LEVELS, DISTRIBUTIONS AND SOURCES OF PARTICULATE ORGANOCHLORINE PESTICIDES IN THE SURFACE SEAWATER FROM THE SOUTHERN SOUTH CHINA SEA

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Abstract

11 particulate samples were collected from surface water of the southern South China Sea (SCS) in May, 2004 and analyzed for 15 organochlorine pesticides (OCPs) compounds, including α-, β-, γ-, and δ-epoxidehexachlorocyclohexanes (HCHs), DDT, DDD, DDE, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, heptachlor, heptachlor and methoxychlor. Total OCPs concentrations in the particles ranged from 0.84 ng/l to 6.44 ng/l with a mean value of 2.90 ng/l. The concentrations of total HCHs in particulates of surface seawater varied from 0.06 ng/l to 3.53 ng/l with an average value of 1.48 ng/l, to which γ-HCH contributed 74% - 93%. Concentrations of total DDT varied from N.D. to 1.38 ng/l with a mean value of 0.44 ng/l. The ratio of α-HCH to γ-HCH ranged between 0.03 and 1.25 (0.33 in average) in the southern SCS, which might imply the presence of a possible emission source of lindane nearby this region. The low ratio of DDT/ (DDD + DDE) suggested that DDT has not been used recently in studied area. This study provided the first data on the levels,distribution and sources of particulate OCPs in the southern SCS, which might be also the most southern place in China where OCPs has ever been detected.

Introduction

Organochlorine pesticides (OCPs), most of which are important persistent organic pollutants (POPs), are of environmental significance for their widespread distribution in the natural environment and potential toxicity to organisms. OCPs, such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs), are also known as endocrine-disrupting chemicals (EDCs).

It is well known that such kinds of OCPs have been widely used in China during the period of 1950s and 1980s. The amounts of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs) used in China accounted for about 33% and 20 % of the total world productions, respectively[1]. Although their usage had been banned more than 20 years ago in China, OCPs were recently found in natural environment, such as air, water, sediments and organisms[2, 3]. These results suggest that it is still very necessary to investigate and clarify their concentration levels and distributions of OCPs in surrounding areas, and to assess their geochemical processes. Many previous studies have shown that OCPs can be easily absorbed by particulates in the air, and then deposit into the sea through long-distance atmospheric transport (LRAT), which pose potential hazard to the human beings and marine ecosystems. In this case, particulate in the seawater is a significant medium for some important processes, such as air-sea exchange and sedimentation. For example, the fractions of ∑DDT associated with suspended particulate materials (SPM) were up to 90% in the Pearl River Estuary[4]. Thus, the determinations of concentration and fate of OCPs in particles could provide crucial information on anthropogenic impact on the environment. This study aimed to evaluate the occurrence of the most important organohalogenated pollutants, such as OCPs (DDTs, HCHs) in the suspended particles of surface seawater from the southern South China Sea. To our knowledge, no data on concentrations of particulate OCPs in seawater from the southern SCS have been presented in the literature before and our work might supply a gap of the OCPs in this sea area.

Materials and Methods

Sampling. Particulate OCPs in SPM samples were collected in 11 stations from the southern SCS on board the

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R/V *Experiment Ⅲ* in May, 2004 (Fig. 1). For each sample, 40~50 L surface seawater sample (1m) was collected and filtered through an on-deck pumping system. The particles were separated on glass fiber filters (0.7μm). The filters were wrapped in aluminum foil, and kept in a deep freezer at -20℃ until further chemical analysis.

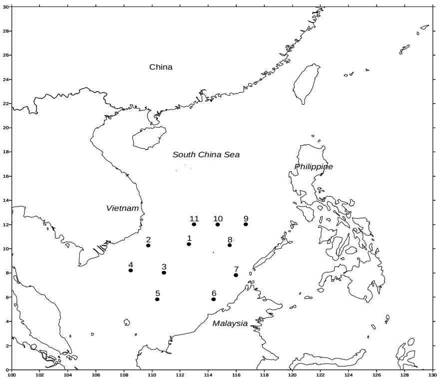

Fig. 1. Map of sampling sites

Sample Extraction and clean-up. OCPs standards (α-, β-, γ-, and δ-HCH, DDT, DDD, DDE, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, heptachlor, heptachlor epoxide) in a mixture and 2,4,5,6- tetrachloro-m-xylene and decachlorobiphenyl were all obtained from Supelco Inc.(North arrison Road in USA). All organic solvents were purchased from Tedia Inc.（USA）and re-distilled with glass system. Neutral silica gel (80-100 mesh) and alumina (100–200 mesh) were baked at 450℃ for 4 hours, and then 2% distilled water (m/m) was added for deactivation assisted by supersonic. Sodium sulfate were baked at 450℃ and stored in sealed containers. All the filters and aluminum foils were also pre-burned at 450℃ for at least 4 hours.

