

# REPORT

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## Synthesis Report on Practical Implications and Opportunities for Transfer to Field Scale Project acronym: OXIRED-2

by

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## Title

Synthesis Report on Practical Implications and Opportunities for Transfer to Field Scale

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# Chapter 1

## Introduction

### 1.1 Background and Objectives

Underground passage as utilized during riverbank filtration and artificial groundwater recharge is widely used as pre-treatment of drinking water within a multi-barrier concept. Additionally it represents an important step within the framework of water-reuse. Especially particulate and particle-bound substances (e.g. algae and bacteria) are efficiently removed by physical straining. Additionally, multiple bio- and geochemical reactions in the subsurface lead to a reduction of many dissolved substances as well (e.g. pharmaceuticals and industrial chemicals).

There are, however, limitations to this system, as some trace organic substances have shown to break through and sufficient removal of high concentrations of dissolved organic carbon (DOC) can only be ensured for long residence times (in Berlin: 1 month under aerobic and 3 to 6 months under anoxic / anaerobic conditions). As shown in the NASRI project, not all trace organics are removed during subsurface passage and thus, may be present in the raw water for drinking water production. For trace organics removal, but also for more conventional parameter such as nitrate the redox conditions in the subsurface are the key drivers of removal.

Several factors can drive the need to enhance artificial recharge: The depletion of groundwater resources due to intensive pumping for agriculture or supply of growing urban areas and the possible decrease in natural groundwater recharge which is expected due to climate change. New legislations might include the need for trace organic removal before infiltrating water to the subsurface. The need for increasing infiltration volumes to ensure water supply in Berlin will lead to shorter retention times in the subsurface and may thus result in lower removal of DOC and trace organics. Reasons for short retention times at other sites are spatial constraints such as the lack of aquifer volume or high hydraulic conductivities. Less natural flow during summer (drought) periods will also lead to an increased share of treated sewage in the surface waters, resulting in higher source water concentrations of DOC and trace organics for drinking water production.

The project OXIREM was initiated in order to deliver a sound solution ready for application to overcome the aforementioned challenges. It investigated the possibility to influence degradation processes via redox control and, as the main issue, to combine subsurface passage with technical oxidation processes. Ozonation or advanced oxidation processes (AOP) are powerful tools to remove trace organics and to enhance the degradation of DOC. Additionally; they offer an additional barrier against microorganisms. Thus, a combination of oxidation technologies with the natural degradation capacity of a subsurface passage could help to maintain the semi-natural drinking water production in Berlin also under changing climatic and hydraulic conditions.

Both treatment methods – underground passage and oxidation – have been investigated separately in different projects at KWB (e.g. NASRI-1, TECHNEAU, PILOTOX). The KWB project OXIREM combined these two strategies to optimize water treatment for DOC and trace organic removal.

Within the first phase of the project (OXIRED 1) substances with high potential for breakthrough in subsurface passage were identified (s. Table 1).

**Table 1: Persistent substances with high, medium and uncertain potential for breakthrough in BF/AR systems ((Wiese and Grützmaier 2009); \*results from field site and lab trials not conclusive, adapted from OXIRED 1)**

potential for breakthrough	pharmaceuticals	x-ray contrast media	pesticides	industrial chemicals
high	Carbamazepine Primidone	AOI Amidotrizoic Acid		MTBE EDTA ETBE 1,5-NDSA
medium	Diclofenac Sulfamethoxazole*	Iopamidol	Bentazone Atrazine Desethylatrazine Linuron Diuron	1,7-NDSA 2,7-NDSA

The reactivity of these trace organics with oxidants is quite variable (s. Table 2), thus even for the combination of oxidation and managed aquifer recharge (MAR) the composition of the source water needs to be evaluated carefully. Some trace organics e.g. carbamazepine are only poorly degraded in subsurface but easily removed via ozonation. MTBE on the other hand is a compound difficult to remove both with MAR and oxidation processes. Thus, for carbamazepine the combination ozone + MAR seem applicable, while for MTBE other solutions are necessary.

**Table 2: Trace organic compounds from the priority list of the report OXIRED 1, D1.1a classified by their removal (transformation) for different oxidation processes (for ozonation: ozone dosing ~ 1 mg O<sub>3</sub>/mg DOC; adapted from (Calderara et al. 2001; Wiese and Grützmaier 2009) and own results,\*\* formation from atrazine during ozonation but also transformation; taken from OXIRED 1)**

Transformation	O <sub>3</sub>	O <sub>3</sub> / UV	O <sub>3</sub> / H <sub>2</sub> O <sub>2</sub>
> 90 %	carbamazepine Diclofenac, sulfamethoxazole Diuron, Bentazone	carbamazepine Diclofenac	carbamazepine Diclofenac
> 50 %	Linuron, 1,5-NDSA, 1,7-NDSA, 2,1-NDSA	Atrazine Iopamidol	Atrazine Iopamidol
< 50 %	Atrazine MTBE Iopamidol	MTBE	MTBE
uncertain	primidone, amidotrizoic acid, desethylatrazine**		

On the basis of these encouraging results, the 2<sup>nd</sup> phase of the project was initiated in 2009 of which the main results will be documented in the following report.

## 1.2 Strategy

In the 2<sup>nd</sup> phase of the project (OXIRED 2), trials at lab and technical scale were conducted to validate the results for trace organic and DOC removal from OXIRED 1 and to gain a more reliable knowledge about oxidation by-product formation for surface water from Berlin. To assess the stability of the process, a pilot unit was operated at Lake Tegel. Moreover the effect of oxidation + MAR on toxicological parameters was investigated (s. D 1.1).

To prepare a field study three sites in Germany were evaluated regarding their suitability including parameters such as aquifer depth and composition, source water quality and possibility of authorization (s. D 2.1). The results were that none of the sites (Hobrechtsfelde, Braunschweig WWTP or artificial recharge site in Görlitz) was identified as suitable.

The current state-of-the-art for influencing the redox zonation in the subsurface was reviewed (D 3.1) and the options to assess the quantity, composition and activity of the microbial population in the soil samples were summarized (D 2.2).

To investigate the dynamic of redox processes, short term column tests were conducted (D 3.2). On the basis of these results reactive flow and transport modelling was carried out (D 3.2 and 3.3).

The aim of this report is to give a summary of the main results from OXIRED 2 and to identify promising opportunities for further experiments and transfer to field scale.

