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DOC and Trace Organic removal via ozonation & underground passage – expected benefit and limitations

Project acronym: OXIRED

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Title

DOC and Trace Organic removal via ozonation & underground passage – expected benefit and limitations

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Abstract

The project OXIRED was initiated to assess the potential of a combination of natural systems such as bank filtration (BF) and artificial recharge (AR) and oxidation processes in order to improve the degradability of DOC and the removal of trace organics during water treatment.

In this literature study, treatment schemes, which combine subsurface passage with oxidation processes, were evaluated with regard to the potential removal of DOC and trace organics, by theoretical considerations and case study analyses. The objectives were i) to estimate the degradation of bulk organic matter and trace organics in such combined systems, ii) to assess the potential for toxic by-products and iii) to describe different possible schemes combining natural systems (BF & AR) and oxidation processes.

Available data generally shows good removal of the substances identified as persistent during BF & AR by oxidation processes. Carbamazepine, for example, is poorly degradable during bank filtration, but ozonation leads to a transformation of more than 97%. If ozonation alone does not suffice, advanced oxidation processes may enhance the transformation. E.g. literature gives a values of < 50% removal of Iopamidol by ozonation. However, transformation increases up to 88% using advanced oxidation processes, such as O_3/H_2O_2 and O_3/UV.

Investigations on the formation of possible toxic by-products have shown the general possibilities to control the formation of bromate by decreasing the pH, avoiding free dissolved ozone in the reactor and/or by adding H_2O_2. Only a low risk of exposure of the potentially forming nitrosamines in drinking water after artificial recharge could be identified. Especially the cancerogenic metabolite NDMA is degraded during subsurface passage.

Three reference treatment schemes were identified:

- A: surface water is treated via oxidation before infiltration into artificial recharge ponds.
- B: a river bank filtration with short retention times (<5 days) is used as a pre-treatment step before the successive oxidation and artificial recharge (AR).
- C1/C2: oxidation is applied subsequent to subsurface passage after bank filtration and artificial recharge.

Due to the possible formation of toxic by-products and the increased assimilable DOC in scheme C (Examples for C1 Mülheim Styrum-East and Le Pecq Croissy & C2 Prairie Waters Project and the Bi´eau Process) a post-treatment including disinfection after oxidation is necessary.

Additional post-treatment in schemes A (implemented at Mülheim Dohne) and B depends on the redox conditions and the travel times during the subsurface passage. However, although there is a lack of practical data, the enhancement of BDOC via oxidation prior to the underground passage seems theoretically more promising than the reverse configuration.

It is therefore recommended that any further experimental program in OXIRED should focus on the schemes A and B and include a cost-benefit analysis of the additional first BF step.

Acknowledgements

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We especially thank all involved persons at the technical divisions and research and development departments as well as the technical committee for the valuable discussions and provided information.

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Thank you!

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Glossary

AR	Aquifer recharge
BAC	Biological activated carbon filtration
BDOC	Biodegradable DOC
BF	Bank filtration
DMS	N,N-Dimethylsulfamid
DOC	Dissolved organic carbon
degradation	Removal of substances via biological processes
NDMA	N-Nitrosodimenthylamin
POC	particulate organic carbon
removal	All processes but mixing/dilution which result in a decrease of concentration (degradation, transformation, adsorption)
STP	Sewage treatment plant
TOC	Total Organic Carbon
transformation	Changes in chemical structure of substances

Chapter 1
Introduction

In the last two decades more and more polar trace organics such as pharmaceuticals, pesticides or x-ray contrast media have been detected in the water cycle due to widespread use and advances in analytical chemistry. This has lead to scientific as well as public debates about the safety of direct or indirect drinking water production from surface waters. Especially in (indirect) water-reuse systems, that often include a step of subsurface passage (e.g. aquifer recharge, soil-aquifer-treatment), persistent organic substances (trace organics or parts of the bulk DOC) may accumulate and endanger the sustainable functioning of the system.

Previous studies have shown that DOC degradation in BF systems may reach up to 50 %, but is often less (Ziegler 2001). The IC-NASRI project Wiese et al. (2009a) showed that in BF and AR systems used for drinking water production in Berlin, 8 trace organic substances out of the 19 investigated were well removable (> 75 % removal), irrespective of the redox zone or under oxic conditions. 11 substances showed either partial removal (30 % – 75 % removal) or persistence (< 30 % removal). Although it was shown that the decrease in concentration was not due to mixing, a differentiation between (bio-)degradation, transformation or adsorption was not possible.

A promising approach to increase the removal of organic substances are pre- or postoxidation processes, such as ozonation or advanced oxidation processes. The KWB project PILOTOX (Bahr et al., 2005) analysed the transformation of organic substances by ozonation of sewage treatment effluent. The results show the transformation of persistent trace organic substances, e.g. carbamazepine and estron, already at low ozone concentrations.

Within the framework of the ongoing OXIRED project, the removal of organic carbon and specific trace organics in different combinations of BF/AR and oxidation systems will be investigated. As the particulate organic carbon (POC) is removed in the first few meters of infiltration these investigations focus on trace organic and the bulk DOC removal only.

This report gives a preliminary analysis of the expected benefits and limitations on the basis of available literature, and reviews existing drinking water production schemes using similar processes. Recommendations will be given to choose the most promising combinations between oxidation and BF/AR for the experimental trials.

Chapter 2
Removal of organic compounds and trace organics during BF and AR

2.1 Behavior of dissolved organic carbon (DOC) in BF and AR

Investigations from different sites worldwide show a wide range of removal of DOC during subsurface passage: DOC removal during bank filtration ranges between 24 % and 50 % (Drewes and Summers, 2002; Jekel, 2006; Kühn and Müller, 2000; Ziegler, 2001). The following table 1 summarizes the results of several sites, most in Germany.

Table 1- Removal of dissolved organic carbon by bank filtration (Grützmacher et al., 2009)

site	DOC surface water	DOC well	removal	Travel time/distance or comments
	[mg/L]	[mg/L]	[%]	
BF River Rhine (Brauch et al., 2000)1)	2.5 to 2.7	*1.3*	50	including dilution
BF River Rhine (Denecke, 1997)1)	3.1 to 3.4	*1.7 to 1.9*	44	
BF Tegel + Wannsee, Berlin (Jekel, 2006; Wiese and Nützmann, 2009)	7.1 to 7.2	4 to 5	25 to 44	weeks to months
BF Tegel + AR Tegel, Berlin (Grünheid et al., 2005)	7.3	4.2 to 4.7	35 to 42	BF: up to 4 months (anoxic) AR: up to 50 days (aerobic)
BF River Elbe (Kühn and Müller, 2000)	6.2	4.5	27	
BF River Rhine (Kühn and Müller, 2000)	2.9 to 6.0	1.1 to 2.7	50	DOC decrease in surface water from 1975 to 1997
33 BF sites across Europe (Lenk et al., 2005)	1.4 to 9 (4.4)	0.2 to 5.1 (2.1)	14 to 84 (46)	80-90% bank filtrate share in wells, average in brackets
BF River Elbe (Ludwig et al., 1997) 1)	6	*3.9*	35	
BF River Neckar (Simon & Kußmaul 1996) 1)	3 to 5 (*4*)	*2.4*	40	after 1 m (50% in total) average in brackets
BF Tegeler See (Ziegler, 2001)	8.5	5.4, 5.2	37, 39	after 32 m, 80 m
BF Müggelsee (Ziegler, 2001)	6.9	4.3 to 4.9	29 to 35	
BF River Ohio (Weiss et al., 2002)	2.7	*0.7 to 1.1*	58 to 74 (66)	61 to 177 m, 3 to 19 d average in brackets
BF River Wabash (Weiss et al., 2002)	4.1	*0.5 to 1.5*	64 to 88 (76)	27 to 122 m average in brackets
BF River Missouri (Weiss et al., 2002)	3.6	*2.3*	36	37 m

1) adapted from (Ziegler, 2001) 2) calculated values in italic

The removal of DOC depends on the composition of the infiltrated water and the different fractions of DOC. Figure 1 shows a LC-OCD (Liquid chromatography – organic carbon detection) chromatogram of samples from a bank filtration site at Lake Tegel (Berlin).

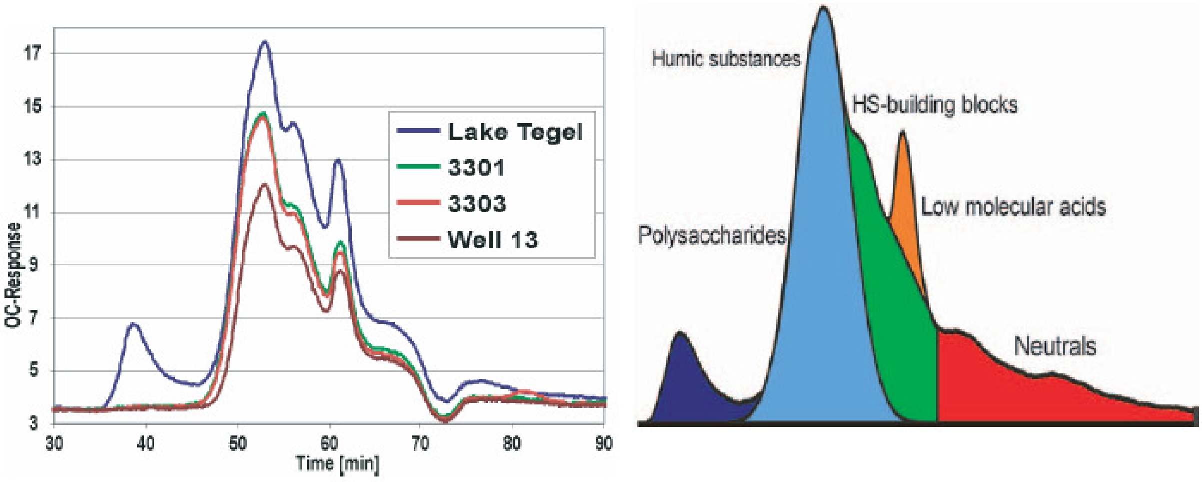


Figure 1- LC-OCD chromatogram of samples from a bank filtration site at Lake Tegel, Berlin (Grünheid et al., 2005)

Starting from small retention times at the left the first peak represents the fraction of biopolymers (easily bio-degradable). The second peak represents the fraction of humic substances (HS) and the humic substances’ building blocks are represented by the a small peak on the right shoulder of the HS peak. The following peak represents a fraction of low molecular weight acids. The latter three fractions are only partially bio-degradable, but usually represent the major DOC fractions.

