

AN INTENSIVE STUDY OF THE FORMATION AND DISTRIBUTION OF 2,3,7,8-TCDD AND  
2,3,7,8-TCDF DURING BLEACHING OF KRAFT PULP

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ABSTRACT

A wide range of Kraft bleaching operations were studied at 23 mills to investigate 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) formation sites in bleach plants, factors influencing the amounts formed, and their partitioning between pulps and filtrates. Analyses of interstage pulp and filtrates provided the information needed to calculate mass balances about each bleaching stage.

All the 2,3,7,8-TCDD and 2,3,7,8-TCDF were formed in the chlorination stages. The amounts formed increased with both molecular chlorine use and the amounts of dibenzodioxin and dibenzofuran in the brownstock. The presence of precursors to TCDD formation other than dibenzodioxin were indicated. Little difference was observed in the amount of 2,3,7,8-TCDD and 2,3,7,8-TCDF formed at the low molecular chlorine usage at mills employing either oxygen delignification or high chlorine dioxide substitution.

The amount of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the final bleached pulps ranged between 6 and 83 percent of the total bleach plant exports. Of the balance, most left the bleach plant with the extraction stage filtrate. No operating conditions could be discerned as influencing the partitioning between pulp and filtrate.

KEYWORDS

2,3,7,8-TCDD, 2,3,7,8-TCDF, Dioxin, Bleaching, DBD, DBF.

INTRODUCTION

Results of the U.S. EPA/Paper Industry Cooperative Dioxin Screening Study released in 1988 provided the first comprehensive information on the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in bleached Kraft mills. This study prompted the EPA to initiate a new cooperative study to define exports of TCDD and TCDF from all 104 pulp mills in the U.S. that practiced bleaching; and it prompted the industry to intensively study TCDD and TCDF formation and distribution between export vectors at 23 carefully selected bleached Kraft mills. These mills were sampled from early 1988 to early 1989.

This paper summarizes the results of this intensive study. This study was unique in that material balances for TCDD and TCDF were carefully constructed about each bleaching stage to locate formation sites and to trace the movement of these materials in the bleach plant. The study was designed to examine the effects of precursor levels, delignification practices, wood species, routinely monitored bleach plant operating conditions, and chemical use on the formation and distribution of TCDD and TCDF within the bleach plant.

It is significant to note that the investigators had limited ability to control or monitor all mill variables that could influence the formation and distribution of TCDD and TCDF in the bleach plant. Consequently, many of the observations presented are not conclusive and will require verification by well designed and controlled laboratory experiments.

Compared to the 104-mill study, which estimated the amount of TCDD and TCDF released to the environment through the vectors of pulp, sludge, and effluent, results of the intensive study are more representative of the amounts of TCDD and TCDF formed in individual bleaching lines.

#### STUDY DESIGN

The objectives of this study were to: (a) investigate the location of 2,3,7,8-TCDD and 2,3,7,8-TCDF formation in bleach plants; (b) find factors that may influence the amount of 2,3,7,8-TCDD and 2,3,7,8-TCDF formed; and (c) explore factors that may influence the partitioning of 2,3,7,8-TCDD and 2,3,7,8-TCDF between pulp and filtrates.

The total 2,3,7,8-TCDD and 2,3,7,8-TCDF formed was estimated by measuring and summing the mass of these materials in pulps and filtrates leaving each bleach plant. Possible locations of 2,3,7,8-TCDD and 2,3,7,8-TCDF formation were isolated by conducting material balances about each stage in the bleaching process. Samples of filtrates and pulp moving between bleaching stages or leaving the bleach plant were analyzed to calculate material balances.

The 23 bleach plants included in this project were chosen to comprise a wide range of bleaching practices. They bleached both hardwoods and softwoods, and represented all regions of the United States where wood is pulped. Operating practices encompassed a wide range of chlorine application levels and chlorine dioxide substitution levels. Some mills practicing oxygen delignification were included. These bleach plants represented the diverse bleaching technology used by the industry at the time the study was conducted.

All samples were analyzed at a single laboratory (Enseco-Cal) to minimize inter-laboratory biases associated with trace analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF. In spite of the fact that existing analytical methods for interstage pulps and filtrates have not been extensively investigated, target detection limits of 1 ng/kg (1 ppt) for pulps and 10 pg/L (10 ppq) for filtrates were judged reasonable for this study.

Quality control procedures for each sample included: (a) close review of the chromatograms; (b) review of mass spectrum data for proper ion ratios; and (c) a check of internal standard recovery. Samples not meeting quality control criteria were reanalyzed. For each batch of approximately 10 similar samples submitted for analysis, one sample was checked for native spike recovery and a replicate sample was analyzed.

