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Microwave assisted solvent extraction and coupled-column reversed-phase liquid chromatography with UV detection Use of an analytical restricted-access-medium column for the efficient multi-residue analysis of acidic pesticides in soils

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Abstract

A screening method has been developed for the determination of acidic pesticides in various types of soils. Methodology is based on the use of microwave assisted solvent extraction (MASE) for fast and efficient extraction of the analytes from the soils and coupled-column reversed-phase liquid chromatography (LC–LC) with UV detection at 228 nm for the instrumental analysis of uncleaned extracts. Four types of soils, including sand, clay and peat, with a range in organic matter content of 0.3–13% and ten acidic pesticides of different chemical families (bentazone, bromoxynil, metsulfuron-methyl, 2,4-D, MCPA, MCPP, 2,4-DP, 2,4,5-T, 2,4-DB and MCPB) were selected as matrices and analytes, respectively. The method developed included the selection of suitable MASE and LC–LC conditions. The latter consisted of the selection of a 5-μm GFF-II internal surface reversed-phase (ISRP, Pinkerton) analytical column (50×4.6 mm, I.D.) as the first column in the RAM–C_{18} configuration in combination with an optimised linear gradient elution including on-line cleanup of sample extracts and reconditioning of the columns. The method was validated with the analysis of freshly spiked samples and samples with aged residues (120 days). The four types of soils were spiked with the ten acidic pesticides at levels between 20 and 200 μg/kg. Weighted regression of the recovery data showed for most analyte–matrix combinations, including freshly spiked samples and aged residues, that the method provides overall recoveries between 60 and 90% with relative standard deviations of the intra-laboratory reproducibility's between 5 and 25%; LODs were obtained between 5 and 50 μg/kg. Evaluation of the data set with principal component analysis revealed that the parameters (i) increase of organic matter content of the soil samples and (ii) aged residues negatively effect the recovery of the analytes.

Keywords: Microwave-assisted solvent extraction; Restricted-access-medium column; Pesticides, acidic

1. Introduction

The trace analysis of acidic pesticides in environmental samples employing reversed-phase liquid chromatography with UV detection (RPLC-UV) is usually hampered by the co-extraction of humic subtances, viz. fulvic and humic acids. At low wavelength detection, typically at about 220 nm, these interference's show up in the chromatogram as a broad hump causing a severe baseline deviation and frequently obstructing the reliable quantification of the analytes at the required low levels.

As demonstrated recently [1–4] analytical col-

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umns packed with a highly efficient restricted access material (RAM) can be a viable way to adequately control the humic hump problem.

Analytical RAM columns combine an efficient reversed-phase separation of low molecular mass target analytes and a size exclusion of large molecular compounds. Originally, they have been successfully developed in the field of biomedical analysis for the direct processing of body fluids. Overviews on the various types of RAM materials, columns and their applications in biomedical analysis have been published [5,6].

In several studies we investigated the feasibility of RAM materials to enhance the RPLC-UV trace analysis of acidic compounds in environmental water [2,3] and soil samples [1].

In a comprehensive study involving the screening of acidic pesticides in water samples [3] it appeared that single RAM column operations could not provide sufficient resolution between interferences and analytes. However, coupled-column RPLC (LC–LC) employing at least one analytical column packed with a highly efficient restricted access material (RAM) considerably eliminates the bad chromatographic behaviour of interferences.

Nowadays, LC with mass spectrometric detection (LC–MS) has proven to be an attractive alternative technique for the determination of acidic pesticides in water [4,7–13] and soil [14]. In comparison to UV detection, base-line deviations caused by humic substances are distinctly less using single MS detection [4,8–10] or absent in case of highly selective tandem MS (MS–MS) detection [7,11,13].

Nevertheless, for several reasons the use of UV detection in the screening and quantification of acidic pesticides in more complex matrices, such as soils, can be very attractive. Beside advantages such as low price, simplicity, robustness and large linear range, calibration with UV detection is usually not hampered by co-eluting non-detectable matrix compounds.

However, in LC–MS analyte responses (ionization) can be effected by matrix interferences and, especially, in the processing of concentrated and uncleaned extracts of solid samples, e.g. soils, matrix effects such as ion-suppression can be expected.

