

Article

Effectiveness of Carbaryl, Carbofuran and Metolachlor Retention in Soils under the Influence of Different Colloid

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Abstract: The affinity of different soil colloids to retain carbaryl, carbofuran and metolachlor in sandy loam and loam soil from mineral, surface horizons was investigated. The undisturbed soil samples and soils amended with colloids—kaolinite (K), montmorillonite (Mt), illite (Il), goethite (G), humic acid (HA)—were mixed with the pesticides for sorption–desorption studies. Their sorption magnitude in pristine soils followed the sequence metolachlor > carbaryl > carbofuran, with loam soil being a better pesticides retarder than sandy soil. The biggest magnitude of carbaryl sorption in light soil was observed in samples with the addition of HA (92.7%), Il (92.3%) and Ge (87.5%), whereas for carbofuran it was goethite (52.3%). Metolachlor uptake was significantly enhanced by 2:1 clays (Mt-85.0%, Il-69.4%), goethite (73.3%) and humic acids (75.4%). The loamy soil sorption capacity of the studied pesticides was blocked by the natural organic matter potentially due to the formation of organo-mineral complexes. HA (66.8%) was the most effective sorbent for carbaryl in the loamy soil, whereas Mt (55.1%) and HA (40.3%) for carbofuran. Metolachlor was retained to the same extent in all loamy soil variants (75.8–83.6%) and its desorption values were the lowest. Carbofuran demonstrated the greatest ability to leach among the studied chemicals.

Keywords: pesticides; carbaryl; carbofuran; metolachlor; clay minerals; goethite; humic acids; sorption; desorption



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1. Introduction

An increase in organic and inorganic pesticide use in agriculture brings the risk of direct or indirect soil and water contamination. Most of these substances once applied on target organisms also reach the soil environment, where they undergo many different processes. The fate and behavior of pesticides in soil is governed by their immobilization, transport and various transformations [1]. Many different factors play a role in their degradation and retention, which occur mainly through adsorption. Mineral particles of different sizes, organic matter and soil microorganisms can profoundly influence the fate of pesticides [2]. The most significant of them, affecting the interactions between soil and chemicals, are soil colloids responsible for the adsorption–desorption phenomenon [3].

Clay minerals (CM), humic substances and hydr(oxides) are the most abundant of the colloidal components of soil and also the most active in binding chemicals [4–12]. Colloid characteristics such as the specific surface area, type of structure, the charge distribution and type of cations sorbed [7,9,12], besides the physio-chemical nature of pesticides, play the most important role in pollutant immobilization. Soil colloids regulate the mobility of pesticides and, hence, are regarded as the main retarders of organic compounds in the downwards transport. The type of soil clay mineral becomes especially important when the soil organic carbon contents are low [13]. The extent to which clay minerals contribute to sorption depends on the nature of the pesticide, as well as the ratio of clay mineral to organic carbon fractions of the soil [14,15]. The latter is particularly important in soils abundant in organic matter, as both—mineral and organic types of colloids—might interfere

with each other, modulating the number of potential sorption sites for xenobiotics. This should be taken into consideration when predicting a pesticide's fate in the environment.

Clay minerals are mainly negatively charged and hydrophilic moieties [16,17] and their reactivity may be influenced by soil pH and the kind of exchangeable cations present in the soil solution [18,19]. Both, CM and hydr(oxides), adsorb preferentially polar compounds through the dissociation of Si-OH, Fe-OH and Al-OH active surface groups. Among CM, smectites, due to their high surface areas connected with an expandable internal surface accessible to water and polar molecules [16], are believed to be one of the most efficient pesticides sorbents. Some studies indicate that illites also have the significant share in the adsorption and transport of polar herbicides by waters in contact with soils or fine-sized soil separates [17]. Fe and Al oxides or kaolinite are regarded to be important agrochemicals reservoirs, as they are abundant in hydroxyl edge surface sites that are available for adsorption by means of the ligand exchange mechanism [18]. Hence, the inorganic colloids' surface properties and the accessibility of the functional active groups of the pesticide molecule to those surfaces are of vital importance. This applies especially to the reactions and interactions of soluble, polar compounds in the soil. Non-polar organic chemicals, which are hydrophobic, are believed to have a higher affinity to soil organic matter (SOM) [1]. It is estimated that about 95–99% of the SOM surface area is formed by micropores and configurational diffusion together with hydrophobic interactions have been proposed as the primary transport mechanisms of non-ionic organic contaminants in the SOM structure [19]. Humic acid (HA) is a representative of natural OM and the most frequently found organic compound in soil, possessing abundant hydroxyl and carboxylic groups that facilitate its adsorption onto minerals and its role in binding of xenobiotics [18,20]. It has been widely shown that HA can effectively interact with pesticides, through sorption or covalent bond formation, and, thus, affect their mobility and transformation in soil and sediments [20,21].

In the last few decades, a lot of attention has been paid to the role of organic components of soil in pesticides' binding and inactivation [20,21]. At the same time, significant progress has been made in terms of variability of these processes, when clay minerals were used as active mineral components in chemical–soil colloid reactions occurring in the soil matrix. Both natural and modified clays, as well as inorganic minerals, have been proposed as sorbents of various types of pollutants, for the remediation on contaminated waters and soils [22–25]. Nevertheless, most of the studies were conducted on model systems, where pure or modified clays and inorganic minerals were applied to immobilize the pollutant [11,23,26–28]. This type of research is valuable as, in many cases, it enables to understand the mechanisms upon which the chemicals are retained on certain sorbents. However, they do not mimic the environmental conditions and do not evaluate the influence of other co-sorbents present in such natural and complex systems as soils. Hence, studies of clay and organic matter in their natural systems are of vital importance, as the interaction between the two soil components may reduce the surfaces available for pesticide adsorption [29]. Extending the studies of sorption–desorption processes of pesticides on model compounds to natural soils enriched with different colloids is a step forward to understand and determine their optimal retention conditions. This knowledge, in turn, is essential to design formulations or an optimal composition of soil materials to protect potential “hot spots” of soil contamination and water pollution.

