# PCDD/PCDF CONGENER PATTERNS IN SEDIMENTS DEPOSITED DURING FLOODING DOWNSTREAM OF BLEACHED KRAFT PULP MILLS

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## Introduction

The confirmation of PCDDs and PCDFs in bleached kraft pulp mill effluents has heightened interest in the environmental impacts of the pulp and paper industry. Chlorine-bleached kraft pulp (CBKP) production effluents are characterised by a distinctive congener pattern. This pattern is dominated by the TCDD and TCDF congeners, in which the most toxic isomers, 2,3,7,8-TCDF and 2,3,7,8-TCDD, are the most abundant, followed by 1,2,7,8-TCDF.[1,2] 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD have also been noted, and more recently, many pulp and paper mill effluents have also been characterized by the presence of OCDD at levels at or above those found for the tetrachlorinated congeners[3,4]. Hexa- and hepta- chlorinated dioxins and furans have also been observed in mill export vectors[5]. In all cases the 2,3,7,8-isomers are prominent in the pattern, and the total dioxins are generally found at much lower concentrations than furans.

The transport and fate of these compounds in aquatic ecosystems is less well established. Based on the limited data available, PCDD/F patterns in the sediments downstream of CBKP mills do not appear to mirror those patterns established in export vectors from the mills. This paper examines the PCDD/F patterns of river sediments near the outfalls of CBKP mills, as well as the patterns in river sediments deposited on the banks of some rivers during seasonal flooding episodes, over 100 km downstream. This paper will review the typical pattern of PCDD/F congeners in effluent and sediment samples obtained from the vicinity of pulp mills, and discuss historical deposition patterns and transformation mechanisms which result in the evolution of the PCDD/F profile with increasing distance from the outfall.

## Methodology

In assessing the changes in congener profile with increasing distance from the CBKP mill source, available data from the literature is reviewed to establish the patterns commonly observed in CBKP mill export vectors, as well as the patterns established

in the sediments near the outfalls. The sediment data is restricted, for the purposes of comparison, to those studies where the source was located on a river system.

In addition, PCDD/PCDF data is presented from sediments deposited during flooding episodes on the banks of two rivers downstream of CBKP mills. These samples were analyzed for 2,3,7,8-isomers and total PCDD and PCDF homologues by high resolution GC/high resolution MS.

**Results and Discussion**

Figure 1 shows the normalized homologue profile typically associated with chlorine-bleached kraft mill discharges.[7] This profile reflects a normalized average of 54 effluent analyses from 9 CBKP mills. As discussed in the introduction, the prominent congeners are the tetra- and octachlorinated dioxins and the tetrachlorinated furans.

Figure 2 shows the pattern observed in sediments downstream of the outfalls of CBKP mills as established in a Canadian study of bottom sediments.[6] Only the results from samples downstream of inland mills are considered, and those mills where dioxins and furans were not detected, or where the authors suggested the data was not as reliable, are not included. The data represent the normalized average from the analysis of 23 samples from 10 mills. Samples from this study were collected within 2 km of the mill outfalls.

It is evident from Figure 2 that higher chlorinated congeners in general are more prominent in the sediment than in the effluent, and OCDD makes a considerably larger contribution. Notable in this profile is the increased contribution of hexa, hepta, and octachlorinated dibenzofuran congeners to the pattern, and the relatively small contribution of tetrachlorinated dibenzodioxins, compared to the effluent profile.

Figure 3 indicates the congener profiles observed in samples collected from the banks of two rivers at locations approximately 65, 100, and 130-150 km downstream of two CBKP mills (Mill #1 and mill #2) located in the United States. The sampling locations for these data were chosen to reflect the deposition of river sediments during many years of periodic flooding episodes. The shifts in homologue profile observed in Figure 2 become increasingly pronounced with increasing distances from the mills, and the proportionally greater increase in octachlorinated dioxin suggests that other sources are also contributing to the pattern. In many cases, octachlorodioxin levels were elevated well above the levels generally considered to be background in urban or rural areas[7] and that no obvious sources were noted near the sampling area. In addition, a control soil sample was taken outside the floodplain of mill #2, and the OCDD levels were an order of magnitude or lower than those observed in the nearby sediment samples.

