Implications from Long-Term Monitoring of Two ZVI Reactive Barriers in Germany

M. Ebert,
A. Parbs, V. Plagentz, D. Schäfer, A. Dahmke, M. Wegner, H. Schad

PRB's in Germany

- *first field applications in 1998*
- *actually 7 installed, 4 planed*
  - *full and pilot scale*
  - *commercial and RD projects*
  - *preference of ZVI or GAC*
  - *preference for F&G systems*
- *monitoring results show not always the expected efficiency*

Some Examples (Strongly Simplified)

- *hydraulic problems due to a regional rising water table*
- *fast degradation of several 100 mg/l of the main contaminant (TCE) – but by-products are not degraded*
- *contaminants down-gradient, a short time after barrier construction*
- *by-passing the barrier due to clogging effects*

Reasons and Effects

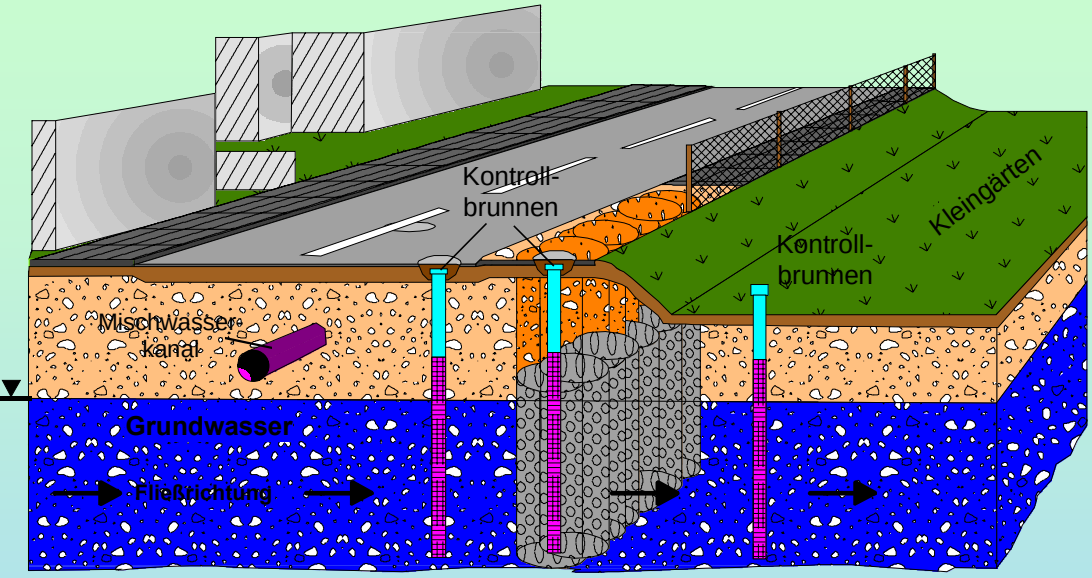
- *reasons often not obviously*
- *critical review of the monitoring results leads to confusion*
  - *not the appropriate sampling frequency or too small analytical suites*
  - *missing monitoring wells*
  - *etc.*

➢ *the opposition to PRB technology feels to be on top again*

Research Activities at Two ZVI PRB's

- part of the German R&D-network RUBIN
- continuous PRB (Rheine) and F&G (Tübingen)
  - ☑ "standard" ground water monitoring
  - ☑ extended analytical suite
  - ☑ multi-level low flow sampling
  - ☒ passive sampling (dosimeter)
  - ☑ core drilling
    - ☑ column experiments, solid phase, microbes
  - ☑ stable carbon isotopes
  - ☑ pump and tracer tests

Rheine Pilot Scale PRB – Site Description



construction in June 1998 (R&D project)

aquifer thickness: 2 – 3 m

aquifer bottom: ~6m bs

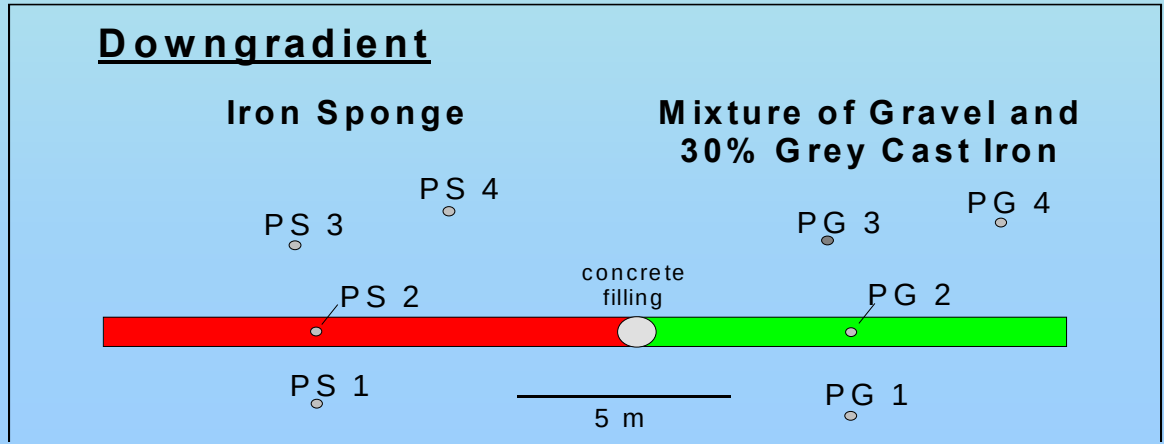
regional ground water flow velocity: 6 – 8 cm/d

main contaminant: PCE (up to 30 mg/l

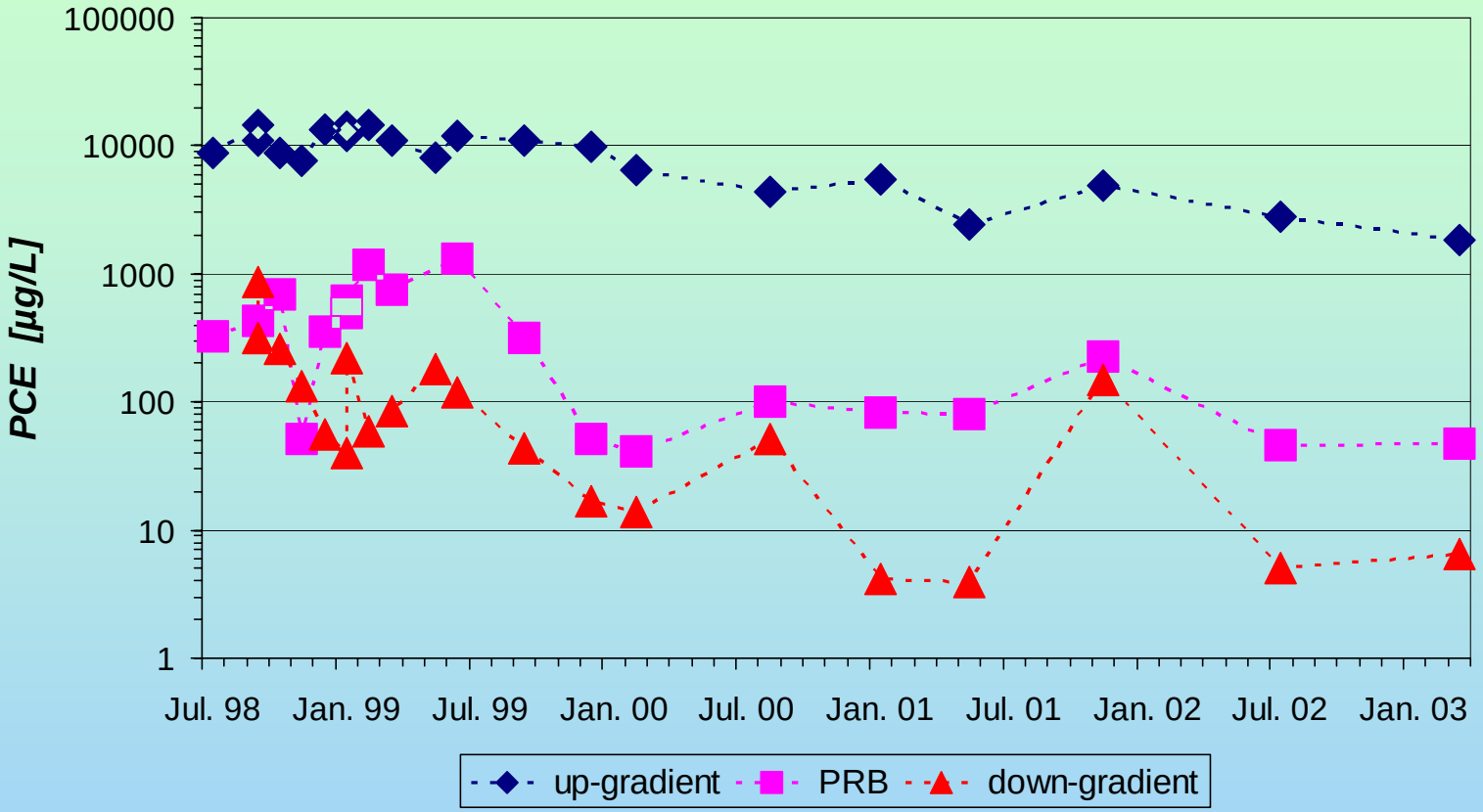
source: dry cleaning, ~800 m up-gradient)