Carbaryl, carbofuran and metolachlor, which are non-ionic, moderately mobile pesticides, were chosen for the study as their properties are intermediate between polar and non-polar compounds. They vary in water solubility, type of functional groups present in their structure and hydrophobicity. What is more, during the past years, residues of the two carbamates, were found in many arable soils in Poland [30]. Carbaryl (1-naphthyl-N-methylcarbamate) is one of the most widely used carbamate insecticides in both agriculture and horticulture. In the environment, it is believed to be prone to degradation and vulnerable to leaching [31]. The adsorption and breakdown of carbaryl in soil systems have been investigated by a number of scientists, but there are many discrepancies concerning its fate

in the soil environment. For example, de Oliveira et al. [26] investigated the sorption of carbaryl on smectite and found that it strongly depends on the nature the exchangeable cations (Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} or Ba^{2+}). It was indicated that carbaryl sorption is due, in part, to site-specific interactions between the carbamate functional group and exchangeable cations [32], though several studies underline insecticide's great affinity to soil organic carbon [33,34]. Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-methylcarbamate) is an insecticide (nematicide), commonly applied directly to soil or pasture. It is soluble in water and highly mobile, which significantly increases the risk of environmental water pollution [13]. The pesticide exhibits a moderate sorption to soil, depending both on the organic matter [35] and clay mineral content [36], though it is not clear to which soil component its affinity is the highest. Metolachlor (2-chloro-N-(6-ethyl-o-tolyl)-N-((1RS)-2-methoxy-1-methyl-ethyl)) is a selective pre-emergence herbicide frequently used for potato, sugar beet, tomato, soyabean and corn annual weed control in Europe and the USA [37]. The herbicide shows a moderate to long persistence in soil (depending on clay and organic matter content) and high water solubility, which is why its use poses a risk of contaminating surface and ground waters [38,39]. Due to the variance in the literature, concerning possible scenarios of carbaryl, carbofuran and metolachlor immobilization in soil, further studies are required to understand the influence of different soil components on their fate in this complex environment.

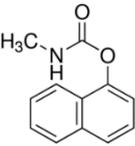
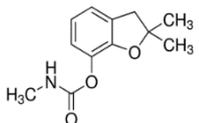
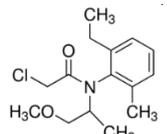
The objective of the study is to estimate the effect of particular colloid addition on the sorption–desorption behavior of carbaryl, carbofuran and metolachlor in sandy and loamy soil materials of a different organic carbon content. Performing the studies on soil materials amended with naturally occurring clay minerals (illite, kaolinite, montmorillonite), iron ores (goethite) or fractions of organic matter (humic acids) would enable to compare the effectiveness of the sorbents in the retention of the studied pesticides. It is of particular importance in preventing the contamination of the soil profile and, as a consequence of that, the ground waters.

2. Materials and Methods

2.1. Chemicals

Carbaryl (1-naphthyl-N-methylcarbamate, 97%), carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranol N-methylcarbamate, 98%) and metolachlor solution in acetonitrile 100 $\mu\text{g}/\text{mL}$ (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(–2-methoxy-1-methylethyl)acetamide, 98%) were of analytical grade and were purchased from Sigma-Aldrich (Schnelldorf, Germany). Table 1 shows the chemical structure and properties of the compounds. Ultrapure water was obtained from a Milli-Q water purification system. Acetonitrile was supplied in analytical reagent grade from Merck (Darmstadt, Germany) and all other chemicals were purchased from POCH (Gliwice, Poland). All materials were used without further treatment or purification.

Table 1. Basic properties of pesticides under study * [40].

Pesticide	Chemical Structure	Water Solubility (mg L ⁻¹) at 20 °C	Octanol–Water Partition Coefficient Log P
Carbaryl		9.1	2.36
Carbofuran		322	1.8
Metolachlor		530	3.4

* Data from PubChem Open chemistry database and PPDB: Pesticide Properties Data Base University of Hertfordshire.

2.2. Sorbents

The kaolinite (KGa-1b, well-crystallized kaolin), illite (IMt-2, 85–90% of illite and 10–15% quartz) and montmorillonite (STx-1b, Ca-rich montmorillonite) were purchased from the Clay Minerals Society Repository (Chantilly, USA). Basic characteristics of CM are presented in Table 2.

Table 2. Selected properties of clay minerals used in the study.

Clay Minerals	Lattice Structure	CEC (cmol _c ·kg ⁻¹) (NH ₄ Ac Method)	Specific Surface Area (m ² g ⁻¹) (N ₂ BET Method)
Kaolinite (KGa-1b)	1:1	3.0 ^a	13.1 ^b
Illite (IMt-2)	2:1	25.0 ^c	24.2 ^d
Montmorillonite (Stx-1b)	2:1	84.4 ^e	83.8 ^e

^a—[41]; ^b—[42]; ^c—[43]; ^d—[44]; ^e—[45].

Humic acid (HA) utilized in the studies was extracted from the topsoil horizon of Gleyic Phaeozem [46] derived from loam, located in the area of Domaniów (near Wrocław, Poland), according to the Schnitzer's method, recommended by the International Humic Substances Society (IHSS) [47,48]. Evaluation of its basic chemical and spectroscopic properties is presented elsewhere [21].

Pure crystalline goethite (α-FeOOH) was synthesized following the method of Schwertmann and Cornell [49]. X-ray powder diffraction confirmed the goethite structure.

The specific surface area of the goethite was 38 m² g⁻¹, determined by a multipoint N₂-BET method (Gemini 2360, Micromeritics, Norcross, GA, USA) [50].

2.3. Soil Sampling and Methods

The study area was located in the south west part of Poland (51.243 E, 17.0453 N) near Wrocław in Ligota Piękna. The research was carried on two arable soils: L—light-textured soil; C—heavy-textured soil. According to the WRB classification [46], the soils were mostly Phaeozems and Umbrisols. The soil material was taken from the A horizon (0–30 cm). The

average analytical soil samples were prepared after mixing samples of each soil from a dozen or so points in the study area. The samples were air-dried and organic elements (roots) were removed. Mineral fractions were ground and sieved using a 2 mm sieve.

Soil fractions smaller than 2 mm were analyzed in the laboratory to characterize the following basic properties: soil texture with a hydrometric method [51]; soil organic carbon content (Corg) using a CS-MAT 5500 analyzer (Ströhlein GmbH & Co., Kaarst, Germany, currently Bruker AXS Inc., Madison, WI, USA); pH in 1 M KCl analyzed in a suspension 1:5 (*w/v*) using a potentiometric method (METTLER TOLEDO, Columbus, OH, USA); hydrolytic acidity (Hh), measured by the Kappen method [52,53]; base exchangeable cations (Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+}) were extracted with 1 M NH_4OAc at pH 7.0 (1:10 *w/v*) and their concentration in extracts was measured using a Microwave Plasma–Atomic Emission Spectrometry (MP-AES 4200 Agilent Technologies, Santa Clara, CA, USA). Cation exchange capacity (CEC) was estimated from sum of hydrolytic acidity and exchangeable base cations. The amount of available forms of P and K was assessed with the Egner–Riehm method [54], and Mg was analyzed on MP-AES 4200 after extraction with 0.0125 M CaCl_2 , at soil to solution ratio of 1:10 [55].