The above data demonstrates that characteristic PCDDs and PCDFs can be detected over 100 km downstream from a chlorine bleached kraft mill source. The

PCDFs detected in the soil samples shown in Figure 3 are not usually seen in typical rural and urban samples. The changes in homologue profiles with increasing distance from CBKP mills reflect the sum total of a number of processes. Rather than the snapshot profile pattern observed in mill export vectors, the downstream floodplain samples show the accumulation of PCDDs and PCDFs from periodic deposition over the lifetime of input from the mill. In addition, the downstream samples mirror specific transformation and deposition processes, and the influence of sources other than the upstream CBKP mill. These processes include dissolution, adsorption, volatilization, photolysis, biodegradation and biouptake.[8]

When PCDDs and PCDFs are discharged to water there is a tendency to partition into the sediments which increases with increased chlorination. Generally, organic micropollutants favour fine sediments with high surface areas, high organic carbon content and high lipid content. The finer sediments would be transported further and are more likely to be deposited on the river banks during flooding episodes. In addition, the higher chlorinated congeners degrade more slowly and are less readily taken up by aquatic organisms, if at all.[9] The observed shift to a greater proportion of higher chlorinated homologues with increasing distance from the mill sources is consistent with the predicted fate and transport of PCDDs and PCDFs based on their physical and chemical properties.

**References**


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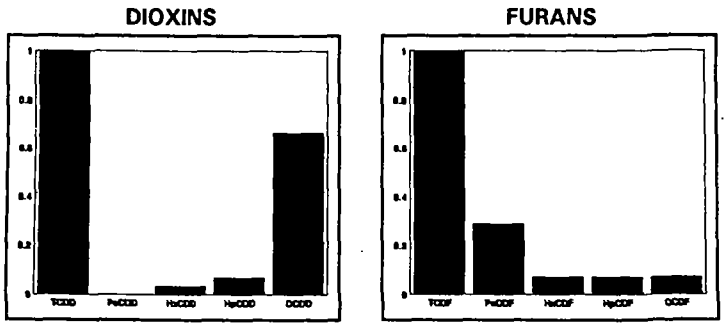


**Figure 1**
PCDD/Fs in Effluent

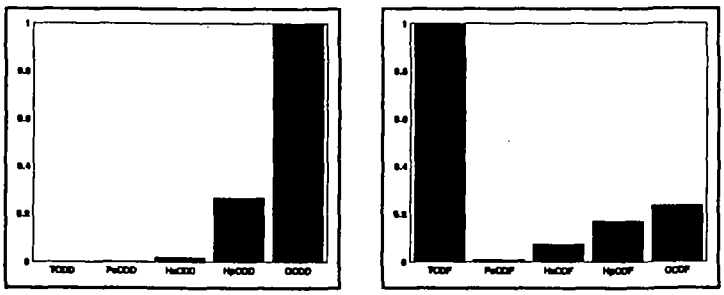

**Figure 2**
PCDD/Fs in Sediment 0 to 2 km Downstream

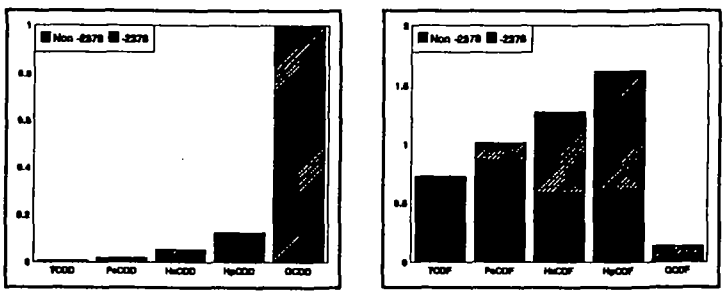

**Figure 3**
PCDD/Fs in Sediment 65 km Downstream

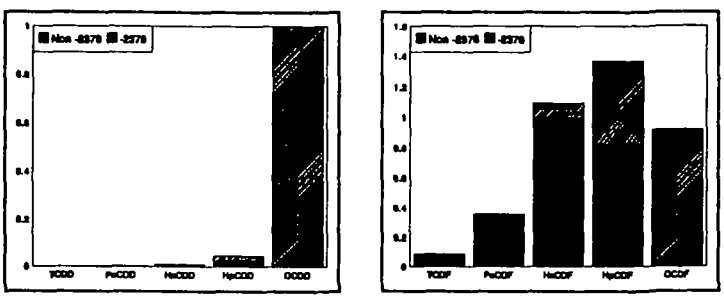

**Figure 4**
PCDD/Fs in Sediment Approximately 100 km Downstream

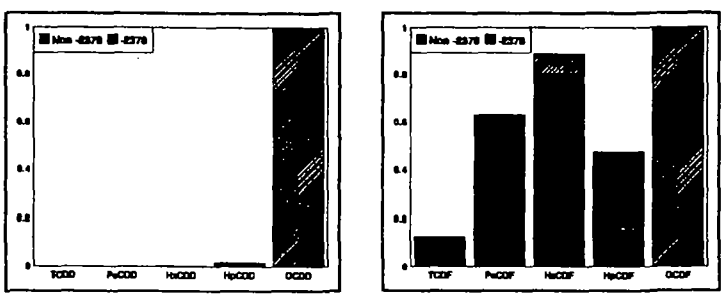

**Figure 5**
PCDD/Fs in Sediment 120 to 150 km Downstream