On-site measurement of excess N_2 “under pressure”

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Section L2.6/B2.3 – Hydrogeochemistry

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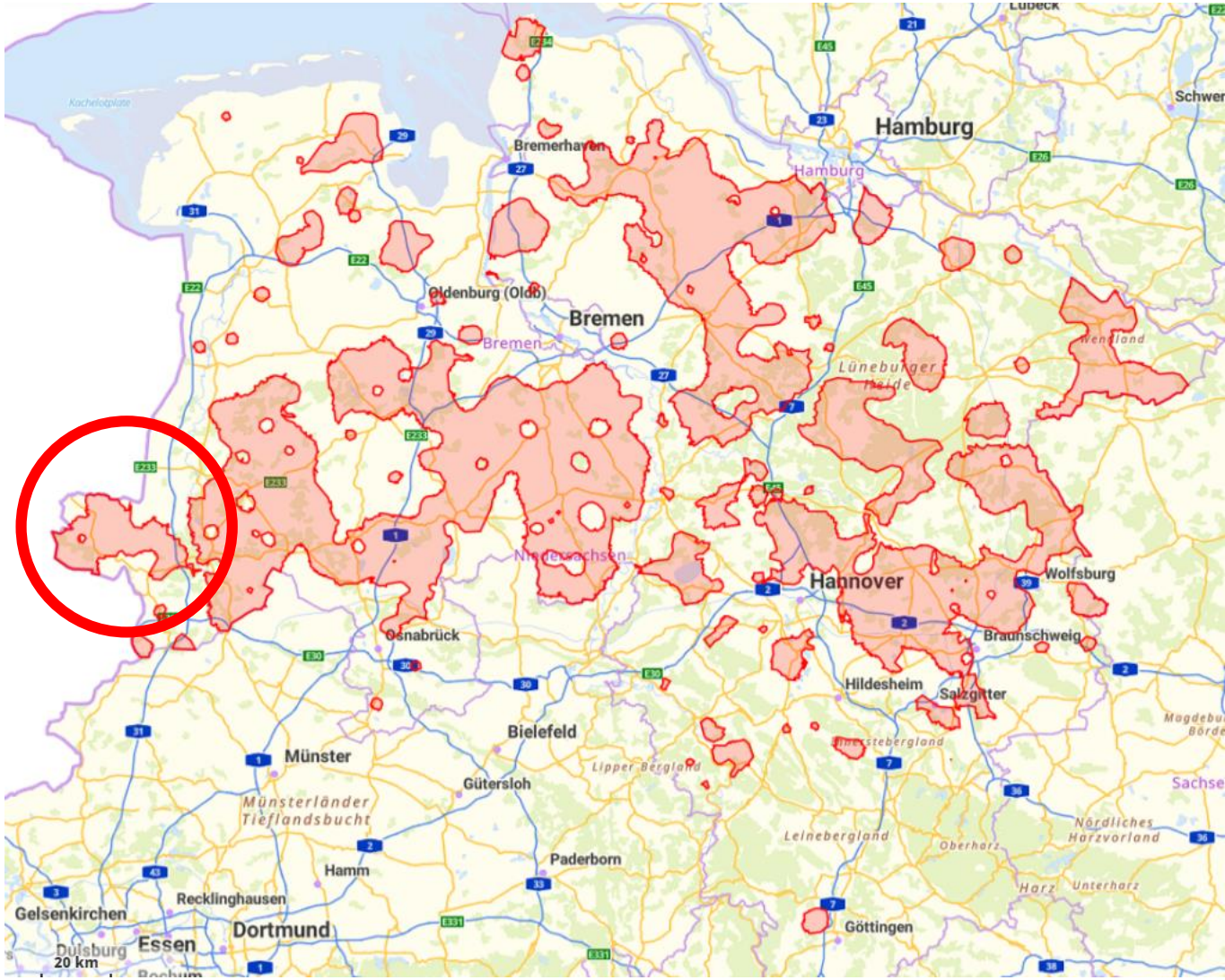
Nitrate input and nitrate pollution

- groundwater bodies affected by **rising nitrate concentrations** → **„red areas“**
- „Red Areas“→ restrictions regarding the use of N-fertilizers (including manure, etc.)
- Recent changes to Groundwater ordinance → future definition of red areas via **nitrate + denitrification** (amount of reduced nitrate)

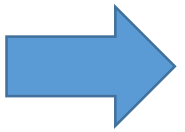


Nitrate input and nitrate pollution

- Method of choice for quantification: **N_2/Ar-method** (Excess-N_2) (e.g. Vogel et al., 1981)
- All 16 federal states need to provide N_2/Ar data by the end of 2025
- LBEG hosts the nationwide interlaboratory tests for N_2/Ar-measurements and developed a QC tool for N_2/Ar data (N_2ArCheck)

miniRUEDI application

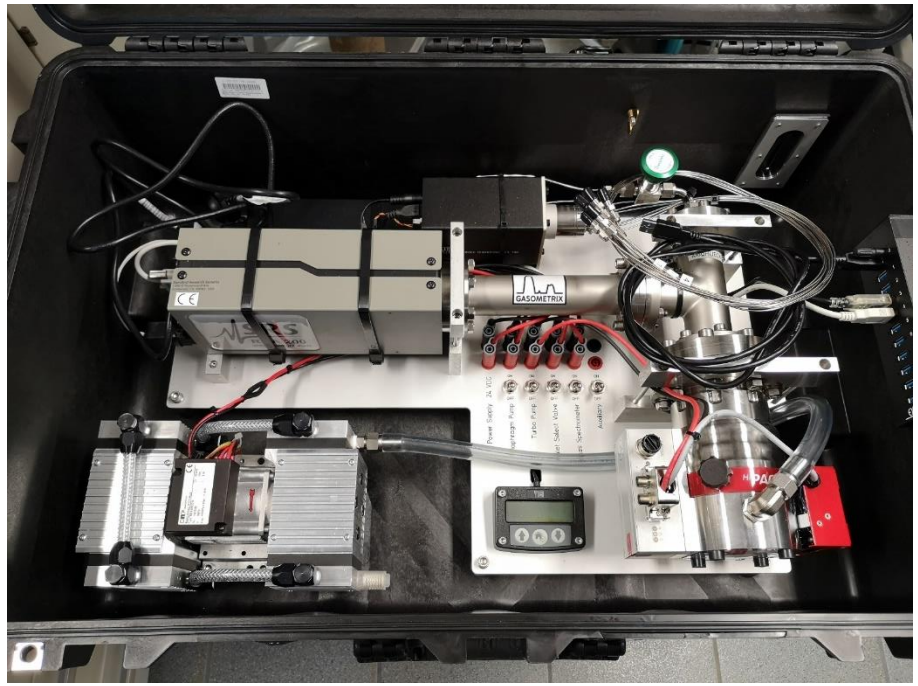
- Better understanding of excess air components (not only N_2 and Ar data)
- evaluate degassing effects (e.g. shallow denitrification, sampling artifacts)
- **independent method for comparison with lab data (MIMS, MIGCMS, HSGC-TCD)**