Specific surface area (SSA) of fractions <2 mm and <2 μm was measured in both studied soils with the glycerol vapor sorption method [56]. The mineralogical composition of the clay fraction (<2 μm) of both soils was analyzed with an X-ray diffractometer with $\text{CuK}\alpha$ radiation (λ for $\text{CuK}\alpha 1 = 1.54056$) in the 2θ range of 5–30° (for natural, saturated with ethylene glycol and heated at 550 °C soil fractions). The obtained data were analyzed with X Powder (X PowderX Ver. 2021.01.03, X PowderXTM, Granada, Spain), a software package for powder X-ray diffraction analysis [57].

2.4. Sorption and Desorption Experiments

Sorption of the investigated pesticides on the L and C soils amended with different soil colloids (experimental variants are presented in Table 3) was determined using a simplified batch equilibrium method [58]. To compare the effect of the utilized sorbents, adsorption was measured using single-point concentration of the pesticides: 30, 15 and 10 mg L^{-1} for carbaryl, carbofuran and metolachlor, respectively. The concentrations were selected based on the preliminary batch experiments of pesticides on L and C soils. Isotherms were measured in the concentration range of 0–50 mg L^{-1} for each of the agrochemical (data not shown).

Table 3. Composition and labelling of the studied experimental variants.

No.	Variant Name	Soil Mass (g)	Colloid Added (g)
1	L/C	2.5 g of L or C soil	-
2	LK/CK	2.0 g of L or C soil	0.5 g of kaolinite
3	LGe/CGe	2.0 g of L or C soil	0.5 g of goethite
4	LMt/CMt	2.0 g of L or C soil	0.5 g of montmorillonite
5	LIl/CIl	2.0 g of L or C soil	0.5 g of illite
6	LHA/CHA	2.4 g of L or C soil	0.1 g of freeze-dried humic acid

LK: L soil amended with kaolinite; LGe: L soil amended with goethite; LMt: L soil amended with montmorillonite; LIl: L soil amended with illite; LHA L soil amended with humic acid.; CK: C soil amended with kaolinite; CGe: C soil amended with goethite; CMt: C soil amended with montmorillonite; CIl: C soil amended with illite; CHA: C soil amended with humic acid.

Briefly, 10 mL of each pesticide solution and either 2.50 g of solely L/C soil, or 2.00 g of each soil with 0.500 g of tested colloid (K, Mt, Il, Ge) or 2.40 g of soils studied and 0.100 g of humic acid were placed in 15 mL volume falcons (see Table 3). Before the pesticide addition, samples were homogenized on dry basis by their physical mixing on rotary shaker for 1 h (Biosan, Multi RS-60). For L and C soils, a pre-study was conducted to estimate the sorbent:

solution ratio of 1:4 (*m/v*). Aqueous 10 mM CaCl₂ was used as a background solution to maintain the constant ionic strength.

In the next step all sealed samples were agitated at 80 rpm and 20 ± 0.5 °C for 24 h. Preliminary tests showed that sorption equilibrium was reached for all the investigated pesticides within less than 24 h and no sorption occurred on the falcon wall. Then, samples were centrifuged for 25 min at 10.000 rpm followed by the solutions prefiltration and a subsequent filtration through a 0.45 µm membrane prior to LC-MS/MS analysis. The amount of pesticide sorbed (*S*) was calculated from the difference between the initial and final concentrations of the pesticide in the solution phase. All experiments were carried out in triplicate.

Desorption experiment was conducted immediately after the taking up of the solutions for sorption studies, according to the procedure described in the literature [15]. After the removal of 7.5 mL of supernatant, the same volume of fresh background solution containing no pesticide was added and the falcons were agitated for an additional 24 h, centrifuged and sampled as described before. Pesticide concentration was calculated as the amount of the investigated compound that desorbed from the samples back to the solution after additional 24 h of equilibration with 10 mM CaCl₂, excluding amount of pesticide that remained in the solution after sorption. Desorption variants were labelled with additional “d” letter at the beginning of the sample name, e.g., dCK for the pesticide solution after desorption from C soil amended with kaolinite.

The equilibrium concentrations of pesticides (both after the sorption and desorption steps) were analyzed immediately after the filtration, using high pressure liquid chromatography coupled with tandem mass spectrometer (LC-MS/MS, Thermo Scientific TSQ Quantum Access MAX, Thermo Fisher Scientific, Waltham, MA, USA). Conditions of the measurements can be found in our previous work [21].

Additionally, in all the experimental variants, pH in 10mM CaCl₂ after 24 h of shaking was measured (METTLER TOLEDO pH-meter, METTLER TOLEDO, Warsaw, Poland). It was conducted to determine whether pH was a variable, which might have influenced sorption affinity of the studied pesticides.

3. Results and Discussion

3.1. Soil Characteristics

The basic properties of soil material are presented in Tables 4 and 5. The textures of soils in a topsoil horizon were loamy sand (L soil) and loam (C soil). The higher content of fraction < 0.002 mm in C soil determined the slight differences in chemical properties of both soils. Their CaCO₃ content was low, between 0.6% and 1.1%. The pH of the soils was similar—7.2 for the L soil and 7.4 for the C soil. The organic carbon content (*C_{org}*) was 0.95% in the L soil and 1.5% in the C soil, N content was 0.1% (L soil) and 0.2% (C soil), giving a similar *C_{org}*: N ratio which was 7.2 for the L soil and 8.4 for the C soil (Table 4). The participation of individual cations in the sorption complex can be arranged as follows: Ca²⁺ > K⁺ > Na⁺ > Mg²⁺. The dominant exchangeable cation in both tested soils was Ca²⁺ (Table 5). The cationic exchangeable capacity (CEC) was much higher for the C soil and equaled 42.3 cmol_c·kg⁻¹, while for the L soil it was 26.4 cmol_c·kg⁻¹. The hydrolytic acidity (Hh) was low—about 0.3 cmol_c·kg⁻¹ in both soils.

Table 4. Basic physiochemical properties of L and C soils.

Soil	pH (H ₂ O)	pH (KCl)	CaCO ₃ (%)	C _{tot}	C _{org} %	N	C _{org} :N	Sand	Silt (%)	Clay
L	7.3	7.2	0.6	1.3	0.95	0.1	7.1	76	17	7
C	7.6	7.4	1.1	1.6	1.5	0.2	8.4	47	34	19

Table 5. The summary of exchangeable cations on studied soils and their specific surface areas.

Soil	Ca	Mg	K	Na	Σ	Hh	CEC	SSA <2 mm	SSA <2 μm
	cmol _c ·kg ⁻¹						m ² g ⁻¹		
L	23.9	0.3	1.3	0.6	26.1	0.3	26.4	40.3	370.4
C	39.1	0.6	1.3	1.0	42.0	0.3	42.3	80.5	309.6

The specific surface area as related to the soil texture and organic matter content was also twice higher in the C soil (40.3 m² g⁻¹ and 80.5 m² g⁻¹ for L and C soils, respectively). The SSA of fraction <2 μm in the L soil was 370.36 m² g⁻¹ and 309.63 m² g⁻¹ for the fraction in the C soil. Such results were related to the mineralogical character of a fraction <2 μm of these soils, in which the montmorillonite and kaolinite were the major clay minerals. The highly dispersed quartz was also observed in both <2 μm fractions of soils.

