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Bentazone adsorption and desorption on agricultural soils

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Abstract – Herbicide fate and transport in soils greatly depend upon adsorption-desorption processes. Batch adsorption and desorption experiments were performed with the herbicide bentazone using 13 contrasted agricultural soil samples. Bentazone was found to be weakly sorbed by the different soils, showing average Freundlich adsorption coefficients (K_f) value of $1.4 \pm 2.3 \text{ mg}^{1-n_f} \text{ L}^{n_f} \text{ kg}^{-1}$. Soil organic matter content did not have a significant effect on bentazone sorption ($r^2 = 0.12$), whereas natural soil pH appeared to be a key factor ($r^2 = 0.68$). A large part (average of $96.9 \pm 4.1\%$) of the sorbed bentazone was released into aqueous solution after successive desorption steps, although some hysteresis was observed for each soil. Whereas soil pH was found to also influence bentazone desorption, other soil properties did not show well-defined relationships with sorption.

bentazone / adsorption / desorption / pH

1. INTRODUCTION

The abundant use of pesticides on cultivated fields is known to compromise soil and water quality. Several studies have shown their presence in both surface and groundwater (IFEN, 2004). Contamination of surface water and underlying water resources is a major concern since pesticides can pose immediate and/or long-term risks for ecosystems and humans (Garcia, 2003; Miersma et al., 2003; Wong et al., 2003).

Since pesticide behavior in soil strongly depends on adsorption-desorption phenomena, knowledge of these processes is important to accurately predict the mobility and fate of these chemicals in the subsurface (Bailey and White, 1970; Barriuso and Calvet, 1991; Coquet, 2003). Sorption influences pesticide degradation and leaching, and hence ultimately determines their fate in the environment (Laabs et al., 2000; Coquet, 2002; Wauchope et al., 2002; Coquet et al., 2004). While sorption of neutral compounds has been widely studied (Johnson and Sims, 1993; Gao et al., 1998a), sorption of weakly acidic chemicals such as bentazone (IUPAC name: 3-isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one 2,2-dioxide) has been far less investigated (Dubus et al., 2001).

Bentazone is a selective contact herbicide used for many crops. Its application to cultivated areas is a main concern since

this pesticide is frequently detected in both surface and ground water (Lagana et al., 2002). Previous studies with bentazone have shown a very low mineralization rate, with the chemical being readily available for leaching immediately after application to three contrasted agricultural soils (Boivin et al., 2004). Bentazone and other ionized pesticides have anionic groups that cause sorption to be affected by pH. This pH dependency of sorption is generally determined by artificially modifying the soil pH (Clausen et al., 2002).

Understanding pesticides desorption processes is also important since desorption determines the release rate and hence the potential mobility of pesticides in the subsurface (Huang et al., 1998; Gouy et al., 1999; Lesan and Bhandari, 2003). Several studies have shown the occurrence of hysteresis in the adsorption-desorption process (van Genuchten et al., 1974; Kan et al., 1994; Huang and Weber Jr., 1997; Weber Jr. et al., 1998). This suggests that sorption of pesticides occurs with only a limited degree of reversibility depending upon both the chemical itself (e.g. its structure and solubility) and the soil properties involved (e.g. texture and soil physico-chemical parameters) (Gramatica and Di Guardo, 2002). Thus, soil can be regarded as an entity that is initially able to bind pesticides by functioning as a quasi-permanent sink, but then also may release those products back into the soil solution (Gao et al., 1998b; Ding et al., 2002). The

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Table I. Selected physico-chemical characteristics of bentazone.

	Molecular formula	M.W. g·mol ⁻¹	pKa	Solubility in water mg·L ⁻¹ ; pH 7, 22 °C
Bentazone		240.3	3.3	570

exact mechanisms of hysteretic adsorption/desorption of anionic pesticides remain largely unknown (Ding et al., 2002).

