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Sorption of Acetochlor, Atrazine, 2,4-D, Chlorotoluron, MCPA, and Trifluralin in Six Soils From Slovakia

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Abstract Sorption of the herbicides (acetochlor, atrazine, 2,4-D, chlorotoluron, MCPA and trifluralin) in their commercially available formulations was characterized on six agricultural soils from Slovakia. Weak acid herbicides (2,4-D and MCPA) were the least sorbed, whereas weak base such as atrazine and nonionic herbicides were the most sorbed in the order: atrazine $<$ acetochlor $\approx$ chlorotoluron $<$ trifluralin, which was closely related to the hydrophobicity of herbicides expressed as $\log K_{OW}$. The K_F values positively correlated with soil organic carbon content for all herbicides. Moreover, all herbicides were the most sorbed by Vertisol with relatively high smectite clay content in proportion to organic carbon content. The K_{OC} values for each herbicide showed a smaller variation among soils (excluding Vertisol) than the K_F and were used to compare soil mobility potential of herbicides.

Keywords Herbicide · Mobility · Soil · Sorption

Herbicides, or chemical weed killers, are one of the major achievements of modern agriculture. However, increasing agricultural use of the herbicides leads to their occurrence in those parts of the environment where it is not desirable (e.g. groundwaters). Sorption, which removes a herbicide from the mobile phase of a soil, is one of the main processes influencing its mobility in soil under laboratory conditions (Socías-Viciana et al. 1999), as well as under field conditions (Laabs et al. 2000). Sorption tends to decrease the degradation rate of herbicides and their bioavailability (Yu et al. 2006). Therefore, the first step in understanding of the environmental fate of herbicides is to study their sorption characteristics. Many studies have shown that soil organic carbon is in general the most important soil property that affects herbicide sorption (Boivin et al. 2005; Wang et al. 1999), but pH, clay content, and clay mineralogy are also important (Baskaran et al. 1996). The objectives of this study were to determine sorption of acetochlor, atrazine, 2,4-D, chlorotoluron, MCPA, and trifluralin in six soils from Slovakia, and to identify the main soil properties affecting their sorption. The batch equilibration method was used to determine sorption of the six herbicides in the six soils. The herbicides represent a wide range of properties and chemical groups and are intensively used in agricultural crops of relevant significance in Slovakia, such as maize, sunflower and cereals. Although, herbicide sorption in soils has been extensively studied throughout the world, there are only few data concerning the sorption of acetochlor, chlorotoluron, MCPA and trifluralin in soils and none for the slovak soils. Quantitative determination of sorption of this range of herbicides in a variety of different agricultural soils is therefore needed information for their safe and effective use in Slovakia.

Materials and Methods

Soils used in this study were collected from five different locations in Western Slovakia. Soil samples were taken

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Table 1 Properties of the soils

	RE	LL 1	CA	LL 2	VL	CM
Location	Lozorno	Chynorany	Stupava	Chynorany	Gbely	Ziharec
Type	Regosol	Luvisol	Chernitsa	Luvisol	Vertisol	Chernozem
Texture	Sand	Loam	Sandy loam	Loam	Clay loam	Clay loam
Sand (%)	85.5	32.2	73.8	38.5	38.5	32.4
Silt (%)	13.9	44.9	15.2	39.4	24.3	37.9
Clay (%)	0.60	22.9	11.0	22.1	37.2	29.8
pH_{H_2O}	5.76	7.30	7.96	7.86	6.11	8.38
OC (%)[a]	0.48	0.89	1.19	1.53	1.57	2.41
Main clay minerals[b]	Ill > Chl	Ill > K	Ill > Chl	Sm > Ill > K+Chl	Sm > Ill > K	Sm > Chl > K

[a] OC, organic carbon content

[b] Ill, illite; Chl, chlorite; K, kaolinite; Sm, smectites

from the surface layer (0–20 cm), air-dried, passed through a 2-mm sieve, and stored in the dark. The soils differ with respect to organic carbon content, clay content, and mineralogy of soil clay fraction (Table 1).