3.2. Sorption of Pesticides

In all the experimental variants, the pH in 10mM CaCl₂ was measured, as it is one of the major factors influencing sorption of pesticides in soil. In pure L and C samples, as well as in their variants containing K, Il, Mt or Ge, it was in the range of 6.8–7.0. Only in the LHA and CHA samples the pH value was 5.85 and 6.15, respectively. Such a decrease in pH is normal due to the acidifying properties of humic acids, which originate from the protonated functional groups on the surface of these macromolecules. For the undisturbed sorption of carbamates it is important to maintain the pH below the value of 7.0, as in alkaline conditions they undergo chemical degradation [21,59].

3.2.1. Carbaryl

The results obtained showed a different sorption ability towards carbaryl in unamended L and C soils (Figure 1; 29.4% and 53.6%, respectively). It suggests that the soil texture and organic carbon content did influence the retention of the pesticide. When the studied soils were enriched in different soil colloids, there was a diversification of their sorptive properties observed. The greatest and comparable effects were obtained in the L soil with the addition of humic acid (HA), illite (Il) and goethite (Ge), where carbaryl sorption increased from 29.4% of the applied dose in soil to 92.7%, 93.3% and 87.5%, respectively. The introduction of kaolinite and montmorillonite into the L soil caused a smaller, though significant, increase in the sorption of this pesticide to, respectively, 50.4% and 51.8% of the initial dose.

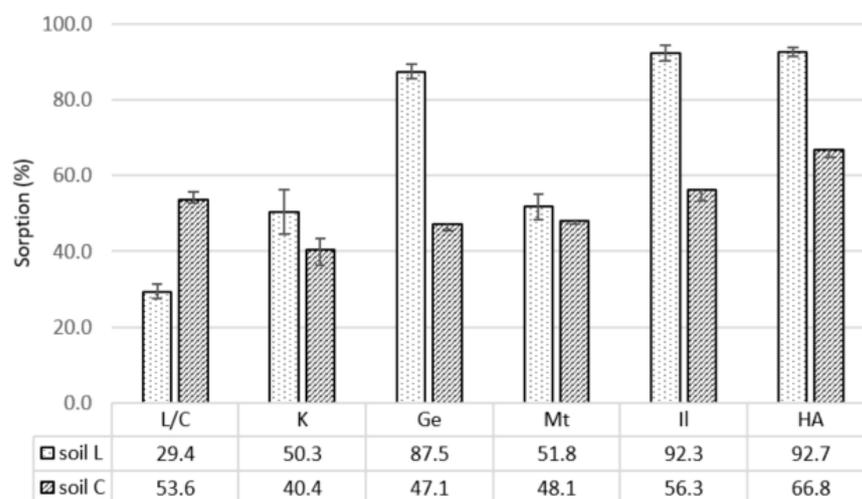


Figure 1. Comparison of carbaryl sorption on soils L and C in the studied variants range. Error bars represent standard deviation of the measurements.

As it can be deduced from the results, in the sandy, low organic carbon content L soil material, the role of mineral soil colloids in carbaryl retention was crucial. It was in agreement with the studies of Chen et al. (2009) [11], who demonstrated that adsorption capacity for carbaryl was significantly impacted by the presence of minerals, though he showed that montmorillonite was a better sorbent of carbaryl than goethite, opposite to our results. This discrepancy may be due to the different composition of the sorbing materials as the study of Chen et al. was conducted on pure, model clays and minerals—without the soil matrix involved—as it is in our study. What is more, minerals such as goethite contributed to the sorption of organic compounds through the dissociation of Si-OH, Fe-OH, and Al-OH active surface groups [60]. The carbaryl two ring-electron system may have participated in the formation of electron donor–acceptor complexes with the siloxane surfaces of minerals [61]. Our results also confirmed the conclusion determined by Polati [62], that in the case of neutral, hydrophobic compounds, montmorillonite was a more effective sorbent than kaolinite.

The higher affinity of carbaryl to 2:1 phyllosilicates (illite—LII sample, 92% of carbaryl dose sorbed, Figure 1) rather than to 1:1 CM (kaolinite—LK sample, 50.35%) was also stated in other studies [63]. A significant increase in carbaryl sorption in the L soil after the addition of humic acid indicated its enhanced affinity toward organic carbon [64]. Hydrogen bonding via the carbaryl's amide carbonyl group was postulated as a main mechanism of carbaryl sorption in the presence of HA [65]. However, what needs to be taken into account, is that the lower pH of the LHA sample (5.85), in comparison to the other experimental variants (6.75), may also have favored carbaryl sorption, as the pesticide is preferentially adsorbed in acidic soils [33].

In contrast to the L soil, the addition of soil colloids to the C soil did not significantly affect the sorption of carbaryl (Figure 1). Its highest value was observed after the HA addition (66.8%), confirming the pesticide's great affinity to organic carbon. The addition of Il caused only the slight and insignificant growth (by 3%), whereas in other cases (LK, LGe, LMt), carbaryl sorption fluctuated below the level of the pure L sample sorption (Figure 1), with a significant decrease in the case of K addition (40.4%). Such observations might be explained by the formation of clay–organic matter complexes [18] and decrease in the sites available for the adsorption of carbaryl. According to Balcke et al. (2002) [66], humic substances (HS) can be adsorbed by a kaolinite clay from the aqueous solution via hydrophobic bonding, though it becomes more favorable at low pH values, when hydroxyl and carboxyl groups of HS are protonated. Ligand exchange (between carboxyl and hydroxyl groups of the HS and surface hydroxyl groups of the minerals) has been discussed as one of the mechanisms for the HS binding of clays [67]. Therefore, the differences on carbaryl sorption on the studied mixtures might be connected with the higher organic carbon content in the C than in the L soil and the mutual blocking of SOM active centers by the minerals added. This phenomenon may explain the greater contribution of soil organic matter toward carbaryl adsorption compared to the clay content of the soils [68].

3.2.2. Carbofuran

The studied soils sorbed less carbofuran from the introduced dose (Figure 2) than it was observed in the case of carbaryl (Figure 1). The carbofuran adsorption capacity of the soils was generally low and assumed to depend on clay and organic carbon contents [69]. The pristine L soil sorbed only 21% of the insecticide dose introduced, while the C soil—38%. It was in accordance with the studies of Farahani et al. who found that in sandy clay soils, the adsorption of carbofuran is weaker than in the clay soils [70]. The highest increase in carbofuran sorption occurred in the L soil after Ge addition (52.3%). Such an observation may be explained by the formation of inner and outer sphere complexes between the pesticide and the singly coordinated surface sites of goethite, which were previously observed for the (4-Chloro-2-methylphenoxy)acetic acid (MCPA, [71]).

