INTAKE FRACTIONS OF PBDES AND PBDD/DFS

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Abstract

Environmental fate and exposure model for PBDEs and PBDD/DFs were developed and intake fractions for PBDEs and PBDD/DFs were calculated. Debromonation of PBDEs to lower-brominted diphenyl ethers and formation of PBDFs from PBDEs were considered in the environmental fate model. The model predicted that the concentration of daughter PBDEs caused by debromination were 2 to 4 orders of magnitude lower than those of their parent PBDEs. Concentrations of PBDEs and PBDD/DFs were calculated based on two emission scenarios which focused mainly on DecaBDE sources. The estimated concentrations of PBDD/DFs were about 2 to 4 orders of magnitude lower than the observed concentrations of PBDD/DFs. This result suggests that the emission sources of PBDD/DFs and the emission sources of DecaBDE are quite different. Lower brominated PBDEs and PBDD/DFs had higher intake fractions than higher brominated compounds.

Introduction

Recent studies have shown that PBDEs are debrominated into lower-brominated compounds by photolysis[1, 2]. Formation of PBDFs by the photolysis of PBDEs is also reported[3]. In our previous study, we reported the importance of PBDFs and lower-brominated diphenyl ethers in the life cycle impact assessment of commercial DecaBDE products[4]. These studies suggest the debromination and PBDFs formation in the environmental fate of PBDEs are important. In this paper, we developed environmental fate and exposure model for PBDEs and PBDD/DFs and calculated the intake fractions (iFs) for these compounds.

Methods

We used a Mackay-type level III multimedia fate model[5]. Our model has three geographical scales: local, national (Japan), and global (Northern Hemisphere). Each geographical scales consists of air, soil, water, and sediment. Debromination rate constants in air and water by photolysis were derived from Schenker et al. (2008)[1]. Debromination in soil and sediment were assumed to be negligible in our model. Rate constant for formation of PBDFs during the photolysis of PBDEs were derived from Kajiwara et al. (2008)[3]. No debromination of PBDDs/PBDFs was assumed.

To calculate iFs[6] for PBDEs and PBDD/DFs, exposure from inhalation, drinking water, soil ingestion and food were considered. Intake of vegetables, meat and fish were considered in the intake of food.

Results and Discussion

Fig. 1 and Fig. 2 show the distribution of PBDEs among environmental compartments after emission of each PBDE homologue. Fig. 1 shows that the higher-brominated diphenyl ethers are more persistent than the lower-brominated compounds. Fig. 2 shows that lower-brominated diphenyl ethers are more likely to be found in air compartment than the higher-brominated compounds.

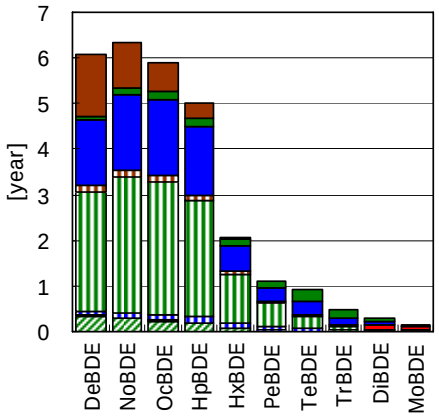

Fig. 1 Average residence time of PBDE homologues in environmental compartments after emission to air. (Unit: year)

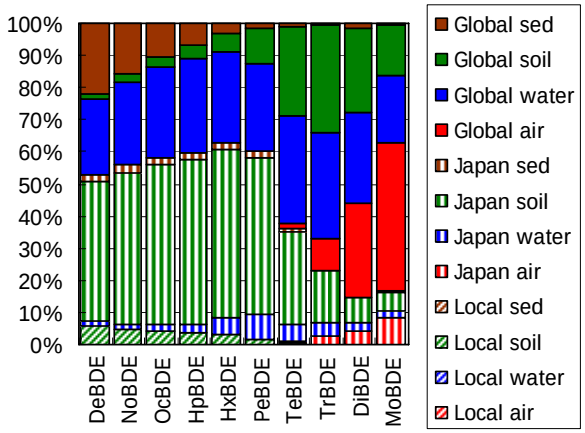

Fig. 2 Distribution of PBDE homologues among environmental compartments after emission to air.