The aim of this work was to identify the main parameters affecting bentazone adsorption/desorption and to assess its potential mobility in the subsurface. To meet these objectives, thirteen contrasting agricultural soils (coarse, medium and fine-textured soils) were selected and analyzed for their specific characteristics. Batch adsorption and desorption experiments were carried out and correlations between the standard Freundlich parameters (K_F , n_F) and soil characteristics were established using descriptive statistical analyses.

2. MATERIALS AND METHODS

2.1. Herbicides

¹⁴C-ring-labelled bentazone was used in our experiments (radiochemical purity > 99%; specific activity 6.69 MBq mg⁻¹). Selected bentazone molecular characteristics are reported in Table I. Non-radio-labeled solutions were prepared separately with aqueous calcium chloride solution (0.01 M) and then mixed with ¹⁴C-labelled methanol solutions to achieve the desired concentrations (0.25; 1; 5 and 10 mg L⁻¹). Methanol represented less than 0.01 percent of the total volume in the final solutions.

2.2. Selected soils

Samples were taken from the surface layers (0 to 15 cm) of thirteen cultivated soils. The soils were selected on the basis of their texture, organic matter content and pH (Tab. II). Twelve soils were from the Lorraine area (France) and one soil from Brittany (Experimental station of Kerlatic, France). Soil types were classified into cambisols, calcisols and regosols according to the FAO classification (WRB, 1998). Soil samples were air-dried, sieved to 2-mm, stored in the dark at room temperature (20 ± 2 °C) and sheltered from humidity.

2.3. Sorption/desorption experiments

Sorption isotherms were carried out using the standard batch equilibration method (OECD, 2000). In the first experiment, aqueous calcium chloride solutions (0.01 M, 10 mL) were added to three replicates of 2 g of air-dried, sieved soil, in 25 mL CorexTM glass centrifuge tubes, in order to bring the samples to water saturation. Tubes were shaken with a rotary agitator (60 rpm) for 1 h at 20 ± 2 °C in the dark and then centrifuged at 5000 g for 25 min using a Beckman, AvantiTM J-25 (Beckman Instruments, Inc, Fullerton, CA, USA). Next, supernatants were taken (8 mL), replaced by labeled solutions, after which the tubes were shaken again (same conditions as before). According to previous kinetic studies, equilibrium was assumed to be reached within the 16 h equilibration period (results not shown). Samples were next centrifuged similarly as before. The radioactivity of the supernatant solution was measured using a Packard 1900 tri-carb liquid scintillation analyzer (Packard Instrument Company, Meriden, CT, USA) after adding 10 mL of a scintillation cocktail (UltimaGoldTM, Packard Bioscience). The counting time was 10 min and a quench correction was made by the scintillator analyzer after calibration. Several tubes without soil were also shaken to serve as a control; they showed no loss of ¹⁴C. Thus, differences between the initial and equilibrium

Table II. Selected characteristics of the 13 cultivated soils. Soils are listed according to their organic matter content (from high to low).

Soil type	Clay (%)	Loam (%)	Sand (%)	O.M. (%) ^a	pH _{H2O}	C/N ^b	C.E.C. ^c (cmol kg ⁻¹)
Dystic Cambisol	17.7	45.2	37.1	6.03	5.3	10.50	13.5
Stagnic Cambisol	53.6	39.7	6.7	5.81	6.7	9.00	31.5
Calcaric Regosol ²	38.1	34.2	27.7	5.59	8.2	8.83	24
Fluvic Gleyic Cambisol	51.6	42.9	5.5	4.80	6.2	8.66	25.4
Eutric Cambisol ²	10.4	19	70.6	3.66	6.2	10.47	7.9
Calcaric Regosol ¹	33.4	25	41.6	3.63	7.9	8.66	14.7
Cambic Calcisol	45.5	44.3	10.2	3.64	8.1	10.59	16.9
Vertic Stagnic Cambisol	41.1	48.6	10.3	3.32	7	9.90	18.7
Cambic Stagnic Vertic Calcisol	50.9	34.8	14.3	2.77	8	7.92	21.2
Stagnic Luvisol	30.9	50	19.1	2.62	5.9	9.13	14.8
Fluvic Stagnic Cambisol	11.4	22.5	66.1	1.50	5.8	9.60	5.5
Eutric Cambisol ¹	12.7	13.8	73.5	1.43	6.4	10.13	4.6
Fluvic Cambisol	20.1	55.4	24.5	1.08	5.5	9.29	9.6

