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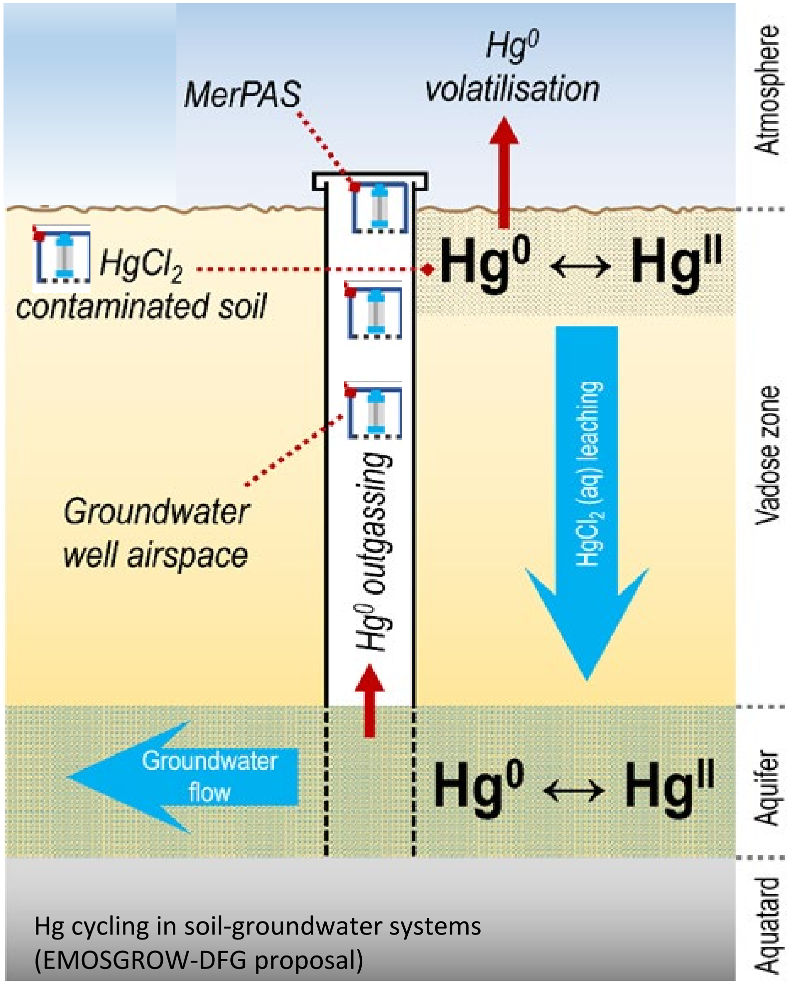
Assessment of mercury reduction and elemental mercury outgassing from groundwater-soils system using subsurface deployments of passive air samplers (MerPAS)

