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**EXTRACTION OF PESTICIDE RESIDUES FROM SOILS
USING DIFFERENT METHODS**

by

Peter N. Githira, M.Sc. M.Ed.

**A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy**

Department of Chemistry

Carleton University

Ottawa, Ontario

March, 1995

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USING DIFFERENT METHODS"**

submitted by

Peter N. Githira, M.Sc. M.Ed.

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University

March, 1995

ABSTRACT

The effectiveness of extraction of lindane, DDT and dieldrin from two soils was compared using Soxhlet extraction, Sonication, High Temperature Distillation (HTD) and Supercritical Fluid Extraction (SFE). The work described in this thesis was carried out mainly with two soils from Kenya which were field contaminated with the pesticides. However, extraction from both spiked and unspiked materials was investigated.

It was found that the optimum parameters for spiked materials were not always optimum for field contaminated matrices. The contact time between the analyte and the matrix apparently produced stronger interactive forces which required harsher conditions than those encountered with freshly spiked matrices. Despite extensive reported use of spiked analytes in method optimization, the results thus obtained often overestimate what is practical for field contaminated soils. Results obtained with the standard Soxhlet method indicated that it is necessary to continue the extraction for a very long period of time. The choice of extraction fluid is also important, as was found in the extraction of the acidic pesticides used in the preliminary experiments.

Extraction with ultrasound was found more effective at low temperatures and for short exposure times. The results

also revealed that ultrasound is more effective with less volatile pesticides e.g. DDT due to volatilization losses.

Experiments done with SFE showed that the extraction process from any matrix is governed by many parameters such as extraction time, temperature and the use of an appropriate collection system and solvent. Methanol and acetone were effective collection solvents relative to dichloromethane which was plagued by restrictor clogging. Although supercritical CO₂ is an effective extractant for the non-polar organochlorine pesticides, higher recoveries were obtained when methanol modified supercritical CO₂ at 125°C was used. The high temperature might enhance the desorption process, while the modifier could displace the analytes or simultaneously modify the matrix structure.

High flow rates were found necessary for effective HTD. Despite its non-selectivity, HTD at an appropriately set temperature was found simple and effective. HTD extracted an extra amount ($\approx$ 1-2%) of DDT and lindane from soil KE#2 samples that had been previously extracted with one of the other three methods.

The results obtained with this work revealed that none of the methods could be termed as the ultimate extraction method. Although there is much optimism that SFE will replace conventional methods in the future, each method can be made quite effective by optimizing the controlling factors. Aspects such as cost of equipment, time required

and wastes generated are briefly considered for the four methods.

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DEDICATION

This work is dedicated to my wife Anne Njeri Njuguna and our lovely children, Caroline, George, Eric, David and Vionnah. Thank you very much for your continuous and unending support during my studies.

I salute you all and may God bless you.

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1 INTRODUCTION

Protection of plants by spraying with pesticides coupled with seed and fertilizer applications constitute a vital factor in increasing food production. Pesticides are also of importance in helping to eliminate disease vectors such as insects. Pesticides must be effective and safe to use where they are needed as control agents for hitherto intractable pest problems. They must persist long enough to control the pest, but preferably no longer. Highly persistent materials, however efficient (e.g. DDT), may ultimately prove undesirable because of the risks resulting from residues in the environment. This type of environmental pollution may have adverse effects on humans and/or other species.

During the application of a pesticide to crops, it comes into contact with plants, soils, and occasionally with water. It is essential, therefore, to consider the fate of various pesticides in plants and soils with a particular emphasis on the analysis of soils and crops for residues. Extraction and quantitation of these residues are important aspects in determining the impact of pesticides on the ecology of the land and in designing toxicological studies.

The quantitative determination of these pesticides in various matrices falls in the realm of analytical chemists.

Different extraction techniques are used by them in quantification of these pollutants. There are many extraction methods, including the standard Soxhlet method, thermal desorption, sonication, microwave oven extraction, and a more recently introduced technique called supercritical fluid extraction (SFE). Past investigations on extraction of organic compounds by Junk and Richards (1986) have shown that there is neither a single extraction technique nor a single solvent that is effective for the efficient extraction of all organic compounds from all types of matrices.

The Soxhlet extraction method has been in use for a long time. During this period, the pros and cons of this process have been evaluated. Soxhlet extraction takes a long time, and the use of large volumes of solvents in the method has had adverse effects on the environment. This is why research organizations like the EPA have looked to supercritical fluid extraction as a potentially advantageous method.

Although it has been alleged that supercritical fluids have better extraction efficiencies, results are far from being conclusive. This work was undertaken to investigate the advantages and disadvantages of different extraction methods.

The methods that were compared were Soxhlet, sonication, high temperature distillation (HTD), which is

often referred as thermal desorption, and supercritical fluid extraction (SFE).

In the following chapter, the four methods that were used in this work will be discussed with respect to their merits and demerits as reported in the literature. Special emphasis is placed on a review of SFE, as this seems to have the potential to replace conventional methods for extraction. At the end (section 2.6) there is a summary of reports which compare the effectiveness of these methods.

2 EXTRACTION METHODS

2.1 Solvent Extraction

Extraction procedures constitute an important step in the scheme of analysis. These procedures are of two types: the removal of an active ingredient from a heterogeneous mixture, and the removal of an undesirable material from an impure product. Separation of the active ingredient from a crude drug mixture is an example of the first type, while the preparation of a derivative and its subsequent purification is an example of the second type.

Steinwandter (1985) has pointed out that the extractability of lindane isomers used as pesticides from various matrices depends very strongly on solvent or solvent mixtures, and on the period of presoaking with water. Grosjean (1986) studied the determination of organic carbon in atmospheric aerosols and noted that the extraction efficiency of a solvent depends on various types of solute-solvent interactions. These interactions include dipole orientation, dispersion forces, and hydrogen bonding for either proton donor or proton acceptor solvents. He further pointed out that the efficiency of the extraction process depends on solute-solvent interactions combined with the ability of the solvent to desorb the organics from the matrix.

Others have also indicated that the solvent plays a very important part as a competitor for the active sites on

the matrix (Burk, 1990). If the matrix has a higher attraction for the solvent molecules than for the solute molecules, then they are preferentially attracted to the matrix and in so doing, the solute molecules are desorbed from the matrix.

Snyder (1974), showed that the extraction efficiency depends on the overall polarity of the solvent, which is the net effect of the various solvent-solute interactions. He further noted that solvent extraction efficiencies correlate well with polarity parameters, but a single solvent is usually unable to extract all the organics. Binary extraction solvents, or successive extractions using a polar and a non-polar solvent, were much more efficient.

Analytical methods for determination of PAHs in particulate matter invariably have involved extraction of the PAHs into an appropriate solvent prior to analysis. The most widely used procedures have been Soxhlet (sec.2.1.1) and ultrasonic (sec.2.2) extractions of samples with 50-250 mL of low boiling solvents such as benzene, toluene and dimethylbenzene. Extraction times used have varied from a few hours to days in some cases (Bjorseth, 1977).

After extraction, the solvents are evaporated and the residues are redissolved in 1-2 mL of an appropriate solvent before analysis by means of chromatography. Once the analytes are isolated, they are identified using various techniques like mass spectrometry (Broddin et al., 1977).

Solvent extractions are limited by the incomplete extractions of the analytes. Fassel et al.(1983) have indicated that the many conflicting reports on the effectiveness of the various extraction methods imply that the methods are all suspect. Many extractions are lengthy in duration; this limits the number of samples that can be effectively analyzed in one single day. Improved methods should be governed by the following criteria:

(i) They should have high extraction efficiency of a wide range of organic and inorganic compounds and should also cover a wide range of molecular weights.

(ii) It should be feasible to carry out extraction from small size samples, e.g. 10 mg.

(iii) The methods used should have short extraction durations so as to increase the number of samples, thereby increasing the overall efficiency of the system.

(iv) Small solvent volumes should be used in order to reduce solvent wastage in an endeavour to increase the profit margin of the whole operation.

(v) The methods should use solvents that are compatible with the available analytical techniques.

Direct analysis of the samples without many concentration steps would be an added advantage, as it minimizes the losses encountered when one has to carry out intermediate concentration steps.

Afghan et al.(1986) compared the different extraction

methods used in ultratrace analysis of dioxins and related halogen compounds. These authors reported that a considerable amount of work had been done in enhancing the extraction processes for ultratrace levels from a variety of samples. They indicated that there was a wide variation in the extraction efficiency and the ability of certain techniques to quantitatively extract dioxins. The choice of an extraction technique was found to depend upon the type of sample and the amount of interfering material in the sample.

Coover et al.(1987) have also indicated that extraction efficiencies vary with the concentration of the analyte; hence there is a need to investigate recovery efficiencies over the entire range of concentrations expected. These authors compared extraction efficiencies of the Soxhlet and Tisumizer techniques and found that the Soxhlet method was more efficient than the latter.

In determining the sample weight in the analyzed extract however, the water in the sample extract and therefore in the original sample must be known. The above problem can be overcome if the extraction and partition steps can be combined into one step by saturating the extraction solvents with sodium chloride and simultaneously driving away the water by dichloromethane or hexane.

The basis of the technique (Steinwandter, 1985) is the use of an electrolyte (salting out effect) for the partitioning of the pesticides into the organic phase. The

following steps are deemed necessary in the extraction process.

- (i) mixing of the sample with the appropriate solvent,
- (ii) filtration of the sample mixture,
- (iii) partitioning of the pesticides into the organic phase by addition of sodium chloride,
- (iv) removal of water from the organic phase by use of appropriate organic solvents,
- (v) drying of the organic phase with an appropriate drying agent,
- (vi) evaporation of the organic phase as a concentration step prior to analysis.

Forbes (1987) noted that most procedures for pesticide residue analysis involve sample preparation, extraction, purification of the extract, quantitative determination and confirmation of the identity. Although the aim of extraction is to isolate the analyte of interest quantitatively from the matrix, many co-extracted materials are usually present in the crude sample extract. These co-extractives can interfere directly with the determination of the pesticide residue by masking analyte peaks on a chromatogram, or indirectly by leading to the rapid deterioration of chromatographic columns and detectors. Consequently, it is usually necessary to purify the crude extract before the determination steps.

2.2 Soxhlet Extraction

The Soxhlet extraction method has been for many years the standard method of extraction of various components from solid matrices. It is a form of liquid-solid extraction which entails the dissolving of one or more components from a solid matrix by simple solution or by formation of a soluble form through a chemical reaction. The process can be achieved in form of leaching, washing or by diffusion.

The leaching process involves the contacting of a liquid and a solid and establishing an equilibrium between the soluble component in the liquid with the adsorbed component on the matrix under investigation (see figure 2.2.1, p 14). In the washing process, the solid is crushed to break the cell walls, permitting the desired product to be washed from the matrix, e.g. as found in the sugar industry. In the diffusional process on the other hand, the product diffuses across the denatured cell walls and is washed out of the solid. No crushing of the matrix is involved. In all the above cases, particle size is vital since extraction is a direct function of the available surface area.

The processes are fast enough in extracting cellular materials due to the fact that the denatured cells expose more surface area to the solvent. In the case of ore extraction, porosity and pore size distribution greatly affect the rate of extraction. The solvent must flow into

the pores to allow the solute to diffuse out to the surface.

The rate of extraction can involve both mass transfer and homogeneous chemical reactions taking place in either or both phases. Mass transfer rates are rapid and the overall extraction equilibrium should occur within a minute or two except when one or more of the chemical reactions are sluggish. The rate of a Soxhlet extraction is difficult to determine due to inability to maintain a constant cycle time. The procedures seldom specify the solvent cycle, even though it is deemed to have a pronounced effect on the recovery of the analytes of interest.

The time for effective extraction has not been agreed upon by the scientific community. Some extractions have been run for four hours while others have been run for a minimum of twenty hours. During the extraction, the removal of the desorbed molecules from the surface or interstices of matrix particles is determined by solvation of the desorbed particles from the adsorption sites.

Klein et al.(1959) found that complete recovery of DDT was only feasible after a prolonged extraction period. These authors found that they could extract 89% of the DDT on spinach leaves after a 24 hour extraction period with ethyl ether. The pesticide could not be removed fully when the operation was repeated for 9 hours with benzene followed by 5 hours with a mixture of benzene and isopropyl alcohol.

Soxhlet extractions can produce co-extractives which

can be as much as 10 times greater than those obtained from 19 hour contact time by normal blending (Klein, 1958). These co-extractives can interfere directly with the determination of the pesticide residues through masking analyte peaks on a chromatogram. They can also interfere indirectly by leading to the rapid deterioration of chromatographic columns and detectors. The crude extracts are normally cleaned before the analysis.

In order to minimize possible contamination, it is essential that the solvents used be of high purity. Many extractions have been carried out with the use of pre-extracted thimbles as a precautionary measure to avoid contamination. Nowicki et al. (1979) reported that glass thimbles offer less contamination than cellulose thimbles, but they can cause cross contamination if not properly cleaned after every extraction. Schwartz (1978) studied glass wool as a source of artifacts in chromatography and found that there was need to pretreat the glass wool used in Soxhlet with methylene chloride for 24 hours.

Jenkins (1994) cautioned that thermally labile compounds can be a problem with the Soxhlet method because the extract is maintained at the boiling point of the solution in the receiver for an extended period of time. Other limitations of the Soxhlet method involve low recoveries of analytes which are encountered in the extraction process. The use of large volumes of solvents

can also be a hazard to laboratory personnel and the disposal of spent solvent can be expensive.

A number of concentration steps are always involved before final analysis, and these add more time to the extraction process and increase the probability of greater sample loss. Loss of the analytes of interest due to evaporation or due to adsorption on glassware also occurs. This lowers the accuracy of the results obtained. Some of the above difficulties could be minimized by working at low temperatures, but this increases the time necessary for efficient extraction. It would also require vacuum apparatus and this would increase the already high costs of the entire Soxhlet operation.

Although the Soxhlet method dates back to 1930s when Soxhlet discovered it, the procedure needs critical evaluation as a result of the findings that many compounds are unstable in it. Tetryl (N-methyl-N,2,4,6-tetranitro-aniline, a common component of USA military explosives) has been found to be unstable in Soxhlet extraction. Research done by Harvey et al.(1992) revealed the formation of a distinct greenish hue, indicating that tetryl had undergone decomposition to new products during the extraction process using Soxhlet method. The chromatograms obtained by these authors on tetryl extracts using GC-MS showed the presence of new products.

Due to the shortcomings of the Soxhlet method, the

Soxtec method was devised as a replacement. This technique is based on the Soxhlet principle and was developed to facilitate and accelerate ether extraction without sacrificing accuracy and reproducibility.

The Soxtec consists of a multiple unit for simultaneous extraction of six samples and complete recovery of the solvent at the end of the operation (see figure 2.2.1, P 14). It has also a heating unit which is separate from the extraction module and provides maximum safety. The extraction procedure in the Soxtec consists of three stages which incorporate:

- (i) initial extraction with the boiling solvent in which the sample is immersed,
- (ii) final extraction with a condensing solvent (typical Soxhlet extraction), in which the extraction thimbles containing the sample are not immersed in the solvent and are washed back by condensation. This facilitates solvent recovery at the end of the extraction and avoids the wastage characteristic of the Soxhlet method.
- (iii) solvent recovery. At the end of the extraction, the analytes are retained in the extraction cup, the matrix remains in the thimble, while the solvent is recovered inside the condensor, ready for a new extraction cycle. For major components, such as those determined during proximate analysis, quantitation can be based directly on the weight

of the extraction cup plus extracted component or indirectly, on the weight lost by the thimble plus cup. Figure 2.2.1 shows the Soxhlet and the Soxtec apparatus in stage (ii) of operation.

Figure 2.2.1 Soxhlet and Soxtec Apparatus

2.3 Use of Ultrasound in Extractions

Ultrasound has become quite common for accelerating chemical reactions and for cleaning processes. Such uses of ultrasound are possible because of the phenomenon of cavitation. The cavitation process involves the formation, growth and implosive collapse of the bubbles. The collapsing of cavitation bubbles generates extreme transient conditions of temperature which can induce high energy chemical reactions. Various research groups have recorded cavitation temperatures $>5000\text{K}$ and pressures $>500\text{ atm}$ (Flint and Suslick, 1991; Suslick, 1986). The high temperatures and pressures are generated within a timescale of a microsecond (Mason and Lorimer, 1988). Although these conditions are very short lived, they may initiate formation of reactive species in solution such as $\text{OH}\cdot$, $\text{HO}_2\cdot$, and $\text{H}\cdot$ (Henglein, 1987).

Chemical ultrasonics started in 1927 when Loomis and Richards reported the acceleration of conventional reactions and redox processes by ultrasound. In recent years, attention has been directed to the use and application of ultrasonic energy to problems associated with water and soil pollution, especially in removing toxic organic compounds from contaminated environmental matrices. Ultrasound is believed to completely destroy or convert the toxic organics to non-hazardous materials, and not simply to convert them to another form (Jiann et al., 1992).

The many chemical effects of ultrasound are associated with cavitation, although there is uncertainty as to how the effects arise. Most research results can be explained through a "hot spot" theory, as the high temperatures and pressures are produced during sonication. However, Margulis et al.(1985) have shown that there are some phenomena which cannot be explained completely by the hot spot theory and have coined an alternative "electrical theory". This theory considers the charge distribution due to dipoles in a solvent and their distribution around the cavitation bubble. These authors showed that during bubble formation and subsequent collapse, enormous electrical field gradients of the order of 10^{11} V m^{-1} are possibly generated, and these are sufficiently high to cause bond breakage accompanied by increase in the chemical activity of the system.

Three zones in a cavitation system have been identified as possible places for chemical effects. These are:

- (i) the bulk liquid, in which no primary sonochemical activity takes place, although subsequent reactions with ultrasonically generated intermediates may occur;
- (ii) the centre of the bubble where extreme conditions cause reactions in the vapor form;
- (iii) the interfacial region, where there are large gradients of temperature and pressure, and also extremely high shear gradients due to shock waves and motion of solvent molecules around the collapsing bubble.

There are many factors which affect the cavitation process. Some of these include the type of dissolved gas used, the presence of air in the system, temperature effects, intensity and frequency of the ultrasound used. Some researchers have shown that at constant intensity, cavitation and hence the sonochemical effects, decrease at higher frequencies. This might be due to the fact that the bubble has less time to grow and collapse at higher frequencies, resulting in lower final temperatures and pressures. The effect of any shock waves are therefore lessened. Recent work done in our laboratory by Entezari and Kruus (1994) has however shown that a higher frequency actually increases the sonochemical effects in the reaction involving the dissociation water.

Solvents with high densities, surface tensions and viscosities have a higher threshold for cavitation, but more harsh conditions once cavitation sets in. Solvents with high vapor pressures lead to relatively high pressures in the bubble and also "cushion" the collapse. In most cases, high sonochemical activity is obtained in solvents with low vapor pressure. This means that it is often advantageous to use low temperatures for extraction by sonication.

At solid-liquid surfaces, surface tension and viscosities can induce the formation of jet streams and shock waves which are thought to be responsible for localized erosion. According to Lauterborn et al. (1984) the

jet is usually fragmented into a cluster of many small bubbles whose direction depends on shock direction, shock strength and interaction between the bubbles and a solid surface. The jet is set into a turbulent motion with locally high velocities. The impact of these high velocities on a solid surface can enhance the extraction process. The liquid around the solid is vigorously whirled around in a turbulent motion. The resulting chaotic motion might be the major factor responsible for effective disruption of cells and also for high extraction efficiency in ultrasound.

The acceleration of solid particles during the erosion has also been observed. The resultant particle collisions are responsible for inducing dramatic changes on the surface morphology, composition and even at times altering the activity of the surface (Suslick, 1989). These factors have been found to be responsible for the enhancement of the efficiency of reactions in heterogeneous systems by ultrasound. Sonication also causes enhanced macroscopic motion which leads to very efficient mass transfer and mixing. The enhanced effectiveness could be due to an increase in mass transfer (Repic, 1982); increase in the reactive surface area (Lindley, 1986) and removal of passive coatings which hinder the cleaning process (Suslick, 1989).

The removal of contaminations from surfaces was studied by Rozenburg in 1960 by means of high speed photography and

led to proposition of two mechanisms for the removal of contaminant films. The first mechanism involved the partial tearing of a film from the surface by the collapse of the bubble while the second one involves the penetration of small bubbles into all pores and gaps between the contaminant layer and the surface.

Chendke and Fogler (1975) have reviewed the use of ultrasound in extraction and Skauen reviewed the degradation due to ultrasound in 1971. These authors suggested that the mechanisms responsible for the increase in extraction rates are cavitation, subsequent cell disruption at lower ultrasonic frequencies and microstreaming around the solute boundary at higher frequencies.

Ultrasound was used in our work to extract pesticide residues from different soil matrices with variable degrees of success. The results obtained are contained in the latter part of this work and is reported in sections 5.2.1 to 5.2.3.

2.4 Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) is a technique that employs a fluid phase which has properties intermediate between those of a gas and those of a liquid (see figure 2.4.1) to effect the solubilization of solutes. The unique properties of supercritical fluids (SFs) offer certain advantages in the extraction processes relative to classical extraction methods. Surfaces are completely made wet by SFs as there is only one fluid phase. Supercritical fluids have lower viscosities and higher diffusivities, facilitating more efficient mass transfer of solutes from sample matrices. These fluids have adjustable solvent power which is achieved through mechanical compression, a property which not only allows selective extraction but also facilitates the concentration of the analytes after extraction.

Until recently, SFE has been used mainly for large scale processing operations (e.g., decaffeination of coffee and extraction of hops); but for a decade or so the use of SFE for analytical applications has drawn considerable interest. The potential for SFE in analytical applications comes from the unique properties of supercritical fluids.

SFE has had an extraordinary growth in food processing and analysis. In the extraction of cholesterol from foods, the process is always complicated by the presence of lipids, oils and fats (Gere, 1992). These interfering compounds lead to long-term retention problems which complicate

identification and quantitation when injected into a chromatographic column. SFE can however selectively extract cholesterol and leave the interfering compounds in the matrix. SFE has also been shown to be rapid, suitable for thermally labile compounds and more selective than classical methods such as Soxhlet and solid/liquid extractions (Janda, 1989; Hawthorne, 1991).

SFE often offers a cost effective alternative to conventional liquid extraction, Soxhlet extraction and even steam distillation. The behavior of a pure compound when its pressure and temperature are altered is represented with the help of figure 2.4.1.