Therefore, a comprehensive study has been carried out on the feasibility of LC–LC-UV as an efficient technique for the screening of acidic pesticides in various types of soils. In a previous study [1] a RAM–C_{18} column combination involving a full size separation internal surface reversed-phase (ISRP) column as a first column was successfully applied in the (single) residue analysis of mecoprop in soils. The powerful cleanup performance of LC–LC allowed the processing of uncleaned aqueous soil extracts obtained after a simple extraction procedure.

In this study, the potential of this approach as regards multi-residue analysis of acidic pesticides in various types of soils was investigated. Representing different chemical families and relevant as regards their actual and/or historical agricultural use in The Netherlands, the ten acidic pesticides listed in Table 1 were selected as test compounds.

2. Experimental

2.1. Chemicals

All the ten acidic pesticides listed in Table 1 were from Dr. S. Ehrenstorfer (Promochem, Wesel, Germany) and had a purity of >99%. Acetone, acetonitrile, dichloromethane, ethyl acetate and methanol, all of HPLC-grade, were from J.T. Baker (Deventer, The Netherlands). Trifluoroacetic acid (TFA, 99%) was from Merck (Darmstadt, Germany). HPLC-grade water was obtained by purifying demineralized water in a Milli-Q system (Millipore, Bedford, MA, USA).

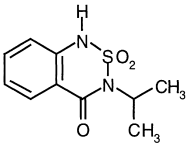
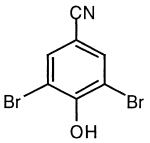
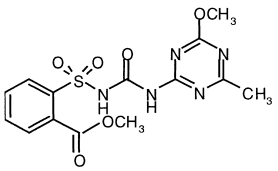
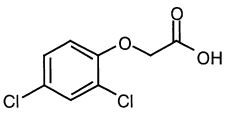
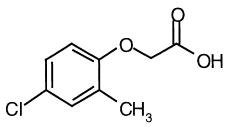
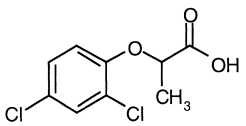
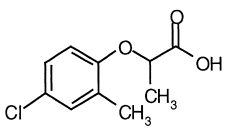
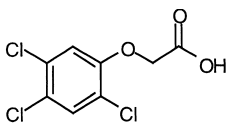
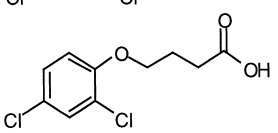
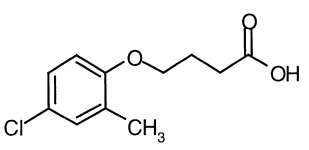
Stock standard solutions (ca. 1000 μg/ml) of the pesiticides were prepared in acetonitrile. For spiking or LC-analysis the stock solution was diluted in methanol or acetonitrile–0.05% TFA in water (20:80, v/v), respectively.

A dichloromethane–methanol–TFA (90:10:0.1, v/v/v) solution was used for Microwave assisted solvent extraction (MASE).

2.2. Instrumentation and columns

MASE was performed with a MES-1000, 950-W laboratory Microwave Extraction System (CEM, Mathews, NC, USA) configured with a 12-position carousel. The instrument controls in closed vessels either pressure or temperature.

Table 1
Information on selected acidic pesticides

Name and chemical family	Structure	pK_a	λ (nm)	ϵ (l mol^{-1} cm^{-1})
Bentazone Benzothiadiazole		3.3	215	27 000
Bromoxynil Hydroxybenzonitrile		3.9	217	30 000
Metsulfuron-methyl Sulfonyl urea		3.3	236	25 000
2,4-D Phenoxy acid		2.6	228	8000
MCPA Phenoxy acid		3.7	228	8300
2,4-DP Phenoxy acid		3.0	228	8000
MCPP Phenoxy acid		3.8	228	8200
2,4,5-T Phenoxy acid		n.a[a]	228	8800
2,4-DB Phenoxy acid		4.8	228	3100
MCPB Phenoxy acid		4.8	228	5800

[a] Information not available.

