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Identification of denitrification by measurement of N_2, Ar and N_2O as aid for the modelling of the nitrate transport in groundwater

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Introduction

- Many catchments of groundwater resources are agriculturally used.
- If nitrate is low in groundwater, in raw water => process of nitrate elimination => main reason

For water supply following questions are important:

- When can raised nitrate concentrations be expected in wells?
- How will measures which decrease emission of nitrate from soil influence water quality at different points in groundwater body?

- *Models are valuable tools for planning soil and water management.*

-*Following conditions should be considered, applying such models:*

- Realistic depiction of groundwater balance + flow.
- Sufficient knowledge about kinetics of nitrogen metabolism, about distribution in the subterranean space.
- Knowledge about metabolism often is only inadequately available.
- In such cases, kind of kinetics, their characteristics need to be based on assumptions.

Introduction

Our investigations were carried out at

=> 3 hydrogeological different aquifers in North German => map => red points

=> pleistocene formations, used for drinking water supply.

Content

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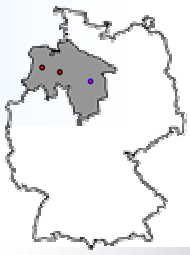


Elimination of nitrate in groundwater

9 types of reactions are known, **denitrification most effective** process of elimination

Heterotrophic: $4\ NO_3^- + 4\ H^+ + 5\ Corg$ **=> $2\ N_2 + 5\ CO_2 + 2\ H_2O$** (1)

1st partial reaction of **autotrophic denitrification**:

$14\ NO_3^- + 5\ FeS_2 + 4\ H^+$ **=> $7\ N_2 + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2\ H_2O$** (2)

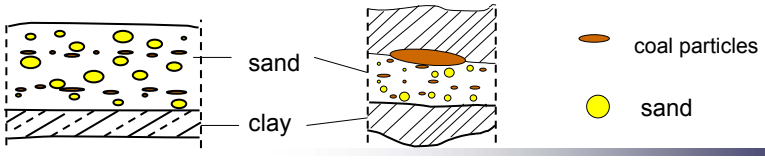
Process (1) is observed in root zone of soils but also in groundwater.
Process (2) is determined frequently in saturated zone of unconsolidated sediments.

Denitrification occurs in **steps from NO_3^- ⇨ NO_2- ⇨N_2O to ⇨ molecular N_2,** if the reaction can progress completely.

Organically bound **carbon or sulphidic compounds** act as **reducing agents**:

In unconsolidated sediments the **agents are distributed**

- **as fine particles** in the hydraulically active parts of the layer like sands
- or **at the edges of layers** as clay



Direct and indirect methods to identify denitrification

Modelling nitrate transport => **mark off cells of 3D - model net** in which denitrification occurs.

On this basis => **characteristic values λ** of the reactions **shall be to assigned** to cells, e.g. for equation $c(t) = co \cdot e^{(-\lambda \cdot t)}$ (3)

Different ways for identification of denitrification are possible:

First step, on the base of **dates of water quality**:

- **Prerequisite**: network of gauging stations that consider 3D - groundwater body.
- **Indications:**

=> No denitrification at **$O_2 \geq 5$ mg · L^{-1}** in pore water,

=> If O_2, NO_3^- ~ 0, => **rise of HCO_3^-** ⇨ heterotrophic **denitrification**, compared with gauging stations in the neighbourhood at which no denitrification occurs.

=> **rise of SO_4^{2-}, partly Fe^{2+} or...** ⇨ autotrophic **denitrification**.

=>**Dates do not supply secure proof** ⇨ concentration can be influenced by other processes. **=> Therefore second step of identification**

Direct and indirect methods to identify denitrification

Second step, the gases N_2, Ar and N_2O should be measured at the gauging stations. => they give a reliable identification on denitrification.

In groundwater ratio of gases N_2/ Ar determined by balance with atmosphere is 37.6 at 10 ^{0}C

NO_3^- => converted to N_2 => increase of N_2/Ar, => Ar remains unchanged.

Excess di-nitrogen:

cN_2 excess = {(N_2/Ar) measured - (N_2/Ar) balanced} · cAr measured [µMol ·L^{-1}] (4)

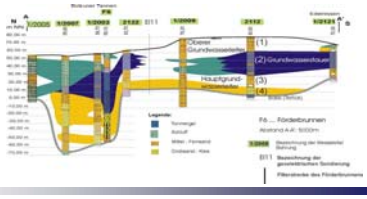
Determination of **ratio N_2/Ar** and of **"excess di-nitrogen"** => relatively **secure proof** => denitrification on flow path between groundwater table and screen of gauging station.

