

Article

Influence of SOM Composition, Clay Minerals, and pH on 2,4-D and MCPA Retention in Peri-Urban Soils

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Abstract: The use of ionic herbicides in urban and peri-urban areas has serious environmental and health consequences due to their common overapplication and mobility in the soil profile. The specific objective of this study was to evaluate the influence of soil organic matter (SOM) fractions and clay minerals on the retention of 2,4-D and MCPA on loamy sand and loam topsoil materials under the pH range of 3–7. The results obtained indicate their weak, unfavorable, and physical sorption, presumably governed by partitioning. 2,4-D exhibited high affinity for polar SOM fractions as well as to kaolinite and montmorillonite, both present in the studied peri-urban soils. MCPA sorption was mainly related to soil fulvic (FA) and humic acid (HA) content; however, the pesticide was sorbed to a lesser extent than 2,4-D due to its great water solubility. This was reflected in MCPA's low K_{oc} values (41.33 and 84.21), indicating its very high mobility and leachability in the studied soils. Meanwhile, 2,4-D was moderately mobile in sandy soil while classified as a non-leacher in the loam topsoil material. Both herbicides were preferably retained at a low soil pH (3–4), which, together with soil amendment with exogenous, well-humified organic matter, could minimize the potential health and environmental risks of their application.

Keywords: phenoxyacetic acids; peri-urban soils; fulvic acids; humic acids; sorption; soil colloids



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1. Introduction

A pesticide's fate in an agroecosystem, in most cases, occurs in the soil, which strongly influences its health and fertility [1]. Although the target organisms of the sprayed agrochemical are mainly plants, insects, or fungi, part of it accumulates in the soil as a drift-off with rain, post-harvest residues, or is translocated by plants [2,3]. Therein, it may undergo many dissipation reactions, resulting in pesticide immobilization, degradation, or leaching, depending on the magnitude of their sorption. The extent to which any organic chemical partition between solid and liquid phases in the soil depends both on its properties (solubility in water, logP, chemical structure) and the environmental conditions (pH, texture, colloid content). These factors also regulate the release of pesticide molecules back into the soil solution, determining whether the solid phase becomes their permanent sink, or only a temporary reservoir [4].

In urban and peri-urban environmental areas such as lawns, home gardens, parks, and greenhouses or arable lands, the application of herbicides is a common practice worldwide [2,5]. In fact, it is estimated that the use of pesticides by homeowners in the urban and peri-urban environment is approximately ten times higher compared to rural areas where sustainable agriculture prevails [6]. The overapplication of pesticides may evoke health problems in the non-target organisms as well as severe consequences in the urban environment. Therefore, it is essential to identify the potential adsorbents of agrochemicals and, since most of them accumulate in soils, determine the components responsible for their permanent binding and immobilization.

Organic matter is an important adsorbent for many pesticides, and it is well-known that non-ionic chemicals of a lipophilic nature respond directly to its increased content in soil [7,8]. In turn, according to some studies, the adsorption of organic compounds with polar, ionic, or ionizable features is rather correlated with the clay content of soils than with the organic matter content [9,10]. This is partly caused by the solubility effect, governed by the initial diffusion and affinity of the ionic chemicals for the hydrophilic sorption sites in soil. However, it has to be kept in mind that apart from clay minerals and hydroxides, individual SOM fractions (e.g., humic and fulvic acids) may also contribute to the fate of polar compounds [11–13], either by their immobilization or by acting as a transport vector for those compounds in natural systems. The major binding sites in humic (HA) and fulvic acids (FA) are usually carboxylic and phenolic groups, whose dissociation is regulated by the pH and inert electrolyte concentration [14,15].

Therefore, SOM adsorption capacity is attributed to the magnitude of the surface charge and the proportion of neutral and ionic sorbate forms, both governed by the pH [16–18]. This was highlighted by Chianese et al. [19], who reviewed the ability of humic acids to sorb cationic organic pollutants by electrostatic interaction with the COO^- groups of HA. Picollo et al. [20] proved that HA complexes with polyvalent cations are important binding sites for glyphosate in soils. Similarly, Jing et al. [21] demonstrated that polar functional groups in the humic acid control the sorption of a macrolide biopesticide and its derivatives by the soil. Therefore, the amount and ratios of humic and fulvic acids subsequently determine the specific pesticide reactivity with the soil colloidal fraction [22–24]. As a consequence, polar SOM fractions may serve as potential sinks for these substances in soils.

The pesticides chosen for the study, namely 2,4-D and MCPA, belong to the group of phenoxyacetic acids. This is a group of anionic herbicides commonly used in agriculture and horticulture in urban and peri-urban areas [2,5,25]. Both agrochemicals are approved for use in the European Union as well as many other countries, despite the fact that they are equivocal endocrine disruptors [26–28]. They pose a potential risk for water sources due to their relative mobility and poor biodegradability in aqueous systems, which is related to their acidic carboxyl group [29,30]. With respect to this structural feature, both phenoxyacetic acids are mostly present in their anionic forms when applied to managed or urban soils, as their pH is usually maintained within 5.5–7.5 [31,32], which is far above the pK_a levels of herbicides. This may induce their enhanced mobility in soil, as the solubility effect primarily governs their fate, especially when the soil lacks for potential herbicide sorbents.

Concerning the pool of factors decisive in 2,4-D and MCPA adsorption in soil, the important role of soil organic carbon, inorganic colloids, and low pH in the sorption of herbicides has been previously confirmed by other researchers [15,33–35]. According to the study of Werner et al. [36], soil organic matter and iron oxides are the most relevant sorbents for phenoxy herbicides. Indeed, hydrous oxides of aluminum and iron have been proven to be efficient sorbents of 2,4-D and MCPA in soil [24,37]. Meanwhile, some contrasting studies can be found concerning the affinity of montmorillonite and kaolinite for the investigated phenoxyacetic acids, pointing out their either favorable [38,39] or minimal sorption onto clay minerals [38,40]. A particularly important finding was made by Haberhauer et al. [23], who observed that soils amended with polar organic material sorbed more MCPA than those amended with hydrophobic organic matter. The results of their study implied that the origin and type of the soil organic matter may play a greater role in the sorption of MCPA in soil than the overall organic matter content, which was corroborated by Waldner [30]. Hiller et al. [41] showed that MCPA sorption was positively correlated with SOM as well as the humic and fulvic acid carbon contents of soil. Both phenoxyacetic acids exhibited a high affinity for freeze-dried humic acid in a single-sorbent system, although a substantial desorption of 2,4-D from HA was also observed [12]. Despite the extensive studies, the behavior of 2,4-D and MCPA in soils needs further research, as there is a lack of understanding of the mutual share of different soil components and their associations (i.e., the presence of the soil organic matter of various humification degree,

individual SOM fractions, or humic acid–clay complexes) to the retention of this still currently used herbicide group.

Considering the importance, the study aimed to evaluate the sorptive behavior of 2,4-D and MCPA herbicides in peri-urban soils under agricultural use. As the investigated agrochemicals are equivocal endocrine disruptors, it is vital to monitor which soil parameters are decisive in terms of their retention in the soil or mobility to groundwater. Therefore, the specific objective of the paper was to determine which individual soil organic matter fraction and/or clay minerals are the most efficient sinks for the tested agrochemicals in sandy loam and loam topsoil materials, and to find the optimal pH conditions of their immobilization. The obtained results may contribute to the health and environmental risk assessment in urban and peri-urban areas, and serve as a theoretical base on which to model efficient strategies for the sustainable use of agrochemicals.

