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ADSORPTION, DESORPTION AND DEGRADATION OF CARBENDAZIM IN THE LOESS-LIKE SOIL

ADSORPCJA, DESORPCJA I DEGRADACJA KARBENDAZYMU W GLEBIE LESSOWATEJ

Abstract: Studies on the adsorption, desorption, reaction kinetic and degradation of carbendazim in samples from Ap, Eg, Bt and 2C_{ca} horizons of gleyed lessivé soil formed from loess-like formations (Gleyic Luvisol) were carried out. Degradation experiments were performed at 5 and 25 °C. Degradation data fitted very well to the exponential form of the three-half kinetic model and, to a much lesser extent, to the first-order kinetic model. This was probably due to the changes in microbial activity of biomass during the degradation process. Therefore, the zero-order kinetic equation was also used. The *DT50* values from first-order equation at 25 °C were 12.3, 20.2, 76.6 and 183.1 days for the Ap, Eg, Bt and 2C_{ca} horizon, respectively. The activation energies *E_a* for all soil horizons were in the range of 52–67 kJ · mol⁻¹. The adsorption process proceeded very quickly, within 2 hours equilibrium was achieved, and after maximum 8 hours in the case of desorption. Kinetics data fitted well to the two-site kinetic model. The achieved Freundlich isotherms were of L-type. The estimated *K_d^{ads}* values were the largest in samples from Bt horizon – 32.89 and the smallest in samples from 2C_{ca} horizon – 0.656. The same was in the case of desorption: 34.99 for Bt and 1.105 for 2C_{ca} horizon. The results suggest that clay minerals play an important role in sorption-desorption processes of this compound in the soil. The calculated Groundwater Ubiquity Score (GUS) index assessed carbendazim on the border between non-leaching and transient compounds.

Keywords: carbendazim, adsorption, desorption, kinetics, degradation, loess-like soil, GUS index

Carbendazim (methyl-1H-benzimidazol-2-ylcarbamate) is a systematic fungicide that controls a wide range of pathogens of cereals, vegetables, fruits, grapes and ornamental plants [1] and is used at a large scale in agriculture throughout Europe [2]. In soils with acid reaction this basic compound accepts a proton and may be adsorbed as a conjugated acid on organic matter and mineral clays by ion exchange [3]. Optimal adsorption occurs near the pH numerically equal to the *pK_a* of the conjugate acid, that is 4.53 [4], but an enhanced protonation [3] may occur which can shift the maximum adsorption even to 2.5–3.5 pH units above the *pK_a* of the fungicide [5, 6]. Also hydrogen bonds and van der Waals forces are probable mechanisms of retention of this

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compound [1, 3]. Organic matter is probably the most important fraction related to carbendazim adsorption in soils [1]; values of K_{oc} are mostly in the range of 400–2800 [6, 7]. The compound is slowly degraded with half-lives in the range of 3–15 weeks in the topsoils with natural moisture [2, 8] and about 8–15 weeks in anaerobic conditions [8]. 2-Aminobenzimidazole is its primary degradation product in soils [9].

Despite of relatively strong sorption carbendazim was found in groundwater at concentrations exceeding the maximum allowable concentration for drinking water in the European Union [10]. Such translocation is probably connected with the macropore transport. Therefore, detailed adsorption/desorption and degradation studies on this compound in various soils are necessary to assess the potential risk of water contamination [6]. Almost all investigations concerning this fungicide were concentrated on topsoils, whereas, successful modelling of its translocation to the groundwater requires realistic sorption-desorption and degradation data on the whole soil profile.

The aim of the presented study was to provide detailed data concerning adsorption, desorption and kinetics of these processes, as well as degradation data in horizons of typical Polish loess-like soil, and also preliminary estimation of the leaching potential of carbendazim in this soil on the base of GUS index. The cover of the soil taken into investigations is only 80 cm deep, and because of this it may have a larger potential for substance translocation down the profile and groundwater contamination than the typical loess soil.

