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Herbicides residues in soil and water from sugarcane area in Brazil

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INTRODUCTION

Harmful insects, mites, infectious fungi, bacteria and invasive weeds have been controlled by pesticides and herbicides involving a huge world market of more than 20 billions dollars annually (10). 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 crucial points on the environmental contamination, mainly of groundwater, causing problems of water quality. The evaluation of these impacts is difficult and expensive because demands high standard analytical equipment and qualified personnel.

The region of Ribeirão Preto city, (São Paulo State) located in Southeast of Brazil is one of the most important sugarcane producing area, with high levels of agrochemicals utilization. This region is also an important recharge area for groundwater supply for the Botucatu aquifer which comprises areas of eight Brazilian states plus parts of Argentina, Uruguay and Paraguay, with approximately 1,200,000 Km². Geological studies have identified a watershed, Espraiado, as a good research area selecting it as a model for studies of water and agrochemicals movement toward groundwater.

A previous study, made in 1994, by the Institute of Agricultural Economy (IEA, São Paulo) has defined 16 production units in the Espraiado watershed involving sugarcane, pasture for cattle, coffee plantation, and small properties with diversified crops. However, this diversification is not representative since sugarcane plantation occupies about 80% of the total area of the watershed. The information on the agricultural practices and herbicides utilization were collected through a farm survey. The following herbicides have been identified as the most commonly used in the area: atrazine, simazine, ametryne, tebuthiuron, diuron, 2,4-D, and picloran.

MATERIAL AND METHODS

P04	4.4	2.33	11.0	8.3	56.5	67.3	28.1	22.1	Clay
P06	4.4	3.88	14.3	15.59	58.7	60.9	22.5	19.6	Clay
P26	5.0	3.39	13.4	12.42	61.5	62.8	20.1	21.4	Clay
P20	14.3	13.9	27.7	31.33	10.3	45.1	47.6	9.57	Loam
P27	24.3	22.3	62.3	68.83	2.35	7.10	11.5	1.72	Sandy
P33	41.6	35.2	42.9	46.87	10.8	14.5	4.70	3.48	Sand loam
P35	29.3	26.5	65.0	68.33	2.40	2.65	3.30	2.50	Sandy
P23	46.1	48.6	34.1	39.49	4.20	9.70	15.6	2.21	Sand loam
P24	56.4	45.7	35.2	42.26	7.25	9.70	3.15	2.34	Sandy

HERBICIDES DETERMINATION IN WATER.

Surface water samples (1L) were collected from Espirado watershed during the period from January to July 1996 from different points. 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 0.22µ porosity. The filtrates were extracted with 12 mL dichloromethane and mechanical shaking for one hour (1,2,3).

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.(4,7,8,9). 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 sensitive 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.

HERBICIDES DETERMINATION IN SOILS.

Soil samples were grounded and passed through a 2mm sieve to obtain particles between 120 - 270 mesh. Five grams aliquots were extracted with 10 mL 1mM NaOH + 20mL ethylacetate for 30 min in ultrasound bath, followed by 16h in waterbath at 50°C with stirring (100 cpm). Organic phases were transferred to tubes, centrifuged during 5 min a 1800xg, and 10mL of ethylacetate fraction evaporated to dryness. Residues suspended in 1.1mL in water were submitted to purification in Supelclean envi-18 columns. Herbicides were eluted with 500uL methanol: ethanol (1:1), v/v. 100uL were applied to a liquid chromatograph.

RESULTS AND DISCUSSION

The analyses, in laboratory experiments, have shown the Clay (“Latossolo roxo”, “Latossolo” dark red), Sandloam, and Loam soils presented medium infiltration potential of water as opposed to Sandy soil which showed a high infiltration potential.

(Table 2), as expected. The Sandy soil, showed as blue area in Fig. 1, is located at the area of least declivity in the watershed making it much more susceptible for infiltration.

Table 2. Infiltration potentials and runoff of different types of soils of the Espiraiado watershed.

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

The pH determination of the soil samples revealed acidic pH, except in the point designated P04, classified as Clay and “latossolo roxo”. A significant seasonal variation of around 2 units was observed, with drop of pH in July samples as illustrated in the Figure 3 with samples from points P06, P33 and P35. In general clay samples were more acidic than the sandy one (P35). The pH of the 80-90 cm soil samples were usually (6 out of 9) more acidic than the surface samples (6).

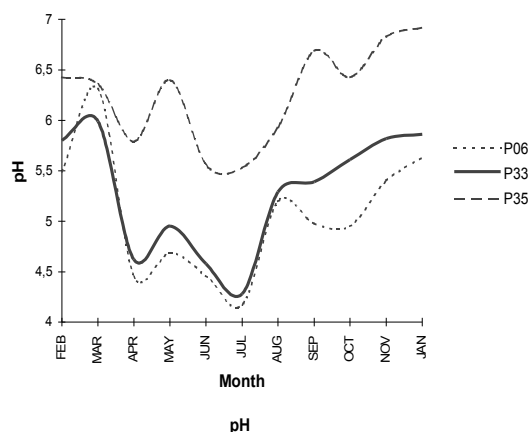
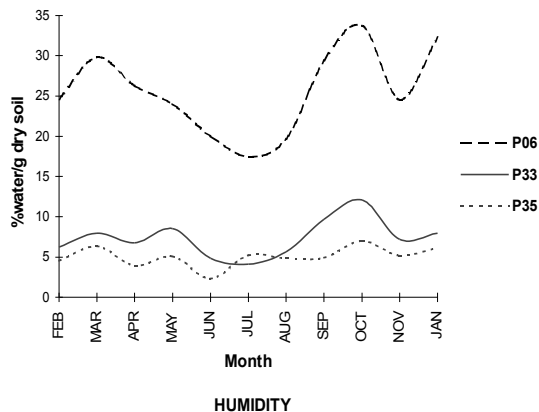


Figure 3 - pH values of soil surface samples from points P06, P33, and P35.



