

## Retention Characteristics of Acetochlor in Soils Collected from Different Depths in Relation to Soil Properties (Žitný ostrov Area, SW Slovakia)

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### Abstract

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Determination of the sorption-desorption of herbicides within soil profile is one of the first steps in predicting their leaching potential. Batch experiments were performed to evaluate the influence of soil properties on acetochlor retention. Soil samples were taken from horizons A, B, and C of three soil types representative of the Žitný ostrov area. The sorption and desorption isotherms were fitted to the Freundlich equation. The Freundlich sorption coefficient ( $K_{fs}$ ) values ranged from 0.71 to 6.58 mg<sup>(1-1/n)</sup>·l<sup>(1/n)</sup>/kg and were correlated positively with soil organic carbon, humic and fulvic acid carbons, amorphous aluminum oxides, and negatively with soil pH. The Freundlich desorption coefficient ( $K_{fd}$ ) values were greater than those for sorption, showing that not all acetochlor sorbed was desorbed after four washing steps. The percentage of acetochlor desorbed ranged from 7.80 to 54.5% with decreased desorption from soil horizons B and C. The higher sorption capacity of surficial soil horizons in the three soils may be a limiting factor for penetration of acetochlor through soil profiles into groundwater.

**Keywords:** chloroacetanilide herbicide; desorption; leaching potential; sorption

Groundwater reservoirs are usually used as a source of drinking water for inhabitants, and therefore should be protected from any kind of contamination. Large aquifers often underlie agricultural land-use areas. Application of pesticides is inevitable in modern agriculture, however, it may represent a serious threat to groundwater quality (ANDRADE & STIGTER 2009). Pesticide parent compounds or their metabolites have frequently been detected in groundwater, even at concentrations exceeding the EU limit value for drinking water (0.1 µg/l) (MALAGUERRA *et al.* 2012). Penetration of pesticides through the soil profile is controlled mainly by their sorption and desorption in soil. These processes are significantly influenced by the pesticide nature and the physico-chemical properties of soils (YEN *et al.* 2005; KODEŠOVÁ *et al.* 2011; ČADKOVÁ *et al.* 2013).

The SW part of Slovakia (Žitný ostrov area) is well-known for the largest groundwater resources in Central Europe. The groundwater supplies make about 10<sup>6</sup> km<sup>3</sup>

while the groundwater requires minimum treatment before being used as drinking water (MUCHA *et al.* 1999). The shallow groundwater table underlies the area at the depth of just 0.5 to 3 m. Therefore, groundwater in the region is susceptible to contamination with herbicides used in agriculture. Maize, cereals, sunflower, sugar beet, and oilseed rape are the most often cultivated plants in the area and acetochlor is commonly used for weed growth regulation.

Acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide) is the most common active ingredient in chloroacetanilide herbicide products. It is a selective systematic pre-emergent herbicide with a weakly polar character. Acetochlor is absorbed by roots and leaves, and inhibits synthesis of proteins in germinating weeds (TOMLIN 2001). The herbicide is rapidly degraded in surface and subsurface soils (MA *et al.* 2000; CAI *et al.* 2006) with a half-life of 2–63 days (MA *et al.* 2004; DICTOR *et al.* 2008; OLIVEIRA *et al.* 2013) depending

on the particular agroenvironmental conditions (e.g. soil organic carbon and moisture contents, pH, and temperature) and initial concentration of acetochlor in soil. It is not highly mobile in soils (MA *et al.* 2000; JURSIK *et al.* 2013), but under unfavourable environmental conditions it may reach groundwater and surface water as evidenced by its detection in natural water resources (MALOSCHIK *et al.* 2007; HLADIK *et al.* 2008). The propensity of acetochlor to leach downward through the soil profile is dependent primarily on its sorption and desorption behaviour in soil. The sorption of acetochlor in different soil types has been studied by various authors (WANG *et al.* 1999; LENGUEL & FÖLDÉNYI 2003; TAYLOR *et al.* 2004; HILLER *et al.* 2009; BEDMAR *et al.* 2011) who proved it to be moderate to strong depending on the soil physico-chemical properties. Reported Freundlich and distribution coefficient ( $K_f$  and  $K_d$ ) values for the sorption of acetochlor in soils range from 1.44 to 16.9  $\text{mg}^{(1-1/n)} \cdot \text{l}^{(1/n)} / \text{kg}$  and from 0.84 to 7.11  $\text{l/kg}$ , respectively (NEMETH-KONDA *et al.* 2002; ZHENG & YE 2002; HILLER *et al.* 2008, 2009). Sorption of acetochlor decreases with soil depth and becomes negligible in sandy aquifer materials with low organic carbon contents (JANNICHE *et al.* 2011). Soil organic carbon content is the key soil property affecting positively the sorption of acetochlor in soils, whereas the other soil properties are less important (WANG *et al.* 1999). By contrast, the desorption of acetochlor from soils into the soil solution is less well known, but this reverse process to sorption is equally important because it facilitates leaching and runoff into water bodies and makes the herbicide more available to microorganisms, thereby facilitating its biodegradation. Available studies have documented that the desorption of acetochlor from soils was hysteretic (i.e. desorption is not complete even when multiple desorption cycles are applied), however, no conclusive statements about the effects of soil properties on the acetochlor desorption were shown (NEMETH-KONDA *et al.* 2002; TAYLOR *et al.* 2004). Studies on the distribution behaviour of acetochlor in soils are still of great importance because understanding the relationship between soil properties and sorption-desorption of acetochlor is essential for predicting its potential for leaching to groundwater as well as its ecological effects on living organisms and plants. It has been shown that acetochlor may affect negatively a range of aquatic and soil organisms (HE *et al.* 2013) and agricultural crops (CHAO *et al.* 2007).

