Decision basis for implementation of oxidation technologies

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Summary: Oxidative treatment is one of the options to eliminate emerging pollutants (EPs) from drinking water or wastewater. For drinking water treatment, the ozonation technology is already implemented at many sites all around the world, so far mostly for disinfection purposes. However, in some countries such as the Netherlands surface water contains relatively high bromide concentrations, which leads upon reaction with ozone to the formation of bromate, a suspected carcinogen. In such a case, UV/H_2O_2 treatment is considered a useful alternative, despite the fact that energy requirements are substantially higher compared to treatment with ozone or O_3/H_2O_2. Only in recent years, the oxidative treatment of wastewater has been investigated to not only protect our water resources, but also the ecosystem from pollution with chemicals used in our daily life. In Switzerland, the first permanent full scale plant with ozonation, WWTP Neugut in Dübendorf, is running since March 2014. Its performance was investigated in detail in the DEMEAU project. The goal of this paper is to present a decision basis for the implementation of oxidation technologies to eliminate EPs. Depending on the composition of the water in different European regions, one or the other treatment is recommended. The different parameters that influence the efficiency of oxidation and the formation of by-products are discussed. A decision tool is presented to decide if oxidative treatment of wastewater is recommended and under which circumstances the treatment of drinking water with ozone, O_3/H_2O_2, or UV/H_2O_2 may be the treatment of choice.

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Oxidative treatment is one of the options to eliminate emerging pollutants (EPs) from drinking water or wastewater. For drinking water treatment, the ozonation technology is already implemented at many sites all around the world, so far mostly for disinfection purposes. However, in some countries such as the Netherlands surface water contains relatively high bromide concentrations, which leads upon reaction with ozone to the formation of bromate, a suspected carcinogen. In such a case, UV/H_2O_2 treatment is considered a useful alternative, despite the fact that energy requirements are substantially higher compared to treatment with ozone or O_3/H_2O_2. Only in recent years, the oxidative treatment of wastewater has been investigated to not only protect our water resources, but also the ecosystem from pollution with chemicals used in our daily life. In Switzerland, the first permanent full scale plant with ozonation, WWTP Neugut in Dübendorf, is running since March 2014. Its performance was investigated in detail in the DEMEAU project.

The goal of this paper is to present a decision basis for the implementation of oxidation technologies to eliminate EPs. Depending on the composition of the water in different European regions, one or the other treatment is recommended. The different parameters that influence the efficiency of oxidation and the formation of by-products are discussed. A decision tool is presented to decide if oxidative treatment of wastewater is recommended and under which circumstances the treatment of drinking water with ozone, O_3/H_2O_2, or UV/H_2O_2 may be the treatment of choice.

1   Introduction

Oxidative treatment is one of the available options to eliminate emerging pollutants (EPs) from drinking water or wastewater. For drinking water treatment, the treatment with ozone is already implemented at many sites all around Europe, but mainly for disinfection. Only in recent years, the oxidative treatment of wastewater has been investigated to not only protect our water resources, but also the aquatic ecosystems from pollution with chemicals used in our daily life which enter the aquatic environment continuously through the effluent of municipal wastewater treatment plants.

For wastewater treatment, an efficient and cost- effective elimination of EPs can be achieved with ozone treatment or sorption to activated carbon. In Germany, several plants with powdered activated carbon (PAC) application are in operation and in Switzerland the ozonation at WWTP Neugut was set into operation in spring 2014. Treatment with ozone or with powdered activated carbon exhibit similar costs, but are cheaper relative to other treatment options (e.g. treatment with UV/H_2O_2) or filtration technologies such as nanofiltration. The treatment with granular activated carbon (GAC) is most promising as an alternative to PAC treatment and is implemented in full scale in Germany.

For drinking water treatment, sometimes ozone-based (advanced) oxidation is applied for eliminating EPs. However, in some countries such as the Netherlands, surface waters contain relatively high bromide concentrations. Upon reaction with ozone this results in the formation of bromate, a suspected human carcinogen. Therefore, UV/H_2O_2 treatment is considered a useful alternative. UV/H_2O_2 also oxidizes EPs efficiently with no bromate formation, but energy requirements are substantially higher compared to treatment with ozone or O_3/H_2O_2 (Katsoyiannis et al. 2011). The goal of the DEMEAU pilot research study by KWR in the Netherlands was to decrease the energy demand of the UV/H_2O_2 process, as it is considered to be its main disadvantage. Another important issue is the formation of possibly mutagenic byproducts, and knowledge on the parameters that prevent or minimize their production is required.

The goal of this report is to present a decision basis for the implementation of oxidation technologies to eliminate EPs. Depending on the composition of the water in different European regions, one or the other treatment is recommended. The different parameters that influence this decision are discussed and a decision tool is presented to evaluate if oxidative treatment of wastewater as well as drinking water treatment is possible.

2 Advanced wastewater treatment

2.1 Choice of technology and costs

Ozonation or treatment with powdered activated carbon (PAC) are the technologies that were proposed to most effectively remove EPs from wastewater. These technologies were tested in several small- and pilot-scale studies around the world. A detailed assessment was performed within the project "Strategy MicroPoll" of the Swiss Federal office for the environment FOEN at the WWTP Regensdorf close to Zurich by Eawag (Hollender et al. 2009, Zimmermann et al. 2011) and the WWTP Lausanne at Lake Geneva by EPFL (Margot et al. 2011) together with various partners. With ozone or PAC, EPs can be reduced by over 80% with reasonable doses, reducing the overall toxicity of the effluent at the same time (Kienle et al. 2011, Stalter et al. 2010a and 2010b). Some ecotoxicological investigations have shown a temporary increase of toxicity after ozonation in certain tests, which can be reduced again by a subsequent treatment step with biological activity such as sand filtration. Based on these investigations, a biological treatment after ozonation is recommended. Other technologies could reach the same goals (e.g. adsorption to granular activated carbon, tight membrane filtration, advanced oxidation processes such as UV/H_2O_2 or O_3/H_2O_2), but current considerations of technical feasibility and costs favor the treatment with conventional ozonation or PAC. The treatment with GAC is a potential alternative to PAC and is implemented in full-scale in Germany at WWTP Gütersloh-Putzhagen and Düren-Merken (NRW, D) (Benstöm et al. 2014). Studies have shown that about 3-5 times more carbon is needed with GAC than with PAC for the same elimination of EPs (Boehler et al. 2012, Böhler et al. 2013), which makes the application more expensive and therefore less favorable. However, beneficial for GAC treatment is that it can be regenerated and filled into existing deep bed filters (e.g. sand filters) with a low footprint and it does not require a post-treatment, e.g. a filtration, to remove carbon from the water.

