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# Waste combustion as a source of ambient air polybrominated diphenylethers (PBDEs)

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## ABSTRACT

The first comprehensive set of U.S. data on polybrominated diphenylether (PBDE) concentrations from municipal waste combustion (MWC), with more than 40 PBDE congeners reported, was compared to ambient air levels of PBDEs in the U.S. The PBDE profiles in the raw MWC flue gas reflected the historical production and usage pattern of PBDE-based flame retardants in North America, which favored Pentaand Deca- BDE formulations. The pattern of selected, routinely measured in the environment, PBDEs (TeBDE-47, PeBDE-99, PeBDE-100, HxBDE-153 and DcBDE-209) was similar in the MWC emissions and profiles most commonly reported for the U.S. atmosphere.

The mean  $\Sigma$  PBDE concentrations in the clean flue gases collected from the stack were 0.13 and 1.7 ng dscm<sup>-1</sup> during the steady state and transients of MWC, respectively (which was 98.6% reduction compare to the levels in the raw flue gases). The major PBDE congeners in the MWC flue gases were those typically found in PBDE technical mixes (TeBDE-47, PeBDE-99, PeBDE-100, HxBDE-153, HpBDE-183, OCBDE-197, NoBDE-206, NoBDE-207, NoBDE-208, DCBDE-209). The profile of the PBDEs in the raw flue gas was dominated by heavier congeners, especially DcBDE-209, while the profile of the stack flue gases profile was dominated by the lighter congeners (TeBDE-47, PeBDE-99, PeBDE-100 accounted for around 80% of total stack emissions). Some of the MWC flue gas samples exhibited enrichment of lower brominated congeners that are minor or not present in the technical mixtures, suggesting that debromination occurs during combustion. Congeners substituted in non- and mono-ortho positions (TeBDE-77, PeBDE-126, HxBDE-156 and -169) were detected mostly during the transients of MWC.

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## 1. Introduction

Numerous studies suggest that concentrations of polybrominated diphenylethers (PBDEs) in the North American environment, as well as their body burden in the general population of the U.S. and Canada, have been steadily increasing over the past 25 years and are among the highest in the world (Schecter et al., 2007, 2006, 2003; Mazdai et al., 2003; Hale et al., 2003). The elevated levels of PBDEs in environmental samples originating from North America are usually attributed to the extensive use of brominated flame retardants (BFRs) in the past. Historically, PBDE-based formulations were the most widely used brominated flame retardants in the U.S., e.g. comprising 65% of the total volume of BFRs used in 2005 (Birnbaum

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and Staskal, 2004). After numerous reports on elevated levels of PBDEs in humans, including breast milk, the manufacture of PentaBDE and OctaBDE technical mixes in the U.S. voluntarily ended in 2004, with use restrictions regulated by state legislation (BSF, 2007; Schecter et al., 2006; Birnbaum and Staskal, 2004; Hites, 2004; Hale et al., 2003). In December 2009, in an agreement with the U.S. Environmental Protection Agency (U.S. EPA), Albemarle and Chemtura, which produce decaBDE in the U.S., and Israel's ICL Industrial Products (IP), the largest U.S. importer of the chemical, have agreed to voluntarily phase out the production of decabromodiphenylether by December 2012. The sales for all remaining "essential uses" will stop by the end of 2013 (U.S. EPA, 2009).

There are numerous reports about PBDE evaporative releases from commercial formulations manufacture and use, including estimates of emissions during product service use and recycling, but there is very little information on the PBDE emissions from post-consumer processes, including incineration of municipal solid waste (MSW) (Allen et al., 2007; Cahill et al., 2007; Wang et al., 2010a, 2010b; Morf et al., 2005; Wilford et al., 2005; Agrell et al.,

