VERTICAL DISTRIBUTIONS OF ORGANOCHLORINE PESTICIDES (OCPs) IN SEDIMENT, LAKE NAKAUMI

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Introduction

The Stockholm Convention can be divided as three groups such as organochlorine pesticides (OCPs), unintentional persistent organic pollutants (POPs) and PCBs which is UPOPs as well as commercial product such as Aroclor, Kanechlor, etc. Among these OCPs, aldrin, dieldrin, endrin, chlordane, heptachlor and DDT have been widely used for 1950–1970s, but mirex and HCB have never been used and produced in the past in Japan. Despite being banned now in many countries, someresidues of their products are still being found in water, sediment or biota. POPs are hydrophobic and therefore, easily bind to the particle phase in water system and then deposited to the bottom via sedimentation processes. They remain very long in sediment due to their long half-life times[1]. Sediments cores are one of the most easily accessed natural archives used for theevaluation and reconstruction of historical trends of pollution levels in theenvironment[2,3].In terms of assessing the levels of contamination,recovery of POPs from environmental samples is important[4].

The lake Nakaumiis located at the Shimane and Tottori prefectural border in the central part of the Sanin Region, western Japan. The lakeNakaumicovers approximately 9200ha and is the 5th largest lake in Japan, with an average depth of 5.4m and a salinity level that reaches as much as 1/2 seawater.Thus, Lake Nakaumi has rich biodiversity in the brackish water system. However, vertical distributions andhistorical trends of OCPsin the lake Nakaumihave not been reported. To evaluate the overall environmentalpollution state and to delineate the historical trends of OCPs in this study area, concentrations of each kindof OCPs were determined in the sediment cores usingHRGC-HRMS.This study would provide the valuable informationto understand the behavior of POPscaused from OCPs,such as dichlorodiphenyltrichloroethane and its metabolites(DDTs), hexachlorobenzene (HCB), heptachlor, chlordanecompounds (CHLs), Drins (aldrin, dieldrin, endrin), mirexand isomers of hexachlorocyclohexane (HCHs) in sediment cores of Lake Nakaumi.

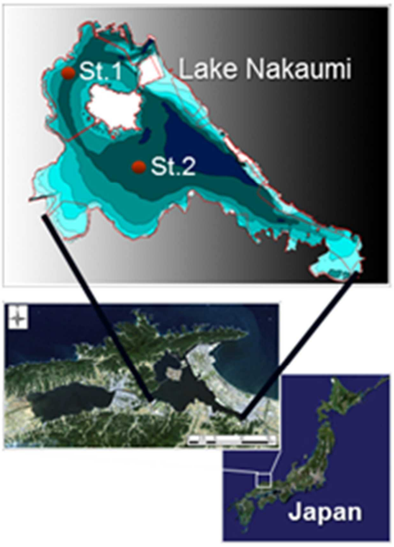


Fig. 1. Map of surface sediment sampling sites of Lake Nakaumi (St.1 and St.2).

Materials and methods

The sampling locations are shown in Fig. 1. Surface sediment samples were collected attwo stations, St.1 (Honjyo, depth 6.3m, N35º30′34″and E133º08′64″) andSt.2 (the center of a lake, depth 6.8m, N35º27′59″ and E133º11′29″) in the lake Nakaumi. Commercially available POPs, DDTs, HCB, heptachlor,CHLs, aldrin, dieldrin, endrin and mirex and persistentorganochlorines such as isomers of HCHs were used. Theirsurrogate substances of stable isotopically labeled internalstandards were purchased from Cambridge Isotope Laboratories, Inc (CIL).The sediment samples wereextracted, fractionated and analyzed following the methodsreported by Eun*et al.*[5]. All data presented here were corrected for each blankvalue.GC–MS analysis was performed using a high-resolutionmass selective detector (HRMS) (MicromassAutospec-Ultima) interfaced to a HP6890 series high-resolution gaschromatograph (HRGC). The SIMmode was constituted by tracing M^+ and $(M^{+2})^+$ ions ofeach compound. The range from m/z 210 to 300 for low mass compounds,HCHs, aldrin, dieldrin, endrin, DDTs, heptachlor, HCB,mirex and m/z 350–420 for high mass compounds, heptachlor-epoxide, chlordane, nonachlor and oxy-CHL wasused for the identification and quantification. Quantificationof the individual compound of POPs in the sampleswas conducted by the internal standard method using aRRF. Two surrogate standardsof ^{13}C-labeled PCB, #81 and #153 were spiked intothe final eluate to calculate recovery as internal standard.Recovery of POPs in spiked samples ranged from 50% to120% except aldrin (less than 30%). In addition, reproducibilityof each individual POP compounds showed less than10% except the mirex (23%) only. The detection limit (ND)was calculated to 3-fold value of the blank value for eachPOP. HRGC–HRMS system conditions are as follows: Asample injection separated an autosampler onto a 30 mENV-8MS column (i.d.0.25 mm, film thickness 0.25 µm,Kanto Chemical Co., Japan). The sediment cores were analyzed for ^{210}Pband^{137}Cs by direct gamma assay using a high purity germaniumdetect. The sedimentation rate and radiometricdates were calculated from the ^{210}Pb records based onthe constant initial concentration mode. The age determination with ^{210}Pb isotope revealed that the sedimentary rate in Station 1 and 2 were 3 and 2.5 cm per year, respectively.

