Assessing groundwater nitrate reduction on a national scale in Denmark

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Acknowledgement of my co-authors at GEUS

- Jens Aamand
- Rasmus Jakobsen
- Hyojin Kim
- Lærke Thorling
- Denitza Voutchkova

Aim

- To show how **nitrate trend analyses** can be used
- To estimate groundwater **denitrification extent and reaction rates**

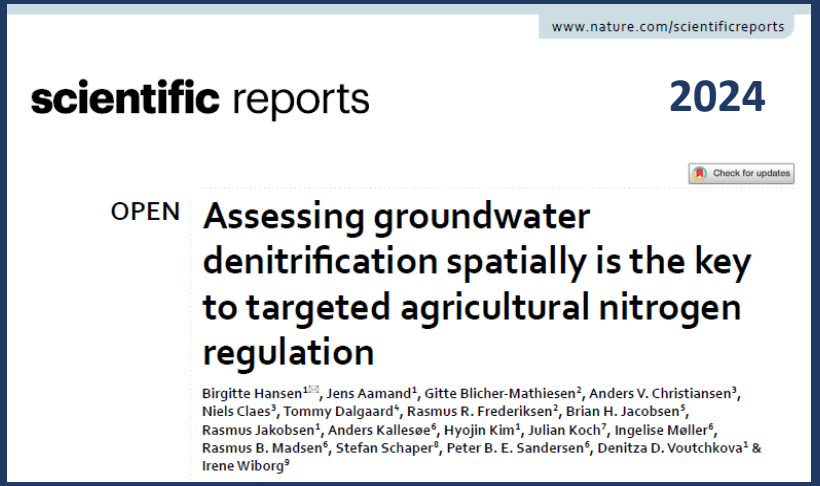
Why focus on denitrification

- It's crucial for national assessment of N retention which is the bottleneck for a new Danish agricultural N regulation model

  (Anker Lajer Højberg's talk)

- There are many different available approaches showing a high degree of variation - no one is optimal

  (Denitza Voutchkova's talk)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Assessing groundwater denitrification spatially is the key to targeted agricultural nitrogen regulation

Birgitte Hansen[1✉], Jens Aamand[1], Gitte Blicher-Mathiesen[2], Anders V. Christiansen[3], Niels Claes[3], Tommy Dalgaard[4], Rasmus R. Frederiksen[2], Brian H. Jacobsen[5], Rasmus Jakobsen[1], Anders Kallesøe[6], Hyojin Kim[1], Julian Koch[7], Ingelise Møller[6], Rasmus B. Madsen[6], Stefan Schaper[8], Peter B. E. Sandersen[6], Denitza D. Voutchkova[1] & Irene Wiborg[9]