In Table 1, the average energy consumption and costs for smaller and larger WWTPs in Switzerland are presented (after Abegglen et al. 2011 and 2012).

Table 1: Energy consumption & costs of ozonation and treatment with PAC (after Abegglen et al. 2011 and 2012). The costs are calculated for a small (14'400 p.e.) and a large (590'000 p.e.) WWTP and include amortization and operation.

	Energy WWTP kWh/m^3	Primary energy kWh/m^3	Costs CHF/m^3 14'400 p.e.	Costs CHF/ m^3 590'000 p.e.
Ozonation (5 g/m^3)	0.06	0.27	0.15–0.19	0.04–0.06
Ozonation (5 g/m^3) with sand filtration	0.1	0.39	0.32–0.36	0.09–0.11
PAC (10 g/m^3)	0.02	0.32	0.25–0.3	0.1–0.15
PAC (10 g/m^3) with sand filtration	0.06	0.44	0.42–0.47	0.15–0.2

The costs of advanced treatment, including operation and investment costs, increase the regular costs of a small WWTP by 20-50% and for a large WWTP by 10-20% (current costs: 0.80 CHF/m^3 for a small, 0.55 CHF/m^3 for a large WWTP). As listed in Table 1, the costs of ozonation are slightly lower than the costs for PAC treatment. However, the costs highly depend on the costs of electricity. Ozonation has a higher energy demand on the WWTP as ozone needs to be produced locally with an ozone generator from liquid oxygen. For PAC treatment, the production of PAC is very energy intensive. The available data for PAC production are not very robust, and the environmental burden of PAC production is only approximately known. Calculations are done for the treatment itself and including a sand filtration as post-treatment. Post-treatment is required after ozonation to eliminate potentially problematic oxidation by-products (mainly from matrix) and after PAC treatment to eliminate residual PAC.

In Germany, several pilot plants are in operation with either GAC or ozone treatment (www.koms-bw.de; www.masterplan-wasser.nrw.de). In Switzerland, the first permanent full-scale plant with ozonation has been built at the WWTP Neugut in Dübendorf and is running since March 2014. A PAC treatment is installed at the WWTP Bachwis in Herisau and is in operation since June 2015.

At WWTP Neugut, wastewater with a load corresponding to 105,000 population equivalents is treated. The plant had already an installed sand filter. The recommended ozone dosing is relatively low because of low DOC values after the biological treatment (2.0 - 3.3 mg/L ozone corresponding to 0.55 g ozone /g DOC). Due to these preconditions, the costs are relatively low with:

- Investment costs: CHF 3.27 Mio

- Additional energy consumption: 0.03 kWh/m^3

- Additional operating costs: CHF 0.013/m^3

- Total costs incl. amortization: CHF 0.06/m^3. This corresponds to a theoretical increase of the costs of wastewater treatment in Dübendorf by about 10%. However, thanks to optimizations at other ends at the WWTP Neugut, the cost of wastewater treatment does not increase for the end user.

2.2 Benefits and limitations of ozonation versus powdered activated carbon

Ozonation and treatment with PAC have both advantages and disadvantages. Table 2 summarizes the most important issues.

Table 2: Benefits and limitations of ozonation and treatment with PAC

	Facts and Benefits	Limitations
Ozonation	- 2-5 mg/L ozone is necessary, depending on the water flow Q and on the DOC content - 10 min retention time required for storm water conditions, and 20-40 minutes for dry weather conditions - Most substances are oxidized	- Target substances are transformed to mostly unknown transformation products - Post-treatment with biological activity needed - High energy demand at WWTP from ozone production - Regulation of ozone dose is crucial - Safety measures (ozone toxicity)

	- Partial disinfection - Reduction of color	- formation of oxidation by-products - bromate formation from bromide
PAC	- 10-20 mg/L necessary for 5-10 mg DOC/L - 20-30 min hydraulic retention time (HRT) necessary - Most substances are removed - removal of substances (not just transformation) - Reduction of color - DOC is also removed up to 40%	- Post-treatment required (textile or sand filter) to reduce loss of the fine fraction of PAC after tertiary clarifier - PAC step requires sand filter after contact tank for PAC retention, because the retention time SRT_{PAC} = 1-2 days >> HRT to reach sorption equilibrium - production of PAC needs high energy - EPs are removed from water but are still sorbed to PAC, which must be properly disposed (incineration). Bromide may be formed in incineration. - Recirculation into biology improves elimination (10-50%) but also increases sludge production (5-10%) in biology => reduction of SRT (reduction of safety for nitrification) - Safety measures (respiratory protection)

2.3 Regulations for installation of advanced wastewater treatment

Currently, no country is requiring or regulating an EP removal step in wastewater treatment, except Switzerland.

In Switzerland, a new water protection act was accepted, first by the federal council, then the council of states, and finally by the Swiss national council on March 3, 2014. The new water protection act will be implemented in January 2016. According to this new act, certain wastewater treatment plants will need to be upgraded with an additional advanced treatment step to eliminate EPs. The goal of the measure is to improve water quality of surface and ground water and to protect aquatic ecosystems.

To evaluate the effectiveness of the measures taken, twelve substances were defined (Table 3) (Götz et al. 2015, new GSchV). These substances need to be removed in average by at least 80% over the whole WWTP. Currently, it is discussed to replace mecoprop by the corrosion inhibitor mixture 4-/5-methylbenzotriazole because the biocide is only occurring irregularly in the WWTP. 5-Methylbenzotriazole is reacting slightly faster with ozone than mecoprop at pH 7 (von Sonntag and von Gunten, 2012).

