THE CONGENER PROFILES OF PCDD/DFs AND DIOXIN-LIKE PCBs IN SOIL ANIMALS FROM JAPANESE FALLOW

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Introduction

In recent years, polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and non- and mono-*ortho*-substituted polychlorinated biphenyls (dioxin-like PCBs) have received considerable attention because of their extreme persistence, bioaccumulation and toxic potential to wildlife. The concentrations of these compounds in wildlife were reported in recent years [1, 2]. And particularly PCDD/DFs were detected at extremely high concentrations in raptors; in spite of the general low soil concentrations. Therefore, the mechanisms of bioaccumulation especially for terrestrial wildlife should be investigated. But very few researches have been done in this area. Almost all the PCDD/DFs in terrestrial field exist in soil because of their high adsorption affinity to soil organic fraction. The soil organisms, on the other hand, which constitute soil ecosystem, feed on soil. The soil ecosystem is the starting point of terrestrial food web. The soil animals intake pollutants in soil and passes them through other biota to raptors [3]. Thus, concentrations of PCDD/DFs of soil animals should be measured and the accumulation characteristics in soil ecosystem should be clarified.

In Japan, the two main sources of PCDD/DFs were combustion and agrochemicals such as pentachlorophenol (PCP) and chloronitrofen (CNP) [4]. The emissions from agrochemicals were far greater than those from combustion sources in the past, and they still remain in the rice field soil. However, there is no report for soil animals in rice field, so rice field was chosen as target of study.

Materials and Methods

Sample Collection:

Soil, earthworm, and mole samples were collected from the fallow in Kanagawa prefecture, Japan (**Figure 1**). The fallow is the farm land which was used for rice farming formerly. We set 5 grids randomly in 10 m ×10 m fallows. Each grid size was 50 cm ×50 cm with depth of 20 cm. Soil sample was collected from each grid and mixed to one sample. Soil and earthworms (Megascolecidae and Lumbricidae) were collected in August 2005. The mole (*Mogera imaizumi*) (n=1) was collected near the fallow in October 2005. Earthworm samples were collected by hands, starved on the wet filter paper for three days. Mole was collected by trap. All samples were kept -30˚C until analysis.

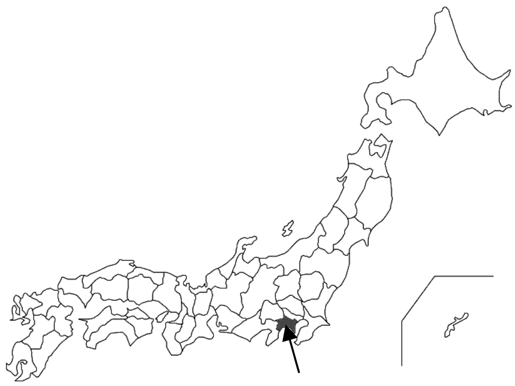

Figure 1 The location of Kanagawa prefecture

Analysis:

Whole body of earthworm and mole's liver, kidney, and muscle of shoulder were used for analysis. All samples were freeze-dried prior to analysis. Details of the analytical procedures were based on the official method established by Ministry of the Environment (MOE) of Japan [5]. The ^{13}C-labeled internal standards were added to all samples and then extracted in a Soxhlet apparatus with distilled toluene for 16 hours. The extracts of earthworm and mole samples were concentrated to 10 ml and 1 ml of the concentrate was used for measuring the lipid contents by gravimetric method. Multilayered silica gel chromatographic column and activated carbon column were used as cleanup procedures. Finally, ^{13}C-labeled recovery standard was spiked for HRGC/HRMS analysis. Tetra to octa-chlorinated PCDD/DFs and dioxin-like PCBs were quantified with DB-5 column (J&W Scientific) [6].

Results and Discussions

The Observed Concentration:

The total PCDD/DFs and dioxin-like PCBs concentration of soil was 19,000 pg/g, on dry weight basis, and those of earthworm, mole's liver, kidney, muscle were 28,000, 6,900, 2,500, 460,000 pg/g, on fat weight basis, respectively. When WHO-TEFs for mammal were used to estimate toxic equivalency (TEQ), the concentrations of total PCDD/DFs and dioxin-like PCBs were 42 pg-TEQ/g dry weight for soil. By way of comparison, the concentration of rice field soil in Japan (2002) reported by MOE ranged from 0.0017 to 200 pg-TEQ/g dry weight [7]. And earthworm and mole's liver, kidney, muscle were 450, 290, 220 and 6,700 pg-TEQ/g fat weight, respectively.

