Bull. Environ. Contam. Toxicol. (2005) 75:264–271

DOI: 10.1007/s00128-005-0747-3

Bulletin of Environmental Contamination and Toxicology

Atrazine Sorption Dynamics in Acid-Surface Soils

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Received: 23 December 2004/Accepted: 8 June 2005

The fate and behaviour of pesticides in soils are governed by a variety of physical, chemical and biological processes, including sorption-desorption, volatilization, chemical and biological degradation, plant uptake, surface runoff, and leaching. Atrazine is a herbicide widely used on corn crops and is relatively recalcitrant in soils. The accessibility of atrazine by target organisms and its potential to reach non-target organisms are both dictated largely by its sorption dynamics which has been widely studied in soils and clays (Ma and Selim 1996; Celis et al. 1997). Atrazine desorption was studied in less extent than its adsorption (Roy and Krapac 1994; Moorman et al. 2001), but has a crucial influence on mobility in soils. Hysteresis, which reflects differences between sorption and desorption, has frequently been observed in this pesticide (Brusseau and Rao 1989). In Galicia (NW Spain), soils are mostly acid. The typical climate of this region, which features moderated average temperatures, delays mineralization of organic matter in soil (Carballas et al. 1978). Therefore, Galician soils exhibit special chemical reactivity as their charge is pH-dependent. The aim of this work was to elucidate the dynamics of atrazine sorption and desorption in these soils with a view to recommending agricultural practices for preserving soil quality and productivity while avoiding detrimental changes in the surrounding waters.

MATERIALS AND METHODS

Atrazine (98.5 % in purity) (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) was obtained from Dr. Ehrenstorfer Lab. Other reagents used included methanol from Aldrich; hexane, iso-octane and water from Merck; and benzene and sodium chloride from Panreac. Soil samples were obtained from the plough layer (0-20 cm) of four corn fields in Galicia (NW Spain). Samples were air dried and sifted through a 2 mm mesh. The properties of the soils are summarized in Table 1. The particle size fractions above 0.05 mm were determined by wet sieving and those below 0.05 mm using the International Pipette method. The organic carbon content was determined by oxidation with potassium dichromate (Guitián and Carballas 1976). Total nitrogen and sulphur were determined on an autoanalyser.

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Table 1. Physico-chemical properties of selected soil samples.

Soil	Clay (%)	Silt (%)	Sand (%)	pH (H_2O)	pH (KCl)	C (%)	N (%)	S (%)	CEC (cmol $_{(c)}$ kg^{-1})	Fe$_d$ g kg^{-1}
1	26	36	38	5.1	4.6	6.6	0.8	0.8	6.8	52
2	28	38	34	5.1	4.5	6.8	0.6	0.3	5.5	44
3	10	16	74	4.4	3.7	3.0	0.2	0.1	4.4	2
4	9	10	81	4.1	3.6	3.3	0.3	0.4	4.3	4

The cation exchange capacity (CEC) was estimated by addition of alkali elements (Na, K, Ca and Mg) extracted with ammonium chloride (Sumner and Miller 1996) plus the exchangeable-Al extracted with 1 M potassium chloride. Finally, *free Fe* (Fe_d) was extracted with the sodium dithionite-citrate mixture (Holmgren 1967).

All HPLC measurements were made by using a Thermo Separation Products (TSP) P2000 binary pump, equipped with a TSP AS1000 autosampler, a TSP SCM1000 vacuum membrane degasser and a Spectra-System UV2000 ultraviolet/visible detector. Chromatographic data were acquired and processed by the using Chrom-Card software package. The optimized instrumental parameters for the chromatographic determination of atrazine were as follows: *Injection loop volume*: 100 μL; *Columns*: A 5 cm x 4.6 mm i.d. stainless steel guard column packed with 40 μm Pelliguard LC-18 (Supelco), followed by a 15 cm x 4.6 mm i.d. stainless steel analytical column packed with 5 μm Symmetry C_{18} (Waters); *Elution conditions*: isocratic elution with 40:60 acetonitrile/water at room temperature. *Flow rate*: 1.5 mL/min. *UV detection wavelength*: 230 nm.

