PRESENCE OF ATRAZINE IN WATER IN A RECHARGE AREA OF GUARANY AQUIFER IN BRAZIL

A. L. Cerdeira[1], N. A. G. Santos[2], M. C. P. Y. Pessoa[1], S. Smith Jr[3], V. L. Lanchote[2].

[1]Embrapa, Research Division of the Brazilian Ministry of Agriculture, Jaguariuna, SP, Brazil. (cerdeira@cnpma.embrapa.br)
[2]Pharmacy School of Sao Paulo University, USP, Ribeirao Preto, SP, 14100, Brazil.
[3]USDA-ARS- National Sedimentation Laboratory, Oxford MS, USA.

ABSTRACT. The region of Ribeirao Preto City located in Sao Paulo State, southeastern Brazil, is an important sugarcane, soybean and corn producing area. This region is also an important recharge area for groundwater of the Guarany aquifer, a water supply source of the city and region. The cultivation of grain and sugar cane in this area demands the frequent use of the herbicide atrazine (2-chloro-4- (ethylamino)-6-(isopropylamino)-S-triazine). This research was conducted to characterize the potential contamination of groundwater with atrazine. Surface water samples were collected in the Espraiado stream in a selected watershed on the area, during the years of 1995-1998. Groundwater was also collected in wells located at the edge of the watershed during the years of 1999 to 2002. The water samples were analyzed by HPLC (High Performance Liquid Chromatography) procedure followed by GC-MS for confirmation. To predict the atrazine leaching in the area, the CMLS-94 (Chemical Movement Layered Soil) simulation model was also used. Only four atrazine detections in surface water were found, however, none of them were confirmed with GC-MS. No atrazine was detected in groundwater samples. The results obtained by the CMLS-94 simulations predicted that atrazine, after four years from the application date, would not have reached the depth of the confined aquifer (40m).

INTRODUCATION

Ribeirao Preto City, Sao Paulo State, Brazil, is an important sugarcane, soybean and corn producing area (Fig. 1). This region is also an important recharge area for groundwater of the Guarany aquifer, a water supply source of the city and region. It has an intercontinental extension that reaches areas of eight Brazilian states, as well as significant portion of other South American countries like Argentina, Uruguay, and Paraguay, with a total area of approximately 1,200,000 Km^2.

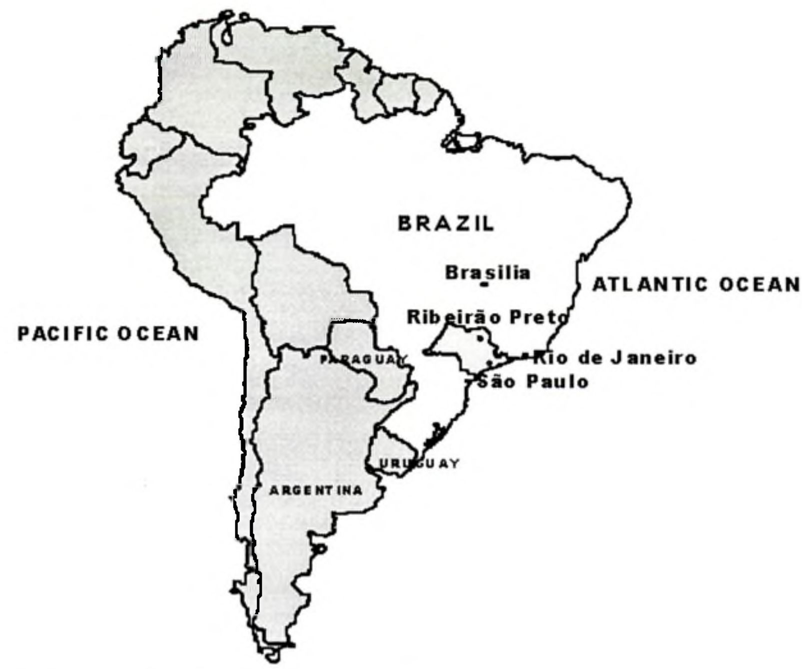

Figure 1. Map of South America showing the city of Ribeirao Preto, Brazil, where the watershed is located.

Due to the high permeability of some soils present in this region, the high mobility of the herbicides and fertilizers applied, and being a recharge area, it is important to investigate the potential transport of applied herbicides to underlying aquifer. Since the crops in this area demand the frequent use of the herbicide atrazine (2-chloro-4- (ethylamino)-6-(isopropylamino)-S-triazine), this research was conducted to characterize the potential of the herbicide leaching to groundwater.