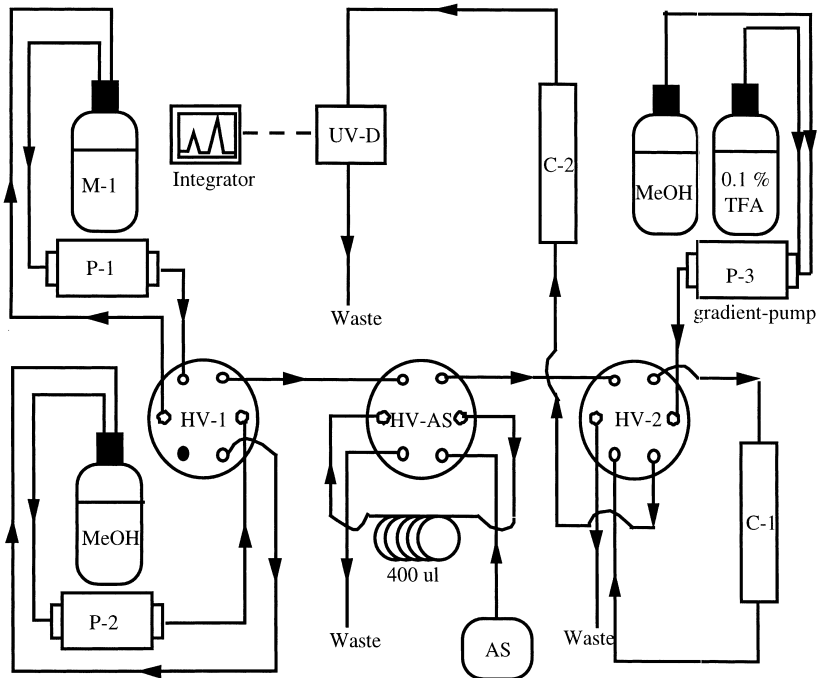


Fig. 1. Set-up of LC-system (cf. Table 3). HV-AS=Autosampler (injection valve); HV-1 and HV-2=high pressure valves; P-1 and P-2=isocratic LC-pumps; P-3=gradient LC pump; C-1 and C-2=first and second separation column; M-1=mobile phase; MeOH=methanol (for rinsing C-1); UV=UV detector (228 nm).

The LC system, schematically presented in Fig. 1, consisted of a Model 231XL autosampler, AS, from Gilson (Villiers-le Bel, France) equipped with two additional programmable high pressure valves, HV-1 and HV-2, Model Valvemate from Gilson; two Model 1050 isocratic LC pumps, P-1 and P-2, from Hewlett-Packard (Waldbron, Germany); a Model 1050 gradient pump, P-3, from Hewlett-Packard; and a Model 118 UV detector (wavelength at 228 nm), UV-D, from Gilson.

A 10×2 mm I.D. precolumn connected to a 50×4.6 mm I.D. column both packed with 5-μm GFF II from Pinkerton (Regis, Morton Grove, IL, USA) was used as the first column, C-1, and a 50×4.6 mm I.D. column packed with 3-μm C_{18} Microspher (Chrompack, Middelburg, The Netherlands) was used as the second column, C-2.

The mobile phase, M-1, applied on C-1 consisted of methanol–0.05% TFA in water (25:75, v/v). The solvents (A and B) to perform a binary gradient consisted of 0.1% TFA in water (solvent A) and methanol (solvent B); the starting mobile phase composition on C-2 corresponds to that of M-1, viz. 25% B. A rinsing mobile phase, M-R, consisting of 100% methanol, was for the cleanup of C-1 in between analyses.

The columns were kept at 30°C with a laboratory made column oven connected to a Model 1441 circulating water system from Braun (Melsungen, Germany).

2.3. Soil samples

Characteristics of the tested standard soils are given in Table 2. The water content was determined

Table 2
Information on the various type of standard soils

Type of soil	Location	Water content (%)	Organic matter content (%)
Sand	Hulshorst	1.2	0.3
Clay	Houten	16.1	3.9
Peat-1	Eeserveen	28.1	10.4
Peat-2	Schoonerwoerd	39.8	12.9

Table 3
Time schedule of the LC–LC analysis (cf. Fig. 1)

Time (min)	Event	Description
0.0	HV-AS injects 400 μl of sample on C-1	Start of analysis and cleanup
2.5	HV-2 switches C-1 on-line C-2; P-3 starts linear gradient elution from 25 to 55% methanol in 20 min	End of cleanup; Start of transfer analytes from C-1 to C-2 with a gradient elution
7.5	HV-2 switches C-1 off-line C-2; HV-1 solvent switch to methanol	End of transfer; Rinsing C-1
22.5	P-3 performs isocratic elution with 55% methanol	
27.5	HV-1 solvent switch to M-1	Conditioning C-1
30	P-3 is set to 100% methanol.	Rinsing C-2
35	P-3 is set 25% methanol	Conditioning C-2
40	End of total run time	

by drying the sample to constant weight at a temperature of 105°C. The organic matter content was determined by heating air-dried samples over 3 h at a temperature of 550°C.