Data comparision - instruments

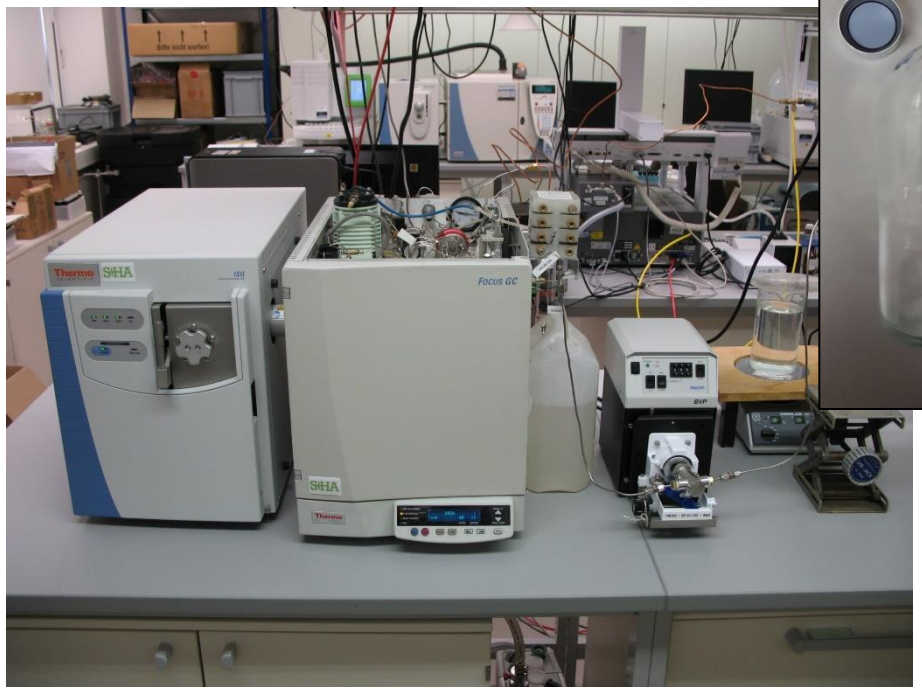
Mobile setup

- miniRUEDI (GE-MIMS)
- 3M mini module (water flow: lumen side)
- OMEGA pressure sensor (pmax=3.5 atm)
- Grundfos MP1 submersible pump, solid PVC-tubing (diam. 20 mm)



Lab setup

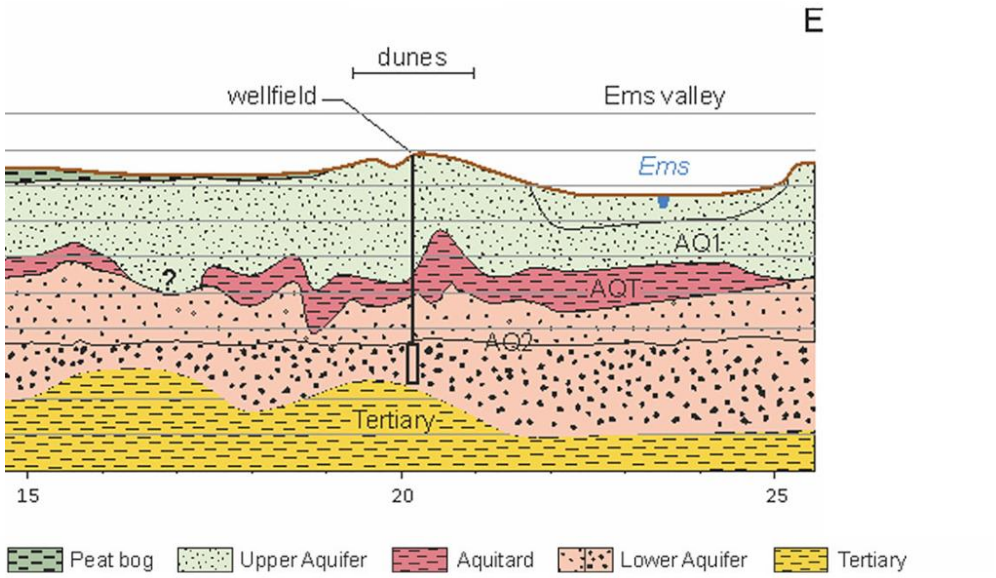
- MI-GCMS with silicone membrane
- samples in 120 ml serum vials
- He-flow @ 20ml/min, 1 ml sample loop
- Columns: PorapakQ, 5 Å molsieve