Figure 2.4.1 Pressure-Temperature Phase Diagram of a Pure Compound (Carbon Dioxide)

Current trends with regard to theory and models for SFE involve both thermodynamic (solvation, partitioning and diffusion) and kinetic contributions. Bartle et al.(1992) proposed a model for dynamic SFE based on the effect of solubility on extraction kinetics, as well as solute diffusion out of the sample matrix. Pawliszyn (1993), presented a kinetic model of SFE which includes several factors (e.g. desorption kinetics, swelling, analyte diffusion in the organic component of the sample and fluid-matrix distribution coefficient) that could potentially contribute to slow extraction rates.

The use of supercritical fluids in analytical chemistry has had a tremendous growth in recent years. More and more scientific research groups are realizing the favorable aspects of using supercritical fluids. The large interest in SFE may be due to its simplicity in the extraction process and also the ease with which the analyses are carried out. Analyses are normally without concentration steps in contrast to other methods. SFE apparently has an edge in the analytical laboratory, and the recent EPA approval of one method using SFE in 1993 is an indication that SFE will eventually be the method of choice in most laboratories.

2.4.1 Advantages of Supercritical Fluids

The potential advantages of supercritical fluids are due to the physical properties of a solvent at temperatures and pressures above its critical point. In this region, a small increase of pressure induces a large increase in density (Rosset et al., 1986; see figure 2.4.1). The viscosity of supercritical fluids is lower than that of liquids and the diffusion coefficient is about 100 times greater than that of liquids. These properties allow a more rapid mass transfer of solutes than is normally obtained in liquids. At high densities, molecular interactions are higher due to shorter intermolecular distances, and solvating properties can approach those in the liquid phase. Table 2.4.1.1 shows some physical parameters of liquids, gases and supercritical fluids for comparison.

Table 2.4.1.1 Physico-Chemical Constants of Supercritical Fluids Compared to Liquids and Gases (Bruno et al.1991)

Parameter	Gas (1 atm)	Supercritical Fluid	Liquid
Density (g cm ⁻³)	(0.6-2) · 10 ⁻³	0.2-0.90	1
Viscosity (cp)	(1-3) · 10 ⁻²	10 ⁻² -10 ⁻¹	10
Diffusion Coeff.	(1-4) · 10 ⁻¹	<10 ⁻⁵	10 ⁻⁴ -10 ⁻³

The advantages that supercritical fluids have over

conventional extraction methods have been applied to many different operations including:

(i) Relatively non-volatile compounds can be dissolved by supercritical fluids.

(ii) The properties of supercritical fluid media can be varied within limits by means of pressure and temperature changes.

(iii) Separation of the extracted materials from the supercritical fluids can be achieved (wholly or partially) by altering the pressure and/or temperature of the fluid.

(iv) Fractionation of different components from the same matrix may be feasible.

A further advantage in SFE of solids is that there is no problem of the fluid in wetting the solid, i.e. in reaching crevices where contaminants may be adsorbed. There is only one fluid phase above the critical point. The fluid is not kept from the solid surface by a gaseous phase as can be the case with liquid extraction.

The efficiency of extraction depends on temperature, pressure, contact time between the extraction fluid and the matrix, the ability of the supercritical fluid to penetrate the matrix, and the solubility of the analyte of interest in the extracting fluid. Many solvents have been used in supercritical fluid extractions. These solvents should have easily attainable critical parameters if they are to be effectively utilized in the extraction process. Table

2.4.1.2 summarizes the properties of some common solvents that have been used in SFE.

Table 2.4.1.2 Critical Property Data for Commonly Used Supercritical Fluid Solvents (Bartle, 1991)

Substance	T_c (K)	P_c (MPa)	ρ_c (g cm ⁻³)
Methane	190.6	4.60	0.162
Ethylene	282.4	5.03	0.218
Carbon dioxide	304.2	7.38	0.468
Propane	369.8	4.24	0.217
Ammonia	405.6	11.30	0.235
Water	647.30	22.00	0.322
Methanol	512.6	8.09	0.272
Nitrous oxide	309.5	7.14	0.457
Ethane	305.4	4.88	0.203

(Note: 1 MPa = 9.865 atm)

ρ_c = Critical density

King (1989) suggested that there are four basic parameters which are extremely useful in understanding solute behavior in compressed gas media. These are:

(i) The pressure or density at which the desired analyte becomes soluble or miscible with the supercritical fluid "the threshold pressure". Control of solubility via applied pressure might allow stepwise extraction of various components of a compound.

(ii) The condition when maximum solubility of the solute

is attained.

(iii) The fractionation pressure range, which is the region between the threshold pressure and the solubility maximum pressure; and when applicable,

(iv) physical and chemical properties of the analytes.

The great interest in PCBs and PAHs with respect to environmental pollution has aroused interest from many research groups. Schantz and Chester (1986), and Hawthorne and Miller (1986), developed SFE methods for extracting PCBs and PAHs from environmental solids. Other pollutants which have been extracted with the use of supercritical carbon dioxide or supercritical nitrous oxide from environmental solids include PCDDs, PCDFs and triazine herbicides. Sugiyama and Saito (1988) used an off-line SFE-GC to investigate the components of lemon peel oil. Ma et al.(1991), have investigated SFE of Chinese Herbal medicines and found good extraction efficiency and selectivity, especially for the higher molecular weight components.

2.4.2 Solubility of Solutes in Supercritical Fluids

Dadge et al.(1986), reported that the solubility of solutes in supercritical carbon dioxide depends primarily on solvent density, with the actual temperature above or below the critical value of 31.04°C being irrelevant. The solvent density of a supercritical fluid can vary considerably with temperature and pressure. Schmitt and Reid (1986) however, have reported that there was no significant increase in solubility of stearic acid when the pressure was raised from 140 to 370 atm. The solubility was higher at the lower pressure but they could not think of a feasible explanation of this behavior.

Broglie (1982) also noted that improvement in product quality or purity can be obtained with conditions that are actually below those which would result in highest solubility and yield. Olive-oil extracts obtained at maximum solubility were found to be darker and less appealing than those extracted at slightly lower conditions.

The solubility of a solute in a supercritical fluid as a function of temperature and pressure is illustrated with figure 2.4.2.1 which shows the solubility of naphthalene in ethene (Bruno and Ely, 1991). The solubility of a solute is expressed in terms of mole fraction rather than mol L⁻¹.

Figure 2.4.2.1. Variation of Solubility with Temperature and Pressure

x = Mole fraction of solute

The solute exhibits a "threshold pressure" above which solubility increases significantly (Giddings et al., 1986). The region of maximum rate of increase of solubility with pressure is near the critical pressure, where the rate of increase of density with pressure is also high. This is because the relationship between log solubility and density is approximately linear in this range (Smith et al., 1986).

In contrast to the above, if the solute volatility is low and at densities less than or near the critical density, increasing temperature (pressure constant) will result in a decrease in the solubility due to a decrease in density.

Supercritical gases such as carbon dioxide and ethane are not "super solvents" for all substances (Stahl et al., 1978). On the contrary, they are relatively poor solvents in comparison with many liquids. However, supercritical fluids have a very selective and highly pressure dependent solvent power for substances of medium molecular weight and relatively low polarity. This variable but limited solvent power is an important advantage. Without it, no selective extraction of such compounds as caffeine from coffee beans or nicotine from tobacco can be achieved.

The relative solvent power of a supercritical fluid can be approximated by the Hildebrand solubility parameter (designated by the Greek letter δ). It can be estimated as $\delta \approx (H_v - RT)/V_m^{1/2}$ in ordinary liquid solvents. In supercritical fluids, it can be estimated as:

$$\delta = 1.25\sqrt{p_c(\rho_r/\rho_{liq})}$$

where p_c is the critical pressure of the fluid, ρ_r is the reduced density of the supercritical fluid and ρ_{liq} is the reduced density of the near liquid fluid at conditions approaching infinite compression (Giddings et al., 1968).

The solubility parameters of CO_2 under various pressures are compared with those of other solvents in figure 2.4.2.2. Under the conditions used in SFE (sec. 5.3) the SFCO_2 has a solubility parameter close to those of cyclohexane and hexane. Methanol, a common co-solvent has a significantly higher solvating power around 14.5 (sec.5.3.4 and 5.3.5)

Extraction pressures between 80-300 bar have been found necessary to achieve adequate densities. Although the occurrence of further dissolution phenomena at higher pressures cannot be excluded, higher pressures are often avoided for economic reasons. In the extraction of hops, Hubert et al.(1973, 1978) have indicated that there are several combinations of extraction conditions that can be used to obtain hop and spice extracts.

In the reduced density and reduced pressure diagram of a supercritical fluid (figure 2.4.2.3), it is found that important density variations are induced by small pressure changes when constant temperature is maintained. The dotted lines in figure 2.4.2.1 show the relevant range for SFE purposes. In this dotted area, the compressibility is

normally high and at the critical point, the compressibility increases to infinity (IUPAC, 1976).

Figure 2.4.2.2 Solubility Parameter Scale for Liquids and Supercritical Fluids Relative to Various Densities of Carbon Dioxide

Figure 2.4.2.3 Reduced Pressure - Reduced Density Diagram
for Carbon Dioxide
(Adapted from Burk, 1990)

2.4.3 The Use of Supercritical Fluids in Pesticide Residue Removal from Soils

Several investigations have highlighted the dependence of chlorinated hydrocarbon adsorption on soils on organic matter content (Hague et al. 1974, Liechtenstein et al. 1977). Brady et al. (1987), concluded that the desorption rates of PCBs, DDT and toxaphenes were proportional to their solubilities in the fluid phase. The solubility of a compound of low volatility in a supercritical fluid near its critical point is orders of magnitude higher than the ideal solubility (the vapor pressure).

Several supercritical fluids have been evaluated for the extraction of pesticide residues from soils. Spiteller (1982) and Spiteller and Ashauer (1985) used a number of solvent mixtures in supercritical states for organic matter extraction. These authors assessed the potential for SFE to remove specific components from the soil. They concluded that SFE had considerable potential as an extractant for humic acids under relatively mild conditions.

Supercritical carbon dioxide has been used in the removal of trace amounts of PCBs from sediment and PAHs from urban particulate matter (Schantz and Chester, 1986). Hawthorne and Miller (1989) also studied these compounds and showed that they could be only poorly extracted. However, non-polar insecticides like lindane and DDT could be selectively extracted from the soil in the presence of a small amount of methanol.

In the extraction of triazine herbicides from solid matrices, Papilloud and Haerdi (1994) found that prolonged SFE extraction times were not beneficial. Due to aerosol formation during depressurization, a certain fraction of the analytes of interest are actually lost into the air. These results are shown with the help of table 2.4.3.1.

Table 2.4.3.1 Comparison of Atrazine/2-Hydroxyatrazine Stripping from Soil

Time (Min)	Atrazine Remaining (%) n=6	2-Hydroxyatrazine (n=6)
30	98±03	98±03
60	98±03	92±05
120	91±05	77±06

Table 2.4.3.1 shows that there are no significant differences between thirty and sixty minute extraction times. However, there are significant losses when extractions are extended for longer periods.

Papilloud (1994) has emphasized the importance of non-polar washing of the matrix prior to extraction in the case of soils. It is likely that the interfering material present in the matrix is partially eliminated before extraction. In the case of spiked materials, the interfering components can be eliminated before or after spiking. The pesticides are deemed to have reduced

interactions with the matrix components, so that their desorption from the matrix sites was thus enhanced.

2.4.4 Sample-Matrix Interactions in SFE

The nature of a sample matrix can have profound effects on the results which are obtained during supercritical fluid extraction. King et al.(1990) have indicated that it is unfortunate that a knowledge of analyte solubilities in supercritical fluids does not always allow a prediction of the effectiveness of SFE. Extraction of real sample matrices should be carried out experimentally, rather than extrapolating from the results obtained with spiked neat analytes.

Studies carried out by Snyder et al.(1984) showed that the geometric size of the matrix particles influenced the speed and the completeness of an SFE process. Enhancement of matrix porosity should promote a more efficient and rapid extraction in SFE as in solid-liquid extractions. Caution should be exercised however in that very fine matrix particles will hinder the extraction efficiency due to restrictor clogging. Fine grinding of the matrix also can result in large pressure drops within the extraction vessel.

Another important parameter that influences the extraction efficiency in SFE is the amount of moisture present in the matrix. The presence of water has been found to reduce the extraction efficiency in SFE in some cases while in other cases, the presence of water increased the extraction efficiency of the extraction process. King et al.(1989) showed that the removal of water had dramatic

effects on the recovery of lipid moieties from meat products. Similar trends have been highlighted by Yamaguchi et al.(1986) and Ramsey et al.(1989).

In other cases the water behaved as a co-solvent and enhanced the extraction process. Brady and his coworkers (1987) concluded from their work that the desorption of a compound from soils is controlled by the water present, their physical and chemical properties, and also soil structure and capillary condensation.

The rate of removal of an analyte from a matrix is dependent on the solubility in the fluid and also on its ability to diffuse through the matrix to the bulk supercritical fluid. There are four major mass transport mechanisms that facilitate the transport of analyte from the matrix. These are:

- (i) analyte diffusion through the internal volume of the sample,
- (ii) surface desorption of the analyte,
- (iii) diffusion of the analyte from the matrix through a surface boundary layer, and
- (iv) transport in the bulk supercritical fluid phase.

If intraparticle diffusion is the rate determining step, then the rate of extraction with the supercritical fluid is dependent on the matrix particle sizes. Swelling of the matrix when exposed to supercritical fluids facilitates mass transport from the matrix. This has led

polymer scientists to use supercritical fluids in the analysis of polymer additives in the plastics industry (Nicholas and Clifford, 1990).

2.4.5 Use of Modifiers in SFE

Experimental work carried out by Brady et al.(1987) and Dooley et al.(1987) showed conclusively that a high organic content contaminated soil could not be effectively extracted with supercritical carbon dioxide alone. It has however been shown that carbon dioxide is very effective in contaminant removal if the soil is of low organic content as found in some clays. They found out that supercritical carbon dioxide with 5% methanol as co-solvent was very effective in contaminant removal from top soils. The carbon dioxide methanol mixture rapidly removes almost all the contaminants and does not leave solvent behind in the soil. The presence of water in the soil slowed the extraction rate, but they found that the co-solvent mixture was very effective in reducing the extraction times from wet soils.

Many research groups (e.g. Burk, 1990, Levy et al., 1989) are currently working on modifiers in an attempt to answer the following questions:

(i) Do co-solvents increase the extraction efficiency by enhancing the solubility of the contaminant in the supercritical fluid phase ? or

(ii) Do co-solvents increase the extraction efficiency by displacing the contaminants from the matrix adsorption sites or by increasing contaminant diffusivity within the matrix ?

In an attempt to answer the foregoing questions, Dooley et al.(1990) reported that the organic matter content in the

soil has very high influence in the adsorption/desorption process. This could be due to two reasons:

(i) Quartz and many silicates have weak affinity for most organic compounds.

(ii) Many of the iron and aluminum oxides have large amounts of Al^{3+} and Fe^{3+} which adsorb both ionic and some polar non-ionic compounds which are saturated with water. They suggested that the observed extraction rates from wet soils should be fast for a desorption process at equilibrium.

Janda et al. (1989) have studied SFE of s-triazine herbicides from sediment material using supercritical carbon dioxide. The extractions were performed at a supercritical carbon dioxide pressure of 230 bar and a temperature of 48°C . The carbon dioxide density under these conditions is about 0.80 g mL^{-1} . The extraction was done for 30 minutes and during this period, 18 mL of carbon dioxide (as SF) was pumped into the SFE system. Table 2.4.5.1 shows the results obtained using supercritical carbon dioxide alone and supercritical carbon dioxide modified with 5% methanol in the extraction process.

Table 2.4.5.1 Recovery of s-triazine (ppb) with Supercritical Carbon Dioxide without Methanol (B) and with Methanol (C)

Compound	Concentration in Sediment	Percentage Recovery	
		B	C
	(ppb)		
Propazine	60.8	96.4	96.4
Terbutylazine	40.2	91.8	91.8
Atrazine	60.2	86.2	91.0
Simazine	28.0	42.5	92.0
Cynazine	81.2	94.4	90.2

The foregoing results show that there was no major difference in the effectiveness of the two processes except for simazine. They found however that a further addition of a 20% methanol into the SFE cartridge before the extraction increased the extraction efficiency dramatically.

Hill and Hill (1991) carried out derivatization work of reactants in the SFE reaction vessel and found that derivatization could play a significant role in shifting the equilibrium in favour of either the reactants or products. Like modifiers, derivatization can shift the extraction equilibrium either in favor of the solvent or the matrix. It is more likely that the derivatized analyte is less strongly bound to the matrix surface. Covering polar moieties by derivatization enhances solute solubility into the supercritical fluid while at the same time derivatizing the matrix active sites, which subsequently hinders the

resorption of the analytes onto active sites. This keeps the analyte in the extracting solvent which shifts the equilibrium in favor of more solubilization of the solute.

Solute-modifier interactions have been investigated by Rao et al.(1990), who concluded that solubility enhancement was mainly attributed to dipole-dipole, dipole-induced dipole, hydrogen bonding and other forces due to polarity differences, and only to a slight extent by the increased solvent density.

Stahl (1987) demonstrated that supercritical carbon dioxide could extract compounds which were either non-polar or medium polar in character. The introduction of polar groups such as OH and COOH into the molecule makes extraction more difficult or impossible in moderate pressure ranges.

Two alternative methods of adding modifiers to the sample are practised. These include the direct addition of the modifier to the extraction vessel; and the dynamic addition of the modifier into the supercritical fluid, by means of an auxiliary pump.

Practical aspects of using modifiers have been highlighted by Levy et al.(1992) and also by Famhy et al.(1993) who used a high pressure sapphire view cell to observe the swelling of modifier saturated plant materials and clays. They determined a relationship between the extractability and swelling of these materials.

2.4.6 SFE Coupled to Other Procedures

The many advantages of supercritical fluids have opened up new avenues in environmental control. Hawthorne et al. (1992) presented a review on the SFE approach to environmental analysis. This group of researchers also discussed the development and evaluation of off-line and on-line SFE methods for petroleum industry products and wastes in 1993.

SFE is increasingly being applied for the isolation of a wide variety of analytes from complex matrices. Many applications involve the coupling of SFE/SFC for combined extraction and analysis with a single instrument (Andersen et al. 1989). The ability to couple SFE to other analytical techniques is a straight forward procedure and in many cases gives SFE advantage over other extraction methods.

Many research groups have reviewed on-line coupling of SFE with other chromatographic techniques and have highlighted the advantages that coupled on-line systems have over other methods. Some of these advantages include the use of very small sample sizes and the enhancement of sensitivity due to direct introduction of the sample into the gas chromatograph. In direct coupling, the solvent peak is eliminated and the analysis of compounds which may elute with the solvent becomes possible. On-line coupling also reduces sample handling, so that the possibility of sample contamination and sample loss is reduced to a

minimum. Research carried out by Richter et al.(1993), and Levy et al.(1992) confirm the above.

The different types of coupling with other instruments include SFE-GC which involves the extraction, depressurization, venting of the supercritical fluid, collection and focusing of the extract onto a GC column for analysis. This coupling process provides a rapid and convenient method for the analysis of air and water samples and is a convenient method for the analysis of trace components. The SFE-SFC system includes an extraction cell which is temperature controlled or held in an oven, a switching valve, a cryogenically cooled trap and a chromatographic oven housing the column and a detector. The system is made in such a way that a single pump or dual pump can be used when in operation (Cotton et al.1992). Cortes et al. (1991) has described a coupled SFE-HPLC for the determination of chlorinated phenols from various solid matrices. This method allows for quantitative determinations down to the sub- $\mu\text{g/g}$ level without clean-up.

SFE has also been combined with various bioassay procedures. France and King (1991) combined SFE with an enzyme assay to screen metal products for pesticides. This technique offers major advantage in that the analyst is not exposed to organic solvents during the extraction. Wolfe et al.(1993) have also used SFE for sample preparation of aqueous pesticide samples for bioassay analysis.

2.5 High Temperature Distillation (HTD) or Thermal Desorption

Thermal desorption (also called high temperature distillation) is involved in hazardous waste incineration, one of the recent technologies effective for the remediation of contaminated soils. This method results in the destruction of many organic compounds. Most current research related to this method involves the determination of the rates of desorption of contaminants from various matrices.

Effective thermal desorption is dependent upon the nature of the contaminants, the nature of the matrix used and the interaction forces between them. The removal of a contaminant from a matrix is governed by the ease of volatilization of the solute, the mass transfer of the desorbed solute and the heat transfer in the matrix.

Thermal desorption is also involved in investigating the composition of airborne particulates. This area has gained prominence in recent years, as some of the polycyclic aromatic hydrocarbons (PAHS) are known to be carcinogenic and pose health risks to society. This awareness has led the scientific community to look for ways and means to qualitatively and quantitatively account for the presence of these components in air, water and food.

Most of the work in thermal desorption has been carried out with air particulates, or with contaminants dissolved in extraction solvents which are eventually adsorbed onto

adsorbent material such as Tenax-GC. The mode of investigation often used in the organic analysis of atmospheric suspended particles involves filtration of a certain volume of air, removal of the organic compounds on the filter by solvent extraction, concentration of the extract and fractionation of the components by liquid chromatographic methods. The quantitation of the different components is subsequently carried out by means of either GC or GC-MS methods.

Higgins et al.(1983) noted that many experiments have been conducted to determine whether organic compounds can be thermally desorbed from air particulate matter directly onto a chromatographic column. Despite the acceptance of thermal desorption as an extraction procedure, a great deal of uncertainty about the process still remains. There is uncertainty as to its validity in quantitative measurements, optimal design of the apparatus used, its optimal operating conditions, and its performance when compared with commonly used techniques still remain unanswered (Sievers et al., 1985).

Although thermal desorption has to a great extent been used for gaseous and solution phase sampling, it can be used with solid samples. The weighed sample material would be placed in a tared sample container and distilled under vacuum for varying lengths of time. The thermally desorbed material would be isolated in a cold trap and then

transferred into a sample loop apparatus that interfaces the GC (Kopczynski, 1984). This method has been used in the determination of contaminants in polymers and can also be used in the determination of volatile components in non-volatile materials such as waxes and oils.

Thermal desorption in this work is used to indicate a heating process which volatilizes the organic contaminants. It is a physical separation process, although chemical transformation of the organic contaminants may occur depending on the thermal stability and the operating temperatures required to achieve adequate decontamination efficiency. In this process, the compounds are vaporized at temperatures above 250°C. The adsorbed analytes are collected in various solvents such as acetone and hexane and are subsequently analyzed by means of GC-MS or GC-ECD.

