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The role of gases in an arsenic contaminated aquifer: Van Phuc, Vietnam

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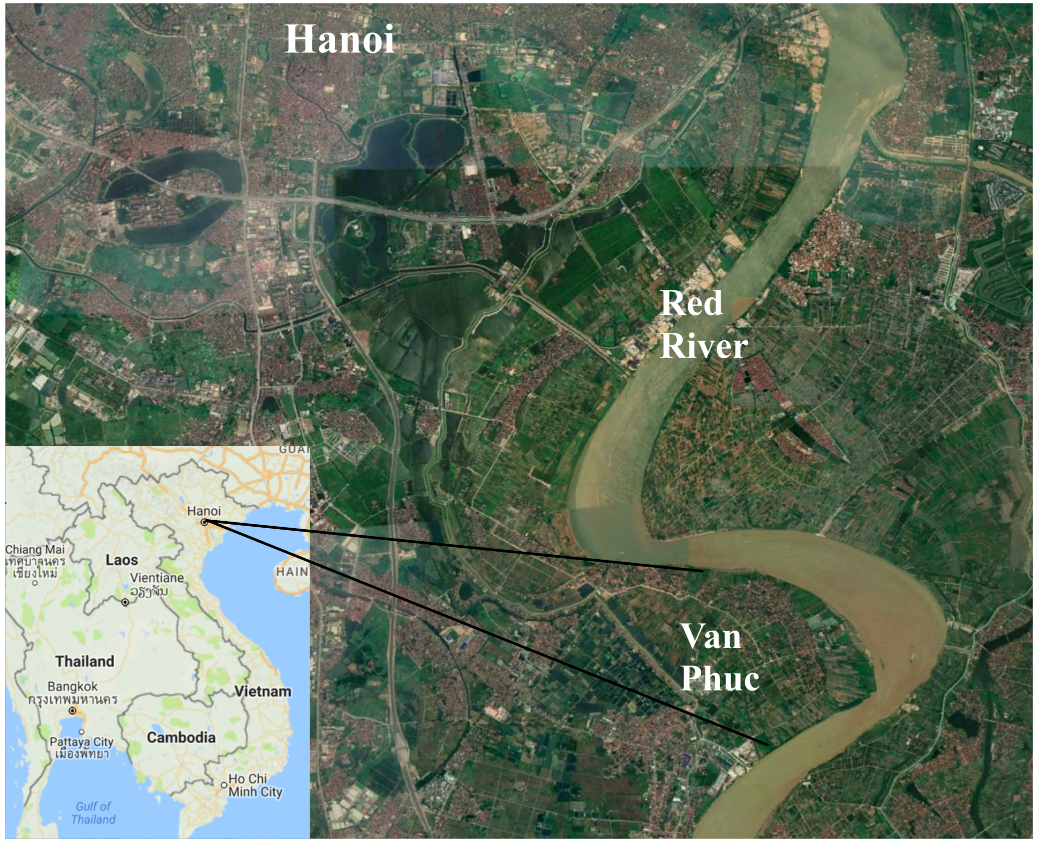
Field Site: Van Phuc village, Vietnam



Overview of field site. Van Phuc is situated ~15km SE of Hanoi, inside a meander of the Red River.

- Van Phuc village is situated inside a meander of the Red River, ~15km SE of Hanoi, and is a typical region associated with high As concentrations.
- Currently, more than 11million people live in the Red River delta region.
- In large quantities, As is hazardous to human health (WHO limit is 10μg/L).
- The problem of As in groundwater is currently common in many south-east Asian countries.

Aim: determine flow dynamics of groundwater in a region where **Arsenic contamination of groundwater is an issue.**

