# Atrazine Adsorption Behavior on a Fluvo-Aquic Soil as Influenced by Contact Periods[*1]

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## ABSTRACT

A batch experiment was performed to investigate nonequilibrium adsorption behavior of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) on a fluvo-aquic soil. The amount of atrazine sorbed increased with increasing adsorption contact periods. For a range of initial atrazine concentrations, the percentage of atrazine sorbed within 24 h ranged from 24% to 77% of the observed total amount sorbed for the longest contact period; when adsorption contact periods were more than 72 h, the deviations in curves fitted using a nonlinear Freundlich equation gradually became less. The opposite trend was observed for the atrazine concentrations in solution. The effect of adsorption contact periods on atrazine adsorption behavior was evaluated by interpreting the temporal variations in linear and nonlinear Freundlich equation parameters obtained from the phase-distribution relationships. As the adsorption contact period increased, the nonlinear Freundlich capacity coefficient $k_f$ showed a significant linear increase ($r^2 = 0.9063$, $P < 0.001$). However, a significant negative linear correlation was observed for the nonlinear coefficient $n$, a dimensionless parameter ($r^2 = 0.5666$, $P < 0.05$). Furthermore, the linear distribution coefficient $k_d$ ranged from 0.38 to 1.44 and exhibited a significant linear correlation to the adsorption contact period ($r^2 = 0.72$, $P < 0.01$). The parameters $k_f$ and $n$ obtained from a time-dependent isotherm rather than the distribution coefficient $k_d$ estimated using the linear Freundlich equation were more appropriate to predict the herbicide residue in the field and thus more meaningful for environmental assessment.

*Key Words*:    adsorption contact periods, atrazine, fluvo-aquic soil, Freundlich equation parameters

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), one of the most widely used herbicides, is registered in more than 70 countries worldwide (Kauffmann *et al.*, 2000; Zhang *et al.*, 2004). Since 1958, it has been used as a pre- and postemergent herbicide to control broad-leafed weeds in the production of corn (*Zea mays* L.) and grain sorghum (*Sorghum bicolor* L. Moench). The widespread use of atrazine, however, is associated with an increasing incidence of contamination of drinking water supplies, with atrazine concentrations above the maximum contaminant level (MCL) of 0.1 $\mu$g L$^{-1}$ (Commission of the European Communities, 2001) reported in some regions (Thurman *et al.*, 1992; Lambropoulou *et al.*, 2002; Cai *et al.*, 2004).

The behavior of atrazine in the environment depends upon several factors, including adsorption to soil components, uptake by plants, transport *via* runoff and leaching, biodegradation, photodegradation, volatilization, and chemical degradation. Efforts have been made to study the adsorption mechanisms of atrazine to soil humic substances and clay minerals (Piccolo *et al.*, 1998; Herwig *et al.*, 2001). These researchers used X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy, in-

frared (IR) spectroscopy, electron spin resonance (ESR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to study the atrazine complexed with soil humic acids and/or smectite. Their results established proton transfer, electron transfer, and hydrogen bonding as the most important adsorption reaction mechanisms.

Solid-solute contact periods can result in "aging effect" that affects the sorption-desorption behavior of the hydrophobic organic solutes in soils and sediments. Xing and Pignatello (1996) used dichloroben-zene, dichlorophenol, and metolachlor as target solutes to describe a "fast fraction" of solute that was rapidly sorbed to soil organic matter (SOM) within the first day, and a "slow fraction" which continued to migrate deeper in the SOM matrix for the duration of the experiment. Adsorption of the "fast fraction" was primarily due to partitioning, whereas that of the "slow fraction" was attributable to the site-specific sorption with time. Pignatello and Xing (1996) have presented a discussion on the mechanisms of slow sorption.

Systematic studies of the effect of contact periods on adsorption, desorption, and extractability of agrichemicals to surface soils remain scarce. Such studies have the potential to significantly contribute to a better understanding of post-application herbicide dynamics in agricultural fields (Lesan and Bhandari, 2003; Bhandari and Lesan, 2003). The objective of this study was to evaluate the time-dependent phase distribution of atrazine on a fluvo-aquic soil by fitting the atrazine adsorption data to linear and nonlinear Freundlich equations.