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2004; Borgnes and Rikheim, 2004; Alaee et al., 2003; Hale et al., 2003; de Witt, 2002; Sakai et al., 2001; Sjödin et al., 2001; Danish EPA, 1999). The presence of PBDEs in waste streams is expected to continue for years, as a consequence of extensive use of BFRs in everyday products, which ultimately will be disposed of or recycled. In addition, after the ban of all bromodiphenvlether-based flame retardants, evaporative releases from consumer uses should decrease over time, while the relative importance of PBDE emissions from various waste treatment processes should increase. The intensity of this trend will logically depend on the lifetime of flame retarded products, as well as trends in generation and disposal patterns of MSW. The U.S. generation of MSW per capita has not changed over the past 20 years (U.S. EPA, 2006). Based on U.S. EPA data on composition of municipal solid waste in the U.S. in 2006, waste products potentially containing BFRs comprised almost 22.3% of total MSW by weight before recycling (plastics -11.7%) rubber and leather and textiles 7.3%, other 3.3%) (U.S. EPA, 2006). Assuming an average recycling rates of 32.5%, in 2006 the amount of waste containing BFRs can be estimated at about 15.1%, so roughly 37.9 million tons of possibly "flame retarded waste" have been generated. In 2006, approximately 12.5% of total MSW (251 million tons) was combusted with energy recovery in the U.S. (U.S. EPA, 2006). The combustion of "flame retarded waste" obviously raises the question of effective thermal treatment of PBDEs, including problems related to potential incomplete incineration. The work of Sakai et al. (2001) on combustion of PBDE flameretarded polyethylene plastic (PBDE/PE) has demonstrated that decomposition of PBDEs in experimental systems (rotary klin furnace at 500–900 °C. with the secondary combustion chamber at 800-1200 °C) was more than 99.9% (Sakai et al., 2001). PBDE concentrations in the flue gas ranged from below detection limit to  $670 \text{ ng Nm}^{-3}$ , with increases in the PBDE concentrations during flue gas cooling process observed in more than fifty percent of the runs (Sakai et al., 2001). Wang et al. (2010a) suggested that the elevated PBDE contents  $(20.4-186 \text{ ng g}^{-1})$  in the bottom ashes of MWCs show that the PBDEs in the feeding waste may not be completely destroyed (Wang et al., 2010a). Agrell et al. (2004) have reported atmospheric levels of nine PBDE congeners near MWCs in Sweden, with mean concentrations in the range of  $2.24-21.3 \text{ pg m}^{-3}$  (Agrell et al., 2004). The Danish Environmental Protection Agency emission estimate for BFRs from incineration assumes, in a worst case scenario, that 1% of the BFRs pass the combustion chamber, and 0.01% pass the flue gas cleaning system and are emitted to the atmosphere. In Denmark this would result in the emission of <0.04 tons per year of BFRs from MWCs (Danish EPA, 1999). In general, studies on the fate of BFRs in incineration suggest that the operating temperatures of MWCs destroy almost all flame retardants, allowing only trace amounts to pass the air pollution control devices (Danish EPA, 1999).

The data presented in this study are the first comprehensive measurements of mono- to deca- BDEs emitted from a U.S. MWC plant. The frequency of sampling, with flue gases collected after the combustion chamber for 5 min every 20 min, allowed measurements of PBDEs in a time scale relevant to operational transients. This work provides information on the destruction and transformation of PBDEs not only during normal MWC operation (steady state), but also during disrupted combustion (shut-down, start-up). This study also provides the first data on the efficiency of a spray dryer absorber/fabric filter (SDA/FF) air pollution control system (APCS) for PBDE removal. Moreover, it gives information on differences of PBDE congener and homologue distribution between raw and cleaned flue gas from combustion of the U.S. municipal solid waste. This study also aims to propose an initial estimate of the PBDE atmospheric emissions from thermal treatment of MSW in the U.S., with connection to atmospheric profiles of PBDEs reported for North America.

