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Transport, sorption and degradation of atrazine in two clay soils from Mexico: Andosol and Vertisol

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ABSTRACT

Although atrazine has been banned in the European Union, it is still one of the most widely used herbicides in the world. It is has been detected in surface and groundwater and has been shown to be associated with major human health problems. Atrazine fate in the environment, e.g. sorption, leaching and degradation depends, *inter alia*, on soil characteristics. Independent static and dynamic experiments were conducted to identify and uncouple the processes governing the fate of atrazine. Two agricultural soils from Mexico with contrasting characteristics in terms of organic matter content and degree of decomposition as well as clay types were selected. Soil organic matter was the main sorbent for atrazine, followed by montmorillonite clays in the Vertisol, and iron oxides and allophanes in the Andosol. Humic acids were predominant in the Andosol's organic matter and favored atrazine sorption, compared to more recalcitrant organic matter such as humin fractions in the Vertisol. Atrazine mobility was enhanced because of the occurrence of preferential flow in the upper layer of the Vertisol and because of the formation of mobile complexes between dissolved organic carbon and atrazine in the Andosol. Our detailed soil characterization and the independent sorption, degradation and transfer experiments allowed identifying the main processes affecting atrazine's fate in the two contrasting soils: In the Vertisol, preferential flow was enhanced because of the lower affinity of the soil's organic matter for atrazine compared to the Andosol. The application of atrazine to Vertisol soils poses a higher risk for groundwater contamination than its application to Andosols.

1. Introduction

Atrazine is one of the most widely used herbicides over the world; however, it may also pose risks to the environment and human health. The herbicide has been detected in surface and ground water in the United States and Mexico (Abdelhafid et al., 2000; Azevedo et al., 2000; Hernández and Hansen, 2011; Lerch et al., 2011). The amounts of atrazine detected in water bodies were directly correlated to the high rates of application and conventional agricultural practices (Mudhoo and Garg, 2011). In the United States, for example, percentages of atrazine and its metabolites in water bodies adjacent to agricultural fields were equivalent to 1 to 3% of the applied atrazine amounts (Graymore et al., 2001). Understanding the processes that govern atrazine's fate will help to better handle the herbicide and avoid the application of excessive rates. This is important given the toxic effects of atrazine in humans, which may be acute, such as severe irritation of eyes and skin, or chronic, such as reproductive disorders. The use of atrazine was banned in the European Community in 2004; nevertheless, in the United States, it is the most widely used herbicide for weed control, and in countries like Mexico, it is still used without any control.

The persistence and fate of atrazine are affected by various soil characteristics such as clay content and type, content of iron oxides, ionic strength of the soil solution (Ureña-Amate et al., 2005), soil pH (McGlamery and Slife, 1996), particles' specific surface areas (Tang et al., 1998), soil porous structure (Li et al., 1996; Wang and Keller, 2008), and soil organic matter content (Francioso et al., 1992; Graber and Borisover, 1998; Seol and Lee, 2000). According to several authors, the latter is the most important factor (Barriuso et al., 1992; Dousset et al., 1994; Nicholls, 1988; Payá-Pérez et al., 1992; Shea, 1989). The addition of organic amendments or nutrients may modify the pH of soils, which can alter the charge of some soil constituents of variable charge (organic matter and allophanes) as well as the speciation of organic pollutants such as atrazine. Kulikova and Perminova (2002) reported that atrazine sorption to soil humic substances was closely related to the

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aromaticity of soil organic matter. The quality of the soil organic matter plays an important role in the sorption equilibrium processes and hysteresis (Kempf and Brusseau, 2009). In addition to the organic fraction of soil, it is documented that some pesticides can be sorbed to clays (Spark and Swift, 2002). Bailey and White (1970) showed that the sorption capacity for herbicides to clays follows the order montmorillonite > ilite > kaolinite.

In the eighties, studies showed that microbial degradation is the main mechanism for the decrease of atrazine concentrations in the environment (Cook, 1987). Other authors considered atrazine a recalcitrant compound (Kaufman and Kearney, 1970). Half-lives of atrazine in soils are ranging from 53 to 113 days (Burkhard and Guth, 1981). One reason for the differences between the reported half-lives lies in the different characteristics of soils, notably in their ability to sorb the herbicide, which causes the pollutant to be less available for microorganisms responsible for biodegradation. Furthermore, in agricultural soils, tillage affects the structure and degree of connectivity of macropores, particularly at the surface (Prado et al., 2009). Previous studies reported the rapid transport of various solutes due to rapid flow into connected macropores: nitrate (Prado et al., 2006), organic compounds (Wehrer and Totsche, 2008), metals (Roulier et al., 2008), pesticides (Kahl et al., 2008), and colloids (Burkhardt et al., 2008). Preferential flow reduces the residence time and the contact surface of a solute when it passes through the soil, thereby decreasing the buffering capacity of the soil. Therefore, the analysis of processes involved in atrazine fate should also consider the physical characteristics of the medium through which it is transported.