MATERIALS AND METHODS

Standard atrazine powder with purity above 99% was purchased from Riedel-de Haenag Seelze, Hannover, Germany. The p$K_a$ and the water solubility of atrazine are 1.68 and 33 mg L$^{-1}$, respectively. The logarithmic value of $K_{ow}$, the $n$-octanol/water distribution coefficient, is 2.7. Technical grade atrazine with purity of 97.03% used in this experiment was supplied by Ruize Pesticide Ltd. Co. of Wuxi, Jiangsu, China.

The soil is a fluvo-aquic soil from the Fengqiu Agro-ecological Experiment Station, Henan, China, and is a typical agricultural soil in this region. The soil samples from the A$_p$ horizons were air-dried and ground to pass through a 2-mm sieve before visible roots and organic residues were removed. Physical and chemical properties of the soil samples are listed in Table I.

TABLE I

Selected physical and chemical properties of the fluvo-aquic soil

| Depth | Clay (< 0.002 mm) | Silt (0.002–0.02 mm) | Sand (0.02–2 mm) | pH (1:2, soil/water ratio) | Organic matter | Bulk density | Cation exchange capacity |
|---|---|---|---|---|---|---|---|
| cm | | g kg$^{-1}$ | | | g kg$^{-1}$ | g cm$^{-3}$ | cmol$_c$ kg$^{-1}$ |
| 0–10 | 136.1 | 113.3 | 750.6 | 8.27 | 4.3 | 1.49 | 6.0 |

The adsorption of atrazine on the fluvo-aquic soil was studied using a batch experiment technique (Chefetz $et\ al.$, 2004). Solutions with different initial atrazine concentrations ($c_i$) of 50, 100, 500, 1 000, and 2 000 $\mu$g L$^{-1}$ in 0.01 mol L$^{-1}$ CaCl$_2$ were used in triplicate. Adsorption was initiated by mixing 12.5 g of air-dried soil sample with 25 mL of the various atrazine solutions in 40-mL Teflon centrifuge tubes. The slurries were mechanically shaken for 2, 8, 24, 48, 72, 96, 120, 144, and 168 h at 25 $\pm$ 2 °C. Then, the suspensions were centrifuged at 4 024 $g$ for 10 min. A 10-mL aliquot was sampled from the supernatant and analyzed using gas chromatography. A blank without soil was prepared for each initial atrazine concentration. Adsorption of the atrazine on the centrifuge tubes was tested to be negligible (< 1%). Solid-phase atrazine concentrations, $c_s$, were determined according to Equation 1:

$$c_s = \frac{(c_i - c) \times v}{w} \tag{1}$$

where $c_s$, $c_i$, and $c$ represent the amount of atrazine sorbed on the fluvo-aquic soil ($\mu$g kg$^{-1}$), atrazine initial concentration ($\mu$g L$^{-1}$), and atrazine concentration in solution ($\mu$g L$^{-1}$), respectively; $v$ is the volume of the solution (mL), and $w$ is the mass of soil in centrifuge tubes (g).

The extracted atrazine was analyzed using gas chromatography (Agilent-6890, USA), using a 30.0 m $\times$ 0.25 mm $\times$ 0.25 $\mu$m film cross-linked with 5% phenyl methyl silicone capillary column and a N/P detector. The operational conditions of the gas chromatography were: injector temperature 250 °C, detector temperature 320 °C, initial oven temperature 80 °C with a holding time of 2.5 min, increased to 230 °C at 40 °C min$^{-1}$ with a final holding time of 3 min, and carrier flow rate 1.5 mL min$^{-1}$. The retention time of atrazine was 7.25 min. All the solutes were rectified using external standard solutions of atrazine. The detection limit was below 5 $\mu$g L$^{-1}$.

The linear and nonlinear forms of Freundlich model, which is commonly used to describe the distribution of atrazine between soil solid phase and solution for both adsorption and desorption processes (Lesan and Bhandari, 2003; Ben-Hur *et al.*, 2003), were used to fit the atrazine adsorption data. The linear and nonlinear Freundlich equation can be respectively expressed as:

$$c_s = k_d c \qquad\qquad\qquad (2)$$

where $k_d$ is the linear Freundlich distribution coefficient, and

$$c_s = k_f c^n \qquad\qquad\qquad (3)$$

where $k_f$ is the capacity parameter and $n$ is a dimensionless parameter, which is usually less than 1.

