

## Environmental Fate and Origin Estimation of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans by the Dynamic Multimedia Environmental Fate Model

Noriyuki Suzuki<sup>§#</sup>, Koji Tosa<sup>§</sup>, Masashi Yasuda<sup>§</sup>, Takeo Sakurai<sup>\*#</sup> and Junko Nakanishi<sup>\*\*#</sup>

§Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

\*National Institute of Environmental Studies, 16-2 Onogawa, Tsukuba 305-0053, Japan

\*\* Institute of Environmental Science and Technology, Yokohama National University, 79-7 Tokiwadai, Hodogaya, Yokohama 240-8501, Japan

# CREST, Japan Science and Technology Corporation

### Introduction

Three major sources of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in Japan are identified as the mixture of municipal solid waste incinerator (MSWI), impurities in pentachlorophenol (PCP) and chlornitrofen (CNP) based on the source estimation efforts. It is well recognized that congener pattern and/or homologue profiles of the sources are different each other. The different homologue/congener patterns and different emission nature of the sources should affect the fate of the emitted compounds.

Recently, source identification based on the multivariate analysis using congener-specific analytical data was presented<sup>1,2,3</sup>. These studies described the relative contribution of sources in the specific samples and the relation to the source estimation was discussed. However, mechanistic understanding of the relation between the estimated contribution and the sources is not well described in the studies.

In this study, source contribution estimates in the sediment media based on the dynamic multimedia environmental fate model are described. Because the estimates are strongly dependent on the model structure and parameter settings, some effects of the parameters are tested for the validation of the model estimates.

### Methods

#### Model formulation

Modeling approach of this study is essentially same as already described<sup>4</sup>. A dynamic multimedia environmental fate model was developed based on the fugacity level IV model<sup>5</sup>, which is the extension of the steady-state level III model<sup>6</sup>.

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

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

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

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

where,  $E_i^j$ : emission rate of homologue  $j$  to the compartment  $i$ ;  $f_i^j$ : fugacity of homologue  $j$  in the compartment  $i$ ;  $D_{ii}^j$ : transportation parameter;  $D_{Ri}^j$ : degradation parameter of homologue  $j$  in

the compartment  $i$ ;  $j$  : homologue number;  $Z_{Bi}$  : bulk phase  $Z$  values.

Ten unit models, each corresponding to one of ten 4 to 8 chlorine substituted PCDD/PCDF homologues, were prepared<sup>7</sup>.

The term  $f_i^{j+1}D_{Ri}^{j+1}$  means the assumption that the degradation of the homologue with  $j+1$  chlorine substitution results in the formation of the homologue with  $j$  chlorine substitution. All modeling effort was performed on the homologue total amount. Flux of soil particles into air by wind erosion was formulated as:  $N = U_E \rho_S C_S$ , 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 ( $m/h$ );  $\rho_S$  : 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.<sup>8</sup>

The above differential equation was numerically solved and the results were calculated in 5-year interval. The time resolution of 5 year was thought to be enough for this long-term trend analysis.

### *Physical/chemical and emission data*

Most of the parameters were estimated by the similar method from literature data<sup>9</sup>. Emissions from three sources, MSWI and impurities in PCP and CNP were adopted from Masunaga<sup>3</sup> with additional assumption of the similar scenario of the previous report<sup>4</sup>. Emission rates from MSWI were assumed to decrease after 1995 by regulation or controlling measures. The PCP impurity was assumed to have largest cumulative emission during simulation period, followed by the CNP impurity, then finally followed by the MSWI emission. Emission from PCP impurity was assumed to reach maximum at 1965, the emission from CNP impurity at 1975, and the emission from MSWI at 1995.

### *Source identification*

Because the formulation is linear for the fugacity variable  $f$ , separate calculation based on the separate source term could give simply the separate source contribution in each media from that source. Potential source contribution was calculated using the total PCDD/Fs concentration from the model estimates.

## **Results and Discussions**

Table 1 shows the cases a to d for estimation.

The results of sensitivity analysis in the previous report<sup>10</sup> showed the relatively high sensitivity for the degradation half-lives in soil and sediment. The above cases a to d were set to cover possible range of half-lives in the soil and sediment media. In case a, increasing half-lives were assumed for higher-chlorinated homologues. Half-lives in sediment were assumed to be 2-fold values for the corresponding soil half-lives. In case b, all half-lives in case a were reduced to one-half values. In case c, half-lives in sediment were assumed to have same values with those in soil in addition to case b assumption. In case d, uniform half-lives were assumed in sediment in addition to the case a assumption.

