

Project no.: 511254 (STREP)



SEDBARCAH

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

Reactive Transport & Biodegradation Model (Part I)

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Short Lecture at the Meeting
Wageningen, January 2006

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

Duration: 2 years
UIT GmbH Dresden

Reactive Transport and CAH-Biodegradation Model



SEDBARCAH

1 Basic Equations

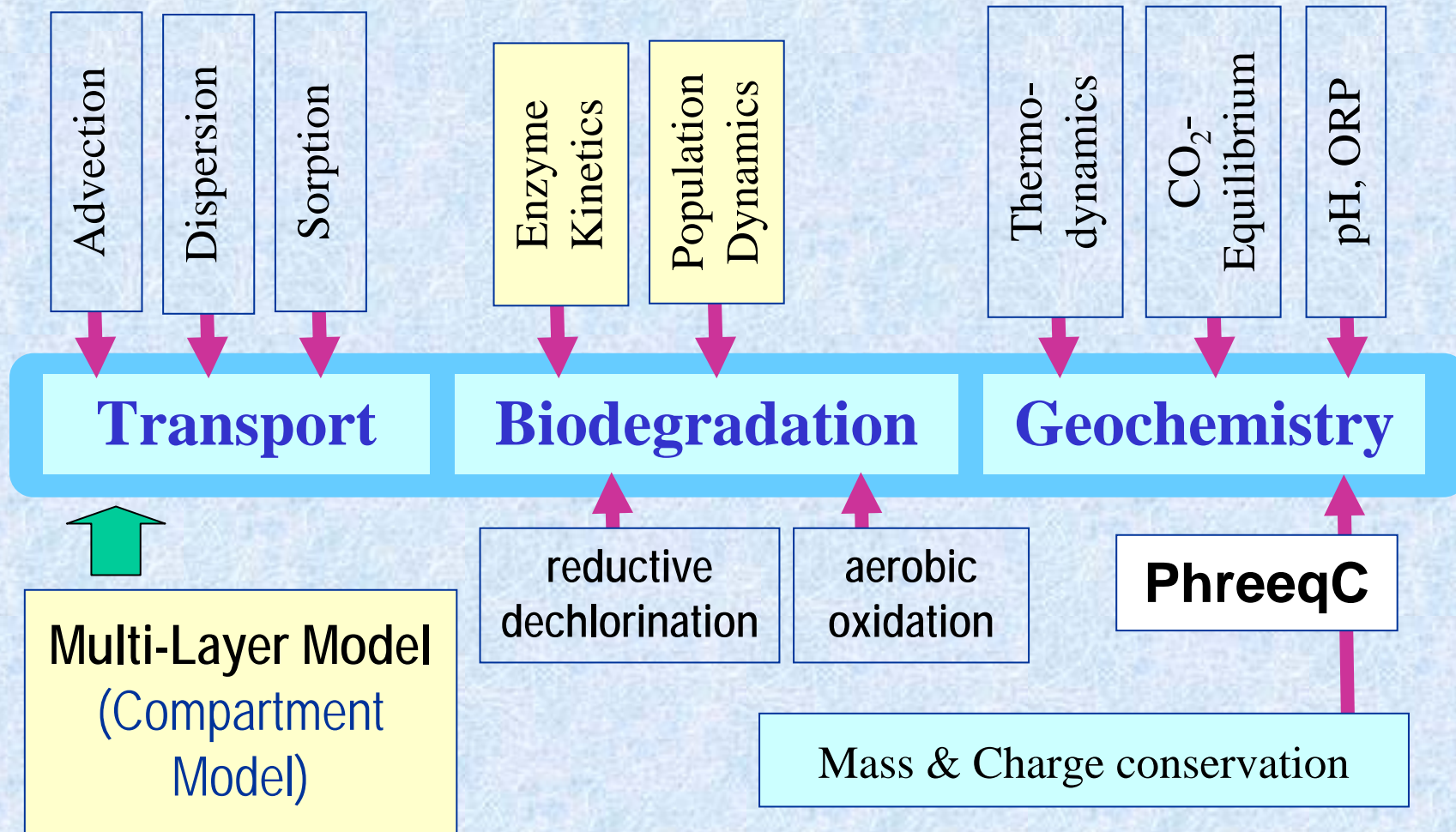
2 Transport Phenomena

3 Enzyme Kinetics

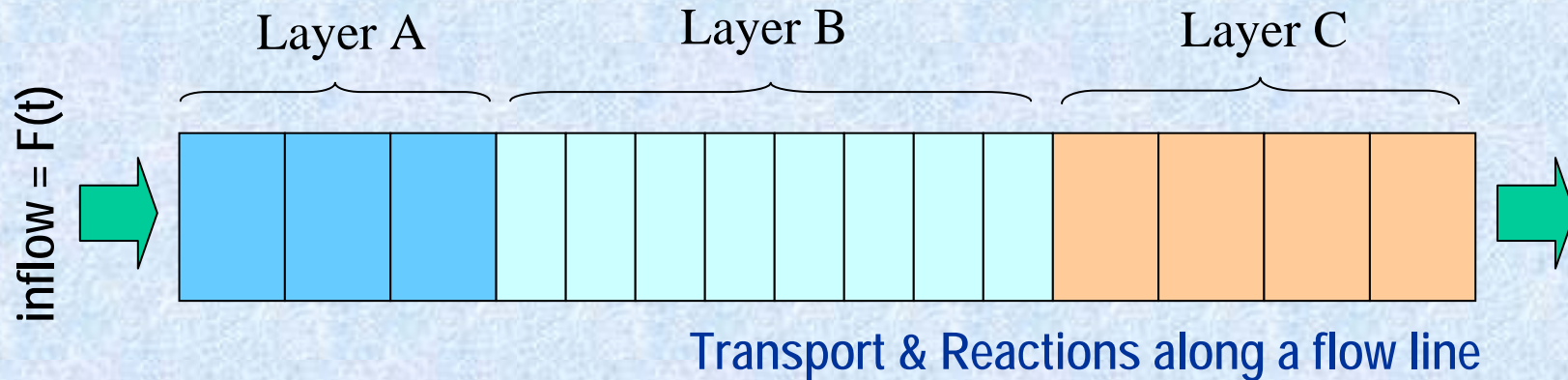
4 Model Parameters

5 Software Presentation / Examples

Main Processes



Multi-Layer Model (Compartments)