Herbicides examined in this study were a commercially available formulations of acetochlor (Guardian Max), atrazine (Atranex 50 SC), 2,4-D (Desormone Liquid 600 SL), chlorotoluron (Lentipur 500 FW), MCPA (Aminex Pur), and trifluralin (Triflurex 48 EC). These formulations were obtained with a kind consent from Istrochem SA (Bratislava, Slovakia). Physico-chemical properties of the herbicides are shown in Table 2. Herbicide solutions (except trifluralin) were prepared directly in a background solution of 0.01 M $CaCl_2$ and 10^{-4} M NaN_3 to keep ionic strength constant and to prevent biological activity, respectively. Stock solution of trifluralin was prepared by dissolving appropriate amount of Trifluralex 48 EC in HPLC-grade methanol, and then it was diluted using background solution to obtain a series of solutions with different initial trifluralin concentrations. Methanol content was less than 1% in all prepared solutions of trifluralin. The following concentration range was used in the sorption tests (in mg L^{-1}): acetochlor (0.1–1.6), atrazine (0.2–5.0), 2,4-D (0.3–5.0), chlorotoluron (0.1–4.0), MCPA (0.3–5.0) and trifluralin (1.0–60).

Duplicate 50 mL (20 mL for MCPA) aliquots of each herbicide solution were added to 10 g (1 g for trifluralin) of soil in 100 mL glass flasks. Flasks were closed with a glass lids and shaken automatically for 48 h. At the end of shaking period, 15 mL suspension was taken and centrifuged at 3,000 rpm for 30 min. The herbicide concentrations in supernatants were analyzed by high-performance liquid chromatography with pre-concentration step using solid phase extraction (PLRP-S cartridge, 10 × 2 mm) and ultraviolet detection composed of HP 1090 LC device (Hewlett-Packard, Waldbronn, Germany) and HP 1090 Series II UV detector. The analytical column used was LiChrosphere 100 RP-18, 125 × 4.0 mm i.d., 5 μm (Merck, Germany). The detector was set at 220, 230, 245 and 275 nm for determination of acetochlor, atrazine, 2,4-D and MCPA, chlorotoluron and trifluralin, respectively. Two mobile phases with gradient elution were used: the mobile phase A was a mixture of 5% (m/v) acetonitrile and 0.5% (m/v) phosphate acid solution and the mobile phase B was 100% acetonitrile. The flow rate of 1 mL min^{-1} was used. The injection volume was 25 μL. Quantification was performed by external calibration by measuring the peak areas. The average uncertainty for the measured concentrations was about ±8% and the detection limit of 0.01 mg L^{-1} was achieved. The amounts of herbicides sorbed were calculated

Table 2 Physico-chemical properties of the herbicides[a]

Herbicide	Molecular weight (g mol^{-1})	Solubility in water at 25°C S_W (mg L^{-1})	*n*-Octanol – water partition coefficient $\log K_{OW}$	Ionizability (pKa)
Acetochlor	269.8	223	4.14	Nonionic
Atrazine	215.7	33 (pH 7)	2.50	Basic (1.7)
2,4-D	221.0	23,180 (pH 7)	0.33 (pH 5)	Acidic (2.73)
Chlorotoluron	212.7	74	2.50	Nonionic
MCPA	200.6	273.9 (pH 7)	−0.71 (pH 7)	Acidic (3.07)
Trifluralin	335.3	0.221 (pH 7)	4.83	Nonionic

[a] From Tomlin (2001)

as the difference between the initial and equilibrium concentrations in the aqueous phase. Sorption data were fitted to the Freundlich sorption isotherm in a linear form:

$$\log S = \log K_\mathrm{F} \times 1/n \ \log C$$

where S is the amount of herbicide sorbed (mg kg^{-1}), C is the equilibrium concentration in solution (mg L^{-1}), K_F is the Freundlich constant (mg$^{1-1/n}$ kg^{-1} L$^{1/n}$), and $1/n$ is the Freundlich exponent reflecting the degree to which sorption is a function of concentration (Socías-Viciana et al. 1999). The Freundlich constant is considered to be a simple partition coefficient K_D (L kg^{-1}) at hypothetical equilibrium herbicide concentration of 1 mg L^{-1}. Coefficients K_OC were calculated by normalizing the corresponding K_F values to the total organic carbon content of the soils:

$$K_\mathrm{OC} = (K_\mathrm{F}/OC\%) \times 100$$

where K_OC is the organic carbon partition coefficient (L kg^{-1}).