Thermal desorption circumvents the need for lengthy solvent extraction procedures prior to chromatographic analysis. It has the potential to be as simple as possible with a minimum of direct sample handling. However, samples for thermal desorption are often adsorbent tubes from environmental air sampling, geological samples and polymers. The volatile compounds are concentrated on such an adsorbent bed and then thermally desorbed to the GC for analysis.

Renkes et al. (1983) showed that several critical factors control the efficacy of the thermal desorption process. These factors include:

- (i) duration of extraction;
- (ii) thermal decomposition reactions in the hot carrier gas and at the surface of the inorganic particulate which may account for lower recoveries;
- (iii) separation of the extract from the particulate, which must be accomplished rapidly to avoid readsorption.

The foregoing factors were also highlighted by Ellis et al. (1986) who showed that flash thermal desorption of oil shales yielded a hydrocarbon mixture which in some cases is chromatographically identical with that obtained from solvent extraction. In most cases, it was found that compounds eluting after C_{15} are more abundant than those eluting after C_{35} , as compared to solvent extraction.

The effectiveness of thermal desorption to decontaminate soil containing contaminants has been studied both on bench and on pilot scale tests. William and coworkers (1987) found that thermal desorption can be combined with a photolysis reaction to improve on the efficiency of the extraction process. They used the procedure to decontaminate soil samples from Air Force camps and could reduce the contaminant level to less than 10^{-9} of the original contaminant value.

Further work in the decontamination of soil was carried out by Williams et al. (1986) using thermal desorption in conjunction with UV photolysis. The technique involved the desorption process, collecting the volatilized material in a

suitable solvent (scrubbing) and finally photolysis. This converts the contaminants to relatively non-hazardous residues through photochemical reactions (Helsel, 1986). They obtained total recoveries and achieved complete conversion of toxic constituents to potentially non-hazardous, easily disposable residues.

There are problems with the use of thermal desorption techniques. Helling and Krivonak (1987) reported on the physicochemical and biological characteristics of bound herbicides in soils. It is apparent from their results that the total pesticide residues are difficult to determine quantitatively by thermal desorption due to strong associations between the soil particles and the herbicides.

2.6 Comparison of Extraction Methods

The main objective of this thesis is to compare the effectiveness in extraction of pesticide residues from soil using the four methods described in sections 2.1, 2.2, 2.3, and 2.4. The comparative studies which have been reported in literature are reviewed in this section.

2.6.1 Comparison of SFE to Solvent and Soxhlet Extraction

Monin et al. (1987) have studied the extraction of hydrocarbons from sedimentary rocks using supercritical carbon dioxide. They compared their results with those obtained by chloroform extraction and concluded that SFE extracts hydrocarbons up to C_{35} but that the recovery was not as good as that obtained with chloroform. They found smaller amounts of heteroatomic compounds in the SFE extract in comparison to the amount obtained by chloroform extraction. These authors also indicated that the hydrocarbons could be extracted quantitatively by solvent extraction.

Although many research groups have implied that SFE is superior to Soxhlet, DeRoos and Biking (1990) found out that the percentage recovery of dioxins from spiked soils with SFE were approximately 30-50% of the levels obtained with the Soxhlet extraction method. These lower levels suggest matrix related effects were present and that physical entrapment in the three dimensional soil matrix is possible.

Apart from solubility, the manner in which the substance to be extracted is bound to the matrix has considerable influence on the efficiency of the extraction process. It has been found that the strength of the binding of nicotine in tobacco varies. Whereas some of the nicotine can be extracted very easily, the rest is probably present as a complex salt with the tobacco components such as chlorogenic acid, citric acid etc., and is more difficult to extract (Hubert and Vitzthum, 1978).

Alexandrou and Pawliszyn (1989) found that SFE leaching of fly-ash material for one hour using supercritical nitrous oxide was more effective than a 20 hour Soxhlet extraction under the same conditions. These authors found that extraction times could be further reduced when higher pressures were used. They also reported that carbon dioxide was a poor extractant for dioxins when high pressures were used.

They were able to extract a standard of heptachloro-p-dioxin and ^{13}C labelled TCDD from an empty extractor tube, and also when it was deposited directly onto the fly-ash. These results imply that solute solubility is not the limiting factor, but rather that the pollutants of interest are strongly adsorbed onto the matrix and cannot be removed from the matrix with supercritical carbon dioxide at the conditions under which the extraction was done. A stronger solvent might be necessary to release them from the matrix.

They concluded that the time required to analyze fly-ash could be reduced substantially by incorporating an isolation step based on SFE.

Hawthorne and Miller (1987) had indicated that the time could be further reduced if direct on-column deposition could be used. Table 2.6.1.1 shows the relative time scales that have been used in some SFE and Soxhlet extractions under similar conditions (Hawthorn and Miller, 1987).

Table 2.6.1.1 Comparison of SFE and Soxhlet Extraction Times

Analyte Extracted	Matrix Type	SFE Time (min)	Soxhlet Time (hr)
DDT	Soil	5 - 10	8-20
Tocopherol	Food and feeds	37	8
Arochlor 1254	Soil	2	8-12
Dioxins and TCDDs	Sediments	30	18-24
PAHs	Urban dust	15	16

SFE performs most extractions in 5-45 minutes with similar or better recoveries than liquid or Soxhlet extractions. The reasons that make SFE so rapid is that the supercritical fluids have a penetration power into the matrix which is one or two orders of magnitude higher than the liquids. This is due to higher diffusivities of the supercritical fluids into the matrix. Liquid solvent may also not be able to penetrate all the crevices in the matrix

due to surface tension effects. There are no such matrix penetration problems with SFE.

2.6.2. Comparison of Solvent Extraction with HTD

Bowers et al.(1983) and Allen et al.(1984) have found that HTD (also referred to as thermal desorption) could have several advantages over the more traditional solvent extraction procedure. These groups found that large amounts of information could be obtained with a minimum of time and sample handling. A typical solvent extraction and fractionation scheme requires about 8-12 hours to complete, while with thermal desorption these steps are not necessary. Thermal desorption as mentioned above requires no solvent or fractionation columns, thus minimizing the possibility of sample contamination.

Crouch (1984) compared thermal desorption with solvent extraction and found that thermal desorption is about 100 times more sensitive than the solvent extraction method. This is because the entire sample is injected into the GC for analysis. The elimination of extensive sample handling in thermal desorption reduces the number of artifacts that alter the sensitivity of any instrument. Although solvent extraction provides adequate sample volumes for replication, Randal (1985) indicated that the accuracy of the method is limited by the effectiveness of the extraction and the introduction of the artifacts in the prefractionation steps. In thermal desorption, the entire sample is used up, but replicate samples are easily collected.

Cautreels and coworkers (1976) examined whether solvent

extraction removes all the organic compounds from a high volume filter by exposing sections of a solvent extracted filter to thermal desorption. They found that an additional 20% of each of the components originally present could be removed by thermal desorption. The strongly adsorbed aromatic components could also be removed to a small extent. The inefficiency of solvent extraction for the quantitative removal of the organic constituents in airborne particulate matter has also been highlighted in the work of Griest et al., (1980).

2.6.3. Comparison of SFE with Thermal Desorption

Raymer and Pellizari (1987) compared the recovery efficiency of supercritical carbon dioxide extraction and thermal desorption of radiolabeled hexachlorocyclohexane (γ -BHC), hexachlorobiphenyl (HCBP), anthracene and parathion. The experiment was meant to demonstrate the ability of supercritical carbon dioxide to desorb environmentally significant compounds from the polymeric sorbent Tenax-GC.

The thermal desorption experiments for the four compounds were carried out at two different flow rates of helium. These authors used a relatively low flow rate of 1.5 mL min^{-1} as measured with the cartridge at 260°C for 8.5 minutes (50 void volumes). The higher flow rate experiment was carried out under similar conditions as the lower but at a flow rate of 6.4 mL min^{-1} for 10 minutes (260 void volumes). The supercritical fluid extraction was carried out at 40°C and at pressure of 210 atmospheres, for 13 minutes (14 void volumes).

The control used for these experiments was analogous to that used for supercritical fluid desorption, where the compound being studied was deposited in the system immediately after the sorbent. The amounts of the analytes applied to the Tenax-GC ranged from $4.5 \text{ }\mu\text{g}$ for the HCBP to $20.5 \text{ }\mu\text{g}$ for γ -BHC. All solvent evaporation was done by nitrogen blowdown. They found that thermal desorption was

less efficient, as shown by the experimental results in table 2.6.3.1

Table 2.6.3.1 Recoveries of Thermal Desorption Compared with Supercritical Fluid Extraction

Mode of desorption	Compound	Void volumes used	Percentage Recovery
Thermal (helium)	γ -BHC	50	27
	anthracene	50	10
	HCBP	50	13
	parathion	50	12
Thermal (helium)	γ -BHC	260	88
	anthracene	260	99
	HCBP	260	13
	parathion	260	12
Supercritical fluid (CO ₂)	γ -BHC	14	100
	anthracene	14	81
	HCBP	14	95
	parathion	14	92

It is evident from table 2.6.3.1 that very poor recoveries were obtained for the test compounds when thermal desorption was used with low flow rates. Increasing the number of column volumes of the helium gas used to 260 improved the recoveries of γ -BHC and anthracene but not for the HCBP or parathion.

Pankow et al.(1983), suggested that improved recoveries can often be obtained by increasing the desorption time, carrier gas flow rate and/or temperature. Increasing the carrier gas flow rate helps to minimize degradation on the cartridge since it reduces the residence time in the desorber. These authors also concluded that the recovery efficiency seems to parallel the number of substitutions on the ring, the overall polarity of the molecule and the number of rings.

o

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2.6.4 Comparison of Ultrasound and Soxhlet Methods

Soxhlet and ultrasonic methods (sonication) have been compared for their extraction efficiency. Many reviews on PAH analysis include references to the inferior efficiency of the Soxhlet method. Sonication (high intensity mechanical disruption) using cyclohexane, benzene or other solvents for 20 - 30 minutes appears to be more efficient than 6 - 8 hours with the Soxhlet for extracting PAH or benzene solubles (Bove et al., 1975). Ultrasonic extraction recoveries of phenanthrene and anthracene of 95% or greater have been reported by Jackson and Cupps (1978); the reproducibility is also better than that obtained with the Soxhlet method.

This led Golden and Sawicki (1978) to compare the extraction efficiency of Soxhlet and sonication methods using glass fibre filters on which air particulates had been collected. They found that the chromatographic peaks obtained by both methods were virtually identical, except that the peaks obtained from sonication were larger than those obtained with the Soxhlet method.

Sonication extracted 49±02% of the PAH. Soxhlet extracted at most 30%, with half the extractions giving amounts which were not even detectable.

Other comparative studies have been carried out by Nash et al. (1973) who compared Soxhlet and shaker extraction methods using nine chlorinated pesticides. Shaking also

involves mechanical disruption. These authors reported nearly identical recoveries with the two methods. Coover et al.(1987) reported that Soxhlet and homogenization with a blender yielded equivalent recoveries in the extraction of 15 PAHs from a sandy loam and a clay loam soil. Similar results had been obtained when comparing the efficiencies of Soxhlet and sonication methods for the extraction of PAHs from sediments (Holoubek et al., 1990).

2.6.5 Comparison of Soxhlet, Sonication and SFE Methods

Many environmental samples have been analyzed for PAHs, PCBs and PCDD/PCDFs using SFE and Soxhlet extraction techniques side by side. The results have consistently shown that SFE is a more effective extraction process than Soxhlet of complex organics from difficult environmental matrices.

Richards and Campbell (1991) compared SFE of sixteen environmentally significant semi-volatile compounds with conventional Soxhlet and sonication methods. They used a soil matrix as the test substrate and analyzed the extracts using GC-MS. Their results showed that SFE using supercritical carbon dioxide modified with 2% methanol was more efficient than Soxhlet and sonication techniques for all but three of the compounds studied. The SFE extraction was performed at 80°C and 390 atm. Extraction times for the 2 g samples used were typically 30 - 40 minutes.

From their results (shown in table 2.6.5.1), the Soxhlet extraction process also appears more efficient than the sonication process. This is contrary to the results obtained by Bove et al.(1975) and by Cupps in 1978 which showed the sonication process to be more efficient. These authors also used only 15 mL of the supercritical fluid solvent relative to the large quantities of flammable solvents used with the other two methods.

Table 2.6.5.1 Comparison of Extraction of Base-Neutral and Acidic Compounds by Soxhlet, SFE and Sonication Methods

Compound	Soxhlet	Sonication	SFE
	Percentage	Recovery	
Phenol	69.0	60.0	70.4
2-Chlorophenol	73.2	63.8	74.9
1,3-Dichloro-benzene	53.8	46.4	73.8
1,4-Dichloro-benzene	54.2	49.1	76.0
Hexachlorobenzene	73.0	75.3	86.2
Naphthalene	57.8	53.0	74.2
2,4,6-Trichloro-phenol	68.8	69.0	83.1
2-Fluorobiphenyl	74.6	60.4	88.0
2,4,6-Tribromophenol++	-----	-----	95.1

++ Analyzed as the methylated derivative.

The data is an average of five (Soxhlet) and nine (sonication and SFE) replicate determinations. The spike level was 25 µg/g; the sample size was of 2 g of soil.

Recent work by Snyder et al (1994) compared supercritical fluid extraction using carbon dioxide mixed with 3% methanol with sonication methods. They compared the extraction efficiencies from field contaminated soils with those from spiked samples. Their results showed equivalent recoveries of some selected pesticides from four different soil samples. The work also demonstrated identical precisions in the results between the two methods.

Janda et al. (1994) used supercritical fluid extraction

for the isolation of antioxidant aromatic amines from tire rubber. These authors found that the efficiency of SFE was comparable with that of Soxhlet microextraction. In experimenting with aromatic amines from different matrices, they found that the extraction efficiency depended to a large extent on the nature of the matrix.

Recent work by Hawthorne et al. (1994) compared the relative extraction rates of native PAHs and those of spike deuterated PAHs from heterogeneous environmental samples. These authors found that the extraction rates of most of the spiked analytes were about 10 times higher than those of the native contaminants irrespective of the spiking method used. In most cases it was found that SFE extraction efficiency was quantitative (>90%) with the spiked material whereas the native contaminants removal ranged between 25-80% in a sequential SFE extraction. Similar extraction efficiencies were obtained by sonication of these same matrices.

Wenclawiak (1994) found that the extraction efficiency of using SFE for extracting chlorobenzene from soils was only 60-85% of the Soxhlet values. The extraction efficiency in SFE was however strongly dependent on method of analyte collection after SFE, in addition to many other parameters.

3 FACTORS DETERMINING EXTRACTION EFFICIENCY

Most pesticides in the environment find their way into the soil in one way or another; the soil functions as a sink for many contaminants. In order to understand the behavior of pesticides in the environment, it is vital to consider pesticide dynamics in the soil. One of the important factors controlling pesticide behavior in the soil is the sorption/desorption process. In order to understand this process, the interaction of the pesticides with the soil matrix must be known.

The soils used in this work are clay-like in structure. The structure of the clay minerals must be considered in order to fully appreciate the interactions involved between the pesticides and the soils.

3.1 The Structure of Clay Minerals

Soils are complex mixtures of minerals, organic matter and water. The most active mineral constituent of soils is clay. Most of the clay minerals have a large specific surface area and are characterized by inherent structural features. They are made up of layered lattice silicates which are divided into two main structural groups on the basis of the ratio of tetrahedral sheets to octahedral sheets in the unit layer.

Figure 3.1.1 shows the structural differences of Kaolinite and Montmorillonite clays.

Figure 3.1.1 Structures of Clay Minerals: Kaolinite and Montmorillonite
(Adapted from Tan, 1993)

Kaolinite

Montmorillonite

The Kaolin group is an example of the 1:1 structure and consists of one sheet of tetrahedrally coordinated cations (Si-O or Al-O tetrahedra) with one sheet of octahedrally coordinated cations (Al^{3+} , Mg^{2+} , Fe^{2+} etc). These minerals are either electrically neutral or possess a very low negative charge. They do not swell (except Halloysite) under normal conditions, and they have an active surface area which is limited to the external surfaces only. These minerals interact with pesticides to a very limited extent (White, 1976).

The Smectite (Montmorillonite), Vermiculites and Micas constitute the 2:1 type silicates. This group consists of two sheets of tetrahedrally coordinated cations (Si-O or Al-O tetrahedral) with one sheet of octahedrally coordinated cations. These are negatively charged due to isomorphous substitutions in which some Si^{4+} in tetrahedral positions are replaced by Al^{3+} , or Al^{3+} by Mg^{2+} in octahedral sites. The negative charges are balanced by positively charged ions or groups of atoms which occur between successive 2:1 layers. Smectites have high cation exchange capacity and high surface areas.

Clay minerals influence the fate of pesticides; an understanding of clay-organic interactions is thus of considerable environmental importance. It is also important in predicting the behavior of pesticides and their effectiveness for pest control (Theng, 1974) as clays

greatly influence the reactivity of the organic molecules. Clays change continuously, generating new surface areas. New surface areas are generated through isomorphous substitution and also through dissociation of exposed hydroxyl groups in acidic and basic media.

Electrostatic bonding takes place between organic cations and anions and clays. The organic cations are adsorbed on the negative clay surfaces, whereas the organic anions are more attracted towards the edge surfaces of clays (Van Olphen, 1977). Adsorption of low molecular weight organic compounds is limited to interlamellar adsorption; this results in an increase in the basal spacing between the layers (Tan and McCreery, 1975). Glycerol and ethylene glycol will however adsorb to all surfaces on dry clays. When interlamellar adsorption occurs, the organic molecule adsorbed may displace the water molecules present in the interlamellar spaces.

Uncharged organic molecules can also be adsorbed by clay minerals. The adsorption can be direct or indirect, and physical forces are responsible for the adsorption. Indirectly the uncharged organic compounds are adsorbed by the silicate surface through linkage to the exchangeable cations. Competition for ligand sites usually occurs between the organic compounds and the water molecules around the exchangeable cations. The organic compound can react directly, or indirectly with the cation through linkage with

the water molecules in the hydration shell by means of ion-dipole reaction.

The importance of layer silicate clays is best illustrated by their cation exchange capacity. The presence of permanent negative sites in certain clays accounts for the ability of many soils to hold cations against leaching, but in a form that supplies nutrients to plants. The exchangeable ions have variable hydration spheres that influence the shrinking and swelling of clay soils as the water content changes. The pioneering research of Ensinger and Gieseking (1941) showed that organic cations are held on interlayer surfaces and influence the interlayer spacing of Smectites, thus demonstrating the site of cation exchange.

Table 3.1.1 shows some of the important characteristics of three important clays.

Table 3.1.1 Characteristics of Clay Minerals
(adapted from Haque and Freed, 1975)

Clay	Type	Surface area m ² /g	CEC* meq/100g
Kaolinite (non-expanding)	1:1	25 - 50	2 - 10
Montmorillonite (expanding)	2:1	700 - 750	80 - 120
Illite	2:1	75 - 125	15 - 40

* (CEC = Cation Exchange Capacity)

3.2 Pesticide Adsorption to Soils

Adsorption of pesticides by soil matrices and their subsequent degradation are the two most important processes affecting their leaching and mobility through soil profiles (Alva and Singh, 1990). The intrinsic properties of both the adsorbate and the adsorbent greatly influence the degree of adsorption of pesticides, which in turn determines their potential to move through different soil profiles (Chiou and Shoup, 1985), degradability and persistence. The soil organic matter and clay content play vital roles in the adsorption process by partitioning the pesticides between them, especially when the materials are non-ionic and hydrophobic (Davis, 1993). The mineral content and cation exchange capacity of a soil also influence adsorption (Dragun, 1988).

3.2.1 Soil-Pesticide Bonding

The chemical properties of pesticides, their molecular size, polarity, polarizability, ionizability, etc. are of primary importance in determining the bonding mechanisms, and hence affect the magnitude of adsorption and mobility in soils (Weber and Weed, 1974). Generally organic pesticides with low water solubility and high K_{ow} (octanol/water partition coefficient) are strongly adsorbed to soil matrices (Briggs, 1981).

When a pesticide molecule comes into contact with a

soil surface, it is usually quickly adsorbed. The adsorption depends upon the energies of the surfaces of the various constituents of the soil. The factors influencing pesticide adsorption-desorption include: soil organic matter, humic material present, water solubility of the pesticide, pH, temperature, and molecular structure of the pesticide. They have been discussed at length by many research groups (Hamaker and Thomson, 1972; Freed and Haque, 1973).

The bonding mechanisms for pesticide retention by soils include ion-exchange, hydrogen bonding, protonation, van der Waals, and ligand exchange mechanisms. Some of these factors are discussed below.

Van der Waals forces are common to all molecules. These include the interaction between the permanent dipoles, and between permanent dipoles and induced dipoles in the molecules. There is also a contribution from transient dipole-dipole interactions known as London or dispersion interactions (Moore, 1962). Fluctuations of the electron density in their orbitals produce instantaneous dipoles which amount to zero over fairly long distances on the molecular scale. However, over short molecular times, the dipoles produced bring about attractions between atoms and molecules at distances up to the van der Waals radii, and cause repulsions at shorter distances (Higgins, 1985).

Hydrophobic bonding is an entropy effect resulting from

the rearrangement of water molecules around the solute molecules in the aqueous phase. The hydrophobic sorption involves the partitioning of the non-polar organics out of the polar aqueous phase onto hydrophobic surfaces in the soil. These surfaces are mainly present in soil organic matter, but may also include -Si-O-Si- bonds at the mineral surface (Hassett and Banwarth, 1989).

Although it is difficult for organic molecules to be adsorbed onto clay surfaces, studies by McBride et al. (1977) have shown that clay surfaces can be made hydrophobic by placing on their surfaces organic molecules which have some hydrophobic properties, but which also possess a polar group such as alkylammonium ions which allow adsorption. This process enhances the adsorption of organic molecules onto clay surfaces and helps hydrocarbon groups to associate with one another and with hydrophobic surfaces.

This also hinders the association of water molecules that were initially bound to the clay surfaces. The overall process results in the displacement of a large number of water molecules from the surface cluster and therefore increases the entropy of the system which is a favorable contribution for a reaction to occur.

Charge transfer results from partial overlap of electron rich groups and electron poor groups. The process involves the partial overlap of the respective molecular orbitals and a partial exchange of electron densities.

