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Joint use of $^{3}H/^{3}He$ apparent age and on-site helium analysis to identify groundwater flow dynamics and transport of PCE in an urban area

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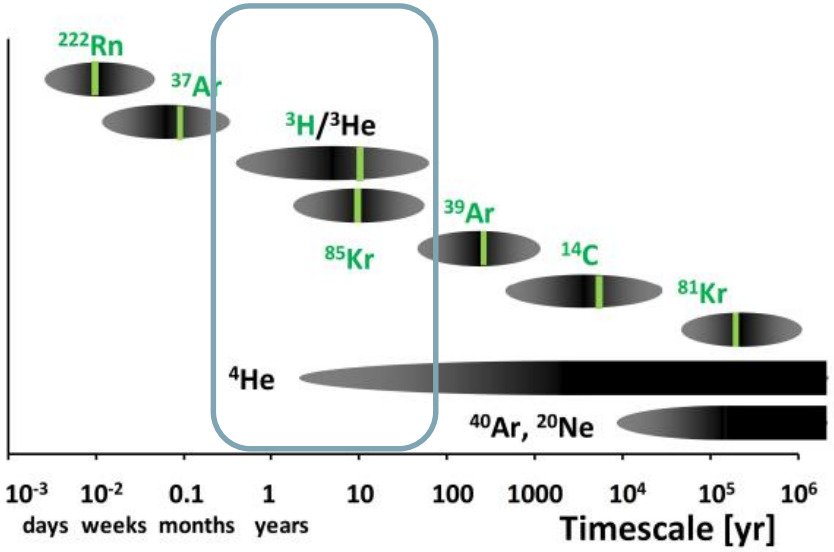
Introduction

- **Majority of groundwater contamination** has occurred in recent times **(< 100 years**), **tritium (^{3}H) is a suitable tracer** for younger groundwater.

- **Radiogenic ^{4}He is a by-product of the ^{3}H/^{3}He method** and used as an **additional indicator for older groundwater**

- **New developments in portable field-operated GE-MIMS system** provides a unique opportunity to measure dissolved gas concentrations, such as ^{4}He, in groundwater systems



Gerber, C. (2017). Groundwater Dating with Noble Gases – from Groundwater-Surface Water Interaction and Contaminant Transport to Paleohydrogeology.

Laboratory & On-site Mass Spectrometer (MS)

Laboratory-based MS

- Analytical precision
- Small amount of water is needed
- **Capable of providing an apparent age**

- High cost (acquisition, operation, and maintenance)
- Labor- and time-intensive

Portable gas equilibrium membrane inlet MS (GE-MIMS)

- Comparat recision inexpensi
- Relatively mental easy to s) on operate
- High- mount of throughpu vater)

