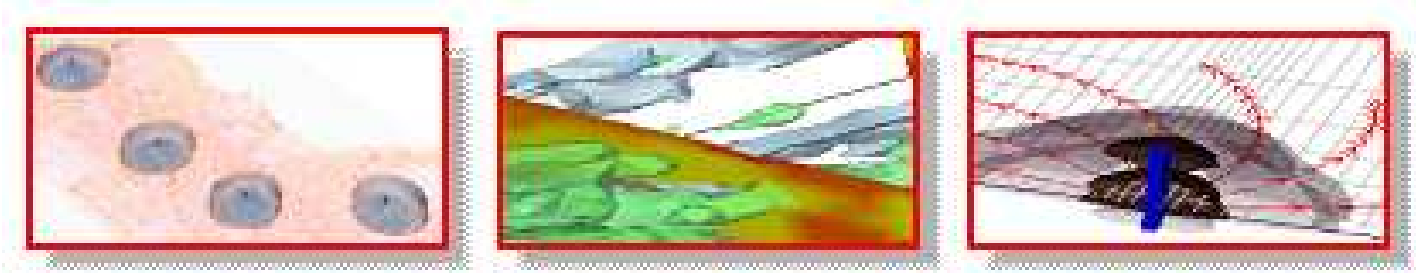

Modelling the fate of oxidisable organic compounds: From a conceptual to a numerical model

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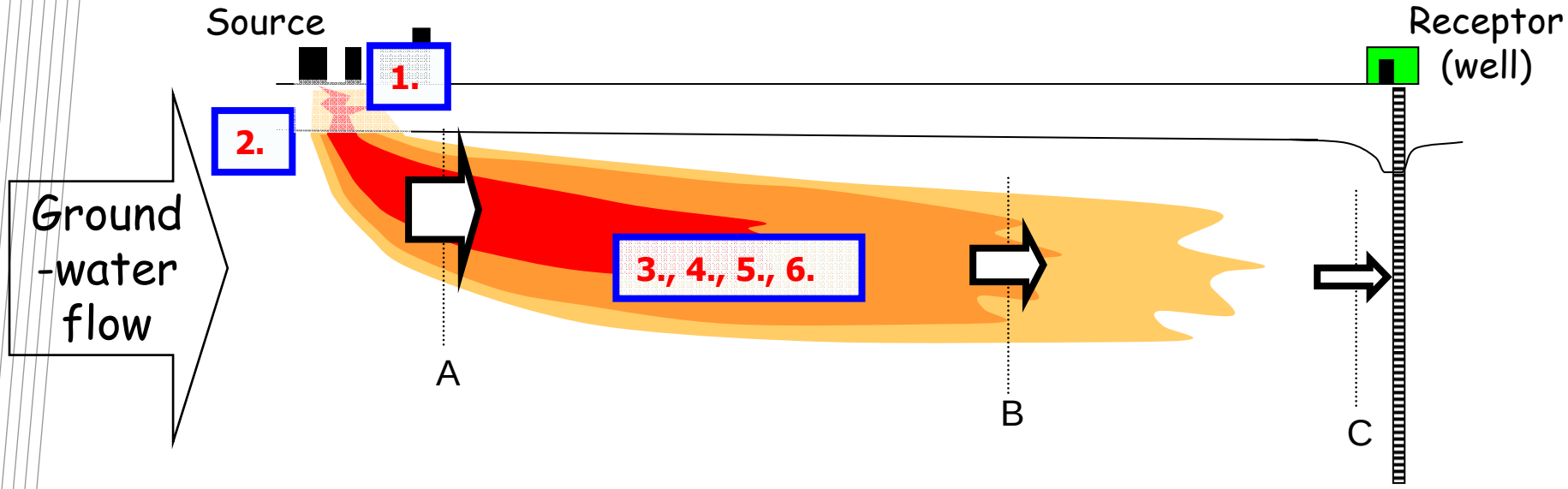
Outline

- Processes
- Modelling *monitored natural attenuation* (MNA)
- From a conceptual model to a numerical model
- Example: Borden Creosote Release Experiment

Processes of a generalised conceptual model for the natural attenuation of oxidisable organic compounds



1. Migration of LNAPLs through the unsaturated zone, formation of contamination source
2. Dissolution from a LNAPL phase into the (passing) groundwater
3. Advective transport
4. Dispersive transport in longitudinal and transversal direction
5. Sorption to the aquifer material
6. Biologically mediated or abiotic degradation, i.e., transformation and/or mineralisation

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From a conceptual model to a numerical model

- Formulation of a proper ‘conceptual’ hydrogeological and hydrochemical model should always be the starting point for any reactive transport simulation
- The conceptual model defines which chemicals are considered to participate or influence the processes that are mainly studied
- The conceptual model is qualitative. The same conceptual model can be translated into many different numerical implementations
- Conceptual model $\rightarrow$ Governing equations $\rightarrow$ Numerical model

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From a conceptual model to a numerical model Example 1

Conceptual model:

- Transported chemical undergoes radioactive decay, but no sorption, degradation
- Governing equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}(D_{ij}\frac{\partial C}{\partial x_j}) - \frac{\partial}{\partial x_i}(v_i C) - k_1 C$$

Numerical model:

- Single species transport model in MT3DMS with advection, dispersion and first-order decay reaction (which is not a function of the concentration of any other species)

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From a conceptual model to a numerical model Example 2

The Borden Emplaced Source Experiment

- Field study by Jim Barker and co-workers at the University of Waterloo
- Modelling study in collaboration with the University of Tübingen (MSc thesis Simon Gossmann)
- The Borden aquifer is one of the best studied aquifers in the world: Several hydrogeological studies have been conducted at this location over the last twenty years and, consequently, many of the parameters affecting the fate and transport of solutes in ground water have been evaluated in exceptional detail
- Previous field experiments at Borden CFB and elsewhere typically focussed on studying slug-type contaminant injection, migration and degradation
- In contrast, the ‘Emplaced Creosote Source’ study focussed on the long-time behaviour of contaminants eminating from a well-defined NAPL source

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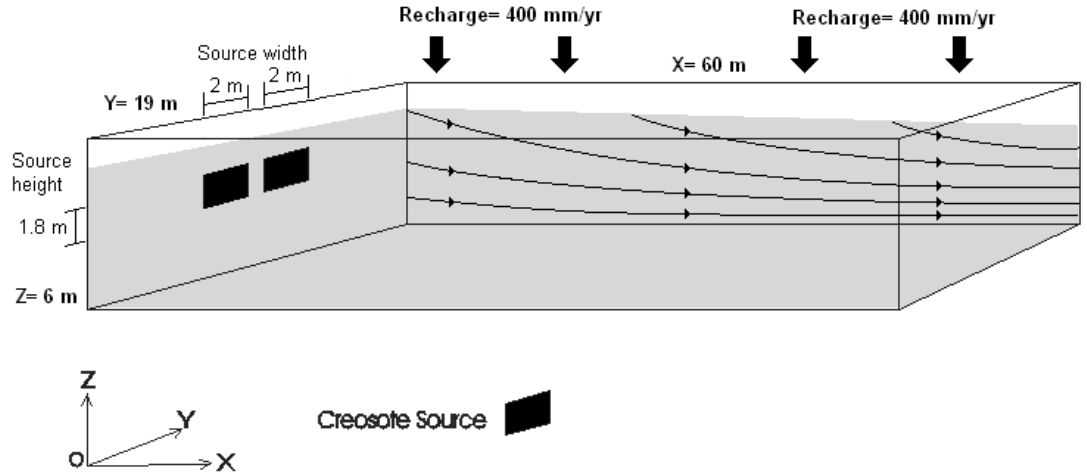
From a conceptual model to a numerical model

