POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS, PENTACHLOROPHENOL, PENTACHLOROANISOLE AND HEXACHLOROBENZENE IN SEDIMENTS OF THE YANGTSE RIVER AND THE LIAO-HE RIVER IN CHINA

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Introduction

The Yangtse River is the third largest river in the world draining with over 700 tributaries an enormous area in South China. PCP-Na has been sprayed widely in this area to control the spread of schistosoma japonica in lakes and rivers since 1960[1]. In order to estimate the impact of this treatment on the water quality of the Yangtse River, the contamination of sediments with pentachlorophenol (PCP), its conversion product pentachloroanisole (PCA)[2] and possible by-products of PCP-Na such as hexachlorobenzene (HCB) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) were investigated. As reference, sediments of the Liao-He River in the north-east region of China, where the schistosomiasis was a minor problem, were examined.

Methods

Sampling: Sediment samples were taken and prepared according to the procedures described in detail elsewhere[3]. Samples were taken at several sites across the rivers at four stations of the Liao-He River in the area of Xinmin and at four stations of the Yangtse River in the area of Nanjing during five sampling campaigns in May, Dec. 1998 and March, June, Sep. 1999.

PCDD/F Analysis: The procedure was described in detail elsewhere[4]. The analysis of PCDD/F in sediments includes isotope dilution, Soxhlet-extraction with toluene, several clean-up steps and measurement by HRGC/HRMS.

Analysis PCP, PCA and HCB: The analysis PCP, PCA and HCB is part of a procedure for the determination of chlorinated organic compounds in sediment and suspended solids[5] and includes isotope dilution, ultrasonic extraction with water/methanol/n-hexane (10/10/25), clean-up on silica gel, acetylation of PCP and measurement by GC/MS.

Analysis of organic carbon (Corg): Corg was determined by acidification, dry combustion and thermal conductivity detection according to ISO 10694.

Results and discussion

Table 1: Concentrations of PCP, PCA, HCB and Corg in sediments of the Yangtse and Liao-He

