GQ 2019 Conference, Liége, Belgium

11.9.2019

Quantification of nitrate reduction potential and kinetics of soil samples obtained from sandy aquifers, Germany

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Inspiration

IWW

Background

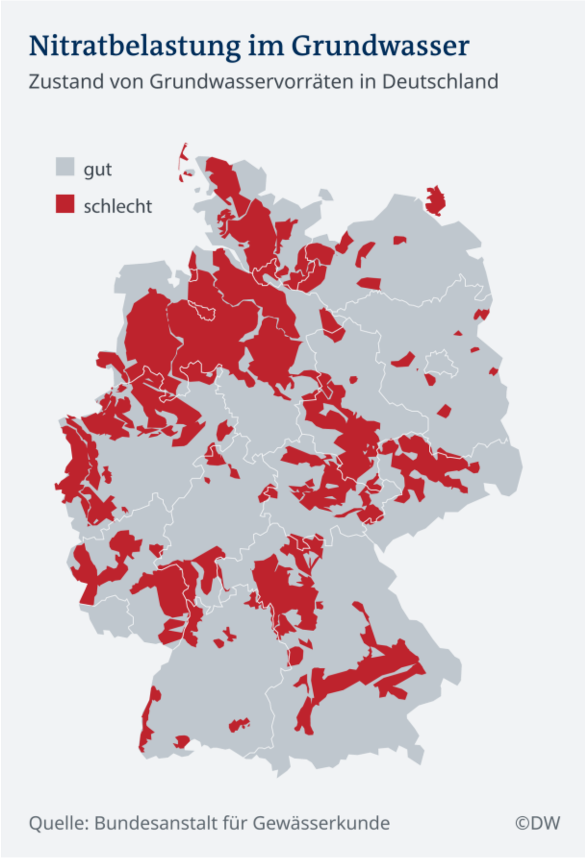
- Intense agricultural activity in Germany
- High nitrate concentrations (almost 30 % of the shallow groundwater bodies > 50 mg/l nitrate)
- **Low concentrations due to denitrification**

continuous nutrient input


dw.com/en/eu-sues-germany-over-water-tainted-by-nitrate-fertilizer/a-19225653

EU sues Germany over water tainted by nitrate fertilizer

The European Commission has lost patience with Germany over the high concentration of nitrate fertilizer in its ground water. Taxpayers could now end up paying hundreds of millions of euros in fines.



Denitrification potential can be depleted → **Propagation of redox front**

Methodology

Denitrification

- Natural nitrate attenuation process
- Anaerobic conditions, microbial activity!

Autolitotrophic denitrification (pyrite)

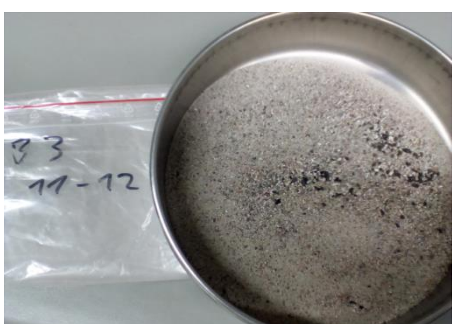
$5\ FeS_2 + 14\ NO_3^- + 4\ H^+ \Rightarrow 7\ N_2 + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2\ H_2O$

Heterotrophic denitrification (organic carbon)

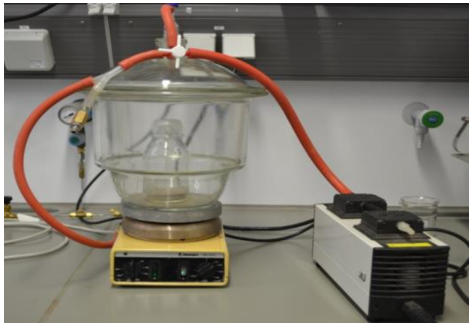
$5\ CH_2O + 4\ NO_3^- + 4\ H^+ \Rightarrow 5\ CO_2 + 2\ N_2 + 7\ H_2O$

Laboratory batch experiments

1. Sediment samples were collected in northern Germany
2. **Solid phase analysis** (sulfide, organic carbon content)
3. **Scanning electrone microscope (SEM)**
4. **Denitrification potential was investigated** from **laboratory batch experiments** containing sediments with different concentrations of sulfide and organic carbon



