ICCE 2017 OSLO

Abiotic reductive deiodination of contrast media and the influence of corrinoids

Fatima El-Athman[1], Anke Putschew[1], Lorenz Adrian[2], Martin Jekel[1]

[1]Chair of Water Quality Control, Dept. of Environmental Technology, Technische Universität Berlin, D-10623 Berlin
[2]Dept. of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research, D-04318 Leipzig

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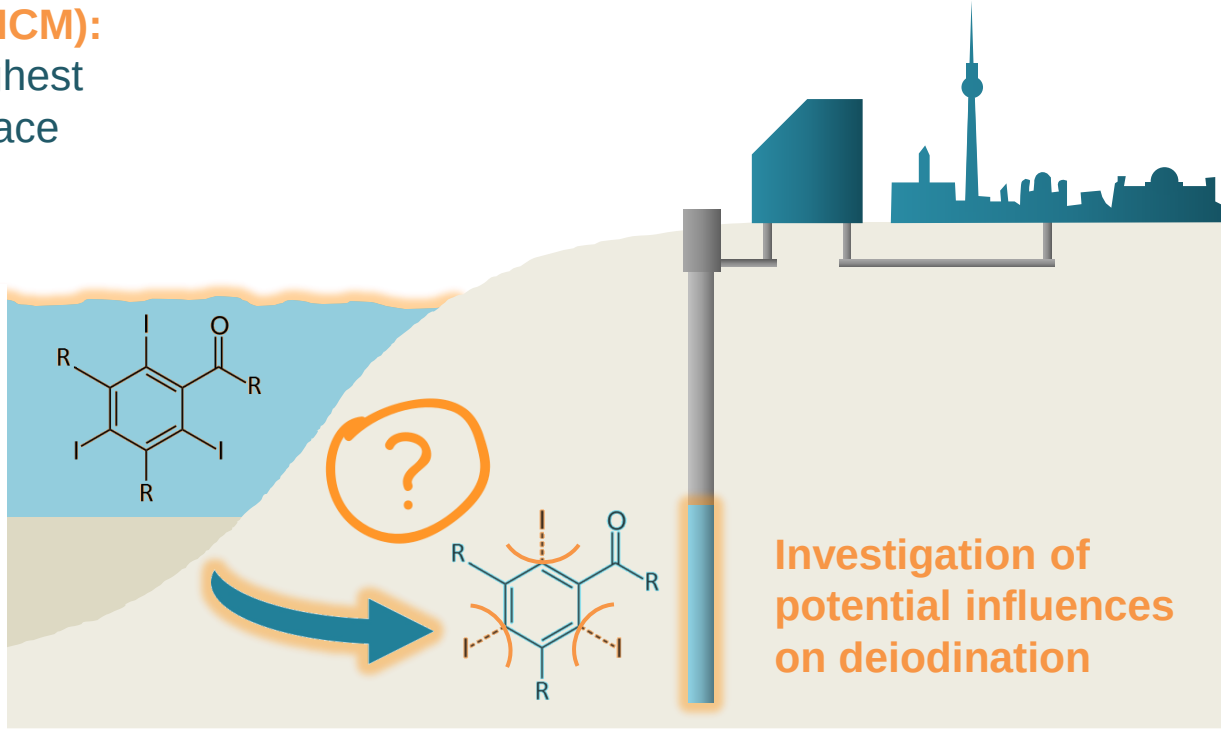
Urban Water Interfaces (UWI)

DFG

Iodinated contrast media in the aquatic environment

- **Iodinated contrast media (ICM):** pharmaceuticals with the highest concentrations in urban surface water
- **Aerobic:** transformation of ICM but no deiodination
- **Anoxic/anaerobic:** field data show deiodination during bank filtration



