DYNAMIC PCDD/F LEVEL MODELING USING STELLA SIMULATION IN TAIWAN

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1. Introduction

Food intake takes over 95% if PCDD/Fs exposure for human. Therefore, the PCDD/Fs levels in food and the human intake rate are crucial factorsto human PCDD/Fs exposure.Due to its high lipophilicity (i.e., octanol/water partition coefficient) and low water solubility, once PCDD/Fs deposit from atmosphere to land surface and ingestedby biota, they tend to adsorb strongly to animal's lipid tissue and accumulate along thefood chain, which is called bioaccumulation.PCDD/Fs emissions can transport from one country to another, therefore, high levelsare found even in remotepolar area.In order to estimating PCDD/Fs levels in biota, this study focuses on theintermedia movement and the mass balance of PCDD/Fs among environmental media, rather than addressing levels of different PCDD/Fs congeners or their transformation mechanisms, such as oxidation, photolysis, or biodegradation. The model's domain included the terrestrial territory of 35,980 km^2, including area of 500 km^2 under freshwater bodies, and also Taiwan's exclusive economic zone of 180,000 km^2(Figure 1). This domain was divided into four compartments—air, soil, freshwater, and seawater—PCDD/Fs levels in both terrestrial and aquatic biota could be estimated by the bioaccumulation factors calculated in this study.

Figure 1 Model domain includingexclusive economic zone for Taiwan.

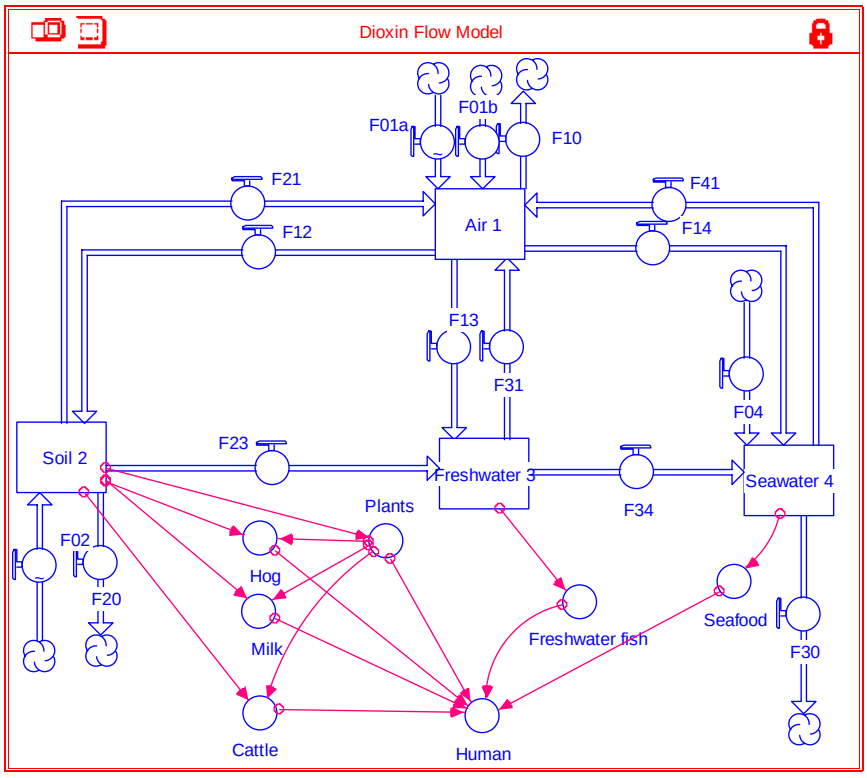
International toxic equivalent (I-TEQ), calculated by toxic equivalency factors (TEFs), is a unit for health risk assessment[1]. TEF value for the most toxic dioxin, 2,3,7,8-TCDD, is assigned as 1and 0–0.5 for other PCDD/Fs congeners and dioxin-like PCBs. This study used I-TEQ as unitsfor PCDD/Fs levels measured in the environmentalmedia and biota for the consequent human exposure assessment.

2. Materials and methods

*Model Construction.*Figure 2demonstrates the Dynamic Dioxin Flow model,which was depicted using the STELLA v.9.0 (isee^{TM} systems, USA)and was modified from a model for PCBs in ariver basin[2].

*Initial Reservoir Mass.*ThePCDD/Fs mass in each environmental reservoirin the beginning of simulation year 1979 was estimated by multiplying the concentration with the volume, which is derived as aproduct of the area and the depth of the environmental reservoir. The depths of atmosphere, soil, freshwater, and seawater were assumed to be 5,000 m, 0.2 m, 5 m, and 50 m, respectively.Due to the fact that there are no domestic measurements for PCDD/Fs in 1979, present background levels from Taiwan EPA were used as surrogate.

