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ScienceDirect
Chemosphere 67 (2007) 847–854
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Atrazine sorption and fate in a Ultisol from humid tropical Brazil

F.V. Correia [a,*], A. Macrae [a], L.R.G. Guilherme [b], T. Langenbach [a]

[a] *Instituto de Microbiologia, Universidade Federal do Rio de Janeiro – CCS Bloco I, Cidade Universitária, Ilha do Fundão, 21941-590 Rio de Janeiro, Brazil*
[b] *Departamento de Solos, Universidade Federal de Lavras, Lavras, Minas Gerais, Brazil*

Received 24 May 2006; received in revised form 6 November 2006; accepted 12 November 2006

Abstract

This study combined laboratory based microcosm systems as well as field experiments to evaluate the mobility of atrazine on a Ultisol under humid tropical conditions in Brazil. Results from sorption experiments fit to the Freundlich isotherm model [K_f 0.99 mg kg^{-1}/(mg l^{-1})$^{1/n}$], and indicate a low sorption capacity for atrazine in this soil and consequently large potential for movement by leaching and runoff. Microcosm systems using ^{14}C-atrazine to trace the fate of the applied herbicide, showed that 0.33% of the atrazine was volatilized, 0.25% mineralized and 6.89% was recorded in the leachate. After 60 d in the microcosms, 75% of the ^{14}C remained in the upper 5 cm soil layer indicating atrazine or its metabolites remained close to the soil surface. In field experiments, after 60 d, only 5% of the atrazine applied was recovered in the upper soil layers. In the field experiments atrazine was detected at a depth of 50 cm indicating leaching. Simulating tropical rain in field experiments resulted in 2.1% loss of atrazine in runoff of which 0.5% was adsorbed onto transported soil particles and 1.6% was in solution. Atrazine runoff was greatest two days after herbicide application and decreased 10 fold after 15 d. The use of atrazine on Ultisols, in the humid tropics, constitutes a threat to water quality, causing surface water and ground water pollution.

Keywords: Atrazine; Runoff; Leaching; Mineralization; Volatilization; Soil pollution

1. Introduction

Pesticide use in Brazil has more than doubled in the last 10 years (Sindag, 2003); which is linked to Brazil's ranking as a global leader in agricultural exports. Brazil is also home to the largest sources of fresh water globally and 25% of the planets biodiversity (Pessoa et al., 1998; Cerdeira et al., 2005). Given that herbicides are being increasingly used in Brazil and throughout the tropics and that they are not easily substituted on a large scale, then knowledge of the fate of these chemicals in tropical environments is required to minimize bioaccumulation and polluting fresh water reserves.

There have been relatively few reports on the behaviour of pesticides in soils from the humid tropics. Soil parameters such as organic matter, structure and texture have similar effects on pesticide distribution and degradation globally but specific characteristics are strongly influenced by climatic conditions and lessons learned from temperate climates cannot always be applied in the tropics (Langenbach et al., 2001). The climate in the Brazilian humid tropics is dominated by large seasonal differences in rainfall and not large differences in temperature common in temperate climes. In the Southeastern region of Brazil, the average annual temperature variation is small (about 7 °C during the year) but pluviometric indices change considerably from between 20 mm (winter) to 300 mm rain month^{-1} (summer). Pesticides are more intensively applied in the spring season, which coincides with main crop planting period, increased rainfall and high temperatures. Application at this time results in enhanced pesticide mobility through the soil, on the soil (runoff) and from the soil surface (evaporation). In this region, the summer rains are torrential, resulting in surface runoff that occurs as overland flow in

* Corresponding author. Tel.: +55 21 2562 6743; fax: +55 21 25608344.
E-mail address: fabioverissimobr@yahoo.com.br (F.V. Correia).

0045-6535/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2006.11.034

excess of infiltration (OFXIN), resulting in considerable erosion (Bertoni and Lombardi-Neto, 1993) and pesticide transport.

Atrazine (2-chlorine-4-etil-6-isopropil-1,3,5-triazin), is a herbicide that continues to be used extensively in Brazilian agriculture, specifically for corn, cotton, sorghum and sugar-cane. It is one of the largest pollutants of groundwater in many countries (Dörfler et al., 1997) and was selected for study because of its widespread use. Here we report on an approach which combined a microcosm mass balance study with a field experiment in order to describe the fate of Atrazine in a Ultisol. Runoff was measured in an area of known slope, on tilled soils and in the dry season. Working in the dry season facilitated simulating torrential rain fall common to the season in which atrazine is applied.

