Tracing the fate of nutrients in agricultural catchments by stable isotope techniques

Part I: The Hessian Ried Story

Christoph Kludt, Alexandra Giber, Christine Kühbeck, Frank-Andreas Weber, Christoph Schüth, Kay Knöller

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Outline

Background

- The nitrate problem in Europe
- The monitoring/analytical/experimental approach

Results

- Part I: The Hessian Ried Story:
  Denitrification in groundwater
- Part II: The Selke Story:
  Denitrification hot spot in a river stretch
- Part III: The Bode Story:
  Denitrification potential in a mesoscale river catchment

Conclusions

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European Commission - Press release

Water: Commission re... ...tice of the EU over water pollution cause...

Brussels, 28 April 2016

Germany in Court over w...

The European Commission is referring **Germany** ... take stronger measures to combat water pollution caused by nitra... ...nts to grow and they are widely used as fertilisers. H... ...ause ... ...tion, with consequences for people's ... Today's decision ... s a reason... ...2014.

GERMANY

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.

EU takes Germany to court over high nitrate levels

EU sues Germany over environmental standards

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Nitrogen surplus in Europe in kg/ha (2005)

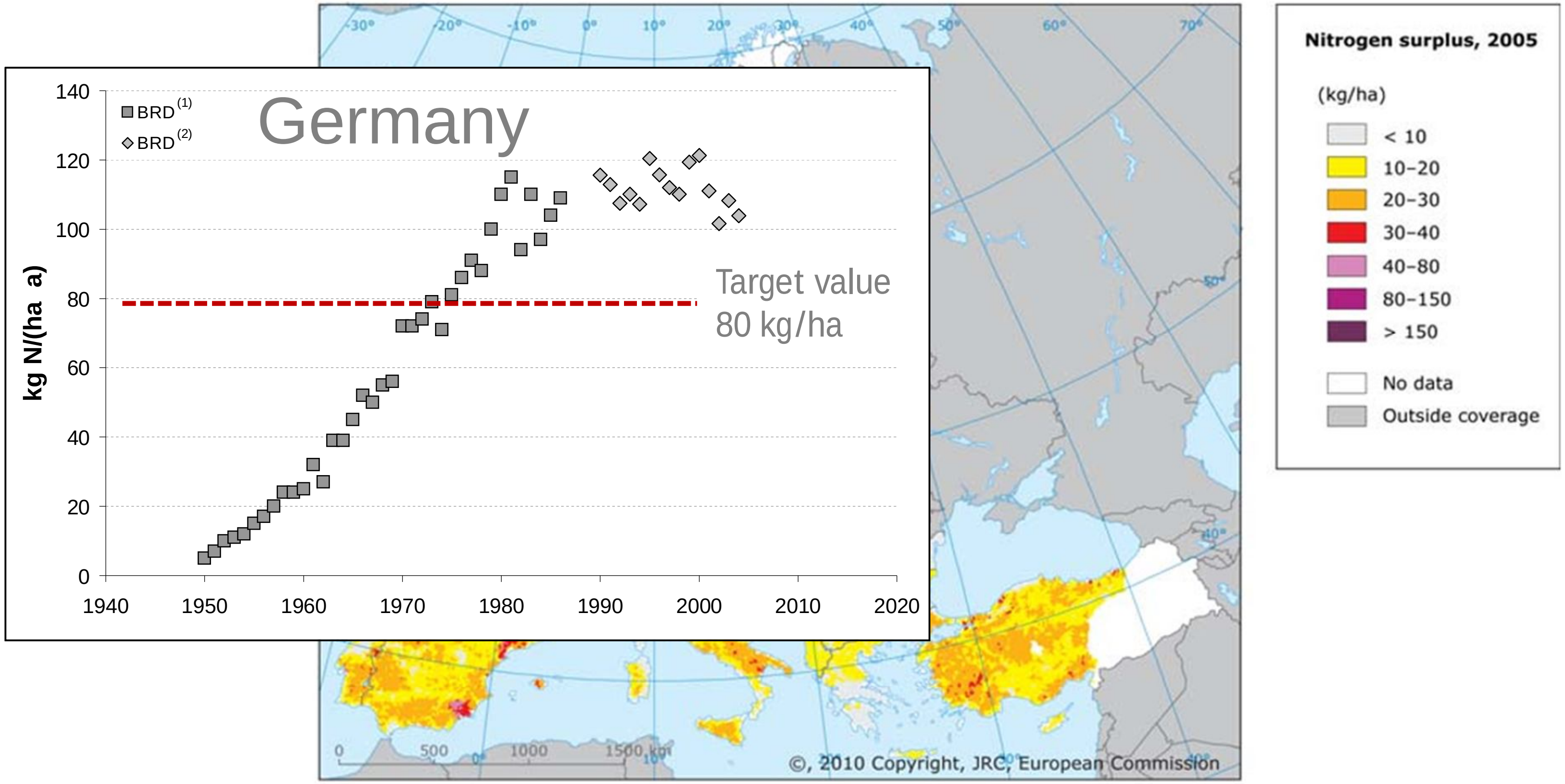


Figure 4: Estimated nitrogen surplus (the difference between inputs and uptake by crops, meat or milk production) in 2005 for Europe. Surplus nitrogen in the soil as a result of excessive application rates and/or low plant uptake can cause an increase in the mineralisation of organic carbon, which in turn leads to an increased depletion of carbon from soils.

Source: JRC/Bouraoui et al., 2009.

Nitrogen surplus and nitrate in groundwater

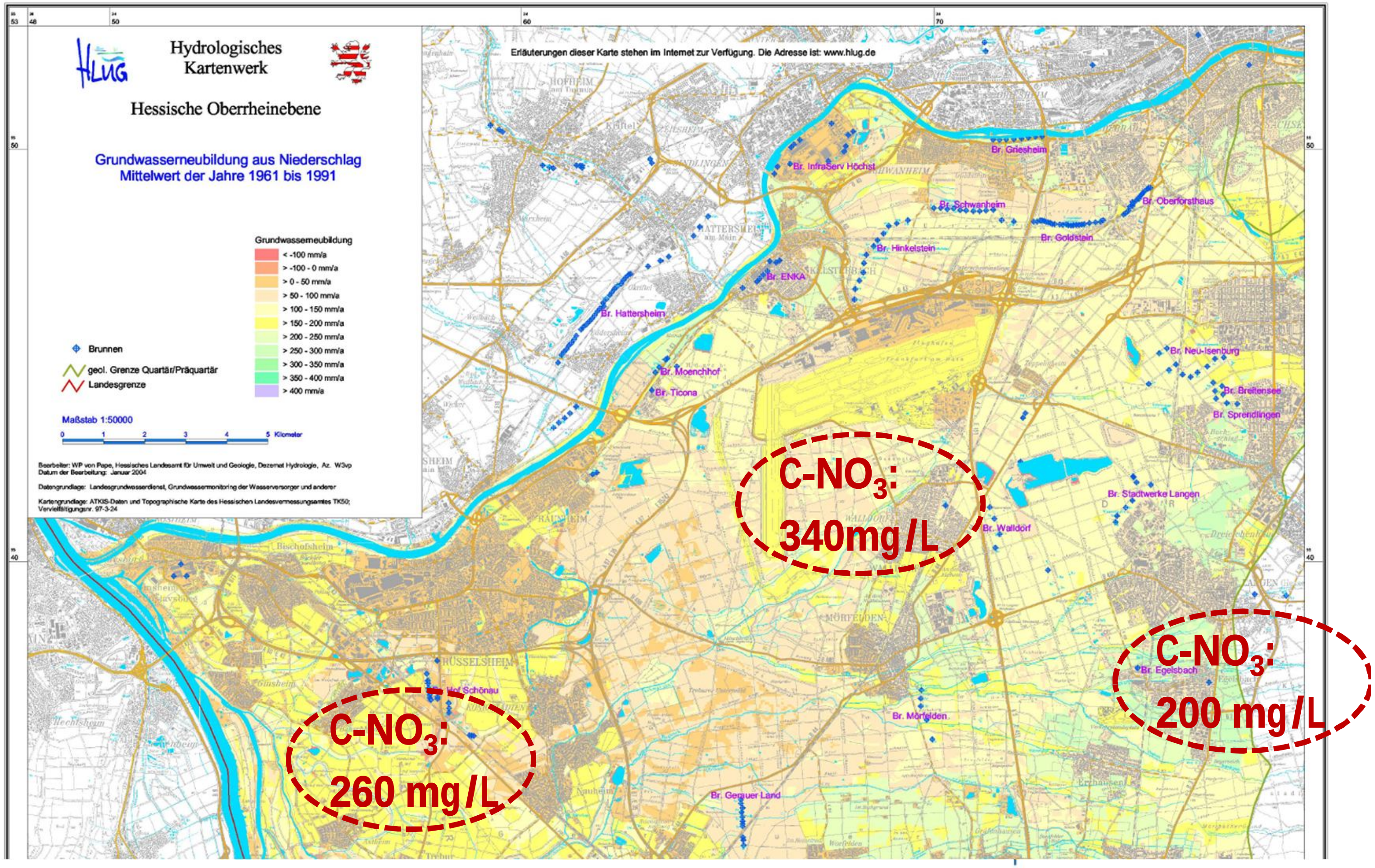
What are the resulting nitrate concentrations in leachate water considering nitrogen surplus ?

$$c_{NO_3} = \frac{440 \cdot N}{Q_{SW}}$$

$c_{NO_3^-}$ =
Nitrate in leachate (mg/l)

N =
Nitrogen excess (kg/h)

Q_{SW} =
Groundwater recharge
(mm/a)



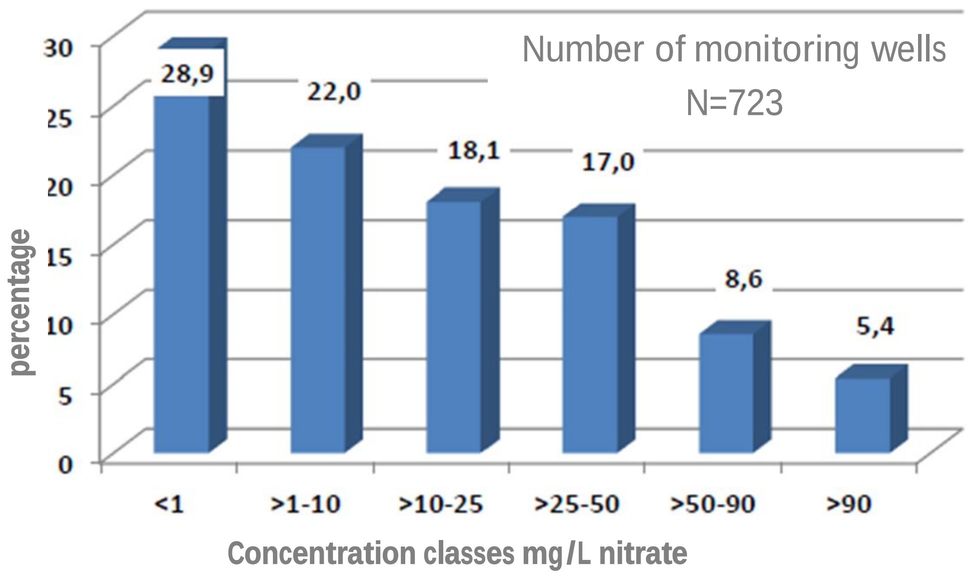
Nitrate in groundwater - Germany

Status of groundwater bodies with respect to nitrate

Situation

About 27% of all GW bodies in Germany are in a poor chemical state due to high nitrate concentrations.

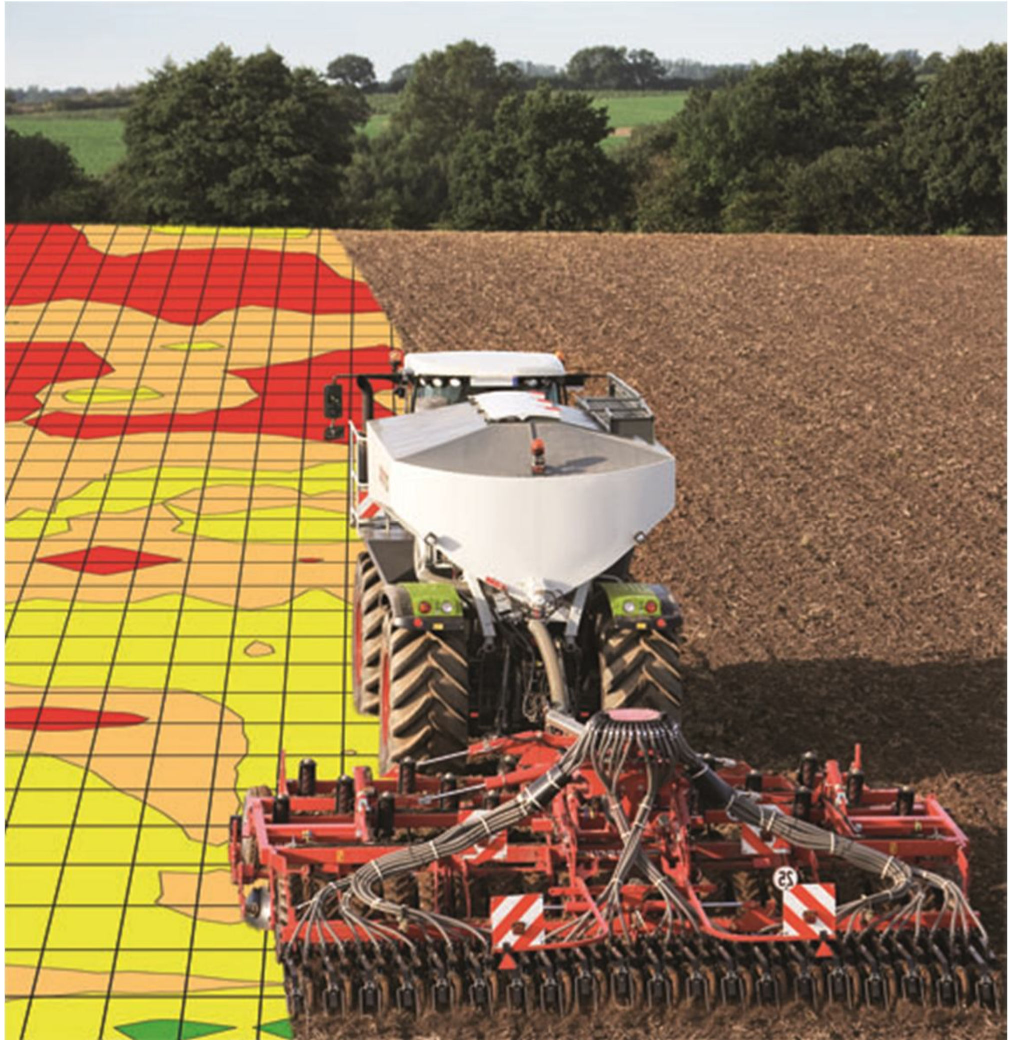
Distribution of nitrate concentrations in network monitoring wells



Potential solutions for the nitrate problem

Sustainable solution:

Reduction of N-surplus by good agricultural practice.



Potential solutions for the nitrate problem

Sustainable solution:

Reduction of N-surplus by good agricultural practice.

