

*Paper for presentation at the 2005 Conference on Incineration and Thermal Treatment Technologies, Galveston, TX, May 9-13, 2005*

**A Pilot-Scale Study on the Combustion of Waste Carpet in a Rotary Kiln: Dioxin and Furan Emissions**

**Paul M. Lemieux**

**U.S. EPA**

**Office of Research and Development  
National Homeland Security Research Center  
Research Triangle Park, NC 27711**

**Chris Winterrowd**

**ARCADIS G&M**

**Durham, NC 27709**

**Matthew Realff, Jim Mulholland**

**Georgia Institute of Technology**

**Atlanta, GA 30332-0100**

**ABSTRACT**

Post-consumer carpet is a potential substitute fuel for high temperature thermal processes such as cement kilns and boilers. In addition, cleanup of contaminated buildings can result in the need to dispose of potentially significant quantities of carpet, which may or may not be contaminated, and will possibly have decontamination chemicals present. Data gaps exist regarding the potential for the production of increased levels of oxides of nitrogen (NO<sub>x</sub>), organic pollutants such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs), and engineering issues such as pre-sizing requirements for the carpeting in order to achieve effective combustion. To respond to these data gaps, US EPA, in collaboration with the Carpet and Rug Institute (CRI) and the Georgia Institute of Technology, performed experiments to address some of these data gaps. This paper reports on results examining emissions of PCDDs/Fs from a series of pilot-scale experiments performed on the EPA's rotary kiln incinerator simulator facility in Research Triangle Park, NC.

**INTRODUCTION**

Building decontamination and cleanup efforts from a biological warfare (BW) or chemical warfare (CW) agent terrorist attack typically result in a significant quantity of building decontamination residue (BDR). This BDR consists mainly of porous materials, such as carpeting or ceiling tiles, which were removed from the building either before or, after decontamination efforts. The BDR is likely to have been decontaminated but due to its porous nature and the limitations of sampling methodologies, the possibility exists for the presence of trace quantities of agents, as well as the likelihood of the presence of varying quantities of decontamination chemicals (e.g., bleach solutions). One likely disposal technique for the BDR is high temperature thermal incineration. Regardless of the issue of whether or not residual agent is

present in the BDR, disposal facilities must be able to operate within relevant permit restrictions while processing BDR, and data gaps exist as to the behavior of BDR in high temperature combustion devices. In addition, certain types of materials that are found in BDR, such as waste carpeting, may be useful as auxiliary fuels for high temperature combustion devices, and similar data gaps exist relative to operational and permit issues for the purposes of the use of those materials for that purpose. The EPA instituted a pilot-scale test program to investigate issues related to the thermal destruction of contaminated BDR (1) including carpeting, ceiling tile, and wallboard.

In the US, approximately 2.2-2.7 billion kg (5-6 billion lbs) of carpet is sold annually, of which 60% is for replacement (2). In spite of considerable effort in the past decade to develop recycling technologies for carpet wastes, most carpet continues to be disposed of in landfills (3). The development of economically viable, environmentally sound, high volume, robust systems for dealing with carpet waste would move the carpet industry closer to its goals of environmental stewardship and protection. Since carpet has a heating value similar to that of coal, the application of carpet as a fuel for high temperature combustion devices such as cement kilns or boilers is potentially attractive, but there are potential environmental and operational issues that need to be addressed in order to promote this as a viable practice for industry. For example, some of the elemental components of carpeting (e.g., nitrogen) could potentially result in the formation of pollutants of concern (e.g., nitrogen oxides [ $\text{NO}_x$ ]). In response to this data gap, the US EPA performed testing on a pilot-scale rotary kiln, which showed only a slight increase in  $\text{NO}_x$  emissions from co-firing carpeting with natural gas (4). This study also showed only minor increases in organic pollutants and no measurable emissions of mercury (Hg). A follow on study showed that no other nitrogen-containing species such as  $\text{NH}_3$  or  $\text{N}_2\text{O}$  could be accounting for the fuel nitrogen, and that the burnout characteristics of the carpet were relatively independent of the cut size of the carpet (5).

This paper describes experiments that were performed in a pilot-scale rotary kiln incinerator simulator to evaluate the combustion characteristics of carpeting as a component of BDR in an effort to aid in the selection of appropriate disposal facilities and to aid facilities in maintaining permit compliance while processing potentially contaminated carpet. This paper reports on emissions of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) while combusting carpet with and without a simulated decontamination chemical (in the form of a 10% bleach solution) present on the carpet.

