Project no.: 511254 (STREP)

**SEDBARCAH**

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

# Reactive Transport & Biodegradation Model

# (Part I)

Harald Kalka

Short Lecture at the Meeting
Wageningen, January 2006

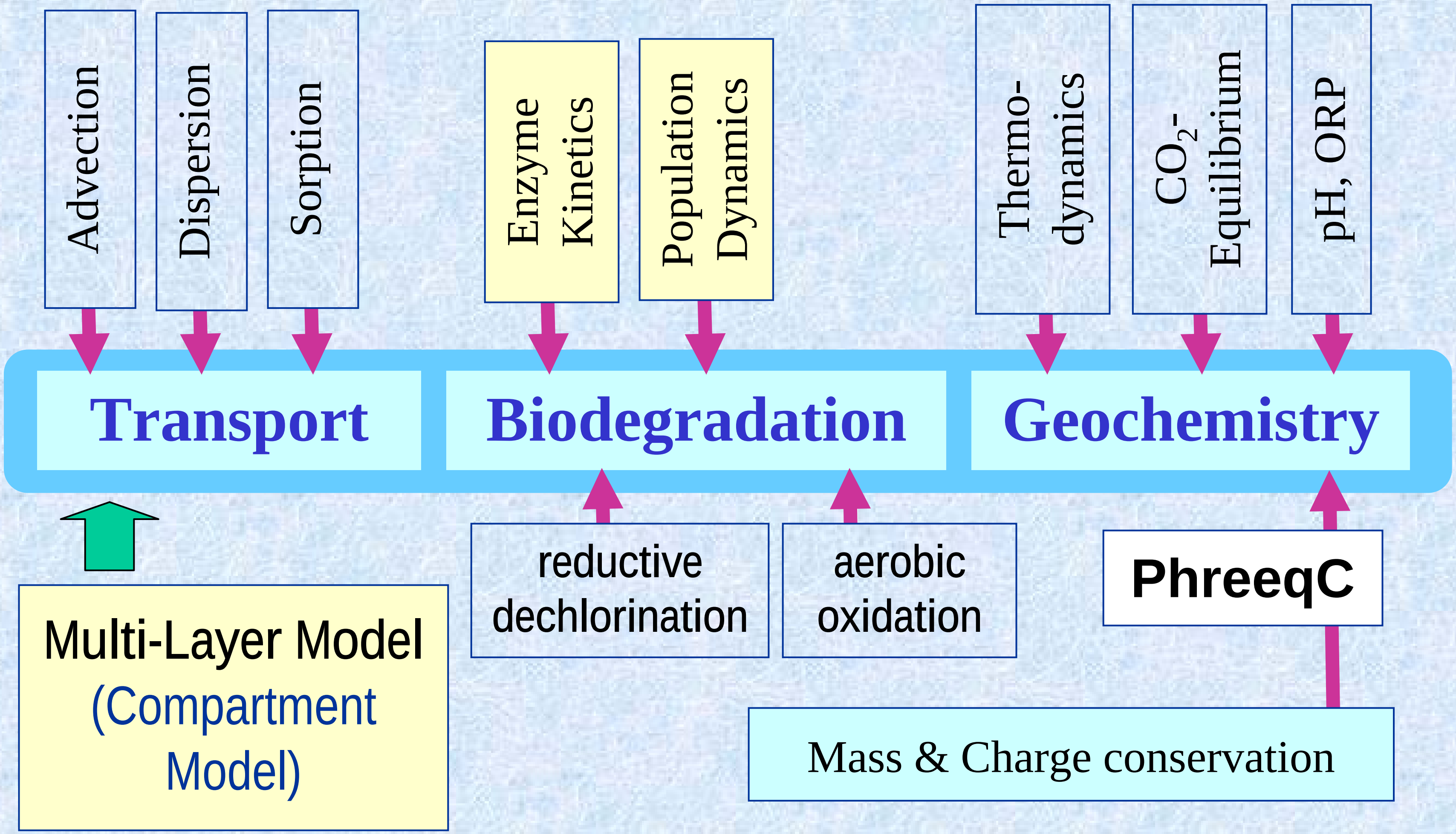
Start date of project: 01/01/2005 Duration: 2 years
Lead contractor for Work Package 5 (Modeling): UIT GmbH Dresden

# Reactive Transport and CAH-Biodegradation Model

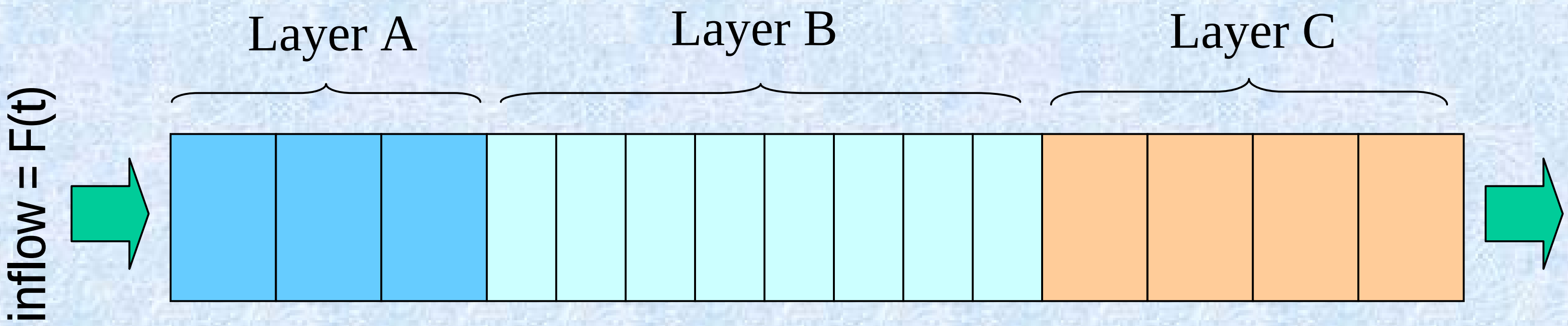
SEDBARCAH

| | |
|---|---|
| 1 | Basic Equations |
| 2 | Transport Phenomena |
| 3 | Enzyme Kinetics |
| 4 | Model Parameters |
| 5 | Software Presentation / Examples |