Freshly spiked soils were prepared by weighing 10.0 g of a soil type into a glass bottle followed by the addition of 1 ml of spiking solution. The samples in the open bottles were allowed to stand for 24 h at ambient temperature in a fume hood before extraction. Samples with aged residues were stored after air-drying in the dark for 120 days at about 4°C.

Fortifications were made at levels of 0.1, 0.05 and 0.02 mg/kg for freshly spiked samples and at levels of 0.2 and 0.05 mg/kg for samples with aged residues, respectively.

2.4. MASE procedure

A 10.0-g blank or spiked soil sample was transferred to the PTFE-lined extraction vessel. Next, 20 ml of MASE extraction solvent was added to the samples before the extraction vessels were closed. At a setting of 100% instrument power (950 W) and a pressure limit of 690 kPa, extractions were performed at 60°C for 10 min. After cooling to room temperature, the organic solvent was dried over sodium sulphate and 5 ml of solvent (equivalent of 2.5 g of soil) was taken and evaporated to dryness under a gentle stream of nitrogen. The residue was dissolved by adding 400 μl of methanol and 1600 μl of 0.05% TFA in water.

2.5. LC analysis

All mobile phases were adjusted to a flow-rate of 1 ml/min. A volume of 400 μl obtained after the MASE procedure was injected on to C-1. After cleanup with 2.5 ml of M-1 (injection volume included), C-1 was switched by means of HV-2 on-line with C-2 for 5.0 min for the transfer of the fraction containing the ten herbicides from C-1 to C-2. After the transfer, the high-pressure valve HV-1 was switched to rinse C-1 with 20 ml of methanol (M-R).

After the cleanup time (2.5 min), a linear gradient elution was performed using 25–55% of methanol (solvent B) in 20 min. Next, C-2 was rinsed with about 5 ml of methanol.

An overview of the various steps involved in the LC–LC analysis is given in Table 3.

Quantification of the analytes was done by external calibration with standard solutions (range=0.01–5 μg/ml).

3. Results and discussion

3.1. General aspects

The aim of this study was to investigate whether the single residue method (SRM) approach developed for mecoprop [1] can be extended to a multi-residue method (MRM) approach for acidic herbicides of different chemical families in various types of soils.

In the SRM approach, small volumes, typically less than 100 μl, can be used for the transfer of the analyte from the first to the second column making the cleanup performance of LC–LC most powerful.

For example, in a comprehensive study on the trace analysis of acidic herbicides in water containing dissolved organic carbon (DOC), it was illustrated that in comparison to the MRM approach, the SRM approach offers higher selectivity [3].

In comparison to water samples more chromatographic difficulties can be expected in the analysis of extracts of soil samples. Moreover, the wide range in polarity and, consequently, the large difference in retention times of the selected analytes in the MRM approach (see Table 1) severely counteracts the cleanup performance of LC–LC because of the unfavourable volumes that will be required for cleanup (small volume) and transfer (large volume), respectively.

Therefore, on the basis of our previous study, method development optimisation was focussed at reducing matrix effects by selecting adequate LC–LC elution conditions and improving the extraction procedure.

3.2. LC analysis

Based on both good performance and robustness obtained for the analysis of mecoprop in soils [1] the short analytical 5-μm ISRP Pinkerton column (50× 4.6 mm I.D.) and the 3-μm C_{18} column (50×4.6 mm I.D.) were also selected in this study to be used in LC–LC as C-1 and C-2, respectively.

In the MRM analysis of a heterogeneous group of compounds one must consider the relatively large differences in efficiency, retention capacity and selectivity between the Pinkerton and the C_{18} column [3]. The reversed elution order and less efficient elution on C-1 of analytes counteracts the efficient separation on C-2. Fortunately, the distinctively lesser retention capacity of the ISRP column in comparison to C_{18} makes it possible to restore the elution order on C-2 in the case of LC–LC [3].

Providing a capacity factor of about five for the first eluting analyte (bromoxynil), methanol–0.05% TFA in water, pH 2.5 (25:75, v/v) as the first mobile phase, M-1, performed an adequate cleanup.