Figure 1 shows that the biopolymer fraction is clearly visible in the Lake Tegel sample. It is no longer present in the samples from observation wells 3301 and 3302 (average travel times of about 80 d) and from the production well (significant amount of mixing of older bank filtrate and landside groundwater, travel time from nearest bank about 140 d). For the other three fractions only little changes are observed.

The readily biodegradable fraction of DOC (BDOC) is highly variable. It is usually degraded within the first meters of infiltration where conditions are still oxic (Wiese et al., 2009a). Here, 25-30% of the DOC removal can be achieved within travel times of some days or a few weeks. A slower DOC removal is detected under anaerobic conditions. In Berlin, the water from the production wells (figure 1) is a mixture of young and old infiltrated water and is also affected by mixing with ambient groundwater (Jekel, 2006).

A statistical analysis of the results from NASRI Wiese et al. (2009b) did not indicate a significant difference in removal between oxic and anoxic/anaerobic conditions. This may be due to the fact that all samples from observation wells – also those classified as anoxic/anaerobic – are likely to have undergone a short aerobic passage directly after infiltration.

Most publications dealing with DOC removal during subsurface passage have not taken DOC fractions of different biodegradability into account. Lenk et al. (2005), for example, developed different non-linear regression model formulas based on surface water concentration and retention time to calculate bulk DOC elimination during bank filtration for different local conditions. The equation for high DOC surface water concentrations (5.3 – 9 mg/L) for all redox zones reads as follows (variance: R^2= 0,89):

(eq. 1) $Y= -3.236+2.350*\ln(X_1)+0.320*\ln(X_2)$

Y = DOC elimination [mg/l]

X_1 = DOC concentration in surface water [mg/l]

X_2 = retention time in the subsurface [d]

Figure 2 shows the corresponding graph for a DOC surface water concentration of 7.1 mg/L as observed in average in Berlin during the NASRI project (2002 – 2005). Wiese et al. (2009b) calculated a similar regression curve for the oxic bank filtrate concentrations measured during this time, which is also given in Figure 2. These investigations show that even under the relatively long travel times as encountered in Berlin (100 – 200 days) DOC removal will not exceed 35 %, leaving a residual of 4-5 mg/L. A further reduction is due to mixing with ambient groundwater that exhibits geogenic DOC values between 2.5 and 2.9 mg/L.

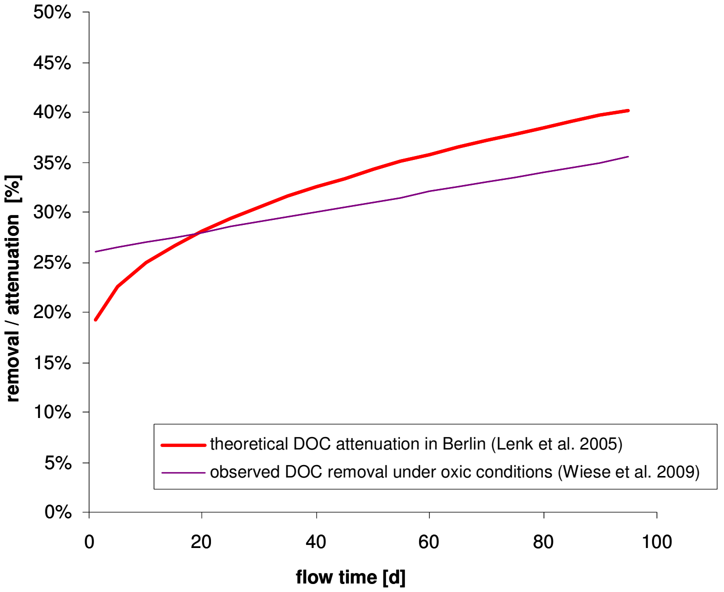


Figure 2: Theoretical DOC attenuation in Berlin according to the formula by (Lenk et al., 2005) and regression curve of removal observed at the field sites during the NASRI project (Wiese et al., 2009a).

- ⇨ DOC is only partially removed by saturated subsurface passage (in Berlin 26 – 35 %)
- ⇨ a high share of biodegradable DOC (BDOC) is decisive for maximum removal
- ⇨ DOC in Berlin’s surface and groundwater consists to a relevant share of poorly bio-degradable humic substances, their building blocks and low molecular organic acids (70-80%)
- ⇨ Mixing is a relevant process and has to be taken into account in field site investigations

2.2 Behaviour of organic trace pollutants during bank filtration and aquifer recharge

Trace organic compounds in surface water may originate from different sources. Due to agricultural land-use in the catchment, pesticides are emitted into lakes and rivers, which are used for drinking water production. The use of x-ray contrast media and pharmaceuticals in medicine leads to an emission of trace organics to surface waters via the discharge of STP effluents.

The intermediate report of NASRI and the results from other bank filtration sites showed that many factors influence the elimination of substances in underground. Biological degradation processes mainly drive elimination and the main impact factors are redox conditions and residence time (amongst others: (Schmidt, 2007; Stuyfzand et al., 2007; Wiese et al., 2009b)).

For Berlin, for example, Grünheid et al. (2005) reported a removal of 60-70% AOI (adsorbable organic iodine) under primarily anoxic / anaerobic conditions (bank filtration site Lake Tegel), whereas no reduction was observed under aerobic conditions (artificial recharge site Tegel).

Processes that can lead to a reduction of trace organics' concentrations in the water cycle are (bio-) degradation, adsorption and dilution. Concentrations of polar and poorly/not biode-gradable compounds, such as EDTA, diclofenac, benzotriazole and carbamazepine will often only be reduced by dilution (Reemtsma et al., in press). Ternes et al. (2002) showed that no significant elimination of bezafibrate, clofibric acid, carbamazepine and diclofenac can be determined in batch experiments under natural aerobic and anoxic conditions. This indicates low sorption properties and high persistence of these substances with non-adapted microorganism.

In the IC-NASRI project different substance groups were classified according to their persistence in the subsurface if no dilution occurs (Grützmacher et al. submitted). Trace organic substances (disinfection by-products, pesticides, pharmaceuticals, endocrine disruptors, chlorinated hydrocarbons, aromatic hydrocarbons) were classified to show partial removal due to bio-degradation or adsorption (depending on substance and redox conditions) based on data from literature and the observations during the NASRI project. For most trace organics with exception of disinfection by-products and x-ray contrast media, aerobic conditions seem to favour removal. E.g. most antibiotics investigated during the NASRI project in Berlin were removed by > 96 % within the first few meters of infiltration (Heberer et al., 2002).

On the other hand degradation for some substances occurs only (carbamezepin) or preferentialyl (e.g. sulfamethoxazol, iopamidol) under anoxic/anaerobic conditions (Schmidt, 2005)

In the first phase of OXIRED 1 a priority list of 18 trace organic substances out of originally 300 substances was identified for further investigations (Wiese and Grützmacher, 2009). The compounds were classified according to the frequency of observed breakthrough or limited removal (< 25 %) in two publications (1. database on trace organics during AR and BF: (Schmidt, 2005), 2. (Stuyfzand et al., 2007)) and in the NASRI project (Wiese et al., 2009b)). In addition a weighting was applied by experts from Veolia Environnement and Berliner Wasserbetriebe on the relevance for their drinking water supplies (a combination of occurrence, average concentrations and removal by conventional drinking water treatment). The substances of 1st priority are MTBE, sulfamethoxazole, EDTA, ETBE and the sum parameter for iodinated x-ray contrast media AOI. Possible target substances of 2nd priority are carbamezepine, primidone, 1,5-NDSA, iopamidol, bentazone, 1,7-NDSA, 2,7-NDSA, atrazine, desethylatrazine, linuron, diuron, diclofenac and amidotrizoic acid. The complete table with the breakthrough potentials, the occurrence in managed aquifer recharge (MAR) and the relative elimination of nearly 40 substances are presented in table 11 in the appendix.

Table 2 shows the 18 substances classified as medium to high potential for breakthrough in BF/AR systems. These substances showed low removal < 25 % (Schmidt, 2005; Stuyfzand et al., 2007; Wiese et al., 2009a) in more than one study. Substances with medium or uncertain removal showed varying removal or the results depend on one study only (Wiese and Nützmann, 2006).

Table 2- Persistent substances with high, medium and uncertain potential for breakthrough in BF/AR systems ((Wiese and Grützmacher, 2009); **results from field site and lab trials not conclusive)

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

- ⇨ Trace organic substances show a large range of removal during subsurface passage (from below 1 % up to > 99 %).
- ⇨ Especially polar substances that are poorly biodegradable (e.g. x-ray contrast media) tend to be persistent in BF / AR schemes.
- ⇨ In the course of rising awareness and possibly increasing concentrations (due to higher share of reuse), measures should be taken to enhance the removal of persistent trace organic substances either at the source (additional wastewater treatment step) or by optimizing drinking water treatment.

Chapter 3
The transformation of DOC and trace organic substances by ozonation and advanced oxidation processes

3.1 Background of ozonation and AOP

Based on the fact, that some polar and persistent substances are not reliably removed via bank filtration and artificial recharge an advanced purification based on oxidation processes is one option to enhance the removal. The oxidation processes dealt with are ozonation and advanced oxidation process (AOP).

Ozone added to water can react directly with organic and inorganic compounds or indirectly after decay by the formation of OH-radicals (eq. 2 and 3). The OH^--ion initiates the decay of ozone in water. High pH values therefore enhance this reaction. The formed OH-radicals react very quickly with other water constituents.