1 Model for 2 Tasks

● Column Experiments

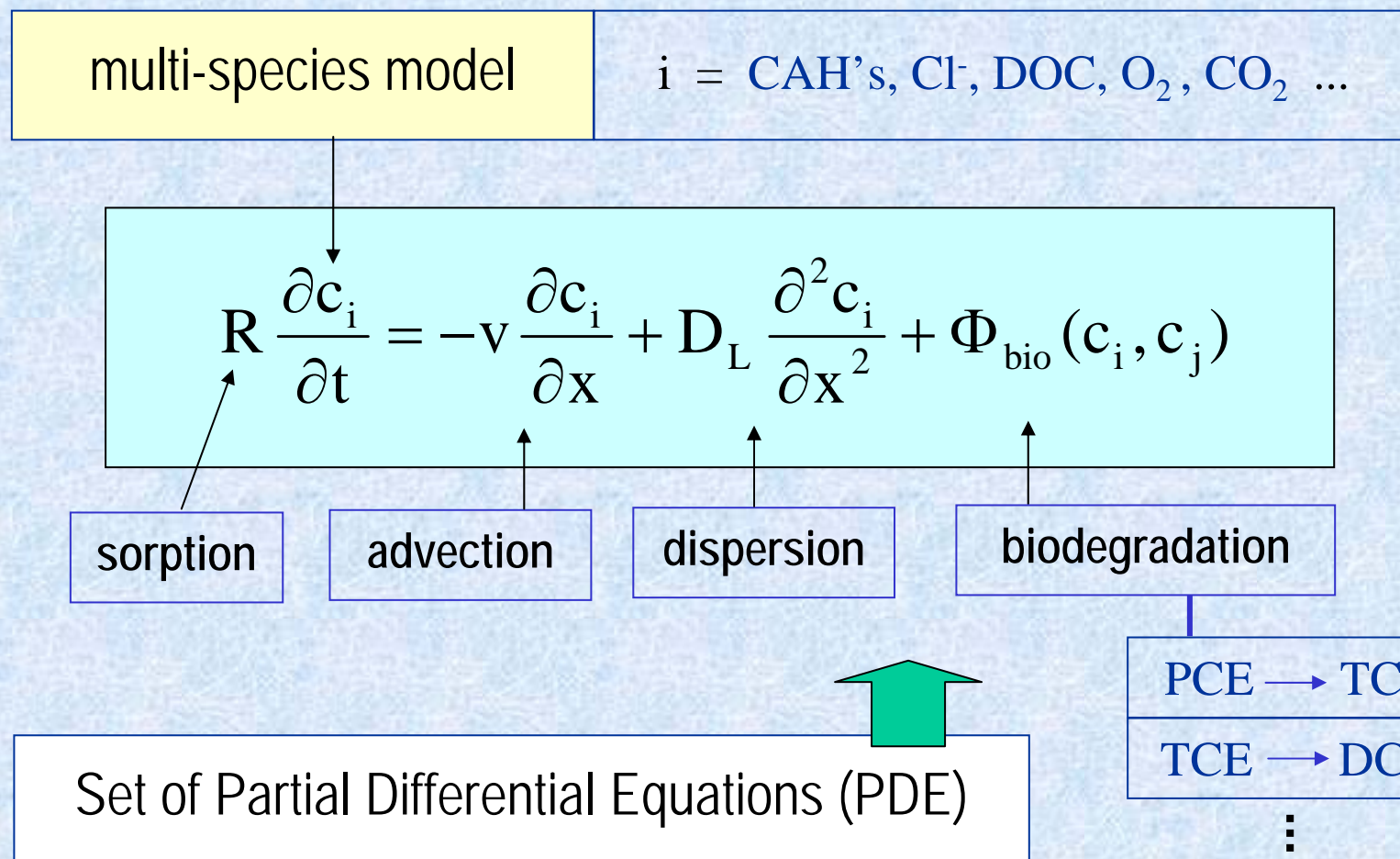
● Field-Scale Applications

Batch Reactions (only kinetics)

Zenne Site

Pelhrimov Site

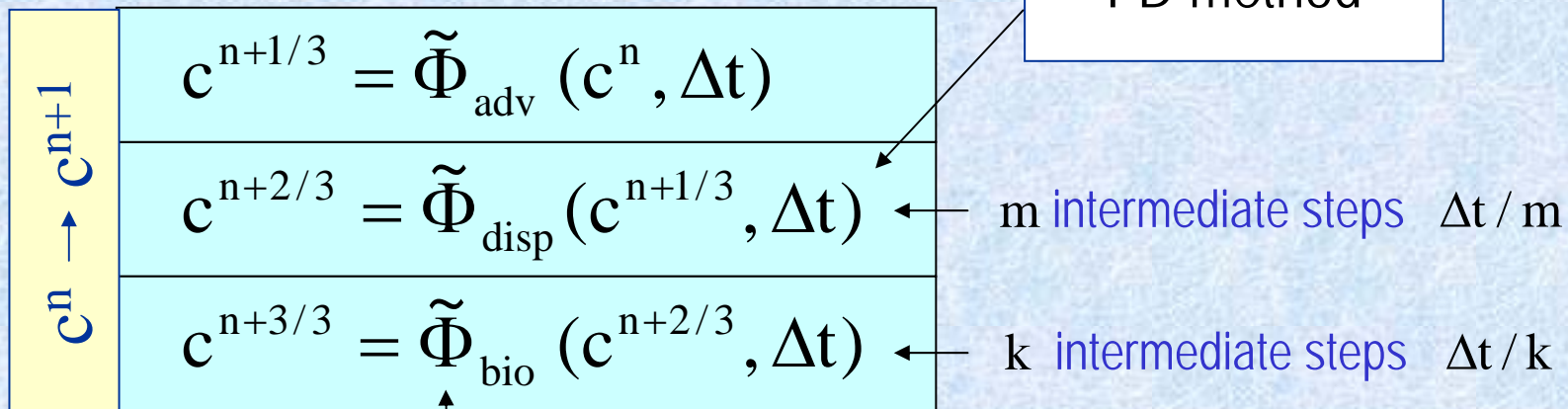
Basic Equation (ADR)



Operator Splitting

$$\frac{\partial c}{\partial t} = \Phi c$$

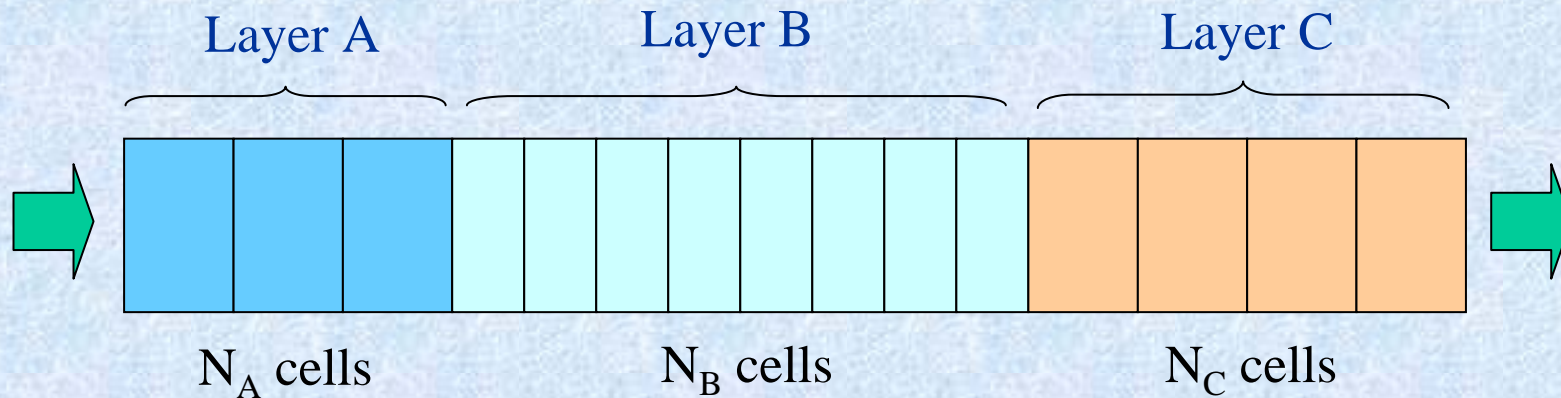
$$\Phi = \Phi_{\text{adv}} + \Phi_{\text{disp}} + \Phi_{\text{bio}}$$