Although the sorption of herbicides in soils has been extensively studied throughout the world, there are only limited data concerning the sorption of acetochlor in soils, and even more limited knowl-

edge of acetochlor desorption from soils collected at different depths. Therefore, the main objectives of the present work were (i) to determine the sorption and desorption isotherms of acetochlor in individual soil horizons of three soil types sampled in the Žitný ostrov area, (ii) to identify the main soil properties influencing acetochlor sorption and desorption, and (iii) based on the results, to discuss about the leaching of acetochlor through soils to groundwater.

## MATERIAL AND METHODS

The sampling area is located in the upper part of the Žitný ostrov (SW Slovakia). Three soil types are characteristic for this area altogether covering 98% of the land: Calcaro-Haplic Chernozem (53%), Fulvi-Calcaric Phaeozem (27%), and Calcaric Fluvisol (18%). The soil samples representative of the Žitný ostrov area were taken from manually excavated soil pits ( $2 \times 1$  m) at various depths corresponding to the occurrence of the individual soil horizons (Table 1). Soil samples were air-dried, passed through a 2 mm sieve, and thoroughly mixed.

Total organic carbon content (TOC) was determined using dichromate oxidation (NELSON & SOMMERS 1996). Humus components (HA – humic acids, FA – fulvic acids) were measured using the method proposed by KONONOVA and BELCIKOVA (1961). Soil pH was measured by electrode in a 1:2.5 (wt:wt) soil-water (active pH) and soil-1M potassium chloride solution (exchangeable pH) suspensions. Calcium carbonate content ( $\text{CaCO}_3$ ) was measured using a volumetric device (JACKSON 1958). The pipette method was used for the determination of the particle size distribution (GEE & BAUDER 1986). Cation exchange capacity (CEC) was measured with 1M ammonium acetate at pH 7 (ISRIC 1995). Amorphous Al and Fe oxides ( $\text{Al}_o$  and  $\text{Fe}_o$ , respectively) were determined by extraction with acidified ammonium oxalate in the dark (MCKEAGUE & DAY 1966). Clay minerals were identified by X-ray diffraction analysis (MOORE & REYNOLDS 1997). The physico-chemical and textural properties of the tested soils are given in Table 1.

Acetochlor of analytical grade used in this work was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Sorption-desorption experiments were performed using the batch method according to the OECD guideline No. 106. The stock solution of acetochlor was prepared directly in a background solution of 0.01M  $\text{CaCl}_2$  and 0.0015M  $\text{NaN}_3$  to keep ionic strength constant and to inhibit microbial activity, respectively. For pre-equilibration, 2 g of each soil was shaken in 15 ml glass tubes with 9 ml of 0.01M  $\text{CaCl}_2$  and 0.0015M  $\text{NaN}_3$  solution for 24 h

at 20°C in the dark. Afterwards, an adequate amount of the stock solution of acetochlor was added to the suspensions to reach a final volume of 10 ml with five initial concentrations of acetochlor: 0.45, 2.47, 5.03, 10.37, and 20.02 mg/l. These concentrations were determined with respect to the expected concentration of the herbicide in the topsoil and the detection limit of the analytical method. Tubes were rotated for another 24 h and subsequently centrifuged at 1160× g for 15 min, followed by filtration (Whatman, 0.45 µm, nylon). Previously, HILLER *et al.* (2008, 2009) showed that the sorption and desorption of acetochlor in soils similar to those used in the present study reached an equilibrium state within 12 h. Soil extracts were transferred in glass vials and analyzed for acetochlor by high-performance liquid chromatography (HPLC) as described below. Desorption experiments followed immediately after sorption with an initial concentration of 20.02 mg/l. After the removal of 8 ml of supernatant, the same volume of aqueous solution containing no herbicide was added and the tubes were rotated for 12 h in the dark, centrifuged, filtered, and the supernatant was analyzed. Desorption procedure was repeated four

times. All sorption-desorption experiments were performed in two replicates. The control samples for each concentration without soil were also included and used to account for possible losses due to volatilization, degradation or sorption of acetochlor onto the glass tube surface.