Part 1: Conceptual hydrogeological model:



The Borden Emplaced Source Experiment

- More or less uniform, parallel groundwater flow within a homogeneous (?) aquifer. Flow (Darcy) velocity approximately 0.028 m d^{-1}
- Groundwater recharge 400 mm yr^{-1}
- Flow is steady-state, i.e., transient changes in groundwater flow direction and gradients are negligible
- Dispersivities after Sudicky et al. (1983) and Freyberg (1986):

  α_L: 0.39 m, α_{TH}: 0.036 m, α_{TV}: 0.008 m

From a conceptual model to a numerical model

Part 1: Conceptual hydrogeological model:

- Dissolution, transport and degradation of creosote compounds in an aerobic aquifer
- Creosote compounds degrade at different rates
- 7 ‘major’ compounds identified among the > 200 PAHs:

  Phenol, naphtalene, phenantrene, m-xylene, dibenzofuran, carbazole, 1-methylnaphtalene
- Degradation of all compounds takes place exclusively (?) under aerobic conditions
- The organic compounds ‘compete’ for the available oxidation capacity, mainly at the plume fringe

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From a conceptual model to a numerical model

Part 1: Conceptual hydrogeological model:

- Sorption/retardation behaviour differs strongly between compounds
- Microbial growth and decay is assumed to affect degradation dynamics and thus contaminant concentrations
- A single microbial population is responsible for the degradation of all organic compounds
- Complete mineralization to CO_2 is assumed (no significant intermediate production)
- Microbial growth is perhaps nitrogen limited

From a conceptual model to a numerical model

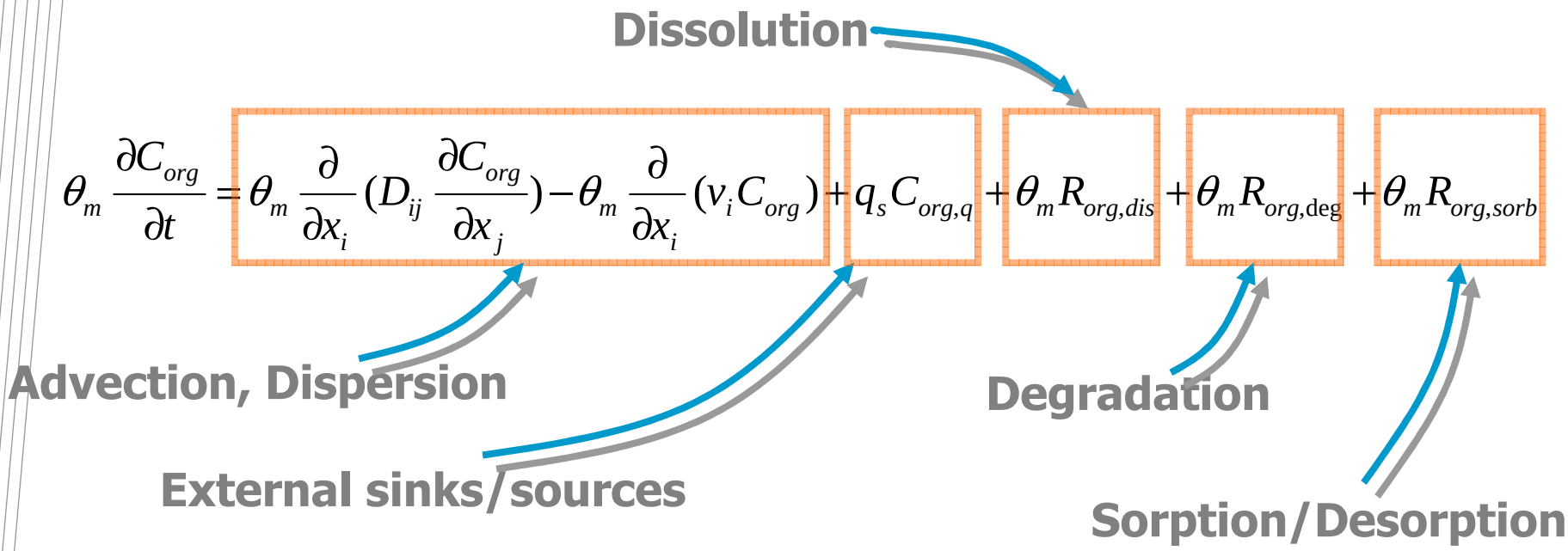
Part 2: Governing equations

To model the hydrochemistry correctly (e.g., mass conservative):

- Selection of the reaction network
- Transport equation(s)
- Formulation of the equations describing the reaction rates
- Determination of the reaction stoichiometry of the biodegradation reactions is required

Transport Equation

For each of the organic compounds:



Reaction terms can take many different forms !

From a conceptual model to a numerical model

First-order model:

$$R_{\mathrm{deg},org} = -k_1 C_{org}$$

Instantaneous reaction model:

$$R_{deg,org} = -\frac{C_{org}}{\Delta t} \quad \text{if} \quad C_{org} \le \frac{Y_{org}}{Y_{EA}} C_{EA}$$

$$R_{deg,org} = -\frac{Y_{org}}{Y_{EA}} \frac{C_{EA}}{\Delta t} \quad \text{if} \quad C_{org} > \frac{Y_{org}}{Y_{EA}} C_{EA}$$

From a conceptual model to a numerical model

One Monod-type reaction term:

$$R_{org,deg} = -k_1 C_{org} \frac{C_{EA}}{K_{EA} + C_{EA}}$$

... or two ?

$$R_{org,deg} = -k_2 \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{EA}}{K_{EA} + C_{EA}}$$

... however, those equations do not model explicitly microbial growth and do not consider a potential growth limitation by nitrogen availability

From a conceptual model to a numerical model

Mass balance for microbes:

$$\frac{\partial X}{\partial t} = \frac{\partial X_{growth}}{\partial t} + \frac{\partial X_{decay}}{\partial t}$$

with

$$\frac{\partial X_{growth}}{\partial t} = v_{max} Y_x \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{EA}}{K_{EA} + C_{EA}} \frac{C_{Nit}}{K_{Nit} + C_{Nit}} X$$

and

$$\frac{\partial X_{decay}}{\partial t} = -v_{dec} X$$

From a conceptual model to a numerical model

In those cases where the microbes are growing from only one organic substrate, the degradation rate of the organic compound

$$R_{org,deg} = v_{max} \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{EA}}{K_{EA} + C_{EA}} \frac{C_{Nit}}{K_{Nit} + C_{Nit}} X$$

is proportional to the growth rate of microbes:

$$\frac{\partial X_{growth}}{\partial t} = v_{max} Y_x \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{EA}}{K_{EA} + C_{EA}} \frac{C_{Nit}}{K_{Nit} + C_{Nit}} X$$

where Y_x depends on the stoichiometry

From a conceptual model to a numerical model

If the microbes can grow from more than one organic substrate, the growth term in the mass balance equation can be modfied to:

$$\frac{\partial X_{growth}}{\partial t} = \sum_{n=1,n_{org}} \frac{\partial X_{growth,n}}{\partial t}$$

i.e., multiple subtrates, e.g., phenol, naphtalene, phenantrene, etc. contribute to the growth, where

$$\frac{\partial X_{growth,n}}{\partial t} = v_{max}^{n} Y_X^n \frac{C_{org,n}}{K_{org,n} + C_{org,n}} \frac{C_{EA}}{K_{EA} + C_{EA}} \frac{C_{Nit}}{K_{Nit} + C_{Nit}}$$

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From a conceptual model to a numerical model

Determination of the reaction stoichiometry:

- Note the difference between reaction equations that neglect and those that consider microbial growth.
- Assume a specific composition for microbes, typically $C_5H_7O_2N$
- Assume how efficient the microbes work: How much of the (organic) carbon (within phenol, ...) is incorporated into microbial mass and how much of it is transferred to CO_2. For aerobic degradation 50 % (or 0.5) might be appropriate. Efficiency decreases for more reducing conditions (sulfate reduction, etc)
- To determine stoichiometric coefficients, balance biodegradation reaction
  - (1) ‘by hand’
  - (2) or use spreadsheet

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Balanced equations for aerobic degradation without microbial growth

- **Phenol:**
- $C_6H_5OH + 8\ O_2 \rightarrow 6\ CO_2 + 3H_2O$
- **Naphthalene:**
- $C_{10}H_8 + 12\ O_2 \rightarrow 10\ CO_2 + 4H_2O$
- **Phenanthrene:**
- $C_{14}H_{10} + 21\ O_2 \rightarrow 14\ CO_2 + 5H_2O$
- **m-Xylene:**
- $C_8H_{10} + 10.5\ O_2 \rightarrow 8\ CO_2 + 5H_2O$
- **Dibenzofuran:**
- $C_{12}H_8O + 13.5\ O_2 \rightarrow 12\ CO_2 + 4H_2O$
- **Carbazole:**
- $C_{12}H_9N + 15.5\ O_2 \rightarrow 12\ CO_2 + 4H_2O + H^+ + NO_3^-$
- **1-methylnaphthalene:**
- $C_{11}H_{10} + 13.5\ O_2 \rightarrow 11\ CO_2 + 5H_2O$

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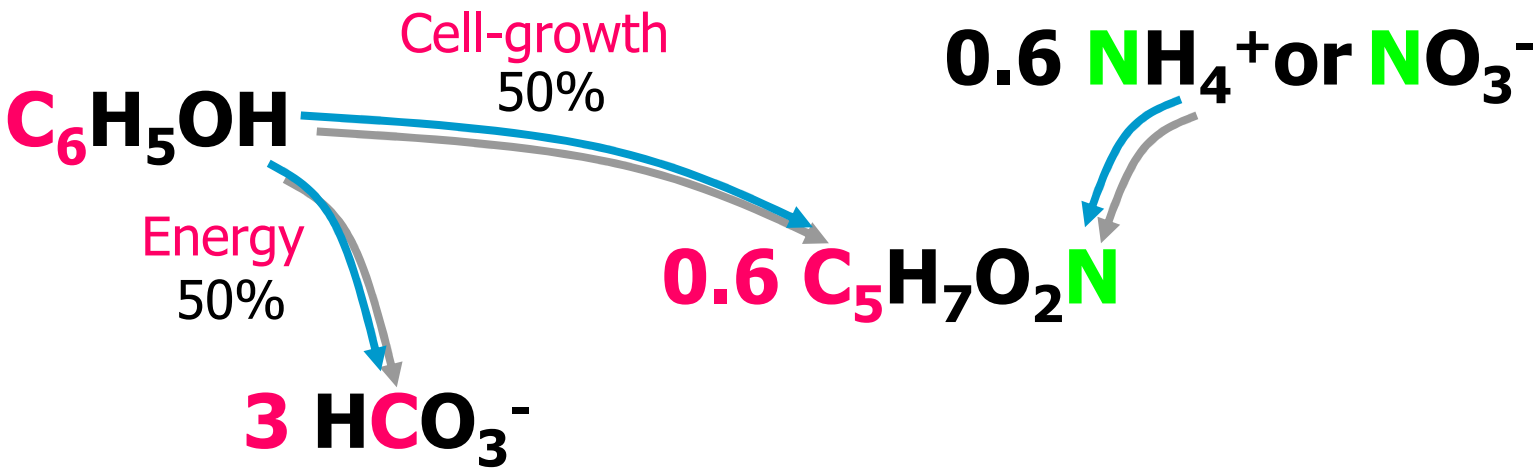
Incorporation of microbial growth



Phenol - Balanced equation with microbial growth:

- $C_6H_5OH + 0.6\ NO_3^- + 2.8\ O_2 + 1.8\ H_2O$
  $\rightarrow 3\ HCO_3^- + 0.6\ C_5H_7O_2N + 2.4\ H^+$

Balanced equations for aerobic degradation with microbial growth

- **Phenol:**

$C_6H_5OH + 0.6\ NO_3^- + 2.8\ O_2 + 1.8\ H_2O \rightarrow 3\ HCO_3^- + 0.6\ C_5H_7O_2N + 2.4\ H^+$

- **m-Xylene:**

$C_8H_{10} + 0.8\ NO_3^- + 4.9\ O_2 + 1.4\ H_2O \rightarrow 4\ HCO_3^- + 0.8\ C_5H_7O_2N + 3.2\ H^+$

- **Naphtalene:**

$C_{10}H_8 + NO_3^- + 5\ O_2 + 4\ H_2O \rightarrow 5\ HCO_3^- + C_5H_7O_2N + 4\ H^+$

- **Dibenzofuran:**

$C_{12}H_8O + 1.2\ NO_3^- + 5.1\ O_2 + 5.6\ H_2O \rightarrow 6\ HCO_3^- + 1.2\ C_5H_7O_2N + 4.8\ H^+$

- **Phenanthrene:**

$C_{14}H_{10} + 1.4\ NO_3^- + 6.7\ O_2 + 6.2\ H_20 \rightarrow 7\ HCO_3^- + 1.4C_5H_7O_2N + 5.6\ H^+$

- **1_methylnaphthalene:**

$C_{11}H_{10} + 1.1\ NO_3^- + 5.8\ O_2 + 3.8\ H_20 \rightarrow 5.5\ HCO_3^- + 1.1\ C_5H_7O_2N + 4.4\ H^+$

- **Carbazole:**

$C_{12}H_9N + NO_3^- + 1.5\ O_2 + 4\ H_20 = 2\ HCO_3^- + 2\ C_5H_7O_2N + H^+$

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From a conceptual model to a numerical model

The stoichiometry and the kinetics for organic substrate degradation, microbial growth and microbial decay are determined now, what about the electron acceptors ?

From a conceptual model to a numerical model

PHREEQC-2 does it all for us, at least as long as the partial equilibrium assumption holds, that is:

- the kinetically controlled oxidation step is rate-limiting
- the electron-accepting step is fast

Why does it work ?

- For each mol or mmol that is removed from the organic compound mass, the appropriate mass of carbon and hydrogen (e.g., C_6H_6 for benzene, C_7H_8 for toluene, etc) will be added to the aqueous solution (containing, among other species, the electron acceptors)
- The redox-state will be adjusted accordingly as the valence of C_6H_6, C_7H_8 .... etc ... is automatically and correctly computed by PHREEQC-2

