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Journal of Chromatography A, 957 (2002) 79–87

JOURNAL OF CHROMATOGRAPHY A

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Analysis of Metribuzin and transformation products in soil by pressurized liquid extraction and liquid chromatographic–tandem mass spectrometry

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Abstract

A method developed for study of metribuzin degradation in soil is presented. LC–MS–MS and electrospray ionisation was used for analysis of metribuzin and the metabolites deaminometribuzin (DA), diketometribuzin (DK) and deaminodiketometribuzin (DADK). Soil samples were extracted by pressurized liquid extraction using methanol–water (75:25) at 60°C. In general, recoveries were about 75% for metribuzin, DA and DADK and their detection limit in soil was 1.25 μg/kg. Lower sensitivity was observed for DK, with detection limit at 12.5 μg/kg and recovery about 50%.

Keywords: Soil; Pressurized liquid extraction; Metribuzin; Deaminometribuzin; Diketometribuzin; Deaminodiketometribuzin; Pesticides

1. Introduction

When aiming at means to predict the risk that pesticides may leach through the soil and reach the ground water level, it is insufficient to consider the original pesticide only, as chemical and microbial degradation often transforms the pesticides into more polar compounds. Some of these are rather stable in the environment and their physical and chemical properties may increase the risk of leaching [1]. Thus, studies of possible degradation pathways and the biotic and abiotic effects on degradation pathways and degradation rates are important in relation to the pesticide risk assessment. In this work a method was developed for studying the degradation pathways and degradation rates of metribuzin in different sandy soils.

Metribuzin is a selective herbicide used for pre- and post-emergence control of grass and broad-leaved weed in specific crops like potatoes, soybeans, and tomatoes among others. Metribuzin belong to the group of triazinone herbicides, it is highly water-soluble (1050 mg/l) and adsorption in low-organic sandy soils is rather weak, sorption coefficients vary from 0.56 in a very sandy loam to 31.7 in a soil containing 60% organic matter [2]. In Denmark, metribuzin is allowed for potato growing only, with a maximal dose of 0.350 kg/ha per year (0.245 kg a.i.) [3]. The possible pathways of metribuzin degradation in soil are illustrated in Fig. 1.

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0021-9673/02/$ – see front matter
PII: S0021-9673(01)01453-4

The main metabolites from chemical and microbial degradation are deaminometribuzin (DA), diketometribuzin (DK) and deaminodiketometribuzin (DADK). Total microbial degradation of metribuzin into CO_2 and water takes place via the metabolite DADK, but in laboratory experiments mineralisation has not exceeded 20% [4,5].

Due to high water-solubility and weak adsorption, metribuzin as well as the transformation products possesses a risk of leaching to the groundwater. In Wisconsin, USA, metribuzin was found in well water samples in concentrations reaching 10.2 μg/l whereas the metabolites DA, DK and DADK were measured in the range 0.1–1.9 μg/l; in some cases metabolites were found even when metribuzin was absent [6]. In a Danish field experiment on a potato-growing sandy loam soil the metabolites DK and DADK were measured in pore water 1–2 m below ground surface, 6 months after metribuzin application [7]. Furthermore, DK and DADK derived from earlier applications were measured in the young groundwater (<10 years, depth 3–6 m), DK often in concentrations above the European Union threshold limit of 0.1 μg/l. In opposition to results from Wisconsin, USA, metribuzin occurred in much lower concentrations than DK and DADK, and the metabolite DA was totally absent, indicating different rates and pathways of degradation.

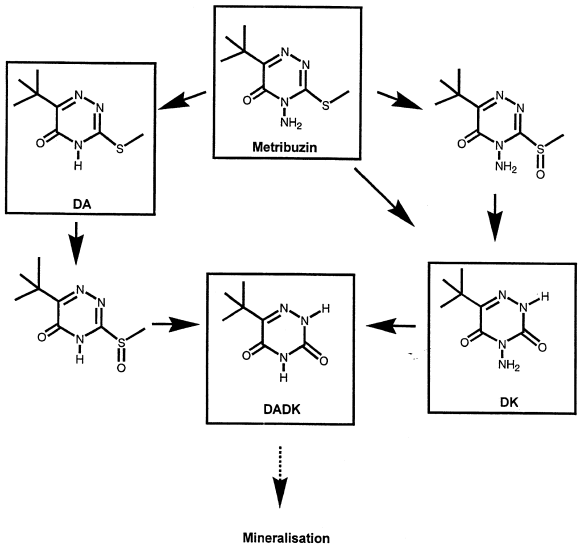

Fig. 1. Likely degradation pathways of metribuzin in soil. Redrawn from Ref. [2].