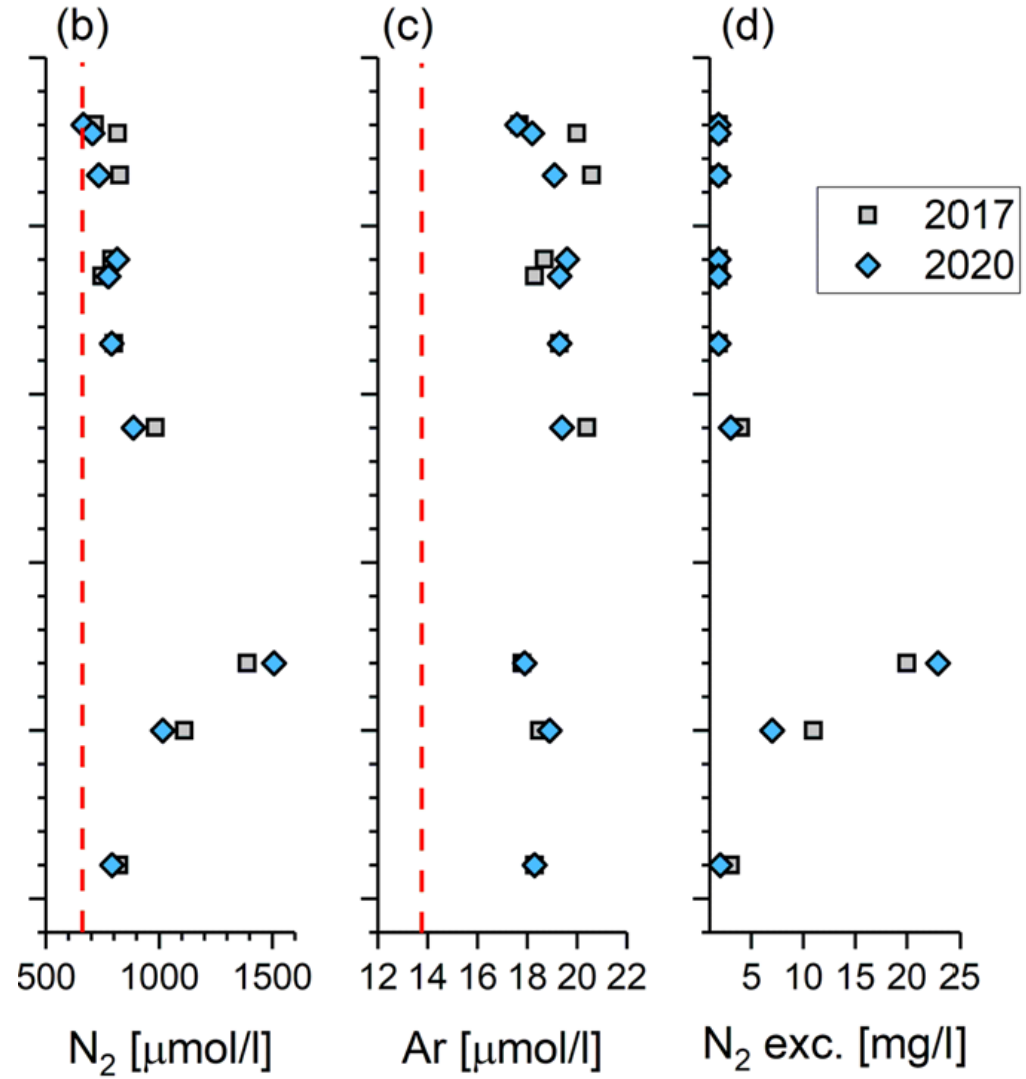


Data comparision – study site

(Hydro)Geological setting

- Two quarternary aquifers (glaciofluvial deposits of the Ems valley), partially separated by an aquitard (NW Germany)
- Lower aquifer used for public water supply
- Screen depths of monitoring wells approx. 5 to 50 m





Houben et al. (2021)