Fig. 3 and Fig. 4 show the amount of PBDEs and PBDD/DFs in the environment caused by continuous emission of DecaBDE to the air, water and soil. The homologue profile of PBDEs show the effect of debromination. The concentration of daughter (lower-brominated) PBDEs were 2 to 4 orders of magnitude lower than those of their parent PBDEs.

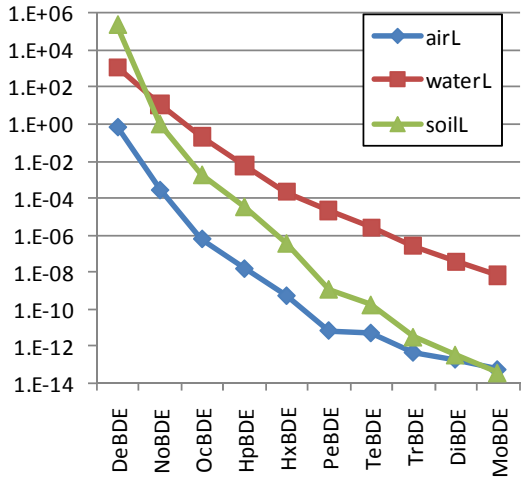

Fig. 3 Amount (mol) of PBDEs homologues in the environment at steady state caused by continuous emission of 1mol/h of DecaBDE.

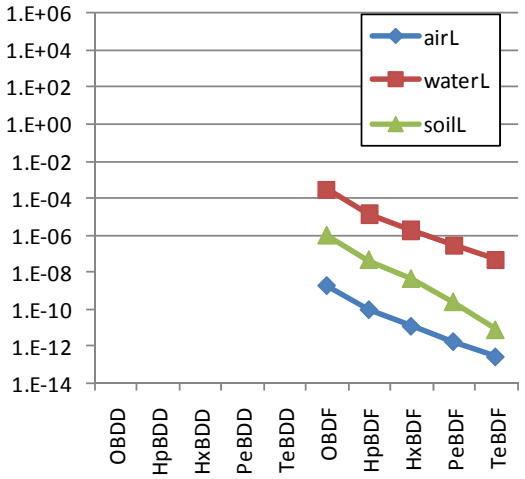

Fig. 4 Amount (mol) of PBDD/DFs homologues in the environment at steady state caused by continuous emission of 1mol/h of DecaBDE.

Fig. 5-Fig. 8 compare the estimated and observed concentrations[7] of PBDEs and PBDD/DFs in air and soil. Two emission scenarios were used to estimate the PBDEs and PBDD/DFs concentrations.

In scenario I, our previous result on homologue specific emission inventory of PBDEs and PBDD/DFs were used[4]. This emission inventory focused mainly on lifecycle of DecaBDE. As a result, the estimated concentrations of PBDEs in scenario I were about 2 orders of magnitude lower than the observed concentrations. This result suggests the underestimation of our previous study.

In scenario II, atmospheric emissions of PBDEs were calculated based on the observed atmospheric depositions of PBDEs[7]. As to PBDD/DFs, atmospheric depositions were not available, so atmospheric emission of PBDD/DFs were estimated by multiplying the DecaBDE emission in scenario II and the raio of PBDD/DFs emission over DecaBDE emission in scenario I. Fig. 5 and Fig. **7** show that the estimated concentrations of higher-brominated diphenyl ethers in both air and soil agreed well with the observed concentrations. However, estimated concentrations of lower-briminated diphenyl ethers in soil were lower than the observed concentrations (Fig. 7). This result may suggest the effect of commercial PentaBDE mixtures. PentaBDE mixtures were used in the past and the effects of these past emissions are not likely to be accounted for in scenario II. Fig. 6 and Fig. 8 show that the estimated PBDD/DFs concentrations were about 2 to 4 orders of magnitude lower than the observed concentrations. These results suggest that the emission sources of PBDD/DFs and the emission sources of DecaBDE are quite different.

