105 - HERBICIDE LEACHING ON A RECHARGE AREA OF GUARANY AQUIFER, BRAZIL.

Lixiviação de herbicidas em área de recarga do aquífero Guarani no Brasil.

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ABSTRACT: The region of Ribeirao Preto city, located in Southeast of Brazil, Sao Paulo State, is an important sugarcane, soybean, and corn producing area with a high level of pesticide utilization. This region is also an important recharge area for groundwater supply of the Guarany aquifer. A survey has shown the following herbicides as the most commonly used in the area: atrazine, simazine, ametryn, tebuthiuron, diuron, and 2,4-D. In order to study a possible leaching of the herbicides into the aquifer, surface and ground water samples were collected during the years of 1996 to 2003 from different points. Groundwater samples were collected from sites near the river during the same period. It was used a GC-MS to detect and quantify the herbicides (gas chromatograph/mass spectrometry). The method was linear over the range of 0.02 to 2.0 µg/L. Analysis of tebuthiuron, diuron, atrazine, simazine and ametryn residues showed no significance amount of these products in ground water. Only two out of nine points of surface water collected in one year, presented ametryn concentrations above (0.17 and 0.23 ug/L) the allowable 0.1 ug/L, European safety level. It was also used the simulator model CMLS-94, "Chemical Movement Layered Soil" which indicated no leaching to the depths of the water table at 40m.

Key words: Herbicides, water, residues, Brazil.

Palavras-chave: Herbicidas, água, resíduos, Brasil.

INTRODUCTION

Pests and weeds have been controlled by pesticides and herbicides involving a huge world market of more than 20 billions dollars annually. The practice of long-term, sometimes indiscriminate and abusive use of herbicides in the agriculture and the high persistence of some of them have been important on the environmental contamination, mainly of groundwater, causing problems of water quality, Williams et al. (1988). The region of Ribeirão Preto city, São Paulo State, located in Southeast of Brazil is one of the most important agricultural producing area, with high level of herbicide utilization. This region is also an important recharge area for groundwater supply for the Guarany aquifer which extends to eight Brazilian states plus parts of Argentina, Uruguay and Paraguay, with approximately 1,200,000 Km^2. Geological studies have identified a watershed in the region, Espraiado, as a good research area, selecting it as a model for studies of water and agrochemicals movement toward groundwater. A survey of herbicides used in the area have identified as the most commonly used as atrazine, simazine, ametryne, tebuthiuron, diuron, and 2,4-D. Based on this information, it was developed an analytical method using a GC-MS to detect and quantify the herbicides (gas chromatograph/mass spectrometry). Surface and ground water samples were collected during the years of 1996 to 2003 from different points. It was also used a simulator - CMLS-94 ("Chemical Movement in Layered Soil"), Nofziger & Hornsby (1994), to evaluate the depths reached by the herbicides in the area.

MATERIALS AND METHODS

Surface and ground water samples (1L) were collected from Espraiado watershed during the period Groundwater samples were collected from the sites near the river during the same period. For the herbicides determination 100 mL of the water samples were initially filtered under vacuum through a membrane of 0.22u porosity. The filtrates were extracted with 12 mL dichloromethane and mechanically shaking for one hour. After phase separation, 6 mL of the organic phases were transferred to conic test tubes and evaporated to dryness under nitrogen at 35°C. The residues were dissolved in 200 µL of the 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. The triazine herbicides were detected at 220 nm, whereas tebuthiuron and diuron were detected at 254 nm. The recovery obtained in 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 level of detection at 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.

In order to predict the atrazine leaching in the area, the CMLS-94, Chemical Movement Layered Soil, (Nofziger & Hornsby (1994) simulation model was used. Data obtained by the simulations were then evaluated with those of depths of the groundwater levels. 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) herbicide properties: K_{OC} and half life ($t_{½}$). Different simulation scenarios were made to evaluate the herbicide movement in the vertical profile

RESULTS AND DISCUSSION

Analysis of tebuthiuron, diuron, atrazine, simazine and ametryn residues showed no significance amount of these products in ground water. Only two out of nine points of surface water collected in one year, presented ametryn concentrations above (0.17 and 0.23 ug/L) the allowable 0.1 ug/L. The results obtained by the CMLS-94 simulations predicted that the herbicides, 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 theoretical potential of the herbicide reaching the aquifer and that leaching was higher in sandy soil type (Table 1).

Table 1. Results obtained by mathematical simulation with CMLS 94 model for different herbicides during four years.

HERBICIDE	SOIL TYPE	DEPTH (m)	AMOUNT (Kg/ha)
Hexazinone	Sandy	30.0	3.7×10^{-5}
	Latossolo Roxo (Clay)	4.7	3.7×10^{-5}
Diuron	Sandy	4.9	1.5×10^{-4}
	Latossolo Roxo (Clay)	0.55	1.5×10^{-4}
Atrazine	Sandy	20.5	5.5×10^{-6}
	Latossolo Roxo (Clay)	3.1	5.5×10^{-6}
Ametryn	Sandy	8.0	4.1×10^{-6}
	Latossolo Roxo (Clay)	0.99	4.1×10^{-6}
Tebuthiuron	Sandy	10.7	3.5×10^{-6}
	Latossolo Roxo (Clay)	2.1	3.5×10^{-6}

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