2. Materials and Methods

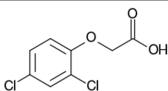
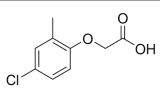
2.1. Chemicals and Sorbents

The pesticides chosen for this study (Table 1) were 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-methyl-4-chlorophenoxyacetic acid (MCPA), which were purchased as analytical standards from Merck (Darmstadt, Germany). Stock solutions of all pesticides were prepared in 10 mM CaCl₂ using ultrapure water (Merck Millipore DirectQ3 system, Warsaw, Poland). The working standard pesticide solutions were used straight after their preparation or stored at 4 °C.

The following clay minerals—kaolinite (KGa-1b) and montmorillonite (STx-1b)—were purchased from the Clay Minerals Society Repository (CMS, Chantilly, VA, USA). According to the source literature [42], utilized kaolin KGa-1b clay is a well-crystallized colloidal material, composed mainly of SiO₂ (44.2%), Al₂O₃ (39.7%), TiO₂ (1.39%), Fe₂O₃ (0.13%), and FeO (0.08%). Its cation exchange capacity (CEC) is estimated to be 2.0 meq 100 g^{−1}, while the surface (N₂ BET) area is 10.05 ± 0.02 m² g^{−1}. In general, kaolinite consists of one silica layer (silicon tetrahedrally coordinated with four oxygen atoms) and an adjacent alumina octahedron (aluminum octahedrally coordinated with two oxygen atoms and four −OH groups) [43]. The exposed planar clay surface of kaolinite consists of a layer of oxygen and a layer of the hydroxyl groups [44]. STx-1b montmorillonite is abundant in SiO₂ (70.1%), followed by minor amounts of Al₂O₃ (16.0%), TiO₂ (0.22%), Fe₂O₃ (0.65%), and FeO (0.15%). It is a Ca-rich montmorillonite with a CEC of 84.4 meq 100 g^{−1} and N₂ BET area equal to 83.79 ± 0.22 m² g^{−1}. Structurally, it contains a layer of silica tetrahedrons (silicon coordinated with four oxygen atoms) on each side of an alumina octahedron. In this structure, each exposed planar surface consists of an oxygen atom [44].

The humic acid (HA) utilized in the present study was extracted according to the procedure recommended by the International Humic Substances Society [45]. It was derived from the loam topsoil material of Gleyic Phaeozem (Domaniów near Wrocław, Poland), followed by freeze-drying of the sample at −46 °C. It is a low ash organic sorbent (1.19% w/dw), characterized by the total acidity of 5.46 meq g^{−1} with the prevalence of phenolic functionalities (69%) over the carboxylic groups [12].

Table 1. Physicochemical properties of the studied phenoxyacetic acids [46].

Compound	2,4-D	MCPA
Molecular structure		
Solubility in water (mg L ^{−1}) at 20 °C	24,300	250,000
Octanol-water partition coefficient Log <i>P</i>	−0.82	−0.81
pKa	3.40	3.73

2.2. Characterization of the Peri-Urban Soils under Study

Two topsoil samples (0–30 cm) from peri-urban areas near Wrocław, Poland were collected for the study. Materials were air-dried, sieved, and the fraction of the soils <2 mm were further analyzed. Details concerning the methodology and their basic physicochemical properties (Table 2) were discussed in our previous study [32]. The soils were mostly Phaeozems and Umbrisols [47] of the sandy loam (L) and loam (C) texture of A horizon, representing the light and heavy groups of soils that are most commonly found in the studied area [48]. Mineralogical composition of the clay fraction revealed that montmorillonite and kaolinite were the dominant clay minerals, followed by minor amounts of the highly dispersed quartz [32].

Table 2. Basic physiochemical properties of sandy loam (L) and loam (C) soil material under study *.

Soil	pH (KCl)	CaCO ₃ [%]	CEC [cmol _c ·kg ^{−1}]	Ca	C _{tot}	C _{org} [%]	N	C _{org} :N	Sand	Silt	Clay
L	7.2	0.6	26.4	23.9	1.3	0.95	0.1	7.1	76	17	7
C	7.4	1.1	42.3	39.1	1.6	1.5	0.2	8.4	47	34	19

* Previously published by Ćwieląg-Piasecka et al. [32].

2.2.1. Fractionation of Soil Organic Matter of L and C Soils

Humic material of the L and C soils was fractionated (Table 3) according to the method recommended by the IHSS, described in Swift [45] with some modification [31,49]. Briefly, carbon of the low-molecular fulvic fraction was obtained by soil sample decalcification with 0.05 M H₂SO₄, followed by the centrifugation of the mixture. The soil residue was further washed with distilled water until a neutral reaction was reached and subjected to the extraction procedure with 0.1 M NaOH, where the total extractable carbon (TEC) content was measured. In the next step, sulfuric acid was utilized to precipitate HA from the alkaline extract by decreasing the pH below the value of 2, followed by the determination of carbon of humic acids (CHA). The carbon of fulvic acids (CFA) fraction was calculated as the difference between the TEC and CHA contents. It was then centrifuged to separate the solid HA from the FA. Residual carbon (CR) was calculated by subtracting the sum of the humic and fulvic acids carbons from the total organic carbon (TOC) using the following equation:

$$CR = TOC - (CHA + CFA) \quad (1)$$

Table 3. Fractional composition of the organic carbon in the studied soil materials.

Fraction	TOC	CAC	TEC	CHA	CFA	CR	CHA/CFA
	g·100 g ^{−1}			% of TOC			
soil L	0.95	6.87	61.76	40.07	21.69	31.37	1.847
soil C	1.50	4.64	35.65	20.17	15.47	59.71	1.304

TOC—total organic carbon; CAC—carbon of low-molecular fulvic fraction, TEC—total extractable carbon (sum of CHA and CFA), CR—residual carbon. Previously published by Ćwieląg-Piasecka et al. [49]. Additionally, the CHA/CFA index was calculated to evaluate the humification degree of the studied peri-urban topsoils.

2.2.2. Amendment of L and C Soils with Inorganic and Organic Colloids

L and C soils amended with kaolinite (20% of KGa-1b w/dw), montmorillonite (20% of STx-1b w/dw), and humic acid (4% w/dw) were prepared according to the proportions given in Table 4. Sorption of the studied phenoxyacetic acids on the eight variants (including natural and amended L or C soils) was determined using a simplified batch equilibrium method [32]. Adsorption was measured using single-point concentration of the pesticides: 20 and 30 mg L^{−1} for 2,4-D and MCPA, respectively.

Table 4. Composition of the L and C soils amended with colloids.

Labelling	Soil Mass [g]	Mass and Type of Colloid Added [g]
L or C	2.5 g of soil L/C	-
LK or CK	2.0 g of soil L/C	0.5 g of KGa-1b *
LMt or CMt	2.0 g of soil L/C	0.5 g of STx-1b *
LHA or CHA	2.4 g of soil L/C	0.1 g of HA *

* KGa-1b—standard kaolinite, STx-1b—standard montmorillonite, HA—freeze-dried humic acid.

2.2.3. Preparation of Soil Materials of Varying pH (3–7)

Two sets of soils (L and C) varying in pH (3–7) were prepared according to the procedure described in a previous paper [49]. Briefly, the soils were saturated with distilled water and 1 M HCl solution was added dropwise to the soil slurry, followed by the equilibration of the mixtures until the desired final pH values were obtained. In the next step, the air-dried and ground soil materials were subjected to the final pH test where they were mixed with 10 mM CaCl₂ solution (1:2 m:v ratio to validate that the experimental pH values would be maintained). Adsorption was measured using a single-point concentration of 20 mg L^{−1} both for 2,4-D and MCPA. The pH range of 3–7 was chosen as it is common for undisturbed soils. pH values above 7 were excluded to avoid the enhanced SOM fractions, which results in the loss of the potential solid sorbent of the phenoxyacetic acids under study.

