Effects of Potassium, Ammonium, and Calcium Chlorides on the Sorption of Metamitron in Soil

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Abstract

The effects of three electrolytes (KCl, NH_4Cl, and $CaCl_2$) on the sorption of the herbicide metamitron in a loamy soil was studied. The sorption of metamitron was measured using the batch equilibrium technique. The experimental data were fitted to the Freundlich and Dubinin-Radushkevich isotherm equations. It was noted that the fraction of metamitron sorbed in soil decreased with the increasing initial concentration of the herbicide in soil solution. In soil with organic matter removed, the sorption of metamitron was lower than in the original soil. The soil-herbicide solution contact time ranging from 60 to 720 minutes and had only a slight effect on metamitron sorption. In soil with the addition of KCl and NH_4Cl, significantly higher sorption of metamitron was observed than in the soil system without these electrolytes. The extent of sorption increased with increasing concentrations of aqueous KCl or NH_4Cl solutions, but the increase of sorption in the presence of NH_4Cl was lower compared to the presence of KCl. A similar effect of the two electrolytes on the sorption of metamitron was observed in the soil with organic matter removed. In the single-component systems with $CaCl_2$, a decrease of metamitron sorption was observed in the original soil. Whereas the presence of $CaCl_2$ in the two-component systems $KCl+CaCl_2$ and $NH_4Cl+CaCl_2$ limited the extent of sorption of metamitron in relation to that obtained in the single-component systems with KCl or NH_4Cl, the adsorbed amount of metamitron was still much higher than in soil systems with no electrolyte.

Keywords: herbicide, metamitron, sorption, soil, electrolyte

Introduction

The application of herbicides, apart from the practical aspect related with the control of plants competing for nutrients in cultivations of crops, has also undesirable effects resulting from the possibility of migration and accumulation of these xenobiotics in various compartments of the environment. In soils, herbicides can undergo three fundamental processes: sorption, degradation, and migration into deeper layers of the soil profile. The intensity and the actual course of sorption processes can have significant effects on the other sorption-related processes of herbicides as its non-sorbed part may be subject to transport, degradation, and uptake by plants and other organisms [1].

Sorption of herbicides is related to the structure of these compounds and the physical and chemical properties of soils [2-8], as well as to soil moisture and the chemistry of soil solution [9, 10]. Moreover, it has been shown that sorption of organic compounds depends on the type of cations present in the soil solution and the degree to which the soil is saturated with these cations. Cations present in soils, such as K^+, NH_4^+, and Ca^{2+}, are either of natural origin or introduced in excess by the fertilization of plants. Intensity of pesticides and other organic compounds sorption in the soil cannot change or be decreased or increased in the presence
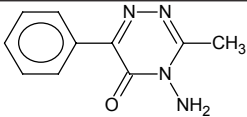
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Table 1. Physicochemical properties of soil.

Percent of soil fraction			pH	TOC (%)		Specific surface area (m²·g⁻¹)	Cationic exchange capacity (mmol(+)·kg⁻¹)
2.0-0.05 mm	0.05-0.002 mm	< 0.002 mm		G	G-OM		
35	40	25	5.6	1.012	0.230	49.09	357.8

Table 2. Properties of metamitron [27].

Structural and molecular formula		Molecular mass (g·mol⁻¹)	Solubility in water (g·L⁻¹) in 20ºC	n-Octanol – water distribution coefficient, K_{OW} in 21ºC
	$C_{10}H_{10}N_4O$	202.2	1.8	7.079

of Ca^{2+} and K^+. This effect depends on the properties of the organic compound, soil, and cations [11-16]. A similar effect has been observed for the adsorption of pesticides on clay minerals (smectites) saturated with K^+ [17, 18]. Observed effects of cations on the sorption of organic compounds in soils and soil components were shown to be due to changes in their ability to dehydrate surfaces of soil minerals, which became more hydrophobic/hydrophilic and thus more accessible/inaccessible for molecules of organic compounds. The sorption of pesticides on minerals saturated with exchangeable cations may proceed according to the following mechanisms: the formation of hydrogen bonds between the functional group of an organic compound and water molecules polarized by exchangeable cations, protonation of the functional group of an organic compound by hydrated cations, and direct ion-dipole effect between the cation and the functional group of the compound [11].

Metamitron, i.e. 4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one, is a herbicide from the group of triazinones, used primarily for the control of annual dicotyledonous weeds in cultivation of sugar and fodder beets [19]. The literature shows a notable effect of organic matter and clay minerals on the level of metamitron sorption in soils [20-21]. Research conducted by Coquet [22], Autio et al. [23], and Matallo et al. [24] confirms the weak sorption of metamitron, especially in soils with low organic matter content, which indicates its high mobility. Low sorption of metamitron in conjunction with its relatively good solubility in water indicates the possibility of leaching of the herbicide from the soil and consequently pollution of ground and surface waters [25].

Poland is one of the leading sugar beet producers in Europe, and Lublin Province is one of the most important areas of its cultivation. Sugar beet is very susceptible to weed infestation, requiring frequent treatments and use of, among others, high doses of fertilizers. According to new agronomic recommendations, metamitron can be used 3-4 times during the growing season. The herbicide may be applied both to the soil and as foliar application [26]. Therefore, due to repeated application of metamitron, there is a possibility to use this herbicide directly after introduc-

ing the fertilizer cations into the soil, e.g. K^+, NH_4^+. Therefore, the presence of these cations may have an impact on the sorption-desorption processes of metamitron, and thus on its mobility and effectiveness. Available literature still lacks uniquivocal information about the effect of fertilizer cations on metamitron sorption in soils. The main aim of our study was to determine:

(i) The sorption of metamitron in original soil and soil with removed soil organic matter
(ii) The effect of electrolytes on the sorption of metamitron in both soils

Material and Methods

Soil samples used in the study were taken from A_p horizon of a brown soil developed from boulder loam classified in the agronomic category – heavy soil. The soil samples were air-dried, then passed through a 2-mm sieve and averaged. The soil was characterized for grain size distribution with the method of Cassagrande as modified by Prószyński, total organic carbon content (TOC) on a Schimadzu TOC-VCSH analyzer, pH in 1 mol·L⁻¹ KCl electrometrically, specific surface area with the method of water vapour adsorption, hydrolytic acidity (H_h), and sum of base exchangeable cations (S) using the method of Kappen. Sorptive capacity of the soil was calculated as the sum of H_h and S. The physico-chemical properties of the soil are presented in Table 1. The chemical formula and the properties of metamitron are given in Table 2.

