# EVALUATION OF HERBICIDES AND CHEMICAL ELEMENTS AND ITS RELATIONSHIPS WITH BIOASSAY TOXICITY OF WATER AND SEDIMENT OF CORUMBATAI RIVER, SP, BRAZIL

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## INTRODUCTION

The Corumbatai River watershed is of great socioeconomic importance, provisioning water to seven municipal district of central part of Sao Paulo State. The basin is explored mainly by the culture of sugarcane and composed of soils with different physicochemical characteristics and relief varying from mountainous to plan. A great concern appears around the environmental behavior of pesticides and fertilizers employed in this basin. The Corumbatai river basin and tributaries (Claro Stream, Passa Cinco River and Cabeça River) extend over an area of 1,710 km$^2$, about 170 km$^2$ of extension. It is populated and affected by domestic and industrial wastes, with about 80% of the taken water coming back as effluents.

## OBJECTIVE

With the purpose of identifying the relationships of water and sediment toxicity along the river basin, ecotoxicological tests with aquatic organisms of different trophic levels such as: *Hydra attenuata, Daphnia magna* and *Pseudokirchneriella subcapitata* were correlated with chemical elements and herbicide residue analyses.

## METHODOLOGY

Water samples were collected in the middle of the channel at the surface using a 10 L bucket. Dissolved oxygen, pH, temperature and electric conductivity were measured in situ. Sediments samples were collected at the same time as water samples and transported refrigerated in plastic bags to the lab as recommended by USEPA (2000) and Burton (1992). Sampling were carried out every three months, from 2004 to 2006. The concentration of chemicals elements was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and the herbicides were determined by multiresidues analyses by CG/NPD and HPLC. The studied area, sampling points and sediment collection are shown in Fig. 1. The ecotoxicological tests were carried out as OECD (1998), Trottier et al. (1997), Blaise et al. (2000) and Fonseca and Rocha (2004). The sediments were used as elutriate from 1:4 sediment/water (w/w) mixture being tested organisms exposed to 100%, 75%,50%, 25 and 12.5% of elutriate and the results expressed as CL50 (48h) for Daphnia, CE50 (96) for Hydra, CL50 (72h) to algae (Fig. 2)

