SIMULATION OF TIME TREND DYNAMICS OF DIOXINS IN SEDIMENT CORE SAMPLES USING THE DYNAMIC MULTIMEDIA ENVIRONMENTAL FATE MODEL

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Introduction

Long-term trends of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were recently studied using the sediment core samples[1,2,3]. Trends and/or homologue profiles of PCDD/F concentrations in each core sample were different from each other, presumably reflecting the difference of the various environmental condition of the sampled site. Three largest emission sources of PCDD/Fs in Japan were municipal solid waste incinerator (MSWI), impurities in herbicide chlornitrofen (CNP) and pentachlorophenol (PCP)[8]. Other sources were of course listed in the emission inventory, however, above three sources were probably much larger than other sources[8]. This implies that the different relative contribution from three sources in an area could roughly determine the different core profiles in that area. Other environmental/chemical conditions, such as land/water ratio, climatic condition and nature of each compound, could significantly modify the trend/chemical profiles.

In this study, a dynamic multimedia environmental fate model including the sediment core layers and nested paddy-field sub-compartment was developed for the simulation of core concentration profile. The paddy-field sub-compartment was included because the majority of CNP and PCP entered into the environment as the herbicides in the paddy-field area. Two model environments, representing the Tokyo bay basin and Lake Kasumigaura basin were tested for calculation. Homologue total concentrations from 4 to 8 chlorinated PCDD/Fs were studied for the purpose of the discussion of environmental dynamics, instead of the toxic 2378-substituted congeners.

Methods

Model formulation

Modeling approach of this study is essentially same as already described[4]. A dynamic multimedia environmental fate model was developed based on the fugacity level IV model[5]. Sediment-core layers were included as the separate 50 compartments each representing the one core layer. Time span across 50-years range could be simulated by the model settings. The model formulations were as follows:

$$V_1 Z_{B1} \left(df_1^j / dt \right) = E_1^j + f_2^j D_{21}^j + f_3^j D_{31}^j + f_w^j D_{w1}^j - f_1^j \left(D_{R1}^j + D_{A1}^j + D_{12}^j + D_{13}^j + D_{1w}^j \right) \qquad \text{(Air)}$$

$$V_2 Z_{B2} \left(df_2^j / dt \right) = E_2^j + f_1^j D_{12}^j + f_3^j D_{32}^j + f_w^j D_{w2}^j + f_s^j D_{s2}^j + f_4^j D_{42}^j$$

$$- f_2^j \left(D_{R2}^j + D_{42}^j + D_{21}^j + D_{24}^j \right) \qquad \text{(Water)}$$

$$V_3 Z_{B3} \left(df_3^j / dt \right) = E_3^j + f_1^j D_{13}^j - f_3^j \left(D_{R3}^j + D_{A3}^j + D_{31}^j + D_{32}^j \right) \qquad \text{(Soil)}$$

$$V_4 Z_{B4} \left(df_4^j / dt \right) = E_4^j + f_2^j D_{24}^j - f_4^j \left(D_{R4}^j + D_{A4}^j + D_{42}^j \right) \qquad \text{(Sediment)}$$

$$V_w Z_{Bw} \left(df_w^j / dt \right) = E_w^j + f_1^j D_{1w}^j + f_s^j D_{sw}^j - f_w^j \left(D_{Rw}^j + D_{Aw}^j + D_{w1}^j + D_{ws}^j \right) \qquad \text{(Water-Paddy)}$$

$$V_s Z_{Bs} \left(df_s^j / dt \right) = E_s^j + f_w^j D_{ws}^j - f_s^j \left(D_{Rs}^j + D_{As}^j + D_{sw}^j \right) \qquad \text{(Paddy-Soil)}$$

where, E_i^j : emission rate of homologue j to the compartment i; f_i^j : fugacity of homologue j in the compartment i; $D_{ii'}^j$: transportation parameter; D_{Ri}^j : degradation parameter of homologue j in the compartment i; j : homologue number; Z_{Bi} : bulk phase Z values.

The k-th sediment core phase were formulated as follows:

$$V_k Z_{Bk} \left(df_k^j / dt \right) = E_k^j - f_k^j \left(D_{Rk}^j + D_{Ak}^j + D_{k,k-1}^j + D_{k,k+1}^j \right) + D_{k-1,k}^j f_{k-1}^j + D_{k+1,k}^j f_{k+1}^j \qquad \text{(Sediment-}k\text{)}$$

where, E_k^j : emission rate of homologue j to the core-compartment k; f_k^j : fugacity of homologue j in the core-compartment k; $D_{kk'}^j$: transportation parameter; D_{Rk}^j : degradation parameter of homologue j in the core-compartment k; j : homologue number; Z_{Bk} : bulk phase Z values. k : core-compartment number $\left(1 \leq k \leq 54 \right)$.

The above differential equation was numerically solved for the ten fugacity variables, each corresponding to one of ten 4 to 8 chlorine substituted PCDD/F homologues[6].

