Laboratory study of retention and release of weak acid herbicide MCPA by soils and sediments and leaching potential of MCPA

E. Hiller[1], M. Khun[1], L. Zemanová[1], Ľ. Jurkovič[1], M. Bartaľ[2]

[1]*Department of Geochemistry, Faculty of Natural Sciences, Comenius University Bratislava, Slovak Republic*
[2]*National Water Reference Laboratory for Slovakia, Water Research Institute Bratislava, Slovak Republic*

ABSTRACT

MCPA sorption and desorption in five surface soils (denoted as A1-5), three bottom sediments (S1-3), two river sediments (L1-2) and one subsurface soil (SS) at two initial concentrations in aqueous solution – C_0 = 0.5 and 10 mg/l were studied. No significant effect of the initial concentration on MCPA equilibrium distribution between soil/sediment and aqueous solution was observed. The difference between distribution coefficient K_D at C_0 = 0.5 mg/l and K_D at C_0 = 10 mg/l was found only in the case of one bottom sediment (S2). A simple regression analysis between K_D at C_0 = 0.5 and 10 mg/l and soil/sediment properties indicated that the most important property which determined the variation in MCPA sorption is organic carbon (r = 0.886*** and r = 0.926***, respectively). Similarly, desorption of MCPA was inversely proportional to organic carbon content of the soils and sediments used (r = –0.862* and r = –0.842**). These observations showed that MCPA sorption and desorption in soils and sediments were primarily controlled by organic components of the geosorbents used. Overall, the percentage of MCPA sorption in soils and sediments was low ($P_{sorp} \approx$ 3–53%; K_D = 0.077–2.827 l/kg) and the percentage of MCPA desorbed was relatively high ($P_{des} \approx$ 11–70%), especially in the soils and sediments with lower organic carbon content. The experimental results and calculated values of groundwater ubiquity score GUS and relative leaching potential index RLPI imply that MCPA is very mobile in all the surface soils and has a potential to contaminate groundwater.

Keywords: sorption; desorption; MCPA; groundwater ubiquity score; soil; sediment

Herbicides, or chemical weed killers, are one of the major achievements of modern agriculture. An increasing agricultural use of these products results in the presence of these compounds in the parts of the environment where it is not desirable.

The mobility of herbicides in soils and their tendency to migrate to other compartments (such as air and water) can be evaluated from sorption-desorption data. Sorption to soil matrix controls the concentration of the chemical in the aqueous solution and influences the rate of other processes such as volatilization, biodegradation, mobility and transport in soil, bioavailability and toxicity (Bekbölet et al. 1999, Jensen et al. 2004). Sorption studies are essential for evaluating the mobility of herbicides in soils. The distribution coefficients are used in mathematical modelling of herbicide transport in soils (Kodešová et al. 2005). Desorption is of a high importance as well. It determines the amount of herbicide that can be released back to aqueous solution and thus controls the final distribution of the herbicides in soil (Haberhauer et al. 2000, Boivin et al. 2005).

MCPA (4-chloro-2-methylphenoxyacetic acid) is a herbicide widely used to control annual and perennial weeds, mostly in cereals. It belongs to the group of anionic herbicides with pK_a = 3.07. In natural environment such as soil and water with usual pH between 5–8, MCPA is found in the anionic form. Many studies showed that sorption and desorption of acid anionic herbicides depend on soil pH – sorption increases with decreasing pH

(Thorstensen et al. 2001, Dyson et al. 2002, Boivin et al. 2005). Total soil organic carbon content and its nature is believed to be another important factor influencing sorption-desorption of anionic organic chemicals (Bekbölet et al. 1999, Socías-Viciana et al. 1999, Haberhauer et al. 2000, 2001). In general, herbicides of acid nature seem to be weakly sorbed in most of agricultural soils. This may be explained by the fact that acid herbicides are in anionic form in the pH range of the soils. Consequently, repulsion between negative charge of the molecule and the net negative charge of organic matter and clays occurs (Dubus et al. 2001, Celis et al. 2005).

Being weakly sorbed by the solid phase, there is a concern about their potential to leach to groundwater. The results of monitoring in European countries showed that acid herbicides pose a threat to water resources, as they were detected in numerous samples of surface- and groundwater (Celis et al. 2005, Sørensen et al. 2006). Good knowledge of the processes controlling behaviour of these herbicides after their agricultural application is important for the ability to predict their mobility in soils and to lower the risk of groundwater contamination.

