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Soil Type and 2,4-D Leaching on a Sugarcane Watershed in Brazil.

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ABSTRACT

The region of Ribeirao Preto, SP, Brazil, is located on the Guarani aquifer, the most important source of ground water in the South Central region of the country. The recharge area of this aquifer is located in the Espraiado watershed. The presence of sandy soil and a sugar cane crop treated with high rate of pesticides applied makes the aquifer vulnerable to groundwater contamination. The herbicide 2,4-d (2,4-dichlorophenoxyacetic acid) was among the pesticides used. To study its behavior, a gas chromatography analytical method for residue analysis was developed and 2,4-D was measured during the years of 1996 until 1999. The movement also was evaluated with simulation using the software CMLS-94-"Chemical Movement in Layered Soils". The gas chromatography analytical method resulted in a 99.9% correlation of the area in the graphics and the herbicide concentration, and indicated that it was highly effective. No residue of 2,4-D was detected in water in any year. The simulation model CMLS have indicated the leaching down to 60 cm., far from the water table, in both types of soils, "Latossolo Roxo" and "Latossolo Vermelho-Escuro" in the second year after the application when the herbicide residues would already been dissipated.

INTRODUCTION

Harmful insects, mites, infectious fungi, bacteria and invasive weeds have been controlled by pesticides and herbicides and there is a huge world market for these products. The practice of long-term, sometimes indiscriminate and abusive use of pesticides in agriculture and their persistence has resulted in environmental contamination, especially groundwater, which causes water quality problems (CARNEY, 1991, WALKER et al., 2000).

The region of Ribeirao Preto city, (Sao Paulo State) located in the southeast of Brazil is one of the most important sugarcane producing area, with high levels of agrochemicals use (Figure 1). This region also is an important recharge area for the groundwater supply for the Guarani aquifer. The Guarani aquifer, approximately 1,200,000 Km^2, comprises areas in eight Brazilian states and parts of Argentina, Uruguay, and Paraguay. Geological studies have identified a 4000 ha watershed, Espraiado, located at the recharge area, as a research area and it was selected as a model for studies of water and agrochemical movement. (CERDEIRA et al., 1988). The herbicide 2,4-D (2,4-dichlorophenoxy acetic acid) is regularly used in the area and some studies have shown residues in water in the United States and Canada (SANCHES et al., 1999), this study monitored the presence of 2, 4-D residues in the Guarani aquifer.

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

A 1994 study by the Institute of Agricultural Economy (IEA, Sao Paulo) has defined 16 production units in the Espraiado watershed that included sugarcane fields, cattle pastures, coffee plantations, and small properties with diversified crops. However, this diversification is not representative of the area since sugarcane plantations occupy about 80% of the total. Information on the agricultural practices and herbicides use was collected through a farm survey. The following herbicides have been identified as the most commonly used in the area: atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2,4-diamine), simazine (6-chloro-N2,N4-diethyl-1,3,5-triazine-2,4-diamine), ametryn (N2-ethyl-N4-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine), tebuthiuron (1-(5-tert-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea), diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), 2,4-D, and picloram (4-amino-3,5,6-trichloropicolinic acid). 2,4-D is applied at rate of 2.0 Kg/ha of active ingredient. To determine the leaching potential of 2,4-D, this study was conducted during the years of 1996 to 1999 by measuring soil properties, determining the levels of 2,4-D residues, and using mathematical simulation models.

MATERIAL AND METHODS

To understand the behavior of 2,4-D in the area, soil samples from nine selected points of the Espraiado watershed were sampled and pH was determined in a DMPH-2 pHmeter (Digimed) with 2g of soil suspended in 5.0 mL deionized water after 15 minutes stirring.