Non-sustainable solution:

Natural attenuation concept

Natural Attenuation

“Variety of physical, chemical, or biological processes that are at work in-situ, under favourable conditions, acting without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants” (NRC 2000)

Main processes “Nitrate Attenuation”:

- Assimilation and conversion to biomass (soil)
- Microbial nitrate reduction (denitrification)
- Dilution (mixing, diffusion, dispersion)
- *Sorption*

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Potential solutions for the nitrate problem

Sustainable solution:

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Denitrification - Reactions:

$4\ NO_3^- + 5\ CH_2O \rightarrow 2\ N_2 + 4\ HCO_3^- + CO_2$

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

➢ Microbial nitrate reduction (denitrification)

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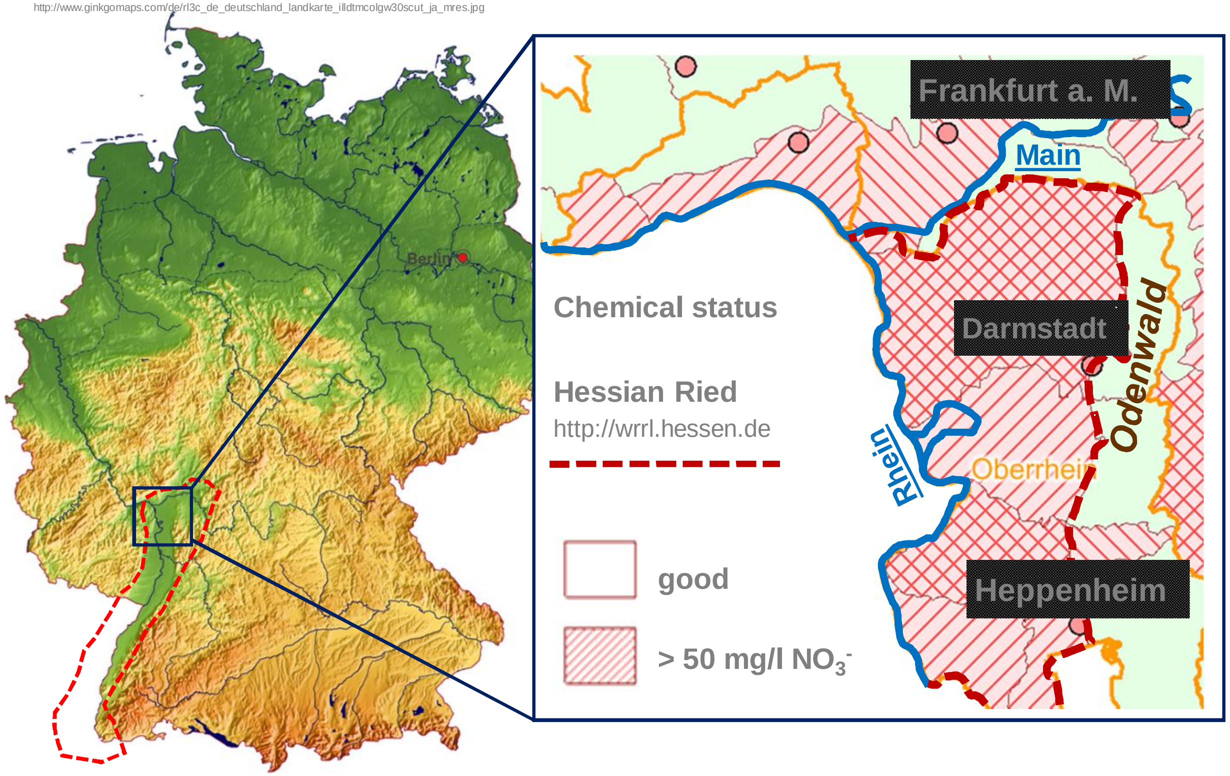
The field site: Hessian Ried

http://www.ginkgomaps.com/de/rl3c_de_deutschland_landkarte_illdtmcolgw30scut_ja_mres.jpg



Alluvial plain in the upper Rhine valley between the rivers Main (north), Rhine (west), Neckar (south), and the Odenwald mountains (east).

Thick sedimentary fill of the graben structure → great aquifer.

Covers an area of approx. 1200 km^2.

33% of the area is intensively used for agriculture.

Serves as a major drinking water source for the Frankfurt metropolitan area

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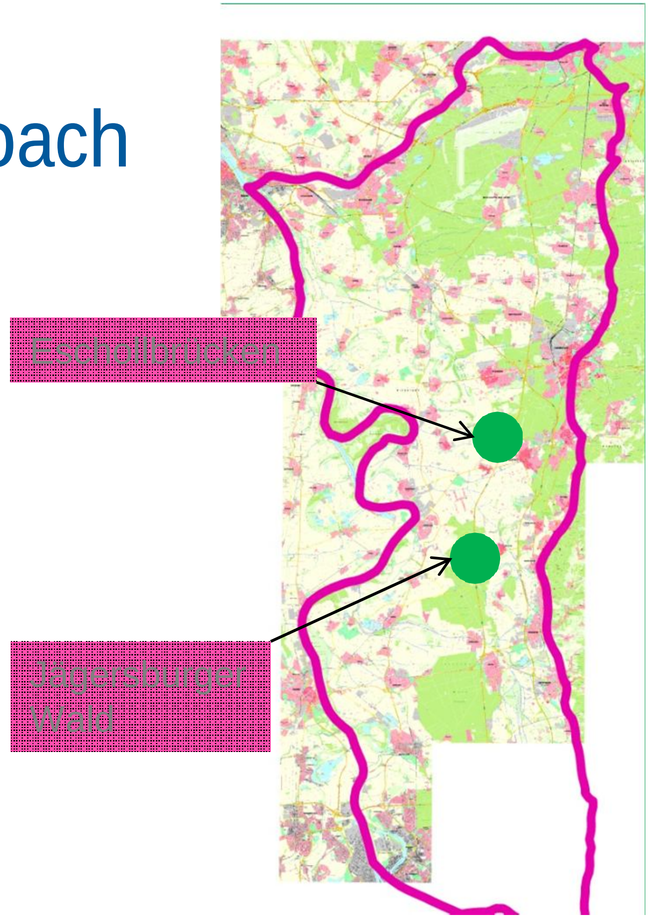
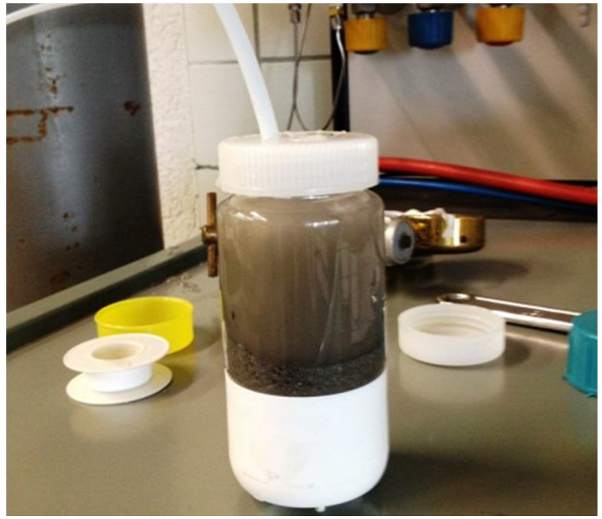
The experimental/monitoring approach



- Estimation of the denitrification potential using sediments from drilling cores
  - Sulfide- / Disulfide sulphur (CRS- Method, extern)
  - Organic carbon (Liquitoc II, TUD)

The experimental/monitoring approach



- Estimation of the denitrification potential using sediments from drilling cores
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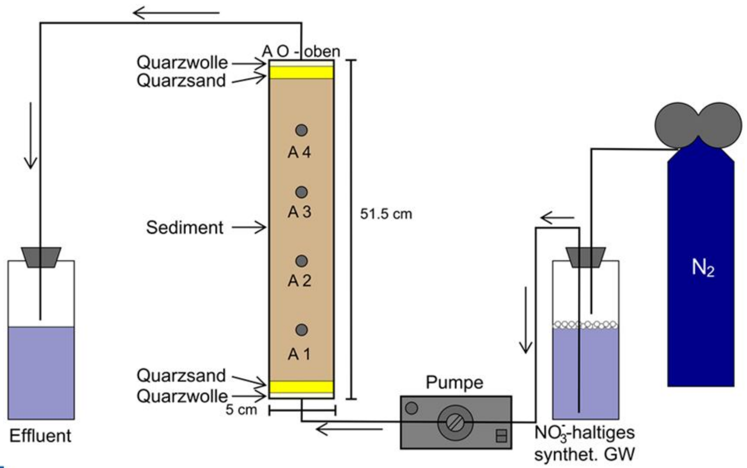
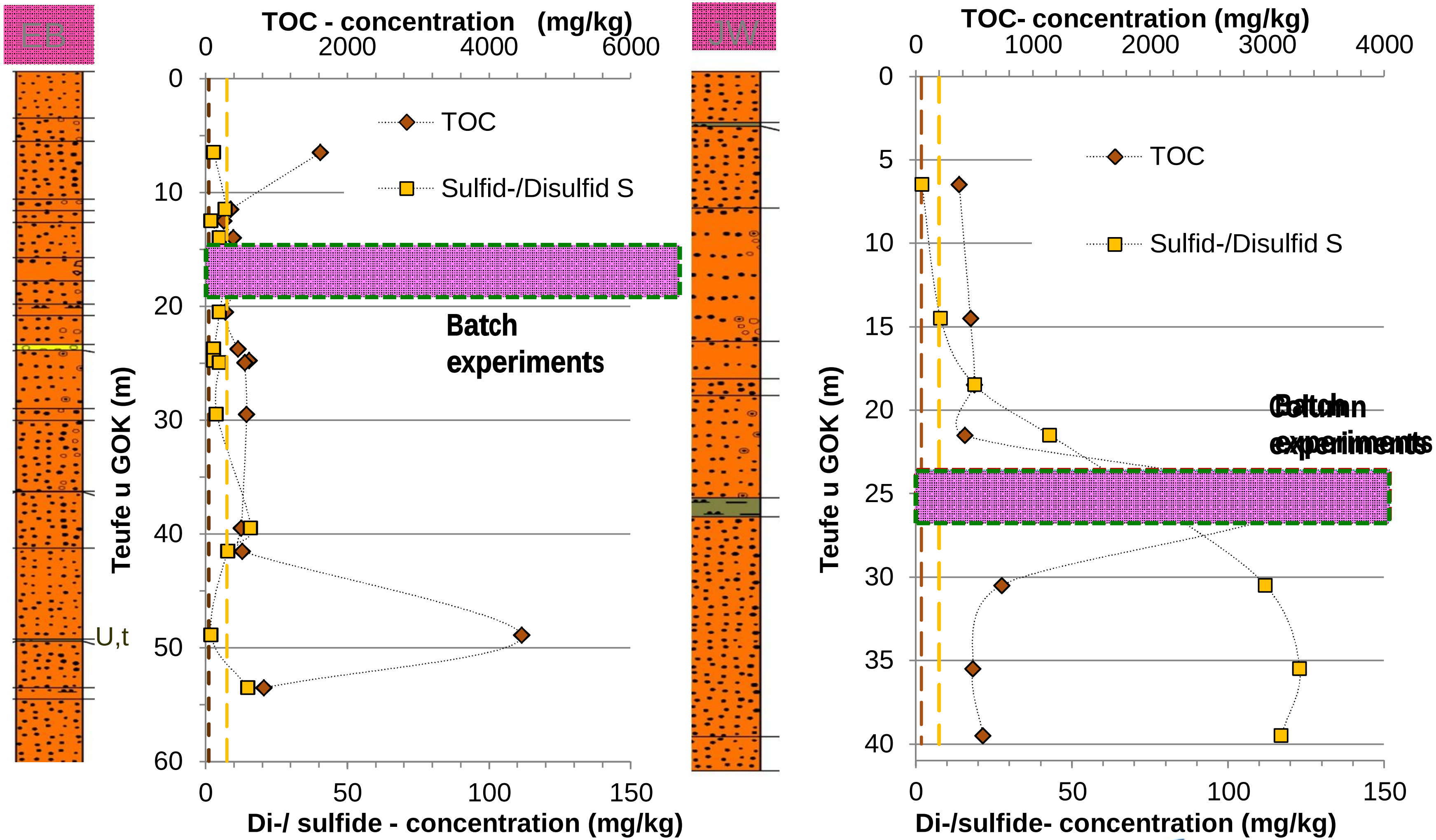
- Determination of prevailing denitrification pathways
  - Batch experiments
  - Column experiments



Nitrate reduction potential in drilling cores



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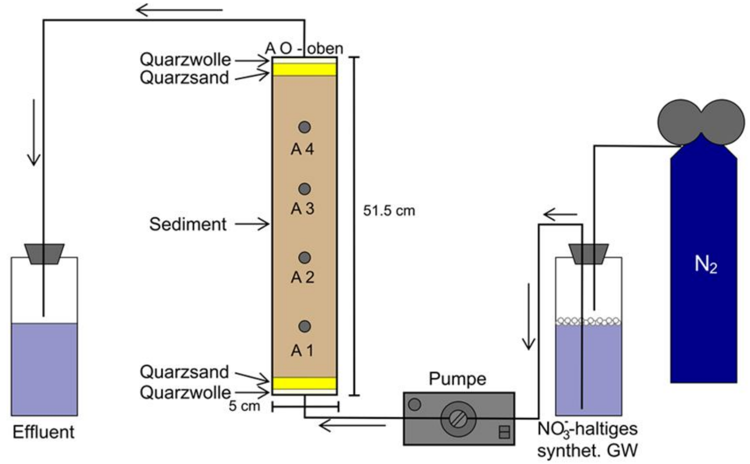
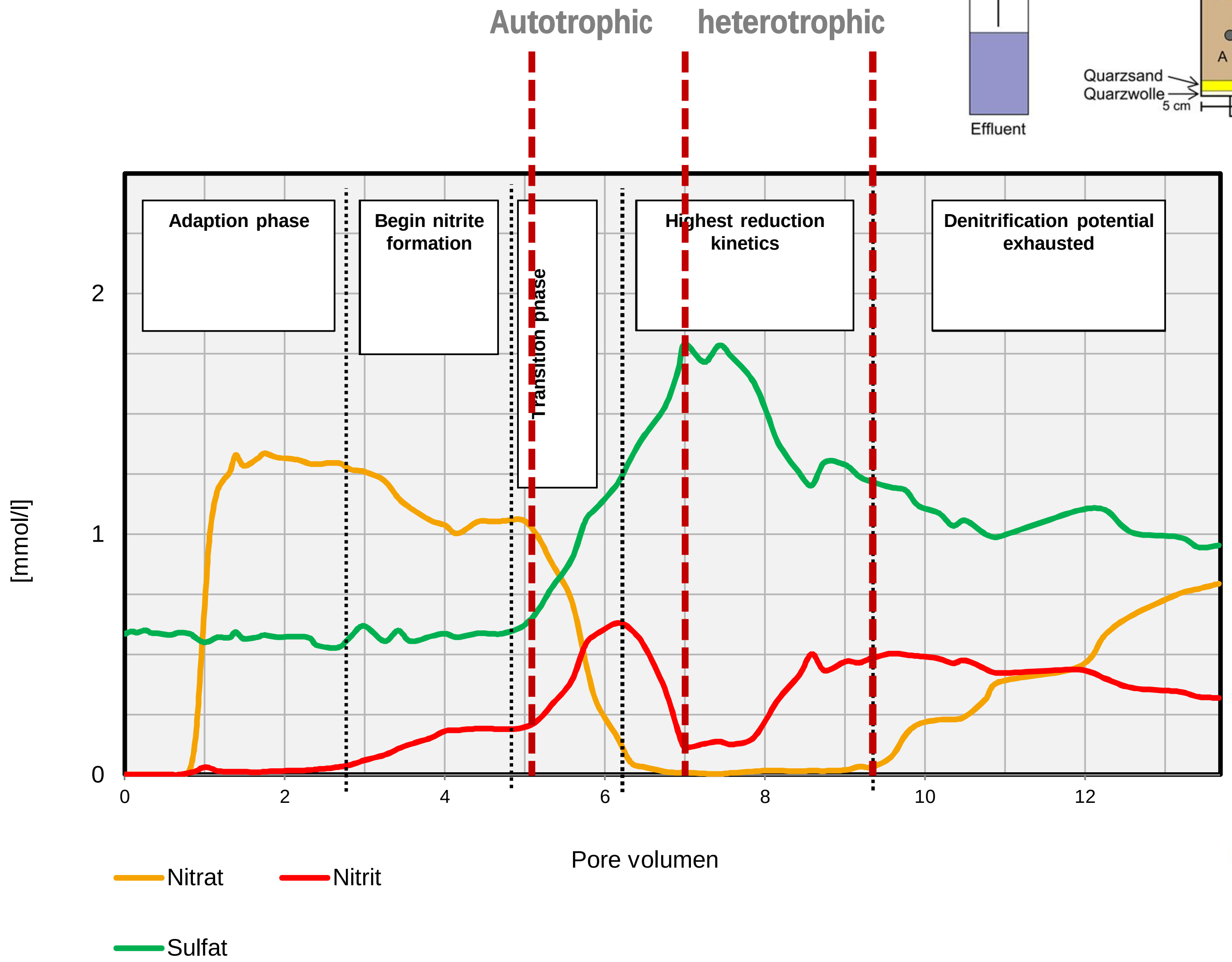
Column experiments





