



Sorption and desorption of atrazine on soils: The effect of different soil fractions

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ABSTRACT

The study of atrazine (AT) sorption and desorption was carried out, employing three Brazilian soils (Typic Acrudox, Typic Argiudoll and Oxic Argiudoll), using horizons A and B, as well as their clay fractions – natural clay, clay after H₂O₂ treatment, clay after iron removal and after treatment to concentrate iron oxides. A contact time of 12 h was defined as adequate for sorption studies. Sorption and desorption curves were adjusted by the Freundlich equation, and satisfactory linear responses were observed, between 0.8332 and 0.9998 for the sorption process. Multiple regression analyses were performed considering the mineralogy, organic carbon content, specific surface area and texture of the soils, and the Freundlich parameter K_f . The principal influence for AT sorption was attributed to organic carbon content and physical bonding on quartz for soil samples. Positive correlation with goethite was observed for clay fractions. The K_f values for sorption ($K_{f(S)}$) obtained for soil samples were between 0.60 and 3.9, and for clay fractions were between 1.90 and 5.30, suggesting an important role of the mineral phase in the sorption of AT. Environmental risks of groundwater contamination were evaluated using the partition coefficient normalized by the soil organic carbon content (K_{oc}), hysteresis index (HI), groundwater ubiquity score (GUS) and leachability index (LIX). Both horizons for the three soils presented leaching potential for AT based on GUS and LIX parameters.

1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has been used as a pre- and postemergence herbicide for weed control in cultures of corn, sorghum, sugar cane, maize, wheat and rice (Xu et al., 2011). Atrazine (AT) is among the herbicides most widely employed with high persistence in soils, and has some physicochemical characteristics that provide high potential for runoff and leaching. AT has an octanol–water partitioning coefficient log (log K_{ow}) of 2.70, water solubility of 35 mg L⁻¹ (20 °C), p K_a of 1.7 and half-life in soil of 66 days (Singh et al., 2014). The persistence of AT in soils, its potential for leaching and moderate water solubility can explain the frequent detection of AT in groundwater in the United States (Toccalino et al., 2014) and in Europe (Vonberg et al., 2014), as well as in Brazilian waters (Montagner et al., 2014).

There are a lot of environmental impacts caused by AT, it being harmful for fish (Xu et al., 2011), amphibians (Rohr and McCoy, 2010), algae and plants (Graymore et al., 2001). The toxic effects in animals and humans caused by AT have been presented by Rouimi et al. (2012), and AT presents carcinogenic potential (Mudhoo and Garg, 2011).

Because of the contamination of waters and the toxicity of AT, its use was prohibited in the European Union in 2004 (Prado et al., 2014), but it is still used in the United States and in many other countries. AT and the degradation product 2-hydroxyatrazine have been detected in soils, even 22 years after application (Jablonowski et al., 2009), suggesting high persistence in soils, and consequently a high risk of groundwater contamination due to gradual desorption. Also, AT was detected in groundwater even 20 years after its prohibition in Germany (Vonberg et al., 2014).

Based on the environmental impacts, some recent investigations have been dedicated to evaluating the behavior and fate of AT in soils (Prado et al., 2014; Singh et al., 2014), especially the sorption and desorption processes between soil and AT which influence its availability for weeds and mobility in soils, and also the role of soil particles, to better understand the binding mechanisms involved (Laird et al., 1994; Polati et al., 2006). The main soil characteristics associated with sorption and desorption are texture, mineralogy and total organic carbon (TOC) content (Wang and Keller, 2009; Huang et al., 2015), which involve physical and chemical processes. Clay minerals and organic matter have a key role in the process, and understanding the

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Table 1
Some soil characteristics and the content of hematite, goethite, kaolinite, and gibbsite in the Clay fraction. Results in g kg^{-1} .

Soils	Results for soils			Results for Clay fraction			
	Clay ^a	Silt ^a	Sand ^a	Hematite ^{a,b}	Goethite ^{a,b}	Kaolinite ^{b,c}	Gibbsite ^{b,c}
Typic Acrudox – HA	704	236	60	199	ND ^d	526	168
Typic Acrudox – HB	831	122	47	231	ND ^d	540	177
Typic Argiudoll – HA	439	434	126	55	21.9	428	ND ^d
Typic Argiudoll – HB	655	228	117	99	12.6	457	ND ^d
Oxic Argiudoll – HA	561	392	47	77	18.5	565	486
Oxic Argiudoll – HB	674	284	42	112	16.8	556	520

^a Data from Hanke et al. (2015).

^b Results for the clay fraction.

^c Results obtained in the present work.