^a Organic matter content, ^b Organic carbon-nitrogen ratio, ^c Cation exchange capacity.

concentrations were assumed to be due to sorption onto soil. Sorption isotherms were obtained by plotting the amount of chemical sorbed per unit weight of soil at equilibrium (Q_e , mg kg⁻¹) versus the amount of chemical per volume of solution at equilibrium (C_e , mg L⁻¹). The sorption data were described using the Freundlich equation:

$$\ln Q_e = \ln K_f \times n_f \ln C_e \quad (1)$$

where K_f and n_f are the Freundlich parameters, characteristic for a particular herbicide-soil combination.

Desorption experiments were conducted immediately after the sorption experiments, starting at a concentration of 1 mg·L⁻¹, by successive dilution. First, supernatants were replaced with an aqueous calcium chloride solution (0.01 M, 8 mL), after which the tubes were shaken at 20 ± 2 °C for 16 h. The suspensions were subsequently centrifuged and the radioactivity of the supernatant was measured (similarly as for the sorption experiments). The desorption process was repeated using the above procedure until the supernatant radioactivity became three times less than the liquid scintillation analyzer background noise (1.7 Bq).

Descriptive statistical analyses were carried out using the Statistica® software package version 6 (StatSoft France, Maitson-Alfort, France). This included the construction of linear correlation models and a Principal Component Analysis.

3. RESULTS AND DISCUSSION

3.1. Bentazone sorption parameters

Freundlich parameters (K_f and n_f) and the corresponding sorbed percentages calculated for bentazone are given in Table III. The K_f parameter is an empirical constant of the Freundlich model expressing soil sorbent capacity (sorption isotherm slope) for a given range of pesticide concentrations. In our study, bentazone K_f values ranged from 1.2 to 1.9 mg^{1-n_f} L^{n_f} kg⁻¹. The highest K_f value was observed for the dystic cambisol, a loamy-sandy soil with high organic matter content and low pH, while the lowest K_f values was found for the calcaric regosol¹ (Ca²⁺ saturated soil with 3.63% organic matter). We noticed that the distribution of K_f values did not differ significantly from normal (Fig. 1). Also, the highest K_f value (for the dystic cambisol) appears to be much different (an outlier) compared with those of the other soils. Thus, only a small amount of bentazone was generally held by the soils (average K_f = 1.4 ± 2.3 mg^{1-n_f} L^{n_f} kg⁻¹) during the sorption experiments.

Bentazone is a polar chemical with a strong affinity for the liquid phase (von Gotz and Richter, 1999). Both characteristics can influence the sorption of bentazone. First, bentazone comprises a carboxylate group which may cause specific sorption reactions such as hydrogen bonding, while stable Fe³⁺ coordination bonding may be possible also (Clausen and Fabricius, 2001). This may cause some soils to exhibit a relatively strong sorption. On another hand, because of its high solubility, bentazone may be subject to relatively rapid diffusion in the soil matrix (Von Open et al., 1991).

Table III. Bentazone Freundlich constants (K_f in mg^{1-n_f} L^{n_f} kg⁻¹ and n_f) and corresponding sorbed percentages (% adsorbed). Percentages correspond to the average of the four sorbed percentages calculated for the four concentrations tested. Standard deviations of the sorbed percentages are also indicated.

