WATER MONITORING PROGRAM IN A RECHARGE AREA OF THE GUARANY AQUIFER IN SOUTH AMERICA

Antonio Luiz Cerdeira[1]
Carlos Farjani Neto[2]
Otavio Balderrama Pinto[3]
Paulo Eduardo Rampazzo[3]

[1] Embrapa Meio Ambiente, Ministry of Agriculture, C. P. 69, Jaguariúna, SP, Brazil, 13820-000 (cerdeira@cnpma.embrapa.br)
[2] DAERP, Departamento de Águas e Esgotos de Ribeirão Preto. (Water Laboratory). Rua Amador Bueno 22, Ribeirão Preto, SP, Brazil. 14100-000.,
[3] Mogi Mirim Regulatory Laboratory, Dow AgroSciences, Mogi Mirim, SP, Brazil, 13800-970 (obalderrama@dow.com)

The Guarany aquifer is the greatest groundwater reservoir of water in South America and its extension covers the central-south part of Brazil, northern Argentina and part of Uruguay and Paraguay. The region of Ribeirao Preto, Sao Paulo State, Brazil, is located on a recharge area of Guarany aquifer and has sugar cane as its main agricultural activity. Based on the use of a number of pesticides and fertilizers in the sugar cane crop management and the natural vulnerability of recharge area, the Brazilian Agricultural Research Agency (EMBRAPA-Environment) carried out a number of studies in this region to study the quality of the Guarany aquifer water from 1995 to 1999. Results of these studies are published in a number of papers and showed no evidence of contamination of Guarany aquifer water. Tebuthiuron, (N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea), is a phenylurea herbicide used in sugar cane for pre-emergence control of weeds and was one of the pesticides monitored in the area. During the years of 2000 and 2002, EMBRAPA-Environment and Dow AgroSciences established a partnership in order to continue monitoring tebuthiuron in wells used in this region to supply drinking water to the population of Ribeirao Preto city region. Nine different sampling points were selected in the region and their wells were sampled from November 2000 to November 2002, covering samplings in rainy and dry seasons during this period. An analytical method using HPLC and UV detection was established to perform residue analysis. The limit of quantification used was 0.1 µg/Kg (ppb, part per billion) for the first three sampling carried out and 0.03 µg/Kg for the following five samplings. The majority of samples showed no detectable residues of tebuthiuron and two samples showed residues below the 0.03 µg/Kg limit of quantification, well below EPA's Lifetime Healthy Advisory limit of 500 µg/L for tebuthiuron in drinking water. The results confirm no changes in the quality of water in this recharge area of Ribeirao Preto region for the specific compound monitored in the present study.

1. Introduction

The region of Ribeirão Preto city, located in Southeast of Brazil, São Paulo State, (Figure 1) is an important sugarcane producing area, with agrochemical utilization. This region is also an important recharge area for groundwater supply for the Guarany aquifer which comprises areas of eight Brazilian states plus parts of Argentina, Uruguay and Paraguay, with approximately 1,200,000 Km^2. Geological studies have identified a watershed (4000 ha) as very susceptible to groundwater contamination by agrochemicals, so it was chosen as research site to study the movement of different herbicides and other compounds, including tebuthiuron (1).

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

The intensive cultivation of sugar cane in that area has been demanding the constant use of pre-emergent herbicides. The behavior of those products in soil, normally reapplied annually, have been object of study "in loco" to analyze the risk of leaching to the groundwater. The high permeability of some soils present in the area, and products with high mobility, constitute factors that make important to study the movement of some compounds in the area. Also, 100% of water for urban consumption of cities close by is

supplied by the aquifer. The purpose of this work was to monitor the herbicide tebuthiuron in municipal wells located at the edge of the watershed to make sure that the quality of the water will be preserved.

The herbicide tebuthiuron is regularly applied in the watershed (1). Tebuthiuron (N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea) is a phenylurea herbicide used in sugar cane culture for pre and post-emergence control of weeds (2). The herbicide is applied once or twice per crop cycle, which depend on crop variety but lasts about 5 to 6 years as an average. Application rate is about 1.0 Kg/ha (Kilogram per hectare) of active ingredient on the first treatment and reduced to about 50 to 70% of this rate in case of a second treatment during same crop cycle. Analysis of tebuthiuron and of other phenylurea herbicides in environmental samples can be performed by HPLC, or by gas chromatography using selective detectors such as nitrogen-phosphorus detector (NPD), electron-capture detector (ECD) or a mass spectrometer (MS), (3, 4, 5, 6).

2. Materials and Methods

The study area is located in Espraiado watershed, north of the São Paulo State, Brazil, in the municipal districts of Ribeirão Preto, Cravinhos and Serrana, in the geographical coordinates 21°05 ' and 21°20 ' of south latitude and 47°40'e 47°50' of west longitude. The climate of the area is tropical with dry winter savanna. The annual medium temperature is 22°C, with rain varying between 1300 and 1500 mm/year. The potential evapotranspiration reaches 1000 mm/year, based on the method of Thorntwaite. The area holds the Botucatu Aquifer where the recharge area and the watershed is located.

