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Review of literature to determine the uses for ozone in the treatment of water and wastewater

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Executive Summary

This paper responds to a CREW call down request submitted by Scottish Water.

A review of literature to determine the uses for ozone in the treatment of water and wastewater; in particular:

- point of use disinfection of water supplies
- inactivation of cryptosprodium oocysts
- bulk disinfection of potable water supplies at treatment works
- oxidation of organics, iron and manganese
- other uses

Wastewater:

- impact of ozone on filamentous bacteria
- disinfection of final effluent
- other uses

Disinfection of potable water using ozone

In most water treatment plants ozone is used for multiple applications. Ozone is now used as a disinfectant, an oxidant of organic and inorganic molecules, a coagulant aid, removing taste and odour, a means of controlling algae and as a way of biologically stabilising water. Ozone is very effective for disinfection against bacteria, viruses and protozoa. However, when used in a disinfection capacity, it is often used when contaminants are highly resistant to more conventional disinfectants.

It has been described as the only chemical form of disinfection to provide effective inactivation of *Cryptosporidium* and *Giardia* at doses similar to those used routinely for water treatment. For drinking water, the CT concept or derivations of it are usually suitable for determining the required dosage. Inactivation of *Cryptosporidia* in final effluent following wastewater treatment differs from drinking water treatment due to the different water quality parameters. This renders the CT approach much less effective for wastewater disinfection.

There is substantial variability across studies on ozone inactivation of *Cryptosporidium* spp. which makes them difficult to summarise or directly compare. This is due to differences in the way studies are performed (e.g. lab *vs*. pilot *vs*. full scale; synthetic or real water sources, artificial seeding with oocysts and continuous *vs*. discontinuous ozone supply) and way in which the values are reported, for example applied or transferred/residual ozone doses; differences in the level of detail with respect to water quality parameters.

Despite this, log inactivation of *Cryptosporidium* following ozone application is frequently reported to be within the 2-3 log range. Of the literature data evaluated graphically (45 data points from 12 studies), 61 % showed greater than 2-log inactivation. The CT relationship was not clear due to the study differences highlighted above. Because *Cryptosporidium* is highly resistant to external stressors including disinfectants, log inactivation cannot be reliably derived from studies of other pathogens or indicator organisms. For example, in a study evaluating *Cryptosporidium* inactivation in river water, Owens et al (2000) demonstrated that the CT required for 2-log inactivation of *Cryptosporidium* (*C. parvum* and *C. muris*) was 12 times greater than that required for the same

degree of inactivation of *Giardia muris* cysts. *Bacillus subtilis* spores show some promise as conservative indicators for *Cryptosporidium* inactivation, however.

Sequential disinfection schemes involving two disinfectants have been proposed to provide a certain level of synergism, which may allow greater levels of inactivation to be achieved in drinking water treatment plants (Gyurek et al., 1996; 1997; Liyanage et al., 1997). Rennecker et al. (1999b) indicated that sequential disinfection with ozone followed by free chlorine was promising for the treatment of oocysts.

A number of water quality parameters strongly influence the efficacy of the ozone to disinfect:

- Temperature: as temperature increases, the disinfecting power of ozone increases. Temperature influences inactivation of *Cryptosporidium*, with a 4.5-fold increase in CT suggested for a 10 degree C rise in water temperature.
- pH: changes in water pH changes the balance of available O_3 and OH An increase in pH from 6 to 9 reduces the amount of O_3 available for disinfection by a factor of 40 (Elovitz *et al*., 1999). There is conflicting evidence in the literature relating to the effect of pH on inactivation of *Cryptosporidium*. It has been suggested that in batch systems, increasing pH is correlated with increasing inactivation, but where ozone is continuously bubbled through the system there is limited effect of pH. Inactivation rates of different *Cryptosporidium* species were not substantially different, although a few studies have noted that oocysts of different ages may show differential responses to ozonation.
- Suspended solids and other ozone scavengers: the presence of contaminants other than the target microorganisms may consume ozone and reduce the disinfection capacity of the water. As for other disinfectants, constituents within the water, primarily NOM, EfOM, BDOC, bromide, synthetic organic compounds and alkalinity exert an ozone demand. It is therefore critical to know what is in the water to understand ozone doses and contact necessary to achieve a specific water quality objective.

When applying ozone at a WTW facility, there are four requisite components: (1) oxygen gas feed system (either air or pure oxygen); (2) ozone production and delivery, (3) an ozone contactor and (4) ozone off gas destruction.

One of the key challenges faced when using ozone as an oxidising agent is the formation of disinfection by-product (DBPs) compounds. Ozone tends to produce DBPs in the categories of oxyhalides, aldehydes and carboxylic acids. While many organic and inorganic ozonation disinfection/ oxidation by-products have been identified, bromate is generally considered to be of greatest concern (von Gunten, 2003) and aldehydes are also important although they are not currently regulated (Silva et al., 2010). Where bromide is present in raw waters, bromo-organic by-products can form during ozonation.

There are a number of factors that influence bromate formation. These are:

- Bromine concentration: given that bromide is oxidised by ozone to bromate, an increase in bromide leads to an increase in bromate for a constant ozone dose and contact time.
- pH: As the pH of the water is increased during ozonation, more bromate is formed.
- Alkalinity: The presence of inorganic carbon (IC) species increases bromate formation.
- Ammonia concentration: Ammonia can remove a significant intermediary from the bromate formation path and reduce the amount of bromate formed.

- Transferred ozone dose and contact time: The relationship between bromate formation and CT follows a linear function, with an increase in CT leading to an increase in bromate formation

The formation of disinfection by products of ozonation has been studied with respect to water reclamation and is also pertinent where treated effluent significantly influences raw water for abstraction.

In a study evaluating DBP concentrations across 12 drinking water treatment plants in the US in which sites using all four major disinfectants (chlorine, chloramines, ozone, and chlorine dioxide) were covered, the highest concentration of the DBP dichloroacetaldehyde occurred at a plant using chloramine and ozone disinfection. Therefore, although the use of alternative disinfectants minimized the formation of the four regulated THM, some unregulated DBPs were present in higher levels than where traditional chlorine disinfection was applied. The literature is contradictory, and ozonation can increase THMS where organic loadings of wastewater are still high, however it has also been shown to reduce the formation of both THMs and HAAs where ozone is introduced in combination with chlorination of effluent.

Oxidation of contaminants in water

Compounds present in water can react with ozone directly or indirectly through OH• radicals. Direct ozonation is usually the most important oxidative reaction if the radical reactions are inhibited due to the lack of initiating compounds to begin the chain reaction or due to the presence of too many radical scavengers. The direct pathway normally dominates under acidic conditions (pH <4) and changes to the indirect pathways above pH 10. Both pathways will therefore play a role in most ground and surface waters (pH ~ 7).

A number of compounds can be directly degraded by ozone. These include taste and odour compounds (geosmin and methylisoborneol (MIB)), phenolic compounds and pesticides such as atrazine. The importance of ozonation in the treatment of industrial wastewaters targeting the degradation of dyes, pharmaceuticals and personal care products has also grown in recent years. Ozone is also used for oxidation of organic macropollutants and its application is used for bleaching of colour, increasing the biodegradability of organic compounds, removal of THM precursors and reducing total organic halide formation potential or chlorine demand. One of the most important ozone applications in water treatment is the oxidation of iron and manganese.

Ozone is capable of destroying a range of volatile micropollutant compounds, in particular alkenes and aromatic organics under the conditions of treatment applied to drinking water. In the past, micropollutant removal was not a primary task for ozone but was considered a positive side effect. However, due to ever lowering detection limits and stricter regulatory requirements for more chemicals in drinking water, the interest in micropollutants has grown in recent years.

The most common taste and odour associated compounds are MIB and geosmin and these have a very low reactivity with ozone. However, despite this, studies with natural waters have shown good removal efficiencies of these compounds when using ozone. It is likely that ozonation is most effective in waters that support the OH• radical pathway. However, the action of ozone in natural waters is variable and depends on the quality of organics present as well as the treatment conditions.

It has been observed for more than 30 years that pre-ozonation ahead of solid-liquid separation processes can improve the removal of particles. Positive effects of pre-ozonation are also seen for algae removal. Ozone readily kills or lyses many types of algae and it has also been observed to enhance the removal of algae by coagulation and settling. Ozone can also be applied to inactivate zooplankton and actinomycetes. A number of laboratory studies have reported the effect of ozonation on the removal of cyanotoxins and it was shown that complete removal of the toxins can be achieved when ozone is included in the treatment process. Ozoflotation is a new process combining the physical phenomenon of flotation with the oxidising properties of ozone and is usually used as a pre-treatment stage in order to reduce the treatment load.

Point of Use systems

There are a range of commercially available point of use (POU) and point of entry (POE) ozonation devices. There is limited scientific literature available on the performance and reliability of these devices and most of the below information has been taken from commercial sources and, as such, limited validation of performance can be gleaned from this data. Independent testing of POU ozone devices is required because to date, most, if not all, claims made by manufacturers have not been verified.

Application of ozone in wastewater treatment

Similarly to drinking water treatment, ozone can be applied to satisfy a number of objectives in wastewater treatment, including:

- Disinfection
- Oxidation of inorganic compounds
- Oxidation of organic compounds
- Enhancement of sludge degradability

Ozone disinfection mechanisms in wastewater are less well understood. Ozone reacts strongly with many substances, therefore it is generally deemed more appropriate for use on pre-treated effluents (Paraskeva and Graham, 2002). In a wastewater of high organic content, inactivation of total and faecal coliforms and *E. coli* has been reported at an applied ozone dose of 10 mg/L for a 5 minute contact time. Ozone doses commonly presented in the literature ranged from 0.3 µg/L to fully saturated, with contact times generally between 1.5 and 18 minutes. This provided a range of inactivation rates, broadly in the range of 1-2.5 log inactivation for coliforms, *Enterococci* and *Clostridia,* while some higher reductions were noted for bacteriophages used as surrogates for human viruses

The critical parameter for disinfection of indicator organisms appears to be the optimisation of mass transfer of ozone, which is usually low due to its poor solubility. Hydraulic retention time appears less important. Meeting the initial ozone demand leads to a substantial microbial inactivation as the microbial cells actually exert a significant proportion of that ozone demand (Xu et al 2002).

Filamentous organisms are a normal part of the activated sludge microflora and, in low numbers, are thought to promote floc formation. Excessively long filaments or presence in high numbers can lead to sludge bulking (Eckenfelder, 1992). Ozone can be used as a “non-specific” approach to reducing filamentous organisms and therefore reducing bulking and foaming in activated sludge systems. Low

dose ozonation can inhibit the activity of filamentous bacteria and has been applied to control bulking and improve floc settling (Foladori et al, 2010).

The efficiency of sludge ozonation depends on the following parameters (Foladori et al; 2010):

- Wastewater or Sludge quality
- Reactor configuration
- Ozone gas flow rate and concentration
- Sludge flow rate and solids concentration
- Ozone transfer efficiency
- Contact time
- Ozone dosage per mass of TSS

Studies have reported improved floc structure directly after the start-up of ozone treatment with few filamentous bacteria remaining inside the sludge flocs. One author reported the number of filaments to be an order of magnitude lower in the ozonated treatment than the control. The authors also indicted that ozonation promoted nitrification and biological removal of organic material without affecting phosphate removal.

The influence of ozone on other wastewater treatment parameters is critical to the success of its use to reduce filaments or excess sludge. Paul and Debellefontaine (2007) noted that there was a linear relationship between the log of biomass activity (reported as maximal oxygen uptake rate) and log ozone dose between 0.001 and 0.2 g O_3 transferred per g COD in the sludge). They concluded that ozonation does not affect any of the capabilities of an AS biological process; however other studies have reported contrary indications. For example, a decrease in nitrification rate has been shown to be proportional to increasing ozone dose (Dyctzak et al (2007), although other studies indicate no effects on nitrification. Reid et al (2007) suggested that a more cost effective ozone process for excess sludge reduction would follow the principle “partial oxidation as low as possible and biological oxidation as high as possible”. This minimises the use of ozone but maximises conversion of solids into biodegradable materials which can then be removed in cheaper biological reactors.

Water quality and ozone demand can be used to determine the best point of application. Broadly, high ozone demand in raw water, indicative of high levels of organic material can lead to increased biodegradability of natural organic matter (NOM) (Beltrán et al. 1999; Ternes et al. 2006) following ozonation. This may then require a biological treatment step to remove BDOC which can lead to bacterial growth in the distribution system. Water with a high ozone demand and high turbidity would be considered the most difficult water to treat with ozone, for example, surface water with a high loading of organic material and inorganic particles therefore selecting a point in the treatment train where particulates and organic matter have been removed substantially would be advisable. However, because ozone can also break down organic material, antibiotics and pharmaceuticals, incorporating ozonation at more than one stage of treatment may be effective. Thus low doses of ozone prior to existing treatment can capitalise on some of these effects.

For wastewater, ozonation is often part of a multistage treatment process to reduce ozone consumption. Most often a chemical-biological process includes biodegradation at least before and also often after the chemical oxidation step (Gottschalk et al, 2010). Ozone quantities and generation costs tend to be reduced when utilising these combined systems.

Dissolved organic carbon (DOC) concentrations are typically greater in wastewater than in surface water, resulting in faster O_3 decomposition rates and increased hydroxyl radical ($^{\bullet}OH$) exposures (Buffle et al., 2006). As a result, higher O_3 dosages are required to meet wastewater treatment goals, potentially leading to increased DBP formation.

One of the aims of ozone application in wastewater treatment is to remove toxic inorganic substances and this mainly involves the removal of cyanide (CN-) mostly associated with metal processing and electronics industry wastewaters. Nitrite (NO_2^-) and sulphide (H_2S/S^{2-}) react quickly with ozone and therefore their removal is sometimes carried out using ozonation, however more cost-efficient biological treatment alternatives are more often employed for these contaminants.

Most often in industrial wastewater treatment, ozone is applied to remove target organic compounds that can be present at a wide range of concentrations. These wastewaters include landfill leachate, textile, pharmaceutical and chemical industry wastewaters that can contain many refractory organics including humic compounds, aromatic compounds containing metals, pesticides and surfactants. The main aims of ozonation in this case are (Gottschalk et al., 2000):

- The transformation of toxic organics that are often present in low concentrations and as complex mixtures
- The improvement of biodegradability of refractory organics by partial oxidation
- The removal of colour

Ozonation is a widely used chemical method to improve anaerobic degradability of sludge. Ozonation has also been combined with anaerobic digestion as a pre-treatment or post-treatment with a recycle back to the anaerobic digester. Better performance and lower ozone consumption has been observed in the case of post-treatment and recycling in the digester. The advantages of ozonation pre-treatment of secondary sludge is that it can improve the sludge solubilisation and it can also simultaneously degrade organic pollutants.

