TEMPORAL CHANGE IN ORGANOCHLORINE PESTICIDES CONTAMINATION IN JAPANESE PADDY SOILS

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Abstract
Organochlorine pesticides and their metabolites (OCPs) were analyzed in preserved paddy soils periodically collected from 14 sites around Japan since 1960 to trace the changes in concentrations and to estimate their half-lives in Japanese paddy fields. Temporal change in OCPs concentrations in paddy soils were reflected the use of pesticides. Namely, HCHs and DDT had been used as insecticides for paddy rice and their use were banned at early 1970s. Concentrations of HCHs and DDT were drastically decreased since end of 1960s. Chlordanes (CHLs) was used to control domestic pest insects until 1986 but not used in paddy fields. The concentrations of CHLs in paddy soils increased during the period of 1970s through 1980s. Afterward, the concentrations have been successively decreased up to present, suggesting that CHLs was transported via atmosphere and (or) water during the period which chlordane was used. The half-lives of OCPs for disappearance from the paddy soils were estimated to be 3 to 17 years. It was found that octanol-water partition coefficient (*K*ow) of compounds, total carbon content in soils and temperature at sampling sites are one of the important factors for the disappearance of OCPs from paddy soils.

Introduction
In order to prevent and reduce the global environmental contamination caused by persistent organic pollutants (POPs) through cooperation with countries around the world, the Stockholm Convention on Persistent Organic Pollutants was adopted in May 2001 and entered force from May 2004. Most of the compounds specified as POPs in this agreement are the organochlorine pesticides, such as DDT, dieldrin and chlordane. After the Convention is put into effect, it should be managed some problems concerning POPs, such as prohibition of use, reduction of emission to environment, prediction of contamination change in the future.

The paddy field accounts for approximately 10% of the agricultural field in the world[1]. In Japan, the paddy field accounts for more than half of them[2]. The amounts of use (active ingredient basis) of organochlorine pesticides, such as HCHs, DDTs, ardrin, dieldrin, endrin, chlordane, heptachlor, from 1958 were from 260 to 390×10^6 kg in Japan[3] (Fig.1). HCHs and DDT were commonly used as paddy insecticide. These pesticides were banned from the end of 1960s to the early 1970s (HCHs and DDT, 1971; ardrin, dieldrin, endrin and heptachlor, 1975; Chlordane, 1968) in Japan. These pesticides are detected in sediments and air from Japan as well as polar environment[4-6]. It can be indicated that organochlorine pesticides applied to paddy fields have not only flowed out into the surrounding catchments but also transferred across borders and are accumulated in polar organisms. Thus, paddy fields have played an important role as a secondary source of organochlorine pesticides in the aquatic and atmospheric environment for half a century. It is therefore important to understand the temporal trends of OCP levels in paddy soils for the prediction of future contamination status.

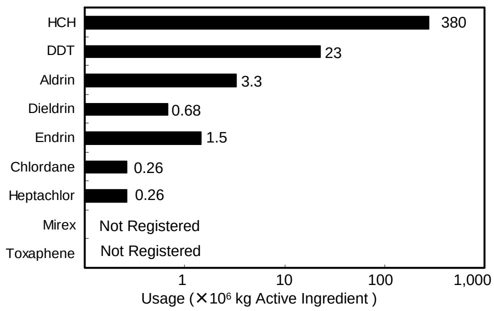

Fig. 1 Usage (×10^6 kg, active ingredient base) of organochlrine pesticides in Japan

We have archived paddy soils collected from all over Japan since 1960s. Results from analysis of these archived soils can derive the temporal change of POPs contamination status exactly compared with sediment core analysis[7]. In this study, organochlorine pesticides and their metabolites (OCPs) such as HCHs (α-, β-, γ-), ΣDDTs [*p,p'*-DDT and *o,p'*-DDT (DDTs), *p,p'*-DDD and *o,p'*-DDD (DDDs), and *p,p'*-DDE and *o,p'*-DDE (DDEs)], CHLs (*trans*-Chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor and oxychlordane), HPCLs (heptachlor, heptachlorepoxide), Drins (aldrin, dieldrin, endrin), HCB (hexachlorbenzene), and Mirex were analyzed in these soils in order to elucidate the status of contamination in the Japanese paddy fields from the 1960s up to the present, and to predict future changes in contamination with these compounds.

