Natural attenuation at petroleum hydrocarbon contaminated sites

Anita Peter [1,2], Benedict Miles [2], Georg Teutsch [3]

[1] *Institute for Geosciences, University of Kiel, Germany*
[2] *formerly at Tübingen Groundwater Reserach Institute, Germany*
[3] *Helmholtz Centre for Environmental Research - UFZ GmbH, Germany*

Summer School on Contaminated Soils, Paris, 22.06.2012

Natural Attenuation: Definitions

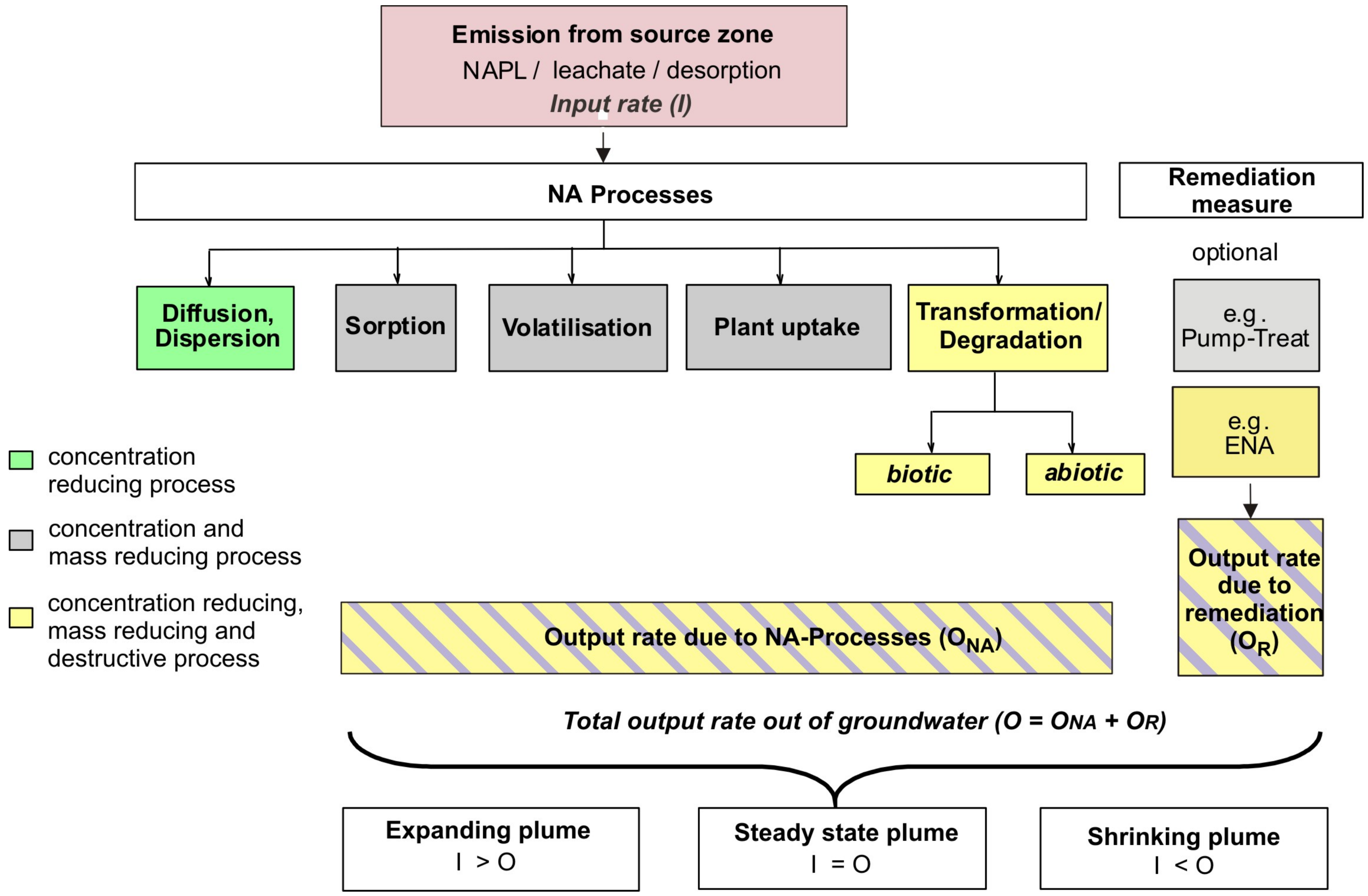
Definition Natural Attenuation (NA), US EPA (1999)

“NA processes (...) include a variety of physical, chemical, or biological processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants.”

Definition Monitored Natural Attenuation (MNA), US EPA (1999)

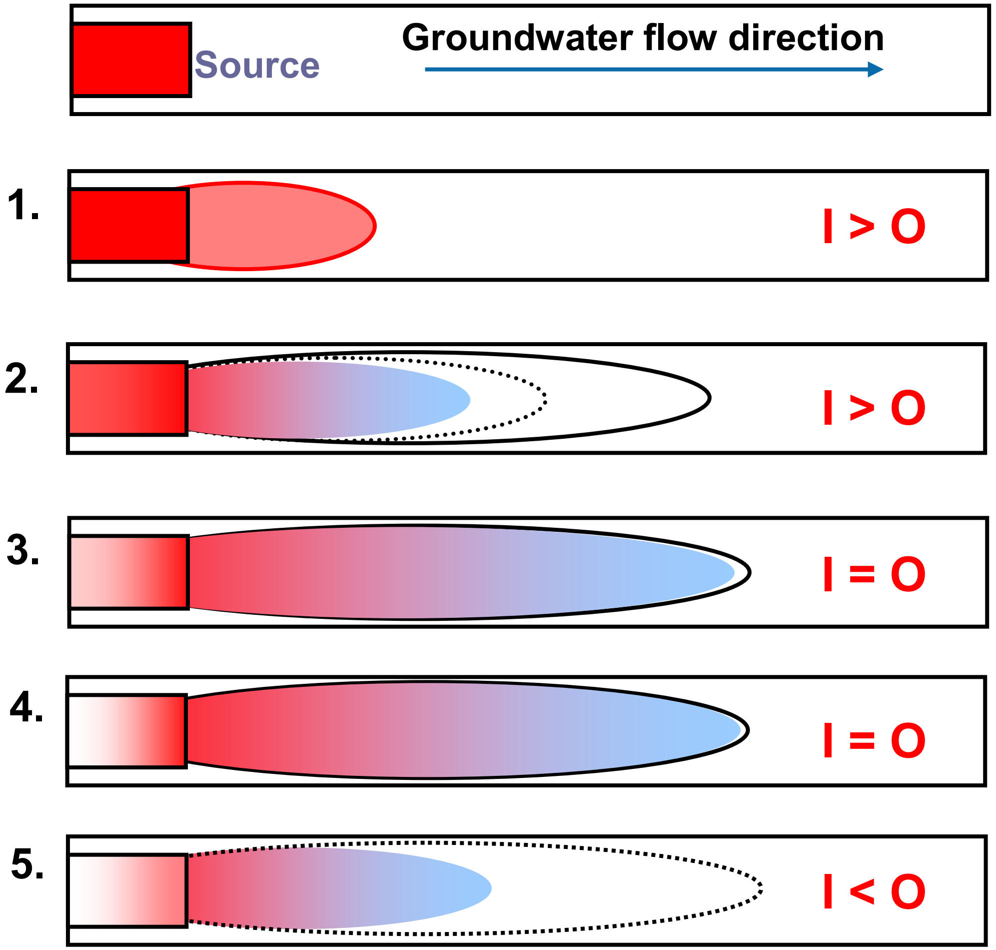
„Monitored natural attenuation (…) refers to the reliance on natural attenuation processes to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods.“

Natural Attenuation processes



Peter et al., (2011), adapted from Grandel & Dahmke (2008)

Temporal development of a plume



1. Beginning of contaminant release: contaminant dissolution and spreading in groundwater
2. Initiation of natural attenuation processes: decelerated contaminant spreading
3. Attaining steady-state: input rate equals output rate
4. Steady-state plume continues
5. Plume shrinking due to source alteration

Teutsch & Rügner (1999)

Prerequisites for Monitored Natural Attenuation

Two essential challenges exist for the implementation of ***Natural Attenuation (NA)***:

(1) **Proof** that NA is taking place, i.e. that it is efficient to reduce contaminant concentrations / mass in the groundwater

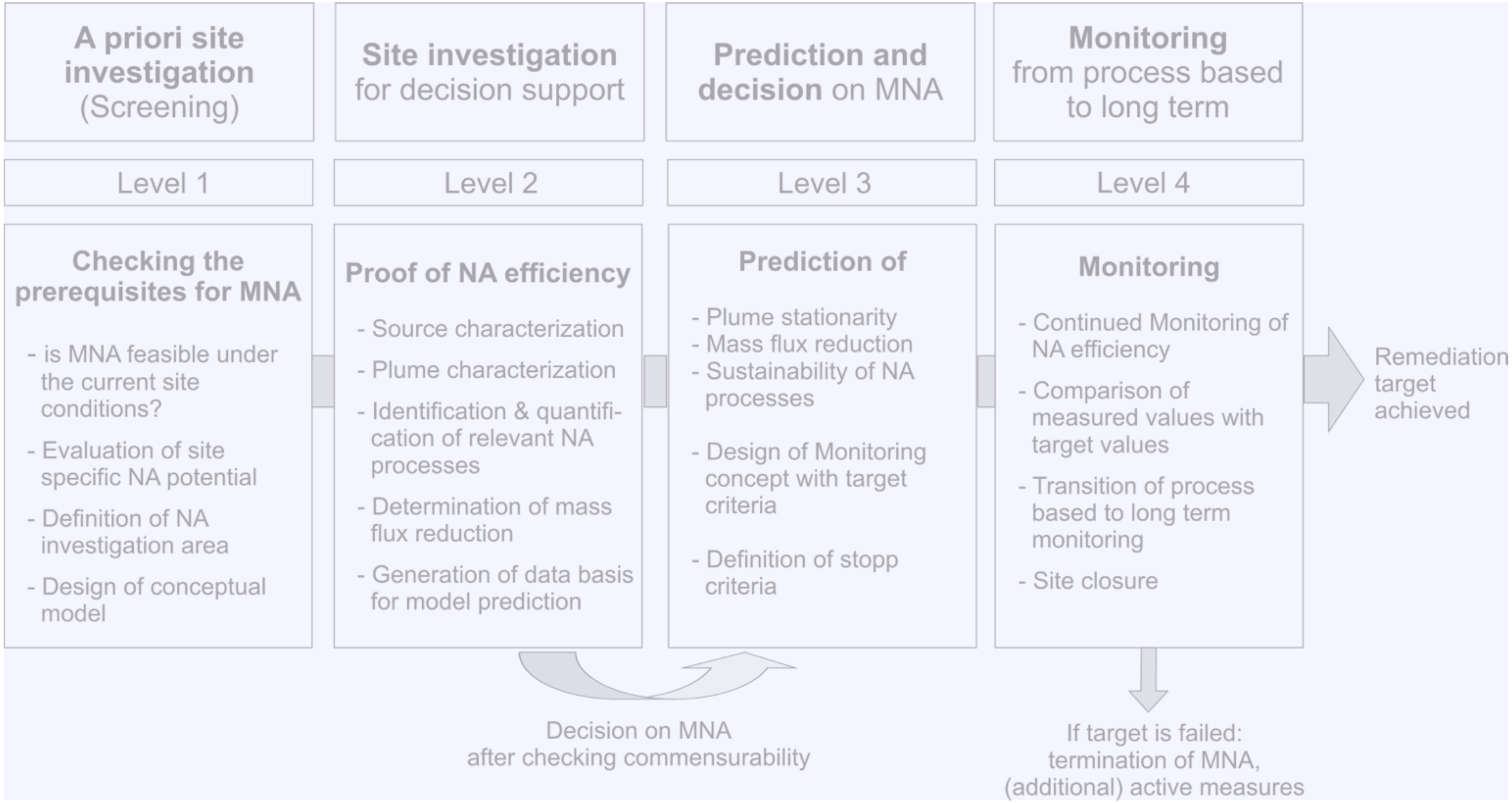
(2) **Prediction** that NA will be efficient in future

↓

(3) **Monitoring** of NA processes

Stepwise approach to investigate NA and to implement MNA according to the German Policy Document on MNA

Christian-Albrechts-Universität zu Kiel

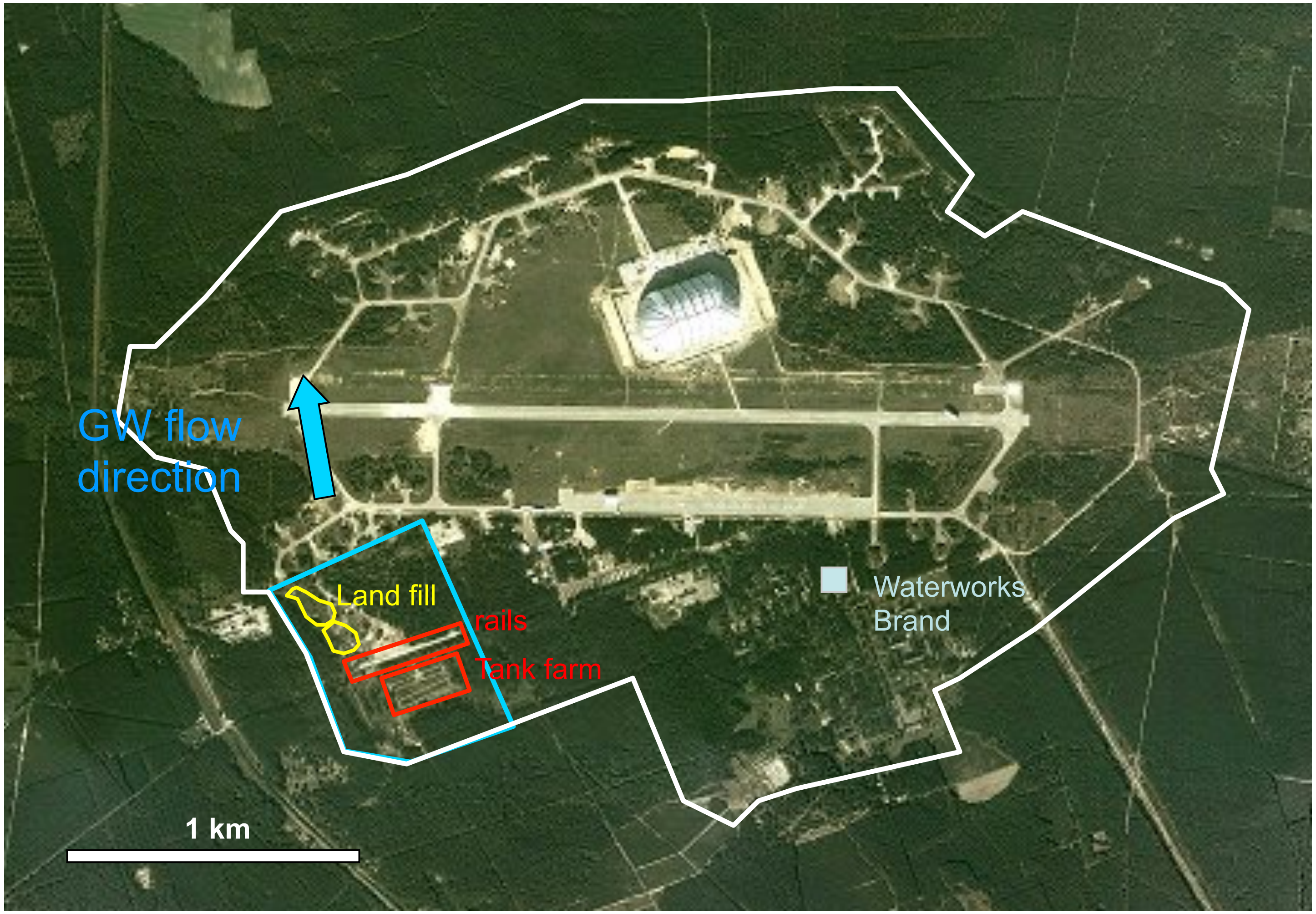


Adapted from Grandel & Dahmke (2008)

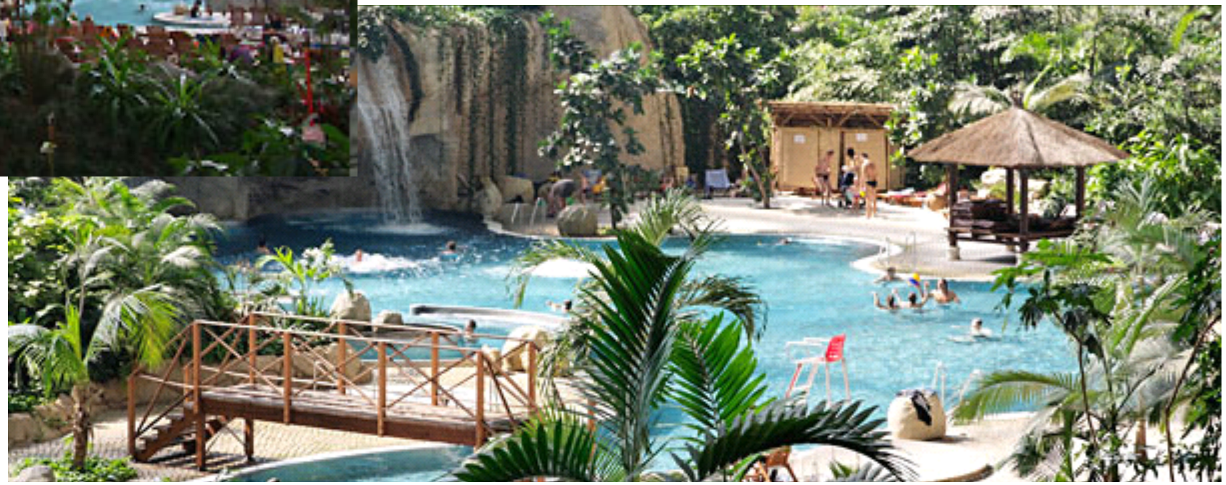
Case Study: Former Military Air Field (1939-1992) Brand / Germany

C | A | U

Christian-Albrechts-Universität zu Kiel



Airship Factory Building „CargoLifter“(1998-2002) Nowadays „Tropical Islands“ (since 2004)



