Method development for the analysis of polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzo-furans in single extract of sediment samples

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Abstract

A comprehensive method was developed for quantitative analysis of polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) in one single extract of environmental samples. The sample preparation procedure included two fractionation steps using silver nitrate silica chromatography to separate PBDEs from PCBs and PCDD/Fs and florisil column to separate PCBs from PCDD/Fs. Acidic silica, acidic alumina and gel permeation chromatography (GPC, for PCBs) or activated carbon column (for PCDD/Fs) were used for further clean-up. The sample extracts were analyzed by using high-resolution gas chromatography/high-resolution mass spectrometry. The entire method was validated from the analysis of mixed standards of PBDEs, PCBs and PCDD/Fs ($n = 3$); the analysis of certified reference biota (WMF-01). The method was applied for the analysis of 10 sediment samples collected from Haihe River and Dagu Drainage River in Tianjin City. No significant PBDEs pollution was found in the areas.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) have been of great concern due to their toxicity and potential health risks [1–5]. However, most of the currently available methods involve two or three individual sample preparation procedures followed by instrument analysis, which is time and solvent consuming. Thus, a rapid and reliable procedure for the simultaneous sample preparation for PBDEs, PCBs and PCDD/Fs is needed.

Separation of PBDEs from PCBs and PCDD/Fs is difficult and vital in the simultaneous sample preparation procedure and consequent gas chromatography/mass spectrometry (GC/MS)

analysis because the compounds often have co-elution problem on various types of GC-column with the same isobaric ions [6–9]. Multi-layer silica column has been used to separate PBDEs from PCBs and PCDD/Fs. In the multi-layer silica column, silver nitrate silica was found to play an important role in the separation procedure. It was reported that PBDEs could not be separated from PCBs and PCDD/Fs by using the multi-layer silica column if the layer of acidic silica was overloaded with sample extracts due to the severe matrix effect on separation efficiency [6]. In these cases, a new multi-layer silica column was needed to clean the sample prior to the separation of PBDEs, which not only affected the recovery but also spent much more time and solvent. In this study, investigation was conducted to use silver nitrate silica to replace the multiple-layer silica to separate PBDEs from PCBs and PCDD/Fs after the clean-up by individual acidic silica and acidic alumina column chromatography. Further clean-up of the PCBs and PCDD/Fs fractions were achieved by using GPC and active carbon col-

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umn chromatography, respectively. The method was validated through the analysis of mixed standards and certified reference tissue sample (WMF-01) and applied for the determination of PBDEs along with PCBs and PCDD/Fs in sediment samples collected from Haihe River and Dagou Drainage River in Tianjin City.

2. Materials and methods

2.1. Chemicals

All solvents were absolute grade and were purchased from Tedia. Silica gel (0.063–0.100 mm) was obtained from Merck. Bio-Beams SX-3 was purchased from Bio-Rad. Standard solutions of PCDD/Fs (1613-LCS (Labeled Compound Stock Solution), 1613-ISS (^{13}C -1, 2, 3, 4-TCDD and ^{13}C -1, 2, 3, 7, 8, 9-HxCDD Internal Standard Spiking Solution) and 1613-PAR (Native PCDD/Fs, Precision and Recovery Stock Solution)), PCBs (WP-LCS (WHO ^{13}C -PCBs Surrogate Spiking Solution), WP-ISS (WHO ^{13}C -PCBs, Internal Standard Solution), MXP) and PBDEs (^{13}C -labeled MBDE-MXC, MBDE-139-IS) were obtained from Wellington Laboratories. Certified reference material WMF-01 (reference fish tissue for organic contaminant analysis) was also obtained from Wellington Laboratories. Ten sediment samples were collected from Haihe River and Dagou Drainage River in Tianjin City of China in November 15–16, 2003. Detailed sample collection and extraction procedures were described elsewhere [10,11].

