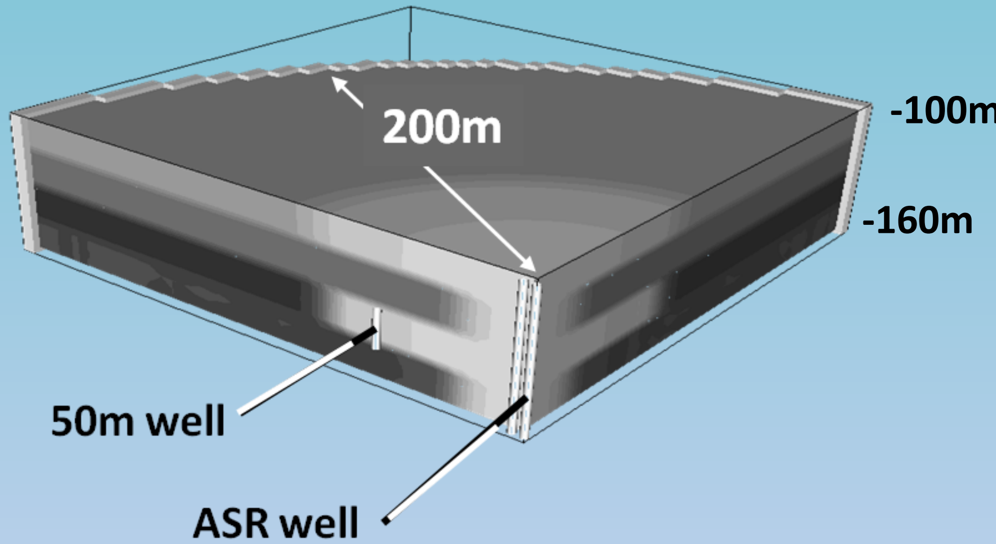


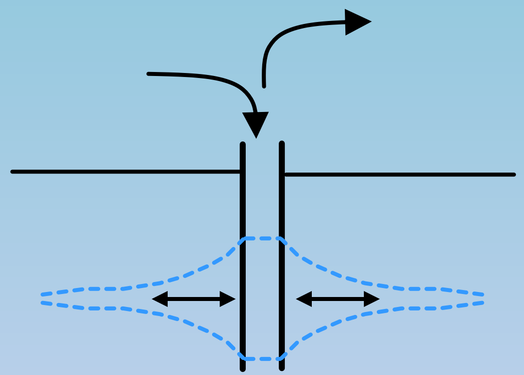
Model-based quantification of groundwater quality changes during Managed Aquifer Recharge

MARSOL Meeting, April 21-23, Pisa, Italy

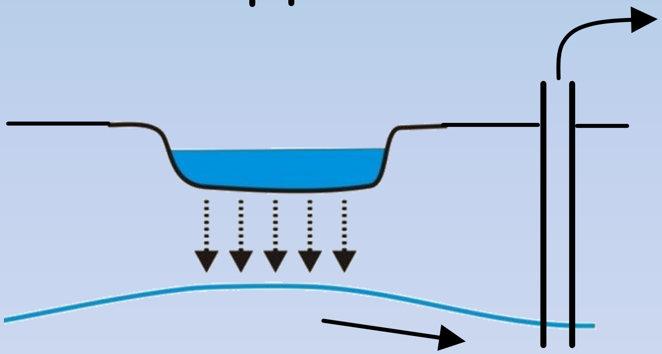
Janek Greskowiak
Carl von Ossietzky University of Oldenburg, Germany

Henning Prommer
CSIRO Land and Water, Australia
University of Western Australia
National Centre for Groundwater Research and Training (NCGRT), Australia

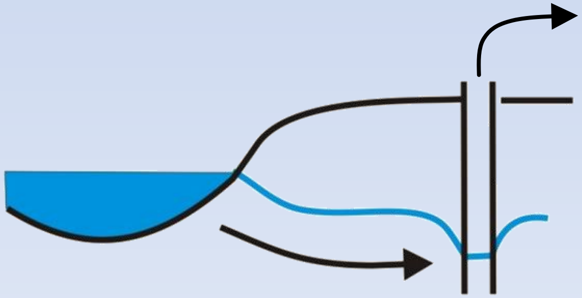
Types of Managed Aquifer Recharge (MAR)



Well injection and recovery
Aquifer storage and recovery (ASR)



Ponded infiltration
Soil aquifer treatment (SAT)



Riverbank filtration

Adapted from Dillon (2005)

Groundwater quality issues for MAR

Injection/infiltration of reclaimed, non-highly treated water:

- Degradation of (labile) dissolved organic carbon → extremely anaerobic conditions
- C, N, P → biomass accumulation → Risk of clogging

Injection/infiltration of aerobic water into anoxic aquifers

- Acid production by pyrite**,** mineral buffering

Fate of trace metals/metalloids, e.g., As

- Mobilisation in conjunction with pyrite oxidation, desorption, …

Fate of organic micropollutants (e.g., pesticides, pharmaceuticals) and pathogens

- Where surface waters or non-highly treated waste water are the source for MAR, e.g., river bank filtration (RBF), infiltration ponds

Fate of disinfection byproducts

- Trihalomethanes (THM), haloacetic acids (HAAs), …

Particle mobilisation / physical clogging

- Injection of low ionic strength water (e.g., RO water) into aquifers exceeding a critical clay fraction

Model-based identification and quantification of reactive processes

Detailed model of groundwater flow and conservative transport

- Use of measured breakthrough curves of conservative species as model calibration constraint (e.g. Chloride, Stable Isotopes)
- Use of additional constraints such as temperature to increase model reliability

Conservative transport simulation for all relevant chemical species

- Comparison of results from non-reactive model runs with data allow the identification of the reactive processes

Model for the "macro-chemistry"

- Successive addition of reactive processes to reduce discrepancies between model results and observations, starting with reaction "drivers"
- Modelling the spatial and temporal changes of the redox zonation

Model for micropollutants, metals, pathogen, ….

- Model refinement/extension for species of "concern" that often do not affect the macro-chemistry (pH, redox,…)

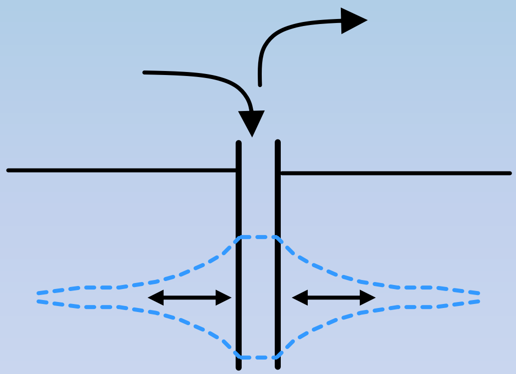
Field scale Examples

Used software:

- Flow modelling: **MODFLOW** (USGS)
- Reactive transport modelling: **PHT3D** (www.pht3d.org)
  - **PHT3D** couples MT3DMS (Zheng and Wang, 1999) and PHREEQC-2 (USGS)

Using these software was personal preference ! Any other state-of-the art flow and reactive transport modelling code could do the same!

Well injection and recovery



Aquifer storage and recovery of reclaimed water at Bolivar, South Australia

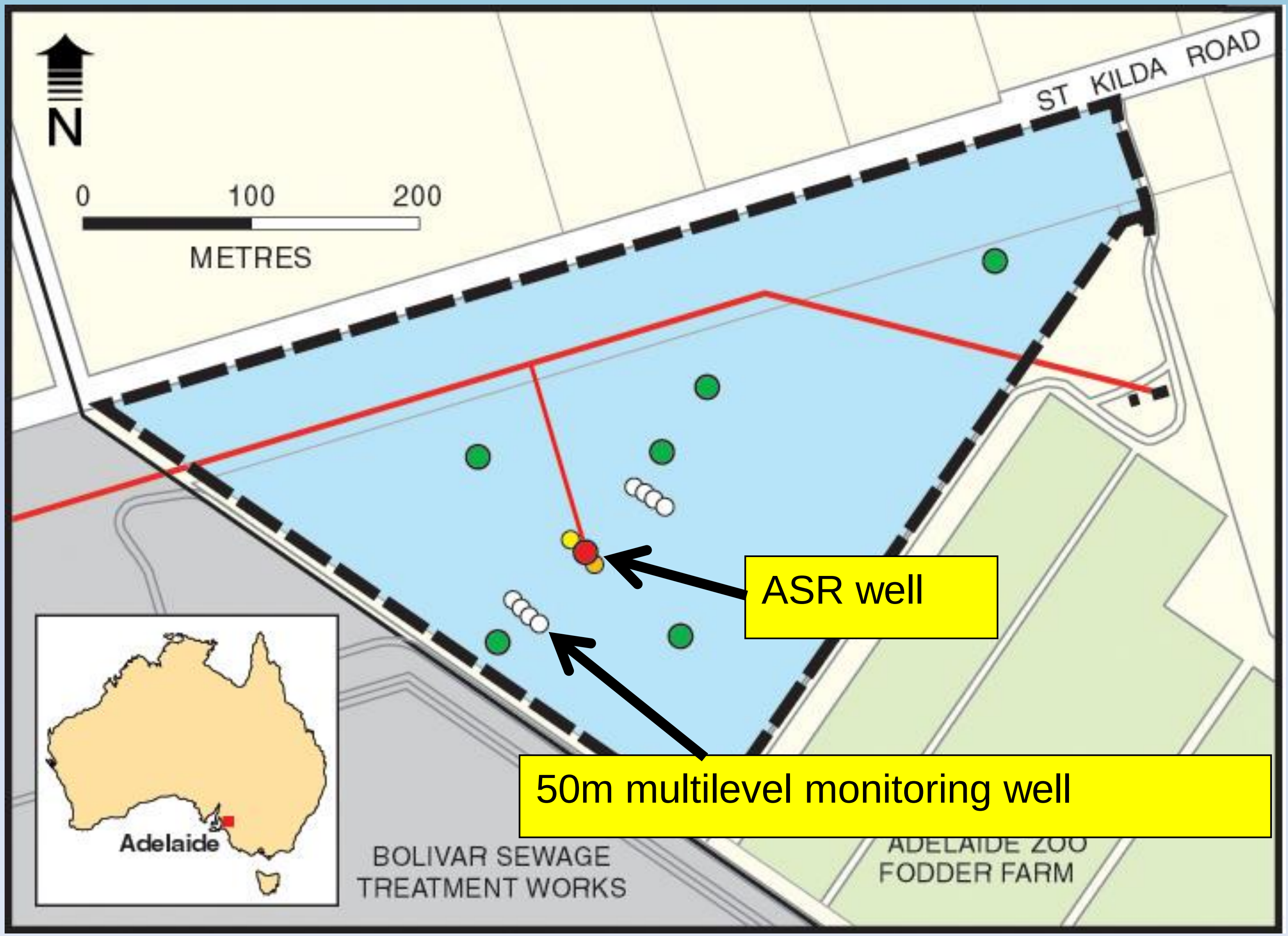
Janek Greskowiak, Henning Prommer, Joanne Vanderzalm, Paul Pavelic, Peter Dillon

(Greskowiak et al., 2005, WRR)

