# CONTAMINATION EVALUATION IN THE REGION AROUND THE SUBMARINE EMISSARY OF ARACRUZ CELLULOSE BY ORGANOCHLORINATED COMPOUNDS

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**ABSTRACT**

The organochlorinated are very dangerous compounds, because they are not biodegradable, they persist in nature for a long period of time. They are toxic to living organisms in certain concentrations and they can be incorporated to the trophic chain. It is know that in pulp mills that use chlorine in the bleaching process are the ones considered as the main sources of these compounds. This way, it is extremely important to monitor the presence of these compounds in the region round about those mills effluent launching, especially in the sediment, once it works as the final tank of most contaminants. The EOX analysis comprehends all organic halogens able for extraction present in the environment and it works as a pre-diagnosis of the environmental quality of the area being studied, so that, if the results are positive, it will be possible to go through a more accurate evaluation, which makes this kind of study economically more feasible, once each compound analysis separately requires higher expense. Thinking about this, the objective of this study was to evaluate the sediment contamination in the region around the submarine emissary of Aracruz Cellulose by halogen compounds.
Marine sediment samples were collected from 9 collection stations during two years of study (2001/2002). The EOX extraction was made by using polar solvents and the reading was made in the EUROGLAS equipment. The results showed that the region did not show contamination in the sediment of almost the whole region, concentration being statistically similar to the reference, except at station 7A which, although it had presented low concentration of EOX, it was considered different from the other stations, according to the multivariate analysis of Cluster. It is worthwhile to inform that the station 7A is located at 1,5 km from the submarine emissary, where the effluent of Aracruz Cellulose flows. Moreover, this is the only station that presents muddy sediment, so it can be seen as a dismissal area.

**KEY WORDS:** Organic halogen compounds, EOX, sediment, pulp mill, bleaching, modernization.

## INTRODUCTION

Among several contaminants that can be launched into an effluent, the POPs (heavy metals, organochlorinated, PCB etc) must be carefully observed. They are not biodegradable, they persist in nature for long time, they are toxic to living organisms in certain concentrations (Mhatre, 1991), and they can be incorporated to the trophic chain (Baby e Menon, 1987).
According to Hayer e Pihan (1996) and David *et al*. (1995), EOX represents a group of chemical compounds that can be naturally found in the environment, however, the anthropogenic contribution is considered one of the biggest environmental problems nowadays, because the organochlorinated can be found in industrial effluents, combustion processes, in the making and use of pesticides and in the mill effluent with chlorine-based bleaching, and this one is the most important. The organochlorinated compounds can be analyzed in many ways, one of them is by the EOX analysis, which is represented by the organic extractible halogens.
According to Sibley *et* al. (1997) since past decades, the paper and pulp mill has been increasing its actions towards the practices of environmental protection, focusing mainly the aquatic environment, which reflects a global concern about the chlorinated compounds, such as dioxins and furans, launched in the bleaching effluents. The impacts that have been already documented in recipient environments of this kind of effluent show effects in the biochemical and physiological systems, and

cause morphological abnormalities in fish and benthic invertebrates. Due to its toxicity, it is very important to quantify the EOX (Sibley *et al*., 1998).

It is known that, once in the environment, the compounds that are present in the effluent may complex to the material in suspension in the water and then deposit and accumulate in the sediment. According to Chapman (1990), Sundelin and Eriksson (1996), many contaminants, including the EOX (Palm e Lammi, 1996), have the characteristic of linking chemically or adsorb physically to non consolidated sediments for such long periods of time, turning the sediments into very enriched tanks when compared to the water, and it may cause chronic effects either to the benthic or epibenthic organisms, as well as to organisms that live indirectly on those organisms. Palm and Lammi (1996) showed that the analysis of the sediments is a good environmental indicator to the destiny of the organochlorinated in dismissal areas, when the study is combined to an estimative of the sedimentation rate.
This way, the purpose of this study was to evaluate the sediment contamination of the region around the submarine emissary from Aracruz Cellulose by halogen compounds.