Column experiments

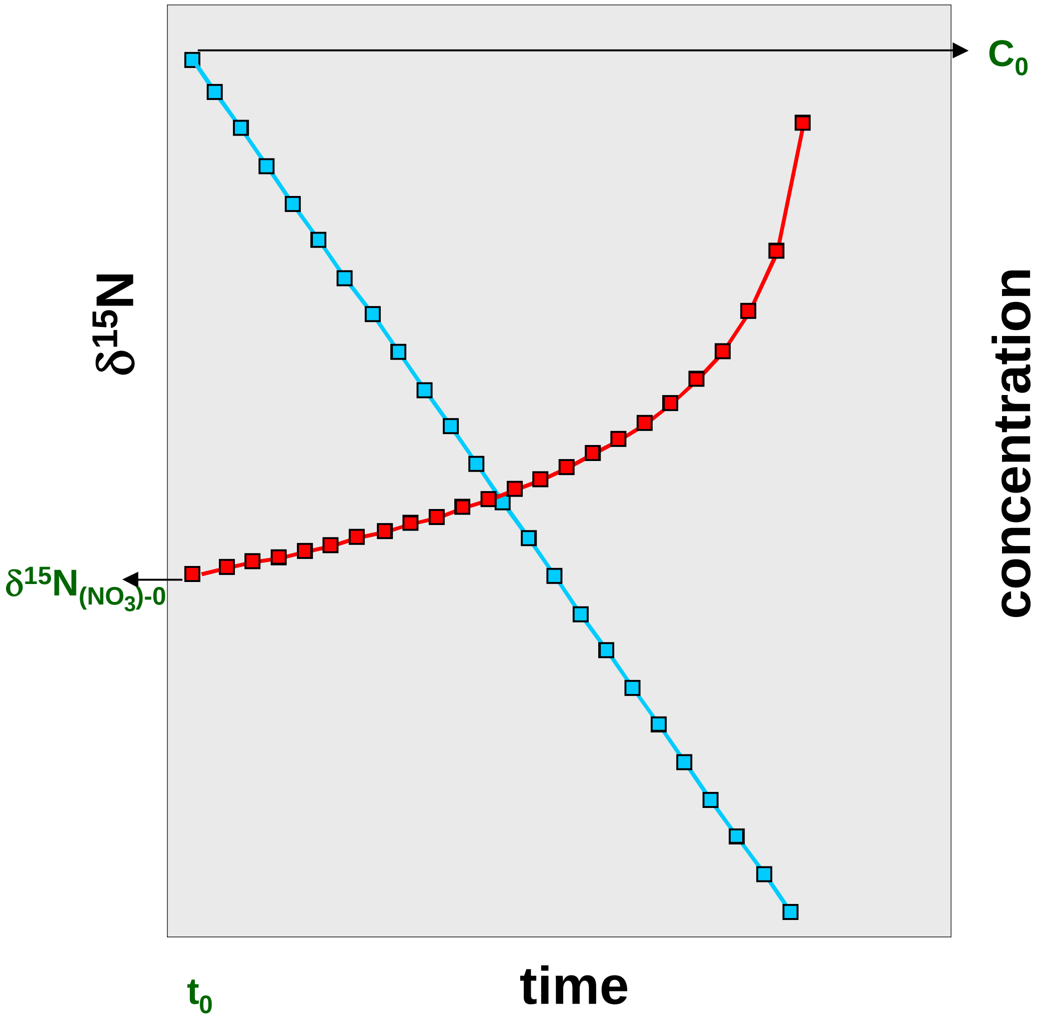
Isotope effects during denitrification

enrichment of heavy N and O isotopes in residual nitrate

(Rayleigh fractionation)

$$\delta_{NO_3} = \varepsilon \ln f + \delta_{NO_3-\text{initial}}$$

$(f = C/C_0)$



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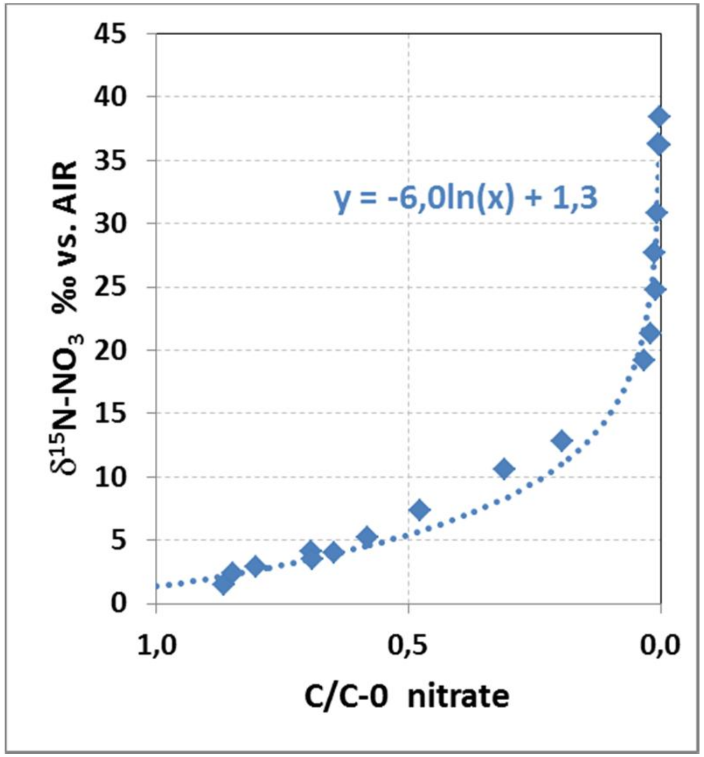

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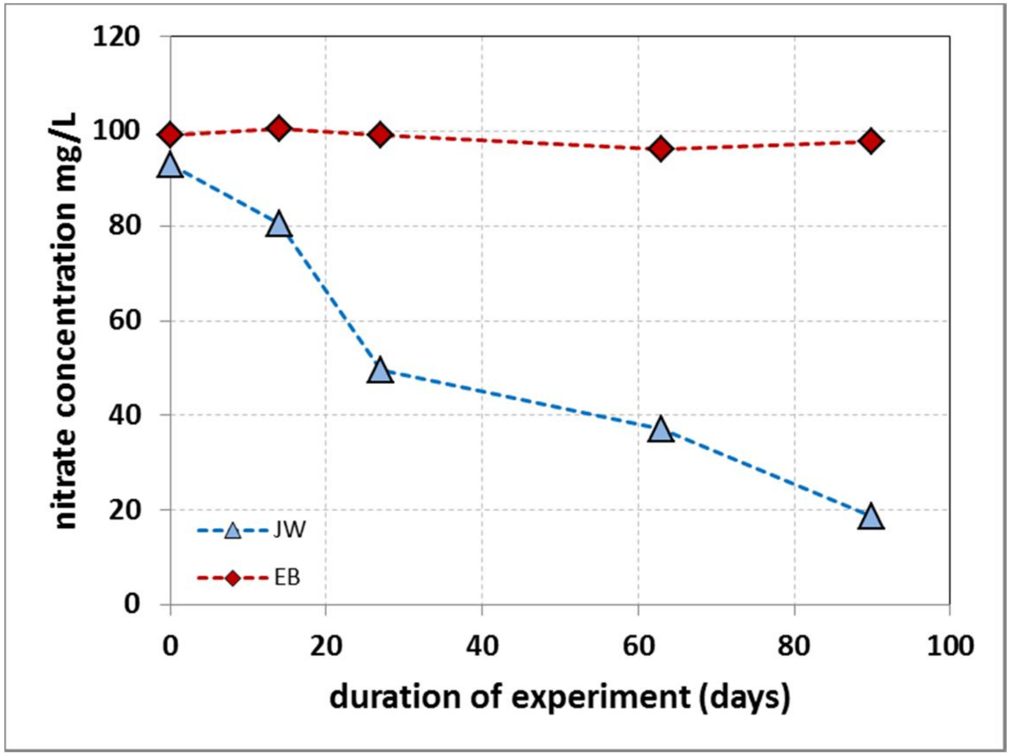
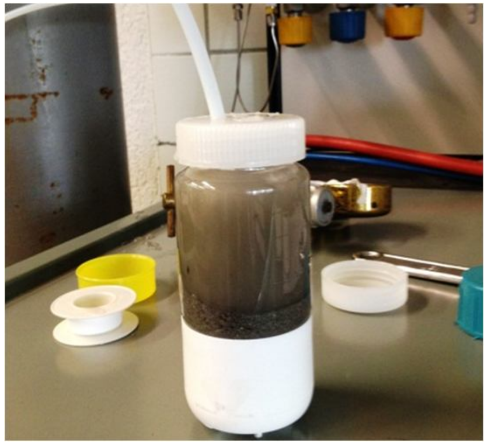
Batch experiments

5 identical batches with aquifer sediment from two different drilling cores

140 g sediment + 177 mL synthetic groundwater (NO_3: 100 mg/l, SO_4: 125 mg/L)

nitrate concentrations





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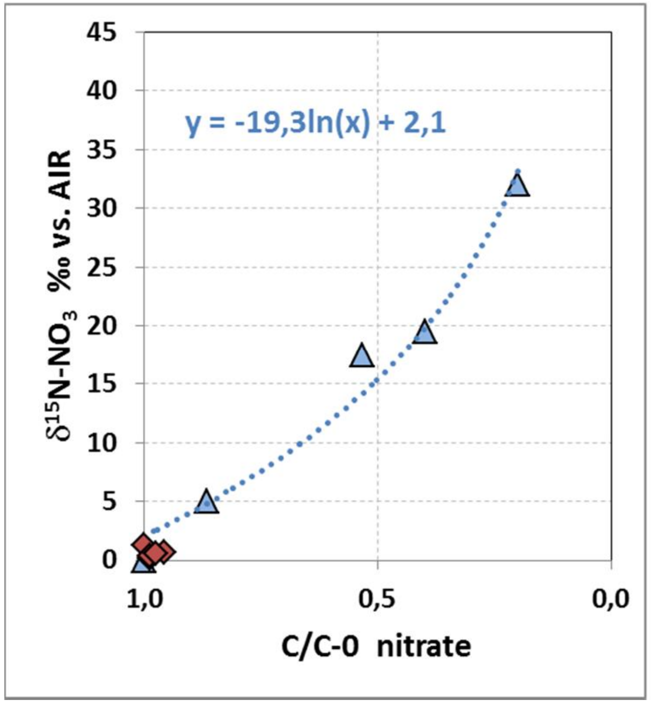
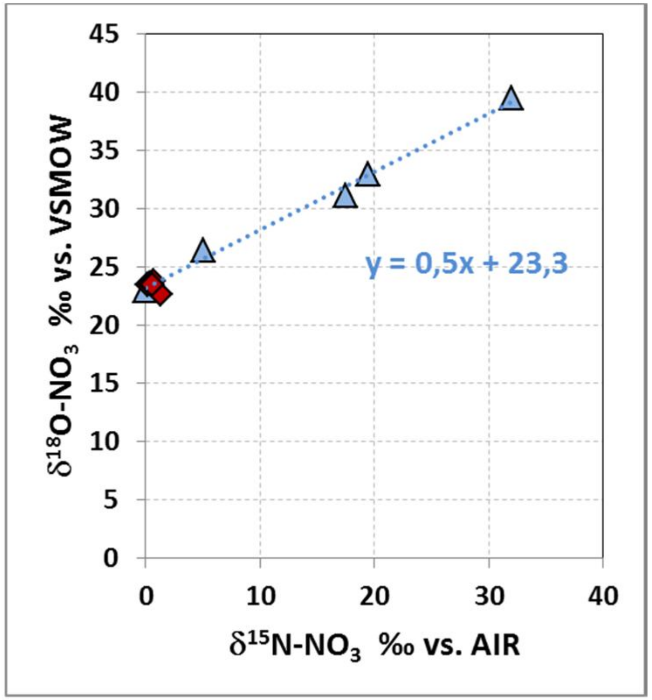
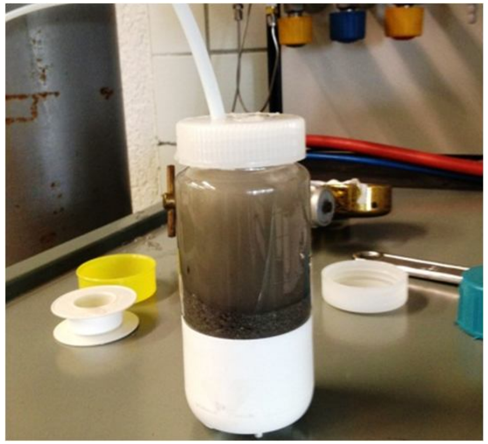
nitrate isotopes







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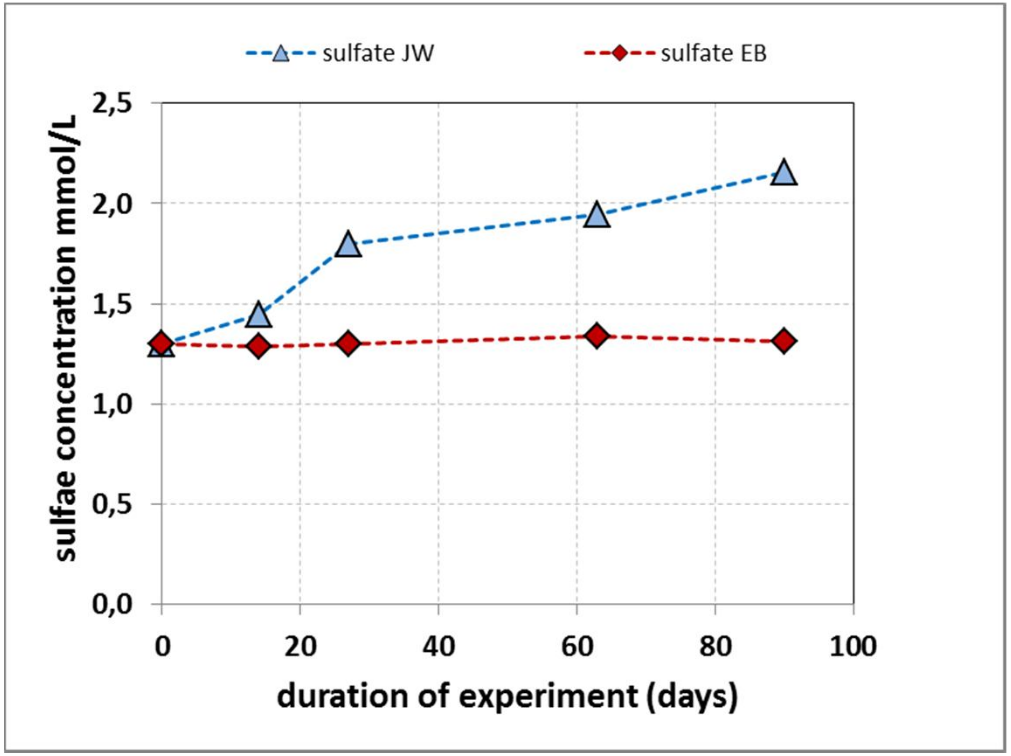
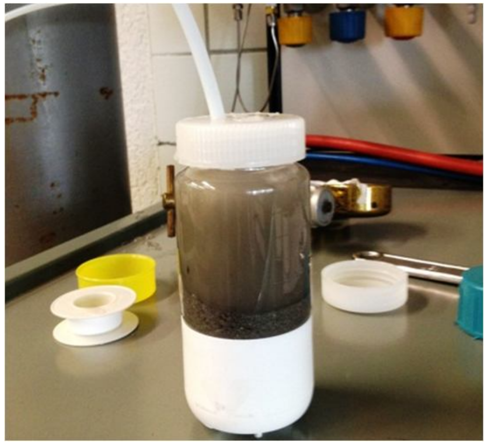
sulfate concentrations





