SIMULATING THE TRANSFER AND FATE OF PCDD/Fs IN BEIJING, CHINA USING A MULTIMEDIA FUGACITY MODEL

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1. Introduction

Polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs) are highly toxic to humans, bioaccumulative in ecosystems and persistent in various environmental compartments. Once formed, they can immediately release to the environmental systems, e.g., atmosphere, and then are able to transfer to the soils and sediments via dry/wet deposition and accumulate in these environmental compartments. Due to such accumulation process, the PCDD/Fs concentration in soil adjacent to combustion source is often found to be higher than typical soil without PCDD/Fs sources nearby. Simulating the transfer flux and content of PCDD/Fs in the environmental multimedia has been proposed as a useful method in order to assess the environmental fate of PCDD/Fs. A few studies on multimedia fate of persistent organic pollutants (POPs) in China have been carried out; *however*, these studies are mainly focused on organic chlorinated pesticide (OPCs) such as DDTs, HCBs whereas the studies on PCDD/Fs are very rare. The reasons are likely due to the facts that 1) public concerns on PCDD/Fs have just boomed in recent years as rapid economic development of China, and thus monitoring data of PCDD/Fs is still limited; 2) from the technical point of view, there are only a few laboratories in domestic China that have the capability of analyzing PCDD/Fs. Numerical simulation method can provide a valuable overall description of the fate of PCDD/Fs and help to further enhance our understanding of the processes controlling PCDD/Fs concentrations in various environmental media. The simulation results provide technical support for ecological and environmental risk assessment and thus for environmental policy formulation and implementation, correspondingly.

In this study, we used a Level III multimedia fugacity model to simulate the transfer processes and fate of PCDD/Fs in Beijing area. Distribution of PCDD/Fs concentration in air, water, soil and sediment and transfer fluxes among these media was then estimated. Model predictions are compared against data from several field campaigns to evaluate model accuracy and applicability.

2. Materials and Methods

2.1 Model framework

The concept and framework of Level III fugacity models have been described by Mackay and co-authors. Basically, the study area was divided into four bulk compartments, i.e. air, water, soil and sediment. The bulk compartments were then divided into more sub-compartments. For example, the air consists of gas and airborne particles. The water is composed of liquid and suspended particles. The soil constitutes gas, liquid and solids. The sediment comprises liquid and solid. The mass balance equations for the four compartments are as follows assuming the steady-state was achieved:

$$E_1 + G_{A1}c_{B1} + f_2D_{21} + f_3D_{31} = f_1 (D_{12} + D_{13} + D_{R1} + D_{A1}) \quad (1)$$

$$E_2 + G_{A2}c_{B2} + f_1D_{12} + f_3D_{32} + f_4D_{42} = f_2 (D_{21} + D_{24} + D_{R2} + D_{A2}) \quad (2)$$

$$E_3 + f_1D_{13} = f_3 (D_{31} + D_{32} + D_{R3}) \quad (3)$$

$$E_4 + f_2D_{24} = f_4 (D_{42} + D_{R4} + D_{A4}) \quad (4)$$

Where E_i is the emission rate into the compartment i, $G_{Ai}c_{Bi}$ is the advection input into compartment i, f_i is the chemical fugacity in the compartment i, D_{ij} is the transfer coefficient from compartment i to j, D_{Ri} is degradation reaction rate in compartment i, D_{Ai} is the advection outflow of compartment i, The single subscript of 1,2,3, and 4 represents the four bulk compartments of air, water, soil and sediment, respectively.

2.2 Processes and parameters

The PCDD/Fs sources in Beijing mainly include municipal solid waste incineration, heating and power supply as well as advection input from neighboring region. The environmental processes of PCDD/Fs within the environmental system include advection, reaction and intermedia transfer such as air-soil deposition, soil-water runoff, sediment-water diffusion, etc. The outgoing processes of these chemicals consist of degradation in each compartment and advection outflow via air and water.

There are totally 62 parameters associated with this model, which can be roughly grouped into emission rate, advection inflow (outflow), physic-chemical properties of PCDD/Fs and environmental properties of studied area.

