Temperature effect on the vaporization of organic groundwater contaminants considering multi-component contaminants and dissolved natural gases

Alexander Schwardt, Andreas Dahmke & Ralf Köber

Institute of Geosciences
Kiel University

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ENERGIESPEICHER
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ANGUS II

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Content

- Introduction:
  - Subsurface temperature increases / thermal energy storage
  - Effects of thermal energy storage on contaminated sites
- Henry‘s law constants
  - Literature review
  - Laboratory measurements
- Temperature effect on gas phase formation in contaminated aquifers
  - PHREEQC calculations & laboratory experiments
- Conclusions

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Institute of Geosciences
Kiel University

Subsurface temperature rise

- Reasons for temperature increases
  - Urban heat islands
  - Thermal Remediation
  - Thermal energy storage

    “Aquifer-”/”Borehole-” Thermal Energy Storage (ATES/BTES)
  - Beneficial to increase the share of renewable energies and to realize the energy transition
  - High potential especially in urban areas

    → High heat/cold demand

    → existing infrastructure

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TES in urban areas

- **But:** the urban geological subsurface is often contaminated by organic pollutants
- Effects on contamination expected due to temperature increase

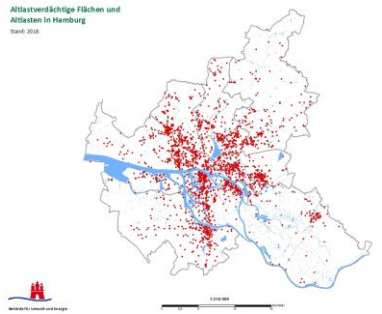
→ **Thermal use of contaminated subsurface is so far not permitted!**

→ **Heating of contaminated aquifer is established for remediation**

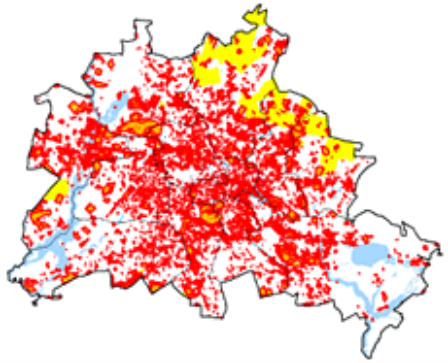
➢ ***Solution:***

➢ ***Combination of TES and Remediation?!***

Suspected contamination areas in large cities



Behörde für Umwelt und Energie Hamburg



Senatsverwaltung für Umwelt, Verkehr und Klimaschutz - Berlin

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Advantages of combining TES and remediation

- Various synergetic approaches for the combination of TES and remediation of contaminated sites
  - better approval & acceptance regarding bio-geochemical changes
  - better energy and cost balance for the remediation of contaminated areas that might otherwise not be decontaminated
    - thermal energy for the heat market can be used for remediation
  - Avoidance of the use of potential drinking water areas
  - Better area availability and area reuse