Although the use of herbicides is limited mainly to agricultural fields, part of herbicides can enter in surface water systems due to a surface runoff, a subsurface flow from fields and their improper handling and application (Laabs et al. 2002). To study the sorption-desorption behaviour of herbicides in aquatic sediments is of a great importance as well. Sorption and desorption can strongly affect the transport and overall dynamics of herbicides in water systems, and hence their input to food chain.

The aim of this study was to investigate MCPA sorption and desorption ability in soil and sediment samples. The obtained sorption parameters were used to evaluate MCPA potential to leach and contaminate groundwater. Another goal of the study was to investigate the effect of different soil characteristics on MCPA sorption and desorption in soils.

MATERIAL AND METHODS

The experiments were conducted with five surface soil samples (denoted as A1-5), three samples of bottom sediments from three different
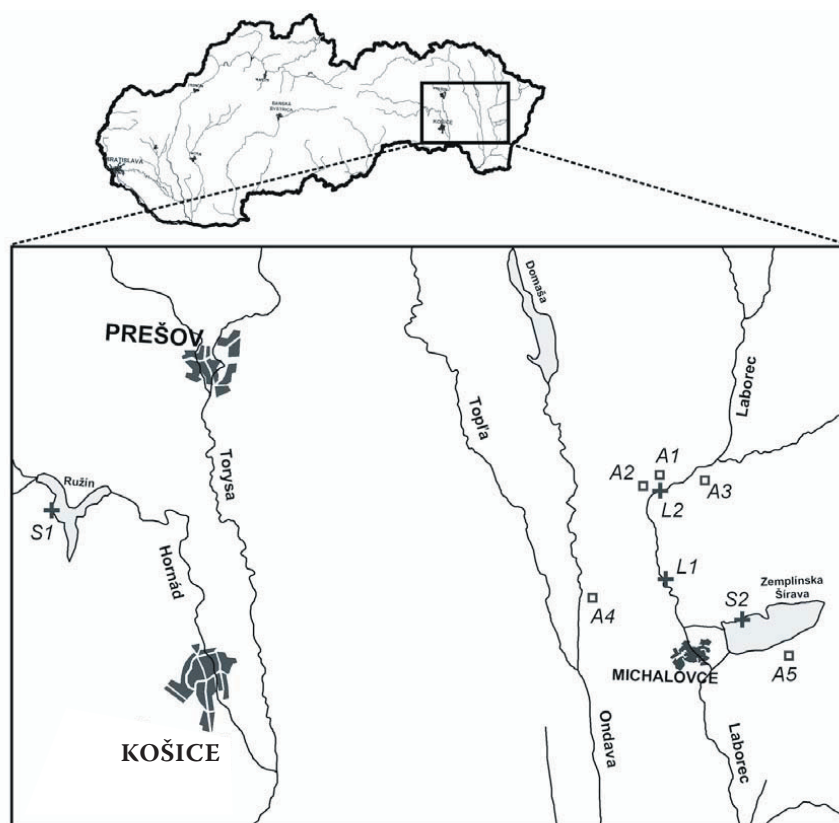

Figure 1. Geographical location and sampling sites of surface soils (denoted as A), bottom sediments (denoted as S) and river sediments (denoted as L) used

basins (denoted as S1-3), two river sediments from Laborec River (denoted as L1-2) and one subsurface soil sample (SS). All the samples were collected in the Eastern part of Slovakia (Figure 1) with the exception of the S3 bottom sediment sampled in Central Slovakia and the SS subsurface soil sampled from a depth of 2 m in the Bratislava airport area. Surface soil samples were collected from the topsoil horizon (A-horizon) and come from fields and pastures of the Laborec River area (Slovakia). The S1 bottom sediment was sampled in the Ružín water basin, S2 in the Zemplínska Šírava water basin and S3 comes from the Veľké Kozmálovce water basin. Physical and chemical properties of the soils and sediments used were determined according to Fiala et al. (1999) and are shown in Table 1. Major differences in soil and sediment properties include total organic carbon content, clay content (< 0.001 mm) and overall sorption capacity T. Soil and sediment samples were air-dried, homogenized and passed through a 2-mm sieve.