All the statistical analysis in this study was performed using statistical software SPSS (version 10.0).

RESULTS AND DISCUSSION

*Adsorption of atrazine on the fluvo-aquic soil*

A phase-distribution relationship (PDR) relates the solid phase concentration of a target chemical to its aqueous phase concentration (Weber and Huang, 1996; Lesan and Bhandari, 2003). The PDRs of atrazine for different adsorption contact periods between the surface of soil particle and the solution are shown in Fig. 1. As expected, an increase in the amount of atrazine sorbed to fluvo-aquic soil was observed with the increase in contact period. The opposite trend was observed for atrazine concentration in solution. As the contact period increased from 2 to 168 h, the deviations in curves fitted using the nonlinear Freundlich equation gradually became less. When the adsorption contact periods were more than 72 h, these fitting curves tended to overlap, indicating a shift of atrazine sorption process in fluvo-aquic soil from nonequilibrium to equilibrium conditions. Furthermore, the contact periods of 2, 8, 24, 48, 72, 96, 120, 144, and 168 h corresponded to the nonlinear Freundlich equations $c_s = 3.49c^{0.6935}$ ($r^2 = 0.9657$), $c_s = 4.482c^{0.6968}$ ($r^2 = 0.9507$), $c_s = 5.3c^{0.7526}$ ($r^2 = 0.9894$), $c_s = 12.38c^{0.6628}$ ($r^2 = 0.9894$), $c_s = 8.446c^{0.7396}$ ($r^2 = 0.9985$), $c_s = 13.04c^{0.6690}$ ($r^2 = 0.9912$), $c_s = 15.93c^{0.6440}$ ($r^2 = 0.9952$), $c_s = 16.79c^{0.6433}$ ($r^2 = 0.9995$), and $c_s = 24.24c^{0.5874}$ ($r^2 = 0.9997$), respectively.

Fitting of the atrazine adsorption data using the linear Freundlich equation showed that the adsorption contact periods from 2 to 168 h correspond to $c_s = 0.3813c$ ($r^2 = 0.9021$), $c_s = 0.508c$ ($r^2 = 0.8868$), $c_s = 0.9138c$ ($r^2 = 0.9541$), $c_s = 1.184c$ ($r^2 = 0.9138$), $c_s = 1.407c$ ($r^2 = 0.963$), $c_s = 1.319c$ ($r^2 = 0.9198$), $c_s = 1.363c$ ($r^2 = 0.9141$), $c_s = 1.444c$ ($r^2 = 0.9267$), and $c_s = 1.412c$ ($r^2 = 0.8895$), respectively. Nonlinear parameter $n$ values ranging from 0.5874 to 0.7526 were significantly less than one ($P < 0.001$) for all the adsorption contact periods. Moreover, based on the $r^2$ values, atrazine adsorption could be better described by the nonlinear Freundlich equation than by the linear equation used in this study.

The solid-phase atrazine concentrations on the fluvo-aquic soil as a function of contact period for different initial atrazine concentrations described in Fig. 2 showed that the amount of atrazine sorbed
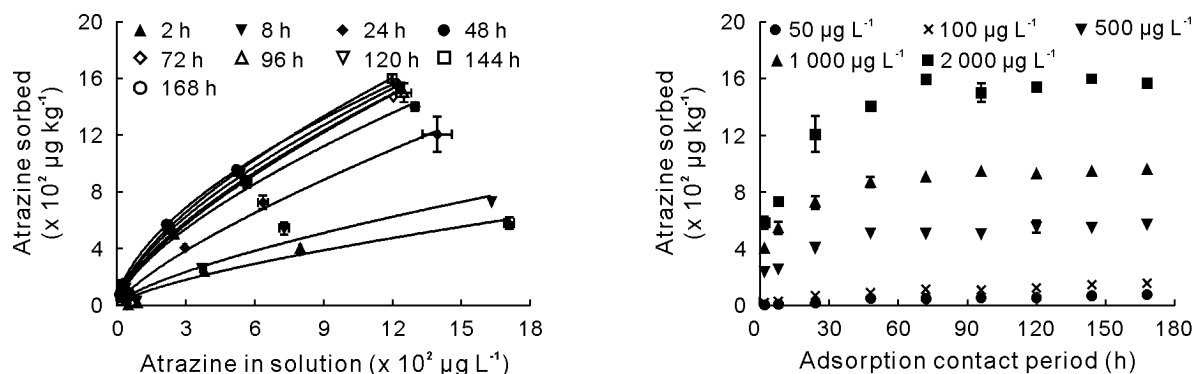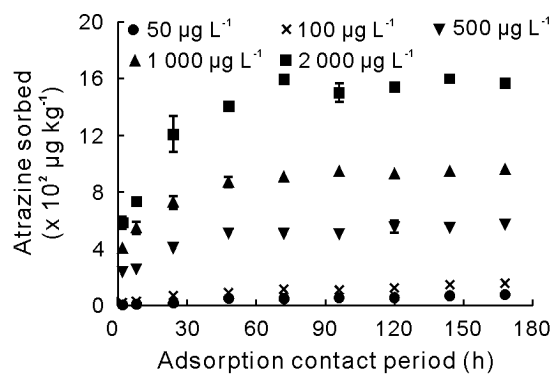
Fig. 1   Phase-distribution relationships of atrazine between the fluvo-aquic soil particle surface and solution. Symbol and error bars represent mean±standard deviation.

