

Toxicants in Terrestrial Ecosystems
A Guide for the Analytical and Environmental Chemist

T.R. Crompton

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and Environmental Chemist

With 18 Figures and 45 Tables

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Preface for Toxicants in Terrestrial Ecosystems

This book discusses the methods currently available in the world literature up to 2005 for the determination of organic, organometallic and metallic impurities in soil and plant materials, vegetables and fruit. Radioactive substances and anions are also discussed.

In the case of soils, the presence of deliberately added or adventitious toxicants can cause contamination of the tissues of crops grown on the land or animals feeding on the land and, consequently, can cause adverse toxic effects on man, animals, birds and insects. Drainage of these substances from the soil can also pollute adjacent streams, rivers and eventually the oceans. Some of the organic substances included in this category are pesticides, herbicides, growth regulators, and organic fertilisers.

Individual chapters deal with the determination of metals, non-metals, organic compounds and organometallic compounds in soil and in plants that grow in soil. A separate chapter deals with sampling procedures. A relationship between toxicant levels in soil and plants that grow in that soil has been established and is the subject of the concluding chapter.

Examining for toxicants combines all the exciting features of analytical chemistry. First, the analysis must be successful and in many cases, must be completed quickly. Often the nature of the substances to be analysed is unknown, might occur at exceedingly low concentrations and might, indeed, be a complex mixture. To be successful in such an area requires analytical skills of a high order and the availability of sophisticated instrumentation.

The work has been written with the interests of the following groups of people in mind: agricultural chemists, agriculturists concerned with the ways in which inorganic and organic chemicals are used in crops and soil treatment that permeate through the ecosystem, biologists and scientists involved in plant life, and also people in the medical profession, such as toxicologists, public health workers and public analysts. Other groups or workers to whom the work will be of interest include environmentalists and not least members of the public who are concerned with the protection of our environment.

Finally it is hoped that the work will act as a spur to students of all subjects mentioned above and assist them in the challenge that awaits them in ensuring that the pollution of the environment is controlled so as to ensure we have a worthwhile environment to protect.

Anglesey, United Kingdom, July 2006

T.R. Crompton

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1 Sampling for the Analysis of Soil and Plant Sample

1.1 Soil

1.1.1 Soil Sampling

An HMSO publication covers the subject of soil sampling methods very extensively, including a detailed discussion on matters such as regular sampling methods, random sampling methods, grab sampling, systematic square sampling of fields, alternative random field sampling methods, auger sampling, depth profiling, and sampling by pedogenetic horizons. As this detailed information is readily available elsewhere it will not be discussed further here [1].

The whole field of the sampling of soils has been reviewed by Stoeppler [2], Lijtha et al. [3] and Fortunati et al. [4]. Fortunati et al. discuss the strategies of soil sampling. What is good practice in soil sampling has been discussed by Epps [5], including the effect of sampling variation on test results and the need for standardisation of soil sampling methods.

For individual investigations of contaminated soil, sampling errors are much greater than analytical errors, so the theory and practice of sampling contaminated soils needs to be developed further and much remains to be done in this field [6].

Van Der Veen and Alink [7] have reviewed methods for evaluating the performance of sampling, sample preparation and subsampling. Several new methods and apparatus for sampling solid matrices have been described recently [5–12] and, in particular, a new sampling method has been developed that is especially adapted to the specific conditions of sampling contaminated bulk soil masses [8].

Eccles and Redford [9] have investigated the use of dynamic (window) sampling in site investigations of soil.

Lancaster and Keller-McNulty [10] showed that reduced costs and improved statistical performance can be achieved by applying composite sampling methods to soil.

Various new devices that have been used in soil sampling include a gravity-driven, hydraulically sampled multi-piston corer for fine-grained soils [11] and time-series trap that can collect 21 samples of soil at programmed intervals [12].

Dong et al. [13] evaluated sampling and analytical errors for the determination of manganese in soils, and no doubt the conclusions reached in this work could be applied to other elements.

On the organic chemicals side, Thiboutot et al. [14] devised protocols for a sampling campaign for sites contaminated by explosives.

Brown and Reinsch [15] have discussed the collection and preparation of soil samples for the US Federal Soil Survey Laboratory Programme.

Burton [16] discussed factors affecting the realism of the collected samples of soil.

Various aspects of the sampling and analysis of soils for total petroleum hydrocarbons and benzene, toluene, ethyl benzene and xylenes have been discussed [202–205].

