

Project no.: 511254 (STREP)



SEDBARCAH

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

CAH-Modeling & Batch Reactions (Part II)

Harald Kalka

Short Lecture at the Meeting
Munich, June 2006

Start date of project: 01/01/2005
Lead contractor for Work Package 5 (Modeling):

Duration: 2 years
UIT GmbH Dresden

CAH-Modeling

SEDBARCAH

1

Batch Reaction Model

2

Kinetic Data

3

Mass Balance

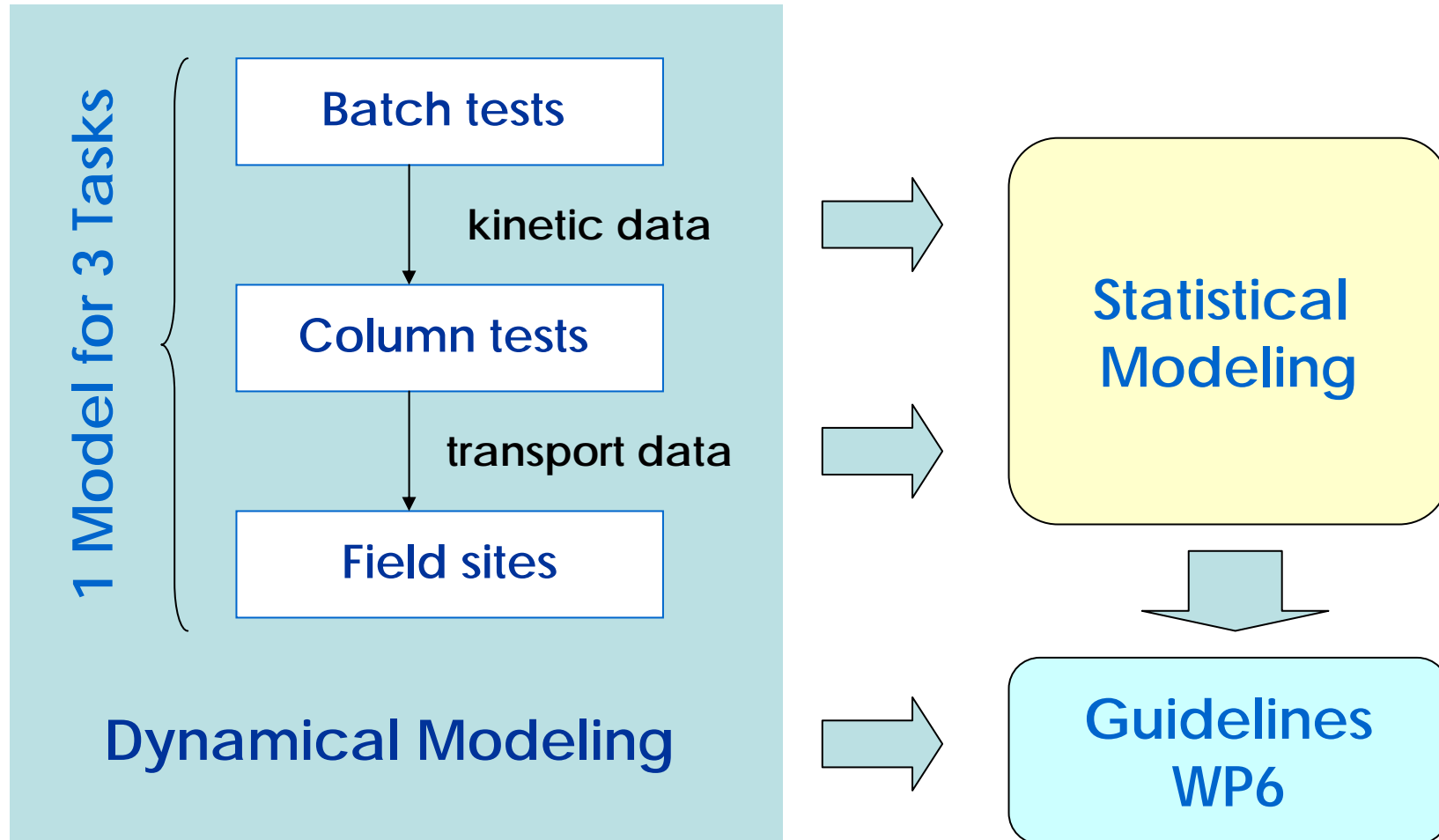
4

Model Capabilities

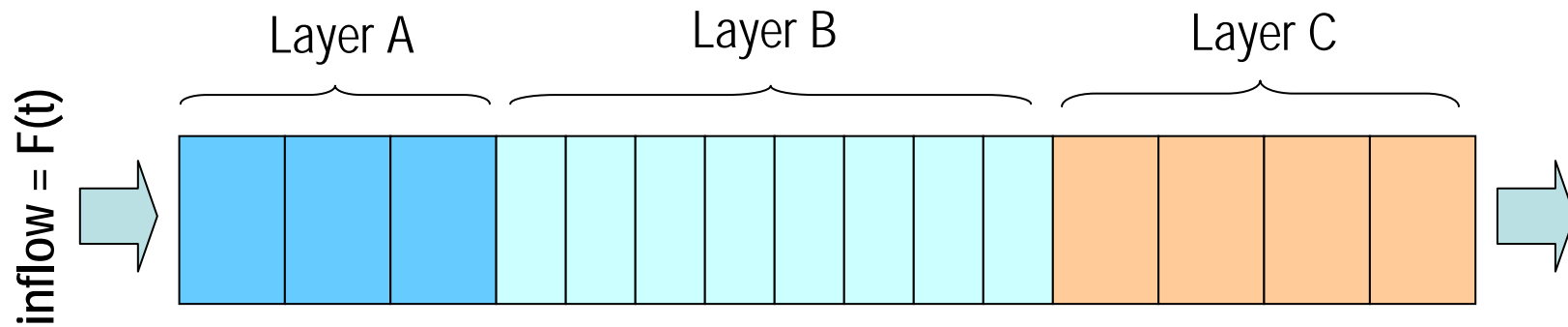
5

Basic Principles / Further Steps

Modeling in WP5

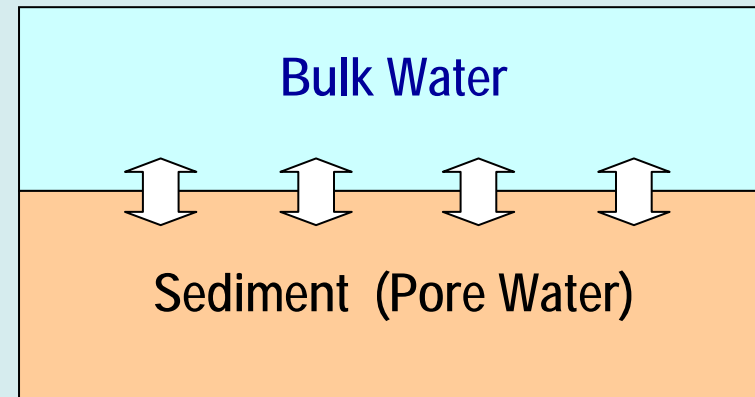


Two Options of the CAH-Model

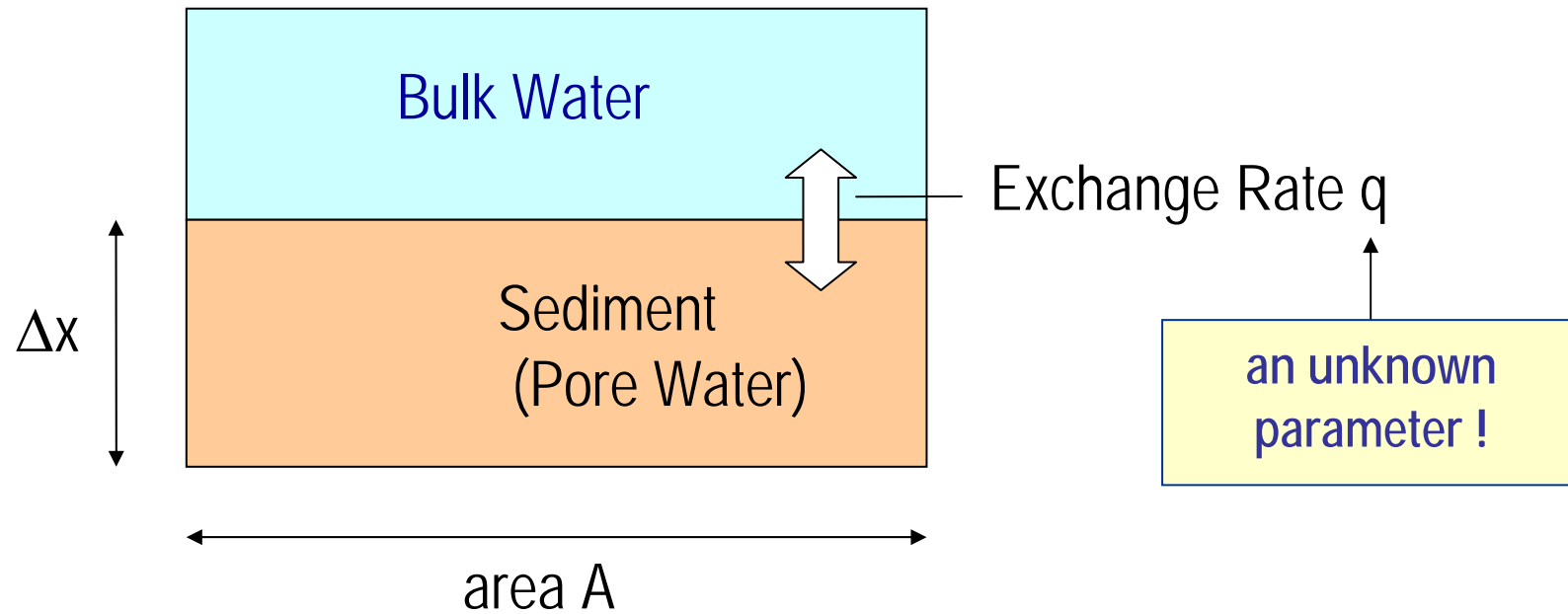


Reactive Transport

Batch Test
(Kinetics only)

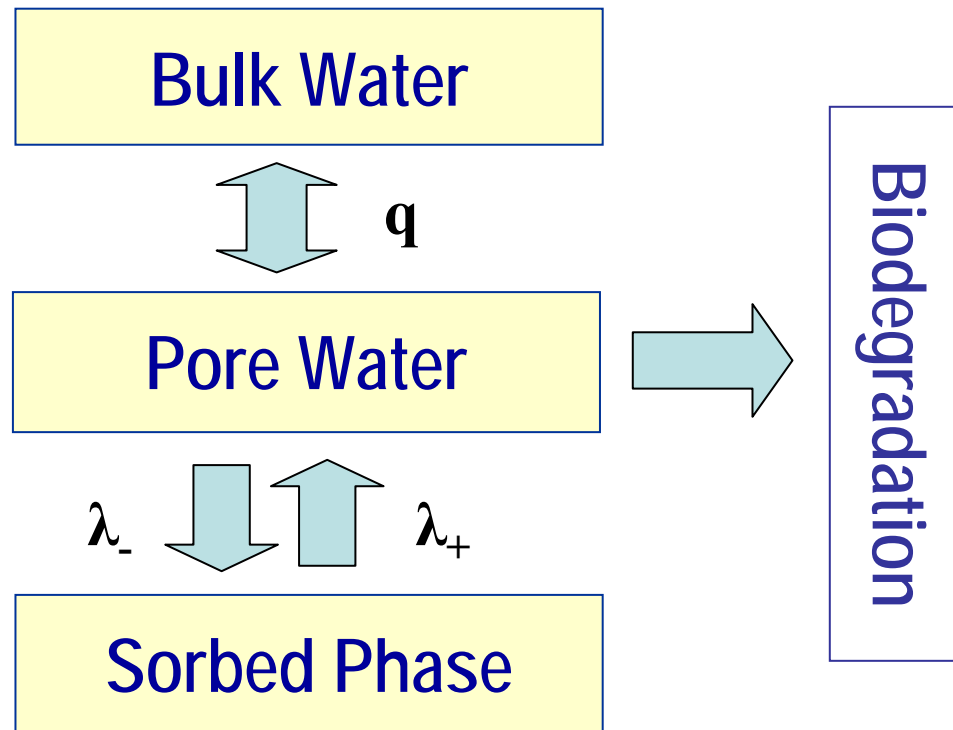


Batch Reactions – Set-up



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

Batch Reactions – 3 Phases



Batch Reactions – Mass Transfer

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

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

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

Biodegradation

Sorption

Biodegradation – Part I

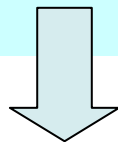
$$\frac{d [\text{PCE}]}{dt} = -\Lambda_{\text{P} \rightarrow \text{T}}^{\text{ana}}$$

$$\frac{d [\text{TCE}]}{dt} = \Lambda_{\text{P} \rightarrow \text{T}}^{\text{ana}} - \Lambda_{\text{T} \rightarrow \text{D}}^{\text{ana}}$$

$$\frac{d [\text{DCE}]}{dt} = \Lambda_{\text{T} \rightarrow \text{D}}^{\text{ana}} - \Lambda_{\text{D} \rightarrow \text{V}}^{\text{ana}} - \Lambda_{\text{D} \rightarrow \text{C}}^{\text{aer}}$$

$$\frac{d [\text{VC}]}{dt} = \Lambda_{\text{D} \rightarrow \text{V}}^{\text{ana}} - \Lambda_{\text{V} \rightarrow \text{E}}^{\text{ana}} - \Lambda_{\text{V} \rightarrow \text{C}}^{\text{aer}}$$

$$\frac{d [\text{ETH}]}{dt} = \Lambda_{\text{V} \rightarrow \text{E}}^{\text{ana}} - \Lambda_{\text{E} \rightarrow \text{C}}^{\text{aer}}$$



