

MASTER  
96-165L



**CHLORINATED PHENOLIC COMPOUNDS IN  
BLEACHED KRAFT PULP MILL EFFLUENT  
RESULTING FROM 80% CHLORINE  
DIOXIDE SUBSTITUTION RATE**

**C. Alcaraz Zini and K.A. Terry**

**NWRI CONTRIBUTION NO. 96-165**

TD  
226  
N87  
No. 96-  
165  
c.1

**CHLORINATED PHENOLIC COMPOUNDS IN BLEACHED KRAFT PULP MILL  
EFFLUENT RESULTING FROM 80% CHLORINE DIOXIDE SUBSTITUTION RATE**

**Cláudia Alcaraz Zini<sup>1</sup> and Ken A. Terry**

**Aquatic Ecosystem Protection Branch  
National Water Research Institute  
Department of the Environment  
Burlington, Ontario, L7R 4A6**

**<sup>1</sup>Environmental Chemistry  
Riocell Technological Center  
Guaíba, RS, Brazil.**

**NWRI Contribution No. 96-165**

## **ABSTRACT**

Chlorinated phenolic compounds were analyzed in raw and treated effluents from Riocell - a kraft pulp mill located in South Brazil. The mill uses oxygen delignification as a prebleaching stage and 80% chlorine dioxide substitution in the first stage of bleaching process. The analytical methodology consists of extraction /in situ acetylation and high resolution gas chromatography / electron capture detector analysis. High resolution gas chromatography / mass selective detector is used to confirm the presence of monochlorinated compounds. Experimental difficulties occurred with some samples and are discussed. The results were compared with literature data and a preliminary evaluation of the toxicity of treated effluent was performed using toxicity equivalent factors. Cumulative reductions in secondary and tertiary treatment for AOX (adsorbable organic halogen) are 85% and for chlorinated phenolic compounds 84%.

## RÉSUMÉ

Des composés phénoliques chlorés ont été analysés dans les effluents bruts et traités, produits par Riocell, une usine de pâtes kraft située dans le sud du Brésil. Cette usine emploie un procédé de délignification à l'oxygène comme étape de préblanchiment et un mélange à 80 % de dioxyde de chlore dans la première étape du blanchiment. La méthode analytique comprend l'extraction/acétylation in situ et la chromatographie en phase gazeuse haute résolution, avec détecteur à capture d'électrons. Un système spectromètre de masse/chromatographe en phase gazeuse haute résolution sert à confirmer la présence des composés monochlorés. On examine les difficultés expérimentales rencontrées avec certains échantillons. En comparant les résultats avec ceux présentés dans la documentation scientifique, on a procédé à une évaluation préalable de la toxicité de l'effluent traité grâce à des facteurs d'équivalence de la toxicité. La réduction cumulative grâce au traitement secondaire et tertiaire est de 85 % pour les HOA (halogènes organiques absorbables) et de 84 % pour les composés phénoliques chlorés.

## **MANAGEMENT PERSPECTIVE**

**This report summarizes work completed during Ms. Claudia Zini's stay and training at the National Water Research Institute, Aquatic Ecosystem Protection Branch at the laboratory of Dr. Francis I. Onuska. The study presents the results of the analyses of raw and treated effluent from the Riocell kraft pulp mill in Southern Brazil. High resolution gas chromatography / mass spectrometry analyses of effluent from several pulp mill plants were used for comparative purposes. Toxicity equivalent factors were used to assess the environmental impact. Riocell (Brazil) uses the oxygen delignification process and 80% chlorine dioxide substitution to reduce the formation of chlorinated phenolic compounds.**

## **SOMMAIRE À L'INTENTION DE LA DIRECTION**

Le présent rapport résume les travaux effectués lors du séjour et du stage de formation de Claudia Zini au laboratoire de Francis I. Onuska, de la Direction de la protection des écosystèmes aquatiques (Institut national de recherche sur les eaux). L'étude présente les résultats de l'analyse de l'effluent brut et de l'effluent traité, produits par l'usine Riocell de pâtes kraft dans le sud du Brésil. Les résultats d'analyses par spectrométrie de masse/chromatographie gazeuse haute résolution des effluents de plusieurs usines de pâtes ont été utilisés à des fins de comparaison. Les facteurs d'équivalence toxique ont permis d'évaluer l'impact environnemental. Riocell (Brésil) emploie le procédé de délignification à l'oxygène et à 80 % de dioxyde de chlore pour réduire la formation de composés phénoliques chlorés.

## INTRODUCTION

About 90% of the chlorine used in the bleaching of kraft pulp ends up as salt at the end of the process and only 10% is found as organically bound chlorine. Eighty percent of these organochlorine compounds are of high molecular weight ( $>1000$ ) and they are commonly called chlorolignins. Only a small portion of the remaining 20% contains potentially harmful compounds, especially those with the capacity to penetrate cellular membranes and to bioaccumulate in adipose tissue of living organisms. The presence of chlorinated phenolic compounds (CPC) has received special emphasis because some of them are toxic, persistent and lipophilic.<sup>1-9</sup> Recently Folke et al.<sup>9</sup> suggested the presence of CPC as an indicative quality parameter of effluent from bleached pulp mills.

The environmental relevance of these compounds has led researchers from all over the world to develop appropriate analytical methodologies for matrices such as pulp mill effluent and sludge.<sup>7,10-15</sup> Practical analytical methods for the determination of toxics in wastewater are necessary for controlling their discharge and for evaluating their environmental impact.<sup>16</sup>

The concentration of CPC in effluent can be reduced through different internal process modifications or through external treatment. Riocell is already using oxygen delignification and 80 % substitution of chlorine dioxide in first D/C stage (D= chlorine dioxide, C= molecular chlorine). This results in a minor load of chlorine and a reduced Kappa number. The Kappa number is proportional to the lignin content of the pulp and reduced levels of both lignin and chlorine are essential factors necessary for lower levels of CPC. Riocell is an eucalyptus kraft pulp mill in South Brazil, currently producing 300,000 air dried market pulp(ADMT) a year, 10% of which are converted into paper. This work aims at presenting a preliminary analysis of Riocell effluent, considering the efficiency of the wastewater treatment plant, the levels of CPC in other pulp mill effluent, and related toxicological concerns. Another goal is to present the results of the analysis of effluents coming from wastewater treatment plants in several countries .

The main CPC may be classified in 5 different groups: phenols, guaiacols, catechols, syringols, and vanillins. Two other groups can be mentioned; syringaldehydes, and veratrols, in spite of the absence of hydroxyl group.