Congener Patterns:

The homologue pattern of PCDD/DFs in soil, agrochemicals (CNP and PCP) and atmospheric deposition are shown in **Figure 2**. The similarity between soil and CNP suggested that CNP was sprayed in the past. So, this field can be regarded as a representative one, contaminated by CNP originated PCDD/DFs in Japan.

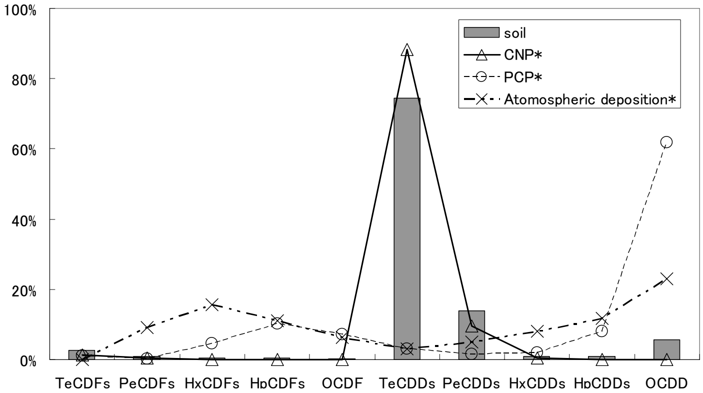

Figure 2 The PCDD/DFs homologue pattern in soil

* CNP and PCP data is reported by Masunaga et al. (2001) [8], and atmospheric deposition data is by Ogura et al. (2001) [9].

For all samples, PCDD/DFs and dioxin-like PCBs homologue pattern are shown in **Figure 3**. The pattern of earthworm was similar to that of soil. Mole samples, however, were quite different. Probably, internal metabolism of dioxins or intake of the food other than earthworm made this difference. As for the homologue patterns of tissues, liver and kidney were similar, but muscle was quite different. This result suggested that each homologue behaved differently in mole. The report for mole carcass (*Mogera Imaizumi*) by Kunisue et al. showed that composition of PCDDs was especially high and OCDD and 1,2,3,4,6,7,8-HpCDD were dominant [10]. In this study, the same trend was observed.

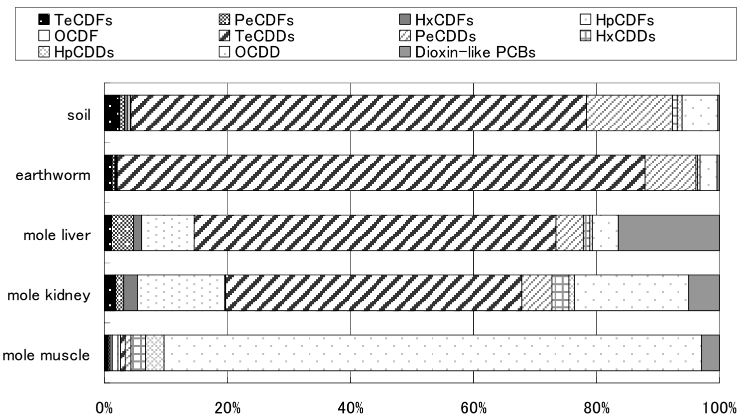

Figure 3 Proportions of each PCDD/DFs homologues and dioxin-like PCBs in total dioxin concentration in soil, earthworm, mole's liver, kidney and muscle

Figure 4 shows the details of congener profiles in soil and earthworm. Congener profiles were shown in percentage in each homologue. OCDF and OCDD were not shown, because only one congener was present in these homologues. Earthworm's profile was very similar to that of soil. This suggested that earthworm reflected the pollution in soil. Moles are said to live on almost exclusively on earthworms. However, mole's profile was different (**Figure 5**). This suggested that each congener behaved differently in mole.

