

## Report by UWI doctoral researcher Marcel Yuki Sorgler (H3)

Project number: H3

First and last name of doctoral researcher: **Yuki Sorgler**

(Working) title of doctoral project: **Abiotic transformation of halogenated organic compounds during bank filtration**

Name of supervisors: Dr. Anke Putschew (TUB), Prof. Dr. Lorenz Adrian (TUB & UFZ), Prof. Dr.-Ing. Martin Jekel (TUB), Dr. Jörg Lewandowski (IGB),

### 2. Description of doctoral project and research results achieved to date:

#### State of the art

Iodinated X-ray contrast media (ICM) are found at much higher concentration than any other pharmaceutical compound in waste water, surface water connected to municipal treatment plants and even in the following ground water as well as in drinking water (Fabbri et al. 2016, Pérez and Barceló 2007, Putschew et al. 2000, Putschew et al. 2001, Sacher et al. 2005, Seitz et al. 2006). Several studies showed that ICM are persistent to deiodination in aerobic environments, but side chain transformations lead to various metabolites (Kalsch 1999, Redeker et al. 2014, 2018, Schulz et al., 2008). The stability of the basic structure, the triiodinated benzoic acid, was shown during waste water treatment (Oleksy-Frenzel et al. 2000, Ternes and Hirsch 2000). Even the oxidation with ozone lead to no decrease of the AOI (adsorbable organic bound iodine) using economical ozone dosages (Putschew et al. 2007). In contrast, a deiodination has been achieved by reductive processes such as metal-catalysed hydrodeiodination (Knitt et al. 2008, Stieber et al. 2011), electrochemical reduction (Radjenovic et al. 2013, Zwiener et al. 2009) and disinfection (Duirk et al. 2011).

A partly deiodination has been found for diatrizoate in anaerobic biotic batch tests with sediment taken from a polishing pond (Redeker et al. 2014). A complete deiodination of iopromide and two of its aerobic formed transformation products was found in anaerobic batch experiments with sediment taken from a sulphate-reducing zone of a polishing pond (Redeker et al. 2018). In the field, a partial deiodination of ICM was detected during anoxic/anaerobic bank filtration by an AOI reduction of around 63% (Grünheid et al. 2005, Schittko et al. 2004, Wiese et al. 2011). El-Athman et al. (2018a) examined the deiodination under anaerobic biotic conditions using *Dehalococcoides*. The biotic tests showed just a very slight deiodination and no organism growth, whereas the abiotic controls showed a distinct deiodination. It could be shown that an abiotic deiodination catalyzed by corrinoids (electron shuttle) can be responsible for the deiodination under reducing conditions. The deiodination depends on several parameters like pH, temperature, type of corrinoid as well as the number and the substitution pattern of the bound iodine atoms.

Considering climate changes, increasing temperature and/or enhanced aerobic degradation due to higher concentrations of contaminants will decrease the thickness of the aerobic zone at the water/sediment interface and with that, the anoxic/anaerobic zone will develop earlier and transformation processes under oxygen depleted conditions will become more important.

#### Motivation and research idea

As shown for diatrizoate (Redeker et al. 2014) and iopromide (Redeker et al. 2018) the deiodination plays a major role in the anaerobic transformation pathway of the ICM. However, the deiodination of iodinated organic compounds during bank filtration is scarcely investigated so far. El-Athman et al. (2018a, 2018b) showed, to our best knowledge for the first time, that an abiotic deiodination in the presence of corrinoids can be responsible for the deiodination in the presence of reducing agents respectively electron donors (Figure 1). The corrinoids like vitamin B<sub>12</sub> serving as electron shuttle and catalyst are ubiquitous in nature, but the used reducing agents are commonly applied in biological tests and cannot be found in nature. For that reason, the relevance of the abiotic deiodination of organic compounds catalysed by electron shuttles will be investigated under natural conditions using other reducing agents/electron donors as well as other electron shuttles.

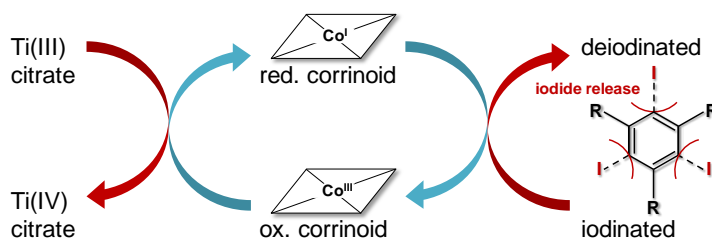


Figure 1: reaction scheme of the electron-shuttled deiodination (El-Athman et al. 2018a)

## Scientific project relevance

Berlin's water cycle is partially-closed meaning that treated waste water is discharged into surface water, which is mixed after bank filtration with ground water and pumped up for drinking water treatment. Within the water cycle, polar persistent organic trace compounds such as ICM are hardly removed. Under anoxic/anaerobic conditions a partly deiodination is observed in the field. It is very important to determine the deiodination mechanism and the kinetics under natural conditions to obtain a comprehensive understanding of the reductive deiodination. With that, the prediction of the contaminant fate during bank filtration is improved and the knowledge can be applied for (managed) artificial groundwater recharge. Furthermore, the behaviour of the resulting transformation products must be studied concerning adsorptive uptake by soil and during subsequent drinking water treatment. Studying the behaviour of other environmental relevant halogenated compounds such as diclofenac can broaden the scientific relevance. To obtain a profound chemical understanding about the kinetics of the dehalogenation, the dependence of the kind (chlorine (Cl), bromine (Br), iodine (I)), the number and substitution pattern of the bound halogens is of great interest (Figure 2).

