TEMPORAL CHANGE OF PERSISTENT ORGANOCHLORINES CONCENTRATIONS AND COMPOSITIONS IN PADDY SOIL

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Introduction

Sediment core[1), 2)] and vegetation[3)] are an important media to investigate temporal trend of persistent organic pollutants (POPs) such as, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), DDTs, HCHs,. These results showed that artificial POPs contamination was started from last century. The next POPs contamination was clearly observed during 1950s – 1980s. In the case of PCDD/Fs in Japanese paddy soils[4)], both concentration and composition of PCDD/Fs in paddy soils changed significantly after the nationwide use of the PCP and CNP had started from 1960s through 1970s. From 1980s onward, only a negligible change in PCDD/Fs compositions could be observed because of reduced PCDD/Fs emission from PCP and CNP. Instead, the proportion of PCDD/Fs of incinerator origin was gradually increased in paddy soils in the last 20 years. Even though environmental POPs levels has been reduced in recent years, it is important to clarify status of POPs contamination in the past for future predictions.

We have preserved paddy soils collected from all over Japan since 1960s. In this study, organochlorines such as HCHs (α-, β-, γ-, δ-), DDTs (*p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE), CHLs (*trans*-Chlordane, *cis*-Chlordane, Oxychlordane, *trans*-Nonachlor, *cis*-Nonachlor), Heptachlor, Heptachlorepoxide, Drins (Aldrin, Dieldrin, Endrin), HCB were analyzed in one site to evaluate the time trend of organochlorines contamination in paddy soils.

Materials and Methods

Paddy soils were preserved in polyethylene bottles after dryness at our institute from 1960. Before extraction, surface layer of these soils in polyethylene bottles were removed. Approximately 10g of soils were soxhlet extracted with acetone for 24 hours. ^{13}C-HCHs (α-, β-, γ-, δ-), ^{13}C-*p,p'*-DDT, D8-*p,p'*-DDD, ^{13}C-*p,p'*-DDE, ^{13}C-*trans*-Chlordane, ^{13}C-Oxychlordane, ^{13}C-*trans*-Nonachlor, ^{13}C-Heptachlor, ^{13}C-Heptachlorepoxide, ^{13}C-Aldrin and ^{13}C-HCB were used

as internal standards. Purification and separation were carried out by Gel Permeation Chromatography (PAE-2000, Shodex) and silica gel column chromatography. Samples were analyzed by HRGC/LRMS (HP6890/5973N) equipped with a RH-12ms (INVENTEX).

Results and Discussion

HCHs

Temporal change of HCHs isomer (α-, β-, γ-, δ-) concentrations from 1963 to 1999 were shown on Fig.1. HCHs concentrations were drastically decreased since 1960s. Use of HCHs was stopped at 1971 in Japan. It was thought that recent levels of HCHs in all over Japanese paddy soils were much lower than 30 years ago.

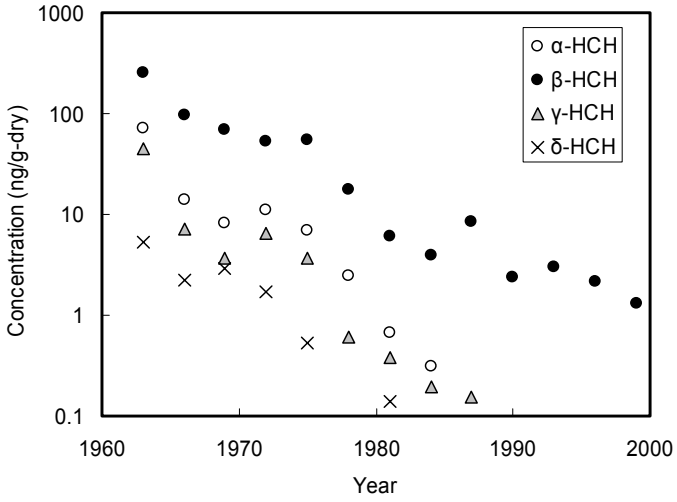

Fig.1 Temporal change of HCHs isomer (α-, β-, γ-, δ-) concentrations in paddy soils

Despite technical HCHs contain mainly four isomers (α:β:γ:δ=67:7:1:0.5), β-HCH was dominantly detected all over the periods. Further, concentrations of α-HCH, γ-HCH and δ-HCH were more rapidly decreased than that of β-HCH. In India[5], most of the HCHs applied to the field were found to volatilize rapidly as low residue levels in water and paddy soil. After two weeks of an application, more than 90% of the HCHs, in particular α-HCH and γ-HCH were found in the air and less than 10% in water, soil and rice plants. It was found that β-HCH is the most persistent isomer among HCHs in paddy soils.