HPLC analyses were carried out by the chromatographic system Elite LaChrom (Merck-Hitachi, Darmstadt, Germany) consisting of L-2130 pump provided by quaternary low-pressure gradient with solvent degasser, L-2200 autosampler, L-2400 UV detector, L-2300 column oven, organizer, and PC data station with the software EZChrom Elite vers. 3.1.4. Separation was done using an isocratic elution with the mobile phase acetonitrile-water (70:30 v/v). Flow rate was 1.0 ml/min. The analytical column was LiChrospher 100 RP-18 column (125 mm × 3 mm i.d., 5 µm) and the guard column was LiChrospher 100 RP-18 column (4 mm × 4 mm i.d.). The column temperature was set at 25 ± 0.1°C. The injection volume of samples was 10 µl. The limit of detection was 0.02 mg/l and relative standard deviation was lower than 0.5%. All measurements were done at 205 nm. Data were acquired by EZChrom Elite vers. 3.1.4. software.

Table 1. Selected physico-chemical and textural properties of soils; the same soils were previously used in a study on the 4-chloro-2-methylphenoxyacetic acid (MCPA) sorption in soils by HILLER *et al.* (2012)

Soil type	Calcaro-Haplic Chernozem			Fulvi-Calcaric Phaeozem		Calcaric Fluvisol	
Label	1A	1B	1C	2A	2B	3A	3B
Location	Most pri Bratislave			Lehnice		Most pri Bratislave	
Vegetation at sampling time	sugar beet			oilseed rape		maize	
Soil depth (cm)	0–15	30–40	90–110	0–15	30–40	0–15	40–60
TOC (%)	2.09	1.39	0.58	4.41	2.31	1.47	0.89
HA (%)	0.42	0.30	0.13	0.89	0.53	0.23	0.13
FA (%)	0.29	0.23	0.10	0.76	0.34	0.28	0.17
Active pH	7.83	8.03	8.24	7.69	7.99	7.91	8.12
Exchangeable pH	7.28	7.55	7.67	7.31	7.53	7.42	7.55
CaCO <sub>3</sub> (%)	19.2	28.0	9.30	16.1	27.4	24.3	27.4
CEC (cmol <sup>+</sup> /kg)	26.2	26.5	21.1	41.6	33.0	19.3	18.7
Fe <sub>o</sub> (mg/kg)	220	226	94.8	457	176	321	361
Al <sub>o</sub> (mg/kg)	217	263	135	484	374	154	127
Sand (%)	22.7	21.9	18.9	39.4	42.9	29.1	31.1
Silt (%)	62.3	61.7	63.4	53.4	43.9	60.1	59.0
Clay (%)	15.0	16.4	17.7	7.20	13.2	10.8	9.90
Clay minerals	Chl/Ill	Chl/Ill/Sm	Chl/Ill/Sm	Chl/Ill	Chl/Ill	Chl/Ill/Sm	Chl/Ill/Sm
Clay/TOC <sup>1</sup>	7.19	11.8	30.6	1.63	5.71	7.33	11.2

TOC – total organic carbon content; HA, FA – humic and fulvic acid carbon contents; CEC – cation exchange capacity; Fe<sub>o</sub>, Al<sub>o</sub> – ammonium oxalate extractable iron and aluminium; Chl – chlorite, Ill – illite, Sm – smectite; <sup>1</sup>ratio of clay content to total organic carbon content

All sorption and desorption data were fitted to the linear form of the Freundlich equation:

$$\log S = \log K_f + 1/n \log C \quad (1)$$

where:

$C$  – equilibrium concentration of acetochlor in solution (mg/l)

$S$  – equilibrium concentration of acetochlor sorbed by soil and calculated as the difference between the initial and the equilibrium solution concentrations (mg/kg)

$K_f$  – Freundlich coefficient ( $\text{mg}^{(1-1/n)} \cdot \text{l}^{(1/n)} / \text{kg}$ )

$1/n$  – Freundlich exponent

$K_{fs}$  and  $1/n_s$  will hereafter refer to sorption, and  $K_{fd}$  and  $1/n_d$  to desorption. Organic carbon distribution coefficient ( $K_{oc}$ ) was calculated by normalizing the corresponding  $K_{fs}$  values to the organic carbon content of the soils:

$$K_{oc} = (K_{fs} / \text{OC}\%) \times 100 \quad (2)$$

Desorption hysteresis index (HI) was calculated as the ratio between  $1/n_d$  and  $1/n_s$  (Cox *et al.* 1997).

The relationship between soil properties and sorption-desorption parameters was analyzed using the Pearson's correlation coefficient  $R$ . All analyses were assessed at significance levels of 0.05 or lower and were processed using STATISTICA software package, Version 7.1, 1984–2005.

## RESULTS AND DISCUSSION

**Sorption of acetochlor and its relationship with soil properties.** Sorption-desorption isotherms of acetochlor in soils are shown in Figure 1. Data were fitted adequately to the linear form of the Freundlich equation with  $R^2$  values being significant at the 0.05 probability level. The values of  $K_{fs}$  and  $1/n_s$  are summarized in Table 2. Most of the sorption isotherms were of L- or C-type. According to GILES *et al.* (1960), L-type isotherms correspond to a decrease in number of sites available for sorption as the solute concentration increases. On the other hand, C-type isotherm indicates that the proportion of the solute sorbed to solid phase does not change with the solute concentration. The sorption isotherm for horizon B of Chernozem (sample 1B) had the slope ( $1/n_s$ ) higher than 1, which was indicative of S-type isotherm. In such a case, as acetochlor concentration in solution increased, the proportion of acetochlor sorbed to soil increased. The different shapes of sorption isotherms might be attributed to the occurrence of more sorption mecha-

nisms included in the acetochlor sorption, likely due to differences in composition of the soils and their heterogeneous nature. Several authors have reported non-linear isotherms of L- and S-types for acetochlor sorption in soils with contrasting physico-chemical properties (TAYLOR *et al.* 2004; HILLER *et al.* 2008; BEDMAR *et al.* 2011).