FD method

Runge-Kutta for ODE

Cell size & Time step



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

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

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

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

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

Analytical Solution

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



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

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

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

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

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

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

Numerical Test

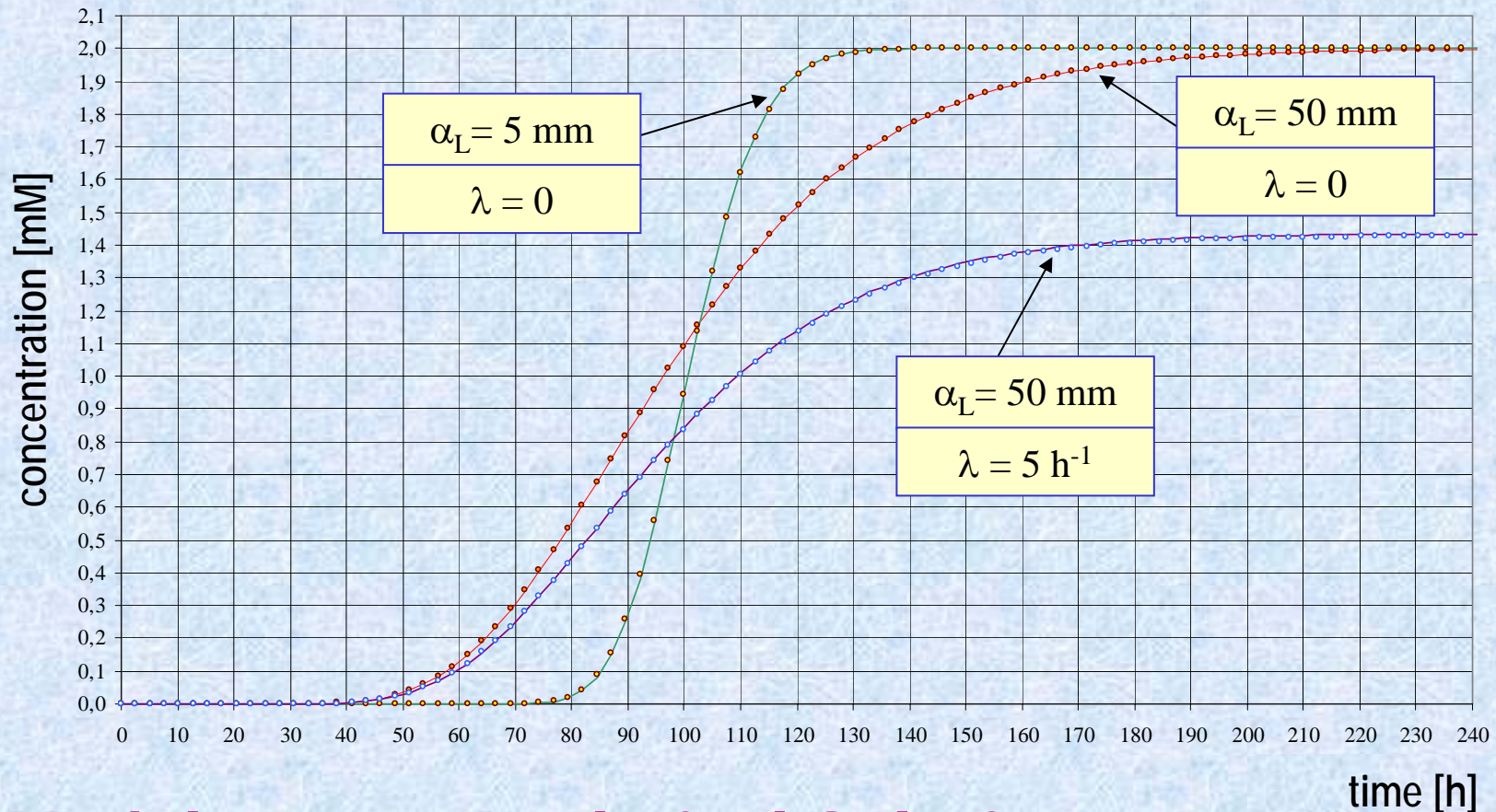
$N = 40$ cells

$v = 9.8$ mm/h

$\Delta t = 2.56$ h

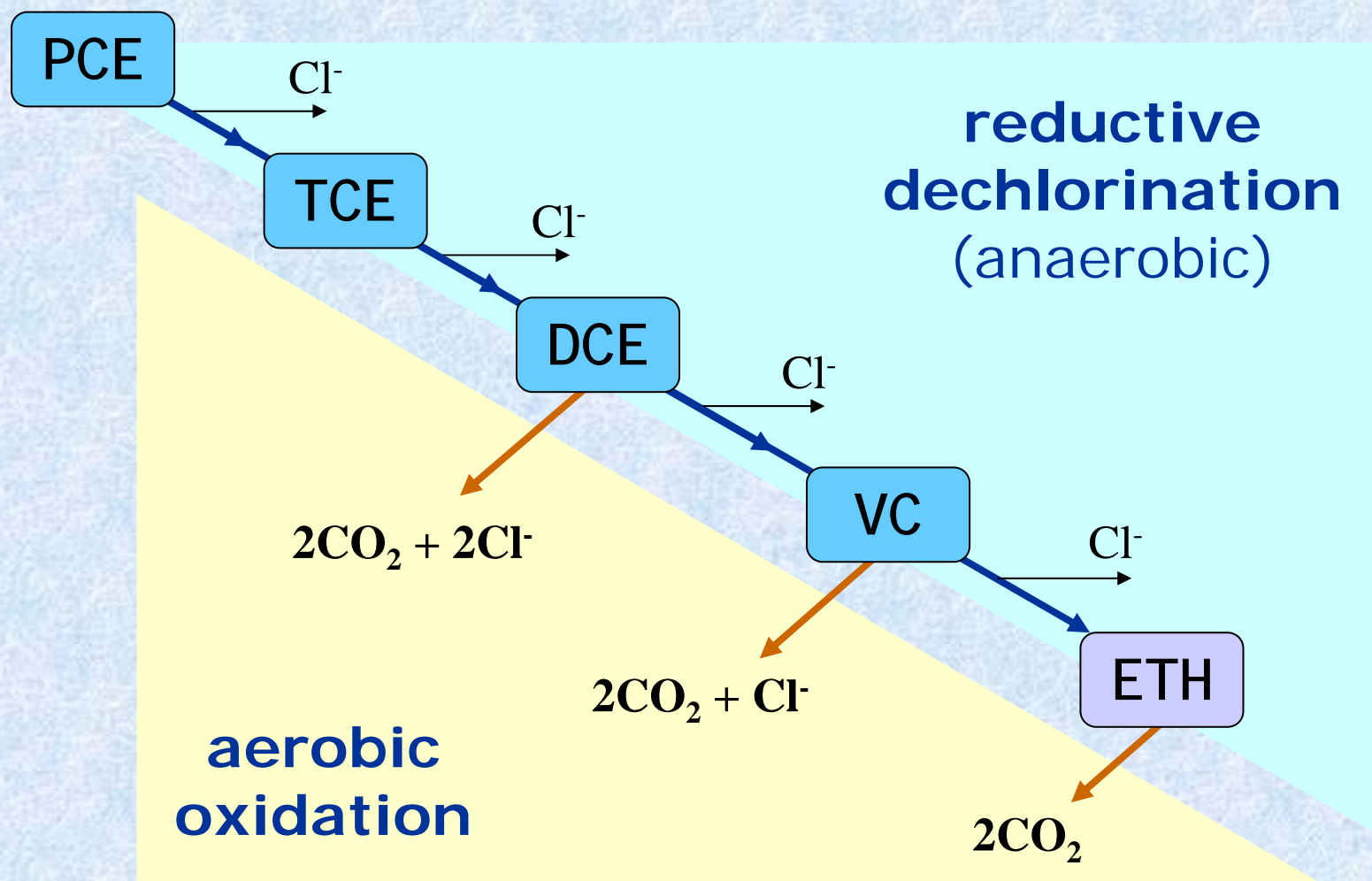