## 2. Materials and methods

## 2.1. Sampling

Field sampling was performed in December 2006 at a U.S. municipal waste combustor burning approximately 400 tons of refuse derived fuel (RDF) daily in a grate furnace technology. Sampling was performed during various stages of normal ("steady state") and transient ("shutdown" and "startup") boiler operation. The shutdowns and startups of the boiler were scheduled at the request of the sampling team. Around 70 samples of raw flue gases were taken isokinetically according to a modified version of U.S. EPA Method 23 (M-23) prior to the APCS using "short" (5 min) and "long" (>1 h) sampling durations. Samples of the clean stack flue gases were collected in time regimens corresponding to the total "long" sampling length of the raw flue gases (stack emissions during monitored shutdowns and subsequent startups were sampled jointly, and are together referred as post-APCS transient samples). The M-23 sampling protocol (U.S. EPA, 1996), routinely used for determination of PCDD/F from municipal waste combustors, was modified for simultaneous analysis of bromoorganics by addition of <sup>13</sup>C<sub>12</sub>-labeled PBDEs and PBDDs/Fs pre-sampling spikes and by measures to avoid photodegradation and debromination due to ultraviolet light exposure (Wyrzykowska et al., 2009). Terms: "exit of the boiler flue gas", "raw flue gas" and "pre-APCS flue gas", are used synonymously. Similarly - "stack flue gas", "clean flue gas" and "post-APCS flue gas", are also used interchangeably.

## 2.2. Analysis/QAQC

Extraction of train samples was performed by means of sequential Soxhlet extraction with methylene chloride (3.5 h) with restricted exposure to light (Wyrzykowska et al., 2009), followed by 16 h extraction with toluene to ensure removal of other target organics (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 PBDEs were determined by high resolution gas chromatography-high resolution mass spectrometry (HRGC/ HRMS). Details on the complete analytical procedure used in this study including volumes and concentrations of elution solvents and HRGC-HRMS analysis parameters are published elsewhere (Wyrzykowska et al., 2009). The recovery rates were 77.7% ( $\pm 11.7\%$ SD) for di- through deca- <sup>13</sup>C<sub>12</sub>-labeled BDE internal standards (the mean recovery of mono-<sup>13</sup>C<sub>12</sub>-labeledBDE internal standard was below 10%; recoveries of mono-BDEs might be lower due to volatilization during solvent evaporation). Routine procedural blanks were performed and analyzed. Only seven PBDE congeners were detected in some of the procedural and field blanks in this study (TeBDE-47, PeBDE-99, PeBDE-100, NoBDE-206, NoBDE-207, NoBDE-208, and DcBDE-209); however, their concentration never exceeded their concentrations in the flue gas (total concentration of PBDEs detected in blanks was on average 2.8% of average total PBDEs detected) (Wyrzykowska et al., 2009). The field blank was not subtracted from the field samples. Reported values were recovery-compensated and non-detects were set to equal zero. The total PBDE concentration is a sum of 42 congeners (SI Table S-1); the concentrations of  $\sum$  PBDE in the flue gases are expressed in picograms or nanongrams per normalized dry standard cubic meter (pg dscm<sup>-1</sup> or ng dscm<sup>-1</sup>) – normalized metered volume of sample run at ambient temperature of 20 °C (293.15 K) and under

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Fig. 1. PBDE concentrations and homologue group pattern in the pre-APCS the post-APCS flue gas.

atmospheric pressure of 101.325 kPa (1 atm); the corresponding emissions are calculated in micrograms per minute ( $\mu g \min^{-1}$ ). Relative standard deviations (RSD%) are calculated for averages of consecutive sampling days.

## 3. Results and discussion

## 3.1. PBDE concentrations and patterns in the MWC flue

## gas - steady state versus transients

The mean concentrations of  $\Sigma$  PBDE in the raw pre-APCS flue gas were: 9.2 and 33 ng dscm<sup>-1</sup> for steady state and transients, respectively (Fig. 1). The mean  $\Sigma$  PBDE concentrations in the flue gases collected from the stack (post-APCS) were 0.13 and 1.7 ng dscm<sup>-1</sup> during the steady state and transients, respectively (Fig. 1).

Eight-fold differences in average day-to-day PBDE concentrations (RSD = 83%) (Table 1) were observed during steady state operations probably due to heterogeneity of the bromodiphenyl based flame retardants in the RDF feedstock. Even higher variation (RSD = 105%) in average PBDE concentrations was observed during the transients (shut-down and start-up raw flue gas data are presented separately in Table 1), perhaps due to additional differences in overfire air supply causing dissimilarities in oxygen supply and turbulent flow in the

boiler. Similarly, the average concentrations of PBDEs in the clean stack gas were more variable during the transients (RSD = 120%), than during steady state combustion (RSD = 39%).

