Soil sorption and degradation of Agritox herbicide formulation containing Na-K-DMA MCPA salt as an active ingredient

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Abstract: This study deals with the evaluation of soil sorption and degradation of Agritox herbicide formulation, which contains Na-K-DMA MCPA salt (dimethyl ammonium-potassium-sodium salt of (4-chloro-2-methylphenoxy)acetic acid) as an active ingredient. It is important to quantify these two processes as they are crucial for the migration of undesirable organic compounds into surface- and groundwater. Three agricultural soils were tested using column experiments to determine the sorption of MCPA salt and incubation batch experiments to measure its dissipation kinetics. The sorption of MCPA salt in these soils was relatively low with Freundlich constant values between 0.33–4.87 mg^{I-1}/ⁿ×I^{1/n}/kg. Despite the small number of soil samples tested, the effect of clay and organic carbon content on MCPA salt sorption was demonstrated. This herbicide was subject to rapid degradation in soil with half-lives of 4.5–7 days and degraded most rapidly in the soil with the highest microbial activity. Due to its rapid degradation, MCPA salt could be classified as a non-leacher into groundwater. **Key words:** degradation, geochemical behaviour, MCPA, pesticide, soil, sorption

1. INTRODUCTION

Sorption is the most important interaction process of herbicides with the soil, which determines and influences their mobility, leaching, biological efficacy against target weeds, decomposition by chemical and microbial pathways and plant uptake (Bailey et al., 1968; Karickhoff, 1984; Rae et al., 1998; Dubus et al., 2001; Spark & Swift, 2002). The amount of herbicides accumulated in soil, and more generally, of all pesticides and shape of their adsorption isotherms depend primarily on the properties of soil as well as physicochemical properties of pesticide (Senesi, 1993). Pesticide sorption in soils is governed mainly by soil organic carbon content (OC), i.e. in a series of soils with different OC, pesticide sorption is linearly related to OC (Madhun et al., 1986). Another important sorbents of pesticides in soils are minerals, mostly, secondary minerals, such as clays and oxyhydroxides of Fe and Al. However, their role in the pesticide sorption is often masked due to coverage of mineral surfaces by humic substances, and therefore, clays and other secondary minerals sorb pesticides only when organic carbon content is not too high. It was shown by several classical studies that the sorption of pesticides in soils containing more than 1-2 wt. % of organic carbon was completely controlled by OC, and only in soils with lower OC, the clay content appeared to contribute substantially to the overall pesticide sorption (Bailey & White, 1964; Karickhoff, 1984; Calvet, 1989; Ying & Williams, 2002; Liu et al., 2008).

Degradation of a pesticide has an influence on its persistence in soil, and thus influences considerably the ability of the pesticide to be transported into the groundwater and surface water. Similarly to sorption, degradation is influenced by many factors involved in the interactions among microorganisms, chemical and soil components. Sorption can inhibit the degradation of pesticides due to decrease of their concentration in the soil solution, where pesticide molecules are more bioavailable to microorganisms than those sorbed in the surface and structure of organic matter and minerals. Many researchers showed that the slow-down of degradation was proportional to the increase in sorption for a variety of pesticides, including herbicides (Mueller et al., 1992; Dyson et al., 2002; Jensen et al., 2004; Hiller et al., 2009). However, the slow-down of pesticide degradation in soils was not correlated with sorption in many other cases (Sørensen et al., 2006; Hiller et al., 2012; Peña et al., 2015). This indicates that other factors must be considered, such as soil OC, microbial population and activity or soil pH (Beulke & Malkomes, 2001).

MCPA ((4-chloro-2-methylphenoxy)acetic acid) and its dimethyl ammonium-potassium-sodium salt belong to the systematic herbicides from a group of carboxylic acids (Cremlyn, 1985; Tomlin, 2001). MCPA has a medium solubility in water (279 mg/l at pH = 7 and at a temperature of 25 °C), which increases in the case of its alkaline metal salts; for example, the solubility of sodium salt of MCPA is up to 270 g/l at 25 °C (Tomlin, 2001). MCPA and its salts are used post-emergently to control broad-leaved weeds in cereals, potatoes, beans and pastures (Cremlyn, 1985).