List of deliverables OXIRED 2:

- D 1.1: Results and recommendations from experimental trials (TUB Prof. Jekel)
- D 2.1: Demonstration site configuration and technical planning (KWB)
- D 2.2: Biomass determination from sediment samples (KWB)
- D 3.1: Presentation of results from literature study (KWB)
- D 3.2: Documentation of laboratory scale experiments (TUB Scheytt)
- D 3.3: Documentation of reactive transport modelling (UIT)
- D 3.4: Synthetic report on practical implications and opportunities for transfer to demonstration scale (this report)

## Chapter 2

### Results for oxidation and infiltration from laboratory, technical and pilot scale trials and preparation of field scale investigations (WP 1 + 2)

For detailed information see:

- D 1.1: Results and recommendations from experimental trials (TUB, U. Hübner, M. Jekel)
- D 2.1: Demonstration site configuration and technical planning (KWB)
- D 2.2: Biomass determination from sediment samples (KWB)

#### 2.1 Effect on removal of dissolved organic carbon

1. How much can we increase DOC degradation during infiltration via pre-ozonation?

The trials with lab and technical scale columns and as well the pilot unit with ozonation and slow sand filtration (SSF) showed the same trend: Pre-ozonation increases the degradation of DOC (s. Table 3). Even at very short retention time (HRT: 12-48 h) as in the SSF the degradation increases from 23 % to 34 % in average. The DOC in the SSF effluent reached a similar level (4.7 mg/L) as the water after 30 d travel time at the artificial recharge site in Berlin Tegel (s. (Grünheid et al. 2008)), while the effluent of the lab scale columns (HRT: 5-7 d) were already in the range of tap water in Berlin (~3.8 mg/L) which has several months of travel time. Nevertheless, the increase of DOC degradation via ozonation is less pronounced in technical scale or the SSF compared to the lab scale columns. Most probably differences in water temperature are the reason.

**Table 3: Comparison of DOC results from laboratory and technical scale with pilot plant (table from D 1.1, Hübner et al. 2011)**

	laboratory scale		technical scale	pilot plant
	exp.1	exp.2		
<b>surface water DOC [mg/L]</b>	6.85	6.41	7.06	7.19
<b>O<sub>3</sub> consumption [mg O<sub>3</sub>/mg DOC<sub>0</sub>]</b>	0.94 ± 0.05	0.69 ± 0.05	0.83 ± 0.27	0.8
<b>DOC removal without pre-ozonation [%]</b>				
0.5 – appr. 2 days retention time			19	23
5 to 7 days retention time	22	22	26	
42 days retention time			37	
temperature	22°C	22°C	12°C	15 - 23°C
<b>DOC removal after pre-ozonation [%]</b>				
0.5 – appr. 2 days retention time			21	34
5 to 7 days retention time	45	40	28	
42 days retention time			42	
temperature	22°C	22°C	12°C	5 – 15°C

2. Which is the optimal ozone dose for DOC removal?

The degradation of DOC depends on the applied ozone dose: Increased dosing also increases the biological degradability. Batch tests (OXIRED 1, D 3.1) showed that increasing the ozone dose from zero to 0.9 mg O<sub>3</sub>/mg DOC improved the degradation from ~9% to 29%. An additional increase to 2.5 mg O<sub>3</sub>/mg DOC increased the degradation only to 37%, thus the additional benefit of applying an ozone dose > 1 mg O<sub>3</sub>/mg DOC is low. Applying 0.7-0.9 mg O<sub>3</sub>/mg DOC increased the DOC removal in lab scale columns from 22% to 40-45% after 5-7 d travel times (s. Table 2). For full scale application a specific ozone dose of 0.7 - 1.0 mg O<sub>3</sub>/mg DOC is recommended. This ratio is applicable for surface water (DOC range 5-7 mg/L) and as well as for WWTP effluents (DOC 10-13 mg/L, see OXIRED 1, D3.1). Short tests to assess the possible degradation enhancement via oxidation therefore should also apply this specific ozone dose.

3. How much energy is needed for ozonation + MAR?

The energy consumption for the combination of oxidation and MAR is driven by two main factors: Ozone production and pumping. For a specific ozone dosage of 0.7 mgO<sub>3</sub>/mg DOC the energy demand for ozonation of surface water (DOC 4-10 mg/L) is in the range of 42-105 Wh/m<sup>3</sup> (assuming a minimal energy demand of 15 kWh/kg O<sub>3</sub> including production of pure oxygen; remark: depending on size/operation > 20 kWh/kg O<sub>3</sub> possible). The energy demand for pumping depends on the type and size of the pump, on its efficiency and lifting height. Typical values of currently market-available pumps are in the range of 4.2 Wh/m<sup>3</sup>/m. In Figure 1 the relation between DOC and energy demand is shown for two different pump sizes for a lifting height of 15 m. It shows that for low DOC the energy demand for pumping is higher than for ozonation.

Rule of thumbs for decision makers:

$$10.5 \text{ Wh/m}^3/\text{mg DOC} + 4.2 \text{ Wh/m}^3/\text{m} \cdot \text{lifting height [m]}$$

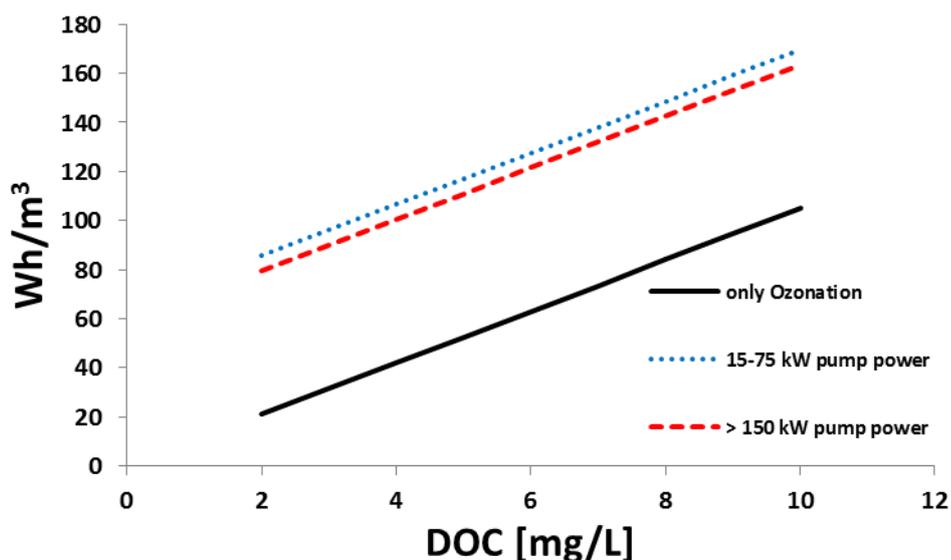


Figure 1: Energy demand for ozonation and recovery from the aquifer for two different sizes of pumps (15-75 kW and > 150 kW) depending on the source water DOC (assumptions: 15 m lifting height; 15 kWh/kg ozone)