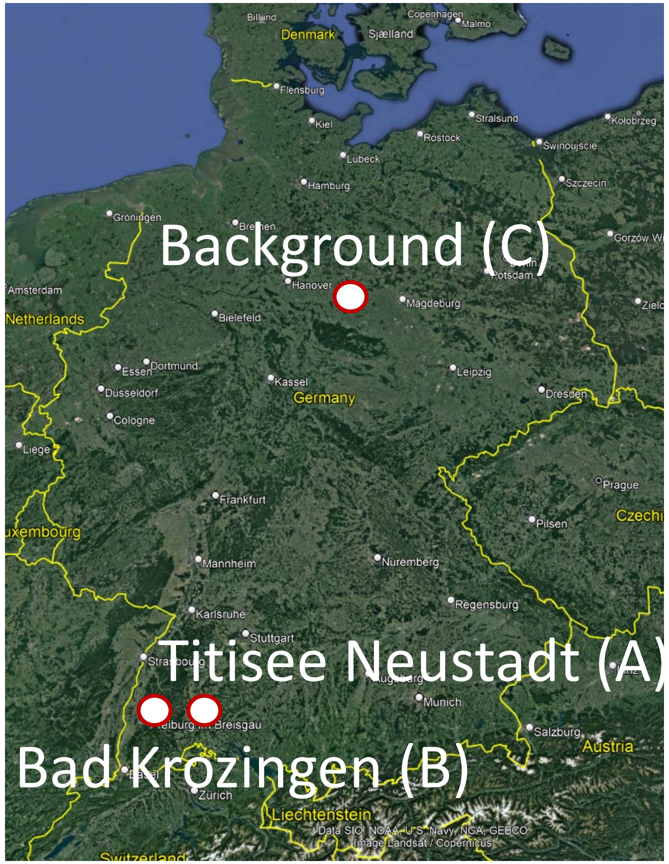


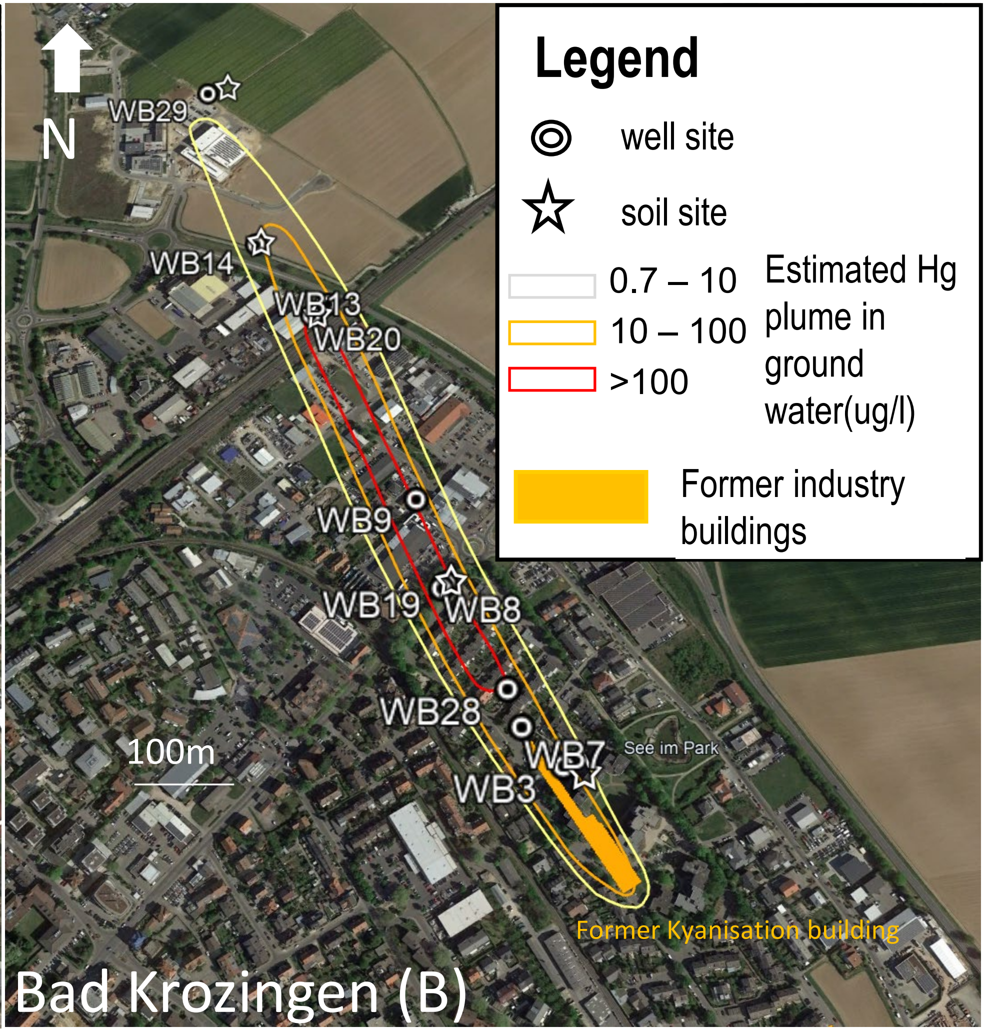
Hg cycling in soil-groundwater systems (EMOSGROW-DFG proposal)

Objectives:

- Explore the application MerPAS for assessing Hg^0 concentration gradients and potential losses from groundwater (GW) to overlying soils, GW wells headspace, and the atmosphere across 3D subsurface space
- Combine GW physicochemical properties and isotopic compositions to identify the mechanisms driving Hg reduction