Materials and Methods

Samples. Air-dried and sieved (<2mm) paddy soils collected from 15 sites throughout Japan since 1960 are preserved in polyethylene bottles with a double stopper in a dark room at room temperature. After the surface of the soil was removed, a sample for OCPs analysis was taken out on a stainless steel spoon. OCPs were analyzed in topsoil samples collected from 14 of the sites.

Analysis of OCPs. Paddy soil samples (approximately 5g) were weighed, and 10 ng of $^{13}C_6$-HCHs (α-, β-, γ-, δ-), $^{13}C_{12}$-*p,p*'-DDT, D_8-*p,p*'-DDD, $^{13}C_{12}$-*p,p*'-DDE, $^{13}C_{10}$-*trans*-chlordane, $^{13}C_{10}$-oxychlordane, $^{13}C_{10}$-*trans*-nonachlor, $^{13}C_{10}$-heptachlor, $^{13}C_{10}$-heptachlorepoxide, $^{13}C_{12}$-aldrin, $^{13}C_{12}$-dieldrin, $^{13}C_{12}$-endrin and $^{13}C_6$-HCB, and $^{13}C_{10}$-mirex obtained from Cambridge Isotope Laboratories, Inc. were added as a recovery surrogates. The sample was Soxhlet extracted with acetone for 16 h. The extract was rotary evaporated and transferred with 25 mL of *n*-hexane into a separatory funnel and then washed twice with 100 mL water pre-cleaned with *n*-hexane, and excess water removed over Na_2SO_4. The solution was concentrated using a rotary evaporator to 1 mL, and interferences were removed by passing the extract through a column packed with 5 g of florisil (Mega Bond Elute FL, Varian). The column was eluted with 30mL of *n*-hexane containing DDEs, HCB, aldrin, heptachlor and mirex, followed by 80mL of *n*-hexane/dichloromethane (1 : 3, v/v), containing HCHs, DDTs, DDDs, CHLs, dieldrin, endrin and heptachlorepoxide. The latter fraction was concentrated in a rotary evaporator to 1 mL and applied to 500 mg of graphite carbon column (Envi-Carb, Supelco), then eluted with 10 ml of *n*-hexane. Both fractions which eluted by *n*-hexane on florisil and graphite carbon column were combined and concentrated, and then, 5 ng of $^{13}C_{12}$-labeled 3,4,4',5-tetrachlorobiphenyl and 2,2',4,4',5,5' -hexachlorobiphenyl (Wellington Laboratories) were added as a syringe spike. Finally, this solution was concentrated to 200µL under a gentle stream of N_2. The cleaned-up samples were analyzed on a high-resolution gas chromatography – high-resolution mass spectrometry gas chromatographic mass spectrometer (HRGC/HRMS) (Micromass AutoSpec-Ultima) equipped with ENV-8MS (30m × 0.25mm i.d. 0.25 mm film thickness, Kanto Kagaku). Recovery rates of the recovery surrogates were between 48% and 123%.

Results and Discussion

Temporal changes in OCPs concentrations in paddy soils reflected the use of pesticides (Fig.2).

HCHs. HCHs concentrations were drastically decreased since end of 1960s. Use of HCHs was banned in 1971 in Japan. It is thought that recent levels of HCHs in all over Japanese paddy soils are much lower than 40 years ago. Despite technical HCHs contain mainly three isomers (α : β : γ = 55-80 % : 5-14 %: 8-15%)[8], β-HCH was dominantly detected all over the periods (Fig. 3). Further, concentrations of α-HCH, γ-HCH and δ-HCH were more rapidly decreased than that of β-HCH. In India, most of 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[9]. It was found that β-HCH is the most persistent isomer among HCHs in paddy soils.