Material and methods

Studies were carried out using the samples taken up from the Ap, Eg, Bt and 2C_{Ca} horizons of a gleyed lessivé soil formed from loess-like formations (Gleyic Luvisol) from Olszanka (22°43'00"N, 51°02'05"E) located in the central part of the Gielczew Elevation of Lublin Upland. Soils from this area are described in details in literature [11–13]. The loess and loess-like soils belong to the best Polish arable soils and cover about 7 % of their total area. The loess-like formations contain slightly more sand and clay than typical deep loesses. The underlying materials of the examined soil are Upper Cretaceous marls [12]. Soil sampling was performed in different horizons taking care that no contamination by other soil layers occurred. The depth of samples was chosen taking into account changes in microbial biomass of soil. The main characteristic of the soil is given in Table 1.

The soil samples for incubation experiments were dried to 40 % of their water holding capacity (WHC), passed through 2 mm sieve, averaged and stored in the dark at 4 °C. The period between collecting from the field and the beginning of the experiments was no longer than 1 month. Substrate-induced respiration (SIR) was used for determination of soil microbial biomass (C_{mic}) [14]. The soil samples for kinetic and adsorption/desorption experiments were air-dried, sieved using a 2 mm mesh diameter sieve and averaged.

Incubation experiments were performed according to the OECD guideline [15]. Before the start of the experiments the soil samples stored at 4 °C were preincubated for a 5 day period in the dark at 25 °C. Then, 50 g dry mass samples of soil were placed in

Table 1

Summary of the physical, chemical and biological characteristics of the soil

Soil horizon	Ap	Eg	Bt	2C _{Ca}
Depth [cm]	5–15	25–35	50–60	80–90
Sand [%]	27	19	27	39
Silt [%]	68	71	49	48
Clay [%]	5	10	24	13
pH (CaCl ₂)	5.9	5.9	6.0	7.3
C _{org}	1.06	0.26	0.24	0.11
WHC [%]	38.3	33.6	65.5	34.0
C _{mic} [μg · g ⁻¹]	273.9	111.9	3.85	1.85
Mineral. comp.*	S > I > K	S > I ≥ K	S >> I	S >>> C

* Mineralogical composition determined by X-ray diffraction (S – dioctahedral smectite + chlorate(III), I – illite, K – kaolinite, C – calcite).

incubation flasks and spiked with carbendazim solution to obtain concentration of 5 mg · kg⁻¹ dry mass. Analytical pure carbendazim (certified purity 99.1 %) purchased from Sigma-Aldrich was used for the experiments. At the end, the water content was adjusted with the sterile redistilled water to 40 % of WHC of each soil horizon. The last operation was repeated weekly. On 0, 4, 9, 16, 30, 60, 90, 120 day for the Ap and Eg and 0, 2, 5, 11, 33, 68, 100 and 131 day for the Bt and 2C_{Ca} the 5 g dry mass samples were taken from the incubation flasks to polypropylene tubes. Then, 10 cm³ of methanol was injected and the tubes were agitated on a rotary shaker for 1 h and centrifuged (10 min, 4000 rpm) to separate the liquid phase for analyses. The recoveries were in the range of 76–93 %. All degradation experiments were performed in duplicate at 5 and 25 °C.

The batch kinetic and adsorption/desorption experiments were performed according to the OECD guideline [16] at 22 ± 1 °C. Selection of an appropriate soil/solution ratio (1:5) was made in the preliminary study.

In the kinetic adsorption experiments tubes with 2 g of air-dried soil and 9.0 cm³ of 0.01 mol · dm⁻³ CaCl₂ were equilibrated overnight and 1 cm³ of 50.0 μg · cm⁻³ carbendazim in 0.01 mol · dm⁻³ CaCl₂ was added. Afterwards, the tubes were agitated on a rotary shaker for 2, 4, 6, 8, 24 or 48 h, centrifuged (10 min, 4000 rpm) and the liquid phase was sampled for analyses. In the kinetic desorption experiments the tubes with 2 g of soil and 9 cm³ of 0.01 mol · dm⁻³ CaCl₂ were equilibrated overnight, then 1 cm³ portions of 50.0 μg · cm⁻³ carbendazim in 0.01 mol · dm⁻³ CaCl₂ were dosed and tubes were shaken for 24 h, centrifuged and the aqueous phase was recovered as much as possible and analyzed. The volume of solution removed was replaced by an equal volume of 0.01 mol · dm⁻³ CaCl₂, agitated for 2, 4, 6, 8, 24 or 48 h and centrifuged to separate the liquid phase for analyses. All kinetic experiments, including the controls (9 cm³ of 0.01 mol · dm⁻³ CaCl₂ and 1 cm³ of 50.0 μg · cm⁻³ carbendazim in 0.01 mol · dm⁻³ CaCl₂) and blanks (2 g of soil and 10 cm³ of 0.01 mol · dm⁻³ CaCl₂) were performed in duplicate.

