

# PRELIMINARY STUDY ON OCCURRENCE AND POSSIBLE SOURCES OF PCDD/Fs AND DL-PCB IN SURFACE SEDIMENTS IN NANTONG AND WUXI, CHINA

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## Introduction

PCDD/Fs mainly originate from natural or industrial processes associated with thermal pyrolysis, municipal solid waste incineration, sintering, secondary metal refinery and electric arc furnace steel making are reported the principal PCDD/Fs emission sources. Wild fires, pesticide usage (especially pentachlorophenols) also contribute to environmental PCDD/Fs. PCBs are a series of technically formulated chlorine-containing compounds, from 1965 to 1974 there are about 10000 tons PCBs are produced in China<sup>1</sup>, primarily as fluid in electric transformers and power capacities in China. Although PCBs production and usage were banned in 1974 the environmental concern on PCBs remains since PCBs sources still exist during disposal of the obsolete electric transformers and power capacities improperly, or still keep in use as an additive of painting<sup>2-3</sup>. It is reported that thermal process can be attributed to PCB production as well. dl-PCBs are components in the PCB technic mixture. PCDD/Fs and dl-PCBs are of the extreme high toxicity POPs for human and biota, thus are paid more attention.

Yangtze River Delta (YRD) is a region with the rapidest economic development in China, consisting of intensive industries and trade activities. As a sink of regional pollutant, sediment is often chosen to investigate the regional pollution status and temporal variations. Although there are reports on the POPs existence in the surface sediment in YRD, few attention were paid to the relations among cities and the local industrial development mode. In this study two cities of Nantong, Wuxi are studied to investigate the occurrence and characteristics of PCDD/Fs and dl-PCB, and try to identify the possible sources. The studied region is also characterized by comprise two important logistic transportation waterways, the Beijing-Hangzhou Grand Canal and Yangtze River, which bring the prosperous logistic transportation there.

YRD is at the Yangtze River's mouth to the Yellow sea in south China. The Beijing-Hangzhou Canal across the city of Wuxi, in northeastern direction and not far away locates Nantong at the side of Yangtze River. Both two cities have intensive light industries of chemical engineering, textile, electronic appliance production and logistic transportation, while Nantong have more transportation proportion comparing to Wuxi. 16 surface sediment samples were collected in the rivers of Nantong and Wuxi, the Beijing-Hangzhou Grand Canal and Yangtze River, from October to November, 2009, sampling locations are shown in Fig.1. A grab sampler were used to collect the surface sediments about 5cm in depth, samples then were put to a prewashed stainless steel can using a clean steel spoon. After wrapped by a self-sealed plastic bag the cans were transferred to the laboratory on ice and keep in a freezer before analysis.

