Geochemical effects of hydrogen intrusions into shallow groundwater

– an incidence scenario from Underground Gas Storage

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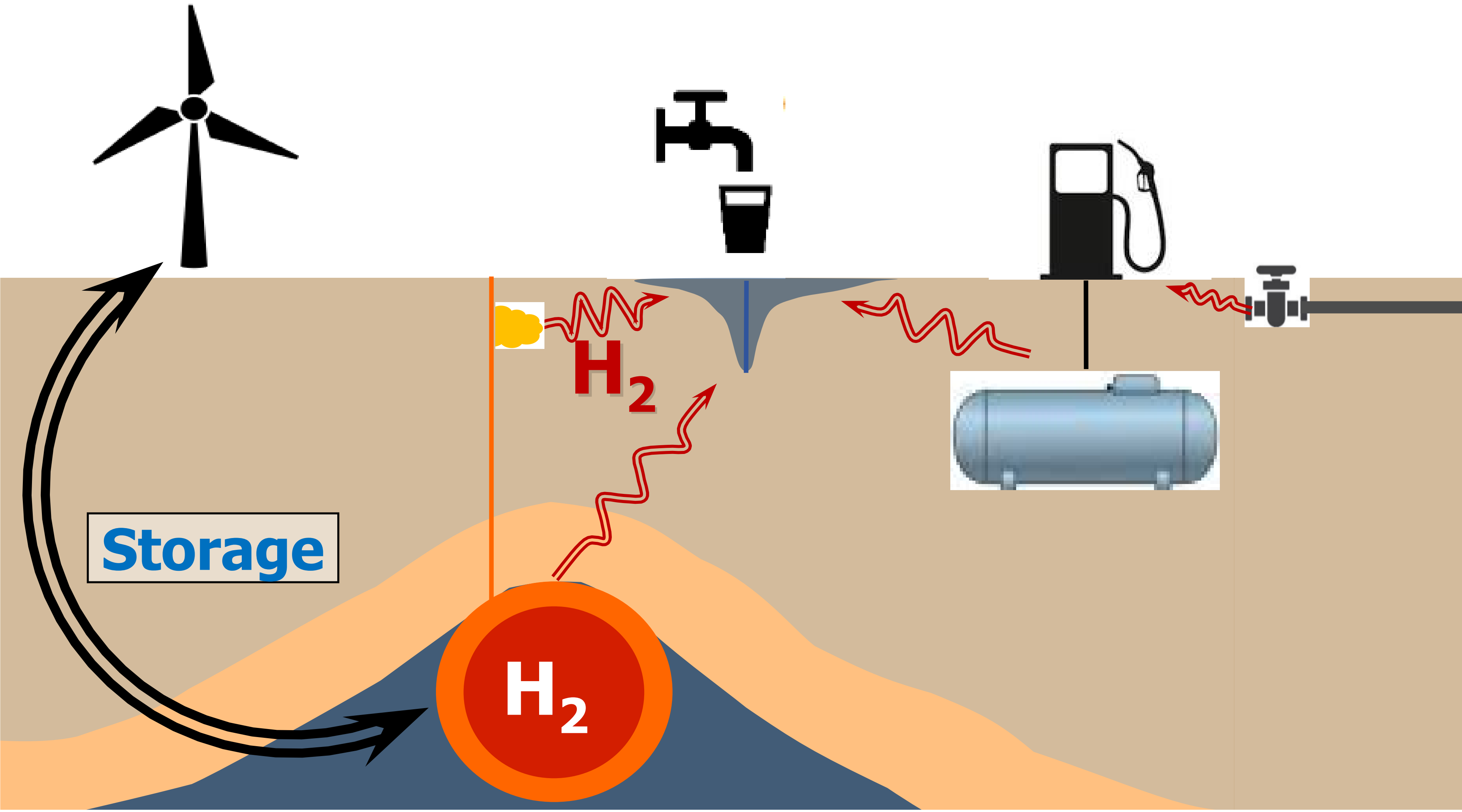
Underground Hydrogen Storage (UHS)



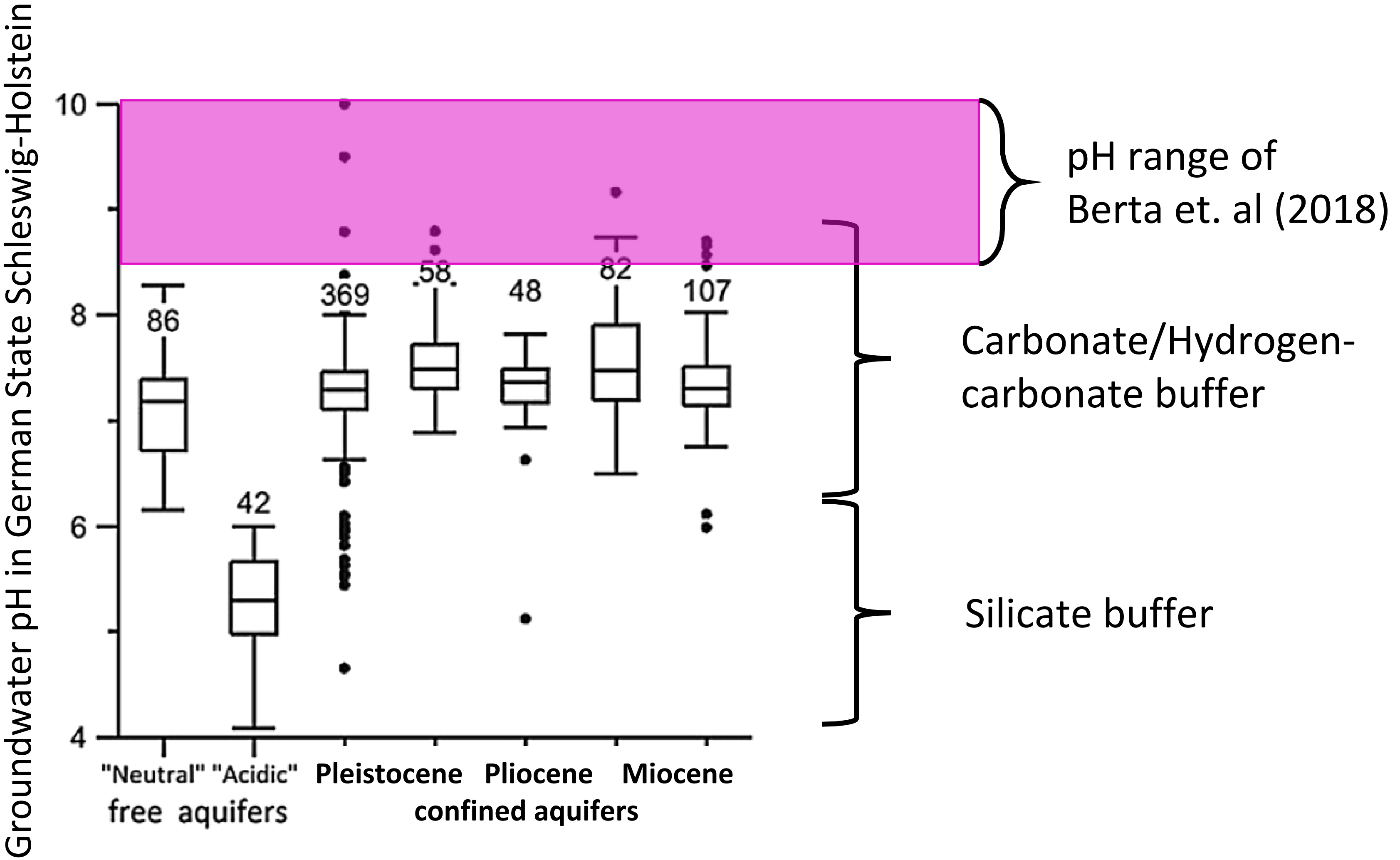
Berta et al. (2018):

previous exp. study on hydrogen intrusions into aquifer:

