ANALYSIS OF THE BROMINATED DIOXIN AND FURAN EMISSION CONGENER PATTERN FROM DIFFERENT SOURCES

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Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) have been studied for several decades and are well-known as unintentionally generated persistent organic pollutants (POPs), which pose serious health and environmental risks on a global scale[1]. Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/F) have similar properties and effects to PCDD/F, as they are structural analogs with all the chlorine atoms substituted by bromine atoms[2-3]. PBDD/F have been found in various matrices such as air, sediments, marine products, and human adipose samples[4-7].

In comparison to PCDD/F, analytical difficulties mean that little is known about the occurrence, levels and characteristics of PBDD/F in various environmental matrices and their emission sources. In recent years, extensive use of brominated flame retardants (BFRs), especially polybrominated diphenyl ethers (PBDEs), has provided more available bromine and increased the chance of PBDD/F formation in both natural environment and industrial processes. Consequently, PBDD/F as well as PCDD/F should be the focus of attention.

Weber and Kuch[8] summarized the main categories of thermal processes that release PBDD/F into the environment, and suggested that PBDD/F might share a similar de novo or precursor mechanism as PCDD/F[9].

The similar chemical properties of chlorine and bromine suggest that the two elements behave comparably during thermal processes; in fact, brominated dioxin-like compounds, have formation mechanisms similar to those of chlorinated dioxin-like compounds due to the similar chemical properties of chlorine and bromine[8].

In the present work, a review of the data in literature concerning brominated dioxins and furans emissions has been done. Data has been found for different sources, including incineration units, vehicle exhaust, clinker furnaces, air sampling and metal treatment plants among other.

Discussion

In the last seven years different studies have been performed on the presence of polybrominated dioxins and furans (PBDD/Fs). In the present work, only those studies presenting the congener distribution have been considered, although there are some other studies considering the total amount of PBDD/Fs. In this way, Gullett et al.[10] only presents the total amount of these compounds generated during open burning of residential waste dump, Brykovska et al.[11] presents data on all congeners grouped by the degree of substitution during the operation of a municipal waste combustor, and Hutson[12] only presents the total emission in a coal fired power plant operation during injection of brominated activated carbon.

From all literature data found, sixty-one samples have been selected. Table 1 presents the samples considered together with the code used during the present study, and the reference to the original works. Only 2,3,7,8- congeners are considered, and the data in literature have been normalized to the total amount of PBDD+PBDFs, in such a way that the sum of all congener emissions is unity. In any case equivalent toxicity has been used. Unfortunately, many studies did not measure the emission of hepta- nor octabrominated D/Fs due to its difficulty. Table 2 presents the data used in the present study, and Figure 1 shows the congener distribution, presented in increasing order of furan emissions, i.e., we find to the right sources with the higher dioxins emissions, and to the left appear more furans emitting sources.

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Sample code	Facility or sampling point	Reference
MSWI-M1 to MSWI-M9	Nine Municipal Solid Waste Incinerators	6
IWI-I1 to IWI-I9	Nine Industrial Waste Incinerators	6
Rural	Air rural area	13
Urban	Air urban area	13
Indust	Air industrial park	13
Science	Air science park	13
PCB-TTT	Seven runs of thermal decomposition of printed circuit board (PCB) sample at different temperatures (TTT represents the temperature in ºC).	14
HWI-Du	Hazardous Waste Incinerator	15
MSWI-Du	Municipal Solid Waste Incinerator	15
CreP	Crematoria	15
CreT	Crematoria	15
IOSinter	Iron Ore Sinter	15
Steel	Steel production	15
S.Pb	Secondary lead	15
S.Al	Secondary aluminium	15
S.Cu	Secondary copper	15
S.Zn	Secondary zinc	15
TPP-Tu	Coal fired power plant stack flue gas	16
MSWIA-Tu MSWIB-Tu	Municipal Solid Waste Incinerators stack flue gas	16
FAPA-Tu FAPB-Tu	Fly Ash Pits of MSWIA and MSWIB	16
BRA-Tu BRB-Tu	Bottom residue of MSWIA and MSWIB	16
SHA-Tu SHB-Tu	Fly ashes from superheaters of MSWIA and MSWIB	16
ECA-Tu ECB-Tu	Economizers of MSWIA and MSWIB	16
SDA-Tu SDB-Tu	Semi-dry scrubbers of MSWIA and MSWIB	16
BFA-Tu BFB-Tu	Fabric filters of MSWIA and MSWIB	16
WoodSludge	Wood chips with sewage sludge	17
BA-WoodS	Bottom ash combustion wood with sewage sludge	17
CA-WoodS	Cyclone ash combustion wood with sewage sludge	17
FA-WoodS	Bag Filter Ash combustion wood with sewage sludge	17
Gas-WoodS	Stack Flue gas combustion wood with sewage sludge	17
Diesel	Diesel engine exhaust	18
Cement-BDE	Cement kiln feeding BDE contaminated soils	19
EAF	Electric Arc Furnace	20