# Main Processes



# Multi-Layer Model (Compartments)




Transport & Reactions along a flow line

1 Model for 2 Tasks

- Column Experiments
- Field-Scale Applications
  - Zenne Site
  - Pelhrimov Site

Batch Reactions (only kinetics)

# Basic Equation (ADR)

multi-species model

$i = CAH's, Cl^-, DOC, O_2, CO_2$ ...

$$R \frac{\partial c_i}{\partial t} = -v \frac{\partial c_i}{\partial x} + D_L \frac{\partial^2 c_i}{\partial x^2} + \Phi_{bio}(c_i, c_j)$$

sorption

advection

dispersion

biodegradation

$PCE \rightarrow TCE$

$TCE \rightarrow DCE$

⋮

Set of Partial Differential Equations (PDE)

# Operator Splitting

$$\frac{\partial c}{\partial t} = \Phi\, c \qquad \Phi = \Phi_{adv} + \Phi_{disp} + \Phi_{bio}$$

$c^n \to c^{n+1}$

$$c^{n+1/3} = \tilde{\Phi}_{adv}\,(c^n, \Delta t)$$

$$c^{n+2/3} = \tilde{\Phi}_{disp}\,(c^{n+1/3}, \Delta t)$$

$$c^{n+3/3} = \tilde{\Phi}_{bio}\,(c^{n+2/3}, \Delta t)$$

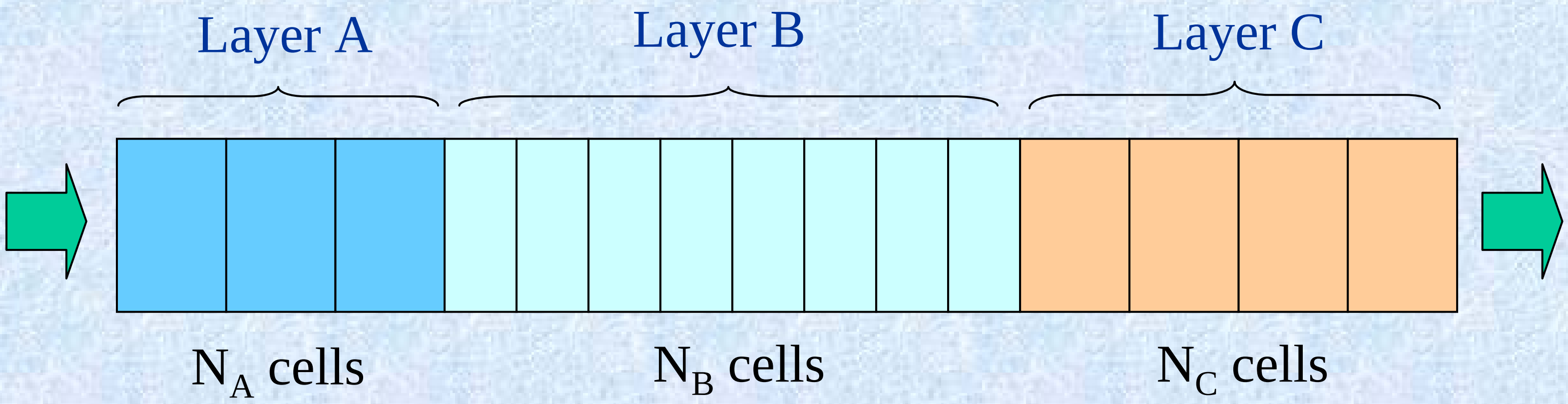
FD method

$m$ intermediate steps $\Delta t / m$

$k$ intermediate steps $\Delta t / k$

Runge-Kutta for ODE

# Cell size & Time step




$$\Delta V_{pore} = \text{const} = \varepsilon_A A \Delta x_A = \varepsilon_B A \Delta x_B = \ldots$$

$$\Delta x_L = \frac{L_L}{N_L}$$

flow: $$Q = \frac{\Delta V_{pore}}{\Delta t} = \text{const}$$

pore velocity: $$v_L = \frac{Q}{\varepsilon_L A} = \frac{\Delta x_L}{\Delta t}$$

$$\Delta t = \frac{\Delta V_{pore}}{Q} = \frac{A \varepsilon_L \Delta x_L}{Q} = \text{const}$$

# Analytical Solution

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D_L\frac{\partial^2 c}{\partial x^2} - \lambda c$$