- flow though column with natural sediment and groundwater
- pH range slightly alkaline (8.5-10)
  (due to CO_2 degassing in experimental setup)
- 8 months of experimental runtime

- rapid and simultaneous H_2 oxidation with
  - reduction of DIC (CO_3^{2-} and HCO_3^-), NO_3^-, Fe^{III} and SO_4^{2-}
  - release of i.e. acetate (CH_3COO^-), NH_4^+, Fe^{2+} and HS^-
    - influence on groundwater quality possible

Typical pH ranges in Schleswig-Holstein aquifers



Modified after Dethlefsen et al. (2017)

Deduction of study aims

Known influence of pH on:

- precipitation / dissolution processes
- sorption / desorption processes

governing i.e. concentrations of **dissolved nutrients and trace elements**

- **microbial consortium** → **influence on bio-geochemical reactions**

➢ pH influence on reactions with mM hydrogen concentrations not investigated yet

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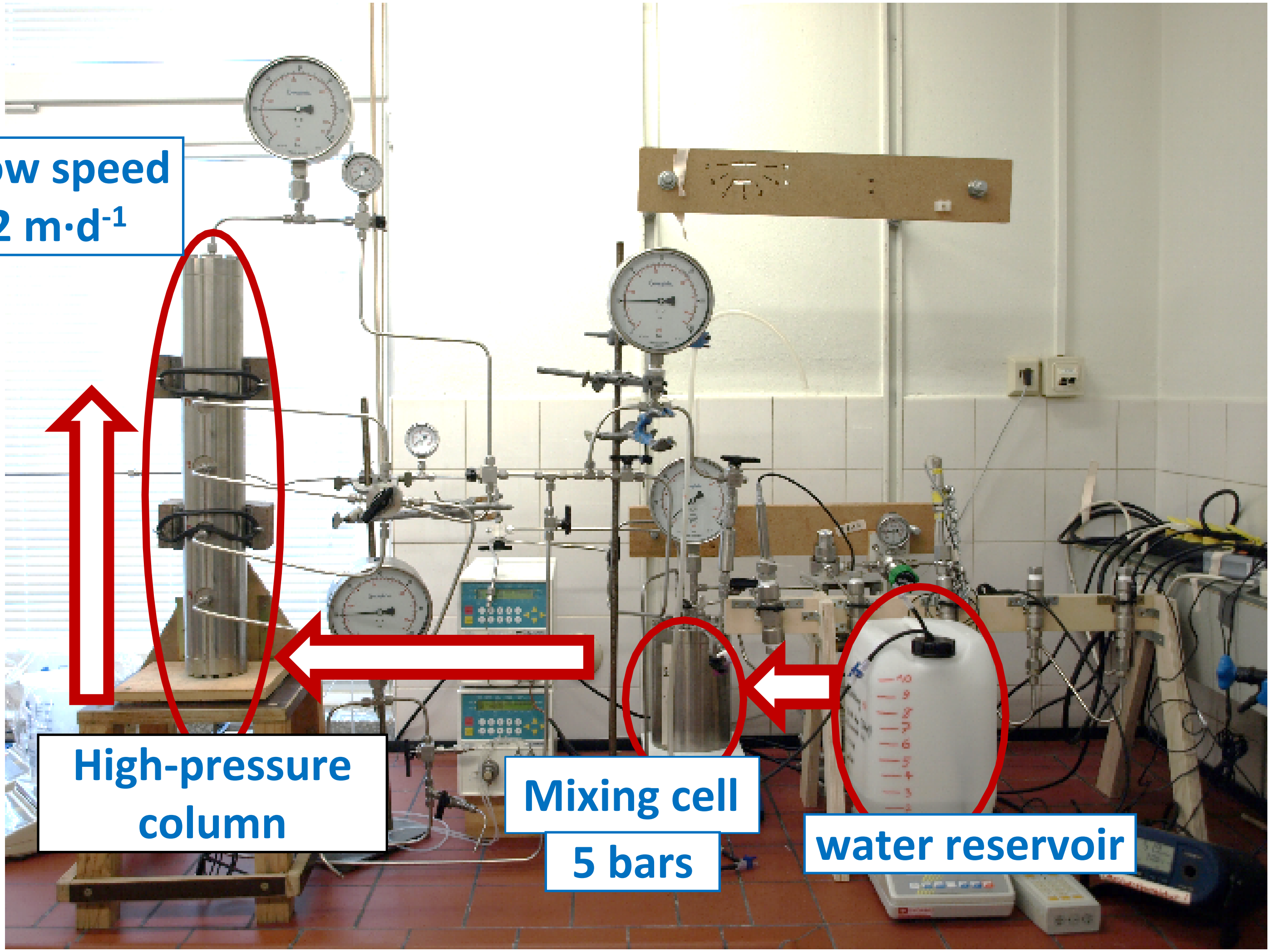
1. Does changing the **pH range to neutral** (6.9-7.7) and **slightly acidic** (5.5-6.2) change the reactions as a consequence of hydrogen intrusion into groundwater?