Based on the PBDE congener profile, the occurrence of bromodiphenylethers in the raw flue gas appears to be related to common PBDE technical formulations used as flame retardants in the U.S. (concentrations of all individual 42 PBDE congeners analyzed in this study are given in Table S-1 and Fig. S-1 of Supplementary Data). The major PBDE isomers in the raw flue gas are those present in the decaBDE technical mix (with decabrominated diphenylether, DcBDE-209, being the most abundant and followed by three NoBDE congeners: -206, -207, and -208) and the penta- and octa- BDE technical formulations (TeBDE-47, PeBDE-99, PeBDE-100, HxBDE-153, HxBDE-154, HpBDE-183 and OcBDE-197) (Supplementary Data, Table S-1; Fig. S-1). The PBDE congeners found in the flue gas at highest concentration are presumably products of thermal desorption from waste treated with PBDE-based flame retardants. This hypothesis is supported by observation of certain congener patterns typical for technical bromodiphenylether mixtures (Supplementary Data, Fig. S-1). For example, the deca- and nona- homologue groups were dominated by one congener - DcBDE-209, which is characteristic of the DecaBDE technical product. The relative proportion of DecaBDE technical congeners was to some extent altered, though.

Table 1

Total PBDE ( $\Sigma$ 42 congeners of mono- through decaBDE) concentrations in the pre-APCS and post-APCS MWC flue gas (ng dscm<sup>-1</sup>) and emissions estimates ( $\mu$ g min<sup>-1</sup>).

	Pre-APCS*											
	Steady state			Shut down				Start up				
	Mean	Min	Max	n	Mean	Min	Max	n	Mean	Min	Max	n
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
	Post-APCS <sup>b</sup>											
	Steady state			Transients			Emissions					
	Mean	Min	Max	п	Mean	Min	Max	п	Mean	Min	Max	п
Day 1	0.092	0.079	0.104	2	0.262	0.262	0.262	1	0.373 <sup>s</sup>	0.241	0.541	3
Day 2	0.162	0.162	0.162	1	3.189	3.189	3.189	1	4.845 <sup>t</sup>	0.799	8.891	2

n – number of samples; s average of steady state for both sampling day (Day 1 and 2), t average of transients for both sampling days (day 1 and 2).

<sup>a</sup> M-23 samples taken from the boiler for 5 min in 20 min intervals.

 $^{\rm b}$  M-23 samples taken from the stack for >1 h.

For example BDE-208 which is reportedly a minor  $(0.06\% \sim 0.07\%)$  (La Guardia et al., 2006) component of DecaBDE formulation, in our study comprised on average 3.2% and 3.3% of the seven DecaBDE-related congeners (4 and 2.4% of the total PBDE detected) in the raw and clean flue gases, respectively. Interestingly, similar phenomenon was reported in other combustion emissions, including those that have no technical PBDE mixture in the fuel (Wang et al., 2010b). Wang et al. (2010b) reported that BDE-208 emissions from the exhaust of vehicles were  $2\% \sim 3\%$  of the total PBDEs, and has suggested that highly brominated congeners may be preferentially formed during combustion processes (Wang et al., 2010a).

