

Article ID: 1001-0742(2003)03-0383-05

CLC number: X52; X131.3

Document code: A

Sorption of a triazol derivative by soils: importance of surface acidity

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Abstract: The sorption of a triazol derivative, 1-(4-chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)penten-3-ol with a common name of S3307D, on fifteen soils and three H₂O₂-treated soils was investigated. The sorption isotherm for each untreated and treated soil was non-linear, and was best fitted to Freundlich sorption equation. Soils containing high amount of clay content or organic matter or both sorbed much higher amounts of the chemical than soils that had low contents of these soil constituents. H₂O₂-treated soils showed considerable sorptive affinity for S3307D. It was concluded that both organic matter and mineral fraction in natural soils contributed to the sorption of the basic compound. Sorption by the H₂O₂ treated soils increased as suspension pH decreased, but all suspension pHs exceeded the pK_a of the compound by more than two units. This implies that organic base protonation can occur on surfaces of soil components, and surface acidity (exchangeable acidity) is important in sorption process of the organic base rather than suspension pH.

Keywords: sorption; organic base; soil; surface acidity

Introduction

Since sorption is a major factor controlling pesticide persistence, bioavailability, and mobility in soils, an extensive literature exists on the study of this process. Many nitrogen-containing organic compounds, such as s-triazines and pyridinones, are weakly basic in nature. Sorption mechanism of weak organic bases on clay minerals from non-polar organic solvents is an acid-base interaction (Wu, 1992; 1997; 2002). In aqueous solutions, it has been also accepted that weakly basic organic substances can be sorbed by soil components through cation exchange mechanism when they are protonated at low pH levels to form a positively charged molecule (Carringer, 1975; Zierath, 1980; Senesi, 1980; Zachara, 1986; Koskinen, 1990). If the pK_a of an organic base is known, the relative proportion of charged and uncharged forms can be predicted according to the relationship:

$$\text{pH} = \text{pK}_a + \log(\text{B})/(\text{BH}^+),$$

where (B) and (BH⁺) are the activities of a base and its conjugate acid in solution. At pH values greater than two pH units above the pK_a, only < 1% of the weakly basic compounds are protonated. Hence, other physical sorption mechanisms such as hydrophobic attractions and H bonding become more important (Hayes, 1970; Bouchard, 1985). In soils and sediments at pH values above pK_a, the sorption of three nitrogen-heterocyclic compounds (acridine, biquinoline, and dibenzocarbazole) follow the K_{oc}-K_{ow} and K_{oc}-S relationships (Banwart, 1982). These relationships were commonly observed for neutral and hydrophobic aromatic compounds (Chiou, 1989). In contrast, Bailey (Bailey, 1968) suggested the importance of organic compound protonation at sorbent surface, which may have an acidity of 2—4 pH units below that of the bulk solution. Later, other workers also pointed out the possibility that protonation may occur on sorbent surface at suspension pH levels more than two units greater than the pK_a of a basic compound (Weber, 1970; 1986; Shea, 1983; Zachara, 1986). However, the importance of this sorption mechanism in natural soils was not well understood.

With respect to the relative importance of organic matter and mineral fraction in the sorption of weakly basic compounds, the most important soil fraction governing the sorption of weakly basic compounds is often organic matter, and sorption by clay minerals is low (Banwart, 1982; Bouchard, 1985; Borggaard, 1988). On the other hand, Weber and his coworkers argued that both organic matter and mineral surfaces in soils could contribute to the sorption of basic compounds (Weber, 1970; 1986; Shea, 1983). Thus, accurate information about the relative importance of the soil constituents is still lacking. However, the extent of sorption by soil mineral fraction should depend upon whether surface protonation can occur. In this paper, sorption of a triazol derivative, 1-(4-chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)penten-3-ol (a common name, S3307D, will be used hereafter for convenience) was investigated on some soils, so as to evaluate the importance of

protonation of the chemical on mineral surface and the relative contribution of soil mineral fraction to the sorption.

1 Materials and methods

1.1 Materials

Fifteen soil samples were collected from plow layer of paddy fields at different agricultural experimental stations in Japan. They were air-dried, and ground to pass a 20-mesh sieve. Selected properties concerning these soils are given in Table 1.