Conclusions and recommendations

- Key consideration of ozone treatment for any of the above processes include improved ozone transfer technologies, correct dosage and an awareness of the importance of key water quality parameters such as organic, particulate and bromide loadings.
- Implementation of ozone treatments is likely to be most effective if evaluated on a site by site basis as this not only promotes a thorough evaluation of how to implement the technology for effective disinfection, but would also allow the operators to determine whether ozone interventions at multiple points would be more cost effective for overall treatment and/or whether the inclusion of additional treatment stages before or after ozonation would be required.
- Ozone disinfection of drinking water is highly effective against a wide range of pathogens, including *Cryptosporidium*.
- Cyst and sporular forms of protozoans and bacteria present the most difficult treatment challenge for ozone disinfection. High CT values can control these pathogens, but it is recommended that a physical barrier is also provided for water sources containing these micro-organisms.

- The main limitation of applying ozone in drinking water systems is the production of bromate as a DBP. Methods of controlling bromate formation have been developed, principally through controlling pH and understanding prevailing water quality conditions.
- POU/POE systems are widely available, mainly from North American suppliers that can generate and deliver ozone from mains electricity. A filtration system needs to be supplied after the ozone when these are used in order to prevent precipitated solids from being present in treated water – it is not always evident that the proprietary systems have these as supplied. Who manages and replaces spent filtration systems and adequate off-gas control must therefore be also considered for POU systems.
- A wide range of organic and inorganic contaminants can be degraded by ozone. High concentrations of ozone are needed for effective degradation of bulk natural organic matter and is therefore not recommended for this application. The most effective use of ozone is for oxidation of metals and organic micro pollutants in combination with a physical/adsorptive process.
- The higher contaminant and scavenging load in wastewater means that much higher doses must be applied for these waters in order to achieve satisfactory levels of removal/disinfection. There are many examples of ozone having been used in wastewater for small scale and pilot treatment systems, but few cases of large WWTWs using ozone due to the high cost of having to add such high concentrations of ozone.
- Ozonation of final effluent can be effective, however higher ozone doses tend to be required which increases the likelihood of formation of disinfection by products.
- Ozone can be an effective non-specific inhibitor of filamentous organisms in activated sludge systems but effects on the overall treatment process are variable
- Ozone is a widely used chemical in water and wastewater treatment as well as numerous industrial applications. The ability of ozone to effectively oxidise a wide range of contaminants and disinfect a broad sweep of micro-organisms have made it an essential component of many treatment flowsheets across the world.

Key words

Disinfection, iron, manganese, ozone, oxidation, point of use, wastewater, water.

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A review of literature to determine the uses for ozone in the treatment of water and wastewater; in particular:

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Wastewater:

- impact of ozone on filamentous bacteria
- disinfection of final effluent
- other uses

1.0 Disinfection of potable water using ozone

1.1 Introduction to ozone

In most water treatment plants ozone is used for multiple applications: as a biocide (disinfection), as an oxidant or as a pre-treatment to improve performance of subsequent processes (for example, prior to GAC, sand filtration and coagulation) (Langlais et al., 1991). Due to these multiple uses, ozone may be applied at a number of points in the water treatment train (Figure 1). At all of these stages, ozone may disinfect the water, but its primary use may be for another application (for example oxidation or enhancing biodegradability). At many locations, multiple stages of application of ozone (usually two) have proven to be the most appropriate and cost effective way of meeting specific water quality objectives. The action of ozone may be enhanced by combining ozone with additional chemicals or physical processes to enhance its mode of action. This includes the downstream of adsorption processes such as GAC or the addition of hydrogen peroxide, UV radiation, ultrasound and metallic catalysts (such as reduced iron). In these cases, the aim is to promote the formation of reactive radicals that may enhance the degradation of contaminants and microbes (Glaze, 1987).

For drinking water treatment, ozone is typically applied to the raw water or the water after flocculation and clarification. Water quality and ozone demand can be used to determine the best point of application (Table 1). Broadly, high ozone demand in raw water, indicative of high levels of organic material can lead to increased biodegradability of natural organic matter (NOM) (Beltrán et al. 1999). Here, large organic molecules are converted into smaller organic molecules of more biodegradable dissolved organic carbon (BDOC). This may then require a biological treatment step to remove BDOC which can lead to bacterial growth in the distribution system. High turbidity may indicate the presence of particulate matter which may contain both organic and inorganic components. Organic content is considered to exert more influence on the ozone demand than suspended solids (Janex et al., 2000). The presence of oxidizable organic constituents or bromide ions will generate disinfection by-products upon ozonation. Water with a high ozone demand and

high turbidity would be considered the most difficult water to treat with ozone, for example, surface water with a high loading of organic material and inorganic particles (Table 2). Ozone generally leads to a reduction in disinfectant demand of finished water (USEPA, 1999).

Ozone is frequently used before coagulation to help the downstream coagulation efficiency (Langlais et al., 1991). However, this is usually for lowland reservoir water sources of low organic content. Ozone has been reported to have widely varying effects on the adsorption of NOM to aluminium hydroxide. In raw water, ozone appeared to be more reactive with the humic (FA and HA) fraction of NOM. This led to a decrease in the efficacy of a subsequent alum coagulation step for NOM removal. If humic substances were removed by pre-coagulation with alum and then ozonated, the remaining fractions adsorbed more effectively to alum (Bose et al., 2007). The authors therefore recommended a strategy of staged coagulation with intermediate ozonation for waters containing both humic and non-humic NOM, in order to achieve maximal removal of dissolved organic carbon.

Ozone can also increase the biodegradability of other compounds such as antibiotics and other pharmaceuticals including fibrates (which lower LDL cholesterol) and estrogens (Larcher 2012 and references therein). Thus low doses of ozone prior to existing treatment can capitalise on some of these effects.

Table 1. Water Quality based determination of ozone point of application for drinking water treatment – (Modified from DeMers and Renner 1992; USEPA 1999).

Ozone Demand	**Turbidity**	**Water Characteristics**	**Potential Issues**	**Where to add:**	**Reason**
Low	Low	High quality raw water	-	Raw water	Only practical point of application
Low	High	Inorganic materials (clay, silt)	May produce some DBPs	After pre sedimentation or conventional sedimentation	Reduced ozone demand
High	Low	Dissolved constituents e.g. bromide, iron, manganese, colour, organics	Production of DPB and/ or BDOC	Raw water or post sedimentation. If biodegradable organics produced, best upstream of biological treatment.	Biological treatment may be required to remove biodegradable organics
High	High	High concentrations of organic and inorganic materials	Production of DPB and/ or biodegradable organics	After sedimentation and possibly after filtration If v. high O3 demand, dual O3 feed points may be required	V. high organics may require biological treatment

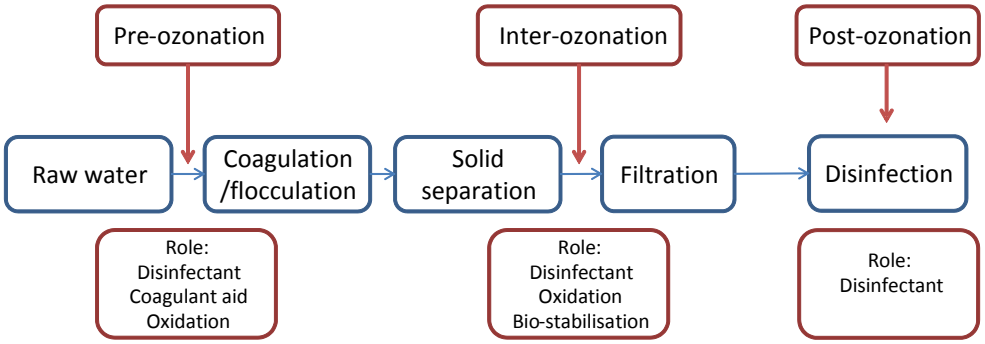


Figure 1. Usual range of dosing positions for ozonation in bulk disinfection of drinking water.

Table 2. Effects of Ozone addition on common water treatment processes.

Process	Effects	References
Biologically Active Filtration (BAF)	↑biodegradability of dissolved organics ↑ DO_2 and efficacy of biological filters ↓ BDOC Removes NOM, reducing potential for DBP formation ↓ Demand for residual disinfectant Helps remove by products of ozonation	USEPA (1999)
Slow Sand Filters	O_3 addition before slow sand filtration ↑TOC and BDOC removal	Rachwal et al. (1988); Zabel (1985); Eighmy et al. (1991); Malley et al. (1993)
Rapid Rate Filters	May ↓ assimilable organic carbon (AOC) but extent of BDOC unclear	USEPA (1999)
All filtration	O_3 oxidation of iron and manganese ↑insoluble oxides and requirement for↑sedimentation or filtration. ↑ backwash frequency.	USEPA (1999)
Granular Activated Carbon	↑ efficiency of GAC removal of BDOC Variable removal of AOC.	Katz (1980); Langlais et al. (1991)
Disinfection	Usually ↓ subsequent chlorine, chlorine dioxide, or monochloramine demand of finished water Possible ↓ NH_4^+ and ↑in NO_3^- presence of ammonium (literature contradictory)	Martinez et al. (2011) and references therein

1.2 Disinfection capability of ozone

Although the widespread use of ozone across the world did not occur until the 1950-60's, the understanding that ozone was an extremely effective way of disinfecting polluted water had been apparent since the end of the 19th century (Langlais et al., 1990). Ozone is now used as a disinfectant, an oxidant of organic and inorganic molecules, a coagulant aid, removing taste and odour, a means of controlling algae and as a way of biologically stabilising water (Table 3). However, in most full-scale applications, the main driver for implementing ozone is for disinfection purposes (von Gunten, 2003a). This is because ozone is an exceptionally good disinfectant that has faster disinfection kinetics and is more potent to most microorganisms when compared with other widely used chemical disinfectants (Table 4). Ozone is very effective for disinfection of bacteria, viruses and protozoa. However, when used in a disinfection capacity, ozone is often preferentially used when contaminants are present that are highly resistant to more conventional disinfectants. For example, as is expanded on elsewhere in this report, ozone is often chosen for disinfection of water contaminated with protozoan cysts (such as *Cryptosporidium* and *Giardia*) because it is far more effective at destroying these organisms at low concentrations and contact times when compared with chlorine based chemicals.

The CT concept (CT being the disinfectant concentration multiplied by the contact time) is an underpinning approach for determining and evaluating disinfection processes in drinking water without attempting to measure actual pathogen inactivation where pathogen numbers are generally too low to enumerate (Broséus et al., 2008). Disinfection is brought about through the combination of disinfectant dose and the length of time for which a given organism is in contact with that chemical. Thus, for inactivation to occur, either a high dose and short contact time or a lower dose but a longer contact time is required. Typically used in the design of drinking water disinfection systems, at its simplest, the CT value is obtained by multiplying the disinfectant residual concentration, C, by the contact time, T, in the water system from the point where the disinfectant is applied to the point where the residual is measured (USEPA, 2009). C is usually measured at the end of the contactor, therefore reflecting minimal oxidant concentration and T is usually represented by T_{10}, the time taken for 10% of the water to pass through the reactor. The basic CT_{10} concept, while conservative does not take into account the effects of water quality (other than temperature and pH which are incorporated into CT reference tables) and modifications of the equation have been developed (e.g. Broséus et al, 2008) with the aim of providing better estimates of CT under full scale conditions. These are extensively reviewed by Rakness (2005).

The linear Chick-Watson model describes the inactivation of microorganisms with chemical disinfectants as a first order chemical reaction.

$\ln (N/No) = -kCnt$ where:

N = number of microorganisms present at time t
N0 = number of microorganisms present at time 0
k = coefficient of specific lethality
C = coefficient of disinfectant
n = coefficient of dilution (constrained to unity in the linear form)
t = time

A constant rate of kill is not realistic for some organisms and disinfectants and models incorporating additional parameters, for example to account for tailing off in survival curves (Hom model) have been applied. However, they do not always provide a better fit (Oppenheimer et al., 2000) in which case the linear Chick-Watson model is as effective.

Advanced CT models provide an effective tool for evaluating effective microbiological CT of disinfection processes under different conditions and controlling CT can reduce DBP formation (Broséus et al, 2008). The CT required to achieve a given level of inactivation is unique (Driedger et al., 2000), although some authors have suggested that doses of 5-15 mg ozone per L is required for adequate disinfection (Martinez et al, 2011). Since long contact times can only be facilitated by large volume contacting systems, which have large footprints and require large capital investments, high dissolved ozone concentrations are likely to be advantageous Meyer et al. (2000).

Table 3. Overview of ozone applications in water treatment (adapted from Langlais *et al*., 1991).

Application	**Point of ozonation in the treatment train**	**Ozone dose**	**Best pathway**	**Comments**
Iron and manganese removal	pre-, inter-	medium	direct	inter- application may be best with high DOC waters
Colour removal	inter-	medium to high	direct	two-step stoichiometry
Taste and odour control	inter-	high	indirect	T and O may be produced by low ozone doses
Synthetic organic compounds	inter-	medium to high	indirect	direct pathway can be best for some compounds
Particles	pre-	low	unknown	may require high calcium concentration
Algae	pre-, inter-	Low to medium	unknown	can be used with flotation
Pathogens	pre-, post-	medium to high	direct	pre- (US), post- (Europe)
Chlorination disinfection by-products	pre-, inter-	Low to high	direct	high levels of removal require radicals (indirect pathway)
Biodegradable compounds	inter-	medium	unknown	design of downstream filtration process is important

Escherichia coli has been shown to be reduced by 4-logs in less than 1 minute at 0.09 mg/L ozone residual concentration. *Legionella pneumophilia* was reduced by over 2-logs when contacted with an ozone level of 0.21 mg/L for 5 minutes. Similar sensitivity to ozone has been seen for *Staphylococcus* and *Pseudomonas* and *Salmonella*. The most resistant species to ozone were *Streptococcus* and vegetative bacteria and those that produce sporular forms, such as *Bacillus* and *Mycobacterium*, but all are effectively killed by relatively low ozone concentrations (US EPA, 1999). Viruses are also effectively removed by ozone. Rotavirus, phage, polio and coxsackie viruses have all been demonstrated to be removed by ozone. Over 5 log removal of coxsackie virus was observed at an ozone dose for 1.45 mg/L in lake water giving a 0.28 mg/L ozone residual (US EPA, 1999).