## METHODOLOGY

• *Mill description*
Aracruz Cellulose S.A. is located in the State of Espírito Santo (Brazil) and it is among the main bleached cellulose pulp supplier worldwide, whose annual production is 2 million dry tones to the air (dta).
The plant has three pulping units and it is in the bleaching sector that the pure and clean product is obtained, through three different bleaching sequences. The sequence for production with bleaching Standard (STD) is C/D ($E_o$) $D_1$ ($E_2$) $D_2$, for ECF (Elementary Chlorine Free) it is D ($E_{OP}$) $D_1$ ($E_2$) $D_2$ and for ACF (Aracruz Chlorine Free) it is D $E_{OP}$ A Ch POP.
The factory effluents are submitted to primary (dry sump) and secondary treatments, where they are oxygenated during five days in aeration lagoons and finally, on the sixth day, the go to the stabilitization lagoon. The final effluent is taken to the sea through a submarine emissary, located at 1,7 km from the coast.

• *Sediment Sampling and Analysis*
The sediment samples were collected in 9 collection stations located round about the submarine emissary from Aracruz Cellulose, being two of the collections made in the Summer and two in the Winter, during the years of 2001 and 2002. Those stations were called 1A, 2A, 03, 4A, 05, 6A, 6B, 6C and 7A (Table 1). The points 03 and 05 are located close to the submarine emissary, i.e., place that receives the effluent discharge, while the stations 6A, 6B and 6C are considered reference and they farther from the submarine emissary.
The sediment samples were collected by a diver through a cylindrical tube with 10cm in diameter, in order to collect only the sediment from the surface because, according to Hakanson et al (1998), the greatest concentrations of EOX are limited to the first 5 cm of the sediment. After the collection was made, the samples were taken to the laboratory at Aracruz Cellulose S.A., where they were distributed into aluminum recipients and kept in the freezer. Then, the samples were defreezed, lyophilized and kept in amber bottle, rightly identified.
The EOX extraction method is not patterned yet and numerous methods have been applied for such purpose (Sibley *et al*.,1998).
The methodology used for the EOX extraction in the present work followed as a pattern the same method used by Palm and Lammi (1996) and it went through some modifications. The EOX analysis proceeded the following way: 50g of the sediment were extracted with apolar solvents (acetone and hexane). From this, two phases were generated (one layer of water and, over this one, an extractive layer). The supernatant was again separated, filtrated with sodium sulphate (to remove the water excess) and evaporated in the steam rotor until approximately 10ml. Following, 100 μl of hexadecane was added to the sample and it was then evaporated to 1ml with gaseous nitrogen. The sample reading was made in the EUROGLAS equipment model ECS 2000 (made in The Netherlands) at a temperature of 850°C. For each sample, two to three replicas were made and the result was expressed in mg/Kg and the detection limit was 0,1 mC (micro Coulomb).

