Dating Groundwater in The Netherlands

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Contents and context

Contents

• National groundwater quality monitoring network, tritium survey
• Regional 3H/3He dating (+ CFCs and SF6)
• Degassing of noble gases by N2 from denitrification
• 3H/3He survey in springs

Context

• PhD research at Utrecht University and Deltares (TNO): “Trends in groundwater quality”

• Funded in part by:
  Integrated project AquaTerra of the EU sixth framework: better understanding of river–sediment–soil–groundwater systems

• Also data from national and regional surveys
National groundwater quality monitoring network

- Total of ~450 multilevel sampling wells
- Screens (2m) at ~8 and ~25 m depth
- Installed in 1980 (original) and 1990 (extended)
- Concept of groundwater flow (Vogel): age increases with depth → sampling specific age (range)

\[ t_z = \frac{\varepsilon D}{N} \ln \left( \frac{D}{D - z} \right) \]


“Groundwater dating and gases in groundwater”, Utre
Monitoring locations

- Shallow: ~8 m
- Deep: ~24 m
Tritium survey in national monitoring network

- Selection of 332 screens of 187 (multilevel) wells in sandy areas in the Netherlands
- Tritium sampled 1 year after installation of networks
- Fitting tritium profile to measurements at two depths (still assuming exponential age increase with depth → estimating: thickness of aquifer, recharge rate


“Groundwater dating and gases in groundwater”, Utrecht, 14 May 2009
3H/3He dating

- Sampling in 2001, 2005 and 2008 in dry sandy areas in the south
- Total of 95 3H/3He samples

Groundwater sampling
Submersible pump: Grundfos MP1

P > TDG

NO BUBBLES!!!

USGS guidelines:
http://water.usgs.gov/lab/
http://water.usgs.gov/lab/3h3he/sampling/
Groundwater dating and gases in groundwater, Utrecht, 14 May 2009

- $^3$H/$^3$He sampling
- Copper sample tube
- Metal frame
- Pressure gauge
- Total Dissolved Gas (TDG) pressure sensor (mmHg)
- EC/pH
- $O_2$
- Time
Groundwater sampling

pH/EC/O₂ sensors

flow through cell

inflow

outflow

BUBBLES!!!
Measuring **Total Dissolved Gas** pressure

- **TDG probe:**
  - Coiled silicone tubing
  - Diffusion of gases into tubing
  - Pressure in tubing = **Total Dissolved Gas** pressure

$$TDG = \sum_{i=1}^{n} P_i = C_i \ast K_{H,i}$$

T300E, In-Situ (Manning, 2003, Ground Water)
$^3$H/$^3$He sampling
Sample analysis: Uni. Bremen

Dr. Jürgen Sültenfuß
\(^3\)He, \(^4\)He and Ne in groundwater

Atmospheric solubility equilibrium
Excess air: air entrapment during infiltration
Radiogenic: U/Th/Li decay \(\rightarrow\) \(^3\)He + \(^4\)He

Tritiogenic: 
\(^3\)H decay

\[ \tau = \frac{12.32}{\ln(2)} \cdot \ln\left(1 + \frac{\text{He}_{\text{trit}}}{\text{H}}\right) \]

Graph showing relative contributions of tritiogenic, radiogenic, and excess air to \(^3\)He, \(^4\)He, and Ne in groundwater.
noble gas concentrations below atmospheric equilibrium

→

“degassing” of groundwater

22Ne excludes diffusive degassing

- 22Ne isotope ratio indicates → no diffusive degassing

Degassing is caused by denitrification

Pyrite oxidation and nitrate reduction:

$$5 \text{FeS}_2 + 14 \text{NO}_3^- + 4 \text{H}^+ \rightarrow 5 \text{Fe}^{2+} + 10 \text{SO}_4^{2-} + 2 \text{H}_2\text{O} + 7 \text{N}_2(g)$$

No nitrate in degassed samples ($\Delta\text{Ne} < 0$)


Bubbles and degassing

\[ \text{NO}_3^- (aq) \rightarrow \text{N}_2 (aq) \]

- Ne(aq)
- \(^4\text{He}(aq)\)
- \(^3\text{He}(aq)\)

- Ne(g)
- \(^4\text{He}(g)\)
- \(^3\text{He}(g)\)

\[ \text{N}_2 (g) \]
Concepts

- **Secondary** partitioning of NGs: new gas phase formation
  - production of gas (bubble) \(\rightarrow\) re-partitioning or re-equilibration
  - “new” gas often methane or nitrogen