The emission data of PCDD/Fs in Beijing area in 2010 was adopted from Yao et al. (2006) assuming that the discharges of PCDD/Fs via gas, water and residues fully entered into the environmental compartments of air, water and soil, respectively. And the emission rates of $E_{1,2,3}$ in the above equations can be derived accordingly, which are 1.95×10^{-5} mol h^{-1}, 1.10×10^{-6} mol h^{-1} and 5.76×10^{-6} mol h^{-1}, respectively. The phsysico-chemical properties of PCDD/Fs used in the model were collected from literature. The data adopted herein are the most commonly used in the model calculation. The environmental property data are obtained from statistical books of Beijing area and from published literature, respectively.

3. Results and discussion

3.1 Simulated concentration and model validation

We herein selected 2,3,7,8-TCDD of highest TEF and OCDD of lowest TEF as representatives of 17 2,3,7,8-substitued PCDD/Fs to simulate the concentration distribution and fate of dioxins in Beijing. These are two extreme cases by assuming that the 17 2,3,7,8-subsituted PCDD/Fs congeners are all 2,3,7,8-TCDD or OCDD. Therefore, the modeled PCDD/Fs concentration are considered to fall into the range defined by 2,3,7,8-TCDD and OCDD if 17 congeners were applied. Figure 1 illustrated the simulated concentrations of 2,3,7,8-TCDD(OCDD)-represented PCDD/Fs (simplified as 2,3,7,8-TCDD or OCDD throughout the rest of paper) and actual monitored concentrations of PCDD/Fs in the four environmental compartments. Monitoring data in air and soil is adopted from our field campaigns in Beijing, respectively. Ambient PCDD/Fs concentrations are obtained by analyzing the consecutive 6-day samples at 6 selected sites in Beijing area and averaging the measured results. PCDD/Fs concentrations in soil are obtained by measuring and averaging the 8 soil samples taken at open ground surface in Beijing. Note that the calculated PCDD/Fs concentrations represent the average level of the entire studied area, whereas the observed concentrations were obtained in specific sites. Therefore, the comparison must be taken as indicative in terms of orders of magnitude. Due to the lack of monitoring data of PCDD/Fs in water and sediment in Beijing, we applied the measured concentrations in Xijiang River that winds through Guangzhou for water and those in Yangtze River estuary into the East China Sea. These two regions are also megacities with highly economic development as Beijing. The results are referential. The results indicate that the modeled concentrations of 2,3,7,8-TCDD and OCDD are 0.32 and 0.34 pg m^{-3} in air and 0.33 and 1.14 ng kg^{-1} in soil, respectively. The monitored concentrations of PCDD/Fs are 0.33 pg m^{-3} in air and 1.48 ng kg^{-1} in soil, respectively. The modeled and measured results agree very well for air, whereas the modeled 2,3,7,8-TCDD in soil is 3.5 times lower than the measured concentration. The reason can be attributed to that the half-time of 2,3,7,8-TCDD in soil is lower than the other congeners leading to more rapid degradation and thus lower concentration in soil. The modeled concentrations in water and sediment are 0.094 ng m^{-3}, 0.38 ng kg^{-1} (2,3,7,8-TCDD) and 0.11 ng m^{-3}, 0.47 ng kg^{-1} (OCDD), respectively. The reference data are 0.039 ng m^{-3} in water and 0.54 ng kg^{-1} in sediment. Overall, the residuals between calculated and measured concentrations are less than one log unit in all four environmental compartments. The results verified the applicability of this model for the Beijing area and suggest that OCDD may be suitable representative substance to simulate the PCDD/Fs concentration in soil. Based on the modeled concentrations, the PCDD/Fs are calculated to account for 0.144%~0.456%, 0.003%~0.009%, 96.7%~98.8% and 1.045%~2.791% in air, water, soil and sediment, respectively, of total residual amount of PCDD/Fs in the environmental compartments. Soil is demonstrated to be the largest bulk reservoir of PCDD/Fs that release into the environment.

It must be emphasized that the comparison between the simulated results and observed data is extremely difficult, unless the observed concentrations are obtained from specific measurements for model evaluation

purpose. Moreover, the calculated vs. measured results in water and sediment could be further improved if the observed concentrations were available for the studied area specifically.