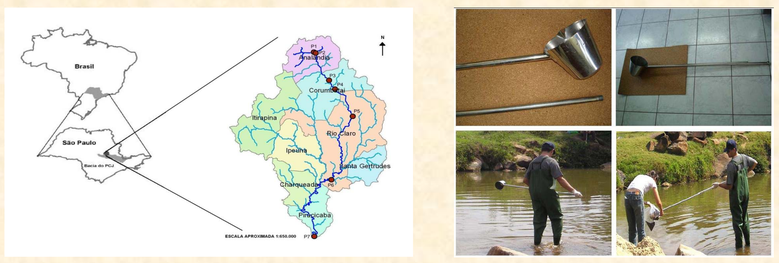




**Fig. 1.** The Corumbatai River basin and the sampling points

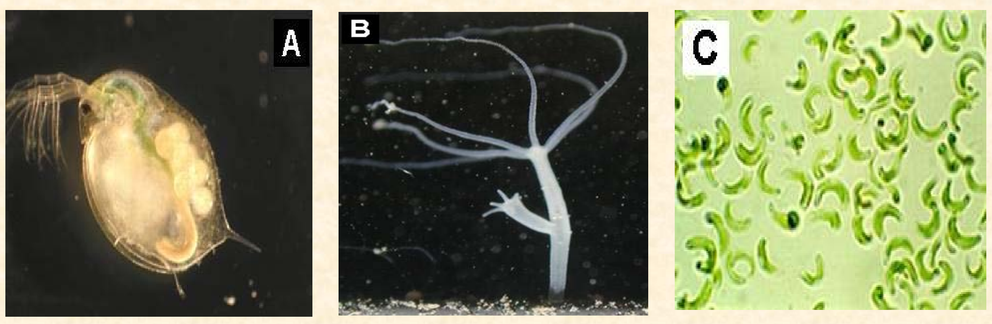


**Figura 2.** (A) *Daphnia magna*; (B) *Hydra attenuata*; (C) *Pseudokirchneriella subcapitata*

## RESULTS

For eight sampling times, every three month in different season of the year, from nov. 2004 to sep. 2006, the pH ranged from 6 to 7.5, with exception for Analândia point in dez. 2005, with a acidic condition (pH 4). Water physical and chemical quality harshly decreased after Rio Claro city. The D.O. (mg L$^{-1}$), electric conductivity (µS cm$^{-1}$), BOD and Turbidity are shown at Fig. 3. This values as BOD, nitrogen, phosphorus, total solids had shown a sharp increased showing the domestic sewage loading at point 6 and 7.

Water samples did not severally affected *Daphnia* population, on the other side, sediments samples were more toxic than water in all points sampled and for all organisms tested. *Hydra* (Fig.5), was more sensitive than *Daphnia* and less sensitive than *Pseudokirchneriella* (Fig. 6).

The dissolved chemical elements Al, Fe and the total Hg, Mn and Cd were in discordance with the legislation for drinking water, and the sediments did not show high concentration of elements. Table 1 shows the range of the total chemical elements determined in the water samples, in the seven points along Corumbatai River, in the period of 05-06.

The herbicide analyses residues of water sample showed mainly triazines and picloran, clomazone, hexazinone and glyphosate were present seasonally in some points (Fig.7).

