

Influence of chlorine ratio and oxygen bleaching on the formation of PCDFs and PCDDs in pulp bleaching

Part 1: a laboratory study

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ABSTRACT *In a laboratory bleaching study, we assessed the influence of the chlorine ratio and oxygen bleaching on the amounts of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxin (PCDDs) formed. A significant factor affecting the amounts of PCDF and PCDD is the chlorine ratio. On well-washed laboratory pulp, oxygen bleaching has little or no effect. The beneficial effects of oxygen bleaching on the amounts of PCDFs and PCDDs observed in mill-scale studies is therefore likely the result of the much greater efficiency in pulp washing through the oxygen bleaching stage.*

KEYWORDS

Bleaching
Chlorine
ratio
Dioxin
Environmental
control
Isomers
Oxygen
bleaching
Toxicity

Polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxin (PCDDs) are two series of tricyclic planar aromatic compounds that are highly toxic and environmentally persistent. Each series consists of a number of chlorinated homologs (monochloro to octachloro) and a large number of isomers (135 PCDF isomers and 75 PCDD isomers). Those isomers chlorinated at all four lateral positions (2,3,7,8-) possess extraordinary toxicity (1-2). Thus, these compounds are the subject of concern in recent years, and reviews have been published

describing their formation and occurrence (3-4).

Recently, PCDFs and PCDDs have been identified in pulp mill sludges, in pulp bleach plant effluents, and in pulp and paper products (5-8). Preliminary work on our series of studies showed that these compounds form during the bleaching processes and are a result of the use of chlorine (9). The PCDFs and PCDDs appeared in the first chlorination stage and were in greatest quantity in the pulp. Among the PCDFs, the TCDFs were present in highest concentration, and of the TCDFs, the 1,2,7,8- and 2,3,7,8-TCDF isomers dominated the profile (9). The PCDDs were present at lower

concentrations than the PCDFs. Of the PCDDs detected, the TCDDs were in highest quantity, and of these, 2,3,7,8-TCDD was present at the highest concentration. The PCDF and PCDD amounts decreased in the stages subsequent to the first chlorination (C) stage—i.e., the first alkaline extraction (E) stage and the hypochlorite (H) stage—but increased slightly in the first chlorine dioxide stage. The overall PCDF and PCDD patterns observed in the first chlorination stage were also detected in the subsequent stages (9).

This study was carried out to determine on a laboratory scale the importance of such factors as chlorine ratio

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and oxygen bleaching on the amounts of PCDFs and PCDDs formed. Oxygen bleaching and the use of low chlorine ratio are measures that may reduce discharges of chlorinated organic matter from pulp bleach plants (10). Variations in concentrations between C and E stages, partitioning between pulp and liquor, and the effects of adding peroxide in the E stage were also considered. Only softwood kraft pulps, well washed in the laboratory, were included. In Part II, we will apply the laboratory results in a full mill-scale study. Results from this mill-scale study will be presented in a later article.

Experimental procedures

Choice and preparation of pulp

Unbleached, softwood kraft pulp was obtained from a pulp mill producing 850 tons of bleached pulp per day. The pulp was produced without condensates in the washing operations and had a kappa number of 31. Before laboratory bleaching, the pulp was washed once again in the laboratory, reducing the kappa number to 30.5.

Bleaching processes

The chlorine gas, obtained from AGA, Special Gas, Sweden, consists of 99.8% Cl_2 and 0.2% CO_2 . The chlorine dioxide used was prepared from sodium chlorite in one of our laboratories. All pulp suspensions were formed using tap water from the City of Stockholm. Pulp washings were also performed using tap water.

In accordance with normal laboratory procedures, all (C85+D15)-stage and E-stage experiments were performed in heat-sealed polyethylene bags. To examine whether the polyethylene may influence the rate of formation or the amounts of PCDFs or PCDDs, one series of (C85+D15)-stage and E-stage experiments was duplicated in glass.

The effect of chlorine ratio was studied by treating 120 g of the pulp in a (C85+D15)-stage, varying the chlorine ratio (as active chlorine) between 0.05 and 0.25. Chlorine ratio is defined as the charge of elemental chlorine and chlorine dioxide, expressed as active chlorine in percent of pulp divided by the kappa number. The conditions used in the (C85+D15) stage were 3.5% pulp consistency, a temperature of 40°C, and a reaction

time of 60 min. In all experiments, the chlorine was almost completely consumed at the end of the reaction time. The chlorinated sample was filtered on a Buchner funnel and washed twice, each time with 500 mL of cold water. The spent liquor and a portion (30 g) of the pulp were reserved for analysis.