Methodology



Treatment of the sediment with vacuum and N_2 gas in a desiccator + stirring → **oxygen can be almost completely removed**

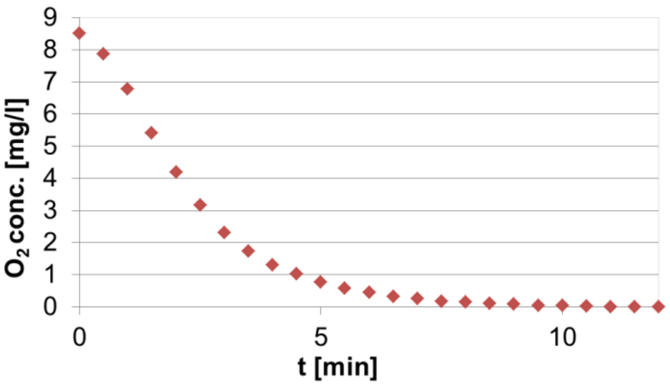
Preparation of oxygen-free, nitrate containing distilled water solution (N_2 gas flushing)

Filling up the soil samples with the solution and sparging with N_2 gas

Chemical optical sensing system, Presens GmbH

5 mm oxygen sensing spot

→ Control unit → Software

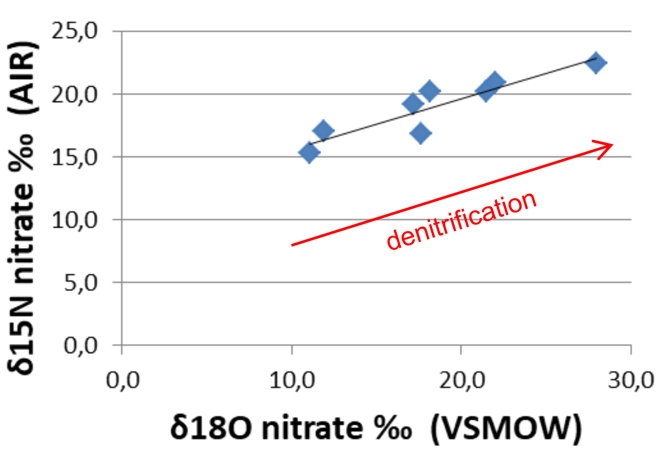


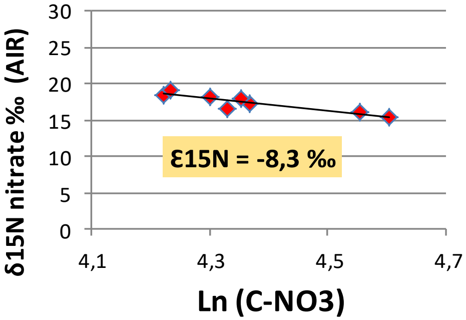
Methodology

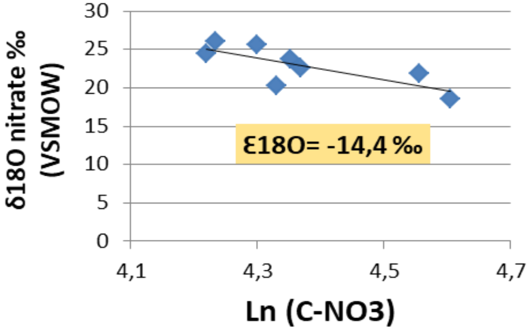
Measurement:

- Major cations, anions: sulfate, nitrate, nitrite…(IC Metrohm AG)
- Dissolved organic and inorganic carbon (LiquiTOC)
- Heavy metals: Fe, Mn, Cr, Cu, Ni, As (contrAA 300 AAS)
- Oxygen concentration (Presens GmbH)
- Isotopic fractionation of nitrate (δ15N, δ18O /NO_3) - UFZ, Germany

Denitrifier method: The technique is based on microbial transformation of nitrate to NO_2 and the isotopic composition of both nitrogen and oxygen can be investigated







