Model Simulation of the Long-term Environmental Fate and Profile Transformation of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans by the Dynamic Multimedia Environmental Fate Model

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Introduction

The environmental fate of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans are not still clear, because many processes could have complex contribution in the environment. Homologue profiles and/or congener patterns are utilized for the study on the fate of the compounds, together with the simple mass-balance approach. However, a modeling approach, which could combine the possible environmental processes into a system, could be a useful complement for the analytical study on the fate of the compounds[1].

In this study, a dynamic multimedia environmental fate model of PCDD/PCDF was developed for the Japanese environmental condition. Dynamic modeling was necessary to include temporal emission from impurities in pentachlorophenol (PCP) and chlornitrofen (CNP), and to simulate the long-term change of environmental levels and transformations as the result of the emission control of municipal solid waste incinerator (MSWI) and others. A monte-carlo simulation was also performed to examine the sensitivity of the model to the parameter fluctuation.

Methods

Model formulation

Dynamic multimedia environmental fate model was developed based on the fugacity level IV model[2], which was the extension of the steady-state level III model[3]. Ten unit models, each corresponding to one of ten 4 to 8 chlorine substituted PCDD/PCDF homologues, were prepared as previously reported[4]. The formulation was as follows:

$$V_1 Z_{B1}\left(df_1^j/dt\right) = E_1^j - f_1^j D_{T1}^j + f_2^j D_{21}^j + f_3^j D_{31}^j + f_1^{j+1} D_{R1}^{j+1} \quad \text{(Air, } i\text{=1)}$$

$$V_2 Z_{B2}\left(df_2^j/dt\right) = E_2^j + f_1^j D_{12}^j - f_2^j D_{T2}^j + f_3^j D_{32}^j + f_4^j D_{42}^j + f_2^{j+1} D_{R2}^{j+1} \quad \text{(Soil, } i\text{=2)}$$

$$V_3 Z_{B3}\left(df_3^j/dt\right) = E_3^j + f_1^j D_{13}^j - f_3^j D_{T3}^j + f_3^{j+1} D_{R3}^{j+1} \quad \text{(Water, } i\text{=3)}$$

$$V_4 Z_{B4}\left(df_4^j/dt\right) = E_4^j + f_2^j D_{24}^j - f_4^j D_{T4}^j + f_4^{j+1} D_{R4}^{j+1} \quad \text{(Sediment, } i\text{=4)}$$

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_{ir}^{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 term $f_i^{j+1} D_{Ri}^{j+1}$ was introduced to express the degradation of the homologue with $j+1$ chlorine substitution to the homologue with j chlorine substitution. All modeling effort was performed on the homologue total amount basis.

Physical/chemical and environmental data
Most of the parameters were estimated by the previous method[4] from literature data[5,6]. Emissions from impurities in PCP and CNP were estimated by literature data. Emission rates from MSWI were assumed to decrease after 1995 by regulation or controlling measures. Figure 1 shows the assumed emission rates of total PCDD/PCDF from the three sources.

Flux of soil particles into air due to wind erosion
Flux of soil particles into air by wind erosion was formulated as follows:

$$N = U_E \rho_S C_S$$

where, N : flux of dioxins due to soil particles into the air by wind erosion $(mg/m^2 \cdot h)$; U_E : wind erosion velocity (m/h); ρ_S : Density of soil particles (kg/m^3); C_S : dioxin concentration in soil particles (mg/kg).
The flux N was then incorporated into D values of the formulation. Parameter U_E was determined to obtain the fixed mixing ratio of soil particles in the total air particles (x). Central estimate of x was set to 0.3 based on the result of the receptor modeling[7].

Sensitivity analysis
Target parameters of monte-carlo analysis were assumed to follow log-normal distribution with standard deviation corresponding to 2-fold variance from central estimates, with some exceptions according to the nature of parameters. Standard deviations of fugacities were calculated from 1000 times trials for each parameter. The results were expressed as the ratio of input standard deviation to the output standard deviation, σ_{out}/σ_{in}.

