

Characterization of the Atrazine Sorption Process on Andisol and Ultisol Volcanic Ash-Derived Soils: Kinetic Parameters and the Contribution of Humic Fractions

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ABSTRACT: Atrazine sorption was studied in six Andisol and Ultisol soils. Humic and fulvic acids and humin contributions were established. Sorption on soils was well described by the Freundlich model. K_f values ranged from 2.2–15.6 $\mu\text{g}^{1-1/n}\text{mL}^{1/n}\text{g}^{-1}$. The relevance of humic acid and humin was deduced from isotherm and kinetics experiments. K_{OC} values varied between 221 and 679 mLg^{-1} for these fractions. Fulvic acid presented low binding capacity. Sorption was controlled by instantaneous equilibrium followed by a time-dependent phase. The Elovich equation, intraparticle diffusion model, and a two-site nonequilibrium model allowed us to conclude that (i) there are two rate-limited phases in Andisols related to intrasorbent diffusion in organic matter and retarded intraparticle diffusion in the organo–mineral complex and that (ii) there is one rate-limited phase in Ultisols attributed to the mineral composition. The lower organic matter content of Ultisols and the slower sorption rate and mechanisms involved must be considered to assess the leaching behavior of atrazine.

KEYWORDS: atrazine, sorption, variable-charge soils, Andisols, Ultisols

■ INTRODUCTION

Atrazine (2-chlorine-4-ethyl-6-isopropil-1,3,5-triazin) is one of the most frequently detected pesticides in ground and surface waters^{1–3} being also found in seawater and ice in remote areas.⁴ It is considered as a potential long-term threat to the environment because of its persistence in water and soils.^{4–6} Nevertheless, this herbicide is still widely used worldwide.

Volcanic ash-derived soils have a great importance in the agricultural economy of countries of Asia, Oceania, and America. These soils are abundant and widespread in Central-Southern Chile accounting for 70% of the arable land. The main common characteristics for Andisols and Ultisols are variable surface charge and acidic pH (4.5–5.5). Andisols are rich in organic matter and allophane and present high specific surface area, low bulk density, and high structural stability and water retention capacity. Ultisols have lower organic matter than Andisols and contain Kaolinite type minerals and more crystalline iron oxides.⁷ They present high bulk density and are sensitive to compaction. In agricultural practices on these types of soils, frequent adjustments of soil pH and mineral fertilization are required. The high organic matter content and the variable surface charge in volcanic ash-derived soils allow a high sorption capacity for some organic contaminants. Thus, K_f values describing the sorption of acidic organic compounds such as bensulfuron-methyl and metsulfuron-methyl are higher than those reported in the literature for different kinds of soils.^{8–10}

Sorption, leaching, and transport mechanisms of atrazine on different soils have been intensively studied,^{11–14} as well as the role of different soil components in sorption and desorption processes.^{15–20} Thus, low sorption coefficients and the influence of the amount and composition of soil organic matter in the variability of sorption affinity have been widely discussed. However, there are only a few reports on the

behavior of atrazine in volcanic ash-derived soils.^{13,21,22} The higher sorption affinity of atrazine in allophanic soils compared to nonallophanic soils was established, but none of the measured soil properties could alone adequately explain its sorption behavior.¹³ In field experiments, runoff and leaching were detected in an Ultisol from humid tropical conditions.²²

In soils, sorption is commonly studied in apparent equilibrium systems at constant temperatures; however, the pesticide–sorber interaction is a time-dependent process which often progresses rapidly over the short-term (minutes or hours), but it can take a long time to reach equilibrium (days, weeks, or months). During the short-term, sorption has influence on the transport of pesticides in the soil environment; therefore, time-dependent aspects must be considered for assessing potential leaching and bioavailability. Nowadays, leading model systems can describe sorption as an instantaneous equilibrium or a two-site equilibrium-kinetic process, one- or two-site kinetic sorption, and sorption in the matrix to equilibrium, kinetic, and irreversibly binding sites.²³

Kinetics of atrazine sorption has been studied for different soils under different conditions. Influence of soil aggregate size,²⁴ time-dependent phase distribution and apparent desorption hysteresis,²⁵ and nonequilibrium transport originated in rate-limited mass transfer process²⁶ have been discussed; nevertheless, nothing is known about the kinetics of atrazine sorption on volcanic ash-derived soils.

The aim of this work was to compare sorption behavior of atrazine on six volcanic ash-derived soils belonging to Andisol and Ultisol orders given their distinctive physical and chemical

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properties and the scarce antecedents related to this process in soils of variable charge. All of these soils have an agricultural use. Furthermore, the individual contribution of humic and fulvic acids and humin-mineral residue extracted from three of them was assessed. The short-term kinetics parameters of sorption were obtained by using the pseudo-first- and pseudo-second-order models,²⁷ and sorption mechanism and potential rate controlling stage were examined by applying the Elovich equation, the intraparticle diffusion model, and a two-site nonequilibrium model.^{28–33}

MATERIALS AND METHODS

Chemicals. Analytical reference standard of atrazine was obtained from Dr. Ehrenstofer, Germany. All reagents used for analytical determination of atrazine and organic matter fractionation were of analytical or HPLC grade. The stock solution for all purposes was 1 mg mL⁻¹ atrazine in acetonitrile, and it was stored at 4 °C under darkness.

Soil Samples. Fresh samples from six volcanic ash-derived soils (0–20 cm) located in the central southern region of Chile (from 37°15' to 40°45' S) were collected: three Andisols, Piedras Negras (medial, isomesic, typic dystrandept, PN), Temuco (medial, mesic, entic dystrandept, TEM), and Pemehue (ashy, mesic, hydric, dystrandept, PEM), and three Ultisols, Metrenco (fine, mesic, palehumult, MET), Cudico (fine metahalloysitic, mesic, typic palehumult, CUD), and Collipulli (fine, mesic, xeric, palehumult, COLL).³⁴ All of these soils have an agricultural use, and they are dedicated to the cultivation of cereals such as wheat and oats or to artificial prairies, according to their physical properties. Soils were air-dried for 24 h, sufficient time to allow sieving through a 2 mm diameter sieve, and stored in hermetic bottles at room temperature until use.

