

LEVELS OF BROMINATED DIPHENYLETHER, DIBENZO-*p*-DIOXIN, AND DIBENZOFURAN IN FLUE GASES OF A MUNICIPAL WASTE COMBUSTOR

Barbara Wyrzykowska^{1, #}, Brian K. Gullett¹, Dennis Tabor¹, Abderrahmane Touati²

¹U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, E305-01, Research Triangle Park, NC 27711, USA.

²ARCADIS Inc., P.O. Box 13109, Research Triangle Park, NC 27709, USA.

[#]Joint Program with Oak Ridge Institute for Science and Education Research Participation Post-doctoral Program

Introduction

Municipal waste combustors (MWCs) reduce dependence on fossil fuels by providing energy and lower the amount of landfilled solid waste, but potential emissions of toxic air pollutants are of concern. Due to the extensive use of brominated flame retardants (BFRs), including brominated diphenylether (BDE) formulations, for various domestic and industrial applications, the presence of brominated chemicals in the waste stream is to be expected for decades. While bromine-based chemicals are used for purposes other than flame retardancy, the U.S. Geological Survey estimated that as much as 40% to 50% of the domestic consumption of bromine was for use in BFR chemicals.¹ Therefore, the potential emissions of BFRs and their thermal breakdown byproducts – polybrominated dibenzo-*p*-dioxins, and polybrominated dibenzofurans (PBDDs/Fs), from waste incineration and recycling are of growing concern. Exposure to bromoorganics is of importance for the U.S. as levels of PBDEs in human breast milk and blood levels are amongst the highest in the world.^{2,3,4}

Data presented in this paper provide the first known measurements of polybrominated diphenylethers (PBDEs), polybrominated dibenzo-*p*-dioxins (PBDDs), and polybrominated dibenzofurans (PBDFs) in a U.S. waste combustor. Measurements were made during varied incineration conditions including shutdowns and startups both prior to the air pollution control system (APCS) and at the stack. This provides information on the formation and behavior of bromoorganics during waste combustion and an estimate of the efficiency of the spray dryer absorber/fabric filter (SDA/FF) air for PBDE and PBDD/F removal.

Materials and Methods

The field sampling was performed in December 2006 at a U.S. municipal waste combustor burning approximately 400 Mg of refuse derived fuel (RDF) daily. Sampling was performed during various stages of the normal (“steady state”) and transient (“shutdown” and “startup”) boiler operation. Samples of flue gases were taken isokinetically according to a modified version of U.S. EPA Method 23 (M-23),⁵ prior to the air pollution control system (pre-APCS) and at stack locations, using “short” (5 min) and “long” (>1h) sampling durations. The M-23 sampling protocol, routinely used for determination of PCDD/F from municipal waste combustors, was modified for simultaneous sampling of bromoorganics by addition of ¹³C₁₂-labeled BDE and BDF pre-sampling spikes and by measures to avoid photodegradation and debromination due to ultraviolet light exposure. Extraction of train samples was performed by means of sequential Soxhlet extraction with methylene chloride (3.5 h) with restricted exposure to light, followed by 16 h extraction with toluene to ensure removal of other target organics *e.g.*, PCDDs/Fs, from the carbonaceous matrix. All raw extracts were concentrated using the three-ball Snyder columns, filtered, and concentrated further with nitrogen to 0.5 mL using an automated evaporator (Zymark Turbovap). The samples were cleaned and fractionated using an automated liquid chromatography multi-column (multilayer silica, basic alumina) Power Prep Dioxin System (FMS Fluid Management Systems, Inc., USA). Concentrations of PBDE and PBDD/F were determined by the HRGC/HRMS analysis using Hewlett-Packard gas chromatograph 6890 Series equipped with a CTC Analytics Combi PAL autosampler (CTC Analytics, Switzerland) and coupled to a Micromass Premiere (Waters Inc., UK) double-focusing high resolution mass spectrometer. The HRMS was operated in an electron impact (35 eV and 650 μ A current) selective ion recording (SIR) mode at resolution $R > 10000$ MU (5% valley). Routine procedural blanks were performed and analyzed. The recovery rates were 77.7% (\pm 11.7% SD) for di-

through deca- $^{13}\text{C}_{12}$ -labeled BDE internal standards, and 85.8% (\pm 14% SD) for tetra- through octa- $^{13}\text{C}_{12}$ -labeled PBDDs/Fs, respectively. Reported values are recovery-compensated.