(eq.2) $O_3 + OH^- \rightarrow HO_2^- + O_2$

(eq.3) $O_3 + HO_2^- \rightarrow OH\bullet + O_2^-\bullet + O_2$

The direct reaction of ozone with organic and inorganic compounds is very selective but slower than the indirect reaction. Ozone reacts with the functional groups of organic compounds, the double-bond structures and aromatic structures. The indirect reaction is quicker and non-selective (Schumacher, 2006). The type of reaction depends on the different constituents present which can promote or suppress this radical reaction (KWB, 2005). Generally, the direct ozonation is important if the radical reaction is inhibited or the water contains many substances, which terminate the radical chain reaction (scavengers). Main scavengers are HCO_3^-, CO_3^{2-}, PO_3^{4-} and humic acids (Gottschalk et al., 2000).

In advanced oxidation processes an enhanced formation of hydroxyl radicals is provoked, which have a higher oxidation potential and react faster with the most of organic compounds. The most common AOP are UV/H_2O_2, O_3/UV and O_3/H_2O_2 (perozone) given in Figure 3 (Gottschalk et al., 2000).

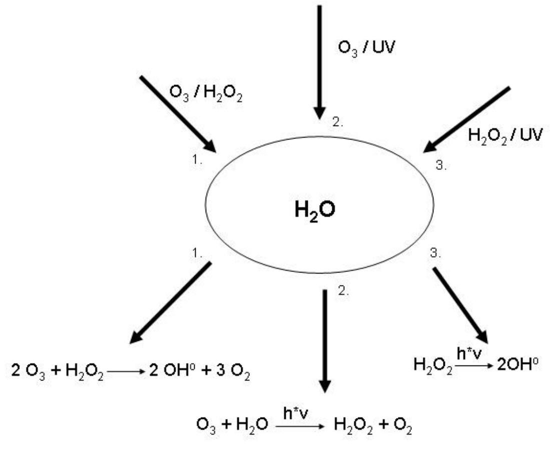


Figure 3 – The three most common advanced oxidation processes (modified from (Gottschalk et al., 2000))

3.2 Transformation of dissolved organic carbon (DOC)

Ozonation of water decreases the color and UV-absorbance and enhances the degradability of the natural organic matter by forming oxidized organic compounds of lower molecular weight. Depending on applied ozone dose, color can be removed by 90 % or more. UV absorbance at 254 nm is commonly reduced to 20-50 % of the initial value. For optimal production of biodegradable DOC a specific O_3-consumption of about 1-2 mg O_3/mg DOC is advised (Gottschalk et al., 2000).

Volk et al. (1997) showed, that over a 10 min contact time, the optimum oxidant dose for BDOC production was approximately 1mg O_3/mg DOC for a fulvic acid solution. The BDOC value reached 0.80 mg/L with an initial BDOC of 0.23 mg/L and an initial DOC of 2.84 mg/L. Initially only 8 % of the DOC were biodegradable and after ozonation 28 %. Ernst & Jekel (1999) likewise observed a total reduction of 60 % of DOC after ozonation and 14 days of biodegradation with a specific ozone dosage of 1.7 mg O_3/mg DOC. The initial DOC of this nanofiltration concentrate was 20-30 mg/L.

First investigations of the combination ozonation and BF/AR have been carried out in parallel to the NASRI project. Remy et al. (2006) applied ozonation (0.6-1 mgO_3/mg DOC) before and after a short soil passage (s. Table 3). The DOC removal after 30 d was 47 % and with ozonation + soil passage (8 d) 44 %. Thus at lab scale high DOC removal was possible with a shorter retention time by applying ozone.

Table 3- Comparison of DOC removal during soil passage with and without ozonation (DOC_0 = 6.5-7.2 mg/L, Lake Tegel, (Remy et al., 2006))

Treatment	HRT [days]	Final DOC [mg/L]	DOC removal [%]
Soil column (SC)	30	3.8	47
O_3 + SC	8	4.1	44
SC + O_3 + SC	8+5	3.9	45

⇨ Ozonation increases the biodegradability of DOC

⇨ Combining ozonation with subsurface passage seems promising as high absolute removal might be achieved in shorter retention times

3.3 Transformation of persistent trace organic substances by ozone and AOP

Several studies have shown that trace organics can be removed during drinking or waste water treatment by ozonation or advanced oxidation processes: (Abegglen et al., 2009; Bahr et al., 2005; Schumacher, 2006; Snyder et al., 2006; Ternes et al., 2003; Von Gunten, 2003).

Ternes et al. (2002) showed, that the direct ozone reaction depends on the chemical structure (see figure 4). E.g. substances with mono- and disubstituted benzene rings are only partly removed. Clofibric acid was stable even at 3 mg/L ozone dose (DOC ~2.4 mg/L) whereas diclofenac or carbamazepine with their aromatic structures and double-bond structures were transformed by more than 97 % at a small ozone dose of 0.5 mg/L.

Acero er al. (2001) reported, that compounds without aromatic- and double-bond structures, like MTBE are poorly oxidisable by ozone alone. For MTBE 30-40%

transformation with 2-4 mg/l of ozone was achieved (DOC 2.7 mg/L). The combination of ozone and H_2O_2 lead to a reduction in concentration of MTBE between 37 and 70% with an ozone dosage of 4 mg/L and 1.36 mg/L H_2O_2.

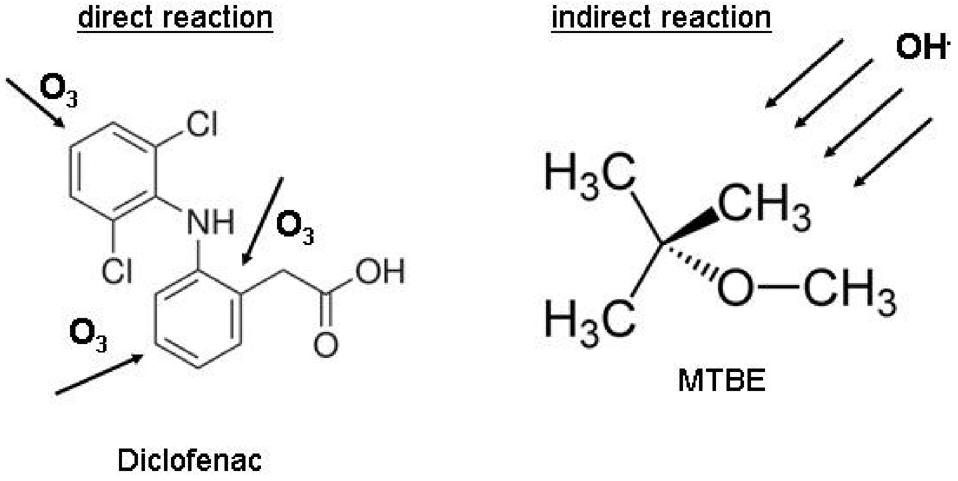


Figure 4 – Examples for direct and indirect oxidation reactions with diclofenac and MTBE

Teunissen (2009) compared several AOP regarding the oxidation performance towards trace pollutants. The most stable compounds were MTBE followed by atrazine. For transformation of MTBE chemical and energy demand are given in table 4.

Table 4- Chemical and energy demand for the removal of MTBE by different AOP (adapted from (Teunissen, 2009), *own calculation assuming 10 kWh/kg for H_2O_2 production)

Process	H_2O_2/UV	O_3/H_2O_2	O_3/UV
Removal [%]	55	50-70	32
Oxidants/ UVC-dosage	12 mg/L H_2O_2 20,500 J/m^2	5 mg/L O_3 15 mg/L H_2O_2	4.6 mg/L O_3 5,800 J/m^2
Energy demand [kWh/m^3]	0.66	0.2-0.25*	0.24-0.3*

For ozonation, Abegglen et al. (2009) reported an energy consumption for the production from pure oxygen at a dosage of 4-5 mgO_3/L with about 0.04 kWh/m^3. The ozone consumption depends on the background DOC, thus water with high DOC content consume more ozone and therefore more energy is required.

The energy consumption for different treatment purposes is shown in table 5 (Haberkern et al., 2008). The data shows that high input of ozone is necessary for the transformation of x-ray contrast media. The table also shows that the production of ozone from pure oxygen consumes only about 45 % of the energy which is necessary to produce it from air. Other authors report different energy consumptions for the ozone production from pure oxygen (e.g. 0.04 kWh/m^3 by (Abegglen et al., 2009)).

Table 5– The energy demand for the transformation of pollutants with ozone (adapted from (Haberkern et al., 2008))

Objektive of purification	real O_3 dosage [mg/L]	energy consumption (ozone generation from pure oxygen)	energy consumption (ozone generation from air)
transformation of pollutants with a high ozone reactivity	6	0.036-0.09 kWh/m³	0.086-0.2 kWh/m³
transformation and disinfection	12	0.072-0.18 kWh/m³	0.17-0.4 kWh/m³
including the transformation of x-ray contrast media	24 (+ 8 mg/L $H_2O_{2)}$	0.14-0.36 kWh/m³	0.34-0.8 kWh/m³

Table 6 summarizes the transformation of the 18 trace organic substances identified as high priority substances in the report OXIRED 1 – D1.1a by treating them with O_3 alone and AOP. The complete table is given in table 12 in the appendix. For water with low organic background (TOC < 3 mg/L) the removal of MTBE can reach up to 75 % at 1.6 mg O_3/ mg TOC (Liang et al., 1999).

Table 6- Trace organics compounds from the priority list of the report OXIRED 1, D1.1a classified by the removal (transformation) for different oxidation processes (for ozonation : ozone dosing ~ 1 mg O_3/mg DOC; adapted from (Calderara et al., 2001; Wiese and Grützmacher, 2009) and own results, formation from atrazine during ozonation but also transformation)**

Transformation	O_3	O_3 / UV	O_3 / H_2O_2
> 90 %	Carbamazepine Diclofenac, Primidone 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 (AOP), Amidotrizoic acid, Desethylatrazine**		

The removal of some substances such as amidotrizoic acid or desethylatrazine is uncertain. Due to a lack of data regarding advanced oxidation there is a need of further investigations for the following compounds: primidone, amidotrizoic acid, bentazone, desethylatrazine, 1,5-NDSA, 1,7-NDSA, 2,7-NDSA, linuron and diuron.