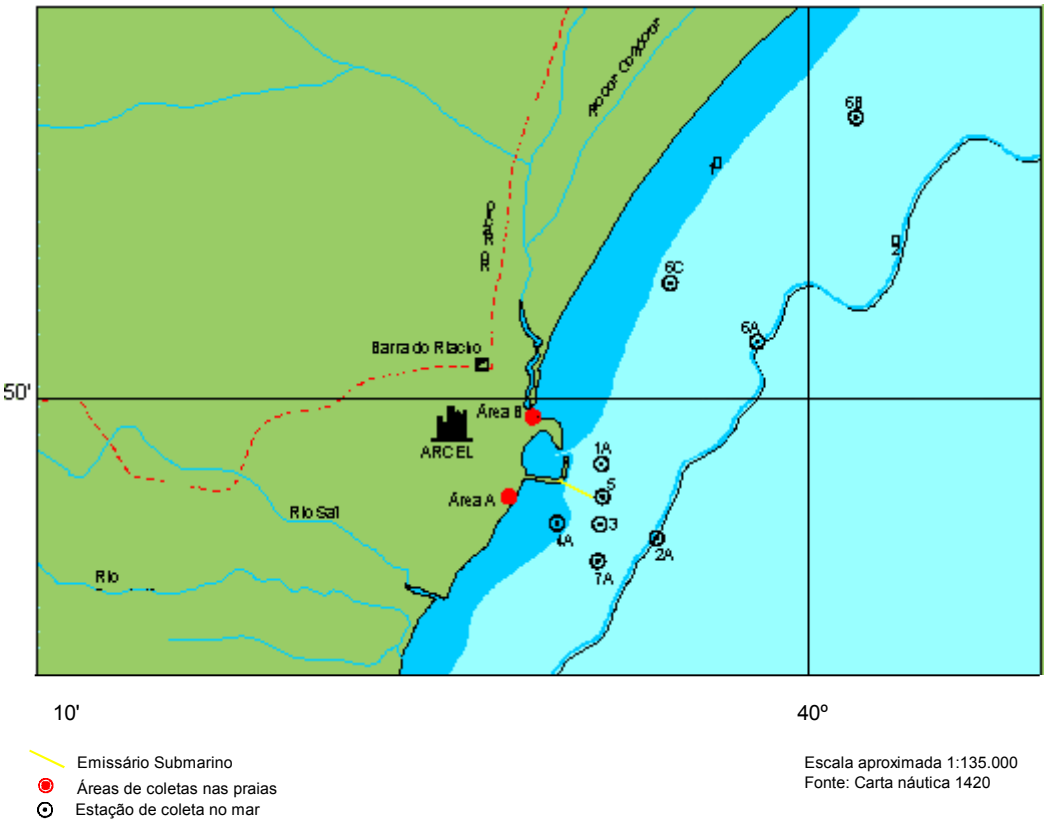


**Figure 1: Schematic Map of the Monitored Region.**

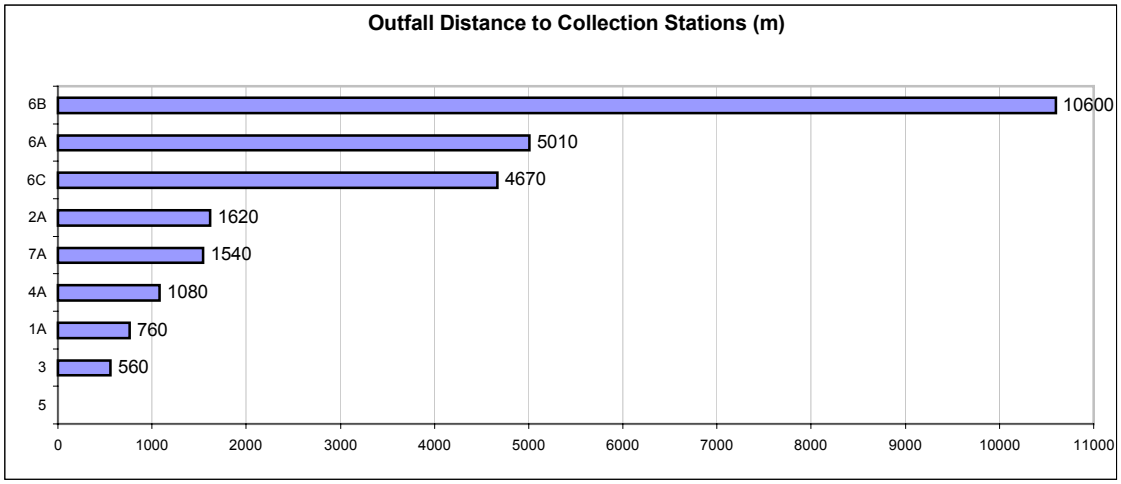


**Figure 2 – Distance in meters from the submarine emissary to each collect station.**

**RESULTS**

The results from the EOX sediment analysis found in this study were low in the whole study area, even in the closest spots to the submarine emissary from Aracruz (Table 1 and Figure 3).

**Table 1 – Results of EOX at the collected sediment in four sampling campaigns at the recepient body from ARACRUZ CELLULOSE INC.**

| Stations | RESULT (mg/Kg) | | | |
|---|---|---|---|---|
| | **08/15/01** | **12/18/01** | **07/09/02** | **12/04/02** |
| 1A | n.d. | n.d. | 0,13 | 0,12 |
| 2A | 0,12 | 0,17 | 0,05 | n.d. |
| 03 | 0,22 | 0,05 | 0,06 | 0,06 |
| 4A | 0,22 | 0,08 | n.d. | 0,03 |
| 05 | 0,13 | 0,12 | 0,17 | 0,06 |
| 6A | n.d. | n.d. | n.d. | n.d. |
| 6B | n.d. | n.d. | n.d. | n.d. |
| 6C | 0,05 | 0,04 | n.d. | 0,06 |
| 7A | 0,13 | 1,00 | 0,17 | 0,44 |