The remaining, chlorinated pulp was treated in an E stage using the following conditions:

- Pulp consistency: 10%
- Charge of alkali: equivalent to 15–20 kg NaOH/ton of pulp
- Temperature: 60°C
- Reaction time: 60 min.

Thereafter, the pulp was again filtered in a Buchner funnel and washed. The filtrate and pulp were reserved for analysis.

A part of the commercially produced softwood kraft pulp was bleached in the laboratory in an oxygen stage using the following conditions:

- Pulp consistency: 25%
- Alkaline charge: 2%
- Temperature: 100°C
- Pressure: 8 bar
- Reaction time: 30 min.

After oxygen bleaching, the pulp was washed extensively to reach a kappa number of 21.6.

The oxygen-bleached pulp was further bleached in a (C85+D15)-stage and E-stage under conditions identical to those described. The chlorine ratios used were 0.10, 0.20, and 0.25, respectively. Bleaching with a chlorine ratio of 0.20 was carried out twice. In one of the samples, 0.20% hydrogen peroxide calculated on pulp was added in the E stage.

PCDF and PCDD analyses

PCDF and PCDD analyses were performed separately on three fractions from each pulp suspension. These fractions were:

1. The filtered, air-dried pulp
2. Fine particulate matter filtered from the pulp-free aqueous liquor using a 0.45- μm membrane filter
3. The aqueous liquor itself.

The analytical methods used are described elsewhere (8, 14).

The solid samples (pulp and fine particulate matter) were Soxhlet

extracted with toluene, and the aqueous liquor filtrates were extracted in a separatory funnel with dichloromethane. A three-column cleanup of the samples followed. The three columns used were:

1. 40% H_2SO_4 on silica gel
2. Activated basic alumina (Woehlm basic akt.I)
3. 18% Caropak C (Supelco) on Celite 545.

The extracts were analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using a VG 70-250E or VG 70-250S mass spectrometer operating in the selected ion monitoring mode. PCDFs and PCDDs were identified by matching responses of the characteristic ions in the molecular ion cluster with the theoretical ion abundances ($\pm 10\%$) and by matching retention times (± 3 s) of *tetra*- through *octa*-PCDF and -PCDD to those of actual isomers established through periodic analysis of retention time standards.

The PCDFs and PCDDs were quantified by comparing the isomer responses to the response of authentic 2,3,7,8-isomers in quantification standards that were analyzed at intervals of no more than once every 8 h of instrument operation. Monitoring the response of the quantification standard was also one important aspect of the quality assurance program to assure consistent instrument calibration and response. The quality assurance program for these samples also included preparation and analysis of laboratory blanks, which were prepared in series with the actual samples.

Another important aspect of the quality assurance program was the inclusion of ^{13}C -labeled compounds as internal standards for the PCDF and PCDD homologs. A total of six ^{13}C -PCDFs and -PCDDs were added to each sample before extraction and cleanup. Two additional ^{13}C -labeled isomers were added to each cleaned up extract before analysis. The response of all eight ^{13}C -isomers was measured in each sample to monitor variations in sample preparation efficiencies and in instrument response and to determine possible matrix effects. The recovery of these ^{13}C -surrogate compounds was calculated for each sample. These recovery