Results and discussion

The changes in organochlorine pesticides usage in Japan are showed in Fig.2. In Japan, the period of intensive use of pesticideswas the decade from the mid-1960s to the mid-1970s, which represented over 50% to the total OCP pesticideuse during the past 35 years.

From 1949 to 1971, approximately 280,000 tons (A.I. base) of HCHswere produced and imported.The use of HCHs was the highest among the OCPsin Japan peaked in 1968.About22,000 tons of DDTs (1947-1971) and17,000 tons of chlordane (1958-1986) have been applied. However, HCB and Mirex have never been used in Japan. Residual concentrations of the POPs caused from pesticidessuch as DDTs, HCHs, CHLs, HCB, heptachlors, Drinsand mirex in sediment cores in the lake Nakaumiare presented in Fig. 3.The vertical distribution of POPs in sediment cores was relatively considered with historical term.The vertical distributionand total OCPs concentrationobserved in sediment core fromthe St.1(102 ng g^{-1} dry wt) from 1941 to 2005is not significantly different from that ofthe sediment corein the St.2(91 ng g^{-1} dry wt) from 1943 to 2005.The highest concentrations of OCPs weremeasured at both sampling locations in sedimentsin the period between 1960s and mid-1970s.In Japan, DDTs and HCHs were widely usedin industries and in agriculture during the 1950s and 1960s,a period of rapid development. The maximum concentration of DDTs and HCHs was presented during the mid-1960s. The results showed that the relatively high concentrations of DDTs and HCHs in the core ranged from 0.03 to 3.85 ng g^{-1} dry wtand 0.01 to 8.27 ng g^{-1} dry wt, respectively. The concentration profiles of HCHs and DDTs were similar to those of Tokyo Bay[6] and Ariake bay[3], Japan. These substances began suddenly increasing in the early 1950s, showing the peak near 1960-70s. OCPscan enter the aquatic environment throughrunofffrom agricultural areas and atmospheric depositioninsediments.

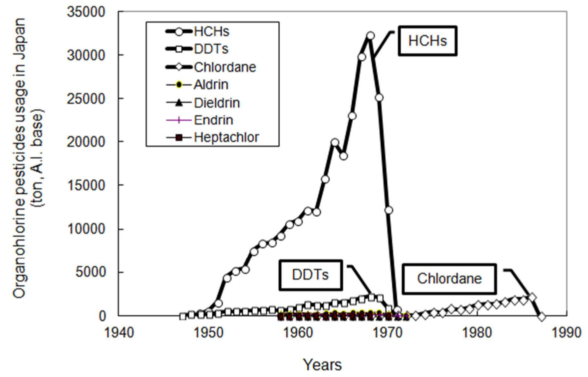
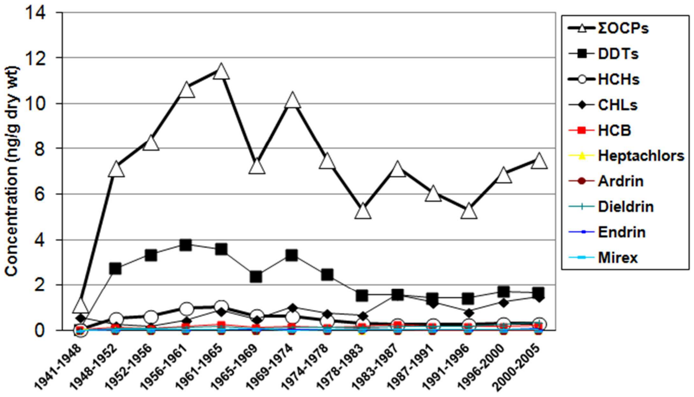


Fig.2Changes in organochlorine pesticides usage in Japan. The information is taken from Nouyaku Youran (Pesticide Usage Survey Report for Japan).

