
*In situ* activated carbon-based technology for groundwater remediation:
Overview, best practices, and case studies

# AC-Fe composites: Combination of sorption and chemical degradation

**EPA Webinar, June 25, 2018**

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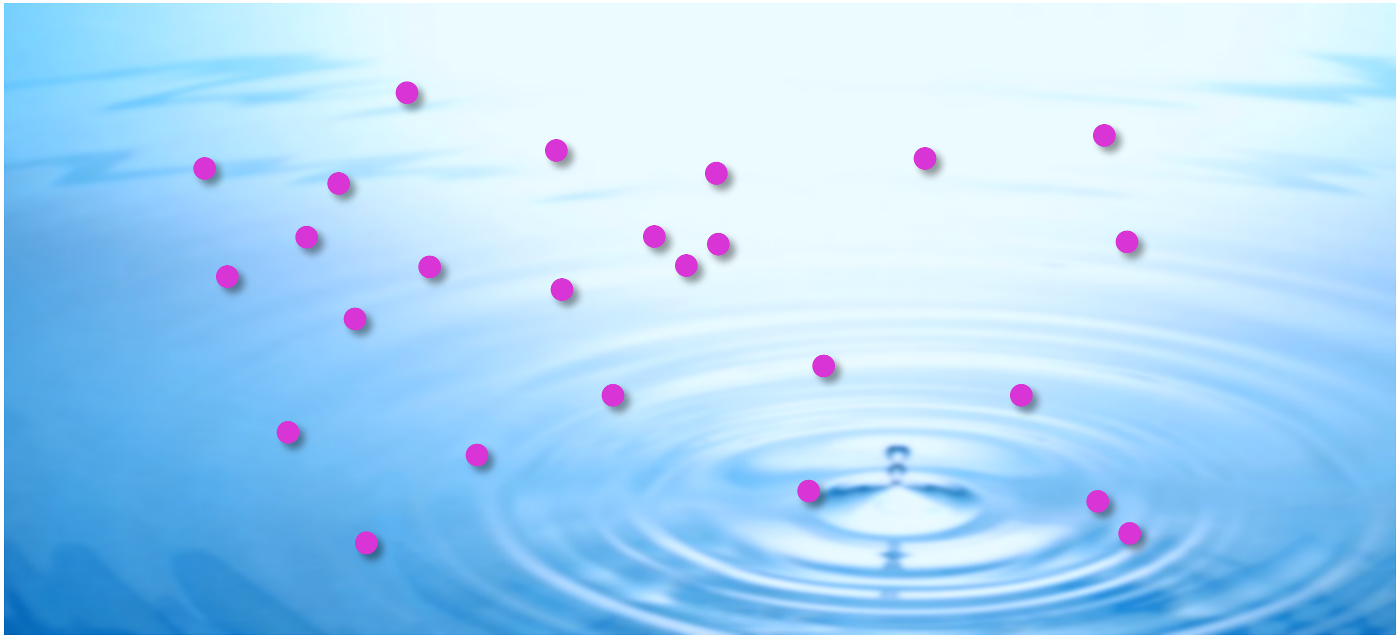
# Outline

- When is it useful to combine sorption and reaction?
- How can I decide?
- How did we design particles?
- How did we prepare the pilot tests?
- Pilot test
- Biological component
- Address plume or source?
- Ecotox tests

# Approach for chemical treatment of “diluted” solutions



coupling of sorption and reaction

**in adsorber pores**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# Coupling of sorption and reaction

## perspective #1 regeneration of the sorbent

- ✓ Reaction prolongs retardation within treatment zone due to *in-situ* regeneration
- ✓ **BUT:** Reaction influences effluent composition, sorption efficiency may vary for transformation products.

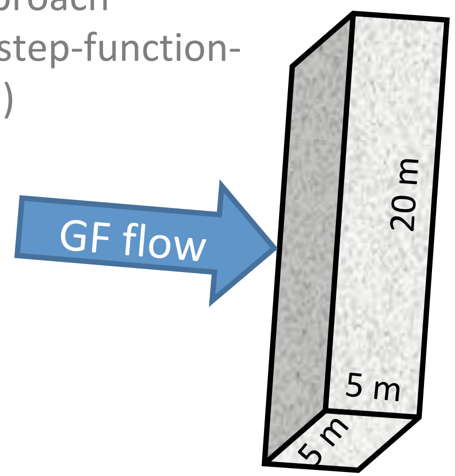
## perspective #2 support of the reaction

- ✓ Sorption increases contact time with reagent
- ✓ Reaction is better to control
- ✓ Reaction is more efficient than in diluted water bulk phase
- ✓ Less reagent is necessary – less side consumers
- ✓ Sorptive binding may have influence on selectivities

# Decision-making: Sorption alone or Sorption+Reaction?

$$R_i = \frac{u}{u_i} = 1 + \frac{\rho}{\varepsilon} f_{adsorbent} K_{d,i}$$

Simplified approach (constant $K_d$, step-function-breakthrough)




| | |
|---|---|
| $R_i$ | retardation coefficient of pollutant i |
| u | linear velocity of groundwater (0.5 m/d) |
| $u_i$ | linear velocity of pollutant i |
| ρ | bulk density of aquifer sediment (2.5 x 0.7 kg/L = 1.75 kg/L) |
| ε | porosity of sediment (0.3) |
| f | mass fraction of adsorbent on sediment (0.1….1 wt%) |
| $K_{d,i}$ | sorption coefficient of i (1000….100,000 L/kg) |

$$t_{breakthrough,i} = \frac{l_{barrier}}{u} \cdot R \approx l_{barrier} f_{adsorbent} \cdot \frac{\rho}{\varepsilon \cdot u} \cdot K_{d,i}$$

barrier aquifer adsorption

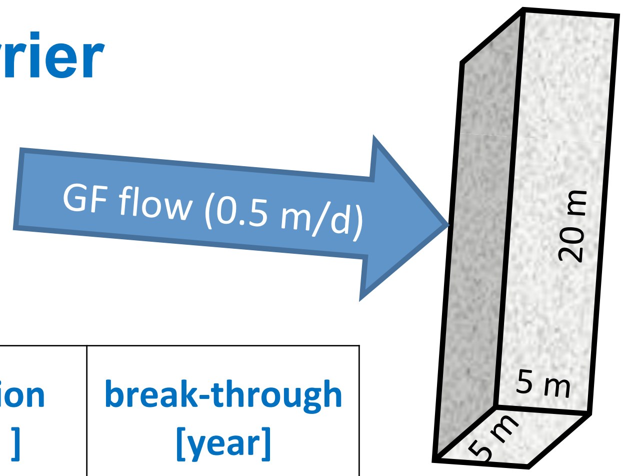
With $l_{barrier} f_{adsorbent} = \frac{m_{adsorbent}}{A_{barrier} \cdot \rho}$ results:

$$t_{breakthrough,i} = \frac{m_{adsorbent}}{A_{barrier}} \cdot \frac{1}{\varepsilon \cdot u} \cdot K_{d,i}$$

Adsorbent mass injected per cross-sectional area of barrier zone or product of $l_{barrier} \times f_{adsorbent}$ determines lifetime of the sorption barrier

# Prediction of lifetime of a sorption barrier

0.1 wt% adsorbent on sediment
= 875 kg/barrier segment
= 8.75 $kg/m^2$ cross-sectional area




| | wt% adsorbent on sediment | pollutant $K_d$ [l/kg] | retardation factor [ ] | break-through [year] |
|---|---|---|---|---|
| **1 mg/L PCE at AC** | 0.1 | 65,000 | 380 | 10 |
| **10 mg/L PCE at AC** | 0.1 | 20,000 | 118 | 3 |
| **100 mg/L PCE at AC** | 0.1 | 3,000 | 19 | 0.5 |

Effect of sorption barrier strongly depends on

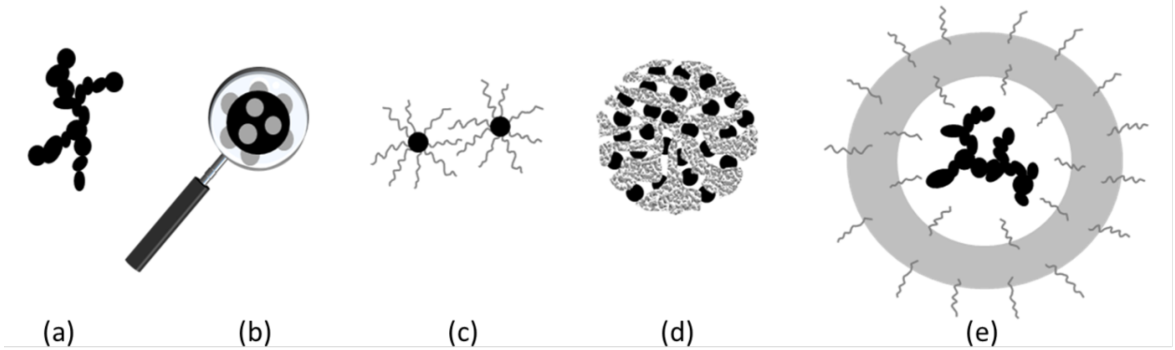
- sorption coefficient
- pollutant concentration (non-linear isotherms!!)
- adsorber mass per cross-sectional area
- GW velocity

**Decision based on site conditions** → **Sorption alone** or → **Degradation in adsorbed state**

# *In-situ* abiotic reactive particles

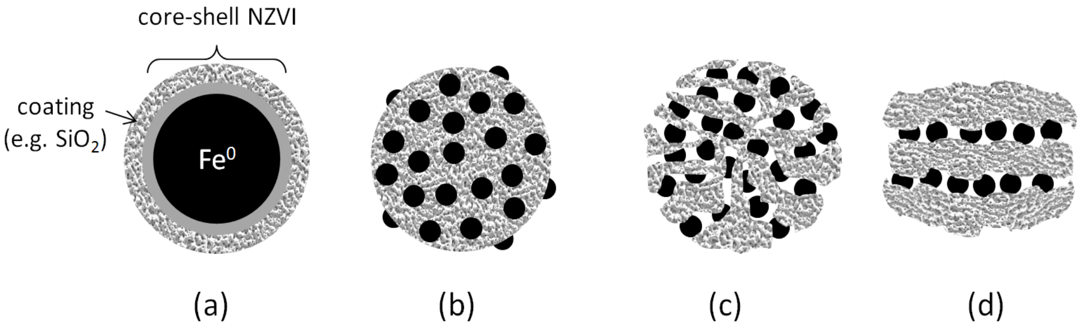
## Reduction means in most cases Fe(0)

**NZVI** in various variations (shells, formulations…)




NZVI types: (a = Bare NZVI, b = Bimetallics, c = Polymer-modified NZVI, d = Supported ZVI, e = Emulsified NZVI

$Fe^0$-containing **composites**




NZVI-support combinations (a = Coated NZVI, b = Nanoiron clusters attached to the outer support surface, c = Nanoiron clusters within porous supports, d = Intercalated nanoiron clusters)

# *In-situ* abiotic reactive particles


## Own developments:

### Reduction

- Carbo –Iron®
  = colloidal AC with up to 30 wt% Fe(0)
- Corrosion-suppressed Carbo-Iron®


### Oxidation

- Trap-Ox®
  = colloidal sorption-active
  Fenton catalysts
- In preparation:
  colloidal sorption-active
  persulfate activator

→ field experience

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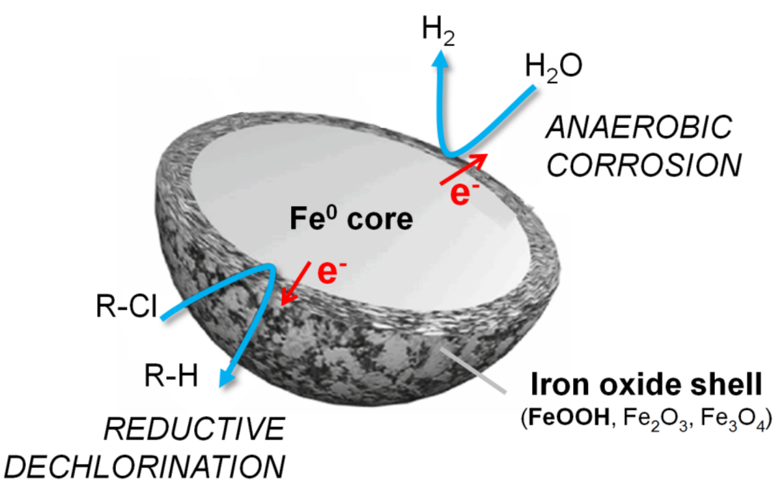
# What do we know about nano-iron?