According to the data from Taiwan EPA, observed PCDD/Fs backgroundconcentrations in air, soil, freshwater and seawater approximated0.341 pg I-TEQ/Nm^3, 3.89 pg I-TEQ/g, 0.043 pg I-TEQ/L, and 0.019 pg I-TEQ/L, respectively.



Note: The four PCDD/Fs reservoirs—air, soil, freshwater, and seawater—were numbered 1, 2, 3 and 4, andthe input/outputfluxes between themwere represented by Fij, where i, j = 1, 2, 3, or 4, i≠j.

Figure2 The Dynamic Dioxin Flow model.

*Anthropogenic Emissions.*Trendsin the anthropogenic PCDD/Fs emissionshave beenreported by Taiwan EPA since 1999. Emissions before 1999 were estimatedin this study based onemission factors and activities forelectric arc furnaces, steel smelters, and municipal waste incinerators (MWIs), which were major (70%) contributors, from 1979 to 1999.Figure 3 shows that anthropogenic emissions increased from 34.04 g I-TEQ/yr in 1979, climaxedat 327.45 g I-TEQ/yr in 2002, and then decreased to 52.8 g I-TEQ/yr in 2009.Emissions after 2009 were predicted to grow slightly for each year till 2029 (Figure 3).

*Natural Emissions.*Natural PCDD/Fs emissionsarecorrelated withreemissions from land and water surface. Once deposited to soil, PCDD/Fs bound strongly to colloids and particles and volatilization half-life from soil may be as long as 12 years. Most of PCDD/Fs occurring in water are expected to be associated with sediments or suspended materials. Due to its adsorption to sediment, the removal half-life may be over 50 years. The volatilization rates were determined as 0.027–0.47pg I-TEQ/m^2-hr,depending on air-surface concentration gradients[3]. The evaporationdurationapproximated 225 days yr^{-1}based on meteorological data.

Wet and Dry Deposition. PCDD/Fs emitted to the atmosphere can be removed by wet and dry deposition. Wet deposition flux of PCDD/Fs is associated with both vapor dissolution into rain and the removal of suspended particulates by precipitation. PCDD/Fs levels in raindrops can be estimated by atmosphericPCDD/Fs concentration and both gas and particle scavenging ratios, which were determined as 741 and 4.2E+4 (dimensionless)[4].Average atmospheric PCDD/Fs concentrationsapproximated6.2fg I-TEQ/m^{3}on the marine and

51 fg I-TEQ/m^3on the land[5,6]. These concentrations were assigned for gas and particlephase using a constant gas/particle partitioning factor of 0.25[7].The estimated wet deposition rates were200 pg I-TEQ/m^2-yr on the marine and 4,303 pg I-TEQ/m^2-yr on the land. Dry deposition involves dry particulate deposition by gravitational settling or turbulent diffusion and vapor phase deposition by diffusion. The deposition flux is derived as the product of the vapor/particle phaseconcentrations and the deposition velocity of vapor or particle, which were 0.01 cm/s or 0.3–0.44 cm/s, respectively[8,9]. The estimated dry deposition rates were242 pg I-TEQ/m^2-yr on the marine and 2,805 pg I-TEQ/m^2-yr on the land. The total deposition rates were estimated as 0.44ng I-TEQ/m^2-yr on the marine 7.11ng I-TEQ/m^2-yr on the land.

DynamicModeling. A static mass balance, that is, the sum of PCDD/Fs inflow fluxes equal to the outflow, was set foreach of the four environmental reservoir—air, soil, freshwater and seawater—in the initial year 1979. The parameterization for dynamic modeling in this study was simply assumed that there were linear relationships between atmospheric deposition rate and reservoir mass and between reemission rate and reservoir level.Consequently,the variablesofdimensionless coefficients were derived.The simulation used a *dt* of 1 day, and a duration of 50 years (1979–2029).

Bioaccumulation.PCDD/Fs enter the terrestrial food chain by deposition onto plant surfaces or the soil which are subsequently adsorbed by plants via roots or ingested by animals. The variables of uptake rate and metabolism factors for plant and animals were drawn from the US EPA algorithms[10]. As shown in Figure 2, the PCDD/Fs levels for agricultural crops and livestock, such as hog, cattle, and milk, commonly ingested by residents in Taiwan, are associated with both soil and plants concentrations. Fish can stronglybioaccumulatePCDD/Fsthrough aquatic food chain.The biomagnification factor (BMF)isthe ratio of PCDD/Fs level in fish tissue to its concentration in the water, and the BMF values for the freshwater and seawater fish were setas 5,800 and 58,660, respectively, suggested by US EPA[11].