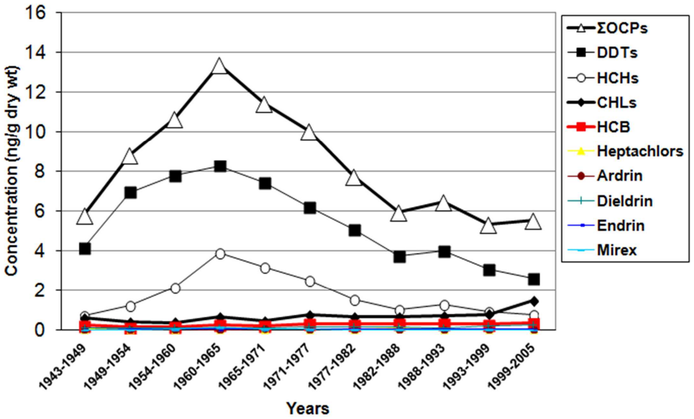
DDTs

The vertical concentrations of DDTs are shown in Fig.4. Concentrations and compositions of DDT isomers werefound to be in order DDE > DDD > DDT (including o,p′- and p,p′-) in almost all cores. Particularly, the concentrationof p,p′-DDE dominated in most of all layers. Thismetabolite was indicated higher persistency. Although, inJapan, about 22,000tons of DDT was used up until 1971, the highest residual concentrationof 8.27ng g^{-1} dry weight in St .2core in years 1960-1965 wasobserved. After that, the DDT concentration decreased. This indicates that a large amount of DDTs discharge had occurred before that period. The concentrations of DDTs in Lake Nakaumiwerelower than those of TokyoBay (0.22–26 ng g^{-1} dry wt.), Japan[6], Lake Taihu (0.65–

38 ngg^{-1} dry wt.), China[7] and San Francisco Bay (4–21 ng gg^{-1} drywt.), CA[8]. It is assumed that thelake Nakaumi seemed to be relatively less contaminated withDDT compounds than other areas.The composition of organochlorines and their metabolitiescan provide some information for a better understandingof the origin and transport of these contaminants in the environment.Peng*et al.*[7]reported a possibility of the continuousillegal use of DDT in China using the ratio of(DDD + DDE)/ΣDDTs. Microbial degradation of DDT,DDDandDDEis generally slow, resulting in environmentalpersistence of these compounds and DDT may degrade toDDD with a half-life of a few days under certain conditions[9]. The ratios of (DDE+DDD)/ΣDDTsin St.1 and St.2 ranged from 0.38 (years 1941-1948) to 1 and 0.88 to 0.94, respectively. Therefore, the ratios were declining toward downcores, which it could be explained that DDT emissionoccurred in the past input.



(a) St.1 (Honjyo area)



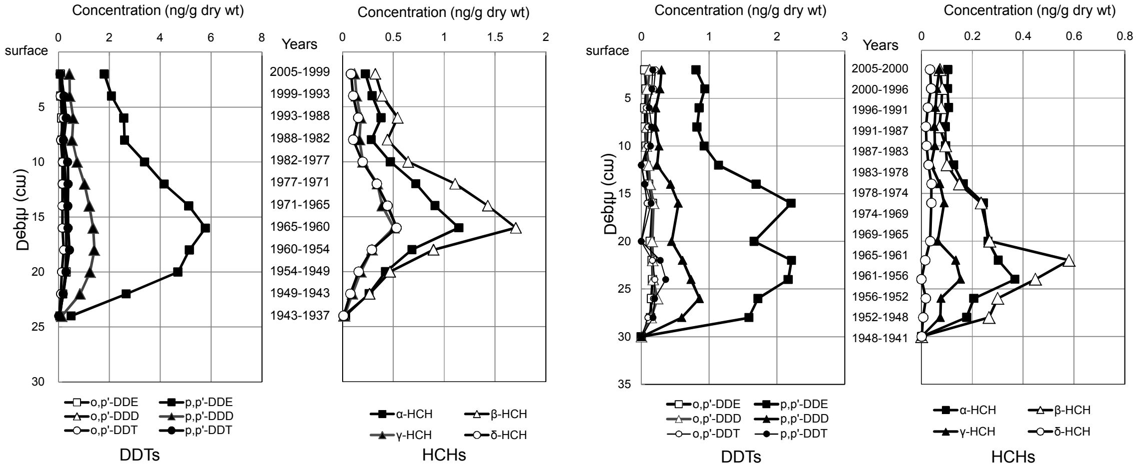
(b) St.2 (the center of a lake)

