Summary of 1996-98 Dioxin/Furan Testing at Lime Plants

Introduction

This report summarizes the findings of two dioxin/furan emissions test programs at lime plants. One was a NLA-sponsored program at a facility in Canada; the other was an EPA program at nine US plants.

NLA-sponsored testing took place in August 1996, and the EPA Office of Air Quality Planning and Standards (OAQPS) Emission Standards Division (ESD) investigation occurred in 1998. The primary objective of both programs was to characterize the uncontrolled and controlled emissions of selected HAPS, including dioxins and furans, from lime kilns.

Testing by EPA took place in three states including Alabama, Ohio, and Texas representing nine lime plants with a total of 12 kilns. NLA-sponsored testing took place at a Canadian plant with two kilns, located in Quebec. The kiln types included pre-heater, vertical, and Calcimatic™ kilns that use a variety of air pollution control devices including baghouses, scrubbers, and ESPs. Two U.S. lime plants (National Lime and Stone and Redland Stone Products) tested in program have since closed.

For the EPA program, PCDD/PCDF samples were collected at the inlet and outlet to the APCD simultaneously and analyzed using Method 23 for 17 individual dioxin and furan congeners. NLA-sponsored sampling at Graybec, Quebec sampled the baghouse outlet only. Results for both programs were expressed as Total PCDD/PCDF (ng/dscm) and Total 2,3,7,8-toxic equivalencies (TEQ) (ng/dscm) adjusted to 7 percent oxygen.

Discussion of Results

Results are summarized below by state and province. Overall, all the 2,3,7,8-toxic equivalencies (ng/dscm at 7% O_2) detected at the stack location were generally one to two orders of magnitude below the Portland Cement MACT limit of 0.2 ng/dscm (TEQ) at 7% O_2. Throughout, detected concentrations of individual PCDD/PCDF congeners were very low[1].

NLA-sponsored testing at Graybec in Quebec included a vertical gas-fired kiln and a pre-heater rotary kiln. Emissions, in terms of the type and concentrations of various congeners were similar for both kilns. Frequency of detection, concentrations ranges, and method detection limits were comparable to most US kilns.

Kilns tested in Alabama (Carmeuse Longview, Lhoist Montevallo, and Lhoist Alabaster) had the lowest PCDD/PCDF concentrations and the lowest frequency of detections. Two of the four kilns tested (Longview kiln 4 and Alabaster kiln 1) were entirely non-detect for the calculated

[1] NLA raised at the time that the EPA contractor (Pacific Environmental Services) reported the individual detection limits for non-detects, which is contrary to EPA Method 23, (Section 9.9) which states "Any PCDD's or PCDF's that are reported as non-detected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample". NLA further observed that the results tables included Estimated Maximum Possible Concentrations (EMPCs). EMPC values represent results for compounds that co-elute from the GC column and have similar mass spectra as the target PCDD/PCDF congener, but do not meet the mass spectral criteria for the expected chlorine isotopic pattern of a dioxin/furan.

TEQs at the stack location. The remaining kilns had no more than two congeners detected at very low concentrations at the stack.

Tests performed at kilns in Ohio had PCDD/PCDF detections at slightly higher concentrations and frequencies than Alabama. However, even the highest emitter (National Lime and Stone Company in Cary, OH) had a stack concentrations of 0.037 (TEQ) ng/dscm at 7% O_2. This particular kiln was a gas-fired Calcimatic™ kiln that has since closed.

Other Ohio kilns included Martin Marietta kilns 1 and 2 and Huron Lime kiln 3. Although several individual dioxin/furan congeners were detected, TEQs at the stack location were again one to two orders below the cement MACT limit. At each kiln, the majority of detections were of pentachlorinated furans, followed by tetra and hexa-chlorinated furan congeners with far lesser concentrations of tetra- and penta-chlorinated dibenzodioxins.

Kilns tested in Texas included Austin White, Lhoist Marble Falls, and Redland Stone Products Austin White kilns 2 and 3, despite being tested under non-representative conditions (pre-heater inlet and kiln exit temperatures were not in their normal operating ranges) had low frequency of detection and low concentrations at the stack, and the concentrations at the stack location (0.002 – 0.003 (TEQ) ng/dscm) were two orders of magnitude below the cement MACT limit.

