

Sorption Behavior of Prochloraz in Different Soils

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The sorption behavior of the imidazole fungicide prochloraz [PCZ; *N*-propyl-*N*-[2-(2,4,6-trichlorophenoxy)ethyl]imidazole-1-carboxamide] was studied in batch experiments with different soils. The soil organic matter content was found to control the amount sorbed by different soils. K_d values ranged from 56 ± 0 to 552 ± 10 (mean = 221 ± 5) and K_{OC} values from 7273 ± 0 to 16250 ± 1300 (mean = 11829 ± 303). As calculated from a linear regression of K_d versus %OC, K_{OC} was 12900 ± 1300 . Additionally, the pH value of the soil had considerable influence on the sorption of the weakly basic PCZ ($pK_a = 3.8$), giving rise to stronger sorption at lower pH. K_d values determined on pH-modified soils confirmed the pH dependency. Sorption isotherms on two soils were recorded, initial concentrations ranging from 0.09 to 5.71 mg L⁻¹. The Freundlich isotherm was fitted to the values measured. The Freundlich exponents calculated were significantly smaller than unity, indicating nonlinear sorption. Sorption experiments with two metabolites of PCZ (PCZ-formylurea and PCZ-urea) revealed K_d values one-fourth to one-third those for PCZ on two soils.

Keywords: Prochloraz; metabolites; soil; sorption; pH dependency

INTRODUCTION

Prochloraz [*N*-propyl-*N*-[2-(2,4,6-trichlorophenoxy)ethyl]imidazole-1-carboxamide, PCZ] belongs to the group of imidazole fungicides that inhibit ergosterol biosynthesis. It is widely used to control eyespot disease and powdery mildew on cereals, and it is also effective against a broad spectrum of fungal diseases on fruits and vegetables (Birchmore et al., 1977; Lafuente and Tadeo, 1985; Kapteyn et al., 1992). The recommended application rate in cereals is 400–600 g of active ingredient ha⁻¹ (Tomlin, 1994).

Owing to its imidazole moiety, prochloraz is weakly basic, with a pK_a of 3.8. It exhibits a low water solubility of 34.4 mg L⁻¹ and a high lipophilicity with a log P_{OW} of 4.38. Photolysis in aqueous solution with a half-life of 10 days has been reported. Dissipation half-lives in soil range between 5 and 37 days under field conditions, whereas in laboratory studies half-lives between 92 and 171 days have been observed (Tomlin, 1994; ARS/USDA, 1997). The main metabolic pathway of prochloraz in rats starts with *N*-formyl-*N*-propyl-*N*-[2-(2,4,6-trichlorophenoxy)ethyl]urea (PCZ-FU), which is then hydrolyzed to *N*-propyl-*N*-[2-(2,4,6-trichlorophenoxy)ethyl]urea (PCZ-U) (Needham and Challis, 1991). Both substances are found as metabolites in soil as well (Höllrigl-Rosta et al., 1998). Chemical structures of all three substances are presented in Figure 1.

Sorption of organic chemicals on soils substantially influences their fate, because mechanisms, such as

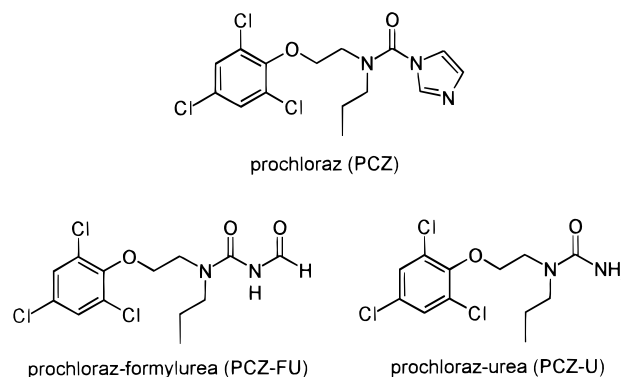


Figure 1. Chemical structures of PCZ and its metabolites PCZ-FU and PCZ-U.

transport, microbial uptake, or metabolization, are only operative on the fraction of nonsorbed molecules (Weber and Miller, 1989; Pignatello, 1989). A field study on the residual situation of prochloraz revealed that it was transferred to deeper soil layers by tillage rather than by leaching (Gottesbüren et al., 1992). Quantitative data on PCZ sorption are sparse. Only a K_{OC} value of 7500 and K_d values of 152 and 256 for a sandy loam and a silty clay loam, respectively, have been published (ARS/USDA, 1997; Tomlin, 1994).