Sampling in former wood treatments ($HgCl_2$) facilities





Sampling in former wood treatments ($HgCl_2$) facilities

- Hg^0-MerPAS deployment and Hg^0-MerAAS (Lumex) measurement in well

- Hg^0-MerPAS deployment in sub-soil

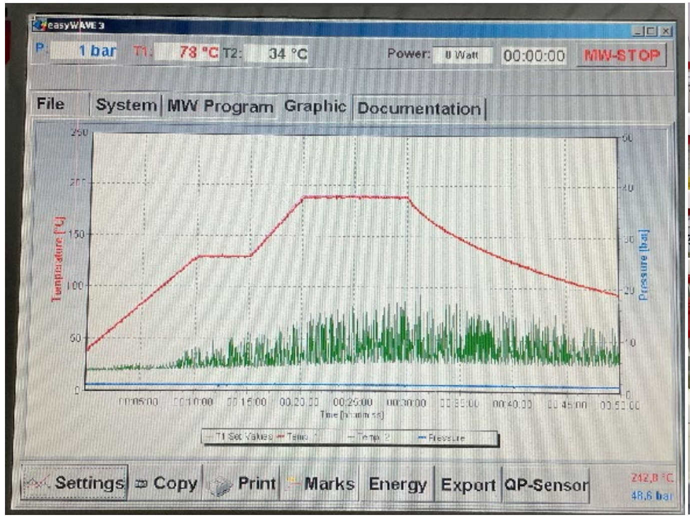
- GW collection:
  - Hg species: Hg^0, Hg_T, Hg^{IIa}, Hg^{IIb}, Hg_{part}
  - Water Level, T, RDO, pH, ORP, Conductivity…
  - DOC
  - Trace metals: Fe, Mn, Cr…
  - Ions: Br^-, Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-} PO_4^{3-}

