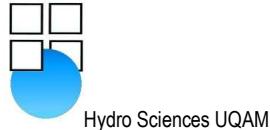


# Analyses of discrete (ground)water dissolved gases samples using the miniRUEDI

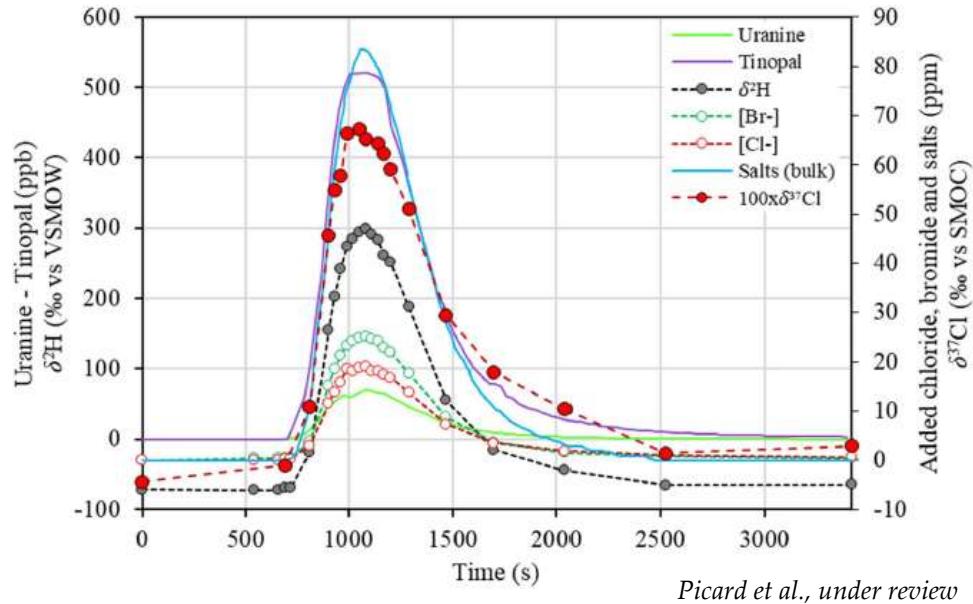
Antoine Picard<sup>1</sup>, Matéo Lacheux<sup>1</sup>, Florent Barbecot<sup>1</sup>, Christin Müller<sup>1</sup>, José Corcho<sup>2</sup>

<sup>1</sup>*Hydro-Sciences UQAM, Geotop, Université du Québec à Montréal*

<sup>2</sup>*Spiez Laboratory, Federal Office for Civil Protection*



# Example 1: rivers

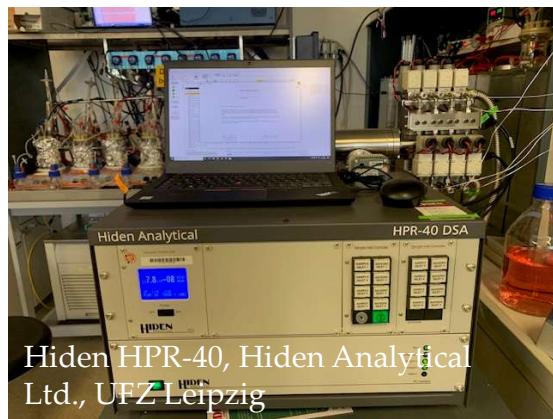


- Is there a cross-sectional heterogeneity in artificial solute concentrations?
- How does it evolve from upstream to downstream?

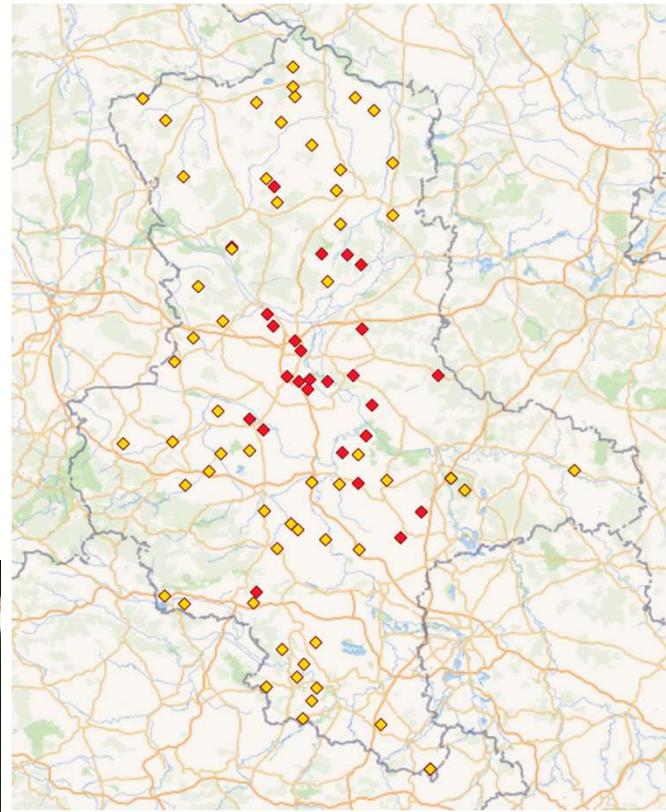
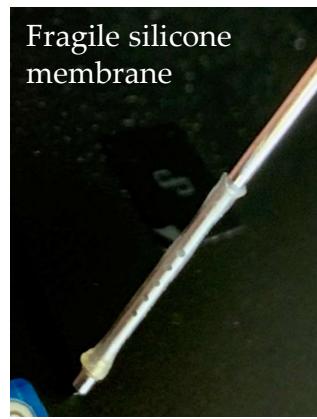
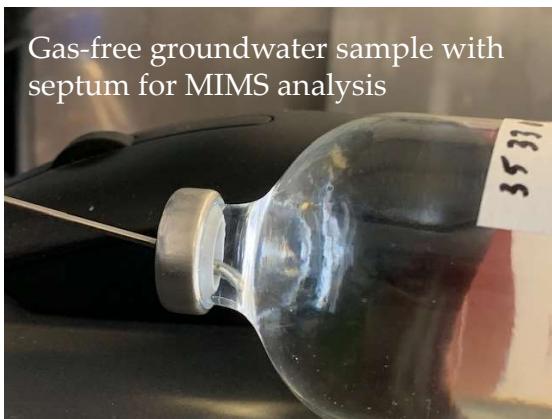
# Example 2: groundwaters



- MIMS: measure N<sub>2</sub>/Ar-ratio + NO<sub>3</sub><sup>-</sup> concentrations and δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> in groundwater samples
- Task: determination of aquifer **denitrification potential**
- **Challenge: sample contamination** during measurement, adequate measuring probe