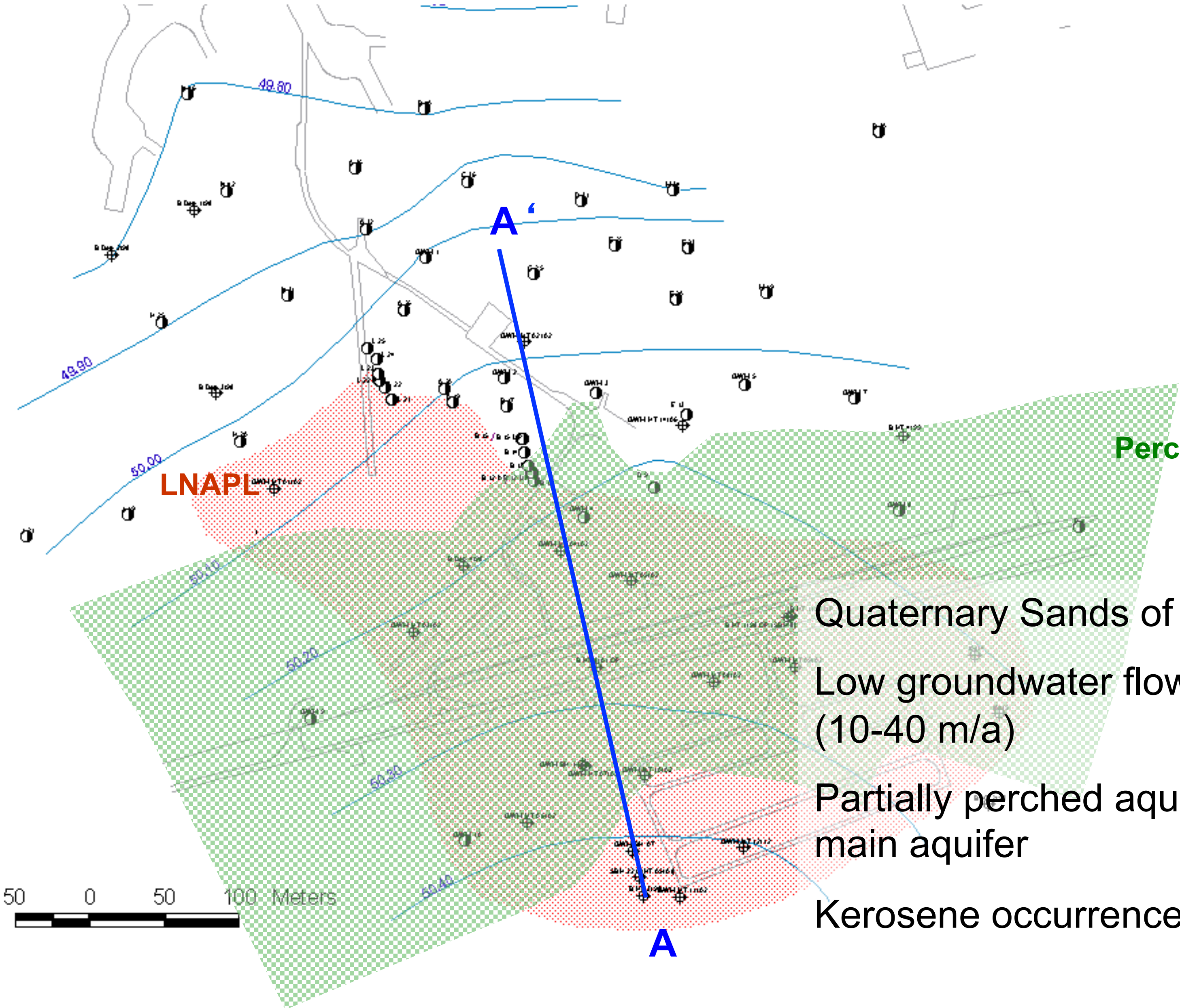
Air Field Brand: Former Main Tank Farm

Christian-Albrechts-Universität zu Kiel

Area North of Tank Farm

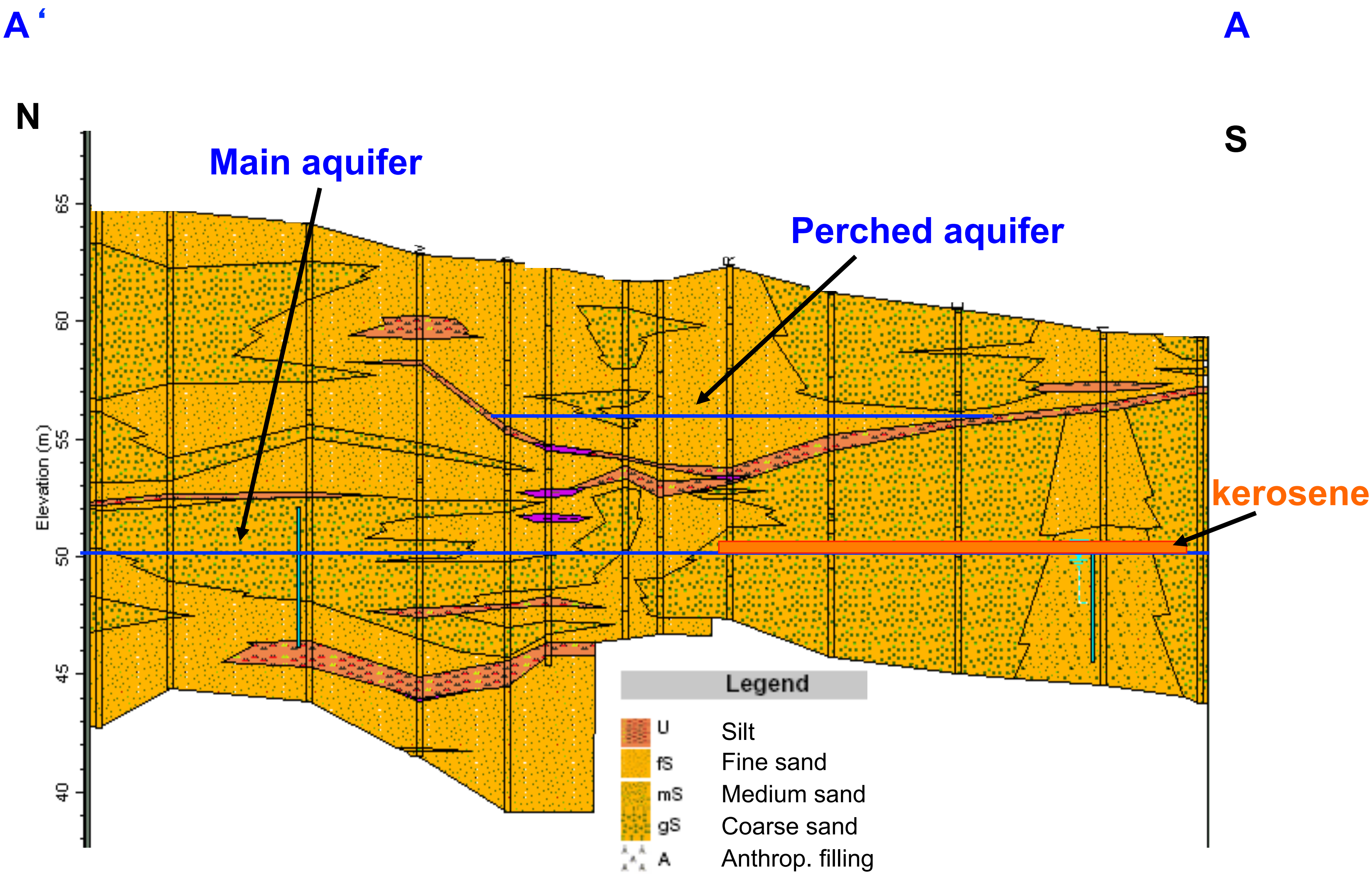
Former Tank Farm at Military Air Field Brand: Geological and contamination situation

Christian-Albrechts-Universität zu Kiel



- Quaternary Sands of >100m thickness
- Low groundwater flow velocities (10-40 m/a)
- Partially perched aquifer above the main aquifer
- Kerosene occurrence 120 ‘000 m²

Geological Cross Section A - A`



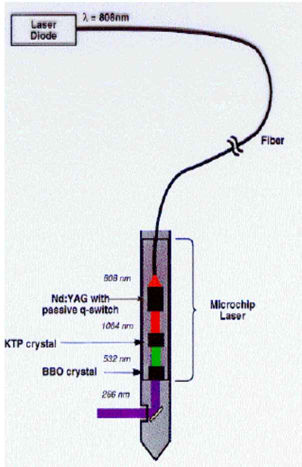
Proving Natural Attenuation

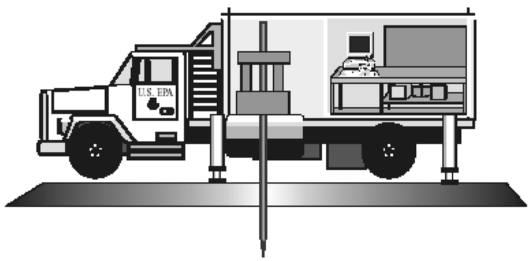
Contaminant source characterization	• Extension of the source (NAPL) and NAPL mass • Source inventory • Source emission and source lifetime
Contaminant plume characterization	• Plume length • Temporal plume development / stationarity • Mass flow rate reduction
Qualitative and quantitative evaluation of NA processes	• Data supporting qualitatively biodegradation and other NA processes • Data supporting quantitatively biodegradation and other NA processes
Prediction of NA processes	• Flow and reactive transport modelling

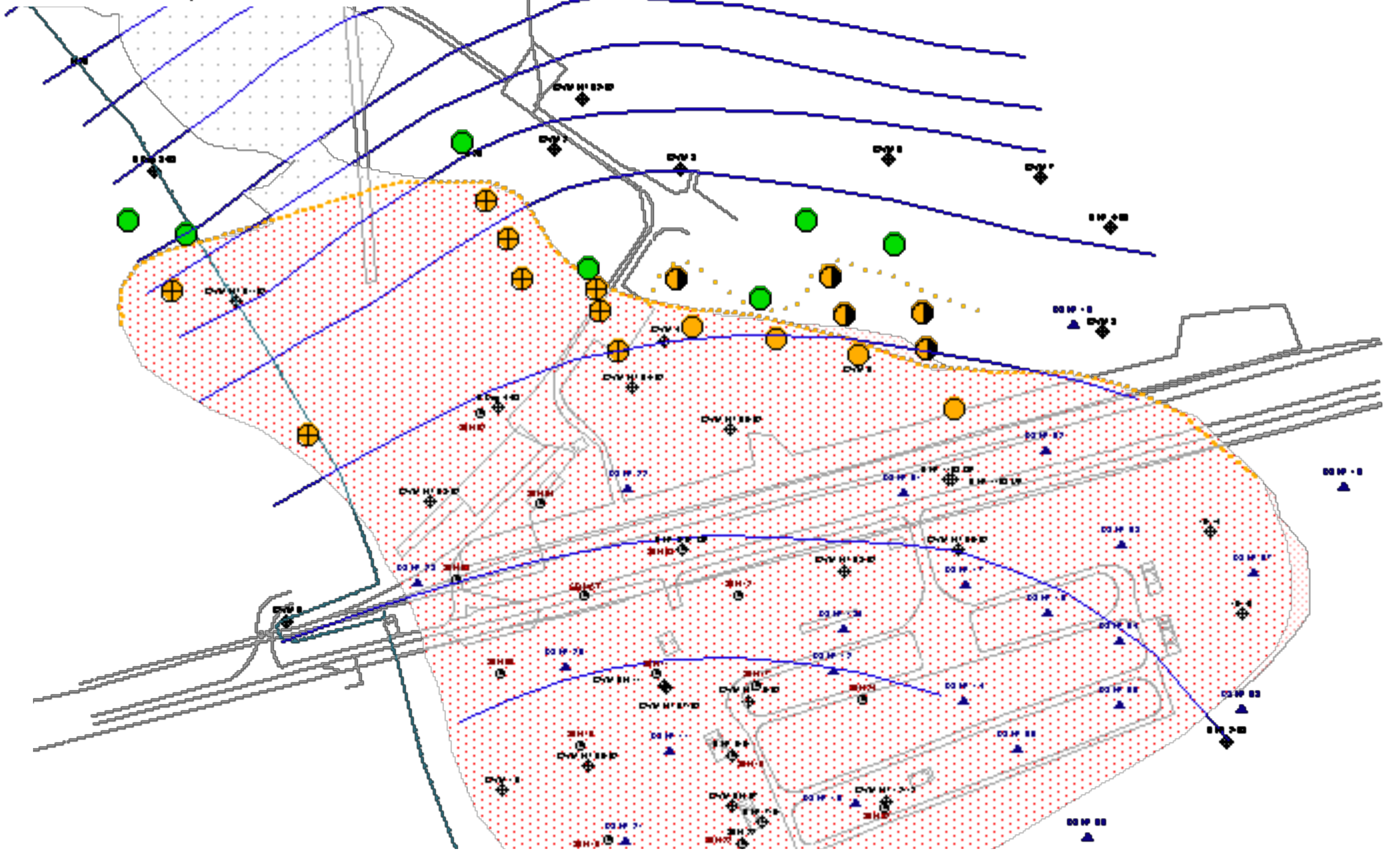
Source zone characterization: Source extension

C A U
Christian-Albrechts-Universität zu Kiel

Adaptive application of Laser-induced Fluorescence (LIF) Measurements







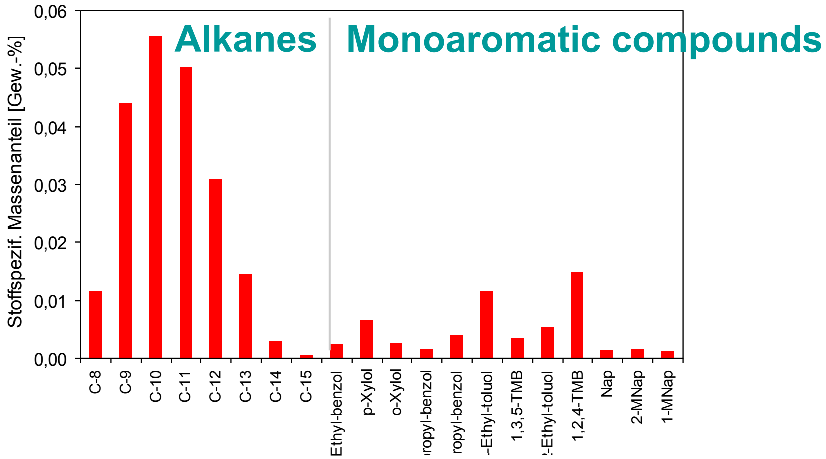
100 m

Legend

- LIF sounding (detect / non-detect)
- MIP sounding
- Multi-level monitoring well
- NAPL outline

Source zone characterization: Source composition in groundwater and soil gas phase

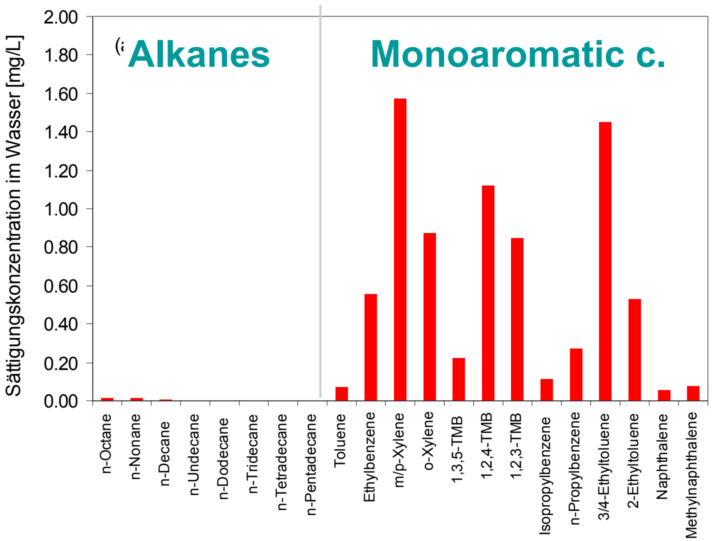
Kerosene composition



Phase transition
NAPL - water
„NAPL dissolution“

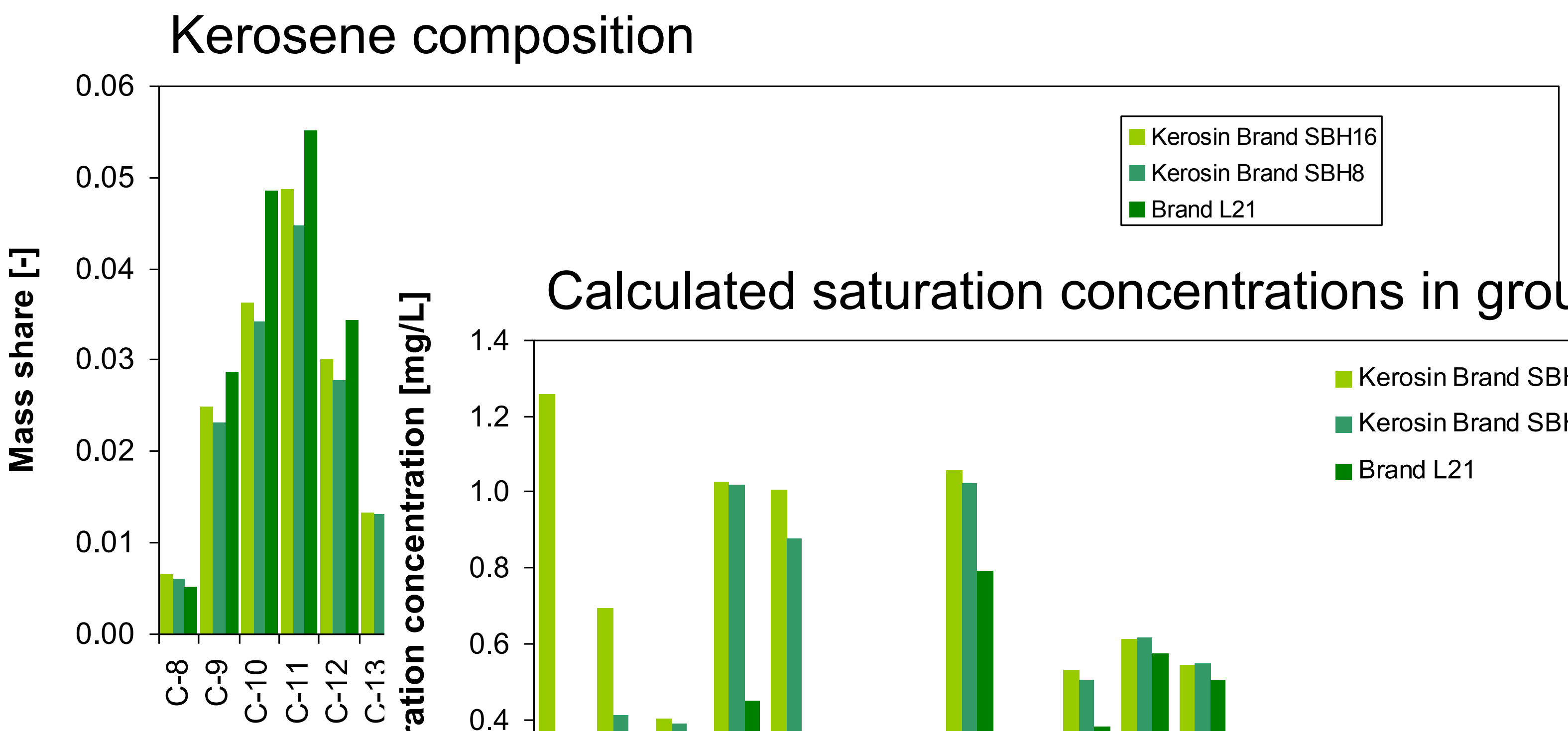
Phase transition
NAPL – gas phase
„Volatilisation“