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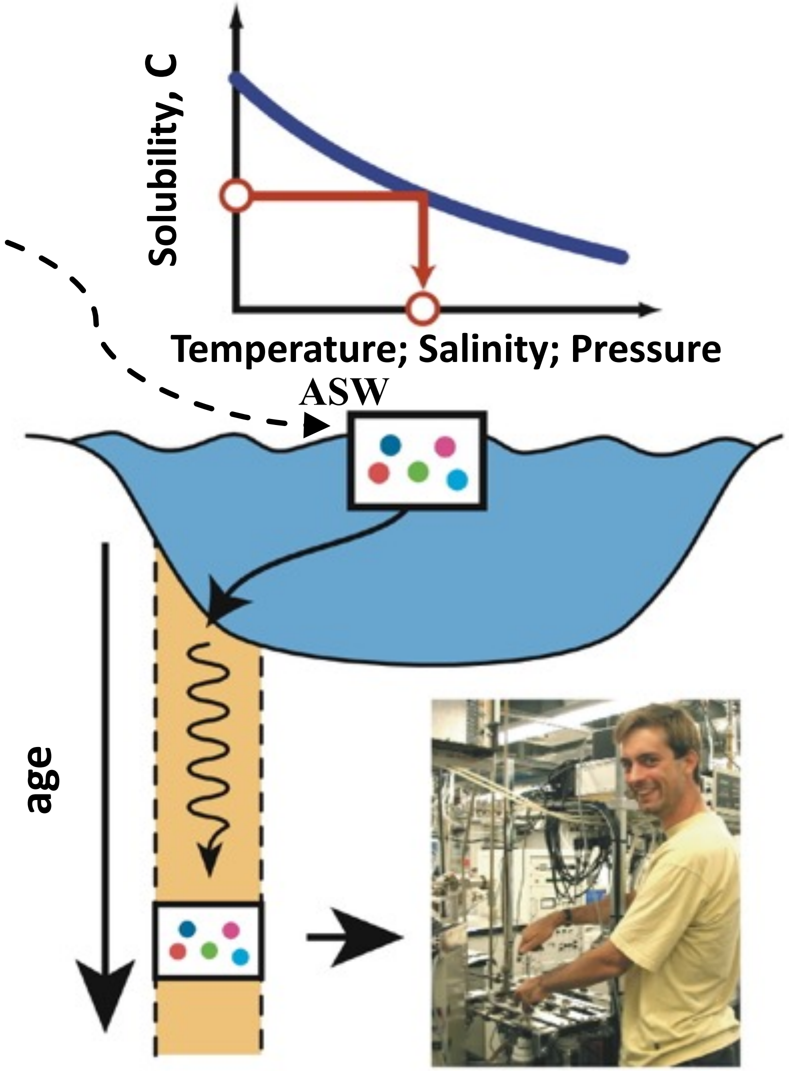
Background: Noble gases(NG) as tracers for groundwater flow

- Similarly to other atmospheric gases, NG's enter the water cycle through gas partitioning at the air/water interface.
- NG's have typical concentrations known as their "air saturated water" (**ASW**) concentrations for a specific Temperature, Salinity and Pressure (Henry's Law).
- The five most well known NG's are **He, Ne, Ar, Kr and Xe.** They are extant in different abundances in our atmosphere.



- Noble gases can be used as environmental tracers because they are biogeochemically inert.
- **The only way to alter noble gas concentrations is by PHYSICAL PROCESSES**

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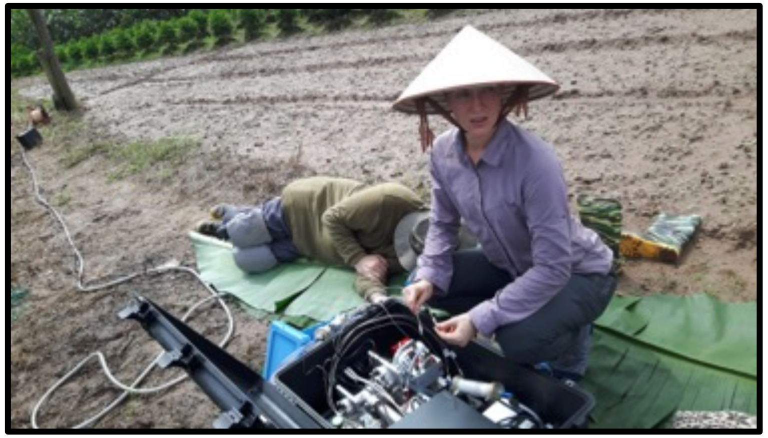
Sampling/Analysis with the miniRUEDI

- The MiniRUEDI[1] is a portable mass spectrometer, able to measure **both** noble and reactive gas concentrations in groundwater including: **He, Ar, Kr,** H_2, **CH_4,** CO_2, O_2, **N_2.**

- Continuous water flow is necessary for operation.

Above: miniRUEDI mass spectrometer including pumps, electronics and switching valve to measure from different ports. Left and right: MiniRUEDI during operation in field.