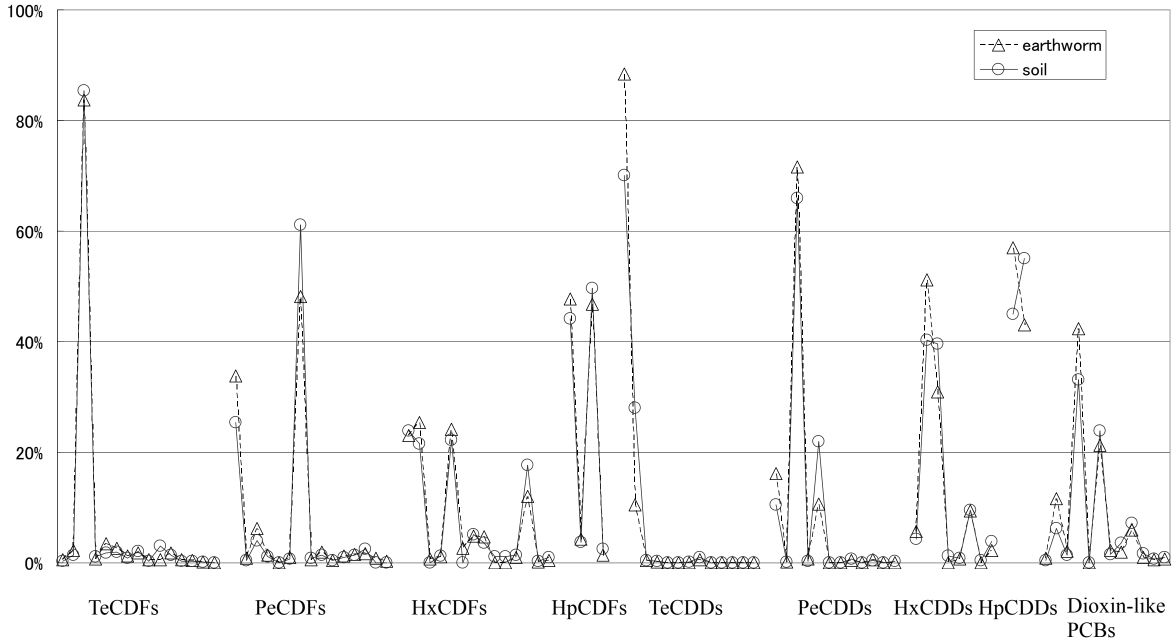

Figure 4 Congener profiles of soil and earthworm. The plots show the proportion of a congener within each homologue.

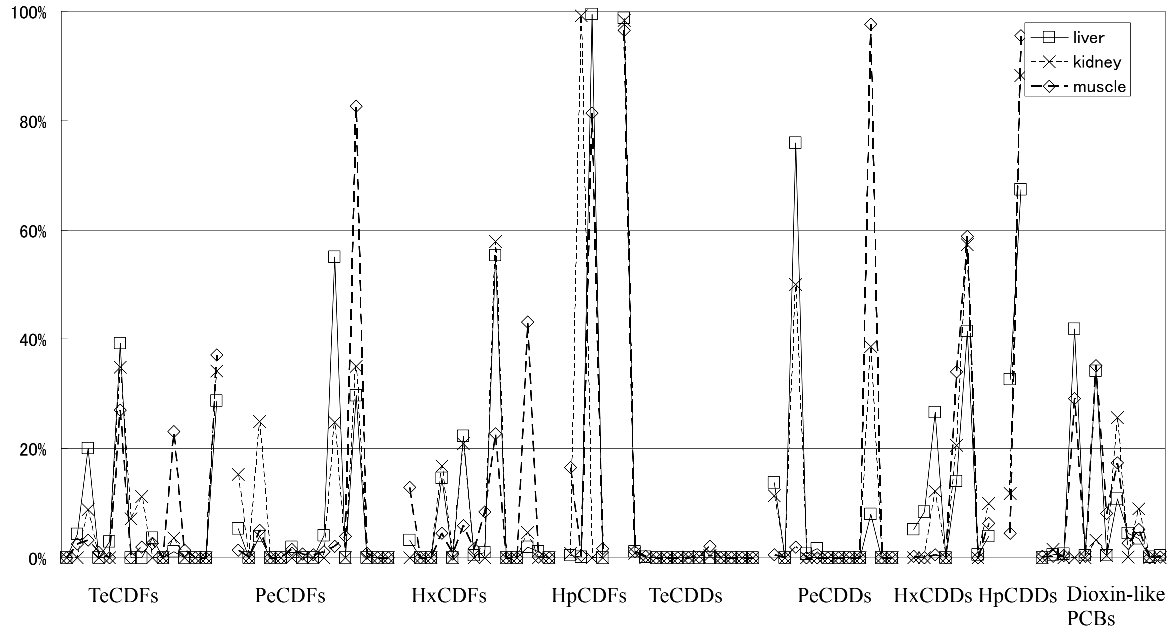

Figure 5 Congener profiles of mole's liver, kidney, muscle. The plots show the proportion of a congener within each homologue.

Conclusions

Dioxin levels and its congener profiles were studied for soil animals in fallow in Japan. The homologue profile in soil showed CNP was once used in the fallow. The congener pattern in earthworm reflected that in the soil, but the mole's congener pattern was different from the earthworm. Probably the metabolism in the mole made such difference. To clarify the effect of metabolism on dioxin congener profiles, it is necessary to investigate the mole's food other than earthworm.

Acknowledgements

This study was supported by the 21st Century COE Program, "Bio-Eco Environmental Risk Management" of Ministry of Education, Culture, Sports, Science and Technology of Japan.

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