The tetra- and pentabromodiphenylether homologue pattern had tetraBDEs and pentaBDEs in approximately equal amounts, with TeBDE-47 and PeBDE-99 being the most abundant congeners, which is the typical fingerprint of the PentaBDE technical product (SI Table S-1; Fig. S-1) (La Guardia et al., 2006). In the transient operation samples, congeners that are minor or not present in the technical mixtures (e.g., DiBDE-15, TriBDE-17, TriBDE-28, TeBDE-49) were more abundant than during steady state conditions (Supplementary Data Table S-1; Figs. S-1 and S-2). The higher contribution of lower brominated congeners during the transients suggests that debromination likely occurs at some point of during disturbed combustion. Thermal debromination of highly brominated PBDEs leading to the formation of lower brominated diphenyl ethers has not been studied under laboratory conditions (Weber and Kuch, 2003). However, there are reports suggesting that debromination reactions are generally observed during thermal degradation of polybrominated aromatics above 500 °C (Weber and Kuch, 2003). Touati et al. (2004) showed that, for PCDDs/Fs in the combustion flue gas, the concentrations of lowly chlorinated congeners (mono- and di-) seem to be governed by gas temperature. PCDDs/Fs with a higher degree of chlorination (greater than two) were suggested to be products of a constant formation mechanism, as indicated by invariant isomer profiles (Touati et al., 2004). In our study profiles of di- to tri- BDEs seem to be dependent on combustion temperature and are different between steady state and transients. The profiles of PBDE congeners with more than four bromine atoms however, are very similar for transients and steady state and seem to be mainly products of thermal desorption (Supplementary Data Fig. S-2; Table S-1). Fig. S-2 of Supplementary Data shows debromination products in the stack flue gas during the transients with specific enrichment of diand tri- brominated homologues when compared to steady state profile.

In addition to observance of di- and tri- brominated congeners originating most likely from debromination, several higher brominated PBDE congeners that were not likely of technical bromodiphenyl mixture origin were detected in a number of steady state and transient samples (Supplementary Data Table S-1). These "non-technical" congeners include those substituted in non-, mono- and di-ortho positions (TeBDE-77, PeBDE-126, HxBDE-156, HpBDE-169, and HpBDE-180) (Supplementary Data Table S-1). Interestingly only one of the non-ortho congeners (PeBDE-126) was so far reported as a minor component (together with HxBDE-155 < 1% w/w) of technical PentaBDE mixtures (Bromkal 70-5 DE and DE-71) (La Guardia et al., 2006). The TeBDE-77 (3,3',4,4'-TeBDE), PeBDE-126 (3,3',4,4',5-PeBDE), HxBDE-156 (2,3,3',4,4',5-HxBDE), HpBDE-169 (3,3',4,4',5,5'-HxBDE), and HpBDE-180 (2,2',3,4,4',5,5'-HpBDE), are brominated counterparts of dioxin-like PCBs, and thus structurally resemble PCDDs/Fs. Therefore it is possible that "dioxin-like PBDEs" can be a product of the dimerisation or condensation of brominated precursors, like polybrominated benzenes (PBBz), or less likely phenols (PBPhs), present in the flue gas. The generation of both PBPhs and PBBz has been reported during thermal degradation and incineration of the common flame retardant tetrabromobisphenol A (TBBPA) (Weber and Kuch, 2003). Rupp and Metzger (2005) reported formation of polybrominated benzenes and phenols, along with polybrominated dibenzofurans and dibenzodioxins (PBDFs, PBDDs), and brominated-chlorinated benzenes, from TeBDE-47 and HxBDE-153 exposed to low temperatures between 250 °C and 500 °C (Rupp and Metzger, 2005). The enhanced precursor-based formation of PCDD/F congeners of certain chlorination patterns (1,3,6,8- and 1,3,7,9-TeCDD, 1,2,4,6,8-PeCDD) has been reported as indicative of transient combustion conditions (Aurell and Marklund, 2009). In our study higher concentrations of PBDEs that lack two or more Br atoms in the ortho- position seem to be more typical for transients than for the steady state (Fig. S-3 of Supplementary Data). Fig. S-3 of Supplementary Data shows changes in the relative contribution of PBDE congeners that most likely originate from thermal desorption from PBDE flame retardants present in the MSW (referred to as "technical BDEs"), congeners that are not present/ minor in commercial BDE formulations ("other BDEs"), and analyzed non-, mono-, di- *ortho* PBDEs ("coplanar PBDEs") in the total BDE (" $\Sigma$ BDE") detected in the raw and clean flue gas during different operating conditions of the MWC. Fig. S-4 of Supplementary Data shows dynamic changes of technical and non-technical PBDEs in the total mass of PBDEs detected during the first day of sampling plotted against oxygen levels as an indicator of the boiler shut-down and startup periods.