Preliminary experiments indicated that the successful MRM approach for DOC-containing water samples [3] involving two isocratic elutions on C-1 and C-2, and a step gradient on C-1, is not feasible for this type of analysis. The sudden release of the high amount of matrix interferences as a result of the step gradient and the required large transfer volume (about 2 min) severely hampers the quantification of compounds in the first part of the chromatogram. Lowering the eluotropic strength of M-2, significantly decreased the hump, but for the late eluting compounds the increase in retention provided a considerable loss in sensitivity (peak height).

Improved chromatographic conditions were obtained with the use of moderate steep linear gradient elution, starting when the columns are switched on-line. The selected conditions are given in Table 3. As shown, the LC–LC procedure includes the rinsing of both columns during each run. This appeared to be a viable approach in the processing of series of soil samples in order to completely eliminate chromatographic distortions such as shifting of retention times and/or chromatogram distortions caused by the matrix substances of previous injections.

3.3. Extraction

In our previous study [1], a convenient extraction procedure was applied involving (i) hydrolysis/extraction of a soil sample by boiling with aqueous alkaline solution, (ii) centrifugation of the extract, and (iii) the acidifying of an aliquot of the clear extract before the instrumental analysis. Optionally an off-line solid-phase extraction (SPE) step on a 100-mg C_{18} cartridge can be used to improve both sensitivity and selectivity.

When testing the procedure with freshly spiked sand and clay samples (0.2 mg/kg) recoveries of about 100% were obtained for all compounds, except

for metsulfuron-methyl (0%), which was caused by decomposition at elevated temperatures during hydrolysis. Furthermore, for peat samples a turbid solution was obtained after the acidifying step. Unfortunately, processing of this solution with LC or SPE caused a severe clogging of the packing material, while an additional centrifugation step resulted in distinct losses of the compounds.

Because of our successful experience with microwave assisted solvent extraction (MASE) for the efficient extraction of various type of polar pesticides from soils [15–17], the feasibility of this technique was investigated. In our previous applications, a mixture of dichloromethane–methanol (90:10, v/v) appeared to be a convenient and efficient extraction solvent. In order to avoid decomposition of metsulfuron-methyl, the rather mild extraction conditions used before in the analysis of sulfonyl urea herbicides [15] were also selected in this study.

Experiments with freshly spiked sand samples (level of 0.2 mg/kg) showed good recoveries for bentazone, bromoxynil and metsulfuron-methyl, however, the seven chlorophenoxy pesticides were poorly recovered (range=10–40%).

The solvent mixture of acetone–ethyl acetate (75:25, v/v) used for the efficient MASE of carbendazim from soils [17] decreased further the recoveries (range=0–18%) of these compounds.

Satisfactory results were obtained in performing MASE with an acidified extraction solvent by the addition of 0.1% TFA (v/v) to the dichloromethane–methanol solvent. Under these conditions (see Section 2) all acidic pesticides were recovered very well (range=90–100%) from the sand soil.

3.4. Results

The final procedure employing MASE and LC–LC-UV (228 nm) was validated by the analysis of freshly spiked soil samples ($N=49$) and soil samples ($N=28$) with aged residues. A total of 77 recovery experiments employing four types of soils (see Table 2) spiked at different levels (see Section 2) were analysed on 24 different days in a 3-month period.

The performance of the screening multi-residue method is displayed in Fig. 2, showing the LC–LC-UV (228 nm) analysis of clay soil freshly spiked with acidic pesticides to a level of 200 μg/kg. As experienced before [15], in comparison to an aqueous extraction [1] the humic acid hump is distinctly less pronounced in MASE. Nevertheless, Fig. 2 clearly indicates the advantageous effects of LC–LC in eliminating (background) interferences and, by this effect, providing slightly improved resolution between the analytes.

The performance of the method was determined by processing the recovery data with CALWER 2.2, a computer spreadsheet program for calibration using weighted linear least square regression analysis [18]. For all compounds, various types of calibration models, linear/non-linear, with/without intercept were tested. The contribution from both intercept and non-linearity appeared to be non-significant. Therefore, the most simple model, viz. a straight line through the origin, was used.

The average recoveries and the intra-laboratory reproducibilities of the pesticides for each type of soil and type of spiking are summarised in Table 4. The standard deviations (s_o) of the lowest calibration point of the analytical procedure were used to establish the detection limit ($3s_o$) of the analytes in the various types of soils. An overview of these results is made in Table 5.