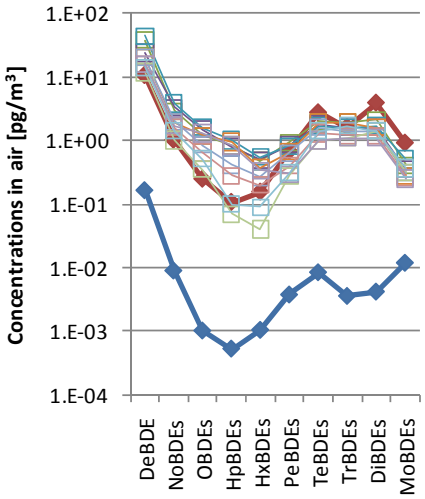

Fig. 5 Estimated and observed concentrations of PBDEs in air [pg/m^3]

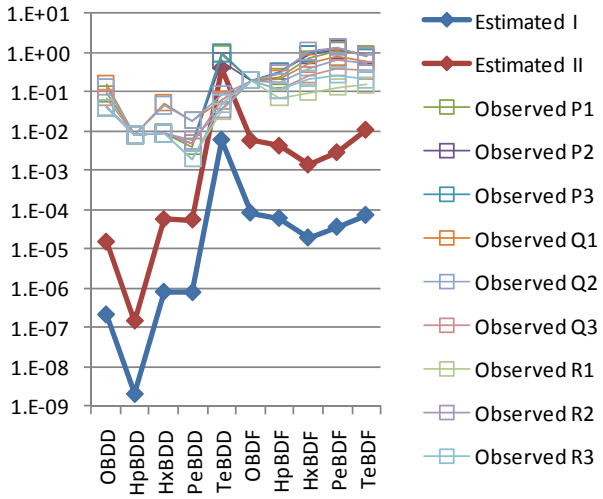

Fig. 6 Estimated and observed concentrations of PBDD/DFs in air [pg/m^3]

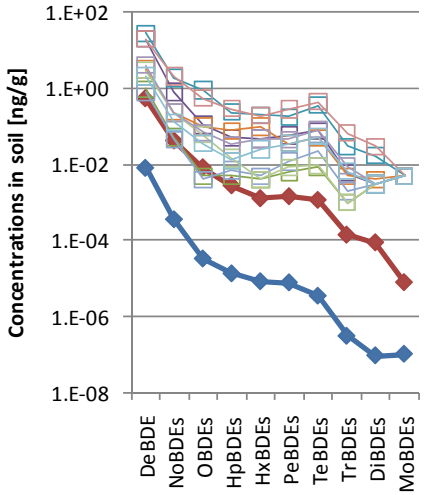

Fig. 7 Estimated and observed concentrations of PBDEs in soil [ng/g]

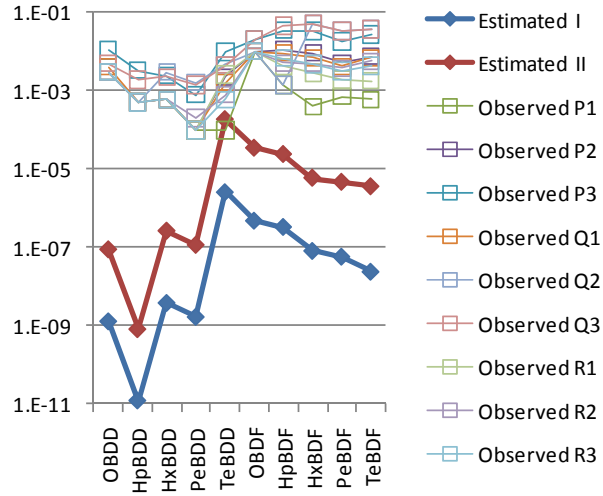

Fig. 8 Estimated and observed concentrations of PBDD/DFs in soil [ng/g]

Table 1 shows the intake fractions of PBDEs and PBDFs caused by atmospheric emission of PBDEs. The environmental fate model in this paper considers the debromination to lower brominated compounds and formation of PBDFs, so not only the original compounds which are released to the environment but also the debrominated compounds and PBDFs are listed in Table 1. Table 2 shows the intake fractions of PBDD/DFs caused by the emission of these compounds to air, water, and soil. Lower brominated PBDEs and PBDD/DFs had higher intake fractions than higher brominated compounds.

Table 1 Intake fractions of PBDEs and PBDD/DFs caused by emission of PBDEs to air.