Purpose of the Bolivar ASR trial

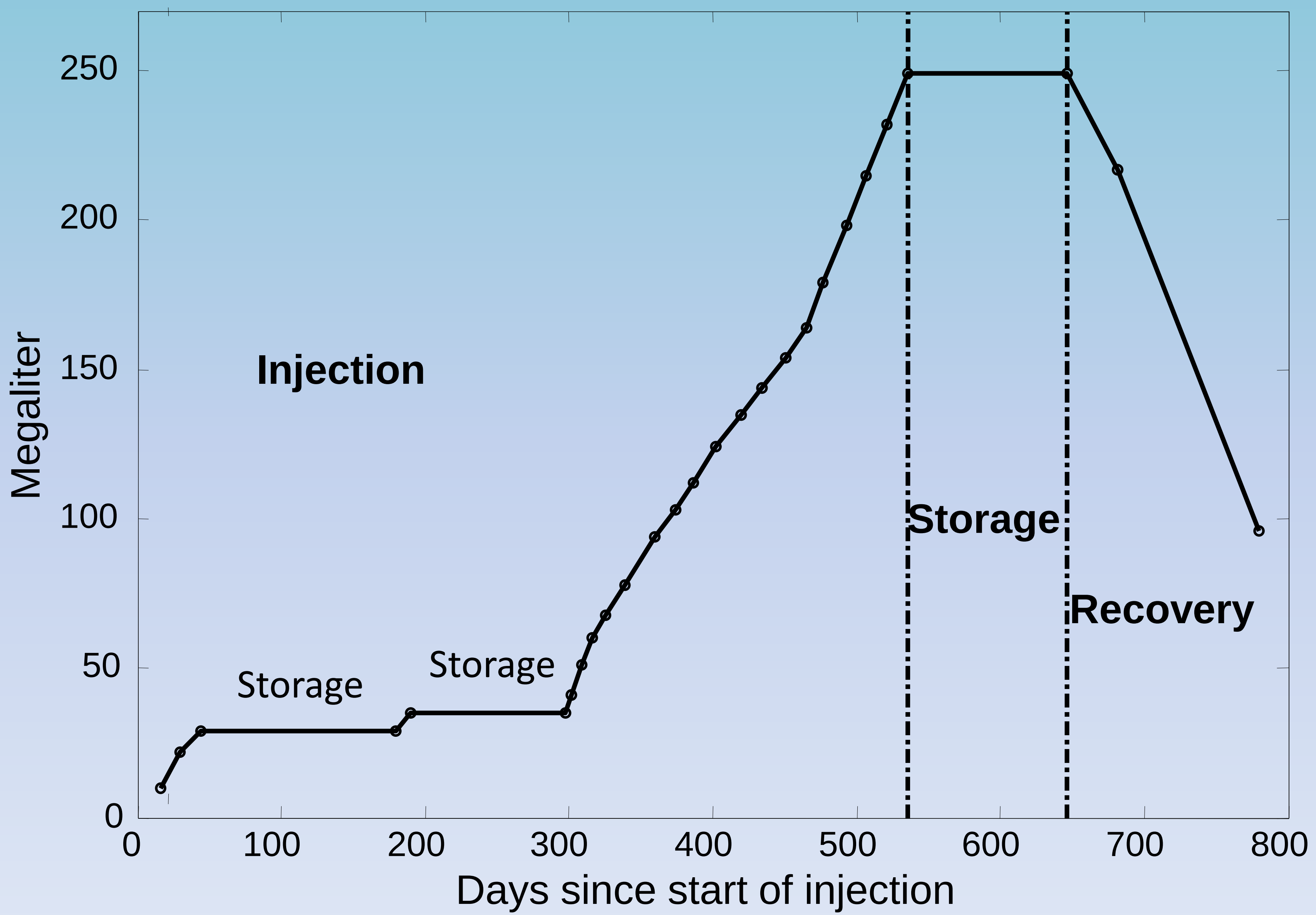
- Investigation of the viability of storage of reclaimed water
- The recovered water is supposed to compensate the greater demand of irrigation water during summer

Field site



N
0
100
200
METRES
ST KILDA ROAD
ASR well
50m multilevel monitoring well
Adelaide
BOLIVAR SEWAGE
TREATMENT WORKS
ADELAIDE ZOO
FODDER FARM

First ASR cycle (1999-2001)



Water quality

Ambient groundwater

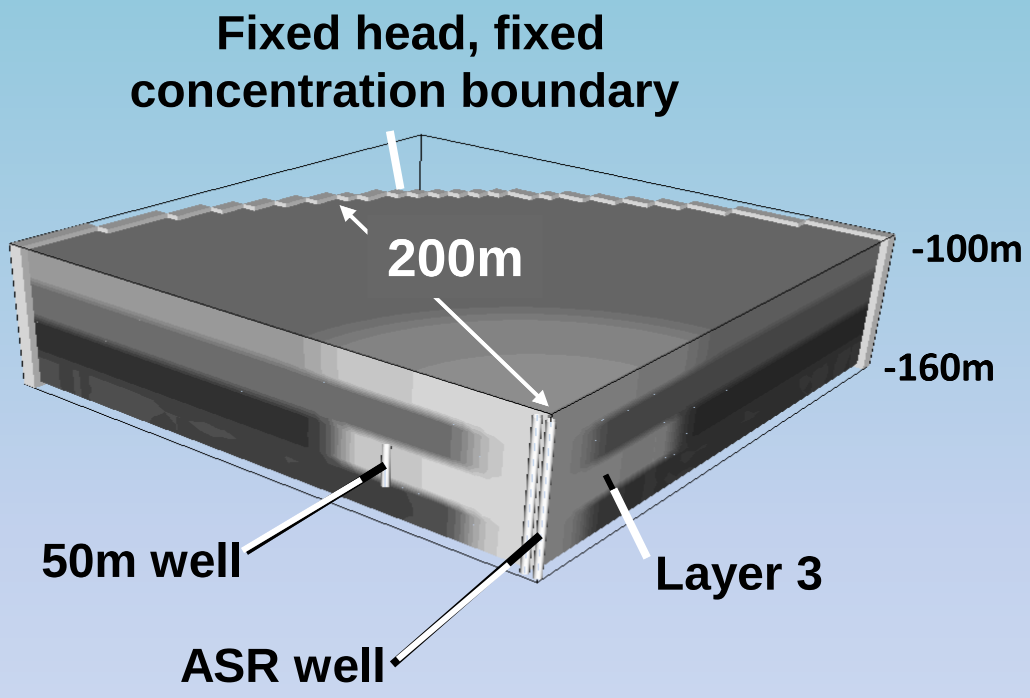
- Brackish (Salinity of ~ 2000 mg/L)
- High chloride and sulfate concentrations
- Anoxic conditons

Injectant

Total organic carbon (TOC)	~ 1.5 mmol/L
Dissolved organic carbon (DOC)	~ 1.4 mmol/L
Particulate organic carbon (POC)	~ 0.1 mmol/L
O_2	0 – 0.3 mmol/L
NO_3^-	0 – 0.3 mmol/L
NH_4^+	0 – 2.1 mmol/L

(Vanderzalm et al., 2002)

Flow and non-reactive transport



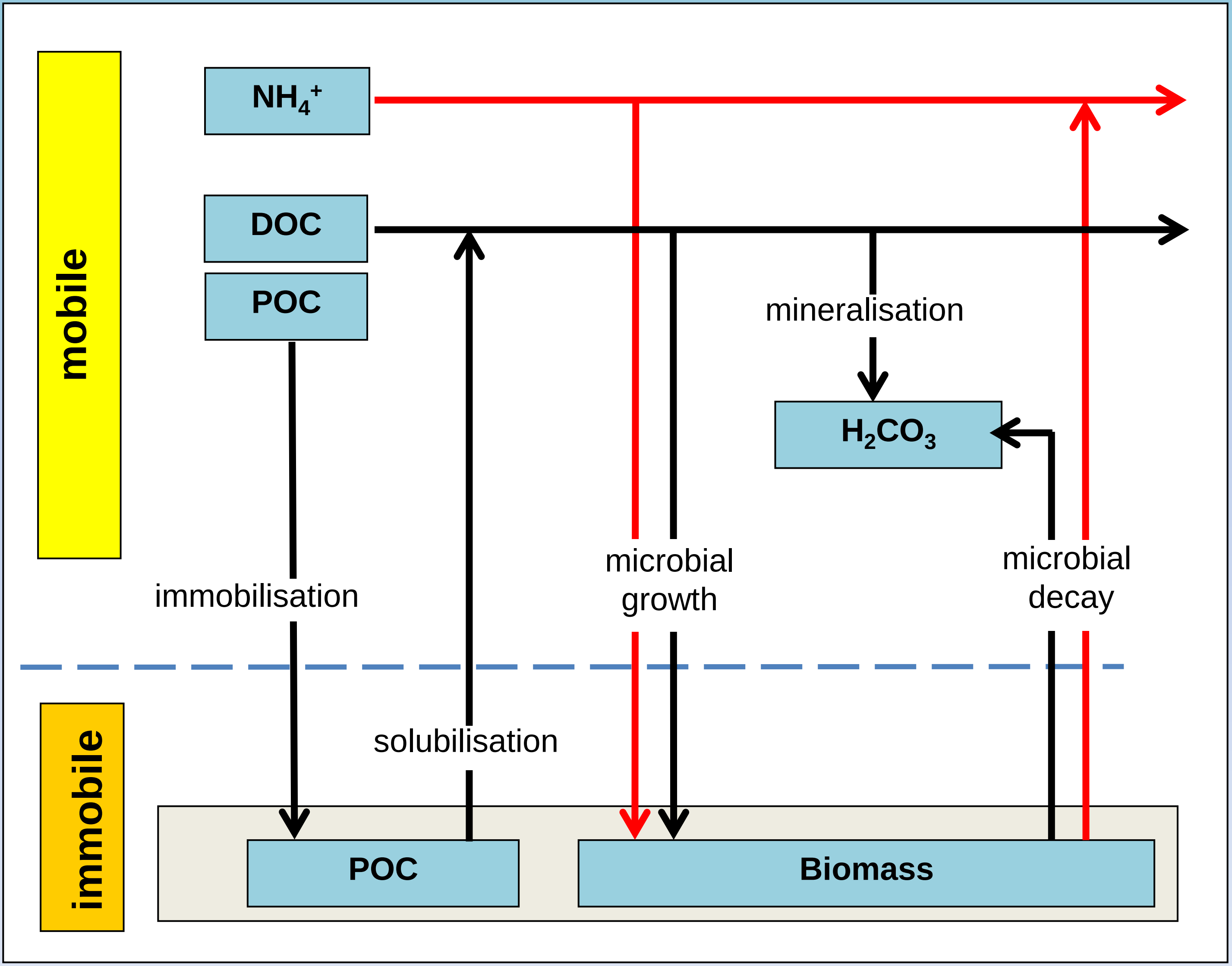
- Radial flow and conservative transport model with MODLFOW and MT3DMS
- Calibration against chloride at the 50m well by adjusting K values and dispersivities
- Subsequent reactive transport modelling was carried out only for layer 3

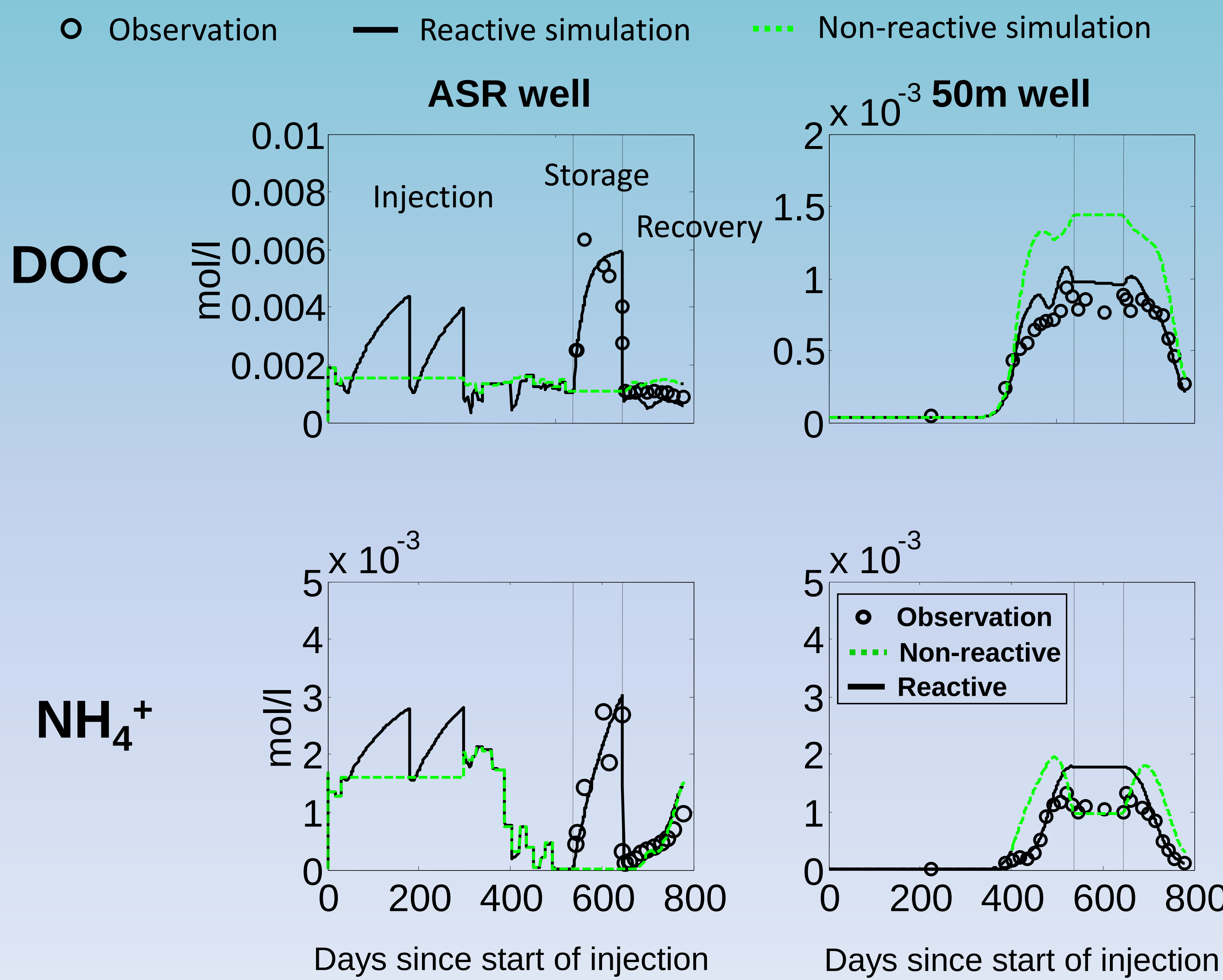
Reactive model: Components

Kinetic components	Equilibrium components	Minerals
POC	All major ions	Calcite
DOC	Oxygen	Hematite
2 Microbial groups ▪ Aerobic/denitrifying ▪ Iron- /Sulfate reducing/methanogenesis	1 Cation exchanger site	Amorphous FeS

