Project no.: 511254 (STREP)

SEDBARCAH

SEDiment BioBARriers for
Chlorinated Aliphatic Hydrocarbons
in ground water reaching surface water

CAH-Modeling & Batch Reactions (Part II)

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Short Lecture at the Meeting
Munich, June 2006

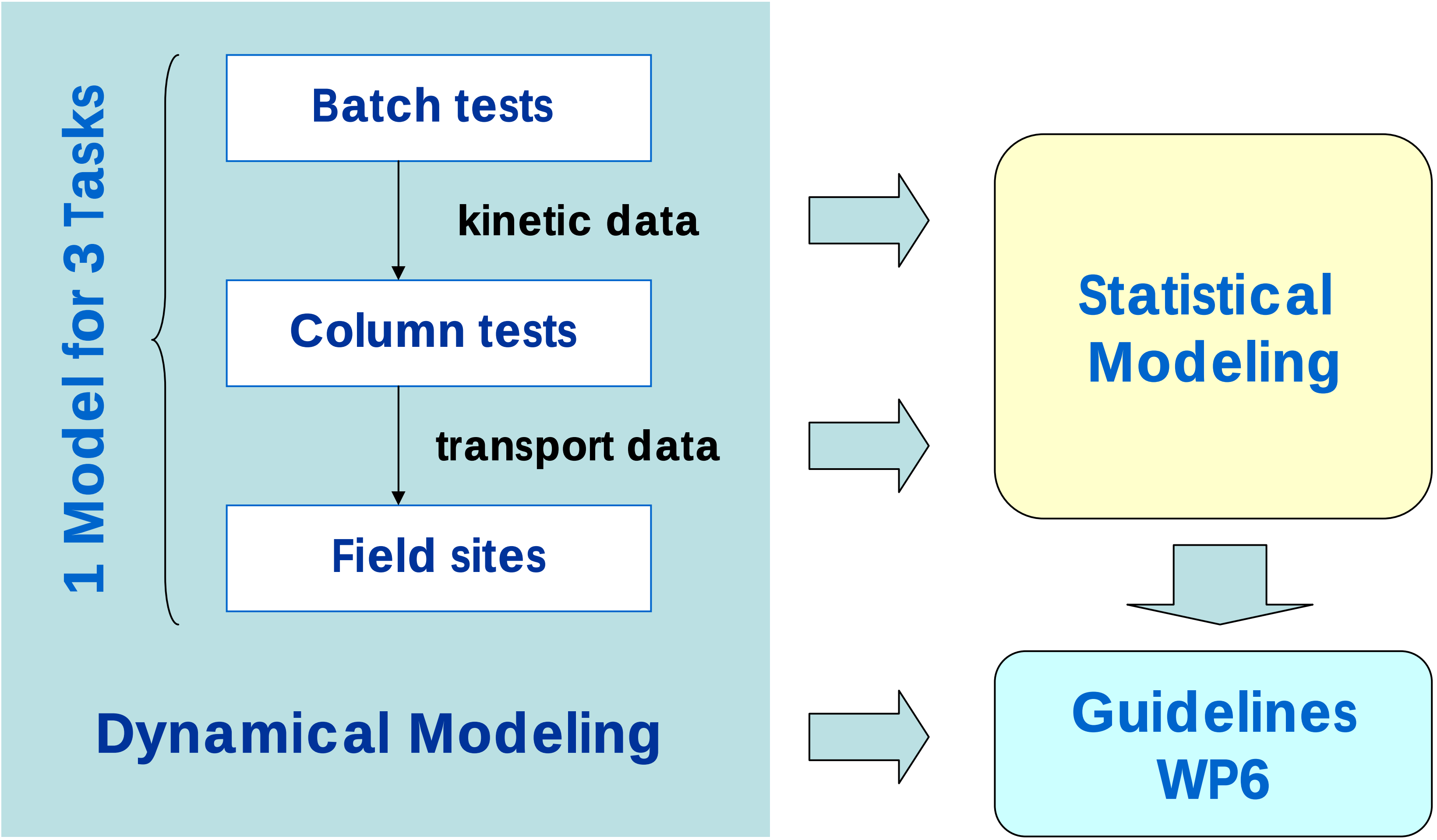
Start date of project: 01/01/2005 Duration: 2 years
Lead contractor for Work Package 5 (Modeling): UIT GmbH Dresden

CAH-Modeling

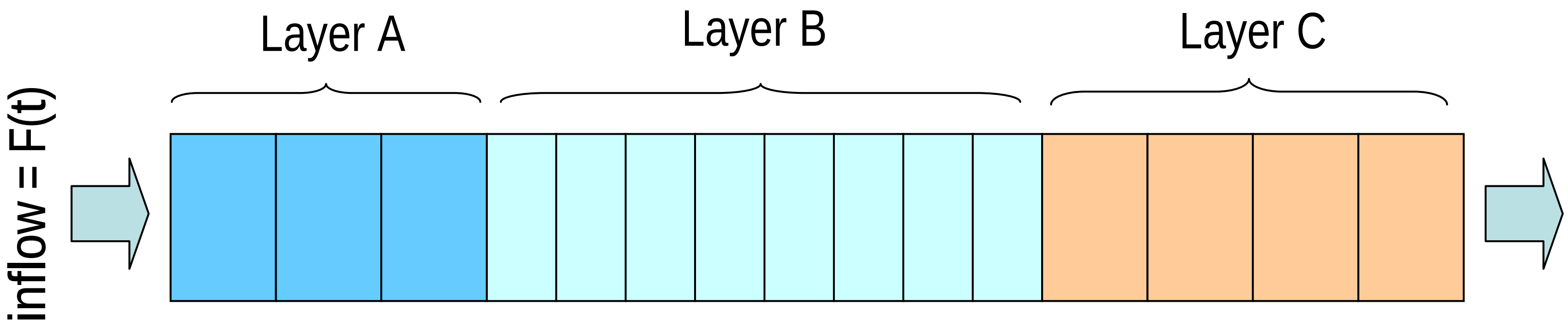
SEDBARCAH

1. Batch Reaction Model
2. Kinetic Data
3. Mass Balance
4. Model Capabilities
5. Basic Principles / Further Steps

Modeling in WP5

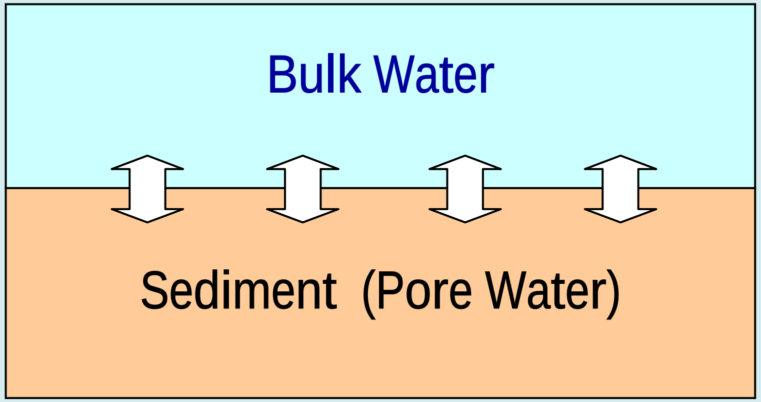


Two Options of the CAH-Model

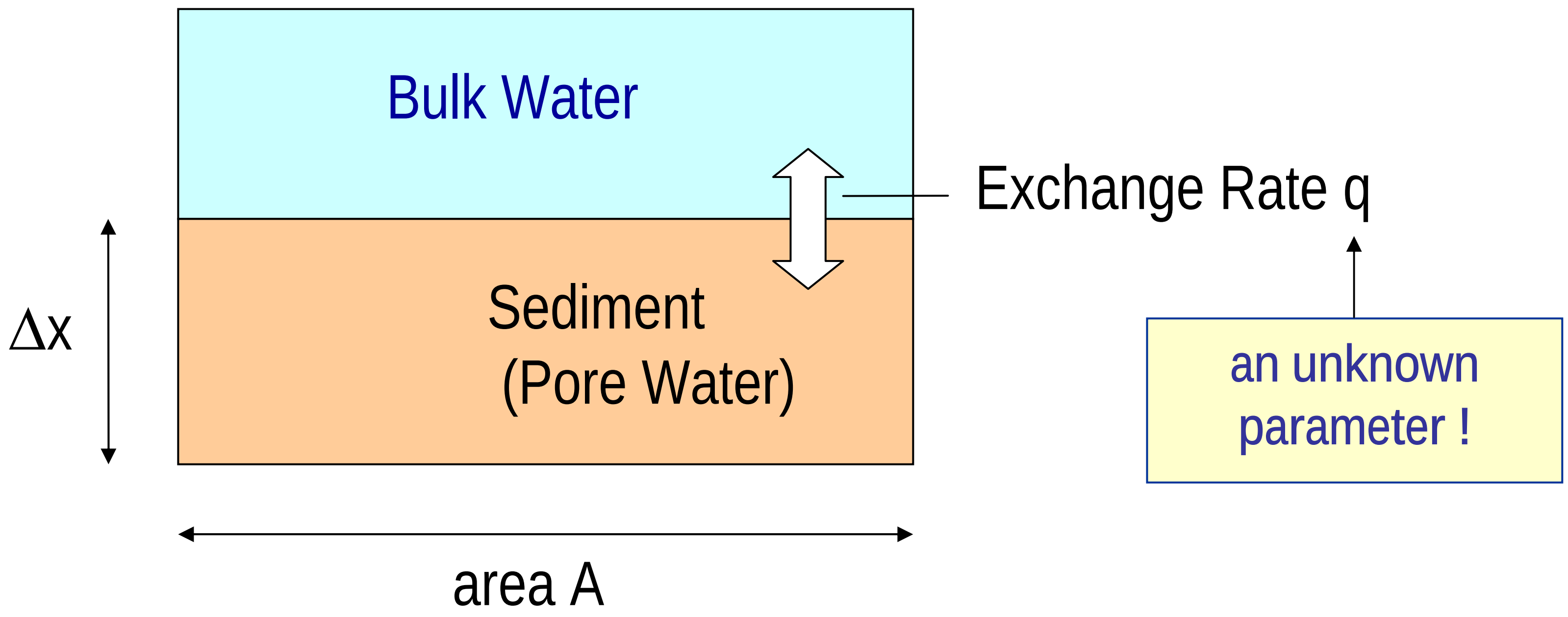


Reactive Transport

Batch Test
(Kinetics only)

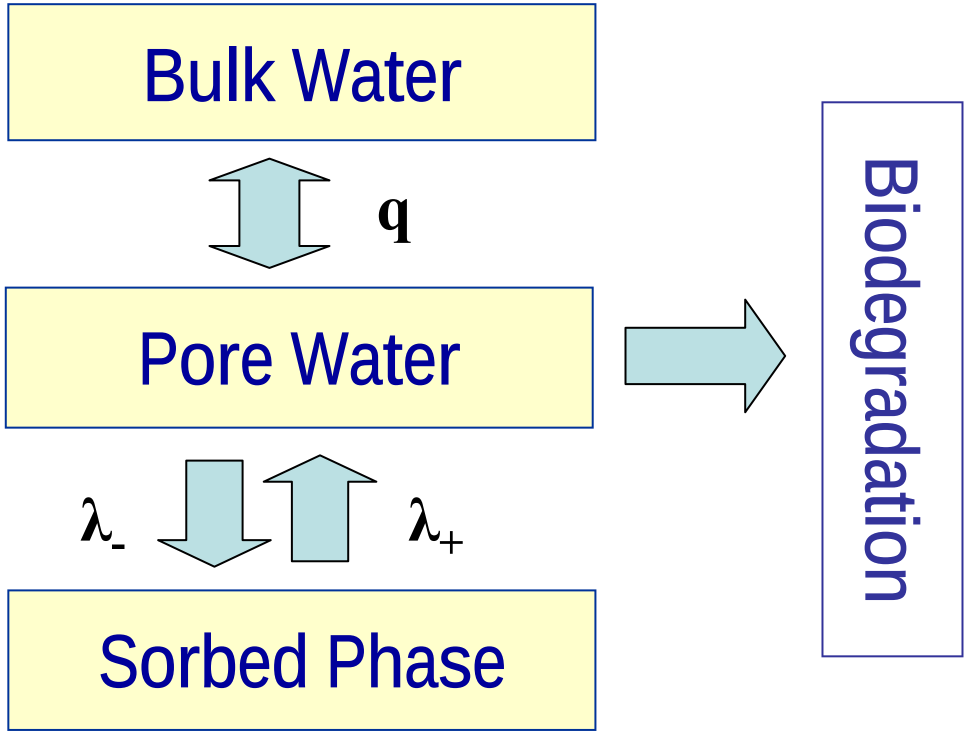


Batch Reactions – Set-up



Pore Water	$V_P = \varepsilon \cdot V_{sed} = \varepsilon \cdot A \Delta x$
Sediment	$m_{sed} = \rho_b \cdot V_{sed}$