Table 1. Emission sources considered in the study.

Facility	MSWI-Du	HWI-Du	CreP	CreT	IOSinter	Steel	S.Pb	S.Al	S.Cu	S.Zn	Rural	Urban
2,3,7,8-TBDF	0,109	0,268	0,283	0,267	0,108	0,106	0,155	0,213	0,717	0,272	0,288	0,239
1,2,3,7,8-PeBDF	0,154	0,107	0,071	0,207	0,183	0,186	0,198	0,124	0,096	0,132	0,279	0,214
2,3,4,7,8-PeBDF	0,039	0,209	0,199	0,059	0,042	0,046	0,099	0,119	0,044	0,272	0,315	0,259
1,2,3,4,7,8-HxBDF	0,168	0,08	0,136	0,059	0,415	0,411	0,276	0,195	0,052	0,238	nd	nd
1,2,3,4,6,7,8-HpBDF	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
OBDF	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
2,3,7,8-TBDD	0,042	0,083	0,055	0,076	0,044	0,036	0,082	0,055	0,024	0,056	0,025	0,045
1,2,3,7,8-PeBDD	0,07	0,118	0,046	0,036	0,098	0,099	0,112	0,06	0,025	0,011	0,03	0,07
1,2,3,4,7,8+ 1,2,3,6,7,8-HxBDD	0,168	0,08	0,105	0,148	0,093	0,099	0,069	0,133	0,035	0,012	0,054	0,14
1,2,3,7,8,9-HxBDD	0,251	0,054	0,105	0,148	0,017	0,017	0,009	0,099	0,008	0,008	0,009	0,032
1,2,3,4,6,7,8-HpBDD	nm	nd	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
OBDD	nm	nd	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm

Facility	Indust	Science	WoodSludge	BA-WoodS	CA-WoodS	FA-WoodS	Gas-WoodS	Diesel	Cement BDE	EAF	MSWIA-Tu	MSWIB-Tu
2,3,7,8-TBDF	0,218	0,137	nd	0,047	nd	nd	nd	nd	0,003	0,075	nd	0,209
1,2,3,7,8-PeBDF	0,283	0,253	0,019	0,047	nd	nd	nd	nd	0,004	0,025	nd	0,09
2,3,4,7,8-PeBDF	0,348	0,527	0,019	0,057	nd	nd	nd	nd	nd	0,18	nd	0,04
1,2,3,4,7,8-HxBDF	nd	nd	0,019	0,094	nd	nd	nd	0,06	0,019	0,2	0,032	0,061
1,2,3,4,6,7,8-HpBDF	nm	nm	0,204	0,283	0,42	0,47	0,27	0,32	0,116	0,262	0,297	0,182
OBDF	nm	nm	0,741	0,472	0,58	0,53	0,73	0,62	0,856	0,258	0,471	0,307
2,3,7,8-TBDD	0,028	0,013	nd	nd	nd	nd	nd	nd	0,003	nd	nd	0,033
1,2,3,7,8-PeBDD	0,039	0,03	nd	nd	nd	nd	nd	nd	nd	nd	nd	0,015
1,2,3,4,7,8+ 1,2,3,6,7,8-HxBDD	0,065	0,022	nd	nd	nd	nd	nd	nd	0	nd	0,044	0,024
1,2,3,7,8,9-HxBDD	0,018	0,019	nd	nd	nd	nd	nd	nd	nd	nd	nd	0,009
1,2,3,4,6,7,8-HpBDD	nm	nm	nd	nd	nd	nd	nd	nd	nd	nd	0,03	0,014
OBDD	nm	nm	nd	nd	nd	nd	nd	nd	nd	nd	0,125	0,015