## EXPERIMENTAL

Testing was performed at the EPA's Rotary Kiln Incinerator Simulator (RKIS) facility located in Research Triangle Park, NC. The RKIS has been used in the past to test a wide variety of solid and liquid wastes (4, 6, 7). The RKIS (shown in Fig. 1) consists of a 73 kW (250,000 Btu/hr) natural gas-fired rotary kiln section and a 73 kW (250,000 Btu/hr) natural gas-fired secondary combustion chamber (SCC). Following the SCC is a long duct that leads into a dedicated flue gas cleaning system (FGCS) consisting of another afterburner, baghouse, and wet scrubber. The RKIS is equipped with continuous emission monitors (CEMs) for oxygen ( $\text{O}_2$ ), carbon dioxide ( $\text{CO}_2$ ), carbon monoxide (CO), nitrogen oxides ( $\text{NO}_x$ ), and total hydrocarbons (THCs). A series of Type-K thermocouples monitor the temperature throughout the system. For the initial tests,



the rotary kiln combustion air was flowing at a rate of  $85.0 \text{ m}^3/\text{hr}$  ( $3000 \text{ scfh}$ ) and the main burner natural gas fuel was flowing at a rate of  $5.66 \text{ m}^3/\text{hr}$  ( $200 \text{ scfh}$ ). The static pressure in the rotary kiln section was maintained at  $-0.05 \text{ in. w.c.}$  For the purposes of these tests, the SCC was not operated, and the temperature in the transfer duct was maintained at approximately  $300\text{--}350^\circ\text{C}$  ( $572\text{--}662^\circ\text{F}$ ) to promote the formation of PCDDs/Fs so that the differences between the test conditions could hopefully be maximized.

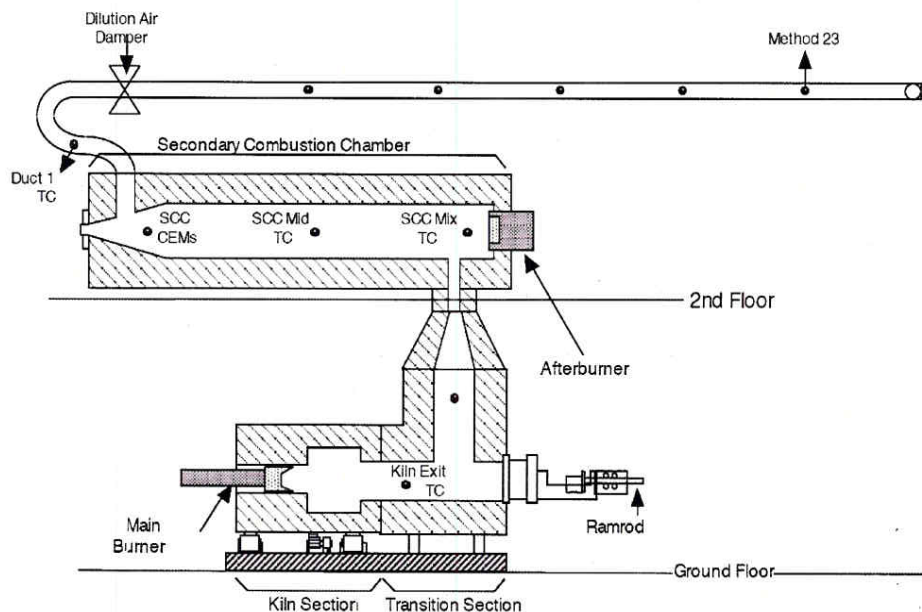


Fig. 1. Rotary Kiln Incinerator Simulator

A series of experiments were performed where approximately  $0.45 \text{ kg}$  ( $1 \text{ lb}$ ) bundles of  $7.6 \text{ cm}$  ( $3 \text{ in.}$ ) square pieces of carpeting, banded together using  $1.3 \text{ cm}$  ( $0.5 \text{ in.}$ ) polypropylene straps, were fed into the RKIS every 10 minutes over a 3-hour period, while samples were acquired to measure PCDDs/Fs (8). The purpose of these tests were to evaluate the potential for combustion of carpeting resulting from building decontamination operations to result in an increase in PCDD/F emissions. The bundles of carpet were wetted with deionized water (approximately 50% of the total charge mass) in one set of experiments and they were wetted with a 10% bleach (sodium hypochlorite) solution to a similar degree of wetness in another set of experiments. The wetting was performed by quickly dunking the banded bundle of carpeting in a plastic bucket containing the desired wetting agent, and allowing the bundle to drain until drops of liquid no longer dripped from the bundle. The bundles of wetted carpet were then manually charged into the RKIS using the ram feeder at 10-min intervals. Method 23 sampling was initiated at the time of the first charging event and terminated 10 minutes after the final charging event, for a total of 3 hours of sampling. A 3-hour combustion blank test was also performed on the RKIS burning natural gas only prior to the other testing. Analyses were performed using high-resolution gas chromatography (HRGC) with high-resolution mass spectrometry (HRMS). The test matrix is shown in Table I.