2.2. Sample preparation and purification

Freeze-dried environmental sediment samples were spiked with ^{13}C -labeled surrogate standards prior to a 24-h Soxhlet extraction with 1:1 dichloromethane (DCM):hexane. After the extraction, acidic silica was added to remove lipid in the tissue samples. The extract was concentrated by using a rotary evaporator, and the residue was dissolved in 7 ml hexane in the vial. Eight millilitres of concentrated sulphuric acid was added and the vial was shaken and then allowed to stand for an hour. The above extraction, concentration and acidic treatment steps were not needed during the development of the chromatographic clean-up procedure, for which a solution of mixed chemical standards was used. The organic layer in the vial was sequentially subjected to acidic silica gel, acidic alumina, silver nitrate (AgNO_3) silica (10%, w/w) for the separation of PBDEs from PCBs and PCDD/Fs and florisil for the separation of PCBs and PCDD/Fs. Activated carbon chromatography columns and gel permeation chromatography (GPC) were used for further clean-up of PCBs and PCDD/Fs, respectively. The activated carbon column was packed by using a glass pipette from bottom to top with glass wool, 0.15–0.2 ml silica gel, 0.35–0.4 ml 18% activated carbon/celite 545 mixture, 0.15–0.2 ml silica gel and glass wool. The GPC was packed with pre-swollen and washed Bio-Beads SX-3 corresponding to 30 g dry material by using 1:1 DCM:hexane as the solvent. The eluted sample was collected in three fractions, which were concentrated to dryness. Then, ^{13}C -labeled internal standards, WP-ISS (for PCBs), MBDE 139

(for PBDEs) and 1613-ISS (for PCDD/Fs), were added prior to the GC injection.

2.3. Instrumental analysis

The instrument analysis of PBDEs, PCDD/Fs and PCBs was performed on an Agilent 6890 gas chromatography coupled with an Autospec Ultima mass spectrometer operating with EI source in SIM mode. Two microliters of sample extract was injected with splitless mode into a DB-5MS fused silica capillary column (60 m $\times$ 250 μm i.d. $\times$ 0.25 μm film thickness) with helium as carrier gas. The details of the MS analysis and quality control are described in the EPA methods 1614-draft, 1613B and 1668A.

3. Results and discussion

3.1. Method development

3.1.1. Separation of PBDEs from PCBs and PCDD/Fs by using silver nitrate silica column

The key work of the method development for the analysis of PBDEs, PCBs and PCDD/Fs in one single sample was to separate PBDEs from PCBs and PCDD/Fs in the sample extract. Martínez et al. reported that separation of PBDEs from PCBs could be achieved by using neutral silica as absorbents [12]. Therefore, separation of PBDEs from PCBs and PCDD/Fs were investigated on neutral silica column (9 mm i.d., 8 cm). Different silica gel activation processes, baked at 170 °C for at least 24 h and baked at 550 °C for 6 h and keep in 170 °C for at least 24 h, were investigated. The results showed that neutral silica under the current conditions could not effectively separate PBDEs from PCDD/Fs and PCBs. Neutral silica baked at 550 °C for 6 h is less adsorptive than the one baked at 170 °C. The different results of separation efficiency between our experiments and that reported by Martínez et al. may be due to the difference of characteristics of the silica sorbents or their preparation procedure.

AgNO_3 silica was then selected for the separation of PBDEs from PCBs and PCDD/Fs. The results showed that the orders of elution depended on the levels of chlorination or bromination of the compounds, but in different patterns. For PCBs and PCDD/Fs, mono-CBs and 2,3,7,8-TCDD were the last eluted congeners, respectively; while mono-BDEs were first eluted out of the AgNO_3 silica column among the PBDEs. Therefore, in order to separate PBDEs from PCBs and PCDD/Fs, the separation of BDE-28 from PCB-28 and 2,3,7,8-TCDD, which are the first or the last elution congeners among our target compounds, was the most difficult. Chromatograms of 2,3,7,8-TCDD/F, PCB-28 and BDE-28 in different fractions were presented in Fig. 1. As shown in Fig. 1, 100% 2,3,7,8-TCDD and PCB-28 were eluted in the first 80 ml hexane, and 90% of 2,3,7,8-TCDD was eluted in 90 ml hexane, while BDE-28 was only detected in the 6% DCM in hexane eluting solvent, indicating that a complete separation of PBDEs from PCBs and PCDD/Fs was achieved. Therefore, 100 ml of hexane was selected to elute PCBs and PCDD/Fs, followed by 40 ml of 6% DCM in hexane for the elution of PBDEs.

