Adsorption, degradation and mobility of carbendazim in profiles of Polish mineral soils

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ABSTRACT

Herein, we report the results of a study aimed at estimating the potential of carbendazim for translocation into groundwater and its retention in 27 profiles of the most common Polish arable soils, including Arenosols (AR) formed from sand, Luvisols (LV) formed from loamy sand or loam and Luvisols or Cambisols (LV&CM) formed from loess or loess-like formations. The adsorption of carbendazim was characterized by very high variability because the distribution coefficients were in the range of 0.86–16.71 mL g^{-1} for AR, 1.92–184.41 mL g^{-1} for LV and 0.65–57.11 mL g^{-1} for the LV&CM profiles. The effectiveness of desorption from the soil using 0.01 M CaCl$_2$ was in the range of 35.7–87.0%, 9.5–76.7% and 22.5–75.5% for the AR, LV and LV&CM profiles, respectively. The obtained half-lives for the selected soil profiles, which were recalculated at 10 kPa and 20 °C, were in the range of 13.3–39.7 d in the Ap horizon and increased to 368 d down the soil profile. A comparison of the horizons from the same depth indicated that the degradation rate was the highest in soils with the highest microbial activity and pH. The simulations using FOCUS PELMO indicated that carbendazim was retained in the Ap horizon, and its concentration in groundwater at a depth of 1 m was not expected to exceed the European Union contamination limit. The nonlinear regression modeling studies of the pH-dependent adsorption of this fungicide have shown that it is well described in typical arable soils assuming that the protonated form of carbendazim adsorbs on clay and the neutral form adsorbs onto organic matter. In sandy soils with a low pH and low content of organic matter, the adsorption of carbendazim cations onto the sand should also be incorporated into the model.

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1. Introduction

Adsorption and degradation are key processes that determine the retention of pesticides in soil profiles and their translocation into groundwater. Understanding the effects of the physicochemical and biological properties of soil and pesticide on the course of these processes is important because it allows for the prediction of the environmental fate of pesticides. Ionizable pesticides comprise a significant and increasing proportion of the active substances used in Europe. However, methods that predict their behavior in soils are poorly developed (Kah and Brown, 2006, 2007).

Carbendazim (methyl benzimidazol-2-ylcarbamate) is a systemic, basic fungicide with a pKa of 4.2, that has been used in agriculture on a large scale throughout the world (Berglöf et al., 2002; Cancela et al., 1992; Tomlin, 1997). It is strongly adsorbed in soils and usually desorbs only to a minor extent (Berglöf et al., 2002; Nemeth-Konda et al., 2002). Both soil organic matter and clay minerals participate in the adsorption of this compound in soils (Berglöf et al., 2002; Cancela et al., 1992; Paszko, 2012), but soil pH influences both the adsorption mechanisms and the contribution of the soil components in the total sorption (Paszko, 2012).

Carbendazim exhibits moderate persistence in soils (EFSA, 2010) with half-lives (DT_{50}) in the range of 3–15 weeks in topsoils with natural moisture (Aharonson and Kafkafi, 1975; EFSA, 2010; Jones et al., 2004). The fungicide is primarily degraded by soil microorganisms (Helweg, 1977), and its primary degradation product in soil is 2-aminobenzimidazole (EFSA, 2010; Helweg, 1977).

Many authors have demonstrated the positive impacts of an increase in soil pH on the total microbial biomass and their activity (Anderson and Joergensen, 1997; Bezdicek et al., 2003; Pietri and Brookes, 2008). Therefore, the degradation of ionizable organic compounds is typically higher at higher pH. However, when abiotic degradation is dominant, the pH typically has a negative influence on the rates of degradation (Kah et al., 2007). Adsorption and degradation are often correlated with each other because sorption processes affect biodegradation by modifying the chemical bioavailability of the adsorbed species (FOCUS, 2009; Kah et al., 2007; Villaverde et al., 2008). According to EFSA (2010), the existing studies on the aerobic degradation of carbendazim in soils are not sufficient. Studies on the adsorption and degradation of this fungicide have been primarily limited to topsoils (Carbo et al., 2007).

Carbendazim is currently approved in the European Union (EU) as a plant protection product with restrictions on crop uses and application rates. However, the preliminary simulations performed with the FOCUS PELMO software using the Freundlich organic carbon adsorption coefficient and degradation parameters obtained by EFSA (2010) indicated that

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that in the coarsest Polish soils with low organic matter content, the concentration of carbendazim in the groundwater at a depth of 1 m can exceed the EU contamination limit.

The first aim of the current study of the adsorption and degradation processes of carbendazim in the most common types of Polish mineral soils was to estimate the capability of this fungicide to be retained in the soil profiles and to translocate into groundwater. The second objective was to estimate the extent to which the previously developed model (Paszko, 2012) describes the pH-dependent adsorption of carbendazim in soils in which the pH was artificially modified is applicable to soils at their native pH.