The objective of this study was to characterize the sorption behavior of PCZ on six typical agricultural soils from Lower Saxony, Germany. Sorption isotherms were recorded, and the influence of soil properties (pH values, organic carbon, and clay contents) was examined. Numerical values of Freundlich parameters (K_f , $1/n$) and soil–water distribution coefficients (K_d) were determined, which allowed the assessment of leaching potential and risk of groundwater contamination. Additionally, K_d values for the more polar metabolites PCZ-FU and PCZ-U were determined.

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Table 1. Properties of the Soils from the Investigation Sites Neuenkirchen (NK) and Nienwohlde (NW), Lower Saxony, Germany

soil	USDA terms	texture			%OC	pH
		% sand	% silt	% clay		
NK1	silt loam	2	80	18	0.97	7.1
NK2	silt loam	3	69	28	0.77	7.8
NW1	loamy sand	76	19	5	1.52	5.3
NW2	sand	86	11	3	0.53	5.8
NW3	loamy sand	77	15	8	2.52	6.8
NW4	loamy sand	81	13	6	4.44	5.9

MATERIALS AND METHODS

Chemicals. PCZ was obtained as analytical standard material (chemical purity > 99%) from Riedel-de Haën, Seelze, Germany, and as phenyl-ring ¹⁴C-labeled material (radiochemical purity = 97.8%, specific activity = 1.473 MBq mg⁻¹) from Campro Scientific, Emmerich, Germany. Nonlabeled metabolites PCZ-FU and PCZ-U were supplied by AgrEvo, Saffron Walden, U.K.

Soils. Soils in this study were taken from the two catchment areas of the German Research Society's Special Collaborative Program 179 (Water and Matter Dynamics in Agro-Ecosystems) in Lower Saxony, Germany. They represent major types of agricultural soils in Germany: two silt loam soils (NK1, NK2) were selected from the foreland of the Harz mountains, and a sand (NW1) and three loamy sands with different organic matter contents (NW2, NW3, NW4) were obtained from the Lüneburger Heath. Soil samples were taken from the surface layer (0–5 cm), air-dried, and passed through a 2-mm sieve. After the water content had been adjusted to 40% of maximum water holding capacity, soils were stored in the dark at ambient temperature. Selected soil properties are shown in Table 1. Soil texture was determined according to the sedimentation vessel method (Moschrefi, 1983). Soil pH was measured in a 1:2.5 (w/w) mixture of soil with CaCl₂ solution (0.01 mol L⁻¹). After carbonate removal by treatment with HCl, the organic carbon content (%OC) was determined using a TOC analyzer (DC-90, Dohrmann, Munich, Germany); combustion at 900 °C in a stream of O₂, 200 mL min⁻¹).

Sorption Experiments. Sorption–desorption behavior was examined using the batch equilibration technique. A 0.01 mol L⁻¹ solution of CaCl₂ was used as aqueous phase, to ease phase separation and to keep ionic strength similar to that of a natural soil solution (OECD, 1981; von Oepen et al., 1991). Following Boesten (1990), the soil–water ratio of 1:5 recommended by OECD Guideline 106 was lowered to 1:1.4, which, moreover, more closely resembles natural conditions (Gottesbüren, 1991).

For the sorption experiments, 25 µg of PCZ in methanolic solution was put into a 75-mL centrifuge tube. The solvent was removed in a gentle stream of N₂ and the substance redissolved in 5 mL of CaCl₂ solution. Twenty-five grams of soil (dry matter) was added, and the total water content was adjusted to 35 mL with CaCl₂ solution to give an initial PCZ concentration (C_i) of 0.71 mg L⁻¹ in the aqueous phase. The centrifuge tube was closed with a Teflon-lined screw cap and mechanically shaken for 24 h at 22 ± 2 °C on a horizontal shaker at 250 rpm. Afterward, the suspension was centrifuged at 4000 rpm for 30 min and the supernatant removed for determination of radioactivity. The radioactivity remaining in the soil phase was also determined.

For kinetic studies, samples were shaken for 1, 6, 24, 48, and 72 h. For determination of sorption isotherms, C_i ranged from 0.09 to 5.71 mg L⁻¹. Nonlabeled PCZ and radiolabeled PCZ were mixed in spiking solutions to keep the total amount of applied radioactivity constant.