Table I. Test Matrix

Run	Feed	Time Fed to Kiln	Dry Carpet Mass (g)	Banded Carpet Mass (g)	Water or 10% Bleach Solution Mass (g)
1	Natural Gas	-	-	-	-
2	Natural Gas Carpet DI Water				
		1134	453.4	478.7	429.3
		1144	453.0	477.1	439.6
		1155	448.5	472.1	367.9
		1205	451.8	475.8	455.3
		1215	458.3	483.8	515.2
		1225	457.0	481.6	515.4
		1235	451.0	474.6	452.4
		1245	456.2	480.1	379.6
		1255	453.8	477.2	419.3
		1305	460.0	486.0	385.7
		1315	450.0	476.3	460.5
		1325	456.7	484.9	378.0
		1335	456.1	482.8	410.9
		1345	452.3	477.1	396.7
		1355	456.9	482.5	426.7
		1405	456.0	480.7	397.4
		1415	455.1	479.9	385.2
		1425	454.6	479.2	380.9
3	Natural Gas Carpet DI Water				
		1021	450.0	472.3	484.7
		1031	459.0	481.3	509.4
		1041	453.0	475.6	476.3
		1051	454.0	476.7	459.7
		1101	454.5	476.5	474.9
		1111	458.7	480.8	459.9
		1121	452.8	474.3	452.8
		1131	457.2	478.9	436.7
		1141	454.6	476.4	403.7
		1151	451.8	474.3	447.8
		1201	454.0	476.7	480.4
		1211	454.7	476.6	444.9
		1231	451.9	474.4	445.4
		1241	459.4	482.3	482.9
		1251	457.2	480.1	485.2
		1301	459.0	481.7	410.7
		1311	455.2	478.3	414.8
		1321	451.4	475.2	485.8
4	Natural Gas Carpet 10% Bleach				
		1055	455.2	478.5	531.7
		1104	452.0	477.8	571.0
		1114	454.0	476.8	555.4
		1124	457.0	484.7	535.6
		1134	453.7	482.0	473.7
		1144	456.1	478.9	479.6
		1154	448.8	474.6	502.8
		1204	452.1	471.7	510.0
		1214	449.0	470.1	472.7

Run	Feed	Time Fed to Kiln	Dry Carpet Mass (g)	Banded Carpet Mass (g)	Water or 10% Bleach Solution Mass (g)
		1224	455.3	475.0	511.3
		1234	458.2	477.9	485.1
		1244	451.3	469.8	476.1
		1254	455.3	474.1	502.7
		1304	457.4	475.0	498.2
		1314	450.2	472.6	496.4
		1324	452.8	475.4	506.8
		1334	454.9	477.4	500.4
		1344	454.1	476.5	443.0
5	Natural Gas Carpet 10% Bleach				
		1202	457.3	480.1	462.5
		1212	458.5	482.3	522.8
		1222	457.7	482.1	493.4
		1232	455.8	480.6	524.8
		1242	453.2	477.2	355.8
		1252	457.1	481.5	506.4
		1302	450.6	474.6	470.1
		1312	455.5	479.8	495.1
		1322	455.0	478.1	468.3
		1332	450.0	474.2	402.6
		1342	451.8	475.5	487.7
		1352	452.5	477.4	418.0
		1402	458.6	483.6	460.6
		1412	454.5	483.2	526.4
		1422	453.0	480.4	388.9
		1432	453.7	479.4	395.3
		1442	454.5	479.0	388.8
		1452	460.2	484.0	396.4

## RESULTS

Table II lists the kiln temperature, the duct O<sub>2</sub> and CO<sub>2</sub> concentrations, and the flue gas temperature and moisture conditions at the Method 23 sampling point. It must be noted however, that due to the batch feed nature of the experiments, there were a series of transients in gas species concentrations and temperatures associated with each charging event. Fig. 2 shows a sample from one of the run days (Run 2) showing the O<sub>2</sub> and CO<sub>2</sub> concentrations, the CO concentrations, and the kiln and duct temperatures. This shows the perturbations from baseline conditions associated with the batch charging of carpet.