- Analysis was made of gases in groundwater from existing wells in the village

- 21 wells were analysed in-field

[1] https://gasometrix.com/; *A Portable and Autonomous Mass Spectrometric System for On-Site Environmental Gas Analysis:* Matthias S. Brennwald et. al. *ES&T* **2016** *50* (24), 13455-13463, DOI: 10.1021/acs.est.6b03669

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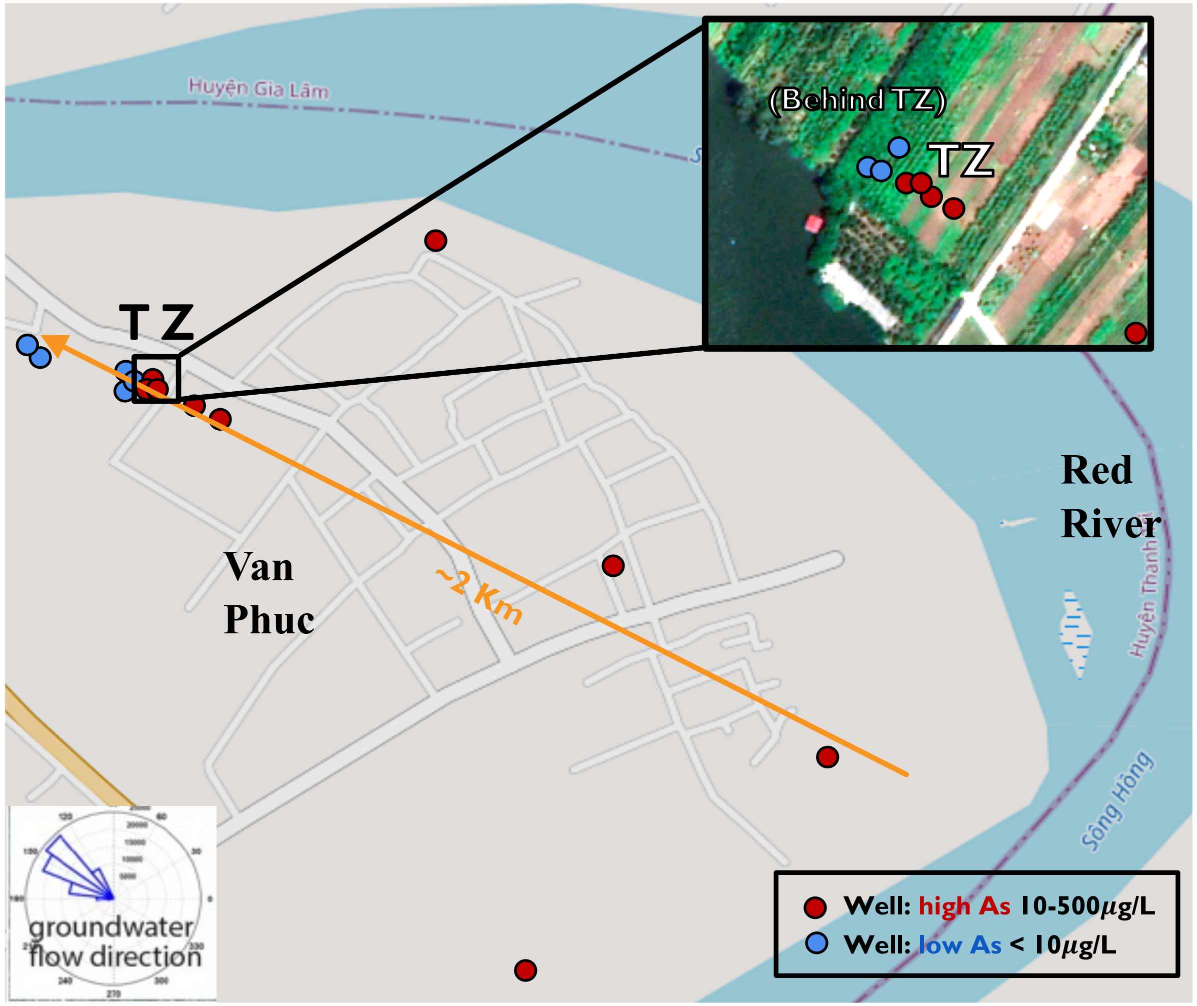
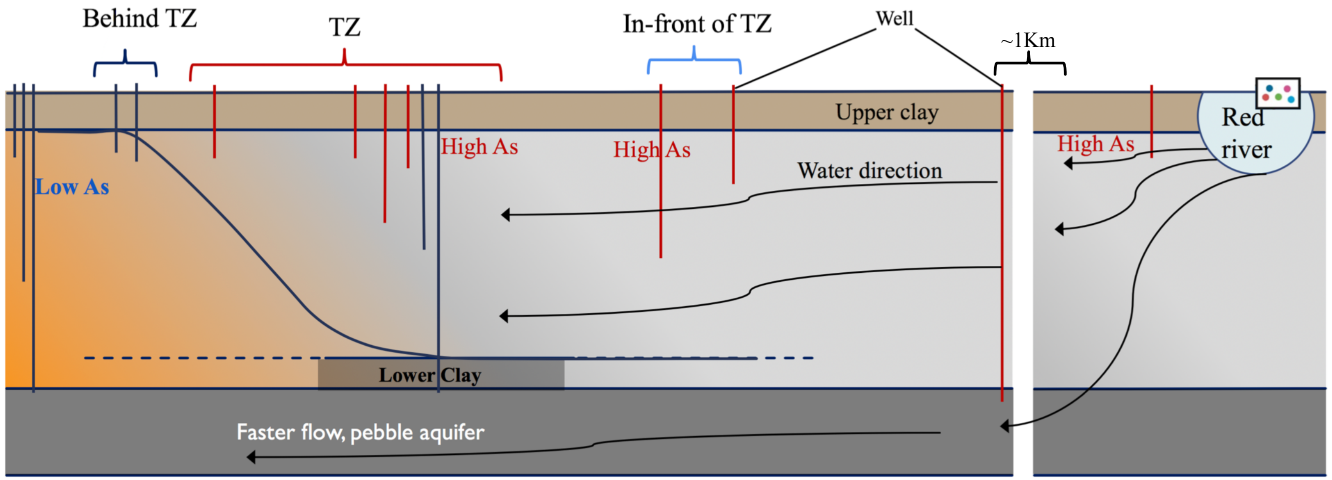
Sampling locations:

- The ‘transition zone’ (TZ) is an important feature of the field site.
- The TZ is characterized by contrasting redox conditions, a common feature at aquifer boundaries (e.g. Holocene and Pleistocene, as is here).
- Water flows from contaminated Holocene aquifer into the uncontaminated Pleistocene aquifer[2].



Circles mark sampling wells within the field site, Van Phuc village, with specific attention paid to the TZ.



2D sub-surface schematic of left image, as followed by the arrow, SE to NW of the village (Red river → Hanoi).

[2] van Geen et al., *Retardation of arsenic transport through a Pleistocene aquifer*. *Nature* **501,** 204–207 (2013). https://doi.org/10.1038/nature12444.

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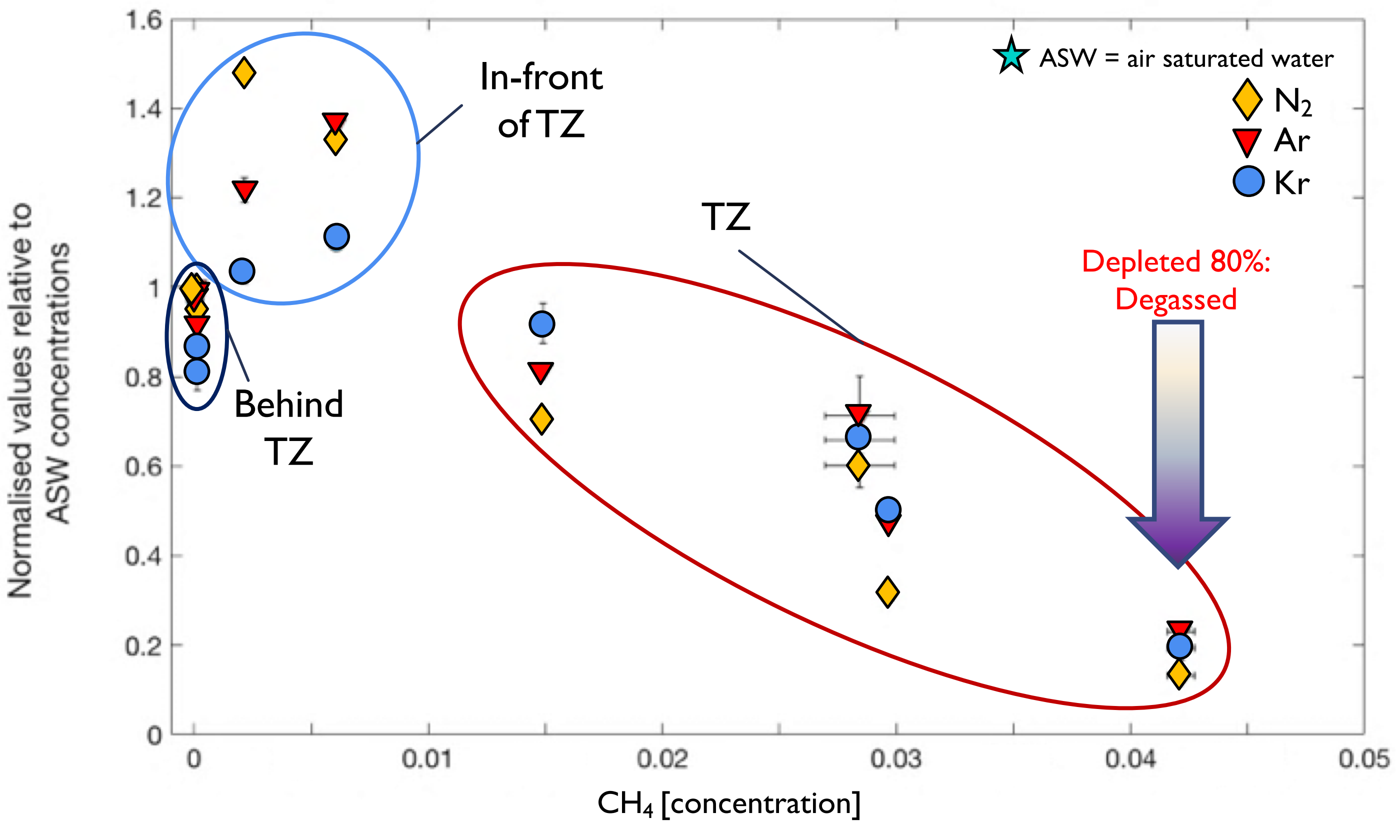
Results 1.1

