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Polychlorinated Organic Compounds (PCOCs) in the Yangtse River Water Samples Using SPE and GC/ECD

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One of the most widely used chemicals at the past were the Polychlorinated Organic Compounds (PCOCs), particularly the organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). They were banned or restricted because of their toxicity, chronic persistence and bioaccumulation in the environment (Barcelo 1991; Wolf et al. 1991; Bacci et al. 1988; Tanabe 1988). Most PCOCs have been included in the list of priority pollutants in many countries and their presence in the environment has attracted a lot of attention (Research group on environmental priority detection 1989) In China, PCOCs were widely used in highly developed industrial activities and agricultural protection for about 20 years and were discharged after use without any precautions to reduce the environmental impact (Wang 1991; Fan 1982). PCOCs can move from water into other media, such as plant, fish, birds and marine mammals. They might ultimately pass onto people through consumption of traditional food. The determination of PCOC residues in water samples is helpful to evaluate the safety of water body, to predict their distribution in other media, and to solve some environmental problems.

The chromatographic techniques used for the analysis of organic compounds at low concentrations require efficient isolation and concentration procedures, which can make determination a time-consuming and laborious process involving large volumes of organic solvents (Wells 1988; Onuska 1984). To overcome these problems, solid-phase extraction (SPE) has been extensively applied to the extraction of organic compounds present in water samples (Junk and Richard 1988; Font et al. 1993; Eisert et al. 1995; Hennion and Pichon 1994; Brinkman and Ureuls 1996).

In this study, 18 organic contaminants from the water samples of the Yangtse River have been qualitatively and quantitatively analyzed. An improved method for the determination of PCOCs was investigated by using SPE and gas chromatography coupled with electron capture detection (GC/ECD). The results have been applied to evaluate the water quality and should be helpful for assessments of the impact of the organic components in the Yangtse River.

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MATERIALS AND METHODS

The reagents used were all HPLC grade and were purchased from BDH Laboratory Supplies Poole, BH15 ITD (UK). A mixture of standard solution containing PCBs (IUPAC No. PCB28, 52, 101, 138, 153 and 180), a mixture of standard solution containing OCPs, i.e. α, β, γ–Hexachlorocyclohexane (α, β, γ – HCH), Hexachlorobenzene (HCB), Aldrin (Ald), Dieldrin (Diel), Heptachlor epoxide (HE), Octachlorostyrene (OCS), Heptachlor (HC), 4,4'-DDT (DDT), 4,4'-DDE(DDE), 4,4'-DDD (DDD), a standard solution of Pentachlorobenzene and a standard solution of PCB209 were purchased from Dr. Ehrenstorfer Chemicals (German). The other materials such as SPE-Filtration device with a vacuum pump and 8 connectors, SPE units, 1g C_{18} cartridges and 0.7 um glass-fibre filters were supplied by Technical University of Graz. An SPE unit including a vacuum regulating valve, a 1000 ml suction flask, a rubber stopper, a connection needle and a SPE cartridge adapter connected with a steel capillary (out diameter: 3.2 mm, inner diameter: 2 mm, length: 0.5 m).

The SPE cartridge was conditioned before it was used to adsorb the PCOCs in the water samples. The SPE cartridge was filled with 5ml methanol and distilled water twice, respectively. It should be paid attention that the solid phase does not run dry.

