THE APPLICABILITY OF THE ENVIRONMENTAL FATE ESTIMATES OF CURRENT-USE-PESTICDES USING A MULTIMEDIA MODEL BASED ON POLY-PARAMETER LINEAR ENERGY RELATIONSHIPS

Kobara Y[1], Nishimori M[2], Wei Y. G[3], Ishihara S[1], Yokoyama A[1], Horio T[1]

[1]Organochemicals Division, National Institute for Agro-Environmental Sciences, Tsukuba, Ibaraki, 305-8604, Japan; [2]Division of Agro-Meteorology, National Institute for Agro-Environmental Sciences, Tsukuba, Ibaraki, 305-8604, Japan; [3]River Basin Research Center, Gifu University, Gifu, 501-1193, Japan

Introduction

Persistent organic compounds (POPs) have been detected in remote areas such as polar region, due to long-range atmospheric transport (LRAT) from source regions to more remote locations. Furthermore, semivolatile organic compounds (SOCs) of many kinds such as current-use-pesticides (CUPs) have been detected in measurable quantities in water, sediments and biota in remote regions where they were neither used nor produced[1]. Many of these CUPs are known or suspected toxicants to humans and wildlife. Therefore, there is great interest in understanding, modeling and predicting their environmental fate and transport. In the near future, actions for part of CUPs other than current POPs may be necessary. In the view of the precautionary principles, tools to decide priority-setting of CUPs researches are needed according to criteria of their inherent properties, such as their distribution tendencies, potential for long-range transport (LTRP) and overall environmental persistence (Pov). We are developing the global-scale multimedia model (NIAES-MMM-global) that is able to characterize LTRP and Pov of CUPs emitted from Japan and the whole Asian region.

Conventional multimedia models based on the fugacity approach are generally applicable to non-polar organic chemicals, and inapplicable to CUPs since most CUPs have some polarities. Reliable estimates of environmental phase partitioning are essential for accurate predictions of the environmental fate of CUPs, but these multimedia models are not yet specified in detailed, because single-parameter linear free energy relationships (SP-LEFRs) is generally used to quantify equilibrium phase partitioning. The applicability of such SP-LFERs is limited because no single parameter is able to describe appropriately all the molecular interactions that contribute to environmental phase distribution processes. Ranges for several environmental partitioning equilibria are identified, where such errors can result in significantly different fate predictions for individual bulk model compartments. It is possible to reduce such errors and uncertainties by implementing polyparametric LFERs (PP-LFERs) approaches in multimedia fate models. Breivik *et al.* proposed how to expand the applicability of multimedia models towards polar organic chemicals by expressing environmental phase partitioning with the help of PP-LFERs.[2,3]

We tried to evaluate the environmental fate of polar organic compounds such as CUPs with the use of PP-LEFRs. PP-LFERs were incorporated into a Level III fugacity multimedia model that can be used for detailed investigation of a particular fate process using a generic environmental scnnario. The model calculates Pov, concentrations and intermedia fluxes of CUPs between air, water, soil and sediments at steady-state. A comparison of modified and unmodified models for a set of CUPs shows that the approach chosen to simulate environmental phase partitioning can have a large impact on model results, including LTRP, Pov, and concentrations in various media. The key objectives of this paper are (a) to present a modified multimedia fate modeling approach that may be utilized to predict CUPs behavior in the environment, and (b) to present illustrative modeling results for selected CUPs exemplified.

Materials and Methods

Model description

In this study we used a modified version of the Level III model. The level III model is a fugacity-based non-equilibrium, steady-state multimedia mass balance model and includes for bulk environmental compartments; air, water, soil and sediment[4], and includes expression for inter- and intermedia transport by diffusion and advection as well as degradation in all environmental media. The partitioning properties of chemicals are characterized by five linear free energy relationships (PP-LEFRs), rather than SP-LFERs based on vapor pressure, water solubility, and octanol-water partition coefficient.[2,3] Solvation parameter models are commonly expressed in Fig.1. SP refers to the phase partition property of interest.

$$\log SP = c + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + vV_\chi \qquad \text{(eq. 1)}$$

SP: Solvation Parameter i.e. the phase partition properties of interest

The solute descriptor

R_2: excess molar refraction, ($cm^3/10$)

π_2^H: dipolarity / palarisability

$\sum\alpha_{2i}^H$, $\sum\beta_{2i}^O$: Abraham's hydrogen bond parameters relating to electron acceptor and donor parameters, respectively

V_χ: McGowan's characteristic volume, (cm^3/mol)

The media system constants

c, r, s, a, b, v

Fig. 1 Linear solvation energy relationships (PP-LFERs) for environmentally relevant phase equilibria by Abraham[6]