^d Not detected.

interaction between AT and soils may prevent water contamination. Humic acid, bentonite and montmorillonite interact with AT by hydrogen bonding and protonation, whereas the surface of kaolinite contributes to AT hydrolysis (Davies and Jabeen, 2003). Therefore, studies involving bulk soil and its respective fractions with AT are of particular importance. Wang and Keller (2009) investigated the sorption/desorption behavior of AT using four soils and their clay, silt and sand fractions. The authors concluded that the clay fraction was the most significant in AT retention, and a hysteresis effect was observed, owing to the higher TOC content and microporous structure. Dick et al. (2010) carried out a study using four soil samples, and the AT sorption behavior was verified in the presence and absence of iron oxide and organic matter fractions. Similar behavior was observed before and after the removal of iron oxide, suggesting that this fraction is not relevant for AT retention. On the other hand, the inorganic fraction presented AT sorption between 8 and 44% after iron oxide removal, while AT sorption by organic matter was between 56 and 85%. Huang et al. (2015) studied AT sorption in bulk soil and clay, silt and sand fractions using six different soil samples. The most important parameter in AT retention for bulk soil was TOC. However, the clay fraction showed the highest AT sorption and lowest AT desorption in some samples. On the other hand, the sand fraction showed the lowest AT sorption and highest AT desorption. Based on sorption and desorption studies and deviations between the respective isotherms (hysteresis effect), it is possible to predict the groundwater contamination risk, by using groundwater ubiquity score (GUS) (Gustafson, 1989) and leachability index (LIX) (Spadotto, 2002) parameters, which provide information about leaching potential.

Because of the great diversity of soils, sorption studies involving samples with different characteristics and their clay fractions are of prime importance, in order to better understand AT behavior and the fate of AT in the environment. Therefore, the main objectives of the present work were: *i*) to investigate AT sorption/desorption with three different soils, from horizons A and B, using the batch equilibration technique, *ii*) to evaluate the role of the clay fractions in the AT sorption/desorption process, *iii*) to evaluate the hysteresis index and GUS and LIX parameters, in order to estimate the possibility of AT leaching, based on sorption/desorption data. Although AT sorption/desorption processes have been extensively studied in soil samples, in the present work, not only the contribution of Brazilian soils of different nature but also that of their respective fractions was evaluated. The results presented here contribute to better understanding the importance of clay fractions and, especially, to knowledge of the risks of groundwater contamination.

2. Experimental

2.1. Materials and reagents

The AT standard (98.9%) was supplied by Sigma-Aldrich Chemie

GmbH (Steinheim, Germany). AT stock solution at 1.00 mg mL^{-1} was prepared in methanol, and stored at -18°C . Working standard solution at $5.00 \mu\text{g mL}^{-1}$ was prepared in 0.01 mol L^{-1} CaCl_2 by dilution of the stock solution. Acetonitrile (HPLC grade) was supplied by Carlo Erba (Rodano, Italy), and employed for preparation of the mobile phase. The water used in all the experiments was obtained by a reverse osmosis system, and purified by using Millipore Simplicity UV equipment (Molsheim, France), to provide ultrapure water (resistivity of $18 \text{ M}\Omega \text{ cm}$).

2.2. Soil samples

Three soil samples from horizons A and B (HA and HB, respectively) were selected for this study, classified as Typic Acrudox, Typic Argiudoll and Oxic Argiudoll according to Soil Taxonomy. Based on the Köppen classification, the region climate is type Cfa, a humid subtropical climate with rain in all seasons and the possibility of dry periods in the winter. Typic Acrudox was collected from Cândido Mota, SP, Brazil, Typic Argiudoll from Maravilha, Londrina, PR, Brazil and Oxic Argiudoll from Guaravera, Londrina, PR, Brazil. The depth for HA was 0–10 cm for the three soils, while for HB the following depths were employed: 83–90 cm (Typic Acrudox), 57–64 cm (Typic Argiudoll) and 70–77 cm (Oxic Argiudoll). The soils were air-dried, and the fraction $< 2 \text{ mm}$ was ground using a pestle and mortar to pass through a 0.20 mm sieve. These soil samples were characterized by specific surface area (SSA) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Part of the soil samples was used for separation of the clay fractions. Some characteristics of these soils are the presence of mica, chlorite and smectite in Typic Argiudoll samples (HA and HB), and their absence in Typic Acrudox and Oxic Argiudoll. Complete characterization of these soil samples was previously presented by Hanke et al. (2015), and some of the main results are shown in Table 1.

2.3. Clay fractions

A mass of 20 g of each soil sample ($< 2.00 \text{ mm}$) was mixed with 50 mL of 0.20 mol L^{-1} NaOH solution and kept under orbital stirring for 8 h at 200 rpm. The sand fraction was separated from the soil matrix suspension using a $53 \mu\text{m}$ sieve. The silt and clay fractions were transferred to 1.0 L glass cylinders and separated by sedimentation. The sample was dried in an oven at 40°C and identified as Clay. The whole procedure was repeated until approximately 30 g was obtained. A fraction of the sample was reserved for the sorption/desorption studies, and the remaining part was employed for elimination of organic matter.

The organic matter in the Clay fraction was eliminated by adding H_2O_2 (10% w/v) in approximately 20 g of each sample (Jackson, 1979; Melo et al., 2009). The sample was named Clay H_2O_2 . Part of the sample was reserved for sorption/desorption studies, and the other part was employed for obtaining the mineral fractions.

Afterwards, a procedure was performed to remove iron oxide from

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