Results from Lhoist Marble Falls (a gas-fired vertical kiln) were found to be the highest of all kilns tested, with positive detections of all PCDD/PCDD congeners at the stack location. The total was again driven by penta- and tetra-chlorinated furans with lesser concentrations of tetra- and penta-chlorinated dibenzodioxins. However, despite all congeners being detected at the stack location, the total concentration (0.045 (TEQ) ng/dscm at 7% O_2) was well below the current cement MACT.

A summary graph showing inlet and outlet concentrations in ng/dscm at 7% O_2 (expressed as 2,3,7,8 TEQ) for all kilns in the EPA study compared to the cement MACT limit is shown in Attachment 1

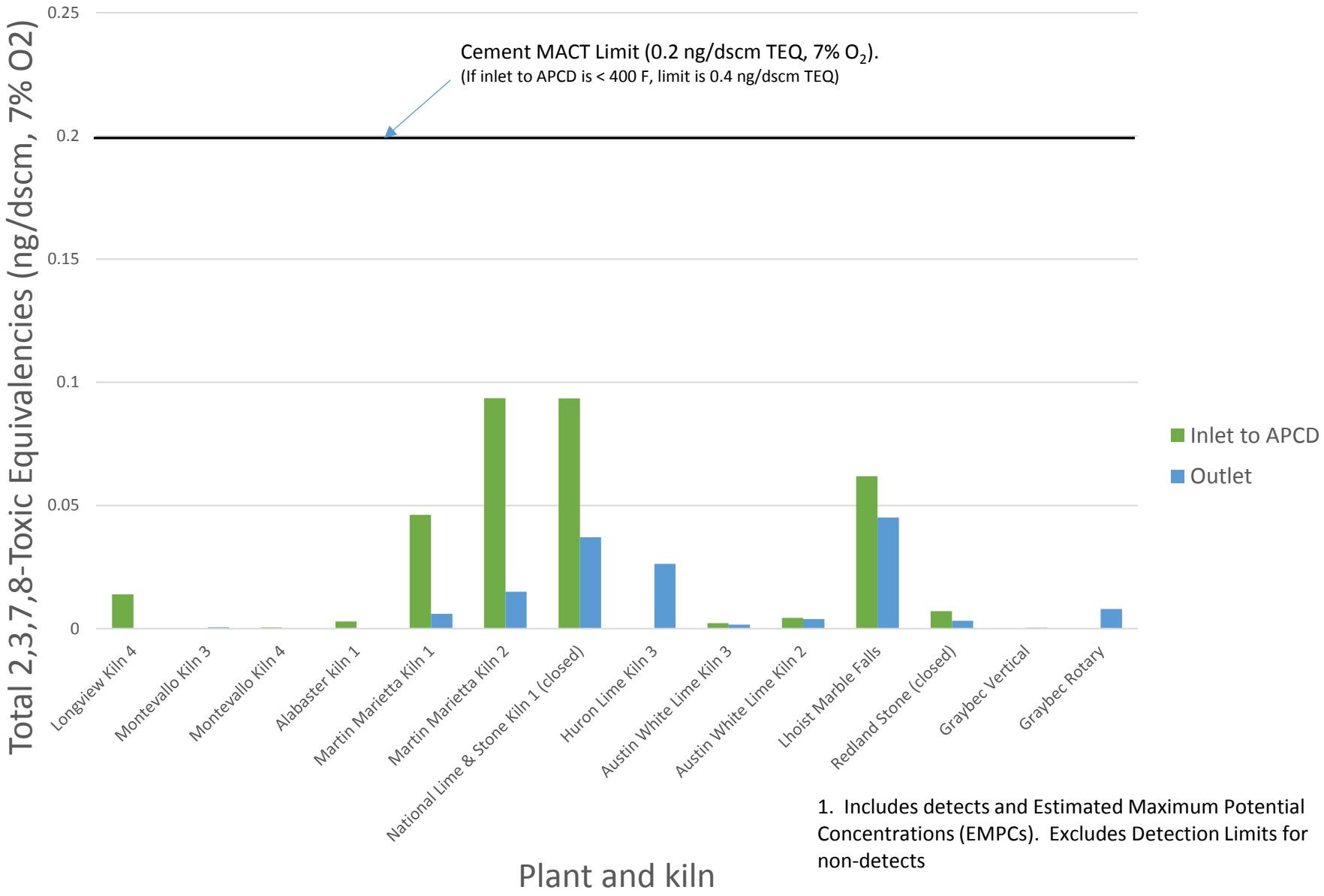
Of the 17 target dioxin and furan congeners tested for under Method 23, the most commonly detected at the inlet and outlet locations was 2,3,7,8-tetrachlorodibenzofuran. At the inlet, this congener was detected in 10 out of 11 samples at concentrations ranging from 0.00023 to 0.0127 (TEQ) ng/dscm at 7% O_2 (with corresponding detection limits ranging from 0.000178 to 0.0158 (TEQ) ng/dscm at 7% O_2. Similarly at the outlet, it was detected in 9 out of 12 samples at concentrations ranging from 0.00019 to 0.010 (TEQ) ng/dscm at 7% O_2. The next most frequently detected congeners were 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF, and 1,2,3,4,6,7,8,9-OCDD at comparable concentrations at the inlet and outlet locations.