2. Materials and methods

2.1. Soils

The examined soil profiles were selected from the database and soil collection of Polish arable soils from the Institute of Agrophysics Polish Academy of Sciences (Gliński et al., 1991). Eleven profiles, which are classified according to FAO (2006) as Arenosols, represented 27% of the coarsest arable soils that are formed from sand. Nine profiles, which are classified as Luvisols, represented 24.7% of the soils formed from loamy sand or loam. Seven profiles, which are classified as Luvisols or Cambisols, represented 6.9% of the soils formed from loess or loess-like formations. The soil groups are denoted in the text as AR, LV and LV&CM, respectively. The locations of the selected profiles reflected the main areas of occurrence of the examined soil groups in Poland. The content of clay (C_{clay}) in the AR, LV and LV&CM profiles was in the range of 0.8–3.1%, 3.5–28.0% and 2.1–19.7%, respectively. The content of organic carbon (C_{oc}) was in the range of 0–1.42%, 0.06–1.69% and 0.12–1.8%, respectively. The pH values (in 0.01 M $CaCl_2$) were in the range of 3.9–6.6, 4.2–6.8 and 4.9–7.7, respectively. Details concerning the properties of the soils and their locations are presented in the Supplementary Data, SD 1. It should be mentioned that some areas in Poland are not represented by any of the nine FOCUS scenarios because in most cases, the prevailing soil types are coarser or contain lower organic carbon contents (FOCUS, 2009). The soil samples from all twenty-seven soil profiles were air-dried, passed through a 2 mm sieve, homogenized and then used for adsorption–desorption experiments.

Three soil profiles (i.e., 611, 590 and 564) were selected for degradation experiments. The main criterion for selection was the pH of the soils, which was in the range of 4.1–4.6 for profile 611, 4.7–5.0 for profile 590 and 6.2–6.6 for profile 564. The changes in the pH of the selected profiles reflected differences between the examined soil groups. The sampling depth was chosen by taking into account changes in soil microbial activity. The samples for the degradation experiments were passed through a 2 mm sieve, homogenized, moisture adjusted to 40% of the maximum water holding capacity (MWHC) and stored in the dark at 4 °C (not for longer than a month after collection from the field). The main properties of the soils are presented in Table 1.

2.2. Soil analyses

The particle size distributions of the sand, silt and clay fractions of the soil were determined using the pipette method (ISO 11277, 2009). The sand and silt subfractions were determined using a Mastersizer 2000 particle size analyzer with a Hydro 2000G adapter (Malvern Instruments) according to Ryżak and Bieganowski (2011), and results from the laser analysis were corrected for the pipette method results according to Taubner et al. (2009). The soil mineralogy was determined using X-ray diffraction analysis. The pH was determined with a glass electrode, and the organic carbon content was determined using a Shimadzu TOC-VCSH analyzer. The content of exchangeable Al was determined after extraction with 1.0 M KCl (Bertsch and Bloom, 1996) using a Varian 820-MS inductively coupled plasma mass spectrometer.

The maximum water holding capacity of the soils was determined at 1 kPa using a porous plate and burette apparatus (ISO 11274, 1998). The soil microbial biomass was determined using the substrate-induced respiration method (ISO 14240-1, 1997). The soil microbial activity was determined based on the dehydrogenase activity (the method of Casida et al. (1964) using the modification of Brzezińska et al. (1998)) and the fluorescein diacetate hydrolysis (Schnürer and Rosswall, 1982).

2.3. Batch adsorption and desorption experiments

Five concentrations of carbendazim (2.0, 10.0, 26.0, 38.0 and 50.0 μg mL^{-1}) in 0.01 M $CaCl_2$ (acidified to pH 4 using HCl and contained 1% methanol) were prepared from the analytical standard carbendazim PESTANAL® (purity 99.1%), which was purchased from Sigma-Aldrich (Poznań, Poland). The other chemicals and solvents used in the study were of analytical or HPLC grade. The batch adsorption and desorption experiments were performed according to the OECD guideline 106 (OECD, 2000) at 22 ± 1 °C. The selection of the appropriate soil/solution ratio (1:5) and kinetic experiments were made in the preliminary study. The results of the experiments on the kinetics of the carbendazim adsorption and desorption indicated that, as in the

Table 1
Main properties of the soils selected for degradation experiments.

Soil profile number	611			590			564		
Soil group	Arenosol (AR)			Luvisol (LV)			Cambisol (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
C_{sand} (%)	87.5	92.6	96.1	80.1	79.8	60.0	25.5	18.5	21.3
C_{silt} (%)	10.1	5.7	2.4	16.5	15.3	20.6	64.8	71.7	68.3
C_{clay} (%)	2.4	1.7	1.5	3.5	4.9	19.4	9.7	9.8	10.4
C_{oc} (%)	0.68	0.09	0.03	0.93	0.12	0.08	1.23	0.53	0.49
C_{Al} (mg kg^{-1})	35.20	25.38	24.50	25.57	6.22	19.63	0.13	0.03	0.01
pH ($CaCl_2$)	4.1	4.6	4.3	4.7	5.0	4.9	6.6	6.3	6.2
MWHC (%)[a]	23.0	18.1	16.1	29.4	22.1	35.3	44.5	38.1	33.7
C_{mic} (μg g^{-1})[b]	276	185	112	380	165	105	424	177	147
DHA (nm kg^{-1} min^{-1})[c]	17.2	12,6	12.9	53.6	13.3	13.4	51.2	13.0	5.9
FDA (μg g^{-1} h^{-1})[d]	1.64	0.19	0.1	2.71	0.56	0.13	1.72	0.48	0.14
Mineralogy[e]	CQKIG	CQKI	CQKI	VIKQ	VQKI	VIKQ	SIQK	SQK	SQKI

[a] Maximum water holding capacity.
[b] Soil microbial biomass.
[c] Soil dehydrogenase activity.
[d] Rate of fluorescein diacetate hydrolysis.
[e] C — chlorite, G — goethite, K — kaolinite, I — illite, Q — quartz, S — smectite and mixed smectite–illite structures, V — vermiculite and mixed vermiculite–chlorite structures (data for fractions <20 μm).