Results and Discussion.

PBDE. Total PBDE concentrations in the raw flue gases (pre-APCS) are given in Table 1.

Table 1. Total PBDE (Σ 42 congeners of mono- through decaBDE) in the raw (pre-APCS) MWC flue gas

	Steady State				Shut down				Start up			
	Mean*	Min	Max	n	Mean*	Min	Max	n	Mean*	Min	Max	n
Σ PBDE [ng/dscm]												
Day 1	16.6	7.64	29.5	6	78.6	5.90	289	4	5.12	1.78	7.31	5
Day 2	8.06	6.67	9.52	3	6.95	2.57	16.2	5	91.7	3.53	312	5
Day 3	2.06	1.62	2.77	3	11.8	3.88	18.5	5	17.3	4.66	29.9	2
Day 4	4.16	3.45	5.12	4	8.38	2.63	19.2	5	41.0	4.22	110	3

* M-23 5 min samples, n – number of M-23 samples taken for 5 min in 20 min intervals.

Based on the congener profile (data not shown), the occurrence of bromodiphenylethers in the raw flue gas appears to be related to common PBDE technical formulations (which are assumed to be present in the waste stream). The anticipated inter-day heterogeneity of the PBDE content in the RDF waste might explain the variation of Σ PBDE concentrations in the raw flue gas. The major PBDE isomers in the raw flue gas are those also present in the DecaBDE technical mix (with decabrominated diphenylether, DcBDE-209, being most abundant) and the penta- and octaBDE technical formulations (TeBDE-47, PeBDE-99, PeBDE-100, HxBDE-153, HxBDE-154, HpBDE-183 and OcBDE-197). Not only were the technical congeners at the highest concentrations, but they also exhibited the fingerprint typical for technical bromodiphenylether mixtures. For example, the deca- and nona- homologue groups were dominated by one congener – DcBDE-209 (profile typical for the decaBDE technical product), while tetra- and pentabromodiphenylether homologue pattern typically showed tetraBDEs and pentaBDEs in approximately equal amounts, with TeBDE-47 and PeBDE-99 being the most abundant congeners (which is characteristic for the pentaBDE technical product).^{6,7} Both the shutdown and the startup of the MWC were found to considerably increase the yields of Σ PBDE in the flue gas (with at least 10- to 30-fold increases in concentrations during transients compared to steady state). The transients also have an effect on the BDE congener and homologue patterns in the flue gas. Even though the isomers found in technical product BDEs dominated all stages of the combustion process, some of the transient samples exhibited specific enrichment of congeners which are minor or not present in the technical mixtures, (e.g., DiBDE-15, TriBDE-17, TriBDE-28, TeBDE-49). The higher contribution of di- through tetraBDE congeners during the transients suggests that debromination likely occurs at some point of the disturbed combustion. The Σ PBDE homologue trends in samples of raw flue gas collected during the transient operating conditions of the boiler for the period of approximately one hour (“long sampling”) are shown in Figure 1a. Congeners with reportedly high potential for dioxin-like toxicity, (i.e., substituted in non-ortho and mono-ortho position including BDE-77, -126, -156 and -169), were detected in several samples collected during the transients.

PBDD/F. Total PBDD/F concentrations in the raw flue gases (pre-APCS) are given in Table 2. Similar to Σ PBDE levels in the flue gas, Σ PBDD/F were affected by the incomplete combustion. The highest yields were found during shutdown and startup, when 3- to 30-fold increases in Σ PBDD/F concentrations were observed compared to the maximum levels during the steady state.