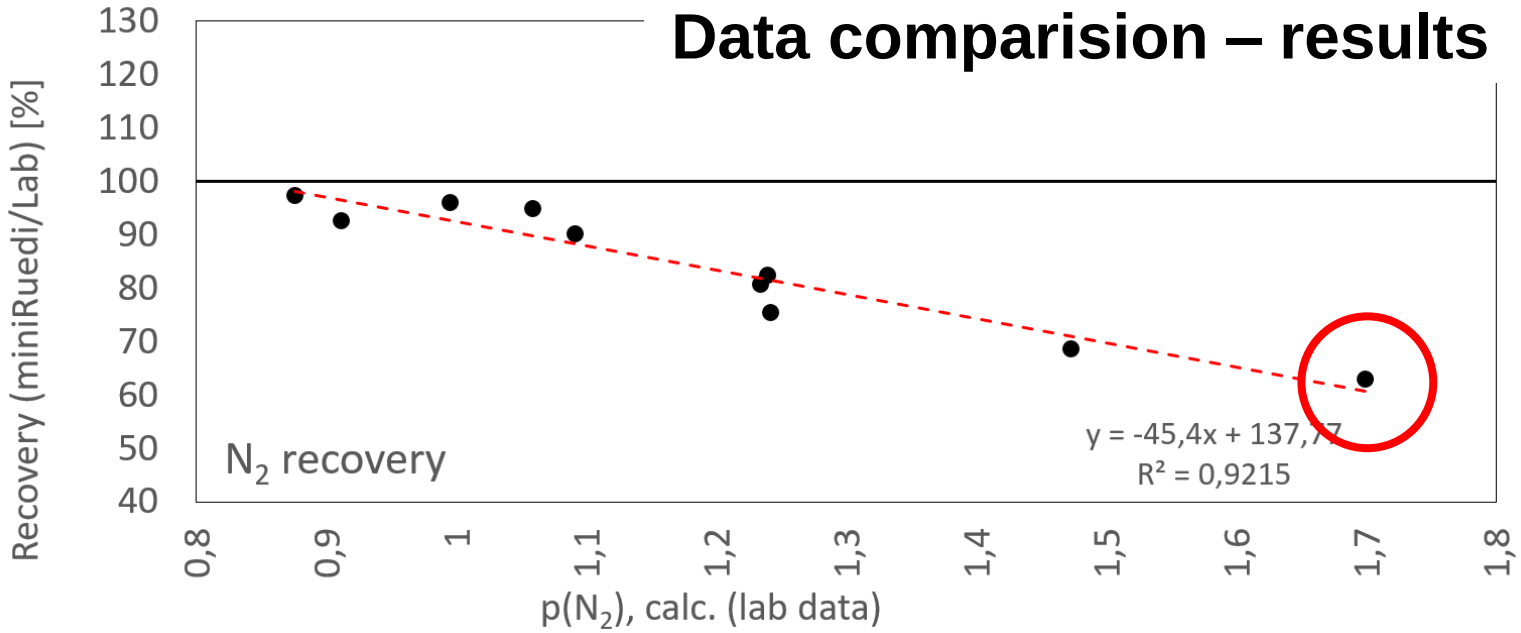
Data comparision – results

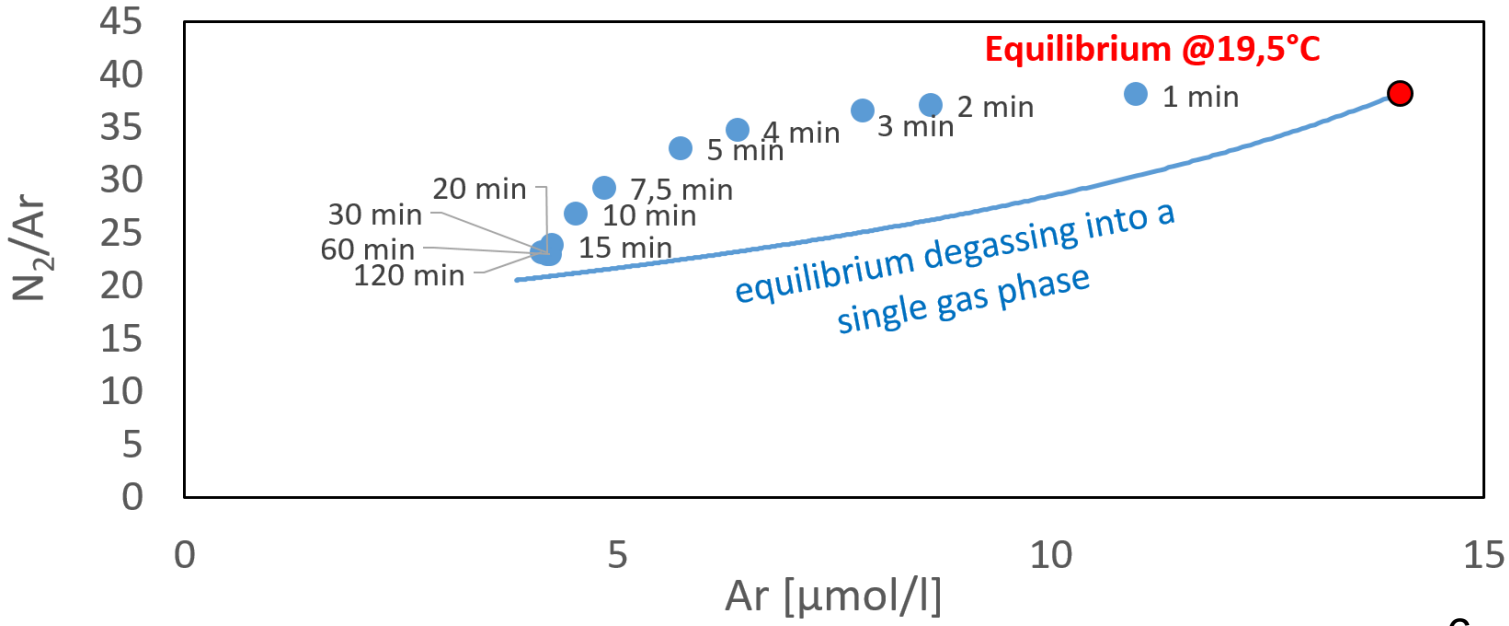
miniRUEDI vs. MIGCMS

- miniRUEDI GE-MI-module flow rates
  75 - 100 l/h
- 10µm water filter and 5 m hose, diameter 20 mm
- miniRUEDI → **major gas losses**
- increases with increasing TDGP
- **Can‘t be easily identified in the field**
- **Shift in N_2/Ar ratios**

→ limits of GE-MIMS?

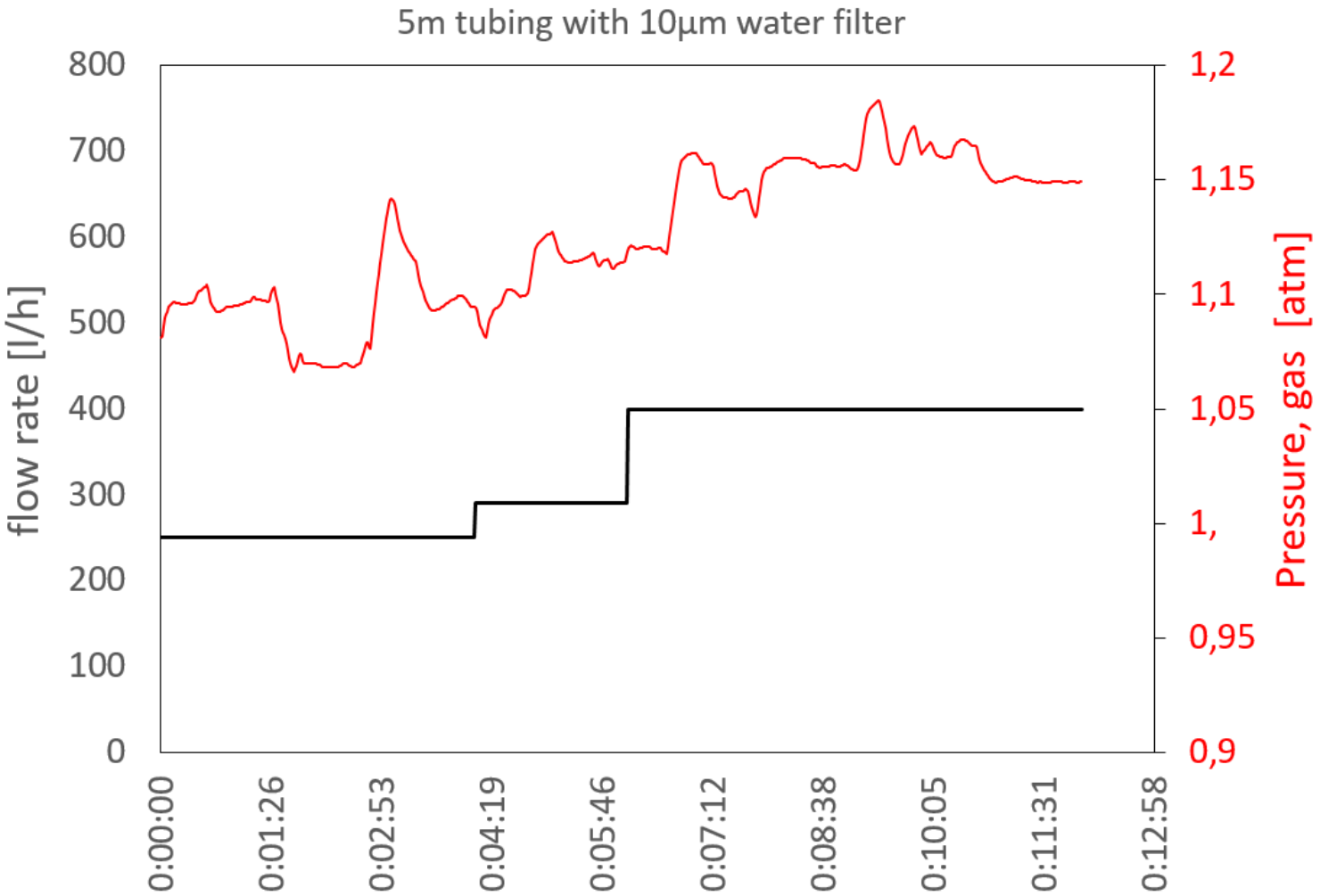
→ Quality/degassing check?





