Scientific Paper

DETERMINATION OF TRIAZINES AND ATRAZINE METABOLITES IN SOIL BY MICROWAVE-ASSISTED SOLVENT EXTRACTION AND HIGH-PRESSURE LIQUID CHROMATOGRAPHY WITH PHOTO-DIODE-ARRAY DETECTION

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Abstract

With our study microwave-assisted solvent extraction followed by chromatographic separation and quantification of selected triazines and atrazine metabolites were used. Soil matrix interferences negatively influenced the quantitation step, narrowing the linear range of the method. With the optimized microwave-assisted solvent extraction using 50:50 methanol/water mixture as the extraction solvent recoveries in the range 67-130% were reached, depending on the soil and the compound. The energy of microwaves was high enough to break down almost all sorption bonds between triazines/metabolites and soil. Due to matrix interferences desethyldesisopropylatrazine, desisopropylhydroxyatrazine and desethyldesisopropylhydroxyatrazine could not be determined. While higher organic matter content in soil seemed to slightly decrease the desorption, no correlation was proven between the clay content or soil pH and extraction efficiency.

Key words: microwave extraction, HPLC-DAD, triazines, metabolites, soil

Introduction

Triazines are a group of herbicides with great consumption all over the world, especially in the USA where atrazine is the second largest-selling herbicide.[1] Triazines are being used as selective pre- and postemergence herbicides on crops such as maize, sorghum, sugarcane, pineapples, and nursery conifers as well as in forestry conservation.[1] Their extensive use causes pollution of soil and consequently pollution of food and drinking water by pesticides' unmetabolised forms and their degradation products (metabolites).

The majority of published extraction methods for determination of triazines in soil include classical extractions with solvents. In spite of the advantages (standard methods, large samples), the disadvantages (long extraction times, large solvent volumes, solvent

exposure, high operating costs) mainly contribute to abandoning these procedures for extraction of solid samples. In recent years, especially microwave-assisted solvent extraction (MASE), besides supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE), has shown comparable results to classical extraction methods. Microwave-assisted extraction technique is suitable for the extraction of pesticides with a wide range of polarities.[2] In comparison to classical procedures the benefits of MASE are speed, high throughput (up to 14 samples simultaneously), low solvent volumes, high efficiency, precision and reproducibility.

In general, the effect of MASE can be explained by the solvent's ability to absorb microwaves, triazine solubility in solvents and triazine sorption in soils.[3] Kaune et al.[4] determined logK_{ow} for all of the investigated compounds. K_{ow} stands for *n*-octanol-water partition coefficient and is a measure of non-polarity (or hydrophobicity) of compounds. LogK_{ow} values expand from 2.99 for nonpolar prometryne to -0.46 for extremly polar desethyldesisopropylhydroxyatrazine. For these compounds different solvents were tested for MASE: methanol (ε=32.63 at 25 °C[5]), water (ε=78.30 at 25 °C[3,5]) and mixtures of dichloromethane/methanol (90:10, v/v) and acetone/*n*-hexane (50:50, v/v).[2,3,6-9] The recoveries with methanol, dichloromethane/methanol and acetone/*n*-hexane proved to be the most efficient; and yet water alone also showed very high recoveries due to highly efficient absorption of microwave energy. The only unknown parameter for recoveries is sorption of these compounds onto soil. The most important factor for triazine adsorption is believed to be the organic matter with its complex tridimensional fulvic and humic acids.[5,10,11] In recent study[12] it was demonstrated that the direct processing of uncleaned MASE extract was only possible, if the organic matter content was below 5%. Consequently, investigations were performed to determine whether bonds are Van der Waals forces, hydrogen bonds, charge transfer bonds, ionic bonds and/or cation bridges.[12] In the case of atrazine electron-charge transfer dominates due to electrophilic character of chlorine and nitrogen atoms[11] while for hydroxyatrazine hydrogen bond dominates because of the hydroxyl group.[5] The sorption is also a pH-dependent process. Ben-Hur et al.[10] reported that the maximum effect of soil pH on triazine sorption by soil organic matter was at pH levels in the vicinity of the pK_a of the respective compounds (e.g. the pK_a value of protonated atrazine is 1.68). Likewise, they observed that at soil pH values > 6 the effect of pH on

triazine sorption was low.[10] Wang et al.[13] determined the highest extent of triazine bonding onto humic substances at pH approximately 3.