Photo: EOS Remediation, LLC

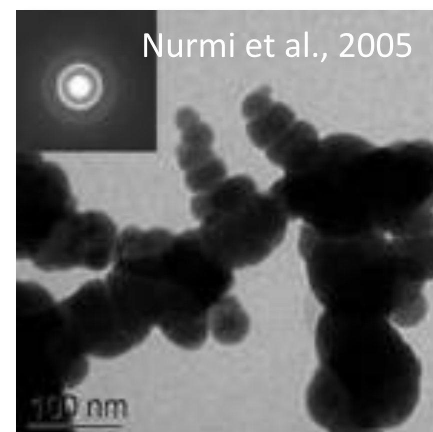
**Potential:**
- → forms injectable suspensions
- → high reactivity towards halogenated hydrocarbons

**Limitations:**
- → strong agglomeration tendency
- → low subsurface mobility
- → does not “like” organic phases
- → not easy to handle (pyrophoric as dry powder)

$$C_2HCl_3 + Fe^0 \longrightarrow C_2H_4 + C_2H_6 + Cl^- + Fe^{2+}$$

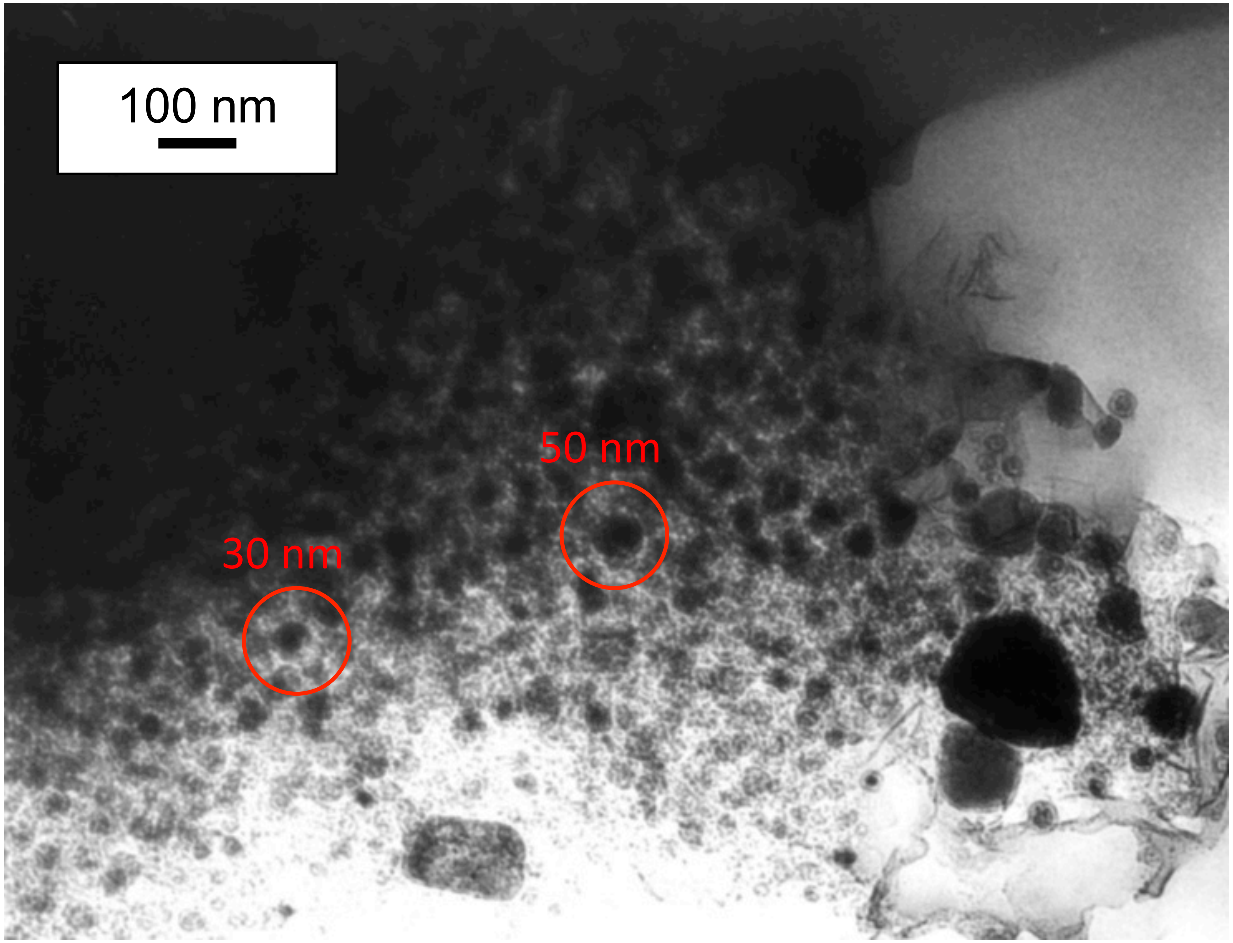



based on Fulekar 2010




*Nano-iron*

# Carbo-Iron®




TEM tight contact of both components in Carbo-Iron (20 wt-% $Fe^0$)

- iron nano clusters in AC framework

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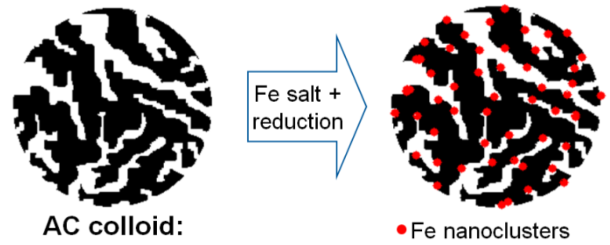
# “Mixing” of the Fe and AC properties




**AC colloid:**
$D_{50}$ = 0.8 µm
$S_{AC,\ BET}$ = 1200 m²/g

up to 30 wt% Fe(0)

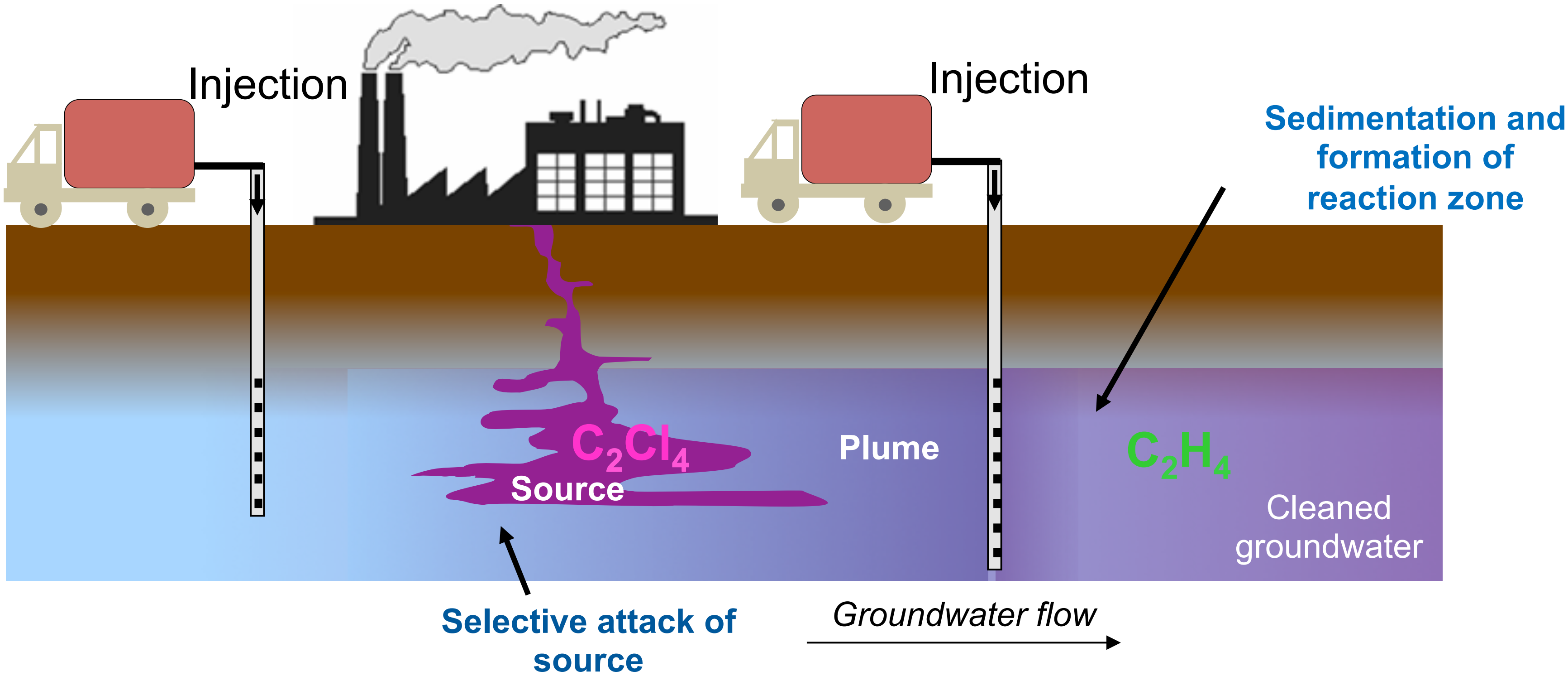
**Nano-iron**

- less agglomeration (shielding of iron)
- higher suspension stability
- higher subsurface mobility
- sorption-assisted reaction
- high affinity to residual phases

**Carbo-Iron**

# Reagent perspective: Particles as *in-situ* reagent

Carbo-Iron® particles as AC-based nano-iron alternative

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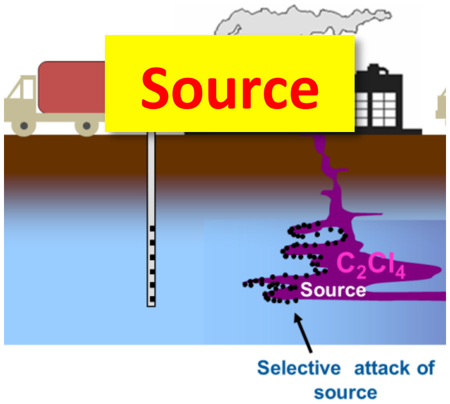
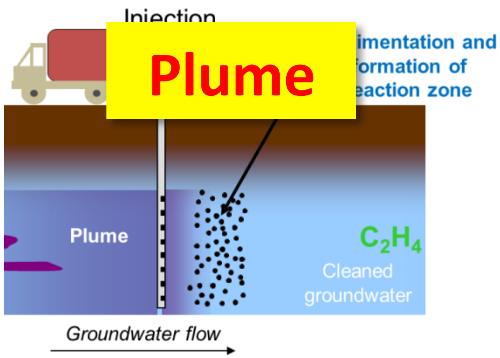
# Carbo-Iron as *In-situ*-Reagent – Requirements




- selective source attack
- particle placement close to source zone
- addition of "enough" reagent
- "affinity" of particles and source
- particles entering the phase?




- high mobility
- immobilization of particles?
- generation of broad zone (high retention, efficient degradation)
- no blockage

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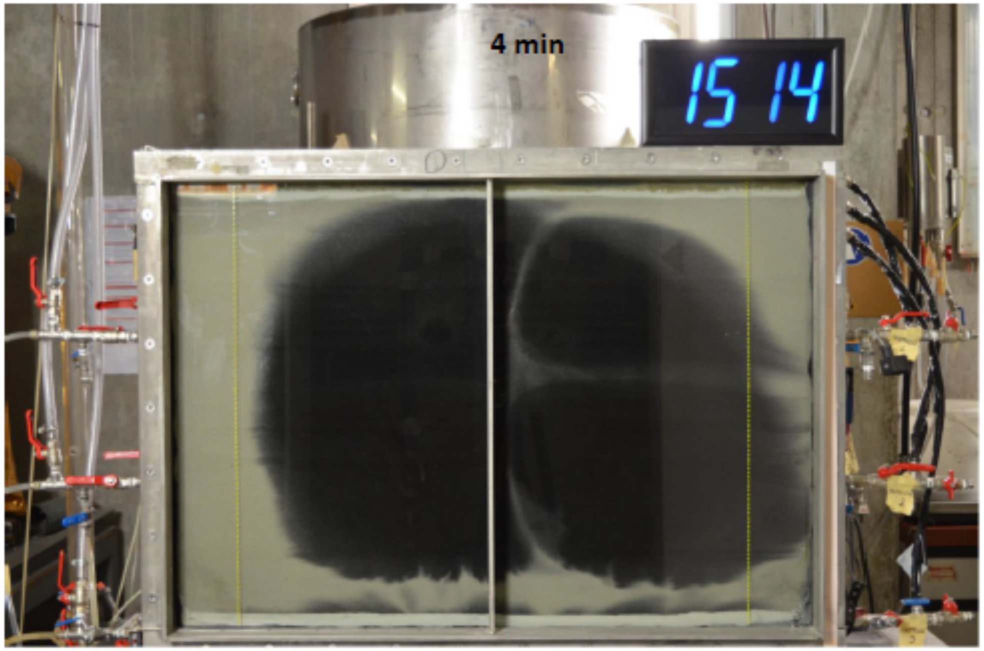
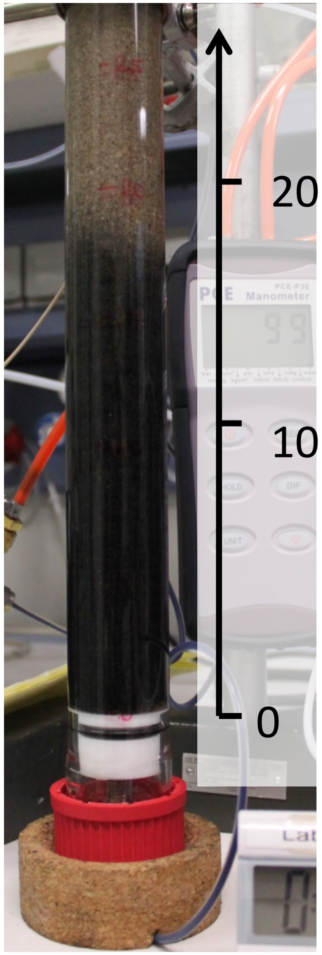
# 1D- and 2D-transport tests (Uni Stuttgart and UFZ)