The determination of humidity has shown results compatible with those published in the literature. Figure 4 shows the seasonal variation of humidity of 3 samples (P06, P33, and P35). The clay point has revealed a variation from 17 to 34% water content (g/dry soil), while the points P33 and P35 an oscillation between 2.3 to 12% humidity. The lower values coincided with the dry and winter season of this region (6).

Figure 4 - Humidity variation as observed with samples from points P06, P33 and P35.

The studies with simulation analysis of the herbicides with soil types of the Espiraiado watershed showed the compounds hexazinone, atrazine, and tebuthiuron had the highest potential of reaching the groundwater level.(Table 3).

Table 3. 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 Dark Red (Clay)	7.3	3.7×10^{-5}
	Latossolo Roxo (Clay)	4.7	3.7×10^{-5}
Diuron	Sandy	4.9	1.5×10^{-4}
	Latossolo Dark Red (Clay)	0.77	1.5×10^{-4}
	Latossolo Roxo (Clay)	0.55	1.5×10^{-4}
Atrazine	Sandy	20.5	5.5×10^{-6}
	Latossolo Dark Red (Clay)	4.7	5.5×10^{-6}
	Latossolo Roxo (Clay)	3.1	5.5×10^{-6}
Ametryne	Sandy	8.0	4.1×10^{-6}
	Latossolo Dark Red (Clay)	1.5	4.1×10^{-6}
	Latossolo Roxo (Clay)	0.99	4.1×10^{-6}
Tebuthiuron	Sandy	10.7	3.5×10^{-6}
	Latossolo Dark Red (Clay)	4.6	3.5×10^{-6}
	Latossolo Roxo (Clay)	2.1	3.5×10^{-6}

Table 4. Average concentrations of herbicides $\mu\text{g/L}$ at surface water samples at nine points of Espiraiado ridge during the months of January, February, May, and July, 1996.

POINT	MONTH	HERBICIDES				
		Tebuthiuron	Diuron	Simazine	Atrazine	Ametryne
01	January	n.d.	0,05	n.d.	n.d.	0,06
	February	0,04	n.d.	n.d.	n.d.	n.d.
	May	n.d.	n.d.	n.d.	n.d.	n.d.
	July	n.d.	n.d.	0,02	n.d.	n.d.
02	January	n.d.	0,06	n.d.	n.d.	0,06
	February	0,04	n.d.	n.d.	n.d.	n.d.
	May	n.d.	n.d.	n.d.	n.do	n.d.
	July	n.d.	n.d.	0,08	n.d.	n.d.
03	January	0,02	0,07	n.d.	n.d.	0,08
	February	0,02	0,02	n.d.	n.d.	0,03
	May	n.d.	n.d.	n.d.	n.d.	n.d.
	July	0,06	n.d.	0,09	n.d.	n.d.
04	January	n.d.	0,07	n.d.	n.d.	0,06
	February	n.d.	0,04	n.d.	n.d.	0,03
	May	n.d.	n.d.	n.d.	n.d.	n.d.
	July	n.d.	n.d.	n.d.	n.d.	n.d.
05	January	n.d.	0,06	n.d.	n.d.	0,05
	February	n.d.	0,04	n.d.	n.d.	0,03
	May	n.d.	n.d.	n.d.	n.d.	0,02
	July	0,07	n.d.	0,03	n.d.	n.d.
06	January	n.d.	n.d.	n.d.	n.d.	n.d.
	February	n.d.	n.d.	n.d.	n.d.	0,03
	May	0,03	n.d.	n.d.	n.d.	0,05
	July	0,05	n.d.	n.d.	n.d.	n.d.
07	January	0,02	0,06	n.d.	n.d.	0,08
	February	0,03	0,09	n.d.	n.d.	0,05
	May	0,04	0,04	n.d.	n.d.	0,03
	July	0,05	n.d.	n.d.	n.d.	n.d.
08	January	n.d.	n.d.	n.d.	n.d.	n.d.
	February	n.d.	0,02	n.d.	0,03	0,03
	May	0,03	n.d.	n.d.	n.d.	0,02
	July	0,04	n.d.	n.d.	0,04	n.d.
09	January	0,05	0,21	n.d.	n.d.	0,13
	February	n.d.	0,07	n.d.	n.d.	0,06
	May	0,02	0,04	n.d.	n.d.	0,06
	July	0,03	n.d.	n.d.	n.d.	n.d.

Detection Limit: 0,02 µg/L n.d. = not detected (< 0,02 µg/L)

Surface water samples were collected during January to July 1996. Analysis of tebuthiuron, diuron, atrazine, simazyne and ametryne residues showed no significance amount of these products (above the Maximum Allowable Concentration) in the water ridge (Table 4), although in December, 1995, only two out of nine points presented ametryne concentrations above (0.17 and 0.23) the allowable 0.1 ug/L.

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