2. Are there any developments which can be observed during **long-term operation** of the experiment?

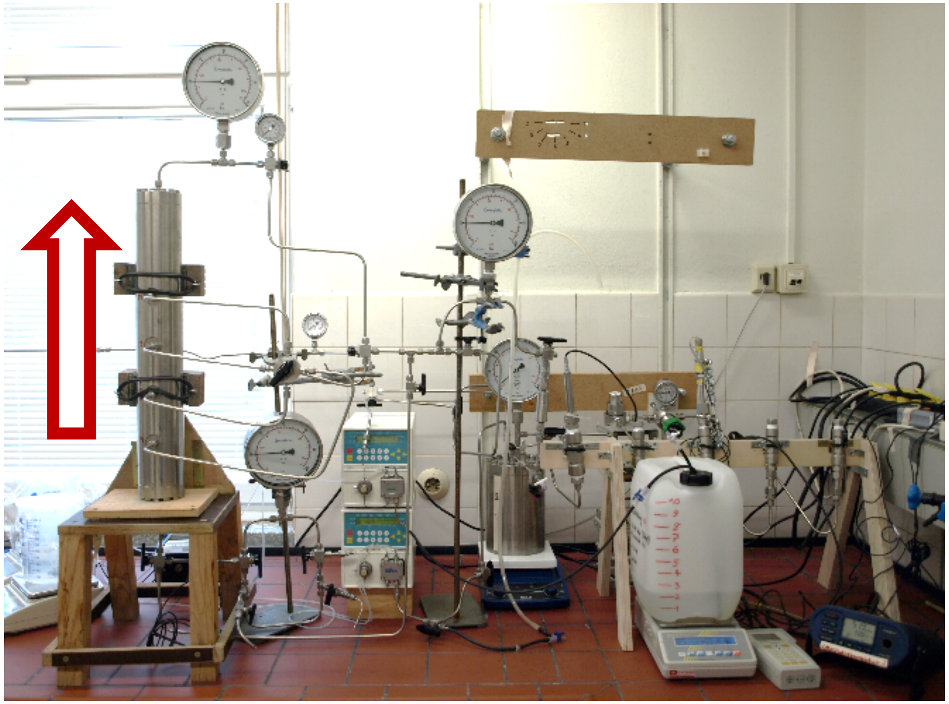
Long-term laboratory column experiment



Further information in Berta et al. (2018)

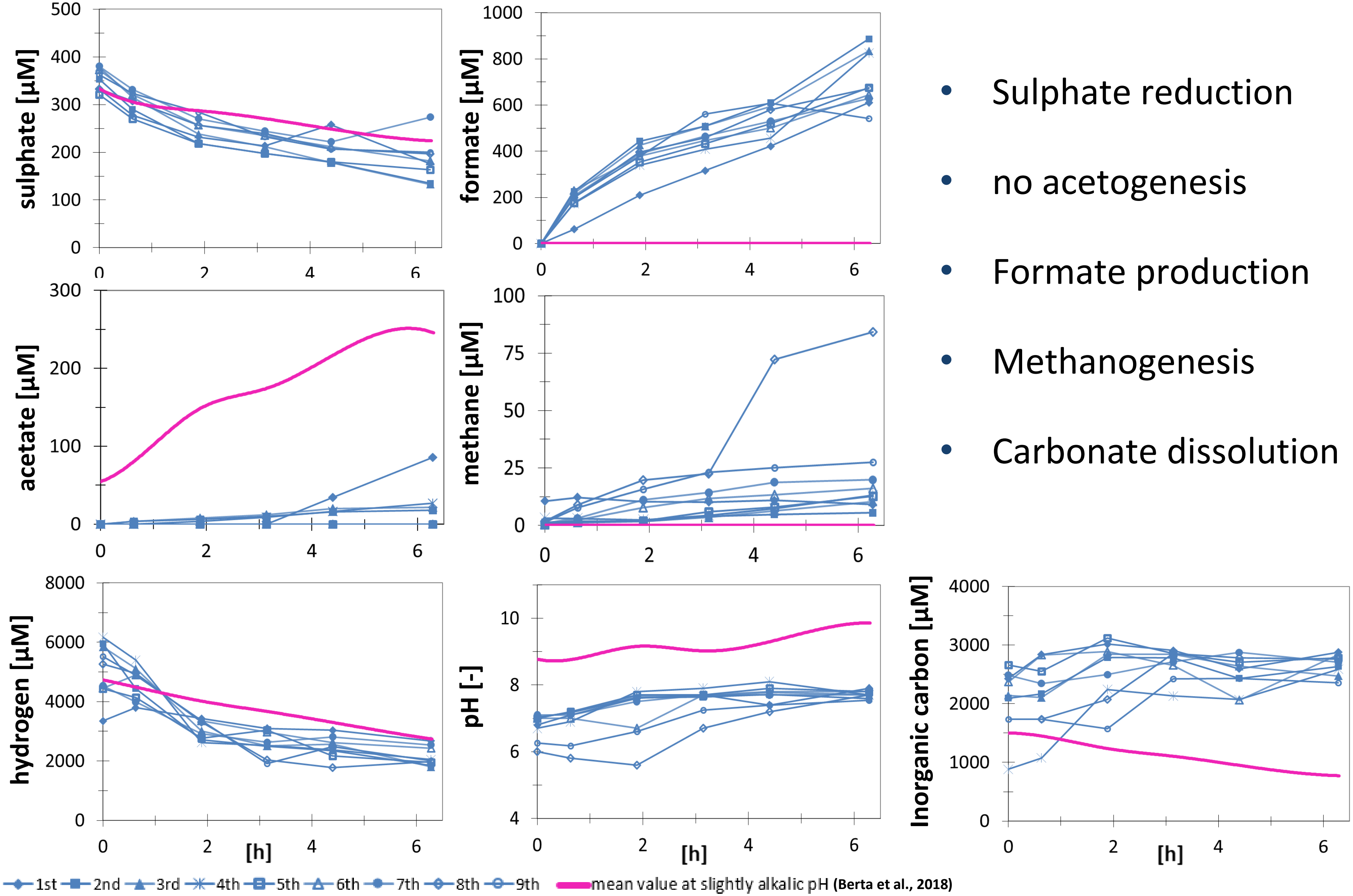
Long-term laboratory column experiment

- Sediment and water from pleistocene aquifer (4-12 m mbgs)
- So far 8 months of runtime at slightly alkaline pH conditions (Berta et al., 2018)