Batch Reactions – 3 Phases



Batch Reactions – Mass Transfer

$$\frac{dm_i^W}{dt} = qV_P\,(c_i^P - c_i^W)$$

$$\frac{dm_i^P}{dt} = -qV_P\,(c_i^P - c_i^W) - \left\{\lambda_- m_i^P - \lambda_+ m_i^S\right\} + \left(\frac{dm_i^P}{dt}\right)_{bio}$$

$$\frac{dm_i^S}{dt} = \left\{\lambda_- m_i^P - \lambda_+ m_i^S\right\}$$

Biodegradation

Sorption

Biodegradation – Part I

$$\frac{d[PCE]}{dt} = -\Lambda^{ana}_{P\to T}$$

$$\frac{d[TCE]}{dt} = \Lambda^{ana}_{P\to T} - \Lambda^{ana}_{T\to D}$$

$$\frac{d[DCE]}{dt} = \Lambda^{ana}_{T\to D} - \Lambda^{ana}_{D\to V} - \Lambda^{aer}_{D\to C}$$

$$\frac{d[VC]}{dt} = \Lambda^{ana}_{D\to V} - \Lambda^{ana}_{V\to E} - \Lambda^{aer}_{V\to C}$$

$$\frac{d[ETH]}{dt} = \Lambda^{ana}_{V\to E} - \Lambda^{aer}_{E\to C}$$

$$\frac{d[CAH]}{dt} = -\left(\Lambda^{ana}_{V\to E} + \Lambda^{aer}_{V\to C}\right)$$

abbreviations:

$$\Lambda^{ana} = \Lambda^{ana}_{P\to T} + \Lambda^{ana}_{T\to D} + \Lambda^{ana}_{D\to V} + \Lambda^{ana}_{V\to E}$$

$$\Lambda^{aer} = \Lambda^{aer}_{D\to C} + \Lambda^{aer}_{V\to C} + \Lambda^{are}_{E\to C}$$

Biodegradation – Part II

$$\frac{d\,[Cl^-]}{dt} = \Lambda^{ana} + 2\Lambda^{aer}_{D\rightarrow C} + \Lambda^{aer}_{V\rightarrow C}$$

$$\frac{d\,[C_{org}]}{dt} = y_{Corg}\,\Lambda^{ana}$$

$$\frac{d\,[O_2]}{dt} = 2\Lambda^{aer}_{D\rightarrow C} + \tfrac{5}{2}\,\Lambda^{aer}_{V\rightarrow C} + 3\Lambda^{aer}_{E\rightarrow C}$$

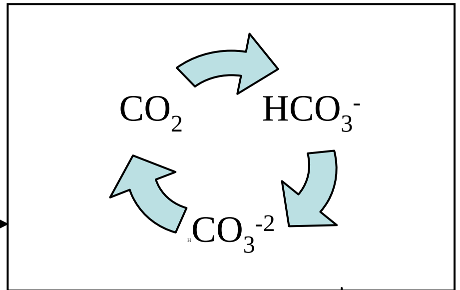
$$\frac{d\,[CO_2]}{dt} = y_{CO2}\,\Lambda^{ana} + 2\Lambda^{aer}$$

stoichiometric coefficients

for CH_2O as C_{org}

$$y_{Corg} = \tfrac{1}{2}$$

$$y_{CO2} = \tfrac{1}{2}$$



$$\frac{d\,[H^+]}{dt} = \frac{d\,[Cl^-]}{dt} + (\,CO_2 \text{ equilibiurm}\,)$$

PhreeqC

Enzyme Kinetics – Rate Equation

transition rates

biomass

temperature dependence

pH dependence

$$\Lambda^{ana}_{i \to j} = X^{ana} f_{i \to j}(CAH) \cdot f_2(C_{org})\, f_3(T)\, f_4(pH) \cdot F_{inh}$$

$$\Lambda^{aer}_{i \to j} = X^{aer} f_{i \to j}(CAH) \cdot f_2(O_2)\quad f_3(T)\, f_4(pH)$$

MICHAELIS-MENTEN and HALDANE

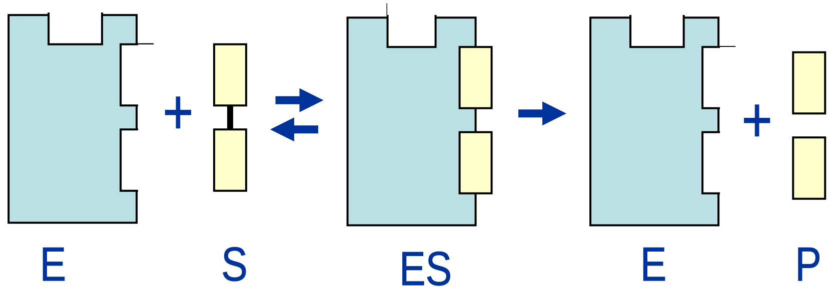
$$f_2(c) = \frac{[c]}{K_c + [c]}$$

$$F_{inh} = \frac{K_{inh}}{K_{inh} + [O_2]}$$

non-competitive inhibition

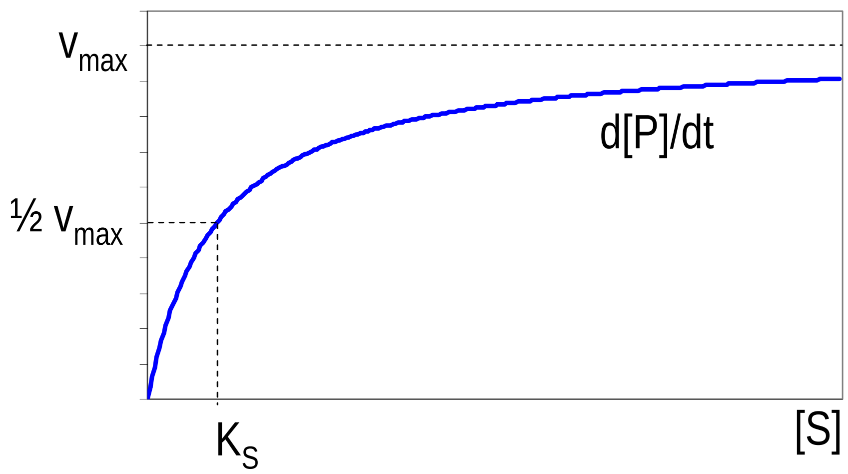
Michaelis-Menten

$$E + S \underset{k_-}{\overset{k_+}{\rightleftarrows}} ES \xrightarrow{k} E + P$$



steady state

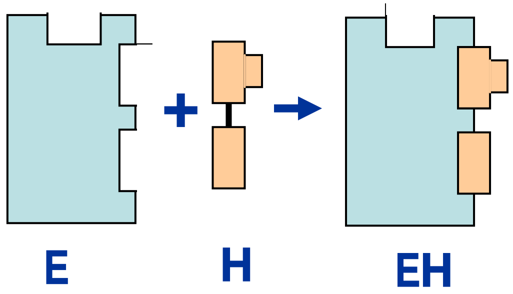
$$\frac{d[P]}{dt} = \frac{v_{max}\,[S]}{K_S + [S]}$$



$$K_S = \frac{k_- + k}{k_+} \qquad v_{max} = k[E_0]$$

$$[E_0] = [E] + [ES]$$

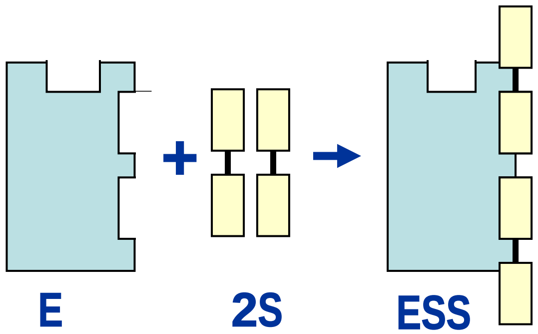
Enzyme Kinetics – Inhibition



competitive inhibition

$$\frac{v_{max}\,[S]}{K_S I_1 + [S]}$$

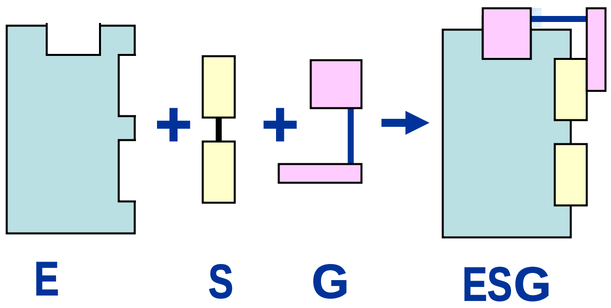
$$I_1 = 1 + \frac{[H]}{K_1}$$



self-inhibition (HALDANE)

$$\frac{v_{max}\,[S]}{K_S + [S] I_2}$$

$$I_2 = 1 + \frac{[S]}{K_2}$$



non-competitive inhibition

$$\frac{v_{max}\,[S]}{K_S + [S]} \cdot \frac{1}{I_3}$$

$$I_3 = 1 + \frac{[G]}{K_3}$$

Kinetic Data

	k_i	K_i	K_{ii}	K_{i-1}	K_{i+1}
	µmol/µg/d	µM	µM	µM	µM
PCE	$12.4 \cdot 10^{-3}$	1.6	0	0	1.8
TCE	$125 \cdot 10^{-3}$	1.8	900	1.6	1.8
DCE	$14 \cdot 10^{-3}$	1.8	750	1.8	62
VC	$8 \cdot 10^{-3}$	62	750	1.8	0

$$\text{rate} = \frac{k_i X}{K_i I_i + [i] + [i]^2 / K_{ii}}$$

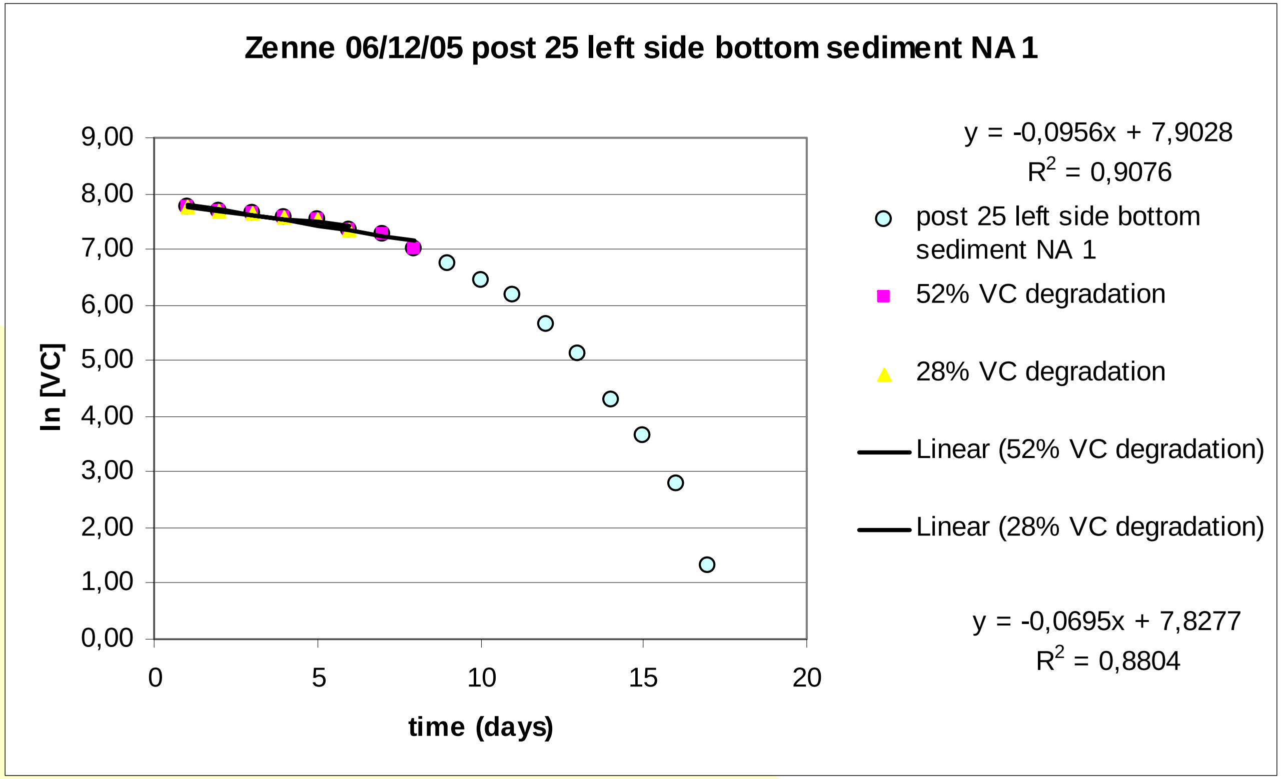
$$I_i \approx 1 + \frac{[i-1]}{K_{i-1}} + \frac{[i+1]}{K_{i+1}}$$

