# Assessment of the impact of pesticides in water quality of Ribeira de Iguape River Basin, São Paulo.

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### ABSTRACT

This research was focused on the assessment of the water quality of Ribeira de Iguape River Basin, located in the Southeastern region of São Paulo State, where the ratio of water availability against demand is high. Remainder of Atlantic Forest represents high occupation of this area in Brazil. Agriculture is the main economic activity in the region, being tea and banana the main crops. The agricultural activities impacts on environment have been characterized in both surface water areas of catchments and drinking water. Water samplings were carried out during March/2002 to February/2003 period, and during January/2004, in 10 different catchments points along River Ribeira de Iguape and its main tributaries. Solid-phase extraction followed by high performance liquid chromatography coupled with UV/Vis detection was used to monitor several classes of pesticides such as carbamates, triazines, and nitroanilines. The results revealed that the water quality is associated with the season of rains and dries. Pesticide residues were found in most samples collected in the beginning of the rainy season, and high variability in their physicochemical properties was observed, due to the high precipitation index. From 152 samples analyzed, only 24% presented pesticides.

Key words: pesticide, water surface, water supply.

### **INTRODUTION**

The Ribeira do Iguape River Basin, an area of 25,000 km<sup>2</sup>,  $(23^{\circ} 30' \text{ S} - 25^{\circ} 30' \text{ S} \text{ and } 46^{\circ} 50' \text{ W} - 50^{\circ} 00' \text{ W})$  is the main of Brazil's Atlantic Florest intact remnants, with more than a million hectares of native vegetation, occupying less than 64% of this region's territory in 1998. Seven state parks, two ecological station and environmental protected areas have been created. More than a half million hectares are protected, economic activities are restricted. Its is the least urbanized region of the state of São Paulo. Seven state parks, two ecological station and tree environmental protected areas have been create. More than a half million hectares are protected areas have been create. More than a half million hectares are protected, restricting economic activities. This is the least urbanized region of São Paulo state. The watershed is 17.180,09 km<sup>2</sup>. The from Ribeira River hydrographic basin has a large agriculture influence on limnologic, physic and chemical characteristics. The surface water is used for agriculture, public supplying and far other uses.

Together with environmental and cultural elements of great interest, Ribeira Valley presents some lowest social values indicators of São Paulo State and Paraná, including the highest rates of child mortality and illiteracy. The population (about 350 000 inhabitants), does not have economical alternatives for sustainable development that

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could permit the rational use of huge environmental and cultural inherited patrimony. The economy in the Ribeira Valley is based on agriculture (bananas, tea), mining and extraction of forest products (palm heart). According to the Agricultural Secretary of São Paulo State, many different fungicides, insecticides and herbicides are applied in the region plantations and these substances belong to different chemical groups. The objective of this study is to investigate the seasonal and spatial variability in pesticides concentration in superficial and supplying water in Ribeira de Iguape River Basin and in supply water. The concentration of atrazine, simazine (triazines); aldicarb, carbaryl, carbofuran (carbamate) and trifluralin (nitroaniline) were measured in this work used Solid-phase extraction followed by high performance liquid chromatography coupled with UV/Vis detection.

# MATERIAL AND METHODS

#### SAMPLING SITES

Water samplings were carried out during March/2002-February/2003 period, and during January/2004 in 10 different catchments points along Ribeira de Iguape River and its main tributaries (Table).

City	Catchments	Latitude and longitude
Registro	Ribeira de Iguape River	Catchment S: 24° 28 24,5 WO: 47° 50 36,2
		ETA S: 24° 29 05,5" WO: 47° 50 58,9
Sete Barras	Ribeira River	Catchment S: 24° 23 32,0 WO: 47° 55 41,7"
		ETA S: 24° 23 <sup>°</sup> 28,7 <sup>°</sup> WO: 47° 55 <sup>°</sup> 42,7 <sup>°</sup>
Cajati	Jacupiranguinha River	Catchment S 24° 43' 48,9" WO: 48° 07' 55,0"
		ETA: S 24° 43' 39,8" WO 48° 07' 59,2"
Barra do Turvo	Pardo River	Catchment S 24° 45' 38" WO 48° 30' 26,2"
		ETA S 24° 45' 33,7" WO 48° 30' 14,3"
Cananéia	Itapirangui River	Catchment S: 24° 55' 55,0" WO: 47° 53' 39,3"
		ETA S: 24° 55' 55,0" WO: 47° 53' 39,3"
Eldorado	Ribeira River	Catchment S: 24° 31 09,0 WO: 48° 06 52,1/
		ETA S: 24° 31 <sup>°</sup> 12 <sup>°</sup> WO: 48° 06 <sup>°</sup> 51,2 <sup>°</sup>
Juquiá	Juquiá River	Catchment S: 24° 19 09,6 WO: 47° 37 31,4
		ETA S: 24° 18 <sup>°</sup> 46,0 <sup>°</sup> WO: 47° 38 <sup>°</sup> 25,3 <sup>°°</sup>
Iguape	Ribeira de Iguape River	Catchment S: 24° 40' 52,5" WO: 47° 35' 49,7"
		ETA S: 24° 42 <sup>°</sup> 28,2 <sup>°</sup> WO: 47° 33 <sup>°</sup> 58,8 <sup>°</sup>
Juquitiba	Godinhos` stream	Catchment S 23° 55' 29,6" WO 47° 03' 36,3"
		ETA: S 23° 55' 49,9" WO 47° 03' 54,3
Iporanga	Iporanga	Catchment: S: 24° 34 47,9 WO: 48° 35 29,6"
		ETA S: 24° 35 <sup>°</sup> 03,7 <sup>°</sup> WO: 48° 35 <sup>°</sup> 45,2 <sup>°</sup>

TABLE: Sampling sites description.

