Recharge rates to deep aquifer layers estimated with $^{39}\text{Ar}$, $^{85}\text{Kr}$ and $^{14}\text{C}$ data: A case study in Odense (Denmark)
Increasing interest in pre-modern groundwater due to
- Overexploitation
- Contamination
- Effects of climate change
- Investigation of potential and limitations of tracers beyond the 50 years age limit.
- Determination of recharge rates, residence times and renewal rates
- Combination of tracer methods and numerical modelling
Odense Water Ltd is one of the largest water utilities in Denmark with a groundwater abstraction permission of ~14 mill. m³/year.

The groundwater is mainly abstracted from rather shallow aquifers (quaternary sand deposits) on 7 wellfields around the city of Odense.

The catchments of the wellfields are dominated by conventional farming and urban areas.

The groundwater table is close to the surface and the low lying areas are generally drained by tile drains.
The catchment area is characterised by two high areas rising to 130 m above sea level divided by a wide and shallow depression stretching NE–SW.

from Hansen et al, 2009
Several ice advances and subsequent ice retreats during the Weichselian glaciation have formed the present landscape and geology (Houmark-Nielsen & Kjær 2003).

Main aquifers are found in semi-confined units of glaciofluvial sand and gravel deposits at varying depths overlain by glacial till.

Tertiary marls and clay forms the lower boundary of the Quaternary aquifer system.

Geology of the quaternary deposits is rather complex and heterogeneous.

Interconnected hydrostatigraphic units with a typical thickness of 10-15 meter.

Troldborg, 2004
Timescales of groundwater dating methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>Dating range (years)</th>
<th>Half-life (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{222}\text{Rn}$</td>
<td>$10^1$</td>
<td>10.7</td>
</tr>
<tr>
<td>$^3\text{H}/^3\text{He}$</td>
<td>$10^2$</td>
<td></td>
</tr>
<tr>
<td>$^{85}\text{Kr}$, FCKW, $\text{SF}_6$</td>
<td>$10^3$</td>
<td>269</td>
</tr>
<tr>
<td>$^{39}\text{Ar}$</td>
<td>$10^4$</td>
<td></td>
</tr>
<tr>
<td>$^{14}\text{C}$</td>
<td>$10^5$</td>
<td></td>
</tr>
<tr>
<td>$^{36}\text{Cl}$, $^{81}\text{Kr}$</td>
<td>$10^6$</td>
<td></td>
</tr>
<tr>
<td>$^4\text{He}$</td>
<td></td>
<td></td>
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</tbody>
</table>
**85Kr-39Ar: Key data**

- **Half-life:** 10.7
- **Decay mode:** β
- **Modern isotope ratio (2008):** ~$3 \cdot 10^{-11}$
  - **39Ar/Ar:** $8.1 \cdot 10^{-16}$
- **Atoms/Liter water:** 58‘000
  - **85Kr:** 8‘700
- **Activity (Bq/L water):** $1.2 \cdot 10^{-4}$
  - **39Ar:** $7.1 \cdot 10^{-7}$ → 22 decays/yr

**Input function**

**Water sample volume:** 1-2 tons!

**Note:**
- Based on a isotope ratio ($39\text{Ar}/\text{Ar}$, $85\text{Kr}/\text{Kr}$ etc) and insensitive to addition of excess air, recharge temperature and degree of degassing (both in nature and during sampling).
- Based on absolute concentrations.
Sampling and detection method

Water degassing in the field

39Ar and 85Kr activity measurement by Low Level Counting

Active and passive shielding in underground lab

Sampling for 85Kr, 39Ar and 14C
Spontaneous fission

\[ U (n) \rightarrow \text{Th} \]

Al, Mg..(\( \alpha, n \))

Subsurface production

\[ {^{39}}K(n,p)^{39}\text{Ar} \]

\[ 3^{9}\text{Ar production} \]

Pore-Water

Subsurface secular equilibrium

Atmospheric Production

\[ ^{40}\text{Ar}(n,2n)^{39}\text{Ar} \]

0.104 dpm/L Argon (100% modern)

\[ T_{1/2} = 269 \text{ years} \]

\[ 40\text{Ar}(n,2n)^{39}\text{Ar} \]

Groundwater residence time (years)

% modern

0 200 400 600 800 1000
39Ar depth profile

- Screen depth (m)
- 39Ar (% modern)
- 0.15m/yr

Graph showing the relationship between screen depth and 39Ar (% modern) with a trend line indicating a rate of 0.15m/yr.
$^{39}$Ar spatial distribution

- Screen depth (m)
- $^{39}$Ar (% modern)
- 0.15 m/yr

- Northing
- Easting

Locations:
- Odense
- Holmehaven
- Borreby
- Lunde
- Soeby
$^{39}$Ar-$^{85}$Kr depth profile

- **Screen depth (m)**
- **$^{39}$Ar (% modern)**
- **$^{85}$Kr (dpm/cc Kr)**

- Modern water

- Mean screen depth (m): 85

- $0.15 \text{ m/yr}$
$^{39}$Ar-$^{85}$Kr depth profile
Single well age gradient

Top screen
Bottom screen

the same borehole
averaged value.
Expected age distribution and dispersion in heterogeneous alluvial aquifer system