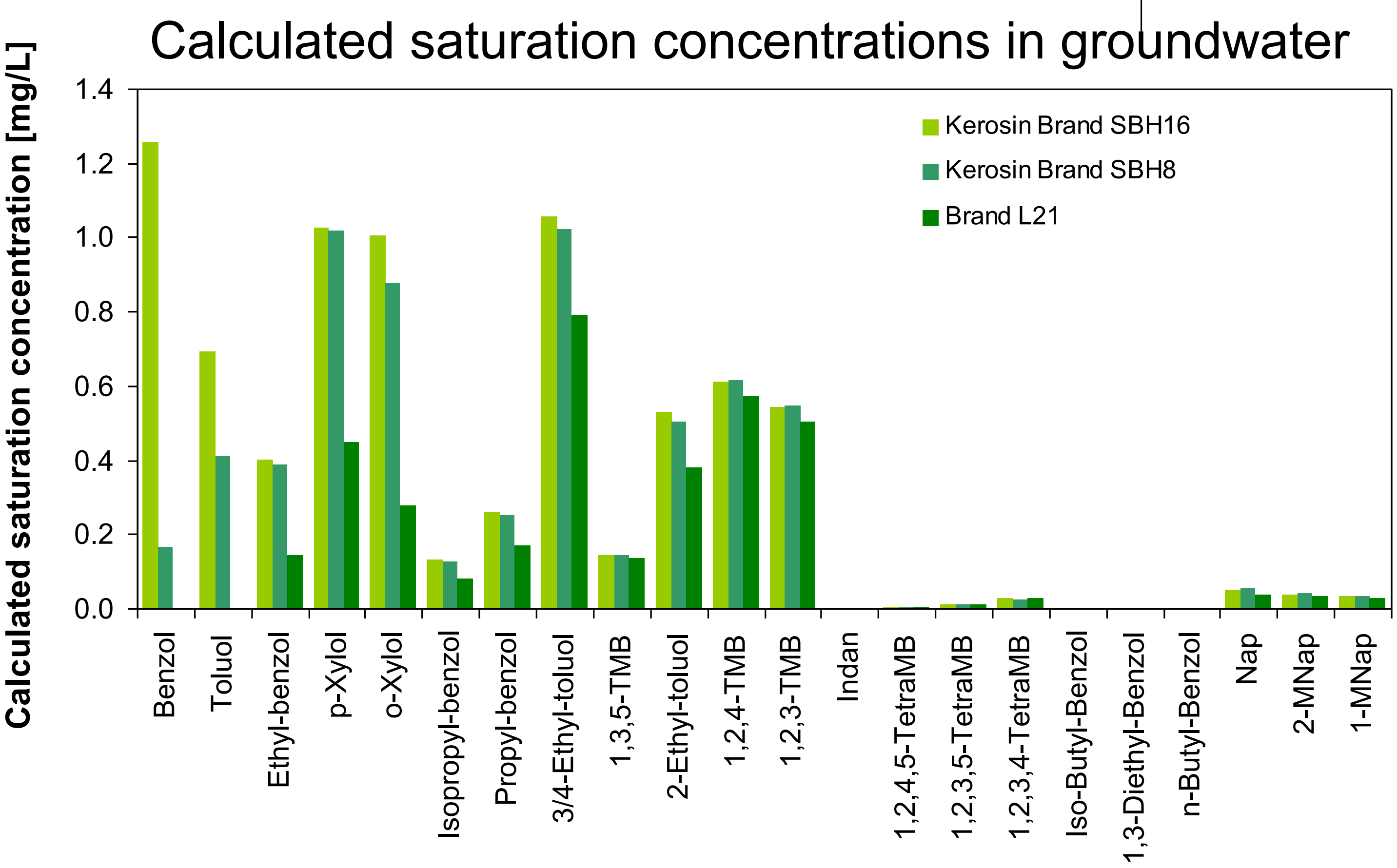
Saturation concentration in groundwater



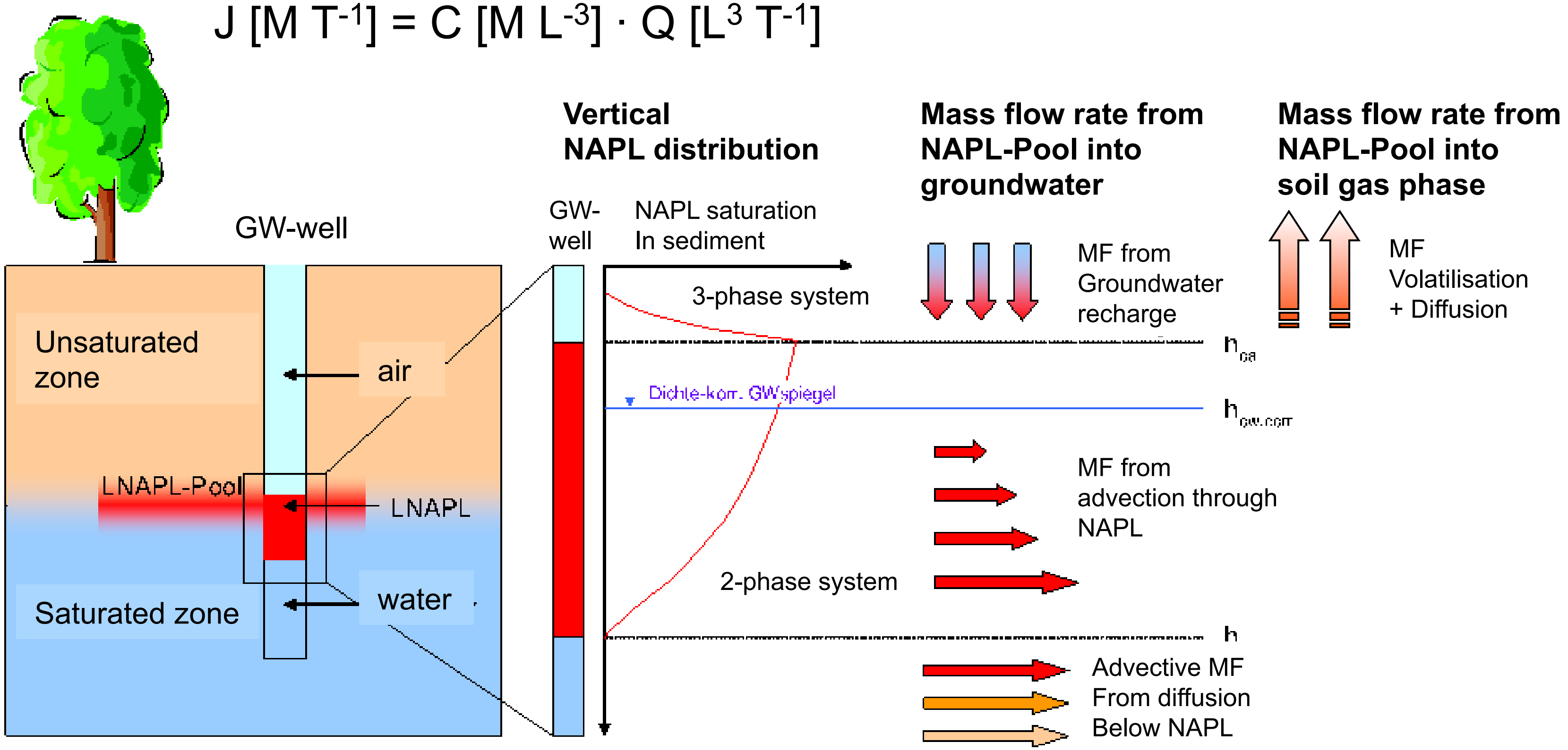
Source zone characterization: Source inventory

Christian-Albrechts-Universität zu Kiel





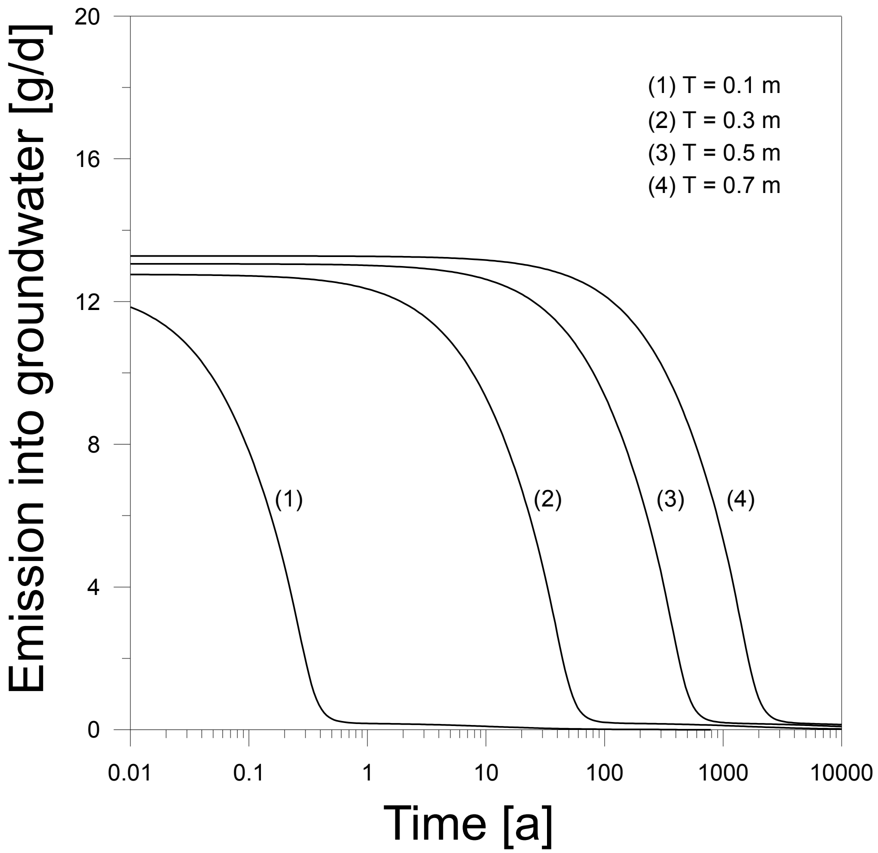
The source zone emission is the mass flow rate (mass/time) out of the NAPL into groundwater and / or soil gas phase.
Mass flow rate is the product of concentration and flow rate, i.e.
J [M T^{-1}] = C [M L^{-3}] · Q [L^3 T^{-1}]



$$J_{total,i} = J_{w,i} + J_{a,i} = C_{w,i}^{sat}\, B_P\, L_p \left(q_{gwr} + \frac{\bar{q}_{gw}}{L_p} + \sqrt{\frac{4D_{v,i}\, n_e\, q_{gw}^S}{\pi\, L_p}} + \frac{C_{a,i}^{sat}}{C_{w,i}^{sat}} \frac{\bar{D}_{ea,i}}{\left(z^{sur} - z^{P1}\right)} \right)$$

Peter et al., Env. Geol. 2008

Impact of NAPL thickness (T) on source emission into groundwater

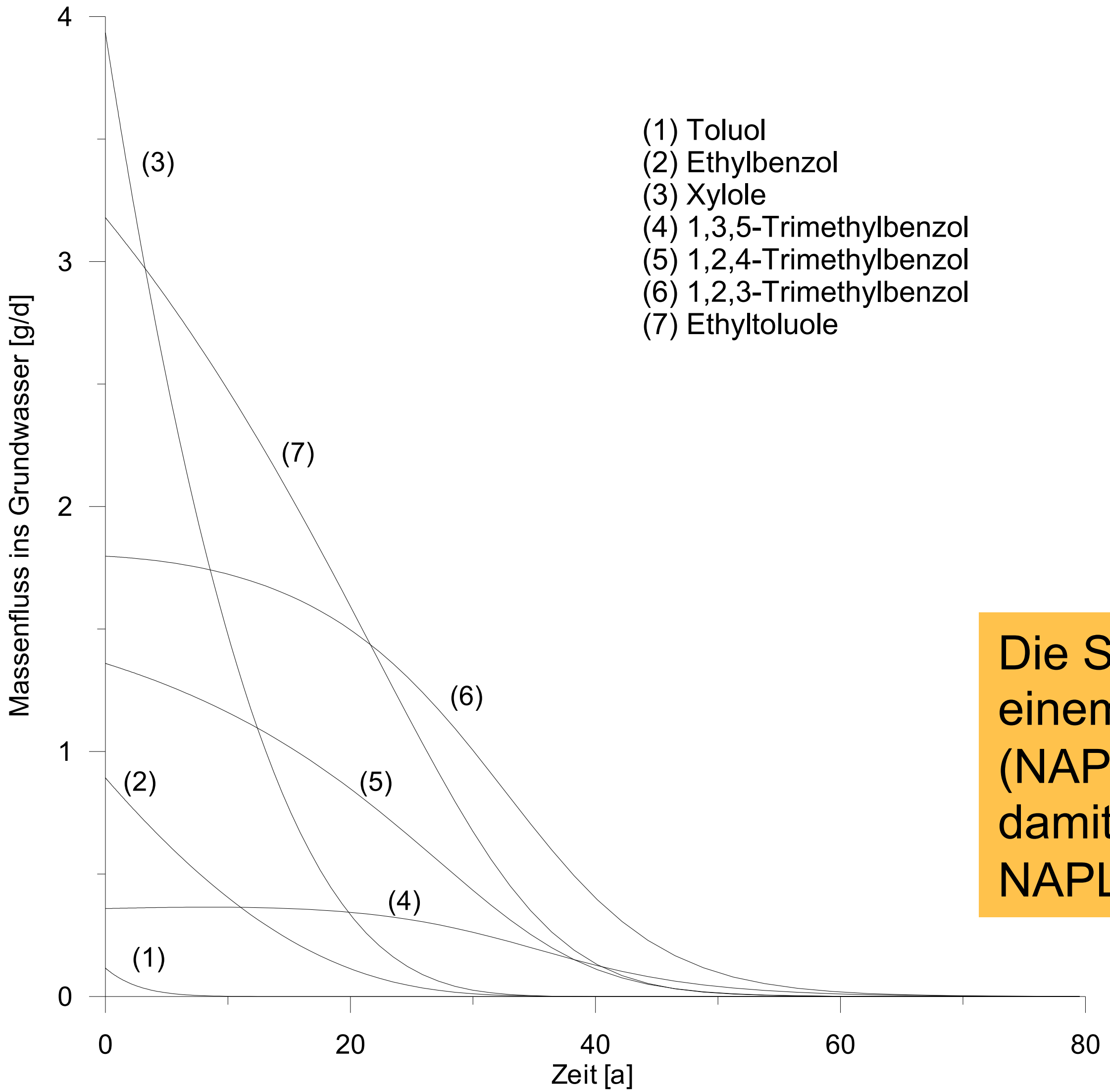


→ NAPL thickness does not have a significant influence on emission into groundwater (important for phase extractions!)

→ NAPL thickness does have a significant influence on source lifetime!

Peter et al., Env. Geol. 2008

Raoult ‘sches Gesetz zur Lösung von NAPL



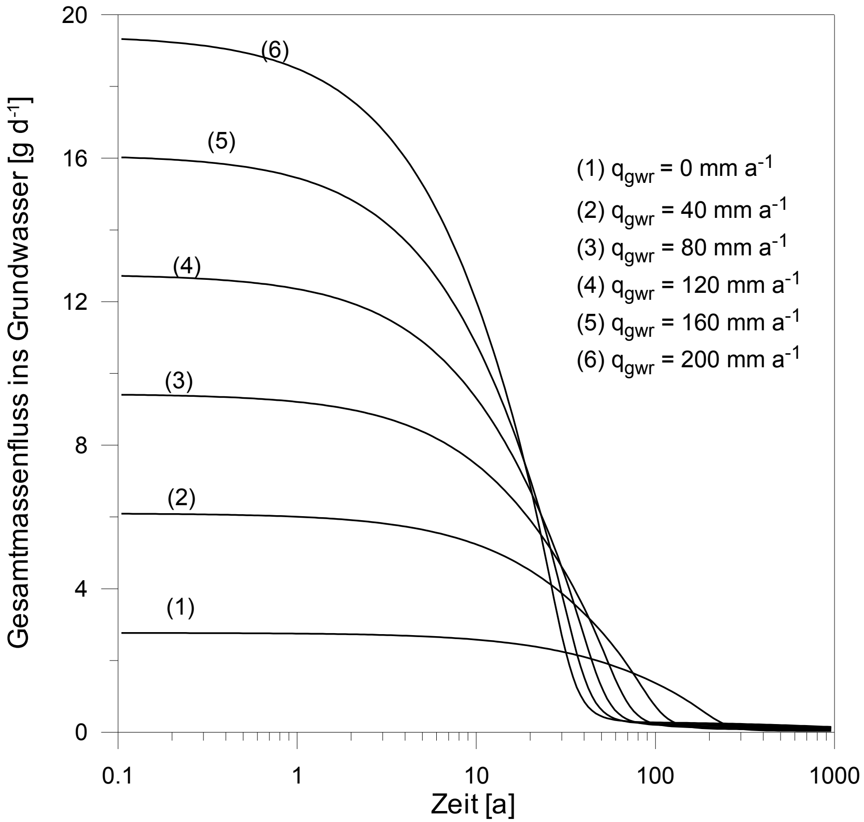
Peter et al., Env. Geol. 2008

$$C_{w,i}^{sat} = \chi_i \, \gamma_i \, S_i$$

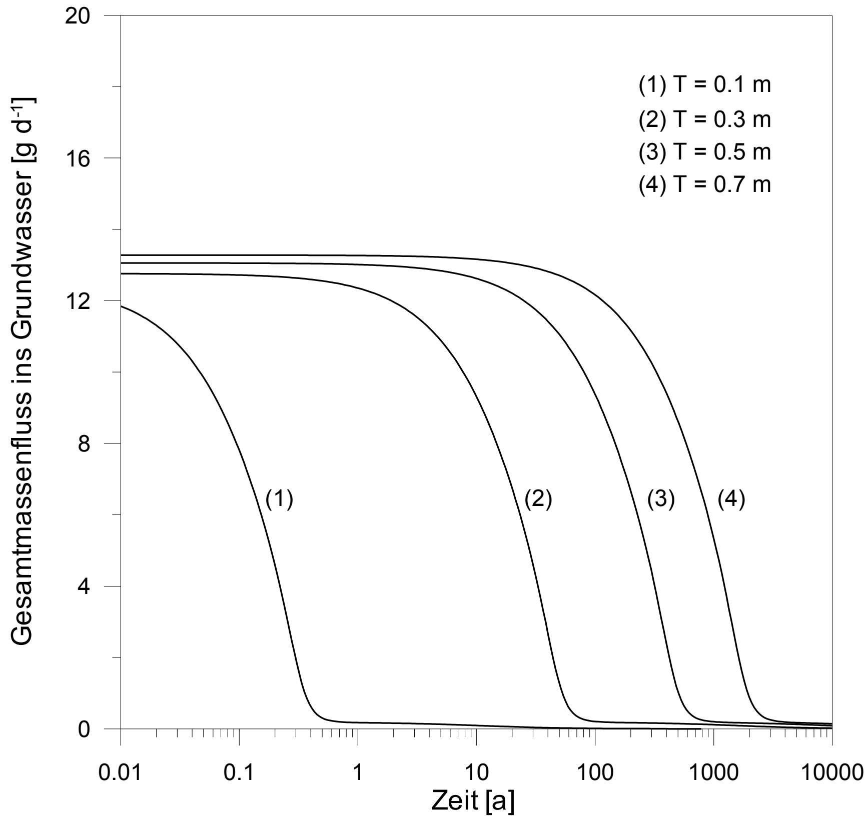
C_{wi}^{sat}:	Sättigungskonzentration des Stoffes i
x_i	Molfraktion des Stoffes i im NAPL Gemisch
γ_i	Aktivitätskoeffizient des Stoffes i
S_i	Löslichkeit des Stoffes i

