

# ECOLOGICAL ACCIDENT DUE TO RESIDUE SPILL FROM A PAPER INDUSTRY - DETERMINATION OF PCDD\_F, VOLATILE AND SEMI-VOLATILE COMPOUNDS

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## Introduction

Due to the rupture of a residual tank from a paper industry, a toxic mixture was spilled and contaminated the rivers Pomba and Paraíba do Sul, as well as the seaboard in the north of Rio de Janeiro. This last location is one of the main water supply sources and also an important port in the city. As part of the mixture's compounds, there were toxic residual substances as caustic and metals such as lead in addition to other extremely toxic compounds, including dioxins and furans. It is believed that 1.2 to 1.6 billion litres of residues have been spilled from the tank. For this reason, thousands of people from several cities within the two states of the Federative Union had been out of water supply. Fauna died due to contamination. Recent and future damage caused to the environment and human health is still to be monitored and evaluated.

The quality of water in these points has been a major concern for the emergency work developed by the public institutions. The water supply has been interrupted in those regions, and so have fishing and agriculture practices.

## Methods and Materials

Several samples have been collected from various points of the rivers Pomba and Paraíba do Sul, where the accident took place, and also from the boroughs nearby. The sampling and preservation methods were applied under the USEPA regulations (United States Environmental Protection Agency). Fruit and vegetables samples have been collected as well.

These samples have been through an extensive volatile and semi-volatile search analysis using gas chromatography and mass spectrometry, under the methods suggested by USEPA 8260 (Purge and Trap) and 8270. PCDD/F's have also been analyzed for there was a high probability for the detection of such contaminants, once the material spilled could have been generated during the manufacturing of cellulose.

## Results and Discussion

It is important to note that the recovery program and the evaluation of the area affected by the accident is still in its initial step. Water quality has been prioritized, since the spill had affected its supply in the region.

Investigations have been implemented concerning the consequences of the accident towards the ecosystem's fauna and flora. Fish and sediment samples have been being collected for future analyses, which will determine toxic effects and bio-magnificence associated to these animals. Still, biologists estimate that the area will be fully recovered at least in a 10-year period.

It is possible to divide the organic volatile and semi-volatile compounds into two categories. First, the samples which have been contaminated directly by the accident, and then the samples that have been contaminated after the water treatment process and the exceeding  $Cl_2$  during one of its steps. This can be seen by the presence of contaminants classified as trihalometans. The conditions for such determination can be found in the location studied, that is, exceeding quantities of organic material and chlorine.

174 water samples have been tested during the monitoring. 143 samples were tested after the water had been treated, whereas 31 samples were collected from the rivers Pomba and Paraíba do Sul. Table 1 shows the total average drifts among three different groups of contaminants. It can be seen that there has been the presence of trihalometans after the water had been treated. The samples collected directly from the rivers present organic acids and phenols contamination only. True, it is noticed that in the samples collected after the water was treated didn't present any contamination by organic acids and phenols, but by trihalometans.

**Table 01: Total average values of contaminants found in the water samples**

Contaminants	Number of water samples (non-treated)	Average Concentration in water samples (non-treated, ppb)	Number of water samples (treated)	Average Concentration in water samples (treated, ppb)
Trihalometans	31	0,0	143	106.3
Organic acids	31	32.5	143	0.0
Phenols	31	56.9	143	0.0

Sixteen fruit and vegetable samples have been collected in the state's market suppliers. Analyses did not determine any contaminant, however it is recommended that a deep study be carried on this matter for these samples are considered non-representative ones.

Only eight samples have been through PCDD/F analysis. Right after the residue spill, two water samples from the river Pomba were collected and tested. As expected, they hadn't been contaminated. Though, about three weeks after the accident there had been collected samples from each river. Sediments samples had also been collected from the location next to the cellulose manufacture area. Since contamination was recent, the sample collected represented the first layer of the river's sediment.

Table 2 shows the results obtained according to the sampling locations.

**Table 02: PCDD/F's drifts in sediment samples**

Location	PCDD/F Concentration, pg/kg, I-TEQ
Porto do Moisés	320
Porto do Ceabra	120
Water Capture	270
Foz do Rio dos Macacos	10
Foz do Rio Paraíba	190
Porto das Barcas	87

According to the results, no high concentrations were observed. However, it should be emphasized that the samples were collected right after the accident. In addition, some of the rivers under analysis present high water flow, so they are considered to have a low sedimentation range.

Detailed research is still to be carried in order to determine an effective result related to the impact caused by this accident. After that, it will be possible to develop a recovery program for the areas affected. Studies concerning fauna (fish) in these rivers shouldn't be ignored either. However, any sample collection or analysis at this moment could lead to inaccurate results.

### References

1. Greenpeace, informativo na Internet, 03/04/2003.