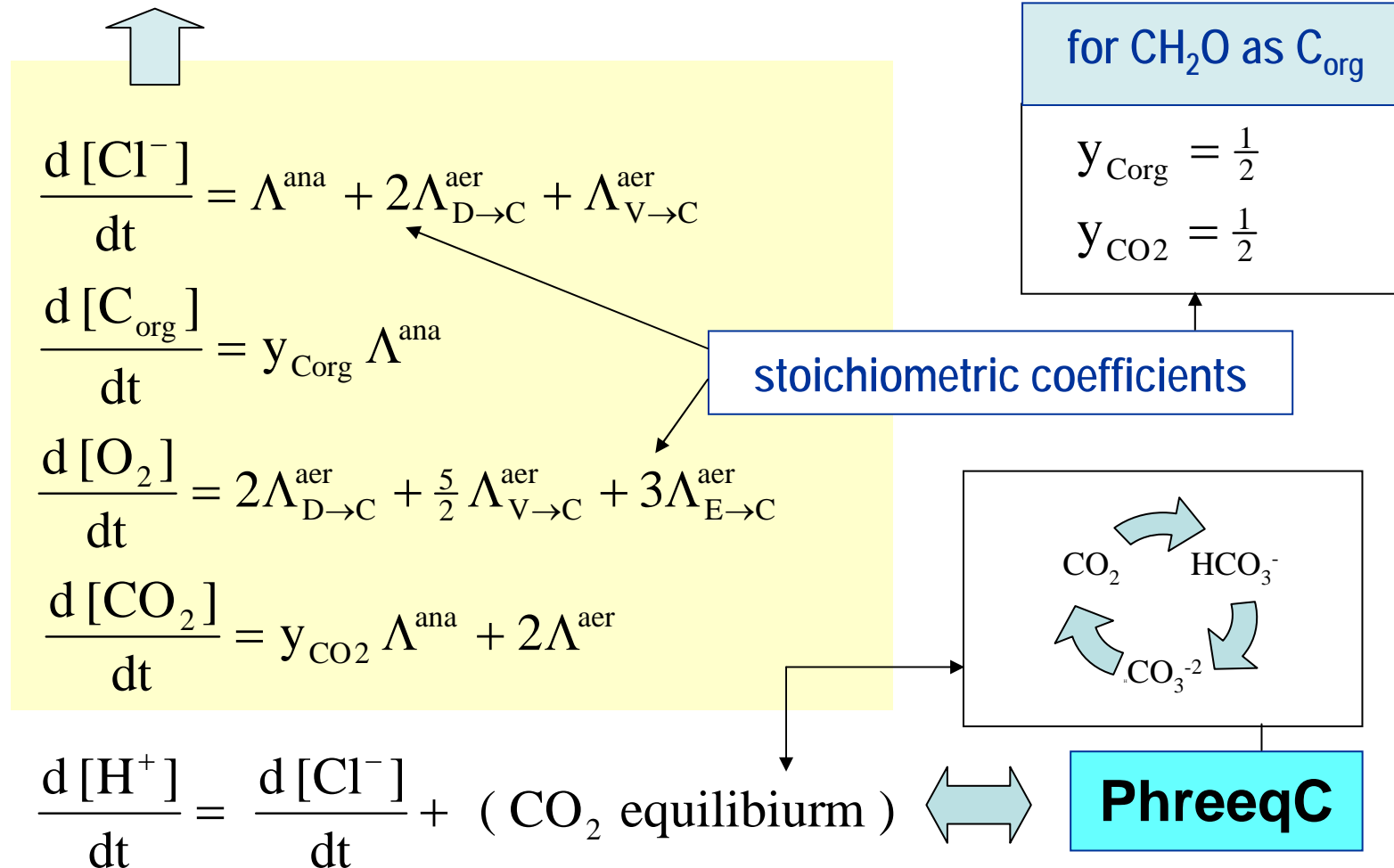
$$\frac{d [\text{CAH}]}{dt} = - \left(\Lambda_{\text{V} \rightarrow \text{E}}^{\text{ana}} + \Lambda_{\text{V} \rightarrow \text{C}}^{\text{aer}} \right)$$

abbreviations:

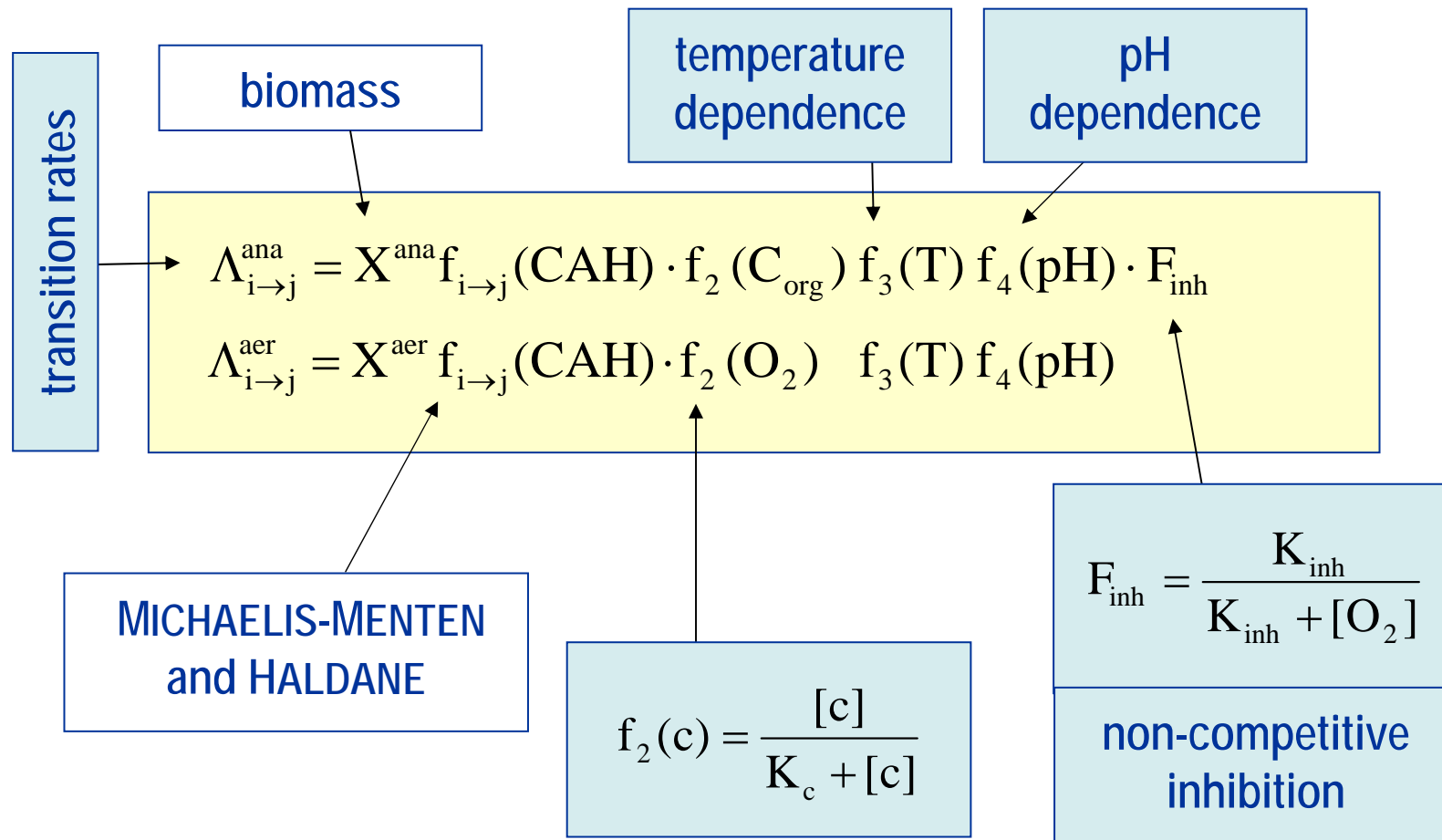
$$\Lambda^{\text{ana}} = \Lambda_{\text{P} \rightarrow \text{T}}^{\text{ana}} + \Lambda_{\text{T} \rightarrow \text{D}}^{\text{ana}} + \Lambda_{\text{D} \rightarrow \text{V}}^{\text{ana}} + \Lambda_{\text{V} \rightarrow \text{E}}^{\text{ana}}$$

$$\Lambda^{\text{aer}} = \Lambda_{\text{D} \rightarrow \text{C}}^{\text{aer}} + \Lambda_{\text{V} \rightarrow \text{C}}^{\text{aer}} + \Lambda_{\text{E} \rightarrow \text{C}}^{\text{aer}}$$

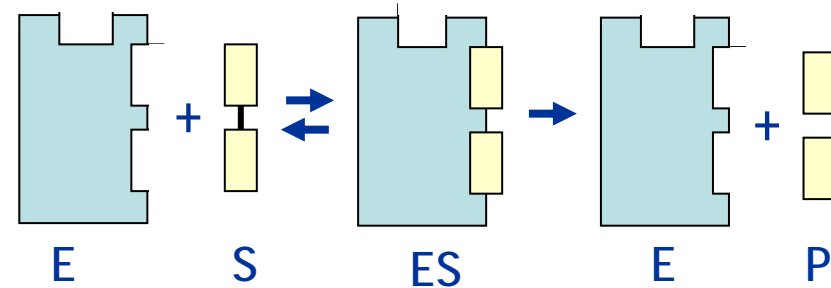
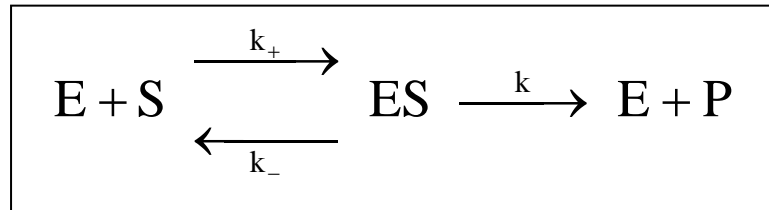
Biodegradation – Part II



Enzyme Kinetics – Rate Equation



MICHAELIS-MENTEN

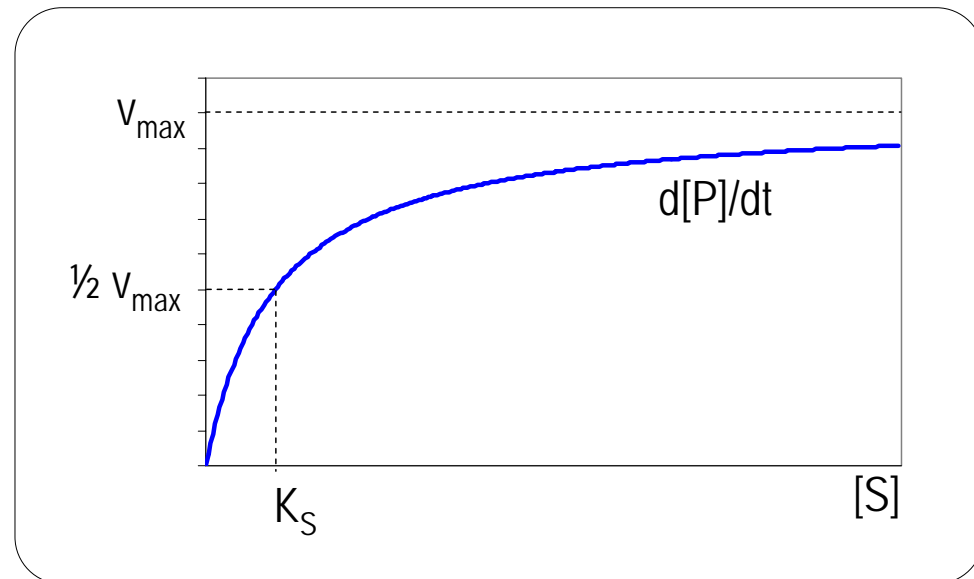


↓ steady state

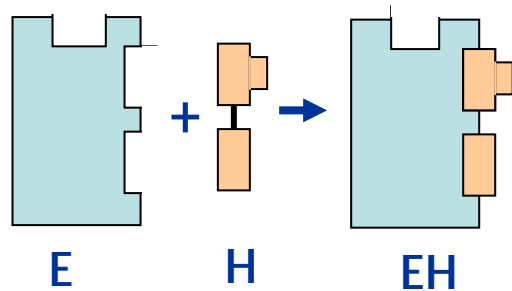
$$\frac{d[P]}{dt} = \frac{v_{\max} [S]}{K_S + [S]}$$