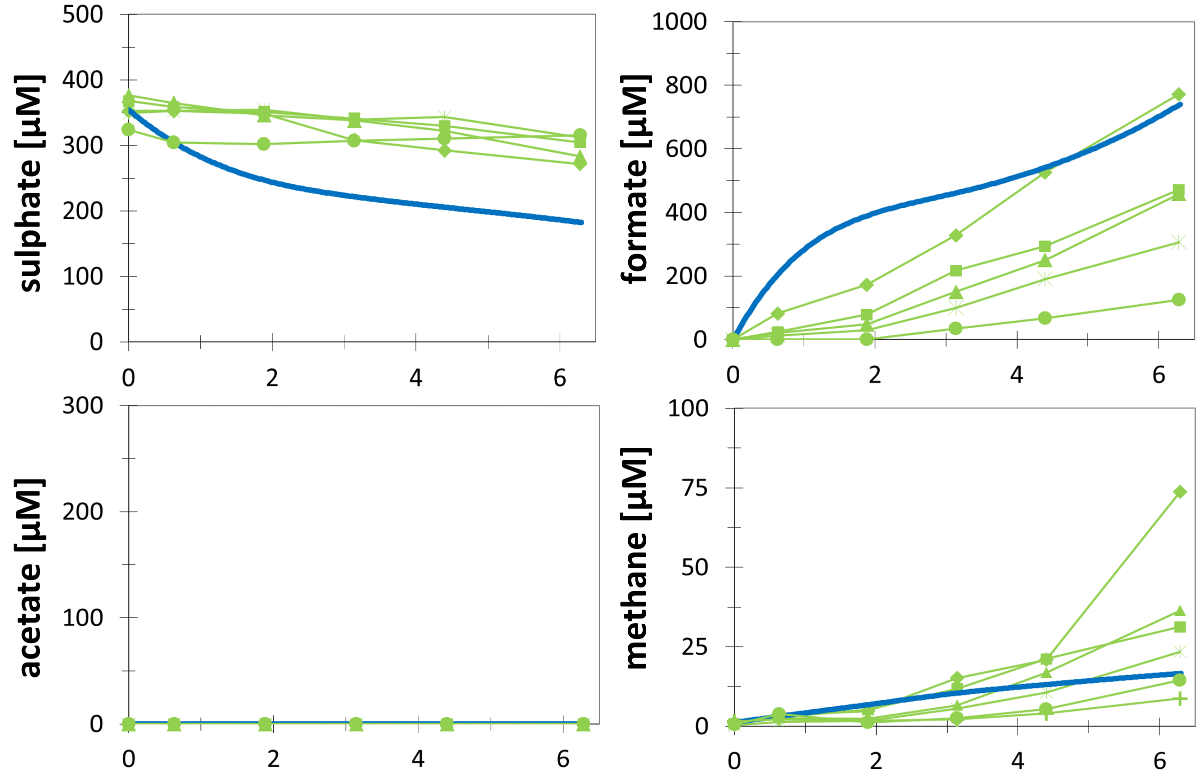
composition of inflow solution	µmol/l
Hydrogen	4950
Nitrate	2.05
Sulphate	**337**
Calcium	**1310**
Iron	1.11
Manganese	0.59
Inorganic Carbon	**2230**

Results at circumneutral pH conditions (pH 6.9 – 7.7)

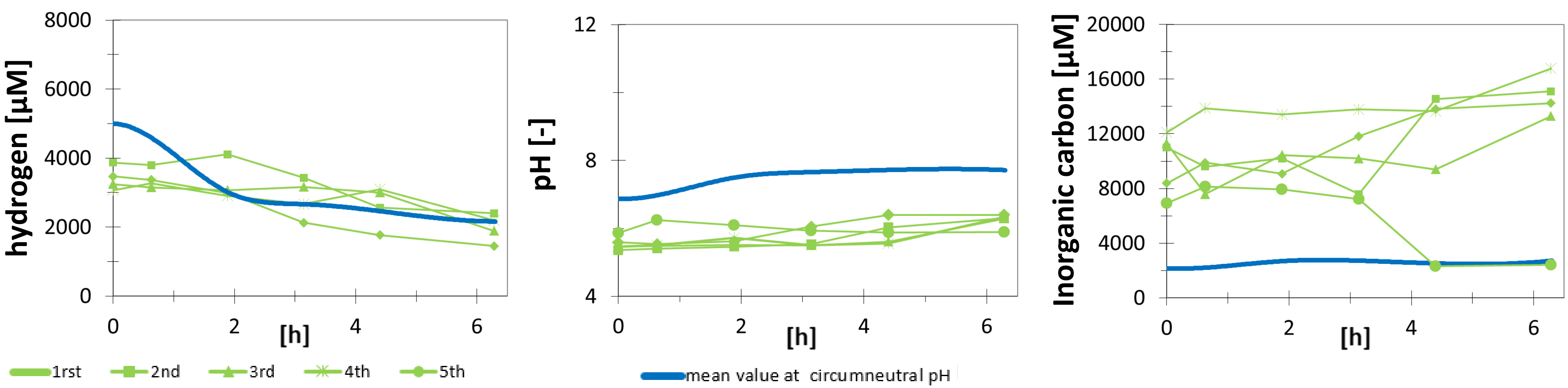


- Sulphate reduction
- no acetogenesis
- Formate production
- Methanogenesis
- Carbonate dissolution

Results at slightly acidic pH conditions (pH 5.5 – 6.2)



- **Progressively decreasing** reaction rates
- At this point: **23 months** of experimental **runtime**



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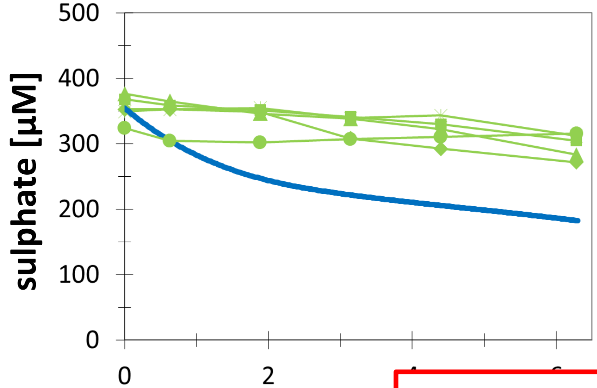
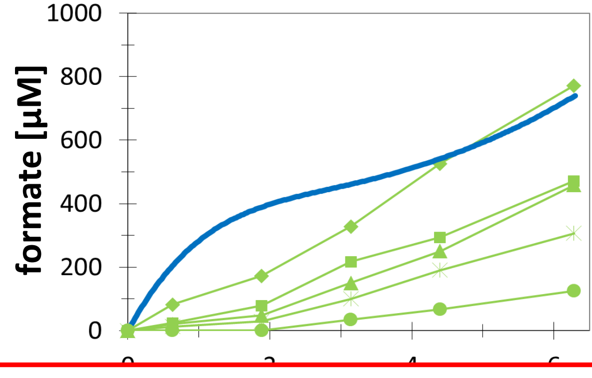
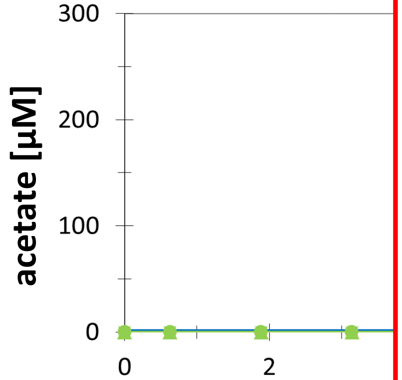