Several techniques can be chosen for analysis of metribuzin and the metabolites, being suitable for both gas and liquid chromatography and for various types of detectors like GC-flame ionization detection (FID) [8], GC–MS [9], GC with nitrogen–phosphorus detection (NPD) [10], RP-TLC–UV [11] and LC–UV [6,9,12,13]. HPLC is preferred for soil analyses even though GC–FID was used for this purpose too. Extensive clean-up procedures for the soil extracts are described in order to remove matrix materials, causing high background signal in the UV detector. Using LC–MS or LC–MS–MS this problem is remarkably reduced since most background noise is removed by the selective measurement at characteristic m/z values. Analysis of metribuzin by LC–MS is mostly performed as a part of multiresidue screening methods using either atmospheric pressure chemical ionisation (APCI) [14,15] or electrospray/ionspray ionization [16]. Specific methods are developed for analysis of metribuzin and the metabolites DA, DK and DADK in plant tissue or foods using LC–MS in combination with thermospray ionisation [17] and APCI [18].

Shaking moisture soil samples with solvent, typically methanol in mixture with aqueous buffer, followed by filtering or centrifugation is the most common technique used for soil extraction of metribuzin [11,12,19]. Pressurized liquid extraction (PLE; Dionex trade name ASE for accelerated solvent extraction) is a new, automated extraction method for solid matrices, using traditional organic solvents or water at elevated temperature and pressure, below the supercritical point. Advantages of this technique may be a less labor-intensive sample preparation, automatisation and less consumption and handling of organic solvent. An evaluation for extraction of atrazine and alachlor, comparing PLE with Soxhlet and flask shaking, demonstrated that recovery in case of short incubation (2 weeks) were about the same, no matter which method used, whereas best recovery was obtained by PLE after 8 and 26 weeks [20].

Aiming at developing a method that can be used for routine analysis, a high degree of automatisation is required. High sensitivity is required too, in order to detect the early formation of transformation

products in very low concentrations. Therefore the method development was based on the use of PLE for soil extraction and analysis by LC–MS–MS.

2. Experimental

2.1. Chemicals

Metribuzin (CAS RN 21087-64-9) and the degradation products deaminometribuzin (35045-02-4), diketometribuzin (56507-35-0) and deaminodiketometribuzin (52236-30-3) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Purity of metribuzin was 99.5%, DA 99% and DK and DADK 98%. A stock solution of metribuzin was made in acetonitrile and stored at 5°C. Before use, the solution was sonicated for 5 min. DA, DK and DADK were delivered in acetonitrile solutions at 10 mg/l. After breaking the ampoules, the standard solutions were kept in closed vials and stored at 5°C for no more than a month.

Methanol, acetonitrile and ethylacetate were HPLC grade from Romil (Cambridge, UK), isopropanol was pro analysis grade from Merck (Darmstadt, Germany). Water passed through a Millipore Milli-Q system (Molsheim, France) was used for soil extraction and standard dilutions, whereas HPLC-grade water from Ratburn (Walkerburn, UK) was used for LC mobile phase.

Ottawa Sand Standard, 20–30 mesh, purchased from Fischer Scientific (Fair Lawn, NJ, USA) was used as inert filling material in soil extractions.

2.2. HPLC

Analysis was performed with an HPLC system from Waters (Milford, MA, USA), model 2690. Complete separation of the compounds was obtained using an XTerra RP_{18} column from Waters, 100×2.1 mm, 3.5 μm particle size. The mobile phase composition was methanol–water (45:55, v/v) isocratic, with flow-rate at 150 μl/min. The injected volume was 10 μl. Temperature in the autosampler chamber was set to 5°C.

2.3. Mass spectrometry

Detection was made using a Quattro Ultima triple quadrupole mass spectrometer from Micromass (Manchester, UK), equipped with electrospray ionisation (ESI) and APCI. ESI was chosen for these analytes, working in both positive and negative mode. Analytes were quantified by selective reaction monitoring, measuring a single characteristic fragment ion of each analyte obtained by collision-induced dissociation of the protonated/deprotonated molecular ion.