Four sampling stations in the Yangtse-River (the sections of Nanjing and Zhenjiang) were selected, i.e. Y01-the upstream to Nanjing, Y02-the downstream closed to Nanjing, Y03-the downstream far from Nanjing (40km), Y04-the downstream closed to Zhenjiang (120km from Nanjing). In each sample station, the water samples were taken from 3 sampling points, i.e. one is in the south side of the River, the second is in the middle of the River, and the third in the north side of the River. The sampling campaign was carried out in May 1998. Water samples were collected at 0.5m below the water surface with a specially designed iron bucket. Samples (1 L) were filled into a glass bottle thoroughly cleaned and rinsed with acetone and distilled water prior to use. The samples were labeled and transported to the laboratory for immediate processing. At the laboratory the water samples were passed through 0.7 μ m glass micro-fibre filters on the SPE-Filtration device to separate the particulate fraction from the liquid phase. Then the conditioned SPE-cartridge was filled with 5mL distilled water and connected with the SPE adapter and steel capillary. The other end of steel capillary was immersed to the filtrates. The vacuum was adjusted by the valve to control the water sample at the flow of max 1L/h. After the extraction, the SPE cartridges were stored at below 0°C to be analyzed later. Two of the samples in each point were analyzed in our department. The other two were determined using GC coupled with mass spectrometer (GC-MS) at GSF-National Research Centre for Environment and Health, German.

Before elution, the solid phase should be dried. Therefore, the cartridge was centrifuged at 5000rpm for 5 min, and then was dried for 5 min with nitrogen gas.

A 25mL pear shaped flask was placed inside the SPE-unit below the cartridge. 5mL dichloromethane (DCM) was drawn through the solid phase at about 1 mL/min. The elution was repeated by 5mL DCM/n-hexane (1: 1). The collected elute was dried and cleaned up on a cartridge containing 0.5g anhydrous Na_2SO_4, and 1g silica gel. The analyte in the column was eluted with 10mL 5% 2-propanol in n-hexane. Then the solution was concentrated by means of a rotary evaporator to nearly 0.5mL. After 150 µ L nonane was added, the solution was further concentrated to nearly 200 µ L. The solution was finally concentrated under a gentle stream of nitrogen to nearly 100 L. 10 µ L of the internal standard (PCT and DCB: 10ng/ µ L) was added and the extract was transferred to a glass micro-vial for GC injection.

The purified extracts were analyzed using HP 6890 GC (DB-5 capillary column: 30m×0.25mm) equipped with ECD. The operational conditions were as follows: Inlet, 220°C ; Electron capture detector, 280°C ; Oven temperature, started at 60 C, and increased to 140°C at 12°C per minute , then increased to 280°C at 8°C per minute, and held 280°C for 5 minutes; Column pressure, 10 psi; Carrier gas, He; Injection volume, 1 µ L with the splitless mode.

The analytical procedure used for the present survey has been subjected to the following tests aiming at the assessment of both the reproducibility (precision) and the accuracy of the results:

1. Analysis of 3 blanks, prepared at one-week intervals and covering the entire analytical procedure (from the extraction to the GC analysis).
2. Assessment of the overall recovery rates through analysis of a known amount of external standard.
3. GC analysis was repeated three times for each replicate sample.
4. Analytical results were compared between the laboratories of Nanjing University and GSF-National Research Centre for Environment and Health.

RESULTS AND DISCUSSIONS

In all water samples, the temperature was approximately 20°C, the pH ranged from 7.3 to 7.6 and the conductivity from 120 to 160 µ S/cm.

The recovery of organic compounds from water samples depends on a number of factors such as the type of water samples (presence of particulate mater, ionic strength of the water), sample volume, pH, different sorbent and sorbent treatment (Font et al. 1993). The effect of pH on the retention of compounds in a solid phase has been studied (Wells and Michael 1987; Coquart and Hennion 1991; Manes et al. 1989). The pH values can change the nature of bonded phases and the recommended pH values are between 2 and 8. If the studied system can not meet these demands, it is necessary to adjust the pH of the sample to ensure that the analyzed compounds are in the appropriate form to achieve the efficient retention by the solid phase. As far as the sorbent treatment is concerned, a typical

sequence involves the following steps: activation of the sorbent, enrichment on solid phase and elution of concentrated organic compounds. Once the sorbent and elution solvent are selected, control of sample elution flow rate is important. According to the studies on analytical performance, it was determined that stable and high recoveries were obtained when the sample flow rate was controlled below 1L/h and the elution flow rate at about 1ml/min.