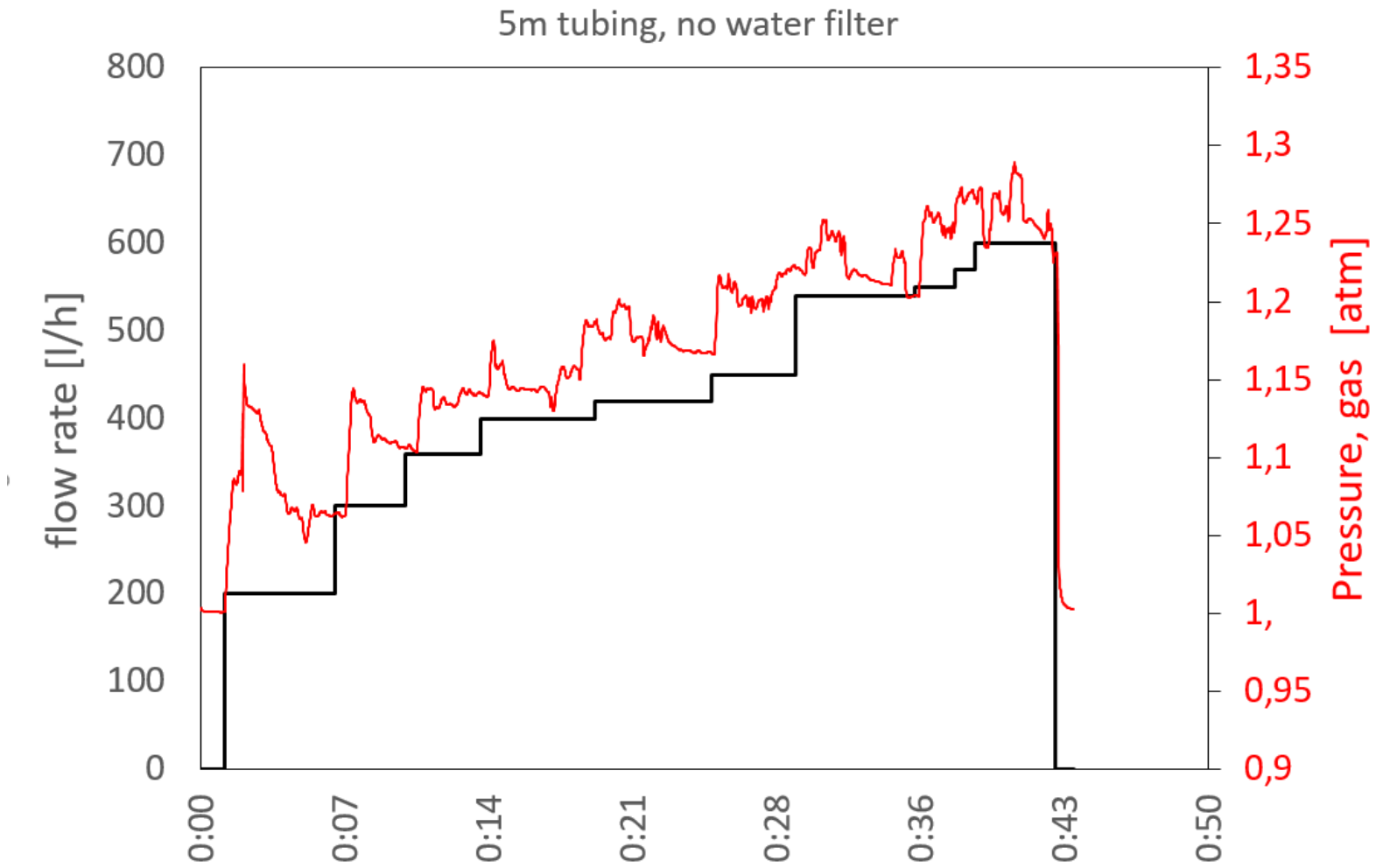
Field tests


miniRUEDI test M5


5m tubing with 10µm water filter
flow rate [l/h]
800
700
600
500
400
300
200
100
0
Pressure, gas [atm]
1,2
1,15
1,1
1,05
1,
0,95
0,9
0:00:00
0:01:26
0:02:53
0:04:19
0:05:46
0:07:12
0:08:38
0:10:05
0:11:31
0:12:58