- **Not capable of providing an apparent age**

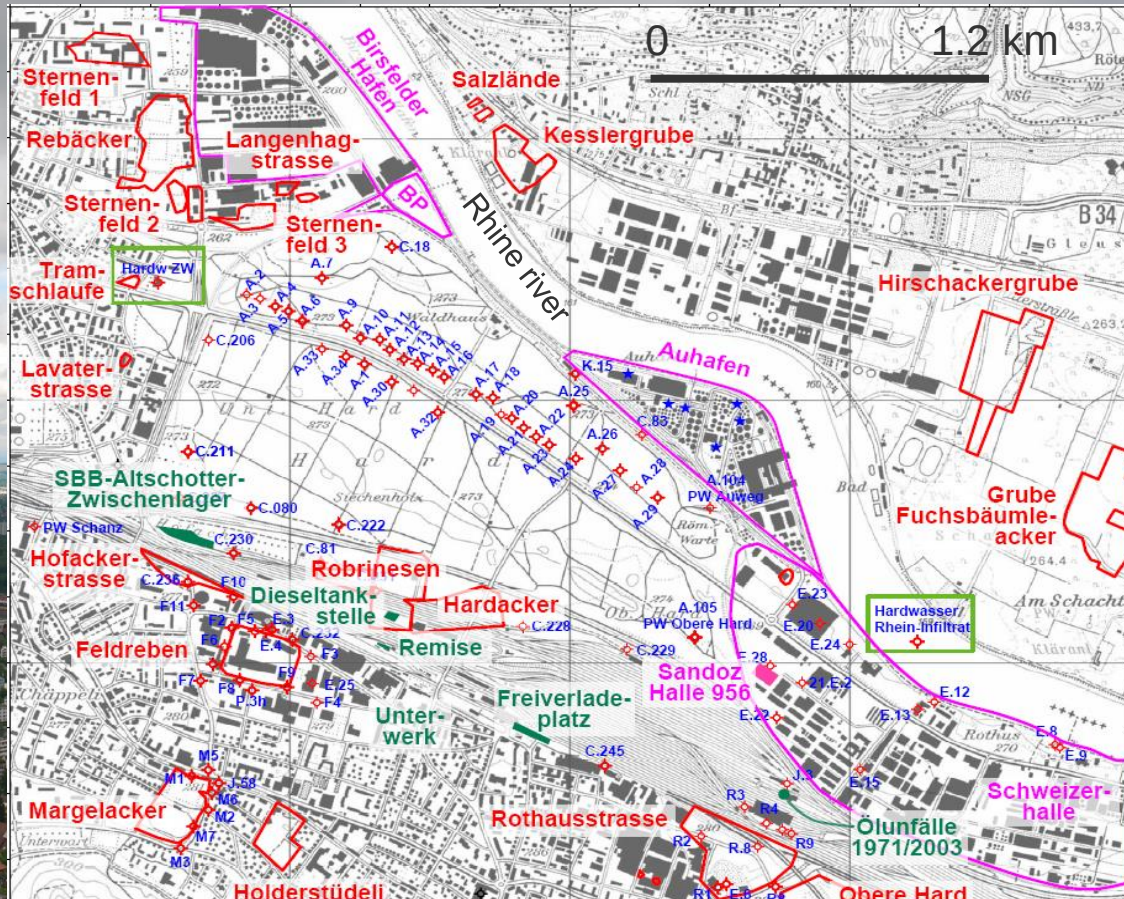
Objective and Study Area

- ^{4}He accumulation rates are often obtained from $^{3}H/^{3}He$ ages.
- And it has been shown that ^{4}He concentrations measured using laboratory and field-based (GE-MIMS) methods closely agree.

→ We aimed to determine the relationship between field-measured ^{4}He concentrations analyzed with a GE-MIMS system and lab-based apparent $^{3}H/^{3}He$ ages.

Study Area

- Important water supply site
- Drinking water supply combined with artificial infiltration
  - Artificial Infiltration 95.000 ($m^3\ d^{-1}$)
  - Pumping rates 45.000 ($m^3\ d^{-1}$)
- Study Site History
  - Contaminated areas
- Avoiding regional groundwater water
- Two main aquifers:
  - i) Overlying Sand-Gravel aquifer
  - ii) Bedrock: Kartisfied limestone aquifer