Mathematical modeling simulator

The CMLS-94 "Chemical Movement in Layered Soils" (Nofziger & Hornsby, 1994) was used to study the movement of chemicals in the vertical profile of the soil. The simulator evaluates the pesticide concentration and the depths reached by it. The program works with up to 20 soil horizons layers and includes chemical data, partition coefficients, and half-life data for each of the soil horizons. The following data were supplied to the model:

a) Sugar cane crop data
Sugar cane cultural coefficient (Kc). The (Kc) of the annual sugar cane culture was obtained in Paranhos (1987).

b) Soil data
The soils, typical of tropical areas, possess peculiarities that are not found in North American similar soils present in the database of the CMLS-94. For this reason, the inclusion of the information on each one of those soils was incorporated to the database of the CMLS-94. For each soil type the following information was supplied: a) name of the soil; b) code of the name; c) number of horizons (depths); d) for each horizon: depth (m); % of organic carbon; density ($Mg.m^{-3}$); volumetric content of water (%): field capacity, and wilting point and saturation (PESSOA et al., 1997).

c) Climate data
Temperatures (maximum and minimum), rain and evaporation data were used in the format demanded by the CMLS-94 (temperatures in integer values and considering Julian year) for a period of four years.

d) 2,4-D pesticide data
Since K_{OC} and half life (t½) of these products vary with soil type, temperature, and percentage of organic matter, among other factors, it was included in the simulation model using the available values for the Brazilian soils.

e) Simulation scenarios

2,4-D leaching was simulated according to the following scenery base: culture of annual sugarcane harvested on September 20 of the first year, with only one application of the herbicide on October 20 of the same year, and simulation ending four years after the application of the product on December 31.

Herbicides determination in water.

Analytical method

HPLC was used to analyze herbicides when they could be detected with ultraviolet light, being possible to measure levels even below 0.1µg/l in water (LEE et al., 1983). Other methods such as ELISA (WALKER et al., 2000), and other variations also were used (VINK & POLL, 1996; FARRAN et al., 1999; HOUBEN et al., 1999).

Surface water was collected during all years, from 1966 to 1999. Water from well located inside the watershed was collected in December of last year, 1999. Samples were analyzed according to the following protocol (EDGELL et al., 1993; WANG & HUNG, 1985):

A stock solution of 2,4-D (99 %, Merck) was prepared at concentration of 19,80 µg/mL then was diluted to 1,584, 0,792 e 0,396 µg/mL. A internal standard was made with 3,4 dichlorobenzoic acid at 40,0 µg/mL (BERTRAND et al., 1987; BOGUS et al., 1990)

2, 4-D was measured after the regular analytical procedures using a gas chromatograph GC17-A equipped with electron detector (split/ splitless) (Shimadzu) according to WALISZEWSKI & SZYMCZWSKI, 1983; SILTANEN et al., 1985; and GURKA et al., 1986

RESULTS AND DISCUSSION

The physical properties of the soils found in the area are defined in Table 1. The sampled soils were classified as Clay, Loam, Sandloam and Sandy, according to Oliveira et al, 1992.

Table 1.Texture composition of different sampling points at different depths (cm.).

SAMPLING POINTS	Sand		Sand (fine)		Clay		Silt		Soil Class	
	Depth		Depth		Depth		Depth		Depth	
	0-20	80-90	0-20	80-90	0-20	80-90	0-20	80-90	0-20	80-90
P01	4.4	3.88	14.3	15.59	58.7	60.9	22.5	19.6	Clay	
P02	14.3	13.9	27.7	31.33	10.3	45.1	47.6	9.57	Loam	
P03	41.6	35.2	42.9	46.87	10.8	14.5	4.70	3.48	Sandloam	
P04	29.3	26.5	65.0	68.33	2.40	2.65	3.30	2.50	Sandy	

Core soil samples were taken to the laboratory and hydraulic conductivity studies performed. These experiments indicate that the Clay ("Latossolo roxo", "Latossolo" dark red), Sandloam, and Loam soils had medium infiltration potentials in contrast to the to Sandy soil, which showed a high infiltration potential (Table 2). The Sandy soil is located in the area of least declivity in the watershed making it much more susceptible to infiltration.

Table 2. Infiltration potentials and runoff for different soil types in the Espraiado watershed.

