FATE I

Modeling the Profile Transformation of PCDDs and PCDFs in the Environment

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1. INTRODUCTION

Homologue profiles of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been used for the assessment of the environmental fate of these compounds. Source and sink specific homologue profiles are well known for many samples until now. Although profile transformation in the environment are thought to be occurring[1] and possible transformation mechanisms have been studied already[1,2], a systematic approach is necessary to understand the whole environmental transformation process.

In this study, a multimedia environmental fate model was developed to simulate the environmental transformation of homologue profiles for PCDD/PCDF. Model validation and sensitivity analysis were performed as the discussion.

2. METHODS

2.1. Multimedia environmental fate model

The level III multimedia environmental fate model by Mackay et al.[3] was employed as the basis of the unit model. Ten unit models were prepared, each corresponding to one of five 4 to 8 chlorine substituted PCDD and PCDF homologues. All unit models have same geographical parameters but different homologue specific chemical/physical parameters.

2.2. Combined Mackay-type model

Degradation of higher-chlorinated PCDD/PCDF to lower chlorinated homologues were simulated using the combination of the unit models. In this study, degradation of a homologue was assumed to result in the formation of one-chlorine less chlorinated homologue. The five unit models for PCDDs and another five for PCDFs were combined respectively, so that degradation term of higher

chlorinated homologues were added as the emission input of the one-chlorine less chlorinated homologues. The formulations of the combined models were as follows.

$$\left(E_1^j + f_1^{j+1} D_{R1}^{j+1}\right) + f_2^j D_{21}^j + f_3^j D_{31}^j = f_1^j D_{T1}^j \qquad \text{(Air, } i\text{=1)}$$

$$\left(E_2^j + f_2^{j+1} D_{R2}^{j+1}\right) + f_1^j D_{12}^j + f_3^j D_{32}^j + f_4^j D_{42}^j = f_2^j D_{T2}^j \qquad \text{(Soil, } i\text{=2)}$$

$$\left(E_3^j + f_3^{j+1} D_{R3}^{j+1}\right) + f_1^j D_{13}^j = f_3^j D_{T3}^j \qquad \text{(Water, } i\text{=3)}$$

$$\left(E_4^j + f_4^{j+1} D_{R4}^{j+1}\right) + f_2^j D_{24}^j = f_4^j D_{T4}^j \qquad \text{(Sediment, } i\text{=4)}$$

where

E_i^j Emission rates 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 chlorine number.

The term $f_i^{j+1} D_{Ri}^{j+1}$ means that the degradation of the homologue with $(j+1)$ chlorine substitution results in the formation of the homologue with j chlorine substitution. Other model structures and parameter definitions are essentially same as the level III model by Mackay et al.[3]

2.3. Model parameters

Geographical parameters were adopted for Japan, and chemical/physical properties for PCDD/PCDF were taken from literature[4,5]. Emission of PCDD/PCDF into the environment was assumed only from municipal waste incinerator stack gas. Total emission rates in Japan from this source were taken from Hiraoka[6] and the homologue emission rates were estimated according to the profile of the stack emission[7] and total emission rate.

3. RESULTS AND DISCUSSION

3.1. Model validation

The estimated total PCDD/PCDF concentrations were 1.1 pg/m^3 for air, 40 pg/l for water, 40 pg/g for soil and 6900 pg/g for sediment, all of which were within the range of measured environmental levels in Japan[8,9,10]. Deposition rate calculated from the model was 350 $ng/m^2 \cdot year$ in total, and this deposition rate was also within the range of observed value[11]. Calculated vapor to particle ratio in the air were 0.98 for TCDD, 7.9×10^{-4} for OCDD, 1.7 for TCDF and 8.4×10^{-4} for OCDF, which were again within the suggested range of V/P ratio[12].

3.2. Estimated profiles and sensitivity analysis

Estimated profiles are shown in Figure 1 to 9. Figure 1 shows the input emission profile. Table 1 summarizes the representative parameter for sensitivity analysis from case 1 to case 4.