Five concentrations of carbendazim (70.0, 50.0, 38.0, 26.0 and 10 $\mu\text{g} \cdot \text{cm}^{-3}$ for Ap, Eg and Bt samples and 50.0, 38.0, 26.0 10.0 and 5.0 $\mu\text{g} \cdot \text{cm}^{-3}$ for 2C_{Ca} samples) in 0.01 $\text{mol} \cdot \text{dm}^{-3}$ CaCl₂ were used for adsorption/desorption experiments. The 2 g soil samples were placed in 50 cm^3 polypropylene tubes and equilibrated with 9 cm^3 of 0.01 $\text{mol} \cdot \text{dm}^{-3}$ CaCl₂ overnight (12 h). Afterwards, 1 cm^3 of the appropriate carbendazim solution was added. The tubes were agitated for 24 h to achieve equilibrium and centrifuged. The aqueous phase was recovered as completely as possible and analyzed. In the step performed to examine the desorption process, the volume of solution removed was replaced by an equal volume of 0.01 $\text{mol} \cdot \text{dm}^{-3}$ CaCl₂. The new mixture was agitated for 24 h, and then centrifuged to separate the liquid phase for analyses. The amounts of adsorbed/desorbed carbendazim as a function of time were calculated from the difference between the initial and the final substance concentrations in solution [16]. All adsorption/desorption experiments were performed in triplicate.

A 20 mm^3 portion of solution was injected into a WellChrom (Knauer, Berlin, Germany) HPLC equipped with two K-500 pumps, a K-2500 UV-VIS detector and a Hypersil Gold C₁₈ column (100 × 3.0 mm i.d., 3 μm particle size, Thermo Electron Corporation, Runcorn, United Kingdom) preceded by a Hypersil Gold C₁₈ guard column (10 × 3.0 mm i.d., 3 μm particle size). The mobile phase was 26:74 (v/v) acetonitrile/citrate buffer (pH 6.5). The flow rate of the mobile phase was 0.7 $\text{cm}^3 \cdot \text{min}^{-1}$, the run time was 6 min per sample and the detection wavelength $\lambda = 223$ nm. The detection limit was 0.5 $\mu\text{g} \cdot \text{dm}^{-3}$ and reproducibility of the results with the relative standard deviation lower than 5 %.

The zero-order kinetic model $C_t = C_0 - k_0 \cdot t$ (C_0 and C_t [$\text{mg} \cdot \text{kg}^{-1}$] – masses of compound in the soil at the beginning of the experiment and at time t [d], k_0 – zero-order degradation rate coefficient), first-order kinetic model $C_t = C_0 \exp(-k \cdot t)$ (k – first-order degradation rate coefficient) and three-half kinetic exponential model [17] $C_t = C_0 \cdot \exp(-k_1 \cdot t - E_0/\mu(\exp(\mu \cdot t) - 1))$ (k_1 – initial rate constant, μ – growth rate constant and E_0 – starting cell concentration) was used for estimation of parameters from incubation experiments. In the last equation assumption $k_1 = 0$ was made. For calculating activation energy E_a [$\text{kJ} \cdot \text{mol}^{-1}$] the transformed form of Arrhenius equation was used: $E_a = R \ln(DT50_1/DT50_2)/(1/T_1 - 1/T_2)$ ($DT50_1$ and $DT50_2$ – 50 % dissipation times at temperature T_1 and T_2 (K), R [$\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$] – gas constant); the details are described in [18].