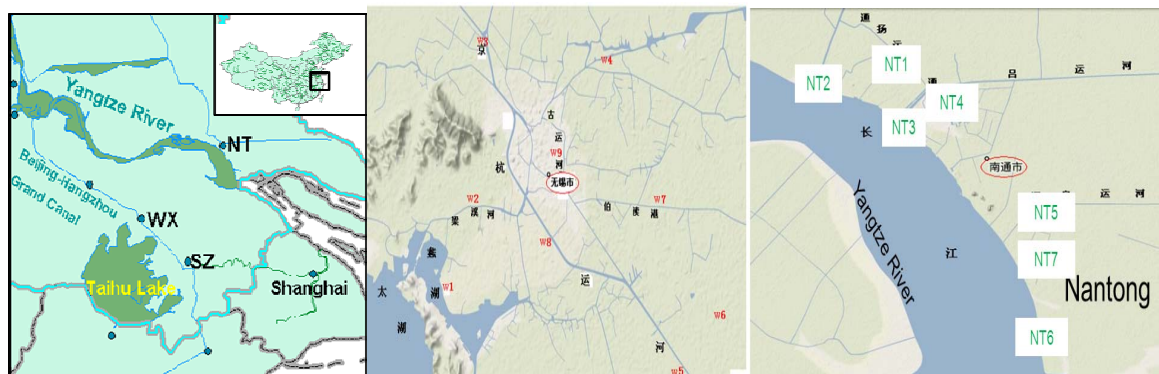


Figure 1 Sampling sites of surface sediments in Nantong and Wuxi

### Materials and methods

The analytical method for PCDD/Fs and dl-PCBs employed is a modified version of the US EPA method 1613 for PCDD/Fs by isotope dilution, high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS). The method can be described in brief as follows: The samples are cool-dried, ground and pass through a 1mm mesh sieve. Soxhlet extraction are performed with solvent toluene for 16 h and meanwhile the activated copper beads are added to remove the Sulfate in the samples. After concentrate and change solvent to hexane, the extracts are spiked with clean up internal standards, <sup>13</sup>C-labeled substituted PCDD/Fs (EPA-1613LCS, Wellington Lab, Canada) and dl PCBs (EDF-5324, Cambridge Isotope Laboratory, USA). The extracts were firstly applied to a sulfuric acid treatment and then cleaned through a multilayer silica column packed, from the bottom to the top, with 3 g anhydrate sodium sulfate, 1 g neutral silica gel, 3 g 2% NaOH silica gel, 1 g neutral silica gel, 4.5 g 44% sulfuric acid silica gel, 6 g 22% H<sub>2</sub>SO<sub>4</sub> silica gel, 1g neutral silica gel, and 2g anhydrate sodium sulfate, then eluted with 200 mL hexane. Concentrated extracts were then fractionated with an activate carbon column (1 g anhydrate sodium sulfate, 1 g embedded activate carbon silica gel, and 1 g anhydrate sodium sulfate) by eluting with 200 mL 25% hexane/dichloromethane (F1, containing mono-ortho PCBs) and 250 mL toluene (F2, containing PCDD/Fs and non-ortho PCBs). The fractions were concentrated and evaporated to near dryness by a gentle nitrogen stream. Before instrument analysis, <sup>13</sup>C-labeled syringe internal standards of PCDD/Fs (EPA-1613ISS, Wellington Lab, Canada) and dl PCBs (EDF-5325, Cambridge Isotope Laboratory, USA) were spiked.

Instrumental analysis are performed with an Agilent high resolution gas chromatography (HRGC) couple to a Autospec-Ultma NT high resolution mass spectrometry (HRMS) using electron impact ionization (ionizing energy 35ev at a resolution over 10000). A DB-5MS (60 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column (J&W Scientific; CA, USA) was used for separating PCDD/Fs and dl-PCB in splitless injection mode. The target compounds include 17 2, 3, 7, 8-chlorine substituted PCDD/F congeners, 12 dl-PCBs congeners with WHO toxic equivalent factor values. Dl-PCBs results are obtained by combining the F1 and F2 fraction for each sample.

The recoveries of the <sup>13</sup>C-labeled PCDD/Fs ranging from 17% to 181% met the criteria of EPA 1613 method for PCDD/Fs. The recoveries of the <sup>13</sup>C-labeled dl-PCB, ranged from 40% to 130% can be accepted by the USEPA method 1668A. The detection limits for PCDD/Fs and dl-PCBs are 0.15 to 6.5 ng/kg d.w. and 0.71 to 3.65 ng/kg d.w., respectively.

### Results and discussion

#### Concentrations and site distributions

The analytical results for PCDD/Fs and dl-PCBs are listed in Table 1 and 2.

Table 1 PCDD/Fs in the surface sediments in Yangtze river middle and lower reaches (ng/kg d.w.)

