PBDE CONTAMINATION EPISODE IN VEGETATION AND SILAGE NEAR PBDE OPERATION FACTORIES IN TAIWAN

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Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardents and known as persistent organic pollutants (POPs). PBDEs are easily adsorbed with non-dissolved oganic carbon in soil due to the characteristic of high lipophilic[1]. Zhang et al. reported that soil samples from surrounding areas of e-waste recycling activities had been polluted by PBDEs[2]. Vrkoslavová et al. proved that tobacco and nightshade can absorb and translate PBDEs from sewage sludge[3]. These evidences raise a caution that the soil-plant system near PBDE operation factories might be serious polluted. PBDEs have potential adverse health effects on thyroid function, endocrine disrupting effects, and developmental neurotoxicity[4, 5]. If the vegetation or silage were polluted by PBDEs, the high level predaters may accumulate high level PBDEs by bioaccumulation. The aim of the present study is to investigate the pollution situations of vegetation and silage near PBDE operation factories in Taiwan.

Materials and methods

The present study was conducted from 2012 to 2013. We collected data of production and usage amounts of PBDEs from toxic chemical management system from Taiwan EPA. The factories which reported high usage amounts of PBDEs in database were selected as target factories. The farmlands which distance from the factory within 1 kilometer and at the leeward side were selected as sampling site. The vegetation and silage which have long growth period have top priority to be sampled to represented to bioaccumulation. The roots of vegetation and silage were cut down and discarded on the sampling site to prevent the soil on the roots may contaminate samples during transportation. Samples were freeze-dried without water clean, then homogenized, and frozen at −20 °C until analysis. The analytical method was slightly modified from USEPA Method 1614A[6]. Seven grams samples were spiked with a suite of ^{13}C-labed-PBDE recovery standards and extracted using n-hexane/acetone (1:1) for 6 h with Soxhlet extractors. The extracts were clean-up by sulfuric acid, acidic silica-gel, and an acidic alumina column. High-resolution gas chromatography/high-resolution mass spectrometry with a 15m Rtx-1614 column was used to quantify PBDE using isotope dilution method. Twenty-four PBDE congeners (tri- through deca-PBDE) were selected for quantification.

Results and discussion

Six factories were selected as target, and 46 vegetation and silage samples from the farmland around the target factories were collected in the present study. Table 1 summarizes the analytical results of 46 samples. The highest concentration of PBDEs was found in pasture sample (348062 pg/g wet weight) around factory D. The lowest PBDEs level (26.3 pg/g w.w.) was found in tomato sample around factory B. The average PBDEs concentration of 46 vegetation and silage samples was 27769 pg/g w.w.. The dominant homologues in all samples were deca-, nona- and octa-BDE. The average $\sum$PBDE level of samples around all factories was decreased in the following order: factory D (108940 pg/g w.w.) > factory E (7125 pg/g w.w.) > factory F (3587 pg/g w.w.) > factory A (3129 pg/g w.w.). We investigated the usage amounts of DecaBDE in these factorys in early 2013 and decreased in the following order: factory E (46.2 tons) > factory D (38.0 tons) > factory A (20.0 tons) > factory F (4.2 tons). This suggests that the levels of PBDEs in vegetation and silage around the PBDE operation factories were increased with the amounts of PBDEs usage. The average concentrations of almost all homologues are higher than 2012 Taiwan FDA fresh food survey impliy the PBDE operation factories are truely the pollution sources to the vegetation and silage.

We pick the top 11 samples which $\sum$PBDE levels were higher than 10000 pg/g w.w. to further discuss (Table 2). The $\sum$PBDE levels decreased in the following order: three pasture samples (348062, 260925, 245334

pg/g w.w.) > two sweet potato vine samples (61203, 36980 pg/g w.w.) > ganges amaranth (26758 pg/g w.w.) >lettuce (22236 pg/g w.w.). The dominant homologues in these samples were deca-, nona- and octa-BDE. The dominant congeners were BDE-209, BDE-206, BDE-207, BDE-196. However, BDE-183 was also a major congener (430- 21100 pg/g w.w.) in pasture samples which were sampled near factory D. If the contaminated pasture samples were provided to feed cows, the high levels of PBDEs would be transferred through food web by bioaccumulaton and biotransformation. The levels of Deca-BDE in the 11 samples were exceed the Federal Environmental Quality Guidelines for wildlife diet (9000 pg/g w.w.) from Canada EPA[7]. Once animal or human intake the contaminated vegetation and silage, the high levels of PBDEs may threaten their health. Debromination seems to be found in pasture samples that high levels of low brominated BDE was detected.

The present study rise a concern that vegetation and silage around the PBDE operation factories were serious polluted. PBDEs may transport by air through dry and wet deposition and absorb in soil. The vegetation and silage on the contaminated soil may absorb and translate PBDEs to food web. The debromination in soil is another important issue. This mechanism will certainly help low brominated BDE to distribute widely before we ban Deca-BDE.

