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Sensitivity Analysis for a Level-III Multimedia Environmental Model: A Case Study for 2, 3, 7, 8-TCDD in Seoul

Jung-Hwan Kwon and Dong Soo Lee[1,*]

Environmental Chemistry Laboratory, Korea Institute of Toxicology, 100
Jangdong, Yusong, Daejon, 305-343, Republic of Korea
[1]*Graduate School of Environmental Studies, Seoul National University,*
San 56-1, Shillimdong, Kwanaku, Seoul, 151-742, Republic of Korea

다매체환경거동모형(level-III)의 민감도분석기법: 서울지역의 2, 3, 7, 8-TCDD 사례연구

권정환, 이동수[1,*]

한국화학연구원 환경화학실, [1]서울대학교 환경대학원

요 약

유해물질의 거동에 대한 이해를 돕기 위해서 대도시지역을 대상으로 하여 fugacity를 이용한 level-III 다매체환경거동모형이 개발되었다. 이 모형에 의한 거동의 예측결과에 민감한 영향을 주는 입력과정과 변수들을 찾아내기 위하여 체계적으로 민감도분석을 수행할 수 있도록 하는 기법을 개발하고 사례연구로서 서울지역과 2,3,7,8-TCDD을 대상으로 그 기법을 적용하였다. Sensitivity index에 의한 평가한 결과, 일정한 배출속도조건에서는 대기중의 바람속도, 그리고 대기에서 수체나 토양으로 전이되는 건식 및 습식 침적과정이 다매체거동에서 전체적으로 가장 중요한 과정인 것으로 나타났다. 또한 이들 거동과정 자체에 영향을 미치는 변수들에 대한 민감도 분석의 결과 건식침적의 경우 중력에 의한 입자들의 침강속도가, 습식침적의 경우 평균 강우속도가 대단히 중요한 변수임이 파악되었다. 물질의 물리화학적 특성 가운데에서는 z-값에 직접 영향을 주는 변수들, 즉, 헨리상수와 옥타놀-물 분배계수 등이 결과에 민감한 영향을 주는 것으로 나타났다. 이러한 사례연구는 본 연구에서 개발된 민감도분석기법이 유해물질의 다매체 거동모형을 개선하고 좀더 중요한 거동과정에 대한 이해를 넓히는데 효율적으로 사용될 수 있다는 것을 보여주고 있다.

Key words : Sensitivity analysis, Multimedia environmental model, Fugacity, 2,3,7,8-TCDD

INTRODUCTION

Multimedia environmental models have drawn much attention as a valuable tool describing the fate of chemicals in the first step of human and ecological risk assessment (Cohen and Ryan, 1985; Devillers *et al.*, 1996; Diamond *et al.*, 2001; Mackay, 1991; Mackay and Paterson, 1991; Mackay *et al.*, 1996; Suzuki *et al.*, 2000; Van de Meent and de Bruijn, 1995). As use of the models are considered for effective chemical management in a number of jurisdictions, the models' performance in describing and predicting the chemicals' environmental fate becomes a

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[*] To whom correspondence should be addressed.
Tel: 02-880-8522, E-mail: leeds@snu.ac.kr

significant concern. The reliability of the multimedia environmental models is undoubtedly a function of the accuracy of the various model input parameters. However, it is often difficult to choose a proper value for each parameter in the models, especially when the range of reported or possible value of the parameter is wide. Whatever value is chosen, it is necessary to analyze the uncertainty associated with the model outcomes for their appropriate use. Usually the uncertainty analysis is resource demanding when the number of the uncertain parameters is large. Therefore, it is critical to reduce the number by limiting the analysis to the most influencing parameters. Sensitivity analysis is a means used to identify the influencing parameters. An additional benefit from identifying the influencing parameters is that research effort can efficiently be focused to reduce the uncertainties of the influencing parameters.

A typical sensitivity analysis is conducted by correlating the model results with the parameter variation based on numerous repetitive calculations. Such a procedure is time consuming and may mask combined effects of interrelated parameters when the number of model parameters is large as in multimedia environmental models. This drawback could be overcome by introducing systematic concepts as exemplified by Cohen (1986). Therefore, a principal objective of this study was to develop a more systematic and mathematical method that could assist in conducting parametric sensitivity in efficient manners. A steady-state multimedia environmental model (Level III), originally developed for an urban environment using fugacity approach by Kwon (1998), was used to screen the parametric sensitivity for the multimedia environmental behavior of 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (2, 3, 7, 8-TCDD) in Seoul.

Fugacity model

Fugacity means "escaping tendency" of a chemical in a medium, having a unit of pressure by definition. The concept of fugacity, which was introduced by Lewis in 1901 as a more convenient thermodynamic equilibrium criterion than chemical potential, has been widely used in chemical process calculations. Its convenience has become apparent by D. Mackay and his co-workers (Mackay, 1979; Mackay, 1991; Mackay and Paterson, 1981; Mackay and Paterson, 1982; Mackay and Paterson, 1991) for multimedia models where chemical equilibrium or partitioning calculations are frequent.

In fugacity models, the contaminant mass balance equations are derived in terms of fugacity in the multimedia. Then the fugacity is converted to concentration or mass. To relate fugacity to concentration, a parameter termed fugacity-capacity is defined for each medium: the Z-value [$\mathrm{mol/m^3Pa}$]. The analogy between the Z-value in a medium and the heat capacity of a material is shown in (1) and (2) (Mackay, 1991). Therefore, the concentration in a medium is a product of fugacity and Z-value, a constant in a given medium.

$$\text{Amount of Heat (J)} = \text{Mass (g)} \times \text{Heat capacity (J/g°C)} \times \text{Temperature (°C)} \quad (1)$$

$$\text{Amount of Matter (mol)} = \text{Volume (m}^3\text{)} \times \text{Fugacity capacity (mol/m}^3\text{Pa)} \times \text{Fugacity (Pa)} \quad (2)$$

When the environment is at equilibrium as assumed in equilibrium models, the pollutant concentration (C_i) in a medium can be calculated simply by multiplying the fugacity (F_i), the same in all media, with fugacity capacity, Z_i.

$$F_1 = F_2 = F_3 = \Lambda = F_i \quad (3)$$

$$C_i = Z_i F_i \quad (4)$$

In non-equilibrium models, steady-state input, transformation, and inter-compartmental transfers are represented by D-values. D-values used in this level of calculation are defined as the value of mass flow rate divided by the fugacity in a medium (5) Environmental loss mechanism includes biological and chemical degradation, advection, and intermedia mass transfer.