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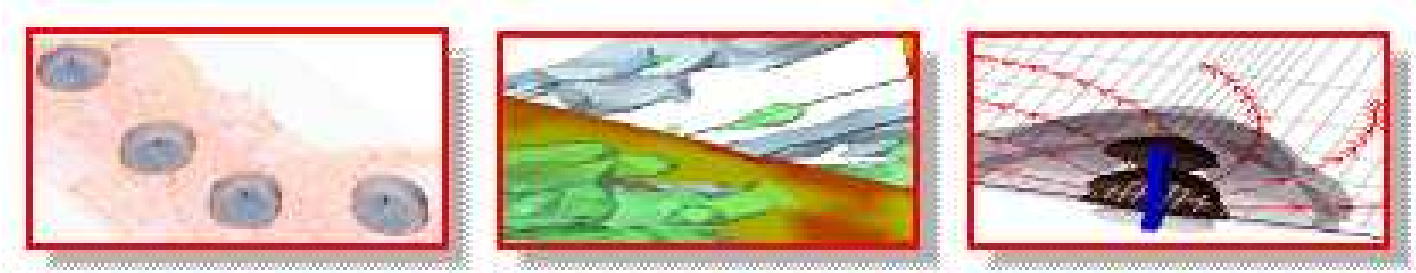
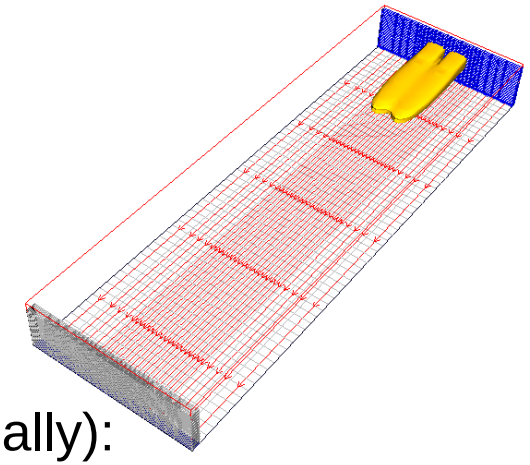


Reactive Transport Modelling of the Borden Emplaced Creosote Source Experiment

In collaboration with:
Simon Markus Gossmann, Lirong Cheng*

University of Tübingen, Centre for Applied Geoscience

Borden Emplaced Source Experiment: Model Setup



- 3D model: 60 m x 19 m x 6 m
- (61 x 26 x 30 grid-cells)
- Homogeneous aquifer:
- Symmetry allows simulation of half-model
- Compounds/components considered (initially):
  7 organic compounds, oxygen, aerobic degraders
- Compounds/components Simulation time:
  Day 0 – day 1360 after source emplacement
- Discretisation into 5 different stress-periods to account for varying source concentrations

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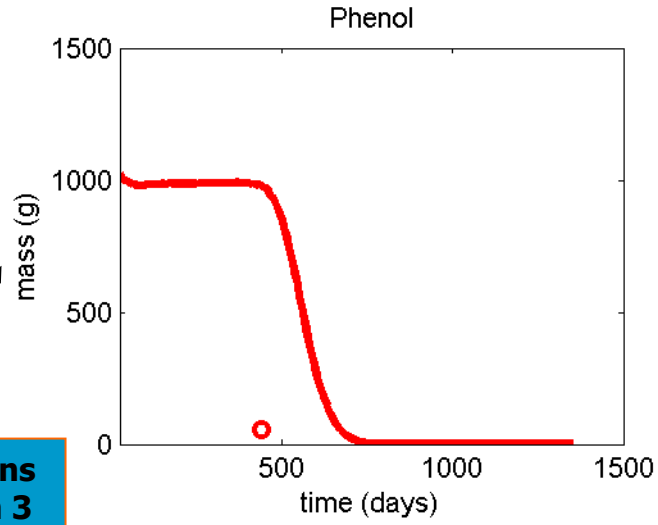
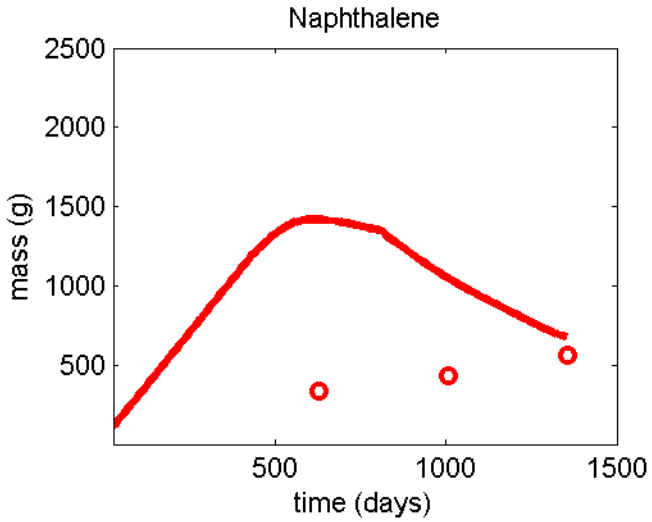
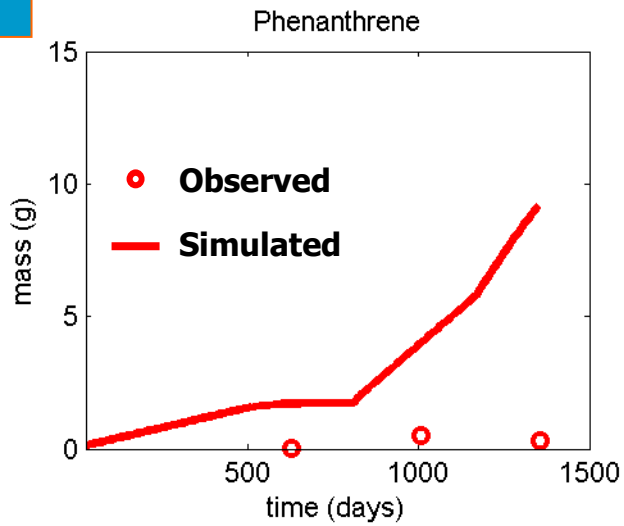
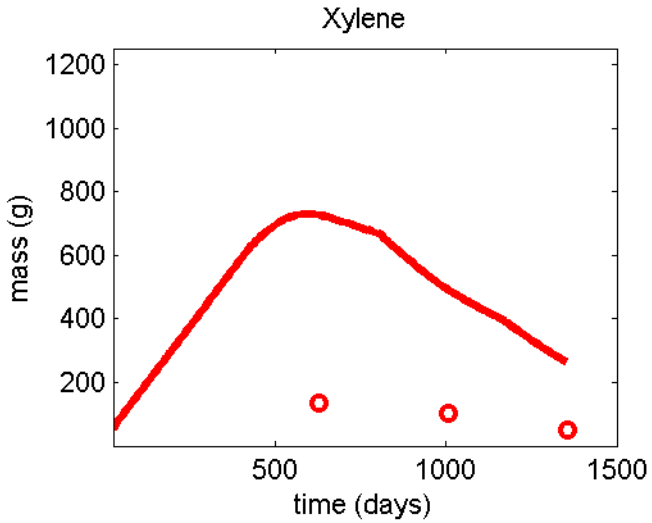
Borden Emplaced Source Experiment: Advective and Dispersive Transport (no Reaction)