A summary table showing inlet and outlet minimum and maximum concentrations and frequency of detection is given in Attachment 2. Minimum and maximum sample detection limits by congener are presented in Attachment 3. A method blank detection limit comparison between analytical laboratories is given in Attachment 4, and a summary spreadsheet showing APCD inlet and stack total PCDD and PCDF concentrations and total TEQs, by plant and kiln is given in Attachment 5

Attachment 1

Graph showing Inlet and Outlet Total PCDD/PCDF Concentrations

APCD Inlet and Outlet PCDD/PCDF Toxic Equivalence Summary Chart [1]



1. Includes detects and Estimated Maximum Potential Concentrations (EMPCs). Excludes Detection Limits for non-detects

Attachment 2

Summary Table showing Inlet and Outlet minimum and maximum concentrations and frequency of detection

Attachment 2

PCDD/PCDF Frequency of Detection and Concentration Ranges

	CONCENTRATION (ng/dscm, 7% O_2)[1]													
Dioxins	**Frequency of Detection**			**Inlet to APCD**			**MIN**	**MAX**		**OUTLET**			**MIN**	**MAX**
2,3,7,8-TCDD	16	/	25	7	/	11	0.00100	0.00798		9	/	14	0.00052	0.00605
1,2,3,7,8-PeCDD	14	/	25	6	/	11	0.00018	0.00791		8	/	14	0.00026	0.00454
1,2,3,4,7,8-HxCDD	10	/	25	4	/	11	0.00367	0.00600		6	/	14	0.00068	0.00196
1,2,3,6,7,8-HxCDD	15	/	25	7	/	11	0.00034	0.00722		8	/	14	0.00048	0.00487
1,2,3,7,8,9-HxCDD	16	/	25	7	/	11	0.00099	0.01000		9	/	14	0.00052	0.00500
1,2,3,4,6,7,8-HpCDD	18	/	25	8	/	11	0.00282	0.04220		10	/	14	0.00155	0.02490
1,2,3,4,6,7,8,9-OCDD	20	/	25	10	/	11	0.00847	0.11700		10	/	14	0.00210	0.09910
Furans														
2,3,7,8-TCDF	21	/	25	10	/	11	0.00292	0.15800		11	/	14	0.00186	0.10000
1,2,3,7,8-PeCDF	18	/	25	9	/	11	0.00091	0.09440		9	/	14	0.00131	0.04390
2,3,4,7,8-PeCDF	18	/	25	9	/	11	0.00025	0.09530		9	/	14	0.00083	0.04340
1,2,3,4,7,8-HxCDF	19	/	25	10	/	11	0.00135	0.30900		9	/	14	0.00113	0.02570
1,2,3,6,7,8-HxCDF	20	/	25	10	/	11	0.00054	0.07480		10	/	14	0.00058	0.01010
2,3,4,6,7,8-HxCDF	16	/	25	8	/	11	0.00034	0.02670		8	/	14	0.00035	0.00601
1,2,3,7,8,9-HxCDF	7	/	25	4	/	11	0.00281	0.00620		3	/	14	0.00054	0.00220
1,2,3,4,6,7,8-HpCDF	19	/	25	10	/	11	0.00195	0.76000		9	/	14	0.00140	0.04110
1,2,3,4,7,8,9-HpCDF	11	/	25	5	/	11	0.00075	0.02110		6	/	14	0.00039	0.00608
1,2,3,46,7,8,9-OCDF	14	/	25	7	/	11	0.00109	0.13500		7	/	14	0.00209	0.04820