Concerning the physico-chemical properties of triazines there are several options for the chromatographic separation and detection system. A few years back gas chromatography (GC) was predominantly used - usually with nitrogen-selective (NPD)[3,7] or electron-capture (ECD)[12] detectors. Other options are also mass spectrometric detector (MS)[14-16] or thermionic sensitive detector (TSD).[12] Recently determinations with high-performance liquid chromatography (HPLC) prevail. Diode-array detector (DAD)[2,8,17-20] is used due to its simplicity while expensive MS detection systems rarely appear.[17] In comparison studies between GC and HPLC methods[14-16] HPLC is favourised due to the same reproducibility and accuracy of the results as in GC,[16] but simultaneous determinations of triazines and their polar metabolites in uncleaned soil extracts are possible.[14] One of the advantages is also possible separation of very polar degradation products.[15,16]

Only few studies[19,21-29] report of soil extraction methods for both triazine herbicides and their degradation products. A cause for this is their different chemical and physical properties which make the simultaneous extraction and further determination rather complex. Therefore the purpose of this study was to select an optimum microwave extraction conditions. Determinations were accomplished by HPLC-DAD and matrix effects of 12 selected soils were observed.

Experimental

Reagents

Atrazine (2-chloro-6-ethylamino-4-isopropylamino-1,3,5-triazine; A) (99.2%), prometryne (4,6-di(isopropylamino)-2-methyltio-1,3,5-triazine; Prom) (99.7%), propazine (2-chloro-4,6-di(isopropylamino)-1,3,5-triazine; Prop) (99.5%), simazine (2-chloro-4,6-di(ethylamino)-1,3,5-triazine; Sim) (99.3%), hydroxyatrazine (6-ethylamino-2-hydroxy-4-isopropylamino-1,3,5-triazine; HA) (96.0%), desethylatrazine (6-amino-4-isopropylamino-2-chloro-1,3,5-triazine; DEA) (99.9%), desisopropylatrazine (6-amino-4-ethylamino-2-chloro-1,3,5-triazine; DIA) (96.1%), desethyldesisopropylatrazine (2-chloro-4,6-diamino-1,3,5-triazine; DeDiA) (98.3%), desethyldesisopropylhydroxy-atrazine (4,6-diamino-2-hydroxy-1,3,5-triazine; DeDiHA) (98.5%),

desethylhydroxyatrazine (4-amino-2-hydroxy-6-isopropylamino-1,3,5-triazine; DeHA) (98.7%) and desisopropylhydroxyatrazine (6-amino-4-ethylamino-2-hydroxy-1,3,5-triazine; DiHA) (96.0%) were purchased as solid standards of Pestanal quality from Riedel-de-Haën (Seelze, Germany).

Methanol (HPLC grade, ≥ 99.8%) and phosphate salts Na_2HPO_4 and NaH_2PO_4 (HPLC grade, ≥ 99.0%) were from Fluka (Buchs, Switzerland). Deionised water was made with ultrapure water system NanoPure Infinity™ (Barnstead, USA).

Stock standard solutions of 100 mg/L were prepared by weighing solid standards in 50 mL flasks and adding methanol up to the marked level. In some cases (metabolites) the addition of phosphoric acid was necessary to achieve complete solubility of solid standards. Standard solutions at lower concentration levels were made from the aliquots of stock standard solutions diluted with water.

Equipment

An HPLC system (1100 Series, Agilent Technologies, Palo Alto, CA, USA) consisted of a standard thermostated autosampler, a standard quaternary pump, an injecton valve (Rheodyne series 7725i), a column thermostat and a diode-array detector.

MASE was performed with a MSP 1000, Microwave Sample Preparation System (CEM, Mathews, NC, USA) with maximum power of 1000 W, maximum pressure of 200 psi and maximum temperature of 200 °C. The pressure was sensed by a transducer and displayed graphically and digitally on the display screen. The carousel contained 12 extraction sites.