Results and Discussion

Representative sorption isotherms of the six herbicides in LL 2 are shown in Fig. 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 K_F and $1/n$ values are summarized in Table 3. Most of the isotherms were of L type (Giles et al. 1960), indicating a decrease in specific sorption sites when herbicide concentration in solution increases. Recently, the nonlinearity of sorption isotherms has been attributed to the occurrence of specific interactions for herbicides with limited active sites in soil organic matter at low herbicide concentrations (Spurlock and Biggar 1994). However, some of the isotherms exhibit a certain C character, (e.g. atrazine in LL1 and LL2 or trifluralin in RE, LL1, LL2 and CA), indicating a constant partition between soil and solution over the concentration range examined. Although the K_F values and the corresponding K_OC values may be difficult to compare with literature data if K_F values are derived from different units of S and C or if $1/n$ values differ (Chen et al. 1999), the results are roughly within the range of previously reported values (Baskaran et al. 1996; Boivin et al. 2005; Liu and Qian 1995; Socías-Viciana et al. 1999; Wang et al. 1999).

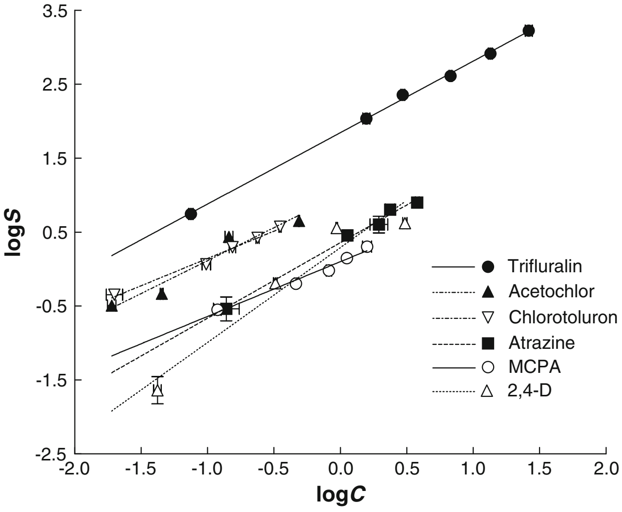

Fig. 1 Sorption isotherms of the six herbicides in LL2. Error bars indicate standard errors of the mean

The anomalously high K_F and K_OC values for all herbicides, and particularly for nonionic herbicides, were found in soil from Gbely (Vertisol) with a high smectite content (more than 21% of the total soil weight), therefore this soil was excluded from correlations between K_F, K_OC and soil/herbicide properties. It has been shown that smectite clays in natural soils effectively sorb many relatively nonionic herbicides, such as triazines and phenylureas (Sheng et al. 2001). For the same soil, the K_F and K_OC values increased among the herbicides in the order: MCPA $\leq$ 2,4-D $<$ atrazine $<$ acetochlor $\approx$ chlorotoluron $<$ trifluralin, which is closely related to the hydrophobicity of herbicides expressed as $\log K_\mathrm{OW}$. The influence of the hydrophobicity on herbicide sorption was confirmed by significant correlation between the $\log K_\mathrm{OC}$ and the $\log K_\mathrm{OW}$ ($p < 0.05$). As expected, the sorption of acidic herbicides at approximately neutral soil pH was lower than that of basic or nonionic herbicides due to repulsion of the anionic herbicide molecules by the negatively charged soil minerals and organic matter. For each pesticide, K_F increased in the following order: RE $<$ LL1 $<$ CA $<$ LL2 $<$ CM $<$ VL. In general, sorption of all six herbicides was highly correlated with organic carbon content of soils, when VL soil was excluded, as discussed above. The relationship was linear for acetochlor, atrazine, 2,4-D, chlorotoluron and trifluralin ($R^2 = 0.87$*, $R^2 = 0.97$**, $R^2 = 0.88$*, $R^2 = 0.95$** and $R^2 = 0.90$*, respectively; * $p < 0.05$ and ** $p < 0.01$) and curvilinear for MCPA ($R^2 = 0.94$*). Knowing the strong relationships between the K_F values and the organic carbon content, the corresponding K_OC values were calculated (Table 3). K_OC values are generally assumed to be a constant for a particular organic chemical where sorption is related to the quantity of soil organic carbon, but, it is now well recognized that sorption may also be affected by the quality of soil organic carbon and the contributions from mineral sorption (Ahmad et al. 2001; Sheng et al. 2001). However, the obtained K_OC values for all six herbicides are nearly uniform among different soils (except Vertisol), suggesting that organic matters of the soils have approximately the same sorption affinity. The higher K_OC values for mainly nonionic herbicides in Vertisol with a high smectite content could be attributed to the sorption by smectite clays, in addition to sorption by soil organic matter.