1.1.2

Soil Preparation for the Analysis and Determination of Metals

It is very important that the subsample analysed represents the original sample, otherwise the analytical result will be of little value. Each sample must be treated according to the analysis required. A very good guide covering the initial preparation of samples which is applicable to most samples has been published [1]!

The former UK Ministry of Agriculture and Food has also published [17] recommended soil preparation techniques for the determination of a wide range of metals and for the preparation of plant samples for analysis by dry combustion and the determination of ash.

Contamination problems can arise during the preparation and analysis of soils. Sources of trace elements can be atmospheric dust contamination after the initial sample was taken, laboratory equipment, adventitious contaminants such as cosmetics, and reagents used during the analysis. The analyst should take suitable precautions to reduce these to a minimum. Some of these problems have been reviewed by Mitchell [18].

Special precautions are necessary during the initial preparation of soil for certain analyses, such as for boron, mercury and selenium, and details of these precautions are given in any well-written published analytical method. Any analytical method for such elements that does not include such information is not worthy of further consideration.

For volatile and labile determinands, particularly in the field of the analysis of nonvolatile organic or organometallic substances, special attention should be given to methods of drying or reducing the sample. Drying must not be

used in the case of soils in which it is necessary to determine volatile organic compounds.

Samples can be dried and moisture content determined by special methods [19] and soil samples can be homogenised with a blender or a similar device.

For many analyses, soil is brought to the air-dried condition. This term refers to soil conditioned to ambient temperature and humidity, although in the case of the determination of organic or inorganic nonvolatile-containing samples, artificial heating at a temperature not exceeding 30 °C may be used in the drying process.

The length of time required to dry a sample to produce a friable material for subsequent sieving will depend on the nature and type of the soil.

In order to sieve samples that are to have their inorganic constituents determined, the soil is ground to pass through a nylon sieve meeting the requirements of BS 410i77. This avoids sample contamination associated with the use of metallic sieves. When sieving samples prior to the determination of organic constituents, a metal sieve may be used provided it does not react with the determinand of interest.

Methods of sample drying, sieving and sample volume reduction as well as long piles and quartering, sifting, core quartering, rotating pie wedge sampling, particle size reduction, sample storage, sample blending and blending homogeneity determination have been discussed in detail elsewhere [1] and will not be discussed further here.

Recent work on soil sample preparation is reviewed below. Rubio and Une [20] have discussed the risks of soil sample contamination using inappropriate materials, containers and tools as well as possible analyte loss during sample loading.

Houba et al. [21] studied the influence of grinding procedures and found that for some soils the availability of some analytes was significantly influenced by the degree of grinding.

1.1.3

Extraction of Inorganic Substances from Soil

Reynolds [25] has reviewed digestion procedures for the analysis of metal-contaminated soils.

Extraction of Metals

Microwave extraction methods are now being developed [22–25]. Krishnamurti et al. [22] found that the microwave extraction of cadmium in a soil reference material gave results comparable to those obtained by conventional soil extraction methods. In another study, Kingston and Walter [23] compared

microwave *versus* conventional dissolution of soils. About 90% of the lead and cadmium were extracted from soils and dusts by a microwave digestion procedure [24].

An extraction procedure based on ethylene diamine tetraacetic acid has been evaluated for the extraction of metals from soils [26]. In a collaborative study between 54 different laboratories, all of the laboratories produced some extreme outlying results, but most results were in good agreement once the outliers had been removed.

An ultrasonic bath extraction procedure gave acceptable accuracy and precision in the determination of metals [27].

In an interlaboratory study involving 160 accredited hazardous materials laboratories reported by Kimbrough and Wakakuwa [28], each laboratory performed a mineral acid digestion on five soils spiked with arsenic, cadmium, molybdenum, selenium and thallium. Analysis of extracts was carried out by atomic emission spectrometry, inductively-coupled plasma mass spectrometry, flame atomic absorption spectrometry and hydride generation atomic absorption spectrometry.

At most concentrations, inductively coupled plasma mass spectrometry exhibited higher precision and accuracy than the other techniques, but also the highest rates of false positives and negative results.

Much work has been reported on the evaluation of sequential extraction procedures. The three-stage sequential extraction procedure for speciation of heavy metals proposed by the Commission of the European Communities Bureau of References (BCR) was found to be acceptable and reproducible with some modifications [29]. In another study, when applied to real soils and sediments, this (unmodified) BCR method was queried [30]. Lopez-Sanchez et al. [31] found that significant results can be obtained when different sequential extraction procedures are used.