2.3. Batch Sorption Studies of 2,4-D and MCPA

Sorption–desorption studies of 2,4-D and MCPA, performed individually on the L and C soil, were conducted according to the OECD 106 and USEPA guidelines for the testing of chemicals [50]. A soil to solution (10 mM CaCl₂) ratio of 1:2 adopted in the preliminary investigation was used in all of the sorption experiments.

Soil aliquots (2.5 g of each soil material in triplicate) were mixed with 5 mL of pesticide aqueous solution at 20 ± 2 °C for 24 h [32] in the concentration range of 1–100 mg L^{−1} for 2,4-D and 1–130 mg L^{−1} for MCPA. In the next step, the samples were centrifuged (15 min, 10,000 rpm), filtered (0.45 µm), and the pesticide concentrations were analyzed with LC/MS-MS (TSQ Quantum Access MAX, Thermo Scientific, Waltham, MA, USA). The detailed quantification procedure can be found in our previously published papers [12,49,51]. In brief, the measuring conditions were as follows: analytical column—TS Hypersil GOLD column, 50 mm × 2.1 mm, with a 1.9 µm particle size; flow rate: 0.50 mL min^{−1}; mobile phase A: deionized water with 0.1% of formic acid and 90% acetonitrile; mobile phase B: 10% of deionized water and 0.1% of formic acid; elution conditions: 100% of eluent A at the beginning of the measurement was gradually replaced by eluent B, achieving 100% in 20 min, with a subsequent re-equilibration time of 7 min. The mass spectrometer measuring conditions: SRM mode; argon in the collision cell (99.995%, 1.87 × 10^{−3} mbar); capillary voltage: 4 kV, negative ionization mode; temperature of ion transfer capillary: 380 °C, vaporizer of the ESI probe: 400 °C.

The measured equilibrium concentrations of the studied pesticides (C_e; mg L^{−1}) were further used to calculate their amount sorbed in the L and C soils (Q_s; mg kg^{−1}) by subtracting their initial (C₀) and equilibrium concentrations (C_e) [52]:

$$Q_s = [(C_0 - C_e)V]/m \quad (2)$$

where V is the volume of solution (L) and m is the mass of soil (kg). The sorption magnitude (S, %) was defined as the percentage of substance adsorbed on the soil related to the quantity present at the beginning of the experiment [50].

Desorption studies were conducted on the soil samples remaining after the sorption experiment. Briefly, the samples were refilled with aliquots of 10 mM CaCl₂ and agitated for 24 h to evoke the potential release of the pesticide back to the solution. After centrifugation,

the supernatants were subjected to quantitative analysis by LC/MS-MS. The desorption magnitude (D) was calculated using the following formula:

$$D (\%) = Q_{de}/Q_{ad} \cdot 100\% \quad (3)$$

where Q_{de} is the amount of pesticide released from the soil (mg kg^{-1}) and Q_{ad} is the pesticide quantity initially adsorbed in the soil [52].

Sorption–desorption experiments aiming to determine the influence of pH and the addition of various colloids on the selected phenoxyacetic acids' adsorption to L and C soils were performed following the experimental procedure and conditions described above.

2.4. Mathematical Modelling of Sorption Isotherms

Results of the experimental batch sorption studies were approximated by Henry's (linear), Freundlich, and Temkin models. The constructed adsorption isotherm curves and values of important variables were determined based on the linearized isothermal equations.

2.4.1. Henry's Model

Henry's isotherm model is a linear relationship between the equilibrium adsorption capacity of the adsorbent (Q_e) and the equilibrium concentration of the adsorbate (C_e). It is derived from Gibbs adsorption and utilized to determine the adsorption equilibrium state of the isolated adsorbates at a relatively low concentration, at a constant temperature [53]. The model can be described with a linear expression:

$$Q_e = K_d C_e \quad (4)$$

where Q_e is the equilibrium adsorbate concentration (mg kg^{-1}); K_d is the Henry's adsorption binding constant (also called linear partition or distribution coefficient) of the adsorbate on the adsorbent surface (L kg^{-1}); C_e is the concentration of the adsorbate at equilibrium (mg L^{-1}).

Furthermore, the estimated K_d parameters were used to calculate the organic carbon normalized distribution coefficients K_{oc} for 2,4-D and MCPA on the L and C soils. K_{oc} , also known as the organic carbon-water partition coefficient, was determined following the equation below:

$$K_{oc} = (K_d/OC) \cdot 100\% \quad (5)$$

where OC is the organic carbon content of the soil (%).

K_{oc} is an important parameter describing the partitioning of pesticides in soil, which indicates the chemical's affinity for the organic fraction of the soil [4], being a measure of their relative potential mobility in soils. High values of organic carbon partition coefficient suggest an effective immobilization of the agrochemical in the soil organic matter fraction, at the same time pointing to a small risk of its leaching in the soil profile.

To measure the chemical percolation ability (leaching) in the soil profile and the risk of groundwater contamination, a groundwater ubiquity score (GUS) index must be determined [54], using the following equation:

$$GUS_{index} = (\log t_{1/2}) \cdot (4 - \log(K_{oc})) \quad (6)$$

where $t_{1/2}$ is the half-life of the chemical. According to the GUS classification, index values below 1.8 characterize non-leachers, while those above 2.8 indicate a very high mobility and potential leachability of the compound in the soil profile.

2.4.2. Freundlich Model

The Freundlich isotherm is a purely empirical formula for microporous and heterogeneous adsorbates, describing a multilayer adsorption [52,55]. The energetically favored binding sites are assumed to be occupied by the chemicals first, and the binding strength

decreases sequentially with their increased coverage. The following equation can be used to characterize the model:

$$Q_e = K_f C_e^{n_f} \quad (7)$$

where Q_e is the equilibrium adsorbate amount (mg kg^{-1}); C_e is the concentration of the adsorbate at equilibrium (mg L^{-1}); K_f is the Freundlich affinity coefficient ($(\text{mg kg}^{-1})(\text{mg L}^{-1})^{-n}$), being the measure of the pesticide affinity for soil. High K_f values indicate a strong adsorption of the pesticide to a sorbent, limiting the potential mobility of the substance in the soil profile [56,57]. n_f is the parameter associated with the energy distribution of the adsorption sites, reflecting the sorption favorability (values from 0 to 1) [58].

The linearized form of the Freundlich isotherm is expressed by the below equation:

$$\ln Q_e = \ln K_f + n_f \ln C_e \quad (8)$$

It yields a plot in which the n_f (slope) characterizes the nonlinearity of the isotherm. When $n_f \neq 1$, then K_d is often calculated to evaluate the extent of adsorption under equilibrium conditions [59].

Based on the Freundlich affinity coefficient (K_f), the thermodynamic parameter determining the spontaneity of the sorption process, namely, the standard Gibbs free energy (ΔG°), can be determined. However, prior to the ΔG° calculations (Equation (10)), the K_f parameters must be converted to the dimensionless standard equilibrium constants (K_c) using the following equation [60]:

$$K_c = K_f \cdot \rho \cdot 10^{-3} \cdot (10^6 / \rho)^{(1-n_f)}, \quad (9)$$

$$\Delta G^\circ = -RT \ln K_f \quad (10)$$

where ρ is the water density (1.0 g mL^{-1}); T is the temperature (K); R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). A negative ΔG° value informs that the process can conduct spontaneously, whilst the opposite indicates its non-spontaneous character [61].