Fig. 1. GC/MS chromatograms of 2,3,7,8-TCDD/F, PCB-28 and BDE-28 in different fractions separated on the AgNO_3 silica column. F1 represents the fraction eluted by using 60 ml hexane. F2 and F3 were the fractions eluted with additional 20 and 30 ml hexane, respectively. F4 represents the fraction eluted by 40 ml 6% DCM in hexane, and F5 was with additional 20 ml of 6% DCM in hexane.

Table 1

Recoveries and relative standard deviation (R.S.D.) ($n = 3$) of PCBs, PCDD/Fs and PBDEs from the analysis of the standard mixture of 1613-LCS, WHO-LCS, MXP and MBDE-LCS

Compounds	#1	#2	#3	Average	R.S.D.
¹³ C-BDE-15	62	43	44	50	22
¹³ C-BDE-28	87	74	81	81	8
¹³ C-BDE-47	125	117	116	119	4
¹³ C-BDE-99	79	79	78	79	1
¹³ C-BDE-153	88	87	84	86	2
¹³ C-BDE-154	98	98	98	98	0
¹³ C-BDE-183	66	62	61	63	4
IS ¹³ C-2378-TCDF	83	65	58	69	18
IS ¹³ C-12378-PeCDF	80	67	65	71	12
IS ¹³ C-23478-PeCDF	82	72	61	72	15
IS ¹³ C-123478-HxCDF	90	75	60	75	20
IS ¹³ C-123678-HxCDF	89	72	60	74	19
IS ¹³ C-234678-HxCDF	88	75	60	74	18
IS ¹³ C-123789-HxCDF	80	72	57	70	17
IS ¹³ C-1234678-HpCDF	78	73	61	71	13
IS ¹³ C-1234789-HpCDF	71	70	60	67	9
IS ¹³ C-2378-TCDD	67	63	53	61	11
IS ¹³ C-12378-PeCDD	79	71	59	70	15
IS ¹³ C-123478-HxCDD	92	80	60	77	21
IS ¹³ C-123678-HxCDD	89	81	57	76	22
IS ¹³ C-1234678-HpCDD	82	73	58	71	17
IS ¹³ C-OCDD	66	62	52	60	12
¹³ C-CB-77	100	88	94	94	6
¹³ C-CB-81	99	90	96	95	5
¹³ C-CB-105	80	90	100	90	11
¹³ C-CB-114	82	87	100	89	11
¹³ C-CB-118	66	84	93	81	17
¹³ C-CB-123	79	89	100	90	12
¹³ C-CB-126	76	79	90	82	9
¹³ C-CB-156	84	89	97	90	8
¹³ C-CB-157	85	89	100	91	8
¹³ C-CB-167	89	87	94	90	4
¹³ C-CB-169	90	88	96	91	5
¹³ C-CB-189	96	89	100	95	6
¹³ C-CB-28	34	60	72	56	35
¹³ C-CB-52	52	68	74	65	17
¹³ C-CB-101	70	72	80	74	7
¹³ C-CB-153	83	79	86	83	4
¹³ C-CB-180	65	84	87	79	15
¹³ C-CB-194	62	77	74	71	12
¹³ C-CB-206	61	76	83	73	16
¹³ C-CB-209	112	144	151	136	15

3.1.2. Further separation and purification of fractions containing PCBs and PCDD/Fs

The separation of PCBs and PCDD/Fs was studied by using different chromatography columns with various solvent mixtures. Florisil chromatography column was found simpler and more efficient, which is accord with previous reports [6,13,14]. Eight centimetres of florisil was filled in the 9 mm i.d. glass column. Thirty-five milliliters of 6% DCM in hexane was selected to elute PCBs, followed by 150 ml of 100% DCM for the elution of PCDD/Fs.

A gel permeation chromatography column was used to remove high molecular weight interferences in the fraction of PCBs. After loading the sample extract containing PCBs, high molecular weight interferences were removed in the first 84 ml

Table 2

Data on PBDEs, PCBs and PCDD/Fs obtained from the analysis of the Certified Reference Material (WMF-01)