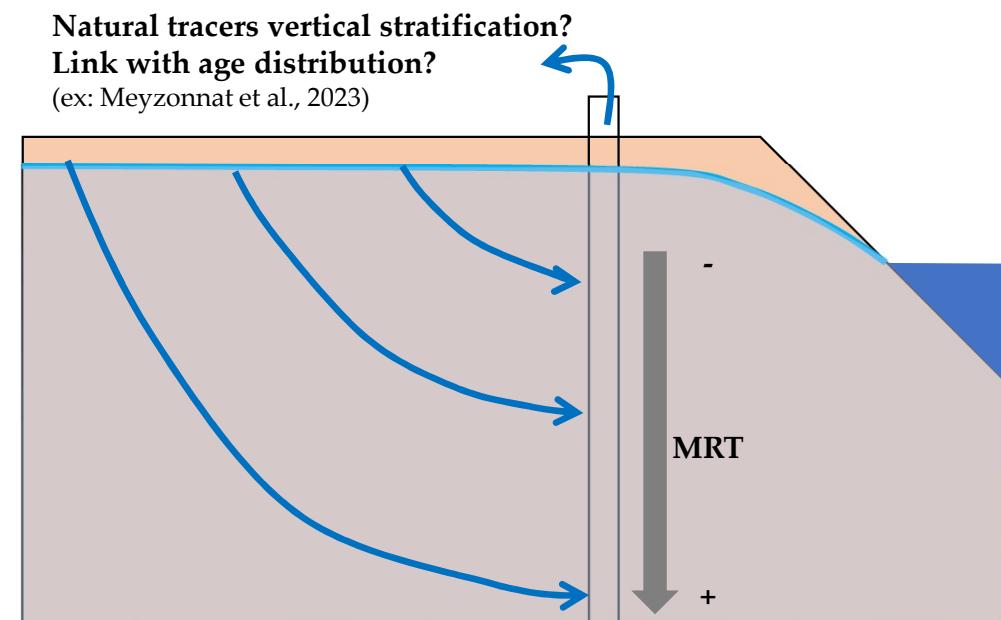


Hiden HPR-40, Hiden Analytical  
Ltd., UFZ Leipzig



Analysis of 80 new boreholes (2021-23) in  
Saxony-Anhalt, Germany

# Example 3: groundwaters



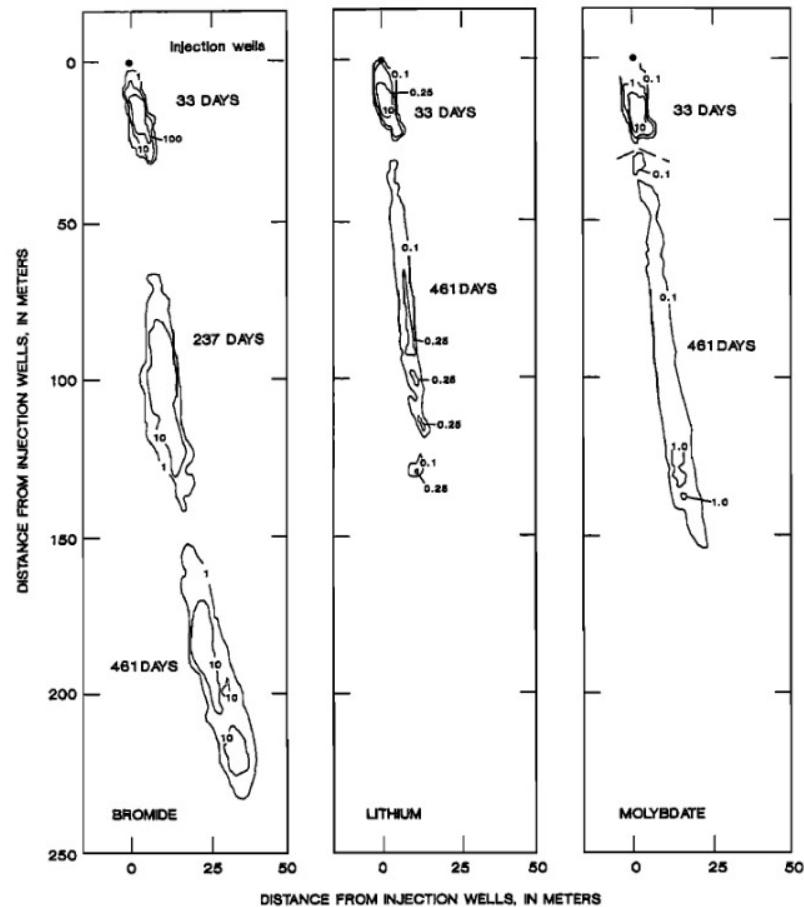
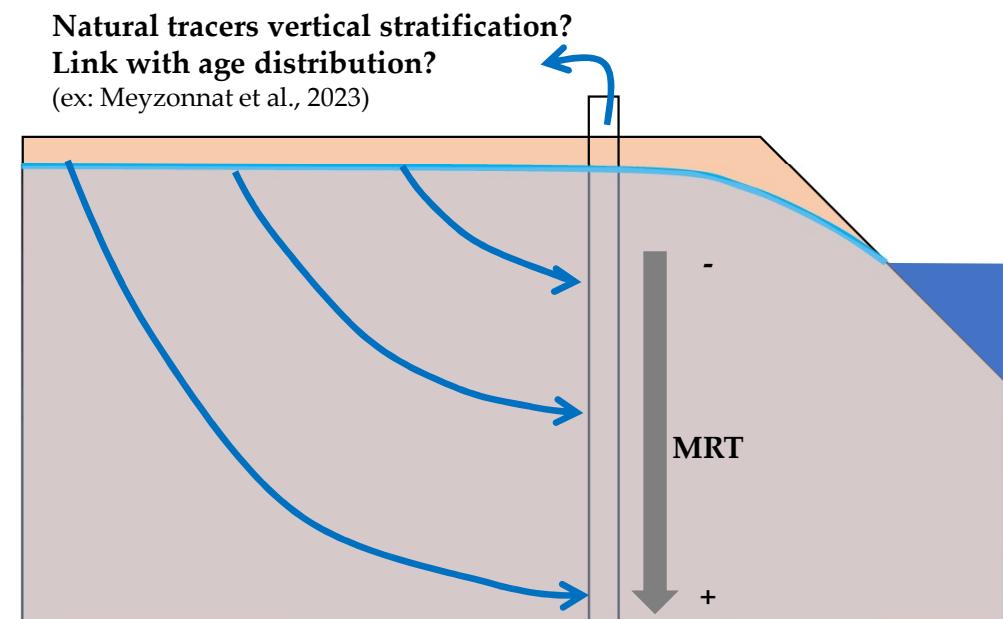
- How could we facilitate the study of vertical and lateral heterogeneity of (gaseous) tracers ?



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2023 - miniRUEDI symposium

# Example 3: groundwaters



- How could we facilitate the study of vertical and lateral heterogeneity of (gaseous) tracers ?



# Objectives of the work



*LeBlanc et al., 1991*



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# Objectives of the work

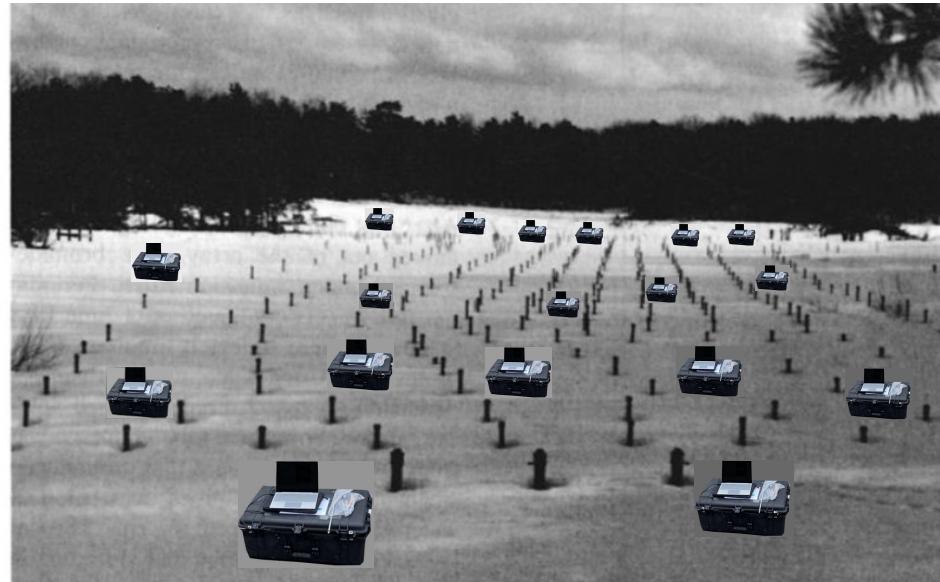


*A non cost effective way to achieve spatial resolution - Modified from LeBlanc et al., 1991*



# Objectives of the work

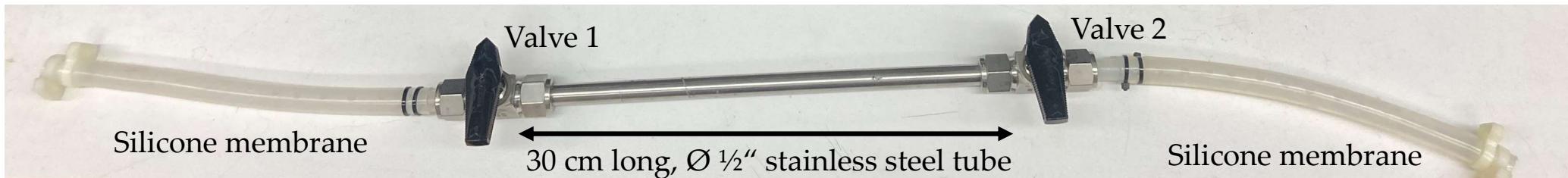
- The miniRUEDI helps to have a high time-resolution: what about **spatial resolution**?
- Objectives:
  - Development of a **cost-effective set up** allowing for the analysis of discrete gas samples (in **finite volume**)
  - Development of a robust, verified **lab method**



A *non* cost effective way to achieve spatial resolution - Modified from LeBlanc et al., 1991

