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Distribution of polybrominated diphenyl ethers (PBDEs) in sediment and food-web of mangrove ecosystem at Pichavaram, Tamil Nadu, India

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Abstract: The contaminations of polychlorinated diphenyl ethers (PBDEs) in under water sediment and food-web samples collected from Pichavaram mangrove ecosystem have been investigated. To evaluate the distribution of PBDEs, fifteen under water sediment samples and fifteen food-web samples have been collected from fifteen different sampling sites. Gas chromatography–Mass spectrometry (GC-MS) technique was used to quantify and qualify the PBDEs. Ten PBDE congeners including BDE-17, 28, 71, 47, 100, 99, 154, 153, 138 and 183, Σ PBDEs (sum of ten BDE congener in sediment and food-web) ranged from 5.70 to 24.59 pg g^{-1} (dw) in underwater sediment whereas 1.36 to 9.66 pg g^{-1} in food-web samples have been identified in the present study area. Among the congeners of PBDE, BDE- 47 was identified with major quantity in entire sediment and food-web samples.
Key words: PBDEs, GC-MS, Mangrove forest, Pichavaram.

Introduction

Polybrominated diphenyl ethers (PBDEs) are anthropogenic chemicals that have been extensively used as flame-retardants. The compounds are incorporated into many types of polymers used in electric circuit boards, paints, textiles, foam, rubber and other casing materials. As a result, they can be found in many commercial and household products, such as computers, televisions, furniture and carpets[1]. They are of environmental concern due to their persistence, potential for bioaccumulation and widespread distribution via atmospheric transport, and possible adverse effects in wildlife and humans[2].

In Asia, deca-BDE is produced and used in large quantities although the use of penta-BDE was largely ceased in the mid-1990's[3]. PBDEs have been widely detected in air, water, fish, birds, marine mammals and humans in recent years. The levels of PBDE contamination have increased over the last 20-25 years in the environment, concomitant with a decrease of concentrations for other halogenated chemicals such as polychlorinated biphenyls[4]. PBDEs, due to their lipophilic, hydrophobic and relatively low

volatile characteristics, are often associated with soils and sediments, particularly coastal sediments. Many studies have reported the contamination of PBDEs in sediments around the world[5-7]. Mangroves are often under pollution stress and are sinks or receivers for various man-made pollutants[8]. The unique features of mangrove ecosystems, including high primary productivity, abundant detritus, rich organic carbon and anoxic /reduced conditions make them a preferential site for the uptake and preservation of persistent organic pollutants. PBDEs at relatively low concentrations in mangrove sediments were reported in Singapore[9], India[10] and Senegal[11]. A recent review on organic contaminants in mangrove ecosystems also concluded that PBDEs could not be detected in water (<80 pg L^{-1}) or sediment (< 1 pg g^{-1} dry weight) in Singapore mangroves, but were detected in sediments in India and in Senegal[12]. These studies indicated that the distribution and accumulation of PBDEs in mangrove ecosystems varied significantly among mangrove swamps and information on PBDE contamination is still rare.

Material and methods

Study site

Pichavaram is located 13 km northeast of Chidambaram, Cuddalore district, Tamil Nadu between latitude 11°29′ to 11°30′ north and longitude 70°45′ to 79°55′ east. It is an estuarine type of mangrove situated in the Vellar, Kollidam estuarine complex and has many islands separated by intricate water ways covering an area of over 2335.5 ha, of which only 24.1 ha is occupied by dense mangrove vegetation (Fig. 1). The area between the two rivers is identified as brackish water with mangrove vegetation. Fifteen different locations were selected for sediment sampling and fifteen different locations were selected for food web collections in Pichavaram mangrove forest area. Global positioning system (GPS) was used to locate the sampling sites.

Fig. 1. Sampling locations of Pichavaram mangrove forests

Sample collection

Sediment samples, collected from the entire sampling stations using stainless steel grab sampler were placed on ice and transported to the laboratory, then frozen and stored at –4 °C until further analysis. Fish samples, collected with the help of local fisherman were wrapped in aluminium foil and placed in polythene bags, tagged and frozen on wet ice. The information tag on the samples included species, size, date and locations of collection. The samples were kept in frozen condition until extraction.