2.4.3. Temkin Model

The Temkin isotherm assumes that the adsorption heat of all molecules in a layer decreases linearly with the coverage increase. The model ignores extremely low and very high concentrations of solute [52], assuming the uniform distribution of binding energy up to some maximum. It is described by the following equations:

$$Q_e = (RT/b_T) \ln C_e + (RT/b_T) \ln A \quad (11)$$

$$Q_e = B \ln C_e + B \ln A \quad (12)$$

where Q_e is the equilibrium amount of the adsorbed chemical (mg kg^{-1}) and C_e is the equilibrium concentration of the adsorbate in solution (mg L^{-1}). B is a constant related to the heat of adsorption and it is defined by the expression $B = RT/b_T$, where b_T is the Temkin constant (J mol^{-1}), T is the absolute temperature (K), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and A is the Temkin isotherm binding constant (L kg^{-1}). From the plot of Q_e vs. $\ln C_e$ (Equation (12)), B and A can be calculated from the slopes (B) and intercepts ($B \ln A$), respectively.

2.5. Statistical Analysis

The presented data reflect the mean values ($n = 3$) including the standard deviation (SD). The mean values of the pesticides' sorption and desorption magnitude on the studied soils, experiments on the pH influence as well as soil amendments with various colloids were subjected to the Shapiro–Wilk normality test, followed by the Student's t -test (at $p < 0.05$). Data were processed with Microsoft Excel 2019 and GraphPad Prism 9.5.1.733 software.

3. Results and Discussion

3.1. Isothermal Approximation of the Experimental Data

Batch studies upon the sorption of 2,4-D and MCPA on sandy loam (L) and loam (C) topsoil materials resulted in various shapes in the obtained sorption isotherms (Figure 1). MCPA on soil L revealed a C-type (linear) isotherm, while an S-type of Q_s to C_e relationship (concave-up [62]) was observed for 2,4-D on both the studied soils and MCPA on soil C. The linear isotherm is indicative for the relative adsorption of the chemical, being the same across the whole concentration range tested, whereas the concave-up is associated with unfavorable equilibrium caused by the weak adsorbent–adsorbate interaction [63]. The latter might suggest that the adsorption of the studied anionic pesticides on (SOM) and negatively charged surfaces (montmorillonite and kaolinite clays present in both soils) is weakened by the initially rather repulsive interactions, leading to their reduced uptake. It has also been hypothesized that at low concentrations, polar compounds are in competition with water for adsorption sites [64], which may explain the concave-up shape of the resulting isotherms. In the next phase, the increasing concentration of pesticide molecules facilitates the ongoing adsorption, leading to the S-type of isotherms [65].

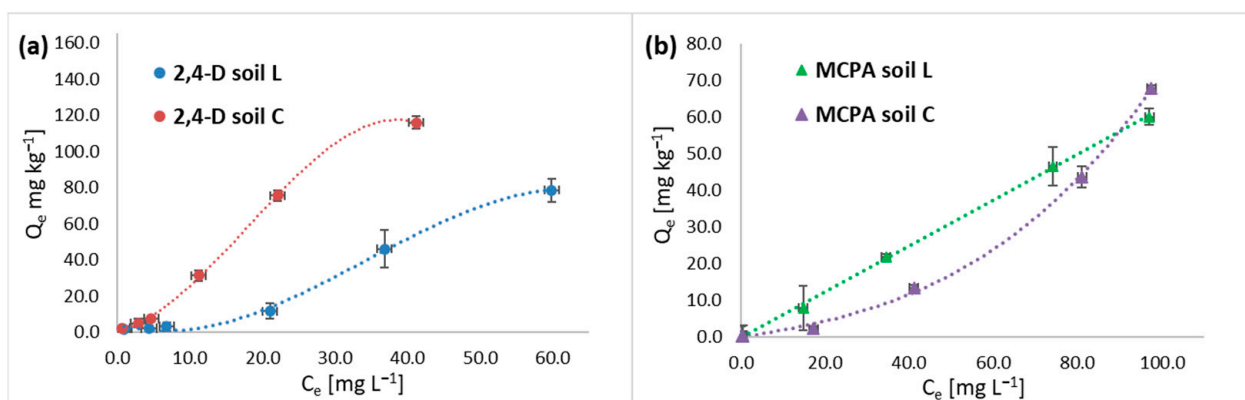


Figure 1. Adsorption isotherms of 2,4-D (a) and MCPA (b) on loamy sand (L) and loam (C) soil. Error bars denote standard deviation ($n = 3$).

The evaluated isotherms were approximated with Henry's, Freundlich, and Temkin models and their linear sorption parameters are summarized in Table 5. High correlation coefficients ($R^2 > 0.95$, Figure 2) were obtained for all of the models except for the Temkin model describing MCPA sorption on C soil. The good fitting of the linear and Freundlich approximations for the experimental isotherms may suggest that partitioning played an important role in the sorption mechanism of the agrochemicals [66,67].

Table 5. Linear sorption isotherm parameters of 2,4-D and MCPA evaluated for the L and C soils.

Soil	Pesticide	Linear		Freundlich			Temkin		
		$Q_e = K_d C_e$	R^2	$Q_e = K_f C_e^{n_f}$	n_f	R^2	$Q_e = (RT/b_T) \ln C_e + (RT/b_T) \ln A$	A	R^2
L	2,4-D	1.35	0.996	0.24	1.432	0.996	88.34	0.20	0.940
	MCPA	0.80	0.965	0.45	1.075	0.997	90.70	0.08	0.960
C	2,4-D	2.98	0.984	1.31	1.254	0.985	49.36	0.21	0.961
	MCPA	0.62	0.999	0.01	1.952	0.998	70.45	0.05	0.858

Q_e —amount of adsorbate at equilibrium (mg kg^{-1}); K_d is the Henry's adsorption binding constant (linear coefficient, L kg^{-1}), C_e —equilibrium concentration of the adsorbate (mg L^{-1}); K_f —Freundlich affinity coefficient ($\text{mg kg}^{-1}(\text{mg L}^{-1})^{-n_f}$); n_f —exponential coefficient expressing isotherm nonlinearity; R —gas constant, $8.31 \text{ (J mol}^{-1} \text{ K}^{-1})$; T —absolute temperature (K); b_T —Temkin isotherm constant (J mol^{-1}); A —equilibrium binding constant (L kg^{-1}).