Fig. 2   Effect of adsorption contact periods on atrazine adsorption on the fluvo-aquic soil particle surface. Symbols and error bars represent mean±standard deviation.

increased as the adsorption contact periods increased. The percentages of atrazine sorbed within 24 h by the soil ranged from 24% to 77% of the observed total amounts sorbed for the longest contact period. In adsorption studies for different initial atrazine concentrations, Lesan and Bhandari (2003) found that the amount of atrazine sorbed by agricultural and woodland soils with SOM content of 3.4% and 6.2% were 70% and 80% of the total amount of atrazine sorbed by both soils within 24 h, respectively. In this study, however, the adsorption at the lower initial atrazine concentrations of 50 and 100 $\mu$g L$^{-1}$ appeared to occur for the entire duration of the study. The longer equilibration periods observed at lower initial atrazine concentrations appeared to be indicative of an attenuated diffusive flux of the solute caused by smaller concentration gradients and stronger sorption at the lower aqueous concentrations of the solute. The longer equilibration periods were likely related to the SOM content of the fluvo-aquic soil. An increase in the ratio of the occupied, low-energy adsorption sites to the occupied, high-energy adsorption sites results in increase of adsorption with increase of initial concentration (Huang and Weber, 1998). A limited number of high-energy sites were available and most of them were occupied at low concentrations and a considerably longer time was required for low initial concentrations of atrazine to reach adsorption equilibrium. At high concentrations, several molecules occupied low-energy binding sites and, therefore, can readily attain adsorption equilibrium within shorter contact periods (Gao et al., 1998; Gunasekara and Xing, 2003). However, it could not be ruled out that the solutes continued to redistribute within soil matrices beyond their respective apparent equilibrium periods, without significant external manifestations.

*Effect of adsorption contact periods on Freundlich equation parameters*

Figs. 3 and 4 summarize the changes in the nonlinear Freundlich equation parameters $k_f$ and $n$ as a function of the adsorption contact periods. $k_f$ showed a very significant linear increase with adsorption contact periods ($r^2 = 0.9063$, $P < 0.001$). However, a negative linear correlation was observed for $n$ ($r^2 = 0.5666$, $P < 0.05$). Time-dependent variations in Freundlich parameters were explained in terms of the dual-domain sorption model. Weber and Huang (1996) provided mechanistic interpretations for the temporal evolution of $k_f$ and $n$ during the sorption of phenanthrene on various geosorbents by invoking a three-domain particle-scale model comprising exposed mineral surfaces, "young" or amorphous SOM, aged or condensed organic matter. An assumption of four adsorption stages was proposed. At the first stage, the solutes accessed the mineral domain and $k_f$ and $n$ remained constant with time. At the second stage, the solute accessed the rubbery and condensed domains simultaneously. During this stage, $n$ decreased and $k_f$ increased with time. At the third stage, $n$ became constant, suggesting