Sample preparation and analysis

Soxhlet extraction method was followed for sediment and food web samples. The sediment was wet-sieved to separate the slit and clay fractions and subsequently air-dried and lightly ground in a mortar and pestle to break up the aggregates. Five grams of sediment was extracted with 20 g of anhydrous sodium sulfate for sixteen hours in a soxhlet apparatus with 200 mL of dioxine grade *n*-hexane acetone (1:1 v/v). Then the extracts were evaporated to dryness in a speed-vacuum concentrator. All the fractions were concentrated to a final volume of between 4 and 10 mL and were ready for analysis.

The removals of biological tissues were carried out under the supervision of an experimental biologist. Muscle samples should be collected from the left side of the fish, above the lateral line, and between the dorsal fin and caudal fin (Fig. 3) 10 g of tissue samples was extracted with 30 g of anhydrous sodium sulfate for sixteen hours in a soxhlet apparatus with 300 mL of dioxine grade *n*-hexane/acetone (1:1 v/v) for 16–18 h with 4–6 cycles h^{-1}.

Then the extracts were evaporated to dryness in a speed-vacuum concentrator. All the fractions were concentrated to a final volume of between 4 and 10 mL and were ready for analysis.

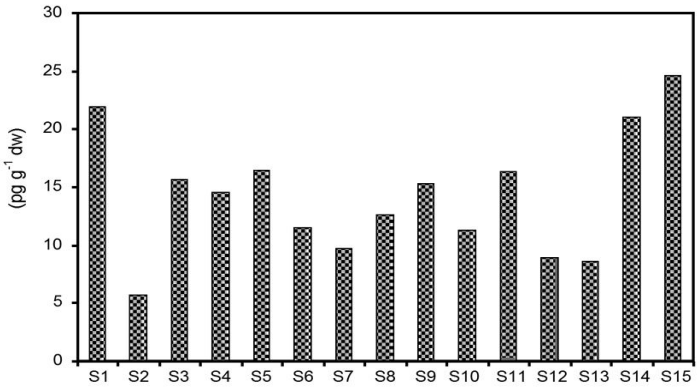

Fig. 3. Polybrominated diphenyl ethers (Σ_{10}BDEs) concentration (pg g^{-1} dw) in sediments from Pichavaram mangrove forests, Tamil Nadu

The extract in aliquot (6 mL) was spiked with ^{13}C-labelled PBDEs for quantification. The aliquot was cleaned by passing it through a multilayer silica gel column (neutral, 70–230 mesh, Merck) using 200 mL of hexane (dioxine analysis grade, Aldrich chemicals India). The eluted fractions were purified on an activated alumina column (neutral, 70–230 mesh, Merck) using successive portion of 3% methylene chloride (dioxine analysis grade, Aldrich chemicals India) in hexane and 50% methylene chloride in hexane. The second fraction was used for the determination of PBDEs.

PBDEs were analyzed using gas chromatograph (GC) (Konik system 4000 series) equipped with Konic-Q_{12} model mass spectrometer (MS) and fused silica capillary column (HP-5, 30 × 0.25 m i.d. with 0.5 µm film thickness). The GC system was operated in a split less mode 1 µL of each sample was injected. The temperature program during the run was as follows: 120 °C (2 min hold) to 180 °C at a rate of 30 °C min^{-1}, to 240 °C (2 min hold) at 1 °C min^{-1} and then to 270 °C at 2 °C min^{-1} with a final hold time of 10 min. Injector and detector temperatures were maintained at 250 and 300 °C, respectively. Helium (purity >99.9%) was employed as carrier gas at a flow rate of 2.32 mL min^{-1}. GC peaks were identified based on the retention time of individual authentic standards (±0.3%).

Qualification was carried out using retention times and mass ratios. The retention time of a component peak should be exactly equal to that of corresponding standard and the mass ratio between the two single ions of a compound was within 0.8–1.0. Quantification was carried out directly using each ^{13}C-labelled internal standard. All the results were corrected with blanks and results were reported as not detectable (nd) when concentrations were lower than the detection limits.

Results and Discussion

Polybrominated diphenyl ethers (PBDEs) are a class of compounds with a common diphenyl ether skeleton. Different PBDE congeners corresponding to varying degree of bromination (Fig. 2). Major commercial products principally contain penta-octa-or deca-BDE mixtures.