Although, it was also proven that van der Waals forces dominate the sorption of nonpolar organic compounds to goethite [72].

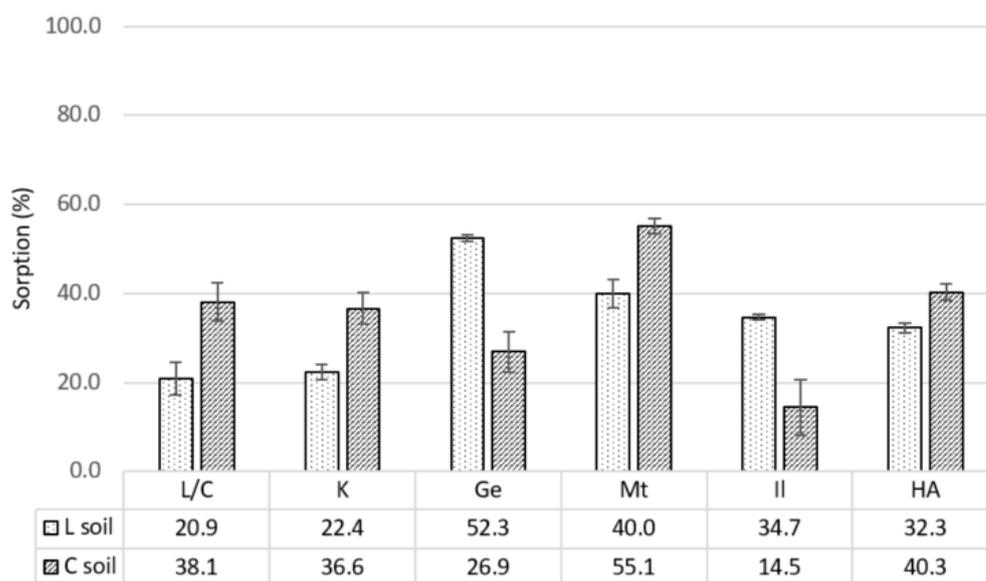


Figure 2. Comparison of carbofuran sorption on soil L and C in the studied variants range. Error bars represent standard deviation of the measurements.

The addition of Mt, Il and HA affected the pesticide sorption to similar extent, resulting in its increase (40%, 34.7% and 32.3% of the introduced carbofuran dose, for the LMt, LIl and LHA sample, respectively; Figure 2). The inorganic amendment of the L soil material evoked a higher affinity of carbofuran to the soil than the addition of humic acids. It was in accordance with studies of Singh and Srivastava, (2009) [73] who found that carbofuran is better correlated with the mineral content of the soils than with their organic matter. Nevertheless, kaolinite's presence in the L soil material had no effect on the carbofuran sorption (22.4%), indicating that other (2:1) clay minerals (illite and montmorillonite) were better pesticide sorbents [62,74] in the studied case.

In the C soil, the added colloids had a more diversified effect on carbofuran sorption; the addition of Il and Ge decreased the sorption to 14.5% and 26.9% in comparison with the C soil sample (Figure 2). This phenomena can be attributed to a decrease in the number of "active" binding sites, similarly as for the carbaryl sorption on Il and Ge in C soil. What is more, this effect in the CGe sample may be explained as a result of the binding of introduced iron oxide to SOM [75]. The addition of K and HA to the C soil had no significant effect on the sorption—36.7% and 40.3%, respectively, whereas in the CMt sample, an increase in sorption to 55.1% was noticed. This may be attributed to an enhanced physical diffusion of pesticide into Mt interlayers as, according to the literature, a fast adsorption process is responsible for carbofuran sorption in acidic soils, governed by intraparticle diffusion [69].

3.2.3. Metolachlor

Metolachlor had the highest water solubility as well as the highest affinity for organic phases among the studied pesticides (see Table 1). The magnitude of its sorption was also the highest among the investigated agrochemicals, both in L and C soils (Figure 3; 51.4% and 82.6% of the dose of this pesticide introduced into L and C soils, respectively). The adsorption of the herbicide was greater in the higher-organic-matter C soil than in the L soil, which followed the trends observed in the literature [76].

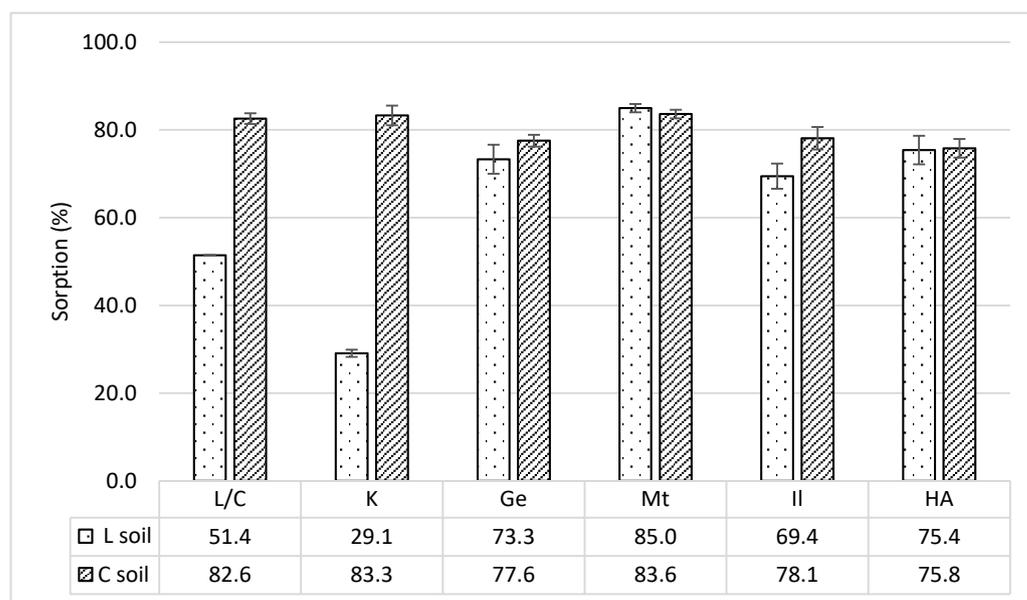


Figure 3. Comparison of metolachlor sorption on soils L and C in the studied variants range. Error bars represent standard deviation of the measurements.