Sampling

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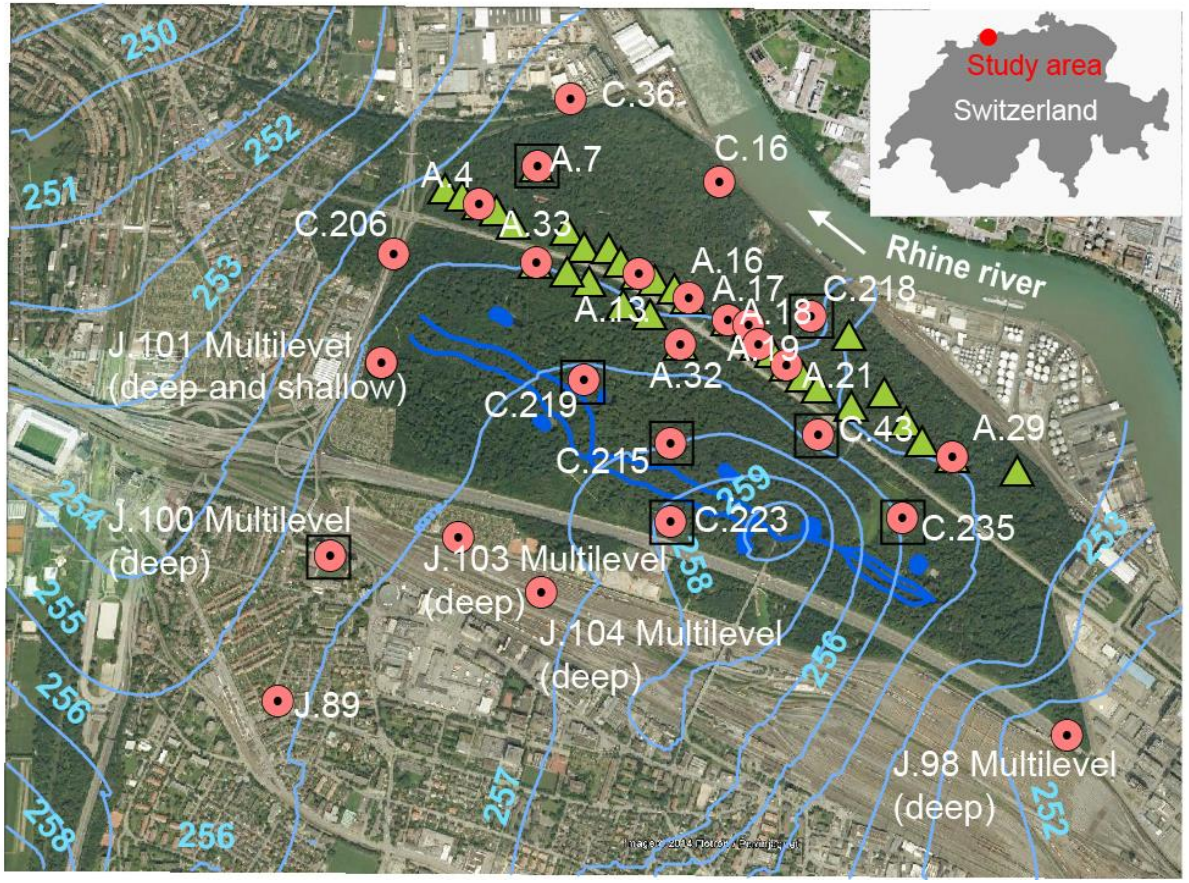
Legend

- Groundwater abstraction well
- Groundwater level (masl)
- Infiltration system
- Sampling ($^3H/^3He$ apparent age & GE-MIMS)
- Sampling (only GE-MIMS)