$$\text{D (mol/h Pa)} = \text{Loss rate (mol/h)} / \text{Fugacity (Pa)} \quad (5)$$

Therefore, introducing mass-balance equations into a fugacity model gives a set of general equations for mass conservation (6) in unsteady state conditions.

$$V_i Z_i \frac{dF_i}{dt} \sum_j D_{ji} F_j - \sum_j D_{ij} F_i + E_i \qquad (6)$$

where D_{ij} and E_i denote intermedia transport from i compartment to j compartment and emission rate [mol/h], respectively. Thus the fugacity in each medium is calculated by simultaneously solving n linear equations derived from a system of n compartments. At steady state conditions, the equation (6) reduces to (7).

$$\sum_j D_{ij} F_i = \sum_j D_{ji} F_j + E_i \quad \text{(for compartment i)} \qquad (7)$$

Processes in the model

The schematic diagram is shown in Fig. 1 for the model used in this study. The Z-values, used in the model, are listed in Table 1 and 2. The detailed derivation of Z-values is referred to Mackay (1991). In a six-compartment model used in this study (Kwon, 1998), equilibrium is assumed within a bulk compartment containing more than two phases, such as air and water. Mass transport processes described in Fig. 1 are presented in terms of D-values in Table 3. Further discussion and the derivation of D-values are well documented in several literatures (Mackay, 1991; Kwon, 1998; Trapp and Matthies, 1995). Calculating the D-values requires the transport parameters described in Table 4.

Sensitivity model

The set of governing equation of fugacity model (7) is represented in N×N matrix form for N compartments (8).

$$\frac{d}{dt}\begin{bmatrix} V_1 Z_1 F_1 \\ V_2 Z_2 F_2 \\ M \\ V_N Z_N F_N \end{bmatrix} = \begin{bmatrix} -D_{T1} & D_{21}\,\Lambda & D_{N1} \\ D_{12} & -D_{T2}\,\Lambda & D_{N2} \\ \Lambda & \Lambda\ \ \Lambda & \Lambda \\ D_{1N} & D_{2N}\,\Lambda & -D_{NN} \end{bmatrix} \begin{bmatrix} F_1 \\ F_2 \\ M \\ F_N \end{bmatrix} + \begin{bmatrix} E_1 \\ E_2 \\ M \\ E_N \end{bmatrix} \qquad (8)$$

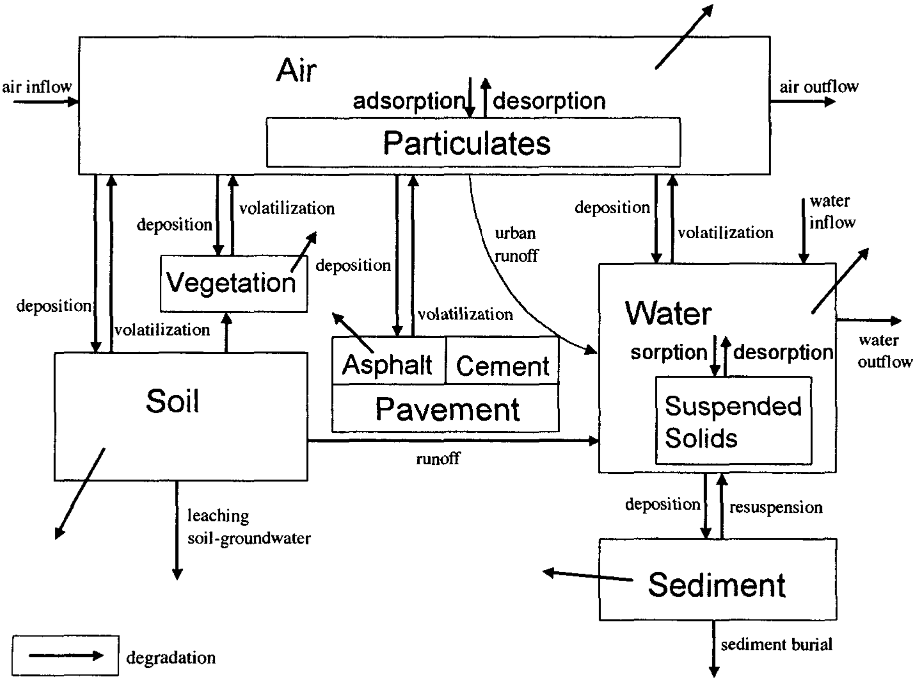

Fig. 1. Schematic diagram and mass flow of the model.

Table 1. Z-values used in this study

Medium	Z-value (mol/m^3 Pa)	
Air (Z_A)	$1/RT$	R : gas constant (8.3145 Pa m^3/mol K) T : temparature (K)
Particulates (Z_P)	K_{PA}/RT	K_{PA} : dimensionless particle air partition coefficient
Water (Z_W)	$1/H$	H : Henry's law constant (Pa m^3/mol)
Soil (Z_S)	$K_{PS}\rho_S/H$	K_{PS} : soil water partition coefficient (L/kg) ρ_S : soil bulk density (kg/L)
Sediment (Z_X)	$K_{PX}\rho_X/H$	K_{PX} : sediment water partition coefficient (L/kg) ρ_X : sediment bulk density (kg/L)
Suspended solids (Z_{SS})	$K_{PSS}\rho_{SS}/H$	K_{PSS} : suspended solids water partition coefficient (L/kg) ρ_{SS} : suspended solids bulk density (kg/L)
Asphalt pavement (Z_{AS})	$K_{PAS}\rho_{AS}f_{AS}/H$	K_{PAS} : asphalt water partition coefficient (L/kg) ρ_{AS} : asphalt bulk density (kg/L) f_{AS} : fraction of asphalt
Vegetation (Z_v)	K_{PW}/H	K_{PW} : dimensionless plant water partition coefficient

where V_i, Z_i, F_i, E_i are volume, fugacity capacity, fugacity, and source emission rate including advection for compartment i, respectively. D_{Ti} is total transfer D value from compartment i.