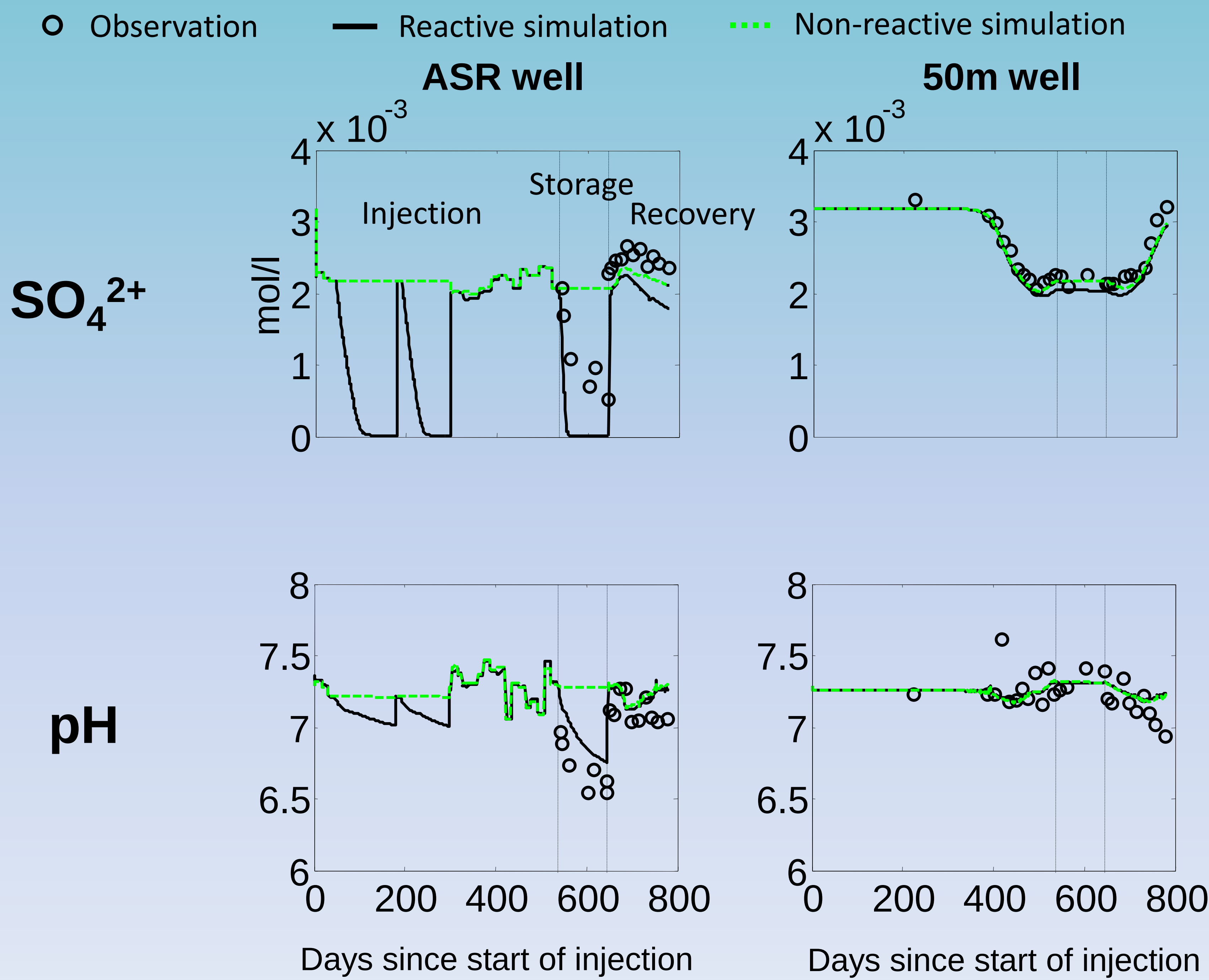
- Redox reactions (e.g., oxygen, nitrate reduction) were linked to microbial model via Mond-kinetic formulations

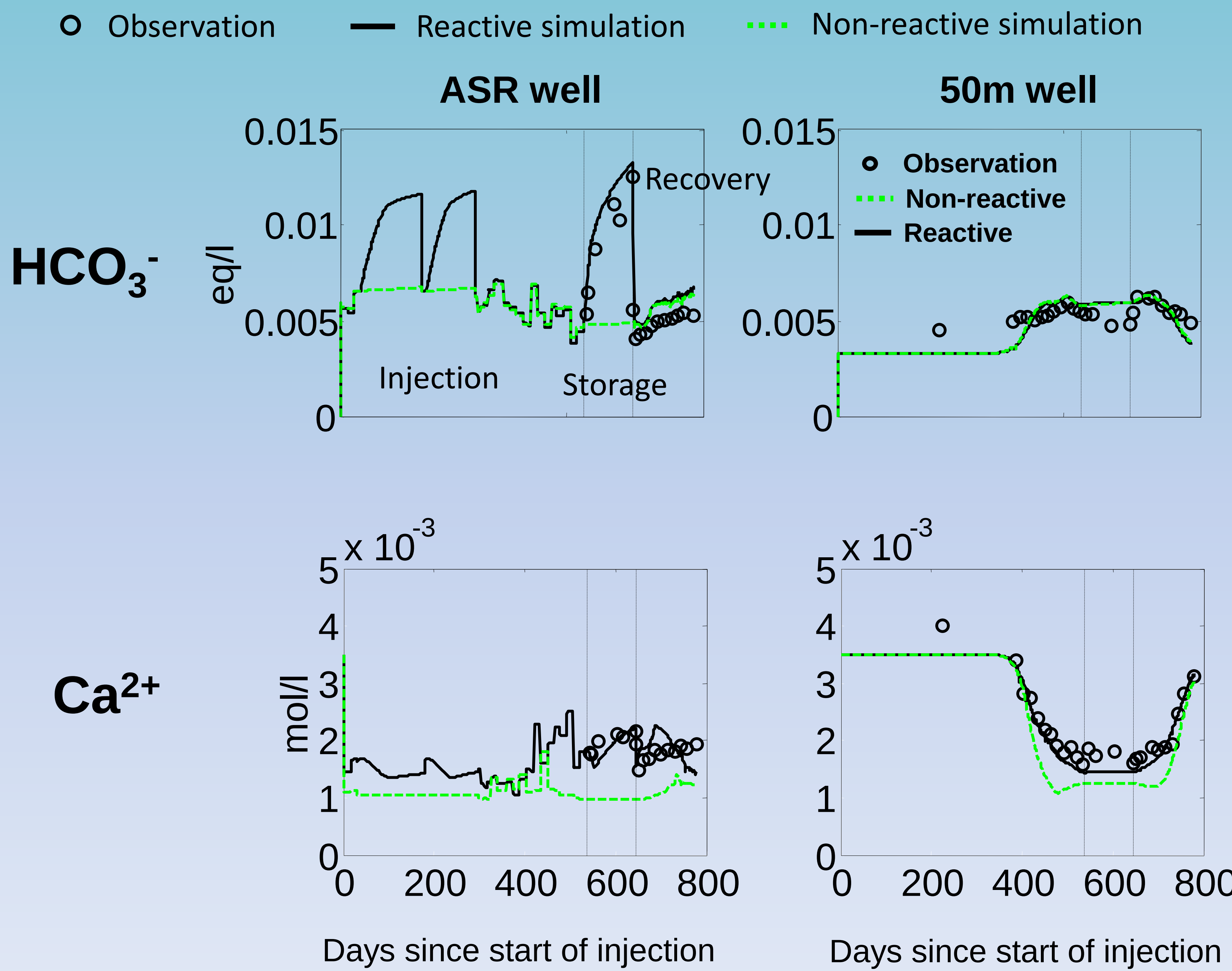
Reactive model: Nutrient cycling





Observation
Reactive simulation
Non-reactive simulation
ASR well
50m well
DOC
NH4+
mol/l
mol/l
Injection
Storage
Recovery
0.01
0.008
0.006
0.004
0.002
0
x 10-3
2
1.5
1
0.5
0
x 10-3
5
4
3
2
1
0
x 10-3
5
4
3
2
1
0
Observation
Non-reactive
Reactive
0
200
400
600
800
0
200
400
600
800
Days since start of injection
Days since start of injection


Observation
Reactive simulation
Non-reactive simulation
ASR well
50m well
SO_4^{2+}
pH
x 10^-3
mol/l
Injection
Storage
Recovery
Days since start of injection
Days since start of injection

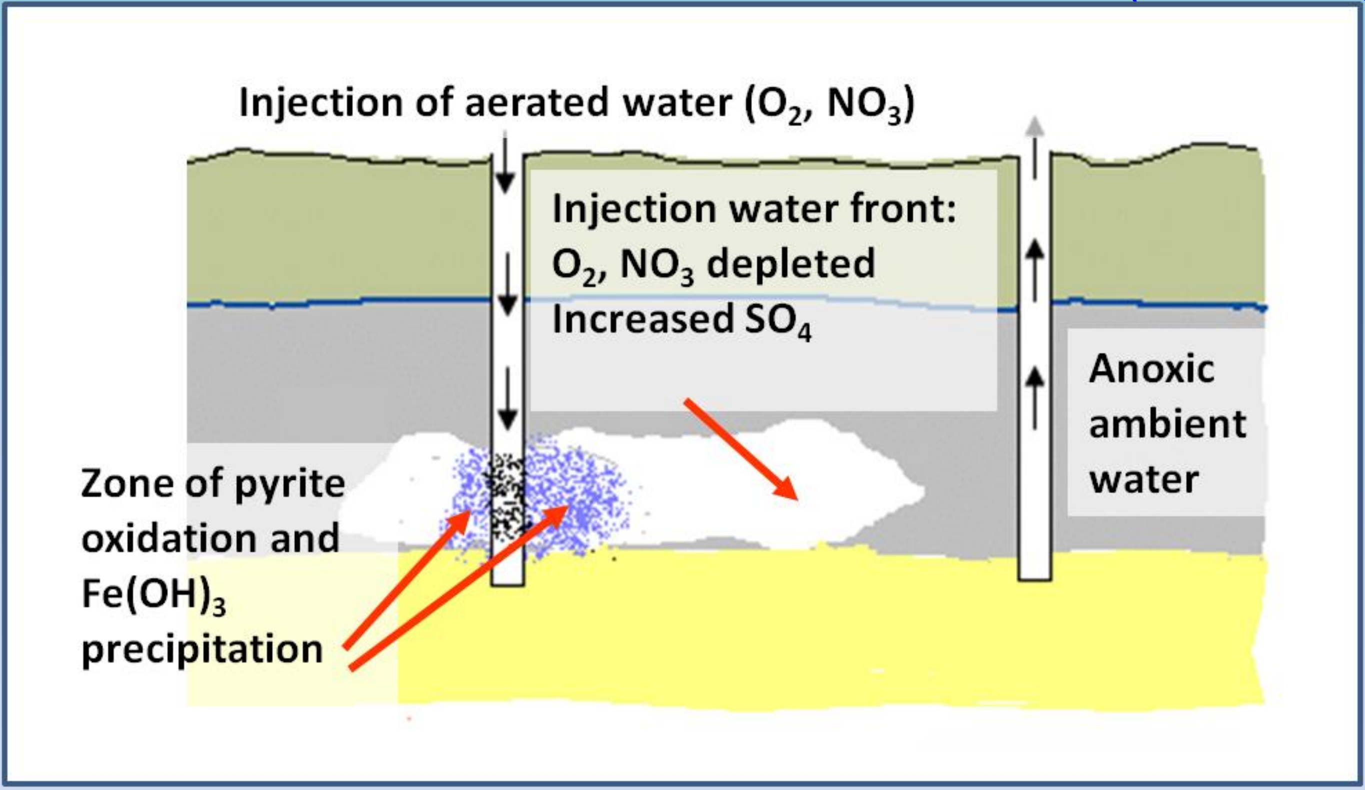


Observation
Reactive simulation
Non-reactive simulation
ASR well
50m well
HCO3-
Ca2+
eq/l
mol/l
Recovery
Injection
Storage
Observation
Non-reactive
Reactive
0.015
0.01
0.005
0
x 10-3
5
4
3
2
1
0
200
400
600
800
Days since start of injection
Days since start of injection

