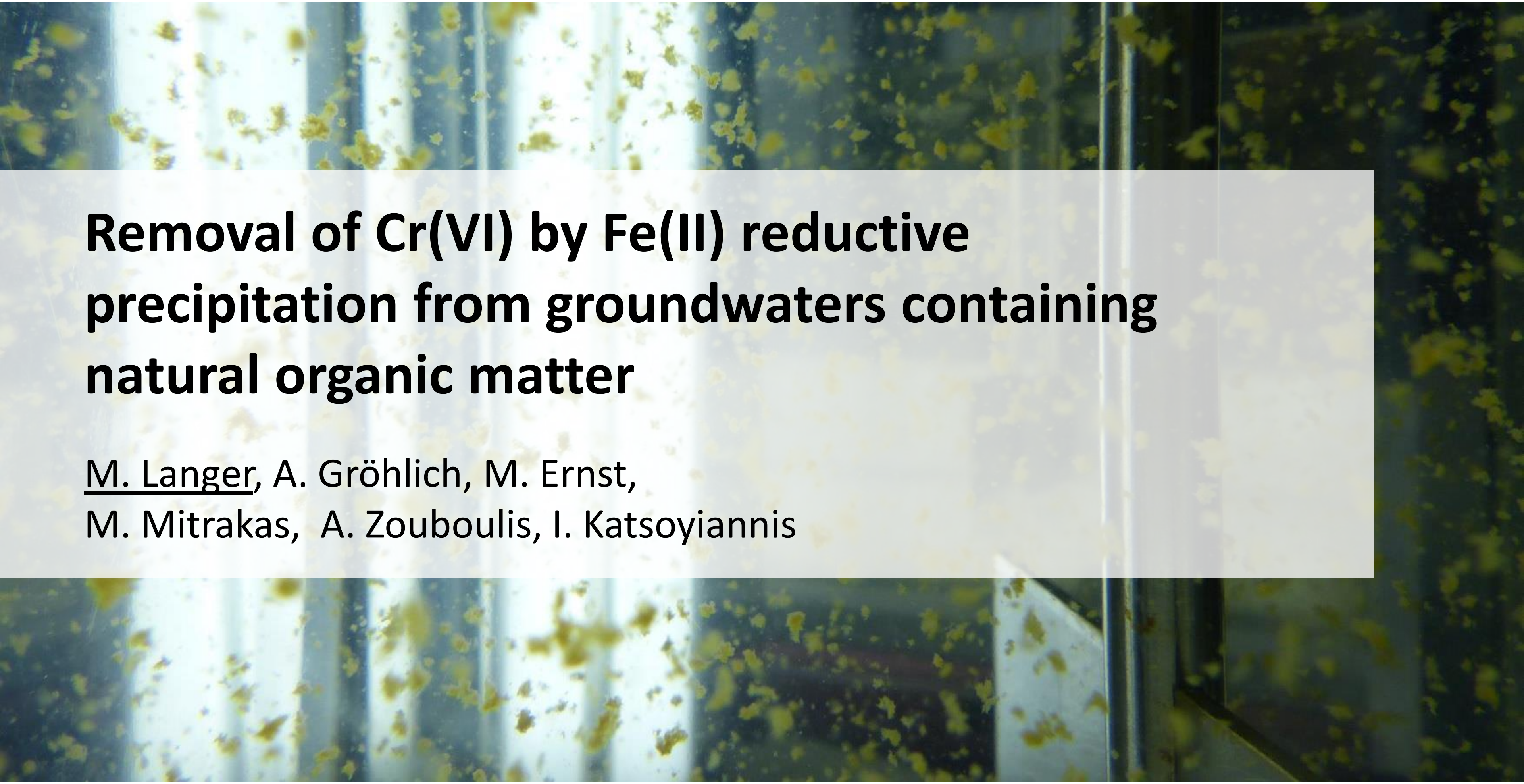
Institute for
WATER RESOURCES
AND WATER SUPPLY

TUHH
Technische Universität Hamburg-Harburg



Removal of Cr(VI) by Fe(II) reductive precipitation from groundwaters containing natural organic matter