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

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

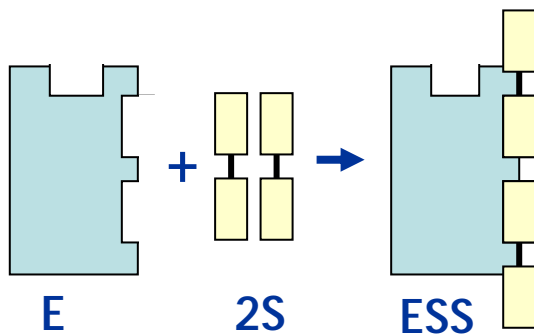


Enzyme Kinetics – Inhibition



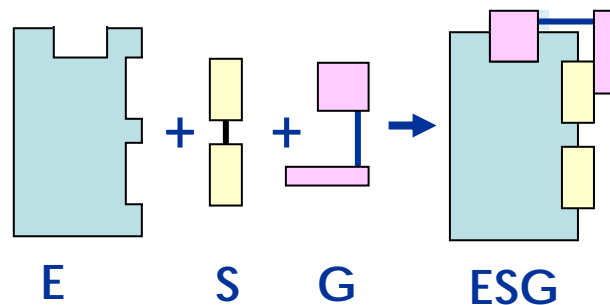
competitive
inhibition

$$\frac{v_{\max} [S]}{K_S I_1 + [S]} \quad I_1 = 1 + \frac{[H]}{K_1}$$



self-inhibition
(HALDANE)

$$\frac{v_{\max} [S]}{K_S + [S] I_2} \quad I_2 = 1 + \frac{[S]}{K_2}$$



non-competitive
inhibition

$$\frac{v_{\max} [S]}{K_S + [S]} \cdot \frac{1}{I_3} \quad I_3 = 1 + \frac{[G]}{K_3}$$

Kinetic Data

	k_i	K_i	K_{ii}	K_{i-1}	K_{i+1}
	$\mu\text{mol}/\mu\text{g}/\text{d}$	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

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

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

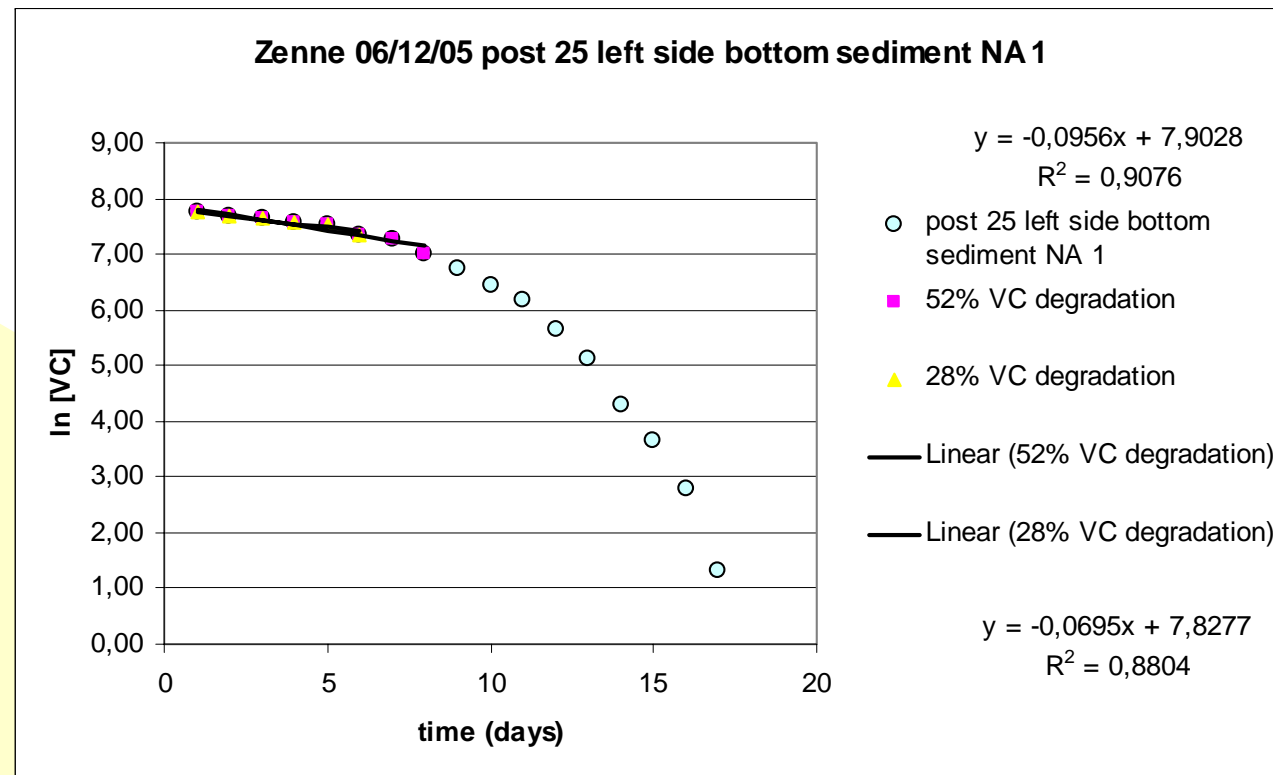
CAH-Modeling

EXAMPLE CALCULATIONS

Zenne VC

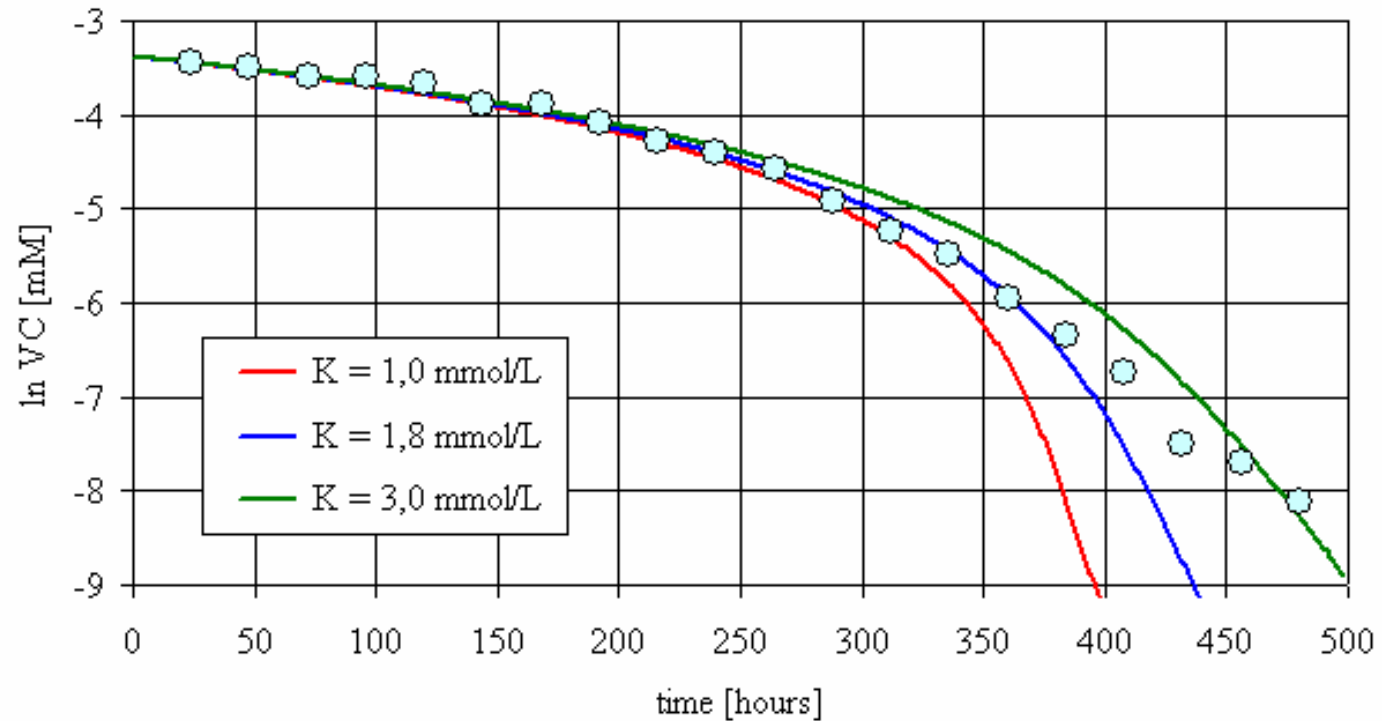
Zenne VC – Degradation Order ??

“KELLY’s Approach”



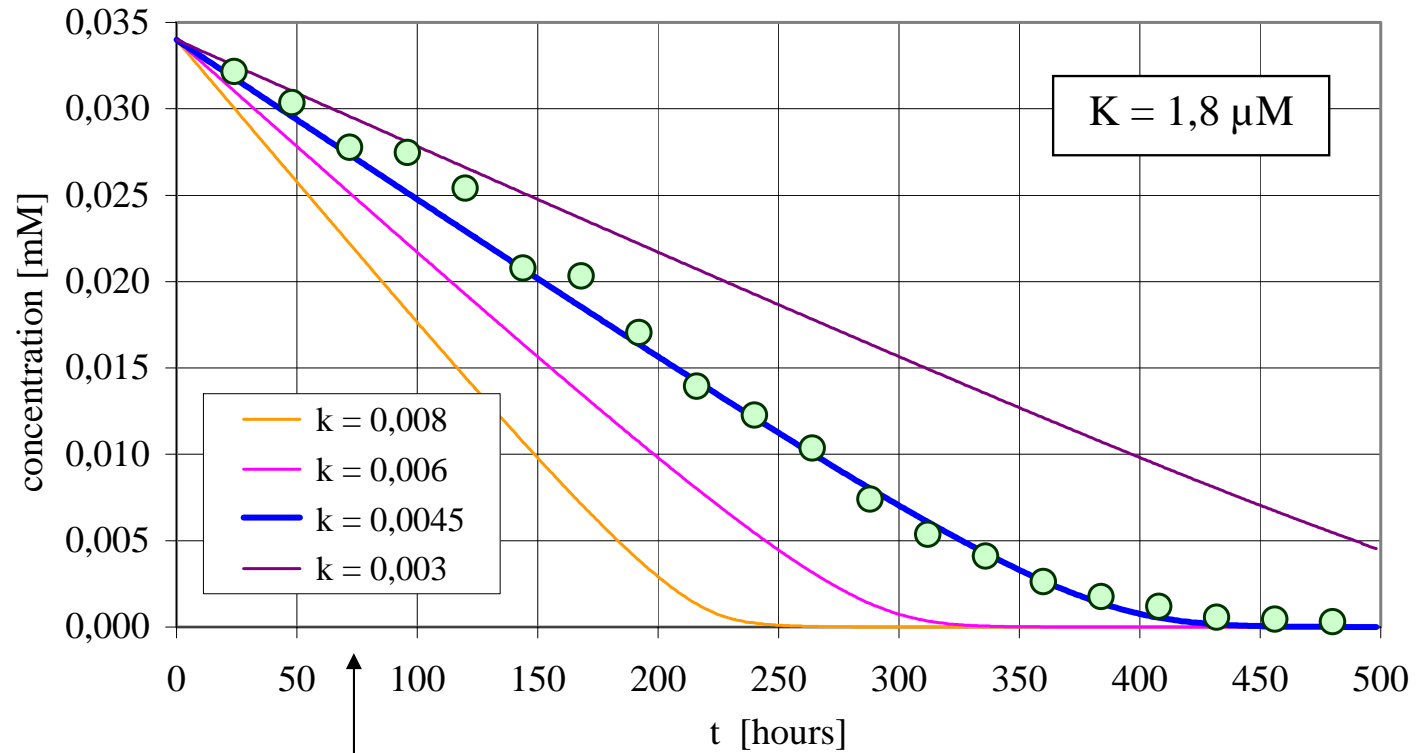
Zenne VC – Degradation Order

log-Scale



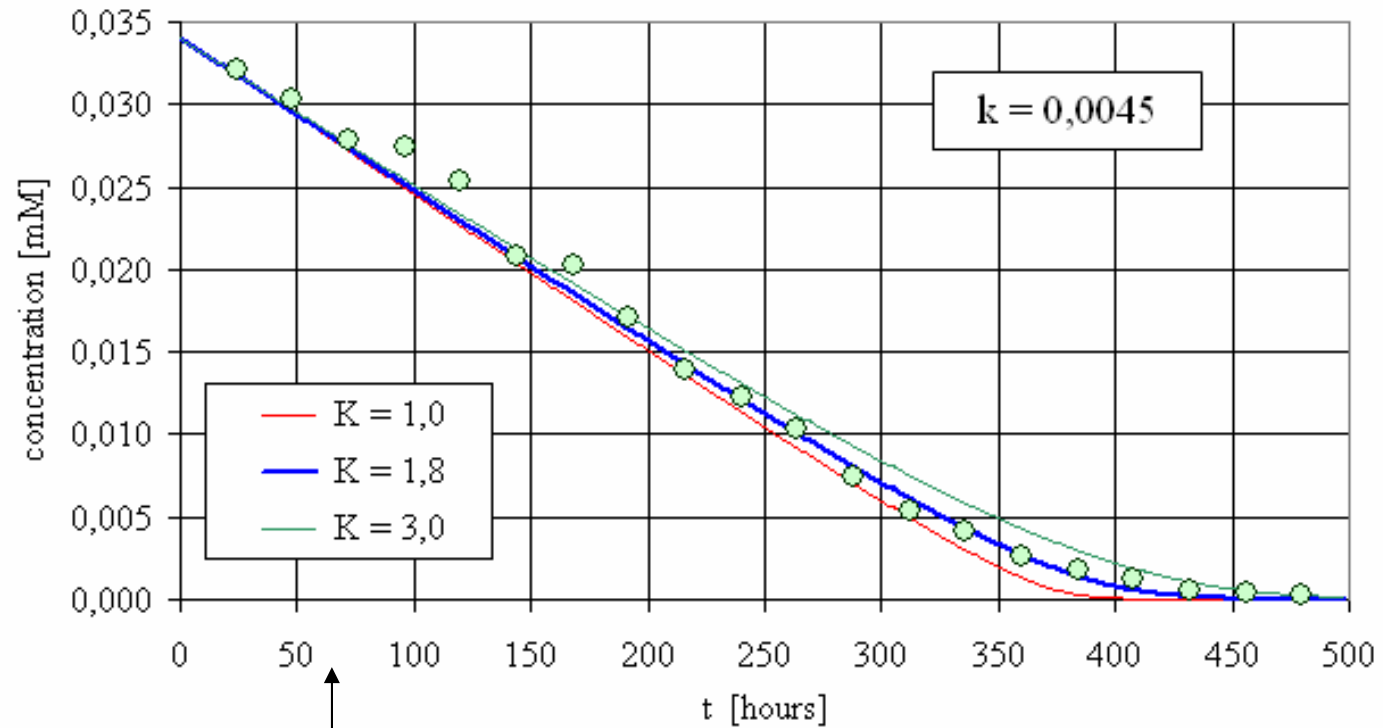
Michaelis-Menten = Kinetic 1st order + Kinetic 0th order