When experiments were performed with nonlabeled PCZ and its metabolites in the soils NK1 and NW1, C_i had to be higher due to reduced sensitivity of high-performance liquid chromatography (HPLC). Values were 2.86 mg L⁻¹ for the metabolites in both soils, as well as for PCZ in NK1, and 5.71 mg L⁻¹ for PCZ in NW1. To determine K_d values of nonlabeled

compounds, 20 mL of the supernatant was salted out with 2 g of NaCl and extracted with 40 mL of acetone and 40 mL of cyclohexane (Koinecke et al., 1994). The organic extract was dried over Na₂SO₄, passed through a 0.45-µm membrane filter (Macherey-Nagel, Düren, Germany), and evaporated. The residue was redissolved in 1 mL of 2-propanol and subjected to HPLC analysis.

Desorption experiments were conducted immediately after the corresponding sorption experiments. The supernatant removed was replaced by the same amount of a fresh CaCl₂ solution (0.01 mol L⁻¹). Shaking and subsequent separation of soil and aqueous phase were conducted as described above. Shaking time for desorption was always 24 h. All sorption and desorption experiments were performed at least in duplicate.

Modification of Soil pH. To investigate the influence of soil pH on the sorption of PCZ, the pH of two soils (NK1 and NW1) was modified following the procedure used by Zachara et al. (1986). Twenty-five grams dry soil was suspended in 63 mL of CaCl₂ solution (0.01 mol L⁻¹). Over the period of 2 days, pH values of the soil suspensions were adjusted four times by adding HCl (0.1 mol L⁻¹) or KOH solution (0.1 mol L⁻¹). Prior to the third adjustment, the supernatant liquid was exchanged against fresh CaCl₂ solution. Soil samples were transferred to centrifuge tubes containing 25 µg of PCZ in 5 mL of CaCl₂ solution, the total amount of water was adjusted to 35 mL (C_i), and the sorption experiments were performed as described above.

Radioassay. To analyze aqueous solutions (C_w), two 10-mL aliquots were mixed with Quicksafe A scintillation cocktail (Zinsser, Frankfurt, Germany). Radioactivity was directly measured with a Packard Tri-Carb 2500 liquid scintillation analyzer (Meriden, CT). Radioactivity in soil samples (C_s) was, first, determined by combustion of four aliquots of each soil in a Harvey oxidizer (Hillsdale, NJ) and liquid scintillation counting of the combustion gases absorbed in OxySolve C-400 scintillation cocktail (Zinsser). Second, radioactivity was calculated as the difference between the total amount of PCZ in the suspension (C_i) and the amount recovered in the aqueous phase (C_w).

The concentration of PCZ in pore water was assumed to be the same as in the supernatant. Thus, the amount of radioactivity entrained therein was magnitudes smaller than that actually sorbed to the soil. As compared to the inherent variability of parallel K_d determinations, its effect on calculations proved to be negligible.

HPLC Analysis. Solutions containing nonlabeled PCZ or metabolites were analyzed by HPLC. Analyses were performed using an HP 1050 system with an HP 1040A diode array detector (Hewlett-Packard, Avondale, PA). The column was an RP-select B 125-4 (Merck, Darmstadt, Germany). The mobile phase consisted of acetonitrile and phosphate-buffered water (0.001 mol L⁻¹ KH₂PO₄, adjusted to pH 8 by addition of KOH). The following gradient was applied: 0 min, 30% acetonitrile; 2 min, 30% acetonitrile; 20 min, 66% acetonitrile. Detection wavelengths were 205 and 225 nm.

RESULTS AND DISCUSSION

Kinetics. Sorption kinetics were studied in the silt loam NK1 and the loamy sand NW1. Results indicate that PCZ was sorbed to both soils through a two-step process. During the first hour, sorption was rapid; thereafter, the system slowly approached a steady state (Figure 2). This may be interpreted as a weak binding of the molecules to outer sorption sites in the first and subsequent diffusions to inner sorption sites in the second step (Gilchrist et al., 1993). Even after 72 h, no actual equilibrium was reached, as proven by desorption experiments using the batches with sorbed PCZ. Ratios of the K_d values for adsorption within 1–72 h to the corresponding K_d values for desorption within 24 h (K_d^{ads}/K_d^{des}) were always below unity, indicating sorption nonideality (Beck et al., 1993, 1996a). These