Fig. 3 OCPs profiles in sediment cores from Lake Nakaumi.

HCHs

The HCH residues are among the most widely distributedand frequently detected organochlorine contaminantsin the environment. The use of HCHs (approximately 280,000 tons) was the highestamong the OCPs in Japan(Fig. 2). This is an extremely large amount whencompared with DDTs. However, the residualconcentration of HCHs (0.03 to 3.85ngg^{-1} dry wt.) was lowerthan those of DDTs in the sediment cores. Thisimplies that more is transferred to the atmosphere afterusage in agriculture. The concentrations of HCHs in sedimentcores of Lake Nakaumishowed and increasing trendfrom the early 1950sand a peak in the mid-1960s.The HCH isomers have a relativelyhigher mobility than other OCP compounds, based on thephysical chemical properties, for instance, relatively lowlog octanol–air partition coefficient (K_{OA} = 6 to 8), relativelyhigh log vapor pressure (P_L = –2 to 0), and relativelylow temperature of condensation (–10 to –50ºC)[10]. The four major isomers discussed in this profile areα-HCH,β-HCH,γ-HCH, andδ-HCH. γ-HCH is also commonly knownas lindane. Technical-grade HCH consists of at least five isomers (approximately 60–70% α-HCH, 5–12% β-HCH, 10–15% γ-HCH, 6–10% δ-HCH, and 3–4% ε-HCH).The HCH isomer composition was β-HCH>α-HCH>γ-HCH,δ-HCH in almost all sediment layers (Fig.4). Decreasing concentrationafter mid-1970s might be reflected to that prohibited theproduction and use of HCHs in the early 1970s in Japan.Regarding the composition of HCH isomers in the environment,α-HCH was overall predominant in sedimentcores. The composition ofβ-HCH has beenreported predominant in environment because it is moststable among HCH isomers and resistant to microbialdegradation[11, 12].Therefore, itcan be assumed that HCHs contamination might haveoccurred through the use of technical-grade HCHs untilthe early 1970s. On the other hand, the decreasing trend forcomposition ofα-isomer and the increasing trend for theβ-isomer after they were officially banned in the early1970s were observed in upper sediment cores. This impliesthat HCHs contamination in upper cores might have originatedfrom a relatively remote source or long-time accumulationafter dispersing.

Unlike the above mentioned compounds, HCB, CHLs, Drins and heptachlors concentrations were observed in very low levels until the 1990s and then detected rather an increasing trend toward the current. The emission sources of HCB in sediment cores were considered as follows: impurities in pesticides such as pentachlorophenol (PCP), incineration of HCB-containing waste from tetrachloroethylene production, and incineration of municipal solid waste[13].Kim *et al.*[3] reported that the origin of HCB insediment core of Ariake Bay was atmosphericdeposition of incomplete combustion on the basis of relationamong the HCB concentration, PCP consumption and OCDDconcentration.As mentioned above, HCB was never registered for use as a pesticidein Japan. Therefore, we suggestthat HCB contamination in sediment of Lake Nakaumiwas caused by PCP.



(a) St.1 (Honjyo area)(b) St.2 (the center of a lake)

Fig.4 Vertical distributions of DDTs and HCHs concentration in the sediment core of lake Nakaumi.

Acknowledgements

The authors would like to acknowledge Dr. Seike N. ofNational Institute for Agro-Environmental Sciences for providing information on the data of organochlorine pesticides usage in Japan.

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