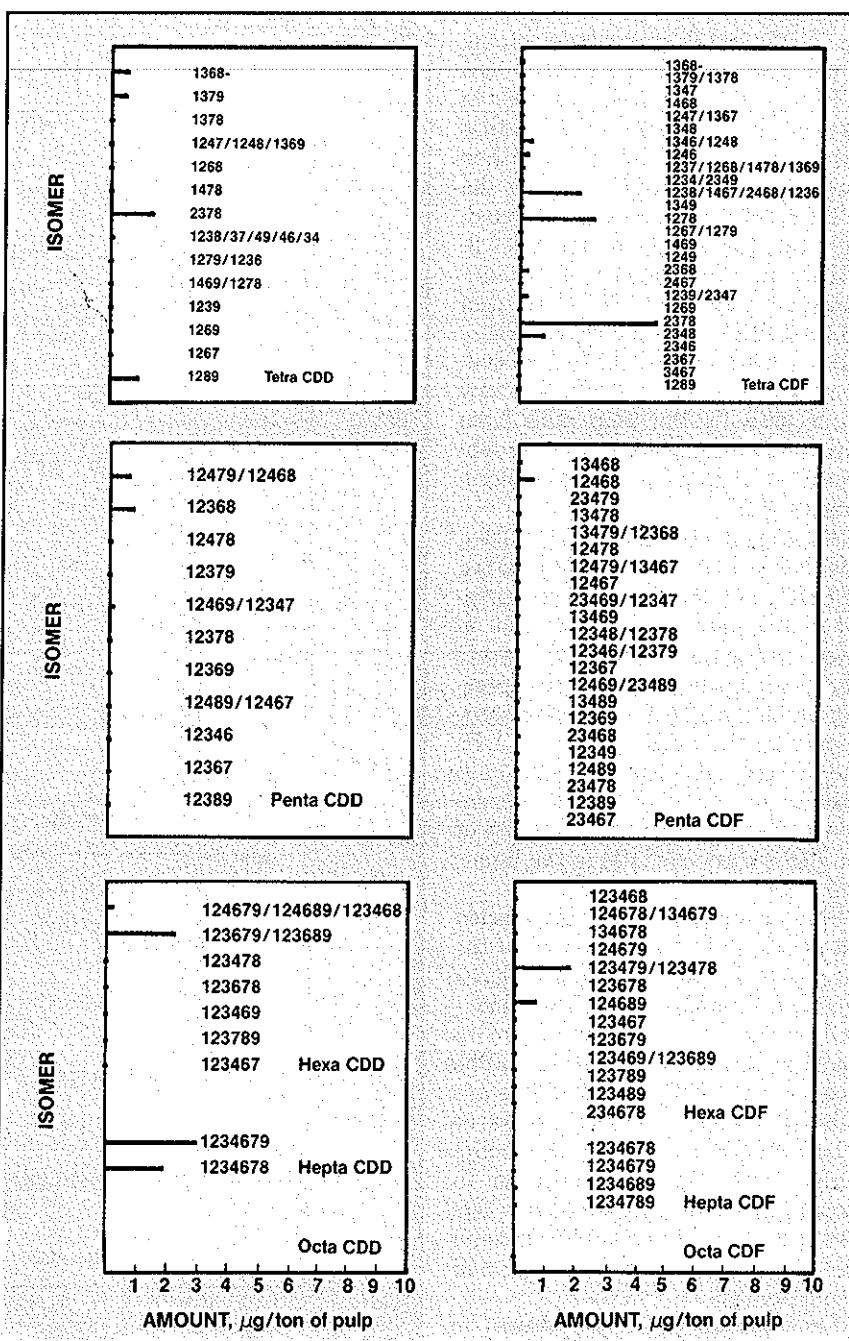
I. Detection limits for isomers in Figs. 1 and 2

Isomer	Detection limit, $\mu\text{g}/\text{ton of pulp}$
TCDF	0.002
TCDD	0.004
PeCDF	0.005
PeCDD	0.005
HxCDF	0.01
HxCDD	0.02
HpCDF	0.01
HpCDD	0.02
OCDF	0.5
OCDD	0.5

II. Weighting factors for calculation of USEPA and Nordic TCDD toxic equivalency factors

Isomers	USEPA	Nordic
2, 3, 7, 8-TCDF	0.1	0.1
Non-2, 3, 7, 8	0.001	0
1, 2, 3, 7, 8-PeCDF	0.1	0.01
2, 3, 4, 7, 8-PeCDF	0.1	0.5
Non-2, 3, 7, 8	0.001	0
2, 3, 7, 8-HxCDF	0.01	0.1
Non-2, 3, 7, 8	0.0001	0
2, 3, 7, 8-HpCDF	0.01	0.01
Non-2, 3, 7, 8	0.0001	0
OCDF	0	0.001
2, 3, 7, 8-TCDD	1	1
Non-2, 3, 7, 8	0.01	0
2, 3, 7, 9-PeCDD	0.5	0.5
Non-2, 3, 7, 8	0.005	0
2, 3, 7, 8-HxCDD	0.04	0.1
Non-2, 3, 7, 8	0.0004	0
2, 3, 7, 8-HpCDD	0.001	0.01
Non-2, 3, 7, 8	0.00001	0
OCDD	0	0.001

1. Distribution of *tetra*- through *octa*-CDFs and -CDDs in (C85+D15)-stage pulp suspension samples from laboratory bleaching of softwood kraft pulp at a chlorine ratio of 0.20. (Detection limits are in Table II.)



values were used to correct the measured results to compensate for analyte loss during work-up and for instrument variation.