$$c = 0 \quad \text{for} \quad t = 0, \quad x > 0$$

$$c = c_0 \quad \text{for} \quad x = 0, \quad t > 0$$

$$c = 0 \quad \text{for} \quad x = \infty, \quad t > 0$$

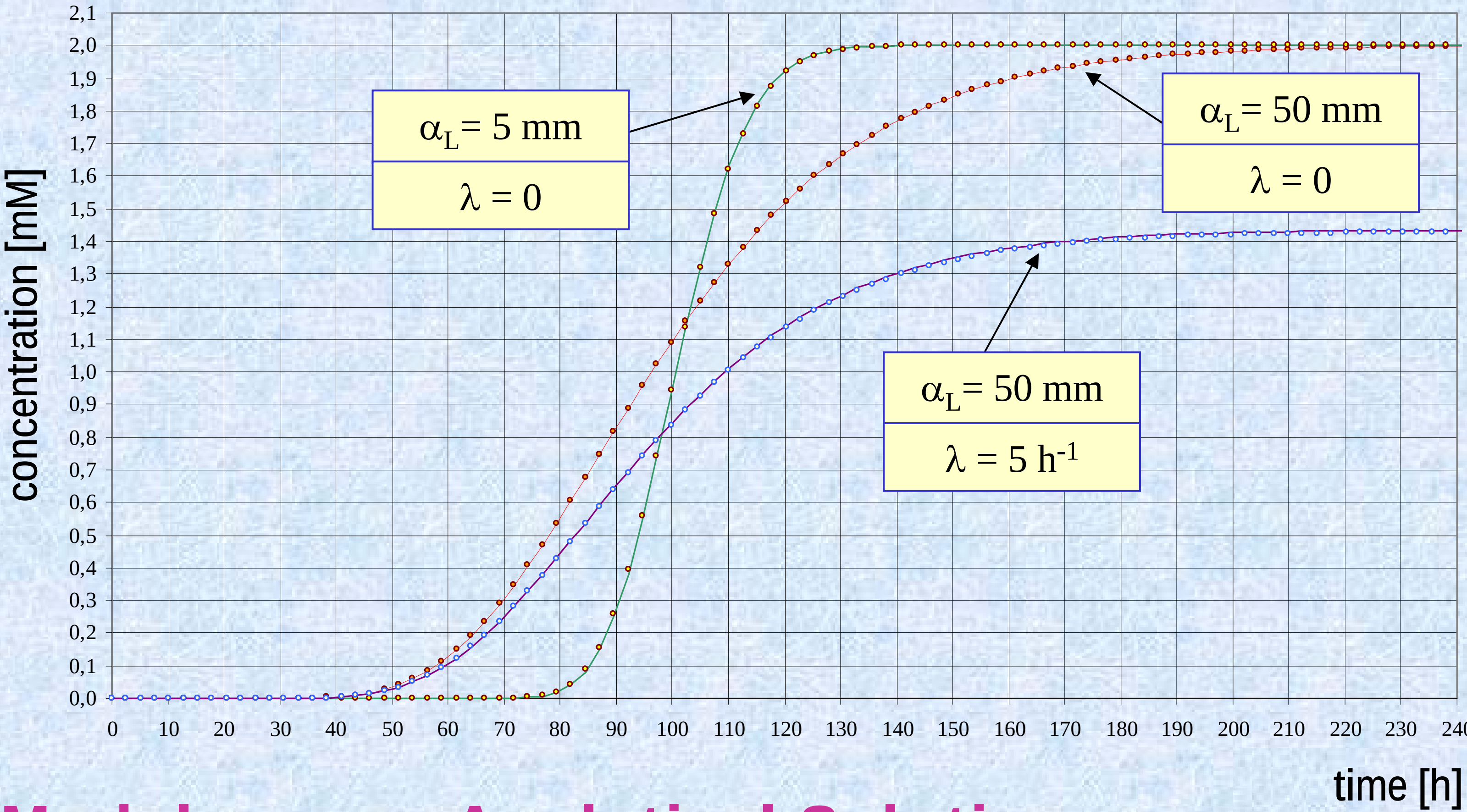
$$c(x,t) = \frac{c_0}{2}\left\{ \exp\frac{x(v-w)}{2D} \cdot \operatorname{erfc}\frac{x(v-w)}{\sqrt{4Dt}} + \exp\frac{x(v+w)}{2D} \cdot \operatorname{erfc}\frac{x(v+w)}{\sqrt{4Dt}} \right\}$$