Table 3 Parameters of the Freundlich equation and corresponding organic carbon partition coefficients

	RE	LL 1	CA	LL 2	VL	CM
Acetochlor						
K_F	1.44 (0.39)	6.16 (0.31)	6.98 (0.18)	10.07 (2.9)	16.94 (1.4)	11.59 (0.9)
$1/n$	0.83 (0.10)	0.91 (0.02)	0.78 (0.01)	0.89 (0.09)	0.78 (0.02)	0.92 (0.03)
R^2	0.93	0.99	0.99	0.94	0.99	0.99
K_{OC}	300	692	587	654	1,076	481
Atrazine						
K_F	0.50 (0.13)	1.60 (0.20)	2.18 (0.27)	2.27 (0.20)	5.46 (0.19)	4.31 (0.47)
$1/n$	1.27 (0.21)	0.95 (0.11)	0.77 (0.10)	1.02 (0.07)	0.84 (0.03)	0.77 (0.08)
R^2	0.90	0.90	0.91	0.96	0.99	0.93
K_{OC}	104	180	183	148	348	179
2,4-D						
K_F	0.16 (0.02)	1.43 (0.15)	1.46 (0.14)	1.94 (0.27)	3.03 (0.21)	2.62 (0.45)
$1/n$	0.95 (0.06)	0.72 (0.10)	0.92 (0.04)	1.28 (0.15)	1.03 (0.09)	0.86 (0.07)
R^2	0.91	0.90	0.99	0.92	0.96	0.95
K_{OC}	33	161	123	127	192	109
Chlorotoluron						
K_F	3.56 (0.19)	6.64 (0.31)	6.55 (0.43)	7.59 (0.56)	37.6 (11.4)	12.50 (1.4)
$1/n$	0.81 (0.04)	0.89 (0.02)	0.63 (0.03)	0.74 (0.03)	0.99 (0.10)	0.76 (0.05)
R^2	0.98	0.99	0.98	0.99	0.94	0.98
K_{OC}	742	746	550	496	2,395	519
MCPA						
K_F	0.55 (0.07)	1.10 (0.04)	1.21 (0.09)	1.26 (0.06)	1.89 (0.20)	1.32 (0.13)
$1/n$	0.61 (0.10)	0.64 (0.03)	0.53 (0.06)	0.74 (0.04)	0.46 (0.08)	0.73 (0.08)
R^2	0.91	0.98	0.93	0.97	0.91	0.91
K_{OC}	114	124	102	82	120	55
Trifluralin						
K_F	18.0 (3.68)	45.9 (7.93)	52.3 (2.91)	70.0 (1.78)	n.d.	223 (29.3)
$1/n$	1.07 (0.07)	1.02 (0.07)	0.98 (0.04)	0.97 (0.01)	–	0.81 (0.08)
R^2	0.96	0.96	0.98	0.99	–	0.94
K_{OC}	3,750	5,157	4,395	4,575	–	9,253

