# The Occurrence, Distribution, and Fate of Di- and Tri- Chlorinated Dibenzo-p-dioxins [CDDs] and Dibenzofurans [CDFs] in Pulp Mill Effluent, Bottom Sediment and Biota

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The substitution of chlorine dioxide in Canadian bleached kraft mills [BKME] has resulted in major reductions of tetrachloro-dibenzo-p-dioxin, tetrachloro dibenzofuran, and chlorophenol emissions[1]. The purpose of this study was (1) to analyze for di- and trichlorodibenzo-p-dioxins and dibenzofurans (2,3-, 2,7-/2,8-, and 2,3,7-dioxins congeners and 2,8- and 2,3,8-furan congeners) in samples of effluent, depositional sediment, and biota and (2) to determine if these congeners could be used as hydrophobic organic markers for BKME. The work was part of a larger study of the fate, distribution, and cumulative effects of contaminants in the Athabasca and Peace Rivers in northern Alberta.

Samples of mill effluent, bottom surficial sediments, and mountain whitefish were collected upstream and at 5 sites up to 180 km downstream of the mill. Samples were analyzed for CDDs and CDFs using high resolution GC/high resolution MS modified to include the surrogate $^{13}C_{12}$-2,7/2,8-CDD [2]. 2,7-CDD and 2,8-CDD are reported as a sum parameter because these two congeners cannot be separated chromatographically on a Hewlett Packard Ultra 2 chromatographic column.

2,7-/2,8-CDD were detected only once in the effluent from four kraft bleaching mills as shown in Table 1. The concentration amounted to 20 pg/L. The detection limit based on 1 L of effluent sample was 4.6-13 pg/L. 2,3-CDD was only detected twice in effluent samples taken from four kraft bleaching mills [Table 1]. The concentrations were 15 and 57 pg/L, respectively and the detection limit was 5.6-14 pg/L. 2,3,7-CDD was detected in 3 effluent samples at 2 mills at concentrations between 7.6 - 53 pg/L. 2,8-DCF was detected in all effluent samples studied at concentrations from 35 - 570 pg/L. 2,3,8-CDF was detected in all effluent samples studied and concentrations varied between 42 - 270 pg/L. 2,3,7,8-CDF was detected in most effluent samples and concentrations varied between 4.3 - 29 pg/L. The ratio between 2,3,8-CDF and 2,3,7,8-CDF was approximately 10:1 for 7 of the 14 effluents samples suggesting a similar mechanism of formation.

**TABLE 1 Di-, Tri-, and Tetra-CDD/CDF in BKME (pg/L)**

| Sample | 2,7/2,8-CDD | 2,3-CDD | 2,3,7-CDD | 2,8-CDF | 2,3,8-CDF | TCDF |
|---|---|---|---|---|---|---|
| Mill 1 | < 5.8 | < 5.6 | < 2.0 | 110 | 65 | 9.7 |
| Mill 1 | < 7.8 | < 7.5 | < 5.8 | 430 | 160 | 8.8 |
| Mill 1 | < 7.2 | < 6.8 | < 4.8 | 220 | 76 | 7.3 |
| Mill 1 | < 11 | < 11 | < 3.8 | 240 | 75 | 5.5 |
| Mill 2 | < 9.6 | < 9.4 | < 6.6 | 130 | 57 | < 4.2 |
| Mill 2 | < 5.6 | < 5.4 | < 4.7 | 340 | 64 | 6.1 |
| Mill 2 | < 5.6 | < 5.4 | 7.6 | 200 | 92 | 33 |
| Mill 2 | < 13 | < 14 | < 4.3 | 140 | 88 | 7.0 |
| Mill 3 | < 5.6 | < 5.4 | 53 | 490 | 270 | 29 |
| Mill 3 | 20 | 57 | <4.9 | 280 | 110 | 11 |
| Mill 3 | < 6.8 | < 6.5 | 8 | 570 | 180 | 15 |
| Mill 3 | < 12 | < 13 | < 5.6 | 180 | 120 | 15 |
| Mill 4 | < 4.6 | < 4.2 | < 6.2 | 51 | 42 | 4.3 |
| Mil 4 | < 5.4 | < 11 | < 3.1 | 35 | 100 | 5.9 |

Table 2 summarizes the data obtained for the analysis of depositional sediments taken downstream of a kraft mill discharge [KMD]. The most commonly detected CDDs/CDFs include 2,7-/2,8-CDD, 2,8-CDF, 2,3,8-CDF and 2,3,7,8-CDF. The most prominent component was 2,8-CDF which is consistent with data obtained for BKME effluent. These data suggest that CDD/CDF may be transported in the aquatic environment on suspended solids like the higher congeners[1,3]. For depositional sediments the ratio of 2,3,8-CDF to TCDF was 10:1 for three of the six samples analyzed an observation that is similar to that obtained for BKME effluent.