In the L soil, the addition of all the studied colloids, except for kaolinite, caused a significant increase in metolachlor sorption (70–85% of the introduced metolachlor dose adsorbed, Figure 3). It was in agreement with the studies of Nennemann et al., who proved that bentonites and montmorillonites are effective sorbents of metolachlor [77]. They indicated that montmorillonite shows a general higher sorption capacity towards derivatives of chloroanilines with respect to illite, goethite or kaolinite [78], which was in accordance with our studies. Presumably, the herbicide adsorbed at the uncharged and hydrophobic siloxane groups of the clays silicate surface and was held there by accepting hydrogen bonds from water molecules around the interlayer cations.

Sorption clearly decreased in the L soil to 29% only after the introduction of kaolinite (LK sample). Kaolinite is a 1:1 phyllosilicate with a relatively low specific surface area (Table 2) and, presumably, its addition to the L soil blocked potential metolachlor sorptive centers, such as the active sites on organic matter. Some studies with mixtures of clay and organic matter indicated that the interaction between the two soil components reduced the surfaces available for metolachlor adsorption [29]. Hence, in the case of metolachlor, the adsorption process might be preferentially influenced by association mechanisms between the organic and inorganic soil constituents in soils with a reduced OM content.

In all variants studied in the C soil, metolachlor sorption achieved values in the narrow range between 75.8% and 83.6% of the pesticide dose introduced (Figure 3). In soil C, the effect of the colloid addition had no significant impact on the sorption of pesticide. For the case of such a nonionizable herbicide, the organic matter plays a fundamental role for specific and nonspecific adsorption mechanisms (hydrophobic bonding to lipophilic sites of OM and humic substances, charge–transfer mechanisms, van der Waals forces and H-bonds on polar surfaces of clay minerals) [60].

3.3. Desorption of Pesticides

The adsorption and desorption characteristics determine the movement of pesticides through the soil profile [79]. Hence, it was important to obtain information on which particular sorbent (if any) was the most effective in immobilizing the compounds under study. Desorption of all the studied pesticides was comparably low on the pristine L soil (dL samples, 1.4–5.8% of the pesticide dose introduced, Figure S2a).

On the pure C soil, however, carbaryl and metolachlor desorbed only slightly (dC samples, up to 4% of initial dose), whereas approximately 25% of introduced carbofuran

dose was released back to the soil solution in the desorption cycle (Figure S2b). It was in agreement with other studies, which proved that carbaryl desorption increases rapidly at C contents below 4% and the pesticide is more rapidly desorbed than it is adsorbed in soil [69].

3.3.1. Carbaryl

The weakest carbaryl desorption was observed on unamended soil L (Figure 4a). The addition of any of the studied colloids resulted in an increase in the desorption of the pesticide on soil L, which indicated that its retention was partly governed by the weak, un-specific processes (e.g., electrostatic interactions, dipole interactions or hydrophobic effects). The highest reversibility of carbaryl sorption was achieved for the L soil amended with illite or humic acid (dII and dHA samples, 11.8% and 15.4%, respectively; Figure 4a). Hydrogen bonding together with van der Waals interactions may explain the relatively weak interaction and, hence, the high desorption of carbaryl in the dLHA [21] and dLII samples, where carbaryl was potentially present on the outer surfaces of the clay aggregates and desorbed relatively rapidly [80]. Nevertheless, it should be noted that carbaryl desorption was proportional to the sorption magnitude in the tested variants and its values for dMt, dGe and dK were 3.6%, 6.7% and 7.5% of the pesticide dose introduced, respectively. The above results may imply that the binding strength of carbaryl on soil L enriched with colloids examined, followed the sequence montmorillonite > goethite > kaolinite > illite = humic acid.

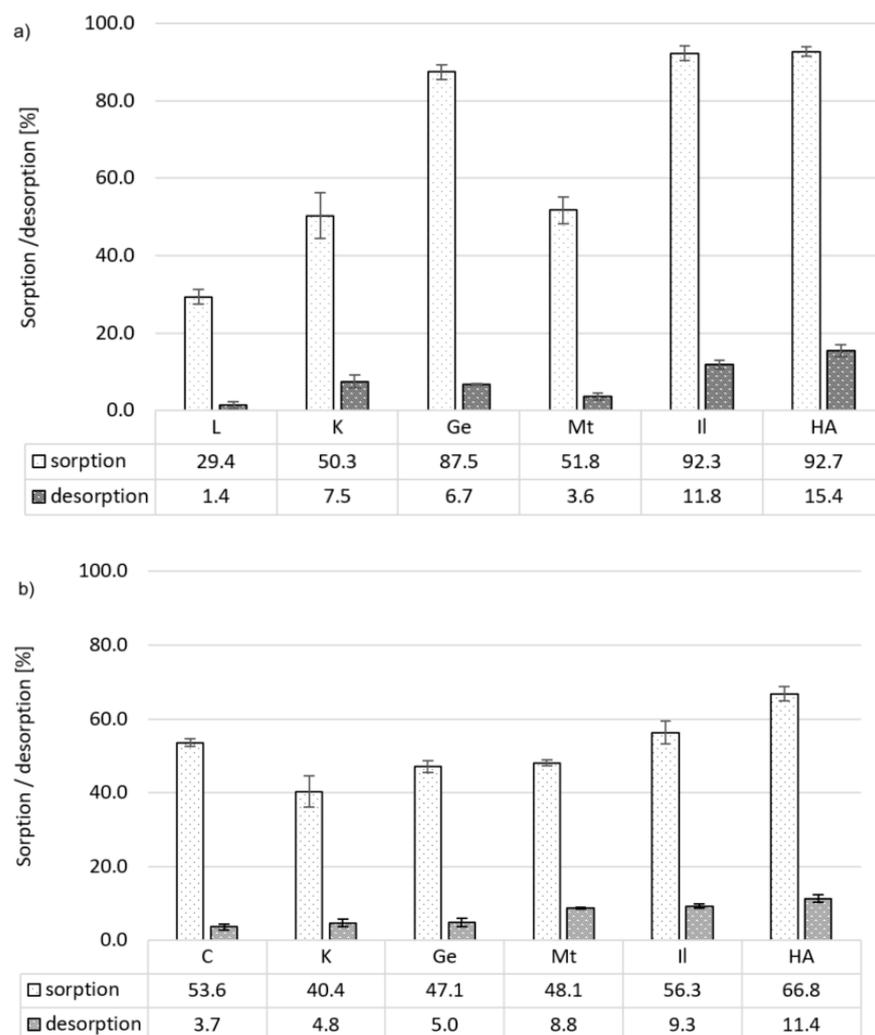


Figure 4. Comparison of sorption and desorption magnitude for carbaryl in (a) soil L and (b) soil C. Error bars represent standard deviation of triplicate samples.

