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Effect of pH on the adsorption of carbendazim in Polish mineral soils

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HIGHLIGHTS

- ► Adsorption of carbendazim in soils was inversely correlated to soil pH.
- ► At low pH carbendazim was adsorbed predominantly by clay minerals.
- ► Al^{3+} influenced adsorption of the protonated form of carbendazim on clays.
- ► Created models predict pH-dependent sorption processes in the whole soil profiles.

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ABSTRACT

The study aimed to determine the influence of pH on the adsorption of carbendazim in soil profiles of three mineral agricultural soils: Hyperdystric Arenosol, Haplic Luvisol and Hypereutric Cambisol. In the examined pH range between 3 and 7 the adsorption of carbendazim was inversely correlated to the pH of the soil. The adsorption coefficients were in the range between 0.3 and 151.8 mL g^{-1}. Decreasing the pH in the soil suspensions from 7 to 3 increased the value of this coefficient by 3 to 70 times. A decrease in the amounts of organic matter down the soil profiles was not associated with weaker carbendazim adsorption. In the samples from all soil horizons, at pH values between 3 and 6, the predominant sorption process was carbendazim adsorption on clay minerals. The adsorption of carbendazim on organic matter prevailed over that on clays only at $pH > 6$ and only in the Ap horizon of the examined soils. The developed mathematical models yielded very good results when the adsorption of the protonated form of carbendazim was assumed to be the predominant adsorption process on clays together with the adsorption of neutral molecules on organic matter and clays. The results from both the model fitting and the experiments revealed the negative effect of Al oxides and hydroxides and Al cations on the adsorption of the protonated form of carbendazim on clay minerals. The developed models successfully described the pH-dependent adsorption processes of carbendazim for both data from particular soil horizons and those from all three examined soil profiles.

1. Introduction

Carbendazim (methyl-benzimidazol-2-ylcarbamate) is a systemic fungicide that controls various fungal pathogens of cereals, fruits and vegetables and is used on a large scale throughout the world (Berglöf et al., 2002; Cancela et al., 1992; Tomlin, 1997). Due to the slow rate of degradation and the relatively high adsorption of carbendazim, it may remain in an immobilized state in the soil for a long time (Berglöf et al., 2002; Lewandowska and Walorczyk, 2010). As a potential environmental hazard, both the parent compound and its degradation products have become the subject of considerable research (EFSA, 2010; Lewandowska and Walorczyk, 2010; Li et al., 2011).

Previous studies (Aharonson and Kafkafi, 1975a, 1975b; Berglöf et al., 2002; Cancela et al., 1992; Leistra and Matser, 2004; Nemeth-Konda et al., 2002) have shown that the adsorption of carbendazim onto organic matter and clay minerals plays a significant role in its retention by soils. The interaction of organic bases with soil components usually involves more than one sorption mechanism, including hydrophobic sorption, van der Waals interactions, hydrogen bonding, charge transfer, and ion exchange after protonation (Berglöf et al., 2002; Cancela et al., 1992; Kah and Brown, 2006).

Smectites exhibit a high affinity for carbendazim, and its adsorption is inversely correlated to pH (Aharonson and Kafkafi, 1975a). No significant adsorption of this compound has been observed on either illite and kaolinite (Cancela et al., 1992) or on Al oxides (Aharonson and Kafkafi, 1975a). The results of a few reports in which the effect of pH on the adsorption of carbendazim in soils was considered are not consistent. Aharonson and Kafkafi (1975b), Nicholls and Evans (1991) and Berglöf et al. (2002) have reported that the adsorption of carbendazim was inversely correlated to the soil pH, but a positive correlation (Berglöf et al., 2002) and a lack of correlation have also been observed (EFSA, 2010). Furthermore, there are very few studies examining carbendazim adsorption in soil profiles (Carbo et al., 2007). In addition, the current modeling of the adsorption of ionizable pesticides in soils has focused primarily on acidic compounds (Jafvert, 1990; Lee et al.,

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1990; Regitano et al., 1997; Spadotto and Hornsby, 2003). The studies performed by Franco et al. (2009) and Kah and Brown (2007) have shown that general models that assume the adsorption of ionizable pesticides onto organic matter and estimate the adsorption based on their octanol–water partition coefficient corrected for pH satisfactorily described the adsorption of acidic pesticides, but failed to do so for basic compounds. According to Kah and Brown (2007) relatively little experimental evidence is available concerning the adsorption processes of weak organic bases in soils and the balance between them in soil components is not fully understood.