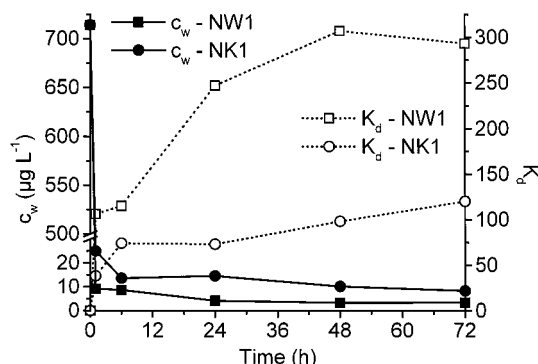


Figure 2. Concentrations of PCZ in the aqueous phase and calculated K_d values versus sorption time on two different soils.

quotients increased from $38/75 = 0.51$ to $120/141 = 0.85$ for the silt loam and from $106/366 = 0.29$ to $293/396 = 0.74$ for the loamy sand with increasing time of adsorption. Intraparticle diffusion and intrasorbent diffusion are frequently cited as causes for the nonattainment of equilibrium (Beck et al., 1993). The low desorption rates in samples subjected to short adsorption times may be ascribed to a negative concentration gradient in the soil particles that hinders molecule diffusion toward the aqueous phase. The gradient's slope becomes smaller as the system approaches equilibrium state, allowing the sorption process to become more reversible (Streck et al., 1995).

Because there is a large discrepancy between the contact times of soil and water under natural conditions and the time periods that are necessary for a soil–water system to obtain equilibrium as determined in laboratory batch studies, most soil–water systems never reach their equilibrium state under field conditions. As Beck et al. (1996b) pointed out, short-term transport and bioavailability of organic chemicals within soils are mainly governed by the initial rapid sorptive uptake. Therefore, K_d values after 24 h were used to compare sorption behavior as affected by various soil properties and to investigate the concentration dependence of K_d values.

Sorption Isotherms. Sorption isotherms were determined for the silt loam NK1 and the loamy sand NW1. Because they are based upon distribution coefficients after 24 h, they do not represent an actual thermodynamic equilibrium. For both soils, the isotherms observed were nonlinear. Fitting the Freundlich equation to the experimental data resulted in exponents $1/n$ of 0.82 ± 0.02 and 0.88 ± 0.04 and Freundlich constants K_f of 110 ± 8 and 251 ± 23 for NK1 and NW1, respectively (all results given as mean \pm standard error of the mean). Correlation coefficients were $r = 0.996$ (NK1) and 0.990 (NW1). A linear model was also fitted to the data. When including all data points, K_d values (as expressed in units of $L\ kg^{-1}$) from linear regression were 35 ± 2 and 123 ± 8 with correlation coefficients $r = 0.982$ and 0.975 for NK1 and NW1, respectively. Significant deviation from linearity occurred only at the highest initial concentration ($5.71\ \mu\text{g}\ L^{-1}$). Therefore, linear regression was also performed excluding these data points. K_d values calculated this way were 59 ± 2 and 226 ± 19 with correlation coefficients of $r = 0.997$ and 0.969 for NK1 and NW1, respectively. Thus, within the range from 0.09 to $2.86\ \mu\text{g}\ mL^{-1}$, the soil–water distribution coefficient appears to be independent of the initial PCZ concentration. At the highest initial PCZ concentration, the relative amount of PCZ sorbed after

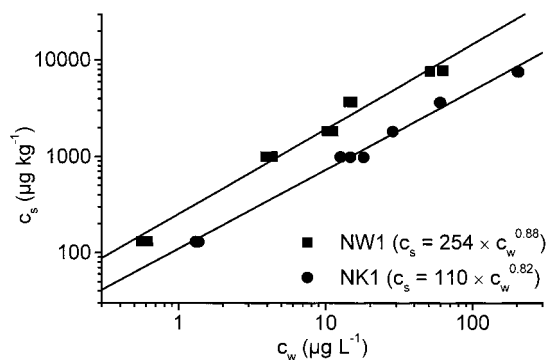


Figure 3. Freundlich isotherms fitted to sorption data of PCZ on two different soils.

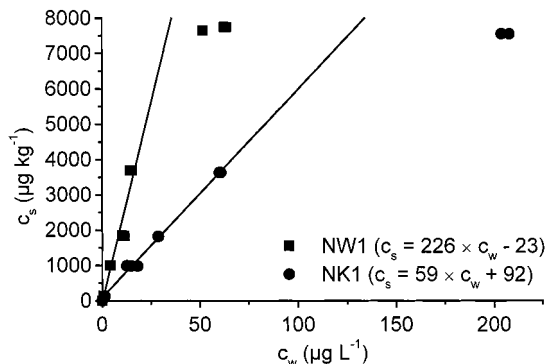


Figure 4. Linear isotherms fitted to sorption data of PCZ on two different soils (highest concentrations c_w excluded in both cases).