The effect of the atrazine concentration on adsorption was monitored as follows: 0.02 M NaCl aqueous solutions (25 ml) containing atrazine concentrations ranging from 0.9 and 46 μM at a fixed pH of 5.0 were added to the soil samples (5 g) in 50 mL Pyrex centrifuge tubes. The samples were shaken on a rotary shaker at 200 rpm at room temperature (20 ± 2°C) for 48 h. After equilibration they were centrifuged for 30 min at 4000 rpm and the atrazine concentrations in the clear supernatants were analyzed by HPLC-UV. The amount of atrazine adsorbed by the samples was calculated as the difference between the initial concentration of atrazine in the solution and that remaining after equilibration with the soil. All assays were carried out in triplicate. The influence of pH on atrazine adsorption was examined at pH 2, 5 and 8, using a constant atrazine concentration of the 3.7 μM. The experimental procedure used is described above. The effect of Cu and Zn on atrazine adsorption was determined by using an atrazine concentration of 3.7 μM, and Cu and Zn concentrations of 1.6 mM in various tests. The experimental procedure used is described above.

For desorption tests, soils were equilibrated with atrazine solutions at initial concentrations of 23, 32 and 46 μM. At the end of the adsorption period (48 h), three quarters of the supernatant for each system was replaced with the same volume of 20 mM NaCl. The systems were then allowed to re-equilibrate and treated as in the adsorption tests. The desorption steps were repeated twice.

RESULTS AND DISCUSSION

Experimental data were fitted to the Langmuir equation in its non-linear form:

$$X = \frac{K_L X_m C}{1 + K_L C} \qquad \text{Eq. 1}$$

where X (µg g^{-1}) is the amount adsorbed per unit mass, K_L (L µg^{-1}) a constant related to the adsorption process, X_m (µg g^{-1}) the maximum adsorption capacity, and C (µg L^{-1}) the equilibrium concentration. Data were also fitted to the Freundlich equation:

$$X = K_F C^{1/n} \qquad \text{Eq. 2}$$

where X and C have the same meaning, and $K_F(L\ g^{-1})$ and $1/n$ (a dimensionless parameter) are two constants. Fitting was done by using the Levenberg-Marquardt least-squares algorithm.

The results obtained by fitting the experimental data for atrazine adsorption (X *vs.* C) to eqs. 1 and 2 are shown in Table 2. Both equations provided significant R^2 values (higher than 0.95). X_m as obtained from Langmuir equation was 15-25 µg g^{-1} for all soils (Table 1). K_L values were extremely low and exhibited no significant differences among soil samples. K_f and *1/n* were similar for all soils, even though soils 1 and 2 had higher Fe_d and clay contents than soils 3 and 4 (Table 1).

Table 2. Fitting parameters (average ± standard deviations; n=3) obtained from the Langmuir and Freundlich equations as applied to atrazine adsorption.

	Langmuir			Freundlich		
Soil	K_Lx1000	X_m	R^2	K_F	1/n	R^2
1	0.22 ± 0.09	22 ± 4	0.953	0.05 ± 0.03	0.64 ± 0.08	0.955
2	0.38 ± 0.09	25 ± 2	0.978	0.11 ± 0.06	0.58 ± 0.07	0.956
3	0.30 ± 0.09	15 ± 2	0.971	0.06 ± 0.03	0.58 ± 0.06	0.963
4	0.29 ± 0.10	24 ± 4	0.964	0.07 ± 0.04	0.62 ± 0.07	0.958

The adsorption process can be described in terms of K_d, the atrazine distribution coefficient, which reflects a balance between atrazine levels bound to the solid phase and dissolved into the liquid phase (µg g^{-1}/µg L^{-1}). A large K_d value reflects a high affinity of the soil for atrazine. As can be seen in Figure 1, K_d decreased with increasing initial atrazine concentration, but also with decreasing CEC and pH (KCl) in soil (Figure 1 and Table 1). The decrease in K_d with increase in initial concentration of atrazine may be a result of atrazine being adsorbed at high-affinity sites at low concentrations (specific adsorption) and at low-affinity sites at