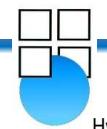
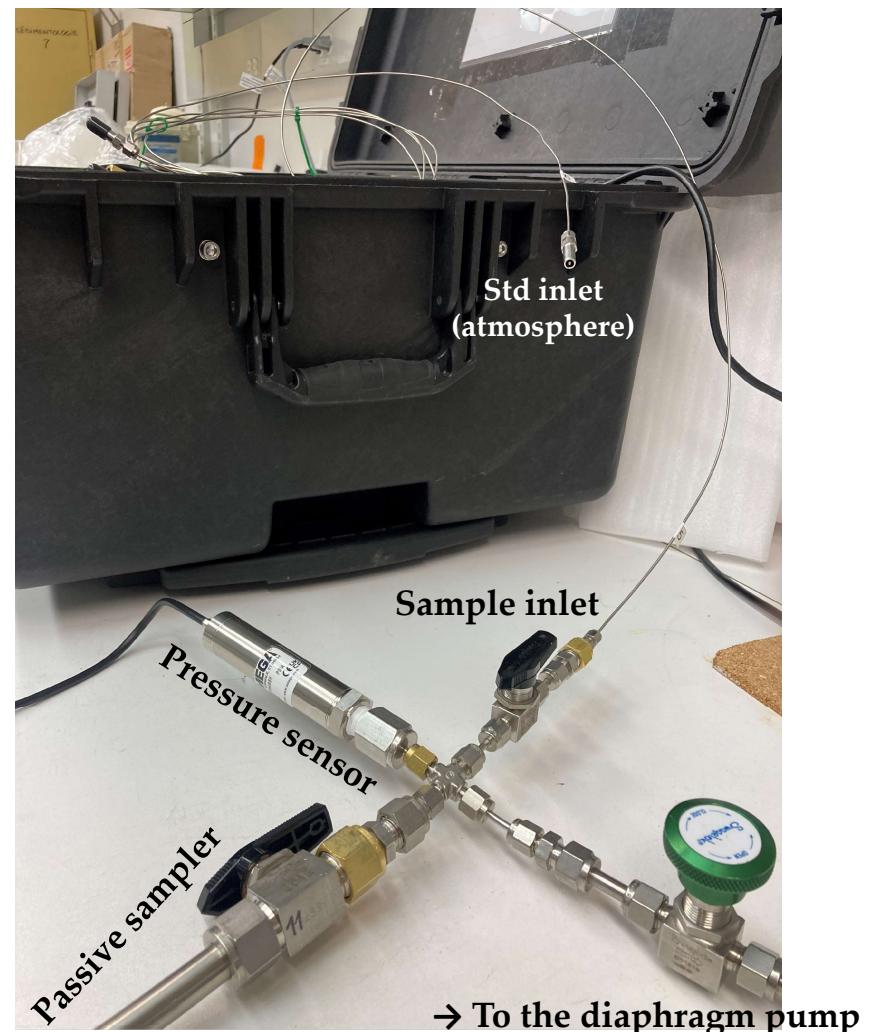
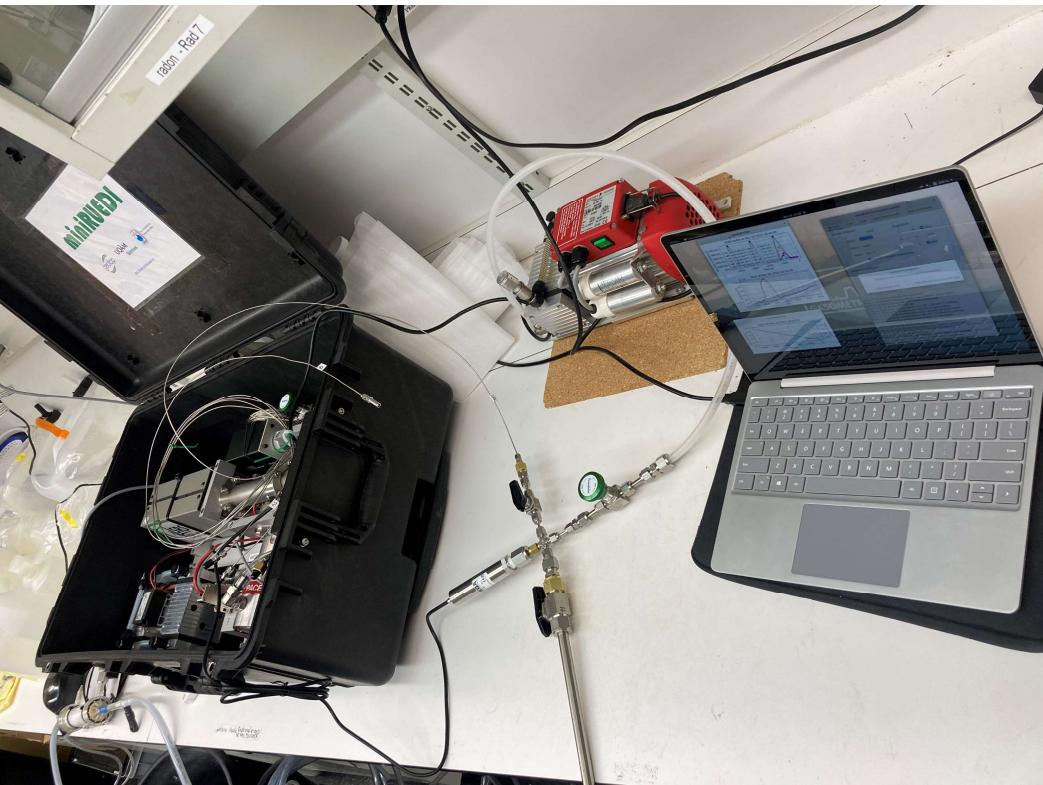


# Materials & Methods : gases passive sampling



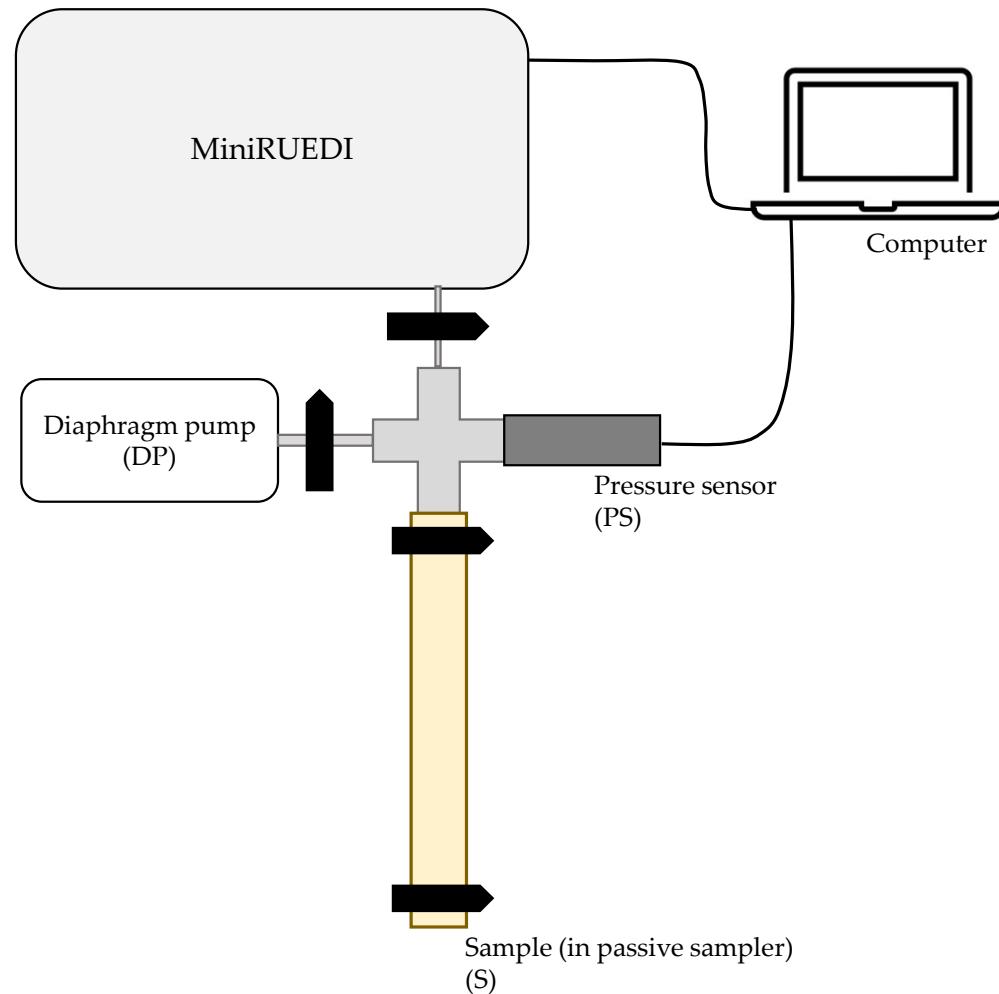
- Gases permeable **silicone membranes** (e.g. *Gardner & Solomon, 2009 ; Arnoux, 2018 ; Meyzonnat et al., 2023*)
- $\approx 25 \text{ mL}$  ; **reusable** stainless-steel sampler
- Equilibration time controlled by **temperature and membrane gas permeation coefficient**
- Large spatial deployment allows for the spatial mapping of (noble) gases concentration (**artificial tracing experiment, vertical groundwater stratification**)
- **No groundwater abstraction** (ex : application for *in situ* sampling for  $^{85}\text{Kr}$ : *Musy et al., 2021*)