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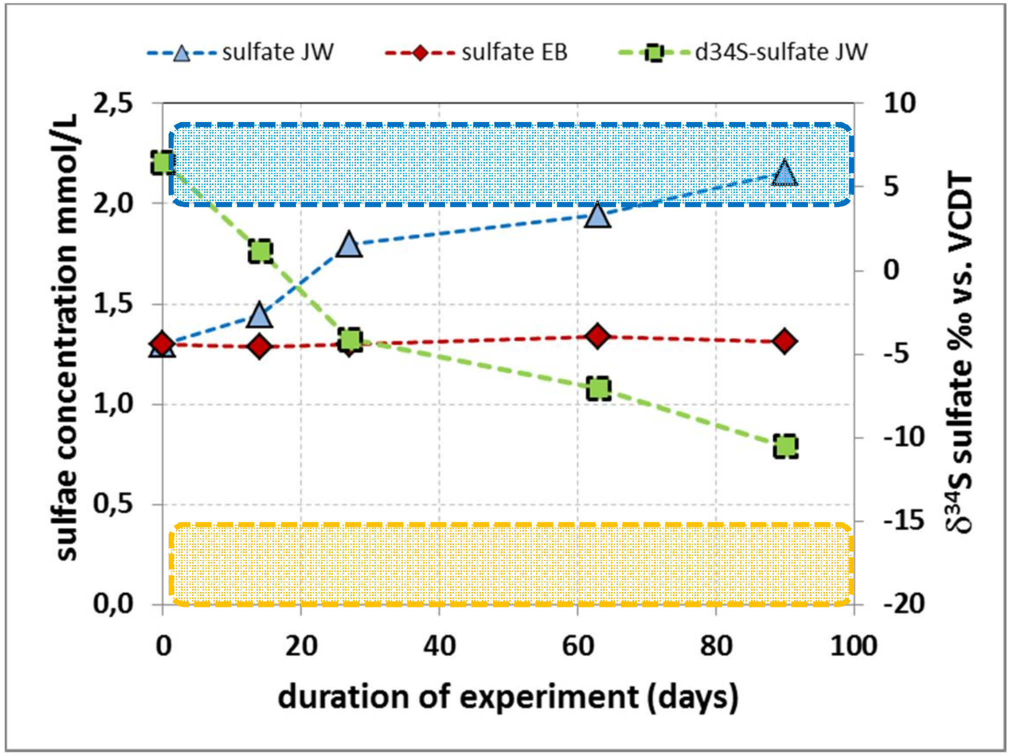
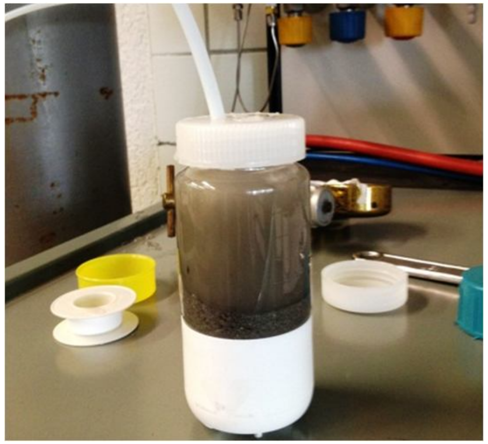
sulfate concentrations and isotopes





$\delta^{34}S$-SO_4-background: +5...+8 ‰,

$\delta^{34}S$-SO_4 from sulfide oxidation: -15..-20 ‰

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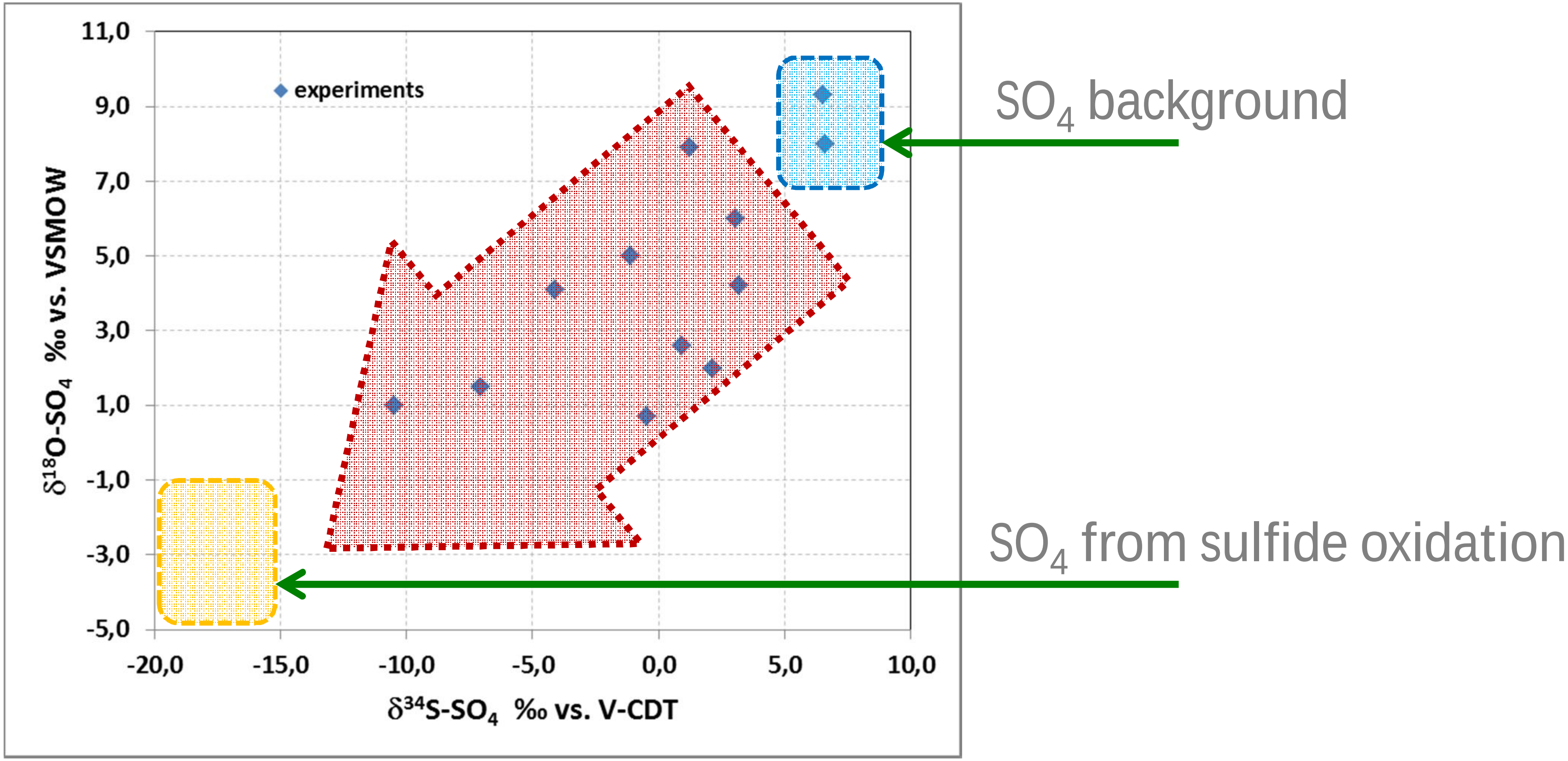
Insights from isotopic composition of sulfate



Autotrophic denitrification seems to be the prevailing pathway during experiments

despite TOC >> FeS_2

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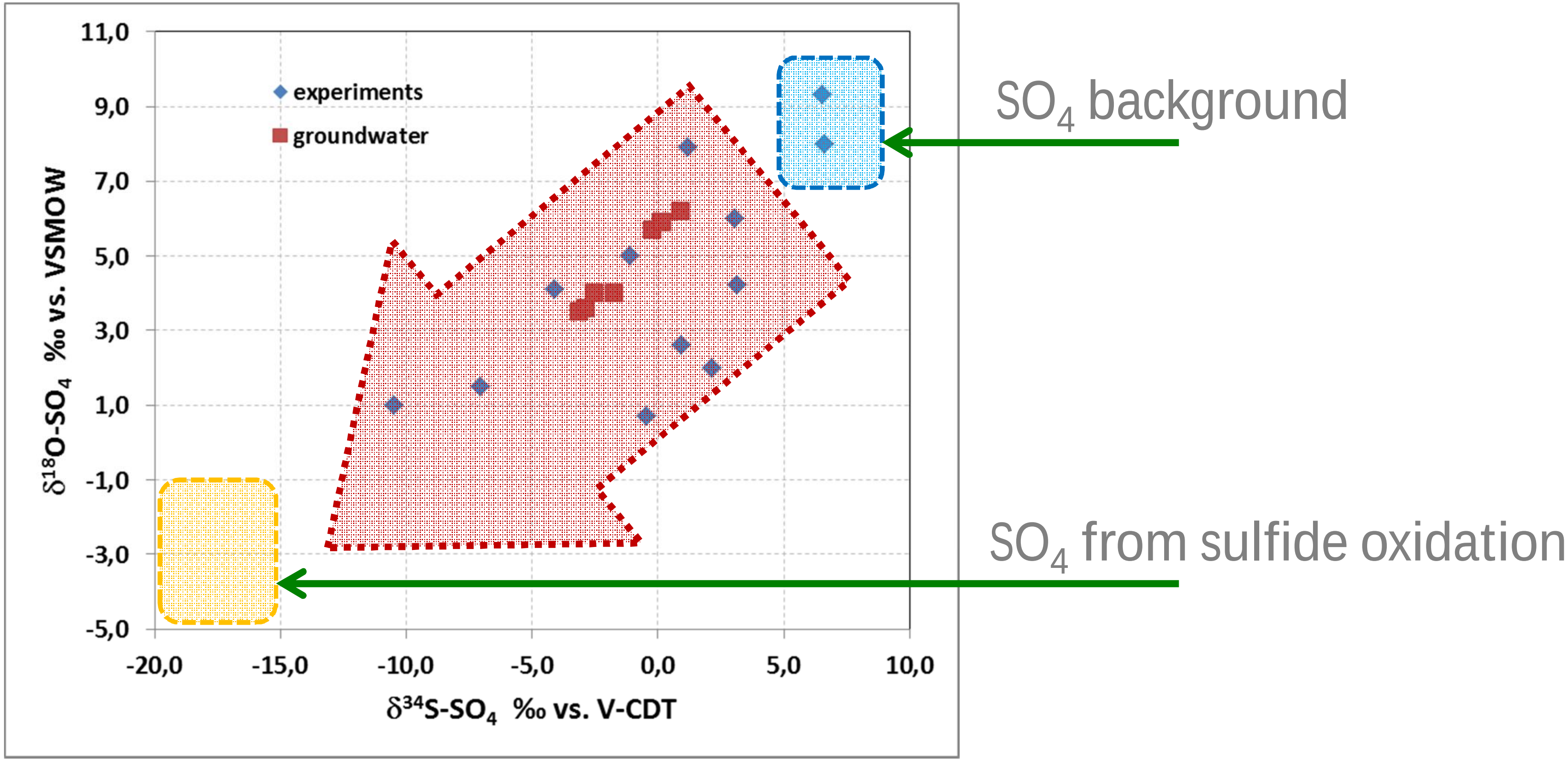
Insights from isotopic composition of sulfate



Autotrophic denitrification seems to be of major importance in the aquifer

despite TOC >> FeS_2

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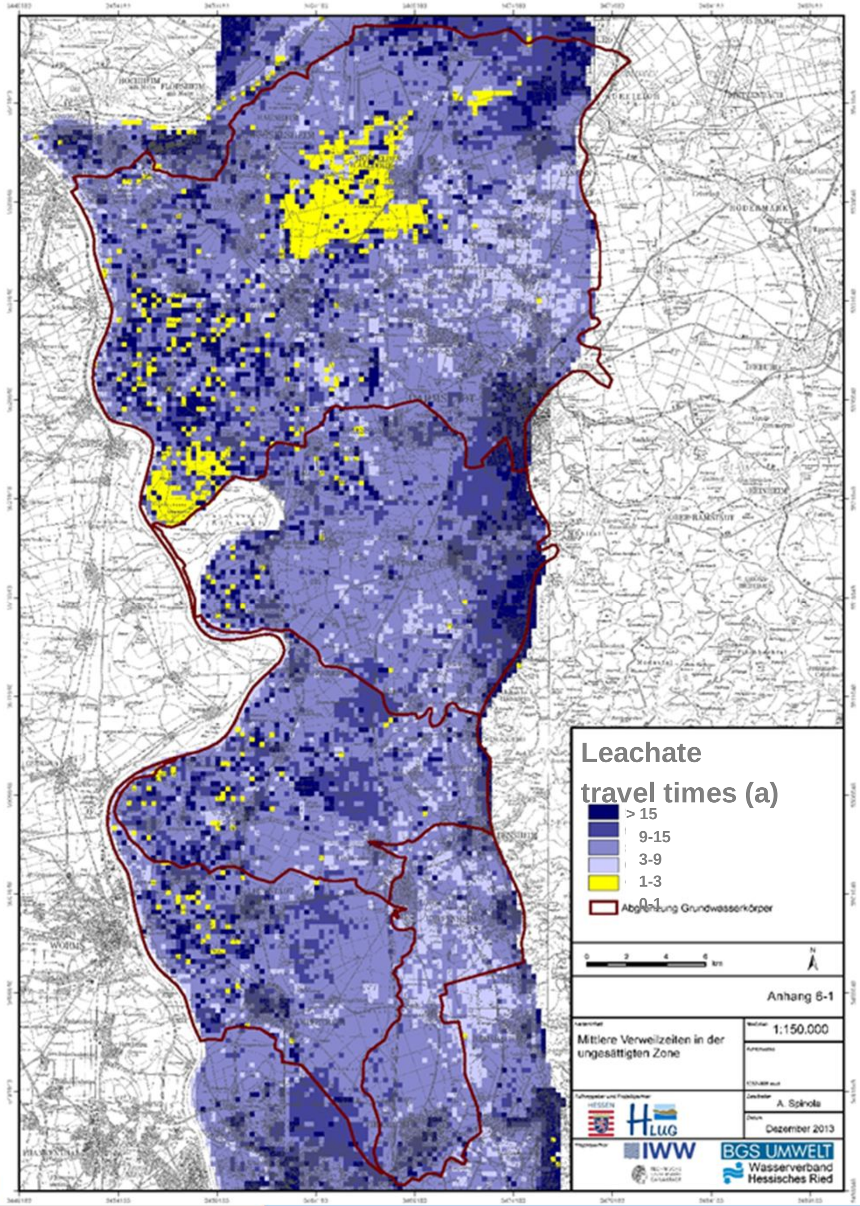
Implication for Water Framework Directive

Meeting the targets of the WFD (good chemical status of groundwater) at the groundwater surface:

Time frame is dependent on (i) time needed to change agricultural practices <u>plus</u> (ii) travel time of leachate through the unsaturated zone.

In the Hessian Ried targets could be met at the groundwater surface e.g. for 17% of the area within 3 years after changing agricultural practices and for 10 % in more than 15 years.

For some monitoring wells of the WFD with deeper screens, concentrations will be high for decades to come or will even increas due to exhausted reduction potential on a flowpath.