Standard errors shown in parentheses

n.d., not determined

McCall et al. (1980) used K_{OC} values of pesticides for classification of their mobility potential through soils. According to this classification 2,4-D and MCPA exhibit very high to medium mobility in all soils. Socías-Viciana et al. (1999) reported that MCPA was very mobile in soils from Spain. On the other hand, trifluralin would be classified as slightly mobile to immobile, but this does not necessarily imply that trifluralin is completely immobile. Run-off of trifluralin bounded to small soil particles or preferential transport through macropores may lead to its occurrence in surface- and ground-waters (Albanis 1992; Laabs et al. 2000). Based on this study, atrazine shows high to medium mobility, which is consistent with its high leaching potential in soil lysimeter studies (Laabs et al. 2000). Acetochlor and chlorotoluron may be considered as herbicides with medium to low mobility. However, other processes like degradation should be considered in the evaluation of contamination risk of the water resources, resulting from the herbicide use in fields. The soil from Gbely exhibits the highest sorption affinity for acetochlor, atrazine, 2,4-D and chlorotoluron when compared with other soils, and hence their potential to move through this soil might be somewhat reduced.

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References

Ahmad R, Kookana RS, Alston AM, Skjemstad JO (2001) The nature of soil organic matter affects sorption of pesticides. 1. Relationships with carbon chemistry as determined by ^{13}C CPMAS spectroscopy. Environ Sci Technol 35:878–884

Albanis TA (1992) Herbicide losses in runoff from the agricultural area of Thessaloniki in Thermaikos Gulf, N. Greece. Sci Total Environ 114:59–71

Baskaran S, Bolan NS, Rahman A, Tillman RW (1996) Pesticide sorption by allophanic and non-allophanic soils of New Zealand. New Zeal J Agr Res 39:297–310

Boivin A, Cherrier R, Schiavon M (2005) A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. Chemosphere 61:668–676

Chen Z, Xing B, McGill WB (1999) A unified sorption variable for environmental applications of the Freundlich equation. J Environ Qual 28:1422–1428

Giles CH, MacEvan TH, Nakhwa SN, 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 measurement of specific surface areas of solids. J Chem Soc 111:3973–3993

Laabs V, Amelung W, Pinto A, Altstaedt A, Zech W (2000) Leaching and degradation of corn and soybean pesticides in an Oxisol of the Brazilian Cerrados. Chemosphere 41:1441–1449

Liu J, Qian CH (1995) Hydrophobic coefficients of s-triazine and phenylurea herbicides. Chemosphere 31:3951–3959

McCall PJ, Swann RL, Laskowski DA, Unger SM, Vrona SA, Dishburger HJ (1980) Estimation of chemical mobility in soil from liquid chromatographic retention times. Bull Environ Contam Toxicol 24:190–195

Sheng G, Johnston CT, Teppen BJ, Boyd SA (2001) Potential contributions of smectite clays and organic matter to pesticide retention in soils. J Agric Food Chem 49:2899–2907

Socías-Viciana MM, Fernández-Pérez M, Villafranca-Sánchez M, González-Pradas E, Flores-Céspedes F (1999) Sorption and leaching of atrazine and MCPA in natural and peat-amended calcareous soils from Spain. J Agric Food Chem 47:1236–1241

Spurlock FC, Biggar JW (1994) Thermodynamics of organic chemical partition in soils. 2. Nonlinear partition of substituted phenylureas from aqueous solution. Environ Sci Technol 28:996–1002

Tomlin CDS (2001) The e-pesticide manual, 12th edn. CD-ROM form, version 2.0. British Crop Protection Council

Wang Q, Yang W, Liu W (1999) Adsorption of acetanilide herbicides on soils and its correlation with soil properties. Pestic Sci 55:1103–1108

Yu YL, Wu XM, Li SN, Fang H, Zhan HY, Yu JQ (2006) An exploration of the relationship between adsorption and bioavailability of pesticides in soil to earthworm. Environ Pollut 141:428–433