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# Persistent Pollutants in Sediments of the Yangtse River

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The Yangtse River, the third largest river in the world and the largest river in China, is subject to environmental pollution by wastewater and agriculture run-off (Chen et al. 1996). However the shortage of available water resources due to rapid industrial development makes it necessary to use Yangtse River water for production of drinking water. Thus resources water contamination by persistent pollutants has become an increasing important issue. Of all the pollutants, some persistent substances like organochlorine pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and heavy metals have received added attention in this regard because of their ubiquity, potential for magnification in the food chain, and harmful biological effects.

Since sediment acts as the main potential source for persistent chemical pollution, its analysis has therefore been widely used to detect PCBs, pesticides, heavy metals and other persistent compounds contamination and to assess ecological risks (Ahmad et al. 1996; Botello et al. 1998: Norena-Barroso et al. 1998; Phuong et al. 1998). Thus it is necessary to determine the residues of these substances in Yangtse River sediment regularly. The investigation of pollutant distribution in sediment can not only provide a close sight on the present environmental quality of the Yangtse River (Nanjing section), but also serves as a baseline for future research of sediment with different contaminants.

Several investigations have been undertaken in some special sections of the Yangtse River (Zhanxiong et al. 1988; Xinrong et al. 1988; Bao et al. 1990) to assess the water quality, but persistent pollutants in sediments still need much more attention. Therefore, the main object of this study is to understand the pollution status of the Yangtse River and to obtain information of chemicals that might persist in the environment.

## MATERIALS AND METHODS

Sediment samples were collected in the Yangtse River (Nanjing section) on May 16-17, 1998. Four fixed stations (Y01 to Y04) were chosen for sampling. Y01

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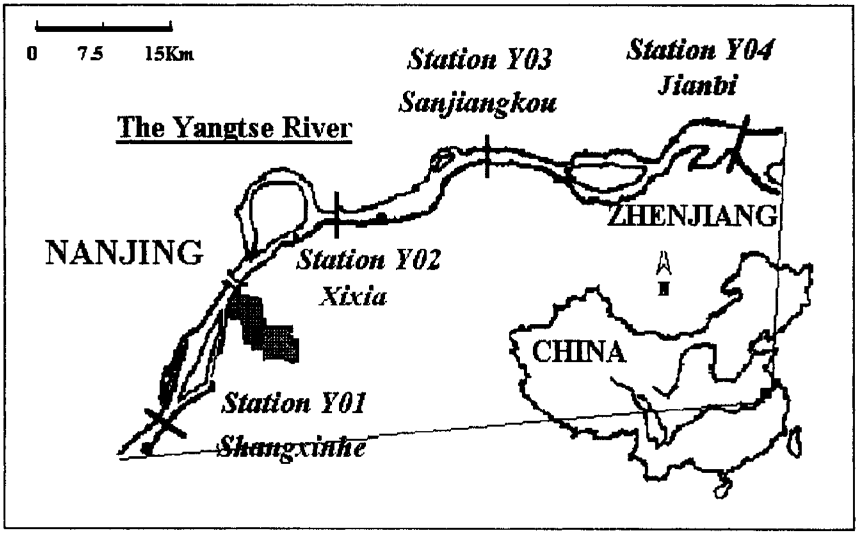


**Figure 1.** The location of the sediment sampling stations in the Yangtse River (Nanjing section)

(Shangxinhe): The first sampling station is in the upper reaches of Nanjing and characterizes the stream's water quality before passing Nanjing, the capital of Jiangsu Province; Y02 (Xixia): The second sampling station is typical for the situation in the zone of Nanjing; Y03 (Sanjiangkou): The third sampling station is situated in the stream after having passed Nanjing; Y04 (Jianbi): The fourth sampling station lies nearby the city of Zhenjiang, in attempt to reflects the river pollution situation before entering the well studied estuary zone of Shanghai. The extra sediment sample for Quality Control was collected in stationY02. Figure 1 gives an overview of the whole sampling area situated in Jiangsu province,

For PCBs and organochlorine compounds determination, the optimal experimental procedure was set up according to the Standard Operation Procedure (SOP) of the German Federal Environmental Specimen Bank (Oxynos et al. 1992). 5g of dried sediment sample and 25mL mixed solvents (10mL dichloromethane and 15mL n-hexane) were added in the extraction vessel, and extracted in an ultrasonic bath for 1hr. The concentrated extract (0.5-1mL) was passed through a silicagel column (6mL) with a layer of 0.5g $Na_2SO_4$ on the top. The silicagel column was eluted with 7mL 5% iso-propanol in n-hexane and the eluate was concentrated into 2mL. 150µL nonane was added to the concentrated solution before being further concentrated into 100µL. 10µL of the internal standards (pentachlorotoluene and decachlorobiphenyl--50pg/µL) was added and the purified extract was transferred to a glass vial for GC-ECD analysis.

