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TEMPORAL VARIATION OF DIOXIN COMPOUNDS IN JAPANESE UPLAND

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Introduction

In the case of Japanese farmland, especially paddy, organochlorine pesticides (OCP) used in the past, contained dioxin precursors such as 2,4,6-trichlorophenyl 4-nitrophenyl ether (Chlornitrofen:CNP) or pentachlorophenol (PCP) as contaminant, hence, related researches have been performed on remnant of dioxin compounds[1,2,3,4]. In the previous work, we found that time trends of dioxin and related compounds concentration in paddy were gradually decreased year by year[5]. The paddy mainly produces rice, but upland produces various crops yearly and adequate fertilizer and herbicide on the crops are introduced to the upland. Because the weather is different depending on the regions in the country, cultivation method and kinds of the crops are also different and agricultural resources being used for crop cultivation show diversity. In addition, in the case of upland, the intention of land-usage has also been changed along with variation of environment.

Case studies of dioxin, however, related to upland that has these variations have not been found. In this study, we investigated the temporal variation of dioxin compounds in upland that was gathered all throughout Japan for about half a century. It was elucidated that the distributions and time variation of dioxin compounds were dependent on the regions, showing different patterns over

the regions for the first time from this research.

Methods and Materials

All PCDD/Fs and co-PCBs used as internal, recovery and calibration standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All other chemical used were for organic trace analysis and were obtained from Kanto Kagaku (Tokyo, Japan).

Upland soil samples in all parts of Japan were collected and preserved every year from 1960 at our institute. All the samples were extracted with toluene in a Soxhlet apparatus for 24h. Detection of PCDD/Fs and co-PCBs were determined by of GC (6890 plus, Hewlett Packard, US) with a DB 5MS column (J&W Scientific, US) and an SP 2331 column (Supelco, Inc., US), coupled to a HRMS (AutoSpec-Ultima, Micromass, UK) operation on a resolution of 10,000 using a positive electron ionization source and operating in the selected ion monitoring (SIM) mode. Verification of resolution in the working mass range was obtained by measuring perfluorokerosene (PFK) reference peaks. The current trap was 500 μA and the ionization energy was 30 eV. Ion source and injector temperatures were 260 ºC. The samples were injected in the splitless mode.

Results and Discussion

The upland of A region shows dioxin compounds came through air, formed by combustion processes until early 1960's, whose pattern is different from that starting from 1970' in which, 2,4,6,8-TeCDF congener was detected in most abundant amounts. The latter pattern of dioxin compounds lasted over 30 years (Fig. 1). The patterns of the upland of B region show that not only was 2,4,6,8-TeCDF congener detected as a major compound starting from 1980's, but 1,2,4,6,8-, 1,2,3,6,8-, and 1,2,3,7,9-PeCDD congeners were also found in abundant amounts. When considering a characteristic dioxin of CNP (prohibition of production and sale by manufacturer, 1996; registration withdrawal, 1998), paddy herbicide, in which 2,4,6,8-TeCDF, 1,2,4,6,8-,

1,2,3,6,8-, and 1,2,3,7,9-PeCDD congeners contains 1,3,6,8- and 1,3,7,9-TeCDD as major impurities (Fig. 2), it can be seen that CNP was used in regions A and B at different times in different amounts.