Facility	SDA-Tu	DFA-Tu	FAPA-Tu	BRA-Tu	SHA-Tu	ECA-Tu	BRB-Tu	SHB-Tu	ECB-Tu	SDB-Tu	BFB-Tu	FAPB-Tu
2,3,7,8-TBDF	0,002	nd	0	0,005	nd	nd	0,002	nd	0,001	0,137	0,081	0,235
1,2,3,7,8-PeBDF	0,004	nd	0,003	0,009	nd	nd	0,005	0,009	0,003	0,008	0,007	0,019
2,3,4,7,8-PeBDF	nd	nd	0,002	0,012	nd	nd	0,011	0,009	0,008	0,02	0,037	0,035
1,2,3,4,7,8-HxBDF	0,043	0,102	0,036	0,083	nd	nd	0,068	0,095	0,07	0,017	0,061	0,053
1,2,3,4,6,7,8-HpBDF	0,458	0,171	0,448	0,373	0,094	0,141	0,39	0,551	0,254	0,126	0,238	0,123
OBDF	0,464	0,727	0,432	0,514	0,906	0,859	0,516	0,301	0,63	0,555	0,494	0,299
2,3,7,8-TBDD	nd	nd	nd	0	nd	nd	0	nd	0	0,003	0,004	0,01
1,2,3,7,8-PeBDD	nd	nd	nd	0	nd	nd	0	nd	0	0,002	0,004	nd
1,2,3,4,7,8+ 1,2,3,6,7,8-HxBDD	nd	nd	nd	0	nd	nd	0	nd	0	0,016	0,007	0,035
1,2,3,7,8,9-HxBDD	nd	nd	nd	0	nd	nd	0	nd	0	0,01	0,004	0,018
1,2,3,4,6,7,8-HpBDD	0,003	nd	0,005	0,001	nd	nd	0,001	0,007	0,005	0,085	0,023	0,155
OBDD	0,026	nd	0,074	0,002	nd	nd	0,005	0,027	0,028	0,021	0,04	0,017

Facility	PCB-625	PCB-500	PCB-400	PCB-325	PCB-275	PCB-250	PCB-20	MSWI M1	MSWI M2	MSWI M3	MSWI M4	MSWI M5
2,3,7,8-TBDF	0,288	0,392	0,302	0,217	0,068	0,165	0,027	0,132	0,087	0,061	0,111	0,053
1,2,3,7,8-PeBDF	0,192	0,039	0,069	0,104	0,085	0,046	nd	0,062	0,09	0,061	0,104	0,126
2,3,4,7,8-PeBDF	0,144	0,098	0,216	0,174	0,153	0,294	0,036	0,03	0,17	0,51	0,258	0,197
1,2,3,4,7,8-HxBDF	0,173	0,245	0,259	0,304	0,381	0,183	0,33	nd	nd	nd	nd	nd
1,2,3,4,6,7,8-HpBDF	0,048	0,078	0,086	0,13	0,28	0,275	0,491	nm	nm	nm	nm	nm
OBDF	nd	nd	nd	nd	0,008	0,009	0,071	nm	nm	nm	nm	nm
2,3,7,8-TBDD	0,115	0,078	0,052	0,052	0,017	0,009	0,009	0,007	0,027	nd	0,039	0,021
1,2,3,7,8-PeBDD	0,029	0,059	0,017	0,017	0,008	0,018	0,009	nd	nd	nd	nd	0,063
1,2,3,4,7,8+ 1,2,3,6,7,8-HxBDD	0,01	0,01	nd	nd	nd	nd	0,009	0,439	0,5	0,368	0,488	0,308
1,2,3,7,8,9-HxBDD	nd	nd	nd	nd	nd	nd	nd	0,329	0,125	nd	nd	0,231
1,2,3,4,6,7,8-HpBDD	nd	nd	nd	nd	nd	nd	0,009	nm	nm	nm	nm	nm
OBDD	nd	nd	nd	nd	nd	nd	0,009	nm	nm	nm	nm	nm