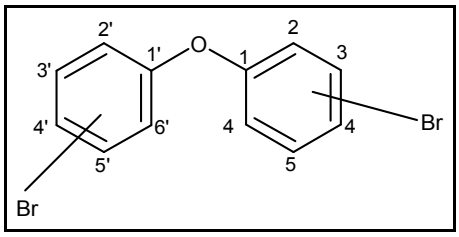

Fig. 2. Polybrominated diphenyl ethers

Concentration of PBDEs in under water sediment and core sediment

Fifteen samples of underwater sediment have been collected around Pichavaram mangrove ecosystem. The samples were analysed to quantify and qualify ten PBDE congeners including BDE-17, 28, 71, 47, 100, 99, 154, 153, 138 and 183 by GC-MS technique. The obtained results on the analysis of PBDE congeners in underwater sediment are presented in Table 1.

Table 1. Polybrominated diphenyl ethers (PBDE) concentration (pg g^{-1} dw) in sediments from Pichavaram mangrove forests, Tamil Nadu

PBDE congeners	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	Total PBDE
BDE 17	4.20	Nd	6.30	nd	5.70	nd	Nd	6.20	nd	1.21	1.42	1.42	0.87	6.32	7.31	40.95
BDE 28	3.52	Nd	1.23	nd	nd	0.96	1.21	nd	0.87	nd	nd	1.15	nd	nd	1.21	10.15
BDE 71	Nd	Nd	nd	4.31	2.16	nd	Nd	nd	4.67	7.81	3.64	nd	1.12	nd	nd	15.90
BDE 47	3.12	1.57	2.86	5.32	4.31	5.64	3.85	1.63	1.87	nd	1.23	5.41	3.00	6.11	7.81	61.54
BDE 100	2.15	Nd	nd	1.80	nd	nd	0.96	nd	nd	nd	1.75	nd	nd	1.81	nd	8.47
BDE 99	3.12	Nd	1.51	nd	2.62	nd	Nd	nd	1.65	nd	nd	1.82	1.67	nd	2.83	15.22
BDE 154	1.12	1.52	1.31	0.96	0.87	0.91	1.57	2.63	1.16	0.52	2.53	1.23	0.74	3.11	0.86	21.04
BDE 153	0.92	Nd	0.75	1.52	nd	0.82	Nd	nd	3.53	nd	nd	2.81	nd	2.11	1.62	14.08
BDE 138	1.12	1.10	0.51	nd	nd	0.86	Nd	1.56	nd	nd	2.61	1.22	nd	nd	0.97	9.95
BDE 183	2.62	1.51	1.23	0.63	0.76	2.31	2.15	0.62	1.55	1.78	3.12	3.83	1.22	1.55	1.98	26.86
Σ_{10} BDEs	21.89	5.70	15.70	14.54	16.42	11.50	9.74	12.64	15.30	11.32	16.30	8.91	8.62	21.01	24.59	

nd = not detected

Total concentration of PBDEs in each sampling rate is varied from 8.47 to 61.54 pg g^{-1} (dw). In addition, we found Σ_{10} PBDEs are in the range between 5.70 and 24.59 pg g^{-1} (dw) (Fig. 3). Among the PBDE congeners analyzed, BDE-183 was present in all the samples. Next to BDE 183, BDE 47 was also identified in all the sampling sites except S_{10}. In total concentration of PBDE congeners, BDE 47 shows high abundance when compared with the other nine congeners (61.54 pg g^{-1} dw) whereas BDE 100 were found minimum in quantity (8.47 pg g^{-1} dw).

Among the sampling sites, S_{14}, S_{15} and S_1 and highly contaminated by PBDE congeners while the site S_2 was less affected by there congeners. In the present study, total concentration of PBDE congeners are found decreased in the order of BDE 47 > 17 > 183 > 154 > 71 > 99 > 153 > 28 > 138 > 100.

Core sediment analysis

A total of seven sites along Vellar river from the estuary were selected fore core sediment sampling. In each site, three replicated core sediments in a depth range 0-24 cm were randomly collected using core sampler. The data obtained in core sediment analysis in given in Table 2.

