On the propagation of reaction fronts in aquifers – the Bourtanger Moor sites revisited after 20 years



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## Problems (1): intensive farming



#### Cattle density per hectare



#### Nitrogen surplus



Agricultural areas (sandy soils, deep ploughed) high nitrate concentrations in groundwater (up to 125 mg/l) high potassium concentrations in gw (up to 12 mg/l)



# Problems (2): legacy of acidification (?)

Forested areas ("acid rain")

- sandy soil
  - pH as low as pH 2.5
  - cation exchangers loaded with aluminum
- groundwater:
  - pH as low as pH 3.6
  - aluminum up to 1.2 mg/l

But: improvement expected (flue gas desulfurization installed during 1990s)











### Now and then - main questions

#### How fast do the reaction fronts move?

#### PhD project RWTH Aachen: 1996-2000

- core drillings (agriculture, forest, peat bog): analysis of reactive components
- column experiments
- multi-level wells: hydrochemistry, stable isotopes, tritium, CFC dating
- 1D reactive transport modeling (PHREEQC) → front velocity prediction

#### What has happened during the last 20 years? Let's do it all a again!

How accurate were the model predictions? Did I really deserve my PhD degree?



### Development of rain water chemistry





### Acidification of forest soils



1 mmol(eq)/100 g ≈ 540 mg/l Al





### Forest site: acidification of groundwater





### Agricultural site: denitrification front 1998



(all observation wells)

Autotrophic denitrification via framboidal pyrite





Bundesanstalt für Geowissenschaften und Rohstoffe

Houben et al. (2001, 2017)

## Depth of denitrification front: cores

1998: 11.40 m



2018: 11.26 m



Reaction front 2018 14 cm higher than 1998?

- flat terrain! no topography effect (4 m distance)
- natural variation?
- drilling artefact: core loss, compaction!

Marker horizont (charcoal) shows little vertical denitrification front propagation (1-2 cm)

- $\rightarrow$  front velocity ca. 0.5-1.0 mm/a
- $\rightarrow$  as predicted by models (Houben et al. 2001, 2017)
- $\rightarrow$  reason: relatively high pyrite content



#### Agricultural site: gw trace elements 1998 vs. 2017





#### Nitrogen excess as denitrification indicator N<sub>2</sub> - argon method





### Hidden denitrification: not just an artefact





How much "hidden nitrate"?

N<sub>2</sub>/Ar data: ca. 5-20 mg/l N<sub>2</sub> excess  $\rightarrow$  25-100 mg/l nitrate

Sulphate conc. multi-level wells: ca. 50-150 mg/l sulphate  $\rightarrow$  45-135 mg/l nitrate



### How does the "ghost nitrate" get into lower aquifer?



Clay pinches out towards west but: reducing conditions (bog)  $\rightarrow$  low nitrate, low recharge

"Holes" in aquitard? Close to pumping wells: water level difference between aquifers: up to 2 m

Abandoned leaky boreholes? No holes? Just flow through aquitard?

MODFLOW model on its way ...



### **Conclusions (official)**

- Reproducibility 1998 vs. 2017/18 surprisingly good ☺
  - despite different sampling & analysis techniques, different labs & people
- Forest site, acidification:
  - rain: pH and sulphuric acid input have improved markedly ☺
  - soil: pH and cation exchange composition show no improvement ⊗
  - groundwater: pH and aluminum mobilisation deteriorated ⊗
- Agricultural site: denitrification front propagation
  - very slow vertical propagation in upper aquifer, as predicted by models  $\odot$
  - But: hidden denitrification in lower aquifer (flow through holes in aquitard?) ●\*
- So, did I deserve my PhD? You decide ...



# Conclusions (inofficial) - 20 years later Still haunted by the ghost of nitrate

"Antigonish" (based on a ghost story) by William Hughes Mearns (1899)

Anti-nitrogen (ode to nitrate) by myself (2019)

"Yesterday, upon the stair,

I met a man who wasn't there!

He wasn't there again today,

Oh how I wish he'd go away!"

*"20 years ago, in my aquifer, I analyzed a contaminant that wasn't there! It wasn't there again today,* 

Oh how I wish this nitrate would go away!"



# Thank you for your attention!

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Terrestrial sedimentary pyrites as a potential source of trace metal release to groundwater – A case study from the Emsland, Germany



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**Cases and Solutions** 

Assessing the reactive transport of inorganic pollutants in groundwater of the Bourtanger Moor area (NW Germany)

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More is on its way ...



### How old is the groundwater?





### **Stable isotopes**