EXAMPLE CALCULATIONS

Zenne VC

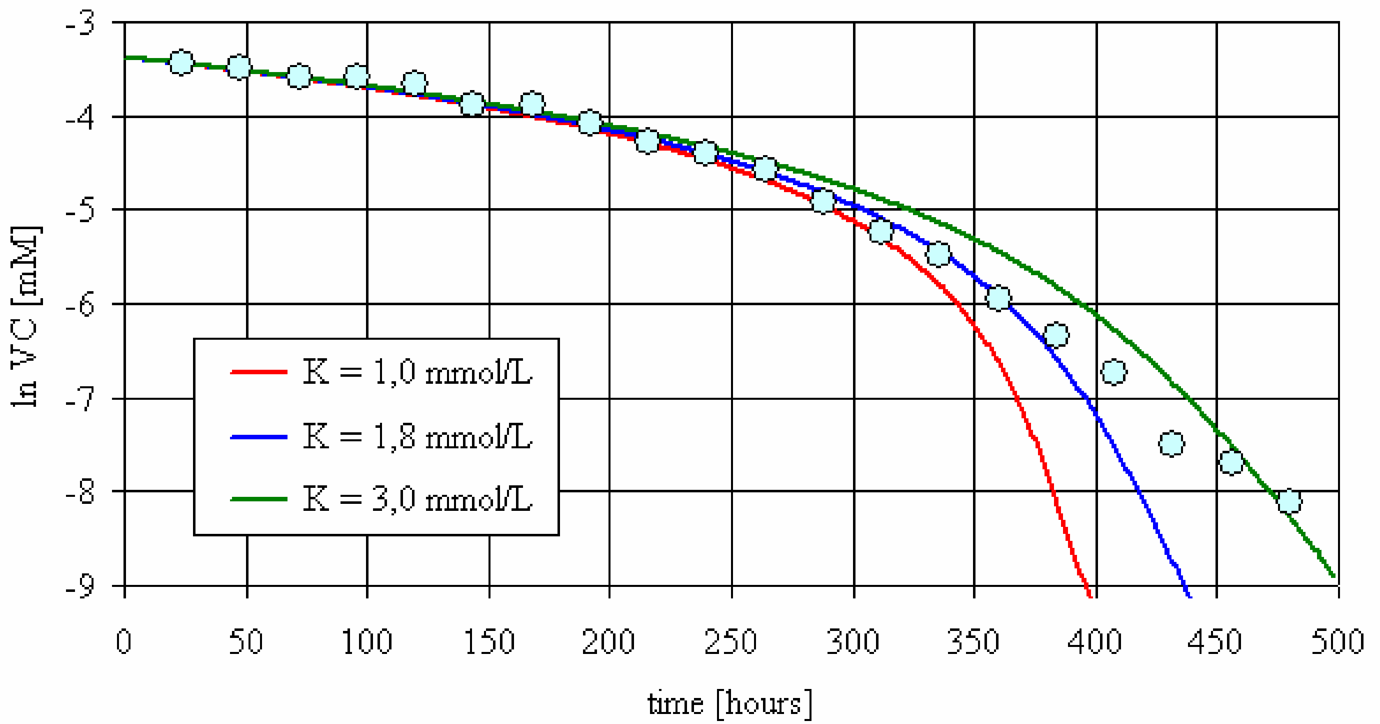
Zenne VC – Degradation Order ??

"KELLY's Approach"



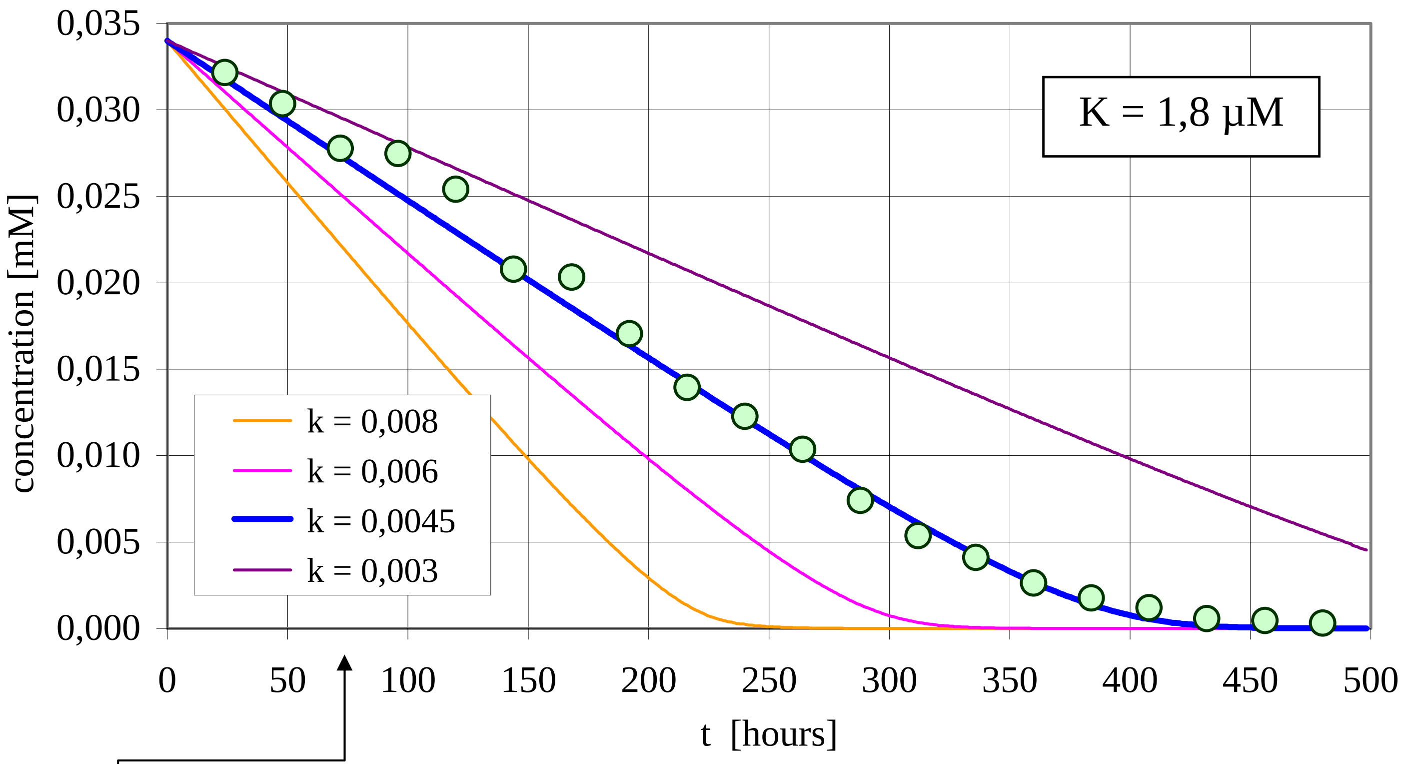
Zenne VC – Degradation Order

log-Scale



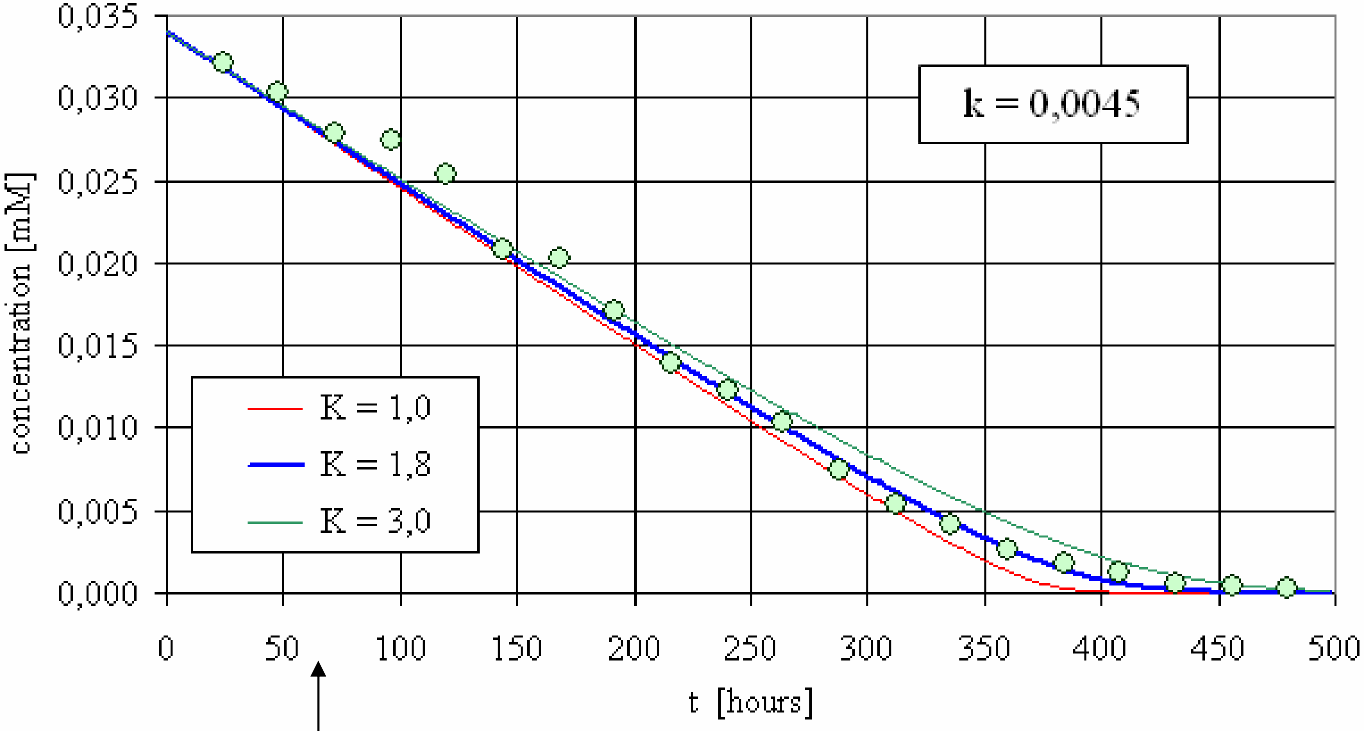
Michaelis-Menten = Kinetic 1st order + Kinetic 0th order