In order to simplify the subsequent analysis, the systems of linear equations (8) can be written more conveniently in the following.

$$VZ\frac{d}{dt}\vec{F} = A\vec{F} + \vec{S} \tag{9}$$

where $\vec{F}$, $\vec{S}$, V, and Z are the fugacity and source (vectors), the volume and Z value (matrices), respectively. A is the intermedia D value matrix whose coefficients are represented in (8).

In the multimedia fugacity model described in (9), fugacities vary with the parameters of matrix A and the source vector $\vec{S}$. Consider a parameter α which is subject to a small variation $\Delta\alpha$ from α_0, the original value of the parameter for the multimedia system for which the solution is $\vec{F}_0$. the change in the solution of (9) due to the variation $\Delta\alpha$ can be expressed by a Taylor series expansion (10-11).

$$\alpha = \alpha_0 + \Delta\alpha \tag{10}$$

$$\vec{F} = \vec{F}_0 + \frac{\partial\vec{F}}{\partial\alpha}\Big|\Delta\alpha + \frac{\partial^2\vec{F}}{\partial\alpha^2}\Big|_{\alpha_0}\frac{\Delta\alpha^2}{2} + \Lambda \tag{11}$$

Limiting $\Delta\alpha$ to small variations, the second and higher order terms in (11) may be neglected. Then (11) reduces to:

$$\vec{F} = \vec{F}_0 + \sigma_\alpha\Delta\alpha \tag{12}$$

where $\sigma_\alpha = \frac{\partial\vec{F}}{\partial\alpha}\Big|_{\alpha_0}$ is termed output sensitivity function.

After differentiating (9) with respect to α, the following sensitivity model is obtained:

$$VZ\dot{\sigma}_\alpha = A_0\vec{\sigma}_\alpha + \varphi_\alpha\vec{F}_0 + \vec{\tau}_\alpha \tag{13}$$

where $\dot{\sigma}_\alpha$ is the time derivative of σ_α and

$\vec{\tau}_\alpha = \frac{\partial\vec{S}}{\partial\alpha}\Big|_{\alpha_0}$, $\varphi_\alpha = \frac{\partial A}{\partial\alpha}\Big|_{\alpha_0}$

If the source vector $\vec{S}$ is independent of the parameter α, then $\vec{\tau}_\alpha$ is becomes a zero vector (14).

$$VZ\dot{\sigma}_\alpha = A_0\vec{\sigma}_\alpha + \varphi_\alpha\vec{F}_0 \tag{14}$$

Table 2. Z-values for bulk environmental phases

Media	Z-value
Air (Z_1)	$Z_A + v_P Z_P$
Water (Z_2)	$Z_W + v_{SS}Z_{SS}$
Soil (Z_3)	Z_S
Sediment (Z_4)	Z_X
Asphalt pavement (Z_5)	Z_{As}
Vegetation (Z_6)	Z_V

v_P and v_{SS} denote volume fractions of particulates and suspended solids, respectively

Table 3. Intermedia D-values

Process		Individual D-value	Overall D-value
Air (1) - Water (2)	Diffusion	$D_{VW}=\dfrac{1}{\dfrac{1}{k_{AW}A_{12}Z_A}+\dfrac{1}{k_{WW}A_{12}Z_W}}$	$D_{12}=D_{VW}+D_{RW}+D_{QW}+D_{DW}+D_{RL}+D_{QL}$ $D_{12}=D_{VW}$
	Rain	$D_{RW}=A_{12}U_RZ_W$	
	Wet deposition	$D_{QW}=A_{12}U_RQv_QZ_Q$	
	Dry deposition	$D_{DW}=A_{12}U_pv_QZ_Q$	
	Rain to LC*	$D_{RL}=de(A_C+A_{15})U_RZ_W$	
	Wet deposition to LC	$D_{QL}=de(A_C+A_{15})U_RQv_QZ_Q$	
Air (1) - Soil (3)	Diffusion	$D_{VS}=\dfrac{1}{\dfrac{1}{k_{SA}A_{13}Z_A}+\dfrac{Y_3}{A_{13}(B_{AE}Z_A+B_{WE}Z_W)}}$	$D_{13}=D_{VS}+D_{RS}+D_{QS}+D_{DS}$ $D_{31}=D_{VS}$
	Rain	$D_{RS}=A_{13}U_RZ_W$	
	Wet deposition	$D_{QS}=A_{13}U_RQv_QZ_Q$	
	Dry deposition	$D_{DS}=A_{13}U_Pv_QZ_Q$	
Air (1) - Asphalt (5)	Diffusion	$D_{VAS}=\dfrac{1}{\dfrac{1}{k_{SA}A_{13}Z_A}+\dfrac{Y_5}{B_{MAS}A_{15}Z_{AS}}}$	$D_{15}=D_{VAS}$ $D_{51}=D_{VAS}$
Air (1) - Vegetation (6)	Diffusion	$D_{GD}=A_{16}LAgZ_A$	$D_{16}=D_{GD}$ $D_{61}=D_{GD}$
Soil (3) - Vegetation (6)	Uptake	$D_{XY}=Qt \cdot TSCF \cdot Z_W$	$D_{36}=D_{XY}$ $D_{63}=0$
Land (3, 5) - Water (2)	Water runoff	$D_{WW}=A_{13}U_{WW}Z_W$	$D_{23}=0$
	Solid ruoff	$D_{SW}=A_{13}U_{SW}Z_S$	$D_{32}=D_{WW}+D_{SW}$
Water (2) - Sediment (4)	Diffusion	$D_{TX}=\dfrac{1}{\dfrac{1}{k_{XW}A_{24}Z_W}+\dfrac{Y_4}{B_{WX}A_{24}Z_W}}$	$D_{24}=D_{TX}+D_{DX}$ $D_{42}=D_{TX}+D_{RX}$
	Deposition	$D_{DX}=A_{24}U_{DX}Z_{SS}$	
	Resuspension	$D_{RX}=A_{24}U_{RX}Z_X$	
Reaction		$D_{Ri}=k_{Ri}V_iZ_i$	
Advection		$D_{Ai}=G_iZ_i$	
Sediment burial		$D_{BX}=U_{BX}A_{24}Z_X$	
Leaching to groundwater		$D_{LS}=U_{LS}A_{13}Z_W$	

* LC denotes Land covering materials, i.e., cement and asphalt pavement.