Herbicide formulations based on MCPA and its salts are still utilized in agriculture in the Slovak Republic. According to Lichvár et al. (1998), up to 21 different formulations with MCPA as an active ingredient were applied to the soil in Slovakia during 1995–1997. One of the most used formulations was Agritox, containing 500 g/l Na-K-DMA MCPA salt as an active ingredient. Current data suggest that consumption of MCPA and its Na-K-DMA salt is gradually decreasing and was approximately 17 tons in 2012. Nevertheless, it is still included in the list of relevant pesticides for groundwater pollution of the Slovak Republic (Patschová et al., 2014).

MCPA and its Na-K-DMA salt are weak organic carboxylic acids with the pK_a value of 3.07, meaning that they occur predominantly as negatively charged species (anions) in the soil solution at natural range of pH values (5-8). Anionic forms of organic acids are weakly sorbed by soils with neutral or weakly alkaline pH values (Nicholls & Evans, 1991; Paszko et al., 2016) due to electrostatic repulsion between the negatively charged molecules of organic acids and the organic matter/mineral surfaces whose net charge is also negative under neutral and alkaline conditions (Rocha et al., 2002; Spark & Swift, 2002). Due to ability of organic acids to accept and donate H⁺ ions, their sorption in soils is often controlled by soil pH (Villaverde et al., 2008). The occurrence of MCPA in European groundwaters is widespread (Spliid & Køppen, 1998; Loos et al., 2010) and also in surface waters (Laganá et al., 2002; Schreiner et al., 2016) with concentrations reaching up to 6.1 µg/l. In the Slovak Republic, the occurrence of MCPA and its metabolites was documented in several wells used as drinking water supplies, although the concentrations of MCPA in drinking water from the wells did not exceed the limit value of 0.1 μ g/l (Lichvár et al., 1998). The

frequent occurrence of MCPA in natural waters, especially in groundwaters, is mainly due to its low sorption in soils, and therefore high leaching potential (Hiller et al., 2006, 2010, 2012; Tatarková et al., 2013; Paszko et al., 2016), despite relatively rapid microbial degradation of MCPA in surface soils (Hiller et al., 2009, 2010, 2012; Paszko et al., 2016).

The main aim of this work was to (i) determine the adsorption isotherms of the herbicide formulation Agritox with Na-K-DMA MCPA salt as an active ingredient in three surface soils of different physicochemical properties using soil column tests, (ii) discuss the influence of soil properties on the sorption of Na-K-DMA MCPA salt, (iii) measure its degradation kinetics in soils and (iv) evaluate the leaching potential of the herbicide formulation to groundwater.

2. MATERIAL AND METHODS

2.1. Soil samples

The three soil samples (two Calcaric Fluvisols (soil 1 and soil 2 in Fig. 1) and one Eutri-Humic Fluvisol (soil 3 in Fig. 1) (according to WRB, 2015) from agricultural fields near the village Žihárec, Galanta district, Slovak Republic) represented surface



Fig. 1. Location of soil sampling sites. Soil 1 and soil 2 are Calcaric Fluvisols and soil 3 is Eutri-Humic Fluvisol.

A horizon and were collected from a depth of 0-20 cm using a stainless steel auger. Each soil sample was taken from four corners and from the centre of a square with a side length of 2 m. These five soil sub-samples were mixed to obtain one average soil sample. The obtained soil samples were air-dried at room temperature, sieved to <2 mm and then analysed for selected soil properties using standard methods (Fiala et al., 1999). For the degradation experiments and determination of soil microbial activity, the soil samples were dried to 40 % of their water holding capacity (WHC), sieved to <2 mm and kept in the dark at 4°C. Soil microbial activity was measured as dehydrogenase activity (DHA) with 2-*p*-iodophenyl-3-*p*-nitrophenyl-5-phenyl tetrazolium chloride (INT) (García et al., 1993). The properties of the soil samples are shown in Table 1.