$$\operatorname{erfc} x = \frac{2}{\sqrt{\pi}}\int_x^\infty \exp(-t^2)\,dt$$

$$w = \sqrt{v^2 + 4D\lambda}$$

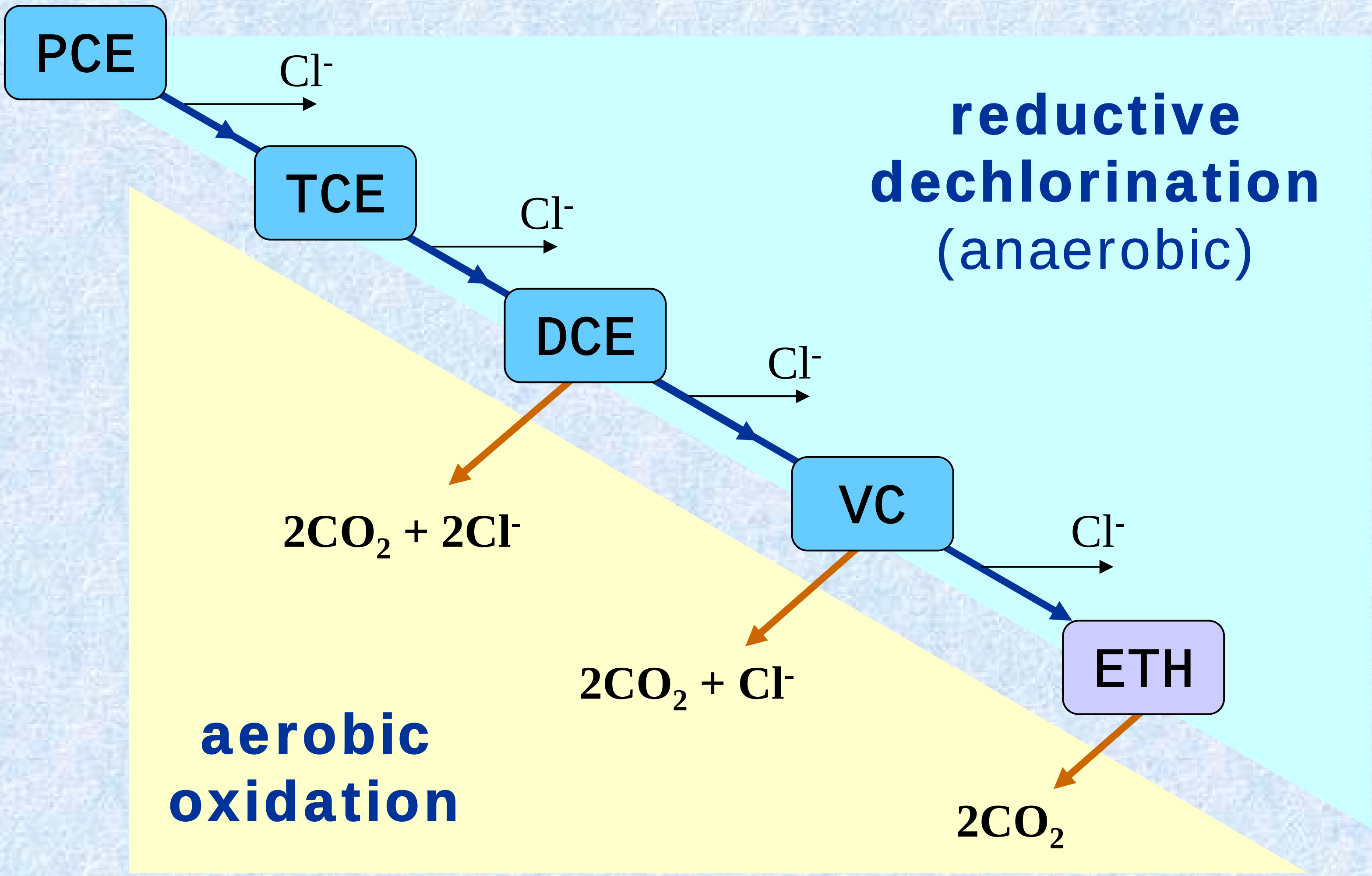
# Numerical Test

| | |
|---|---|
| N = 40 cells | |
| v = 9.8 mm/h | L = 1 m |
| $\Delta t$ = 2.56 h | $c_0$ = 2 mM |

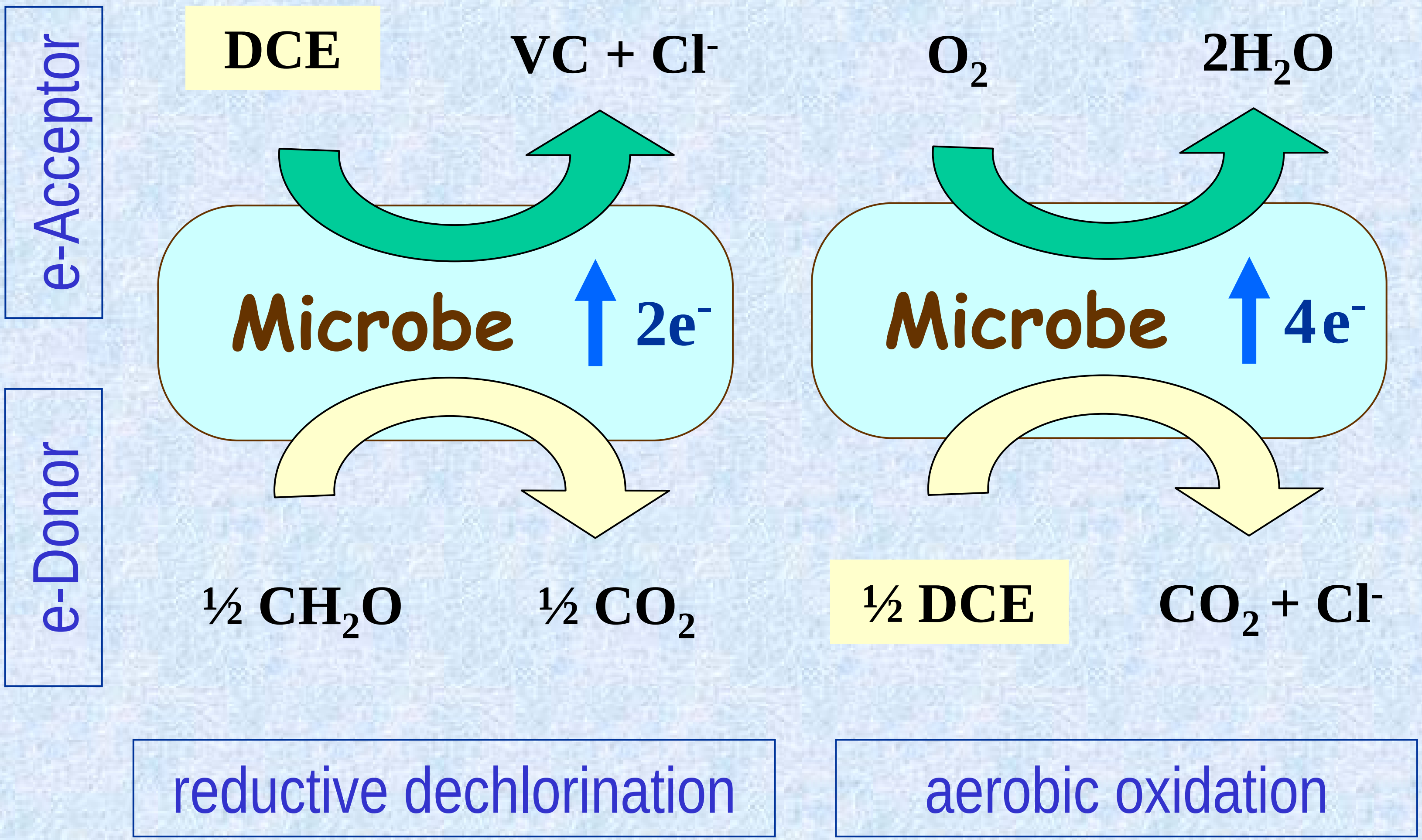



# Model versus Analytical Solution

# Degradation Pathways



# Electron Transfer



# Electron Balance

$$CHCl{=}CHCl + H^{+} + 2e^{-} \rightarrow CHCl{=}CH_2 + Cl^{-}$$

$$CH_2O + H_2O \rightarrow CO_2 + 4H^{+} + 4e^{-}$$

$$DCE + \tfrac{1}{2}C_{org} + \tfrac{1}{2}H_2O \rightarrow VC + \tfrac{1}{2}CO_2 + H^{+} + Cl^{-}$$