For some compounds (e.g. diuron, linuron) the high removal by ozonation is more linked to their reaction with OH-radicals formed during ozonation than with the direct reaction with O_3 (Chen et al., 2008). Thus, scavengers will have negative impact on the removal of this compounds.

- ⇨ Depending on their chemical structure, some trace organics that are persistent during subsurface passage can be transformed by oxidation processes (e.g. carbamazepine, diclofenac, primidone, sulfamethoxazole).
- ⇨ AOP may enhance the transformation of some of these substances (atrazine, iopamidole, MTBE), for others, however, conclusive data on necessary operational conditions is lacking.
- ⇨ Energy consumption and formation of by-products have to be taken into account as possible limitations for practical implementation.
- ⇨ O_3/H_2O_2 is the most energy efficient AOP, but still requires more energy than ozonation.

3.4 The formation of oxidation by-products and their possible prevention or elimination

In addition to higher energy demand the main drawback of oxidation technologies is the formation of possible toxic by-products. The by-product of most concern is the bromate ion (BrO_3^-), a potential human carcinogen, which is formed by applying oxidation technologies to bromide ion (Br^-) containing waters. The German Drinking Water Ordinance (TVO 2001) and similarly the WHO have set a maximum level of 10 µg/L for bromate in drinking water (WHO 2004).

A second by-product of concern is the carcinogenic N-Nitrosodimethylamin (NDMA). The maximum level in drinking water has been set to 10 ng/L. This is an orientation value for a lifelong uptake in Germany (UBA, 2003). NDMA-formation during ozonation has especially been observed in regions with specialized cultivation, e.g. of strawberries (Schmidt, 2007). As important NDMA-precursor N,N-Dimethylsulfamid (DMS) has been identified. DMS is a metabolit of the pesticide Tolyfluanid, which used for these cultivations. No significant removal of the precursor DMS during soil passage and activated carbon is noticed (Schmidt, 2007). Other precursors are DMST (N,N-Dimethyl-N´-(4-methyl)-sulfamid) and it's metabolites OH-Methyl-DMST and COOH-DMST. In general, all chemical compounds with N-N-bond are possible precursors of NDMA.

Figure 5 shows the factors that influence bromate- and NDMA- formation during ozonation.

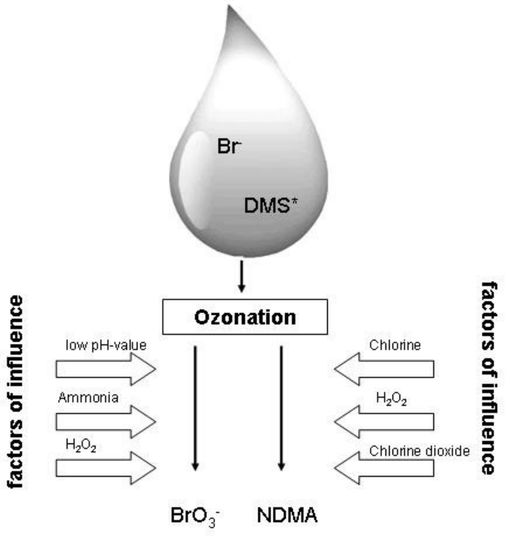


Figure 5– Factors that influence bromate and NDMA formation during ozonation (* or other compounds with N-N-bond) (adapted from (Pinkernell and Von Gunten, 2001; Schmidt et al., 2007; Von Gunten, 1996))

For an optimized water treatment the main goal is to find the optimum dose of ozone to minimize the formation of by-products but with sufficient removal of trace organic substances. The formation of bromate will be reduced up to 50% at low ph-values and the addition of ammonia (Pinkernell and Von Gunten, 2001). A reduction of BrO_3^- formation is also possible by avoiding free dissolved ozone in the reactor e.g. by adding H_2O_2 or optimized process control (Von Gunten, 1996). Free ozone concentrations especially occur at low DOC or TOC concentrations, which leads to high specific ozone dosing and thus to increased bromate formation. Liang et al. (1999) found bromate formation of 100-140 µg/L at 1.6 mg O_3/mg DOC (DOC 2.3-2.7 mg/L) which could be reduced to 14-96 µg/L by adding H_2O_2. Even with a perozone process bromate formation become critical if high free ozone concentrations occur due to a low ozone consumption of the DOC.

Yasunaga (2005) showed the influence of carbonate radicals and that some kinds of organic radicals generated by NOM decomposition participate in BrO_3- formation. If the concentration of NOM is high, ozone dosage should be carefully limited. Because of this, the challenge is not only to control the dissolved ozone concentration, but to know the organic composition of target water for drinking water production in order to control radical reactions that basically dominates BrO_3^--formation.

Von Gunten (1996) postulated that control of micropollutants, minimization of bromate, and disinfection may not be feasible in one treatment step. Therefore it is necessary to combine biological with oxidation steps. Full scale trials at the STP Regensdorf (Abegglen et al., 2009) with a effluent flow of 8,500 m^3/d showed clear decrease of endocrine- and herbicidal effects as well as acute toxicology (*Vibrio fischeri*). No formation of stable toxic by-products in relevant concentrations for ecotoxicology by combining ozonation and sand filtration was observed. Further investigations on the identity of possible toxic by-products are necessary.

NDMA is biodegradable, so that it is at least partly removable by sand filter, soil aquifer treatment or biofiltration (Schmidt et al., 2007). The final report of the Regensdorf project (Abegglen et al., 2009) showed an elimination of 50% NDMA by sand filtration after ozonation. Furthermore, results from the RECLAIM WATER project yielded, that NDMA is completely removed during groundwater recharge. Therefore, just a low risk of nitrosamine exposure after subsurface passage could be identified (Krauss et al., 2008). Nevertheless, if water with very high NDMA concentrations (> 1000 ng/L) is infiltrated, elevated concentrations in observation wells (50-600 ng/L) and productions wells (< 10 ng/L) occurred (Zhou et al., 2009).

The Global Water Research Coalition (DVGW, 2007) found, that biodegradation is the dominant mechanism of NDMA removal. However, it depends on the adaptation of microorganism, the nutrient status of the water, and the availability of competitive substrates. One other option to remove NDMA is intense UV irradiation (>10,000 J/m^2) or oxidation via AOP (Lee et al., 2007). Unfortunately, the ozone demand to transform NDMA is high resulting in increased bromate formation also if high amount of H_2O_2 are added (Lee et al., 2007). Thus neither UV irridiation nor AOP are suitable options to lower the NDMA concentration.

One other group of oxidation by-products are aldehydes such as formaldehyde and acetaldehyde. Liang et al. (1999) reported a slightly higher aldehyde formation by applying perozone than with ozonation alone. Abegglen et al. (2009) assume aldehydes to be responsible for a slight increase in chronic toxicity (reproduction test) after ozonation. The subsequent sandfilter seems to be able to remove these substances and thus no chronic toxicity was observed in the filter effluent.

- ⇨ Bromate and NDMA are the main known toxic oxidation by-products.
- ⇨ Their formation depends on the presence of pre-cursors (e.g. DMS, NOM, bromide) and the ozone dose.
- ⇨ NDMA is removed easier via biodegradation than by chemical oxidation.
- ⇨ Whereas NDMA is biodegradable by adapted microorganisms during subsurface passage, conclusive investigations on the removal of bromate in the subsurface are so far lacking.

Chapter 4
Review of the possible and existing concepts

Figure 6 presents four different concepts for combining subsurface treatment and oxidation processes. In the following, existing case studies for drinking water production from surface water that follow these scenarios will be described.

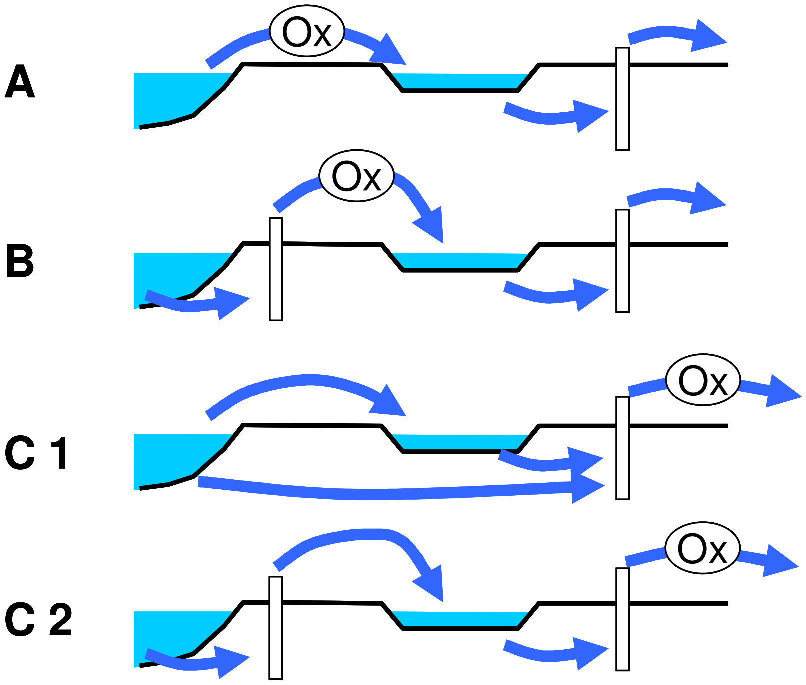


Figure 6- Possible concepts for the combination of subsurface treatment and oxidation systems (OX = oxidation process)

Scenario A

Scenario A is based on an oxidation (OX) step followed by pond infiltration using surface water as feed water. Pre-treatment by coagulation/flocculation and rapid filtration will usually be necessary for the removal of particles (e.g. algae) and colloids to reduce the oxidant demand. With surface waters of low suspended solids content (<10 mg/L), micro-sieves might be sufficient. For this scenario there is a possible need for final post-treatment as iron and manganese could be mobilized under anaerobic conditions during subsurface passage.

