Characterization and Source of Chlorinated Aromatic Compounds in ECO LOGIC Process Stack Outputs

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Abstract

Chlorinated organic compound data from various stages in the ECO LOGIC Process was examined to determine the possible source of low levels of PCDFs in stack gas following the treatment of high-strength PCB oil. Results indicated that gas produced from the reduction of PCBs contained low levels of chlorobenzenes and non-detect PCBs, whereas ambient air drawn into the burner train where product gas is combusted contained measurable levels of PCBs. It is speculated that the PCDFs present in the stack gas were produced during the combustion of the "dirty" combustion air. To avoid this possibility in future projects, combustion air will be filtered or drawn from off-site.

Introduction

In April and May, 1996, ECO LOGIC conducted commercial-scale performance testing of the ECO LOGIC Process at a site in Ontario, Canada. During this testing, high-strength PCB oil containing dioxins and furans was processed. Levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalents (dioxin TEQs) in the stack gas were approximately 15 picograms per cubic metre of air. Levels of PCBs, dioxins and furans were calculated to be approximately 10,000 times lower than Ministry of Environment and Energy (MOEE) criteria at the nearest receptor (point of impingement).

While recognizing these levels of dioxin TEQs are well below criteria, the environmental community is concerned about the presence of even minute quantities of dioxins and furans in industrial outputs. This document examines the possible source of dioxins and furans in ECO LOGIC stack gas during performance testing. This is accomplished through characterization and evaluation of dioxins, furans, and their possible precursors, at various stages in the ECO LOGIC Process.

Analytical Results

Table 1 provides a summary of dioxin TEQs for the performance test samples in the input oil, combustion air, product gas and stack gas. Because of the high strength of the oil, considerable dilution was required during sample cleanup, resulting in high detection limits. Note that the analyses were carried out on three samples of oil from the same tank. The relative variation between the samples may be almost totally due to analytical standard deviation.

Table 1 DIOXIN TEQS IN PERFORMANCE TEST SAMPLES

Location	*Method Blank*	*Field/Filter Blank*	*Test 1*	*Test 2*	*Test 3*
Input Oil (pg/g)	-	-	113030	145919	298506
Product Gas (pg/m³)	35	68	38	32	25
Combustion Air (pg/m³)	0.21	0.38	0 48	0.62	0.48
Stack Gas (pg/m³)	5.8	7.9	21	19	16

Input Oil Characteristics

The PCB oil input to the reactor during performance testing contained approximately 50 percent PCBs and from 25 to 35 percent chlorobenzenes. Table 2 shows the congener-specific PCDD and PCDF data for the input oil. All PCDF congeners were detected at very high levels; all dioxin congeners except OCDD were below detection limits.

Table 2 PCDDS AND PCDFS IN INPUT OIL (pg/g)

Dioxin/Furan Congener	*Test 1*	*Test 2*	*Test 3*
2,3,7,8-TCDD	< 400	< 680	< 360
1,2,3,7,8-PeCDD	< 590	< 800	< 470
1,2,3,4,7,8-HxCDD	< 1,000	< 870	< 760
1,2,3,6,7,8-HxCDD	< 750	< 650	< 570
1,2,3,7,8,9-HxCDD	< 890	< 770	< 670
1,2,3,4,6,7,8-HpCDD	< 710	< 820	< 770
OCDD	3,600	1,800	3,500
2,3,7,8-TCDF	100,000	120,000	130,000
1,2,3,7,8-PeCDF	38,000	56,000	160,000
2,3,4,7,8-PeCDF	160,000	180,000	380,000
1,2,3,4,7,8-HxCDF	510,000	590,000	1,200,000
1,2,3,6,7,8-HxCDF	65,000	73,000	230,000
2,3,4,6,7,8-HxCDF	100,000	140,000	310,000
1,2,3,7,8,9-HxCDF	1,600	81,000	30,000
1,2,3,4,6,7,8-HpCDF	340,000	330,000	410,000
1,2,3,4,7,8,9-HpCDF	180,000	210,000	290,000
OCDF	2,200,000	1,800,000	1,700,000

Product Gas Characteristics

Product gas is created by the reduction of the PCB molecules in the presence of hydrogen at temperatures of 850°C. As shown in Table 1, the dioxin TEQs for the product gas are in the range of 25 to 38 pg/m³. Of note, however, are the high levels of dioxin TEQs in both the method blank and the field blank (Table 3 and Figures 1a and b).