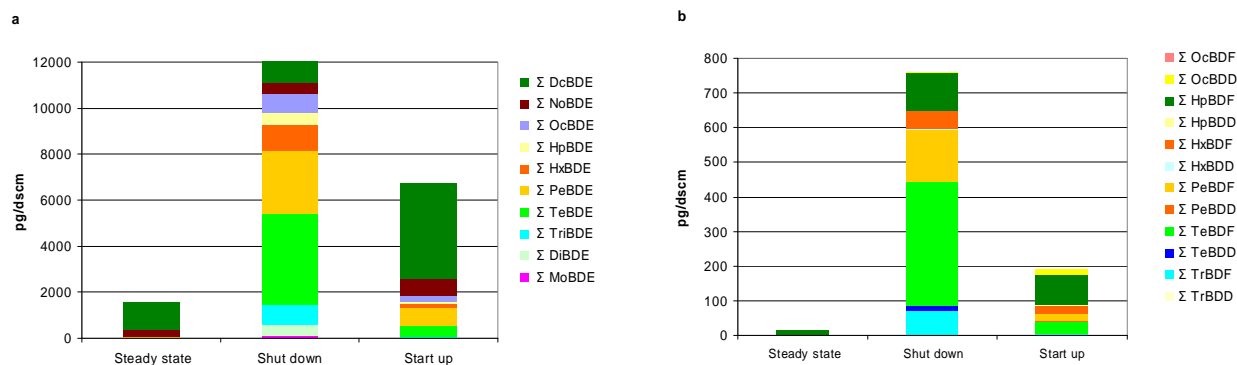
Table 2. Total PBDD/F ($\Sigma 17$ congeners of 2,3,7- and 2,3,7,8-Br-substituted tri- to octa-PBDD/F) in the raw (pre-APCS) flue gas

	Steady State					Shut down					Start up				
	Mean*	Min	Max	n	Ratio**	Mean*	Min	Max	n	Ratio**	Mean*	Min	Max	n	Ratio**
	ΣPBDD/F [ng/dscm]														
Day 1	0.025	n.d.	0.070	6	0.62	0.31	n.d.	0.63	4	0.93	0.20	n.d.	0.76	5	0.66
Day 2	0.14	0.051	0.28	3	0.70	0.30	0.029	0.58	5	0.96	1.78	n.d.	7.17	5	0.95
Day 3	0.16	0.071	0.30	3	0.66	0.75	0.056	1.19	5	0.97	0.58	0.14	1.02	2	0.93
Day 4	0.026	0.0045	0.046	4	0.38	0.56	0.22	0.97	5	0.70	0.55	0.16	1.22	3	0.63

* M-23 5 min samples, n – number of M-23 samples taken for 5 min in 20 min intervals; ** ratio between Σ PBDF/ Σ PBDD

As shown on Figure 1, trends in the bromodibenzo-*p*-dioxin and bromodibenzofuran homologue patterns during the transients closely mirrored those observed for bromodiphenylether. For samples showing higher concentrations of lowly-brominated diphenylethers, the homologue pattern of PBDD/F was also dominated by the lower brominated congeners. Samples with a higher relative proportion of highly-brominated diphenylethers also had a higher concentration of more highly-brominated PBDDs/Fs (Figure 1 a and b). During the transients, especially the shutdowns, PBDFs were favored over PBDDs (average Σ PBDF/ Σ PBDD ratios are given in Table 2). It might be due to favored PBDF formation from lowly- versus from highly-brominated diphenylethers (intramolecular elimination of two bromine substituents in highly-brominated BDEs is energetically less favorable than elimination of HBr in lowly-brominated BDEs).⁸ The occurrence of PBDFs in the raw flue gases might be also due to release from technical BDEs, which reportedly contain PBDF impurities.⁹

Figure 1. The Σ PBDE (a) and Σ PBDD/F (b) homologue concentrations in the raw (pre-APCS) flue gases collected for approximately one hour (“long sampling”, Day 3) during steady state, shutdown and startup.



The mean PBDD/F concentration (sum of tri- to octa- 2,3,7,8-Br-substituted PBDD/F) in the stack gases during steady state conditions, 1.45 pg/dscm (1.41-1.53 pg/dscm; n=3), is similar to values (2.28 pg/Nm³, sum of tetra- to hexa-BDD/F) recently reported for MSWIs in Taiwan.¹⁰ The mean PBDD/F concentration during the transients, 9.53 pg/dscm (2.54-16.5 pg/dscm; n=2), are comparable to PBDD/F stack concentrations of 18.2 pg/Nm³ reported for industrial waste incinerators.¹⁰ The mean PBDEs concentrations in flue gases collected from the stack were almost 10-fold higher than those of PBDDs/Fs: 115.5 pg/dscm (79.8-162 pg/dscm; n=3) for the steady state and 766 pg/dscm (262.1-3189 pg/dscm; n=2) during the transients.