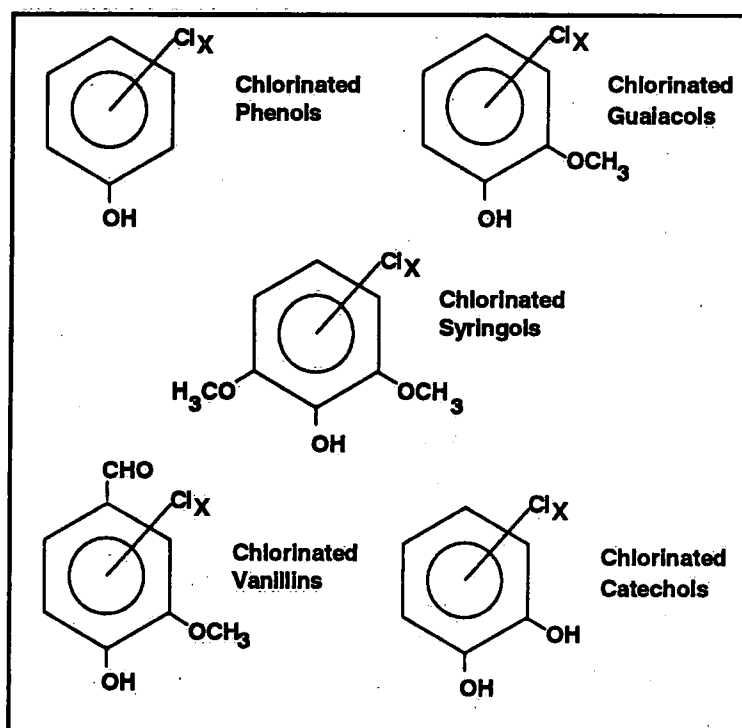


Figure 1: Chemical structures of the analyzed chlorinated phenolic compounds.



## EXPERIMENTAL

During the past 15 years efforts have been directed towards the identification and quantitation of these compounds.<sup>12</sup> Several extraction and derivatization procedures, and diverse chromatographic techniques have been used for the analysis of these compounds at trace levels. Although underivatized phenols can also be analyzed, derivatization techniques are preferred, because they improve peak shape, separation, and sensitivity.<sup>16</sup> Among derivatives registered in the literature some are acetates,<sup>10-12,14,17,18</sup> polyhalogenated derivatives such as pentafluorobenzyl ethers, pentafluorobenzoate, and heptafluorobutyrate esters.<sup>12</sup> Other derivatization reagents have been used like diazomethane, diazoethane<sup>19</sup>, and silanizing reagents.<sup>11,16</sup>

GC detection systems currently used for CPC analysis are electron capture (ECD), flame ionization (FID), and mass spectrometry (MSD), in either full scan or selected ion monitoring (SIM). ECD offers high sensitivity for compounds with two or more chlorine atoms, but both ECD and FID are nonspecific methods of detection. Full scan technique is not as sensitive as ECD but provides identification of the compounds. SIM and negative ion mode can be used to enhance sensitivity.<sup>12</sup> In this work the detection of chlorophenols was done by ECD and confirmation by MSD-SIM.

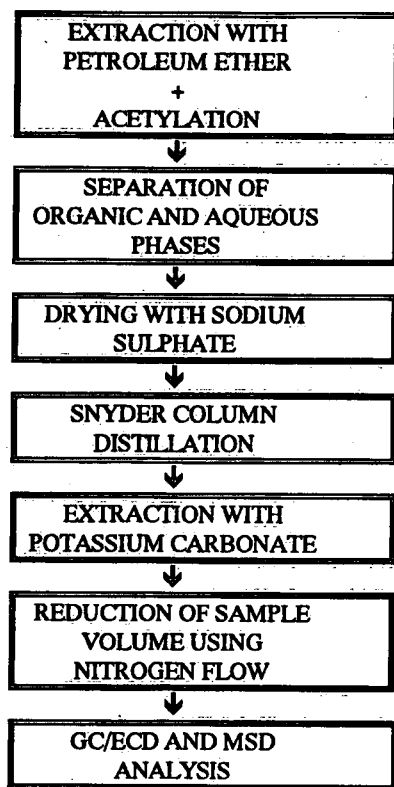


Figure 2: Simplified scheme of the methodology used for the analysis of CPC in pulp and paper effluent.

## METHODOLOGY

### Sampling

Grab samples of raw and treated effluent were collected in polyethylene bottles allowing for the residence time through the wastewater treatment plant. Sample containers were kept at 0 to 4°C .

### Reagents and Material

Glassware should be washed with detergent and water, cleaned by solvent rinse and baked at 450°C for one hour minimum.<sup>14</sup>

When standard solutions are not being directly used in the laboratory, they are stored in the dark at  $-20^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$  in screw capped vials with Teflon lined lids. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected and the level restored if solvent losses occur. Samples should also be stored at  $-20^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$ . Chlorovanillins are subject to gradual methylation, if dissolved in methanol. Therefore, the standards for these compounds must be prepared in acetone.<sup>14</sup>

Solvents used during analytical procedure were all distilled in glass (DIG).

(a) Analytical standards: 98% purity chlorinated phenolic compounds from Helix Biotech Scientific Ltd. (Vancouver, BC, Canada) and Aldrich Chemical Co. (Milwaukee, WI, USA). Standard solutions were prepared according to Lee et al.<sup>6</sup>

(b) Organic free water: distilled water extracted three times with DIG hexane or DIG petroleum ether.

(c) Sodium sulphate: reagent grade, baked overnight ( $400^{\circ}\text{C}$ ) and stored in clean glass bottle.

(d) Acetic anhydride: 3 times distilled. The fraction collected was at  $138-140^{\circ}\text{C}$ . It should be kept at  $-20^{\circ}\text{C}$  in the dark to minimize decomposition to acetic acid.

### **Instrumental Analysis<sup>10</sup>**

Analysis of the samples were performed using two 5890 Series II/GC Hewlett-Packard gas chromatographs, one of them coupled to an ECD with a  $\text{Ni}^{63}$  source, and the other equipped with a model 5989A mass spectrometer and data system. The volume of injection was  $1\mu\text{L}$ . On-column injector temperature was preset by oven tracking feature at a

temperature 3°C above oven temperature. The initial injector pressure and temperature were 18 psi and 70°C respectively. The oven was programmed at 70°C for 2 min, with an increase of temperature at 20°C/min up to 120°C for 1 min and a second programming rate at 5°C/min up to 270°C. SE-54 and HP-5 columns ( 25 m - 0.32 mm - 0.25  $\mu$ ) were used to separate compounds. High purity helium was used as the carrier gas set at 18 psi at 50° C and using constant flow on with electronic pressure programming (EPP).

For ECD system, the make up gas was argon-methane (95+5) and the temperature of the detector was 350°C.

In the GC/MSD system the temperature of the source was 200°C and the transfer line temperature was 250°C. The electron multiplier voltage was kept at 2000 V and electron energy at 70 eV. Ions used to confirm the presence of chlorinated phenols, guaiacols, vanillins, and syringols were: M+, (M - 42)+, (M - 42 - 15)+ and (M - 42 - 42)+.

