A MULTIMEDIA MODEL FOR THE EVALUATION OF ENVIRONMENTAL BEHAVIOR OF DIOXINS

M. Kawashima*, T. Tobe*, A. Kaga*, A. Kondo*, Y. Inoue*, D. Matsumoto*, and Y. Dong**

Graduate School of Engineering, Osaka University, 2-1 Yamada oka, Suita, Osaka, 565- 0871, Japan
** School of Chemical and Environmental Science, Henan Normal University, 148 Jianshe Road, Xinxiang, Henan 453002, P. R. China*

ABSTRACT

Recently, various chemical substances have been discharged in the environment because of the developments of the industrial activities and so on. To evaluate the behavior in the environment and the risk to human health and the ecosystems, we have constructed a multimedia model and a food chain model. These models enable us to calculate concentrations of dioxins simultaneously in the every media, such as air, water, soil, sediment and aquatic organisms. These models were applied to Hyogo Prefecture, Japan. In the result of calculation from 1960 to 2010, the concentration of dioxins (TCDDs + TCDFs + Co-PCBs) in every media was predicted. It was clarified that dioxins were not accumulated in the air and water but easily accumulated in soil and sediment, and that dioxins concentrate in aquatic organisms through food chain. In the fate prediction, the concentration of dioxins is expected to decrease lower than the environmental standard in the near future in every media in Hyogo Prefecture.

The possibility to apply the same models to Vietnam was also discussed.

KEYWORDS

dioxins, environmental circulation, food chain model, multimedia model, numerical simulation

INTRODUCTION

Recently, various chemicals have been discharged in the environment, because of the development of industrial activities in the world. In these chemicals, many hazardous chemicals which damage the human health and ecosystems are included. Some chemicals like as environmental hormones such as dioxins effect human health with very small amount and are accumulated easily in the organisms. The affect continues for a long term and over several generations. In the Vietnamese case, between 1962 and 1971, tremendous amount of herbicides called "Agent Orange" including dioxin (TCDD) were sprayed for defoliation on southern Vietnam. This was the largest dioxin contamination known to data. In this contamination, previous studies [1] documented the increase of liver cancer and congenital malformation. And even now, many people potentially have sickness linked to dioxins exposure in Agent Orange.

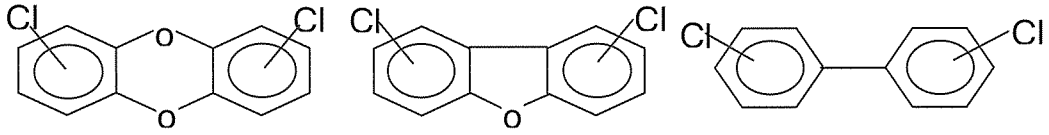
Strong persistent chemicals such as dioxins circulated and were accumulated in the environmental media such as air, soil, water, and sediments once they were discharged to environment. Therefore even though after the amounts of generation of these chemicals are reduced, it will be possible that the persistent chemicals discharged long time ago were accumulated in organisms and effect human health and ecosystems in later time. It is also possible that people who live far from generation point are exposed to persistence chemicals. To clarify how the persistent chemicals discharged in environment circulate through media and are accumulated in media, a multimedia model which can calculate concentration of dioxins simultaneously in the every media

and give us information such as the effect of dioxins contaminant in the past and in the future is required.

MATERIALS AND METHODS

Dioxins

Dioxins is the generic name of poly- chloro- dibezo- para- dioxin (PCDDs), poly- chloro- dibezo-flan(PCDFs), and coplanar PCBs(Co-PCBs). The structures of PCDDs, PCDFs, and Co-PCBs are shown in Fig.1. PCDDs, PCDFs, and Co-PCBs have many isomer and different toxicity depend on the number and the site of chlorine combining. TCDDs and TCDFs have two benzene rings combined with one or two oxygen. Since their structures are similor, chemical properties and toxicities of PCDDs and PCDFs also are similar. Co-PCBs are parts of the poly-chloro-biphenyl (PCB) which have plane structure. They have the same toxicities as PCDDs and PCDFs. Dioxins have a very strong toxicity. Effects to the creatures are reported as carcinogenicity, immunotoxicity, and reproduction toxicity. In this study, these dioxins are picked up as the target substances in the fate simulation.



(a) PCDDs (b)PCDFs (c)Co-PCBs

Fig. 1 Structures of dioxins

Multimedia Model

Outline of multimedia model

As described above, after chemicals are discharged, they circulate through various media. Therefore, to analyze the circulation, a model which includes multiple media, not single medium, is needed. The structure of our multimedia model is shown in Fig. 2. Seven media are assumed in this model. They are mainly air, soil, water, and sediment. Air consists of particles and gas. Water consists of liquid, biota and SS (suspended substances).

