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

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

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

- 21 wells were analysed in-field.

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\(^1\) [https://gasometrix.com/](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
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 aquifer².

Results 1.1

- Simultaneous measurements of noble and reactive gas concentrations suggest **in-situ degassing** of Ar and Kr via oversaturation of CH$_4$.

- **Degassing means:** Saturation of e.g. CH$_4$ or CO$_2$ in groundwater $\rightarrow$ gas bubble formation (+escape) $\rightarrow$ removal of noble gases from water phase into the gas bubble $\rightarrow$ depletion signature seen in NG analysis.

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

Presence of a free gas phase within the aquifer affects groundwater flow and residence times; information necessary to determine As evolution.
Results 1.2

✓ $^4$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?

$^4$He concentrations increase with increasing CH$_4$ in the same wells where Ar and Kr show severe depletion.
Results 2

As concentrations vs. total dissolved gas pressure (TDGP)

- TDGP is the total pressure of all gases in the groundwater as measured by the miniRUEDI at sampling.
- If values exceed 1 atm, 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.

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.
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?
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 a 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.

- \(^4\)He 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 \(^4\)He can accumulate significantly.
  - Addition of an older water component of high \(^4\)He 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.
AdvectAs project team!