Reductive dehalogenation

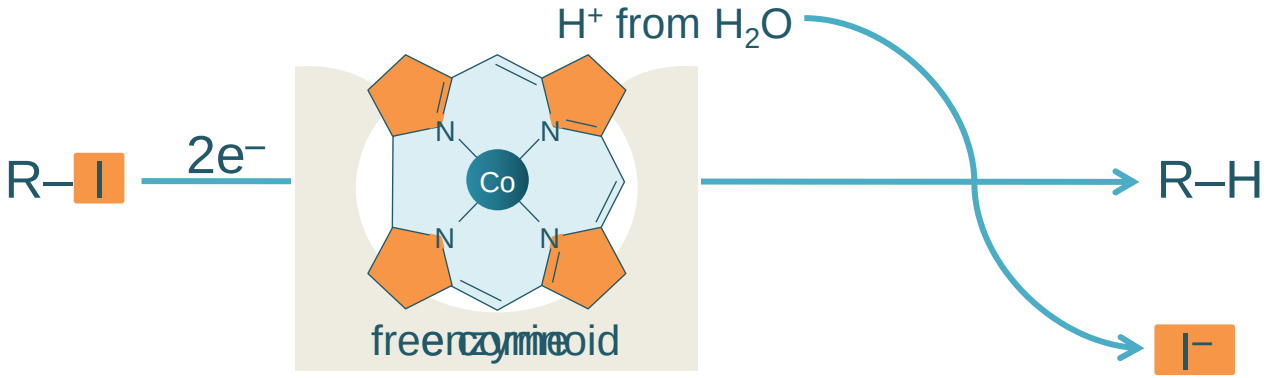
Dehalogenation by microorganisms:

- Dechlorination and debromination known for several trace compounds
- Catalyzed by corrinoid-containing enzymes

Abiotic dehalogenation by corrinoids:

- Dechlorination shown with heat-inactivated enzymes and free corrinoids

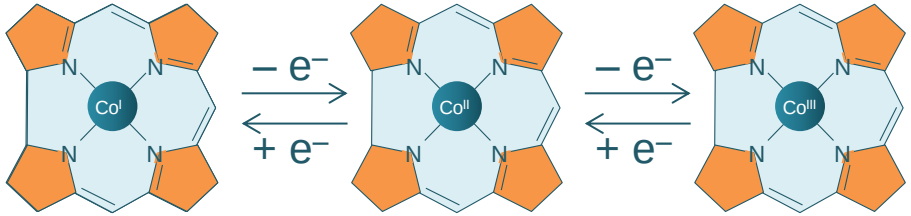
Deiodination of ICM catalyzed by corrinoids?



Corrinoids as electron shuttle

- Corrin ring as basic structure
- Metal-containing corrinoids: central cobalt ion
- Cobalt center can exist in three oxidation states:

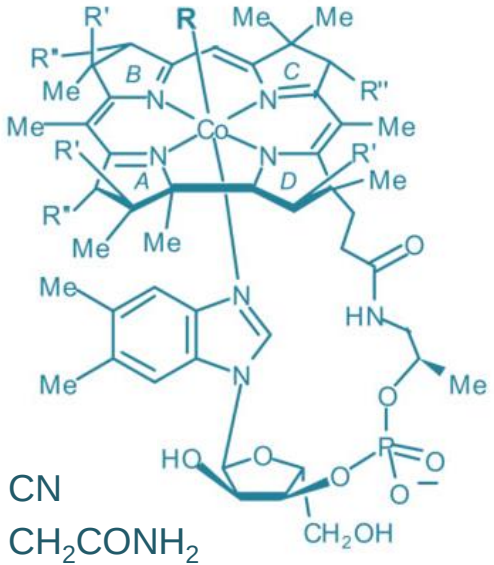
I+ II+ III+



- Ready transition between oxidation states

➡ important redox catalyst

Cyanocobalamin (Vitamin B_{12}):