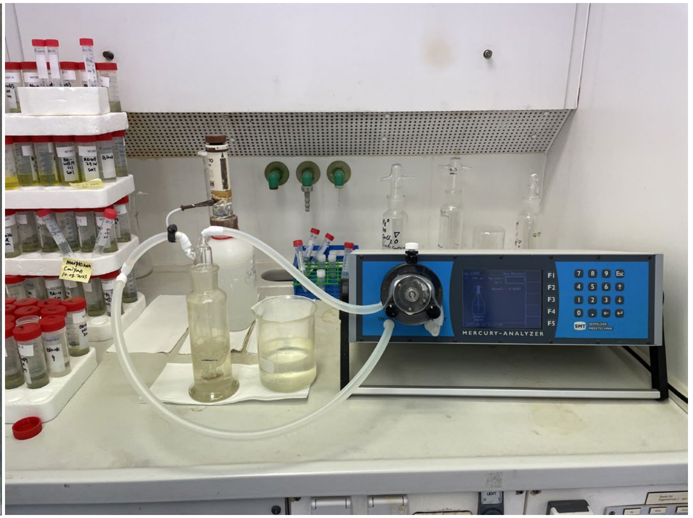
- Sub-soil collection:

Hg_T analysis

Methodology (MerPAS)

- Microwave aqua regia digestion + CVAAS /CVAFS/MC-ICPMS analysis





- DMA-80

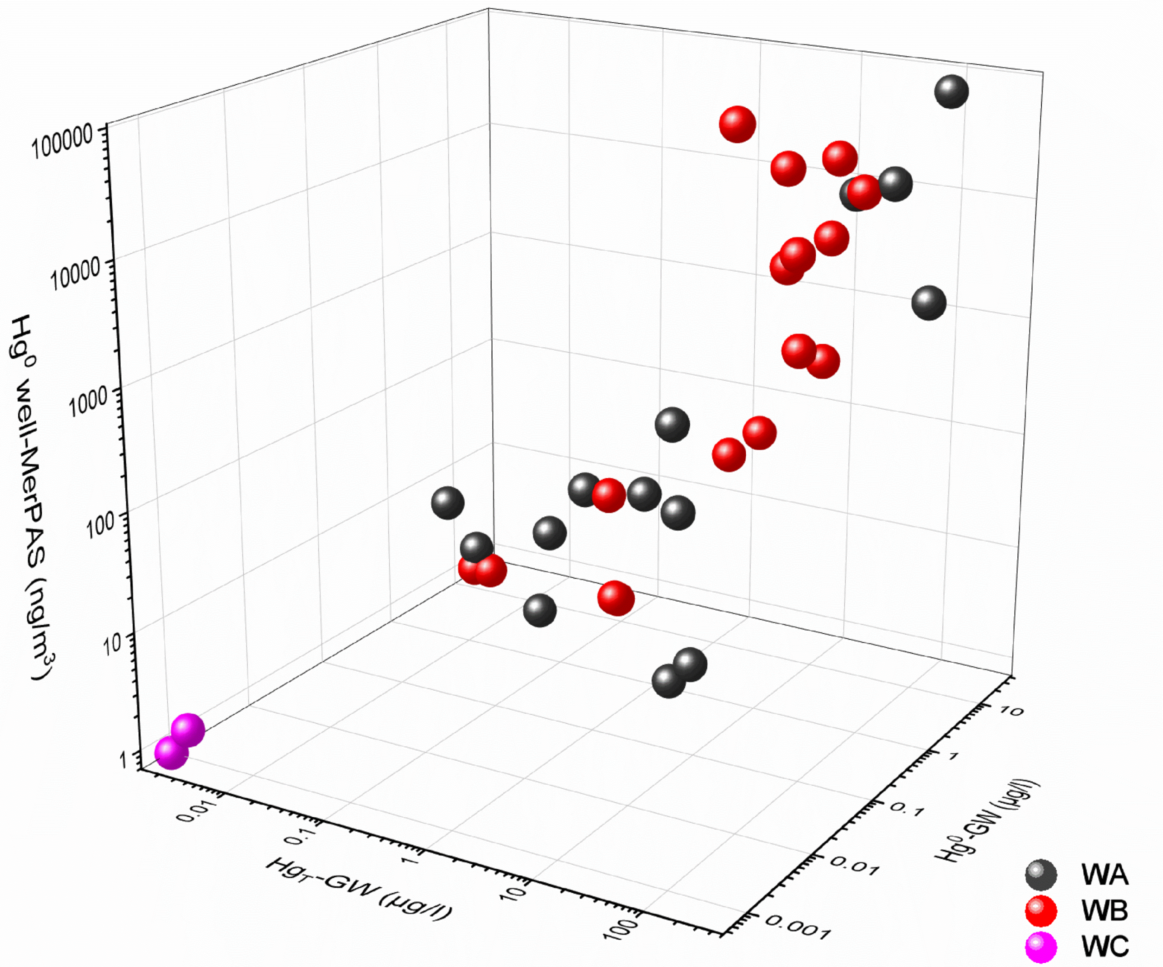
- **Gaseous Hg^0 concentrations (ng/ m^3)**

$$C = {}^{m}/_{(SR * t)}$$

- **m**: mass of absorbed Hg (g)
- **SR**: sampling rate (m^3 /day)
- **t**: length of time the samplers were deployed (day)