AOX analysis was performed using an Euroglas BV Delft Holland analyzer.

### **Extraction and Acetylation Procedure**

The procedure is shown schematically in Fig. 2. Measure 50 mL of effluent and a convenient volume of the spike solution in a 250 mL Erlenmeyer flask. Adjust to pH 7 using either 1 N H<sub>2</sub>SO<sub>4</sub> or 1 N NaOH. Add 1 mL of 75 % K<sub>2</sub>CO<sub>3</sub>, 5 mL of triple-distilled acetic anhydride, and 30 mL petroleum ether. Stopper and stir with Teflon-coated stirring bar on magnetic stirrer. Separate the layers in 500 mL separatory funnel, drain water sample back into the original flat-bottom flask and collect organic layer in 250 mL round-bottom flask. Repeat this procedure twice using 30 mL petroleum ether and 1 mL acetic anhydride portions each time. Discard aqueous fraction after third extraction. Rinse separatory funnel twice with 10 mL petroleum ether portions and add rinses to petroleum ether extracts.

Pass the total extract through 4 cm anhydrous sodium sulphate column placed inside an Allihn funnel into another 250 mL round-bottom flask. Wash the sodium sulphate column with

25 mL petroleum ether and at the end of this operation apply the vacuum until sodium sulphate is dry. Remove the funnel, add boiling chips to extract and attach 3-stage Snyder column with 3 mL iso-octane and clamp the flask securely in a heating mantle. Adjust distillation to a moderate rate and reduce sample volume to 5 - 7 mL. Avoid a fast heating rate to minimize loss of the volatile compounds.

Let apparatus cool and wash the Snyder column with 3 mL of petroleum ether and quantitatively transfer the concentrated extract to 15 mL centrifuge tube. Further evaporate extract to 3 mL with a gentle stream of nitrogen and then dilute to 5.0 mL with iso-octane. Transfer the final extract to another 15 mL centrifuge tube containing 1 mL 1%  $K_2CO_3$ . Mix on a vortex mixer for 1 minute. Pass the organic layer through 9 mm Pasteur pipet packed with 5 cm anhydrous sodium sulphate supported by glass wool. Rinse aqueous layer twice with small portions of petroleum ether and pass them through the pipet also.

Evaporate the organic extract to 5 mL with a gentle stream of nitrogen and analyze by GC/ECD. The presence of monochlorophenols, catechols, and guaiacols should be confirmed by GC/MSD - SIM mode using a final volume of 1 mL. Samples were run in duplicate.

A blank and standard solution for calibration should be prepared concurrently with effluent samples, following the methodology described above, using 50 mL of organic free water and spike solution in order to achieve 0.4 ppm in the standard solution. The internal standard was 2,4,6-tribromophenol and the recoveries obtained were 107% for raw effluent and 80% for treated effluent.

For the sake of simplicity, the following abbreviations are used to denote various phenolics throughout this report; P for chlorophenols, G for chloroguaiacols, C for chlorocatechols, S for chlorosyringols, and V for chlorovanillins. The prefixes are the positions of chlorine substitutions. As an example, 345G stands for 3,4,5-trichloroguaiacol.

## RESULTS AND DISCUSSION

According to Lee et al.<sup>10</sup> this method tends to give low results for catechols. Catechols are susceptible to degradation by active sites on injection port liners and columns, and are subject to oxidation to the corresponding chloro-o-benzoquinones. They are also rapidly oxidized by atmospheric oxygen, particularly in alkaline solutions to the respective quinonoid compounds, and phenolic aldehydes are easy to oxidize to the respective carboxylic acids. Morales et al.<sup>12</sup> reported improved recoveries for catechols, vanillins and syringaldehydes in the presence of ascorbic acid. A small amount of ascorbic acid may be added to samples to prevent auto-oxidation. However, for pulp and paper industry in-process streams and untreated effluent, the addition of ascorbic acid may convert chloro-o-quinones to catechols if these quinones are present.<sup>14,20</sup>

Regarding procedures for breaking emulsions during effluent and sludge samples treatment, 6 different trials were tested. The addition of a saturated solution of  $\text{Na}_2\text{SO}_4$  was the most effective, although it is a laborious and time consuming method. Addition of methanol is not recommended because methanol promotes methylation of the aldehyde group of vanillins.<sup>10-12,14</sup>

Other suggestions in the literature are to reduce the sample initial volume and dilute it with organic free water,<sup>14</sup> or to pass the emulsion layer through a 2-cm internal diameter column containing 10 cm of loosely packed glass wool that had been washed with diethyl ether.<sup>16</sup>

Comparisons among concentrations of CPC in pulp and paper effluent are difficult because literature data are extremely variable regarding analytical approach and process characteristics of the mills. Data can be found concerning effluent of each of the bleaching stages or of total effluent; they can be presented as a general parameter (AOX for example) or presented one by one, or as a sum of each of the compounds analyzed. Dissimilarities in bleaching sequences and general process conditions also influence CPC concentrations found

in mill effluent. The focus of this discussion will be to compare CPC concentrations of different discharged effluent into the environment, and secondly to compare the characteristics of industrial process involved. Tables 1, Figures 3, and 4 show CPC concentrations in some different mill effluent. The legend of Tables 1, Figures 3, and 4 shows some characteristics of these mills.

Table 1 shows total CPC concentrations in effluent of 3 softwood bleached pulp mills (*B*, *F* and *G* mills), 3 hardwood bleached mills (*A*, *D* and *E* mills) and one mill using both hard and soft wood (*C* mill). Most of mills are kraft mills, except *G* mill which uses sulfite process. Mills *B*, *D*, *E*, and *G* have a low reduction of CPC concentrations during biological treatment. Tri- and tetra- chloroguaiacols and phenols were not degraded after a retention time of 5 days in the aerated lagoon at *B* mill.<sup>11</sup>

CPC concentrations of *E* mill raw effluent are similar to that of Riocell; however the efficiency of its secondary treatment is low. Both factories use a delignification process and a high chlorine dioxide substitution.