➢ ***Easier permission process***

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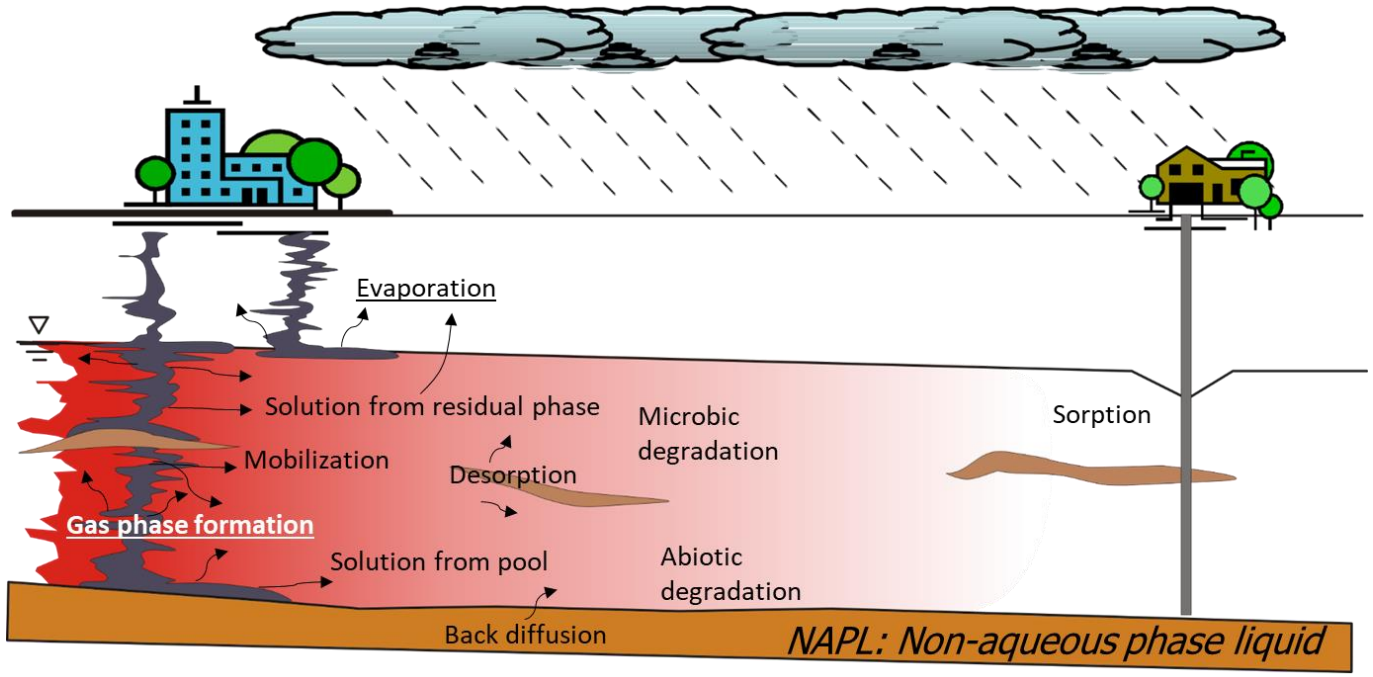
Temperature-dependent processes in case of contamination

Temperature changes of the contaminated subsurface leads to changes in e.g.

- solubility (Koproch et al. 2019),
- mobility,
- degradation (Metzgen et al. in prep/ Schwardt et al. in prep)
- **gas phase formation** (Schwardt et al. in prep)



Research objectives of ANGUS$^+$ (ended), **ANGUS II**, "ANGUS III" (planned)

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Gas phase formation

- **Influences on gas phase formation**
  - Temperature
    - Composition of water / contaminants, dissolved components or gases (N_2, O_2, CO_2)
      - Henry's law constants
      - Vapor pressure

} temperature dependent

- **Consequences of gas phase formation**
  - Outgassing/devolatilization of pollutants
  - Migration of contaminants (potential hazard)
  - Changes of porosity/permeability of an aquifer
  - **Remediation effect** (combination of volatilization and soil air extraction)

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Objectives

- Are available data appropriate for predictions about gas phase formation?
  - Literature review on **Henry‘s law constants** of volatile organic compounds (VOC)
  - Measurements of Henry’s law constant to close data gaps of several compounds
- Influence of **dissolved atmospheric gases and temperature** on gas phase formation in case of a contamination with VOCs
- Influence of temperature and **Multi-component NAPL (non aqueous phase liquid) composition** on temperature induced gas phase formation
  - PHREEQC calculations
- Development of a **new laboratory experiment** to determine the gas volume resulting from a temperature increase of contaminated water

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Theoretical background

- **Henry's law** – The concentration of a dissolved gas is directly proportional to the partial pressure of the gas above the liquid.
- Henry's law constant: $$H = \frac{C_g}{C_{aq}}$$

H	Henry's law constant [-]
C_g	Concentration in gaseous phase
C_{aq}	Concentration in aqueous phase