# 3.2. Efficiency of SDA/FF air pollution control system for PBDE removal

The SDA/FF (sprav drver absorber/fabric filters) APCS had a significant effect on reduction of  $\Sigma$  PBDE emissions from the stack. The removal efficiency varied somewhat between the sampling days (from 96.3% to 99.6%), with an average reduction of 98.6%. Efficiencies of SDA/FF APCS for PBDE removal were determined based on the pre- and post-APCS "long sampling duration" data; flue gases were collected in the same time regimens; Supplementary Data Table S-2. The PBDE homologue patterns in the clean post-APCS gas (Fig. 1) show that the average proportion of higher brominated homologues decreased in the stack versus the raw (pre-APCS) flue gas during the transients. It is probably due to fact that higher-brominated PBDE congeners, especially DcBDE-209, are more likely to condense and bind to particulate matter aiding their capture on fabric filters (Shoeib et al., 2004). In addition, gas phase lower-brominated PBDE analogues are preferentially released to the atmosphere. The average proportion of DcBDE-209 in  $\Sigma$  PBDE detected in the raw flue gas seems to have a slight effect on removal rates. On the first sampling day (day 1) DcBDE-209 contributed 70.5% to all congeners detected in the raw flue gas, while on the second day (day 2) only 55.3% (by mass). The PBDE removal efficiency by the APCS was, on average, 99.6% and 97.5% for those two days, respectively. These results seem to suggest that dust collectors are effective in reducing PBDE air emissions from MWC.

## 3.3. The levels and congener pattern of PBDE releases from MWC

The data on air emissions of PBDEs from full-scale MWCs are scarce and rarely discussed as potential source of PBDEs in atmosphere. In our study we calculated average stack emissions for steady state as  $0.37 \ \mu g \ min^{-1}$  (RSD = 41%). Average emissions of 4.84  $\ \mu g \ min^{-1}$  observed for transients were almost 15-fold higher, but characterized by larger variation (RSD = 120%). The investigated plant has frequent, atypical shutdowns triggered primarily by CO excursions. The average daily ratio of steady state combustion to disturbed combustion in the investigated plant was estimated as ~23 h (1370 min) to ~1 h (70 min) per day (Supplemetary Data,

Appendix). Based on the steady state PBDE emission value per amount of waste burned per day, the emissions of PBDEs from MWC plants in the U.S. are 150 kg/year (based on 12.5% of total municipal waste combusted in the U.S. in 2006 with 99% PBDE removal efficiency; see Appendix of Supplementary Data for details). This annual PBDE emission rate would increase to 240 kg/ vear if these transient operation were relevant to all U.S. MWCs. These emission estimates are subject to large uncertainty concerning the assumed differences of APCS efficiencies for PBDE removal, number and duration of transients, and waste composition. A most significant limitation of our emission estimate is the complete lack of measurement data from other plants, as MWCs are not tested for PBDEs. Nonetheless, data from this one plant demonstrate PBDE releases to the air and the impact of ignoring transient operation modes (such as start-ups and shut-downs) on emission estimates.

Unfortunately, our estimate is hard to compare to other estimates of source-specific PBDE atmospheric emissions in the U.S, as literature data are very limited. One option is to compare our estimate to vapor pressure (Vp) based estimates of evaporative PBDE emissions from products in service. A Vp approach was previously described by Prevedouros et al. (2004) as suitable to estimate solid to gas-phase PBDE releases from flame retarded solid matrices, under ambient temperature, and is described by following equation (Prevedouros et al., 2004):

emissions by volatilization per year (%) =  $1.1 \times 10^6 \times V_p^*$ 

<sup>\*</sup>*Vp* = (*mmHg at 20* °*C*);  $3.52 \times 10^{-7}$  for pentaBDE mix,  $4.94 \times 10^{-8}$  for octaBDE mix,  $3.47 \times 10^{-8}$  for decaBDE mix (Environment Canada, 2004).