The concentration and mass of PCBs and chlorobenzenes in the product gas for each test are presented in Table 4. Product gas contains chlorobenzenes at levels up to approximately 5000 µg/test, although the blank levels would indicate that there is considerable interference from background. No PCBs were detected above detection limits ranging from 37 to 60 µg/test.

Combustion Air Characteristics

Combustion air is ambient, on-site air which is drawn into the catalytic steam reformer to provide air for combustion of the product gas. It is not produced by the waste processing system. Dioxin TEQs for combustion air are only slightly higher than the blank values (i.e. in the same order of magnitude) (Table 1). The congener-specific data (Table 5 and Figures 2a and b), shows some interference in the PCDD data from the field blank. This is particularly evident in the tetra-, penta- and hexa-substituted PCDD congeners in the field blank, which have levels essentially the same as found in the combustion air. Hepta- and octa-substituted PCDDs are higher for the three test samples, but higher levels of these congeners is a typical feature of environmental samples. Hexa-substituted PCDFs found in the combustion air are essentially the same level as the field blank samples (Figure 2b). Other PCDFs are present at levels somewhat higher than the blank data, although within the same order of magnitude.

Table 6 presents the concentration and mass of PCBs and chlorobenzenes in combustion air for each test. Combustion air contains predominantly PCBs ranging from approximately 20 µg to 6500 µg per test. Some trichlorobenzenes are found at levels up to 1800 µg/test.

Stack Gas Characteristics
Stack gas is produced from the burning of product gas and combustion air. Table 1 shows the levels of dioxin TEQs for the three tests, and corresponding blank data. While higher than the blank data, all test data was in the same order of magnitude as the blank data.

Levels of tetra-substituted PCDDs are similar to those found in the field blank (Table 7 and Figure 3a). With the exception of Test 1, penta- and hexa-substituted PCDDs are also present at similar levels to those found in the field blank. The level of penta-substituted PCDDs in Test 1 is higher than in the field blank, but in the same order of magnitude. Levels of hepta- and octa-substituted congeners show typically higher levels, as is common in combustion samples. Levels of all PCDD congeners are in the same order of magnitude as the field blank. Levels of PCDF congeners are generally higher than the blank data (Table 7 and Figure 3b). In some cases (particularly Test 3), levels are more than an order of magnitude higher.

Discussion

A review of the data for combustion air and product gas (which are burned in the catalytic steam reformer to produce stack gas) reveals that lower chlorinated chlorobenzenes are present in the product gas, while PCBs are predominant in the combustion air. Combustion of chlorobenzenes produces both PCDDs and PCDFs, with the levels of each product dependent on the level of oxygen present, temperature and residence time. Combustion of PCBs, on the other hand, results primarily in the formation of PCDFs (1).

If combustion of the product gas, which contained primarily chlorobenzenes, were the source of PCDFs in the stack gas, then it would be expected that both PCDDs and PCDFs would be created. However, PCDD levels in the stack gas appear to be a result of sampling and analytical interference. It is more likely that the PCDFs in the stack gas are the result of PCBs present in the combusion air.

Occupational testing of ambient air around the site during typical waste processing activities shows that levels of PCBs are below occupational standards. It is possible that the slightly higher levels of PCBs present during the performance test were a result of the increased sampling that was required during the testing program, which necessitated the opening of some system components (such as scrubbers and filters) which would not normally be exposed during typical waste processing activities. One method of preventing this type of potential interference would be to draw air from an area that is known to have little or no PCBs in the air.