**anaerobic**

**aerobic**

$$CHCl{=}CHCl + 4H_2O \rightarrow 2CO_2 + 10H^{+} + 8e^{-} + 2Cl^{-}$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow H_2O$$

$$DCE + 2O_2 \rightarrow 2CO_2 + 2H^{+} + 2Cl^{-}$$

# Biodegradation ODE (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 ODE (part II)

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

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

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

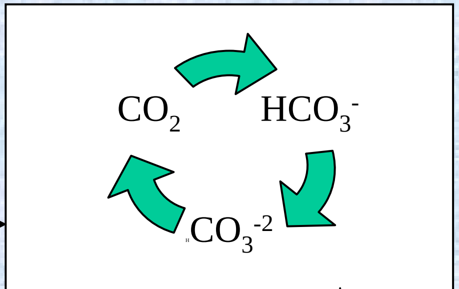
$$\frac{d[CO_2]}{dt} = y_{CO2}\,\Lambda^{ana} + 2\Lambda^{aer}$$

for $CH_2O$ as $C_{org}$

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

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

stoichiometric coefficients




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

**PhreeqC**

# Population Dynamics

biomass

2 populations

$$\frac{dX^{ana}}{dt} = Y^{ana}\Lambda^{ana} - k_d^{ana} X^{ana}$$

$$\frac{dX^{aer}}{dt} = Y^{aer}\Lambda^{aer} - k_d^{aer} X^{aer}$$

yield coefficient

death rate

stationarity

$$\frac{dX}{dt} = 0$$

# Environmental Factors

- Temperature (ARRHENIUS behavior)
- pH microorgs prefer pH = 6.5 .. 7.5
  **but:** production of org. acids, HCl
- ORP ( anaerobic / aerobic )
- Moisture Content
- Nutrients C:N:P = 120:10:1
- Inhibiting or Toxic Compounds

# Enzyme Kinetics (part I)

transition rates

biomass

temperature dependence

pH dependence

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

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

MICHAELIS-MENTEN and HALDANE

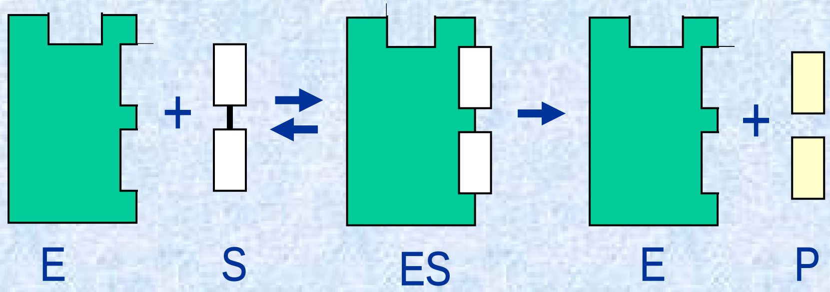
$$f_2(c) = \frac{[c]}{K_c + [c]}$$

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

non-competitive inhibition

# MICHAELIS-MENTEN Kinetics

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

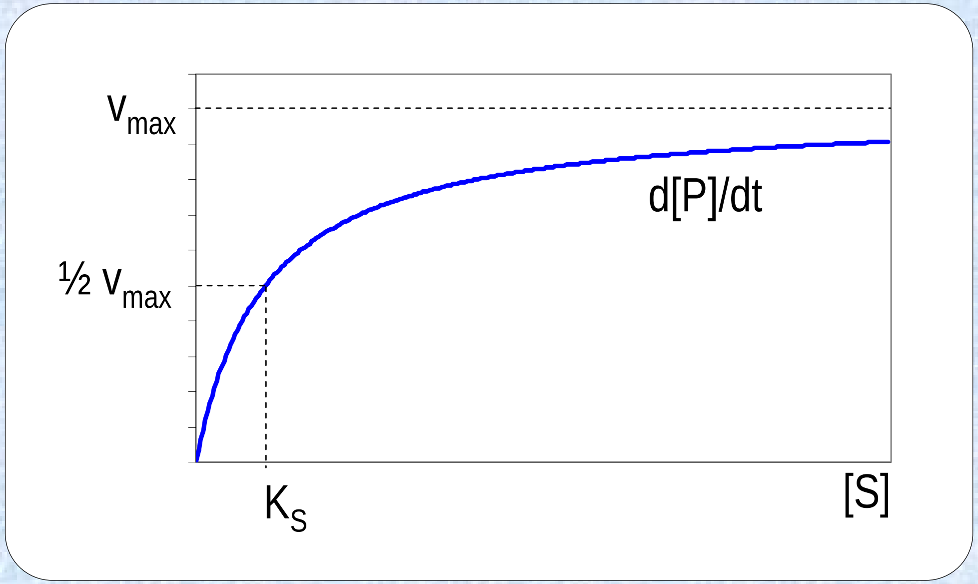



steady state

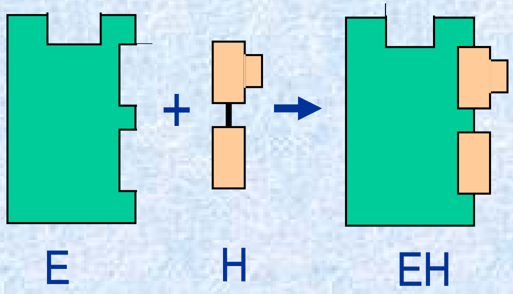
$$\frac{d[P]}{dt} = \frac{v_{max}\,[S]}{K_S + [S]}$$