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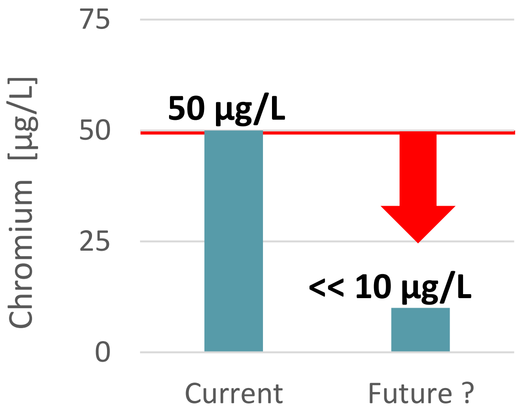
Chromate in drinking water

- Worldwide people suffer from groundwater contaminated with chromium
- Sources: Broad application in industry and erosion of natural ophiolitic or ultramafic rocks
- Predominant redox species are Cr(VI) and Cr(III)
- Recent studies reclassified Cr(VI) as toxic, carcinogenic and mutagenic

→ Current discussion about reducing the acceptable limits in in drinking water



Chromium removal

- Reduction through Fe(II):

$$Cr(VI) + 3\ Fe(II) \rightarrow Cr(III) + 3\ Fe(III)$$

[Cr(VI)]:[Fe(II)] = 1:3

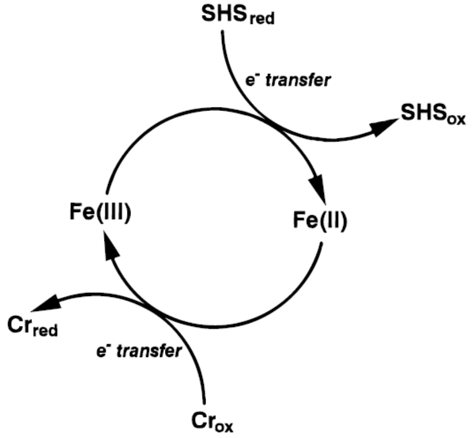
- Resulting Cr(III) has low solubility:
  Precipitates as Cr(III) hydroxide, adsorbs onto or co-precipitates with iron hydroxides
- Removal of produced solids e.g. by filtration
- Known to be influenced by:
  - pH value
  - Fe(II)/ Cr(VI) ratio
  - Temperature
  - Water composition

(Mitrakas et al. 2011)

→ Fe(II) reductive precipitation widely used, but so far, role of natural organic matter rarely investigated

Natural organic matter in water

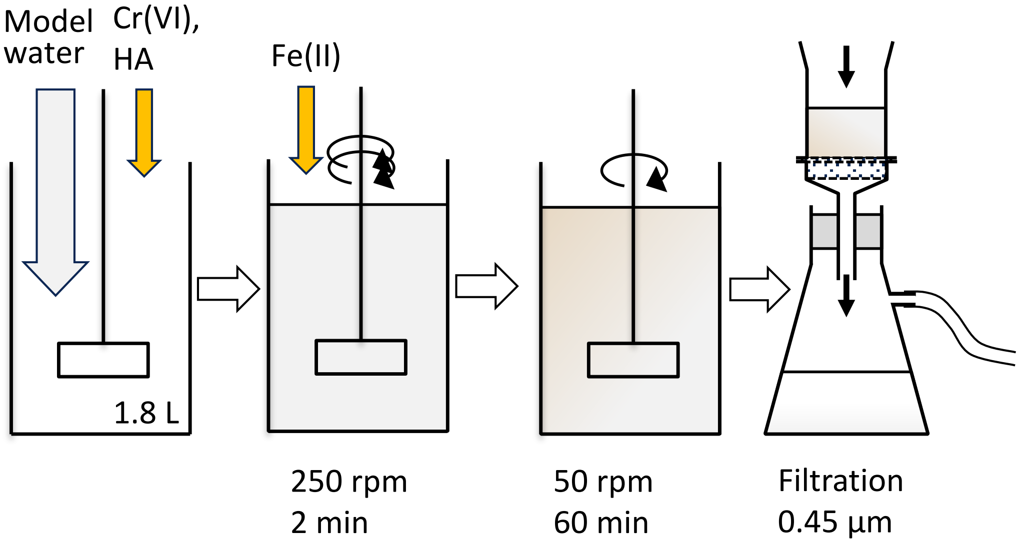
- Commonly found in natural waters and soils
- Wide variety of substances (e.g. lignin, polysaccharides, lipids); Most important humic and fulvic acids
- **Influence on chromium removal:**
    - Formation of soluble complexes of Fe(III), Cr(III) and humic substances (Buerge, Hug 1998)
    - Catalyzing/Accelerating effect on Fe(II) reductive precipitation at pH<6 (Hori et al. 2015)
    - Dependent on the type of organic substances