Deep well injection experiment Langerak/Netherlands

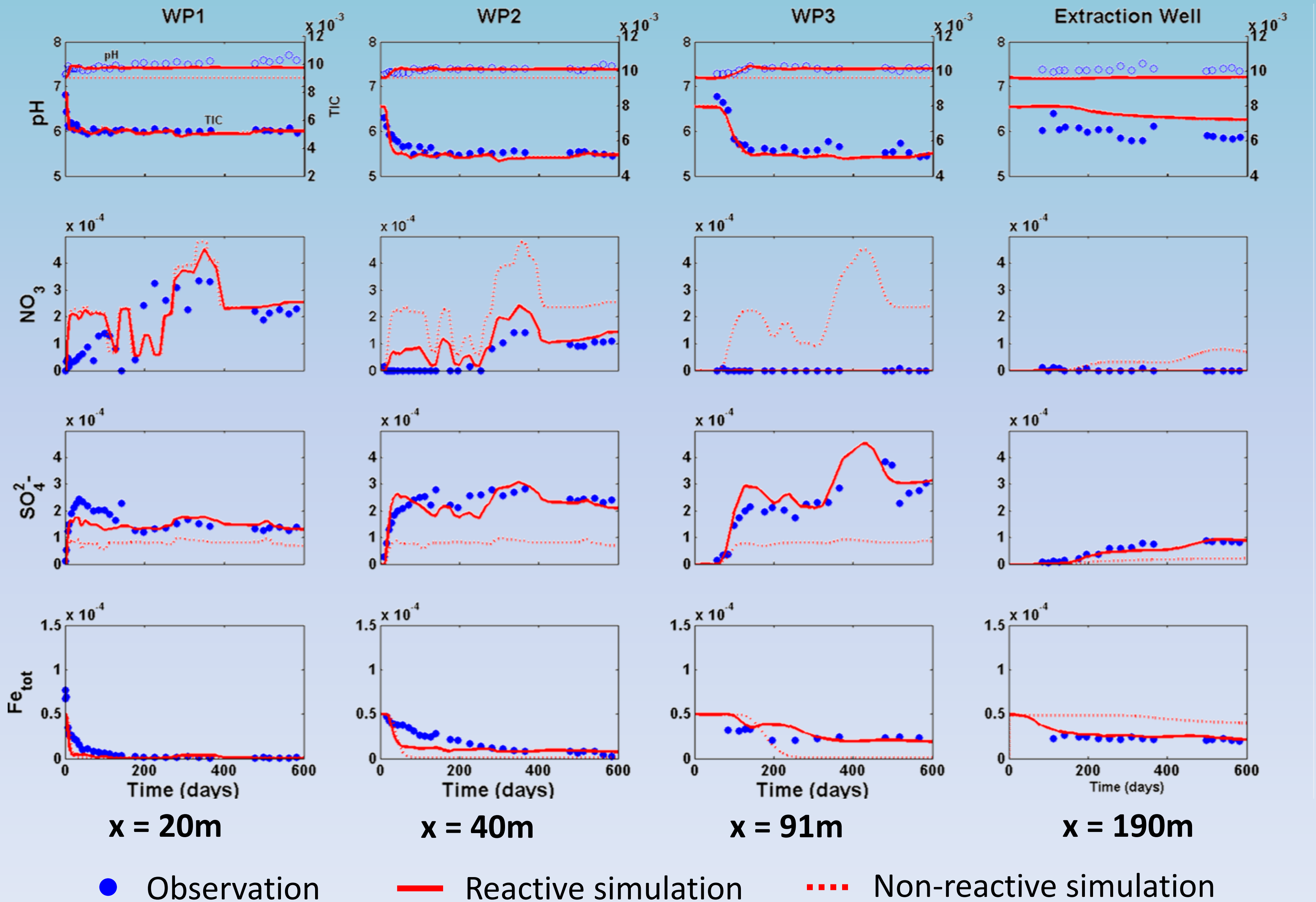
Ilka Wallis, Henning Prommer, Craig T. Simmons, Vincent Post and Pieter J. Stuyfzand

(Wallis et al., 2010, ES&T)

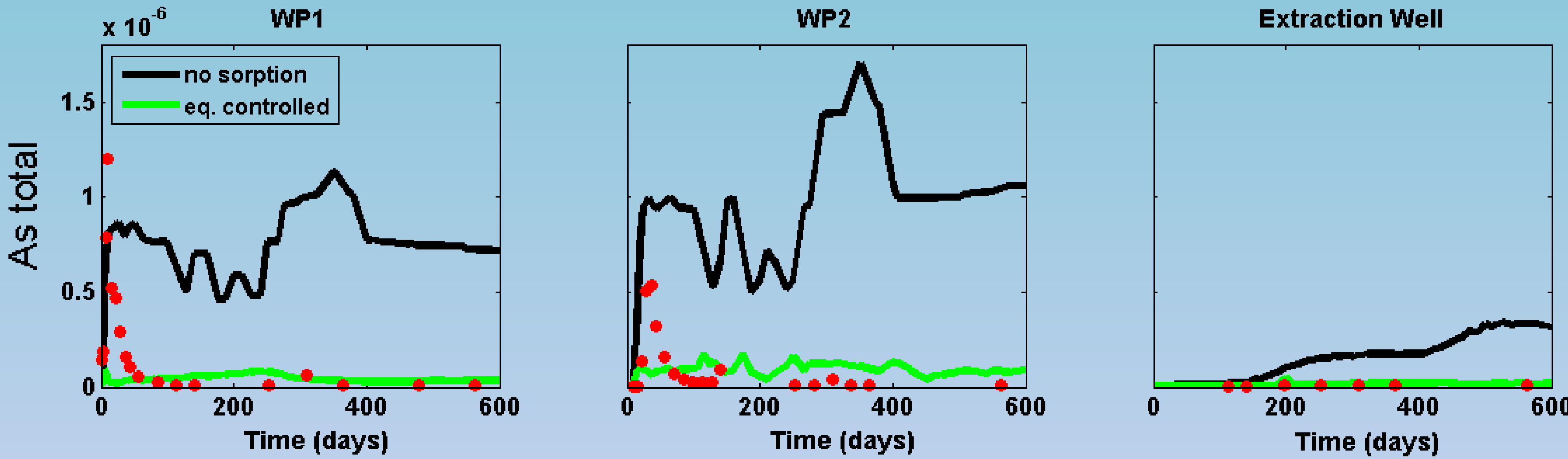


- Pyrite oxidation occurs in response to injection of aerobic water (Saaltink et al., 2003, JCH)
- Stoichiometric release of arsenic linked to pyrite oxidation
- Ferrous iron is oxidised and precipitates as $Fe(OH)_3$, thus providing a successively increasing sorption capacity for As.
- Sorption of As assumed to occur as a surface complexation reaction with Fe(OH)3 (ala Dzombak and Morel)

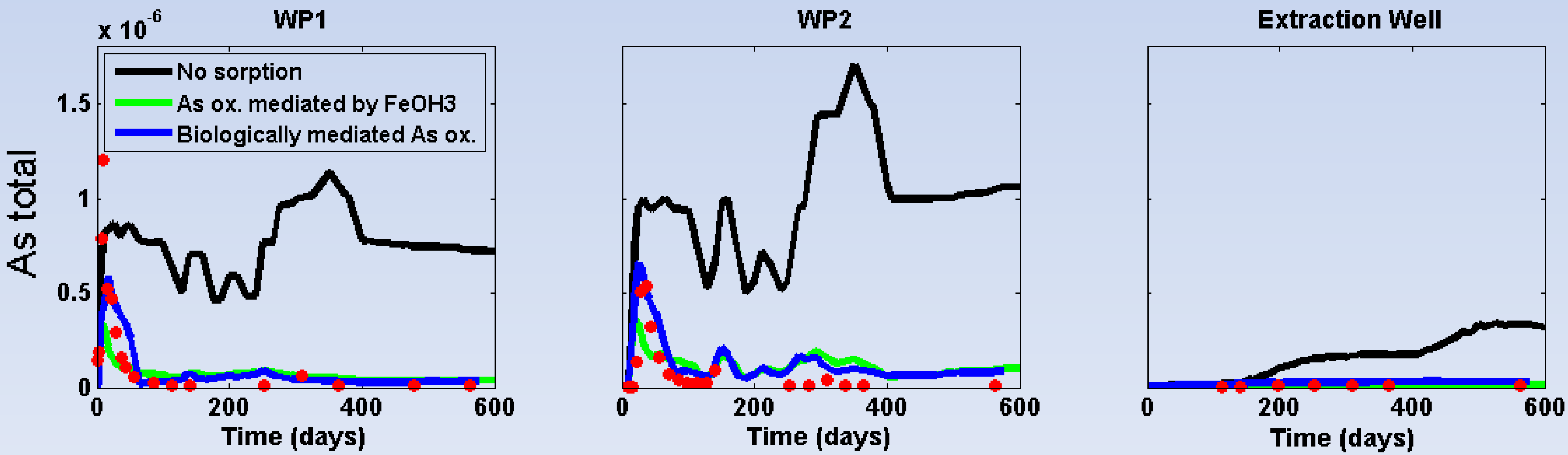
Reactive Transport (Major Ion/Redox Chemistry)



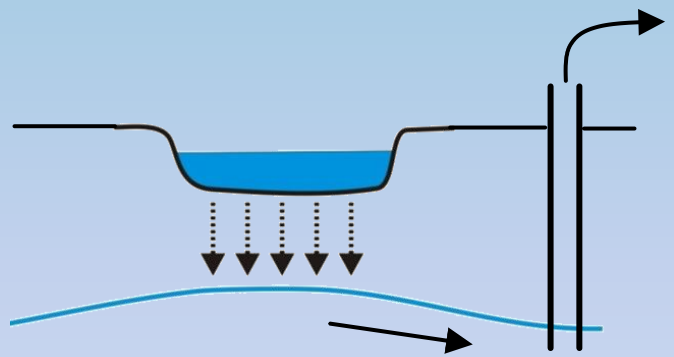
As(III)/As(V) Redox-equilibrium



Kinetic oxidation of As(III) to As(V)