Travel times for leachate through the unsaturated zone

Modell: MIKE-SHE (BGS Umwelt)

Tracing the fate of nutrients in agricultural catchments by stable isotope techniques

Part II: The Selke Story

N. Trauth et al. (UFZ Department Hydrogeology), K. Knöller

mass twin

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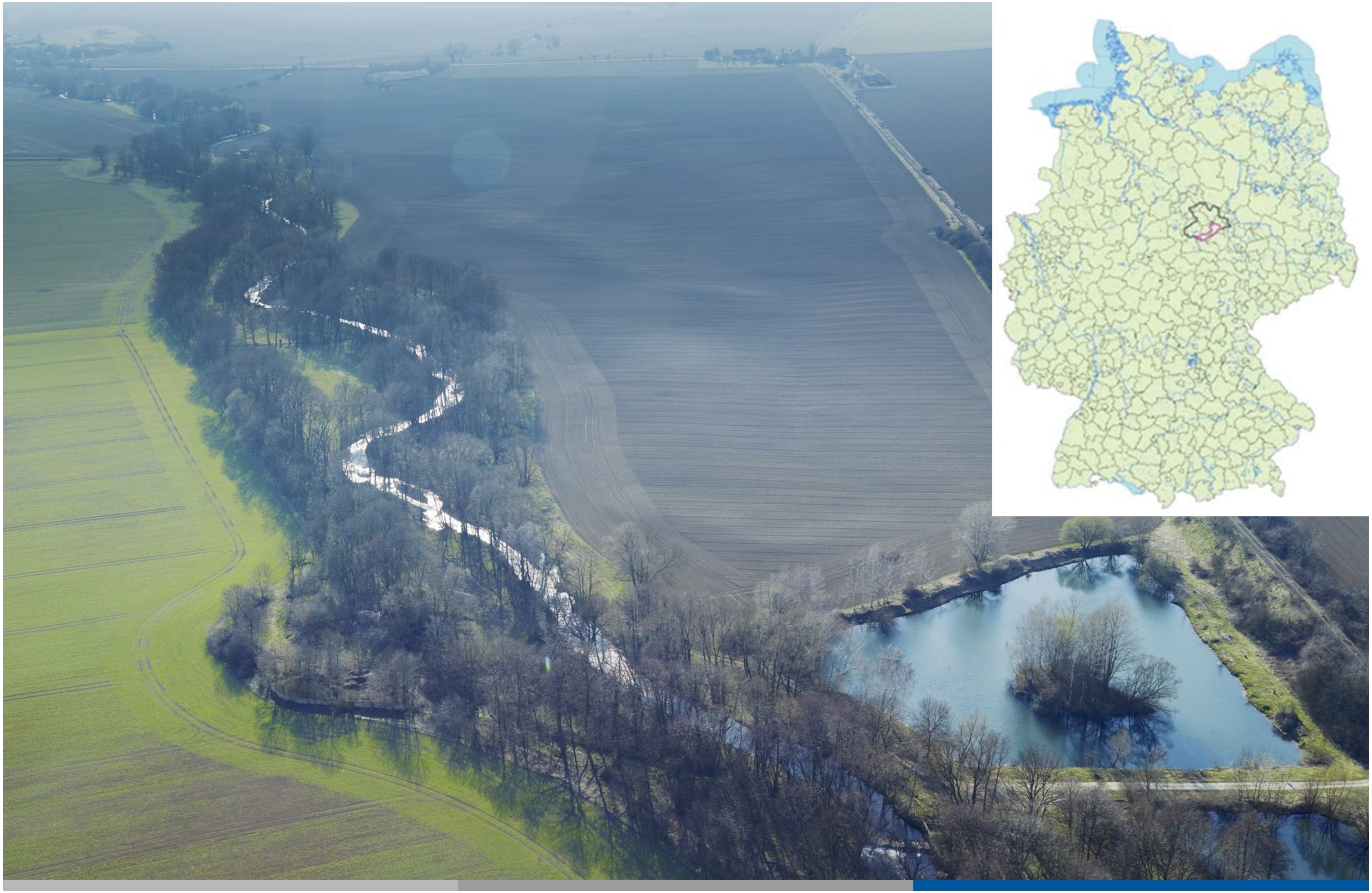
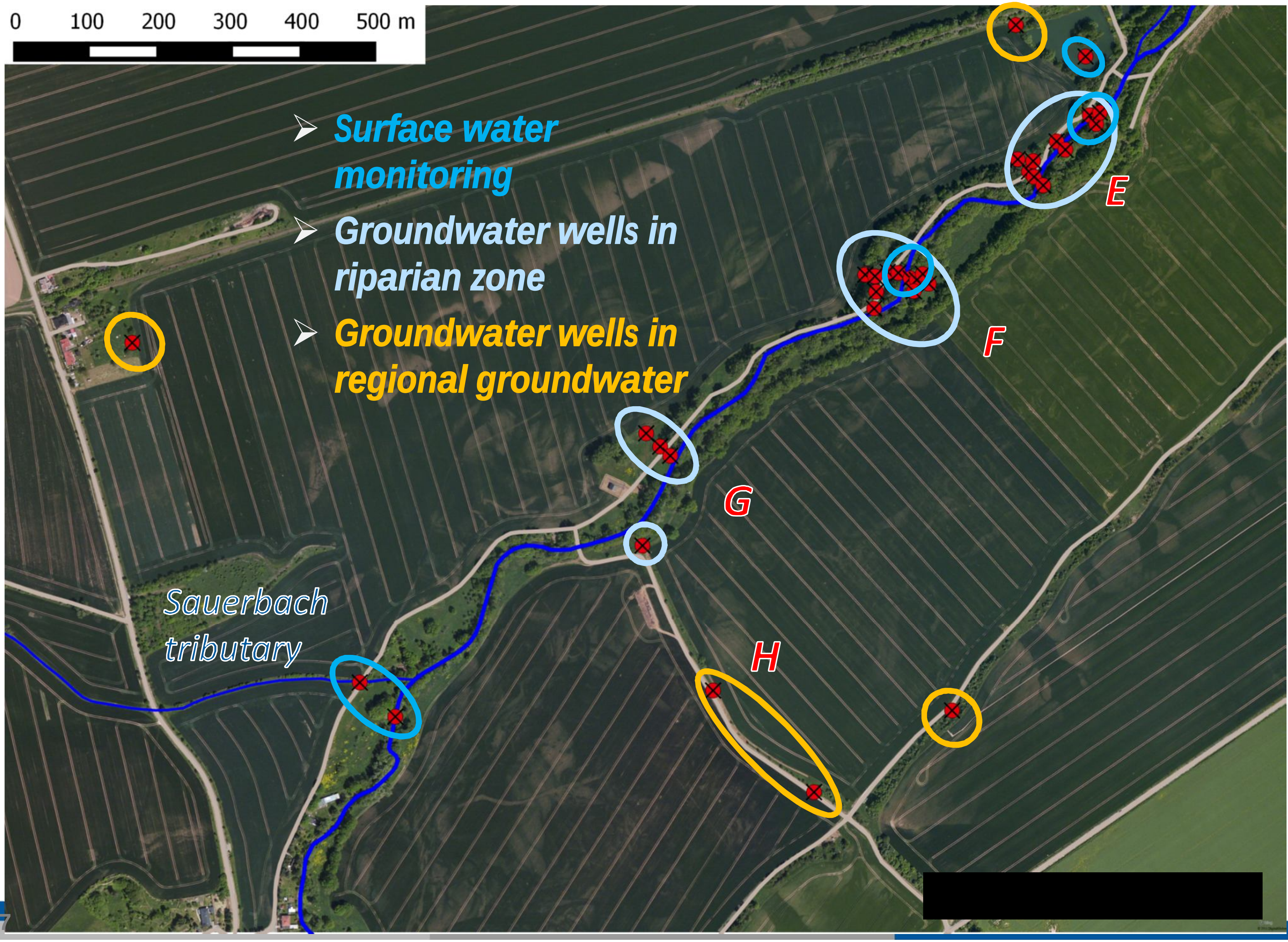
Impact of groundwater/ surface water exchange on the fate of nitrate in groundwater

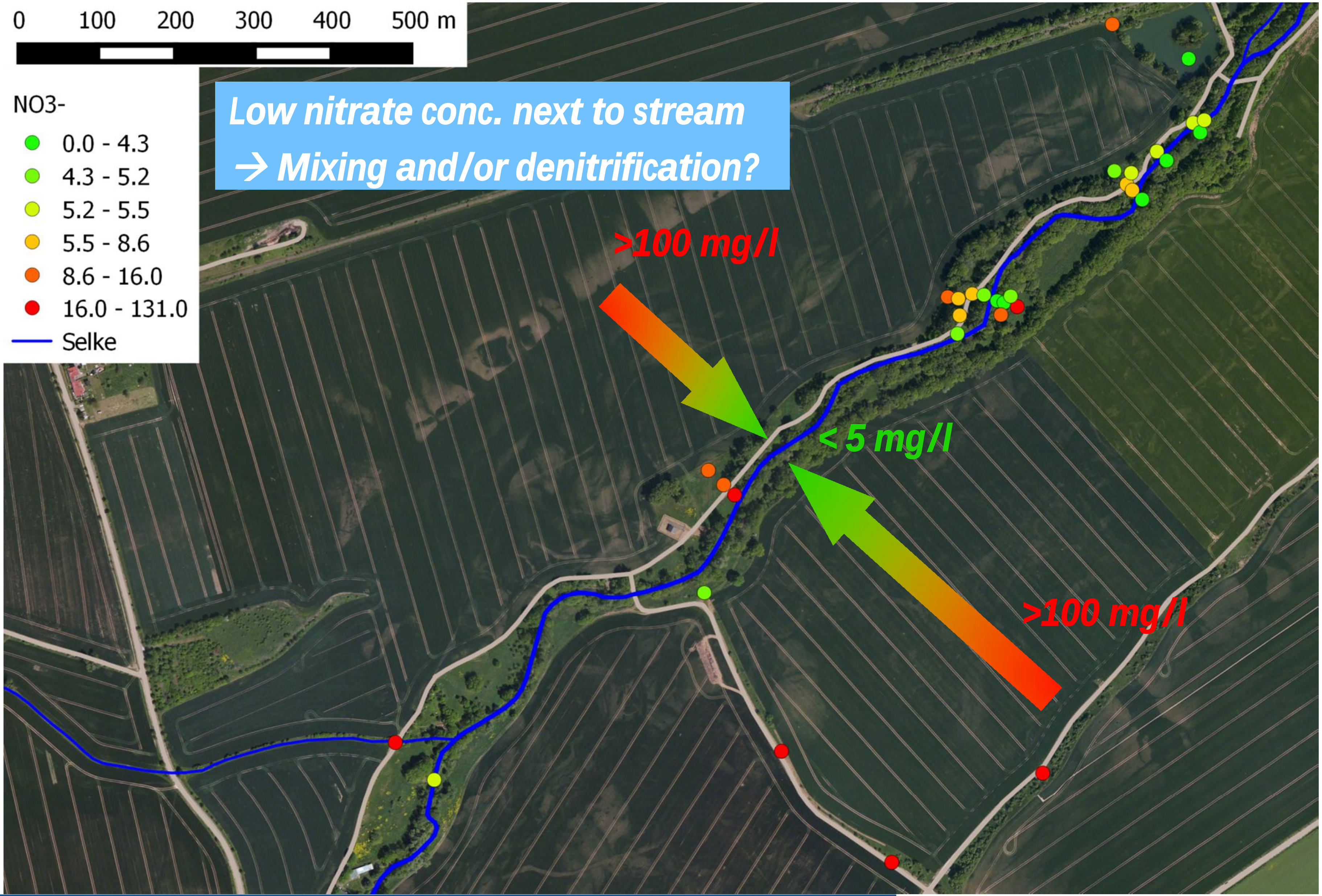


Installations



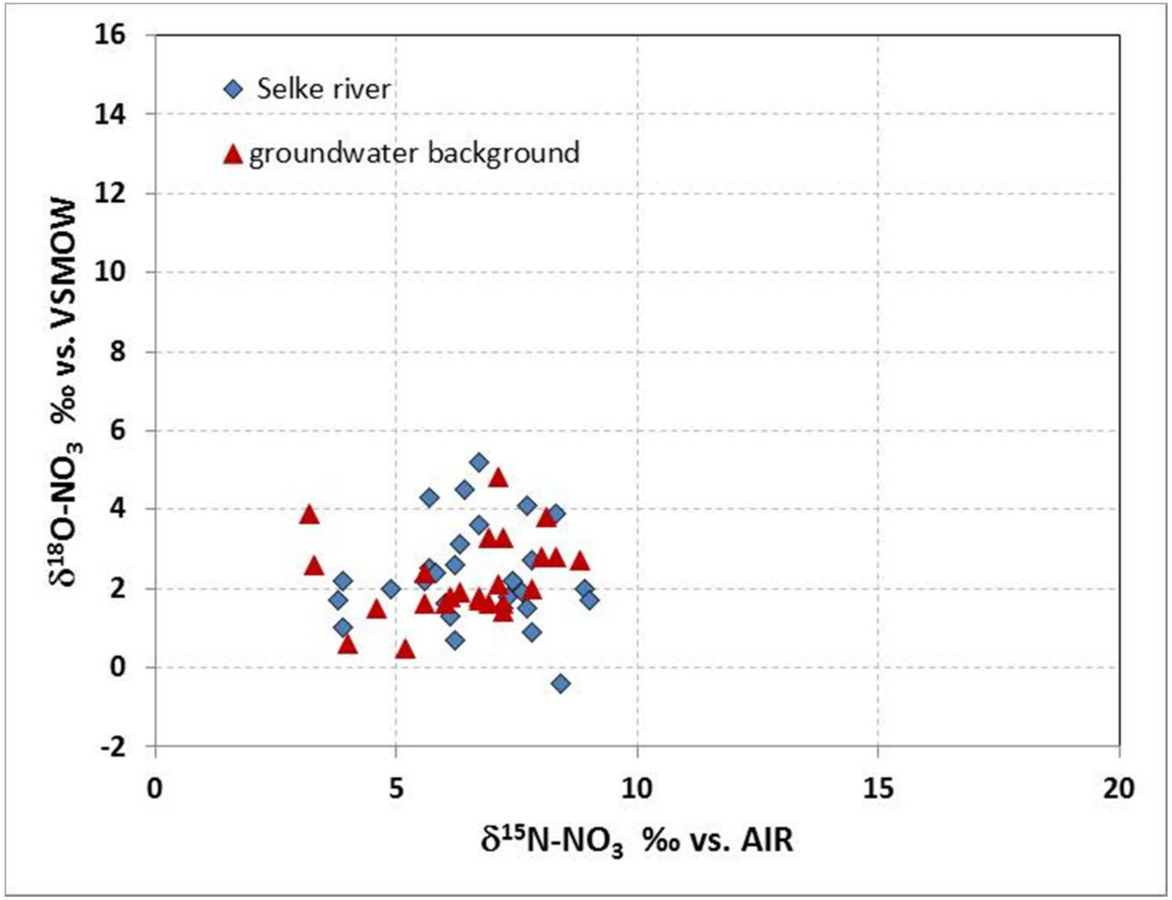
[redacted]