**2-D Small Channel (Uni Stuttgart)**




**Column (UFZ)**




Suspension stability and particle placement are in principle controllable

NanoRem

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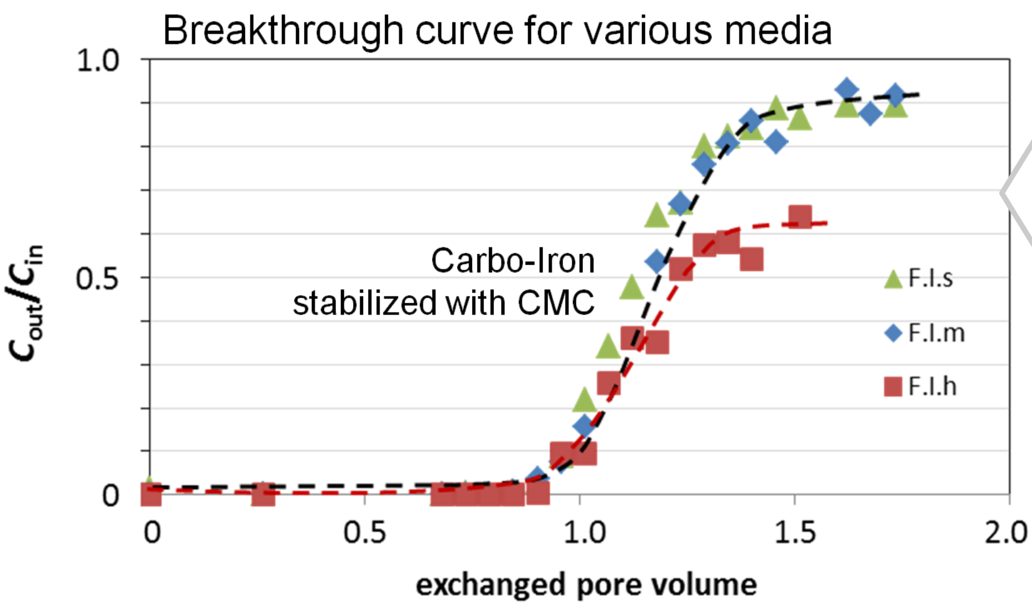
# Lab: Transport of Carbo-Iron for Plume treatment

## Carboxymethyl cellulose (CMC) as adaptable stabilizer

→ Injectable stable suspensions
→ High transport length achievable
→ Particle placement by stabilizer adjustment

Column studies (l = 1 m, middle sand, EPA artificial ground water medium hard (F.I.m), $v_{injection}$ = 10 m/d, $m_{Fe(0)}$ = 1 g/L, $c_{CMC}$ = 1 g/L)




Column studies (l = 25 cm, middle sand as porous medium with $d_{50}$ = 0.51 mm, EPA artificial ground water soft (F.I.s), medium hard (F.I.m) and hard water (F.I h), $v_{injection}$ = 10 m/d, $m_{Carbo\text{-}Iron}$ = 6 g/L, $c_{CMC}$ = 1.1 g/L)

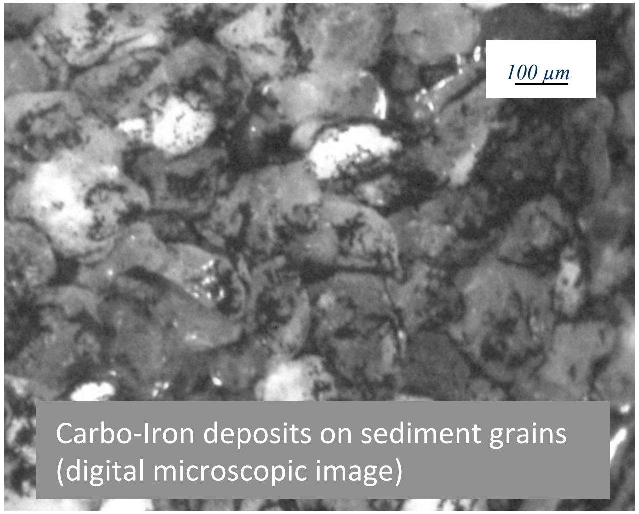
**2 aPV**

- Transport distance calculatable from breakthrough curves ($L_{T,50}$, $L_{T,67}$, $L_{T,99}$)
- CMC concentration decisive for transport distance

# Transport of Carbo-Iron in water-saturated sediments

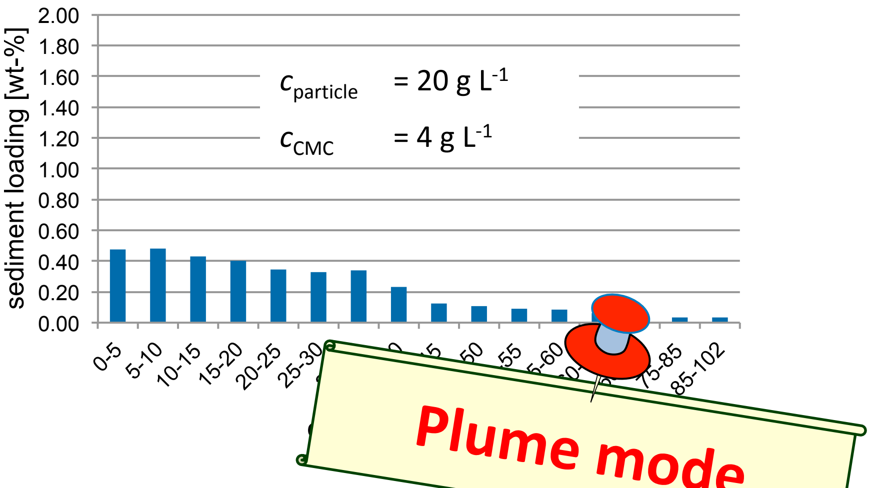
Control of Carbo-Iron mobility and particle mass loading necessary

Influence of suspension stabilizer on **sedimentation profile** and colloid mobility

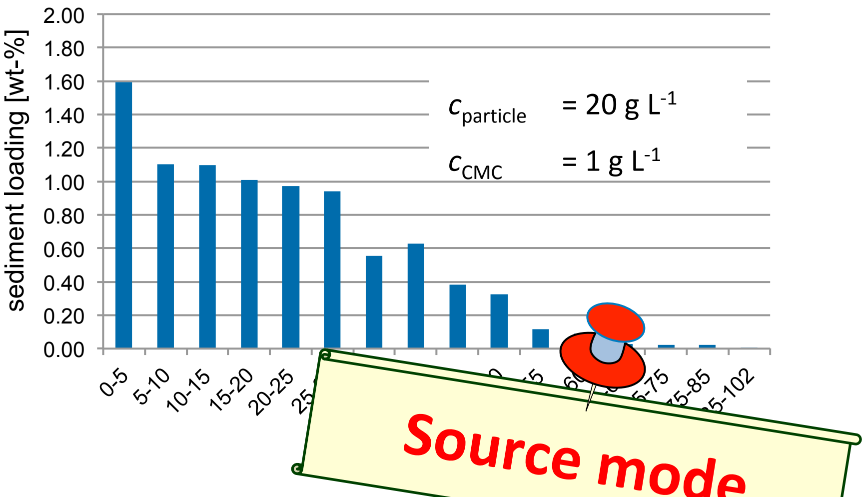



Carbo-Iron deposits on sediment grains (digital microscopic image)

decrease of $c_{CMC}$




$L_{T,99} \approx 12$ m




$L_{T,99} \approx 1$ m

# Field experience with Carbo-Iron

Third-party funded projects and commercial application

55,8 Fe 26 Nanosit

ContaSorb

Funding by German Federal Ministry of Education and Research (BMBF)

NanoRem

European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 309517

Sites in Germany (near Celle in Lower Saxony, Braunschweig, at present Langenhagen), site in Hungary

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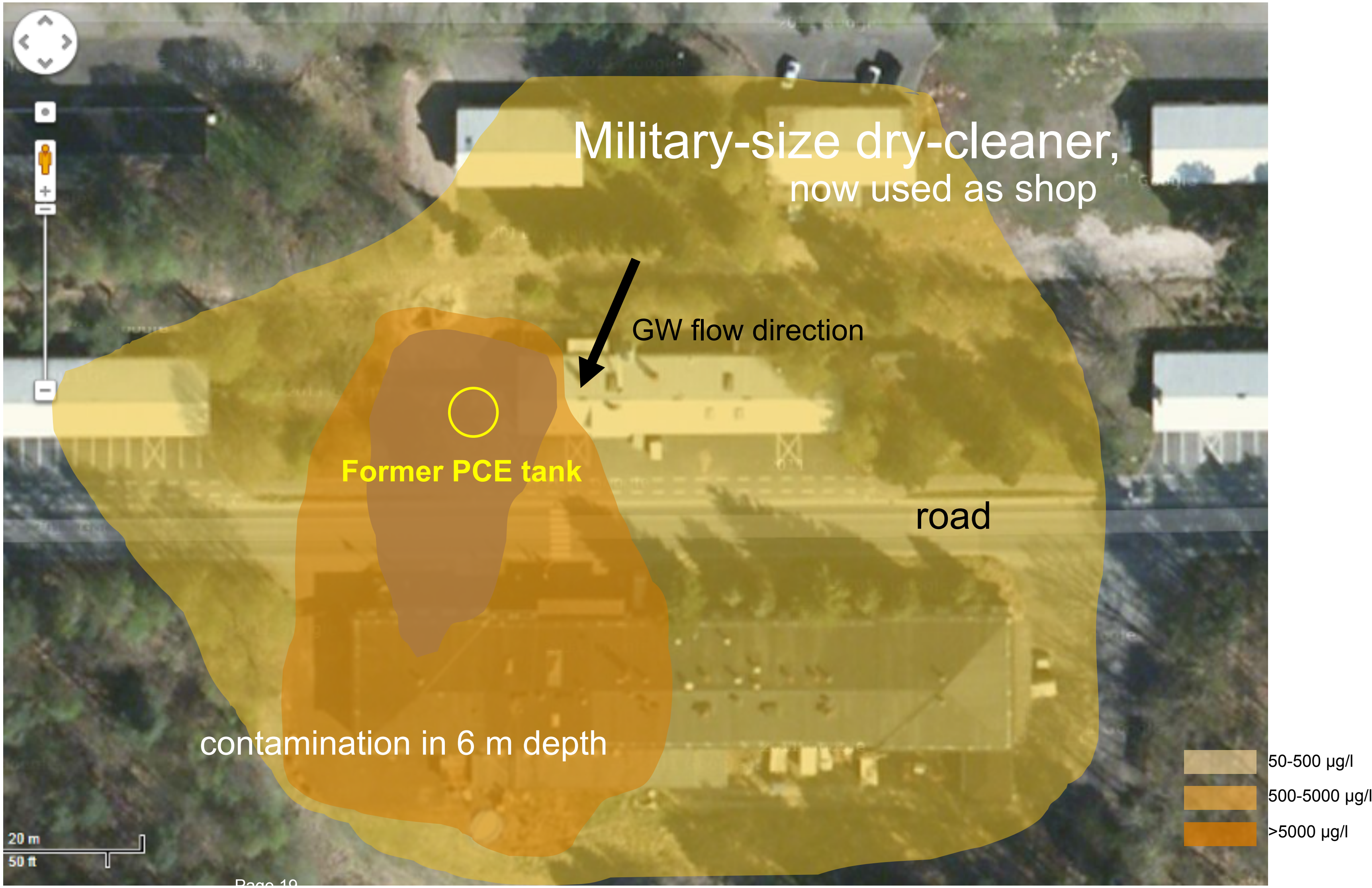
# First field test in Lower Saxony, Germany

