Comparative Analysis of Polychlorinated Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs) in Suspended Solids of Three Wastewater Types - Pulpmill, Municipal and Combined Sewer Overflow

Derksen George
Pollution Abatement Division, Environment Canada, 224 West Esplanade, North Vancouver, B.C. Canada. V7M 3H7

1. Introduction

Studies incorporating ^{14}C added as glucose have demonstrated that suspended biological solids (biosolids) do not readily settle out in the receiving environment and are concentrated and incorporated by benthic invertebrates [1,2]. Highly hydrophobic compounds (log K_{ow} >6) such as tetra-chlorinated dibenzo dioxin/furans (TCDD/DF) seek to remove themselves from water by partitioning into the organic pools of colloidal and solids materials in the aquatic environment.

There is ongoing interest in the fate of hydrophobic compounds in the aquatic environment [3,4,5]. Considering that biosolids and any associated contaminants can be incorporated directly into the aquatic foodchain, Environment Canada initiated a program to look at contaminants associated with the suspended solids matrix of several wastewater sources including pulpmills [6], municipal sewage, and combined sewer overflows. The focus of this effort has been on the Fraser River, as part of the Fraser River Action Plan [7].

2. Approach and Methods

Effluent solids were obtained using a submersible pump and an Envirodat Sedisamp II continuous-flow centrifuge operated at a flow rate of 4L/m. A description of operating procedures, cleanup and sample handling is reported in detail elsewhere [8].

In addition to PCDDs/PCDFs, suspended solids were tested for carbon/nitrogen, chlorophenolics, PAHs, PCBs and heavy metals. For PCDDs/PCDFs, a subsample of wet sample was ground with sodium sulphate and extracted by refluxing in a soxhlet apparatus for 20h. The extract was back washed with base and then acid, and processed through the four cleanup columns (silica, alumina, carbon, alumina). Each sample was spiked with an aliquot of surrogate standard solution containing nine ^{13}C-labelled dioxin and furan congeners for measuring extraction efficiency. An aliquot of ^{13}C-

labelled recovery standard was added to each extract prior to analysis by HRGC/HRMS. Carbon and nitrogen were determined on an air-dried sample with a Carlo-Erba elemental analyzer.

3. Results and Discussion

The reduction in pulpmill biosolid dioxin/furan concentrations as a result of the implementation of improved mill operations, including high levels of chlorine dioxide substitution, is evident in Figure 1. Wastewater source details are given in Table 1. In 1990/91, 2,3,7,8-TCDD levels in biosolids in the three mills tested ranged between 85 to 560 pg/g (n=4) [6]. In 1993/1994, for three of the five mills sampled, 2,3,7,8-TCDD concentrations ranged between <0.8 to 7.2 pg/g (n=5). The high concentration (81 pg/g 2,3,7,8-TCDD) at Mill 6 is considered to be a result of dredging operations within the aerated stabilization basin a month earlier. The higher concentration (47 pg/g 2,3,7,8-TCDD) at Mill 3 is unexplained.

The ratio of 1,2,3,6,7,8-H6CDD to 1,2,3,4,7,8-H6CDD for the different wastewaters is reported in Table 1. The low ratio (2.0-5.3) for the municipal wastewaters is similar to levels (2.5-3) reported to reflect atmospheric sources [9]. The combined sewer overflow had the lowest carbon (24.5%) and nitrogen (3.2%) content.

A comparison of pulpmill biosolids with municipal sewage and combined sewer overflow suspended solids(Figure 2) show the two latter wastewaters to generally have a higher overall toxic equivalent concentration then the pulpmills tested (Mill 6 data point removed).

4. References

1) Costa, H.S., J.J. McKeown, and D.L. Borton (1980) : Fate of Suspended Biological Solids Discharged to Receiving Waters. Journal WPCF. 52, 2432-2441.

2) NCASI (1978) : A Study of the Fate of Biosolids from Biologically Treated Effluent in Laboratory and Constructed Streams. Technical Bulletin 308, 14pp.