The reproducibility in analysis of blood, human milk, liquid and solid samples from incinerators, and pulp and bleach plant liquors using appropriate ^{13}C -surrogates was previously found to be approximately 20–30% for *tetra*- and *penta*-CDFs and -CDDs (11–12).

Results and discussion

The influence of chlorine ratio with unbleached pulps

As mentioned, certain characteristic patterns appear for the various PCDFs and PCDDs (6, 7, 9) in the analysis of bleach plant samples. In these patterns, the 2,3,7,8-TCDF and 2,3,7,8-TCDD isomers often dominate the profile. Other isomers are also detected, however, including the

1,2,7,8-TCDF and *penta*- and *hexa*-CDFs and -CDDs. Occasionally, even *hepta*- and *octa*-CDFs and -CDDs are detected. Figure 1 shows the quantities of each of the *tetra*- through *octa*-CDFs and -CDDs found in the bleaching of softwood kraft pulp using a chlorine ratio of 0.20. Only values for the (C+D) stage are presented. In the figure, each line represents the sum of the respective isomers in the pulp, in fine particulates, and in the liquor,

with this sum calculated as $\mu\text{g}/\text{ton}$ of pulp. Detection limits (DL) are given in Table I.

The graphs show that not all existing PCDFs and PCDDs are detectable in the samples. Of the PCDFs and PCDDs present, the TCDFs appear in highest quantity, and the dominating isomer is 2,3,7,8-TCDF. Another isomer is 1,2,7,8-TCDF. Among the TCDDs, four isomers were detected, with the highest level for 2,3,7,8-TCDD. In the analysis of the unbleached pulp, 1,3,6,8-TCDD and 1,3,7,9-TCDD were detected. These isomers have been identified as contaminants in chlorophenols. The raw water used by the pulp mill, from which the bleached pulp was obtained, is known to contain chlorophenols (13).

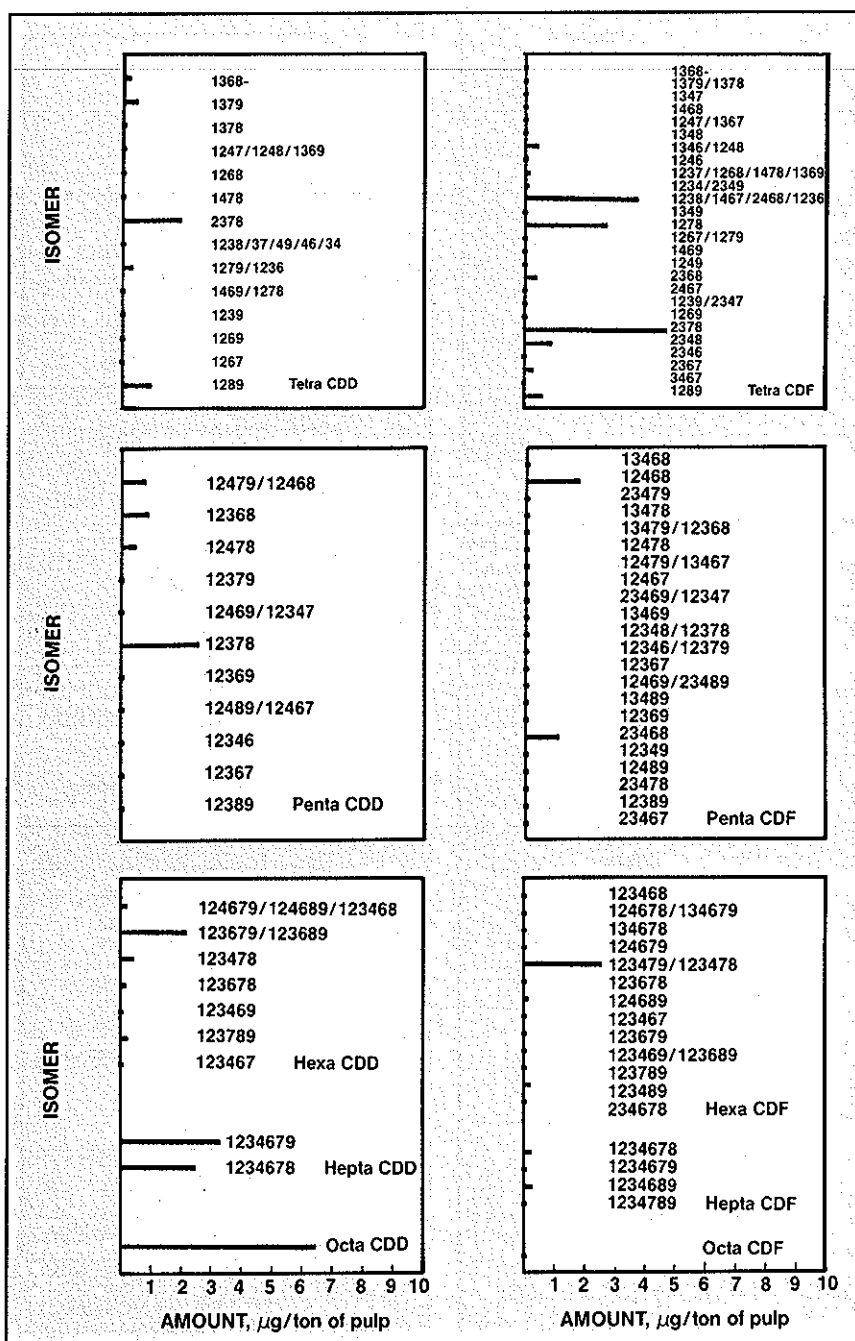
Significant quantities of PeCDFs, PeCDDs, HxCDFs, HxCDDs, HpCDFs, and HpCDDs are also present in the pulp suspension. Also, in these congener groups, the toxic 2,3,7,8-substituted isomers are present in the highest concentrations. Generally, the major part of PCDFs and PCDDs were detected in the pulp fraction of the (C+D)-stage suspension, with only approximately 10% of the PCDFs and PCDDs in the liquor and fines.