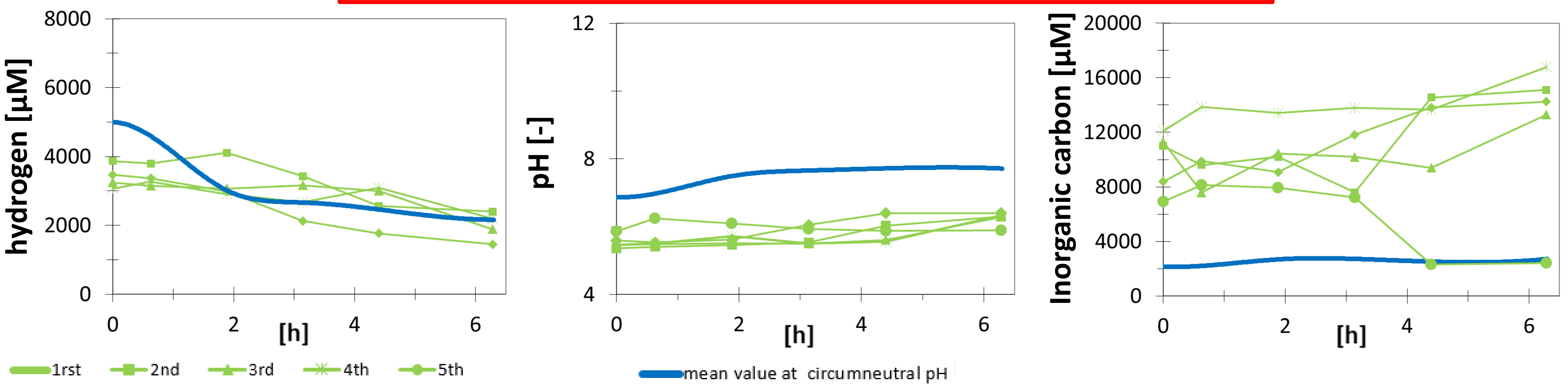




- **Progressively** ...**easing** reaction ...s

After 31 months:

- returning to neutral pH
- reactions did not re-establish



Supplementary phase

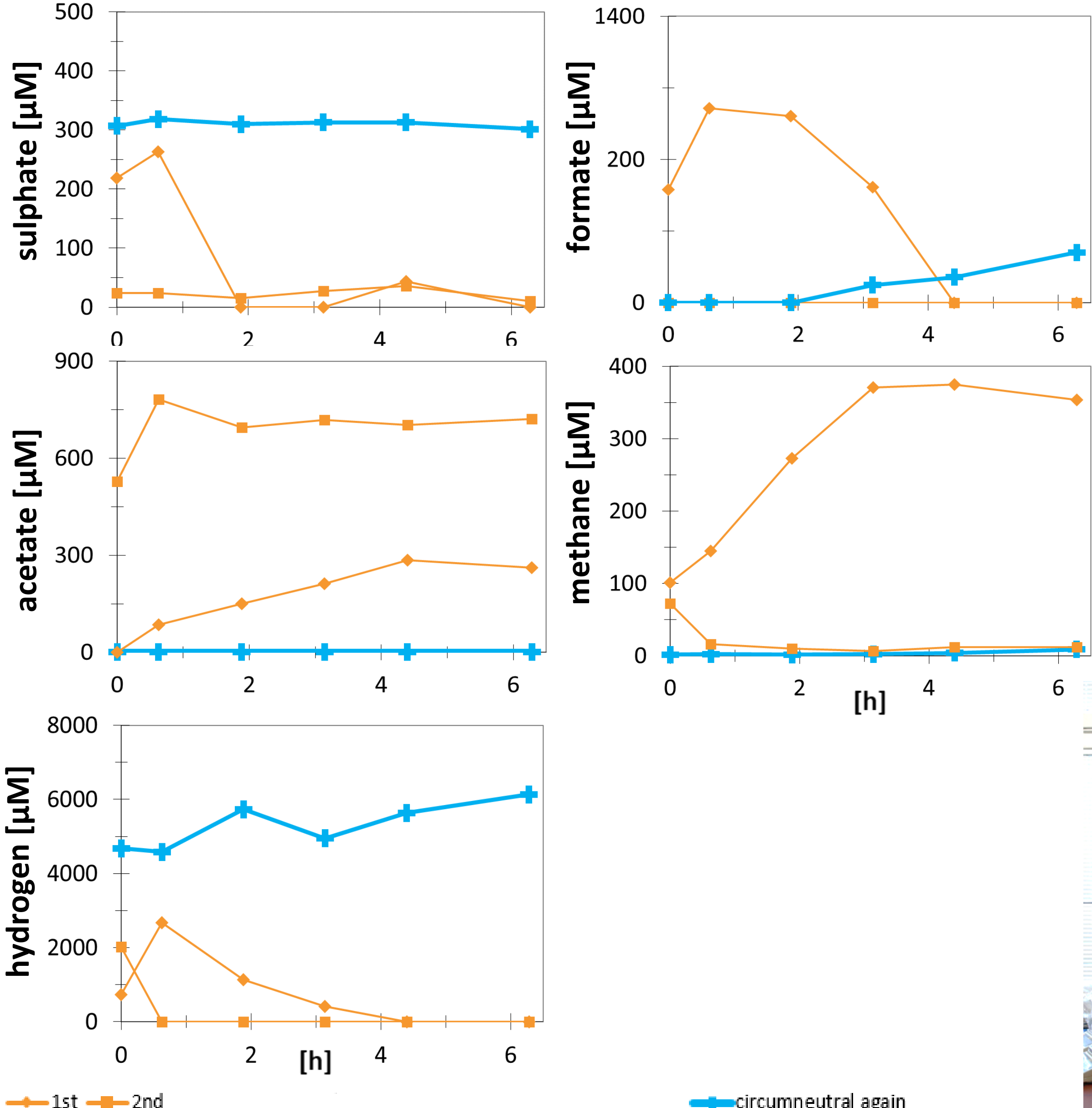
- **New assumption:**
  - long experimental runtime (**33 months now**)
  - appearing lack of nutrients and trace elements
  - increasingly limited microbial activity

➢ Reenhancing microbial activity by supply of:
- NH_4^+ 9.34 mM
- PO_4^{3-} 3.67 mM
- trace element solution 10 (DSM, 2017)

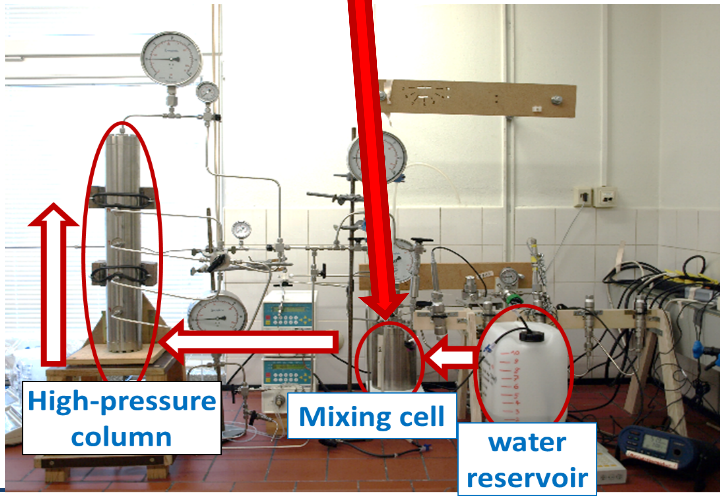
trace elements in trace element solution 10	*nmol/l*
iron	521
manganese	24.6
zinc	34.6
cobalt	1.70
molybdenum	19.8
nickel	0.44
boron	2.49
copper	5.90

in cooperation with the Centre for Environmental Research UFZ Leipzig (M. Löffler, C. Vogt, HH. Richnow)