Compounds	Measured (pg/g)	Certified (pg/g)	Z-score
BDE-28	3243	3124 ± 290	0.41
BDE-47	123287	123200 ± 24800	0.00
BDE-99	37377	37500 ± 220	0.03
BDE-100	40733	35870 ± 14500	0.34
BDE-153	14165	17040 ± 8000	0.36
BDE-154	18535	19790 ± 2880	0.44
BDE-183	392	532 ± 400	0.35
CB-77	2425	2233 ± 720	0.27
CB-81	154	201 ± 58	0.80
CB-105	60933	49050 ± 14200	0.84
CB-114	4846	3523 ± 1670	0.79
CB-118	154207	130100 ± 32500	0.74
CB-123	4719	4233 ± 2620	0.19
CB-126	848	739 ± 260	0.42
CB-156	17472	14890 ± 5020	0.51
CB-157	4225	3488 ± 870	0.85
CB-167	9351	9750 ± 3090	0.13
CB-169	92	76 ± 30	0.54
CB-189	2263	2016 ± 611	0.40
2378-TCDF	13.75	13.10 ± 4.9	0.13
12378-PeCDF	0.07	1.53 ± 1.4	1.04
23478-PeCDF	7.61	7.15 ± 2.2	0.21
123478-HxCDF	0.27	0.86 ± 1.0	0.59
123678-HxCDF	0.30	0.51 ± 0.7	0.30
234678-HxCDF	0.31	0.68 ± 1.2	0.31
123789-HxCDF	0.05	0.25 ± 0.4	0.50
1234678-HpCDF	0.30	1.01 ± 1.9	0.37
1234789-HpCDF	0.03	0.30 ± 0.5	0.54
OCDF	0.72	1.38 ± 2.1	0.31
2378-TCDD	14.39	13.10 ± 4.4	0.29
12378-PeCDD	3.01	2.72 ± 1.3	0.22
123478-HxCDD	0.03	0.22 ± 0.3	0.63
123678-HxCDD	0.77	0.88 ± 0.4	0.28
123789-HxCDD	0.03	0.27 ± 0.4	0.59
1234678-HpCDD	0.39	0.59 ± 0.7	0.29
OCDD	4.83	3.91 ± 6.2	0.15

of 1:1 DCM:hexane, and PCBs were then eluted with additional 30 ml of 1:1 DCM:hexane. It was found that GPC was efficient for removing the chemicals that interfered with the quantification of PCBs, which is consist with the literature reports [15–17].

Further clean-up for the PCDD/Fs fraction was achieved by using the carbon column chromatography. The sample extract was loaded with 1:1 DCM:cyclohexane and the PCDD/Fs were eluted with 30 ml toluene.

Table 3

Background contamination of PCBs and PBDEs in method blanks ($n = 5$)

Congeners	Average (pg/sample)	R.S.D. (%)
PCB-77	0.21	17.5
PCB-105	2.82	19.3
PCB-118	6.30	17.8
BDE-47	6.94	12.4
BDE-99	3.43	20.5
BDE-153	ND	–

Table 4

Concentrations of PCBs, PCDD/Fs, and PBDEs detected in sediment samples from Haihe River and Dagou Drainage River (pg/g dw)