Soil type	n_f	K_f	% adsorbed
Dystic Cambisol	0.99	1.9	28 ± 1
Stagnic Cambisol	1	1.4	22 ± 1
Calcaric Regosol ²	0.99	1.2	20 ± 2
Fluvis Gleyic Cambisol	1	1.5	23 ± 1
Eutric Cambisol ²	1	1.3	21 ± 1
Calcaric Regosol ¹	1	1.2	20 ± 2
Cambic Calsisol	1	1.3	20 ± 4
Vertic Stagnic Cambisol	1	1.2	20 ± 1
Cambic Stagnic Vertic Calcisol	1	1.3	20 ± 1
Stagnic Luvisol	1	1.4	22 ± 1
Fluvis Stagnic Cambisol	1.01	1.4	22 ± 1
Eutric Cambisol ¹	0.99	1.2	20 ± 1
Fluvis Cambisol	0.99	1.5	23 ± 2
Average value	1	1.4	22
Standard deviation	0.01	0.2	2.3

Figure 1. K_f distribution (histogram) for bentazone assuming normal distribution.

Bentazone sorption isotherms were found to be linear (n_f = 1), with insignificant differences between the different soils; (Tab. III and Fig. 2). Thorstensen et al. (2001) previously obtained non-linear sorption isotherms of bentazone for three Norwegian soils. Non-linearity was especially evident for a forest soil (gleyic podzol) with highly decomposed organic material (37.7%) and a very low pH (2.9). In addition, the relatively high standard deviations could be due to the use of a commercially available triple formulation product. On the other hand, the sorption isotherm n_f values of the other two soils in that same study (a dystic fluvisol and a stagnic pozoluvisol), representative of the most frequent soil types in cultivated areas of Norway, were close to those observed in our study (n_f ≈ 1); this even

Figure 2. n_f distribution (histogram) for bentazone assuming normal distribution.

though the Norway experiments involved much higher bentazone concentrations.

In our work, no explicative variable produced a significant improvement in the n_f value predictions. Obviously, no significant differences existed between the n_f values calculated for the 13 soils, and hence the n_f value may be considered constant. Our results are consistent with those by Coquet (2002; 2003) who also found it difficult to assess differences between n_f values.

A preliminary descriptive statistical analysis was carried out for K_f , n_f , and several soil parameters (texture, organic matter content, pH, CEC, Ca, Fe) (results not shown). According to this preliminary analysis we decided to focus on soil organic matter content and pH, since both presented clear correlations with bentazone sorption.

3.2. Effect of soil organic matter content and pH on bentazone sorption

Several previous studies of weakly acidic chemicals have indicated little or no effect of soil organic matter content on sorption (e.g. Barriuso and Calvet, 1991). This lack of correlation between sorption of anionic molecules and organic matter content has been attributed to repulsion caused by the negative charge of these compounds and the net negative charge of organic matter and clay minerals (Hamaker and Thompson, 1972). Our data do not suggest significant correlation between bentazone sorption and soil organic matter content (Fig. 3). This shows that bentazone has a relatively high affinity for the liquid phase irrespective of the soil organic matter content. For instance, the bentazone K_f was estimated to be $1.4 \text{ mg}^{-1-n_f} \text{ L}^{n_f} \text{ kg}^{-1}$ for the stagnic cambisol and $1.5 \text{ mg}^{-1-n_f} \text{ L}^{n_f} \text{ kg}^{-1}$ for the fulvic cambisol having organic matter contents of 5.81% and 1.08%, respectively (Tab. II). This is probably due to bentazone's physicochemical properties (i.e. solubility), and the nature of the interactions involved. The type of organic matter may also have an effect, but this aspect was not investigated as part of our study.

Several laboratory studies (e.g., Halfon et al., 1996; Carrizosa et al., 2000) have demonstrated an effect of soil pH on the sorption of weakly acidic compounds. The lower the pH, the more

Figure 3. Bentazone K_f in relation to the soil organic matter content of the 13 soils. The solid line represents the fitted curve; the coefficient of determination is also shown.