Organic Fractions. The humic acid, fulvic acid, and humin fractions were extracted from PN, COLL, and CUD soils according to their solubility properties in acids or bases. Humic acids were purified by washing with a 1:1:6 (v/v/v) = HF/HCl/H₂O solution. Hydrofluoric and hydrochloric acids were 48 and 37%, respectively. Fulvic acids solutions were eluted from an ionic exchange resin (Dowex X8 resin), concentrated in a rotary evaporator, and finally dialyzed by using a 2 kDa MWCO membrane. The residual soil without HA and FA was washed by successive shaking and centrifugation steps until a neutral pH was obtained. Finally, all fractions were dried at 40 °C to constant weight and stored at room temperature. The original weight of the soil was 50 g.³⁵

Characterization of Soils. Total organic carbon (TOC) was determined through elemental analysis (Elemental analyzer Vario El). The pH of soils was measured in soil suspension made with deionized water at a 1: 2.5 w/v ratio and with 1 M KCl. Samples were stirred during the first 5 min of contact time, and determinations were made after 2 h. For all soils, cation exchange capacity (CEC) was calculated from the total exchangeable bases (i.e., amounts of Mg, Ca, K, and Na extracted by 1 M ammonium acetate at pH 7.0) plus extractable acidity of soils. Extractable acidity was determined by using 2.5 g of sample through extraction with 0.25 M BaCl₂ + 0.2 M triethanolamine at pH 8.2, during 16 h. Iron, Al, and Si contents were extracted with acid ammonium oxalate, representing active or poorly crystalline compounds, and later determined by atomic absorption spectroscopy. The extraction was carried out by a single 4 h treatment, in darkness, with oxalic acid-ammonium oxalate at pH 3.³⁶ Allophane content was estimated from Si extractable with acid ammonium oxalate.³⁷ The point of zero salt effect (PZSE) was determined by potentiometric titration at 0.01, 0.1, and 1 M KCl: 1 g of soil was equilibrated with 100 mL of KCl solution, and later, the titration was done with 1 M HCl and 1 M KOH, at 28 ± 0.1 °C, under N₂ atmosphere, and constant stirring during 30 min between measurements. The PZSE value was determined as the common intersection point of the three curves in the graph of surface charge vs pH. The total specific surface

area was determined gravimetrically by using the retention method of ethylene glycol monoethylether.³⁸

Characterization of Organic Fractions. Organic fractions were passed through a 60 mesh sieve, and TOC was determined as described above. Total acidity was determined by potentiometric titration with Ba(OH)₂ to neutralize the acidic groups in the polymer. Carboxylic acidity was determined through an indirect method by using (CH₃COO)₂Ca, and the CH₃COOH produced during the reaction was titrated with NaOH. Phenolic acidity was calculated as the difference between total and carboxylic acidities.³⁹

Batch Sorption Experiments. Adsorption isotherms of atrazine on soils were determined at 30 ± 1 °C. Duplicate samples of 2 g of air-dried soil were equilibrated with 10 mL of aqueous herbicide solution (with 0.01 M CaCl₂) in 30 mL centrifuge tubes (polypropylene copolymer). The initial concentration for each solution was 2, 4, 6, 8, and 10 µg mL⁻¹. The tubes were shaken end over end at the natural pH of soils during 16 h.

Suspensions were centrifuged at 2750 g for 15 min; the supernatant was filtered through a 0.22 µm membrane (Durapore, PVDF, from Millipore). The concentration of atrazine in solutions was determined by HPLC-DAD (Waters, Milford, MA, USA) at 224 nm. Organic fraction isotherms were determined as described above, but these experiments were carried out with 50 mg of humic acid and fulvic acid, and 200 mg for humin being shaken during 16 h. No degradation products were detected during a 24 h equilibration with the more complex matrices, an aqueous solution obtained from PN soil and its corresponding humic acid. The presence of coeluting compounds of soil matrices was discarded through the evaluation of the spectral purity test and the spectral matching test of atrazine peak by using the analytical standard.

Sorption was described by the Freundlich equation:

$$Q_{ads} = K_f \times C_e^{1/n} \quad (1)$$

where Q_{ads} (µg g⁻¹) is the amount of herbicide adsorbed by the corresponding soil or organic fraction. C_e is the equilibrium concentration in solution (µg mL⁻¹), and K_f and $1/n$ are empirical constants. The organic carbon distribution coefficient (K_{OC}) was calculated as follows:

$$K_{OC} = \frac{K_d}{\%OC} \times 100 \quad (2)$$

where K_d is the distribution coefficient at a determined concentration from the isotherm range.

Sorption Kinetic Experiments. Kinetic experiments were performed for PN and COLL soils at 30 ± 1 °C, both soils being representative of Andisols and Ultisols and presenting the high and lower organic matter content, respectively. Duplicate samples of 2 g were mixed with a 10 mL aliquot of an aqueous solution of atrazine at 6 µg mL⁻¹ (0.01 M CaCl₂); tubes were shaken during 15, 20, 30, and 60 min and 2, 4, 8, 15, 24, 30, 40, and 48 h. Humic acid and humin fractions from PN soil were used to clarify the kinetic behavior of this soil, but in this case, samples were shaken up to 6 and 16 h, and weights were 50 and 200 mg, respectively. The same procedure described for isotherm experiments was used to establish the concentration of atrazine in solutions.

Pseudo-First-Order Equation. For this model, integrating the rate equation for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$ and rearranging the terms gives the corresponding linear equation

$$\log(q_{max} - q_t) = \log q_{max} - \frac{k_1}{2.303} t \quad (3)$$

where q_t is the sorbed quantity per unit mass of sorbent at time t , t is the solid-solution contact time (min), q_{max} is the maximum sorbed amount per unit mass of sorbent and k_1 is the first-order rate constant (min⁻¹).⁴⁰

Pseudo-Second-Order Equation. This model considers that the driving force is proportional to the available fraction of active sites on the sorbent, and the kinetic rate equation is the following:⁴⁰

Table 1. Physical and Chemical Properties of Soils (Mean Values, $n = 2$)

soils	TOC ^a (%)	pH _{H₂O}	pH _{KCl}	CEC ^b (meq (+) /100g)	Al ^c (%)	Fe ^c (%)	Si ^c (%)	allophane (%)	PZSE ^d	specific surface area (m ² g ⁻¹)
Andisols										
PN	14.8	4.8	4.3	97.0	3.4	2.3	0.8	5.7	3.8	251
TEM	5.6	5.5	4.6	63.3	2.9	3.1	0.9	6.4	4.7	229
PEM	3.8	5.2	4.5	37.8	2.0	2.1	0.7	5.0	4.8	85
Ultisols										
CUD	7.4	5.2	4.0	52.6	1.0	0.9	0.1	0.7	4.4	274
MET	3.6	5.4	4.2	37.0	0.5	1.9	0.1	0.7	4.6	166
COLL	2.5	5.0	3.9	39.9	0.5	1.2	0.1	0.7	4.4	231

^aTotal organic carbon. ^bCation exchange capacity. ^cAl, Fe, and Si extracted with 1 M acid ammonium oxalate solution. ^dPZSE measured by potentiometric titration.

Table 2. Adsorption of Atrazine on Volcanic Ash-Derived Soils: Freundlich Parameters (K_f , $1/n$, and Determination Coefficients) and K_{OC} Values

soil	K_f ($\mu\text{g}^{1-1/n} \text{ mL}^{1/n} \text{ g}^{-1}$)	n	R^2	K_d^a (mL g ⁻¹)	K_{OC} (mL g ⁻¹)
Andisols					
PN	15.6 (0.4) ^b	0.78 (0.02)	0.996	17.8	120
TEM	7.3 (0.2)	0.71 (0.02)	0.994	7.2	128
PEM	4.2 (0.2)	0.77 (0.02)	0.994	4.0	103
Ultisols					
CUD	9.2 (0.2)	0.90 (0.01)	0.999	9.8	132
MET	6.4 (0.2)	0.73 (0.02)	0.993	6.3	176
COLL	2.2 (0.1)	0.80 (0.03)	0.993	2.3	90

^a K_d values obtained for a 2 $\mu\text{g mL}^{-1}$ solution (in 0.01 M CaCl₂). ^bThe standard error for each parameter is in parentheses.

$$\frac{dq_t}{dt} = k_2(q_{\max} - q_t) \quad (4)$$

where q_t and q_{\max} have the same meaning as before, and k_2 is the reaction-rate constant ($\text{g } \mu\text{g}^{-1} \text{ min}^{-1}$).