two sections: *iron sponge* and a *mixture of gravel and 30% grey cast iron*

for each section one monitoring transect



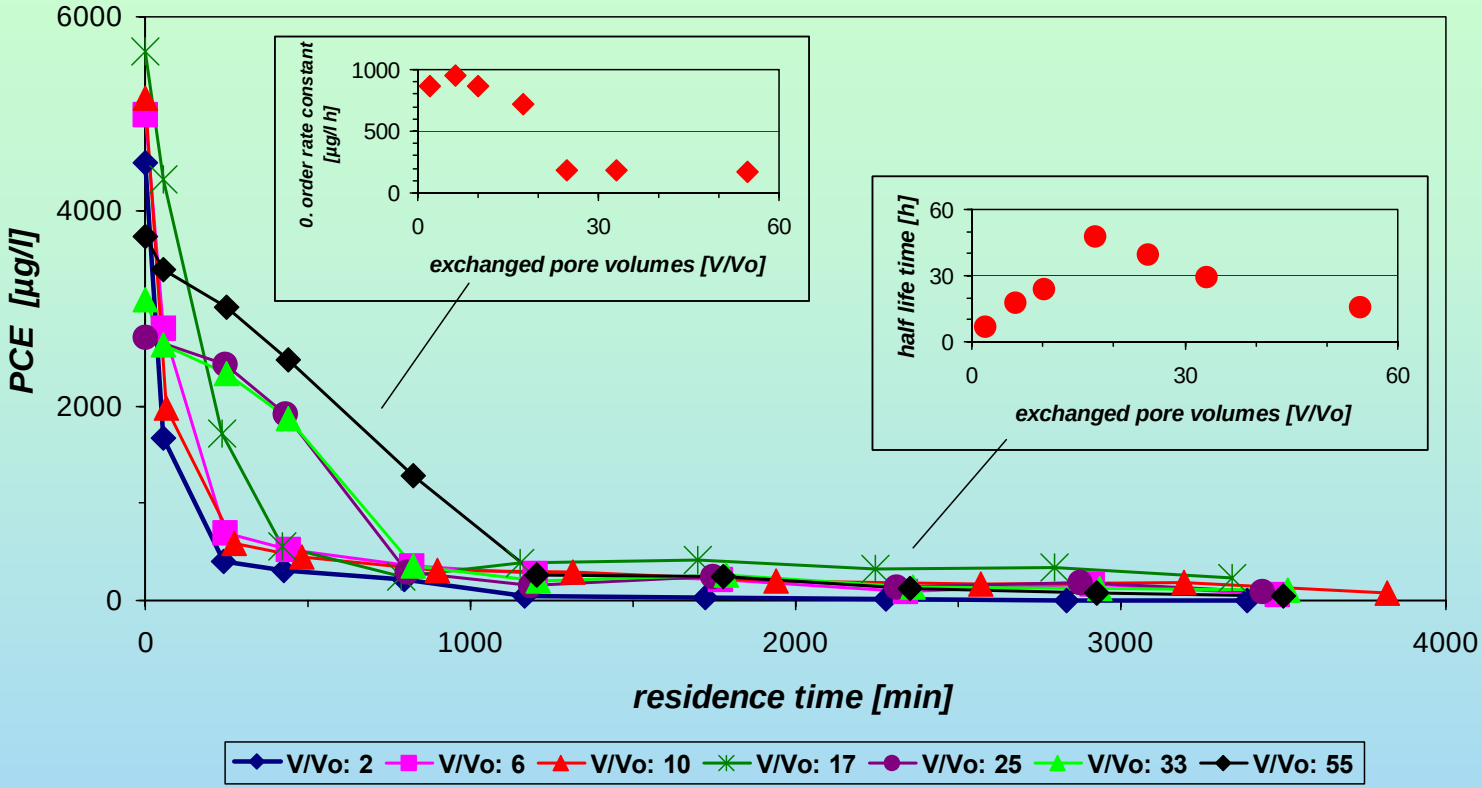
Monitoring: PCE, Iron Sponge Section



- **cleaning efficiency is still >99%**
- **during the first year smaller efficiency**

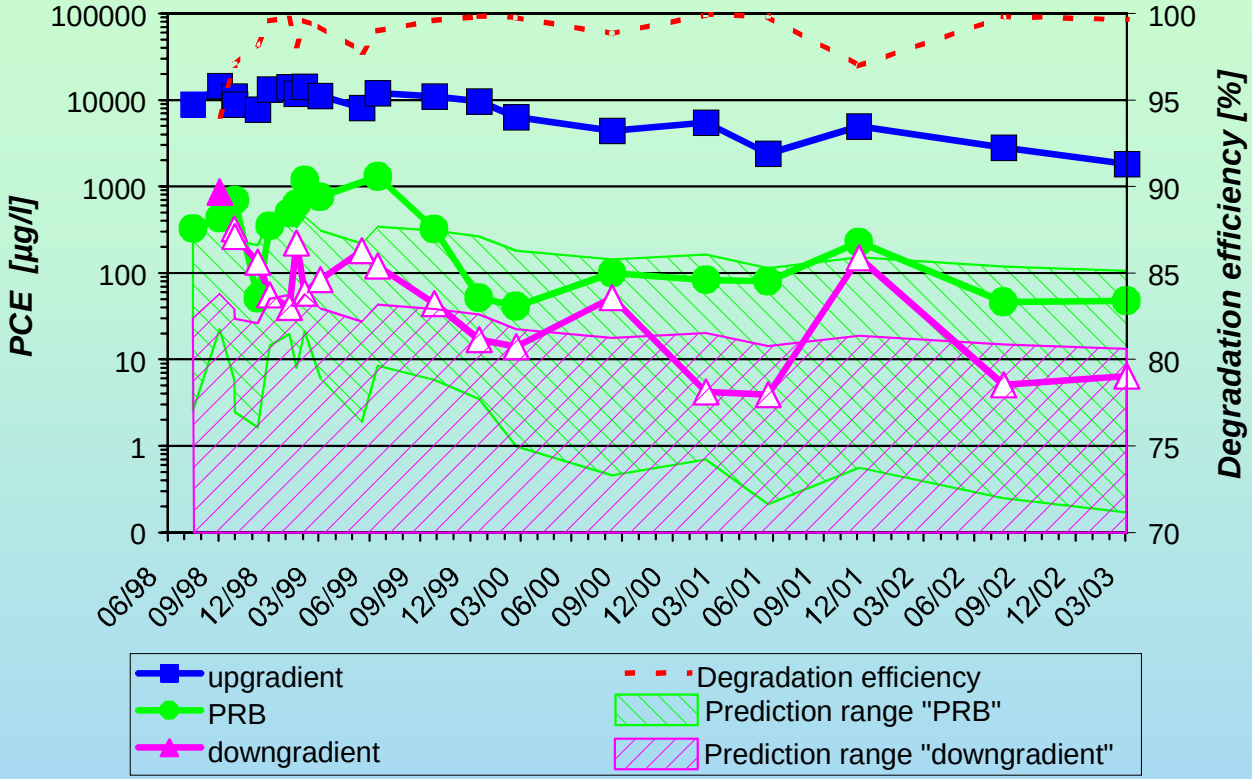
(decreasing up-gradient PCE concentration is due to P&T at the source)

Column Experiment Using Iron Sponge



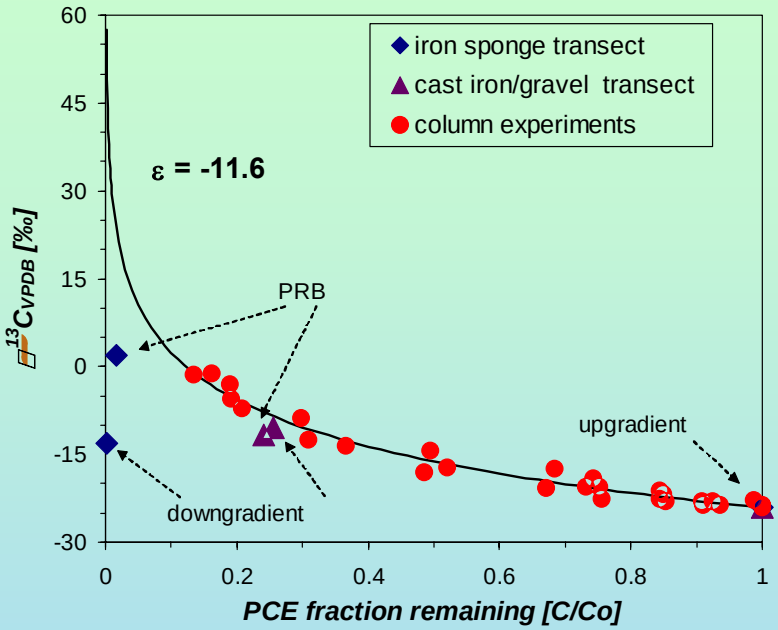
- zero order and first order degradation combined
- steady state conditions were not reached
- simple mixed kinetic equation
- prediction: 10 days residence time => at least 5 years life time

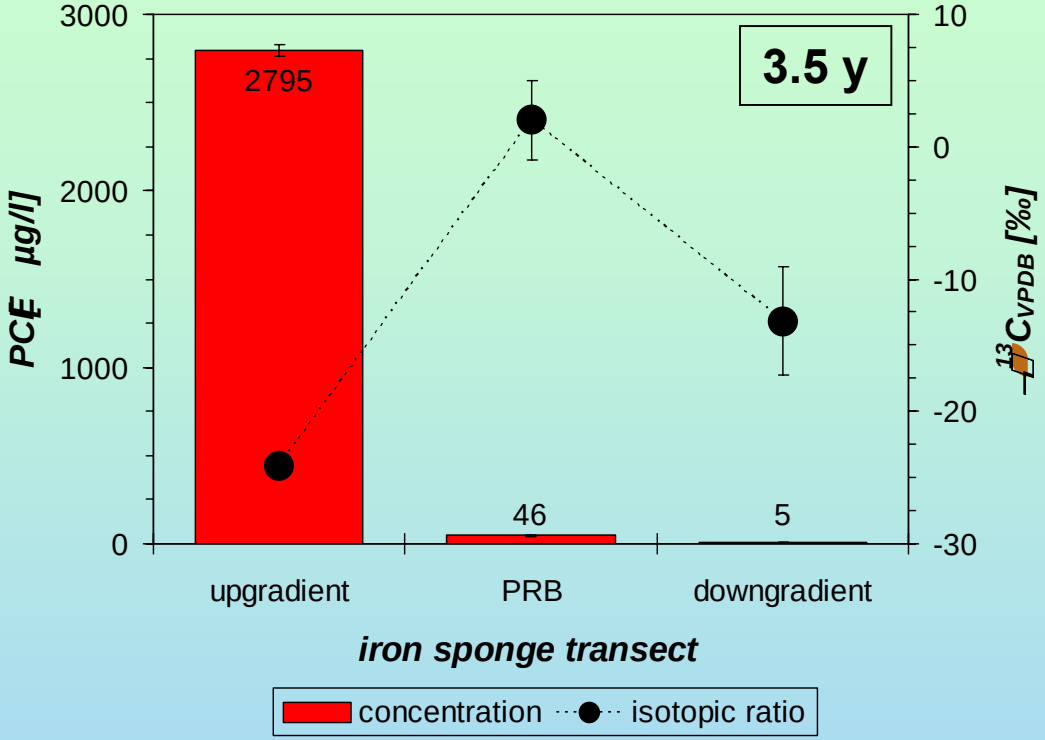
Comparison of Prediction and Field Results