3) Muir, D.C.G., W.L. Fairchild, and D.M. Whittle (1992) : Predicting Bioaccumulation of Chlorinated Dioxins and Furans in Fish Near Canadian Bleached Kraft Mills. Water Pol. Res. J. Canada. 27, 487-507.

4) Comba, M.E., and K.L.E. Kaiser (1990) : Suspended Particulate Concentrations in the St. Lawrence River (1985-1987) Determined by Centrifugation and Filtration. Sci. Total Environ. 97/98, 191-206.

5) NCASI (1995) : Mass Transfer of TCDD/F from Suspended Sediment Particles. Technical Bulletin 689, 13pp.

6) Derksen, G., and G. Mitchell (1994) : Characterization of Fraser River Basin Bleached Kraft Pulpmill Biosolids. Environment Canada, North Vancouver. Draft Report, 35pp.

7) Fraser River Action Plan (1993) : 1992-93 Progress Report. Environment Canada, North Vancouver. DOE FRAP 1993-02, 20pp.

8) Mitchell, G. (1994) : Field Operating Procedures for Envirodat Sedisamp II Centrifuge for the Measurement of Dioxins and Furans is Suspended Sediment. Environment Canada, North Vancouver. RPR 94-01, 34pp.

9) Horstmann, M., A. Kaune, M.s. McLachlan, M. Reissinger, and O. Hutzinger (1992) : Temporal Variability of PCDD/F Concentrations in Sewage Sludge. Chemosphere. 25, 1463-1468.

TABLE 1: Wastewater Sources - Biosolids Carbon/Nitrogen Content and 1,2,3,6,7,8-H6CDD:1,2,3,4,7,8-H6CDD Ratio - 1993/94

Wastewater	(C%/N%)	H6CDD Ratio
Mill 1 BK-ASB	39.4/6.3;47.7.7	-
Mill 2 BK-ASB	52.4/5.5;51.9/6.1	36:1
Mill 3 BK-ASB	37.1/4.4	73:1
Mill 4 CTMP-ASB	42.9/7.0	-
Mill 5 BK-LRAS	46.2/4.5	-
STP 1 Partial 2^0	41.6/7.6	5.3:1
STP 2 1^0	41.3/5.3	2.0:1
STP 3 1^0	47.7/6.6	4.3:1
CSO 1	24.5/3.2	3.3:1;2.2:1

BK-ASB = Bleached Kraft-Aerated Stabilization Basin
BK-LRAS = Bleached Kraft-Low Rate Activated Sludge
CTM = Chemical Thermal Mechanical

FIGURE 1: TCDD, TCDF, and Other PCDD/PCDFs EXPRESSED AS TOXIC EQUIVALENTS

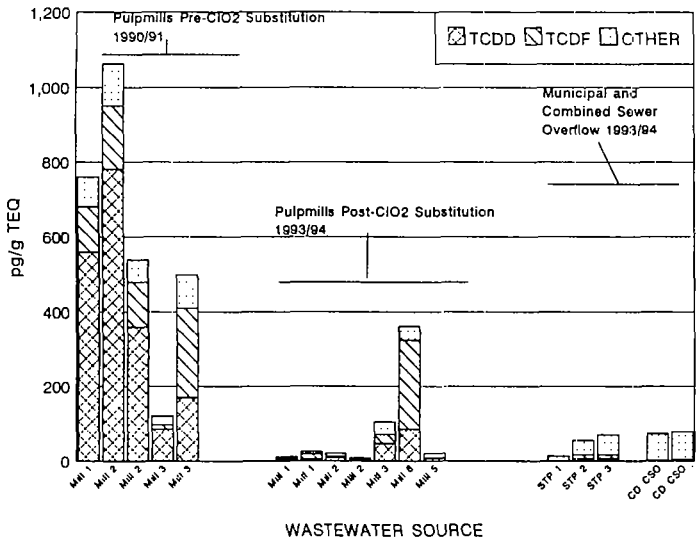

FIGURE 2: TCDD, TCDF, and Other PCDD/PCDFs EXPRESSED AS TOXIC EQUIVALENTS