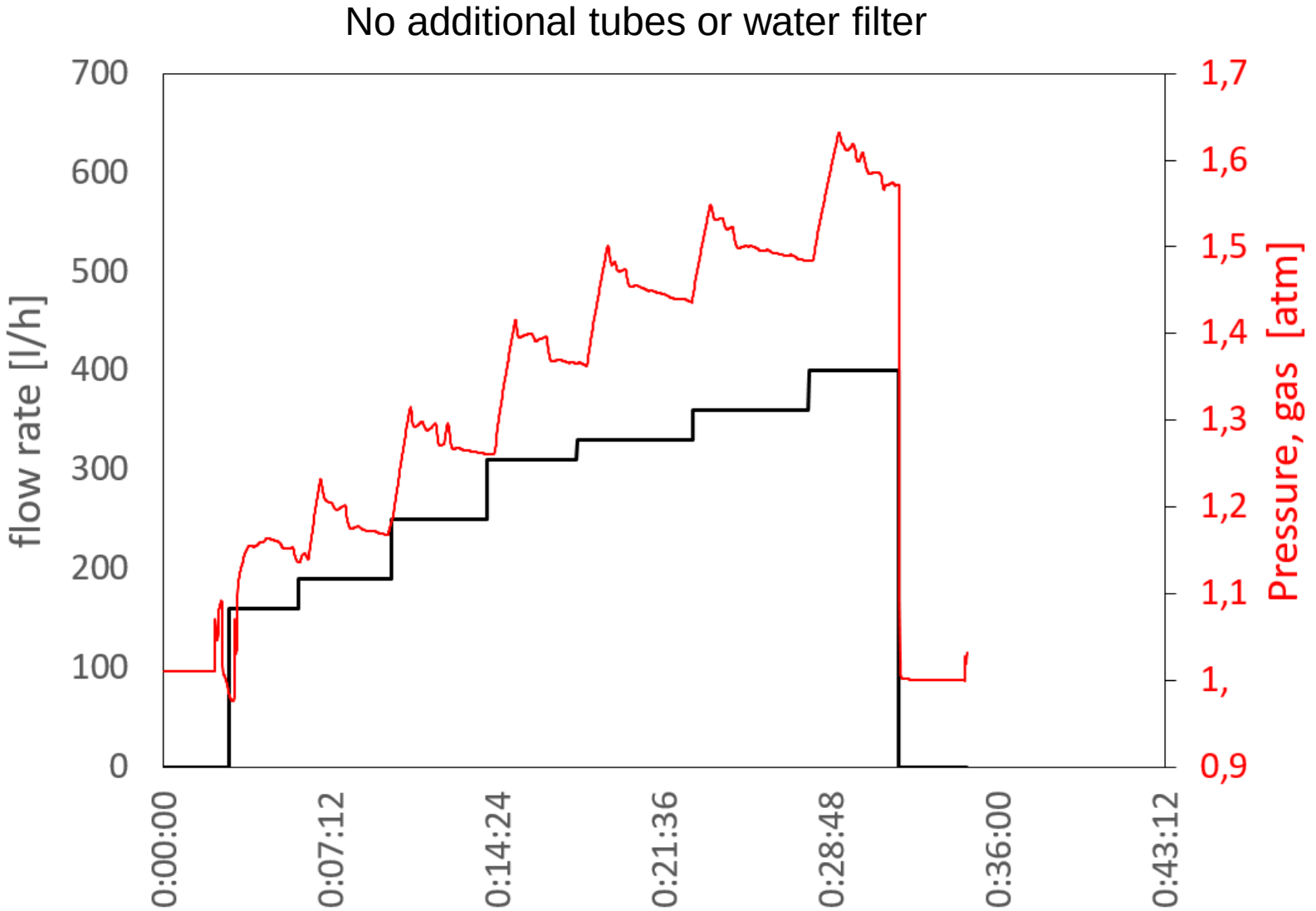
Field tests


miniRUEDI test M6


5m tubing, no water filter
flow rate [l/h]
800
700
600
500
400
300
200
100
0
0:00
0:07
0:14
0:21
0:28
0:36
0:43
0:50
1,35
1,3
1,25
1,2
1,15
1,1
1,05
1,
0,95
0,9
Pressure, gas [atm]