3.2 Calculated mass residues of PCDD/Fs in bulk- and sub-compartments

The residual amounts of PCDD/Fs in the environmental compartments were calculated using the estimated concentrations and volumes of the bulk compartments. Upon calculation, soil was the dominant sink for PCDD/Fs in Beijing, accounting for 96.7% of 2,3,7,8-TCDD and 98.8% of OCDD residual amount in the environment, respectively. The residue of 2,3,7,8-TCDD and OCDD in sediment accounts for 2.8% and 1.0% of the total amount in the environment, respectively. The different proportions in soil and sediment of 2,3,7,8-TCDD and OCDD reside in the physicochemical properties in these two compartments and in multimedia exchange behavior.

The mean concentrations and amount of 2,3,7,8-TCDD and OCDD were also calculated in each sub-compartment of bulk media. For example, 2,3,7,8-TCDD concentrations in the gas and particulate phases of air were 7.81×10^{-19} and 3.94×10^{-8} mol m^{-3}. In other words, in Beijing area, more than 99% of PCDD/Fs in air were bound to particles. This is higher than the ratios reported through experimental findings (Li et al., 2008). In the water compartment, the amount of PCDD/Fs in the suspended particles ranged from 51.3% to 53.1%, one to two orders of magnitude higher than that in water phase. For the soil and sediment compartments, more than 99% of PCDD/Fs were bounded to solid phase.

3.3 Transfer fluxes and processes

The intermedia transfer fluxes was simulated and displayed in Fig. 2. As shown in Fig. 2, the predominant transfer process of PCDD/Fs in the Beijing area is deposition from air to soil, accounting for 92.8% of the total transfer fluxes on average followed by air-water deposition, water-sediment deposition, sediment-water diffusion, soil-water runoff, water-air diffusion and soil-air diffusion. The degradation of PCDD/Fs in air and soil was found to be the major eliminating pathways for these chemicals, accounting for 99.1% of the total loss. The degradation in water and sediment contributes as low as 0.87% of the total loss. The results also suggest that the overall degradation rate of PCDD/Fs in Beijing within the four bulk environmental compartments is 23.3%, in other words, nearly three-fourths of the PCDD/Fs emissions would reside in the environment and biota. Figure 2 also details the reaction degradation, advection inflow (outflow), and intermedia exchange fluxes of 2,3,7,8-TCDD among the environmental compartments in Beijing. Due to the fact that the environmental conditions differ from place to place, e.g., total suspended particles in the air, precipitation, and wind speed etc, the transfer fluxes of PCDD/Fs exhibit the regional characteristics. In other words, the simulated intermedia transfer fluxes and processes herein are applicable for Beijing area alone.

3.4 Sensitivity analysis

In order to evaluate the inherent variability and uncertainty in the input parameters, the most sensitive input data should be identified. The sensitivity coefficients herein were defined as the relative change of the output to the relative change of the input parameters:

$$S = \frac{(Y_{101\%} - Y_{100\%})/Y_{100\%}}{(X_{101\%} - X_{100\%})/X_{100\%}} \quad (5)$$

In this model, the sensitivity coefficients of all the input parameters to the concentration of 2,3,7,8-TCDD in four bulk compartments were calculated. The results indicate that the environmental properties affect the predicted concentrations more significantly than physico-chemical properties for air. Air depth and emission rate have a positive influence on the calculated concentrations while the remaining parameters have negative influences. For water, the environmental properties have obviously increasing effects except for air residence time, e.g. precipitation and scavenging ratio, which probably enhance the air-water deposition. In contrast, the physico-chemical properties have reducing effects. The influences of the input parameters for predicting PCDD/Fs concentrations in soil are consistent with those in water. In sediment, the physico-chemical properties are more influential than the environmental properties, among which *K*ow is the most sensitive input parameter. Overall, precipitation and scavenging ratio are the most sensitive parameters in the four environmental compartments, which have negative effects on the calculated concentration for air while positive effects for the other three environmental compartments. The reason could be that a significant fraction of PCDD/Fs in air

deposited on the ground via precipitation and then followed by variety of transfer processes between the water, soil and sediment.