Under certain conditions, a number of organic compounds may develop positive charges within the molecule by a process suggested by Mortland in 1970. After adsorption by the clay, organic pesticides become positively charged by accepting protons as shown by the following reactions:

(i) H^+ -saturated clays can donate the proton

(ii) Water can be polarized by a cation and can then donate a proton to the organic pesticide compound:

(iii) The presence of a protonated species that may donate a proton to the organic molecule:

Protonated	organic
species	molecule

The organic molecules, having acquired a positive charge, may replace inorganic cations on exchange positions or in the interlayer surfaces of clays. Hendricks (1941) has shown that the exchange occurs in a stoichiometric manner and reaches a maximum when the exchange value equals the cation exchange capacity of the clay. Theng (1974) has indicated that if the organic cation occupies the interlamellar spaces, analysis of basal spacings of the clays indicate that the organic ion is adsorbed with its shortest axis perpendicular to the silicate layer.

3.2.2 Pesticide Properties of Importance

The rate of desorption of heavy organics from soils to the atmosphere is controlled by many factors. Some of these factors include: the compound's vapor pressure, its solubility in the water present in most soils, and the physical and chemical properties of the soil. The soil parameters which have been studied are total organic carbon, porosity, pore size distribution, clay content, water content and temperature.

The nature of the adsorption of a pesticide on a soil surface can be elucidated from the magnitude of the heat of adsorption. The adsorption of a highly soluble pesticide such as diquat cation $[(C_5H_4NCH_2)_2Br_2]^+$ on clay surfaces involves a cation exchange mechanism as shown by the following equation:

The reaction as written above proceeds to a large extent (Weber and Weed, 1968). Diquat and paraquat are two important members of the bipyridinium quaternary salts which are highly water soluble (Brian et al., 1958) and are readily adsorbed on clay and soil surfaces.

It should be noted that most pesticides are aromatic or heterocyclic in character. The acidity of the functional group has a key role in determining the interaction between the mineral surface and the pesticide: acidic, basic or amphoteric. These have a key role in determining the

reaction involving the mineral surface and the pesticide under investigation.

The water present in the soils greatly affects the observed vapor pressure of contaminants as it competes with them for the active sites on the soil. In the presence of non-polar or weakly polar groups on organic material, water is preferentially adsorbed onto the organic soil particles. This preferential adsorption weakens the bonding between the contaminant and the soil, which in turn increases the vapor pressure of the contaminant. This enhances the desorption of the contaminant from the soil.

Glotfelty et al. (1989) have indicated that the interaction of non-ionic pesticides with the soil is primarily through the soil organic matter. The soil organic matter and the vapor pressure of pesticides are inversely proportional as shown in table 3.2.1, which depicts the drop in the vapor pressure of trifluralin (2,6-dinitro-N,N-di-propyl- α,α,α -trifluoro-p-toluidine) with an increase in the organic matter content. This has also been confirmed by Chio and Shoop (1985) who indicated that clay content has little effect on non-ionic pesticide adsorption. Bailey et al. (1970) demonstrated that the adsorption capacity of clays for herbicides was highest for Montmorillonite, intermediate for Illite and least for Kaolinite.

2

PM-1 3½" x 4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

PRECISIONSM RESOLUTION TARGETS

Table 3.2.1 Variation of Vapor Pressure of Trifluralin in Three Soils of Differing Organic Matter Content

Soil	% Soil Organic Matter	Trifluralin vapor pressure $\times 10^{-5}$
Imperial Clay	0.20	24
Gila Silt Loam	0.58	13
Kentwood Sandy Loam	1.62	4.7

Pesticides can be detoxified at clay surfaces via hydrolysis or molecular rearrangement. This is controlled by the adsorption capacity of the soil. The adsorption capacity is the ability of the adsorbent to reduce the amount of the pesticide in solution to a level which is chemically undetectable. Pesticides may be detoxicated by clay surfaces through hydrolysis or through molecular rearrangement.

Compounds like the organochlorine pesticides and the PCBs, which are hydrophobic in character, can be adsorbed by the silicate surface through linkage to the exchangeable cations. Competition for ligand sites usually occurs between the pesticides and the water molecules around the exchangeable cations. The pesticides might react directly with the cation or can be indirectly coordinated to the cation by linkage to the water through the hydration shell. This forms the basis of an ion-dipole reaction which is dependent on the polarizing power of the cation, the

basicity of the pesticide, and on the nature of the packing when adsorbed in interlamellar spaces (Hovarth and Melander, 1978).

It has also been shown that the geometric fit of a pesticide on soil surfaces depends on surface charge density of the clay and the size/shape of the organic molecule. The orientation of a pesticide in the clay structure allows for either parallel or longitudinal adsorption on the clay surface.

3.3 Characteristics of the Soil Influencing Adsorption

To understand the adsorption phenomena, the nature of the soil being used in the investigations must be known. Clay and organic matter are the soil components most often implicated in pesticide adsorption. The individual effects are not clearly defined as in most cases the organic matter is intimately bound to the clay in the form of a clay-metal-organic complex (Tan et al., 1971). Two types of adsorbing surfaces are normally available to the pesticide, namely clay-humus and clay alone. Comparative studies between known clay minerals and organic soils suggest that most but not all pesticides have a greater affinity for organic surfaces than for mineral surfaces.

3.3.1 Interaction with Clays

The work reported here used one form of Smectites, the Montmorillonite which has been used to a large extent to explain the double diffuse layer of soils. They are responsible for the shrinking and swelling that is common in soils; they are also responsible for the adhesive properties that help to prevent soil erosion. They have however been found to play a destructive role when they adsorb large quantities of water. This decreases the strength of soils causing destructive landslides. The expansive nature of smectites and their negative surface charges cause them to be extremely reactive in soil environments.

The organic cations are mostly adsorbed on the negative clay surfaces while anions are more attracted towards the edge surface of the clay (Van Olphen, 1975). In the adsorption process, the pesticides may displace adsorbed water molecules from the clays. Interactions of pesticides with soils are influenced by characteristics of the adsorbent (soil) and the adsorbate (pesticide) as well as the magnitude, distribution and intensity of the electrical field at the surface (Bailey and White, 1970).

As seen in table 3.1.1, the 1:1 Kaolin minerals have low cation exchange capacity and low surface area; they have therefore very limited adsorption capacities. The 2:1 minerals (Montmorillonite and Vermiculite) have however very high CEC and also very high surface areas and subsequently have very high adsorption capacities. The non-expanding 2:1 minerals (e.g. Illite) have intermediate surface area and intermediate surface charges and are therefore of intermediate adsorption capabilities.

Solomon and Hawthorne (1983) proposed a model of the soil structure that depicts the structure as a stack of rectangles (figure 3.3.1). Depending on the degree of hydration of the mineral, various types of surface functional groups are available. These functional groups play a key role in mediating the interactions of the clay surface with guest organic molecules.

Figure 3.3.1. Illustration of Surface Functional Groups in Smectites
(Adapted from Solomon and Hawthorne, 1983)

In the model shown above, the silicate layers are represented as stacked rectangles with various functional groups. These functional groups mediate the interactions of the clay surface with guest organic molecules. The bottom of the figure shows smectite clay under idealized conditions of complete dehydration. The galleries are collapsed and inaccessible and no interlamellar adsorption or ion exchange reactions are anticipated unless the guest molecule is highly polar and capable of swelling the interlayers.

The Lewis acid sites and hydroxyl groups are of primary importance under these conditions. As the degree of hydration increases, or in the presence of liquid water, terminal hydroxyl groups and equated Lewis acid sites become

predominant on edge positions increasing acidity at external surfaces as shown by the following equations:

The coordinatively unsaturated Lewis acid sites (Al^{3+}) are capable of forming adducts with organic donors as shown above. Mortland and Raman (1968) showed that as water content decreases, the proton donating ability of the clay surface increases due to polarization effects by the cation or residual water molecules.

3.3.2 Interaction with Organic Matter

Adsorption by organic matter is a key factor in the behaviour of many pesticides in the soil. Numerous reviews dealing with bioactivity, persistence, leachability and volatility have been shown to bear a direct relationship to the organic matter content in the soil (Stevenson, 1972). Adsorption by organic matter depends to a considerable degree upon the physical and chemical properties of the pesticide.

The organic matter of the soil has great potential for promoting the non-biological degradation of many pesticides. Many pesticides contain nucleophilic groups such as amino,

phenolic, etc.; these are responsible for producing chemical changes in a wide variety of pesticides. These nucleophilic functional groups are easily oxidized and lead to the formation of transformation of the pesticides to other compounds. The new compounds may be more or less toxic than the original pesticide.

Unless the nature and chemical composition of the organic fraction of soils are well known, potential pesticide-organic matter relationships will remain obscure. The ability of a particular soil to retain or release pesticide residues is greatly influenced by the interaction between the physical and chemical properties of both the soil and the pesticides applied, as well as the living and nonliving components of the soil system. The living and the non-living components of the soil are either fungi or bacteria. In general, soils high in organic matter or clay content tend to retain pesticides residues longer than sandy soils or soils low in organic matter (Burns, 1971).

3.4 Models for Adsorption and Diffusion

3.4.1 Adsorption Models

The sorptive capacity of soils for neutral pesticides is determined by an "active" organic fraction which, in its sorptive characteristics is essentially similar in soils of widely divergent origin (Lambert, 1968). At very low concentrations, a simple distribution coefficient appropriately describes adsorption by the most energetic sites:

$$K_d = (x/m) (v/Y_{eq}).$$

Experimentally, the quantity of a pesticide adsorbed (x) was estimated as the difference between total pesticide in the system (Y_t) and that in the supernatant at equilibrium. The mass of adsorbent (m) was varied at constant aqueous volumes. To estimate K_d by least squares, ($Y_t - Y_{eq}$) was substituted for x in the equation above and the expression rearranged to: $Y_t/Y_{eq} = 1 + K_d(m/v)$ (the Freundlich equation). Here K_d is the slope of the line which intercepts the vertical axis at $Y_t/Y_{eq} = 1$ when the adsorbent is present.

Another model that has been used is the Langmuir model (1918) which has the form: $x/m = k_1 C / (1 + k_2 C)$ where: x = amount adsorbed; m = amount of adsorbent; k_1 and k_2 are constants; and C = concentration of equilibrium solution. The equation differs from the Freundlich equation in that at very high concentrations $k_2 C$ reaches such a value that the factor 1 can be neglected. This makes the formula

take the form: $(x/m) = (k_1/k_2)$, making x/m a constant at high concentrations. This makes the surface of the adsorbent saturated and adsorption subsequently reaches a maximum.

A different model by Brunauer et al. (1938) was developed for the adsorption of multilayers of nonpolar substances. This model is the basis of Brunauer, Emmett, and Teller equation and takes the form:

$$\frac{p}{V(p_o - p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{p}{p_o}$$

where p = equilibrium vapor pressure; p_o = saturation vapor pressure; V = volume of gas adsorbed; V_m = volume of gas adsorbed when solid is covered with monolayer; and C = constant related to heat of adsorption.

The equation above is an extension of the Langmuir for application to multilayer adsorption. It assumes strong adsorption of the first layer of gas by the surface by perhaps van der Waals forces. The second and any subsequent layers are held to the surface by weaker forces and the number of layers becomes infinite when p/p_o becomes unity.

It is apparent from the literature that there is no general agreement of the nature of adsorption isotherms. Some authors, e.g. Bailey and White (1970), believe that adsorption of organic compounds can be better described with the Freundlich equation, but Weber (1970) reported that adsorption of organic compounds follows the Langmuir equation.

The Freundlich equation predicts that adsorption increases indefinitely with increasing concentration. On the other hand, the Langmuir equation assumes that adsorption of organic compounds on the clay surface reaches a maximum limit. The latter theory predicts that the soil and clay particles do not have an infinite capacity to adsorb but rather, they eventually become saturated if exposed to excess adsorbate.

Gupta et al. (1993) have shown that the values of the distribution coefficient, K_d for benzene, toluene and xylene isomers were lower in Kaolinite than in Montmorillonite or Illite. The K_d values reported in their study match the reported adsorption coefficients of sorbents with organic content less than 1% (Walton et al., 1988). Similar results of the adsorption of the hydrophobic compounds by clays have been reported by Bailey and White (1970).

One explanation of the above phenomenon is that Montmorillonite is a 2:1 clay with a large surface area (table 3.1.1), whereas Illite is a non-expandable 2:1 clay. Kaolinite on the other hand is a non-expandable 1:1 clay with very small surface area relative to the other two (Mingelgrin and Prost, 1989). Gibbons and Soundarajan (1988) showed that aromatic hydrocarbons can fit between the interlamellar space of clay minerals and that C-H bonding between clay surface and hydrocarbon has been confirmed using infrared spectroscopy.

3.4.2 Diffusion Models

Investigation of the mechanisms responsible for slow sorption processes have been confounded by the complexities and heterogeneity of natural systems. Studies have implicated both restricted diffusion through soil organic matter (Rao et al., 1989) and restricted diffusion through intra-aggregate pores (Ball and Grathwohl, 1993) as responsible for the persistence of contaminants in the environment. The difficulties encountered in the understanding of the diffusion processes in the soil are illustrated through consideration of the pore diffusion model.

It has been found that capillary condensation leads to filling by water of internal pores of solute particles and aggregates. In both the saturated and the unsaturated zones, desorption of contaminants bound within soil aggregates requires diffusion through water filled pores. The pore diffusion model provides a framework for understanding solute mass transfer within porous particles and aggregates.

Sorption may be limited by diffusion through small pores and may be retarded by sorption to cell walls. The retardation is proportional to the strength of the sorptive interaction between the sorbate and the matrix.

Effective diffusion reflects the rate at which the solute appears to diffuse through the aggregates. It thus accounts for the fraction of time that the diffusing species are adsorbed on the solid surface and are therefore

immobile. Kearney et al.(1970) indicated that removal of pesticides from soils is a far more complex process, since the system is static and not conducive to flow-through operations. Pignatello (1989) has indicated that the fate of many compounds in nature are sensitive to their distribution between sorbed and nonsorbed states.

3.5 The Influence of Water in Soil Extractions

An important factor in any soil extraction is the water content of the soil. The presence of water in the soil effectively represents an extra phase that will affect the partitioning properties of the solute and the solvent under investigation. Brady et al.(1987) found that the presence of 20 wt % water in laboratory spiked soils contaminated with DDT and PCBs resulted in slower extractions although the final extent of extraction was unchanged with respect to the dry soils used. This result was also duplicated in a later study by Dooley et al. in 1990 using CO₂ with 5% methanol as a cosolvent in the extraction of PCBs from soils.

Hess et al.(1991) also examined the influence of water on the extraction of phenols from soils. These authors used a static apparatus in which the distribution coefficient of the phenol between the supercritical phase and the soil was measured. The addition of 10% water to the soil at 152 atmospheres and 37°C increased the extraction by 10 - 15% when compared with dry soils. However, when water was added to soil containing 6.4% methanol, the extraction fell slightly.

It is possible that this slight fall in extraction efficiency was due to a slower extraction similar to that observed by Dooley et al. in 1990. The conflicting influence of water on the extraction efficiency observed for

phenol (Hess et al., 1990) and DDT and PCBs (Dooley et al. 1990; Brady et al., 1987) is due to both the different experimental techniques used and the different solute - systems investigated. Although none of the three solutes studied was strongly polar, phenol extraction was enhanced while DDT and PCB extraction was lowered.

The addition of water to supercritical CO_2 enhanced the desorption of anthracene from soil by reducing the measured adsorption distribution coefficient by a factor of three (Andrews et al., 1990). The experimental work involved utilized a circulation batch equilibrium cell in which the adsorption and desorption of several polycyclic aromatic hydrocarbons from supercritical CO_2 onto the soil were measured. The addition of water to the supercritical fluid phase was observed to have no further effect on desorption above a concentration of 0.6 mol%. This concentration represents saturation of the CO_2 - H_2O system and further additions of water would not be soluble in the supercritical phase. The foregoing results implied a competition between the water and the anthracene for polar adsorption sites on the soil. If this is true, the wet soils should offer higher extraction efficiencies than dry soils in which the water molecules have been removed from the polar adsorption sites.

The preceding paragraphs effectively demonstrate that water has a strong influence on the extraction efficiency of

contaminants from soils and the high natural water content of most soils means that water cannot be ignored. Despite several investigations as alluded above, the influence of water on contaminant removal from soils remains poorly understood. It is clear from the available data however, that the presence of water can alter extraction behavior and that the effect is apparently system specific and a sweeping statement that water **INCREASES** extraction efficiencies from soils is not justifiable. Results from experiments on soils (wet or dry) must be interpreted with caution.

The results in this work were obtained with soils that had less than 1% water, and for all practical aspects are treated as obtained from dry soils.

4 EXPERIMENTAL

4.1 Materials

4.1.1 Chemicals

In the initial stages of this project, we intended to use soil spiked with eight chlorinated compounds:

1. Lindane γ -(1,2,3,4,5,6-hexachlorocyclohexane)
2. DDT (2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane)
3. Dicamba (2-methoxy-3,6-dichlorobenzoic acid)
4. Aldrin (1,2,3,4,10,10'-hexachloro-1,4,4a,5,6,7,8,8a-hexahydro-1,4,4,5,8-endo,exo-dimethanonaphthalene)
5. 2,4-D (2,4-dichlorophenoxyacetic acid)
6. Picloram (4-amino-3,5,6-trichloro-picolinic acid)
7. Dieldrin (1,2,3,4,10,10'-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,1,2-3,4,10,10'-hexa-8-dimethanonaphthalene)
8. Endrin (1,2,3,4,10,10'-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,endo-5,8-dimethanonaphthalene)

These compounds were used to spike the various soils which had been obtained from Agriculture Canada.

After using these soils for about four months, it was found that the results obtained with aldrin were always difficult to quantify due to the presence of dieldrin in the extracts. Some photodieldrin was also obtained in some of the extracts. The conversion of aldrin to dieldrin made it difficult to quantitatively determine the amount of dieldrin

or aldrin in the sample mixture. Aldrin was therefore left out from the list.

Harris and Liechtenstein (1961) showed that 15-30% of aldrin was converted to dieldrin under their experimental conditions. These authors had also found that some aldrin was lost due to evaporation and suggested that the losses could have been due to:

(i) Immediate epoxidation of aldrin to dieldrin as soon as aldrin was added to the soil,

(ii) Rapid epoxidation when the spiking levels are low. The chemical and structural similarity of endrin to dieldrin led us to also remove endrin from the original list. It was apparent that the results obtained with dieldrin would be applicable to endrin as well.

Picloram and 2,4-D were also removed from the list after it was found that they were very difficult to remove from the soil matrix in most cases. It is likely that they were strongly held onto the soil and were not easily eluted. The extracts obtained showed no traces of these two compounds, especially when their concentrations were at ppb levels.

The chemicals were of 99.5% purity and were supplied by Polyscience Corporation as reference standards. Although pesticide grade solvents should have been used, the solvents used (hexane, dichloromethane and acetone) were all of spectrograde standard (99.5% purity). These solvents were

found to have no interfering peaks with the extracts on analysis. They were obtained from Caledon Laboratories, Georgetown, Canada.

The structures of the above compounds are shown in figure 4.1.1.1.

Figure 4.1.1.1 Structures of Pesticides Used

Supercritical grade carbon dioxide (99.99% purity) was supplied by Air Products Ltd. (Canada) under a helium pressure head. The helium head was necessary for maintaining the pressure and facilitating smooth flow of the supercritical fluid.

4.1.2 Soils

Initial work was carried out with soil samples that were obtained from some reference soils kept by Land Resources Centre (Agriculture Canada) at the Central Experimental Farm in Ottawa. The selected samples were fully characterized with regard to pH, total percentage carbon, particle size distribution, exchangeable cations and extractable iron and aluminum. These soils, in particular ECSS#7, were used in preliminary experiments (sec.5.1.1).

Two other soils used in this study were obtained from Kenya under licence from Agriculture Canada. The preliminary work with these soils showed that one contained lindane and DDT while the other contained lindane, dieldrin and DDT as "native" or "field" contaminants. It was therefore decided to do most of the experiments with these two soils, as much as was practically feasible. Spiked samples were however used in some experiments which were intended to investigate the differences in the extraction efficiencies between field contaminated soils and laboratory spiked soils.

The soils were used as obtained and were not modified in any way. The characteristics of the two soils (hereafter referred to as KE#2 and KE#4) are presented below, together with soil ECSS#7 obtained from Agriculture Canada.

Table 4.1.3.1. Soil Characteristics

Soil Type	ECSS#7	KE#2	KE#4
% Carbon	4.30	0.80-1.00	12.2
% Clay	29.0	68.0±0.50	26.50
% Sand		9.8±0.5	16.60
% Silt		22.2±0.1	56.90
CEC (meq/g)	33.0	N.A	N.A
pH (0.01M CaCl ₂) _{aq}	7.30	6.50	5.80
% Nitrogen	0.35	N.A	N.A
Extractable Fe (%)	0.60	N.A	6.90
Extractable Al (%)	0.10	N.A	0.33

N.A. means that the parameter was not analyzed for.

The determination of the organic matter content in soil KE#4 was carried out by Dr. Torrence of the Geography Department at Carleton University. This was carried out by putting 2.97 g in a muffle furnace for three hours at a temperature of 400°C. After cooling for 30 minutes, the soil in the crucible was reweighed. The difference between the initial mass and the final mass was the loss due to ignition and this was the organic component.

The soil KE#2 used in this work was brought from an area in Kenya where organochlorine pesticides had been used before being banned in 1980. Its pH was determined in 0.01 M CaCl_2 solution (2:1 ratio with soil) and was found to be 6.50. Another soil (KE#4) was obtained from Kenya at the end of December, 1993. It was brought from a suburb around the capital city, Nairobi. This area is a coffee and maize growing area where the use of organohalogen pesticides had been prevalent.

Although the banning order of these pesticides took place over fifteen years ago, the soils in these areas are still contaminated with pesticides. This soil was transferred into white plastic containers and was brought to Canada under permit from Agriculture Canada. The soil was also cleared by the ministry of Agriculture in Nairobi, Kenya.

The soil KE#4 was characterized by Dr. Wang of Agriculture Canada. It is a clay loam soil with about 30% clay. The extractable iron content in soil KE#4 is about eight times more than in soil KE#2 and has a higher aluminum content. The soil used was sieved through a 3.8 mm sieve and this fraction is the one that contained the clay fraction.

4.2 Apparatus

4.2.1 Soxhlet

The Soxhlet apparatus is normally used for liquid-solid extractions. The solid sample is put into a tared porous thimble, which is covered with the hot solvent. The Soxhlet apparatus (see figure 2.2.1, p 14) must have enough solvent to fill the siphon so that the system does not dry up. The solid in the thimble is bathed in fresh solvent at regular time intervals, the solvent cycle of the apparatus.

In most cases, different solvent cycles were used due to the use of different rheostats which apparently supplied different amounts of heat to the mantles despite the same calibration setting. The three extractors used were run at a rate of 6 -10 cycles per hour. The insoluble matrix is left in the thimble while the analytes of interest are carried along into the solvent reservoir.