Table 2. Concentration of PBDEs (pg g^{-1} dw) in core sediments at seven sampling sites in Vellar river wetland

	Depth (cm)	BDE 17	BDE 47	BDE 99	BDE 154	BDE 153	BDE 138	BDE 183	Σ_{10} PBDEs
CS_1	0–8	2.12	3.52	0.32	2.81	0.96	0.63	2.18	12.55
	8–16	2.04	2.69	Nd	2.52	0.85	0.47	1.78	10.35
	16–24	1.52	2.12	Nd	1.62	0.52	nd	1.52	7.30
CS_2	0–8	1.78	1.52	Nd	1.89	1.62	nd	1.72	8.53
	8–16	0.81	0.89	Nd	1.80	1.35	nd	1.35	3.20
	16–24	nd	nd	Nd	1.76	1.29	nd	0.92	3.97
CS_3	0–8	0.89	2.12	0.89	0.82	nd	0.52	0.95	6.19
	8–16	nd	1.15	0.62	0.52	nd	0.43	0.72	3.44
	16–24	nd	0.62	0.42	nd	nd	0.40	0.80	2.24
CS_4	0–8	nd	0.52	0.52	0.47	0.62	0.67	1.52	4.32
	8–16	nd	0.42	Nd	nd	0.32	0.52	1.11	2.37
	16–24	nd	nd	Nd	nd	nd	nd	0.67	0.67
CS_5	0–8	1.67	nd	1.50	1.78	nd	nd	1.12	6.07
	8–16	1.21	nd	0.76	1.32	nd	nd	0.92	4.21
	16–24	0.89	nd	0.52	1.30	nd	nd	0.85	3.56

CS_6	0–8	0.92	0.98	Nd	2.82	1.89	1.12	1.43	9.16
	8–16	0.75	0.72	Nd	2.14	1.12	0.92	1.27	6.92
	16–24	0.32	0.35	Nd	1.47	0.92	0.72	0.64	4.42
CS_7	0–8	1.52	1.52	1.12	0.82	0.58	0.75	1.98	8.29
	8–16	0.65	0.69	0.98	0.48	nd	0.62	1.54	4.96
	16–24	nd	nd	0.69	nd	nd	0.64	0.69	2.02

nd = not detected

Unlike underwater sediment analysis, BDE47 were not identification in all the sampling stations whereas BDE 183 was found in all the seven sites. When depth of core increased from 0-24 cm, the entire congener's concentrations are either decreased in quantity or in non detectable limit (Fig. 4).