Using MerPAS in-well deployments to detect Hg redox chemistry and Hg^0 outgassing in groundwater: Hg^0 source tracking

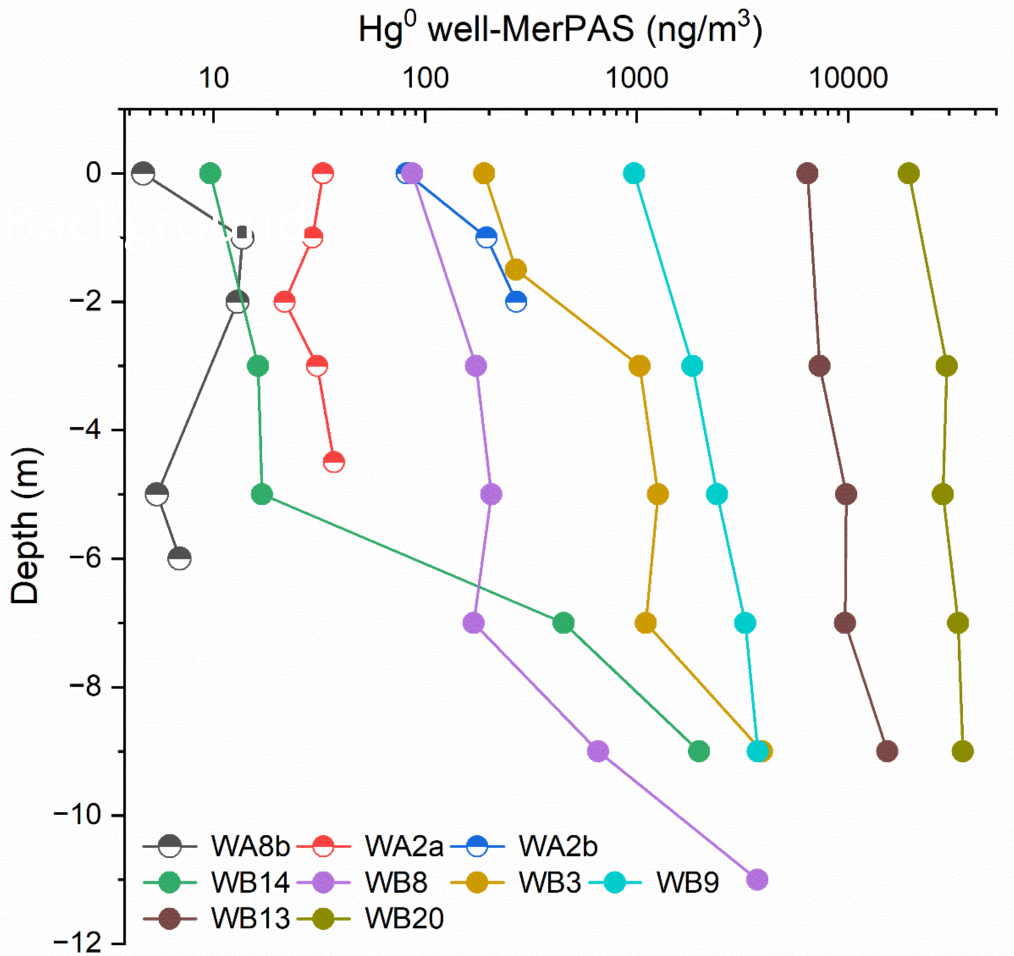
- Hg^0 well-MerPAS concentrations in well surface changed with GW-Hg contamination



- Hg^0 well-MerPAS concentrations varies in orders of magnitude
- Significant correlations between surface Hg^0 well-MerPAS and Hg_T-GW($r=0.819$, $P<0.01$), Hg^0-GW ($r=0.707$, $P<0.01$)
- Offset of peak values between Hg^0 well-MerPAS and Hg_T-GW

Using MerPAS in-well deployments to detect Hg redox chemistry and Hg^0 outgassing in groundwater: Hg^0 source tracking