Results: Supplementary phase



- reestablished microbial activity
  - indicative for previous limitation
- reactions mainly upstream the column in the mixing cell



Implications for short-term intrusions

Observed **reactions** in context of H_2 oxidation:

- **rapid** and **simultaneous** (no redox zonation)
- with **differing IC reaction products** in different pH – regimes
  - slightly alkaline pH → acetate
  - circumneutral pH → formate and methane

Expectations for natural groundwater environments:

- **relatively short H_2 plumes**
- **H_2S** produced during sulphate reduction

Suggestion for monitoring:

- focus on **anion screening** (sulphate, organic acids)

Implications for long-term intrusions

Concerning long-term hydrogen intrusions:

- limited nutrient and trace element availability in groundwater environments
  - can lead to ceasing microbially catalysed reactions
- slightly acidic pH may intensify limitation

Consequences for natural groundwater environments:

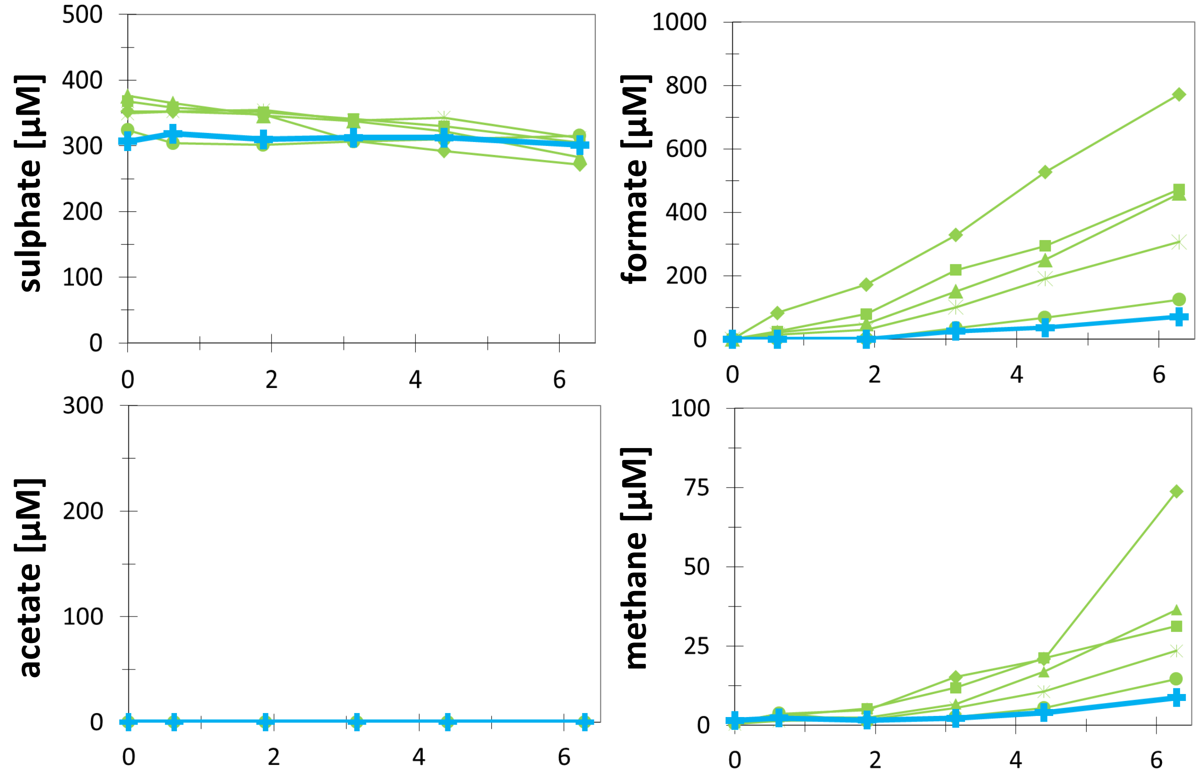
- limited attenuation potential → prolonged H_2 plumes

Possible intervention measures:

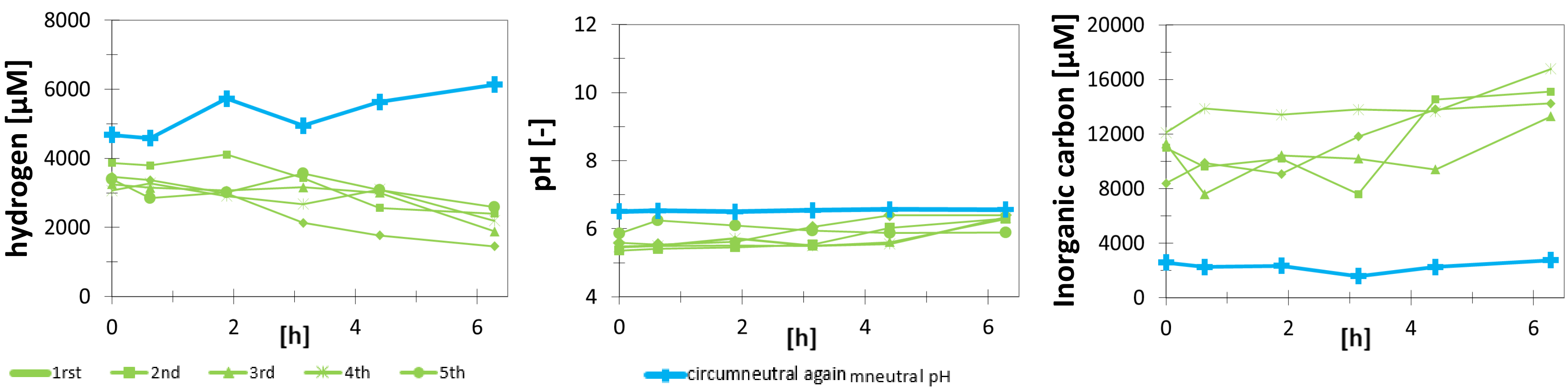
- supplementation of nutrient solution
  - ➢ stimulates microbial activity

Thank you for your attention

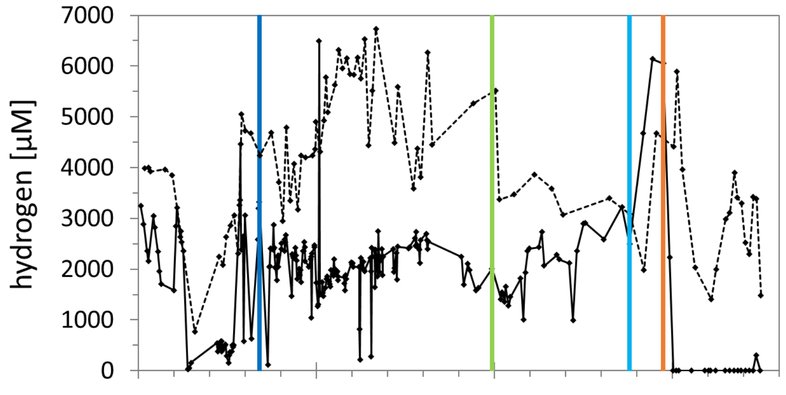
Returning to circumneutral pH conditions