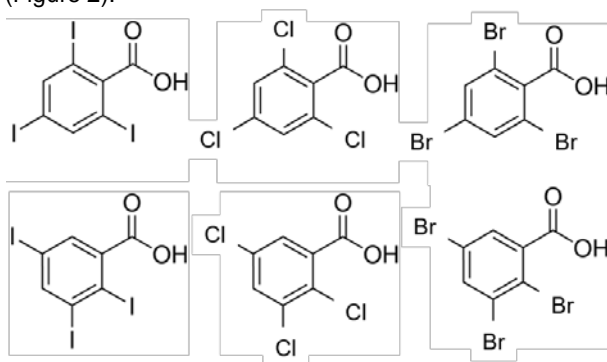


Figure 2: Examples of differently halogenated benzoic acids halogenated in positions 2,4,6 (top row) and 2,3,5 (bottom row)

## Research demands

To further clarify the scope of the project, the following scientific questions are designed to be answered during this project:

- 1) What kind of natural-occurring compounds/mineral phases can provide electrons for the abiotic deiodination?
- 2) Beside of the corrinoids, which other natural-occurring electron-shuttles can catalyse the deiodination?
- 3) How does the (partly) deiodinated compounds behave during bank filtration and subsequent drinking water treatment?
- 4) How does the kinetics depend on the kind (Cl, Br, I), the number and substitution pattern of the bound halogens?
- 5) Is a deiodination/dehalogenation already in the reducing micro-environments of the hyporheic zone possible?

## Objectives

The study consists of the following main objectives:

- 1) Determination of the behaviour of the (partly) deiodinated ICM during bank filtration and drinking water treatment.
- 2) Determination of the reacting agents (reducing agent and electron-shuttle) responsible for the deiodination/dehalogenation under natural reducing conditions and determination of kinetic data.
- 3) Examination of the relevance of the dehalogenation in environmental samples.

## Work programme incl. proposed research methods

### WP 1

### 'Behaviour of the partly deiodinated ICM'

The behaviour of the (partly) deiodinated ICM during bank filtration and subsequent drinking water treatment will be examined. In detail the i) adsorptive uptake by soil during bank filtration, ii) the biodegradability under aerobic conditions (subsequent drinking water treatment), iii) the behaviour during ozonation and iv) adsorption on activated carbon will be determined. The (partly) deiodinated transformation products (TP) will be produced by reproducing experiments of El-Athman et al. (2018a, 2018b). As reactants titanium-III-citrate and cyanocobinamide will be used because of the high reaction constant ( $k_{\text{obs}}$ ) determined for this combination. The reaction will be stopped at different times to have mixtures with one TP in highest concentration (Figure 3).

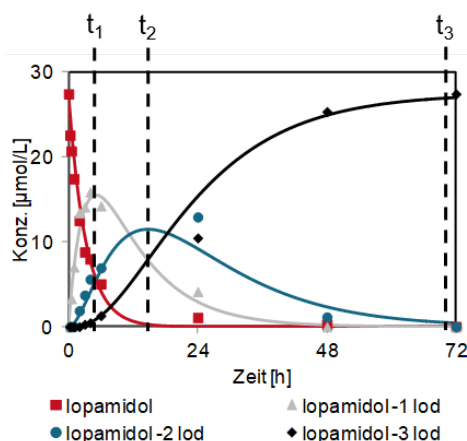


Figure 3: Kinetics of the stepwise deiodination of Iopamidol (El-Athman et al. 2018b): Stopping the reaction at the marked points where the highest concentration of the partly deiodinated Iopamidol is reached

The production of the TPs as well as the investigation of the adsorption to soil will be conducted under anaerobic conditions in a glovebox with a nitrogen atmosphere. The TPs will be monitored based on the response area obtained by liquid chromatography with UV-detection (LC-UV), liquid chromatography with electrospray ionization mass spectrometry (LC-ESI-MS) and/or AOI. Up to now, the concentration of the partly deiodinated TP can just be estimated due to the lack of standards. A quantification might be possible via the still bound iodine and can be done by liquid chromatography with inductively coupled plasma mass spectrometry (LC-ICP-MS), which could be realized by a cooperation or an internship.

The duration of this package will be 8 months and will end at the beginning of 2019.