Table 1 shows the retention time (t_R), % recovery of each PCOC, and the concentrations of PCOCs determined in the 12 water samples, Mean values were also presented. Of these PCOCs, Heptachlor, Heptachlor epoxide and PCB138 were not detected. Because the retention time of DDE was same as that of Dieldrin, it was difficult to quantitatively determine DDE and Dieldrin. Therefore, the concentrations of DDE and Dieldrin were not reported.

The recoveries of PCOCs distribute from 36.6% to 105.9%, but most of relative standard deviations (RSD) were less than 15%. Therefore, it could be concluded that some of PCOCs were difficult to be adsorbed by C 18 solid phase, the method produced the results in a good reproducibility and repeatability. The external standard recoveries were merely used to monitor method performance. After correcting for concentrations, the analytical results showed a good agreement with known samples. As far as the analytical quality control is concerned, blank runs revealed no impurities.

Table 1. Qualitative and quantitative results of PCOCs in the Yangtse River

	t_R	Recov	Y01*			Y02*			Y03*			Y04*			Mean
	(min)	(%)	S	M	N	S	M	N	S	M	N	S	M	N	
α-HCH	12.529	83.8	3.3	4.5	5.9	2.9	1.9	1.5	2.3	3.5	3.3	3.3	2.1	2.6	3.3
β-HCH	12.170	105.9	1.7	2.0	1.8	2.7	2.3	1.2	3.2	2.7	3.4	1.4	3.3	3.3	2.3
γ-HCH	13.319	105.2	1.9	2.7	3.9	2.1	2.0	1.6	1.6	2.0	2.0	2.0	2.5	2.1	2.1
HCB	12.708	60.8	0.5	0.7	0.4	1.2	0.5	0.4	1.3	0.7	0.6	0.7	0.8	1.1	0.8
Ald	15.811	49.4	1.5	1.1	1.7	1.6	0.6	0.3	1.3	1.6	0.7	0.4	0.4	0.5	1.0
OCS	16.661	36.6	4.3	4.2	7.1	4.8	3.4	2.7	3.5	4.6	4.7	3.7	4.2	4.2	4.4
DDD	19.070	91.8	0.3	0.4	0.5	0.5	0.4	0.4	0.3	0.5	0.5	0.3	0.4	0.3	0.4
DDT	19.898	73.5	0.4	0.5	0.5	0.9	1.2	1.5	0.5	0.6	0.7	1.5	1.7	1.7	0.9
PCB28	14.662	55.3	2.6	2.0	1.5	1.8	1.8	1.6	3.7	2.7	2.4	1.2	1.5	1.5	2.2
PCB52	15.474	64.2	0.7	0.8	0.8	1.6	0.6	0.5	0.8	1.3	1.3	0.4	0.6	0.7	0.9
PCB101	17.477	45.5	0.8	0.5	1.0	0.4	1.8	0.8	1.5	1.1	1.5	1.7	1.6	0.5	1.2
PCB153	19.382	48.0	0.2	0.3	0.3	0.2	0.2	0.2	0.7	0.6	0.5	0.2	0.2	0.2	0.4
PCB180	21.230	38.2	0.9	0.7	0.7	0.8	0.6	1.3	0.6	0.8	0.8	0.9	0.9	0.9	0.8

* S, M and N represent the sampling points at the south side, middle and north side of the Yangtse River respectively, and the data are the average concentration of samples (ng/L).

As shown in Table 1, the average concentrations of the PCOCs determined are in the range of 0.3 to 4.4 ng/L.. With the exception of HCHs, OCS and PCB28, the mean values of most analytes in the 4 sample stations were lower than 1.2ng/L. The concentrations of individual PCOC in different sampling points of each station are close to each other, as well as those of different stations, which shows mostly uniform distributions of PCOCs along and across the rivers.