Scenario B

In scenario B, the scheme A is supplemented with a short bank filtration step (< 5 d) as pre-treatment before the oxidation step. As the BDOC is eliminated by this first underground passage, less oxidant is required in the oxidation process. A pretreatment is probably not necessary. However, one additional cost factor to keep in mind is the energy demand for additional pumping. Möller et al. (2009) compared nine water works in Schleswig-Holstein (Norther Germany) operated with groundwater. The values ranged from 0.05 to 0.23 kWh/m³ with an average of 0.11 kWh/m³ for the extraction of water.

This configuration stands as a viable option when the spatial setting of the plant (i.e. lack of space along the banks, close setting of the wells or presence of horizontal wells below the river bed) causes short travel times (in the range of a few days) to the well. Depending on the redox conditions during the short bank filtration, i.e. if anaerobic conditions already occur in the short BF iron and manganese mobilization is to be expected. Dissolved Fe^{2+} or Mn^{2+} would result in an increased oxidant demand.

No direct application of such a scheme has been found in the literature.

Scenario C

The scenario C is divided into C1 and C2. In both cases the oxidation process is implemented subsequent to subsurface passage. Treatment is required prior to oxidation to ensure the removal of iron and manganese which are most probably mobilized during subsurface passage. In addition, a biofiltration step is required subsequent to ozonation ensuring the removal of biodegradable organic matter produced during oxidation to prevent regrowth in the distribution network. Also, a disinfection step after oxidation is necessary to eliminate detached microorganisms from the biofilters. The difference of both cases is the long subsurface passage by C1 and the additional short underground passage in C2.

4.1 Scenario A case study

Mülheim-Dohne:

Scenario A is applied at the Mülheim water facilities operated by RWW (Rheinisch-Westfälische Wasserwerksgesellschaft). This company is one of the biggest water service companies in Germany and developed a specific water treatment train - the Mülheim process - after 1976 as a response to the new German drinking water act (1975) and the restrictions on chlorine usage for any drinking water treatment.

Mülheim-Dohne is essentially not a pure scenario A scheme, because the oxidation is part of an extensive pre-treatment for the river water prior to infiltration (figure 7).

The main objective of the overall treatment is to remove DOC (which occurs at concentrations up to 5 mg/L in the river Ruhr) in order to reduce the need of disinfecting agents and avoid re-growth of pathogens in the distribution networks. Water from the Ruhr is treated successively by pre-ozonation, flocculation and sedimentation, ozonation, and biologically activated carbon (BAC) filtration before it is infiltrated into the quaternary aquifer. After a short soil passage of 1-2 days, the water is pumped for a final disinfection step (chlorine 0.10 to 0.15 mg/L) and deacidification with NaOH (Bundermann, 2006).

The process combines artificial groundwater recharge/soil passage and advanced treatment steps in order to produce drinking water from surface water. The same process was implemented at three different sites in the region: Dohne, Kettwig and Styrum-West.

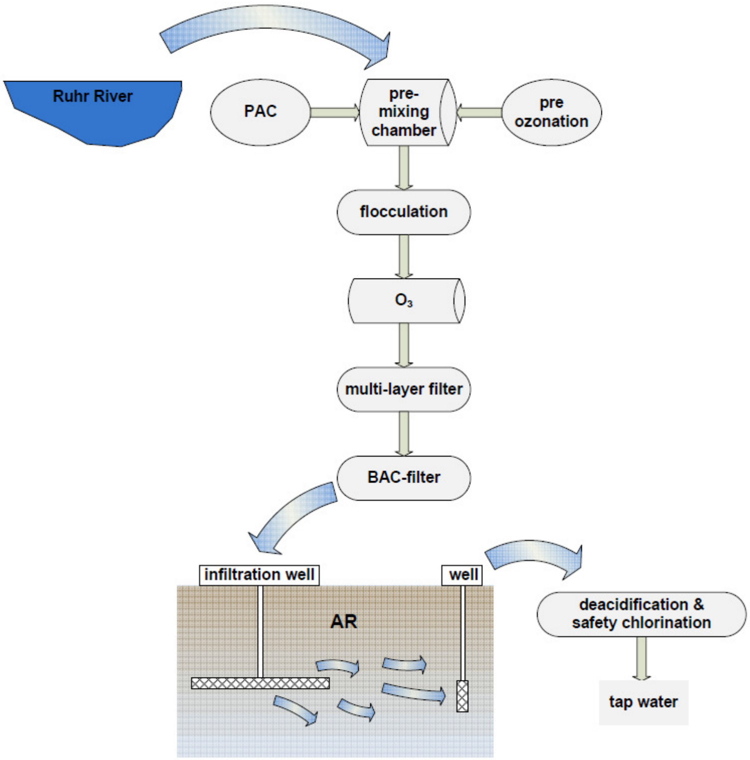


Figure 7- Treatment process at Mülheim-Dohne (PAC dosing only on demand; from (Bundermann, 2006))

The removal of different raw water compounds in the overall treatment process are presented in table 7. Regarding the DOC concentration, the treated water has a very good quality with less than 1.0 mg/L. Pesticides, as an indicator for trace organic compounds are also not detectable in the drinking water.

Table 7- Comparison of raw water and water treated by the "Mülheim Process" at Styrum-West, Dohne and Kettwig (LOQ = limit of quantification) (Bundermann, 2006)

Parameters	Raw water	Treated water
Turbidity [NTU]	≤ 100	≤ 0.1
Ammonia [mg/L]	≤ 5	0.01
DOC [mg/L]	≤ 5	0.8 – 1.0
HPC (20/36°C) [1/mL]	≤ 10^5	0
Coliforms [1/100 mL]	≤ 10^4	0
E-Coli [1/100 mL]	≤ 10^4	0
Parasites (*Giardia, Crypto.*) [1/100 L]	<100	0
Pesticides (Atracine, Diurone..) [ppb]	>0.5	< LOQ

4.2 Scenario C1 case study

Mülheim Styrum-East and Le Pecq Croissy

At one site operated by RWW, Styrum-East, the standard Mülheim treatment presented in scenario A could not be implemented due to specific spatial constrains. The alternative process designed (figure 8) includes direct artificial recharge of surface water with a 1-2 day subsurface passage, and post-treatment consisting of ozonation, BAC filtration, UV disinfection and diacidification by NaOH. A stand-by chlorination is available for emergency cases.

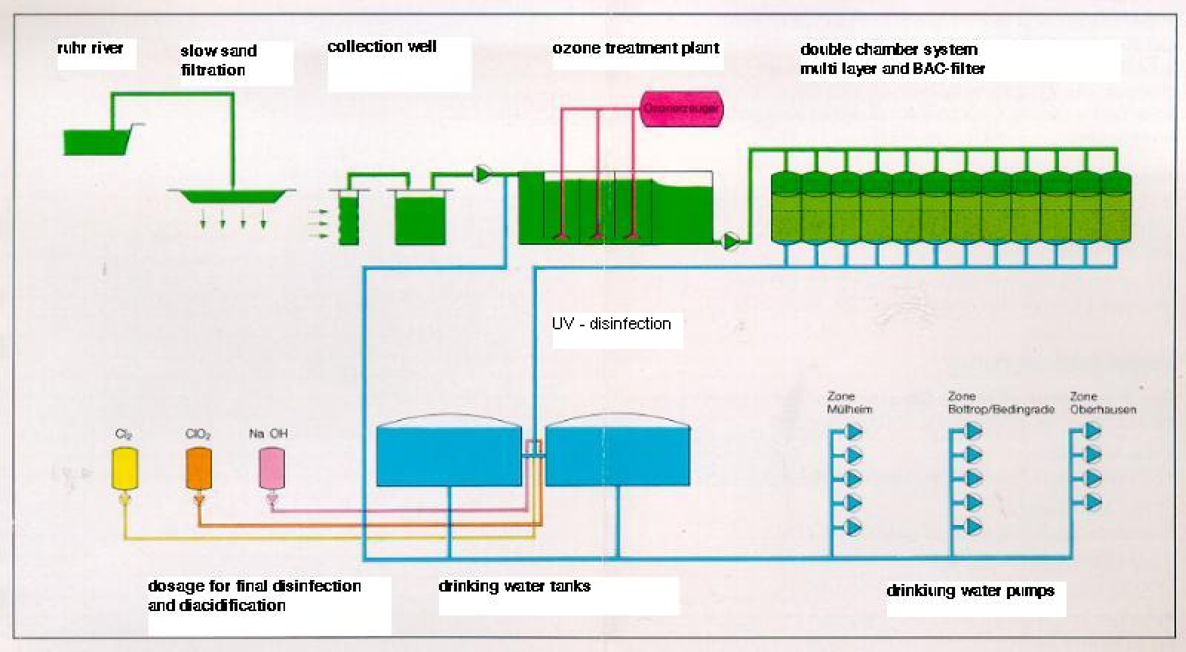


Figure 8- Treatment train at Mülheim-Stryrum-East (Bundermann, 2006)

The produced water quality in Styrum-East is given in table 8. Similar to the classical Mülheim process DOC is reduced from max. 5 mg/L in the raw water to 0.8 – 1.0 mg/L in the treated water. Trace organics like endocrine disruptors and pharmaceuticals are reduced to below detection limit.

Table 8- Comparison of raw water and treated water at Styrum-East waterworks (LOQ = limit of quantification) (Bundermann, 2006).

Parameters	Raw water	Treated water
DOC [mg/L]	≤ 5	0.8 – 1.0
HPC (20/36°C) [1/mL]	≤ 10^5	0
Coliforms [1/100 mL]	≤ 10^4	0
E-Coli [1/100 mL]	≤ 10^4	0
Endocrines (Estrogenes..) [ppb]	>0.10	< LOQ
Pharmaceuticals (e.g. Diclofenac, Ibuprofen,Carbamazepin..) [ppb]	0.08 – 0.14	< LOQ

Figure 9 shows the effect of subsurface passage and ozonation on the assimilable organic carbon (AOC), which is a fraction of the BDOC. The first, short subsurface passage enables a 90% reduction of the AOC. Then, the ozonation step enhances the bioavailability of the organic compounds resulting in an increase of the AOC by 400%. Subsequent filtration steps reduce the AOC to about 20 % of the original value.