Field tests

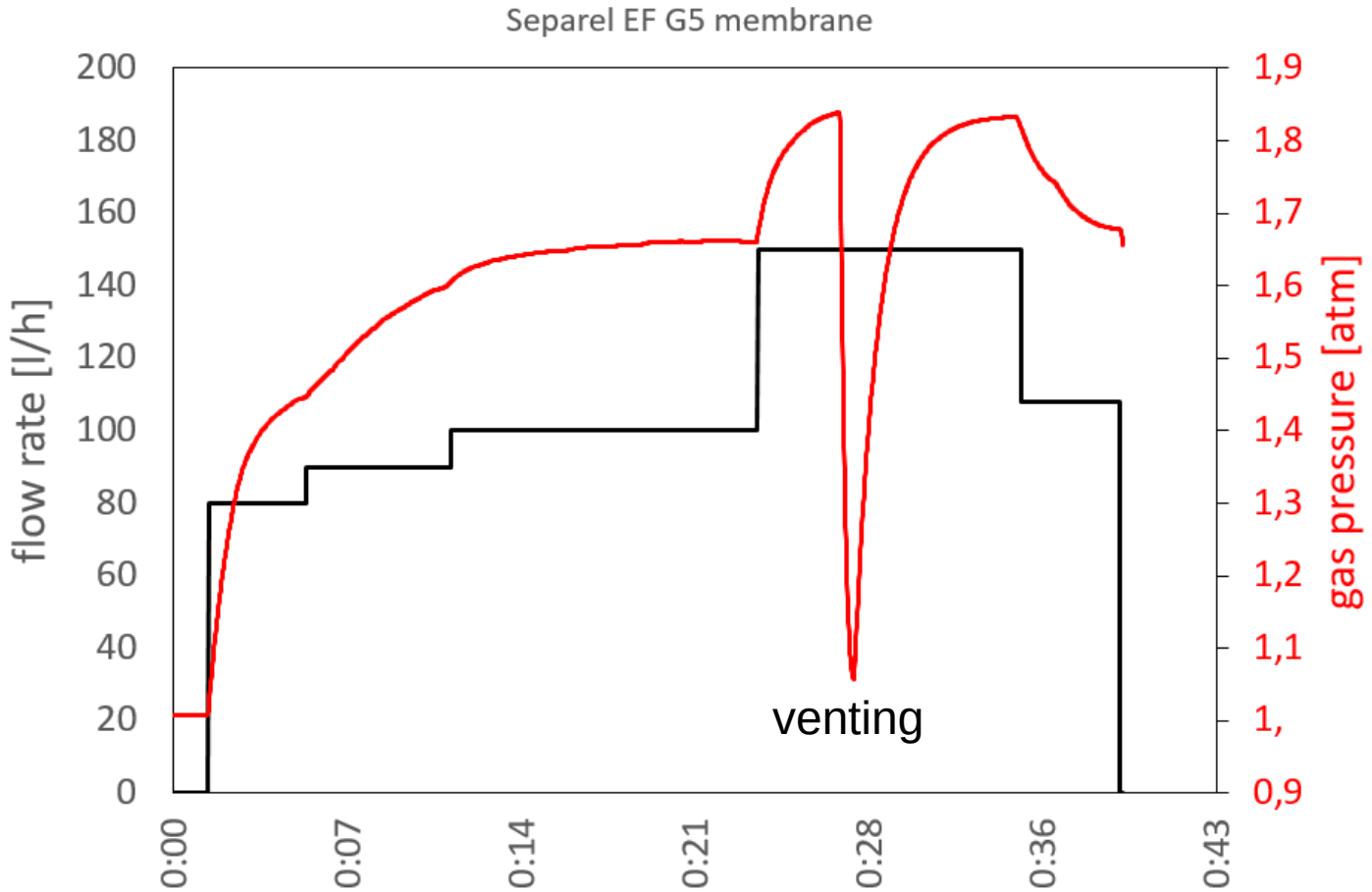

miniRUEDI test M7


No additional tubes or water filter
flow rate [l/h]
Pressure, gas [atm]
700
600
500
400
300
200
100
0
1,7
1,6
1,5
1,4
1,3
1,2
1,1
1,
0,9
0:00:00
0:07:12
0:14:24
0:21:36
0:28:48
0:36:00
0:43:12

External flow modul

- Water flow: **shell side** (outside hollow fibers)
- max. applied flowrate 150 l/h
- **TDGP measurement**

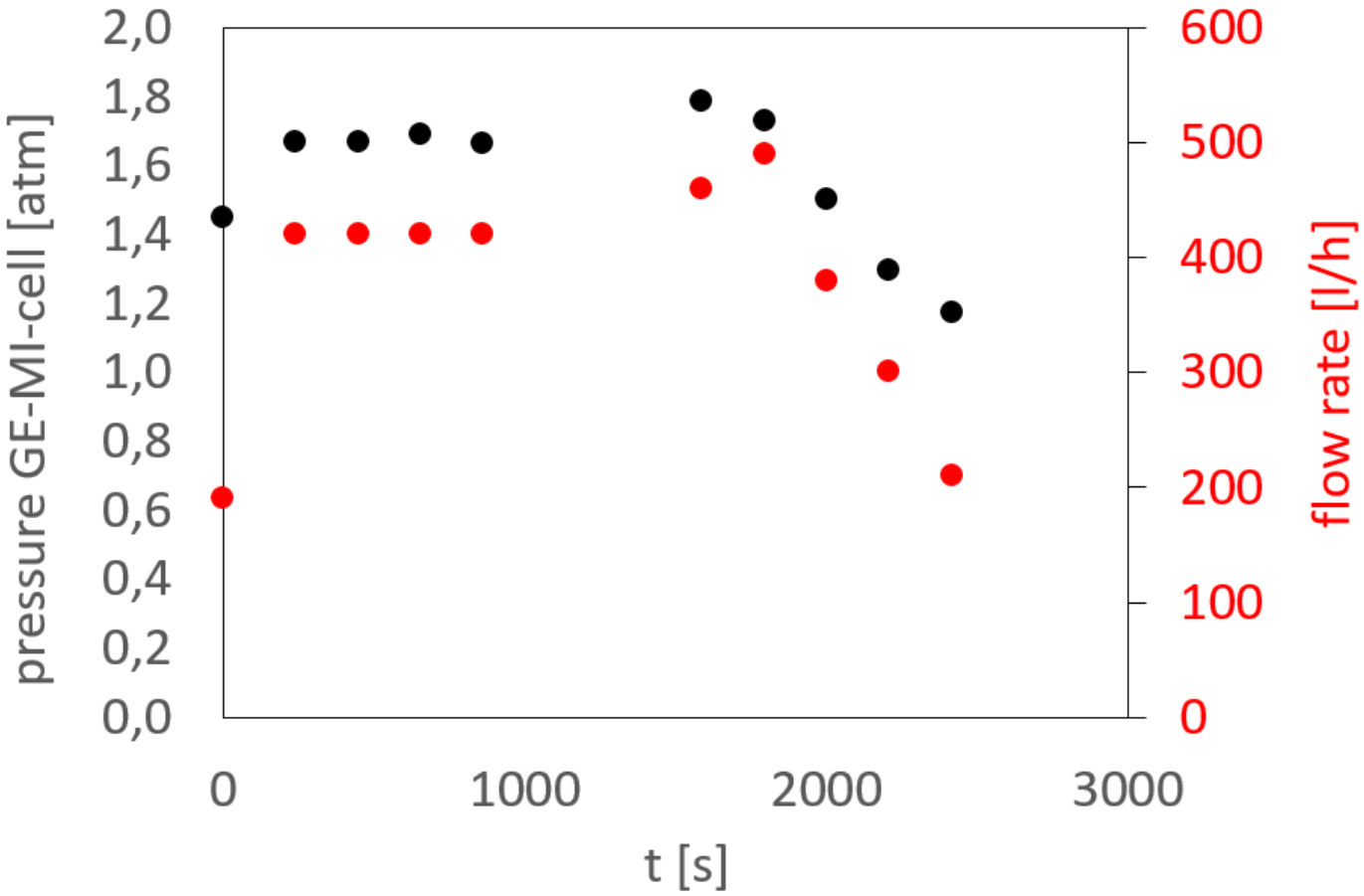
→ **Independent pressure check for miniRUEDI**



miniRUEDI final test

- miniRUEDI GE-MI-module flow rates **400 - 500 l/h**
- no water filter, membrane module directly connected to well head
- **constant pressure and flow rate**
- **clogging** of the membrane module starts after approx. 30 min