# Materials & Methods

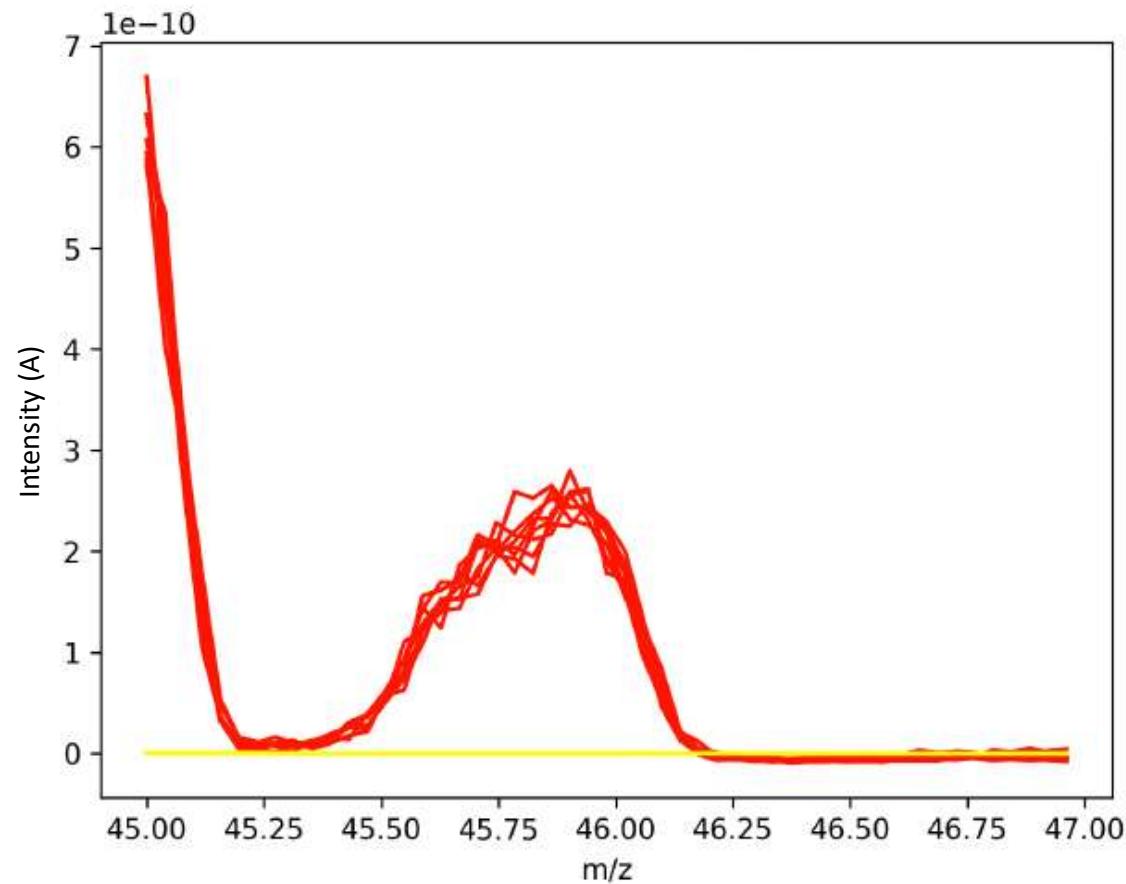


# Materials & Methods

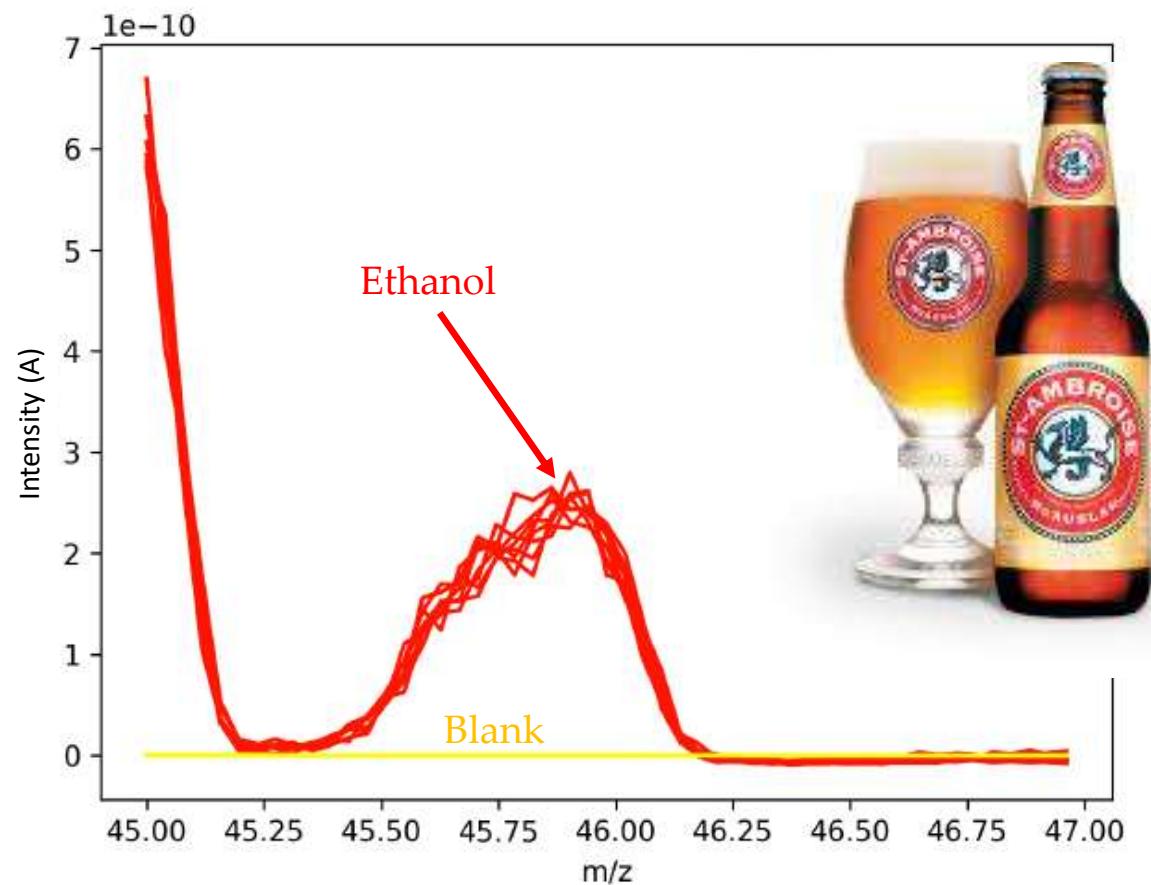
- System made of Swagelok **gas-tight pieces**
- A **crux** (dead volume of 5.57 mL) connects:
  - miniRUEDI inlet (with valve)
  - Diaphragm pump (Pfeiffer, vacuum  $\approx$  6-7 hPa) with valve
  - Pressure sensor (Omega, range 0-30 psi – same as GE-MIMS system)
  - Passive sampler (stainless steel,  $\approx$  25.50 mL) with valve
- Modification of **miniRUEDI programs**
  - Adding the pressure sensor
  - Modifying the sampling inlet and the default analysis sequence