2.2. Dissipation kinetics experiments

These experiments were performed in duplicates for each time period. One week before incubation, soils originally stored at 4 °C were pre-incubated in the dark at 20±2 °C. Then 20 g of each dried soil were placed in incubation glass flasks and spiked with Agritox solution to obtain an initial MCPA concentration of 10 mg/kg. The soil water content was adjusted with deionized water to 40 % of the respective WHC value of each soil and kept constant during the entire incubation experiment. The incubation flasks were placed in the dark at 20±2 °C. After 0, 7, 14, 21, 28 and 35 days, the flasks were discarded and extracted for MCPA from the soil. Soil MCPA was ultrasonically extracted for 2 hours using 20 ml acetonitrile-acetic acid solution (0.5 % acetic acid) at a ratio of 50:50 (v/v). After centrifugation at 3000xg for 10 minutes, the extract was analysed by HPLC. The recoveries ranged from 74–98 %. All results were adjusted with the respective recoveries to give precise concentration of MCPA in the soil samples.

2.3. Sorption experiments

Sorption of Agritox in soils was performed in flow-through glass columns that were connected to the peristaltic pump using plastic tubes. Duplicate glass columns (height of 17 cm and 2.5 cm internal diameter (i.d.)) for each initial concentration of MCPA and each soil were uniformly packed with 50 g of air-dried soil. Together, this represented 24 soil columns. Filter paper and 1.0 cm thick layer of acid washed sand was placed at bottoms and tops of the columns to avoid soil losses. The volume of Agritox solution percolated through the columns was 250 ml and initial concentrations of MCPA were set at 0.05, 0.10, 0.15 and 0.20 mg/l. The sorption experiments were done in the dark and at 20 ± 2 °C. After 24 hours, the column leachates were centrifuged and analysed for equilibrium concentration of MCPA.

2.4. Analysis of MCPA

The concentration of MCPA in the soil extracts and column leachates was determined by high-performance liquid chromatography (HPLC) using Hewlett-Packard Agilent 1100 chromatograph equipped with Hewlett-Packard 1046 fluorescence detector (FD). The following chromatographic conditions were used: Lichrosphere 100 RP-18 column (4.6x125 mm i.d., 5 μ m particle size), a mixture of 50 % acetonitrile and 0.1 % phosphate acid solution at a ratio of 50:50 (v/v) as the mobile phase, flow rate of mobile phase was 0.75 ml/min, sample injection volume of 20 μ l and detection wavelength of 232 nm. The detection limit was 0.02 mg/l and the reproducibility expressed as the relative standard deviation (RSD) was lower than 8 %.

2.5. Data analysis

The sorbed concentration of MCPA in the soils (S in mg/kg) was calculated as the difference between its initial and equilibrium concentration in the solution (C_i and C_e in mg/l, respectively) according to the relation:

$$S = \frac{(C_{\rm i} - C_{\rm e}) \times V}{m}$$

• where V(in l) is the volume of solution and m(in kg) is the soil weight used in column sorption experiments. The equilibrium concentrations of MCPA versus S were plotted in a graph, which gives an adsorption isotherm, and fitted to the Freundlich adsorption isotherm:

$$S = K_{\rm f} \times C_{\rm e}^{1/n}$$

• where K_f (in mg^{l-1/n}×l^{1/n}/kg) is the Freundlich constant, which is simply *S* at $C_e = 1$ mg/l and 1/n (dimensionless) is the Freundlich exponent, representing the curvature of adsorption isotherm. The measured adsorption isotherms were also fitted to the linear (Henry) adsorption isotherm:

$$S = K_{\rm d} \times C_{\rm e}$$

• where K_d (in l/kg) is the linear distribution (sorption) constant. From K_d , K_{oc} values were also calculated according to the equation:

$$K_{\rm oc} = \frac{K_{\rm d}}{\rm OC\%} \times 100$$

• where K_{oc} (in 1/kg) constant expresses the sorption of organic compounds only by soil organic matter and is an important indicator of mobility of organic contaminants in unsaturated and saturated zone of the soil environment. The degradation kinetics of MCPA salt in soils was fitted to the first-order kinetic equation:

$$C_{\rm t} = C_0 \times e^{-k_1 \times t}$$

• where C_t (in mg/kg) is the herbicide concentration in soil at any time t, C_0 (in mg/kg) is the initially applied herbicide concentration in soil at t = 0 and k_1 (in 1/d) is the first-order rate constant. From the first-order kinetic equation, the half-life (DT₅₀ in d; the time required for the concentration to reduce to half of its initial value) could be calculated as follows:

$$\mathrm{DT}_{50} = \frac{\mathrm{ln2}}{k_1}$$

Tab. 1. Phy	vsicochemical	and biological	properties of the soils.