Concentrations integrated in 3 dimensions

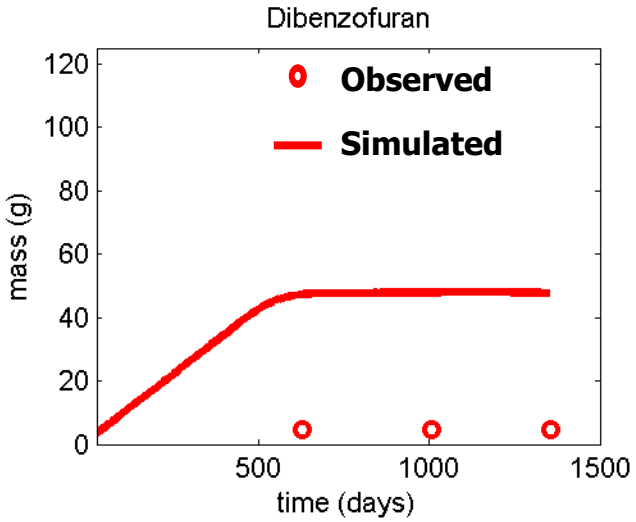


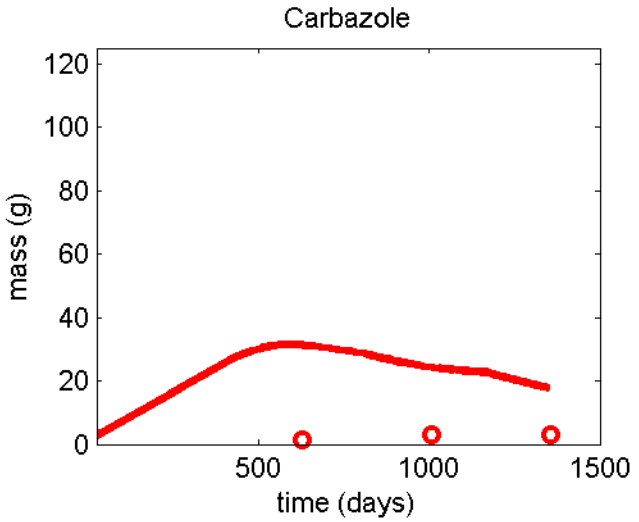


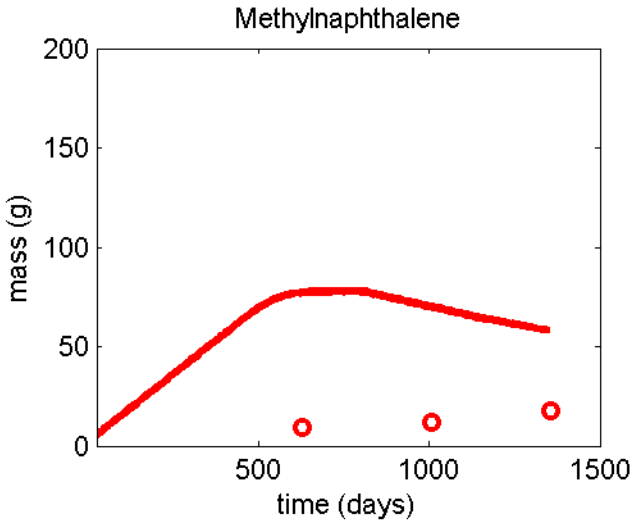




Borden Emplaced Source Experiment: Advective and Dispersive Transport (no Reaction)







Borden Emplaced Source Experiment: Sorption (King et al., 1999)

Site-specific retardation coefficients from batch-tests:

Phenol	1.05
Naphtalene	2.2
Phenanthrene	10.87
m-Xylene	1.6
Dibenzofuran	4.67
Carbazole	5.55
1-Methylnaphthalene	2.31

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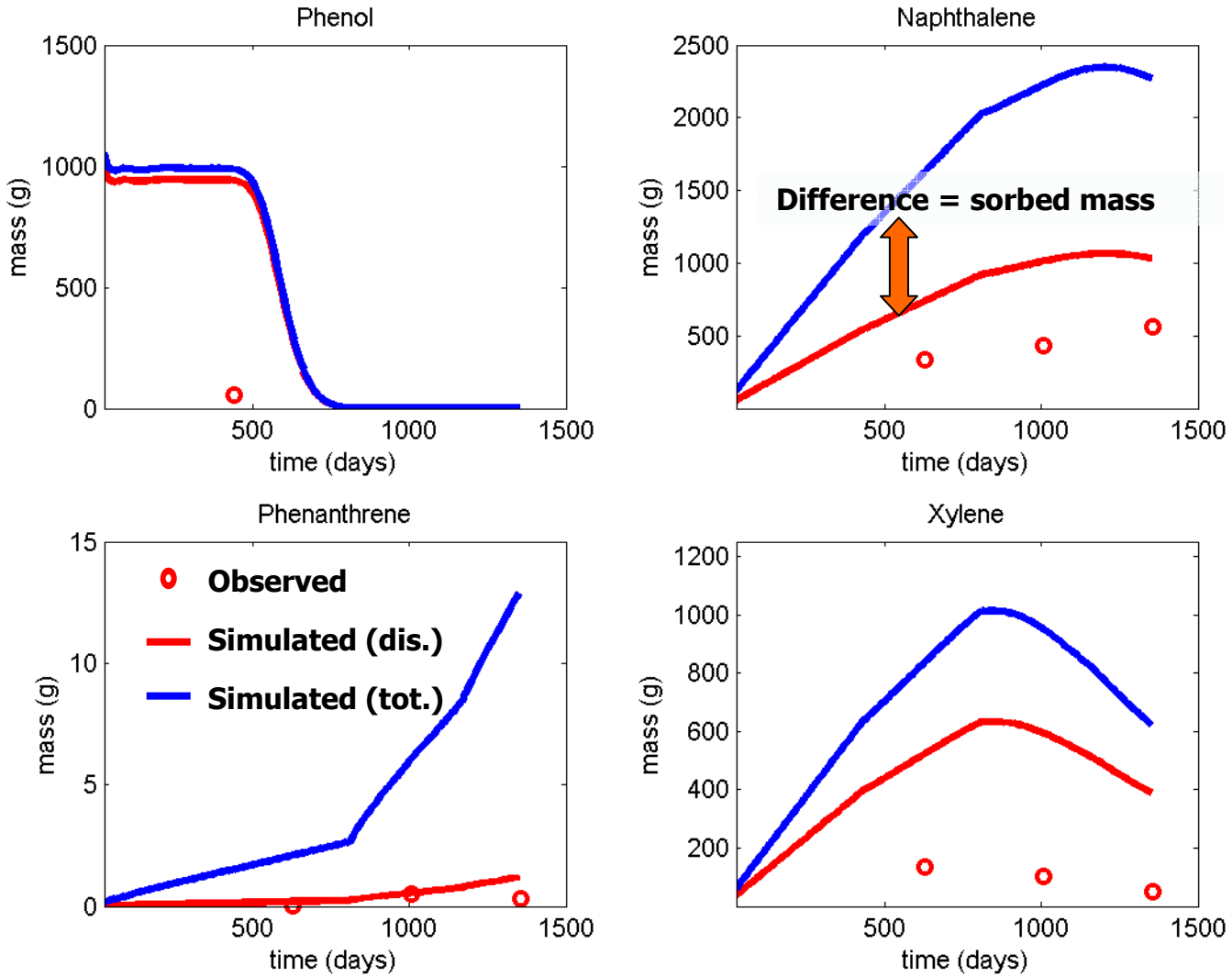
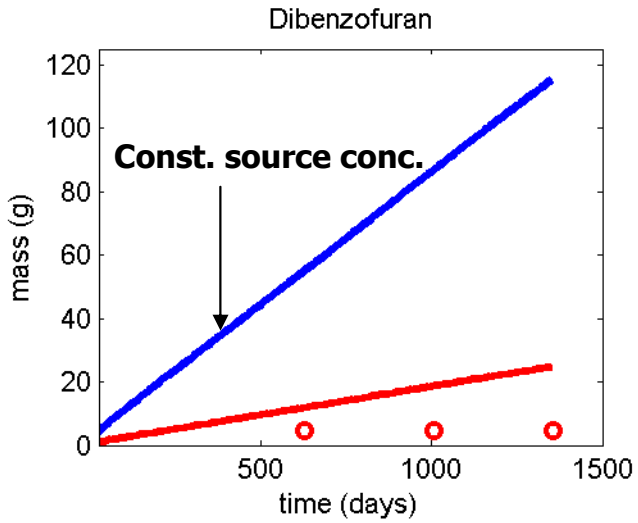
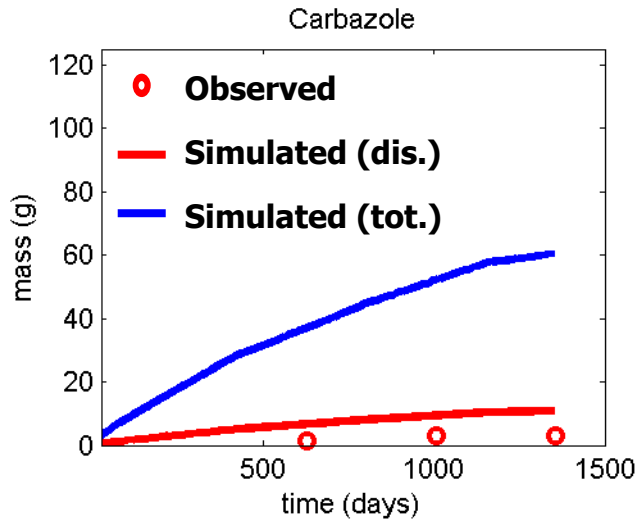
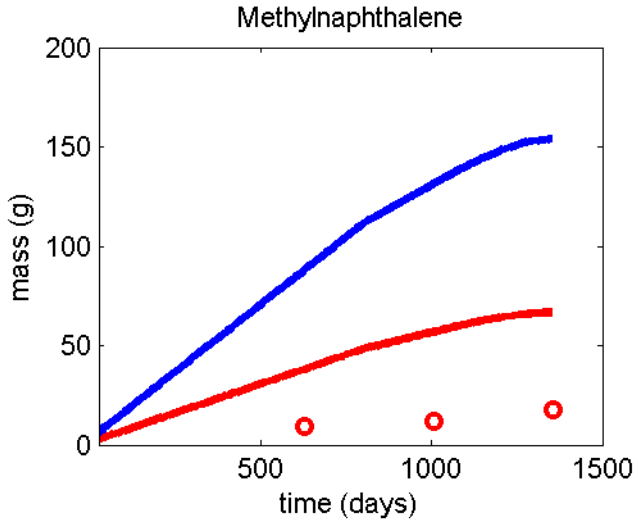
Borden Emplaced Source Experiment: Advective and Dispersive Transport with Sorption