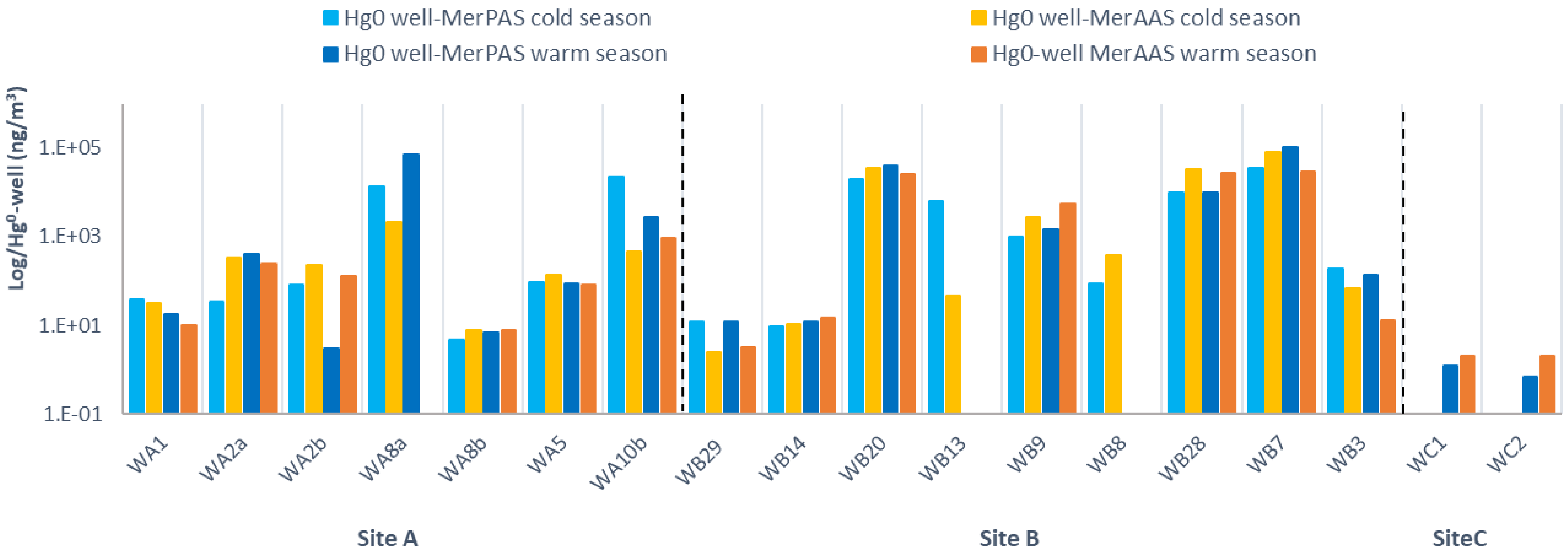
- Hg^0 well-MerPAS concentrations increased along the vertical well depths



- More significant correlation between bottom Hg^0 well-MerPAS and Hg^0-GW (r=0.846, P<0.01)
- Hg^0 well-MerPAS concentrations in less soil contaminated areas were higher or comparable to those in highly soil contaminated (industrial) areas
- GW is the main source of Hg^0 in well

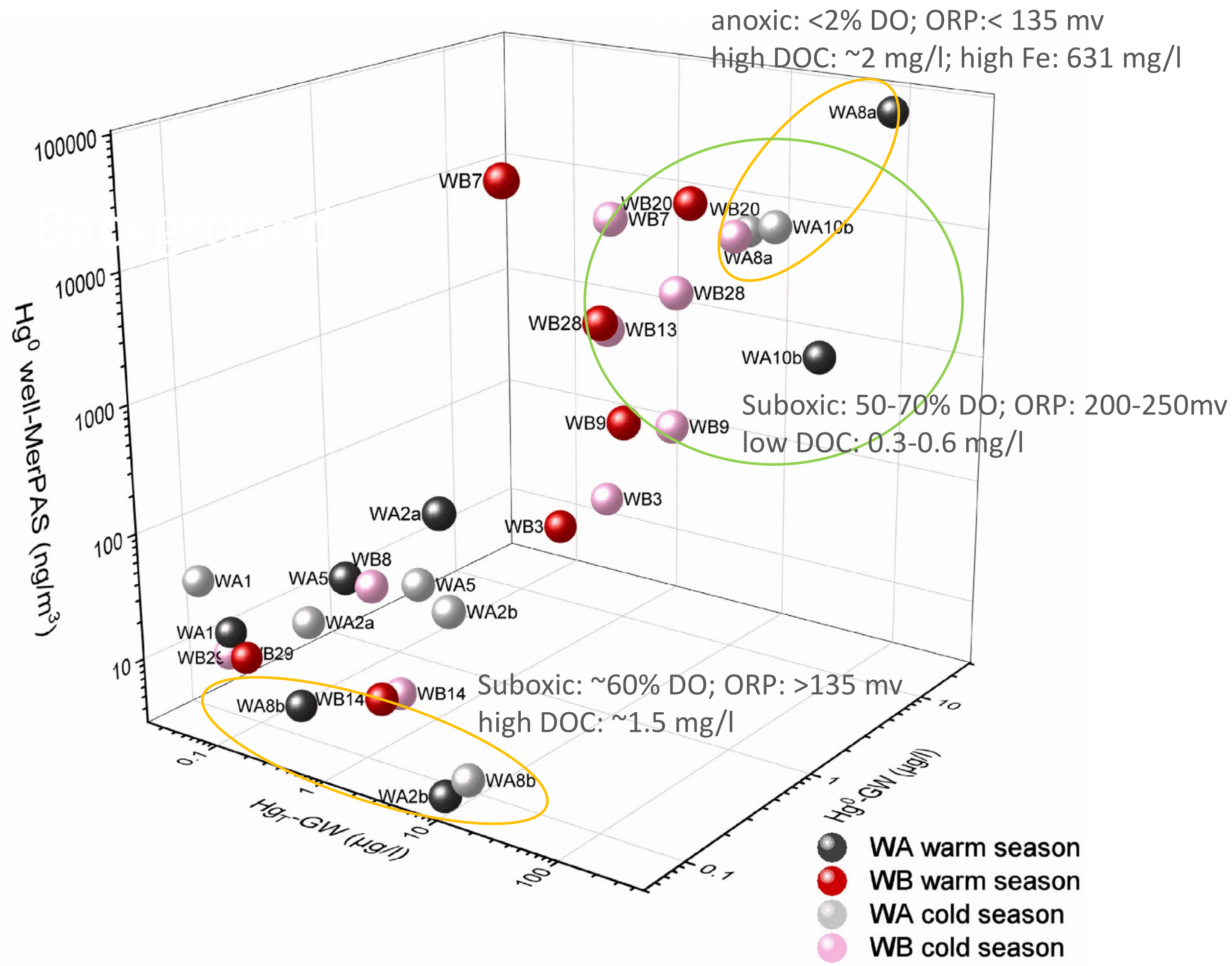
Using MerPAS in-well deployments to detect Hg redox chemistry and Hg^0 outgassing in groundwater: Hg^0 source tracking