Table 3:   The twelve substances proposed in Switzerland to evaluate the effectiveness of measures

substance	class	Elimination with ozone / PAC
Amisulpride	antipsychotic	Very good (>80%)
Carbamazepine	antiepileptic	Very good
Citalopram	antidepressant	Very good
Clarithromycin	macrolide antibacterial	Very good

Diclofenac	antiinflammatory / antirheumatic	Very good
Hydrochlorothiazide	diuretic	Very good
Metoprolol	beta blocking agent	Very good
Venlafaxine	antidepressant	Very good
Benzotriazole	corrosion inhibitor	good (50-80%)
Candesartan	antihypertensive agent, angiotensin II antagonist	good
Irbesartan	antihypertensive agent, angiotensin II antagonist	good/ Very good
Mecoprop	biocide, plant protection	good

2.4 Decision basis for the choice of ozonation as advanced treatment

2.4.1 Parameters to consider for implementation of ozonation

Ozonation of wastewater is only recommended if several prerequisites are fulfilled. On one side, several parameters have to be considered which influence the costs of the installation. On the other side, no undesired and potentially toxic transformation or oxidation by-products should be formed.

1) A very good biological pre-treatment and elimination of easily degradable compounds is beneficial, as it produces a wastewater with low DOC and nitrite concentration for subsequent ozonation. A higher DOC requires more ozone because the bulk organic matter is mainly responsible for ozone consumption, so less ozone is available for the elimination of EPs. Nitrite in the water is reacts very fast with ozone, consuming 1 mol O_3/mol NO_2^- (or 3.4 g O_3/g NO_2^--N). Therefore, the preceding biological treatment should have a well-functioning nitrification.

2) The installation of an ozonation is only recommended with a biologically active post-treatment, e.g. a sand filtration, to eliminate easily degradable substances (assessed as AOC, assimilable organic carbon, or as BDOC, biodegradable organic carbon) produced in ozonation which may be potentially problematic.

3) A reserve area for the installation of an ozone reactor with about 10 minutes hydraulic retention time during peak load and 30 minutes for average dry weather flow should be available.

4) The reserve capacity should be sufficient, so no upcoming costly enlargements are foreseeable.

5) Ozonation might not be the choice for a WWTP with high fractions of industrial wastewater. If a wastewater contains significant amounts of "unknown" chemicals, which can be the case when industries are connected to municipal wastewater treatment plants, ozonation might lead to the formation of undesired transformation products.

6) Problematic ozonation by-products (bromate, NDMA) have to be investigated.

7) The toxicity of the wastewater after ozonation needs to be assessed. EPs are not completely removed with ozone, but transformed to new, mostly unknown products. They can be best evaluated by ecotoxicological assessment of the whole effluent.

Schindler Wildhaber et al. (2015) have recently proposed a modular laboratory decision tool based on the findings of previous investigations to test the feasibility of ozonation as an option for advanced wastewater treatment. In these modules, the assessment of four parameters is proposed (Figure 1): the matrix effects on ozone stability, the efficiency of EP removal, the formation of oxidation by-product, and bioassays to measure specific and unspecific toxicity of the treated wastewater.

The modules 1-4 can be assessed in the laboratory. If necessary, a fifth module can be included to test certain parameters on-site at the wastewater treatment plant. In the following chapters, each of the modules will be explained in detail.

The proposed tests can be easily performed and implemented by a private environmental laboratory. Estimated time for all the tests is about 3 months, so it needs to be planned in due time. The costs are estimated to be about CHF 30'000 - 40'000. In Switzerland, this test procedure will be included in the planning of future advanced treatment steps in WWTPs to reduce EPs. The Swiss water association will therefore publish a recommendation including a description of the methodology and a guideline for helping to interpret the results.

Figure 1: Overview of the five modules of the decision tool for suitability of ozone treatment (from Schindler Wildhaber et al. 2015, with permission).

2.4.2 Module 1: ozonation matrix effects on ozone stability

in a comparison of ten different municipal WWTPs from Switzerland, Australia and the USA, Lee et al. (2013b) found that the elimination of EPs in municipal wastewater effluents with varying water quality can be predicted from only a few parameters. These key parameters are the DOC-normalized ozone dose, the rate constants for the reaction of the selected EPs with ozone and •OH, and the measurement of the ozone

and •OH exposure. Ozone exposure is calculated from the area under the ozone decay curve in a specific wastewater (Bader and Hoigné 1981), while •OH exposure is calculated from the elimination of an ozone-recalcitrant compound like *para*-chlorobenzoic acid (Elovitz and von Gunten 1999, Lee et al. 2013b).

This predictability of EP elimination in a "regular" wastewater defines reference values of ozone and •OH exposures to be compared to for any other municipal wastewater. If the exposure data measured at several ozone doses are not in the expected range, the wastewater matrix might contain unknown ozone-consuming constituents, which may lead to undesired or even toxic transformation products. In this case, ozonation may not be recommended.

2.4.3 Module 2: efficiency of EP removal

The ozone and •OH exposure values at specific ozone doses determined in module 1 are used to calculate the elimination of phenytoin and atrazine. The rate constants for the reaction of these two compounds with ozone and •OH are well known, and their elimination is largely controlled by their reaction with •OH as their reactivity with ozone is very small (k_{03} <10 M^{-1}s^{-1}) what corresponds to a contribution of less than 5%. Therefore, ozone exposure data are not necessary for this prediction.

Phenytoin and atrazine are spiked to the WWTP effluent at concentrations of 1 µM and analyzed after several hours, e.g. by HPLC with UV detection (Lee et al. 2013b). The measured elimination rates can then be compared to the calculated rates. This relation is usually very good, and in WWTP with higher •OH exposure, the elimination is higher. With this module, elimination of ozone-refractory EPs can be predicted for each wastewater, and the comparison to measured elimination confirms the assessed •OH exposure data in module 1. The plants with very low •OH exposure values show low elimination, where ozonation may not be recommended. Compounds that react well with ozone are not considered in this module as they pose no limiting factor for ozonation.