R = CN

R‘ = CH_2CONH_2

R“ = $CH_2CH_2CONH_2$

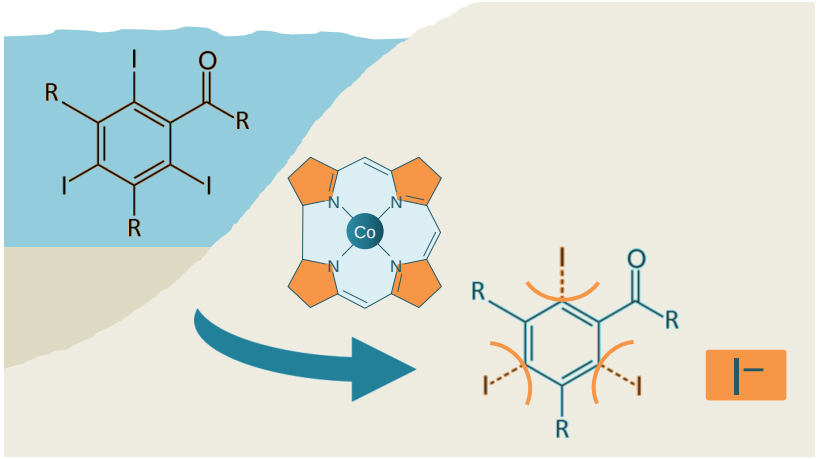
Aim of the study

- Deiodination during bank filtration:

  Are abiotic processes responsible?

- Free corrinoids as redox catalyst:

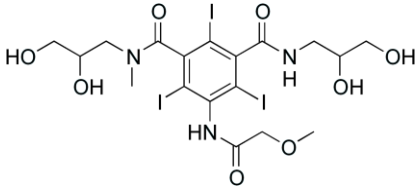
  Can deiodination be catalyzed by corrinoids?



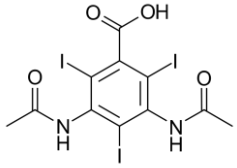
Investigation of the deiodination of non-ionic iopromide and anionic diatrizoate in the presence of different corrinoid types with varying concentrations

Materials and methods

Batch tests under anaerobic conditions:

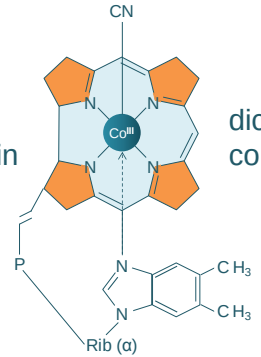


iopromide

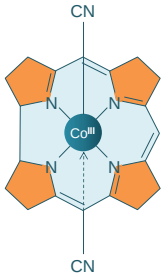


diatrizoate

cyano-cobalamin



dicyano-cobinamide

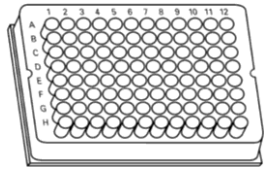


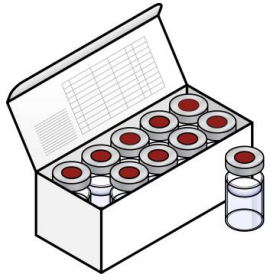
Iodinated contrast media:
iopromide, diatrizoate

Pure water (buffered to pH 5.8)

Reducing Agent:
titanium(III) citrate, methyl viologen, dithiothreitol (DTT), cysteine

Corrinoid:
cyanocobalamin (B_{12}), dicyanocobinamide (DCC)





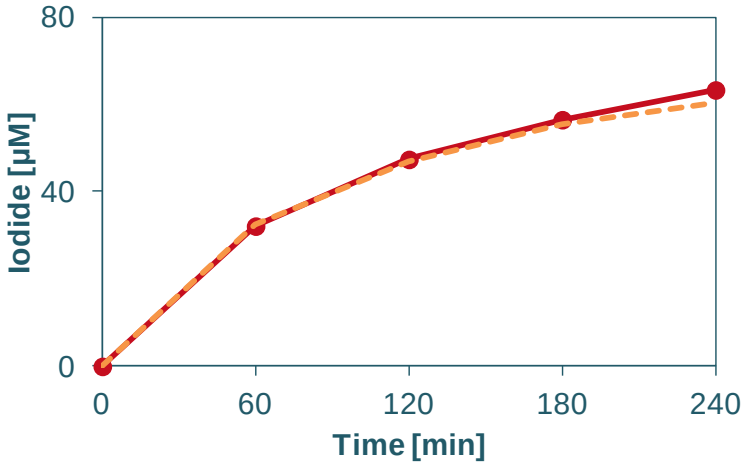
Materials and methods

Quantifying the iodide release:

- IC-UV for tests conducted in vials
- Calculated using the extinction decrease of methyl viologen:

$$RX + 2MV^{\bullet} + H^{+} \rightarrow RH + 2MV + X^{-}$$

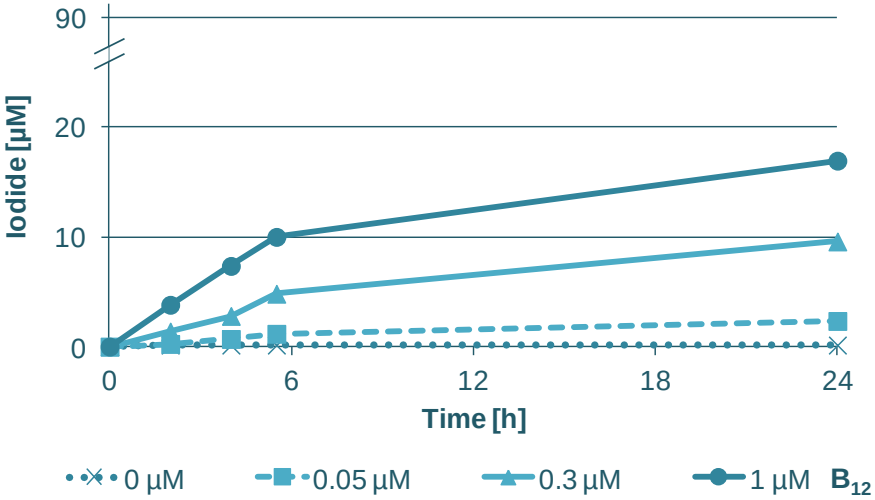
$$c_{t\_Iodide} = \frac{E_0 - E_t}{\varepsilon_{MV} \cdot d \cdot 2}$$



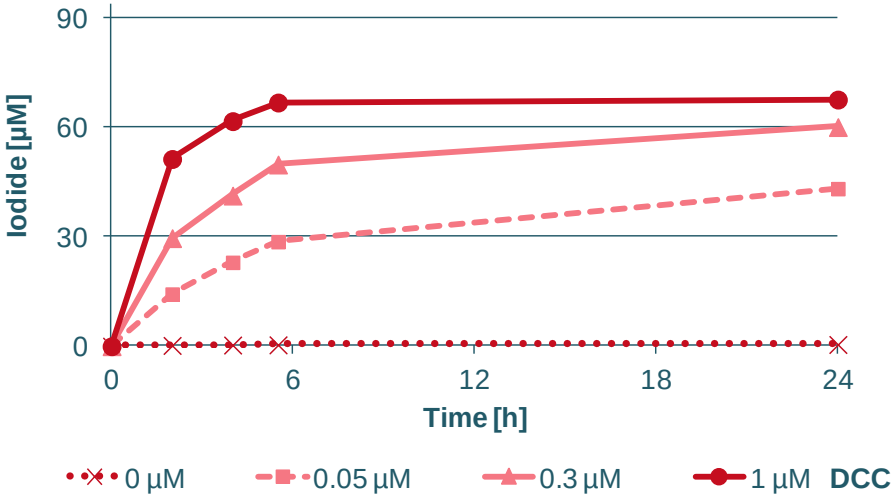
Results and discussion

Influence of the corrinoid type and concentration:

- 30 µM iopromide with **B_{12}** (0–1 µM)



- 30 µM iopromide with **DCC** (0–1 µM)