Shan and Chen [32] reported that various proportions of metals released from exchangeable, carbonate-bound iron, manganese oxide-bound and organic-bound fractions were reabsorbed onto the other solid geochemical phases during sequential extractions.

Some work on sediments is reported here in the belief that it may also be useful in the analysis of soil samples. Thus Asikainen and Nikolaides [33] have carried out a sequential extraction study of chromium from contaminated aquifer sediments and found that 65% of the chromium was extractable. Of this amount 25% was exchangeable, 11% was bound to organic matter and 30% was bound to iron and manganese oxide surfaces. Thomas et al. [34] also investigated the use of BCR sequential extraction procedures for river sediments, and found the method to work well. Real et al. [35] improved sequential extraction by optimising microwave heating.

Martens and Suarez [37] employed sequential extraction and hydride generation atomic absorption spectrometry to analyse soil for arsenic and selenium and achieved excellent precision.

Ren and Salin [36] showed that direct analysis of solid samples is possible, by using furnace vaporisation with Freon modification and inductively coupled plasma mass spectrometry. The relative standard deviations obtained for several metals in marine reference sediments varied from 3 to 15%.

A number of studies on sequential extractions of trace metals have been reported [42–49]. Metal distributions were significantly different among three compared sequential extraction procedures [43]. Silty soils may have a relatively high heavy metal retention capacity due to the presence of carbonate, and this retention capacity can be comparable in magnitude to that of certain clayey soils [47]. Soil amended with sewage sludge exhibited a different distribution of metals in the soil [48]. Bodog extended the sequential extraction procedure of Ure, and observed good agreement with a total acid extraction procedure [49].

The effects of soil sample preparation procedures for the determination of chromium in soils have been reported [38]. The optimum conditions included the use of an homogeneous sample with a mass of less than 4 kg, a grain diameter of less than 0.25 mm, digestion with a solution of nitric acid plus perchloric acid (3:2) and hydrochloric acid after dry ashing, with the addition of 1% lanthanum or 1% ammonium chloride to eliminate interferences.

Mierzwa and Dobrowolski [39] determined selenium using combined slurry sampling, microwave-assisted extraction and hydride atomic absorption spectrometry. Lopez-Garcia et al. [40] also used slurry sampling in the determination of arsenic and antimony in soil.

Direct solvent extraction of soil by an organic solvent containing an organic complexing has been used. Thus Reddy and Reddy [41] showed that extraction of soil with a chloroform solution of xanthate completely extracted cadmium. Compared to untreated soil or sediment, none of the three drying methods studied – freeze drying, air drying and oven drying – completely preserved the distribution of selected metals in the various geochemical fractions [50].

Reviews have been conducted on the problems associated with techniques and strategies of soil sampling [4] and on the collection and preparation of soil samples for the Federal Soil Survey Laboratory Program [51]. Factors affecting the realism of the collected sample were discussed by Burton [16]. Various sampling schemes for soils have been described [52–56]. Different sampling designs are needed, depending upon whether the soil contamination is expected to be “spread” over the whole area or to exist in localised “hot spots” [52]. A decision support system for the sampling of aquatic sediments in lakes was described by Wehrens and was applied to a real environmental problem [53]. Lame showed that the *fundamental* sampling error for soils only affects the analytical variance when sample sizes are less than 10 g [54]. For larger samples, the variance is determined by the *segregation* error. A sampling board method of estimating the *segregation* error has been described. Skalski showed that a two-way compositing strategy could be used to attribute detected contamination in composited samples directly to constituent samples without further analyses [55].

Evaluations of various soil and sediment samplers have been reported [56, 57]. The sediment shovel proved highly practical, but was limited because small particles tend to be lost when the shovel is lifted [56]. A cryogenic sediment sampler was less convenient to use, but allowed the collection of almost undisturbed samples. Houba described a different device for the automatic subsampling of soil, sediment and plant material for proficiency testing [57]. In another study, Thoms showed that freeze-sampling collects representative sediment samples, whereas grab-sampling introduces a bias into the textural composition of the 120 mesh fraction, due to washout and elutriation of the finer fractions [58].

1.1.4

Extraction of Organic Substances from Soils

Analysis of organic pollutants in environmental soil samples is an important task with respect to the protection of the environment.

