushed and sieved through a 120  $\mu\text{m}$  filter prior to storage at  $-21^\circ\text{C}$ . Despite the solubility of pirimicarb in supercritical  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CHClF}_2$ , all proved to be ineffective at quantitatively extracting the insecticide from the soil over the range 50 to  $100^\circ\text{C}$  at 30 MPa. The addition of a basic modifier e.g. triethylamine or pyridine to a supercritical  $\text{CO}_2$  proved to be the ideal combination for the efficient extraction ( $100^\circ\text{C}$ , 30 MPa and 20 ml of supercritical  $\text{CO}_2$  with 5% triethylamine) of pirimicarb from the contaminated soil. An extraction mechanism was suggested. As only basic modifiers were effectual it was suggested that a specific competition between the pirimicarb and the modifier for the same sites on the soil matrix was the prevailing factor for quantitative SFE. Furthermore, the dominant binding mechanism to the soil matrix was postulated to be due to acidic sites present on the soil. Experimental results also suggested that SFE offers better precision, shorter

Table 2  
Properties of supercritical fluids evaluated<sup>a</sup>

Compound	Critical temperature/ $^\circ\text{C}$	Critical pressure/MPa	Dipolar moment/D	Solubility parameter ( $\text{cal}/\text{cm}^3$ ) <sup>0.5</sup>
$\text{CO}_2$	31.1	7.38	0	10.8
$\text{N}_2\text{O}$	36.6	7.24	0.2	10.6
$\text{CHClF}_2$	96.3	4.97	1.4	8.8

<sup>a</sup> From [59].

Table 3  
Physical properties of modifiers used<sup>a</sup>

Compound	Acid/base, p <i>K</i> <sub>a</sub>	Dipolar moment/D	Potential solvent interactions of modifiers
Methanol	16	1.70–2.87	Induced dipole, hydrogen bonding
Toluene	NA	0.36–0.43	Induced dipole, dispersion, $\pi$ – $\pi$
Pyridine	5.2	2.19	Induced dipole, dispersion, $\pi$ – $\pi$ , acid–base
Triethylamine	11.01	0.66	Induced dipole, acid–base
Pyrrolidine	11.3	NA	Induced dipole, acid–base

<sup>a</sup> From [59].

NA = not available.

analysis time and a reduction in solvent usage by a factor of 10, compared with Soxhlet extraction.

The following points have been concluded as important for the extraction of pesticides from soils

1. Soil characteristics, e.g. organic matter, should be experimentally determined or estimated using appropriate models, and their relationship to pesticide recovery determined. This may allow the development of appropriate extraction models.
2. The soil–water partition coefficient ( $K_d$ ) is indicative of the adsorption of pesticides on soil. Knowledge of  $K_d$  may allow appropriate extraction solvents to be selected.
3. The solubility of the pesticide in supercritical CO<sub>2</sub> is important.
4. Solubility in supercritical CO<sub>2</sub> does not guarantee quantitative extraction.
5. Modified supercritical fluids are more likely to overcome matrix effects. The type of modifier to be used should be evaluated; mixed modifiers may be needed.
6. Problems may be encountered due to the extraction of co-extractives when using modified supercritical fluids. The use of alternative chromatographic detection systems may be required.
7. High pressure leads to high recovery.
8. Soils may be washed with a non-polar wash to remove humic substances prior to SFE (care needs to be taken that analytes of interest are not lost).
9. Soil organic matter appears to be an important parameter (deleteriously) affecting analyte recovery.

10. In situ derivatization may lead to improved recovery.

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