Hydrochemistry - Nitrate



Nitrate isotope monitoring Selke-site 2014/15

Inventory:
Background isotope signatures



No obvious difference between river nitrate and groundwater background

↓

any change in isotope signatures related to biogeochemistry

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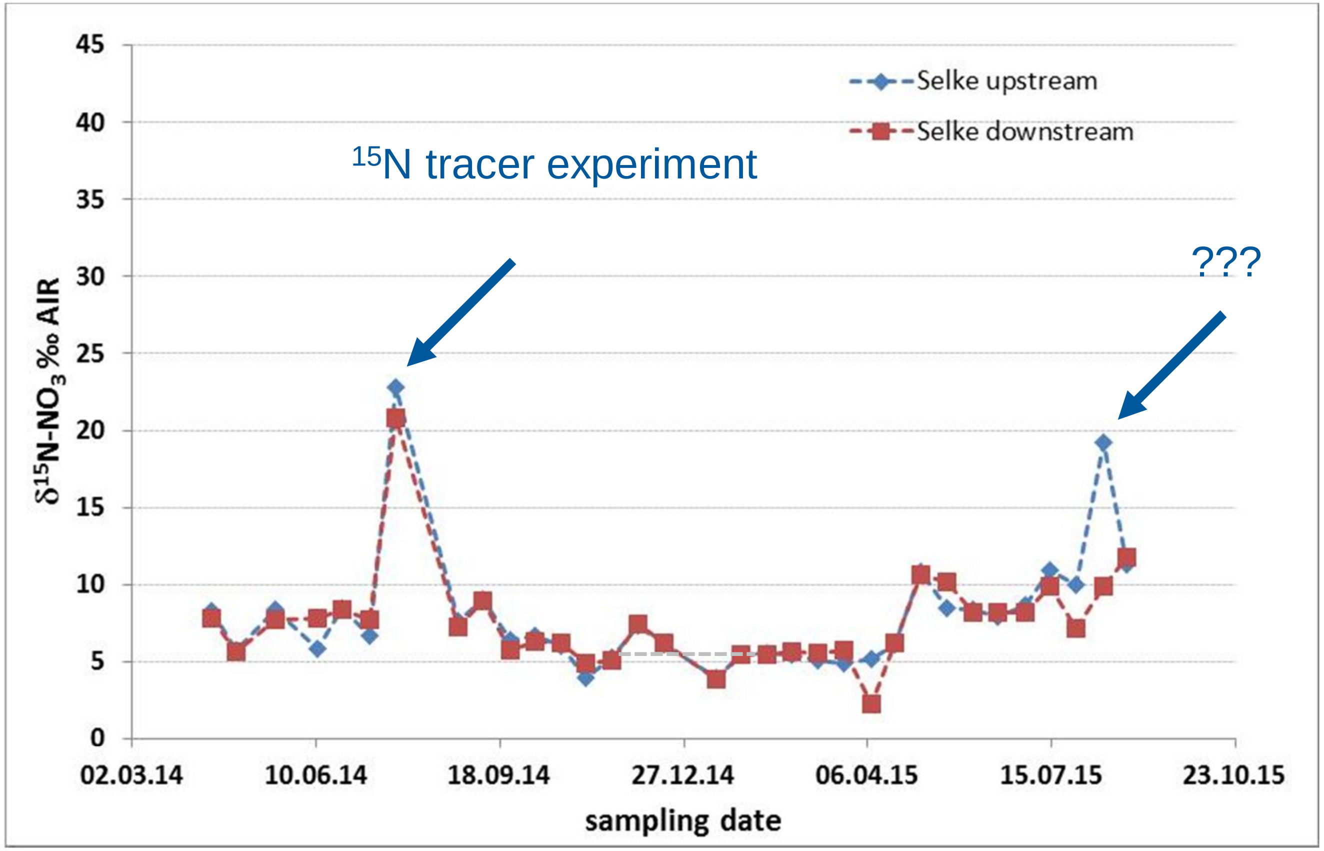
Nitrate isotope monitoring Selke-site 2014/15

Temporal variation of **nitrogen** isotope signatures in nitrate

river

water



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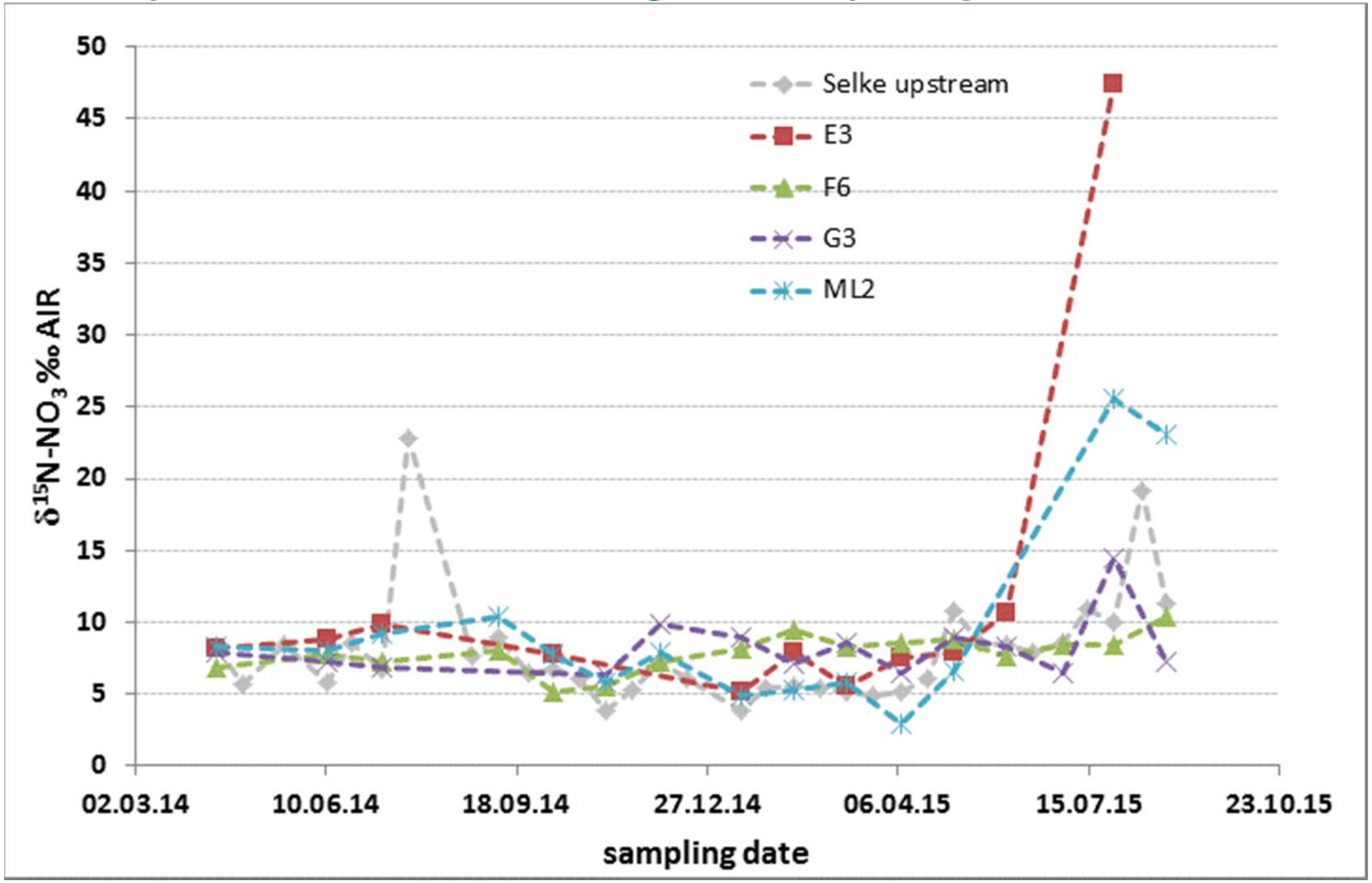

ground water

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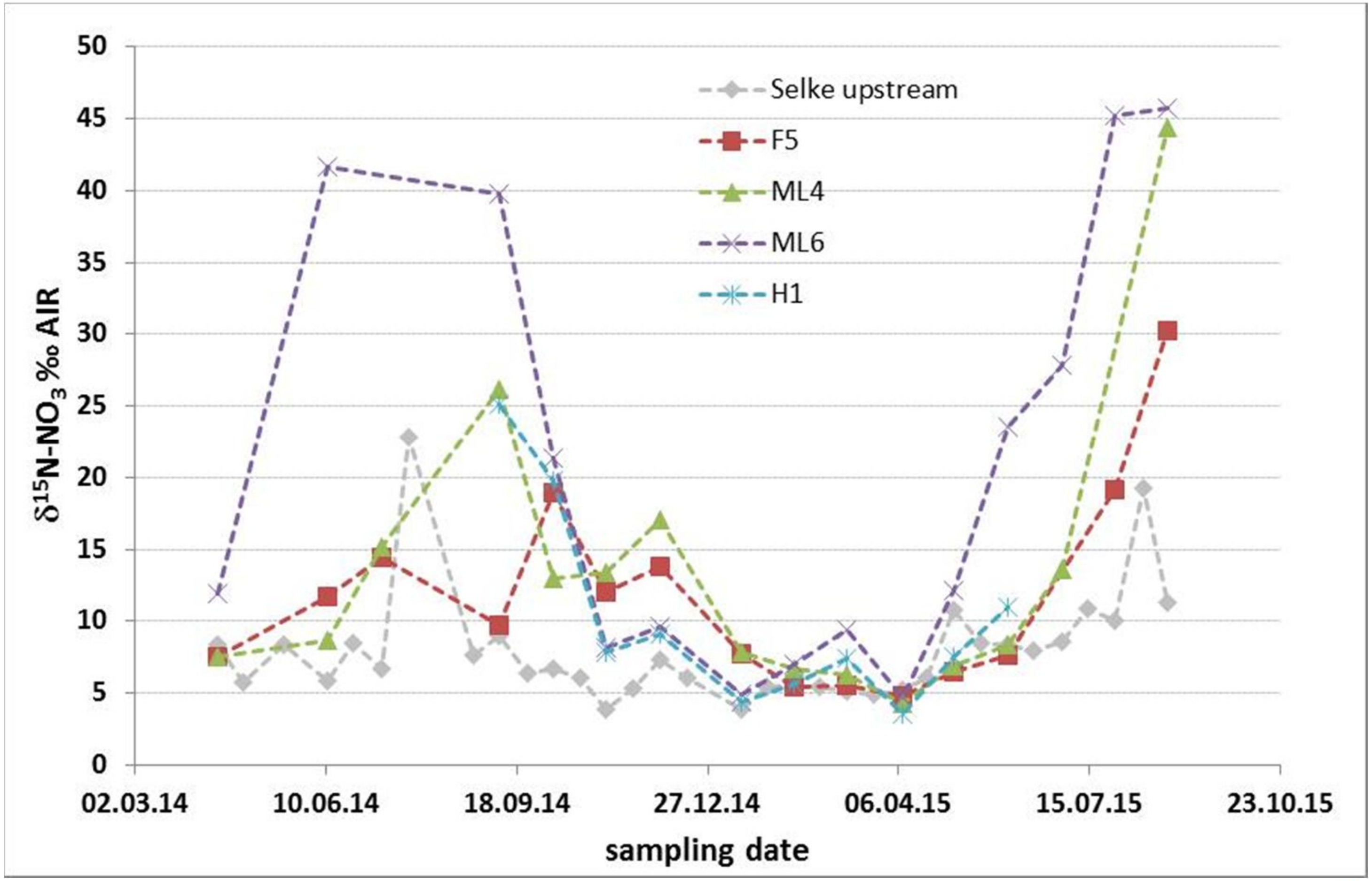

ground water

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Nitrate isotope monitoring Selke-site 2014/15

Validation of denitrification in biogeochemical hot spots:

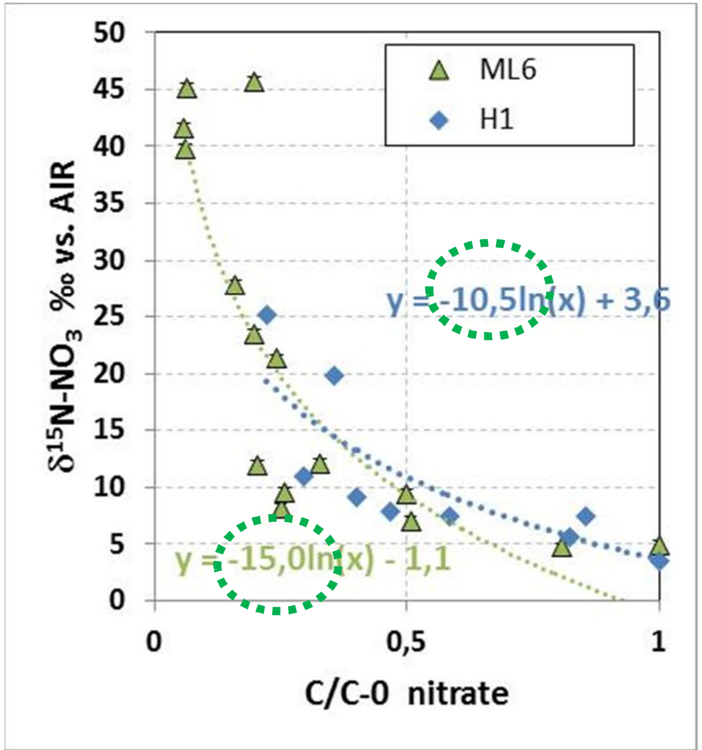
Expected parameters:

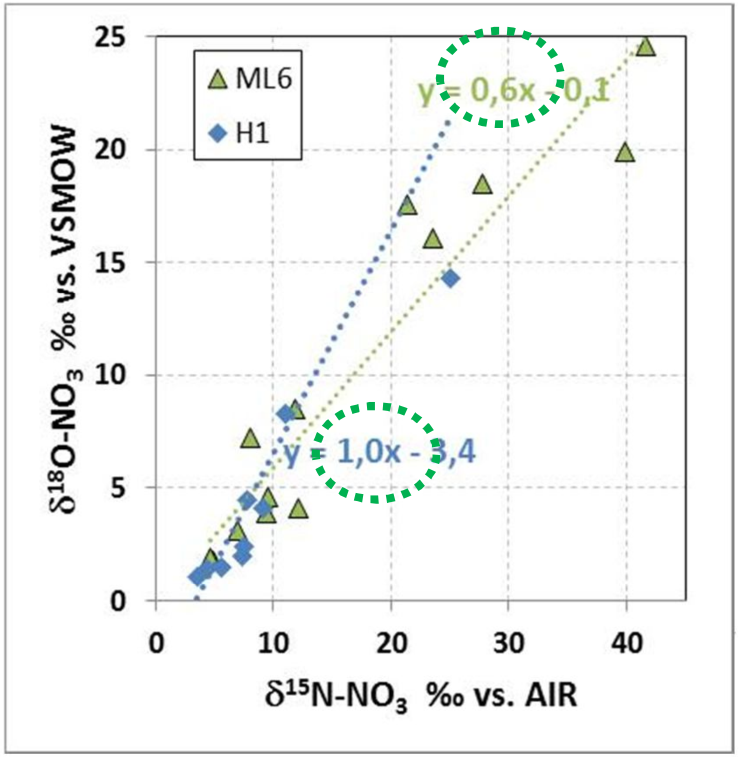
Nitrogen isotope enrichment factor:

-15 to -10 ‰

Slope in the dual isotope plot:

0.5 to 1.0





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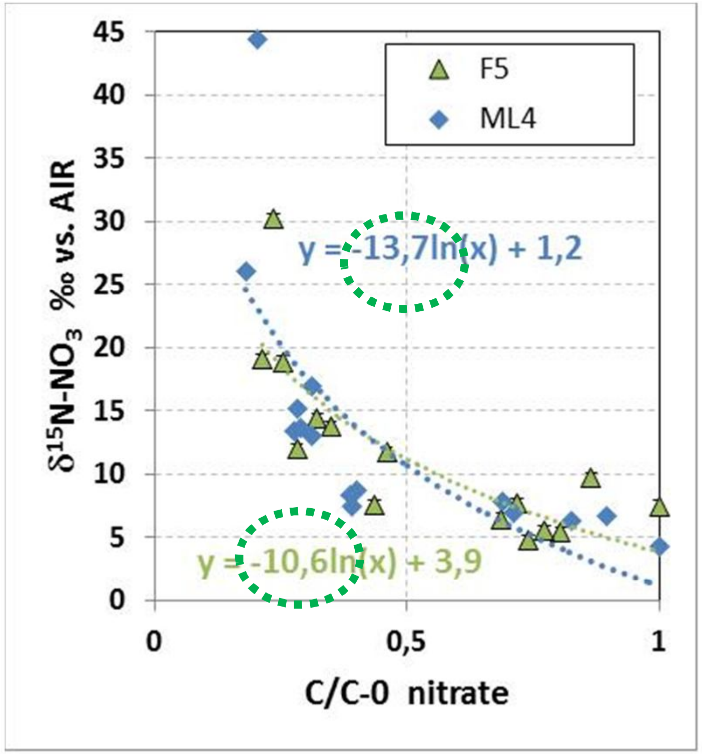