Die Sättigungskonzentrationen in einem Mehrkomponentengemisch (NAPL) sind zeitabhängig und damit auch die Emission aus einem NAPL

Einfluss der Grundwasserneubildung auf die Emission



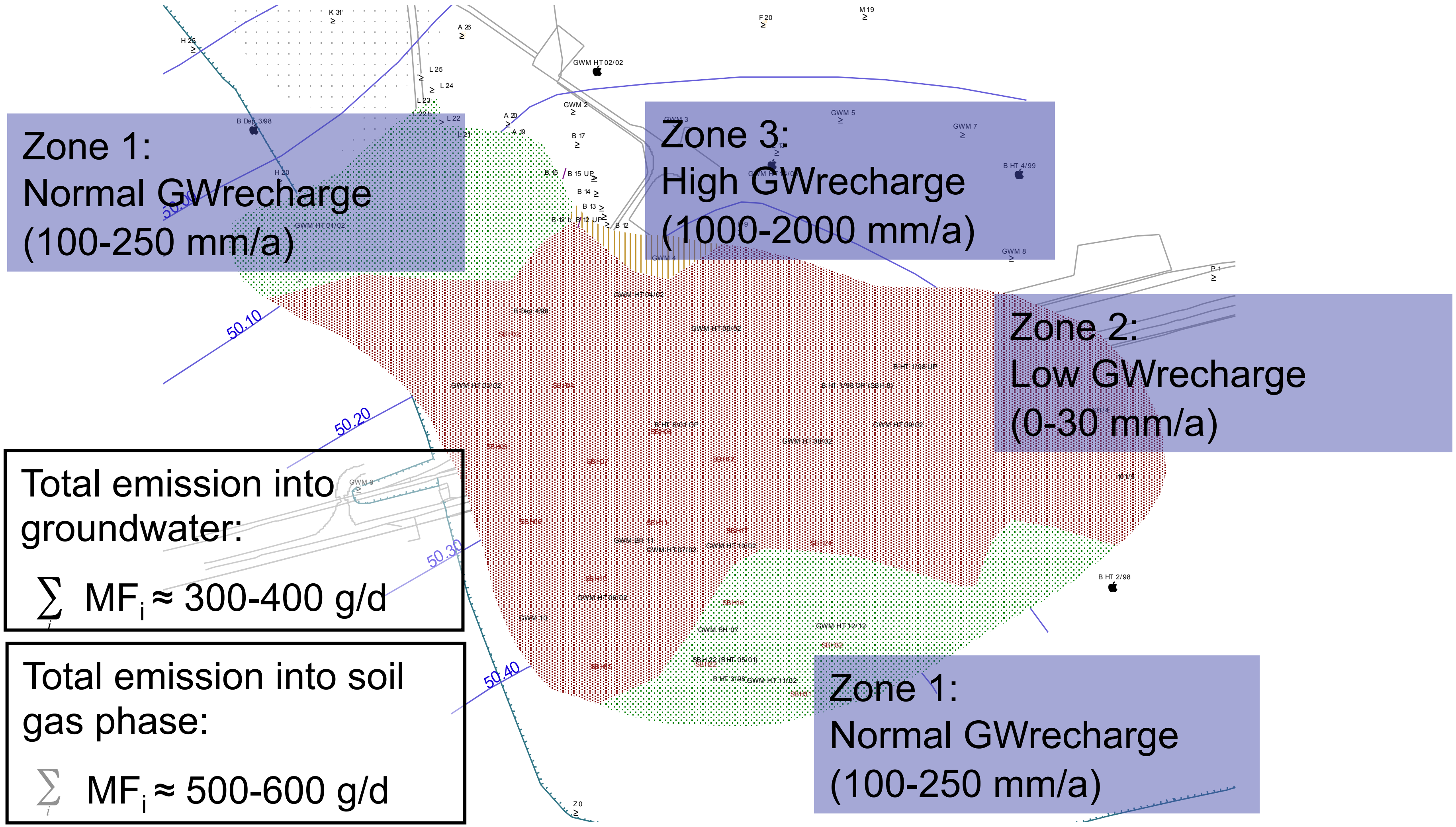
Einfluss der NAPL-Mächtigkeit auf die Emission



Peter et al., Env. Geol. 2008

Source zone characterization: Source emission
Analytical calculation of LNAPL emissioin

Source emission at Tank Farm Brand, calculated assuming different areas of groundwater recharge



Total emission into groundwater:

$\sum_i MF_i \approx 300\text{-}400$ g/d

Total emission into soil gas phase:

$\sum_i MF_i \approx 500\text{-}600$ g/d

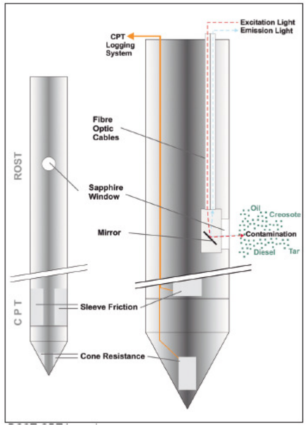
Proving Natural Attenuation

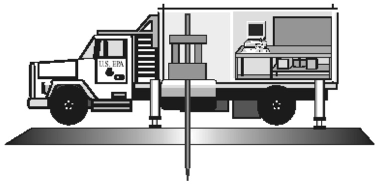
Contaminant source characterization	• Extension of the source (NAPL) and NAPL mass • Source composition / inventory • Source emission and source lifetime
Contaminant plume characterization	• **Plume length** • **Temporal plume development / stationarity** • **Mass flow rate reduction**
Qualitative and quantitative evaluation of NA processes	• Data supporting qualitatively biodegradation and other NA processes • Data supporting quantitatively biodegradation and other NA processes
Prediction of NA processes	• Flow and reactive transport modelling

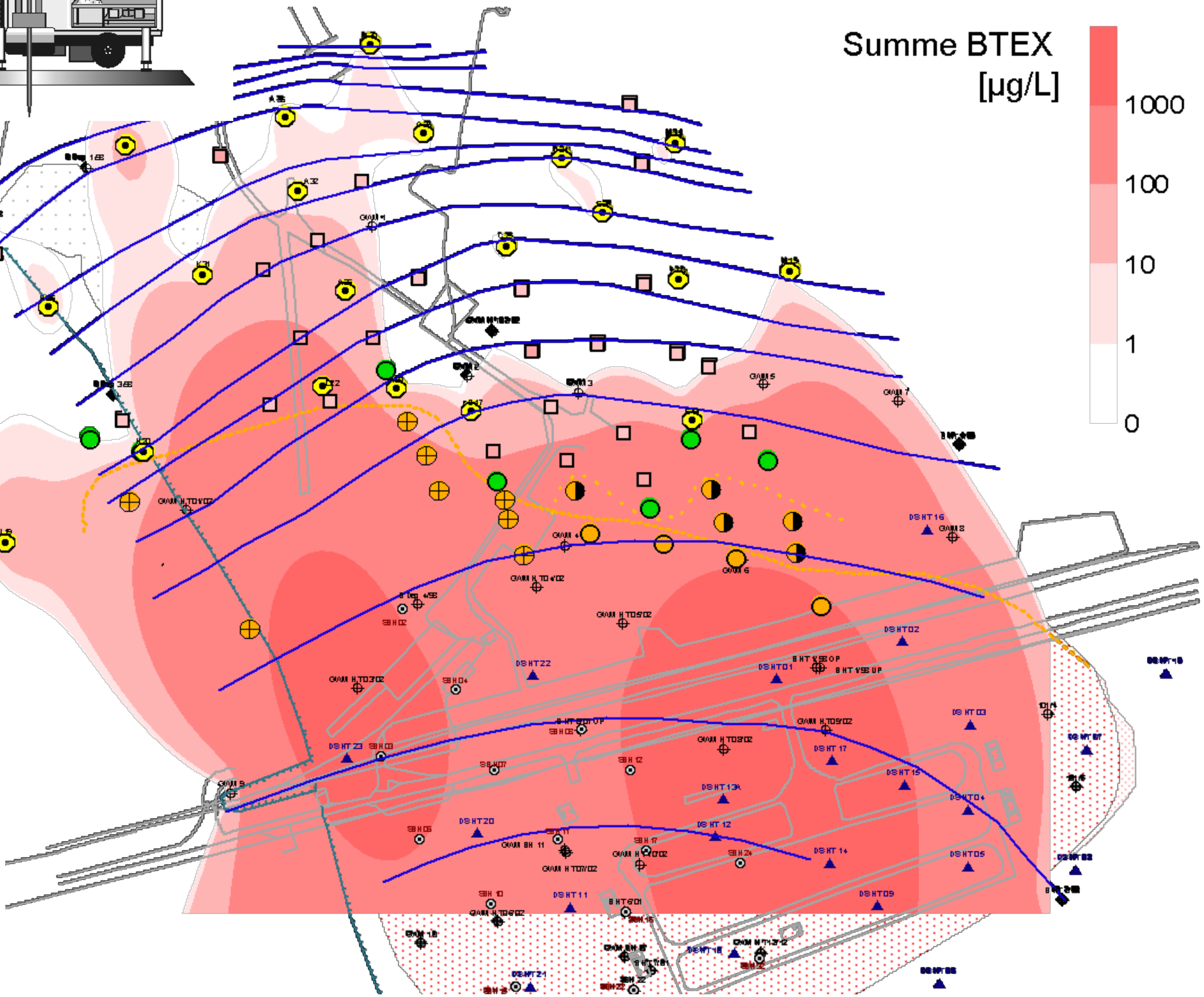
Source characterization	Source mass Source emission Source lifetime
Plume characterization	Plume length Temporal plume development Plume composition Mass flow rate reduction
Qualitative and quantitative indication of biodegradation	Electron acceptor distribution Distribution of degradation products Compound specific isotope analyses Reactive transport modelling

C | A | U
Christian-Albrechts-Universität zu Kiel

Adaptive application of Membrane Interface Probing (MIP) and GW monitoring well installation



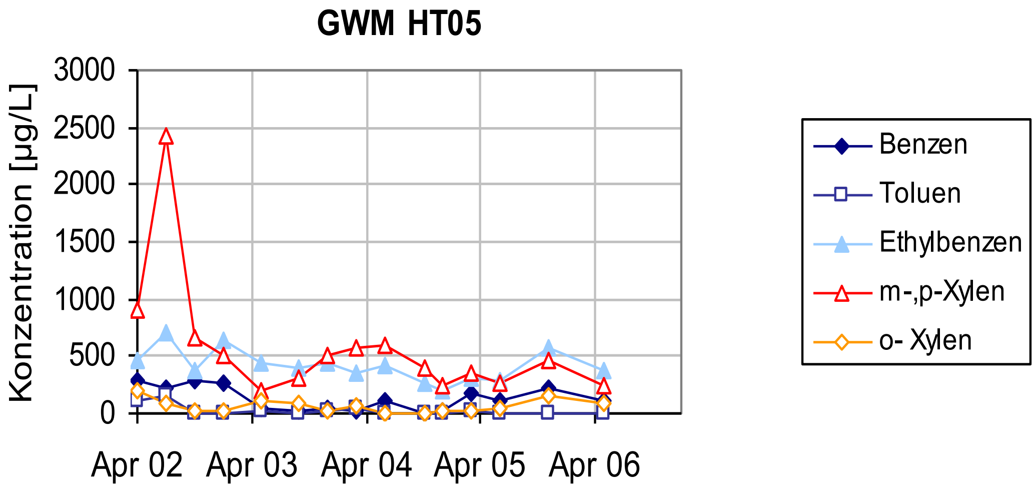


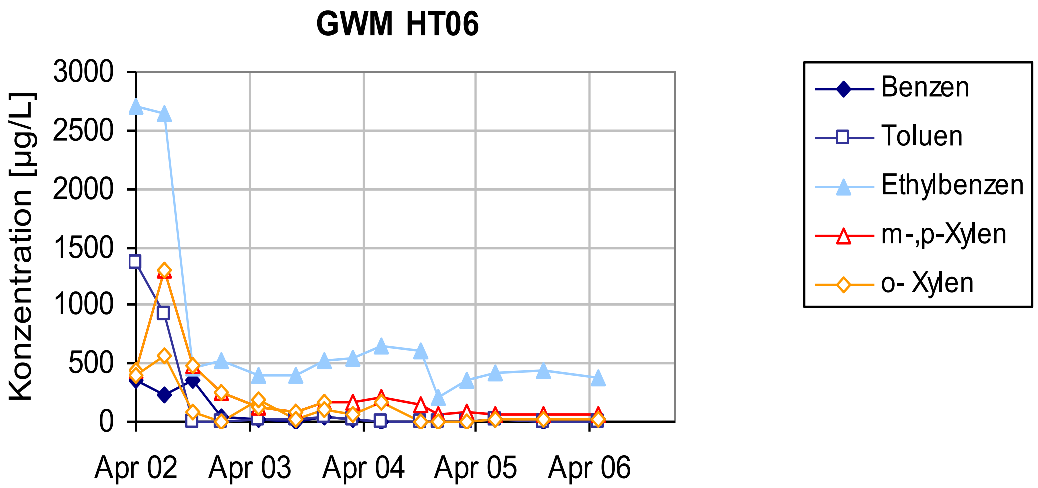


Legend

- LIF sounding (detect / non-detect)
- MIP sounding
- Multi-level monitoring well
- NAPL outline

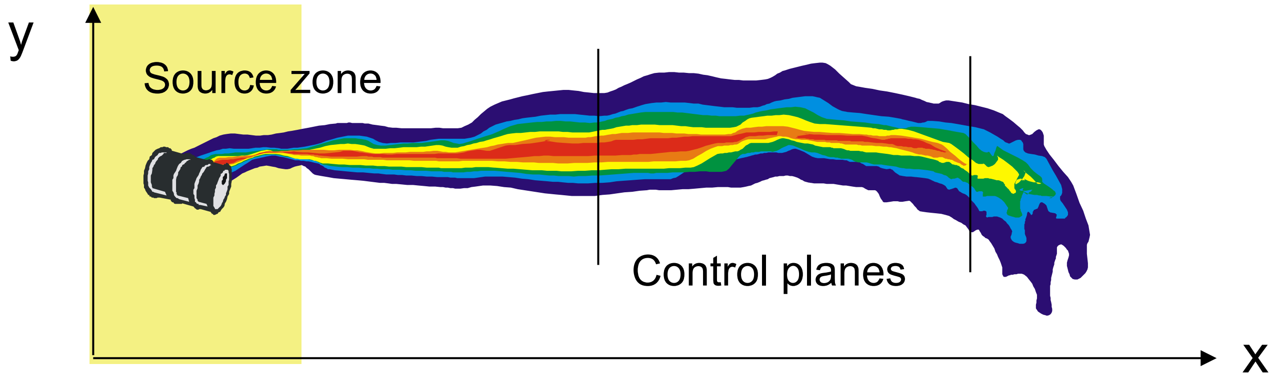
Stationarity of contaminant plume:
Concentration time series at monitoring wells near the source



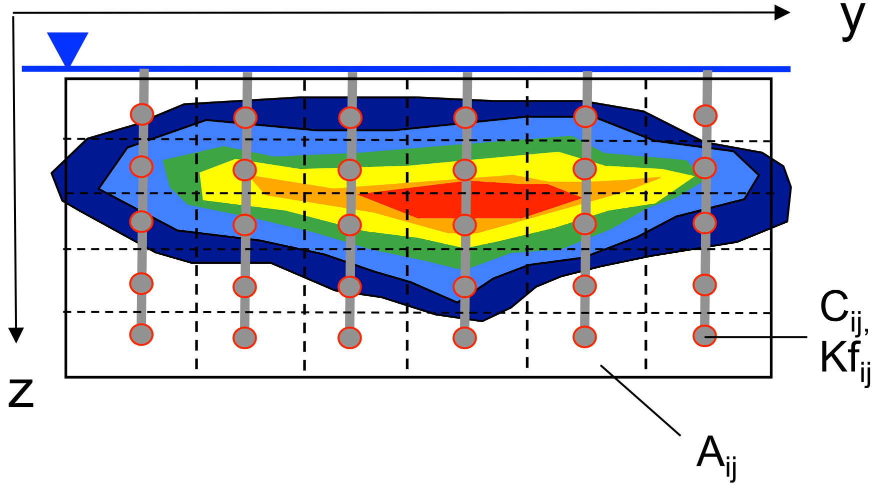


Determination of mass flow rates using the groundwater fence method

C | A | U
Christian-Albrechts-Universität zu Kiel



Cross section through control plane:

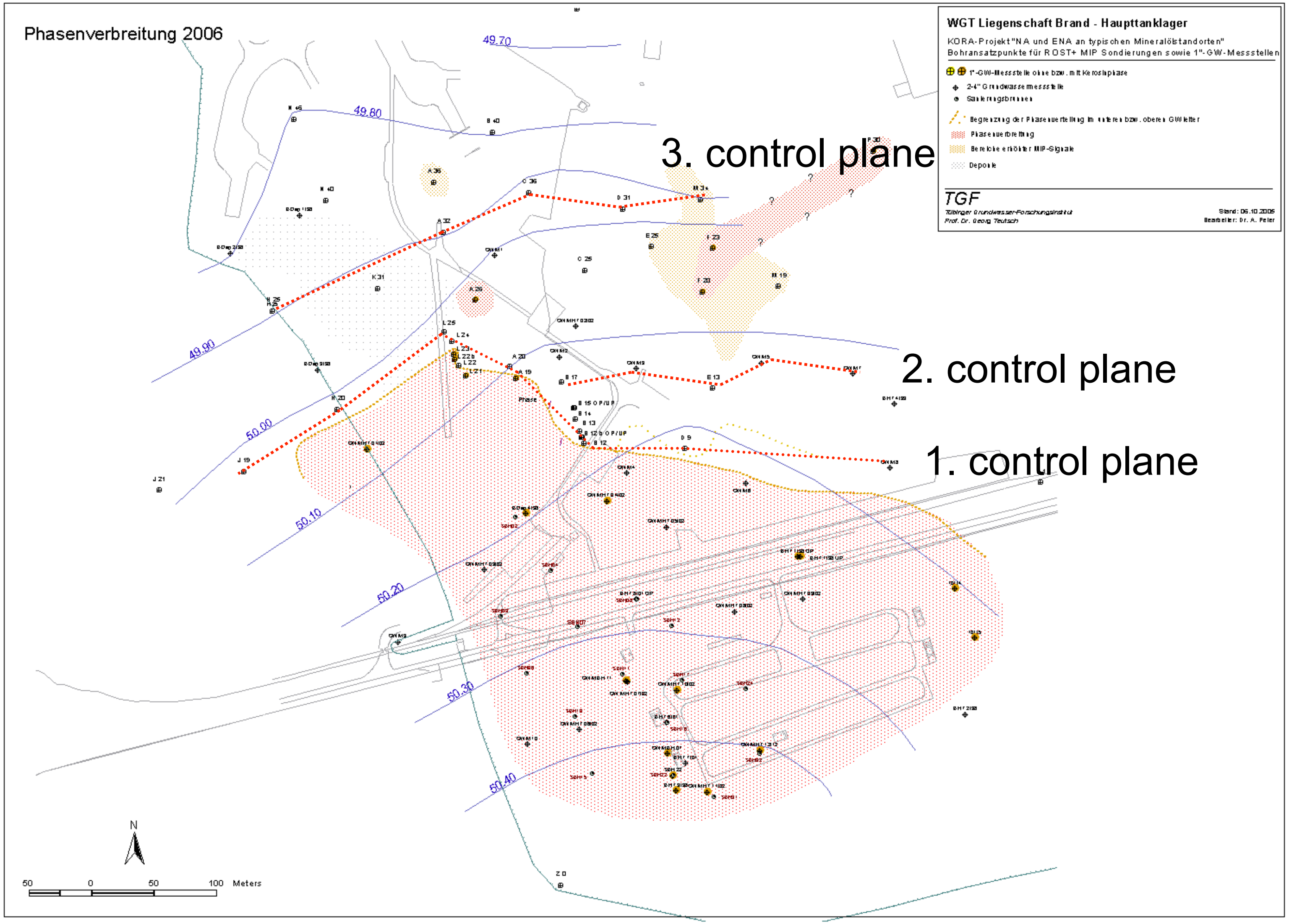


1.	Multilevel well	→	$C_{i,j}$
2.	Injection Logging	→	$Kf_{i,j}$
3.	Polygone area	→	$A_{i,j}$
4.	Hydraul. gradient	→	I

Contaminant Mass Flow rate $= \Sigma\ (C_{ij} \cdot Kf_{ij} \cdot A_{ij}) \cdot I$