Nitrogen was used as desolvation gas at a flow-rate of 400 l/h. The desolvation temperature was 250°C, the ion source was kept at 100°C. Capillary voltages were 2.80–3.20 kV and cone voltages 50–80 V, depending on the analyte. For MS–MS, argon was used as collision gas at operating pressure of 1.5 mTorr (0.2 Pa), with collision energies in the range 18–20 eV. The exact settings and ion traces for each analyte are shown in Table 1.

2.4. Preparation and spiking of soil samples

Since the extraction method must be usable for many different soils, sampled in various depths, two sandy soils were used for method development, representing the variation through an average Danish soil profile with respect to the content of organic matter. Soil taken from the plough layer (topsoil)

Table 1
Specified MS–MS conditions for detection of each compound

	M_r	Ionisation mode	Ion trace	Capillary voltage (kV)	Cone voltage (V)	Collision energy (eV)
Metribuzin	214.29	ESI (+)	215⇒187	3.2	80	20
DA	199.28	ESI (+)	200⇒172	2.6	50	18
DADK	169.18	ESI (−)	168⇒97	2.8	60	18
DK	184.20	ESI (−)	183⇒139	2.8	80	18

contained 2.31% organic carbon, and the sediment soil (subsoil) contained 0.023%.

Soil samples for each run of a maximum of 24 samples were prepared simultaneously. Aliquots of 30.0±0.1 g soil were weighted into a 100 ml blue cap bottle and 1000 μl aqueous pesticide standard was added slowly all over the soil surface concerning not to deposit it on the glass. The bottles were then capped and incubated for 2–6 days at 10°C.

2.5. Soil extraction

PLE using an ASE 200 system connected to a four-bottle solvent controller, both from Dionex (Sunnyvale, CA, USA), performed extraction of soil samples. Nitrogen at a pressure of 10 bar was supplied to assist the pneumatic system and to purge the extraction cells. For extraction, methanol–water (75:25; v/v) was used at 60°C for 10 min static time, in one extraction cycle. Other extraction conditions were as follows: pressure 1500 p.s.i., preheat 3 min, flush volume 60% and purge time 60 s (1 p.s.i.= 6894.76 Pa).

The volume of the extraction cells was 33 ml, sufficient to contain 35–40 g of moist soil. Since water was a part of the final extraction solvent, no drying agent was added to the cell. To protect the end cap from particulate substances a cellulose filter was mounted inside the cell towards the outlet direction. Soil samples were quantitatively transferred to the extraction cell using a narrow spoon and rubber scraper. The remaining cell volume was filled with Ottawa Sand.

A soil extract of 35–40 ml was obtained. After thoroughly mixing an aliquot was filtrated through a 0.45 μm nylon filter for HPLC analysis without further clean-up.

3. Results and discussion

3.1. LC–MS–MS analysis

Ionisation and fragmentation conditions were optimised for each compound by continuous flow injection of pure standard solution using a syringe infusion pump at 10 μl/min.

Ionisation of metribuzin, DA, DK and DADK was performed using both ESI and APCI. However, the response using APCI was at least ten times less than the response obtained by ESI. Therefore, further method development described below was done for ESI only.

At first the precursor ion was selected by scanning the first quadrupole in both positive and negative mode, followed by optimising the capillary voltage and cone voltage in order to obtain the highest response of the selected ion. In the positive mode metribuzin and DA were detected as $[M+H]^+$ whereas DK and DADK were detected by negative ionisation as $[M-H]^-$. Only poor ionisation, or none at all, was observed when analysing the compounds in the opposite mode, respectively.

Being a weak base, the formation of protonated metribuzin in the positive ionisation mode was expected, as confirmed in other LC–MS methods published [14–16]. The ionisation of the three metabolites was less predictable, as only DA was detected in the positive mode. The formation of negative ions from DK and DADK may be explained by keto–enol tautometry of these molecules, as described by Hatzios and Penner [21], creating weakly acidic enolic forms. The fact that the ionisation yield of DADK, being about five to ten times higher than the yield of DK, is in good agreement with this theory, since both keto groups in DADK are available for tautomery but only one of the keto groups in DK. Opposite to DK and DADK, the positive ionisation of DA was clearly favoured in this work, even though it has been demonstrated that also the metabolite DA does exist in several tautomeric forms [22]. Using thermospray ionisation, all the metabolites were detected as positive ions; DA as $[M+H]^+$ at m/z 200 and DK and DADK as $[M+NH_4]^+$ at m/z 202 and 187, respectively [17]. Additional adduct ions were observed for DADK at m/z 246 and 247. DADK was the least sensitive of the four compounds analysed, whereas it was the next most sensitive compound in the present work. Using APCI, metribuzin and DA were ionised in both the positive and the negative mode [18], and the negative mode was selected for DA in the final method. DK and DADK were only ionised in the negative mode. Even though it seems that the three metabolites have potential for both modes of ionisation, positive ionisation of DADK and DK by