Similar analyses were also carried out on the pulp suspension from the successive E stage. Figure 2 shows the *tetra-* through *octa-*CDFs and -CDDs. The basic pattern shown in Fig. 1 is also apparent in Fig. 2. The levels in the (C+D) and E stages are similar, except for the levels of 1,2,3,7,8-PeCDD and -OCDD being higher in the E stage suspension. In this suspension, approximately 30–50% of the total amount of PCDFs and PCDDs was found in the liquor and fine material.

Four parameters were chosen to illustrate the influence of the chlorine ratio on the formation of PCDFs and PCDDs. These were the amounts of 2,3,7,8-TCDF, 2,3,7,8-TCDD, the U.S. EPA TCDD Toxic Equivalence Factor (TEF) and the Nordic TEF (14, 15), respectively.

These parameters were selected to best illustrate the toxic aspects of the PCDFs and PCDDs found. Table II shows the U.S. EPA and Nordic TCDD Toxic Equivalence Weighting Factors. Figure 3 illustrates the effect of chlorine ratio on the four

2. Distribution of *tetra-* through *octa-*CDFs and CDDs in E-stage pulp suspension samples from laboratory bleaching of softwood kraft pulp at a chlorine ratio of 0.20. (Detection limits in Table II.)

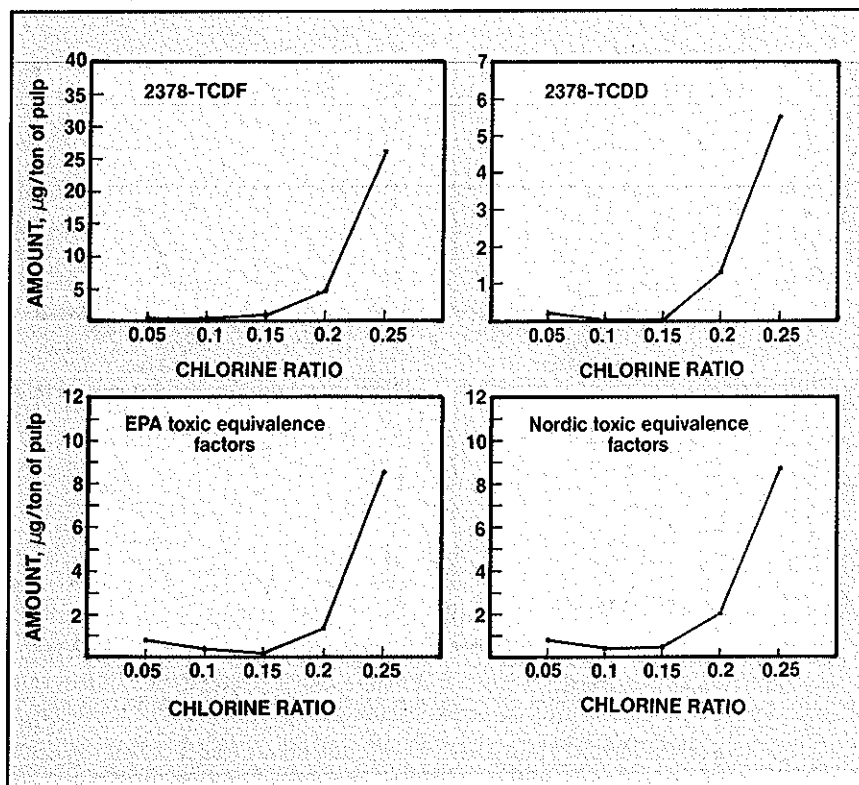


parameters as found in the (C85+D15)-stage suspension. Figure 4 illustrates the results obtained for the respective successive E stages. The results in these figures, expressed in $\mu\text{g}/\text{ton}$ of pulp bleached, are the combined results of analysis of the pulp, liquor, and fine particulate fractions in the suspensions.

