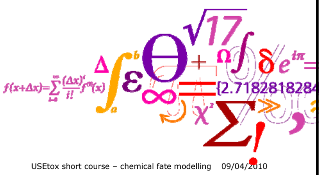
Chemical fate modelling

Overview of typical mass balance concepts and introduction to transport and degradation rate calculations as well as matrix solutions

Assistant professor
Morten Birkved
birk@man.dtu.dk



DTU Management Engineering
Department of Management Engineering

Learning objective and outline

Objectives:

- To understand what fate modelling is
- To understand the role of fate modelling in USEtox
- To understand how fate modelling is applied in USEtox

Outline

1. What is chemical fate
2. Chemical fate processes
3. What is chemical fate modelling
4. How is chemical fate modelling applied in USEtox
5. Exercise
6. Presentation of solution to exercise
7. Questions

What is chemical fate
A matter of (important) details?

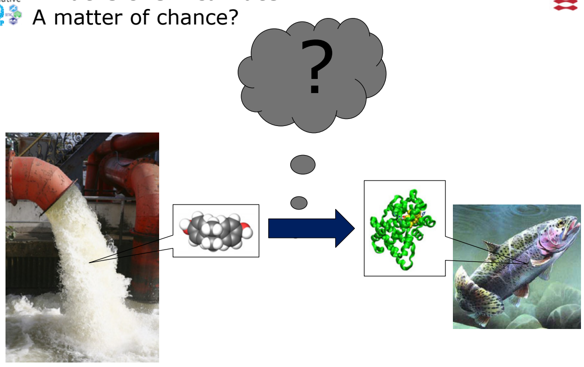
What is chemical fate modelling
Do we need fate and exposure models in LCA?

Fate and exposure models serves one purpose only in impact assessment of chemical emissions:

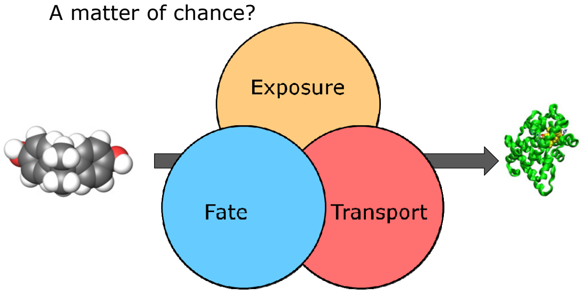
Prediction of chemical behavior in the environment

The prediction power of the chemical fate and exposure models facilitates the quantification of the marginal toxicological impacts occurring in LCIA caused by chemical emissions.

What is chemical fate
A matter of chance?



What is chemical fate
A matter of chance?



What is chemical fate
Severity of chemical emissions

a) What main fate properties determines the fate pattern of a chemical emission - i.e. which overall properties controls the fate of a chemical emission?

1. It's mobility (transport potential)
2. Is ability to avoid degradation (persistence)

b) What factors determines the severity/impact potential of a chemical emission – i.e. which factors controls the impact potential of a chemical emission?

1. It's toxicity (affinity for a specific receptor)
2. It's exposure pattern (availability to interact with a receptor)
3. It's fate pattern (ability to reach (i.e. mobility) and have time (i.e. persistence) to interact with a receptor)

What is chemical fate
Adressing chemical behaviour in the environment in LCA

Assessment resolution:
"Single compound" assessment (CAS number resolution)

Impact potential

IP = Q × CF

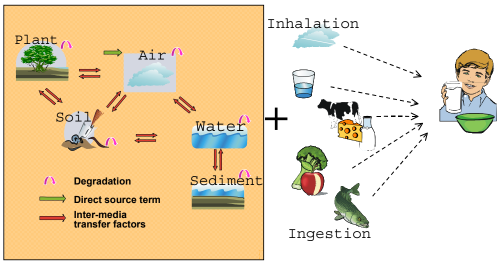
Assessment of ecotoxicological impacts :

CF = EF × FF × XF

Assessment of human toxicological impacts:

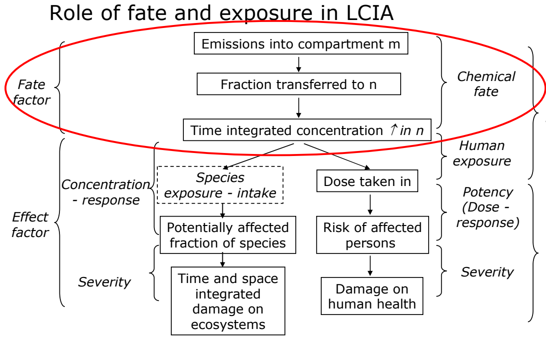
CF = EF × FF × XF = EF × IF

What is chemical fate
Role of fate models in LCA



Environmental distribution of chemical – resulting human exposure

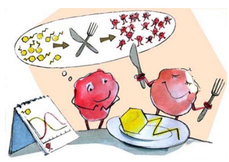
What is chemical fate
Role of fate and exposure in LCIA

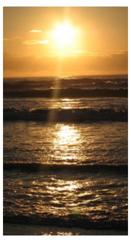


Chemical fate processes
Major grouping

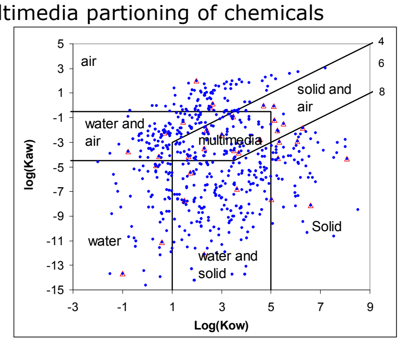
Biological processes
- Biodegradation/bio-transformation
- Biotransfer

Abiotical processes
- Degradation
- Sorption
- Advection
- Convection

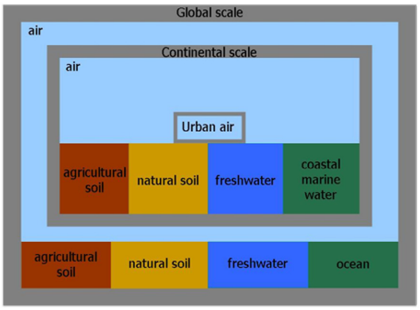




Chemical fate processes
Multimedia partioning of chemicals

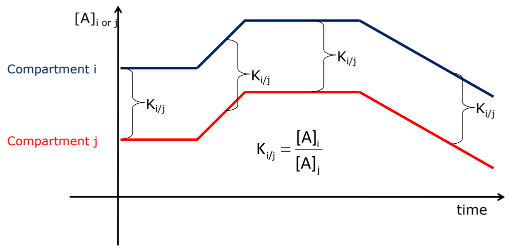


Chemical fate modelling
Nested models

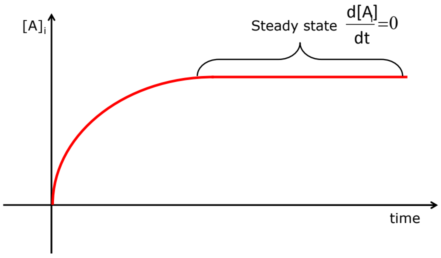


Huijbregts et al. 2010

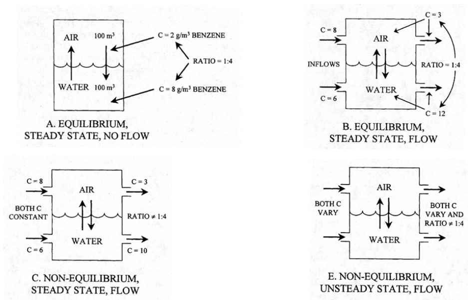
Chemical fate modelling
Modelling principles – model approaches



Chemical fate modelling
Modelling principles – model approaches



Chemical fate modelling
Modelling principles – model approaches

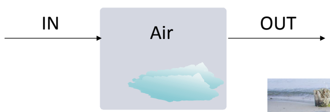


Mackay (2001)