0 0.25 0.5 1 Kilometers

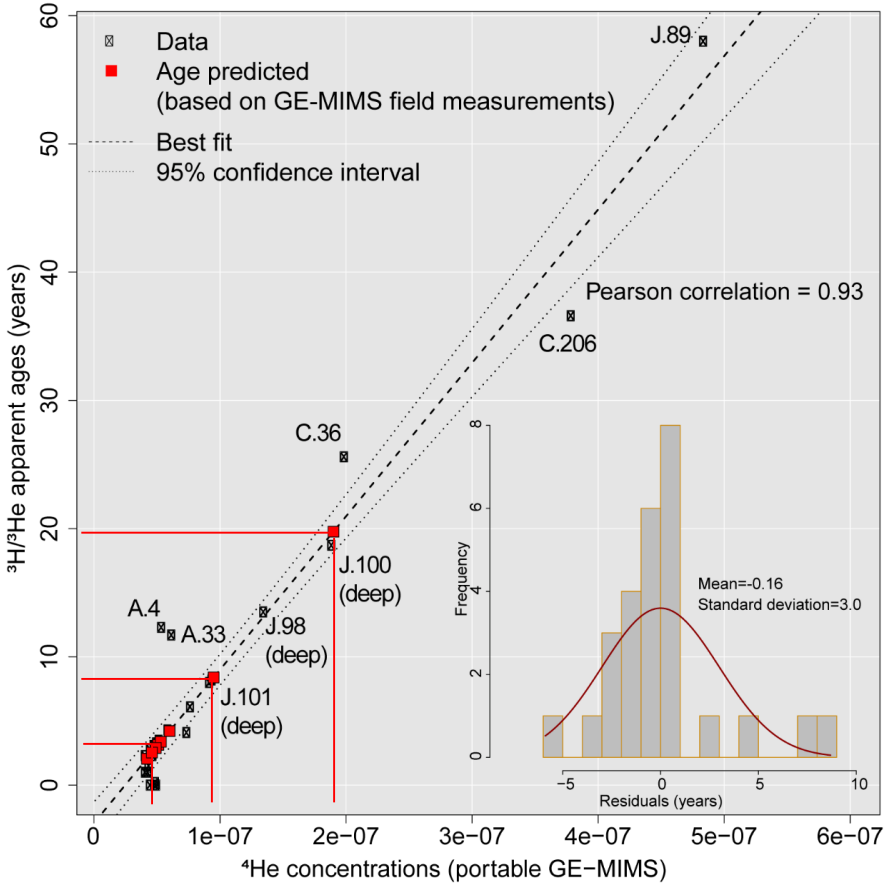
N W E S



Relationship between $^3H/^3He$ apparent ages and GE-MIMS measurements

- Linear relationship between field-measured ^4He concentrations collected with the GE-MIMS system and the estimated laboratory $^3H/^3He$ apparent ages.

- Apparent ages can be predicted for sampling locations where only ^4He concentration from the GE-MIMS measurements are available.



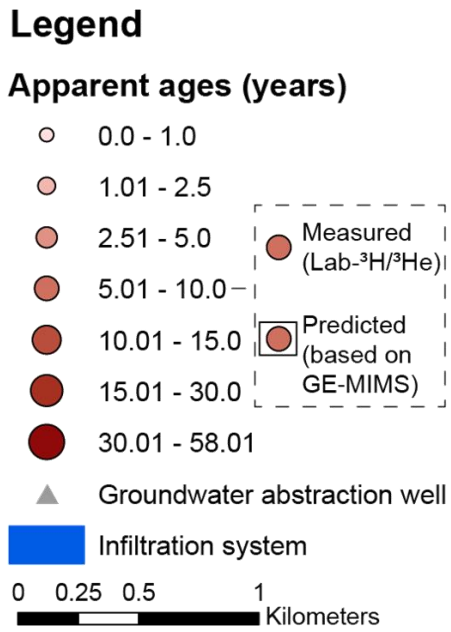
Spatial Distribution Apparent Ages

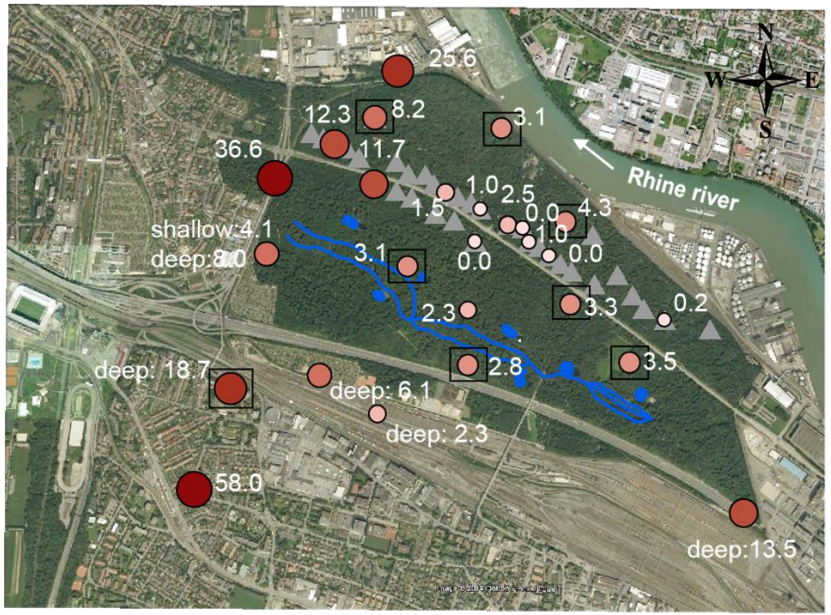
Relatively young water → close to the artificial infiltration system.

Oldest water → in the south and at western edge.

Multilevel wells → increasing trend with increasing depth.