2.4.4 Module 3: oxidation by-product formation

In this module, two well-known and problematic ozonation by-products are assessed: bromate and *N*-nitrosodimethylamine (NDMA).

Bromate is formed during ozonation of bromide-containing waters. Bromide sources are geogenic, from industries, from the washing water of ash of waste incinerator plants, and from landfill leachates, but up to 50% still from unknown industrial sources. Bromide and bromate can be measured by ion chromatography followed by a post-column reaction with UV detection down to 20 µg/L for bromide and 2 µg/L for bromate (Salhi and von Gunten 1999).

At specific ozone doses below 0.5 gO$_3$/gDOC, only little bromate is formed, as, due to the quick decomposition of ozone, the ozone exposure is only very small at these doses (Lee et al. 2013b). With increasing ozone doses, a gradual increase of bromate formation can be found (Soltermann et al., 2015; Deliverable 31.1). The yield of bromate formed from bromide ($[BrO_3^-]/[Br^-]_0$) is between 10-20% at a specific ozone dose of 1 gO$_3$/gDOC.

The environmental quality standard proposed by the Ecotox Centre Eawag-EPFL to protect the aquatic organisms is 50 µg/L bromate. Bromate is a suspected human carcinogen, and, therefore, the drinking

water standard has been set to 10 µg/L bromate by EU, Germany and Switzerland. In the Netherlands, the drinking water standard is only 1 µg/L bromate and is associated with a 10^{-6} lifetime excess cancer risk. Therefore, the concentration of bromate after dilution in the receiving water should not exceed the value of 10 µg/L, and preferentially not exceed 1 µg/L to be on the save side for drinking water production. That means that, for a receiving water body with a typical dilution factor of 10, the concentration of bromate in the WWTP effluent should be below 10 µg/L to be in line with the Dutch drinking water standard. Bromate is very persistent and is not degraded in a biological post-treatment step, nor in rivers or under aerobic riverbank filtration conditions. Only under anaerobic conditions, bromate is reduced to bromide.

N-nitrosodimethylamine (NDMA) can be formed from the reaction of secondary amine precursors with ozone. Usually, yields are low, but for a limited set of precursors containing hydrazines (e.g. unsymmetrical dimethylhydrazine and semicarbazides) or sulfamide functional groups, yields could be ≥ 50% (Kosaka et al. 2009; Schmidt and Brauch 2008; von Gunten et al. 2010; Krasner et al. 2013). For example, *N,N*-dimethylsulfamide, a degradation product of the fungicide tolylfluanide, resulted in high NDMA formation in ozone treatment of German drinking water (Schmidt and Brauch 2008). Chloramination, however, is the major cause of nitrosamine formation in drinking water in the US (Krasner et al. 2013). NDMA needs to be enriched by solid phase extraction and analyzed either by HPLC with post-column UV photolysis/Griess reaction down to 3 ng/L (Lee t al. 2013a) or with LC followed by high resolution mass spectrometry down to 1 ng/L (Krauss et al. 2008).

Drinking water concentrations in the low ng/L level are associated with a 10^{-6} lifetime excess cancer risk. Accordingly, California's Department of Public Health (CDPH) set a 10 ng/L notification level for NDMA, and the Dutch drinking water standard is 12 ng/L. The WHO recommendation for NDMA in drinking water is 100 ng/L.

The formation of NDMA does not significantly correlate with the ozone dose (Hollender et al. 2009, Zimmermann et al. 2011, Schindler Wildhaber et al. 2015, our findings in deliverable 31.1). Thus, the composition of the secondary clarifier effluent with likely changing concentrations of different NDMA precursors and varying NDMA formation rates affects the NDMA formation rate more than the ozone dose. The formation of NDMA varies greatly from plant to plant. At an ozone dose of 1 gO$_3$/gDOC, NDMA formation of more than 100 ng/L was observed in one case (Schindler Wildhaber et al. 2015). NDMA was at least partially reduced in biological post-treatment steps in all studies, but degradation is very variable. In some WWTPs, NDMA is already present in high concentration in the primary effluent before biological treatment (Krauss et al. 2009; Sedlak et al. 2005). A large daily variation and variation among different WWTPs was noted (influent or primary effluent concentration from below detection limits to 990 ng/L). In biological treatment, NDMA concentrations usually decreased. In the secondary effluent of 20 investigated Swiss WWTP, concentrations varied from below detection limit to 188 ng/L (Krauss et al. 2009). In the US, concentrations in not chlorinated effluents were found up to 380 ng/L (Sedlak et al. 2005; Pehlivanoglu-Mantas et al. 2006; Plumlee and Reinhard 2007). The Californian drinking water alert level of 10 ng/L may be exceeded in the receiving river water, even with a dilution of a factor of 10 and higher. Therefore, and because the formation of NDMA by unknown precursors is unpredictable, the assessment of the fate of NDMA is considered an important step in the test system.

2.4.5   Module 4: Bioassays

In this module, the (eco)toxicity of the ozonated wastewater before and after biological treatment is assessed with a range of bioassays, including *in vitro* and *in vivo* tests. The results are compared to effects in the untreated effluent of the WWTP. Five different bioassays are proposed: The Ames test, the Yeast Estrogen Screen (YES), and the combined algae assay (performed with solid phase extracted (SPE) samples to be sensitive enough), as well as the *Ceriodaphnia dubia* reproduction assay and the fish embryo toxicity test with *Danio rerio* (performed with native wastewater effluent samples to include the effect of very polar compounds not well extracted by SPE).

If a toxicity increase is found after ozonation, further clarifications are necessary.

1) With the **Ames test**, the mutagenicity of the water is evaluated. In this assay, mutants of the bacteria *Salmonella typhimurium* are used (Ames et al. 1975), and in the Ames fluctuation test, three different strains (TA98, TA100, YG7108) are tested (Mestankova et al. 2014).

    Increased mutagenicity was observed after ozonation of several WWTP secondary effluents, especially with the YG7108 strain without metabolic activation. After biodegradation, the observed mutagenicity disappeared.