$L = 1$ m

$c_0 = 2$ mM

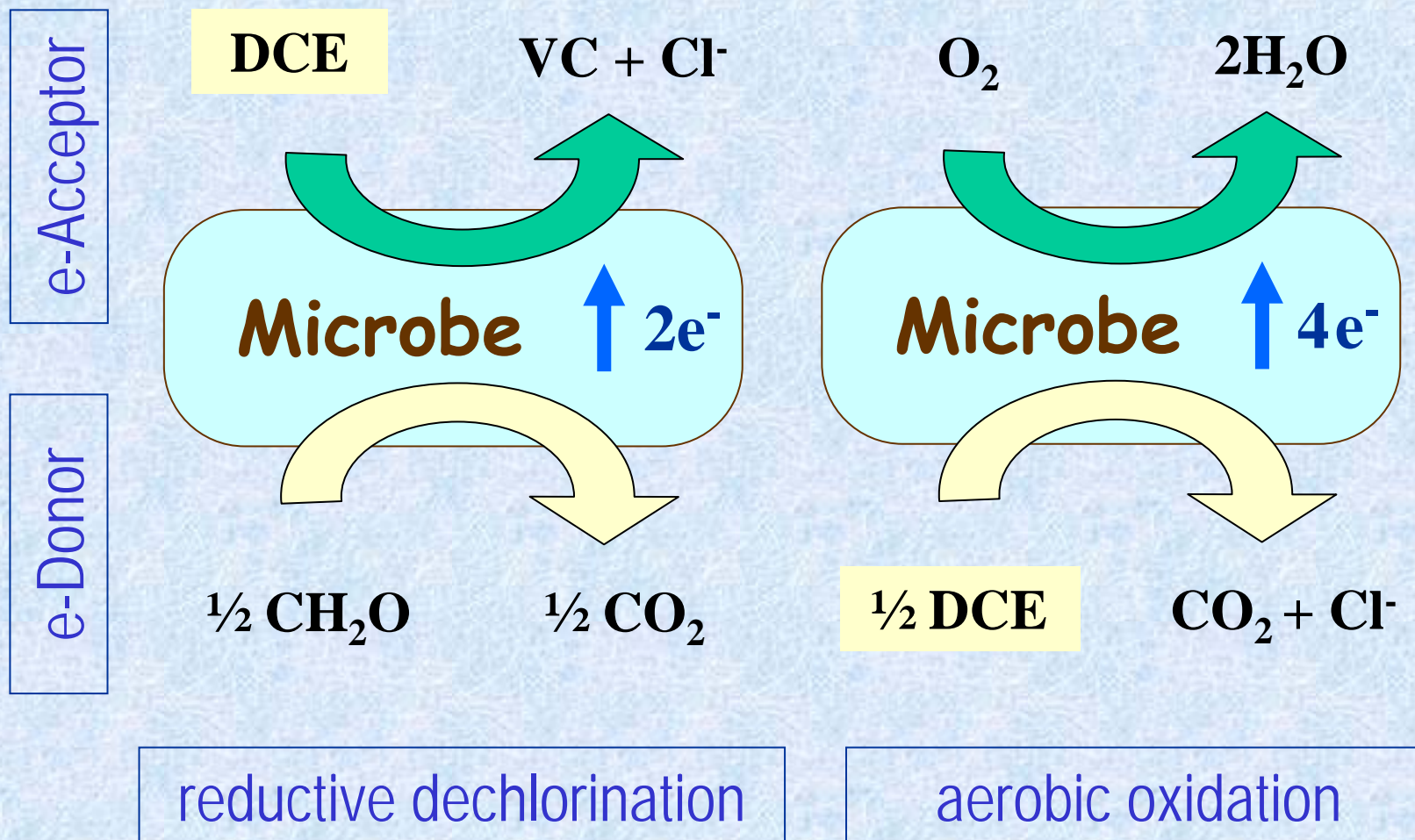


Model versus Analytical Solution

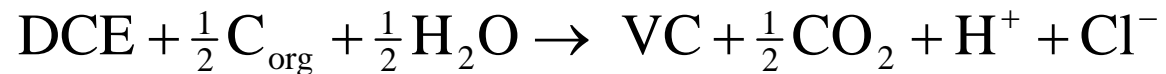
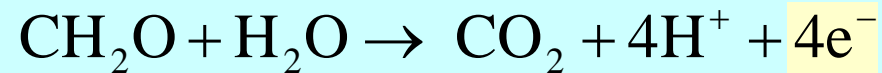
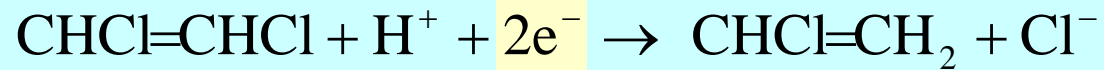
Degradation Pathways



Electron Transfer

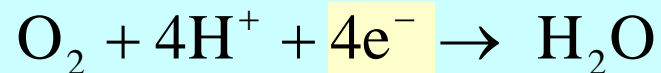


Electron Balance



anaerobic

aerobic



Biodegradation ODE (part I)

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

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

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

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

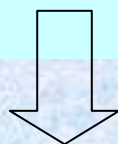
$$\frac{d [\text{ETH}]}{dt} = \Lambda_{\text{V} \rightarrow \text{E}}^{\text{ana}} - \Lambda_{\text{E} \rightarrow \text{C}}^{\text{aer}}$$

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

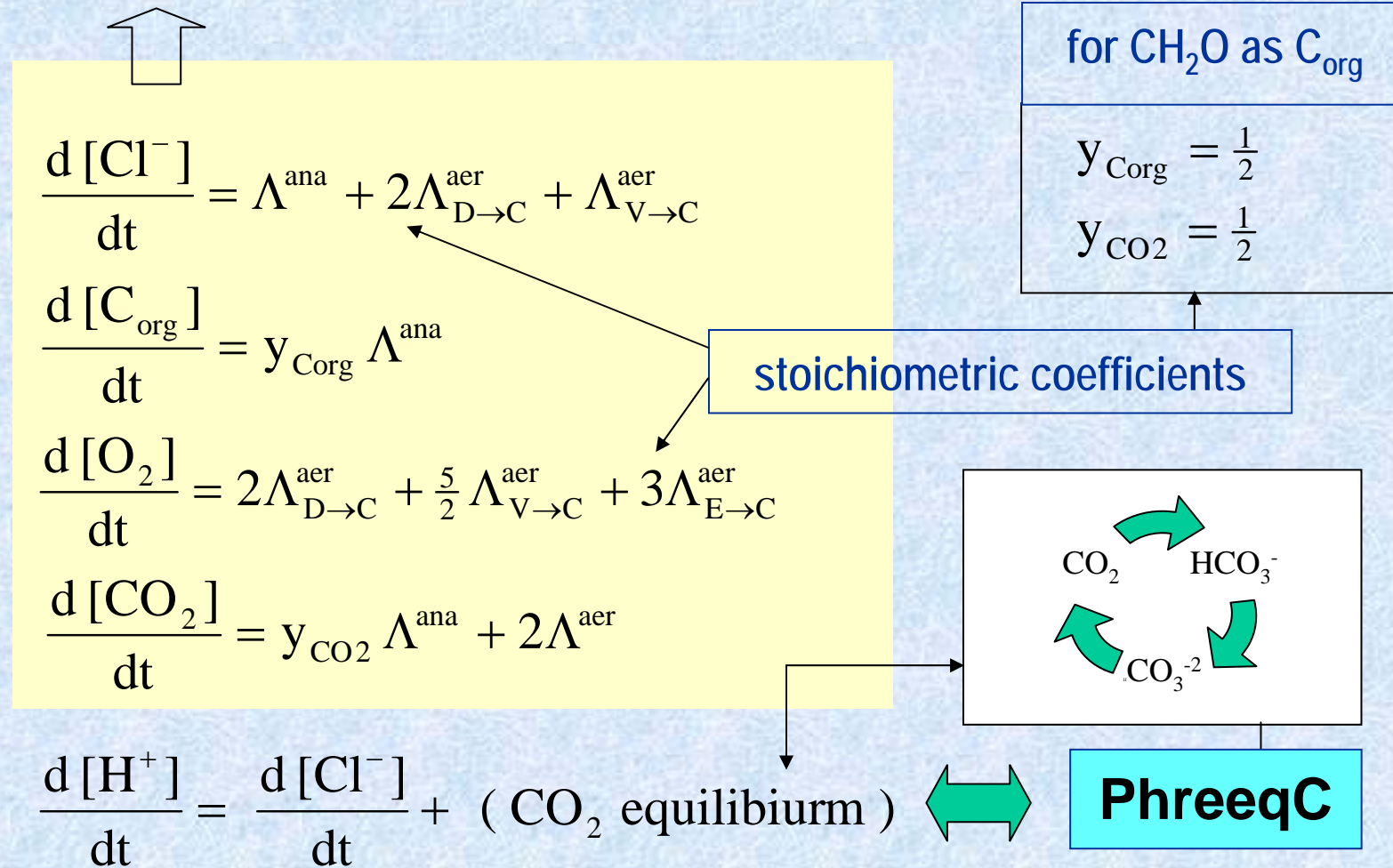
abbreviations:

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

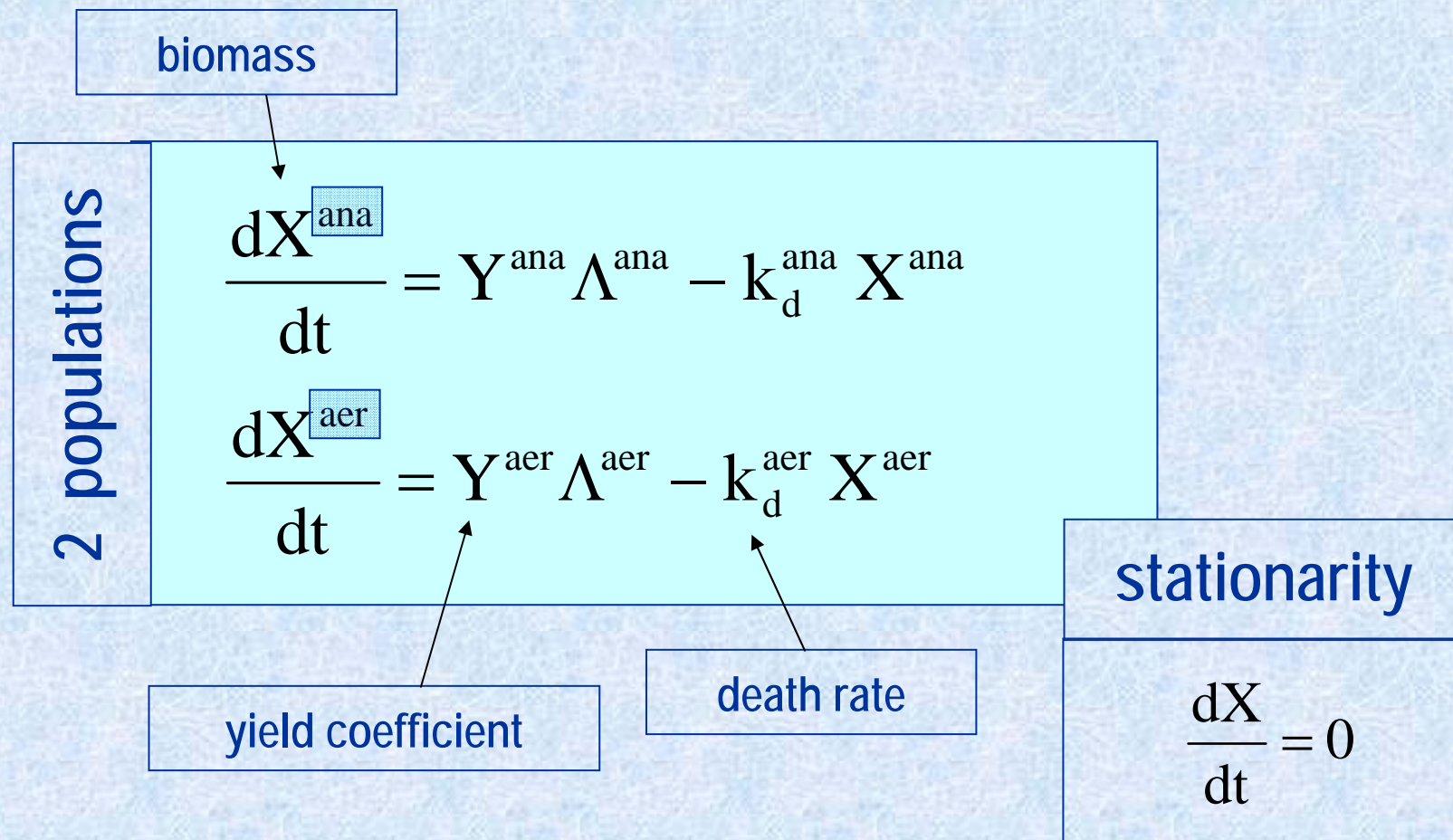
$$\Lambda^{\text{aer}} = \Lambda_{\text{D} \rightarrow \text{C}}^{\text{aer}} + \Lambda_{\text{V} \rightarrow \text{C}}^{\text{aer}} + \Lambda_{\text{E} \rightarrow \text{C}}^{\text{aer}}$$



Biodegradation ODE (part II)



