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Mobility of atrazine in soils of a wastewater irrigated maize field

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A R T I C L E I N F O

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A B S T R A C T

The behavior of atrazine has been studied mainly in laboratory experiments, seldom directly in the field, and even less in agricultural plots irrigated with wastewater. In the Mezquital Valley, central Mexico, maize (*Zea mays* L.) crops have been irrigated with untreated municipal wastewater for more than 100 years. The herbicide atrazine has been applied to maize for weed control for 20 years. The research objectives of this study were: (i) to monitor the persistence and migration of atrazine and its main metabolites (hydroxyatrazine (HyA) and deethylatrazine (DEA)) in a wastewater irrigated maize field along a cropping cycle; (ii) to assess their sorption behavior in batch experiments; and (iii) to determine the degradation of atrazine under field conditions. Soil samples (0–15 and 25–40 cm) were collected before and after three irrigation events within a 2 ha plot. Additionally,percolation water was collected below the rooting zone and down to 5.0 m depth. Atrazine degradation was studied by calculating dissipation rates considering field data. Atrazine was detected in soil and percolation water during the first two irrigation events after application. HyA was detected only in the soil samples from the first and third irrigation events (~0.08 mg kg^{-1}) while DEA was found only in the percolation water of the second irrigation event (0.03 mg L^{-1}) and also in the groundwater (~0.02 mg L^{-1}) from a deep piezometer. Batch experiments showed, that the soil has a higher affinity for atrazine (Kd = 5 L kg^{-1}) than for HyA and DEA (Kd = 1.3 L kg^{-1}). The atrazine half-life value was 16 days under field conditions. The moderate filter capacity of the soil and the relatively fast degradation rates seem to prevent the transport of atrazine and its metabolites into the unsaturated zone. Nevertheless it is recommended to establish a monitoring program with more narrow time intervals during the first days after atrazine application. We concluded that the large wastewater volume applied for irrigation explains themobility of these compounds.

1. Introduction

In many countries irrigation is increasingly done with treated or even untreated wastewater to optimize the use of short water resources (Jiménez and Asano, 2008). This is the case in China (14.8 Mm^3 d^{-1}), Mexico (14.3 Mm^3 d^{-1}), United States of America (7.6 Mm^3 d^{-1}), Egypt (1.9 Mm^3 d^{-1}) and Saudi Arabia (1.8 Mm^3 d^{-1}), among many other countries. In the Mezquital Valley, southwest of Hidalgo State in central Mexico, maize (*Zea mays* L.) and alfalfa (*Medicago sativa* L.) crops have been irrigated by overflow using untreated municipal wastewater for more than a century, and atrazine has been applied to maize for weed control for about 20 years.

In over flow irrigation a large water volume is applied to a field, which favors quick transport of fertilizers and pesticides into deep soil layers (Nelson et al., 2000). Additionally, wastewater contains large concentrations of dissolved organic matter (DOM), which may form soluble complexes with atrazine reducing its sorption and increasing the herbicide solubility in the soil solution. DOM also competes for sorption sites, and the alkaline pH of the wastewater as well as its ionic compounds may affect the sorption of atrazine (Müller et al., 2007; Xia et al., 2015, 2013). It could therefore be expected that atrazine is more mobile in soil irrigated with wastewater. On the other hand, irrigation with wastewater does not only moisten the soil but also adds nutrients and increases the microbial activity (Cook, 1987; Friedel et al., 2000). Atrazine degradation could be favored under these conditions, although it has also been reported that large nitrogen availability in fields fertilized with mineral fertilizer inhibits atrazine degradation, since bacteria prefer to use more labile N and C sources rather than decompose the atrazine (Guillén-Garcés et al., 2007).

Atrazine (*6-chloro-N^2-etyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine*) is a systemic selective herbicide, which has been used since the 1950s to control broad leaf herbs in agriculture. Currently, it is one of the most popular herbicides used to protect crops like maize, sorghum (*Sorghum spp*) and sugar cane (*Saccharum officinarum*) (LeBaron et al., 2008). In

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the European Union its use has been prohibited since 2004 (2004/248/EC), because several studies evidenced its potential to pollute the groundwater (Mudhoo and Garg, 2011; Panshin et al., 2000).

This compound is highly persistent in the environment; its reported half-life ranges between 10 and 5824 days (Hansen et al., 2013). Its adsorption to soil components is moderate with K_d values between 0.4–3.1 L kg^{-1} (Laird et al., 1994; Moreau and Mouvet, 1998; Müller et al., 2012). Therefore, and due to its wide use, atrazine represents a risk for groundwater contamination. Reported concentrations in groundwater ranged formerly from 0.0002 to 0.006 mg L^{-1} (Domagalski and Dubrovsky, 1992; Sadeghi and Isensee, 1994), however this trend has changed, since in recent studies the concentration of atrazine in groundwater has decreased to values between 0.000003 to 0.00002 mg L^{-1} (Toccalino et al., 2014). Some health problems related to the presence of triazines in drinking water include acute effects like severe eye irritation, abdominal pain and diarrhea, or chronic effects as reproductive harm and fetal growth. For this reason the maximum permissible limits for atrazine in drinking water in the United States of America is 0.003 mg L^{-1} (USEPA, 2003), while in the European Community it is of 0.0001 mg L^{-1} (European Parliament, 1998).