Redox cycling of ferrous and ferric iron in the presence of soil humic acids (SHS) (Wittbrodt, Palmer 1996)

Materials and Methods

- Model groundwater spiked with Cr(VI) and humic acid (Carl Roth)
- Procedure and conditions:

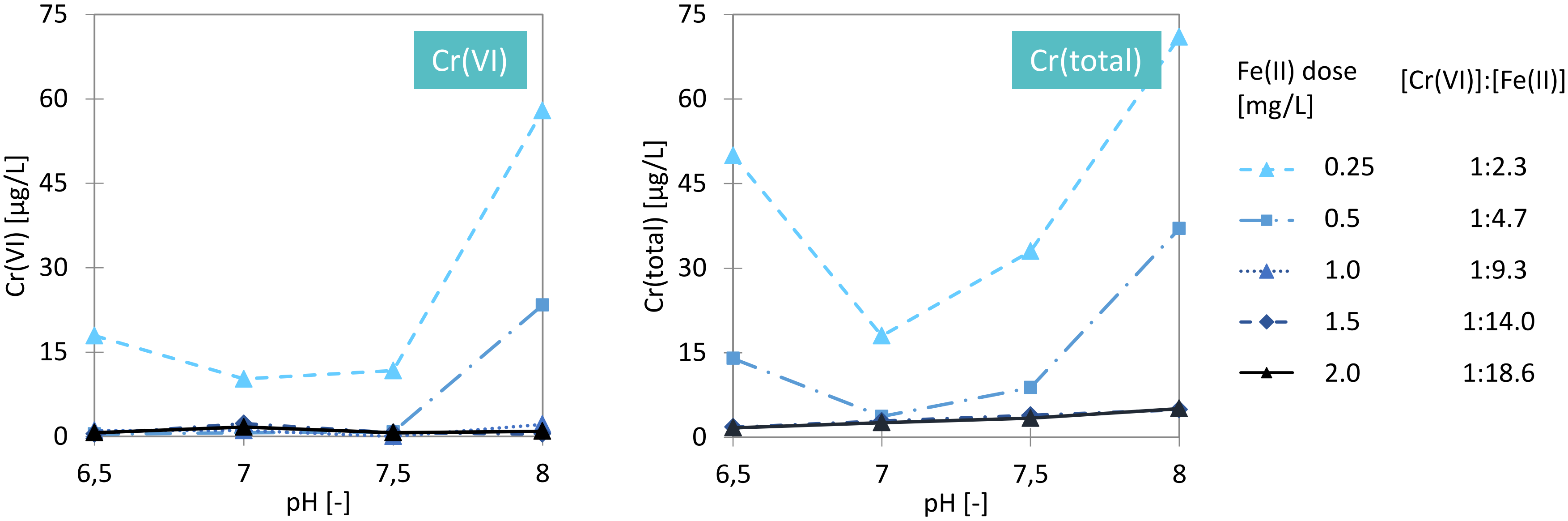


Cr(VI):	100 µg/L
Humic acid:	0-5 mg/L DOC
pH:	6.5 - 8.0
$FeSO_3$ dose:	0.25 - 2.0 mg/L Fe(II)
[Cr(VI)]:[Fe(II)]	*1:2.3 - 1:18.6*

at TUHH and AUTh

- Analytics:
    - Cr(VI) photometric with DPC complexation (100mm cuvette)
    - Cr(total) ICP-MS or GFAAS