Zenne VC – Variation of k



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

Zenne VC – Variation of K



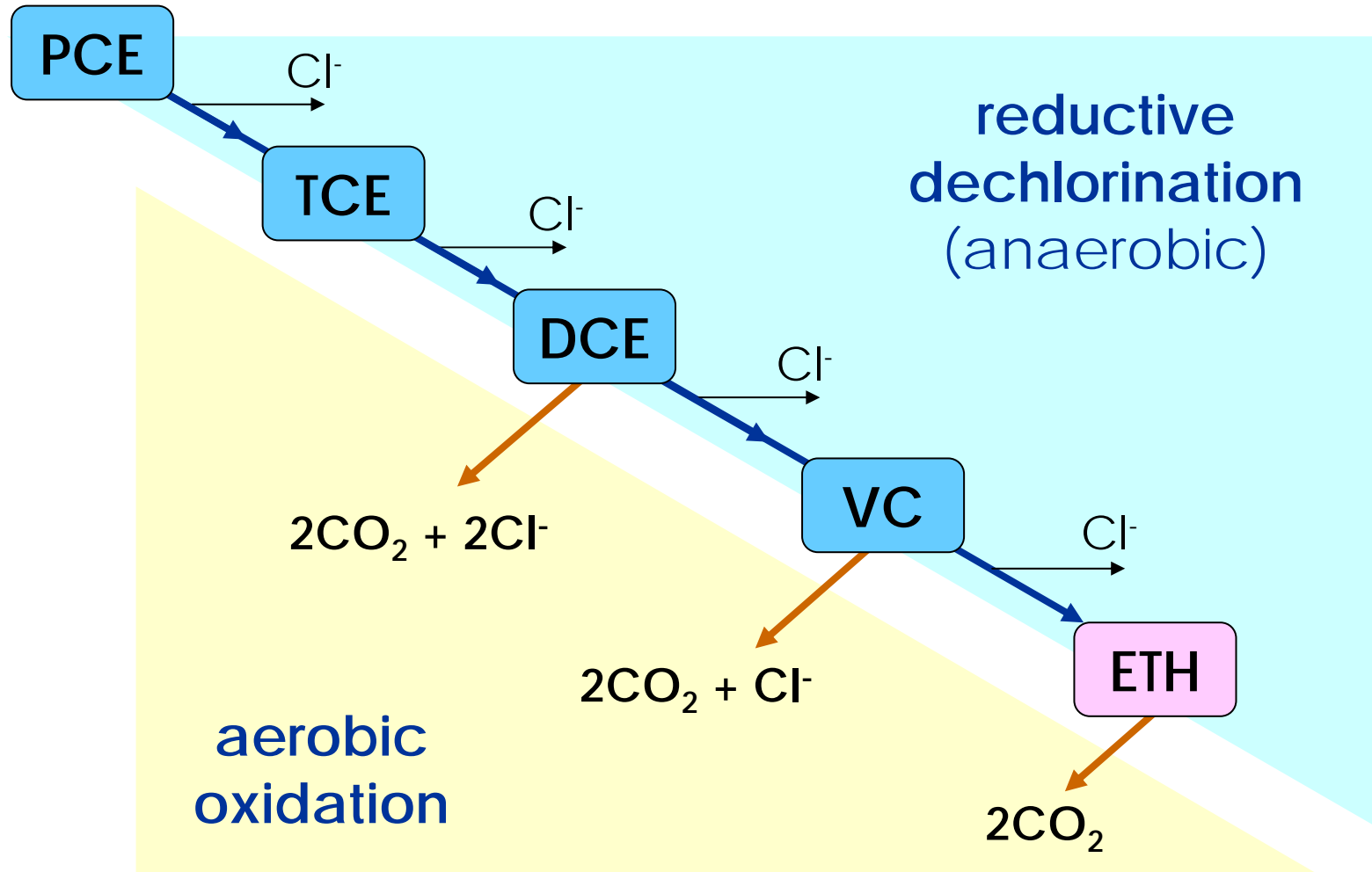
$$\text{rate} = \frac{kX}{K + [i] + [i]^2 / K_{ii}}$$