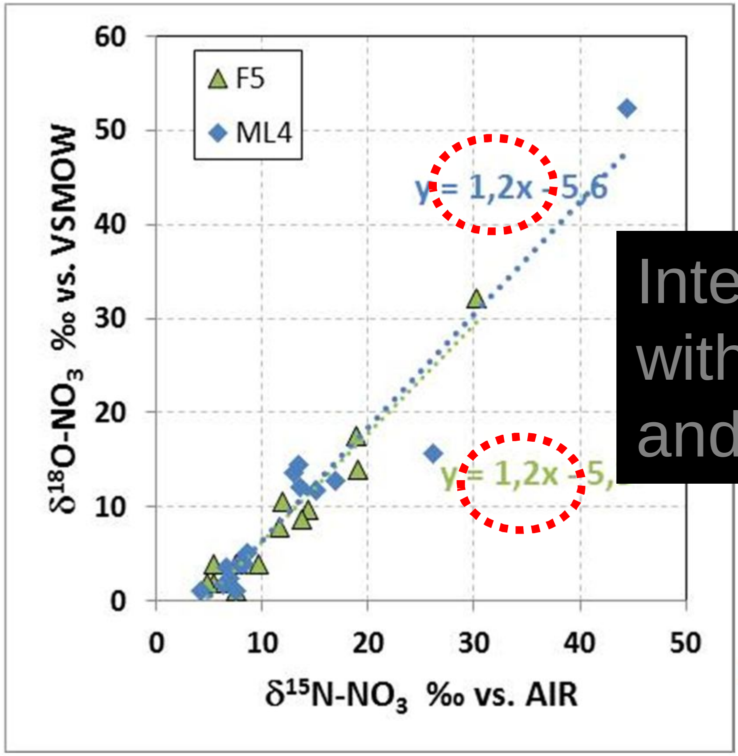

Interference with nitrification and/or dilution

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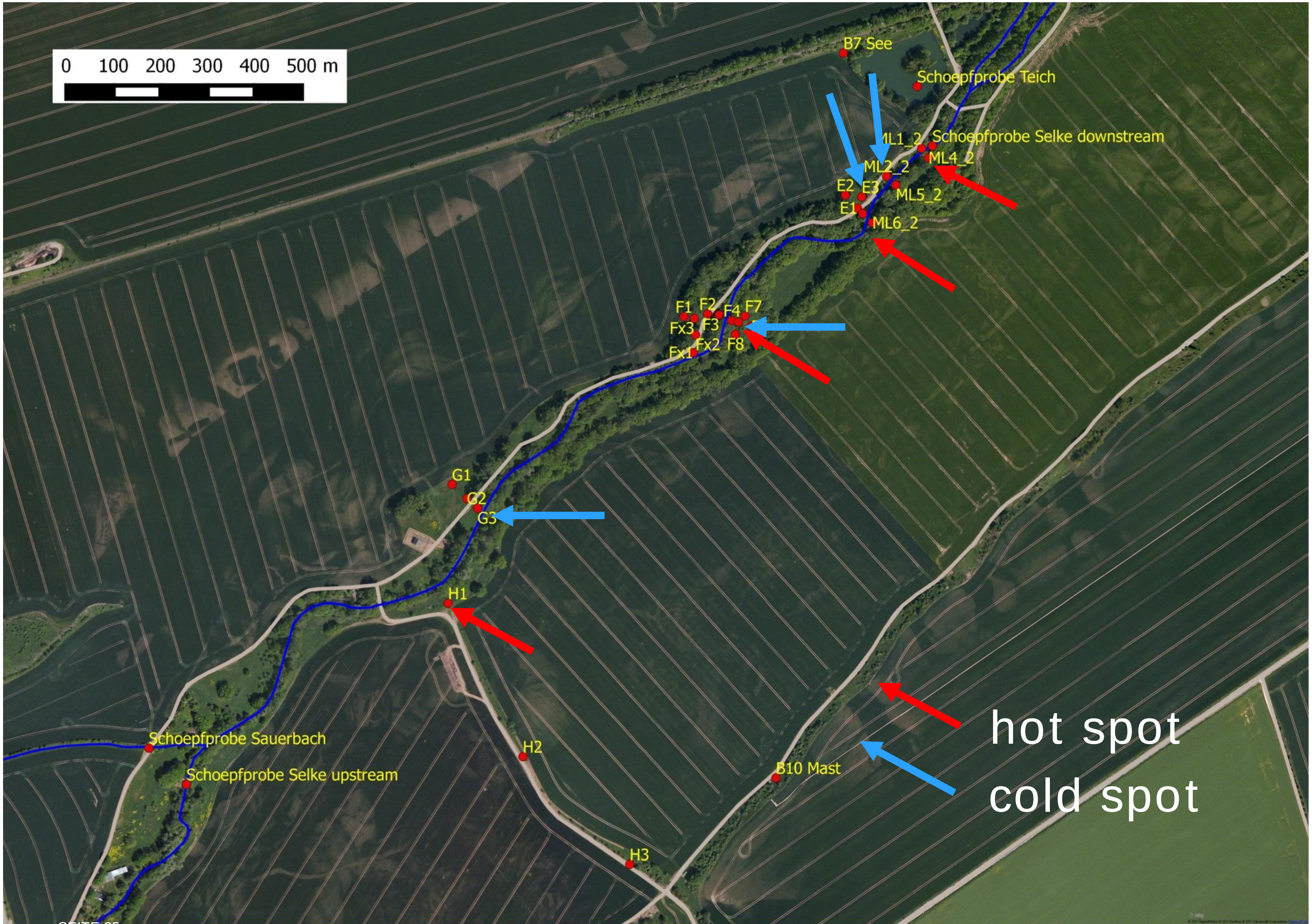
0 100 200 300 400 500 m
B7 See
Schoepfprobe Teich
ML1_2
Schoepfprobe Selke downstream
ML4_2
ML2_2
E2
E3
ML5_2
E1
ML6_2
F1
F2
F4
F7
Fx3
F3
Fx2
F8
Fx1
G1
G2
G3
H1
Schoepfprobe Sauerbach
Schoepfprobe Selke upstream
H2
B10 Mast
H3
hot spot
cold spot

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Part III: The Bode Story

Christin Müller, Matthias Zink, Luis Samaniego, Ronald Krieg, Michael Rode, Ralf Merz, Kay Knöller

mass twin

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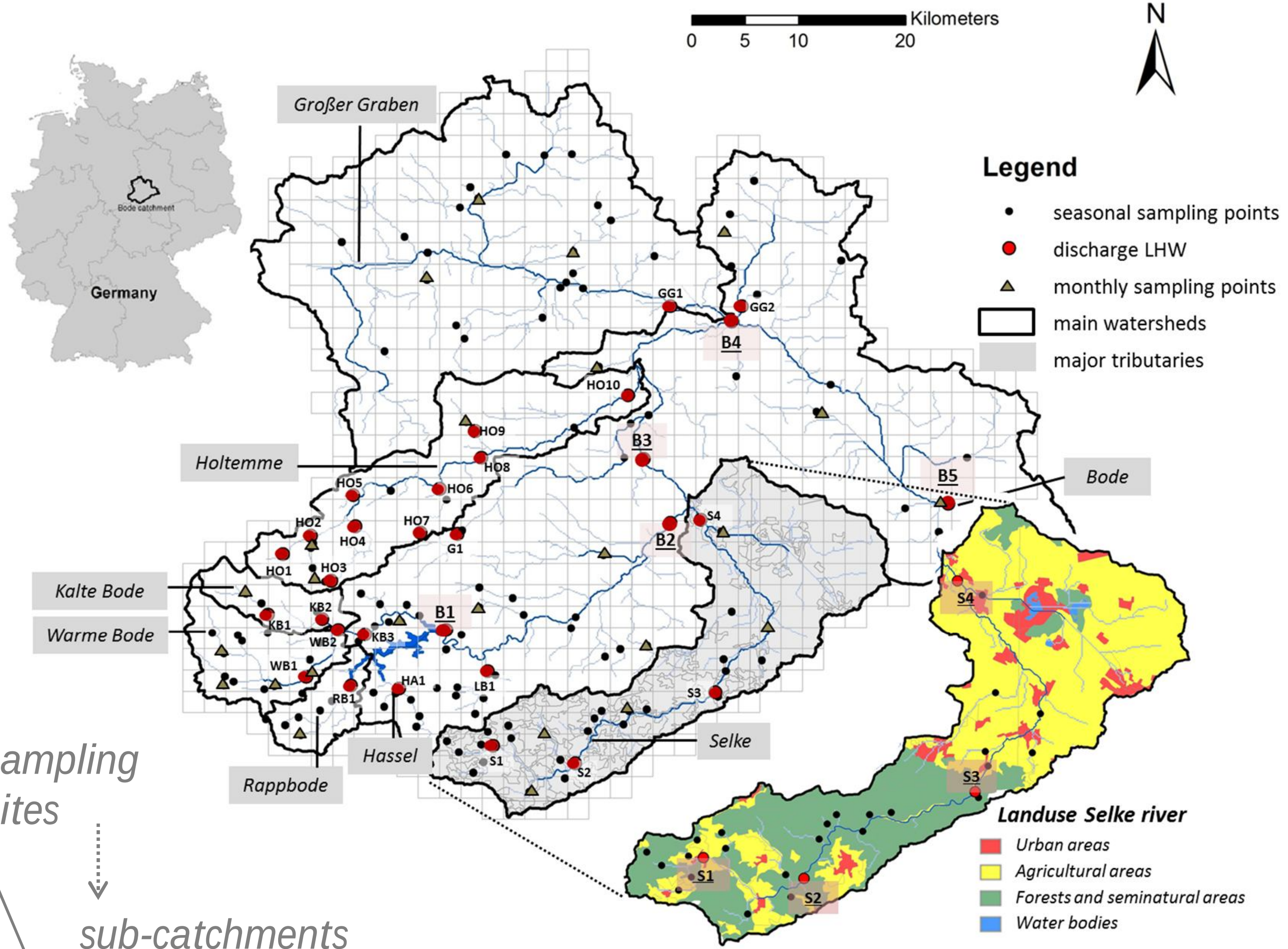
Isotope monitoring in the Bode river catchment