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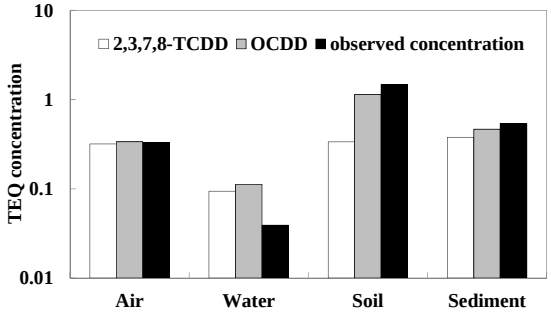

Fig. 1 Comparison between modeled and observed concentrations

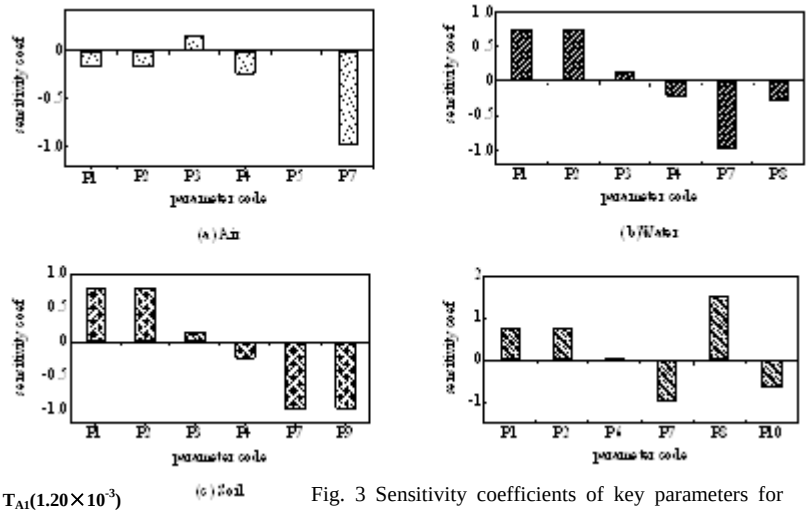

Fig. 3 Sensitivity coefficients of key parameters for 2,3,7,8-TCDD simulation

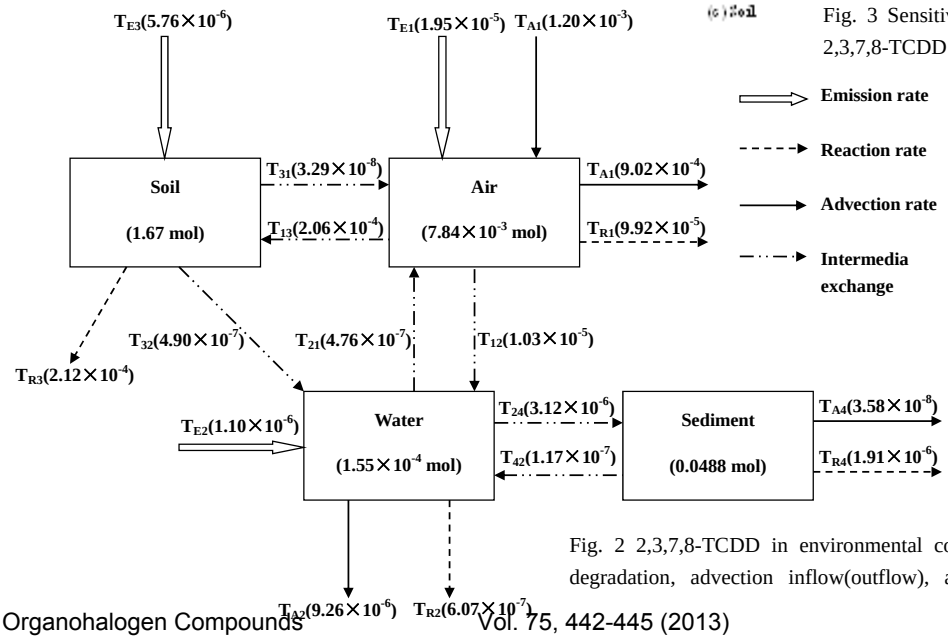

Fig. 2 2,3,7,8-TCDD in environmental compartments and reaction degradation, advection inflow(outflow), and intermedia exchange