	2,3,7,8 TOXIC EQUIVALENCIES (ng/dscm, 7% O2)[1]													
Dioxins	**Frequency of Detection**			**Inlet to APCD**			**MIN**	**MAX**		**OUTLET**			**MIN**	**MAX**
2,3,7,8-TCDD	17	/	25	8	/	11	0.00023	0.00798		9	/	14	0.00040	0.00605
1,2,3,7,8-PeCDD	14	/	25	6	/	11	0.00009	0.00396		8	/	14	0.00010	0.00227
1,2,3,4,7,8-HxCDD	10	/	25	4	/	11	0.00037	0.00060		6	/	14	0.00007	0.00020
1,2,3,6,7,8-HxCDD	15	/	25	7	/	11	0.00003	0.00072		8	/	14	0.00005	0.00049
1,2,3,7,8,9-HxCDD	15	/	25	7	/	11	0.00010	0.00100		8	/	14	0.00005	0.00050
1,2,3,4,6,7,8-HpCDD	18	/	25	8	/	11	0.00003	0.00042		10	/	14	0.00000	0.00025
1,2,3,4,6,7,8,9-OCDD	18	/	25	9	/	11	0.00001	0.00012		9	/	14	0.00001	0.00010
Furans														
2,3,7,8-TCDF	21	/	25	10	/	11	0.00023	0.01270		11	/	14	0.00017	0.01000
1,2,3,7,8-PeCDF	19	/	25	8	/	11	0.00005	0.00472		11	/	14	0.00007	0.00219
2,3,4,7,8-PeCDF	17	/	25	8	/	11	0.00013	0.04760		9	/	14	0.00041	0.02170
1,2,3,4,7,8-HxCDF	18	/	25	9	/	11	0.00014	0.01000		9	/	14	0.00002	0.00257
1,2,3,6,7,8-HxCDF	18	/	25	9	/	11	0.00005	0.00748		9	/	14	0.00001	0.00101
2,3,4,6,7,8-HxCDF	15	/	25	7	/	11	0.00003	0.00267		8	/	14	0.00001	0.00060
1,2,3,7,8,9-HxCDF	6	/	25	4	/	11	0.00028	0.00439		2	/	14	0.00005	0.00020
1,2,3,4,6,7,8-HpCDF	16	/	25	7	/	11	0.00005	0.00140		9	/	14	0.00000	0.00041
1,2,3,4,7,8,9-HpCDF	9	/	25	5	/	11	0.00001	0.00021		4	/	14	0.00003	0.00010
1,2,3,4,6,7,8,9-OCDF	12	/	25	6	/	11	0.00000	0.00014		6	/	14	0.00000	0.00005

1. Includes EMPCs (EMPC values represent results for compounds that co-elute from the GC column and have similar mass spectra as the target PCDD/PCDF congener, but do not meet the mass spectral criteria for the expected chlorine isotopic pattern of a dioxin/furan.)

Attachment 3

Min and Max Sample Detection Limit Summary for EPA Contractors

Attachment 3
Sample Detection Limit Summary for EPA Contractors
(ng/dscm and 2,3,7,8 TEQ ng/dscm)

Dioxins	**MIN DL (ng/dscm @7% O_2)**	**MAX DL (ng/dscm @7% O_2)**
2,3,7,8-TCDD	0.00106	0.0124
1,2,3,7,8-PeCDD	0.000255	0.0216
1,2,3,4,7,8-HxCDD	0.000137	0.0278
1,2,3,6,7,8-HxCDD	0.00176	0.0247
1,2,3,7,8,9-HxCDD	0.00176	0.0247
1,2,3,4,6,7,8-HpCDD	0.00355	0.0309
1,2,3,4,6,7,8,9-OCDD	0.00717	0.0333
Furans		
2,3,7,8-TCDF	0.00178	0.00414
1,2,3,7,8-PeCDF	0.00142	0.00999
2,3,4,7,8-PeCDF	0.00142	0.0133
1,2,3,4,7,8-HxCDF	0.00178	0.0133
1,2,3,6,7,8-HxCDF	0.00178	0.0133
2,3,4,6,7,8-HxCDF	0.000159	0.0185
1,2,3,7,8,9-HxCDF	0.000159	0.0216
1,2,3,4,6,7,8-HpCDF	0.00249	0.02
1,2,3,4,7,8,9-HpCDF	0.000238	0.0309
1,2,3,4,6,7,8,9-OCDF	0.00182	0.0333
Dioxins	**MIN DL 2,3,7,8 TEQ (ng/dscm @7% O_2)**	**MAX DL 2,3,7,8 TEQ (ng/dscm @7% O_2)**
2,3,7,8-TCDD	0.00106	0.0124
1,2,3,7,8-PeCDD	0.000127	0.0108
1,2,3,4,7,8-HxCDD	0.0000137	0.00278
1,2,3,6,7,8-HxCDD	0.0000297	0.00247
1,2,3,7,8,9-HxCDD	0.000176	0.00247
1,2,3,4,6,7,8-HpCDD	0.0000355	0.000309
1,2,3,4,6,7,8,9-OCDD	0.00000717	0.0000896
Furans		
2,3,7,8-TCDF	0.000178	0.0158
1,2,3,7,8-PeCDF	0.000071	0.00324
2,3,4,7,8-PeCDF	0.00071	0.0324
1,2,3,4,7,8-HxCDF	0.000178	0.00309
1,2,3,6,7,8-HxCDF	0.000178	0.00154
2,3,4,6,7,8-HxCDF	0.0000159	0.00185
1,2,3,7,8,9-HxCDF	0.0000159	161
1,2,3,4,6,7,8-HpCDF	0.0000249	0.0002
1,2,3,4,7,8,9-HpCDF	0.00000238	0.000309
1,2,3,4,6,7,8,9-OCDF	0.00000182	0.0000333