Figure 4. Bentazone K_f in relation to $\text{pH}_{(\text{H}_2\text{O})}$ for the 13 soils. The solid line represents the fitted curve; the coefficient of determination is also shown.

sorption generally occurs. Such behavior has been observed mostly by artificially modifying the pH, but very rarely by using contrasting soil samples (de Jonge and de Jonge, 1999; Carrizosa et al., 2001; Dubus et al., 2001). A descriptive statistical analysis would allow one to assess a possible link between soil pH and bentazone sorption since a significant correlation was observed in our study ($r^2 = 0.68$; $P \leq 0.05$; Fig. 4). For the wide range of pH values investigated (5.30 to 8.20) some of the bentazone should be present in neutral form (1 to 3%). Thus, bentazone sorption may be more sensitive to soil pH variations due to ionization. An ionization state is crucial when assessing the mechanisms of soil sorption, including non-specific or specific sorption interactions (Calvet, 1989). Sorption of the neutral form likely involves non-specific interactions along with hydrophobic interactions and the presence of hydrogen bonds (Hamaker and Thompson, 1972). Sorption of the ionized form would be stronger than the neutral form due to repulsion between electro-negative charges of soil constituents and those of the ionized molecules.

Direct sorption involving the relatively few positive charges generally present in soils, may not be a significant mechanism for weakly acidic chemicals (Dubus et al., 2001). However, sorption could involve bivalent cations such as those between the ionized molecule and negatively charged surfaces of phyllosilicates or organic matter. In the case of bentazone, sorption

Table IV. Multiple linear regression results for bentazone sorption. The model was established for 13 soils. Both O.M. (organic matter content) and pH, significantly contributed to the regression ($P = 0.05$). The multiple correlation coefficient between the observed (K_f) and predicted K_{fp} values indicated significant correlation (*).

Sorption multiple linear regression	Multiple correlation coefficient
$K_{fp} \text{ bentazone} = 0.060 \text{ O.M.} - 0.146 \text{ pH} + 2.129$	0.82*

Figure 5. Principal component analysis representation (projection on 1, 2 planes) obtained for bentazone and selected soil characteristics from the 13 soils studied. 94.57% of the total variability could be explained by the two selected principal component axes.

of both neutral and ionized forms could explain the increased sorption at low pH values. Thus, the slight variation in bentazone sorption observed between the different soils (K_f ranging from 1.16 to 1.91, corresponding to soil pH values of 8.2 and 5.3 respectively) may have been mainly caused by soil pH.

3.3. Descriptive statistical analyses for linear sorption

The relationship between soil characteristics and bentazone sorption was studied by means of a Principal Component Analysis (Fig. 5). The analysis (plane 1, 2) shows that bentazone sorption on cultivated soils is inversely related to pH, while soil organic matter content has very little or no effect. In addition, multiple linear functions were derived in order to correlate the various soil characteristics with the K_f values; (Tab. IV). Multiple linear regression combines relationships between the various soil parameters and the K_f values, and leads to a linear predictive model for K_f value (denoted by K_{fp} here) (Golfopoulos and Arhonditsis, 2002). The predicted K_{fp} values in our study may be considered reliable since they were established using a wide array of soils that exhibited significant correlations (Tab. IV). The simple linear model may be useful for identifying areas (homogeneous soil types) where surface water resources could be threatened by pesticide contamination. The

Table V. Observed (data from R. Cherrier, unpublished) and predicted K_{fp} values calculated for 3 soils (Brittany, France). The ratios K_f/K_{fp} were calculated for each soil.

Brittany soils	K_f	K_{fp}	K_f/K_{fp}
Kerlavic	1.72	1.54	1.12
Kerguéhennec	1.6	1.22	1.31
Champ Noël	1.53	1.12	1.37

predictive model would be useful also for identification of pesticides which are more easily leached through the soil profile.

The linear model was used to compare measured bentazone K_f values obtained for three agricultural soils in Brittany, France (Cherrier R., unpublished data) with predicted values using the linear model for K_{fp} (Tab. V). Although the values obtained with the experiments and the linear model were different, the ranking between the three soils was found to be the same for the experimental and predicted data. The ratios of K_f/K_{fp} were systematically higher than 1 (1.12 to 1.37), with only small differences between the data sets. This indicates that a simple correction factor should lead to K_{fp} values that would closely approximate the measured data. This approach corroborates the fact that linear models constitute useful tools for predicting the adsorption of pesticide onto soil.