# Detecting leaks when you can't measure the pressure...

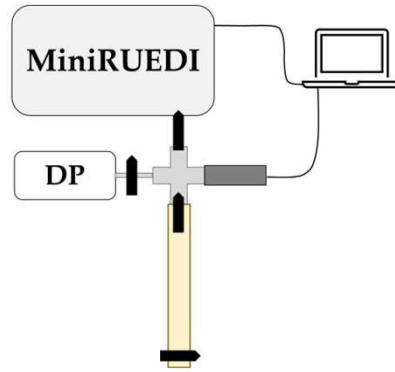


# Detecting leaks when you can't measure the pressure...

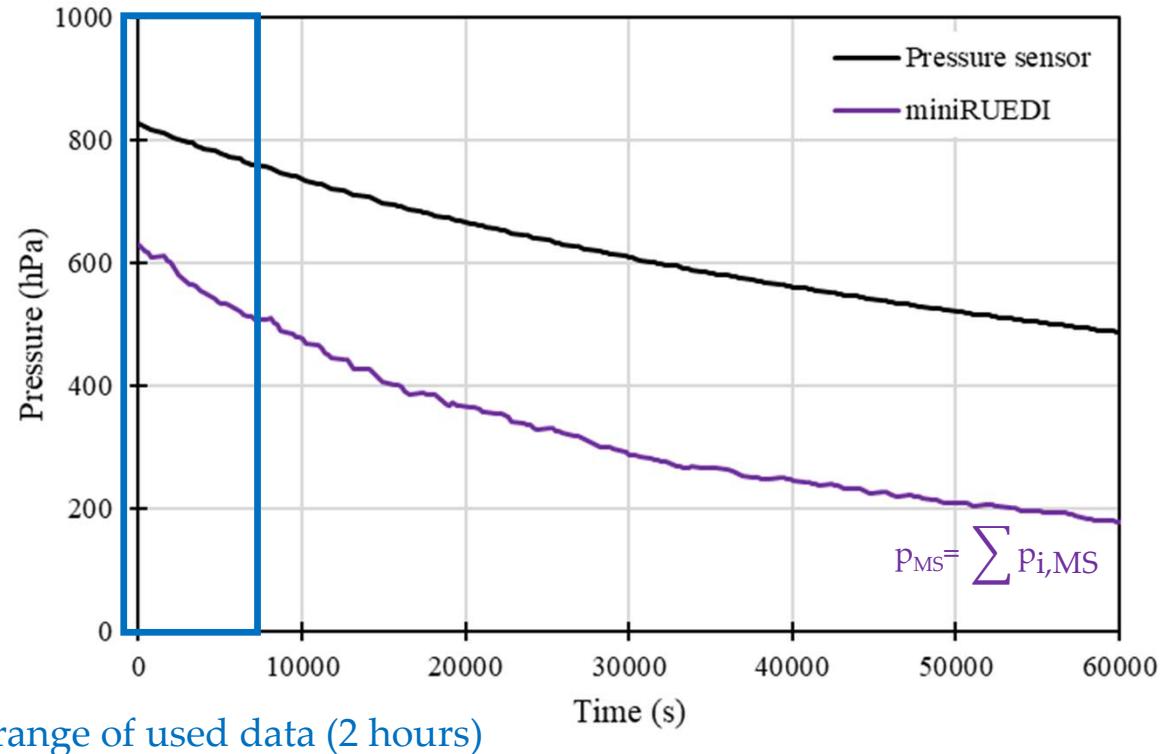


# Experiments – short analyses

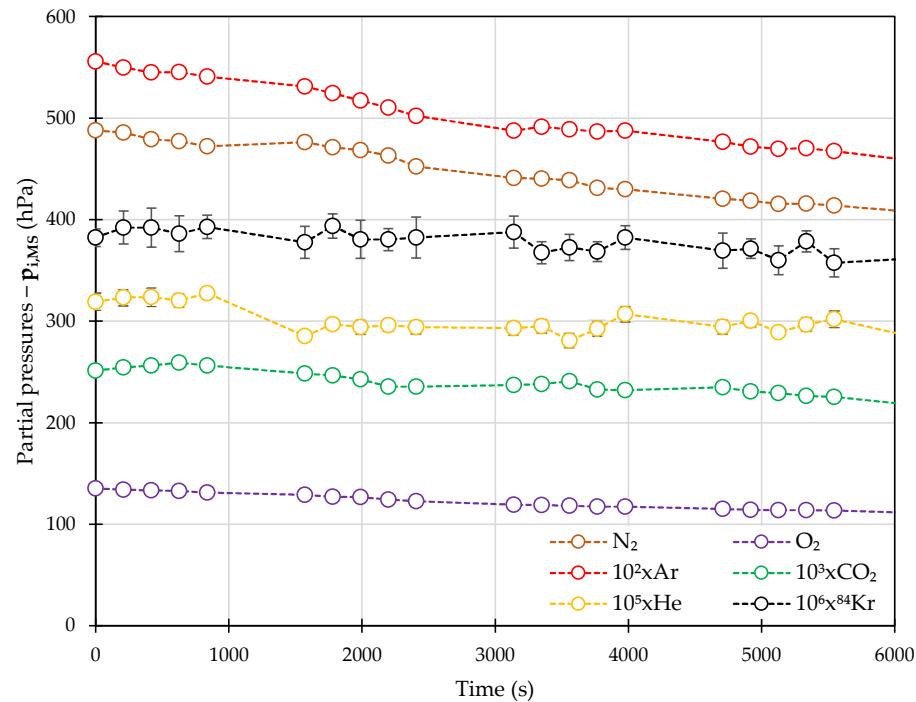
- Measurement of **atmosphere as a sample**
- **Analytical sequence**
  - 2 blanks
  - 1 std
  - 5 samples }  $\times 4$
  - 2 blanks



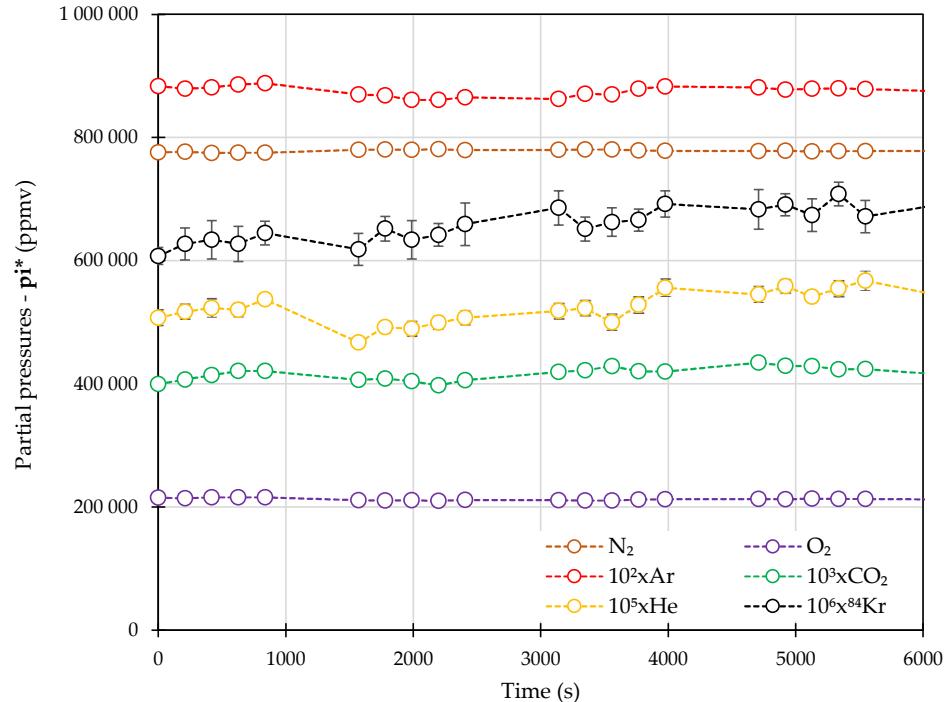
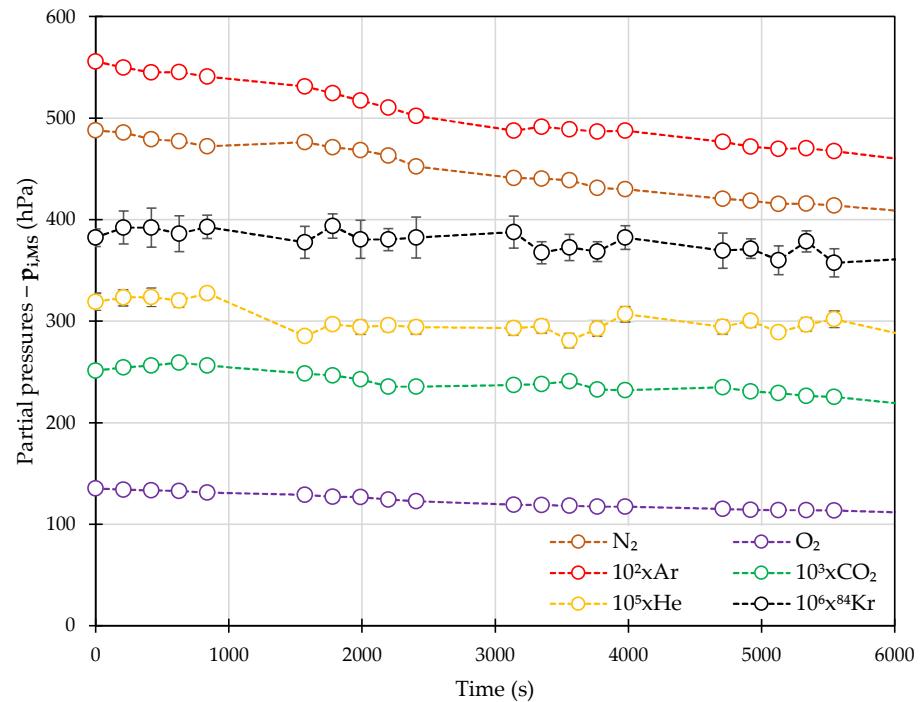
Sample analysis



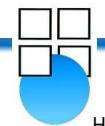
# Experiments – short analyses



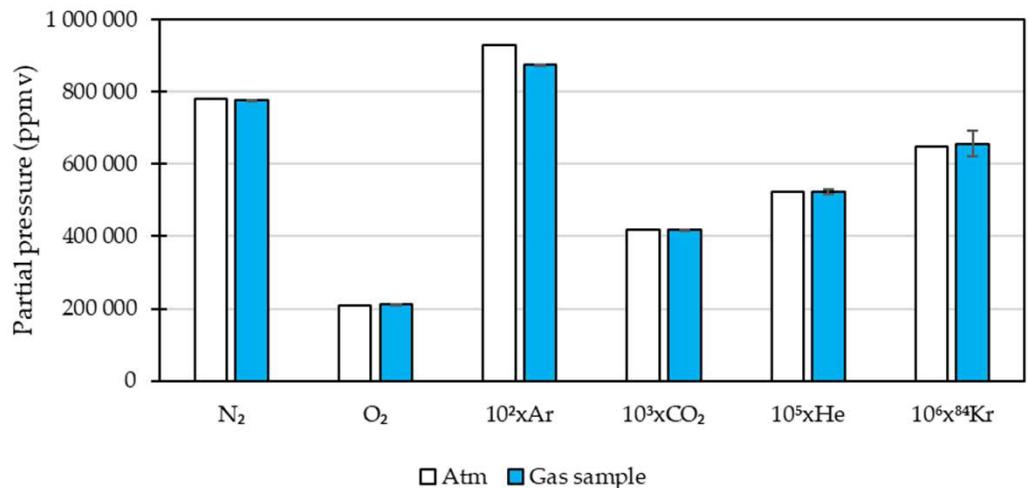
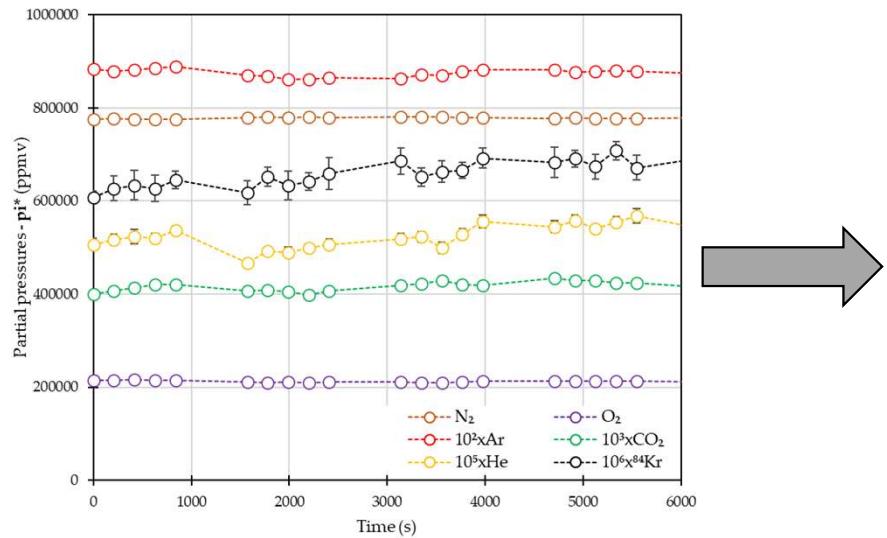
# Experiments – short analyses