Determination of mass flow rates at three control planes in Brand

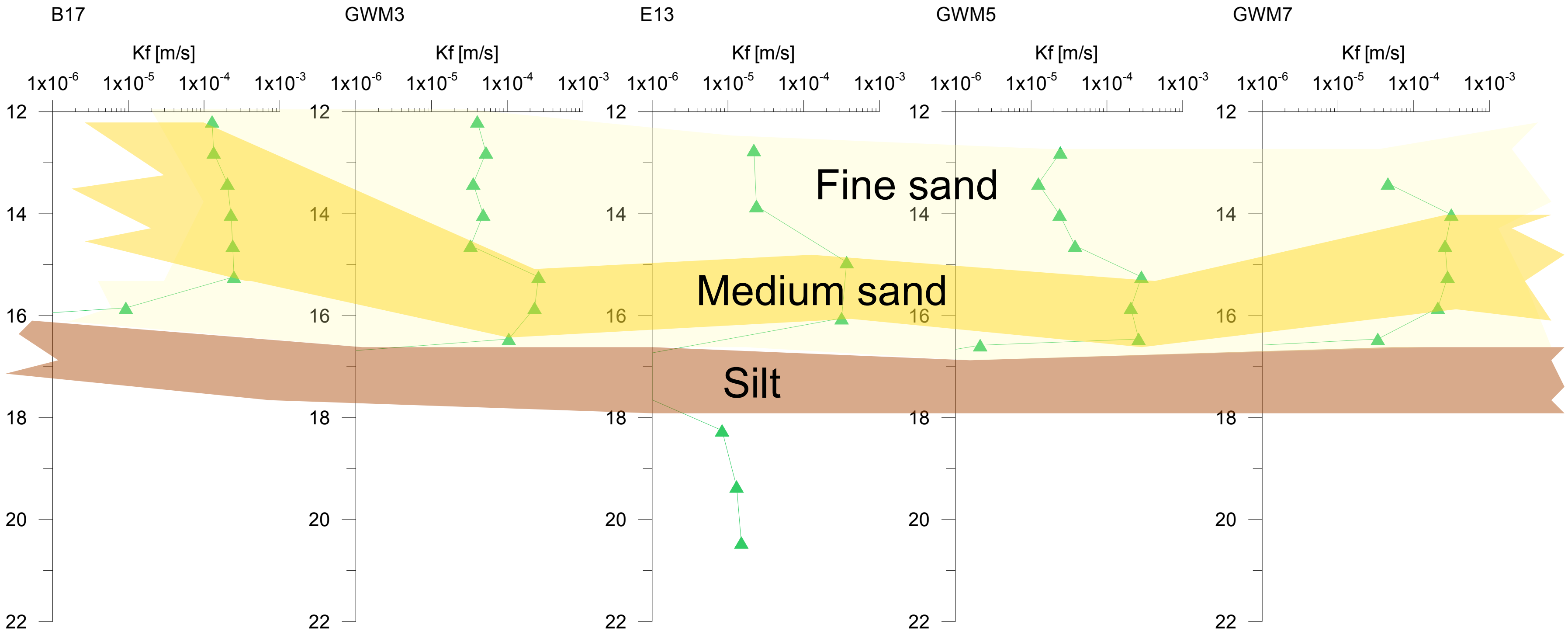
C | A | U
Christian-Albrechts-Universität zu Kiel



Determination of depth profiles of Kf at each control plane

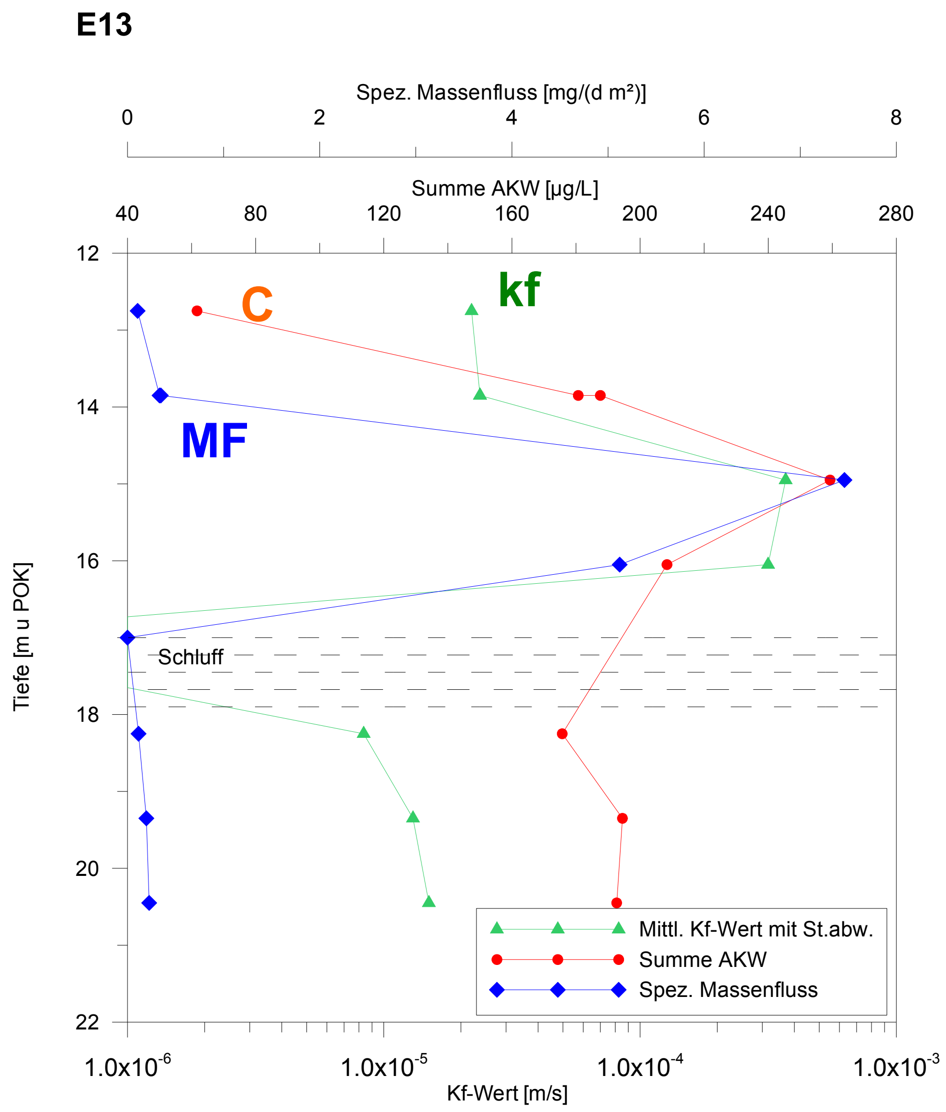
Christian-Albrechts-Universität zu Kiel

Depth profiles of Kf from Injection Logging and Slugtests: 2. Control plane



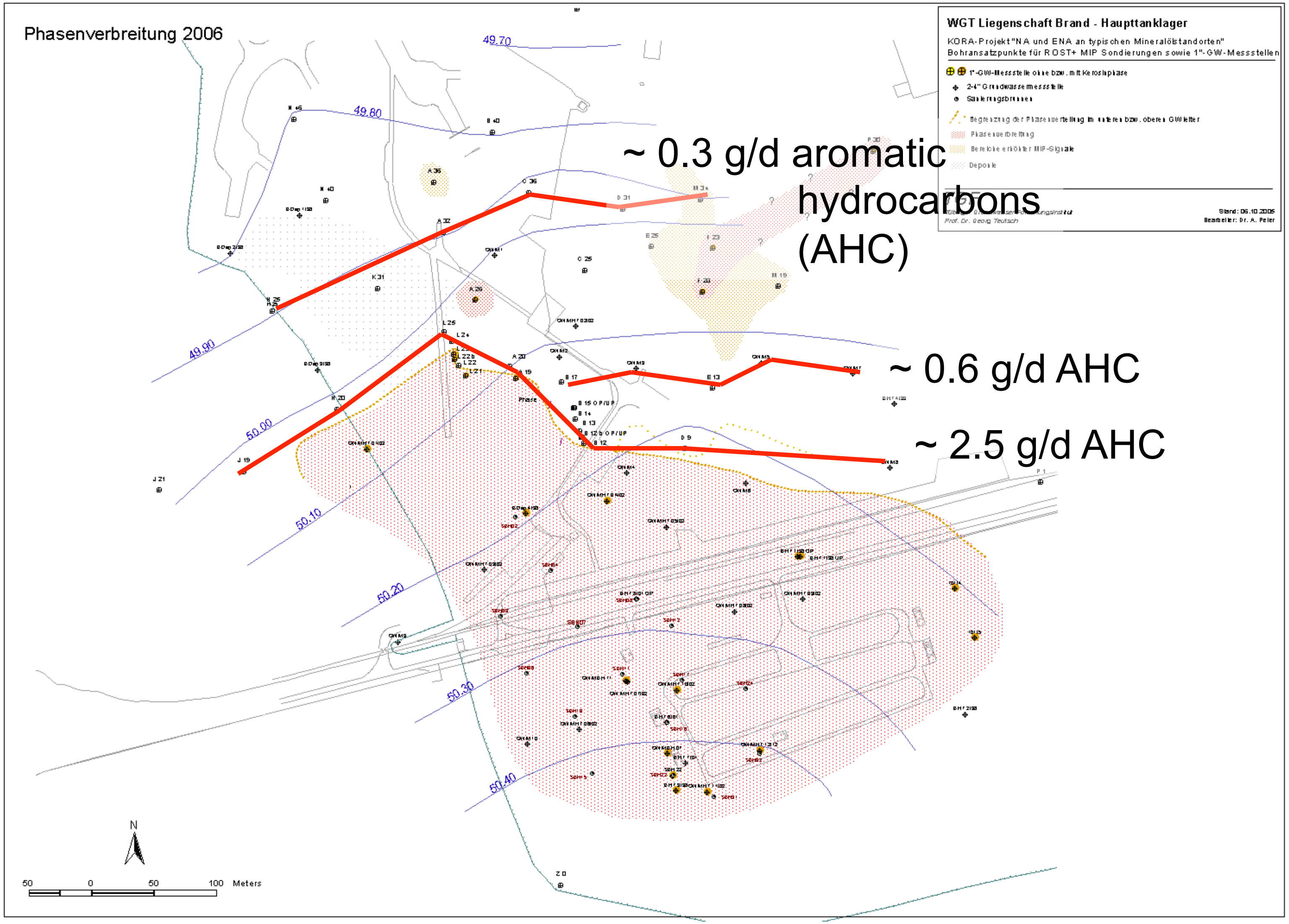
Determination of mass flow rates in Brand

Determination of contaminant mass flow rates at a single well:
Depth-profiles of concentration, Kf-values and specific mass flow rates



Determination of mass flow rates at three control planes in Brand

C | A | U
Christian-Albrechts-Universität zu Kiel

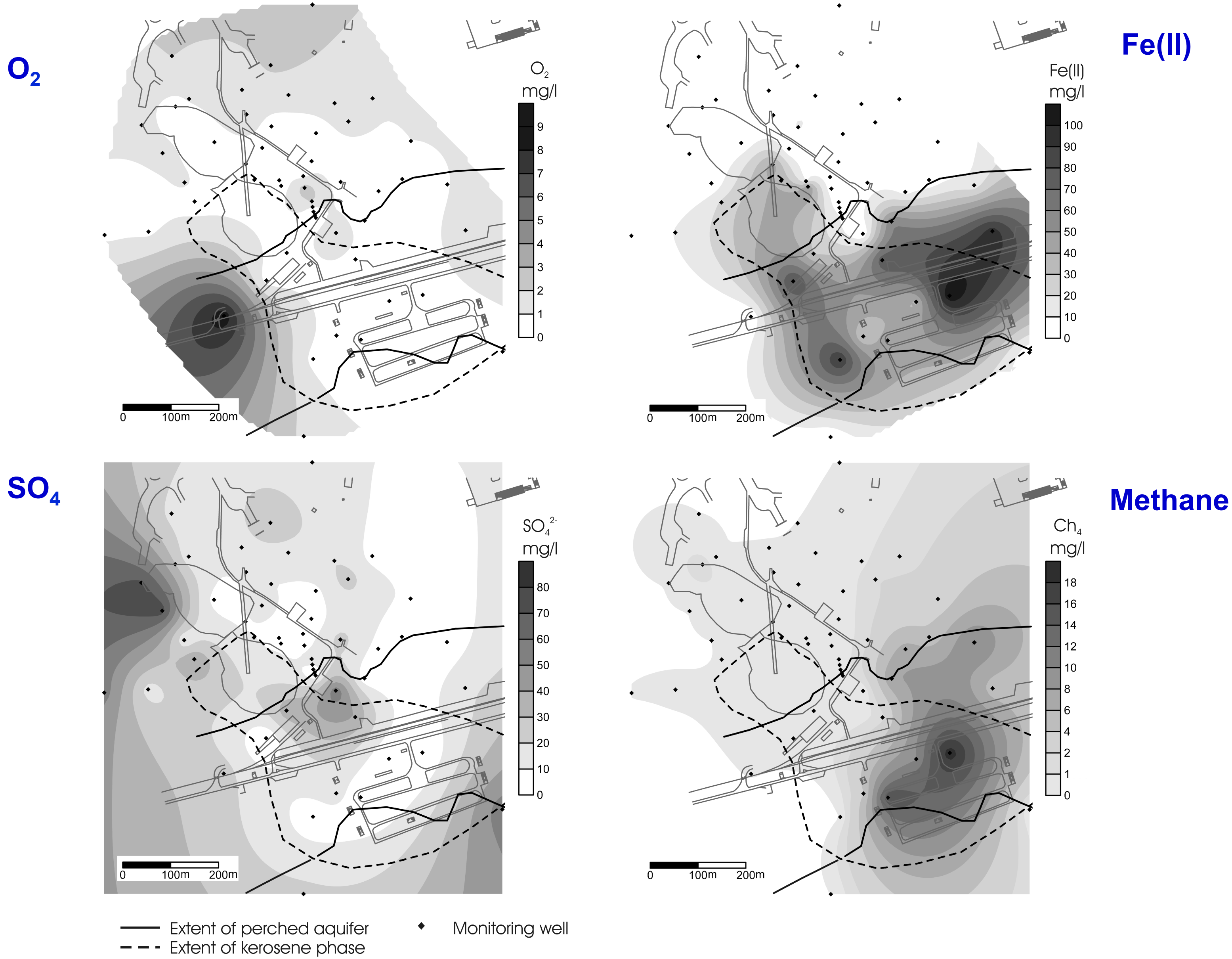


Proving Natural Attenuation

Contaminant source characterization	• Extension of the source (NAPL) and NAPL mass • Source composition / inventory • Source emission and source lifetime
Contaminant plume characterization	• Plume length • Temporal plume development / stationarity • Mass flow rate reduction
Qualitative and quantitative evaluation of NA processes	**• Data supporting qualitatively bio-degradation and other NA processes** **• Data supporting quantitatively bio-degradation and other NA processes**
Prediction of NA processes	• Flow and reactive transport modelling

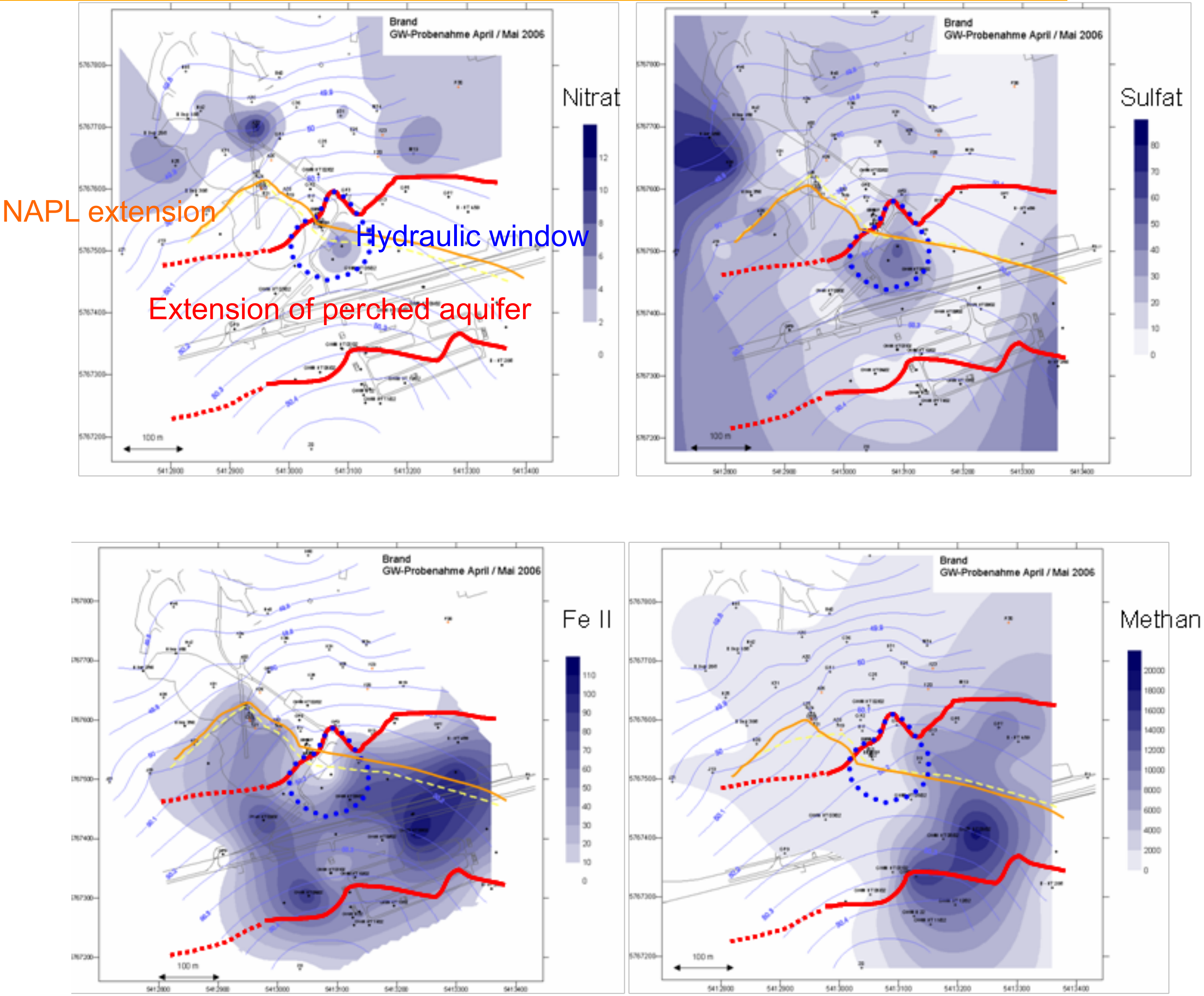
Distribution of electron acceptors and reaction products in the source and plume