PP-LFERs for various environmentally relevant, dimensionless partition coefficients are listed in Fig. 2. The water-air partition coefficient logK_{WA}, the octanol-water coefficient logK_{OW} and the organic carbon (OC)-water partition coefficient log$K_{OC,W}$ are based on McGown's chracteristic volume (V_X).[2,3]

$$\log K_{WA} = -0.99 + 0.58R_2 + 2.55\pi_2^H + 3.81\sum\alpha_2^H + 4.84\sum\beta_2^H - 0.87V_\chi \qquad \text{(eq. 2)}$$

$$\log K_{OW} = 0.09 + 0.56R_2 - 1.05\pi_2^H + 0.03\sum\alpha_2^H - 3.46\sum\beta_2^H + 3.81V_\chi \qquad \text{(eq. 3)}$$

$$\log K_{OC,W} = 0.21 + 0.74R_2 - 0.31\sum\alpha_2^H - 2.27\sum\beta_2^H + 2.09V_\chi \qquad \text{(eq. 4)}$$

Fig. 2 The water-air partition coefficient logK_{WA}, the octanol-water coefficient logK_{OW} and the organic carbon-water partition coefficient log$K_{OC,W}$ based on McGown's chracteristic volume (V_X)

Model input data

The model was parameterized to reflect the typical environmental conditions of Japan. An evaluation area is 10,000 km², and environmental properties and dimensions that were used in the model calculations are listed in Table 1. Selected chemicals are atrazine and diuron as CUPs, and included benzo[α]pyrene, hexachlorobenzene and aniline as reference chemicals. Physicochemical properties, half-lives and solute descriptors of individual chemicals are presented in Table 2. Data on half-lives in individual environmental media were estimated using the EPWIN software. For the purpose of direct comparability at this PP-LFERs approach, we applied a similar emission rate and mode of release for all selected chemicals. Emission rate to the atmosphere is 10,000 kg/year and there is no inflow of these chemicals from outside the model region.

Results and Discussion

Unlike the SP-LFER based approach to phase partitioning, the PP-LFER based approach facilitates mechanistic insights into the various interactions that influence the environmental distribution of CUPs. The various

Table 1 Environmental input data

Envirtonmental dimensions and properties

	Air	Water	Soil	Sediment
Area (m^3)	1.00E+10	1.00E+09	9.00E+09	1.00E+09
Depth (m)	1.50E+03	5.00E+01	1.00E-01	5.00E-02
Fraction organic carbon (g g^{-1})		2.00E-01	2.00E-02	4.00E-02
Density (Kg m^{-3})	1.19	1.00E+03		
		2.12E+03	2.37E+03	2.34E+03
Advctive flow (m^3 h^{-1})	2.42E+12	2.19E+08		
Temperature (°C)	25	25	25	25

Volume fractions and scavenging ratio (-)			
Aerosols in air	5.00E-12	Water in sediment	8.60E-01
Air in soil	2.00E-01	Particles in water	2.00E-06
Water in soil	3.00E-01	Scavenging ratio	6.80E+04

Mass transfer coefficients (m h^{-1})			
Air-water diffusion (air-side mtc)	5.00E+00	Sediment-water diffusion mtc	1.00E-04
Air-water diffusion (water-side mtc)	5.00E-02	Sediment deposition raet	4.60E-07
Soil-air diffusion (boundary-layer mtc)	5.00E+00	Sediment re-suspension rate	1.40E-07
Soil-air diffusion (air-phase mtc)	2.00E-02	Sediment burial rate	3.40E-07
Soil air diffusion (water-phase mtc)	1.00E-05	Soil water runoff	7.00E-05
Dry deposition velocity	1.03E+00	Soil solids runoff	4.00E-10
Rain rate (m^3 rain /m^2 area/h)	1.94E-04	Leaching to ground water	4.00E-06
Transfer rate to stratosphere	0.00E+00		

Properties of atmospheric particles and phase densities			
Volume fraction OC particles (-)	1.00E-01	Density of mineral matter (Kg m^{-3})	2.40E+03
Density of octanol (Kg m^{-3})	8.20E+02	Density of organic matter (Kg m^{-3})	1.00E+03

Table 2 Molecular weight (g/mol), pKa, solute descriptors and environmental half-lives of

Chemical				Descripters						Half lives (day)			
	CAS RN	MW	pKa	R_2	π_2^H	$\sum\alpha_2^H$	$\sum\beta_2^H$	$\sum\beta_2^O$	V_χ	Air	Water	Soil	Sediment
Atrazine	1912-24-9	215.7	1.70	1.51	1.24	0.33	0.94	0.94	1.62	0.39	60	120	542
Diuron	330-54-1	233.1		1.28	1.60	0.57	0.70	0.70	1.60	0.98	38	75	338
Benzo[a]pyrene	50-32-8	252.3	-	3.63	1.98		0.44	0.44	1.954	0.21	60	120	542
Hexachlorobenzene	118-74-1	284.8	-	1.49	0.99		0.00	0.00	1.451	39.63	180	360	1621
Aniline	62-53-3	93.1	4.61	0.96	0.94	0.26		0.50	0.816	0.10	15	30	135