- variation of flow velocity and best/worst kinetic coefficients
  => predicted concentration range
- field results in agreement with prediction (after ~1.5 y)
- after five years of operation a decreasing reactivity is not indicated

Stable Carbon Isotope Fractionation



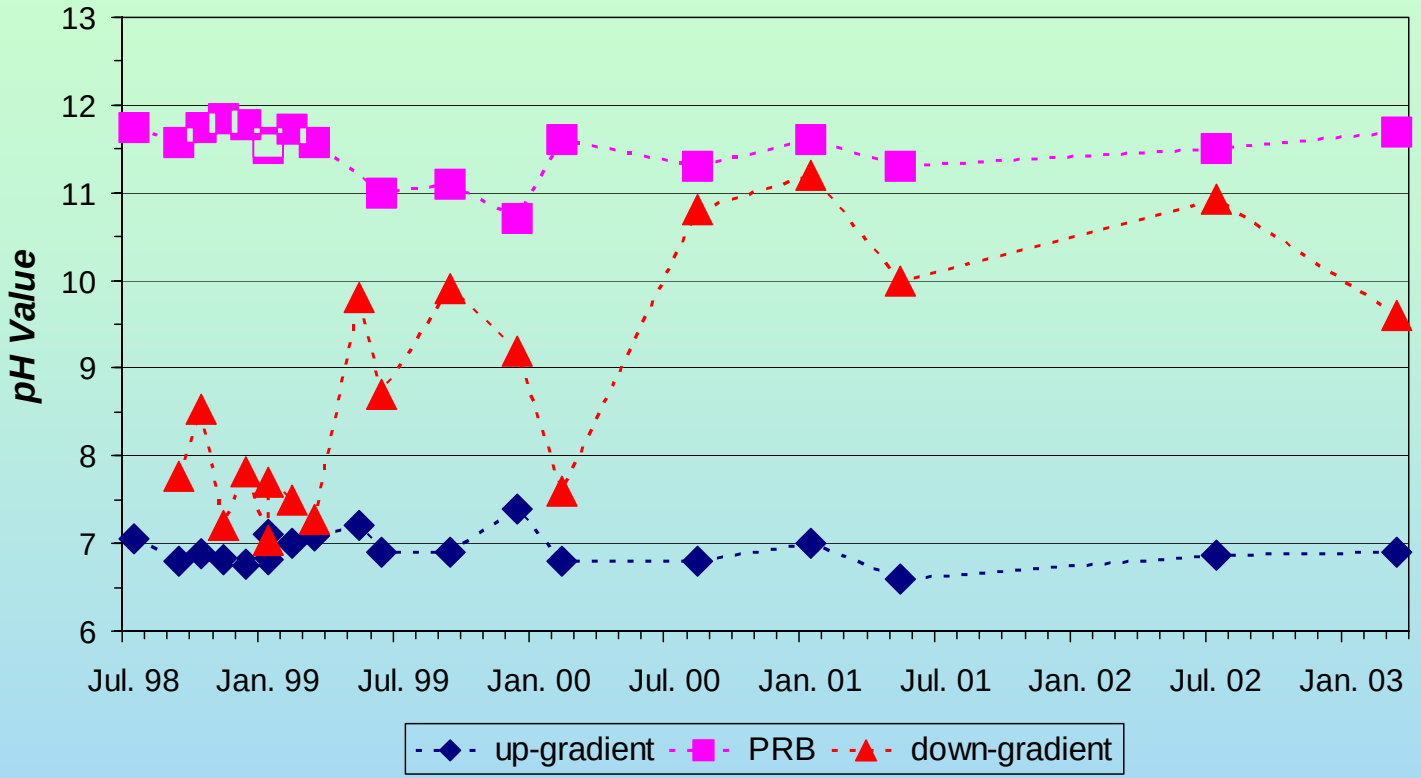


- fractionation factor determined in three column experiments using material excavated from the PRB and site ground-water
- isotopic ratio within and behind the PRB is smaller than expected from concentration measurement
- more significant at the iron sponge transect

Stable Carbon Isotope Fractionation

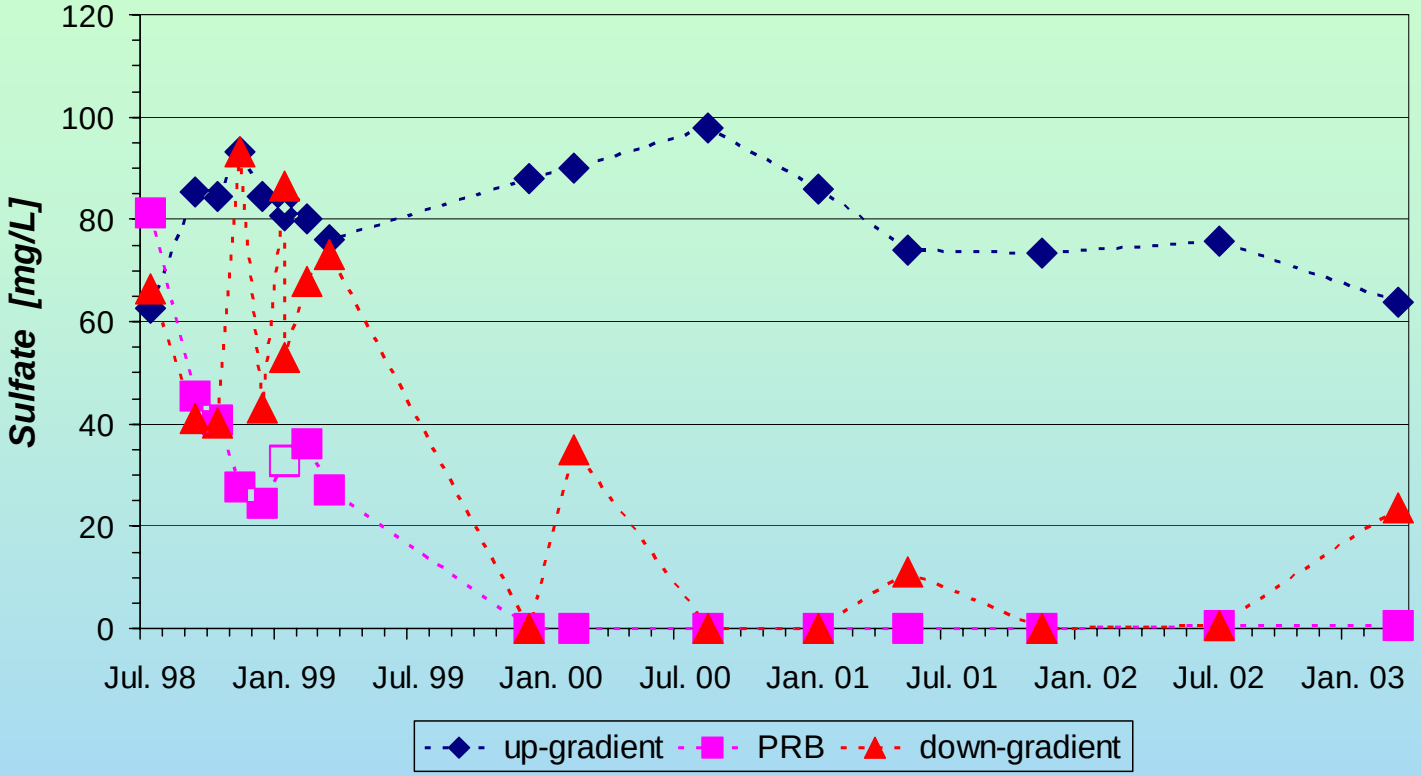
- ***the observations can be explained by:***
  - ***mixing effects within the PRB***
  - ***desorption processes down-gradient of the PRB***
- ***desorption processes effects the contaminant concentration down-gradient of the PRB over years***
- ***under-estimation of the efficiency***