C | A | U
Christian-Albrechts-Universität zu Kiel



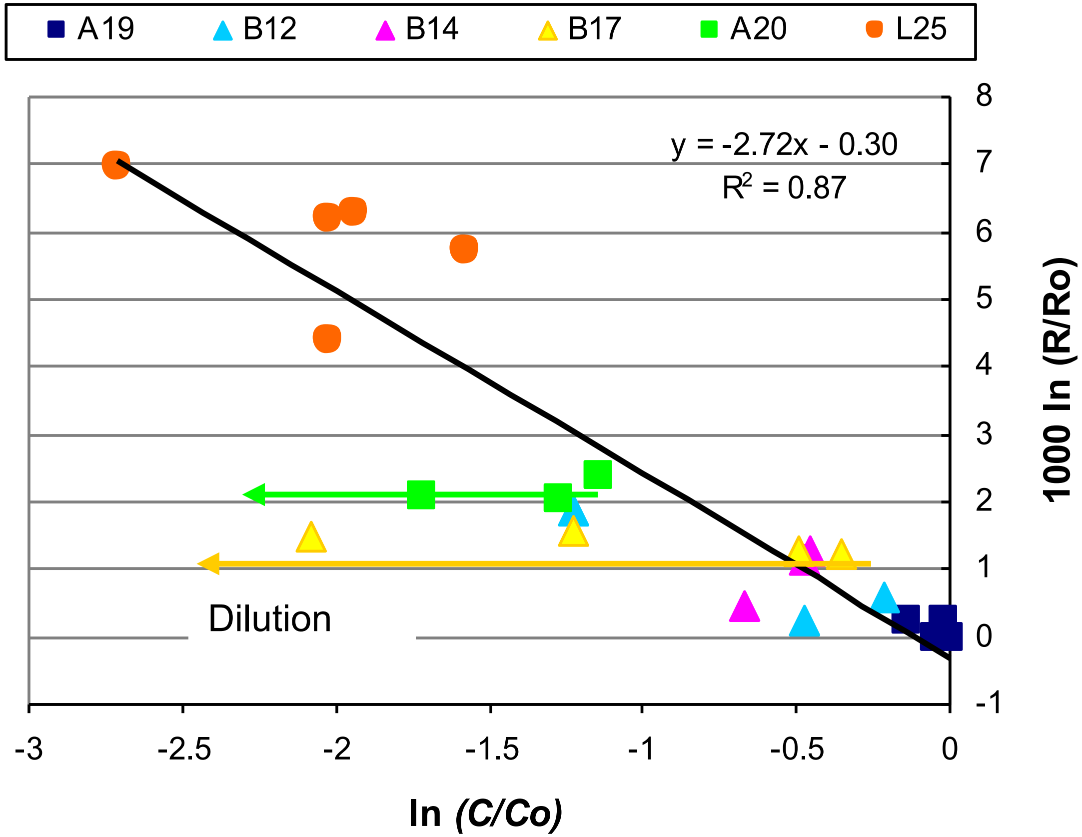
Distribution of electron acceptors and reaction products in the source and plume

Christian-Albrechts-Universität zu Kiel



Quantitative investigation of biodegradation using $^{13}C/^{12}C$ isotope analyses of aromatic hydrocarbons

Benzene



Blessing, 2007

→ Isotopic fractionation according to Rayleigh equation is a proof for biodegradation

→ Concentrations from wells in the area of the hydraulic window show no fractionation, only dilution

Contaminant specific biodegradability at the field site Brand determined using $^{13}C/^{12}C$ isotope analyses

	West part of plume	East part of plume
Benzene	97 %	79 %
Toluene	+(+)	
Ethylbenzene	+	34 %
Xylenes	+	
1,3,5-TMB u. 1,2,4-TMB	++	
1,2,3-TMB	+	
Propylbenzene u. Isopropylbenzene	++	
Ethyltoluenes	++	

Numbers: Percental share of contaminant mass, that has been beiodegraded

+: qualitative hint for biodegradation

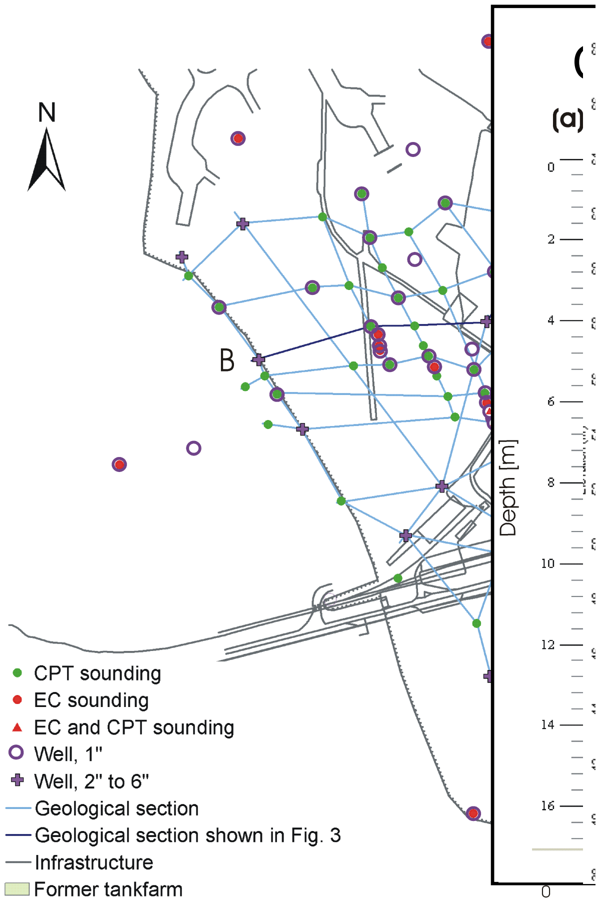
++: strong qualitative hint for biodegradation

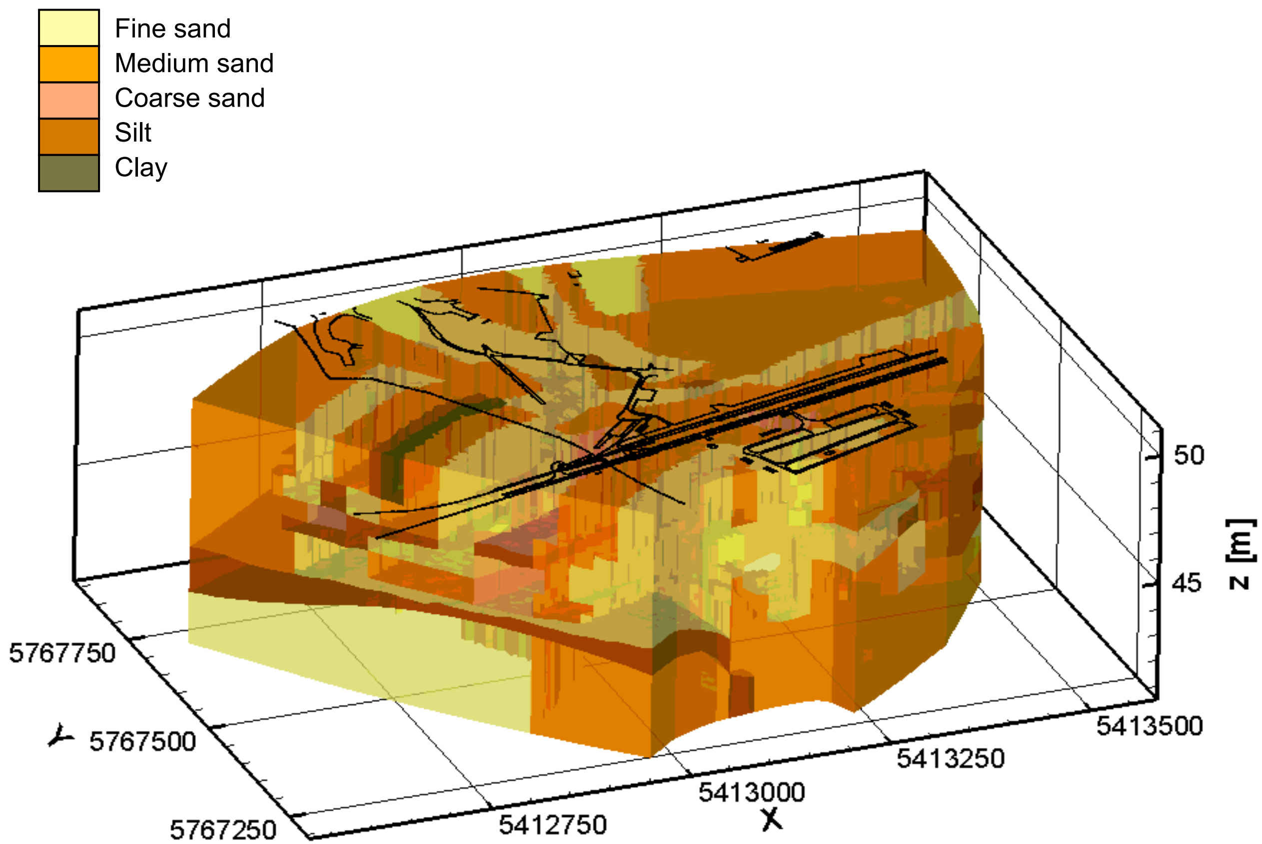
Blessing, 2007

Contaminant source characterization	• Extension of the source (NAPL) and NAPL mass • Source composition / inventory • Source emission and source lifetime
Contaminant plume characterization	• Plume length • Temporal plume development / stationarity • Mass flow rate reduction
Qualitative and quantitative evaluation of NA processes	• Data supporting qualitatively bio-degradation and other NA processes • Data supporting quantitatively bio-degradation and other NA processes
Prediction of NA processes	• **Flow and reactive transport modelling**

3D Geological structure and flow model

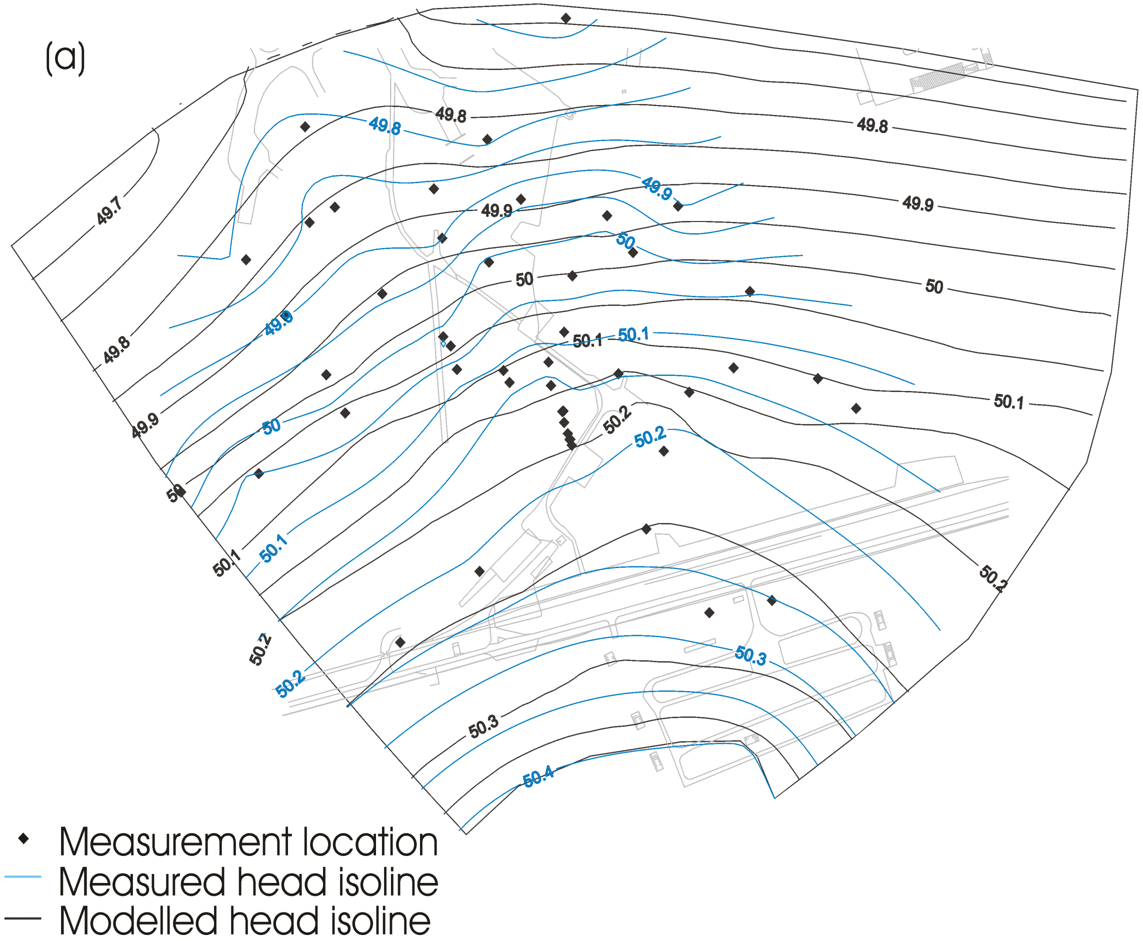
C | A | U
Christian-Albrechts-Universität zu Kiel

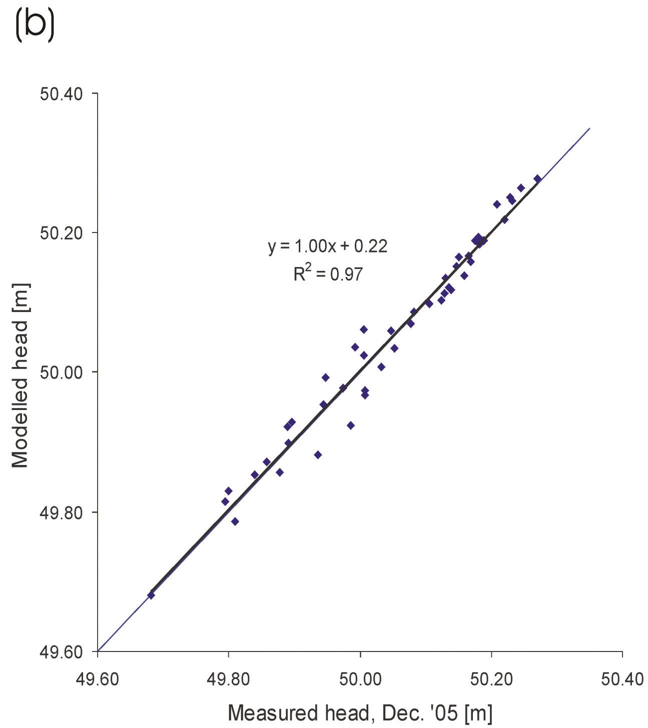




Miles et al., Env. Geol. (2007)

3D Geological structure and flow model

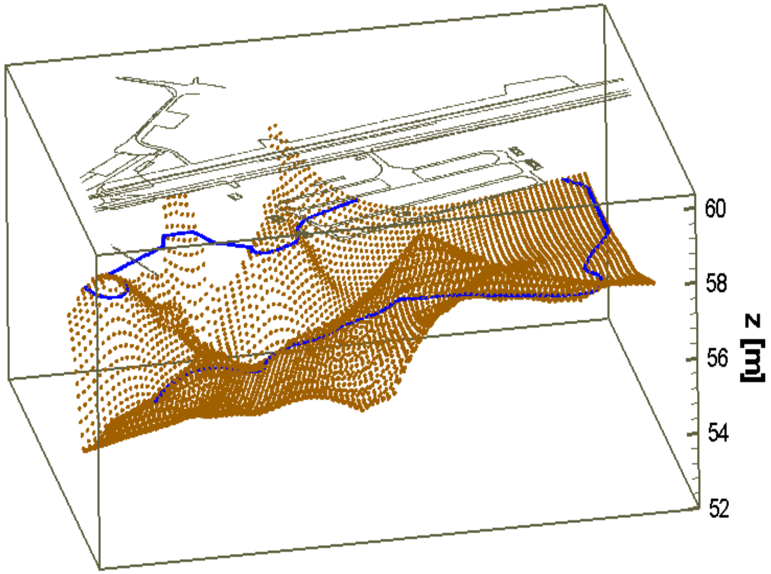




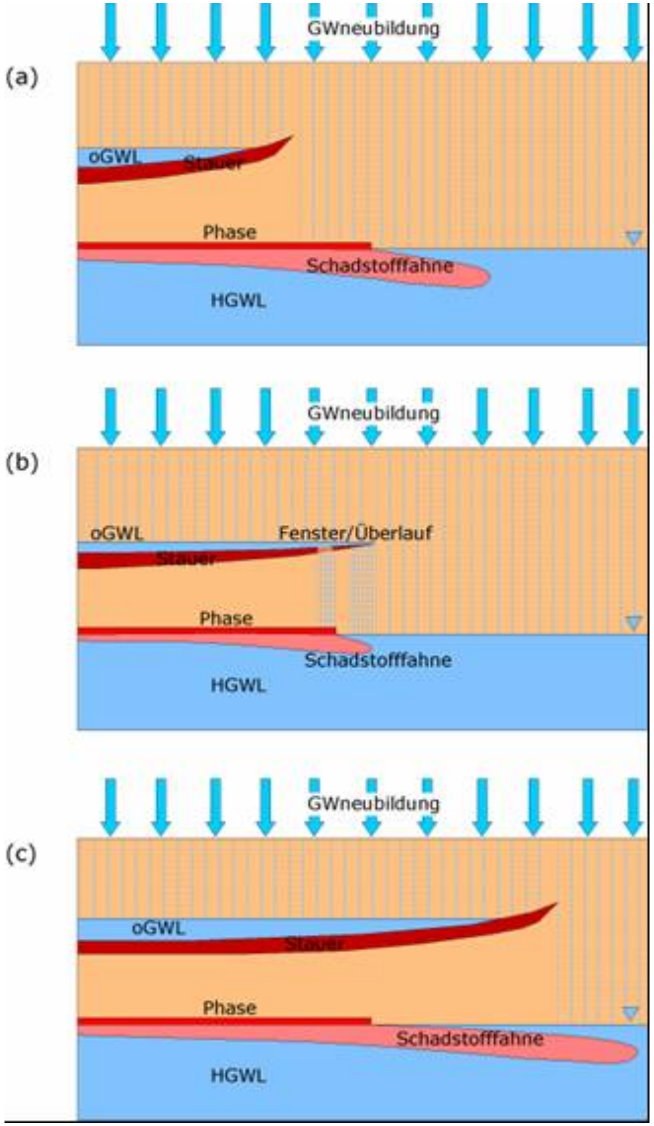
Miles et al., Env. Geol. (2007)