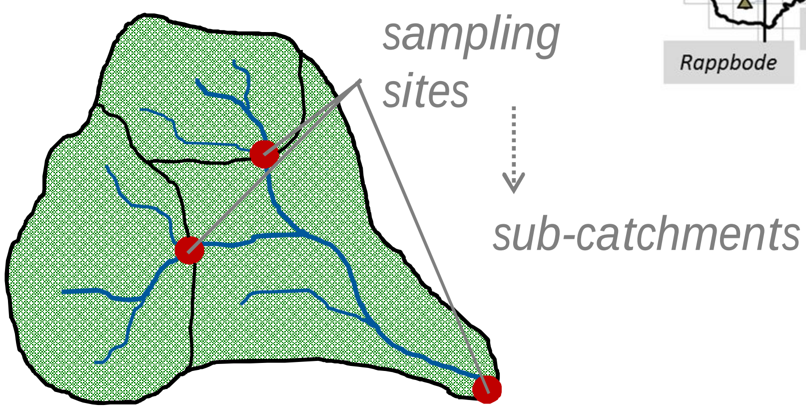
133 surface water sampling sites

seasonal sampling

25 intensive sites

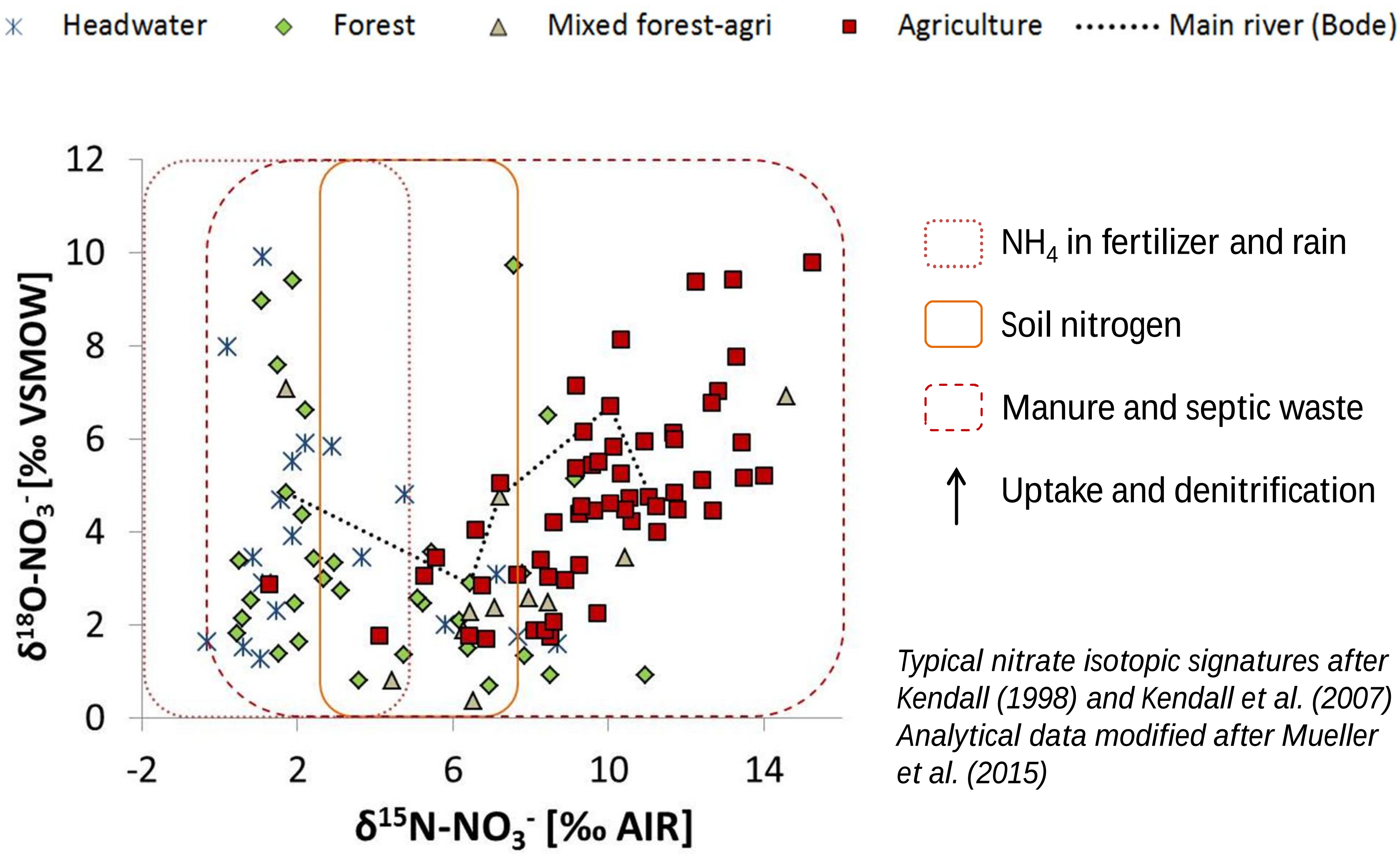
monthly sampling





Nitrate isotopes along the main river

Spatial distribution



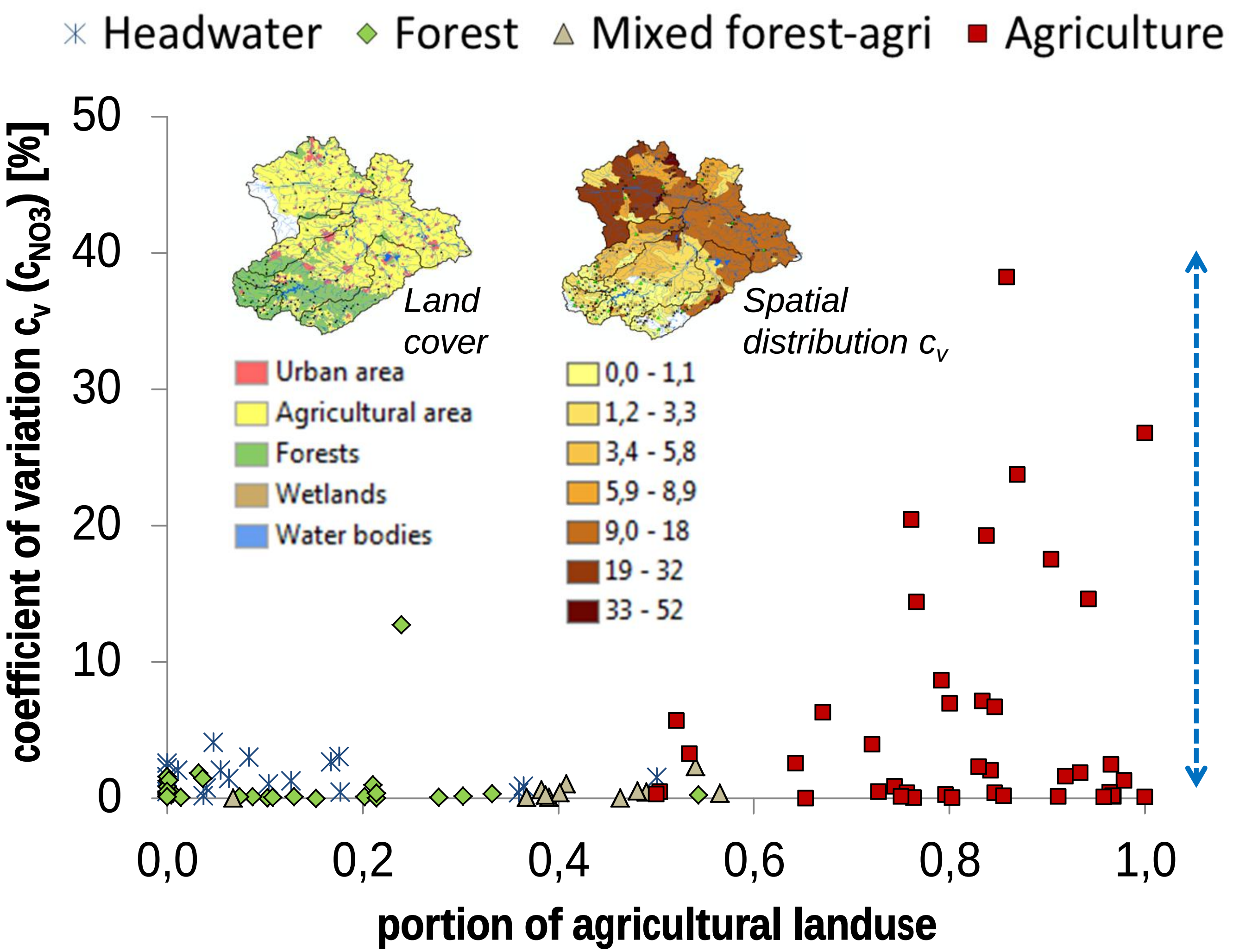
Typical nitrate isotopic signatures after Kendall (1998) and Kendall et al. (2007) Analytical data modified after Mueller et al. (2015)

Mueller et al. (2016, ES&T)

Nitrate isotope fingerprinting in the mesoscale Bode River catchment:

temporal variability of nitrate concentrations

$$c_v = \frac{Std\ Div}{mean\ \mu}$$



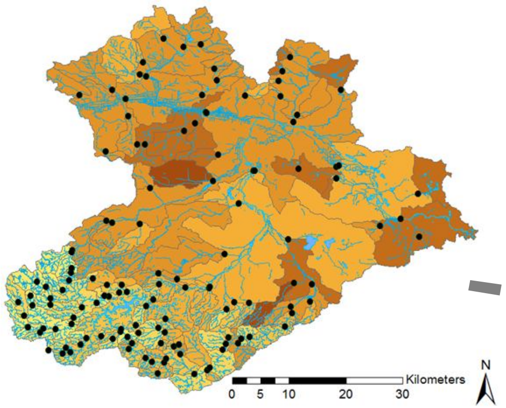
Large variation in agricultural tributaries in the northern sub-basins due to

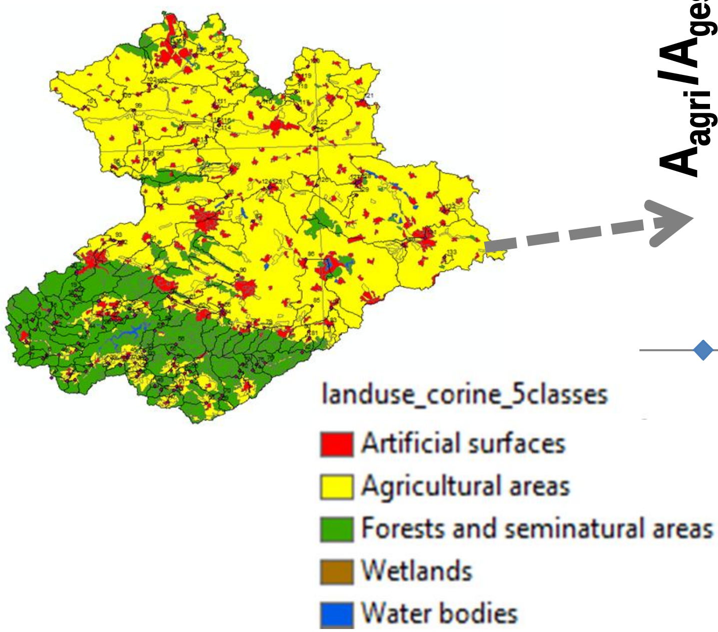
seasonal fertilizer application

Mueller et al. (2016, ES&T)

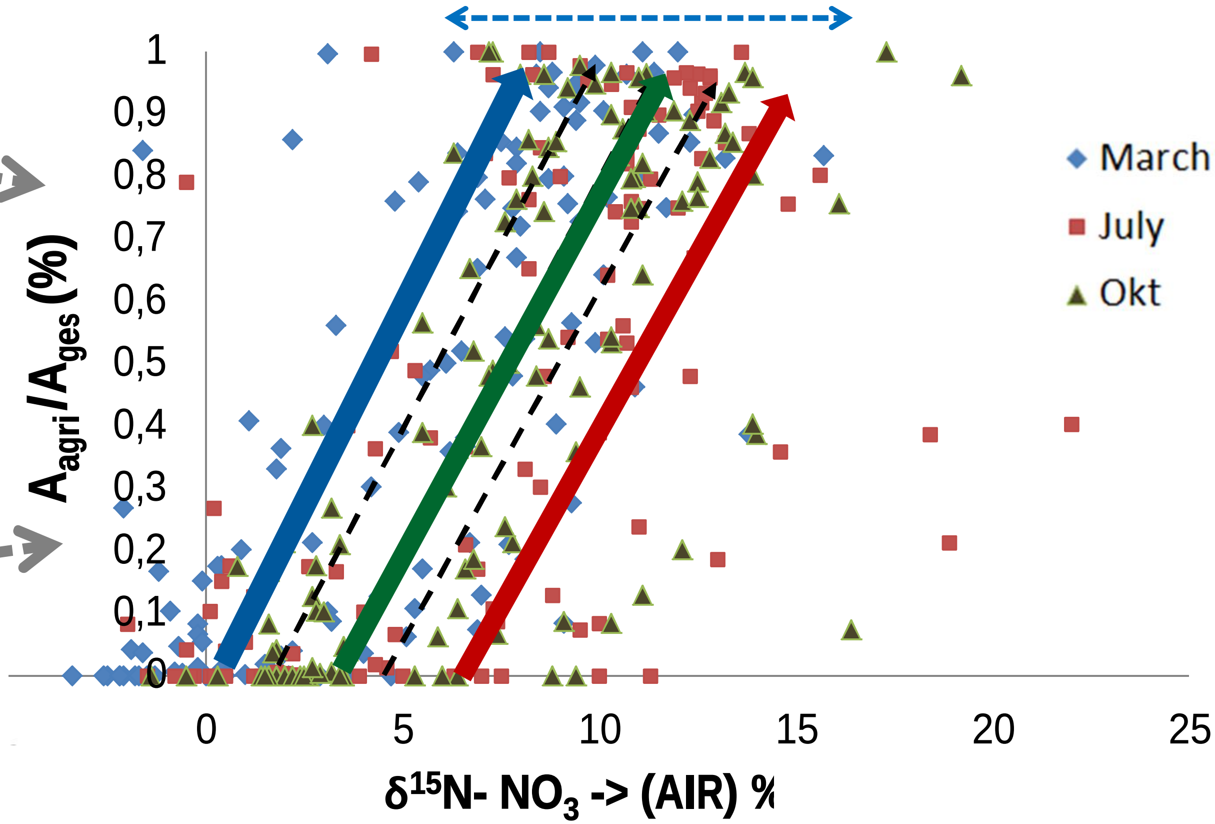
Nitrate isotope fingerprinting in the mesoscale Bode River catchment:

Regional relevance and variability of N-sources and sinks





Seasonal variability of denitrification impact?

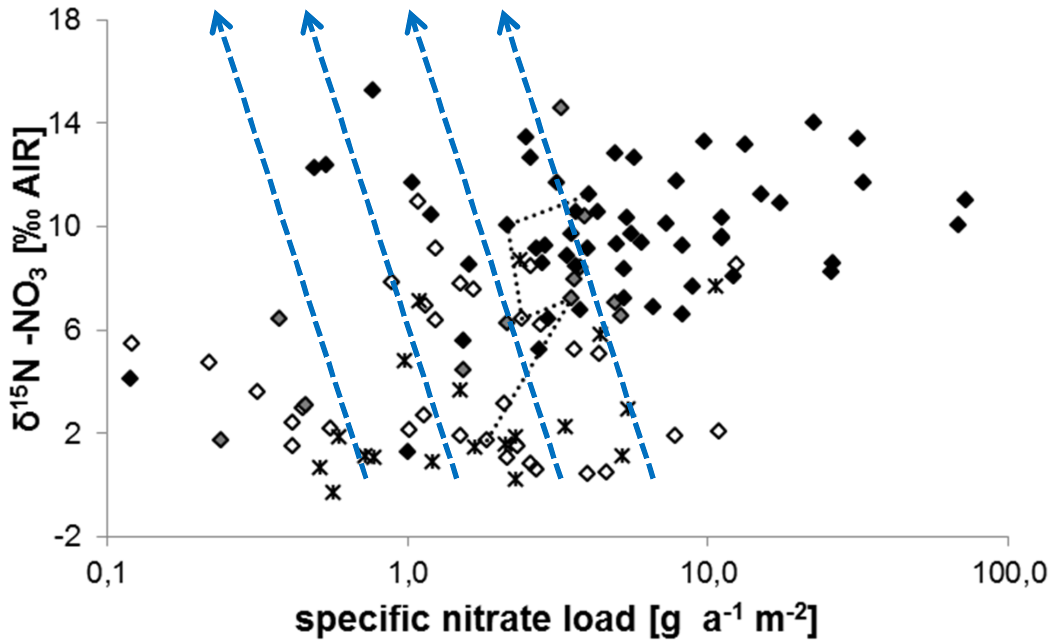


Subcatchment $A_{agri\ ratio}$ vs. $\delta^{15}N_{NO3}$

Nitrate isotope fingerprinting in the mesoscale Bode River catchment:

Regional vs. local impact of denitrification

Potential denitrification vectors



No indication that denitrification has a significant impact on regional scale

⁎ Headwater ◇ Forest ◆ Mixed forest-agri ◆ Agriculture ········ Main river

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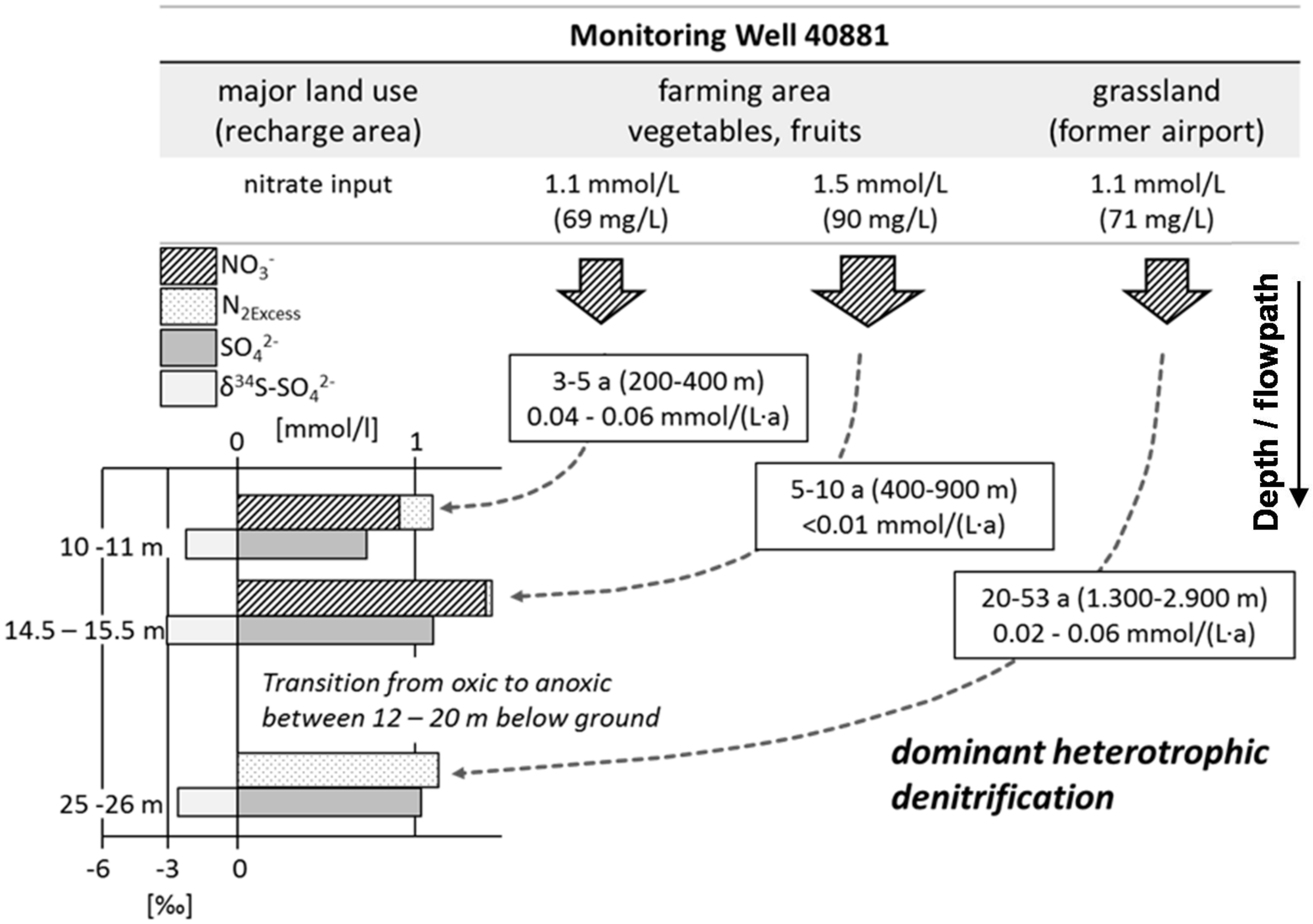
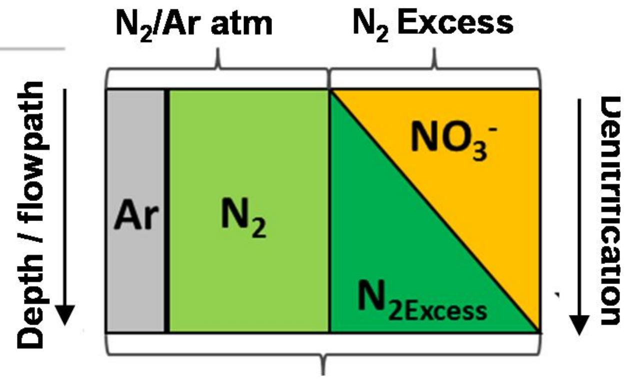
Thank you for your attention!

Denitrification pathways in the aquifer





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Denitrification pathways in the aquifer