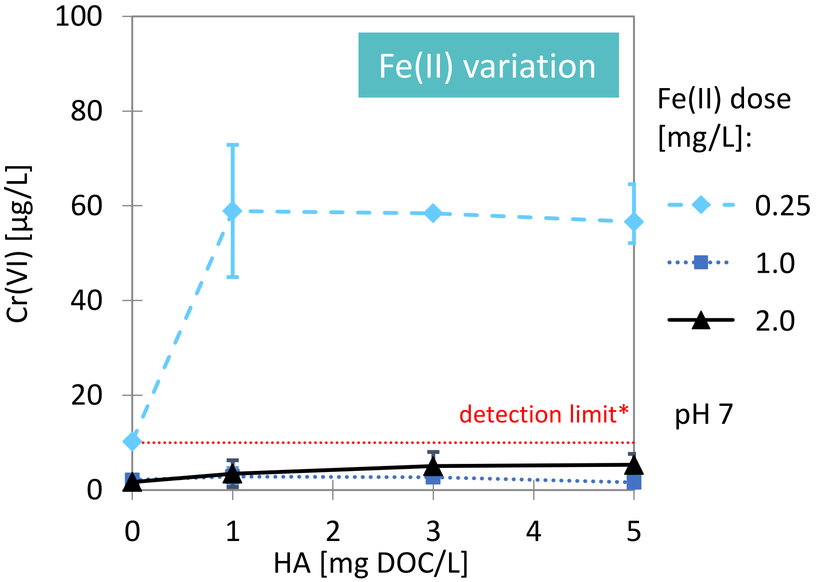
Influence of pH and Fe(II) dose

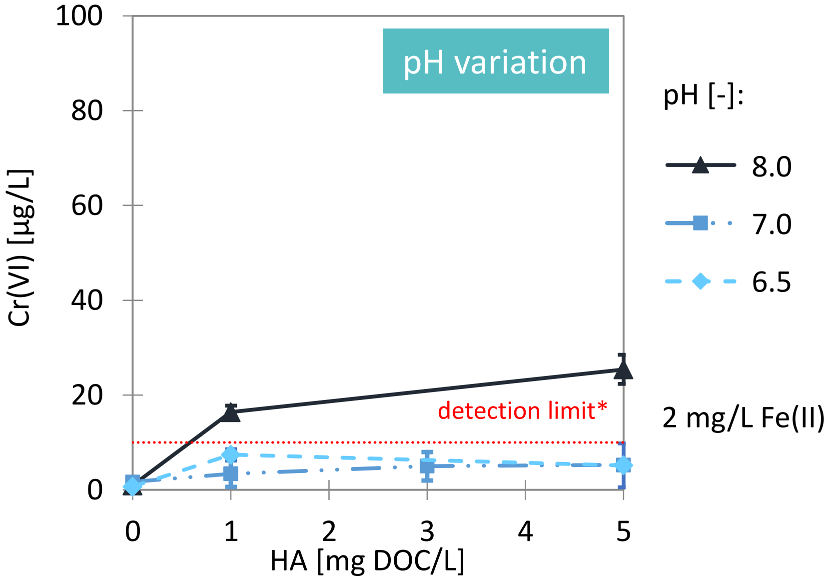


- With 1 mg/L Fe(II) total Cr concentrations of 5 µg/L can be achieved over wide pH range when humic acid is absent
- At pH 8 Fe(II) oxidation competition through oxygen

(Gröhlich et al. 2017)