Sample sites	WX1	WX2	WX3	WX4	WX5	WX6	WX7	WX8	WX9	NT1	NT2	NT3	NT4	NT5	NT6	NT7
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2378-TCDF	6.36	3.44	12.28	7.44	2.45	0.50	7.27	1.97	N.D.	3.28	N.D.	1.47	0.49	0.80	N.D.	0.47
12378-PeCDF	14.7	15.2	5.89	8.93	6.36	0.99	3.39	1.48	N.D.	1.41	N.D.	0.98	1.98	0.40	N.D.	N.D.
23478-PeCDF	19.6	9.35	5.89	11.4	8.81	N.D.	9.21	N.D.	N.D.	3.75	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
123478-HxCDF	17.1	21.6	10.3	11.4	23.0	N.D.	26.2	N.D.	3.46	10.8	N.D.	3.91	5.44	2.00	3.95	N.D.
123678-HxCDF	18.6	26.1	5.89	10.9	21.0	2.97	10.2	1.97	1.98	9.85	N.D.	3.91	4.45	1.00	3.46	2.37
123789-HxCDF	N.D.	1.48	0.98	0.99	N.D.	N.D.	N.D.	N.D.	N.D.	0.94	N.D.	N.D.	N.D.	N.D.	N.D.	0.95
234678-HxCDF	18.1	23.1	6.88	11.4	32.8	2.97	8.24	1.97	1.48	6.10	N.D.	3.42	4.45	0.60	3.95	3.32
1234678-HpCDF	27.4	101	31.43	32.8	133	12.9	27.6	8.87	5.44	40.8	5.20	17.6	20.3	6.19	14.8	9.00
1234789-HpCDF	3.91	60.0	3.44	3.47	28.4	1.49	7.27	1.48	1.48	10.8	N.D.	3.91	1.48	0.40	3.46	1.90
OCDF	19.6	142	64.83	12.4	126	12.9	31.5	15.3	N.D.	97.1	N.D.	31.3	36.6	59.9	18.8	N.D.
2378-TCDD	0.98	N.D.	N.D.	N.D.	N.D.	N.D.	0.48	N.D.	N.D.	0.47	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
12378-PeCDD	4.89	1.48	N.D.	1.99	N.D.	N.D.	0.97	N.D.	N.D.	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
123478-HxCDD	2.94	1.48	N.D.	N.D.	3.42	N.D.	1.45	N.D.	N.D.	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
123678-HxCDD	3.91	0.00	N.D.	2.48	6.36	N.D.	2.42	N.D.	N.D.	1.88	N.D.	2.93	1.98	N.D.	N.D.	N.D.
123789-HxCDD	2.94	1.97	N.D.	1.99	5.87	N.D.	1.45	N.D.	N.D.	1.41	N.D.	N.D.	1.98	N.D.	1.48	N.D.
1234678-HpCDD	11.3	35.4	20	16.4	66.0	8.92	18.9	4.93	3.46	21.6	13.0	55.7	34.6	5.59	23.7	12.3
OCDD	72.9	175	216	71.0	283	85.7	141	69.0	51.9	327	202	893	708	109	425	97.6
TCDFs	444	159	420	166	79.0	40.0	119	44.0	20.0	98.0	31.0	55.0	75.0	33.0	43.0	42.0
PeCDFs	333	155	245	140	109	34.0	126	31.0	25.0	109	25.0	52.0	73.0	32.6	44.0	54.0
HpCDFs	41.0	216	53.0	47.0	228	19.0	49.0	12.0	10.0	72.0	10.0	40.0	33.0	10.4	30.0	18.0
HxCDFs	167	162	80.0	101	186	28.0	89.0	19.0	19.0	78.0	9.9	36.0	40.0	11.6	31.0	28.0
OCDF	N.D.	142	65.0	N.D.	126	N.D.	31.0	N.D.	N.D.	97.0	N.D.	31.0	37.0	59.9	N.D.	N.D.
TCDDs	124	36.0	60.0	28.0	14.0	19.0	30.0	6.4	9.4	28.0	2.8	13.0	17.0	6.6	5.4	16.0
PeCDDs	117	20.0	45.0	59.0	21.0	18.0	25.0	3.5	7.4	30.0	5.2	8.3	17.0	3.6	5.9	26.0
HxCDDs	44.0	30.0	28.0	40.0	51.0	7.9	34.0	7.9	3.5	29.0	4.2	19.0	21.0	4.6	14.0	23.0
HpCDDs	23.0	81.0	44.0	34.0	125	20.0	40.0	14.0	9.9	55.0	30.0	130	83.0	13.6	54.0	28.0
OCDD	73.0	175.0	216.0	71.0	283	86.0	141	69.0	52.0	327	202	893	708	109	425	98.0
1-TEQ	21.5	16.4	7.70	12.4	16.9	1.03	12.2	0.90	0.85	6.99	0.38	3.31	3.29	0.75	2.15	1.04
WHO-TEQ <sub>1998</sub>	23.8	16.8	7.45	13.3	16.5	0.94	12.5	0.83	0.80	6.61	0.20	2.48	2.62	0.60	1.75	0.95
Σ PCDFs/Σ PCDDs	2.59	2.44	2.20	1.96	1.47	0.80	1.53	1.05	0.90	0.97	0.31	0.20	0.30	1.07	0.29	0.74

ND: not detected

Table2 dl-PCBs in the surface sediments in Yangtze river middle and lower reaches (ng/kg d.w.)

