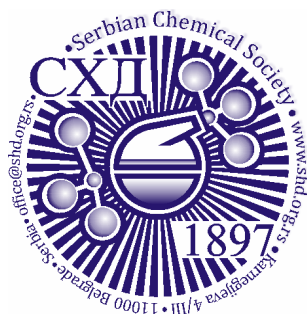




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Adsorption-desorption behaviour of clomazone in Planosol and Vertisol agricultural soils

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Abstract: Understanding of the processes that affect soil herbicide behaviour enables the prediction of their fate in the environment. Soil-herbicide interactions are governed by adsorption-desorption processes as only the free herbicide fraction participates in all other processes occurring in or on the soil. Given the agricultural and environmental significance of clomazone, its adsorption-desorption behaviour was investigated in two widely distributed Serbian agricultural soil types, Planosol and Vertisol. Both processes were well-described by Freundlich isotherms, and the obtained sorption parameters show that clomazone sorbed to both organic matter and mineral soil components. Vertisol, characterized by higher organic matter and clay content, demonstrated greater sorption capacities ($3.67\text{--}21.23 \text{ mg}^{(n-1)/n} \text{ dm}^{3/n} \text{ kg}^{-1}$ for $1.5\text{--}15 \text{ mg dm}^{-3}$) and lower desorption rates (the amounts desorbed of $29.49\text{--}28.48 \%$ during 72 h for $1.5\text{--}15 \text{ mg dm}^{-3}$) compared to Planosol ($3.15\text{--}18.35 \text{ mg}^{(n-1)/n} \text{ dm}^{3/n} \text{ kg}^{-1}$ and $33.32\text{--}29.97 \%$ for $1.5\text{--}15 \text{ mg dm}^{-3}$). The more pronounced desorption hysteresis observed in Vertisol is likely attributable to the presence of a higher number of high-energy sorption sites compared to Planosol. These findings highlight the crucial role of soil composition in determining the environmental fate of clomazone, providing a valuable basis for developing agronomically effective and environmentally safe application recommendations.

Keywords: pesticides; sorption; soil; Freundlich modelling.

INTRODUCTION

Chemical weed control is essential for large-scale agriculture, but given the manner and amount of herbicide application, soil contamination is a central concern. The retention time of herbicides in soil depends on many factors, including especially the soil's sorption capacity, fluid flow dynamics, and the solute transport in addition to degradation rates. Understanding the processes that

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herbicide molecules undergo after contact with soil is crucial for predicting herbicide efficacy and the fate of these agrochemicals in the environment.¹

Soil-herbicide interactions after the herbicide is found in the soil and/or soil solution are driven by sorption processes (sorption/desorption) of this compound, since all detoxification mechanisms, such as mobility, degradation (primarily microbiological) and plant uptake, relate only to the free (unsorbed) fraction of the molecules.² Knowledge of sorption constants (K_d , K_{oc} , K_{om}) and sorption isotherms (described by the Freundlich coefficients K_f and n_f) enables assessment of the mobility of pesticide molecules in the environment, especially their potential to enter groundwater.

In general, herbicides of concern for aquatic systems are those with water solubility $\geq 30 \text{ mg dm}^{-3}$, a sorption coefficient (K_d) $< 5 \text{ dm}^3 \text{ kg}^{-1}$ or a sorption coefficient normalized to organic carbon content (K_{oc}) in the range of 300-500 $\text{dm}^3 \text{ kg}^{-1}$, a hydrolytic half-life ($t_{1/2}$) > 6 months, a photolytic half-life ($t_{1/2}$) > 3 days, and/or a microbiological degradation half-life ($t_{1/2}$) $> 2-3$ weeks.³⁻⁵ Clomazone (IUPAC: 2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one), an isoxazolidinone herbicide, is a good example of such a herbicide.

Clomazone is a nonionic herbicide with relatively high water solubility (1100 mg dm^{-3}), moderate mobility (K_{oc} : 150-562 $\text{dm}^3 \text{ kg}^{-1}$) and persistence in soil (DT_{50} : 30-135 days), and moderate resistance to photolytic degradation ($t_{1/2}$: > 30 days).⁶ These properties, along with the potentially harmful effects this compound may have on cultivated plants after crop rotation,⁷ make clomazone a possible environmental contaminant of agricultural relevance.