## 2.2 Effect on removal of trace organics

### 4. Can we increase trace organics removal during infiltration via pre-ozonation?

Two different aspects need to be differentiated:

- i. The transformation of trace organics via ozonation and
- ii. The possible enhancements of degradation in the soil column or slow sand filter subsequent to the oxidation step.

Table 4 gives the results from the pilot unit at Lake Tegel. The removal of compounds via degradation in the filter is in line with the literature data (s. Table 1). The ozonation step reduced the concentration of single compounds from 50 % (ETBE, AMDOPH) up to more than 98 % (carbamazepine, < LOQ) for an average dosing of 0.8 mg O<sub>3</sub>/ mg DOC. Thus, the optimal dosing range for DOC removal seems also applicable for the removal of most of the investigated trace organic compounds. Nevertheless some compounds e.g. primidone or MTBE can only be removed to limited extent. For the SSF (and the lab scale columns) after ozonation no removal could be calculated for most compounds, as the residual concentration in the influent was already below the limit of quantification. For benzotriazole and AMDOPH no degradation could be observed in the SSF for the residual concentration after oxidation (0.07 - 0.73 µg/L and 0.02 - 0.08 µg/L respectively). Thus, for non/poorly degradable trace organics the removal is only driven by the oxidation step itself. Nevertheless, the infiltration step via a slow sand filter after the ozonation brings additional benefits such as: degradation of formed BDOC and degradable oxidation by-products, particle and parasite removal (e.g. helminth eggs).

**Table 4: Removal of trace organics at pilot plant (n. c.: not calculated, because c<sub>0</sub> was too low for calculation of removal efficiency; table from TUB report, Hübner et al. 2011)**

Substances	LOQ [µg/L]	Removal in SSF without ozonation	Removal via ozonation	Removal in SSF after ozonation	Total removal (ozone + SSF)
ETBE	0.03	> 96% <sup>1</sup>	~ 50%	n. c.	> 90% <sup>1</sup>
AMDOPH	0.02	< 10%	~ 50%	< 10%.	~ 50%
Carbamazepine	0.02	< 10%	> 98% <sup>1</sup>	n. c.	> 98% <sup>1</sup>
Phenazon	0.05	> 70% <sup>1</sup>	> 70% <sup>1</sup>	n. c.	> 70% <sup>1</sup>
AAA	0.05	> 70% <sup>1</sup>	> 90% <sup>1</sup>	n. c.	> 90% <sup>1</sup>
FAA	0.05	~ 70%	> 90% <sup>1</sup>	n. c.	> 90% <sup>1</sup>
Primidone	0.02	< 10%	~ 70%	n. c.	~ 70% <sup>2</sup>
p-TSA	0.05	< 10%	> 50% <sup>2</sup>	n. c.	> 50% <sup>2</sup>
BSA	0.03	< 10%	> 50% <sup>2</sup>	n. c.	> 50% <sup>2</sup>
Sulfamethoxazole	0.03	~ 30%	> 80% <sup>1</sup>	n. c.	> 80% <sup>1</sup>
Metoprolol	0.03	~ 60%	> 90% <sup>1</sup>	n. c.	> 90% <sup>1</sup>
Benzotriazol	0.02	< 10%	~ 85%	< 10%.	~ 85%
Tolyltriazol	0.02	< 10%	> 94% <sup>2</sup>	n. c.	> 94% <sup>2</sup>

<sup>1</sup> removal below LOQ in all samples, samples below LOQ calculated as ½ LOQ

<sup>2</sup> several samples below LOQ, data shown as minimum reduction, samples below LOQ calculated as ½ LOQ

5. For which trace organics is the combination of ozonation and subsurface passage a suitable solution?

Ozonation and infiltration removed most investigated compounds by more than 70 % (with oxidation being the most important step). For 9 out of 19 compounds the concentration after treatment was under the limit of quantification (s. Table 5). Nevertheless some substances (6 out 19) were only removed by 30 – 70 %. All these trace organics show low biodegradation and in addition a low reactivity towards ozone (e.g. MTBE or primidone). For these compounds the use of advanced oxidation via e.g. ozone & H<sub>2</sub>O<sub>2</sub> could be beneficial.

**Table 5: Trace organics removal during ozonation and slow sand filtration/artificial recharge: Summary of results from laboratory, technical and pilot scale experiments**

(++: complete removal (below LOQ in all samples); +: good removal (> 70%); + / - : partial removal (30 % -70 %); data from D 1.1 Hübner et al. 2011)

Removal	++	+	+/-
<b>High potential for breakthrough in RBF / AR systems</b>	Sulfamethoxazole	ETBE*	MTBE
	Carbamazepine		Primidone
<b>Medium / uncertain potential for breakthrough in RFB / AR systems</b>	Bentazone	Linuron	
	Diuron		Atrazine
	Diclofenac		
<b>Other substances detected in Lake Tegel water</b>	Phenazon	Benzotriazole	AMDOPH
	AAA	Tolyltriazole	p - TSA
	FAA		BSA
	Metoprolol		

\* Degradation results not fully conclusive

## 2.3 Formation of oxidation by-products

6. Which by-products were formed?

The investigations in this study focused on the two frequently occurring by-products of ozonation: Bromate and nitrosamines (including NDMA). Both are well known carcinogenic compounds. In ozonation trials with water from Lake Tegel, none of the samples contained NDMA or one of the other seven analysed nitrosamines (LOQ: 5 ng/L). The bromate formation depends on the applied ozone dosage: to avoid formation of bromate above the limit for drinking water (WHO, US EPA, EU: 10 µg/L) the dosage should be limited to 0.9 mg O<sub>3</sub>/mg DOC for the treatment water for Lake Tegel (Bromide: ~100 µg/L).