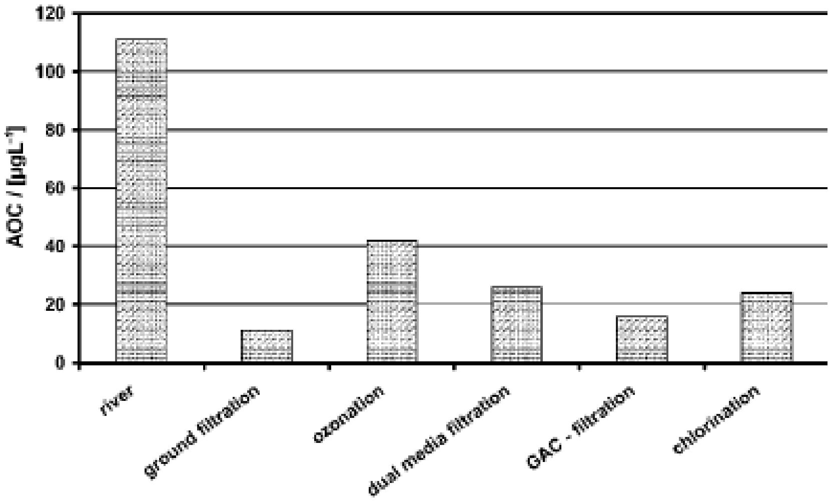


Figure 9- AOC concentrations after the different treatment steps within the Mülheim process (Uhl, 2000).

A similar scheme is implemented at the Pecq-Croissy water plant that is operated by Suez. The Seine water undergoes coagulation and sand filtration as pre-treatment before artificial recharge (infiltration rate: 1 m/d). Post-treatment steps for polishing and disinfection include nitrification, advanced oxidation process (O_3 and H_2O_2) and GAC filtration. Water quality data for DOC and trace organic substances is not available.

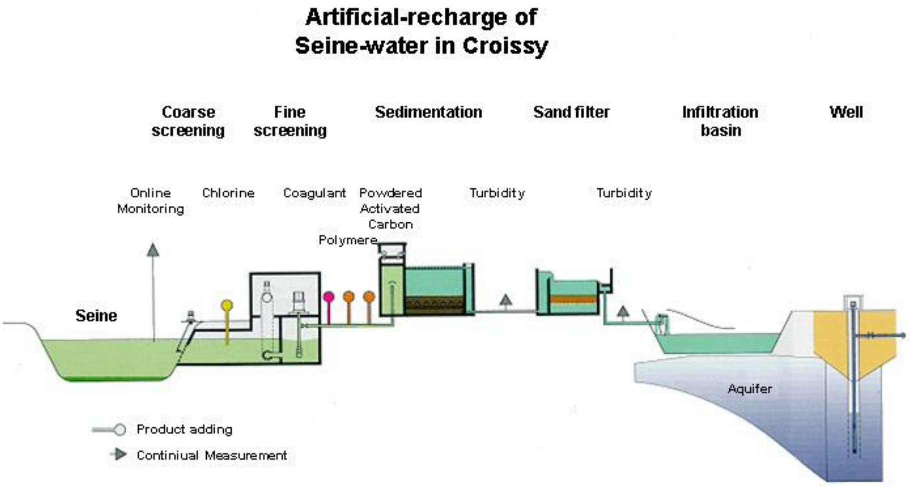


Figure 10 - Treatment of the Seine at Pecq-Croissy plant, part 1 (eau-de-seine, 2009)

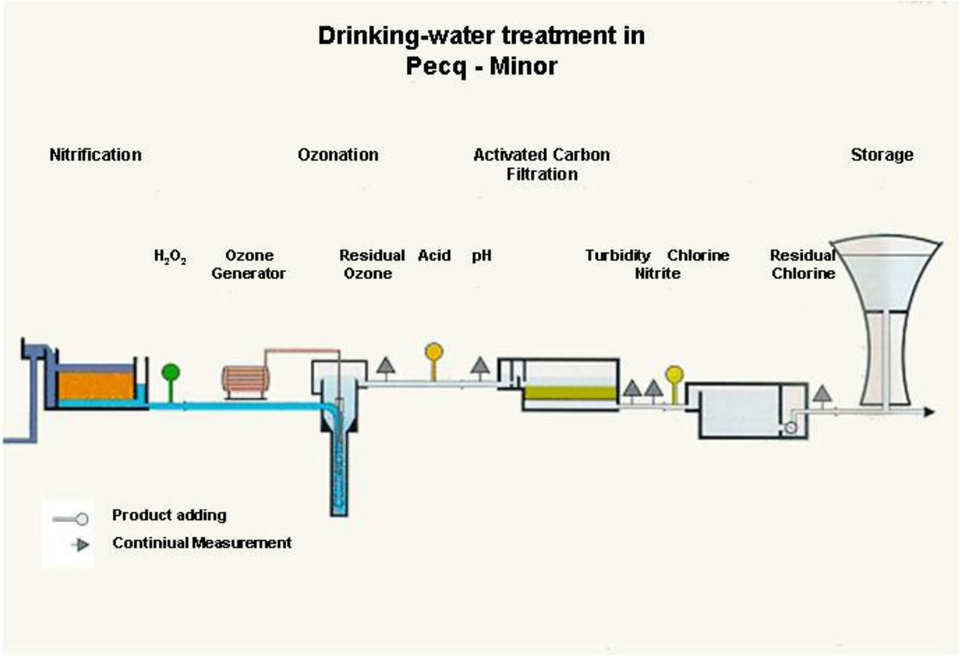


Figure 11- Post-treatment at Le Pecq-Croissy plant, part 2 (eau-de-seine, 2009)

4.3 Scenario C2 case study

<u>Prairie Waters Project by CH2M-Hill / Aurora Water in Colorado and Bi'eau Process at Flins-Aubergenville / Suez</u>

In these cases, advanced treatment steps (including oxidation) take place subsequent to subsurface passage. The mentioned case studies have just recently been established and they indicate that the combination of underground passage with adapted water treatment offers a relevant and promising perspective in regards to meeting water capacities and reducing sludge management costs.

Unfortunately, no specific data regarding the removal of TOC and trace organics have been published yet.

CH2M-Hill plans a multi-barrier approach including natural and mechanical/physical treatment in order to meet the water demands in Aurora (Colorado, US) starting in 2011. As it shown in Figure 12, the natural subsurface treatment steps (BF + AR) is followed by advanced treatment. After subsurface passage the treatment train at the Aurora Reservoir Water Purification Facility consists of precipitation/softening, AOP (UV/H_2O_2), sand filtration, GAC adsorption and blending processes will successively take place.

The construction of the ARWPF and the piping system will be completed in 2010. From 2006 to 2008, only pilot experiments at the BF and AR sites were carried out. From early results, the BF - with a 10-day travel time - presents a removal of TOC (from an average concentration of 8 mg/L for the South Platte river to less than 4 mg/L), turbidity and nitrogen which is independent of stream flow and season. Thus, BF and AR are identified as useful barriers.

Persistent trace organics will be treated at ARWPF using UV/H_2O_2 and granular activated carbon (GAC). Figure 13 presents the different treatment steps and the parameters on which they will have an impact.

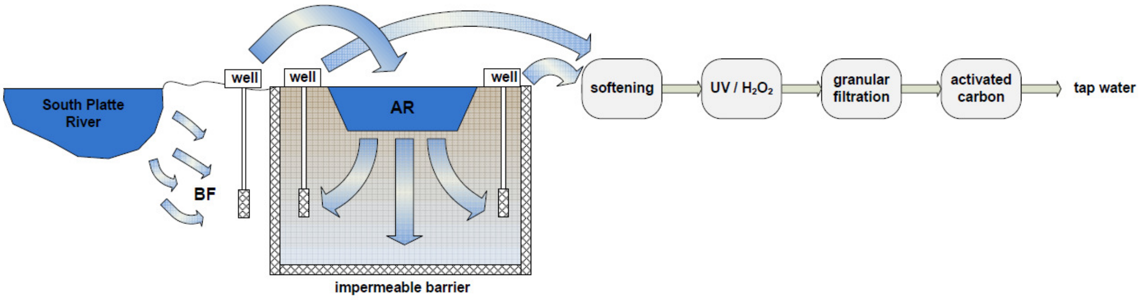
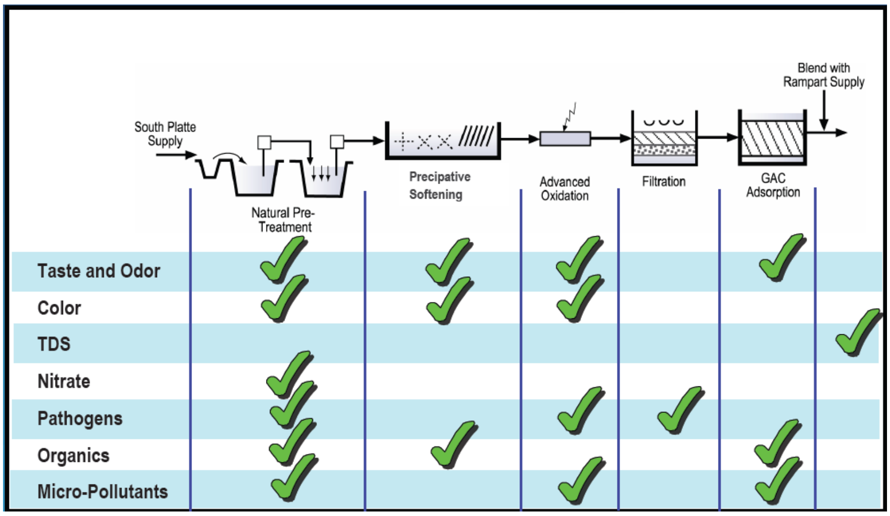


Figure 12 - Treatment scheme at Aurora Water



	Natural Pre-Treatment	Precipative Softening	Advanced Oxidation	Filtration	GAC Adsorption	
Taste and Odor	✓	✓	✓		✓	
Color	✓	✓	✓			
TDS						✓
Nitrate	✓					
Pathogens	✓		✓	✓		
Organics	✓	✓			✓	
Micro-Pollutants	✓		✓		✓	

Figure 13 - Advanced treatment scheme at ARWPF (Binney, 2006)

<u>Bi’eau Process at Flins-Aubergenville / Suez</u>

Similarly, but without oxidation is the Bi’Eau process (patented by SUEZ). It is implemented in order to obtain natural in-situ treatment using different redox conditions through both BF and AR (see figure 14). Since September 2006, the process has been implemented at the Flins-Aubergenville well field which is located downstream of the Parisian urban area. The Seine water is recovered after a short anoxic bank filtration and is pumped to infiltration ponds. In the AR ammonia and dissolved iron are removed. The post-treatment consists of activated carbon filtration and disinfection (ozone and chlorine). The main reason for implementing this process were i) avoid sludge production from flocculation of surface water, ii) increase the AR to avoid increasing nitrate level from groundwater influenced by agricultural areas and iii) reduce oxidant demand (Haeffner and Gandguillaume, 2007).