Impact of perched aquifer on gw-recharge distribution

Aquitard of hanging aquifer with groundwater level

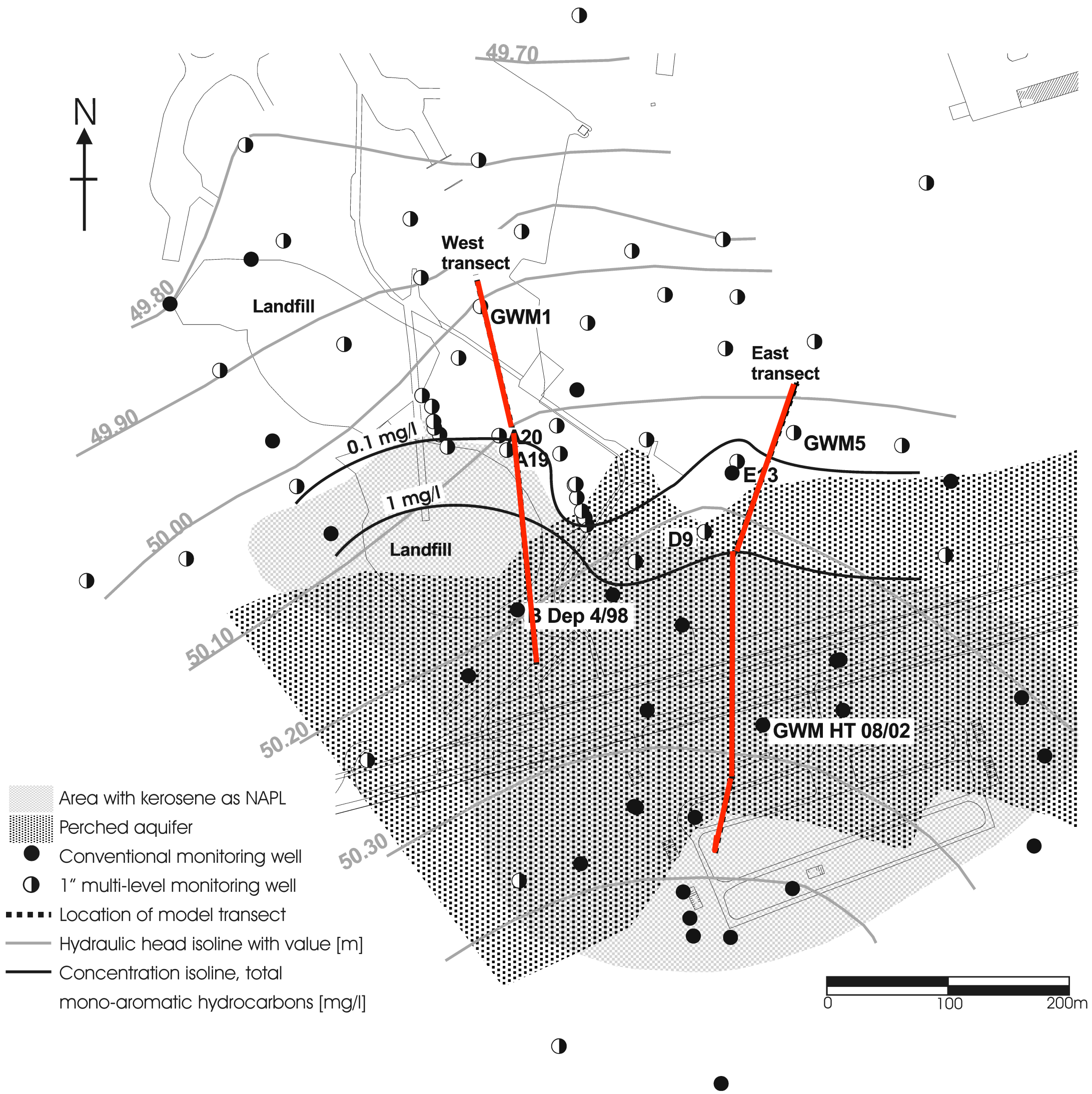


Miles et al. (2007)



Predicting NA:
Multicomponent Reactive Transport Modelling

Christian-Albrechts-Universität zu Kiel



East Transect

- Long BTEX plume
- High Fe(II) downstream
- High CH_4
- Low SO_4

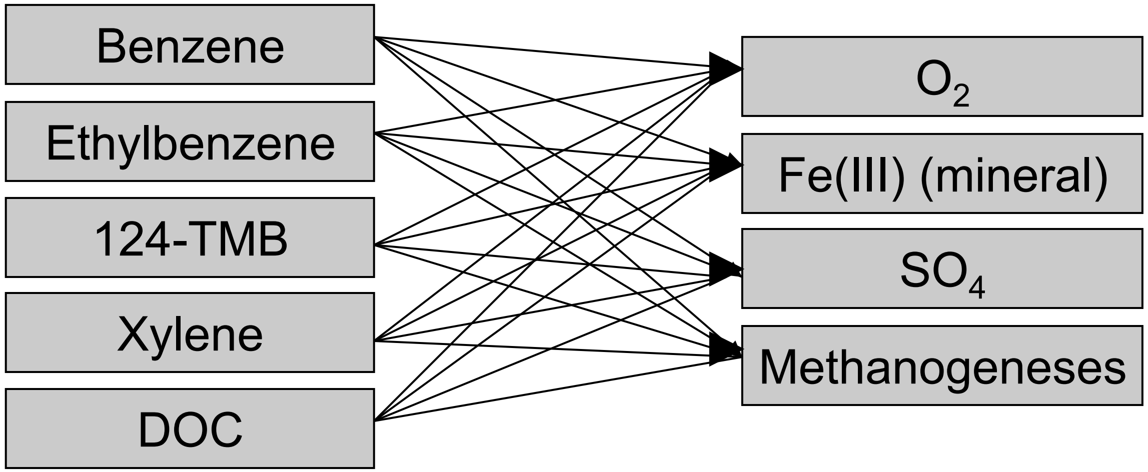
West Transect

- Short BTEX plume
- Lower Fe(II)
- Low CH_4
- Higher SO_4

Miles et al., Ground Water (2008)

Reaction Scheme: 22 degradation reactions

Contaminants **Electron Acceptor**



Electron Acceptor	Kinetics	Inhibition
O_2	Monod	
Fe(III) (mineral)	1st order	O_2
SO_4	Monod	O_2,Fe(III)
Methanogeneses	1st order	O_2,Fe(III),SO_4

Additional Fe reactions

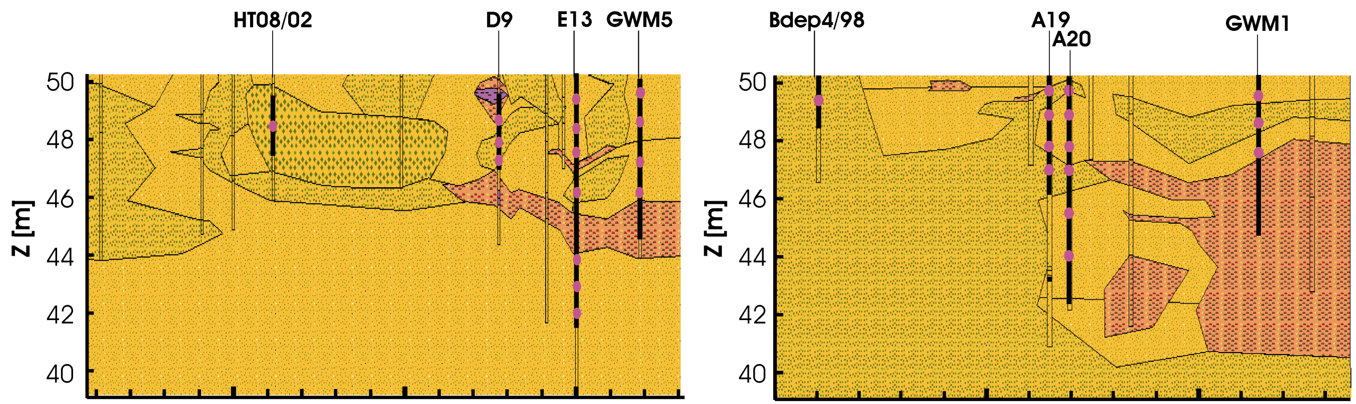
- **Fe(II) reoxidizes to Fe(III) in presence of O_2**
- **Precipitation of Fe(II) as 1st order reaction**

Predicting NA:
Multicomponent Reactive Transport Modelling (MIN3P)

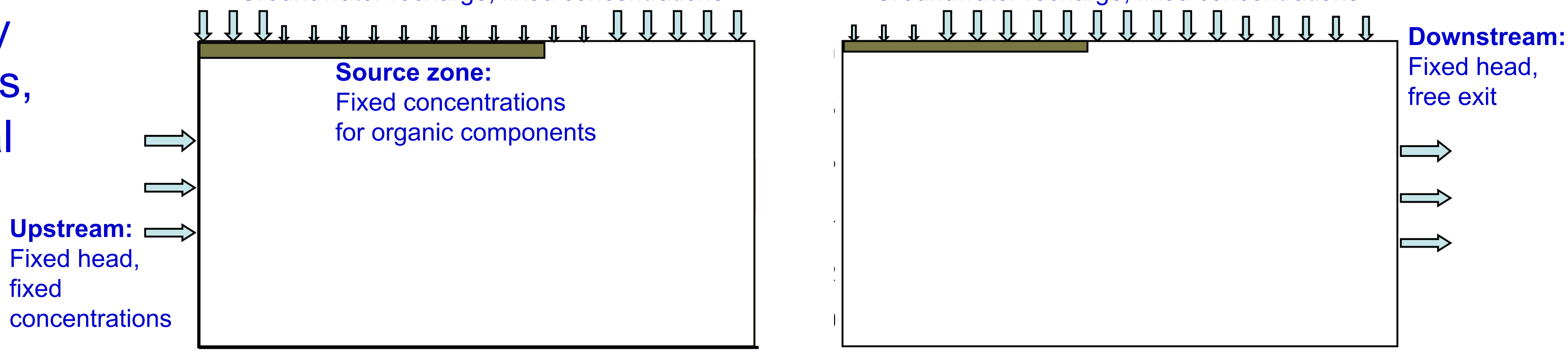
C | A | U
Christian-Albrechts-Universität zu Kiel

East transect | West transect

Geological cross section



Boundary conditions, numerical model



Calibration of degradation parameters using multilevel concentration data

Implementation of degradation scheme without further calibration

Miles et al., Ground Water (2008)

Prediction:
Multicomponent Reactive Transport Modelling

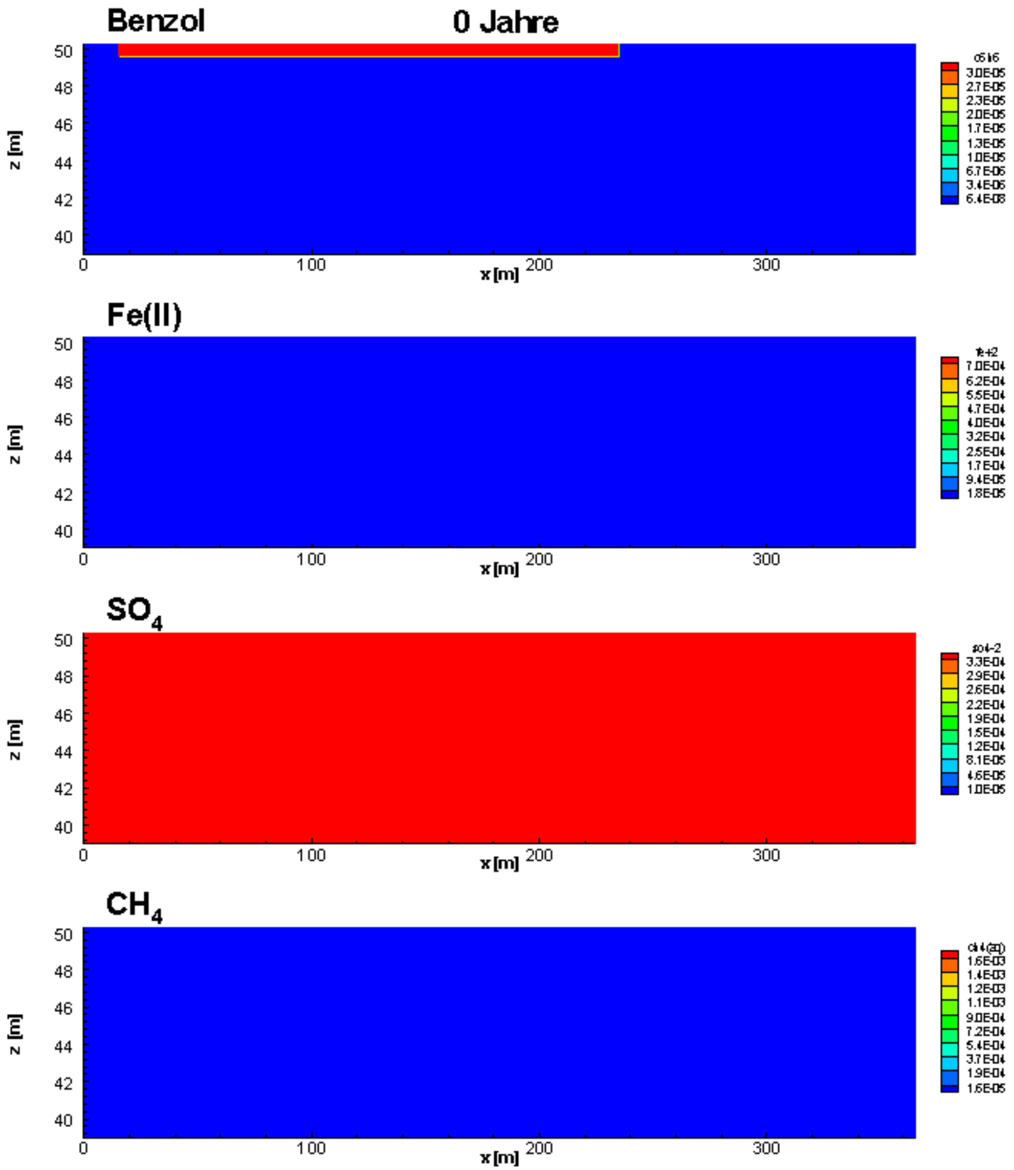
Simulation of plume development

Benzene

Fe(II)

Sulfate

Methane



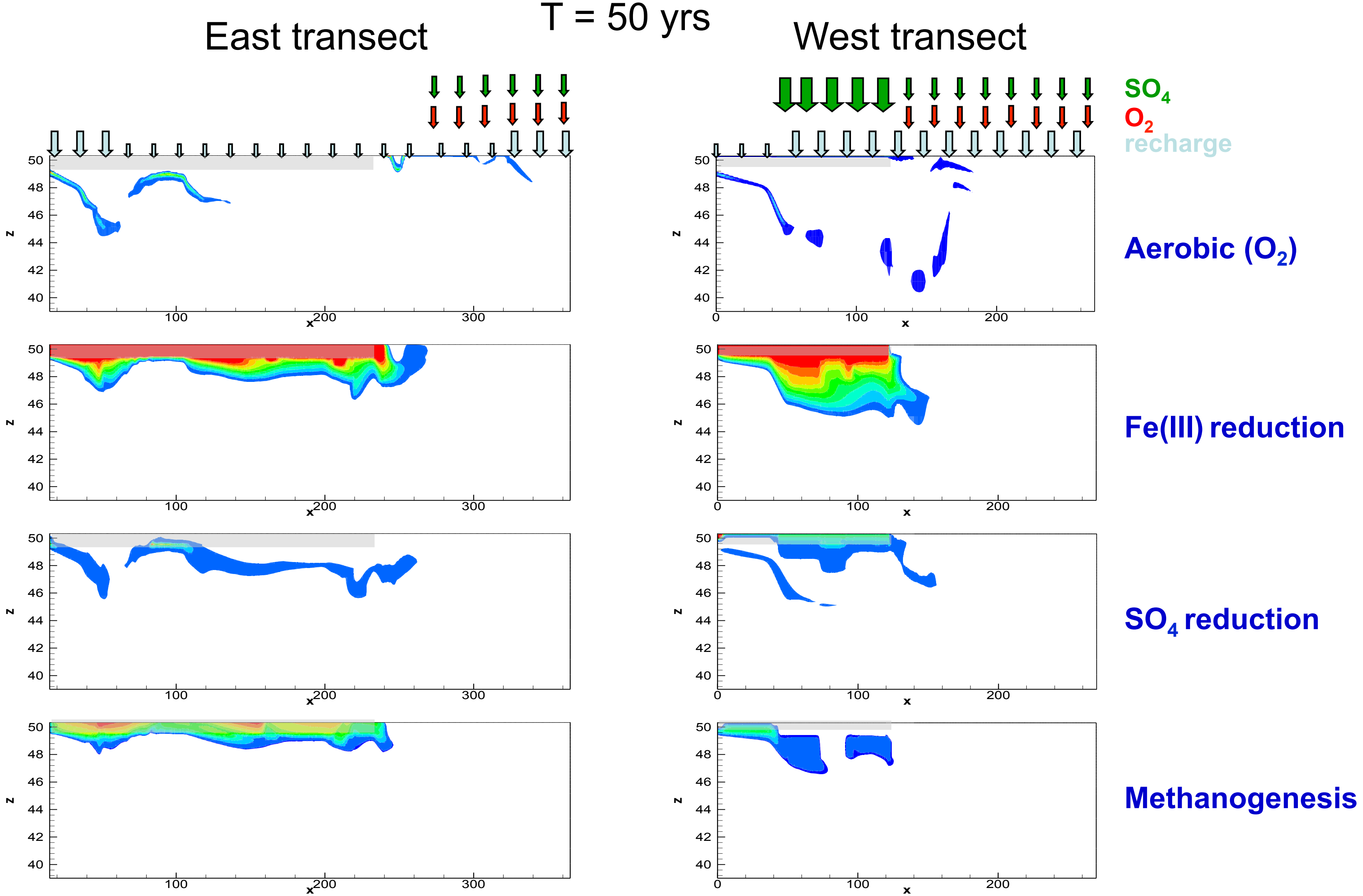
Miles et al. (2008)