- Simultaneous measurements of noble and reactive gas concentrations suggest **in-situ degassing** of Ar and Kr via oversaturation of CH_4.

- **<u>Degassing means:</u>** Saturation of e.g. CH_4 or CO_2 in groundwater → gas bubble formation (+escape) → removal of noble gases from water phase into the gas bubble→ depletion signature seen in NG analysis

DEGASSING is the ONLY **physical process** that can explain depletion of the NG's Ar and Kr.

Ar, Kr and N_2 vs. Methane concentrations



In the TZ, there is clear depletion of the NG's with increasing CH_4 concentrations. 'In-front' of the TZ, there are 'normal' groundwater signatures, while after, the water signals are slightly degassed.

Presence of a free gas phase within the aquifer affects groundwater flow and residence times; information necessary to determine As evolution.

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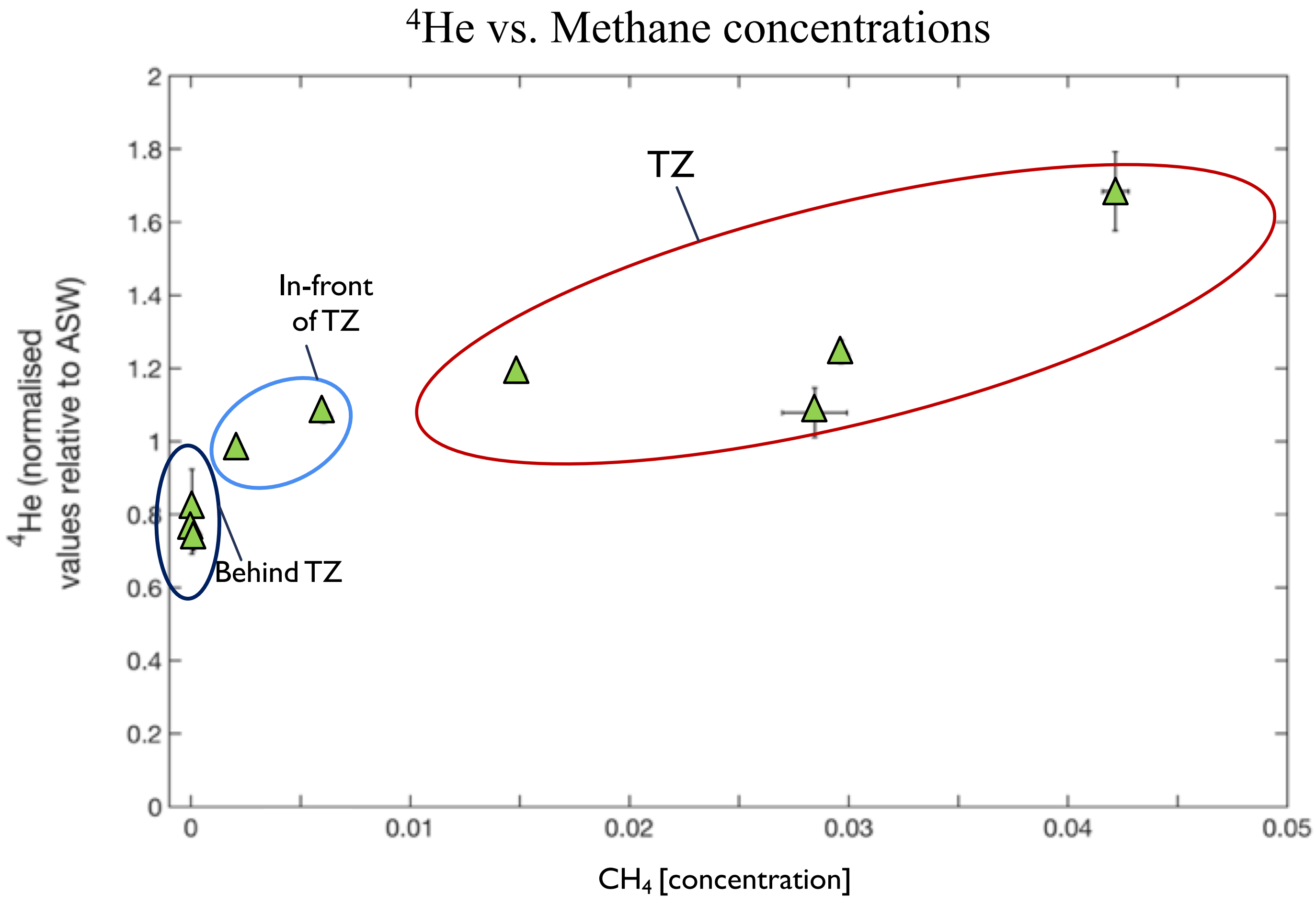
Results 1.2