Facility	MSWI M6	MSWI M7	MSWI M8	MSWI M9	IWI I1	IWI I2	IWI I3	IWI I4	IWI I5	IWI I6	IWI I7	IWI I8
2,3,7,8-TBDF	0,229	0,072	0,084	0,212	0,254	0,123	0,207	0,22	0,234	0,111	0,335	0,54
1,2,3,7,8-PeBDF	0,167	0,025	0,097	0,104	0,17	0,165	0,275	0,183	0,285	0,183	0,237	0,229
2,3,4,7,8-PeBDF	0,277	0,197	0,165	0,46	0,395	0,222	0,401	0,202	0,375	0,459	0,311	0,127
1,2,3,4,7,8-HxBDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
1,2,3,4,6,7,8-HpBDF	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
OBDF	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
2,3,7,8-TBDD	0,004	0,144	0,004	0,034	0,011	0,101	0,006	0,018	0,016	0,01	nd	0,057
1,2,3,7,8-PeBDD	0,029	0,011	0,088	0,047	0,013	0,148	0,052	0,149	0,036	0,088	nd	0,035
1,2,3,4,7,8+ 1,2,3,6,7,8-HxBDD	0,168	0,504	0,516	0,081	0,033	0,191	0,015	0,052	0,014	0,039	0,017	0,006
1,2,3,7,8,9-HxBDD	0,126	0,048	0,046	0,061	0,124	0,052	0,043	0,176	0,039	0,11	0,1	0,008
1,2,3,4,6,7,8-HpBDD	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
OBDD	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm

Table 2. PBDD/Fs emission profile from different sources (data are normalized to the total emission).

nm= not measured. nd= not detected.