Table II. Operating Conditions

Run	Average O <sub>2</sub> (% dry)	Average CO <sub>2</sub> (% dry)	Average Moisture (%)	Average Kiln Temperature (°C)	Sampling Temperature (°C)
1	13.4	3.8	10.7	892	293
2	11.4	5.3	10.2	957	292
3	11.8	5.1	10.2	953	303
4	10.7	5.7	11.4	1000	291
5	11.5	5.3	9.51	1010	308



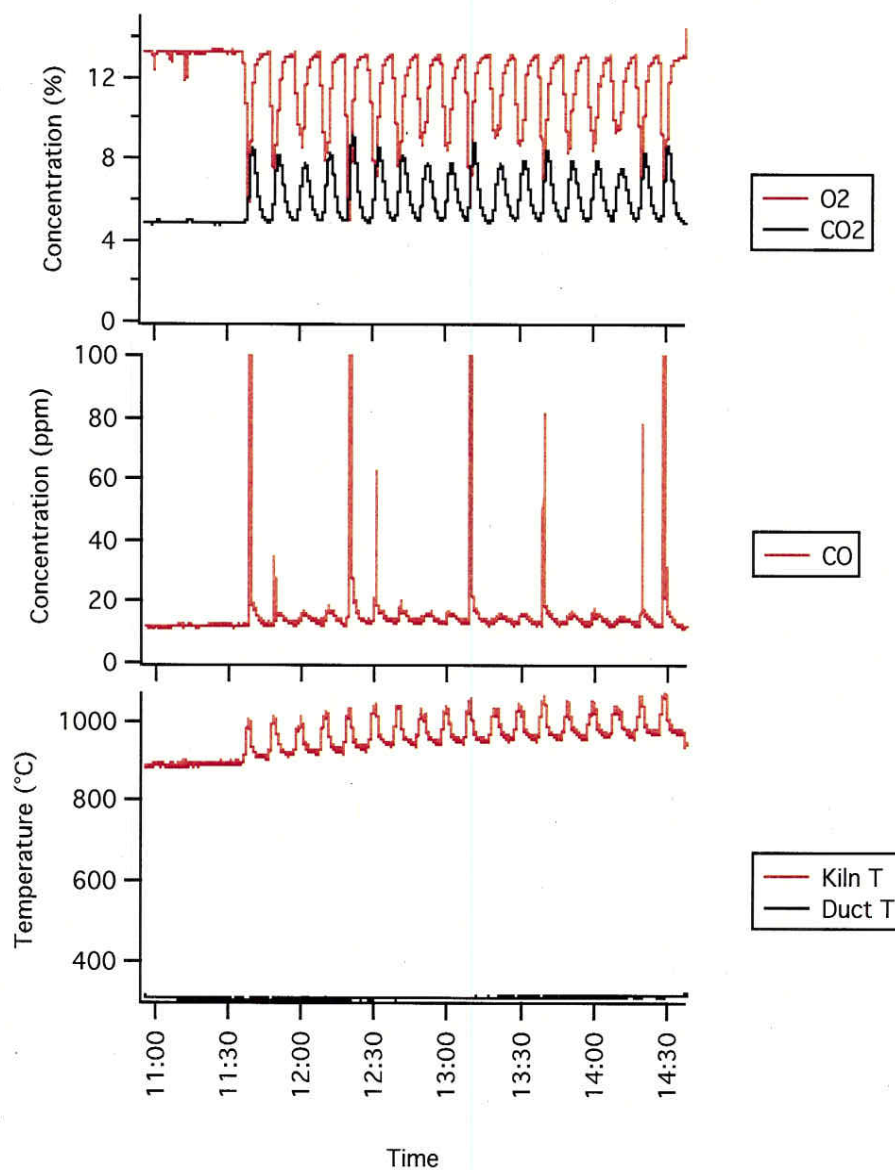


Fig. 2. Sample CEM Traces from Run 2.

Table III lists the PCDD/F results from Runs 1 through 5, as well as the concentrations in terms of the international toxic equivalency (TEQ) units (9). It must be noted that these data were generated at conditions specifically intended to maximize formation of PCDDs/Fs, by not operating the SCC of the RKIS facility, and by adjusting the transition duct temperature to be within the optimal temperature window for PCDD/F formation (300-350 °C). In addition, the samples were acquired prior to any flue gas cleaning devices. These experiments are not designed to duplicate concentrations that might be seen in practice, but rather to elucidate relevant qualitative trends that might be seen in practice. Although there were variations between the duplicate runs, the variations between the duplicates were significantly less than the variations between run conditions.

Table III. PCDD/F Results (ng/dscm).