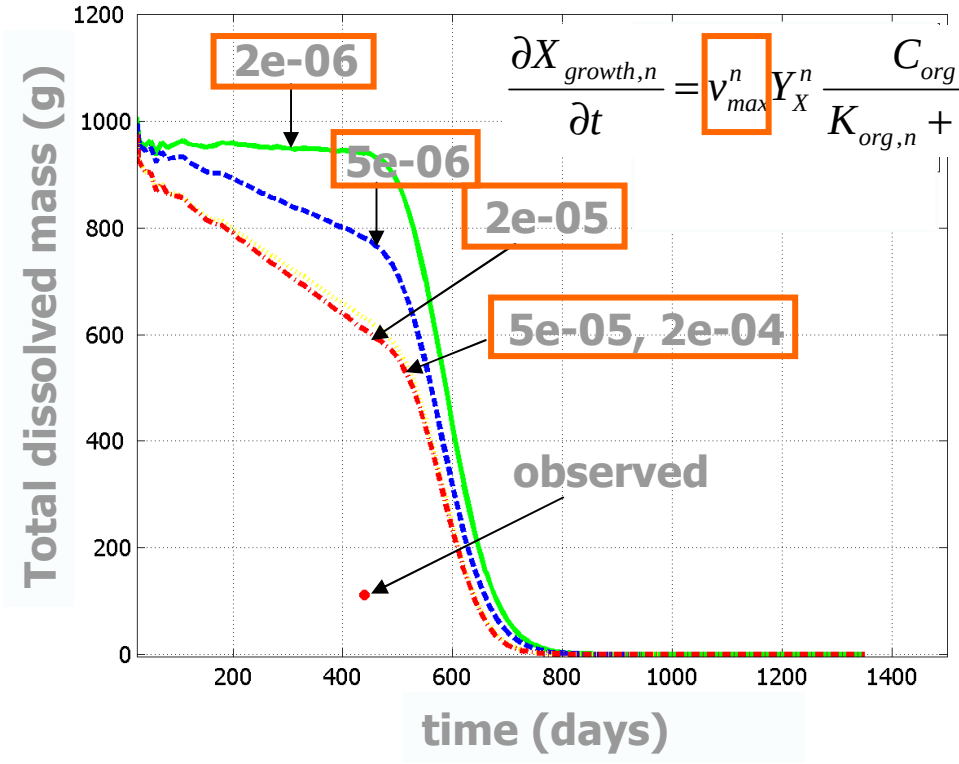
Borden Emplaced Source Experiment: Advective and Dispersive Transport with Sorption







Advective and Dispersive Transport with Sorption and Aerobic Biodegradation: Phenol Mass vs Time



$$\frac{\partial X_{growth,n}}{\partial t} = \nu_{max}^{n} Y_X^{n} \frac{C_{org,n}}{K_{org,n} + C_{org,n}} \frac{C_{EA}}{K_{EA} + C_{EA}} \frac{C_{Nit}}{K_{Nit} + C_{Nit}}$$

Variation of reaction rate constant for phenol:

- Transition from reaction rate control to supply (dispersion) controlled plume
- Not enough mass is degraded for assumed dispersivities after Sudicky et al.

Advective and Dispersive Transport with Sorption and Aerobic Biodegradation

Potential reasons for unsufficient mass removal:

- Accumulation of reaction intermediates (organic acids). Less oxidation capacity (i.e., oxygen) is used for transformation, compared to mineralisation
- Dispersivities are larger than estimated. However, reactions are controlled by local-scale dispersion which should rather be smaller than the macrodispersivity estimates from nonreactive transport (e.g., Cirpka, 1999)
- Anaerobic processes contribute to mass removal
- Some phenol mass remained unaccounted for during the integration of the 'observed mass'

Modification of conceptual model is needed and different options need to be investigated

Use of moment analysis to identify most likely 'model'