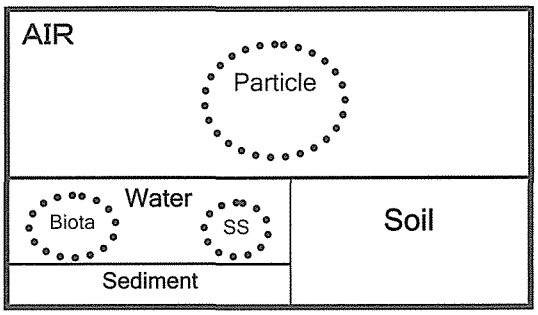


Fig.2 Structure of Multi Media Model

The circulation of the dioxins is shown in Fig. 3. Assumptions are as follows[2]:

- There are inflow and outflow of dioxins by advection in air and water.
- PCDDs and PCDFs are discharged from pesticides and incinerator plants, and Co-PCBs are discharged from incinerator plants and lost electric products such as condensers and transformers.
- Dioxins are decomposed with each decomposition rate in each media.
- Between adjoined media, dioxins move toward the equilibrium by diffusion.
- Between gas and particles, and liquid and SS, the equilibrium state is kept always.
- Particles in air deposit on the surface of soil and water, and SS in water deposit on sediment.
- Particles are re-suspended from soil to air, and

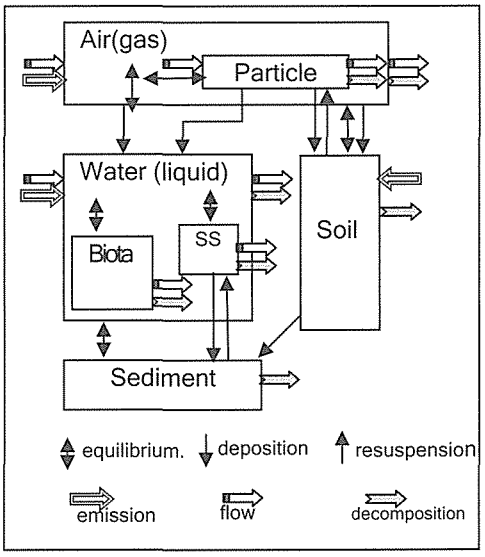


Fig. 3 Circulation of dioxins in the environment

SS are re-suspended from sediment to liquid.

- Soil particles inflow into water by runoff of rainwater and deposit on sediment.

Fundamental equation in multimedia model

Fundamental equation is shown in equation (1) on the basis of the assumptions described above. The fundamental equation consists of diffusion flux, discharge flux, advection flux, decomposition flux, and deposition/run off/ re-suspension flux.

$$\frac{dM_i}{dt} = \sum_{j=1}^{j=MN}(f_{dif})_{ij} + (f_{dis})_i + (f_{ad})_i + (f_{dec})_i + \sum_{j=1}^{j=MN}(f_{dprs})_{ij} \quad (1)$$

Here i, j: discrimination subscript for media, MN: number of total media, M_i:amount of dioxins in media i (mol), f_{dif}: diffusion flux between media (mol/s), f_{dis}: discharge flux (mol/s), f_{ad}: advection flux (mol/s), f_{dec}: decomposition flux, f_{dprs}: deposition /run off /re-suspension flux (mol/s).

Model parameters

Parameters of tetra-chloro-dibezo-para-dioxin (TCDD) used in this model are shown in Table 1. TCDD have the strongest toxicity among dioxins, and dioxins contained in Agent Orange sprayed in the Vietnam War were mainly TCDD. In Table1, H_{ij}: equilibrium constant, K_{ij}: mass transfer constant, D: decomposition rate, M: Molecular weight, gs, pt, sl, lq, ss, sd, bt: air(gas), particle, soil, water(liquid), suspended solids, sediment, biota.

Table 1 Model parameters in multimedia model

Parameter	$H_{gs\text{-}pt}$	$H_{gs\text{-}lq}$	$H_{gs\text{-}sl}$	$H_{lq\text{-}sd}$	$K_{gs\text{-}lq}$	$K_{gs\text{-}sl}$	$K_{lq\text{-}sd}$	D_{gs}	M
Value	10^{-10}	1.33	$6*10^{-8}$	$1*10^{-6}$	2.0	$4*10^{-5}$	$1*10^{-7}$	$2*10^{-2}$	322
Unit	-	-	-	-	m/day	m/s	m/s	1/day	g/mol

Food Chain Model

Outline of food chain model

Dioxins, especially Co-PCBs, are easily concentrated in fat of aquatic biota. Vietnamese heavy consumers of fish are contaminated at a high level [(1)]. Consequently it is important to predict concentration in not only environmental media, but also in aquatic biota in detail. For this purpose, food chain model is constructed. The structure of food chain model is shown in Fig. 4.

