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Distribution and sources of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in surface waters of Jinzhou Bay in China

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Abstract

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in surface water collected from the Jinzhou Bay in North China were analyzed using gas chromatography to reveal their horizontal distribution tendencies and trace their sources. Total PCB concentrations ranged from 215.4 to 3161 ng/L. The level of PCB in the opening of the Bay was higher than the inner Bay. The predominated components were 5- and 6-chlorinated PCBs, indicating these residual PCBs derived from paint additives. Total OCP concentrations ranged from 4.165 to 136.8 ng/L, whose isomer concentrations' ratios implied the usage of technical HCH and lindane.

Key words: polychlorinated biphenyls; organochlorine pesticides; Jinzhou Bay; surface water; gas chromatography

1. Introduction

Persistent Organic Pollutants (POPs) have triggered an increasing concern world widely for several decade years. POPs have high toxicity, last for a long time in environment, and may travel long distance far from their sources of usage, release and emission. Furthermore, they can accumulate in fatty tissue of organism and result to negative effect associating with the occurrence of immunologic and teratogenic dysfunction, reproductive impairments and endocrine disruption [1].

In the last century, large quantities of chlorinated persistent organic pollutant have been produced in relation to a variety of human activities. For example, organochlorine pesticides (OCPs), such as HCHs, DDTs, dieldrin and chlordane, were used in agricultural production and for sanitation purposes.

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Meanwhile, DDTs were widely used in World War II to protect soldiers and civilian from malaria, tyhus, and other diseases spread by insect [2]. From 1981 to 1984, it was estimated that about 184,000 tons of HCHs and 311,000 tons of DDTs were consumed in 103 countries annually [3]. PCBs are one group of anthropogenic aromatic congeners with the H atoms of the biphenyl rings substituted by Cl atoms. PCBs were produced from 1930 to 1983 in the form of complex mixtures serving as dielectric fluids in transformers and capacitors, as plasticizers in paint and rubber sealants [4]. Although PCBs have not been produced since their usage history, they will remain in the environment for a long time.

To carry out a risk assessment, it is vital that the residue levels in the study matrices are accurately determined [5]. A lot of researchers have analysed and reported the distribution of PCBs and OCPs in waters samples. The objectives of this paper were to reveal the horizontal distribution tendencies of PCBs and OCPs and trace their resources in surface water of the Jinzhou Bay, North China.

2. Materials and Methods

2.1. Sampling area

Jinzhou Bay locates in Huludao city in the eastern of Bohai area, whose area is 151.5 km^2. In the past 30 years, because of its half-enclosed geochemistry characteristics, a large amount of industrial and life sewage discharged into the Jinzhou Bay exchanged with the opening water slowly and tended to accumulate in the aquatic environment, causing large area water pollution [6]. In the May of 2012, fifteen superficial water samples were collected from Jinzhou Bay, as Fig. 1 shown.

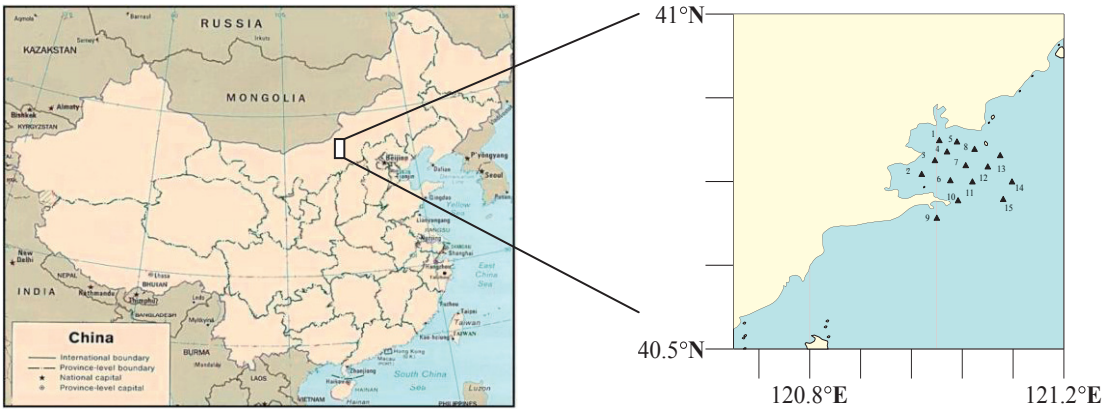


Fig. 1. Location of the stations in Jinzhou Bay, 2012.