- Vapor pressure
  - Miscible fluids: $$p_{total} = \sum x_i p_i$$
  - Immiscible fluids: $$p_{total} = \sum p_i$$

p_i	Vapor pressure of compund i
x_i	Mole fraction of compund i

➢ Dissolved components or gases like N_2 act like miscible fluids

➢ For mixtures of immiscible fluids (e.g. PCE + Water), the vapor pressures must be added, reducing the boiling point

➢ **Co-boiling temperature**

Compound	bp. [°C]	Co-bp [°C]
Water	100	-
PCE	121	88
TCE	87	73-74
PCE+TCE	-	86

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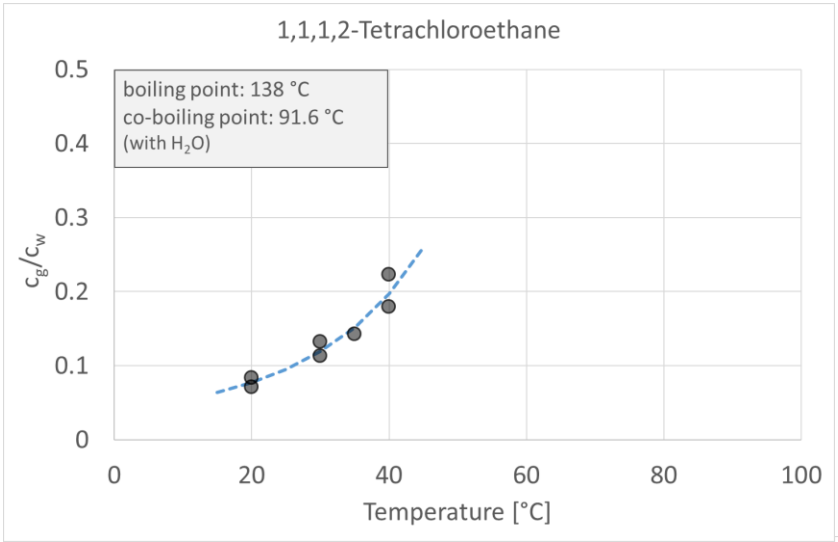
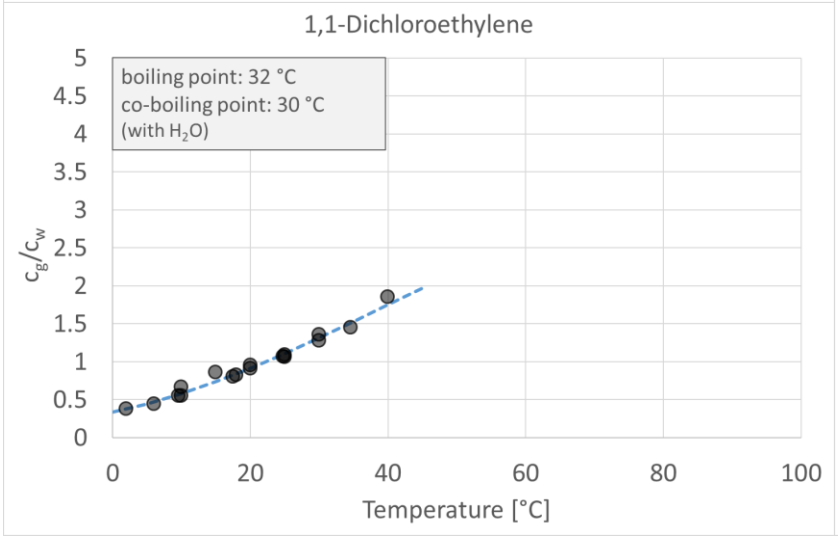
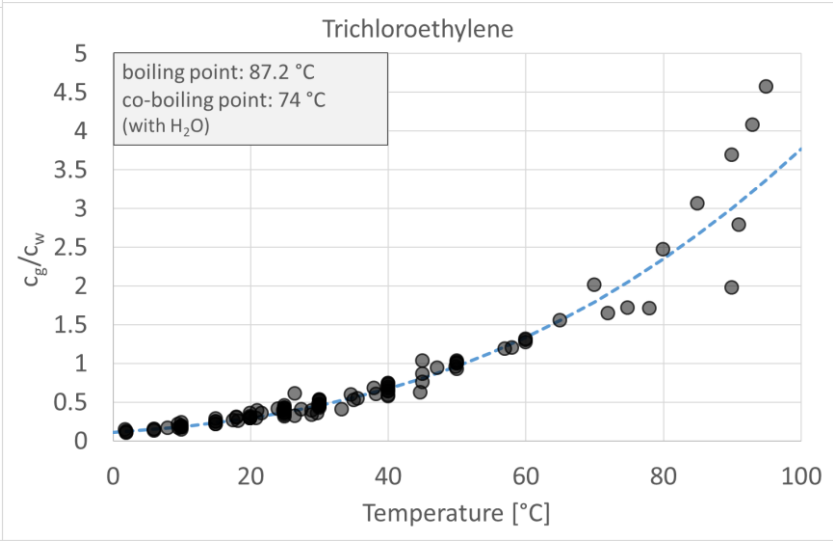
Henry's law constants – Literature review