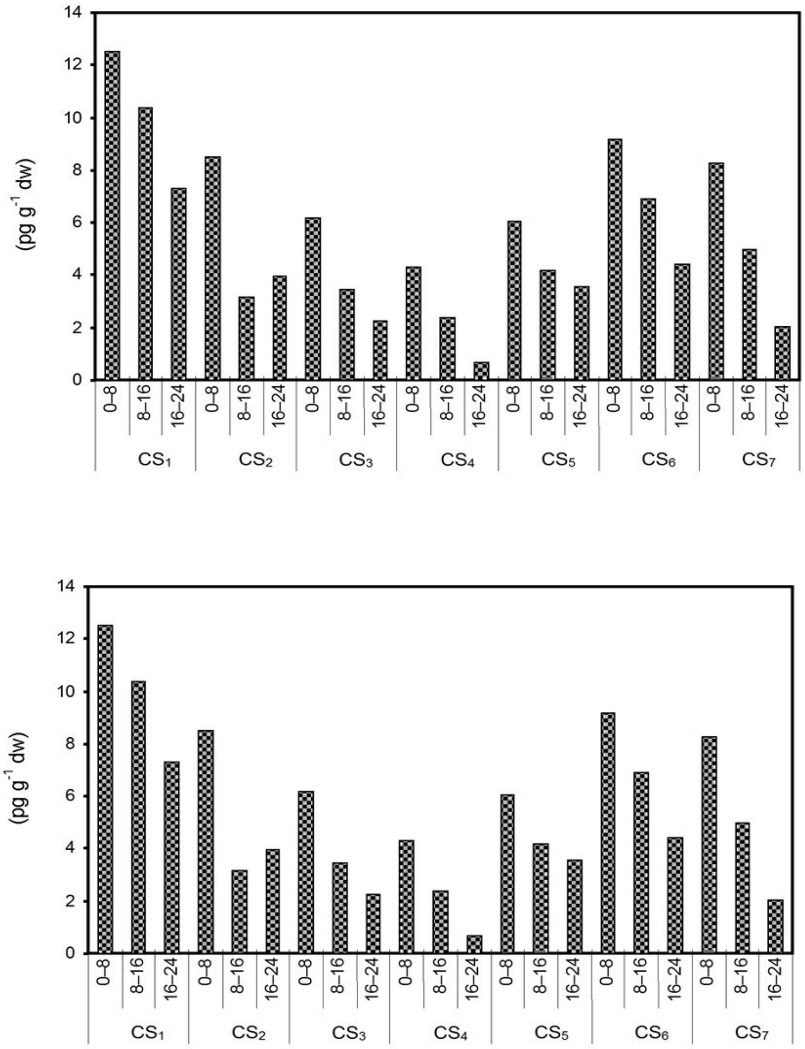

Fig. 4. Polybrominated diphenyl ethers (PBDE) concentration (pg g^{-1} dw) in core sediments from Vellar river wetland

These observations imply the recent accumulation of BDE congeners along Vellar river.

An overall enrichment for majority of the congeners was pronounced at sampling station, which is very close to the estuary (CS_1) which reached the maximum level of 15.55 pg g^{-1} dw (Table 2) at 0-8 cm sediment layer. Although tetrabromodiphenyl ether BDE-47 was found in all samples, followed by hexabromodiphenyl ether BDE-183, both were the dominant congeners. The pollution level decreases along the river side while moving from estuary.

Although we recognize that the direct comparability is somewhat compromised by the fact that different studies considered different BDE congeners and that OC-normalized data (organic carbon) were not generally used, still it is important to evaluate the quantitative patterns of PBDE contamination to get a sense of

regional similarity. Concentrations of PBDEs is Asian coastal environments ranged from 0.01 to 59 ng g^{-1} dw and BDE 47, BDE-99 and BDE-153 were the most frequently reported congeners. Although sediments from some rivers of the United Kingdom and Belgium were found to be extremely high, most European samples showed concentrations ranging from 0.5 to 27 ng g^{-1} dry weight (Table 3).

Table 3. Comparative data from the literature on total PBDE levels in sediments

Location	PBDEs (ng g^{-1} dw)	References
Several Japanese rivers	21-59	Watanabe *et al.* (1987)[13]
Industrialized areas of Japan	0.01-2.35	Choi *et al.* (2003)[14]
Hong Kong marine sediments	1.7-53.6[a]	Liu *et al.* (2005)[15]
Pearl river delta	0.15-13.03	Zheng *et al.* (2004)[16]
Singapore coasts	3.4-13.8	Wurl and Obbard (2005)[17]
Some UK rivers	Upto 1700	Sellstrom *et al.* (1999)[18]
Some Belgium rivers	Upto 200	Sellstrom *et al.* (1999)[18]
Scheldt estuary (The Netherlands)	15-23[b]	Verslycke *et al.* (2005)[19]
Coastal sediments of Portugal	0.5[c]	Lacorte *et al.* (2003)[20]
River sediments of Portugal	20[c]	Lacorte *et al.* (2003)[20]
Marine sediments from Barcelona and Tarragona (NE Spain)	0.86-2.49	de la Cal *et al.* (2003)[21]
Lake Mjosa (Norway)	0.6-27	Schlabach *et al.* (2004)[22]
Danube delta (Romania)	13[d]	Covaci *et al.* (2006)[23]
San Francisco estuary (USA)	<LOD-211.8[e]	Oros *et al.* (2005)[24]
Sundarban mangrove wetlands (India)	0.08-29.03[f]	Binelli *et al.* (2007)[25]

[a]sum of 15 PBDEs; [b]sum of 15 PBDES (excluding BDE-209); [c]sum of 20 PBDEs;[d]BDE-209 excluded; [e]<Limit of detection (LOD); [f]sum of 12 PBDES

Food web analysis

Fifteen food web samples have been collected and analyzed for ten PBDE congeners (Table 4). The total concentration of PBDEs in entire samples are varied from 3.97 to 17.20 pg g^{-1} and Σ_{10} BDEs are ranged from 1.36 to 9.66 pg g^{-1} (Fig. 5). All the ten congeners are not found in all fifteen food-web samples. In each sample, few congeners are in not delectable range.