Literature data indicate that clomazone sorption in soil occurs either through organic matter (OM)⁸⁻¹³ or through both OM and soil clay¹⁴. López-Piñeiro *et al.*¹⁵ found that clomazone sorption to soil increased with increasing soil acidity, while Gunasekara *et al.*¹⁰ and Xu *et al.*¹⁶ reported that soils with a history of fire events tend to have higher clomazone retention. Some studies indicate that clomazone sorption to soil decreases as herbicide concentration increasing,^{10,17,18} while some authors found that OM contained in various biochars used as soil amendments significantly increases clomazone sorption.^{12,15,16,19-23} The desorption of pesticides is also an important process, as it affects the amount of pesticide released from the soil to the soil solution and can further contribute to the processes of mobility, degradation, and plant uptake, thereby determining the activity of the compound in the environment. However, with the exception of our earlier study on clomazone desorption from Regosol and Chernozem soils,⁹ to our knowledge, there are only a few papers addressing clomazone desorption from soil^{10,12,15,20}. All of these studies have been conducted in rice production and flooded conditions, where clomazone may pose a particular environmental risk due to its relatively high solubility in water. Considering that these studies, as well as all other previously referenced papers, have examined clomazone adsorption behaviour in waterlogged

soils, it is clear that further research is needed on the adsorption/desorption behaviour of this herbicide in agricultural soils.

As previously mentioned, our previous study⁹ included Chernozem and Regosol, both developed under terrestrial environmental conditions without water excess. These alkaline, loam soils differed in humus content and clay mineralogy. The present study extends to Vertisols and Planosols²⁴ which are also widespread in crop production, predominantly occurring on level plains and covering 335 and 130 million hectares worldwide²⁵, and approximately 700,000 and 400,000 hectares in Serbia, respectively²⁶. Natural Vertisols and Planosols are characterised by a challenging water regime, where water excess and moisture stress alternate according to distinct wet and dry seasons. Vertisols are heavy soils, with a high proportion of swelling clays that cause a difficult water regime but also confer high chemical fertility. The waterlogging problem in Planosols can be mitigated by tillage practices in agricultural crop production.²⁵ Compared to the alkaline Chernozem and Regosol, investigated Vertisols and Planosols are acidic. Considering the all mentioned, the aim of this study was to determine the adsorption/desorption behaviour of clomazone in Planosol and Vertisol²⁴, two Serbian widespread soils used in crop production that may have problematic water regimes. The main objective was to establish whether, and to what extent, the amount of OM and clay in these soils influence the retention and release of clomazone, as well as to assess the extent to which different clomazone concentrations affect its adsorption/desorption behaviour.

EXPERIMENTAL

Reagents and materials

Analytical standard of clomazone (99.5 % purity) was supplied by Dr Ehrenstorfer, Germany. Its stock solution (1.5 g dm⁻³) was prepared in acetonitrile (J. T. Baker, Holland) and stored at -18 °C until further use.

Calcium chloride was purchased from Merck (Germany), and highly purified deionized water (Purelab Option – R7, Elga, UK) was used for preparation of 0.01 M CaCl₂ solution.

Working standard solutions of clomazone (0.5, 1.5, 3, 6, 9, 12 and 15 mg dm⁻³) were prepared by diluting its stock solution with 0.01 M CaCl₂ solution.

Samples of two agricultural soils, Planosol and Vertisol, were collected in October 2022 from the top 25 cm soil layer in fields where soybean had been grown that year. Planosol was sampled in Varna (44°41'N, 19°38'E; 110 m a.s.l.), and Vertisol in Umka (44°39'N, 20°17'E; 111 m a.s.l.). Clomazone had not been applied to these fields for at least 3 years prior to sampling. Soil samples were air-dried and sieved (2 mm mesh), and subsequently characterized by standard methods: soil texture by combining the sieving and pipette methods, using 0.1 M sodium pyrophosphate as a dispersing agent; organic carbon (OC) by the dichromate method; soil pH by the potentiometric method (soil/water 1/2.5)²⁷; and the soil textural class according to the USDA triangle²⁸ (Table I).

Planosol is a clay loam, strongly acidic, with low OC, and clay composed mainly of illite, with a small amount of smectite and chlorite. Vertisol is a clay, moderately acidic, with moderate OC, and clay consisting mainly of smectite, but also containing illite and kaolinite.