Likewise, φ_α becomes a zero matrix when A is independent of α (15).

$$VZ\dot{\vec{\sigma}}_\alpha=A_0\vec{\sigma}_\alpha+\vec{\tau}_\alpha \qquad (15)$$

At steady state, (14) and (15) are readily solved to yield the solutions (16) and (17), respectively:

$$\vec{\sigma}_\alpha=A_0^{-1}\varphi_\alpha\vec{F}_0 \qquad (16)$$

$$\vec{\sigma}_\alpha=A_0^{-1}\vec{\tau}_\alpha \qquad (17)$$

Because concentration is more tangible than fugacity in the notion, the parametric sensitivity may be written in terms of concentration as:

$$\frac{\partial C_i}{\partial\alpha}=Z_i\frac{\partial F_i}{\partial\alpha}+F_i\frac{\partial Z_i}{\partial\alpha}=Z_i\sigma_{\alpha i}+F_i\frac{\partial Z_i}{\partial\alpha} \qquad (18)$$

Table 4. Parameter values used in the model

Parameter	Symbol	Value
Correction exponent for differences between plant lipids and octanol	B	0.95[a]
Drainage efficiency	de	0.8[b]
Correction factor for differences between asphalt pavement and octanol	f_{Oas}	1.2[c]
Conductance in air-vegetation interface (m/h)	G	3.6[a]
Air side mass transfer coefficient over asphalt pavement (m/h)	k_{AsA}	1[d]
Air side mass transfer coefficient over water (m/h)	k_{AW}	5[e]
Air side mass transfer coefficient over soil (m/h)	k_{SA}	1[e]
Water side mass transfer coefficient (m/h)	k_{WW}	0.05[e]
Water side mass transfer coefficient over sediment (m/h)	k_{XW}	0.01[e]
Leaf surface area (m^2/m^2)	LA	5[a]
Lipids contents in vegetation (kg/kg)	L_P	0.02[a]
Density of particulate matter (kg/L)	Pd	2[a]
Vegetation bulk density (kg/L)	ρ_P	0.5[a]
Scavenging ratio	Q	20,000[e]
Transpiration stream (m^3/h)	Qt	4.14×10^{-5}[a]
Sediment burial rate (m/h)	U_{BX}	3.4×10^{-8}[e]
Sediment deposition rate (m/h)	U_{DX}	4.6×10^{-8}[e]
Soil-groundwater leaching rate (m/h)	U_{LS}	3.9×10^{-5}[e]
Sediment resuspension rate (m/h)	U_{RX}	1.1×10^{-8}[e]
Volume fraction air in soil	v_A	0.3[e]
Volume fraction water in soil	v_W	0.2[e]
Volum fraction water in sediment	v_X	0.63[e]
Water content in vegetation (g/g)	W_P	0.8[a]
Diffusion path length in soil (m)	Y_3	0.05[e]
Diffusion path length in sediment (m)	Y_4	0.005[e]
Diffusion path length in asphalt pavement (m)	Y_5	1×10^{-6}[c]

a. Trapp and Matthies (1995), b. typical runoff coefficient for urban area is about 0.8 (Kiely, 1996), c. Kwon (1998), d. Assumed the same as k_{SA} in Mackay (1991), e. Mackay (1991)

Then, sensitivity index, which is defined as % change in concentration over % change in the parameter α, is obtained by multiplying $\frac{\alpha_0}{C_0}$ with the output sensitivity function (19).

$$\frac{\frac{\Delta C}{C}}{\frac{\Delta \alpha}{\alpha}} = \frac{\frac{\Delta C}{C_0}}{\frac{\Delta \alpha}{\alpha_0}} \approx \frac{\partial C}{\partial \alpha} \times \frac{\alpha_0}{C_0} \tag{19}$$

Physico-chemical properties of 2,3,7,8-TCDD

Physico-chemical properties and environmental life-time of TCDD have been studied by several researchers (Atkinson, 1987; Eitzer and Hites, 1988; Friesen and Webster, 1990; Friesen *et al.*, 1996; Koester and Hites, 1992; Kowk *et al.*, 1994; Kowk *et al.*, 1995; McCrady and Maggard, 1993; Pennise and Kamens, 1996; Shiu *et al.*, 1988). The dominant environmental degradation of TCDD is photodegradation in the atmosphere and surface water. Typically, photolysis half-lives of TCDD are about several days and a few weeks in the atmosphere and surface water, respectively (Atkinson, 1987; Friesen *et al.*, 1996). In this paper, physico-chemical properties and degradation rate constants of TCDD were selected mostly from suggested values in Mackay *et al.* (1992), after reviewing several literature mentioned above (Table 8). Degradation rate constant in asphalt pavement was assumed to be ten times higher than in soil, because thin effective thickness of asphalt pavement was considered favorable to surface

Table 5. Compartment depths

Compartment	Depth (m)
Air (Mixing height; MH)	1000
Water (Water depth; WD)	3.0
Soil (Effective soil depth; SD)	0.10
Sediment (Effective sediment depth; XD)	0.10
Asphalt pavement (Effective asphalt pavement; AsD)	1.0×10^{-5}
Vegetation (Volume of vegetation per unit area; VD)	0.002

Table 6. Interface areas

Interface	Area (m^2)[a]
Air-Water (A_{12})	2.48×10^{7}
Air-Soil (A_{13})	2.40×10^{8}
Air-Cement concrete (A_C)	2.71×10^{8}[b]
Air-Asphalt pavement (A_{15})	7.05×10^{7}[c]
Air-Vegetation (A_{16})	7.20×10^{7}[d]
Water-Sediment (A_{24})	2.48×10^{7}[e]

a. Areas were obtained using TM (May, 1993) band 2, 3, 4 through supervised classification, b. obtained by the deduction of the asphalt pavement area from urban land use area, c. Seoul Metropolitan Government (1996), d. assumed 30% of soil is covered with vegetation, e. assumed the same as the air-water interface area