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Property	Soil 1	Soil 2	Soil 3
Sand (wt. %)	20	27	22
Silt (wt. %)	61	53	40
Clay (wt. %)	19	20	38
OC ^a (wt. %)	0.96	1.62	1.86
pH (H ₂ O)	8.20	8.23	7.70
pH (KCl)	7.46	7.37	6.75
CEC ^b (mmol/100 g)	11.3	16.6	20.9
Fe ₂ O ₃ (wt. %)	3.30	3.70	4.60
Al ₂ O ₃ (wt. %)	9.50	10.1	14.9
DHA ^c (mg/g×h)	0.94	0.97	1.35

^a organic carbon content; ^b cation exchange capacity; ^c dehydrogenase activity.



Fig. 2. Measured adsorption isotherms of the Na-K-DMA MCPA (Agritox formulation) salt in three agricultural soils (soil depth of 0–20 cm). Lines are fitted Freundlich adsorption isotherms. Mean values of C_e and S from duplicates are shown.

Tab. 2. Sorption and degradation kinetic parameters for the MCPA salt.

Parameter	Soil 1	Soil 2	Soil 3
K_{f}^{a} (mg ^{l-1/n·} l ^{1/n} /kg)	0.33	0.85	4.87
1/n ^b	0.69	1.03	1.24
R ²	0.93	0.97	0.99
K _d ^c (l/kg)	0.67	0.80	2.50
K _{oc} ^d (l/kg)	70	49	134
R ²	0.79	0.97	0.98
% Sorption	14.2	16.8	34.5
k ₁ ^e (1/d)	0.104	0.099	0.155
DT ₅₀ ^f (d)	6.7	7.0	4.5
R ²	0.97	0.99	0.99
GUS ^a	1.78	1.95	1.22
RLPI ^h	104	70	298

^a Freundlich constant; ^b Freundlich exponent; ^c linear distribution constant; ^d organic carbon sorption constant; ^e first-order rate constant; ^f half-life; ^g Groundwater Ubiquity Score; ^h Relative Leaching Potential Index. The data were processed in GraphPad Prism program, version 5.00 for Windows (Graph-Pad Software, San Diego, California, USA).

3. RESULTS AND DISCUSSION

3.1. Sorption of MCPA salt

The values of sorption characteristics of the Na-K-DMA MCPA salt in soils are shown in Table 2, and the adsorption isotherms are shown in Fig. 2. According to the K_f and K_d values, the sorption rate of MCPA in soils decreased in the order of: Soil 3 > Soil 2 > Soil 1. At the same time, the soil organic carbon and clay contents decreased in the sorption of MCPA salt in soils, as it is consistent with the previous literature (Paszko et al., 2016 and references cited herein).

The K_f and K_d values as well as sorption percentage (Table 2) indicated a low sorption efficiency of the MCPA salt in these soils with weakly alkaline soil reaction. The herbicide MCPA is a weak organic acid with a low pK_a value of 3.07, so it is predominantly present as an anion in the weak-alkaline region of the soils investigated. The relationship $\phi_a = [1 - 1/(1 + 10^{pH-pKa})]$ x100 % shows that under the pH conditions of all three soils, nearly 100 % of the MCPA molecules are in the form of anions. Since soil organic matter and secondary soil minerals have negatively charged surfaces at such high pH values, there is a mutual repulsion between MCPA anions and negatively charged soil colloids, resulting in low MCPA sorption. Weak to negligible sorption of MCPA and chemically related pesticides in soils, especially in sandy soils with low OC, is a commonly observed phenomenon, only in acidic soils can sorption be significant (Wauchope et al., 2002). In all cases, the K_f and K_d values found in this study are in the range of values that were recorded for MCPA in other soils (Paszko et al., 2016). Despite the anionic nature of MCPA in these weakly alkaline soils, a positive relationship was observed between the $K_{\rm f}/K_{\rm d}$ of the MCPA salt and the OC or clay content in this study. Similar dependencies for MCPA and the related herbicide 2,4-D have been found in previous studies (Hiller et al., 2011 and references cited herein).