Name	H1	H2	H3	H6	H7	H8	H9	H10	N1	N3
BDE-15	28.4	40.3	37.4	50.2	19.5	50.0	829.8	363.7	1480.4	9985.6
BDE-17	2.7	2.0	5.3	5.3	2.3	9.8	3.3	1.6	31.7	7.4
BDE-28	12.6	10.1	28.8	16.9	8.1	28.9	17.2	6.7	168.1	201.3
BDE-47	45.1	67.8	158.5	30.3	24.7	69.7	17.4	8.2	756.4	23.0
BDE-49	14.4	13.2	40.0	19.7	9.1	30.4	10.3	4.0	281.3	9.6
BDE-66	10.4	8.6	22.0	8.1	6.9	18.4	2.5	1.0	88.5	3.1
BDE-71	0.7	0.5	1.1	1.2	0.4	2.0	0.3	0.1	2.3	0.3
BDE-77	2.3	1.7	3.6	2.1	1.4	5.7	0.5	0.2	13.3	0.5
BDE-85	1.4	2.5	1.8	1.9	2.0	3.3	0.4	0.1	40.4	1.8
BDE-99	31.2	59.9	183.7	25.5	29.2	26.5	8.8	4.2	983.1	15.8
BDE-100	7.9	22.4	43.4	6.0	5.0	5.4	2.8	1.1	198.3	4.7
BDE-119	0.4	0.4	0.8	0.3	0.2	0.9	0.1	0.1	0.6	0.4
BDE-126	6.4	5.0	8.0	5.9	1.6	16.9	0.6	0.3	12.3	10.0
BDE-138	3.2	1.9	4.1	2.5	2.0	7.7	0.9	0.6	9.8	2.5
BDE-153	18.9	29.9	1.2	29.4	24.6	18.4	4.1	2.1	308.1	6.6
BDE-154	7.0	16.0	19.0	9.2	4.9	4.9	2.0	1.0	113.7	2.4
BDE-183	49.9	19.1	61.0	137.9	48.0	64.2	18.6	5.3	487.5	26.5
Total-PBDEs	242.9	301.3	619.5	352.3	189.8	362.9	919.5	400.4	4975.8	10301.7
CB-77	31.5	112.5	186.3	357.2	173.5	53.2	29.9	13.1	235.0	121.7
CB-81	1.3	1.4	5.8	19.0	1.8	2.6	0.6	0.3	14.7	2.3
CB-105	34.7	48.6	230.6	504.6	84.1	102.7	26.5	11.6	256.8	98.3
CB-114	2.2	2.4	11.1	14.7	2.3	4.2	1.3	0.7	17.4	3.5
CB-118	75.4	102.9	429.1	1094.0	145.9	159.0	99.5	45.9	407.4	633.9
CB-123	3.8	3.8	21.3	44.1	6.7	10.5	5.7	4.5	19.5	73.2
CB-126	2.9	4.6	8.1	31.6	5.1	11.5	5.0	1.7	15.6	30.6
CB-156	9.3	16.0	72.7	156.5	25.8	73.4	13.7	6.5	54.5	62.8
CB-157	3.0	4.8	16.5	53.8	7.3	36.7	5.5	2.3	15.0	29.8
CB-167	4.2	7.4	26.4	66.7	10.9	51.5	9.8	4.0	24.9	57.0
CB-169	0.7	1.0	1.4	8.5	1.4	4.0	0.8	0.3	22.6	2.7
CB-189	1.4	3.1	5.2	32.1	3.5	37.7	5.3	2.0	11.1	22.2
CB-28	381.0	568.4	3591.1	5009.1	1092.8	535.6	294.1	172.3	5767.1	456.5
CB-52	151.0	215.0	727.6	1831.1	342.5	244.7	166.4	121.0	1403.2	247.0
CB-101	89.8	114.8	560.4	1318.1	221.1	361.4	186.7	82.0	725.2	790.5
CB-138	90.5	117.3	622.9	1236.2	209.7	406.5	106.3	59.4	437.4	278.4
CB-153	87.5	118.8	610.4	1533.9	253.7	437.6	186.2	84.0	500.4	577.9
CB-180	28.0	43.7	163.1	712.0	96.9	444.6	100.0	38.0	205.6	313.5
CB-209	31.4	60.9	200.8	933.5	156.8	495.3	1522.8	242.3	225.5	7187.7
Total-PCBs	1029.5	1547.4	7490.6	14956.4	2841.7	3472.5	2766.0	891.7	10358.7	10989.4
2378-TCDF	2.1	1.8	3.5	4.2	1.7	3.5	1.6	0.9	7.2	3.4
12378-PeCDF	2.1	2.0	0.9	1.7	0.5	5.5	1.3	0.3	8.6	4.9
23478-PeCDF	2.2	0.7	1.8	1.4	0.9	7.3	0.7	0.4	2.1	0.3
123478-HxCDF	3.6	6.6	6.5	13.6	4.7	76.5	17.9	7.4	37.8	125.3
123678-HxCDF	2.1	2.0	0.6	5.1	1.6	24.3	2.4	0.1	5.7	15.1
234678-HxCDF	1.5	1.9	0.9	3.9	1.4	21.5	3.2	1.4	6.2	35.0
123789-HxCDF	0.3	0.7	1.3	0.1	0.1	0.1	0.1	0.1	0.2	0.2
1234678-HpCDF	5.9	10.5	13.3	28.7	9.6	335.0	25.5	8.6	37.1	423.4
1234789-HpCDF	1.0	2.6	1.5	6.0	2.2	54.1	6.1	2.1	7.4	98.9
OCDF	7.8	19.3	25.9	69.5	23.9	721.9	141.2	47.0	71.6	3119.6
2378-TCDD	0.4	0.7	0.9	0.5	0.1	0.5	0.5	0.3	0.1	1.8
12378-PeCDD	0.1	0.4	0.8	0.1	0.1	0.1	0.9	0.5	0.2	0.2
123478-HxCDD	0.4	0.9	0.9	2.7	0.8	11.0	17.9	5.7	12.3	74.4
123678-HxCDD	0.3	2.3	0.9	13.1	5.3	61.6	12.6	3.8	13.0	141.3
123789-HxCDD	0.6	1.4	0.9	7.5	2.0	32.9	7.0	2.3	9.8	41.7
1234678-HpCDD	8.7	60.0	69.6	199.8	57.9	1056.6	271.2	80.8	215.0	3091.8
OCDD	63.4	333.1	326.7	984.1	317.2	5360.6	2928.6	992.3	2171.6	54147.4
Total-PCDD/Fs	102.7	446.7	457.1	1342.0	429.8	7773.1	3438.6	1153.8	2605.8	61324.7