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He, Ne, Ar, Kr, Xe
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He, Ne, Ar, Kr, Xe
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He, Ne, Ar, Kr, Xe
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He, Ne, Ar, Kr, Xe
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He, Ne, Ar, Kr, Xe
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He, Ne, Ar, Kr, Xe
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He, Ne, Ar, Kr, Xe
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- “Depletion” noble gases: concentrations below atmospheric equilibrium
  - \(\Delta\)He, \(\Delta\)Ne, \(\Delta\)Ar, \(\Delta\)... below zero
  - \(\Delta^{22}\)Ne non-zero \(\rightarrow\) diffusive fractionation

"Groundwater dating and gases in groundwater", Utrecht, 14 May 2009
Examples of NG re-partitioning (degassing)

- **Groundwater:**
  - Borden landfill, Ontario: methane? (Solomon, 1992, WRR)
  - Voldby, Denmark: nitrogen (Blicher-Matthiesen, 1998, JoH)
  - Banisveld, The Netherlands: methane (Van Breukelen, 2003, JoCH)
  - Bemidji, Minnesota: methane (Amos, 2005, WRR)
  - The Netherlands: methane (Fortuin, 2005, JoH)
- **Lake sediments:**
  - Soppensee, Switzerland: methane (Brennwald, 2005, EPSL)
- **Lake water:**
  - Black Sea, methane (Holzner, 2008, EPSL)
- **Peat pore water:**
  - Silver Flowe bog, Scotland (laboratory): methane (Laing, 2008, GCB)
Borden Landfill, Ontario (Solomon, 1992, WRR)
Degassing of groundwater by methanogenesis at water table

- High methane and CO₂
- He and N₂ below atm. equilibrium
- → gas stripping (degassing) by methane + CO₂ exsolution
Voldby, Denmark (Blicher-Matthiesen, 1998, JoH)
Degassing of groundwater by denitrification

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>Cl</th>
<th>CI</th>
</tr>
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<tbody>
<tr>
<td>T °C</td>
<td>11.08</td>
<td>11.2</td>
<td>11.22</td>
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<td>P atm</td>
<td>1.146</td>
<td>1.079</td>
<td>1.083</td>
<td>1.121</td>
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<td>Ar µM</td>
<td>17.58</td>
<td>17.31</td>
<td>15.92</td>
<td>15.83</td>
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<td>ΔAr</td>
<td>5%</td>
<td>3%</td>
<td>-5%</td>
<td>-6%</td>
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<tr>
<td>N2-N µM</td>
<td>1569</td>
<td>1676</td>
<td>1703</td>
<td>1704</td>
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<tr>
<td>ΔN</td>
<td>25%</td>
<td>33%</td>
<td>35%</td>
<td>35%</td>
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<td>NO3 µM</td>
<td>1433</td>
<td>1192</td>
<td>879</td>
<td>981</td>
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<td>O2 µM</td>
<td>97.93</td>
<td>52.28</td>
<td>12.06</td>
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</table>

"Groundwater dating and gases in groundwater", Utrecht, 14 May 2009
The Netherlands (Fortuin, 2005, JoH)
Degassing of groundwater by methanogenesis (or denitrification)

- Nitrogen most abundant at low total gas pressures
  High methane abundance at high total gas pressures
Degassing calculations

Denitrification of 200 mg/l nitrate at 5 m below the groundwater table:

Solubility of N₂ at atmospheric pressure: 0.83 mmol/l
Solubility of N₂ at 1.5 bar (= 5 m below gwt): 1.2 mmol/l

Atmospheric equilibrium concentration: 0.65 mmol/l

“Dissolution space”: (1.2 – 0.65 =) 0.55 mmol/l

→ 200 mg/l NO₃ = 3.2 mmol/l NO₃ → 1.6 mmol/l N₂

“Excess” N₂ (above solubility): (1.6 – 0.55 =) 1.05 mmol/l = 16.3 ml gas per liter (=1.6% !!)