The determinations of sorption were conducted under static conditions: 2 g of soil (G) were shaken with 5 mL of metamitron solution with concentrations of 5, 7.5, 10, 12.5, and 15 mg·L⁻¹ for 6 hours at room temperature, and then the samples were left for 18 hours to achieve sorption equilibrium. The effect of electrolytes on metamitron sorption was studied using the following solutions: KCl and NH₄Cl with concentrations of 0.1, 0.2, 0.3, and 0.5 M; CaCl₂ with concentrations of 0.05, 0.1, 0.2 M, and mixtures of two electrolytes in the following systems: 0.3 M KCl+0.05 M CaCl₂, 0.3 M KCl+0.1 M CaCl₂, 0.3 M KCl+0.15 M CaCl₂,

0.3 M NH$_4$Cl+0.05 M CaCl$_2$, 0.3 M NH$_4$Cl+0.1 M CaCl$_2$, and 0.3 M NH$_4$Cl+0.15 M CaCl$_2$. In the first stage of the experiment, 2 g of soil were shaken with 5 mL of electrolyte solution for 6 hours at room temperature. After 18 hours, samples with electrolyte were centrifuged at a speed of 4,000 rpm for 10 min. In the next stage, specific volumes of solution (0.110, 0.165, 0.220, 0.275, 0.330 mL) were taken from the samples, and identical volumes of metamitron solution (227 mg·L^{-1}) were added to the samples. In this manner metamitron solutions with initial concentrations of 5, 7.5, 10, 12.5, and 15 mg·L^{-1} and volume of 5 mL were obtained in the test tubes, and then they were shaken again with soil (saturated with the electrolyte) for 6 hours at room temperature, and then left for 18 hours to achieve the sorption equilibrium. All experiments were conducted in three replicates. Sorption experiments were conducted also with soil in which a considerable part of organic matter was oxidized with 30% solution of H$_2$O$_2$ at a temperature of 80ºC (G-OM). Metamitron sorption in the soil treated with H$_2$O$_2$ and the effect of 0.5 M of KCl or NH$_4$Cl electrolytes on the metamitron sorption on G-OM soil were carried using the method described above. The experimental conditions were the same as described above, except the mass of soil (1 g) and volumes of solutions (2.5 mL). The tests were made in two replicates. After the shaking and equilibrating, the soil suspension was centrifuged at 4,000 rpm for 20 min, and metamitron concentration in the solution was analyzed by high-performance liquid chromatography (HPLC) using a Supelcosil LC-PAH RP-18 column and a UV-VIS detector (K-2500, Knauer, Germany) at λ=300 nm. The mobile phase used was a mixture of acetonitrile and water (29:71, v/v). The flow rate applied was 1 mL·min^{-1}. The amount of metamitron sorbed per unit weight of soil (S, [mg·kg^{-1}]) was calculated using the equation:

$$S = (C - C_{eq}) \cdot V/m \qquad (1)$$

...where C and C_{eq} are the initial and equilibrium concentrations of metamitron, respectively (mg·L^{-1}), V is the volume of the solution (L), and m is the mass of soil (kg).

The kinetics of sorption were studied by shaking 2 g of soil with 5 mL of metamitron solution with initial concen-

trations of 10 and 15 mg·L^{-1} for 60, 180, 300, 360, 480, 600, and 720 minutes. The sorption kinetics experiments were done in three replicates.

Equilibrium sorption data were fitted to the following sorption isotherm equations:
a) the Freundlich equation:

$$S = K_F \cdot C_{eq}^n \qquad (2)$$

...where K_F is the Freundlich constant (mg·kg^{-1}) and n is the Freundlich exponent [28];

b) the Dubinin-Radushkevich equation (D-R):

$$S = X_m \cdot \exp\left[-K \cdot (R \cdot T \cdot \ln(1+1/C_{eq}))^2\right] \qquad (3)$$

...where S (mol·kg^{-1}), C_{eq} (mol·L^{-1}), X_m is the DR constant (mmol·kg^{-1}), R is the gas constant (8.314 J·mol^{-1}·K^{-1}), T is the thermodynamic temperature (K), and K is the coefficient (mol^2·J^{-2}) related with the energy of sorption E (kJ·mol^{-1}) and given by the formula: $E = (-2K)^{-1/2}$ [29-30].

The parameters of the Freundlich and Dubinin-Radushkevich equations were determined with the method of non-linear regression. According to Armagan and Toprak [31] the non-linear method is a more appropriate technique to estimate the adsorption isotherm parameters than the linear method, whereas the quality of fitting of the models to the experimental data was estimated on the basis of the normalized deviation (Δq) expressed in % and the values of coefficients of determination (R^2). The values of Δq were calculated from the formula [32-34]:

$$\Delta q = (1/N \sum_{i=1}^{N} (|(Si,e - Si,c)|/Si,e))) \cdot 100\% \qquad (4)$$