Results and Discussions

Simulated environmental levels and model validation
Table 1 shows the description of cases 1 to 5, which examine the effect of some model processes on the simulation results. Table 2 summarizes the simulated concentration.
Estimated concentration from basic case 1 suggests that the concentration of soil and depositions seem to become closer to the measured environmental concentration and depositions[8,9,10,11] than the result of the previous report[4]. However, the concentration in air still seems lower, and that in sediment seems higher than the real environmental level[8,12].
Figures 2 to 4 show the time trend of fugacities in case 1 for TCDD, OCDD and TCDF, respectively. Figures 2 to 4 suggest that non-steady state environmental condition lasts for

Table 1 Description of Cases

Case 1	Base simulation (Sources=MSWI+CNP+PCP) without Degradation-Emission link
Case 2	Case 1+Degradation-Emission link ($P_nCDD/F \rightarrow P_{n-1}CDD/F$)
Case 3	Omit soil mixing ratio in air from Case 1
Case 4	Steady state simulation (Level III) with Case 1 parameters (Source=MSWI only)
Case 5	Non-steady state simulation with Case 4 parameters (Source=MSWI only)

Table 2 Simulated concentrations and depositions (Total PCDD/Fs) in 1995

	Concentration				Deposition	
	Air (pg/m^3)	Water (pg/l)	Soil (pg/g)	Sediment (pg/g)	Dry $(ng/m^2 \cdot y)$	Wet $(ng/m^2 \cdot y)$
Case 1	1.8	303	2340	51300	63	113
Case 2	1.8	339	2630	57600	64	113
Case 3	1.8	303	2340	51300	63	112
Case 4	1.6	11	57.4	1999	59	104
Case 5	1.6	4	20.5	657	59	104

several decades, especially for OCDD, which is assumed to have the longest degradation half-lives. Comparison of Figures 2 to 4 to Figure 1 shows that the response of fugacities in sediment is simulated to be delayed maybe for decades from emission input. Fugacities in air, water and soil are simulated to follow more immediately to the emission change. The results suggest the possible long response time to reach steady-state condition, although the assumed degradation half-lives and other parameters could significantly affect this implication.

Effect of process assumptions to the simulation

Comparison of cases 1 and 2, reveals that the degradation-emission formulation has relatively minor importance on the estimated total concentrations in the dynamic simulation. Comparison of cases 1 and 3, and the result of sensitivity analysis for parameter x, suggest that relatively small contribution of soil wind erosion for the air concentration. However, when soil concentration is very high, probably the soil wind erosion could have a significant contribution in the air concentration. Comparison of cases 4 and 5 suggests that the steady-state model give smaller concentration than the dynamic model with similar parameter set.

Sensitivity analysis

Table 3 shows the examples of σ_{out}/σ_{in} values for parameters with significant sensitivity. Degradation half-lives in soil may have most significant sensitivity for all homologues, which is suggested by the large σ_{out}/σ_{in} values in Table 3. Scavenging ratio, Q, may be another uniquely sensitive parameter, which give fluctuations in relatively wide range of media and homologues. In other parameters, geographical assumption like the height of air compartment, and some parameters controlling the partition in the media like organic carbon-water partition coefficient, give relatively large σ_{out}/σ_{in} values mainly for the concentration in the corresponding media.

Long term trend in environmental homologue profiles

Figures 5 to 7 show the simulated homologue profiles in air for case 1. Long-term change of

Table 3 Examples of σ_{out}/σ_{in} value from Monte-Carlo sensitivity analysis

Parameter	Media	Year	TCDD	PeCDD	HxCDD	OCDD	TCDF	PeCDF	HxCDF	OCDF
Half Life in Soil	Soil	1975	*0.27*	*0.41*	*0.35*	0.11	**0.63**	**0.52**	*0.46*	*0.22*
		1995	*1.71*	**0.52**	*0.44*	*0.33*	**0.78**	**0.68**	**0.61**	**0.64**
		2015	***3.45***	***1.32***	***1.17***	**0.55**	***1.96***	***1.92***	***1.73***	***1.07***
Scaveng-ing Ratio	Soil	1975	0.00	0.19	0.17	0.00	*0.38*	*0.26*	*0.23*	0.00
		1995	0.00	*0.25*	*0.25*	0.00	*0.40*	*0.28*	*0.26*	0.00
		2015	0.00	*0.26*	*0.25*	0.00	*0.40*	*0.28*	*0.26*	0.00

profile may occur as a result of emission change and transformation processes. Figure 5 to 7 shows that profiles in air could be affected by the soil TCDD concentration.