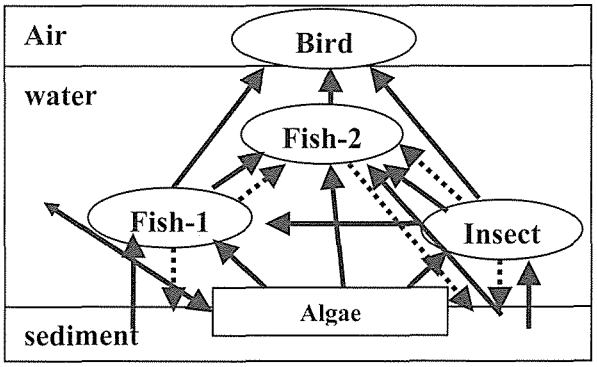


Fig. 4 Structure of food chain model

Assumptions in the food chain model are as follows[(3)].

- Dioxins concentrations in water and in Algae are kept always in the equilibrium state.
- Insects eat Algae, Fish-1 eats Insect and Algae, Fish-2 eat Algae, Insects and Fish-1, Birds eat Insect, Fish-1, and fish-2. When eating food, they intake dioxins.
- Insect, Fish-1, and Fish-2 intake dioxins from sediment when eating Algae.
- Eighty percents of Dead Insect, Fish-1, and Fish-2 are eaten by Fish-2, and 20 % of those are deposed on sediment.
- Concentration of dioxins in each biota is uniform.
- Concentration of dioxins in water and sediment is obtained by a result of calculation of multimedia model.

Fundamental equation in food chain model

The model equations used in our food chain model is shown in equation (2):

$$V_{lq}\frac{dN_k^m M_k^m}{dt} = Q(C_k^n - C_k^m) + \sum_{k'=1}^{DTN}(F_{k-k'\to k}\alpha_k M_k N_{k-k'})^m V_{lq} - \sum_{K'=1}^{UTN}(F_{k+k'\to k}M_{k+1}N_k)^m V_{lq} - (D_k M_k N_k)^m V_{lq} - (E_k M_{ki} N_k)^m V_{lq} \quad (2)$$

Here k: discrimination subscripts for biota, m: discrimination superscripts for region, n: discrimination superscripts for background, DTN: number of lower level biota, UTN: number of higher level biota, M: mass of biota in water (g/m^3), N: amount of dioxins in biota (mol/g), V: water volume (m^3), C: concentration in water (mol/m^3), F: eating rate of biota per weight of biota (g/s/g), α: absorption rate of dioxins (-), D: dying rate of biota (1/s), E: extinction rate of dioxins in biota (1/s)

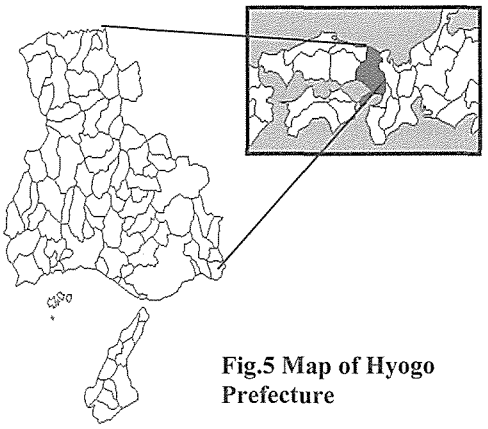


Fig.5 Map of Hyogo Prefecture

RESULT AND DISCUSSION

Environmental circulation of dioxins in Hyogo Prefecture, Japan was estimated using multimedia model and food chain model. The map of Hyogo Prefecture is shown in Fig.5. Emission sources were assumed to be pesticide and incinerators. Calculation results are shown in Table 2, in which observed data of dioxins are compared with calculated values for annual average in 2000.

Table 2 Comparison of calculation and observation (TCDDs+TCDFs)

media	Unit	Calculation	Obserbvation (number of sumples)
Air	(pgTEQ/m^3)	0.023	0.13(20)
Soil	(pgTEQ/g)	0.69	0.55(24)
River	(pgTEQ/l)	0.07	0.29(26)
Sediment	(pgTEQ/g)	1.0	2.6(24)

In the result of the comparison, calculation data agrees with observation data within one order. Consequently, in this simulation, circulation of dioxins in Hyogo region was reproduced by multimedia model successfully.