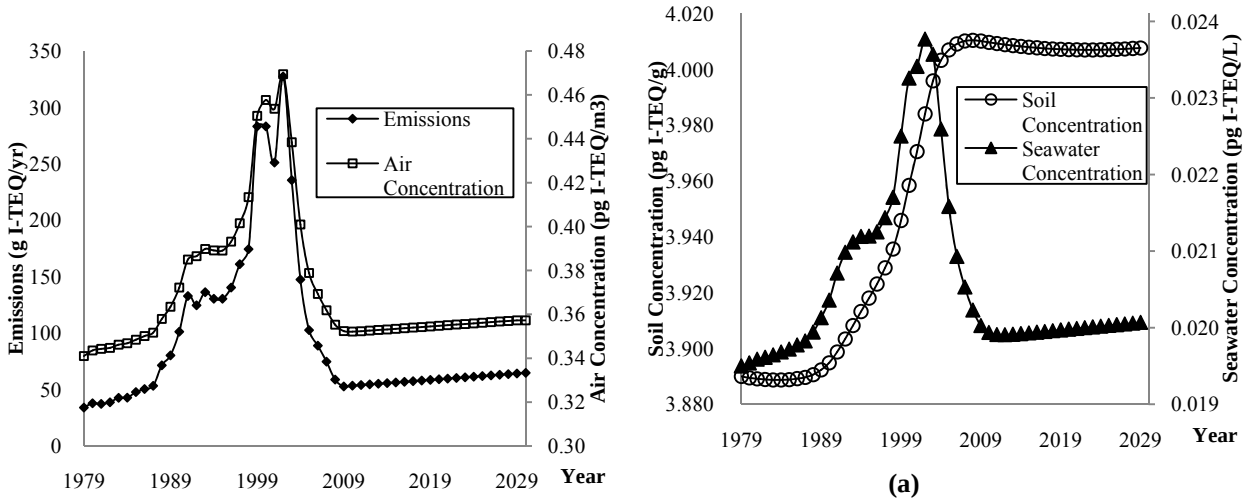


Figure3 Temporal trends of the (a) annual anthropogenic emissions and the simulated annual average PCDD/Fs concentration forair, (b)freshwater, and seawater.

3. Results and discussion

Results.As shown inFigure 3, the PCDD/Fs levels for air and seawater are consistent with the trends of anthropogenic emission. However, levels for surface soil did not significantly decline while the emission dramatically decreasedduring 2002 and 2009, attributing to regulations for electric arc furnaces and MWIs emission standards. It is mainly because the soil keeps the bulk of PCDD/Fs among the reservoirs[12], so its concentration tends to be relatively stable.By comparing the simulated PCDD/Fs concentrations with the observed (Table 1), it showsthat there was acceptable corroboration between simulated and observedvalues.This

result reveals that the Dynamic Dioxin Flow model is pretty accurate on predicting PCDD/Fs concentrationsnot only for environmental media, but also for aquaticand terrestrial food chain.

Table 1 Comparison of simulated and observed PCDD/Fs concentrations in various media.

Media (units)	Time	Observed	Simulated
air(pg I-TEQ/m^3)	2008	0.21 [a]	0.36
soil(pg I-TEQ/g)	2005	3.89 (0.254–15.2) [a]	3.95
freshwater(pg I-TEQ/L)	2007	0.044 (0.008–0.079) [a]	0.045
seawater(pg I-TEQ/L)	2008	0.019 [a]	0.020
plants(pg I-TEQ/g)	2003	1.33(for pasture sampled) [b]	1.81
beef(pg I-TEQ/g)	2004	0.967±0.692 [b]	0.973
milk(pg I-TEQ/g)	2004	1.34±0.84 [b]	0.256
	2010	0.564 [b]	0.256
pork (pg I-TEQ/g)	2004	0.306±0.214 [b]	0.128
freshwater fish(pg I-TEQ/g)	2004	1.850±0.36 [b]	0.319
seawater fish(pg I-TEQ/g)	2004	4.700±3.82 [b]	1.297

[a] Taiwan Environmental Protection Administration.[b]Taiwan Ministry of Health.

*Discussion.*The Dynamic Dioxin Flow modeldeveloped by the STELLA softwareis low-cost, simple and fast. Moreover, this model showed good performance oncurrent concentrations for both environmentalmedia and biota. On health risk or exposure assessment, it could be a substitute for complexenvironment model, such as atmospheric dispersion model for anthropogenic emission and water quality model for rivers,especially in long-term prediction,such as modeling fish PCDD/Fs level after dozens of years or even one hundred years later.However, parameterization for dynamic modeling in this study should be more sophisticated, such as, in the calculation of dynamic atmospheric deposition rate and the consideration of sediment burial, degradation and photolysis. Thismodel (Figure 2)illustrates the human PCDD/Fs exposure for a more comprehensivestudy related to health risk assessment, which could be carried outby incorporating parameters like food intake rates for residents in different countries.

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