Nanjing, the capital of Jiangsu (one of most developed area in China), is situated on the lower reaches of the Yangtse River. The River water is presently a sole resource for the production of drinking water. This survey illustrates the concentrations of most PCOCs are less than 5ng/L (Table 1), far lower than lug/L of the standards for the State Drinking Water. Therefore, the River water is safe as the resource of drinking water. Comparatively speaking, the Yangtse-River is still one of the cleanest rivers in China. This is closely related to the characteristics of the Yangtse-River. It is well known that the Yangtse-River is the longest river in China and the third longest in the world in terms of its length and flux ($9604x10^{8}m^{3}$/year). Although the Yangtse River in sections of Nanjing and Zhenjiang (one of the most industrialized areas in China) is influenced by the pollution from the industries such as automobile, textile, chemical and electronic production and strong naval activity, the ratio of running water to waste water is 99:l (She 1997). It is also because the Yangtse-River has strong ability to complete self-cleaning that it is still a good and safe drinking resource in China at present.

The values of PCOCs determined in present study were significantly lower than those measured in previous report (Bao and Zhang 1990). The average concentration of PCOCs in water samples collected in 1988 was between 0.01 to 0.05 μg/L, which is about 10 times higher than that in water samples collected in 10 years (1998). This illustrates that, in general, the contamination of PCOCs in the Yangtse River has been decreased. Since most of PCOCs interested in this study have been banned for around 20 years in China, their concentrations should naturally diminish.

Table 2. Comparison of PCOCs concentrations (ppt) via ECD & MSD

	α-HCH		β-HCH		γ-HCH	
	ECD	MS	ECD	MS	ECD	MS
Y01-S	3.3	3.1	1.7	4.4	1.8	1.4
-N	5.9	2.9	1.8	3.9	3.9	4.0
Y02-S	2.9	3.1	2.7	3.8	2.1	2.8
-N	1.5	2.9	1.2	4.9	1.6	1.5
Y03-S	2.3	2.7	3.2	4.9	1.6	1.3
-N	3.3	2.8	3.4	2.8	2.0	2.2
Y04-S	3.3	2.9	1.4	4.1	2.0	1.9
-N	2.6	2.8	3.3	4.1	2.1	1.9

Though ECD has many attributes, its ability to identify individual PCOCs relies on retention time alone. Using GC/ECD requires the use of a reference standard comprising all compounds present in the environment. By comparison, the use of mass spectrometric detectors not only enhance selectivity, but by using selected ion monitoring (SIM) and isotope ratios, qualitative information is provided to supplement retention time supplied by GC. The analysis for the SPE extracts of the water samples from the Yangtse River done by GCIMS-SIM at GSF-National Research Centre for Environment and Health of German made it is possible to compare with the results obtained from detection methods of two laboratories, and to validate the methods. A comparison of the results for three of the most abundant PCOCs indicated a satisfactory agreement for the two different methods of detection (Table 2).

Compared with the classical method (Oxynos et al. 1992) and other similar researches (Junk and Richard 1988; Eisert et al. 1995; Hennion and Pichon 1994), this investigation has employed a specific filtration and extraction device, which can simultaneously be applied to 8 water samples. This is important for a sampling campaign having more than 3 sample points. Moreover, the quality control of analysis was performed between different laboratories by using different detection, which produces a very high reliability of analytical results.

It has also been seen from the analysis that if the pH of the water samples could be controlled at certain value and the temperature programs could be developed, this method can be extended to detect other chlorinated compounds.

In summary, the use of SPE of C_{18}-bonded silica coupled with GC/ECD provides a sensitive and reproducible method for the simultaneous determination of PCOCs in water, This research demonstrates that the method is applicable to detect PCOCs in a large water body of China. In the view of the concentration of PCOCs, the water quality of the Yangtse River in Nanjing section is quite good.

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