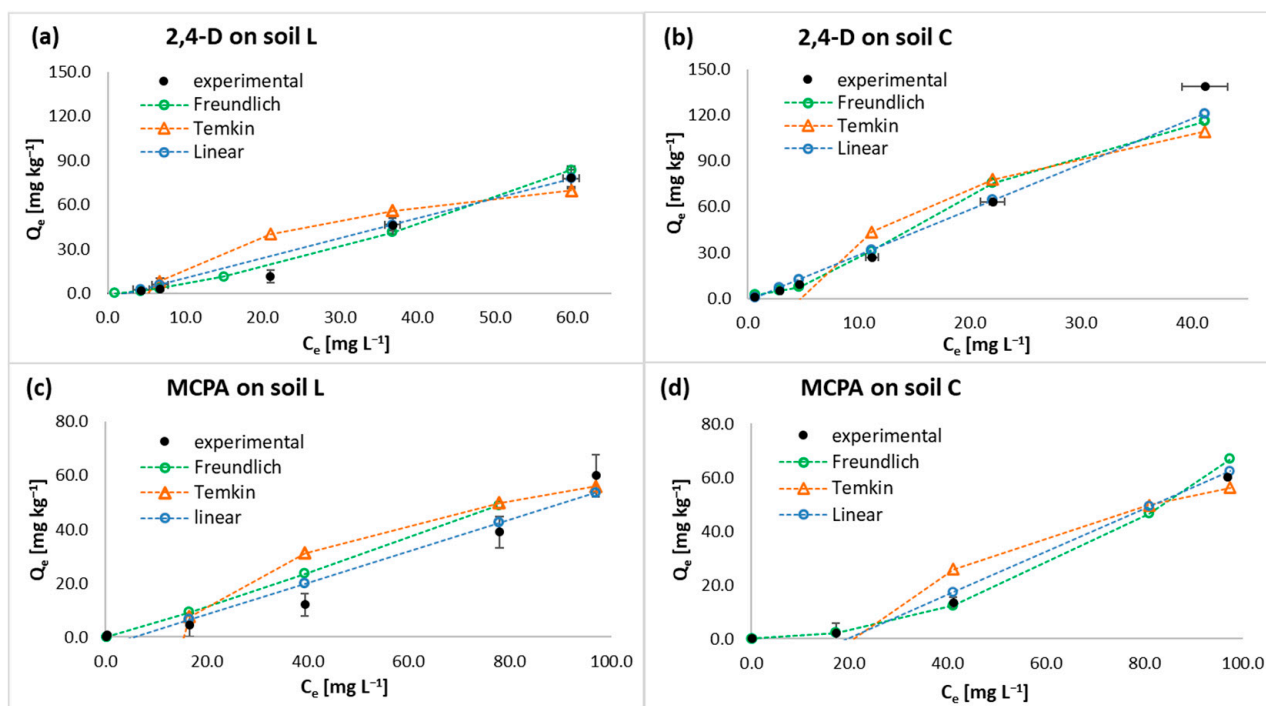


Figure 2. Comparison of the experimental data obtained for 2,4-D (a,b) and MCPA (c,d) on the studied L and C soils, with the calculated linear, Freundlich, and Temkin isotherms. Error bars denote the standard deviation ($n = 3$).

The adsorption intensity value (n_f) for the sorption of phenoxyacetic acids on the studied soils was in the range of 1.075 to 1.952. The n_f magnitude slightly exceeded 1, calculated for MCPA sorption on L topsoil, which confirms the pesticide linear adsorption. This corroborates the C-shape of the isotherm, pointing out that the primary mechanism regulating the adsorption of the agrochemical is presumably a constant partitioning between the soil components and the pesticide molecules [68]. In general, n_f values above one are often observed for compounds containing a polar functional group [64], which is in accordance with the results presented herein.

The Temkin b_T constant (amount of energy that is released), revealed a decreasing trend when comparing soil L to C. It can be concluded that the lower values of the constant obtained for loamy soil indicate the higher degree of surface coverage with the pesticides, compared to sandy loam soil material [69]. In addition, the values of the b_T parameter (Table 5) suggest that the sorption of 2,4-D and MCPA on L and C soil is presumably of a physical nature, due to the energy magnitude lower than $4.184 \text{ kJ mol}^{-1}$ (1 kcal mol^{-1}) [70].

The linear partition coefficients (K_d) for MCPA on both of the studied soils were much lower than for 2,4-D. This reveals the higher 2,4-D affinity for active sorption sites on L and C soils compared to MCPA. Such behavior might be partly related to MCPA's over ten times higher water solubility compared to 2,4-D (Table 1) as well as its relatively high soil pH, dictating the prevalence of the herbicide's anionic form in the solution. In addition, the K_d coefficient's magnitude (0.62 to 2.98 L kg^{-1}) was higher than the analogous Freundlich constants (K_f), which ranged from 0.01 to 1.31 (Table 5). The lowest value of the parameter was elaborated for MCPA on C soil (0.01), confirming the extremely low potential of the soil to sorb the agrochemical. This is particularly well-illustrated when the sorption magnitudes of 2,4-D and MCPA on both of the studied soils are compared (Figure 3).

The unfavorable MCPA and 2,4-D sorption on the investigated soils was corroborated by the magnitude of the standard free Gibbs's energy (ΔG°). The calculated ΔG° parameters for 2,4-D and MCPA on L soil were equal to 35.44 and $21.66 \text{ kJ mol}^{-1}$, respectively. Their positive value corroborates the non-spontaneous sorption of the phenoxyacetic acids on L soil. The ΔG° determined for loamy topsoil reached 15.19 and $51.17 \text{ kJ mol}^{-1}$ in the case of

2,4-D and MCPA, respectively, which is in agreement with the herbicides' calculated low K_d values and concave-up isotherm shape (Figure 1).

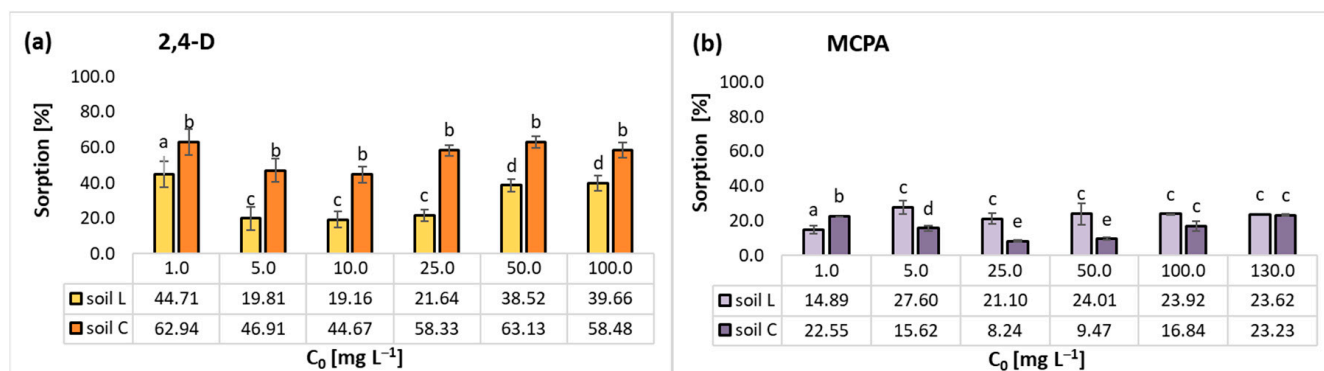


Figure 3. Sorption magnitude of 2,4-D (a) and MCPA (b) on L and C soils with respect to the herbicides' initial concentration (C_0). Error bars denote the standard deviation ($n = 3$). Different letters represent the statistical difference at the significance of $p < 0.05$.

3.2. Leaching Potential of the Phenoxyacetic Acid Herbicides in the Studied Topsoils

Parameters of K_d calculated from linear approximation were further used to calculate the K_{oc} values and GUS indices, determining the pesticide's mobility and leachability, respectively (Table 6). The obtained K_{oc} was below 500, which specifies the minimum or no adsorption at all of a pesticide to the soil and indicates the high probability of runoff or leaching [10,71]. According to McCall's soil mobility classes, MCPA belongs to a group of compounds of very high mobility ($K_{oc} < 50$) and are highly mobile ($50 < K_{oc} < 150$ [72]) in the L and C soils, respectively. 2,4-D exhibits high mobility (142.62) on L soil, whereas on C soil, it can be classified as a medium mobile compound.

Table 6. Parameters expressing the mobility (K_d , K_{oc} , $\log K_{oc}$) and leaching potential (GUS) of the studied pesticides on the L and C soils.