Results of the fate simulation of dioxins using multimedia model are shown in Fig. 6. Much pesticide (CNP, PCP) including much dioxins were emitted in farm (soil) between 1960 and 1980, and until 1998 when the law which regulates the emission of dioxins was instituted, dioxins had been discharged in air and water from incinerator. In Fig. 6, concentrations of dioxins in air and water change in same rate. This rate resembles the discharging rate of emission. It shows that dioxins are not concentrated in air and water. The concentration in soil decreased from 1970 gradually, but the concentration in sediment didn't not decease from 1980. From this result, dioxins are easily accumulated in soil and sediment. Especially in sediment, dioxins are accumulated heavily. This model could adequately reproduce our knowledge about the behavior of dioxins.

The results of fate simulation of dioxins using food chain model in Hyogo Prefecture are shown in Fig.7. The higher the trophic level becomes, the higher the concentration of biota becomes. Although the concentration of water decreased from 1998, concentrations in high trophic level biota

such as Fish-2 didn't decrease significantly. Consequently, it is known that dioxins are easily accumulated through food chain in high trophic level biota.

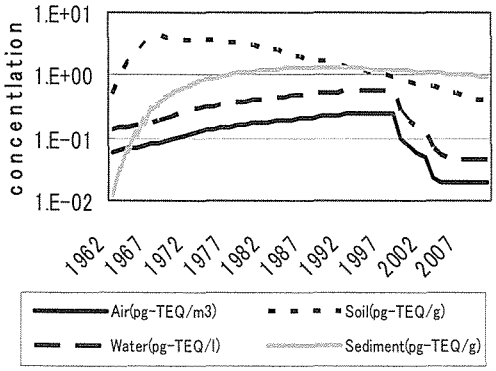


Fig.6 rusult of fata simulation of Multi Media Model

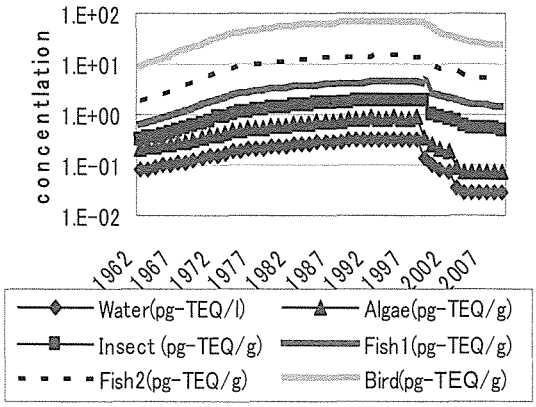


Fig.7 rusult of fatasimulation of Food chain model

Possibility of Application to Vietnam

From this study, it was demonstrated that dioxins are accumulated in sediment, the concentration in biota become higher through food chain, and finally dioxins are accumulated in human body at high level. Arnold S. [(1)] recently reported that the concentration of dioxins in the blood of Vietnamese who had lived nearby the places contaminated by dioxins and ate fishes heavily was at very high level. It may be useful that these models developed here are applied to clarify the fate of dioxins included in Agent Orange and to make a risk assessment of Vietnamese dioxins contamination. Data shown below will be needed.

- The information of the region where Agent Orange were sprayed.
- The concentration of dioxins in Agent Orange sprayed in Vietnam.
- The altitude data of the sprayed region to know the basin.
- Other emission data of dioxins except for Agent Orange.
- The environmental information of sprayed region such as the flow rate of the river, the amount of rainfall, and wind conditions.
- The observed data for of dioxins concentration in the environment for the comparison with the model result to check the model accuracy.

CONCLUSIONS

In this study, multimedia model and food chain model are constructed for clarifying circulation and the fate of dioxins in the environment and aquatic biota. In the result of comparison between observed data and calculated values in Hyogo Prefecture, they agree well. Consequently it is thought that the models constructed in this study can reproduce the circulation of dioxins. In the result of fate simulation of dioxins, it is found that dioxins in soil and sediment are easily concentrated. Especially in sediment, dioxins are accumulated heavily, and dioxins are easily accumulated also in higher trophic level biota.

It was thought that the application to Vietnam of the same model maybe useful for environmental risk assessment. The collection of required data is a future subject.

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One of the authors is now staying in Hanoi University as a short-term student for a research of the dioxin problem in Vietnam. The authors express their sincere thankfulness to Prof.Viet, CETASD, Hanoi University of Science, for his acceptance and kind instruction, and to AIEJ (Association of International Education, Japan) for their financial support.

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