2.2. Material and Methods

All organic solvents were of pesticide analysis quality and were purchased from Tedia Company (Cincinnati, USA). Standard materials were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

2.3. Gel permeation chromatography (GPC) optimization

The Gel permeation chromatography (GPC) is based on the difference molecular size to going to cleaning. An aliquot of 1 ml PCB congeners (Accustandard, Inc, USA), HCHs and DDTs standard

solution (the commission of the national standard measuring, China), with the concentrations of 50 ng/ml, was transferred into the GPC column. The mobile phase was the mixture of cyclo hexane: ethyl acetate (1: 1, v: v) with a flow rate of 4.7 ml/min. The elution was dumped from beginning to 8th min because of the bigger molecules, such as oil, protein and fat, were rinsed, subsequently, the target compounds were eluted. In this procedure, the elution solvents were collected very minutes from 8 min to 16 min.

2.4. Extraction and analysis

Generally, PCBs, HCHs and DDTs can be analysed using a common procedure, which shares the same extraction, cleanup and GC-ECD analysis. Within the analysis sequence, extraction and cleanup are the key step and are also perhaps the greatest source of waste in environment analysis laboratories [7]. An aliquot of 800 ml seawater sample with PCB 209 spiked as surrogate was mixed with dichloromethane (DCM) (50 ml) and shaken about 15 min, and then the funnel was left undisturbed until the hexane and water phases had been clearly separated without visible emulsion or cloudiness. The lower layer of DCM was carefully discarded into a flask. The extraction procedure was repeated with additional 30 ml DCM twice, subsequently, the triple extraction solutions which had been eliminated moisture previously through a layer of anhydrous Na_2SO_4 were combined in the flask. After extraction, the solvent was concentrated to 2 ml using a rotary evaporator (Büchi, R-215, Switzerland) and exchanged to the mixture of cyclo hexane and ethyl acetate (1: 1, v: v) as solvent in order to further clean up by GPC. Then the elution was condensed and exchanged to 1 ml hexane. An internal standard of 2,4,5,6 -TCMX was spiked in the condensed solvent prior to analysis.

GC apparatus equipped with ECD detector (Shimadzu 2010, Japan) was applied to analyse target compound using a DB-5 capillary column of length 30 m (0.25 mm i.d., 0.25μm film thickness). The column temperature program was as followed: initial temperature 80°C, ramped to 180°C at a rate of 20°C/min; then increased at a rate of 5°C/min to 250°C and held for 2 min; finally, the temperature was elevated to 280°C at 30°C/min and held for 5 min.