The main positive outcome of this implementation is the economical savings due to the reduction of sludge production. 1,000 t/yr of sludge and 2 Mill. € of investment costs for sludge treatment were avoided, according (Haeffner and Gandguillaume, 2007).

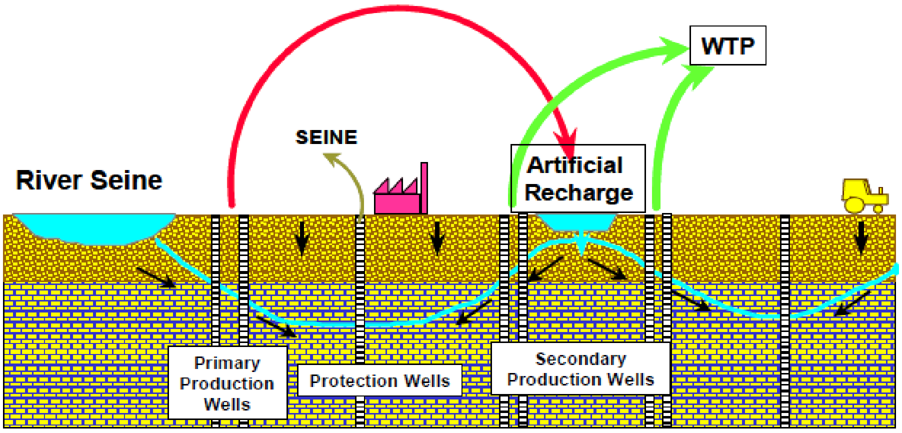


Figure 14 - Bi'Eau Process (Haeffner and Gandguillaume, 2007)

4.4 Summary of the case studies

Table 9 gives an overview of the mentioned case studies with the necessary pre- or post-treatment steps.

Table 9 - Overview of the different cases

	Mülheim Dohne Germany	**Mülheim Styrum East - Germany**	**Pecq-Croissy France**	**Bi´Eau Suez France**	**Prairie Waters USA**
examples for scheme:	A	C1	C1	C2	C2
bank filtration		X	X	X	X
artificial recharge	X	X	X	X	X
travel time	1-2 days	1-2 days	no data	no data	BF 5-10 days AR 20-30 days
additional pre-treatment before oxidation	preozonation & flocculation	slow sand filtration	coagulation & sand filtration		softening
additional post-treatment after oxidation	biolog. double layer filter & BAC filtration	biolog. double layer filter & BAC filtration & deacidification and UV-disinfection	GAC filtration		granular filtration & activated charcoal filtration
source DOC concentrations	~ 5 mg/L	~ 5 mg/L	no data	no data	~ 4-6 mg/L
treated water (DOC)	0.8-1.0 mg/L	0.8-1.0 mg/L	no data	no data	no data
oxidation process	O_3	O_3	O_3 / H_2O_2	O_3	UV / H_2O_2
disinfection		UV			

Chapter 5 Conclusions

The literature study on the theoretical and practical potential of combined subsurface passage and oxidation processes for water treatment gave rise to the following conclusions:

Limited DOC removal during subsurface passage can be enhanced by prior oxidation, by raising the share of biodegradable DOC (BDOC) which is then rapidly removed by infiltration. For optimal performance of the oxidation process, the BDOC of the source water should be as low as possible (e.g. by pre-treating it with slow sand filtration or short subsurface passage) and substances that raise the oxidant demand like total suspended solids, dissolved Fe(II) and Mn(II) or ammonia should be removed prior to oxidation.

Many trace organics that persist or are only poorly removable during subsurface passage are transformed by ozone or AOP (e.g. carbamazepine, diclofenac, sulfamethoxazole). The transformation products may be better degradable than the parent substance offering potential for removal via subsequent subsurface passage or BAC. For high performance the oxidant dose needs to be optimized with respect to maximum trace substance transformation and low formation of toxic by-products, i.e. minimization of the free ozone concentration by limiting the dosing or adding of H_2O_2. The oxidation step should be performed prior to infiltration to allow for degradation of transformation products in the subsurface.

O_3/H_2O_2, O_3/UV and H_2O_2/UV are the most common advanced oxidation processes. These combinations enable a high transformation of most trace organics and poorly degradable DOC, however, the energy consumption of AOP is generally higher (e.g. H_2O_2/UV requires 5-10 times more energy: up to 0.66 kWh/m^3) compared to ozone alone (~0.04-0.09 kWh/m^3 for 5-6 mg/L O_3).

The main known toxic oxidation by-products are bromate and NDMA. In order to minimize their formation the dose should be kept as low as possible by removing O_3-demanding substances (e.g. DOC, Fe(II), Mn(II), NH_4^+) to maximum degree – e.g. by short, aerobic subsurface passage. On the other hand, subsurface passage subsequent to oxidation offers the potential for by-product removal in the subsurface without advanced technical methods.

Concerning the sequence of the two treatment steps theoretical considerations have shown that oxidizing the water prior to infiltration will make most use of the self-purification capacity of the subsurface. If oxidation is applied subsequent to infiltration (and recovery) – as considered in scenarios C1 and C2 – reduced Fe and Mn as well as ammonia might have to be removed prior to oxidation in order to minimize the ozone dose. In addition, an extra-filtration step (in practice usually through BAC) and disinfection is required to remove the newly-formed BDOC and to reduce the number of microorganisms. That could be avoided if the oxidation takes place prior to the subsurface passage (scenarios A and B). Further treatment would only be necessary in case of the iron and manganese mobilization which can be avoided by ensuring aerobic conditions (short travel times).

In order to reduce the reagent demand during oxidation, pre-treatment options may be relevant in scheme A. For the removal of particles it is possible to establish a flocculation/sedimentation like in Mülheim-Dohne. For source waters with a low suspended solids content (< 10 mg/L) microsieving might be sufficient. Another option to eliminate particles and also DOC is to use bank filtrate before oxidation and subsequent artificial recharge as given in Scenario B.

Whereas scenarios A and C1 have already been implemented in water treatment plants in Germany and France, it can be noticed that the innovative scheme B which offers two natural barriers is - to our knowledge - currently not operated in practice. Other scenarios, C1 and C2, which also benefit from both BF and AR have recently been launched on new field sites with distinct objectives: i) to increase the water storage capacity for Aurora Waters, ii) to decrease the nitrate level and avoid sludge/waste production. The removal of TOC and trace organics was not especially targeted in those cases.

Further literature research should focus on obtaining additional data from practice on this subject. Nevertheless the enhancement of BDOC via oxidation processes prior to the underground passage seems promising and more efficient than the reverse configuration. It is then recommended that any further experimental program in OXIRED should focus on the schemes A and B and include a cost-benefit analysis of the additional first BF step in scenario B. The energy demand for pumping the short bank filtrate to the oxidation plant is estimated with 0.11 kWh/m³. Due to this fact scheme B will require more energy for pumping then scheme A, but additional energy consumption for pre-treatment is avoided.

The most promising scheme for future investigations seems to be scheme A. There are no additional costs for pumping energy and it is very simple to implement in existing plants. On the other hand, pre-treatment is probably be necessary for suspended solids removal

Table 10 - Overview of the advantages and disadvantages of the investigated schemes

Case	**A**	**B**	**C1**	**C2**
existing examples	**Mülheim Dohne Germany (advanced pre-treatment including O_3 prior to infiltration)**	**No example found**	**Mülheim Styrum East - Germany Pecq-Croissy France**	**Prairie Waters USA Bi´Eau Suez France**
oxidation before subsurface passage	X	X		
oxidation after subsurface		X	X	X
additional pre-treatment necessary prior to oxidation	filtration for TSS removal	recommended in case of anoxic / anaerobic subsurface passage for Fe(II), Mg(II) and NH_4- removal		
additional treatment necessary after oxidation	probably no (although Mühlheim Dohne has BAC implemented prior to recharge)		biofiltration & disinfection	
Advantages				
insufficient permeability of bank is no criteria for exclusion	X		X	
no filtration step necessary prior to oxidation		X (in case of aerobic conditions)	X (in case of aerobic conditions)	X (in case of aerobic conditions)
simple implementation in existing AR facilities	X		X	
oxidation by-products are degraded during subsurface passage	X	X		
Disadvantages				
treatment necessary prior to oxidation, otherwise high ozone demand	X (TSS removal)		X (Fe, Mn, NH_4-removal)	X (Fe, Mn, NH_4-removal)
additional pumping costs due to 2nd subsurface passage		X		X
additional post-treatment necessary after oxidation for removal of oxidation by-products and disinfection			X	X

Appendix

Table 11 - Classification of trace organic substances investigated by OXIRED 1.1.a