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

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



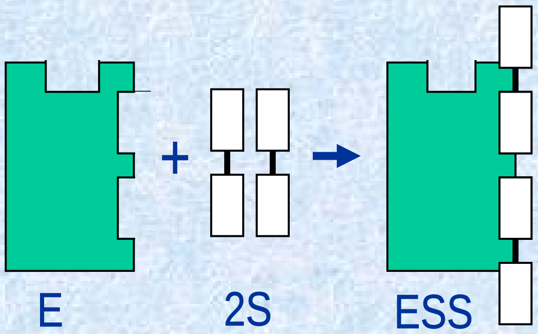
# Enzyme Inhibition




competitive inhibition

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

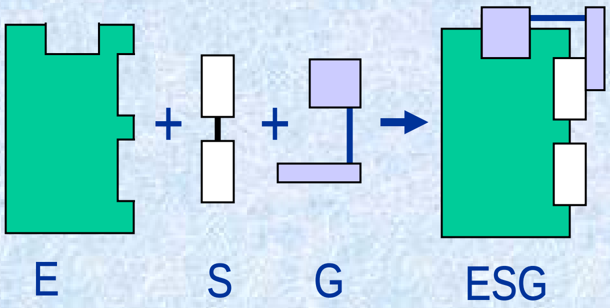
$$I_1 = 1 + \frac{[H]}{K_1}$$




self-inhibition (HALDANE)

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

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




non-competitive inhibition

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

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

# Enzyme Kinetics (part II)

$$k_i = v_{max}^{(i)} / X$$

CAH species

$$f_{i \to j} = \frac{k_i [i]}{K_i I_i + [i] + [i]^2 / K_i^H}$$

competitive inhibition

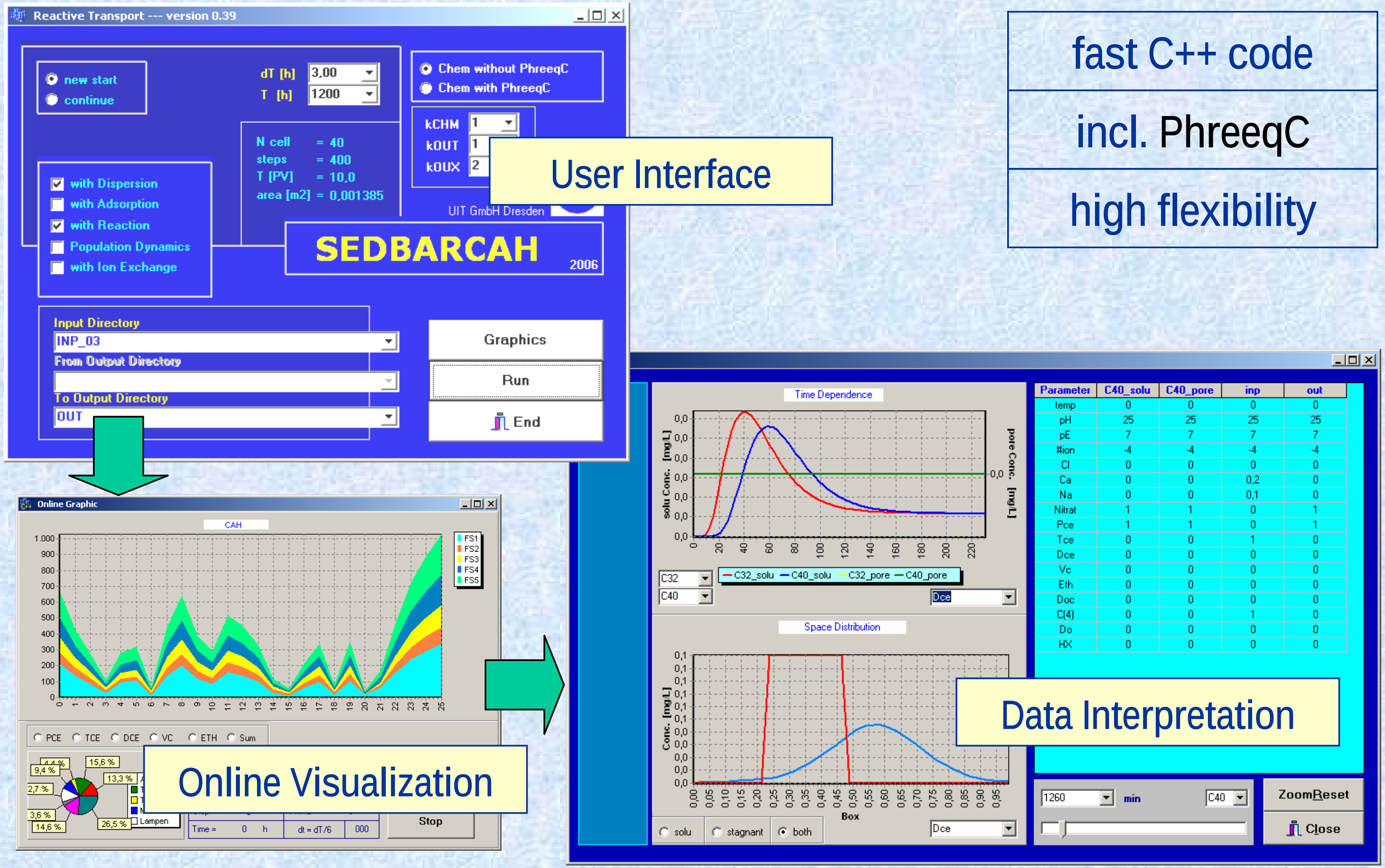
self-inhibition (HALDANE)

$$I_i = 1 + \prod_{j \neq i} \frac{[j]}{K_{ij}^{inh}}$$

assumption: $K_{ij}^{inh} \approx K_j$

**many kinetic parameters !**

# Software (1st version 0.40)




fast C++ code

incl. PhreeqC

high flexibility

# High Flexibility

| | |
|---|---|
| number of layers (compartments) | unlimited |
| number of cells per layer | unlimited |

| | |
|---|---|
| number of chemical elements (PhreeqC) | unlimited |
| number of inflow compositions | unlimited |

- Clearly arranged Input / Output structure
- Stop-and-Go (calculation with interrupts)

Open for future extensions

# Input Data (part I)

| | | |
|---|---|---|
| time-step width | $\Delta t$ | h |
| end time | T | h |
| cross section area | A | $m^2$ |
| number of layers | $N_L$ | |
| inflow solution | inp.sol | |