...where N is the number of measurements, Si,e is the experimentally determined value of metamitron amount sorbed by soil (mg·kg^{-1} or mol·kg^{-1}), and Si,c is the value of metamitron amount sorbed by soil obtained from isotherm equations (mg·kg^{-1} or mol·kg^{-1}). Generally it is assumed that values of Δq < 5% indicate good fit of model to experimental data [35]. The experimental data were statistically processed by ANOVA (the Tukey's test at significance level p=0.05) using the Statgraphics Centurion XVI program (Statpoint Technologies, Inc.).
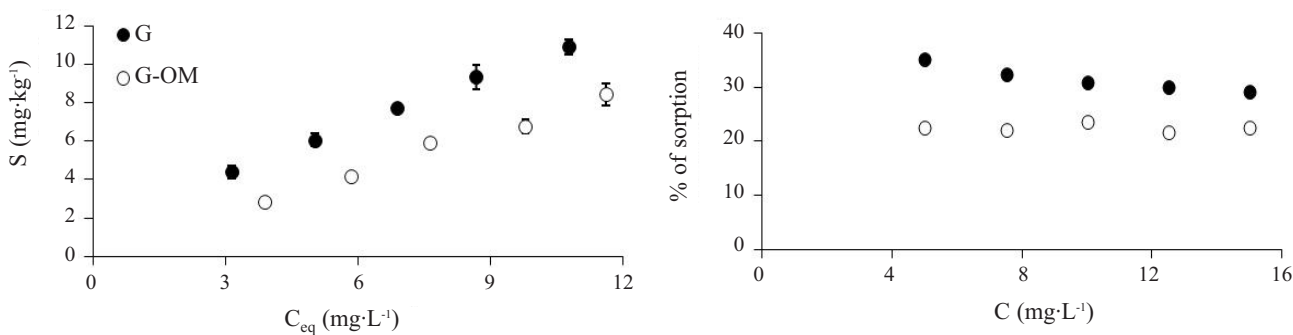

Fig. 1. Sorption isotherms and percentage of metamitron sorption in soil: S – equilibrium sorbed amount, C$_{eq}$ – equilibrium concentration, C – initial concentration, G – original soil, G-OM – soil with removed soil organic matter. Error bars represent standard deviation of triplicate assays.

Table 3. Parameters determined from the Freundlich isotherm equation.

System	K_F (mg·kg^{-1})	n	R^2	Δq (%)
G	1.841	0.748	0.999	0.927
G + 0.1M KCl	1.903	0.833	0.997	1.381
G + 0.2M KCl	2.864	0.696	0.994	1.908
G + 0.3M KCl	4.474	0.752	0.992	2.718
G + 0.5M KCl	5.438	0.701	0.982	4.134
G + 0.1M NH$_4$Cl	1.808	0.834	0.993	2.240
G + 0.2M NH$_4$Cl	2.876	0.672	0.999	0.697
G + 0.3M NH$_4$Cl	3.170	0.819	0.993	2.258
G + 0.5M NH$_4$Cl	3.568	0.850	0.999	1.111
G + 0.05M CaCl$_2$	1.122	0.902	0.997	1.390
G + 0.1M CaCl$_2$	1.077	0.944	0.995	2.011
G + 0.2M CaCl$_2$	0.795	0.975	0.998	1.628
G + 0.3M KCl + 0.05M CaCl$_2$	3.153	0.799	0.992	2.568
G + 0.3M KCl + 0.1M CaCl$_2$	2.231	0.924	0.993	2.364
G + 0.3M KCl + 0.15M CaCl$_2$	2.680	0.799	0.999	0.563
G + 0.3M NH$_4$Cl + 0.05M CaCl$_2$	2.983	0.830	0.987	3.688
G + 0.3M NH$_4$Cl + 0.1M CaCl$_2$	2.427	0.856	0.997	1.665
G + 0.3M NH$_4$Cl + 0.15M CaCl$_2$	2.683	0.841	0.999	1.255
G-OM	0.731	0.994	0.991	2.815
G-OM + 0.5M KCl	8.817	0.704	0.987	3.823
G-OM + 0.5M NH$_4$Cl	5.033	0.793	0.999	0.471

K_F – Freundlich constant, n – constant indicative of sorption intensity, R^2 – coefficient of determination, G – original soil, G-OM – soil treated with H_2O_2, Δq – normalized deviation.

Results and Discussion

Metamitron Sorption from Water in Soil

Fig. 1 presents the isotherms and the percentage values of metamitron sorption in the original soil (G) and treated soil (G-OM). The process of sorption was analyzed with the use of two-parameter equations of Freundlich and Dubinin-Radushkevich (Tables 3 and 4). Values of $\Delta q <$ 3% and $R^2 > 0.99$ indicated that both equations described well the sorption of metamitron in the G and G-OM systems.

Original soil (G) had higher sorption capacity for metamitron in comparison with G-OM soil (Fig. 1). The same conclusion can be drawn on the basis of the K_F value, which is 1.841 mg·kg^{-1} for G soil and two-times higher than that for G-OM soil. The lower sorptive ability of the soil treated with H_2O_2 (G-OM) indicates that soil organic matter participates significantly in metamitron binding in the original soil (G). As reported by Cox et al. [21], apart from organic matter, clay minerals also play a significant role in metamitron sorption in soil. According to Sànchez-Martin et al. [20], the contribution of clay minerals to the sorption of metamitron increases notably in soils with organic matter content below 2%. In this study, the content of organic carbon in the original soil (G) was 1.012% (Table 1). For this reason, and on the basis of literature data, one can suppose that in the soil studied, metamitron was bound to a considerable extent also by clay minerals.

Comparing the intensity of the sorption process is possible due to dimensionless parameter n in the Freundlich equation, which is also used in determining the nature of the sorption isotherms describing metamitron in analyzed systems. Values of *n* lower than one are characteristic for isotherms of type L and indicate a decrease in the proportion between the level of metamitron sorption and its equilibrium concentration (ratio S/C_{eq} decreases with increasing concentration C_{eq}). This type of isotherm is characteristic for the systems with poor competition between molecules of the solvent and the substance sorbed during sorption, as well as a possibility of "flat" orientation of sorbate molecules relative to the sorption surface [12, 36]. If n values are

Table 4. Parameters determined from the Dubinin-Radushkevich isotherm equation.