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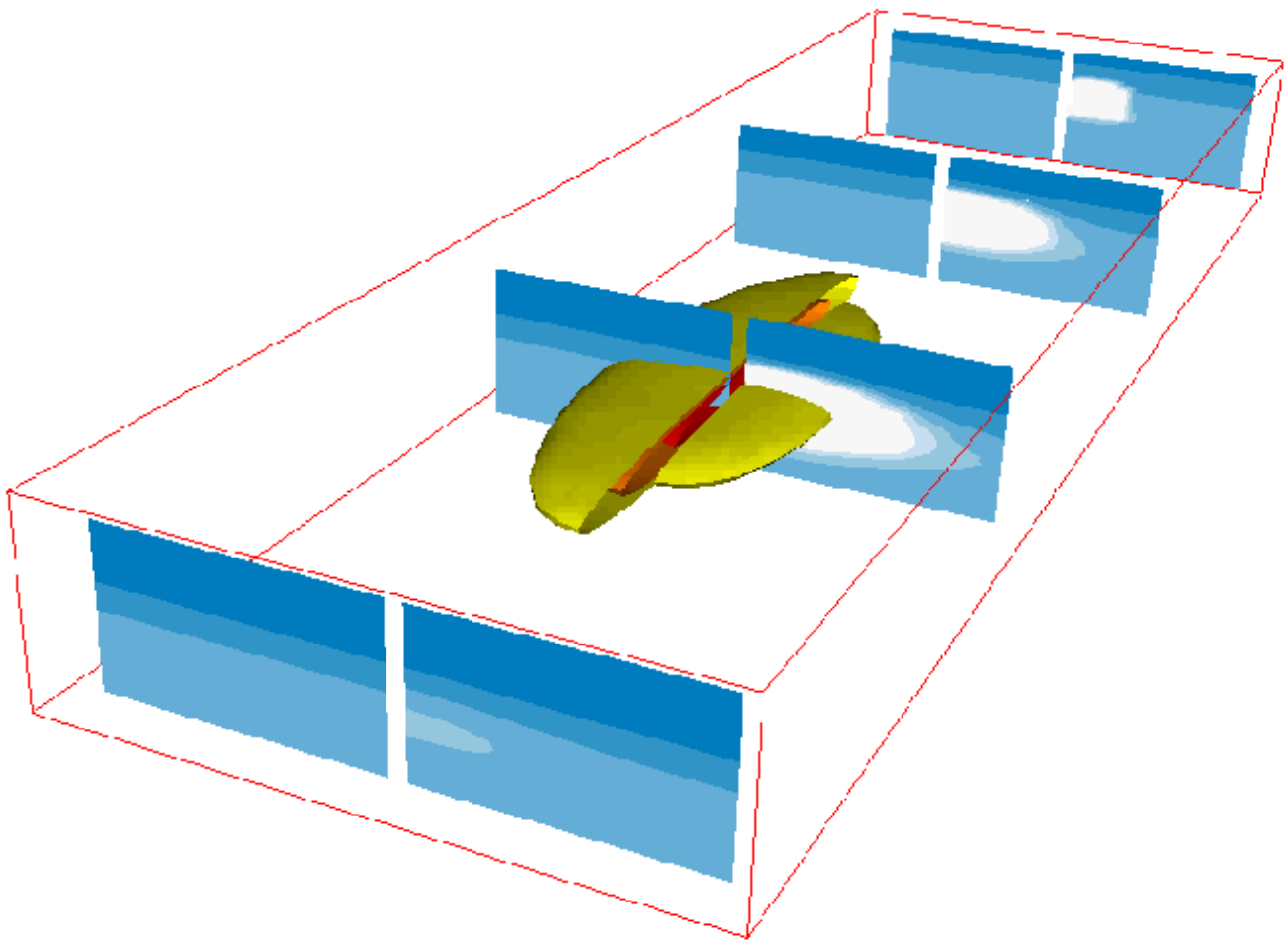
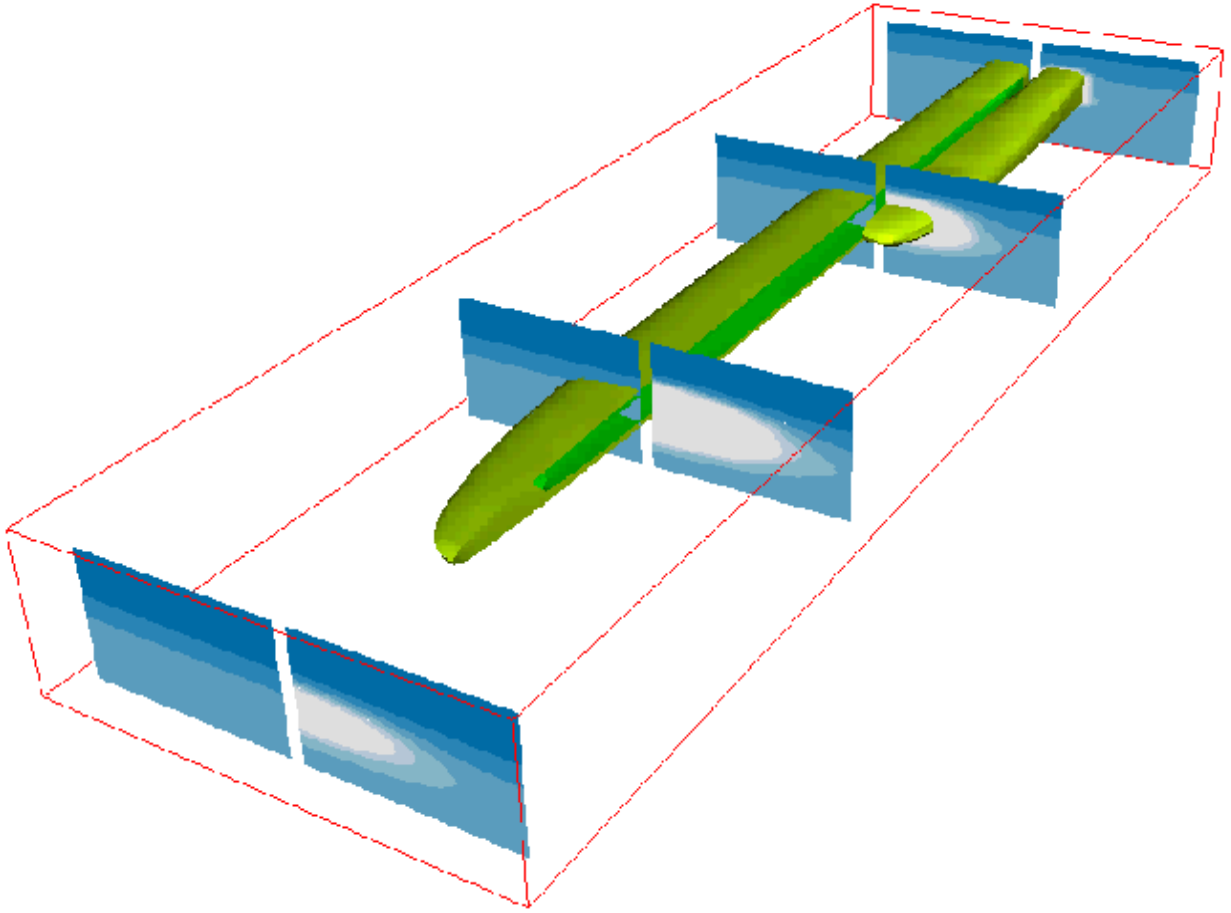
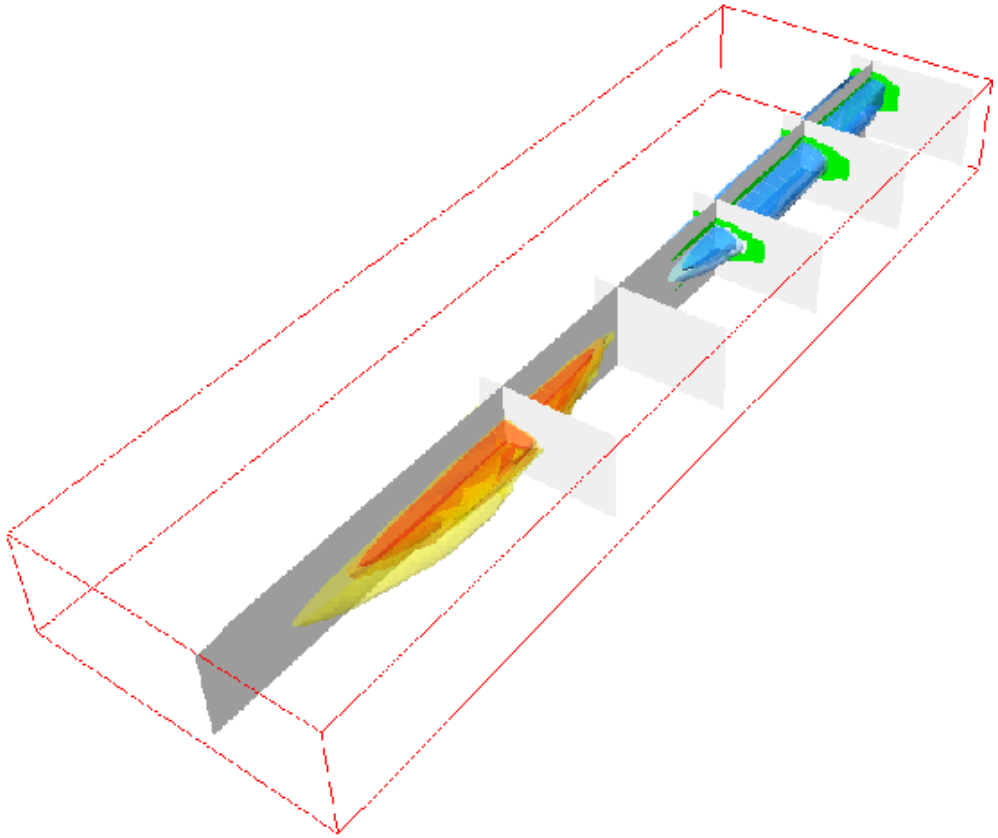
Aerobic and Anaerobic Biodegradation vs Nonreactive Transport: Phenol, Oxygen