Population Dynamics

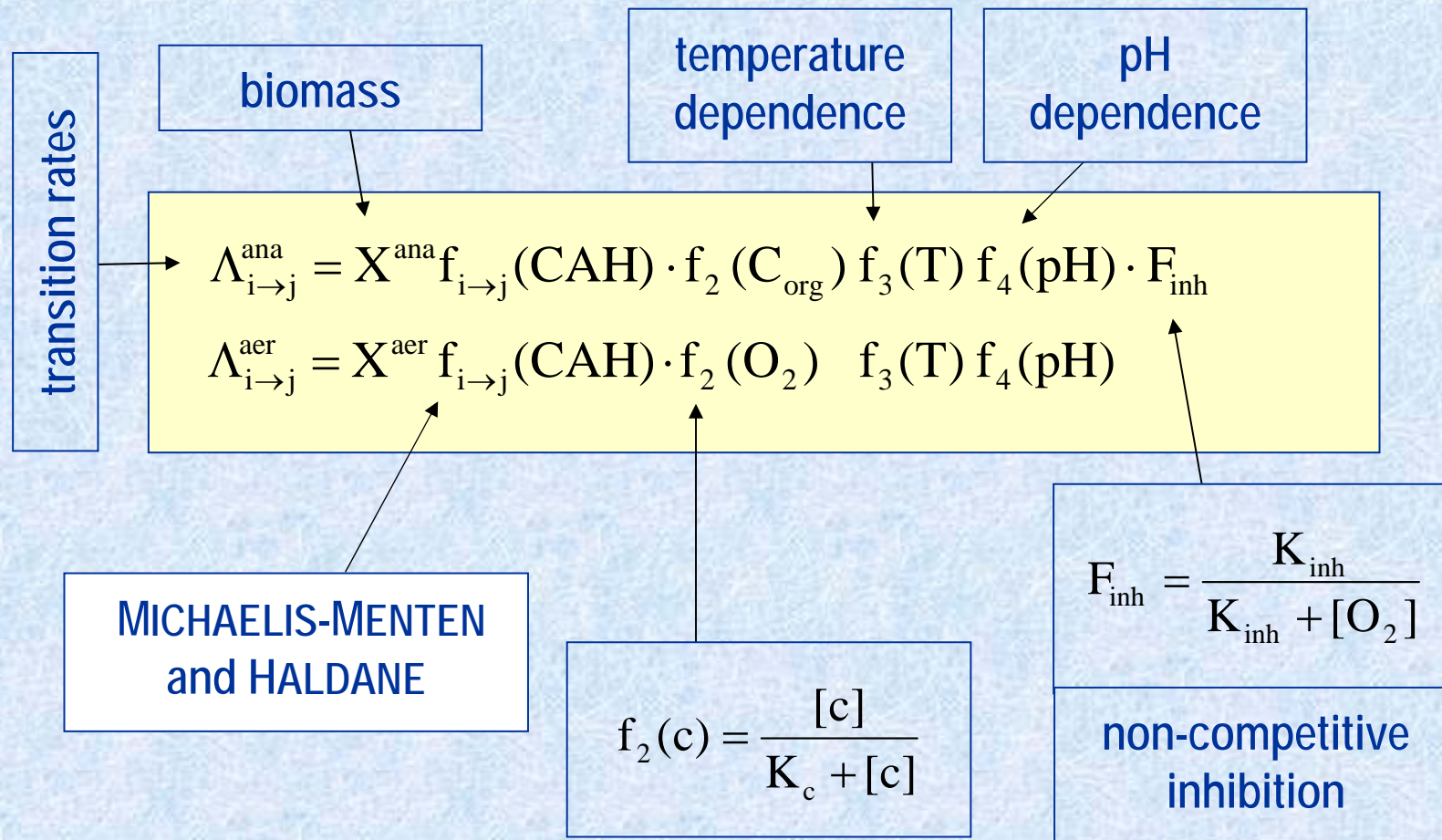




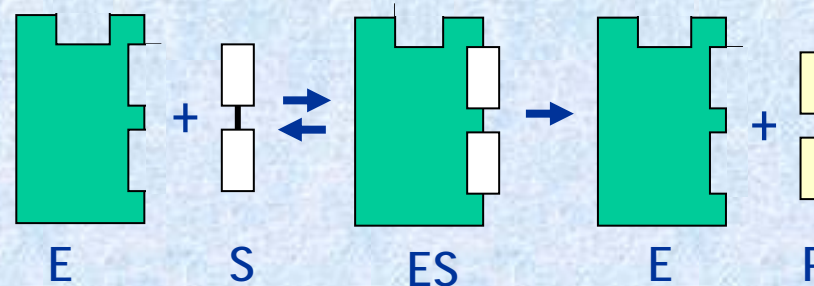
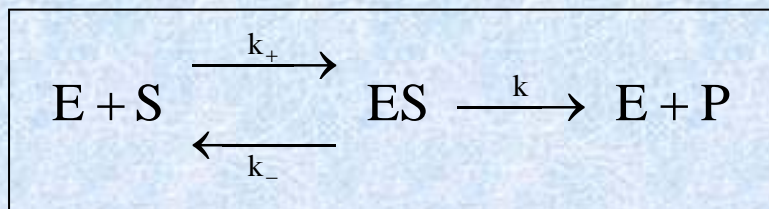
Environmental Factors

- ➔ 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)



MICHAELIS-MENTEN Kinetics

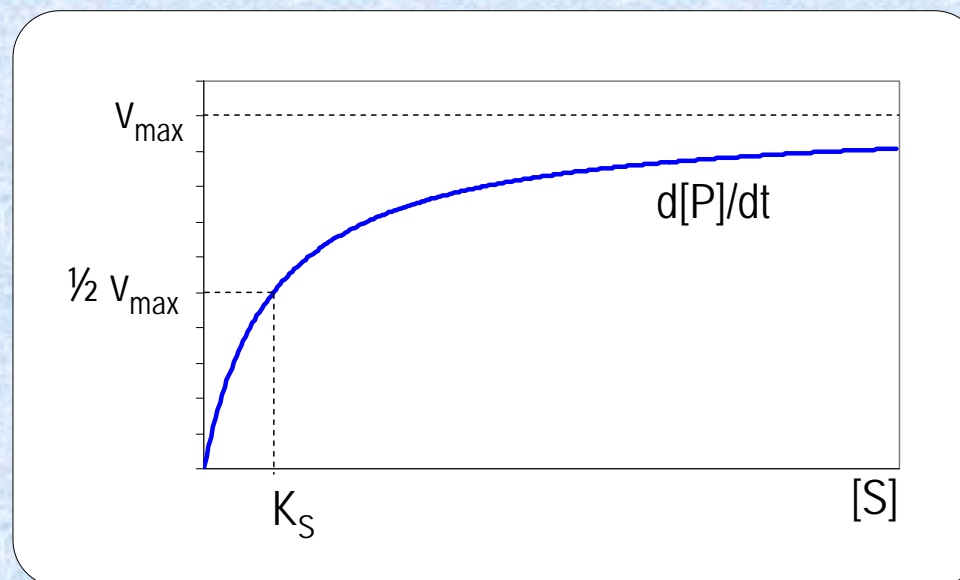


steady state

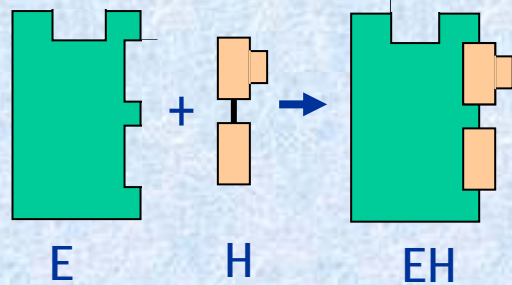
$$\frac{d[P]}{dt} = \frac{v_{\max} [S]}{K_S + [S]}$$

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

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

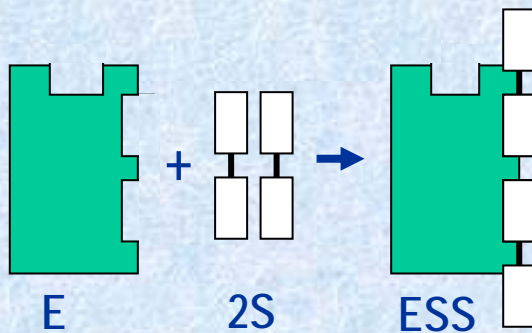


Enzyme Inhibition



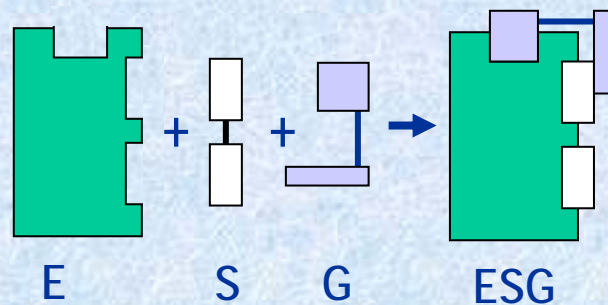
competitive inhibition

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



self-inhibition
(HALDANE)