Table 4. Polybrominated diphenyl ethers (PBDE) concentration (pg g^{-1}) in food-web collected from Pichavaram mangrove forests, Tamil Nadu

PBDE congeners	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F13	F14	F15	Total PBDE
BDE 17	1.21	nd	nd	nd	1.52	0.81	nd	nd	nd	0.62	nd	nd	nd	0.66	0.32	5.14
BDE 28	nd	0.71	nd	nd	0.62	nd	nd	1.55	0.56	nd	nd	0.22	0.31	nd	nd	3.97
BDE 71	0.32	nd	nd	1.52	0.73	nd	nd	0.55	nd	nd	1.12	nd	0.52	nd	nd	4.76
BDE 47	1.12	0.93	nd	1.52	2.31	3.12	nd	1.55	0.75	0.66	nd	1.44	nd	2.11	1.69	17.20
BDE 100	nd	nd	0.15	0.62	0.73	nd	nd	1.12	nd	0.76	0.82	nd	nd	0.62	nd	4.82
BDE 99	1.12	nd	1.31	0.85	nd	nd	nd	0.52	1.15	nd	nd	0.44	nd	nd	0.32	5.71
BDE 154	0.86	0.62	0.43	nd	1.31	1.15	0.91	0.79	nd	0.82	1.15	1.23	nd	0.76	0.82	10.85
BDE 153	0.55	nd	1.21	1.61	1.11	0.82	nd	nd	nd	nd	0.16	nd	0.22	0.31	nd	5.99
BDE 138	nd	1.16	0.52	nd	0.21	nd	nd	0.51	0.77	nd	nd	0.55	nd	nd	0.25	3.97
BDE 183	0.42	0.35	0.22	nd	1.12	0.56	0.45	0.52	nd	nd	0.51	0.64	1.15	nd	0.94	6.88
Σ_{10} BDEs	5.60	3.77	3.84	6.12	9.66	6.46	1.36	7.11	3.23	2.86	3.76	4.52	2.20	4.45	4.34	

nd = not detected

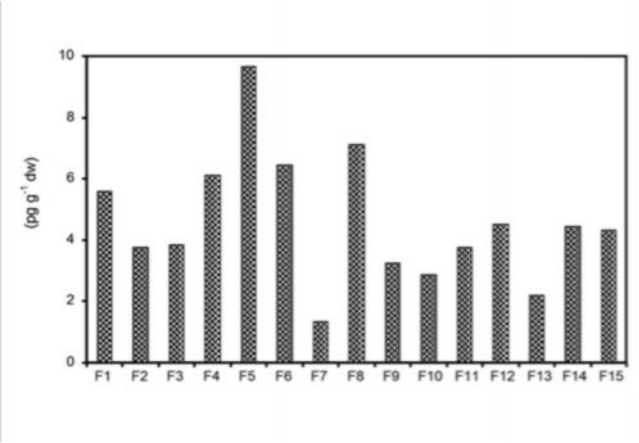

Fig. 5. Polybrominated diphenyl ethers (Σ_{10}BDEs) concentration (pg g^{-1}) in food-web collected from Pichavaram mangrove forests, Tamil Nadu

Among the congeners identified, BDE 47 was found in maximum quantity. Σ_{10} BDEs are found high in sample F_5 (9.66 pg g^{-1}) and low in sample F_7 (1.36 pg g^{-1}). The values imply that the total concentration of PBDEs follows the order BDE-47 >154>183> 153>99>17>100>71>138 and 28.

Conclusions

The present study exhibited that ten congeners of PBDE were ubiquitous in underwater sediment and food-web of Pichavaram mangrove ecosystem. The level of PBDEs contamination varied from very low to moderate compared with values of aquatic sediment in Asian region. The data reported here are pioneer one on the distribution of PBDEs in present study area. The dominant BDE congener in all sediment and food-web samples was BDE 47. In core sediment sample analysis, high contamination was observed only in surface sediment of depth 0-8 cm. The contamination level (ΣPBDEs) was low in food-web when compared with sediment of the same area. The mechanism of PBDEs entry and distribution is still under investigation. Hence an increasing trend of PBDEs contamination might pose potential risk of exposure to human through aquatic animals.