The linear equation is obtained by using the same procedure as that described above.

$$\frac{t}{q_t} = \frac{1}{q_{\max}^2 k_2} + \frac{1}{q_{\max}} t \quad (5)$$

Elovich Equation. The integrated form of the Elovich equation is simplified to obtain a linear equation by assuming that t is much larger than t_0 , with $t_0 = 1/\alpha\beta$.

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (6)$$

The constant α ($\mu\text{g g}^{-1} \text{ min}^{-1}$) is regarded as the initial rate, the intercept would correspond to the amount sorbed during the initial equilibrium phase (fast reaction phase), and β ($\text{g } \mu\text{g}^{-1}$) is related to the extent of surface coverage and activation energy for chemisorption.

Intraparticle Diffusion (Weber–Morris Model). For this model, the mathematical dependence of uptake $q(t)$ of the sorbate on $t^{1/2}$ is given by the following equation:

$$q_t = k_{\text{int}} t^{1/2} + C \quad (7)$$

where k_{int} ($\mu\text{g g}^{-1} \text{ min}^{1/2}$) is the intraparticle diffusion rate constant, and C is a constant related to the thickness of the boundary layer.

Two-Site Nonequilibrium Model (TSNE).³⁰ The two-site concept presumes that sorption or exchange sites in soils can be classified into Type 1, where sorption is assumed to be instantaneous, and Type 2, where sorption is considered time-dependent. The equation used to calculate the relative concentration (C/C_{in}) as a function of time is

$$\frac{C}{C_{\text{in}}} = \frac{1}{R} + \left(\frac{1}{\beta R} - \frac{1}{R} \right) \exp \left[- \left(\frac{k_2}{\beta} \right) t \right] \quad (8)$$

where C is the solute concentration in water ($\mu\text{g mL}^{-1}$), C_{in} is the initial added solute concentration ($\mu\text{g mL}^{-1}$), R is the retardation factor, β is the fraction of retardation for the instantaneous region, and

k_2 (h^{-1}) is the kinetic rate coefficient for desorption from Type 2 sites. Parameters are determined by using nonlinear curve fitting procedures on C/C_{in} versus time data. Once R and β are calculated, the linear sorption partition coefficient at equilibrium K (mL μg^{-1}) and the fraction of the total sorption in the Type 1 region when the system is in equilibrium F are determined according to the following equations:

$$R = 1 + \frac{M}{V} K \quad (9)$$

$$\beta = \left(1 + F \frac{M}{V} K \right) / R \quad (10)$$

where M is the mass of soil (g), and V is the volume of water (mL).

Statistical Analysis. The Freundlich parameters (K_f and $1/n$) were established through nonlinear analysis of data for all soil and organic matter fractions. Linear analysis was used to establish kinetic parameters for all models except for the TSNE model where nonlinear analysis was employed. In all cases, the corresponding standard error values and the coefficient of determination (adjusted R^2) were obtained. The statistical significance of relationships between variables was established through ANOVA.

RESULTS AND DISCUSSION

Adsorption of Atrazine and Soil Properties. Soils presented acid pH both in water and 1 M KCl (Table 1). Iron, Al, and allophane were similar in order of magnitude to those obtained for 16 surface horizons of Andisols and Ultisols.⁴¹ The sign of ΔpH (pH KCl – pH H₂O) value has been proposed as the sign of the electric charge of a soil.⁴² According to this criterion, soils have a negative net charge, and this is more pronounced in Ultisols than Andisols, in agreement with PZSE, with lower values than the corresponding pH.

Adsorption data were well described by the Freundlich model with $R^2 \geq 0.993$ (P value < 0.05) (Table 2). A significant adsorption was produced on all soil samples except for COLL soil, and $1/n$ values were lower than 1, which corresponds to L-type isotherms, indicating heterogeneous sorption sites (Figure

1). According to its pK_a value (1.8) and the pH of the soils, the neutral form of atrazine was the sole species present.

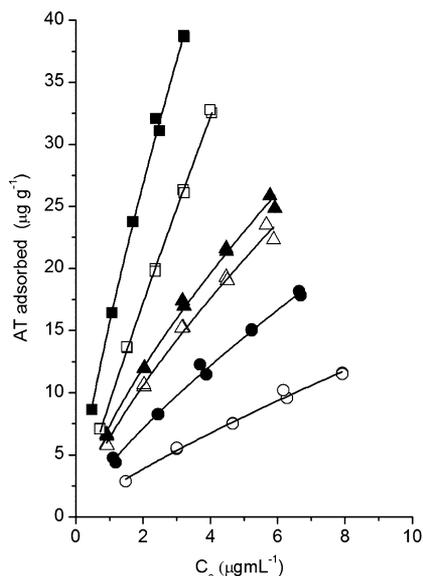


Figure 1. Adsorption isotherms of atrazine on Andisol and Ultisol soils: (■) PN, (Δ) MET, (●) PEM, (▲) TEM, (○) COLL, and (□) CUD.

Consequently, ionic interactions cannot be expected because of the negative net charge of soils, and sorption will occur mainly through hydrophobic interactions or van der Waals forces. The highly significant linear relationship between K_f values and TOC ($R^2 = 0.944$, P value < 0.05) showed that the main interactions between atrazine and soil surfaces could be attributed to organic matter. Even though a significant relationship with CEC was also obtained, the combined influence of both factors was not well described through a multiple regression model. K_f values did not correlate with any other physical or chemical individual characteristic of soils.

Taking into account that isotherms were not linear and to compare data with those reported in the literature for volcanic ash-derived soils, K_{OC} values were calculated from the distribution coefficient (K_d) determined for a concentration of $2 \mu\text{g mL}^{-1}$. Similar K_{OC} values were obtained for Andisols, whereas for Ultisols a wider range was observed probably as a consequence of the mineral composition ($103\text{--}120 \text{ mL g}^{-1}$ vs $90\text{--}176 \text{ mL g}^{-1}$). Ranges of K_{OC} reported for atrazine in allophanic soils of New Zealand include $25\text{--}79^{21}$ and $46\text{--}375^{13}$. However, the higher values of K_d (mean value 8.5 L kg^{-1}) for the second set of soils compared to those of nonallophanic soils were attributed to the different nature of the organic matter within allophanic soils and to the contribution of clays to the sorption process. In general, low K_f or K_d values ($< 4 \text{ mL g}^{-1}$) have been obtained for agricultural soils with low to medium organic matter content.^{11,14,22,24,26} However, enhanced sorption capacities have been obtained through amendments with different organic materials (K_f values from 0.81 to 2.20).¹⁴ In this case, the amendment with higher aromatic carbon content led to an increased K_{OC} value, great significance being attributed to hydrophobic interactions. Great differences have been also observed in the behavior of atrazine in carbonatic soils, with K_{OC} values significantly lower than those found in noncarbonatic soils.^{30,43} These differences were mainly attributed to the composition of organic matter with a