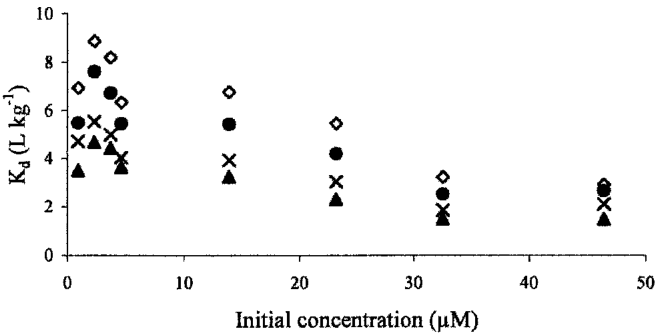

Figure 1. Variation of the atrazine distribution coefficient (K_d) with the initial atrazine concentration. Soils: 1 (◇), 2 (●), 3 (x) and 4 (▲).

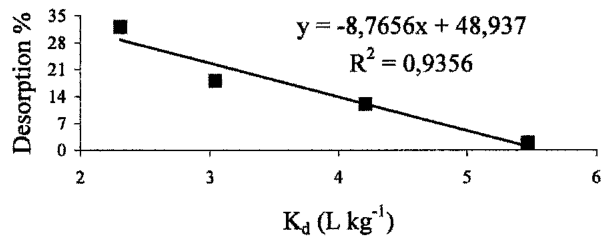

Figure 2. Percent desorption of atrazine as a function of its distribution coefficient (K_d).

high concentrations (non-specific adsorption). The rate of decrease of K_d is low (from 10 to 2 L kg^{-1}), which suggests that this behaviour results preferentially from atrazine being governed by electrostatic interactions This hypothesis was previously formulated for the soil adsorption of cations such as Cu, Pb, Zn and Ni (Basta and Tabatabai 1992); atrazine in acid media has positive charge, so it may behave similarly. Previous studies based on data for surface and near-surface soils revealed atrazine sorption to be proportional to their organic matter content (Koskinen and Clay 1997; Moorman et al. 2001). The only clear correlation we found was that with CEC, however.

The influence of pH on the adsorption process was examined at an initial concentration of atrazine of ca. 3.7 μM and a pH of 2, 5 or 8 (Table 3). Atrazine adsorption by the soils was found to decrease with increasing pH and to peak at a pHs close to its pK_a (1.7-2.6) when cationic atrazine accounted for 50% of all atrazine. At pH values above its pK_a, the cationic atrazine was lower and electrostatic interactions with negative charge in the soil was weaker as a result.

Table 3. Atrazine adsorption (µg g^{-1}) as a function of pH. Atrazine input level = *3.7 µM.*

	pH		
Soil	2	5	8
1	3.3 (82.5)	2.5 (62.5)	1.9 (47.5)
2	3.0 (75.0)	2.3 (57.5)	1.6 (40.0)
3	2.6 (65.0)	1.9 (47.5)	1.2 (30.0)
4	2.7 (67.5)	2.0 (50.0)	1.4 (35.0)

*adsorption percentages are shown in brackets. The standard deviation was less than 3% in all cases.

Table 4. Influence of Cu and Zn on atrazine adsorption. Atrazine input level = 3.7 µM; Cu and Zn levels: 1.6 mM.

	Adsorbed atrazine (µg g^{-1})		
Soil	Alone	Cu	Zn
1	2.50 ± 0.05	2.60 ± 0.01	2.30 ±<0.01
2	2.30 ± 0.00	2.40 ± 0.03	2.20 ± 0.04
3	1.90 ± 0.05	2.00 ±<0.01	1.40 ± 0.00
4	2.00 ± 0.04	2.30 ±<0.01	2.00 ± 0.04

An increase of pH can additional cause the dissolution of some organic matter and reduce atrazine adsorption through a decrease in the number of adsorption sites (Lee and Farmer 1989; Kookana et al. 1998).