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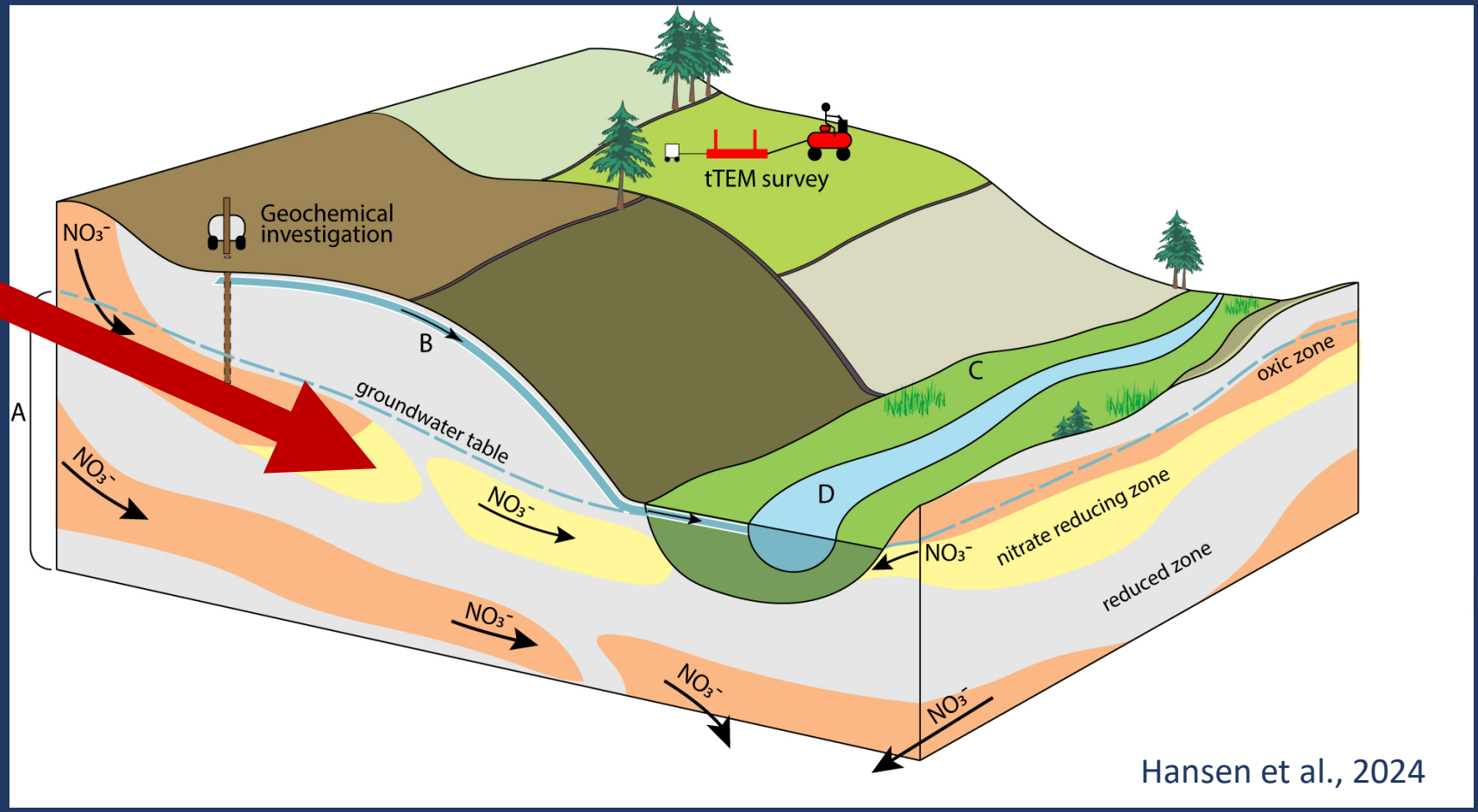
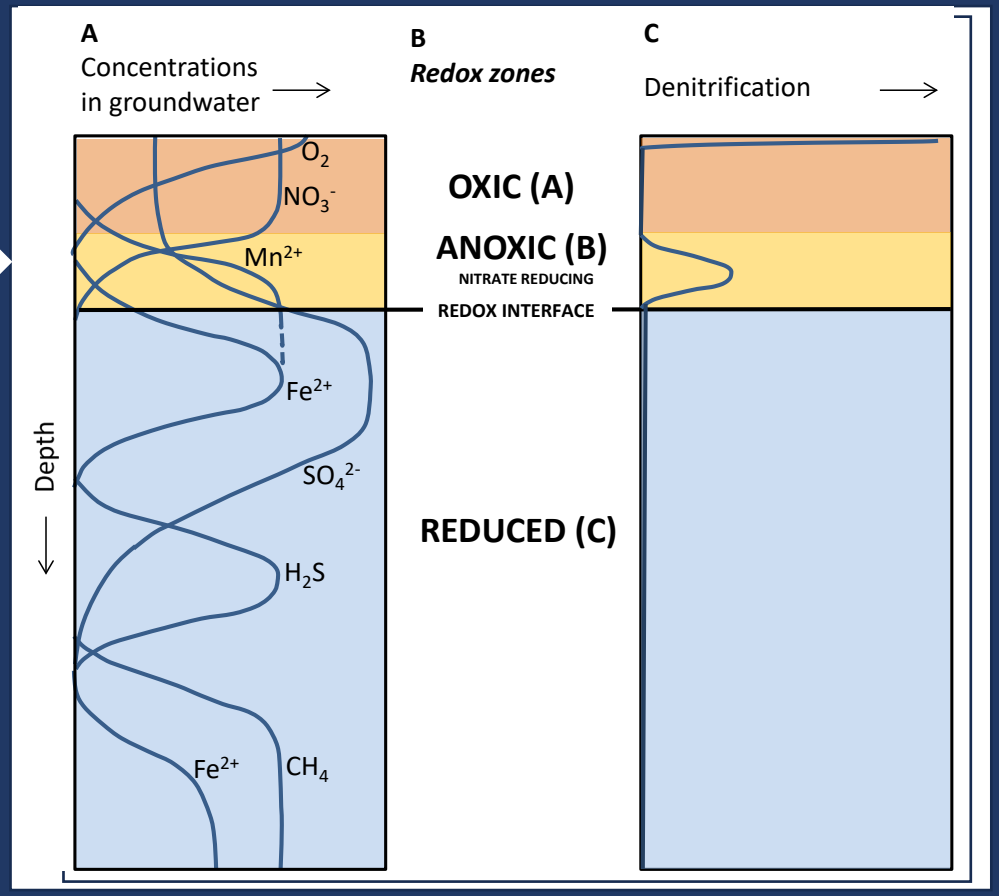
Focus is on the anoxic nitrate-reducing zone



Hansen et al., 2024

Definition



Hansen et al, in review

Nitrate reduction in the anoxic nitrate-reducing zone

- By oxidation of pyrite (FeS_2), organic matter or Fe (II) minerals catalyzed by denitrifiers:

$$NO^-_{3(aq)} \xrightarrow{2e^-} NO^-_{2(aq)} \xrightarrow{1e^-} NO_{(enzyme\ complex)}$$

$$\xrightarrow{1e^-} N_2O_{(gas)} \xrightarrow{1e^-} N_{2(gas)}$$

Denitrification approach

- **Comparison** of nitrate trends in data populations from two redox zones

Reasons for nitrate concentration changes with time

OXIC ZONE:

- Changes in nitrate leaching

ANOXIC NITRATE-REDUCING ZONE:

- Changes in nitrate leaching & **Denitrification**

Denitrification approach

Data demand:

- Long-term nitrate time series from monitoring wells
- Dating of groundwater (e.g. $^{3}H/^{3}He$ or CFC)
- Analyses of redox sensitive parameters to determine redox zone
- Multiscreen monitoring wells for rate determinations