System	X_m (mmol·kg^{-1})	K (mol^2·J^{-2})	E (kJ·mol^{-1})	R^2	Δq (%)
G	1.697	-6.017×10^{-9}	9.116	0.998	1.412
G + 0.1M KCl	3.122	-6.674×10^{-9}	8.656	0.997	1.421
G + 0.2M KCl	1.745	-5.521×10^{-9}	9.517	0.992	2.386
G + 0.3M KCl	3.652	-5.828×10^{-9}	9.262	0.994	2.383
G + 0.5M KCl	2.956	-5.347×10^{-9}	9.670	0.978	4.594
G + 0.1M NH$_4$Cl	3.006	-6.693×10^{-9}	8.643	0.993	2.228
G + 0.2M NH$_4$Cl	1.506	-5.352×10^{-9}	9.666	0.999	0.898
G + 0.3M NH$_4$Cl	4.273	-6.414×10^{-9}	8.829	0.992	2.461
G + 0.5M NH$_4$Cl	5.775	-6.616×10^{-9}	8.693	0.999	0.668
G + 0.05M CaCl$_2$	3.151	-7.316×10^{-9}	8.267	0.996	1.656
G + 0.1M CaCl$_2$	4.057	-7.653×10^{-9}	8.083	0.995	1.957
G + 0.2M CaCl$_2$	3.802	-7.940×10^{-9}	7.936	0.996	2.174
G + 0.3M KCl + 0.05M CaCl$_2$	3.753	-6.276×10^{-9}	8.926	0.992	2.521
G + 0.3M KCl + 0.1M CaCl$_2$	6.513	-7.319×10^{-9}	8.265	0.995	2.116
G + 0.3M KCl + 0.15M CaCl$_2$	3.306	-6.328×10^{-9}	8.889	0.999	0.612
G + 0.3M NH$_4$Cl + 0.05M CaCl$_2$	4.415	-6.529×10^{-9}	8.751	0.988	3.440
G + 0.3M NH$_4$Cl + 0.1M CaCl$_2$	4.381	-6.763×10^{-9}	8.598	0.995	2.184
G + 0.3M NH$_4$Cl + 0.15M CaCl$_2$	4.386	-6.649×10^{-9}	8.672	0.999	0.758
G-OM	4.072	-8.121×10^{-9}	7.847	0.991	2.977
G-OM + 0.5M KCl	4.433	-5.237×10^{-9}	9.771	0.990	3.218
G-OM + 0.5M NH$_4$Cl	5.144	-6.070×10^{-9}	9.076	0.999	0.787

X_m – Dubinin–Radushkevich constant, K – coefficient related to sorption energy, E – energy of sorption, R^2 – coefficient of determination, G – original soil, G-OM – soil treated with H_2O_2, Δq – normalized deviation.

equal or close to unity, the amount of sorbed substance under study increases proportionally to the change in concentration, and the isotherm obtained is linear and belongs to the C-type. Based on the Freundlich exponent values (Table 3), the isotherms were of L-type and C-type for the original soil and the treated soil, respectively [37]. This means that the degree of metamitron sorption in soil G decreases with increasing initial concentration of metamitron, as it is presented in Fig. 1. The decrease of the percentage of sorption with increasing initial concentration may also indicate heterogeneity of active centres that could potentially be occupied by metamitron during its sorption in soil [12]. However, in the G-OM soil, the sorption isotherm of metamitron was linear, and therefore the extent of metamitron sorption remained almost constant at all initial concentrations. In general, it can be concluded that metamitron displayed small affinity to the soil studied. This is evidenced by the relatively low levels of sorption that did not exceed 35.09% in the original soil (G) and 23.58% in the soil treated with H_2O_2 (G-OM) (Fig. 1). Compared to soil G, the decrease of sorption in soil G-OM was the

greatest for initial concentrations of 5 and 7.5 mg·L^{-1} (by 36.07 and 31.81%, respectively), and the smallest (by 22.92%) for an initial concentration of 15 mg·L^{-1}.

Parameter E determined from the Dubinin-Radushkevich equation is related with the energy of sorption. As various values of energy correspond to the particular mechanisms of sorption, some conclusion about the possible sorption mechanism of metamitron may be presented based on the value of E. According to Weber et al. [38], the interactions of organic compounds with soil can be classified as physical, chemical, and electrostatic. The value of energy corresponding to physical sorption is E < 8 kJ·mol^{-1}, whereas values of E > 8 kJ·mol^{-1} are characteristic for chemical sorption [39, 40]. Usually, physical and chemical sorption processes are simultaneous, especially if surface sorption occurs. In G and G-OM systems, the values of parameter E were 9.116 and 7.847 kJ·mol^{-1}, respectively (Table 4). On this basis, it can be assumed that chemisorption contributes to metamitron sorption in original G soil, while sorption of metamitron in G-OM soil is a more non-specific process.

The results presented in Fig. 2 indicate that for the period ranging from 60 to 720 min no significant increase in metamitron sorption was observed. This means that the sorption of metamitron in soil rapidly reached the pseudo-equilibrium state. The fast sorption may suggest that one of the binding mechanisms of metamitron in the soil could be a physical process [41].

Effects of Single Electrolyte on Sorption

High coefficients of determination R^2 and low normalized deviation Δq, presented in Tables 3 and 4 indicate the exact match of the Freundlich and Dubinin-Radushkevich equations to the experimental data for each of the single-component systems.

The results presented in Figs. 3 and 4 show that the presence of KCl and NH_4Cl caused significant changes in the extent of metamitron sorption in the original soil. According to the data given in Table 3, n values for all systems G+KCl and G+NH_4Cl were significantly lower than 1. This indicates that the sorption of metamitron in these systems is described by the isotherm of L-type. Furthermore, the values of K_F increased with increasing concentration of KCl and were higher than the values of K_F determined for sorption in soil without any addition of electrolytes (systems G and G-OM). A similar trend of changes of the K_F values was noted for sorption in the presence of NH_4Cl.