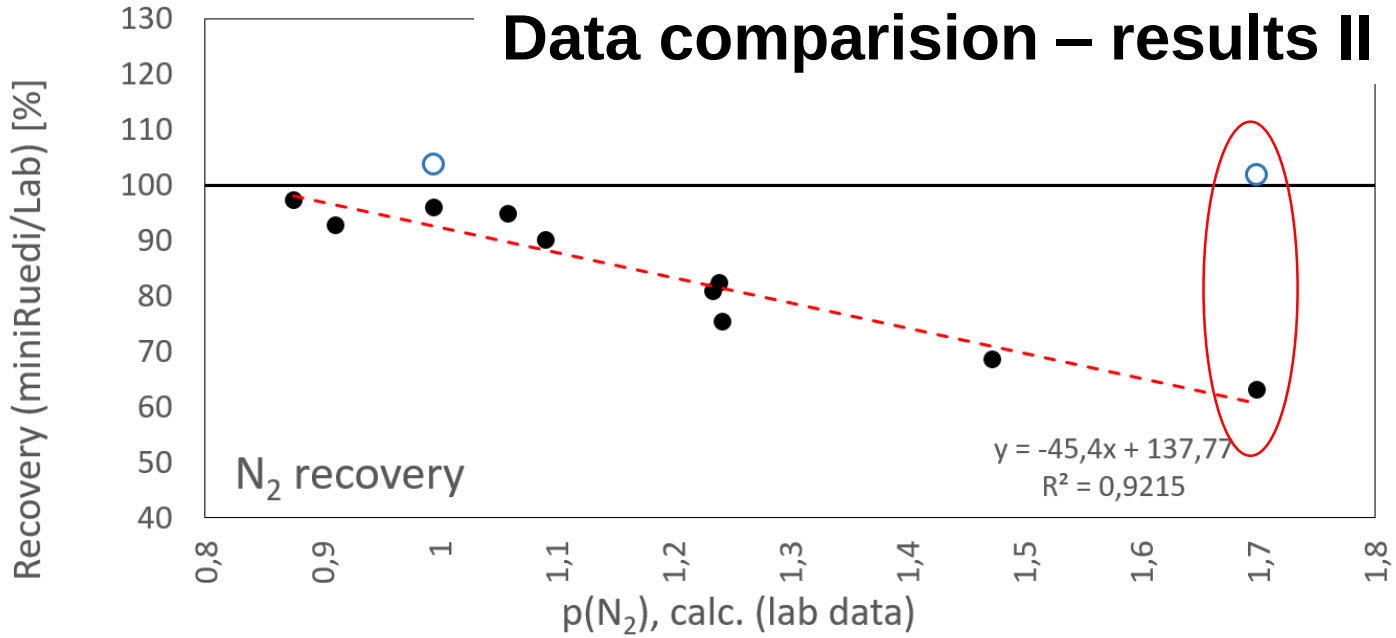
→ **rapid loss of pressure/flow rate** at constant pump frequency

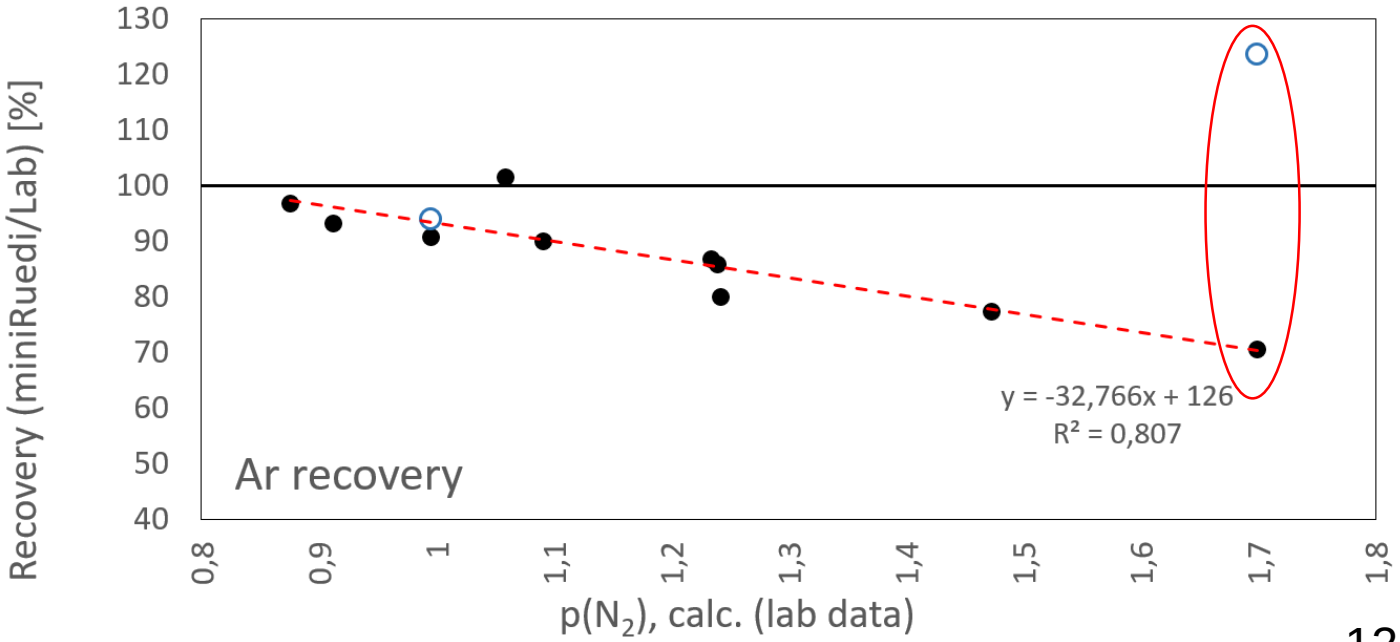


miniRUEDI final test

- **Gas loss compensated by:**
  - High flow rate (400-500 l/h)
  - short tubing
  - removal of water filter
- **Drawbacks:**
  - Leakage
  - Clogging
  - p_{max} probably < 2 atm

Data comparision – results II





Conclusions

- Degassing ist not always obvious → Check the gas pressure at various flow rates
- Use a second independent module for TDGP measurements
- Degassing can be compensated with higher flowrates (TDGP < 2 atm → limit for this setup)

Outlook

- Test other filter systems/membranes for the miniRUEDI setup (e.g. external flow [less clogging? Sufficient gas phase volume?])
- Add restriction at water outlet and monitor water pressure
- Sampling other sites for further data comparision

Thank you!