Dynamic toxicity modelling based on the USEtox matrix framework

Peter Fantke[1], Olivier Jolliet[2], Cédric Wannaz[2]

[1] Quantitative Sustainability Assessment, Technical University of Denmark, Kgs. Lyngby, Denmark
[2]University of Michigan, Department of Environmental Health Sciences, Ann Arbor (MI), USA

E-mail contact: peter@substitute.dk

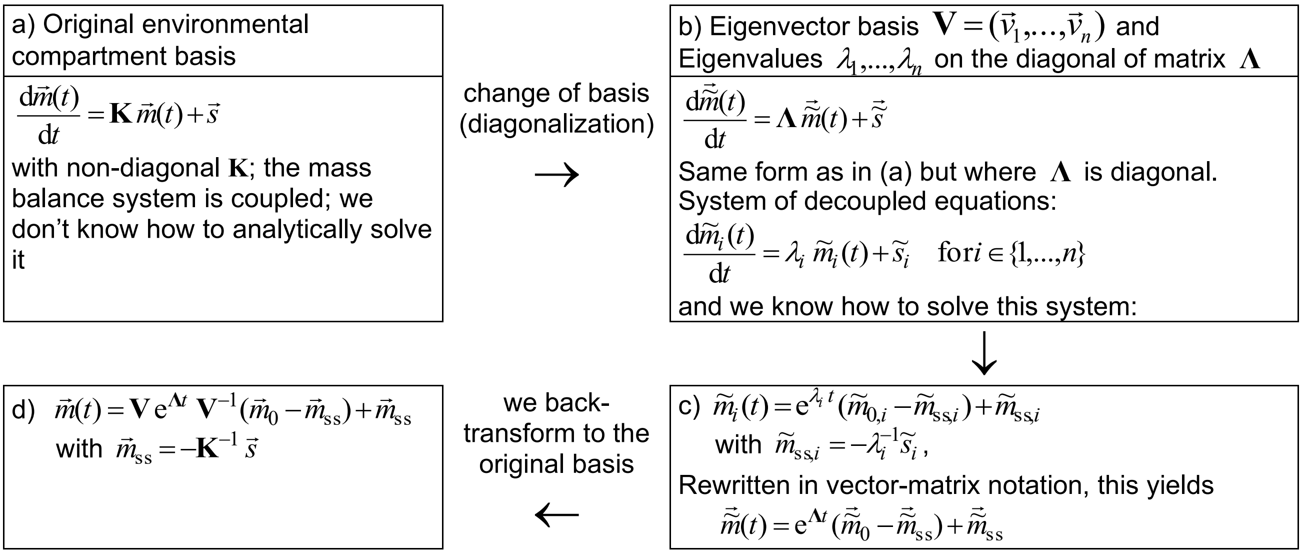
---

1. Introduction

It is recommended to report characterization factors (CFs) in life cycle assessment for different time horizons, e.g. for infinity (steady-state) and after 100 years [1]. While CFs in several impact categories are reported for both time horizons, the UNEP/SETAC human and ecosystem toxicity model USEtox 1.01 only allows for steady-state calculations. To comply with the time perspective of other impact categories and to allow for additionally calculating CFs after different times whenever necessary, there is a need to develop a tool for modeling the dynamics of the system that complies with the matrix framework underlying USEtox. This paper addresses this lack of flexibility and aim to a) develop a dynamic multimedia model based on and fully compatible with the USEtox steady-state framework, b) analyze and interpret the main parameters affecting chemical fate and exposure dynamics, and c) evaluate whether for 3000+ USEtox 1.01 chemicals a 100 years time horizon will yield considerably different results than the steady-state default assumption.

2. Materials and methods

Principle: USEtox characterizes chemical fate by a set of differential equations (one mass balance equation for each compartment), where transfer between and degradation within compartments are expressed by a square matrix $\mathbf{K}$ of rate constants. USEtox solves the steady-state system $(\mathrm{d}m(t)/\mathrm{d}t = 0)$ by inverting $\mathbf{K}$ to yield steady-state fate factors, $\mathbf{FF}$ [2,3]. To solve the dynamics of the system, we apply a classical approach based on Eigenvectors and Eigenvalues of $\mathbf{K}$ (Figure 1): We transform the initial system of n coupled differential equations (1a) into a system of n independent differential equations through an appropriate change of basis (basis of Eigenvectors, 1b). While the original system is difficult to handle, the transformed system, parameterized by a diagonal matrix $\mathbf{\Lambda}$ (Eigenvalues of $\mathbf{K}$ on its diagonal), can be solved easily (1c), as each equation describes the dynamics of a single, independent "abstract" compartment. The solution of the transformed system is then back-transformed into the original basis, yielding an expression for computing the mass at time t based on the initial mass/condition and the mass at steady state (1d).