Predicting NA: Multicomponent Reactive Transport Modelling

Christian-Albrechts-Universität zu Kiel

Spatial distribution of degraded contaminant mass by different EAs

T = 50 yrs

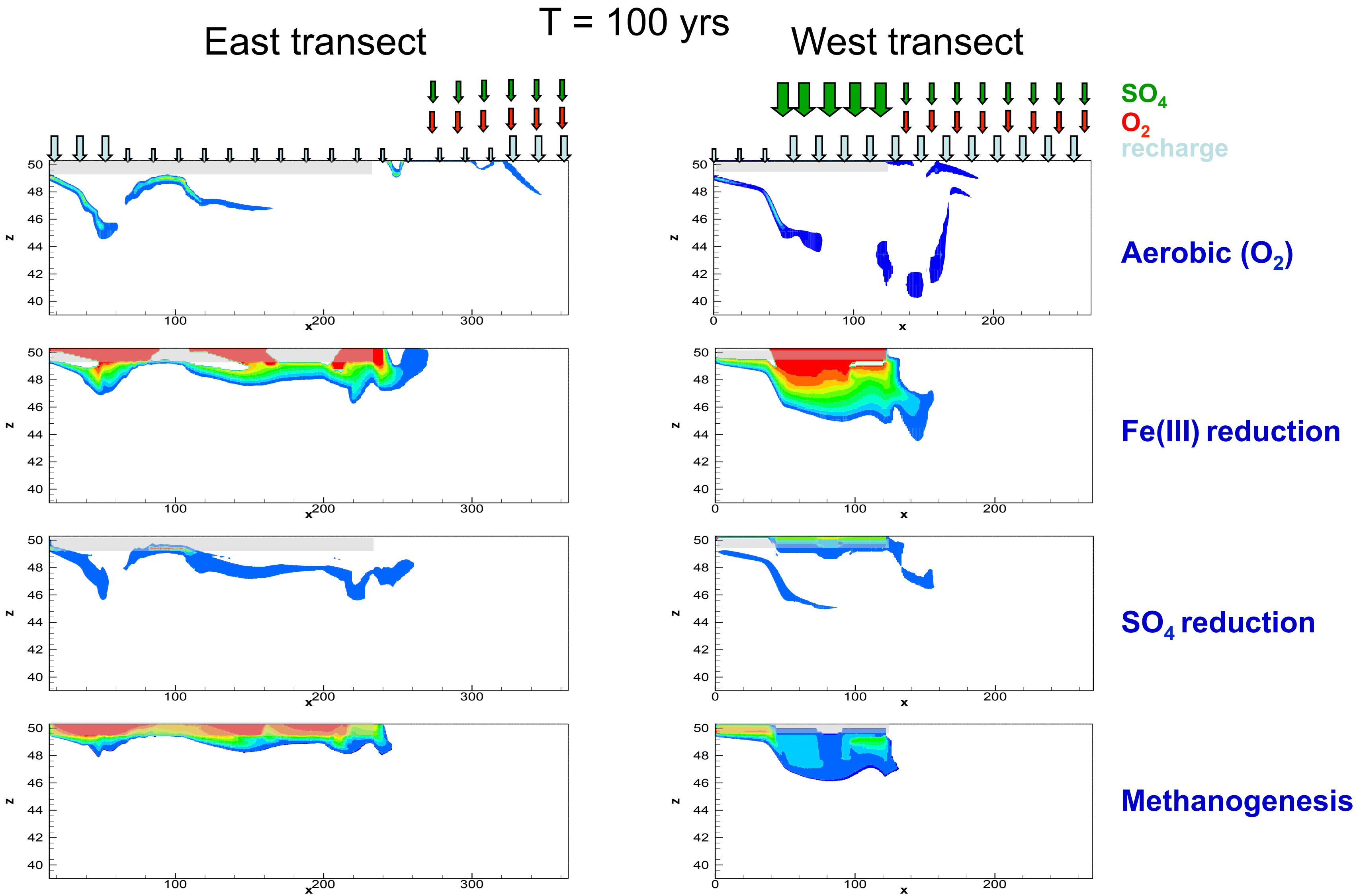


Miles et al. (2008)

Predicting NA: Multicomponent Reactive Transport Modelling

Christian-Albrechts-Universität zu Kiel

Spatial distribution of degraded contaminant mass by different EAs



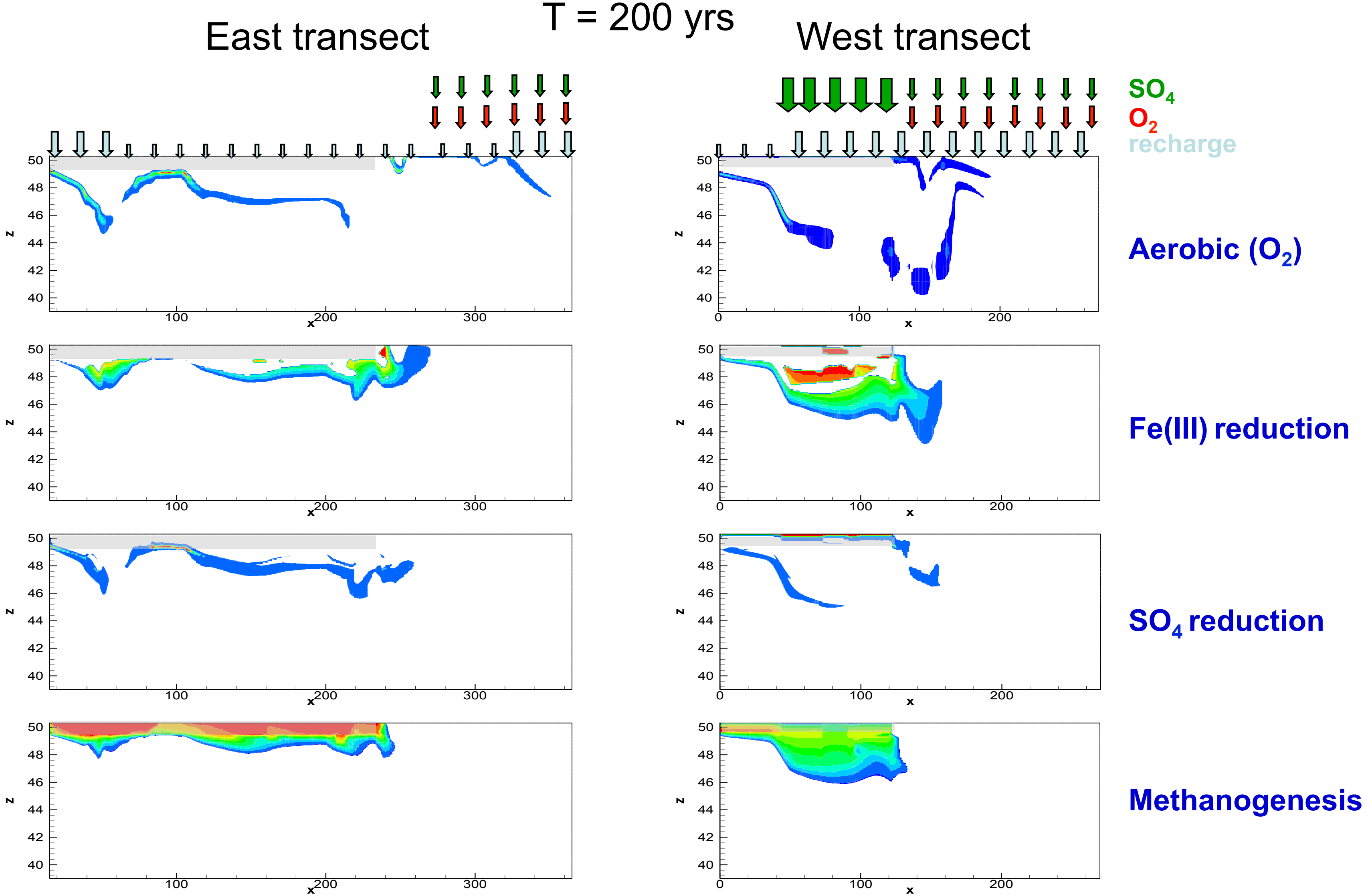
Miles et al. (2008)

Predicting NA:
Multicomponent Reactive Transport Modelling

C A U
Christian-Albrechts-Universität zu Kiel

Spatial distribution of degraded contaminant mass by different EAs

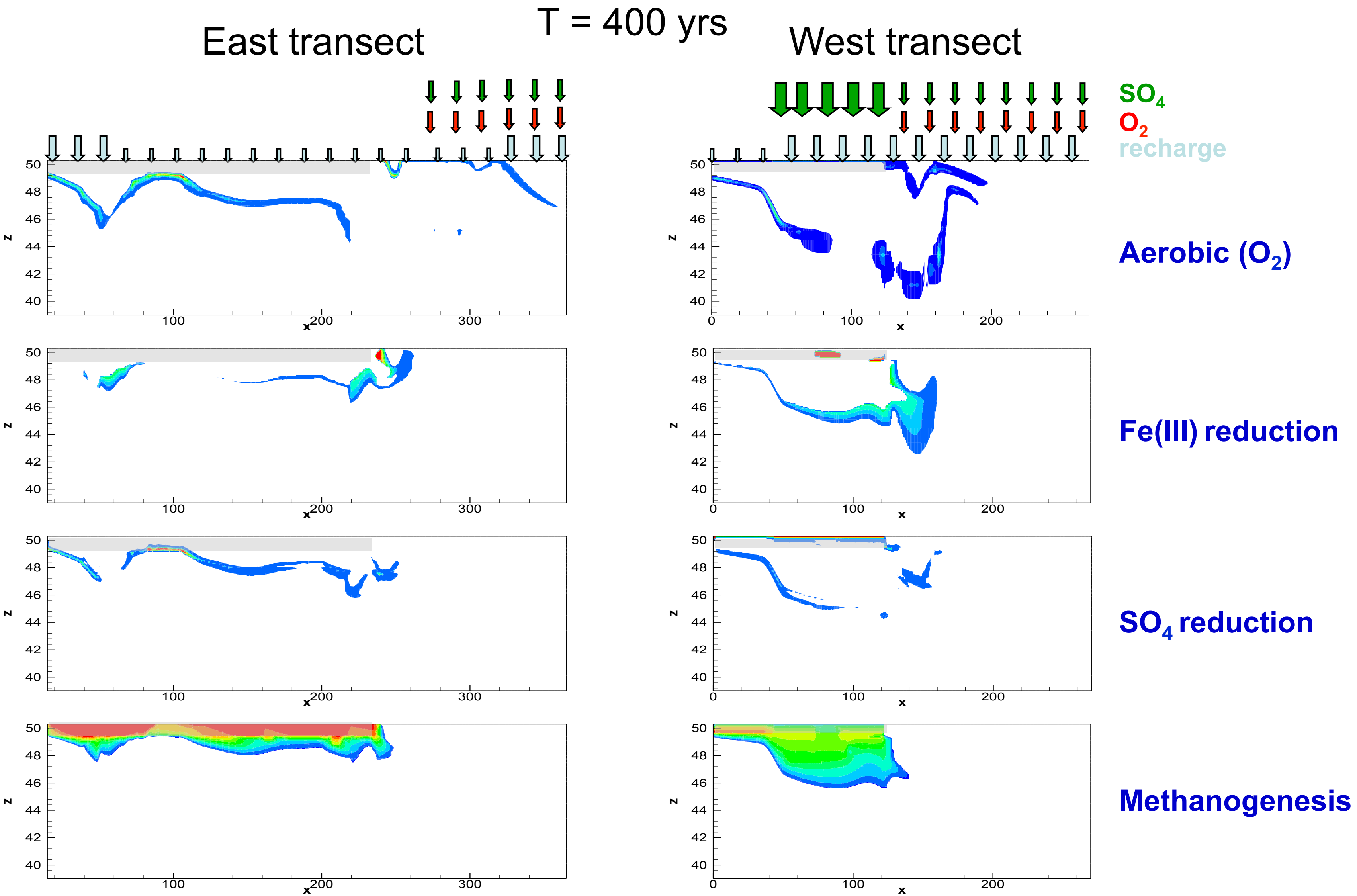
T = 200 yrs



Miles et al. (2008)

Predicting NA:
Multicomponent Reactive Transport Modelling

Spatial distribution of degraded contaminant mass by different EAs

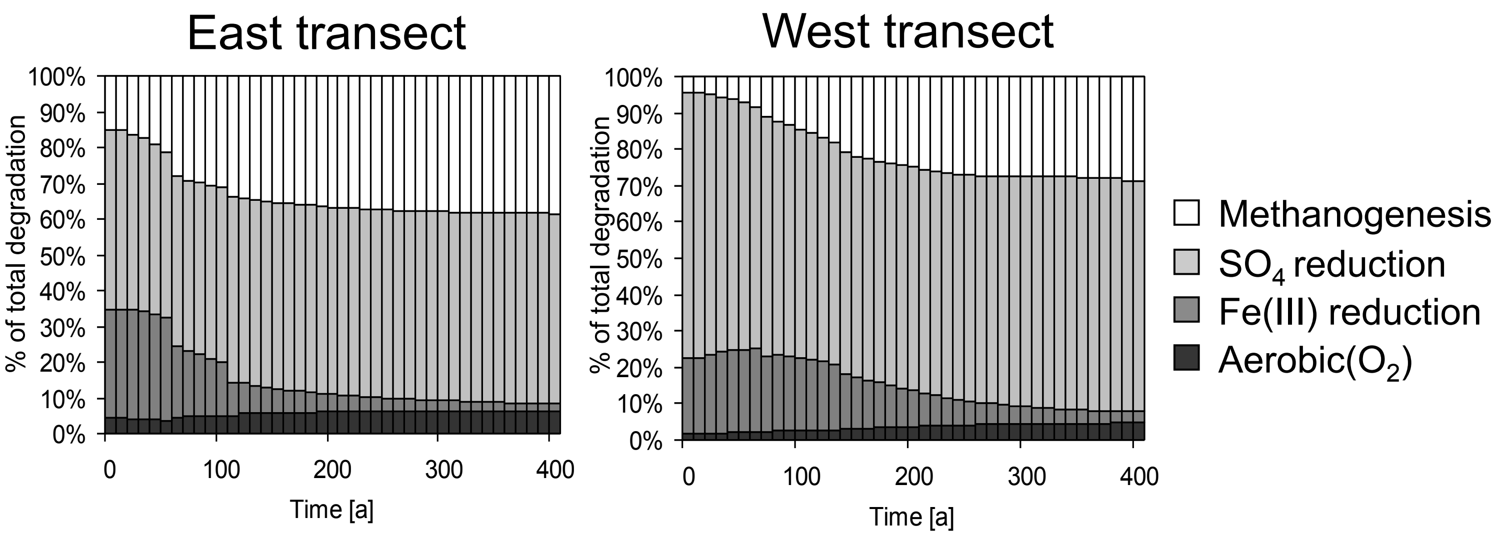


Miles et al. (2008)

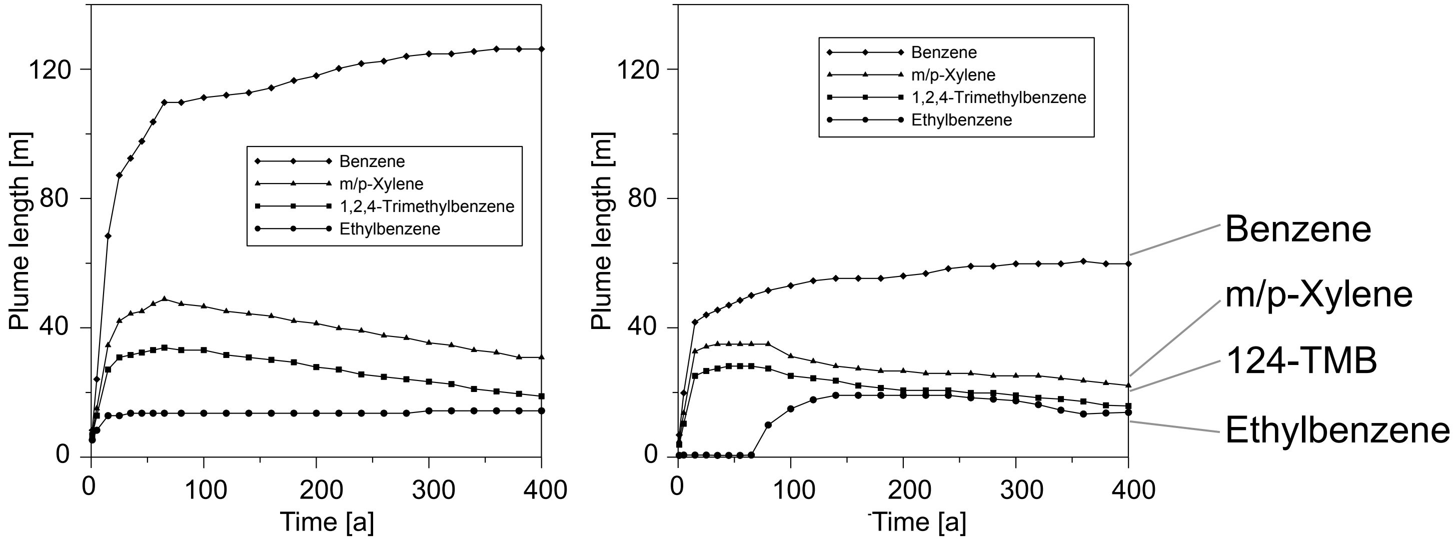
Predicting NA:
Multicomponent Reactive Transport Modelling

Simulated plume lengths and evolution of EA consumption

Contribution of TEAPs to total contaminant degradation



Plume lengths from end of source zone, 5µg/l isoline



Miles et al. (2008)

Conclusions

- Several lines of evidence demonstrate the efficacy of NA processes, like mass flow rate reduction, plume stationarity, electron acceptor distribution, isotope analyses and reactive transport modelling.

- Extensive site investigation is necessary to prove NA efficacy. Direct-Push technologies provide a suitable bundle of methods for time- and cost-efficient site investigations.

- Geological conditions, like a perched aquifer and as a result altered ground-water recharge conditions may have a significant influence on the supply of electron acceptors and thus on biodegradation and plume length.

- Reactive transport modelling suggest that within the contaminant plume, Fe(III) reduction and methanogeneses dominate degradation processes and that after depletion of immobile electron acceptors, methanogeneses might dominate degradation processes *within* the plume, which might lead to a temporal plume expansion.

- Active remediation measures (NAPL phase extraction) were stopped at the site and a MNA concept was implemented to monitor NA processes.

Acknowledgements

C | A | U

Christian-Albrechts-Universität zu Kiel

The KORA-Project „NA and MNA at the sites Brand and Niedergörsdorf“ (2002-2007) was funded by

German Ministery of Education and Research (BMBF)

Brandenburgische Boden GmbH

Bundesministerium für Bildung und Forschung

KORA

BRANDENBURGISCHE BODEN

Project partners

Benedict Miles, Michael Jahn

Michaela Blessing

Olaf Kolditz, Peter Dietrich

Georg Teutsch

Martina Freygang

et al.

Thank you for your attention