This means that the increase in KCl or NH_4Cl concentration resulted in increased sorption of metamitron relative to its sorption in the soil without any electrolyte. Comparison of the amount of metamitron sorbed in soil with KCl or NH_4Cl with its amount sorbed in soil without electrolytes may provide quantitative information about the extent of this effect. For example, for the solution with metamitron initial concentration of 15 mg·L^{-1}, the amounts of metamitron sorbed by soil G in the presence of 0.1 M KCl, 0.2 M KCl, and 0.3 M KCl were 12.73 mg·kg^{-1}, 13.73 mg·kg^{-1}, and 19.16 mg·kg^{-1}, respectively, while in soil G with no KCl it was 10.94 mg·kg^{-1}. This means that the sorption of metamitron with its initial concentration of 15 mg·L^{-1} in the soil after the addition of 0.1 M KCl, 0.2 M KCl, and 0.3 M KCl increased by 16.36%, 25.50%, and 75.14%, respectively, compared to the sorption from solution with no KCl (Fig. 3). The highest sorption of metamitron in the soil G was observed in sorption systems with the highest KCl concentration (0.5 M). The same findings were observed for metamitron sorption in soil G with added NH_4Cl. Moreover, the data in Figs. 3 and 4 show that for the entire range of metamitron initial concentrations the increase of sorption was greater in systems G+KCl than in systems G+NH_4Cl, especially in the presence of 0.3 M and 0.5 M KCl or NH_4Cl. Probably, the addition of KCl or NH_4Cl to the soil contributed to the exchange of cations, e.g., Na$^+$, Ca^{2+}, that naturally occur in the inter-layer spaces of clay
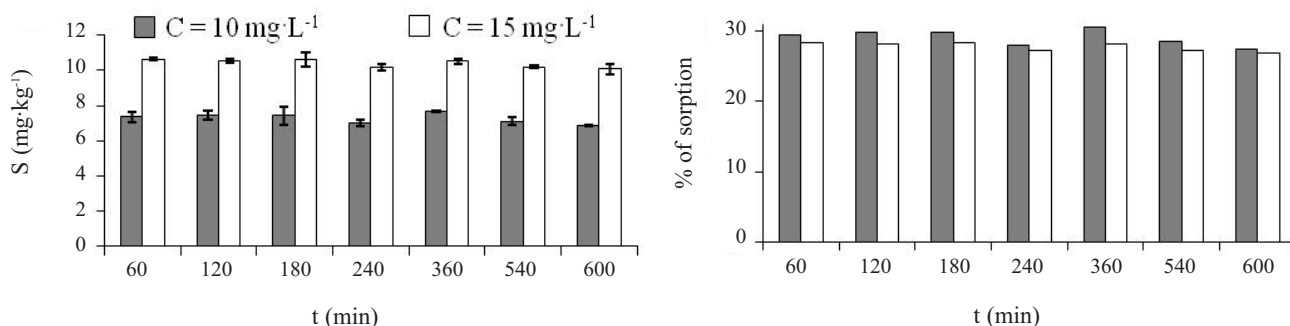

Fig. 2. Kinetics of sorption of metamitron in soil: S – equilibrium sorbed amount, t – time. Error bars represent standard deviation of triplicate assays.
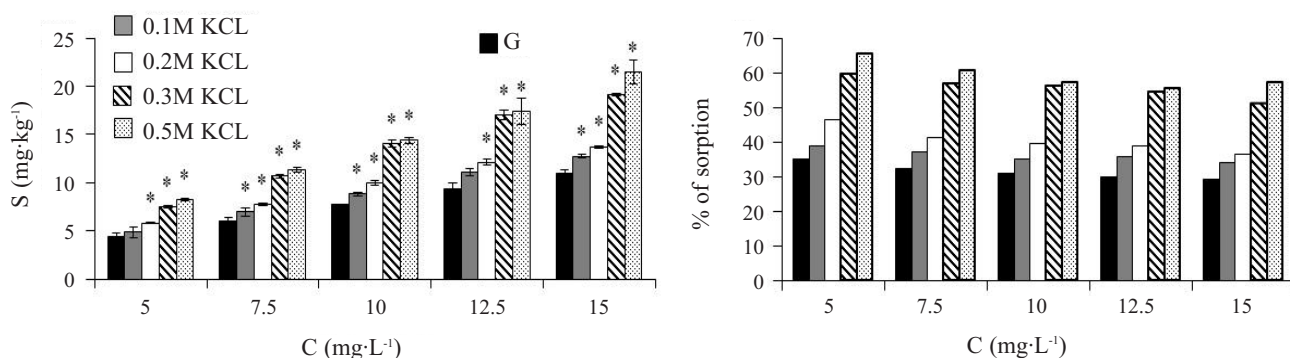

Fig. 3. Effect of KCl on the sorption of metamitron in soil: S – equilibrium sorbed amount, C – initial concentration, G – original soil. Error bars represent standard deviation of triplicate assays. (*) denotes significant differences (p < 0.05) from original soil according to Tukey's difference test.
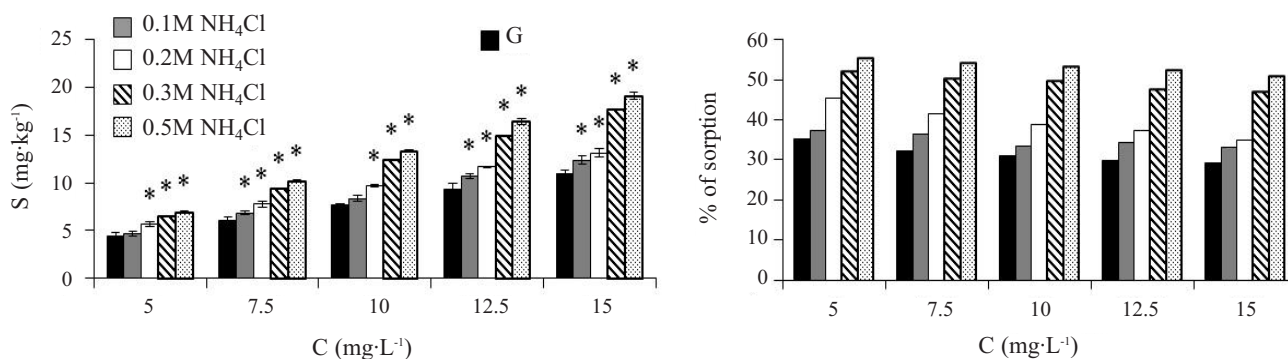
Fig. 4. Effect of NH$_4$Cl on the sorption of metamitron in soil: S – equilibrium sorbed amount, C – initial concentration, G – original soil. Error bars represent standard deviation of triplicate assays. (*) denotes significant differences ($p < 0.05$) from original soil according to Tukey's difference test.