Riocell effluent enters into wastewater treatment plant with 49.9 ppb of CPC and after primary, secondary and tertiary treatment comes out with a total concentration of 7.7 ppb. Among the factories shown in Figure 3, the Canadian *F* mill had the greatest CPC reduction, but its performance is variable and the results are from pilot plant trials.<sup>21</sup>

During wastewater treatment, CPC reduction is a result of processes like volatilization, sorption, and biodegradation.<sup>5</sup> According to Nevalainen et al.<sup>22</sup> (*D* and *E* factories) there is a low accumulation of organochlorine compounds in sludge and volatilization is considered a minor process while effluent is being treated with activated sludge. Other research indicates that biomass adsorption is an important pathway for organochlorine compounds.<sup>5,21</sup> The biodegradation of CPC by activated sludge in the Attisholz (*G*) mill was low, although as a general process, it was predominant. Volatilization was not significant. The experience of the Canadian mill *F* showed a wide range of efficiency of CPC reduction (from 4% to 93%) using

oxygen in the biological treatment. Figure 3 presents the best performance of the *F* mill treatment plant. A substantial elimination of CPC took place during biological treatment with some organochlorine compounds considered resistant to biodegradation according to Rempel et al.<sup>21</sup> Other researchers point at biological treatment as an efficient process for CPC elimination through an adaptation mechanism of microbial population for some difficult to degrade compounds. The literature records a range of CPC reduction from 30% to 80% during biological treatment.<sup>11,21-25</sup> Data and explanations stated in the literature regarding CPC reduction process in bleached pulp mill effluent are not in agreement with observed data and lead to conclusions limited to the individual mills considered. This makes it difficult to extrapolate these conclusions to other biological treatment systems. Consequently a more detailed knowledge of sorption, volatilization, and biodegradation process will necessitate a further extensive study of the Riocell treatment system.



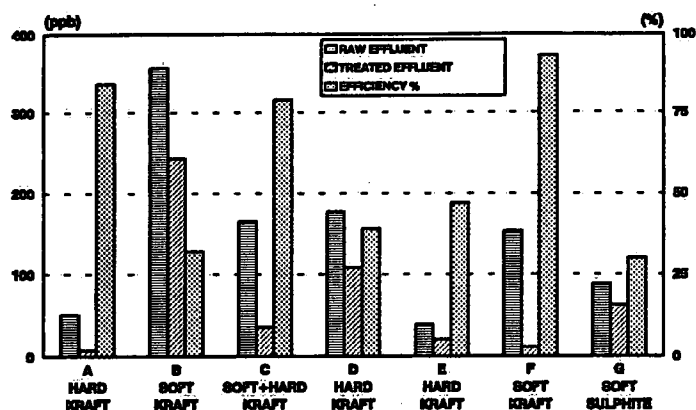


Figure 3: Total CPC reported in 7 bleached pulp mill effluent.

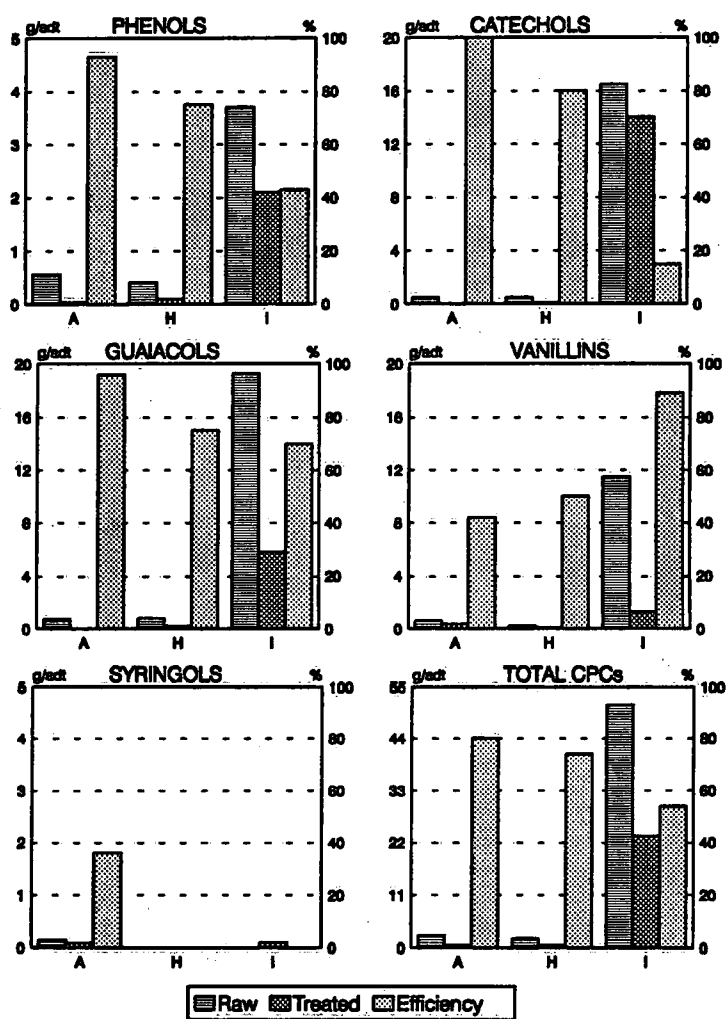


Figure 4: CPC loads in 3 kraft bleached kraft pulp mills.

Table 1: Concentration of chlorinated phenolic compounds in raw and final pulp mill effluent

Effluent CPCs(ppb)	A Brazil Riocell			C Canada <sup>10</sup>			G Swiss		
	raw	treated	reduction %	raw	treated	reduction %	raw	treated	reduction %
2P	*	*	-	-	-	-	-	-	-
3P	*	*	-	-	-	-	-	-	-
4P	*	*	-	-	-	-	-	-	-
26P	*	*	-	-	-	-	-	-	-
24P	9,8	*	100	6,1	*	100	7,1	5,2	27
35P	*	*	-	-	-	-	-	-	-
23P	*	*	-	-	-	-	-	-	-
34P	*	*	-	-	-	-	-	-	-
246P	0,9	*	100	7,9	5,1	35	-	-	-
236P	*	*	-	-	-	-	-	-	-
235P	*	*	-	-	-	-	-	-	-
245P	*	*	-	-	-	-	-	-	-
46G	6,0	*	100	10,3	*	100	b	c	-
345P	*	*	-	-	-	-	-	-	-
45G	6,9	*	100	9,1	*	100	b	c	-
2356P	*	*	-	-	-	-	-	-	-
6V	11,5	6,8 <sup>d</sup>	41	8,4	*	100	-	-	-
2345P	*	*	-	-	-	-	-	-	-
45C	*	*	-	1,8	0,5	72	-	-	-
345G	*	*	-	25,3	2,8	89	20,9	13,3	-
456G	1,5	0,5	67	8,8	1,2	86	3,4	2,2	35
56V	0,5	*	100	15,2	0,9	94	-	-	-
23456P	0,3	0,7	-	1,3	0,6	54	1,9	1,4	26
345C	9,7	*	100	9,9	6,4	35	-	-	-
3456G	*	*	-	34,8	5,5	84	16,2	14,1	-
345S	2,8	1,7	39	5,5	0,6	89	-	-	-
3456C	*	*	-	17,2	10,6	38	-	-	-
2346F	-	*	-	3,1	1,1	64	7,3	4,9	33
346G	-	-	-	-	-	-	3,4	2,8	18
346C	-	-	-	-	-	-	-	-	-
35C	-	*	-	0,6	*	100	-	-	-
phenols	11	0,7	94	18,4	6,8	63	36,1	28,5	21
catechols	9,7	*	100	29,5	17,5	41	-	-	-
guaiacols	14,4	0,5	95	88,3	9,5	89	51,9	33,3	36
vanillins	12,0	6,8	43	23,6	0,9	96	-	-	-
syringols	2,8	1,7	39	5,5	0,6	89	-	-	-

Legend of Table 1, Figure 3, and Figure 4:

\* not detected

- not analysed

A. Riocell ( HBK: hardwood bleached kraft pulp mill) - bleaching sequence is  $O_2$  - D/C (80/20)-EDE<sub>H</sub>D.  $O_2$  is the oxygen delignification process. D/C (80/20) is the bleaching stage where 80% of chlorine dioxide and 20% of elemental chlorine is added to pulp. E is an extraction stage, D is a bleaching stage with chlorine dioxide, and E<sub>H</sub> is an extraction stage with hypochloride. Biological treatment consists of an activated sludge system followed by a aluminum sulphate addition and two clarifiers.