a) Original environmental compartment basis

$$\frac{\mathrm{d}\vec{m}(t)}{\mathrm{d}t} = \mathbf{K}\,\vec{m}(t) + \vec{s}$$

with non-diagonal $\mathbf{K}$; the mass balance system is coupled; we don't know how to analytically solve it

change of basis (diagonalization)

$\rightarrow$

b) Eigenvector basis $\mathbf{V} = (\vec{v}_1,\ldots,\vec{v}_n)$ and Eigenvalues $\lambda_1,\ldots,\lambda_n$ on the diagonal of matrix $\mathbf{\Lambda}$

$$\frac{\mathrm{d}\vec{\tilde{m}}(t)}{\mathrm{d}t} = \mathbf{\Lambda}\,\vec{\tilde{m}}(t) + \vec{\tilde{s}}$$

Same form as in (a) but where $\mathbf{\Lambda}$ is diagonal.
System of decoupled equations:

$$\frac{\mathrm{d}\tilde{m}_i(t)}{\mathrm{d}t} = \lambda_i\,\tilde{m}_i(t) + \tilde{s}_i \quad \text{for}\, i \in \{1,\ldots,n\}$$

and we know how to solve this system:

$\downarrow$

c) $\tilde{m}_i(t) = \mathrm{e}^{\lambda_i t}(\tilde{m}_{0,i} - \tilde{m}_{\mathrm{ss},i}) + \tilde{m}_{\mathrm{ss},i}$
with $\tilde{m}_{\mathrm{ss},i} = -\lambda_i^{-1}\tilde{s}_i$,
Rewritten in vector-matrix notation, this yields

$$\vec{\tilde{m}}(t) = \mathrm{e}^{\mathbf{\Lambda}t}(\vec{\tilde{m}}_0 - \vec{\tilde{m}}_{\mathrm{ss}}) + \vec{\tilde{m}}_{\mathrm{ss}}$$

we back-transform to the original basis

$\leftarrow$

d) $\vec{m}(t) = \mathbf{V}\,\mathrm{e}^{\mathbf{\Lambda}t}\,\mathbf{V}^{-1}(\vec{m}_0 - \vec{m}_{\mathrm{ss}}) + \vec{m}_{\mathrm{ss}}$
with $\vec{m}_{\mathrm{ss}} = -\mathbf{K}^{-1}\,\vec{s}$

Figure 1: Principle of the change of basis to diagonalize (decouple) and solve the set of mass balance equations for any time t

Implementation: The $\mathbf{K}$ matrix was read from USEtox 1.01 for 3000+ chemicals and imported into Matlab to calculate for each chemical Eigenvectors and Eigenvalues. The masses in the different compartments at various times were then calculated using the eq. in Figure 1d. The matrix of fate factors at time t, $\mathbf{FF}(t)$, is then calculated for a time horizon of $t = 100$years as $\mathbf{FF}_{100y} = \mathbf{V}(\mathrm{e}^{\mathbf{\Lambda}t} - \mathbf{I})\mathbf{\Lambda}^{-1}\mathbf{V}^{-1}$ with $\mathbf{I}$ as identity matrix.

3. Results and discussion

3.1. Dynamic solution: Evolution of chemical masses

Figure 2 contrasts the mass evolution in compartments for a continuous emission of 1 kg/day into indoor air, starting at $t=0$. Masses in all compartments saturate (reach steady-state) for the dioxin congener within 100 days, whereas for Pb the soil and deep ocean have not yet reached steady-state after even 100 years. The shortest kinetics is found for both compounds for indoor air, followed by urban air and continental air.