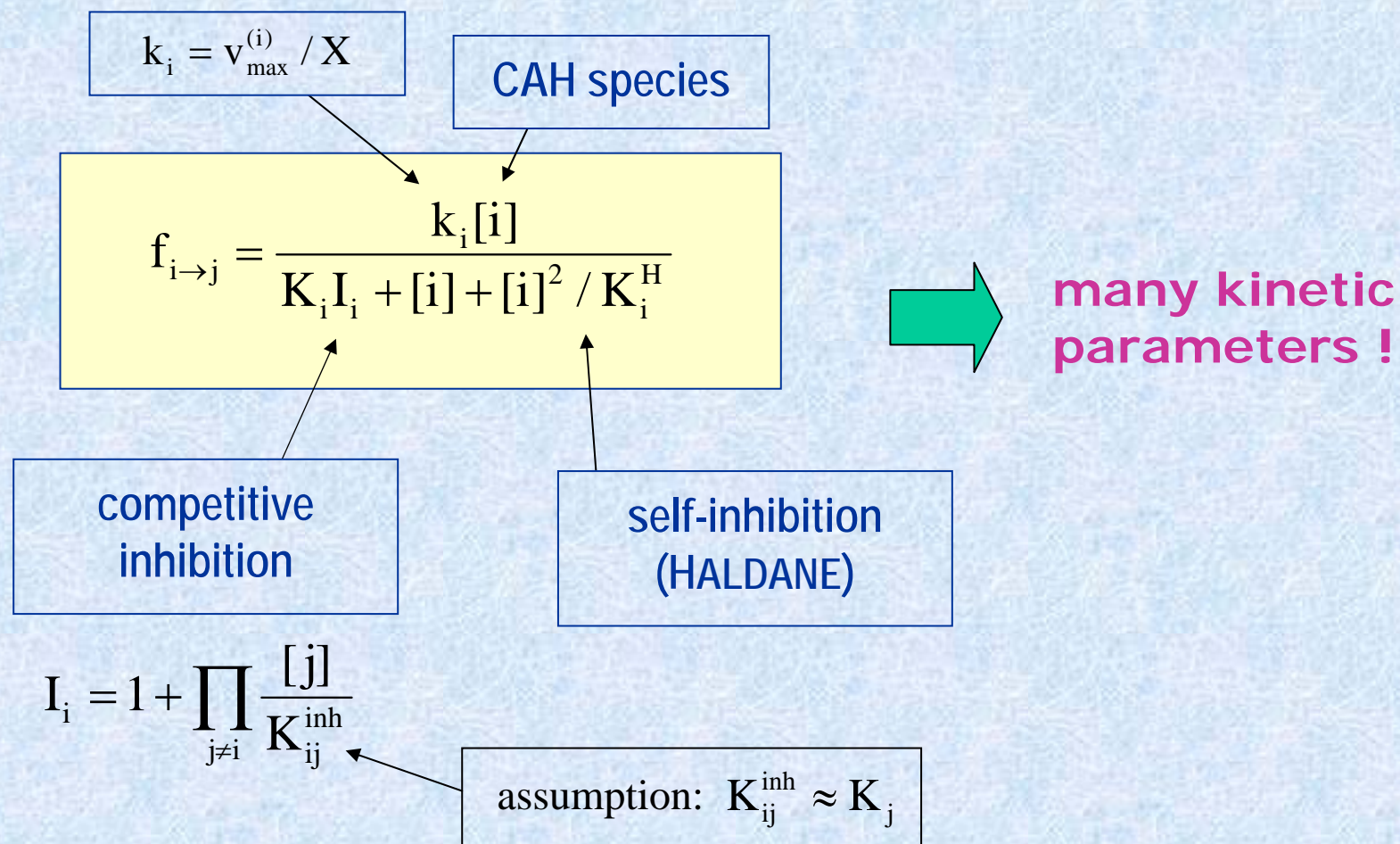
$$\frac{v_{\max} [S]}{K_S + [S] I_2} \quad I_2 = 1 + \frac{[S]}{K_2}$$



non-competitive inhibition

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

Enzyme Kinetics (part II)



Software (1st version 0.40)



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

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

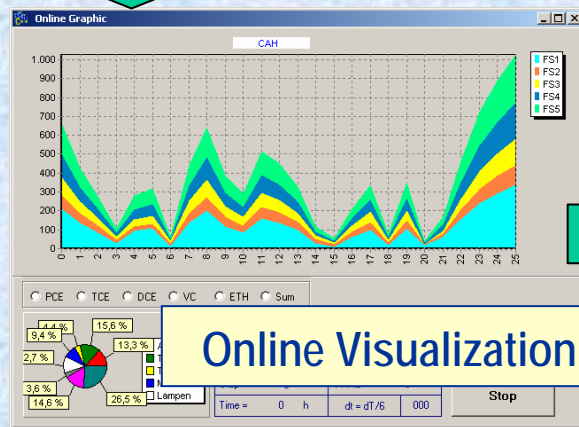
Graphics
 Run
 End

User Interface

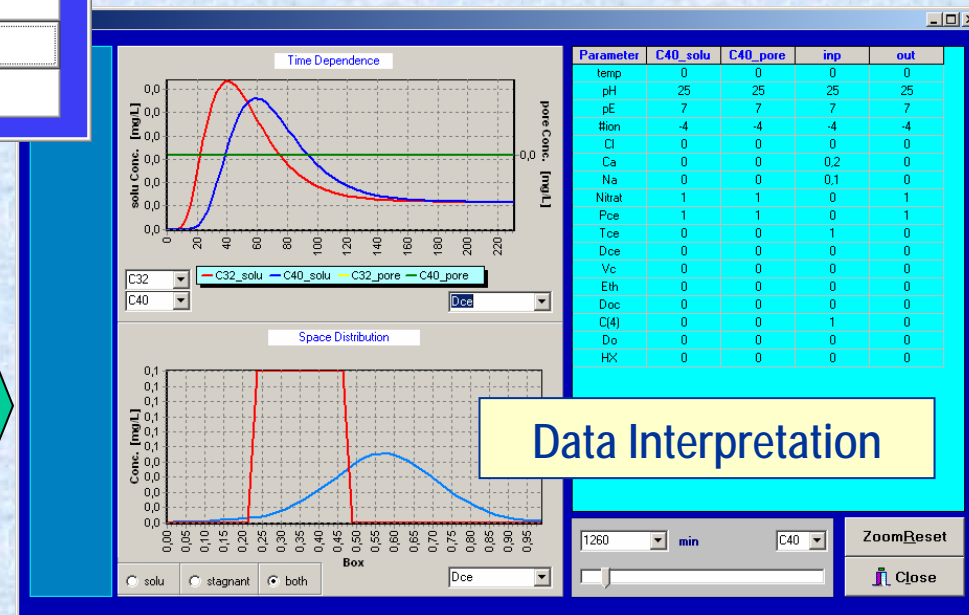
fast C++ code

incl. PhreeqC

high flexibility



Online Visualization



Data Interpretation

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	Δt	h
end time	T	h
cross section area	A	m²
number of layers	N_L	
inflow solution	inp.sol	

Global Data

Data for each Layer

cell number	N	
cell length	Δx	m
porosity	ϵ	
dispersity	α_L	m
bulk density	ρ_b	g/cm³
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	c	mM
TCE		
cis-DCE		
VC		
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}	$\mu\text{mol}/\mu\text{g}/\text{d}$
	half-velocity coefficient	K_i^{ana}	$\mu\text{mol}/\mu\text{g}/\text{d}$
	HALDANE coefficient	K_{Hi}^{ana}	$\mu\text{mol}/\mu\text{g}/\text{d}$

PCE → TCE
TCE → DCE
DCE → VC
VC → ETH

aerobic	max. specific oxid. rate	k_i^{aer}	$\mu\text{mol}/\mu\text{g}/\text{d}$
	half-velocity coefficient	K_i^{aer}	$\mu\text{mol}/\mu\text{g}/\text{d}$
	HALDANE coefficient	K_{Hi}^{aer}	$\mu\text{mol}/\mu\text{g}/\text{d}$

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}	$\mu\text{g}/\mu\text{mol}$
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}	$\lambda = k_i X / K_i$
	$\mu\text{mol/mgP/d}$	μM	μM	d^{-1}
PCE \rightarrow TCE	12	3.0		120
TCE \rightarrow DCE	124	2.0	900	1860
DCE \rightarrow VC	20	1.9	1000	316
VC \rightarrow ETH	5	100	1000	1.5