Analytical grade MCPA (purchased from Dr Ehrenstorfer GmbH) with 825 mg/l water solubility at 25°C and $pK_a = 3.07$ was used. In agriculture it is commonly applied in the dose of 1–2.5 kg/ha, which represents 3.3–8.2 mg/l MCPA in the soil solution (under assumption that sufficient rainfall rises the water content in soil up to 20% vol. to the depth of 15 cm) (Weber et al. 2000).

Sorption experiments were carried out using the batch equilibration method. 2 g of air-dried, sieved soil were weighed into a 10 ml glass centrifuge tubes. Calcium chloride solutions (0.01M, 5 ml) containing the MCPA initial concentrations of 10 and 0.5 mg/l were added. NaN_3 (10^{-4}M) was added to prevent microbial degradation during the experiment. The tubes were shaken for 48 hours. This was followed by centrifugation (2000 rpm, 30 min) and MCPA equilibrium concentration (C_e) in liquid phase was determined by HPLC (High Performance Liquid Chromatography) in National Water Reference Laboratory for Slovakia. Desorption experiments followed immediately. The supernatant removed was replaced by the same amount of MCPA-free 0.01M calcium chloride solution. The tubes were shaken for 48 hours. After centrifugation, desorbed amount of MCPA (C_{des}) in solution was determined. Tubes containing only MCPA solution without soil were included to determine adsorption onto the surface of the

Table 1. Physical and chemical properties of the soils and sediments used. Determined according to Fiala et al. (1999)

	Sample type	[1]OC	[2]C_{HA}	[2]C_{FA}	[3]pH(H_2O)	[4]Clay < 1 μm	[5]$CaCO_3$	[6]T (mol/kg)
		(%)				(%)		
A1	Rendzina	4.586	0.868	0.796	6.93	11.13	1.40	0.399
A2	Fluvisol	1.922	0.301	0.269	7.99	15.32	2.00	0.485
A3	Cambisol	0.893	0.152	0.210	6.76	22.08	0.30	0.203
A4	Pararendzina	2.486	0.351	0.328	7.86	9.08	12.2	0.502
A5	Luvisol	1.212	0.304	0.262	6.32	5.75	0.00	0.127
S1	bottom sed.	3.050	0.440	0.494	7.56	6.41	3.80	0.446
S2	bottom sed.	1.640	0.294	0.182	7.46	7.85	2.20	0.462
S3	bottom sed.	6.385	0.673	0.867	6.45	2.03	0.00	0.361
L1	river sed.	2.456	0.235	0.557	7.17	2.16	0.30	0.505
L2	river sed.	3.457	0.276	0.316	7.22	1.89	3.60	0.506
SS	subsurface soil	0.600	NM	NM	8.20	NM	NM	NM

[1]OC – organic carbon content was determined using the wet oxidation method by Tjurin with a modification by Nikitin; [2]C_{HA} and C_{FA} – humic and fulvic acid carbon content was determined by the method of Kononova-Belcikova; [3]pH(H_2O) – soil pH was measured in a 1:2.5 (wt:wt) soil-water suspension; [4]clay content was determined by the pipette method; [5]$CaCO_3$ content was measured using Janko's limemeter; [6]T – total soil sorption capacity expressed as S + H, where S is the sum of exchangeable basic cations determined by the method of Kappen and H is the hydrolytic acidity estimated by the titration method; NM – not measured

tubes. All sorption and desorption experiments were performed at least in duplicate. No losses of MCPA due to adsorption onto the surface of the tubes or volatilization were observed.

Concentrations of MCPA in initial aqueous solutions as well as in clear supernatants after sorption-desorption experiments were analyzed on a reversed-phase HPLC (Hewlett-Packard model 1100, 5 µm, 4.6 × 125 mm LICHROSPHERE-100 RP column) with a fluorescence detector (Hewlett-Packard 1046A). External solution standards were used to establish linear calibration curves for a fluorescence detector. The mobile phase used was a mixture of acetonitrile and 0.05M phosphate acid solution. The flow rate of this mobile phase was kept at the level of 0.4 ml per minute. The average uncertainty for the measured concentrations was about ±10% and detection limit for the aqueous extracts was 0.02 mg/l.