Using the 2001 North American data on market demand for PBDE commercial formulation (7100, 1500, 24500 tons of penta-, octa-, and decaBDE products, respectively) (Birnbaum and Staskal,

2004), outgassing of a mass of technical PBDEs equivalent to one year of production (assuming 100% domestic consumption with no import) would result in the evaporative emissions of almost 3800 kg of technical bromodiphenylether from flame retarded products, with PentaBDE accounting for 73% of the cumulative Vp based emissions in North America. The recent work of Batterman et al. (2009) on aggregate emissions rates from U.S. houses and garages estimated collective release of about 4100 kg of PBDEs per year, of which around 20% (722 kg  $y^{-1}$ ) would be airborne emissions (Batterman et al., 2009). The MWC PBDE releases, based on steady state measurements made in our study would be 3.9% and 21% of these two evaporative emissions estimates (or 7.1% and 33% using the transient profile data). Our estimate is especially important if we consider the fact that combustion with energy recovery has remained very stable in U.S. for the past fifteen years (1990 – 14.5%; 2000 - 14.2%; 2005 - 13.6%; 2006 - 12.5%) (U.S. EPA, 2006, 2003). Therefore our per annum estimates might be applicable for past atmospheric emissions from MWCs. Interestingly, the profile of bromodiphenylethers in the raw flue gas still reflects late 1990's Northern American production pattern (see Fig. 2 and discussion of technical PBDE profile in the raw flue gas with connection to historical production patterns in the latter section of this section.

This study is the first comprehensive data on PBDE emissions from a U.S. MWC. It reports levels of 42 PBDE congeners; therefore it is not valid to compare the cumulative  $\sum$  PBDE emission estimate with scarce literature data, which usually report only few PBDE congeners. Thus, the congener which is abundant in the stack flue gases in this study, and is often used to deliver emission factors from fugacity models, and moreover routinely reported in the U.S. atmosphere, *i.e.* TeBDE-47 (Venier and Hites, 2008; Gouin et al., 2005; Hoh and Hites, 2004; Alcock et al., 2003; Gouin and Harner, 2003; Hale et al., 2003; Gouin et al., 2002; Strandberg et al., 2001), was selected to compare present study results with other emission estimates available. The TeBDE-



Fig. 2. Profile of selected PBDE congeners abundant in the pre-APCS and post-APCS flue gases of investigated MWC, compared to PBDE commercial formulations usage in the U.S. and Europe, and pattern of those congeners in selected environmental matrices; from references: Agrell et al. (2004), Allen et al. (2007), Birnbaum and Staskal (2004), de Witt (2002), Schecter et al. (2006), Strandberg et al. (2001), Su et al. (2007), Wurl et al. (2006).

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47 MWC emissions in our study are in line with recent calculations of PBDE releases from controlled incineration of waste in North America (Alcock et al., 2003). Alcock and coworkers (2003) assumed that 0.01% of PBDE-based flame retardants entering the system will be emitted, and estimated that in 1999 controlled incineration of North American household waste resulted in atmospheric emissions of 35 kg of TeBDE-47 (Alcock et al., 2003). In our estimate 51 kg per year (99% clean-up scenario; transient concentrations included) of TeBDE-47 is released to atmosphere from MWCs. The estimated PBDE atmospheric emissions, both from this study and based on theoretical releases from controlled incineration, are calculated as emissions per year, and do not reflect actual cumulative releases of PBDEs from combustion sources over past decades, therefore are not sufficient to draw definite conclusions on importance of combustion sources versus production and products-in-service sources.