Analyte	Run 1	Run 2	Run 3	Run 4	Run 5
2,3,7,8-TCDD	0.000263	0.00158	0.000626	0.0369	0.00548
1,2,3,7,8-PeCDD	0.000294	0.00401	0.0012	0.222	0.0431
1,2,3,4,7,8-HxCDD	0.000228	0.00231	0.0012	0.354	0.0911
1,2,3,6,7,8-HxCDD	0.00119	0.003	0.00126	0.745	0.342
1,2,3,7,8,9-HxCDD	0.00119	0.00283	0.0012	0.689	0.361
1,2,3,4,6,7,8-HpCDD	0.0019	0.00828	0.00356	8.27	4.58
2,3,7,8-TCDF	0.000917	0.0302	0.0275	0.805	0.12
1,2,3,7,8-PeCDF	0.00119	0.0229	0.0093	1.49	0.232
2,3,4,7,8-PeCDF	0.00119	0.0641	0.0376	3.88	0.834
1,2,3,4,7,8-HxCDF	0.00119	0.0222	0.00915	3.49	0.759
1,2,3,6,7,8-HxCDF	0.00119	0.0242	0.00605	4.36	1
2,3,4,6,7,8-HxCDF	0.00119	0.0377	0.00903	12.5	4.17
1,2,3,7,8,9-HxCDF	0.000294	0.0124	0.00243	4.19	0.914
1,2,3,4,6,7,8-HpCDF	0.000349	0.0319	0.00915	24.1	7.54
1,2,3,4,7,8,9-HpCDF	0.000349	0.00933	0.002	10.7	3.22
PCDD/F I-TEQ (ND=0; EMPC=0)	0.000147	0.0509	0.0251	5.37	1.41
PCDD/F I-TEQ (ND=0; EMPC=EMPC)	0.000152	0.0509	0.0255	5.37	1.41
PCDD/F I-TEQ (ND=DL/2; EMPC=0)	0.00101	0.0509	0.0253	5.37	1.41
PCDD/F I-TEQ (ND=DL/2; EMPC=EMPC)	0.00101	0.0509	0.026	5.37	1.41
PCDD/F I-TEQ (ND=DL; EMPC=EMPC)	0.00187	0.0509	0.0265	5.37	1.41
Mono-Di--Tri-CDDs	0.0564	0.13	0.0817	6.48	0.145
TCDDs	0.0506	0.0916	0.0771	9.98	0.354
PeCDDs	0.00573	0.0461	0.0161	9.86	1.03
HxCDDs	0.00423	0.0326	0.0113	14.7	3.83
HpCDDs	0.00432	0.0167	0.00699	15.9	8.56
OCDD	0.00499	0.0117	0.00831	12.3	6.3
Mono-Di-Tri-CDFs	0.118	2.4	0.506	130	5.72
TCDFs	0.0204	0.847	0.241	46.5	5.48
PeCDFs	0.0044	0.585	0.208	43.9	10.2
HxCDFs	0.0037	0.273	0.0718	59.3	17.1
HpCDFs	0.00485	0.0648	0.0171	71.8	24.7
OCDF	0.00461	0.0165	0.00759	62.7	19.2

Fig. 3 shows the total PCDD/F emissions and Fig. 4 shows the PCDD/F emissions in terms of the International Toxicity Equivalency (I-TEQs) for the 3 conditions with results from duplicate conditions being averaged. The combustion of the wetted carpet resulted in PCDD/F emissions only slightly higher than the natural gas blank, in terms of both the total PCDDs/Fs and TEQs. Addition of the 10% bleach solution, however, resulted in a significant increase of PCDD/F concentrations both in terms of the total PCDDs/Fs and the TEQs. This suggests that combustion facilities that may process BDR that has been decontaminated with a chlorinated decontamination agent should be aware of the potential for increased emissions of PCDDs/Fs. In general, good combustion practices including minimization of CO emissions and operating the flue gas cleaning equipment at temperatures below 250 °C will effectively minimize emissions of PCDDs/Fs (10). Other operating practices such as rapidly quenching the flue gases so that they spend as little time as possible in the PCDD/F formation temperature window will also minimize emissions of PCDDs/Fs (11). There has been no conclusive study to implicate water concentration in the formation mechanism, probably because at flue gas conditions, water is present in high concentrations.