B.(SBK: softwood bleached kraft pulp mill) - 5 days of biological treatment in aerated lagoons.

C. (HBK + S: hardwood + softwood kraft pulp mill).

D. HBK - it is considered only the sum of chlorinated phenols, guaiacols, and catechols, although the authors do not discriminate which compounds were considered. The values presented should be considered only as an estimation. Bleaching sequence is C-E-H-D-E-D and the effluent treatment was done on a pilot scale. C is a bleaching stage with elemental chlorine and H is a bleaching stage using hypochloride.

E. HBK - the same as D, except the bleaching sequence:  $O_2$ -D/C-E-D-E-D. The authors do not mention the percentage of chlorine dioxide substitution.

F. Western Pulp (SBK) - bleaching sequence D/CEoDED with 30% of chlorine dioxide substitution. Secondary treatment makes use of activated sludge on a pilot scale and long retention times. Eo represents a bleaching oxidative extraction stage.

**G. Cellulose Attisholz Corp. (SBS: softwood bleached sulfite pulp mill) - Effluent is treated through two aeration tanks, each followed by settling tanks. Tables 1 and 2 list the sum of concentrations of chlorinated phenols and guaiacols.**

**H. Aankoski mill operated by Oy Metsa-Botnia Ab. (HBK + S) - The bleaching sequence is (D/C = 66/34) EDED. Effluent is treated by primary clarifier, activated sludge, and secondary clarifier. Data shown in Figure 4 are related to hardwood input for both mills: H and I.**

**I. Kemijarvi mill of Veitsiluoto Oy. (HBK + S) - The bleaching sequence is (D/C =20/80) EHDED. Effluent is treated by primary clarifier and an aerated lagoon with 10% of its area provided with aerators.**

**a. 100% means that it was not possible to detect the CPC in the effluent, that is , if the CPC is present in the samples it would be below detection limit (DL) of applied analytical methods. DL of data listed in Table 2 is in the range of 0.5 - 1.0 ppb.**

**b. Dichloroguaiacol concentrations are expressed as a sum of the 3 isomers: b= 8.0 ppb and c= 3.7 ppb and the reduction is 54%.**

**c. 6V was not confirmed by GC/MSD data.**

CPC concentration in Riocell mill effluent should be calculated using the dilution of these compounds in the receiving body. A rough estimation of the dilution can be done considering the effluent flow and the average flow of the Guaíba River during its low flow period ( $730 \text{ m}^3/\text{s}$ ). Thus the effluent comprises 0.07% of the flow of the river.<sup>26,27</sup>

6V is the prevailing CPC in treated effluent, even after a 57% reduction during the treatment process. According to Voss et al.<sup>28</sup> the presence of substantial quantities of chlorinated vanillins is characteristic of E stage of the bleached kraft mill process. C mill uses hardwood and softwood and has vanillins in its effluent. The Riocell mill effluent results in 3.4 ppt of 6V in Guaíba River. Little is known of the toxicity of chloro-vanillins; however, the smaller the number of chlorine substituents in the molecule the lower its toxicity.<sup>4,29</sup>

456G and 345S concentrations were reduced by 67% and 43% respectively during effluent treatment and their concentrations in receiving waters from the Riocell mill are estimated as 0.3 ppt for 456G and 1.1 ppt for 345S. 456G concentrations in potable water of the Finnish cities Janakka and Jyväskylä are 9 and 25 ppt respectively, about 30 and 83 times higher than that estimated for the Riocell mill contribution to the Guaíba River. 345S presence is characteristic of mills that use hardwood as wood input, like the A and C mills.<sup>28</sup> 345S reduction was better in the C mill than in the A mill.

23456P can originate from wood preservatives, combustion, pesticides and pulp mill bleaching process.<sup>24</sup> Pentachlorophenol concentrations in Riocell effluent are similar to those from other mills listed in Table 2. There appears to be no reasonable explanation for a higher concentration of 23456P in treated effluent compared to raw effluent, and it is necessary to further study the Riocell wastewater treatment plant to have a more precise picture of its performance. The Riocell contribution of 23456P is estimated to result in 0.5 ppt in the river. Pentachlorophenol in potable water of Janakka and Jyväskylä is 46 times (23 ppt) and 10 times (5 ppt) higher than in the Guaíba River. The Swiss Environmental Protection Agency suggests 100 ppt as an acceptable concentration of 23456P in rivers.<sup>8</sup> Considering the toxicities of

trichlorinated phenolic compounds are similar to that of 23456P and summing up the concentrations of 456G, 345S, and 23456P it is possible to estimate the Riocell mill contribution in receiving waters to be 1.9 ppt. Because of the high dilution in the Guaíba River system, the resulting concentration is 52 times smaller than the "acceptable concentration" suggested by the Swiss Environmental Agency for 23456P in river waters. Laboratory studies have shown that degradation of pentachlorophenol is possible aerobically and anaerobically.<sup>29</sup> Aerobic degradation goes through dechlorination and further aromatic ring cleavage.<sup>30</sup> However, this compound is considered resistant to degradation in the environment.<sup>24</sup>

Some modifications that have already been tried in order to reduce the organochlorine content in many different mills are: lower input of chlorine, replacing  $\text{Cl}_2$  by  $\text{ClO}_2$ , temperature of chlorination, chlorination final pH, etc. Among these parameters substitution of  $\text{Cl}_2$  by  $\text{ClO}_2$  appears to be the best alternative. The low concentrations obtained in raw and treated effluent of the Riocell mill confirm that delignification followed by a high percentage of chlorine dioxide substitution can generate a lower environmental impact effluent. Recent trials with 100% chlorine dioxide substitution have demonstrated the practical elimination of CPC.<sup>28,31,32</sup> According to Voss et al.,<sup>11</sup> the use of 100% chlorine dioxide substitution generates only small amounts of 6V, which was also confirmed in the Riocell effluent. Kachi et al.<sup>3</sup> also describe the formation of small quantities of monochlorinated phenolic compounds and the predominance of non-chlorinated phenolic compounds.