Soil samples

After the fresh samples were collected they were air-dried at 35 °C for up to 96 h, sieved through a 2 mm sieve and stored at 4 °C. A selection of 12 soil samples was made according to their characteristics: organic carbon content (determined by sulfochromic oxidation[30]), pH value (determined in KCl solution[31]), clay, sand and silt content (determined by American classification[32]) (Table 1). Each soil sample was then weighted into a polypropylene flask prior to addition of methanol, which was used for washing off the possible residues of pesticides and metabolites in the samples. After the

washing procedure, which was done three times, the samples were again air-dried at 35 °C for up to 96 h[3].

Table 1. Characteristics of soil samples used in experiments.

Soil sample	pH (KCl)	Organic matter (%)	Clay (%)	Silt (%)	Sand (%)
Soil 1	4.1	5.1	7.6	37.9	54.5
Soil 2	6.9	9.7	6.5	31.4	62.1
Soil 3	6.9	5.0	30.6	36.6	32.8
Soil 4	6.9	19.3	18.1	44.2	37.7
Soil 5	4.7	3.4	20.7	51.3	28.0
Soil 6	6.9	10.4	7.9	43.1	49.0
Soil 7	7.1	15.3	13.9	47.9	38.2
Soil 8	4.4	1.6	13.1	25.7	61.2
Soil 9	6.1	3.2	20.6	40.9	28.5
Soil 10	7.0	7.2	32.7	25.1	42.2
Soil 11	7.4	2.1	2.8	25.5	71.7
Soil 12	7.0	6.5	21.5	43.3	35.2

To establish whether the extraction recoveries are influenced by the soil matrix, all soil samples were spiked with investigated triazines and metabolites. The spiking method was as follows: 4 g of soil was spiked with 0.06 mg of triazine or metabolite. A simoultaneous introduction of all substances in each soil sample was done. Then 30 mL of methanol was added, put on a stirrer for 48 h and air-dried at 35 °C until all the methanol evaporated.[3] According to the spiking method the concentrations obtained were 15 μg of each analyte per g of the soil. The samples were then stored for 7 days at 4 °C prior to analysis.

Every soil was extracted with MASE using the optimal conditions, and the obtained blank soil extracts were spiked with the investigated triazines at 0.05, 0.075, 0.1, 0.2, 0.3, 0.4, 0.5, 0.75, 1.0, 2.0 and 5.0 mg/L (corresponding to 0.4, 0.6, 0.75, 1.5, 2.25, 3.0, 3.75, 5.6, 7.5, 15.0 and 37.5 μg/g of air-dried soil at 100% extraction recovery) level for each compound, respectively.

MASE procedure

4 g of blank or spiked soil was weighted into a teflon vessel and 30 mL of mixture methanol/water (50:50, v/v) was added. The moisturized sample inside the teflon vessel was left at room temperature for 24 h prior to extraction due to possible gas

development from organic matter. Our experiences with MASE have shown that without this incubation step, the protective membranes in the extraction vessels were more likely to burst. The MASE conditions (pressure program) were: from 0 to 73 psi in 20 min and then another 20 min at isobaric conditions (73 psi). The vessels were allowed to cool down to room temperature. The contents of the vessels were transferred into glass centrifuge tubes for centrifugation at 3000 rpm for 20 min. The supernatants were collected, filtered through a 0.45 μm pore-sized membrane filter and aliquots put in the HPLC vials. The same procedure was used for all 12 blank or spiked soil samples. All samples were extracted in two replicates and 12 extractions were simultaneously performed. The same procedure was performed with a standard solution (with no soil) of analytes in water and no changes in concentrations after MASE were observed. It can be therefore concluded that the MASE itself does not contribute to any systematic error of the extraction procedure.