$$p_i^*(t) = 10^6 \frac{p_{i,MS}(t)}{\sum p_{i,MS}(t)} [\text{ppmv}]$$



# Experiments – atmosphere as a sample



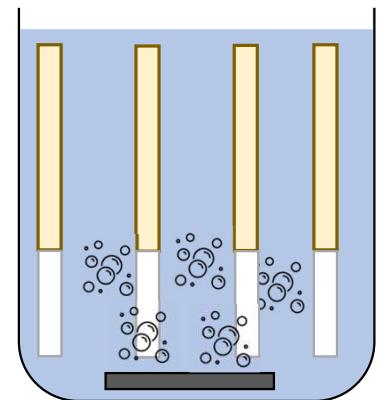
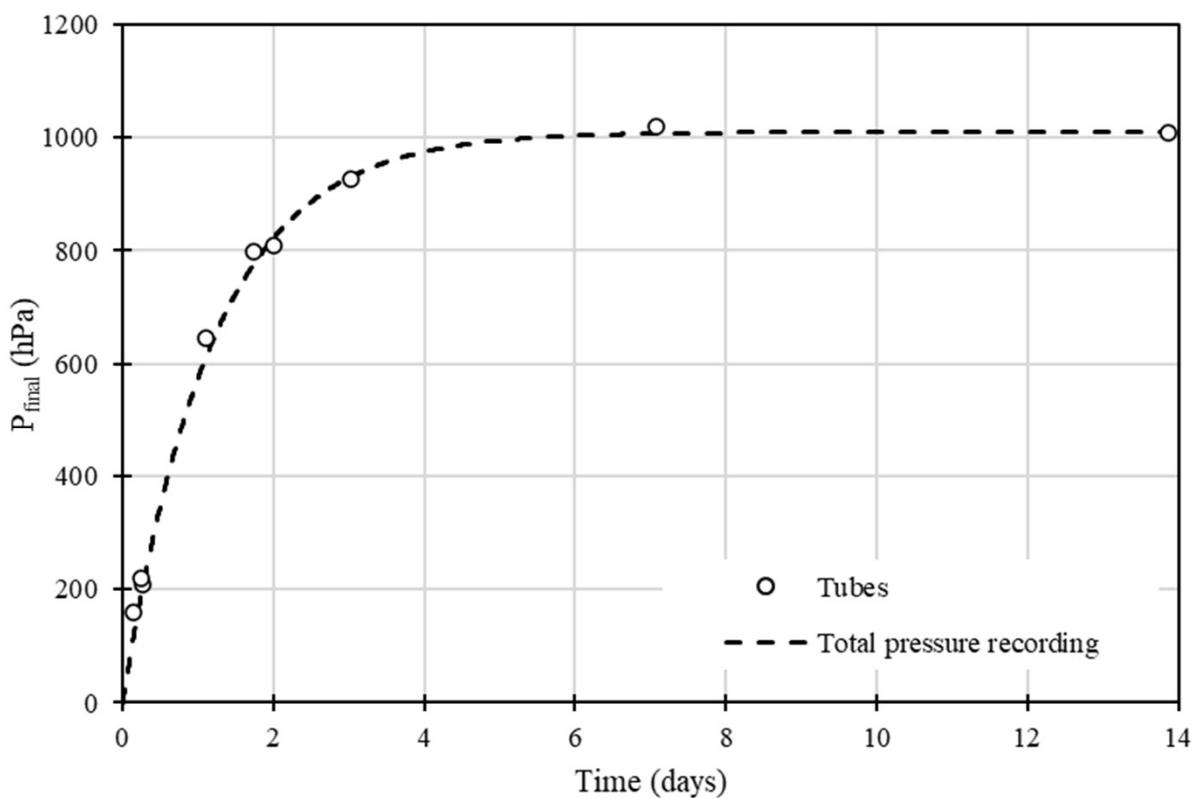
- **Error** between 0.3 % ( $N_2$ ) and 5.9 % (Ar) compared to atmosphere
- **Uncertainties** between 0.5 % ( $N_2$ ) and 4.5 % (Kr)
- **Very good agreement** between sample and atmosphere standard : the methodology is judged to be satisfactory



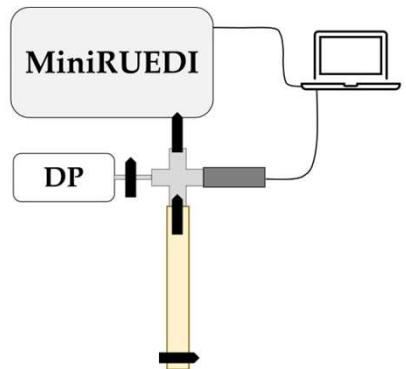
# Experiments – Gas equilibration



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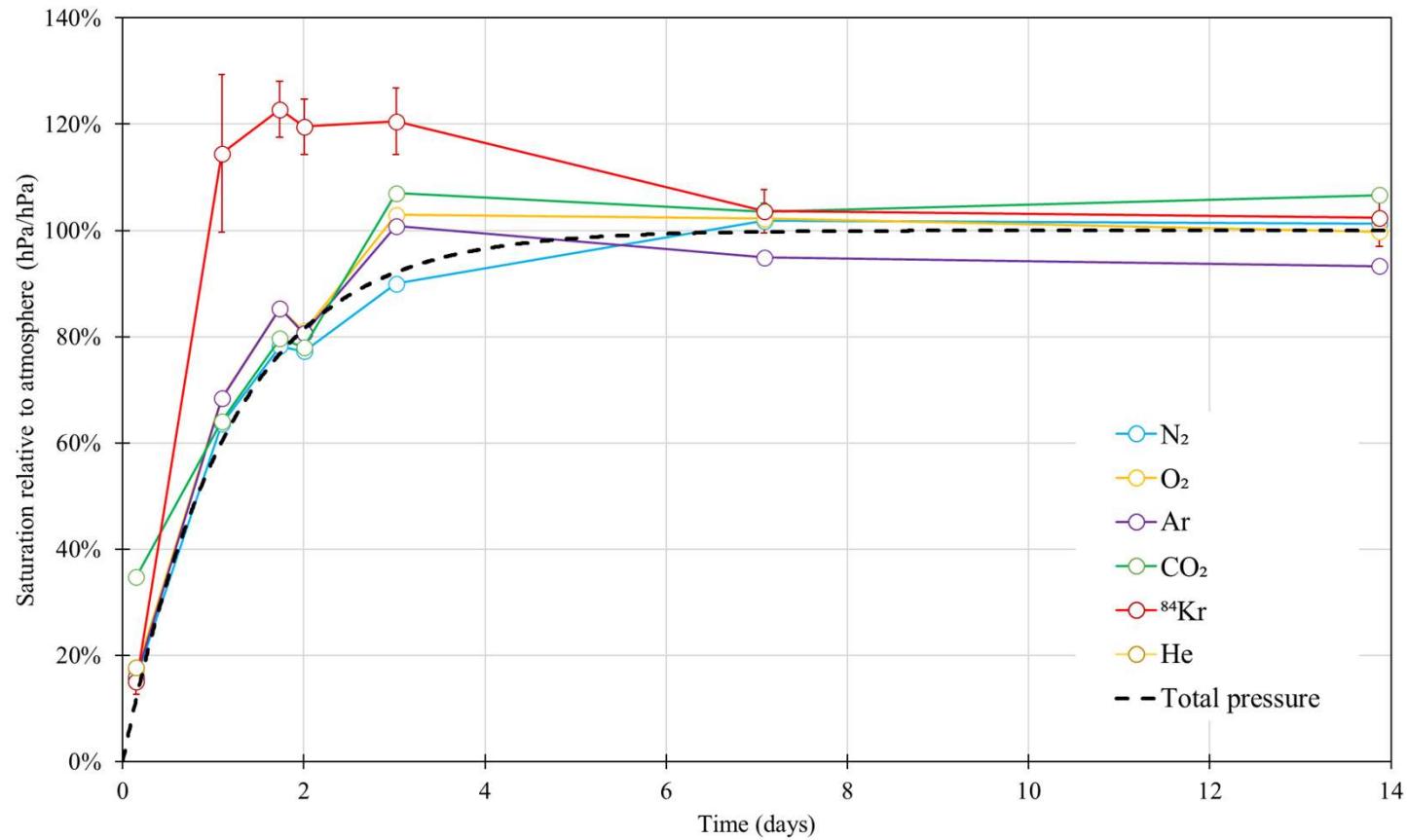
1 – equilibration setup