The C soil was characterized by the similar carbaryl desorption (approx. 3.7% of the initial pesticide dose) to its variants enriched with K and Ge (4.8% and 5.0%, respectively). An over two to three times higher desorption on the C soil was noticed for the dMt, dII and dHA samples (8.8%, 9.3% and 11.4%, respectively). It mostly followed the retention trend for the studied colloids in the L soil, except for montmorillonite (sample dCMt, Figure 4b). For this expanding clay mineral, the desorption value in the C soil in relation to carbaryl was over two times higher (8.8%, Figure 4b) than in the L soil.

3.3.2. Carbofuran

Carbofuran revealed the highest desorption values amongst the studied pesticides—both in the case of L and C soils (Figure 5a,b). The addition of each of the sorbents evoked an increase in the carbofuran release in the L soil in the following order: K < Ge < Mt < II < HA (its value reached almost 25% of the pesticide dose introduced; Figure 5a). Simultaneously, it followed the direction of the decreasing binding force (retention of carbofuran in the investigated variants). On the other hand, in the case of the C soil, desorption oscillated in the range of 22.8–26.1% for the pure C soil and its dCK, dCGe and dCMt variants.

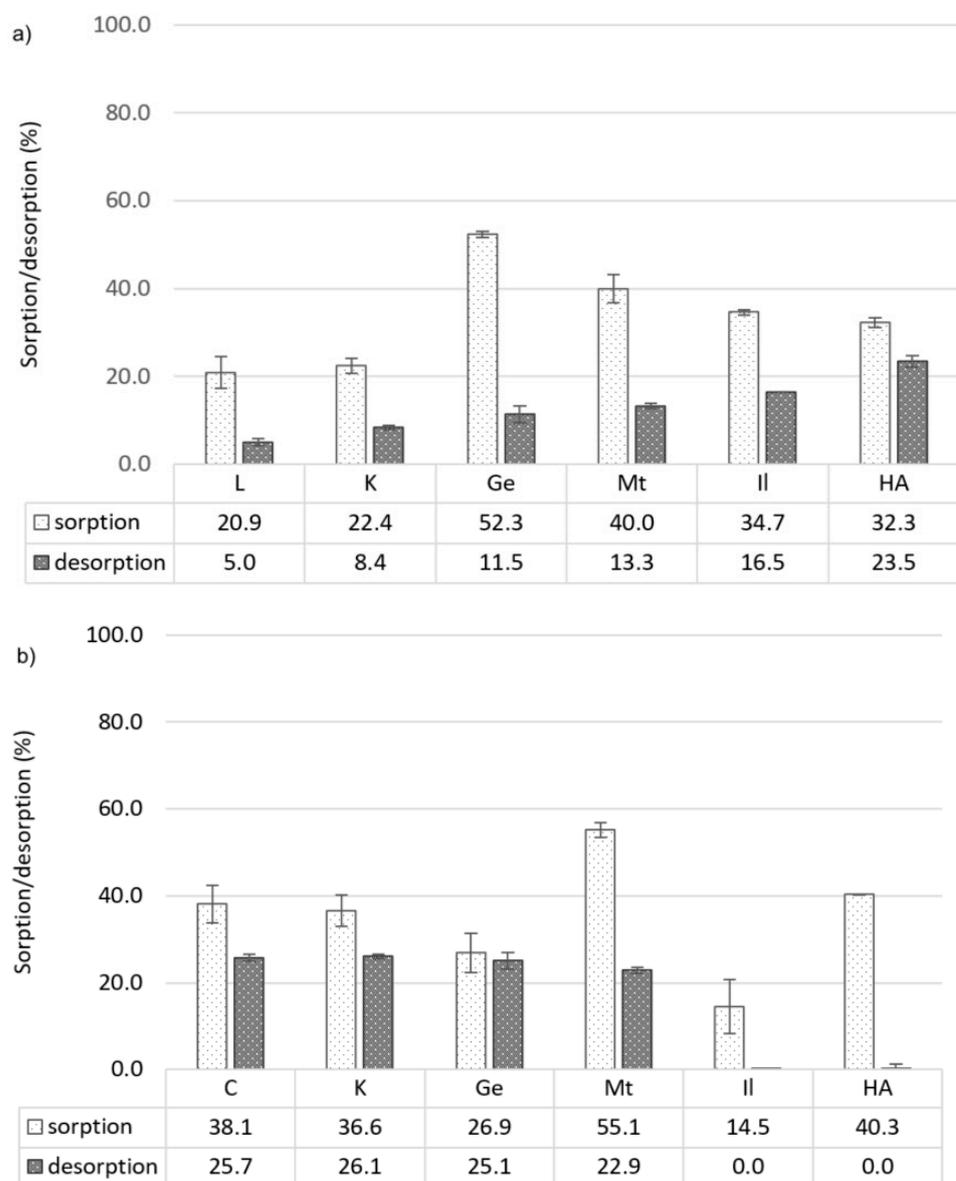


Figure 5. Comparison of sorption and desorption magnitude for carbofuran in (a) soil L and (b) soil C. Error bars represent standard deviation of triplicate samples.

What was interesting was that the carbofuran release observed for the C soil amended with II (dCII) and HA (dCHA) (Figure 5b) was marginal (desorption values of 0.0%). This could be attributed to the formation of more stable complexes in the dCII sample (e.g., between the illite and oxygen of the $>C=O$ group of carbofuran, coordinated by Ca^{2+} ion bridges). Nevertheless, one has to keep in mind that the CII sample was the one with the highest decrease in carbofuran sorption (14.5%) and such a low pesticide concentration in the desorption step may result from its dilution. In turn, the enhanced retention of carbofuran in the dCHA sample may be due to the lower experimental pH than in the other variants, as acidic conditions stabilize carbofuran adsorption in soils [13]. Taking into account the pesticide low sorption and relatively high desorption (except for the dCHA sample), physical diffusion may be postulated as a main, though highly reversible, mechanism of its retention in soil.

3.3.3. Metolachlor

Metolachlor was desorbed to a comparable extent (4.1–5.8%) in all the investigated L soil variants, except for dK (0% of pesticide desorbed) and dMt (10.9% of metolachlor initial dose released back to the solution). Nevertheless, the desorption of metolachlor was marginal in comparison to its sorption (Figure 6a,b). The highest desorption value was obtained for the dLMt sample, which can be partly attributed to the stronger polarizability of water molecules by multivalent cations Ca^{2+} —probably the pesticide was not able to compete with water for all adsorption sites [27].

The C soil revealed an even stronger pesticide retention as only 0.1% up to 3.1% of the metolachlor initial dose was recorded in the solution after the desorption cycle (Figure 6b). Both L and C soils and their variants were very effective in inhibiting metolachlor desorption. In the L soil (Figure 6a), there was more variability observed in its sorptive properties towards metolachlor, than in soil C. It was due to the more pronounced and individual influence of different soil colloids utilized in the studies in the L series of the samples. In the case of the C soil, however, there was a predominant role of soil organic matter exposed. It was manifested in an extensive sorption as well as a marginal desorption of metolachlor; hence, SOM seems to be a major retarder for metolachlor downward transport in soil.

