# PCDD/PCDF Levels in Raw Sewage, Final Effluent, Sludge, and Ash Samples from an Ontario Waste Water Treatment Plant

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## Abstract

Raw sewage, final effluent, sludge and ash samples were taken over a consecutive 5-day period at an Ontario waste water treatment plant (WWTP) and analyzed for PCDD/Fs by triple quadrupole GC/MS/MS and isotope dilution quantitation. The PCDD/Fs levels increased significantly in the heat treated sludge as compared to the raw sewage, suggesting de novo formation of the contaminants. No PCDD/Fs were found in the bottom ash of the multiple-hearth incinerators. Detection limits ranged from 1 to 7 ppt.

## Introduction

Lamparski and co-workers first reported the presence of PCDDs in a sealed 1933 sample of dried municipal sewage sludge[1]. Since then, there have been many of accounts of the presence of PCDD/Fs in sewage sludge and associated with land applications of sludge. These reports include description of PCDD/Fs levels in sewage sludges from various regions worldwide[2-5], incinerator emissions for sludge burning facilities[6-7], investigations of potential sources[8-14], and proposed mechanisms of formation.[15-18]

More recently, discussions of fertilization and land application have surfaced,[19-20] generating concern about the hazards associated with repeated and long-term applications of sewage sludges to agricultural lands. These land use applications are frequently limited by guidelines that address levels of heavy metals in the soils. However, in many jurisdictions, no restrictions have been established for organic contaminants. As a result, land application of sludges has become highly controversial owing to the possibility of introducing these toxic pollutants into food chains.

Numerous other options exist for the disposal of sewage sludge. These include sludge-only landfills (monofills), mixed waste landfills, ocean disposal and incineration. Among these, incineration presents many unique features[21]. In addition to achieving a substantial weight and volume reduction, there is also the potential for heat recovery. Disposal of the sludge may frequently occur at the point of generation, effectively eliminating the hazards and costs associated with transportation. Finally, current incinerators are capable of operating within legislated emission guidelines and as point sources they lend themselves to effective monitoring.

## Experimental

Samples were extracted using liquid/liquid or Soxhlet-based techniques. The resultant extracts were cleaned up using a dual stage open column chromatography procedure consisting of modified silica and alumina stationary phases. Standard PCDD/Fs mixtures were prepared from stock solutions obtained from either Cambridge Isotope Laboratories Inc. or Wellington Laboratories. The internal quantitation standard contained 15 $^{13}C_{12}$ 2,3,7,8-substituted PCDD/Fs (see Table 2 for specific congeners). Prior to injection, the samples were reconstituted with a recovery standard solution containing $^{13}C_{12}$-1,2,3,4-T4CDD and $^{13}C_{12}$-1,2,3,7,8,9-H6CDD at 100 pg/$\mu$L in nonane. All samples were analyzed by GC/MS/MS (Varian 3400 GC/Finnigan MAT TSQ 70 triple quadrupole mass spectrometer), and an ICIS II data system. Samples were chromatographed using a 60m x 0.25 mm i.d. x 0.25 $\mu$m film thickness J&W DB-5 fused silica capillary column. Complete details of the analytical procedure are available elsewhere[22].

## Results and Discussion

Treatment Plant Description

The treatment plant is a conventional activated sludge facility which uses secondary treatment to process an average 170,000 m$^3$/day of influent, serving an estimated population of 290,000. Approximately 22 percent of the flow into the facility is estimated to be industrial in nature[23] (Table 1), 13 percent residential, and 5 percent commercial. The remaining inputs are uncharacterized.

**Table 1 - Summary of Industrial Influents to Wastewater Treatment Plant**

| Industry Type | Number of Establishments |
|---|---|
| Machinery Manufacturing | 165 |
| Printing & Publishing | 134 |
| Electrical and Electronic Components | 80 |
| Metal Finishing | 71 |
| Furniture Manufacturing | 43 |
| Miscellaneous Converted Paper Products | 37 |

Secondary effluent is chlorinated year-round and discharged to Lake Ontario. Sludge treatment

involves dissolved air flotation, anaerobic digestion, grinding, heat treatment by the Porteous process and centrifugal dewatering. The resultant sludge is incinerated using two multiple hearth incinerators, with a combined capacity of 5 tonnes of sludge cake per hour at 30% total solids. The ash and scrub water from the incinerator is lagooned.