minerals, for K$^+$ or NH$_4^+$ cations. It can be supposed that the higher the concentration of the electrolyte added to soil the more intensive the ionic exchange, and therefore the minerals were saturated to a greater degree with K$^+$ or NH$_4^+$ cations. Compared to Na$^+$ and Ca^{2+} cations, K$^+$ and NH$_4^+$ are characterized by significantly lower hydration ability (hydration enthalpy (ΔH) is: for Na$^+$: -375 kJ·mol^{-1}, for Ca^{2+}: -1515 kJ·mol^{-1}, for K$^+$: -304 kJ·mol^{-1}, and for NH$_4^+$: -292 kJ·mol^{-1}) [42, 43]. This means that K$^+$ and NH$_4^+$ cations are surrounded by water molecules to a lesser extent. For this reason the adsorption of K$^+$ and NH$_4^+$ cations inhibits the hydration of soil clay minerals. Due to lower hydration of soil clay minerals by K$^+$ and NH$_4^+$ cations, mineral surfaces become more hydrophobic and thus more accessible for the molecules of organic compounds [44-48]. One should assume that the hydration of soil minerals was inhibited more strongly at higher KCl and NH$_4$Cl concentrations. As a result, metamitron sorption in the soil was higher in the presence of 0.3 M and 0.5 M KCl and NH$_4$Cl than that in the presence of 0.1 M and 0.2 M KCl and NH$_4$Cl. According to Aggarwal et al. [47], Li et al. [49], and Sheng et al. [50, 51], increasing concentration of KCl intensifies the aggregation of clay minerals and quasi-crystals are formed. As quasi-crystals are characterized by a reduced basal distance d$_{001}$, molecules of pesticides and other organ-

ic compounds have simultaneous contact with two silicate surfaces of minerals during sorption and can thus better compete with water molecules for sorption sites within the inter-layer space.

In contrast to KCl and NH$_4$Cl, the CaCl$_2$ solution added to the original soil caused a decrease in the sorption of metamitron. Significantly lower K$_F$ values (Table 3) for the original soil (G) designated in the presence of 0.05 M, 0.1 M, and 0.2 M CaCl$_2$ in comparison with the soil without electrolyte and results presented in Fig. 5 confirmed the observed decrease in metamitron sorption. The effect of CaCl$_2$ on the extent of metamitron sorption could be caused by a reduction of hydrophobicity of the inter-layer space of clay minerals due to the adsorption of Ca^{2+} cations, which hydrated soil minerals more strongly than K$^+$ or NH$_4^+$ cations. Due to considerable energy of hydration of Ca^{2+} ions (-1,515 kJ·mol^{-1}), water molecules are retained more strongly in the hydration zone of Ca^{2+} ions. This hydration effect, on the one hand inhibits the dehydration of metamitron, and on the other hand, intensifies interactions of polar groups of the herbicide with Ca^{2+} cations [52]. Moreover, the stronger hydration ability of Ca^{2+} cations results in an increase of the distance of inter-layer spaces in clay minerals saturated with Ca^{2+} ions to a greater extent compared to clay minerals saturated with K$^+$ or NH$_4^+$ ions [45, 53]. For this reason, molecules of metamitron had

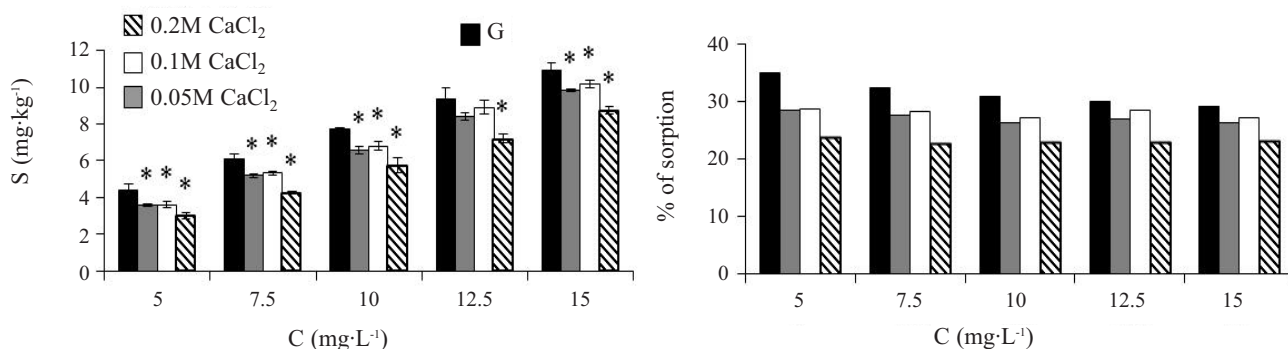Fig. 5. Effect of CaCl$_2$ on the sorption of metamitron in soil: S – equilibrium sorbed amount, C – initial concentration, G – original soil. Error bars represent standard deviation of triplicate assays. (*) denotes significant differences ($p < 0.05$) from original soil according to Tukey's difference test.

Fig. 6. Effect of KCl and NH₄Cl on the sorption of metamitron in soil: S – equilibrium sorbed amount, C – initial concentration, G – original soil, G-OM – soil with removed soil organic matter. Error bars represent standard deviation of duplicate assays. (*) denotes significant differences ($p < 0.05$) from original soil according to Tukey's difference test.
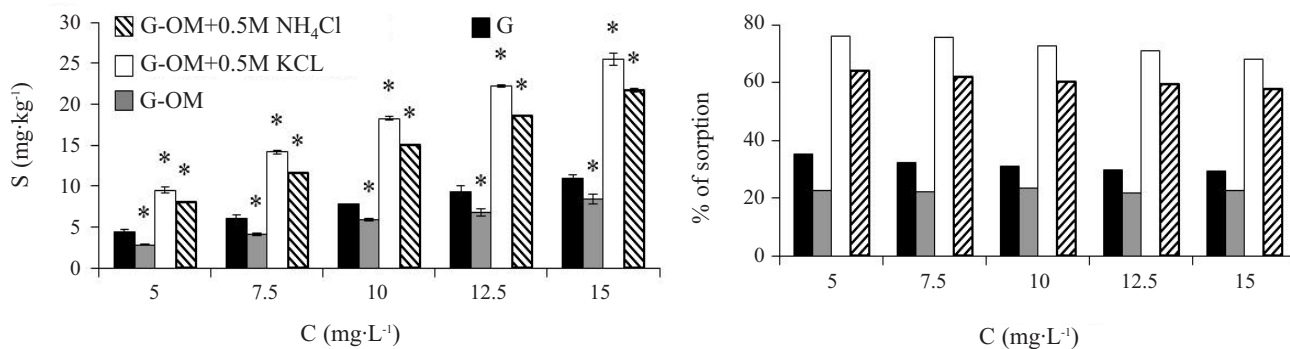
more difficult contact with the siloxane surface of clay minerals, and this resulted in lower sorption of the herbicide. Compared to 0.05 M CaCl₂, the addition of 0.2 M CaCl₂ had a stronger effect on the sorption of metamitron. It should be noted that values of n parameter for G+CaCl₂ systems were higher than for G+KCl and G+NH₄Cl systems. This may indicate greater energy heterogeneity of the surface sorption in component systems with CaCl₂ than with KCl or NH₄Cl. The value of n close to unity (0.975) for the G+0.2 M CaCl₂ suggests that sorption of metamitron occurs as a distribution process between the soil and solution to a large extent.