Sub-samples of three soils (Hiroshima, Touhoku, and Miyagi soil) were oxidized to remove organic matter using H_2O_2 . These three soils were selected to examine the relative importance of soil mineral and organic fraction in sorption since they represent the highest, middle, and the lowest sorptive capacity among the fifteen soils. The resultant “soil mineral fraction” was subjected to the measurement of organic matter content and pH value. The H_2O_2 -treated soils were also air-dried, and ground to pass a 20-mesh sieve.

S3307D was obtained by courtesy of Sumitomo Chemical Co. Ltd., and had the purity of 99.3%. This compound was developed to reduce the height of rice plant so as to prevent it from wind damage of lodging. It has the following properties: pK_a of 1.18

(determined spectrophotometrically during this study); water solubility of 8.3 mg/dm^3 ; melting point of $172.5\text{--}173.5^\circ\text{C}$, and molecular weight of 291.5. A stock solution of S3307D(1200 mg/dm^3) in methanol was prepared and stored in an airtight glass bottle.

1.2 Soil properties

Soil pH measurement was made in 0.01 mol/l $CaCl_2$ solution with soil: solution ratio of 1:2, using a glass electrode pH meter(Jackson, 1958). Exchangeable acidity was determined using potassium chloride method(Jackson, 1958). Oxidizable organic matter contents were determined using chromic acid method(Jackson, 1958). Clay fractions($<2\mu\text{m}$) of each soil were collected by wet sedimentation following ultrasonic dispersion, with all soil samples receiving a prior H_2O_2 treatment for organic matter removal. The clay contents were then quantified and major clay mineral species were identified with X-ray diffraction analyses.

1.3 Sorption

Sorption experiments were carried out on all fifteen soils and the three oxidized soils. 15 cm^3 volumes of 0.01 mol/l $CaCl_2$ and appropriate amount of the stock solution of S3307D(1200 mg/dm^3) in methanol were added to 50 cm^3 polycarbonate centrifuge tubes containing 2.5 g of soil. A microcyringe was used to distribute the stock solution of S3307D. Five initial S3307D concentrations ranged from 0.5 to 6.0 mg/dm^3 . All aqueous solutions were made to contain 0.5% by volume of methanol, because different amount of methanol may affect sorption process. The tubes were then shaken for 48 h at room temperature($21\text{--}26^\circ\text{C}$) for the soil sorption studies. 48 h was found to be enough for S3307D to achieve equilibrium in pre-experiments. After 48 h , the suspensions were centrifuged and the supernatants were filtered to remove suspended substances. The concentrations of S3307D in filtrates were then determined by HPLC.

Blank determinations(that is, sorbent in the absence of S3307D, and S3307D in the absence of sorbent) were always included. The extent of S3307D sorbed to the centrifuge tube was found to be between $7\%\text{--}11\%$ of that added. Therefore, amounts of S3307D sorbed were calculated from differences between equilibrium concentrations with and without the sorbents.

Table 1 Selected properties of the soil samples studied

Soil sample	Major clay minerals	Clay content, %	Soil pH	Organic matter content, %
Hiroshima	Kt	14.7	5.20	1.40
Kouchi	Ch/Vt, Kt	25.7	5.79	2.67
Shikoku	Vt, Kt, It	12.9	5.80	1.41
Saga	Vt, Kt	14.2	5.60	2.31
Nagasaki	Vt, Kt	24.5	5.48	2.45
Ibaragi	Vt, Kt	13.8	4.73	1.76
Shimane	Mt	27.1	5.35	1.90
Chiba, N	Kt	10.4	5.18	1.83
Nagano	Mt, Vt, Kt	33.2	4.98	1.62
Kagoshima	Vt/Ch, It, Kt	15.3	4.71	2.72
Aichi	Kt, Mt	38.9	4.98	1.46
Shiga, K	Vt, Kt, It	25.1	4.88	3.78
Fukui	Kt, Vt/Ch	46.9	5.83	3.94
Touhoku	Ch, Mt, Kt	20.4	5.78	3.50
Miyagi	Mt	33.6	4.16	3.56

Notes: Mt = montmorillonite; Kt = kaolinite; Vt = vermiculite; It = illite; Ch = chlorite; Vt/Ch = vermiculite/chlorite intergrade

From retention times of the peaks on chromatograms, it was recognized that there was no evidence that S3307D degradation by microorganisms occurred during the equilibration period.