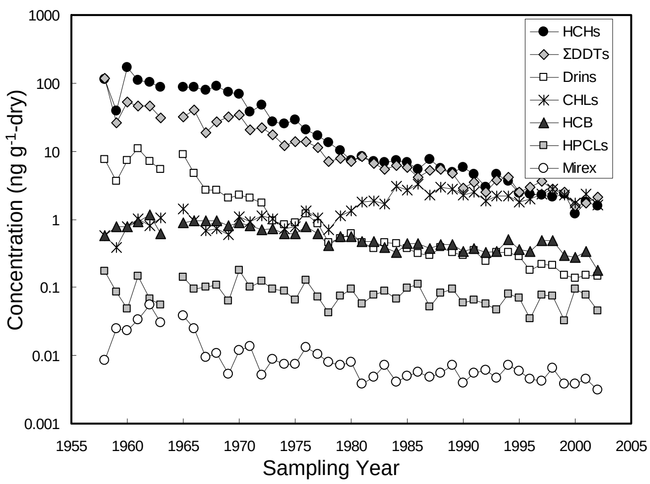

Fig. 2 Temporal changes in OCP concentrations (geometric mean of 14 sites, ng g^{-1} -dry) in Japanese paddy soils

DDT. ΣDDTs concentrations were also decreased since end of 1960s. However, reduction speed of ΣDDTs concentrations was slower than that of HCHs. It is well known that DDEs as well as DDDs are major metabolite of DDTs in paddy soil[10]. The proportions of DDDs and DDEs in ΣDDTs are increased gradually (Fig.4).

Other Organochlorines. Drins were less used on paddy rice until their use was the early 1970s compared with HCHs and DDT; concentrations of these pesticides have decreased dramatically since the end of the 1960s. CHLs was used to control domestic pest insects until 1986 but was not used in paddy fields; concentrations of CHLs in paddy soils increased from the 1970s through the 1980s, but since then they have steadily decrease, suggesting that CHLs was transported via the atmosphere and/or water during the period when it was used. 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[11]. 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) contained as major impurities in PCP was also high during 1960s[7]. Hence, it was thought that major source of HCB in paddy soil during 1960s was impurities of PCP. Mirex, an insecticide, was never used in Japan, but small amounts of mirex have been detected in paddy soils the 1960s up to the present.

Therefore, mirex appears to have been transferred across borders from other countries.

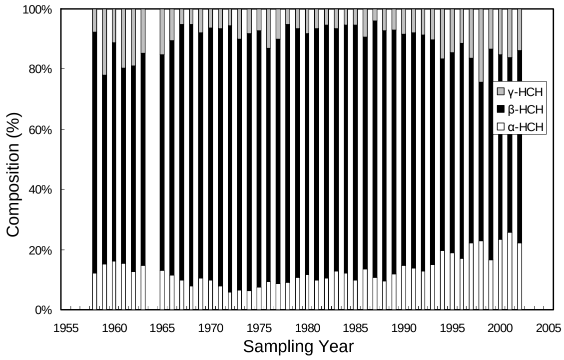

Fig. 3 Temporal changes in percentage compositions of HCHs isomer (mean value from 14 sites) in Japanese paddy soils

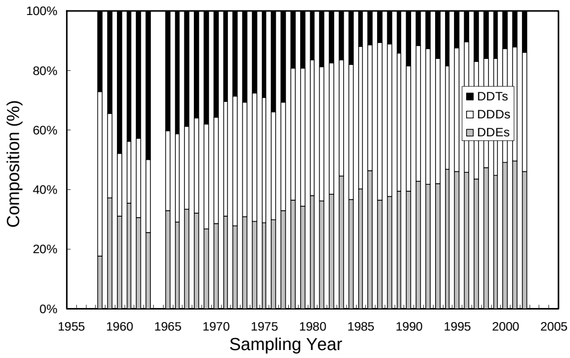

Fig. 4 Temporal changes in percentage compositions of DDT and metabolites (mean value from 14 sites) in Japanese paddy soils