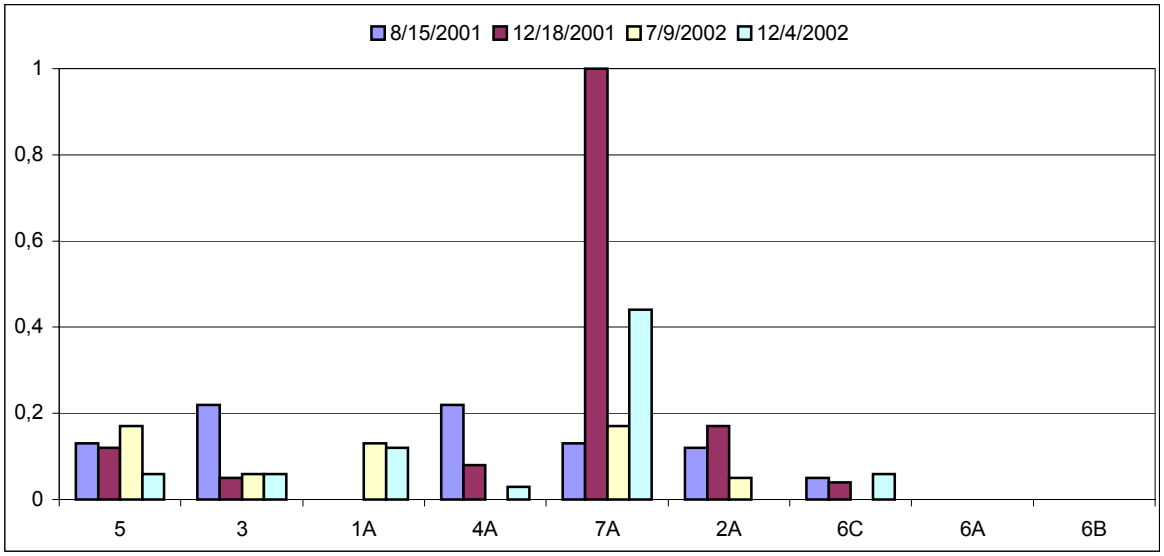


**Figure 2 – Results of EOX (mg/Kg) in growing order of distance from the outfall, about the two campaigns (2001/2002).**

Applying the new ANOVA statistics to the obtained data, it was observed that there was no meaningful seasonal variation (Table 2).

**Table 2 – ANOVA variation analysis comparing Winter x Summer results (2001/2002).**

| Year season | P |
|---|---|
| Inv. 2001 x Ver. 2002 | 0,562 |
| Inv. 2001 x Inv. 2002 | 0,415 |
| Inv. 2001 x Ver. 2003 | 0,842 |
| Inv. 2002 x Ver. 2002 | 0,384 |
| Ver. 2002 x Ver. 2003 | 0,518 |
| Inv. 2002 x Ver. 2003 | 0,692 |

The own ANOVA analysis applied, comparing each monitoring station (1A to 7A) to each reference station (6A, 6B and 6C) (Table 3), showed no significant variation, except at station 05, which is the closest spot to the effluent.

**Table 3 – ANOVA variation analysis comparing results among the monitoring stations.**

| Monitored Stations | P |
|---|---|
| 1A x 6A | 0,134 |
| 1A x 6B | 0,134 |
| 1A x 6C | 0,540 |
| 2A x 6A | 0,064 |
| 2A x 6B | 0,064 |
| 2A x 6C | 0,277 |
| 03 x 6A | 0,054 |
| 03 x 6B | 0,054 |
| 03 x 6C | 0,212 |
| 4A x 6A | 0,141 |
| 4A x 6B | 0,141 |
| 4A x 6C | 0,407 |
| 05 x 6A | 0,002* |
| 05 x 6B | 0,002* |
| 05 x 6C | 0,020* |
| 7A x 6A | 0,073 |
| 7A x 6B | 0,073 |
| 7A x 6C | 0,095 |

* Significant variation

Analysing the spatial variation through Cluster analysis, presented by the dendrogram below (Figure 3), it is possible to notice that the most significant numbers were the ones from station 7A, and this one was considered different from the other stations, concerning EOX concentrations.