Fig. 6 presents the sorption of metamitron in the treated soil, in which most of organic matter was oxidized with H₂O₂ (G-OM) (Table 2). Prior to application of metamitron to G-OM, the soil was saturated with 0.5 M solutions of KCl or NH₄Cl. The values of n (Table 3), show that the sorption isotherms of metamitron in systems G-OM+0.5 M KCl and G-OM+0.5 M NH₄Cl are of L-type. Based on the data given in Fig. 6, one can conclude that in the presence of KCl and NH₄Cl, there was a significant increase of metamitron sorption within all its initial concentrations. This was indicated by the percentages of sorption in the presence of KCl and NH₄Cl ranging from 67.94 to 76.07% and from 57.76 to 64.10%, respectively. The strong impact of KCl and NH₄Cl on the amount of metamitron sorbed in the G-OM soil is also confirmed by the K_F values, which were significantly higher than the corresponding K_F values for sorption in G soil saturated with 0.5 M solutions of KCl or NH₄Cl (Table 3). This implies that in the soil with organic matter removed and saturated with KCl or NH₄Cl solutions, the sorption of metamitron was even higher than that in the original soil saturated with the same cations, although as demonstrated in the study (Fig. 1), removal of soil organic matter caused a decrease of the extent of metamitron sorption. It could be assumed that sorption sites were unblocked after the removal of soil organic mater and became more available for metamitron in the presence of KCl or NH₄Cl. Probably, this effect was large enough to overcome the unfavourable effect of soil organic matter removal on the sorption of metamitron. This idea is supported by comparing the extent

of sorption on unblocked sites in systems G-OM+0.5 M KCl and G-OM+0.5 M NH₄Cl with the difference in sorption extent between systems G and G-OM. The extent of sorption at unblocked sites can be calculated by subtracting from the value of sorption in the system G-OM+electrolyte the amount of metamitron sorbed in the system G-OM and the difference: (sorption in system G+electrolyte) – (sorption in system G). The results of these calculations presented in Fig. 7 indicate that sorption on unblocked sites is greater compared to the difference in sorption extents between G and G-OM systems.

It is worth noting that the E values (Table 4) determined from the Dubinin-Radushkevich equation for the single-component systems with KCl or NH₄Cl were higher in comparison with single-component systems with CaCl₂. This may indicate that the sorption of metamitron in systems G+KCl, NH₄Cl+G, G-OM+0.5 M KCl, and G-OM+0.5 M NH₄Cl are proceeded by a different mechanism than those in G+CaCl₂.

Combined Effects of Two Electrolytes on Sorption

The sorption isotherms of metamitron in binary systems were also fitted adequately to the Freundlich and Dubinin-
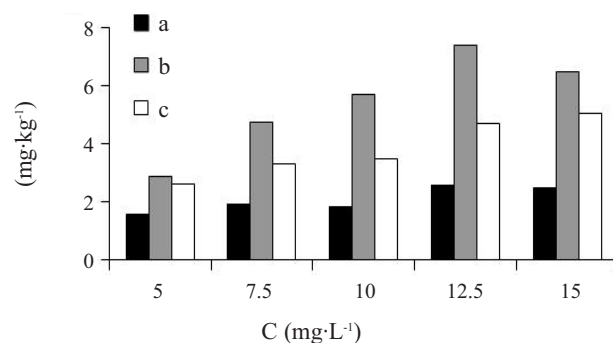

Fig. 7. Differences in sorption extents between systems G and G-OM (a), extent of sorption on unblocked sites in systems G-OM + 0.5M KCl (b), and G-OM + 0.5M NH₄Cl (c), G – original soil, G-OM – soil treated with H₂O₂.

Fig. 8. Effect of KCl + CaCl$_2$ on the sorption of metamitron in soil: S – equilibrium sorbed amount, C – initial concentration, G – original soil. Error bars represent standard deviation of triplicate assays. (*) denotes significant differences (p < 0.05) from original soil according to Tukey's difference test.
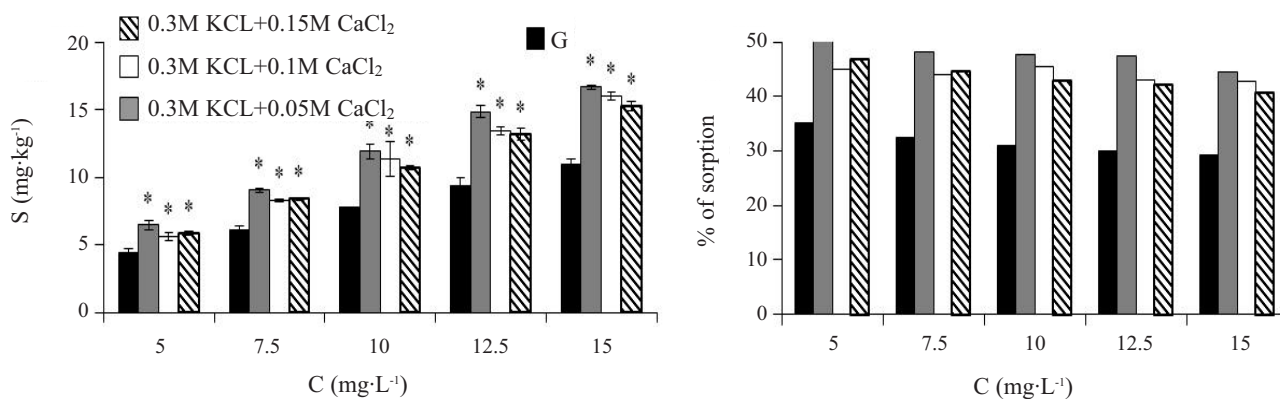