Chemical fate modelling
Mass balance model

Lavoisier principle of mass conservation:

« In all operations of nature, matter cannot be created/destroyed, although it may be rearranged. This implies that for any chemical process in a closed system, the mass of the reactants must equal the mass of the products »



dM/dt = In - Out

Chemical fate modelling
Basic processes for environmental mass balance modeling

INPUTS
- Emission or Source, S_m [kg/hour]
- Intermedia transfer rate coefficient $k_{i,m}$ [$hour^{-1}$]
  - From other compartments
  - From outside the system

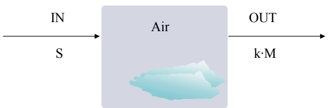
OUTPUTS
- Intermedia transfer rate coefficient $k_{m,i}$ [$hour^{-1}$]
  - To other compartments
  - Burial processes into deep sediments
  - Advection out of the system

TRANSFORMATION
- Degradation processes $k_{m,deg}$ [$hour^{-1}$]
  - biodegr., hydrolysis, photolyis, etc.

Chemical fate modelling

Equilibrium and/or Steady state: IN = OUT

dM/dt = 0



Emission rate: S [kg/day]

Mass in compartment: M [kg]

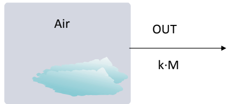
Removal rate coefficient: k [per day]

(fraction of mass eliminated per day)

S =

Chemical fate modelling

Rate Constant - Half-life Relationship



dM/dt = In - Out

dM/dt = -k · M

Per definition: $M(\tau_{½})/M(0)=0.5$

Removal rate coefficient: k [day^{-1}]

(fraction of mass eliminated per day)

Half-life: $\tau_{½}$ [day]

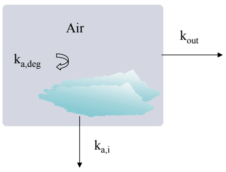
(days to eliminate half of mass)

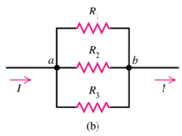
$\tau_{½} = \ln(2)/k$

Chemical fate modelling

Removal rate coefficients k

Like electric resistances





$$k_{a,tot} = k_{a,out} + \sum_i k_{a,i} + k_{a,deg}$$

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}$$

$$\frac{1}{\tau_{½,tot}} = \frac{1}{\tau_{½,1}} + \frac{1}{\tau_{½,2}} + \frac{1}{\tau_{½,3}}$$

Units = time

How is chemical fate modelling applied in USEtox

Matrix Algebra Solution Dynamic and steady state solution

Dynamic: $\dot{M}(t) \; {}_{-}\vec{k} \cdot \vec{M} + \vec{S}$

Fate factor matrix

Steady State: $\frac{dM_a}{dt} = 0 \Rightarrow \vec{M} = -\vec{k}^{-1} \cdot \vec{S}$

Mass vector (kg) | Rate coefficient matrix (1/h) | Source vector (kg/h)

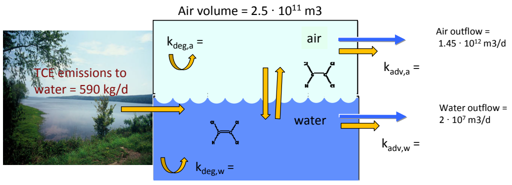
Air Water

Air, Water: $\begin{pmatrix} M_a \\ M_w \end{pmatrix} = -1 \times \begin{pmatrix} -k_{a,t} & k_{wa} \\ k_{aw} & -k_{w,tot} \end{pmatrix}^{-1} \cdot \begin{pmatrix} S_a \\ S_w \end{pmatrix}$

How is chemical fate modelling applied in USEtox

Exercise: Fate of TCE in a two-compart. Syst.