Raw Sewage and Final Effluent

A summary of the data for the four sample types is presented in Table 2. The raw sewage data are dominated by hepta- and octa-chlorinated congeners, with the PCDD levels present in excess of the PCDF levels. The data correspond to 1.6 pg TEQ/L, which falls well under the Ontario Drinking Water Quality Objective of 15 pg TEQ/L. Neither 2,3,7,8-T4CDD nor 2,3,7,8-T4CDF were detected in any of the raw sewage samples taken during the 5-day period. The levels and congener patterns are consistent with those observed at other WWTPs in the Province of Ontario. Analysis of the final effluent did not detect the presence of any PCDD/Fs. Detection limits ranged from 6 to 60 pg/L.

Sludge

Data for the sludge samples, averaged over 5 days, are presented in column 3 of Table 2. In addition to O8CDF and O8CDD, 2,3,7,8-substituted isomers from the H6CDD, H7CDD and H7CDF homologues were also observed. The data correspond to 15.7 pg TEQ/g. Neither 2,3,7,8-T4CDD nor 2,3,7,8-T4CDF were detected in any of the sludge samples. Concentrations of congener groups were found to increase with increasing degree of chlorination, with the pattern dominated by O8CDD at a mean value of 6500 pg/g. Presently, there are no Ontario guidelines defining the maximum levels of PCDD/Fs in sludges.

Ash

Analysis of the incinerator bottom ash did not detect the presence of any PCDD/Fs. Detection limits ranged from 1 to 7 ppt. Ontario currently does not have any guidelines identifying acceptable levels of PCDD/Fs in incinerator ash. However, the data fall within acceptable ranges for both agricultural and residential soils (10 and 100 pg of TEQ/g respectively). Previous incinerator studies at the same facility concluded that the levels of PCDD/Fs were substantially lower than those observed at municipal solid waste incinerators (MSWs) [6]. The facility in question has also been shown to meet emission guidelines with no source related air borne deposition of PCDD/Fs[7]. We conclude that the incinerator operating at the facility offers a viable alternative to land application for the disposal of sewage sludges.

Interpretation

The congener group profile of the heat treated sludge is consistent with most previously reported sludge patterns[3,18,24-26]. A closer examination of the data suggests that the PCDD/Fs present are not indicative of pentachlorophenol (PCP) contamination. The signature congeners, 124689-H6CDF and 1234689-H7CDF, are absent from the chromatograms. Gihr and coworkers[8] concluded that known sources of PCDD/Fs, such as PCP, could not wholly explain sewage sludge contamination, and examined numerous potential pathways of PCDD/F introduction. Possible sources were the textile industry, the pulp and paper industry, car traffic, and air (municipal solid waste incineration, hospital incineration and domestic heating). They concluded that atmospheric deposition, followed by runoff, was a significant contributor of PCDD/Fs. It has