Monitoring: pH, Iron Sponge Section



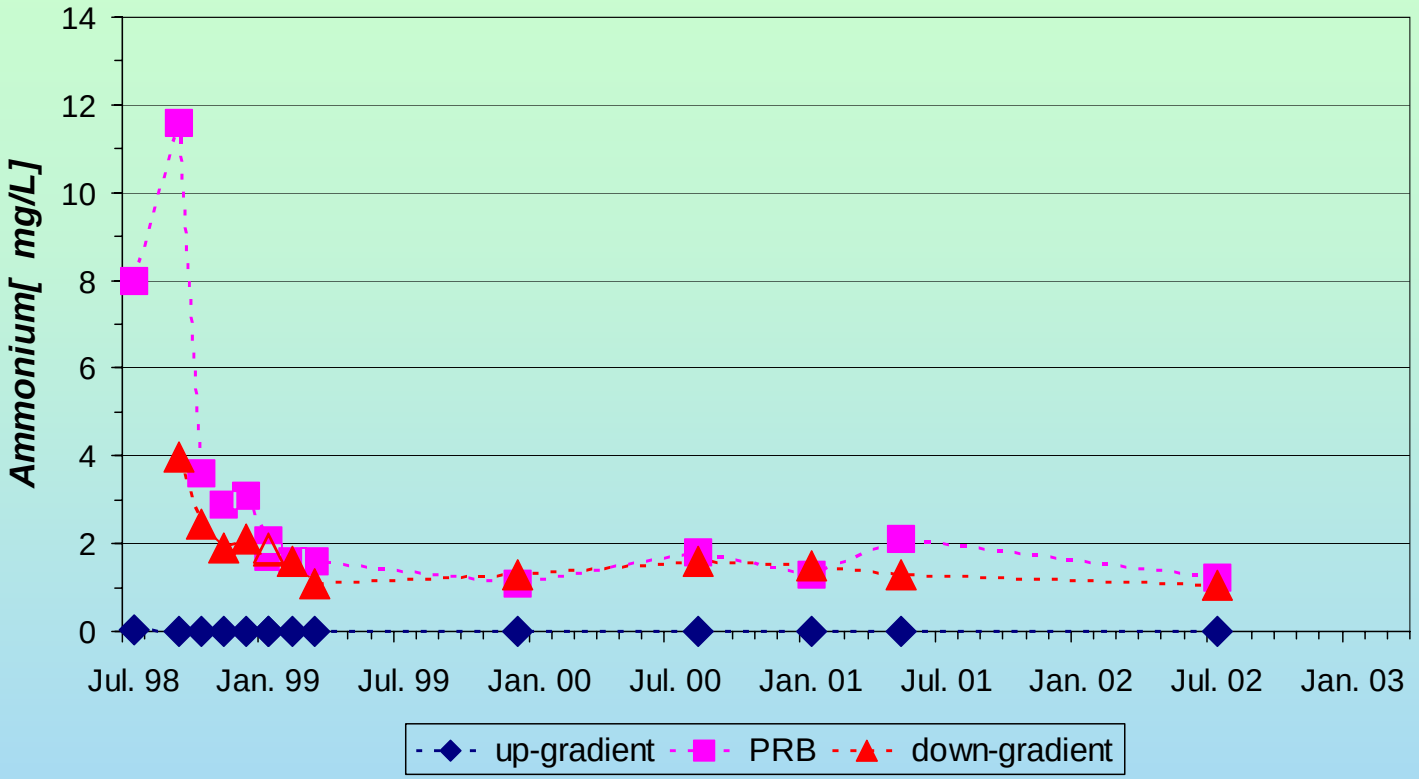
- pH > 11 within the PRB (typical for iron sponge)
  - down-gradient: increasing pH after ~1 year
- pH front movement depends on buffer capacity of the aquifer

Monitoring: Sulfate, Iron Sponge Section



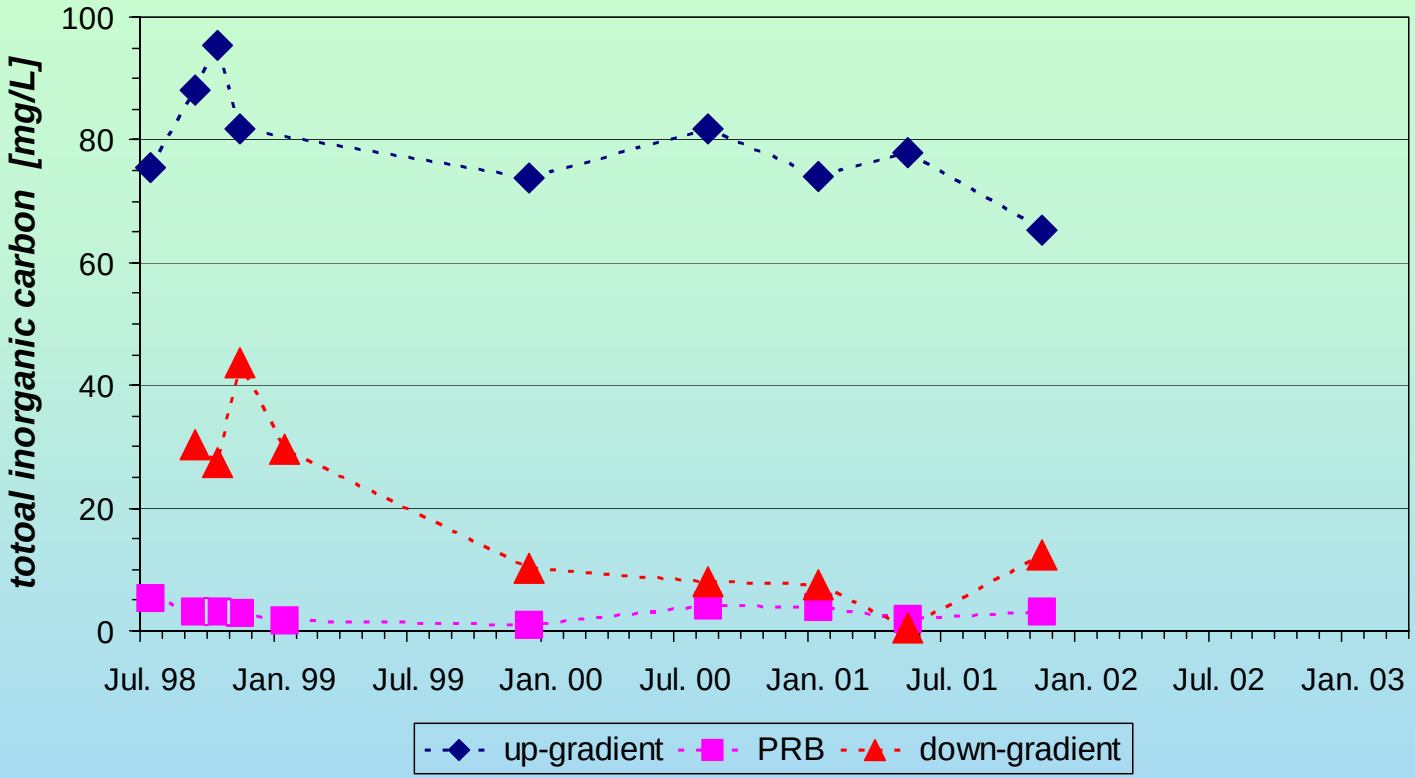
- sulfate concentration decreased during first year of operation
- development of microbial community containing SRB
- hydrogen surplus still exists

Monitoring: NH_4^+ Iron Sponge Section



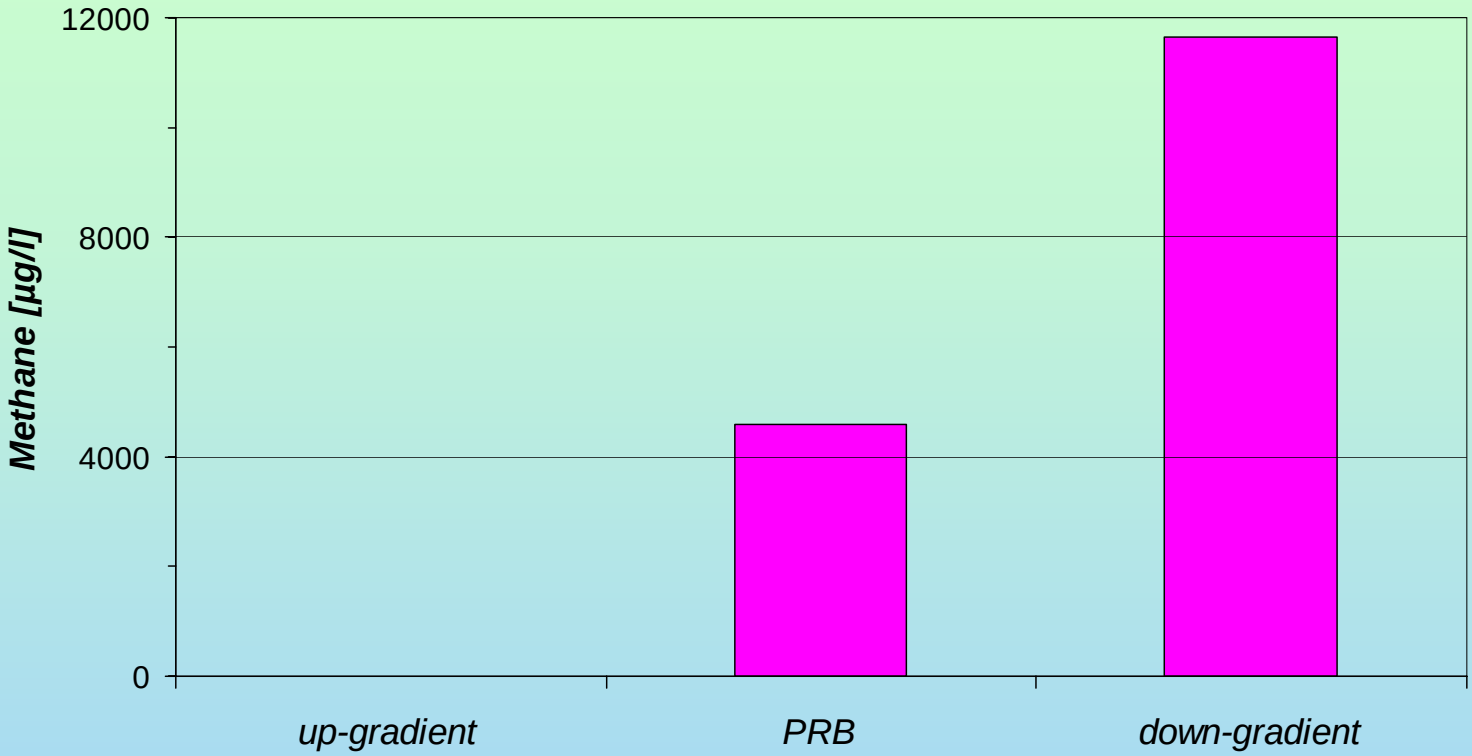
- **30 – 50 mg/l nitrate was lost continuously**
- **ammonium emission (due to abiotic nitrate reduction with Fe^0) decreased during the first ½ y. after installation**
- **dominant nitrate reduction process has changed => effect of microbes**

Monitoring: TIC, Iron Sponge Section



- **continuous loss of ~ 80 mg/l TIC was observed**
- **down-gradient: delayed response**
- **mass of carbonate precipitation is usually calculated from the loss in TIC content**

Monitoring: CH_4 Iron Sponge Section (June 02)