^{4}He concentrations increase with increasing CH_4, in the same wells where Ar and Kr show severe depletion.

- ^{4}He doesn't show degassing like Ar, Kr! WHY?
- ^{4}He instead increases with increasing CH_4 concentrations.
- High ^{4}He signature indicates longer residence time (~1000's years); it is the only NG that is additionally affected by radiogenic decay so can accumulate where groundwater flow is slowed.

→ Flow inhibition due to gas bubbles mean radiogenic ^{4}He can accumulate.
→ Input of ^{4}He from a second water source?

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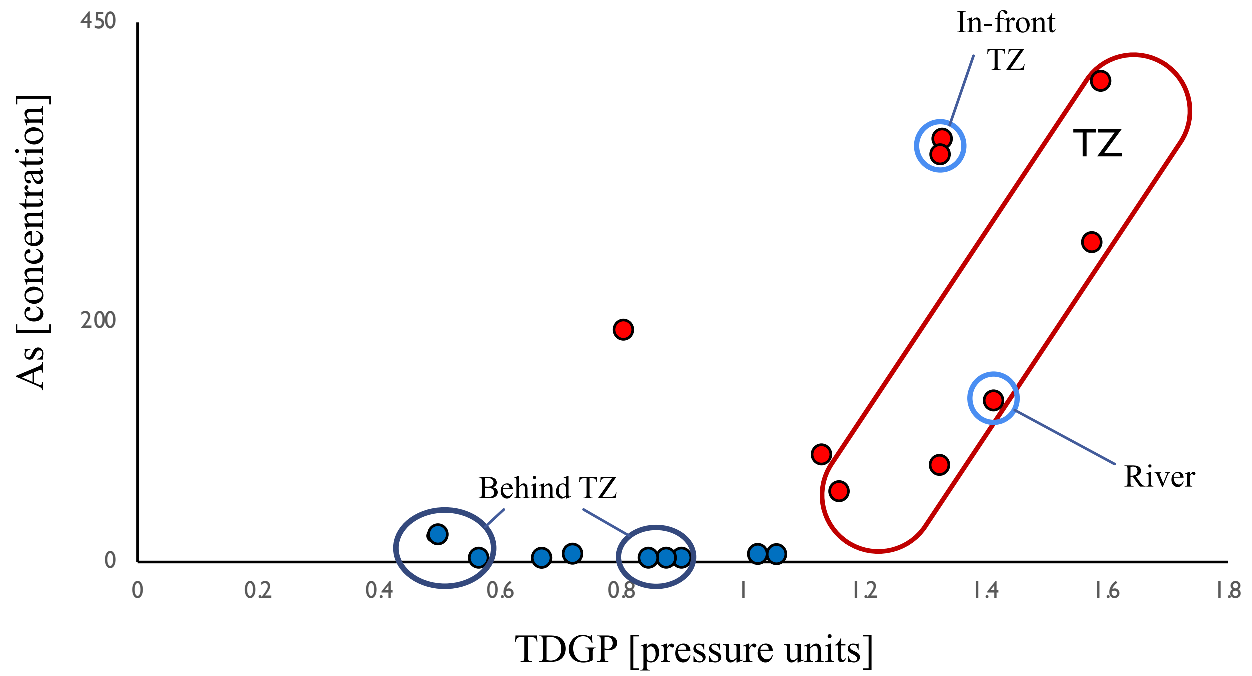
Results 2