However, a variability of K_{oc} values (Table 2) suggested that the sorption of MCPA could not depend solely on the OC of these soils. In the case of polar pesticides, variability of K_{oc} values is very often observed, which is related to (i) soil pH, which determines the speciation of polar pesticide molecules and thus their affinity for soil organic matter and minerals, and (ii) different chemical composition and quality of organic matter in different soils (Haberhauer et al., 2001; Hiller et al., 2006, 2012; Peña et al., 2015). Since the pH values of the three soil samples were very similar (Table 1), the differences in K_{oc} values were probably due to different chemical composition of the organic matter of these soils; however, this aspect was not investigated in this work. The non-linear dependence of K_f and K_d on OC was also reflected by the difference between K_f and OC. The K_f values of MCPA salt differed by up to a factor of ~15 and the OC values among the soils varied only by a factor of ~2. The effect of the clay content on the sorption of MCPA salt in soils was also not clear in nature, despite the observed positive relationship between clay content and sorption magnitude. Similar to the discussion of OC influence, the magnitude of MCPA sorption was not linearly dependent on clay content only, since its content among the soils varied only by a factor of 2.

Several literature sources have suggested that the sorption efficiency of organic compounds in soils does not depend separately on either organic matter or clay content, despite the existence of a positive correlation to both soil components. For example, Celis et al. (1999) found that the sorption of atrazine and simazine in separate soil components (montmorillonite, ferrihydrite and humic acids) was not directly proportional to the sorption in a mixture of two or more of these components, in other words, the total sorption of the two pesticides in the mixture was not expressed as simple sum of pesticide sorption in individual pure components. They explained this phenomenon by reducing the number of available sorption sites and changing their properties due to the formation of specific bonds between soil components. Rebhun et al. (1992) showed earlier that the sorption of indole, fluoranthene and dichlorobenzene on Ca-bentonite and its mixtures with humic acids could not be described as the sum of contributions from pure Ca-bentonite and pure humic acids. The reduction in the contribution of the clay mineral Ca-bentonite to the total sorption of organic compounds in clay-humic acid mixtures was associated with blocking of the available sorption sites on the surface of clay mineral by humic acids.

3.2. Dissipation of MCPA salt

The dissipation of the Na-K-DMA MCPA salt in soils over time is shown in Fig. 3 along with the curve fitting according to the first-order kinetic equation. As can be seen from Fig. 3 and Table 2, the first-order kinetic equation described the measured results very well with $R^2 \ge 0.97$. The lag phase during MCPA dissipation



Fig. 3. Dissipation curves of the Na-K-DMA MCPA salt (Agritox formulation) in three agricultural soils (soil depth of 0–20 cm). Curves that fit the experimental data are according to the first-order kinetic equation. Mean values of C_t from duplicates are illustrated.

has not been observed, although some works reported the lag phase for up to three weeks, especially in lower soil horizons with decreased microbial activity (Jensen et al., 2004; Mortensen & Jacobsen, 2004; Paszko, 2009). The values of DT₅₀ for MCPA salt in the three soils $(DT_{50} = 4.5 - 7.0 \text{ days}; \text{ Table 2})$ were in agreement with those determined in other surface soils from Europe (Crespín et al., 2001; Thorstensen & Lode, 2001; Paszko et al., 2009; Hiller et al., 2012; Peña et al., 2015), which ranged from 1.5 day to 16 days. Lower degradation rates of MCPA and hence higher DT₅₀ values are mostly observed in deeper soil horizons where microbial activity is lower (Paszko et al., 2016). The rate of MCPA decomposition was highest in Soil 3, followed by Soil 1 and Soil 2. Although Soil 3 showed the highest sorption (Table 2), a process that commonly slows down degradation and increases persistence of MCPA in soil (Jensen et al., 2004; Hiller et al., 2009), at the same time, Soil 3 had the highest DHA value (Table 1). From this, it could be concluded that microbial activity had a far greater effect on the dissipation of MCPA salt in these soils than sorption, whose role was completely suppressed by the biological properties of the soil. Dehydrogenase enzyme activity has been shown to be a soil property affecting the degradation of MCPA in the soil. Higher DHA in the soil increased the dissipation rate of MCPA (Paszko et al., 2009) and other phenoxyacid herbicides (Villaverde et al., 2008).