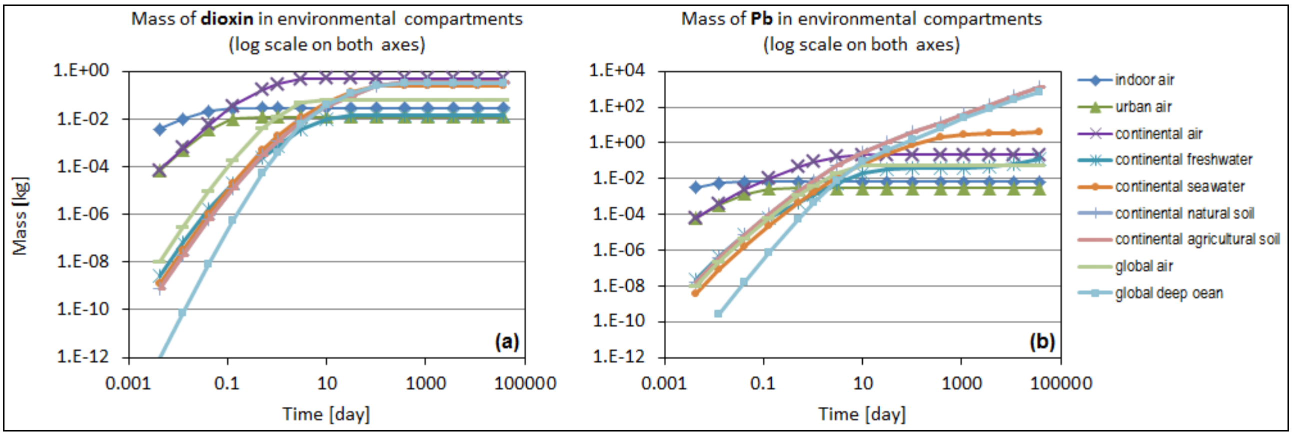


Figure 2: Short and long term dynamics for various USEtox environmental compartments (a) dibenzo-p-dioxin, (b) lead (Pb)

3.2. Model interpretation: Understanding the system dynamics

Interestingly, the inverse of the Eigenvalues are very close but not equal to the steady-state fate factors, which represent the chemical persistence in different compartments (Table 1: up to 221712 days ≈ 607 years for lead in soil).

Similarly, $\vec{v}_1$ for lead is very close to the first vector of the original basis. This suggests that the computation of the fate factors and the importance of intermedia transfers are intimately related to the Eigen decomposition.

Table 1: Fate factors after 100 years and at steady-state, inverse of eigenvalues and 1st eigenvectors for dioxin and Pb

Substance	Dibenzo-p-dioxin				lead (Pb)			
Factor / Comp.	FF_{100y} [day]	FF [day]	$-1/\lambda$ [day]	$\vec{v}_1$	FF_{100y} [day]	FF [day]	$-1/\lambda$ [day]	$\vec{v}_1$
indoor air	0.029	0.029	0.029	0.880	0.007	0.007	0.007	0.997
urban air	0.051	0.051	0.051	−0.472	0.052	0.052	0.052	−0.065
cont. air	1.10	1.10	1.08	0.041	1.90	1.90	1.90	−0.048
global air	1.16	1.16	1.15	<0.001	2.38	2.38	2.38	<0.001
cont. freshwater	7.14	7.14	7.14	<0.001	12.0	12.0	12.0	<0.001
cont. seawater	41.6	41.6	41.6	<0.001	386	436	347	<0.001
global ocean	50.6	50.6	50.6	<0.001	27751	63537	63625	<0.001
cont. nat. soil	98.5	98.5	98.5	<0.001	33675	221712	221712	<0.001
cont. agric. soil	98.5	98.5	98.5	<0.001	33675	221712	221712	<0.001

3.3. Comparison of fate factors after 100 years and at steady-state

The time horizon of 100 years has no influence on the fate factors and related intake fractions compared to the steady-state values, neither for the dioxin congener (Table 1, first set of columns), nor when calculated for the 3000+ organic compounds found in USEtox 1.01. The only difference appears for metals fate in deep ocean and soil, with a reduction of both fate factor in soil and related intake of agricultural produce after 100 years to 15% of the corresponding steady-state factors (i.e. FF_{100y} = 15% $\cdot$ FF). Depending on the considered metal, the 100 years fate factors in soil can be reduced to between 7% and 84% of their steady-state values.

4. Conclusions

The dynamic solution of environmental mass balance problems using matrix algebra enables to elegantly characterize the dynamics of fate and intake of organic and inorganic substances and has previously been shown for pesticides applied to crops [4]. Our results show that considering a 100 years time horizon is different from steady-state values only for metals, espcially via soil-mediated fate and exposure and confirms previous results obtained with USES-LCA. A 100 years time horizon for metals raises the question of consistency between the dynamics of characterization models and the dynamics of inventory releases (emissions), which can span several 1000 years for metals deposited in landfills. This has implications on the results of an assessment of chemical fate and exposure as a function of the considered time perspective.

5. References

[1] Udo de Haes et al., 2002. Life-Cycle Impact Assessment: Striving towards Best Practice. SETAC Press.
[2] Rosenbaum et al., 2007. A flexible matrix algebra framework for the multimedia multipathway modeling of emission to impacts. Environ Int 33: 624-634.
[3] Rosenbaum et al., 2008. USEtox – The UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in Life Cycle Impact Assessment. Int J LCA 13 : 532-546.
[4] Fantke et al., 2013. Dynamics of pesticide uptake into plants: From system functioning to parsimonious modeling. Environ Modell Softw 40: 316-324.