CAH-Modeling

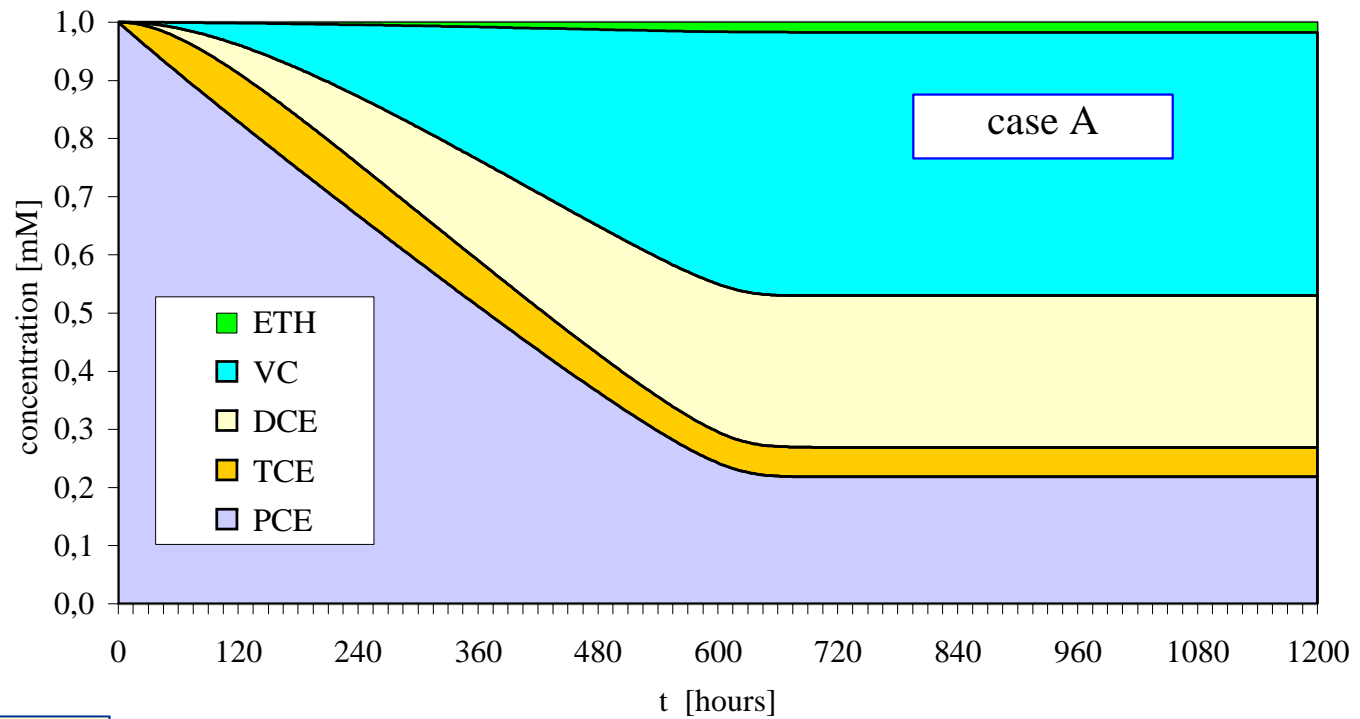
EXAMPLE

Mass Balance in Degradation Chain

Degradation Pathways



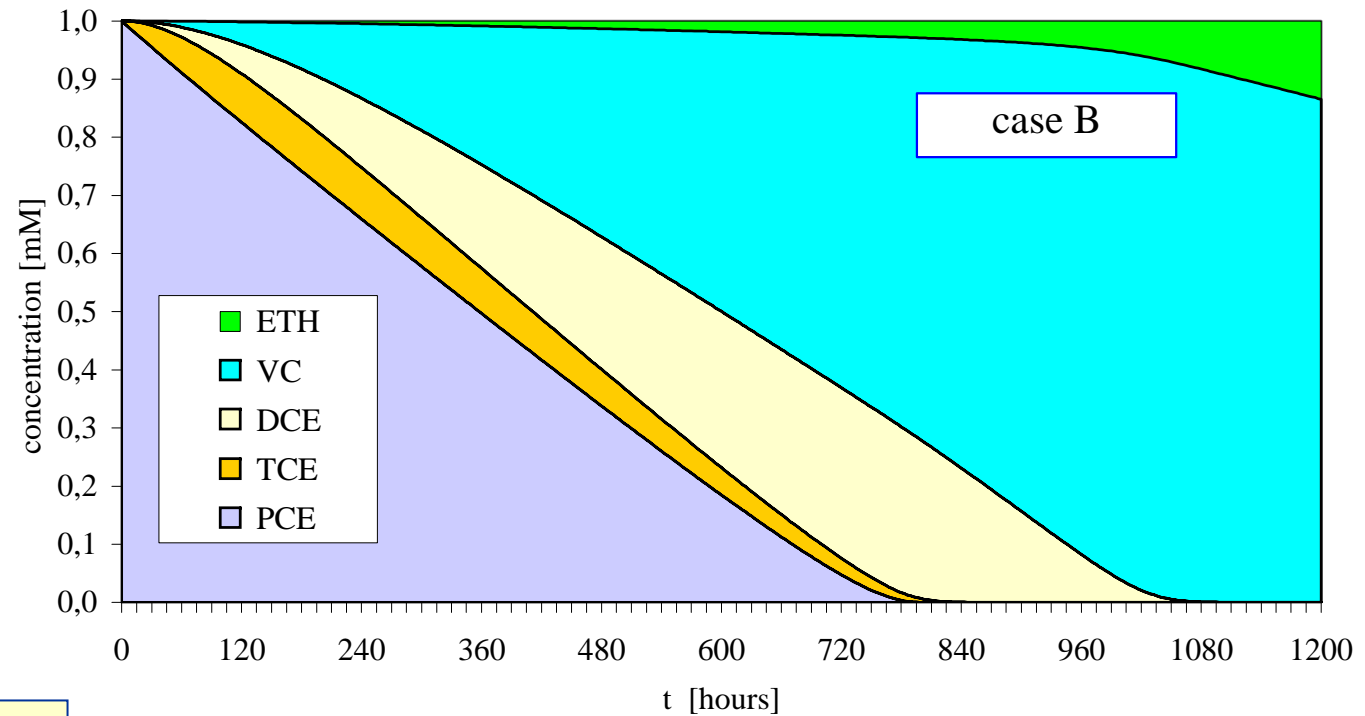
Example A



1 mM PCE
1 mM DOC

↑
DOC is exhausted

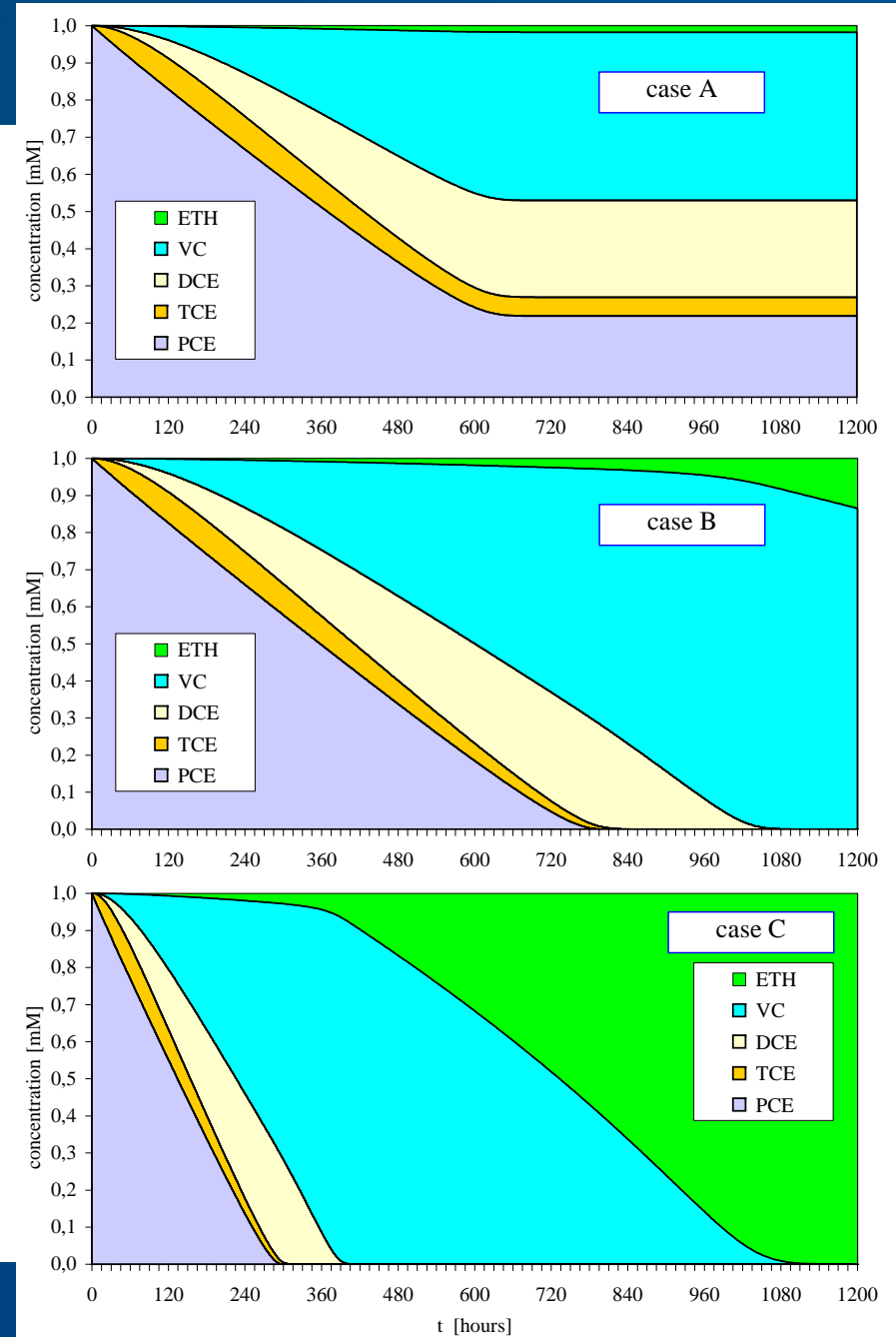
Example B



1 mM PCE
3 mM DOC

Degradation time too short

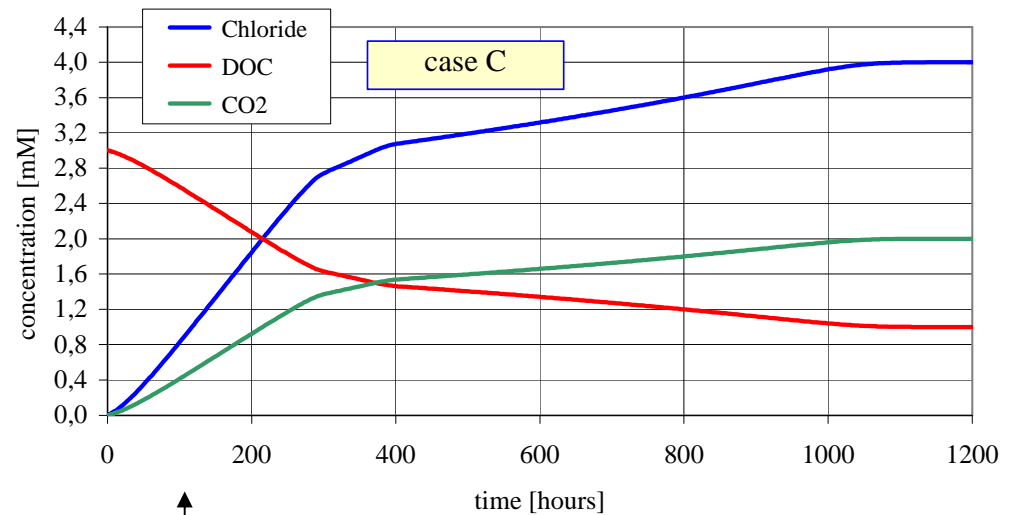
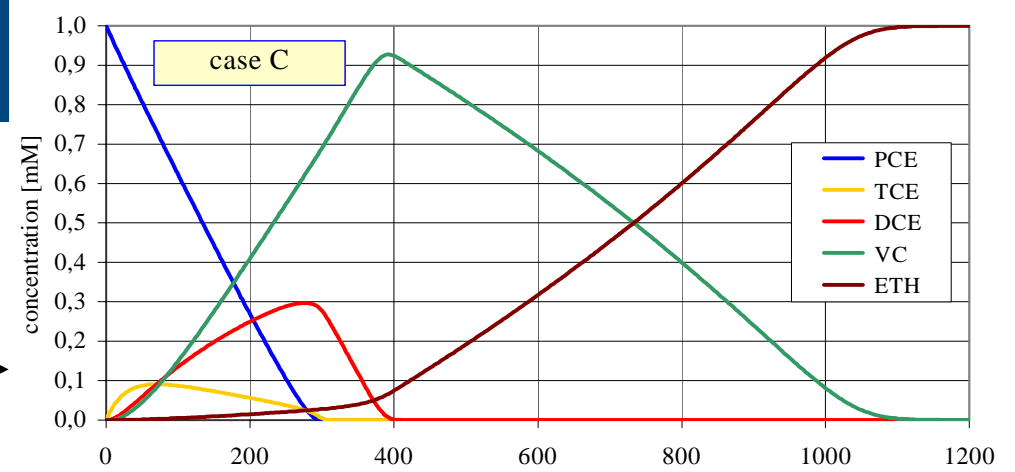
Example C



Complete CAH-Degradation →

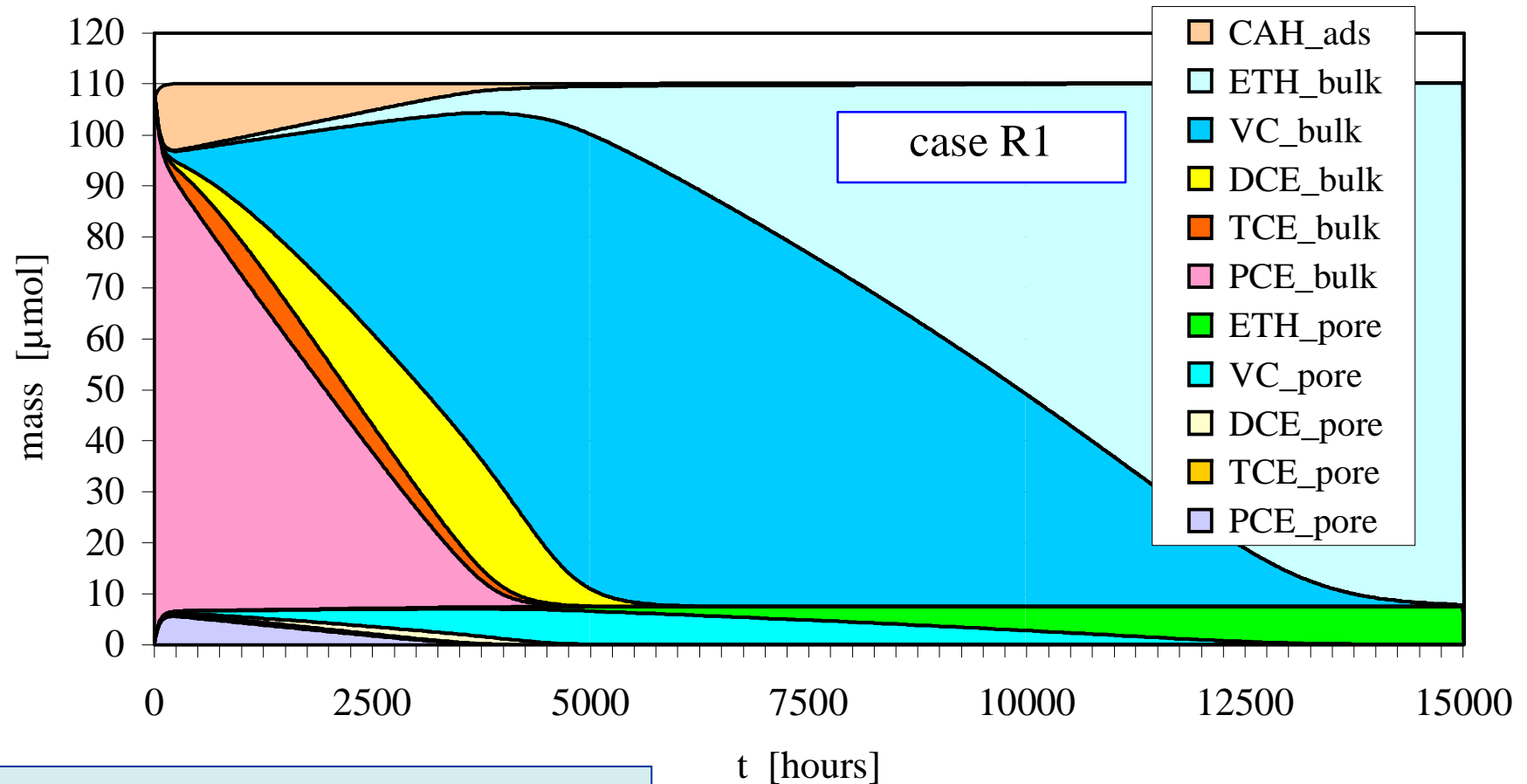
Example C

Intermediate Accumulation of DCE and VC



Degradation Products

Example R1 – Three Phases

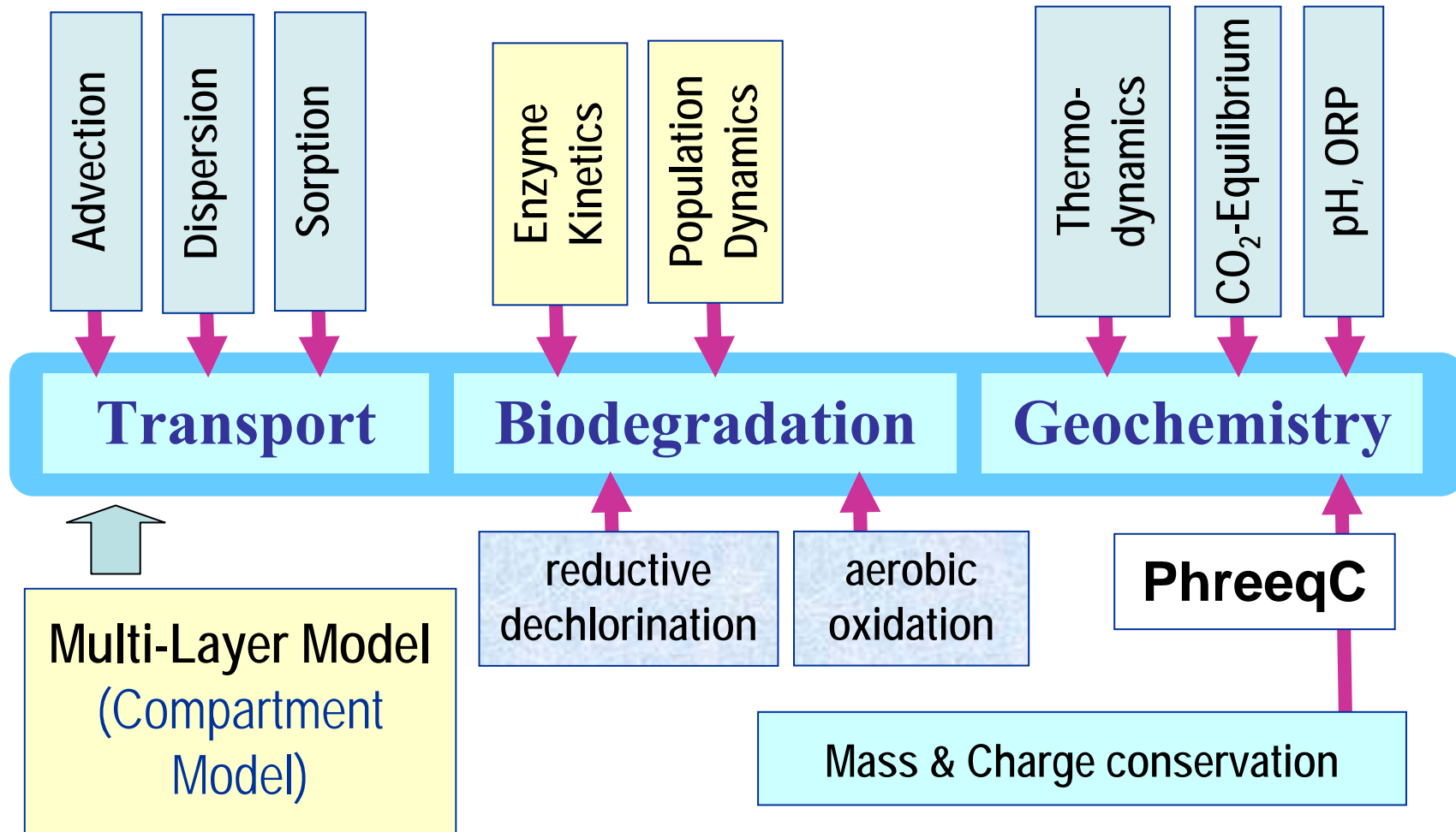


The Most General Case

CAH-Modeling

PROGRAM CAPABILITIES

Dynamical Model – Main Processes



SEDBARCAH Computer Program

Reactive Transport --- version 0.39

new start
 continue

dT [h] 3,00
 T [h] 1200

Chem without PhreeqC
 Chem with PhreeqC

kCHM 1
 kOUT 1
 kOUX 2

N cell = 40
 steps = 400
 T [PV] = 10,0
 area [m2] = 0,001385

with Dispersion
 with Adsorption
 with Reaction
 Population Dynamics
 with Ion Exchange