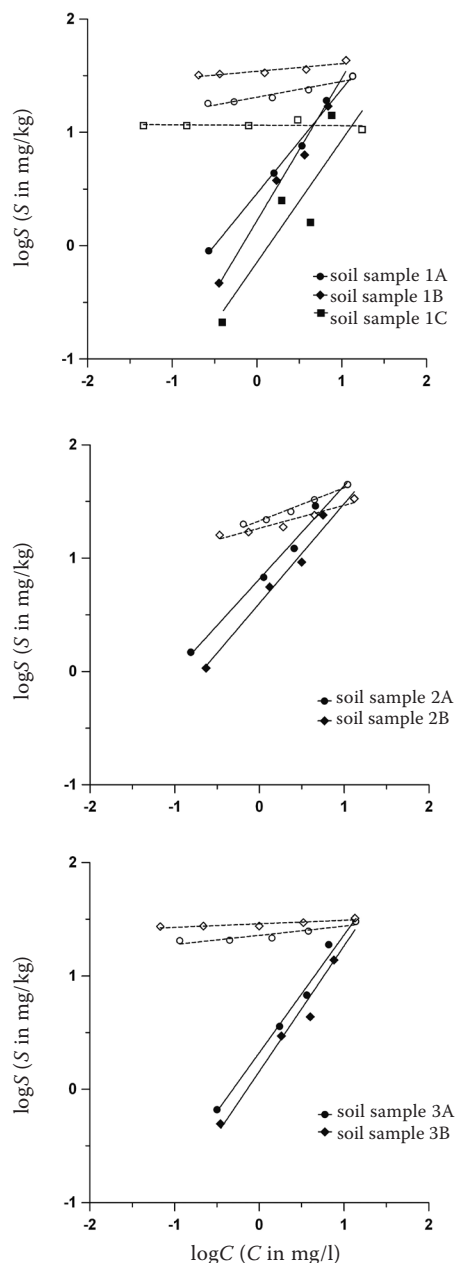


Figure 1. Sorption and desorption isotherms (black and white symbols, respectively) of acetochlor in the soils; soil samples 1A, 1B, and 1C represent soil horizons A, B, and C of Calcaro-Haplic Chernozem, respectively; 2A and 2B are soil horizons A and B of Fulvi-Calcaric Phaeozem, respectively; and 3A and 3B denote soil horizons A and B of Calcaric Fluvisol, respectively; lines are the fitted Freundlich isotherms



Based on the  $K_{fs}$  values, the extent of acetochlor sorption decreased with increasing soil depth for each soil type (Table 2). Considering all the soil samples, the order of decreasing sorption was: horizon A of Phaeozem > horizon B of Phaeozem > horizon A of Chernozem > horizon A of Fluvisol > horizon B of Chernozem > horizon B of Fluvisol > horizon C of Chernozem, and corresponded to the decrease of soil organic carbon content. Statistical analyses (Table 3) showed that the sorption of acetochlor in soils was highly correlated with soil organic carbon content ( $R = 0.99$ ,  $P < 0.001$ ), and the humic acid and fulvic acid carbon contents ( $R = 0.98$  and  $R = 0.97$ ,  $P < 0.001$ ). Several studies have suggested that soil organic matter exhibits a high affinity for acetochlor and plays the most prominent role as a sorbent of acetochlor in soils (WANG *et al.* 1999; HILLER *et al.* 2008; BEDMAR *et al.* 2011). The calculated  $K_{oc}$  values for acetochlor were similar among the soils, confirming that organic matter of the soils had similar sorption affinity for the herbicide and that TOC was the most important factor for acetochlor sorption in soils. Although pH values of the soil samples varied within a limited range (Table 1), a significant negative correlation was found between the soil pH and the  $K_{fs}$  values ( $R = -0.84$ ,  $P < 0.05$ ). There was also a positive significant relationship between the  $K_{fs}$  values and the  $Al_o$  contents ( $R = 0.93$ ,  $P < 0.01$ ). However, positive influence of non-crystalline to poorly crystalline Al oxides on acetochlor sorption should be highly questionable due to positive significant relationship between  $Al_o$  and TOC (Table 3). Unfortunately, there are no studies regarding the adsorption of chloroacetanilides onto Al oxides, but CLAUSEN *et al.* (2001) demonstrated that the uncharged herbicides like isoproturon and atrazine did not adsorb on the Al-surfaces of  $\alpha$ -alumina.