Zenne VC – Variation of k



$$\text{rate} = \frac{kX}{K + [i] + [i]^2 / K_{ii}}$$

Zenne VC – Variation of K

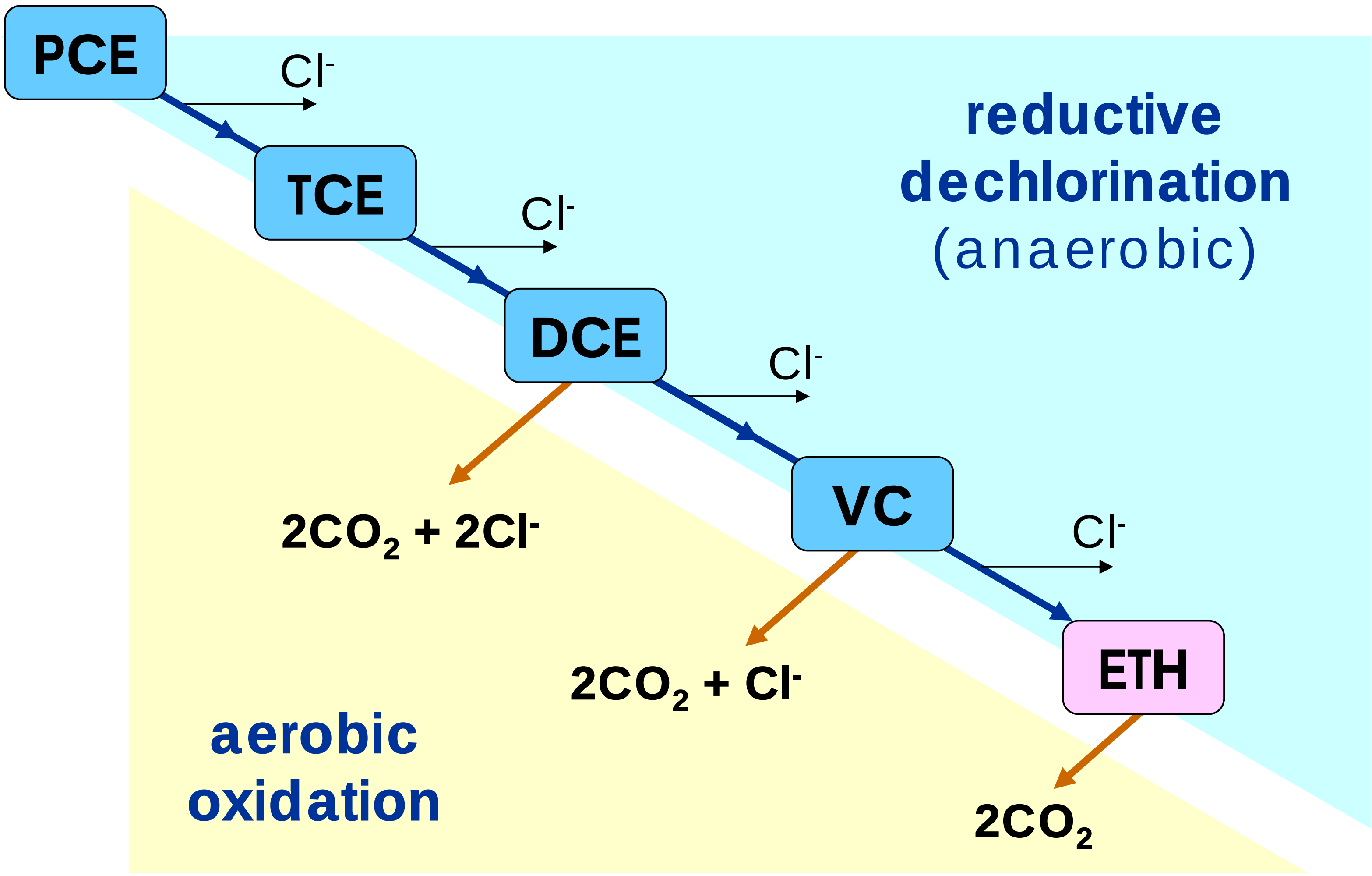


$$\text{rate} = \frac{kX}{K + [i] + [i]^2 / K_{ii}}$$

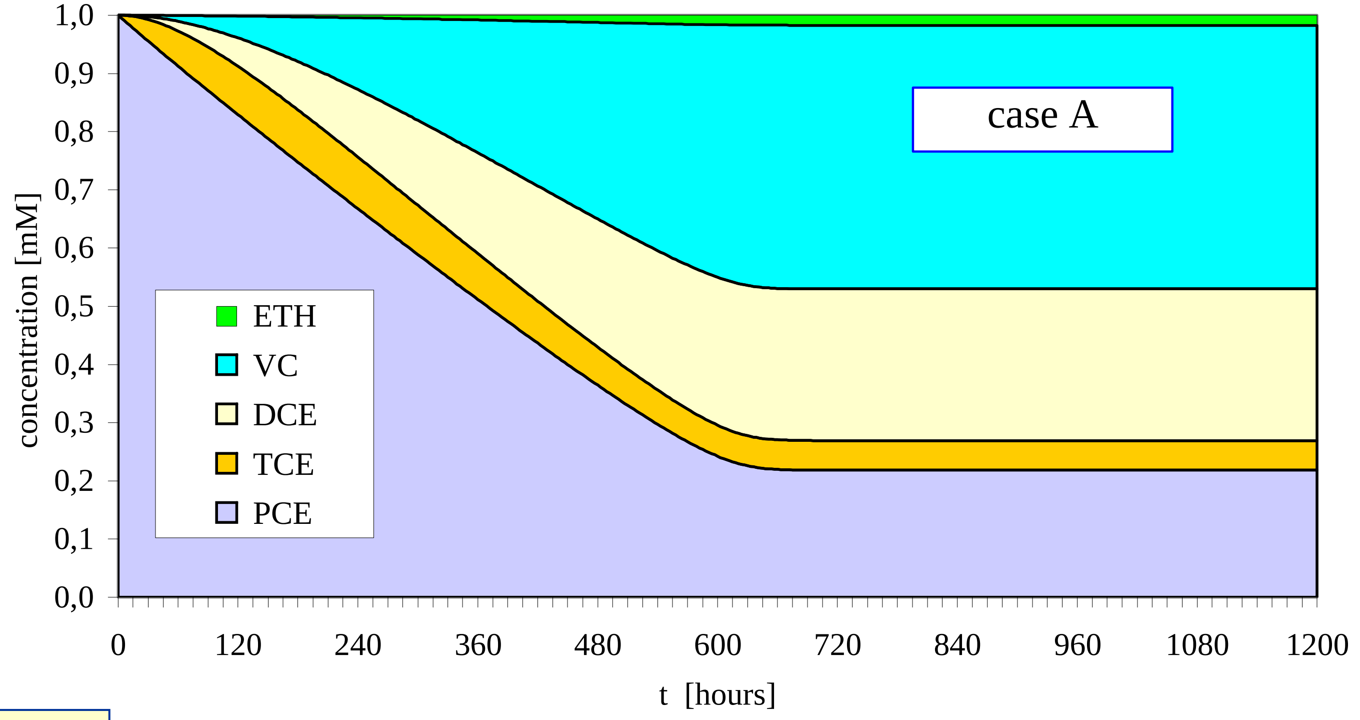
EXAMPLE

Mass Balance in Degradation Chain

Degradation Pathways



Example A

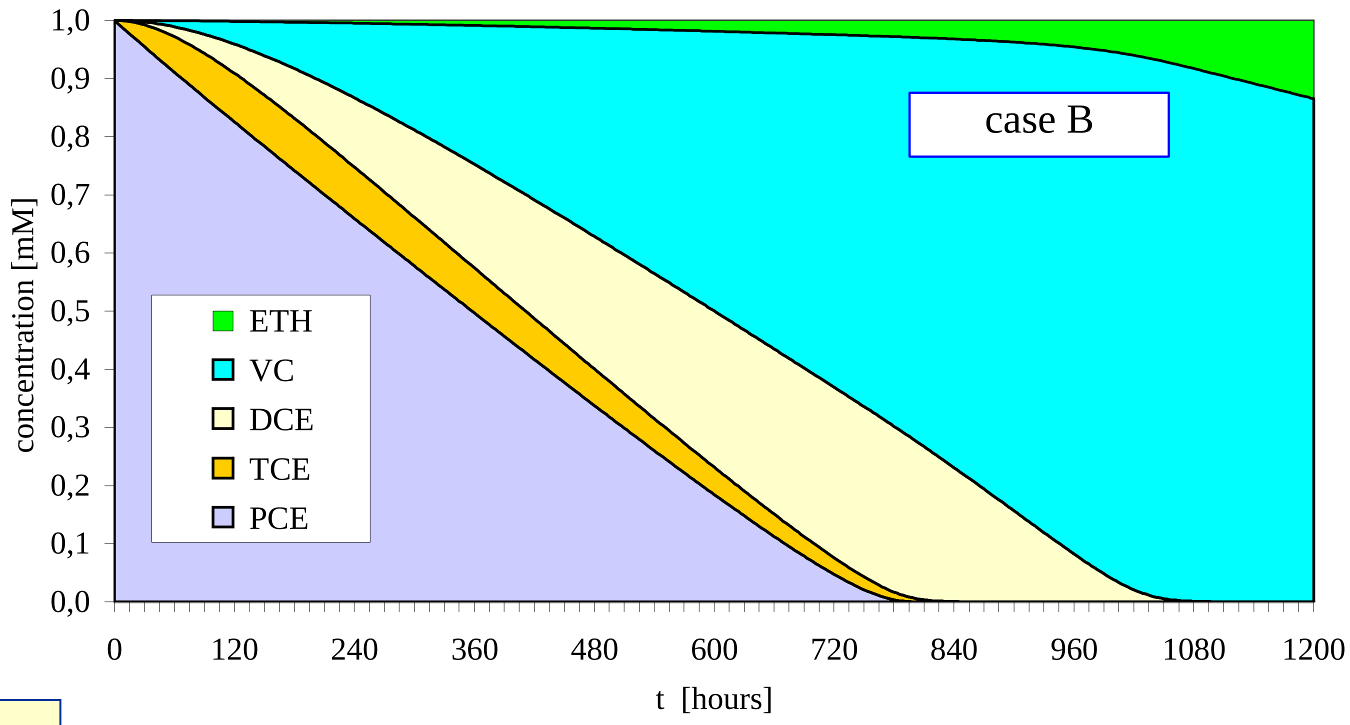


1 mM PCE

1 mM DOC

DOC is exhausted

Example B

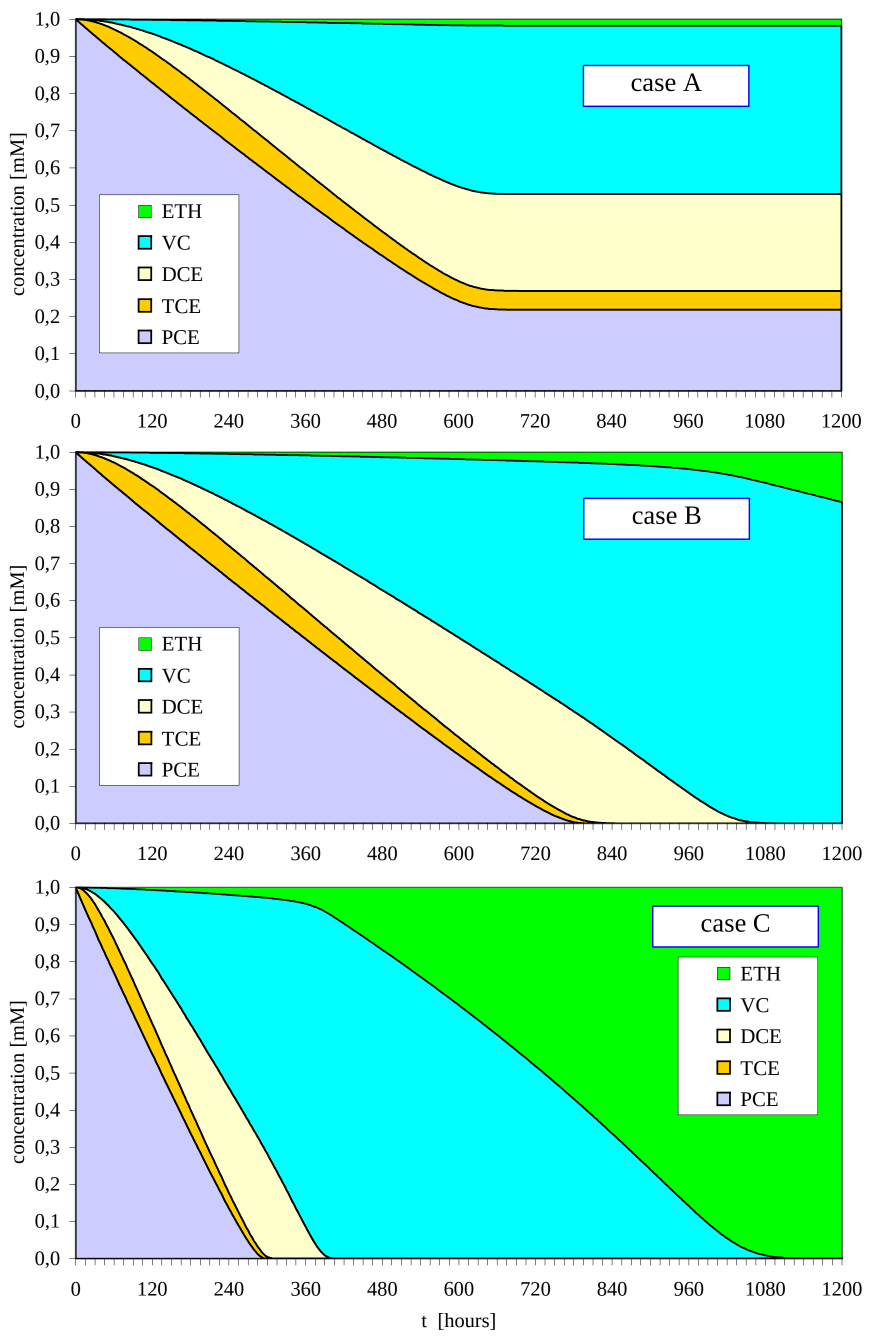


1 mM PCE
3 mM DOC