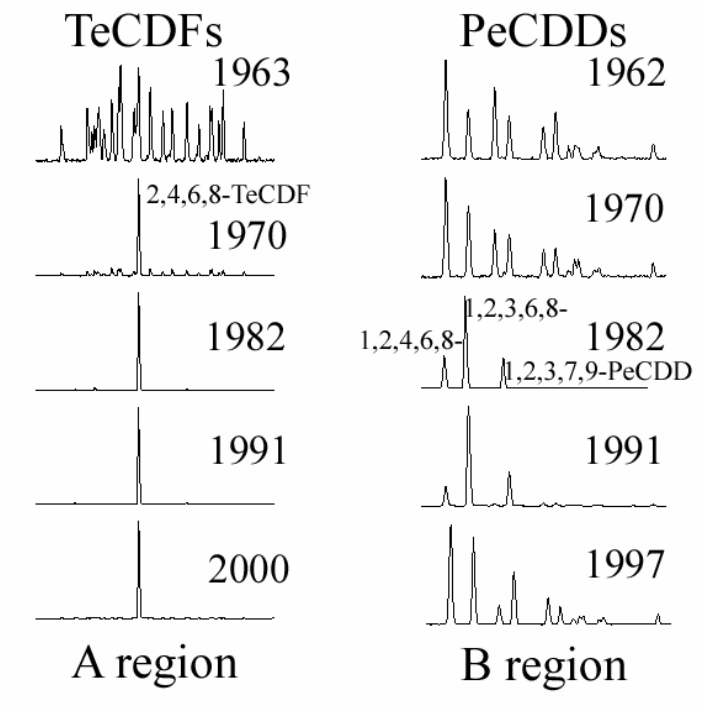

Figure 1. Temporal changes of TeCDFs and PeCDDs pattern in upland soils

It has also shown that remnants of CNP used at that time still affects the soil in those regions to this day. Meanwhile, various patterns could be seen such as regions where the upland only used PCP at different times and amount, and regions where a mixture of CNP and PCP was used. Here, we need to pay attention to this fact that PCP was largely used in 1960's, and CNP started to be used widely in the upland along with emulsion in early and late 1980's. Time variation of dioxin compounds in upland of the country, unlike paddy, display complicated and diverse patterns due to cultivation of various crops. In addition to differences in dioxin distribution between regions, considering the difference in upland-usage, it's difficult to conclude the patterns of dioxin compounds in upland.

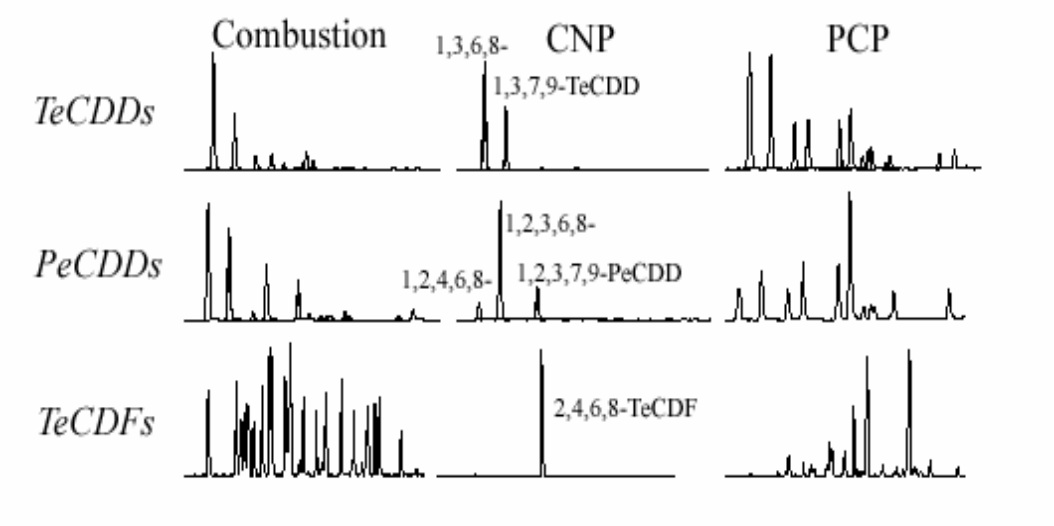

Figure 2. Chromatograms of combustion and organochlorine pesticides pattern

References

1. Seike N., Sakiyama T., Matsuda M., Wakimoto T. (1997). Organohalogen Compounds, 20, 147
2. Seike N., Matsumoto M.., Matsuda M., Kawano M., Wakimoto T. (1998). Organohalogen Compounds, 39, 97
3. Masunaga S., Takasuga T., Nakanishi J. (2001) Chemosphere, 44, 873
4. Masunaga S., Yao Y., Ogura I., Nakai S., Kanai Y., Yamaamuro M., Nakanishi J. (2001) Environ. Sci. & Technol., 35, 1967
5. Seike N., Eun. H., Ishizaka. M., Komamura M., Uegaki R., Kuwahara M., Ueji M. (2002) Organohalogen Compounds, 57, 1