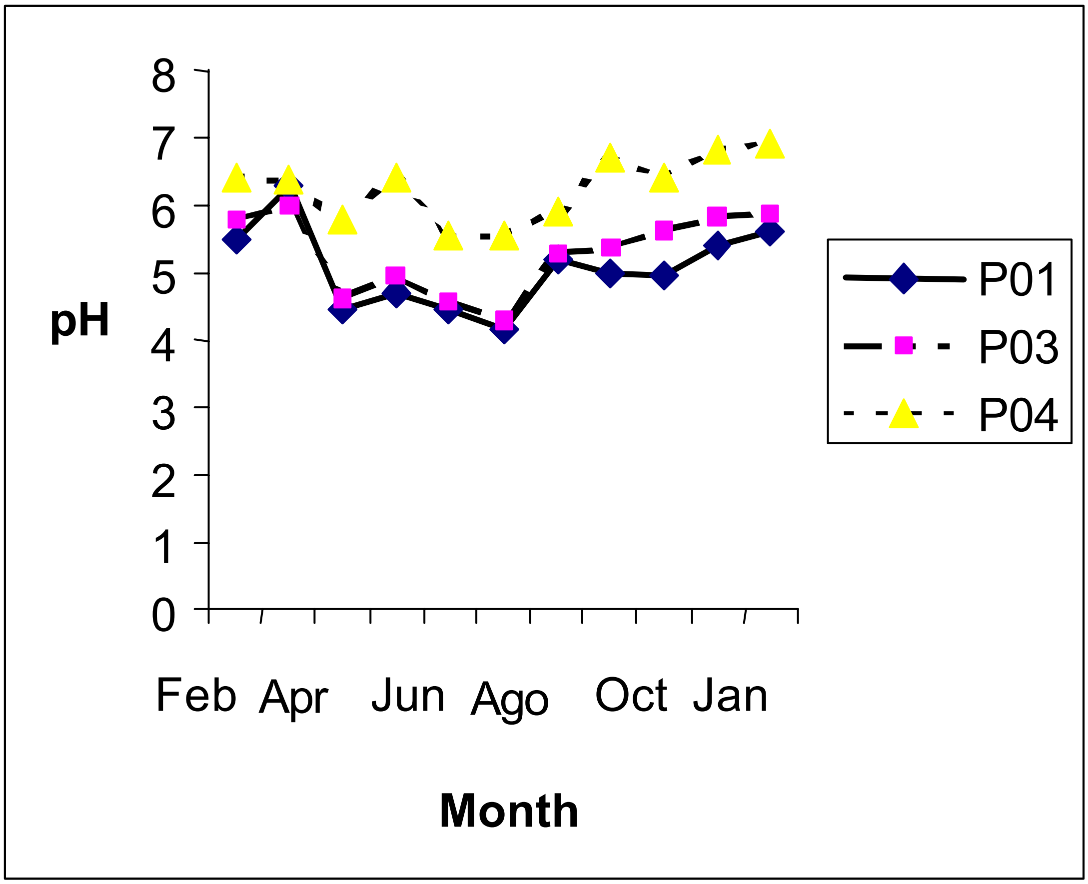
Soil Type	Hydraulic conductivity	Slope	Water infiltration potential	Runoff potential
Latossolo roxo (Clay)	High	High	Medium	Medium
Terra Roxa Estruturada (Clay)	High	High	Medium	Medium
Latossolo Dark Yellow (Loam)	Medium	Slight	Medium	Medium
Latossolo Red Yellow (Sandloam)	Medium	Slight	Medium	Medium
Areia Quartzosa (Sandy)	High	Slight	High	Low

Since pH affects the herbicide behavior, they were measured during the period of the sampling and monthly variations were determined as shown.

pH variations

Analysis of soil pH indicated that they have an acidic pH, A significant seasonal variation of approximately two pH units was observed in the samples (P01, P03 and P04) collected in July (Figure 2). In general, clay samples were more acidic than the sandy ones (P04). The pH of the 80-90 cm soil samples usually were more acidic than the surface samples (data not shown).