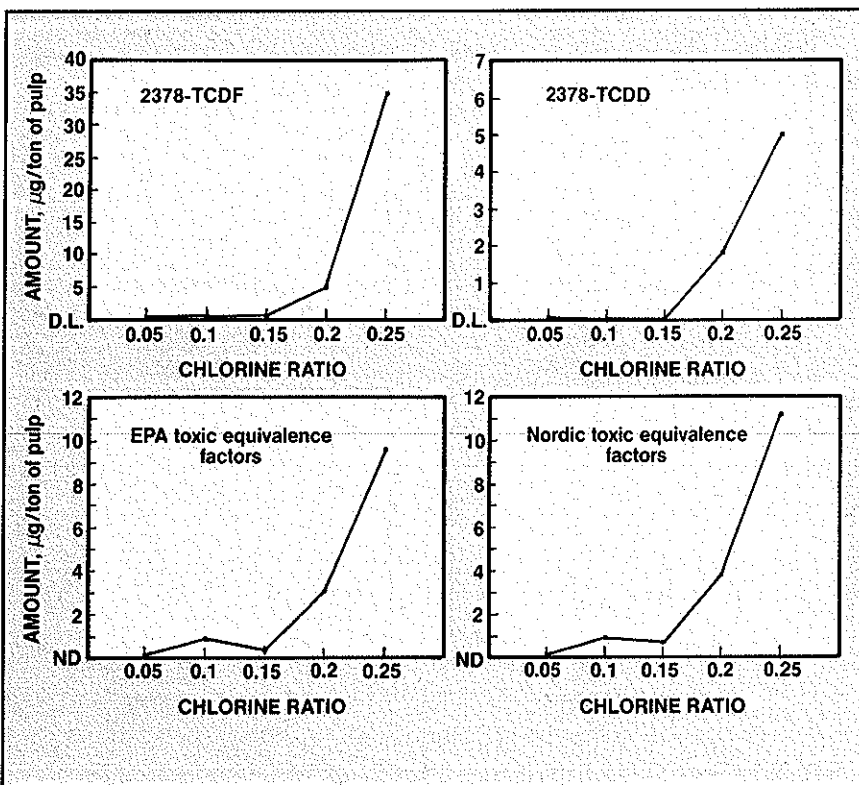
In accordance with the previous observations, the four PCDF and

PCDD parameters already appear in the (C85+D15) stage. In general, the levels in the E stage are the same or slightly higher. A carryover of the PCDFs and PCDDs, formed during chlorination, to the E stage is logical. However, the higher concentrations of 1,2,3,7,8-PeCDD and -OCDD strongly indicate that in addition a *denovo* synthesis may take place in the E stage.

3. Levels of four characteristic PCDF and PCDD parameters calculated per ton of pulp bleached in (C85+D15)-stage pulp suspension samples from the laboratory bleaching of a softwood kraft pulp (kappa no. 30.5) using five different chlorine ratios. (DL = 0.002 $\mu\text{g}/\text{ton}$ for TCDF and 0.004 $\mu\text{g}/\text{ton}$ for TCDD.)



4. Levels of four characteristic PCDF and PCDD parameters calculated per ton of pulp bleached in E-stage pulp suspension samples from the laboratory bleaching of a softwood kraft pulp (kappa no. 30.5) using five different chlorine ratios. (DL = 0.002 $\mu\text{g}/\text{ton}$ for TCDF and 0.004 $\mu\text{g}/\text{ton}$ for TCDD.)



A significant conclusion is that an exponential relationship seems to exist between PCDF and PCDD concentrations and the chlorine ratio used. This relationship is exhibited for all four parameters, and it indicates that even a small reduction in the chlorine ratio may result in a significant drop in the PCDF and PCDD levels.