The Freundlich equation $S^{ads/des} = K_F^{ads/des} C^{1/n}$ ($S^{ads/des}$ [$\mu\text{g} \cdot \text{cm}^{-3}$] – amount of adsorbed/remain after desorption solute per unit mass of soil, $K_F^{ads/des}$ and $1/n$ – empirical constants) was used to fit the adsorption/desorption data and the two-site model $S_t^{ads} = S_1^{ads} \cdot (1 - \exp(-k_1 \cdot t)) + S_2^{ads} \cdot (1 - \exp(-k_2 \cdot t))$ and $S_t^{des} = S_e^{des} + S_1^{des} \exp(-k_1 \cdot t) + S_2^{des} \exp(-k_2 \cdot t)$ ($S_1^{ads/des}$ and $S_2^{ads/des}$ [$\mu\text{g} \cdot \text{g}^{-1}$] – amounts of solute adsorbed/remain after desorption at time t to the sites with the first order adsorption/desorption rate constants k_1 and k_2 , respectively) to fit the results from kinetics experiments. At adsorption/desorption equilibrium $S_e^{ads} = S_1^{ads} + S_2^{ads}$ and $S_e^{des} = S_e^{ads} - S_1^{des} - S_2^{des}$. The details concerning estimations with using of above equations were described in other papers [19, 20].

Parameters of the above equations were estimated by nonlinear regression (Marquardt method, Statgraphics, Manguistic).

Results and discussion

The data from incubation experiments are plotted in Fig. 1. The rate of degradation decreased with the increase of soil depth and with the decrease of temperature. It should be noted that degradation process was only a little slower in the soil samples from Eg horizon in comparison with the respectable samples from Ap horizon despite of large differences with C_{mic} content (Table 1). In the samples from lower horizons, degradation was much slower; clearly the slowest in the $2C_{Ca}$ horizon, although, small C_{mic} content in Bt and $2C_{Ca}$ horizons suggest that both horizons should be in practice biologically inactive. Fitting the first-order kinetic equation to the experimental results gave generally good results ($r^2 > 0.7$), with the exception of samples from Bt and $2C_{Ca}$ horizons at $5\text{ }^\circ\text{C}$ (Table 2). But r^2 values are generally smaller when degradation is slow [21] despite of low RSS values. Values of E_a calculated for particular soil horizons were in the range of $52.0\text{--}67.0\text{ kJ}\cdot\text{mol}^{-1}$. It is probable that larger values of activation energy in the Bt and $2C_{Ca}$ horizons are only the result of difficulties with exact estimation of $DT50$ of the slowly degraded compound.

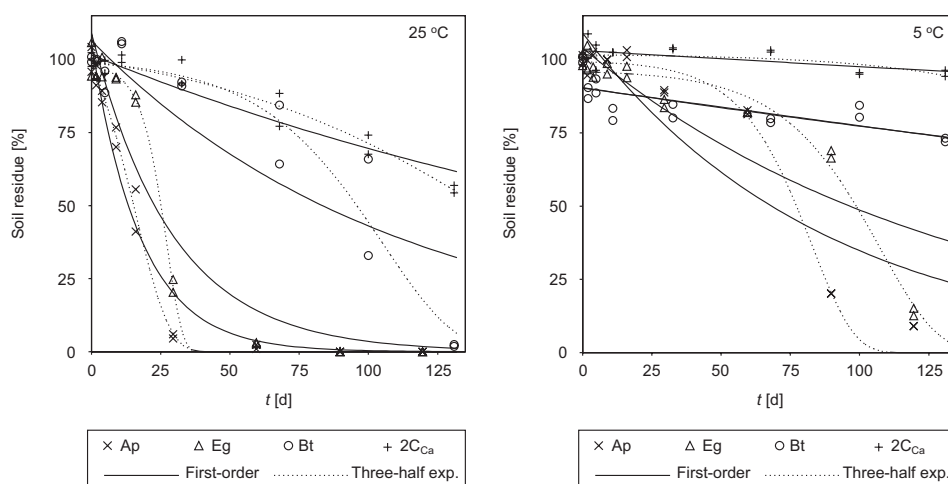


Fig. 1. Fit of first-order and three-half kinetic models to data of carbendazim incubation experiments in soil horizons at $25\text{ }^\circ\text{C}$ and $5\text{ }^\circ\text{C}$

The results of fitting, using the exponential form of the three-half kinetic model are presented in Table 3 and as dash lines in Fig. 1. The values of r^2 in this Table are greater in comparison with the appropriate values in Table 2, and RSS values are lower. This suggests that changes in biomass influence the degradation process of carbendazim. The presence of the lag-phase in the Eg and Bt horizons at $25\text{ }^\circ\text{C}$ and in Ap and Eg horizons at $5\text{ }^\circ\text{C}$ also confirm this (Fig. 1).