Helium partitioning coefficient: 107.4 : 1 (gas : water)
Helium atmospheric equilibrium concentration (initial concentration in groundwater):

\[ \text{He}_{\text{eq}} = 2.07 \times 10^{-9} \text{ mol/l} \]

Water phase (1 liter): 0.75 \times 10^{-9} \text{ mol} (= 36%) \[ \Delta \text{He} = -64\% \]

Gas phase (16.3 ml): 1.32 \times 10^{-9} \text{ mol} (= 64%)
Results $^{3}H/^{3}He$ ages

- Large deviations from average theoretical age profile
- Rather old groundwater with 10 m of groundwater table
- Shows the value of age dating, even in “simple” environments
Check $3H/3He$ ages with tritium in precipitation

$3H + 3He^*$

old $3H$ at time of recharge
- extra check
- "stable" groundwater system?
Comparing $3\text{H}+3\text{He}^*$ with dispersion model

Black-box dispersion model, with dispersion parameter PD

- Most samples can be explained by some dispersion model (but some can’t)
- Is this truly dispersion? Or just fitting lines to data?
- *Is there a “good” way to combine point data of $3\text{H}$ in precipitation from different stations?*
Results of CFCs, SF6 and two-phase model

- CFCs: degradation
- SF6: degassing

Visser et al. (2009) J Contam Hydrol 103, 206-218

Visser et al. (2009) J Contam Hydrol 103, 206-218
Relating groundwater quality to groundwater travel time

- new method to aggregate all groundwater quality monitoring data
- clearly reveals trends, in non-reactive contaminants
Plotting data against recharge year instead of measurement year

Visser et al. (2007) Environmental Pollution 148:797-807

Dating spring water with 3H/3He?
8 selected springs

- Springs in chalk plateau in southern most part of NL
- Thickness of chalk plateaus is between 40 and 80 meter thick
Dating spring water with 3H/3He?
## Results tritium-helium springs

<table>
<thead>
<tr>
<th>Plaats</th>
<th>code KRW</th>
<th>code Meinardi</th>
<th>x [m]</th>
<th>y [m]</th>
<th>$^3$H [TU]</th>
<th>$^3$He* [TU]</th>
<th>$^3$H (2001) [TU]</th>
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<tbody>
<tr>
<td>Epen</td>
<td>z.025</td>
<td>191873</td>
<td>191800</td>
<td>314000</td>
<td>6.75</td>
<td>3.6</td>
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<td>Eys</td>
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<td>315200</td>
<td>6.54</td>
<td>3.6</td>
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<td>317110</td>
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<tr>
<td>Noorbee</td>
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<td>Schin</td>
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<td>Bellet</td>
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<td>Vijlen</td>
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<td>6.75</td>
<td>3.6</td>
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</tr>
</tbody>
</table>

- **Very low $^3$He**
- $^3$He escape to the atmosphere during groundwater flow, fluctuating water levels and drying up of springs
- **$^3$He not useful for dating spring water (in this case)**
- tritium-concentrations are valuable, in combination with tritium-concentrations measured in 2001
Conceptual groundwaterflow
Black-box model: exponential model

“Groundwater dating and gases in groundwater”, Utrecht, 14 May 2009
Example: tritium in St. Brigida-bron

- water in de St. Brigidabron is mixture:
  - ~62% of water younger then 50 years (contains nitrate)
  - 38% old and nitrate free water.
**Resultaten leeftijdsverdeling bronnetjes**

<table>
<thead>
<tr>
<th>bron</th>
<th>code KRW</th>
<th>code Meinardi</th>
<th>Travel time saturated zone</th>
<th>Travel time unsaturated zone</th>
</tr>
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<tbody>
<tr>
<td>Epen</td>
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<td>Stockem</td>
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<tr>
<td>Wittem</td>
<td></td>
<td>81</td>
<td></td>
<td>10</td>
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</tbody>
</table>
Example: nitrate in St. Brigida-spring

- Modeling nitrate concentrations in St. Brigida-spring using “black-box” model and reconstructed surface deposition.
- Fluctuating nitrate concentrations probably the result of fluctuating discharge of the St. Brigida spring, resulting in a varying contribution of old (nitrate-free) water to total discharge.

![Nitrate in St. Brigida-bron](image)
90 new samples taken

- Waiting for analysis
Conclusions

• Large number of wells dater under rather ideal circumstances: well defined monitoring wells with short screens.
• 3H/3He dating showed large variations in groundwater ages, where simple exponential age-increase with depth was assumed.
• Noble gases show signs of degassing, as a result of exsolution of N$_2$ gas produced by denitrification.
• $^3$H/$^3$He groundwater dating can be used, even when degassing has taken place. (Rather then CFCs (in anoxic environments) of SF6
• TDG pressure sensor is essential to calculated timing of degassing, and provides interesting field data.
• $^3$He* is not contained in the spring-system in the south of the Netherlands
• Combining tritium measurements makes exponential model possible (or is it fitting yet another line to two data points?)
• Future work: dating drinking water supply wells…
Acknowledgements

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