Conventionally, organic contaminants in solid samples are examined by Soxhlet extraction, followed by separation and identification. Several methods have been proposed to reduce the use of organic solvents and to increase the speed of analysis, such as supercritical fluid extraction [59, 60], accelerated solvent extraction [61], subcritical fluid solvent extraction [62, 63] and headspace solid-phase microextraction [64–66]. Separation and phase identification methods such as gas chromatography–mass spectrometry are typically used to examine the extracts. Attenuated total reflectance–infra-red spectroscopy [67] provides a direct method for detecting organic species in samples of varying physical composition and is very suitable for handling aqueous solutions because the evanescent wave penetrates into the adjoining medium for a short distance. Examples of these techniques are reviewed below.

Conventional Solvent Extraction

Miellat [80] and Lopez-Avila et al. [81] have reviewed the applications of Soxhlet extraction to the determination of pesticides in soil. This technique has been applied extensively to the extraction of polycyclic aromatic hydrocarbons, volatile organic compounds, pesticides, herbicides and polychlorodibenzo-*p*-dioxins in soils. Details of the extraction procedures and the analytical finish employed are reviewed in Table 1.1.

Accelerated Solvent Extraction

This relatively new technique has been proposed as an alternative to the Soxhlet procedure [92–94]. In this technique the soil sample is packed into an extraction cartridge and the analytes are extracted from the matrix with conventional low

Table 1.1. Conventional solvent extraction procedures for organic compounds in soils (from author's own files)

Compound-pesticides and herbicides	Extractant	Clean-up	Analytical finish	Reference
Organochlorine insecticides Alachlor	Polar solvents Methanol enrichment on C ₁₈ cartridge	Florisil -	- -	[68] [69,70]
Bromoxynil, ioxynil residues	Solvent partitioning	Solvent partitioning	Gas chromatography with ion-trap detector	[71]
Triazine type herbicides	Methanol enrichment on C ₁₈ cartridge	-	Gradient C ₁₈ high- performance liquid chromatography	[72]
Imazapyr	Methanol	None	High-performance liquid chromatography, detection at 250 nm	[73]
Terbuthylazine and degradation products	Hot acetone, then cation exchange solid-phase cartridge	-	High-performance liquid chromatograph with photodiode array detection	[74,75]
Norflurazon herbicide	Methanol	Filtration	C ₁₈ high-performance liquid chromatography	[76]
Isoproturon, dichlorprop-P- bifenox	Solvent	Size exclusion chromatography	High-performance liquid chromatograph	[77]
Fenopropimorph and metabolite fenopropimorphic acid fungicide	Acetone - water, partitioning with methylene chloride	Gel permeation chromatography	Methylation - gas liquid chromatography with NP detection and GC-MS	[78]
Fenoxaprop, Fenoxapropethyl	Solvent	Florisil or alumina	High-performance liquid chromatography	[79]
Polycyclic aromatic hydrocarbons Polycyclic aromatic hydrocarbons	Soxhlet extraction and saponification	Silica gel	1 ppm detected in soil	[82]

Table 1.1. (continued)

Compound-pesticides and herbicides	Extractant	Clean-up	Analytical finish	Reference
Polycyclic aromatic hydrocarbons	BF ₃ in methanol	-	-	[83]
Polycyclic aromatic hydrocarbons	Miniaturised liquid-liquid extractor (100 µl solvents)	-	-	[84]
Polycyclic aromatic hydrocarbons	Automated Soxhlet extraction with ethyl acetate	-	-	[85]
Polycyclic aromatic hydrocarbons	Organic solvent, methanolic hydrolysis	-	-	[86]
Volatile organic compounds	Hot (70 °C) methanol	-	-	[87]
Volatile organic compounds	Comparison of solvent extraction, headspace analysis and vapour partitioning, methanol extraction	-	-	[88]
Volatile organic compounds	Comparison of methanol extraction and purge and trap method	-	Hot methanol extraction is the most efficient	[89]
Polychlorodibenzo <i>p</i> -dioxins and benzofurans	Comparison of Soxhlet extraction using (a) toluene and (b) methylene dichloride-acetone	-	-	[90, 103]
Medium polar and polar analytes	Hot phosphate buffered water extractant	-	-	[91]
Aromatic hydrocarbons	Solvent extraction with methanolic hydrolysis	-	-	[86]
Chlorophenols	Soxhlet extraction	-	-	[99, 100]

boiling point solvents or solvent mixtures at elevated temperatures of up to 200 °C and pressures of up to 20 MPa [93–95] to maintain the solvent in a liquid state.