Ɛ15N: from -20,2 ‰ to -4,7 ‰
Ɛ18O: from -22,8 ‰ to -3,1 ‰

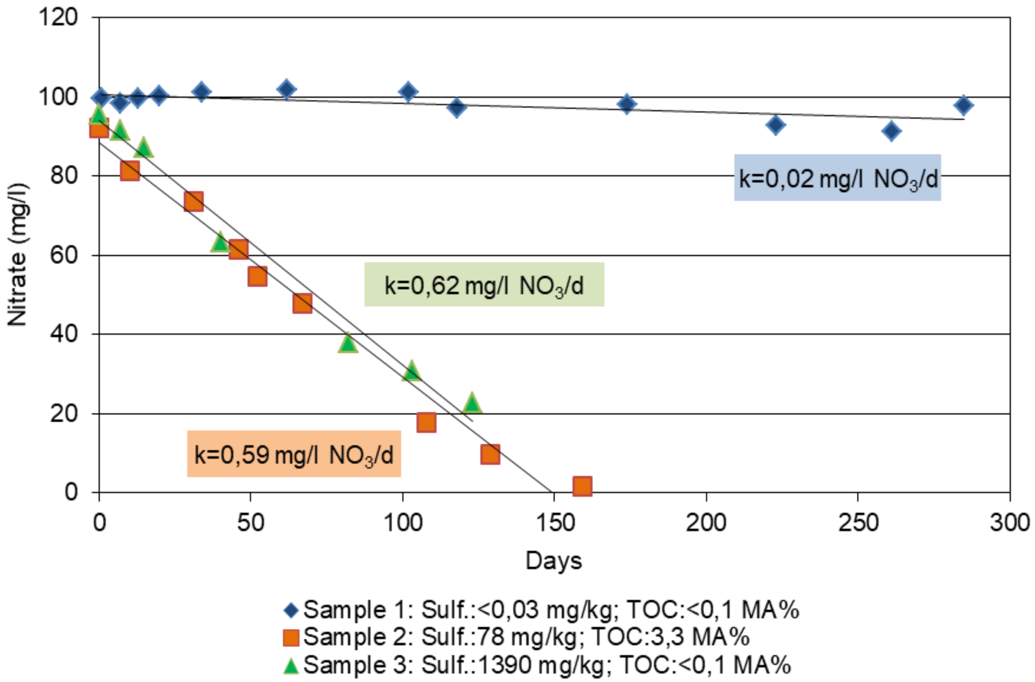
Results

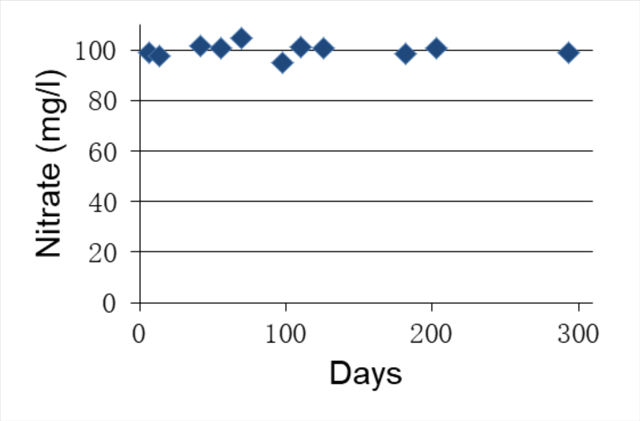
- **Reactive phases** in the sediments (pyrite, organic carbon), however there is **difference in their efficiency** regarding to denitrification.

- Based on the same mass of electron donors, **degradation by organic carbon is slower than by sulfides**

- **Degradation rates:**
TOC: 0,45-2,21 mg/l NO_3 /d
Sulfide-disulfide: 0,1-0,72 mg/l NO_3 /d

- In most cases a **correlation** could be found between the initial electron donor concentration and degradation rate but some **deviations → microbiology? mineral structure?**