Table 4. Relative disinfecting capacity of ozone against a range of microorganisms. Data gives CT (mg.min/L) values for 99% inactivation at 5 °C. Adapted from Langlais et al. (1990). Data in bold indicates the best performing disinfectant.

Micro-organism	Ozone pH 6-7	Chlorine pH 6-7	Chloramine pH 8-9	Chlorine dioxide pH 6-7
E. Coli	0.02	***0.034-0.05***	95-180	0.4—0.75
Polio 1	***0.1-0.2***	1.1-2.5	770-3740	0.2-6.7
Rotavirus	***0.006-0.06***	0.01-0.05	3810-6480	0.2-2.1
Phage f2	-	0.08-0.18	-	-
G. Lambia cysts	***0.5-0.6***	47->150	-	-
G. Muris cysts	***1.8-2.0***	30-630	1400	7.2-18.5

1.3 Ozone Inactivation of Cryptosporidium

Cryptosporidiosis is a predominantly waterborne disease with infections caused by contaminated drinking water, among other routes (HPA, 2008). Between 106 and 1011 *Cryptosporidium* oocysts per g of human faeces are released into wastewater treatment plants and may be released into surface waters if process failure occurs (Wohlsen et al., 2007). Furthermore, *Cryptosporidium* oocysts are shed by livestock and are prevalent in surface waters from both human and animal sources (Pintar et al., 2012). Therefore eliminating the organism during drinking and wastewater treatment processes is important for the protection of human health. *Cryptosporidium* oocysts are particularly resistant to disinfection (Campbell et al., 1982). Korich et al. (1990), in a study comparing the efficacy of ozone, chlorine dioxide, chlorine and monochloramine against *C. parvum*, concluded that, with the possible exception of ozone, disinfectants could not be expected to inactivate oocysts in drinking water.

Ozone is a strong oxidant and has been shown to inactivate many different types of microorganism (Appendices 1-4; Blanc et al.; 2005; John et al., 2005; Chand et al., 2007; Kobayashi et al., 2011). The oxidizing mechanisms of ozone may involve direct reactions of molecular ozone and also free radical-mediated destruction. It is thought to affect cellular components such as proteins lipids, peptidoglycans, enzymes and virus capsids (Voidaru et al, 2007). Ran et al (2010) found that ozone did not damage the DNA and RNA within the oocysts, but appeared to lead to the folding (at 60 seconds) and ultimately shrinking and bursting (at 8 minutes contact time; dose not given but assumed to be 3 mg/L).

Due to the large CT values required for *C. parvum* inactivation, treatment with free chlorine may not result in adequate oocyst inactivation under most conditions relevant to drinking water treatment. Ozone has, however, been proved superior to chlorine and monochloramine for *Cryptosporidium parvum* oocyst inactivation (Driedger et al., 2000; 2001) and has been described as the only chemical form of disinfection to provide effective inactivation of *Cryptosporidium* and *Giardia* at doses similar to those used routinely for water treatment (Irish EPA, 2011). Von Gunten (2003) stated that ozone is “an excellent disinfectant and is able to inactivate even more resistant pathogenic microorganisms such as protozoa (e.g. *Cryptosporidium parvum* oocysts) where

conventional disinfectants (chlorine, chlorine dioxide) fail", although the author also noted that the ozone exposure required to inactivate these microorganisms is quite high. Korich et al.(1990) demonstrated a 99% (2-log) inactivation of oocysts with an ozone concentration of 1 mg/L for 5-10 minutes (Appendix 1), whereas to achieve the same results with chlorine required a dose of 80 mg/L for 90 minutes. Nieminkski and Bradford (1990) applied ozone treatment to two of four parallel continuous flow treatment trains in a pilot reactor employing coagulation/flocculation with ferric chloride and direct filtration. Ozone was applied before coagulation at a CT value of 1.5 mg.min/L (intended to provide 99.9% inactivation of *Giardia lamblia* cysts). Although not the principle focus of the trials, *Cryptosporidium* oocysts were enumerated in the filter backwash water and were detected only in the non-ozonated treatment trains (Table 5).

Table 5. *Cryptosporidium* oocysts detected in 40-L ozonated and non-ozonated treatment trains (after Nieminski and Brandford 1990).

Sampling occasion	**Raw Water**	**Train 1 (O_3)**	**Train 2**	**Train 3**	**Train 4 (O_3)**
1	0	0	0	+	0
2	3	0	3	3	0
3	1	0	3	2	0
4	4	0	+	+	0

Inactivation of *Cryptosporidia* in final effluent following wastewater treatment differs from drinking water treatment because the different water quality parameters lead to a range of issues discussed later in this review. However, several studies have reported on the efficacy of final effluent disinfectant with ozone, specifically in relation to *Cryptosporidium*. In a quantitative microbial risk assessment study, Pintar et al (2012) modelled the mean individual daily probability of *Cryptosporidium* infection under existing conditions (advanced wastewater treatment with ozone disinfection) and also under a scenario where ozone treatment was removed. They demonstrated that the risk of infection increased, albeit less than ten-fold, if ozone treatment ceased. However, in contrast, in a 6-year monitoring study of *Cryptosporidium* oocyst prevalence in source (river) water in Seoul, including a sampling location heavily influenced by a sewage treatment works, Lee et al. (2010) found no significant differences in numbers before and after the implementation of ozone final effluent disinfection, indicating that it may be insufficient to inactivate *Cryptosporidia*. Liberti et al. (2000) also reported that ozone was ineffective (Appendix 1) in inactivating *Cryptosporidium parvum*, however their study utilised clarified secondary treated effluent and the same effluent post filtration through sand and gravel. The initial loading of pathogens was low and it is likely, as the authors concluded, that the low concentrations of *C. parvum* present (10 and 2 oocysts detected) rendered the microbial counts inaccurate.

Overall, for (primarily) drinking water and final effluent, log inactivation of *Cryptosporidium* following ozone application is frequently reported to be within the 2-3 log range (Appendix 1). Of the literature data evaluated graphically (45 data points from 12 studies), 61 % showed greater than 2-log inactivation. The CT relationship was not clear due to the study differences highlighted above (Figure 2).

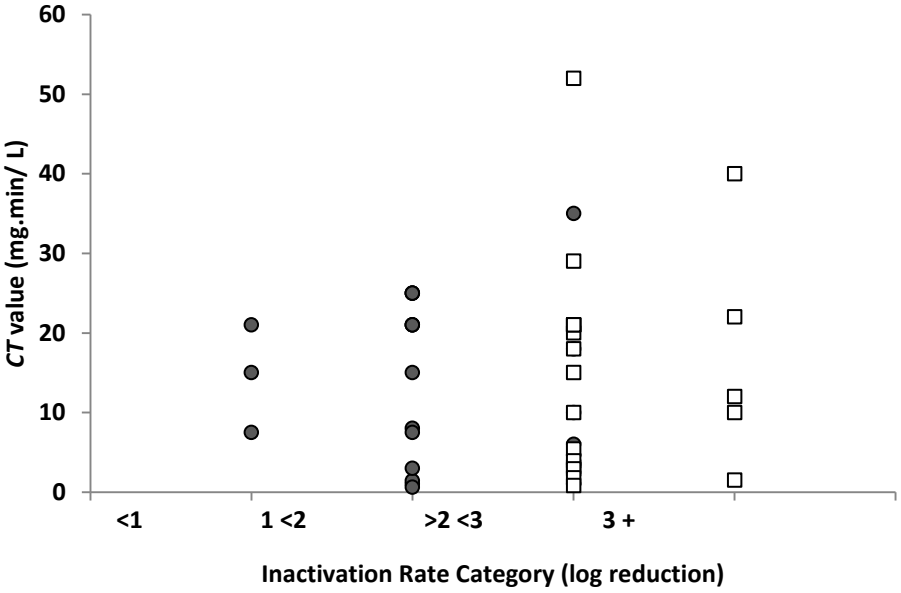


Figure 2. Literature data on inactivation of *Cryptosporidium spp*. across a range of *CT* values. Data were derived from Appendix 1 utilising all studies for which suitable *CT* values and inactivation data were available. Open squares indicate consumed ozone was used in the calculation of *CT*; filled circles represent data where applied ozone was utilised.

1.3.1 Variability across studies on ozone inactivation of Cryptosporidium spp.

As with many microbial-related inactivation reviews, some difficulties arise when attempting to summarise the literature relating to ozone disinfection of *Cryptosporidium spp*. Firstly, there are a number of studies based on laboratory scale reactors (Appendix 1) and few which fully replicate full scale treatment situations. The necessity of seeding test waters with oocysts in many cases is evident from Liberti et al (2000). However, it is encouraging to note that Owens et al, using a pilot scale reactor on natural river water from Ohio, observed comparable results to bench scale studies (Owens et al, 2000). The reactor type is of particular importance as batch studies are most likely to demonstrate proficient disinfection compared with flow through systems (Rochelle et al, 2005). However, it is important to attempt to replicate the conditions of the proposed full scale process when carrying out bench scale tests.

Secondly, data are reported in different forms throughout the literature and single parameters cannot always be readily extracted, for example a CT value may be given or the specific concentration and contact time details may be provided, with or without reference to whether the authors refer to applied, residual or transferred ozone. In other cases, a rate constant for ozone inactivation of *Cryptosporidium* is given. Furthermore, background parameters which may affect ozonation reactions are not always provided in full and a number of studies utilised clean water or buffer solutions only for disinfection trials (Korich et al, 1990; Driedger et al, 2001; Rennecker et al., 1999; Ran et al, 2010a) which, while useful as a starting point do not accurately reflect full scale treatment.

In addition to the above aspects, methods of determining inactivation can also differ significantly among reports and studies. For example, the excystation approach is known to underestimate viable

oocysts and is likely to differ from animal infectivity approaches, which can be quite variable. Burkhari et al (2000) illustrated variability of close to 99% in a comparison of different viability determinations, including application of various stains (DAPI/PI, Syto 9, Syto 59) and excystation. They also considered the relationship with infectivity using a mouse model. Determination of viable and infective *Cryptosporidium* is discussed in depth by Rochelle et al. (2005). With this in mind, Appendix 1 and Tables 1-3 provide a summary of some keys findings on ozone inactivation of *Cryptosporidium*.

1.3.2 Inactivation of Cryptosporidium compared with other microorganisms

Owens et al (2000) tested the efficacy of ozone inactivation of a range of microorganisms in river water from Ohio, using a pilot scale ozonation reactor. The reactor comprised a single stage continuous flow, counter current glass ozone contactor with a liquid depth of 2.65 m and a diameter of 0.15m. Mean operating conditions were: 6.4 L/min liquid flow rate; 0.64 L/min gas flow rate, 0.1 gas-to-liquid ratio and transfer efficiency of >90 % (Owens, 2000).They reported that under these conditions, the CT required for 2-log inactivation of *Cryptosporidium* (*C. parvum* and *C. muris*) was 12 times greater than that required for the same degree of inactivation of Giardia muris cysts. Their data suggested that this ratio may change depending on the log inactivation. Table 6 below (Von Gunten et al., 2003) illustrates the difference in inactivation kinetics among a range of different microorganisms including *C. parvum*.

Table 6. Inactivation Kinetics of *Cryptosporidium* and other pathogens or indicator organisms at pH 7 (adapted from Von Gunten et al, 2003).

Microorganism	***k*o$_3$ (l/mg/min)**	***CT*$_{lag}$ (mg.min/L)**	**Temperature (°C)**
E. coli	130	-	20
B. subtilis spores	2.9	2.9	20
Rotavirus	76	-	20
Giardia lamblia cysts	29	-	25
	12[a]	-	22
Giardia muris cysts	15.4 [a]	-	25
C. parvum oocysts[b]	0.84	0.83	20

[a]= estimated value. Data derived from excystation for *C. parvum. k* refers to the rate constant for ozone disinfection.

It is worth noting that Owens et al. (2000) obtained a similar value of kO_3 for *C. parvum*, while Finch et al (1993) reported a different rate using an animal infection assay. Owens et al (2000) demonstrated the need for relatively high CT values to inactivate *Cryptosporidia* compared with other organisms. *B. subtilis* spores were also resistant (Table 7).

Table 7. Inactivation of a range of microorganisms in natural river water from Ohio, based on simple *CT* values (after Owens et al., 2000).

Microorganism	**n**	**pH**	**Temperature (°C)**	***CT* (mg.min/L)**	**Log inactivation range**
Bacillus subtilis spores	19	7.9	22.7	0.7-18.4	0-2.17
C. parvum oocysts	6	8.2	24.5	2.6-7.2	0.57-2.67
C. muris oocysts	7	8.4	23.6	0.1-11	0.36-2.56
Giardia muris oocysts	5	7.6	25.2	0.3-1.0	1.52-2.70
Poliovirus 1	9	8.1	25.0	0.2-2.5	1.43-3.85
HPC, PCA	6	7.1	15.5	0.3-6.3	0.74-2.16
HPC, R2A	6	7.1	15.5	0.3-6.3	2.10-3.36
TC, P-A broth	6	7.1	15.5	0.3-6.3	2.63-3.95
TC, colilert	6	7.1	15.5	0.3-6.3	2.29-4.10

TC = total coliforms (colilert MPN method or P-A broth MPN method); HPC = heterotrophic plate count on PCA medium or R2A medium.

1.4 Factors affecting ozone disinfection

Ozone reacts with other constituents often present in raw or processed drinking waters. Ozone demand is associated with the following (USEPA 1999):

- Reactions with natural organic matter (NOM) in the water to form aldehydes, organic acids, and aldo- and ketoacids (Singer, 1992).
- Organic oxidation by-products (BDOC).
- Synthetic organic compounds (SOCs), some of which can be oxidized and mineralized under
- favourable conditions, particularly where hydroxyl radical oxidation is the dominant pathway, (as in advanced oxidation processes).
- Oxidation of bromide ion forming hypobromous acid, hypobromite ion, bromate ion, brominated organics, and bromamines .
- Bicarbonate or carbonate ions (alkalinity), forming carbonate radicals (Staehelin et al., 1984; Glaze and Kang, 1988) – this is important in AOPs where the radical oxidation pathway is predominant.