The method is simple, has a fairly good degree of reproducibility and offers data that are comparable from different laboratories. However, it presents some risks due to the exceedingly long extraction times (typically 10 hr), the exposure of personnel to toxic chemicals, and a possibility of explosion.

An extraction involved setting a known amount of a spiked or unspiked soil sample into the thimbles of a 250 mL Soxhlet apparatus. The solvent or solvent mixture (50 mL) was then put into round bottomed flasks and connected to the

Soxhlet extractor. The rate of reflux of the solvent was controlled by the amount of direct current supplied to the heating mantle. When the extraction period was complete, the organic extracts were concentrated in a rotary evaporator and methylated when necessary. The methylation was carried out with diazomethane for about twenty minutes (see sec.4.6.5). After this, 1 μ L was injected into the GC-MS or GC-ECD for analysis.

4.2.2 Extraction with Ultrasound

The ultrasonic equipment that was used for sonication is shown in figure 4.2.2.1. The equipment was a Bransonic Cell Disruptor model VC 600 (Sonics and Materials Inc. Danbury, Connecticut USA), with a titanium tip whose area was 1.1 cm^2 . The cell was operated at 20 kHz at 35 watt. The ultrasonic probe was inserted into the beaker containing 3.5 g of sample in 50 mL of solvent. The extractions were run for 5, 15 and 30 minutes. The extracts were removed, transferred into a centrifuge tube and centrifuged for 25 minutes at 3800 rpm. The centrifuge used was an MSE, Johns Scientific, Toronto instrument. The extracts obtained were concentrated in a rotary evaporator and a $1 \mu\text{L}$ aliquot of each extract was injected into the GC-ECD for analysis. Figure 4.2.2.1 shows the type of the ultrasonic probe used.

Figure 4.2.2.1 The Ultrasonic Probe

4.2.3 Apparatus for SFE

The SFE system used was a Suprex SFE50 , with some runs done on the Suprex Prepmaster at Agriculture Canada. The conditions typically used were 40°C, 400 atm (a density of 0.958 g mL⁻¹ for 30 minutes. The extraction cell used was a 10 cm³ cell and the flow rate was kept between 0.3 and 0.5 mL min⁻¹. The system is made up of four basic parts which include the compressor (pump), an extraction cell, a temperature/pressure control system and a separator or absorber in some cases. The extracted material was collected in a few millilitres of acetone or hexane.

Figure 4.2.3.1 Schematic Supercritical Fluid Extraction System (Ramsey et al., 1994)

In SFE, solvent fluids such as carbon dioxide are typically contacted with a solid or liquid phase at high pressures (e.g. 300 atm) and moderate temperatures (e.g. 40°C). Slight changes in temperatures or pressures of the system can cause large changes in the density of the solvent and consequently in its ability to solubilize contaminants or analytes of interest from the solid or liquid phases. A non-volatile solute can be solubilized and mobilized from the extractor but even a moderate pressure drop during the subsequent transfer to the trapping solvent can cause premature precipitation of this material. For efficient transfer of the solute to the trapping solvent, the pressure drop must be effected at the exit of the transfer line. The supercritical fluid phenomenon offers unique opportunity for separation and recovery in one processing step of materials which are difficult to separate.

Although SFE equipment is available commercially, the equipment can also be constructed easily from a suitable syringe pump, an old GC or any other oven for thermostating the extraction vessel, some stainless steel tubing and on/off valves (Burk, 1991). The homemade equipment has an added advantage in that modifications can be incorporated into it in contrast to the commercial equipment, where there are limitations as to the use of specific extraction vessels, restrictors and analyte collection procedures.

4.2.4 High Temperature Distillation (Thermal Desorption)

A thermal desorption unit is made up of a desorption module consisting of a heater and a carrier gas flow system, as well as a control module which controls the upper desorption temperature and time. The sample is heated with the carrier gas flushing away desorbed material. Detection of the desorbed species can be done by trapping the desorbed species cryogenically, followed by rapid heating on-line to a chromatographic column.

Solid material for thermal desorption should be ground in advance to increase the surface area. This enhances diffusion rates of the analytes out of the matrix and provides a representative sample. Pankow and his coworkers (1983) have indicated that small sample sizes are preferred as they offer faster desorption and their initial peak widths on a chromatographic column are narrower. The minimum sample size is however restricted by analytical sensitivity and the stability of the sample.

Successful thermal desorption should be fast and reproducible. The higher the ramp rate and the final temperatures, the higher the desorption of the analyte from the solid and the narrower the peak widths. When the adsorbed analytes have different boiling points, programmed temperatures can be used, especially in areas where the matrix has very volatile analytes on the surface and less volatile ones in the bulk of the matrix.

During the desorption process, carrier gas flow rates should be fast enough to facilitate sample transfer efficiently to the GC. It has however been postulated by Pankow and Kristensen (1983) that the recovery of analytes by thermal desorption is unaffected by the flow rate of the carrier gas. Their results were found to be in very good agreement with the results that had been previously obtained by Pankow in 1983. The earlier study had shown that very volatile compounds may be cold trapped on whole fused capillary columns with excellent peak sharpness, even at high desorption carrier gas flow rates, provided that trapping temperatures are sufficiently low.

The operation and set up for high temperature distillation is an easy standard process. An amount of soil was weighed into a tared boat which was then inserted in an open ended sample tube and the assembly placed in the groove in the Lindberg instrument (figure 4.2.4.1). One end of the open tube is connected to a helium tank and the flow of the helium gas is adjusted to about 30 mL min⁻¹. The other end of the tube is connected to four traps, two containing acetone and two containing hexane respectively. The traps were eventually reduced to two after it was found that there were no pesticides in the last two. If there were any pesticides in these last two traps, they were below the detection limit of the instrument used.

The equipment is operated to a maximum temperature of

900°C. This maximum temperature was arrived at from previous work done by Khan et al. (1982) which showed that most of the analytes from soils would be dislodged long before the temperature hit the 300°C mark.

Figure 4.2.4.1 shows the schematic of the HTD apparatus.

Figure 4.2.4.1 Schematic Diagram for HTD
(Khan et al., 1982)

4.3 Methods

4.3.1 Preparation of Spiked Soil Samples

The method of preparation of spiked soil samples may have a significant influence on extraction efficiency. Pesticides spiked onto soil matrices should be left for some time for an equilibrium situation to be established. If this is not done, the results obtained are not reproducible due to different degrees of adsorption of the pesticide onto the matrix.

The spiking was carried out by adding a measured amount of the spiking stock solution to a tared amount of soil suspended in dichloromethane (DCM) or acetone with constant stirring. Typically, the spiking solutions were prepared by the appropriate dilution of stock standard solutions which contained $1 \mu\text{g mL}^{-1}$ of each of the test pesticides. The concentration of the spiked soil was determined by adding a fixed volume of the spiking solution to a known mass of the soil sample. The spiked soil was allowed to air dry in a beaker with occasional stirring to ensure even distribution of the pesticides in the sample matrix. The soil was kept for at least two days in a dark bottle in the cupboard, after which it was used for experiments for about a week.

The beaker in which the spiking was done was rinsed with the solvent and the rinse solution was analyzed for the pesticides. This was done to ensure that there were minimal losses due to adsorption of the pesticides onto the glass

walls. The residue on the glass was found to be negligible.

4.3.2 Identification by GC-MS

Identification of the analytes was carried out on a Varian Saturn II GC-MS. The column used was a DB-5 with a diameter of 0.25 mm, a film thickness of 0.25 μm and a length of 30 m. The carrier gas used was helium at a flow rate of 5 mL min^{-1} . The injector temperatures was maintained at 300°C. The ion trap was maintained at 220°C, and the transfer line at 290°C. The column temperature program was : 150°C for 1 min, ramp to 300°C at 6.2°C/min, and hold at 300°C for 5 min.

For the analysis of the extracts, 1 μL of the solvent followed by 1 μL of concentrated extract were drawn up into a 5 μL syringe and injected into the chromatograph. This method assured that the volume injected remained constant.

The identification and some quantitation was done from the chromatographic peaks obtained with the GC-MS. The six pesticides were identified through their retention times which were compared with those obtained from authentic samples. In addition to the retention times, three major ions of each pesticide (including the base peak in the mass spectrum) were incorporated in the identification procedure. The three ions used are shown in table 4.3.2.2. The retention times obtained with the DB-MS column are shown in table 4.3.2.1.

Table 4.3.2.1 Pesticide Retention Times (min) on DB-MS Column

Compound	Retention
Dicamba	5.32
2,4-D	8.08
Lindane	9.25
Picloram	12.13
Dieldrin	17.04
p,p'-DDT	19.51

Disugran represents the ester that is formed from dicamba (2-methoxy-3,6-dichlorobenzoic acid) while the 2,4-D is converted to the 2,4-D methyl ester. The two acids underwent methylation in order to make them more amenable to chromatographic analysis. When analysis was done, one chromatogram containing all the pesticides was used in drawing up the calibration curve for quantitation purposes. The selected ions used in making the calibration curves are shown in table 4.3.2.2.

The underlined ion in table 4.3.2.2 was used as the base peak for each of the pesticide, and was always included in the selection of the ions used to make the calibration curves. When the proper multiplying factor from the dilution was incorporated into the quantitation data, a linear relationship resulted except in the case of lindane. In this case, the linear relationship could only be achieved if only one of the major ions (m/e 181 or m/e 183) was used.

These two ions were of almost equal size in the chromatogram. Although a narrow window (~ 5 sec) was used in the case of lindane, and excellent lindane peaks were obtained, it was not clear as to why the linear relationship was not obtained when the other selected ions were included.

Table 4.3.2.2 Selected Ions from Various Pesticides Used in Quantitation

Disugran	<u>203</u> + 188 + 234
2,4-D-me	<u>199</u> + 175 + 234
Lindane	<u>181</u> + 183 + 219
Picloram-me	<u>196</u> + 168 + 223
Dieldrin	<u>79</u> + 263 + 345
p,p'-DDT	<u>235</u> + 199 + 319

Due to the existence of DDT isomers (o,p-DDT, p,p'-DDT, m,p-DDT etc.), it was felt that the analysis of this compound should be done with only the predominant isomer. The p,p'-DDT was therefore the isomer that was used in all our work. Much effort was put into identifying the DDT breakdown products but unfortunately these were not quantifiable. If any transformation products were present in an extractable form, their concentrations were below the method limit of detection.

Figure 4.3.2.1 shows a GC-MS chromatogram from one of the extracts from soil KE#2 showing the retention times of

the two pesticides used in most of this work.

Figure 4.3.2.1 GC-MS Chromatogram from a Soxhlet (16 hr) Extract Showing the Retention Times for Lindane and DDT from Soil KE#2

Figure 4.3.2.2 shows the spectrum match of DDT from one extract with the library workstation data.

Figure 4.3.2.2 DDT Extract Spectrum Match

4.3.3 Analysis by GC-ECD

Most quantitations were carried out with a Varian 3600 gas chromatograph equipped with an electron capture detector (^{63}Ni source) by the external standard method. The electron capture detector was used due to its higher sensitivity to organochlorine compounds. The column was a DB-17 and the temperature program used was the same as that described in section 4.3.2.

Figure 4.3.3.1 shows a GC-ECD chromatogram of a Soxhlet extract of soil KE#4.

Figure 4.3.3.1 GC-ECD Chromatogram from a Soxhlet (16 hr) Extract Showing the Retention Times of Lindane, DDT and Dieldrin from Soil KE#4

4.3.4. Calibration Standards

Standard stock solutions containing each of the test pesticides were prepared by accurately weighing approximately 0.01 g of each pesticides into a 250 mL volumetric flask. The pesticides were dissolved in acetone and the volume adjusted to the mark. The other dilute solutions were made by serial dilutions of the stock solution. These standards were run on the GC-MS or the GC-ECD and the response obtained with each concentration was used to draw the calibration curves. The analyses were carried out by comparing the sample area counts with those of the standards. The unknowns were run in the linear range of the calibration curves. A typical calibration curve for GC-ECD analysis of DDT is shown in figure 4.3.4.1.

Figure 4.3.4.1 GC-ECD Calibration Curve of DDT

The minimum detectable quantity of each analyte was determined by means of the following procedure. For GC-ECD, the signal to noise limit was set to 5. Thus any peak detectable by the instrument was at least five times greater than the noise level of the instrument. In practice, this was found to be 1 ppb for DDT, about 0.5 ppb for lindane and about 1 ppb for dieldrin.

The detection limits using GC-MS were not as low as those using the GC-ECD. Instrumental detection limit were found by plotting detector response versus mass of analyte injected. The x-axis intercept was the instrumental detection limit for that analyte. The detection limit for DDT was found to be 5 ppb, lindane 10 ppb and dieldrin about 5 ppb.

Much work has been done with the use of internal standards in the analysis of pesticides. The internal standard of choice normally has some similarity to the compounds being analyzed. In the case of multiresidue analysis, it is often very difficult to find one compound that would act as an internal standard for all the compounds under investigation.

EPA does not recommend the use of internal standards in multiresidue analysis. Purcell (1975) indicated that external standardization has an added advantage in that calculations are based on comparisons of the same compounds in the standards as in the unknown samples; and no response

or correction factor is necessary. The accuracy of the results depends much on the ability to inject exact amounts of samples and standards, and having the chromatographic parameters under control.

4.3.5. Derivatization

Although the methylation process adds extra steps to the already labor intensive Soxhlet extraction, it is essential for some compounds, as it allows compounds to elute from the chromatographic column within a reasonable time and increases the sensitivity of trace amounts using selective detectors. McMahon (1985) gave the following reasons as to why derivatization is necessary:

- (i) to facilitate analysis of polar molecules with various functional groups such as -COOH , -OH , and NH_2 ;
- (ii) to reduce tailing and non-linearity of response for polar compounds;
- (iii) to enhance detector response for trace components;
- (iv) to improve temperature stability of components and prevent decomposition;
- (v) to allow analysis of relatively nonvolatile components; and
- (vi) to improve the resolution of closely related compounds.

Diazomethane is a frequently used derivatization reagent for carboxylic acids, whereas silylation with the

various trimethylsilyl reagents are commonly used for hydroxyl compounds.

The diazomethane reagent used in this work was prepared dissolving 6 g of potassium hydroxide in a few mL of water, followed by the addition of 20 mL of methanol. The mixture was put in a round bottom flask fitted with a condenser and a solution of 21 g of diazald in 200 mL of diethylether was added slowly. The yellow distillate (a solution of CH_2N_2 in ether) was collected. This was kept in a refrigerator for subsequent derivatizations. In the preparation of diazomethane, nitrosomethyl urea was at times used as a precursor.

4.3.6 Sampling

Sampling sites were chosen in Nairobi (Kenya) in two coffee farms where organochlorine pesticides had been used ten years before the collection of the soil was done. The soils were collected on the surface. They were shipped to Canada in plastic bags and were kept in the laboratory under air dry conditions. Some characteristics of the soils are contained in table 4.1.3.1.

Although EPA recommends the use of 2-mm sieves for pesticide analysis, a 3.8-mm sieve was used in this work in order to get a larger soil aggregate. All samples used in this study were taken without any pretreatment, except for the removal of large sticks, grass and rocks.

When these soil aggregates were spiked, 50-60 g samples were weighed to ± 0.01 g into a 500 mL beaker and the spiking was done as indicated in section 4.3.1.

5 RESULTS AND DISCUSSION

5.1 Soxhlet Extractions

Initial work related to this research was carried out with the Soxhlet apparatus. The cellulose thimbles used were first Soxhlet extracted to find out whether they had contaminants which would have interfered with our results. The extractions were conducted for about 10 hours initially but this was changed to 16 - 20 hours in the latter part of the investigation after it was found that the extractions carried out for only 10 hours were not quantitative. The extractions were carried out with both field contaminated soils and spiked soils. The experimental work done with soil ECSS#7 (see section 4.1.2) from the experimental farm in Ottawa formed the basis of subsequent work with respect to the solvent used, the extraction duration, and the maturation of the spiked soils.

5.1.1 Preliminary Experiments (Soil ECSS#7)

Three Soxhlet apparatus were set up for use with three different solvents: hexane, acetone, and a 50:50 mixture of hexane and acetone. In the latter part of the experimental work comparing the efficiency of the different extraction solvents, varying proportions of hexane and acetone were used.

Recoveries of the six pesticides from the various spiked soils varied from sample to sample with respect to

the solvent used, the duration of the extraction, and the volume ratio of acetone to hexane in those experiments where mixed solvents were used.

The mean recoveries of the six pesticides (see sec.4.1.3) from soil ECSS#7 (see sec.4.1.2) using acetone are shown in table 5.1.1.1. The standard deviations are for the average of a minimum of three separate experiments with a minimum of three analyses per experiment (see sec.5.1.2 for the magnitude of sampling error).

Table 5.1.1.1 Percent Recovery of Chlorinated Pesticides
Using Acetone by Soxhlet Method
(average of 3 independent experiments)

Compound	Spike (ppb)	%Recovery (16 hr)	%Recovery (10 hr)
Dicamba	160	30 ± 10	20±05
2,4-D	184	20 ± 10	N.D*
Lindane	145	90 ± 20	60±10
Picloram	120	70 ± 30	40±10
Dieldrin	115	80 ± 20	50±20
DDT	105	80 ± 20	40±10

N.D* Non-detectable

As seen in table 5.1.1.1, all the pesticides were extracted but the recoveries of the acidic ones were relatively poor. The results obtained with 50:50 mixture of acetone and hexane were similar to those obtained with acetone.

The three acidic pesticides (dicamba, picloram and

2,4-D) were not readily extracted with hexane. These compounds were also not easily quantified. The extracts were methylated with diazomethane (sec.4.3.5), making the acidic pesticides more amenable to GC due to higher volatility of the derivatized material.

The preliminary Soxhlet experiments suggested that acetone would be the best extraction solvent for the pesticides under investigation; it was thus used for subsequent work. The data in table 5.1.1.1 suggest that at least 16 hours of Soxhlet extraction was required for effective extraction. It was also apparent that the acidic pesticides dicamba, picloram and 2,4-D were more difficult to quantitate from the spiked soils.

Soxhlet extractions from unspiked Kenyan soils KE#2 and KE#4 showed the presence of appreciable amounts of chlorinated pesticides (see sec.5.1.2). The presence of lindane and DDT from the Kenyan soil KE#2 and lindane, dieldrin and DDT in the Kenyan soil KE#4 prompted the use of these soils in all subsequent work, as there was then no need for spiking.

Some experiments were still carried out with spiked material in an effort to investigate the difference in the extraction efficiency between the spiked and the naturally contaminated soils. This might shed some light on how the different pesticides are incorporated into the matrix. In the case of pesticide/clay interactions, the pesticides

could be incorporated into the interlamellar spaces of the clay, on clay edge surfaces or simply adsorbed onto the surface.

5.1.2 Soxhlet Extractions of Kenyan Soils

The Soxhlet extractions were carried out on samples of soil KE#2 by the procedure described in sec.4.2.1. The results are shown table 5.1.2.1.

Table 5.1.2.1 Soxhlet Extraction (20 hr) with Acetone of Unspiked Soil KE#2 (ppb)

Experiment set	DDT	Lindane
1	930 $\pm$ 40	930 $\pm$ 60
2	1000 $\pm$ 50	1010 $\pm$ 20
3	990 $\pm$ 60	1000 $\pm$ 50
Mean	970 $\pm$ 40	980 $\pm$ 40

Six analyses (see sec.4.3.3) were carried out on extracts from each experiment. The value appended to it as ($\pm$) shows the standard deviation due to analyses. An example of the GC-ECD chromatogram is shown as figure A.2.1. The uncertainty due to analysis is of the order of 5% for both DDT and lindane as seen in table 5.1.2.1.

The uncertainty due to sampling was in this case of the order of 5%. However, uncertainties of the order of 20% were obtained in other experiments. This could be due to the nonhomogeneity of the soil particles and to nonuniform distribution of the pesticides in the matrix.

It is of significance to mention that the soils were used "as is", without modification except the removal of pebbles and large fragmented plant materials. The large

soil particles with small surface areas must have adsorbed small amount of pesticides which is reflected in the amount extracted in the field contaminated soils. Cai (1990) has also reported that extraction was less efficient from clays because of small particle size and high adsorptive capacity of the soils.

Soxhlet extractions were also carried out with soil KE#4 under the same conditions as with soil KE#2. Table 5.1.2.2 shows the results obtained.

Table 5.1.2.2 Soxhlet Extraction (20 hr) with Acetone of Unspiked KE#4 in ppb

Experiment Set	DDT	Dieldrin	Lindane
1	140 ± 20	2130 ± 200	20 ± 05
2	150 ± 40	1920 ± 110	30 ± 08
3	130 ± 10	1990 ± 130	20 ± 05
Mean	140 ± 10	2010 ± 110	20 ± 05

The data shown for each set of experiments in table 5.1.2.2 is the mean of at least three analyses. An example of the GC-ECD chromatogram is shown in the appendix as figure A.2.2. The relative standard deviation in dieldrin due to the analytical procedure is of the order of 5% while that calculated for DDT is about 7%. The lindane and DDT concentrations were quite low, as shown in the table. It was at times difficult to quantify the small quantities that were extracted in some samples. A criterion of a signal to

noise ratio of three was used to define a detectable signal.

The lindane found in the extracts of soil KE#4 were so small that in some of the subsequent work with KE#4, we neglected analysis of lindane from the unspiked soils. In the spiked soils, lindane was used in quantitation just like the other two pesticides.

5.1.3 Soxhlet Extraction (20 hr) of Spiked Kenyan Soils

Some investigations were carried out of spiked samples (see sec.4.3.1) with the intention of finding out how the extraction efficiency was influenced by the spike level of the pesticides on the soil. Table 5.1.3.1 gives results for soil KE#2 spiked with DDT.

Table 5.1.3.1 Soxhlet Extraction Efficiency of DDT from Spiked Soil KE#2 Using Acetone

Spike level (ppb)	Recovered (ppb)	% Recovery
1030	1780 $\pm$ 60	88
2120	2790 $\pm$ 200	89
4190	4900 $\pm$ 300	94

N.B. The % calculations include the 1 ppm of native contaminant already on the soil.

The data above represents the mean of eight extractions per spike level, with three analyses for each extraction. It shows an upward trend in the extraction efficiency as the spike level is increased. The high extraction efficiencies are not uncommon considering the relatively high spike level used.