3.4. Bentazone desorption

Desorption controls the vulnerability of a pesticide to be degraded and/or leached at different times (Dur et al., 1998). In our study, desorption of bentazone exhibited hysteresis (results not further shown). Hysteresis is manifested by an increase in the difference between the adsorption and desorption isotherm slopes (Carrizosa et al., 2001; Worrall et al., 2001). Desorption behavior may reflect some of the interactions involved between the chemical and the various soils.

A large part of sorbed bentazone was released (average value of $96.9 \pm 4.1\%$) after successive desorption steps, with no significant differences occurring between the 13 soils (Tab. VI.). Conceptually, the lack of similarity between adsorption and desorption observed due to the hysteresis is likely a result of binding to organic matter and mineral particles, particularly clay minerals (Neville et al., 2000). Though no significant correlation was observed between bentazone sorption, soil organic matter content, and clay content, some of the binding may have been strong enough to induce hysteresis and/or even irreversible sorption. During the sorption experiments, soil pH was shown to have a significant effect on bentazone sorption. Consequently soil pH may also influence the release of the pesticide. Multiple linear regressions carried out with the desorption data indicated some correlation between soil organic matter content, pH and the desorbed percentages of bentazone (Tab. VI). While for the wide range of soils studied, pH and soil organic matter contents did influence bentazone desorption, no significant multiple correlation coefficients could be obtained (Tab. VII).

We believe that pesticide diffusion may also play a role in the desorption process. Physical entrapment can lead to kinetic diffusion restrictions and could explain the slow release of bentazone

Table VI. Bentazone desorbed percentages calculated for the 13 soils. Desorbed percentages pertain to the total amount of pesticides desorbed during the different desorption stages.

Soil type	desorbed %
Dystic Cambisol	99.8
Stagnic Cambisol	98.8
Calcaric Regosol ²	91.5
Fluvic Gleyic Cambisol	99.1
Eutric Cambisol ²	99.3
Calcaric Regosol ¹	86.2
Cambic Calsisol	98.4
Vertic Stagnic Cambisol	99.7
Cambic Stagnic Vertic Calcisol	98.9
Stagnic Luvisol	99.5
Fluvic Stagnic Cambisol	93.4
Eutric Cambisol ¹	99.1
Fluvic Cambisol	95.9
Average value	96.9
Standard deviation	4.1

Table VII. Multiple linear regression for bentazone desorption. The model was established for the 13 soils. Also shown is the multiple correlation coefficient between the observed (K_f) and predicted (K_{fp}) values.

Desorption multiple linear regression	Multiple correlation coefficient
$P_{des. \text{ bentazone}} = 0.271 \text{ O.M.} - 1.946 \text{ pH} + 108.96$	0.48

during desorption (de Jonge and de Jonge, 1999). Bentazone has a high solubility (570 mg L^{-1}), which allows it to diffuse relatively quickly into a large part of the soil matrix. Smaller concentration gradients during the desorption phase reduce the diffusion rates from relatively inaccessible sorption sites, even though they are still connected with the liquid phase, possibly contributing to apparent desorption hysteresis. In addition, if during the diffusion process pesticide molecules encountered new adsorption sites, water may not always be able to reach those sites during overall desorption.

Accurate interpretation of the bentazone desorption data is not easy because of the possible interplay of several processes. Desorption hysteresis appears to be the result of complex physicochemical processes between soils and the chemical involved, leading to multiple sorption processes. The data in this study do not permit a clear separation of the various processes responsible for hysteresis.

4. CONCLUSIONS

Our sorption experiments showed relatively little or no effect of soil organic matter content, while a lower pH statisti-

cally enhanced bentazone sorption onto soil. The latter result was obtained without artificially modifying soil pH values. Simple linear models for predicting bentazone sorption such as those derived in this study may provide useful tools for optimal management of pesticides in field applications, and hence for preventing water contamination. Desorption appeared to be the result of a complex, time dependent interplay of several chemical and physical processes, leading to hysteresis. A more detailed conceptual explanation of the observed sorption and desorption processes requires additional information about the nature of the soil organic matter involved, including diffusion.

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