Sampling sites	WX1	WX2	WX3	WX4	WX5	WX6	WX7	WX8	WX9	NT1	NT2	NT3	NT4	NT5	NT6	NT7
PCB 81	0.001	0.001	0.005	N.D	0.003	N.D	0.003	0.002	0.001	0.033	0.005	0.001	0.001	0.002	0.004	0.001
PCB 77	3.01	19.10	87.98	18.14	87.12	4.61	1.27	24.05	6.98	0.32	4.16	33.55	1.07	50.89	67.49	1.89
PCB123	N.D	0.002	0.026	0.005	0.008	0.001	0.082	0.006	0.022	0.012	0.004	0.004	0.005	0.004	0.002	0.003
PCB 118	0.024	0.039	0.221	0.114	0.154	0.034	1.037	0.100	0.461	1.035	0.026	0.082	0.397	0.040	0.016	0.074
PCB 114	N.D	0.001	0.011	0.013	0.004	0.002	0.018	0.003	0.006	0.048	N.D	0.002	0.008	N.D	N.D	N.D
PCB 105	0.011	0.015	0.084	0.036	0.059	0.015	0.397	0.034	0.138	0.336	0.012	0.037	0.133	0.017	0.007	0.031
PCB 126	N.D	0.002	0.008	0.004	0.005	0.001	0.007	0.003	0.006	0.006	N.D	0.002	0.003	0.006	0.011	0.001
PCB 167	0.002	0.003	0.029	0.008	0.016	0.003	0.052	0.008	0.029	0.057	0.002	0.004	0.027	0.005	N.D	0.006
PCB 156	0.003	0.005	0.022	0.012	0.029	0.005	0.101	0.011	0.061	0.150	0.003	0.011	0.062	0.007	0.003	0.013
PCB 157	0.001	0.002	0.015	0.005	0.008	0.002	0.030	0.004	0.015	0.032	N.D	0.003	0.013	0.002	N.D	0.004
PCB 169	N.D	N.D	0.002	N.D	0.001	N.D	0.001	0.001	0.001	0.001	N.D	0.003	0.001	0.001	N.D	N.D
PCB 189	N.D	N.D	0.006	N.D	0.005	0.001	0.008	0.002	0.005	0.015	N.D	N.D	0.007	0.002	N.D	0.003
WHO-TEQ <sub>1998</sub>	0.348	2.158	9.642	2.225	9.262	0.614	1.102	2.694	1.426	0.930	0.463	3.633	0.526	5.746	7.868	0.333

The sum WHO-TEQ<sub>1998</sub> value of seventeen 2,3,7,8-substituted PCDD/Fs in 16 surface sediments possesses a median of 2.55 ng WHO-TEQ<sub>1998</sub>/kg d.w., with a range of 0.20-23.8 ng WHO-TEQ<sub>1998</sub>/kg d.w.. The sum TEQ value for 12 dl-PCBs are with a median of 1.43 ng WHO-TEQ<sub>1998</sub>/kg d.w., ranges between 0.33 to 9.64 ng WHO-TEQ<sub>1998</sub>/kg d.w., The total WHO-TEQ<sub>1998</sub> ( sum of PCDD/Fs-TEQ and dl-PCB-TEQ) is from 1.18 to 24.7 ng WHO-TEQ<sub>1998</sub>/kg d.w. with a median of 9.95 ng WHO-TEQ<sub>1998</sub>/kg d.w., such TEQ level is slightly higher than that in Liaohhe middle and lower reaches<sup>4</sup>, higher than the data in 2005 for Yangtze river<sup>5</sup>, but much lower than the heavy polluted sites, as Haihe River<sup>6</sup>, Dongjiang River<sup>7</sup> and Pearl River Delta<sup>8</sup>. In this study dl-PCBs derived TEQ account for 41.5% in average of total WHO-TEQ<sub>1998</sub>, a percentage is higher than some areas reported in China, which may be caused by the very low concentration of tetra to hexa CDD congeners in some samples, since zero were assigned to the congener when its results below the detection limit in TEQ calculation.

