

## **Determination of organochlorines contaminants on river sediments and bottom feeding fish from Paraíba do Sul – Guandu River system - Brazil**

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### **Introduction**

The Paraíba do Sul - Guandu River is the unique source of potable water for more than 10 million people in the metropolitan area of Rio de Janeiro city. This watercourse crosses the most industrialised and populated region, water quality studies ought to be complemented with sediment analysis.

Until 1986, agricultural use of chlorinated pesticides also contributed for the contamination of this water body. Moreover, in 1988, a fire accident at Thyssen Foundry released 200 Kg of Askarel (a mineral oil containing PCBs) to River Paraíba Sul River<sup>1</sup>. All of the water treatment plants situated below this place had to stop the pumps until the toxic wave has passed.

This paper is short communication on the presence of chlorinated pesticides and polychlorinated biphenyls - PCBs) on river Paraíba do Sul sediments and bottom feeding fish.

### **Materials and methods**

River sediments were sampled using a metal scoop, adapted at the end of a 4 meter long aluminium rod. They were stored in acetone washed glass jars, and kept at 4 °C until analysis. All the solvents have residue analysis quality, and the glassware was rinsed twice with acetone prior analysis. 2-4 g. of wet sediment mixed with silica gel undergone a soxhlet extraction four 2 h. in a hot water bath (90°C). in order to extract water from the samples, a azeotropic mixture (15 mL) containing 25% of cyclohexane in n-hexane, was used. All contaminants are extracted using 20 mL of this mixture and retained in 2 mL of isooctane. The extract is evaporated down to 0,5 mL in a Kuderna-Danish. The Clean-up method used is described elsewhere<sup>2</sup>. After purification the extracts is fractionated into two phases: n-Hexane phase: This fraction will contain all of the PCBs and part of the organochlorines including HCB, aldrin, heptachlors and part of pp'-DDE to be analysed in the GC-ECD. n-hexane : diethyl ether (9:1) This fraction contains the remaining organochlorines in the GC-ECD (Lindane, endosulfan, dieldrin, endrin, DDT and other metabolites), Gas chromatograph conditions: Shimadzu GC-14B, with auto-sampler AOC-1400. Columns: CBP-1 (SE-30) and CBP-5 (SE-52/54). Injection: Splitless (30seg.) 300 ° C. Temperature program of the oven: 110 °C (1 min.); 15 °C/min up 170 °C; 7.5 °C/min up to 290 ° C, hold for 10 minutes. Total run time: 25 minutes. Electron Capture Detector (<sup>63</sup>Ni) temperature: 310 °C.

### Results and discussion:

All of the reported values express a dry weight basis. The organochlorinated pesticides and the OCs, PCBs and were normalized to 10% of organic matter. Sediments were sampled and analysed between 1994 and 1996. At 9 stations, organic micropollutants were present. In the same period, in other 8 stations, sediment samples were collected at the Guandu River basin. As most stations have coarse sandy sediment, the presence of organochlorines was hardly identified. As referred above, organochlorinated hydrocarbons, including PCBs were detected sparsely on the collected surface sediments. For example, no OC residues could be found neither at Itatiaia nor at Porto Real. After Volta Redonda, a relative low contamination with PCBs could be detected ( $\Sigma$  of PCBs = 19 ng/g). The relative contribution of the lower chlorinated congeners is evident, especially at Pinheiral ( $\Sigma$  of PCBs = 67 ng/g).

Among DDT and its metabolites, *op'*-DDT and *pp'*-DDE, were present between Volta Redonda (densely populated) and Barra do Pirai. The  $\Sigma$  of DDTs near Volta Redonda is around 225 ng/g. Traces of HCB near the first town were below 5 ng/g, while near Barra do Pirai this level was 5 times greater (25 ng/g). At Volta Redonda the presence of the cyclodienes heptachlor-epoxide and aldrin was detected in low levels (5-20 ng/g).

Tomassi in 1985, presented the first Brazilian survey on organochlorine levels in a urban coastal estuary in São Paulo State. These OC results are in the same range as the ones presented here. For example, our highest DDT value, 210 ppb, is similar of Tomassi highest result, 300 ppb. However, on lacustrine sediments from a freshwater reservoir (Lobo-Broa, SP), the highest reported value of DDT was < 8 ppb<sup>3</sup>.