Mineralogical composition of the clay fraction was determined previously by XRD analysis and reported elsewhere.²⁹ Clay mineral composition was determined by X-ray diffraction (XRD) analysis of the clay fraction (<2 μm), following standard oriented aggregate preparation procedures including, ethylene glycol saturation and heating treatments.³⁰

TABLE I. General soil properties

Soil	pH (H_2O)	Content of soil components, %			
		OC	Sand	Silt	Clay
Planosol	5.20	1.28	24.7	39.8	35.5
Vertisol	6.08	1.91	20.7	34.1	45.2

Sorption experiments

Adsorption/desorption isotherms of clomazone were obtained using the batch equilibration method.³¹ Duplicate 2 g soil samples were mixed with 10 cm^3 of 0.01 M CaCl_2 solution with initial clomazone concentrations ranging from 0.5 to 15 mg dm^{-3} in 50 cm^3 polypropylene centrifuge tubes. Samples were equilibrated by shaking at 20 ± 1 $^\circ\text{C}$ on a rotary shaker during 24 h. Although our previous research showed that apparent equilibrium was reached within 8 h in Planosol and 6 h in Vertisol),¹⁸ for practical reasons and to be sure that full equilibrium was attained, 24 h was chosen as equilibration time. The suspensions were then centrifuged at 3000 rpm for 5 min, and the resulting supernatants were filtered through 0.22 μm membranes before further analysis. The amounts of clomazone adsorbed by the soils were calculated from the difference between the initial and supernatant concentrations in each sample.

For initial clomazone concentrations of 1.5, 6 and 15 mg dm^{-3} , desorption studies were conducted immediately after the adsorption process was completed, by replacing 5 cm^3 of the obtained supernatants with 5 cm^3 of clomazone-free 0.01 M CaCl_2 solution. The tubes were equilibrated for an additional 24 h on the rotary shaker, followed by centrifugation at 3000 rpm for 5 min, filtration of the obtained supernatants and chromatographic analysis. For all concentrations, three successive desorption steps were examined.

All sorption and desorption measurements were performed in triplicate.

Chromatographic analysis

Quantification of clomazone in the obtained adsorption/desorption supernatants was performed using the Shimadzu Prominence high performance liquid chromatography (HPLC) system, equipped with a pump model LC-20AD and diode array detector (DAD) model SPD-M20A. The following conditions were used: Eclipse XDB-C18 column (4.6 x 150 mm, 3.5 μm), acetonitrile/water (70:30, v v⁻¹) as the mobile phase at 1.0 $\text{cm}^3 \text{min}^{-1}$ the flow rate, 40 mm^3 injection volume, and quantification at 214 nm. The detection and quantification limits were 0.0009 and 0.003 mg dm^{-3} , respectively.

Data analysis

Adsorption/desorption coefficients (K_d / $\text{dm}^3\text{kg}^{-1}$) were calculated as the ratio of the clomazone concentration in soil after completion of the adsorption/desorption experiments (c_s / mg kg^{-1}) and equilibrium concentration in the solution (c_e / mg dm^{-3}) according to Eq. (1):

$$K_d = \frac{c_s}{c_e} \quad (1)$$

The K_{OC} coefficients were calculated by normalizing K_d coefficients to the soil OC contents according to equation:

$$K_{OC} = \frac{K_d}{\text{Content of OC}} \times 100 \quad (2)$$

Adsorption/desorption isotherms were fitted using the Freundlich equation

$$c_s = K_f c_e^{1/n_f} \quad (3)$$

and the Freundlich constants K_f and n_f were calculated from the linear form of the Eq. (3):

$$\log c_s = \log K_f + \frac{1}{n} \log c_e \quad (4)$$

The desorption percentage (D / %) for all desorption steps was calculated using Eqs. (5) and (6):

$$D = 100 \times \frac{c_{s(\text{ads})} - c_{s(\text{des},1)}}{c_{s(\text{ads})}} \quad (5)$$

$$D = 100 \times \frac{c_{s(\text{des},i)} - c_{s(\text{des},i+1)}}{c_{s(\text{des},i)}} \quad (6)$$

where $c_{s(\text{ads})}$ and $c_{s(\text{des}, i)}$ are the clomazone concentrations in the soil after the completion of adsorption and desorption steps, respectively, and i is the number of desorption steps ($i=1-3$).