Transformation products of trace organics were not analysed within this study. All trace organics which react with ozone will form (mostly unknown) transformation products with an altered but similar molecular structure. This alteration is in many cases associated with the loss of the biological activity of e.g. antibiotics (Yargeau et al. 2008).

#### 7. Can by-products be removed during infiltration?

The formed bromate is not removable under oxic conditions which may prevail beneath infiltration ponds during short subsurface passage. However, in laboratory experiments the concentration decreased in anoxic soil columns by 60 % within 10 - 13 days. Most probably, bromate removal follows similar mechanisms as denitrification, and thus only occurs in presence of a bioavailable carbon source (BDOC) for heterotrophic microorganisms (Kirisits et al. 2001). Taking in account, that for oxidation + MAR the BDOC would be removed under oxic conditions in the first meters of subsurface passage and no BDOC would be left in the anoxic zone, a breakthrough of bromate into the raw water for drinking water production is very likely. Therefore the oxidation step needs to be handled with care to avoid/limit the bromate formation.

For NDMA degradation in the subsurface could not be assessed as no NDMA was found to be formed above the limits of quantification. Data from the EU funded RECLAIM WATER project showed, that NDMA is completely removed after groundwater recharge (Krauss et al. 2008). Nevertheless, under high infiltration rates NDMA can enter the groundwater (Haruta et al. 2008). (Zhou et al. 2009) found increased NDMA concentrations even in a 50 m deep well in a sandy aquifer after unintended groundwater recharge but no increase when infiltration basins were used.

#### 8. Has the treatment an impact on toxicological parameters?

As ozonation might produce unknown harmful oxidation by-products and transformation products, several series of samples before and after treatment with ozone and SSF/soil columns passage were taken. For genotoxicity (Ames/Salmonella microsome assay + Micronucleus assay) all tested samples were negative, thus no toxic effect could be observed. Cytotoxicity was assessed by measuring the generation of reactive oxygen species (ROS), which causes cell damage. One ozonated sample but also some effluents of the SSF without any ozone treatment showed a ROS-induction. Thus, no systematic cytotoxic effect due to ozonation was identified.

To conclude: No systematic effect of ozonation on the chosen toxicological test protocols was observed.

As one general question the usefulness of toxicity test for trace organics related toxicity assessment is uncertain from our point of view. Health related limits for trace organics include safety factors of 10 or more and thus even at concentrations at e.g. 500 % of the (drinking water) limit value for a single compound a toxicity test most probably will not show any effect. To overcome this drawback detailed studies on ecotoxicity are planned together with the TU Berlin and Berlin Water Company within two KWB research projects starting end 2011.

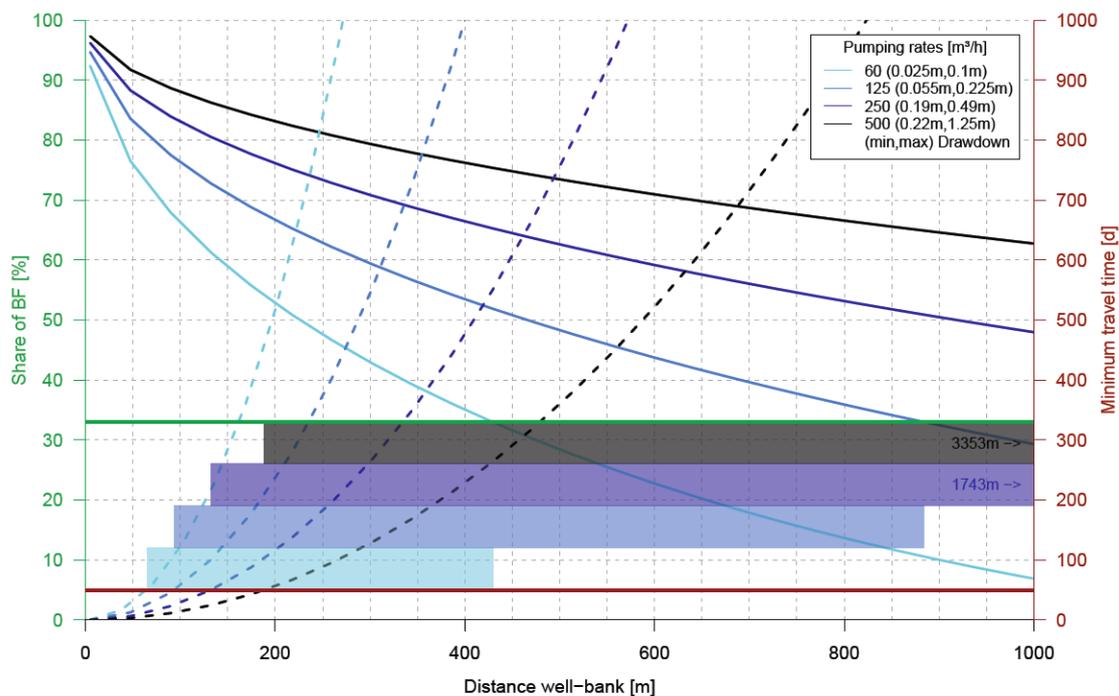
### **2.4 Searching a site for your field study (or full scale application)**

For the planned field study in OXIRE3 three possible sites were checked regarding their suitability as field site. Even though we concluded, that none of the sites was suitable, we identified several pre-requisites for such a site.

#### 9. What hydrogeological setting should be present?

First of all, sufficient land needs to be available in the size of the infiltration ponds (roughly 0.2 - 4 m<sup>2</sup> per m<sup>3</sup> to be infiltrated per day; (DVGW 2007) and for installation of

the production wells in the surroundings. For MAR an unconfined aquifer which enables unsaturated and saturated flow within a range of hydraulic conductivity values between  $10^{-2}$  m/s to  $10^{-4}$  m/s (recommendations from (Grischek et al. 2010) for bank filtration). The ambient groundwater should not be saline (Dillon et al. 2002) and the possibility of dissolution of salts (e.g. chloride, sulphate) or reduced species such  $Mn^{2+}$  or  $Fe^{2+}$  need to be assessed as well (DVGW 2007). The aquifer material should be relatively homogeneous without silt or clay layers. Recommended are quartz-rich, unconsolidated sediments. Generally, prior to field studies or full scale application hydrogeological exploration including drilling, pumping test and hydraulic modeling should be conducted (DVGW 2004). The groundwater level needs to be considered as it drives the cost for the installation of wells and as well the energy demand for pumping (s. Figure 1). The aquifer should be unconfined or protected by a thin layer (< 2-5 m) of low permeability (Grischek et al. 2007). The distance between infiltration pond and production well will primarily depend on the necessary travel time. For riverbank filtration, where pathogen removal is one of the primary targets, a minimum travel time of 50 d has been defined. Figure 2 shows, how for a given bank filtration setting (high hydraulic conductivity, moderate ambient base flow and no clogging) the minimum travel time is influenced by pumping rates and distance between bank and well.