On the basis of a visual interpretation of the data given in Tables 4 and 5, several effects can be observed. For example, as illustrated in Fig. 3, the recovery of most analytes is significantly lower in peat samples with aged residues in comparison to sand (or clay, see Table 4). Consequently, higher LODs are obtained for peat samples with aged residues (see Table 5).

3.5. Principal component analysis

In order to illustrate more clearly the influence of the organic matter content on the recovery of the different analytes, the data of this study were evaluated with principal component analysis (PCA). PCA is a statistical multivariate data analysis to abstract information from a data set [19].

The first principal component, PC-1, is defined as the linear combination of the pesticides that describes the largest possible part of the variance. The second principal component, PC-2, is independent and orthogonal (perpendicular) from the first PC and describes the second largest part of the variance of

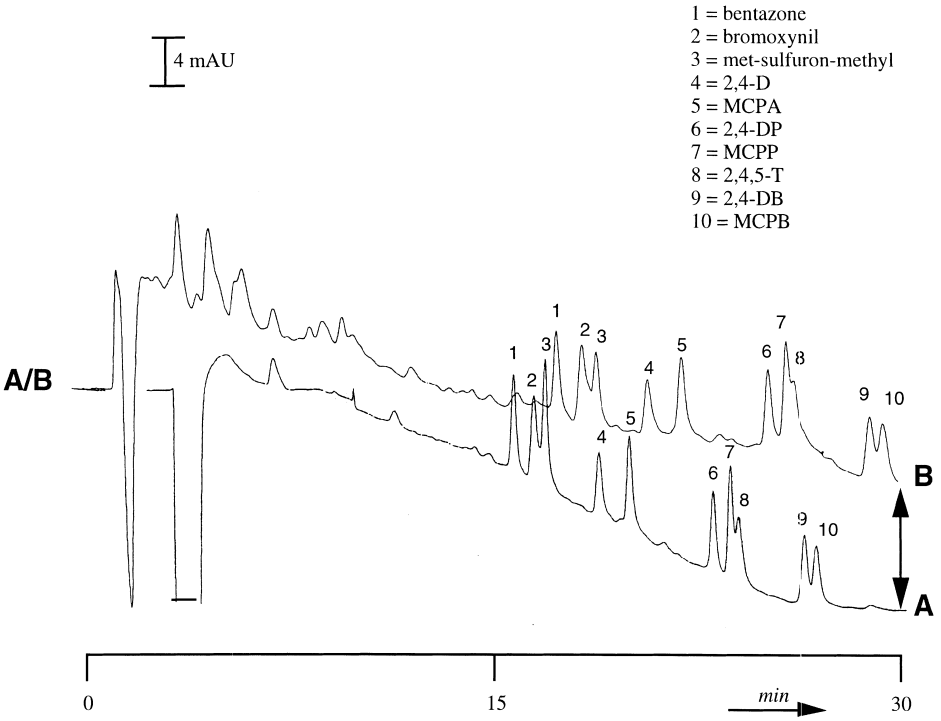


Fig. 2. RPLC-UV (228 nm) of 400 μl of extract of a standard soil clay sample spiked with the acidic pesticides at level of 200 μg/kg. (A) LC–LC (column switching) using 5-μm GF-II ISRP column (50×4.6 mm I.D.) as C-1 and a 3-μm C_{18} column (50×4.6 mm I.D.) as C-2. (B) LC on C-1 and C-2 coupled on-line (without column switching). Elution conditions for both (A) and (B) are given in Table 3.

Table 4
Overall recoveries of acidic pesticides from various types of soils of freshly-spiked and aged residue samples

Soil type	Spiked level (μg/kg)	*N*	Overall recovery and the relative standard deviation (RSD) of the intra-laboratory reproducibility, *R* (%)								
			Bentazone	Bromoxynil	Metsulfuron -methyl	2,4-D	MCPA	2,4-DP	MCPP	2,4,5-T	2,4-DB	MCPB
Sand	100; 50; 20	14	104(12)	105(13)	87(12)	83(18)	82(19)	95(11)	85(12)	76(19)	66(19)	78(16)
Sand[a]	200; 50	7	98(13)	100(11)	40(7)	79(13)	81(11)	82(12)	73(21)	76(21)	66(16)	65(7)
Clay	100; 50; 20	14	61(10)	76(11)	105(30)	47(15)	64(16)	74(12)	85(25)	51(18)	97(14)	93(17)
Clay[a]	200; 50	7	78(9)	67(16)	100(8)	74(6)	84(11)	93(4)	99(9)	69(6)	96(11)	87(8)
Peat-1	100; 50; 20	14	80(29)	91(25)	78(33)	80(26)	94(25)	80(21)	94(31)	122(16)	60(17)	54(18)
Peat-1[a]	200; 50	7	53(23)	73(22)	54(26)	72(29)	48(24)	45(23)	50(18)	47(19)	36(16)	38(14)
Peat-2	100; 50	7	100(4)	101(15)	88(17)	119(13)	95(8)	97(5)	89(5)	105(13)	93(14)	107(12)
Peat-2[a]	200; 50	7	19(35)	11(27)	68(11)	75(15)	66(20)	50(18)	46(18)	55(19)	23(17)	33(12)

