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Levels of methoxylated polybrominated diphenyl ethers and polybrominated diphenyl ethers in hen eggs from China

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ABSTRACT

PBDEs are widely used brominated flame retardant, which are increasingly reported in the environment. MeO-PBDEs are structural analogs to PBDEs, and reported as natural products and novel pollutants present in the environment. Concentrations of thirteen PBDEs and eight MeO-PBDEs in a large number of commercial sales of hen eggs representing 15 different regions and household productions of hen eggs representing 2 different regions collected from Hubei province of China were investigated in this study. An effective isotopic dilution GC–MS method was firstly developed to simultaneously determine thirteen PBDEs and eight MeO-PBDEs in hen eggs in this study. Liquid/liquid extraction, concentrated sulfuric acid and multi-layer silica gel column chromatography cleanup were used, some important steps and crucial parameters were modified and intensified compared with other literatures, and GC and MS conditions were optimized. The limits of quantitation values of 0.2–4, 0.8–4 μg kg^{-1} wet weight in hen eggs were calculated for PBDEs and MeO-PBDEs, respectively. In addition, good repeatability and accuracy of the whole method were achieved. The established methods were therefore suitable for the simultaneous determinations of thirteen PBDEs and eight MeO-PBDEs in hen eggs at trace contamination levels. Using the established methods, PBDEs or MeO-PBDEs emerged in 4 of 40 household productions of hen eggs, and in low-μg kg^{-1} wet weight for these samples.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are one class of halogenated organic brominated flame retardants (BFRs), and have been used industrially in large volumes for flame protection purposes in various commercial products such as electronic equipment and textiles. The commercial PBDEs products predominantly consist of so-called penta-, octa- and decabromodiphenyl ether products. They have been widely distributed in the air, dust, fish and human milk due to their physical, chemical and bio-accumulative characteristics, such as environmental persistence and high lipophilicity [1–8].

Methoxylated polybrominated diphenyl ethers (MeO-PBDEs) are structural analogs to PBDEs, which have been considered synthetic anthropogenic compounds and reported as natural products and novel pollutants present in the marine environment and fish [9–16]. It is very interesting that MeO-PBDEs were found in eggs of white-tailed sea eagles breeding in different regions of Sweden [17].

Following concerns about contamination status of PBDEs and MeO-PBDEs in the environment, the rising attentions were led about the possible adverse health effects to humans. Toxicity studies indicate that the liver, thyroid gland and possibly developmental reproductive organs are particular targets of PBDEs toxicity [18,19]. More and more evidences are emerging that PBDEs show a certain toxicity in vitro and vivo [20–27]. Our study indicates PBDE-209 and PBDE-47 can inhibit the proliferation of Hep G2 cells by inducing apoptosis through ROS or NO generation [28,29]. A few researches about toxicity of MeO-PBDEs indicate the kind of compounds have effects on steroidogenic genes, aromatase activity and steroid hormones in vitro and may have the potential to affect steroidogenesis and reproduction in whole organisms [30,31]. To satisfy the requirements of further accurate risk assessments for these chemicals, especially MeO-PBDEs, it is expected that the trend in generating MeO-PBDEs and PBDEs data will be encouraged to grow in environmental and biotic samples, especially in farm and aquaculture products.

The Hubei province of China has an old farm and aquaculture production tradition. Especially there are a plenty of hen eggs from Hubei exported to other countries. These productions are favorite food for people and their safety has been highly concerned by our previous papers [32,33]. To our knowledge, there is little

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Table 1
The information and the ions monitored of thirteen PBDEs, eight MeO-PBDEs, MBDE-MXFS and MBDE-MXFR.