2) The **yeast estrogen and androgen screen** (YES and YAS) are used to assess estrogenic and androgenic activity (Routledge and Sumpter 1996, Escher et al. 2008b). These assays are performed with genetically modified yeast cells. The estrogenic activity in the sample is assessed relative to a reference substance 17β-estradiol and is expressed as 17β-estradiol equivalent concentrations (EEQ).

    Estrogenic activity was often detected in the effluents of WWTPs, even exceeding the proposed chronic quality criterion for Switzerland of 0.4 ng/L for 17β-estradiol (E2) (Oekotoxzentrum 2014). After ozonation, the estrogenic activity is usually reduced below the quantification level, confirming the high removal efficiency of estrogenicity during ozonation of wastewater (Escher et al. 2009; Margot et al. 2013; Stalter et al. 2011).

    Androgenic, anti-androgenic and anti-estrogenic activity were usually not detected in the assessed wastewater effluents and after ozonation.

3) The **combined algae assay** with the green algea *Pseudokichneriella subcapitata* is used to detect non-specific effects leading to a reduced growth of the algae and the inhibition of photosynthesis (Escher et al. 2008b). The effects are reported as diuron equivalent concentrations (DEQ). This assay responds mainly to inhibitors of photosynthesis as e.g. the herbicides atrazine, diuron, isoproturon and the algicide terbutryn (Margot et al. 2013).

    Ozonation usually reduced algal toxicity in the wastewater, with no further decrease by subsequent biodegradation.

4) The *C. dubia* **reproduction test** is used to assess chronic toxicity. In this assay, the impact of pollutants on the offspring production of daphnids is investigated according to ISO 20665:2008. Results are expressed by the estimated concentration of the sample that induces an inhibition of 50% (EC_{50}) of the population growth with respect to the control at the end of the test.

Ozonation often did not reduce the existing toxicity in the effluent, while partly a lower toxicity after ozonation was observed. In some cases, ozonation also led to an increased toxicity. However, after the subsequent biological step, the wastewater was not toxic anymore (Schindler Wildhaber et al. 2015).

5) The **embryo toxicity test with the fish *D. rerio*** is performed according to the guideline DIN EN ISO 15088:2008. The endpoints mortality and deformation are observed. Results are expressed as the lowest concentration, at which at least 90% of the embryo do not show any effects.

Often, ozonation did not evoke any toxicity. In selected cases, ozonation increased the toxicity, but, after biodegradation, the toxicity was usually gone. However, it has been shown previously that the embryo toxicity test with *D. rerio* is not sensitive enough to assess low levels of toxicity in WWTP effluents (Abegglen et al. 2009; Kienle et al. 2011).

3 Advanced drinking water treatment

3.1 Choice of technology

For using surface water as a source for drinking water production, a high level of purification is required. In the Netherlands 2/3rd of the drinking water is produced from groundwater, whereas 1/3rd is produced from surface water. In Switzerland, 40% of groundwater and 20% of surface water is used, while another 40% comes from natural spring water sources. For current surface water treatment in the Netherlands, mostly flocculation and sedimentation are applied, followed up by filtration steps. In Switzerland, rapid and slow sand filtration and filtration over activated carbon combined with ozonation are commonly used techniques. Finally the water is disinfected, mostly by means of an UV process. These techniques, however, are not really optimized to remove increasing amounts and concentrations of organic EPs, and therefore several drinking water utilities are considering additional or upgraded (oxidation) processes. Both treatments with ozone (O_3 or O_3/H_2O_2) or with UV/H_2O_2 are feasible to remove EPs.

Discovered in 1839, ozone was only applied in full scale in the early 1900s for drinking water disinfection in Nice (France). The number of full-scale ozone applications for drinking water treatment stayed very limited in the years after, mainly because of the lower costs of chlorination. However, from the 1940s, many countries in Europe, North America and Asia started to install drinking water facilities using ozone (von Sonntag and von Gunten, 2012), also for elimination of color and taste and odor. Several hundred of drinking water facilities worldwide are applying ozone nowadays.

The main disadvantage of ozonation processes is the formation of bromate, a suspected carcinogenic compound, formed from the oxidation reactions of bromide with ozone and hydroxyl radicals (see Figure 2). This by-product was shown to be not biodegradable, not removed by conventional biological post-treatments like activated carbon and only slightly removed by UV post-treatment. Consequently, its formation during ozonation reactions has to be mitigated and, for that, its mechanism of formation has to be clearly defined.
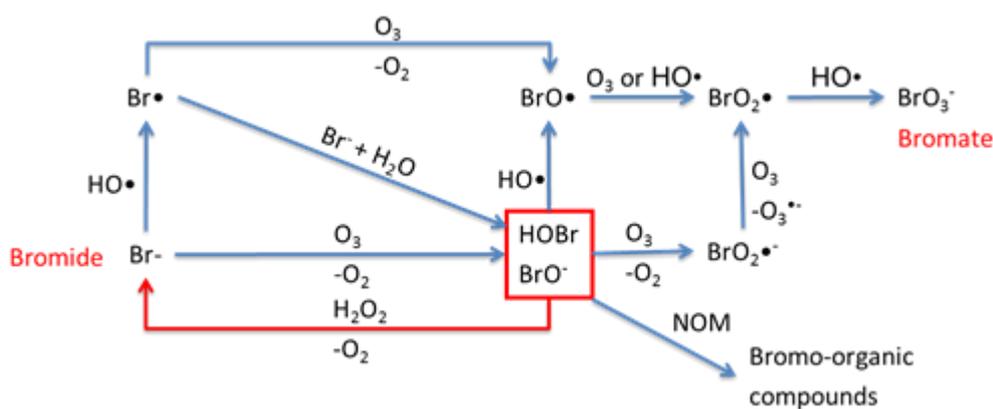

Figure 2: Formation of bromate (BrO_3^-) during ozonation of bromide-containing waters (von Gunten 2003, von Gunten and Oliveras, 1998).

The addition of H_2O_2 leads to a faster decomposition of O_3 to •OH, which are able to abate more persistent EPs. Another benefit from the addition of H_2O_2 in ozone-based processes is the mitigation of bromate formation (Figure 2). In UV treatment, no bromate is formed (von Gunten and Oliveras, 1998).