Denitrification approach

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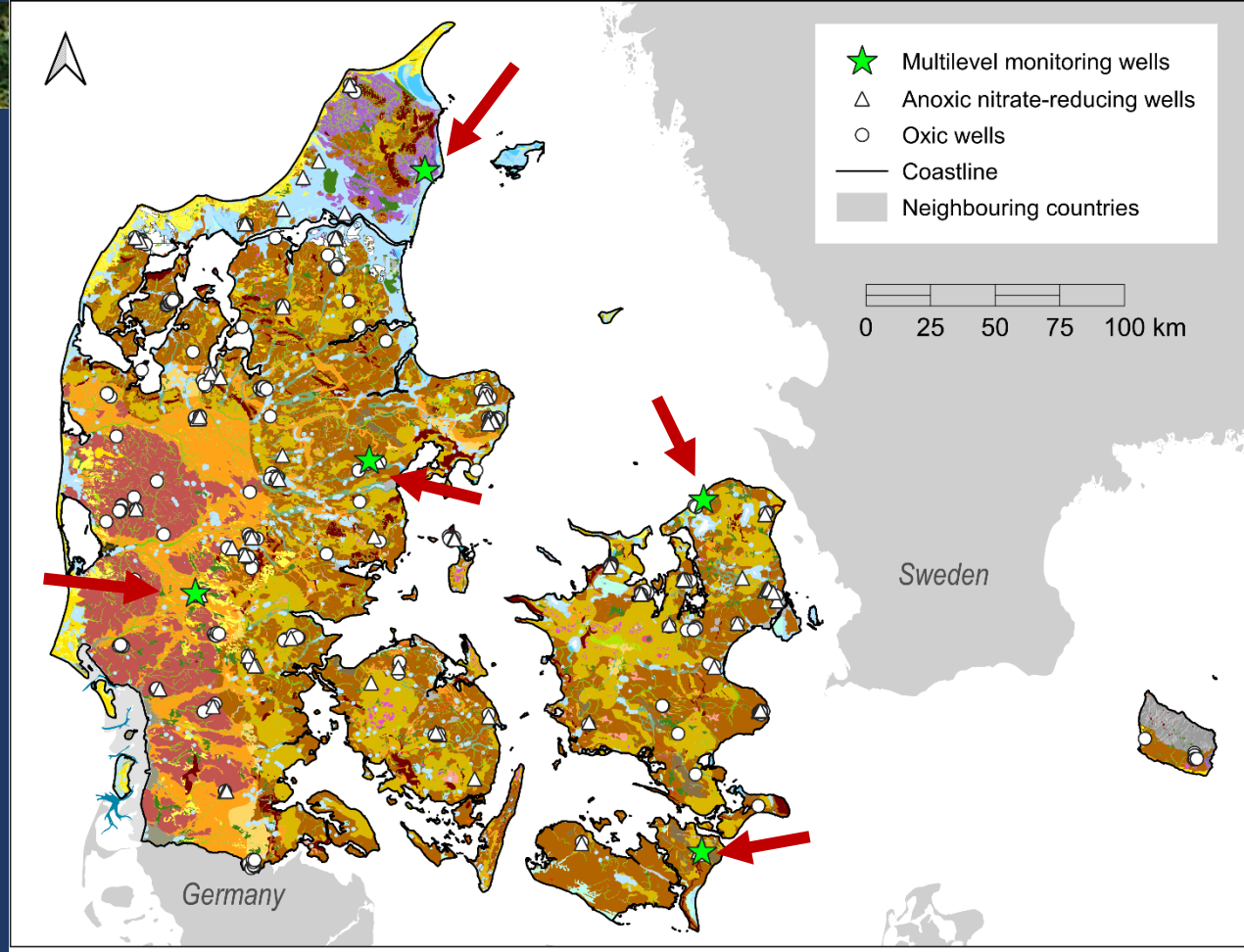


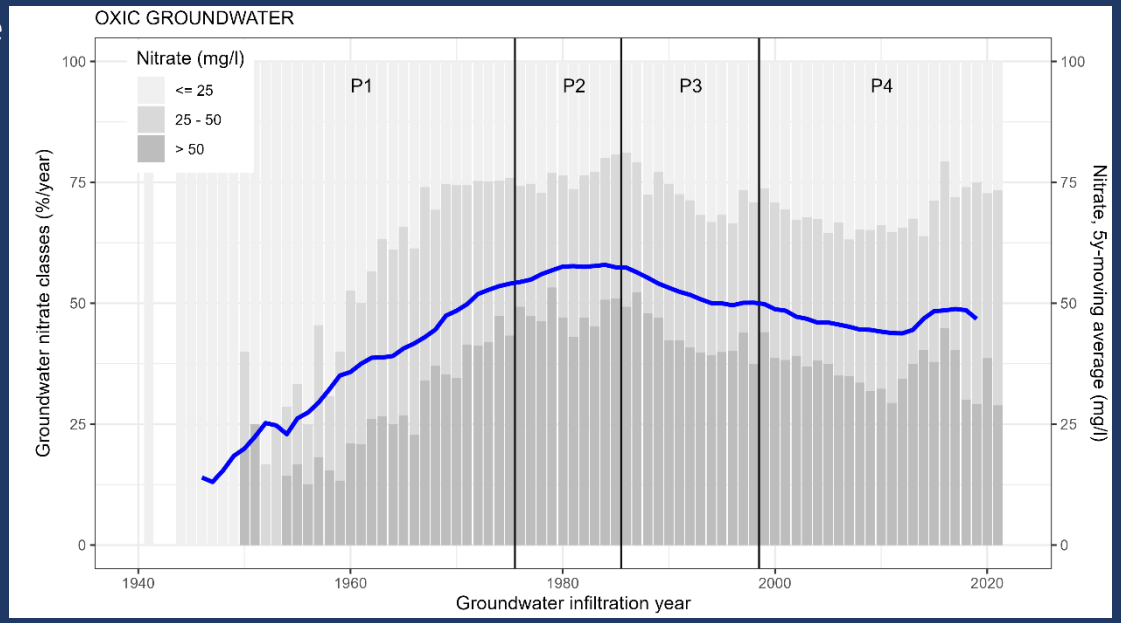
Geomorphology

- Lake
- Till plain
- Drumlin
- Tunnel valley
- Esker
- Hummocky topograhy
- Kettle hole
- Kame
- Marginal moraine
- Transgressed marginal moraine
- Older Till plain
- Outwash plain
- Hummocky outwash plain
- Valley system
- Glacial lake deposit
- Raised late glacial plain
- Raised late glacial beach ridge
- Marsh
- Delta
- Beach ridge
- Marine plain
- Lake plain
- Bog
- Dune
- Aeolian plain
- Tectonic valley
- Reclaimed lake
- Reclaimed marine plain
- Antropogenic landscape
- Bedrock
- Chalk, Bedrock
- Tidal flat
- Tidal inlet
- Neighbouring countries