Note. This table only reflects EPA study detection limits (ng/dscm @7% O_2).
Graybeck summary tables did not include sample detection limits.

Attachment 4

Laboratory Method Blank Detection Limit Comparison

Attachment 4
Detection Limit Comparison
(Method Blanks (ng))

	Paradigm (ng)	TRIANGLE LABS (ng)	
	EPA	Canada (NLA)	EPA
Dioxins			
2,3,7,8-TCDD	0.0012	0.003	0.002
1,2,3,7,8-PeCDD	0.0007	0.005	0.002
1,2,3,4,7,8-HxCDD	0.0013	0.006	0.003
1,2,3,6,7,8-HxCDD	0.001	0.005	0.002
1,2,3,7,8,9-HxCDD	0.0011	0.005	0.002
1,2,3,4,6,7,8-HpCDD	0.0017	0.006	0.003
1,2,3,4,6,7,8,9-OCDD	0.0096	--	--
Furans			
2,3,7,8-TCDF	0.0016	0.003	0.002
1,2,3,7,8-PeCDF	0.0008	0.003	0.002
2,3,4,7,8-PeCDF	0.0007	0.003	0.002
1,2,3,4,7,8-HxCDF	0.0008	0.004	0.002
1,2,3,6,7,8-HxCDF	0.0006	0.003	0.002
2,3,4,6,7,8-HxCDF	0.0007	--	0.002
1,2,3,7,8,9-HxCDF	0.0008	0.004	0.002
1,2,3,4,6,7,8-HpCDF	0.0022	0.003	0.002
1,2,3,4,7,8,9-HpCDF	0.0028	0.005	0.002
1,2,3,4,6,7,8,9-OCDF	0.0041	0.007	0.003
Total D/F			
Total TCDD	0.0012	--	0.002
Total PeCDD	0.0007	0.005	0.002
Total HxCDD	0.001	0.005	0.002
Total HpCDD	0.0017	0.006	0.003
Total TCDF	0.0016	0.003	--
Total PcCDF	0.0007	0.003	0.002
Total HxCDF	0.0006	--	0.002
Total HpCDF	0.0022	0.004	0.002