Table 2

Degradation rate estimates and their standard errors estimated with using the first-order kinetic equation

Horizon/Temp	k [d ⁻¹]	$DT50$ [d]	r^2	RSS	E_a [kJ · mol ⁻¹]	
Ap	25 °C	0.0561 ± 0.0058	12.3 ± 1.3	0.970	1.29	54.9
	5 °C	0.0114 ± 0.0020	60.7 ± 10.4	0.825	4.52	
E _g	25 °C	0.0343 ± 0.0057	20.2 ± 3.3	0.922	4.80	52.0
	5 °C	0.0076 ± 0.0014	91.4 ± 15.7	0.779	5.53	
Bt	25 °C	0.0090 ± 0.0019	76.6 ± 15.3	0.777	7.61	60.4
	5 °C	0.0016 ± 0.0004	441.9 ± 105.5	0.569	0.88	
2C _{ca}	25 °C	0.0038 ± 0.0004	183.1 ± 18.9	0.892	0.88	67.0
	5 °C	0.0005 ± 0.0002	1303.7 ± 449.8	0.381	0.33	

$DT50 = \ln 2/k$ – time required for 50 % dissipation of initial concentration.

Table 3

Degradation rate estimates using the simplified exponential form ($k_1 = 0$) of the three-half kinetic model

Soil horizon	E_0 [d ⁻¹]	μ [d ⁻¹]	r^2	RSS	
Ap	25 °C	0.0223	0.0821	0.993	0.29
	5 °C	0.0003	0.0661	0.988	0.43
E _g	25 °C	0.0013	0.1801	0.996	0.26
	5 °C	0.0003	0.0481	0.965	0.89
Bt	25 °C	0.0007	0.0382	0.938	2.14
	5 °C	0.0014	0.0014	0.563	0.89
2C _{ca}	25 °C	0.0014	0.0152	0.947	0.43
	5 °C	7.7 · 10 ⁻⁵	0.0241	0.441	0.31

Since most of the examined degradation curves did not show the real first-order kinetic behavior and that caused difficulties with the estimation of $DT50$ and E_a values, the zero-order equation was used. Values of r^2 and RSS indicated that this equation gave a better fit of the experimental data than the first-order equation, however worse than the three-half kinetic model. Also the values of E_a from Table 4 are scattered to a lesser extent than those from Table 2. It seems that in the cases in which changes in microbial biomass influence the degradation process, the zero-order kinetic equation may give more reliable results than the first-order one. Values of r in comparison C_{mic} with $DT50$ at 25 °C and 5 °C calculated from zero-order equation were -0.770 and -0.702 , respectively, whereas, for the first order equation -0.738 and -0.695 , which also confirms the above thesis.

The values of $DT50$ for carbendazim in this study are lower or are in the lower range of the results obtained by other authors [2, 8, 22]. Degradation potential of the examined soil was high and an adaptation phase, which in the case of this compound is usually relevant to this process [9, 23], was relatively short. The values of E_a correspond well with mean activation energy 54.1 kJ · mol⁻¹ calculated by Walker et al [24] on the basis

of 114 observations of various pesticides (but without carbendazim) and proposed as a default value for EU.

Table 4

Degradation rate estimates and their standard errors
using the zero-order kinetic equation. $DT50 = C_0/2k_0$

Horizon/Temp	k_0 [$\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$]	$DT50$ [d]	r^2	RSS	E_a [$\text{kJ} \cdot \text{mol}^{-1}$]
Ap 25 °C	0.1184 ± 0.0047	15.6 ± 0.5	0.985	0.27	50.2
	0.0279 ± 0.0022	66.7 ± 4.2	0.909	2.34	
Eg 25 °C	0.1017 ± 0.0144	21.8 ± 2.5	0.833	2.57	50.0
	0.0265 ± 0.0028	87.9 ± 7.7	0.849	3.77	
Bt 25 °C	0.0289 ± 0.0030	79.6 ± 6.6	0.865	4.58	51.4
	0.0057 ± 0.0013	353.3 ± 78.3	0.562	0.89	
2C _{Ca} 25 °C	0.0145 ± 0.0012	159.3 ± 11.3	0.916	0.69	62.0
	0.0024 ± 0.0008	962.8 ± 318.0	0.385	0.33	