Pesticide	L Soil				C Soil			
	K_d	K_{oc}	$\log K_{oc}$	GUS *	K_d	K_{oc}	$\log K_{oc}$	GUS *
2,4-D	1.35	142.62	2.15	1.85	2.98	198.34	2.30	1.70
MCPA	0.80	84.21	1.93	2.90	0.62	41.33	1.62	3.33

* $t_{1/2}$ was taken from [73].

The FAO mobility ranking [64], based on $\log K_{oc}$ values, classifies MCPA as mobile on both the L and C soils studied ($\log K_{oc}$ values of 1.93 and 1.62 on sandy loam and loam soil, respectively), which is in accordance with the literature findings [46]. 2,4-D is moderately mobile on both soils, achieving $\log K_{oc}$ values within the range of 2 to 3. Hence, MCPA is a potential leacher in both L and C soils, with a higher potential to percolate C soil, irrespective of its greater abundance in soil constituents capable of retaining the herbicide.

Overall, based on calculated GUS indices, the lowest risk of C soil percolation, taking into account the average half-life of the agrochemical in soils, was obtained for 2,4-D (1.70). The herbicide exhibited slightly moderate potential for movement toward groundwater in loamy sand soil, achieving a GUS value of 1.85. The MCPA GUS indices calculated for both of the studied soils were higher than 2.8, corroborating the great leaching potential of the pesticide.

The calculated leaching potentials should be consistent with the results of the desorption studies, as they provide information on the release rate of the chemical in soil. 2,4-D and MCPA revealed different patterns concerning their sorption–desorption behavior on the investigated soil materials (Figure 4).

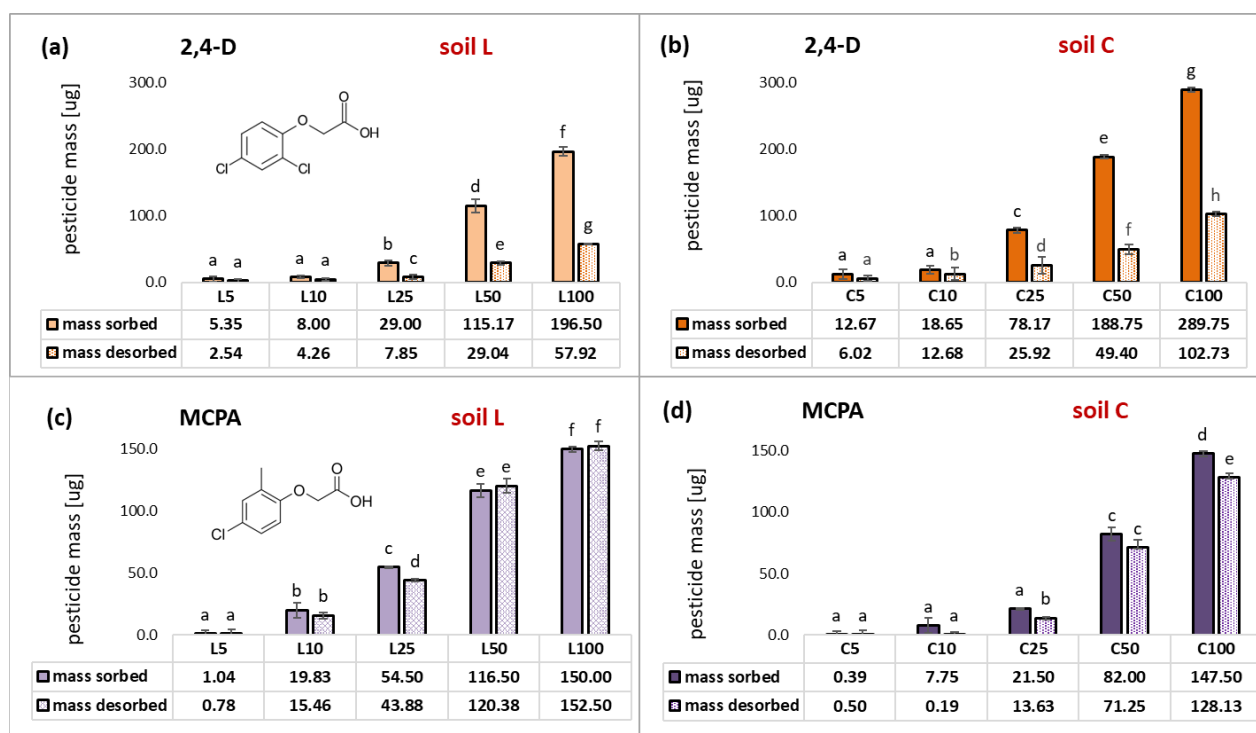


Figure 4. Comparison of the 2,4-D (a,b) and MCPA (c,d) mass initially sorbed and released by the L and C soils with regard to the initial pesticide concentration range. Error bars denote the standard deviation ($n = 3$). Different letters represent the statistical difference at the significance of $p < 0.05$.

Approximately 25–55% and 25–50% of the introduced 2,4-D mass was desorbed from the L and C soils, respectively (Figure 4a,b). The desorption tended to decrease inversely to the herbicide mass introduced. Its release did not exceed 75% of the amount initially sorbed, which according to OECD 106 [50] suggests that the adsorption should be considered irreversible. These results partly corroborate the calculated GUS indices and the moderate mobility of the pesticide in the investigated topsoils.

MCPA, on the other hand, is an evident leacher (Figure 4c,d), achieving desorption magnitude values over 75% over the whole concentration range, which is in agreement with the herbicide's GUS indices. This implies that under the soil pH studied (7.2 and 7.4 for the L and C soils, respectively; Table 2), there seems to be no efficient sorbent for the pesticide among the soil constituents of both of the investigated soils.

3.3. Influence of L and C Soil Components on the Sorption–Desorption Behavior of 2,4-D and MCPA

Generally, weak organic acids such as phenoxy herbicides can bind to soil via several mechanisms. In both their neutral and anionic form, they can adsorb onto endo- and exogenous soil organic matter fractions, which are believed to be an important sink for these herbicides in soils [12,74]. According to the literature, 2,4-D and MCPA sorption in soil is significantly correlated with humic acid carbon (HA) [12,41,75], and is even better with the more polar fulvic acid (FA) carbon fraction in the case of MCPA [76]. However, it is also known that the affinity of the anionic MCPA form to SOM is ten times lower than that of neutral MCPA molecules [74]. Under the experimental conditions (pH of 6.8), the agrochemicals were mostly present in their anionic forms, in which case, the cation bridge mechanism [77] is postulated to play a major role in their binding to SOM. Since FA and HA are abundant in various hydrophilic functional groups (carboxyl, carbonyl, alcoholic, phenolic etc.), they may participate in Ca^{2+} bridging of dissociated 2,4-D and MCPA molecules. Bridging complexes are formed when cations, especially divalent Ca^{2+} , act as a link between the negatively charged sites of the surfaces and the anionic or polar

groups of the adsorbent. Since Ca^{2+} are dominant cations in the sorptive complex of the soils, and the sum of fulvic (FA) and humic acid (HA) fractions of SOM in L soil constitutes 61.76% of the total organic carbon (Table 3), such a mechanism is highly probable.