As concentrations vs. total dissolved gas pressure (TDGP)



Wells in the TZ and follow the same curve of increasing As with increasing TDGP, which, is a result of high CH_4. The well near the river, N_2 is the dominant gas component contributing to total TDGP.

- TDGP is the total pressure of all gases in the groundwater as measured by the miniRUEDI at sampling.
- If values exceed 1atm, there is gas production within the aquifer, when related to high reactive gas concentrations.

→ Arsenic concentrations correlate to gas production within the aquifer. Predominantly, this is related to CH_4, but is also shown in wells with high N_2 values, for example, near the river bank.

→ Two different mechanisms for As mobilisation at the river and in the TZ.

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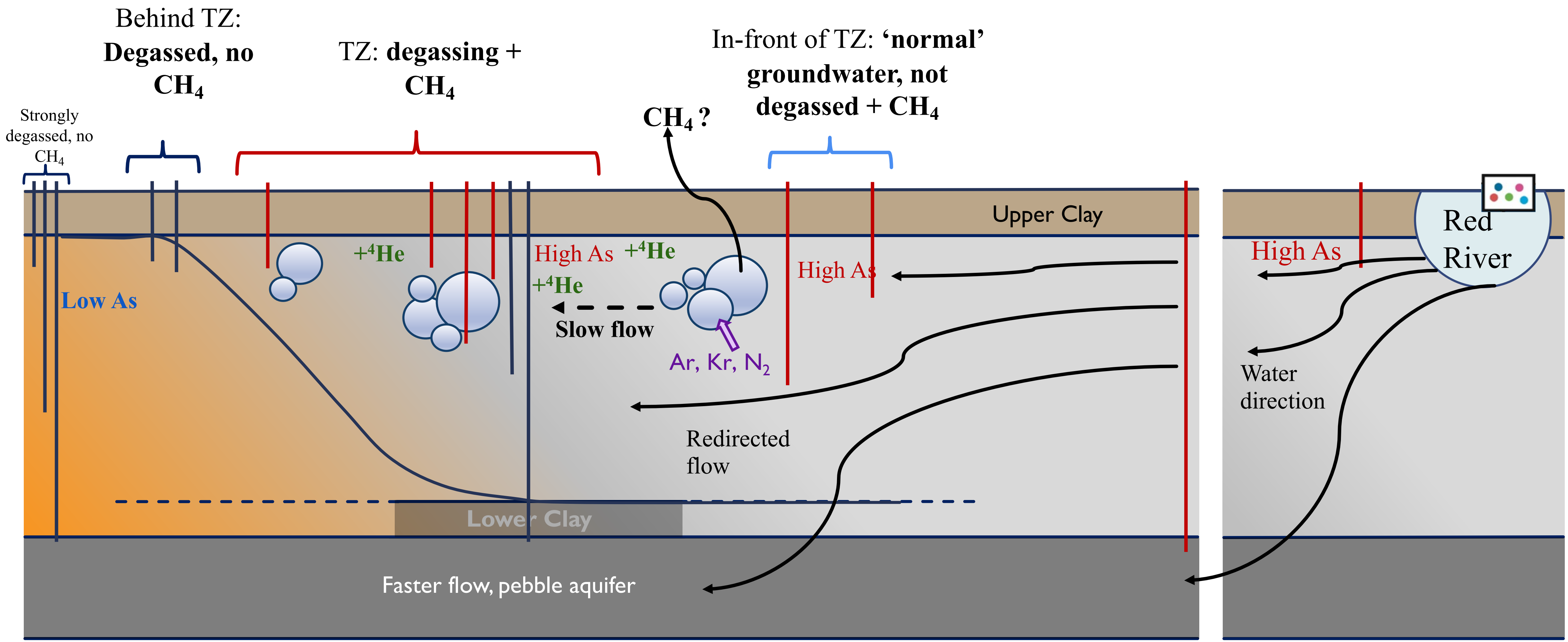
A conceptual model should account for these three points:

Groundwater flow seems complex in nature - could this complexity relate to patchy As distributions?

Is As accumulating in areas where groundwater flow slows as a result of in-situ CH_4 gas bubble production?