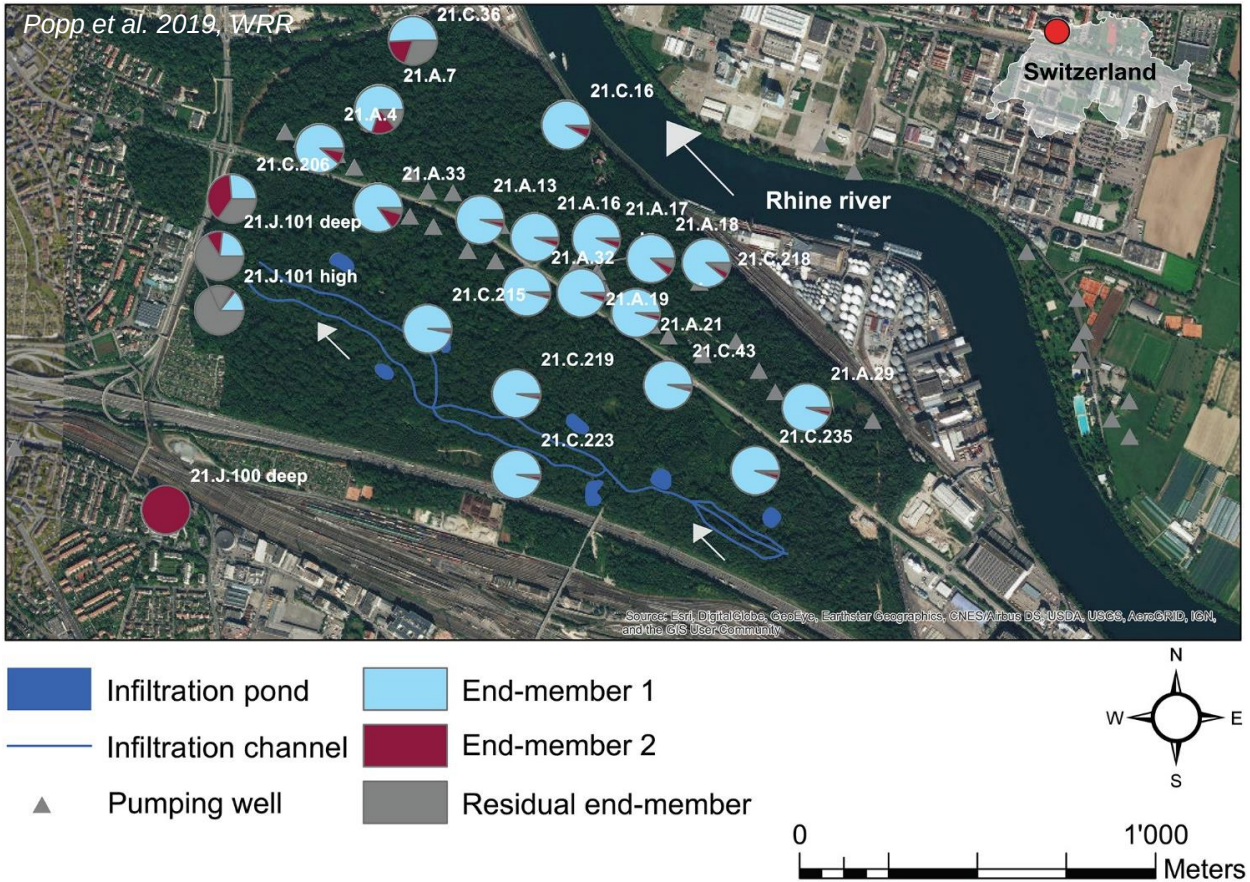
Pumping wells → older ages at wells located at the western edge.