The hysteresis coefficients (H) were calculated for the adsorption/desorption isotherms according to Eq. (7):

$$H = \frac{1/n_{\text{des}}}{1/n_{\text{ads}}} \quad (7)$$

where $1/n_{\text{ads}}$ and $1/n_{\text{des}}$ are the Freundlich slopes obtained for the adsorption and desorption isotherms, respectively.

RESULTS AND DISCUSSION

Clomazone adsorption studies

In order to compare the experimental results with previously published ones for Chernozem and Regosol soils that were obtained under the same experimental conditions⁹, the adsorption/desorption behaviour of clomazone was modelled by the Freundlich equation. Clomazone adsorption/desorption isotherms for the two agricultural soils studied are shown in Fig. 1. Distribution coefficients and Freundlich parameters obtained for clomazone adsorption are presented in Table II.

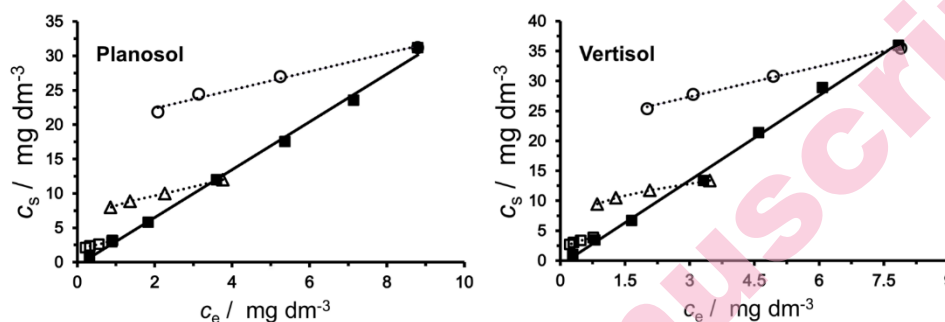


Fig. 1. Adsorption/desorption isotherms of clomazone in two Serbian agricultural soils: (■) adsorption; (□) desorption for 1.5 mg dm⁻³; (Δ) desorption for 6 mg dm⁻³; (○) desorption for 15 mg dm⁻³

TABLE II. Distribution coefficients and Freundlich parameters for clomazone adsorption on the soils

	Soil	
	Planosol	Vertisol
$K_d(ads) / dm^3 kg^{-1}$	3.41 (± 0.05)	4.59 (± 0.08)
r^2	0.998	0.998
$K_{OC(ads)} / dm^3 kg^{-1}$	266.40	240.30
$K_f(ads) / mg^{(n-1)/n} dm^{3/n} kg^{-1}$	3.14 (± 0.01) ^a	4.05 (± 0.01)
$1/n(ads)$	1.04 (± 0.01)	1.07 (± 0.02)
r^2	0.999	0.998

^a Value in parentheses is the 95 % confidence interval.

As Table II shows, clomazone adsorption behaviour is well described by the Freundlich model with correlation coefficients (r^2) of 0.999 and 0.998 for Planosol and Vertisol soils, respectively. According to the Giles classification³², the obtained isotherms (Fig. 1) are C-type, indicating that their slopes are independent of the initial clomazone concentration in the solution. This is further confirmed by the $1/n(ads)$ parameters with values close to 1 for both soils studied (Table II). The same type of isotherms was obtained for Regosol and Chernozem, two other widespread Serbian soils used in crop production⁹, which indicates constant partition of clomazone molecules between all the studied soils and soil solutions.

Across the entire initial clomazone concentration range studied (0.5–15 mg dm⁻³), adsorption in Vertisol was consistently higher than in Planosol (Fig. 1). This observation is further supported by the adsorption coefficients K_d and Freundlich adsorption constants $K_f(ads)$, which were higher for Vertisol than for Planosol (Table II). According to the universal hypothesis, organic matter is the dominant component involved in pesticide adsorption in soils where its content exceeds 5%, while in soils with lower organic matter content, adsorption can occur on both the organic and inorganic fractions of the soil, primarily humic acids and clays.³³⁻³⁵