- Active measurements support the MerPAS results



Using MerPAS in-well deployments to detect Hg redox chemistry and Hg^0 outgassing in groundwater: Hg biogeochemistry

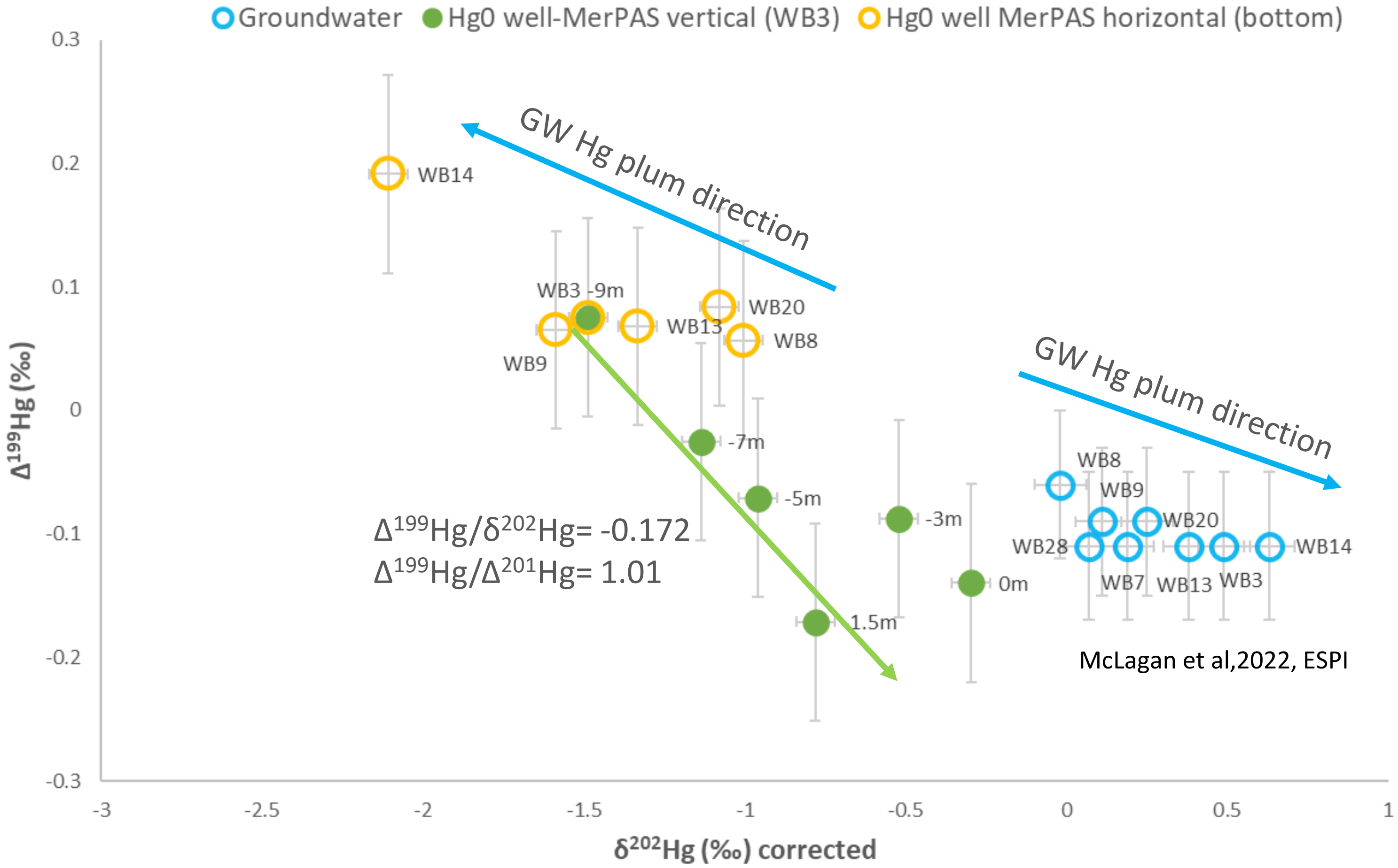
- GW physicochemical properties



- *Temporal variations in reduction*
- *Strong abiotic, DOM and/or Fe^{2+} induced reduction in unconfined well and no obvious reduction in vicinity confined wells*
- *High dissolved inorganic Hg^{2+} controlled abiotic reduction*

Using MerPAS in-well deployments to detect Hg redox chemistry and Hg^0 outgassing in groundwater: Hg biogeochemistry

- Hg isotopic compositions (preliminary results)



- Dark abiotic reduction (NVE) in GW and GW is the main source of Hg^0 in wells
- Equilibrium fractionation between Hg^0 and Hg^{2+} after Hg^0 produced from GW in the closed well system

Using MerPAS soil chamber deployments to detect Hg redox chemistry and Hg^0 outgassing in vadose zone

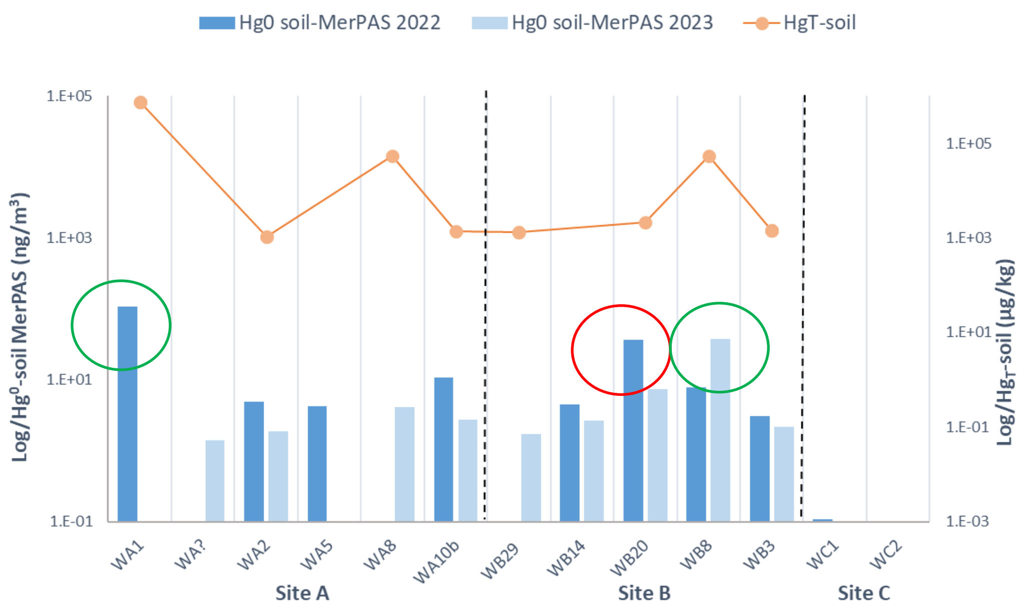
- Hg^0 outgassing from sub-soil is less than from GW

$$\textbf{Enrichment factor}_{soil} = \frac{Hg^0\text{–soil merpAS}}{Hg_T\text{–soil}} = 4 \pm 6 \times 10^{-3}$$