## RESULTS

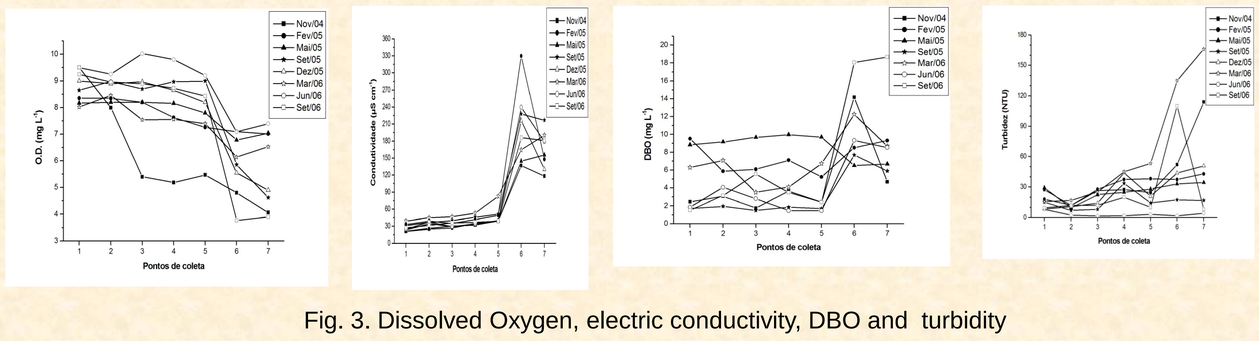


Fig. 3. Dissolved Oxygen, electric conductivity, DBO and turbidity

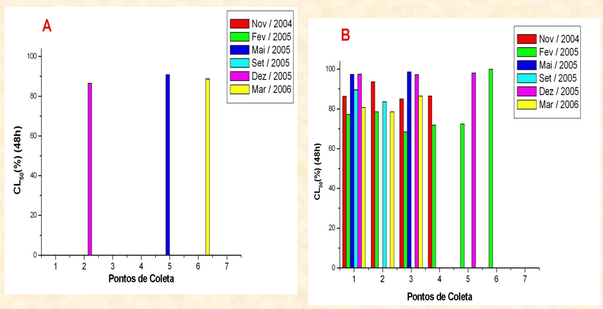


**Fig. 4.** CL50(48h) *Daphnia magna*, (A) water samples (B), sediments

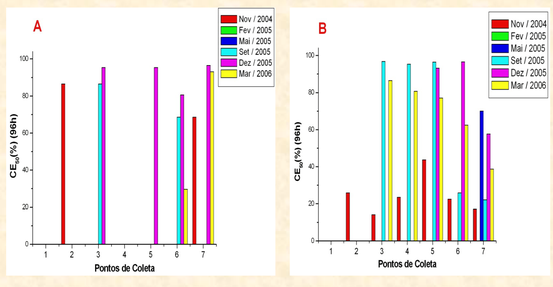


**Fig. 5.** CL50(96h) *Hydra attenuata* (A) water samples (B), sediments

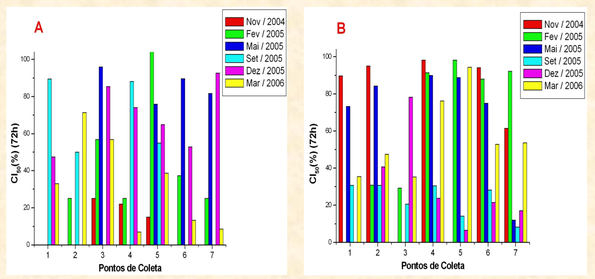


**Fig. 6.** CL50 (72h) *P. subcaptata*, (A) water samples (B), sediments

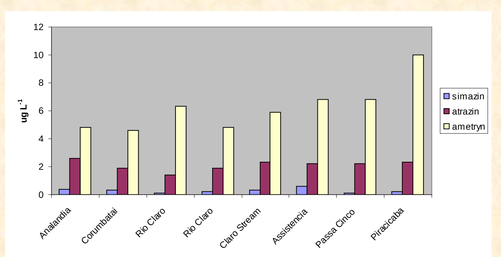


**Fig.7.** Media of triazines residues of water samples during the 2005 period.

**Table 1.** Total Chemical Elements in water sample colleted in set/05 to set/06 (**mg L-1), (*µg L-1)

| Teores totais | set/05 | dez/05 | jun/06 | set/06 |
|---|---|---|---|---|
| Na ** | 1,82-13 | 0,79-15 | 0,60-20 | 0,75-12 |
| Mg ** | 0,67-3,0 | 0,70-5,4 | 0,60-3,6 | 0,69-3,6 |
| Al ** | 0,35-2,2 | 0,15-3,3 | 0,22-0,51 | 0,25-5,5 |
| K ** | 1,2-3,8 | 1,2-3,8 | 0,93-3,0 | 1,5-3,7 |
| Ca ** | 1,2-6,7 | 1,2-8,6 | 0,99-7,9 | 2,0-13 |
| Cr * | 0,21-2,1 | 0,02-2,2 | 0,008-0,47 | 0,40-5,1 |
| Mn * | 0,04-0,15 | 0,05-0,14 | 0,03-0,10 | 0,05-0,20 |
| Fe ** | 1,0-3,4 | 1,31-4,9 | 0,75-2,3 | 1,3-5,6 |
| Ni * | 0,6-1,8 | 0,36-1,8 | 0,01-0,75 | 0,4-3,7 |
| Cu * | 2,0-4,1 | 0,32-4,3 | 0,30-6,3 | 0,07-9,1 |
| Zn * | 3,5-39 | 0,08-46 | 2,5-12 | 0,73-56 |
| As * | 2,0-4,5 | 0,03-1,2 | 0,03-0,4 | 0,2-1,3 |
| Cd * | 0,06-0,15 | 0,03-1,0 | 0,008-0,14 | 0,06-0,20 |
| Ba * | 71-94 | 46-68 | 37-48 | 42-71 |
| Hg * | 0,13-0,21 | 0,13-0,31 | 0,07-0,53 | 0,12-0,70 |
| Pb * | <0,021 | <0,021 | 0,009-0,78 | 0,10-6,6 |

## CONCLUSION

All sampled point had shown toxicity for all organisms tested. The herbicides seems to be the main source of toxicity for this organisms. The sediments had shown to be more toxic than water samples.

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