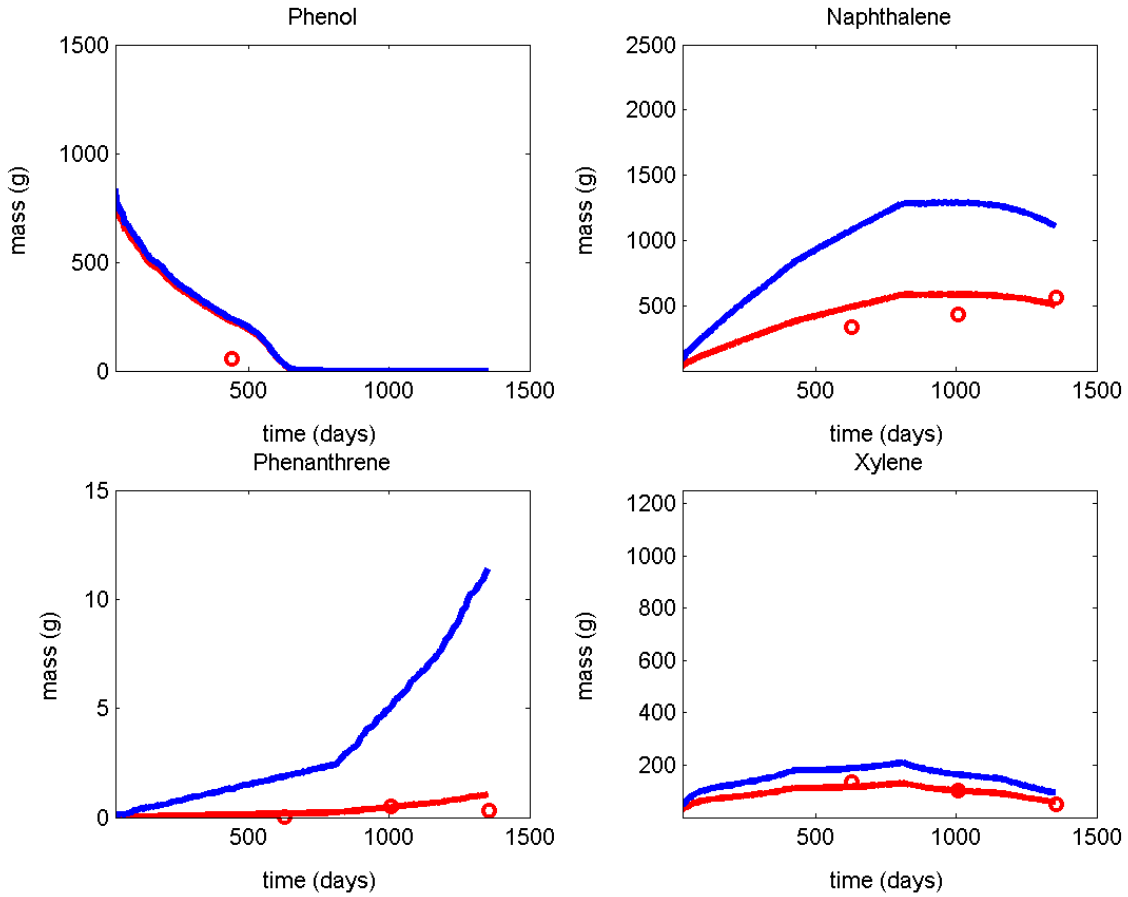
Aerobic and Anaerobic Biodegradation vs Nonreactive Transport: Naphtalene, Oxygen



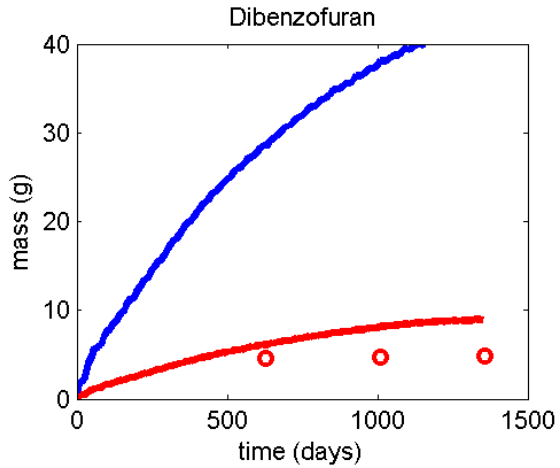
Aerobic and Anaerobic Biodegradation: Phenol, Naphtalene and Bacteria

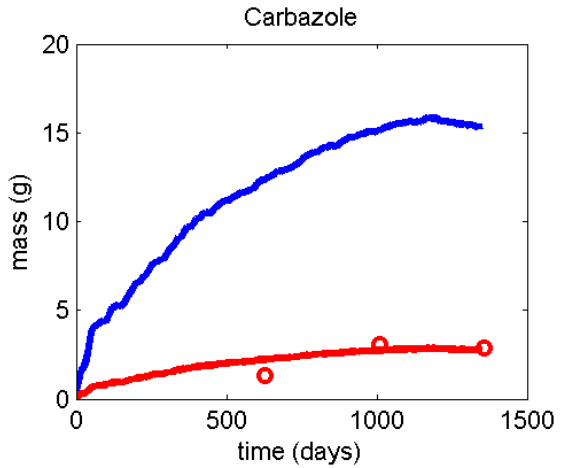


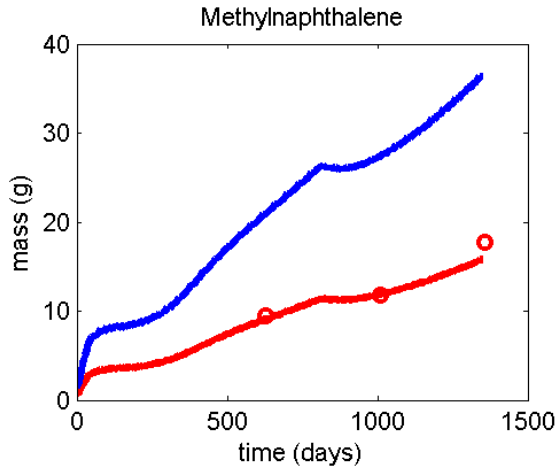
Aerobic and Anaerobic Biodegradation: Total Mass vs Time



Aerobic and Anaerobic Biodegradation: Total Mass vs Time







Summary

- The pathway from the conceptual modelling stage to a numerical model has been discussed
- Conceptual/numerical modelling should be an iterative process
- Numerical models need to be flexible such that they can be easily modified and can so 'accurately' represent site-specific conceptual models
- Generally: Mathematical modelling provides a rational framework to formulate and integrate knowledge that has otherwise been derived from (i) purely theoretical work, (ii) fundamental (e.g., laboratory) investigations and/or (iii) from site-specific experimental investigations

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