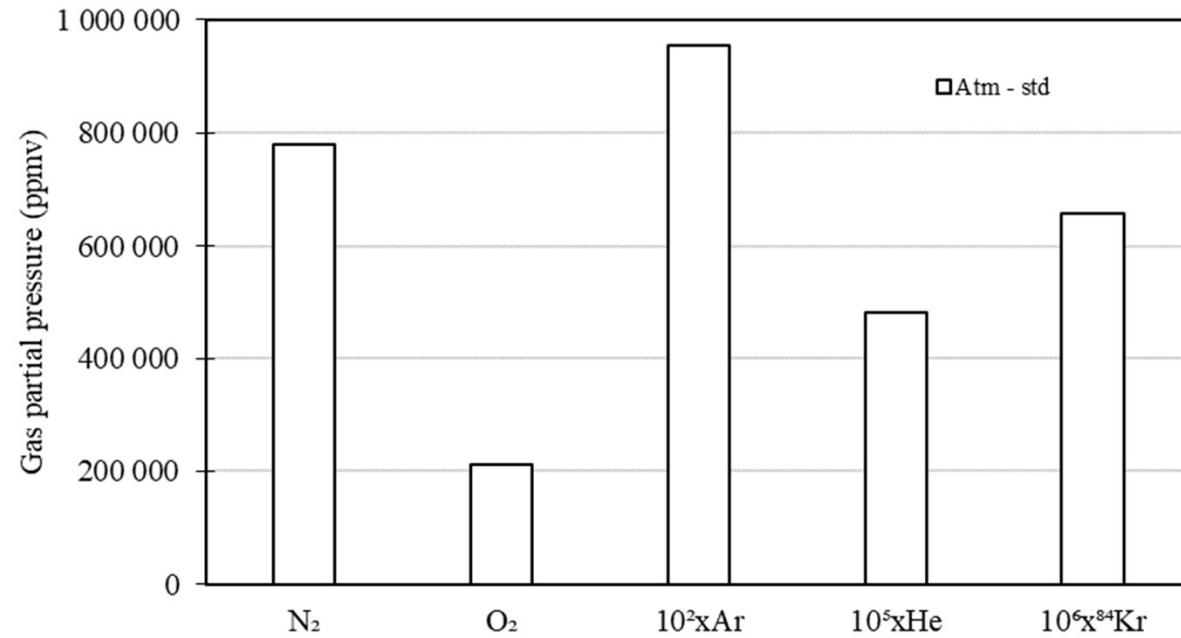
2 – sample analysis



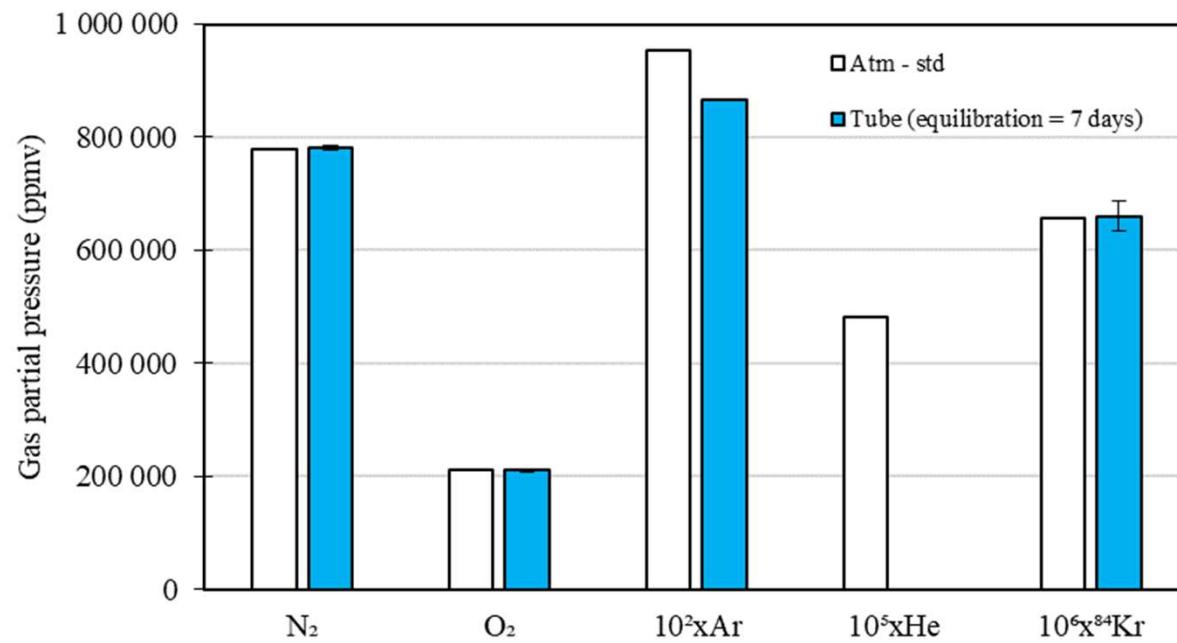
# Experiments – Gas equilibration



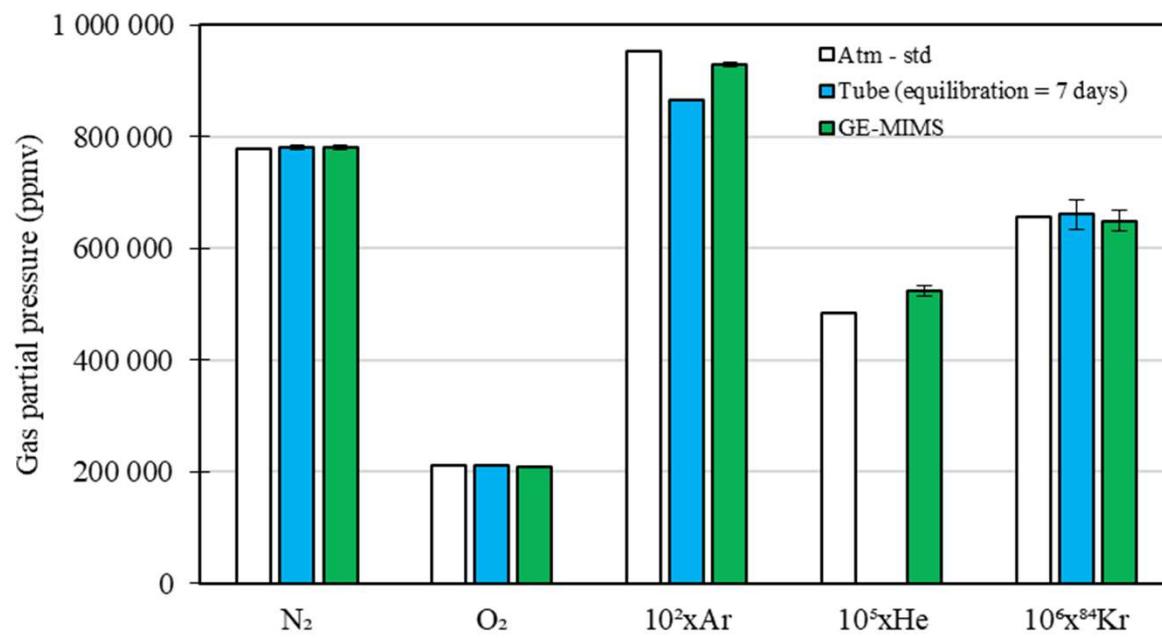
# Experiments – Comparison with GE-MIMS measurements



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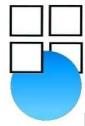


# Conclusions

- **Passive reusable samplers** are analysed using the miniRUEDI
- This allows to achieve spatial resolution at **lower costs**