The amount of MCPA sorbed by the soil or sediment was determined by the difference between the initial and equilibrium MCPA concentrations in solution:

$$S_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where: S_e is the equilibrium amount of MCPA sorbed by the solid phase (mg/kg), C_0 is the initial MCPA concentration in solution (mg/l), C_e is the equilibrium MCPA concentration in solution (mg/l), V is the volume of solution (l) and m is the mass of soil (kg).

The amount of MCPA desorbed was calculated as:

$$S_{des} = \left[C_{des} - \left(C_e \times \frac{V - V_{ex}}{V} \right) \right] \times \frac{V}{m} \tag{2}$$

where: S_{des} is the amount of MCPA released from the solid phase calculated on the mass of soil (mg/kg), C_{des} is the analytically determined concentration of desorbed MCPA in solution (mg/l) and V_{ex} (l) is the volume of the MCPA solution removed from each tube and replaced by the same volume of MCPA-free calcium chloride solution.

The percentages of MCPA sorption were calculated as follows:

$$P_{sorp} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100\% \tag{3}$$

The percentages of MCPA desorbed were calculated as:

$$P_{des} = \left(\frac{S_{des}}{S_e} \right) \times 100\% \tag{4}$$

Distribution coefficient K_D (l/kg) represents the equilibrium distribution of a herbicide between soil/sediment and solution. It is defined as follows:

$$K_D = \frac{S_e}{C_e} \tag{5}$$

Coefficient K_{OC} was calculated by dividing the K_D values for particular soils/sediments by the corresponding organic carbon content of the soil/sediment:

$$K_{OC} = \left(\frac{K_D}{OC} \right) \times 100 \tag{6}$$

where: OC is the organic carbon content (%) and K_{OC} is the organic carbon distribution coefficient representing the equilibrium distribution of a herbicide between soil/sediment with 100% organic carbon content and solution (l/kg).

Definition of K_{OC} results from the assumption that if organic carbon content in the soil or sediment is not lower than 0.1%, organic carbon is the main sorbent of organic compounds within this soil/sediment. In that case, the contributions from soil mineral components to sorption are negligible (Schwarzenbach and Westall 1981). It has been shown that for a certain organic compound and particular group of soils or sediments containing organic matter of approximately the same origin and characteristics, K_{OC} values are nearly constant and differ only within a factor of 2–3 (Hamaker and Thompson 1972, Rutherford et al. 1992).

K_D and K_{OC} values were analysed by t-test, so that the differences among soils/sediments for MCPA and between two MCPA initial concentrations in each soil/sediment were determined. Pearson correlation coefficients between K_D, P_{des} and soil/sediment properties were evaluated for MCPA. Linear regressions between K_D, P_{des} and organic carbon content were performed using GraphPad Prism version 4.00 for Windows (GraphPad Software, San Diego California USA).

RESULTS AND DISCUSSION

Sorption and desorption of MCPA by soils and sediments

Distribution coefficients and percentages of MCPA sorption are shown in Table 2. It can be seen from Table 2 that the initial MCPA concentration used (C_0) had no effect on equilibrium distribution of MCPA between soil/sediment and aqueous

Table 2. Distribution coefficients K_D and K_{OC}, percentages of MCPA sorption P_{sorp} and desorption P_{des} for MCPA; mean ± experimental standard deviation