The data on kinetics of adsorption/desorption in soil are presented in Fig. 2. The course of these processes in all soil horizons was similar. In a less than 2 hours time soil adsorbed an appropriate portion of carbendazim and equilibrium was obtained. Such fast adsorption kinetics was also observed by Dios Cancela et al [1]. Carbendazim desorption was also very fast at first, then slowed down rapidly, the stage of slow desorption started and equilibrium was obtained in a time of about 8 hours. As it was in the case of previous studies [20], kinetics data fitted well to the two-site kinetic model. Values of r^2 for adsorption/desorption for Ap, Eg, Bt and 2C_{Ca} horizons were 0.978/0.872, 0.985/0.962, 0.999/0.872 and 0.728/0.802, respectively. On the basis of these results it may be assumed that both adsorption and desorption of carbendazim

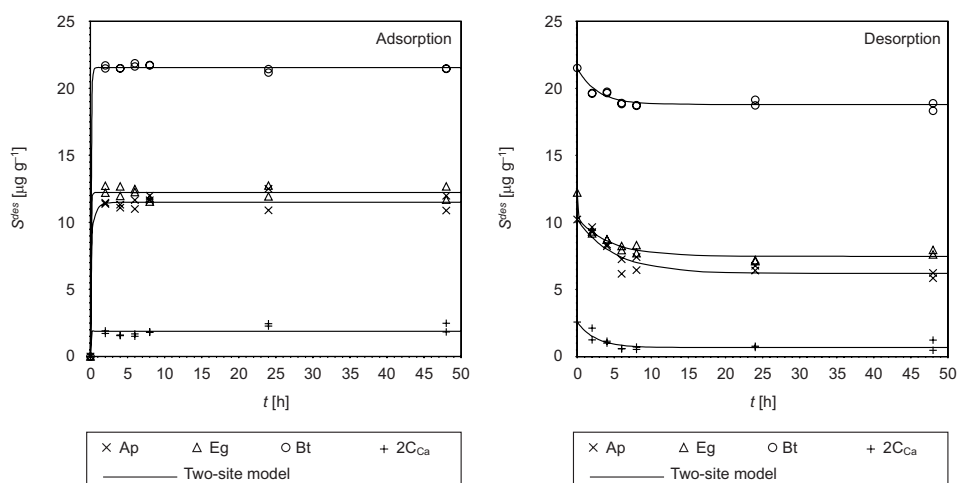


Fig. 2. Carbendazim adsorption and desorption in soil horizons as a function of reaction time

proceeded quickly and 24 hours of equilibration time was long enough to obtain adsorption and desorption isotherms. It also can be concluded that the experiments with these processes were not influenced by degradation of carbendazim.

After desorption, the amounts of non-desorbed carbendazim were high in comparison with the previously adsorbed amounts; in the Ap and Eg horizons 64.3 and 63.5 %, extremely high in Bt horizon – 87.3 % and only 27.1 % in 2C_{Ca} horizon. This suggests existence of strong bonds between the fungicide and the soil constituents (especially in the Bt horizon) in fraction not capable of desorption and weak, probably physical forces, in desorbed fraction.

The adsorption and desorption isotherms are shown in Fig. 3. The estimated values of parameters of Freundlich equation and also K_d values are given in Table 5. The obtained isotherms are of L-type ($1/n < 1$) which is usually attributed to the sorption of high polar or monofunctional ionic substances presenting very strong intermolecular interactions into organic and mineral matrices [25, 26].