Table 3 DIOXINS AND FURANS IN PRODUCT GAS

Dioxin/Furan Congener	Method Blank		Field Blank		Test 1		Test 2		Test 3	
	pg/m³	ng/test	pg/m³	ng/test	pg/m³	µg/test	pg/m³	µg/test	pg/m³	µg/test
2,3,7,8-TCDD	< 11	< 10	32	29	22	18	18	19	14	11
1,2,3,7,8-PeCDD	16	14	30	27	10	8.5	9.3	10	8.4	6.4
1,2,3,4,7,8-HxCDD	< 19	< 17	< 28	< 25	22	18	19	21	15	11
1,2,3,6,7,8-HxCDD	< 12	< 11	< 20	< 18	< 4.3	< 3.6	< 3.4	< 3.7	< 2.9	< 2.2
1,2,3,7,8,9-HxCDD	< 16	< 14	< 23	< 21	< 5.2	< 4.4	< 4.1	< 4.4	< 3.4	< 2.6
1,2,3,4,6,7,8-HpCDD	46	41	< 32	< 29	15	13	14	15	12	9.1
OCDD	320	280	280	250	30	25	31	34	19	15
2,3,7,8-TCDF	13	12	26	23	10	8.4	9.3	10	8	6.1
1,2,3,7,8-PeCDF	< 6.9	< 6.1	< 15	< 14	4.9	4.1	4.8	5.2	3.4	2.6
2,3,4,7,8-PeCDF	< 6.9	< 6.1	< 15	< 14	< 4.9	< 4.1	< 3.5	< 3.8	< 3.3	< 2.5
1,2,3,4,7,8-HxCDF	< 11	< 9.8	< 9.4	< 8.5	< 4.9	< 4.1	< 4.2	< 4.5	< 3.1	< 2.4
1,2,3,6,7,8-HxCDF	< 7.4	< 6.6	< 6.8	< 6.1	3.8	3.2	3.3	3.6	2.7	2.1
2,3,4,6,7,8-HxCDF	< 11	< 9.8	< 11	< 9.9	< 5.6	< 4.7	< 4.9	< 5.3	< 3.6	< 2.7
1,2,3,7,8,9-HxCDF	25	22	40	36	23	19	17	18	13	9.9
1,2,3,4,6,7,8-HpCDF	14	12	< 28	< 25	3.5	2.9	< 3.4	< 3.7	< 2.9	< 2.2
1,2,3,4,7,8,9-HpCDF	< 11	< 9.8	< 38	< 34	< 4.8	< 4.0	< 4.5	< 4.9	< 3.8	< 2.9
OCDF	51	45	< 83	< 75	9.2	7.7	11	12	5.3	4.0