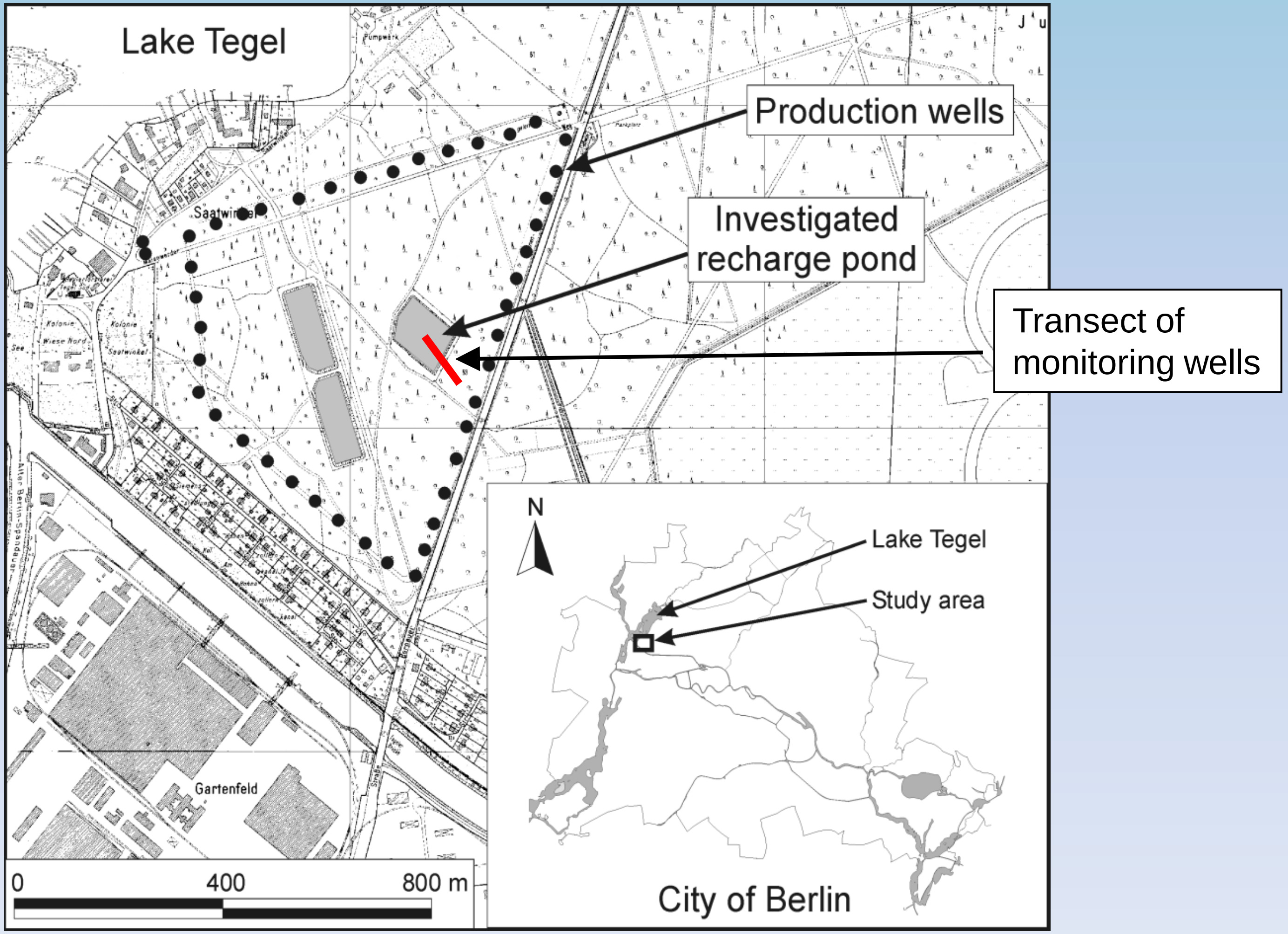
Ponded infiltration



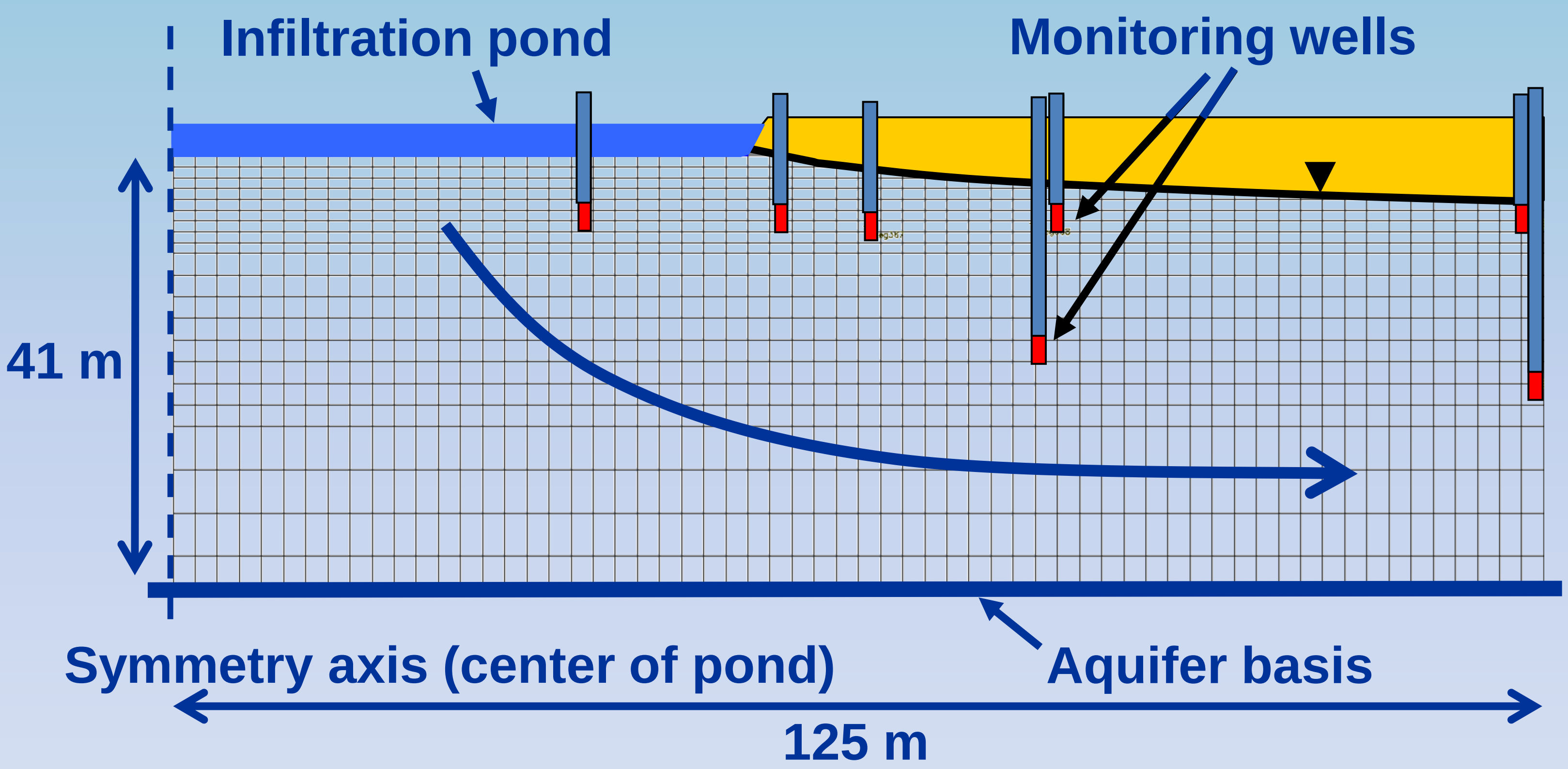
Seasonal redox dynamics during ponded infiltration, Berlin, Germany

Janek Greskowiak, Henning Prommer, Gudrun Massmann, and Gunnar Nützmann

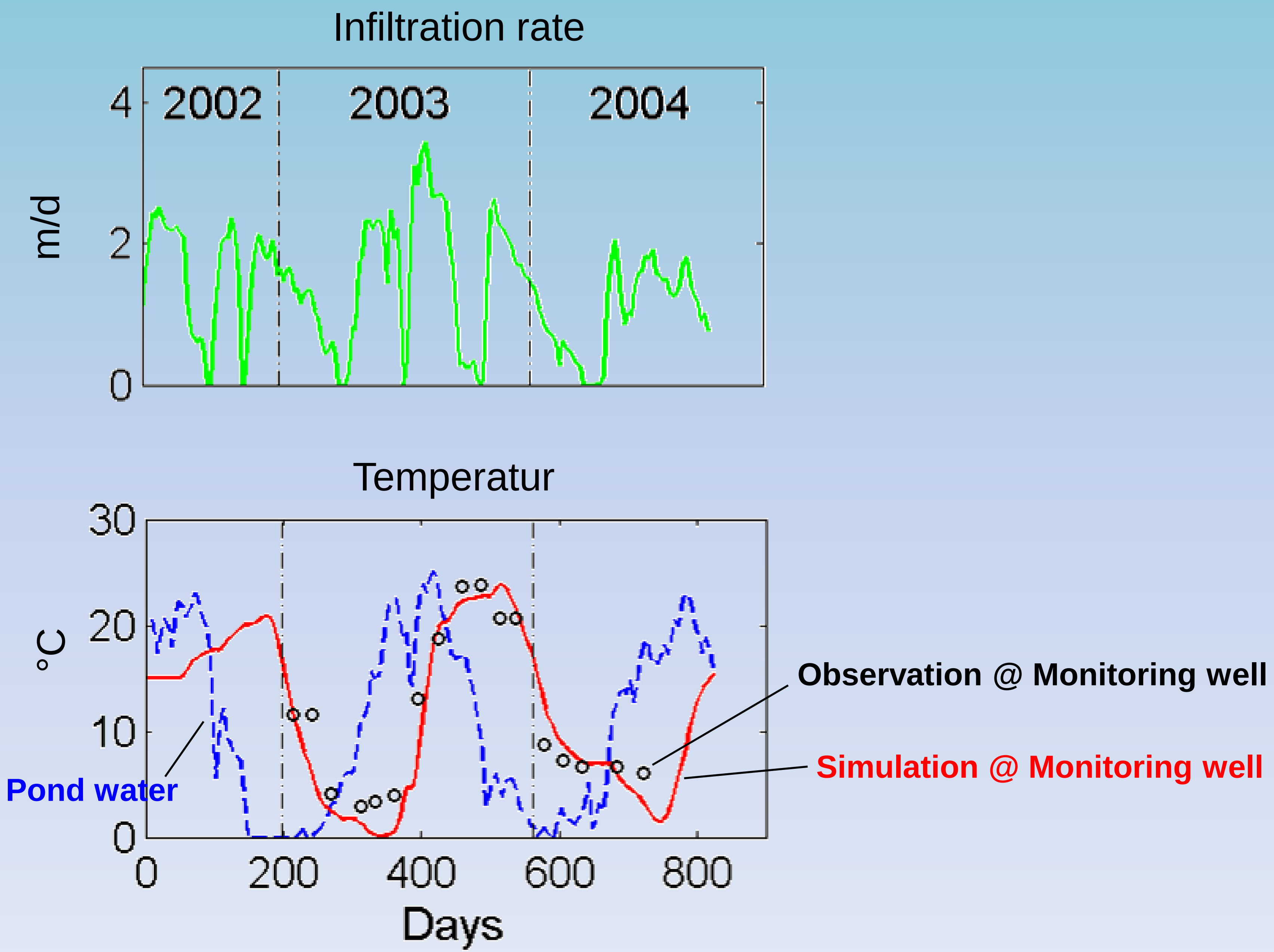
(Greskowiak et al., 2006, ES&T)