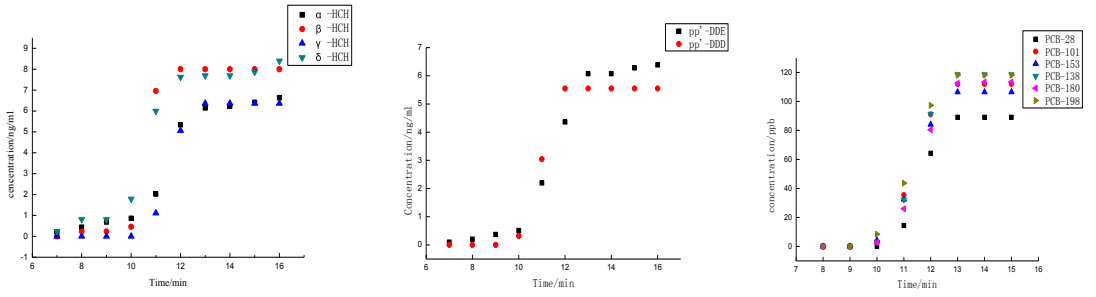
2.5. QA/QC

Quality control was rigorously executed referring to the USEPA methods [8]. In the pretreatment procedure, two method blanks and two matrix spikes were analysed with the 15 samples as a batch. A five-point calibration curve with internal standards method was applied for the quantization of 28 PCB congeners and 16 individual OCP compounds. The method recoveries were calculated by analysing the matrix spike samples. The recoveries of PCBs and OCPs individually range from 85.1% to 91.2% and 83.9% to 93.6%.

3. Results and Discussion

3.1.The curve of elution of Gel permeation chromatography (GPC)

The concentrations of PCBs and OCPs of the eluted solutions were analysed and the accumulating concentrations were obtained through summing up the target compounds' concentrations every minute. The curves of elution were presented in Fig. 2, indicating the elution solutions should be collected from 9 to 12 min for HCHs, 9 to 13 min for DDTs and 9 to 13 min for PCBs. Consequently, the period from 9 to 13 min was the optimized collection duration.

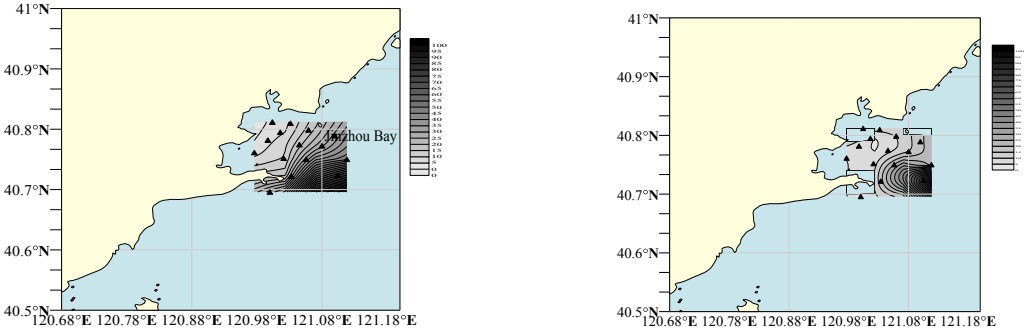


(a) (b) (c)

Fig. 2. Curve of elution solutions of HCHs (a), DDTs (b) and PCBs (c).

3.2. The distribution of PCBs and OCPs in waters samples

In present study, 28 PCBs congeners and 19 OCPs were analysed, whose horizontal distribution tendencies in surface water in Jinzhou Bay was illustrated in Fig. 3. The total concentration of PCBs was in the range of 215-3161 ng/L, and the total concentration of OCPs ranged from 4.165 to 136.8 ng/L with mean of 878.4 ng/L. HCHs concentrations in all samples were summed up as ΣHCHs to evaluate their contamination status. ΣHCHs concentrations were in the range of 4.165-136.8 ng/L with mean of 28.45 ng/L. The total concentrations include p,p′-DDT, o,p′-DDT, p,p′-DDE and p,p′-DDD. The ΣDDTs concentrations ranged from 0.3887 to 15.19 ng/L with the mean value of 3.953 ng/L. The concentrations of PCBs in the majority of the stations were nearly identical; however, which detected in the station 15 was the climax, which located at the mouth of the Jinzhou Bay. The horizontal distribution tendency of OCPs concentrations was quite similar to that of PCBs.



(a) (b)

Fig. 3. Contour concentration diagram of PCBs (a) and OCPs (b).

3.3. The composition and sources of PCBs and OCPs

Twenty eight PCB congeners ranging from 1-CB to 10-CB had been attempted to be analysed, but only the congeners with 2 to 6 Cl atoms were detected. 1-CB might evaporate o in the pretreatment procedure, and the congeners with 8, 9 and 10 Cl atoms were under their detection limits. The compositions of HCHs and PCBs are illustrated in Fig. 4 (a) and (b).