Danish national nitrate trends in groundwater

OXIC GROUNDWATER

Nitrate mg/l



Groundwater infiltration year

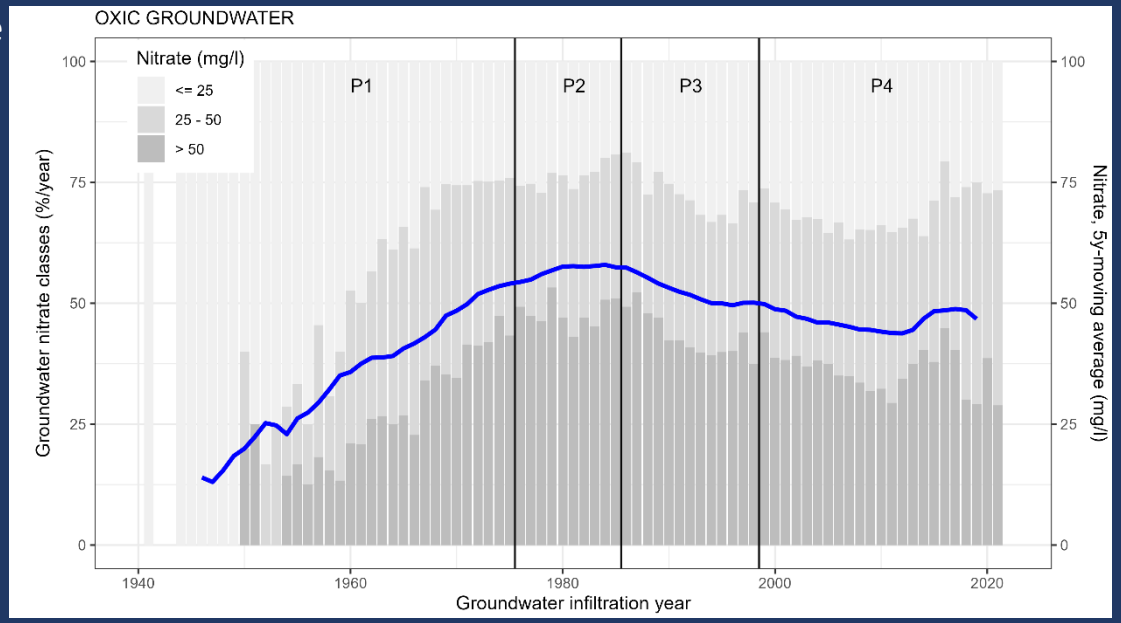
8767 nitrate analyses from 439 monitoring points