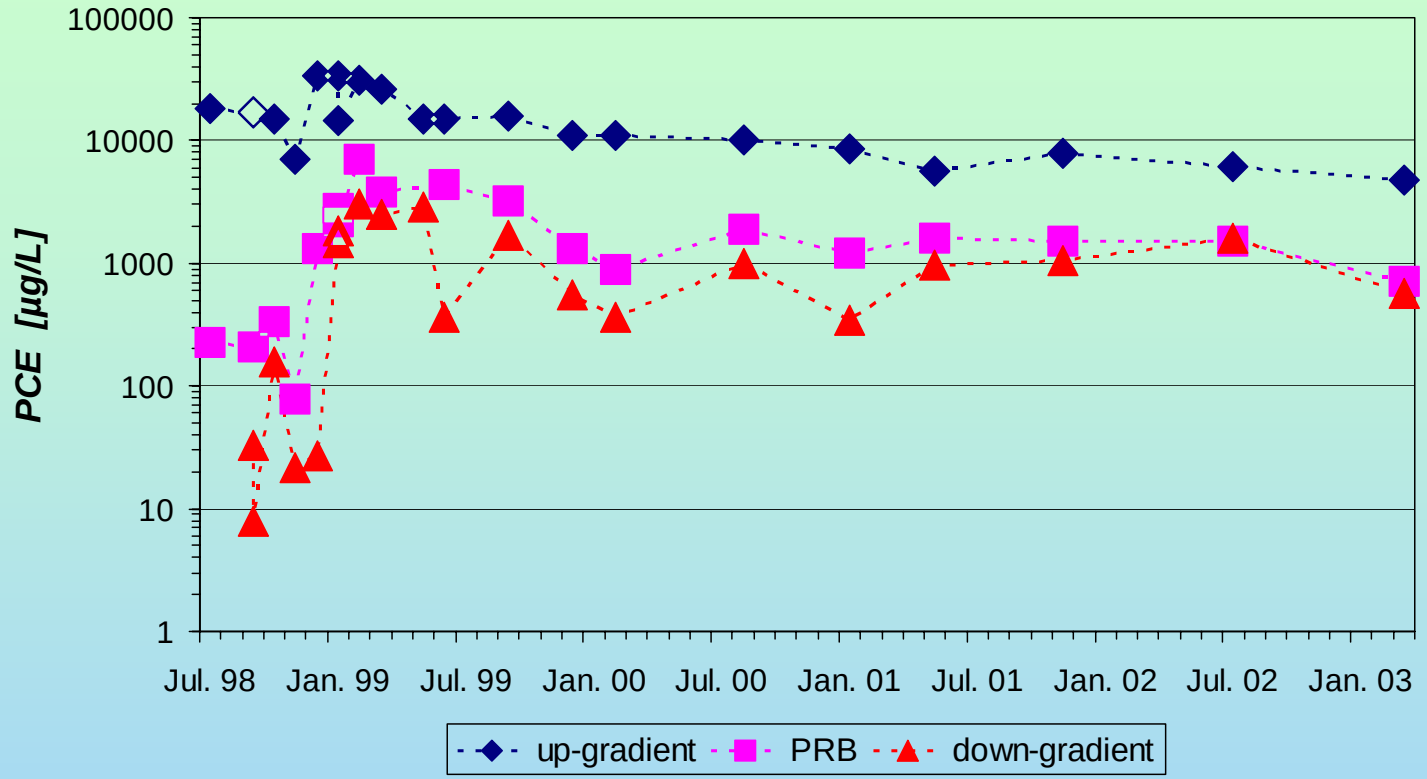
- **methane production not (only) from contaminants**
- **primary carbon source is probably dissolved CO_2**
  (also supported from microbial characterization)
- **longer life time of PRB's due to methane production ?**

Successful PRB Application…

- ***the iron sponge at the Rheine site PRB works high efficiently and also like predicted from a column experiment***
- ***a microbial community was established during the first year of operation***
- ***inorganic ground water constituents were effected by interactions with ZVI, microbes and down-gradient with the aquifer matrix***
- ***effects of methane production not clear***
- ***life time of the PRB is higher than 5 years***

…and the iron/gravel section of the PRB?

Monitoring: PCE, Iron/Gravel-Mixture

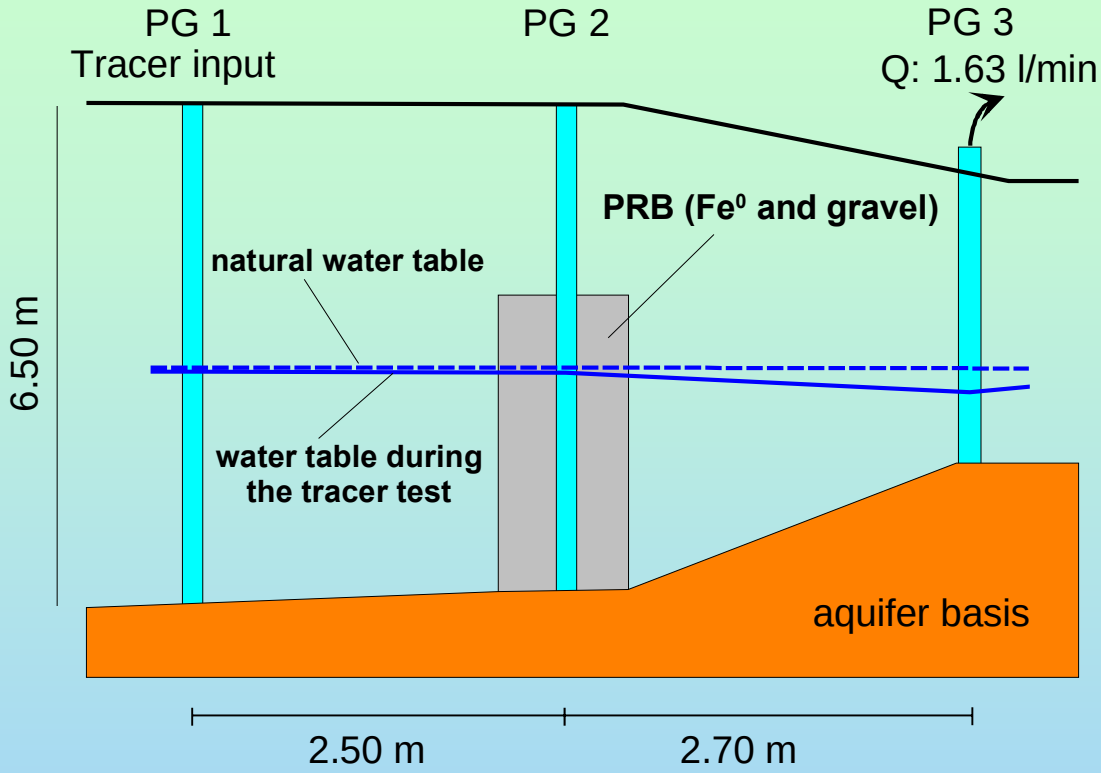


- initially high cleaning efficiency
- increasing concentration down-gradient of the section with iron/gravel mixture just 1 y. after construction
- during the last 4 y. a smaller but ± stable degradation efficiency

…Reasons ?

- *a column experiment was not performed with the mixture (iron/gravel)*
- *hydraulic problem ?*
  - *clogging and subsequent flow by-pass due to loss in permeability*
- *passivation ?*
- *no hints from the standard monitoring*
  - *inorganic constituents comparable to the other section*
- *forced gradient tracer test*
  - *using reactive and conservative tracers*