probable influence of aromaticity.⁴³ Kaolinite and halloysite are the primary clay minerals in Chilean Ultisols³⁴ and could contribute to sorption in this kind of soils. Kaolinite has been described as an active surface for nonionic atrazine sorption.^{15,16} Although kaolin-type clays are the least reactive clays, the hydrophilic and hydrophobic character for octahedral and tetrahedral basal surfaces, respectively, is well established.⁴⁴ Sorption of atrazine on this mineral is associated with hydrophobic bonding through the silanol surface sites of the tetrahedral sheets.¹⁶ Whereas allophane content in Andisols is $> 50\%$ of the total minerals, Ultisols have different mineral composition. Although the dominant presence of kaolinite clays is common for these soils, there is a greater variety of minerals in COLL soil, including allophane, chlorite, gibbsite, and goethite/hematite, which could influence the atrazine sorption capacity of organic matter ($K_{OC} = 90$).

Organic Fractions and Atrazine Adsorption. From the data of elemental analysis (Table 3), TOC contents were quite

Table 3. Chemical Properties of Organic Matter Fractions from Three Soils (Mean Values, $n = 2$)

	C^a (%)	N^a (%)	C/N	pH	total acidity ^b	carboxylic acidity ^b	phenolic acidity ^b
PN							
HA ^c	49.1	4.3	11.3	3.9	476	268	208
FA	38.4	3.0	12.8	3.3	955	177	778
HUM	5.5	0.3	20.3	9.1			
CUD							
HA	51.9	4.0	13.0	3.6	407	229	178
FA	32.3	1.7	18.9	3.3	819	209	609
HUM	3.5	0.3	12.0	8.9			
COLL							
HA	51.6	4.3	12.1	3.6	448	262	186
FA	18.6	1.0	18.8	3.5	569	241	328
HUM	1.1	0.1	15.3	8.3			

^aTotal carbon and nitrogen. ^bcmol (+) kg^{-1} . ^cHA = humic acid, FA = fulvic acid, and HUM = humin fraction.

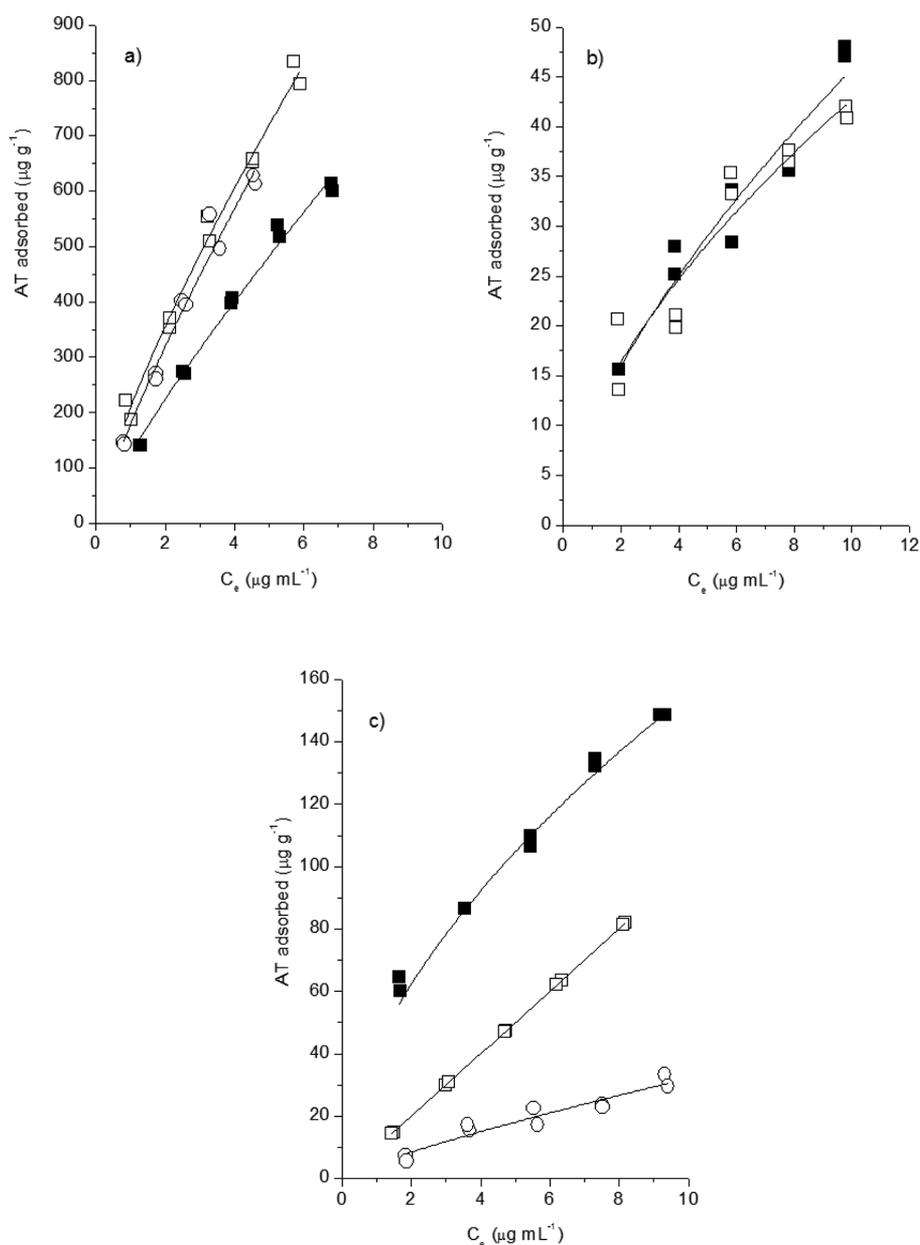
similar for humic acids ($\cong 50\%$), and the most significant differences between fulvic acids were obtained for COLL soil presenting the lowest TOC content and total and phenolic acidity. Humin presented a residual TOC content clearly related to that found in the corresponding soil. Data for adsorption on all humic acid and humin fractions for PN and CUD soils were well described by the Freundlich model ($R^2 \geq 0.966$, P value < 0.05 , Table 4). A lower homogeneity and purity could explain the lower R^2 values for fulvic acid from PN and CUD soils. Sorption for fulvic acid from COLL soil was negligible without any clear trend. Isotherms were not linear, and the coefficient $1/n$ was < 0.65 for humin from PN soil and for fulvic acid from PN and CUD soils (Figure 2).