## → Plume treatment

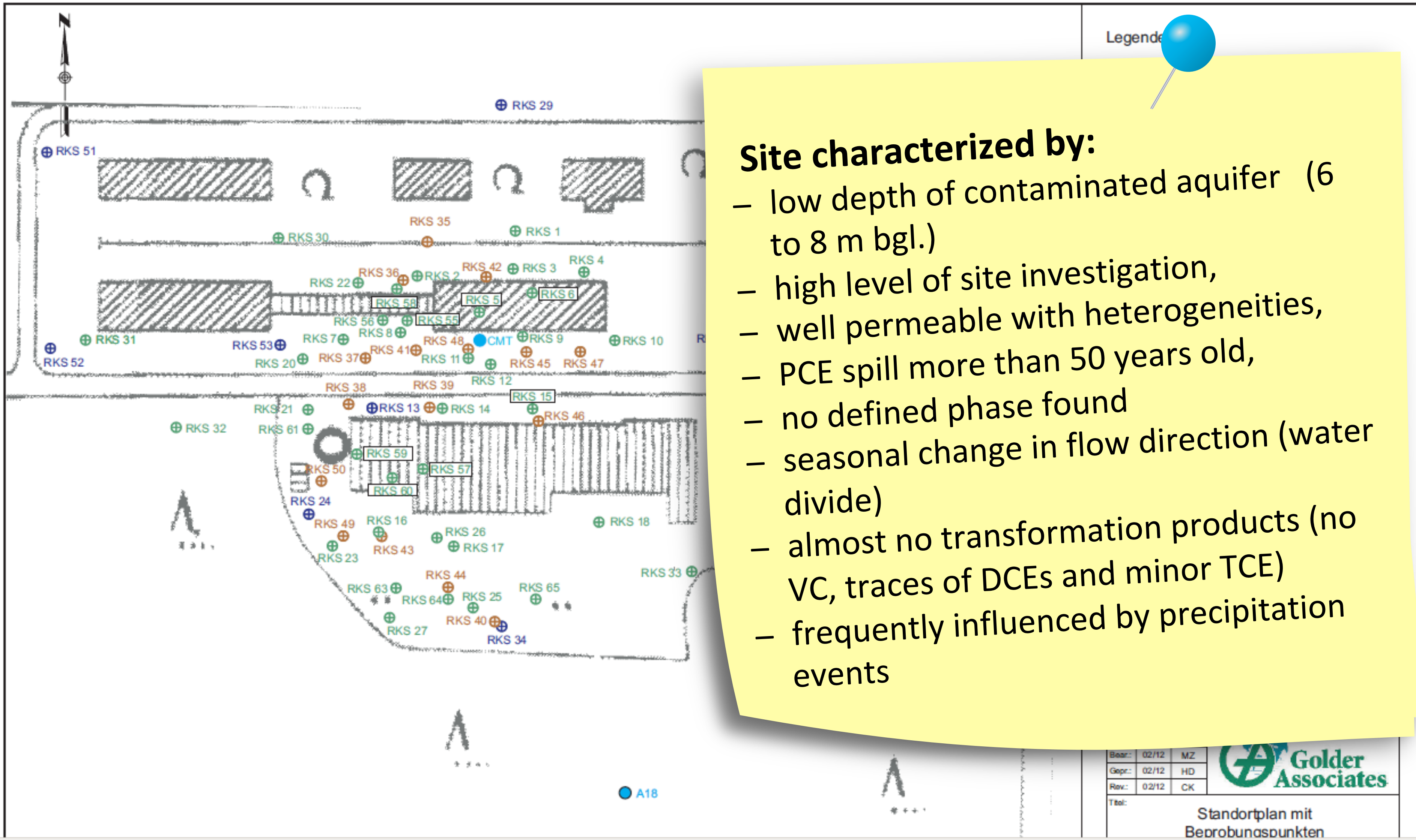
- PCE contamination ($c_{PCE,max}$ = 125 mg/L)
- Sandy aquifer ($K_f$ ~ $1 \cdot 10^{-5} \ldots 5 \cdot 10^{-4}$ m/s)
- Porosity: 15…30 %
- GW distance velocity: 18 cm/d
- $\sigma$ = 360 µS/cm
- $C_{O2}$ = 0.3 mg/L
- $E_H$ < -100 mV

# The site



Military-size dry-cleaner,
now used as shop
GW flow direction
Former PCE tank
road
contamination in 6 m depth
50-500 µg/l
500-5000 µg/l
>5000 µg/l
20 m
50 ft

# The Site

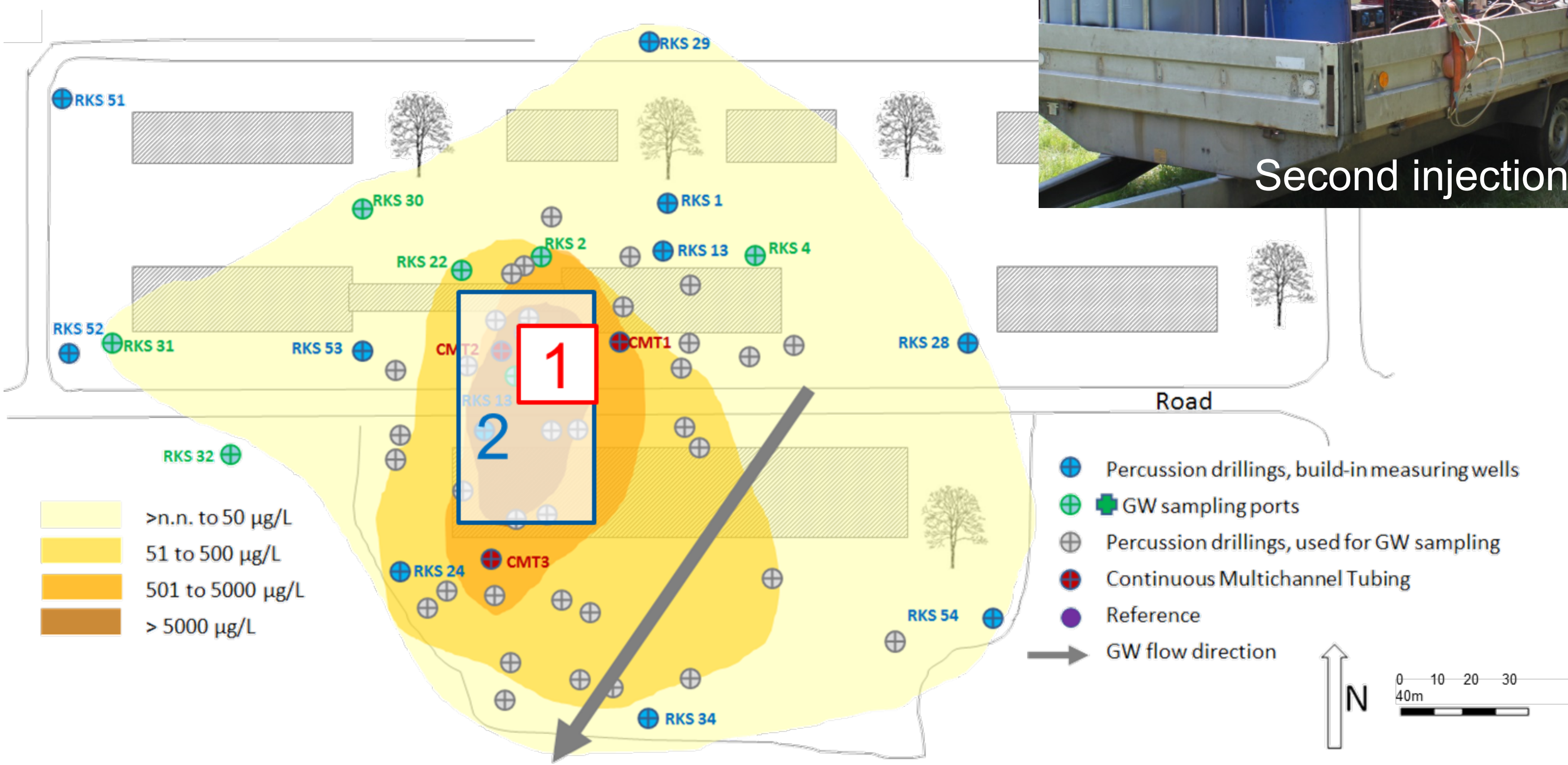



**Site characterized by:**

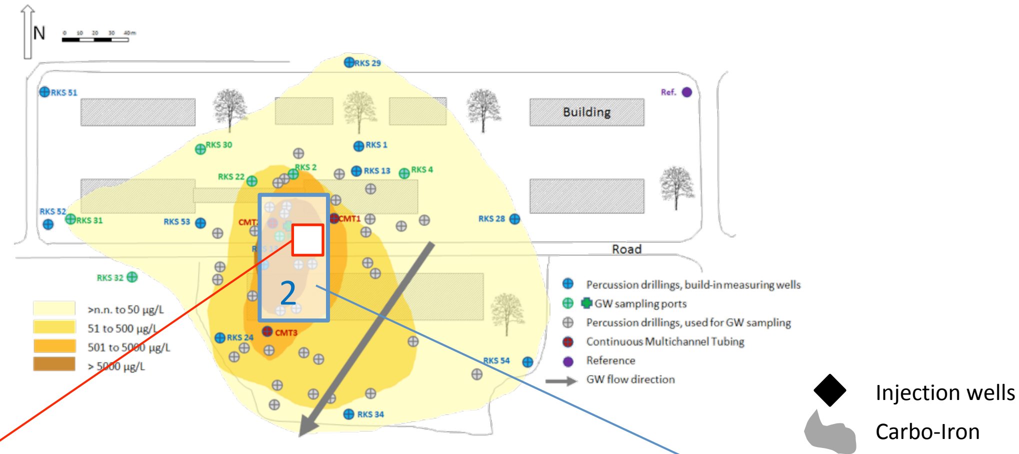
- low depth of contaminated aquifer (6 to 8 m bgl.)
- high level of site investigation,
- well permeable with heterogeneities,
- PCE spill more than 50 years old,
- no defined phase found
- seasonal change in flow direction (water divide)
- almost no transformation products (no VC, traces of DCEs and minor TCE)
- frequently influenced by precipitation events

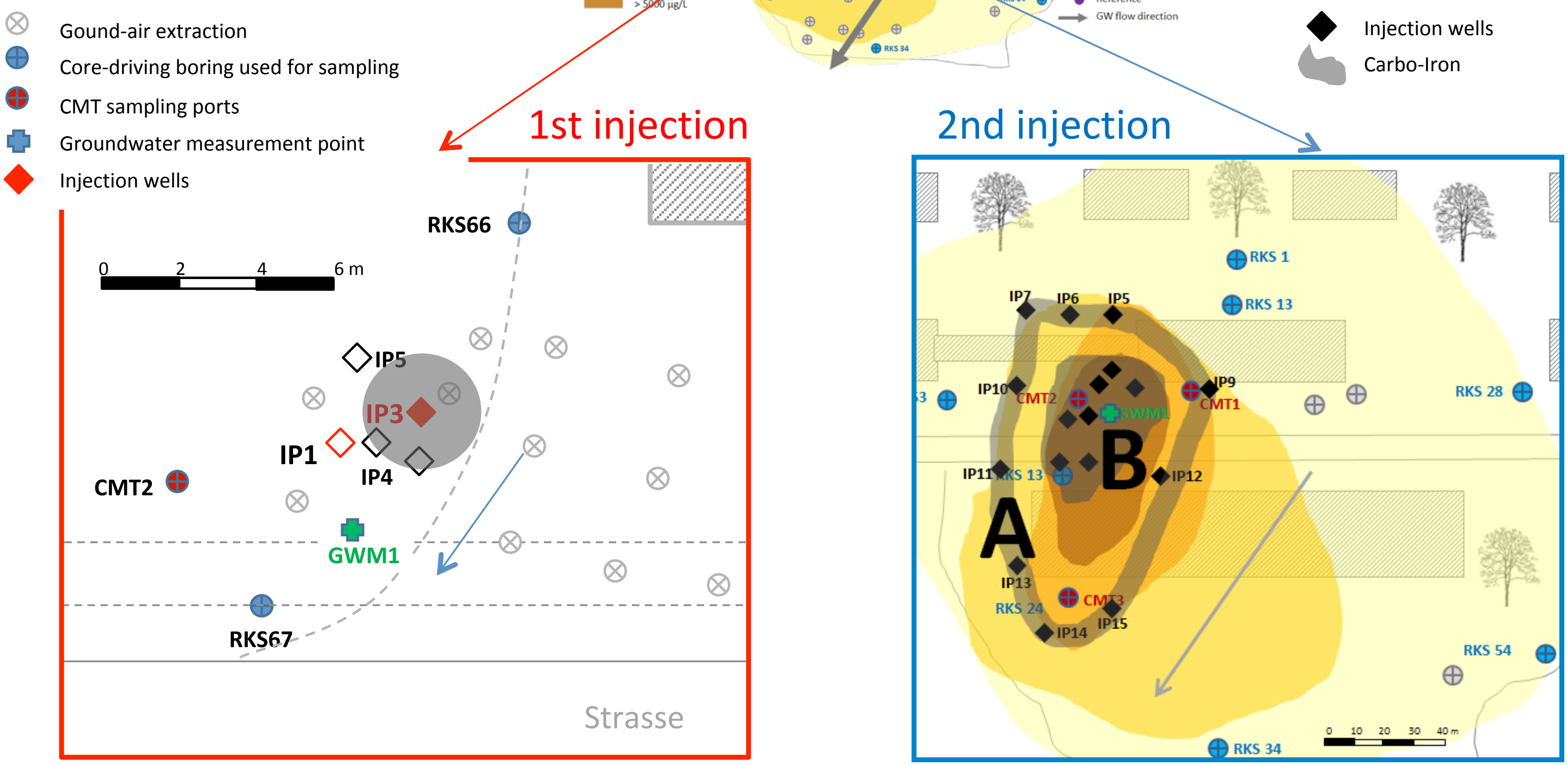
# Two injections





# Two injections




**20 kg Carbo-Iron (10 g/L, 2 g/L CMC)** **120 kg Carbo-Iron (15 g/L, 1,5 g/L CMC)**

# Suspension tank

## Dry Carbo-Iron is added to disperser

(here: during EU project NanoRem)