Two comparative studies have shown that accelerated solvent extracted quantities of pesticides from soils equal to or larger than those found by other extraction techniques [120, 121]. However, only 36 to 72% of phenoxyacetic acid herbicides were recovered by this technique from clay, loam and sand [43]. A further limitation of the accelerated solvent extraction technique, which is shared by several of the other newer extraction techniques reviewed here, is that selective extraction of organics based on their polarities is difficult. For example, in the case of the extraction of soil with a high organic content (9.6%) at 100 °C with methanol or acetone as such or acidified with phosphoric acid with each of these extractants, large amounts of wax-like substances – presumably cellulose, lignin and waxes from plant cells – were coextracted with the herbicides considered. The presence of these high molecular weight compounds in soil extracts caused interference in the final analytical finish employed to determine the herbicides, and can only be avoided in some, not all, cases by tedious and time-consuming clean-up procedures. To a lesser extent these species are also present in soils with a lower organic content. Subcritical water extraction overcomes this difficulty and will be discussed further below [123].

The range of materials for which the technique is proposed includes semi-volatile compounds, including polycyclic aromatic hydrocarbons, organochlorine pesticides, organophosphorus pesticides, chlorinated herbicides and polychlorinated biphenyls [92].

Saim et al. [96] investigated the interdependence of selected operating parameters on the recovery of 16 polycyclic aromatic hydrocarbons from nine highly contaminated soils, including a range of pressures from 1000–2400 psi, operating temperatures from 40–200 °C, and extraction times from 2 to 16 minutes.

At the 95% confidence interval, no significance in terms of the three operating parameters was found when considering the total polycyclic aromatic hydrocarbon recovery. However, recoveries of some individual polycyclic aromatic hydrocarbons were found to be dependent on operating variables. In particular, low operating temperatures of 40 °C were very significant for naphthalene, chrysene and benzo(b)fluoranthene.

Wennrich et al. [97] have described a method for the determination of nine chlorophenols in soil using accelerated solvent extraction with water as the solvent combined with solid-phase microextraction and gas chromatography – mass spectrometry. An extraction temperature of 125 °C and ten-minute extractions were optimal.

Hofler et al. [98] also studied the application of accelerated solvent extraction with an organic solvent, followed by clean-up and preconcentration procedures.

Hubert et al. [101] state that accelerated solvent extraction compared to alternatives such as Soxhlet extraction, steam distillation, microwave extraction, ultrasonic extraction and, in some cases, supercritical fluid extraction is an exceptionally effective extraction technique. Hubert et al. [101] studied the effect of operating variables such as choice of solvent and temperature on the solvent extraction of a range of accelerated persistent organic pollutants in soil, including chlorobenzenes, HCH isomers, DDX, polychlorobiphenyl congeners and polycyclic aromatic hydrocarbons. Temperatures of between 20 and 180 °C were studied. The optimum extraction conditions use two extraction steps at 80 and 140 °C with static cycles (extraction time 35 minutes) using toluene as a solvent and at a pressure of 15 MPa.

Pyle and Marcus [102] achieved low ppb detection limits for the determination of organochlorine insecticides in soil using accelerated solvent extraction followed by gas chromatography ion trap tandem mass spectrometry. Richter et al. [103] showed that accelerated solvent extraction gave essentially equivalent recoveries of chlorinated dibenzo-*p*-dioxins and dibenzofurans from soil compounds to Soxhlet extraction, but in less time and using much less solvent.

Pressurised Liquid Extraction

Pressurised hot water extraction has been used to isolate polycyclic aromatic hydrocarbons from soil [104, 105]. Ramos et al. [106] reported an rapid (ten minutes) miniaturised pressurised liquid extraction method using only 100 µl solvent for extracting polycyclic aromatic hydrocarbons from soil.

Microwave-Assisted Extraction

Lopez-Avila et al. [107] showed that microwave-assisted extraction of pesticides and polycyclic aromatic hydrocarbons from soil is a viable alternative to Soxhlet extraction and needs a smaller sample volume and extraction time [108, 109]. These techniques have also been compared in the case of chlorophenols. Lopez-Avila et al. compared microwave-assisted extraction with electron capture gas chromatography to ELISA for the determination of polychlorinated biphenyls in soils. Both techniques are applicable to field screening and monitoring applications. Microwave-assisted extraction [111, 112] and solid-phase microextraction [113] have been applied to the extraction of pesticides from soil. It was observed by these and other workers [114] that the selectivity of microwave-assisted extraction is highly dependent on the soil composition.