saturation of the amorphous regions, but $k_f$ continued to increase, indicating the continued migration of the solutes into the condensed SOM matrices. Finally, at the apparent equilibrium stage, $k_f$ and $n$ became constant and represented true Freundlich sorption isotherm parameters. Pedit and Miller (1996) used first-order mass transfer, surface-diffusion, and pore-diffusion models and predicted the time-dependent changes in $k_f$ and $n$ similar to those observed by Weber and Huang (1996), with an assumption of a homogenous sorption domain. The pore-diffusion model applied to nonlinear sorption predicted stronger sorption at low solute concentrations, which had the potential to significantly retard the solute diffusion, resulting in longer equilibration time for dilute solutions. Concentration-dependent solute diffusion could, therefore, also result in temporal shifts in $k_f$ and $n$.
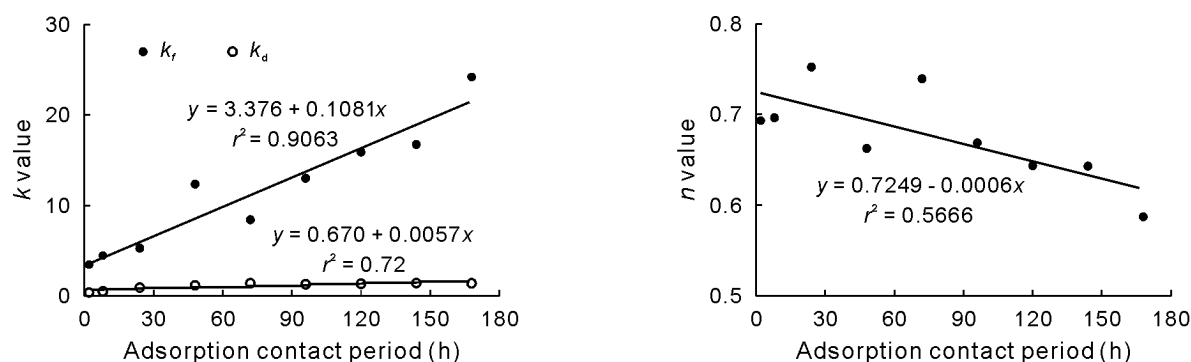


Fig. 3   Relationships of the nonlinear Freundlich equation parameter $k_f$, the capacity parameter, and $k_d$, the distribution coefficient estimated using the linear Freundlich equation, with the adsorption contact periods.

Fig. 4   Relationships of the nonlinear Freundlich equation parameter $n$, a dimensionless parameter, with the adsorption contact periods.

Since the estimated $n$ values derived from the nonlinear Freundlich equation were different for various soils, comparison of the $k_f$ values was not appropriate (Zhu and Selim, 2000). The distribution coefficient $k_d$ values were estimated using the linear Freundlich equation. Result of a statistical correlation analysis for changes in $k_d$ with adsorption contact periods revealed that they were significantly positively correlated ($r^2 = 0.72$, $P < 0.01$) (Fig. 3). $k_d$ values were clearly time dependent for the fluvo-aquic soil, especially in cases of longer adsorption contact periods. Furthermore, these $k_d$ values were within the range of values previously reported. Johnson and Sims (1993) reported atrazine $k_d$ values of 0.66 to 2.96 on six Atlantic coastal plain surface soils, and Pignatello and Huang (1991) reported values of 0.77 to 2.96 on four soils from Connecticut. In this study, atrazine $k_d$ values ranged from 0.38 to 1.44 on a fluvo-aquic soil. The lower $k_d$ values indicated a greater potential mobility of atrazine in soil.

Pignatello and Huang (1991) determined an apparent constant ($k_{app}$) by measuring the sorbed and solution concentrations of atrazine following suspension of a field soil sample in water for 24 h. They also determined the $k_d$ values based on a 24 h sorption isotherm of freshly added herbicide, and found that the $k_{app}/k_d$ ratios varied from 2.3 to 42 and were directly related to the age of the residue. This finding was consistent with the time-dependent adsorption isotherm results of this study (Fig. 3). It was customary to utilize short-term equilibration periods (24 h) for determining herbicide adsorption distribution coefficient $k_d$. Such measured $k_d$ may not be a representative in describing the residue concentrations under field conditions according to the results of this study. Thus, the parameters obtained from a time-dependent isotherm rather than the $k_d$ estimated using the linear Freundlich equation were more appropriate to predict the herbicide residue in the field and thus more meaningful for environmental assessment.

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