The determination of polychlorinated organic compounds (PCOCs) was carried out with a Hewlett-Packard 6890 GC system equipped with a $^{63}$Ni electron capture detector under the splitless mode. The solution was chromatographed on a 30mx0.32-mm i.d. HP-5 capillary column with a film thickness of 0.25µm at a pressure of 50 Kpa. Helium was used as carrier gas at 2.0mL/min and nitrogen as make-up gas at 54.4mL/min. The oven temperature was programmed at 60°C for 1min, from 60 to 140°C at 12°C/min. from 140 to 280°C at 8°C/min, and finally at 280°C for 5min. The injector and the detector were set at 220 and 280°C respectively.

For PAH determination, the same procedure was used, except that clean up of the extracts was performed by l g silica gel first and then separated by semi-preparative HPLC (Gilson, pumps 305 and 307, 250x8mmx5µm Hypersil column, 4mL/min). The fractions with PAHs were then analyzed by GC-MS (Fisons 8000) in the GSF-National Research Centre for Environment and Health, Germany.

Heavy metals in the Yangtse River sediments were analyzed at Joint Research Centre of European Community in Ispra, ltaly.

## RESULTS AND DISCUSSION

PCOCs in ten sediment samples collected from the mentioned river stations were analyzed in triplicate according to the method mentioned above. Blank and quality control samples were analyzed with each set of samples. No disturbance peaks appeared in the chromatograms of the blanks. Standard deviations of PCOCs detected in the QC samples were in the range of 0.005% to 1.87% for each compound. Confirmation was achieved by GC-MS (Fisons-8000) and HRGC/HRMS (Finnigan MAT95, R=10000) in the laboratory of GSF-National Research Centre for Environment and Health, Germany (Platzer et al. 1999).

In the 1970's, the usage of organochlorine pesticides in China was $19.17x10^4$t, accounting for 80.1% of total pesticides production. Among all the PCOCs, HCHs and DDT were the most widely used pesticides from 1960 to 1980 in China. The respective total input of HCHs and DDTs were 68,310t and 8,100t in the 1960s, 171,672t and 18,992t in the 1970s as well as 241,613t and 16,428t in the 1980s. Until they were banned in China on April 1, 1983 (Xiaomei et al. 1996), these organochlorine pesticides had played an important role in protecting crops against insect damage and in developing agriculture production.

It was initially estimated that the sediment samples from the Yangtse River would reveal high PCOCs levels especially to HCHs and DDTs and, thus, the further advanced water treatment technologies could be established to restore aquatic system. But data did not show such high values as forecasted. The concentration levels found were even much lower than those of some well treated European Rivers (Guzzella 1977; Galassi et al. 1993). Furthermore, some PCOCs concentrations were below the detection limits of GC-ECD.

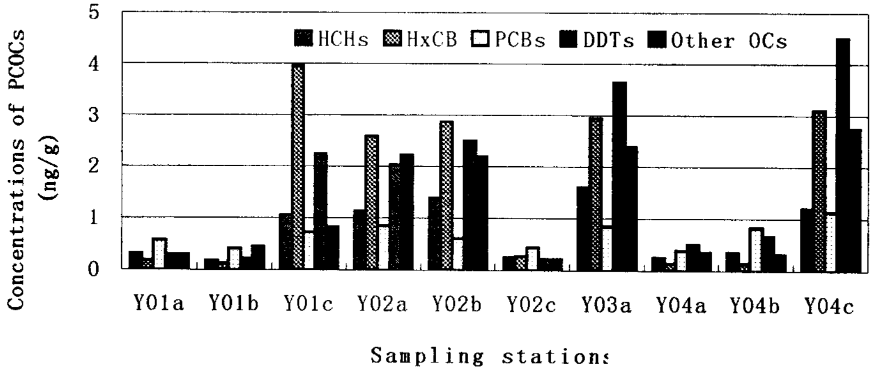


**Figure 2.** Total concentrations of five kinds of organochlorine compounds (OCs) in the sediments of the Yangtse River. Y-the Yangtse River; 01,02,03,04-number of sampling station; a,b,c-sampling point in each station.