It is thought that molecular ozone is primarily responsible for inactivation of micro-organisms within most operational ozonation pH ranges (between 6-9) (Hunt and Marinas, 1999). However the production of hydroxyl radicals (OH·) from the degradation of ozone results in the presence of another highly oxidative species that also has disinfecting capability. Other contaminants present in the water may scavenge both dissolved ozone and hydroxyl radicals, therefore the purity of the water prior to ozone addition has a significant effect on its disinfecting capacity (US EPA, 1999). These water quality parameters are now discussed in more depth:

Temperature: as temperature increases, it is generally thought that the disinfecting power of ozone increases (Langlais et al., 1990). Whilst increased temperature reduces the solubility and stability of ozone, temperature also increases the rates of diffusion of ozone through the cell wall of microorganisms, as well as increased rates of reaction with the microbe. The effect of temperature on *Cryptosporidium* has been clearly shown. A decrease in the required CT product for a 2-log reduction in protozoan infectivity has been observed with an increase in temperature that followed

an Arrhenius type model (where K is the temperature in Kelvin, C is the chlorine concentration and T is the contact time):

$$\frac{1}{CT} = 1.086x10^{18}e^{-12520/K}$$

The model indicates that the CT required for 2-log reduction in *Cryptosporidium* increases by a factor of 4.2 with every 10 °C decrease in water temperature.

Ozone inactivation of *Cryptosporidia* is temperature dependent, because temperature affects the solubility, stability and reactivity of ozone (Martinez et al, 2011). For example, Driedger et al (2001) observed that the rate of *C. parvum* inactivation decreased with decreasing temperature between 1 and 20 °C. Oppenheimer et al (2000) also demonstrated a reduction in CT values with increasing temperature (Figure 2). CT values recommended by USEPA for inactivation of *Cryptosporidium* oocysts by ozone are given in Table 8 below:

Table 8. CT values (mg.min/L) for inactivation of *Cryptosporidium* oocysts by ozone (after IEPA 2011).

Log Inactivation	**Temperature (°C)**				
	≤1	**5**	**10**	**15**	**20**
0.5	12	7.9	4.9	3.1	2.0
1.0	24	16	9.9	6.2	3.9
2.0	48	32	20	12	7.8
3.0	72	47	30	19	12

Source: USEPA, 2006.

By modelling ozone inactivation constants for natural waters across a range of temperatures, Oppenheimer et al (2000) derived an empirical temperature characteristics term (Θ) for *C. parvum*. This was expressed by the following equation:

$k_2/k_1 = \Theta^{T2-T1}$

where T_1 is temperature 1; T_2 is temperature 2; k_1 = coefficient of specific lethality at T_1; k_2 = coefficient of specific lethality at T_2. The coefficient of specific lethality is derived from the change in log inactivation of a particular organism with change in contact time with a specific disinfectant under given conditions e.g. Verhille et al., 2003.

The authors reported that a multiplier of 4.5 for the CT value would be required for every 10 °C temperature increase for *C. parvum*. Interestingly, this was substantially greater than the temperature impact upon Giardia disinfection with ozone, thus demonstrating organism-specificity.

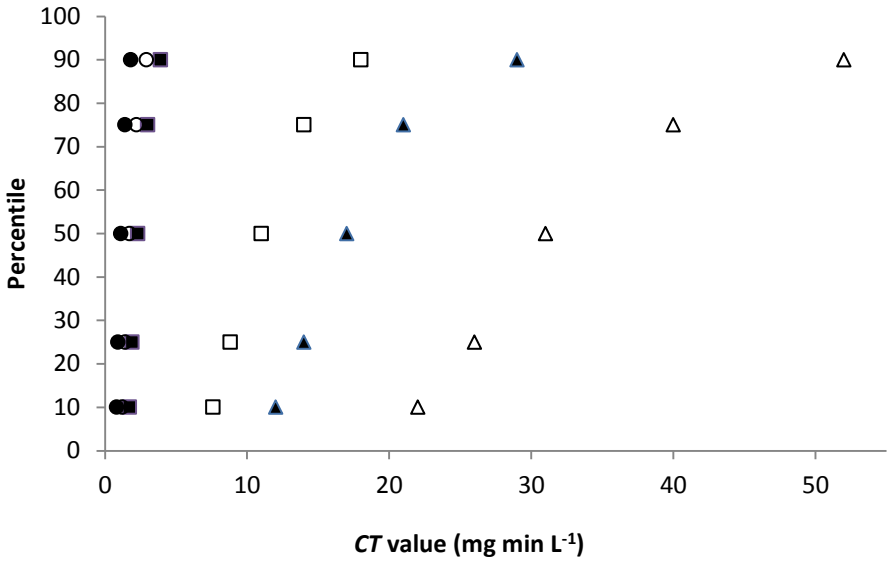


Figure 2. Illustrating the temperature dependence of CT values for 2-log inactivation of C. parvum in natural waters at 3 °C (open triangles), 7 °C (filled triangles), 10 °C (open squares), 20°C (filled squares), 22 °C (open circles) and 25 °C (filed circles). Data source: Oppenheimer et al., (2000).

pH: changes in water pH changes the balance of available O_3 and OH·, with an increase in pH from 6 to 9 reducing the amount of O_3 available for disinfection by a factor of 40 (Elovitz *et al*., 1999). This is because ozone decomposes to other products more quickly in alkaline environments. Over this pH range, the available OH· remains roughly constant, therefore it is thought that pH increases are likely to influence disinfection more than oxidation reactions with inorganic and organic compounds. However, empirical observations do not always confirm this. Hunt and Marinas (1999) saw only an 8% difference in second order inactivation rate for *E. coli* at pH 6 and 8. Driedger et al. (2001) saw no effect on the inactivation of *Bacillus subtilis* spores between pH 6 and 8. It does, however, appear that susceptibility to ozone at different pH is species specific. However, substantial effects of pH on ozone inactivation of *Bacillus subtilis* spores was noted by Cho et al. (2003) by applying a hydroxyl radical scavenger to all treatments, the effect of pH was negated and all CT values were similar. They therefore attributed changes to the presence of hydroxyl radicals rather than pH. Langlais et al. (1991) show evidence for decreased inactivation of poliovirus type 1 and rotavirus with increased pH whilst inactivation of *Giardia muris* cysts increased from pH 7 to 9. A clear understanding of the objective for disinfection must therefore be understood in order to determine how effective the ozonation pH will be on disinfection efficiency.

There are conflicting findings in the literature relating to the effect of pH on ozone inactivation of *Cryptosporidium*. For example, while there was no overall significant effect of pH on ozone disinfection, Ran et al (2010a) demonstrated that in a batch reactor at pH 6 vs. pH 9, 3 mg/L ozone at a contact time of 5 minutes led to a reduction in oocyst extinction from 99-93% respectively. In earlier studies, Farooq et al. (1977) reported pH to have minimal effect where there is no ozone residual i.e. continuous gas bubbling. In contrast, pH has been shown for *Giardia muris* to be significant in batch systems where the O_3 residual is decreasing (Labatiuk, 1992). In a batch study, Kim et al (2007) found that ozone decay rates ranked from lowest to highest in the order pH 6.5<7.5<8.5, reporting a higher exposure ratio of hydroxyl radical to ozone as pH increased and therefore indicating that pH effects on decay rates and production of hydroxyl radicals was a likely

cause of an zone-pH interaction. Oppenheimer et al. (2000) also observed a deviation from a linear regression of pH vs. ozone inactivation of *C. parvum* at pH less than 6.5, indicating some inhibition of disinfection.

Suspended solids & other ozone scavengers: Turbidity is important because it is indicative of the presence of particulates. Firstly, microorganisms tend to associate with particulates and therefore higher turbidities often correlate with higher pathogen loadings. Secondly, microorganisms can be shielded from disinfectants when attached to particles or flocs, and particulates also exert a disinfection demand leaving a smaller proportion of the transferred ozone to inactivate the microbial target (Winward et al, 2008). This has been demonstrated for cell-associated poliovirus and coxsackievirus at applied ozone doses of 4.1 and 4.7 mg/L respectively for 30 seconds. For un-associated viruses, these were inactivated by the application of 0.08 mg/L of ozone for 10 seconds. E. Coli inactivation has been shown to be reduced by the presence of an organic scavenger (tert-butanol) (Hunt and Marinas, 1997). However, the nature of the material present has a big impact on the consumption of ozone, therefore a parameter such as turbidity does not always give a good measure of how the efficacy of disinfection will change. Non-reactive inorganic minerals will not consume large quantities of ozone, but both particulate and dissolved organic substances are highly reactive with ozone.

Several studies have reported an inverse correlation between turbidity and inactivation of *Cryptosporidia* (e.g. Oppenheimer et al, 2000; Falabi et al 2002; Ran et al., 2010). Ran et al (2010) evaluated the ozone-induced reduction in viability of *Cryptosporidium* (determined by fluorigenic staining and microscopy) in distilled water laboratory batch reactors supplemented with different concentrations of Kaolin to provide turbidity. The authors observed a decrease from 99.2 % to 86.2 % when turbidities increased from 0.1-20 NTU at a contact time of 7 minutes (Appendix 1). Oppenheimer et al (2000), noted a significant difference in ozone inactivation in one set of four replicate water samples in of natural waters and attributed this to a difference in turbidity of these particular samples (1 vs. 11 NTU). Across the whole study, thought to represent water typologies representative of around 65 % of those found in the US, high turbidity (>10) was correlated with less effective ozone disinfection.

Dissolved organic matter has been shown to significantly affect the ozone inactivation of *Cryptosporidium* in laboratory model systems in which humic acids were added to distilled water batch systems, reducing the rate of inactivation from 84.9 % at 2 mg/L to 62.1 % at 10 mg/L (Ran et al, 2010). Studies have also indicated a specific association between the number of oocysts present and the ozone demand (Peeters et al., 1989); however Wohlsen et al., (2007) did not find this to be the case. The presence of contaminants other than the target microorganisms may consume ozone and reduce the disinfection capacity of the water (Dietrich et al., 2007). For example, viruses that are associated with cells, or parts of cells, are protected from inactivation by ozone (Emerson et al., 1982).

Strain related differences: *C. parvum* (found in over 150 mammalian species including humans) and *C. hominis* (primary reservoir: Humans) are considered to be the most human and animal-health relevant species of *Cryptosporidium*. There are eleven species in total, with differing primary hosts and characteristics (Carey et al., 2004). Even subtle differences in oocyst size and shape may lead to variations in the propensity to react with ozone, however there is little research on the subject and

compared with water quality factors, these are likely to play a limited role in mediated required dosages of ozone for disinfection. Owens et al (2000) reported similar inactivation of *C. parvum* and *C. muris* oocysts using ozone, although *C. muris* cysts were slightly more resistant than those of *C. parvum*. Oppenheimer et al (2000) noted that at 20-25 °C, the *Ct* requirements of *C. parvum* were 7-10 times higher than that described in the US Surface Water treatment Rule (USEPA, 1991) for *Giardia lamblia*. This rose to 22 times greater at 10 °C. Therefore while intra-genus differences are likely to be insignificant, reliance on disinfection kinetics for other organisms is not recommended. In addition to differences related to genera, species and strains, Corona-Vasquez et al (2002) reported that different "lots" of oocysts showed different levels of inactivation. Studies have illustrated differences in the inactivation response of different ages of oocysts (Bukhari et al, 2000; Driedger et al., 2001), which may have explained some of the findings.

It is therefore critical to know what is in the water to understand ozone doses and contact necessary to achieve a specific water quality objective.

1.5 Ozone dosing and conditions

Under atmospheric conditions, ozone is an unstable gas that quickly decomposes to oxygen and has a half-life of only 20 minutes at room temperature. Ozone is equally unstable when dissolved in water and quickly breaks down to oxygen and a range of other products dependent on the water quality (von Gunten, 2003b). In water, ozone's half-life varies from seconds to hours and is a function of the water pH, alkalinity and natural organic matter (NOM) concentration in the water. Due to its instability, ozone must therefore be generated on site for immediate use. In addition, ozone does not provide a residual disinfecting capacity so is not able to be used for this purpose and an additional disinfectant much be added to the water if a residual is required (for example, using a chemical such as chlorine), albeit usually at a lower dose.

When applying ozone at a WTW facility, there are four requisite components: (1) oxygen gas feed system (either air or pure oxygen); (2) ozone production and delivery, (3) an ozone contactor and (4) ozone off gas destruction.

(1) Gas feed: Ozone can be produced from air, oxygen or a combination of the two. A higher yield of ozone is produced when pure oxygen is used as the feed for the ozone generator but it comes at higher cost because the oxygen must be generated on site or purchased in a pure form. Yields of ozone are relatively inefficient, typically 3.5% (by weight) from air and up to 14% from pure oxygen gas (US EPA, 1999). For all oxygen sources, the gas source needs to be cleaned and dried prior to ozone generation. This requires significant pre-treatment of the gas before it enters the ozone generator, particularly when air is used. Typically, air is compressed, filtered, dried and regulated prior to entering the ozone generator.

(2) Ozone generator and delivery: Ozone is formed when oxygen is broken down into atomic oxygen radicals. In turn, these radicals may react with oxygen molecules to form ozone. The formation of oxygen radicals requires high energy (493-683 kJ/mol) and the processes that are used to do this are those that are able to form high energy electrons, usually from the application of high voltage. This includes plasma corona discharge, chemonuclear sources and electrolytic processes. Corona discharge is the most widely used process for large scale production of ozone. Here, an electrical discharge is passed from a high potential electrode to a grounding electrode across air or pure oxygen gas that has been dried and filtered (Langlais et al., 1990). Two

orientations are seen for corona discharge ozone generation, namely as concentric cylinders or as parallel plates. Parallel plates only tend to be used in small scale ozone generation systems. The concentric cylinders in most commercial systems look similar to conventional fluorescent tube light bulbs and are composed of a high potential electrode encased in a glass dielectric sleeve. The tube is then placed within a stainless steel grounding electrode with the gas passing between the two electrodes (US EPA, 1999). Over 80% of the energy applied to ozone generators is lost as heat, therefore this heat must be quickly dissipated to prevent quickened degradation of ozone and overheating of equipment. Water is therefore circulated between the electrode cells. The frequency of the power supplied to the generator impacts on the efficiency of the ozone generation, with an increase in frequency resulting in an increase in efficiency. However, higher frequencies tend to result in more heat generation and more complicated power arrangements. In the past, low frequency systems were most common (50-60 Hz), put medium (<1000 Hz) and high (>1000 Hz) systems have now become more popular as advancements in electrical robustness have evolved.

(3) *Ozone contactor:* Ozone is contacted with water either via bubble diffusers, injector dissolution or turbine mixers. Bubble diffuser systems are the most commonly applied contacting system due to their relative simplicity, high ozone transfer rates (typically 85- 95%) and flexibility. Here, water is passed through a baffled chamber in deep tanks (5.4-6.7 m) in either a co-, counter- or combined co/counter current direction to the diffused ozone gas. Other ways to dissolve the gas in the water are via injection of ozone into water under negative pressure. This may be directly into the main flow (for small scale systems) or through a sidestream that is pressurised. The sidestream is then mixed with the bulk flow under high turbulence. After the ozone is distributed, a contactor must be provided to enable the appropriate CT to be delivered. Turbine mixers are the final way by which ozone can be rapidly distributed into the flow. Turbine mixers require high energy (4.8-5.9 kWh per kg of ozone transferred) but are able to achieve over 90% ozone transfer. The main advantages and disadvantages of each type of ozone contacting system is summarised in Table 9.