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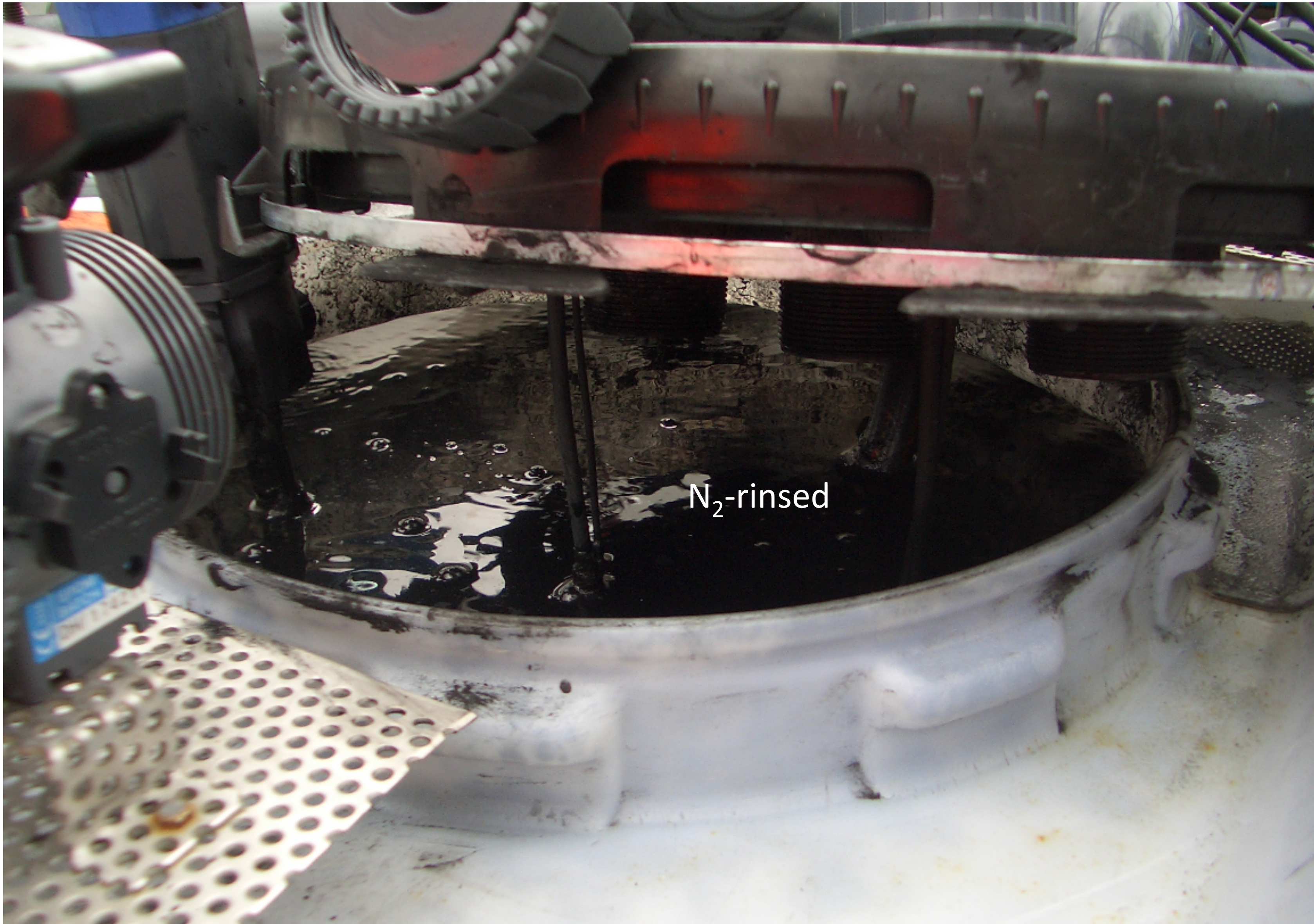
# Particle Suspension ready for Injection



# Particle Suspension ready for Injection

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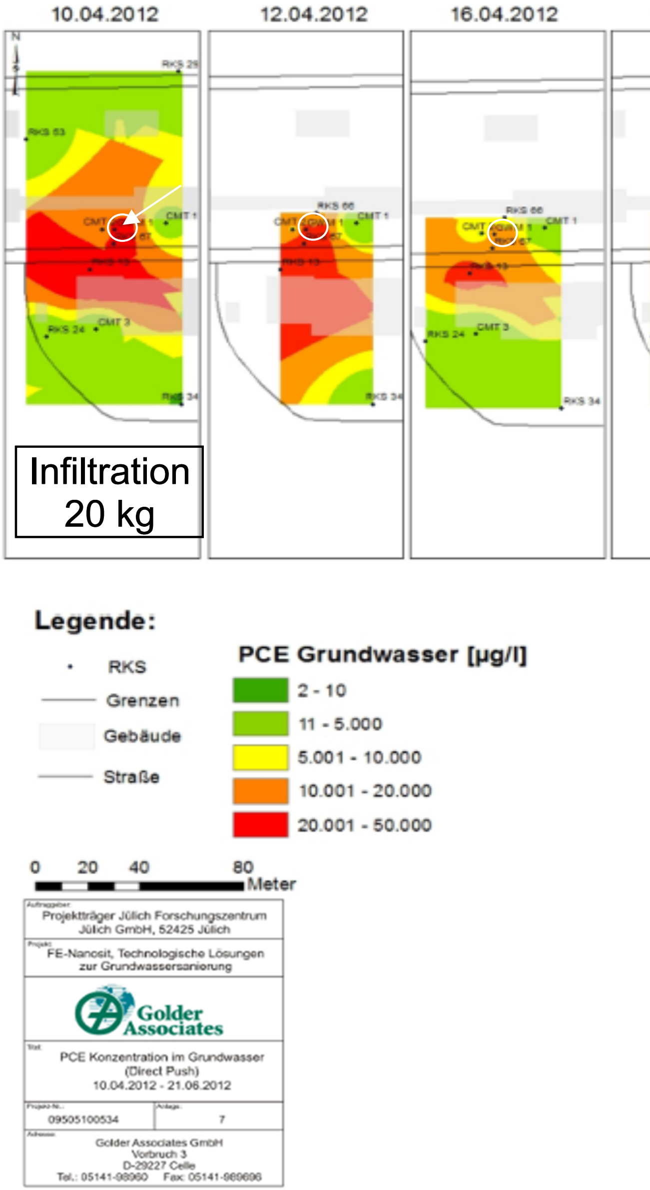
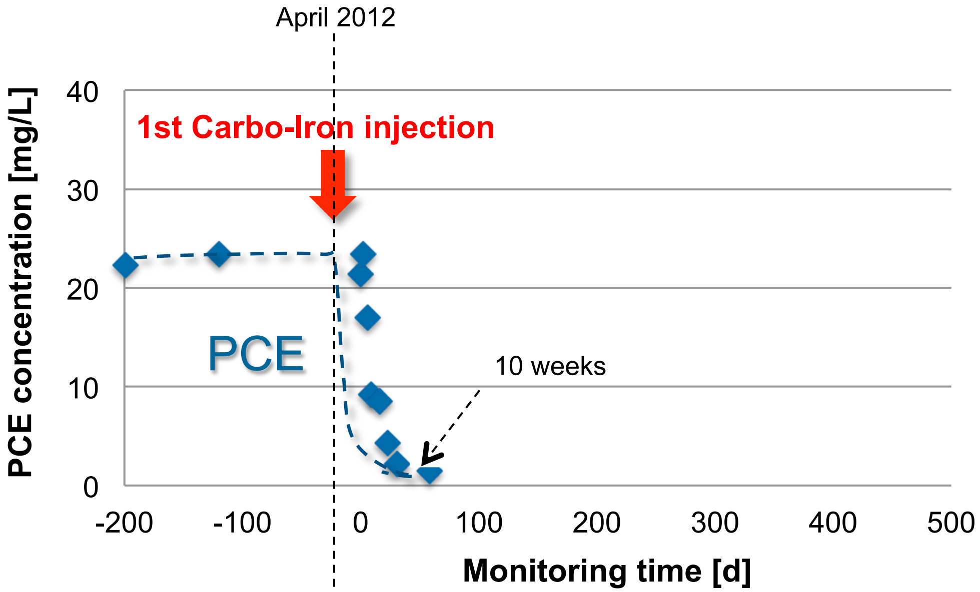
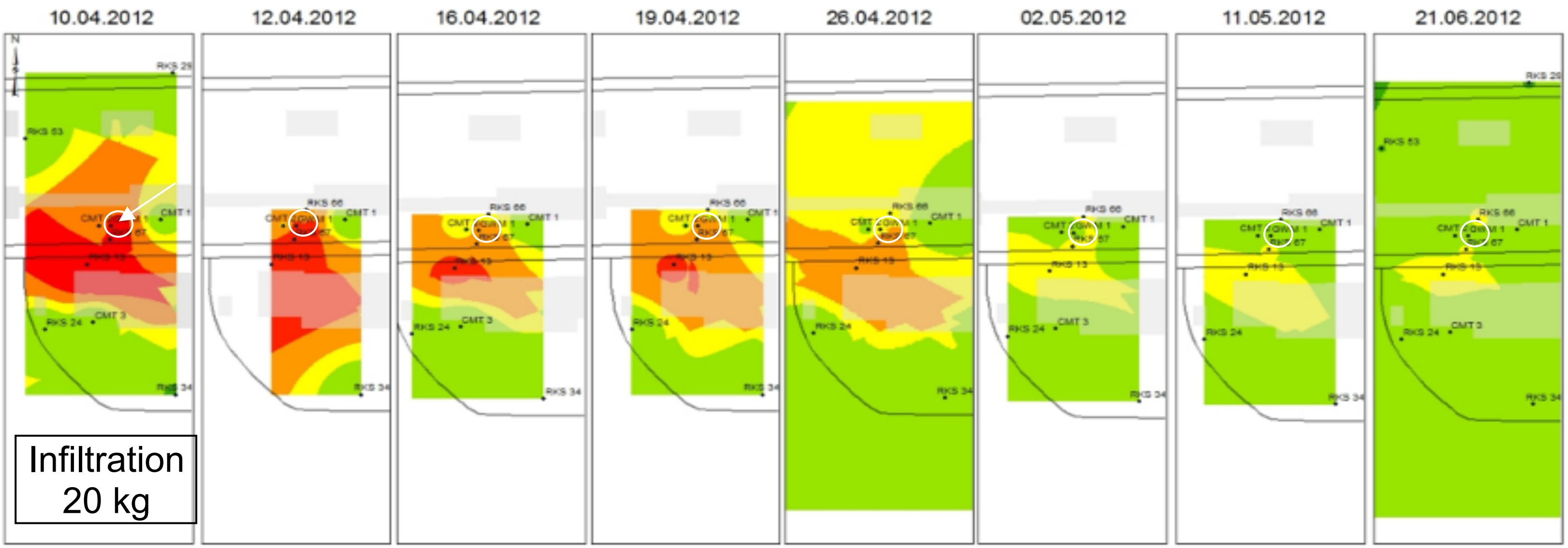
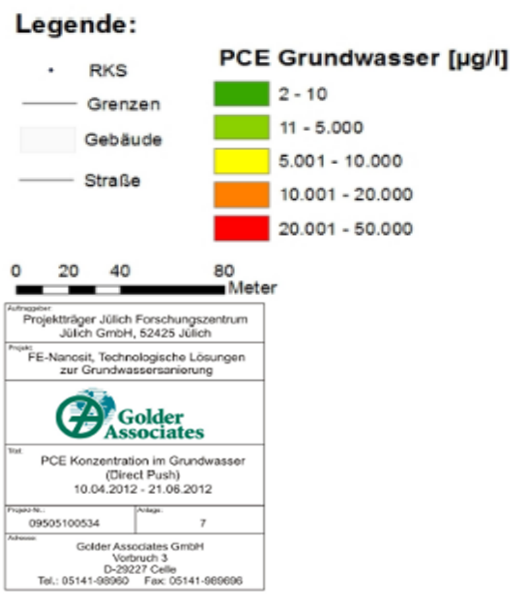
# Pollution profile in first 2 months

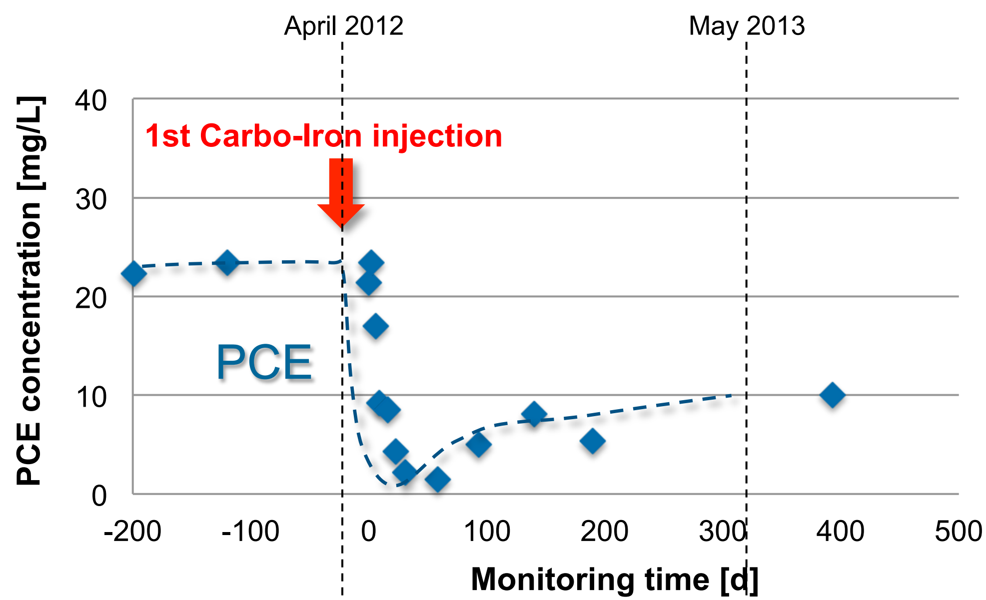


# Pollution profile in first 2 months

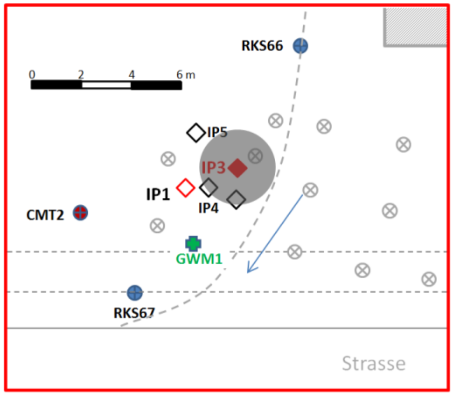


# Effect of sorption

1st injection




$$R = 1 + \frac{1-\varepsilon}{\varepsilon} \cdot \eta_{sed} \cdot K_{d,AC} \cdot f_{AC}$$

| | |
|---|---|
| $R$ | = Retardation factor |
| $\varepsilon$ | = Porosity |
| $K_{d,AC}$ | = Sorption coefficient of AC for PCE |
| $\eta_{sed}$ | = Density of sediment material |
| $f_{AK}$ | = Mass fraction of AC in sediment |