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References

1. Hale RC, LaGuardia MJ, Harvey EP, Mainor TM. 2002. Chemosphere., 2002, 46 : 729-735.
2. McDonald TA, Chemosphere., 2002, 46 : 745-755.
3. Wang YW, Jiang GB, Lam, PKS, Li A. Environ. International., 2007, 7(33) : 963-973.
4. Noren K, Meironyte D. Chemosphere., 2000, 40 : 1111-1123.
5. Zegers BN, Lewis WE, Booij K, Smittenberg RH, Boer WD, Boer J. J. Environ. Technol., 2003, 37 : 3803-3807.
6. Bixian Mai, Shejun Chen, Xiaojun Luo, Laiguo Chen, Quingshu Yang, Guoying, Sheng, Pingan Peng, Jiamo Fu, and Eddy Y. Zhang, 2005. Environ. Sci. Technol., 39, 3521-3527.
7. Haowen Zhu, Ying Wang, Xiaowei Wang, Tiangang Luan, Nora F.Y. Tam. Science of the Total Environment., 2014, 468-469, 130-139.
8. Tam, NFY, Wang, YS. J. Environ. Qual., 1999, (28) : 556-564.
9. Bayen S, Wurl O, Karuppiah S, Sivasothi N, Lee HK, Obbard JP. Chemosphere., 2005, 61, 303-313.
10. Binelli A, Sarkar SK, Chatterjee M, Rvia C, Parolini M, Bhattacharya BD, Bhattacharya AK, Satpathy KK. Mar. Polut. Bull., 2007, 54 : 1220-1229.
11. Bodin N, N Gom, Ka R, Le Loch F, Raffray J, Budzinski H, Peluhet I. Chemsphere., 2011, 84 : 381-327.

12. Bayen S. Environ Int., 2012, 48 : 84-101.
13. Watanabe I, Kashimoto T, Tatsukawa R. Chemosphere., 1987, 16 : 2389-2396.
14. Choi JW, Onodera J, Kitamura K, Hasimoto S, Ito H, Suzuki N, Sakai S, Morita M. Chemosphere., 2003, 53 : 637-643.
15. Liu Y, Zheng JG, Yu H, Martin M, Richardson JB, Lam MHW, Lam PKS. Marine Pollution Bulletin., 2005, 50 :1173-1184.
16. Zheng GJ, Martin M, Richardson BJ, Yu HX, Liu, Y. Zhou CH, Li J, Hu GJ, Lam MHW, Lam PKS. Marine Pollution Bulletin., 2004, 49 : 520-524.
17. Wurl O, Obbard JP. Chemosphere, 2005, 58 : 925-933.
18. Sellstrom U, Kierkegaard A, Alsberg T, Johnsson P, Wahlberg C, de Wit C. Organohalogen Compounds., 1999, 40 : 383-386.
19. Verslycke TA, Vethaak AD, Arijs K, Janseen CR.. Environmental Pollution., 2005, 136 : 19-31.
20. Lacorte S, Guillamon M, Martinez E, Viana P, Barcelo D. Environmental Science and Technology, 2003, 37 : 892-898.
21. de la Cal A, Eljarrat E, Barcelo D. Journal of Chromatography A., 2003, 1021: 165-173.
22. Schlabach M, Fjeld E, Gundersen H, Mariussen K, Kjellberg G, Breivik E. Organohalogen Compounds., 2004, 66 : 3779-3785.
23. Covaci A, Gheorghe A, Hulea O, Schepens P. Environmental Pollution., 2006, 140 : 136-149.
24. Oros DR, Hoover D, Rodigari F, Crane D, Seriano J. Environmental Contamination and Technology., 2005, 39 : 33-41.
25. Binelli, A, Santosh Kumar Sarkar, Mousumi Chatterjee, Consuelo Riva, Marco Parolini, Bhaskar deb Bhattacharya, Asok Kumar Bhattacharya, Kamala Kanta Satpathy.. Marine Pollution Bulletin., 2007, 54 : 1220-1229.

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