Table 2. PCZ Sorption Coefficients for Soils with Different Organic Matter and Clay Contents ($C_i = 0.71\ \text{mg}\ L^{-1}$, 25 g, 35 mL, 24 h, Ambient)

soil	K_d^{ads}	$K_d^{\text{ads}}/K_d^{\text{des}}$	K_{OC}
NK1	73 ± 2 (14)	0.83	7526 ± 206
NK2	56 ± 0 (2)	0.84	7273 ± 0
NW1	247 ± 6 (6)	0.71	16250 ± 395
NW2	78 ± 4 (2)	0.74	14717 ± 755
NW3	322 ± 6 (2)	0.75	12778 ± 238
NW4	552 ± 10 (2)	0.82	12432 ± 225
mean	221 ± 5		11829 ± 303

24 h was markedly lower, suggesting a limitation of outer sorption sites occupied in the rapid first step. Sorption data of NK1 and NW1 together with fitted Freundlich and linear isotherms are depicted in Figures 3 and 4, respectively.

Influence of Soil Properties. Organic matter and clay minerals are often thought to be the soil components responsible for sorption. Their influence was examined by determination of K_d values at 24 h (K_d^{ads}) in all six soils (soil properties are listed in Table 1). To obtain additional information about the non-equilibrium state reached after 24 h, desorption values (K_d^{des}) were also measured. The calculated ratios of K_d^{ads} to K_d^{des} show that no equilibrium state was reached in any of the soils after 24 h (Table 2). Furthermore, none of these ratios was correlated with soil properties (texture, organic carbon content, pH).

A higher clay content appears to have no enhancing influence on the sorption of PCZ, because the silt loam NK2 gave the lowest K_d value. Also, no simple relation between K_d values and texture of the other soils was found. In contrast, organic carbon content and distribution coefficients K_d were positively correlated. From a

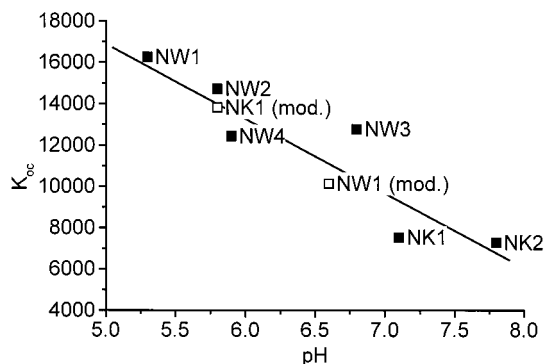


Figure 5. K_{OC} values of PCZ on six unmodified and two pH-modified soils versus soil pH.

least-squares linear regression of K_d values versus organic carbon contents, a K_{OC} of 12900 ± 1300 was calculated as the slope of the fitted straight line with a correlation coefficient of $r = 0.981$. K_{OC} values determined this way are more widely applicable than those obtained by simple division of a K_d value for a particular soil by the corresponding organic carbon content (Payá-Perez et al., 1992). These results for PCZ agree well with those from other sorption studies using poorly water soluble, lipophilic compounds, in which sorption was found to be influenced by organic carbon rather than by clay content. This may be due to the fact that the surfaces of clay minerals are often covered by organic matter or shielded by a "lipophobic" hydration shell and are hence not directly accessible for lipophilic organic compounds (Hamaker and Thompson, 1972; Calvet and Barriuso, 1994; Haderlein et al., 1996).