The persistence of atrazine and its mobility in soil are key factors influencing its potential to contaminate aquifers. The sorption behavior of atrazine is determined by its chemical and structural properties (Dragun, 1998): it is a weak base; therefore if the pH of the soil solution is close to its $pK_a = 1.7$, atrazine protonates even further increasing its solubility. At sites receiving abundant rain or heavy irrigation, the risk of atrazine transport into groundwater or surface water is particularly large (Mobaser et al., 2012). The atrazine binding to organic carbon compounds in soil is well recognized and atrazine has a strong affinity to aromatic and aliphatic compounds, especially to humic acids (HA) (Dutta et al., 2015; Kulikova and Perminova, 2002). The humic substances also influence the transport, bioavailability, degradation, and accumulation of micropollutants. Although atrazine is dominantly sorbed by SOM, clay minerals also contribute substantially to atrazine sorption by soils (Laird et al., 1994), in particular smectites have a large potential for atrazine sorption due to their large surface area. According to Herwig et al. (2001), clay minerals are the most reactive inorganic constituents of soil and form the last barrier to avoid translocation of environmental chemicals by soil leachates into groundwater.

Atrazine sorption-desorption and degradation has been studied dominantly under controlled conditions in the laboratory by batch experiments (Moreau and Mouvet, 1998; Müller et al., 2012), column experiments (Dousset et al., 1995; Müller et al., 2007; Prado et al., 2014a,b) or incubation experiments (Ke-Bin et al., 2008; Mahía and Díaz-Raviña, 2007). However, very few studies have been made under field conditions (Graber et al., 1995), and even less have studied soils irrigated with wastewater (Drori et al., 2005; Müller et al., 2012). Wastewater irrigation has to be done by overflow, particularly if the effluents are untreated, since suspended particles clog the water dispersion systems as sprinklers or drippers.

The Mezquital Valley is the largest continuous area irrigated with wastewater in the world. It currently receives 52 m^3 s^{-1} of untreated sewage effluents from Mexico City to irrigate mainly alfalfa and maize. Three main soil types can be found in the Mezquital Valley: Leptosols, Phaeozems and Vertisols (Siebe et al., 2016). The Leptosols have a silt loam texture and a limited depth, less than 25 cm. The Phaeozems are loamy clay soils of medium depth (25–70 cm) and the Vertisols are generally deeper and have a clayey texture with a dominance of smectites. In general, these soils have a neutral to slightly alkaline pH and medium organic matter contents. The use of atrazine in doses of 1.5–3.5 kg ha^{-1} per crop cycle has been a common practice for the last 20 years. The objective of this investigation was to study the atrazine dynamics in a wastewater irrigated field in the Mezquital Valley. We hypothesized that the large wastewater volume applied with each irrigation, would transport the compound readily into deeper depths and out of the rooting zone where most of the bacterial activity occurs. The DOM contained in the wastewater should enhance the atrazine mobility even further so that we expected a high risk of groundwater pollution with atrazine or its metabolites. We therefore collected soil samples periodically at two depths over the field before and after three irrigation events during one maize crop cycle. We also collected soil solution and deep percolation water and determined atrazine as well as its main metabolites, namely hydroxyatrazine (HyA) and deethylatrazine (DEA). Batch experiments were conducted to establish the sorption coefficients of the herbicide and its metabolites. All the obtained results allowed evaluate the mobility of atrazine in the studied agricultural land use system.

2. Materials and methods

2.1. The study site

The Mezquital Valley is located 80 km North of Mexico City and in the southern part of the Hidalgo state. It has received the discharge of untreated wastewater (40 m^3 s^{-1}) from Mexico City mixed with the surface runoff during the rainy season (12 m^3 s^{-1}) for over a century. The reuse of wastewater for irrigation has increased significantly the maize yields from 2 t ha^{-1} to more than 10 t ha^{-1} in the last decades (Siebe et al., 2016). The large water volumes applied to the fields have led to an artificial groundwater recharge of up to 25 m^3 s^{-1} (BGS et al., 1998; Del Arenal, 1985). This aquifer supplies water to more than 700,000 inhabitants in the region (Lesser-Carrillo et al., 2011).

We selected a 2 ha plot, which has been irrigated by overflow with wastewater for more than 70 years, located in a piedmont at Tlahuelilpan, a village in the Mezquital Valley. The piedmont is formed out of layers of volcanic tuff deposits covered by alluvial material transported out of the dominantly dacitic to andesitic mountain ranges. The soil developed in this alluvium was classified as a pachic vertic Haplustoll (fine clayey, montmorillonitic, thermic) (United States Department of Agriculture and Natural Resources Conservation Service, 2010), or vertic Phaeozem (IUSS, 2006). These soils have a neutral to slightly pH, a clay content of 28% that increases with depth and medium total carbon contents (Table 1). To optimize infiltration the piedmont has been terraced, so that each plot has a slope of less than 2°, and the soil depth within the plot varies from 40 cm in the upper part to 120 cm at the edge of the terrace.

Atrazine is applied to maize to prevent competition with broad leaf herbs. It is applied at the beginning of the crop cycle, 2 days after sowing and immediately before the irrigation.

Table 1
Selected soil properties.

Depth	pH	ρ (g cm^{-3})	θ (cm^3 cm^{-3})	% Clay	%TOC	%N	TOC/N	Clay/TOC
0–15 cm	7.1	1.17	0.40	28	2.6	0.27	9.6	11
25–40 cm	7.5	1.20	0.45	40	1.4	0.14	10.0	29

ρ: soil bulk density, θ: volumetric water content, C: total carbon, N: total nitrogen, OC: organic carbon.
Note: The soil pH was measured in water using a soil:water ratio of 1:2.5. Total organic carbon (TOC) was analyzed by dry combustion using an automatic carbon analyzer (TOC, Shimadzu 5000). Bulk density was measured from intact soil cores of 104 cm^3, sampled from each studied soil depth, and dried 24 h at 105 °C to constant weigh. Soil texture was determined by the pipette method after eliminating organic matter with peroxide and dispersion of the soil with sodium hexametaphosphate.