Microwave-assisted extraction [115] has been compared with ultrasonic extraction [116] in the context of soil extraction. Microwave-assisted extraction [117, 195–198] and supercritical fluid extraction coupled with on-line infrared spectroscopy detection [118, 119] have been compared as methods for the extraction of hydrocarbons from soil.

Subcritical Water Extraction

This technique, as discussed above under “Accelerated Solvent Extraction”, has the outstanding advantage that extraction with water as opposed to organic solvents does not cause contamination of the extract with potentially interfering organic components such as cellulose, lignin and waxes originating in plant cells or interference due to contamination by the solvent or impurities therein.

Crescenzi et al. [122] evaluated the feasibility of selectively extracting phenoxyacetic acid herbicides with subcritical hot water and collecting the analytes on a Carbograp-4 solid-phase extraction cartridge set on-line with the extraction cell. Final analysis was by liquid chromatography–mass spectrometry with an electrospray ion source. With few exceptions, recoveries were in the range 81 to 93% (with the exception of 24 DB and MCPB, which gave 63%) recovery and detection limits of between 1.7 and 10 ng/g. Other applications of subcritical water extraction are reviewed in Table 1.2.

Table 1.2. Applications of subcritical water extraction to the determination of organic compounds in soil (from author’s own files)

Determinand	Subcritical water extractant	Sorbent trap	Analytical finish	Reference
Mixtures of herbicides	Water	Miscellaneous traps		[123]
Terbuthylazine and metabolites	Phosphate buffered water	Graphitised carbon block cartridge		[123]
Herbicides and breakdown products	Water	Miscellaneous traps		[124]
Polycyclic aromatic hydrocarbons	Static subcritical water	Styrene-divinylbenzene discs		[124]
Polycyclic aromatic hydrocarbons	Water	Solid phase	High-performance liquid chromatography, post column fluorimetric detection	[125]
Polychlorobiphenyls	Water at 250 – 300 °C and 50 atmospheres pressure	–		[126]
Polychlorobiphenyls	Water	Solid-phase microextraction		[63]

Solid-Phase Microextraction

This technique seems to have been introduced in late 1998, and consists of extracting organic contaminants from the soil with a solvent, generally subcritical water, and then passing the extract through a small disc of solid sorbent. The solid sorbents discussed to date include graphitised carbon black [123], styrene-divinyl benzene [124], Carbograph-4 [122] and polyisobutylene [193].

An example of the application of subcritical water extraction–solid-phase microextraction is that of Crescenzi et al. [122] (see above).

Water extraction is also occasionally combined with solid-phase microextraction. Thus Wennrich et al. [97] determined chlorophenols in soil by using accelerated water extraction to remove the chlorophenols from the soil followed by adsorption onto a solid sorbent for ten minutes at 125 °C. Low ppb detection limits were thus achieved.

Other applications of subcritical water extraction–solid-phase microextraction are the determination of terbuthylazine and its metabolites [123], polycyclic aromatic hydrocarbons [124, 125] and polychlorobiphenyls [63]. Yang and Her [193] collected 1-chloronaphthylene, nitrobenzene and 2-chlorotoluene in soil on a hydrophobic polyisobutylene disc prior to analysis by attenuated total reflectance Fourier transform infrared spectroscopy.

Supercritical Fluid Extraction

This is an attractive technique for recovering organic compounds from soils. Carbon dioxide is currently the fluid of choice, due to its low toxicity and environmental acceptability. The physicochemical properties of supercritical fluids, including low viscosity, variable solvent strength and high diffusivity, contribute to faster extractions compared to conventional extraction techniques such as Soxhlet extraction or sonication. Supercritical fluid extraction methods have been successfully developed for nonpolar compounds that exhibit high solubilities in carbon dioxide, such as polycyclic aromatic compounds [127–133], polychlorobiphenyls [134–136], chlorodioxins [137–142], amines [143], pyridine [144], triaryl and trialkyl phosphates [145], hydrocarbons [146], volatile organic compounds [147–150], phenols [151], organic acids [152], ketones [152], enteroviruses [153], organochlorine pesticides [154] and miscellaneous herbicides and pesticides [155–165]. With methanol as a modifier, supercritical carbon dioxide becomes more amenable to the extraction of moderately polar pesticides including triazines [160, 166], organophosphorus insecticides [167, 168], sulfonyl ureas [161–163], organochlorine insecticides [167, 170], flumetron [171], and other herbicides [172]. Further details of the methods are given in Table 1.3. The work of Field et al. [165] is quoted as an example of the application of supercritical carbon dioxide and subcritical (hot) water extraction of the widely used pre-emergent herbicide dacthal and its mono and diacid metabolites in soil. These compounds were sequentially

extracted from soils by first performing a supercritical hot water extraction for 15 minutes at 150 °C and 400 bar to recover dacthal, followed by a subcritical hot water extraction to recover the metabolites, which were then trapped *in situ* on a strong anion exchange disc placed over the exit frit of the extraction cell. Dacthal was combined with the metabolites by placing the disc into a gas chromatograph autosampler vial containing the supercritical fluid extract. The metabolites are then simultaneously eluted from the disc and derivatised to their ethyl esters by reaction with ethyl iodine at 100 °C.