A freeze-dried sample was spiked with surrogated standards (tetrachlor-m-xylene). Add 50mL dichloromethane and store overnight. Then extract the sample three times with supersonic. Activated Cu was added for desulfurization. The extract was concentrated by rotary evaporator to approximately 5ml, and then subject to a 2:3 alumina/silica gel glass column (Ø100×5 mm) with 1cm anhydrous sodium sulfate on the top. The column was eluted with 5ml n-hexane and 10ml ethyl acetate successively, and the first eluate which contains alkanes was discarded, while the second part containing OCPs was further concentrated to 0.5 ml under a gentle nitrogen stream.

Analysis. The samples were analyzed by a Hewlett-Packard (HP) 5890 series II gas chromatograph (GC), equipped with a ^{63}Ni electron capture detector (ECD) and an 50 m (i.d. 0.32 mm, film thickness 0.17um) HP-5 silica fused capillary column(J&W,Angilent,USA). The samples were injected splitlessly (split opened after 5 min) at 270℃. High purity nitrogen was used as carrier gas with a flow rate of 1.0 ml/min. The oven temperature program was as follow: initial temperature was 60℃, heated at 20℃ min^{-1} to 160℃, held for 1 min, heated at 3º min^{-1} to 265℃, held for 5 min. The temperatures of injector and detector were 250℃ and 280℃, respectively. In this study, the target analytes are 15 OCP compounds, including α-, β-, γ-, and δ-HCH, DDT, DDD, DDE, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, heptachlor, heptachlor epoxide，Methoxychlor. Quantification was performed by the internal calibration method based on five-point calibration curve for individual component. Decachlorobiphenyl was used as internal standard for quantification of OCPs in GC-ECD analysis. For each set of 10 samples, a procedural blank and spike sample consisting of all reagents was run to check for interference and cross contamination. The detection limits (DL) of OCPs were determined as the concentrations of analyses in a sample which gives rise to a peak with a signal-to-noise ratio (S/N) of 3. The results showed detection limit for individual OCPs with a sample size of 50 l was 0.008 ng/l. Tetrachlor-m-xylene was used as surrogated standard. For all the samples analyzed, the mean surrogate recoveries of most OCPs were between 81% and 110%; and the recoveries of DDE, DDD, and methoxychlor were relatively high (around 120%).

Results and Discussion

Total 15 OCPs Compounds. In this study, Total concentrations of 15 OCPs compounds of the particulates (expressed as ∑OCP) ranged from 0.84 ng/l to 6.44 ng/l with a mean value of 2.90 ng/l. The distribution of ∑OCP in the southern SCS is presented in Fig. 2. It showed that the concentrations of ∑OCP decreased from the southeast to northwest in the southern SCS. The highest ∑OCP occurred at the Station 7 located in coastal seawater near Palawan Island, where terrestrial runoff may exceed atmospheric deposition input and contribute large amounts of OCPs to coastal sea area. In other stations, most OCPs found in the open-sea were likely from atmospheric deposition input and by water-mass transportation, which are the two major sources of OCPs in the southern SCS.

HCH isomers. It is well known that isomers of HCHs were widespread global pollutants[5]. Concentrations of total HCHs (∑HCH, sum of α-, β-, γ-, and δ-HCH isomers) in the SPM samples were in the range of 0.06 ng/l to 3.53 ng/l (mean 1.48 ng/l), which contributed about 51% to the total OCPs. The overall trend of spatial distribution of HCHs was also the same as that of total OCPs. The highest value of ∑HCH was found in the southeast of the studied area which is located in the west of Kalimantan. The concentration of ∑HCH decreased from southeast to northwest, which might be due to the LRT and seawater mass exchange in SCS (Fig.3). γ-HCH was found in 8 of 11 stations and the highest concentration was 2.63 ng/l in Station 6, which is in the coastal sea of Kalimantan. Compared to other stations, the water depth in this station is only 995 m. In more than half stations, the predominant pesticide of SPM was γ-HCH, which contributed 74% - 93% to the total HCHs. While the four isomers of HCHs were almost in the same level in station 10 and 11, where the water depths are 4 368 m and 4 300 m, separately.

DDTs. The total concentrations of DDTs (∑DDT, sum of DDD, DDE and DDT) ranged from N.D. to 1.38 ng/l with an average value of 0.44 ng/l. The contents of ∑DDT were much lower in the surface SPM from the southwest of SCS near Vietnam (Station 1 to 5), while they were comparable with the DDT levels in other stations. There were different spatial distribution patterns of ∑DDT in different parts of the southern SCS (Fig.4). In the south of studied area, the distribution of ∑DDT showed a distinctive gradient from the likely sources near Kalimantan Island, Station 6, to off-shore stations, and low values in the southwest part near the coast of Vietnam, Station 1 to 4. While in the north, the concentrations of ∑DDT were quite uniform with a slight variation of 0.2 ng/l. We suggest that there did not has point source of OCPs in the middle of SCS, and the spatial distribution patterns of ∑DDT might probably be controlled by atmospheric deposition input and water mass exchange.

