

Effects of Organic Matter and Clay Content in Soil on Pesticide Adsorption Processes

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SUMMARY

The effect of organic matter and clay content on the adsorption of atrazine, acetochlor, clomazone, pendimethalin and oxyfluorfen in soil samples was studied. In order to determine whether and to what degree different soil properties affect the process of determination of selected pesticides, three soils with different clay and organic matter contents were used.

An optimized liquid-solid extraction procedure followed by SPME measurement was applied to analyse the selected pesticides in soil samples. Detection and quantification were done by gas chromatography-mass spectrometry (GC/MS). Relative standard deviation (RSD) values for multiple analyses of soil samples fortified at 30 µg/kg of each pesticide were below 19%. Limits of detection (LODs) for all compounds studied were less than 2 µg/kg. The results indicate that soils with different physico-chemical properties have different effects on the adsorption of most pesticides, especially at higher concentration levels.

Keywords: Solid phase microextraction; Pesticides; Soil; Adsorption; Clay; Organic matter

INTRODUCTION

The fate and mobility of pesticides in the environment involve complex mechanisms that are influenced by many processes, including volatilization, leaching, adsorption, as well as chemical and biological degradation. Of these processes, adsorption is the key process in soil because detoxification mechanisms, such as degradation, metabolism, microbial uptake and mobilization, involve only the nonsorbed fraction of molecules (Huang and McKercher, 1984; Welhouse and Bleam, 1992, 1993; Pignatelo and Xing, 1996). The extent of adsorption depends on various soil properties, including organic matter content, type and amount of clay, ion exchange capacity and pH. Moreover, various phys-

ico-chemical parameters of these compounds, such as water solubility and octanol-water partition coefficient, also play an important role in determining adsorption extent (Singh et al., 1990; Barriuso et al., 1992). Generally, it has been found that adsorption of pesticides is positively correlated with octanol-water partition coefficient and negatively correlated with their water solubility (Singh, 2002).

The sorption interactions of pesticides in soil may involve either the mineral or organic components, or both. In soils that have higher organic matter levels (> 5%), pesticide adsorption depends on organic matter content, the nature of organic matter having little influence on the adsorption processes (Bailey and White, 1964; Hayes, 1970; Arienzo and Buondonno, 1993;

Jenks et al., 1998; Bekbolet et al., 1999). In soils with low organic matter contents, the adsorption of pesticides often depends on active components of the inorganic fraction, which is predominantly the clay fraction. An increase in clay content results in increasing adsorption of a pesticide (Barriuso et al., 1992; Murphy et al., 1992; Welhouse and Bleam, 1992; Baskaran et al., 1996).

The objective of this study was to investigate sorption behaviour of 5 herbicides with distinct chemical structures and belonging to different pesticide groups. The main parameters affecting the sorption process, such as organic matter and clay content in soil, were studied.

MATERIAL AND METHODS

Reagents and materials

The pesticides chosen for this study were: clomazone, acetochlor, pendimethalin, oxyfluorfen (Dr Ehrenstorfer) and atrazine (Syngenta). The pesticides studied and some of their physico-chemical properties are presented in Table 1. Stock solutions (1 g/l) of each pesticide standard were prepared by dissolving the weighed amount in acetone (J.T. Baker, Deventer, Holland). The solutions were stored at -18°C. Working standard mixed solutions were prepared weakly by diluting each individual stock solution with acetone and storing at 4°C. Sodium chloride (99.5% purity) was purchased from Merck (Darmstadt, Germany) and methanol from J.T. Baker (Deventer, Holland).

The 100 µm polydimethyl-siloxane (PDMS) fibres (Supelco, Bellefonte, PA, USA) were used for SPME measurements. Extraction, mixing included, was performed in 4 ml vials (Supelco).

Polypropylene centrifuge tubes with caps (50 ml) (Sarstedt, Germany), filter papers IPS, 150 mm diameter (Watman Int. Ltd., Maidstone, UK) and a centrifuge (UZ 4, Iskra, Slovenia) were used in the soil preparation procedure.

Instrumentation

A gas chromatograph-mass spectrometer (GC/MS) was used as a detection device (CP-3800/Saturn 2200, Varian, Australia) with 30 m x 0.25 mm x 0.25 µm VF-5ms column (Varian). Experimental parameters and conditions for GC/MS measurements performed have been described in detail elsewhere (Đurović et al., 2008).