MATERIAL AND METHODS

Nine surface water sample points were selected in the Espraiado stream in the watershed. Samples were collected, during the years of 1995-1998, in the months of October, November, December, January, March, May, and July of each year. Four replications were collected at each site for a total of 252 surface water samples per year. Groundwater was also collected during the same months from county groundwater wells located at the edge of the watershed during the years of 1999 and 2002. The following seven wells were studied: Palmares, Sao Jose, Sao Sebastiao Velho, JP, Higienopolis, Schimidt, Jardim Recreio, and DAERP Central. The water samples were analyzed using an HPLC (High Performance Liquid Chromatography) procedure followed by GC-MS for confirmation.

The water samples (1-liter) were stored in amber flasks and kept at 4°C until analysis using the following HPLC (High Performance Liquid Chromatography) procedure: A standard solution of atrazine (100%, Supelco) was prepared in HPLC-grade methanol (Merck) at a concentration of 1.0 mg/ml. Working solutions at concentrations of 0.08, 0.20, 0.32, and 0.40 µg/ml, were prepared by appropriate dilution. A caffeine solution (used as the internal standard) for confirmation of herbicide residues by GC-MS was prepared in methanol at a concentration of 5.0 µg/ml.

HPLC analysis were performed with a Shimadzu liquid chromatograph (Kyoto, Japan) consisting of an LC-10AD pump, a UV detector (SPD-10AV) operating at 220 nm, an automatic injector (SIL 10A) with a 100 μl loop and a Chromatopac C-R6A integrator. The presence of atrazine in water samples was confirmed using a Shimadzu GC-MS system model QP5000 (Kyoto, Japan) that consists of a gas chromatograph equipped with a split/splitless injector (t_V = 240°C, splitless, 0.75 min sampling time) and coupled to a mass selective detector operating in the SIM mode. The calibration curves were obtained by spiking 100 mL aliquots of water purified in a MILLI Q®-plus system (Millipore) with 25.0 μL of each standard solution, resulting in concentrations of 0.02 to 0.1 μg/L water. In the GC-MS analysis the water samples were also spiked with 25.0 μL of internal standard solution, caffeine 5 μg/mL (Lanchote et al., 2000).

To predict the atrazine leaching in the area, the CMLS-94, Chemical Movement Layered Soil, (Nofziger and Hornsby, 1994) simulation model was used. Data obtained by the simulations were then evaluated with those of depths of the groundwater depths. The input data used were: a) crop cultural coefficient (Kc); b) soil type by levels: percent of organic carbon, density (Mg m^{-3}), volumetric content of water (%), field capacity, wilting point, and saturation; c) weather: daily maximum and minimum temperatures, rainfall and evaporation, for a period of four years; d) atrazine properties: K_{OC} and half life (t½). Different simulation scenarios were made to evaluate the atrazine movement in the vertical profile of Clayey Eutroferric Red Latosol (LVefb), Psamitic Distrofic Red Latosol (LVdfq), and Quartzarenic Neosol (RQ), (EMBRAPA, 1999).

RESULTS AND DISCUSSION

Only four atrazine detections in surface water were found in the year 1996, with residues varying from 0.02 to 0.09 ppb. However, none of them were confirmed with GC-MS. No atrazine was detected in groundwater samples.

The results obtained by the CMLS-94 simulations predicted that atrazine, after four years from the application date, would not have reached the depth of the confined aquifer (40m). However, as a non-confined more superficial watertable exists in the study area (with depths varying between zero and 20 m) it was shown that there is a risk of the herbicide reaching the aquifer (Table 1).

Since the half-life ($t_{1/2}$) of atrazine is highly influenced by the soil pH and by organic matter content (Walker and Blacklow, 1994), also Quartzarenic Neosol (RQ) has pH values varying from 7.3 at 0-50 cm to 7.0 at 50-60 cm (Cerdeira et al. 2000), those characteristics would favor the mobilization of the atrazine molecules and result in leaching to greater depths (Table 1). In Clayey Eutroferric Red Latosol (LVefb) and Psamitic Distrofic Red Latosol (LVdq), the respective values of pH remained acidic and favored a little movement of atrazine in those soils (Table 1). In that situation, the final amount projected by simulation scenarios was mainly influenced by t½ values of atrazine in the respective soil type. Atrazine has shown no potential to reach groundwater when evaluated by the CMLS-94. This result agrees with the information obtained by means of monitoring wells located in the study area, where atrazine was not detected in the water.

Table 1. Partition Coefficient (Koc), half-life (t½) of atrazine, depth values (DPT, m) and amount (AMT, kg/ha) reached at the end of simulations for each type of soil.

SOIL TYPE	ATRAZINE			
	characteristics		movement	
	Koc(L/kg)	t½(days)	DPT	AMT
LVdq (Psamitic Distrofic Red Latosol)	224.3	54	1.67	9.2×10^{-7}
Lvefb (Clayey Eutroferric Red Latosol)	187.1	262	1.43	1.4×10^{-1}
RQ (Quartzarenic Neosol)	305.7	181	2.88	3.4×10^{-2}

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