SEDBARCAH 2006

Input Directory: INP_03
 From Output Directory:
 To Output Directory: OUT

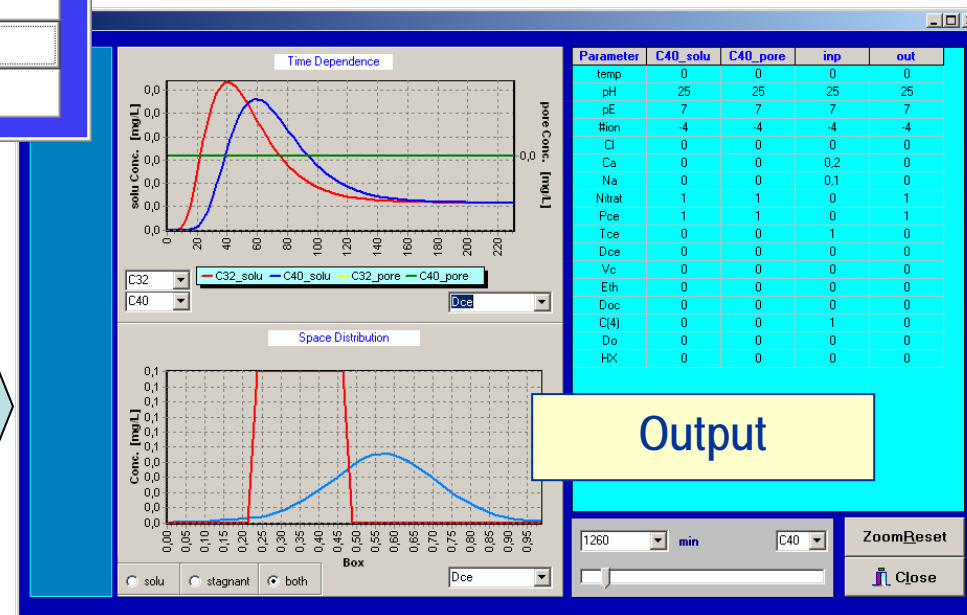
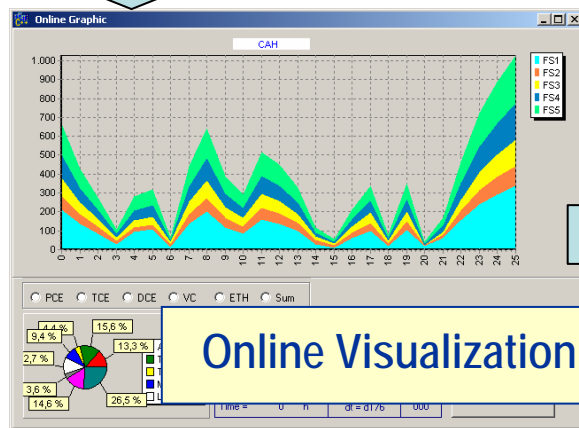
Graphics
 Run
 End