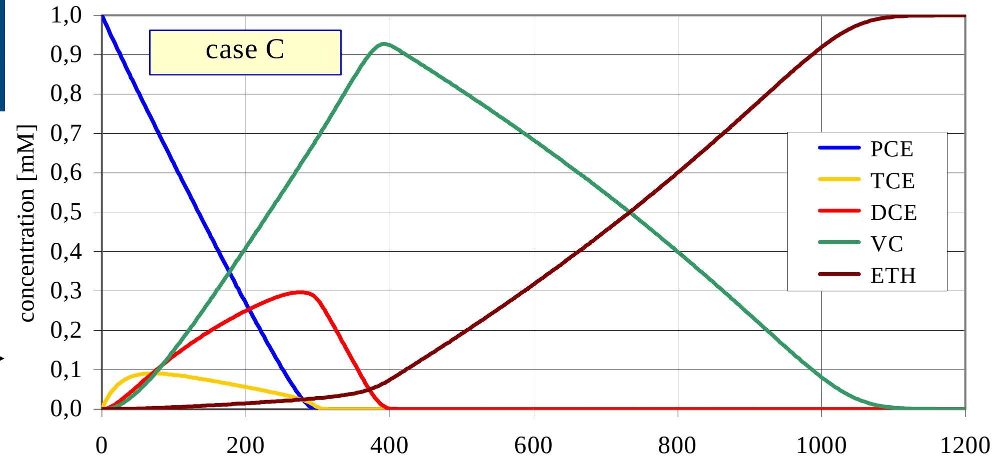
Degradation time too short

Example C

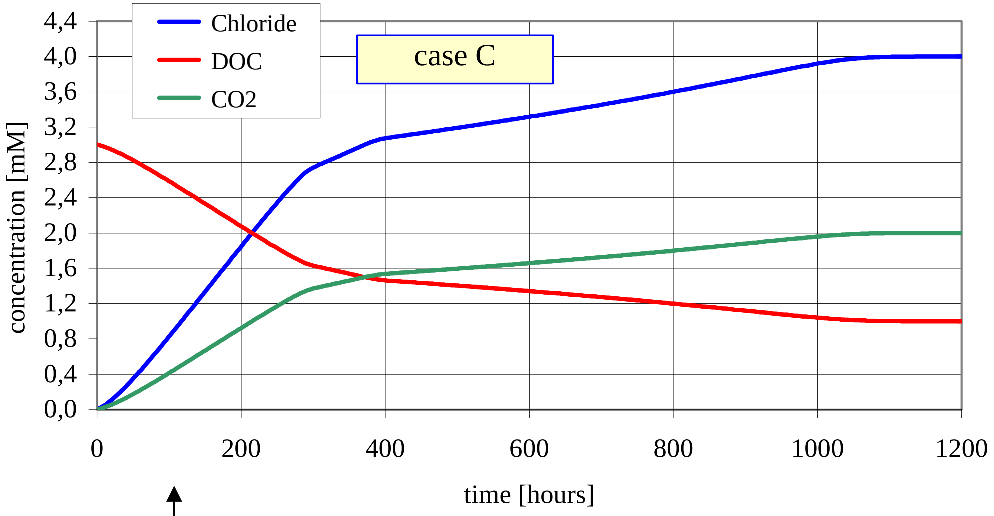
Complete CAH-Degradation



Example C

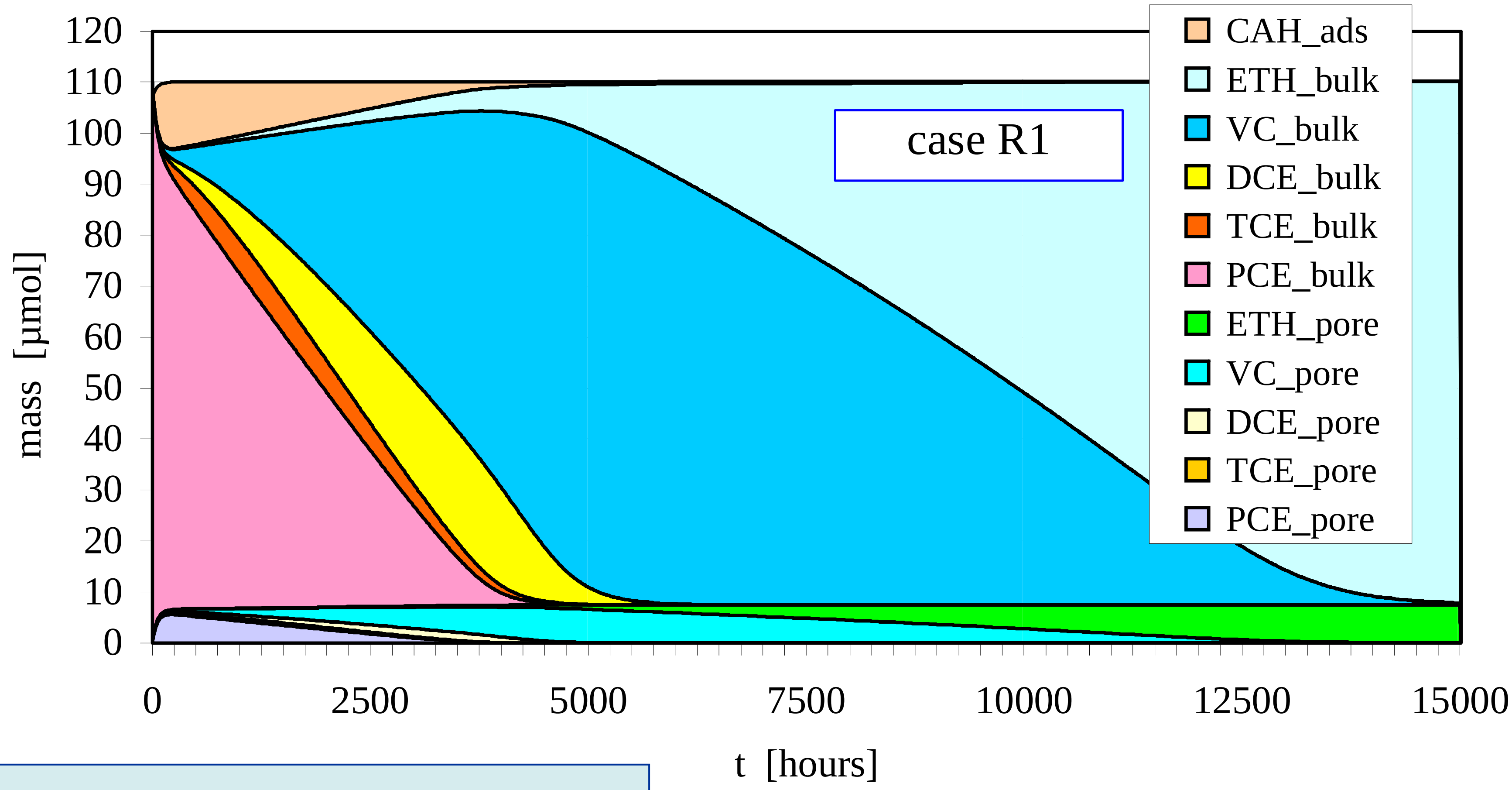


Intermediate Accumulation of DCE and VC



Degradation Products

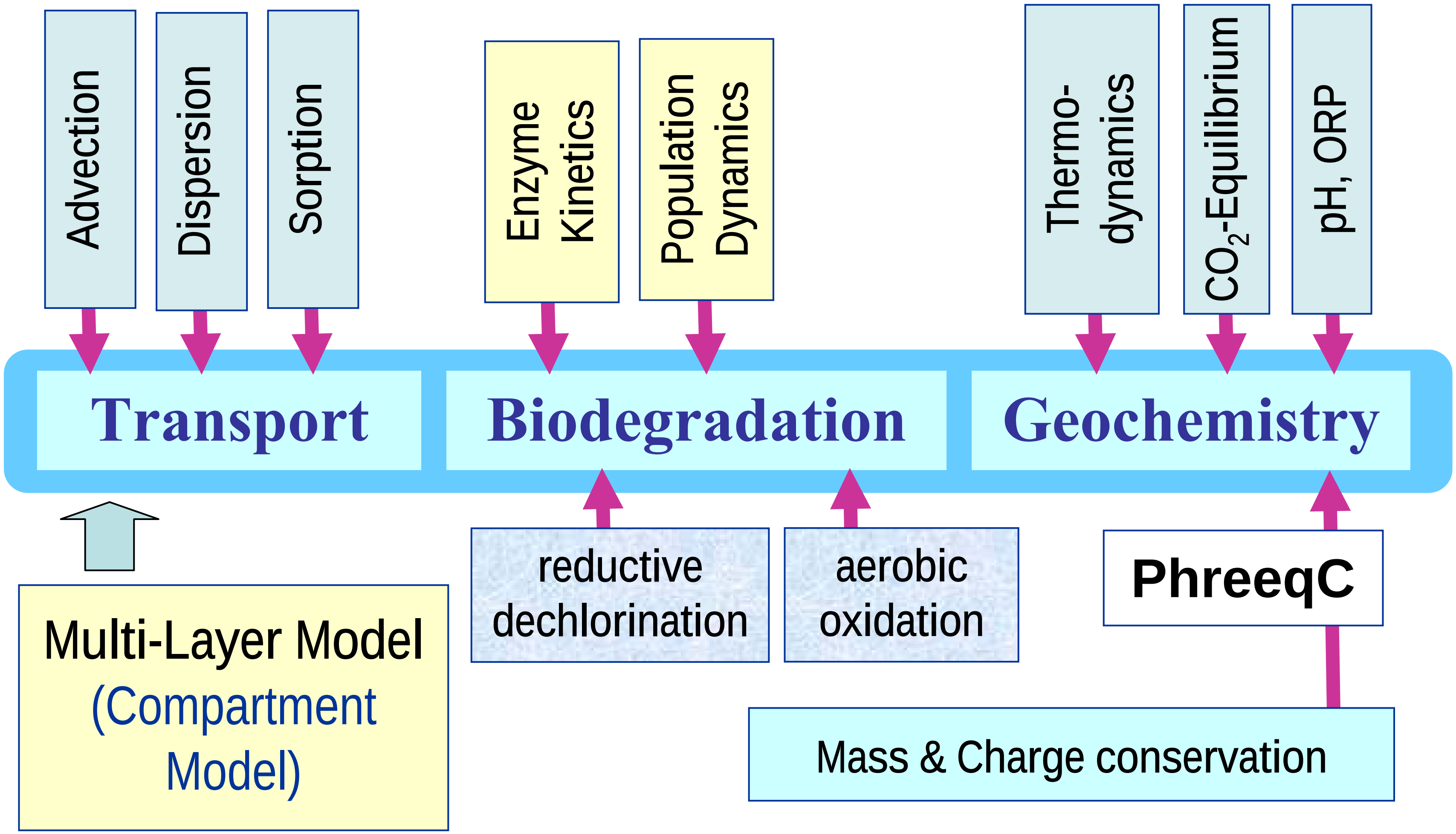
Example R1 – Three Phases



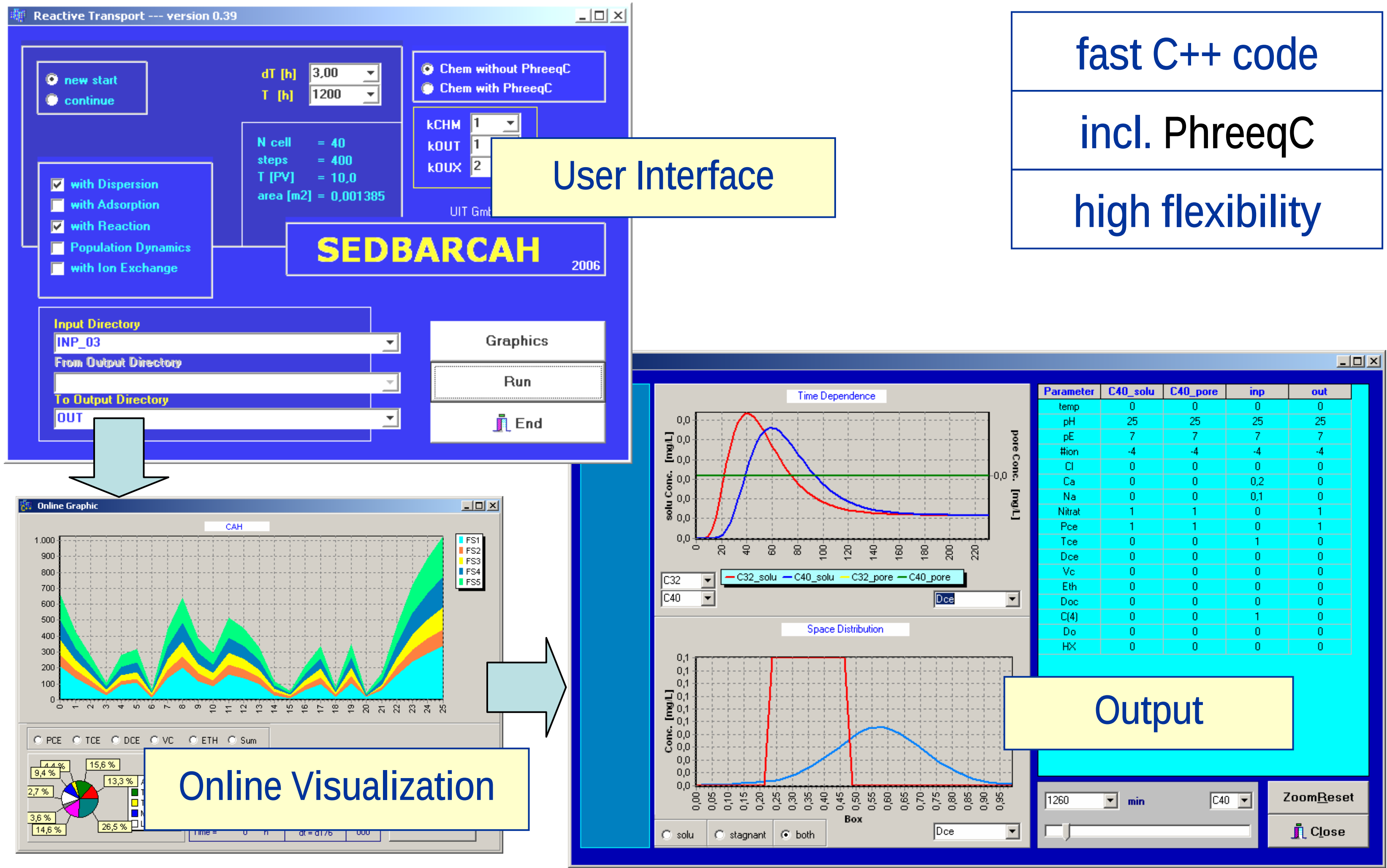
The Most General Case

PROGRAM CAPABILITIES

Dynamical Model – Main Processes



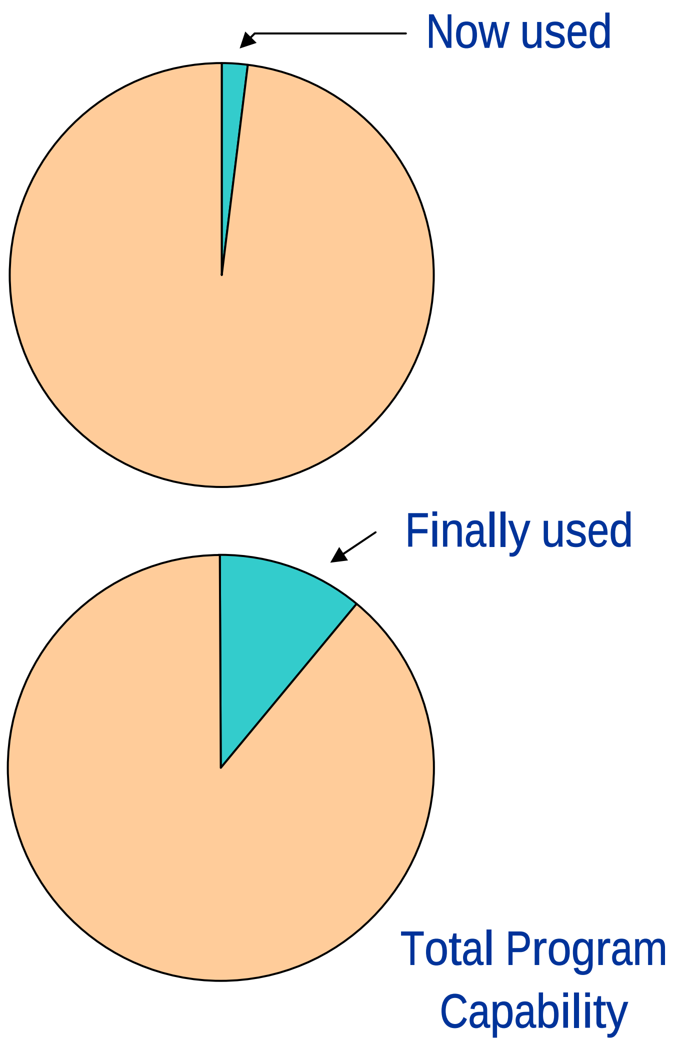