Meyer et al. [173] showed that supercritical fluid extraction results can give recoveries comparable to Soxhlet extraction methods, even for soils with high carbon contents. McNally et al. [174] have studied factors affecting the supercritical fluid extraction of soils. It was shown that soil type affects the recovery of moderately polar analytes. In general the organic carbon content of the soil governs analytical recovery.

Online coupling of supercritical fluid extraction and high-performance liquid chromatography considerably decreases sample preparation time and analysis time [175]. Dunkers [128] showed that by using dilute dichloromethane as a static modifier, 20–30 minute supercritical fluid extractions gave results comparable to those obtained by conventional four-hour sampling methods in soil extractions.

Fahing et al. [176] studied the effect of the addition of modifiers such as methanol and water on the SCFE of organic solutes from soils and clays. Hawthorne et al. [177] compared the application of sub- and supercritical water in the extraction of organics from soil, and found that both were effective extractants.

Headspace Analysis

This technique is, of course, only applicable to organic compounds in soil that are sufficiently volatile at room temperature or slightly above that they exist in the headspace above the samples. For such samples, the technique is elegant in that it is solventless, *i.e.*, there is no solvent interference, is amenable to automation, and can be directly coupled to a gas chromatograph and/or alternate techniques such as mass spectrometry to ensure unequivocal identification of the organics.

Headspace analysis is the method of choice for determining volatile organic compounds in soil [178–183]. A limitation of this method is the incomplete desorption of the contaminants in soil–water mixtures, but this problem can be overcome through the addition of methanol to the sample [181]. Good recoveries of volatile organic compounds in soils were obtained via thermal vaporisation of the sample followed by Tenax GC trapping and gas chromatography–mass spectrometry.

Stuart et al. [184] studied the analysis of volatile organic compounds in soil using an automated static headspace method. Recoveries increased in the or-

Table 1.3. Determination of organic compounds from soil by supercritical fluid extraction (from author's own files)

Determinand	Extractant	Conditions/comments	Analytical finish	Reference
Polycyclic aromatic hydrocarbons	Dichloromethane modified CO ₂	30 minute extraction	-	[128]
Polycyclic aromatic hydrocarbons	CO ₂	-	High-performance liquid chromatography	[129]
Polycyclic aromatic hydrocarbons	Water-methanol dichloromethane	Comparison with CO ₂	-	[130]
Polycyclic aromatic hydrocarbons	CO ₂ -dichloromethane	Comparison with CO ₂ and CO ₂ -methanol. CO ₂ recommended	-	[131]
Polycyclic aromatic hydrocarbons	CO ₂	Use of liquid-solid traps compared to analyte trapping	-	[133]
Polycyclic aromatic hydrocarbons	Pretreatment of sample with (a) 15% water, (b) 5% (ethylenedinitrilo) tetraacetic acid tetrasodium salt or (c) 50% methanol then extraction with CO ₂	60-98% recovery using Na ₄ EDTA-CO ₂ . Only 7-63% recovery with CO ₂ alone	-	[146, 147, 195-198]
Diesel hydrocarbons	CO ₂	-	Gas chromatography	[149]
Petroleum hydrocarbons	CO ₂	Comparison of sorbent trapping with solvent trapping	Gas chromatography	[148]
Petroleum hydrocarbons	Argon	500 atm at 150 °C	Infrared spectrometry	[148]
Volatile organic compounds	CO ₂	-	-	[150]
Phenols, cresols	CO ₂	-	-	[151]
Organic acids and ketones	CO ₂	-	-	[152]

Table 1.3. (continued)