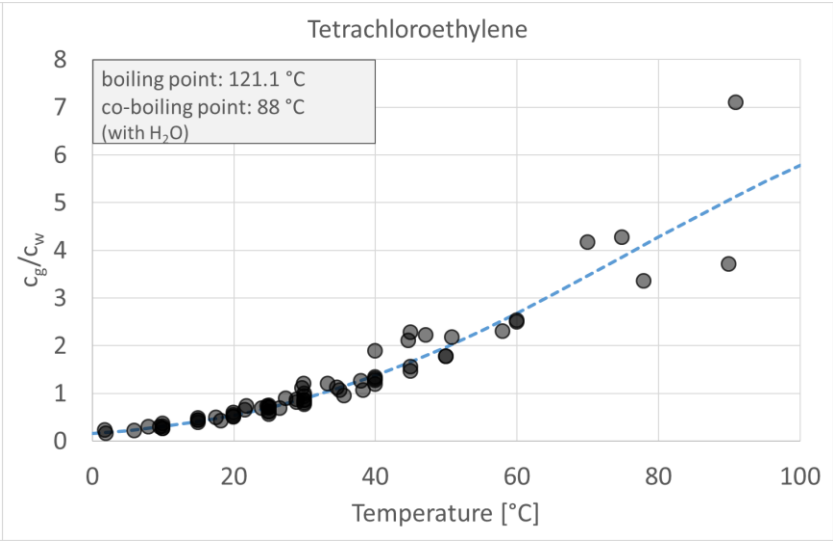


- 44 compounds, 46 publications
- Only a few studies with H > 40 °C, and/or large variations of H at higher T

➢ **further measurements of H are necessary**







measured data (literature) Regression (of literature data)

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Institute of Geosciences
Kiel University

Measurements of Henry's law constants

- EPICS procedure (Equilibrium Partitioning In Closed Systems) by Gossett (1987)
  - 4 pairs of two equal bottles V = ~100 mL, filled with different amount of water (20 mL/80 mL), but equal mass of the compound, GC-Analysis of the gas phase
- 17 substances with insufficient data will be studied between 10 & 90 °C
- Fit of measured data: $\ln(H) = A - \frac{B}{T} + C\ln(T)$ (Heron et al., 1998)

Substances which will be measured

Carbon Tetrachloride
1,1-Dichloroethane
1,2-Dichloroethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,1,1,2-Tetrachloroethylene
1,1,2,2-Tetrachloroethylene
Vinyl Chloride
1,1-Dichloroethylene
1,2-trans-Dichloroethylene
Trichloroethylene
Tetrachloroethylene
Ethylbenzene
Chlorobenzene
p-Xylene
o-Xylene
m-Xylene