## METHODOLOGY

Pesticides were extracted by using solid-phase extraction (SPE) cartridges from SPE ENVI C<sub>18</sub> 500mg 3mL (polipropilene) Supelco and compounds were separated and quantifield by reverse phase using Liquid Chromatographic–HPLC with UV detection at 220 $\eta$ m (Lebre, 2000). Water samples (02 glass bottles, 1.000 mL from each sampling site) were buffered with monochloroacetic acid and potassium acetate in pH =3. Samples stored at 4 °C, transported to laboratory on São Paulo City and analyzed until 15 days past sampling. The analyses were realized at the Laboratory of Environmental Chemistry of the IPEN (Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil).

# **RESULTS AND DISCUSSION**

The monitoring showed that from 76 analyzed surface water samples: aldicarb, simazine and atrazine were detected in one sample, carbofuran was detected in sixteen samples and trifluralin was detected in three samples.

From the 76 drinking water samples: carbaryl and trifluralin were detected in a sample each, atrazine was detected in two samples, simazine was detected in four samples and carbofuran in seven samples. Although the concentrations detected were extremely low ( $\leq 2,25 \ \mu g L^{-1}$ ).

From total samples analysed, 15% (23 samples) were detected carbofuran. This result has been expected, because carbofuran is the more consumed active principle in the study region.

From twelve (12) analyzed samples of each catchment point, the biggest number of positive samples was detected at points cities as following: Iguape seven samples, Juquitiba six samples, Iporanga five samples and Sete Barras four samples.

The high pluviometric index had influences on carry of the pesticides for the Basin River, therefore it had greater incidence of positive samples in the rain period, as is presented on graph at the follow Figure.

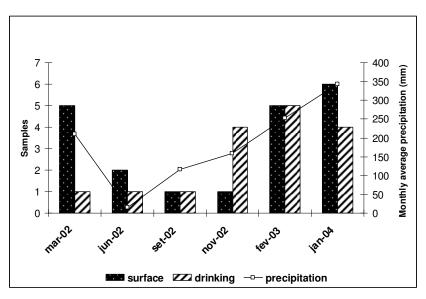


FIGURE - Comparative graph of the precipitation with the number of positive samples for pesticides residues.

### CONCLUSIONS

It was verified that the water quality is influenced by the seasonality. In rain periods, a higher pesticides concentration was detected in the surface water due to the runnof. It was observed that the surface water sample presented a bigger incidence of carbofuran residues due to the great mobility in water. The positive samples presented greater frequency during the rain periods, mainly, when the pluviometric index exceed 300 mm in the monthly average. One of the main contributory factors for this runoff effect was the floods, which frequently occur in this period. Although, the observed concentrations of the pesticide residues were low concentrations, the results denote contamination and impact of agriculture on the Ribeira de Iguape River Basin watershed. The control actions for preservation of the catchments points must be observed. The first line of defense is to protect the water of the contamination.

# REFERENCES

BARCELÓ, D.; Journal of Cromatography, 643(1993) 117-143.

BRASIL. MINISTÉRIO DO DESENVOLVIMENTO URBANO E MEIO AMBIENTE. CONSELHO NACIONAL DO MEIO AMBIENTE (CONAMA). Resolução nº 357 de 18/06/86, D.O.U., de 17/03/2005, Brasília. BRAZIL.

BRASIL. MINISTÉRIO DA SAÚDE. Portaria n<sup>0</sup> 518 de 25/03/2004, D.O.U., Brasília.

BRASIL. MINISTÉRIO DO MEIO AMBIENTE. Perfil Nacional da Gestão de Substâncias Químicas – PNGSQ, Brasília, www.mma.gov.br, janeiro 2003.

EPA Drinking Water Standasds and Health Advisories 822-B-00-001, SUMMER 2000, Office of Water 4304

HOGAN, D. J.; CARMO, R. L.; ALVES, H. P. F.; RODRIGUES, I. A. Desenvolvimento sustentável no Vale do Ribeira (SP): conservação ambiental e melhoria das condições de vida população. www.unicamp.br/nepo/staff/roberto/valeribeira.htm – 16/12/01.

LEBRE, D.T. Desenvolvimento de metodologia para a determinação de herbicidas e inseticidas em águas superficiais utilizando extração líquido - sólido e cromatografia líquida de alta eficiência. Dissertação de mestrado, IPEN, 140p. Maio 2000.

MARQUES, M.N.; COTRIN, M.E.B.; PIRES, M.A.F.: Pesticide Monitoring in Ribeira Valley, Southeastern Brazilian. In Anais do XI World Water Congress – Water Resources Management in the 21<sup>st</sup> Century, Madrid, 2003. 1 CD-ROM.

MARQUES, M.N. Avaliação do Impacto de Agrotóxicos em Áreas de Proteção Ambiental, Pertencentes à Bacia Hidrográfica do Rio Ribeira de Iguape, São Paulo. Uma Contribuição à Análise Crítica da Legislação sobre Padrão de Potabilidade. *Tese de Doutorado*, Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brasil, 2005.

PIRES, M.A.F; MARQUES, M.N.; COTRIN, M.E.B. Avaliação de novos herbicidas no controle de qualidade da água dos mananciais. In: Anais do II Congresso Brasileiro de Pesquisas Ambientais, Santos, Brazil, 03-04 junho 2002, CD ROM, 5p 2002.

PIRES, M.A.F.; et al. Revista Brasileira de Pesquisa e Desenvolvimento, vol 3, fascículo 2, novembro, 2001, p 127-138.

SABIK,H.; et al Journal of Chromatography A, 885(2000) 217-236

BIZIUK, M.; et al Journal of Chromatography A, 754(1996) 103-123.