- Carbo-Iron mass in 20 $m^3$ sediment volume
- $K_{d,AC} = c_{PCE,\ sorbed}/c_{PCE,water\ phase} > 10000\ L\ kg^{-1}$

**R = 38** (PCE travels 38 times slower than water)

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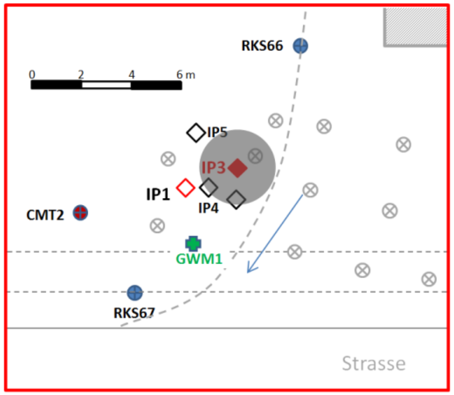
# Reaction of Iron




*Anaerobic iron corrosion:*

$$Fe^0 + 2H_3O^+ \xrightarrow{k_{korr}} Fe^{2+} + H_2 + 2H_2O$$

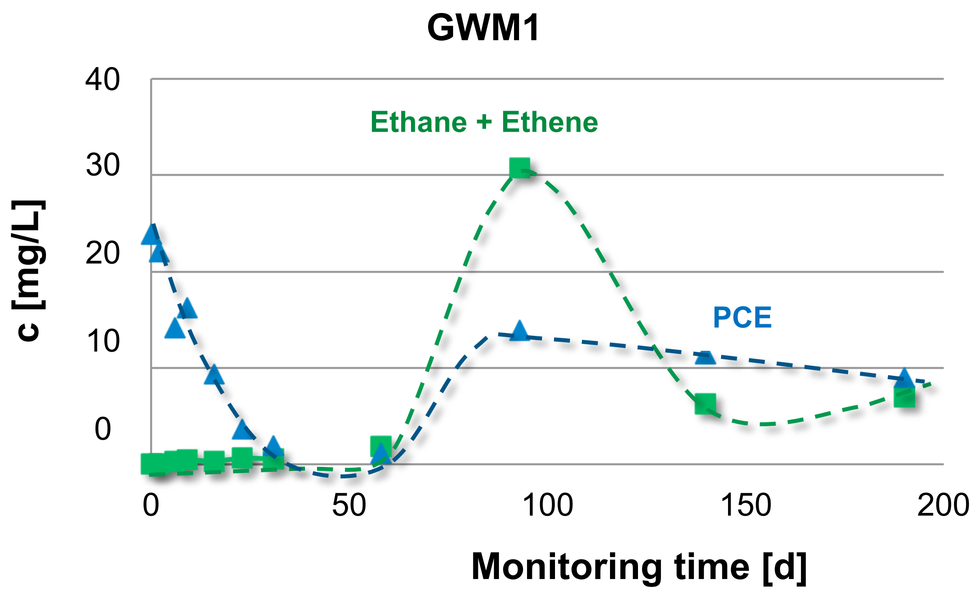
*Reductive dechlorination of PCE:*

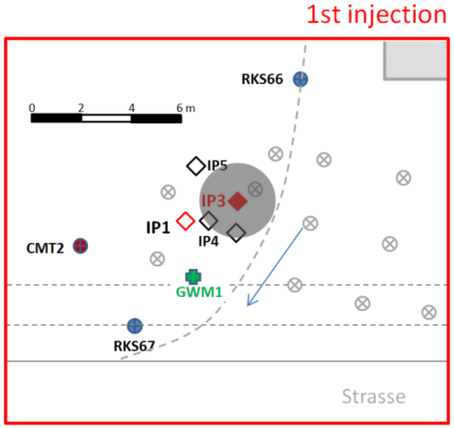
$$n\,Fe^0 + C_2Cl_4 + (2n-4)\,H_2O \xrightarrow{k_{dechl}} n\,Fe^{2+} + C_2H_{(2n-4)} + (2n-4)\,OH^- + 4\,Cl^-$$

**Products:** $H_2$ ~~TCE~~, DCEs, ~~VC~~, ~~Acetylene~~ **Ethylene, Ethane,**

**Proof for abiotic dechlorination reaction**

# Analytical data



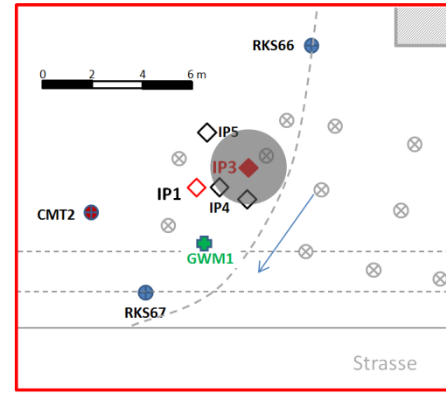



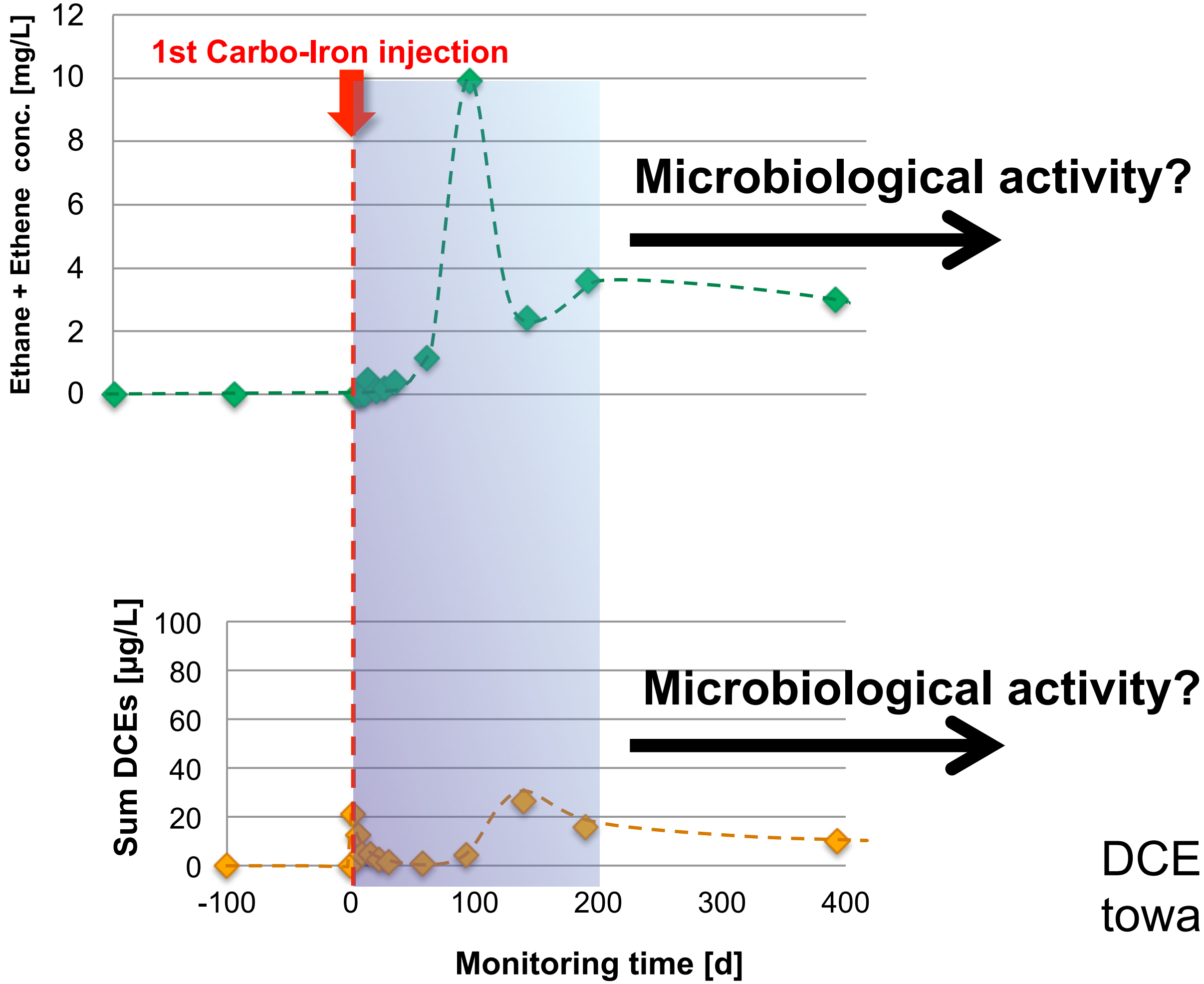

- ✓ Marked reduction of **PCE**
- ✓ → slow rebound after 2 months
- ✓ **Ethane and Ethylene** form with a time shift
- ✓ **DCEs** only in traces

  → No enrichment of intermediates!

# Reaction beyond Carbo-Iron lifetime

1st injection

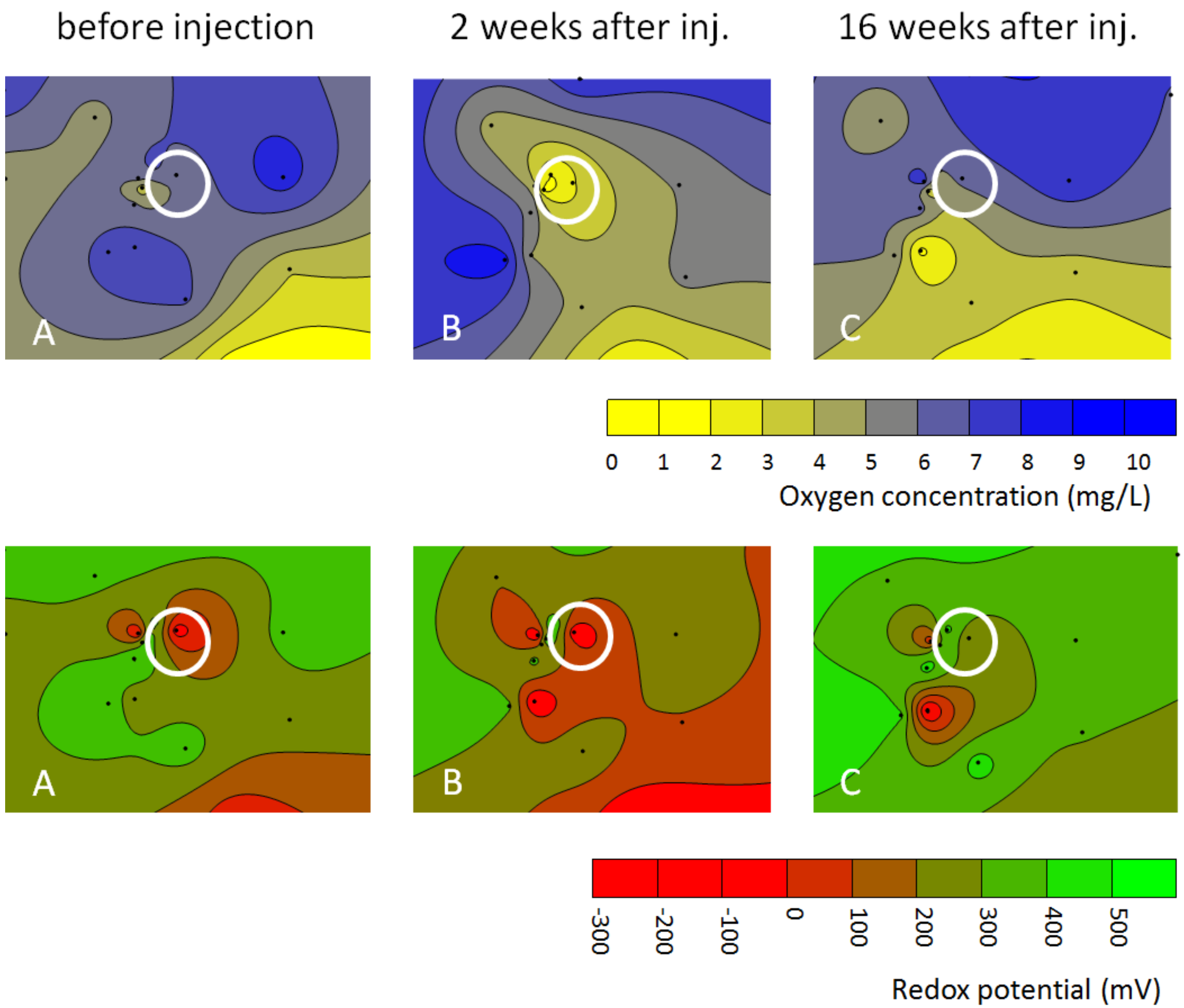



DCE selectivity pattern changes towards cis-DCE

**No VC is formed!**

# Redox conditions




Oxygen introduction always after rainfall event

Fluctuation of redox

Instead of expected *Dehalococcoides sp.* another MO type dominated: *Polaromonas sp.* strain JS666