Table 7. Characteristic environmental parameters for Seoul

Environmental parameters	Value
Atmospheric temperature (T)	293 K
Soil bulk density (ρ_S)	1.5 kg/L
Sediment bulk density (ρ_X)	2.0 kg/L
Suspended solids bulk density (ρ_{SS})	1.2 kg/L
Asphalt pavement bulk density (ρ_{As})	2.5 kg/L[a]
Organic carbon content in soil (f_{Ocs})	0.01 g/g
Organic carbon content in sediment (f_{Ocx})	0.03 g/g
Organic carbon content in suspended solids (f_{Ocss})	0.06 g/g
Total Suspended Particulates (TSP)	80 $\mu g/m^3$[b]
Volume fraction suspended solids (v_{SS})	5×10^{-6} m^3/m^3[c]
Asphalt content in asphalt pavement (f_{As})	0.05[a]
Advective inflow rate in air (G_{A1})	1.12×10^{11} m^3/h[d]
Advective inflow rate in water (G_{A2})	3.6×10^{6} m^3/h[e]
Dry deposition velocity (U_P)	10.8 m/h
Rain rate (U_R)	1.63×10^{-4} m/h[f]
Water runoff rate from soil (U_{WW})	3.26×10^{-5} m/h[g]
Solids runoff rate from soil (U_{SW})	3.26×10^{-8} m/h[h]

a. Traxler (1961), b. Ministry of Environment (1992-1996), c. Ministry of Environment (1996), d. from average wind speed (Korea Meterological Administration, 1992-1997), e. from water flux (Ministry of Construction and Transportation, 1996a; Ministry of Construction and Transportation, 1996b), f. average rainfall (Korea Meterological Administration, 1992-1997), g. assumed that the amount of surface runoff is 20% of total rainfall, h. assumed that particulates matter in runoff water is 0.1% by volume.

photolysis.

Environmental parameters

Environmental characteristics for Seoul are listed in Table 5, 6, and 7. Compartment depths are generally assumed values (Table 5). Air-water and air-soil interface areas were obtained using TM (May, 1993) band 2, 3, 4 through supervised classification. Asphalt pavement area was obtained from the statistical data (Seoul Metropolitan Government, 1996). Air-cement interface area was calculated by deduction of asphalt pavement area from urban land use area. Air-vegetation interface area was calculated by assuming that 30% of soil is covered with vegetation. Water-sediment interface area was considered as the same as the air-water interface area. Parameters describing the sorption characteristics of the asphalt pavement were from Traxler (1961). Advective inflows of air and water compartment were calculated using average wind speed and flow rate appeared in annual statistics published by the government (Korea Meteorological Administration, 1992-1997; Ministry of Construction and Transportation, 1996a, b). Total suspended solids (TSP) and volume fraction of suspended solids were chosen as the average value of the reported data (Ministry of Environment, 1992-1996; Ministry of Environment, 1996). Precipitation rate was calculated by averaging rainfall (Korea Meteorological Administration, 1992-1997). Water and solids runoff from soil to water were calculated assuming that the amount of surface runoff is 20% of total rainfall and particulates matter in runoff water is 0.1% by volume. The values of the remaining parameters (i. e., temperature, bulk densities, organic carbon contents, dry deposition rate) were assumed values in Mackay (1991).

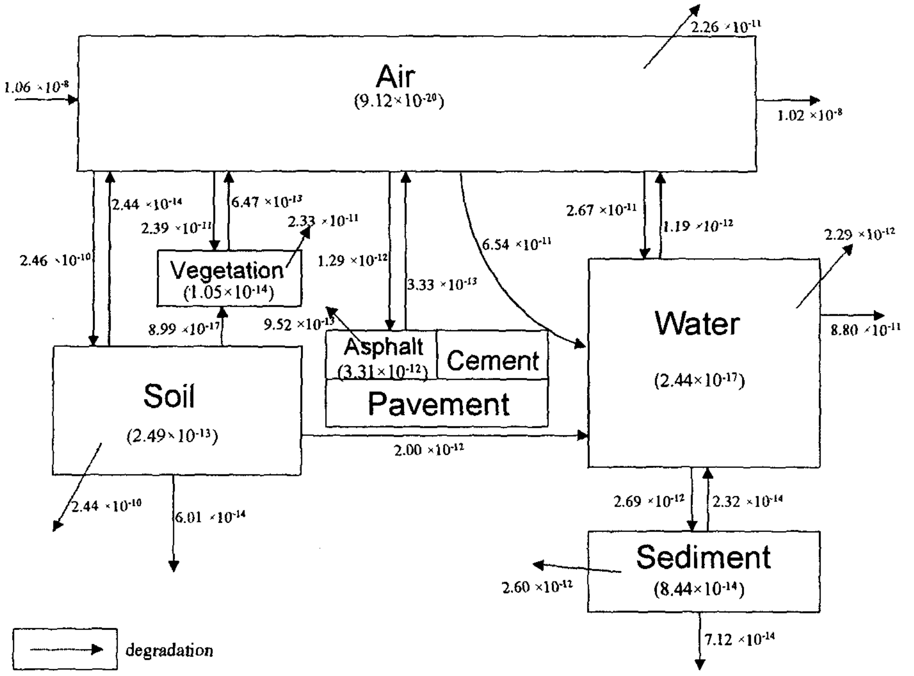

Fig. 2. Illustrated fate of 2, 3, 7, 8-TCDD in multimedia environment. Parenthesized values are concentration (mol/m^3) and other values on arrows are mass flow rate (mol/hr).

Emission scenario

To provide a hypothetical emission scenario of 2, 3, 7, 8-TCDD in Seoul, domestic waste incinerators were assumed a major source in Seoul. For a total of five identical incinerators, the effluent gas flow of each incinerator is 3.425×10^4 Nm^3/hr, under the assumption of 300 days/yr working day, 5000 Nm^3/waste ton of effluent gas, and 200 ton/day of amount of disposal. A measured average emission concentration of 0.1 ng/Nm^3 (Oh *et al.*, 1999) was used. Therefore, the total emission rate of 2, 3, 7, 8-TCDD was 34.3 μg/hr (10.6 nmol/hr) into air.