Previously, the sorption of 4-chloro-2-methylphenoxyacetic acid (MCPA), which is another commonly used herbicide in the Žitný ostrov area, was determined in the same soil samples as used in the present study (HILLER *et al.* 2012). Comparing the sorption of MCPA with that of acetochlor in the soils, the extent of MCPA sorption (a range of  $K_{fs}$  values was  $0.37\text{--}1.03\text{ mg}^{(1-1/n)}\cdot\text{l}^{(1/n)}/\text{kg}$ ) was approximately 2–8 times lower than that of acetochlor sorption, although soil properties controlling both MCPA and acetochlor sorption were identical (Table 3 and Table 3 in HILLER *et al.* 2012). Thus, differences in the soil sorption between MCPA and acetochlor can be explained by the different physico-chemical properties of the two herbicides. MCPA has relatively high water solubility (825 mg/l at 25°C) and low octanol-water distribution coefficient ( $\log K_{ow} = -0.71$  at 25°C and pH 7), whereas water solubility and  $\log K_{ow}$  of acetochlor are 223 mg/l and 4.14 at 25°C, respectively (TOMLIN 2001) indicating a tendency of MCPA to remain in the soil solution rather than to be sorbed by the soil solid phase. Moreover, MCPA, as a weak organic acid with a  $pK_a$  value of 3.07, is almost completely dissociated to negatively charged ions when soil pH is approximately 3 pH units above its  $pK_a$  value (KAH & BROWN 2006). This shift in the speciation of MCPA towards anionic forms at slightly alkaline pH of the soils (Table 1) contributed to the observed low sorption of MCPA in the soils. Because acetochlor is not subject to dissociation, it occurs in a form of neutral molecules that have higher sorption affinity for soil solid organic and inorganic components than more soluble anionic species of MCPA.

**Desorption of acetochlor and its relationship with soil properties.** Desorption isotherms were fitted to the linear form of the Freundlich equation

Table 2. Sorption and desorption parameters for acetochlor in soils ( $K_{fs}$ ,  $1/n_s$ ,  $K_{oc}$ ,  $K_{fd}$ ,  $1/n_d$ ), hysteresis index (HI), and percentage of acetochlor desorbed of its total amount sorbed in soils after four successive desorption cycles ( $P_d$ ); values of  $K_{fs}$  and  $1/n$  appear as mean  $\pm$  standard error

Soil sample	1A	1B	1C	2A	2B	3A	3B
$K_{fs}$ ( $\text{mg}^{(1-1/n)}\cdot\text{l}^{(1/n)}/\text{kg}$ )	$2.90 \pm 0.21$	$1.67 \pm 0.24$	$0.72 \pm 0.26$	$6.57 \pm 0.91$	$4.00 \pm 0.48$	$2.10 \pm 0.22$	$1.44 \pm 0.26$
$1/n_s$	$0.92 \pm 0.04$	$1.26 \pm 0.09$	$1.08 \pm 0.26$	$0.82 \pm 0.05$	$0.88 \pm 0.07$	$1.04 \pm 0.06$	$1.11 \pm 0.10$
$R^2$	0.99	0.99	0.85	0.99	0.98	0.99	0.98
$K_{oc}$ (l/kg)	139	119	122	149	174	145	163
$K_{fd}$ ( $\text{mg}^{(1-1/n)}\cdot\text{l}^{(1/n)}/\text{kg}$ )	$20.42 \pm 0.68$	$34.59 \pm 0.89$	$11.56 \pm 0.42$	$21.33 \pm 0.76$	$18.37 \pm 0.87$	$22.80 \pm 0.80$	$28.84 \pm 0.49$
$1/n_d$	$0.14 \pm 0.02$	$0.07 \pm 0.02$	$0.02 \pm 0.01$	$0.29 \pm 0.03$	$0.20 \pm 0.03$	$0.08 \pm 0.02$	$0.03 \pm 0.01$
$R^2$	0.93	0.84	0.57	0.98	0.93	0.84	0.80
HI	0.15	0.06	0.02	0.35	0.23	0.08	0.03
$P_d$ (%)	38.6	25.9	7.80	54.5	50.1	30.3	15.7

(Figure 1) and the Freundlich desorption parameters are shown in Table 2. Desorption of acetochlor from all soil samples was lower than the amount initially sorbed as indicated by much lower slopes of acetochlor desorption isotherms ( $1/n_d$ ) than those of the sorption isotherms ( $1/n_s$ ). These results showed that sorption-desorption isotherms for acetochlor were hysteretic and indicative of a positive hysteresis with  $HI < 1.0$ . This is consistent with other reports describing desorption hysteresis of acetochlor (TAYLOR *et al.* 2004) and the related chloroacetanilide herbicides like butachlor (YU *et al.* 2006) and metolachlor (ZHENG & COOPER 1996).