no DCE, no VC

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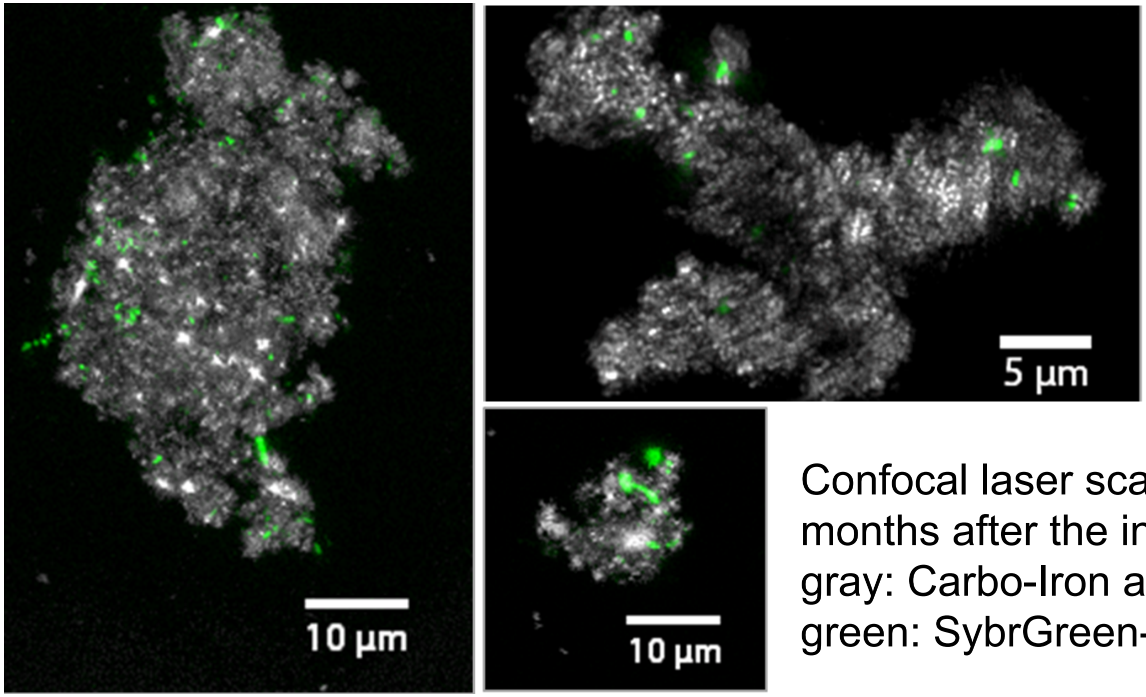
# Microbiological Activity

*Trend over several months:*

→PCR screening
→product distribution (PCE removal, DCE appearance and further removal)
→correlation with groundwater conditions ($O_2$, ORPs…)
→Isotope signature ($\delta\ ^{13}C$)

OTUs related to Polaromonas sp. strain JS666




Confocal laser scanning microscopy three months after the injection.
gray: Carbo-Iron agglomerates,
green: SybrGreen-dyed microorganisms

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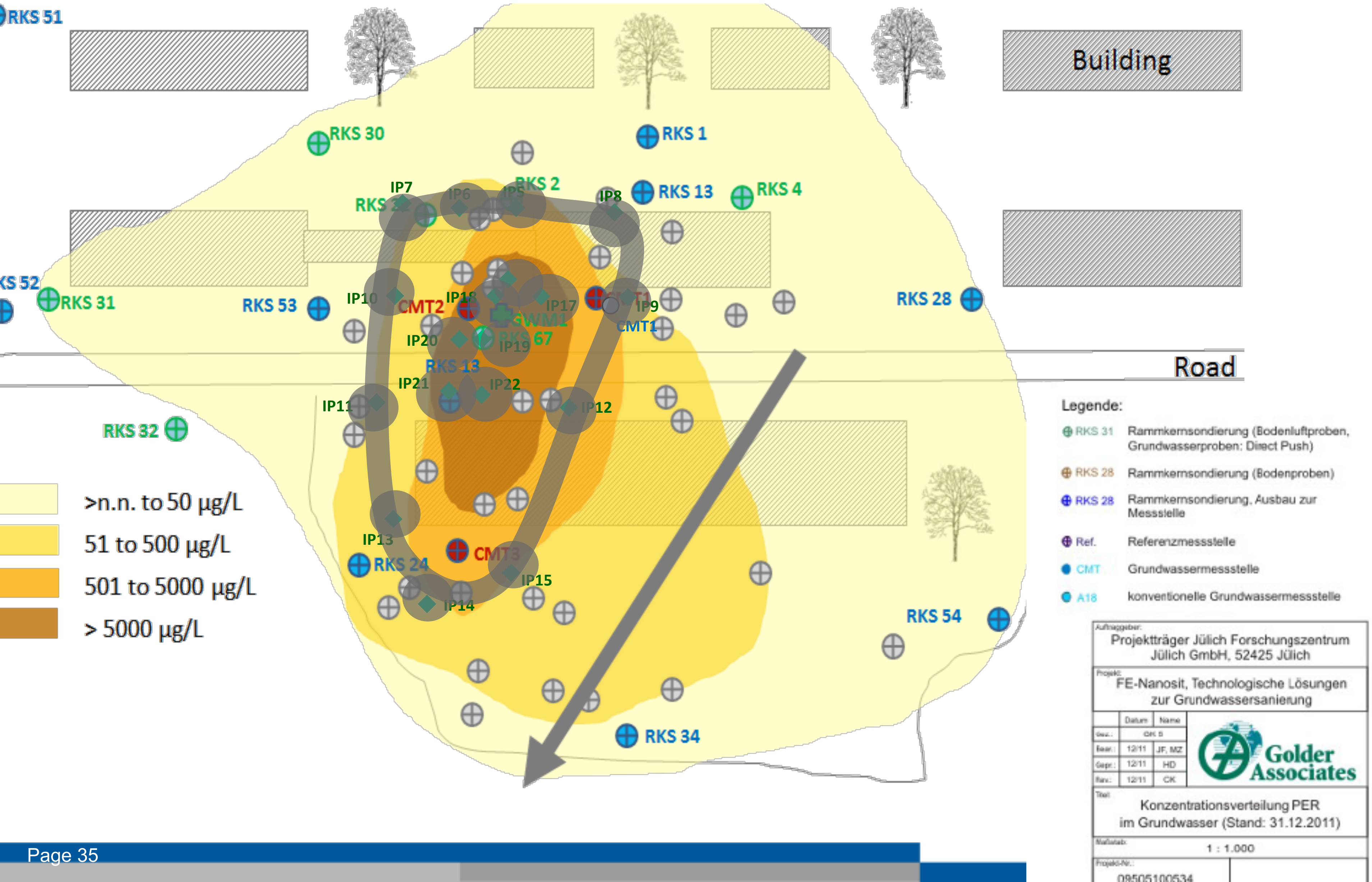
# 2nd Injection



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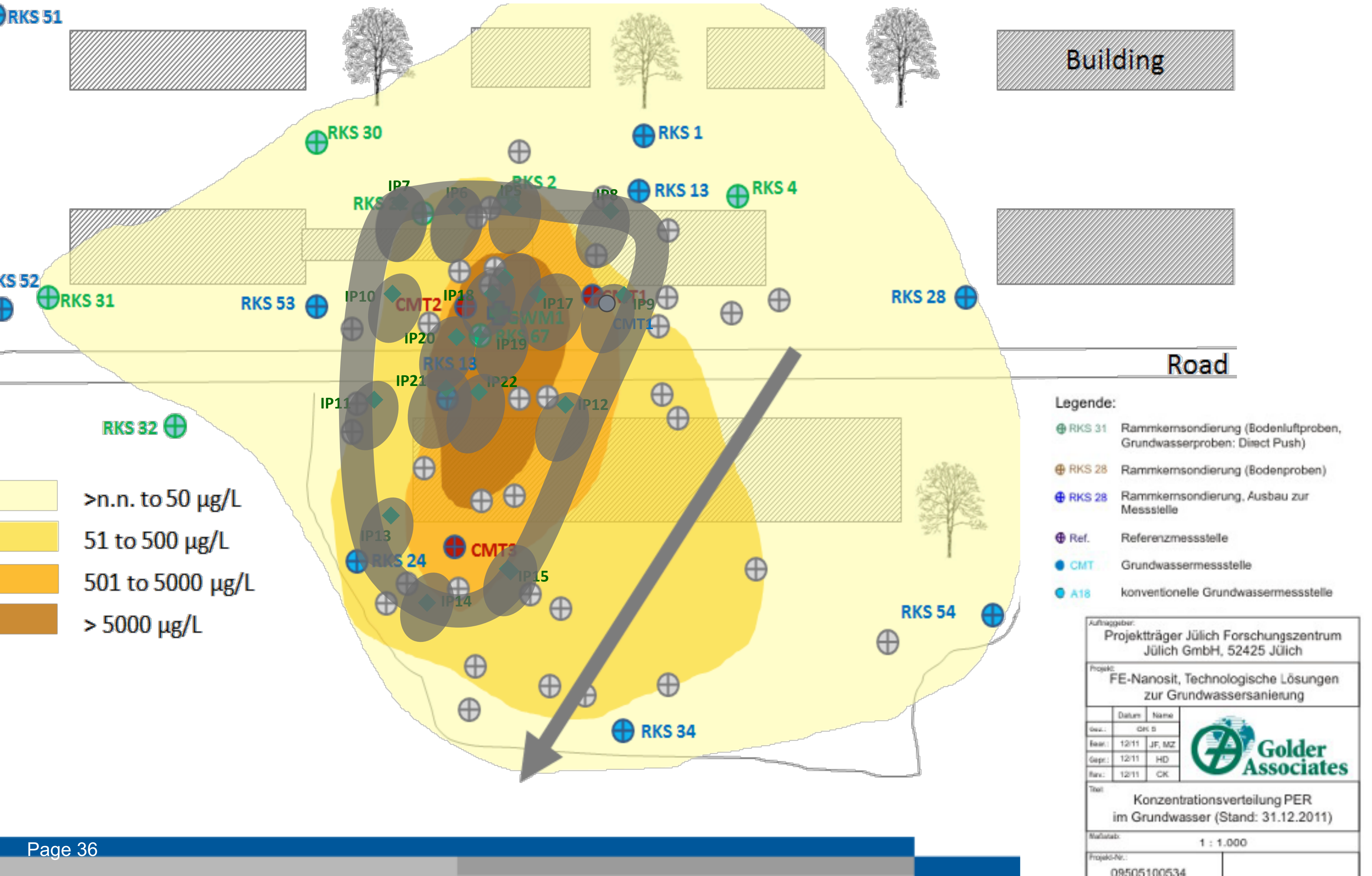
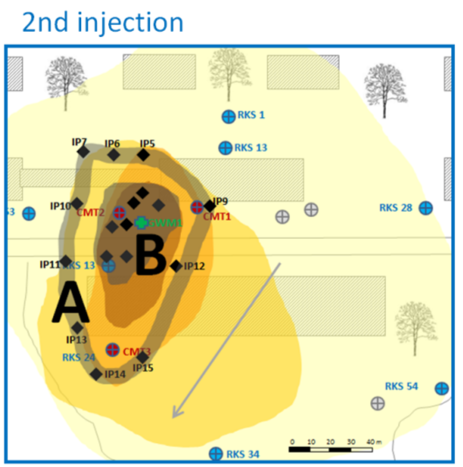
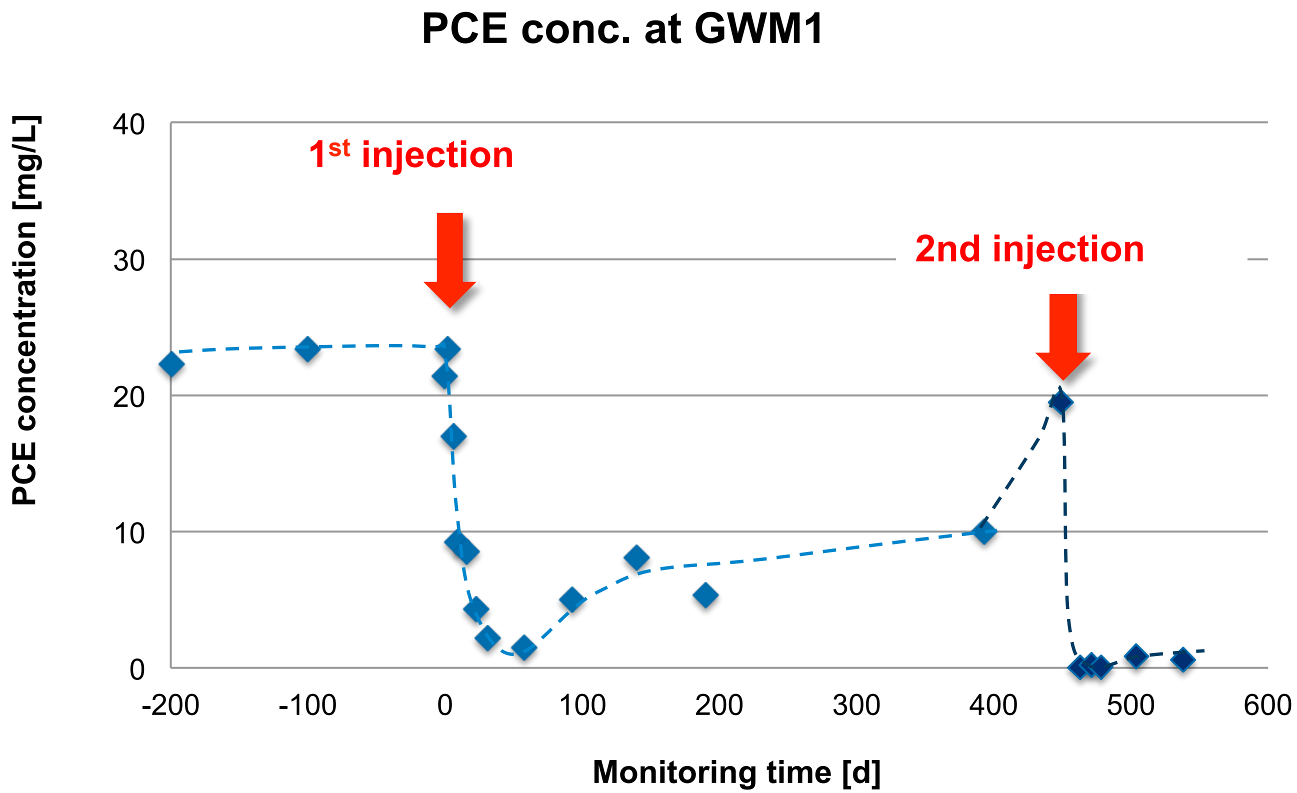