**Figure 2: Nomogram for scenario 1: high hydraulic conductivity, moderate ambient baseflow, no clogging (from Grützmaier et al. in prep.).**

10. Which source water quality should be available for a field study? For which water qualities could oxidation & MAR potentially bring benefits?

During the search for a suitable site for pilot studies it became obvious that not at all sites water of specific quality is available to produce useful results for the process combination ozonation + MAR. In return, this may indicate for which water qualities oxidation & MAR could potentially bring advantages compared to other treatment methods.

First of all the source water should bring a need for advanced treatment, e.g.

- Elevated DOC values which are supposed to be reduced. One reason could be the limitation of disinfection by-product formation; e.g. for Germany the DOC level for application of chlorine dioxide should be < 2.5 mg/L (DVGW 224)
- Necessity to remove of odour and colour
- Elevated trace organic contents which are not (completely) removed during subsurface passage e.g. carbamazepine and thus are found in the drinking water (see also Table 1).

Unfavourable conditions are:

- Presence of saline groundwater as it will deteriorate the produced water quality,
- High bromide concentrations as the bromate formation increases
- DOC with more aliphatic than aromatic character: Aliphatic compounds have a lower reactivity towards ozone, thus the demand for ozone increases. The energy demand to achieve some DOC removal rises and the formation of bromate concentrations is very likely. Water with a specific ultraviolet absorption (SUVA) of > 2 mg/L\*m (e.g. surface water in Berlin) shows a high ozone consumption while a tested groundwater with a SUVA of ~1.2 mg/L\*m showed only marginal reactivity to ozone and a very high bromate formation.
- High concentrations (> 10 mg/L of suspended solids) lead to rapid clogging of the infiltration ponds. In Berlin, the target value before infiltration is 2 mg/L TSS. In case of overstepping additional pre-treatment (e.g. micro sieving or dual media filtration) before infiltration is required.

11. Which effect would ozonation of the artificially recharged water at Tegel waterworks (Berlin) have on raw water quality?

To estimate the effect of ozonation of the water for artificial recharge (16 % of all water recharged in the waterworks' catchment) on the concentrations of carbamazepine and DOC in the raw water for drinking water production, a calculation based on mixing of different water sources (bank filtrate, recharged water, natural groundwater) was carried out.

The following assumptions were made for this calculation:

- Share of bank filtrate + water from artificial recharge
  - Case A: 80 % (64 % BF + 16 % AR)
  - Case B: 70 % (54 % BF + 16 % AR)
- DOC levels and degradation:
  - ambient groundwater: 2.5 mg/L
  - Lake Tegel 7 mg/L
  - Degradation during BF and AR: 30 %
  - Degradation for ozonation + AR: 50 %
- Carbamazepine
  - Lake Tegel: 500 ng/L
  - ambient groundwater: 0 ng/L
  - Degradation during bank filtration: 80 % (anoxic conditions)
  - Degradation during artificial recharge: 0 % (fully oxic conditions)

- Removal in the artificially recharged water via ozone: 100 %
- Bromate: worst cases scenario with 10 µg/l bromate for ozonated water

The outcomes of these calculations are summarized in Table 6. The calculated raw water concentration for carbamazepine without ozonation is in the range of the measured values in WW Tegel (120 -140 ng/L). Ozonation of the water for artificial recharge reduces the calculated concentration by 49 % and 56 % for case A or B respectively. For bromate only concentrations below 2 µg/L are expected in the raw water, if 10 µg/l are formed via ozonation. Even at bromate levels up to 60 µg/L in the ozonated water, less than 10 µg/L would occur in the raw water. Restricting the bromate formation during ozonation would reduce the risk of bromate occurrence in the production well to negligible levels. The DOC concentration is expected to change only slightly (5 %).

**Table 6: Calculated raw water quality for WW Tegel with and without ozonation of the water for artificial recharge (Case A+B: quality in production well)**

	<b>Carbamazepine</b> ng/L	<b>Bromate</b> µg/L	<b>DOC</b> mg/L
<b>Lake Tegel</b>	500	0	7
<b>Case A</b>	142	0.0	4.42
<b>Case B</b>	132	0.0	4.18
<b>Case A + Ozone</b>	68	1.6	4.20
<b>Case B + Ozone</b>	58	1.6	3.96

## 2.5 Preparing the control of work force (Assessing the biological activity)

The degradation processes in MAR are driven by the microbial community present. The (mostly heterotrophic) bacteria live in biofilms attached to filter or aquifer material and metabolize the delivered organic carbon and electron-acceptors (O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and other). As a result of their activity redox conditions change and compounds such as DOC, nitrate and most trace organics are removed. (The removal of trace organics in the subsurface could theoretically also be caused by adsorption or chemical transformation. Most authors, however, agree that biodegradation is the major removal process as those substances present in surface water will usually be hydrophilic and not readily transformed by chemical reactions). In many studies focussed on trace organics the microbial community, its composition, its density, or its activity is not addressed or only indirectly observed via substrate consumption. Advances in microbiology and especially biomolecular methods offer a broad variety of approaches to include microorganisms in the study. Some selected methods are recommended (s. D 2.2) for future projects to answer the following two questions.

### 12. How to count your microbial co-workers?

Counting bacteria in soil or filter material samples bring two main challenges: the sample preparation and the counting method itself. As the bacteria are attached to surface of sand grains and other solid matter, they need to be detached for further analysis. This can be done with special extraction kits. Another approach is the buried slide technique:

A glass microscope slide is embedded in a soil or filter compartment. The microorganisms attach and grow on the glass surface and thus can be removed from the sampling spot and analyzed afterwards.