A wide rather than a piston piston-flow-like age distribution can be expected because of

- The heterogeneity of the system
- The spatially distributed recharge
- Mixing in the extended screen intervals of the extraction wells
Age distribution: $^{39}$Ar and $^{85}$Kr data

- Measured $^{85}$Kr and $^{39}$Ar activities can consistently be interpreted if dispersive mixing is taken into account (AD2-AD3)
- Modern $^{39}$Ar values in samples low in $^{85}$Kr are suspicious for produced underground
Age spectra $^{39}$Ar-$^{14}$C

$^{39}$Ar (35 samples)

350 yrs

$^{14}$C (7 samples)

<2000 yrs

Explanation?
Geochemical correction of $^{14}$C activities

- Two component mixing is not consistent (or at least very unlikely) within the hydro-geological context
- Geochemical correction models are not sufficient to eliminate the discrepancy between $^{39}$Ar and $^{14}$C ages
Diffusive exchange with stagnant zones (Sudicky, 1981)

Averages estimates (System of parallel layers; Sanford, 1997)

Porosity (Active & stagnant): 0.3
Thickness flow zone: 20 m
Thickness stagnant zone: 40 m
Diffusion coeff. ($^{14}$C): $3.15 \times 10^{-3}$ m$^2$/yr
Diffusion coeff. ($^{39}$Ar): $2.6 \times 10^{-3}$ m$^2$/yr
Dispersive mixing reduces the apparent decay rate of $^{39}$Ar relative to $^{14}$C.
Summary: The combined contribution of isotope exchange with the aquifer rocks, diffusive exchange with aquitards, dispersion and eventually underground production resolves the discrepancy between $^{39}$Ar and $^{14}$C ages: The resulting age span ranges between recent and 500-700 years (and not up to 2000 years as indicated by $^{14}$C data)
Age spectra

Uncorrected $^{39}$Ar ages

Corrected $^{14}$C-$^{39}$Ar tracer ages
Problems with heterogeneity in physically based agricultural catchment models

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A good-looking catchment can turn into a modeller’s nightmare

Jens Christian Refsgaard & Jeppe Rølmer Hansen

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Stable isotopes $\delta^{18}O-\delta^{2}H$

$\frac{d^{18}O}{100m} \approx 0.28\% \Rightarrow \Delta h \approx 150m$

(Poage, 1996)

$\frac{d^{18}O}{d^\circ C} \approx 0.56\% / ^\circ C \Rightarrow \Delta T \approx 0.8^\circ C$

(Schrag, 1996)

Geological cross section

Till Fractured till Sand Prequaternary

Middle aquifer

Lower aquifer

Reconstructed Temperature

Medieval Warm Period

Little Ice Age

IPCC 2001, Mann et al, 1999
Water Budget

* Data from Hansen, 2006

- Precipitation*: 600-1000 mm (av: 840 mm) 880
- Evaporation*: 500-600 mm (av. 550) -575
- Recharge*: ~290 mm 303 (100%)

Volumes Mio m³ (%)

- Drain to river, (run off, shallow aquifers*): 203 mm 212 (70%)
- Other boundaries, storage change*: 35 (13%)
- Abstraction* (2006) 17 mm 14 (4 %)
- Recharge to deep layers 40 mm 42 (13%)

* Data from Hansen, 2006

- Shallow layers (< 50-60 m)
- Deep layers (>50-60 m)

~1046 km²
Spectral GammaLog

Well U 341

<table>
<thead>
<tr>
<th>Total</th>
<th>K</th>
<th>U</th>
<th>Th</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>2 ppm</td>
<td>7 ppm</td>
</tr>
</tbody>
</table>

1%
High $^{39}$Ar values: Hypothesis

Shallow water table $\rightarrow$ Residual CR flux in saturated zone

Confining layer $\rightarrow$ Sufficient time for activity build up
Conclusions

- The relation between $^{85}$Kr and $^{39}$Ar indicates pronounced dispersive mixing in accordance with the heterogeneous structure of the aquifer.
- Uncorrected $^{39}$Ar- and $^{14}$C-model age scales differ by ~1 order of magnitude (Note: $^{14}$C model ages consider geochemical corrections).
- The consideration of a whole set of processes (rather than a single one) results in a consistent $^{14}$C- and $^{39}$Ar-age range between 20 years and ~700 years.
- Underground production of $^{39}$Ar is locally relevant in particular in the northern part of the study area. A general assessment of this effect needs more detailed investigation.
- Combined and integrated tracer data including $^{39}$Ar allow for the estimation of flow dynamic and recharge rate of groundwater in deeper aquifer layers that are out of range of transient tracers ($^{3}$H/$^{3}$He, SF$_6$ etc).
- Vertical age profiles have potential as climate records on the millennium scale (instead of horizontal “flow lines” with notorious limited sampling points)
Thank you
Spatial variation of recharge rates

from Dubgaard et al., 2007

Symbol size ~ $^{85}$Kr activity