Residue analysis of environmental samples was also conducted near important agricultural areas from Parana State in Brazil. They found that in 43% of the samples HCB could be detected. In 38% Aldrin was found and Heptachlor residues were present in 18% of the samples<sup>4</sup>. In water samples, other authors have found low levels in the Parana and São Paulo state water courses<sup>4,5</sup>. Twenty years ago, a report from CETESB, the Environmental Agency of Sao Paulo State (SE Brazil), presented concentrations of some organochlorines on bottom sediments from PSR basin, upstream from the Funil Dam that were 1000 times higher than the ones found in this work<sup>6</sup>. Ten years after, this contamination virtually disappear and no PCBs or organochlorinated residues were present on sediments collected in the Funil dam near the boarder between São Paulo and Rio de Janeiro states<sup>7</sup>.

In our study, the last agriculture area is now being industrialised. This helps to explain the low levels of organochlorine insecticides found. The presence of PCBs is more marked, reflecting the urbanisation and industrial Development of the Paraíba do Sul River Valley.

The core sample collected in 1996 presented high levels of PCBs, specially the highly chlorinated ones, that are in general less mobile. The increasing concentration pattern in deeper layers may reflect a higher input of these contaminants in recent past, which remounts to the accidental spill of ASKAREL<sup>1</sup>. Another core sample was collect at the same station in the same month of subsequent year. The concentrations are somewhat lower in the second core sample, but the same pattern persists with the contamination appearing to be quite stable. In this reservoir, dredging activities should be avoided in order to avoid a more pronounced water contamination.

Figure 1 presents a chromatogram of an extract of a deep layer of a sediment core sample collected in 1997 at Santana reservoir (part of the Rio Paraíba do Sul – Guandu River system that supply water for RJ city) and summarises PCB contents in this core sample. The other two chromatograms are from bottom feeding fish collected at the same place.

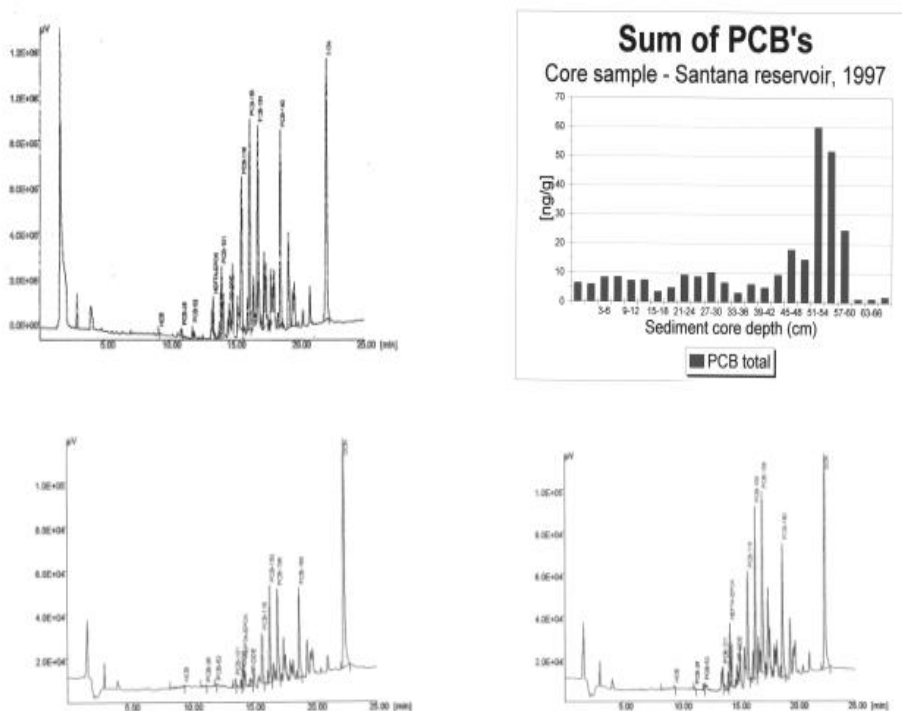


Figure 1- PCBs contamination at the Santana Reservoir (1997).

In 1997, two bottom feeding fishes that were also collected near the same area within the Santana reservoir were analysed and the pattern of contamination found was similar to Aroclor 1260, confirming that bioaccumulation of PCBs is prone to occur in this aquatic system.

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