- By means of further parameters as SO_4^- or HCO_3^- the kind of the reaction can be deduced.
- NO_2^-, N_2O => indicator of incompletely running denitrification:
- N_2O may also occur when O_2 > 5 mg · L-1 in the pore water.

Application of methods

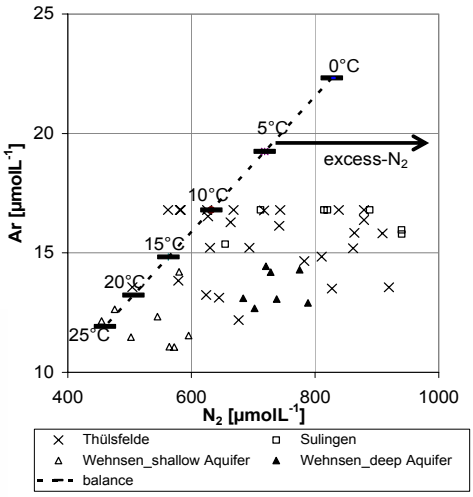
nitrogen studies carried out in investigation areas "Wehnsen", "Sulingen", "Thuelsfeld"
=> hydraulical active zones consist of sand/gravel
=> **K between 10^{-6} and 10^{-2} m · s^{-1}.**
=> thickness of aquifers 50 – 170 m
=> area "**Wehnsen" vertically subdivided into storeys** through silt and clay.
=> share of **agriculture** => between **56 % and 90 %,** residual part => mainly forests.

reactive material is very heterogeneously distributed in the hydraulically active sands. According to that distribution, the NO_3^- varies between < 0,1 and 298 mg · L^{-1} in a short distance.
Denitrification was investigated up to depths of **80 m below ground with help of core material and in situ investigation.**



Application of methods

gas \ temperature	0°C	10°C	25°C
N_2 [µmol·l^{-1}]	827,0	632,1	460,2
Ar [µmol·l^{-1}]	22,3	16,8	11,9
N_2/Ar - balanced	37,1	37,6	38,6



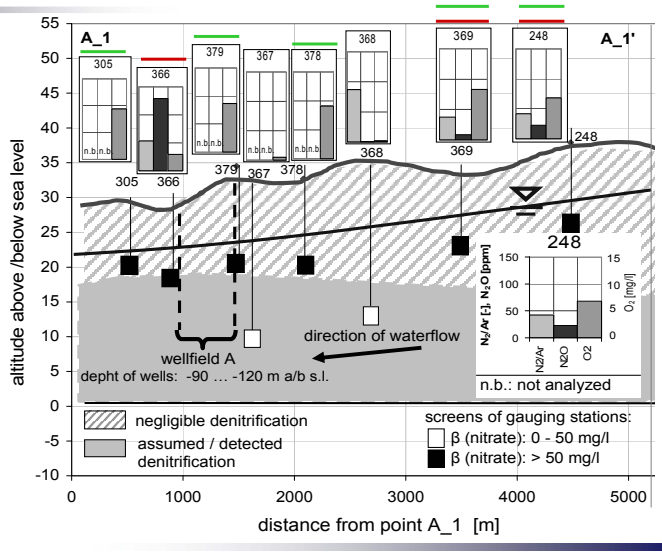
Application of methods

„Thuelsfeld, well field A“

station	FUK [m_NN]	Denitr. accord. water quality	N_2/Ar [-]	Denitr. on flow path accord. N_2/Ar	N_2O [µg L^{-1}]	Denitr. near the screen
1	2	3	4	5	6	7
248	24.95	no	41.84	no	48.21	Exist
353	7.47	heterotrophic	33.47	no	0.66	low
368	11.31	possible	87.24	exist	0.79	low
369	22.13	no	37.20	no	21.01	exist

N_2/Ar = 37.6 at 10 °C

Application of the methods



Conclusion

- Models that depict metabolism and transport of nitrate in a groundwater catchment of a waterworks are very suitable tools in order to plan measures to minmize emissions into groundwater.
- But until today models are still seldom build up and applied by enterprises of water supply.
- If a model of nitrate transport is supposed to be adapted to an aqifer, the metabolism of nitrate have to be known.
- In this case the measurement of the gases N_2, Ar, N_2O can be a good aid.
- The measurement of this gases should become an indispensable support during the development of transport model in future.

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Thank you for your attention

A view of Dresden and river Elbe