Soil samples

Three samples of uncontaminated Serbian soils originating from Kosjerić (soil A), Kikinda (soil B) and Bela Palanka (soil C) were used in the study. The main physico-chemical properties of these soils are given in Table 2. The soils were air dried and sieved (2 mm) before using.

Sample preparation and analysis

The method based on conventional liquid-solid procedure, followed by SPME determination of the selected pesticides, is described in a previous paper (Đurović et al., 2008). Optimization both of the microextraction conditions (such as the fibre type, desorption temperature and time, extraction time and NaCl content) and extraction efficiencies of several solvents (water, hexane, acetonitrile, acetone and methanol) and the optimum number of extraction steps within a sample preparation step were explained in detail. According to the results obtained in these experiments, two successive extrac-

Table 1. Physico-chemical properties of pesticides studied ^a

Pesticide	Chemical group	M _r ^b (g/mol)	Water solubility (mg/L)	Log K _{ow} ^c	H ^d (Pam ³ /mol)
Atrazine	Triazine	215.7	33	2.5	1.5 x 10 ⁻⁴
Acetochlor	Chloroacetamide	269.8	223	4.14	3.83 x 10 ⁻¹
Oxyfluorfen	Diphenyl ether	361.7	0.116	4.47	9.40 x 10 ⁻²
Pendimethalin	Dinitroaniline	281.3	0.3	5.18	2.73 x 10 ⁻³
Clomazone	Isoxayolidinone	239.7	1100	2.5	4.19 x 10 ⁻³

^a Data cited refs. (Pesticide Manual, 2000–2001; www.sitem.herts.ac.uk/aeru/footprint/en/index.htm, 2008)

^b Molecular weight

^c Partition coefficient between n-octanol and water (as the log value)

^d Henry's constant

Table 2. Physico-chemical properties of soils

Soil	pH (H ₂ O)	O. M.* (%)	Sand (%)	Silt (%)	Clay (%)
A	6.72	3.43	28.40	47.96	23.64
B	8.39	3.17	73.96	22.60	3.44
C	7.54	8.69	52.08	24.48	23.44

* Content of organic matter

tions with methanol as the extraction solvent were chosen as the optimal sample preparation procedure, while the following conditions were found to be most efficient for SPME measurements: 100 μ m PDMS fibre, desorption for 7 min at 270°C, 30 min extraction time and 5% NaCl content (w/v) (Đurović et al., 2008).

In order to determine whether, why and to what extent different soil properties are able to influence the sorption of selected pesticides on a soil matrix, i.e. to affect SPME efficiency, the proposed method was applied to analyze the selected pesticides in three different soil types. In this part of the study, sub-samples of 8 g were placed in polypropylene centrifuge tubes and fortified at 30 μ g/kg level of each pesticide using 1 mg/L mixed standard solution. The spiked samples were homogenized for 15 min using a mechanical stirrer and left to rest for 24 hours prior to further analysis.

RESULTS AND DISCUSSION

The optimized liquid-solid extraction procedure followed by SPME measurement (Đurović et al., 2008) was applied to analyze the selected pesticides in three different soil types. The main physico-chemical properties of these soils are given in Table 2.

Linearity of the method was tested in a concentration range from 2 to 600 μ g/kg. The obtained arrangements and correlation coefficients (R) for all pesticides and soils under study are presented in Table 3. It shows that the correlation coefficients obtained exceeded 0.99 in all cases.

The limit of detection was computed as three times the base line noise (S/N=3) at the lowest detectable concentration. LODs for all pesticides and soils studied were less than 2 μ g/kg (Table 4).

Precision and confidence of the developed method were determined by performing four consecutive measurements of the soil samples spiked at 30 μ g/kg level. Both relative standard deviation (RSD) and recovery values are presented in Table 4. The table shows that RSDs for all pesticides and soils under study were below 19%. For most of the analyzed pesticides, the recovery values were higher than 67%. An explanation of the lower recoveries obtained for pendimethalin and oxyfluorfen (soils B and C) can be the strong influence of soil matrix on those pesticides and/or the insufficient power of methanol as extraction solvent in the sample preparation step (Sparks, 1995).