The percentages of acetochlor desorbed from soils after four successive desorption cycles ranged from 7.80 to 54.5% (Table 2) and were correlated positively with TOC (Table 3). The relationship suggested that more acetochlor was desorbed from soil samples that had higher TOC content and adsorption capacity (horizon A of all three soil types and horizon B of Phaeozem) than from soil samples with lower TOC content and adsorption capacity. It was unusual to observe positive significant correlation between the adsorption capacity (i.e.  $K_{fs}$ ) and the desorption percentage as in our case ( $R = 0.92$ ,  $P < 0.01$ ). However, high capability of a soil to sorb pesticide is not an indication of binding strengths involved in soil-pesticide interaction. The percentages of acetochlor desorbed were correlated negatively to clay/TOC ratio (Table 3), suggesting that the extent of acetochlor desorption was controlled by soil organo-mineral complexes rather

than by individual organic or inorganic components of the soils. Additionally, the soils containing smectite clays exhibited lower desorption of acetochlor than those with the absence of these mineral components. TORRENTS and JAYASUNDERA (1997) investigated the desorption of two chloroacetanilide herbicides from pure Na-montmorillonite and humic acid-coated Na-montmorillonite and observed that herbicide desorption was lower from humic acid-coated clay than from pure clay and humic acid. This might indicate that stronger and multiple bondings operated simultaneously in the interaction of chloroacetanilide herbicides with organic matter-coated clays, while this sorptive interactions with individual soil components were governed by weaker bonding mechanisms.

Desorption of acetochlor was compared to MCPA desorption (HILLER *et al.* 2012) from the same soils as used in the present study. Although the sorption-desorption of MCPA was also hysteretic with  $HI$  values of 0.34–0.77, hysteresis was low and percentages of MCPA desorbed from the soils after four successive desorption cycles were between 48.4–80.6% and not correlated with soil properties (HILLER *et al.* 2012). Consistently higher desorption of MCPA from soils compared to desorption of acetochlor could be attributed to a weaker sorption affinity of MCPA for soil organic and mineral components and its relatively high solubility.

**Environmental implications.** Considering the relatively high desorption extent of acetochlor in surficial soil horizons A and its lower extent of sorption in

Table 3. Pearson's correlation coefficient ( $R$ ) values between the soil properties as well as between the soil properties and the selected sorption/desorption parameters; significant  $R$  values are given by bold numbers

	TOC	HA	FA	Active pH	CEC	Fe <sub>o</sub>	Al <sub>o</sub>	Clay	Clay/TOC <sup>1</sup>	$K_{fs}$	$P_d$	HI
TOC	1											
HA	<b>0.99***</b>	1										
FA	<b>0.99***</b>	<b>0.96***</b>	1									
Active pH	<b>-0.88**</b>	<b>-0.83*</b>	<b>-0.87*</b>	1								
CEC	<b>0.93**</b>	<b>0.97***</b>	0.89**	-0.69	1							
Fe <sub>o</sub>	0.60	0.48	0.69	-0.64	0.35	1						
Al <sub>o</sub>	<b>0.92**</b>	<b>0.96***</b>	0.88**	-0.69	<b>0.99***</b>	0.38	1					
Clay	-0.62	-0.52	-0.70	0.60	-0.38	<b>-0.93**</b>	-0.43	1				
Clay/TOC <sup>1</sup>	-0.72	-0.67	-0.69	<b>0.84*</b>	-0.55	-0.68	-0.61	0.69	1			
$K_{fs}$	<b>0.99***</b>	<b>0.98***</b>	<b>0.97***</b>	<b>-0.84*</b>	<b>0.93**</b>	0.58	<b>0.93**</b>	-0.65	-0.73	1		
$P_d$	<b>0.90**</b>	<b>0.91**</b>	<b>0.84*</b>	<b>-0.85*</b>	<b>0.85*</b>	0.41	<b>0.88**</b>	-0.50	<b>-0.84*</b>	<b>0.92**</b>	1	
HI	<b>0.97***</b>	<b>0.98***</b>	<b>0.94**</b>	<b>-0.81*</b>	<b>0.94**</b>	0.47	<b>0.94**</b>	-0.56	-0.69	<b>0.99***</b>	<b>0.94**</b>	1

\*, \*\*, \*\*\*significant at  $P < 0.05$ , 0.01 and 0.001; TOC – total organic carbon content; HA, FA – humic and fulvic acid carbon contents; CEC – cation exchange capacity; Fe<sub>o</sub>, Al<sub>o</sub> – ammonium oxalate extractable iron and aluminium; HI – hysteresis index; <sup>1</sup>ratio of clay content to total organic carbon content

subsoil horizons B and C, leaching of the herbicide into groundwater might be of a potential concern in the studied area. However, groundwater monitoring performed by Slovak Hydrometeorological Institute (SHMI) in the Žitný ostrov shows that acetochlor concentrations are below the method detection limit of 0.02 µg/l (personal communication by A. LUPTÁKOVÁ from SHMI), suggesting a very low potential of acetochlor to leach through the soils into the groundwater. This might be due to rapid degradation of acetochlor in soils at ambient temperatures (DICTOR *et al.* 2008) and its strong sorption in upper soil layers (JURSÍK *et al.* 2013), thereby decreasing significantly its concentration in the soil solution.