HPLC conditions

For separation the guard column 4.0 x 3.0 mm C18 (ODS, octadecyl) (Phenomenex, USA) was used in front of the analytical column Luna C18(2), 250 x 4.6 mm (5μm) (Phenomenex, USA). The mobile phases consisted of phosphate buffer (pH 7, 10 mmol/L) as phase A and methanol as phase B. Gradient elution was used according to the timetable: from 0 to 4 min 95% A and 5% B; from 4 to 30 min from 5% to 100% B; the flow-rate was 1 mL/min. Absorbances were measured at two wavelengths: 213 nm for polar compounds (DiA, DeDiA, DeDiHA, DiHA and DeHA) and 220 nm for less polar compounds (DEA, HA, Sim, A, Prop, Prom). The column temperature of 22 °C was kept with the column thermostat. A 50 μL volume of the sample was injected.

Results and discussion

HPLC performance

The described chromatographic procedure enables separation of polar atrazine metabolites and nonpolar triazine compounds (Figure 1). The linearity of the method was tested with weighted regression calculations for all the compounds in the concentration range from 0.05 mg/L to 10.0 mg/L. In the case of standard solutions the

linearity was proven in the whole range, except for DeDiA and DiHA, which were no longer efficiently separated at concentrations above 5.0 mg/L and their quantitation was not possible due to wider and overlapping peaks. LODs for individual compounds were 0.05 mg/L. The calibration curves for atrazine are presented in Figure 2: standard solutions and blank soil extract spiked with the analytes. Because of the background of blank samples a method of spiked blank soil extracts at 11 levels was used (see Experimental), but the calibration curves obtained in this way were linear only from 0.05 to 2.0 mg/L because of matrix effects. The LODs of the compounds differed for every soil sample, ranging from 0.05 to 0.10 mg/L, which would correspond to 0.4 – 0.75 μg/g of soil at 100% extraction recovery.

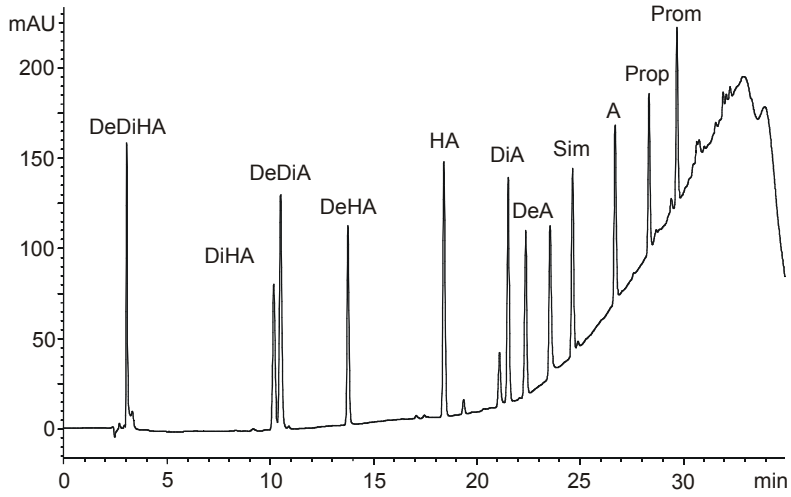

Figure 1. HPLC-DAD chromatogram of standard solution of selected trazines and atrazine metabolites at concentration level of 2 mg/L.

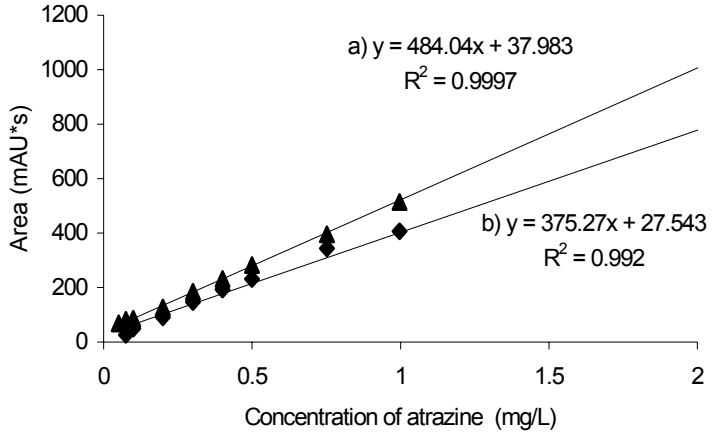

Figure 2. Calibration curves for atrazine: a) standard solutions, b) spiked blank soil extracts for Soil 12.

