

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

Methodology for the Exposure Assessment of Soil for Organic Chemicals. Part I: Extraction Procedure of Non-volatile Organic Chemicals

Ursula Wahle^a; W. Kördel^a; W. Klein^a

^a Fraunhofer-Institut für Umweltchemie und Ökotoxikologie 5948, Schmallenberg-Grafschaft, FRG

To cite this Article Wahle, Ursula , Kördel, W. and Klein, W.(1990) 'Methodology for the Exposure Assessment of Soil for Organic Chemicals. Part I: Extraction Procedure of Non-volatile Organic Chemicals', International Journal of Environmental Analytical Chemistry, 39: 2, 121 – 128

To link to this Article: DOI: 10.1080/03067319008027688

URL: <http://dx.doi.org/10.1080/03067319008027688>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

METHODOLOGY FOR THE EXPOSURE ASSESSMENT OF SOIL FOR ORGANIC CHEMICALS

Part I: Extraction Procedure of Non-volatile Organic Chemicals

URSULA WAHLE, W. KÖRDEL and W. KLEIN

*Fraunhofer-Institut für Umweltchemie und Ökotoxikologie 5948
Schmallenberg-Grafschaft, FRG*

(Received 11 November 1988; in final form 29 February 1989)

A widely applicable clean-up scheme for the analysis of anthropogenic organic chemicals in soil, comparable to the "master-analytical-scheme" for organic compounds in water, is not available. Isotopically-labelled compounds representing seven classes of chemicals with a broad range of physico-chemical properties have been used to develop a general procedure for extraction, clean-up, and analysis. Two different soil-types have been spiked with these chemicals for at least four weeks prior to analysis. For non-volatiles, best results have been obtained by the extraction of soil by the system of water/dichloromethane resulting in a recovery of about 95%. For amines the recovery from aged residues is only 40%. A large amount of soil-borne impurities can be eliminated by subsequent gel chromatography, resulting in samples ready for further separation and quantification by HPLC, GC or for MS analysis.

KEYWORDS: Analytical scheme, soil, extraction procedure, organic pollutants.

INTRODUCTION

Most chemicals enter the environment via air and water. Therefore analyses of pollutants in these media are well advanced. A widely applicable clean-up scheme for the analysis of anthropogenic organic chemicals in soils, comparable to the "master analytical scheme" for organic compounds in water,¹ is not available.

For soil analysis, research is mostly restricted to single substances or classes of substances.²⁻⁷

Soils may be contaminated by anthropogenic organic chemicals by several pathways, and an unpolluted "zero-soil"⁸ is not available. Contaminations can interfere with organic compounds which have been added in order to prove extraction methods.

This especially is of importance when working at low concentration levels and may result in irreproducible recovery rates. Some groups have tried to prepare a "zero soil",⁸ but the qualities may influence the adsorption of the applied anthropogenic chemicals. Therefore in this research project, isotopically-labelled substances representing important classes of chemicals have been used. Thus the efficiency of each working step (extraction, clean-up, concentration, and partitioning) can be controlled and optimized separately.

Table 1 Characterisation of selected soils

Soil type	pH	Corg %	CEC mval/100 g	CaCO ₃ %	Sand %	Silt %	Clay %
Alfisol	6.7	1.25	12.3	0.43	69.7	14.4	15.9
Spodosol (forest)	2.8	4.82	15.1	—	88.1	3.4	1.4

Sorption of the individual chemical and the clean-up procedure depend on characteristics of the soil used. Soils have been selected which differ particularly in their organic carbon content, clay content, and the cation exchange capacity (Table 1).

Sorption processes in soil and, therefore, extractability of a chemical are time dependent. Realistic and environmentally relevant recovery rates are only obtained if, prior to extraction, the soil has been exposed to the chemical for a relatively long period of time. In order to avoid biodegradation during this incubation time, the moist soil has to be sterilized before spiking. To suppress biotic degradation in soil, different methods such as γ -radiation, ethylene oxide or propylene oxide fumigation, autoclaving, or addition of fungicidally and bactericidally active components are commonly used. We prefer the autoclave method because of its minimal influence on sorption properties and its sufficient suppression of biodegradation during testing.⁹

EXPERIMENTAL SECTION

Sample Source

The alfisol was obtained from Schönberg (Holstein), the agricultural spodosol was taken from Wasbeck (Holstein), and the forest-spodosol from Lauenburg (Holstein).¹⁰ The soil was air dried, sieved (particle size <2 mm), and stored at 4 °C. The characterisation of the soil is shown in Table 1.