Table 8. Physico-chemical properties of 2, 3, 7, 8-TCDD

Henry's law constant	3.337 Pa · m^3/mol
Log Kow	6.8
Modified Antoine equation constant A	124001 J/mol^a
Modified Antoine equation constant B	287.6 J/mol · K^a
Melting point	578 K
Molecular weight	322.0 g/mol
Molar volume	275.6 cm^3/mol
Degradation rate constant in air	4.08×10^{-4} /h
Degradation rate constant in water	1.26×10^{-3} /h
Degradation rate constant in soil	4.08×10^{-5} /h
Degradation rate constant in sediment	1.24×10^{-5} /h
Degradation rate constant in asphalt pavement	4.08×10^{-4} /h^b
Degradation rate constant in vegetation	1.54×10^{-2} /h^c

a. Rordorf (1989), b. assumed to be one order of magnitude higher in asphalt pavement than in soil, c. selected degradation rate constant including biodegradation and photolysis from Chrostowski and Foster (1996). All other values are from Mackay *et al.* (1992)

RESULTS AND DISCUSSION

Model simulations were conducted with the prescribed emission scenarios and the input parameter values in the Tables 4 through 8. The resulting multimedia movements of 2, 3, 7, 8-TCDD are illustrated in Fig. 2. Only 4% of the total 2, 3, 7, 8-TCDD emitted into the environment is retained in the system and the major portion of the mass is transported out

Table 9. Sensitivity indices for D−values

Process	Sensitivity indices					
	Air	Water	Soil	Sediment	Asphalt pav.	Vegetation
D_{VW}	−7.34e−6	8.31e−4	−7.34e−6	8.31e−4	7.34e−6	7.34e−6
D_{RW}	−5.08e−6	5.74e−4	−5.08e−6	5.74e−3	−5.08e−6	−5.08e−6
D_{QW}	−5.48e−4	**6.20e−2**	−5.48e−4	**6.20e−2**	−5.48e−4	−5.48e−4
D_{DW}	−1.81e−3	**2.05e−1**	−1.81e−3	**2.05e−1**	−1.81e−3	−1.81e−3
D_{RL}	−5.59e−5	6.33e−3	−5.59e−4	6.33e−3	−5.59e−5	−5.59e−5
D_{QL}	−6.03e−3	**6.83e−1**	−6.03e−3	**6.83e−1**	−6.03e−3	−6.03e−3
D_{VS}	−2.53e−6	−2.13e−7	1.07e−4	−2.13e−7	−2.53e−5	−2.53e−5
D_{RS}	−4.98e−5	−4.19e−6	2.09e−3	−4.19e−6	−4.98e−4	−4.97e−5
D_{QS}	−5.37e−3	−4.52e−4	**2.26e−1**	−4.52e−4	−5.37e−3	−5.37e−3
D_{DS}	**−1.78e−2**	−1.50e−3	**7.49e−1**	−1.50e−3	**−1.78e−2**	**−1.78e−2**
D_{VAs}	−6.65e−5	−6.65e−5	−6.65e−5	−6.65e−5	**7.41e−1**	−6.65e−5
D_{GD}	−2.14e−3	−2.14e−3	−2.14e−3	−2.14e−3	−2.14e−3	**9.71e−1**
D_{XY}	2.27e−10	−7.53e−9	−3.65e−7	−7.53e−9	2.27e−10	3.75e−6
D_{WW}	5.90e−8	5.30e−4	−2.04e−4	5.30e−4	5.90e−8	5.83e−8
D_{SW}	2.29e−6	**2.06e−2**	−7.92e−3	2.06e−2	2.29e−6	2.26e−6
D_{TX}	−3.93e−9	−3.50e−5	−3.93e−9	1.20e−3	−3.93e−9	−3.93e−9
D_{DX}	−3.18e−6	**−2.83e−2**	−3.18e−6	**9.70e−1**	−3.18e−6	−3.18e−6
D_{RX}	2.73e−8	2.43e−4	2.73e−8	−8.32e−3	2.73e−8	2.73e−8
D_{R1}	−2.13e−3	−2.13e−3	−2.13e−3	−2.13e−3	−2.13e−3	−2.13e−3
D_{R2}	−2.73e−6	**−2.43e−2**	−2.73e−6	**−2.43e−2**	−2.73e−6	−2.73e−6
D_{R3}	−4.65e−6	**−2.11e−2**	**−9.92e−1**	**−2.11e−2**	−4.65e−6	−8.37e−6
D_{R4}	−2.67e−8	−2.38e−4	−2.67e−8	**−9.65e−1**	−2.67e−8	−2.67e−8
D_{R5}	−2.33e−5	−2.33e−5	−2.33e−5	−2.33e−5	**−7.41e−1**	−2.33e−5
D_{R6}	−5.93e−5	−5.93e−5	−5.93e−5	−5.93e−5	−5.93e−5	**−9.73e−1**
D_{A1}	**−9.64e−1**	**−9.64e−1**	**−9.64e−1**	**−9.64e−1**	**−9.64e−1**	**−9.64e−1**
D_{A2}	−1.05e−4	**−9.35e−1**	−1.05e−4	**−9.35e−1**	−1.05e−4	−1.05e−4
D_{BX}	−7.33e−10	−6.52e−6	−7.33e−10	**−2.65e−2**	−7.33e−10	−7.33e−10
D_{LS}	−1.15e−9	−5.19e−6	−2.44e−4	−5.19e−6	−1.15e−9	−2.06e−9

Expressed in bold if the absolute value is greater than 0.01.

to neighboring regions. It represents that pollution caused by an air−born chemicals, persisting in the environment long time, has wide range. Careful examination of the rates of transfer in Fig. 2 roughly identifies the processes significantly affecting the distribution and migration in the given multimedia system. By combining the results shown in Figs 2 and 3, it could be shown that 2, 3, 7, 8−TCDD accumulates mostly in soil and sediment via atmospheric deposition.

To quantify the response of the model outputs to the input parameters, the sensitivity analysis was performed by calculating sensitivity indices. Sensitivity indices for intermedia D values were calculated to screen dominant processes affecting the multimedia fate of 2, 3, 7, 8−TCDD. Based on the sensitivities of D values, the sensitivity indices were further calculated for transfer coefficients, physico−chemical properties, and environmental parameters strongly affecting the results of the simulation.