This work aimed to determine the influence of pH on the adsorption of carbendazim in the soil profiles of three mineral soils that had different physical and chemical properties. The results were examined to discriminate and estimate the contribution of the main adsorption processes and the main soil components that affected the retention of carbendazim. In addition, an attempt was made to create a mathematical model describing the pH-dependent adsorption of this fungicide.

2. Materials and methods

2.1. Soils

Three soils–Hyperdystric Arenosol (location 22°14′N, 51°24′E), Haplic Luvisol (location 22°10′N, 51°26′E) and Hypereutric Cambisol (location 23°22′N, 50°51′E)–were selected as representative for the Polish agricultural soils. In this text, the soils are denoted as AR, LV and CM respectively. These soils were selected based on the database from the Institute of Agrophysics, Polish Academy of Science (Gliński et al., 1991). Some areas in Poland are not represented by FOCUS scenarios, primarily because their prevailing soil types are coarser or have a lower organic carbon content (FOCUS, 2009). Although the soil composition is typical of Poland and parts of other countries in Central Europe (FOCUS, 2009; Gliński et al., 1991), the FAO reference soil groups of the selected soils are common in most of Earth's temperate regions (Driessen and Deckers, 2001).

The samples were collected from the Ap, BC and C horizons of AR, the Ap, E and Bt horizons of LV and the Ap, Bw and BC horizons of CM; then, the samples were air-dried, passed through a 2 mm mesh diameter sieve and homogenized. The characteristics of the soil properties are provided in Table 1; further details have been presented elsewhere (Paszko, 2009). The soil mineralogy was determined by X-ray diffraction analysis, the organic carbon content (C_{oc}) was determined using a Shimadzu TOC-VCSH analyzer, and the pH was determined with a glass electrode and iron and aluminum oxides using the dithionite–citrate–bicarbonate (DCB) method (Mehra and Jackson, 1960). The effective cation exchangeable capacity (ECEC) and the percentage of Al^{3+} saturation ($C_{Al\ sat}$) were determined in an unbuffered 1.0 M NH_4Cl solution with desorption using 1.0 M KCl, according to Skinner et al. (2001).

Table 1
Selected properties of the soils.

Soil	Hyperdystric Arenosol			Haplic Luvisol			Hypereutric Cambisol		
	(AR)			(LV)			(CM)		
Soil horizon	Ap	BC	C	Ap	E	Bt	Ap	Bw	BC
Depth (cm)	5–15	35–45	65–75	5–15	35–45	65–75	10–20	35–50	65–75
Sand (%)	89	95	96	73	73	58	15	11	14
Silt (%)	9	4	3	24	20	19	77	81	77
Clay (%)	2	1	1	3	7	23	8	8	9
pH (H_2O)	4.35	4.68	5.05	4.85	4.96	5.04	5.97	6.08	5.85
pH (KCl)	4.03	4.43	4.39	4.27	4.48	4.30	5.82	5.66	5.62
C_{oc} (%)	0.68	0.09	0.03	0.93	0.12	0.08	1.23	0.53	0.49
C_{Fe} (%)[a]	0.094	0.073	0.077	0.167	0.249	0.511	0.314	0.327	0.262
C_{Al} (%)[a]	0.055	0.051	0.030	0.068	0.05	0.076	0.033	0.049	0.041
ECEC (meq/100 g)	2.15	1.67	1.81	4.41	3.26	12.32	15.88	12.72	12.03
$C_{Al\ sat}$ (%)	19.96	29.05	19.11	9.58	5.85	2.98	0.49	0.50	0.45
Mineralogy[b]	CQKIG	CQKI	CQKI	VIKQ	VQKI	VIKQ	SIQK	SQK	SQKI

[a] Values obtained using the Mehra and Jackson (1960) method.