In order to determine matrix effects on determination of the selected pesticides, three different soils were chosen. As organic matter and clay mostly participate in the sorption of pesticides in soil (Sparks, 1995), soils with different organic matter and clay contents were chosen. Table 2 shows that soil C has similar clay and higher organic matter content than soil A. It was therefore assumed that the effect of organic contents on recoveries could be determined. On the other hand, soil A has a similar organic matter content as soil B, but also a higher clay content. Considering the recoveries obtained for these two soils, we were able to determine the effect of clay on the efficiency of the proposed method. However, considering the recoveries (Table 4) and precision of measurements (stand-

Table 3. Linearity ranges (μ g/kg) and correlation coefficients (R) for investigated pesticides and soils

Pesticide	Soil A		Soil B		Soil C	
	Concentration range (μ g/kg)	R	Concentration range (μ g/kg)	R	Concentration range (μ g/kg)	R
Atrazine	2-600	0.999	2-600	0.996	2-600	0.999
Acetochlor	2-600	0.999	2-600	0.998	2-600	0.997
Oxyfluorfen	2-600	0.998	2-600	0.999	2-600	0.999
Pendimethalin	2-600	0.999	2-600	0.999	2-600	0.996
Clomazone	2-600	0.997	2-600	0.999	2-600	0.999

Table 4. Recoveries (%), relative standard deviations (RSDs, %) and limits of detection (LODs, $\mu\text{g}/\text{kg}$) obtained for investigated pesticides and soils

Pesticide	Soil A			Soil B			Soil C		
	Recovery (%)	RSD (%)	LOD ($\mu\text{g}/\text{kg}$)	Recovery (%)	RSD (%)	LOD ($\mu\text{g}/\text{kg}$)	Recovery (%)	RSD (%)	LOD ($\mu\text{g}/\text{kg}$)
Atrazine	94.30	6.27	1.61	89.93	9.45	0.67	90.89	5.33	1.00
Acetochlor	84.02	2.22	0.22	93.77	7.79	0.18	89.32	9.80	0.17
Oxyfluorfen	67.23	16.70	0.14	62.82	19.20	0.27	56.64	7.95	0.75
Pendimethalin	52.24	17.50	1.68	51.66	18.56	1.52	49.23	16.14	1.96
Clomazone	84.30	4.28	0.82	89.87	4.31	0.12	90.10	1.68	0.49

ard deviation values are not shown), the soils with different physico-chemical properties were not found to have effect on the recoveries. This conclusion was not surprising because similar results had been reported by Bouaid et al. (2001).

However, considering the dependences of the extracted pesticide amounts as a function of pesticide concentration in different soil samples, it was noticed that the matrix effects of the soils studied were different. Figure 1 shows the effects of different soil matrices on determination of the selected pesticides. It shows that the sorption of each pesticide in different soils is similar at lower concentrations, which explains the initial conclusion in which only recoveries (fortification of $30 \mu\text{g}/\text{kg}$) had been considered. However, it is obvious that different soil properties do affect the efficiency of the method at higher concentration levels.

Finally, in terms of linear dependency of all pesticides and soils under study, the pesticides can be classified in three groups. The first pesticide group consists of more hydrophobic pesticides such as pendimethalin and oxyfluorfen, compounds whose sorption to soil was mainly determined by organic matter content in the soil. These pesticides have low water solubility (0.3 and $0.116 \text{ mg}/\text{l}$, respectively) and high $\log K_{ow}$ values (5.18 and 4.47 , respectively) (Table 1). Actually, these results are in accordance with a frequent assumption that soil organic matter acts as a non-polar phase or surface, and consequently is the main sorbent for pesticides of low polarity (De Jonge et al., 2000; Sparks, 1995). For these two compounds sorption decreased (recoveries increased) in the order: soil C > soil B > soil A. Thus, soil C with higher organic matter content than the other two soils sorbed pesticides stronger. In soil A, a part of the organic matter was probably blocked by clay particles that produced a weaker sorption of analytes by the organic surface than soil B.