Yangtse station /site	date	River Corg. %	PCP ng/g	PCA ng/g	HCB ng/g	Liao-He station /site	date	River Corg. %	PCP ng/g	PCA ng/g	HCB ng/g
1/3	May 98	0,07	x	0,08	0,09	1/1	May 98	0,03	x	nd	0,05
1/4	May 98	0,08	0,49	0,11	0,10	1/2	May 98	0,26	0,17	0,06	0,15
1/5	May 98	0,83	1,52	1,02	6,92	1/3	May 98	0,06	0,15	nd	0,06
2/1	May 98	0,53	2,11	0,57	3,08	1/4	May 98	0,14	0,15	nd	0,08
2/2	May 98	0,66	3,33	0,77	4,12	1/5	May 98	0,04	0,15	nd	0,06
2/6	May 98	0,08	0,49	0,15	0,29	1/6	May 98	0,06	0,17	nd	0,07
2/R	May 98	x	2,38	0,47	3,12	1/7	May 98	0,21	0,16	nd	0,12
3/5	May 98	0,78	3,86	0,83	4,11	2/1	May 98	0,46	0,25	0,11	0,23
4/1	May 98	0,07	x	0,10	0,15	2/2	May 98	0,16	0,19	nd	0,10
4/2	May 98	0,07	x	0,10	0,12	2/3	May 98	0,29	0,18	0,05	0,13
4/3	May 98	0,11	0,45	0,13	0,13	2/4	May 98	0,33	0,17	nd	0,11
4/6	May 98	0,74	2,06	0,61	4,86	2/5	May 98	0,38	0,17	0,05	0,16
1/1	Dec 98	0,55	2,67	0,61	4,56	3/1	May 98	0,10	0,21	0,13	0,21
1/5	Dec 98	0,52	1,48	0,77	2,68	3/2	May 98	0,06	0,22	0,16	0,20
2/2	Dec 98	0,15	0,59	0,36	0,57	3/3	May 98	0,91	0,18	0,05	0,09
2/6	Dec 98	0,48	1,70	0,34	3,90	3/4	May 98	0,08	0,21	0,15	0,30
3/1	Dec 98	0,40	0,74	0,43	1,42	3/5	May 98	0,77	0,19	0,10	0,16
3/5	Dec 98	0,58	2,14	0,65	3,75	4/1	May 98	0,43	0,27	0,05	0,09
1/1	Mar 99	0,65	2,46	0,54	0,40	4/3	May 98	0,12	0,18	nd	0,08
1/5	Mar 99	0,34	3,80	0,58	3,63	4/4	May 98	0,47	x	0,15	0,41
2/2	Mar 99	0,15	0,52	0,20	1,41	4/5	May 98	0,25	0,17	0,06	0,13
2/6	Mar 99	0,16	0,31	0,13	0,29	1/3	Dec 98	0,19	0,13	nd	0,07
3/1	Mar 99	0,60	1,55	0,40	1,02	2/5	Dec 98	1,28	0,15	0,11	0,16
3/5	Mar 99	0,25	0,89	0,20	1,00	3/2	Dec 98	0,02	nd	nd	nd
1/1	**Jun 99**	**0,31**	**512,61**	**12,28**	**14,13**	4/2	Dec 98	0,08	0,10	0,06	0,06
1/5	**Jun 99**	**0,48**	**11,11**	**2,10**	**4,10**	1/3	Jun 99	0,44	0,10	0,05	nd
2/2	Jun 99	0,47	1,55	0,46	3,16	1/5	Jun 99	0,10	nd	0,06	nd
2/6	Jun 99	0,72	3,92	1,50	7,89	2/3	Jun 99	0,03	nd	nd	nd
3/1	Jun 99	0,65	1,65	0,52	3,65	2/5	Jun 99	1,05	0,24	0,18	nd
3/5	Jun 99	0,68	3,37	1,08	4,47	3/2	Jun 99	0,07	nd	nd	nd
1/1	Sep 99	0,51	3,43	1,00	6,09	4/2	Jun 99	0,63	0,25	nd	nd
1/5	Sep 99	0,65	1,89	0,70	3,87						
2/2	Sep 99	0,55	1,87	0,86	4,61						
2/6	Sep 99	0,81	2,23	0,65	5,08						
3/1	Sep 99	0,37	1,18	0,27	0,54						
3/5	Sep 99	0,66	x	1,74	5,85						

High variations of PCP, PCA and HCB in sediments of the Yangtse River could be observed between the sampling sites but also between the sampling dates at the same sampling site. The concentrations of PCP, PCA and HCB were significantly correlated to the organic carbon content (Corg) of the sediments (n=29, 33, 33; $p<0.01$). It can be assumed that the concentrations of these chlorinated compounds were the result of the concentrations in water and the sorption properties of the sediment. Except station 1 in June 99 the sediments show no obvious input of the organochlorines in the area of Nanjing. It can be assumed that the treatment with PCP-Na to

control the schistosomiasis was the main source of the PCP contamination in sediments of the Yangtse River. PCA was found in each Yangtse sediment and the concentrations were significantly correlated to the PCP concentrations (n=29; $p<0.01$). HCB was the most abundant compound in nearly all Yangtse sediments. It was an intermediate of the PCP production[4] and could be a by-product of technical PCP, but it was also used as pesticide in China[4].

The sediments of the sites 1/1 and 1/5 from June 30th exhibited much higher PCP, PCA and HCB concentrations, while the concentrations of Corg and other contaminants like PCBs, DDE and lindane remained low. The high concentrations at site 1/1 were probably the result of an accidental discharge of PCP formulation or another kind of PCP containing product upstream to this sampling point. The discharge had also slightly influenced the sediment 1/5 at the other side of the river, which also exhibited an elevated PCP concentration, but the stations 2 and 3 downstream were not affected.