Processes involved in atrazine fate through soil are usually investigated in independent experiments: these experiments provide basic relevant information for the understanding of the herbicide's mobility through soil. However, processes are coupled: for example, when the compounds are adsorbed, transport and biodegradation processes become slower leading to the accumulation of the compound in the upper layers of the soil, reducing the risk of leaching to the groundwater but increasing the risk of direct contact with people, transport of particles in the air and increasing the compound's half-life. Evaluating the mobility, adsorption and degradation processes during dynamic experiments in intact soil columns provides more realistic estimates of degradation and sorption rates than those measured by static incubation and batch experiments. Factors such as soil:solution ratio and contact between soil matrix, microorganisms and the herbicide are closer to field conditions.

The objective of this study was to investigate atrazine transport, degradation and sorption processes in two soils, Andosols and Vertisols. We chose two soils important for agriculture in Mexico with contrasting characteristics relevant for the fate of atrazine, namely content and degree of decomposition of organic matter (OM), and content and type of dominant clays. The above processes were evaluated by independent static experiments, and the fate of the herbicide was determined dynamically with intact soil columns. The set of results obtained allowed a realistic analysis of the risk of groundwater contamination under the two soil types.

2. Materials and methods

2.1. The sites

Atrazine is an herbicide widely used for corn production. The herbicide is used in more than 70 countries, and Mexico is one of the top five corn-producing countries in the world. In Mexico, 55,000 t of pesticides are applied annually (INE, 2000), of which 28.7% are herbicides. Atrazine constitutes the 3rd herbicide applied (12.8%) in Mexico. Atrazine 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine is a white crystalline solid with a pKa of 1.7 (at 20 °C), vapor pressure of 2.9×10^{-7} mm Hg at 298 °K and a water solubility of 33 ppm at 20 °C and pH 7 (Tomlin, 1997).

2.1.1. Andosol

The Andosol studied was sampled in the Valle de Bravo watershed, which is part of the Cutzamala system and is located 300 km west of Mexico City. The Cutzamala system provides 16 $m^3 s^{-1}$ water (35% of total water usage of Mexico City) to Mexico City's water supply system. The main land use in the Valle de Bravo watershed is agriculture, and its outlet is an artificial lake, which is the main reservoir within the Cutzamala system. One sub-catchment of Valle de Bravo, La Loma, has been the site of numerous studies on runoff, erosion (Viramontes et al., 2008), and water and agrochemical movement in the vadose zone (Duwig et al., 2008; Prado et al., 2006, 2011). This sub-catchment is representative of the soil types and land-use in the region. The dominant soil type in La Loma was classified as Pachic Andosol (FAO-ISRIC and ISSS, 1998), and its main mineralogical, physical and chemical characteristics were determined by Prado et al. (2007). The soil studied here was sampled in a 3-ha plot with 28% slope (19°16′48.6″ North and 99°58′13.7″ West) in La Loma. The main crop of the plot was non-irrigated maize, to which atrazine was applied at a total annual rate of 1 kg a.i. ha^{-1} for weed control.

2.1.2. Vertisol

The Vertisol studied was sampled in the Bajío region, which is located 300 km north of Mexico City and where 35% of the cereals consumed in Mexico are produced (Sagarpa, 2010). The experimental plot is situated in the Penjamo Municipality, in the Negrete Province (Guanajuato State) (20°18′58.9″ North and 101°46′59.5″ West). The plot has 16 ha and 0.5% slope, and was cultivated with sorghum and wheat under irrigation. Atrazine was applied at an annual application rate of 1.3 kg a.i. ha^{-1}. The soil is classified as Vertisol (FAO-ISRIC and ISSS, 1998).

Table 1 presents the main physical and chemical characteristics of both soils, and Fig. 1 shows the locations of the studied soils in Mexico.

2.2. Soil samples

At both sites, intact soil samples and bulk soil samples for chemical and mineralogical analyses were collected at two depths, 25 cm and 85 cm for the Andosol, and 20 and 90 cm for the Vertisol, respectively. The samples nearest to the soil surface were taken in the plowed zone, thus, the original soil structure was modified. The samples at 85/90 cm depth were located at the base of the rootzone, where the soil structure was intact and only affected by roots and soil fauna. At the time of collecting the soil columns and the bulk soil samples the plots at both sites were bare and recently plowed.

The intact soil cores used for the displacement experiments were of 8.5 cm internal diameter and 15 cm length, and were collected in triplicate from each soil depth. Soil cores of about 9 cm diameter and 20 cm length were hand sculpted. These were then properly cut with a metallic ring of 8.5 cm internal diameter and cut off the ground. The ring was removed, and a PVC tube of 9 cm internal diameter and 15 length was placed around the soil monolith. The space between the soil and the tube was filled with chemically pure paraffin (Merck, 107157) heated at 60 °C. The columns were carefully transported to the laboratory and kept at 4 °C before the experiments. One column (25 cm Andosol, A2-3) was treated with chloroform during storage at 4 °C to avoid development of biofilms.

2.3. Sorption studies

The fresh soil samples were sieved (<2 mm) and stored at 4 °C until the start of the experiments and analyses of soil properties. Standard batch experiments were conducted to obtain atrazine sorption and one-step desorption isotherms. The isotherms were determined at five atrazine concentrations, 25, 50, 100, 150 and 200% of the total concentration applied at each site, namely 6.8 μg g^{-1} for the Andosol and 4.5 μg g^{-1} for the Vertisol. The atrazine solutions were prepared from atrazine standards (Chem Service, West Chester, USA, 99.8% purity). A