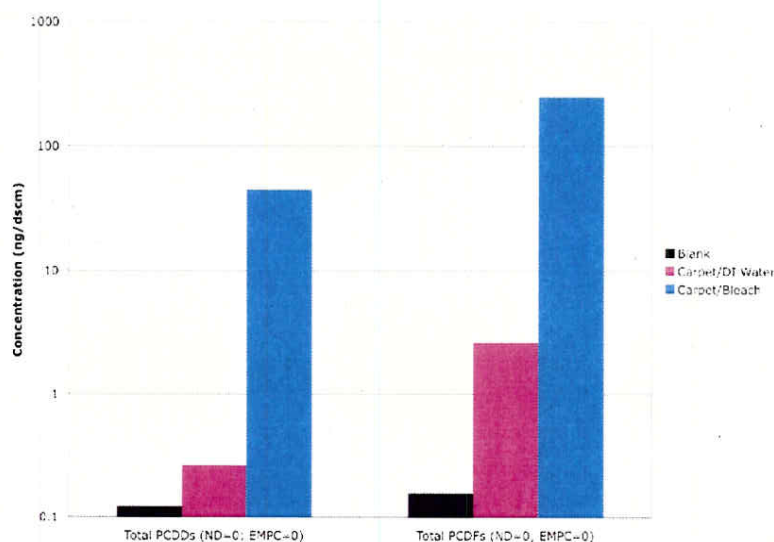


Fig. 3. Total PCDD/F Emissions

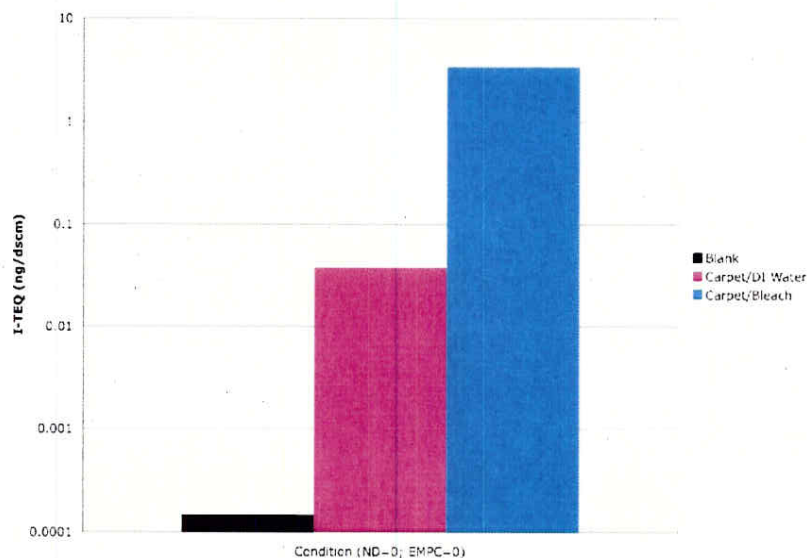


Fig. 4. PCDD/F I-TEQ Emissions

Fig. 5 shows the normalized distribution of the homologue groups. In all cases the furans were present at higher concentrations than the similarly chlorinated dioxin species. The homologue distribution for the natural gas combustion blank is heavily weighted towards the mono-tri chlorinated dioxins and furans, with some tetra-substituted dioxins contributing to the distribution. Most of the higher chlorinated species were present at very low levels relative to the lower chlorinated species. The samples with the carpet/DI water conditions showed a greater diversity in homologue groups present in significant concentrations, although the distribution was monotonically decreasing with higher degree of chlorination. The samples with the carpet/bleach conditions showed a relatively flat homologue distribution. The octa-chlorinated species were present at levels similar to the lower chlorinated species.