protonisation was not observed in any case and higher sensitivity was obtained by negative ionisation. Regarding the metabolite DA, the sensitivity of each ionisation mode may depend on the actual conditions like the mechanisms of ionisation and the solvent and additives used for LC separation.

Fragmentation of the parent ion was examined at different collision energies by increasing the accelerating voltage inside the collision cell in the range 10–25 eV. Full scan spectra of the fragments were obtained in the second quadrupole for each 5 eV increases, and the spectra compared to select the characteristic fragment and the optimal collision energy. It was found that some peaks in the fragment mass spectrum were derived from solvent clusters, having the same m/z value as the precursor ion. In case of DK, additional peak injections of the pure standard were necessary to select a correct ion trace.

The sensitivity and selectivity of the analysis are demonstrated in Fig. 2, showing the chromatogram from the analysis of a topsoil sample, spiked with the analytes at 12.5 μg/kg. This level is close to the detection limit for DK, the least sensitive metabolite.

3.2. Soil extraction

PLE consists of several steps: filling the cell with solvent and heating until equilibrium; a static soaking of the sample in the heated solvent; flushing the sample with fresh solvent while collecting the first portion of solvent and finally purging the sample with nitrogen forcing the remaining solvent out of the cell. When more than one extraction cycle is performed, the cell is flushed with a fraction of the volume and the static step is repeated with fresh solvent. In order to optimise the extraction, temperature, solvent, pressure, soaking/static time, flush volume, purging time and number of cycles can be varied.

In this work, optimisation of the extraction conditions was primarily performed with metribuzin as model compound. The metabolites were only added to a few samples in each run, representing the extremity in the conditions evaluated. In almost all cases recovery of the metabolites followed the same tendencies as for metribuzin. Method development was performed for one soil type at the time, starting with the subsoil. Since some of the experience

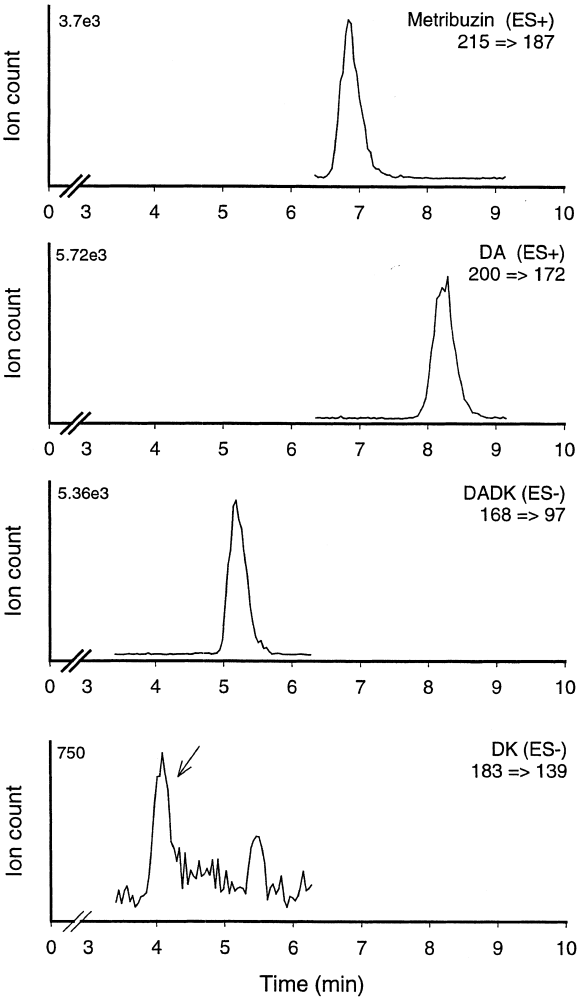

Fig. 2. Analysis of extracted soil sample. The sample was spiked with metribuzin, DA, DK, and DADK in the concentration 12.5 μg/kg and incubated at 10°C for 5 days before extraction. Analyte concentrations were 5–10 μg/l. MS–MS traces used for detection of each compound are shown in their respective chromatograms.

obtained during this work was utilized in the following, the extraction conditions for the subsoil was more thoroughly evaluated than for the topsoil.