Half-lives of OCPs in paddy soils. To elucidate the decline in OCPs and horizontal differences, we calculated half-lives for the disappearance of OCPs in paddy soils on the basis of the first-order reaction

$$k = - [\ln (C/C_0)]/t \qquad (1)$$

where k is the rate constant, C_0 and C are the initial and final residue concentration of OCPs and their metabolites in preserved paddy soils, and t is years from start (t = 0) to end. The start is the year with the highest concentration, and differs by site and compounds. It was assumed that no significant inputs of OCPs in the point of start have been occurred. The end is the last year of sampling.

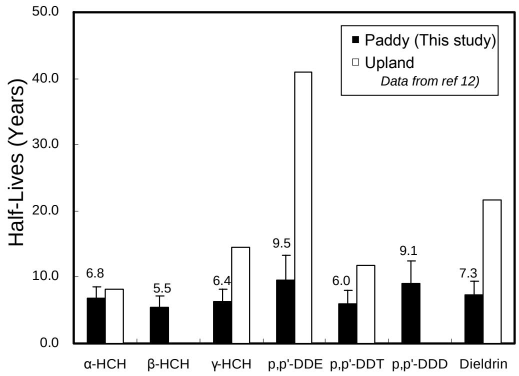

Fig. 5 Calculated OCPs half-lives (mean ± SD years) in Japanese paddy soils. The numbers and bars denote mean of half-lives and SD, respectively.

The half-lives for the disappearance of OCPs were estimated to be 3 to 17 years, shorter than in upland fields[12] (Fig. 5). It can be indicated that OCPs in submerged condition likely paddy fields might be easily reduced than upland condition. The calculated mean half-lives of POPs (OCPs and their metabolites, and dioxin congeners) were significantly (r = -0.41, P < 0.05) correlated with octanol-water partition coefficient (*K*ow)[13] (Fig. 6). The half-lives of OCPs at all sites in this study tend to be correlated with the total carbon content (T-C) in soils, and annual mean temperature at sampling sites (Table 1). These results suggest that *K*ow of compounds, T-C in soils and temperature at sampling sites are one of the important factors for the disappearance of OCPs from paddy soils.

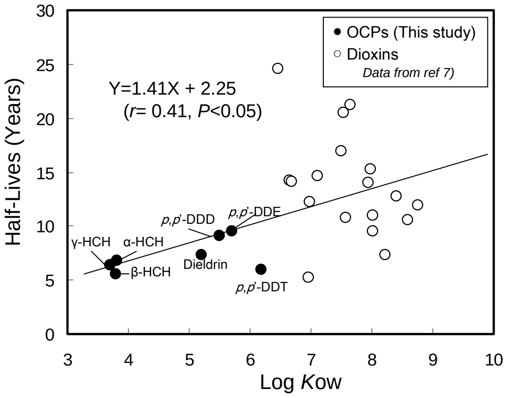

Fig. 6 Relationship between half-lives of POPs (OCPs and dioxins[7]) in Japanese paddy soils and *K*ow[13].

Table 1. Correlation coefficient between half-lives of OCPs in paddy soils and soil properties. Bolded numbers are significant as determined by ANOVA(P<0.05)

Compound	T-C	Annual mean temp.	pH (H2O)	Clay content
α-HCH	0.506	**-0.686**	-0.216	0.515
β-HCH	**0.601**	**-0.541**	-0.040	0.522
γ-HCH	0.475	-0.030	-0.126	0.376
p,p'-DDE	**0.704**	-0.366	-0.006	0.516
p,p'-DDT	0.237	-0.032	-0.451	0.350
p,p'-DDD	**0.722**	**-0.600**	0.073	0.448
Dieldrin	0.444	-0.304	0.040	0.011

Acknowledgements
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