1.4 Effect of pH on sorption

The dependence of sorption on suspension pH was examined using the three oxidized soils. Two grams of each oxidized soil in the presence of 15 cm³ of 0.01 mol/L CaCl₂ were adjusted to desired pH levels by adding 1.0 mol/L NaOH or HCl. After standing for 24 h with intermittent shaking by hand, the pH was determined and recorded. The sorption studies were performed using an initial S3307D concentration of 2.0 mg/dm³.

1.5 Analysis

Concentrations of S3307D in solutions were measured with a Shimadzu HIC-6A liquid chromatograph, installed with a SPD-6A UV spectrophotometric detector at 240 nm. A sumipax ODS A-212 column was used with a mixture of methanol/water (4:1, v/v) as a mobile phase. Peak areas were determined with a CR-6A CHROMATOPAC integrator.

2 Results and discussion

2.1 Sorption by soils

Sorption data were best fitted by the empirical Freundlich sorption isotherm. The linear form of the equation can be expressed as:

$$\log X = \log K + n \log C,$$

where *X* is the amount sorbed by unit mass of sorbent (mg/kg); *C* is the equilibrium concentration in solution (mg/dm³); *n* and *k* are constants specific to each soil. Representative isotherms are shown in Fig.1, and sorption constants in Table 2.

For all soils, the value of *n* was less than unity, indicating a convex or non-linear isotherm. This implies that the sorption of S3307D was not a single hydrophobic partition process between water and soil organic matter, which was observed for many nonionizable and hydrophobic compounds (Chiou, 1989). In addition, the *n* values obtained were approximately similar (ranging from 0.78 to 0.87), thus, the *k* value is a measure of the degree of S3307D sorption by the soil.

An examination of *k* values in Table 2 shows that, of the soils studied, Miyagi soil had distinctively high sorptive affinity for S3307D. This soil contains high amounts of organic matter(3.56%) and montmorillonite clay(33.6%). It particularly has a low pH value(4.16) relative to the other soils. Soils containing high amounts of clay content (33.2%—46.9%, Nagano and Aichi) or organic matter(2.72%—3.78%, Touhoku, Shiga, K., and Kagoshima) or both(Fukui) also had much higher *k* values than soils that had low contents of these soil constituents. The results indicated that both organic and clay surfaces in natural soils were contributing to the binding of weakly basic compound. This agrees with the observations of Weber and his coworkers (Weber, 1970; 1986; Shea, 1983). Linear regression analyses indicate, however, that *k* values were poorly

Table 2 Freundlich constants for S3307D sorption by soils

Sample	<i>K</i>	1/ <i>n</i>	<i>r</i> ²
Hiroshima	9.10	0.828	0.999
Kouchi	9.25	0.823	0.999
Shikoku	10.00	0.788	0.997
Saga	11.86	0.863	0.999
Nagasaki	12.36	0.800	0.998
Ibaragi	13.55	0.821	0.999
Shimane	13.84	0.868	1.000
Chiba, N	14.29	0.790	0.999
Nagano	14.69	0.808	0.999
Kagoshima	17.18	0.835	0.999
Aichi	19.06	0.859	1.000
Shiga, K	26.79	0.824	0.999
Fukui	28.05	0.778	1.000
Touhoku	30.20	0.834	0.999
Miyagi	72.78	0.868	1.000

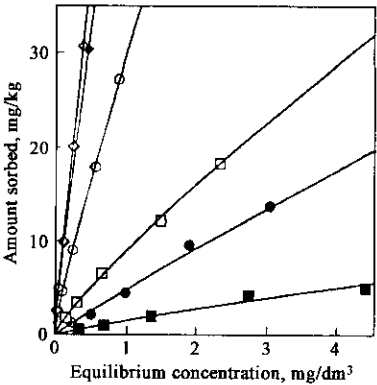


Fig. 1 Sorption isotherms of S3307D from aqueous solutions by Hiroshima soil (□), Touhoku soil (○), and Miyagi soil (◇) untreated and treated with H₂O₂ for organic matter removal (closed symbol)

correlated with all soil properties determined (correlation coefficients for organic matter content, pH, and clay content were 0.63, -0.53, and 0.42, respectively). This was probably because of that in natural soils, each of different origin, many factors vary simultaneously (types and composition of soil's mineral and organic fractions) and the effect of individual parameters can not be easily isolated.