Figure 1a DIOXINS IN PRODUCT GAS

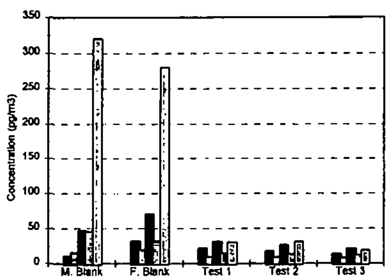


Figure 1b FURANS IN PRODUCT GAS

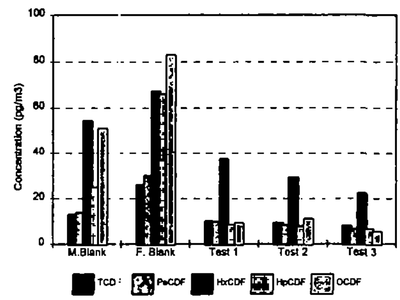


Table 4 PCBS AND CHLOROBENZENES IN PRODUCT GAS

Compound	Method Blank		Field Blank		Test 1		Test 2		Test 3	
	µg/m³	µg/test	µg/m³	µg/test	µg/m³	µg/test	µg/m³	µg/test	µg/m³	µg/test
1,2-Dichlorobenzene	< 0.11	< 98	0.32	286	2.6	2168	0.43	466	0.42	322
1,3-Dichlorobenzene	< 0.11	< 98	0.15	131	6.1	5136	0.96	1040	1.3	1026
1,4-Dichlorobenzene	< 0.11	< 98	4.0	3617	4.3	3652	1.2	1315	0.96	733
1,2,3-Trichlorobenzene	< 0.11	< 98	1.6	1428	0.76	639	0.59	634	0.24	183
1,2,4-Trichlorobenzene	< 0.11	< 98	7.7	6853	3.4	2853	2.8	2989	1.1	806
1,3,5-Trichlorobenzene	< 0.11	< 98	< 0.050	< 45	0.080	65	< 0.060	< 60	< 0.050	< 37
1,2,3,4-TetraCB	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
1,2,3,5- 1,2,4,5-TetraCB	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Pentachlorobenzene	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Hexachlorobenzene	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Chlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Dichlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Trichlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Tetrachlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Pentachlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Hexachlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Heptachlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Octachlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Nonachlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Decachlorobiphenyl	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37
Total PCBs	< 0.11	< 98	< 0.050	< 45	< 0.070	< 57	< 0.060	< 60	< 0.050	< 37

Table 5 DIOXINS AND FURANS IN COMBUSTION AIR

Dioxin/Furan Congener	Method Blank		Field Blank		Test 1		Test 2		Test 3	
	pg/m³	ng/test	pg/m³	ng/test	pg/m³	ng/test	pg/m³	ng/test	pg/m³	ng/test
2,3,7,8-TCDD	< 0.04	< 0.20	0.22	3.1	0.27	3.6	0.31	4.6	0.24	3.1
1,2,3,7,8-PeCDD	0.12	1.7	0.10	1.4	0.11	1.5	0.13	1.9	0.11	1.4
1,2,3,4,7,8-HxCDD	< 0.05	< 0.70	0.24	3.4	0.27	3.6	0.26	39	0.27	3.5
1,2,3,6,7,8-HxCDD	< 0.04	< 0.60	< 0.04	< 0.60	0.06	0.80	0.05	0.70	0.08	1.0
1,2,3,7,8,9-HxCDD	< 0.05	< 0.70	< 0.05	< 0.70	< 0.05	< 0.70	< 0.05	< 0.70	0.09	1.2
1,2,3,4,6,7,8-HpCDD	0.17	2.4	0.13	1.9	0.27	3.6	0.38	5.6	0.42	5.5
OCDD	0.36	5.1	0.14	2.0	0.65	8.6	0.79	10	1.54	11
2,3,7,8-TCDF	0.11	1.6	0.10	1.4	2.1	28	0.37	5.5	0.21	2.7
1,2,3,7,8-PeCDF	0.04	0.60	< 0.05	< 0.70	0.36	4.7	0.18	2.7	0.12	1.6
2,3,4,7,8-PeCDF	0.05	0.70	< 0.05	< 0.70	0.21	2.9	0.11	1.6	< 0.05	< 0.70
1,2,3,4,7,8-HxCDF	< 0.05	< 0.70	< 0.05	< 0.70	0.14	1.8	0.19	2.8	0.09	1.2
1,2,3,6,7,8-HxCDF	0.06	0.90	< 0.04	< 0.60	< 0.12	< 1.6	0.13	1.9	0.05	0.70
2,3,4,6,7,8-HxCDF	< 0.06	< 0.90	< 0.06	< 0.90	0.10	1.3	0.09	1.3	< 0.06	< 0.80
1,2,3,7,8,9-HxCDF	0.41	5.8	0.22	3.1	0.22	3.0	0.23	3.4	0.24	3.1
1,2,3,4,6,7,8-HpCDF	0.06	0.90	0.17	2.4	0.17	3.0	0.35	5.2	< 0.14	< 1.8
1,2,3,4,7,8,9-HpCDF	0.08	1.1	< 0.10	< 1.4	< 0.10	< 1.3	< 0.11	< 1.6	< 0.10	< 1.3
OCDF	0.15	2.1	0.20	2.9	0.20	2.6	0.19	2.8	0.56	7.3