WATER SAMPLING. Water was collected from wells located at the edge of the watershed during the years of 2000 to 2002 using dark bottles. The water samples (1000 ml) were stored in amber flasks and kept at 4^{o}C prior to extraction.

TEBUTHIURON DETERMINATION IN WATER. Tebuthiuron was analysed by HPLC using a Agilent model 1110 Series, Column Agilent Eclipse XDB-C8 5-Micron, 4,6 mm ID x 150 mm. Solid phase extraction was made with Octadecyl column C18, (SPE) J.T.Baker. Mobile phase was 40% acetonitrile + 60% water.

3. Results and Discussion

Efficiency of methodology was checked based on recoveries of fortified water samples performed on the range of 0.025 to 10 µg/Kg. Average from 39 recoveries performed during the 2 years is 90%. Overall standard deviation from same data points is 9%.

The statistical limits of detection and quantification (7), calculated as 3 and 10 times the standard deviation from the replicate analysis at quantification limit of analytical method (0.025 µg/Kg) resulted in 0.008 and 0.025 µg/Kg. The quantification limit of analytical method applied was 0.03 µg/Kg.

Typical calibration curve used in the study is presented in Figure 1.

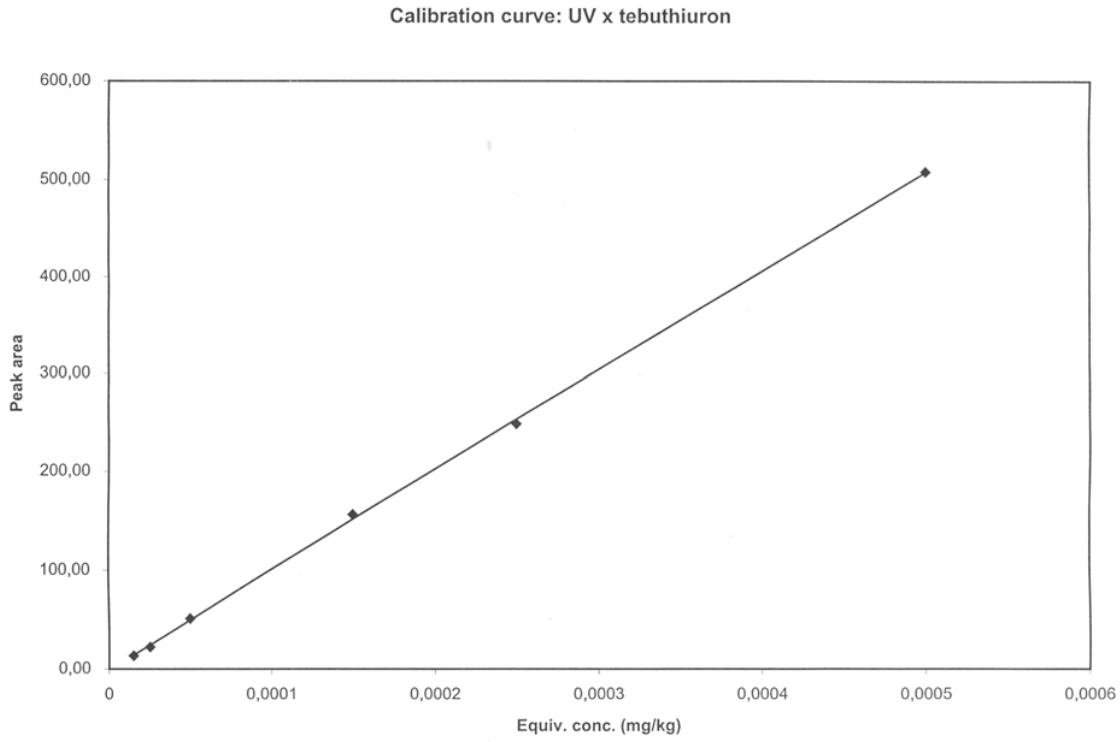

FIGURE 1. CALIBRATION CURVE FOR TEBUTHIURON ANALYSIS IN WATER ($Y = 1E+10^6X - 0.9847$).

Typical chromatograms of analytical standard solution at concentration of 0.05 ug/L and water sample collected in a Ribeirão Preto Municipal well are presented in Figures 2 and 3, respectively.