Table 9. Advantages and disadvantages of ozone mixings systems. Adapted from USEPA (1999).

	Advantages	**Disadvantages**
Bubble diffusion	- No moving parts - Low hydraulic headloss - Simple to operate	- Deep contactors needed - Bubble channelling - Maintenance required of diffusers, piping and gaskets
Injection	- No moving parts - Effective ozone transfer - Shallow contactors needed	- High headloss from static mixers needed - More difficult dosing flexibility - Complex operation and high cost
Turbine mixing	- High ozone transfer - Shallow contactor needed - Aspirating turbines able to re-use off-gas from other chambers - No filter clogging concerns	- High energy required - Maintenance of motor and turbine

(4) *Off gas destruction*: the final component for any ozonation system is off-gas removal. As ozone is a very toxic gas and because not all gas is transferred to the water, residual ozone must be destroyed to prevent accumulation of ozone to harmful levels in working environments. Off gas removal is carried out using heat, catalysts or a combination of the two.

The amount of applied ozone and the contact time required for disinfection is highly dependent on the water quality being treated and the treatment target required. Typically applied ozone doses range from 1-3.5 mg/L ozone, with most applications between 1.5-2.5 mg/L. Specific case study examples for full-scale ozonation systems being used primarily for disinfection are shown in Table 10. Investigation of these applications of ozone show that tools such as online UV_{254}, CT and CFD modelling are all being used in order to optimise ozone doses for maximum pathogen control (Bouland et al., 2004; Zhang et al., 2008; Audenaert et al., 2010).

Table 10. Ozonation case study sites for potable water disinfection.

Case study	Ozonation procedure	Objective of ozonation	Typical ozonation conditions	Other information
A. H. Weeks Water Treatment Plant, Windsor, Canada Mazloum et al. (2004)	Pre ozone	*Cryptosporidium* and *Giardia* control	1-3.5 mg/L	-Improvements in coagulation observed -Increase from 1 to 2 log reduction of *Cryptosporidium* and *Giardia* throughout year
Kluizen WTWs, Belgium Audenaert et al. (2010)	Post ozone	Disinfection Taste & odour removal Biostabilisation	2.5 mg/L	-UV absorbance (at 254 nm) used to help control ozone dosing on-line
DesBaillets WTP, Montreal, Canada Zhang et al. (2008)	Post ozone	Disinfection	2.2 mg/L	-CFD used to model disinfection efficacy – strong agreement between observed and modelled results -Areas of short circuiting identified -CFD used for the first time as for an ozone residual monitoring strategy
Orly WTWs, Paris, France Bouland et al. (2004)	Pre and Post ozonation	Disinfection Taste & odour removal Biostabilisation	Minimum CT set at 1.6 mg/min/L 11-20 minutes contact time	-Authors suggest that the CT should include contact with downstream processes (e.g. GAC) due to higher levels of bromate formation observed on site.

1.6 Disinfection by-products

One of the key challenges faced when using ozone as an oxidising agent is the formation of disinfection by-product (DBPs) compounds. DBPs are an unwanted consequence of adding strong chemicals to water, and can be a range of hazardous compounds. Disinfection by-products (DBPs) form as a result of reactions between chemical disinfectants, organic and inorganic matter (NOM and IOM respectively) in water during the water disinfection process (Figure 3). Predominantly a problem in drinking water treatment because of the direct risk of human consumption of water containing harmful compounds, DBP formation could also be an issue in wastewater treated for

reclamation or where drinking water sources are significantly influenced by WWTP effluent (Wert et al., 2007; Muller et al., 2012). Some DPBs associated with the halogens present either in raw water or added for disinfection purposes, are known to be hazardous to health and can also be toxic to aquatic systems. However, there is a requirement to protect human health from waterborne disease, hence disinfection is essential. It is therefore important to achieve a balance between effective disinfection and concentrations and types of DBPs formed.

There are two approaches to reduce the formation of DBPs during drinking water treatment. The first is to reduce the presence of DBP precursors (principally NOM and bromide) prior to applying a chlorine based disinfectant. This can be achieved through the use of combinations of chemical and physical treatments (Chin et al, 2005), and may include ozonation. The second approach is to use a non-halogen primary disinfectant (such as ozone) followed by the addition of a chlorine residual. This reduces the amount of chlorine required and likewise the amount of chlorine-associated DBP formation. However, as has already been noted, ozone is also known to produce a range of other DPBs.

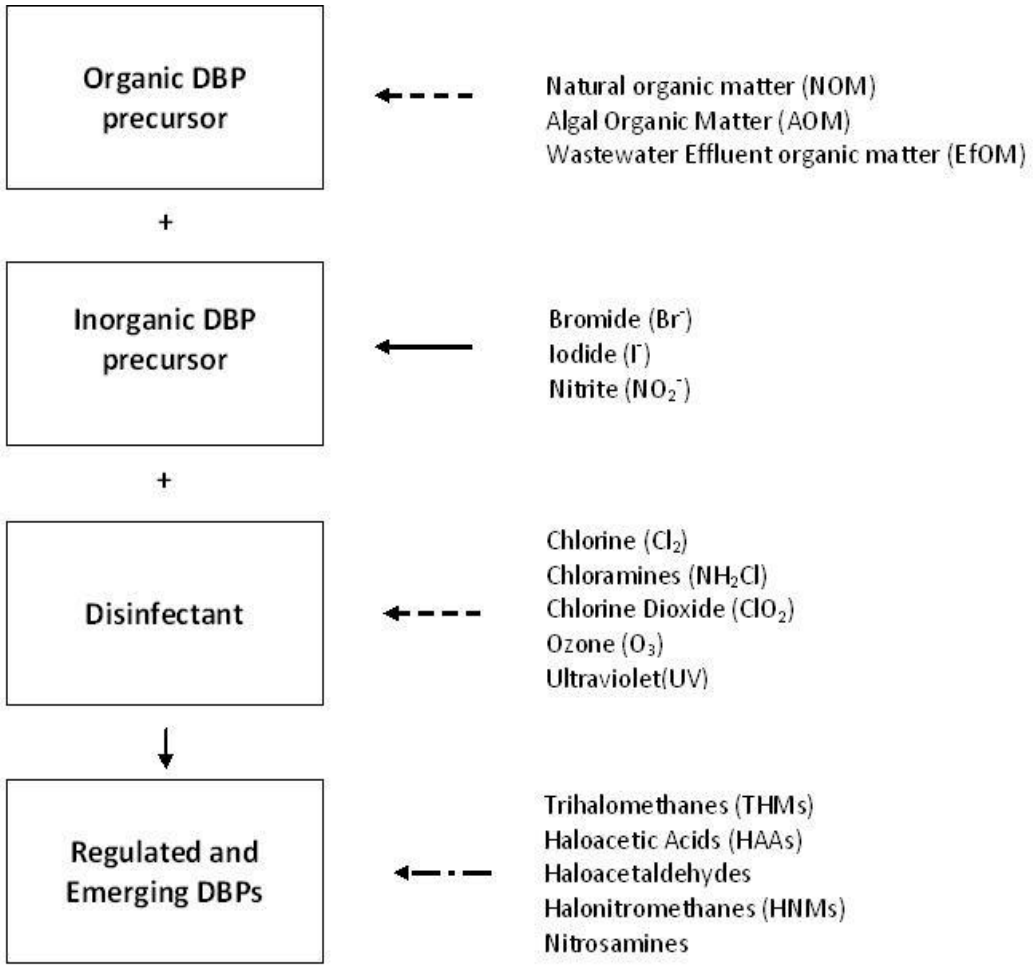


Figure 3. Schematic diagram of the reaction of organic and inorganic DBP precursors with disinfectants to form regulated and emerging DBPs (After Krasner, 2009).

1.6.1 Types and concentrations of DBP formed with ozonation

The formation of ozonation by products has been well documented and DBPs (Table 8) form when disinfectants react with organic matter, bromide, iodide and anthropogenic pollutants (Richardson and Postigo, 2012). DBPs may be organic (e.g., assimilable organic carbon (AOC), aldehydes, carboxylic acids, and ketones) and inorganic (e.g., bromate). Nitrogen-containing DBPs, such as N-nitrosodimethylamine (NDMA) which can form during the ozonation of the tolylfluanid fungicide metabolite N, N-dimethylsulfamide (Schmidt and Brauch, 2008) are thought to be generally more genotoxic and cytotoxic than those without nitrogen (Muller et al., 2012).

A comprehensive assessment by Richardson et al. (1999) identified the presence of hundreds of halogenated (halo- alkanes/alkenes, aldehydes, ketones, dicarbonyls, acetonitriles, acids, alcohols, nitromethanes) and unhalogenated (aldehydes, ketones, dicarbonyls, carboxylic acids, nitriles and aldo and keto acids) DBPs from ozone, ozone-chlorine, ozone-chloramine samples, typically at very low concentrations (ng-μg/L ranges). When ozone is used alone, no halogenated DBPs will usually form. However when ozone was dosed in addition to chlorine based disinfectants a number of halogenated DBPs were formed at a concentration significantly higher than that formed with the chlorine disinfectant alone. At present, the presence of these compounds do not present a regulatory risk, but as future water quality regulation becomes stricter in the coming years, it is important to understand the presence, concentration and toxicity of these DBPs.

While many organic and inorganic ozonation disinfection/ oxidation by-products have been identified (Table 11), bromate is generally considered to be of greatest concern (von Gunten, 2003) and aldehydes are also important although they are not currently regulated (Silva et al., 2010; Table 12). Where bromide is present in raw waters, bromo-organic by-products can form during ozonation (Figure 2). Ozone and bromide react to form hypobromous acid, which then reacts with organic matter to produce the DPBs. These include: bromoform, bromopicrin, dibromoacetonitrile, bromoacetone, bromoacetic acid, bromoalkanes, bromohydrins, but most tend to be present in low concentrations (von Gunten, 2003).

Iodate is formed by the ozone-oxidation of naturally occurring iodide and is of no toxicological concern (von Gunten, 2003). Bromate is the only specific DPB of ozone regulated in drinking water in a range of countries, including the UK and the US, with a limit of 10 μg/L (Table 12).

Aldehydes, primarily formaldehyde, acetaldehyde, glyoxal, and methylglyoxal are formed as a result of the oxidation of organic matter from wastewater (Melin and Odegaard, 2000; Huang et al., 2005; Silva et al., 2007). Silva et al (2010) determined concentrations of ozonation by products generated from anaerobic (USAB) wastewater effluent in a bench scale continuous ozonation system. Aldehydes were present at up to 187 μg/L and glyoxal up to 46 μg/L. These are regulated in only a few countries, and then usually for specific compounds such as formaldehyde and trichloroacetaldehyde (Table 12). Contact time did not appear to affect the degree of aldehyde formation, for contact times between 5 and 15 minutes and doses of 5, 8 and 10 mg O_3/L. In contrast, Nawrocki et al (2003) found strong contact time dependency of formaldehyde and acetaldehyde during the ozonation of drinking water.

Weinberg et al (2002) carried out a National Occurrence study, evaluating DBP concentrations across 12 drinking water treatment plants in the US in which sites using all four major disinfectants

(chlorine, chloramines, ozone, and chlorine dioxide) were covered. It is notable that the highest concentration of dichloroacetaldehyde occurred at a plant using chloramine and ozone disinfection. Therefore, although the use of alternative disinfectants minimized the formation of the four regulated THM, some unregulated DBPs were present in higher levels than where traditional chlorine disinfection was applied.

Table 11. Some key DBPs generated by Ozone and their Health Effects (adapted from Lipmann, 2009).

Compounds Group	**Oxyhalides**	**Aldehydes**	**Carboxylic Acids**
Health Effects	Animal, possible human carcinogen (Bromate) Limited knowledge on toxicity of chlorate	Can be carcinogenic at high levels but low concentrations present in water contribute little to calculated cancer risk. Questionable importance as carcinogens *via* ingestion (formaldehyde and acetaldehyde). (Lippmann, 2009)	Possible developmental toxicity (Moudgal et al, 2000)
Specific DBPs	Bromate	Formaldehyde	2-Methylpropanoic acid
	Chlorate	Acetaldehyde	Butanoic acid
	Chlorite	Cyanoformaldehyde	Pentanoic acid
		Glyoxal	Hexanoic acid
		Methylglyoxal	Heptanoic acid
		Propanal	Octanoic acid
		Butanal	Oxalic acid
		Pentanal	Malonic acid
		5-Keto-1-hexanal	Succinic Acid
		Trans-2-Hexanal	

Table 12. DBP Regulations worldwide (adapted from Hrudley and Charrois, 2012).

DBP	Guideline value (μg/L) by Country/Agency					
	WHO	**EU**	**USEPA**	**Australia**	**Canada**	**Japan**
Chloroform	300	-	-	-	-	60
Bromodichloromethane	60	-	-	-	-	30
Chlorodibromomethane	100	-	-	-	-	100
Bromoform	100	-	-	-	-	90
Monochloroacetic acid	20	-	-	150	-	20
Dichloroacetic acid	50	-	-	100	-	40
Trichloroacetic acid	200	-	-	100	-	200
Trichloroacetaldehyde	-	-	-	20	-	-
Formaldehyde	-	-	-	-	-	80
Bromate	10	10	10	20	10	10
Chlorate	700	-	-	-	1000	-
Chlorite	700	-	1000	800	1000	-
Dichloroacetonitrile	20	-	-	-	-	-
Dibromoacetonitrile	70	-	-	-	-	-
N-Nitrosodimethylamine	0.1	-	-	0.1	0.04	-
Total THMs	-	100	80	250	100	100
HAA5	-	-	60	-	80	-
Cyanogen Chloride	-	-	-	80	-	-

However, undoubtedly the DBP of most concern at present when using ozone is bromate. Due to its power as an oxidising agent, ozone is able to oxidise bromide to bromate. Bromate is a known carcinogen in mammals and is therefore strictly controlled at 10 μg/L in Europe in drinking water supplies. There are a number of factors that influence bromate formation. These are:

- ***Bromine concentration***: given that bromide is oxidised by ozone to bromate, an increase in bromide leads to an increase in bromate for a constant ozone dose and contact time (Legube et al., 2004). Conversion of bromide to bromate is relatively high (typically between 10-50 %), with higher conversions observed in summer compared with winter (Song et al., 1996). Typical concentrations of bromide in natural waters usually range from 30-200 μg/L, with an average of 100 μg/L (Amy et al., 1993), however this can be greater than 500 μg/L (Legube et al., 2004). Amy et al. (1993) approximated that up to 30 μg/L of bromate can form from a bromide concentration of 100 μg/L, which is a similar conversion ratio to that seen by others. High bromide in water sources can result from road run-off, ingress by saline water and from the dissolution from sedimentary rocks (Magazinovic et al., 2004; Butler et al., 2005). General rules for bromide containing waters are that those containing <20 μg/L of bromide do not present a problem for bromine-derived DBP's, whilst waters containing >100 μg/L of bromide are likely to cause significant bromate problems (von Gunten 2004a). Data from full-scale water treatment plants show that other chemical factors than just bromine concentration are important when understanding bromate formation rates (Table 13). These factors are listed below.