Figure 2 and 3 show the profiles in air and soil by the basic case 1 calculation. In this case the half lives in gas phase in air was assumed to 10 to 30 days and particulate phase in air was to 100 to 300 days. Half lives in soil and sediment were assumed to 10 to 100 years and 20 to 200 years, respectively. The profile in Figure 2 is similar to the measured air profile[7]. The soil profile in Figure

Table 1 Half lives for sensitivity analysis

Parameter	Case 1		Case 2		Case 3		Case 4	
	TCDD	OCDD	TCDD	OCDD	TCDD	OCDD	TCDD	OCDD
Half life in air (gas) (day)	10	30	1	10	10	10	10	30
Half life in air (particulate) (day)	100	300	100	300	100	100	100	300
Half life in soil (year)	10	100	10	100	10	100	10	10
Half life in sediment (year)	20	200	20	200	20	200	20	20

3 is qualitatively similar to the typical measured soil profile[1,10], but further examination may be necessary for quantitative comparison.

Figure 4 shows the profile in air by case 2, which assumed shorter half lives in gas phase in air, but the difference was negligible. Figure 5 shows the profile in air by case 3, which assumed uniform half lives in air phase. No significant change occurs in the air and other profiles in this case. Figure 6 show the profile in soil by case 4, which assumed uniform half lives in soil. This assumption created clearly different profile from the typical soil one.

Figure 7 and 8 show the profile in air and soil by case 5, which omitted the degradation-emission link in the formulation (the term $f_i^{j+1} D_{Ri}^{j+1}$) with other parameters being same as case 1. Figure 9 shows the profile in soil by case 6, which also omitted the degradation-emission link using the case 4 parameters. Profiles in Figure 7 to 9 are slightly different from original case 1 and 4, but the difference was not significant.

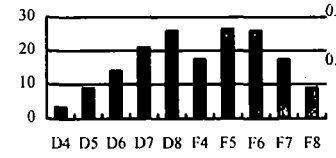

Figure 1 Emission profile

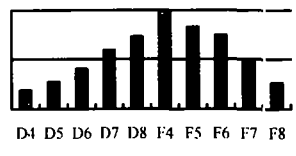

Figure 2 Case-1, Air

Figure 3 Case-1, Soil

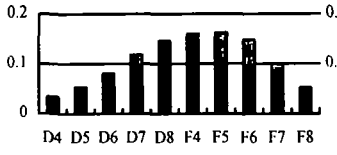

Figure 4 Case-2, Air

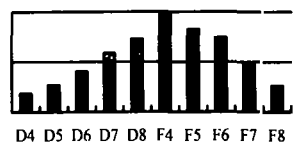

Figure 5 Case-3, Air

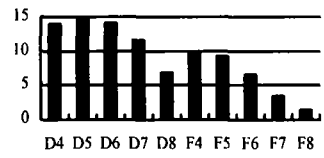

Figure 6 Case-4, Soil

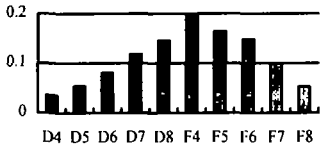

Figure 7 Case-5, Air

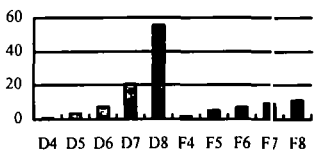

Figure 8 Case-5, Soil

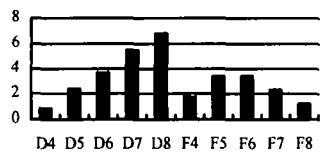

Figure 9 Case-6, Soil

3.3. Discussion

Profile transformation in the environment was qualitatively well simulated by the simple combination of Mackay type environmental fate model. The profiles in air was mainly determined by the selective homologue elimination by particle deposition and was not determined by the degradation in air. Degradation rates in air may have no significant effects on the profile transformation into soil, although soil half lives have much larger effects on profiles in soil. This suggests profile transformation from air to soil is determined by the homologue specific degradation in soil. This suggestion may be somewhat unusual, and further model modification may be necessary. Washout ratios were calculated from the model results, which were 700 to 1300 for gas (Wg) and 200,000 for particles (Wp). This range is different from reported washout ratios by Eitzer and Hites[13] and the estimated profiles in rain and deposition were also somewhat different from measured profiles in rain[2]. This point should be examined further.

In conclusion, the model calculation could give not complete but acceptable simulation of profile transformations. The multimedia fate model could be an useful complement of analytical work for the study of the whole environmental transformation processes.

4. REFERENCES

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