User Interface

fast C++ code

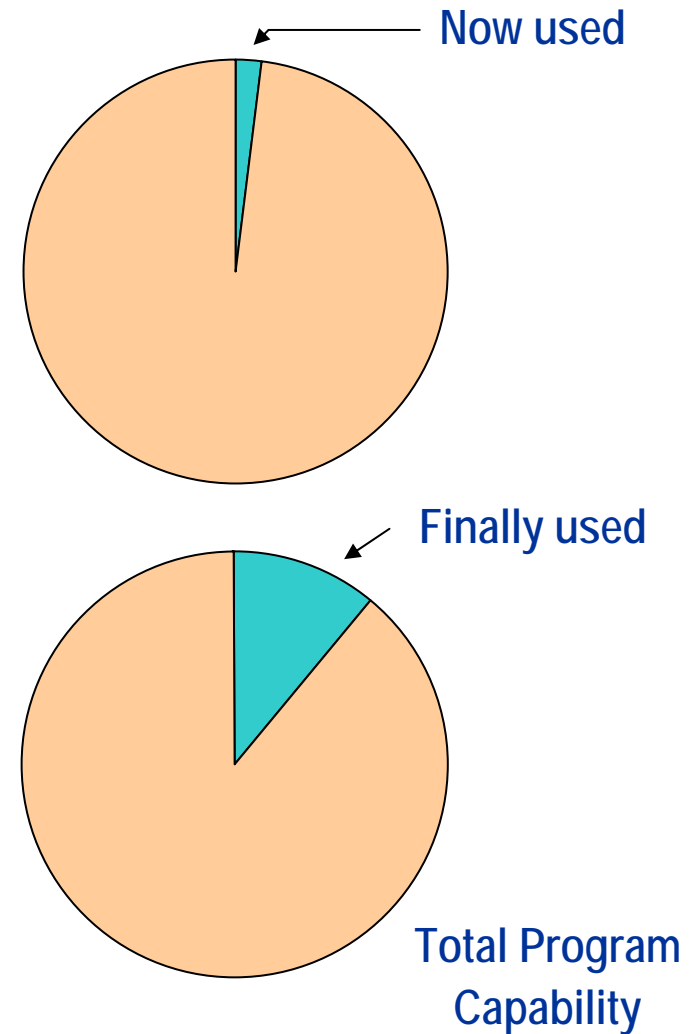
incl. PhreeqC

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		



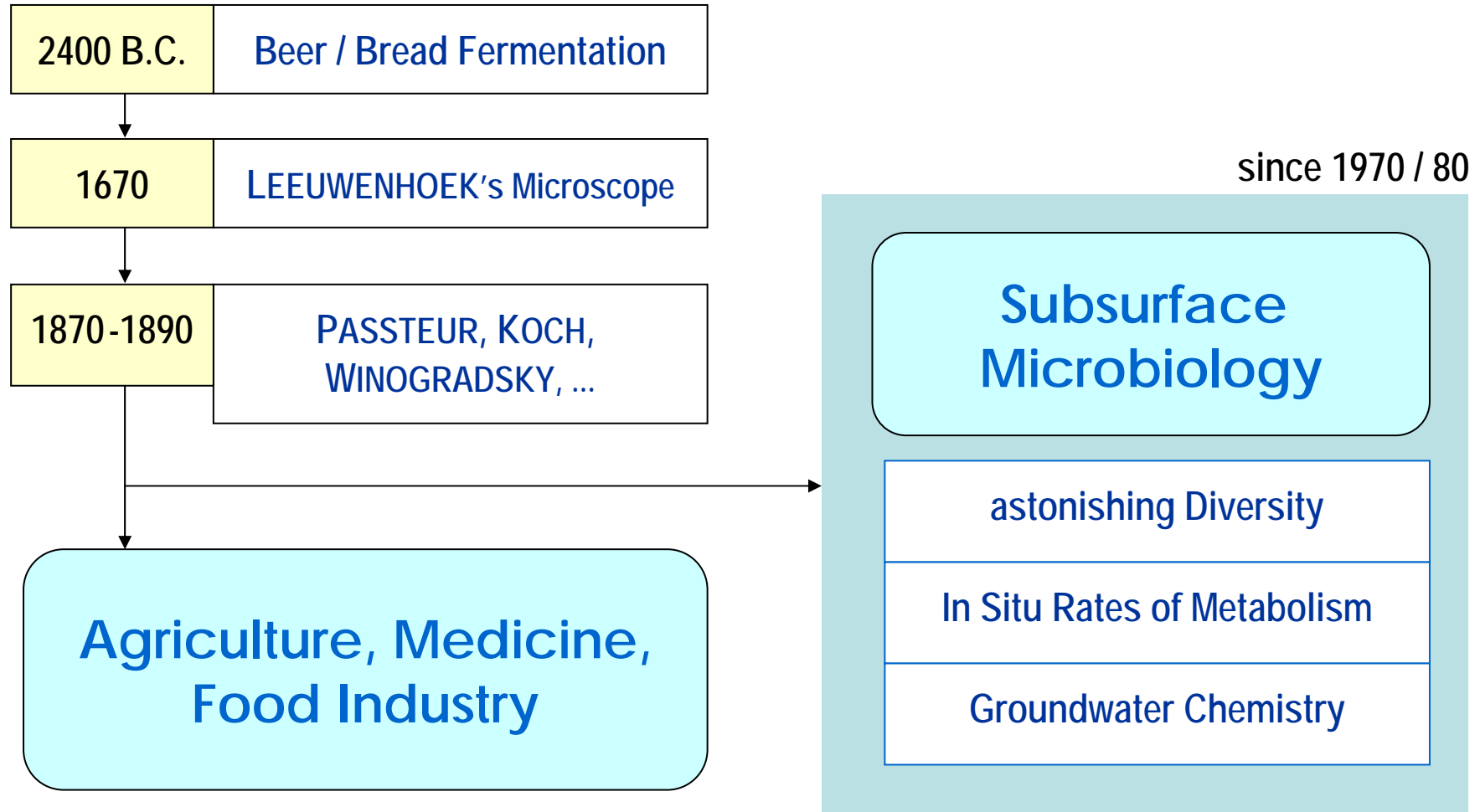
CAH-Modeling

BASIC PRINCIPLES

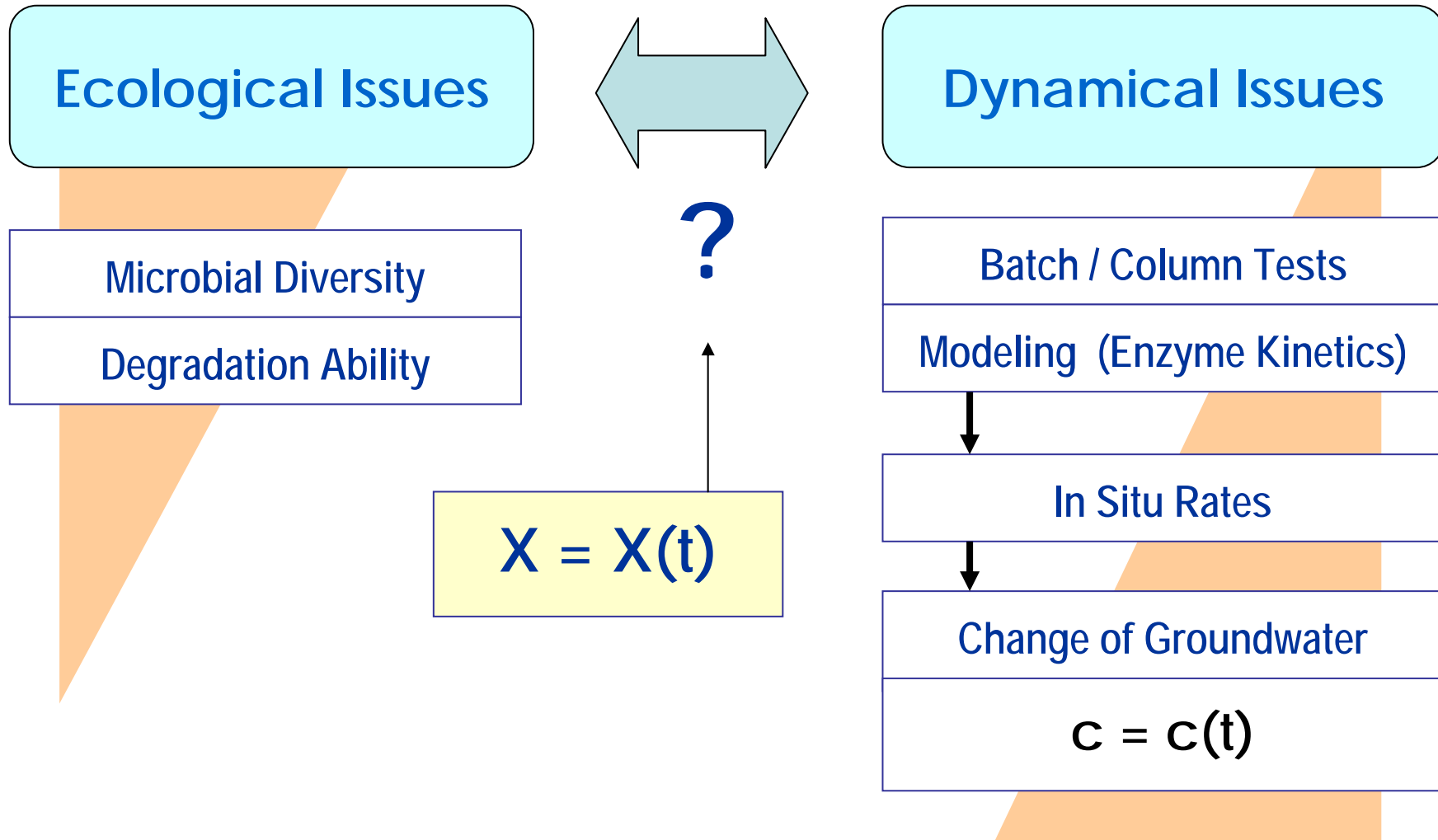
and

Open Questions

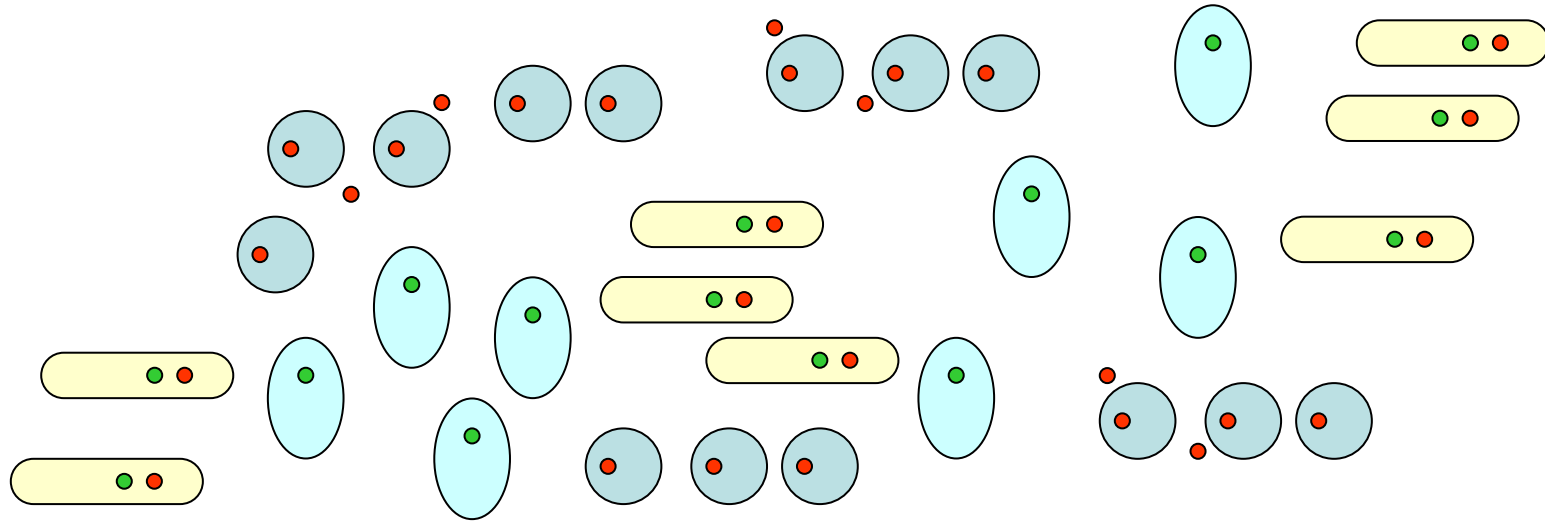
Microbiology



Interplay of Different "Sciences"



Population Density ?