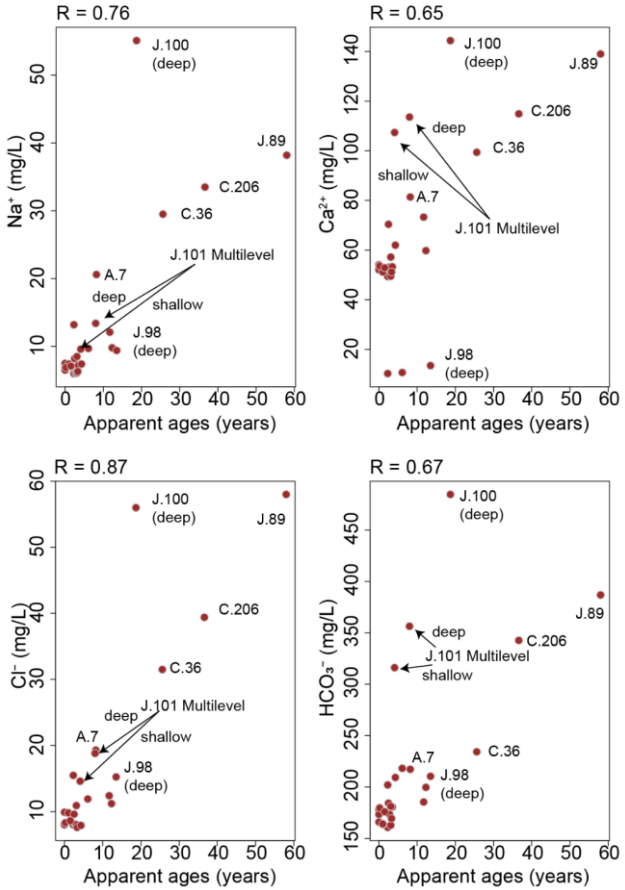
Groundwater Mixing

- **Bayesian Mixing Model**
- Explicitly considers the possibility of unknown end-members
- Fully accounting for tracer uncertainties
- Tracer set, which includes helium (^{4}He) analyzed on site with a newly developed Gas Equilibrium Membrane Inlet Mass Spectrometer (GE-MIMS)



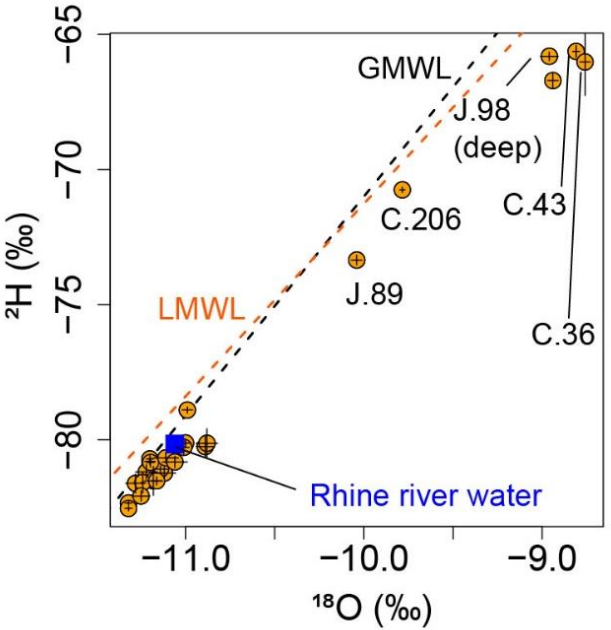
Apparent Ages and Hydrochemistry

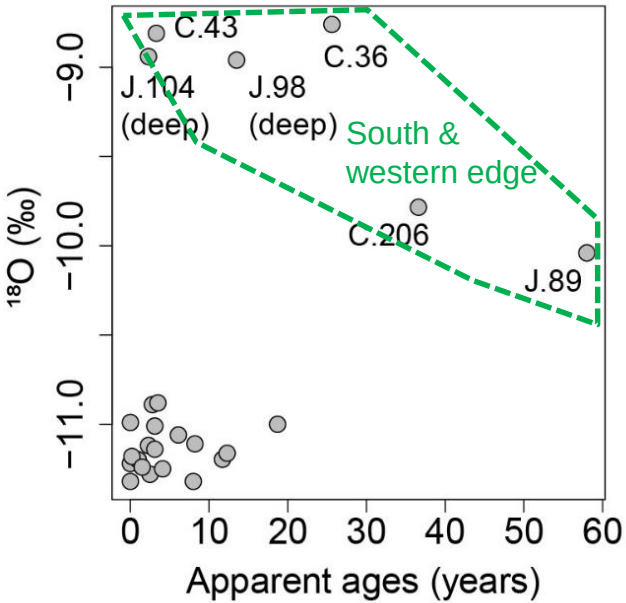
- Trend between hydrochemical data and the apparent age.
- Muschelkalk water has significantly different hydrochemistry than the artificial infiltrated surface water, including an increase in Ca^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-}.
- At pumping wells where the impact of artificial infiltration is low (e.g. A.7), a higher concentration can be observed.
- Older groundwater → higher concentration (~Muschelkalk water).