[b] C—chlorite, G—goethite, K—kaolinite, I—illite, Q—quartz, S—smectite and mixed smectite–illite structures, V—vermiculite and mixed vermiculite–chlorite structures.

2.2. Batch adsorption experiments

The 50.0 μg mL^{-1} carbendazim stock solution in 0.01 M $CaCl_2$ (acidified to pH 4 with HCl and containing 1% of methanol) was prepared from analytical standard carbendazim PESTANAL® (purity 99.1%) purchased from Sigma-Aldrich (Poznań, Poland). The other solvents and chemicals used in this study were of analytical or HPLC grade. The selection of the appropriate soil/solution ratio (1:5) was determined in the preliminary study. Preliminary experiments on the kinetics of the carbendazim adsorption were performed according to the OECD guideline 106 (OECD, 2000). The results indicated that, as in the previous studies (Paszko, 2006), the process occurred rapidly; equilibrium was most often achieved in 1–2 h and no later than 8 h, and the adsorption kinetics was not influenced by carbendazim degradation (data not shown).

For the experiments that examined the influence of pH on adsorption, 9 mL of 0.01 M $CaCl_2$ was added to the duplicate 2 g soil samples. Then, for approximately 8 h, the pH was adjusted to the desired values in the range of 3–7 using either 0.05 M HCl or 0.024 M $Ca(OH)_2$ (i.e. saturated solution at room temperature (Elert et al., 2008)). Afterwards, 1 mL aliquots of 50.0 μg mL^{-1} carbendazim in 0.01 M $CaCl_2$ were added to the samples, the tubes were agitated for 24 h, the final pH values of the soil suspensions were measured, and, after centrifuging (10 min, 2790 g), aliquots of the aqueous phase were collected for analysis. The initial carbendazim concentration in the solution was 5 μg mL^{-1}; this value is in the range of typical field application rates for this fungicide (i.e., from 0.065 kg ha^{-1} (EFSA, 2010) to 2 kg ha^{-1} (Berglöf et al., 2002)).

The effects of Al and Fe oxides and hydroxides on the adsorption of carbendazim were examined using duplicate 2 g soil samples prepared using the Mehra and Jackson (1960) method. The DCB procedure was repeated three times for each soil sample. Afterwards, the samples were saturated twice with 20 mL of 1.0 M KCl, agitated for 30 min and washed three times with 20 mL of 0.01 M $CaCl_2$ after centrifuging. The reference samples that were not subjected to the DCB procedure were saturated twice with 20 mL of 1.0 M KCl and washed three times with 20 mL of 0.01 M $CaCl_2$. The purpose of the above step was to eliminate the differences in the sorption capability of the reference and altered soil samples that result from their differences in saturation with exchangeable cations after the DCB procedure.

Then, in all soil samples, the volume of the liquid phase was adjusted to 9 mL, and the pH values of the altered samples were adjusted to that of the reference samples. Next, 1 mL aliquots of 50.0 μg mL^{-1} carbendazim in 0.01 M $CaCl_2$ were added to the samples, the samples were agitated for 24 h, and then, the pH was measured. After centrifuging, the aqueous phase was collected for analysis.

For the experiments that examined the influence of Al^{3+} on the adsorption of carbendazim duplicate 2 g soil samples were equilibrated for 8 h with 9 mL of a 1.25 mM $AlCl_3$ solution in 0.01 M $CaCl_2$ or of a 6.0 mM $AlCl_3$ solution in 0.01 M $CaCl_2$. In the reference soil samples, which were only equilibrated with 0.01 M $CaCl_2$, the pH in the soil suspension was adjusted to the values obtained in the respective samples equilibrated with $AlCl_3$ in $CaCl_2$. Then, 1 mL aliquots of 50.0 μg mL^{-1} carbendazim in 0.01 M $CaCl_2$ were added to the altered and reference samples; the subsequent part of the experiment was performed as described above.