Due to the toxicity of bromate, the drinking water standard has been set to 10 µg/L bromate by WHO, EU and Switzerland. The Dutch drinking water act has set the value to 1 µg/L bromate. Consequently, the concentration of bromide in the raw water is crucial for the choice of the treatment technology.

An estimation of energy calculations was given recently for the 3 processes (conventional ozonation, O_3/H_2O_2 and UV/H_2O_2) (Table 4; Katsoyiannis et al. 2011). This estimation was realized based on a 90%-abatement of an ozone-refractory compound (para-chlorobenzoic acid, pCBA), assuming an average energy requirement of 15 kWh/kg and 10 kWh/kg for O_3 and H_2O_2 production, respectively. Table 4 shows that the energy requirement for the conventional ozonation varied depending on the water matrix between 0.035 and 0.2 kWh/m^3 for 90% pCBA abatement, while it ranged 0.043 - ~0.25 kWh/m^3 for the ozone-based AOP. This latter is therefore slightly more energy demanding (by 23%) than the conventional ozonation, due to the demand from H_2O_2 production. However, this increase in energy demand is compensated by a reduction of hydraulic residence time (due to a faster kinetic) and a reduction of bromate formation.

Table 4: **Energy requirements (kWh/m^3) for 90% pCBA abatement in different water matrices by conventional ozonation, O_3/H_2O_2, and UV/H_2O_2, using 1, 5 and 10 cm path length and 0.2 mM H_2O_2 (after Katsoyiannis et al. 2011).**

Water matrix	Ozonation	O_3/H_2O_2	UV/H_2O_2		
			1 cm	5 cm	10 cm
Lake water 1	0.035	0.043	0.75	0.23	0.17
Lake water 2	0.035	~ 0.043	1.28	0.45	0.36
Lake water 3	0.065	~ 0.080	1.92	0.61	0.48
Wastewater	0.2	~ 0.25	2.28	0.82	0.70

The UV/H_2O_2 process was shown to require significantly more energy (between 0.17 and 2.28 kWh/m^3) depending on the water matrix and the path length. In every case, the UV/H_2O_2 process was more energy demanding than the ozone-based processes by a factor of 3.5 - 36.5. This factor is generally increasing inversely to UV path length and alkalinity and to a smaller extent to the concentration of DOM.

Despite higher costs, an UV/H_2O_2 treatment may be considered in case of very high bromide concentration in the raw water. A decision tool for drinking water treatment by means of oxidation processes is proposed in Figure 3. The exact Br-limit may vary from water to water.

Surface water in the Netherlands contains relatively high concentrations of bromide (100-400 µg/L; Kruithof and Meijers 1995). Therefore, currently only one Dutch drinking water company applies ozone at full scale as a pre-oxidation method before BAC filtration (v.d. Helm et al. 2009; v.d. Aa et al. 2012). Dunea decided to build a two-step process with O_3/H_2O_2 followed by UV/H_2O_2 (Scheideler et al. 2011; Lekkerkerker-Teunissen et al. 2012).

Br⁻ ≤ 100µg/L*
NOM ≥ 5 mg/L → **Yes** → O₃ or O₃/H₂O₂ Depending on type and conc. of pollutants and water quality

No

UV-T <70% → **Yes** → Adsorption, membrane filtration

Yes → Pretreatment with AC or O₃/H₂O₂ (depending on Br- conc.)

No

UV/H₂O₂

[NO₃⁻] > 10 mg/L → **Yes** →

Yes → Pretreatment: Removal of NO₃⁻ and/or NOM

LP UV

No

MP or LP UV

Design of installation, depending on:
- UV-T
- Water matrix
- Type of pollutants
- Formation of transformation products

↔ Optimization:
- MP (if possible) or LP
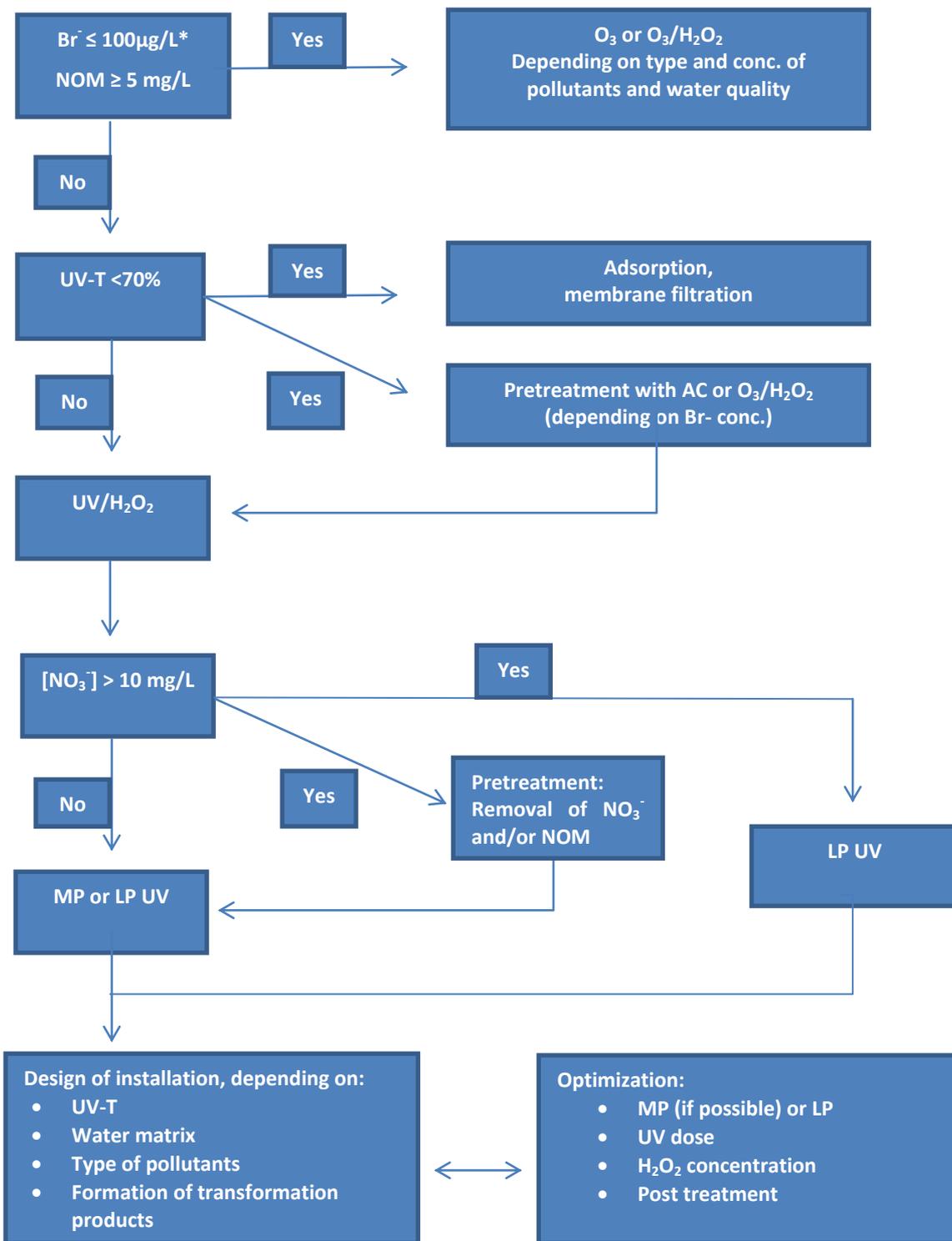- UV dose
- H₂O₂ concentration
- Post treatment