Radial cross-section model

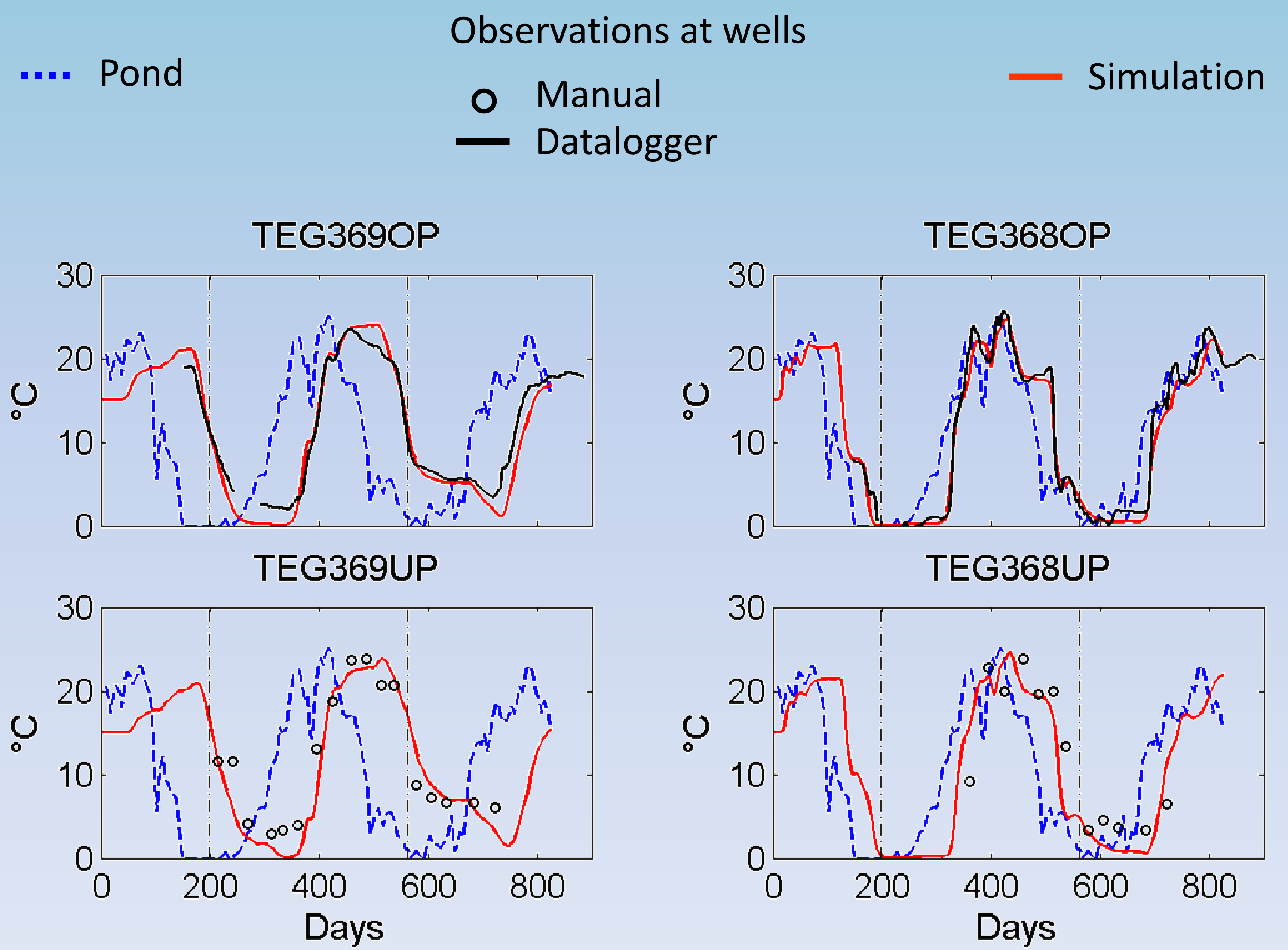


Highly dynamic hydrological boundary conditions



Non-reactive simulation (Temperature)

Temperature retardation R = 2.1 (Derived from breakthrough of water isotopes)



Reactive model: Components

Kinetic components	Equilibrium components	Minerals
Soil organic matter	All major ions	Calcite
	Oxygen	Pyrolusite (MnO_2)

Temperature dependent redox reaction rate formulations

O_2 reduction

$$r_{ox} = f_T k_{ox} \left(\frac{C_{ox}}{K_{ox} + C_{ox}} \right)$$

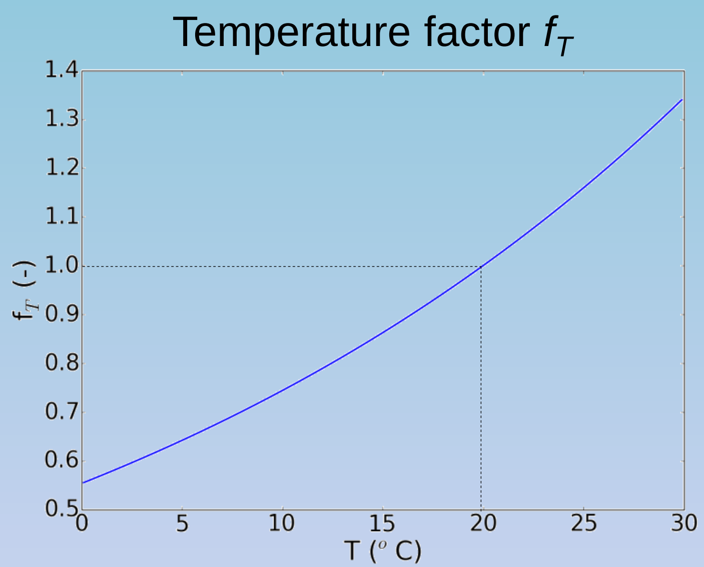
Nitrate reduction

$$r_{nitr} = f_T k_{nitr} \left(\frac{C_{nitr}}{K_{nitr} + C_{nitr}} \right) \left(\frac{K_{ox\_inh}}{K_{ox\_inh} + C_{ox}} \right)$$

Manganese reduction

$$r_{mn} = f_T k_{mn} \left(\frac{K_{ox\_inh}}{K_{ox\_inh} + C_{ox}} \right) \left(\frac{K_{nitr\_inh}}{K_{nitr\_inh} + C_{nitr}} \right)$$

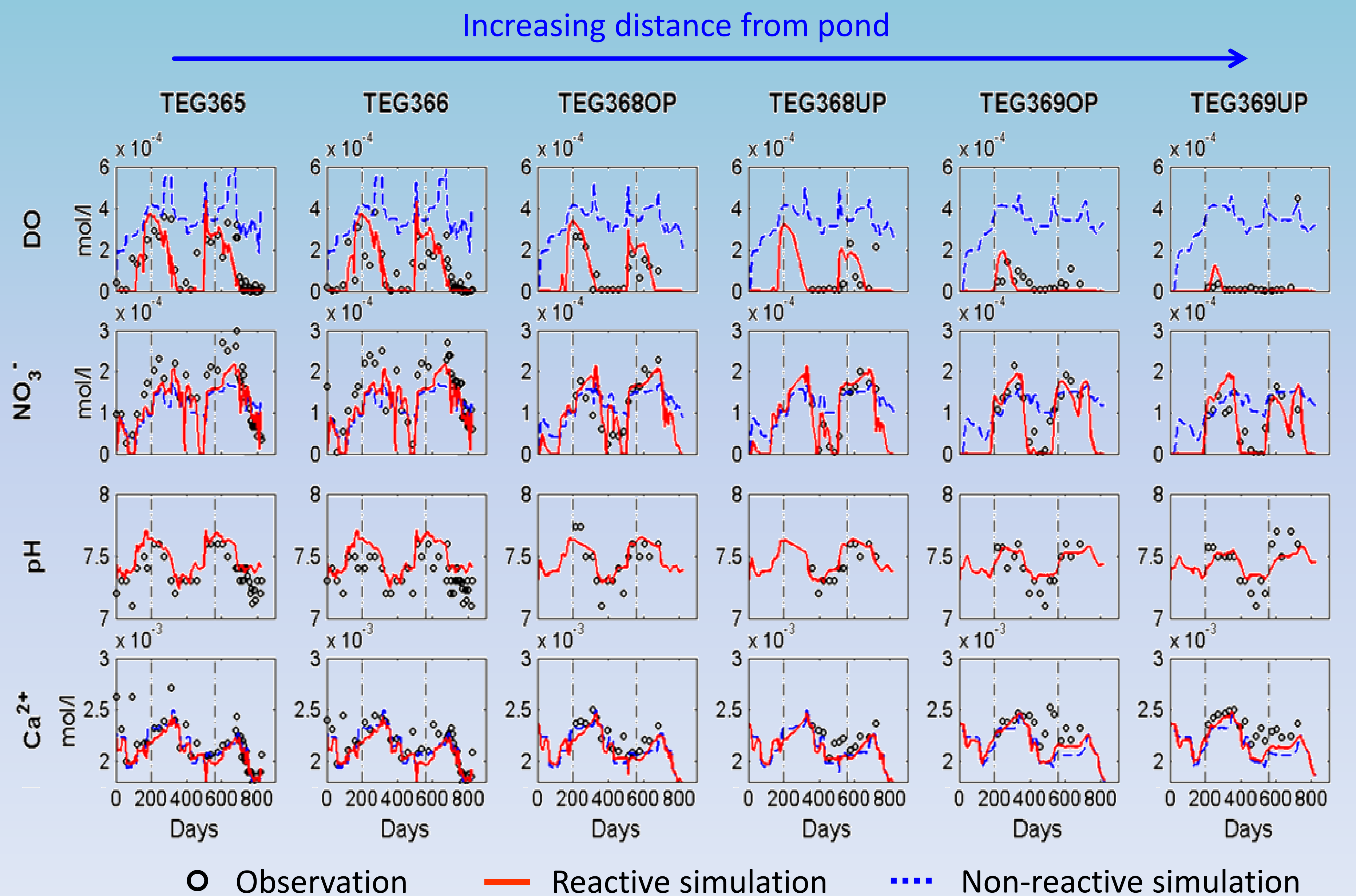
$$f_T = e^{\left(\alpha + \beta T \left((1 - 0.5 \frac{T}{T_{opt}}) \right) \right)}$$



Empirical formulation for decomposition of NOM (forest litter) found by O' Connell, (1990)

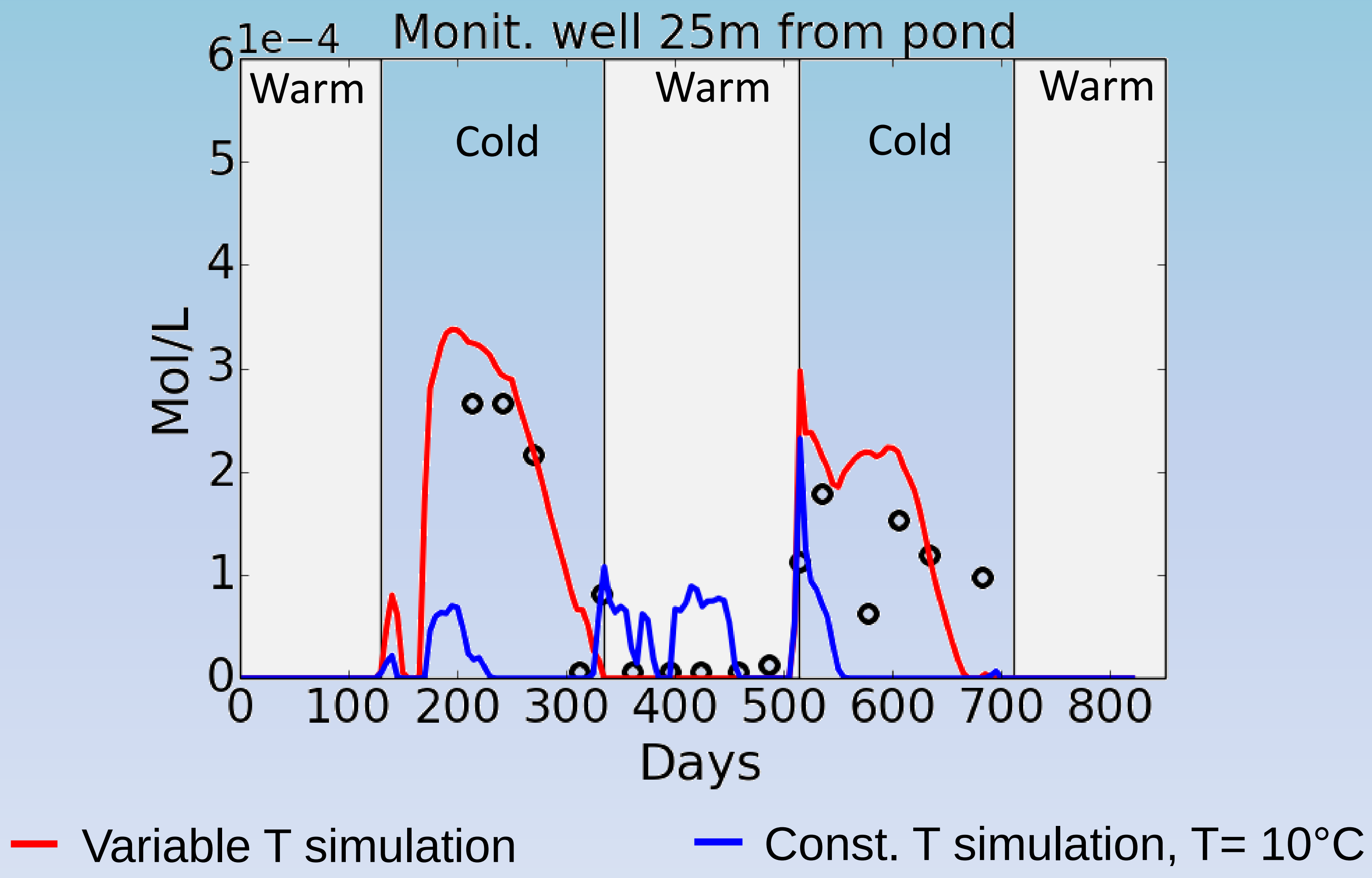
Later applied in soil respiration studies by Kirschbaum (1995, 2000)