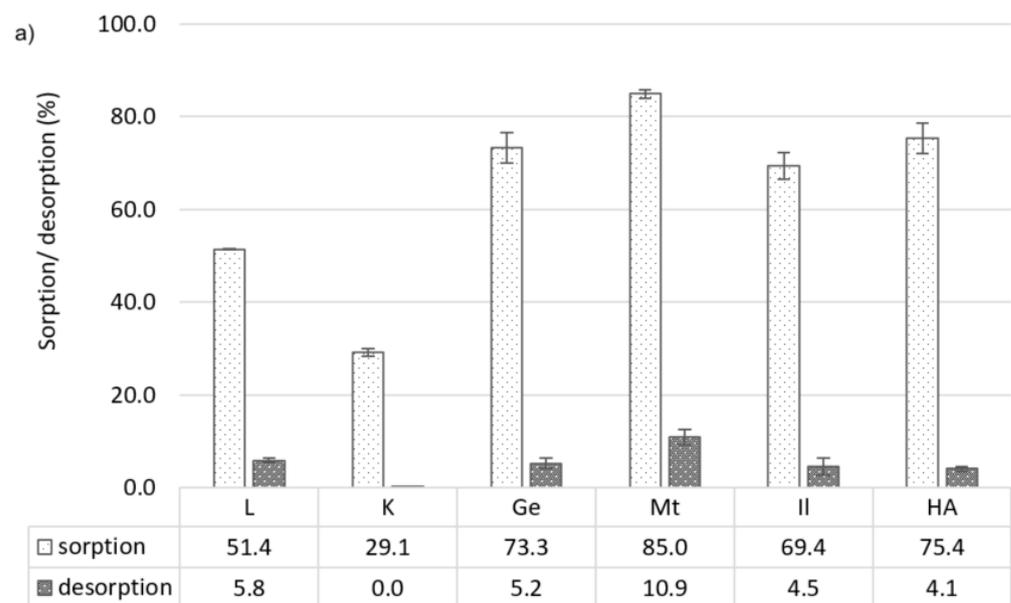


Figure 6. Cont.

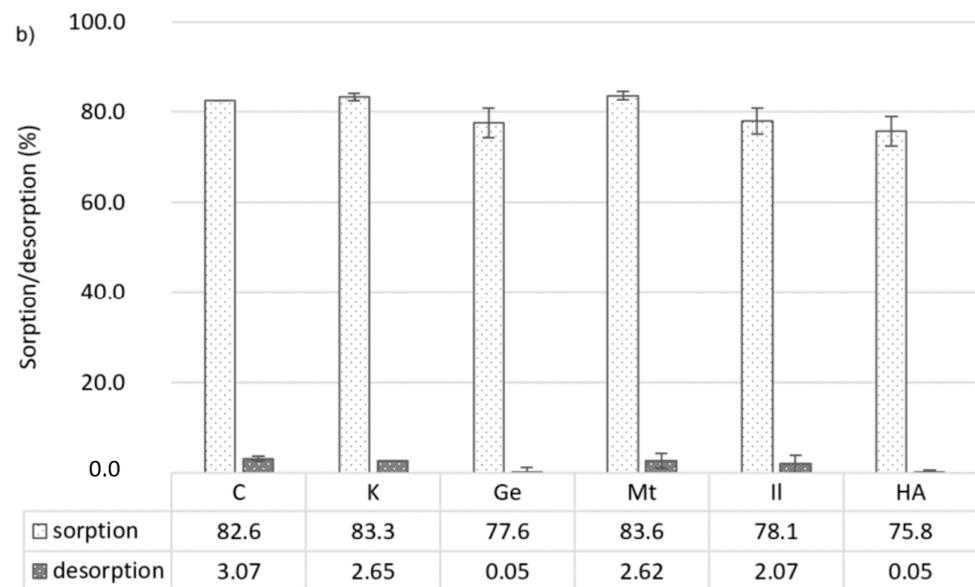


Figure 6. Comparison of sorption and desorption magnitude for metolachlor in (a) soil L and (b) soil C. Error bars represent standard deviation of triplicate samples.

4. Conclusions

The immobilization of carbaryl, carbofuran and metolachlor on the pristine loamy sand soil with a low organic carbon content was less effective than on loamy-textured soil. When the studied colloid addition effect was tested on soil with approximately 0.95% of organic carbon, the role of mineral soil colloids in retaining chemicals was crucial.

Carbaryl was susceptible to all types of amendments which, in few cases, resulted in its nearly total adsorption. Hence, both organic and mineral colloid additions improved insecticide retention in sandy soils. Carbofuran, in turn, was adsorbed in the light-textured soil and its studied variants to a much lesser extent than carbaryl and metolachlor. What is more, it showed a greater affinity to soils enriched with hydrated iron oxide or phyllosilicate 2:1 clays rather than to humic acid, in which case the greatest desorption of insecticide was also observed. In general, carbofuran retention in sandy soil was moderate as the pesticide was probably bound by the weak forces, making its sorption reversible to a considerable extent. The metolachlor uptake was significantly influenced both by 2:1 clays, goethite and humic acids added to the soils. Its desorption in relation to the herbicide dose introduced in the study was scarce, highlighting an important role of colloids in its retention in soil. The presented results emphasized that, in low organic carbon soils (up to an organic carbon content of 1.5%), both organic and mineral surfaces were involved in adsorption.

Based on our results, it can be also concluded that the retention potential of mineral surfaces toward the studied pesticides in natural soils amended with different colloids was suppressed by natural organic matter. The formation of organo-mineral interactions may explain the observed inhibition of carbaryl, carbofuran and metolachlor sorption on loamy soil in which the organic carbon level was 1.5% (m/m). In this case, the enrichment of soil with colloids had no or even negative effect on the tested pesticides sorption in comparison to sandy soil.

According to our studies, SOM acted as a primary reservoir of carbaryl and metolachlor in loamy soil, taking into account their small desorption range in the experimental variants. In turn, carbofuran sorption was noticeably forced only upon the addition of montmorillonite in the loamy soil, potentially due to the physical diffusion of pesticide into clay interlayers. Its lowest retention efficiency was demonstrated by the highest desorption among the pesticides studied - both in sandy and loamy soil variants tested. This corroborated carbofuran's high affinity to leach and, although it is relatively easily biodegraded

in soil, in case of a point-source contamination this soluble-in-water chemical may pose a serious environmental threat.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11090924/s1>, Figure S1: Comparison of the studied pesticides sorption on soils (a) L and (b) C, Figure S2: Comparison of desorption magnitude for the studied pesticides in (a) L soil and (b) C soil.

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