Danish national nitrate trends in groundwater

GEUS

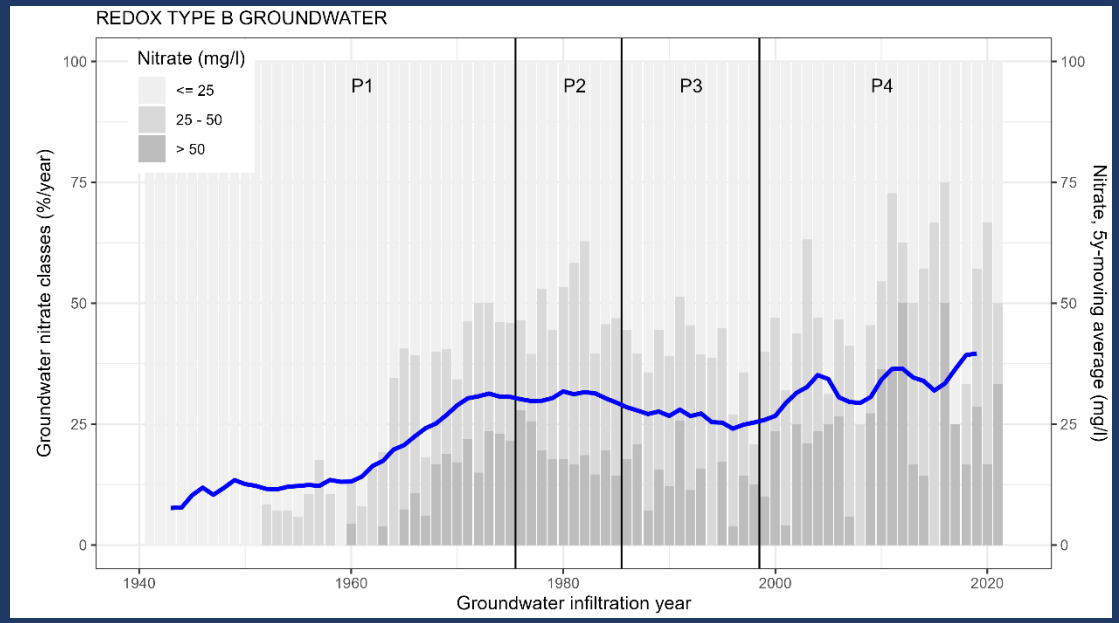
OXIC GROUNDWATER

Nitrate mg/l



8767 nitrate analyses from 439 monitoring points

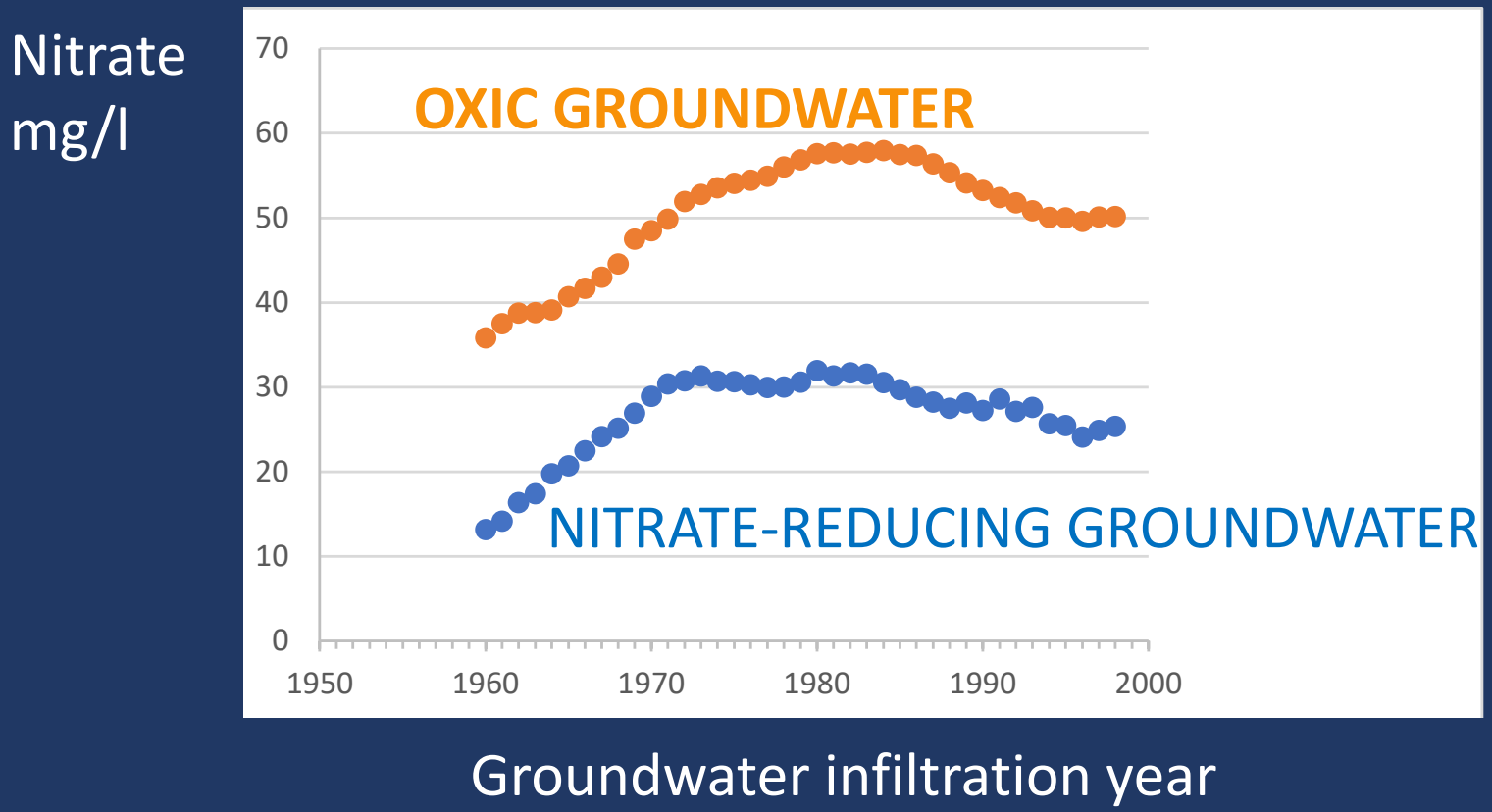
NITRATE REDUCING GROUNDWATER