	MCPA initial concentration C_0 = 10 mg/l				MCPA initial concentration C_0 = 0.5 mg/l			
	K_D (l/kg)	K_{OC} (l/kg)	P_{sorp} (%)	P_{des} (%)	K_D (l/kg)	K_{OC} (l/kg)	P_{sorp} (%)	P_{des} (%)
A1	[2]0.956 ± 0.049	20.9 ± 1.08	27.7 ± 1.04	15.2 ± 0.43	1.098 ± 0.39	24.0 ± 8.54	30.1 ± 7.60	12.8 ± 3.34
A2	[3]0.499 ± 0.037	25.9 ± 1.93	16.6 ± 1.03	29.9 ± 3.61	0.394 ± 0.07	20.5 ± 3.64	13.6 ± 2.09	[1]NM
A3	0.131 ± 0.076	14.7 ± 8.48	4.94 ± 2.74	49.9 ± 20.8	0.173 ± 0.04	19.4 ± 4.87	6.46 ± 1.52	51.5 ± 4.12
A4	0.375 ± 0.002	15.1 ± 0.09	13.0 ± 0.07	20.2 ± 1.62	0.814 ± 0.24	32.7 ± 9.59	24.4 ± 5.44	10.9 ± 0.03
A5	0.200 ± 0.052	16.5 ± 4.26	7.40 ± 1.77	35.7 ± 0.58	0.392 ± 0.05	32.4 ± 4.41	13.6 ± 1.60	34.5 ± 17.4
S1	0.812 ± 0.0002	26.6 ± 0.007	24.5 ± 0.00	21.4 ± 3.43	1.278 ± 0.23	41.9 ± 7.58	33.7 ± 4.06	17.0 ± 11.0
S2	[3]0.436 ± 0.064	26.6 ± 3.90	14.8 ± 1.85	34.2 ± 8.73	0.281 ± 0.06	17.1 ± 3.36	10.1 ± 1.76	42.3 ± 0.01
S3	2.390 ± 0.145	37.4 ± 2.26	48.9 ± 1.51	NM	2.827 ± 0.03	44.3 ± 0.48	53.1 ± 0.27	NM
L1	0.703 ± 0.058	28.6 ± 2.34	22.0 ± 1.41	28.4 ± 4.80	NM	NM	NM	NM
L2	[3]0.563 ± 0.087	16.3 ± 2.51	18.3 ± 2.33	NM	0.383 ± 0.154	11.1 ± 4.47	13.2 ± 4.65	NM
SS	0.077 ± 0.008	12.9 ± 1.27	3.01 ± 0.29	69.3 ± 10.8	0.209 ± 0.178	35.1 ± 29.7	7.53 ± 6.08	55.5 ± 33.2

[1]NM – not measured; [2]the average value from 7 samples (n = 7); [3]the average value from 4 samples (n = 4); in all other cases, the experiments were performed in duplicate (n = 2)

solution as no significant difference was observed between K_D obtained at C_0 = 10 mg/l and K_D at C_0 = 0.5 mg/l for a given soil/sediment (*t*-test, $P > 0.05$). The difference in K_D measured at both initial MCPA concentrations was observed only in the case of the S2 bottom sediment ($P < 0.05$). It can be assumed that the distribution of MCPA between soil matrix and aqueous solution will not significantly vary with changing initial concentration in the range of C_0 = 0.5–10 mg/l. This finding may imply that the sorption capacity of soil and sediment samples used was not fully saturated even when the higher MCPA concentrations were applied. The results are in good agreement with Haberhauer et al. (2000, 2001) who obtained linear sorption isotherms for MCPA, indicating no dependence of sorption strength on the MCPA initial concentration used. However, Socías-Viciana et al. (1999) and Thorstensen et al. (2001) observed non-linear isotherms for MCPA sorption in soils with decreasing distribution coefficients as C_0 increased. This was observed in many other cases and it might be explained by an increased difficulty to access the active sorption sites when pesticide concentrations in solution are elevated (Nemeth-Konda et al. 2002).

Experimentally obtained K_D values for both MCPA initial concentrations were in the range from 0.077 l/kg (for the SS subsurface soil) to 2.827 l/kg (for the S3 bottom sediment). These values are comparable to those obtained by Haberhauer et al. (2000) (K_D = 0.46–1.94) for soils with OC = 0.54–2.70%, Sørensen et al. (2006) (K_D = 0.03–1.89) for a soil profile with OC = 0.10–4.90%, or Socías-Viciana et al. (1999) (K_D = 0.28–1.24) for peat-amended soils with OC = 0.18–4.61%. The K_D values obtained in this study for both initial concentrations indicate that the amounts of MCPA sorbed in soils and sediments are relatively low. For example, the percentage of MCPA sorption in the soils/sediments with organic carbon content < 2.5% was lower than 25% (Table 2). Only in the soils and sediments with OC > 3.0%, more than 25% of the initial amount of MCPA in solution was sorbed by solid phase. The highest sorption strength (P_{sorp} ~ 53%) was exhibited by the S3 bottom sediment with the highest organic carbon content among all the soil and sediment samples used (Table 1). The observed low percentage of MCPA sorption by soils and sediments is likely related to its dissociation.