Similar results were obtained when lindane was extracted from spiked soils KE#2, although the percentage recovery was lower. The lower recovery could be due to the losses that occur during the concentration steps involved. The higher vapor pressures of lindane relative to that of

DDT at any temperature reflects the relatively lower attractive forces in lindane. At 30°C, the vapor pressure of lindane is 4.5×10^{-5} while that of DDT is 7.2×10^{-7} torr.

In all the results obtained, it was found that the extraction efficiency was always higher for higher spike levels than from the lower spiked soils. This is probably because the active sites can only take a fixed amount of material. Any further material added to the soil would not be as strongly bound to the matrix, and would therefore be more easily desorbed from the soil.

Soil KE#4 was spiked with spiking solution containing dieldrin and DDT (see sec.4.6.1). Lindane was left out as the amount present in the "natively" contaminated soil was very low (see table 5.1.2.2). The results obtained are shown in table 5.1.3.2.

Table 5.1.3.2 Soxhlet Recovery (20 hr) of DDT and Dieldrin in ppb from Spiked Soil KE#4
(Eight independent extractions)

Compound	Spike level	Recovery	% Recovery
DDT	1780	1960±70	102±10
DDT	1860	2100±400	104±20
Dieldrin	2410	4100±220	93±10

M.B. The % recovery is calculated on the bases that there is 150 ppb of DDT and 2000 ppb of dieldrin already on the soil. The variation for DDT is about 20% while that for

dieldrin is about 5% from the above results.

The percentage recovery values above 100 reflect the presence of contaminants in the soil prior to the spiking per se. The results show that all the added material (new spike) was totally removed from the matrix, together with additional amount of the material that was already present on the soil under field conditions (see sec.5.1.2). It is likely that the new spike material is more easily removed from the matrix than the weathered residues which were present in the matrix prior to spiking.

The dieldrin and DDT values obtained in some of the experiments were rather high in comparison with others obtained from some previous Soxhlet extractions of the same soil. The differences in the results were probably due to the inhomogeneity of the soil. Small lumps of soil which are highly contaminated with either or both of the pesticides can be present.

5.2 The Use of Ultrasound in Extractions

5.2.1 Extraction of Unspiked Soils

Sonication was carried out as explained in section 4.2.2 on unspiked soil KE#2. The extractions were run at room temperature (about 20°C) for 15 minutes using acetone. During these 15 minute sonications, variable temperature increases between 10-20°C were noticed. The results shown in table 5.2.1.1 were obtained.

Table 5.2.1.1 Extraction of Unspiked Soil KE#2 Using Ultrasound for 15 minutes
(Four independent experiments)

Data Set	DDT (ppb)	Lindane (ppb)
1	690 ± 20	910 ± 40
2	640 ± 40	610 ± 20
3	760 ± 30	720 ± 30
4	780 ± 30	800 ± 30
Mean	720 ± 60	760 ± 130

Investigations on soil KE#2 were also carried out to determine the effect of time on the extraction efficiency. The experiments were carried out under similar conditions as above for 20, 40 and 60 minutes. The results shown in table 5.2.1.2 were obtained.

Table 5.2.1.2 Effect of Sonication Time on The Recovery of DDT from Unspiked Soil KE#2 Using Acetone

Time in Minutes	20	40	60
DDT Recovered (ppb)	620±50	820±30	980±20

The data in the previous table is a mean of four independent experiments. Although the results show an upward trend in the extraction efficiency with time, it is clear that the major part of the contaminant was removed in the first extraction. Slight increases in the extraction at longer time intervals with ultrasound have also been reported by Mason et al.(1994) in the study of enhanced extraction of tannins from tea solids.

Unspiked soil KE#4 was sonicated for two different times at room temperature conditions using acetone. The results are shown in table 5.2.1.3.

Table 5.2.1.3 Sonication of Unspiked KE#4 for Different Times Using Acetone at 20°C
(Mean of at least 5 independent experiments)

Time (min)	Lindane (ppb)	Dieldrin (ppb)	DDT (ppb)
5	40±04	2140±220	180±40
30	13±02	2420±200	190±10

When sonication was carried out on this unspiked soil

for a longer time period, it was found that the amount of dieldrin and DDT obtained had increased relative to the results obtained for shorter time periods, as with the case of table 5.2.1.2. However, the amount of lindane decreased to such an extent that it was in some cases difficult to quantify. This could be due to volatilization. During the sonication it was found that the temperature rise in the reaction vessel was of the order of 15-20°C. This rise in temperature could have been sufficient to vaporise some lindane.

Spectrograde acetone contains approximately 0.5% of water. It is therefore likely that this water breaks down into hydrogen and hydroxyl radicals which would react with the available lindane. This might contribute to the destruction of lindane; thereby contributing to the loss.

In an effort to find out what effect temperature had on the recovery of a pesticide, a series of experiments was done. Each set of experiments was done under controlled temperature conditions using a waterbath. The results shown in table 5.2.1.4 were obtained.

Table 5.2.1.4 Recovery of Lindane from Soil KE#4 under Sonication (20 min) at Different Temperatures Using Acetone
(Four separate experiments)

Temp. °C	20	35	40	50
Recovery	25±04	23±05	15±02	11±03

Results contained in table 5.2.1.4 show that sonication was most effective at the lowest temperature used.

Ultrasound has a greater influence on extraction at lower temperatures where the energy generated upon cavitation bubble collapse is greater (Mason and Zhao, 1994). The decrease in the extraction efficiency with increase in temperature could be due to the volatility of lindane; to a decreased effectiveness of ultrasound; reaction with radicals produced by the dissociation of water or all the foregoing combined. In order to investigate this further, some experiments were carried out with spiked acetone solutions without soil (see section 5.2.3).

5.2.2 Sonication of Spiked KE#4

Between 1-3 grams of soil KE#4 was sonicated as explained in section 4.2.2 after it had been spiked with an acetone solution containing lindane, DDT and dieldrin. The spiking process had been carried out as shown in section 4.3.1. The spike levels used in the experiments are given in table 5.2.2.1.

Table 5.2.2.1 Recovery of Lindane, DDT and Dieldrin under Sonication from Spiked Soil KE#4 Using Acetone for 15 minutes
(Three independent extractions)

Compound	Spike (ppb)	Native Contaminant	Recovery (ppb)	Total % Recovery
Lindane	2900	40±04	2690±200	91.5±08
DDT	3300	180±40	3130±350	90.0±12
Dieldrin	5100	2420±200	9000±40	119.7±05

N.B. The native contaminants are based on 5 minutes recovery for lindane and DDT respectively and 30 minutes for dieldrin extraction.

The above results show very high recovery rates in all the experiments carried out. It is not uncommon to have high recoveries due to the fact that the spiked material is likely to be more loosely adsorbed onto the matrix than the "native" contaminants. The latter would preferentially occupy the strongest (adsorption) sites within the soil matrix.

The spike levels used in these experiments may be too high to be of realistic use in assessing extraction effectiveness. The high spike levels used were in conformity to other works reported in the literature. The unspiked soil had about 2420 ppb of dieldrin extracted (table 5.2.1.3). The recovery of dieldrin from the spiked sample was found to be 9000 ppb, implying a "native" contamination of 3900 ppb. This is far in excess of the values obtained in the major part of this work. This large value was of concern and subsequent experiments with the same spiked soil were carried out to ascertain the validity of the obtained results. It was found that the values obtained were reasonable and ranged between 8500 ppb and 9450 ppb.

Despite the high dieldrin results obtained in these experiments, the results reflect an important indicator to the fact that the soil as a matrix, in unmodified form, has a very high degree of inhomogeneity. The concentration of the contaminants within a soil sample can have wide and varied implications in the analysis. It is also possible that the spiking process (see section 4.3.1) releases more of the field contaminants in the soaking phase (section 5.5). Alterations in the matrix structure have been observed in previous studies (Castrol et al., 1994).

5.2.3 Sonication of Spiked Acetone Without Soil

One mL of an acetone solution containing 1450, 1090, and 2190 ppb of lindane, dieldrin and DDT respectively was added to 50 mL of acetone. The resulting solution was sonicated for 15 minutes, after which the extract was concentrated in a rotary evaporator.

The results in table 5.2.3.1 reflect some loss due to either volatilization or formation of new products from the destruction of the pesticides during the sonication process. Some volatilization is possible as there was increase in temperature of between fifteen and twenty degrees centigrade during a 15 minute sonication. Sonochemical destruction of organochlorine compounds, such as chlorobenzene, have been observed previously (Entezari and Kruus, 1994). Ultrasound has also been effective in the destruction of methylene chloride, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene in variable concentrations (Cheung et al., 1991).

Table 5.2.3.1 Effect of Sonication of Spiked Acetone Without Soil at 20°C (ppb) for 15 Minutes
(4 Independent extractions)

Spike level	Lindane (ppb)	Dieldrin (ppb)	DDT (ppb)
Initial	29.0	21.8	43.8
Final	19±03	18±0.5	32±04
% Loss	34.5	17.4	26.9

The results show that sonication time should be determined in the optimization stage so that it is long enough for effective extraction, yet short enough to minimize volatilization or reaction losses. Effective extractions should be carried out at as low temperatures as is practically feasible and for optimized time.

5.3 Supercritical Fluid Extraction

Effective SFE is governed by the interplay of the attractive forces between the analyte and the fluid, the interaction between the fluid and the matrix, and between the analyte and the matrix. These interactions constitute what has been termed "the SFE triangle" in the SFE literature (Clifford, 1993).

The work reported here was carried out with the use of supercritical fluid carbon dioxide which has an attractive combination of properties for extraction purposes especially for non-polar pollutants. Extractions were done which focused on the recovery of the three pesticides from the two Kenyan soils. Most of the work was done using pure supercritical carbon dioxide, but a few experiments were done using modified supercritical carbon dioxide. The modifier used was methanol. These latter experiments were done at the Experimental Farm in Ottawa.

5.3.1 SFE of Unspiked Soil KE#2

Supercritical fluid extraction of soil KE#2 was carried out at 40°C and 400 atm, giving a supercritical fluid density of 0.958 g mL⁻¹. The extraction cell was filled with 4.5 g of soil; connected to the SFE equipment and brought to the set pressure before equilibration. The whole assembly was equilibrated in the thermostat for 15 minutes. Methanol was used as the collection solvent for three

extractions and acetone for four extractions. The extractions were each for 30 minutes duration, with a flow rate of 0.3 mL/min of SF.

The results obtained with these two collecting solvents are shown in table 5.3.1.1.

Table 5.3.1.1 SFE of Unspiked Soil KE#2 in ppb Using Supercritical CO₂ (T=40°C; p=400 atm ρ =0.958 g mL⁻¹)

Collection Solvent	DDT Recovered	Lindane Recovered
Acetone	900 $\pm$ 200	850 $\pm$ 100
Methanol	1150 $\pm$ 140	820 $\pm$ 80

Experiments were done under conditions similar to the above but using methylene chloride as the collection solvent. There was too much clogging of the restrictor when this solvent was used, so that the results were unreliable. This illustrates the importance of the collection solvent in SFE.

In order to determine the effect of time on the extractability of DDT from the soil, about 3.5 g of soil KE#2 were put into a 5 mL extraction cell and extracted with unmodified supercritical carbon dioxide using the Suprex SFE 50. The extracts were collected at 15 minute intervals for 120 minutes. These data are presented in figure 5.3.1.1. They show that the extraction curve attains a plateau in about 90 minutes. The data in table 5.3.1.1 are thus not for an exhaustive extraction. Since the

extractions were carried out for 30 minutes, figure 5.3.1.1 suggests that only about half of the DDT was extracted.

In the literature, it is often claimed that 20 minutes is a sufficient time for completion of an SFE. With some matrices, contaminant removal is difficult and a 20 minute exhaustive extraction may be overly optimistic.

Figure 5.3.1.1 Variation of DDT Extraction Efficiency with Time from Soil KE#2 Using Supercritical CO₂

5.3.2 SFE of Unspiked KE#4

About 4.5 g of soil KE#4 were weighed into the extraction cell. The temperature and pressure of the Suprex SFE 50 were adjusted to 40°C and 400 atm of pressure respectively. After the pump had been filled with the supercritical fluid CO₂, equilibration was established before extraction was started. Approximately 15 minutes were required for equilibration. The extraction was then carried out for 180 minutes during which different fractions of extracts were collected at 30 minute intervals. The experiment was repeated four times. The results obtained are shown in figure 5.3.2.1.

Although the amount of dieldrin present in this soil is not known with certainty, the results obtained with Soxhlet and sonication suggest that the amount ranges between 2.0-2.5 ppm. The data in the figure suggest that more than 50% of the analyte is extracted within the first 30 minutes extraction. Note however that methanol modified CO₂ extraction at 125°C showed the presence of 6000 ppb (section 5.3.5). Thus a modifier is required for complete SFE of soil KE#4.

The SFE process is governed by the solubility of the solute in the supercritical fluid, the diffusion of the supercritical fluid into the matrix and the solute out of the matrix; and the solute matrix interactions. Although the solubility of the analyte is not limiting, it seems that in

the initial stage of the SFE the extraction is dependent on the solubility of the analyte in the fluid, while the subsequent extractions must be matrix controlled.

It takes time for the analytes enclosed within the matrix to make their way out of the matrix into the supercritical fluid; once in the supercritical fluid, the analytes must be effectively swept out into the collection solvent. The resistance to the foregoing mass transfer phenomena could possibly be the cause for the decline in recovery with time.

Figure 5.3.2.1 SFE Time Dependent Extraction of Dieldrin from Unspiked Soil KE#4

($T = 40^{\circ}\text{C}$; $\rho = 0.958 \text{ g mL}^{-1}$, $p = 400 \text{ atm}$).
(Each data point is a mean of four experiments)

5.3.3 SFE of Spiked Soils

Table 5.3.3.1 shows the variation of extraction from the field contaminated soil KE#2 and spiked samples. It also shows the results for the extraction of soil KE#2 which had been spiked with lindane and DDT at a spike level of 4200 ppb and 5200 ppb respectively and subjected to SFE after on one of incubation before extraction.

Table 5.3.3.1 SFE Recovery of DDT and Lindane (ppb) from Spiked and Unspiked Soil KE#2 (40°C., 400 atm., density 0.958g mL⁻¹)
(Each set of data is a mean of four experiments)

Sample type	Spike level		Recovery in ppb	
	DDT	Lindane	DDT	Lindane
No Spike	-----	-----	900±200	850±100
Spiked	1030	1290	1670±80	1590±60
Spiked	5220	4220	5600±200	5100±200
Incubated	5220	4220	5450±80	4700±100

The incubated spiked samples were extracted for 20 minutes as compared to 15 minutes for the other results shown. Nevertheless, the amount of lindane recovered is significantly lowered.

The aging process during the incubation period may thus facilitate the binding of the lindane more strongly to the soil matrix. Lindane could also have reacted and changed to other forms aerobically. A steady state is not fully established if extraction is carried out immediately after

spiking. The spiked material is simply washed off from the matrix and this would account for the high extraction efficiencies that are reported in the literature.

Supercritical fluid extractions of unspiked and spiked KE#4 were carried out at 40°C, pressure 400 atm (a density of 0.958 g mL⁻¹), and a flow rate of about 0.30 mL/min. The experiments were run for 30 minutes using 3.5 g of the spiked soil for each experiment. The spike levels used were 1480 ppb of lindane, 1680 ppb DDT and 2610 ppb of dieldrin. The results are shown in table 5.3.3.2.

Table 5.3.3.2 Recovery of Lindane, DDT and Dieldrin from Soil KE#4 Using Supercritical CO₂
(Each set of data is a mean of 3 experiments)

Spike level	Lindane	DDT	Dieldrin
Unspiked	N.D	60±10	2250±400
Spiked	1750±60	2200±100	3800±300

Since spiked samples are known to be often less retained on environmental matrices than native contaminants, the efficiency of the extraction methods can be overestimated when based on recovery studies from spiked samples. The data in tables 5.3.3.1 and 5.3.3.2 suggest that the extraction efficiency of analytes is highly dependent on the nature of the matrix under investigation. The recovery from soil KE#2 was significantly greater than from soil KE#4.

5.3.4 SFE of KE#2 with Methanol Modified Carbon Dioxide

Unspiked soil KE#2 was extracted with the Suprex 50 under moderate conditions: 40°C, 400 atm and at a density of 0.958 g mL⁻¹. No modifier was used. Table 5.3.4.1 shows the results.

Further work was done at Agriculture Canada with a modified Suprex SFE 250 (Prepmaster). This instrument is similar to the originally used SFE 50 but is equipped with an additional pump for modifier addition. Although the instrument can be used to carry out four different extractions simultaneously, only one extraction cell was used during the extractions for which the results are reported. The following conditions were used: flow rate 3.5 mL/min; density 0.603 g mL⁻¹; methanol (modifier) 10 mol%; temperature 150°C. The results of extraction of KE#2 are also shown in table 5.3.4.1.

Table 5.3.4.1 SFE Comparison of Extraction Efficiency Using Supercritical CO₂ and Supercritical CO₂ + CH₃OH from Unspiked KE#2 (ppb)
(Extraction conditions given in the text)

Compound	Pure CO ₂	CO ₂ + CH ₃ OH
DDT	900 ± 200	1630 ± 400
Lindane	850 ± 100	810 ± 20

These results show a marked increase in the extraction efficiency of DDT with a methanol modifier. This increased

efficiency might be the result of an increased solvating power of the mixed fluid and/or a preferential adsorption of methanol on the active sites on the soil matrix or to both. The extracted analytes were collected in 5 mL of methanol which was contained in a beaker of water at room temperature.

The high temperature involved could also have played a role in the desorption of the pesticide from the matrix. The adsorption of DDT and other pesticides in soil decreases with increasing temperature. It is therefore likely that the extraction of DDT was enhanced at high temperatures as long as the decreased adsorption is not hindered by a decrease in the extraction fluid density with subsequent reduction of the solvating power of the supercritical fluid. There might also have been a reduction in the adsorption of methanol at higher temperature.

All the parameters discussed in the above paragraphs must be considered before generalizing on the effect of temperature on each of the pesticides under investigation. The nature and character of the soil and the interaction between the pesticides and the soil matrix must also be considered.

The results for DDT shown in table 5.5.4.1 are similar to results obtained from soils by Burk (1990); Cai (1990) and by Hoefler (1992). The improvement in the extraction efficiency of organochlorines when a small amount of

methanol was added to the supercritical CO₂ has also been reported by Dooley et al.(1992). However, work carried out by Liu et al.(1991) indicated a very low extraction yield of DDT from a spiked soil.

The extraction efficiency of lindane with methanol modified CO₂ in the above experiments showed no significant increase. The high fluid flow resulted in aerosol formation; this could also have contributed to some loss due to inefficient trapping, as lindane is more volatile than DDT. The "SFE triangle" for lindane might be different from that of DDT and hence the different behavior in the extraction efficiency.

5.3.5 SFE of KE#4 with Methanol as Modifier

Some extractions of soil KE#4 were done using Agriculture Canada's Suprex Prepmaster (see sec.5.3.4). The experiments were carried out for 30 minutes. The data obtained for unspiked and spiked soil KE#4 is shown in table 5.3.5.1.

Table 5.3.5.1 SFE Recovery of Lindane, DDT and Dieldrin from Spiked Soil KE#4 Using SFCO₂ Modified with 30 Mol% Methanol (p =400 atm., temp = 125°C, ρ =0.63 g mL⁻¹)
(The values are a mean of three separate extractions)

Compound	Lindane	DDT	Dieldrin
Unspiked	25±04	200±20	6200±50
Spike level	1480	1680	2610
Recovery	1350±105	1490±60	8060±210

The data presented above shows that the removal of lindane and DDT from the spiked soil KE#4 was reasonably complete. However, a much greater amount of dieldrin was detected in soil KE#4 using methanol as a modifier and a higher temperature. The extraction methods used previously were unable to remove a part of the dieldrin. An exception was the sonication of spiked KE#4 (sec.5.2.2) which suggested a higher level.

It is likely that the high temperature involved with the modified supercritical fluid extraction has a more important role in the desorption process and the whole procedure might be kinetically controlled by the

elution/desorption process of the analytes. The high temperatures used in these experiments contribute to the desorption of the pesticides from the matrix. This begins to resemble thermal desorption (see section 2.5). The overall removal of the pesticides might be facilitated by both the desorption and the solubility of the analytes in the supercritical fluids.

5.4 High Temperature Distillation (HTD)

The results reported here are based on extraction work from two Kenyan soils which have been referred to as KE#2 and KE#4 in the previous section. The experiments were carried out with the field contaminated soils without any modification. The same soils were also used after being spiked with the pesticides under investigation. The work was carried out with the aim to finding out how strongly the different pesticides were held to the matrix. This could give data that might also be of value for soil remediation purposes.

5.4.1 Temperature Dependence Extraction of Unspiked Soils

Thermal desorption experiments were carried out as indicated in the experimental section with each of the soils under investigation. Helium was passed through the apparatus for about five minutes before heating was begun to avoid oxidation of the material by the oxygen initially present in the tube. Temperature controlled experiments were carried out with about twenty minutes for each temperature step; about 5 minutes were required to reach to the temperature point, which was then maintained constant for about 15 minutes.

The results obtained with unspiked soils KE#2 are shown in figure 5.4.1.1. The results obtained with unspiked KE#4 are shown in table 5.4.1.1.

Figure 5.4.1.1 (HTD) Temperature Dependent Extraction of DDT and Lindane (ppb) from Unspiked Soil KE#2

Note that figure 5.4.1.1 reports the results of experiments where the temperature was increased only to 600°C.

Table 5.4.1.1 Recovery of Lindane, DDT and Dieldrin (ppb)
from Unspiked Soil KE#4 Using HTD

Temp. °C	Lindane	DDT	Dieldrin
0	N.D	N.D	N.D
100	N.D	N.D	N.D
200	20	55±08	350±45
300	30±02	70±05	880±60
400	45±05	90±10	940±50
600	60±09	180±50	980±90
800	60±11	230±35	2100±150
900	N.D	260±45	2890±200

Since the structure of the two soils used were different, the extraction efficiency of one of the pesticides common to both soils was compared. This gave an idea as to how strongly the pesticide was held to each of the matrices. Figure 5.4.1.2 shows that at any temperature, DDT was apparently more tenaciously held to the matrix in soil KE#4 than in soil KE#2. This however can only apply when the pesticide loadings on both soils are equal.

In the experiments reported in figure 5.4.1.1, the temperature was brought up only to 600°C, while for those in figure 5.4.1.2, the temperature was taken up to 900°C. It is obvious that DDT in KE#4 was held more tenaciously than in KE#2.