Efficiency of SDA/FF air pollution control system. The SDA/FF (spray dryer absorber/fabric filters) air pollution control system had a significant effect on reduction of Σ PBDE and Σ PBDD/F emissions from the stack. The maximum reduction rates were observed in the case of PBDEs on the first day of sampling (Day 1). On that day, Σ PBDE emissions from the stack during steady state combustion were 0.34 $\mu\text{g}/\text{min}$ compared to an average 84.5 $\mu\text{g}/\text{min}$ in the flue gas at the exit of the boiler. This is a reduction of 99.6% due to the SDA/FF. Correspondingly, raw flue gas PBDE concentrations of 183 $\mu\text{g}/\text{min}$ observed for transients, were reduced also by 99.6% to 0.80 $\mu\text{g}/\text{min}$. Eventhough, the removal efficiency varied between the days, the average reduction was about 98.6% for PBDEs and 98.5% for PBDDs/Fs, respectively. The BDE homologue patterns (data not shown) show that the proportion of higher brominated congeners, especially decabromodipheylether, decreased in the stack versus the raw (pre-APCS) flue gas. A similar trend was observed for PBDD/F, with higher brominated congeners being removed more efficiently. More highly-brominated compounds are more likely to condense and bind to air particulate matter aiding their capture on fabric filters. Conversely, the more lowly- brominated compounds would be preferentially released to the atmosphere. Interestingly, in the PBDEs profile most commonly reported for the U.S. environment (including human samples) lower brominated congeners are more abundant than higher brominated ones, even though the production and usage pattern of technical BDE in the Northern America favors the higher brominated technical formulations (decaBDE).^{2,3,4,6,10,11} The atmospheric BDE pattern is most commonly dominated by lighter congeners, usually explained by photolytic degradation of decaBDEs, lower volatility of higher brominated BDEs, and differences between actual production and usage rates.^{11,12,13} Interestingly, it has been already suggested that recent regulatory activity, banning many of the lower brominated diphenylethers from production, will increase the relative importance of post-consumer secondary sources, like combustion or recycling, for the emissions of so called “old BDEs” (e.g., BDE-47), whereas emissions of bromodiphenylethers which are still manufactured and used (e.g., BDE-209) should be mostly influenced by primary sources (manufacturing and evaporative emissions from present usage).¹³ The results of this study suggest that MWC emissions should be considered as a source of both lowly and highly brominated PBDEs and PBDDs/Fs to the atmosphere.

Acknowledgments. This research was supported in part by an appointment of the Postdoctoral Research Program at the U.S. EPA National Risk Management Research Laboratory, administered by the Oak Ridge Institute for Science and Education (ORISE). Special acknowledgments to all participants of the 2006 MWC sampling campaign.

Literature cited

1. U.S. Geological Survey, 2006; <http://minerals.usgs.gov/minerals/pubs/commodity/bromine/bromimyb05.pdf>
2. Schecter A., Pavuk M., Pöpke O., Ryan J., Birnbaum L. and Rosen, R. *Environ Health Perspect* 2003; 111: 1723.
3. Mazdai A., Dodder N. G., Abernathy M. P., Hites R. A. and Bigsby R. M. *Environ Health Perspect* 2003; 111:1249.
4. Schecter A., Johnson-Welch S., Kuang C., Harris T. R., Pöpke O. and Rosen R. *J Toxicol Environ Health A* 2007; 70: 1.
5. U.S. EPA. Test Method 23, 1996.
6. Birnbaum L.S. and Staskal D.F. *Environ. Health Perspect* 2004; 112: 9.
7. Sjödin A., Jakobsson E., Kierkegaard A., Marsh G. and Sellström U. *J Chrom A* 1998; 822: 83.
8. Weber R. and Kuch B. *Environ Int* 2003; 29: 699.
9. Hanari N., Kannan K., Miyake Y., Okazawa T., Kodavanti P., Aldous K. and Yamashita N. *Environ Sci Technol* 2006; 40: 4400.
10. Wang L.-C. and Chang-Chien G.-P. *Environ Sci Technol* 2007; 41: 1159.
11. Strandberg B., Dodder N. G., Basu I. and Hites R. *Environ Sci Technol* 2001; 35: 1078.
12. Hale R., Alae M., Manchester-Neesvig J., Stapleton H. and Ikonomou M.G. *Environ Int* 2003; 29: 771.
13. Agrell C., ter Schure A. F. H., Sveder J., Bokenstrand A., Larsson P. and Zegers B. *Atm Environ* 2004; 38: 5139.