Reagents

The individual stock solution for each compound was prepared in ethanol, toluene, or water. All solvents were residue analysis purity, and the unlabelled chemicals were p.a. grade and purchased from Merck, Sigma, and Riedel-de-Haen. The ¹⁴C-labelled compounds were purchased from Amersham, Sigma, or kindly supplied by NATEC and GSF.

Sample Preparation

An 100 g aliquot of soil was loaded into a 250 ml glass bottle. Soil humidity was adjusted to 40% maximum water holding capacity and sterilized at 121 °C for 20 min.⁹ The soil was spiked under sterile conditions by carefully mixing with 1 ppm of the ¹⁴C-labelled compound and 4 ppm unlabelled compound to avoid influences of low concentrations.¹¹ The content of organic solvent did not exceed 1%.¹²

The spiked soil was incubated for at least four weeks at 25°C in darkness prior to extraction.

SHAKE EXTRACTION

Aliquots (5 g) of spiked soil in 80 ml centrifuge bottles were shaken with 5 ml water for 10 min. Then 10 ml of the organic solvent were added and the sample was shaken for another 20 min followed by centrifugation at 5,000 × *g* in order to promote phase separation. This extraction procedure was repeated twice.

Soxhlet Extraction

Aliquots (10 g) of the spiked soil were placed in a soxhlet thimble and extracted with 40 ml methanol for 12 h. Then 10 ml benzene were added and soxhlet extraction continued for 24 h.^{13, 14}

ULTRASONIC EXTRACTION

Aliquots (5 g) of spiked soil in centrifuge bottles were extracted ultrasonically (Bandelin ultrasonic cleaning bath, Sonotex Super RX 255H) with 5 ml water and 10 ml organic solvent for 20 min at 25°C.

The radioactivity in the organic and aqueous phase was determined by liquid scintillation counting. Non-extractable residues were determined by combustion of 100 mg soil aliquots after extraction and drying in a vacuum desiccator at room temperature.

The extracted compounds were identified by thin layer-chromatography to verify the identity of the chemical.

RESULTS AND DISCUSSION

Essentially four methods are in use for the extraction of solid samples: hot extraction with a soxhlet or similar apparatus, shaking, sonication, and extraction with supercritical solvents. Extraction by shaking is an effective and simple method which is preferred to extraction by sonication or soxhlet extraction. Extraction by sonication results in high standard deviations if conditions such as water level, sample size, vessels used are not completely standardized. The results of both methods are comparable. Soxhlet-extraction is not recommended as a routine method since some portions of the substances (e.g., PAHs, Table 2) are distributed in and tightly sorbed to the extraction device. This fact should be considered especially when working at low concentrations near the detection limit.

The classes of chemicals, PAHs, phenols, chlorinated compounds, acids, esters, ketones, and amines were tested separately. The first three chemicals of each class were spiked and extracted in common. For problematic groups, e.g., the amines,

Table 2 Comparison of Extraction techniques for PAHs (naphthalene, anthracene, perylene)

a) Alfisol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
H ₂ O/toluene	74	85	87	±2	2
MeOH/benzene-soxhlet	88			±8	2.0
H ₂ O (pH 11)/CH ₂ Cl ₂	76	93	95	±5	3.0
H ₂ O/cyclohexane	48	65	67	±3	32.0
Cyclohexane	32	—	—	±5	68.0
H ₂ O/ether	77	90	96	±4	3.0
H ₂ O/ <i>n</i> -hexane/CH ₂ Cl ₂	82	84	85	±5	6

b) Spodosol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
H ₂ O/toluene	42	57	67	±6	30
H ₂ O (pH 11)/CH ₂ Cl ₂	41	57	67	±5	30
H ₂ O/Et ₂ O	41	59	65	±6	20
H ₂ O/ <i>n</i> -hexane/CH ₂ Cl ₂	41	50	60	±7	30
1. H ₂ O (pH 11)/CH ₂ Cl ₂					
2. H ₂ O (pH 2)/CH ₂ Cl ₂ successively			93	±5	7

the extraction procedures were repeated with the single substances. The applied chemicals are itemized in Tables 2–7.

A comparison of the different extraction procedures is listed in the Tables 2–7. The results shown are obtained by summing up the respective extracted amounts in the organic layers.

It can be seen clearly that extractions using the two phase system soil/organic solvent give worse results (e.g., Table 2: PAH extraction with cyclohexane) compared with those using a three phase system soil/water (or alcohols)/organic solvent.