Figure 2a DIOXINS IN COMBUSTION AIR

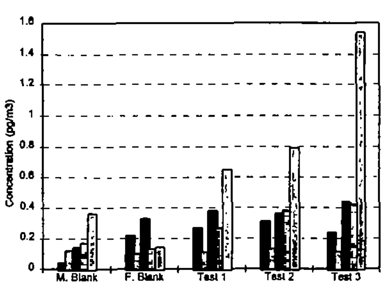


Figure 2b FURANS IN COMBUSTION AIR

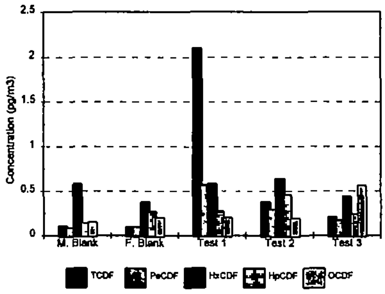


Table 6 PCBS AND CHLOROBENZENES IN COMBUSTION AIR

Compound	Method Blank		Test 1		Test 2		Test 3 FltrBlnk		Test 3	
	ng/m³	µg/test	ng/m³	µg/test	ng/m³	µg/test	ng/m³	µg/test	ng/m³	µg/test
1,2-Dichlorobenzene	< 0.70	< 10	1.5	20	1.8	26	1	14	3.2	42
1,3-Dichlorobenzene	< 0.70	< 10	< 0.73	< 9.2	< 0.70	< 11	< 0.70	< 10	1.5	20
1,4-Dichlorobenzene	34	468	18	240	22	325	52	709	49	638
1,2,3-Trichlorobenzene	< 0.70	< 10	14	183	28	412	5.2	71	27	346
1,2,4-Trichlorobenzene	< 0.70	< 10	58	757	110	1561	30	402	140	1822
1,3,5-Trichlorobenzene	< 0.70	< 10	< 0.73	9.2	< 0.70	< 11	< 0.70	< 10	< 0.70	< 9.1
1,2,3,4-T4CB	< 0.70	< 10	1.5	20	2.9	43	< 0.70	< 10	< 0.70	< 9.1
1,2,3,5- 1,2,4,5-T4CB	< 0.70	< 10	< 0.73	< 9.2	1.3	19	< 0.70	< 10	< 0.70	< 9.1
Pentachlorobenzene	< 0.70	< 10	< 0.73	< 9.2	< 0.70	< 11	< 0.70	< 10	< 0.70	< 9.1
Hexachlorobenzene	< 0.70	< 10	< 0.73	< 9.2	< 0.70	< 11	< 0.70	< 10	< 0.70	< 9.1
Chlorobiphenyl	< 0.70	< 10	84	1108	28.1	434	< 0.70	< 10	8.7	113
Dichlorobiphenyl	< 0.70	< 10	410	5357	103.9	1604	< 0.70	< 10	30.9	401
Trichlorobiphenyl	< 0.70	< 10	490	6465	140.4	2168	< 0.70	< 10	26.7	346
Tetrachlorobiphenyl	< 0.70	< 10	140	1847	46.3	716	< 0.70	< 10	11.2	146
Pentachlorobiphenyl	< 0.70	< 10	29	388	3.1	48	< 0.70	< 10	1.5	20
Hexachlorobiphenyl	< 0.70	< 10	5.2	68	1.4	21	< 0.70	< 10	< 0.70	< 9.1
Heptachlorobiphenyl	< 0.70	< 10	< 0.70	< 9.2	< 0.70	< 11	< 0.70	< 10	< 0.70	< 9.1
Octachlorobiphenyl	< 0.70	< 10	< 0.70	< 9.2	< 0.70	< 11	< 0.70	< 10	< 0.70	< 9.1
Nonachlorobiphenyl	< 0.70	< 10	< 0.70	< 9.2	< 0.70	< 11	< 0.70	< 10	< 0.70	< 9.1
Decachlorobiphenyl	< 0.70	< 10	< 0.70	< 9.2	< 0.70	< 11	< 0.70	< 10	< 0.70	< 9.1
Total PCBs	< 0.70	< 10	1150	15148	323	4987	< 0.70	< 10	79	1020