Atrazine adsorption at different pHs was higher in soils 1 and 2 (with higher contents in Fe_d and clay) than for 3 and 4 (Table 3). Also variability adsorption was similar (about 35%) in all soils. This suggests that the influence of soil pH on atrazine adsorption is exerted via atrazine charge itself than through the negative charge in soil colloids. Agronomic management practices such as liming and fertilisation can result in relative abrupt changes in soil pH and hence affect the behaviour of pesticides applied to soils.

The effect of Cu and Zn on atrazine adsorption was studied at constant concentrations of atrazine and metals, and an initial pH of 5.0. Both Cu and Zn can coexist together with atrazine in soils as a result of agicultural practices. Copper slightly increased atrazine adsorption (Table 4), particularly in sample 4 (with the highest pH). On the other hand, Zn slightly reduced atrazine adsorption (Table 4). The adsorption of Cu and Zn was severely reduced by the presence of atrazine in the soils (Table 5). This can be ascribed to the formation of metal-pesticide complexes that reduce metal affinity for sorption sites and is reminiscent of Mortland's finding (1970) that desorption of the herbicide 3-aminotriazole from clay was greatest when the dominant exchangeable cation was calcium, which was presumably due to coordination of the herbicide to the cation being weakest for this metal.

Table 5. Influence of atrazine on Cu and Zn adsorption (μg g^{-1}). Cu and Zn input levels = 1.6 mM.

Sample	Atrazine Concentration (μM)	Cu adsorption	Zn adsorption
1	0.0	0.8	0.7
	3.7	0.2	0.1
	4.6	0.2	0.1
2	0.0	0.8	0.5
	3.7	0.2	<0.1
	4.6	0.2	<0.1
3	0.0	0.5	0.4
	3.7	0.1	<0.1
	4.6	0.1	<0.1
4	0.0	0.5	0.3
	3.7	0.1	<0.1
	4.6	0.1	<0.1

Table 6. Percent atrazine desorption from the different soil samples after any of the three sequential 24-h equilibration events. The standard deviation was always less than 3%.

		Percent cumulative desorption			
Initial Concentration (μg L^{-1})	**Step**	**Soil 1**	**Soil 2**	**Soil 3**	**Soil 4**
5000	1	2	12	32	18
	2	18	33	65	30
	3	43	59	92	60
7000	1	15	28	49	36
	2	49	65	86	51
	3	91	92	97	95
10000	1	15	28	63	45
	2	45	66	94	65
	3	92	92	98	96

Atrazine desorption was measured after three sequential 24-h equilibration events. The recovery of adsorbed atrazine varied among soils and with the initial atrazine concentration. Cumulative desorption during the sequential events increased, with increase in atrazine concentration (Table 6).

In the first desorption step, desorption decreased in the soil samples with the lowest contents in organic matter. One other clear change occurring during desorption was that, at an atrazine input level of 23.2 μM, more atrazine was retained onto the soils than was predicted from the adsorption isotherms. At higher input levels (32.5 and 46.4 μM), however desorption exceeded 90%;

hysteresis was thus negligible, and so was irreversible binding between atrazine and soil colloids as a result.

The relationship between adsorption and desorption is connected with that between K_d and atrazine desorption. The latter was statistically significant ($p < 0.01$) during the first desorption step (Figure 2): desorption decreased with increasing K_d, which suggests that atrazine desorption depends on the affinity with which was previously adsorbed by the soil surface.

Acknowledgments. Funding by Xunta de Galicia (Ref. PGIDIT03RAG38301PR) and Spanin's Ministry of Science and Technology (Ref. AGL2003-02244) are gratefully. The authors are also grateful to the Spanin`s Ministry of Science and Technology for research contracts awarded to Dr. Arias-Estévez and Dr. López-Periago under the Ramón y Cajal program and to Xunta de Galicia for research contract to Dr. Cancho-Grande under the Parga Pondal program.

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