Soil/sediment pH is greater than pK_a + 2 in all the samples of soils and sediments used. MCPA is almost completely dissociated under these conditions and occurs in the form of anions. Consequently, repulsion between negative charge of the molecule and the net negative charge of soil and sediment colloids occurs (Nicholls and Evans 1991).

Various studies showed that the amount of polar herbicides of acid nature sorbed by soils increases as the total soil organic carbon content is increased (Bekbölet et al. 1999, Socías-Viciana et al. 1999, Boivin et al. 2005, Sørensen et al. 2006). However, some authors observed no influence of organic carbon content on sorption behaviour of acid herbicides in soils and the observed differences were caused mainly by different nature of soil organic matter (especially polarity) and different pH (Wu et al. 2000, Haberhauer et al. 2001, Thorstensen et al. 2001, Dyson et al. 2002). Despite these inconsistent findings, the results of this study showed a positive relation between K_D and the total organic carbon content at both levels of MCPA initial concentration used (Figure 2a). This finding is supported by significant correlations found between total organic carbon content and distribution coefficients for both MCPA initial concentration used, 0.5 and 10 mg/l ($r = 0.886$*** and $r = 0.926$***, respectively) as well as by relatively constant K_{OC} values (Table 2), indicating similar sorption capacity of organic matter present in soil and sediment samples used. However, besides the organic carbon content the composition of the soil and sediment humic components seems to be important for the sorption of MCPA. For example, sorption of MCPA was lesser in the A4 soil (Pararendzina) with higher $C_{HA}:C_{FA}$ ratio than in the L1 river sediment with low $C_{HA}:C_{FA}$ ratio (*t*-test, $P < 0.05$), even though the organic carbon content was almost the same (Tables 1 and 2). Lower $C_{HA}:C_{FA}$ ratio is considered to be an indicator of higher organic matter polarity or smaller degree of polymerisation (Dousset et al. 1994) in

the L1 sample, which can therefore contain more active sorption sites suitable for binding of polar herbicides such as MCPA (Haberhauer et al. 2001) in comparison to majority of soil samples having $C_{HA}:C_{FA}$ ratio higher than 1.

The results showed that there were some differences between MCPA sorption within soils and sediments, although not statistically significant in all the cases. These differences could be observed through the K_{OC} values, reflecting MCPA sorption by soil or sediment organic matter. The higher K_{OC} values observed for sediments with $C_{HA}:C_{FA}$ ratio less than 1 (S1, S3 and L1, Table 2) suggest that the sediment organic matter with the greater fulvic acid fraction is a better sorbent of MCPA in comparison to the soil organic matter with $C_{FA} < C_{HA}$ (Table 1). It is believed that the greater amount of hydrophilic parts of the fulvic acids might favour the amount of polar MCPA retained by soils and sediments (Haberhauer et al. 2002). A similar effect of the organic matter composition on the sorption of organic chemicals by soils and different fractions of fulvic acids, humic acids and humins was shown by Chiou et al. (1986) and Dousset et al. (1994).

Desorption is of high importance as well. Desorption processes can affect microbial breakdown of herbicides and their mobility in the soil environment (Boivin et al. 2005). The highest amounts of MCPA were desorbed to aqueous solution from soils and sediments with lower organic carbon content and from those with relatively low amounts of MCPA sorbed (samples SS, A3, A5 and S2). The amount of MCPA desorbed (extracted) from soils and sediments during 48 hours
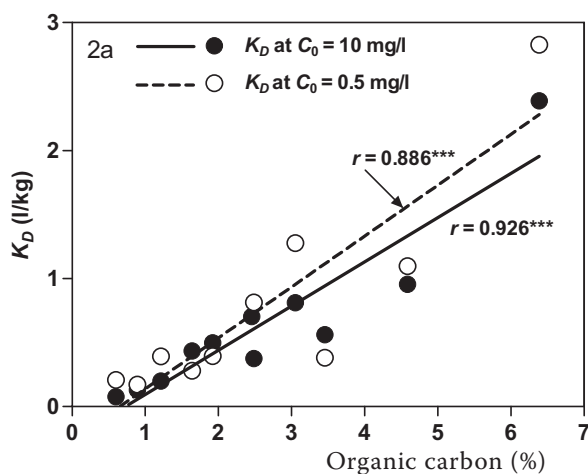
Figure 2a. Relationship between distribution coefficient K_D and soil/sediment organic carbon content for weak acid herbicide MCPA; ***$P < 0.001$
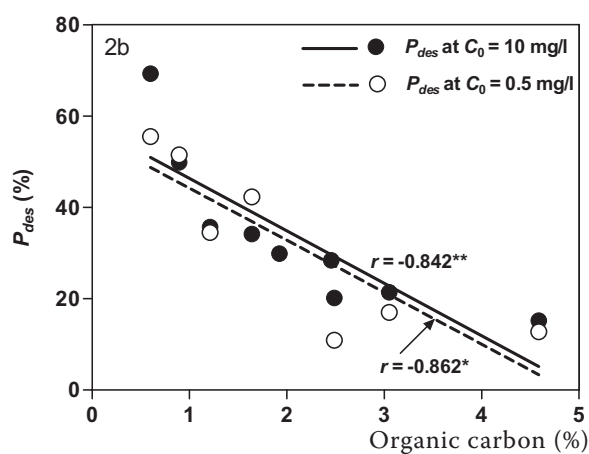
Figure 2b. Inverse relationship between percentages of MCPA desorbed P_{des} and soil/sediment organic carbon content; **$P < 0.01$, *$P < 0.05$