Figure 2 - pH values of soil surface samples from points P01, P03, and P04.



Simulation Studies

Simulation studies indicated that 2,4-D has low persistence in these soils and low leaching potential (Table 3). During the first year of simulation, there were only small amounts of 2,4-D remaining in depths less than one meter; being unlikely to reach groundwater level in the recharge area. At the end of the second year the concentration was very close to zero and it could not be detected at the end of year 3 (Table 3).

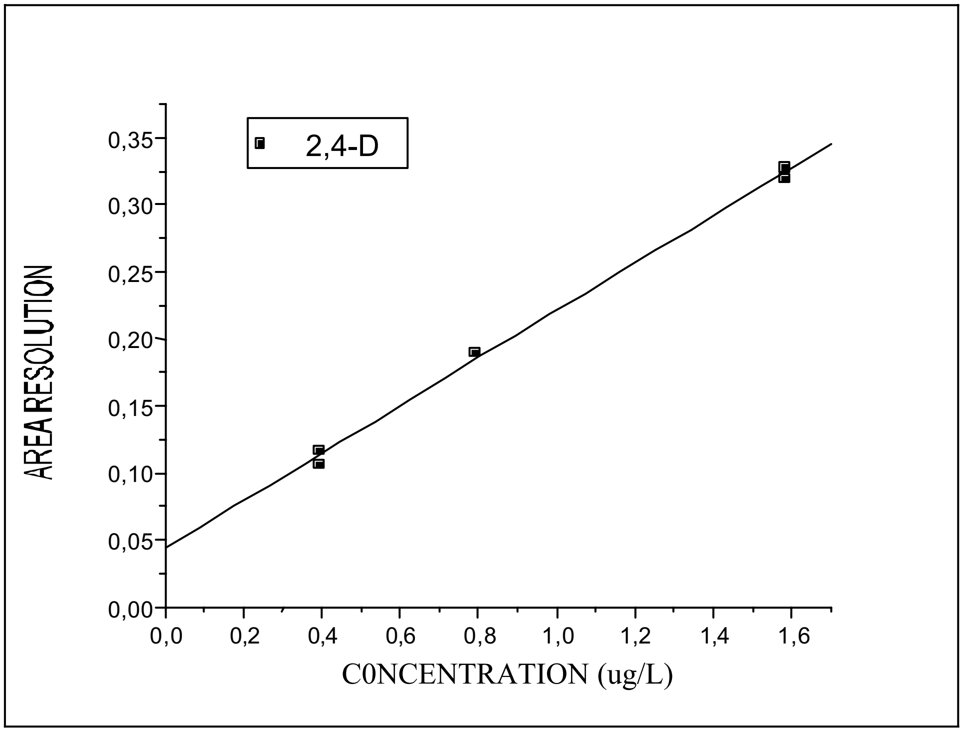
Table 3: Depths reached by 2, 4-D in two different types of clay soils, "Latossolo Roxo" and "Latossolo Vermelho-Escuro" at the Espraiado watershed in Riberao Preto, SP, Brazil. (Amt= Amount, Kg/ha).

	Latossolo Roxo Soil		**Latossolo Vermelho-Escuro Soil**	
	Depth(m)	Amt(kg/ha)	Depth(m)	Amt(kg/ha)
Year 1	0,453	$3,4x10^{-12}$	0,463	$3,4x10^{-12}$
Year 2	0,601	$2,2x10^{-24}$	0,591	$1,4x10^{-23}$
Year 3	0,847	0	0,877	0