Where does the CH_4 go?

Conceptual picture of groundwater flow:



Schematic of groundwater flow in the TZ of the field site. Water tends to deviate around the CH_4 bubbles. Within the 'slow-flow' TZ, Ar, Kr, and N_2 show degassed signatures from the groundwater, while ^{4}He accumulates indicating an longer residence time and/or input from an additional water source.

Conclusions

- By combining noble and reactive gas measurements, we can come up with a conceptual model of groundwater flow within the transition zone of this As contaminated field site.

- Results show depletion of Ar, Kr and N_2 relative to increasing CH_4 concentrations:
  → An indicator for degassing and presence of an in-situ CH_4 gas phase within the aquifer, which subsequently affects groundwater flow.

- ^4He concentrations show the opposite affect; they increase with increasing CH_4 concentrations. This could mean:
  → Flow inhibition caused by the CH_4 gas bubbles means radiogenic ^4He can accumulate significantly.
  → Addition of an older water component of high ^4He content

- **Details on groundwater flow are necessary to fully understand the evolution of As movement in contaminated aquifers.**

- Additionally, high TDGP, which is attributed to high CH_4 in the transition zone, shows there is a link between As concentrations and CH_4 production.

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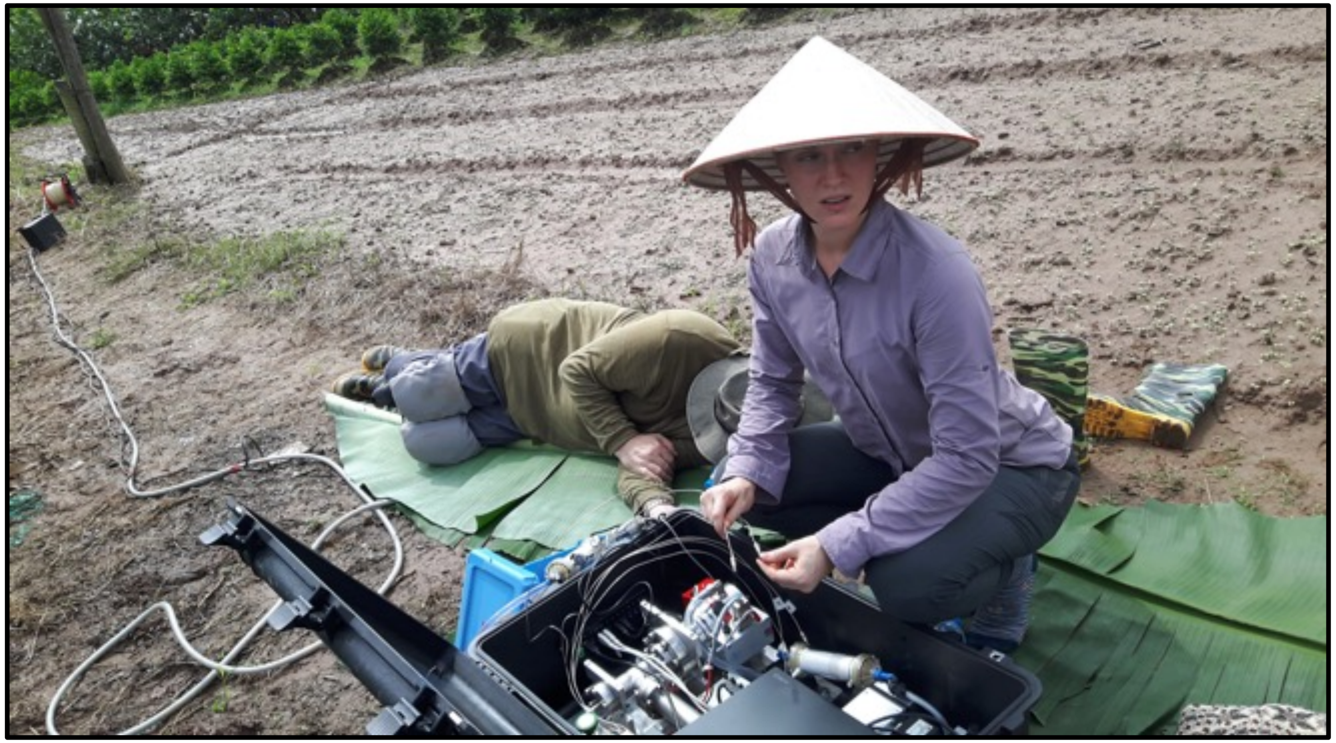
AdvectAs project team!



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