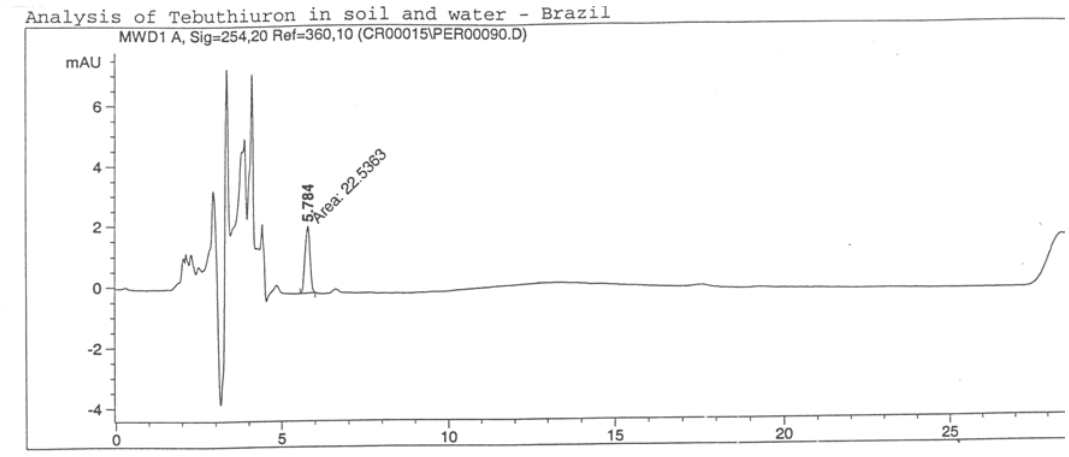

FIGURE 2- CHROMATOGRAM OBTAINED WITH THE HERBICIDE TEBUTHIURON IN WATER AS STANDARD (0.05 ug/L).

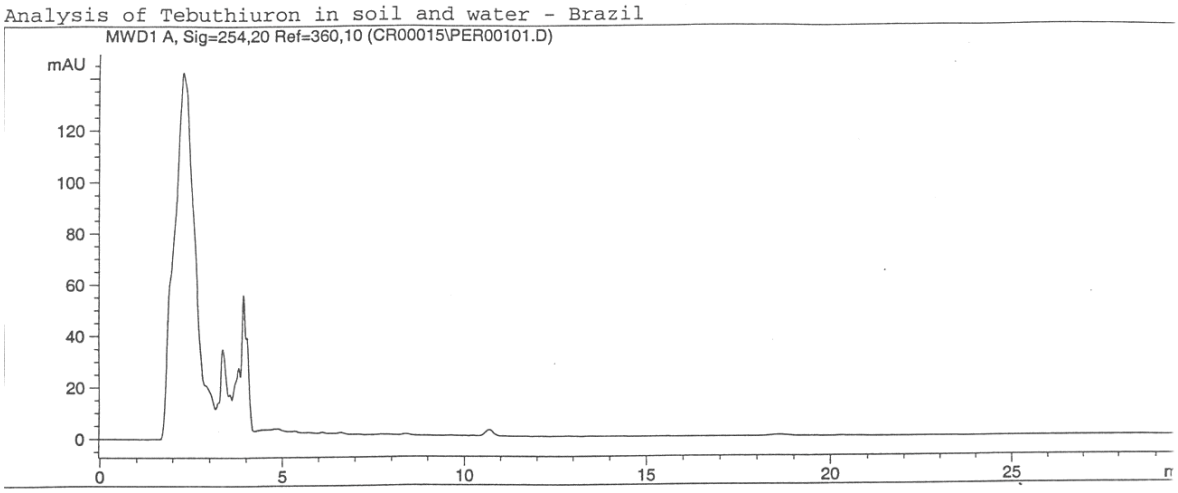

FIGURE 3- GENERAL CHROMATOGRAM OBTAINED FROM WATER COLLECTED FROM MUNICIPAL WELLS.

The majority of samples showed no detectable residues of tebuthiuron and two samples showed residues below the 0.03 µg/Kg limit of quantification, well below EPA's Lifetime Healthy Advisory limit of 500 µg/L for tebuthiuron in drinking water. Due to the difference between residues found in these two water samples and EPA´s limit no confirmatory study was made to certify if residues found were really related to tebuthiuron. Results are presented in Table 1.

	Date of Sampling								
WELLS	nov/00	apr/01	may/01	jul/01	nov/01	mar/02	apr/02	jun/02	nov/02
São Sebastião (Old)	ND	ND	ND		ND	ND	ND	ND	ND
Palmares	ND	ND	ND			ND	ND	ND	ND
JP Hotel	ND	ND	ND		ND	ND	ND	ND	ND
São José	ND	ND	ND		ND	ND	ND	ND	ND
Recreio Internacional	ND	ND	ND		<0,03	ND	ND	ND	ND
Higienopolis		ND	ND		ND	ND	ND		
DAERP Central		ND	ND		ND	ND		ND	ND
São Jose Farm				<0,03	ND				
Dow Cravinhos					ND				

TABLE 1. RESIDUES OF TEBUTHIURON (ppb) IN WATER FROM RIBEIRÃO PRETO MUNICIPAL WELLS . ND MEANS NOT DETECTABLE.

4. Conclusions

Results confirm no changes in the quality of water in this recharge area of Ribeirao Preto region for the specific compound monitored in the present study.

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