## CONCLUSION

The extents of sorption and desorption of acetochlor in agricultural soils of the Žitný ostrov area (SW Slovakia) were positively correlated to soil organic carbon content as well as humic and fulvic acid carbon contents, amorphous Al oxide content, and negatively correlated to soil active pH. The extent of acetochlor sorption and its percentages desorbed were higher in surficial horizons A than in deeper soil horizons. Variations in sorption-desorption behaviour were attributed to the different affinity of acetochlor to soil components. Considering the relatively high desorption extent of acetochlor in surficial horizons A and its lower extent of sorption in the subsoil horizons, leaching of the herbicide into groundwater might be of a potential concern in the studied area. However, more detailed investigations including lysimeter studies and degradation experiments would be required to estimate the actual potential for leaching of acetochlor through soils into the groundwater occurring in the Žitný ostrov area.

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## References

- ANDRADE A.I.A.S.S., STIGTER T.Y. (2009): Multi-method assessment of nitrate and pesticide contamination in shallow alluvial groundwater as a function of hydrogeological setting and land use. *Agricultural Water Management*, **96**: 1751–1765.
- BEDMAR F., DANIEL P.E., COSTA J.L., GIMÉNEZ D. (2011): Sorption of acetochlor, S-metolachlor, and atrazine in surface and subsurface soil horizons of Argentina. *Environmental Toxicology and Chemistry*, **30**: 1990–1996.
- CAI X., SHENG G., LIU W. (2006): Degradation and detoxification of acetochlor in soils treated by organic and thiosulfate amendments. *Chemosphere*, **66**: 286–292.
- CHAO L., ZHOU Q.X., CHEN S., CUI S., WANG M.E. (2007): Single and joint stress of acetochlor and Pb on three agricultural crops in northeast China. *Journal of Environmental Sciences*, **19**: 719–724.
- CLAUSEN L., FABRICIUS I., MADSEN L. (2001): Adsorption of pesticides onto quartz, calcite, kaolinite, and α-alumina. *Journal of Environmental Quality*, **30**: 846–857.
- COX L., KOSKINEN W.C., YEN P.Y. (1997): Sorption-desorption of imidacloprid and its metabolites in soils. *Journal of Agricultural and Food Chemistry*, **45**: 1468–472.
- ČADKOVÁ E., KOMÁREK M., KALISZOVÁ R., VANĚK A., BALÍKOVÁ M. (2013): Tebuconazole sorption in contrasting soil types. *Soil and Sediment Contamination: An International Journal*, **22**: 404–414.
- DICTOR M.C., BARAN N., GAUTIER A., MOUVET C. (2008): Acetochlor mineralization and fate of its two major metabolites in two soils under laboratory conditions. *Chemosphere*, **71**: 663–670.
- GEE G.W., BAUDER J.W. (1986): Particle-size analysis. In: KLUTE A. (ed): *Methods of Soil Analysis. Part 1 – Physical and Mineralogical Methods*. 2<sup>nd</sup> Ed. Agronomy Series 9, American Society of Agronomy and Soil Science Society of America, Madison, 383–411.
- GILES C.H., MACEWAN T.H., NAKHWA S.N., SMITH D. (1960): Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society*, **111**: 3973–3993.
- HE H., CHEN G., YU J., HE J., HUANG X., LI S., GUO Q., YU T., LI H. (2013): Individual and joint toxicity of three chloroacetanilide herbicides to freshwater cladoceran *Daphnia carinata*. *Bulletin of Environmental Contamination and Toxicology*, **90**: 344–350.
- HILLER E., KRASCENITS Z., ČERNÁNSKÝ S. (2008): Sorption of acetochlor, atrazine, 2,4-D, chlorotoluron, MCPA, and trifluralin in six soils from Slovakia. *Bulletin of Environmental Contamination and Toxicology*, **80**: 412–416.
- HILLER E., ČERNÁNSKÝ S., KRASCENITS Z., MILIČKA J. (2009): Effect of soil and sediment composition on acetochlor sorption and desorption. *Environmental Science and Pollution Research*, **16**: 546–554.
- HILLER E., TATARKOVÁ V., ŠIMONOVICHOVÁ A., BARTAL M. (2012): Sorption, desorption, and degradation of (4-chloro-2-methylphenoxy)acetic acid in representative soils of the Danubian Lowland, Slovakia. *Chemosphere*, **87**: 437–444.
- HLADÍK M.L., BOUWER E.J., ROBERTS A.L. (2008): Neutral degradates of chloroacetamide herbicides: Occurrence in drinking water and removal during conventional water treatment. *Water Research*, **42**: 4905–4914.