Tables 2 to 5 show the estimated results from the calculation of cases a to d.

The left part of Tables 2 to 5 show the estimated relative contribution of three sources in the sediment PCDD/Fs at the specified year. The right part of Tables 2 to 5 show the arbitrary ratio of estimated relative contribution of three sources in the sediment PCDD/Fs at the specified year to the relative contribution of cumulative emission amount of three sources at the specified year.

The data on the left part of Tables 2 to 5 generally show that at the year 1965, most of the PCDD/Fs in sediment was estimated to come from PCP. At the year 1980, relative contribution

Table 1 Data set of degradation half lives in soil and sediment in cases a, b, c and d.

	in Soil	in Sediment
Case a	10 to 100 yeas for PCDDs 5 to 50 years for PCDFs	20 to 200 years for all homologues
Case b	5 to 50 years for all homologues	10 to 100 years for all homologues
Case c	5 to 50 years for all homologues	5 to 50 years for all homologues
Case d	10 to 100 years for PCDDs 5 to 50 years for PCDFs	100 years for all homologues

from CNP source is estimated to reach larger values because of the larger emission during this period. At the year 1995, relative contributions from CNP decrease and those from MSWI increase. However, the magnitude of relative contribution of the sources in the sediment does not directly reflect the magnitude of relative contribution of emissions at the sources.

The data on the right part of Tables 2 to 5 suggest that the relative impact of sources to sediment media may different each other. PCDD/Fs emission from impurities of CNP and PCP are assumed to occur in similar manner, both of which are the direct emission into the soil compartment. However, the ratios in the right part of Tables 2 to 5 are significantly different between CNP and PCP. This is suggesting that the homologues from PCP are more strongly concentrated than the homologues from CNP. This phenomenon is possibly come from different chemical/physical parameters of lower chlorinated homologues and higher ones.

### Conclusion

Although the results and discussion of this research depend on the formulation and parameter settings of the model, the discussion could be used as the general, qualitative understandings of the mechanisms of relation in the analytical data.

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Table 2 Relative ratio of origin estimation of sediment PCDD/Fs from case a.

Year	Ratio of origin of sediment PCDD/Fs			(Ratio in sediment)/(Ratio in source)		
	From CNP	From PCP	From MSWI	From CNP	From PCP	From MSWI
1965	0.00	0.99	0.01	0.00	2.68	0.60
1980	0.29	0.71	0.01	0.47	1.91	0.54
1995	0.31	0.68	0.01	0.50	1.83	1.03
2015	0.15	0.84	0.01	0.24	2.26	0.99

Table 3 Relative ratio of origin estimation of sediment PCDD/Fs from case b.

Year	Ratio of origin of sediment PCDD/Fs			(Ratio in sediment)/(Ratio in source)		
	From CNP	From PCP	From MSWI	From CNP	From PCP	From MSWI
1965	0.00	0.99	0.01	0.00	2.68	0.59
1980	0.24	0.76	0.01	0.38	2.04	0.59
1995	0.17	0.81	0.02	0.28	2.19	1.30
2015	0.03	0.95	0.02	0.05	2.57	1.16

Table 4 Relative ratio of origin estimation of sediment PCDD/Fs from case c.

Year	Ratio of origin of sediment PCDD/Fs			(Ratio in sediment)/(Ratio in source)		
	From CNP	From PCP	From MSWI	From CNP	From PCP	From MSWI
1965	0.00	0.99	0.01	0.00	2.68	0.57
1980	0.21	0.78	0.01	0.34	2.11	0.57
1995	0.12	0.86	0.02	0.19	2.33	1.32
2015	0.01	0.97	0.01	0.02	2.63	1.06

Table 5 Relative ratio of origin estimation of sediment PCDD/Fs from case d.

Year	Ratio of origin of sediment PCDD/Fs			(Ratio in sediment)/(Ratio in source)		
	From CNP	From PCP	From MSWI	From CNP	From PCP	From MSWI
1965	0.00	0.99	0.01	0.00	2.68	0.62
1980	0.28	0.71	0.01	0.45	1.93	0.60
1995	0.28	0.70	0.02	0.46	1.90	1.25
2015	0.12	0.86	0.02	0.19	2.34	1.21

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