Four organic extraction solvents – methanol, acetonitrile, ethyl acetate and isopropanol – were evaluated; both as pure solvents and as 1:1 mixtures. Except for the samples extracted with pure isopropanol, recoveries were better than 70% and no significant difference was found between the remaining three solvents. However, methanol was preferred

in the further work because this sample solvent was less harmful to handle than acetonitrile and more compatible to the LC mobile phase than the stronger eluting ethyl acetate, which caused severe peak broadening.

Using pure methanol as extraction solvent, the extraction temperature, time and number of cycles were evaluated for the subsoil. Finally the effect of addition of water to the solvent was examined. The effect of temperature is shown in Fig. 3. Surprisingly, recovery decreased at temperatures above 60°C, whereas increase of temperature is usually recommended to improve recovery. Later, the effect of temperature was tested once again in combination with the addition of 0–25% water to the solvent. In these experiments there was almost no difference, as seen in Fig. 4, but at least higher temperatures did not seem to improve recovery either. Therefore the final extraction temperature was kept at 60°C.

Extraction time was evaluated in the range 3–10 min (Fig. 5). Significant increase of recovery was obtained within this time range and at 10 min the curve starts to flatten out. However, a small improvement might result from increasing extraction time beyond 10 min. The use of one or two extraction cycles was evaluated within the same static time range, but no differences were observed. Locke et al. [19] evaluated extraction time using flask shaking with methanol–water (80:20) for 2×0.5, 4 and 24 h, respectively. Recoveries for 0.5 and 4 h were almost the same, whereas significant improvement was obtained by shaking 24 h. Due to the very different pattern in these two experiments it seems that extraction under PLE conditions causes significantly faster release of the analytes from the soil matrix.

If evaporation of the PLE extract is needed for further increase of the concentration, addition of water to the extraction solvent will prolong the evaporation time significantly. But, as the soil samples will contain water in different amounts anyway,

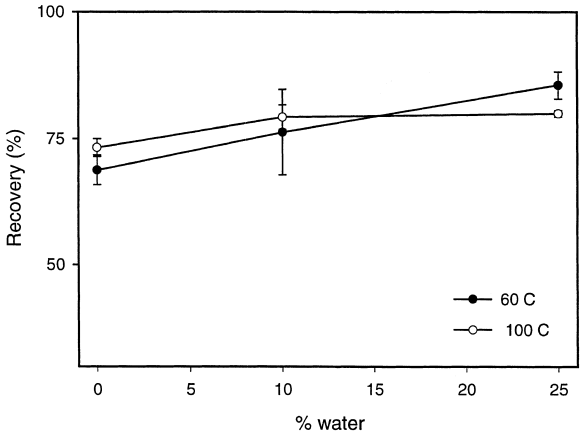

Fig. 4. Effect of methanol–water composition at different temperature. Subsoil samples were extracted with methanol at 60°C or 100°C for min with methanol containing 0, 10 or 25% (v/v) water.

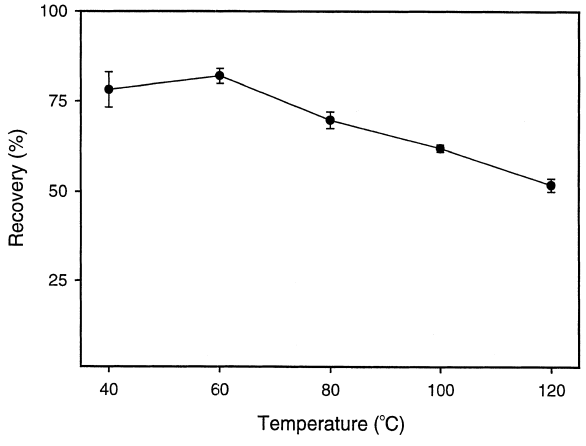

Fig. 3. Effect of extraction temperature. Subsoil samples were extracted with methanol for 5 min. Error bars showing standard deviation of duplicates.