S:2900 mg/kg, TOC: <0,013%

Results

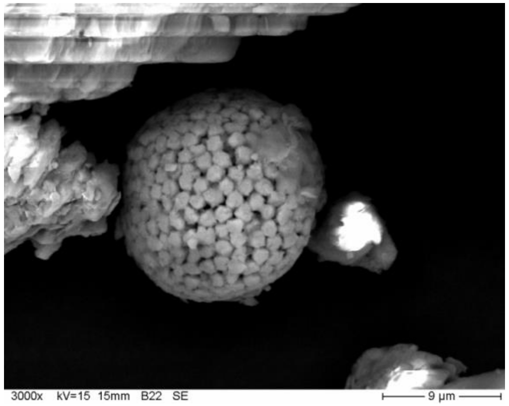
Scanning Electron Microscope

Framboidal pyrite

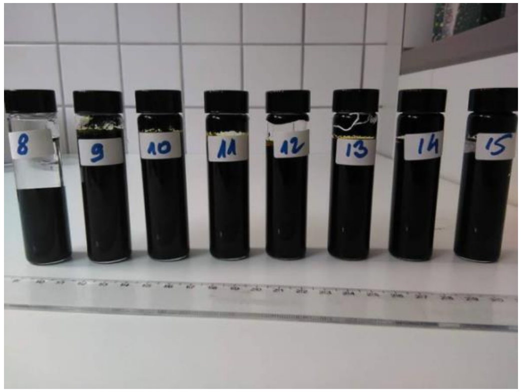
- „framboise”=raspberry in French
- Can be dominant in anoxic environments
- 3 fundamental characteristics:
    - spheroidal to sub-spheroidal in form
    - they are composed of discrete microcrystals
    - The microcrystals are equidimensional and equimorphic

- Studies showed that better available for bacteria → higher surface area
- Can be synthesized in the lab (modified Sweeney and Kaplan's method)