Both methods are applied, but have its specific disadvantages: 1. Extraction method: the detachment is not always fully complete. 2. Buried slide method: since soil microorganisms grow in pores or aggregates, this flat area might not give a representative overview. The counting itself can be done via fluorescent microscopy with DAPI or Acridine Orange, which are useful for the direct count technique. This will result in the count of the total (alive and dead) organisms per gram of dry soil.

Another approach to compare the abundance of organisms in different filter/soil depth is the denaturing gradient gel electrophoresis (DGGE), which is, however, not quantitative as standalone method. Therefore, it should be used together with quantitative PCR (qPCR). The combination of DGGE + qPCR gives quantitative information about the composition of the microbial community and is thus very useful to investigate the influence of external factors (e.g. soil columns run under different temperatures or nutrient status) on the number of different species within the microbial community.

### 13. Are the microbes working or maybe taking a rest?

Most physiological methods are useful to analyse organisms with a specific physiological function. Those organisms can be cultured under specific conditions. Nevertheless, this cannot be applied for column studies where the amount of organisms in a certain depth in the column will be coupled to the attenuation of organic compounds on the same position. Furthermore, it would be too detailed to couple specific species to the degradation of specific substrates.

Therefore, it is recommended to describe the activity of the microbes by LIFE/DEAD staining, to quantify the amount of living cells. In combination with substrate degradation assessments by BDOC (or AOC) measurements and direct counts of organisms stained with the CTC redox dye (an indicator for respiratory activity) the microbial activity in certain column depths can be compared. The quantification of ATP (Adenosine triphosphate) to assess the activity is not recommended as it is known to be quite unreliable.

## Chapter 3

# Opportunities for redox control and optimization at AR-ponds (WP 3)

### 3.1 Preliminary question

14. Why should we try to influence the redox conditions?

Biochemical reactions are influenced by redox conditions, but in turn they also influence them as microbial activity leads to a depletion of electron donors (O, NO<sub>3</sub><sup>-</sup>, Mn, Fe). The presence of oxygen is the most important environmental parameter for microorganisms, which are divided into aerobic, facultative anaerobic and obligate anaerobic populations. Thus, the removal of several substances in the subsurface is redox-dependant. For instance, cyanotoxins, ammonium and DOC are best removed under oxic conditions, while nitrates, THMs and some pesticides are best removed under anoxic or anaerobic conditions (D 3.1). Thus, to control the desired subsurface removal processes for a given water quality, the control of redox conditions seems a promising method.

### 3.2 Redox dependence on the degradation of general water quality parameters

15. Which general water quality parameters are redox indicators?

Most water quality parameters are, to some extent, related to the redox potential. Among the general water quality parameters, some major ions are indicators of a redox zone. Dissolved oxygen indicates an oxic zone, while nitrate indicates an anoxic zone and species like iron, manganese or hydrogen sulfide indicate anaerobic conditions.

In turn, redox conditions also influence the chemical reactions and the removal of several water quality parameters (DOC, ammonium, nitrate/nitrite, iron and manganese, trace organics...).

16. Which redox zonation is favourable for DOC removal?

DOC is in most cases an electron acceptor and can be oxidized (only at very low redoxpotentials DOC can be reduced to e.g. methane) – hence, in general, oxic conditions are favourable for DOC removal. It must be noted that DOC is also degraded under anoxic or anaerobic conditions, but to a lesser extent and at lower rates. Table 7 and Table 8 summarize the time-dependent removal of major substances under respectively oxic and anoxic/anaerobic conditions.

### 3.3 Redox dependence of trace organic removal / degradation

17. For which trace organics may removal be optimized via redox control?

Among the priority trace organics (Table 2) several compounds (e.g. carbamazepine, sulfamethoxazole) are highly redox sensitive. For MTBE and iopamidol, the dependence on redox conditions is less marked, with improved removal efficiencies under anoxic and anaerobic conditions respectively. Finally, other substances, such as diclofenac, iopromide or some other types of NDSA are not redox sensitive (Schmidt et al. 2007).

Table 7 and Table 8 show that, for all these substances, long residence times under given redox conditions may significantly improve the removal efficiency.

18. Which redox zonation is favourable for trace organic removal?

This depends on the type of substance and in many cases the redox zonation is exclusive (i.e. only one type of conditions is favourable for an efficient removal). Table 7 and Table 8 summarize the time-dependent removal of the main trace organics under oxic and anoxic/anaerobic conditions respectively.

Generally, maximum benefit for aerobic subsurface passage is reached after 30 d, for anoxic / anaerobic subsurface passage after 100 d. However, already 15 d of aerobic and 2 d of anoxic / anaerobic passage lead to substantial removal or redox-sensitive substances or substance groups.

**Table 7: Time-dependent removal under oxic conditions**

Substance / substance group	Residence time under oxic conditions		
	for up to 25 % removal	for up to 50 % removal	for 99 % removal
cyanobacterial toxins (microcystins)	no information	no information	> 9 d*
ammonium	> 3 d***		
DOC	> 2 d**	> 30 d** (for high DOC not possible)	not possible
some pesticides (ureas, phenoxy-herbicides)	no time-dependency reported		
<i>PhACs and x-ray contrast media</i>			
clindamycine	> 2 d***	> 3 d***	> 25 d***
diclofenac	> 10 d***	> 23 d***	> 200 d***
iopromide	no information	> 7 d <sup>+</sup>	no information
phenazone	no information	> 2 d <sup>+</sup>	no information
propyphenazone, AAA, AMDOPH, AMPH, DP, FAA	no time-dependency reported		
other trace organics (1,7-NDSA, 2,7-NDSA)	no time-dependency reported		
inorganic trace elements	Fe and Mn will be mobilized as soon as anoxic conditions prevail (and Fe and Mn are available in the sediment)		

\* (Grützmacher et al. 2007)

\*\* (Lenk et al. 2005)

\*\*\* NASRI data from Berlin ((Pekdeger et al. 2006) and Wiese et al. 2010))

<sup>+</sup> (Stuyfzand et al. 2007)

**Table 8: Time-dependent removal under anoxic to anaerobic conditions**

Substance / substance group	Residence time under anoxic to anaerobic conditions		
	for up to 25 % removal	for up to 50 % removal	for 99 % removal
nitrate			> 2 d (> 97 % removal)*
disinfection by-products (THMs)	< 20 d**	> 20 – 40 d**	> 100 d**
some pesticides (triazines)	no time-dependency reported		
<i>PhACs and x-ray contrast media</i>			
sulfamethoxazole,	> 20 d***	> 40 d***	> 80 d***
carbamazepine,	no time-dependency reported		
AOI	no time-dependency reported		
highly soluble chlorinated hydrocarbons (PCE)	no time-dependency reported		

\* NASRI data from Berlin (Grützmacher et al. in prep).