According to Folke et al.,<sup>9</sup> the total content of CPC in a modern mill is about 100 ppb and the limit of discharge of CPC to the environment when using BAT (best available technology) is less than 0.5g/air dried ton(ADT). Riocell levels are at 9.7 ppb for CPC concentrations and its discharge is 0.5g/ADT.

Figure 4 shows total CPC and each one of the CPC categories in terms of load per ADT, and compares Riocell data with those found in the literature for 2 Finnish kraft mills. Riocell and Aankoski mills (H) present similar load levels and effluent treatment efficiency,

and this could be expected because both mills use hardwood and modern technologies. Vanillin loads are higher at Riocell than at H mill and the removal efficiency is lower for Riocell.

AOX (adsorbable organic halogen) values in raw and treated effluent are 0.63Kg/ADT (12.41mg/l) and 0.09Kg/ADT (1.78 mg/l) respectively. This represents an 85% reduction in AOX, and the figure of 0.09Kg/ADT is nearly 17 times lower than the Canadian limit stipulated in February 2/93 (1.6Kg/ADT) and 9 times lower than the value that will be stipulated in 1999(0.8Kg/ADT).<sup>32</sup>

Although preliminary analysis of Riocell's effluent have shown CPC concentrations and AOX values below some international standards, further research is needed to minimize environmental impact through industrial process improvement and/or new external treatments.

### Toxicity

Although the CPC are a small part of all chlorinated compounds present in the bleached kraft pulp effluent, these compounds are important because of their acute toxicity to fish, their bioaccumulation, and persistence in the environment.<sup>8,11,24,30,33</sup> However, to date there has been no scientific evidence to show that the discharge of chlorinated phenolics by pulp mills is responsible for actual adverse biological effects in aquatic environments.<sup>4</sup> Biomarkers such as MFO (mixed function oxidase) activity are regarded as sensitive indicators of exposure to contaminants, and have shown increased enzyme activity in bleached and nonbleached kraft mills.<sup>34</sup> Other researches concluded that there were no differences in fish responses between a kraft mill with secondary treatment, a kraft mill producing primarily unbleached pulp and mills using the sulfite process.<sup>35</sup> Effluent from TCF (totally-chlorine-free) sequences (i.e., OQP- oxygen-quelants-hydrogen peroxide - and OZEP - oxygen-ozone-extraction-hydrogen peroxide) were found to show chronic toxicity to *Ceriodaphnia*.<sup>36</sup> Nevertheless, the concern and the controversy around the discharge of CPC compounds by pulp mills remains because there is still a lack of knowledge concerning the relationship between biological response and chemical pollutants.<sup>37-39</sup>

Recently, Kovacs et al.<sup>4</sup> have published a set of toxicity equivalent factors (TEF) to tentatively relate the toxicity of CPC to that of pentachlorophenol, generally the most toxic of the group. Similar method has been used for relating the toxicity of the many different forms of chlorinated dioxins and furans to that of the most toxic member of this family of compounds, namely 2,3,7,8-tetrachlorodibenzo-p-dioxin. Aquatic TEF were estimated using published chronic toxicity data for fathead minnows, rainbow trout, zebra fish, American flagfish, and sea urchins. By using TEF numbers, the potential combined toxicity of complex mixtures of such compounds can be predicted from analytical data by assuming simple additivity of the toxicity of individual components. Table 2 presents TEFs for CPC:

Degree of chlorination of phenolic compound	TEF value
monochloro-	0.04
dichloro-	0.1
trichloro-	0.2
tetrachloro-	0.5
pentachloro-	1.0

Table 2: Toxicity equivalent factors (TEF) for CPC from bleached kraft pulp effluent.<sup>4</sup>

Focusing attention on Riocell's effluent, the total toxicity equivalent of CPC is 6.1 ppb in raw effluent and 1.3 ppb in treated effluent. This is much lower than the predicted value of an 11 ppb mixture that would probably not cause aquatic chronic toxicity. The NOAEL (no observed adverse effect level) of rainbow trout to pentachlorophenol is 11 ppb, and it was the most sensitive species to chlorinated phenolics. The equivalent toxicity (TEQ) of Riocell's treated effluent is roughly 8 times lower than the threshold value recommended for an effluent



in order to prevent chronic toxicity. Considering the dilution of the effluent in receiving waters, the contribution of Riocell can be estimated as 5.4 ppt of CPC and 0.9 ppt of TEQ.

Despite the limitations of the data used to calculate TEFs, this model is useful to provide an estimate of the toxicity of complex mixtures of CPC. Further improvement of this simplified approach will probably provide a fast, simple, and low cost method for toxicity evaluation of this kind of effluent. Acute toxicity tests of treated effluent performed from Jan. 21 to Feb. 1, 1993 using *Daphnia similis* EC 50; 48 h Claus 1879 (Cladocera, Crustacea), indicated a lack of acute toxicity. The chronic toxicity were evaluated from Jan. 25 to Feb. 3, 1993 using *Ceriodaphnia dubia* Richard, 1894 (Cladocera, Crustacea).<sup>27</sup> The NOAEL was 75%, which means that there is no chronic effect in *Ceriodaphnia dubia* after 10 days of exposure to a 75% treated effluent and 25% water solution.

A review dealing with the effects of pulp mill effluents in the aquatic ecosystem concluded that no complete mechanistic link had been shown that relates exposure to contaminants in pulp mill effluents to "within-organism" responses, "whole-organism" effects and effects at the population and community level. The increased environmental concern has become a significant driving force for stricter regulations of potentially noxious compounds in the effluent and for the generation of new technologies in prebleaching, bleaching, and after bleaching stages.<sup>40</sup> Although modern mills present a lower environmental impact than the conventional ones, the remaining impact should still be minimized. Consequently, there is an urgent need to integrate efforts to identify compound(s) responsible for adverse effects on aquatic life and to develop internal and/or external process to minimize the effluent load through recycling.<sup>25,32,34,37,39</sup>