Residue analysis

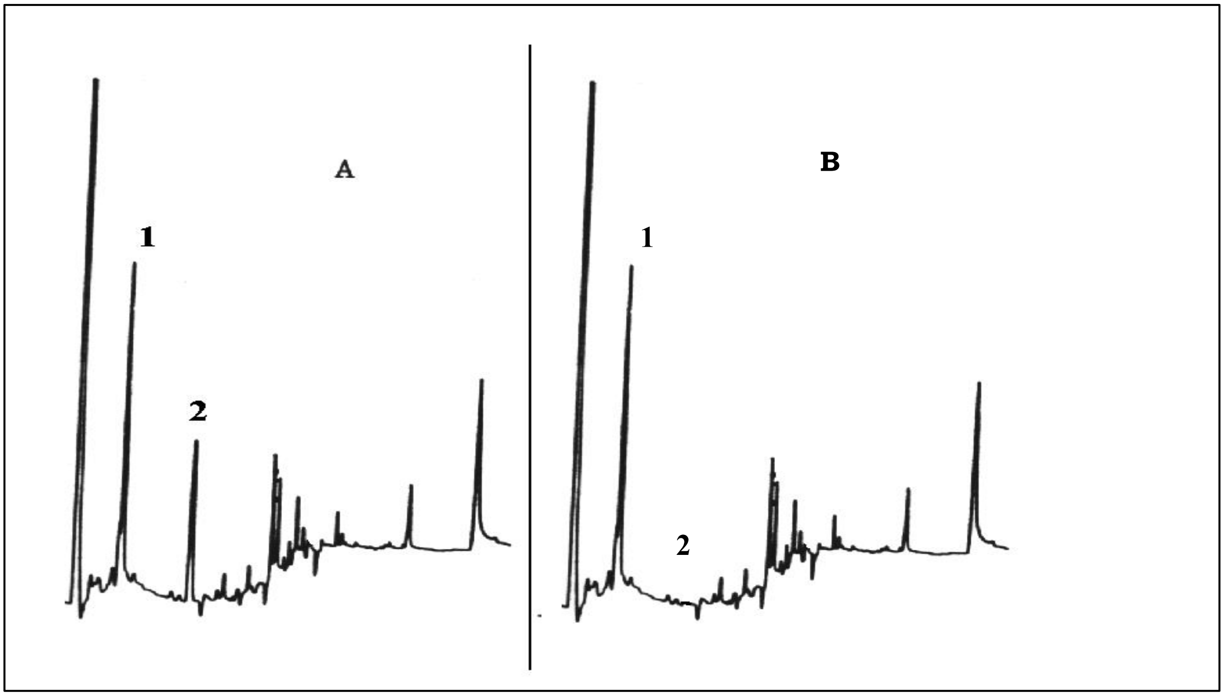
There was a linear relationship between the area, herbicide and internal standard, and the concentrations of 2,4-D in water (Figure 3).

Figure 3. 2,4-D calibration curve (Y = 0,04 + 0,18 X; R = 0,999) in water.



The chromatographic methodology applied to the detection of 2,4-D in water samples was sensitive to concentrations of 0.2 ug/L. The results indicated that there was no residue in the water during the years of 1996 and 1999 (Figure 4).

Figure 4. Chromatographic analysis of 2,4-D in water samples. A: peak 1, water with internal standard; peak 2, 2,4-D peak. B: water collected at Espraiado watershed, peak 1, water with internal standard; peak 2, 2,4-D (none present).
Column db-5 0,25 µm (0,25 mm x 30 m); tv = 220°c for 5 min; 25°c/min to 255°c; td = 255°c. Nitrogen flux = 22,0 ml/min; injection: split = 2 µl; detector = capture of electrons.



CONCLUSIONS

2,4-D was analyzed in surface and groundwater during the years of 1996 to 1999 using a gas chromatograph GC17-A equipped with electron detector (split/ splitless) (Shimadzu). There was a 99.9% correlation between the area of the peaks and the 2,4-D concentration indicating that the method was very efficient. No residue of the herbicide was found in water during the three years of testing.

The mathematical simulator model CMLS-94 "Chemical Movement in Layered Soils" was used to evaluate the leaching tendency of 2,4-D. The results indicated that a maximum depth of 60 cm was reached in soils away from the water table and that there were no residues. This indicates that there was no potential for groundwater contamination.

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