		Compounds emitted to air									
		DeBDE	NoBDE	OBDE	HpBDE	HxBDE	PeBDE	TeBDE	TrBDE	DiBDE	MoBDE
Compounds exposed to	DeBDE	3.3E-05	-	-	-	-	-	-	-	-	-
	NoBDE	5.5E-07	2.0E-04	-	-	-	-	-	-	-	-
	OBDE	1.1E-08	4.1E-06	2.3E-03	-	-	-	-	-	-	-
	HpBDE	4.5E-11	1.4E-08	6.8E-06	4.6E-03	-	-	-	-	-	-
	HxBDE	4.1E-13	7.5E-11	2.0E-08	1.1E-05	4.2E-03	-	-	-	-	-
	PeBDE	2.4E-14	3.6E-12	3.9E-10	7.1E-08	2.1E-05	7.5E-03	-	-	-	-
	TeBDE	3.3E-15	4.7E-13	4.3E-11	2.6E-09	2.0E-07	4.9E-05	1.3E-02	-	-	-
	TrBDE	2.6E-16	3.7E-14	3.3E-12	1.9E-10	8.2E-09	1.2E-06	2.8E-04	1.3E-02	-	-
	DiBDE	3.0E-17	4.2E-15	3.8E-13	2.0E-11	5.6E-10	2.2E-08	3.8E-06	1.4E-04	6.2E-03	-
	MoBDE	3.6E-18	5.2E-16	4.7E-14	2.5E-12	6.2E-11	7.1E-10	2.7E-08	8.4E-07	3.1E-05	2.1E-03
	OBDF	3.6E-13	7.4E-11	2.5E-08	-	-	-	-	-	-	-
	HpBDF	1.5E-14	2.3E-12	3.5E-10	1.3E-07	-	-	-	-	-	-
	HxBDF	1.9E-15	2.8E-13	2.6E-11	2.3E-09	4.4E-07	-	-	-	-	-
	PeBDF	3.2E-16	4.6E-14	4.1E-12	2.3E-10	1.1E-08	2.0E-06	-	-	-	-
	TeBDF	6.7E-17	9.5E-15	8.6E-13	4.5E-11	1.2E-09	2.1E-08	2.8E-06	-	-	-

Table 2 Intake fractions of PBDD/DFs caused by emission of PBDD/DFs to air, water and soil.

	Air	Freshwater	Seawater	Agricultural soil	Industrial soil
OBDD	5.9E-05	1.5E-05	5.3E-08	3.8E-08	1.6E-07
HpBDD	1.5E-04	2.5E-05	1.5E-07	2.6E-07	1.9E-07
HxBDD	8.7E-04	4.6E-05	1.0E-06	1.4E-06	2.6E-07
PeBDD	2.4E-03	8.8E-05	3.0E-06	1.8E-06	4.4E-07
TeBDD	5.1E-03	1.8E-04	1.2E-05	2.8E-06	9.4E-07
OBDF	6.3E-05	2.6E-05	2.7E-08	4.3E-08	1.9E-07
HpBDF	1.9E-04	4.2E-05	8.8E-08	3.5E-07	2.5E-07
HxBDF	6.2E-04	6.6E-05	4.2E-07	7.2E-07	3.7E-07
PeBDF	2.2E-03	1.1E-04	3.6E-06	1.4E-06	6.9E-07
TeBDF	6.6E-04	2.2E-04	4.5E-05	3.7E-07	1.6E-06

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References

1. Schenker U., Soltermann F., Scheringer M., Hungerbuhler K. *Environ Sci Technol* 2008; 42: 9244
2. Soderstrom G., Sellstrom U., de Wit C.A., Tysklind M. *Environ Sci Technol* 2004; 38: 127
3. Kajiwara N., Noma Y., Takigami H. *Environ Sci Technol* 2008; 42: 4404

4. Hirai Y., Sato S., Sakai S. *Organohalogen Compounds* 2008
5. Mackay D., Di Guardo A., Paterson S., Cowan C. E. *Environ Toxicol Chem* 1996; 15: 1627
6. Bennett D.H., Margni M.D., McKone T.E., Jolliet O. *Risk Analysis* 2002; 22: 905
7. Ministry of Environment, Japan. *Results of PBDDs/DFs study in Japan.* 2004-2006; http://www.env.go.jp/chemi/report/h18-11/index.html