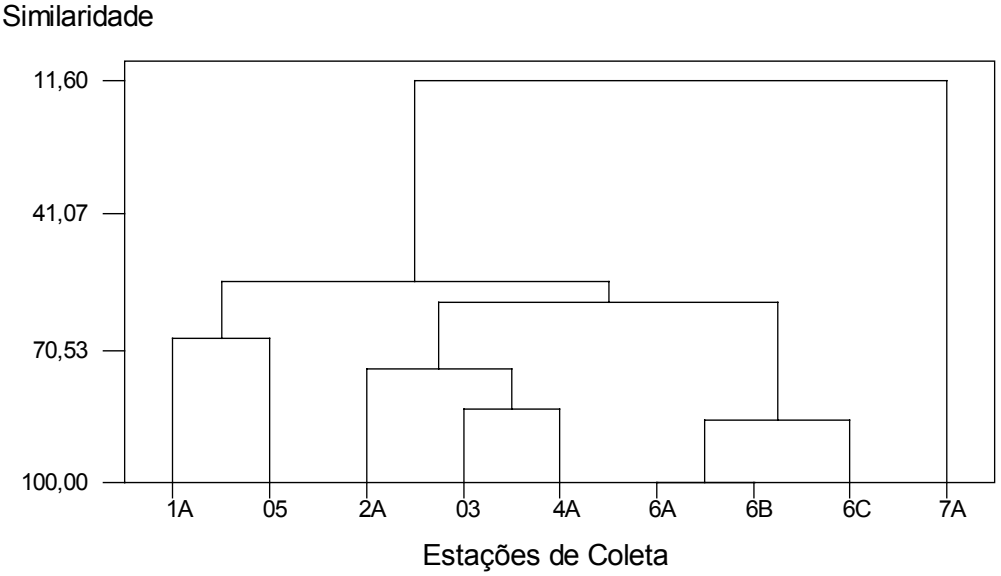


**Figure 3 – Dendrogram from the collection stations for EOX analysis.**

## DISCUSSION

The results found in this study revealed that the close areas to the effluent were insignificant statistically and environmentally.
According to Carlberg and Stuthridge (1996), concentrations of organochlorinated lower as long as the distance from the discharge place of the effluent in the recipient body (Table 4). In the present study, the numbers found were small, either in the collection stations near the outfall or at the farther ones, except for station 7A, which is located at 1,5 km from the effluent and presented the most significant values of this study, although they are still considered low numbers environmentally. However, it is necessary to monitor the sediment at station 7A, which was the muddy kind, indicating dismissal area because, according to Sibley et al (1997), the destination of the EOX is determined by the hydrodynamics and the depositional characteristics of the recipient body. That is why it can also be used to draw the contamination areas.

**Table 4: Comparative Table between the distance and the EOX concentration in three different studies.**

| Compound class | Effluent | Treatment | Recipient body | Country | Distance (Km) | Concentration (mg Kg-1 d.w.) | Reference |
|---|---|---|---|---|---|---|---|
| EOX | BKME | Secondary | River | New Zealand | 1,5<br>20<br>80 | 0,006<br>0,003<br>0,0004 | Stuthridge *et al.,* 1992 |
| | BKME | Secondary | Sea | Sweden | 5<br>15<br>36 | 5,27<br>0,7<br>0,25 | Hakanson *et al.,* 1988 |

## CONCLUSION

After the results obtained in this study, it is to conclude that the sediment exposed to the effluent from Aracruz Cellulose presented no meaningful environmental contamination by EOX, even in the closest areas to the place where the effluent flows neither in the farthest spots. Although it had presented low concentrations of EOX, the station 7A was named significantly different from the other monitored stations, which was due to the low hydrodynamics of the area, proven by the muddy characteristic of the sediment. That is why the place is considered a dismissal area.

There was no interference in the seasonality, once that, either the results obtained in the Summers or in the Winters of the years 2001 and 2002, showed low concentration of EOX.
This results shows that the final effluent treatment of Aracruz Cellulose is being very effective and/or the reduction in the use of ECF bleaching, a low concentration of EOX is coming and settling in the marine sediment of the recipient body from Aracruz.
For a more complete evaluation of the marine environment contamination by EOX, this study will be complemented in the future with EOX analysis in the sludge of the aeration lagoons, which treat the effluent from Aracruz Cellulose, as well as an analysis with clams, which have been the best way to evaluate bioaccumulative compounds, in order to evaluate if the EOX is being effectively hold at the aeration lagoons or if it is being released in the water column (which will be detected in the clams) and maybe being taken to farther areas, besides the studied region.

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