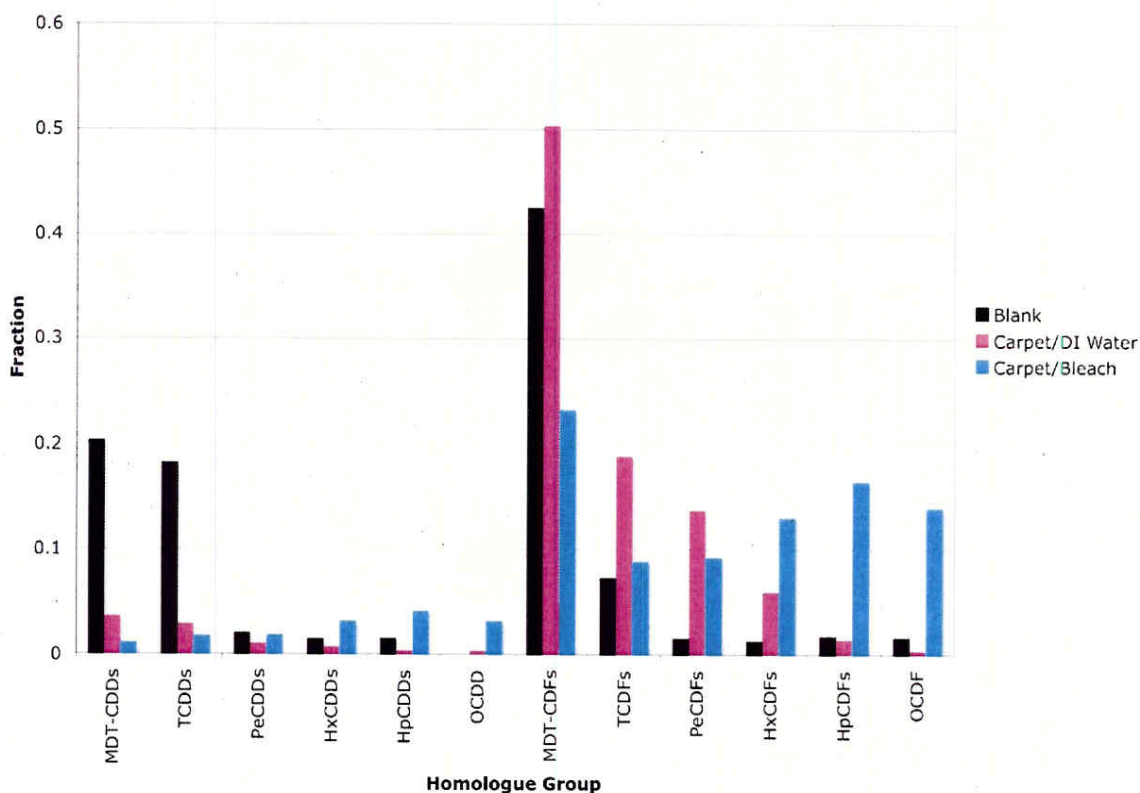


Fig. 5. PCDD/F Homologue Group Distribution.

Fig. 6 shows the normalized distribution of the isomers (the dioxin “fingerprint”). Of the species with the toxic 2,3,7,8 substitutions, there were significant qualitative differences between the fingerprints of the 3 test conditions. The toxic species associated with the combustion blank were almost totally contained in the octa-substituted dioxin and furan. Note that of the homologue groups, the combustion blank showed very low relative concentrations of the higher substituted species. This helps explain why the TEQ levels were very low for the combustion blank. The test condition with the carpet and deionized water showed a significant increase in the 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF. These 2 species have a fairly high toxicity equivalency factor (TEF) which explains the significant increase in the TEQ emissions when compared to the combustion blank. The distribution for the conditions with the bleach solution showed a significant contribution from the higher substituted species, both dioxins and furans.