and at both levels of MCPA initial concentration was mainly affected by the total organic carbon content and P_{des} increased as the total organic carbon content decreased (Figure 2b). The inverse relation was supported by significant correlations found between OC (%) and P_{des} (%) for both MCPA initial concentrations C_0 = 0.5 and 10 mg/l (r = −0.862* and r = −0.842**, respectively). These findings are in good agreement with the results of Sørensen et al. (2006) who studied sorption-desorption behaviour of MCPA and also Bekbölet et al. (1999) who reported the sorption-desorption characteristics of another anionic herbicide (2,4-D). Moreover, the results indicate that the percentage of MCPA desorbed from soils and sediments P_{des} is inversely proportional to the percentage of MCPA sorption P_{sorp} for both MCPA initial concentrations C_0 = 0.5 and 10 mg/l (r = −0.928** and r = −0.830**, respectively). It appears that the binding strength of MCPA sorption by soils and sediments increased when organic carbon content was elevated as the percentage of MCPA desorbed was lower in the samples with higher organic carbon content (Table 2). Thorstensen et al. (2001) reported that sorption and desorption were inversely correlated for dichlorprop, MCPA and propiconazole in the soils from Norway. The results also showed that not all MCPA sorbed by soils and sediments was desorbed within 48 hours, indicating sorption nonideality. This sorption nonideality is a frequently observed phenomenon (Thorstensen et al. 2001, Jensen et al. 2004) that can be attributed to irreversibility in the sorption process caused by slow kinetics of desorption, diffusion-limited transport within the particles and/or irreversible binding of MCPA to the soil/sediment particles.

Evaluation of MCPA potential to leach to groundwater

Low K_D values, low percentages of MCPA sorption and relatively high amounts of MCPA desorbed from surface soils (Table 2) indicate MCPA mobility and its potential to reach groundwater, especially when it is applied to the soils with low organic carbon content (the A3 and A5 soils). Experiments conducted by Haberhauer et al. (2002) showed that MCPA migrated easily through soil profile and the leachate coming out of the soil column contained more than 70% of the MCPA initial amount. Similarly, Socías-Viciana et al. (1999) reported a high leachability of MCPA in soils with 99% of

the herbicide collected in the leachate. Sørensen et al. (2006) investigated sorption-desorption processes and biological breakdown of MCPA in two soil profiles and confirmed the high mobility of this herbicide, especially in the deeper parts of the soil profile containing a low amount of organic carbon. The high mobility was caused by the low amount of MCPA sorbed to the soils as well as by the absence of its biological decomposition.

To evaluate the potential of MCPA to leach to groundwater, the measured organic carbon distribution coefficients (Table 2) and average half-life time (12.67 days) estimated from Müller and Buser (1997), Crespín et al. (2001), Thorstensen and Lode (2001) and Tomlin (1997) were used. The following published models were applied to predict the potential of MCPA to leach to groundwater. Gustafson (1989) introduced an empirical model as follows:

$$\mathrm{GUS} = \log t_{1/2} \times \left(4 - \log K_{OC}\right) \tag{7}$$

where: GUS represents a dimensionless index called the groundwater ubiquity score, K_{OC} is the organic carbon distribution coefficient (l/kg) and $t_{1/2}$ is the half-life time in the soil (days).