Table 7 DIOXINS AND FURANS IN STACK GAS (pg/m³)

Dioxin/Furan Congener	*Method Blank*	*Field Blank*	*Test 1*	*Test 2*	*Test 3*
2,3,7,8-TCDD	1.2	3.8	2.7	5.3	3.9
1,2,3,7,8-PeCDD	1.8	2.8	13	3.7	2.0
1,2,3,4,7,8-HxCDD	2.1	5.5	4.7	7.5	6.4
1,2,3,6,7,8-HxCDD	1.3	1.2	1.2	3.3	1.9
1,2,3,7,8,9-HxCDD	1.7	2.8	5.2	5.7	3.0
1,2,3,4,6,7,8-HpCDD	5.1	11	27	29	27
OCDD	35	60	87	77	150
2,3,7,8-TCDF	1.4	2.3	6.9	16	27
1,2,3,7,8-PeCDF	0.76	0.92	7.9	8.6	5.2
2,3,4,7,8-PeCDF	0.76	0.81	6.7	6.8	8.6
1,2,3,4,7,8-HxCDF	1.2	1.9	8.2	13	10
1,2,3,6,7,8-HxCDF	0.81	1.3	5.2	69.8	5.4
2,3,4,6,7,8-HxCDF	1.2	2.0	1.2	6.4	12
1,2,3,7,8,9-HxCDF	2.8	2.1	2.7	3.3	3.4
1,2,3,4,6,7,8-HpCDF	1.5	3.5	17	26	75
1,2,3,4,7,8,9-HpCDF	1.2	1.0	2.7	4.0	12
OCDF	5.5	3.9	10	13	250

Figure 3a DIOXINS IN STACK GAS

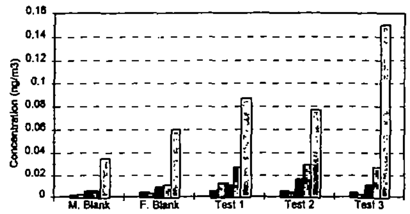
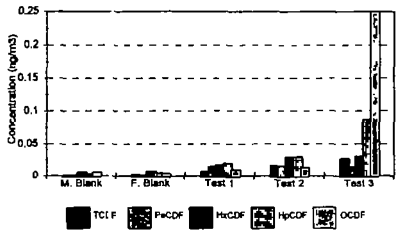


Figure 3b FURANS IN STACK GAS



Conclusions

PCDDs and PCDFs in all samples of product gas, combustion air, and stack gas, with the exception of PCDFs in the stack gas, are either below or within the same order of magnitude as the corresponding blank samples, and are therefore a result of sampling or laboratory interference. PCDFs were detected in the stack gas at levels more than an order of magnitude higher than the blank samples. The levels of PCDFs are still very low (approximately 10,000 times below criteria at point of impingement).

Based on the analysis of the product gas and corresponding blank data, the product gas does not appear to be the source PCDFs the stack. It can be speculated that PCDFs in the stack gas are a result of the presence of PCBs in combustion air taken into the burner train used to heat the catalytic steam reformer. To eliminate this possibility in future projects combustion air will be drawn from a source that is off-site, or filtered through carbon.

Literature Cited

1. Kominsky, J.R. 1984. *The Chemistry of Electrical Transformer Fires.* Hazard Evaluations and Technical Assistance Branch, National Institute for Occupational Safety and Health, Cincinnati, Ohio.