SEDBARCAH Computer Program



- fast C++ code
- incl. PhreeqC
- high flexibility

Dynamical-Model Capabilities

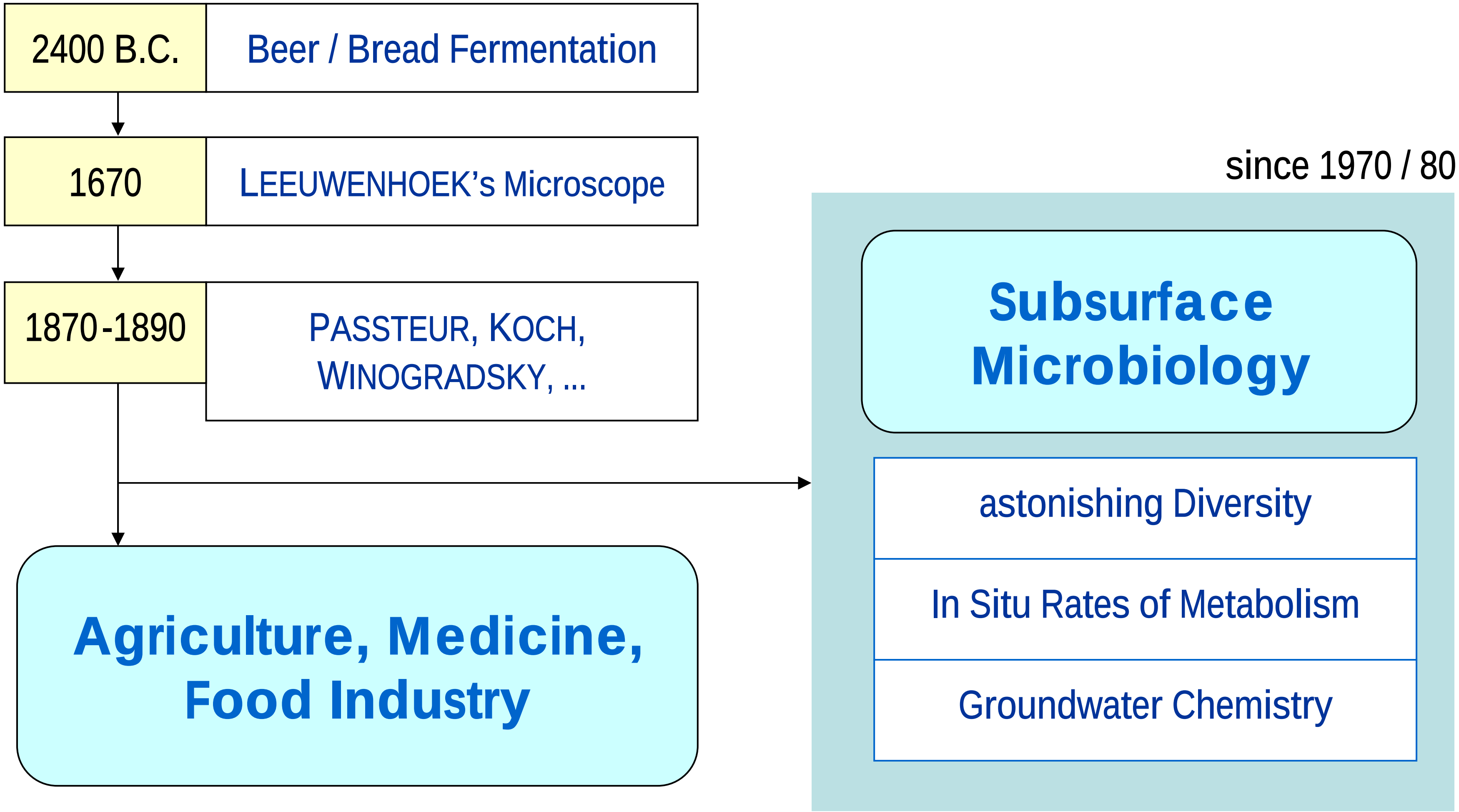
		D12	D13
Enzyme Kinetics	Population Dynamics		X
	Anaerobic Pathway	X	X
	Aerobic Pathway		
	T-Dependence		
	pH-Dependence		
	Nutrient Limitation		
	O2-competition		
Transport	Advection + Dispersion		X
	Time-Dependent Inflow		
	Multi-Layer		
	Heterogeneous Populations		
PHREEQC	Complete Analyses		
	Open CO2-System		
	Phase Equilibrium		
	Ion-Exchange		