[a] Aged residue samples stored for 120 days at 4°C before analysis.

Table 5
Calculated LODs of the acidic pesticides (μg/kg) in the various types of soils

Soil type	Bentazone	Bromoxynil	Metsulfuron-methyl	2,4-D	MCPA	2,4-DP	MCPP	2,4,5-T	2,4-DB	MCPB
Sand	6	7	5	11	11	6	8	11	14	8
Sand[a]	13	11	7	13	11	12	21	21	16	7
Clay	6	8	10	10	12	8	24	21	15	4
Clay[a]	12	25	10	8	14	12	14	24	26	10
Peat-1	13	14	12	17	16	13	27	12	16	5
Peat-1[a]	28	31	21	54	32	28	26	29	34	15
Peat-2	6	19	27	19	13	8	8	18	35	16
Peat-2[a]	32	41	41	21	26	22	25	25	46	27

[a] Aged residue samples stored for 120 days at 4°C before analysis.

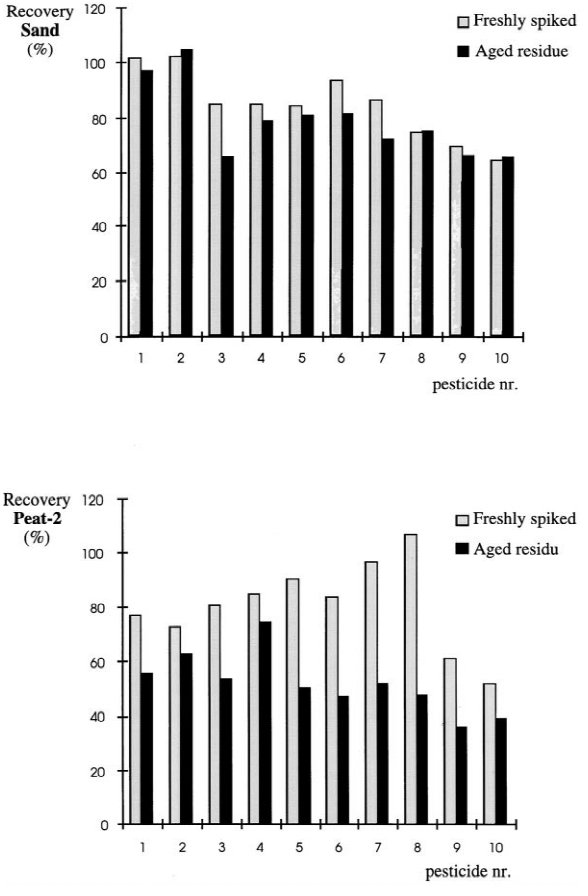


Fig. 3. Recovery plots freshly spiked samples and samples with aged residues of sand (upper) and peat-2 (under) standards soils.

the data set. For our data set, PC-1 describes 55% and PC-2 17% of the variance.

Assuming a linear combination of the original variables, samples (scores) and pesticides (loadings) were projected on the PCs.

Fig. 4 shows the scores plot of the recoveries of the samples. The PC loadings are reflected in Fig. 5 and inform about the amount of variance of the parameters (i) pesticides, (ii) aged-residue analysis and (iii) organic matter contents. A parameter completely described by two PCs will be projected on the circle with radius 1.

For interpretation purposes the scores of artificial samples with recoveries of 25, 50, 75, 100 and 125% for all compounds were added to the plot (Fig. 4). Real samples with scores close to these artificial points will have average recoveries close to the started values. For example, the aged samples with a high organic-matter (OM) content are on average close to 50%. Most fresh sand and peat samples are on average in between 75 and 100%.