Sensitivity indices in Table 9 show the processes determining the concentration in each medium. Advective flow of air (D_{A1}) was a dominant process for all media. As the flow rate of air increases by 1%, the concentrations of 2, 3, 7, 8−TCDD in all media decrease by 0.964%. Dry deposition to water (D_{DW}) and wet deposition to the covering layer (D_{QL}) was the two most important processes for water and

Table 10. Sensitivity indices for transfer coefficients in the model

MTCs	Sensitivity indices					
	Air	Water	Soil	Sediment	Asphalt pav.	Vegetation
k_{AW}	−6.79e−6	7.68e−4	−6.79e−6	7.68e−4	−6.79e−6	−6.79e−6
k_{SA}	−2.93e−8	−2.46e−9	1.23e−6	−2.46e−9	−2.93e−8	−2.93e−8
k_{WW}	−5.58e−7	6.31e−5	−5.58e−7	6.31e−5	−5.58e−7	−5.58e−7
k_{AsA}	−6.57e−5	−6.57e−5	−6.57e−5	−6.57e−5	**7.31e−1**	−6.57e−5
k_{XW}	−4.35e−12	−3.87e−8	−4.35e−11	−1.33e−6	−4.35e−12	−4.35e−12
U_{BX}	−7.33e−10	−6.52e−6	−7.33e−10	**−2.65e−2**	−7.33e−10	−7.33e−10
U_{DX}	−3.18e−6	**−2.83e−2**	−3.18e−6	**−9.70e−1**	−3.18e−6	−3.18e−6
U_{LS}	−1.15e−9	−5.19e−6	−2.44e−4	−5.19e−6	−1.15e−9	−2.06e−9
U_{P}	**−1.96e−2**	**2.04e−1**	**7.47e−1**	**2.04e−1**	**−1.96e−2**	**−1.96e−2**
U_{R}	**−1.21e−2**	**7.51e−1**	**2.21e−1**	**7.51e−1**	**−1.21e−2**	**−1.21e−2**
U_{SW}	2.29e−6	**2.06e−2**	−7.92e−3	**2.06e−2**	2.29e−6	2.26e−6
U_{WW}	5.90e−8	5.30e−4	−2.04e−4	5.30e−4	5.90e−8	5.83e−8
U_{RX}	2.73e−8	2.43e−4	2.73e−8	−8.32e−3	2.73e−8	2.73e−8
g	−2.14e−3	−2.14e−3	−2.14e−3	−2.14e−3	−2.14e−3	**9.71e−1**

Expressed in bold if the absolute value is greater than 0.01.

Table 11. Sensitivity indices for physico−chemical parameters and rate constants

Parameters	Sensitivity indices					
	Air	Water	Soil	Sediment	Asphalt pav.	Vegetation
H	2.57e−4	**−4.70e−1**	−2.68e−3	**−4.70e−1**	**−2.69e−1**	**−2.67e−2**
K_{OW}	−8.74e−5	**4.42e−1**	4.61e−4	**9.58e−1**	**2.69e−1**	**2.56e−2**
A	**−2.23e−1**	**9.04e+0**	**9.96e+0**	**9.04e+0**	**−4.08e+1**	**−4.08e+1**
B	**1.51e−1**	**−6.14e+0**	**−6.77e+0**	**−6.14e+0**	**2.77e+1**	**2.77e+1**
V_m	6.88e−7	1.20e−5	−1.66e−5	−3.99e−4	−3.18e−3	6.88e−7
k_{R1}	−2.13e−3	−2.13e−3	−2.13e−3	−2.13e−3	−2.13e−3	−2.13e−3
k_{R2}	−2.73e−6	**−2.43e−2**	−2.73e−6	**−2.43e−2**	−2.73e−6	−2.73e−6
k_{R3}	−4.65e−6	**−2.11e−2**	**−9.92e−1**	**−2.11e−2**	−4.65e−6	−8.37e−6
k_{R4}	−2.67e−8	−2.38e−4	−2.67e−8	**−9.65e−1**	−2.67e−8	−2.67e−8
k_{R5}	−2.33e−5	−2.33e−5	−2.33e−5	−2.33e−5	**−7.41e−1**	−2.33e−5
k_{R6}	−5.93e−5	−5.93e−5	−5.93e−5	−5.93e−5	−5.93e−5	**−9.73e−1**

Expressed in bold if the absolute value is greater than 0.01.

sediment. Advective flow of water affected the concentrations only in water and sediment. Particle−bound dry deposition to soil (D_{DS}), suspended solids settling to sediment (D_{DX}), and gaseous deposition to asphalt (D_{VAs}) and vegetation (D_{GD}) were significant input processes to those compartments. Degradation processes for soil (D_{R3}), sediment (D_{R4}), asphalt (D_{R5}), and vegetation (D_{R6}) were important removal processes for the corresponding compartments.

Sensitivity indices for intermedia D values are consistent with mass−flow rates in Fig. 2. Although the values in Table 9 do not have physical meaning because of the inter−dependency among D−values, they assist in screening the influencing processes of various environmental media. With the emission made into air, concentrations in other media, excluding air, are controlled primarily by atmospheric deposition. Atmospheric advection is the most important removal process for the whole system. Whereas advection is a major removal process in air