Attachment 5

Dioxin/Furan Testing Program Summary

Attachment 5

Dioxin/Furan Testing Program Summary

State	Company	Plant	Test Date	Kiln	Kiln Type	APCD	L. Kinner Characterization	EPA CHARACTERIZATION				Comment
								Total PCDD/PCDF (ng/dscm)		Total TEQ (ng/dscm)		
								Inlet	Stack	Inlet	Stack	
Alabama	Carmeuse	Longview	3/28/98	4	PRK	RA+	The concentrations of the 17 individual dioxin/furan congeners were below the analytical detection limits. Emissions data reported in Table 2.4 for total 2,3,7,8-Toxic Equivalents corrected to 7% oxygen indicate non-detectable levels for every congener reported at the stack location.	1.11[1]	0.101[1]	0.0162[1]	ND (0.00513)[2]	Common to all; The non-detected D/F congeners should be reported as zero as stated specifically in Method 23. "Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample." (Section 9.9 page 927 40 CFR 60, 7-1-97). If zero values were used instead of the instrument detection limits in the equations, the results indicated in summary tables would be an order(s) of magnitude lower than reported. As reported, the emissions are orders of magnitude lower than that proposed in the recent cement MACT rule.
			3/23/98	4	SRK	Plenum Pulse	**7/25** Congeners	0.226[1]	Common Stack Kiln 4: 0.103[1] (3/23/98) Kiln 3: 0.190[1] (3/24/98)	ND (0.0375)[2]	Common Stack Kiln 4: ND (0.0148)[2] (3/23/98) Kiln 3: 0.00809[1] (3/24/98)	
	Lhoist	Montavello	3/24/98	3	SRK	Plenum Pulse	**1/25** Congeners	4.97[1]		ND (0.0729)[2]		
	Lhoist	Alabaster	3/27/98	1		SC	None of the total reported 25 D/F congeners and classes of congeners were above the instrumental detection limits for this kiln scrubber stack	0.119[1]	ND (0.0341)[2]	0.00794[1]	ND (0.0073)[2]	
Ohio	Martin Marietta	Woodville	8/27/98	2	SRK	PJ-		5.63[3]	1.27[1]	0.0935[3]	0.015[3]	Common to all: The non-detected congeners should be reported as zero, not the laboratory detection limit as stated in Section 9 of Method 23. These concentrations represent the worst possible case scenario because they include *estimated maximum possible concentration* (EMPC) values in the results. The EMPC values represent results for compounds that co-elute from the GC column and have similar mass spectra as the target PCDD/PCDF congener, but do not meet the mass spectral criteria for the expected chlorine isotopic pattern of a dioxin/furan.
			8/28/98	1	SRK	ESP		3.02[3]	0.501[3]	0.0461[3]	0.0061[3]	
	Huron Lime	Huron	8/31/98	3	SRK	Venturi Scrubber		Not tested	2.261[1]	Not tested	0.0271[1]	
	National Lime&Stone - CLOSED	Carey	9/2/98	1	Calcimatic™ - CLOSED	Venturi Scrubber		12.3[3]	9.18[3]	0.0935[3]	0.0372[3]	
Texas	Austin White	McNeil	6/30/98	3	PRK	RA	Non-representative conditions	0.0568[3]	0.0865[3]	0.00231[1]	0.00169[1]	
			7/1/98	2	PRK	SC	Non-representative conditions	0.157[3]	0.176[3]	0.00473[1]	0.00396[1]	
	Lhoist	Marble Falls	6/25/98		Gas-Fired vertical	BH	PCDD/PCDF ng/dscm TEQ was 0.0492 and 0.0348 for inlet and stack respectively	5.63[3]	6.27[4]	0.0579[3]	0.045	
	Redland Stone Products **CLOSED**	San Antonio	6/28/98	1	SRK CLOSED	SC	PCDD/PCDF ng/dscm TEQ was 0.00568 and 0.00275 for inlet and stack respectively	0.304[3]	0.142[3]	0.00726[1]	0.00317[1]	
Canada	Graybeck Calc	Marbleton, Quebec	8/12/96		PRK	BH			1.9511[5]		0.00038[5]	
	Graybeck Calc	Marbleton, Quebec	8/12/96		VERTICAL	BH			0.0871[5]		0.00079[5]	

Terminology

EMPC = Estimated Maximum Possible Concentration. The EMPC values represent results for compounds that co-elute from the GC column and have similar mass spectra as the target PCDD/PCDF congener, but do not meet the mass spectral criteria for the expected chlorine isotopic pattern of a dioxin/furan.

Detection Limits

Instrument Detection Limit is the concentration equivalent to a signal, due to the analyte of interest, which is the smallest signal that can be distinguished from background noise by a particular interest. The IDL should always be below the method detection limit. It may be used for statistical analysis and comparing the attributes of different instruments.

Method Detection Limit is the minumum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte.

Notes

1. The value shown is the sum of **detection limits (for non-detects)**, EMPCs, and detected congeners. (i.e., the value shown is the PCDD/PCDF catch weight)
2. Individual dioxin/furan congengers were not detected. The value shown is the sum of individual congener detection limits. Total may include EMPCs.
3. EMPC (Sum total of detected PCDDs + PCDFs, plus EMPCs)
4. All PCDD/PCDF total congener classes were detected. There are no EMPCs or DLs in the total.
5. The sum of detetcted dioxin/furans (individual congeners plus Totals). Non detectes were reported as "ND", and there are no EMPCs reported.

8/22/2013