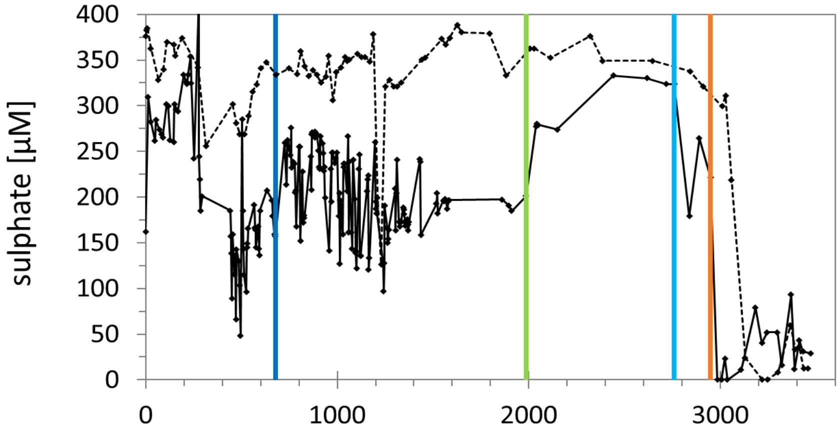


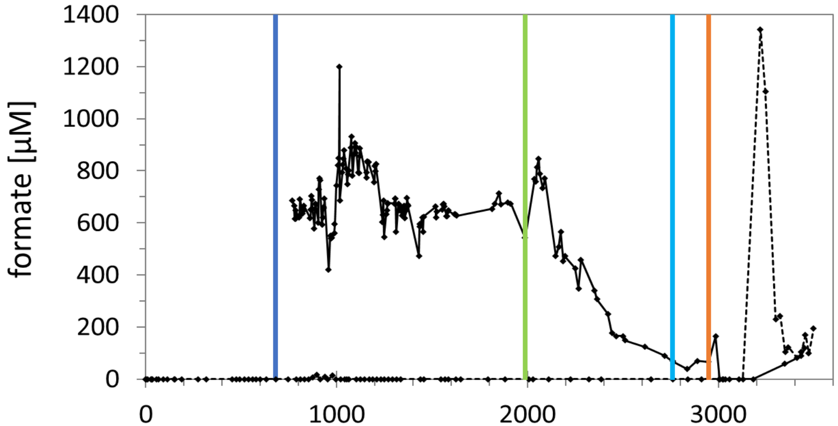
- 58 days of pH-neutral conditions
  - ➢No recovery of microbial activity