Acknowledgements
We are in great debt to our colleagues at the Research Center of Environmental Trace Toxic Substances for sampling and analytical assistance. This study was supported by grants from the Agriculture and Food Agency, Council of Agriculture, Executive Yuan, Taiwan.

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Table 1 Average (range) PBDE level (pg/g wet weight) in 46 samples from 6 decaBDE operation factories.

	2012 Factory A (n=7)	2013 Factory A (n=7)	Factory B (n=6)	Factory C (n=1)	Factory D (n=9)	Factory E (n=11)	Factory F (n=5)	2012 Taiwan FDA survey (n=78)
TriBDE	0.849 (0.03~3.52)	0.172 (0.079~0.352)	0.312 (0.089~1.1)	0.194	5.94 (0.131~28.7)	0.45 (0.045~2.21)	0.872 (0.058~3.1)	0.165 (0.02~1.54)
TetraBDE	8.31 (0.304~34.2)	2.22 (0.636~0.636)	2.19 (0.492~7.54)	2.83	31.7 (1.39~105)	3.96 (0.317~12.8)	15.9 (0.449~64.2)	1.53 (0.167~14.0)
PentaBDE	9.93 (0.205~60.8)	2.61 (0.387~11.1)	0.947 (0.1~2.50)	1.69	107 (0.948~742)	2.47 (0.182~8.26)	13.6 (0.22~59.4)	0.722 (0.086~3.61)
HexaBDE	6.91 (0.09~45.7)	1.74 (0.1~8.95)	1.22 (0.177~4.04)	0.915	639 (0.659~4753)	3.44 (0.224~8.51)	6.87 (0.08~31.2)	0.31 (0.014~5.87)
HeptaBDE	22.1 (0.26~151)	3.56 (0.169~19.7)	0.695 (0.142~1.31)	2.23	3652 (2.14~25654)	8.51 (0.242~22.7)	12.4 (0.115~58.7)	0.539 (0.008~4.53)
OctaBDE	26.1 (0.305~188)	8.55 (0.627~40.9)	0.789 (0.232~1.40)	3.36	3346 (17.2~20904)	23.3 (0.571~67.1)	20.5 (0.613~95.8)	1.91 (0.004~9.75)
NonaBDE	302 (4.59~2062)	96.3 (5.77~357)	16.4 (3.25~39.3)	69.6	20689 (297~64425)	671 (18.1~1814)	317 (5.02~1477)	26.9 (2.15~190)
DecaBDE	2752 (28.3~19694)	496 (39.3~1717)	171 (21.5~411)	691	80467 (1787~299293)	6412 (183~25103)	3200 (44.4~14834)	172 (8.85~1232)
ΣPBDE	3129 (34.8~22236)	611 (47.7~2163)	194 (26.3~454)	772	108940 (2132~348062)	7125 (202~26757)	3587 (53.3~16623)	204 (12.0~1433)

Table 2 The top 11 samples which were detected highest PBDE levels in the present study.

	Factory A	Factory D–site I（summer）		Factory D–site I（winter）			Factory D –site II（winter）	Factory E			Factory F	Canada EPA[7]
	Lettuce	Sweet potato vine	Pasture	Sweet potato vine	Pasture	Pasture	Leaf from paper mulberry	Ganges amaranth	Water convoevueus	Welsh onion	Leaf from paper mulberry	Wildlife diet
TriBDE	0.983	0.274	1.36	1.43	8.88	9.14	28.8	1.01	0.310	0.442	3.10	-
TetraBDE	33.4	3.47	25.8	9.80	55.5	105	77.9	8.69	7.16	7.36	64.2	44,000
PentaBDE (BDE-99)	48.6	3.10	28.7	9.75	54.2	365	33.5	6.01	2.93	2.30	42.1	3,000
PentaBDE (BDE-100)	8.85	0.832	10.8	3.42	18.6	154	9.34	1.43	1.05	0.934	12.8	-
PentaBDE	60.8	4.29	50.9	15.6	95.0	742	47.1	8.16	4.48	3.71	59.4	3,000
HexaBDE	45.7	4.09	181	53.3	734	4,754	17.8	7.73	5.59	5.65	31.2	4,000
HeptaBDE	151	13.2	500	308	6,352	25,655	25.9	15.3	14.0	13.3	58.7	64,000
OctaBDE	188	77.2	1111	1,505	6,298	20,905	157	29.0	29.7	30.8	95.8	63,000
NonaBDE	2,061	3,207	46,898	13,968	62,370	56,601	1,682	1,584	1,085	1,012	1,476	78,000
DecaBDE	19,694	33,669	299,293	45,341	185,010	136,562	11,139	25,103	14,157	11,337	14,834	9,000