Therefore, considering the higher OC and clay contents in Vertisol compared to Planosol (Table I), higher adsorption could be expected in Vertisol, as was experimentally confirmed by K_d and $K_{f(ads)}$. However, if we assume that OC is the dominant soil component involved in clomazone adsorption, the values of the $K_{OC(ads)}$ coefficients calculated for both soils should be very similar. Comparing the $K_{OC(ads)}$ constants presented in Table II, it is clear that clay also plays a role in clomazone adsorption in both tested soils. The lower $K_{OC(ads)}$ constant obtained for Vertisol, which based on the K_d and $K_{f(ads)}$ coefficients adsorbs clomazone more strongly than Planosol, is probably a consequence of partial coverage of organic matter, that is blocking of the active adsorption centres of organic matter by clay. Additionally, differences in soil mineral composition and texture may also influence the sorption process. Vertisols are rich in the clay fraction, dominated by expansive smectite minerals that swell with increased moisture, whereas Planosols are clay loams with illite as the dominant clay mineral.¹⁸ In general, clay minerals may contribute to clomazone retention through hydrogen bonding, dipole-dipole interactions, and surface adsorption on hydroxylated mineral surfaces. Although clomazone does not undergo cation exchange because it occurs predominantly as a neutral molecule, its polar functional groups can interact with exposed hydroxyl groups located on clay mineral edges and external surfaces.³⁶ Although raw smectite is not the most effective sorbent for clomazone, it still exhibits a higher sorption capacity than illite or kaolinite.³⁷ On other side, non-ionic herbicides such as clomazone can be adsorbed to organic matter by physical and chemical sorption mechanisms, including Van der Waals forces, ligand exchange, and hydrogen bonding.³⁷ There are scarce experimental results on clomazone-OM component binding mechanisms. Loux *et al.*³⁷ indicated that hydrophobic bonding is one mechanism of clomazone adsorption on OM, based conclusions on mean Koc values.

Linear and multiple regression analyses between selected soil properties and the distribution coefficients ($K_{d(ads)}$ and $K_{OC(ads)}$) as well as the Freundlich parameters ($K_{f(ads)}$ and $1/n_{(ads)}$) were conducted (Supplementary material, Tables S-I and S-II) based on data from this study and previously published source⁹ using the Data Analysis Tool Pak in Microsoft Excel 2016.

A significant correlation ($p < 0.05$) was found only between the constant $K_{OC(ads)}$ and soil pH ($r = 0.997$, $p = 0.003$) (Table S-I), indicating that $K_{OC(ads)}$ decreases with increasing soil pH ($K_{OC(ads)} = -27.5418 \times \text{pH} + 409.0384$). A decrease in clomazone sorption with increasing soil pH was reported by López-Piñeiro *et al.*¹⁵ who studied the impacts of fresh and aged holm oak biochar on clomazone behaviour in rice cropping soils. A multiple correlation analysis between the sorption data and combinations of two soil parameters showed a significant correlation ($p < 0.05$) of $K_{OC(ads)}$ with both OC and sand contents, as well as with soil acidity and silt content (Table S-II). Therefore, these multiple

correlation analyses provide linear predictive models for $K_{OC(ads)}$. Considering all multiple linear functions of sorption data that were significantly or relatively well correlated with combinations of soil properties (Table S-II), it is clear that in addition to the OC content and acidity of the tested soils, soil texture has a significant influence on clomazone adsorption. A similar conclusion was drawn in a kinetic study of clomazone sorption in four agricultural soils.¹⁸

By comparing our results with literature data, a relatively good agreement between adsorption coefficients $K_{d(ads)}$, $K_{OC(ads)}$ and $K_{f(ads)}$ can be found (Table S-III).^{9,17-19} However, as the clomazone concentration ranges^{8,10} and soil/soil solution ratios^{8,10-12,14-16,20,23,37,38} used in other studies are often not uniform and differ from ours, some discrepancies between our results and those previously published are not surprising. For example, Gunasekara *et al.*¹⁰, Xu *et al.*¹⁶ and Pena *et al.*¹⁹ obtained L-type isotherms, while the reported $K_{d(ads)}$ and $K_{OC(ads)}$ coefficients were higher^{10,14} or lower^{11,12,15,20,21,23} than our findings. Similarly, previously reported $K_{f(ads)}$ values were higher^{10,14} or lower^{16,21,23} than those obtained in this study.

Clomazone desorption studies

Clomazone desorption isotherms for the two agricultural soils studied are presented in Fig. 1, while the Freundlich desorption parameters, hysteresis coefficients and desorption percentages obtained by applying Eqs. (4)-(7) to the experimental data are listed in Table III.