Global Data

Data for each Layer

| | | |
|---|---|---|
| cell number | N | |
| cell length | $\Delta x$ | m |
| porosity | $\varepsilon$ | |
| dispersity | $\alpha_L$ | m |
| bulk density | $\rho_b$ | $g/cm^3$ |
| org. carbon contentent | $f_{oc}$ | |
| biomass „ana“ for t=0 | $X^{ana}$ | µg/L |
| biomass „aer“ for t=0 | $X^{aer}$ | µg/L |
| initial solution fot t=0 | file: cell.sol | |

# Input Data (part II)

| | | |
|---|---|---|
| temperature | **temp** | **°C** |
| pH-value | **pH** | |
| ORP | **pe** | |
| PCE (CAH's) | **c** | **mM** |
| TCE (CAH's) | **c** | **mM** |
| cis-DCE (CAH's) | **c** | **mM** |
| VC (CAH's) | **c** | **mM** |
| ETH | **c** | **mM** |
| $C_{org}$ (dissolved organic carbon) | **c** | **mM** |
| DIC (dissolved inorganic carbon) | **c** | **mM** |
| Cl | **c** | **mM** |
| DO (dissolved oxygen) | **c** | **mM** |
| other anions: S(VI), S(-II), N(V), ... | **c** | **mM** |
| other cations: Ca, Mg, Na, N(-III), ... | **c** | **mM** |

Aqueous Solution Data

file: cell.sol

file: inp.sol

# Input Data (part III)

| | | | |
|---|---|---|---|
| anaerobic | max. specific dechlor. rate | $k_i^{ana}$ | µmol/µg/d |
| | half-velocity coefficient | $K_i^{ana}$ | µmol/µg/d |
| | HALDANE coefficint | $K_{Hi}^{ana}$ | µmol/µg/d |

anaerobic (applies to each of):

- PCE → TCE
- TCE → DCE
- DCE → VC
- VC → ETH

| | | | |
|---|---|---|---|
| aerobic | max. specific oxid. rate | $k_i^{aer}$ | µmol/µg/d |
| | half-velocity coefficient | $K_i^{aer}$ | µmol/µg/d |
| | HALDANE coefficint | $K_{Hi}^{aer}$ | µmol/µg/d |

aerobic (applies to each of):

- DCE → $CO_2$
- VC → $CO_2$
- ETH → $CO_2$

| | | |
|---|---|---|
| $O_2$ inhibition | $K_{inh}$ | µM |
| $C_{org}$ half-velocity coefficient | $K_{Corg}$ | µM |

Population Dynamics

| | | |
|---|---|---|
| yield | $Y^{ana}$, $Y^{aer}$ | µg/µmol |
| death rate | $k_d^{ana}$, $k_d^{aer}$ | $d^{-1}$ |

**27 Kinetic Parameters**

# Example Calculations

| | |
|---|---|
| A | pure advection |
| B | advection + dispersion |
| C | biodegradation with constant inflow |
| D | biodegradation with time-dependent inflow |
| E | biodegradation with population dynamics |
| F | ... other examples |

Software Presentation

# Kinetic Parameter Set (Example)

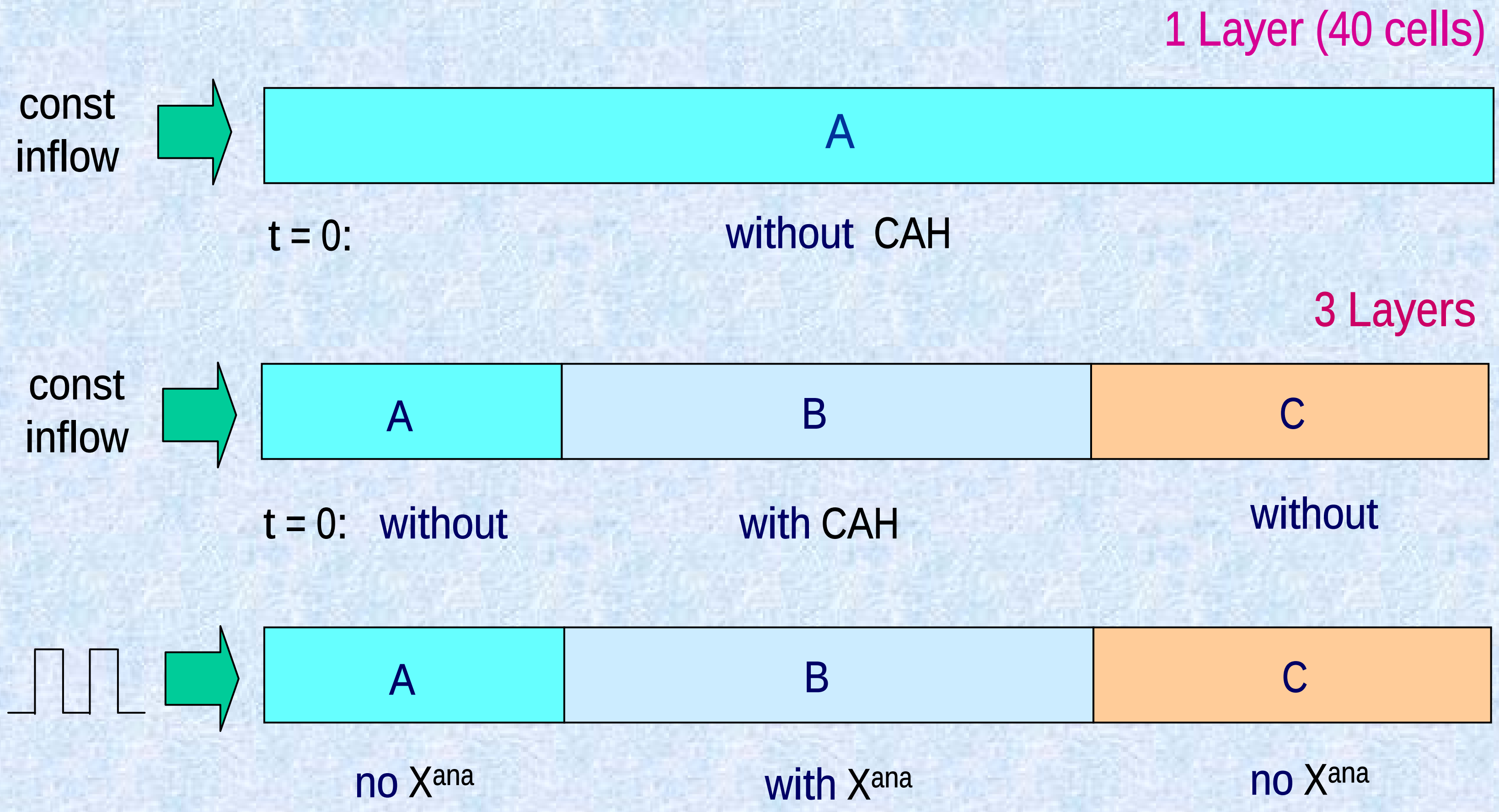
| anaerobic | $k_i$ | $K_i$ | $K_{Hi}$ | $\lambda = k_i X / K_i$ |
|---|---|---|---|---|
| | μmol/mgP/d | μM | μM | $d^{-1}$ |
| PCE → TCE | 12 | 3.0 | | 120 |
| TCE → DCE | 124 | 2.0 | 900 | 1860 |
| DCE → VC | 20 | 1.9 | 1000 | 316 |
| VC → ETH | 5 | 100 | 1000 | 1.5 |