Forced Gradient Tracer Test



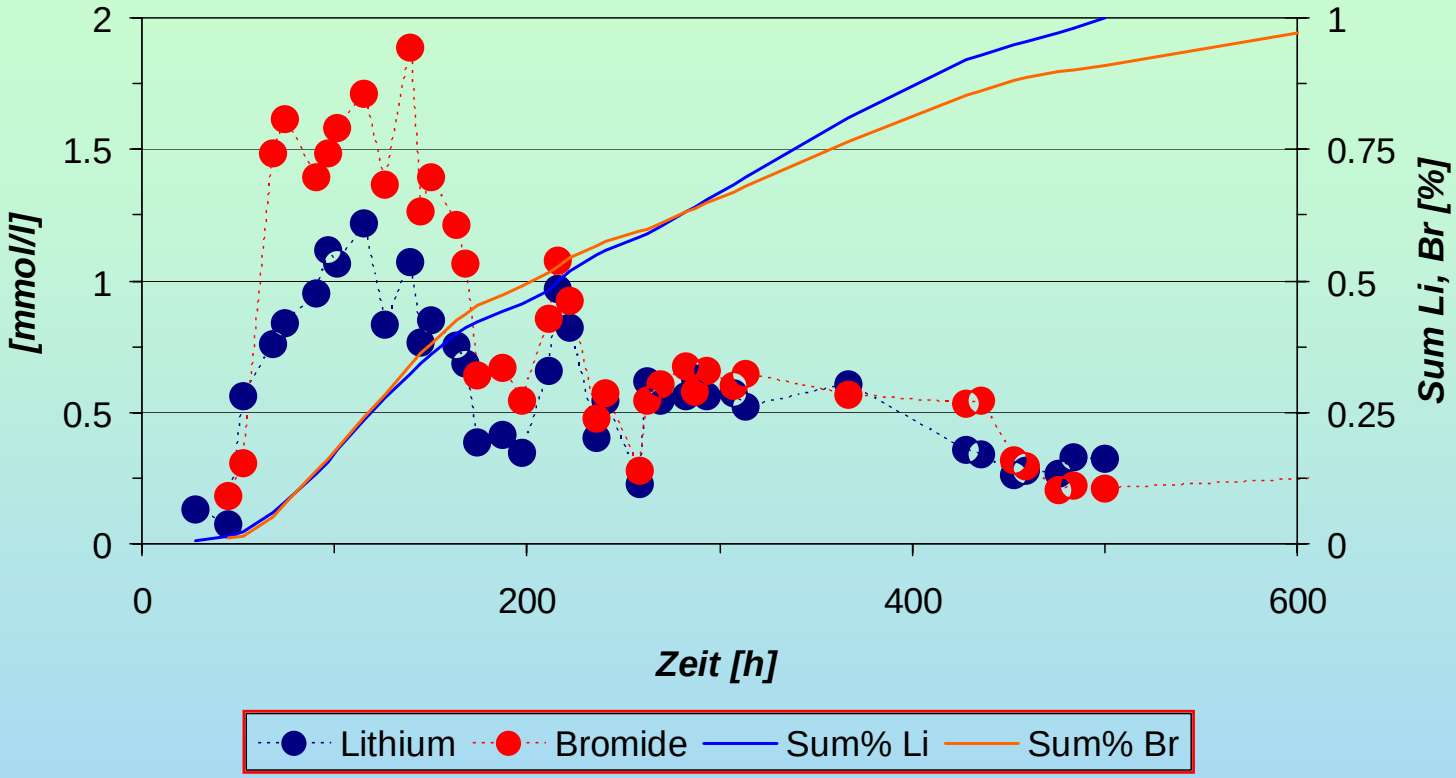
duration: 27 days

tracer input: 280 Liter / 3h / 1 kg LiBr, $NaNO_3$

draw down: PG 3: ~31 cm, PG 2: ~7 cm, PG 1: ~5 cm

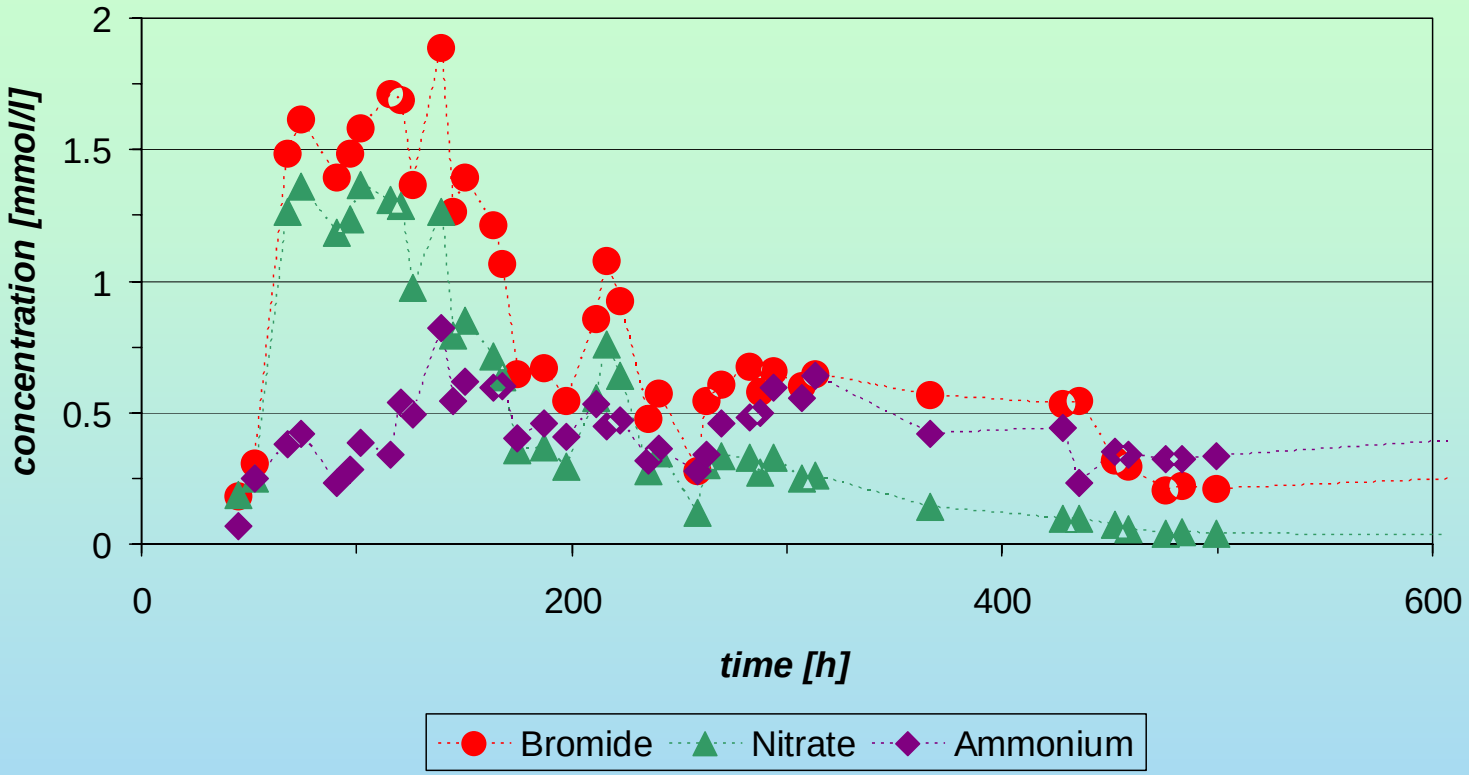
sampling: PG 2 at 3 levels and PG 3

Tracer Breakthrough at PG 2 (PRB), 5 m depth



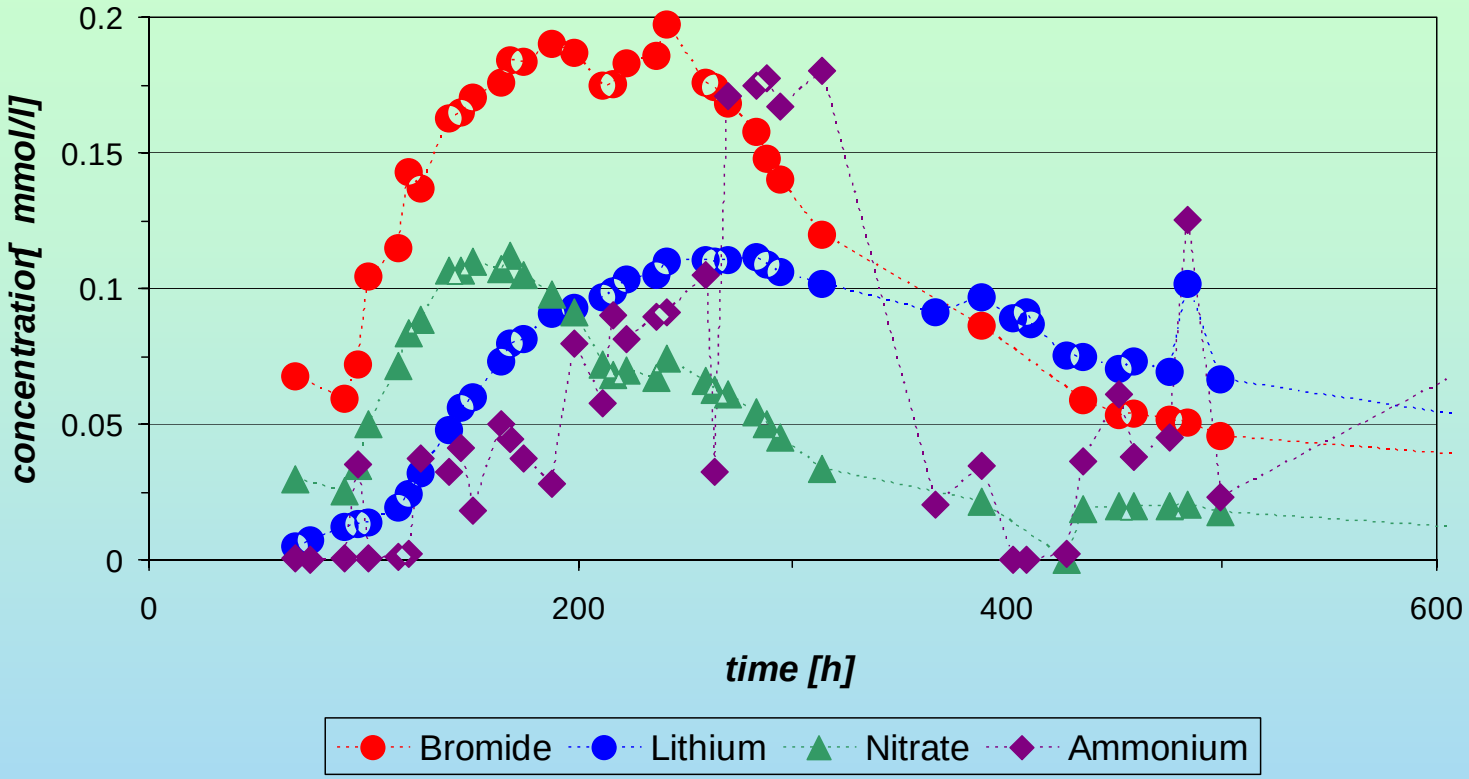
- lithium and bromide breaks through at the same time
- lithium concentration is smaller than bromide concentration
- ~1 day residence time within the reactive fillings

Tracer Breakthrough at PG 2 (PRB), 5 m depth



- **nitrate was not retarded**
- **nitrate transformation to ammonium: 0.4 – 0.8 mmol/l**
- **~25% of nitrate was reduced**

Down-Gradient Breakthrough Curves

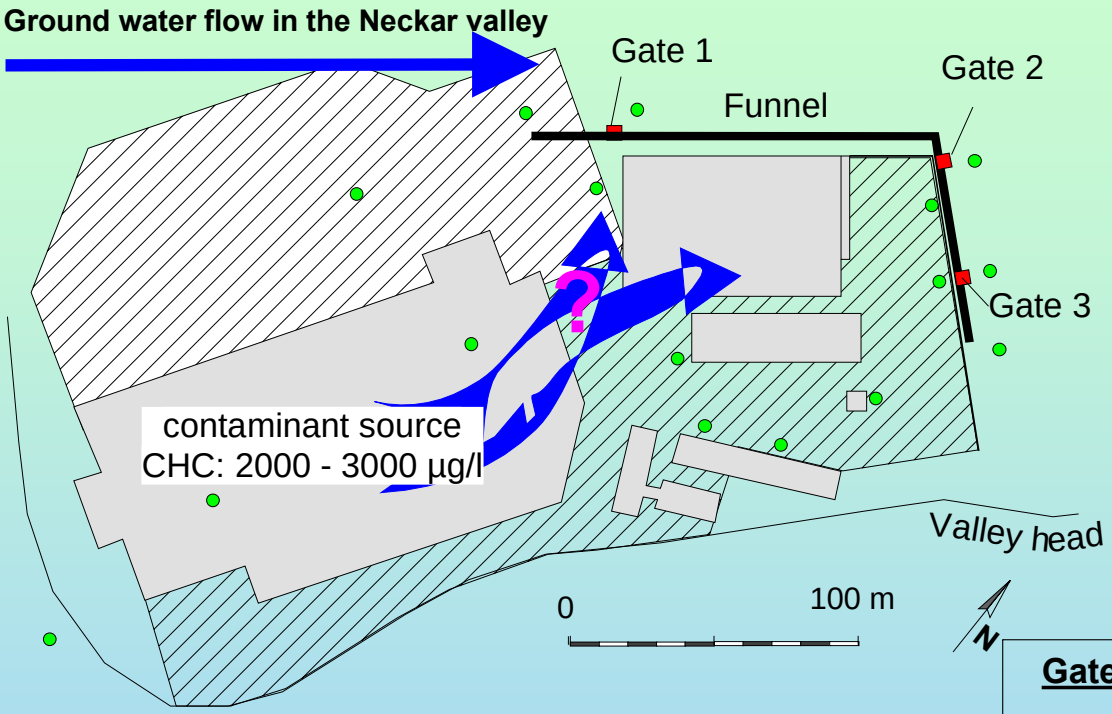


- **down-gradient of the PRB the cations were retarded due to higher pH in the aquifer**
- **~50% of nitrate was reduced**