Table 13. Bromate formation at full scale WTWs in Europe and N America. Adapted from von Gunten (2003b).

Location	Number of plants	Bromide range (μg/L)	Bromate range (μg/L)
France	42	12-658	<2-19.6
Germany	4	30-150	<1-12
Switzerland	86	5-50	<0.5-20
USA	24	2-180	0.1-40

- ***Temperature***: Higher temperatures increase the rate of bromate formation as a result of increased reaction kinetics and because there is a commensurate increase in the acidity constant which promotes the formation of an important precursor of bromate (Legube et al., 2004). The effect of temperature is more pronounced at higher ozone doses. For example, Galey et al. (2004) observed that at an ozone dose of 1 mg/L the bromate formation was 8 μg/L at both 5 and 24 °C whilst at 2.5 mg/L the bromate formation was 22 μg/L at 5 °C and 37 μg/L at 24 °C.
- ***pH***: As the pH of the water is increased during ozonation, more bromate is formed. At low pH, more hypobromous acid remains fully associated with protons, which prevents the formation of an important intermediary (BrO^-) in the bromate formation pathway. At higher pH, the formation of this compound is favoured. Hydroxyl radical formation is also promoted at high pH due to the increased concentration of hydroxyl ions present (Song et al., 1997; Siddiqui et al., 1998). Bromate formation has been shown to increase from 10 μg/L at pH 6.5 to 50 μg/L at pH 8.2 (Legube et al., 2004) whilst Krasner et al. (1994) observed a 60 % decrease in bromate formation for each drop in pH unit. The ozonation pH is the best way of controlling bromate formation at a WTW (Ozekin and Amy, 1997). This must be countered by the increased formation of brominated organic compounds as the pH is reduced (USEPA, 1999) and because high alkalinity waters may require too much acid to reduce the pH to be cost effective (von Gunten, 2003a).
- ***Alkalinity***: The presence of inorganic carbon (IC) species increases bromate formation because both carbonate (CO_2^-) and bicarbonate (HCO_3^-) species can form the carbonate radical ($CO_3^-\bullet$) as a result of oxidation by hydroxyl radicals (von Gunten, 2003a). Once the carbonate radical has been formed, this can convert hypobromite into the hypobromite radical ($BrO^-\bullet$) and then bromate (Kim et al., 2004).
- ***Ammonia concentration***: The presence of ammonia in water acts as a scavenger of hypobromous acid (HOBr) during ozonation, an important intermediate in the formation pathway of bromate (von Gunten, 2003a). HOBr reacts with ammonia to form bromamine compounds, which, in turn, can be converted back to bromide through oxidation by ozone. Ammonia can therefore remove a significant intermediary from the bromate formation path and reduce the amount of bromate formed (Song et al., 1997). Ammonia may be present naturally in waters to be ozonated, or alternatively can be added prior to ozonation as a bromate prevention strategy. The addition of 1.5 mg/L ammonia addition can reduce bromate formation by around 5 μg/L when applied to water containing 100 μg/L Br^- under constant conditions (Ozekin and Amy, 1997). This reduction, although small, may be critical for those WTW where bromate levels are around the maximum permitted concentration.

However, this must be tempered by the fact that above a certain ammonia concentration, the addition of more ammonia has no further effect on bromate reduction. Therefore, for waters that contain naturally high to medium concentrations of ammonia, the addition of further ammonia may offer no further benefit (von Gunten, 2003b). Furthermore, any un-removed ammonia may act as a nutrient for nitrifying bacteria once in distribution (USEPA, 1999a).

- ***Transferred ozone dose and contact time***: As previously discussed, the efficiency of any disinfectant may be characterised by the CT factor (USEPA, 1999b). The combined impact of the concentration of applied ozone and residence time of the ozone in the reactor is an important parameter in the formation of bromate. The relationship between bromate formation and CT follows a linear function, with an increase in CT leading to an increase in bromate formation (von Gunten and Hoigne, 1996 and Legube et al., 2004). Due to its low solubility, typical residual concentrations of ozone found at WTW are in the range 0.1-1 mg/L. In order to achieve 99 % inactivation of *Cryptosporidium* oocysts typical contact times in the range of 4-18 minutes are applied giving CT of 2.4-10 mg min/L (USEPA, 1999a). However, CT is dependent on temperature and the log inactivation of microorganisms required. For example at 13 °C, a 3-log inactivation of *Cryptosporidium* requires a CT of 22 mg min/L whilst at 22 °C a similar inactivation requires a *Ct* of 8 mg min/L (Galey et al., 2004). Any change in CT to control bromate formation must therefore also ensure that adequate disinfection is maintained.

Empirical models have been developed that predict bromate formation based on these water quality and ozonation parameters. The variables important for bromate formation are those mentioned previously (i.e. bromide, DOC or UV_{254}, pH, O_3 dose, NH_3, alkalinity and temperature). The relationship of each of these variables to the output bromate concentration is then found experimentally by fixing all variables but one. The change in bromate formation is then observed with the random variable. By carrying out multiple linear regression (MLR) analysis on the data (or log transformed data), the cumulative relationship and significance of each of the variables can be found. MLR was first applied to bromate formation by Ozekin (1994) and, to date, most bromate formation models using MLR have been of the form:

$$\log Y = b_0 + b_1 \log x_1 + b_2 \log x_2 + b_3 \log x_3 \ldots\ldots + b_n \log x_n$$

where Y is the dependent variable, x_i is an independent variable and b_i is the regression coefficient. The following example shows the regression model for bromate formation from Song *et al*. (1996):

$$\log [BrO_3^-] = -6.11 + 0.880 \log[Br^-] - 1.180 \log[DOC] + 5.110 \log[pH] + 1.420 \log[O_3] + 0.270 \log[t] - 0.180 \log[NH_3\text{-}N] + 0.180 \log[IC]$$

A range of bromate formation models found in the literature of the form shown above are included in Table 14. An alternative form of the equation has been developed by Ozekin and Amy (1997):

$$\log[BrO_3^-] = -3.361 + 1.136 \log[Br^-] - 1.267 \log[DOC] + 0.249 [pH] + 1.575 \log[O_3] + 0.006 [t]$$

DOC has been replaced with UV_{254} in some of the models (Sohn *et al*., 2004). This is advantageous because UV_{254} is an easier and more robust measurement to make on-line and UV_{254} is more suitable for application to waters where staged ozonation is deployed or for post ozonation because UV_{254} is

significantly reduced during the first ozonation process, however the DOC of the sample stays approximately the same. During intermediate and staged ozonation, less ozone is consumed by the DOC compared to un-ozonated water of a similar DOC. The effect of this being an increase in the bromate formation potential. DOC based regression models should therefore only be applied to one-off ozonation situations. A number of the regression models also include ammonia. This gives flexibility to water utilities depending on whether they add ammonia as a bromate control measure or routinely measure ammonia as a water quality parameter (Ozekin and Amy, 1997).

The models show that the parameters that most affect bromate formation are of the following order for increasing bromate formation: pH > O_3 dose > Br^- > IC > time and for decreasing bromate formation: DOC > NH_3-N. When the models have been applied to similar raw waters to those with which the models have been developed (internal validation), good correlation has been seen between the observed and predicted bromate concentrations. For example, Song *et al.* (1996) had an average R^2 value of 0.93 for validation of bromate models on water sources that were used to develop the model for predicted against measured bromate concentrations. Similarly good correlation was seen by Siddiqui *et al*. (1994) and Ozekin and Amy (1997) with R^2 values of 0.98 and 0.91 respectively. However, increased error becomes apparent when the models have been validated with external data. Nevertheless, these models show the key way in which water quality parameters influence bromate formation and if the time can be taken to develop specific formation models for specific waters, a high degree of accuracy on bromate formation can be ascertained.

While there is continuing debate about the issue, there is evidence to show that the risk of infection by waterborne disease can outweigh that from DBPs. For example, the risk of infection with *C. parvum* was considered to outweigh that of getting renal cancer due to consumption of bromate-containing drinking water resulting from ozonation of waters containing bromide (Havelaar et al. 2000). Application of ozone to suitable waters or effluents has the potential to improve human health by maintaining protection against pathogens while removing or reducing the requirement for chlorine application (Wert et al 2007) and consequently reducing the formation of key trihalomethane and haloacetic acids present in drinking water or entering the environment.

Table 14. Regression coefficient value for bromate formation from various locations. Adapted from Jarvis et al. (2007).

Regression coefficient values for listed variables from bromate prediction models (number of variables included is dependent on particular model)										Boundary conditions	Notes	Source
Constant	**Br^- (µg/L)**	**DOC (mg/L)**	**pH**	**O_3*[1] (mg/L)**	**t*[2] (mins)**	**NH_3-N (mg/L N)**	**UV_{254} (cm^{-1})**	**Alkalinity (mg/L as $CaCO_3$)**	**Temp (°C)**			
-5.810	0.730	-1.260	5.820	1.570	0.280	-	-	-	-	70 ≤ **Br^-** ≤ 440 1.1 ≤ **DOC** ≤ 8.4 6.5 ≤ **pH** ≤ 8.5 1.1 ≤ **O_3** ≤ 10.0 1 ≤ **t** ≤ 120	Model developed from 10 raw waters. For raw waters with no ammonia. Limited to 20 °C.	Ozekin (1994)
-5.788	0.730	-1.300	5.790	1.590	0.270	-0.033	-	-	-	70 ≤ **Br^-** ≤ 440 1.1 ≤ **DOC** ≤ 8.4 6.5 ≤ **pH** ≤ 8.5 1.1 ≤ **O_3** ≤ 10.0 1 ≤ **t** ≤ 120 0.02 ≤ **NH_3-N** ≤ 3.0	Model developed from 10 raw waters. For raw waters with ammonia. Limited to 20 °C	Ozekin (1994)
-6.924	0.960	-	5.680	1.307	0.336	-	0.623	-0.201	*[3]	70 ≤ **Br^-** ≤ 440 6.5 ≤ **pH** ≤ 8.5 1.1 ≤ **O_3** ≤ 10.0 1 ≤ **t** ≤ 120 0.010 ≤ **UV_{254}** ≤ 0.280 13 ≤ **Alkalinity**	Developed from Ozekin (1994). For raw waters with no ammonia. Limited to 20 °C.	Sohn *et al.* (2004)
-7.080	0.944	-	5.810	1.279	0.337	-0.051	0.593	-0.167	*[3]	70 ≤ **Br^-** ≤ 440 6.5 ≤ **pH** ≤ 8.5 1.1 ≤ **O_3** ≤ 10.0 1 ≤ **t** ≤ 120 0.02 ≤ **NH_3-N** ≤ 3.0 0.010 ≤ **UV_{254}** ≤ 0.280 13 ≤ **Alkalinity** ≤ 316	Developed from Ozekin (1994). For raw waters with ammonia. Limited to 20 °C.	Sohn *et al.* (2004)
-6.110	0.880	-1.180	5.110	1.420	0.270	-0.180	-	0.180 [says IC]	-	2 ≤ **BrO_3^-** 100 ≤ **Br^-** ≤ 1000 1.5 ≤ **DOC** ≤ 6.0 6.5 ≤ **pH** ≤ 8.5 1.5 ≤ **O_3** ≤ 6.0 0 ≤ **t** ≤ 30 0.02 ≤ **NH_3-N** ≤ 3.0 1 ≤ **Alkalinity** ≤ 216	Model developed from 4 different model waters. Limited to 20 °C	Song *et al*. (1996)

Regression coefficient values for listed variables from bromate prediction models (number of variables included is dependent on particular model)										Boundary conditions	Notes	Source
Constant	**Br^- (µg/L)**	**DOC (mg/L)**	**pH**	**O_3*[1] (mg/L)**	**t*[2] (mins)**	**NH_3-N (mg/L N)**	**UV_{254} (cm^{-1})**	**Alkalinity (mg/L as $CaCO_3$)**	**Temp (°C)**			
-4.267	0.040	-1.080	4.700	1.120	0.304	-	-	-	0.580	70 ≤ **Br^-** ≤ 440 1.1 ≤ **DOC** ≤ 8.4 6.5 ≤ **pH** ≤ 8.5 1.1 ≤ **O_3** ≤ 10.0 1 ≤ **t** ≤ 120		Galey *et al.* (1997)
-2.824	0.610	-0.740	2.260	0.640	-	-	-	-	2.030	250 ≤ **Br^-** ≤ 1500 3.0 ≤ **DOC** ≤ 7.0 6.5 ≤ **pH** ≤ 8.5 1.5 ≤ **O_3** ≤ 17.5 20 ≤ **Temp** ≤ 30	Model developed from 5 surface and ground waters	Siddiqui *et al.* (1994)

*[1]Utilised/transferred ozone; *[2]Time in ozone contactor; *[3]Temperature correction factor can be applied for variations in temperature: $[BrO_3]_{@tempT} = [BrO_3]_{@temp20\,°C}(1.035)^{T-20}$

2.0 Oxidation of contaminants in water

Compounds present in water can react with ozone directly or indirectly through OH• radicals (von Gunten, 2003b). These two different reaction pathways lead to different oxidation products and are controlled by different types of kinetics. Many of the rate constants for the direct reaction with ozone appear to be low and typically in the range 1.0 – 10^3 per M/s (Gottschalk et al., 2000). One of the key molecule characteristic which controls reactivity of a compound with ozone is its charge or polarity. For example, ionised or dissociated forms of organic compounds will react with ozone much faster than a neutral (non-dissociated) form.