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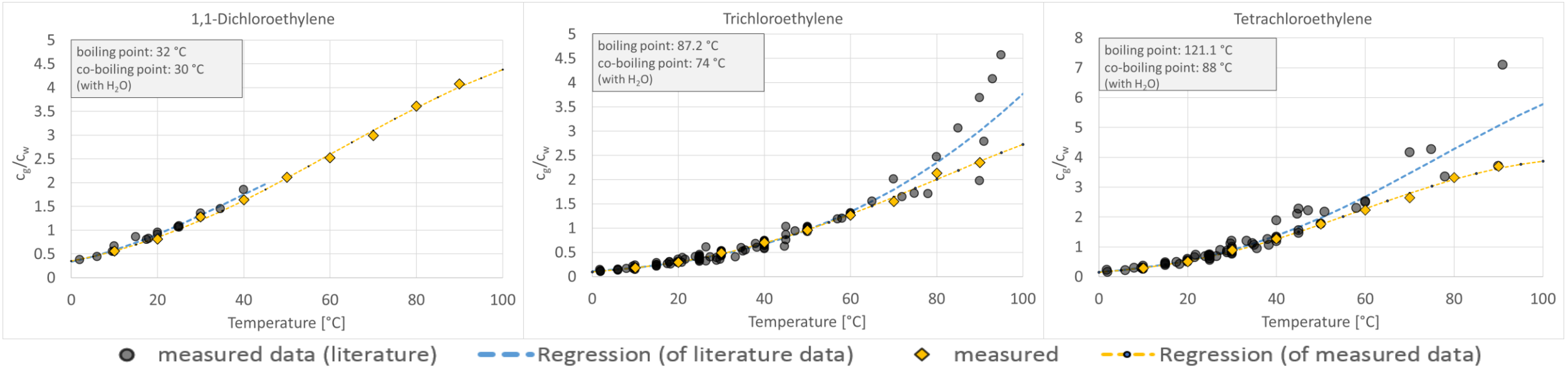
Measurements of Henry's law constants

- Good fit of measured H to literature data up to 40 °C
- for PCE & TCE, measured H are lower than the average of literature data at higher temperatures



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Methods: PHREEQC calculations

- Phreeqc v3: Program for aqueous geochemical equilibrium calculations (by Parkhurst & Appelo)

- Addition of thermodynamic data (solubility by Koproch et al. (2019)/Henry's law constants by Schwardt et al (in prep)) to the database (phreeqc.dat) for the examined compounds (e.g. PCE, TCE etc.)

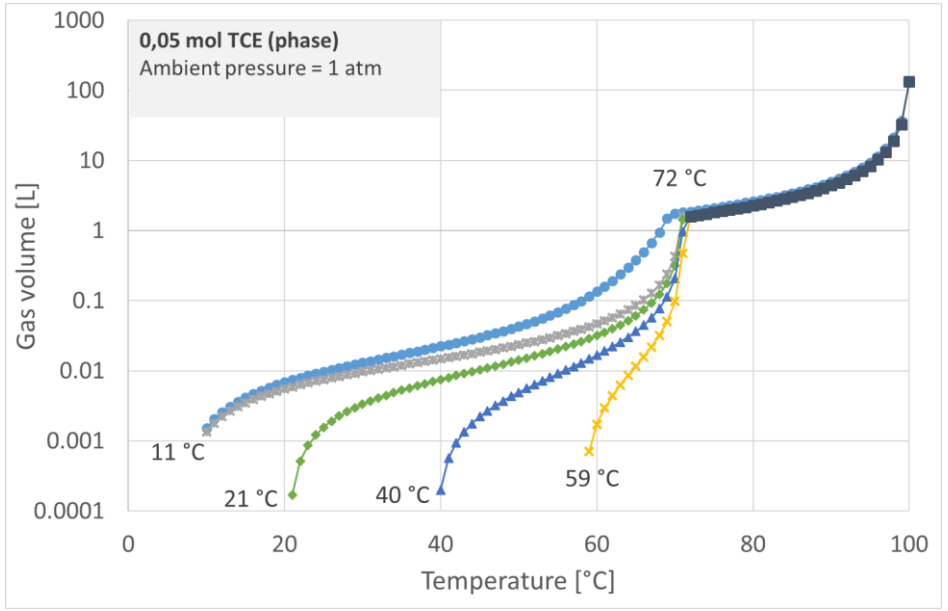
Method of Calculation:

- Heating up of 1 kg pure water from 10 °C to up to 100 °C
- Pressure: 1 atm (constant); (gas-)volume: variable
- The calculations were performed with dissolved NAPL or NAPL phases
- Dissolved atmospheric gases (e.g. $N_2/O_2/CO_2$) were varied, because there are huge variations in dissolved gases in natural aquifers (Lüders et al., 2016)
  - total partial pressure up to 1 atm

Results: PHREEQC calculations – Dissolved atmospheric gases

Influence of dissolved atmospheric gases on single-phase NAPL

- The boiling point is not influenced by $N_2/O_2/CO_2$ at groundwater typical masses
- With increasing N_2, the temperature at which a gas phase is formed decreases
- Due to its higher solubility, dissolved CO_2 has a greater influence on the resulting gas volume than dissolved N_2



➢ **Depending on N_2-Partial pressure the resulting gas volume can be increased by 10 times and more**

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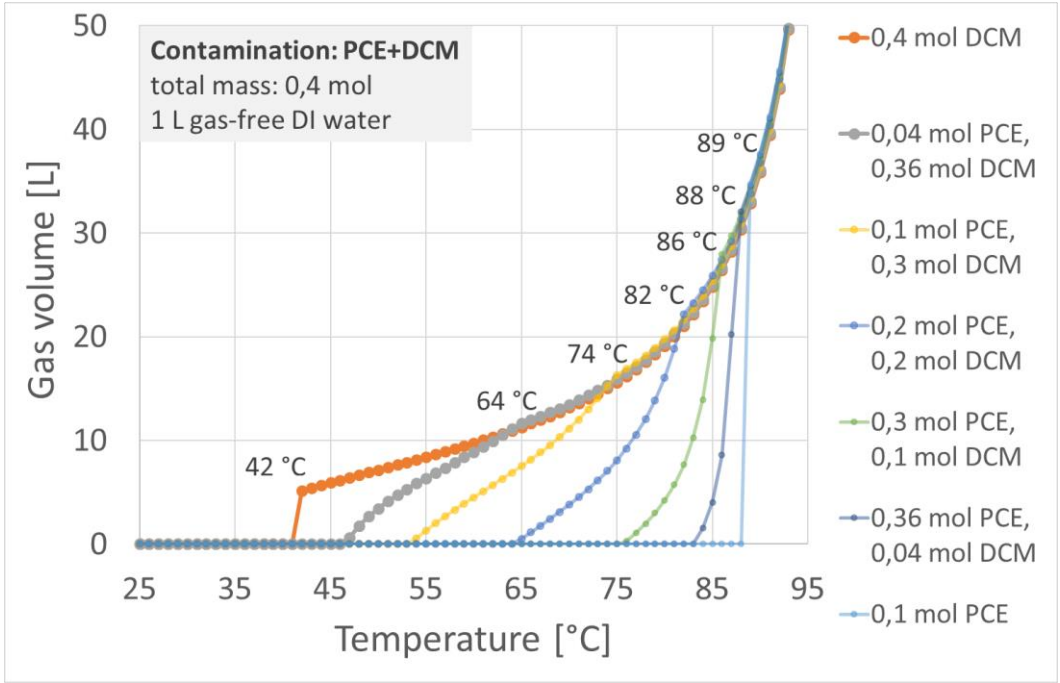
Institute of Geosciences
Kiel University

Results: PHREEQC calculations – Multi-component NAPL

PHREEQC-Calculations
(PCE + Dichloromethane (DCM))

- the co-boiling point of a Multi-NAPL system is controlled by the molar fractions of the involved components

➢ The higher the fraction of the less volatile compound, the higher the boiling temperature of the mixture