HCHs= αHCH+βHCH+γHCH

PCBs=B28+B52+B101+B153+B138+B180

DDTs=pDDE+pDDD+oDDT+pDDT

Other OCs=Aldrin+trans-Heptachlor epoxide +Endrin+Methosychlor+Octachlorostyrene

Among all the PCOCs investigated, the HCB concentrations in sediments were the highest, ranging from 0.14 to 3.96ng/g, whereas for DDTs, their total concentrations were the second highest, ranging from 0.21 to 4.5 ng/g.. Then follows HCHs, ranging from 0.25 to 1.41ng/g. PCBs concentrations were the lowest, ranging from 0.39-1 1.13ng/g.

Especially for DDTs detected in Yangtse River sediment, p,p'-DDE was the dominant component of the DDT family in most of the sampling stations (except for station Y04c, which might indicate recent application in this area), accounting for 58.91% of DDTs on an average. This could be due to the degradation of DDT in environment, and without continuing illegal input in these areas.

On the whole, it was clear from Fig. 2 that PCOCs contamination pattern was similar in the sediments from different sampling stations, although the sediment samples in station Y0lc, Y02a, Y02b, Y03a and Y04c appeared to have higher values of PCOCs than in other stations investigated. Such results could be explained by high water velocity in the Yangtse River, but the properties of sediments and other geochemical factors could not be excluded.

PAHs were predominantly formed as a result of human activities such as oil spill and combustion of fossil fuels (Neff 1979), but may also be the result of decomposition by aquatic organisms (Andelman and Snodgrass 1974). Some PAHs were demonstrated to be mutagenic and carcinogenic (Grimmer 1983; Grimmer 1993). Therefore it was necessary to screen the concentrations of PAHs in Yangtse

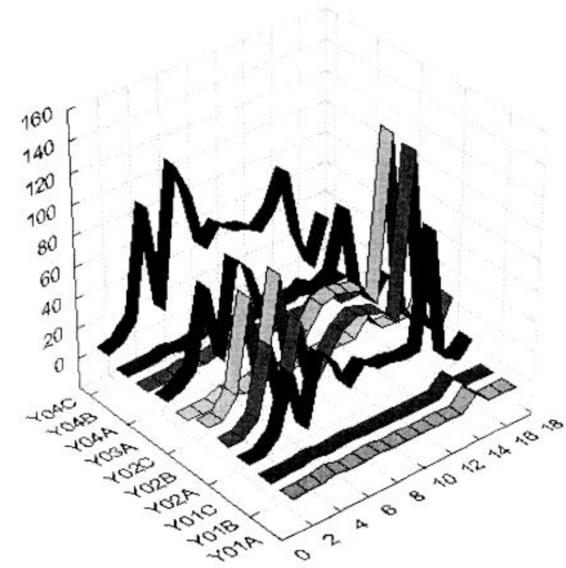


**Figure 3.** Surface plot of PAHs distribution pattern in the sediments of the Yangtse River (PAHs' concentration unit: ng/g of dry weight) X-axis: 1 Acenaphthylene 2. Acenaphthene 3. Fluorene 4. Phenanthrene 5. Anthracene 6.Fluoranthene 7. Pyrene 8. Benzo(a)anthracene 9. Chrysene 10. Benzo(b)fluoranthene 1l.Benzo(k)fluoranthene 12. Benzo(e)pyrene 13. Benzo(a)pyrene 14. Perylene 15. lndeno(1,2,3-cd)pyrene 16. Dibenzo(ah)anthracene 17. Benzo(ghi)perylen

River sediments. Figure 3 showed the ribbons of PAHs distribution in ten stations investigated. It could be seen from the figure that the levels of PAHs followed similar trends of PCOCs'. The PAHs concentrations (sum of 17 individuals) ranged from 15.94ng/g to 765.28ng/g dry weight in the Yangtse River sediments.