H₂O/ether and H₂O/CH₂Cl₂ have been shown in these investigations to be suitable solvent systems for the extraction of PAHs (Table 2), while polar systems (e.g., H₂O/acetone) which are useful for the extraction of esters and ketones (Tables 5 and 6) are unsuitable for PAHs.

For chlorinated compounds and acids (Table 3), the solvent systems H₂O/acetone and H₂O/CH₂Cl₂ are comparably well suited with extraction efficiency rates of more than 95%. Non aqueous systems such as acetone/CH₂Cl₂ give lower efficiencies.

Organic acids were extracted up to pH 11. Thus, an effective extraction system contrasts with group selective extraction. The comparison of the phenols' extraction efficiencies (Table 4) underlines this fact. Under acid extraction conditions, 95% of the radioactivity was found in the organic phase, while alkaline extraction

Table 3 Comparison of Extraction techniques for halogenated substances and org. acids (lindane, pentachloronitrobenzene, buturon, 2, 4-D, chlorobenzoic acid)

a) Alfisol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
H ₂ O/acetone	85	93	97	±5	3.0
Acetone/CH ₂ Cl ₂	68	89	92	±7	3.0
Acetone/hexane	52	56	60	±7	10.2
H ₂ O/CH ₂ Cl ₂	87	93	97	±4	2.5
i-PrOH/cyclohexane	45	56	58	±5	17.0
HAM ^a -soxhlet	50			±10	10.0

^aHAM = hexane-acetone-methanol (8:1:1)

b) Spodosol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
H ₂ O/acetone	75	91	96	±2	4.0
Acetone/CH ₂ Cl ₂	82	91	95	±7	5.0
Acetone/hexane	88	94	96	±6	4.0
H ₂ O/CH ₂ Cl ₂	71	85	93	±4	4.0
i-PrOH/cyclohexane	79	87	87	±10	10.0

Table 4 Comparison of Extraction techniques for phenols (phenol, *p*-nitrophenol, tetrachloroguaiacol)

a) Alfisol

Extraction technique	% extracted (org. phase)			Aquatic phase	S.D.	% residue in soil
	I	II	III			
EtOH/Et ₂ O	77	91	94	1.0	±3	5.0
H ₂ O/toluene (pH < 2)	64	91	95	3.0	±3	2.0
CHCl ₃ /Et ₂ O (pH < 2)	75	93	95	0.5	±3	4.5
H ₂ O/CH ₂ Cl ₂ (pH < 2)	73	92	96.5	0.5	±2	3.0
H ₂ O/CH ₂ Cl ₂ (pH > 11)	6.0	8.0	8.5	88.5	±7	3.0

b) Spodosol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
EtOH/Et ₂ O	68	80	83	±3	16
H ₂ O/toluene	55	68	89	±7	10
CHCl ₃ /Et ₂ O	66	81	89	±5	10
H ₂ O(pH2)/CH ₂ Cl ₂	65	75	89	±3	10

Table 5 Comparison of Extraction techniques for esters (phthalic acid-bis (2-ethylhexyl) ester, benzoic acid butyl ester, warfarin)

a) Alfisol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
H ₂ O/acetone	68	87	92	±1	8.0
H ₂ O/CH ₂ Cl ₂	79	93	95	±2	5.0
Acetone	76	90	92	±3	8.0
Acetone/CH ₂ Cl ₂	87	94	95	±2	5.0

b) Spodosol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
H ₂ O/acetone	74	90	93	±2	7.0
H ₂ O/CH ₂ Cl ₂	70	93	97	±2	3.0
Acetone	70	90	93	±3	7.0
Acetone/CH ₂ Cl ₂	82	92	95	±5	5.0

Table 6 Comparison of Extraction techniques for ketones (cyclohexanone, acetophenone, trichloroacetophenone)

a) Alfisol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
H ₂ O/acetone	80	93	96.5	±2	3.5
H ₂ O/CH ₂ Cl ₂	80	94	96.5	±2	3.5
Acetone	80	90	92	±4	8.0
Acetone/CH ₂ Cl ₂	81	91	92	±4	8.0

b) Spodosol

Extraction technique	% extracted (org. phase)			S.D.	% residue in soil
	I	II	III		
H ₂ O/acetone	74	88	92	±3	8.0
H ₂ O/CH ₂ Cl ₂	75	91	93	±3	7.0
Acetone	70	85	90	±5	10.0
Acetone/CH ₂ Cl ₂	73	83	90	±5	10.0

resulted in 80% of the radioactive material being partitioned into the aqueous phase.