Regarding molecular parameters that can affect the sorption of PCZ, basicity has to be taken into account. Therefore, the impact of soil pH was examined by determining K_d values in pH-modified soils. The pH of NW1 was increased from 5.3 to 6.6 by addition of KOH and that of NK1 lowered from 7.1 to 5.8 by addition of diluted HCl. A control experiment with KCl revealed the same K_d as obtained in the unaltered soil NW1, proving that the addition of potassium ions did not affect the sorption of PCZ in that soil. The observed K_d values were transformed to K_{OC} values by normalization to the soil organic carbon content ($K_{OC} = K_d/\%OC \times 100$). Figure 5 shows the measured K_{OC} values plotted against soil pH for both modified and unmodified soils. The K_{OC} values determined in the other four soils are also included in this graph. A negative correlation between all K_{OC} and pH values was observed ($r = -0.915$). For weakly basic molecules, sorption maxima are often found at pH values near their pK_a (Hamaker and Thompson, 1972; Calvet, 1989). Lowering the pH increases the fraction of protonated molecules having interaction with the soil matrix based on not only van der Waals forces but also cation exchange mechanisms (Weber, 1982). Thus, sorption is increased due to promotion of pesticide-soil interactions. For PCZ, this is also supported by results from laboratory degradation experiments in the dark, showing slightly slower dissipation of PCZ in acidic than in neutral to basic soils (Höllrigl-Rosta et al., 1998). Stronger sorption of the molecules at lower pH seems to reduce bioavailability of PCZ for the degrading microorganisms.

Sorption of Metabolites. Sorption studies with PCZ-FU and PCZ-U were conducted using conventional HPLC analysis. To ensure comparability, K_d values of nonlabeled PCZ were determined accordingly. K_d values

Table 3. Sorption Coefficients of PCZ and Its Metabolites PCZ-FU and PCZ-U for Two Different Soils ($C_i = 2.86 \text{ mg L}^{-1}$, 25 g, 35 mL, 24 h, Ambient; $C_i = 5.72 \text{ mg L}^{-1}$ for PCZ in NW1)

soil	K_d		
	PCZ ^a	PCZ-FU	PCZ-U
NK1	59 ± 5 (2)	28 ± 3 (2)	13 ± 0 (2)
NW1	173 ± 2 (3)	35 ± 1 (2)	49 ± 2 (2)

^a Due to lower sensitivity of conventional HPLC analysis, higher initial concentrations of PCZ were applied than in radiotracer experiments, resulting in smaller K_d values.

of both metabolites were significantly lower than those of PCZ in the silt loam NK1 as well as in the loamy sand NW1 (Table 3). This reflects the higher polarity of the metabolites relative to the parent compound PCZ. Moreover, being urea derivatives, both metabolites are markedly less basic than PCZ and, therefore, cannot undergo cation exchange as readily as PCZ. PCZ-FU as well as PCZ-U exhibited stronger sorption in NW1 with its higher organic carbon content and much lower pH. Sorption of PCZ-U appeared to be much more influenced by soil organic carbon than that of PCZ-FU, because the K_d value of PCZ-U increased by nearly 4 times from NK1 to NW1, whereas that of PCZ-FU rose by only a factor of 1.25. This may indicate that sorption of the two compounds is determined by their different functional groups with dissimilar abilities to form hydrogen bonds; that is, PCZ-U has an amino group with two active hydrogens, whereas PCZ-FU has only an imino hydrogen with which to form a hydrogen bond.

CONCLUSIONS

PCZ was strongly sorbed on all soils examined in this study. With regard to mobility in soil, Fichter and Holden (1992) ascribed a high leaching potential to the following properties: $K_d < 5$; $K_{OC} < 300$; water solubility $> 30 \text{ mg L}^{-1}$; soil half-life $> 14\text{--}21$ days; and hydrolysis half-life > 175 days. Consequently, PCZ is not likely to leach into deeper soil layers or into groundwater despite its relatively long half-life for degradation in soil.

Experimental results indicate that PCZ is sorbed on soil through a two-step process. Rates of sorption are highest within the first hour and significantly smaller over the subsequent course of time. Although no true equilibrium is reached after 24 h, the system can be well described by applying the Freundlich equation. Freundlich exponents $1/n$ below unity indicate that sorption behavior of PCZ is concentration dependent, with sorption efficiency decreasing toward higher initial concentrations.

K_d values of PCZ were well correlated with organic carbon content of the soils but were not affected by clay mineral content. Hence, sorption of this fungicide is primarily determined by its interactions with soil organic matter. Owing to the basicity of PCZ, these interactions are further influenced by soil pH as revealed by increasing K_d and K_{OC} values with decreasing pH.

K_d values of the PCZ metabolites, PCZ-FU and PCZ-U, were markedly smaller than those of the parent compound. Whereas sorption of PCZ-U appeared to be strongly dependent on organic carbon content, corresponding values for PCZ-FU showed only little variation, thus indicating sorption through different functional groups. The risk of groundwater contamination by PCZ metabolites depends on their concentration in

soil and thus on their rates of formation and degradation, which are discussed by Höllrigl-Rosta et al. (1998).

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