In the investigated L and C soils, kaolinite and montmorillonite were the major clay minerals, and despite the fact that the clay fraction constituted only 7% of the L soil (Table 2), it may also have contributed to the uptake of the studied phenoxyacetic acids. According to the literature, the sorption of 2,4-D in soil increases proportionally to the concentrations of metal oxides, organic matter, and also to the clay contents [2,78,79]. Furthermore, the bridging mechanism via the Ca-complexes of 2,4-D and the soil minerals (quartz or kaolinite of silt and sand) was evidenced, although in acidic soils with very low organic matter contents [38]. Similarly, in soils of high ratios of the mineral to organic carbon fraction, clay minerals are believed to be the primary sorbents of MCPA, capable of immobilizing the chemical via hydrogen bonding, ligand exchange, or coulomb interactions [80,81]. However, according to Paszko [80], interactions of MCPA with organic matter are stronger than with soil mineral components. Some contradictory findings [38,40] were also proven, demonstrating a negligible sorption of phenoxy herbicides to kaolinite or Ca-saturated montmorillonite. The majority of these results were obtained for the model of single sorbent systems, which do not fully mirror nor take into account the complexity of soil conditions. This is why in the current study, additional investigations on the L and C soil materials amended with K, Mt, and HA were performed. These were conducted to elucidate the influence of organic and inorganic colloids occurring naturally in the investigated topsoils on 2,4-D and MCPA sorption. Their results (Figure 5) revealed that each colloid added to the L or C soil evoked an increase in the 2,4-D sorption magnitude, corroborating the literature findings. Furthermore, they significantly reduced the 2,4-D release back to the solution in the desorption cycle (Table 7). On the contrary, MCPA uptake was enhanced only upon the addition of humic acid to both of the studied soils, which also declined its desorption, presumably via hydrophobic force to aromatic SOM moieties and hydrogen bonding [82]. Interestingly, C soil amendment with HA seemed to have less of an impact on MCPA sorption than in L soil, resulting in the reduced MCPA uptake by the soil. This may be due to the affinity of HA for the sorption sites on Mt [83], limiting the surfaces available for herbicide adsorption. According to the literature, direct HA hydrophobic and hydrogen interactions with Mt often undergo partial complexation or cation bridging with Ca^{2+} [84], although the intercalation of charged, long-carbon chain organic molecules was also evidenced [85]. Similar observations were made in metolachlor studies, where mutual interaction between the clay and organic matter reduced the surfaces available for pesticide adsorption [86].

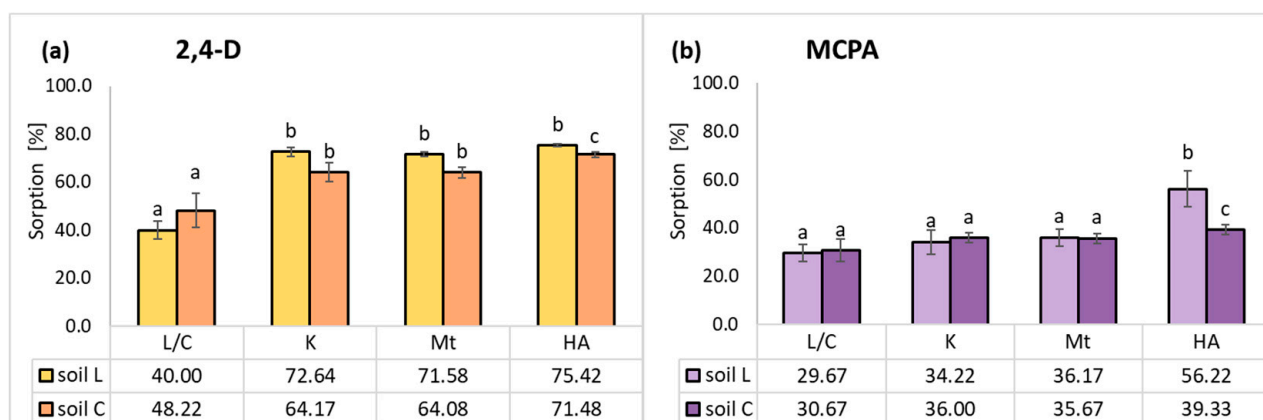


Figure 5. Comparison of 2,4-D (a) and MCPA (b) sorption on L and C soils upon the addition of kaolinite (K), montmorillonite (Mt), and humic acid (HA). Standard deviation ($n = 3$) is expressed with error bars. Different letters represent the statistical difference at $p < 0.05$.

Table 7. Desorption efficiency of 2,4-D and MCPA from the L and C soils under the addition of various amendments. Results are expressed as mean values \pm standard deviation ($n = 3$). Different letters indicate significant differences ($p < 0.05$).

Desorption [%]	2,4-D		MCPA	
	Soil L	Soil C	Soil L	Soil C
soil	40.36 ^a \pm 2.58	8.24 ^b \pm 0.57	21.03 ^a \pm 2.01	41.07 ^b \pm 0.64
K	25.34 ^c \pm 3.20	7.39 ^b \pm 0.25	35.39 ^c \pm 2.18	6.35 ^d \pm 0.45
Mt	21.05 ^c \pm 0.62	7.07 ^b \pm 0.13	79.75 ^e \pm 3.69	11.23 ^d \pm 0.28
HA	16.46 ^d \pm 0.96	5.84 ^c \pm 0.57	7.74 ^f \pm 2.47	23.93 ^g \pm 2.30

The high affinity of 2,4-D (and low affinity of MCPA) for K and Mt may partly explain the great discrepancy in the behavior of the studied phenoxyacetic acids in the batch sorption studies on C soil. Their contribution becomes particularly important in the situation of a reduced share of polar SOM fractions, as observed in C soil. In loamy soil, the amount of organic carbon related to the fulvic and humic acid contents constitutes only 35.65% of the total organic carbon (Table 3), and the calculated CHA/CFA ratio indicates a lower degree of SOM humification compared to the L soil. Therefore, it can be deduced that the enhancement in the retention of 2,4-D on C soil is a combined effect of potential sorption sites on the polar SOM fractions and increased contents of Mt and K in the soil (Table 2), compared to sandy soil. This was corroborated by over 2 and 5.5 times higher K_d and K_f coefficients (Table 5) obtained for the sorption of 2,4-D on soil C in comparison to soil L.

The sorption of MCPA to soil C was of lower magnitude than that in L soil (Figure 3). A negligible effect was observed on the MCPA retention upon the addition of K and Mt to C soil, thus the increased clay fraction content of C soil presumably did not affect the herbicide uptake. Despite a significant increase in the OC content of loamy soil (Table 3), the reduced humic and fulvic acid carbon share and lower humification degree of the organic matter in C soil were presumably responsible for the limited number of sorption sites, capable of Ca^{2+} bridging of the chemical. Our findings corroborate the observation made by Haberhauer et al. [23], who found that the fractional composition and origin of the SOM appear to have a crucial impact on the sorption behavior of MCPA, and a decrease in the soil carbon content does not necessarily imply a reduction in the sorption capacity for polar organic acids such as MCPA. Hence, it appears that soils with higher fulvic and humic acid carbon contents may provide additional sorption sites for polar MCPA molecules, leading to greater herbicide sorption and its more efficient retention [41].

3.4. Influence of Soil pH on the Retention of 2,4-D and MCPA on Loamy Sand and Loam Soils

In accordance with the literature findings [15,33,74], on both of the studied soils, the sorption magnitude of 2,4-D and MCPA gradually decreased, inversely to their pH value (Figure 6a,b). At a pH below the pK_a of the herbicides, the protonated carboxyl group of phenoxyacetic acid may participate in hydrogen bonding with hydroxyl and carbonyl groups of humic or fulvic acids [77]. Some additional interactions may also occur between the chlorine atom of the 2,4-D and MCPA ring and another hydrogen atom of the protonated SOM amine groups, contributing to their strong and effective retention in L and C soils at pH 3. Along with a pH increase, the anionic phenoxyacetic acid form prevails over the neutral molecules, which favors their Ca^{2+} bridging to SOM [74]. The observed decreasing sorption trend with pH corroborates the literature findings, postulating that the affinity of uncharged phenoxyacetic acid molecules to SOM is ten times higher than that of ionic forms [74].