2.2 Sorption by H_2O_2 -treated soils

Data in Table 3 show that although a large proportion of organic matter content was successfully removed by H_2O_2 treatment (93% for Hiroshima, 90% for Tohoku, and 83% for Miyagi soil), the treatment caused some changes in soil reaction. As will be shown later (Table 4), however, sorption of S3307D by the soils was not substantially affected by changes in soil reaction within the pH range which occurred during the organic matter oxidation. Therefore, the comparison of sorption before and after the H_2O_2 treatment may provide a rough estimate of relative importance of mineral and organic surfaces in the S3307D sorption for the soils. The isotherms of S3307D sorption by the H_2O_2 treated soils can also be represented by the Freundlich equation (r^2 was 0.988 for Hiroshima, 0.987 for Tohoku, and 0.998 for Miyagi soil). From Fig. 1, it can be seen that each of the H_2O_2 treated soils showed considerable sorptive affinity for S3307D. In fact, the sorption by Miyagi soil was due mainly to the mineral fraction. The order of sorptive capacity of the H_2O_2 treated soils was: Miyagi > Tohoku > Hiroshima soil.

Table 3 Comparison of soil properties before and after H_2O_2 treatment

Sample	Organic matter content, %		pH value		TEA ^a , cmol/kg	
	Natural soil	Treated soil	Natural soil	Treated soil	Natural soil	Treated soil
Hiroshima	1.40	0.12	5.2	5.4	0.09	0.04
Tohoku	3.50	0.36	5.8	5.0	0.41	0.53
Miyagi	3.56	0.62	4.2	4.0	1.33	1.24

a: Total exchangeable acid

2.3 Effect of pH

High sorptive capacity of weakly basic compounds at low pH levels has been observed and it has been attributed to protonation of the basic compound and sorption through cation exchange forces (Weber, 1970; 1986; Zachara, 1986; Zierath, 1980; Helmy, 1983). Results in Table 4 show that sorption of S3307D also significantly increased as the suspension pH decreased. It should be noted, however, that the lowest pH value achieved was 3.4, being 2.2 units greater than the pK_a . This suggests that the increased sorption was due mainly to an enhanced protonation at sorbent surface, which was expected to have a high surface acidity (exchangeable acidity) by adding 1 mol/L HCl, even though the organic base should exist predominantly in its neutral form in solution. On the other hand, because the addition of 1 mol/L NaOH could progressively neutralize surface acidity, sorption of S3307D decreased when suspension pH was adjusted by 1 mol/L

Table 4 Effect of suspension pH on sorption of S3307D by H_2O_2 treated soils

Sample	Amount added cm ³ , 1 mol/L HCl or NaOH	Suspension, pH	Amount sorbed,	
			mg/kg	%
Hiroshima	0.08(HCl)	3.41	3.36	24
	0.04(HCl)	3.94	1.80	13
	0.02(HCl)	4.46	1.59	11
	0.02(NaOH)	6.84	0.91	7
	0.04(NaOH)	7.58	0.62	4
	0.08(NaOH)	8.51	0.58	4
Tohoku	0.13(HCl)	3.89	7.32	51
	0.07(HCl)	4.17	5.75	40
	0	5.00	4.46	31
	0.07(NaOH)	6.37	4.16	29
	0.14(NaOH)	7.15	3.59	25
	0.28(NaOH)	7.99	3.43	24
Miyagi	0.03(HCl)	3.43	13.51	94
	0	4.01	12.74	89
	0.05(NaOH)	4.50	12.68	88
	0.14(NaOH)	5.31	12.58	87
	0.22(NaOH)	6.32	12.48	87
	0.42(NaOH)	7.72	12.01	81

NaOH. Small reduction in sorption for Miyagi soil with increasing pH was clearly attributed to the much high surface acidity (exchangeable acidity, Table 3) and buffer capacity (Table 4).

3 Conclusion

Both organic matter and mineral fraction in natural soils contributed to the sorption of the basic compound, S3307D.

Sorption by the H₂O₂ treated soils increased as suspension pH decreased. The increase in sorption appears to be due to the enhancement of surface acidity by the addition of HCl.

Sorption of S3307D may occur through acid-base interaction on sorbent surface at suspension pH levels more than two units greater than the pK_a of the chemical. Namely, surface acidity is important in the sorption process rather than suspension pH.

Acknowledgements: The author is grateful to Prof. T. Henmi and Dr. N. Matsue for their encouragement and helpful suggestions. This research was conducted in the Laboratory of Soil Science, Ehime University.

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