Fig. 9. Effect of NH$_4$Cl + CaCl$_2$ on the sorption of metamitron in soil: S – equilibrium sorbed amount, C – initial concentration, G – original soil. Error bars represent standard deviation of triplicate assays. (*) denotes significant differences (p < 0.05) from original soil according to Tukey's difference test.
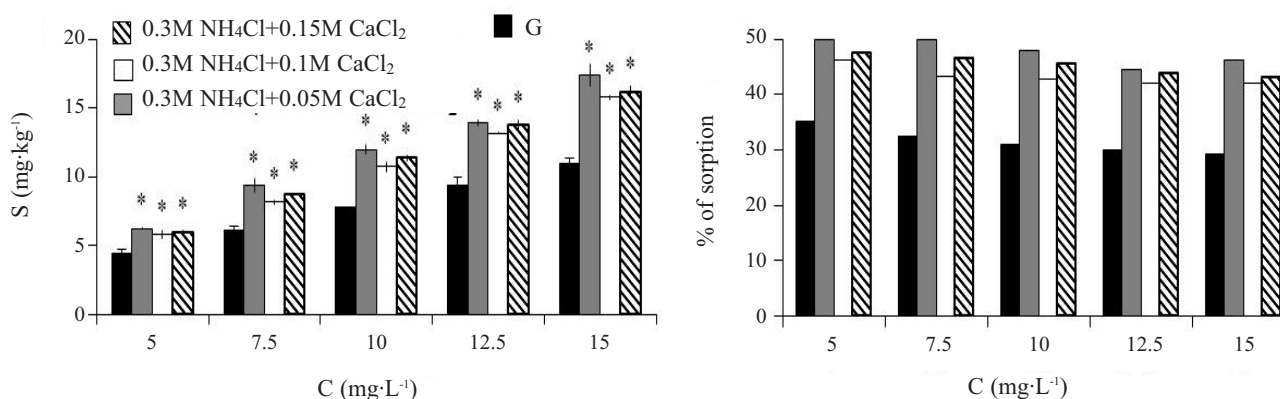
Radushkevich equations with R^2 values of 0.99 and low Δq values (<3.7%) for both tested isotherm equations.

Figs. 8 and 9 present the results concerning the effect of two-component mixtures of electrolytes (KCl+CaCl$_2$ and NH$_4$Cl+CaCl$_2$) on metamitron sorption in soil. The maximum sorption of metamitron was observed in binary systems with the highest electrolyte/CaCl$_2$ ratio, whereas with the decrease in the electrolyte/CaCl$_2$ ratio, metamitron sorption in soil decreased in two-component systems. Li et al. [46] studied the sorption of pesticides by smectites from solutions with various ratios of K$^+$ to Ca^{2+} ions and showed that pesticide sorption decreased at low K$^+$ to Ca^{2+} ratio in the solution. Whereas, a considerable increase of pesticide sorption was observed by those authors at a high ratio of K$^+$ to Ca^{2+}, i.e. under such conditions when the inter-layer spaces of smectites were fully saturated with K$^+$ ions. Based on the n values, which were lower than unity and in the range 0.799-0.924, it can be concluded that sorption isotherms of metamitron in the studied two-component systems were non-linear (L-type). In addition, the values of K$_F$ in two-component systems were lower than those obtained in the single-component systems with KCl or NH$_4$Cl. On

the other hand, in comparison with systems without any addition of electrolyte and the single-component systems with CaCl$_2$, K$_F$ values were higher, indicating that the sorption of metamitron in CaCl$_2$+electrolyte systems was more efficient. It could be assumed that metamitron sorption in two-component systems was affected by both electrolyte components, but in a different manner. It seems justified taking into account the results from studies upon single-component electrolyte solutions in which it was confirmed that KCl and NH$_4$Cl electrolytes had a positive impact on metamitron sorption in soil G, thus opposite to CaCl$_2$. Probably the presence of K$^+$ or NH$_4^+$ cations in two-component systems has a greater impact on the sorption of metamitron than the presence of Ca^{2+} ions. However, negative effect of Ca^{2+} cations on the sorbed amounts of metamitron was also marked. This explains why the sorption of metamitron in two-component systems was lower than in a single-component system with either KCl or NH$_4$Cl, but higher than in the original soil without electrolytes. The negative effect of CaCl$_2$ on the sorption of metamitron in two-component systems could be a result of competition between Ca^{2+} and K$^+$ or NH$_4^+$ cations for sorp-

tion sites on clay mineral surfaces. As mentioned before, Ca^{2+} ions adsorbed in interlayer spaces of clay minerals are surrounded with a greater number of layers of water molecules than monovalent ions, and thus the distance between the planes of the layers of minerals increases, which has a negative effect on the sorption of organic compounds.

It should be noted that values of parameter E for tested two-component systems were within the range of 8.265-8.926 kJ·mol⁻¹ (Table 4), indicating that metamitron sorption in the two-component systems could be a combination of both physical and chemical sorption.

Conclusions

Results of the study indicate that K^+, NH_4^+, and Ca^{2+} cations significantly affect the intensity of metamitron sorption in soil. It has been shown that the presence of K^+ and NH_4^+ cations in soil increased metamitron sorption, whereas in the presence of Ca^{2+} its sorption decreased. As a result of increased metamitron sorption in soil containing K^+ and NH_4^+ cations the availability of the herbicide for weed roots and its mobility can be reduced. Therefore, after the application of metamitron to the soil fertilized with cations K^+ and NH_4^+ its herbicidal effect and leaching to deeper soil layers would be limited. A greater possibility of metamitron leaching through soil profile may occur on limed soils. This negative effect can be eliminated if plants treated by metamitron grow on soils that contain not only the Ca^{2+} cation, but also sufficient amounts of K^+ and NH_4^+ cations.

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