	Breakthrough potential under aerobic conditions (NASRI data, (Wiese et al., 2009b)	Occurence in MAR (Stuyfzand et al., 2007)	Elimination in bank filtration [%] (Schmidt, 2005)			Resulting assessment of possible breakthrough in BF / AR systems
Substance	3: < 25 % removal 2: 25 - 75 % removal 1: 25 - 75 % removal under anaerobic conditions	3: often and >0.1µg/L, 2: often or >0,1 µg/L, 1: sometimes and <0.1 µg/L	aerobic	anaerobic	Number of studies in Schmidt 2005	3: high, 2: medium, 1: uncertain
Carbamazepine	3	3	0	100	9	3
MTBE	3	3	0-50	0-50	3	3
Primidone	3	1	0	0	3	3
EDTA	3		0-50	0-50	28	3
Naphthalene-1,5-disulfonate	3		10	10	15	3
Sulfamethoxazole	2	2	0	100	5	3
Amidotrizoic acid		3	0	100	2	3
Methylbenzene		3	0-100	0-100	2	3
Tris(chloroethyl)phosphate (TCEP)		3	43-50	0-90	6	3
1,2-Dichlorpropane			0	100	3	3
2,4-Dichloraniline			0	0	4	3
2,5-Dichloraniline			0	0	6	3
PFOS / PFOA						3
1,3 and 1,4 dimethybenzene		3	50	75	21	2
1,4 Dioxane		3				2
Chloroform		3	50	85	23	2
Iopamidol		3				2
Iso-Nonylphenol		3	99	34-99	3	2
Bentazone		2	0	25	11	2
AAA (Acetylaminoantipyrine)	2		77	90	2	2
Naphthalene-1,7-disulfonate	2		0	50	4	2
Naphthalene-2,7-disulfonate	2		0	50	5	2
2-Chlorphenol			0	0	2	2
2-Hydroxy-4,6-bis(4-sulfanilo)-1,3,5-Atriazine			0		1	2

Chlortoluron			0-100	0	6	2
Diethylentriaminpentaacetic acid [DTPA]			0	25	4	2
Dikegulac			0	0	5	2
Atrazine		1	25	50	34	2
Phenazone	1	3	85	0	4	1
1,2,4 Trimethylbenzene		2	90		1	1
1,2-Dichlorethane		2	0-70	0-70	4	1
1,3,5 Trimethylbenzene		2	90	0	2	1
Isoproturon			75	0	15	1
Bisphenol A		3	100		2	1
Diglyme		3	100		1	1
2-Naphthol			0		1	1
2-NH2-Naphthaline-4,8-disulfonate			0	0	2	1
Bis(dichlorpropyl)ether			0		1	1
cis-4,4'-Dinitrostilbene-2,2'-disulfonate			0-20		2	1
Desethylatrazin [Atrazine-Metabolite]			0-30	45-79	10	1
Linuron			0		1	1
Sulfonierte Naphthalin-Formaldehyd-Kondensate [SNFC] (n = 5)			0		1	1
Tetrachlorethene [PER]			0	100	30	1
Trichlorethene [TRI]			10	100	26	1
Diuron			25	25	9	1

Table 12 - Removal efficiency of oxidation processes for selected trace pollutants

		AOP		Type of water*	
substance	**O_3**	**O_3 / UV**	**O_3 / H_2O_2**	**(DOC [mg/L])**	
Sulfametoxazole	>97%			SW (1.3)	(Huber et al., 2003)
	>97%			SW (3.7)	(Huber et al., 2003)
	>97%			SW (1.3)	(Huber et al., 2003)
	>97%			SW (3.7)	(Huber et al., 2003)
	>92%			WW (23.0)	(Ternes et al., 2003)
MTBE	~5%	32%	25%	SW (5.0)	(Teunissen et al.)
			55%	SW (5.0)	(Teunissen et al.)
	39%		46%	SW (1.4)	(ACERO et al., 2001)
			71%	SW (1.4)	(ACERO et al., 2001)
	33%		37%	SW (2.7)	(ACERO et al., 2001)
			46%	SW (2.7)	(ACERO et al., 2001)

		AOP		Type of water*	
substance	**O_3**	**O_3 / UV**	**O_3 / H_2O_2**	**(DOC [mg/L])**	
	28%		37%	SW (0.8)	(ACERO et al., 2001)
			65%	SW (0.8)	(ACERO et al., 2001)
Carbamazepine	>97%			SW (1.3)	(Huber et al., 2003)
	>97%			WW (12.0)	(Bahr et al., 2005)
	>97%			SW (~2.4)	(Ternes et al., 2002)
	>97%			SW (1.3)	(Huber et al., 2003)
	>97%			WW (12.0)	(Bahr et al., 2005)
	>97%	>97%	>97%	SW (5.0)	(Teunissen et al.)
			>97%	SW (5.0)	(Teunissen et al.)
	98%			WW(23.0)	(Ternes et al., 2003)
Primidone	>50%			SW (~2.4)	(Ternes et al., 2002)
	90%			SW (~2.4)	(Ternes et al., 2002)
Iopamidol	~30%		~18%	WW (12.0)	(Bahr et al., 2005)
	~65%		~80%	WW (12.0)	(Bahr et al., 2005)
	33%	88%	~80%	WW (23.0)	(Ternes et al., 2003)
Atrazine	20%			SW(~2.0)	(Meunier et al., 2006)
	30%			SW(~2.0)	(Meunier et al., 2006)
	~18%	65%	~35%	SW (5.0)	(Teunissen et al.)
			75%	SW (5.0)	(Teunissen et al.)
	25%			WW (~5.0)	(Abegglen et al., 2009)
	60%			WW (~5.0)	Abegglen, Escher et al. 2009)
Diclofenac	>97%			SW (~2.4)	(Ternes et al., 2002)
	>97%			WW (12.0)	(Bahr et al., 2005)
	>97%			SW (1.3)	(Huber et al., 2003)
	>97%			SW (1.3)	(Huber et al., 2003)
	>97%	>97%	>97%	SW (5.0)	(Teunissen et al.)
	>97%			WW (12.0)	(Bahr et al., 2005)
	>96%			WW (23.0)	(Ternes et al., 2003)
			>97%	SW (5.0)	(Teunissen et al.)
Isoproturon	~ 95%	95%	~88%	SW (5.0)	(Teunissen et al.)
			95%	SW (5.0)	(Teunissen et al.)
Ibuprofen	~50%			WW (12.0)	(Bahr et al., 2005)
	~93%			WW (12.0)	(Bahr et al., 2005)
	~52%	87%	~78%	SW (5.0)	(Teunissen et al.)
			95%	SW (5.0)	(Teunissen et al.)
	48%			WW (23.0)	(Ternes et al., 2003)

		AOP		Type of water*	
substance	**O_3**	**O_3 / UV**	**O_3 / H_2O_2**	**(DOC [mg/L])**	
Iohexol	~12%		~40%	WW (12.0)	(Bahr et al., 2005)
	25%		>97%	WW (12.0)	(Bahr et al., 2005)
Iopromide	~13%		~15%	WW (12.0)	(Bahr et al., 2005)
	~65%		~60%	WW (12.0)	(Bahr et al., 2005)
	42%	90%	89%	WW (23.0)	(Ternes et al., 2003)
Clofibrine acid	10-15%			SW (~2.4)	(Ternes et al., 2002)
	22%		60%	WW (12.0)	(Bahr et al., 2005)
	>97%		96%	WW (12.0)	(Bahr et al., 2005)
	40%			SW (~2.4)	(Ternes et al., 2002)
	50%			WW (23.0)	(Ternes et al., 2003)
1,4 Dioxane	25%		75%	SW (<2.0)	(Iwamoto et al., 2005)
Naproxen	>97%		~70%	WW (12.0)	(Bahr et al., 2005)
	93%		~92%	WW (12.0)	(Bahr et al., 2005)
	>50%			WW (23.0)	(Ternes et al., 2003)
Indomethacine	~85%			WW (12.0)	(Bahr et al., 2005)
	>97%			WW (12.0)	(Bahr et al., 2005)
	>50%			WW(23.0)	(Ternes et al., 2003)
Ketoprofen	~30%		~44%	WW (12.0)	(Bahr et al., 2005)
	>97%		>97%	WW (12.0)	(Bahr et al., 2005)
AMDOPH	~42%			WW (12.0)	(Bahr et al., 2005)
	~84%			WW (12.0)	(Bahr et al., 2005)
Bezafibrate	~17%			WW (12.0)	(Bahr et al., 2005)
	~30%			SW (3.7)	(Huber et al., 2003)
	80%			SW (1.3)	(Huber et al., 2003)
	50%			SW (~2.4)	(Ternes et al., 2002)
	>97%			SW (3.7)	(Huber et al., 2003)
	98%			WW (12.0)	(Bahr et al., 2005)
	80%			SW (~2.4)	(Ternes et al., 2002)
AAA (Acetylamino antipyrine)	>97%			WW (12.0)	(Bahr et al., 2005)
	>97%			WW (12.0)	(Bahr et al., 2005)
FAA ()	>97%			WW (12.0)	(Bahr et al., 2005)
	>97%			WW (12.0)	(Bahr et al., 2005)
Phenazone	>70%			WW (12.0)	(Bahr et al., 2005)
	>70%			WW (12.0)	(Bahr et al., 2005)
Diatrizoate		36%	25%	WW (23.0)	(Ternes et al., 2004)
Ethinylestradiol	>97%			SW (1.3)	(Huber et al., 2003)
	>97%			SW (3.7)	(Huber et al., 2003)

		AOP		Type of water*	
substance	**O_3**	**O_3 / UV**	**O_3 / H_2O_2**	**(DOC [mg/L])**	
	🟨 >97%			SW (1.3)	(Huber et al., 2003)

O_3-concentration [mg/L]	
	🟩 < 0.5
	🟨 1.0 - 2.0
	🟥 2.5 - 5.0
	🟦 >5

	O3	H2O2
O3 /H2O2	🟩 < 2mg/L	0.8 mg/L; ~ 6 mg/L ; 0.17mg/L
	🟨 2-5 mg/L	0.08 mg/L; ~ 15 mg/L
	🟥 5-10 mg/L	2.1 mg/L; 10 mg/L
	🟦 > 10 mg/L	7.7 mg/L

O_3 / UV	4.6 mg/L O_3	5800 J/m²
	15 mg/L O_3	400 J/m²

*SW Seawater

WW Wastewater

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