# Results of 2nd injection




→ PCE concentration drops again, same pattern as for 1st injection

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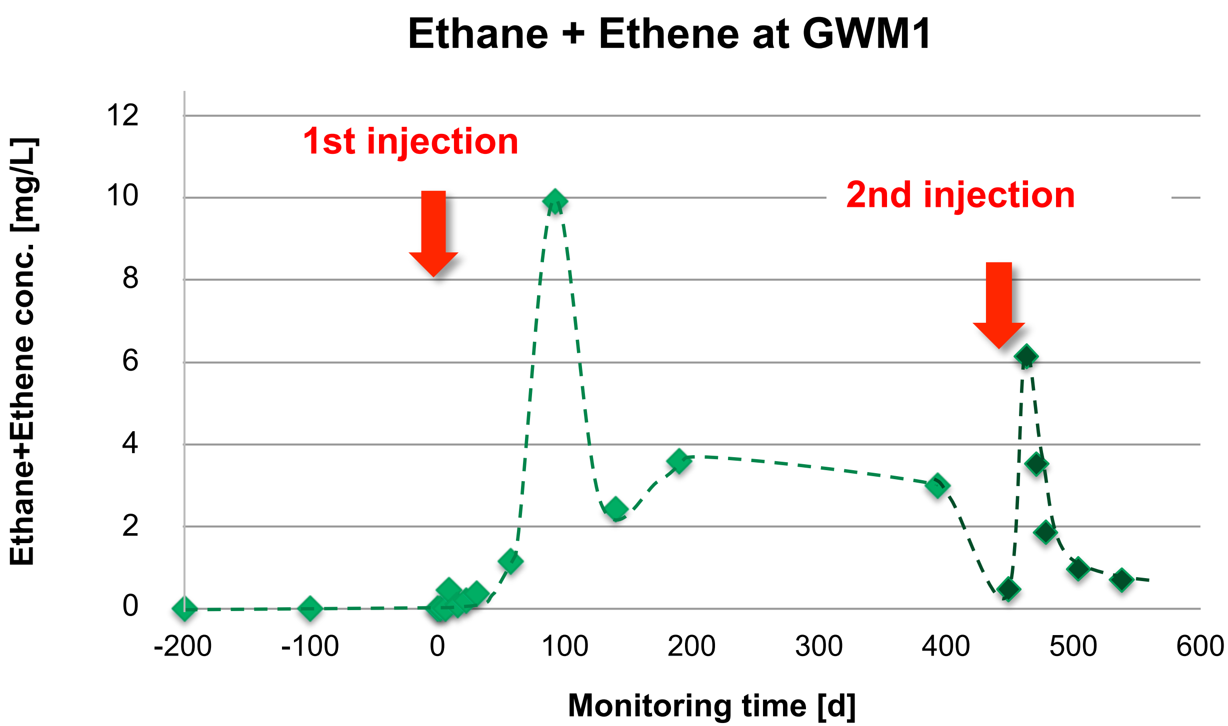
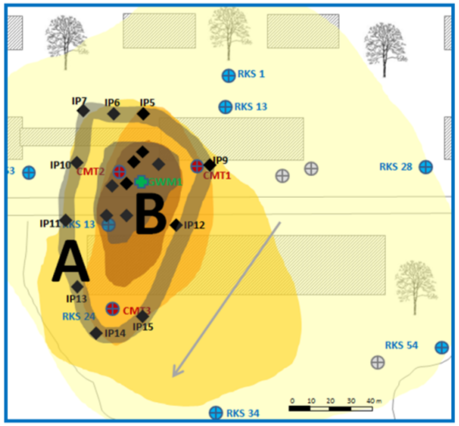
# Results of 2nd injection




2nd injection




→ $C_2$ hydrocarbons are quickly abiotically formed, in the long term also biotically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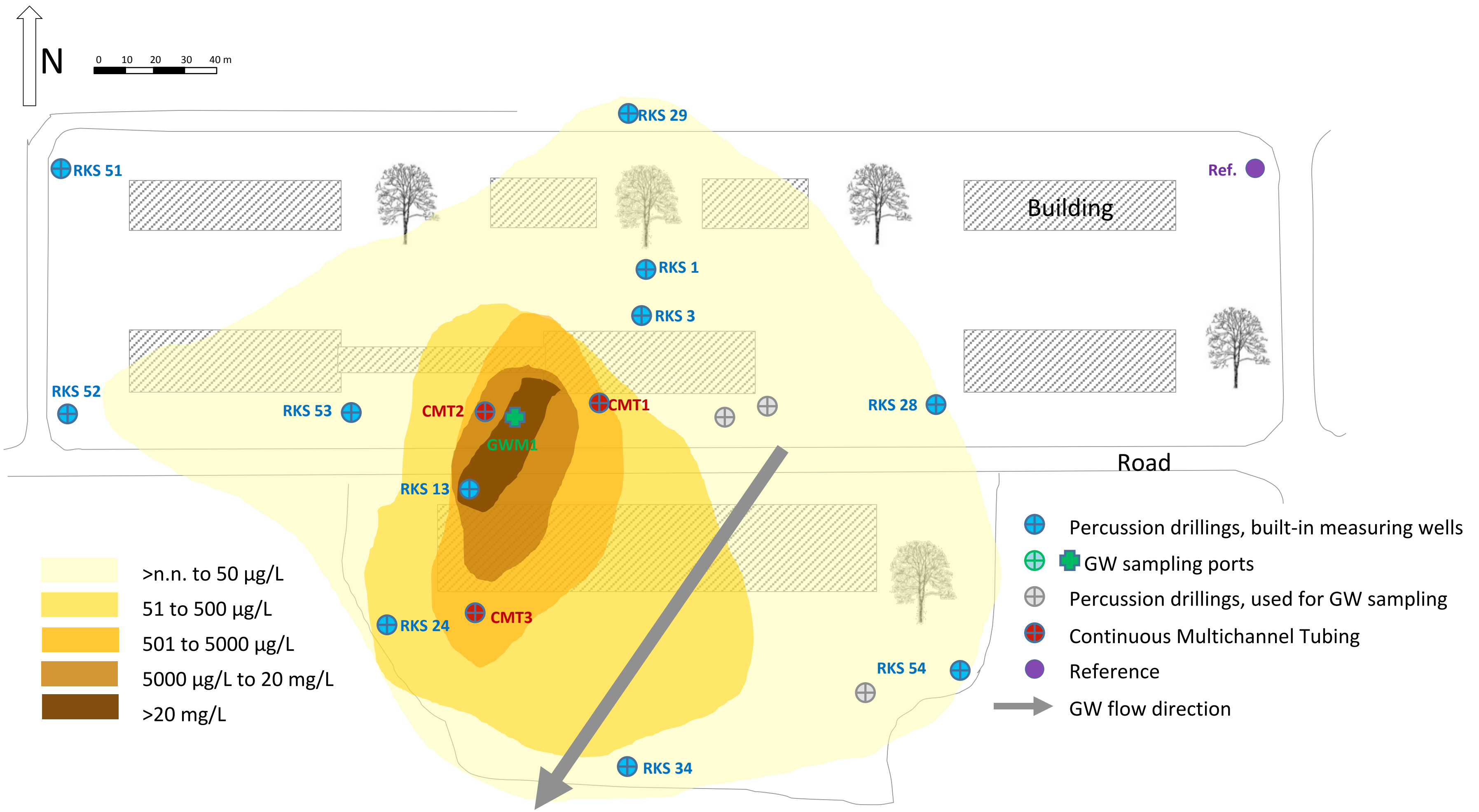
# Contamination profile before injection

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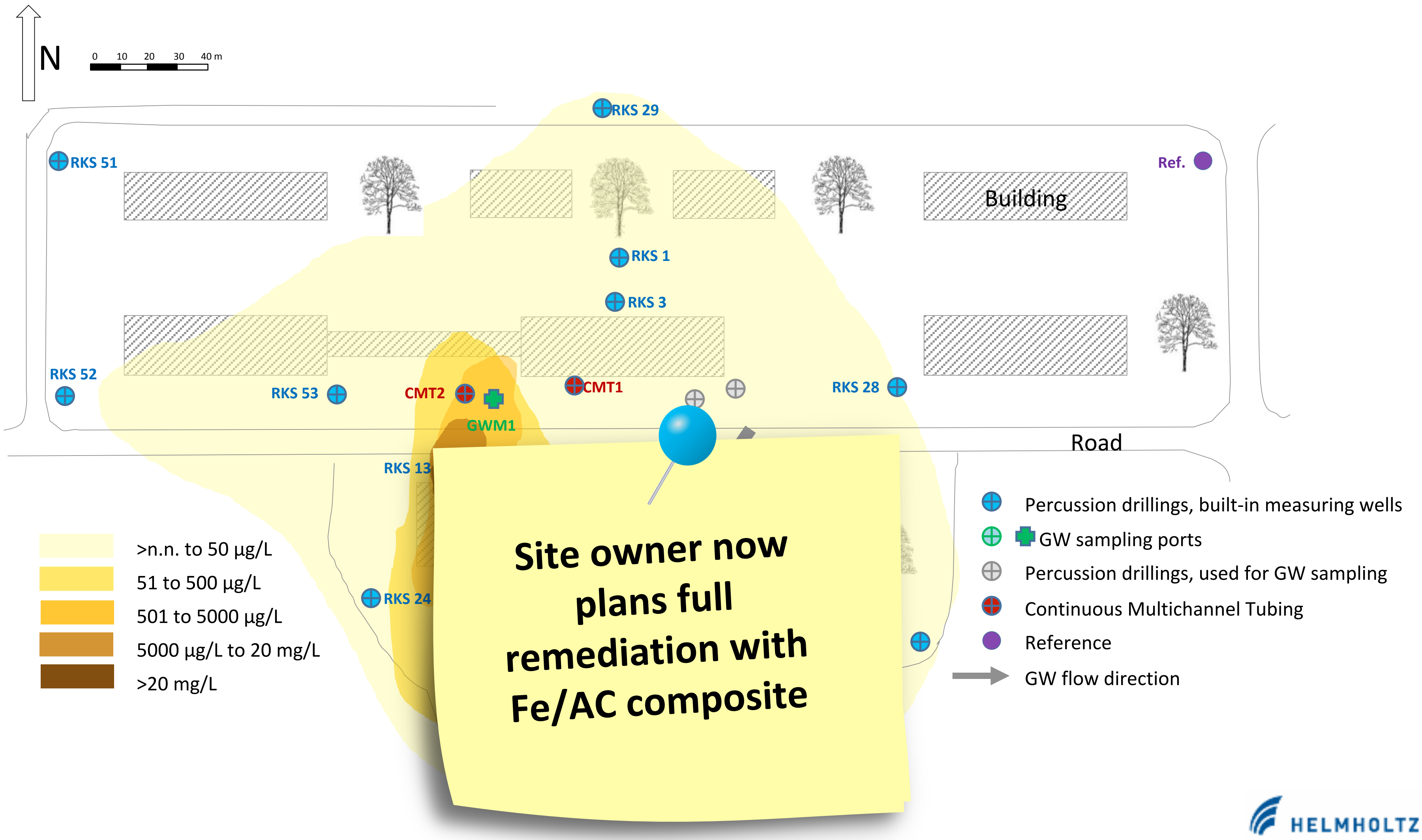
# Contamination profile 2 years after the project

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# Ecotoxicity tests

Study of possible environmental hazards which could result from the particles.






Tests for acute and chronic toxicity

- standard tests with model organisms
- uptake in organisms
- mechanisms

Fish: gene expression pattern (microarrays)
Algae: metabolom

- effect mechanisms
- combination effects with pollutants
- possible development of measures and alternatives

## → no adverse effect up to 1000 mg/l in most assays

(Bacterial luminescence bioassay and algae tests suffered from shading and showed no adverse effect up to 100 mg/L; earthworm survival test as well as seed germination and root elongation tests were performed up to 10 g/L and showed no adverse effects)


Thank you for your attention!