Among 16 surface sediments, WX5, WX1 and WX2 are the three sites with the highest total WHO-TEQ<sub>1998</sub> values of 25.8, 24.1 and 19.0 ng WHO-TEQ<sub>1998</sub>/kg d.w., respectively. Site WX5 belongs to Beijing-Hangzhou Grand Canal, both WX1 and WX2 are park lakes. The boat coating and chlorine-containing herbicides used in the park may contribute to the higher PCDD/Fs in surface sediments, but the exact PCDD/Fs emission sources in

these sites should be further conformed. In general total WHO-TEQ<sub>1998</sub> values in Nantong surface sediments are obviously lower than that in Wuxi, which may be explained by the differences of the industrial plant scale and quantity between these two cities.

Homologue profile and the possible sources

PCDD/Fs homologue profile is shown in Fig.2.

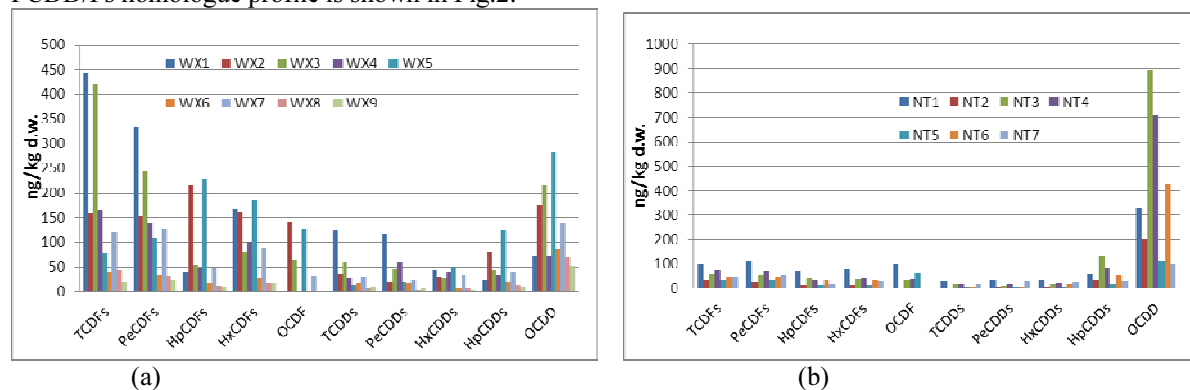


Figure 2 PCDD/Fs homologue profiles in sediments for (a) Wuxi, (b) Nantong

The ratio of  $\Sigma$ PCDFs/ $\Sigma$ PCDDs can be looked as an indicator to identify the possible PCDD/Fs sources. The ratio larger than 1.0 imply the sources associated with thermal pyrolysis, primarily from industrial processes, while a ratio less than 1.0 normally indicate a natural source or usage of pentachlorophenols. As shown in Fig.2 and Table 1, 7 in 9 WX surface sediments have  $\Sigma$ PCDFs/ $\Sigma$ PCDDs ratios larger than 1.0, contrarily there is only 1 sample in 7 NT sediments with a ratio more than 1.0. This phenomenon strongly suggests that more industrial emission sources of PCDD/Fs existed in Wuxi than in Nantong.

The congener patterns of dl-PCB in 16 surface sediments are similar. Differing from the findings of PCB 118 are predominant dl-PCBs congener in the surface sediment in some studies, in this work PCB 77 is found of the most abundance, then followed by PCB 118. It is reported the proportion of PCB (126+169)/PCB(77+126+169) varied according to the different sources<sup>9</sup>. In PCBs technical mixture the proportion is about 1% while in combustion process the proportion increase to about 50%. In this work the proportions are calculated from 0 to 2.14%, indicating the principal dl PCBs source are PCB technical mixture.

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