Other OCPs. The total concentrations of the rest 8 OCPs (including aldrin, dieldrin, endrin, endosulfan I, endosulfan II, heptachlor, heptachlor epoxide and Methoxychlor) changed from 0.65 ng/l to 1.58 ng/l with a mean of 0.99 ng/l. Among them, there were several OCP compounds which had relatively high concentrations. For , Haptachlor ranged from 0.14 ng/l to 0.43 ng/l with an average value of 0.23 ng/L, Heptachlor epxide ranged from 0.20 ng/l to 0.69 ng/l with an average value of 0.34 ng/l, Endosufan ranged from 0.04 ng/l to 0.53 ng/l with a mean value of 0.24 ng/lm, and Aldrin ranged from 0.07 ng/l to 0.17 ng/l with a mean value of 0.10 ng/l.

Sources of OCPs. Ratio of α-HCH to γ-HCH and *p,p'*-DDT to *p,p'*-DDE had been used to estimate the origin and the pathway of air mass in the LRAT of contamination. Generally, HCHs contain the isomers in the following percentages: α, 55–80%; β, 5-14%; γ, 8–15%; δ, 2–16%; with lindane containing more than 90% of γ-HCH. Because of the environmental and biological persistent harms of HCHs, many developed countries had banned or restricted technical HCH usage since 1970s; a ban followed by many developing countries in 1980s. But lindane was still used as seed dressing and human medicinal purpose in many countries, including USA, Canada, and most European countries[6]. If technical HCH mixture was the source, the ratio of α-HCH to γ-HCH

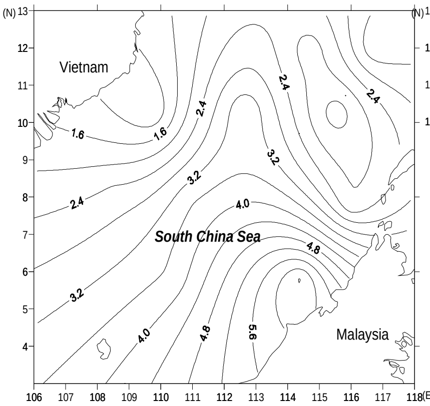

Fig.2. Distribution of concentration of ∑OCP

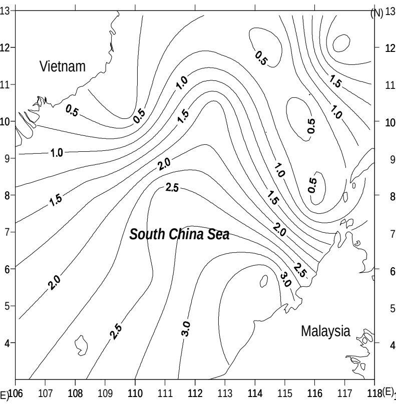

Fig.3. Distribution of concentrations of ∑HCH

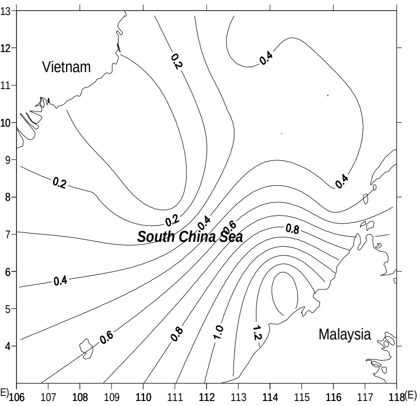

Fig.4. Distribution of concentrations of ∑DDT

should be between 4 and 15, which should range from 0.2 to 1 for the pesticide lindane[7]. These ratios are expected to increase with distance from the sources due to the biotransformation from γ-HCH to α-HCH.

In this study, except for 3 samples in which γ-HCH has not been detected, the ratios of α-HCH to γ-HCH ranged between 0.03 and 1.25 (averaged 0.33) in the southern SCS. The observed low α/γ ratios of HCHs in the Southern SCS may imply the presence of a possible emission source of lindane nearby this region. The similar ratio ranges were found in Daya Bay, China (0.03-1.47)[8] and in the Macau Harbour, China (0.72 - 1.52)[4].

Since metabolite of DDE, it is more stable and persistent in the environment, the ratios of DDT/ (DDE+DDD) and DDD/DDE can be used to trace the degradation degree of DDT and to identify the new input[9]. DDT has not been detected in the southwest sea area, near Vietnam And the DDT/ (DDE+DDD) ratios in other stations ranged from 0.36 to 1.44 with a mean value of 0.71. The DDD/DDE ratios ranged from 5.62 to 48.58 with a mean value of 29.38, except in Station 3 and 4, where DDD was not detected. Both of them implied that DDT has not been used recently in studied area.

Acknowledgements

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