Currently, a chlorine ratio of 0.20–0.25 is quite normal in the bleaching of softwood kraft pulp. A large drop may be observed within a range of chlorine ratios from 0.25 to 0.15. The implication is that within limits dictated by mill operations, the levels of PCDFs and PCDDs can be greatly affected by the chlorine ratio used. In fact, at chlorine ratios at or below 0.15, the concentrations of all four parameters are only slightly above or at the limits of detection.

A similar relationship has been found for higher chlorinated phenols in other studies (15, 16). It is not apparent from our work whether there is a connection between formation and the concentrations of chlorinated phenols, and formation and the amounts of PCDFs and PCDDs.

In our study here, only the two first bleaching stages were investigated. No attention was paid to a final bleaching result with regard to final brightness or other pulp qualities. These aspects will be considered in Part II.

The influence of chlorine ratio with oxygen-bleached pulps

The same general pattern of PCDF and PCDD isomers pattern of PCDF and PCDD isomers found in the bleaching of unbleached softwood kraft pulp was also obtained in the bleaching of pulp prebleached with oxygen to kappa number 21.6. Thus, the relative distribution of PCDFs and PCDDs shown in Figs. 1 and 2 was also detected after bleaching the oxygen-bleached samples with the 2,3,7,8-TCDF and 2,3,7,8-TCDD isomers dominating. In all, there was only a relatively small number of other isomers present, although the PeCDFs and PeCDDs did appear in somewhat higher concentrations.

In Figs. 5 and 6, the same four PCDF and PCDD parameters have been used to illustrate the effect of chlorine ratio. Again, the results are the combined results of analysis of the pulp, liquor, and fine particulate

fractions in these suspension and are expressed in $\mu\text{g}/\text{ton}$ of pulp bleached.

In accordance with what was found for unbleached pulp, Figs. 5 and 6 show that the four PCDF and PCDD parameters already appear in the (C85+D15) stage. An exponential relationship between chlorine ratio and the various parameters seems to exist.

An additional parameter we examined is the addition of hydrogen peroxide in the E stage. Hydrogen peroxide is often added to enhance the delignifying effect of the E stage. Thus, included in Fig. 6 are the four PCDF and PCDD parameter levels in E-stage samples with and without peroxide addition. As shown, the hydrogen peroxide treatment has little effect on the formation of PCDFs and PCDDs.

A comparison of Figs. 3-6 suggests that oxygen bleaching does not have any significant effect on the overall amounts of the four PCDF and PCDD parameters, as calculated per ton of pulp. However, the pulps used in this study were washed extremely well in the laboratory prior to bleaching. Other studies suggest that in full mill-scale operations, oxygen bleaching has an advantageous effect in decreasing PCDF and PCDD concentrations (18). Therefore, this decrease must be a result of the oxygen bleaching in the mill functioning as an effective washing stage, removing PCDF and PCDD precursors.

Conclusions

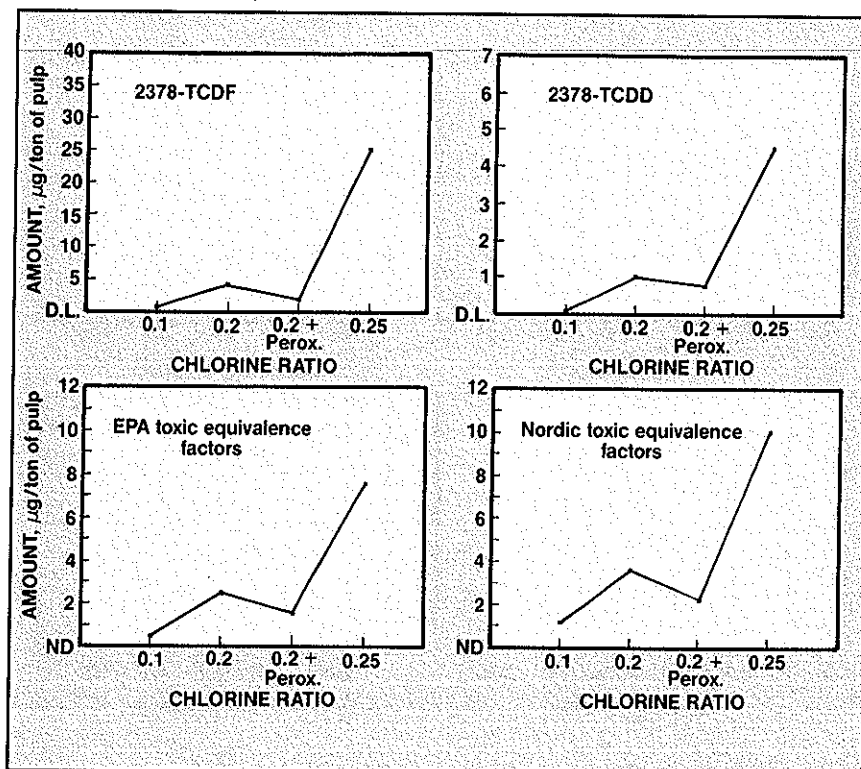
A significant factor that affects PCDF and PCDD formation in the bleaching of pulp using chlorine is the chlorine ratio. Oxygen bleaching may also affect PCDF and PCDD concentrations but probably only through the benefit of effective washing procedures.