The pesticides leaching to groundwater are classified as having scores higher than 2.8. The pesticides having scores lower than 1.8 are improbable to contaminate groundwater. The pesticides with GUS between 1.8 and 2.8 are considered transitional.

The relative leaching potential index (RLPI) defines the relative attenuation of each pesticide in soil and therefore its potential to leach to groundwater (Hornsby et al. 1993). It is defined as follows:

$$\mathrm{RLPI} = 10 \times \left(\frac{K_{OC}}{t_{1/2}}\right) \tag{8}$$

It is important to realize that the smaller the RLPI value of a pesticide is the greater is its potential to leach to groundwater. The pesticides having RLPI lower than 100 are considered to be highly mobile in soil.

K_{OC} and $t_{1/2}$ are key parameters in the two models mentioned above and are also included in the other models proposed for example by Jury et al. (1987) as sorption and biological degradation are believed to be the main processes controlling the pesticide concentration in the mobile soil solution. Criteria of the two above-mentioned models are presented in Figure 3. On the basis of GUS and RLPI criteria it could be concluded that MCPA had
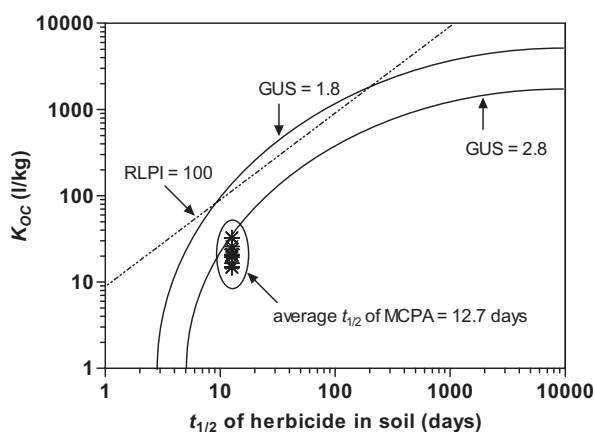
Figure 3. Evaluation of the MCPA potential to leach to groundwater from the organic carbon distribution coefficients K_{OC} determined for surface soil samples (A1-5) and average persistence $t_{1/2}$ estimated from literature data; MCPA in all soils used is considered to be a contamination risk to groundwater because all points (asterisks) are to the right of each line based on the GUS and RLPI criteria as reported in the text

a potential to leach to groundwater in all the soils used, as the calculated GUS and RLPI values are higher than 2.8 or approximately equal to 2.8 and lower than 100, respectively (Figure 3).

Sørensen et al. (2006) observed no MCPA mineralization in the deeper parts of soil profiles, likely caused by the lack of oxygen and low microbial activity. They concluded that MCPA was potentially mobile and the lack of any natural attenuation in the deepest layers might pose a threat of future groundwater contamination. This finding indicates that if a vertical movement of soil solution brings MCPA to the deeper parts of soil profile, the risk of groundwater contamination may be even higher than suggested by the simple analysis presented in this study. High water solubility of MCPA, its low sorption in the soils with low organic carbon content observed in this study (Table 2) as well as in the studies of Thorstensen et al. (2001) and Sørensen et al. (2006), an easy leachability of MCPA in soil columns (Socías-Viciana et al. 1999, Haberhauer et al. 2002) may potentially result in an undesirable occurrence of the herbicide in groundwater. For example, in the period 1993–2003 MCPA was detected in 9.3% (of 118 groundwater samples) of the monitored groundwater wells (Sørensen et al. 2006).

Overall, based on the results measured in this study, MCPA appears to be a highly mobile her-bicide in the soils used. However, a more accurate evaluation of its mobility and leaching potential would require a determination of the exact MCPA half-life time values in all the soils used.

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Corresponding author:

RNDr. Edgar Hiller, PhD., Univerzita Komenského v Bratislave, Prírodovedecká fakulta, Katedra geochémie, Mlynská dolina, 842 15 Bratislava 4, Slovenská republika
phone: + 421 260 296 218, fax: + 421 260 296 217, e-mail: hiller@fns.uniba.sk