3.3. Environmental implications

Sorption quantities (K_{tr} , K_{d} and K_{oc}) express the magnitude and strength of the interaction of an organic contaminant with a solid matrix and are therefore an indicator of its mobility in the rock environment, while degradation quantities, especially DT_{s0} , indicate the rate at which a parent organic contaminant disappears or transforms into metabolites. Together, these two processes determine the resulting concentration of organic contaminant in the soil solution at a given time. Therefore, sorption and degradation are the most important bio-geochemical characteristics of an organic contaminant that play a role in its migration either vertically or laterally into natural waters. The most frequently used empirical model to predict the potential of pesticides to leach to groundwater was introduced by Gustafson (1989) and has the form as follows:

$$GUS = \log DT_{50} \times (4 - \log K_{oc})$$

• where GUS is a dimensionless index, so called the groundwater ubiquity score. When GUS is >2.8, pesticides likely leach to groundwater. Pesticides with GUS <1.8 do not leach very likely to groundwater and pesticides with GUS between 1.8 and 2.8 are considered transitional. Another frequently used empirical model is the relative leaching potential index (RLPI), which defines the relative attenuation of each pesticide in soil, and therefore, its potential to leach to groundwater (Hornsby et al., 1993). The relative leaching potential index is defined by the equation:

$$\text{RLPI} = 10 \times \left(\frac{K_{\text{oc}}}{\text{DT}_{50}}\right)$$

Generally, it is considered that pesticides having RLPI <100 are highly mobile in soil and likely leach to groundwater.

The calculated GUS and RLPI values are given in Table 2. The GUS value for Soil 1 and Soil 3 was less than 1.8 and the RLPI value for the same soils was higher than 100. The GUS and RLPI values for Soil 2 were higher than 1.8 and lower than 100, respectively, suggesting that the MCPA salt may be leached to groundwater, while in Soil 1 and Soil 3 it is unlikely to leach MCPA salt to the groundwater table. The low leaching potential of MCPA salt in the soil samples is mainly due to the rapid degradability of MCPA salt in these soils. However, it is known that MCPA occurs quite frequently in groundwater. It should be noted that leaching of MCPA into groundwater is a complex function of its physicochemical properties, including sorption and degradation characteristics, physicochemical properties of soils and hydro-physical characteristics of the rock environment, while application rate and timing of this herbicide are also important.

4. CONCLUSIONS

The study of sorption and degradation processes of pesticides in soils is of great importance in assessing their mobility and biological activity as well as risk of groundwater contamination by these undesirable compounds. Experimental results of a sorption study of Na-K-DMA MCPA salt, which is an active ingredient in the Agritox herbicide formulation, in three soil samples with different physicochemical and biological properties indicated a relatively low ability of soils to sorb this herbicide due to their weakly alkaline character. The sorption efficiency expressed as % of sorbed concentration of MCPA salt was approximately 14 % and 17 % for Soil 1 and Soil 2 (Calcaric Fluvisols), respectively, and ~35 % for Soil 3 (Eutri-Humic Fluvisol), which had the highest organic carbon and clay content. This implies that most of the MCPA remains in the soil solution. On the other hand, the degradation of MCPA salt was rapid with the estimated first-order half-life values ranging from 4.5 day to 7 days, with significantly the most rapid dissipation of MCPA salt in Soil 3, which exhibited the highest microbial activity expressed as dehydrogenase activity. In view of the potential for migration of MCPA salt to groundwater based on the obtained sorption and degradation characteristics and calculated GUS and RLPI values, it could be concluded that there was a low probability of herbicide leaching into groundwater.

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