**TABLE 2: Analytical Results for Polychlorinated Dibenzo-p-dioxins And Polychlorinated Dibenzofurans**

| | AVERAGE VALUES FOR 5 CONSECUTIVE DAYS | | | |
|---|---|---|---|---|
| | Raw Sewage pg/L | Final Effluent pg/L | Sludge pg/g | Ash pg/g |
| T4CDD | ND(9) | ND(7) | 200[5] | ND(2) |
| P5CDD | ND(10) | ND(8) | 530[3] | ND(2) |
| H6CDD | ND(20) | ND(10) | 250[5] | ND(1) |
| H7CDD | 34[2] | ND(6) | 730[2] | ND(2) |
| O8CDD | 1300 | ND(60) | 6500 | ND(2) |
| T4CDF | ND(10) | ND(7) | ND(20) | ND(6) |
| P5CDF | ND(10) | ND(8) | 11[1] | ND(4) |
| H6CDF | ND(20) | ND(20) | 26[3] | ND(5) |
| H7CDF | ND(20) | ND(10) | 81[2] | ND(7) |
| O8CDF | 79 | ND(20) | 250 | ND(3) |
| | 2,3,7,8-Substituted Isomers | | | |
| 2,3,7,8-T4CDD | ND(9) | ND(7) | ND(9) | ND(2) |
| 1,2,3,7,8-P5CDD | ND(10) | ND(8) | ND(6) | ND(2) |
| 1,2,3,4,7,8-H6CDD | ND(20) | ND(10) | ND(6) | ND(1) |
| 1,2,3,6,7,8-H6CDD | ND(20) | ND(10) | 22 | ND(1) |
| 1,2,3,7,8,9-H6CDD | ND(20) | ND(10) | 23 | ND(1) |
| 1,2,3,4,6,7,8-H7CDD | 19 | ND(6) | 400 | ND(2) |
| 2,3,7,8-T4CDF | ND(10) | ND(7) | ND(6) | ND(6) |
| 1,2,3,7,8-P5CDF | ND(10) | ND(8) | ND(5) | ND(3) |
| 2,3,4,7,8-P5CDF | ND(10) | ND(8) | ND(5) | ND(3) |
| 1,2,3,4,7,8-H6CDF | ND(20) | ND(20) | ND(10) | ND(5) |
| 1,2,3,6,7,8-H6CDF | ND(20) | ND(10) | ND(10) | ND(3) |
| 2,3,4,6,7,8-H6CDF | ND(20) | ND(20) | ND(10) | ND(3) |
| 1,2,3,7,8,9-H6CDF | ND(20) | ND(20) | ND(10) | ND(3) |
| 1,2,3,4,6,7,8-H7CDF | ND(20) | ND(10) | 46 | ND(7) |
| 1,2,3,4,7,8,9-H7CDF | ND(20) | ND(10) | ND(4) | ND(3) |

Values are corrected for recovery of isotopically labelled surrogate standards.
"ND" Not detected. Detection limit given in brackets ( ).
Superscripts indicate the number of isomers detected.

recently been observed that the typical sludge pattern still dominates the sludge profiles in samples from totally uncontaminated areas and in samples from cities with MSW incineration, chemical industries or pulp and paper industries[4]. Other interpretive efforts have focussed on laundry wastewater and the textile industry[10,13,14]. Given the variety of inputs that influence the WWTP in the current study (refer to Table 1) it is difficult to attribute the PCDD/F contamination to any single source.

Most attempts at calculating a PCDD/F mass balance for WWTP have been unable to account for the levels present in sewage sludge[24,25]. The inadequacy of these models is suggestive of a de novo formation of PCDD/Fs. Similar conclusions regarding the possibility of sludge as a primary source of PCDD/Fs have been previously offered[1,16,18]. The marked difference in pattern and levels of PCDD/Fs observed in the digested sludge as compared with the levels in the raw sewage is consistent with this hypothesis.

The present study supports the conclusions of Bazler and Pluschke[18], which attributes the formation of PCDD/Fs to the Porteous process. Although no raw or untreated sludges were examined in the current study, there is an obvious enrichment of the PCDD/F levels and profiles when comparing the raw sewage and the final thermally treated sludge. No efforts were made to identify and quantitate the presence of pre-dioxins. In consideration of the variety of industries contributing to the plant catchment (Table 1), it is highly likely that such species might exist.

**Conclusions**

Currently, the level of understanding of the processes governing the introduction and potential formation of PCDD/Fs in sewage sludge is limited. Moreover, the processes by which contaminants within land applied sludge enter the food chains are potentially even more complex. In the face of ever-tightening constraints and legislation, the preferred routes for sewage sludge disposal may conceivably change. When unique patterns of PCDD/F contamination are present, it may be possible to identify and abate the source of contamination, giving rise to a final sludge product which is more amenable to disposal by land application. Given the numerous pathways by which PCDD/Fs (and their precursors) may enter WWTP catchments, the appropriate disposal route may need to be evaluated on a case-by case basis.

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