Effects of Agriculture on Ground Water in a Recharge Area of Guarany Aquifer in Brazil

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ABSTRACT

The region of Ribeirão Preto City located in São Paulo State, southeastern Brazil, is an important and highly mechanized sugar cane producing area. It is also an important recharge area of the Guarany aquifer, which provides water to several cities and rural communities in the region. Research has been conducted in this region since 1995 to assess the behavior of herbicides, such as atrazine, simazine, ametryn, tebuthiuron, diuron, 2,4-D, picloram, and hexazinone, applied in the area. Nitrate applied as nitrogen fertilizer was also evaluated. Espraiado watershed, located over the recharge area, was chosen for this study. Water samples were collected from seven wells located inside the watershed and from surface water of Espraiado stream. Other samples were taken from city wells located at the edge of the recharge area with exception of the control samples that were collected from downtown wells. Results have shown that no residue of herbicide was found in ground water wells and only ametryn was found at levels higher than the Maximum Concentration Level (MCL) of 0.1 μg/L in surface water of the watershed. However, nitrate was detected at levels close to the MCL of 10 mg/L in wells located in downtown, far away from the sugar cane area.

Key Words: Agriculture, Ground Water, Nonpoint Source Pollution, Solute Transport, Water Quality.

INTRODUCTION

Although it was generally accepted that pesticides would not leach to ground water, studies conducted especially in the last decade (Smith et al. 2001, Bower, 1990) have indicated that agrochemical leaching is an important factor of agricultural non-point-source pollution and some North American aquifers were contaminated with both inorganic and organic compounds including some pesticides (Williams et al. 1988).

Herbicide persistence in soil and leaching are potential sources of ground water contamination (Pessoa et al. 2003). The region of Ribeirão Preto city, São Paulo State, located in Southeast of Brazil, is an important area for sugar cane production, with high level of herbicide and fertilizer utilization. This is also an important recharge area of the Guarany aquifer ground water, which extends to eight Brazilian states and part of Argentina, Uruguay, and Paraguay, with approximately 1,200,000 km^2. Geological studies in the region have identified a watershed, called Espraiado (Miklós and Gomes 1996), with high risk of ground water contamination. Certain areas of the Espraiado watershed are highly permeable sandy soil allowing leaching of agrochemicals applied in crops (Gomes et al. 1996).

Several analytical methods were developed using gas chromatograph/mass spectrometry (GC-MS) to detect and quantify herbicides used in the area in Brazil. (Lanchote et. al. 2000, Souza et al. 2000, Souza et al. 2001, Cerdeira et al. 2000, Gomes et al. 2000).

As a tool to understand the interaction among cropping systems, herbicides, soils, and weather factors affecting the fate of the herbicides, various simulation systems can be used, including Chemical Movement in Layered Soils (CMLS-94) (Nofziger and Hornsby, 1994), Pesticide Root Zone Model (PRZM) (Carsel et al. 1995), and Ground water Loading Effects of Agriculture Management System (GLEAMS) (Leonard et al. 1987), among others. Several studies using CMLS-94 to evaluate the tendencies of tebuthiuron, diuron, atrazine, simazine, ametryn, 2,4-D, picloram and hexazinone herbicides in reaching ground water were conducted in the area (Cerdeira et al. 2002, Pessoa et al. 2003). This research was conducted because of the Espraiado watershed vulnerability, and its vicinity was chosen to study herbicides and nitrates movement and potential contamination of the water.

Table 1. Depths and localization of the wells.

Wells	Depths (m)	Localization (South and West)
São Sebastião[1]	197	21°02′59′′ and 47°44′09′′
Palmares[1]	199	21° 10′29′′ and 47°45′44′′
São José[1]	236	21°13′25′′ and 47°45′40′′
Recreio Internacional[1]	134	21°11′09′′ and 47°43′32′′
Central[1]	79	21°10′55′′ and 47°18′01′′
Portinari[1]	220	21°09′44′′ and 47°44′28′′
W1[2]	53	21°13′40″ and 47°42′05″
W2[2]	38	21°14′30″ and 47°42′33″
W3[2]	8	21°14′49″ and 47°43′ 07″
W4[2]	4	21°14′50″ and 47°43′10″
W5[2]	9	21°14′42″ and 47°42′53″
W6[2]	surface	21°15′47″ and 47°43′43″
W7[2]	9	21°14′10″ and 47°43′49″

[1]Denotes municipal wells.[2]Denotes wells on the recharge area, from 1 to 7.