\*\* adapted from Schmidt et al. (2003)

\*\*\* NASRI data from Berlin (Wiese et al. 2010)

### 3.4 Options for influencing the redox zonation

#### 19. How to enhance/prolong oxic conditions?

Enhancing or prolonging oxic conditions requires to establish the highest possible dissolved oxygen content in the recharged water, or to supply more oxygen to the oxygen-depleted subsurface. Three major methods can be distinguished:

- ensuring high flow rates by modifying the pumping regime – hydraulic control of the subsurface passage;
- forcing unsaturated conditions – additional oxygen input from the unsaturated zone surrounding the infiltration ponds ;
- oxygen enrichment of surface water – oxygen input via the infiltration pond and the hyporheic zone.

#### 20. How to enhance/prolong anoxic / anaerobic conditions?

On the contrary, enhancing or prolonging anoxic or anaerobic conditions requires to prevent massive migration of oxygen in the subsurface, or to ensure that other electron acceptors than oxygen are used. These methods focus, on the contrary to the above mentioned methods, on:

- limiting flow rates during filtration – hydraulic control of the subsurface passage;
- manipulating the filtrated water to reach anoxic or anaerobic conditions – e.g. by adding electron acceptors (DOC).

#### 21. Which techniques are established or seem applicable?

Three techniques are to date commercially available:

- Bioxwand® (“biox-wall”): this technique is based on the injection of oxygen via gas injection wells to act like a wall or barrier to which the subsurface water is exposed. By flowing through this wall, the water is oxygenated and aerobic processes (e.g. nitrification) occur. Similar to the redox zonation during infiltration the oxygen content downstream the Bioxwand® will decrease and anoxic/anaerobic zones follow the aerobic zone. This allows nitrification and subsequent denitrification.
- Vyredox: the basic principle of Vyredox is to inject aerated water into an anaerobic aquifer. The aerated water is injected by wells arranged circularly around the water production well, enabling an oxidation of various substances, e.g. Fe and Mn.
- Nitredox: here anaerobic water is injected prior to the Vyredox process. This is only required if there are some issues with nitrate/nitrite contents in the subsurface water. Then, a secondary “barrier” of wells disposed circularly around the Vyredox barrier is installed, and used for the injection of anaerobic water. In this anaerobic zone, nitrate and nitrite are reduced by bacteria.

### **3.5 Key results from short term column experiments and redox modelling**

22. Do redox conditions achieved during short-term column experiments resemble those obtained from field settings?

Column experiments with untreated sand from the AR pond at Lake Tegel yielded constantly oxygen-free conditions after one day (35 cm of sand passage). During the NASRI project the same was true for samples taken in 50 cm depth and 0.5 d travel time under saturated conditions during summer. However, as clogging proceeded, unsaturated conditions developed beneath the infiltration pond, leading to re-oxygenation of the infiltrating water. This cannot be simulated with the chosen column experiment set-up. In addition, during winter oxygen was not completely consumed 50 cm below the infiltration pond. The column experiments carried out at 20°C to 25 °C therefore only represent the summer conditions before relevant clogging has occurred.

23. Does ozonation of the inlet have an influence on redox conditions in the subsurface?

The column experiments with untreated sand from the AR pond at Lake Tegel did not show an impact of ozonation on the redox conditions in the column outlet. The pilot scale experiment carried out within OXIRE2, however, showed a clear break-through of oxygen (average oxygen concentrations 11 mg/L) as soon as the inlet was ozonated (oxygen inlet concentrations constantly around 20 mg/L). There are two reasons for this: firstly, the column experiments were carried out at 20 - 25 °C, whereas the temperatures in the pilot scale experiments were 10.8 °C in average (previous investigations at Lake Tegel had shown that below 14 °C oxygen depletion below the infiltration pond is strongly retarded due to less biological activity in the uppermost layers). Secondly, the ozonation of the inlet was discontinuous in the column experiments so that the inlet oxygen concentrations were considerably lower in average than during the pilot scale experiments.

We therefore assume that ozonation of the inlet will probably influence the redox conditions in the upper layers of the infiltration basin and will lead to aerobic conditions

also at higher temperatures. In combination with the pilot scale experiment these results show that aerobic conditions in the first decimetres of infiltration could be ensured through oxygen super-saturation by ozonation, however, the oxygen content will be sensitive to high temperatures, which are difficult to control in a field setting.

24. Which impact does the POC present in the sediment / filter sand have on redox conditions?

The particulate organic carbon influences the redox conditions tremendously (s. question 22). The columns filled with untreated disturbed sand samples ( $C_{org}$ : 0.19 %) from the infiltration pond reached denitrifying and even sulphate reducing conditions within 3-4 d (ORP < -100 mV). Even during operating of the columns with high dissolved oxygen concentrations (12 to > 20 mg/L) no increase of oxygen in the effluent occurred within several days. On the contrary, a column filled with sand pre-treatment with 550°C ignition ( $C_{org}$ : 0.06 %) remained in oxic conditions with an ORP around 300 mV.

However, the sheer concentration of POC will not be the only key driver – its bioavailability is an additional important factor. In the column experiments the bioavailability of POC is most probably also affected by the way of sampling, as no core sampling was conducted for the sediment from the infiltration pond. For further investigation POC degradation tests with undisturbed samples are recommended. For infiltration ponds it might be useful to assess an “oxygen consumption potential” and “denitrification potential” to predict the behaviour of a field or full scale installation. The “oxygen consumption potential” would mean: How much oxygen is consumed during a defined filtration length or time (or same for nitrate). Both could be done at lab scale with column operated with tap water and defined oxygen/nitrate concentration in the influent.

25. Can we model redox processes in a soil column?

Modelling of redox process is a challenging task, as it needs to include water chemistry, geochemistry and microbial processes. With the data from the column experiments (s. question 22 + 23) a coupled reactive transport modelling was carried out. The hydraulic parameters (pore-velocity, dispersivity) as well as the cation exchange capacity were assessed with a lithium bromide tracer. The column which was pre-treated via ignition (550°C), showed a reduced cation exchange capacity. This is most probably related to the loss in organic matter.