Apparent Ages and Stable Water Isotopes

- Stable water isotopes (^{18}O and ^{2}H) ranged from -11.32 to -8.76‰ & -82.54 to -65.63‰.
- Locations in the south and at the western edge → enriched isotope composition, indicating different water origins.





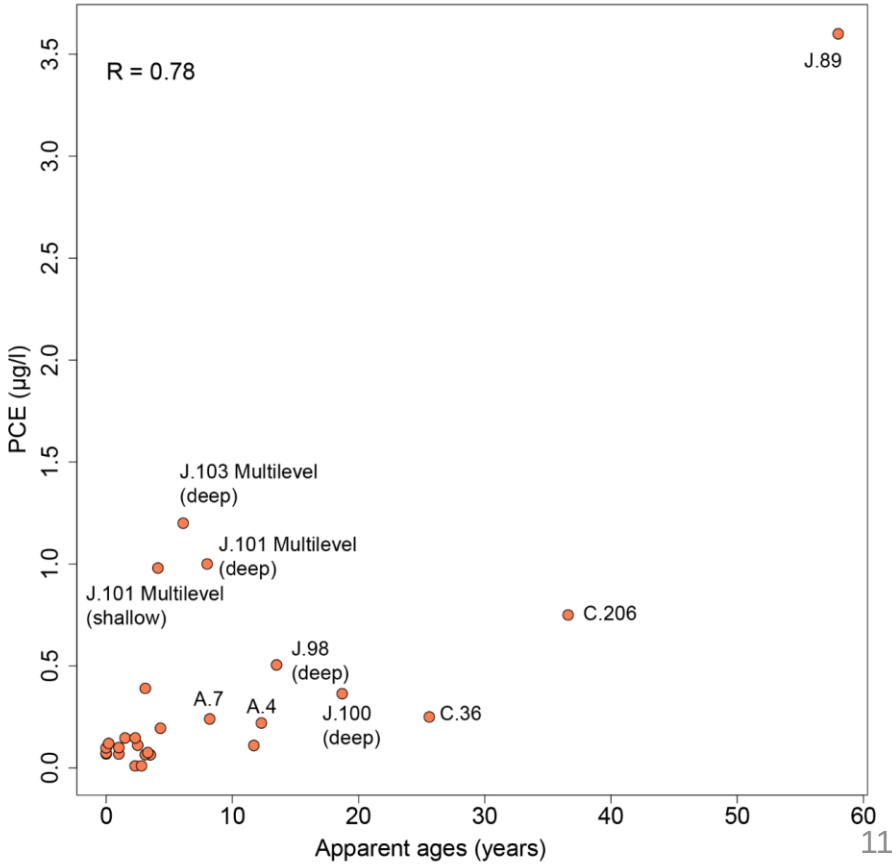
Apparent Ages and PCE

Highest concentration PCE → oldest groundwater.

PCE concentration decreases with decreasing age.

Most multilevel wells with deeper sampling depths indicate higher concentrations of PCE.

Pumping wells in the western part of the pumping well gallery (e.g. A.4 and A.7) show higher concentrations of PCE.