Fig. 2 presents the congener pattern of selected common technical PBDE congeners (TeBDE-47, PeBDE-99, PeBDE-100, HxBDE-153 and DcBDE-209) in our flue gas samples compared to that of the PBDE product usage in North America. According to Birnbaum and Staskal (2004) in 2001 North America consumed almost 50% of the world's total market demand of PBDEs, with the DecaBDE product used most commonly, followed by PentaBDE (importantly, 95% of the world's production of this formulation was consumed in North America). The OctaBDE remained a minor product in the U.S. and worldwide (Birnbaum and Staskal, 2004). Considering the composition of MSW in the U.S and the most common applications of PBDE formulations in U.S. (PentaBDE – polyurethane foams; OctaBDE and DecaBDE – electronics and high impact polystyrene). input waste of investigated municipal waste incinerator should mainly contain congeners typical for DecaBDE and PentaBDE product. Indeed, the profile of TeBDE-47, PeBDE-99, PeBDE-100, Hx-BDE-153 and DcBDE-209 observed in the raw pre-APCS flue gas in this study is very similar to the historical American usage pattern with DcBDE-209 being the most abundant congener, followed by congeners of the PentaBDE product, i.e., tetra-bromo isomer BDE-47 and penta- isomers BDE-99 and BDE-100, and smaller amounts of the hexa- isomer BDE-153 (Fig. S-1). In contrast, the MWC raw flue gas profile from this study is completely different from the European technical PBDE usage pattern (Fig. 2). The resemblance between the North American PBDE usage pattern and pre-APCS gas profiles is especially striking for transient conditions. This might be due to the fact that the incomplete combustion of RDF input material most likely occurs during the start-up and shut-down transients, when the pattern of "technical PBDEs" in the raw flue gas results in the least alteration of the input waste by combustion.

The PBDE concentrations reported in the stack (range 100–3200 pg dscm<sup>-1</sup>, SI Table S-1) are up to three orders of magnitude higher that concentrations reported for the U.S. ambient air samples, which tend to be in the range of few pg per cubic meter to 100s pg per cubic meter (Supplementary Data, Table S-3). The PBDE profiles in the clean stack gas (post-APCS) closely mirrors patterns of TeBDE-47, PeBDE-99, PeBDE-100, HxBDE-153 and DcBDE-209 reported for North American air (Fig. 2). In the average stack profiles observed in the present study, DcBDE-209 is more abundant than in the air collected from two sites from Great Lakes region (Strandberg et al., 2001), which suggests that DcBDE-209 released from stationary sources, is less likely transported in the atmosphere than lighter congeners (Fig. 2). On the other hand, the profiles reported for indoor personal air and food are enriched with DcBDE-209 if compared to stack emissions from this study, suggesting a stronger impact of "near-product" evaporative sources for indoor air PBDE concentrations (Fig. 2; Table S-3 of Supplementary Data presents comparison of total PBDE, TeBDE-47 and DcBDE-209 concentrations in the present study with their levels in the ambient and "near-product" air samples). The atmospheric patterns of TeBDE-47, PeBDE-99, PeBDE-100, HxBDE-153, and DcBDE-209 in air from remote areas of the globe are very similar to the post-APCS flue gas pattern from this study (Fig. 2). The presence of PBDEs in the remote areas of the globe agrees with the Stockholm convention's candidature of commercial PBDEs as suitable for long range transport (Stockholm Convention, 2008), and – naturally – should be considered as a result of various airborne PBDE emissions from a range of global sources.

## 4. Conclusions

The results of this study demonstrate that PBDE emissions during non-optimal, transient combustion conditions are significantly higher than during steady state operations. Emissions during transients have both higher concentrations and altered patterns in the raw and stack flue gases. The results of this study also show that dry scrubber/baghouse air pollution control systems which reduce emissions of polychlorinated dioxins and furans (PCDDs/Fs) are very effective in reducing emissions of PBDEs from MWCs. Nevertheless, thermal treatment of waste containing flame retarded products is a source of PBDEs to North American air. Since environmental releases of PBDEs from manufacturing and primary uses depend strongly on actual production rates, the importance of "product-use" emissions to air will likely decrease over the years, while secondary sources (such as combustion) will probably remain a non-negligible source of PBDEs in the U.S. for years to come.

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## Appendix. Supplementary data

The congener-specific concentrations of PBDEs in the pre-APCS and post-APCS flue gas, stack emissions with efficiency of APCS, average contribution (%) of "technical PBDEs", PBDE congeners which are not present or minor in commercial BDE formulations ("other BDE") and coplanar PBDEs in the raw pre-APCS flue gas and stack post-APCS gas depending on operating condition of MWC, detailed calculations of the PBDE emissions from MWCs in the U.S., and a short literature review of the atmospheric concentrations of PBDEs is available free of charge via the Internet at doi:10.1016/j. atmosenv.2011.04.052.

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