Figure 3: Decision tree for the application of (advanced) oxidation processes (O₃/H₂O₂ or UV/H₂O₂) in drinking water production. *The exact Br⁻ limit may vary from water to water. The NOM criteria does not apply for ozonation.

For other Dutch drinking water companies the use of ozone, even in a combined process e.g. with H_2O_2, often is not possible because of bromate formation, as was shown by research at e.g. PWN, a Dutch drinking water utility (Kruithof et al. 2002). Therefore the UV/H_2O_2 process was studied in the past few years. PWN already has over ten years of experience with this process at full-scale, and other companies, like Dunea and WML, are interested in its application at large scale. The process is also very effective in the removal of a broad range of organic EPs. Apart from the fact that it does not generate bromate, its advantage is that most companies already have a UV-process used for disinfection, which may be extended to an advanced oxidation process. For advanced oxidation the UV dose has to be about ten times higher than for disinfection purposes.

3.2 Comparison of O_3 and O_3/H_2O_2 treatment

Additionally to the energy assessment and the potential formation of by-products, other criteria have to be considered for the implementation of an ozone-based process, concerning the objectives of treatment (EPs elimination and disinfection) and water quality parameters. These criteria are described hereafter.

3.2.1 EPs abatement

Though ozone is known to oxidize directly a wide range of molecules containing reactive chemical functions (olefins, amines, phenols, anilines, sulfides, among others), some compounds are more persistent and react exclusively with OH radicals (*i.e.*, alkanes, amides, benzenes, …). Even though the half-life of •OH is extremely short in aqueous solution (in the microsecond range), they are non-selective and extremely reactive (k_{OH}: 10^8-10^{10} M^{-1} s^{-1}). Therefore, to enhance the O_3 transformation to •OH, ozone-based processes for water treatment may be converted to an advanced oxidation process by (i) addition of hydrogen peroxide, (ii) irradiation with UV-light, (iii) increasing of pH or (iv) decomposition of ozone by catalysts or activated carbon (von Gunten et al. 2003).

The AOP O_3/H_2O_2 is the most used ozone-based AOP where H_2O_2 and ozone are usually dosed with the molar ratio of 1:2. However, additional experiments have been carried out with a greater excess of ozone or conversely with an excess of H_2O_2. However, when the H_2O_2 dose is too high (*i.e.*, for a $H_2O_2:O_3$ molar ratio > 3), OH radicals may be scavenged by H_2O_2 and the efficiency of the treatment may be directly affected (Buxton et al. 1988).

3.2.2 Disinfection

Ozonation was originally proven to be very efficient for the inactivation of microorganisms such as *Escherichia coli*, *Cryptosporidium parvum* or *Giardia lamblia* (Peter 2008).

Nevertheless only the direct reaction of microorganisms with ozone is assumed to occur during the disinfection process (Hoigné and Bader 1975; Hoigné and Bader 1978). For this reason, AOP O_3/H_2O_2 is not recommended for disinfection purposes. However, AOP O_3/H_2O_2 may be implemented as a complement of conventional ozonation: this latter is usually applied first to get the necessary inactivation of microorganisms and hydrogen peroxide is dosed afterwards to decompose ozone to •OH to accelerate abatement of ozone refractory compounds.

3.2.3 Dissolved organic matter and alkalinity

The lifetime of ozone in drinking water is mainly governed by its reaction with dissolved organic matter (DOM). The concentration and the nature of the DOM is indeed influencing the stability of ozone, which is essential for EP removal and disinfection. In the case of drinking waters, the concentration of DOM, measured as DOC, is generally between 0.5 and 5 mg C/L.

Due to its broad range of chemical functions and high concentration in water sources, DOM may readily scavenge ozone and enhance its decomposition to $\bullet$OH (Nöthe 2009; Pocostales 2010). The presence of carbonate and bicarbonate ions, defined as alkalinity, is also an essential parameter involved in the stability of ozone (Hoigné et al. 1985).

However, due to the complexity of the water matrix, especially from the DOM, the estimation of O_3 and $\bullet$OH concentrations is difficult. Therefore, the R_{ct} concept was developed, defined as the ratio of $\bullet$OH concentration to the O_3 concentration (Elovitz and von Gunten 1999). This approach aims first at determining the respective O_3 and $\bullet$OH exposures and then to predict the elimination of EPs in the studied water. The R_{ct} is usually ranging between 10^{-7} and 10^{-10}. The addition of H_2O_2 increases significantly the R_{ct} by decomposing ozone to hydroxyl radicals.