Among these ten stations, significantly high concentration of total PAHs compounds was found in station Y04c (765.28ng/g), followed by station Y02b, Y02a, Y03a and Y0lc with the total concentration of 702.04ng/g, 613.21ng/g, 550.32ng/g and 415.57ng/g in dry weight respectively. The high concentrations may be a result of great anthropogenic input of PAHs in these areas and sources most probably came from the shipyard near the Yangtse River, the traffic along the Yangtse River and coke oven emissions. The other five stations showed relatively low concentrations of PAHs, which should be due to comparatively less urbanization and industrial establishments in these areas.

With regard to PAHs levels in ten sediment samples studied, the 5 ring aromatics presented the greatest percentage (43.69%) of total PAHs, and the 4 ring compounds accounting for 32.57% of total PAHs, then came the 3 ring compounds with 16.59% and 6 ring compounds with 7.15%. These results coincided with the fact that the entry of PAHs into the system had an anthropogenic origin.

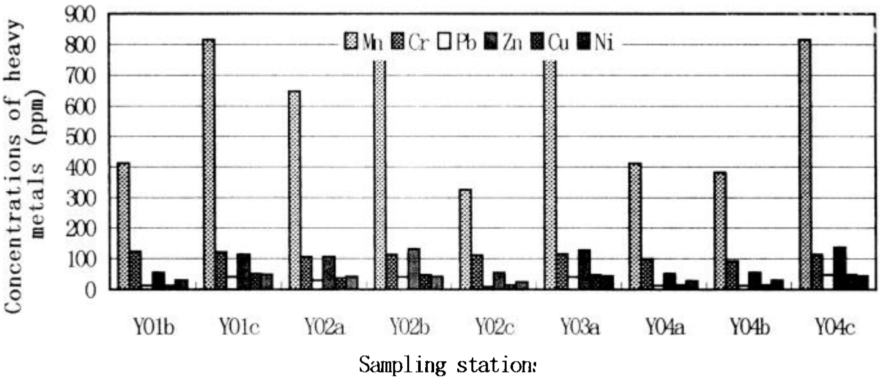


**Figure 4.** Average heavy metal concentrations in the sediments of the Yangtse River

**Table 1.** Correlation coefficient matrix of heavy metals in the sediments of the Yangtse River

| | Mn | Cr | Pb | Zn | Cu | Ni |
|---|---|---|---|---|---|---|
| Mn | 1.00 | | | | | |
| Cr | 0.45 | 1.00 | | | | |
| Pb | 0.99 | 0.41 | 1.00 | | | |
| Zn | 0.98 | 0.40 | 0.99 | 1.00 | | |
| Cu | 0.98 | 0.44 | 0.98 | 0.97 | 1.00 | |
| Ni | 0.97 | 0.45 | 0.96 | 0.93 | 0.97 | 1.00 |

Except for the trace PCOCs and PAHs detected in nearly all the Yangtse River sediments, some other persistent pollutants like heavy metals were also found. The results for trace heavy metal contamination of Yangtse River sediments were delineated in Fig. 4. The exploratory studies of the Yangtse River showed that the spatial distribution pattern of individual heavy metals in sediments was similar to those of PCOCs and PAHs. These results indicated that heavy metals might be mainly associated with fine particles and with the organic carbon. The differences between the Mn concentration of the sediments from one station to another were little, which demonstrated the geochemical origin of the material. Little difference was also found for Cr, Pb, Zn. Cu and Ni concentrations. The correlation matrix for heavy metals was presented in Table 1. A majority of the heavy metals showed excellent positive correlations with each other (except for Cr), indicating a common source of these metals.

Due to the importance of the Yangtse River for water utilization for industrial and agriculture purpose, it should be mentioned that some PCOCs, PAHs and heavy metals were listed by EPA (the Environmental Protection Agency. USA) as priority pollutants, and they were well known to maintain their stability in the aquatic environment. Moreover, Due to their lipophlic properties, most of them could accumulate in high concentrations in the dissolved organic matters, sediments and organisms, which could cause potential harm to human health. Thus, although the levels of persistent pollutants in Yangtse River sediment were not so high as some other rivers in the world, the control of the industrial and municipal discharges along the Yangtse River should still be seriously concerned.

