HISTORICAL TREND OF PCDD/FS IN PADDY SOIL BY PRESERVED SAMPLE ANALYSIS

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Introduction

Sediment core[1), 2)] and vegetation[3)] are an important media to investigate temporal trend of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). These results show that artificial PCDD/Fs contamination was started about year 1900. A foremost PCDD/Fs contamination was clearly observed during 1960s – 1980s. Evan though environmental PCDD/Fs levels has been reduced in recent years, it is important to clarify status of PCDD/Fs contamination in the past for future predictions.

Some pesticides, such as 2,4,6-Trichlorophenyl 4-nitrophenylether (CNP) and Pentachlorophenol (PCP), were used at paddy fields as herbicides in the past. Congeners, such as 1,3,6,8-TeCDD, 1,3,7,9-TeCDD and OCDD are impurities of these herbicides[4)] are widely distributed in aquatic environment[5-7)]. Therefore, It is important to investigate time trend of PCDD/Fs concentration in paddy soils to understand the contamination occurred by such chemicals.

In this study, PCDD/Fs were analyzed in preserved paddy soils collected from throughout Japan since 1960s. Then evaluate the time trend of PCDD/Fs contamination in Japan.

Materials and Methods

After dried, paddy soils were preserved in polyethylene bottles at our institute from 1960. Before extraction, surface layer of these soils in polyethylene bottles were removed. All samples were soxhlet extracted with toluene. Purification and separation were carried out by multiplayer silica gel, alumina and activated carbon column chromatography. Samples were analyzed by HRGC/HRMS (HP6890/ Auto Spec-Ultima) equipped with a SP-2331 (SPELCO) and DB-5ms (J&W SCIENTIFIC).

Results and Discussion

Concentration of PCDD/Fs in paddy soils was increased during 1960s – 1970s. Then the contamination has been reduced in recent years (Fig.1). From these results, it could be estimated that the half-life of PCDD/Fs in paddy fields was about 10-20 years.

Fig.2 shows that historical trend of OCDD and 1,3,6,8-TeCDD concentrations in paddy soils. The highest concentration of OCDD in paddy soil was detected on early 1960s. Then it has been reduced. On the other hand, the highest concentration of 1,3,6,8-TeCDD was detected in the latter half of 1960s or early 1970s. Fig 3 shows that time trends of production of PCP and CNP in Japan. PCP and CNP were used as a paddy field herbicide on early 1960s and the latter half of 1960s, respectively. It can be observed that OCDD and 1,3,6,8-TeCDD concentrations and production of PCP and CNP patterns were well agreed.

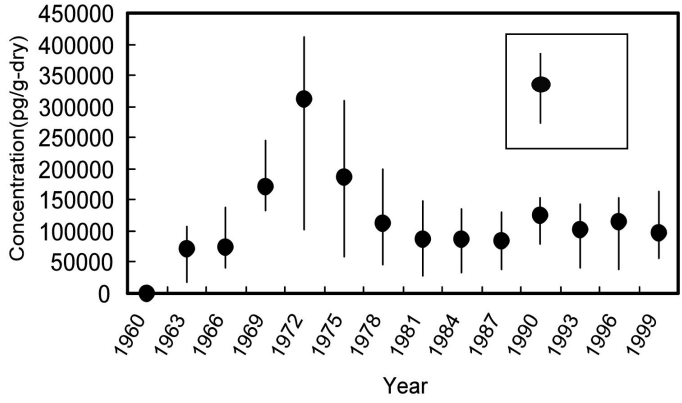

Figure 1. Historical trend of PCDD/F concentrations in paddy soils form Japan

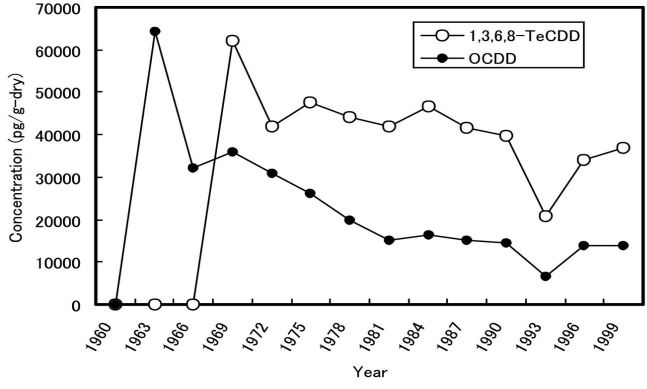

Figure 2. Historical trend of OCDD and 1,3,6,8-TeCDD concentrations in paddy soils

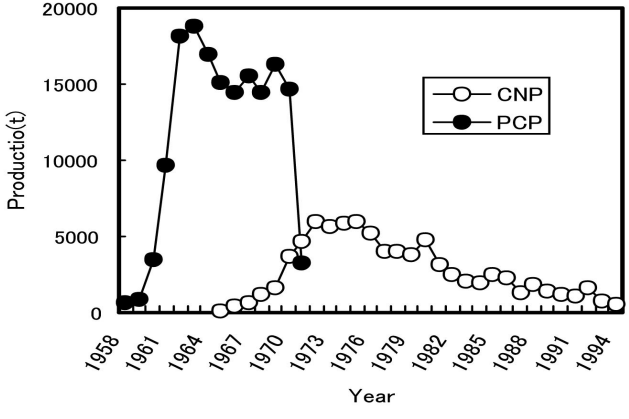

Figure 3. Time trend of production of PCP and CNP in Japan

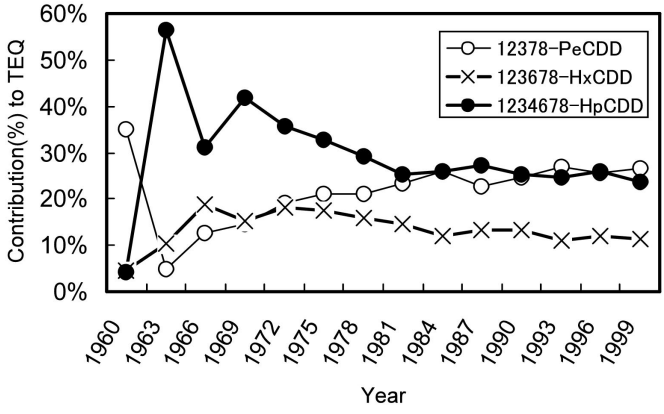

Figure 4. Time trend of contribution (%) to TEQ by some toxic congeners

Time trend of TEQ showed similar pattern with PCDD/F concentration. However, trend of 2,3,7,8-substituted congener contributions to TEQ was different in 1960s compared to 1990s (Fig.4). The contribution by 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD and 1,2,3,4,6,7,8-HpCDD congeners accounted for about 60-70 % of TEQ from 1960 to 1999. The highest contribution by 1,2,3,6,7,8-HxCDD and 1,2,3,4,6,7,8-HpCDD was observed on 1966 and then decreased. 1,2,3,7,8-PeCDD was gradually increased year by year. It can be suggested that major contributors in PCP and CNP are 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8-PeCDD, respectively.

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