

Reviewer comments/suggestions are in *italics* font and our responses are underlined:

Anonymous Referee #2

Overall, this paper reports some useful new data on concentrations of PBDEs in outdoor atmospheric particles. The principal strength of the paper is its provision of data on the particle size distribution of PBDE concentrations. To my knowledge, data on this issue are scarce. A weakness is its focus on the human exposure implications of this. Given the minor role of outdoor air inhalation as a human exposure pathway, I believe the authors should have focused more on the implications of their data for global atmospheric fate and transport. I have a number of other observations.

1. The authors have made an attempt to place outdoor air inhalation exposure in context with other exposure pathways. They do however, fail to identify contact with indoor dust (either through ingestion - e.g. via hand-to-mouth contact - or dermal contact with dust) as being for many individuals and especially young children, the principal exposure pathway.

R: Although we agree with the reviewer, we also realize that what is being suggested will likely take us several years and that is what we are doing. However, the data published in this article is the first of its kind and should help others in assessing the particle size distribution of PBDEs and evaluating the outdoor air inhalation exposure. In view of this situation, we consider any such more quantitative evaluation (either through ingestion - e.g. via hand-to-mouth contact - or dermal contact with dust) is beyond the scope of the present manuscript.

2. The evaluation for the health risk of the exposure assessment should be made against the USEPA's reference doses for PBDEs (e.g. BDE-47, -99, and -100 etc.).

R: In this manuscript, the oral reference doses ($\text{pg kg}^{-1} \text{bw d}^{-1}$) of BDE-47, -99, -153 suggested by USEPA IRIS (www.epa.gov/iris) were 1.0×10^5 , 1.0×10^5 and 2.0×10^5 , respectively. RfD of other tetra-BDE, penta-BDE and hexa-BDE were assumed equivalent reference dose of BDEs congeners with the same bromine atoms. In addition, RfD of tri-BDE and hepta-BDE were assumed to be the same as BDE-47 and BDE-153, respectively. We added this data in new Table 1.

Table 1. Physiochemical properties, *RfD* of the target PBDE congeners and data from Yang et al (2013).

Chemical	Molecule	MW ^a	<i>RfD</i> ^f	$\log p_L^o/p_a$ ^b	$\log K_{OA}$ ^c	Gas phase ^e (pg m ⁻³)	Particulate phase ^e (pg m ⁻³)
BDE-17	2,2',4-tribromodiphenyl ether	406.9	1.0×10 ⁵	-2.71 ^d	9.31	15.64	0.93
BDE-28	2,4,4'-tribromodiphenyl ether	406.9	1.0×10 ⁵	-2.95	9.4	30.04	1.17
BDE-71	2, 3', 4', 6-tetrabromodiphenyl ether	485.8	1.0×10 ⁵	-3.55 ^d	10.2		
BDE-47	2,2',4,4'-tetrabromodiphenyl ether	485.8	1.0×10 ⁵	-4.07	10.1	28.81	5.38
BDE-66	2,3',4,4'-tetrabromodiphenyl ether	485.8	1.0×10 ⁵	-4.27	10.25	6.11	0.38
BDE-100	2,2',4,4',6-pentabromodiphenyl ether	564.7	1.0×10 ⁵	-4.91	10.82	3.38	1.52
BDE-99	2,2',4,4',5-pentabromodiphenyl ether	564.7	1.0×10 ⁵	-5.14	10.96	8.02	5.06
BDE-85	2,2',3,4,4'-pentabromodiphenyl ether	564.7	1.0×10 ⁵	-5.40	11.03	2.58	2.42
BDE-154	2,2',4,4',5,6'-hexabromodiphenyl ether	643.6	2.0×10 ⁵	-5.83	11.66	1.37	2.10
BDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether	643.6	2.0×10 ⁵	-6.08	11.77	1.27	2.39
BDE-138	2,2',3,4,4',5'-hexabromodiphenyl ether	643.6	2.0×10 ⁵	-6.23	11.81	1.09	2.21
BDE-183	2,2',3,4,4',5',6-heptabromodiphenyl ether	722.5	2.0×10 ⁵	-6.75	12.52	1.67	10.01
BDE-190	2,3,3',4,4',5,6-heptabromodiphenyl ether	722.5	2.0×10 ⁵	-7.00	12.71		

^a Molecular weight

^b Subcooled liquid vapor pressure in 292K from Tittlemier et al.(2002)

^c Octanol-air partition coefficient in 292K from Harner and Shoeib.(1998)

^d data from Wang et al.(2008)

^e data from Yang et al. (2013)

^f Oral reference dose (pg kg⁻¹ bw d⁻¹) of BDE-47,-99,-153 were suggested by USEPA IRIS (www.epa.gov/iris) and *RfD* of other tetra-, penta-, hexa-BDE congeners were assumed equivalent reference dose of BDEs congeners with the same bromine atoms. In addition, *RfD* of tri-BDE and hepta-BDE were assumed to be the same as that of BDE-47 and BDE-153, respectively.

3. The theoretical considerations of gas-particle partitioning are fine, but no measurements were made of PBDEs in the gas phase. The authors use instead previously published data from another site. While the authors attempt to highlight the "match" between the two data sets, the absence of spatially and temporal consistent measurements of gas and particle phase concentrations is a weakness.

R: We agree with the reviewer's suggestion, but we were unable to find any reference in Shanghai area associated with gas phase PBDEs' data, except for the current used one.

4. It appears that no sampling efficiency standards (i.e. those that assess any PBDE losses during sampling), were added to the filters BEFORE sampling and monitored at the end. It is usual to add at least 1 such standard.

R: The compounds ¹³C-BDE-28, 47, 99 and 153 were used as internal standards in this investigation. Please see this description in experimental section (line 21-27, page 6).

Method recoveries determined by spiking the sampling process (five replicates) with a standard mixture of PBDEs ranged from 75 to 175%. In addition, isotopically-labelled PBDEs was added as internal standard (added after extraction and clean-up, just prior to GC-MS analysis) to check for instrument performance. Recoveries were between 90 and 110%. As a further quality control step, SRM 2585 (NIST, Gaithersburg, MD, USA) was used as the reference material in this study. Measured PBDE levels in SRM 2585 ranged from 75 to 120% of certified values. Repeatability was evaluated by performing four analyses of a standard PBDEs solution containing the above mentioned PBDEs and the surrogate standards in the same conditions. The relative standard deviations (RSD) of the relative response factors were below the 10% for all PBDEs.

5. Internal standards were added post-extraction and clean-up. They should be added BEFORE extraction.

R: Yes, the internal standards were used for two times in this study, i.e., BEFORE extraction and BEFORE instrumental analysis.

The PBDE-spiked in the sampling process was used to examine the recovery of the analytical methods for the measurements of PBDE concentrations, and the recoveries were generally in the range of 75 to 175% depending on individual congeners.

In addition, isotopically-labelled PBDEs were added as internal standard (added after extraction and clean-up, just prior to GC-MS analysis) to check for instrument performance. Recoveries were between 90 and 110%.

6. The authors do not provide data about their measurements of PBDEs in SRM2585. How did the concentrations they measure compare to the certified/indicative values reported by NIST for this SRM? This is an important measure for the accuracy of the data reported.

R: Since NIST SRM 2585 is a standard reference house dust materials, it is the most appropriate one comparing with urban atmospheric PBDEs studied here, although there is also a little deviation. Thus, we did a simple comparison with the certified/indicative values reported by NIST for this SRM. Measured PBDE levels in SRM 2585 ranged from 75 to 120% of certified values.