Results for O_2, Nitrate, pH and Ca^{2+}



Constant vs. variable temperature simulation

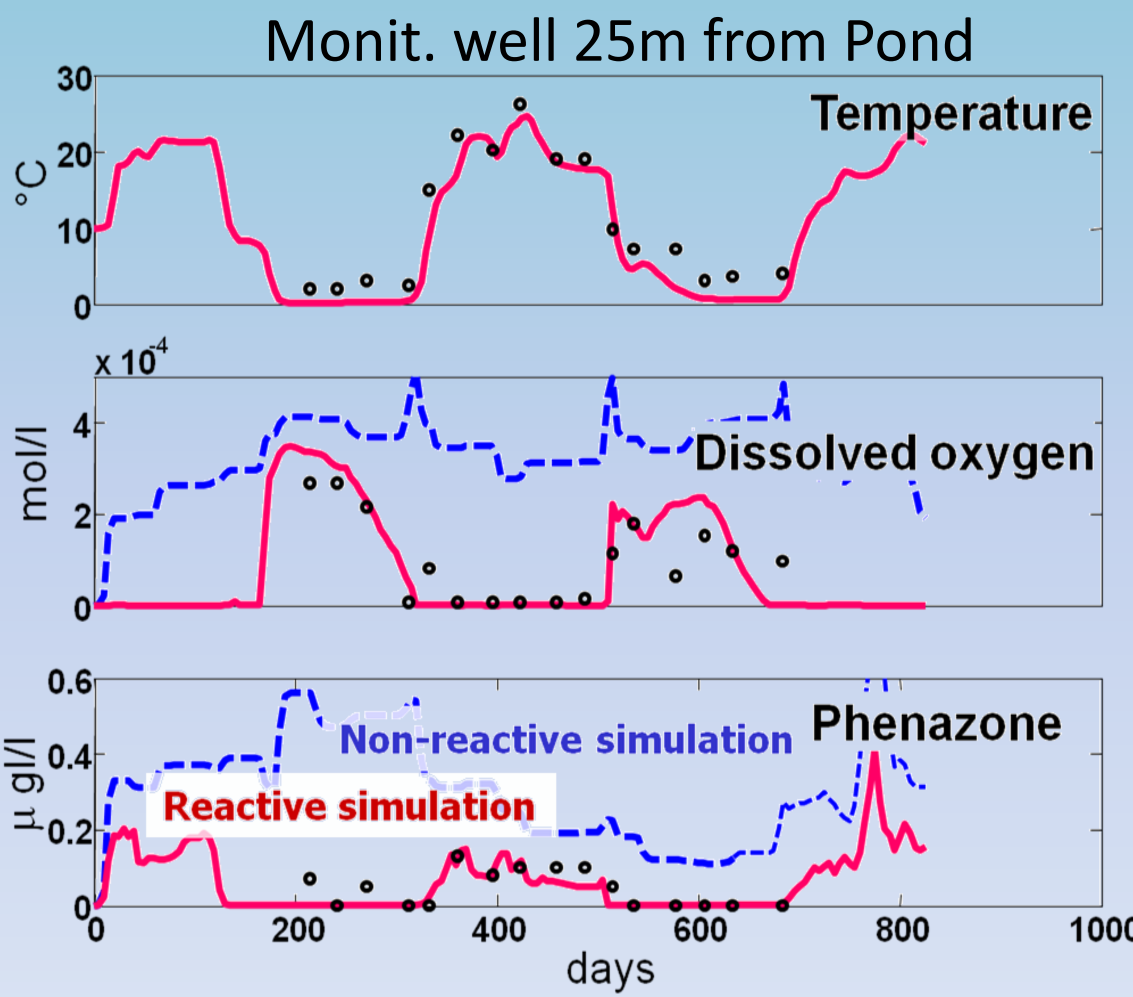
Oxygen



- Constant temperature simulations cannot reproduce the redox dynamics

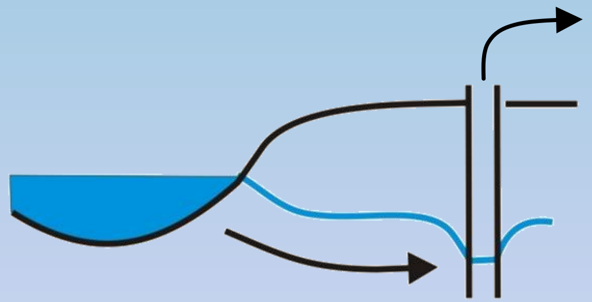
Pharmaceutical residue *phenazone* (analgesic)

Biodegradation only under oxic conditions



- Redox-effect on the phenazone degradation rate was more important here than the direct temperature effect

Riverbank filtration



Modelling temperature dependent redox zonation during river bank filtration

The Rhine case

Laxman Sharma, Janek Greskowiak, Chittaranjan Ray, Paul Eckert, Henning Prommer

(Sharma et al., 2012, J Hydrol.)

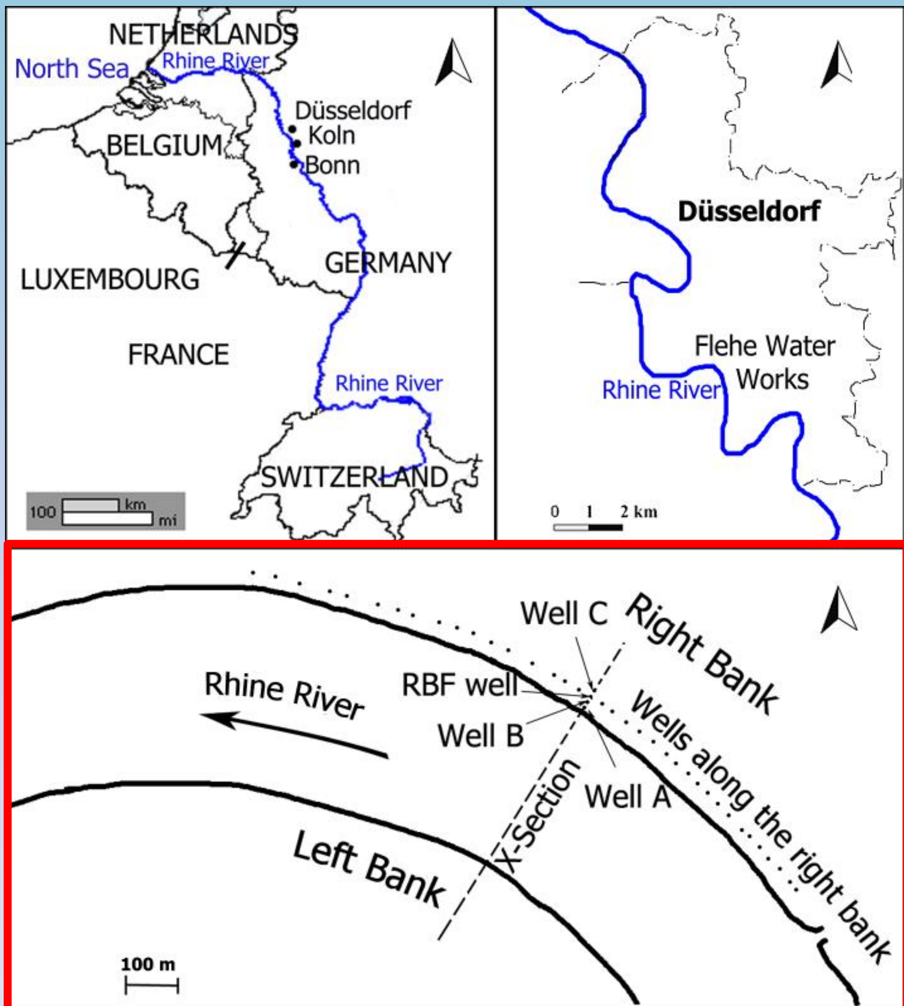
The Lake Tegel case

Aline Henzler, Janek Greskowiak, Gudrun Massmann

(Henzler et al., to be submitted to J Hydrol.)