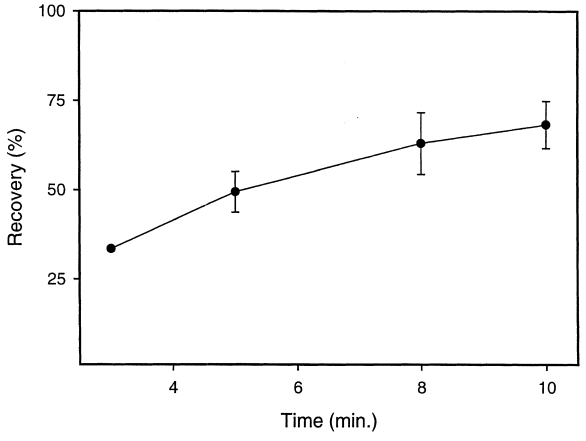

Fig. 5. Effect of extraction time. Subsoil samples were extracted with methanol at 60°C for 3, 5, 8 or 10 min.

and since other experiments have shown that methanol with 20–25% of water or aqueous buffer is more efficient for metribuzin extraction, the effect of methanol–water in different compositions was evaluated as well. Pure water was used, since non-volatile salts like $CaCl_2$ or Na_2SO_4 may suppress the ionisation in LC–MS and cause salt formation in the inlet. Locke et al. [19] found maximum recoveries using methanol–water (80:20) and (70:30). At compositions of 100:0 and 50:50, recoveries were about 10% lower. Results in Fig. 4 are showing the same tendency and a mixture of methanol–water (75:25) was chosen.

Extraction conditions in the topsoil were evaluated at 60, 80 and 100°C; 10 and 25% water in methanol and using one or two extraction cycles. Regarding metribuzin, the only difference compared to results from the subsoil was that the average recovery at 80°C was slightly better than at 60°C. Recoveries at 100°C were lower in all cases. The metabolites were only tested at few conditions and results for 60 and 100°C followed metribuzin. Considering the solvent composition, a clear discrepancy between the analytes was observed. Using 25% water gave the best recovery for metribuzin and DA whereas 10% water was better for extraction of DK and DADK. Differences in recoveries were 10–20% between the two solvent compositions, worst in the case of DK. The reason for the higher recovery at using the less water-containing solvent is not quite clear, since DK and DADK seem to be the most water soluble of the analytes with respect to comparison of retention times in reversed-phase HPLC. However, since the deviation in optimal conditions were relatively few and ambiguous, it was decided due to an overall consideration to use the same extraction conditions in both soils, based on the optimal conditions for the subsoil.

3.3. Evaluation of method performance

Limits of detection (LODs) and relative standard deviations (RSDs) were measured for the LC–MS–MS method. The calculated LODs, RSDs and linear correlation coefficients are listed in Table 2. The lower ionisation efficiency of DK compared to the other analytes can explain the difference in detection limits. Even though most background from co-extracted soil materials was removed from the chromatogram by mass selection, other kind of matrix effects like suppression/enhancement of the analyte ionisation or formation of complexes should still be considered. For this purpose, analytes were added to blank extracts from both types of soil and compared to aqueous standards. However, no differences were observed for any of the spiked soil extracts.

Table 2
Analytical precision (RSD), detection limit (LOD) and linear correlation

	RSD (%)	LOD (μg/l)	Correlation coefficient (r)
Metribuzin[a]	4.8	1.4	0.9998
DA[a]	5.7	0.9	0.9998
DADK[a]	3.5	0.6	0.9965
DK[b]	15.4	5.5	0.9999

RSD and LOD calculations are based on results from repeated injections of pure standard ($n=5$) at concentrations about five times the detection limit. LOD is calculated as: $2t_{(0.95,f)} \cdot \mathrm{SD} = 4.26 \cdot \mathrm{SD}$. Linearity was examined for the range 1–100 μg/l (5–100 μg/l for DK); [a] measured at 5.0 μg/l; [b] measured at 10.0 μg/l.

To examine the extraction recovery and detection capability for the method as a whole, moisture soil samples were spiked with metribuzin and metabolites at four levels: 1.25–2.50–12.5–25.0 μg/kg, and analysed after 5 days of incubation in accordance with the optimised method.