Table 12. Sensitivity indices for environmental parameters

Parameters	Sensitivity indices					
	Air	Water	Soil	Sediment	Asphalt pav.	Vegetation
f_{As}	-2.42e-5	-2.42e-5	-2.42e-5	-2.42e-5	**2.69e-1**	-2.42e-5
f_{OCs}	-2.36e-6	-5.25e-4	5.46e-4	-5.25e-4	-2.36e-6	-6.11e-6
f_{OCss}	-4.50e-6	**4.42e-1**	-4.50e-6	**9.59e-1**	-4.50e-6	-4.50e-6
f_{OCx}	-1.77e-10	-1.57e-6	-1.77e-10	5.39e-5	-1.77e-10	-1.77e-10
ρ_{As}	-2.42e-5	-2.42e-5	-2.42e-5	-2.42e-5	**2.69e-1**	-2.42e-5
ρ_d	4.38e-3	**-1.78e-1**	**-1.96e-1**	**-1.78e-1**	**8.02e-1**	**8.02e-1**
ρ_s	-2.36e-6	-5.25e-4	5.46e-4	-5.25e-4	-2.36e-6	-6.11e-6
ρ_{SS}	-4.50e-6	**4.42e-1**	-4.50e-6	**9.59e-1**	-4.50e-6	-4.50e-6
ρ_X	-1.77e-10	-1.57e-6	-1.77e-10	5.39e-5	-1.77e-10	-1.77e-10
ρ_P	-5.93e-5	-5.93e-5	-5.93e-5	-5.93e-5	-5.93e-5	**2.69e-2**
v_A	-4.51e-6	-3.79e-7	1.90e-4	-3.79e-7	-4.51e-6	-4.51e-6
v_W	-1.02e-6	-8.59e-8	4.30e-5	-8.59e-8	-1.02e-6	-1.02e-6
v_{SS}	-5.20e-5	**1.97e-2**	-5.20e-4	**-4.62e-1**	-5.20e-5	-5.20e-5
v_X	-5.89e-9	-5.24e-5	-5.89e-9	1.80e-3	-5.89e-9	-5.89e-9
Y_3	2.50e-6	2.11e-7	-1.05e-4	2.11e-7	2.50e-6	2.50e-6
Y_4	3.93e-9	3.50e-5	3.93e-9	-1.20e-3	3.93e-9	3.93e-9
Y_5	8.58e-7	8.58e-7	8.58e-7	8.58e-7	-9.55e-3	8.58e-7
G_{A1}	**-9.64e-1**	**-9.64e-1**	**-9.64e-1**	**-9.64e-1**	**-9.64e-1**	**-9.64e-1**
G_{A2}	-1.05e-4	**-9.35e-1**	-1.05e-4	**-9.35e-1**	-1.05e-4	-1.05e-4
b	-3.83e-4	-3.83e-4	-3.83e-4	-3.83e-4	-3.83e-4	**1.74e-1**
LA	-2.14e-3	-2.14e-3	-2.14e-3	-2.14e-3	-2.14e-3	**9.71e-1**
L_P	-5.93e-5	-5.93e-5	-5.93e-5	-5.93e-5	-5.93e-5	**2.69e-2**
W_P	-8.23e-10	-8.23e-10	-8.23e-10	-8.23e-10	-8.23e-10	3.74e-7
Qt	2.27e-10	-7.53e-9	-3.65e-7	-7.53e-9	2.27e-10	3.75e-6
f_{OAs}	-2.42e-5	-2.42e-5	-2.42e-5	-2.42e-5	**2.69e-1**	-2.42e-5
de	-6.09e-3	**6.89e-1**	-6.09e-3	**6.89e-1**	-6.09e-3	-6.09e-3
T	**1.64e-1**	**-6.64e+0**	**-7.34e+0**	**-6.64e+0**	**3.04e+1**	**3.01e+1**
TSP	-4.38e-3	**1.78e-1**	**1.96e-1**	**1.78e-1**	**-8.02e-1**	**-8.02e-1**
Q	**-1.20e-2**	**7.44e-1**	**2.19e-1**	**7.44e-1**	**-1.20e-2**	**-1.20e-2**

Expressed in bold if the absolute value is greater than 0.01.

and water, degradation is a major removal process in other compartments.

Because assumed values were used in this study, sensitivity analysis was performed on transfer coefficients. From Table 10, dry deposition velocity (U_P) and rain rate (U_R) are the most two influencing coefficients. Sediment deposition rate (U_{DX}), air-side mass transfer coefficient over asphalt pavement (k_{AsA}), and conductance for vegetation (g) are also important because they control major input D-values for sediment (D_{DX}), asphalt pavement (D_{VAs}), and vegetation (D_{GD}), respectively. Further elaboration may be needed on the transfer coefficients to improve the predictability of the model. For example, temporal variation of wet deposition may significantly alter the multimedia fate of 2, 3, 7, 8-TCDD. In rainy season, rain rate (U_R) is much greater than the annual average used in this model. About 70% of annual rainfall is concentrated in summer (Korea Meterological Administration, 1992-1997). Therefore, a simple use of the average value might introduce significant errors.

Sensitivity indices for physico-chemical properties are listed in Table 11. Modified Antoine equation constants, Henry's law constants, and octanol-water partition coefficient exhibit high sensitivity indices

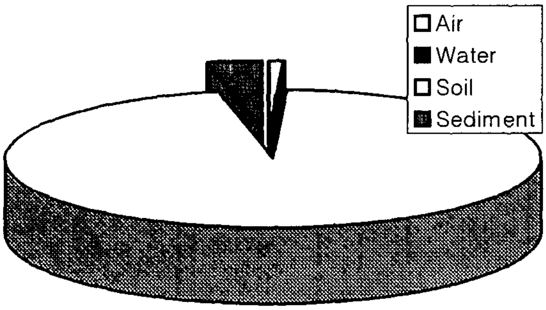

Fig. 3. Total mass distribution of 2, 3, 7, 8-TCDD among environmental media.

for almost all compartments. Sensitivity indices for degradation rate constants for soil (k_{R3}), sediment (k_{R4}), asphalt (k_{R5}), and vegetation (k_{R6}) show high values for the corresponding compartments. Although modified Antoine equation constants (A and B) are the most influencing parameters, the uncertainty associated with the values is small. The reported values for Henry's law constant (H) and octanol-water partition coefficient (K_{OW}) vary by two to three orders of magnitude for the same substance. Henry's law constant and octanol-water partition coefficient are the two most important properties because they determine Z-values. Degradation constants in the solid media strongly affect the concentration. However, their effect remains within the particular medium except in the sediment.

Sensitivity indices for all environmental parameters used in the model are listed in Table 12. Atmospheric advection rate (G_{A1}) has high sensitivity indices for all compartments because it determines atmospheric advection D-value. Organic carbon fraction (f_{OCi}), particle density (ρ_i), and volume fractions (TSP and v_{SS}) show high values as they determine the Z-values. Drainage efficiency (de) is also significant for water and sediment. Atmospheric parameters, such as temperature (T), total suspended particulates (TSP), and scavenging ratio (Q) are of higher sensitivity for almost all compartments. Concentration in asphalt pavement and vegetation is highly dependent on temperature and TSP, since they affect on the particle-air partition coefficient. Because partitioning fraction between air and particle can be changed with the temperature (Chrostowski and Foster, 1996), a careful consideration is needed to describe the fate of TCDD for those compartments. Unsteady state model considering seasonal variation in the environmental parameters may properly reflect seasonal environmental characteristics in the model output.

CONCLUSION

A sensitivity analysis technique, developed for a level-III multimedia environmental model, was applied to a case study for 2, 3, 7, 8-TCDD in Seoul metropolitan area. Important processes were efficiently screened by using the sensitivity analysis technique. Convective flow rate in air and water and deposition processes from air to other compartments are determining processes for the multimedia system. Furthermore, the sensitivities were estimated by one-time simulation for the parameters in the description of the important processes. Among the transfer coefficients, dry deposition velocity and rain rate are the two most influencing ones. Other sensitive parameters include Henry's law constant, octanol-water partition coefficient, and parameters related to the deposition processes such as TSP and scavenging ratio. It is strongly suggested that this technique be used to improve and refine similar models by efficiently identifying important processes and parameters.

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