1891 nitrate analyses from 125 monitoring points

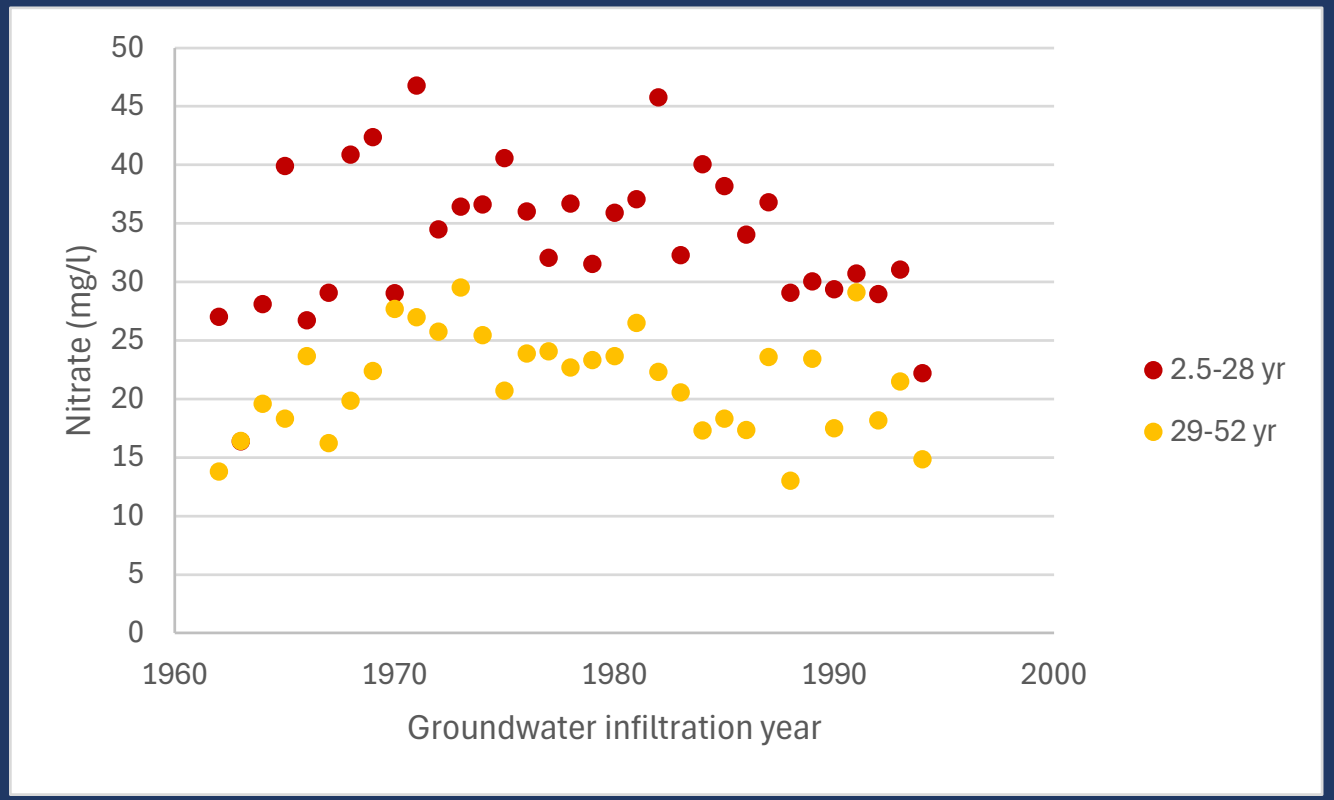
Groundwater infiltration year

The period with highest data density



Denitrification and residence time

Nitrate mg/l



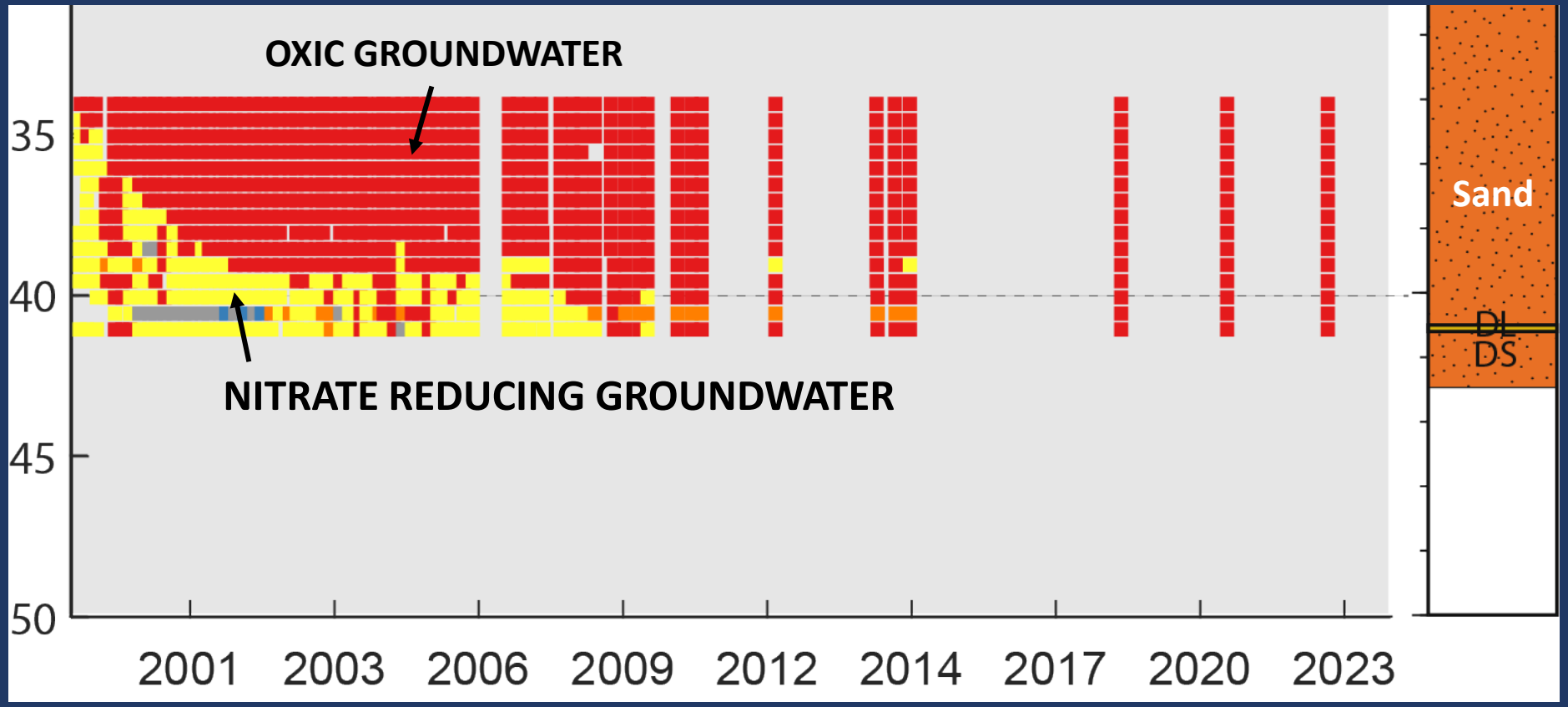
Groundwater infiltration year