Br No.	Abbreviation	Molar mass	Precursor ions, $[M]^+$ and $[M+2]^+$, or $[M-2]^+$ (m/z)	Product ions, $[M-2Br]^+$ and $[(M+2)-2Br]^+$, or $[(M-2)-2Br]^+$ (m/z)	The ions monitored (m/z)	No. of MS scan functions
PBDEs						
3	BDE17	407	406, $[M+2]^+$	246, 248	406, 408, <u>246</u>, 248	2
3	BDE28	407	406, $[M+2]^+$	246, 248	406, 408, <u>246</u>, 248	4
4	BDE71	486	486, $[M-2]^+$	326, 328	484, 486, <u>326</u>, 328	5
4	BDE47	486	486, $[M-2]^+$	326, 328	484, 486, <u>326</u>, 328	6
4	BDE66	486	486, $[M-2]^+$	326, 328	484, 486, <u>326</u>, 328	8
5	BDE100	565	564, $[M+2]^+$	404, 406	564, 566, <u>404</u>, 406	13
5	BDE99	565	564, $[M+2]^+$	404, 406	564, 566, <u>404</u>, 406	17
5	BDE85	565	564, $[M+2]^+$	404, 406	564, 566, <u>404</u>, 406	20
6	BDE154	644	644, $[M-2]^+$	484, 486	642, 644, <u>484</u>,486	22
6	BDE153	644	644, $[M-2]^+$	484, 486	642, 644, <u>484</u>, 486	26
6	BDE138	644	644, $[M-2]^+$	484, 486	642, 644, <u>484</u>, 486	28
7	BDE183	723	722, $[M+2]^+$	562, 564	722, 724, 562, <u>564</u>	30
7	BDE190	723	722, $[M+2]^+$	562, 564	722, 724, 562, <u>564</u>	31
MeO-PBDEs						
4	2′-MeO-BDE68	516	516, $[M-2]^+$	420*, 422*	514, 516, <u>420</u>, 422	9
4	6-MeO-BDE47	516	516, $[M-2]^+$	356, 420*, 422*	514, <u>516</u>, 420, 422, 356	11
4	5-MeO-BDE47	516	516, $[M-2]^+$	356, 358	514, 516, <u>356</u>, 358	14
4	4′-MeO-BDE49	516	516, $[M-2]^+$	356, 358	514, <u>516</u>, 356, 358	15
5	5′-MeO-BDE100	595	596, $[M-2]^+$	434, 436	594, 596, <u>434</u>, 436	18
5	4′-MeO-BDE103	595	596, $[M-2]^+$	434, 436	<u>594</u>, 596, 434, 436	19
5	5′-MeO-BDE99	595	596, $[M-2]^+$	434, 436	594, 596, 434, <u>436</u>	23
5	4′-MeO-BDE101	595	596, $[M-2]^+$	434, 436	<u>594</u>, 596, 434, 436	24
MBDE-MXFS						
3	$^{13}C_{12}$-BDE-28	419	418, $[M+2]^+$	258, 260	418, 420, <u>258</u>, 260	3
4	$^{13}C_{12}$-BDE-47	500	498, $[M+2]^+$	338, 340	498, 500, <u>338</u>, 340	7
5	$^{13}C_{12}$-BDE-100	577	576, $[M+2]^+$	416, 418	576, 578, <u>416</u>, 418	12
5	$^{13}C_{12}$-BDE-99	577	576, $[M+2]^+$	416, 418	576, 578, <u>416</u>, 418	16
6	$^{13}C_{12}$-BDE-154	656	656, $[M-2]^+$	494, 496	654, 656, <u>496</u>, 498	21
6	$^{13}C_{12}$-BDE-153	656	656, $[M+2]^+$	494, 496	656, 658, 494, <u>496</u>	25
7	$^{13}C_{12}$-BDE-183	735	734, $[M+2]^+$	574, 576	734, 736, <u>574</u>, 576	29
MBDE-MXFR						
4	$^{13}C_{12}$-BDE-77	500	498, $[M+2]^+$	338, 340	<u>498</u>, 500, 336, 338	10
6	$^{13}C_{12}$-BDE-138	656	656, $[M+2]^+$	494, 496	656, 658, <u>496</u>, 498	27

The ion of underline was indicated for quantitative analysis.
The symbol "*" indicates that the ion is the product ion, $[M-CH_3Br]^+$.

Table 2
Retention times (RT), start time and end time of retention window, number of MS scan functions, quantitation reference for MeO-PBDEs, PBDEs, MBDE-MXFS and MBDE-MXFR on Elite-5MS, and LOQ of MeO-PBDEs and PBDEs in hen eggs.

Br No.	Compounds	Quantitation reference	Retention times (RT)	Start time and end time of retention window	No. of MS scan functions	LOQ (μg kg^{-1} wet weight)
Compounds using $^{13}C_{12}$-BDE-77 as labeled injection internal standard						
3	BDE17	$^{13}C_{12}$-BDE-28	14.11	13.44–14.53	2	0.2
3	BDE28	$^{13}C_{12}$-BDE-28	14.92	14.24–15.40	4	0.2
4	BDE71	$^{13}C_{12}$-BDE-47	19.69	18.93–20.05	5	0.4
4	BDE47	$^{13}C_{12}$-BDE-47	20.37	19.66–20.87	6	0.4
4	BDE66	$^{13}C_{12}$-BDE-47	21.36	20.64–21.88	8	0.4
5	BDE100	$^{13}C_{12}$-BDE-100	25.06	24.27–25.55	13	0.8
5	BDE99	$^{13}C_{12}$-BDE-99	26.68	25.96–27.05	17	0.8
5	BDE85	$^{13}C_{12}$-BDE-99	29.35	28.61–29.88	20	0.8
Compounds using $^{13}C_{12}$-BDE-138 as labeled injection internal standard						
6	BDE154	$^{13}C_{12}$-BDE-154	30.76	29.86–31.06	22	0.8
6	BDE153	$^{13}C_{12}$-BDE-153	33.02	32.23–33.37	26	0.8
6	BDE138	$^{13}C_{12}$-BDE-153	35.81	35.02–36.20	28	2
7	BDE183	$^{13}C_{12}$-BDE-183	39.00	38.22–39.33	30	2
7	BDE190	$^{13}C_{12}$-BDE-183	42.19	41.46–42.57	31	4
Compounds using $^{13}C_{12}$-BDE-77 as labeled injection internal standard						
4	2′-MeO-BDE68	$^{13}C_{12}$-BDE-100	22.87	22.00–23.21	9	0.8
4	6-MeO-BDE47	$^{13}C_{12}$-BDE-100	23.66	22.81–24.12	11	0.8
4	5-MeO-BDE47	$^{13}C_{12}$-BDE-100	25.25	24.28–25.72	14	0.8
4	4′-MeO-BDE49	$^{13}C_{12}$-BDE-100	25.55	24.66–26.10	15	2