## REFERENCES

1. Berry, R. M., Luthe, C.E., Voss, R. H. et al. June 1991. The Effects of Recent Changes in Bleached Softwood Kraft Mill Technology on Organochlorine Emissions: An International Perspective. Pulp and Paper Canada. v.92, n. 6, p. 43-55.
2. Walden, C.C., Howard, T.E. April 1981. Toxicity of Pulp and Paper Mill Effluents: a Review. Pulp and Paper Canada. V. 82, n. 4, 115-122.
3. Kachi, S., Yonese, N., Yoneda, Y. 1979. Low Molecular Weight Compounds Related to the Toxicity of Beech Spent Bleaching Liquors. In: CPPA/TS ENVIRONMENTAL IMPROVEMENT CONFERENCE, Victoria, Canada. Proceedings...Victoria: CPPA, 1979.
4. Kovacs, T.G., Martel, P.H., Voss, R.H. et al. 1993. Aquatic Toxicity Equivalency Factors for Chlorinated Phenolic Compounds Present in Pulp Mill Effluents. Environmental Toxicology and Chemistry, v. 12, p. 281-289.
5. Bell, J.P., Tsezos, M. 1987. Removal of Hazardous Organic Pollutants by Adsorption on Microbial Biomass. Water Science and Technology, New York, v. 19, p. 409-416.
6. Mc Kague, A.B. 1981. Some Toxic Constituents of Chlorination-Stage Effluents from Bleached Kraft Pulp Mills. Canadian Journal of Fisheries and Aquatic Sciences, v. 38, n. 7, p. 739-743.
7. Starck, B., Bethge, P.O., Gergov, M. et al. Dec. 1985. Determination of Chlorinated Phenol in Pulp Mill Effluents - an Intercalibratory Study. Paperi ja Puu - Papper och Trä, v. 67, n. 12, p. 745-749.
8. Leuenberger, C., Giger, W., Coney et al. 1985. Persistent Chemicals in Pulp Mill Effluents in an Activated Sludge Treatment Plant. Water Research, New York, v. 19, n. 7, p. 885-894.
9. Folke, J., Landner, L., Lehtinen, K.J. et al. 1993. Simplified Bioassays and Chemical Analyses to be Used for Regulatory Purposes in the Pulp Industry. In: ENVIRONMENTAL CONFERENCE, Boston, Massachusetts, Proceedings...Atlanta: TAPPI, v.1, p. 413-425.
10. Lee, H. B., Hong-You, R.L., Fowlie, P.J.A. 1989. Chemical Derivatization Analysis of Phenols. Part VI. Determination of Chlorinate Phenolics in Pulp and Paper Effluents. Journal of the Association of Official Analytical Chemists, v. 72, n6, p. 979-984.

11. Voss, R.H, Wearing, J.T., Wong, A. 1981. A Novel Gas Chromatographic Method for the Analysis of Chlorinated Phenolics in Pulp Mill Effluents. In: Keith, L.H. Advances in the Identification and Analysis of Organic Pollutants in Water. Ann Arbor: Ann Arbor Science, v. 2, p.1059-1095.
12. Morales, A., Birkholz, D.A., Hrudey, S.E. 1992. Analysis of Pulp Mill Effluent Contaminants in Water, Sediment, and Fish Muscle: Chlorophenol and Related Compounds. Water Environmental Research, v. 64, n. 5, p. 669-681.
13. Abrahamsson, K., Xie, T.M. 1983. Direct Determination of Trace Amounts of Chlorophenols in Fresh Water, Wastewater and Sea Water. Journal of Chromatography, Amsterdam, v. 279, p. 199-208.
14. United States Environmental Protection Agency. Method 1653. Chlorinated Phenolics in Wastewater by in-situ Acetylation and GCMS. P. 26.
15. Ionescu, L.G., Moro, C.C. 1989. Isolation and Identification of Toxic Chlorinated Organic Compounds Present in Black Liquor of Bleached Cellulose Pulp from Southern Brazil. Quimica Nova, v. 12, n.1, p. 108-110.
16. Holbom, B. Sept. 1980. A Procedure for Analysis of Toxic Compounds in Pulp and Paper Mill Wastewaters. Paperi ja Puu - Papper och Tra, v. 62, n. 9, p. 523-531.
17. Lee, H.-B., Weng, L.-D., Chau, A.S.Y. 1984. Chemical Derivatization Analysis of Pesticide Residues VIII. Analysis of 15 Chlorophenols in Natural Water by in Situ Acetylation. Journal of the Association of Official Analytical Chemists, v. 67, n. 4, p. 789-796.
18. Lee, H.-B., Weng, L.-D., Chau, A.S. 1984. Chemical Derivatization Analysis of Pesticide Residues. VIII. Analysis of 21 Chlorinated Phenols in Natural Waters by Formation of Pentafluorobenzyl Ether Derivatives. Journal of the Association of Official Analytical Chemists, v. 67, n. 6, p. 1086-1091.
19. Salkinoja-Salonen, M., Saxelin, M.-L., Pere, J. et al. 1981. Analysis of Toxicity and Biodegradability of Organochlorine Compounds Released into the Environment in Bleaching Effluents of Kraft Pulping. In: Keith, L.H. Advances in the Identification and Analysis of Organic Pollutants in Water, Ann Arbor: Ann Arbor Science, v. 2, p. 1131-1164.
20. March, J. 1977. Advanced Organic Chemistry: Reactions, Mechanisms, and Structure. Tokyo: McGraw Hill. p. 1328.
21. Rempel, W., Turk, O., Sikes, J.E.G. 1992. Side-by-Side Activated Sludge Pilot Plant Investigations Focusing Organochlorines. Journal of Pulp and Paper Science, v. 18, n. 3, p. J77-J85.

22. Nevalainen, J., Rantala, P.R., Junna, J. et al. 1991. Activated Sludge Treatment of Kraft Mill Effluents from Conventional and Oxygen Bleaching. Water Science and Technology, New York, v. 24, n. 3/4, p. 427-430.
23. Gergov, M., Priha, M., Talka, M. et al. Dec. 1988. Chlorinated Organic Compounds in Effluent Treatment at Kraft Mills. Tappi Journal, Atlanta, V. 71, n. 12, p. 175-184.
24. Herve, S. 1991. The Effect of Biological Wastewater Treatment in the Pulp and Paper Industry on Organochloride Compounds in the Recipient Waters. In: ENVIRONMENTAL CONFERENCE, 1991. Proceedings...Atlanta: TAPPI, p. 267-269.
25. Sodergren, A. 1993. Bleached Pulp Mill Effluents. Composition, Fate and Effects in the Baltic Sea. Sweden: Swedish Environmental Protection Agency, p. 150 (Final Report 4047).
26. Departamento Municipal de Agua E Esgotos. 1986. Centro de Estudos De Saneamento Basico. O rio. Guaiba - suas caracteristicas fisicoquimicas e biologicas, v. 5, n. 43, p. 361.
27. Gherardi-Goldstein, E., Bertolotti, E., Zagatto, P.A. et al. 1990. Procedimentos para utilização de testes de toxicidade no controle de efluentes liquidos. Sao Paulo: CETESB, 1990, p. 17 (Série Manuais). b. Goldstein-Gherardi, E., Bertolotti, Zagatto, P.A. et al. ii. Implementacao de testes de toxicidade no controle de efluentes liquidos. Sao Paulo, CETESB: p. 7 (Série Manuais).
28. Voss, R.H., Wearing, J.T., Wong, A. March 1981. Effect of Hardwood Chlorination Conditions on the Formation of Toxic Chlorinated Compounds. Tappi Journal, Atlanta, v. 64, n. 3, p. 167-170.
29. Paasivirta, J., Heinola, K., Humppi, T. et al. 1985. Polychlorinated Phenols, Guaiacols and Catechols in Environment. Chemosphere, v. 14, n. 5, p. 469-491.
30. Hendricksen, H.V., Larsen, S., Ahring, B.K. 1991. Anaerobic Degradation of PCP and Phenol in Fixed-Film Reactors: the Influence of an Additional Substrate. Water Science and Technology, New York, v. 24, n. 3/4, p. 431-436.
31. Voss, R.H., Wearing, J.T., Wong, A. Feb. 1981. Effect of Softwood Chlorination Conditions on the Formation of Toxic Chlorinated Compounds. Pulp and Paper Canada, v. 82, n. 2, p. 97-105.