The next sampling in Sept. 99 showed no elevated concentrations anymore. Between June and September was the flood season with high water level, water discharge and current velocity and the force to resuspend the settled particles of sediment; probably the contaminated sediment was simply washed out.

The concentrations of PCP, PCA and HCB were much lower in sediments of the Liao-He River. The schistosomiasis is not a problem of the North East part of China. PCP was also used as wood preservative or perhaps emitted by the washing process of PCP containing clothes[6].

Table 2: PCDD/F (ng/kg)in sediments of the Yangtse River and the Liao-He River.

River	Liao-He	Yangtse	Yangtse	Yangtse
Date	06. 15. 99	05. 16. 98	05. 16. 98	06. 30. 99
Station/Site	2/2	2/R	2/2	1/1
Sum Tetrachlorodibenzo-p-dioxins	nd	nd	1.7	5.4
Sum Pentachlorodibenzo-p-dioxins	nd	0.3	1.2	4.5
Sum Hexachlorodibenzo-p-dioxins	nd	7.7	3.5	74.1
Sum Heptachlorodibenzo-p-dioxins	3.4	40.3	32.3	333.7
Octachlorodibenzo-p-dioxin	12.7	953.4	685.5	22752.6
Sum Tetrachlorodibenzofurans	0.3	1.3	5.0	1.3
Sum Pentachlorodibenzofuran	0.1	0.8	2.1	1.1
Sum Hexachlorodibenzofuran	0.4	1.7	2.3	6.2
Sum Heptachlorodibenzofuran	0.6	4.9	3.5	3.9
Octachlorodibenzofuran	0.8	14.1	14.3	14.2
Sum PCDD and PCDF (Tetra to Octa)	18.2	1024.6	751.3	23197.0
% OCDD of the sum PCDD/F	70	93	91	98
TE (NATO/CCMS)	0.1	1.8	1.2	34.9
TE (WHO 1998)	0.1	1.1	0.6	15.5

The PCDD/F concentration in the sediment 2/5 of the Liao-He was $1^1/_2$ orders of magnitude lower than in the sediments 2/2 and 2/R of the Yangtse River (Table 2). Highest PCDD/F concentration was found in sediment 1/1. In all sediments octachlorodibenzo-p-dioxin (OCDD) was the most

abundant compound. More than 90 % of PCDD/F in Yangtse sediments consisted of OCDD and 70 % in Liao-He sediment.
High concentrations (18 mg/g) of OCDD were found in Chinese technical PCP-Na[7]. The accidental discharge of PCP in the vicinity of site 1/1 was probably responsible for the high PCDD contamination of this sediment. The PCDF concentration remained low and was comparable to the PCDF concentrations of the other Yangtse sediments.
The PCDD/F concentrations of the sediments 2/2 and 2/R were very similar indicating the normal PCDD/F level of the Yangtse sediments near Nanjing. The pattern were predominated by OCDD. It can be concluded, that the widespread use of technical PCP was the main input of PCDD/F in the Yangtse River system. Zheng[8] reported high PCDD/F concentrations with a very high OCDD level in sediments of the Donting Lake as a result of PCP treatment. Wu[4] observed high PCDD/F concentrations with predominance of OCDD in the Ya-Er Lake sediments, which were influenced by effluents of a PCP production plant.

Elevated PCP concentrations were detected in the sediment samples from the Yangtse River. Since PCP is a weak acid with a pKa of 4.9[9] and a pH of the Yangtse water around 8, considerable ionisation and higher PCP concentrations in water can be expected. This could be a serious problem for the health of the Chinese population, because the river water is used as drinking water with only simple pre-treatment.
The particle bounded hydrophobic substances seem to be transported to the estuary, especially during the flood season and contribute to the contamination of the marine ecosystem[10].

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