Influence of humic acid on Cr(VI) reduction



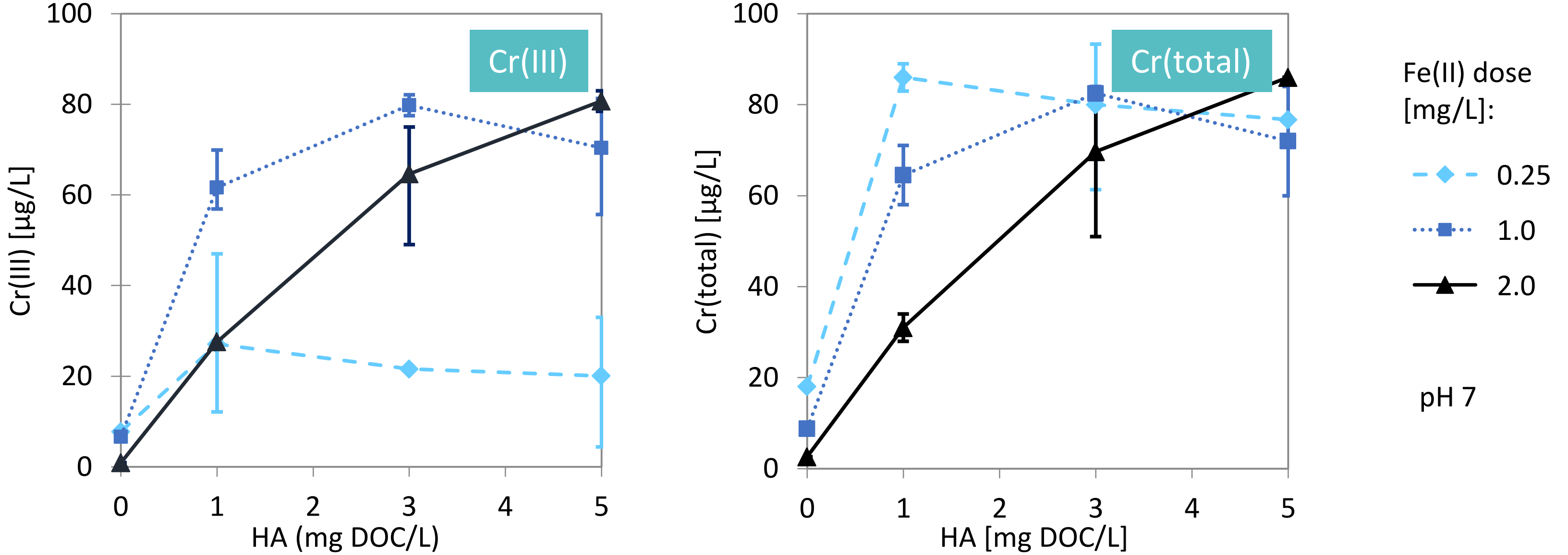


- Reduction of Cr(VI) to Cr(III) only influenced by HA at very low Fe(II) dosage (substoichiometric) and at pH 8
- No explicit catalyzing effects on Cr(VI) reduction through humic acid observed

*Detection limit increased due to interferences with humic acid

(Gröhlich et al. 2017)

Influence of humic acid on Cr(III) removal



- Already at DOC of 1 mg/L removal of Cr(III) heavily impaired
- When Cr(VI) fully converted into Cr(III),
  30 t 80 µg/L Cr(III) left in solution
- Even with 2 mg/L Fe(II) total Cr values <30 µg/L not achievable

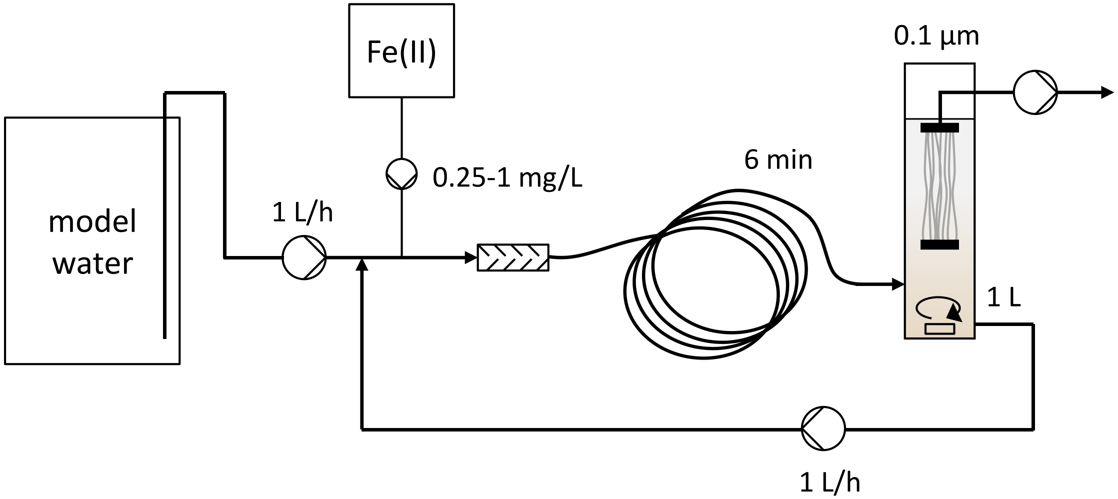
(Gröhlich et al. 2017)