Considering the linear dependency observed, and applying a two-factor analysis of variance (Statistika

'99 Edition, ANOVA/MANOVA), it was evident that there were no significant differences ($p > 0.05$) in sorption between: soils A and B over the entire concentration range under study ($c \leq 600 \mu\text{g}/\text{kg}$), A and C at $c \leq 30 \mu\text{g}/\text{kg}$, B and C at $c \leq 100 \mu\text{g}/\text{kg}$ (for pendimethalin); soils A and B, A and C at $c \leq 250 \mu\text{g}/\text{kg}$, and B and C at $c \leq 400 \mu\text{g}/\text{kg}$ (for oxyfluorfen) (where c is pesticide concentration).

The second group includes only acetochlor. The results indicate that sorption of that pesticide (which is more polar than pendimethalin and oxyfluorfen) by soils was primarily determined by clay content in the soils. Therefore, soil A with high clay and low organic matter contents was the strongest sorbent. In soil C, a part of the clay sorption sites was probably blocked by organic matter, finally producing a similar sorption capacity of that soil and soil B. Differences in acetochlor sorption by the different soils were insignificant between: soils B and C over the entire concentration range under study ($c \leq 600 \mu\text{g}/\text{kg}$), A and B, A and C at $c \leq 30 \mu\text{g}/\text{kg}$.

The third pesticide group consists of compounds whose sorption behaviour could not be explained by considering organic matter and clay contents alone. Our results indicate that there are actually two sorption trends: soil B > soil C > soil A (atrazine) and soil A > soil B > soil C (clomazone). A possible explanation of the „unexpected” behaviour of these pesticides lies either in different sand and silt contents in the analyzed soils (Table 2) or different nature/origin of those soils (soils A and B were grassland soils, while soil C originated from forest) (Oliver et al., 2003a, 2003b, 2005).

Differences in sorption were insignificant between: soils A and B, A and C at $c \leq 30 \mu\text{g}/\text{kg}$, B and C at $c \leq 250 \mu\text{g}/\text{kg}$ (for atrazine); soils A and B, and A and C at $c \leq 30 \mu\text{g}/\text{kg}$, B and C at $c \leq 250 \mu\text{g}/\text{kg}$ (for clomazone).

Generally, considering that soils with different physico-chemical properties had different effect on the recoveries of most of the pesticides studied, i.e. on sorption behaviour (especially at higher concentration levels), it seems that a standard additional method would be more appropriate for quantitative analysis than external calibration. On the other side, knowing that recent trends in sample preparation are based on the use of multiresidue methods, the problem that often occurs

is quantification of analytes for which the method efficiency is not satisfying. For those compounds, external calibration based on standard solutions, is not the best choice (as for pendimethalin and oxyfluorfen in our study). However, if uncontaminated soil with similar physico-chemical properties as the analyzed soil sample is available, external calibration using spiked uncontaminated soil samples can be used. It would help avoid possible errors arising from the influence of the matrix.

ACKNOWLEDGEMENT

This work was realized within the project No TR20041, supported by the Ministry of Science and Environmental Protection of the Republic of Serbia.