Results…

- ***forced gradient tracer test results show:***
  - ***permeability of the PRB is still high***
  - ***nitrate reduction is small in comparison to results from column experiments with fresh iron***
  - ***no significant differences in reactivity between the front and the back part of the PRB***
  - ***the observed increasing PCE concentration is due to a loss in reactivity and not due to flow problems***
  - ***a distinction can not be made between a general loss in reactivity or a strong passivation along single flow paths***
  - ***an inhomogeneous mixture of cast iron and gravel caused by construction factors probably combined with heterogeneities in contaminant load is the favorite reason for decreasing remediation efficiency***

Tübingen Site F&G PRB



construction in autumn 1998

aquifer thickness: 6 - 7 m

aquifer bottom: ~10 m bs.

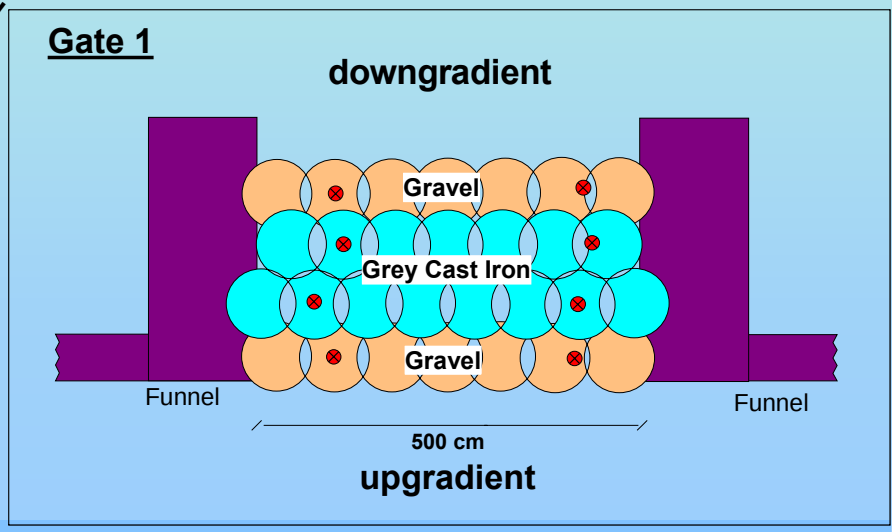
aquifer permeability: 10^{-2} – 10^{-5} m/s

main contaminant at Gate 1: cis-DCE (up to 130 µg/l)