B16 10-11 m

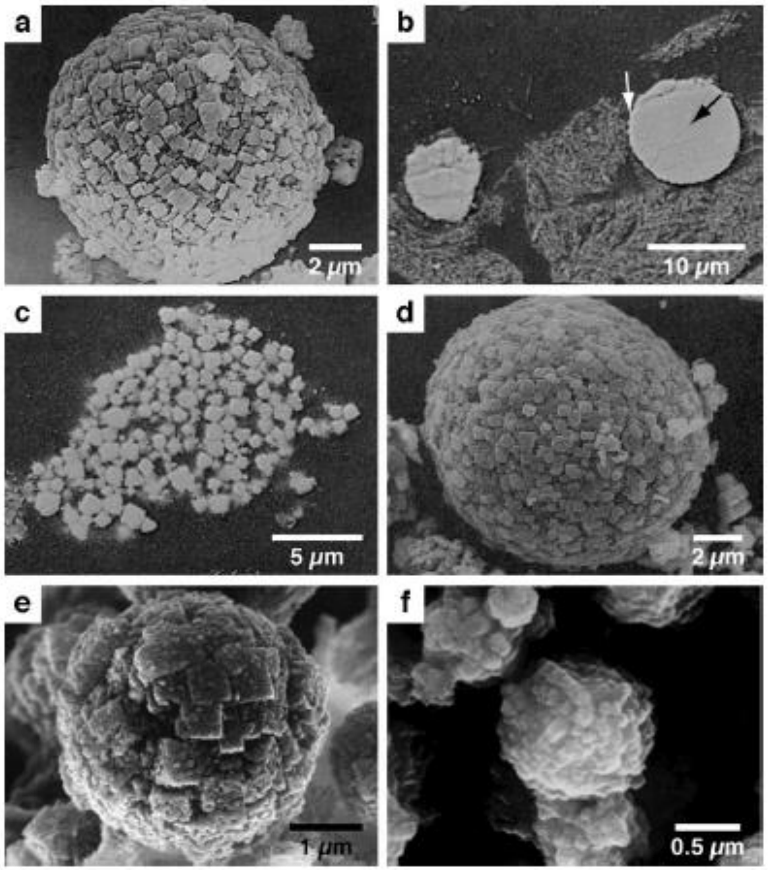


B22 7-8 m



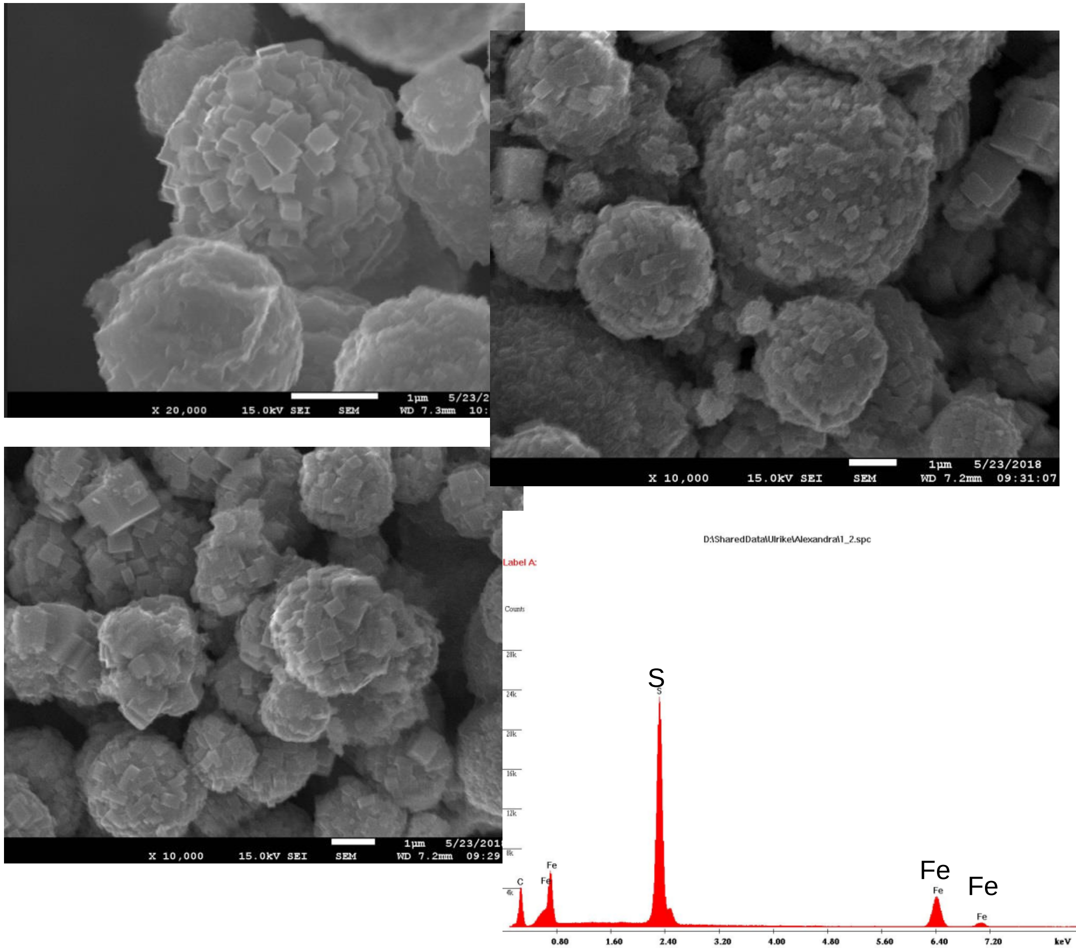
Results

Previous research:

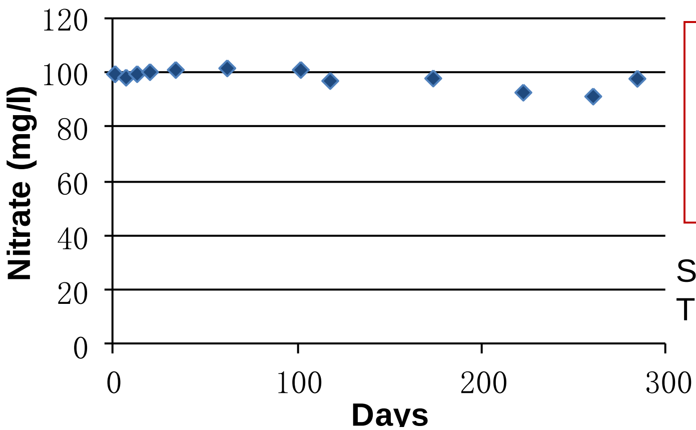


Ohfuji et Rickard, 2005

TU Darmstadt:

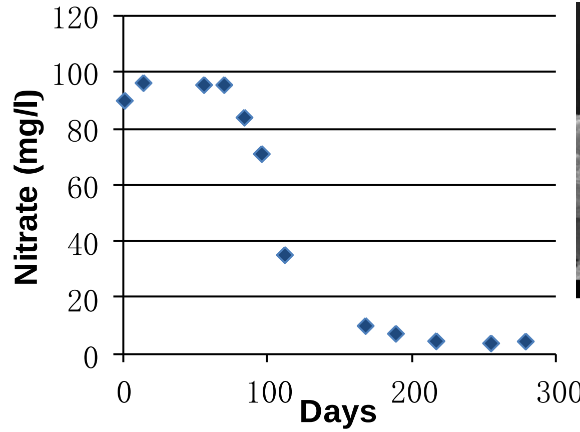


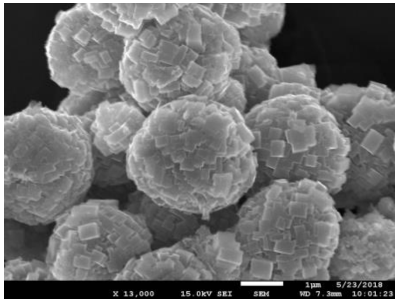
Results



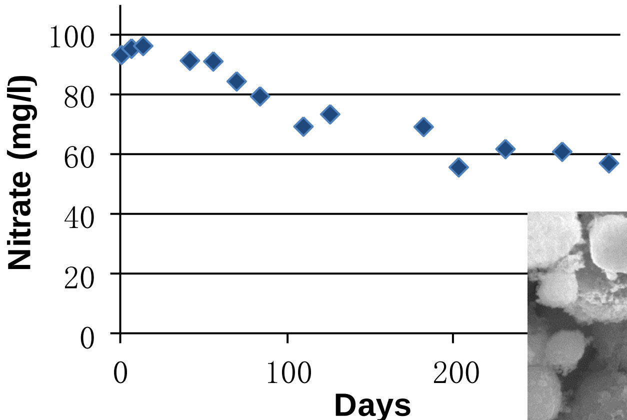
Soil sample without any reactive phases

Sulf.<0,03 mg/kg,
TOC <0,1 MA%

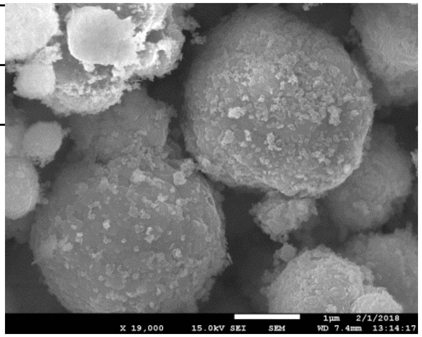


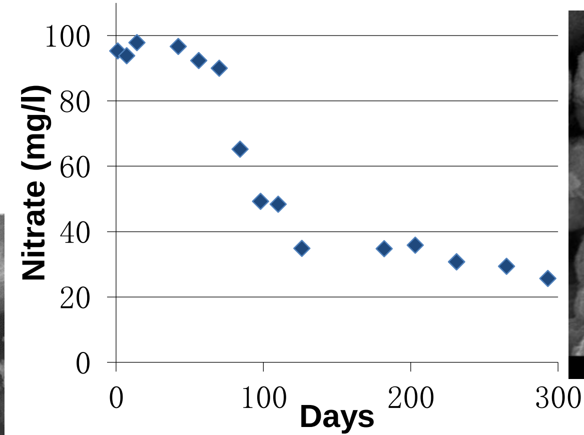


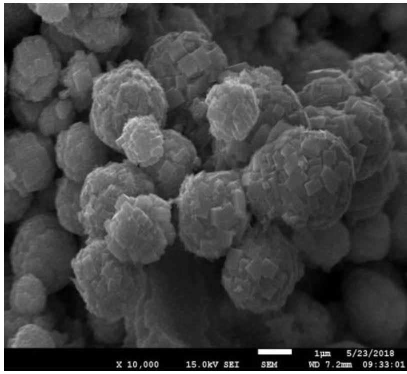
42 % of pyrite reacted



17 % of pyrite reacted







34 % of pyrite reacted

$$5\ FeS_2 + 14\ NO_3^- + 4\ H^+ \Rightarrow 7\ N_2 + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2\ H_2O$$

1 mg NO_3 can react with 0,64 mg pyrite

Conclusion

- The **laboratory method** developed in this study is suitable for the determination of denitrification rates and the identification of different processes during denitrification.