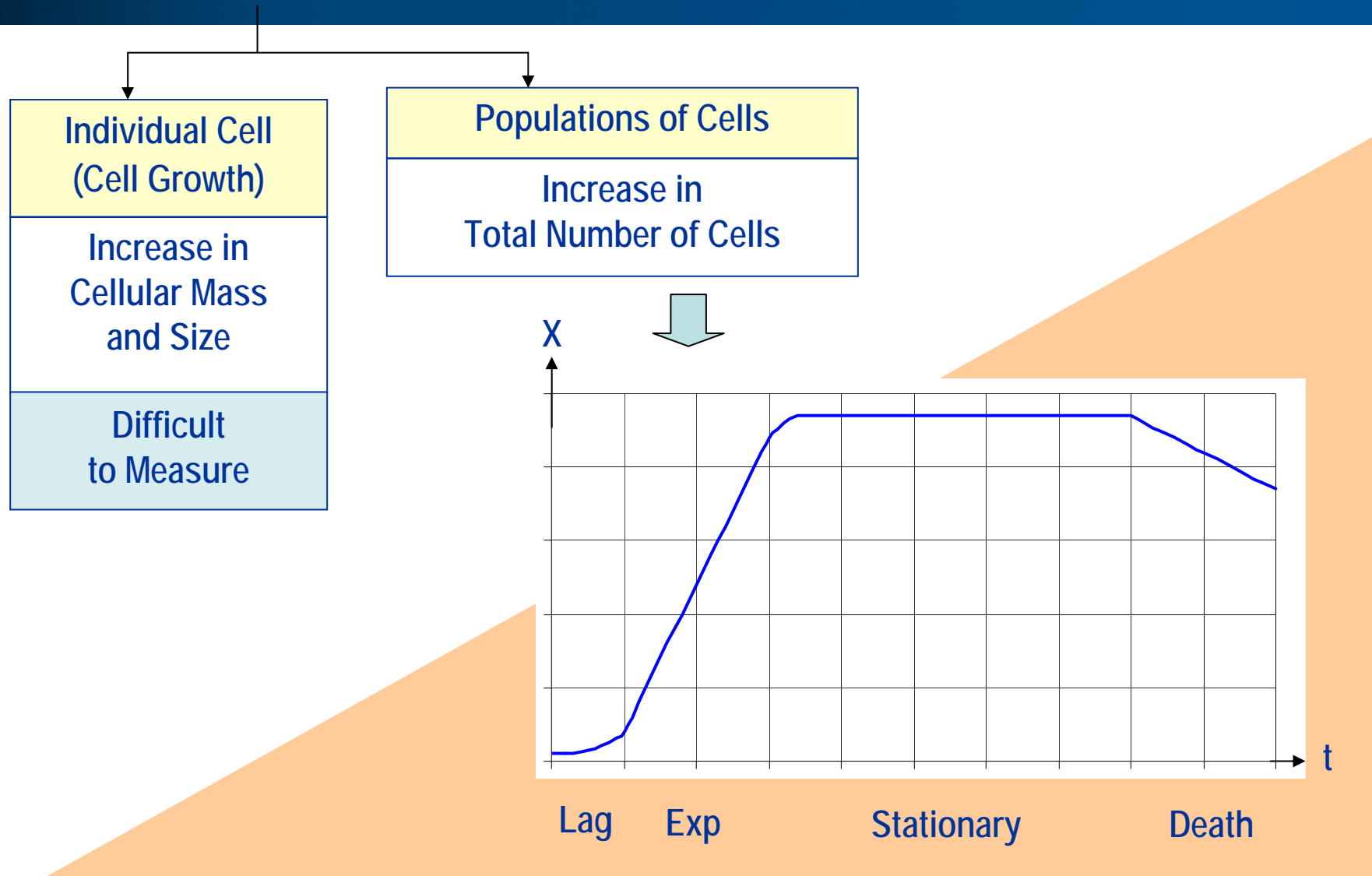


$$X_A \neq X_a$$

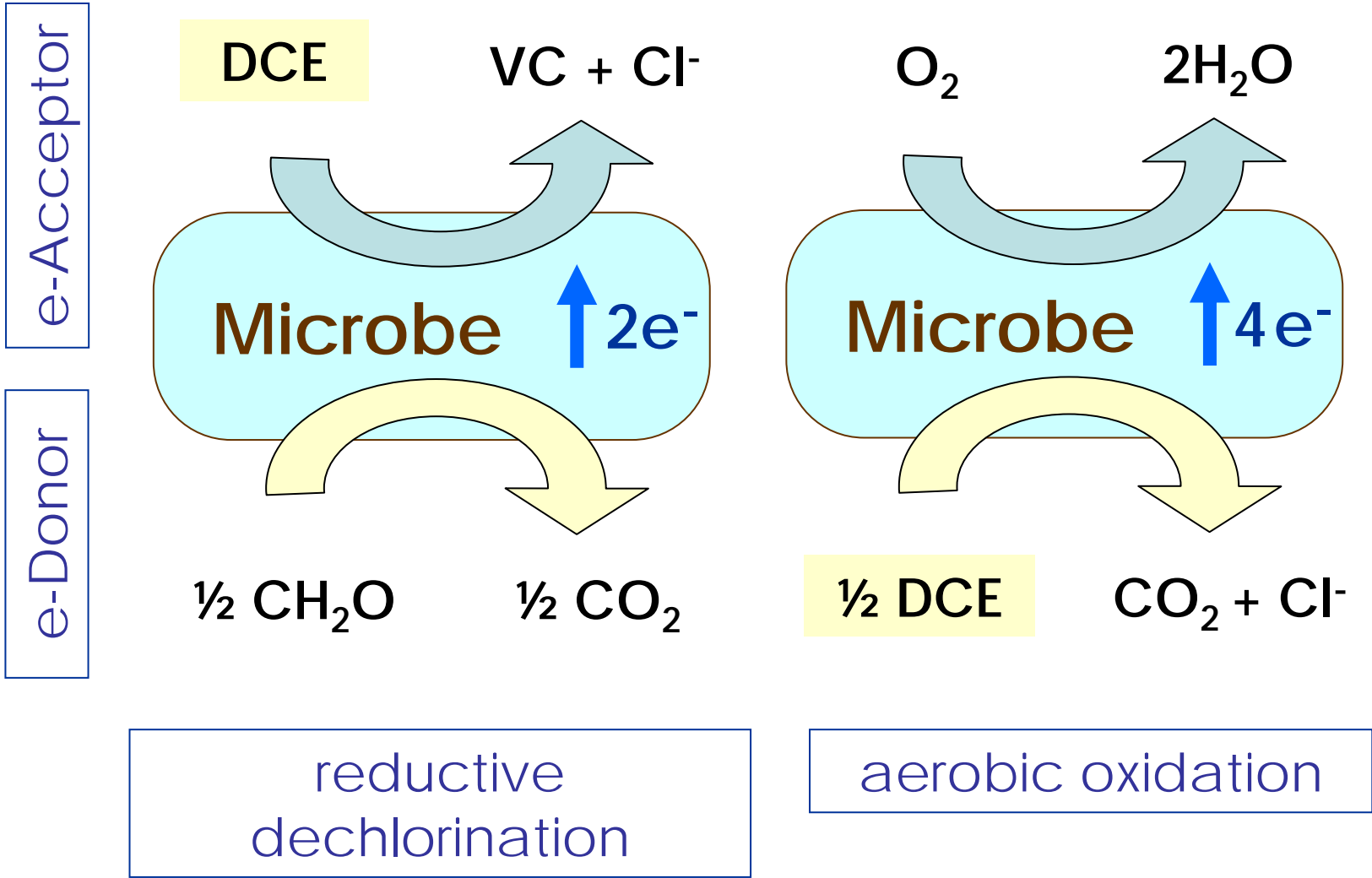
- enzyme A
- enzyme B

- strain a
- ▭ strain b
- strain c

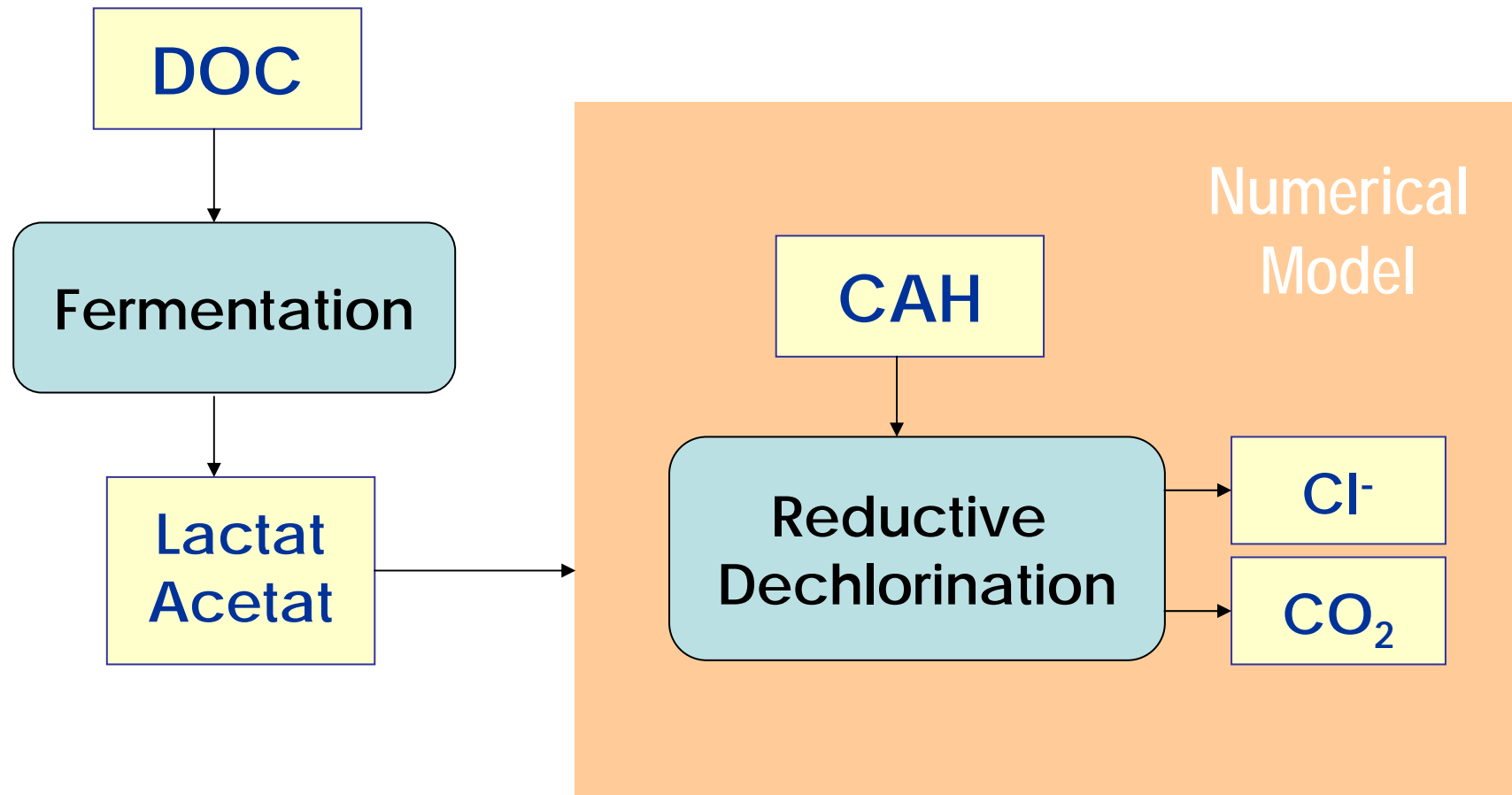
Bacterial Growth



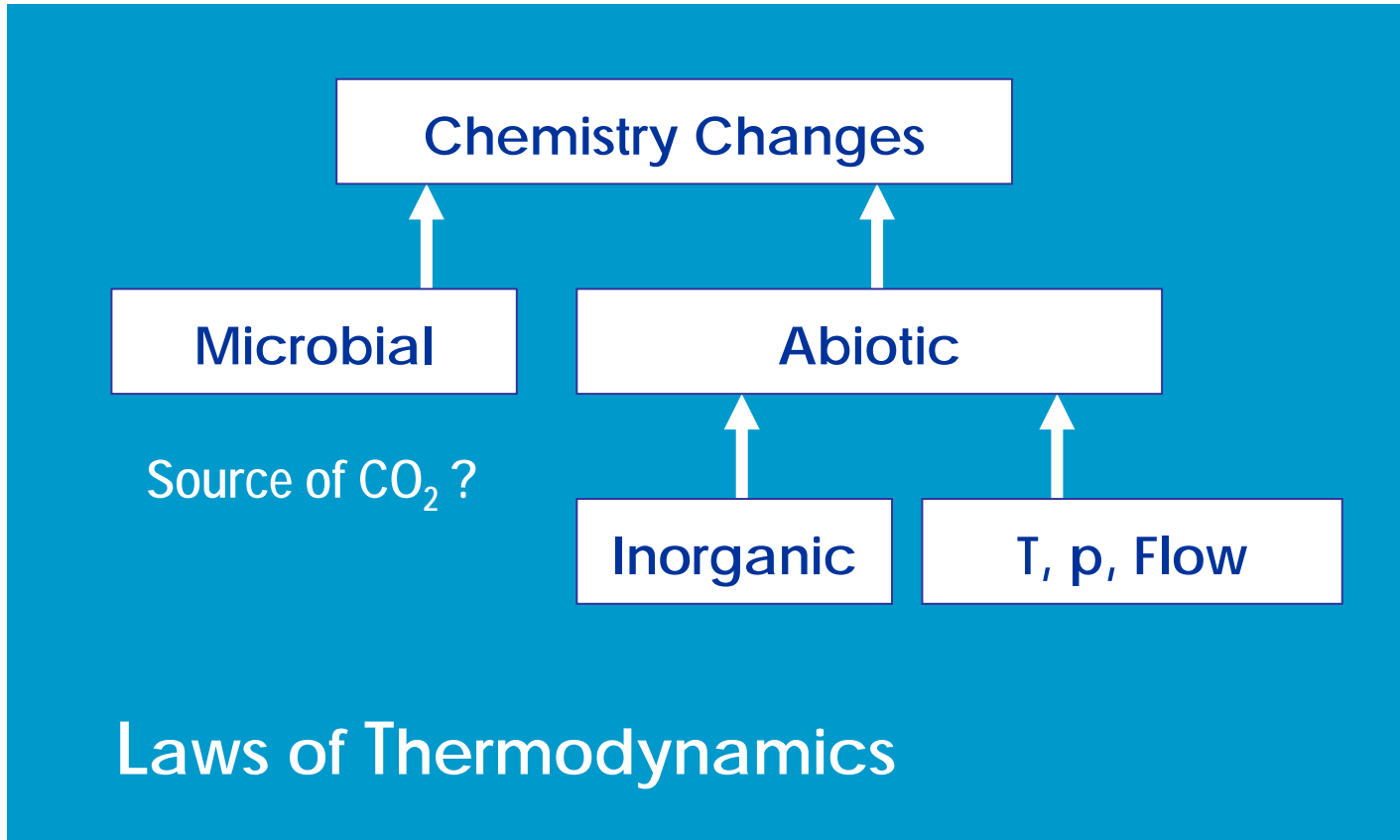
Electron Transfer



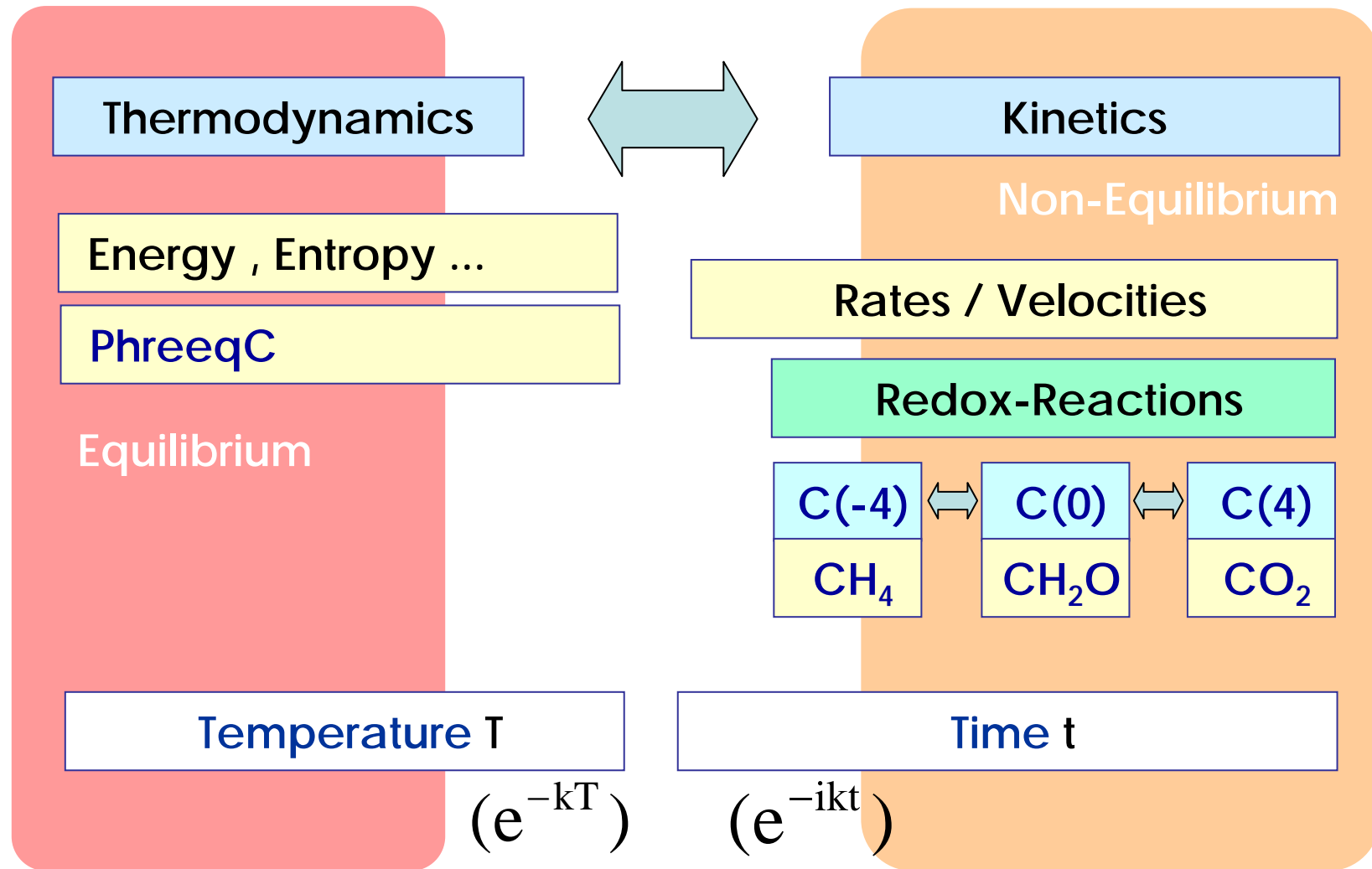
Complete Degradation Chain (Symbiosis)



Impact on Groundwater Chemistry



Equilibrium or Non-Equilibrium ?



CAH-Modeling

LINK TO GEOCHEMISTRY (PHREEQC)

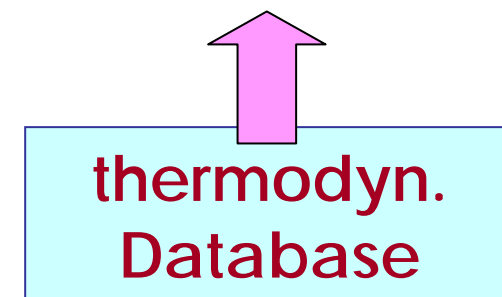
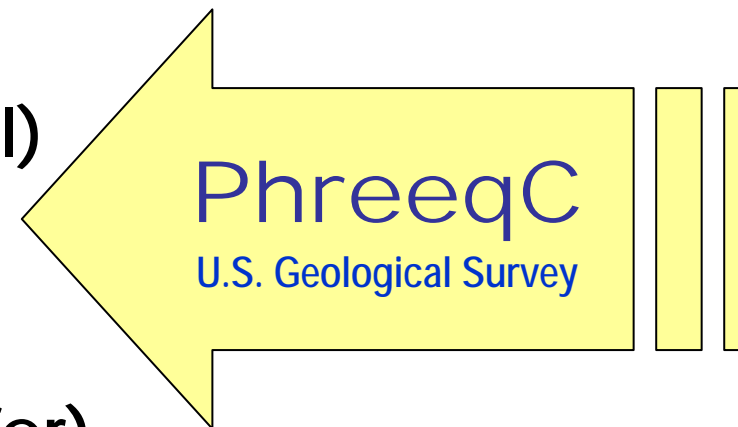
Water is more than H₂O

Dissolved Ions / Complexes:

H⁺, OH⁻, H₂O AlSO₄ Al(SO₄)₂⁻ Al³⁺, Al(OH)²⁺ AlHSO₄²⁺ AlOH²⁺ AlOH₃ Al(OH)₄⁻
CO₂ HCO₃⁻, MgHCO₃⁺ FeHCO₃ CaNCO₃⁺ MnHCO₃⁺ NiHCO₃⁺ ZnHCO₃⁺
NaHCO₃ UO₂CO₃ NiCO₃ PbHCO₃⁺ FeCO₃ MnCO₃ MgCO₃ ZnCO₃ CO₃²⁻
CaCO₃ PbCO₃ NaCO₃⁻ UO₂(CO₃)₂²⁻ Pb(CO₃)₂²⁻ (UO₂)₃(CO₃)₆⁶⁻ Ca²⁺ CaSO₄
CaHSO₄ CaOH⁺ Cl⁻ FeCl⁺ MnCl⁺ NiCl⁺ ZnCl⁺ FeCl₂⁺ UO₂Cl⁺ NiCl₂ MnCl₂ PbCl⁺
ZnCl₂ ZnOHCl FeCl₃ PbCl₂ UO₂Cl₂ MnCl₃⁻ ZnCl₃⁻ PbCl₃⁻ ZnCl₄²⁻ PbCl₄²⁻ Fe²⁺
FeSO₄ FeHSO₄⁺ FeOH⁺ Fe(OH)₂ Fe(OH)₃⁻ FeSO₄⁺ FeOH²⁺ Fe³⁺ Fe₂(OH)₂⁴⁺
Fe(OH)₂⁺ FeHSO₄²⁺ Fe₃(OH)₄⁵⁺ Fe(OH)₃ Fe(OH)₄⁻ H₂, K⁺ KSO₄⁻ Mg²⁺ MgSO₄
Mg(OH)⁺ Mn²⁺ MnSO₄ MnOH⁺ Mn(OH)₃⁻ Mn³⁺ MnO₄²⁻ Na⁺ NaSO₄⁻ Ni²⁺ NiSO₄
Ni(SO₄)₂²⁻ NiOH⁺ Ni(OH)₂ Ni(OH)₃⁻ O₂ PbSO₄ Pb²⁺ Pb(SO₄)₂²⁻ PbOH⁺ Pb(OH)₂
Pb₂OH³⁺ Pb(OH)₃⁻ Pb(OH)₄²⁻ Pb₃(OH)₄²⁺ SO₄²⁻ HSO₄⁻ ZnSO₄ Zn(SO₄)₂²⁻
UO₂SO₄ UO₂(SO₄)₂²⁻ UO₂²⁺ UO₂OH⁺ (UO₂)₂OH³⁺ (UO₂)₂(OH)₂²⁺ UO₂(OH)₃⁻
(UO₂)₃(OH)₄²⁺ (UO₂)₃(OH)₅⁺ (UO₂)₄(OH)₇⁺ UO₂(OH)₄²⁻ (UO₂)₃(OH)₇⁻ Zn²⁺
ZnOH⁺ Zn(OH)₂ Zn(OH)₃⁻ Zn(OH)₄²⁻ ... and so on

Complete Hydrochemistry

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



More Info: SEDBARCAH project
Deliverable D12

www.aquac.de/model.html

*End of
presentation.*