The new denitrification concept - for multiscreen wells

Local rate for the recharge area of the screens:

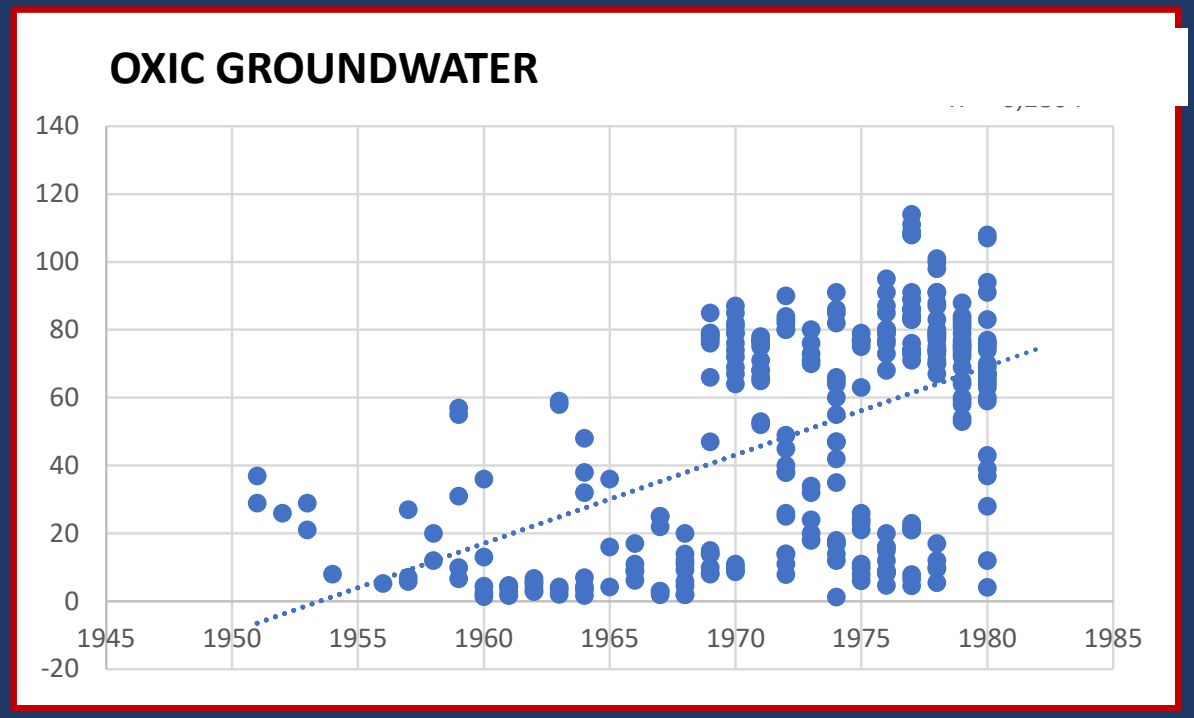
$$Denitrication\ rate = \frac{dC}{dt}(oxic\ zone) - \frac{dC}{dt}(anoxic\ nitrate\ reducing\ zone)$$