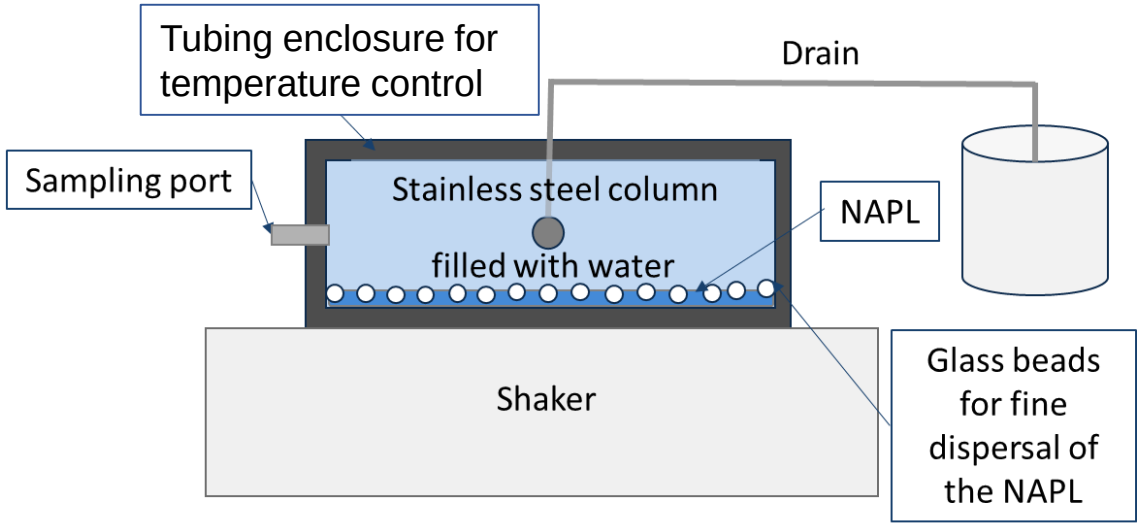


➢ **Even a 10% fraction of PCE in a DCM-PCE-NAPL leads to a significant increase of the co-boiling point (~22 K)**

Methods: Batch experiments

- Gas tight stainless-steel column (40 x 5,5 cm)
- Glass beads & shaking the column contributes to distribute the NAPL phase finely and to establish equilibrium
- NAPL phase: a) TCE 0,05 mol/l; b) PCE+TCE (0,05 mol/l each)

- Water equilibrated at **10°C** with **synth. air** (0,8 atm N_2, 0,2 atm O_2), NAPL was added, the column closed and then heated to **25, 40, 55 & 70 °C**
- Heating the completely filled column leads to gas phase formation in the column, displacing the equivalent volume of solution
- The gas volume was quantified by refilling the resulting gas space in the column with a known volume of water