As can be seen in Fig. 6, metribuzin, DA and DADK were detected at all spike levels applied, whereas DK was not detected below 12.5 μg/kg. Since recoveries were almost constant within the whole range, it might be expected that analyte could be detected even in lower concentrations than 1.25 μg/kg (12.5 μg/kg for DK). However, the analyte concentration in the filtrated extracts at these levels was just above the analytical detection limit. Thus, at the moment, without further extract clean-up the detection limit of the whole method will be about 1 μg/kg for metribuzin, DA and DADK and 10 μg/kg for DK. For comparison, soil extraction with methanol and GC–NPD analysis obtained a detection limit for metribuzin at 10 μg/kg [10]. Extraction recoveries reported from other experiments, using methanol and water/buffer as extraction solvent, are comparable to recovery obtained in this work, being in the range 73–97% [10,11,19]. However, this

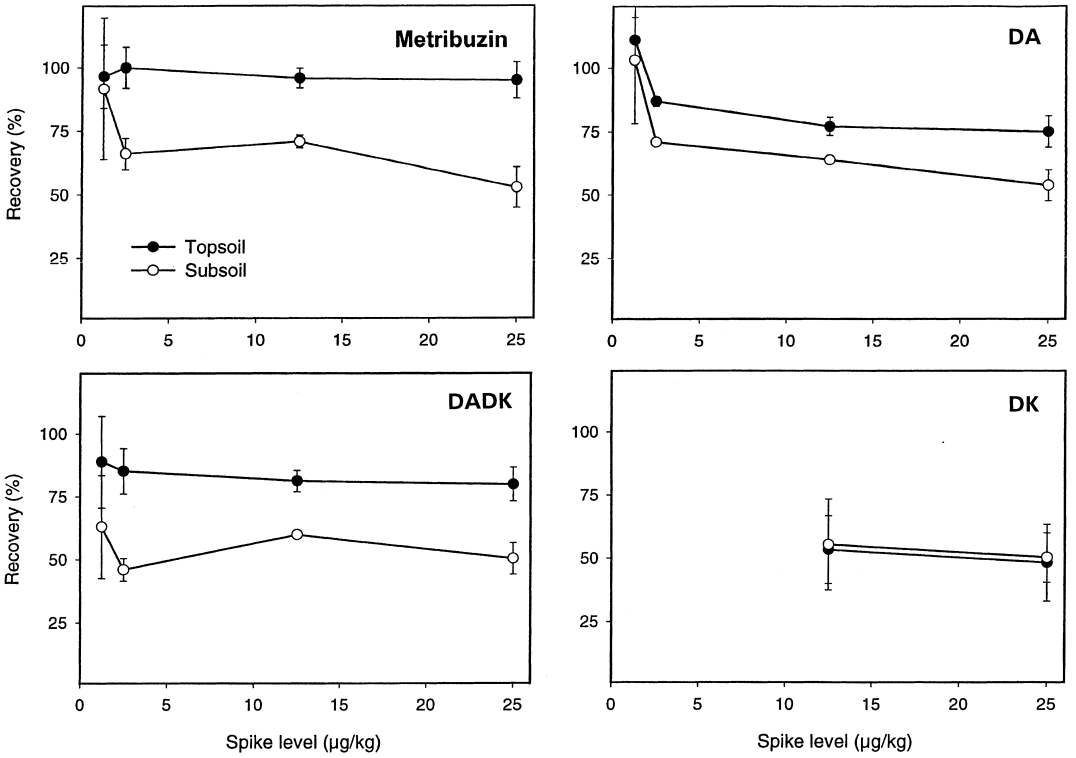

Fig. 6. Recovery at various concentrations using the optimised method. Samples of moisture topsoil (●) and subsoil (○) spiked to the concentrations: 1:25, 2.50, 12.5 and 25.0 μg/kg. Optimised conditions: methanol–water (75:25), 60°C, 10 min static time, and one extraction cycle. Standard deviations of the triplicates are shown.

method is simpler, because it is automated to a great extent.

It is possible to further optimise the detection limit by reducing the volume of the PLE extract. Due to the water content, evaporation of the methanol may cause only a four times increase of concentration. Further optimisation would require solid-phase extraction or liquid–liquid extraction of the remaining aqueous extract.

4. Conclusion

A method was developed for analysis of metribuzin and the three main metabolites, deaminometribuzin, diketometribuzin and deaminodiketometribuzin in soil. Analysis by LC–MS–MS using electrospray ionisation in positive mode for metribuzin and DA and in negative mode for DK and DADK showed high sensitivity and selectivity in the soil extracts. Sensitivity of DK was about ten times lower than the other compounds, probably due to lower ionisation efficiency in the mass spectrometer.