For the investigated chemicals, extraction efficiencies of about 95% were obtained with the H₂O/CH₂Cl₂ system. Variation in pH-value favours the extraction of acidic and basic compounds. This agrees substantially with the

Table 7 Comparison of Extraction techniques for amines (paraquat, 2-chloroaniline, benzylamine, tyramine)

a) Alfisol

Extraction technique	% extracted	S.D.	% residue in soil
H ₂ O/CH ₂ Cl ₂ -soxhlet	57	±8	43
H ₂ O (pH > 11)/CH ₂ Cl ₂	49	±4	51
H ₂ O (pH < 2)/CH ₂ Cl ₂	63	±5	37
1M HCl/MeOH	59	±5	41
Methanolic NaOH	43	±5	57
MeOH/toluene	26	±4	74

b) Spodosol

Extraction technique	% extracted	S.D.	% residue in soil
H ₂ O/CH ₂ Cl ₂ -soxhlet	60	±10	40
H ₂ O(pH > 11)/CH ₂ Cl ₂	73	±6	27
H ₂ O(pH < 2)/CH ₂ Cl ₂	66	±7	34
1 M HCl/MeOH	59	±7	41
Methanolic NaOH	30	±3	70
MeOH/toluene	43	±6	57

results of Lopez-Avila *et al.*² who determined basic and neutral priority pollutants in a sediment.

The group of amines (Table 7) obviously sorb more strongly to soil than the other groups. Using strong solvents, on average 40% of the radioactivity remained bound to the soil. Recovery rates depended on the respective substrates using the H₂O/CH₂Cl₂ system. Worst results were obtained for paraquat (only about 50% was extracted after 1 week aging) and best for chloroaniline and benzylamine (about 70%). Using the H₂O/CH₂Cl₂ system at pH > 11 and pH < 2, successively, the alfisol and spodosol gave different results: the spodosol yielded 10% bound residues, and the alfisol 30% bound residues. This can be related to the higher organic carbon content of the spodosol. A large portion of the humic fraction was extracted with H₂O/CH₂Cl₂ at pH 11 and pH 2 respectively.

Successive extraction of the non-volatiles with H₂O/CH₂Cl₂ at pH > 11 and pH < 2 was followed by gel chromatography to separate high molecular weight impurities. Further liquid-liquid partitioning and column chromatography led to subfractions of neutrals, acids, and basics which could be analysed by GC, HPLC and MS after concentration.

Acknowledgement

This work is supported by a grant of the Federal Ministry for Research and Technology within its soil protection programme, grant-No. 63390 83 A.

References

1. E. D. Pellizzari and A. W. Garrison, *Master analytical scheme for organic compounds in water*. Proceedings of the 188th National Meeting of the American Chemical Society (Philadelphia, 1983), vol. 24, No. 2.

2. V. Lopez-Avila, R. Northcutt, J. Onstot and M. Wickham, *Anal. Chem.* **55**, 881 (1983).
3. Ch. S. Helling and A. E. Krivanak, *J. Agric. Food Chem.* **26**, 1156 (1978).
4. J. B. Ferrario, G. C. Lawler, I. R. DeLeon and J. L. Laseter, *Bull. Environ. Contam. Toxicol.* **34**, 246 (1985).
5. P. H. Kiang and R. L. Grob, *J. Environ. Sci. Health* **A21**, 71 (1986).
6. S. U. Khan and H. A. Hamilton, *J. Agric. Food Chem.* **28**, 126 (1980).
7. T. Rampstad, T. Nestick and T. L. Peters, *American Laboratory*, July (1981).
8. P. H. Kiang and R. L. Grob, *J. Environ. Sci. Health* **A21**, 15 (1986).
9. B. von Oepen and W. Kördel, *Chemosphere*, in press (1989).
10. O. Fränze and G. Kuhnt, *Regionale Repräsentative Auswahl der Böden für eine Umwelt-probenbank—Exemplarische Untersuchung am Beispiel der Bundesrepublik Deutschland*. Umweltforschungsplan des Bundesministeriums des Innern, Forschungsbericht 106 05 028 (1983).
11. J. Katan, T. W. Fuhreman and E. P. Lichtenstein, *Science* **193**, 891 (1976).
12. *OECD-Guideline for testing chemicals No. 304 A, adapted 12 May 81*, Inherent Biodegradability in Soil.
13. W. Giger and M. Blumer, *Anal. Chem.* **46**, 1663 (1974).
14. R. G. Nash, W. G. Harris, P. D. Ensor and E. A. Woolson, *J. Assoc. Off. Agric. Chem.* **56**, 728 (1973).