| | | |
|---|---|---|
| $X^{ana}$ | mgP/L | 30 |
| $Y^{ana}$ | mgP/μM Cl | 0.006 |
| $k_{death}$ | $d^{-1}$ | 0.024 |

data: Yu & Semprini 2004

**Data in literature varies strongly !**

# Demo (3 Example Configurations)



# Open Questions

$e^-$ donor $C_{org}$ : $CH_2O$, $CH_4$ or other ?
fraction of DOC ?

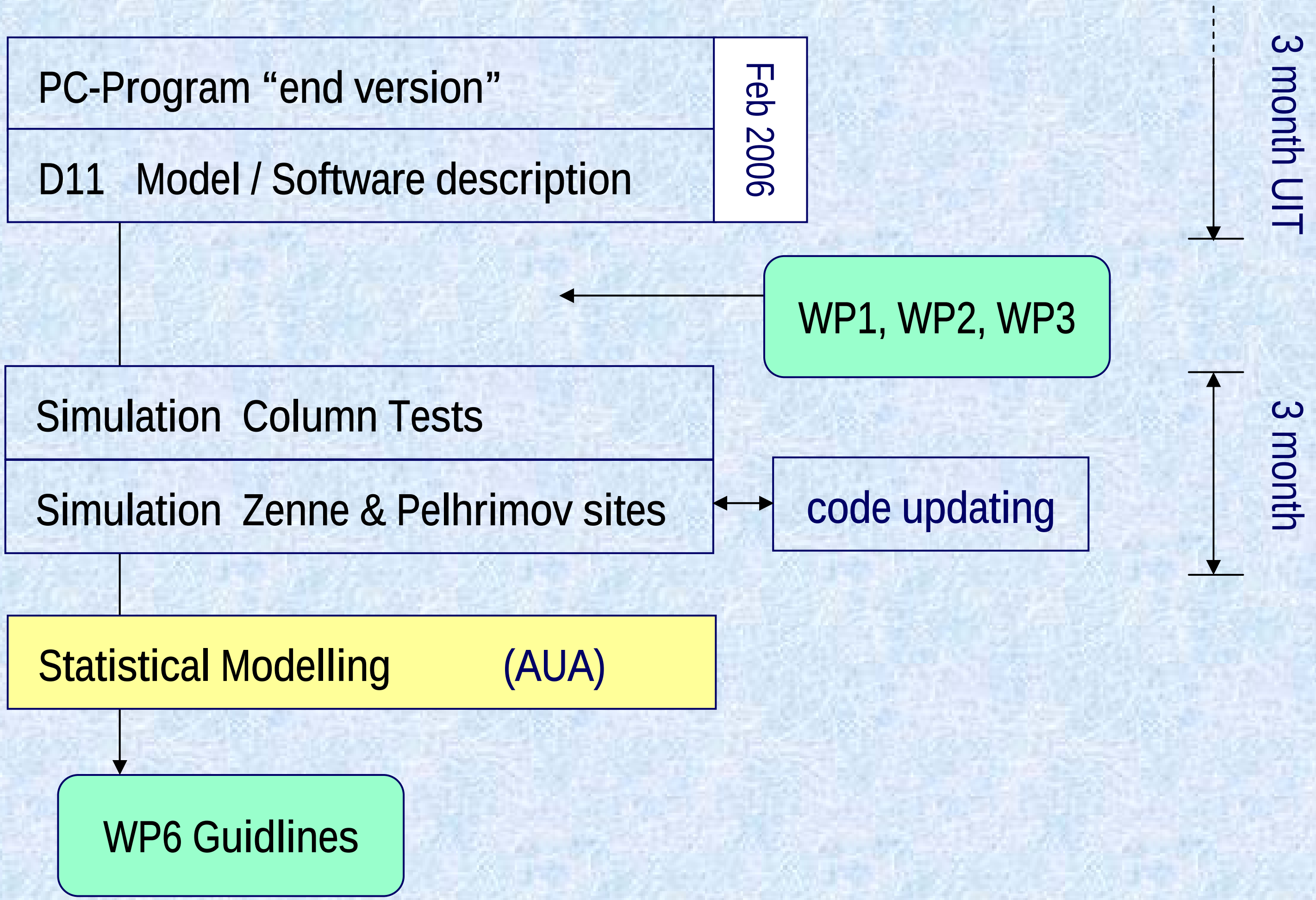
population dynamics: stationarity ?

aerobic oxidation ?

role of other oxidants (NO3 etc.) ?

... and many other questions

# WP5 - Next Steps



More Info: SEDBARCAH project
Deliverable D11

www.aquac.de/model.html

***End of presentation.***