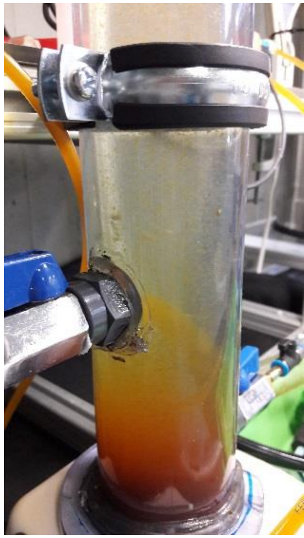
Conclusion

- Cr(VI) is realbly converted into Cr(III) under a wide range of process conditions
- Removal of Cr(III) was observed to be slower and much more prone to be influenced by pH and humic acid
- Without HA Cr(total) values of 5µg/L easily achieved, whereas with HA (1-5 mg/L DOC) 30-80 µg/L Cr(III) remain in solution
- As a likely result of complexation, high amounts of residual Fe (> 0.1 mg/L) were observed

➔ Optimization of Cr(III) removal necessary for a versatile application of Fe(II) reductive precipitation

Future Prospects





- Lab-scale pilot experiments including recirculation and submerged microfiltration:

  ➔ Larger contact surface area for Cr(III) adsorption and removal of undesirable and interfering DOC expected

- First experiences:
  At high sludge concentrations (1 g/L Fe(III)) lower residual concentrations of Cr(VI), Cr(III) and Fe possible