TABLE III. Freundlich parameters ($K_{f(des)}$ and $1/n_{(des)}$), hysteresis coefficients (H) and desorption percentages (D) for clomazone desorption in Planosol and Vertisol

	Planosol			Vertisol		
	Initial concentration, mg dm ⁻³					
	1.5	6	15	1.5	6	15
$K_f^{(des)} / \frac{mg^{(n-1)/n}}{dm^3 kg^{-1}}$	3.15 (± 0.01) ^a	8.22 (± 0.01)	18.35 (± 0.01)	3.67 (± 0.01) ^a	9.82 (± 0.00)	21.23 (± 0.01)
$1/n^{(des)}$	0.27 (± 0.03)	0.28 (± 0.03)	0.24 (± 0.01)	0.19 (± 0.03)	0.25 (± 0.00)	0.24 (± 0.02)
r^2	0.965	0.973	0.992	0.933	0.999	0.987
H	0.261	0.266	0.232	0.176	0.237	0.228
$D(I)^b / \%$	17.18	16.42	13.55	11.86	12.25	13.29
$D(II) / \%$	9.06	11.45	9.49	10.25	10.72	9.88
$D(III) / \%$	11.47	9.82	10.50	10.87	9.99	8.49
Total $D(I-III) / \%$	33.32	33.26	29.97	29.49	29.49	28.48

^a Value in parentheses is the 95 % confidence interval; ^b Number of desorption cycles.

The data indicate that clomazone desorption behaviour is well described by Eq. (4) for all three initial concentration levels of clomazone, with r^2 ranging from 0.965 to 0.992, and 0.933 to 0.999 for Planosol and Vertisol, respectively.

By comparing the $1/n$ Freundlich parameters obtained for adsorption (Table II) and desorption (Table III), it can be concluded that $1/n_{(ads)}$ values are much

higher than $1/n_{(des)}$, regardless of both the initial clomazone concentration and the soil types studied. This indicates that a significant amount of adsorbed clomazone is not easily desorbed and that desorption cannot be predicted on the basis of adsorption isotherms. It has also been reported previously that the sorption of clomazone to soil is not a reversible process.^{9,10,15,20}

The calculated hysteresis coefficients (Eq. 7) range from 0.232-0.266 and 0.176-0.237 for Planosol and Vertisol, respectively (Table III), which are comparable with the values obtained for Regosol and Chernozem in our previous study⁹. However, these values were somewhat higher than those reported for clomazone adsorption-desorption behaviour in four American soils,¹⁰ but given their different origins, types of land use, and management practices, this inconsistency was to be expected. As shown in Table III, for each initial clomazone concentration in the study, the H value obtained for Planosol was higher than that for Vertisol, indicating that Vertisol, with its higher adsorption capacity (Table II), has a lower tendency to desorb clomazone. Considering that only the free fraction (unadsorbed) of clomazone molecules can participate in detoxification mechanisms such as mobility, degradation (primarily microbiological) and uptake of pesticides by plants, i.e. target organisms, it is obvious that there is a greater tendency for Planosol pollution, including a bigger potential for leaching, i.e. pollution of deeper soil layers and even groundwater.

The desorption percentages ($D / \%$) for all three successive desorption steps, as well as the total percentage of clomazone desorbed calculated by Eqs. (5) and (6) are presented in Table III. As shown, regardless of soil type and initial clomazone concentration in the adsorption-desorption study, the amount desorbed decreases with each subsequent desorption step in most cases. These results confirm the hypothesis of bound residues, which states that only clomazone molecules weakly bound to soil can be easily desorbed. Considering the total amounts of clomazone desorbed during all three consecutive desorption cycles (D (I-III)) for both soils studied, it seems that these fractions are highly dependent on the initial clomazone concentration. For both soils, the decrease in D (I-III) values with increasing initial clomazone concentration in the soil-solution system, indicates that high-energy binding sites are limited, and become progressively saturated as the solute concentration increases. By comparing the D (I-III) values obtained for Planosol (33.32-29.97 %) and Vertisol (29.49-28.48 %), it can be stated that desorption is higher from Planosol regardless of the initial clomazone concentration. These results were expected, considering the higher adsorption capacity (Table II) of Vertisol compared to Planosol. The results obtained along with the possible water saturation of Planosols in some parts of the year, highlight the necessity for responsible clomazone application in this soil.