DDTs

Temporal change of DDT related compounds (*p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE) concentrations from 1963 to 1999 were shown on Fig.2. Use of DDTs was also stopped at 1971 in Japan. DDTs concentrations also were decreased since 1960s. However, reduction speed of DDTs concentrations was slower than that of HCHs. It is well known that *p,p'*-DDD is major metabolite of *p,p'*-DDT in paddy soil. Therefore, *p,p'*-DDD was dominantly detected in all over the period.

Concentrations of DDTs on 1972 were *p,p'*-DDD>*p,p'*-DDT> *p,p'*-DDE. On the other hands, that on 1999 were *p,p'*-DDD> *p,p'*-DDE > *p,p'*-DDT. It means that the proportion of *p,p'*-DDE in DDTs was increased gradually. Half life of *p,p'*-DDE is higher than *p,p'*-DDT in upland soil[6]. It is

thought that *p,p'*-DDE is the most persistent compounds among DDTs in paddy soils and *p,p'*-DDE is going to be detected dominantly for the future.

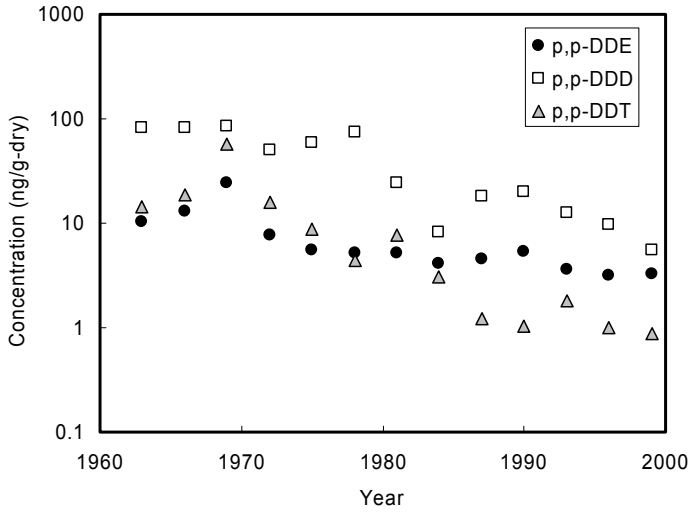

Fig.2 Temporal change of DDTs (*p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE) concentrations in paddy soils

Other Organochlorines

Temporal change of Drins HCB, and CHLs concentrations from 1963 to 1999 were shown on Fig.3. Heptachlor and its metabolite of heptachlorepoxide were not detected in all samples because it was mainly used as upland field insecticide in Japan. Only dieldrin was detected among Drins. Dieldrin concentrations were significantly decreased since 1960s. In the case of upland soil data from Rothamsted Experimental Station[6], half life of dieldrin was estimated to be ~25 years. In this study, half life of dieldrin was roughly estimated to be ~5 years in paddy soils. It can be indicated that dieldrin in submerged condition likely paddy fields might be easily reduced than upland condition.

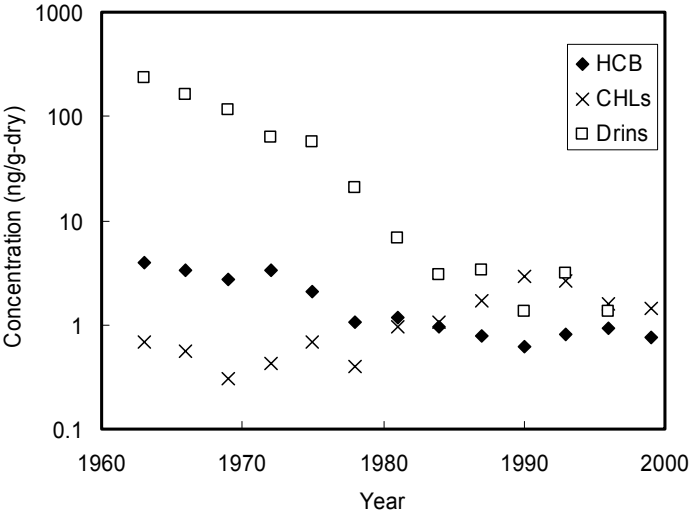

Fig.3 Temporal change of Drins, HCB and CHLs concentrations in paddy soils

HCB concentrations were also decreased since 1960s and lower than HCHs, DDTs and dieldrin. HCB was not used as pesticides in Japan. It was reported that HCB contained in some pesticides, such as PCP and PCNB[7]. Particularly, PCP was nationwide

used as paddy field herbicide during 1960s. However, PCNB was not used at paddy fields in the past. Concentration of octachlorinated dibenzo-*p*- dioxin (OCDD) was also high during 1960s. Hence, it was thought that major source of HCB in paddy soil during 1960s was impurities of PCP.

Concentrations of CHLs were much lower than that of other organochlorines during 1960s-1970s. However, the concentrations were increased during the period of 1980s through early 1990s. Afterward, the concentrations of CHLs have been successively decreased up to present. CHLs were used to control termites and other pest insects in Japan. It was thought that CHLs were not used at paddy fields but transported via atmosphere and (or) water.

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