Physical/chemical and the emission data
Most of the model parameters were estimated by the similar method from literature data[7]. Emissions from three sources, MSWI and impurities in PCP and CNP were adopted from Masunaga[8] with additional assumption in the similar scenario of the previous report[4]. Emissions from MSWI were assumed to be proportional to the population in the basin area. Emissions from CNP and PCP impurities were assumed to be proportional to the paddy-field area in the basin area. Emissions from CNP impurities were arbitrarily reduced to 1/5 of the original data[8] to get the similarity of the resultant homologue profile to the measured one. However, this point needs to be studied further. For the simulation of Lake Kasumigaura basin, the depth of mixing zone in the surface sediment was assumed to 20 cm, according to the field observation[3].

Geographical data
The population, basin area and paddy-field area were calculated by the GIS-based environmental

Table 1 Description of the Tokyo bay and Lake Kasumigaura basin*

Basin	Area $\left(m^2 \right)$	Population	Percentage of paddy-field area (%)
Tokyo bay	1.6×10^{10}	2.8×10^7	11
Lake Kasumigaura	1.2×10^9	6.8×10^5	27

*Numbers in the table 1 may have some error because of the limited resolution of collected geographical mesh data used in the calculation. However, the accuracy of the estimation should be sufficient for the following analysis in this study.

information system. Results calculated for the Tokyo bay and Lake Kasumigaura basins are shown in Table 1.

Results and Discussions

Modification of MSWI emission scenario by the result of core sample analysis
Although total amount of emission from MSWI was set to the same value as Masunaga[8], the time trend of emission was tentatively adjusted to the result of core samples from Lake Haruna-ko[9], which was the relatively isolated lake in Kanto area with closed, narrow catchment area with a negligible small population. The time trend of the core samples from Lake Haruna-ko was assumed to represent the time trend of MSWI emission pattern into the air. The adjusted emission scenario and the trend of total PCDD/Fs flux in Lake Haruna-ko core were shown in Figure 1.

Simulation of Tokyo bay and Lake Kasumigaura basin
The results of the simulated core concentrations for Tokyo bay and Lake Kasumigaura basins
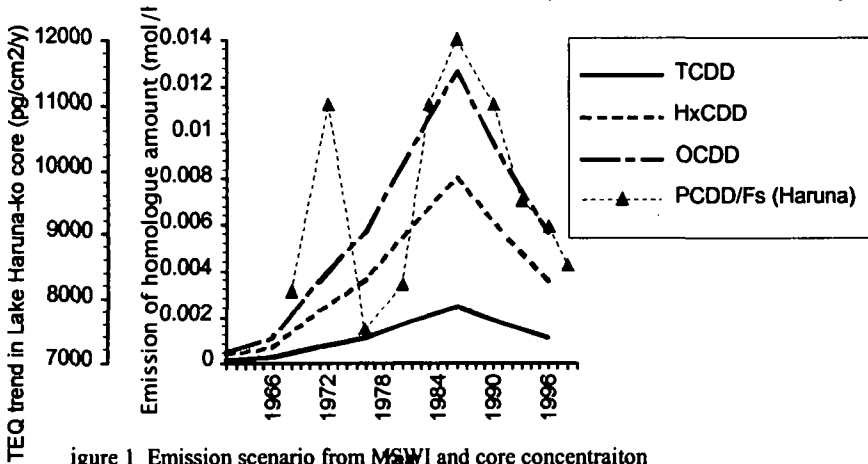

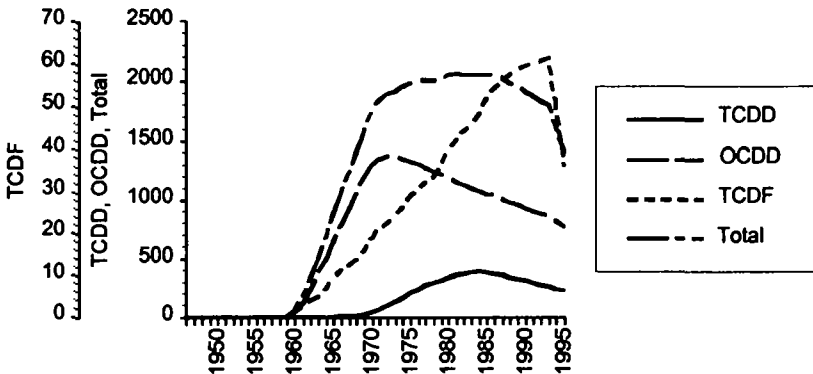igure 1 Emission scenario from MSWI and core concentraiton in Lake Haruna-ko

Figure 2 Simulated core concentration profile of Tokyo bay at 1995

were shown in Figures 2 and 3, respectively. Because the absolute concentration in the simulation largely depends on the model parameters, only the relative curve profiles will be discussed here. The simulation of real absolute concentration needs further study. The results of the simulated core concentrations were shown in Figures 2 and 3.

Figure 2 shows that the increase of OCDD in the Tokyo bay core started in the 1960th, then gradually decreased after the maximum at the 1970th. TCDD started to increase in 1970th, then went to the maximum around 1980. TCDF, which was assumed to be emitted only from MSWI in this simulation, was simulated to increase steadily from 1960th to 1990. Figure 3 shows that the gradual increase of all homologues because of the large mixing zone depth assumed in the calculation. This result suggests that how strong mixing at surface sediment could affect the core-concentration profile. The result shown in Figure 3 is qualitatively similar to the real core sample from the studied area[9].

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