MATERIALS AND METHODS

A survey conducted in the area has indicated that the herbicides atrazine, simazine, ametryn, tebuthiuron, diuron, 2,4-D, picloram, hexazinone and nitrate applied as nitrogen fertilizer, were frequently utilized and they were chosen for this study.

Surface and ground water were collected at four month intervals from seven wells located at the Espraiado watershed and from six municipal wells located outside of the watershed at the vicinity of the recharge area, during the period of 1995 to 2006 (Table 1).

Herbicides Determination in Water

Water samples (1L) were collected. Herbicides measurements were made from 100 mL of water samples, filtered under vacuum through a membrane of 0.22 µm porosity. The filtrates were extracted with 12 mL dichloromethane and shaken for one hour (Ballinova 1993, Durand et al. 1992).

After phase separation, 6 mL of the organic phases were transferred to conic test tubes and evaporated to dryness at 35°C. The residues were dissolved in 200 µL of mobile phase and 100 µL were chromatographed on a Lichrospher 100 RP-8 column (particle 5 µm, 125 x 4 mm, Merck) using 0.05 M phosphate buffer, pH 5.5, and acetonitrile (73:27, v/v) as mobile phase. Triazine herbicides were detected at 220 nm, whereas tebuthiuron and diuron were detected at 254 nm. (Schlett 1991).

The recovery obtained with the extraction procedure was higher than 95% for all herbicides except simazine for which the recovery was 85.6%. Due to the enrichment in the extraction procedure and the sensitive detection at the two wavelengths, it was possible to obtain a quantification limit of 0.02 μg/L for the herbicides studied. The method was linear over the range of 0.02 to 2.0 μg/L.

Nitrate was analyzed by Cadmium Reduction Method according to Greenberg, et al. 1992.

Simulation with CMLS-94 Model

The mathematical model of leaching CMLS-94 was used to understand the behavior of the chemicals on the environment. The input data required to use CMLS-94 were: a) crop cultural coefficient of sugar cane (Kc); b) soil type by depths - percent of organic carbon, density (Mg m^{-3}), volumetric content of water (%) on field capacity, on wilting point, and on saturation; c) weather - daily maximum and minimum temperatures, rainfall (varying between 1300 and 1500 mm/year) and evaporation (the potential evapotranspiration reaching 1000mm/year, based on the Thorntwaite method), d) herbicides properties- adsorption coefficient (K_{OC}) and soil half life (t½); e) spraying - date and initial dose applied; and f) geographical coordinates (Table 1). Koc and t½ were evaluated from the soils collected in the area.

RESULTS AND DISCUSSION

Chemical analysis of tebuthiuron, diuron, atrazine, simazine, and ametryn revealed that no residues of these herbicides were detected in ground water. In one sole collection, ametryn residues at concentrations above the Maximum Concentration Level (MCL) (0.17 and 0.23 μg/L) were detected in samples acquired in two locations out of nine from the Espraiado stream. The acceptable maximum level for European standard is 0.1 μg /L.

Very low amount of nitrates residues were detected in ground water of the Espraido area (Table 2), however, analysis of municipal wells have shown that nitrate levels were detected at higher concentration than the MCL of 10mg/L (Table 3) in downtown well. This well is located away from agricultural sites.

The results obtained by the CMLS-94 simulation (Figure 1) indicate that the applied herbicides did not reach the depth of the confined aquifer (40 m). Hexazinone was found at deepest depth, at 30.0 m. (Figure 1).

In relation to soils, there was a tendency of Quartzarenic Neosol (RQ) soil leaching more than Clayey Eutroferroc Red Latosol (LVef) and Psamitic Distrofic Red Latosol (LVd) (Figure 2).

Table 2. Average values of NO_{-3} (mg/L) during the years of 1996, 1997, and 1998 in ground water from wells located at the Espraiado watershed.