Apparently, the clay samples situated in the upper half of the plot behave different from the other type of soils, which is not caused by the organic matter content.

The loadings information in Fig. 5 suggests that compounds 3, 9 and 10 are relatively high and 8 and 4 are relatively low for clay, indicating that the different acidic compounds behave differently.

The loadings plot also shows that both organic matter and aging reduce the recovery (the variables are plotted on the left side).

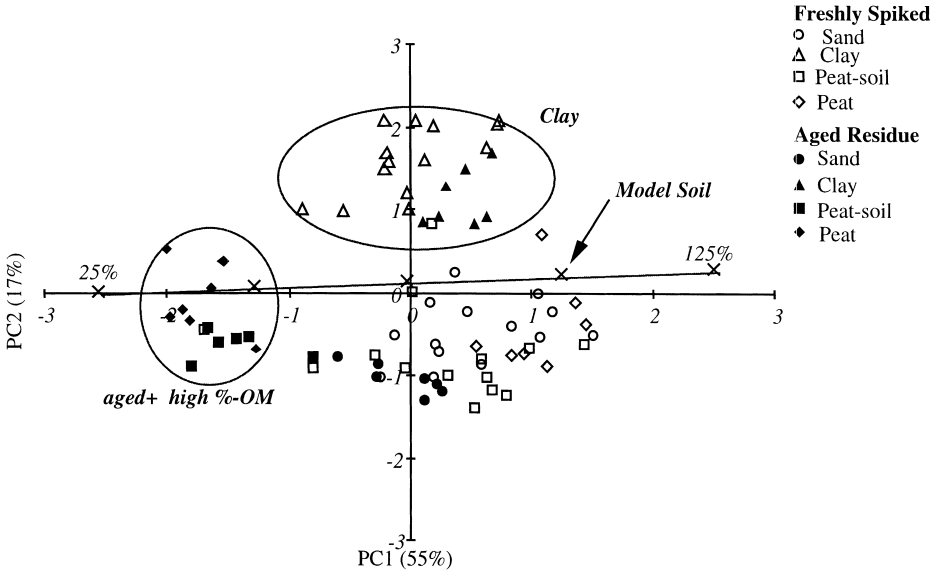


Fig. 4. Scores plot of the PCA performed on the recoveries of the samples.

4. Conclusions

The combination of microwave assisted solvent extraction (MASE) and coupled column RPLC-UV (228 nm) employing an analytical restricted access medium (RAM) column is a viable approach for the multi-residue screening of acidic pesticides of different chemical classes in various types soils with a wide range in organic matter content.

In comparison to a previous extraction procedure [1], MASE offers improved selectivity and avoids degradation of analytes during extraction.

Soil extracts obtained by MASE are automatically processed in 40 min with LC–LC-UV providing a sample throughput of at least 20 samples per day.

In the case of freshly spiked samples, overall recoveries of the ten different acidic pesticides were obtained between 60 and 90% for most soil–pesticide combinations with a relative standard deviation of the reproducibility below 25%.

Similar results were obtained for samples with aged residues, except for the peat soil with the highest organic matter content (12.9%). These samples provided low recovery values (11–33%) for bentazone, bromoxynil, 2,4-DB and MCPB, while for the remaining compounds the overall average recoveries ranged between 45 and 75%.

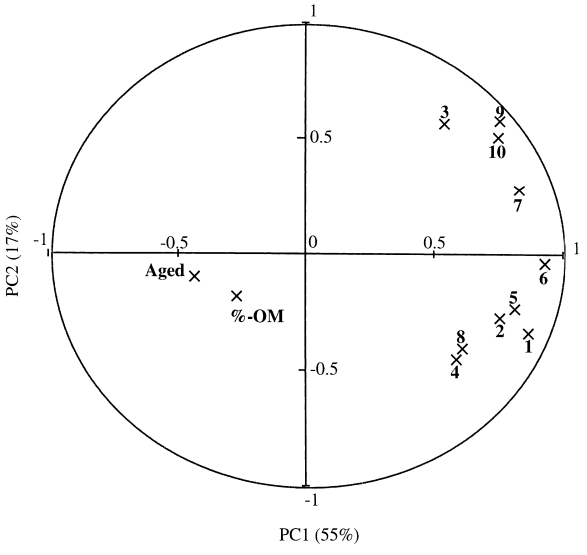


Fig. 5. Loadings plot of the PCA performed on the pesticides, the aging and the organic matter content.

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