Figure 5.4.1.2 (HTD) Temperature Dependent Extraction of DDT from Unspiked Soils KE#2 and KE#4 (ppb)
(Each data point is a mean of at least six experiments)

5.4.2 High Temperature Distillation of Spiked KE#2

The results of high temperature distillation of unspiked KE#2 are shown in figure 5.4.1.1. The above type of experiments were repeated using soil KE#2 which had been spiked with the two pesticides. The results obtained are contained in table 5.4.2.1.

Table 5.4.2.1 Recovery of Lindane and DDT from Spiked KE#2

Compound	Spike level (ppb)	Recovery (ppb)
Lindane	1290	1900±220
DDT	1030	2030±120

For effective collection of the desorbed analytes, two traps were used as shown in figure 4.2.4.1. The hexane trap contained 1750±200 ppb of lindane while 150±30 ppb were contained in the acetone trap. The extraction efficiency of lindane was 83%; besides the 1290 ppb spike, 610 ppb of lindane contained in the field contaminated soil was obtained.

In like manner, a set of eight experiments with the spiked DDT were done. The results showed a total recovery of 2030±120 ppb of DDT, implying an extraction efficiency of 91%. Besides the 1030 ppb spike, 1000 ppb of the native contaminant was extracted. Figure 5.4.1.2 suggests that there is a total of approximately 1200 ppb of native DDT on soil KE#2.

Similar experiments were carried out with spiked soil KE#4 but the maximum temperature was maintained at 600°C for about 30 minutes. The results shown in table 5.4.2.1 were obtained. Each data point in the table is a mean of at least four experiments.

Table 5.4.2.2 Recovery of Lindane, DDT and Dieldrin (ppb) from Spiked Soil KE#4 Using HTD

	Lindane	DDT	Dieldrin
Spike level	1570	1780	2760
Temp. °C			
0	0	0	0
100	1360±60	1240±80	1800±200
200	1500±100	1350±100	3200±300
300	1600±100	1500±200	4300±400
400	1610±200	1690±200	4680±350
600	1630±150	1820±250	4750±500

The results shown in table 5.4.2.2 reflect the ease with which spiked material is extracted. In the case of the field contaminated soil, none of the pesticides was desorbed at the 100°C mark (table 5.4.1.1). However, in the case of the spiked material, a large proportion of the spike was removed in the first 100°C. This implies that the spiked material was superficially adsorbed onto the surface and could therefore be easily desorbed from the matrix.

Figure 5.4.2.1 shows a plot of data from tables 5.4.1.1

and 5.4.2.2. It is again obvious that the "native contaminants" on the soil are held more strongly to the soil than the spiked material. Nevertheless, higher temperature was required to remove the last of the spiked dieldrin.

Figure 5.4.2.1 (HTD) Ease of Extraction of Spiked and Unspiked Dieldrin from Soil KE#4

5.5 Soaking and Shaking Experiments

The extraction of the pesticides with the Soxhlet method involved the washing of the matrix with the appropriate solvent for a certain duration of time. It was therefore felt that unspiked soil KE#4 should just be left soaking in a beaker of acetone in an endeavor to find out how much of the contaminants could be removed simply by soaking the soil. A set of experiments was therefore carried out to find out how much of the native contaminants on the soil would have been dissolved. Another set of experiments were carried out using a wrist action shaker on soil KE#4.

5.5.1 Soaking Experiments

3.5 g of soil KE#4 was weighed into a 250 mL beaker. Approximately 50 mL of spectrograde acetone was added with constant stirring. The beaker and its contents were suspended in a 500 mL beaker containing cold water at room temperature (15°C). This was done to reduce the rate of evaporation of acetone. After 20 hours of incubation, the supernatant was removed, concentrated in a rotary evaporator and subsequently analyzed by GC-ECD. Table 5.5.1.1 gives the results compared to those obtained from Soxhlet extraction (table 5.1.2.2) and from wrist action shaking (sec.5.5.2). In some of the experiments carried out, lindane could not be detected.

Table 5.5.1.1 Relative Extraction Efficiency of Lindane, DDT and Dieldrin (ppb) from Soil KE#4 by Soxhlet (20 hr) and Soaking Methods

Method	Lindane	DDT	Dieldrin
Soxhlet	20±05	140±10	2000±100
Soaking	20±05	190±30	1800±400
Shaking	30±03	270±20	2800±300

The extraction efficiency from soaking is essentially the same as that obtained by Soxhlet.

A "soaking" experiment was also carried out for soil KE#2 spiked with 4200 ppb of DDT. The recovery was 3490 ppb, i.e. about 80% of the 4200 ppb was recovered simply by leaving the spiked soil in contact with acetone.

The contact time between the matrix and the solvent has a very important role; this was noted in some of the Soxhlet experiments. The Soxhlet apparatus with shorter cycle times per hour (more contact time between the matrix and the solvent) always gave more of the pesticides under investigation. The results of the experiments described in sec.5.5.2 further illustrate the importance of contact time.

5.5.2 Shaking Experiments

Between 1.80 - 3.50 g of unspiked soil KE#4 were put in a centrifuge tube containing 40 - 50 mL of acetone. The soils were shaken with the help of a wrist action shaker for about 13 hours. The material was then centrifuged for 25

minutes at 38000 rpm. After the first supernatant solution was removed for analysis, more acetone was added to the soil, and the tube was shaken with the wrist action shaker for a further 13 hours. The procedure was repeated two more times with the same soil sample. The supernatant was then concentrated in a rotary evaporator and was subsequently analyzed by means of GC-ECD. The results obtained are shown in table 5.5.2.1.

Table 5.5.2.1 Recovery of Lindane, DDT and Dieldrin (ppb)
from Soil KE#4 Using Wrist Action Shaker
(Each data point is a mean of 4 experiments)

Time (hr)	13	26	39	52
Lindane	30	N.D	N.D	N.D
DDT	150±08	70±10	30±10	20±05
Dieldrin	1045±100	840±70	600±30	340±60

The amount of each pesticide extracted was found to decline with any subsequent addition of new solvent. The cumulative totals are shown in table 5.5.1.1. More dieldrin is extracted with the shaking experiments than with soaking or Soxhlet. This may be due to greater fragmentation of the soil aggregates with the shaking. After 52 hours the soil was in the form of finer particles than initially.

5.6. Comparison of Extraction Methods

5.6.1 Overview of Methods Used

The objective of this work was to compare the extraction efficiency of the previously mentioned methods. In pursuit of this goal, many experiments were carried out with the four main methods. In addition, a few experiments with soaking and shaking methods (sec.5.5) were incorporated into the schedule of work in an effort to understand better what is actually involved in the extraction process.

The extraction processes with three of the main methods (Soxhlet, SFE and Sonication) involved a leaching process where the analytes were removed from the matrix surfaces, transferred into the solvent and eventually carried into the collection solvent. There is also a diffusion process involved, where the analytes move out of the interior of the matrix to the surface. In addition to the above, extraction with the sonication method may involve the formation of jet streams which enhance the erosion process on the solid-liquid boundary. Many of the foregoing extraction processes are also encountered in the soaking and shaking experiments.

The HTD extraction process involves an indirect removal of the analytes of interest by heating the matrix and sweeping the desorbed analytes with an inert gas such as helium. The desorbed material also encounters kinetic and diffusional limitations especially when large amounts of the matrix (soil) are involved. The desorbed material is

normally collected in a solvent which is subsequently analyzed for the pesticides.

It is of significance to note that dynamic SFE at 125°C at a density of $\approx 0.63 \text{ g mL}^{-1}$ of methanol modified supercritical fluid starts to resemble HTD, and was found to approach HTD in its extraction efficiency (see sec.5.3.5).

Although the extraction processes involved are similar in almost all the methods, there were some differences in the efficiencies of the methods. The following section highlights some of the differences which were encountered.

5.6.2 Re-extraction of Soxhlet Extracted Materials

When the residue material from some Soxhlet extracted soil was re-extracted using supercritical fluid CO_2 , it was found that traces of DDT and dieldrin could still be detected with the GC-ECD (table 5.6.2.1). The lack of lindane in the re-extraction could be due to total removal of lindane from the matrix during the Soxhlet process, or to the loss of lindane during the extraction processes. The high temperatures attained in the Soxhlet apparatus could also have contributed to the volatilization and subsequent loss.

Table 5.6.2.1 Re-extraction of DDT with HTD from a Soil Residue Pre-Extracted with SFE, Soxhlet and Sonication

Method (ppb)	First Extraction (ppb)	Re-extraction Using HTD (ppb)
SFE	980 $\pm$ 90	50 $\pm$ 10
Soxhlet	910 $\pm$ 90	160 $\pm$ 20
Sonication	950 $\pm$ 80	110 $\pm$ 10
HTD	1140 $\pm$ 70	Not Re-extracted*

N.B* The organic material in the HTD extracted soil was altered considerably. It was thus not possible to re-extract it.

6 SUMMARY AND CONCLUSIONS

6.1 Experiments with Spiked Materials

The question as to the validity of the results obtained with spiked materials has lingered on for a long time. Chiba and Morley (1968) thought that fortification techniques for establishing extraction efficiencies were of questionable value. They had found that extraction efficiencies from five different extraction systems ranged from 91 to 97% for a sandy loam soil fortified with dieldrin ^{14}C in the laboratory but for non-fortified field treated soil only 36 to 67% was extractable.

The addition of spiking materials on soils often involves the addition of the analytes dissolved in organic solvents such as acetone or dichloromethane. The organic solvents with the spike could irreversibly alter the soil properties, which in turn would invariably alter the experimental results. Hawthorne et al. (1993) have indicated that spiking analytes onto heterogeneous environmental matrices such as soils, sludges, and air particulate matter may not be a reliable means of representing the extraction behavior of field contaminated analytes.

The spiked analytes may often be less firmly held on or in the environmental matrices than the field contaminated analytes. This may account for the high extraction efficiencies from spiked materials. The results obtained with the use of spiked materials may therefore be an

overestimation of the recoveries that would be achieved for field contaminated samples.

Our results showed that the use of spiked sample soils gave extraction efficiencies over 100% in some cases (sec. 5.1.3 and sec. 5.4.2). Some of the native contaminant was thus extracted together with the spike.

Easy extraction of spiked material could be due to the fact that the pesticides had not had enough time to be adsorbed onto the matrix and to establish an equilibrium. As the incubation period was increased prior to extraction, the amount extracted of each of the pesticides was found to decrease (table 5.3.3.1). During aging, the pesticides had become more tightly bound to the soil matrix. The pesticides might also have found their way into the interlamellar spaces of the clay particles found in the soil; or they might have been occluded within the matrix. This would offer resistance to the penetration of the extractant fluids. The recovery with SFE could certainly be increased with the use of a modifier as found in sec.5.3.5.

The variation of soil moisture, temperature, and biological activity may also be factors in making the adsorption stronger in "natural contamination".

The apparent discrepancies in extraction efficiencies obtained using the same solvent and samples from the same spiked material (sec. 5.1.2) could be due to the spiking technique (sec. 4.3.1). There could be an uneven

distribution of the pesticides on the matrix during the spiking process.

The spiked material is normally on the surface of the matrix and thus quite easy to remove. Material that might have been lodged within the soil matrix (soil micropores) must not only be desorbed during the extraction, but must also diffuse out of the micropores prior to being swept into the extracting solvent. This makes the removal of these materials diffusion limited. For occluded materials on the other hand, disruption of the soil particles is necessary in order to expose the analytes to the extractant.

6.2 Optimization

Soil is a porous medium and is capable of capturing and accommodating organic compounds from fluids which percolate through it. The organic pollutants are held in the soil pore spaces while the fluids pass on to lower layers of the soil. Depending on the nature of the compounds involved and the characteristics of the soil, the pollutants may be trapped at the soil fluid interface or incorporated into the soil matrix. The amount and the nature of the organic compounds trapped within the matrix will influence the ability to remove these materials from the matrix.

Optimization of the extraction conditions with the use of spiked soils should be done with care. As indicated in sec. 6.1, the results obtained with spiked samples often cannot be effectively used when it comes to optimization of field contaminated soils. Thus actual field contaminated soils should be used despite the problems involved with this.

It is always difficult to determine the ultimate total amount of the pesticides present in a field contaminated soil. Thus the "% recovery" can often not be quoted. More work is thus required to do exhaustive recovery of contaminants from the same sample applying different methods.

6.2.1 Soxhlet

It was found from our preliminary experiments that of the three solvents used in the Soxhlet method, acetone was the best for the soil matrices and contaminants under investigation. In Soxhlet extraction there is continuous washing of the matrix at an elevated temperature during the refluxing process. The high temperature (up to $56.2^{\circ}\text{C}^{760}$ for acetone) increases the solubility of the analytes in the solvent, and promotes the desorption process from the matrix.

It was found that for compounds with high vapor pressures, it was possible to have losses due to vaporization, giving low recoveries. This was demonstrated in the case of lindane. In cases where quantitative recovery is possible with other methods, the use of Soxhlet extraction is inadvisable since it produces a high degree of co-extractives, especially where high boiling solvents are used.

The preliminary Soxhlet experiments showed that the acidic pesticides were not easily removed from the matrix. These acids have very low K_d values. The acidic conditions employed during the extraction might not have been acidic enough for effective desorption. These were difficult to quantitate due to very low extraction efficiencies even after the pesticides had been methylated. It is likely that these pesticides experienced extensive hydrogen bonding the

or were entrapped within the soil matrices. The organic matter in one of the soils used in this work was about 12% while the other soil had only 7% organic content. The organic matter content in a soil has a high influence on the adsorptive capacity of the soil. The soil-pesticide complex must break down during the extraction process.

6.2.2. Ultrasound

This work has shown that the ultrasonic process is a promising and effective method for the removal of pesticides from contaminated soils. The results also show that the extraction efficiency was greater at lower temperatures. At higher temperatures, there were losses, especially of the pesticides with high vapor pressures; this resulted in losses due to volatilization.

It is also possible that losses could be due to chemical reactions that result in the destruction of organochlorine compounds. Work carried out by Livengood et al.(1992) has shown that exposure of CCl_4 solutions to ultrasound in the presence of dissolved air resulted in a decrease of the CCl_4 concentrations in the solutions. They attributed this destruction to bond cleavage of water and of CCl_4 in the collapse of the cavitation bubbles.

It was also found that most of the contaminant was extracted in the first five to fifteen minutes from experiments where extractions were done for different

durations. Extractions using ultrasound need not be done for extended periods of time, as pesticides can be lost through volatilization.

Although not conclusive, it is most likely that effective extraction using ultrasound might be due to more than one mechanism. An increase in the agitation and diffusion rates enhances contact between the solvent and the solid particles, and increases frictional forces due to jet stream formation which raises pesticide erosion from the matrix. The erosion process also reduces the size of the soil particles; this would in turn increase the surface area exposed to erosion. The cavitation process releases enough energy that would tear or disrupt the soil structure resulting in disaggregation of the particles. The increase in the reaction temperature in the reaction cell may contribute somewhat to pesticide desorption. The extraction efficiency is apparently due to a synergistic effect of increased interphase mass transfer, enhanced erosion, and microstreaming which facilitates the leaching of the contaminants from the soil.

Due to higher efficiency of ultrasound at lower temperatures, the method would offer opportunities for effective extraction of thermally labile pesticides. The use of ultrasound for these pesticides would also offer a reasonable challenge to supercritical fluid extraction.

6.2.3 Supercritical Fluid Extraction

This work has shown that supercritical CO₂ extracted the organochlorine pesticides from the two soils fairly effectively. It was however found that the presence of a modifier in the extraction of native contaminated soils increased extraction, as shown in the extraction of dieldrin (sec.5.3.4).

SFE at 400 atm and 125°C, in the presence of methanol as a modifier resulted in very high recoveries of dieldrin from soil KE#4. The methanol modified CO₂ extraction at 125°C showed the presence of 6000 ppb (section 5.3.4). Thus a modifier is required for complete SFE of soil KE#4.

The higher temperature used might facilitate the desorption of dieldrin from the matrix. Since the effect of the extraction temperature is the total of the temperature effect on the solute vapor pressure, on the density of the supercritical fluid, and on the adsorption of the contaminant to the soil, all these parameters must be considered before generalizing on the effect of temperature on each of the pesticides under investigation. The nature and character of the soil and the interaction between the pesticides and the soil matrix must also be evaluated.

This work has also shown that the collection solvent in SFE has a prominent role in the success of the extraction. Higher recoveries were achieved with dieldrin when methanol was used as the collection solvent. When methylene chloride

was used, there was too much clogging of the restrictor and this resulted in unreliable results. Acetone was also found quite satisfactory in our work.

It was found that the type of soil used might have a significant role to play in the extractability of the pesticides from the soil. The extraction of DDT from the two Kenyan soils differed to a certain extent. The amount of the organic matter present in the two soils was different and this could have contributed to the lower recovery in one of the two soils relative to the other. It is likely that DDT adsorbed more strongly to the organic matter in soils. The extent to which phyllosilicates or oxides dominated in the soil might also have influenced the extraction processes but more work in this area is necessary.

The amount of clay present in the soil did not seem to influence the extraction efficiency. However, it was found that complete extraction of the analytes from the matrix was not easily achieved (especially when the extractions were done for 20 minutes). This could be due to irreversible binding of the contaminants within the interlamellar spaces or the occlusion of the pesticides within the soil micropores. This might lead to bound residues resulting in stronger binding of the pesticides to the matrix.

The results obtained in our work also indicated that the short extraction durations used in SFE are unrealistic. A twenty minute extraction was found to be inefficient in

our experiments; longer extraction times were required to come close to a quantitative extraction.

6.2.4 Thermal Desorption (HTD)

High temperature distillation (HTD) or thermal desorption entails indirect supply of heat to the contaminated soil. An inert gas such as helium is passed through from one end of the Lieberg apparatus (sec.4.2.4.1). The use of the inert gas is vital as it eliminates the otherwise oxidative processes which could occur within the reaction vessel.

As the name implies, high temperatures are involved in the extraction process and this method is therefore not intended for compounds that are thermally labile. A high and rapid flow of the gas is necessary to minimize the residence time of the desorbed material, thus preventing re-adsorption of the analytes.

The use of this method in our work resulted in quantitative recoveries of some of the compounds such as DDT and dieldrin but gave low results with lindane (sec.5.4.1). The high vapor pressure of lindane could be responsible for its volatilization losses. The method was found non-selective and produced as much co-extractives as a 16 hours Soxhlet extraction, and sometimes more.

Although the ease of removal of the analytes is matrix dependent, it was found that when soil KE#2 samples were

extracted with the different methods, HTD could still remove a bit more of the analytes on re-extraction of the same samples (sec.5.6).

HTD results can be improved if the desorbed components from a matrix are directly desorbed into the GC for analysis. This would offer similar advantages to on-line SFE which allows desorption of cryogenically collected analytes to be desorbed directly into a GC. The method is simple and minimizes sample handling, which eliminates sample contamination. HTD has been used with adsorbent materials which have been conditioned; this helps to reduce the use of solvents. The conditioned sorbents can be reused, making the method more economically feasible.

6.2.5 Soaking and Shaking Experiments

The results from these experiments demonstrated that the extraction efficiencies obtained with these two methods are similar to those obtained with the Soxhlet extraction method from the same matrix. These two methods are however not as complicated as the Soxhlet method.

The low temperatures (room temperatures) used in the soaking and shaking experiments minimize the losses of the more volatile compounds and also reduce the amount of co-extractives encountered in the Soxhlet method. The amount of co-extractives obtained with the soaking and shaking experiments were relatively lower, as evidenced by a

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comparison of the chromatograms obtained with the three methods (see appendix).

Cumulative results obtained from the Shaking method were apparently more effective than the Soxhlet method. This could be due to multiple extractions which enhance the extraction efficiency through partitioning of the solutes between the matrix and the added new solvent. The shaking experiments could also enhance the fragmentation process of the soil particles and thus expose surfaces where the pesticides might be adsorbed. The solvent would then wash out (erode or leach) the new surface with additional removal of the pesticides.

Although the soaking and shaking experiments are similar to Soxhlet in extraction efficiency, they are more cost effective. However, they use large amounts of hazardous solvents just as the Soxhlet method.

6.3 Comparison of Methods

The Soxhlet extraction method has been regarded as the standard extraction method for a long time, but recent research in residue analysis seems to focus largely on SFE (Lopez-Avila et al., 1992). It seems to be favoured over other extraction methods such as sonication and HTD. This work aimed at comparing the relative efficiencies of these methods when applied to the same samples.

Previous work has been carried out in comparing extraction methods (Lindner and Seidel, 1993; Myer et al., 1992). The results reported here are the first in which as many as four methods have been used for the same sample. This work has also mainly been done with unspiked soils. A few experiments were carried out with spiked samples of the same matrix in order to investigate the differences in the extraction efficiency between spiked and unspiked matrices. Methods comparison reported in literature have used spiked soils (Varita et al., 1994; Knipe et al., 1992; Bartle et al., 1992).

Table 6.3.1 presents a summary of method attributes for each of the four different extraction methods/techniques.

Table 6.3.1 Comparison of the Four Extraction Methods

Aspect	HTD	SFE	SOX	SON
Recovery	Highest	90%	85%	85%
Analysis	Poorest	Best	Poor	Poor
Capital	\$5,000	\$30,000	\$750	\$5,000
Time	1.5 hr	30-60 min	10-20 hr	1 hr
Wastes	High	Low	High	Medium

6.3.1 Recovery

Although quantitative recovery seemingly makes a method satisfactory, a comparison with other methods may not always be valid. Less quantitative recoveries may reflect lack of experimental control parameters which might enhance degradation and volatilization of the analytes under investigation.

When extraction efficiency of the four methods were compared with respect to soil KE#2, HTD extracted the greatest amount of contaminant, but the difference is only of the order of magnitude of the variation caused by sampling. In order to test this, some unspiked soil samples were re-extracted with HTD after having been subjected to one of the other three extraction processes. As shown in table 5.6.2.1, HTD extracted further DDT from all the samples previously extracted by SFE, Soxhlet or sonication.

HTD completely destroys the integrity of the soil when carried to higher temperatures. There was therefore no re-

extraction of a soil that was previously extracted with HTD. When soil KE#4 was extracted using methanol modified CO₂, at 400 atm and a temperature of 125°C, SFE was found to approach HTD in extraction efficiency.

6.3.2 Analysis

The term analysis as used in table 6.3.1 is meant to indicate the difficulties in analysis of the extracts due to interferences of co-extracted substances. The extracts obtained with Soxhlet, sonication and HTD methods had many contaminants in them. SFE extracts were cleaner and identification of GC peaks was often straight-forward. Sample chromatograms obtained with each of the methods are shown in appendix 2.

With advanced analytical equipment, the presence of numerous co-extracted compounds is however not a major problem as shown by the chromatograms obtained with SFE extracts which were very clean.