Redox changes in a multiple screen well



Redox changes in a multiple screen well Albæk

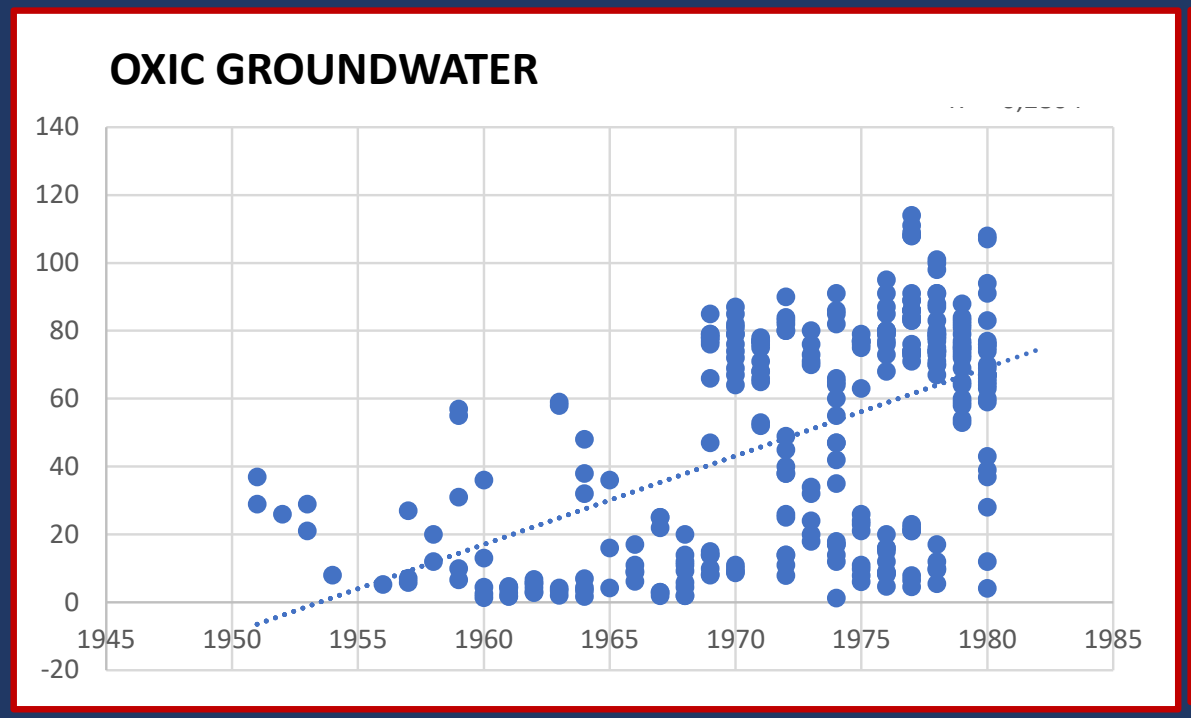
Nitrate mg/l

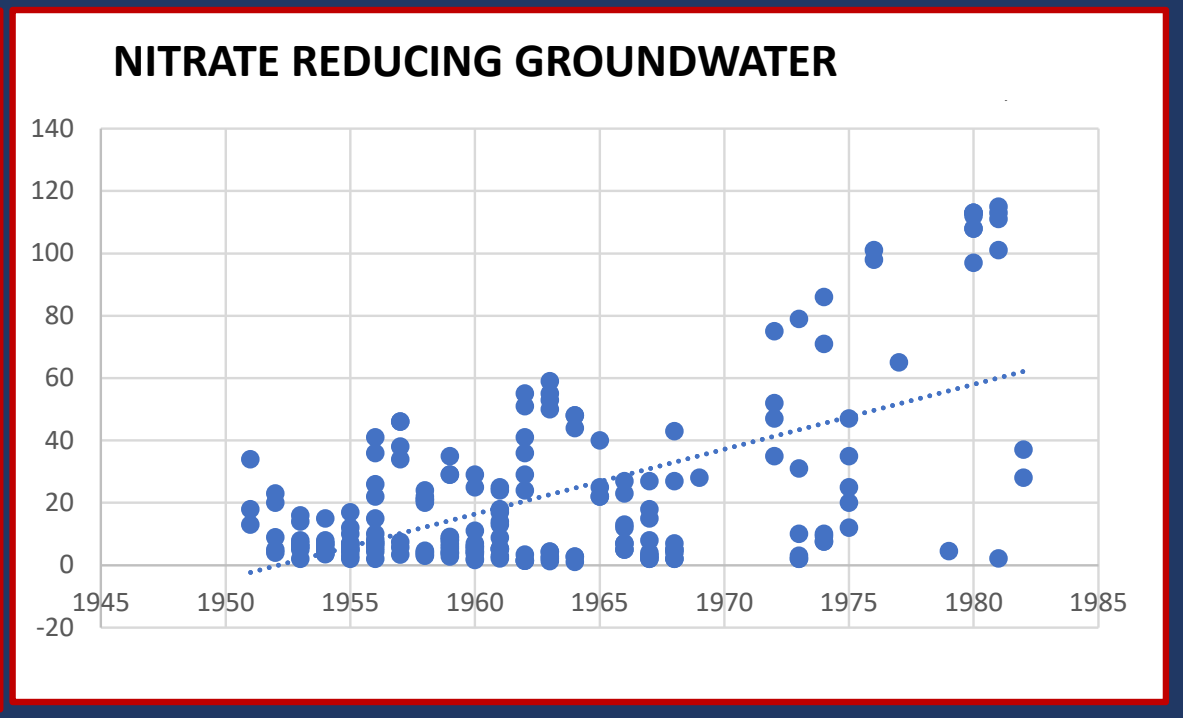


Groundwater infiltration year

Redox changes in a multiple screen well Albæk

Nitrate mg/l





Groundwater infiltration year

Denitrification in a multiple screen well Albæk

OXIC	
mg NO_3/l/yr	**Period**
2.61	1951-1980

Denitrification in a multiple screen well Albæk

OXIC		NITRATE-REDUCING	
mg NO_3/l/yr	**Period**	**mg NO_3/l/yr**	**Period**
2.61	1951-1980	2.08	1951-1982

Denitrification in a multiple screen well Albæk

OXIC		NITRATE-REDUCING		RATE	
mg NO_3/l/yr	**Period**	**mg NO_3/l/yr**	**Period**	**mg N/l/yr**	**µmol N/l/day**
2.61	1951-1980	2.08	1951-1982	0.12	0.023

Denitrification rates in 5 single multiple wells

OXIC		NITRATE REDCING		RATE P<0.05	
Well	**mg/l/yr**	**Period**	**mg/l/yr**	**Period**	**mg N/l/yr**	**µmol N/l/day**
Albæk	2.61	1951-1980	2.08	1951-1982	0.12	0.023
Kasted	1.13	1948-1999	0.42	1949-1984	0.16	0.032
Grindsted	0.93	1974-1993	0.76	1974-1993	0.04	0.008
Vejby	1.30	1993-2008	0.60	1993-2008	0.16	0.031
Sibirien	0.19	1968-1999	-0.76	1963-2011	0.22	0.042

- Low end of Danish acetylen-block determinations on sandy Quaternary deposits (Kim et al., 2021)
- Within the range of derived from in situ gradients using environmental tracers (Groffman et al., 2006)

Conclusion

- Assessing groundwater denitrification spatially is the key to agricultural nitrogen regulation
- The new concept relies on assessment of nitrate trends in oxic and anoxic nitrate-reducing groundwater
- National level analyses shows pronounced reduction in groundwater
- Assessment of local denitrification rates is possible from multiscreen wells

But we need…

- More long-term nitrate time series from groundwater monitoring wells
- More dating of groundwater
- More multiscreen wells

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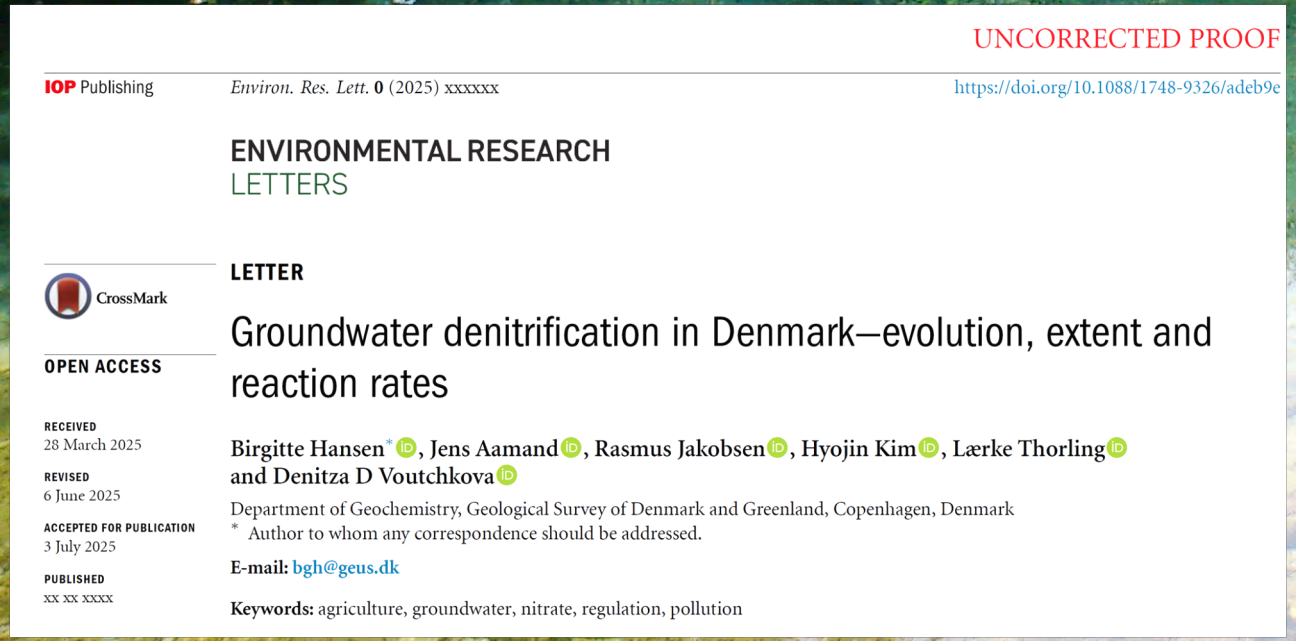
Thank you for listening



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LETTER

Groundwater denitrification in Denmark—evolution, extent and reaction rates

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