When evaluating the PCDF and PCDD concentrations in bleach plant samples, it is advisable to determine the levels in all three fractions: aqueous liquor fraction, fine particulate matter in the liquor, and in the pulp. □

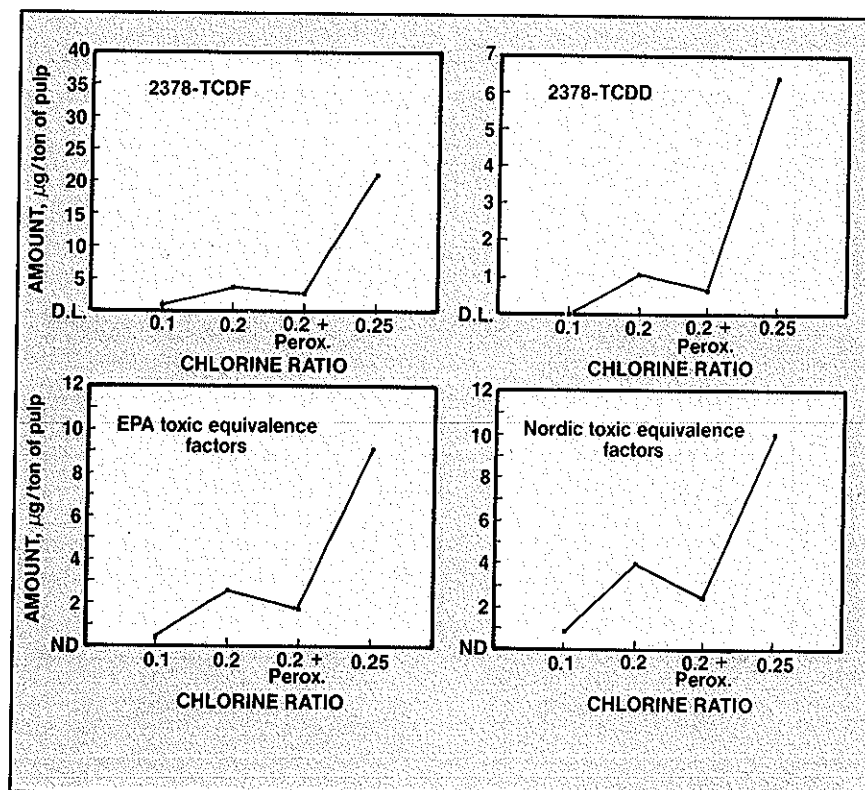
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5. Levels of four characteristic PCDF and PCDD parameters calculated per $\mu\text{g}/\text{ton}$ of bleached pulp in (C85+D15)-stage pulp suspension samples from the laboratory bleaching of an oxygen-bleached pulp (kappa no. 21.6) using three different chlorine ratios. (DL = $0.002\mu\text{g}/\text{ton}$ for TCDF and $0.004\mu\text{g}/\text{ton}$ for TCDD.)



6. Levels of four characteristic PCDF and PCDD parameters in E-stage pulp suspension samples (with and without hydrogen peroxide) from the laboratory bleaching of an oxygen bleached pulp (kappa no. 21.6) at three different chlorine ratios, calculated in $\mu\text{g}/\text{ton}$ of pulp bleached. (DL = $0.002\mu\text{g}/\text{ton}$ for TCDF and $0.004\mu\text{g}/\text{ton}$ for TCDD.)



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This study has been carried out as part of the SSVL (the Swedish Forestry Industries Water and Air Pollution Research Foundation) project "Environment 90, Bleaching Effluents."

Received for review Jan. 6, 1989.

Accepted Jan 17, 1989.

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