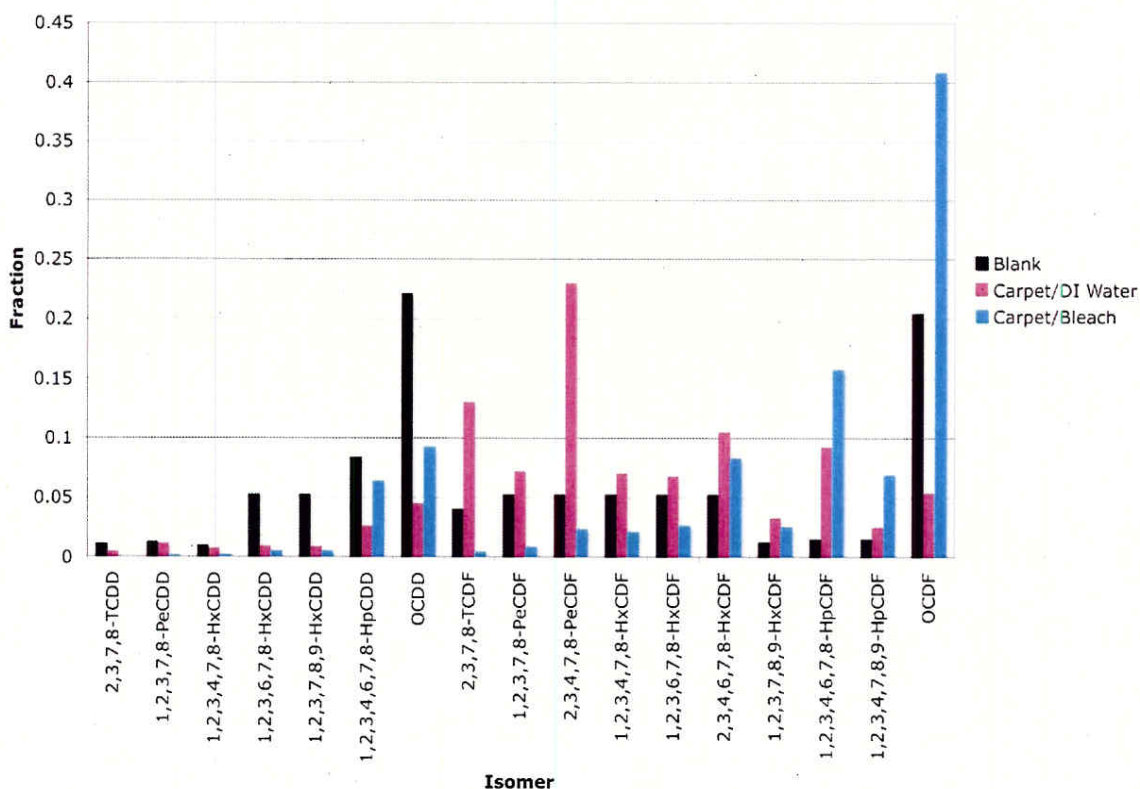


Fig. 6. PCDD/F Isomer Distribution

## CONCLUSIONS

Testing was performed on a pilot-scale rotary kiln incinerator simulator to evaluate the potential for formation of PCDDs/Fs from the combustion of carpeting. Five runs were performed at three test conditions (combustion blank, carpet wetted with deionized water, and carpet wetted with a 10% bleach solution). In order to maximize the differences in measured emissions between the various run conditions, the combustor was operated in such a way as to maximize formation of PCDDs/Fs. In all conditions, emissions of the furan species were higher than emissions of the analogous dioxin species. Emissions of PCDDs/Fs in the combustion blank were extremely low, and exhibited a homologue distribution heavily favoring the lower chlorinated species, although the majority of the toxic 2,3,7,8-substituted isomers were the octa-chlorinated dioxin and furan species. Emissions of PCDDs/Fs from the carpet wetted with deionized water were somewhat higher than the combustion blank, but were still low. The homologue distribution for the deionized water condition was monotonically decreasing as degree of chlorination increased, although unlike the combustion blank, there were significant levels of the higher chlorinated species. The condition with the deionized water showed a significant increase in the 2,3,7,8-TCDF and the 2,3,4,7,8-PeCDF isomers. The homologue distribution for the test condition with the bleach solution was flat, and the contribution of the octa-chlorinated species to the TEQs was significant. These results suggest that although combustion of clean carpet is not likely to increase emissions of PCDDs/Fs from solid fuel-burning facilities, the combustion of carpeting



that has been decontaminated with a chlorinated decontamination agent such as bleach, may require care to prevent an increase in PCDD/F emissions.

## ACKNOWLEDGMENTS

The authors would like to thank Richie Perry and Steve Terril of ARCADIS and Marc Calvi of EPA/NRMRL for their invaluable help in making these tests happen. The authors would also like to thank John Conyers and Steve Bradfield of Shaw Industries for providing the carpet samples.

## REFERENCES

1. Lemieux, P. (2004), "EPA Safe Buildings Program: Update on Building Decontamination Waste Disposal Area," *EM*, Vol. 29-33.
2. Statistical Report, 2001, *Floor Covering Weekly* 50 (18).
3. US EPA, June 2002. Municipal Solid Waste in the United States: 2000 Facts and Figures, Office of Solid Waste and Emergency Response, EPA530-R-02-001. Washington, D.C., 2002.
4. Lemieux, P.; Stewart, E.; Realff, M.; Mulholland, J.A. (2004), "Emissions Study of Co-firing Waste Carpet in a Rotary Kiln," *Journal of Environmental Management*, Vol. 70, pp. 27-33.
5. Realff, M., Lemieux, P., Lucero, S., Mulholland, J., and Smith, P., "Characterization of Transient Puff Emissions from Burning of Carpet Waste Charges in a Rotary Kiln Combustor," Paper to be presented at the IEEE 47th Cement Industry Technical Conference, Kansas City, MO, May 15-20, 2005.
6. Stewart, E.S.; Lemieux, P.M., "Emissions from the Incineration of Electronics Industry Waste," IEEE International Symposium on Electronics and the Environment & the IAER Electronics Recycling Summit Electronics Goes Green 2003 International Congress and Exhibition: Life-Cycle Environmental Stewardship for Electronic Products, Boston, MA, May 19-22, 2003.
7. Lemieux, P.M.; Stewart, E.S. (2004), "A Pilot-Scale Study of the Precursors Leading to the Formation of Mixed Bromo-Chloro Dioxins and Furans," *Environmental Engineering Science*, Vol. 21, pp. 3-9.
8. U.S. EPA, 1991, EPA Test Method 23, "Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources" in Code of Federal Regulations, Title 40, Part 60, Appendix A, U.S. Government Printing Office, Washington, DC, July 1991.
9. US EPA, 1998. The inventory of sources of dioxin in the United States, Review Draft, EPA/600/P-98/002Aa, Washington DC, April 1998.

10. U.S. EPA, 1996 Proposed Rule—Hazardous Waste Combustors; Maximum Achievable Control Technologies Performance Standards (Performance Specifications). Fed. Regist. 1996, 61, 17499-17502.
11. Rigo, G.H.; Chandler, A.J.; Lanier, W.S. The Relationship between Chlorine in Waste Streams and Dioxin Emissions from Waste Combustor Stacks; ASME Research Report CRTD; American Society of Mechanical Engineers: New York, 1996; Vol. 36.