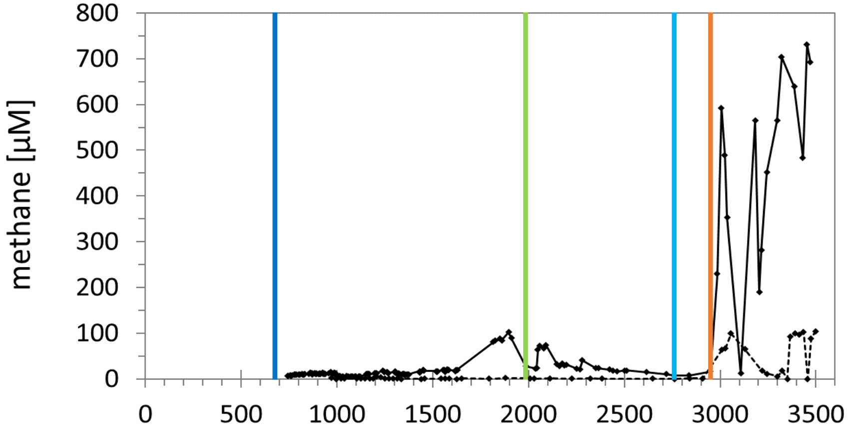


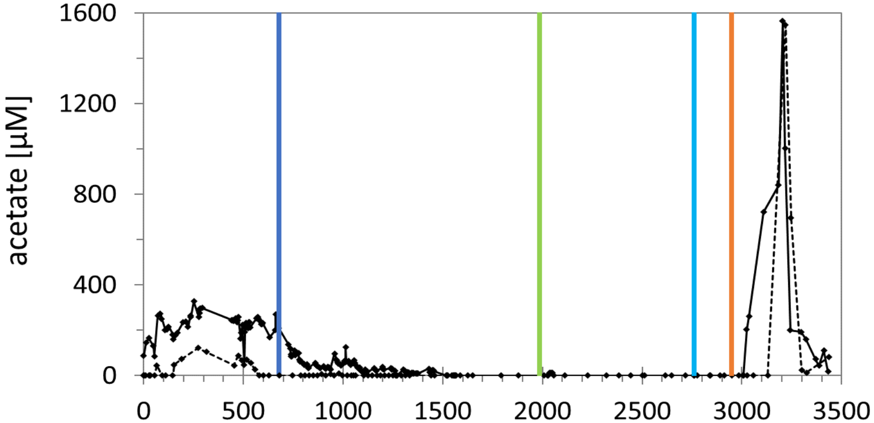
Implications



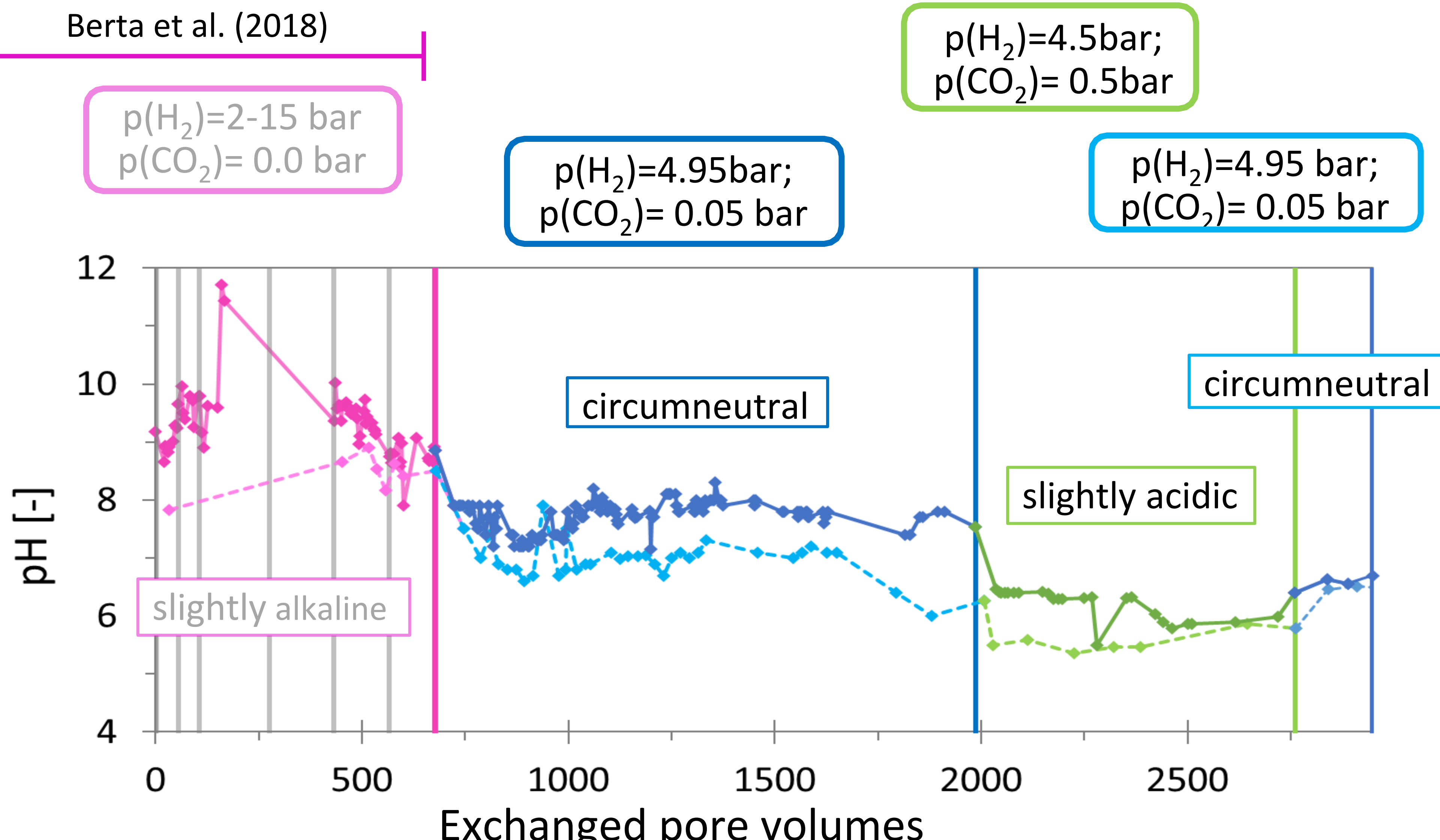








Experimental phases



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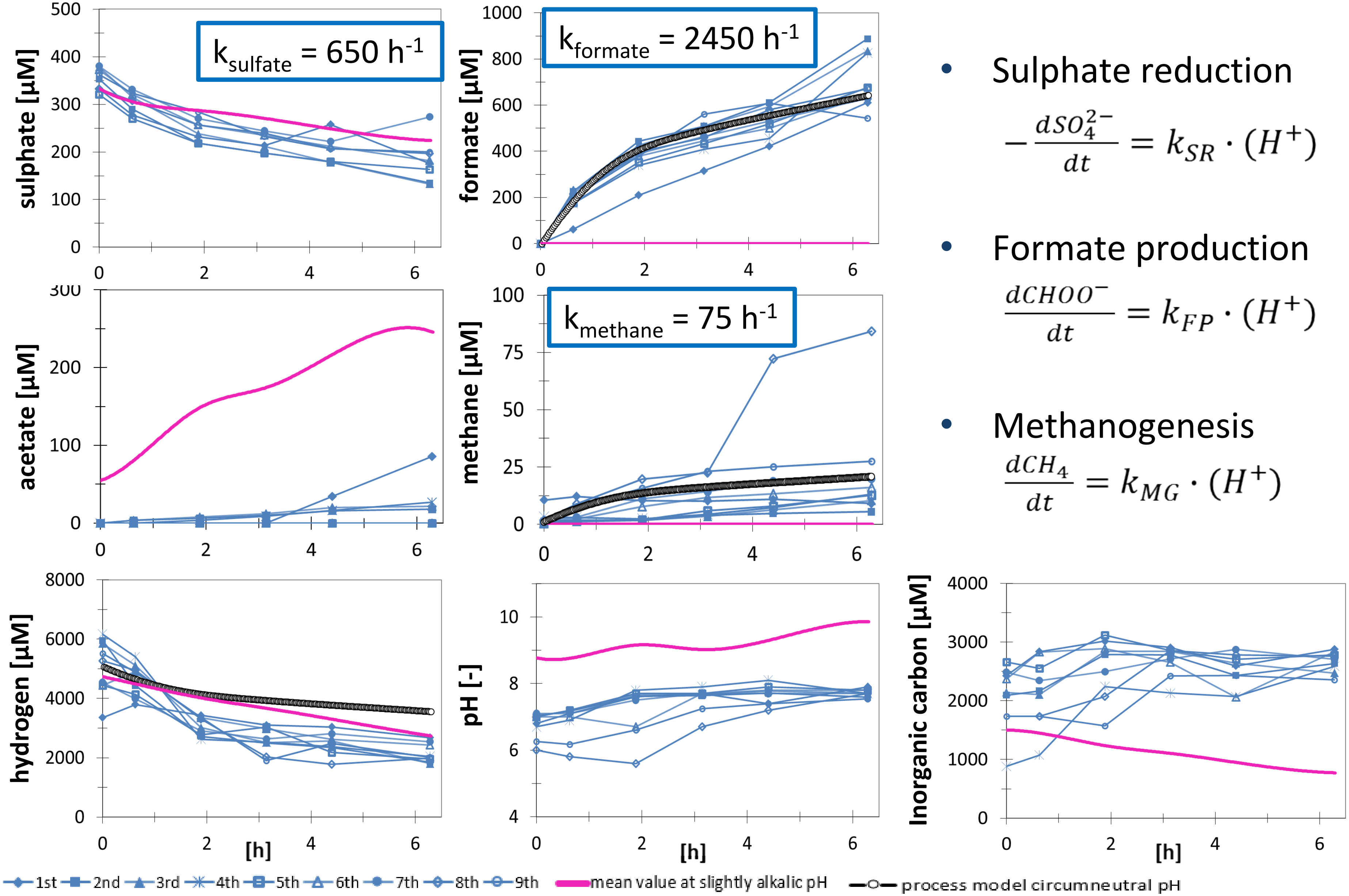

- Sulphate reduction

$$-\frac{dSO_4^{2-}}{dt} = k_{SR} \cdot (H^+)$$

- Formate production

$$\frac{dCHOO^-}{dt} = k_{FP} \cdot (H^+)$$

- Methanogenesis

$$\frac{dCH_4}{dt} = k_{MG} \cdot (H^+)$$

Summary

	slightly alkaline	circum neutral	slightly acidic	supplementary
acetogenesis	1. Order respect to TIC ($0.03\ h^{-1}$)	↓		↑
sulphate reduction	0. Order ($18\ \mu Mh^{-1}$)	1. Order respect to $a(H^+)$ ($650\ h^{-1}$)	↓	↑
formate production		1. Order respect to $a(H^+)$ ($2450\ h^{-1}$)	↓	
Methano-genesis		1. Order respect to $a(H^+)$ ($75\ h^{-1}$)	↓	↑