There was no significant relationship between binding capacity and the different properties of organic fractions. Humic acid and humin from all soils presented high K_{OC} values, whereas sorption of atrazine on fulvic acids was very limited. The aggregation of lower molecular weight fractions of fulvic acid, where a competition with atrazine for active sites on the larger molecular weight fraction is produced, has been mentioned in the literature as a possible origin of diminished binding when total fulvic acid concentration increases.⁴⁵ Maximum adsorption of atrazine has been observed for humic acid at pH 3; however, at this pH the degree of

Table 4. Freundlich Parameters (K_f , $1/n$, and Determination Coefficients) and K_{OC} Values for the Adsorption of Atrazine on Organic Fractions

	K_f ($\mu\text{g}^{1-1/n} \text{mL}^{1/n} \text{g}^{-1}$)	$1/n$	R^2	pH ^a	K_d (mL g^{-1})	K_{OC} (mL g^{-1})
PN						
HA ^b	125.8 (7.8) ^c	0.84 (0.04)	0.989	2.8	108.6	221
FA	10.1 (1.7)	0.65 (0.08)	0.914	3.1	7.3	19
HUM	42.0 (3.2)	0.56 (0.04)	0.966	7.1	37.1	679
CUD						
HA	208.3 (12.8)	0.77 (0.04)	0.984	2.9	221.5	427
FA	10.8 (1.7)	0.60 (0.08)	0.894	3.1	9.0	28
HUM	10.0 (0.1)	1.0 (0)	0.999	7.1	10.0	289
COLL						
HA	179.6 (14.2)	0.83 (0.06)	0.969	2.9	178.1	345
FA				3.1		
HUM	4.7 (1.0)	0.82 (0.11)	0.913	7.2	3.5	326

^apH value for each organic fraction at 0.01 M CaCl_2 and $2 \mu\text{g mL}^{-1}$ atrazine. ^bHA = humic acid, FA = fulvic acid, and HUM = humin fraction. ^cThe standard error for each parameter is in parentheses.

**Figure 2.** Adsorption isotherms of atrazine on humic acids (a), fulvic acids (b), and humin (c): (■) PN, (□) CUD, and (○) COLL.

protonation is low (<5%). Therefore, ionic interactions would be improbable. Nevertheless, the relevance of this type of interactions is proposed on the basis of the progressive sorption decrease with increasing pH for humic and fulvic acids.^{19,45,46} The pH at the equilibrium varied between 3.3 and 3.9 for fulvic and humic acids and was 7 for the humin fraction; therefore, different mechanisms control the behavior of atrazine on soil organic fractions. Binding affinity of atrazine to humic acid and other different humic materials represented as K_{OC} values has been related mainly to the percentage of carbon in aromatic structural groups without a significant relationship with the percentage of carbonylic and carboxylic carbon; thus, a key role is attributed to hydrophobic interactions in the binding of atrazine to humic substances.^{18,46} Phenolic groups have also been associated with an enhanced adsorption capacity of atrazine on humic acid.⁴⁶ The low phenolic acidity of fulvic acid for COLL soil could explain the null capacity in spite of its high TOC content. The contribution of humin fractions was high for all soils, but it was variable and not related to the residual TOC content. A higher carboxylic and phenolic acidity as well as a greater aromatic H content compared to the corresponding humic acid was established for the residual organic matter after the extraction of humic and fulvic acids from a volcanic ash-derived soil.⁴⁷ Consequently, humin would be a sorbent with abundant reactive groups similar to those found in the most reactive humic acid. At the pH of the solution, phenolic groups as well as other functional groups such as SiOH from allophane and SiOH and (Al–OH–Si)^{+0.5} from the exposed edge of kaolinite will be as neutral species making possible hydrophobic interactions in the humin fraction.

In accordance with the results presented above, the most stable organic matter associated with soil mineral colloids is relevant for the sorption of atrazine on Andisols and Ultisols. The high sorption of PN soil can be attributed to the high contribution of humin because of its high K_{OC} . In a similar way, humic acid represents the most important organic fraction for CUD soil.

Given the high relevance of organic matter, PN and COLL soils, representative of Andisols and Ultisols, respectively, and humic acid and humin fractions from the first one were selected for kinetic studies.

Sorption Kinetics. Sorption of atrazine on soils at different solid–solution contact times is shown in Figure 3. Sorbed amounts reached 61–63% during the first 15 min. Kinetics followed a much slower progress toward an apparent equilibrium during the next 30 h where the maximum sorbed amount was observed. Therefore, a rate-limited process is relevant for both soils. A slow sorption taking place over long contact times has been described for soils with different organic matter contents.^{25,32}

Pseudo-First- and Pseudo-Second-Order Models. The results obtained by fitting experimental data to these models are presented in Table 5. The R^2 values for the pseudo-first-order model were >0.95 (P value <0.05) (Figure 4), with a low standard error (SE) for each parameter; however, it fails to explain the q_{max} experimental value. In contrast, for the pseudo-second-order model the predicted values agree well with the experimental ones, describing the whole data set (plot of t/q_t vs t ; Figure 5). The fastest sorption kinetics was obtained for Ultisol.

The interpretation of sorption as a first- or second-order process has some limitations. Several authors⁴⁸ consider that the amount of unoccupied active sites becomes approximately

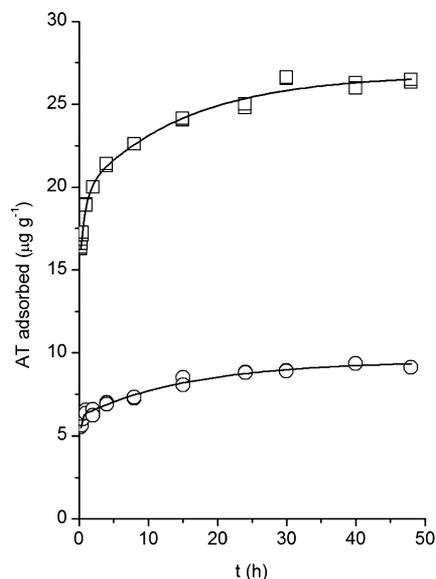


Figure 3. Sorption kinetic of atrazine on volcanic ash-derived soils: (□) PN and (○) COLL.

Table 5. Kinetic Parameters Predicted from the Linear Analysis of Pseudo-First- and Pseudo-Second-Order Kinetic Models

soil	COLL	PN
q_{max} (exp) ($\mu\text{g g}^{-1}$)	9.05	26.00
Pseudo-First-Order Equation		
q_{max} ($\mu\text{g g}^{-1}$)	3.44 (0.13) ^a	8.16 (0.39)
k ($\times 10^3 \text{ min}^{-1}$)	1.21 (0.05)	1.50 (0.08)
R^2	0.974	0.953
Pseudo-Second-Order Equation		
q_{max} ($\mu\text{g g}^{-1}$)	9.29 (0.12)	26.56 (0.19)
k ($\times 10^3 \text{ g } \mu\text{g}^{-1} \text{ min}^{-1}$)	2.06 (0.51)	0.93 (0.21)
R^2	0.997	0.999

^aThe standard error for each parameter is in parentheses.

