

**ENVIRONMENTAL IMPACT OF POLYCHLORINATED DIBENZO-p-DIOXINS
AND DIBENZOFURANS FROM A CEMENT KILN**

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1. INTRODUCTION

The detection of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in cement kiln dust (CKD) and stack emissions from cement kilns in the early 1990's¹⁾ indicated that for the cement industry in particular, those kilns burning hazardous waste may be a significant source of dioxins and furans into the environment. The precursor of cement, clinker, is produced by heating a combination of calcium (limestone), silica and iron oxide that has been crushed and ground together to a temperature of about 1,500°C in a rotary kiln. Raw materials flow countercurrent to the kiln's combustion gases which are used to preheat the raw materials. These exhaust gases carry with them finely ground raw materials, products of combustion of the fuel and partially reacted feed materials¹⁾. CKD, a by-product of cement production, is the fine particles that are trapped by pollution control devices such as cyclones, electrostatic precipitators (ESP) and fabric filters (FF). The clinker is finely ground and mixed with gypsum to form cement. Certain conditions during cement production, including temperature and residence times, can be favourable for the formation of PCDD/PCDFs in CKD and stack emission gases^{2,3,4)}.

The data in this report are from samples collected at St. Lawrence Cement (SLC) located on Lake Ontario in Mississauga, Ontario and from areas surrounding the plant. St. Lawrence Cement produces three types of Portland cement: Type I low alkali, Type II low alkali and Type 10 normal. St Lawrence uses waste solvents and waste oil in the cement kiln as a substitute fuel. The ESP, baghouse (fabric filters) and coal mill all vent to the same stack. CKD from the ESP is recycled into the process while CKD from the alkali dust stream (ADS, captured by FF) is used as land fill. About 30% of the exhaust gases go to the ADS just after the cement kiln. The remaining 70% of exhaust gases flow through the feed materials and the ESP.

2. EXPERIMENTAL

Air samples were collected with a high volume air sampler modified to accept a back-up polyurethane foam (PUF) vapour trap situated after a Teflon coated glass fibre particulate filter⁵. Sampling times were typically 48 hrs with sample volumes of about 3000m³. Air samples were collected when St. Lawrence Cement was burning waste solvents and wind directions were southerly or easterly. Two samplers were placed to the north at the Mississauga Golf Course and one sampler was placed to the southeast at Appleby College.

Vegetation and soil samples were taken at 10 parks in varying directions ranging from 0.8 to 5.9 km from the cement plant. Parks were at least 25 years old with tree species that were common to all sites. Norway maple trees were sampled. Foliage was sampled from the tree canopy facing SLC. At each site, an area of approximately 10m x 10m near the sampled tree was selected for soil sampling. Soil samples consisted of 20 soil cores taken at random with an Oakfield soil corer to a depth of 5cm. Cores were homogenized in a stainless steel bowl.

Samples from St. Lawrence Cement were collected as described previously by Schreiber and Croom⁶. Briefly, samples were composited from 25 grab samples in duplicate. Samples were taken for the clinker, kiln feed, coal, CKD-ESP, CKD-ADS, waste oil and waste solvent.

PUFs and filters, soil, CKD-ESP, CKD-ADS, clinker, coal and kiln feed samples were extracted by Soxhlet extraction with toluene. Vegetation samples were extracted by Soxhlet extraction with acetone/hexane. Waste oil, waste solvent and the above extracts were cleaned using a classical, two stage, open column chromatographic procedure. The first stage used silica packings modified with silver nitrate, sodium hydroxide and sulphuric acid. The second stage used alumina as the stationary phase. Samples with considerable interferences were cleaned further using a semi-automated high performance liquid chromatography (HPLC) cleanup with alumina and carbon columns⁷.

Samples were analyzed by gas chromatography - tandem mass spectrometry on a Finnigan Mat TSQ 70 triple quadrupole mass spectrometer linked to a Varian 3400 GC equipped with splitless injection⁸ or by gas chromatography-high resolution mass spectrometry on a Fisons/VG AUTOSPEC magnetic sector mass spectrometer operated at 10,000 resolution (10% valley). The GC was a Hewlett-Packard 5890 II equipped with a splitless injection system. Both gas chromatographs used a 60 m fused silica, 0.25 mm i.d., 0.25 micron film thickness DB-5 stationary phase capillary column.

3. RESULTS AND DISCUSSION

Listed in Table 1 are data for in-plant samples at the St. Lawrence Cement Company (Part A) as well as air (Part B) and soil (Part C) samples taken at the point of impingement as determined by dispersion modelling of emissions from the kiln stack. PCDDs and PCDFs were not detected in any of the 10 vegetation samples. The detection limits for the vegetation samples ranged from 1 to 3 ppt (picograms (10⁻¹²g) per gram of sample) for 2,3,7,8-TCDD and from 1 to 10 ppt for the other congeners. These results indicate that aerial deposition of PCDDs and PCDF onto foliar surfaces are insufficient to result in detectable PCDD/F levels in foliar tissue.