The first step in the indirect reaction pathway is the decay of ozone which can be accelerated by the presence of OH- ions (Gardoni et al., 2012). The radical pathway is very complex and can be influenced by many substances. The mechanism of the indirect pathway consists of initiation, chain reaction and termination steps. Substances which convert OH·into superoxide radicals promote the chain reaction but if OH·react with a compound, and this does not lead to the formation of a superoxide radical, the chain reaction is terminated and the ozone decay inhibited. Such compounds are often called OH·scavengers and these can include carbonate and bicarbonate ions, humic acid (which can also act as a promoter) and phosphate (Stahelein and Hoigne, 1985).

Direct ozonation is usually the most important oxidative reaction if the radical reactions are inhibited due to the lack of initiating compounds to begin the chain reaction or due to the presence of too many radical scavengers (Gottschalk et al., 2000). The direct pathway normally dominates under acidic conditions (pH <4) and changes to the indirect pathways above pH 10. Both pathways will therefore play a role in most ground and surface waters (pH ~ 7). It is therefore clear that pH has a great effect on the dominant reaction pathway, however it will also depend on the contaminants present in the water or wastewater.

2.1 Destruction of organic and inorganic compounds using ozone

A number of compounds can be directly degraded by ozone. These include taste and odour compounds (geosmin and methylisoborneol (MIB)), phenolic compounds and pesticides such as atrazine (Crittenden et al., 2005). The importance of ozonation in the treatment of industrial wastewaters targeting the degradation of dyes, pharmaceuticals and personal care products has also grown in recent years. Ozone is also used for oxidation of organic macropollutants and its application is used for bleaching of colour, increasing the biodegradability of organic compounds, removal of THM precursors and reducing total organic halide formation potential or chlorine demand (Langlais et al., 1991).

Several options exist to promote OH·formation during ozonation. These include the addition of H_2O_2, TiO_2 and combining ozone with UV (von Gunten, 2003a). The O_3/H_2O_2 process is perhaps the easiest and cheapest option to enhance the process, but low reaction rates have been observed at pH 5 or less (Matilainen and Sillanpää, 2010). Theoretically 0.5 moles of H_2O_2 is needed per 1 mole ozone (0.354 kg H_2O_2/kg O_3) but more ozone is usually required as it is more reactive with the background organic matter. However care must be taken because excess ozone can have a scavenging effect on the hydroxyl radicals formed. In addition, careful control of the H_2O_2 residual is needed because of its higher stability when compared with ozone (Crittenden et al., 2005).

Several studies have looked into the removal of NOM by ozone based AOPs and concluded that these processes increase the removal of NOM but do not always decrease the production of THMs when compared to normal ozonation (Matilainen and Sillanpää, 2010). Catalytic ozonation is a promising technology for the effective removal of pollutants that are resistant to conventional water treatment but the mechanisms of these processes are still unclear (Legube and Leitner, 1999; Ikhlaq et al., 2013).

In all applications ozone is consumed not only in the oxidation reaction with the target compound but also with the background water matrix (non-target demand) as well as through self-decomposition. The overall ozone demand is water quality specific and may vary widely with season and temperature and therefore existing applications on the same water or treatability studies are the only ways of determining the dose requirements.

Optimum contact time can also vary widely depending on the intended ozonation objective and again this is usually determined through treatability studies. Oxidation of easily oxidisable compounds usually happens in a much shorter timeframe than disinfection. The contact time for oxidation applications is usually far less important than the dose itself and this is mainly true for fast ozonation reactions. However the contacting system can have an effect on the reaction rate. Further, contact time does not necessarily have the same meaning for different types of reactors as mixing intensities and rate of transfer can have a dramatic effect on the relative contact time associated with a process.

2.1.1 Iron and manganese removal

One of the most important ozone applications in water treatment is the oxidation of iron and manganese. It is not considered to be a very cost effective strategy in the US but it is successfully applied in Europe in pre or inter- ozonation combined with conventional treatment processes (Crittenden et al., 2005). Stoichiometric requirements are 0.43 mg O_3/mg Fe^{2+} and 0.86 mg O_3/mg Mn^{2+} but often higher doses are required due to competing oxidation reactions that happen during the treatment stage. Ozone can readily oxidise iron and manganese in groundwater and water of low organic content. Uncomplexed iron is oxidised much faster than manganese as kinetics of iron oxidation by ozone are very fast and therefore as a result, if high concentration of iron is present in groundwater, low ozone doses lead to little manganese oxidation. The ozone doses required in such environments are close to stoichiometric doses if no other scavengers (nitrites or sulphides) are present. Excessive ozone doses (2.2 mg O_3/mg Mn^{2+}) will lead to the formation of permanganate leading to pinkish colour of the treated water. The oxidation of manganese by ozone is less dependent on pH than for other oxidants and ozone is more likely to offer kinetic advantages at low rather than high pHs. An additional advantage of groundwater ozonation is re-oxygenation of the water.

The degree of complexed iron oxidation by ozone is likely to be dependent on the pH and the nature and concentration of the organic matter. Ozonation can also lead to the formation of stable iron-organic complexes that cannot be subsequently further oxidised. Therefore it is important to remove organic matter prior to ozone application. It was reported previously that humic substances can successfully compete for ozone leading to higher doses required (Rakness, 2005). For example, for synthetic water (alkalinity 150 mg/L; pH 8.5; [Mn] = 250 μg/L) 0.5 mg O_3/mg Mn as ozonation dose has resulted in a filtered-water manganese residual of less than 30 μg/L and higher ozone doses led

to the formation of permanganate. In another case for a synthetic water ([Mn] = 1 mg/L; pH 6.3; TOC = 2-5 mg/L; 50-200 mg $CaCO_3$/L), 75% manganese removal was achieved after application of ozone dose of 0.2-0.7 mg O_3/mg C in excess of that required for manganese oxidation alone. The excess of ozone required was inversely proportional to the alkalinity and high levels of bicarbonate lead to lower ozone requirements. For this reason, intermediate recarbonation has been used to improve the efficiency of manganese oxidation by ozone (El Araby et al., 2009). Once the manganese is oxidised to Mn(III) or Mn (IV) it can be removed by flocculation and sedimentation, rapid sand filtration or multimedia filtration. Examples of iron and manganese removal by ozone are shown in Table 15 below.

Table 15. Removal of iron and manganese in various case studies (adapted from Langlais et al., 1991).

Water source	Average dose	Contact time	Process Efficiency
Groundwater (average Fe = 50 μg/L and Mn = 75 μg/L)	0.1 mg/L	2 min + 2 min	Fe: 80% removal Mn: >50% removal
River water (Fe = 23-263 μg/L and Mn = 20-300 μg/L)	0.5 mg/L (max 1.9 mg/L)	3 min + 5 min	Concentrations below detection limit
Reservoir water (pilot) (average Fe = 600 μg/L and Mn = 150 μg/L; TOC = 7.5 mg/L	0.8-1.3 mg/L	not available	Fe: 99% removal Mn: 85% removal
Reservoir water (Mn= 30-550 μg/L; TOC = 3.8-4 mg/L)	0.8-1.3 mg/L	2 min	<50 μg/L

If post-ozonation (for disinfection) is included in the treatment train without subsequent filtration, manganese removal by pre- or inter-ozonation must be well controlled to prevent further oxidation of residual manganese in the post-ozonation stage which could lead to the production of an unacceptable pinkish colour in the water. Other inorganic compounds that can be removed by ozone, usually during pre-ozonation, includes nitrite (NO_2^-) and H_2S/S^{-2} (von Gunten, 2003a).

2.1.2 Oxidation of organic macropollutants

The removal of NOM can have a number of objectives, including removal of colour and UV absorbance, an increase in biodegradable organic carbon ahead of biological treatment, reduction of the DBP formation potential and direct reduction of DOC/TOC levels by mineralisation. The principle oxidation by-products from NOM ozonation are aldehydes, ketones and carboxylic acids (Westerhoff et al., 1999). Mineralisation of NOM is usually not achievable at full scale as this requires high ozone as shown in Table 16.

Table 16. Ozone demand for oxidation of organic compounds.

Target objective	Reported ozone demand	Reference
Colour removal	Up to 3 mg O_3/mg C	Langlais et al., 1991; Gottschalk et al., 2000
Increase in biodegradable carbon	1-2 mg O_3/mg DOC	Gottschalk et al., 2000
Reduction of disinfection by-	0.5-2 mg O_3/mg DOC (to achieve	Gottschalk et al., 2000

product formation potential	10-60% reductions)	
TOC/DOC mineralisation	3 mg O_3 mg/DOC (for 20% removal efficiency)	Gottschalk et al., 2000

When used in drinking water treatment, ozonation is usually positioned between settling/flotation and rapid filtration or between rapid filtration and activated carbon filters or other post-treatment units (Gottschalk et al., 2000). Because ozone interactions with NOM causes substantial changes in the organic compound's molecular structure, ozonation can be also applied prior to membrane filtration to reduce membrane fouling (Van Geluwe et al., 2011).

Ozone doses of 1-3 mg O_3/mg C lead to almost complete colour removal (Langlais et al., 1991) but because humic substances can account for over 10 mg/L of DOC in many natural waters, the required ozone doses are likely to be inhibitive due to cost and the likely high rate of DBP formation. Other sources suggest that over 90% colour removal can be achieved with an ozone dose in the range below 1 mg O_3/mg DOC. If sufficient ozone dose is applied it can lead to a reduction in chlorine demand. It has also been shown that beyond a certain threshold, the colour was difficult to remove and further treatment is required (GAC filtration or sand filtration) or multistage ozonation is necessary.

Topley (1987) reported the application of ozone in combination with a biological activated filter process for the treatment of highly coloured water (up to 60 total colour units (TCU)). The ozone dose in the full scale plant was designed to be 4.2 mg/L at full flow with a 5 minute contact time in each of the four contact chambers and it was reported that substantial colour removal occurred at an ozone dosage of approximately 2-3 mg/L with some additional colour removal occurring through the filter (Topley, 1987).

2.1.3 Removal of micropollutants

Ozone is capable of destroying a range of volatile micropollutant compounds, in particular alkenes and aromatic organics, using the conditions of ozone treatment applied in drinking water (Langlais et al., 1991). In the past, micropollutant removal has not been usually a primary task for ozone but was considered to be a positive side effect. However, due to ever lowering detection limits and stricter regulatory requirements for more chemicals in drinking water, the interest in micropollutants has grown in recent years. The oxidation of micropollutants by ozone is only an efficient process for compounds that contain an amino group, an activated aromatic system or a double bond (von Gunten, 2003a). Most micropollutants are poorly accessible to direct ozone attack and an advanced oxidation process is usually required. Micropollutants are usually transformed to metabolites that are often more polar in nature and smaller in molecular weight, but are rarely completely mineralised, therefore it is essential to have a subsequent treatment unit (Gottschalk et al., 2000). The following table (Table 17) summarises the expected removals of a range of micropollutants when using ozone.

Table 17. Degree of removal of trace organics during ozonation in full-scale drinking water treatment plants (Gottschalk et al., 2000).

Substances	**Degree of removal (%)**	**Comments**
Taste and odour	20-90	source specific
MIB, geosmin	40-95	Improvement by AOP (O_3/H_2O_2; O_3/UV)
Alkanes	<10	

Alkenes, chlorinated alkenes	10-100	chlorine content important; AOP support oxidation
Aromatics and chloroaromatics	30-100	highly halogenated phenols are more difficult to oxidise
Aldehydes, alcohols, carbonic acids	low	typical products of ozonation, easily biodegradable
N-containing aliphatics and aromatics	0-50	AOP may increase oxidation rate
Pesticides	0-80	very substance specific; triazines require AOP
Polyaromatic hydrocarbons	High, up to 100	

2.1.4 Taste and odour control

The efficiency of ozone in the removal of taste and odour depends on the compounds causing the issues and if these compounds are saturated structures, ozone can have little impact. The most common taste and odour associated compounds are MIB and geosmin and these have a very low reactivity with ozone. However, despite this, studies with natural waters have shown good removal efficiencies of these compounds when using ozone. It is likely that ozonation is most effective in waters that support the $OH^{\bullet}$ radical pathway. However, the action of ozone in natural waters is variable and depends on the quality of organics present as well as the treatment conditions. It was reported that the combination of ozone with H_2O_2 increased geosmin and MIB elimination by 35% compared to ozone alone (Langlais et al., 1991). The best taste and odour control strategy includes ozonation followed by filtration and adsorption. If combining ozonation with GAC adsorption, it is important to control the ozone dose in order to prevent the formation of certain by-products such as short chain aldehydes which are not very well adsorbed on GAC (Langlais et al., 1991). In most cases only a partial oxidation of the compounds is necessary to eliminate taste and odour problems (von Gunten, 2003a).

2.1.5 Particle removal

It has been observed for more than 30 years that pre-ozonation ahead of solid-liquid separation processes can improve the removal of particles (Gottschalk et al., 2000). Pre-ozonation can have a number of positive effects on coagulation and settling processes and these include a shift in particle size distribution towards larger sizes, the formation of colloidal matter from dissolved DOC, a decrease of coagulant dose and an increase in floc settling velocities. It has been suggested that a certain critical concentration of organic material must be present in order to observe the enhanced coagulation effects of ozone. Further the calcium concentration in raw water also impacts on the coagulation effects of ozone. Ozone gas can be added either before or together with the coagulant at dosages between 0.5-2 mg/L. The mechanisms involved appear to be rather complex and poorly understood. The observed increase in solids removal are often quite variable from site to site (20-90%) which suggests some very specific reactions are taking place from water source to water source (Gottschalk et al., 2000). Positive effects of pre-ozonation are also seen seen for algae removal. Ozone readily kills or lyses many types of algae and it has also been observed to enhance the removal of algae by coagulation and settling. Ozonation of algae can lead to the release of surface active polymers, which may aid aggregation but could also be a source for organic disinfection by-products. Ozone can also be applied to inactivate zooplankton and actinomycetes (Lin et al., 2012). A number of laboratory studies have reported the effect of ozonation on the removal of cyanotoxins and it was shown that complete removal of the toxins can be achieved when

ozone is included in the treatment process (von Gunten, 2003a; Sharma et al., 2012). Ozoflotation is a new process combining the physical phenomenon of flotation with the oxidising properties of ozone and is usually used as a pre-treatment stage in order to reduce the treatment load.

3.0 Point of use disinfection of water supplies

3.1 Applications and dosing conditions

There are a range of commercially available point of use (POU) and point of entry (POE) ozonation devices. In POU systems, ozone is added directly into the water that is being used, for example at the tap. In POE systems, ozone is added to the water as it enters a property before it is distributed throughout the premises. These devices have found application for drinking water treatment, wastewater treatment, aquaculture and agriculture, electronics manufacture, food production and pool water treatment. There is limited scientific literature available on the performance and reliability of these devices and most of the below information has been taken from commercial sources and, as such, limited validation of performance can be gleaned from this data.