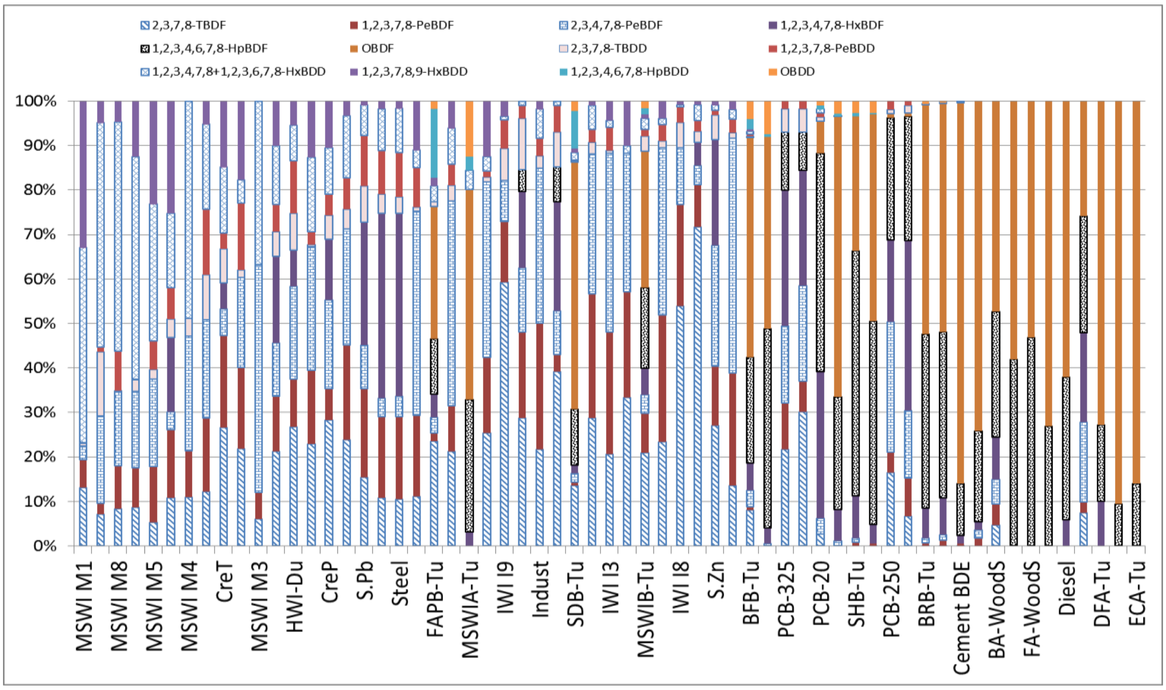

Figure 1. Congener distribution in the sixty-one profiles considered in the study.

References:

1. U.N.E.P. (2005); *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*; Geneva (Switzerland).
2. Birnbaum L S, Staskal D F, Diliberto J J. (2003); *Environment International* 29(6): 855-860.
3. Olsman H, Engwall M, Kammann U, Klempt M, Otte J, Van Bavel B, Hollert H. (2007); *Env. Toxicol. Chem.* 26(11): 2448-2454.
4. Choi J W, Fujimaki S, Kitamura K, Hashimoto S, Ito H, Suzuki N, Sakai S I, Morita M. (2003); *Env. Sci. Technol.* 37(5): 817-821.
5. Malmvärn A, Zebühr Y, Jensen S, Kautsky L, Greyerz E, Nakano T, Asplund L. (2005); *Env. Sci. Technol.* 39(21): 8235-8242.
6. Wang L-C, Chang-Chien G-P. (2007); *Env. Sci. Technol.* 41(4): 1159-1165.
7. Li H, Feng J, Sheng G, Lü S, Fu J, Peng P, Man R. (2008); *Chemosphere* 70(4): 576-583.
8. Weber R, Kuch B. (2003); *Environment International* 29(6): 699-710.
9. Everaert K, Baeyens J. (2002); *Chemosphere* 46(3): 439-448.
10. Gullett B K, Wyrzykowska B, Grandesso E, Touati A, Tabor D G, Ochoa G S. (2009); *Env. Sci. Technol.* 44(1): 394-399.
11. Wyrzykowska-Ceradini B, Gullett B K, Tabor D, Touati A. (2011); *Env. Sci. Technol.* 45(13): 5853-5860.
12. Hutson N D, Ryan S P, Touati A. (2009); *Atmospheric Environment* 43(26): 3973-3980.
13. Wang L-C, Tsai C-H, Chang-Chien G-P, Hung C-H. (2008); *Env. Sci. Technol.* 42(1): 75-80.
14. Duan H, Li J, Liu Y, Yamazaki N, Jiang W. (2011); *Env. Sci. Technol.* 45(15): 6322-6328.
15. Du B, Zheng M, Tian H, Liu A, Huang Y, Li L, Ba T, Li N, Ren Y, Li Y, Dong S, Su G. (2010); *Chemosphere* 80(10): 1227-1233.
16. Tu L K, Wu Y L, Wang L C, Chang-Chien G P. (2011); *Aerosol and Air Quality Research* 11(5): 596-615.
17. Chang S-S, Lee W-J, Wang L-C, Chang-Chien G-P, Wu C-Y. (2013); *Env. Sci. Technol.* 47(21): 12600-12606.
18. Chang Y-C, Lee W-J, Wang L-C, Yang H-H, Cheng M-T, Lu J-H, Tsai Y I, Young L-H. (2014); *Appl. Energy* 113(0): 631-638.
19. Yang Y, Huang Q, Tang Z, Wang Q, Zhu X, Liu W. (2012); *Env. Sci. Technol.* 46(24): 13409-13416.
20. Wu E M Y, Wang L C, Lin S L, Chang-Chien G P. (2014); *Aerosol and Air Quality Research* 14(1): 185-196.