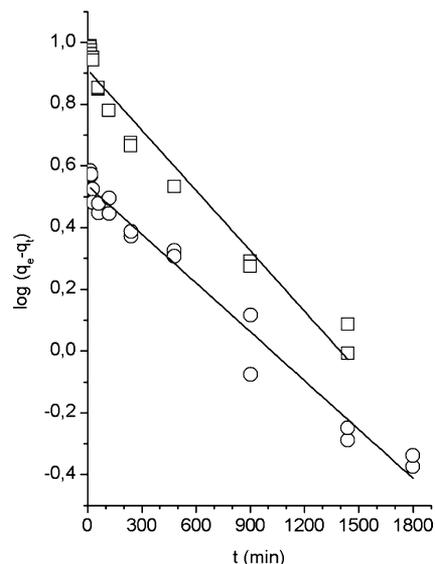


Figure 4. Pseudo-first-order plot for atrazine sorption on volcanic ash-derived soils: (□) PN and (○) COLL.

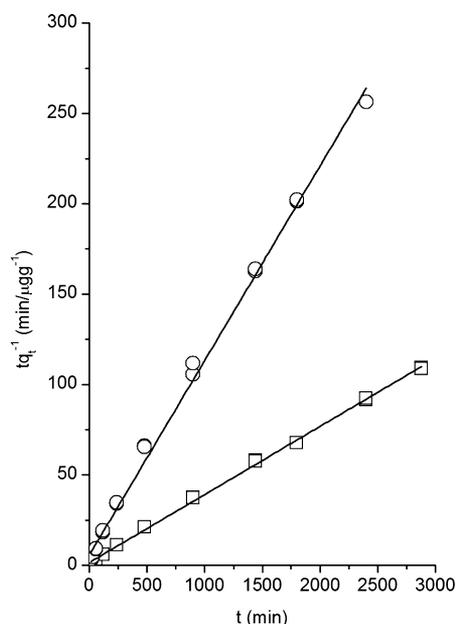


Figure 5. Pseudo-second-order plot for atrazine sorption on volcanic ash-derived soils: (□) PN and (○) COLL.

constant when low coverage of the sorption sites is produced, and in this case, the reaction could show a pseudo-first-order kinetics behavior. Accordingly, this situation could describe mainly the first stages of the sorption process; however, as the sorption reaction proceeds, unoccupied sites and the solute concentration in solution constantly decrease; in this case, sorption becomes a pseudo-second-order reaction. The change in the amount of atrazine sorbed on both soils was very marked during the earlier times of equilibration; consequently, the above conditions are not valid. Azizian²⁷ derived the first- and second-order equations by using a general equation that considers the rate constant of adsorption and desorption of solute in solution, the coverage fraction θ , and C , the molar concentration of solute at any time. According to the

theoretical analysis, the first order equation is obtained when the initial concentration of solute is very high compared to the $\beta\theta$ term, where β is related to the maximum capacity of sorbent. The second-order equation is obtained when the initial concentration of solute is not too high for the $\beta\theta$ term in the general equation to be ignored. The q_{\max} experimental values should indicate that the β term is low for COLL soil. Nevertheless, the amount adsorbed during the first 15 min reached approximately 60% of the amount in equilibrium; therefore, the coverage fraction was high enough to make the $\beta\theta$ term be high compared to the initial concentration of solute in solution. According to this criterion, the better fit of the pseudo-second-order equation might be expected, allowing a better prediction of the corresponding q_{\max} values.

For the pseudo-second-order model, the initial adsorption rate, as qt/t approaches 0, is defined as $h = k(q_{\max})^2$; therefore, it can be calculated directly from the intercept of the straight line. Values were 0.655 and 0.178 $\mu\text{g g}^{-1} \text{min}^{-1}$ for PN and COLL, respectively. The difference was more pronounced and in a direction contrary to that established for the intrinsic rate values, showing a higher initial contribution of mass transport in PN soil probably through the high number of vacant sites accessible to organic matter and/or organic matter Al-Fe complexes, given as a result of an increased concentration gradient between atrazine in solution and atrazine on the soil surface.

Solute Transport Mechanism. By considering that sorption kinetics will depend on soil properties, experimental data must be interpreted to identify the steps involved during sorption and/or to know their relevance within the whole process. Therefore, other kinetic models were used to study the different phases or mechanisms that control sorption kinetics: Elovich equation, the Weber–Morris model, and the TSNE model. The parameters obtained are presented in Table 6.

Elovich Equation. This equation is used successfully to describe second-order kinetics assuming that actual solid surfaces are energetically heterogeneous.⁴⁹ Experimental data fitted adequately to the Elovich equation (R^2 values >0.94, P

Table 6. Kinetic Parameters Predicted from the Linear Analysis of Elovich and Intraparticle Diffusion and Nonlinear Analysis for the Two-Site Nonequilibrium Model (TSNE)

soil	COLL	PN	HA (PN)	HUM (PN)
K_D (exp) (mL g^{-1})	2.1	18.0	58.2	22.2
Elovich Equation				
α ($\mu\text{g g}^{-1} \text{min}^{-1}$)	90 (9) ^a	398 (13)	2406 (47)	215 (55)
β ($\text{g } \mu\text{g}^{-1}$)	1.40 (0.07)	0.50 (0.01)	0.03 (0.00)	0.12 (0.01)
t_0 (min)	0.008	0.005	0.013	0.038
R^2	0.944	0.991	0.965	0.834
Intraparticle Diffusion				
$k_{\text{int } 1}$ ($\mu\text{g g}^{-1} \text{min}^{1/2}$)	0.078 (0.004)	0.54 (0.03)	13.86 (1.05)	1.51 (0.13)
C ($\mu\text{g g}^{-1}$)	5.60 (0.10)	14.33 (0.22)	158.1 (5.5)	45.6 (1.8)
R^2	0.957	0.968	0.961	0.890
$k_{\text{int } 2}$ ($\mu\text{g g}^{-1} \text{min}^{1/2}$)		0.15 (0.01)		
C ($\mu\text{g g}^{-1}$)		19.01 (0.38)		
R^2		0.931		
TSNE				
K ($\text{mL } \mu\text{g}^{-1}$)	2.2 (0.1)	18.0 (0.8)	58.0 (0.7)	22.6 (1.9)
F	0.53 (0.03)	0.30 (0.04)	0.56 (0.04)	0.43 (0.07)
k_2 (h^{-1})	0.07 (0.010)	0.06 (0.01)	2.07 (0.03)	0.15 (0.00)
R^2	0.974	0.965	0.945	0.868

^aThe standard error for each parameter is in parentheses.

value <0.05). The initial rate constant α was $\cong 4.5$ times higher for PN soil, agreeing with data obtained from the pseudo-second-order model, where the h value for PN soil was $\cong 3.9$ times higher than the corresponding value for COLL soil. The intercept of the linear plot of q_t versus $\ln t$ (Figure 6) has been