3.2.4 Bromide concentration in raw water

Bromide is naturally present in water sources in the range of low $\mu g\ L^{-1}$ to low mg L^{-1}. As stated above, the ozonation of bromide-containing waters is problematic when the concentration of bromate in the distributed waters might exceed the guideline values. The initial concentration of bromide in the raw water is therefore an important criterion for the implementation of ozonation. It appears difficult to apply ozonation for the treatment of drinking water with a bromide content higher than 100 µg/L. However, the exact bromide limit may vary from water to water and depends on what needs to be achieved. For disinfection, it is typically harder to comply with bromate standards than for oxidation.

3.2.5 pH

The pH of drinking water resources can generally vary from 6.5-8.5. The pH is an important water quality parameter for the elimination of EPs: some compounds are much more reactive with ozone at higher pH. These are the dissociating compounds, like the phenols or the amines. As an electrophilic compound, ozone is then more reactive with this species and the second-order rate constant of the reaction might be dramatically increased, generally by an order of magnitude per pH unit increase. For instance, the molecular form of phenol has second-order rate constant of $1.3 \times 10^3\ M^{-1}\ s^{-1}$, while the second-order rate constant of the anionic form (phenolate) is $1.4 \times 10^9\ M^{-1}\ s^{-1}$ (Hoigné and Bader 1983). The reactivity of non-dissociating compounds, like olefins, with ozone is not influenced by the pH of the solution. The hydroxyl radicals formed during the ozone-based processes are unselective and very reactive with many chemical functions, but the reactivity of hydroxyl radicals with organic compounds is considered as pH-independent. Since the yield of $\bullet$OH is almost independent of pH, for full O_3 consumption the same elimination can be expected. At higher pH, a higher formation of bromate is observed for a given O_3 exposure. More O_3 is decomposed in the reactor at higher pH, leading to a higher overall oxidant exposure.

3.3 Treatment with UV/H$_2$O$_2$

As the surface water in the Netherlands contains relatively high concentrations of bromide, only one utility, Waternet, applies ozone for disinfection and as a pretreatment technique before BACF (v.d. Helm et al. 2009; v.d. Aa et al. 2012). PWN built a full scale UV/H$_2$O$_2$ installation to deal with organic EPs because of too high bromate formation with O$_3$/H$_2$O$_2$ (Kruithof et al. 2002). Recently, Dunea decided to build a two-step advanced oxidation process (Scheideler et al. 2011; Lekkerkerker-Teunissen et al. 2012). In the first step ozone and H$_2$O$_2$ are added, to degrade part of the EPs and to increase UV-transmission (UV-T). The ozone concentration here, too, has to be kept below a certain limit, in order to comply to the strict Dutch drinking water standard of 1 µg/L bromate. After this reaction step the excess H$_2$O$_2$ is irradiated with UV to obtain sufficient degradation of EPs. As the UV-T is increased by the O$_3$/H$_2$O$_2$ process, the UV/H$_2$O$_2$ process becomes much more efficient.

Another drinking water utility, WML, also is interested in an additional process to eliminate EPs. Here too, bromide concentration is relatively high (ca. 90 µg/L, and is expected to increase due to the presence of a local pollution (Hofman et al. 2013). As a result, the application of ozone will not be possible. However, as the pretreated water of WML has a very high UV-T (ca. 94%), the UV/H$_2$O$_2$ process here is extremely efficient, with a very low energy demand.

Whether or not ozone as (advanced) oxidation can be applied depends on both the bromide and NOM concentrations (v.d. Hoek et al. 1995). This had been discussed above and a decision tool is presented in Figure 3. The values given in the decision tool are rough estimates based on this research performed at Waternet. It should be kept in mind that also temperature is a parameter that may affect the bromate formation, and that for an individual case local conditions should be thoroughly considered. In case of ozone or ozone combined with H$_2$O$_2$ will result in too much bromate formation, UV/H$_2$O$_2$ may be an interesting alternative. Which method will be most effective will depend on the composition of the EPs involved: some will be more sensitive towards oxidation by ozone, whereas others can easily be converted by means of UV photolysis. Combination with H$_2$O$_2$ in both cases results in the formation of hydroxyl radicals, which are very reactive and non-selective, and thus can react with a broad range of compounds.

UV or UV/H$_2$O$_2$ treatment are known to be the only efficient methods for degradation of NDMA due to the strong photolability of NDMA. NDMA contaminated water can be effectively treated by low-pressure or medium-pressure Hg lamps (Stefan and Bolton, 2002; Sharpless and Linden, 2003), and photolytic mechanisms of NDMA degradation have been suggested (Lee et al., 2005a and Lee et al., 2005b).

The main disadvantage of the UV/H$_2$O$_2$ process is its relatively high energy demand, as high doses (in general $\geq$ 500 mJ/cm^2) are required. This strongly is related to the UV-T value of the water: the higher this value, the more efficient the process will become. Especially at high values (>90%) a small increase in UV-T may result in a significant improvement of the efficiency. In case the UV-T is rather low (<70%), another technology should be considered. Another possibility would be to improve the water quality by applying a pretreatment, e.g. filtration over activated carbon or pretreatment with O$_3$/H$_2$O$_2$. This will require a cost-benefit analysis.

In case the previous considerations result in the decision to use UV/H$_2$O$_2$, the nitrate concentration may be an important factor. It was shown that the photolysis of nitrate, in combination with the presence of NOM, may result in the formation of possibly mutagenic byproducts (see DEMEAU deliverable 31.2, Hofman-Caris et al. 2013). To prevent this, at nitrate concentrations > 10 mg/L, photolysis of nitrate may be prevented by applying LP instead of MP UV lamps, by using sleeves which exclude wavelengths in the range 200-240 nm, or possibly to remove nitrate and/or NOM. This depends on the type of EPs present, whether or not a broad range of wavelengths (MP lamps) is more efficient than only 254 nm.

The final design and optimization of the installation strongly depends on local conditions. Depending on the required degree of abatement of the EPs and local concentrations, the required energy may also vary. UV-T and concentration and composition of NOM will play an important role in the operation costs of the process. Therefore, it is difficult to give general cost estimations.

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