Determinand	Extractant	Conditions/comments	Analytical finish	Reference
Polychlorobiphenyls	Comparison of CO ₂ , CHClF ₂ , N ₂ O	CHClF ₂ gave the best recovery of PAH		[135]
Polychlorobiphenyls	CO ₂	-	FT offline IR spectroscopy	[136]
2,3,7,8-Tetrachloro- <i>p</i> - benzo dioxin	CO ₂	-	-	[138-141]
Trialkyl and triaryl phosphates	CO ₂	Microwave extraction	-	[145]
Aromatic amines	CO ₂	-	-	[143]
Pyridine	CO ₂	-	-	[144]
Enteroviruses	CO ₂	-	-	[153]
Insecticides and herbicides				
Dacthal herbicide and acid metabolites	Supercritical CO ₂ at 150 °C and 400 bar, then supercritical water at 50 °C and 200 bar	Metabolites derivatised to ethyl esters	-	[165]
Diuron, Linuron	CO ₂	-	-	[155]
Chlordane	CO ₂	Compared to Soxhlet and accelerated solvent extraction	-	[156]
Chlorpyrifos metabolite	Polychlorobiphenyls	Comparison with subcritical water extraction	-	[157]
Organochlorine insecticides	CO ₂	-	Comparison with Soxhlet extraction	[170]
Imazaquin	CO ₂	-	-	[158]

Table 1.3. (continued)

Determinand	Extractant	Conditions/comments	Analytical finish	Reference
Atrazine	CO ₂	-	High-performance liquid chromatography-mass spectrometry	[159]
Flumetron	CO ₂	-	-	[171]
Atrazine, cyanazine, desethylatrazine	CO ₂	-	-	[160]
Metochlor	CO ₂ -methanol SF extractions			
Sulfonylurea herbicides and metabolites	CO ₂	-	Superfluid chromatography	[161]
Sulfonylurea herbicides and metabolites	CO ₂ -methanol	Using C ₁₈ solid phase extraction disk	High-performance liquid chromatography with UV detection. Dimethyl sulfonyl ureas determined by GC with detection by electron capture or N-P or MS.	[162,163]
Triazine herbicides	CO ₂ -methanol	-	-	[166]
Organochlorine, organophosphorus insecticides	CO ₂ -3% methanol	Comparison with classical sonication and Soxhlet extraction	-	[165,167]
Flumetron, fenpropionmorph, perimicarb, parathion, ethyl triallate, fenvalerate	CO ₂ -5% methanol	Extraction at 60 °C and 3.8 × 10 ⁷ Pa	-	[172]

der: water, pure sand, sandy soil, clay and top soil. A full evaporation technique that uses little or no aqueous phase and higher equilibration temperature gave the most reproducible analyte recoveries. Hewitt [185] compared three vapour partitioning methods, three solvent extraction methods and headspace analysis for the preparation of soil samples for the determination of volatile organic compounds.

Samples Used for the Determination of Volatile Organic Compounds in Soils

Methanol extraction was the most efficient method of recovering volatile organic compound spikes from soils, but results depended on the organic carbon content of the soil.

Various other workers have reported on the determination of volatile organic compounds in soils [186, 187] and landfill soils [188]. Soil fumigants such as methyl bromide have also been determined by this technique [189]. Trifluoroacetic acid is a breakdown product of hydrofluorocarbons and hydrochlorofluorocarbon refrigerant products in the atmosphere and, as such, due to the known toxicity of trifluoroacetic acid, it is important to be able to determine it in the atmosphere, water and in soil from an environmental point of view [190]. In this method the trifluoroacetic acid is extracted from the soil sample by sulfuric acid and methanol, which is then followed by the derivatisation of it to the methyl ester. The highly volatile methyl ester is then analysed with a recovery of 87% using headspace gas chromatography. Levels of trifluoroacetic acid in soil down to 0.2 ng/g can be determined by the procedure.

Purge and Trap Analyses

Kester [191] has reviewed the application of this technique to the determination of a wide range of organic compounds in soil, including ketones, aldehydes, aromatic hydrocarbons, halogenated aliphatic compounds, alcohols and vinyl acetate.

Basically, in these methods the volatiles released by heating the sample are collected on a Tenax GC and subsequently desorbed from the Tenax and determined by gas chromatography-mass spectrometry.

Roche and Miller [192] have shown that ultrasonic extraction gives more accurate results when compared with a heated nitrogen purge in the determination of volatile organic compounds in soils.

Yang and Her [193] have described a rapid method for the determination of down to 200 ppt of semi-volatile compounds such as 1-chloronaphthalene, nitrobenzene and 2-chlorotoluene in soils by coupling solid-phase microextraction with attenuated total reflectance Fourier transform infrared spectroscopy.