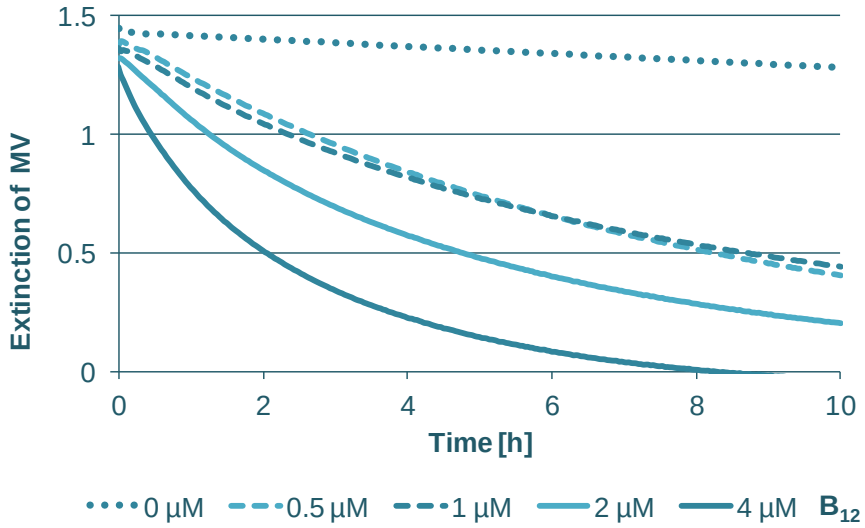


- Deiodination with low corrinoid concentrations, faster deiodination with DCC than with B_{12}

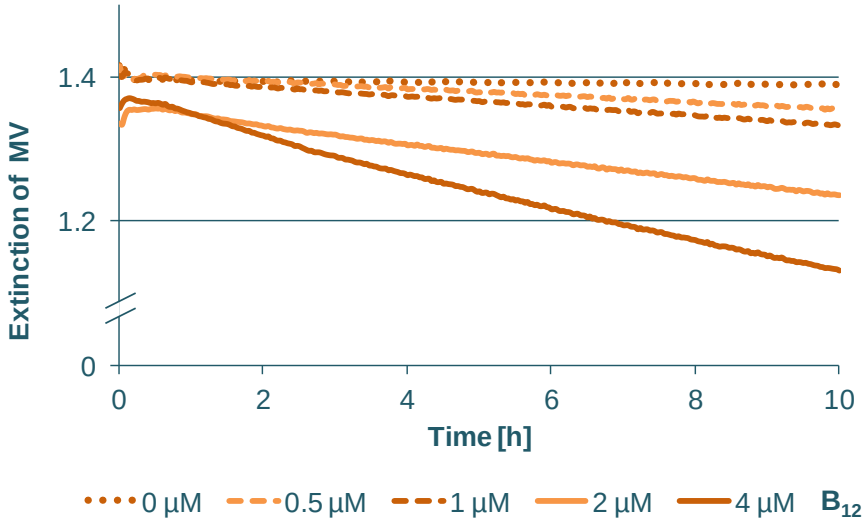
Results and discussion

Different iodinated contrast media:

- **Iopromide** with different B_{12} concentrations

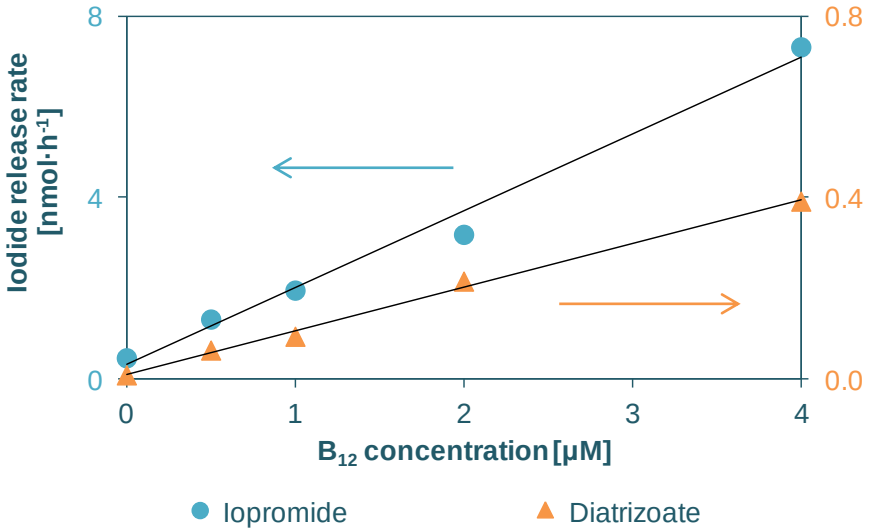


- **Diatrizoate** with different B_{12} concentrations



Results and discussion

- Linear correlation between deiodination rates and corrinoid concentrations



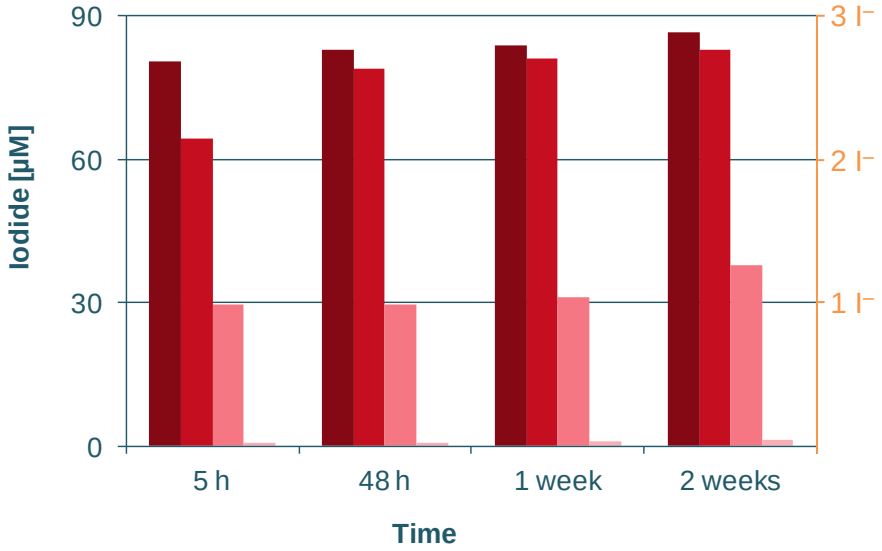
- Deiodination rate of iopromide about 17 times higher compared to diatrizoate

B_{12} conc. [µM]	Specific activity [mol I^- × (mol corrinoid × h) $^{-1}$]	
	iopromide	diatrizoate
0.5	6.8	0.4
1.0	6.0	0.3
2.0	5.5	0.4
4.0	6.9	0.4
1/n × ∑	**6.9**	**0.4**

Results and discussion

Influence of the reducing agent and the respective redox potential:

- 30 µM iopromide with 5 µM DCC and 1 mM reducing agent



Titanium(III) citrate	-480 mV
Methyl viologen	-450 mV
Dithiothreitol	-330 mV
Cysteine	-210 mV

decreasing deiodination rate

- Deiodination is much faster at lower redox potentials

Conclusions

Abiotic deiodination of ICM is strongly catalyzed by corrinoids:

- Dicyanocobinamide, a degradation product of B_{12}, is even a better catalyst than B_{12}

  Possible explanation: better electron transfer with DCC due to two cyano ligands

- Deiodination of iopromide catalyzed by corrinoids is much faster compared to diatrizoate

  Possible explanation: electrostatic repulsion between anionic diatrizoate and Co(I) corrinoid

- Deiodination is much faster at lower redox potentials

Reductive deiodination catalyzed by corrinoids could influence the degradation of ICM under anaerobic conditions during bank filtration

Acknowledgements

Supervisors

Technische Universität Berlin

Prof. Dr.-Ing. Martin Jekel

Dr. rer. nat. Anke Putschew

Helmholtz-Centre for Environmental Research

PD Dr. rer. nat. Lorenz Adrian

Team

Water Quality Control

(TU Berlin)

Collaboration

Functional Genomics and Biochemistry

(UFZ Leipzig)

Students

Corinna Schröder

Lydia Splettstößer

Max Behrens

Research training group Urban Water Interfaces (UWI) funded by the DFG

Thank you for your attention!

QUESTIONS

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