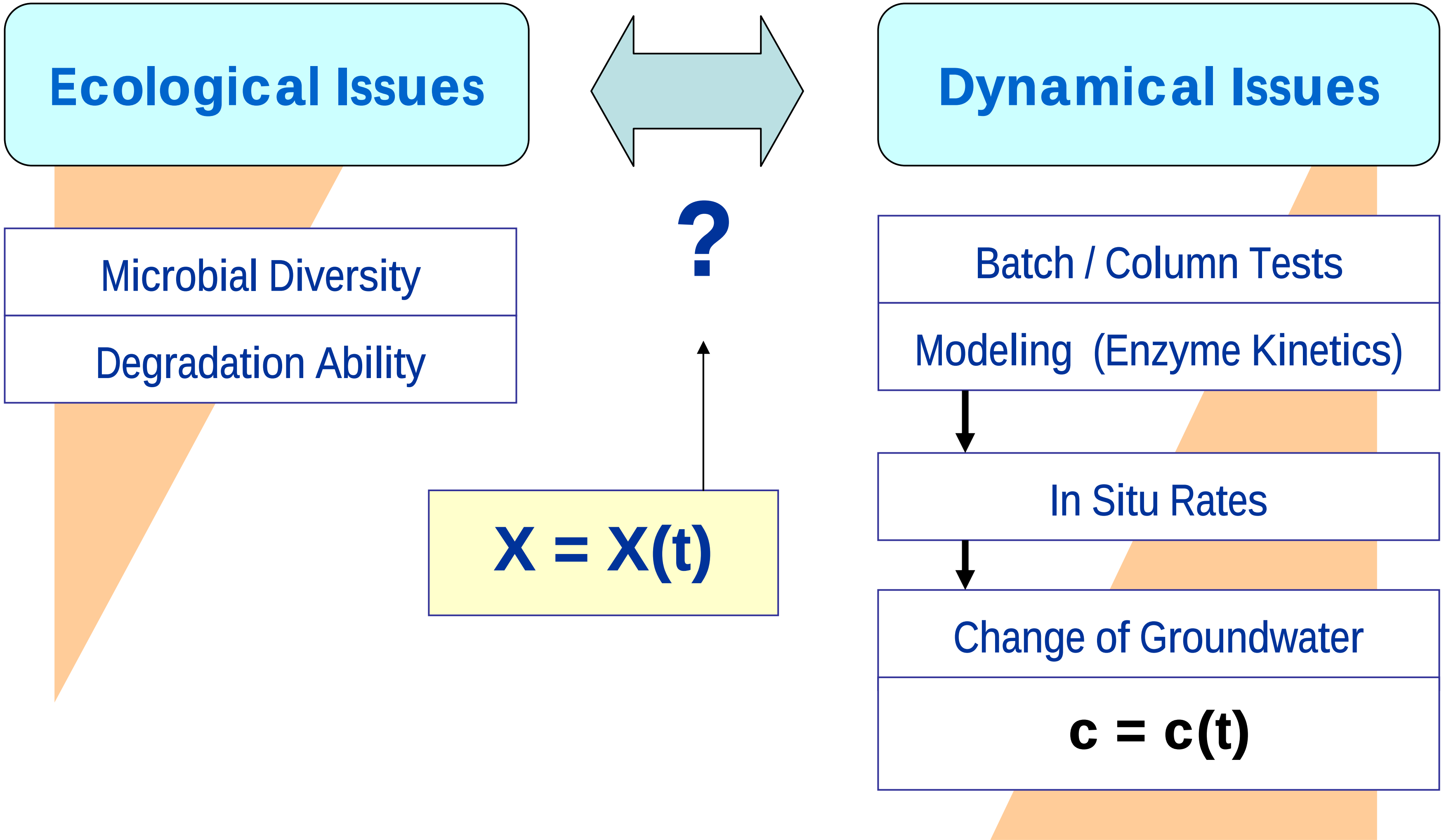
BASIC PRINCIPLES

and
Open Questions

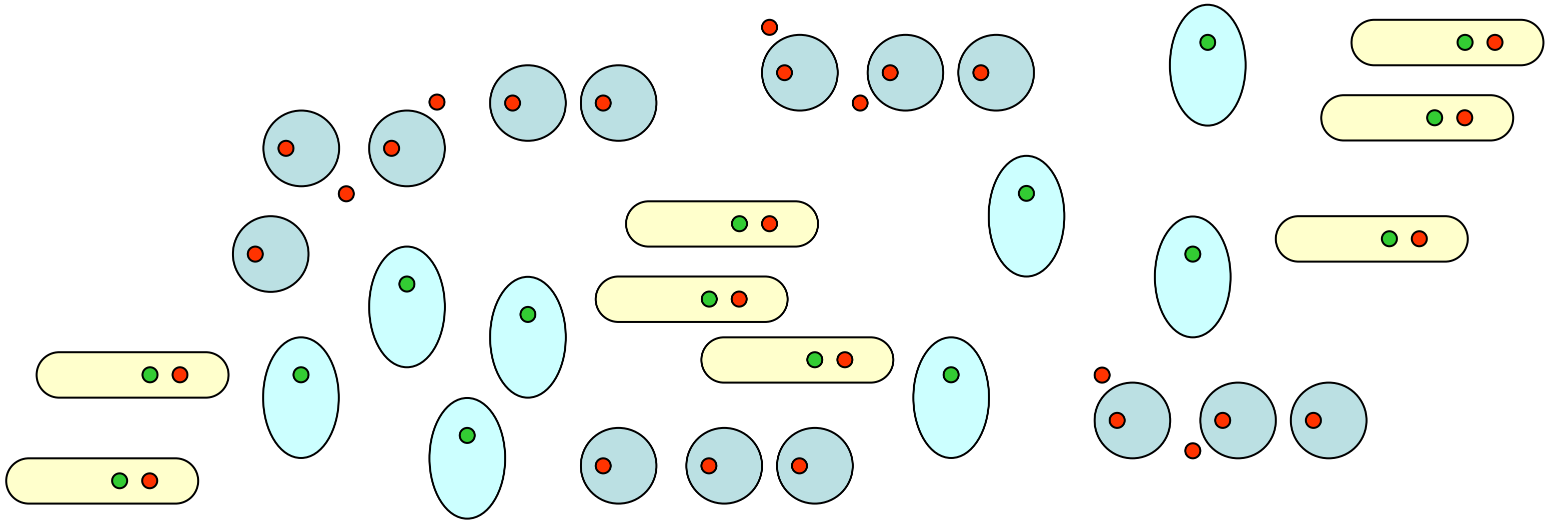
Microbiology



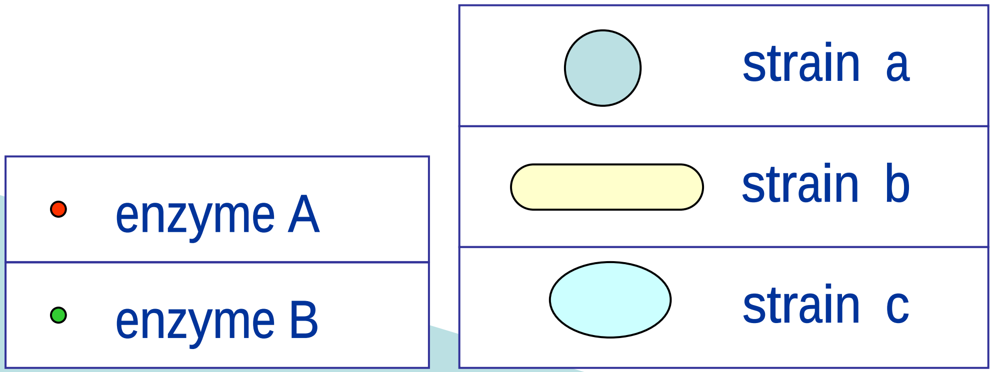
Interplay of Different "Sciences"



Population Density ?



$$X_A \neq X_a$$



Bacterial Growth

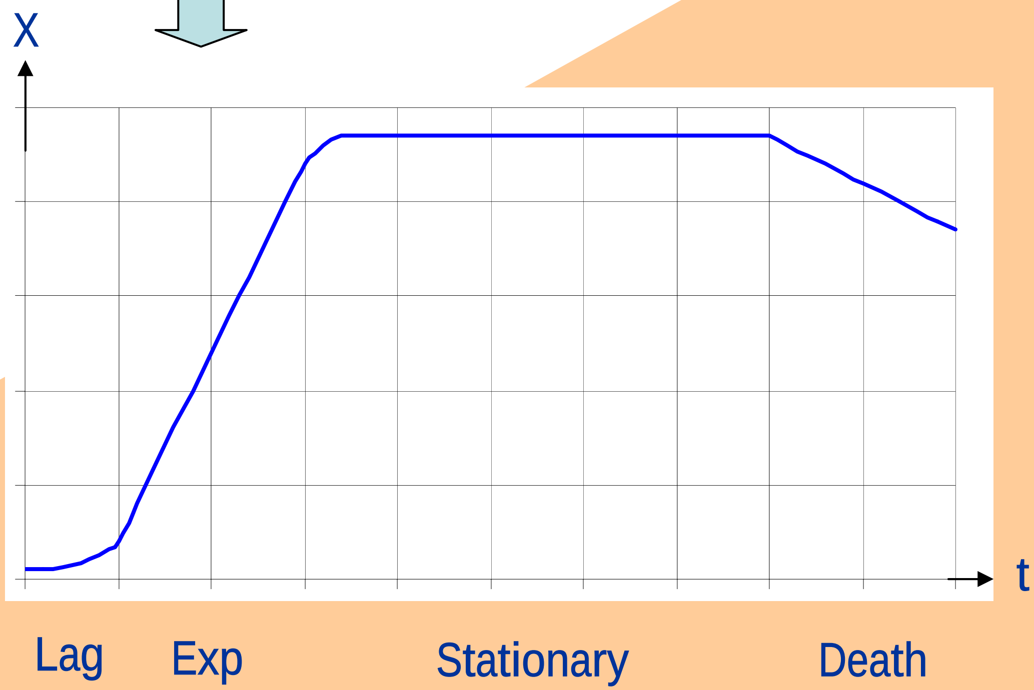
Individual Cell (Cell Growth)