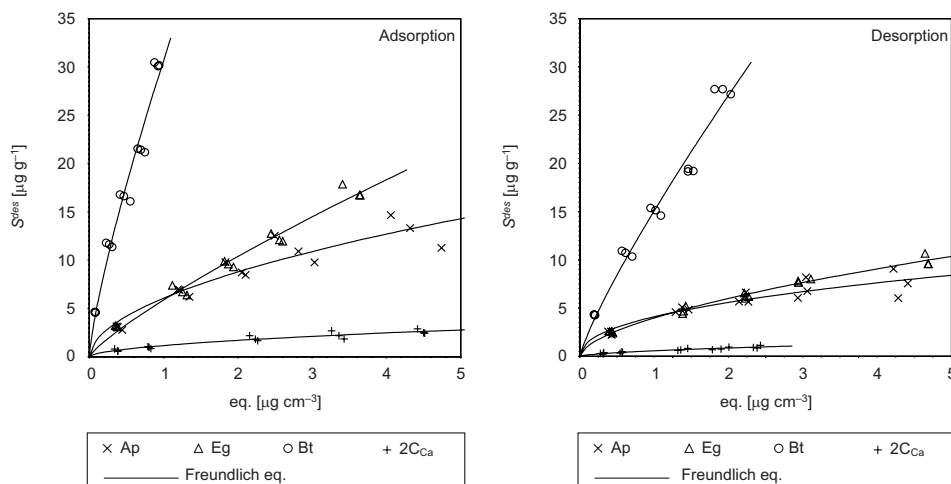


Fig. 3. Adsorption and desorption isotherms of carbendazim in soil horizons

The smallest K_F^{ads} value was calculated for the samples from the 2C_{Ca} horizon (Table 5) larger for Ap and Eg horizons and the largest for the samples from Bt horizon. The same was observed for desorption isotherms; the smallest K_F^{des} value was in the samples from the 2C_{Ca} horizon and the largest again in the samples from Bt horizon. The obtained K_F^{des} and K_d^{des} values were higher than the corresponding K_F^{ads} and K_d^{ads} values. Such commonly found in sorption experiments hysteresis [3, 25] may be caused by eg slow kinetic of desorption, diffusion-limited transport within the particles and, which is supposed to be the most probable in the case of carbendazim, strong or irreversible binding of this compound to soil particles [6, 7].

Comparison values of C_{org} from Table 1 with the respectable values of K_F^{ads} and K_d^{ads} did not give good correlation (-0.159 and -0.207). Enough good positive values of r were obtained in comparison values of these parameters with total clay content (0.842

Table 5

Adsorption/desorption parameters and their standard errors using the Freundlich equation

Soil horizon	Adsorption				Desorption			
	K_f^{ads}	$1/n$	r^2	K_f^{ads}	$1/n$	r^2	K_d^{des}	r^2
Ap	6.059 ± 0.481	0.534 ± 0.069	0.877	4.289 ± 0.263	0.448 ± 0.065	0.726	6.541 ± 0.428	0.584
Eg	5.875 ± 0.301	0.821 ± 0.049	0.975	5.043 ± 0.172	0.595 ± 0.027	0.917	6.995 ± 0.324	0.807
Bt	30.68 ± 1.03	0.785 ± 0.060	0.963	32.89 ± 1.63	0.844 ± 0.057	0.848	34.99 ± 1.32	0.909
2C _{ca}	1.155 ± 0.091	0.547 ± 0.064	0.907	0.656 ± 0.043	0.592 ± 0.068	0.684	1.105 ± 0.060	0.728

and 0.869). It can be concluded from this that clay minerals play an important role in sorption of carbendazim in the examined soil, especially in the deeper soil horizons. The predominant clay minerals of the soil are complexes of dioctahedral smectites and chlorate(III) (Table 1) with significant accumulation in Bt horizon (30 % higher than in Ap horizon). The confirmation of this is the highest WHC of Bt horizon. The samples from 2C_{Ca} horizon composed of cretaceous marls have much higher pH value and because of this its clay minerals have different sorption properties than minerals of upper horizons. Therefore, r values for comparison values of K_F^{ads} and K_d^{ads} with clay content only for Ap, Eg and Bt were higher (0.966 and 0.973). Montmorillonite, the principal clay mineral of smectite group, has a very high selectivity for carbendazim, and illite has a very low one [1]. The largest adsorption of carbendazim on montmorillonite at pH 5–6 is usually explained by an enhanced protonation of its neutral molecules at the clay-solution interface and adsorption by cation exchange [1]. This can explain high adsorption in Bt horizon.

The results of the experiments of Dios Cancela et al [1] showed that organic matter might be the most important soil fraction related to carbendazim adsorption in soils. The optimum pH for maximum adsorption of basic molecules on this soil constituent is usually near the pK_a value of the conjugate acid [3]. This may explain why in the presented study comparison between C_{org} and MCPA sorption parameters did not give positive results. The role of organic matter in sorption of pesticides in soils is very often underestimated [27] and the data presented in this paper also suggest this thesis.