High concentration levels of selected compounds used were deliberately chosen[6] in order to monitor extraction recoveries for crude soil extracts which were obtained after the MASE. Soil extracts were analyzed directly without any preconcentration or clean-up steps.

MASE procedure

Table 2. Average extraction recoveries at different extraction solutions for soils spiked at 15 μg/g level with selected compounds.

Compound	logK_{ow}	Recovery (%)				
		100% H_2O	75% + 25% H_2O+MeOH	50% + 50% H_2O+MeOH	25% + 75% H_2O+MeOH	100% MeOH
Prop	2.89	36	69	78	86	91
DiA	1.01	69	85	91	95	99
DeHA	-0.08	101	105	110	111	108

The influence of different mixtures of methanol and water used for MASE on extraction recoveries from soil for selected compounds is presented in Table 2. With the higher logK_{ow} of the compound, the recoveries increased with higher methanol content. When logK_{ow} was near zero the compound showed almost equal solubility in all solvents, which appears to be a consequence of almost equal solubility in water and *n*-octanol. According to these results a 50:50 mixture of methanol and water was proven to obtain acceptable recoveries for all compounds regardless of the logK_{ow} (see also Table 3).

Extracts of the soil samples

In Figure 3 the chromatograms of soil extracts obtained with different solvent mixtures are shown. In all cases water-soluble and UV-detectable humic substances can be observed. They are eluted at short retention times (from 2 to 5 min) as the most polar compounds in soil extracts. For this reason separation, determination and quantification of the most polar atrazine metabolite DeDiHA was impossible (its retention time is 3.2 min).

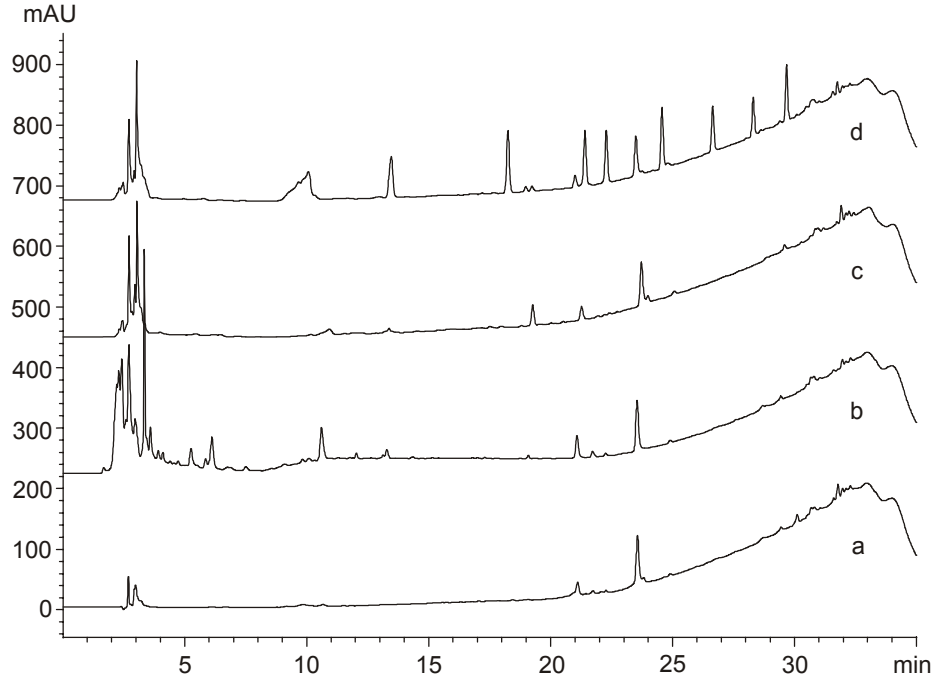

Figure 3. HPLC-DAD chromatograms of extract of Soil 11 at selected wavelength 213 nm: a) extraction with 100% methanol; b) extraction with 100% water; c) extraction with 50:50 (%, v/v) methanol/water; d) extract of spiked Soil 11 (15 μg/g) obtained with 50:50 (%, v/v) methanol/water.