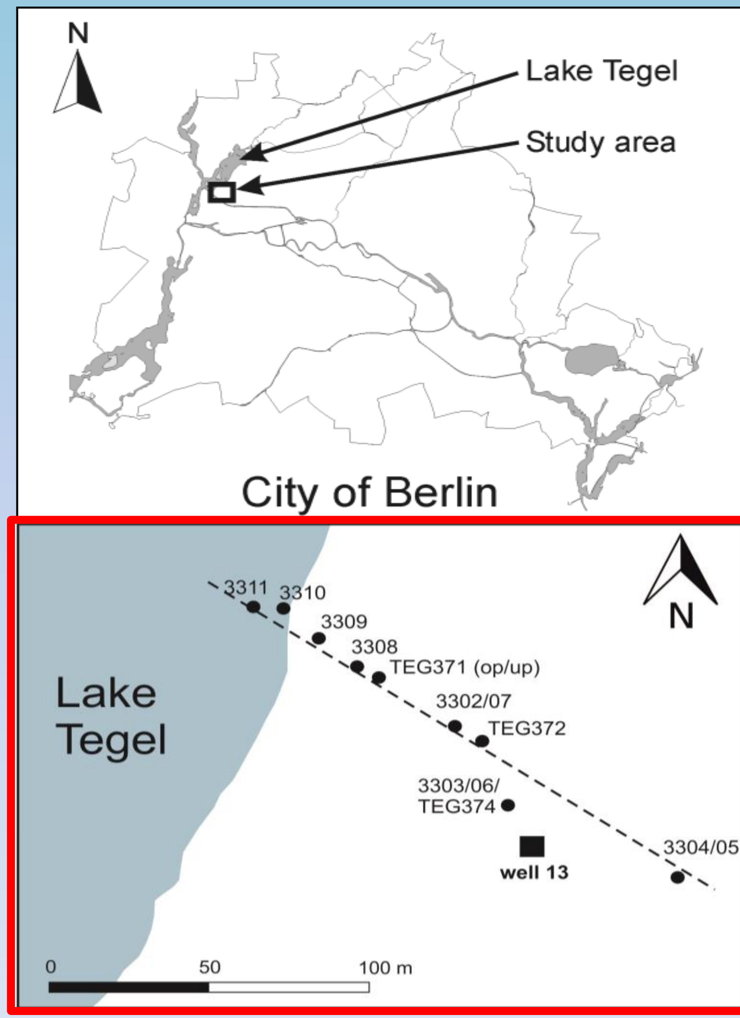
Field sites

RBF River Rhine



Travel time: 10 days - 2 months

RBF Lake Tegel



Travel time: 3 - 4 months

Model approaches

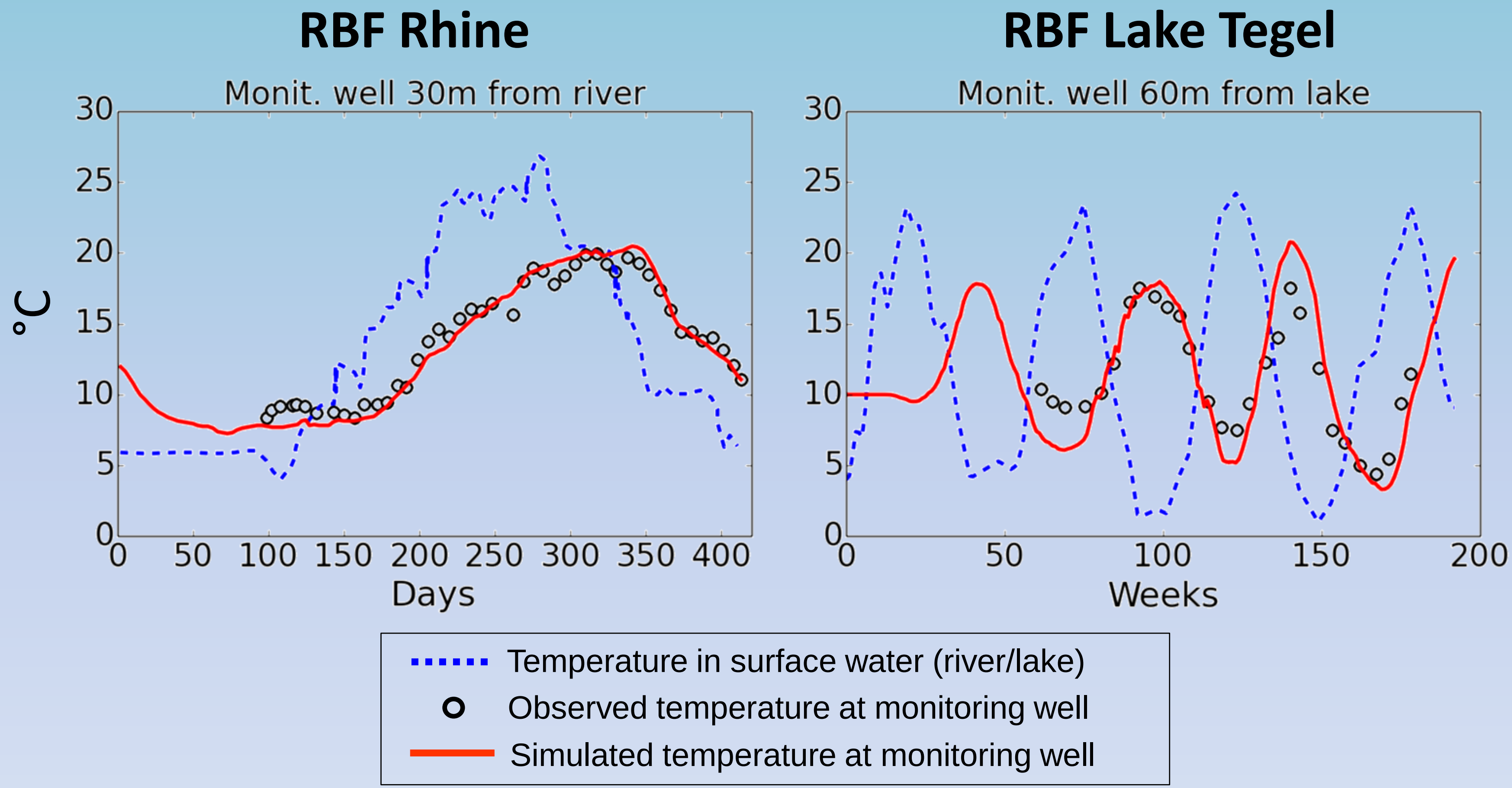
RBF River Rhine

- 2D cross-section model
- Conservative Transport:
  - Chloride, temperature
- Reactive Transport
  - All major ions, O_2, pH
  - DOC and SOM
  - Temperature-dependent redox-reaction rates

RBF Lake Tegel

- 2D cross-section model
- Conservative Transport:
  - Stable isotopes, temperature
- Reactive Transport
  - O_2, nitrate, Mn^{2+},Fe^{2+}
  - SOM
  - Temperature-dependent redox-reaction rates

Non-reactive simulation: Temperature



- Retardation factor R for temperature: 2.1 - 2.2 (compared to measured water isotopes or chloride)

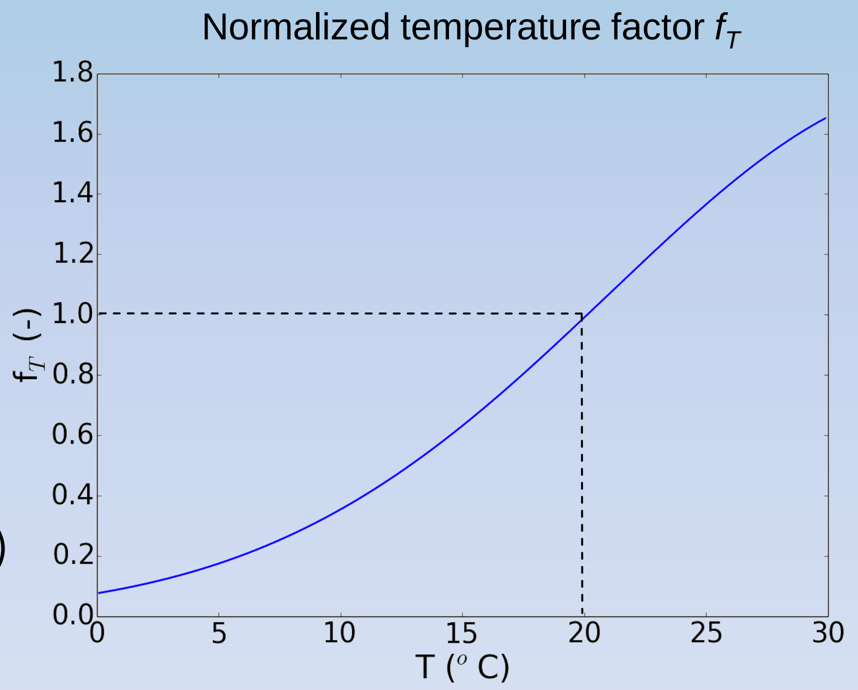
Temperature dependence of redox reaction rate

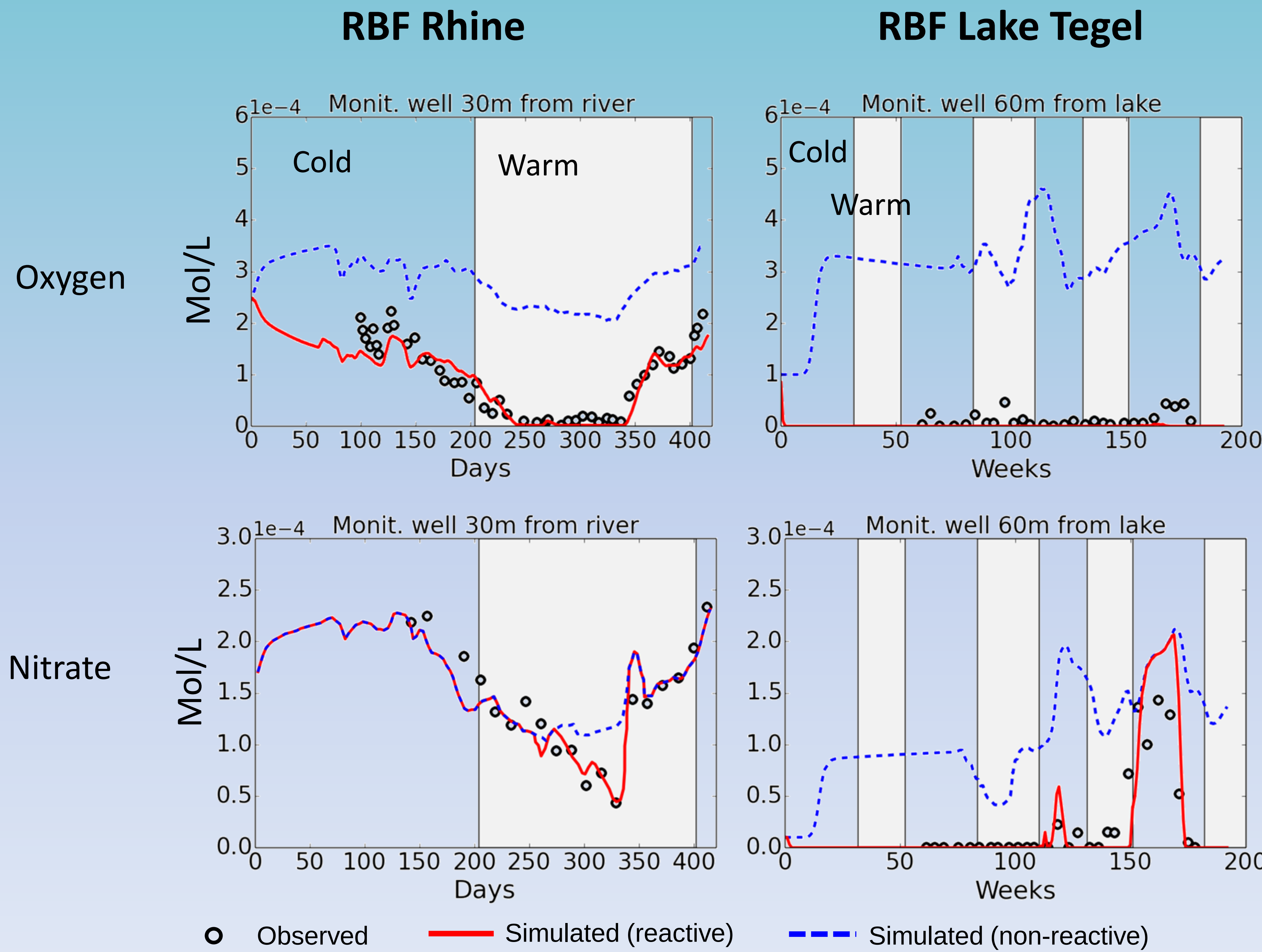
- Identical temperature dependence as in the infiltration pond model

$$f_T = e^{\left(\alpha + \beta T\left((1 - 0.5\frac{T}{T_{opt}})\right)\right)}$$

α	=	-1.5	(-3.5 – -1.2)
β	=	0.18	(0.15 – 0.26)
T_{opt}	=	35.0	(33.1°C – 36.9°C)

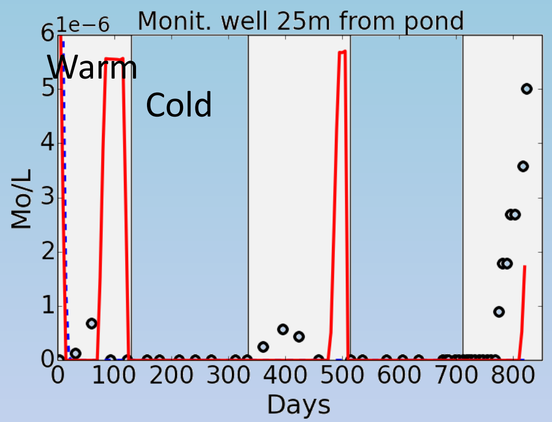
(O'Connell, Kirschbaum)




RBF Rhine
RBF Lake Tegel
Oxygen
Nitrate
Mol/L
1e−4
Monit. well 30m from river
Monit. well 60m from lake
Cold
Warm
Days
Weeks
Observed
Simulated (reactive)
Simulated (non-reactive)

Reactive simulation: Manganese

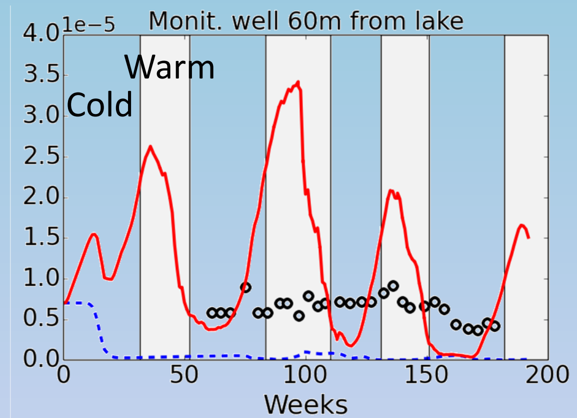
Infiltration pond

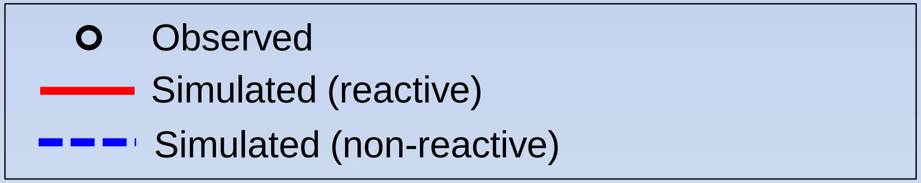


RBF Rhine

No manganese reduction occuring

RBF Lake Tegel





- Manganese involving reactions and effect of temperature not fully resolved

Some concluding remarks

- Water quality changes during MAR result from complex interplay of highly dynamic physical, geochemical and microbiological processes
- So far, reactive transport modeling was mainly used to improve the integrated processes understanding as processes are not regarded isolated from each other
- “*Quantitative models force the investigator to validate or invalidate ideas by putting real numbers into an often vague hypothesis, …* “ (Lichtner et al., 1996)
- Reactive transport modelling becomes increasingly important in predicting long-term sustainability of MAR

  (e.g., Antoniou, E.A., P. J. Stuyfzand, B. M. van Breukelen, 2013, Applied Geochemistry)

Thank you for your attention !