Table 1:

Part A, In Plant Samples from St. Lawrence Cement (1993)

Type of Cement	CKD ESP	CDK-ADS Baghouse	Kiln Feed	Coal	Clinker	Waste Solvent	Waste Oil
I-Low Alkali	16	<1	<1	2.5	<1	170	14
II-Low Alkali	89	0.20*	4.3	4.4	<1	120	28
10 Normal	14	<1	0.14*	0.19*	<1	Not used	17

Results are reported as toxic equivalents (TEQ) of 2,3,7,8-TCDD

All data reported in parts-per-trillion (ppt), picograms (10^{-12} g) per gram of sample

A value of 0 was used in the TEQ calculation for congeners that were not detected

* - Detection limits for some individual congeners are greater than TEQ value

Part B, Air Samples (1989)

Date	MGC - 1	MGC - 2	Appleby College	Toronto Island (Average)
June 7-9	0.029	0.033	0.015	0.063 (Sept 14/88 to Jul 3/89, 6 samples)
June 12-14	0.032	0.035	0.021	

Results are reported as toxic equivalents (TEQ) of 2,3,7,8-TCDD converted from congener group totals using proportional factors⁹⁾

All data reported in pg/m^3

MGC - Mississauga Golf Course

Part C, Soil Samples (1993)

Site (Park)									
1	2	3	4	5	6	7	8	9	10
0.27*	1.1	1.7	5.0	0.22*	0.39*	0.25*	0.92*	0.18*	0.29*
Background PCDD/F Concentration Ranges in Soil From Ontario Cities ¹⁰⁾									
<1 to 160**									

Results are reported as toxic equivalents (TEQ) of 2,3,7,8-TCDD

All results are reported in ppt (picograms/gram of sample dry weight)

A value of 0 was used in the TEQ calculation for congeners that were not detected

* - Detection limit for some individual congeners are greater than TEQ value

** - ppt-TEQ, converted from congener group totals using proportional factors

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Data from Table 1, Part A show that PCDD/F levels were highest for CKD from the ESP during the production of low alkali type-II portland cement (LA-2). Elevated levels of PCDD/Fs were also detected during production of LA-2 cement in the kiln feed and coal. Low or non-detect levels at the ADS, which was sampled at the kiln exit, show that PCDD/Fs are essentially destroyed in the kiln for all three types of cement. Also, the congener pattern observed in the waste solvent and waste oil samples were significantly different from the congener patterns seen in the ESP(CKD), while the congener patterns in the kiln feed and coal samples resembled the congener patterns from the ESP(CKD). These results are consistent with the formation of PCDD/Fs during the preheating/precalcination stage from chlorinated organics present in the raw materials^{3,4}. PCDD/F levels in the low alkali type-I (LA-1) cement were lower than in LA-2. LA-1 cement contains considerably higher levels of iron and alkali (sodium and potassium) than LA-2, which may act as chlorine scavengers, and consequently reduce amounts of PCDD/Fs and their precursors. The range of data reported for CKD in Table 1 Part A, 0.14 ppt to 89 ppt, lies well within the range of 0.008 ppt to 247 ppt previously reported by the U.S. EPA¹. Stack samples have not yet been taken for St. Lawrence Cement, however, levels are expected to be similar to those reported previously by the U.S. EPA¹.

Air samples were taken on two separate occasions and are reported in Table 1 Part B. Both sets of data are in excellent agreement. Samples taken at the Mississauga Golf Course (MGC) and Appleby College were significantly lower than the average value for air samples taken on Toronto Island. The Toronto Island sampling site is located south of Toronto, Ontario, on the Toronto islands and is about 30 km east of St. Lawrence Cement. All samples were considerably lower than the Ontario Ministry of Environment and Energy (MOEE) guideline of 5 pg/m³. Results from MGC are higher than those from Appleby College. MGC is located down wind of the Queen Elizabeth Highway and vehicular traffic may be a prominent source of PCDD/Fs at the MGC location.

Soil samples in Table 1 Part C range from 0.18 ppt to 5.0 ppt and are below the MOEE agricultural soil guideline of 10 ppt and are well below the MOEE residential/parkland/industrial soil guideline of 1 ppb (part-per-billion, ng/g). Also, the results listed above are at the low end of the range of values previously reported for background PCDD/F levels in soil from Ontario cities¹⁰. There was no evidence of a concentration gradient or depositional pattern of PCDD/Fs in relation to St. Lawrence Cement.

Data in Table 1 Part A show that in-plant samples from St. Lawrence Cement are typical of other cement plants burning hazardous waste. Air, soil and vegetation data from samples taken at the predicted point of impingement failed to show any evidence of contamination that could be attributed to emissions from St. Lawrence Cement by the techniques used.

4. REFERENCES

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