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Thanks for you attention

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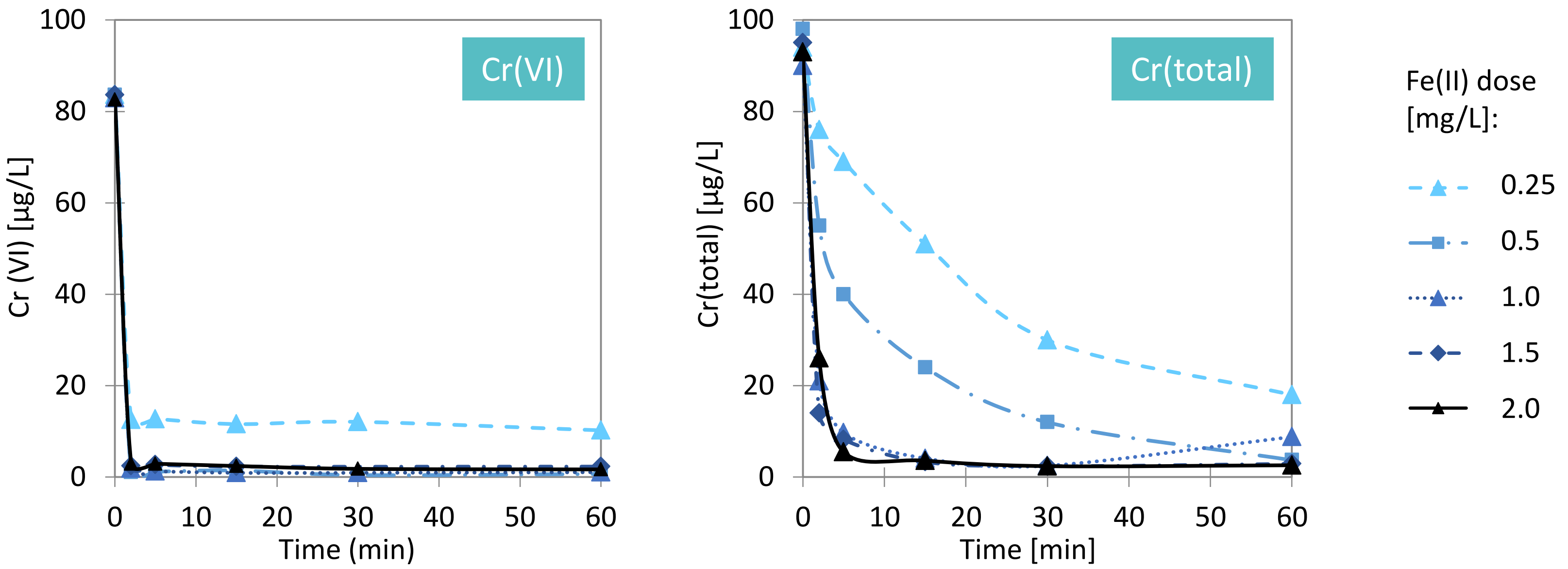
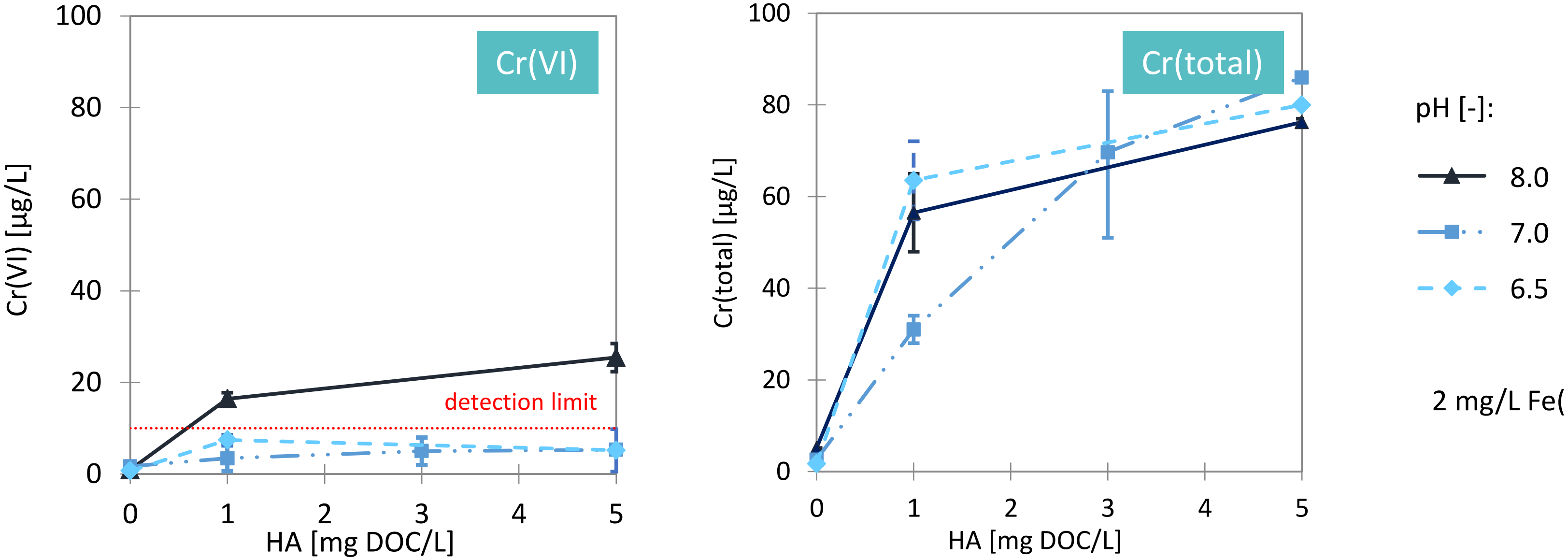
Reaction time



Influence of humic acid and pH



2 mg/L Fe(II)