# Thank you! Questions ?

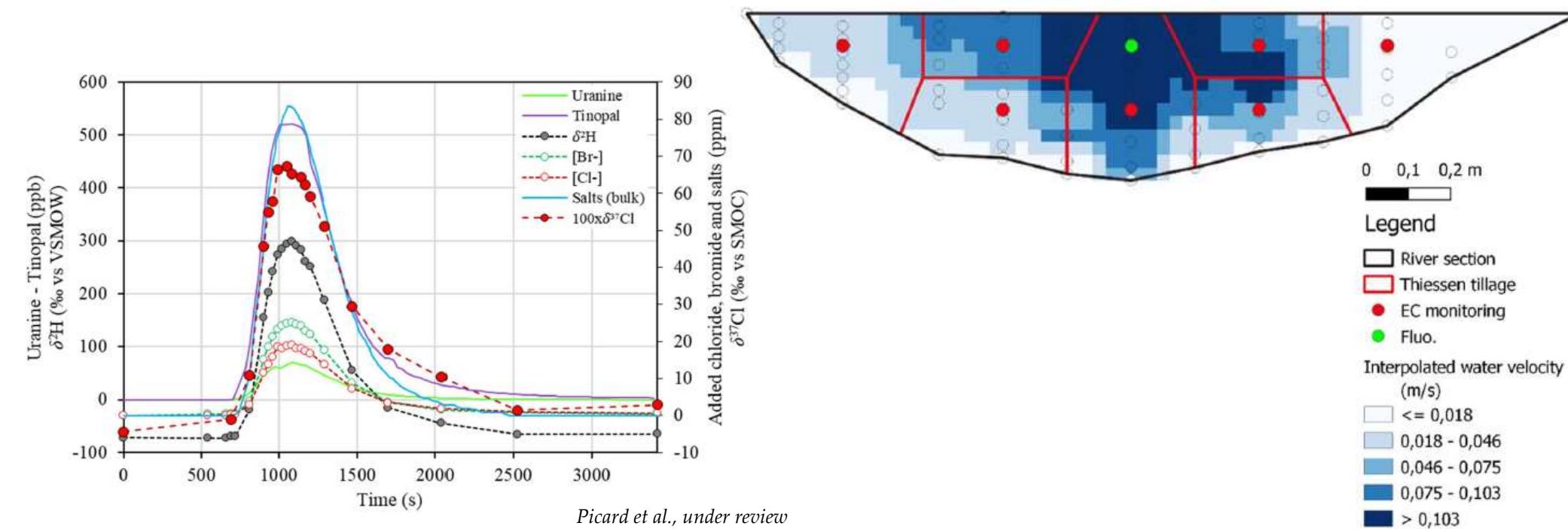


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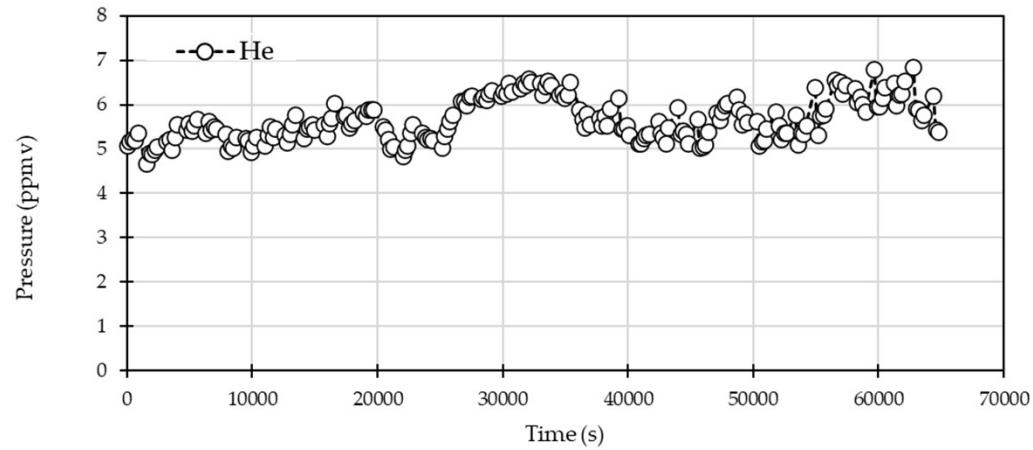
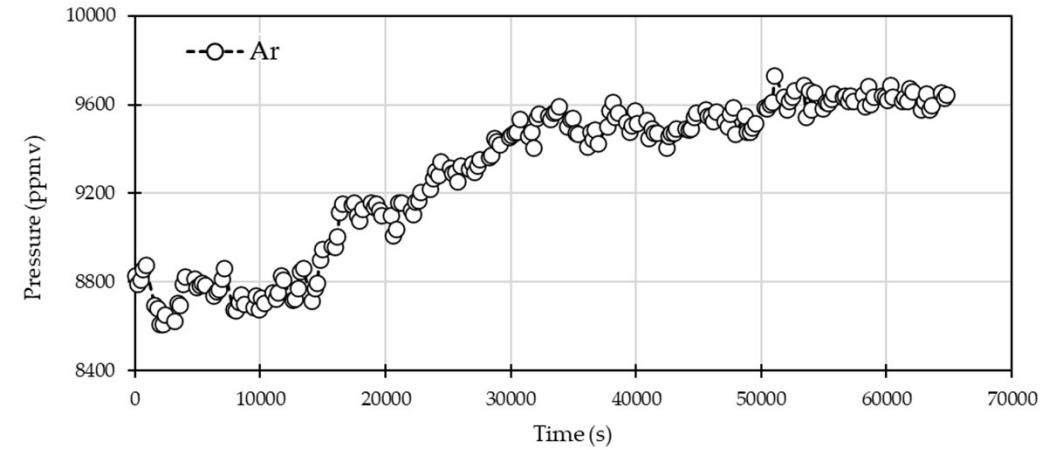
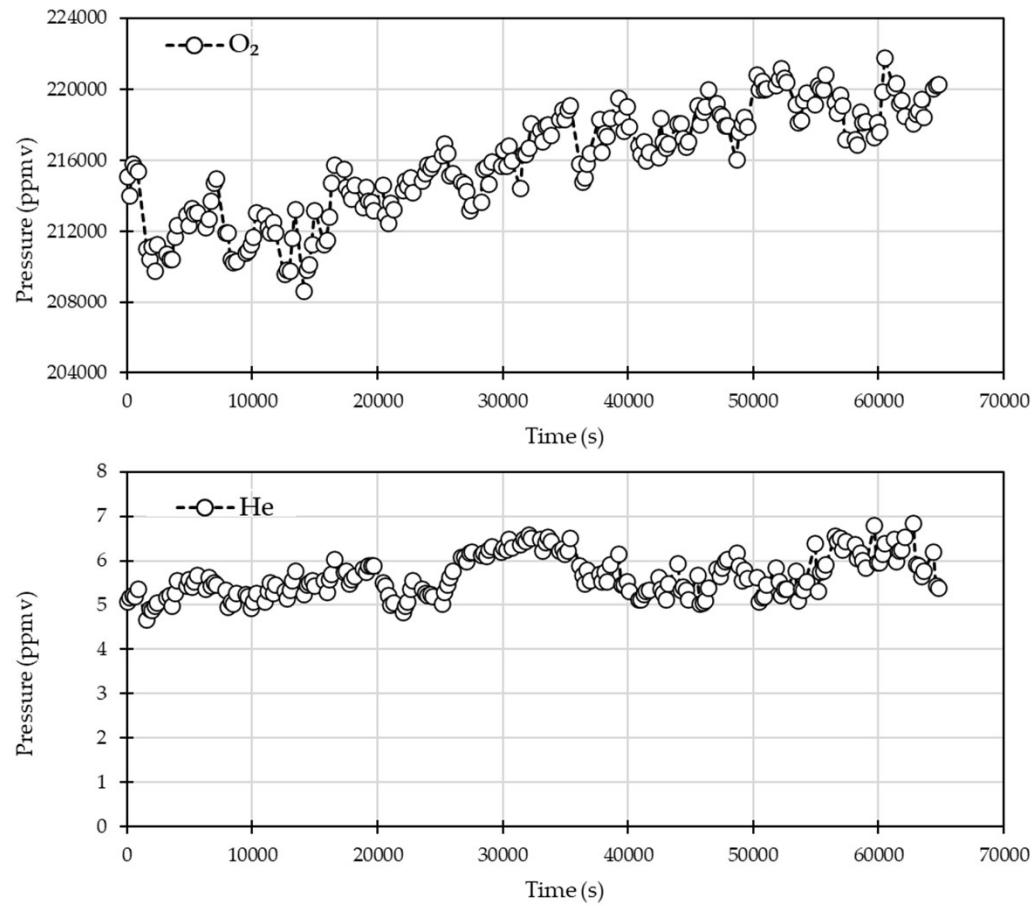
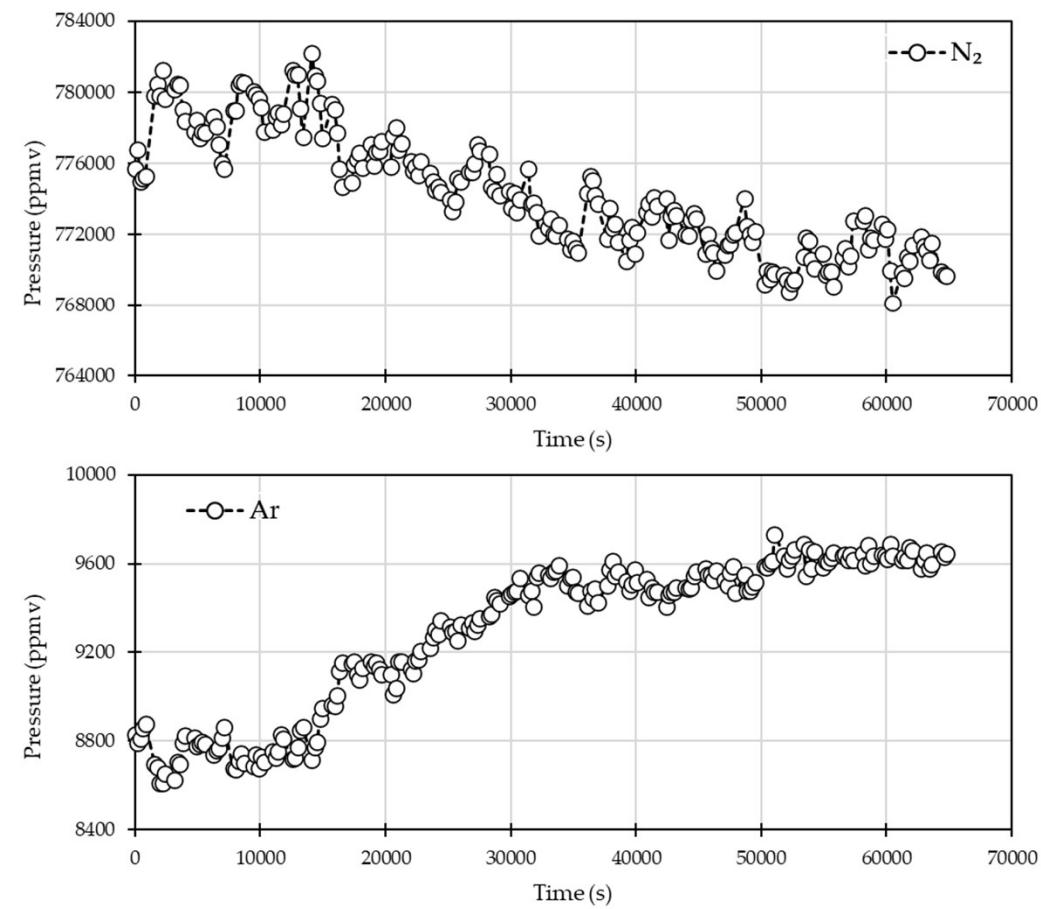
**NSERC  
CRSNG**

# Examples : rivers



- Is there a cross-sectional heterogeneity in artificial solute concentrations?
- How does it evolve from upstream to downstream?

# Open questions – long analyses in a finite volume



# Open questions – long analyses in a finite volume