In some cases the water and material balances relied on a number of poorly measured or estimated flow rates. Thus, considerable uncertainty could be introduced into the calculation of the mass of TCDD and TCDF in liquid streams. The uncertainty was minimized by selecting mills where good measurements of the major flows could be obtained.

#### EXPORT OF 2,3,7,8-TCDD AND 2,3,7,8-TCDF FROM BLEACH PLANTS

The total export of 2,3,7,8-TCDD from the 23 bleach plants studied ranged from <0.6 ng/kg oven-dried brownstock (odbs) to 78 ng/kg odbs. The amount of 2,3,7,8-TCDF exported from the same bleach plants ranged from <1.1 ng/kg odbs to 668 ng/kg odbs. Calculation of the lower values includes the use of some analytical results reported as "non-detect" at the detection limit.

#### FORMATION LOCATION

All of the 2,3,7,8-TCDD and 2,3,7,8-TCDF appeared to be formed in the chlorination stage. The amount formed in the chlorination stage appeared to be greater than the amount measured exiting the bleach plant. At some bleach plants, a portion of the 2,3,7,8-TCDD and 2,3,7,8-TCDF entering the extraction stage could not be accounted for in the mass balances.

Any 2,3,7,8-TCDD and 2,3,7,8-TCDF formation or loss that may have occurred in hypochlorite and/or chlorine dioxide stages was small relative to the amount formed in the chlorination stage.

#### PROCESS CONDITIONS AFFECTING TCDD AND TCDF FORMATION

For the 23 bleach plants studied, observations indicate a trend of increasing 2,3,7,8-TCDD and 2,3,7,8-TCDF exiting the bleach plant with greater molecular chlorine use and with greater amounts respectively of dibenzodioxin (DBD) and dibenzofuran (DBF) in the brownstock entering the bleach plant. Considerable variability remained after accounting for the effect of these two factors. This variability may have resulted from measurement uncertainties or from other unidentified factors influencing the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF. 2,3,7,8-TCDD and 2,3,7,8-TCDF formation measured in this study showed no correlation to either the chlorine factor or kappa factor.

Oxygen delignification and very high chlorine dioxide substitution both resulted in similar low levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF formation.

Mills bleaching hardwood pulp generally generated less 2,3,7,8-TCDD and 2,3,7,8-TCDF than those bleaching softwood pulp. Most mills bleaching hardwood in this study used less active chlorine than those bleaching softwood.

At one mill, when the chlorine dioxide substitution level was increased in four steps, the 2,3,7,8-TCDD and 2,3,7,8-TCDF formation decreased. The ratio of 2,3,7,8-TCDF to 2,3,7,8-TCDD also decreased.

The DBD content of the brownstock ranged from non-detected at 4 ng/kg odbs to 1700 ng/kg odbs. DBF was measured in brownstocks in quantities ranging from 400 to 130,000 ng/kg odbs.

At several bleach plants, more 2,3,7,8-TCDD was generated than could be theoretically formed from the measured DBD entering the bleach plant with the brownstock. These bleach plants had low or non-detectable levels of DBD in the brownstock. 2,3,7,8-TCDD may have formed from precursors other than DBD at these mills.

#### PARTITIONING OF TCDD AND TCDF BETWEEN FILTRATE AND PULPS

The fraction of 2,3,7,8-TCDD and 2,3,7,8-TCDF generated that left the bleach plant with the final pulp was highly variable. For some bleach plants in the study, the bleached pulp contained most of the total 2,3,7,8-TCDD and 2,3,7,8-TCDF measured. At other mills the major fraction was found in the discharged filtrates.

Possible factors that may influence the partitioning of 2,3,7,8-TCDD and 2,3,7,8-TCDF between the pulp and filtrates leaving the chlorination stage were examined using the data collected in this study. No relationship was observed between the partitioning and (a) filtrate discharge rate; (b) chlorination stage temperature; (c) suspended solids in the filtrate; (d) pitch content of the filtrate; (e) pitch content of the washed pulp; (f) pitch content of the brownstock; or (g) ratio of shower water flow to water content of washed pulp.

The first extraction stage effluent carried the majority of the discharged 2,3,7,8-TCDD and 2,3,7,8-TCDF. Factors influencing the partitioning of 2,3,7,8-TCDD and 2,3,7,8-TCDF between pulp and filtrates in the extraction and subsequent bleaching stages remain unclear.

#### COMMENTS

Many changes in bleaching conditions aimed at reducing TCDD and TCDF generation, such as use of low contaminant defoamers and split addition of chlorine, have been reported in the literature and instituted since the sampling for this project was completed. At the time of sampling, many companies were beginning to experiment with strategies to minimize the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF during bleaching. Some of these process modifications may reduce TCDD and TCDF formation below levels found for the bleaching practices included in this study. These and other process changes have not yet been widely implemented or universally evaluated by the industry. General observations made in this report will not include the benefits of these bleaching innovations.