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## REFERENCES

Ahmad S, Ajmal M, Nomani AA (1996) Organochlorines and polycyclic aromatic hydrocarbons in the sediments of Ganges river (India). Bull Environ Contam Toxicol 57:794-802

Andelman JG, Snodgrass JE (1974) Incidence and significance of polynucleararomatic hydrocarbons in water environment. CRC. Crit Rev Environ Control 4:69

Bao Z, Zun Z (1990) Identification and analysis of organics in Yangtse River (Jiangyin section). Huan Jing Ke Xue. 9: 1-8 (in Chinese)

Botello AV, Calva B. LG (1998) Polycyclic aromatic hydrocarbons in sediments from Pueblo Viejo, Tamiahua. and Tampamachoco Lagoons in the southern gulf of Mexico. Bull Environ Contam Toxicol 60:96- 103

Galassi S, Valsecchi S, Tartari GA (1997) The distribution of PCB's and chlorinated pesticides in two connected Himalayan lakes. Wat Air Soil Pollut 99: 717-725

Chen Guojie (1996) The evaluation on water quality of Yangtse River and the decision of its industrial development along the River. China Environ Sci 16:339-344

Grimmer G (1983) Environmental carcinogens: Polycyclic Aromatic Hydrocarbons. CRC Press, Florida, USA

Grimmer G (1993) Relevance of polycyclic aromatic hydrocarbons as environmental carcinogens. Polycycl Aromat Cmpds Suppl 3:31-42

L. Guzzella (1997) PCBs and organochlorine pesticides in lake Orta (Northern ITALY) sediments. Wat Air Soil Pollut 99: 245-254

Neff, J. M. (1979) Polycyclic aromatic hydrocarbons in the aquatic environment. Applied Science Publishers Ltd, London

Norena-Barroso E, Zapata-Parez O, Ceja-Moreno V, Gold-Bouchot G (1998) Hydrocarbon and organochlorine residue concentrations in sediments from bay of Chetumal, Mexico. Bull Environ Contam Toxicol 61:80-87

Oxynos, K., Schmitzer, J.. Duerbeck. H. W., Kettrup. (1992) A: Analysis of chlorinated hydrocarbons (CHC) in environmental samples. In: Specimen Banking. Rossbach, M., Schladot, J.D., Ostapczuk, P. (Eds.), Springer-Verlag, Berlin, ISBN-3-540-55001-1. p 127

Phuong PK, Son CPN, Sauvain J-J, Tarradellas J (1998) Contamination by PCB's, DDT's, and heavy metals in sediments of Ho Chi Minh city's canals, Viet Nam. Bull Environ Contam Toxicol 60:347-334

Platzer B, Martens D, Jiang X. Quan X, Gfrerer M, Gawlik BM (1999). Chlorinated hydrocarbons and other selected pollutants in parts of the Yangtse (Changjiang) and Liao-He- comparison and evaluation of results obtained by all project participants In: On the Presence of Polychlorinated Organic Compounds in the Liao River and Yangtse River in

Eastern China. Gawlik BM. (Eds.). The European Commission. EURl8702EN. p97-144

Xiaomei Hua, Zhengjun Shan (1996) The production and application of pesticides and factor analysis of their pollution in environment in China. Adv Environ Sci 4:33-45

Xinrong Ye, Yang H, Zhu J. Bao G. Qui Y (1988) Distribution features of polychlorinated biphenyls and organochlorine pesticides in the Changjiang estuary and adjacent East China Sea. In: Proceedings of the International Symposium on Biogeochemical Study of the Changjiang Estuary, and Its Adjacent Waters of the East China Sea, Yu Guohui, J. M. Martin, Zhou Jiayi. (Eds.). China Ocean Press, Beijing. p773-781

Zhanxiong Yang, Yunqian Tang. Guihai Zhu. Bing Lu, Jian Zhou (1988) Distribution characteristics of polycyclic aromatic hydrocarbons in the Changjiang estuary. In: Proceedings of the International Symposium on Biogeochemical Study of the Changjiang Estuary and Its Adjacent Waters of the East China Sea, Yu Guohui, J. M. Martin, Zhou Jiayi. (Eds.). China Ocean Press. Beijing. p557-569