Given the widespread and increasing use of pesticides in Brazil, case studies for a number of soil and pesticides are required to evaluate the risk of polluting water reserves. Case studies provide the data required to change agricultural policy and practice in order to limit pollution. Here we present a novel case study combining for the first time a mass balance and runoff experiment on how atrazine moved on and through a Brazilian Ultisol.

2. Materials and methods

Given the complex interactions and processes involved in following the movement of atrazine through soil, three approaches were chosen. Firstly physical, chemical and mineralogical attributes were evaluated together with the sorption capacity of the top soil (layer 0–10 cm) using the Freundlich isotherm (Schiavon et al., 1990). Secondly a mass balance study using ^{14}C-atrazine in microcosms of undisturbed soil to measure volatilization, mineralization, leaching and sorption down the soil profile. Thirdly a runoff experiment in the field was conducted under simulated high rainfall conditions and atrazine and it metabolites were measured in soil layers to 50 cm depth over a 90 d period.

2.1. Soil

A Ultisol soil known as Red-Yellow Argisol in the Brazilian soil classification system was selected as an important and representative soil type for this work (Camargo et al., 1987). The soil was sampled from the Department of *Fitotecnia* experimental area, Universidade Federal Rural do Rio de Janeiro, Seropédica (RJ); an area of 800 m^2, with 12% slope (22°49′ south latitude, 43°38′ longitude). Soil texture was evaluated using the pipette method (Day, 1965) and classified according to USDA (1975). The soil characteristics were: 66% sand; 10% silt; 24% clay; 28 g kg^{-1} organic matter and pH 5.7. Soil was adjusted to pH 6.5 by liming and fertilized in accordance with the recommended conventional agricultural practices for maize (EMBRAPA, 1997).

2.2. Laboratory experiments

2.2.1. Sorption

Sorption experiments were conducted in triplicate and isotherms were measured using the standard batch equilibration method (OECD, 2000). Soil was sieved (<2 mm) and 2 g added to 30 ml centrifuge tubes. Twenty milliliter solutions of atrazine at different concentrations (0.5, 1.0, 2.5, 5.0 and 10 mg l^{-1}) were prepared with the commercial product Gesaprim 500 (500 g l^{-1} of 2-chloro-4-ethylamino-6-isopropylamino-s-triazine) in 0.01 M $CaCl_2 \cdot 2H_2O$. The samples were agitated on a rotary shaker for 24 h at 20 ± 1 °C in the dark to achieve equilibrium. Tubes were centrifuged for 20 min at 756 g and the supernatant liquid collected. Blanks without soil, prepared in the same way, showed no sorption of Gesaprim 500 on the centrifuge tube wall. A pilot kinetic study showed that 80–90% of sorption equilibrium was reached after 24 h of shaking (data not shown) confirming the choice to use the methodology of Ahmad et al. (2001). Sorption isotherms were fit using the Freundlich equation and organic carbon sorption distribution coefficients (K_{oc}) were calculated (Bourg, 1989; Schiavon et al., 1990).

2.2.1.1. Residue analysis using HPLC. Aliquots of the supernatants were filtered using a (0.45 nm) membrane and the atrazine concentration was directly measured by injecting 80 μl into an Shimatzu HPLC equipped with a reverse phase column RP_{18} (250 mm × 4.6 mm i.d.) preceded by a guard column (10 × 3.0 mm i.d.) with 222 nm absorption. The mobile phase comprised methanol + 0.1 mol l^{-1} sodium acetate (pH 5.2) in a proportion of 60:40/v:v. The operational temperature of the column was 75 °C and the flow speed 1 ml min^{-1}.

This method for atrazine analysis in soil and water was based on that of Huang and Pignatello (1990) and Balinova and Balinov (1991), with modifications testing different solvents and agitation times. Calibration curves for atrazine and its metabolites were made using chemical standards from Riedel-de-Haën. Curves were linear up to 5 mg l^{-1} with regression coefficients of 0.999 and detection limits of the 0.2 μg l^{-1}. Reproducibility was appropriate with relative standard deviations less than 5% in all cases and recoveries of atrazine ranging between 75% and 85%.

2.2.2. Microcosm experiment

2.2.2.1. Microcosm system. Undisturbed soil cores were carefully collected 30 d after tillage and fertilization for a maize crop. Stainless steel cylinders of 30 cm height and 15 cm diameter were carefully pushed into the soil by hand to avoid compaction of the soil. Samples were collected from 4 different points. Samples were assembled and placed within a laboratory microcosm system at room temperature (15–25 °C) (Fig. 1). Airflow was controlled by a gas-flow meter at 17 l h^{-1} and using a system of pumps, air entered via irrigation holes in the lid of the microcosm. Airflow was maintained as such throughout the experiment.