From Figure 3 (a, b and c) a difference in solubility of humic substances in pure water, 50:50 methanol/water mixture and pure methanol can be observed. The largest solubility and therefore the greatest interferences were present in water extracts. When the water content in the extraction mixture was lower, the humic substance interferences were consequently also decreased. Other interferences were present at retention times around 10, 13, 21, 23.5 and 25 min. At 10 min matrix interferences eluted at the same retention times as DeDiA and DiHA. Additional confirmation of their identity with UV spectra was only possible at concentrations higher than 2 mg/L, but their quantitation was impossible in the tested concentration range. The same interferences were present in all 12 investigated soils. They mostly contributed to higher extraction recoveries for compounds appearing in the chromatogram in their close vicinity (Table 3).

The MASE recoveries and matrix interferences

In Table 3 the extraction recoveries for those compounds that could be quantified are presented. The recoveries were calculated as the average of two replicate extractions with RSD up to 3%. One sample has been studied in more detail concerning the

repeatability, which was proven to be 9%. All recoveries were in the range from 68 to 138%. The highest values obtained were with DeHA (from 94 to 123%), DiA (from 79 to 118%), Sim (from 84 to 138%) and HA (from 73 to 123%). Especially with DeHA and Sim, in several soils recoveries above 100% were calculated as a consequence of matrix interferences co-eluting in the chromatogram at approximately the same retention times. But for both compounds, the lowest recoveries were obtained in soils with the highest organic matter content (Soils 4 and 7).

Table 3. Recoveries of triazines from spiked soil samples (15 μg/g of each compound).

	Recoveries (%)							
	Prom	Prop	A	Sim	HA	DeA	DiA	DeHA
Soil 1	100	75	86	104	73	83	90	117
Soil 2	94	75	88	84	104	79	94	100
Soil 3	81	80	96	103	118	82	100	116
Soil 4	98	77	85	85	98	86	96	94
Soil 5	99	81	93	113	97	90	105	111
Soil 6	103	76	87	138	113	87	101	120
Soil 7	91	68	74	91	100	67	79	98
Soil 8	109	80	92	103	115	79	92	133
Soil 9	103	89	96	92	92	95	101	100
Soil 10	110	100	104	100	101	98	118	107
Soil 11	102	79	91	101	109	80	91	120
Soil 12	97	101	105	123	123	91	116	123

In general, the recoveries were among the lowest for most of the investigated compounds in Soils 2, 4, 6 and 7 where the organic matter was 10% or higher.

In Figure 4 influences of soil organic matter content on recoveries of Prop, A, DiA and DeHA are shown. These four compounds were chosen for comparison on the basis of their different K_{ow} values (see Table 2) and consequently different position in the chromatogram. As seen from Figure 3, blank soil extracts were generally free of larger interferences at the retention times of these four compounds, except for DeHA. In Figure 4, a slight trend of decreasing recoveries for Prop, A, DiA and DeHA with increasing organic matter content is seen. Although the pesticide/organic matter content ratio in our experiments was much higher than occurring at environmental conditions, sorption of triazines to organic matter would still be possible to some extent. However, the data from our experiments as far as now are not convincing enough for such a conclusion.

Other soil characteristics (clay content, soil pH) did not exhibit any significant influences. The second soil characteristic that could possibly affect the sorption at the pesticides to the soil and thus influence the extraction efficiency was the soil pH. For Soils 1, 5 and 8, the pH in KCl solution was in 4-5 range as compared to other soil samples with pH 6-7.5. However, no observable differences were found in the extraction recoveries between the two groups. This is in agreement with some studies showing that significant sorption of triazines to organic matter, especially humic substances, occurs at pH below 4.[13]