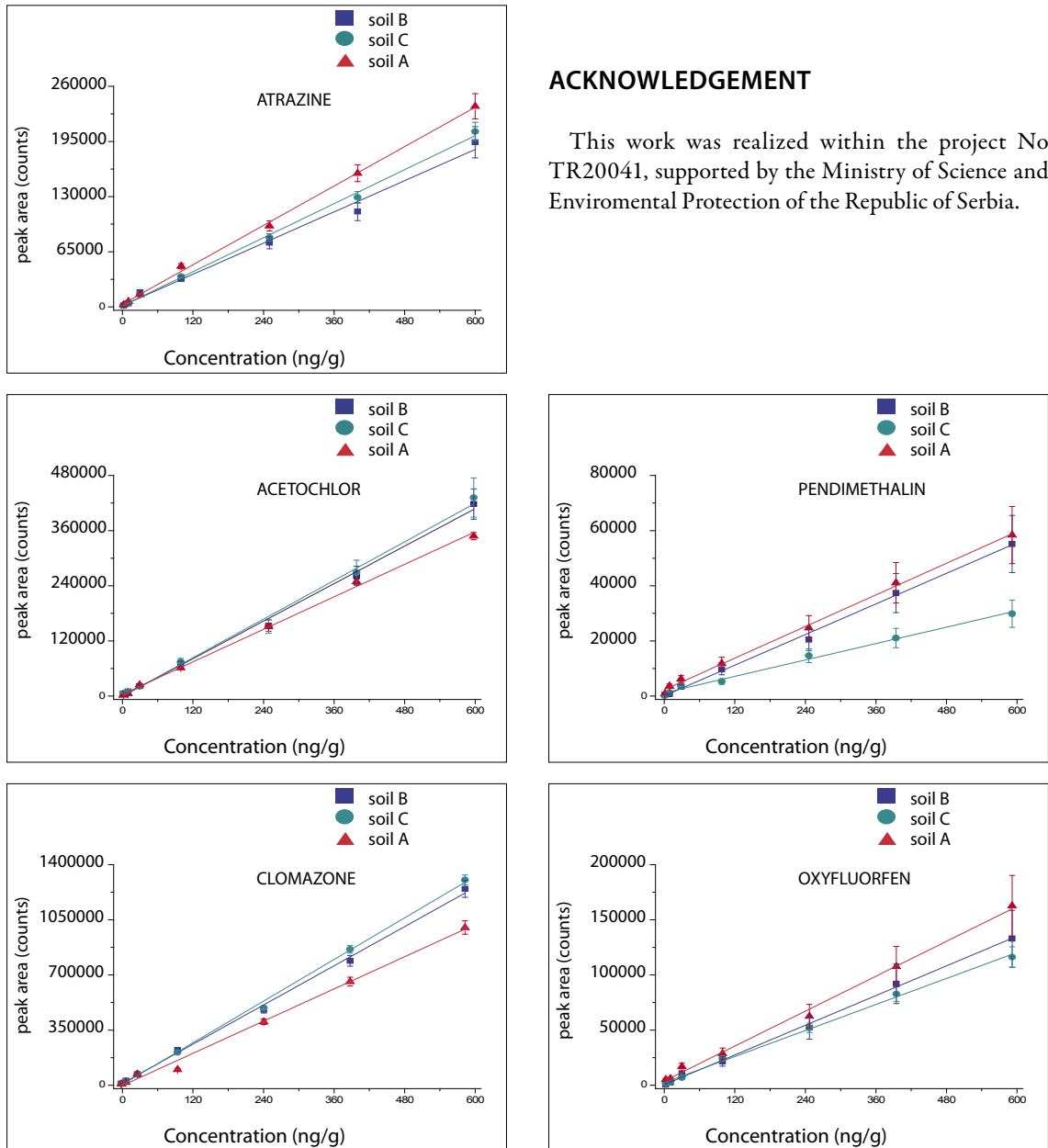


Figure 1-5. Matrix effect of soils with different physico-chemical properties on atrazine, acetochlor, clomazone, pendimethalin and oxyfluorfen determination

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Uticaj sadržaja organske materije i gline u zemljištu na adsorpciju pesticida

REZIME

Proučavan je uticaj sadržaja organske materije i gline u uzorcima zemljišta na procese adsorpcije atrazina, acetohlor, klomazona, pendimetalina i oksifluorfena. U cilju utvrđivanja da li i u kojoj meri različite zemljišne karakteristike utiču na adsorpciju proučavanih pesticida, a time i na njihovo određivanje, izabrana su tri zemljišta sa različitim sadržajem organske materije i gline.

Za određivanje pomenutih pesticida u uzorcima zemljišta korišćena je optimizovana tečno-čvrsta ekstrakciona procedura u kombinaciji sa metodom mikroekstrakcije u čvrstoj fazi (SPME). Detekcija i kvantifikacija analita je vršena gasno-masnim spektrometrom (GC/MS). Vrednosti relativnih standardnih devijacija (RSDs) višestruko ponovljenog merenja uzorka obogaćenog do 30 µg/kg svakog pesticida su ispod 19%. Granice detekcije (LODs) za sve pesticide i zemljišta uključena u ispitivanje su bila ispod 2 µg/kg.

Rezultati ukazuju da zemljišta različitih fizičko-hemijskih karakteristika imaju različit uticaj na sorpciju za većinu proučavanih jedinjenja, što je naročito izraženo kod većih koncentracija.

Ključne reči: Mikroekstrakcija u čvrstoj fazi; pesticidi; zemljište; adsorpcija; organska materija; glina