The GUS index ($GUS = (4 - \log K_{oc}) \log(DT50)$) assesses the leaching potential of pesticides and the possibility of finding these compounds in the groundwater [28]. The values of this index calculated for the topsoil on the basis of $DT50$ values estimated from the zero- and first-order kinetic equations and recalculated to 20 °C are 1.85 and 1.73, respectively. This classifies carbendazim in the examined loess-like soil on the border between non-leaching and transient compound ($1.8 < GUS < 2.8$ transient compound; $GUS < 1.8$ no leacher). Taking into account very high adsorption and low desorption in the Bt horizon it seems to be improbable that it could be found in groundwater of the soil taken into investigations at concentrations exceeding the maximum allowable concentration.

Conclusions

1. A relatively fast degradation of carbendazim occurred in the Ap horizon of the soil and lower in the deeper horizons. The E_a values were in the range of the mean default value for EU. Degradation data fitted very well to the exponential form of the three-half kinetic model and, to a much lesser extent to the first-order kinetic model. This was probably due to the changes in microbial activity of biomass during the degradation process. In the cases in which the lag-phase was observed, the zero-order kinetic equation was more useful for estimation of degradation parameters than the first-order equation.

2. Carbendazim was quickly and strongly adsorbed and only partly capable of desorption. The highest adsorption and the lowest desorption was observed in the Bt

horizon. On the basis of high correlation values between adsorption coefficients and amount of clay it can be concluded that clay minerals played an important role in adsorption of this compound in the examined soil, especially in the deeper soil horizons.

3. The GUS index assessed the behavior of carbendazim on the border between non-leaching and transient compound. Taking into account very high adsorption and low desorption in the Bt horizon it seems to be improbable that carbendazim could be a leacher in the soil taken into investigations.

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ADSORPCJA, DESORPCJA I DEGRADACJA KARBENDAZYMU W GLEBIE LESSOWATEJ

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Abstrakt: Badania adsorpcji, desorpcji, kinetyki reakcji i degradacji karbendazymu przeprowadzono w próbkach z poziomu Ap, Eg, Bt i $2C_{Ca}$ gleby płowej opadowo-glejowej wytworzonej z utworów lessowatych (Gleyic Luvisol). Doświadczenia z degradacją przeprowadzono dla temp. 5 i 25 °C. Dane z degradacji były bardzo dobrze opisywane wykładniczą postacią modelu trzy i półrzędowej kinetyki i w dużo mniejszym stopniu przez model kinetyki pierwszorzędowej. Było to prawdopodobnie spowodowane zmianami mikrobiologicznej aktywności biomasy w czasie procesu degradacji. Dlatego zastosowano również równanie kinetyki rzędu zerowego. Wartości $DT50$ z równania pierwszego rzędu dla 25 °C dla poziomu Ap, Eg, Bt and $2C_{Ca}$ wyniosły odpowiednio 12,3, 20,2, 76,6 i 183,1 dni. Energie aktywacji E_a dla wszystkich poziomów gleby mieściły się w zakresie 52–67 kJ · mol⁻¹. Proces adsorpcji przebiegał bardzo szybko i w czasie 2 godz. ustalała się równowaga, a w przypadku desorpcji po maksymalnie 8 godz. Dane kinetyczne były dobrze opisywane za pomocą modelu kinetyki dwucentrowej. Otrzymano izotermy Freundlicha typu L. Największe wartości K_d^{ads} otrzymano dla próbek z poziomu Bt – 32,89, najmniejsze dla próbek z poziomu $2C_{Ca}$ – 0,656. Tak samo było w przypadku desorpcji: 34,99 dla poziomu Bt i 1,105 dla $2C_{Ca}$. Wyniki wskazują, że minerały ilaste odgrywają ważną rolę w procesach sorpcyjno-desorpcyjnych tego związku w glebie. Wyznaczona wartość indeksu GUS wskazuje, że karbendazym jest na granicy pomiędzy związkami niepodatnymi na wymywanie i przejściowymi.

Słowa kluczowe: karbendazym, adsorpcja, desorpcja, kinetyka, degradacja, gleba lessowata, indeks GUS