6.3.3 Costs

The cost per analysis in SFE and Soxhlet were compared by Myers et al. in 1992. They found that it cost \$22.60 for a Soxhlet analysis relative to \$15.85 for an SFE.

The data in table 6.3.1 refer to capital costs of equipment. The costs of SFE equipment is variable, and can be as low as \$5,000 for a "home-made" apparatus (Burk and

Kruus, 1990) or as high as \$60,000 for a highly automated commercial apparatus. A cost of \$30,000 is set in the summary table.

Equipment for analysis must of course be available in addition to the equipment for extraction. This can add as much as \$70,000 to any one of the methods if a sophisticated GC-MS is used.

6.3.4 Time

The figure in table 6.3.1 is the approximate time of the extraction procedure, including steps required to prepare the sample for injection into a GC. The subsequent analysis time would be the same for each method, unless there are difficulties due to interferences.

As indicated in sec.5.3.2, SFE times (15 -20 min) reported in the literature is apparently underestimated. It was found that more time is necessary for quantitative extraction.

6.3.5 Wastes

Waste solvents are becoming of more concern, especially if these are chlorinated organic compounds. SFE requires only a few mL of solvent, while Soxhlet requires over 50 mL. The amount of solvent used in sonication depends on the size of the probe; it could be less than the 50 mL used in these experiments.

There are minimal disposal problems in SFE; its contribution to environmental hazards are also minimal.

6.3.6 Assessment of SFE Relative to the Other methods

This work has shown that the extraction efficiencies with the methods under investigation are very similar. Although SFE dramatically reduces the extraction time and minimizes exposure of personnel to hazardous solvents, it still offers difficulties due to clogging of restrictors and manipulations in extract collection.

With respect to extractions from soils, it is difficult to achieve total removal of the contaminants due to irreversible binding of some of the components to the matrix. The variability in soil compositions make optimization for extraction purposes difficult; for parameters used with one type of soil may not be equally applicable to another type of soil. Irrespective of the method being used, the role of the matrix in the extraction should always be given a priority for optimization purposes.

Folie et al.(1986), Griest et al.(1980) and Junk et al.(1986) have indicated that conventional methods take several hours to complete, require relatively large volumes of solvent and subsequent concentration steps are necessary. These methods may also yield incomplete recovery and/or degradation of analyte species. SFE on the other hand is used for almost all types of compounds including those which

are thermally labile compounds.

Despite the upsurge in SFE, it is imperative to heed what Bartle and Clifford said in 1991, i.e "SFE must not be considered as a magic technique but as an important weapon in the analyst's armoury".

7 RECOMMENDATIONS FOR FUTURE WORK

Some aspects of this work have raised interesting questions that warrant further experimental work. The major areas where further work is deemed necessary are the outlined below.

** The HTD experiments have used helium as the sweeping gas in the desorption processes. These experiments can be further investigated by using the same extraction set up as in section 4.2.4 but using vapor from heated methanol in carbon dioxide instead of helium. High temperature SFE starts to resemble HTD in that a fluid is passed over a heated sample of the matrix.

** Work in the desorption of pesticides at different temperatures using HTD can be extended to incorporate the calculation of enthalpies of adsorption using the Arrhenius equation. Experimentally, the rate of desorption might be expected to vary with temperature as $K = A.e^{-E_a/RT}$. A is the pre-exponential factor or frequency factor and E_a is the activation energy.

A and E_a can be assumed to be temperature independent when the temperature range under investigation is not too large.

** The use of supercritical CO_2 under a helium head should be investigated due to the solubility of helium in supercritical CO_2 . Helium dissolves in the carbon dioxide to the extent of 1% by volume. By altering the helium head pressure in the CO_2 tank, the density of the supercritical

CO₂ can be altered when pressure is kept constant. The extraction efficiency for the pesticides under investigation with the amount of helium in the supercritical fluid CO₂ would form an interesting study.

** A greater range of contaminated soils would constitute an interesting study due to the structural differences involved.

** More experiments using the shaking method may prove this method to be adequate and economical.

REFERENCES

- Afghan, B.K.; Carron, J.; Goulden, P.D.; Lawrence, J.; Leger, D.; Onuska, F.; Sherry, J.; Wilkinson, R. **Can.J.Chem.** 65:1086 (1987)
- Alva, A.K.; Singh M. **Bull.Environ.Contam.Toxicol.** 45:365 (1990)
- Andersen, R.A.; Knoles, D.E.; Richter, B.E.; Later, D.W. **Research Paper, Lee Scientific, Utah, U.S.A.** (1989)
- Andrews, A.T.; Ahlet, R.C.; Kossan, D.S. **Environ.Prog.** 9(4):204 (1990)
- Bailey, G.W.; White, J.L. **Residue Rev.** 32:29-92 (1970)
- Ball, W.P.; Roberts, P.V. **Environ.Sci.Technol.** 25:1223 (1991)
- Bartle, K.D.; Ashraf, S.; Clifford, A.A.; Moulder, R. **J.High Res.Chromatogr.** 14:29-32 (1991)
- Bartle, K.D.; Clifford, A.A.; Jafar, S.A.; Shilstone, G.F. **J.Phys.Chem.Ref.Data** 20:713 (1991)
- Bjorseth, A. **Anal.Chim.Acta** 94:21 (1977)
- Bove, J.L.; Kukreja, V.P. **Environ.lett.** 10:89 (1975)
- Bowers, W.D.; Hawley-Fedder, R.A.; Parsons, L.; Karasek, F.W. **J.Chromatogr.** 269:161 (1983)
- Brady, N.C. **Ind.Eng.Chem.Res.** 26:261 (1987)
- Briggs, G.G. **J.Agric.Food Chem.** 29:1050 (1981)
- Broddin, G.; VanVaech, L.; Cauwenberghe, K. **Atmos Environ.** 11:1061 (1977)
- Brogie, H. **Chem.Ind. (London)**, 19 June (1982)
- Brunauer, S.; Emmett, R.H.; Teller, E. **J.Am.Chem.Soc.** 60:309 (1938)
- Bruno, J.T.; Ely, J.F. **Supercritical Fluid Technology: Reviews in Modern Theory and Applications** (1991)
- Burk, R.C. **PhD Thesis, Carleton University** (1990)

- Cai, J.Y. **Supercritical Fluid Extraction of Toxic Organics from Soils, Dissertation** (1990)
- Chendke, P.K; Fogler, H.S. **Ultrasonics** 13:31(1975)
- Cheung, H.M.; Bhatnagar, A.; Jansen, G. **Environ.Sci.Technol.** 25(8), (1991)
- Chiba, M; Morley, H.V. **J.Agric.Food Chem.**16(6):916 1968.
- Chiou, C.T.; Shoup, T.D. **Environ.Sci.Technol.**19:1196-1200 (1985)
- Coover, M.D.; Sims, R.; Doucette, W. **J.Assoc.Off.Anal.Chem.**70(6):1018 (1987)
- Cortes, H.J.; Green, L.S.; Campbell, R.M. **Anal.Chem.**,63:2719 (1991)
- Cotterill, E.G. **Pestic.Sci.**11:23 (1980)
- Cotton, N.J.; Raynor, M.W.;Bartle, K.D. In **Supercritical Fluid Extraction and its Use in Chromatographic Sample Preparation**; Westwood, S.A., Ed.; Blackie:Glasgow, (1992)
- Crouch, R.L.; Hawley-Fedder, R.A.; Parsons, M.L. **J.Chromatogr.**303:53 (1984)
- Cupps, J.A.; Jackson, J.O. in **Carsinogenesis**, Vol.3, Polynuclear aromatic hydrocarbons, Jones and Freudenthal (eds), Ranven Press, N.Y., p178 (1978)
- Dandge, D.K.; Heller, J.P.; Wilson, K.V. **Ind.Eng.Chem.Prod.Res.Dev.**24:162 (1985)
- Deroos, F.L.; Biking, M.K.I. **Chemos.**20:1355 (1990)
- Dooley, K.M.; Ghanasghi, D.; Knopf, F.C.; Gambrell, R.P. **Environ.Prog.**9:197 (1990)
- Dragun, J. "**Soil Chemistry of Hazardous Materials**," Hazardous Material Control Research Institute, Silver Springs, Maryland, (1988)
- Ellis, J.; Phillip, C.T. **Anal.Chem.**58:258-261 (1986)
- Ensminger, L.E.; Giesecking, J.L. **Soil Sci.**53:203 (1942)
- Entezari, M.H.; Kruus, P. **Ultrasonics Sonochemistry** 1(2):575(1994)

- Famhy, T.M.; Paulaitis, M.E.; Johnson, D.M.; McNally, M.E.P. **Anal.Chem.**65:1462-1469 (1993)
- Fassel, V.A.; D'Silva, A.P.; Renkes, G.D.; Walters, S.N.; Woo, C.S.; Iles, M.K. **Anal.Chem.**55:2229 (1983)
- Flint, E.B.; Suslick, K.S. **Science** 253:1397(1991)
- Forbes, S. **Anal.Chim.Acta** 196:75 (1987)
- France, J.E.; King, J.W. **J.Assoc.Off.Anal.Chem.**74(6):1013-1016 (1991)
- Freed, V.H.; Haque, R. in "Environmental Dynamics of Pesticides" edited by R.Haque and V.H.Freed (1973)
- Freed, V.H.; Haque, R. **Environmental Dynamics of Pesticides**, (1974)
- Gere, D.R. "Selective Extraction of Cholestrol from fats and butter cookies and other baked food products", Paper presented at Midwest AOAC Annual Meeting, Champaign, Illinois (1992)
- Gibbons, J.J.; Sundarajan, B. **Am.Lab.**20:38 (1988)
- Giddings, J.C.; Myers, M.N.; McLaren, L.; Keller, R.A. **Science** 162:67 (1968)
- Grosjean, D. **W.M Keck Labs. Environ. Eng.**, California Inst. Technol., Pasadena, Ca. 91125 (1986)
- Glotfelty, D.E.; Schomburg, C.J. **SSSA Special Publication No.22**:181-208 (1989)
- Golden, C.; Sawichi, E.; **Anal.Lett.**A11:1051 (1978)
- Griest, W.H.; Yeatts, L.B.(Jr); Caton, J.E. **Anal.Chem.**52:199 (1980)
- Hamaker, J.W.; Thomson, J.M. "Organic Chemicals in the Soil Environment" 1:49 C.I.Goring and J.W.Hamaker, Ed., Marcel Dekker, Inc. New York (1972)
- Hassett, J.J.; Banwart, W.L. **SSSA Special Publication No.22**:31-43 (1989) 79. Moore, W.J. **Physical Chemistry** 3rd ed. Prentice Hall, Englewood Cliffs, NJ. p713-716 (1962)
- Harvey, S.D.; Fellows, R.J.; Campbell, J.A.; Cataldo, D.A. **J Chromatogr.**605:227-240 (1992)

- Hawthorn, S.B.; Krieger, M.S.; Miller, D.J.
Anal.Chem.61:736-740 (1989)
- Hawthorne, S.B. **J.Chromatogr.**541:187 (1991)
- Hawthorne, S.B.; Miller, D.J. **J.Chromatogr.Sci.**24:258-264 (1986)
- Hawthorne, S.B.; Miller, D.J. **Anal.Chem.**59:1705 (1987)
- Hawthorn, S.B.; Miller, D.J.; Langenfield, J.J.
ACS Symp.ser.488:165-178 (1992)
- Hawthorn, S.B.; Langenfeld, J.J.; Miller, D.J.;
Pawliszyn, J. **Anal.Chem.**65:338-344 (1993)
- Helling, C.S.; Krivonak, A.E. **J.Agric.Food Chem.**26
(1987)
- Henglein, A. **Ultrasonics** 25:6-16 (1987)
- Hoeftler, F. **Chem Labor.Biotech.**43(7) 1990
- Hills, J.W.; Hill, H.H. **Anal.Chem.**62:2170 (1990)
- Hills, J.W.; Hill, H.H. **J.Chromatogr.Sci.**31:6 (1993)
- Hirata, Y.; Oikamoto, Y. **J.Microcol.Sep.**1:46 (1989)
- Houloubek, I.J.; Maatela, P.; Holoubkova, I.; Korinek, P.;
Bohacek, Z.; Caslavsky, J. **Toxicol.EnvIRON.Chem.**25:137(1990)
- Hovarth, C.; Melander, W. **Am.Lab.**10:17-36 (1978)
- Hubert, P.; Vitzthum, O.G. **Agnew.Chem.Int.Ed.Eng.**17:710
(1978)
- Janda, V. **J.Chromatogr.**479:200 (1989)
- Janda, J.; Bartle, K.D.; Clifford, A.A.
J.Chromatogr.642:283-299 (1993)
- Janda, V.; Kriz, J.; Vejrosta, J.; Bartle, K.D.
J.Chromatogr.669:241 (1994)
- Khan, S.U. **J.Agric.Food Chem.**30:175 (1982)
- King, J.W. **J.Chromatogr.Sci.**27:355 (1989)
- King, J.W.; Ki-Souk Nam **J.Agric.Food Chem.**42:1469 (1994)

- King, J.W.; Hopper, M.C. **J.Assoc.Off.Anal.Chem.**74:661 (1991)
- Klein, A.K. **J.Assoc.Off.Anal.Chem.** 42(3) (1959)
- Kopczynski, S.L. **Anal.Lett.**17(A2):97 (1984)
- Jiann, M. Wu, Huang, H.S.; Livengood, C.D. **Environ.Progress** 11(3):195 (1992)
- Junk, G.A.; Richards, J.J. **Anal.Chem.**58:962-965 (1986)
- Lambert, S.M. **J.Agric.Food Chem.**16:340 (1968)
- Laird, J. **J.Am.Chem.Soc.**40:1361 (1918)
- Lauterborn, W.; Hentschel, W. **Appl.Opt** 23:3263 (1984)
- Levy, J.M.; Cavalier, R.A.; Bosch, T.N.; Tynaski, A.F. **J.Chromatogr.Sci.**27:341-346 (1989)
- Levy, J.M.; Rosselli, A.C.; Storozynsky, E.; Ravey, R.M.; Dolata, L.A.; Ashraf-Khorassani, M. **LC-GC** 10:386-391 (1992)
- Lichtenstein, E.P.; Harris, C.R. **J.Econ.Entomol.**54(5):1038 (1961)
- Lichtenstein, E.P.; Katan, J.; Anderegg, B.N. **J.Agric.Food Chem.**25:43 (1977)
- Lindley, J.; Lorimer, J.P.; Mason, T.J. **Ultrasonics** 24:292 (1986).
- Lopez-Avila, V.; Beckert, W.F. **J.Am.Chem.Soc.**1992
- Liu et.al. **Chemos.**23(8-10) (1991)
- Ma, X.; Mao, J.; Zheng, Z.; Yu, X. **J.Chromatogr.** (1991)
- Mason, T.J.; Lorimer, J.P. **Sonochemistry, Theory, Applications and Uses of Ultrasound in Chemistry**, Ellis Horwood, Chichester, 1989
- Margulis, M.A. **Russian J.Phys.Chem.**59:882 (1985)
- Margulis, M.A. **Ultrasonics** 23:157 (1985).
- McMahon, B.M. **Pesticide Analytical Manual** 1 (1985)

- Mingelgrin, U.; Prost, R. Surface interactions of toxic organic chemicals with minerals p91-135. In Z.Gerstl, Y. Chen, U. Mingelgrin and B. Yaron (eds). **Toxic Organic Chemicals in Porous Media**, Springer-Verlag, New York, N.Y. 1989
- Monin, J.C.; Barth, D.; Perrut, M.; Espitalie, M.; Durand, B. **Org.Geochem.**13(4-6):1079(1987)
- Mortland, M.M. **Adv.Agron.**22:75-119
- Myer, L.J.D.; Damian, J.H.; Liescheski, P.B.; Tehrani, J. **ACS symp.Ser.**488:221-229 (1992)
- Pankow, J.F.; Isabelle, L.M.; Kriestensen, T.J. **Anal.Chem.**54:1815 (1982)
- Papilloud, S.; Haerdi, W. **Chromatographia** 38(7-8):514-519 (1994)
- Pawliszyn, J.; Alexandrou, N. **Anal.Chem.**61:2270-2276 (1989)
- Pawliszyn, J. **J.Chromatogr.Sci.**31:31-37 (1993)
- Pignatello, J.J. **SSSA Special Publication No.**22:45-80 (1989)
- Purcell, J.E.; Downs, H.D.; Ettre, L.S. **Chromatographia** 8:605 (1975)
- Randall, L.G. **J.Liq.Chromatogr.**9(14):3177 (1986)
- Ramsey, W.; Wachob, G. **Supelco Report No.** 13(1) (1994)
- Ramsey, E.D.; Perkins, J.R.; Games, D.E.; Startin, J.R. **J.Chromatogr.**464:353 (1989)
- Rao, P.S.C.; Nkedi-Kizza, P.L.; Brisseau, M.L.; Hornsby, A.G. **Environ.Sci.Technol.** 23:814 (1989)
- Raman, K.V.; Mortland, M.M. **Clays and Clay Minerals**, 16:393 (1968)
- Renkels et al. **Anal.Chem.**55(14):2229-2231 (1983)
- Repic, O.; Vogt, S. **Tetrahedron Lett.**23:2729 (1982).
- Richards, W.T.; Loomis, A.L. **J.AM.Chem.Soc.**49:3086(1927)
- Richter, B.E.; Knowles, D.E.; Ezzell, J.L.; Porter, N.L. **Am.Chem.Soc.Div.Environ.Chem.** 33:347-350 (1993)

- Rosset, R.; Mourier, P.; Caude, M. **Actual.Chim.**9:17-34 (1986)
- Sawicki, E.; Stanley, T.W.; Elbert, W.C.; Meeker, J. **Atmos.Environ.J.**1:131 (1967)
- Schantz, M.M.; Chesler, S.N. **J.Chromatogr.**363:397 (1986)
- Schwartz, H.E.; Brownlee, R.B. **J.Chromatogr.**353:77 (1986)
- Schmitt, W.J.; Reid, R.C. **Fluid Phase Equilibria** 32:77(1986)
- Seidel, V.; Lindner, W. **Anal.Chem.**65:3677 (1993)
- Skauen, D.M. **Chem Eng Progr. Symp.Ser.**109:35 (1971)
- Smith, R.D; Wright, B.W. **J.High Res.Chromatogr.**9:73-77 (1986)
- Snyder, J.M.; Friedrich, J.P.; Christianson, D.D. **J.Am. Oil Chem.Soc.**61:1851 (1984)
- Snyder, J.M.; King, J.W. **J.Sci.Food Agric.**64:257 (1994)
- Snyder, L.R. **J.Chromatogr.**22:6(1974)
- Snyder, J.M.; King, J.W. **J.Sci.Food Agric.** 64:257 (1994)
- Spiteller, M.; Haeder, K. **Intern.J.Anal.Chem.**53:125 (1993)
- Spitller, M. **Org.Geochem.**8:111 (1985)
- Solomon, D.H.; Hawthorne, D.G. **Chemistry of Pigments and Fillers.** John Wiley and sons, New York (1983)
- Steinwandter, H. **Fresenius Z.Anal.Chem.**320:179 (1985)
- Stevenson, F.J. **J.Environ. Quality** 1:333-343 (1972)
- Stahl, E.; Schilz, W.; Schultz, E.; Willing, E. **Angew Chem.**17(10):731 (1978)
- Sugiyama, K.; Saito, M. **J.Chromatogr.**442:121 (1988)
- Suslick, K.S. **Scientific American**, 260:80 (1989)
- Suslick, K.S. **Modern Synth.Methods** 4:1 (1986)

- Tan, K.H.; King, L.D.; Morris, H.D. **Soil Sci.Soc.Am.Proc.**35:748-751 (1971)
- Tan, K.H.; McCreery, R.A. **Proc.Int.Clay Conf.**Mexico City, Mexico, (1975)
- Theng, B.K.G. **"The Chemistry of Clay-Organic Reactions,** p136, Adam Hilger,London, (1974)
- Van Olphen, H. **Clay Colloid Chemistry,** John Wiley and Sons, N.Y. (1977).
- Weber, J.B. **Soil Sci.Soc.Am.Proc.**34:401-404 (1970)
- Weber, J.B.; Weed, S.B. **Soil Sci.Soc.Am.Proc.**32:485-487 (1968)
- Wenclawiak, B.; Jahn, K.R. **Chromatographia** 26:345 (1988)
- White, J.L. **ACS Symposium Series** No.29:208-218 (1976)
- William, D.; Ronald, C.S.; Mervin, P.C. **J.Assoc.Off.Anal.Chem.**50(14):2122 (1987)
- Wolfe, M.F.; Seiber, J.N.; Hinton, D.E. **Am.Chem.Soc. Div.Environ.Chem.**33:385-387 (1993)
- Yamaguchi, K.; murakami, M.; Nakano, H.; Konosu, S.; Kokura, T.; Yamamoto, H.; Kosaka, M.; Hata, K. **J.Am.Chem.Soc.**(1986)
- Yarita, T. **Microchemical Journal** 49,(2-3)(1994)

APPENDIX 1

Mass Spectrum of Lindane

Mass Spectrum of DDT

Background Subtract E:\NPG-DATA\NPG-DDT11 Date: 07/11/93 09:45:57
Comment: CHECK RT AND COMPOSITION
Average of: 1868 to 1872 Minus: 1890 to 1894 100% = 279604
100% 205

SMP
-
BKG

Mass spectrum of Dieldrin

Mass spectrum of Dieldrin

20
10
0

Mass spectrum of Dieldrin

✓

Sample Chromatogram Obtained with Soaking

Appendix 3 Representative Calibration Curve for Lindane

Representative Calibration Curve for Dieldrin

Appendix 4 GC-MS Chromatogram for Pure DDT

GC-MS Chromatogram for Pure Lindane

Chromatogram Plot D:\PETER\LINDANE Date: 01/02/95 10:14:08
Sample: LINDANE AT 6.94 ppm
Scan No: 982 Retention Time: 8:11 RIC: 229687 Mass Range: 51 - 399
Scanned: 800 to 1300 Range: 1 to 3599 100% = 1550134

GC-MS Chromatogram for Pure Dieldrin

Chromatogram Plot D:\PETER\DIELDRIN
Comment: DIELDRIN AT 1.95 ppm
Scan No: 1700 Retention Time: 14:10 RIC: 618344 Mass Range: 51 - 384
Plotted: 1500 to 2000 Range: 1 to 3600 100% = 968476
3.95%

Appendix 5 Chromatogram Obtained from a Blank Solvent

END

2 1-1 1-9 5

FIN