- The results showed that there are **reactive phases** in the sediments (pyrite, organic carbon), but there is difference in their efficiency with respect to denitrification.

- Sediment samples were examined using a scanning electron microscope (SEM) and in some cases a raspberry-shaped mineral, called **framboidal pyrite** was found – Results of batch experiments indicated that it is a **reactive** mineral.

Outlook

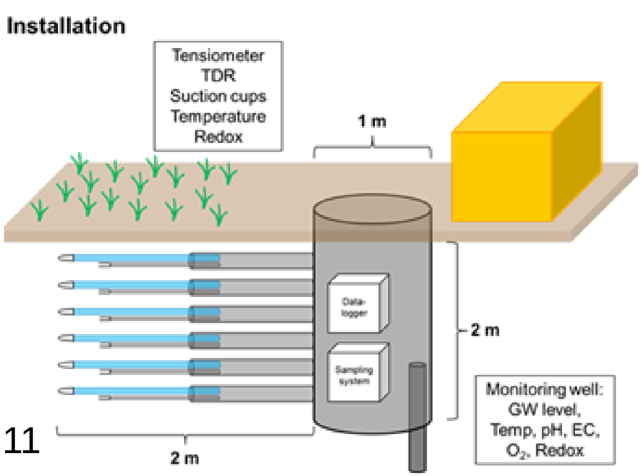
Installation of monitoring tools on the field

Hessian Ried

- Area: 1200 km^2
- Approx. 33 % of the area is intensively used for fertilizer-intense agriculture (asparagus, wheat, strawberries)
- **Monitoring station:**
  - soil moisture (tensiometers)
  - infiltrating water (suction cups)
  - redox conditions (redox probe)
  - groundwater quality (piezometer) (multilevel piezometer)

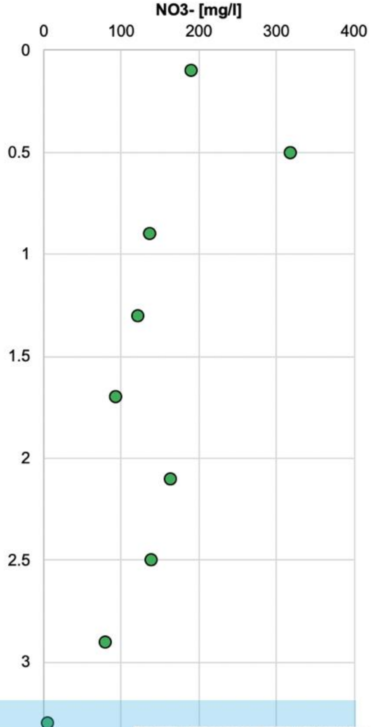
unsaturated z. (soil moisture, infiltrating water, redox conditions)

saturated z. (redox conditions, groundwater quality)



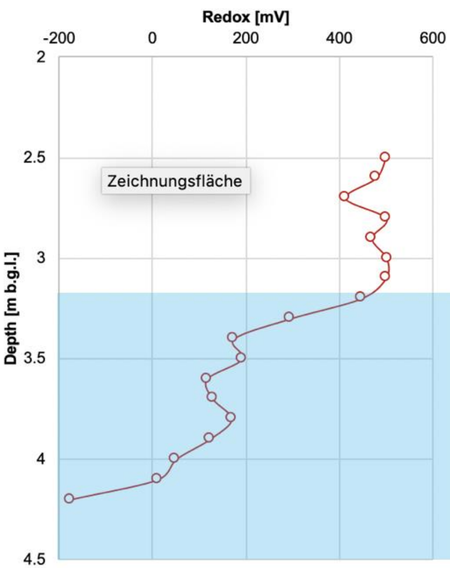
Outlook

Leaching test



Redox probe (Paleoterra)

sensors



Water sampling

- Suction cup (unsat. zone 1 m b.g.l): 89,2 mg/l
- Bailer sample (4 m): 29,4 mg/l
- Bailer sample (10 m): 1,1 mg/l

Results of laboratory and field monitoring → 3D reactive transport model

Thank you for your attention!

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675120

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