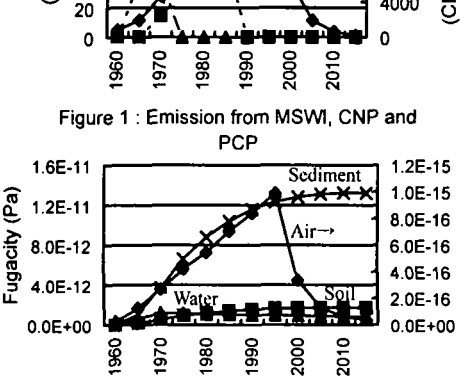

Figure 1 : Emission from MSWI, CNP and PCP

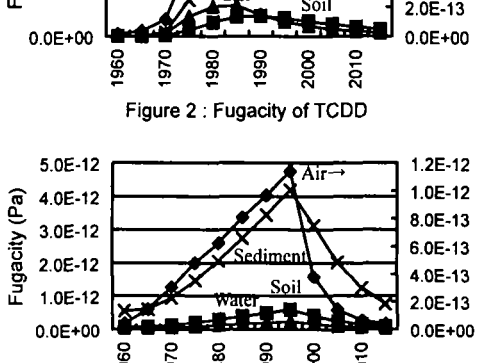

Figure 2 : Fugacity of TCDD

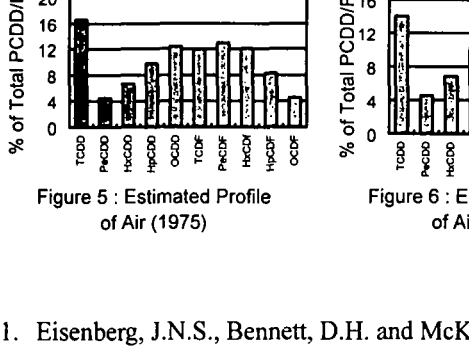

Figure 3 : Fugacity of OCDD

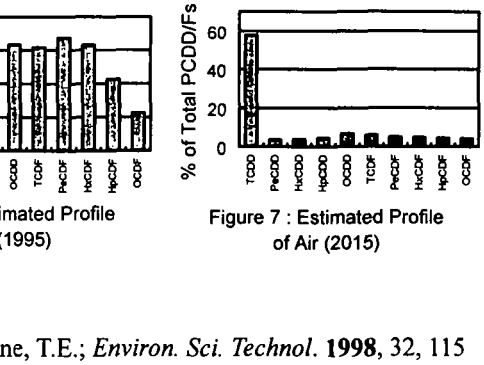

Figure 4 : Fugacity of TCDF

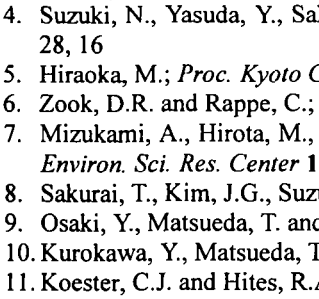

Figure 5 : Estimated Profile of Air (1975)

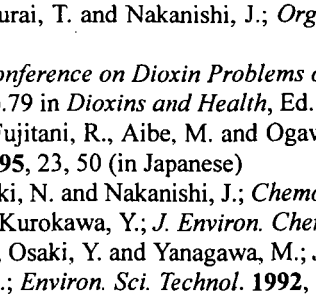

Figure 6 : Estimated Profile of Air (1995)

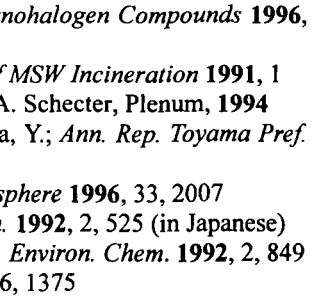

Figure 7 : Estimated Profile of Air (2015)

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