Transport and Sediment Profiles of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ya-Er Lake, China

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Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) are ubiquitous environmental pollutants. Chemical production and combustion processes are the two primary sources of PCDD/F to the environment[1)]. Because of the high toxicity of some individual PCDD/F, it is important to understand their environmental behavior, such as transport, deposition and sink. A lot of work has been done on the emission from incineration and the transport by air[2,3)]. Eitzer and Hites demonstrated that atmospheric transport is the major source of air-born PCDD/F to Great Lakes[2)]. However, source reconciliation studies based on atmospheric release estimates can only account for approximately 10% of environment loading of PCDD/F[4)]. PCDD/F are highly lipophylic, poorly soluble, have a low volatility and adsorb strongly to particles and surfaces. Thus, PCDD/F are immobile once they become incorporated into the sedimentary sink[5)]. Emissions of PCDD/F into water are not as well investigated and have not been analyzed with the same intensity as air emissions of these substances[6)].

Ya-Er lake is located in the eastern part of Hubei, China. It is a shallow and eutrophic lake and has been polluted by organic chlorine e.g. hexachlorocyclohexanes (HCH), chlorobenzenes (CB), chlorophenols (CP) and heavy metals by direct discharge of waste effluent from a large chemical plant[7)]. High amounts of PCDD/F have been detected in the sediment near the effluent entrances[8)]. Though the plant ceased to discharge waste effluent to the lake area in 1992, now it is important to survey the distribution and history input of PCDD/F in this lake area to better understand their environmental behavior and provide valuable information for the lake reclamation and restoration management.

Materials and methods

Sample collection

Sediment cores were taken in the middle of the first three ponds of Ya-Er Lake by a kajak sediment sampler in July 1996. The sampling locations were shown in a previous paper[9)]. The total depth of each core was 60 cm. The cores were immediately sliced into 5 layers with a Teflon knife and each layer was 12 cm in depth. Three cores were taken in each pond and the corresponding layers are mixed. The water depth of the lake is 2-3 m and the pH of the water is 7.5-7.9.

Sample extraction

After homogenization, samples were freeze-dried and ground. 2-20 g of the sample was weighted in shell. Prior to extraction, the sample was spiked with $^{13}C_{12}$ labeled 2,3,7,8-substituted PCDD/F internal standards. Extraction was carried out by Soxhlet using 180 ml toluene for 24 hours.

Clean-up

Following the extraction, in order to remove interferences, a clean up based on several liquid chromatography steps was applied according to the method by Schramm[10]. The multiple column chromatography included basic and super active alumina, sulfuric acid coated and active silica, deactivated florisil™ and small basic and super active alumina. All columns were covered with Na_2SO_4. Prior to analysis, the sample was reconstituted with a recovery standard (1,2,3,4-$^{13}C_{12}$ Cl_4DD, 100 pg/µl)

Instrumental analysis

The identification and quantification were accomplished with capillary GC/MS system where a high resolution gas chromatography (HRGC) is obligatory. After splitless injection, the sample was separated on a Rt_x 2330 polar capillary GC column (60 m x 0.25 mm ID x 0.25 µm) and quantified by Finnigan MAT 95 mass spectrometer at resolution 10000.

Results and discussion

Time estimating of the sediment core

Before 1962, Ya-Er lake was an oligotrophic lake. From 1962-1978, the lake was seriously polluted by HCH isomers and waste effluent from a large chemical plant. In 1979 a series of five ponds were built for the waste effluent treatment by self oxidative purification[7]. Visual inspection of the sediment core revealed that the ground at the basin of the pond was yellow. Most of the black layers (0-48 cm) originated from the waste effluent. We can estimate that the deposition at 48 cm in core of pond 1 is corresponding to the year of 1962, the time when the pollution by the waste effluent started. Sediment layer of 36-48 cm is the deposition from 1962-1970; 24-36 cm layer, 1970-1978; 12-24 cm layer, 1978-1986; 0-12 cm layer, 1986-1996. The sedimentation rate is about 1.2 cm/year. This rate is a little faster than that in other lakes (0.4 cm/year)[11], because Ya-Er lake receives the direct discharge of the waste from the plant. The time is roughly dated, just according to the history of the lake.