X^{ana}	mgP/L	30
Y^{ana}	mgP/ $\mu\text{M Cl}$	0.006
k_{death}	d^{-1}	0.024

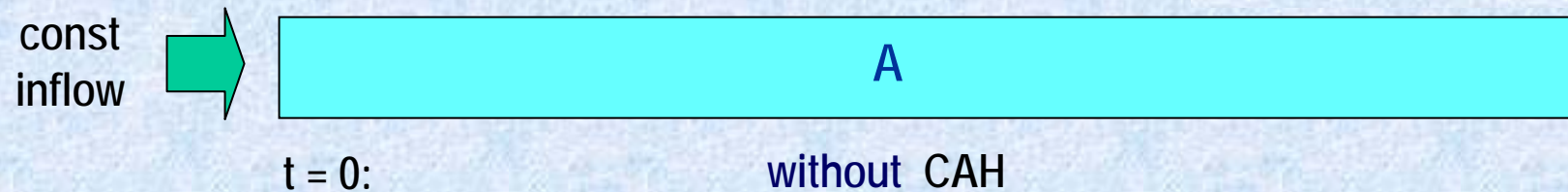
data: Yu & Semprini 2004

Data in literature varies strongly !

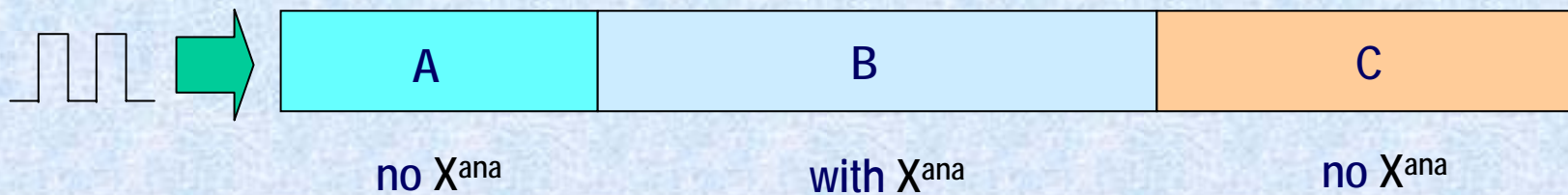
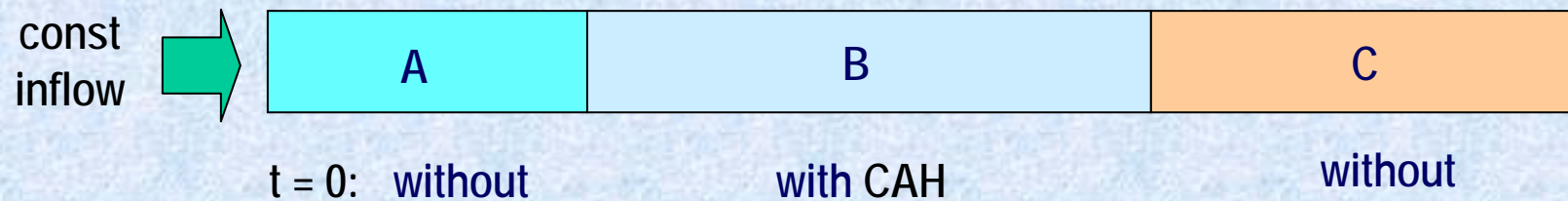
Demo (3 Example Configurations)



1 Layer (40 cells)



3 Layers



Open Questions

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

population dynamics: stationarity ?

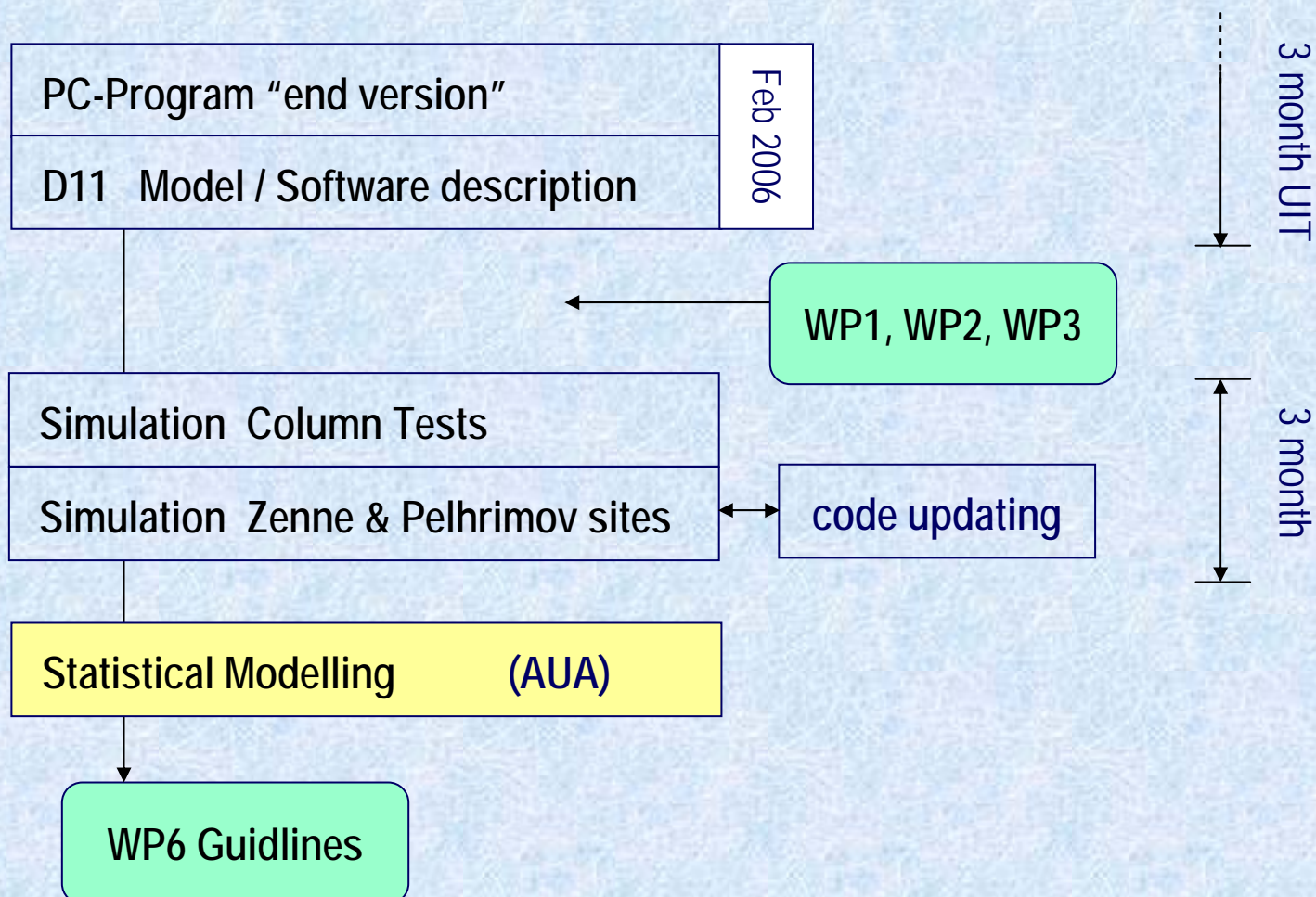
aerobic oxidation ?

role of other oxidants (NO_3 etc.) ?

... and many other questions



WP5 - Next Steps





More Info: SEDBARCAH project
Deliverable D11

www.aquac.de/model.html

*End of
presentation.*