In the case of 2,4-D on L soil, the decline in sorption was relatively sharp (a drop from 80.1% to 20.85%), whereas on C soil, it declined only slightly with a pH increase. This could be attributed to the higher OC content of the C soil and more effective entrapment of 2,4-D by organic matter acting as a molecular sieve [87]. Meanwhile, MCPA sorption on both

soils under various pH was comparable (Figure 4b). The declining trend in the retention of both phenoxyacetic acids on the studied soils with pH may also be partly explained by the increase in the ionization of the surface acid groups of organic matter. This results in enhanced solid OM solubility and a higher share of HA- and FA-bound herbicides in the solution [9], observed as a decline in their uptake in Figure 6.

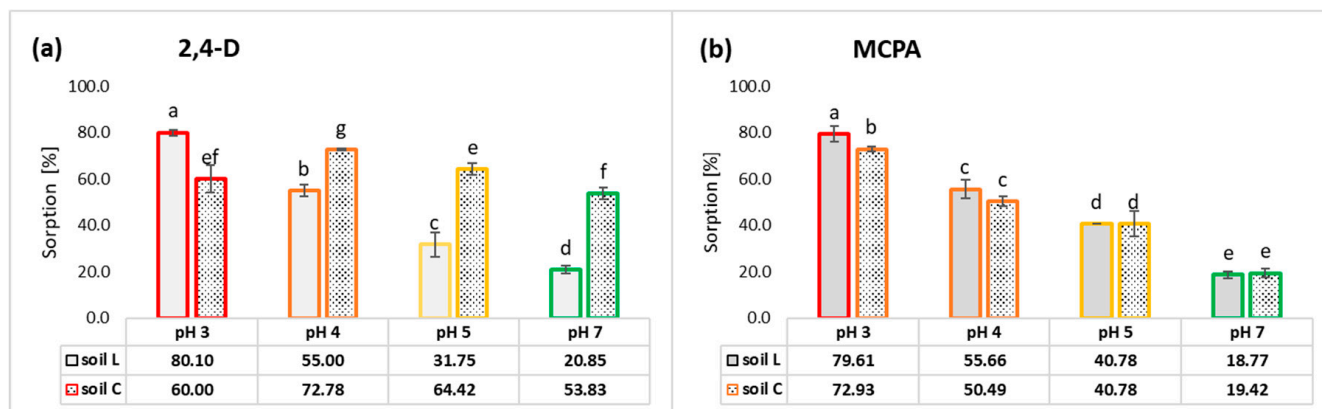


Figure 6. Sorption of 2,4-D (a) and MCPA (b) on L and C soils under a range of pH (3–7). Error bars denote the standard deviation of triplicate samples. Different letters represent a statistical difference at the significance of $p < 0.05$.

In the studied L and C topsoils, kaolinite and montmorillonite might substantially influence 2,4-D and MCPA sorption, although, as evidenced in the present paper, MCPA is not particularly susceptible to interactions with CMs. When 2,4-D comes in contact with clay minerals, the anionic herbicide form can be adsorbed on their surface (Ca^{2+} bridging on the edges of CMs particles) as well as diffuse into the various spatial associations (floculates) of these inorganic soil constituents [44]. The potential share of the discussed cation bridging mechanism on kaolinite and montmorillonite in L and C soils should therefore increase with pH. However, since there was a decline in the sorption capacities of studied soils, it reveals that the postulated mechanism contribution is either negligible or that the active sorption sites of the clay minerals were largely inhibited by the SOM constituents [88,89].

Both phenoxyacetic acids revealed different trends upon their release from the studied soils (Table 8). 2,4-D was desorbed up to 22.41% and 13.59% of the pesticide dose sorbed at pH 4 on L and C soils, respectively. The slightly downward desorption trend on both soils was disturbed at a pH of around 3, where the higher number of neutral pesticide molecules was presumably retained by the stronger hydrophobic types of interactions with the SOM constituents than the cation bridges. A similar observation was made by Meftaul et al. [2], who found that the acidic condition was more conducive for the sorption of 2,4-D, whereas a higher sand content favored phenoxyacetic acid desorption. The content and fractional composition of OC also influenced the desorption behavior of 2,4-D on the L and C soils. According to some studies [86], the intensive desorption of herbicides can be attributed to the soft carbon fraction (humic and fluvic acids) whereas slower desorption can be correlated with the hard carbon fraction (various non-extractable, residual carbon fractions). This partly explains the lowest 2,4-D release from C soil over the various pH studied. Based on the desorption magnitude, it can be concluded that the leaching potential for 2,4-dichlorophenoxyacetic acid on both soils under the pH range of 3–7 is low, contrary to the findings of some other authors, due to which the herbicide is very prone to soil percolation [34,90].

Table 8. Desorption efficiency of 2,4-D and MCPA from the L and C soils under the pH range studied. Mean values of the results \pm standard deviation are given. Different letters represent a statistical difference at the significance of $p < 0.05$.

Desorption [%]	2,4-D		MCPA	
	Soil L	Soil C	Soil L	Soil C
pH 3	13.79 ^a \pm 0.92	10.07 ^b \pm 1.31	14.06 ^a \pm 0.21	13.03 ^a \pm 1.89
pH 4	22.41 ^c \pm 1.45	13.59 ^d \pm 2.74	47.04 ^b \pm 7.21	42.07 ^b \pm 1.03
pH 5	18.63 ^c \pm 1.94	2.29 ^e \pm 0.35	58.01 ^b \pm 2.06	69.82 ^c \pm 2.40
pH 7	17.63 ^c \pm 3.54	1.09 ^f \pm 0.25	68.4 ^b \pm 8.27	88.38 ^d \pm 5.15

The identical desorption trends were observed for MCPA—there was an increase in desorption with pH on L and C soils, with the highest (88.38%) magnitude of MCPA release on C soil at the pH of 7 (Table 8). This confirms the high mobility and leaching potential of the herbicide (Table 6). In general, it could be related to the herbicide's very high water solubility, weak interaction with mineral components, and low share of polar SOM fractions of C soil. The obtained results are in agreement with Paszko et al. [80], who found that both the adsorption and desorption of MCPA in the soil horizons is strongly and negatively related to soil pH, with hydrophobic adsorption playing a dominant role in the MCPA retention in topsoils.

4. Conclusions

The studied phenoxyacetic acids, namely 2,4-D and MCPA, were weakly sorbed on sandy loam and loam topsoil materials of peri-urban areas, revealing moderate and very high mobility, respectively. MCPA was retained to a much lesser extent than 2,4-D, presumably due to its greater water solubility. 2,4-D exhibited a high affinity for the polar SOM fractions as well as kaolinite and montmorillonite, while MCPA sorption was mainly related to the soil fulvic and humic acid contents. Therefore, information on the SOM fractional composition seems to be crucial in predicting the 2,4-D and MCPA mobility and attenuation in soils, both during their sustainable and safe use in agriculture and in urban landscapes, where their inefficient and unregulated application may result in the contamination of soil, water, and food systems [5,18].

Low soil pH favored phenoxyacetic acid sorption in soil, but the management of urban and peri-urban soils often lead to their semi-neutral or slightly alkaline reaction. Maintaining soil pH below 7 should be introduced as a simple strategy to reduce the organic carbon loss in soil, and at the same time, the mobility of 2,4-D and MCPA. Hence, in urban soils, it is advised to implement soil amendment with highly humified exogenous organic matter sources such as composts [91] or biochars abundant in polar functionalities [51] as a sustainable strategy to avoid phenoxyacetic acid contamination in the environment.

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