The redox model included a biodegradation model based on a combined approach of enzyme kinetics and thermodynamics. The degradation of organic matter is solved by enzyme kinetics and the accompanied electron transfer and electron balance is controlled by thermodynamics (using PHREEQC). Altogether the model could predict the time-dependend development of the following parameter with an acceptable accuracy showing the same trends as the lab data: dissolved oxygen, nitrate and redox potential had the best correspondence between model and data, while pH and ammonia showed strong variations.

26. What needs to be done in order to use the model for predicting redox conditions a given field site?

As temperature has been shown to be a key parameter for the velocity of oxygen depletion in the subsurface, the model needs to be upgraded by including temperature

dependency based on experimental data. This means a set of further laboratory experiments in order to calibrate the model.

Then, the model could be used to assess redox conditions at a new AR site with available information on: bulk density, effective pore volume, organic carbon content, cation exchange capacity, water chemistry of the inlet (main anions & cations, pH, T, oxygen content, nitrate, nitrite, ammonium). For given AR sites the model might be used to assess the influence of operation (water level in pond) and maintenance (cleaning intervals) on predominant redox conditions.

## Chapter 4

### Draft decision tree for new sites

For new MAR sites (or existing sites considered for an upgrade with trace organic removal) an easily applicable decision tree could help to assess the potential for substance removal of oxidation together with infiltration. A draft decision tree has been developed within OXIRE2, but will be further developed in the project OXIMAR.

The proposed decision tree will include three main areas (s. Figure 3). As first step the applicability of MAR and the hydrogeological prerequisites need to be assessed. A draft proposal of the domain “trace organics” and “DOC” is given in Appendix A.

#### Hydrogeological prerequisites:

- Is MAR applicable at the foreseen site?
- Which distance between infiltration and production well is necessary to achieve a minimum travel time?
- How high will the share of infiltrated water be in the production well?
- Hydrogeological conditions, etc.

#### Enhancement DOC removal via oxidation:

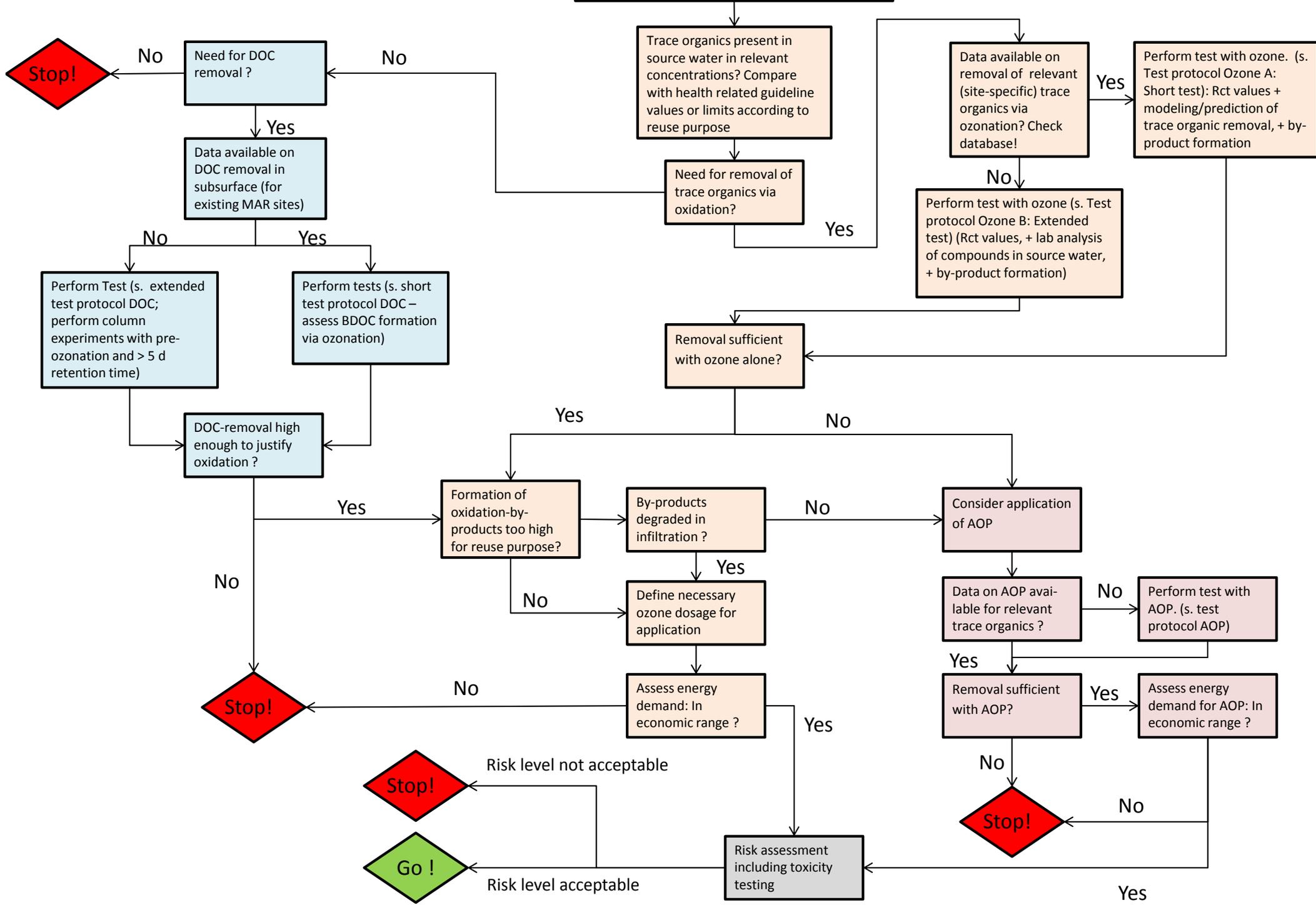
- Which DOC level is targeted for the product water?
- How much DOC removal is achievable with oxidation and MAR?
- Formation of unwanted by-products?

#### Removal of trace organics via ozonation:

- Which trace organics with breakthrough potential are present?
- Which are removable via ozonation?
- Are there unknown compounds?
- Is there a need for additional lab tests?
- Formation of unwanted by-products?

Figure 3: Main domains of the decision tree for new sites with oxidation and MAR

# Evaluation of trace organics and DOC removal via Oxidation and MAR



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