Extraction time and composition of the methanol–water solvent were most important for optimising soil extraction. Recovery using PLE was on average about 75%, showing some variation depending on soil type. However, the recovery of DK was only about 50%.

In spiked soil samples, incubated for 5 days, metribuzin, DA and DADK were detected at 1.25 μg/kg and DK at 12.5 μg/kg. These levels may be regarded as the detection limit, since concentration in the soil extracts were close to the analytical detection limits. However, improvement may possibly be obtained by further clean-up of the extract.

The present method is suitable for studying metribuzin degradation in laboratory experiments, being able to detect formation of metabolites in amounts about 0.5–1.0% of the applied herbicide. Consider-

ing the application dose of metribuzin, measurements of degradation under field conditions may also be possible, at least in the first 20–30 cm depth, where the concentration should be sufficiently high, with respect to the current detection limit.

Acknowledgements

We thank Pernille Stockmarr and Ann Siri Borg Hentze for valuable technical assistance during the method development and optimisation of the soil extraction procedure.

References

[1] D.W. Kolpin, E.M. Thurman, S.M. Linhart, Arch. Environ. Contam. Toxicol. 35 (1998) 385.
[2] T.R. Roberts (Ed.), Metabolic Pathways of Agrochemicals, Herbicides and Plant Growth Regulators, Vol. Part 1, The Royal Society of Chemistry, Cambridge, UK, 2001.
[3] J.E. Jensen (Ed.), Guidelines for Plant Protection (in Danish), Landbrugets Rådgivningscenter, 2001.
[4] P. Mallawatantri, B.G. McConkey, D. Mulla, J. Environ. Qual. 25 (1996) 227.
[5] T.B. Moorman, S.S. Harper, J. Environ. Qual. 18 (1989) 302.
[6] J.R. Lawrence, M. Eldan, W.C. Sonzogni, Water Res. 27 (2001) 1263.
[7] J. Kjær (Ed.), The Danish Pesticide Leaching Assessment Programme – Monitoring results, May 1999–July 2000, Geological Survey of Denmark and Greenland, Copenhagen, 2001.
[8] G.R.B. Webster, G.J. Reimer, Weed Res. 16 (1976) 191.
[9] B. Pepperman, J.W. Kuan, J. Liq. Chromatogr. 15 (1992) 819.
[10] J. Jebellie, S.O. Prasher, Trans. ASAE 41 (1998) 1051.
[11] R.M. Johnson, A.B. Pepperman, J. Liq. Chromatogr. 18 (1995) 739.
[12] M.A. Locke, S.S. Harper, L.A. Gaston, Soil Sci. 157 (1994) 279.
[13] E.W. Pavel, A.R. Lopez, D.F. Berry, E.P. Smith, R.B. Reneau Jr., S. Mostaghimi, Water Res. 33 (1999) 87.
[14] R. Jeannot, E. Sauvard, Ital. J. Food Sci. 12 (2000) 219.
[15] R.B. Geerdink, A. Kooistra-Sijpersma, J. Tiesnitsch, P.G.M. Kienhuis, U.A.Th. Brinkman, J. Chromatogr. A 863 (1999) 147.
[16] R. Curini, A. Gentili, S. Marchese, A. Marino, D. Perret, J. Chromatogr. A 874 (2000) 187.
[17] E. Parker, A.V. Geeson, D.E. Games, E.D. Ramsey, E.O. Abusteit, F.T. Corbin, K.B. Tomer, J. Chromatogr. 438 (1988) 359.
[18] M. Okihashi, K. Akutsu, H. Obana, S. Hori, Analyst 125 (2000) 1966.
[19] M.A. Locke, J.V. Pothuluri, T.B. Moorman, S.S. Harper, Commun. Soil Sci. Plant Anal. 21 (1990) 2141.
[20] J. Gan, S.K. Papiernik, W.C. Koskinen, S.R. Yates, Environ. Sci. Technol. 33 (1999) 3249.
[21] K.K. Hatzios, D. Penner, in: P.C. Kearney, D.D. Kaufmann (Eds.), Herbicides: Chemistry, Degradation and Mode of Action, Marcel Dekker, New York, 1988, p. 191.
[22] H. Dieckmann, R. Kreuzig, M. Bahadir, Fresenius' J. Anal. Chem. 348 (1994) 749.