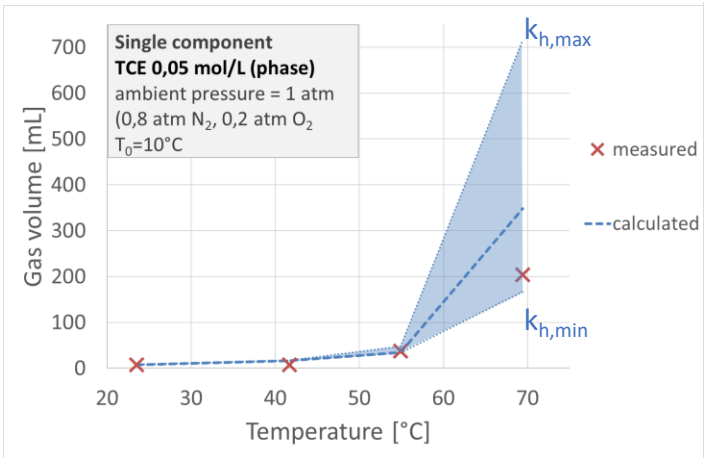


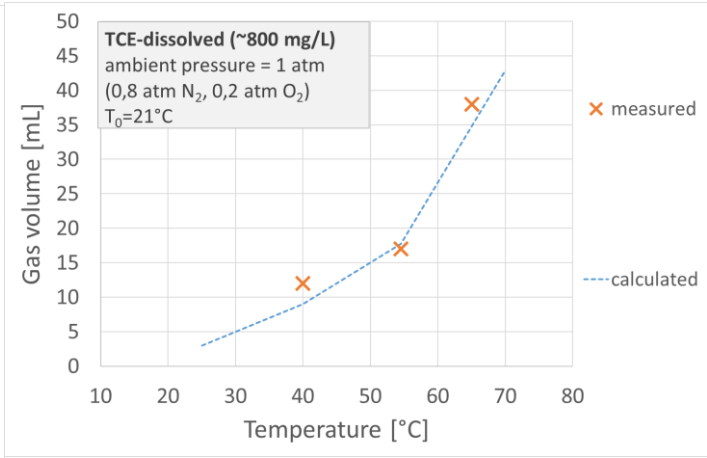
Results of the batch experiments

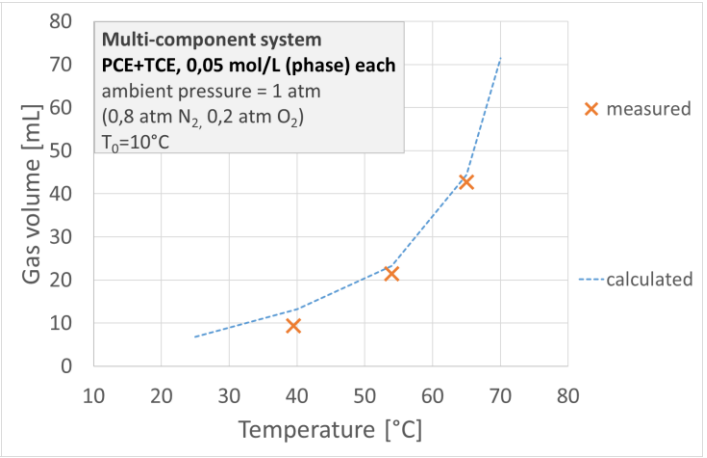
- Experiments with TCE (phase) as single component
- Measured gas volumes at 25, 55 und 70 °C lie within the calculated range of expectations
  - wide range of expectation for experiments with TCE phase at 70 °C due to Henry's law constants (H) and temperature close to the co-boiling point of TCE+H_2O (~73 °C)
- Experiments with TCE (dissolved) and multi-component experiments (PCE+TCE phase)
- Measured gas volumes showed a good fit to the calculations

➢ **The PHREEQC calculations are verified**

➢ **Determination of the resulting gas phase volume is possible even if no or poor thermodynamic data are available**







Conclusions I

- The existing H database of most contaminants at T > 50 °C leads to a **large uncertainty range** in the estimation of gas phase formation (a factor 4 between min. und max. gas volume when heating 1 L of water with 0,05 mol/l TCE phase from 10 to 70 °C)

  - An **improvement of the H database is necessary** for the risk assessment of high-temperature heat storage systems and efficiency of remediation projects in contaminated areas

  - **Measurements of H were already started**, 17 substances between 10 and 90 °C will be studied

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Conclusions II

- (HT-) TES temperatures can lead to a volatilization of pollutants and thus to a reduction of the pollutant mass in the aquifer
- Composition of dissolved atmospheric gases in the groundwater is of importance at temperatures below the co-boiling point
  - ➢ For the assessment of an environmental hazard through outgassing of pollutants or for the evaluation of a remediation efficiency, the composition of dissolved atmospheric gases in groundwater should be analysed within the framework of preliminary investigations
- For multi-components pollutants, the compositions of the contamination is essential to determine the co-boiling point and thus the exact gas phase formation
  - ➢ A shift of the co-boiling point by several degree Celsius is possible
  - ➢ TES can lead to a partly or even complete devolatilization of the NAPL (and thus leading to a remediation of the source of contamination)
  - ➢ Knowing the exact (co-)boiling temperature can significantly decrease the energy demand for remediation

Thank you for your attention!

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