**TABLE 2 Di-, Tri-, and Tetra-CDD/CDF in River Bottom Sediments (pg/g)**

| Sample | 2,7/2,8-CDD | 2,3-CDD | 2,3,7-CDD | 2,8-CDF | 2,3,8-CDF | TCDF |
|---|---|---|---|---|---|---|
| Site 1 | < 0.2 | 0.5 | < 0.1 | < 0.1 | 0.3 | 0.2 |
| Site 1 | 1.8 | < 0.1 | < 0.1 | < 0.2 | 1.1 | < 0.1 |
| Site 1 | < 0.2 | < 0.1 | 0.6 | < 0.1 | 0.7 | 0.4 |
| Site 2 | 3.6 | < 0.1 | < 0.1 | 16 | 6.3 | < 0.2 |
| Site 3 | 4.4 | < 0.1 | < 0.1 | 26 | 8.9 | 1.0 |
| Site 4. | 6.4 | < 0.1 | < 0.1 | 55 | 25 | 2.1 |

Note: Site 1 is approximately 1250 km downstream of a KMD
Site 2 is approximately 1 km downstream of a KMD
Site 3 is approximately 20 km downstream of a KMD
Site 4. is approximately 48 km downstream of a KMD

Table 3 summarizes the data obtained from the analysis of mountain whitefish muscle and liver.

**TABLE 3 Di-, Tri-, and Tetra-CDD/CDF in Mountain Whitefish Muscle (M) and Liver (L) (pg/g)**

| Sample | 2,7/2,8-CDD | 2,3-CDD | 2,3,7-CDD | 2,8-CDF | 2,3,8-CDF | TCDF |
|---|---|---|---|---|---|---|
| Site 1M | < 0.2 | < 0.1 | < 0.1 | 0.9 | 1.5 | 3.6 |
| Site 1L | < 1.4 | < 2.4 | < 0.3 | < 0.2 | 4.0 | 3.1 |
| Site 2M | < 0.2 | < 0.2 | 0.1 | < 0.1 | 1.9 | 4.0 |
| Site 2L | < 0.5 | < 0.9 | < 0.2 | < 0.1 | 2.2 | 6.9 |
| Site 3M | < 0.4 | < 0.4 | < 0.1 | < 0.1 | 1.9 | 19 |
| Site 3L | < 0.1 | < 0.1 | < 0.1 | < 0.4 | 3.0 | 3.0 |

From these results it is apparent that 2,3,8-CDF and 2,3,7,8-CDF are generally detected in all samples of mountain whitefish analyzed, however, the levels are very low. Furthermore, the ratio of 2,3,8-CDF to 2,3,7,8-CDF is not 10:1 as was observed for effluent, and bottom sediment, indicating that 2,3,8-CDF is much more readily eliminated by fish than 2,3,7,8-CDF.

In conclusion, current movement by the kraft bleaching industry towards chlorine dioxide substitution has resulted in reduced effluent discharges of 2,3,7,8-CDD, 2,3,7,8-CDF and chlorinated phenols[1], however, compounds such as 2,8-CDF, 2,3,8-CDF and 2,3,7,8-CDF are still detectable in samples of BKME effluent and river depositional sediment. In many cases the ratio of 2,3,8-CDF concentration to

2,3,7,8-CDF is 10:1 and this was observed during the analysis of effluent and bottom sediment. Analysis of fish muscle and liver samples revealed low levels of 2,3,8-CDF and 2,3,7,8-CDF, however these compounds were detected in all samples analyzed.

Di- and trichloro CDDs/CDFs do not elicit the toxic effects of the 2,3,7,8-tetrachloro-congeners. They have low binding affinities for rat hepatic cytosol Ah receptor and are known to be rapidly biotransformed by mammals[4]. 2,8-CDD was found to be non-toxic to goldfish and readily biotransformed to a hydroxy-di-CDD[5]. 2,3,8-CDF has been shown to induce hepatic mixed function oxidase (MFO) activity in rainbow trout[6] , however, the dose required to elicit such a response was relatively high [300 nanograms per gram of fish administered orally over twenty days]. In light of these studies it seems unlikely that adverse effects on fish can be associated with exposure to di- and tri- CDDs/CDFs, however, they may be useful markers of hydrophobic organics in bleached kraft mill emissions.

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