- ISRIC (1995): Procedures for soil analysis. International Soil Reference and Information Centre, Wageningen, The Netherlands.
- JACKSON M.L. (1958): Soil Chemical Analysis. Prentice-Hall, Englewood Cliffs, New York.
- JANNICHE G.S., MOUVET C., ALBRECHSTEN H.-J. (2011): Vertical small scale variations of sorption and mineralization of three herbicides in subsurface limestone and sandy aquifer. *Journal of Contaminant Hydrology*, **123**: 167–177.
- JURSÍK M., KOČÁREK M., HAMOUZOVÁ K., SOUKUP J., VENCLOVÁ V. (2013): Effect of precipitation on the dissipation, efficacy and selectivity of three chloroacetamide herbicides in sunflower. *Plant, Soil and Environment*, **59**: 175–182.
- KAH M., BROWN C.D. (2006): Prediction of the adsorption of ionizable pesticides in soils. *Journal of Agricultural and Food Chemistry*, **55**: 2312–2322.
- KODEŠOVÁ R., KOČÁREK M., KODEŠ V., DRÁBEK O., KOZÁK J., HEJTMÁNKOVÁ K. (2011): Pesticide adsorption in relation to soil properties and soil type distribution in regional scale. *Journal of Hazardous Materials*, **186**: 540–550.
- KONONOVA M.M., BELCIKOVA N.P. (1961): Speed up methods for humus determination. *Pochvovedenie*, **25**: 125–129. (in Russian)
- LENGYEL Z., FÖLDÉNYI R. (2003): Acetochlor as a soil pollutant. *Environmental Science and Pollution Research*, **10**: 13–18.
- MA Q.L., HOLLAND P.T., JAMES T.K., MCNAUGHTON D.E., RAHMAN A. (2000): Persistence and leaching of the herbicides acetochlor and terbuthylazine in an allophanic soil: comparisons of field results with PRZM-3 predictions. *Pest Management Science*, **56**: 159–167.
- MA Q.L., RAHMAN A., HOLLAND P.T., JAMES T.K., MCNAUGHTON D.E. (2004): Field dissipation of acetochlor in two New Zealand soils at two application rates. *Journal of Environmental Quality*, **33**: 930–938.
- MALAGUERRA F., ALBRECHTSEN H.J., THORLING L., BINNING P.J. (2012): Pesticides in water supply wells in Zealand, Denmark. A statistical analysis. *Science of the Total Environment*, **414**: 433–444.
- MALOSCHIK E., ERNST A., HEGEDÜS G., DARVAS B., SZÉKÁCS A. (2007): Monitoring water-polluting pesticides in Hungary. *Microchemical Journal*, **85**: 88–97.
- MCKEAGUE J.A., DAY J.H. (1966): Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science*, **46**: 13–22.
- MOORE D.M., REYNOLDS R.C. (1997): X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press, Oxford, New York.
- MUCHA I., KOCINGER D., HLAVATÝ Z., RODÁK D., BANSKÝ L., KUČÁROVÁ K., KÚROVÁ E. (1999): Visit to the area of the Gabčíkovo hydropower project. Ground Water Consulting Ltd., Bratislava. Available at <http://www.gabcikovo.gov.sk/doc/green/index.html> (accessed December 2012). (in Slovak)
- NELSON D.W., SOMMERS L.E. (1996): Total carbon, organic carbon and organic matter. In: SPARKS D.L., BARTELS J.M. (eds): *Methods of Soil Analysis. Part 3 – Chemical Methods*. SSSA Book Series No. 5, SSSA, Madison, 961–1010.
- NEMETH-KONDA L., FÜLEKY GY., MOROVJAN GY., CSOKAN P. (2002): Sorption behaviour of acetochlor, atrazine, carbandazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. *Chemosphere*, **48**: 545–552.
- OLIVEIRA JR. R.S., KOSKINEN W.C., GRAFF C.D., ANDERSON J.L., MULLA D.J., NATER E.A., ALONSO D.G. (2013): Acetochlor persistence in surface and subsurface soil samples. *Water, Air and Soil Pollution*, **224**: 1747.
- TAYLOR J.P., MILLS M.S., BURNS R.G. (2004): Sorption and desorption behavior of acetochlor in surface, subsurface and size-fractionated soil. *European Journal of Soil Science*, **55**: 671–679.
- TOMLIN C.D.S. (2001): The E-pesticide Manual. Version 2.0. 12<sup>th</sup> Ed. British Crop Protection Council, [CD-ROM].
- TORRENTS A., JAYASUNDERA S. (1997): The sorption of nonionic pesticides onto clays and the influence of natural organic carbon. *Chemosphere*, **35**: 1549–1565.
- WANG Q., YANG W., LIU W. (1999): Adsorption of acetanilide herbicides on soils and its correlation with soil properties. *Pesticide Science*, **55**: 1103–1108.
- YEN J.H., CHANG S.L., WU C.C., WANG Y.S. (2005): Behavior of acetanilide herbicides in soils and the possibility of groundwater contamination. *Bulletin of Environmental Contamination and Toxicology*, **75**: 1086–1093.
- YU Y.L., WU X.M., LI S.N., FANG H., ZHAN H.Y., YU J.Q. (2006): An exploration of the relationship between adsorption and bioavailability of pesticides in soil to earthworm. *Environmental Pollution*, **141**: 428–433.
- ZHENG H., YE C. (2002): Adsorption and mobility of acetochlor and butachlor on soil. *Bulletin of Environmental Contamination and Toxicology*, **68**: 509–516.
- ZHENG S.-Q., COOPER J.-F. (1996): Adsorption, desorption, and degradation of three pesticides in different soils. *Archives of Environmental Contamination and Toxicology*, **30**: 15–20.

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