Trichloroethylene (TCE) is a colourless, somewhat toxic, volatile liquid belonging to the family of organic halogen compounds. It is a chemical widely used in industry as a solvent in dry cleaning, in degreasing of metal objects, and in extraction processes, such as removal of caffeine from coffee or of fats and waxes from cotton and wool



Air-to-water transfer factor, k_{aw} = 5.57 · 10^{-3} $days^{-1}$

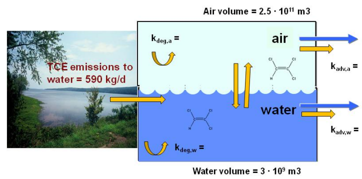
Water-to-air transfer factor, k_{wa} = 1.91 · 10^{-1} $days^{-1}$

Atmospheric degradation half-life = 15 days

Aquatic degradation half life = 150 days

How is chemical fate modelling applied in USEtox

Fate of TCE in a two-compart. syst.

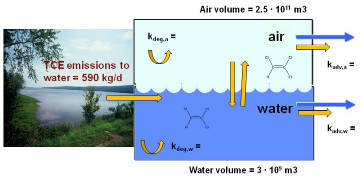


Q1) Determine the total rate coefficients in air and water?

Q2) Which is the dominant removal pathway in air and in water respectively?

How is chemical fate modelling applied in USEtox

Fate of TCE in a two-compart. syst.



Q3: Determine the Mass (or Concentration in air and water respectively)?

Solutions

How is chemical fate modelling applied in USEtox

Fate of TCE in a two-compartment system - Q1

Calculation of rate costants for advective loss

Volume	Advective flow	Rate constant for advective loss
Air		
Vair= 2,50E+11 m^3	Fair= 1,45E+12 m^3/d	Fair/Vair= 5,80 $days^{-1}$
Water		
Vwater= 3,00E+09 m^3	Fwater= 2,00E+07 m^3/d	Fwater/Vwater= 0,0067 $days^{-1}$

Conversions of half-lives to rate coefficients

Half-lives			Rate constants for degradation	
Atmospheric degradation half-life	$\tau_{½}$ (deg_A)=	15 days	$kdeg_A$=ln(2)/$\tau_{½}$ (degA)=	0,0462 $days^{-1}$
Aquatic degradation half-life	$\tau_{½}$ (deg_W)=	150 days	$kdeg_W$=ln(2)/$\tau_{½}$ (degW)=	0,00462 $days^{-1}$

How is chemical fate modelling applied in USEtox

Fate of TCE in a two-compartment system - Q1

Compartment			
Air		Water	
Loss process	Rate constant	Loss process	Rate constant
Advection	5,8000 $days^{-1}$	Advection	0,0067 $days^{-1}$
Degradation	0,0462 $days^{-1}$	Degradation	0,0046 $days^{-1}$
Inter-media exchange (air→water)	0,0056 $days^{-1}$	Inter-media exchange (water→air)	0,1910 $days^{-1}$
Total	**5,85 $days^{-1}$**	**Total**	**0,20 $days^{-1}$**

How is chemical fate modelling applied in USEtox

Fate of TCE in a two-compartment system – Q2

Compartment			
Air		Water	
Loss process	Rate constant	Loss process	Rate constant
Advection	5,8000 $days^{-1}$	Advection	0,0067 $days^{-1}$
Degradation	0,0462 $days^{-1}$	Degradation	0,0046 $days^{-1}$
Inter-media exchange (air→water)	0,0056 $days^{-1}$	Inter-media exchange (water→air)	0,1910 $days^{-1}$
Total	**5,85 $days^{-1}$**	**Total**	**0,20 $days^{-1}$**

Dominant removal process for air

Dominant removal process for water

How is chemical fate modelling applied in USEtox

Fate of TCE in a two-compartment system – Q3

Steady state mass

$$\vec{M} = -\bar{k}^{-1} \cdot \vec{S}$$

Step 1:

Calculate fate matrix $(-\bar{k}^{-1})$

$$-\bar{k}^{-1} = \begin{pmatrix} -0.17 & -0.16 \\ -0.01 & -5.01 \end{pmatrix}$$

Step 2:

Calculate product of and source vectors $(-\bar{k}^{-1} \cdot \vec{S})$

How is chemical fate modelling applied in USEtox
Fate of TCE in a two-compartment system – Q3 step 1

Compartment

Air: Loss process	Rate constant	Water: Loss process	Rate constant
Advection	5,8000 $days^{-1}$	Advection	0,0067 $days^{-1}$
Degradation	0,0462 $days^{-1}$	Degradation	0,0046 $days^{-1}$
Inter-media exchange (air→water)	0,0056 $days^{-1}$	Inter-media exchange (water→air)	0,1910 $days^{-1}$
Total	**5,85 $days^{-1}$**	**Total**	**0,20 $days^{-1}$**

$$\bar{k} = \begin{pmatrix} kair\_tot & kwater\_air \\ kair\_water & kwater\_tot \end{pmatrix}$$

$$\bar{k} = \begin{pmatrix} 5.85 & 0.19 \\ 0.01 & 0.20 \end{pmatrix}$$

How is chemical fate modelling applied in USEtox
Fate of TCE in a two-compartment system – Q3 step 1

Inversion of matrix

For a 2×2 matrix

$$A \equiv \begin{bmatrix} a & b \\ c & d \end{bmatrix},$$

the matrix inverse is

$$A^{-1} = \frac{1}{|A|}\begin{bmatrix} d & -b \\ -c & a \end{bmatrix} = \frac{1}{ad-bc}\begin{bmatrix} d & -b \\ -c & a \end{bmatrix}.$$

Source: *mathworld.wolfram.com*

How is chemical fate modelling applied in USEtox
Fate of TCE in a two-compartment system – Q3 step 1

$$\bar{k} = \begin{pmatrix} 5.85 & -0.19 \\ -0.01 & 0.2 \end{pmatrix}$$

$$\bar{k}^{-1} = \frac{1}{|\bar{k}|}\begin{pmatrix} 5.85 & -0.19 \\ -0.01 & 0.2 \end{pmatrix} = \frac{1}{5.85 \times 0.2 - 0.19 \times 0.01}\begin{pmatrix} 0.20 & 0.19 \\ 0.01 & 5.85 \end{pmatrix}$$

$$\bar{k}^{-1} = \frac{1}{1.17}\begin{pmatrix} 0.20 & 0.19 \\ 0.01 & 5.85 \end{pmatrix}$$

Fate factor matrix

$$-\bar{k}^{-1} = -1 \times \begin{pmatrix} 0.17 & 0.16 \\ 0.01 & 5.01 \end{pmatrix} = \begin{pmatrix} -0.17 & -0.16 \\ -0.01 & -5.01 \end{pmatrix}$$

How is chemical fate modelling applied in USEtox
Fate of TCE in a two-compartment system – Q3

Steady state mass

$$\vec{M} = -\bar{k}^{-1} \cdot \vec{S}$$

Step 1:

Calculate fate matrix $(-\bar{k}^{-1})$ $\quad -\bar{k}^{-1} = \begin{pmatrix} -0.17 & -0.16 \\ -0.01 & -5.01 \end{pmatrix}$

Step 2:

Calculate product of and source vectors $(-\bar{k}^{-1} \cdot \vec{S})$

How is chemical fate modelling applied in USEtox
Fate of TCE in a two-compartment system – Q3 step

Source matrix [kg/day]

$$\vec{M} = -\bar{k}^{-1} \cdot \vec{S} \qquad \vec{S} = \begin{pmatrix} 0 \\ 590 \end{pmatrix} \qquad -\bar{k}^{-1} = \begin{pmatrix} -0.17 & -0.16 \\ -0.01 & -5.01 \end{pmatrix}$$

	Fate matrix [days]			Source matrix [kg/day]			Mass matrix [kg]	
	Air	Water		Air	Water		Air	Water
Original scenario: Air	0.171	0.163	x	0	0	=	0	96.0
Water	0.009	5.008		0	590		0	2954.8