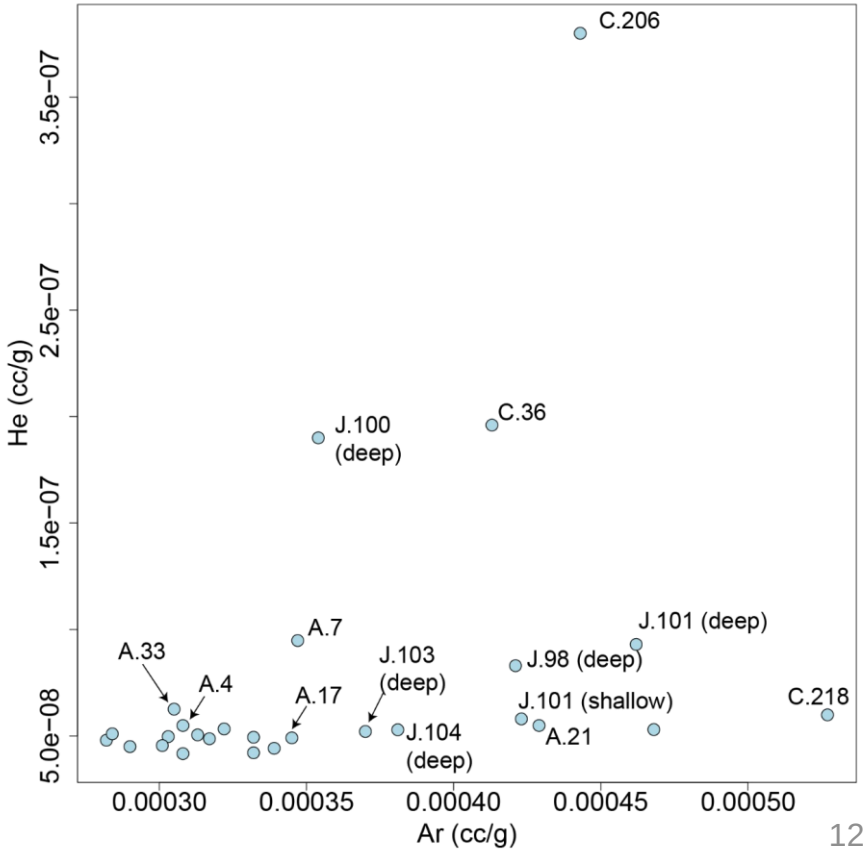
Why both measurements correlate?

Applicability: Radiogenic helium is accumulated in the aquifer by radioactive decay of U and Th within the aquifer matrix → ^{4}He concentration is controlled by the residence time of the groundwater.

But excess air can also explain the relationship.

Approach: Ar concentration is not affected by ^{4}He accumulation in the aquifer, but only by excess air processes.

- Correlation between Ar and He → excess air is controlling the relationship.
- Ar does not vary with the He concentration, then the ^{4}He accumulation in the aquifer leads to the $^{3}H/^{3}He$–^{4}He relation.



Conclusion

- Results of the simpler GE-MIMS system are as satisfactory as those of the highly sophisticated lab-based method.

- The applicability of the method is assured when radiogenic helium is accumulated in the aquifer by radioactive decay of U and Th within the aquifer matrix
  - ^{4}He concentration is controlled by the residence time of the groundwater in the aquifer.

- Pumping well water contains not only artificial infiltrated surface water → Mixing occur, especially at the western edge of study area

- “Old” limestone water has elevated PCE concentration.

- Combined use opens up new opportunities in site characterization, even though laboratory data are still required to establish this relationship.

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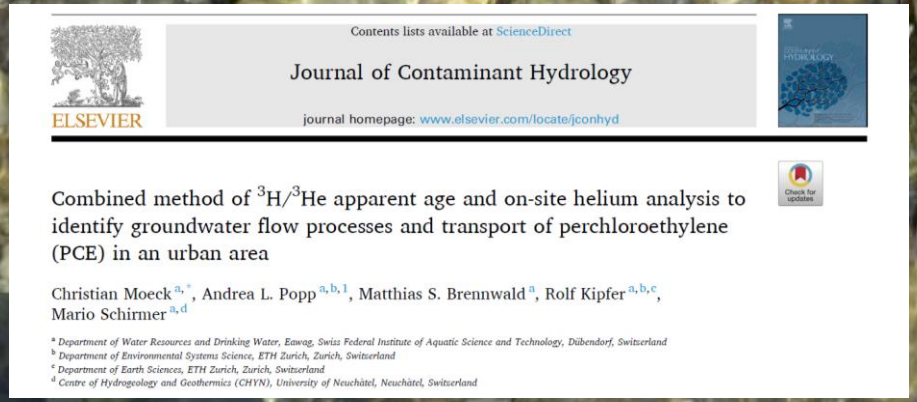
Thank you for your attention



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https://gasometrix.com/

Moeck et al.: Combined method of 3H/3He apparent age and on-site helium analysis to identify groundwater flow processes and transport of perchloroethylene (PCE) in an urban area. *Journal of contaminant hydrology*.

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