## WP 2

### 'Relevance of the abiotic dehalogenation'

In earlier studies, compounds such as titanium-III-citrate, methyl viologen, dithiothreitol and cysteine were used as reducing agents. In general, these substances are applied for biotic tests. Thus, it is necessary to determine the kinetics of the transformation using reducing agents, which can be found in nature like iron, manganese or sulphur species. Regarding the reducing agents, different solid phases must be considered because reduction processes occur mainly on mineral surfaces. Possible minerals are Fe(II)-bearing trivalent iron species such as goethite. Although corrinoids are ubiquitous in nature, other electron shuttles like quinones, which are model compounds of natural organic matter, as well as humic and fulvic acids and porphyrins will be examined. Applicable quinones could be AQDS (anthraquinone-2,6-disulfonate), juglone, lawsone, naphthoquinone, benzoquinone or menadiene which have already shown catalytic effects on dechlorination of polychlorinated compounds. A preliminary test has already shown that quinones can act as electron shuttles for deiodination of ICM. The influence of humic and fulvic acid will be studied using different waters like drinking and surface water enriched with dissolved organic carbon (DOC). Porphyrins have a similar structure to corrinoids and can form different metal-complexes, which can be found in nature such as heme or chlorophyll. Besides the iodinated compounds, other halogenated organic substances having an environmental relevance can be considered within this WP. To compare the kinetics of different halogenated substances, same structured compounds differing in the type (Cl, Br, I), number and substitution pattern of the bound halogens will be investigated.

The experiments will be carried out as batch tests in an anaerobic glovebox. The halogen release rate will be determined for different concentrations and combination of electron shuttle and reducing agent. The halogen concentration will be measured by ion chromatography with UV detection (IC-UV) and the concentration of the compound by LC-UV or LC-MS/MS.

This package will require 20 months and will end in autumn 2020.

## WP 3

### 'Dehalogenation in environmental samples'

To investigate the dehalogenation process in environmental samples, experiments and field studies will be conducted. The experiments will be done with sediment material of Tegeler See and river Erpe. Four core samples will be taken at positions close to each other. Two cores will be used for the determination of the redox zones and the sediment characterisation. The other two cores are divided into sections of few centimetres corresponding to the redox zones. The anoxic and anaerobic sediment samples will be applied for batch tests with selected halogenated compounds, which could be reduced in WP 2. Besides comparison of the biotic/abiotic dehalogenation using sterile/non-sterile tests, other different set-ups can be compared: dehalogenation rate i) with/without additional electron shuttles and ii) with/without additional reducing agents, both successfully used in WP 2. To investigate the dehalogenation in the field, water of the transect at the bank filtration site Tegeler See and the hyporheic zone in the river Erpe will be sampled and analysed concerning transformation products of the selected halogenated compounds.

The experiments will be carried out in an oxygen-free glovebox. The concentration decrease of the halogenated compounds in the batch tests will be measured via AOX/AOI and LC-ESI-MS/MS. The dissolved halide

concentration will be quantified by IC-UV. The redox zones in the core samples will be determined by quantification of nitrate (via IC), iron (via atomic absorption spectroscopy (AAS)), manganese (via AAS), sulphate (via IC) and methane (via gas chromatography (GC)). The sediment characterisation will be done by determining grain size distribution and ignition loss and CNS analysis (elemental analysis of carbon, nitrogen, sulphur). Selected halogenated organic compounds and their TP can be analysed with methods described in WP 1.

This package will require 8 months and will end in spring 2021

### Collaborations

A collaboration is feasible within the WP 3. For this package, an appropriate cooperation partner is the research group of Jörg Lewandowski (H1). The focus of their studies relies on the transformation of trace organic compounds during the hyporheic zone regarding the river Erpe. In the hyporheic zone micro anaerobic/anoxic areas emerge promoting the reduction of trace organic compounds which are known for higher removal rates under anoxic/anaerobic conditions. Under these circumstances it could be attractive to investigate the deiodination potential of the hyporheic zone.

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### 3. Comments on the qualification programme and supervision strategy:

Participation in the following Research Training Group events:

#### 1. Core courses

- Urban interface processes – fluxes, transport, interactions (3 ECTS)
- Urban freshwater ecology (3 ECTS)
- Modelling and measuring concepts of interface processes (3 ECTS)

#### 2. Elective courses

- Language: English for academic purposes (6 ECTS)
- „Einführung in mathematische und statistische Methoden der Umweltforschung“ (6 ECTS)
- Urban soils (6 ECTS)

Research stays or internships at other research institutions both at home and abroad:

To deepen the knowledge in the field of trace compound analysis and to examine different samples searching for transformation products, an appropriate internship could be at the *Federal Institute of Hydrology* in Koblenz, within the research group of Prof. Dr. Thomas Ternes/Dr. Arne Wick. Ternes/Wick are specialists for the detection of transformation products of iodinated X-ray contrast media using high resolution LC-MS/MS and LC-ICP-MS.

Another interesting internship could be the *Center for Applied Geosciences* at *Eberhard-Karls University* in Tübingen. In the research group of Prof. Dr. Stefan Haderlein various redox processes occurring in natural porous media such as sediments, soils and aquifers were investigated. For example, Orsetti et al. (2013) investigated the electron transfer between iron minerals and quinones, which is thematically related to WP 2. Redox processes in the soil are very complex due to the presence of various metals and organic compounds. A better understanding of these processes will be necessary for a comprehensive description of the transformation processes of iodinated/halogenated organic compounds in the aquatic environment.