Wells	1996			1997			1998		
	May	Sep	Nov	May	Sep	Nov	Feb	Apr	Jun
W1	1.0	0.3	0.2	0.8	0.0	0.2	0.0	0.0	0.2
W2	1.0	0.2	0.3	0.5	0.2	0.3	0.3	0.2	0.3
W3	0.3	0.2	0.0	0.0	0.1	0.0	0.0	0.0	0.0
W4	0.6	0.4	0.5	0.7	0.4	0.5	0.5	0.3	0.5
W5	0.4	0.6	0.3	0.4	0.6	0.3	0.0	0.4	0.3
W6	0.8	0.7	0.5	0.6	0.3	0.5	0.2	0.3	0.4
W7	0.5	0.6	0.4	0.5	0.6	0.4	0.4	0.3	0.0

Table 3. Average values of NO_{-3} (mg/L) during the years of 2005 and 2006 in ground water from wells located at the municipal area of Ribeirão Preto city.						
Wells	**July 05**	**March 05**	**Dec 05**	**Mar 06**	**Jun 06**	**Oct 06**
São José	0.5	0.8	0.5	0.2	0.6	0.6
Portinari	0.1	0.1	0.2	0.1	0.0	0.1
Palmares	0.1	0.5	0.3	0.3	0.2	0.0
S. Sebastião	0.3	0.3	0.5	0.2	0.6	0.4
R. Internac.	0.0	0.3	0.4	0.8	0.0	0.1
Central[1]	8.5	11.0	9.3	7.3	8.0	7.0
[1]Well located in downtown away from the recharge area.						

A non-confined superficial water table found in the watershed with depths varying between zero to 20 m increases the risk of ground water contamination particularly in sandy soil. Thus the simulated results indicate that there is a potential risk of few herbicides to enter in contact with the superficial water table and further investigation must continue in monitoring those risk areas.

CONCLUSIONS

Results have shown that no residue of herbicide was found in ground water wells. Only nitrate was detected at levels close to MCL of 10 mg/L in wells located in downtown area, which is at further distance of the sugar cane plantations. Among the herbicides, only ametryn was found at levels higher than the MCL of 0.1 µg/L in surface water of the watershed. Simulation has shown that the herbicide hexazinone could reach the deepest depth, at 30.0 m, and the leaching was higher in sandy soils, Quartzarenic Neosol (RQ).

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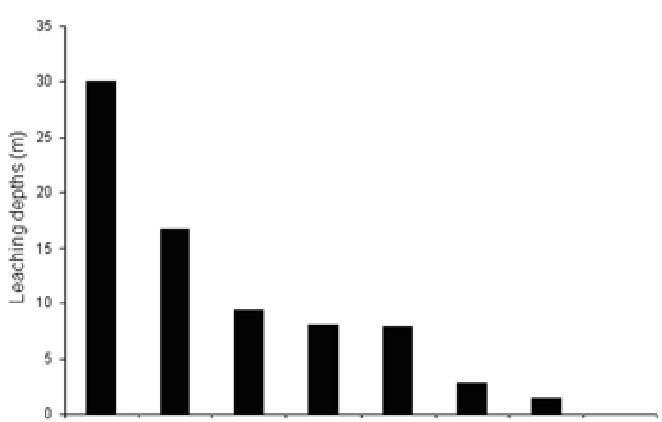

Figure 1. Herbicide depths reached in Quartzarenic Neosol (RQ) soil of the recharge area.

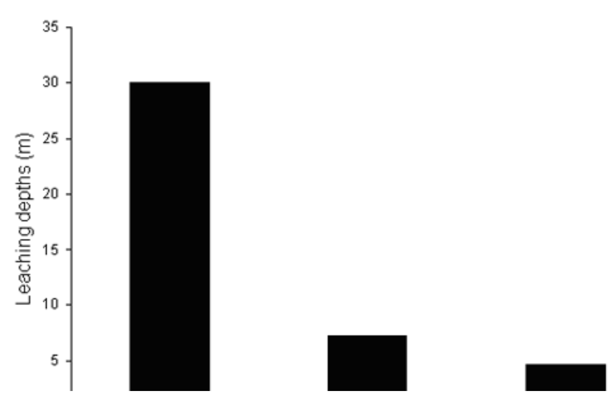

Figure 2. Depths reached by the herbicide hexazinone in different type of soils Quartzarenic Neosol (RQ), Psamitic Distrofic Red Latosol (LVd), and Clayey Eutroferroc Red Latosol (LVef). Simulated for 4 years.

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