Comparison of our results with literature data (Table S-III) indicates good agreement of obtained K_f (des), n (des) and D values with those obtained for

Chernozem and Regosol soils.⁹ However, Gámiz *et al.*²³ obtained $K_{f(des)}$ coefficient lower than our findings, Gámiz *et al.*²³ and Gunasekara *et al.*¹⁰ reported lower $n_{(des)}$ values than those presented in this study, while D values obtained in this study are lower than those published by Vicente *et al.*¹², López-Piñeiro *et al.*¹⁵ and Pena *et al.*¹⁹ Considering that soil/soil solution ratios^{12,15,19,23} and the clomazone concentration range¹⁰ are not uniform and differ from ours, discrepancies between our results and those previously published are not surprising.

CONCLUSION

The study of the adsorption-desorption behaviour of clomazone in two widespread Serbian agricultural soil types showed that, in addition to organic matter and clay as the main sorbing soil components, soil acidity and overall soil texture significantly influence the extent of this herbicide sorption. Regardless of soil type, the distribution of clomazone molecules between the soil and the soil solution is linear, and does not depend on the initial concentration of the herbicide in the system. Clomazone was found to adsorb more to Vertisol, which has a higher content of both organic matter and clay compared to Planosol. At the same time Vertisol showed a lower tendency to desorb herbicide molecules than Planosol. The greater hysteresis effect (lower H values) observed in Vertisol can be explained by the high-energy bonding hypothesis, which suggests that this soil contains more high-energy sorption sites than Planosol. Significant correlations established between the constant $K_{OC(ads)}$ and soil pH, as well as between the $K_{OC(ads)}$ and both OC and sand contents, soil acidity and silt content, provide predictive linear models for calculating the $K_{OC(ads)}$ constant based on soil characteristics. In order to provide more reliable models for predicting the adsorption/desorption behaviour of clomazone in agricultural soils, future studies must include a larger number of agricultural soil types in the type of research presented in this paper. These data are important for making reliable recommendations from both agronomic and environmental perspectives, especially for the protection of groundwater as a source of drinking water.

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ИЗВОД

АДСОРПЦИОНО-ДЕСОРПЦИОНО ПОНАШАЊЕ КЛОМАЗОНА У ПОЉОПРИВРЕДНОМ ЗЕМЉИШТИМА – ПЛАНОСОЛ И ВЕРТИСОЛ

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Познавање процеса који утичу на понашање хербицида у земљишту омогућава разумевање и предвиђање њихове судбине у животној средини. Интеракције земљиште–хербицид су вођене процесима адсорпције–десорпције, с обзиром на то да у свим осталим процесима који се одвијају у/на земљишту учествује само слободна фракција хербицида. С обзиром на пољопривредни и еколошки значај кломазона, његово адсорпционо–десорпционо понашање је проучавано у планосолу и вертисолу, као два широко распрострањена пољопривредна земљишта у Србији. Оба процеса су добро описана Фројндлиховим изотермама, при чему добијени параметри сорпције указују да се кломазон везује и за органску материју и за минералне компоненте земљишта. Вертисол, који карактерише већи садржај органске материје и глине, карактерише већи капацитет сорпције ($3,67\text{--}21,23 \text{ mg}^{(n-1)/n} \text{ dm}^{3/n} \text{ kg}^{-1}$ за $1,5\text{--}15 \text{ mg dm}^{-3}$) и нижи степен десорпције (десорбована количина од $29,49\text{--}28,48 \%$ у току 72 h за $1,5\text{--}15 \text{ mg dm}^{-3}$) у односу на планосол ($3,15\text{--}18,35 \text{ mg}^{(n-1)/n} \text{ dm}^{3/n} \text{ kg}^{-1}$ и $33,32\text{--}29,97 \%$ за $1,5\text{--}15 \text{ mg dm}^{-3}$). Израженији десорпциони хистерезис добијен за вертисол се може објаснити већим бројем високоенергетских сорпционих центара присутних у овом земљишту у односу на планосол. Приказани резултати указују да судбина кломазона у животној средини у великој мери зависи од састава земљишта, при чему представљају и значајну основу за развој агрономски ефикасних и еколошки безбедних препорука за примену.

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