History input of PCDD/F into the lake sediment

The amount of PCDD/F in the sediment core of pond 1 was shown in Table 1. We can see that the concentration of PCDD/F in the layer of 48-60 cm was very low (57.73 ng/kg). This layer was dated before 1962 when there was no chemical plant. 36-48 cm layer corresponds to 1962-1970 when the plant began to discharge waste water. The highest concentration of PCDD/F was found in the sediment layer of 24-36 cm corresponding to the years of 1970-1978. At that time, a lot of HCH was produced for pesticide use. The PCDD/F in this layer may form as the by-product of the HCH production process. The dominate homologues are OCDD and TCDF. Due to the destroy of the ecosystem by the effect of the high concentration of HCH on the aquatic biota and fish, in 1979 a series of pond was built for waste effluent treatment by self oxidative purification. In 12-24 cm layer, the dominate congeners are also OCDD and TCDF, but the pattern changes. The concentration of PCDD was lower, that of PCDF was higher than during 1970-1978, because in 1983 HCH was banned to be used as pesticide and the plant ceased to produce this chemical. The main production of the plant was shifted to chlorophenols (CP). This layer may be due to the by-products of the manufacturing of CP. The 0-12 cm layer represents the last ten years deposition of the waste from the plant. The concentration of PCDD especially OCDD decreased, but the concentration of most PCDF congeners increased. Recently the main contributor of toxicity of the sediment pollutants shifted from PCDD to PCDF.

Transport of PCDD/F along the flow direction

Comparing the upper layer of all the three ponds, we can see that high concentrations of OCDD, TCDD, TCDF can also be detected in pond 3. Though pond 2 and 3 have lower sedimentation rates than pond 1, the 0-12 cm layer may represent the years of 1982-1996, the transportation of PCDD/F can be found from the pond 1 to pond 2 and 3. From Fig 1 we can see that PCDD especially OCDD is easier to be transported than PCDF. In pond 1 the ratio of the concentration of PCDF to PCDD is 2, but in pond 2 and 3 the ratio is only 0.5. More PCDF especially TCDF still stay in pond 1. This transportation of PCDD/F in the lake may be carried by the co-contaminated pollutants and the organic coated particles. The differences of the co-transportation of PCDD and PCDF need more investigation.

Conclusion

Sediment cores of 3 ponds in the contaminated Ya-Er lake area were collected to investigate the history input and transport of PCDD/F in the sediment. The results indicate that the highest concentrations of PCDD are found around 1970-1978, when a lot of lindan was produced in the plant. In recent years, the contributor of toxicity of the sediment pollutants shifted from PCDD to PCDF. PCDD/F can be transported by particles from the source of the effluent to pond 2 and pond 3.

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Table 1. PCDD/F in Ya-Er lake sediment core of pond 1 (ng/kg)

PCDD/F	0-12 cm	12-24 cm	24-36 cm	36-48 cm	48-60 cm
sum TCDD	173.63	165.53	183.31	10.75	0.00
sum PeCDD	16.93	92.32	177.25	25.43	0.00
sum HxCDD	111.39	262.18	387.08	203.06	0.32
sum HpCDD	201.87	431.8	614.23	375.92	3.05
OCDD	2271.9	4578.79	5269.46	3559.41	53.77
sum TCDD to OCDD	2775.71	5530.63	6631.33	4174.57	57.15
2,3,7,8-TCDD	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDD	nd	nd	nd	nd	nd
1,2,3,4,7,8-HxCDD	1.04	29.77	44.51	18.09	nd
1,2,3,6,7,8-HxCDD	nd	1.7	11.39	0.76	nd
1,2,3,7,8,9-HxCDD	nd	nd	1.58	nd	nd
1,2,3,4,6,7,8-HpCDD	57.85	139.55	208.21	102.17	0.23
sum TCDF	2411.35	1696.63	1469.45	321.47	0.39
sum PeCDF	483.39	403.17	386.99	35.56	0.02
sum HxCDF	430.19	378.99	327.73	33.97	0.16
sum HpCDF	292.17	277.93	199.21	28.03	0.02
OCDF	931.2	709.89	563.51	78.34	nd
sum TCDF to OCDF	4548.31	3466.6	2946.3	497.36	0.58
2,3,7,8-TCDF	99.71	77.15	56.35	8.31	0.01
1,2,3,7,8/1,2,3,4,8-PeCDF	67.23	51.18	50.62	8.02	0.01
2,3,4,7,8-PeCDF	114.28	71.71	76.65	4.71	nd
1,2,3,4,7,8/1,2,3,4,7,9-HxCDF	138.94	99.3	93.19	7.66	nd
1,2,3,6,7,8-HxCDF	80.04	47.57	37.71	2.86	nd
1,2,3,7,8,9-HxCDF	nd	1.54	2.62	nd	nd
2,3,4,6,7,8-HxCDF	16.47	18.06	15.6	0.88	0.01
1,2,3,4,6,7,8-HpCDF	195.44	141.18	90.19	14.27	0.02
1,2,3,4,7,8,9-HpCDF	37.81	45.31	35.56	0.4	nd
sum PCDD/F (tetra to octa)	7324.02	8997.23	9577.63	4671.94	57.73
I-TEQ	100.23	74.47	76.32	11.42	0.06

n.d. not detected.

Fig. 1 PCDD/F in Ya-Er lake sediment (0-12 cm)