PCBs have been employed in multitude of applications, in general, 3-Cl PCB as the impregnant of power capacitor, while highly chlorinated PCBs associated with the paint additives. In this study, the 5-, 6-, and 7-CB were the majority components, exceeding 70% of total PCBs, implying PCBs might derive from paint additives.

Two types of HCH products have been manufactured throughout the world: technical HCH (containing about 60%-70% α-HCH, 5%-14% β-HCH, 10%-15% γ-HCH and minor proportions of minor isomers) and lindane (γ-HCH ≥99%). The HCHs with the ratio of α- HCH to γ-HCH in the range of 4-7 generally derived from technical HCH usage, and the ratio close to 1 always imply the usage of lindane. According to the composition in this study, it was possible that the residual HCHs resulted from the multi-use of technical HCH and lindane.

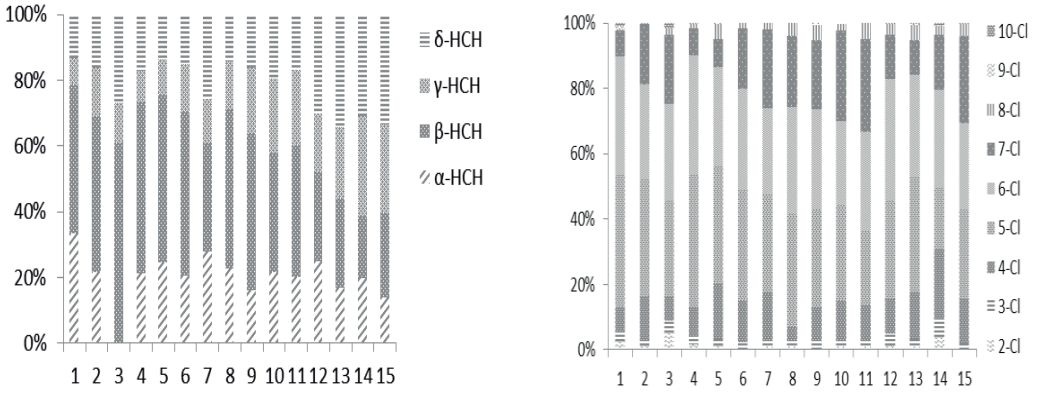


Fig. 4. Compositions of OCPs (a) and PCBs (b).

4. Conclusions

The horizontal distribution tendencies and sources of OCPs and PCBs in Jinzhou Bay have been reported. The distribution trends of OCPs and PCBs in the water samples from the Jinzhou Bay were quite similar. In waters, PCBs and OCPs distributed uniformly in the inner bay, while the highest levels were detected in the same two stations, which were the furthest stations in the sampling area. 5-chlorinated, 6-chlorinated and 7-chlorinated are the main ingredients, implying PCBs might mainly derive from paint additives. With regard to HCHs, the multi-usage of technical HCH and lindane might be source of HCHs residual in Jinzhou Bay. At present, China's water environment pollution of PCBs research mainly concentrated in Yangtze river, Yellow River and the basin of the pearl river, such as the reach, lake and estuary et al. Although the concerning of PCB monomer is different, the ΣPCB detected following in 1000 ng/L. (except the water influenced by the pollution of shipping and channel water). The concentration of OCPs is closed to most water in China. Overall, the level of PCB and OCP in water in Jinzhou Bay are closed to the Yellow River, Yangtze river water[9, 10].

Although PCBs, HCHs and OCPs have been banned exceeding 30 years, due to the great quantity of usage in the past and their persistent characteristics in environment, there is still a certain level of residual in the environment. Therefore, the environment behavior mechanisms of PCBs and OCPs in aquatic environment, as well as their environmental effect research have a long way to go.

Acknowledgments

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