3.2. Method validation

Method performance was evaluated by triplicate analyses of mixed standards including MBDE-MXC, 1613-LCS MXP and WP-LCS. The average recoveries and relative standard deviation (R.S.D.) of PBDEs, PCDD/Fs and PCBs are listed in Table 1. The results met the acceptance criteria specified in the US-EPA methods 1614-draft (25–150%), 1613B (17–185%) and 1668A (25–150%).

CRM sample (WMF-01) was analyzed to validate the developed single analysis method for the PBDEs, PCBs and PCDD/Fs. The results were satisfied with Z -score ≤ 1 for all congeners. The recoveries of PBDEs, PCBs and PCDD/Fs were 91–110, 64–101 and 78–101%, respectively, which again met the criteria specified in US-EPA method 1614-draft, 1668A and 1613B. Congener-specific concentrations of three groups of chemicals in WMF-01 are summarized in Table 2 and compared with the certified values.

3.3. Quantitative analysis of sediment samples

The method was applied for the analysis of 10 sediment samples collected from Haihe River and Dagou Drainage River in Tianjin City. Seventeen 2,3,7,8-substituted chlorinated congeners of PCDD/Fs, 12 WHO toxic congeners of PCBs, 6 indicator PCBs (PCB-28, -52, -101, -138, -153 and -180) and PCB-209 as well as 17 PBDEs (BDE-15, -17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154 and -183) were quantitatively determined. The background contamination of PCBs and PBDEs in method blanks is listed in Table 3. Concentrations of PBDEs, PCBs and PCDD/Fs determined in the sediment samples were listed in Table 4. Average recoveries for PCBs, PCDD/Fs and PBDEs are 45–92, 67–79 and 64–110%, respectively, which met the criteria specified in US-EPA methods 1668A, 1613 and 1614-draft.

The obtained results indicated that sediments from Haihe River were contaminated with PBDEs, PCBs and PCDD/Fs. The concentrations of PBDEs, PCBs and PCDD/Fs in the sediments from Haihe River were 189.8–10301.7 pg/g dry weight (dw), 891.7–14956.4 pg/g dw and 102.7–61324.7 pg/g dw, respectively. Serious PCDD/Fs pollution was found in Dagou Drainage River that is a municipal waste water discharging river. The detected profiles of PCDD/Fs show that the production of pentachlorophenol (PCP) or PCP-Na in this area may be the principal pollution source of PCDD/Fs, which is in accord with previously reported data [10]. The levels of PCBs and PCDD/Fs in site H10 were lower, compared to the results obtained from the previous sediment samples collected in July 2003. The difference in concentration may be due to the different sampling time because the samples analyzed in this study were collected during the flood season and the previously reported data referred to the samples collected in November. The contamination of PBDEs was investigated in this area for the first time. The results indicate that the contamination levels of PBDEs

were low in Haihe River and Dagou Drainage River in Tianjin City.

4. Conclusion

A more convenient and stable sample preparation procedure has been developed to allow the determination of PBDEs, PCBs and PCDD/Fs in one single environmental sample. Silver nitrate silica was successfully used to separate PBDEs from PCBs and PCDD/Fs. The entire method was validated through the analysis of WMF-01 certified reference fish tissue. The performance of the method is satisfied. The method was applied to analyze sediment samples. Contamination levels of PBDEs were first reported for the sediment sample collection areas, along with PCBs and PCDD/Fs levels compared with the data reported previously.

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