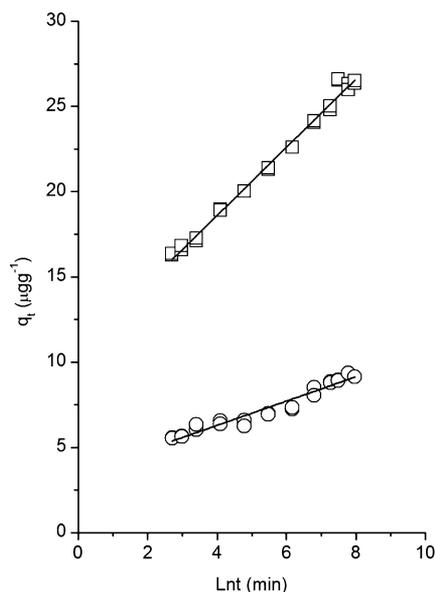


Figure 6. Elovich equation for atrazine sorption on volcanic ash-derived soils: (□) PN and (○) COLL.

considered as the amount sorbed during the initial fast phase reaction.³² The corresponding values were $10.59 (\pm 0.24)$ and $3.44 (\pm 0.21)$ for PN and COLL soil, equivalent to 44 and 36% from the total sorbed amount, respectively. These percentages could represent the contribution of a nearly instantaneous equilibrium to the whole sorption process. These results agree with those obtained for atrazine on soils with low TOC content and similar mineralogy of the clay fraction but with a great variability in texture and specific surface area where the amount sorbed in this phase varied between 34 and 42%.³² The slope of the linear equation is considered as the sorption rate during the slow phase of the reaction.^{32,33} The slopes were $2.00 (\pm 0.041)$ and $0.712 (\pm 0.037)$ for PN and COLL soil, respectively.

A broad range of R^2 values (0.27 to 0.99) was reported when this model was applied to describe the behavior of imidacloprid and diuron in eight different soils.³³ The lower R^2 (0.27–0.72) corresponded to the higher extent of surface coverage (β), this effect being the most pronounced for imidacloprid, with percentages sorbed at the initial phase $>87\%$. The Elovich equation, according to the theoretical analysis carried out by Rudzinski and Pancsyk,⁴⁹ must be applied only in cases of strongly heterogeneous surfaces. These authors emphasize the inapplicability at low surface coverage produced at short adsorption times. Furthermore, they conclude that deviation at higher coverage would be due to the fact that the Elovich equation neglects the effects of the simultaneously occurring desorption. Given the high organic matter content in PN soil and the moderate sorption on COLL soil, a very high coverage cannot be expected. In addition, low surface coverage at short adsorption times would not be expected according to the initial rate observed in both soils. An appropriate fitting of data of humic acid and humin fractions from PN soil was also found. According to TOC contents in both sorbents (humic acid 49%

and humin 4.5%), the initial rate constant α was $\cong 11.2$ times higher for humic acid compared to that observed for humin (2406 ± 47 and $214 \pm 55 \mu\text{g g}^{-1} \text{min}^{-1}$, respectively), and both were 1 or 2 orders of magnitude higher than the rate obtained for the soil. Sorption rates during the slow phase of the reaction were 30.79 ± 2.21 and $8.24 \pm 0.88 (\mu\text{g g}^{-1} \text{min}^{-1})$. For humic acid, the apparent equilibrium was reached throughout the first hour of contact time; however, a very high coverage during the process cannot be expected because of the great abundance of active sites within the polymeric nature of the matrix. This fact is demonstrated for both materials through the β values, which were lower than those observed for soils.

Intraparticle Diffusion (Weber–Morris Model). The intraparticle diffusion rate constants obtained from the slope of linear gradients of the plots q_t versus $t^{1/2}$ and C values for both soils are given in Table 6. In this model, if the value of C is zero, the rate of adsorption is controlled by intraparticle diffusion for the entire adsorption period. However, data found in the literature for different sorbent–solute systems show multilinearity, and plots do not pass through the origin.^{28,29,31,33} Therefore, adsorption proceeds via a more complex mechanism consisting of both surface adsorption and intraparticle transport within the pores. The intercept is related to the extent of the boundary layer effect, namely, the diffusion of solute molecules through the solution to the external surface of the adsorbent. The second and third steps describe the gradual adsorption stage, where intraparticle diffusion through macropores and micropores is rate limiting.^{28,29,31}

The application of this model on both soils gave as a result two different behaviors (Figure 7). A two-linear plot with a

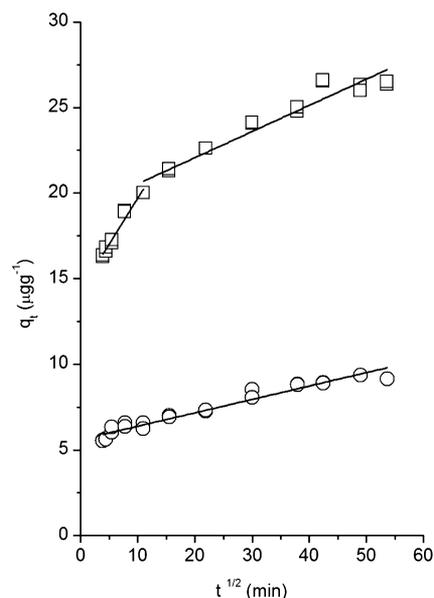


Figure 7. Intraparticle diffusion plot for atrazine sorption on volcanic ash-derived soils: (□) PN and (○) COLL.

clear change of slope was obtained for PN soil; therefore, two pore diffusion constant rates $k_{\text{int}1}$ and $k_{\text{int}2}$ were calculated. The regression estimates of the first linear segment had an intercept value different from zero; consequently, pore diffusion was not the step controlling the overall rate of mass transfer at the beginning of sorption process. For COLL soil, a single linear plot was obtained ($R^2 = 0.96$, P value <0.05), with a lower rate compared to that of the second phase for PN soil. From the

data, we can deduce that pore diffusion is more significant for Ultisol and that different mechanisms are involved in both soils.

Chemical nonequilibrium and rate-limited diffusive mass transfer are considered as the mechanisms involved in sorption-related nonequilibrium.⁵⁰ The presence of instantaneous equilibrium for both soils allows discarding a rate-limited specific interaction between atrazine and soils. Rate-limited diffusive mass transfer involves film diffusion, retarded intraparticle diffusion and intrasorbent diffusion. All of these mechanisms could be present because of the high and intermediate organic matter content in PN and COLL soil, respectively, and the dominant character of kaolinite in the inorganic matrix of COLL soil. Retarded intraparticle diffusion involves the aqueous phase diffusion of solute within pores of microporous particles mediated by retardation resulting from instantaneous sorption to pore walls; therefore, sorption occurs inside the particles.⁵⁰ Sorption of atrazine on kaolinite has been described as a slow process with no significant detection for the first 24-h contact time reaching equilibrium after 48 h.¹⁵ Retarded intraparticle diffusion of atrazine could be originated in the well-packed structure of this mineral. The contribution of organic matter in the rate-limited phase cannot be ignored in any of the two soils. Intraorganic matter diffusion has been established as the predominant rate-limiting mechanism for sorption of hydrophobic organic chemicals,⁵⁰ and the neutral form of atrazine can also exhibit a similar nonequilibrium sorption behavior. The experiments carried out with humic acid and humin fractions obtained from PN soil allowed us to establish that instantaneous equilibrium and rate-limited steps were present on both materials (Figure 8). For humin, a slow