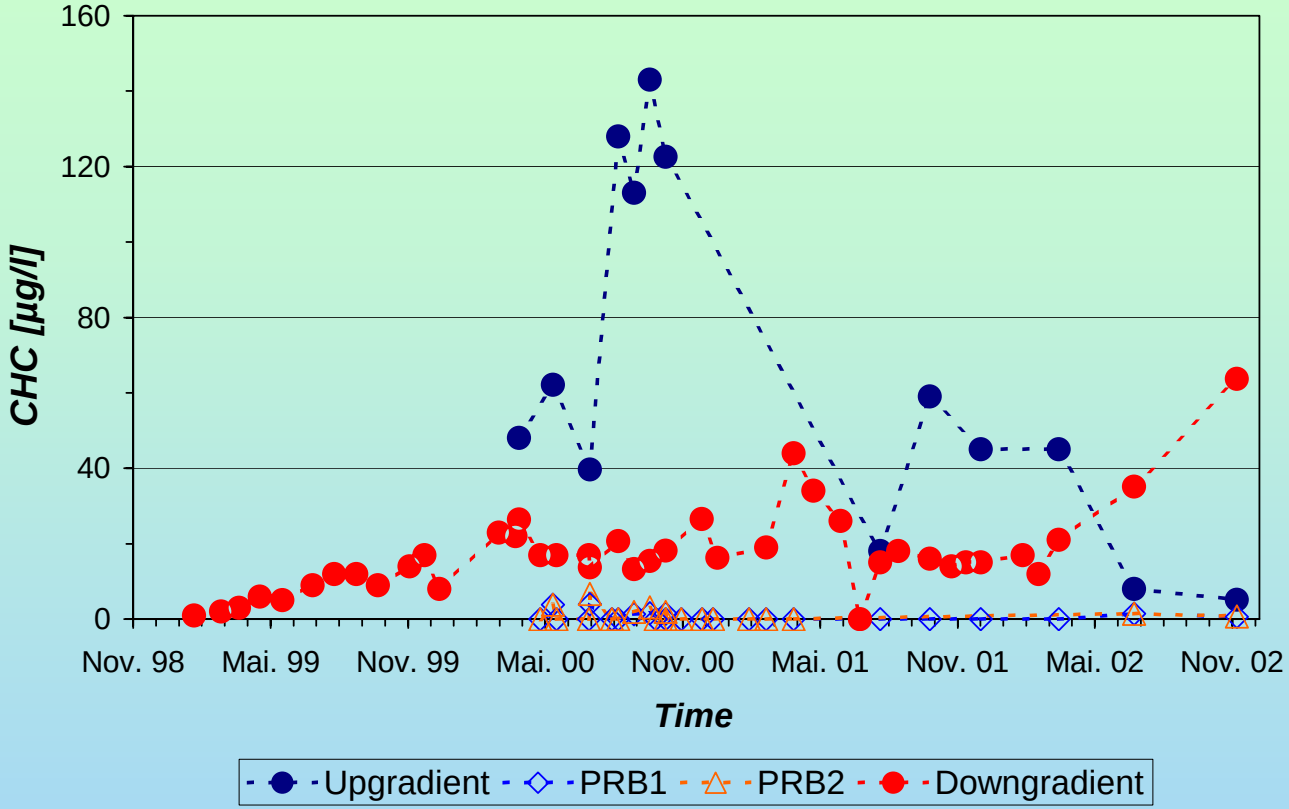
funnel (slurry wall) length: 200 m

3 gates with a flow through thickness of 1.9 to 1.85 m

2 monitoring transects per gate

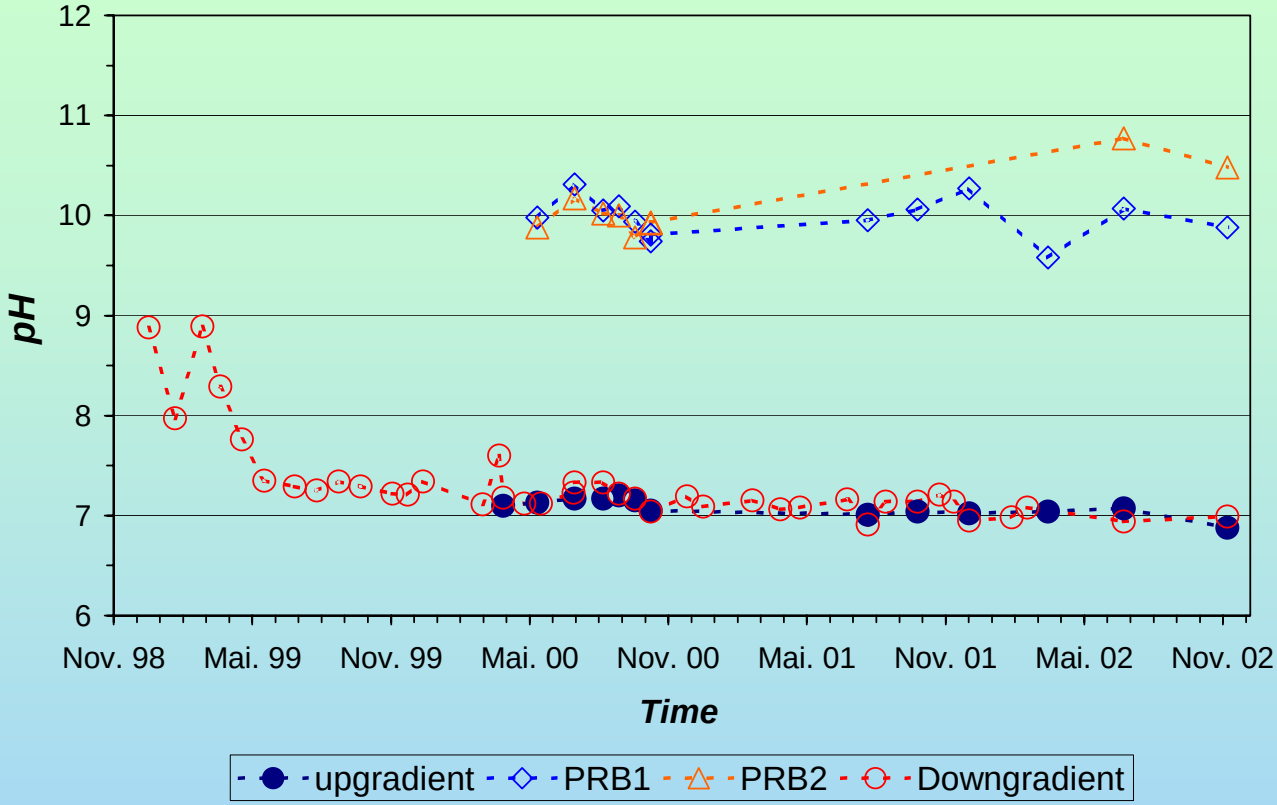


Monitoring: CHC, Gate 1, Left Transect



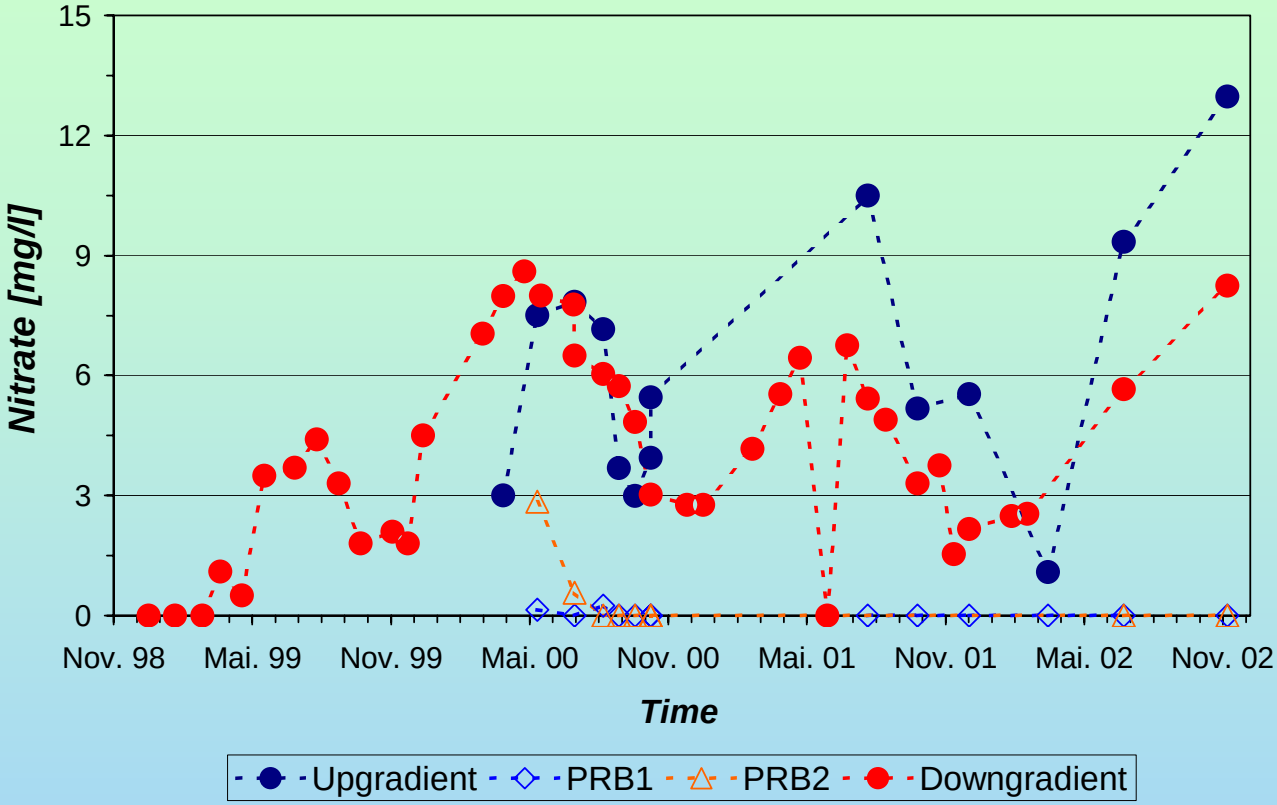
- **increasing CHC concentrations were observed at the down-gradient monitoring well during the first year after construction**
  - **actually: $CHC_{down\text{-}gradient} > CHC_{up\text{-}gradient}$**
- **contaminants within the iron fillings are still below detection limit**

Monitoring: pH, Gate 1, Left Transect



- **a decrease in pH was observed at the down-gradient monitoring well half a year after construction**
  - **actually: $pH_{down\text{-}gradient} = pH_{up\text{-}gradient}$**
  - **the pH within the iron fillings is still high**

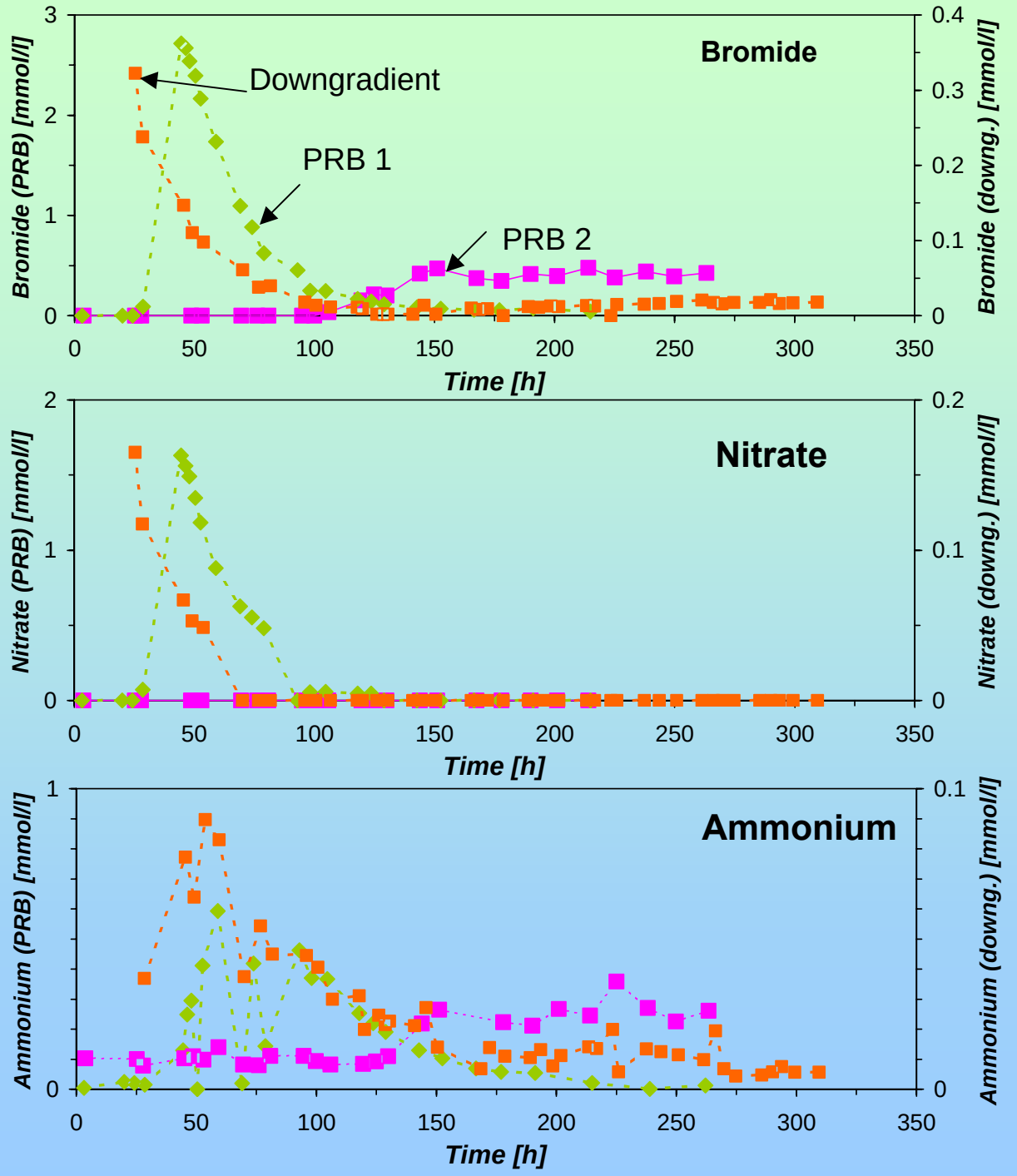
Monitoring: NO_3^-, Gate 1, Left Transect



- an increase in nitrate concentration was observed at the down-gradient monitoring well half a year after construction
  - actually: $\text{nitrate}_{\text{down-gradient}} \approx \text{nitrate}_{\text{up-gradient}}$
  - nitrate within the iron fillings is still below detection limit

Forced Gradient Tracer Test at Gate 1

- the tracers break through down-gradient of the gate earlier than within the gate
- only the decreasing part of the break-through curves was detected due to unexpected high flow velocity
- nitrate was abiotically reduced within the iron filled section



Forced Gradient Tracer Test Results

- ***the results show:***
  - ***a preferential flow path with higher flow velocities and/or minor iron content exits***
  - ***the iron filled section was percolated with lower flow velocity***
  - ***the mass flux at the flow paths can not be estimated due to incomplete breakthrough curves***
  - ***the abiotic nitrate reduction indicates that the iron is still reactive***

- ***a flow path along a section with high permeability and only small iron content probably explains the monitoring results (construction problems)***

Conclusions

- *comparison of prediction and field results show the usability of column experiments*
- *at the Rheine site one section of the PRB (iron sponge) works high efficiently and within the range expected*
- *the section with mixture of iron and gravel works stable but lower efficient probably caused by construction/design "failures"*
- *at the Tübingen site also construction/design "failures" are probably responsible for the small efficiency*
- *in case of performance limitations were observed problems will be indicated in a short time span after construction*
- *forced gradient tracer tests lead to problem identification*
- *use design/applications/construction simple as possible*

Thanks to…

BMBF
R.U.B.I.N.
Mull & Partner GmbH
I.M.E.S GmbH
Wessling GmbH
Hornbach Baumarkt AG
Administration of the City Rheine
Administration of the District Steinfurth
Administration of the City Tübingen
Martin Steioff and Staff (Tech. Uni Berlin)
Alfred Steinbach (Uni Hamburg)
Georg Teutsch and Staff (Uni Tübingen)
Laboratory Staff and many Students