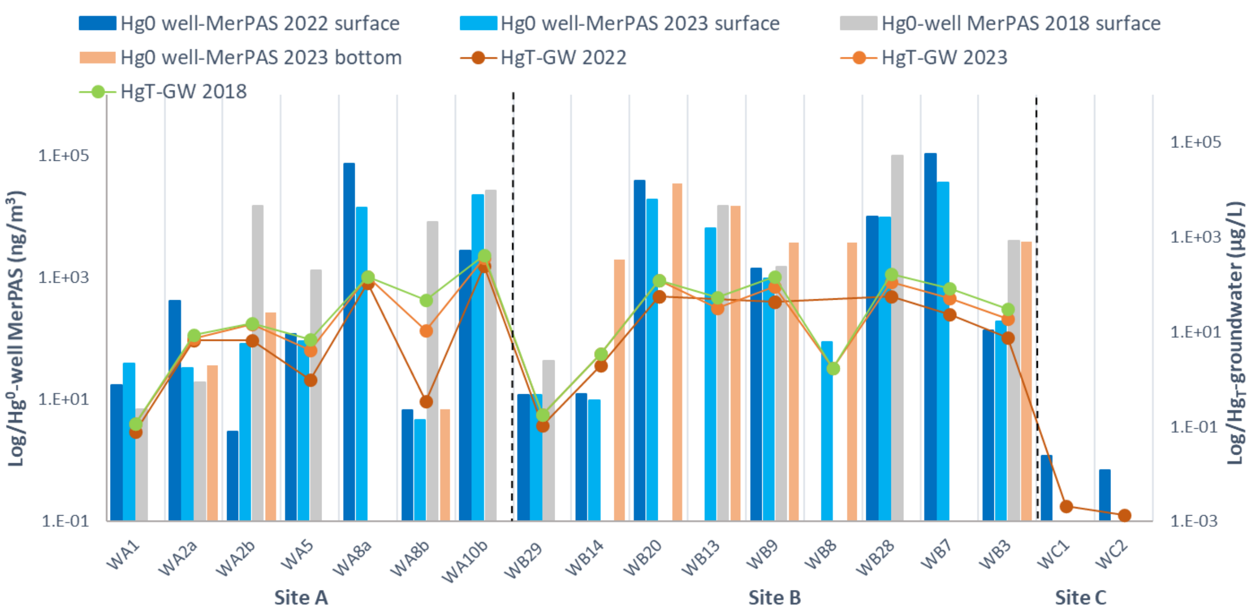
$$\textbf{Enrichment factor}_{GW} = \frac{Hg^0\text{–well merpAS}}{Hg_T\text{–}GW} = 334 \pm 788 \text{ for surface}$$

$$= 827 \pm 1410 \text{ for bottom}$$

<u>*MerPAS Soil chambers*</u>



<u>*MerPAS well deployments*</u>



Conclusions and Perspectives

- Hg^0 well-MerPAS concentration gradients were observed **both horizontally and vertically,** which confirms **GW is the main source of Hg^0 in the wells**
- Combining Hg^0 well-MerPAS data with GW geochemical property and isotopic composition elicits **different levels and mechanisms of Hg reduction and distribution** in GW-soil systems
- Hg^0 concentrations in well were significantly higher than those in soil, suggesting **Hg redox processes are more dynamic and Hg^0 outgasses more readily from GW than subsurface soils**

Subsurface MerPAS deployment methods are powerful tool to derive unique information of **Hg redox chemistry and Hg^0 outgassing within GW-soil systems**

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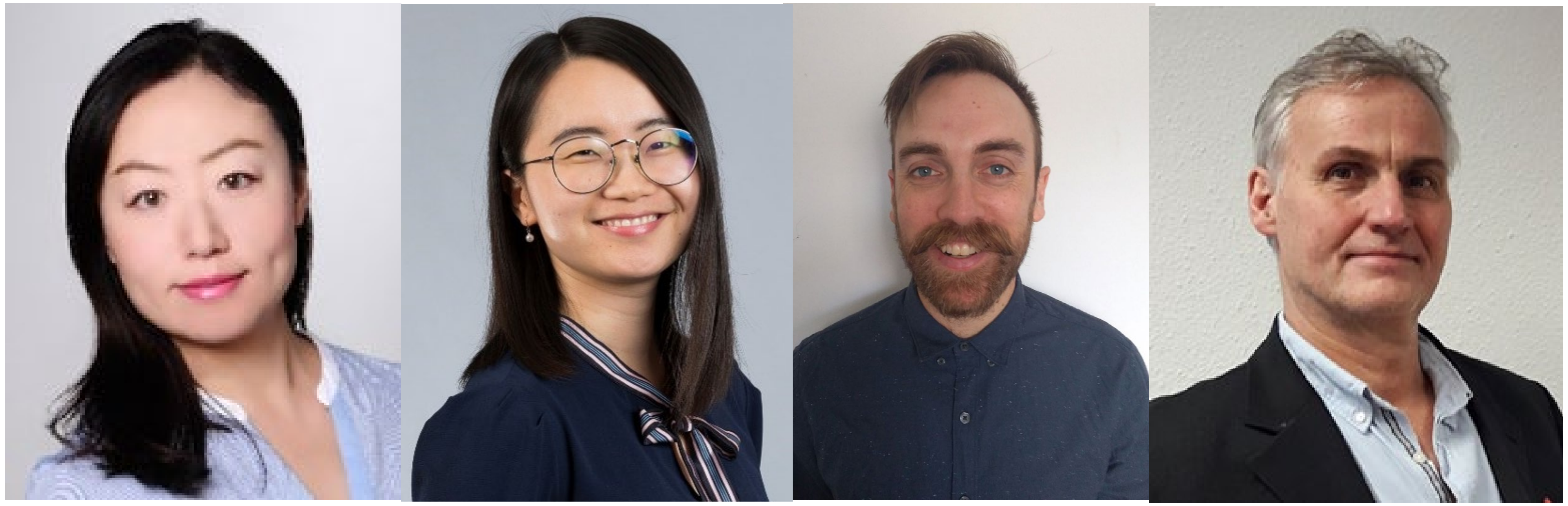
Thank you for your attention!



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