Increase in Cellular Mass and Size

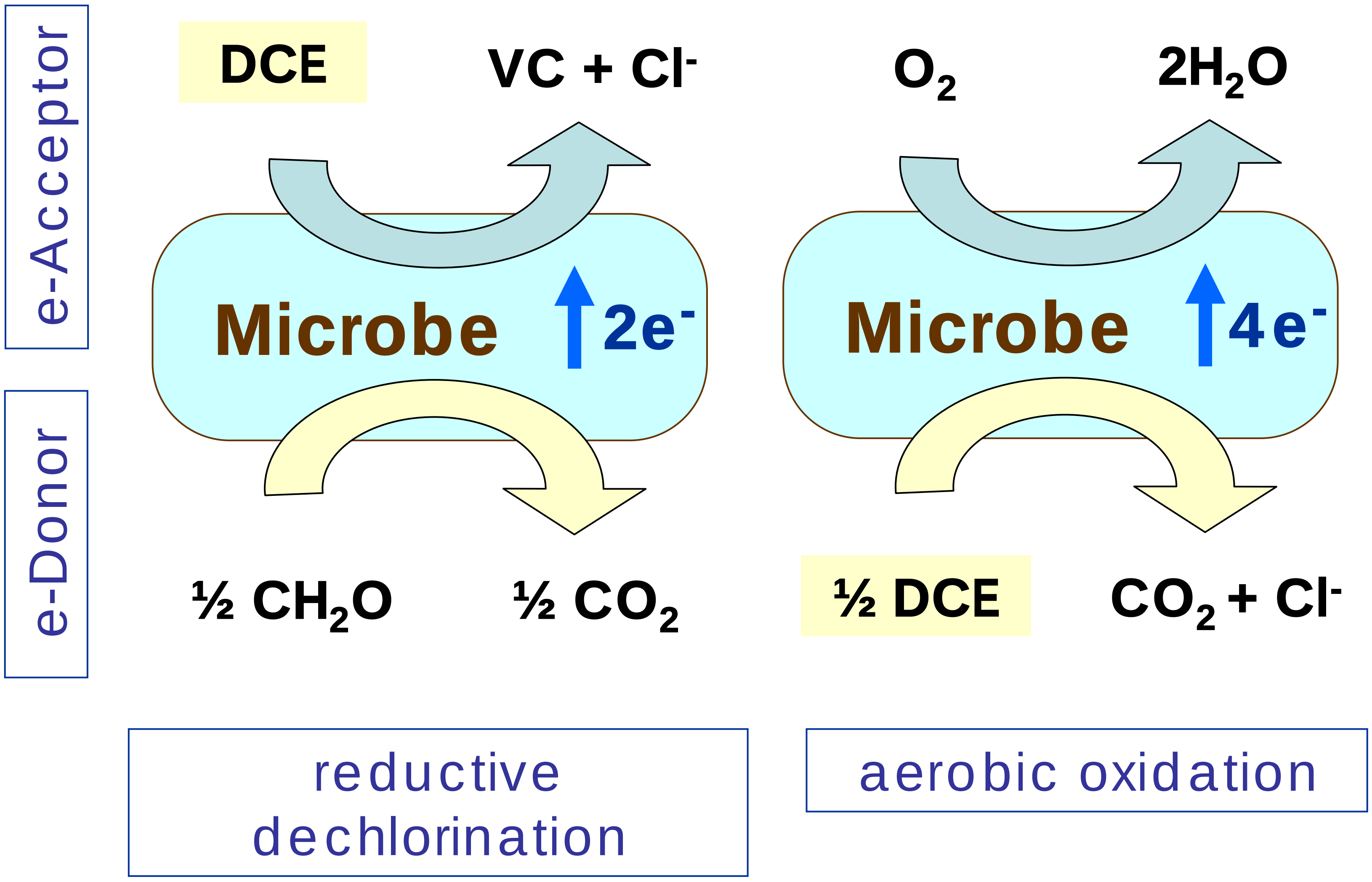
Difficult to Measure

Populations of Cells

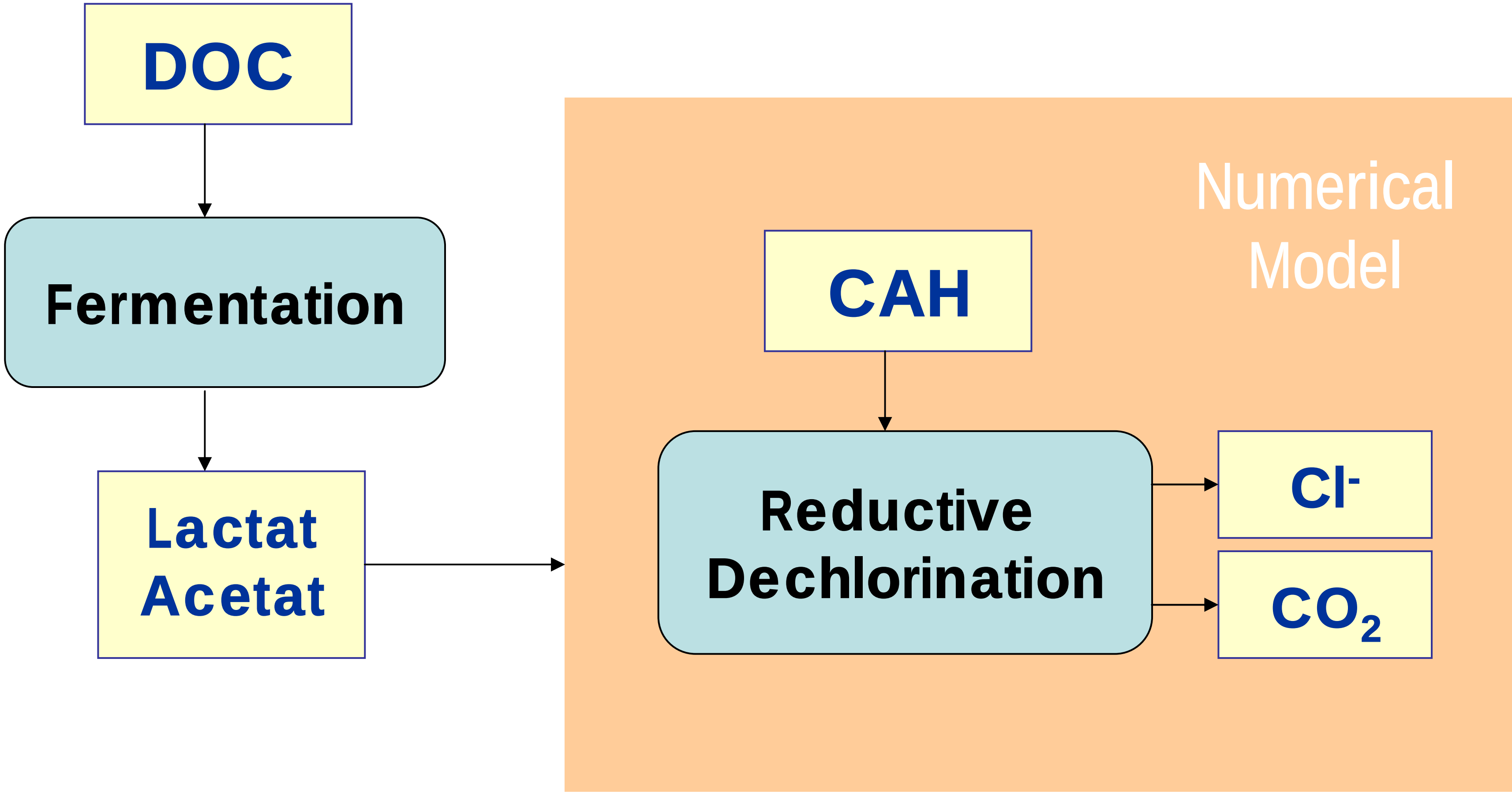
Increase in Total Number of Cells



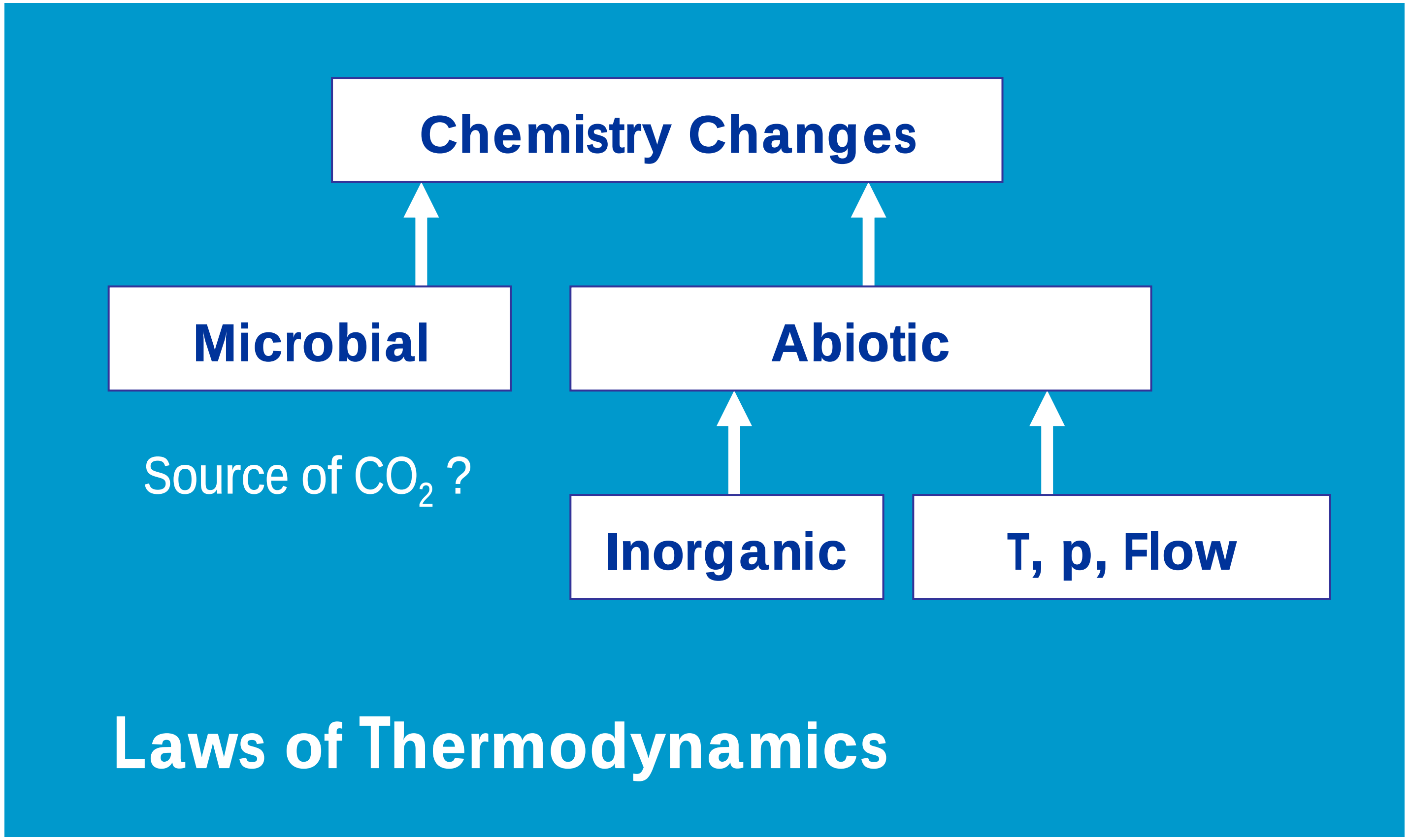
Electron Transfer



Complete Degradation Chain (Symbiosis)



Impact on Groundwater Chemistry



Equilibrium or Non-Equilibrium ?

Thermodynamics

Energy , Entropy ...

PhreeqC

Equilibrium

Temperature T

(e^{-kT})

Kinetics

Non-Equilibrium

Rates / Velocities

Redox-Reactions

C(-4)	C(0)	C(4)
CH_4	CH_2O	CO_2

Time t

(e^{-ikt})

LINK TO GEOCHEMISTRY

(PHREEQC)

Water is more than H_2O

Dissolved Ions / Complexes:

H^+, OH^-, H_2O $AlSO_4$ $Al(SO_4)^{2-}$ Al^{3+}, $Al(OH)^{2+}$ $AlHSO_4^{2+}$ $AlOH^{2+}$ $AlOH_3$ $Al(OH)_4^-$
CO_2 HCO_3^-, $MgHCO_3^+$ $FeHCO_3$ $CaNCO_3^+$ $MnHCO_3^+$ $NiHCO_3^+$ $ZnHCO_3^+$
$NaHCO_3$ UO_2CO_3 $NiCO_3$ $PbHCO_3^+$ $FeCO_3$ $MnCO_3$ $MgCO_3$ $ZnCO_3$ CO_3^{2-}
$CaCO_3$ $PbCO_3$ $NaCO_3^-$ $UO_2(CO_3)_2^{2-}$ $Pb(CO_3)_2^{2-}$ $(UO_2)_3(CO_3)_6^{6-}$ Ca^{2+} $CaSO_4$
$CaHSO_4$ $CaOH^+$ Cl^- $FeCl^+$ $MnCl^+$ $NiCl^+$ $ZnCl^+$ $FeCl_2^+$ UO_2Cl^+ $NiCl_2$ $MnCl_2$ $PbCl^+$
$ZnCl_2$ $ZnOHCl$ $FeCl_3$ $PbCl_2$ UO_2Cl_2 $MnCl_3^-$ $ZnCl_3^-$ $PbCl_3^-$ $ZnCl_4^{2-}$ $PbCl_4^{2-}$ Fe^{2+}
$FeSO_4$ $FeHSO_4^+$ $FeOH^+$ $Fe(OH)_2$ $Fe(OH)_3^-$ $FeSO_4^+$ $FeOH^{2+}$ Fe^{3+} $Fe_2(OH)_2^{4+}$
$Fe(OH)_2^+$ $FeHSO_4^{2+}$ $Fe_3(OH)_4^{5+}$ $Fe(OH)_3$ $Fe(OH)_4^-$ H_2, K^+ KSO_4^- Mg^{2+} $MgSO_4$
$Mg(OH)^+$ Mn^{2+} $MnSO_4$ $MnOH^+$ $Mn(OH)_3^-$ Mn^{3+} MnO_4^{2-} Na^+ $NaSO_4^-$ Ni^{2+} $NiSO_4$
$Ni(SO_4)_2^{2-}$ $NiOH^+$ $Ni(OH)_2$ $Ni(OH)_3^-$ O_2 $PbSO_4$ Pb^{2+} $Pb(SO_4)_2^{2-}$ $PbOH^+$ $Pb(OH)_2$
Pb_2OH^{3+} $Pb(OH)_3^-$ $Pb(OH)_4^{2-}$ $Pb_3(OH)_4^{2+}$ SO_4^{2-} HSO_4^- $ZnSO_4$ $Zn(SO_4)_2^{2-}$
UO_2SO_4 $UO_2(SO_4)_2^{2-}$ UO_2^{2+} UO_2OH^+ $(UO_2)_2OH^{3+}$ $(UO_2)_2(OH)_2^{2+}$ $UO_2(OH)_3^-$
$(UO_2)_3(OH)_4^{2+}$ $(UO_2)_3(OH)_5^+$ $(UO_2)_4(OH)_7^+$ $UO_2(OH)_4^{2-}$ $(UO_2)_3(OH)_7^-$ Zn^{2+}
$ZnOH^+$ $Zn(OH)_2$ $Zn(OH)_3^-$ $Zn(OH)_4^{2-}$ ... and so on

Complete Hydrochemistry

- Speciation (Debey-Hückel)
- Complexation
- Acid-Base (H-Transfer)
- Redox Processes (e-Transfer)
- Homogeneous Reactions (Mixing)
- Heterogeneous Reactions
  (Phases, Gas)
- OF-Adsorption

PhreeqC
U.S. Geological Survey

thermodyn.
Database

More Info: SEDBARCAH project
Deliverable D12

www.aquac.de/model.html

End of presentation.