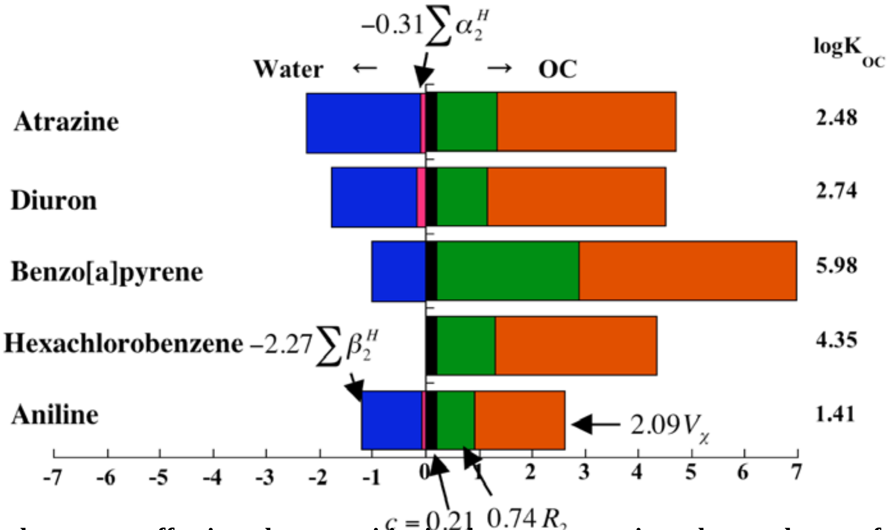

Fig. 4 Product terms affecting phase partitioning between organic carbon and water for selected chemicals

Table 3 Comparison with $\log K_{OC}$ of selected chemicals by a conventional method and pp-LFERs

Chemical	**EPIWIN**		**SP-LFERs**	**PP-LFERs**	
	$\log K_{OW}$	**$\log K_{OC}$**	**$\log K_{OC}=0.41\log K_{OW}$**	**$\log K_{OC}$**	**$\log K_{AW}$**
Atrazine	**2.82**	**2.36**	**1.16**	**2.48**	**7.44**
Diuron	**2.67**	**2.13**	**1.09**	**2.74**	**7.99**
Benzo[a]pyrene	**5.52**	**5.36**	**2.26**	**5.98**	**6.58**
Hexachlorobenzene	**5.86**	**3.53**	**2.40**	**4.35**	**1.13**
Aniline	**1.08**	**1.65**	**0.44**	**1.41**	**2.24**

Table 4 Selected model results, portioning to each medium (%)

Chemical	**SP-LFERs**				**PP-LFERs**			
	Air	**Water**	**Soil**	**Sediment**	**Air**	**Water**	**Soil**	**Sediment**
Atrazine	**0.01**	**43.80**	**56.20**	**0.04**	**0.00**	**5.77**	**93.94**	**0.29**
Diuron	**0.01**	**42.90**	**57.10**	**0.04**	**0.00**	**5.65**	**93.69**	**0.66**
Benzo[a]pyrene	**0.06**	**3.45**	**95.00**	**1.46**	**0.02**	**0.16**	**37.32**	**62.50**
Hexachlorobenzene	**2.50**	**39.00**	**56.40**	**2.13**	**0.08**	**0.07**	**98.54**	**1.31**
Aniline	**0.44**	**48.40**	**51.10**	**0.04**	**0.64**	**36.82**	**62.47**	**0.08**

contribution of a specific intermolecular interaction are shown for individual chemicals in Fig. 1. From this figure, it becomes clear that polar organic chemicals such as atrazine, diuron and aniline have predominant interaction process that leads to affinity by the hydrogen-bond basicity for water phase. The organic carbon-water partition coefficients ($\log K_{OC}$) by PP-LFERs are comparatively larger than values by SP-LFERs in Table 3. Experimental $\log K_{OC}$ values have relatively large uncertainties. Potentially important $\log K_{OC}$ are better estimated with PP-LFERs than by SP-LFERs based $\log K_{OW}$.

A comparison of modified and unmodified models for selected chemicals shows that the approach chosen to simulate environmental phase partitioning can have a large impact on model results because the model results are highly sensitive to the equilibrium partitioning between organic carbon and water, the degradation rate in water. The use of PP-LFERs is generally thought to be superior to the use of SP-LFERs. In Table 4, the model results presented here show that atrazine, diuron and hexachlorobenzene tend to stay predominantly in soil medium by PP-LFERs approach. On another front, these chemicals partitioning in water medium tends to increase by SP-LFERs. Benzo[α]pyrene tends to stay in sediment medium by PP-LFERs, but by SP-LFERs predominantly in soil medium.

The PP-LEFRs based approach indicates that the greatest mobility in aqueous phases may be pesticides that combine a small molecular size with strong H-acceptor properties. Environmental partitioning coefficients predicted by SP-LFERs may thus have errors of up to an order of magnitude. These results presented here illustrate that the PP-LFER based Level III model may be a useful tool to obtain reliable predictions of CUPs' environmental fate, and can be used for detailed investigation of a particular fate process in various environmental scenario.

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