32. Reeve, D.W. 1993. Banning AOX is not Justified: a Response to the Draft Effluent Limits Proposed by the Ontario Ministry of the Environment for the Pulp and Paper Sector. Toronto, Pulp and Paper Centre University of Toronto.
33. Bryant, C.W., Amy, G.L., Alleman, B.C. Oct. 1987. Organic Halide and Organic Carbon Distribution and Removal in a Pulp and Paper Wastewater Lagoon. Journal of Water P.C.F., v.59, n. 10, p. 890-896.
34. Carey, J.H., Hodson, P.V., Munkittrick, K.R. et al. March 1993. Recent Canadian Studies on the Physiological Effects of Pulp Mill Effluent on Fish. National Water Research Institute-Environment Canada.
35. Paper Technology, v. 34, n. 6, p. 3-4.
36. O'Connor, B.I., Kovacs, T.G., Voss, T.H. et al. 1993. A Laboratory Assessment of the Environmental Quality of Alternative Pulp Bleaching Effluents. In: EUCEPA International Environmental Symposium "Pulp and Paper Technologies for a Cleaner World", Paris, France, April 27-29, 1993. Torrendinos: Asociacion de Investigacion Tecnica de la Industria Papelera Española.
37. Pulp Mill Can Still Improve. Sept. 1993. Pulp and Paper International, v. 35, n. 9, p. 5.
38. Congressman: Kicks Out Chlorine. Oct. 1993. Paper, v. 217, n. 10, p. 8.
39. Owens, J.W. 1991. The Hazard Assessment of Pulp and Paper Effluents in the Aquatic Environment: a Review. Environmental Toxicology Chemistry, v. 10, p. 1511-1540.
40. Kinstry, R.B. March 1993. An overview of Strategies for Reducing the Environmental Impact of Bleach-Plant Effluents. Tappi Journal, Atlanta, v. 76, n. 3, p. 105-113.
41. Universidade Federal Do Rio Grande Do Sul. Instituto de Quimica. Desenvolvimento de um laboratorio de Quimica Ambiental no Instituto de Quimica (IQ) da Universidade Federal do Rio Grande do Sul: avaliacao de metodos de analise de organoclorados. Projeto de pesquisa em andamento iniciado em julho de 1993.
42. Hassi, H. June 1992. Closing up the Mill. Paper, v. 217, n. 6, p. 9.
43. Earl, P.F., Reeve, D.W. Jan. 1990. Chlorinated Organic Matter in Bleached Chemical Pulp Production. Part 6: Chlorinated Compounds in Effluents. Tappi Journal, Atlanta, v. 73, n 1, p. 179-184.

44. McCubbin, N., Sprague, J.B., Bonsor, N. March 1990. Kraft Mill Effluents in Ontario. Pulp and Paper Canada, v. 91, n. 3, p. 112-116.
45. Neilson, H.A., Allard, A.N., Hynning, P.A. et al. March 1990. The Environmental Fate of Chloro Phenolic Constituents of Bleachery Effluents. Tappi Journal, Atlanta, v. 73, n. 3, p. 239-247.
46. Atlas, R.M., Barth, A.R. 1981. Microbial Ecology: Fundamentals and Applications, Massachussetts, Addison-Wesley Publishing Company.
47. Martel, P.H., Kovacs, T.J., O'Connor, B. et al. 1993. A Survey of Pulp and Paper Mill Effluents for their Potential to Induce Mixed Function Oxidase Enzyme Activity in Fish. In: Annual Meeting 79, 26, and 27, Jan. 1993. Preprints...Montreal CPPA, p. A165-A177.
48. Martel, P.H., O'Connor, B.I. Sept. 1992. Mixed Function Oxidase (MFO) Enzymes and their Use in the Biological Monitoring of Fish Exposed to Pulp and Paper Mill Effluents. Pulp and Paper Research Institute Of Canada, p. 19.(Miscellaneous Reports - MR 237)
49. Anderson, T., Förlin, L., Härdig, J. et al. 1988. Physiological Disturbances in Fish Living in Coastal Water Polluted with Bleached Kraft Pulp Mill Effluents. Can. J. Fish, Aquatic Sci., v. 45, p. 1525-1533.
50. Morales, A., Birkholz, D.A., Hrudey, S.E. et al. Methodologies for the Measurement of Chlorinated Organic Compounds in the Environment. Chlorlphenols and Related Compounds. Water Environment Research.
51. Yang, J.L., Sacon, V.M., Law, S.E. et al. July 1993. Bleaching of Eucalyptus Kraft Pulp with the EnZone Process. Tappi Journal, Atlanta, v. 76, n. 7, p. 91-96.
52. Oliveira, F.A.C., Lima, M.M. Sept. 1993. Alternativas para a reducao/eliminacao de compostos orgnaoclorados na favricacao de celulose. O Papel, v. LIV, n. 9, p. 49-50.
53. Sodergren, A. 1989. Biological Effects of Bleached Pulp Mill Effluents. Sweden, National Swedish Environmental Protection Agency, p. 139 (Report 3558).

## **ACKNOWLEDGEMENT**

We thank especially Dr. Francis Onuska (Canada Centre for Inland Waters - National Water Research Institute) for valuable technical discussions, and for the critical review of this paper. We gratefully acknowledge Dr. Ralph Daley for kindly providing access to the Institute's facilities. Robert Hong-You of WTC is thanked for providing CPCs standards and profitable technical discussions.

Celso Foelkel from Riocell and also the SENAI - Serviço Nacional da Indústria are acknowledged for their support to this research.

ENVIRONMENT CANADA LIBRARY, BURLINGTON



3 9055 1016 4630 4





**National Water Research Institute  
Environment Canada  
Canada Centre for Inland Waters**

P.O. Box 5050  
867 Lakeshore Road  
Burlington, Ontario  
Canada L7R 4A6

**Institut national de recherche sur les eaux  
Environnement Canada  
Centre canadien des eaux intérieures**

Case postale 5050  
867, chemin Lakeshore  
Burlington, Ontario  
Canada L7R 4A6



Environment  
Canada

Environnement  
Canada

**Canada**