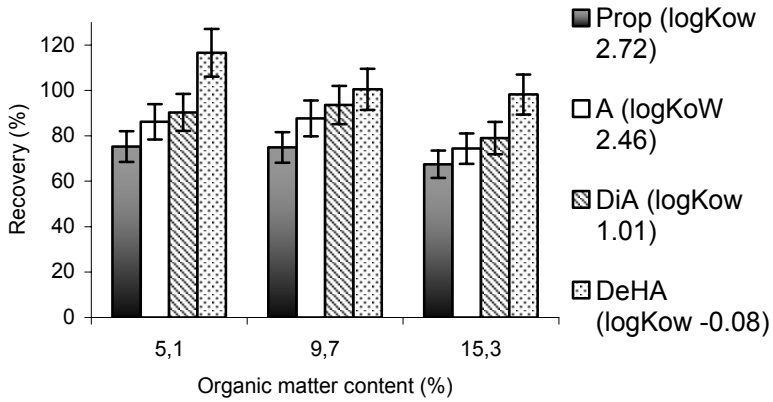

Figure 4. Recoveries for Prop, A, DiA and DeHA influenced by organic matter content of the soil (shown in parenthesis).

As seen from Table 1, there is a high content of clay in both Soil 3 and Soil 10 (over 30%), while organic matter content and soil pH for both samples differ minimally. Although for most of the observed compounds extraction efficiency is approximately the same, there is a significant difference in recoveries for Prom, Prop and DiA, which cannot be explained on the basis of the measured soil properties. Even at the highest content of clay, there seemed to be no negative influence on the extraction. Only if clay to organic matter content ratio is > 30,[5,20] the role of clay on the adsorption of triazines becomes significant, but in our research no such soil samples were used.

There might be another explanation why we could not detect any significant differences in the extraction efficiency for such different types of soils. It is possible that MASE efficiently breaks down most of the sorption bonds between the analytes and the soil matrix. The reason for rather scattered recovery results (see Table 3) might be in possible degradation of the analytes,[5] as well as their different solubilities in the

extraction solvent. Also, pesticides could be partially re-adsorbed during the cooling of the vessels to the room temperature.

Conclusions

MASE followed by HPLC-DAD determination was optimized for selected triazines and some atrazine metabolites from different soils. Best recoveries of selected compounds from the spiked soil samples were obtained by methanol/water mixture (50:50) as the solvent.

For all the investigated compounds, recoveries were in the range from 67% to 138% with RSD up to 9%. For some soils, recoveries were above 100%, which is explained by poor quantitation due to baseline distortion arising from matrix interferences. Because of this reason, the calibration curves were linear only in a narrow range, while some polar atrazine metabolites (DeDiA, DiHA, DeDiHA) could not be quantified. Efficiency of extraction was correlated with some soil properties affecting the sorption of pesticides, e.g. organic matter, clay content and soil pH, but some rather weak correlation was found only for organic matter content.

However, further research should be aimed at proving these findings also in aged soil samples, from which the extraction of pesticide residues is known to be more problematic. Also, the efficiency of MASE has to be tested in a lower concentration range, closer to the levels of triazine residues in agricultural soils.

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Povzetek

Optimizirali smo metodo za ekstrakcijo nekaterih pesticidov iz tal s pomočjo mikrovalov. Ekstrahirane triazine in metabolite atrazina smo določevali s tekočinsko kromatografijo. Ekstrahirale so se tudi nekatere interference iz tal, ki so onemogočale določevanje deetildeisopropilatrazina, deisopropilhidroksiatrazina in deetildeisopropilhidroksiatrazina. Te komponente so tudi zmanjšale naklon umeritvenih krivulj in znižale linearno območje metode. Izkazalo se je, da je ekstrakcija z mešanico metanol/voda (50:50) učinkovita za večino preiskovanih spojin. Izkoristki so bili v območju 67–130%, kar nakazuje, da energija mikrovalov zadošča za desorpcijo večine triazinov oziroma metabolitov. S primerjavo ekstrakcijske učinkovitosti iz tal različne sestave smo ugotovili, da višja vsebnost organskih snovi v tleh nekoliko otežuje desorpcijo, medtem ko vsebnost gline in pH tal ne vplivata na izkoristke ekstrakcije.