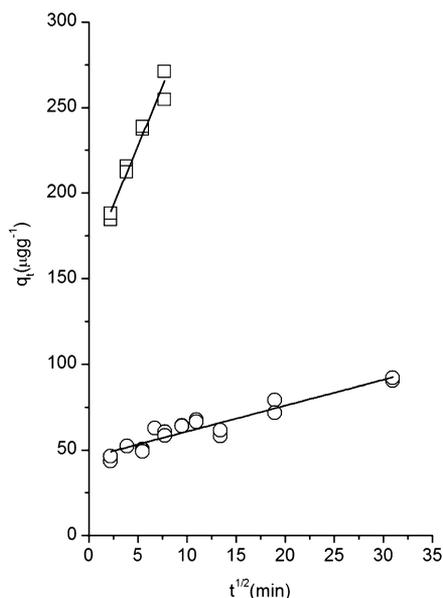


Figure 8. Intraparticle diffusion plot for atrazine sorption on humic acid and humin fractions from PN soil: (□) humic acid and (○) humin.

sorption without attainment of equilibrium was observed through 16 h, whereas for humic acid the final equilibrium was obtained within the first hour. The constant rate was 10 times greater for humic acid (13.86 ± 1.05 and $1.51 \pm 0.13 \mu\text{g g}^{-1} \text{min}^{1/2}$ for humic acid and humin, respectively). Given the TOC content of humic acid and humin, the presence of the boundary layer effect and intra sorbent diffusion for the first

one and retarded intraparticle diffusion for the second one can be suggested as the principal rate-limiting mechanisms. This fact could explain the two phases found in PN soil behavior, especially if the high OM content is taken into account. The first one could represent the more accessible OM domain, and the second one the more complex association between OM and mineral constituents, where a more intensive predominance of retarded intraparticle diffusion would be present.

Two-Site Nonequilibrium Model (TSNE). The TSNE model is based on a bicontinuum first-order mass transfer model, where S_1 is the sorbed-phase concentration in the instantaneous domain, and S_2 is the sorbed-phase concentration in the rate-limited domain. In this model, the first-order desorption rate coefficient k_2 (from Type 2 sites) is interpreted in terms of retarded intraparticle diffusion and intraorganic matter diffusion. It combines factors that control mass transfer such as the diffusion coefficient, molecular size, and molecular weight of the solute and the shape, tortuosity, and diffusion path length characterizing the sorbent.^{30,50}

This model was applied both for soils and the two fractions of PN soil. The kinetic parameters are shown in Table 6, and time-dependent sorption of atrazine on both soils is shown in Figure 9. Data from all sorbents fitted well to the TSNE model,

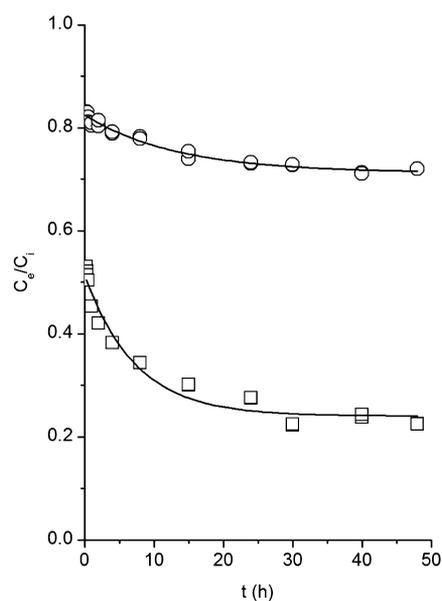


Figure 9. Two-site nonequilibrium model (TSNE) plot for atrazine sorption on volcanic ash-derived soils: (□) PN and (○) COLL.

with an $R^2 > 0.94$ (P value < 0.05) except for humin with 0.87. The predicted K values in all cases agree well with the experimental ones, presenting a low SE. Two kinds of sites were clearly defined for all sorbents agreeing with results obtained for the Elovich and Weber Morris models. The TSNE model has been employed to study the atrazine kinetic behavior in carbonatic and noncarbonatic soils. The presence of two sites was established except for one of them where sorption was better described through a one-site nonequilibrium model.³⁰

The different compositions of each matrix and the contribution of organic and inorganic components in the rate-limiting step could be expressed through the magnitude of the parameters k_2 and F .

The k_2 value for humic acid was 1 order of magnitude larger than that observed for the humin fraction, where the most

stable organic matter is associated with the mineral matrix without a polymeric type nature, as is described for humic acid. We can conclude that a very fast rate-limiting mechanism where the boundary layer effect and intrasorbent diffusion is present in humic acid and that this mechanism could explain the faster but brief phase observed at the beginning of the sorption process on PN soil. Several authors identify free, intra-aggregate and organo-mineral fractions through fractionation procedures of soil organic matter.⁵¹ The behavior observed in PN soil can be associated with the presence of organic matter intra-aggregate as well as organo-mineral fraction, the last one being responsible of the second rate-limited phase. Consequently, from a practical point of view we can hypothesize that the low k_2 value for this soil would represent the total rate-limited process, with a greater contribution of the intraparticle diffusion process inside the organo-mineral complex, with a slow rate. This behavior is consistent with that observed for a soil rich in organic matter, which had the lowest k_2 value.³⁰ However, the humin fraction could be regarded as a model soil because of the association between the mineral matrix, constituted by allophane, Fe and Al oxides, and the residual organic matter. Kinetic behavior observed for this sorbent can be considered as representative of the intraparticle diffusion phase discussed above. A different situation was observed for COLL soil. The lower organic matter content and the predominance of a nonexpanding mineral, although with a likely influence on the atrazine sorption process, would present a mechanism dominated by retarded intraparticle diffusion, explaining the low k_2 value with an order of magnitude similar to that observed for PN soil and its humin fraction.

Humic acid presented a fraction of the total sorption in the Type 1 region (F) higher than that observed in the humin fraction but with the same order of magnitude (56–40). A singular effect is observed for soils, both presenting low and similar F values and with values being specifically low for PN soil. In spite of the great sorbed amounts observed in the initial stage of the sorption process, the fast and brief phase found at the beginning of the sorption process could be estimated as belonging to the initial external mass transfer from the bulk solution to the sorbent surface (boundary layer effect) besides intrasorbent diffusion being highly significant for PN soil.

In this research, the atrazine binding capacity of Chilean agricultural variable charge soils has been assessed. Sorption was clearly related to the organic matter content of soils, and the relevance of humic acid and humin from Andisol and Ultisol soils was deduced both from isotherm and kinetics experiments. Sorption of atrazine was controlled by instantaneous equilibrium followed by a time-dependent phase related to the physical properties of the soil matrix. For the soil representative of the Andisol order, two rate-limited phases were established, the first one attributed to the more accessible organic matter domain and the second one related to the slow diffusion presented inside the complex association between organic matter and mineral constituents. For Ultisols, only one rate-limited phase was found, and the physical contribution of the principal mineral constituent to the slow and progressive sorption was hypothesized.

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Notes

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