POU and POE systems generate ozone in the same way as for full scale systems as applied at WTWs, usually by passing high voltage electricity through air. Details of POU systems found in the literature are shown below:

Ozone Pure Water Inc: http://www.ozonepurewater.com/ozone.htm#2

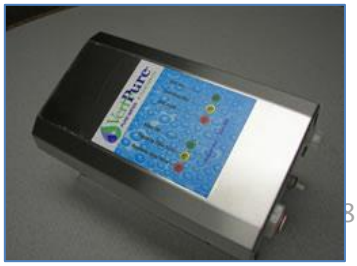
Ozone is generated by high voltage electricity passed through air. An off-gas venting filter and a media filtration unit is supplied as part of the treatment system.

The system treats flows of 26-45 L/min.

Ozomax: http://www.ozomax.com/Residential-products/point-of-use-ozone-systems.html

Ozone is produced electrolitically *in situ* using a precious metal anode and an electricity supply. The manufacturers state that higher ozone levels are formed at higher conductivity levels (up to 600 mg/L total dissolved solids), so this method will not be effective for soft water sources. The units come in a range of sizes and can be fitted to domestic taps under the sink and also incorporate a pre carbon filter to remove chlorine and a post filter to remove precipitated solids. Monthly cleaning of the system is required.

Veripure: http://www.veripurefood.com/index.php



The system is an in-line, low power ozone generation system (30 Watts) with a replaceable filter cartridge after ozonation to

remove particulates from the water. The system is able to treat a flow of 1.9-15 L/min. No information is provided as to how the ozone is generated.

Ozotech point of use ozone generator: http://www.ozotech.com/index.php/residential

A range of different sized systems are available for residential blocks or under the sink application. Ozone is generated by a corona arc discharge. Under the sink systems treat flows of 2.6 L/min, but the residential system (POE) has a much greater capacity. Ozone is dosed to around 1.5 mg/L, leaving a residual of 0.1-0.4 mg/L. The residential system has an activated carbon post filter, whilst nothing seems to be supplied with the under the sink ozonation systems. As with most POU/POE devices, no detail on off gas destruction is mentioned.

DWC: http://www.dwc-water.com/technologies/ozone-disinfection/index.html

This company has a range of POU devices, but the one of most interest is a system that generates ozone from water pressure and therefore requires no electricity. The system is applied directly onto the tap. The suppliers claim that it is able to operate for 5000 hours, can treat 5 L per minute, supplying ozone at a concentration of 0.2-0.3 mg/L.

POU devices are widely available from a range of suppliers (particularly in North America). Unless installed immediately before water exits the tap, POU systems need to include an in-line filter to be able to remove precipitated solids that will form as a result of the ozone application: not all of the ozone generators reviewed have this capability. Off-gas destruction is also not considered in most POU systems. This may be because all gas is transferred into the water or because accumulation of off gas is low, but given that these systems are likely to be installed in customer's homes this aspect needs to be understood thoroughly. Further, appropriate independent testing of POU ozone devices is required because to date, most, if not all, claims made by manufacturers have not been verified.

4.0 Application of ozone in wastewater treatment

Similarly to drinking water treatment, ozone can be applied to satisfy a number of objectives in wastewater treatment (examples of ozone applications in wastewater treatment are presented in Table 10). Ozone is beginning to be employed in wastewater treatment for disinfection, oxidation, improved membrane fluxes, reduced colour and odour, and removal of pharmaceutical and personal care products (PPCPs) or other refractory organics (Sharif et al., 2012). Full scale ozone treatment plants (with an ozone generation capacity of >0.5 kg/h) can be found being used for various applications and treating almost all types of wastewaters:

- Disinfection
- Oxidation of inorganic compounds
- Oxidation of organic compounds

- Enhancement of sludge degradability

Cost implications of full scale ozonation has led to the development of multistage treatment systems as it has been shown that savings can be made by combining ozonation with biodegradation systems (Gottschalk et al., 2000). Full scale wastewater ozonation systems usually employ bubble column reactors as contactors and many are operated at elevated pressure (2-6 bar_{abs})in order to achieve high ozone transfer rates, which in turn increases the process efficiency (Gottschalk et al., 2000).

4.1 Disinfection of final effluent

Disinfection of waste waters is required in some countries, such as the US, before effluent is discharged into receiving waters to meet water-quality standards. While bacteriological standards are not currently part of the EU Urban Wastewater Treatment Directive, disinfection of municipal effluents is implemented where there is a need to protect bathing waters in line with the EU Bathing Water Directive. Chlorine is most commonly used but can cause formation of chlorinated disinfection by-products (DBPs) (Gottschalk et al, 2010).

Although ozone disinfection is a well-established technology for drinking water treatment, ozone disinfection mechanisms in wastewater are less well understood. However, where increasing pressure on water resources has driven demand for water reuse for irrigation, ozone has been utilised. For example, WWTP effluent in Almeria (Spain) is disinfected with ozone, before the water is then applied to 3,189 ha of horticultural greenhouse crops. This provides water and nutrient savings and eliminates pollutants from the wastewater discharge (Martinez 2011). Ozone reacts strongly with many substances, therefore it is generally deemed more appropriate for use on pre-treated effluents (Paraskeva and Graham, 2002).

A number of studies on ozone disinfection have utilised seeding approaches whereby laboratory cultures of microorganisms (bacterial pathogens, viruses or indicators) are applied to buffer solutions or wastewater which is then subject to ozonation. Reductions in faecal coliforms and enteric viruses have been reported to undergo 3-6 log reduction in just a few seconds under these conditions (Finch and Fairbairn, 1991: Herbold et al*.,* 1989; Vaughn et al*.,* 1987). For example, Norwalk virus can be attenuated by ozone to a similar degree to the MS2 phage and was reported to be removed to the order of 3-3.5 log units by 0.37-mg/L ozone for 10 seconds in ozone demand free water (Shin et al, 2003). However, this may not give a realistic approximation of indigenous organisms present in real wastewater treatment systems.

In wastewater systems, the ozone dosage required is dependent on the nature of the wastewater, as for drinking waters (Gottschalk et al., 2010); therefore data from studies on actual wastewaters provide a clearer indication of disinfection requirements. In laboratory semi-batch experiments, carried out in a column reactor, ozone was applied to secondary treated effluent from a sewage treatment plant in Varanasi, India (Tripathi et al., 2011). Following a conventional activated sludge process, effluent was subject to a range of ozone doses and contact times at ambient temperature (not given). Total and faecal coliforms and *E. coli* were inactivated at 10 mg/L at a 5 minute contact time (Appendix 2) in effluent with a COD of 78 mg/L; turbidity of 40 NTU, pH 7.1 and characterised as high in organic content. The authors noted that the applied ozone dose, rather than the transferred dose was reported. Marked resistance of *C. perfringens* to ozone disinfection has been noted by other authors (Tyrrel et al.1995). Ozone doses commonly presented in the literature

ranged from 0.3 µg/L to fully saturated, with contact times generally between 1.5 and 18 minutes. This provided a range of inactivation rates, broadly in the range of 1-2.5 log inactivation for coliforms, *Enterococci* and *Clostridia*, while some higher reductions were noted for bacteriophages used as surrogates for human viruses (Appendix 2).

Xu et al. (2002) reported that hydraulic retention time had no significant effect on disinfection of *E. coli* and faecal coliforms, rather than the critical parameter was optimisation of mass transfer of ozone. Mass transfer tends to be low due to the low solubility of ozone (Zhou and Smith, 2000). For example, Silva et al. (2010) reported transferred ozone percentages to wastewater of between 65 and 79 % in a bench-scale batch system. Many full-scale ozone reactors are operated at elevated pressure (2–6 bar) to allow a high ozone-transfer efficiency, which also increases the overall process efficiency (Gottschalk et al., 2010). When the transferred ozone dose approximates the immediate ozone demand, before there is any measurable residual ozone, a significant log inactivation of faecal coliforms and *E. coli* has been reported (Janex et al., 2000; Xu et al., 2002). Xu et al (2002) noted a 1-3 log inactivation occurred when sufficient ozone was applied to meet the initial ozone demand. Higher initial ozone demand can therefore mean higher inactivation rates at these doses, due to the fact that the bacteria present form part of that ozone demand due to their high reactivity with ozone. Xu et al. (2002) note that because of this, the CT approach used to calculate ozone application for drinking water is inappropriate for disinfection of final effluent. At one of the same wastewater treatment plants (in Indiannapolis) ozone disinfection had been successful, however no ozone residual could be measured (Rakness et al. 2005).

For wastewater, ozonation is often part of a multistage treatment process to reduce ozone consumption. Most often a chemical-biological process includes biodegradation at least before and also often after the chemical oxidation step (Gottschalk et al, 2010). Ozone quantities and generation costs tend to be reduced when utilising these combined systems.

Evaluating the combined effects of ozone and hydrogen peroxide, Gerrity et al (2011) established a pilot HipOX reactor utilising and ozone/ H_2O_2 process for treatment of ultrafiltration (UF) or sand-filtered secondary effluent after activated sludge treatment at a wastewater reclamation facility in Nevada. Ozone was dosed at 5 mg/L and H_2O_2 at 3.5 mg/L with a residence time of 5 minutes. This represented an ozone: total organic carbon ratio of 0.8. The addition of H_2O_2 promotes very rapid decomposition of ozone into hydroxyl radicals, leading to completion of disinfection reactions within seconds. Disinfection was evaluated for the sand filtration treatment train as UF was more effective in eliminating coliforms. The ozone/ H_2O_2 process achieved 2-3-log inactivation of total coliforms and 3-4-log inactivation of faecal coliforms during two sampling campaigns. However, the ozone/H_2O_2 conditions were insufficient to comply with the effluent total coliform levels ranged from 284 to 1069 MPN per 100 mL. Faecal coliform levels ranged from 3.1 to 37 MPN per 100 mL, not meeting US requirements for reuse. Limited inactivation *Bacillus* spores was reported (<1-log), however, bacteriophage MS2 (human virus surrogate) underwent >6.5-log inactivation under the same conditions. The authors stated that significantly higher ozone doses would have to be used to achieve the 2.2 MPN per 100 mL threshold in the sand filtration configuration. However, UF pre-treatment was effective in meeting this target. In contrast, Wert et al. (2007), comparing coliform the efficacy of O_3 and O_3/H_2O_2 on tertiary treated wastewater reported that when similar O_3 dosages are applied, O_3 was a more effective disinfectant. They reported that sufficient disinfection

was achieved with O_3 when applying dosages at or above the instantaneous ozone demand (IOD). They recommended this for process control during full-scale application.

Subsequent BAC processing could also lead to regrowth of coliforms; therefore a final disinfection process would potentially be required (Gerrity et al., 2011). Oh et al (2007) noted suggested that a combined ozone/UV process could overcome the limitations of the ozone alone for the disinfection of sewage effluent water.

While the generation of a measurable ozone residual for disinfection purposes poses problems, it has been shown that combining ozone with a chlorine residual could be beneficial. Wert et al. (2007) observed that ozonation reduced the formation of trihalomethane and haloacetic acids during chlorination by 20%.

4.2 Impact of Ozone on filamentous bacteria

Reduction of excess sludge is a significant challenge for biological wastewater treatment and a good understanding of the microbial ecology of the system is required to maintain an appropriate number of filaments (Guo et al., 2012). Filamentous organisms are a normal part of the activated sludge microflora and, in low numbers, are thought to promote floc formation. Excessively long filaments or presence in high numbers can lead to sludge bulking (Eckenfelder, 1992).

Ozone can be used as a "non-specific" approach to reducing filamentous organisms and therefore reducing bulking and foaming in activated sludge systems. Chlorine is commonly used for this purpose, but doesn't represent an on-going solution as it can affect nitrification (Thirion, 1982). Partial ozonation of the return sludge of an activated sludge process can also substantially reduce the excess sludge. During ozonation, in addition to damaging and inactivating microorganisms present in sludge, organic matter is converted into biodegradable materials and there is some mineralization of soluble organic matter through chemical oxidation (Foladori et al, 2010). Ozonation also improves settling properties of the sludge and reduces bulking and foaming (Vergine et al, 2007). Ozonation has been applied directly within biological wastewater treatment processes or as pre-treatment prior to anaerobic digestion (Yazoo and Shibata, 1994; Weemaes et al., 2000; Goel et al., 2004; Lee et al., 2005; Dytczak et al., 2007) in order to reduce excess sludge. Low dose ozonation can inhibit the activity of filamentous bacteria and has been applied to control bulking and improve floc settling (Foladori et al, 2010, Appendix 3a).

However, there is relatively little understanding of the mechanisms involved and, as with any approach adopted for reducing sludge production, it influences the microbial community which could affect effluent quality (Vergine et al, 2007). Organisms responsible for bulking and foaming are listed in Table 18 below.

The efficiency of sludge ozonation depends on the following parameters (Foladori et al; 2010):

- Wastewater or Sludge quality
- Reactor configuration
- Ozone gas flow rate and concentration
- Sludge flow rate and solids concentration
- Ozone transfer efficiency

- Contact time
- Ozone dosage per mass of TSS

Table 18. Filamentous bacteria found in bulking activated sludge (adapted from Guo and Zhang, 2012).

Types	**Phylum**	**Genus or species according to the reference**	**Reference related to bulking**
Beggiatoa	Proteobacteria	*Beggiatoa*	Williams and Unz, 1985
Cyanobacteria	Cyanobacteria	Unknown	N.A.
Flexibacter elegans	CFB group	*Flexibacter elegans*	Jenkins et al., 1993
Haliscomenobacter hydrossis	Bacteroidetes	*H. hydrossis*	Ziegler et al., 1982
Leucothrix mucor	Proteobacteria	*Leucothrix mucor*	Williams and Unz, 1989
Microthrix cali	Actinobacteria	*Candidatus Microthrixa*	Levantesi et al., 2006
Microthrix parvicella	Actinobacteria	*Candidatus Microthrixa*	Rossetti et al., 1997
Mycobacterium fortuitum	Actinobacteria	*Mycobacterium fortuitum*	Blackall et al., 1991
Nocardiaform-like organisms	Actinobacteria	*Gordonia amarae*	Blackall, 1994
Nostocoida limicola	Firmicutes	*Trichococcus*	Liu et al., 2000
Nostocoida limicola	Actinobacteria	*Tetrasphaera jenkinsii*	Liu and Seviour, 2001
Nostocoida limicola	Planctomycetes	*Isosphaera*	Liu et al., 2001
Rhodococcus globerulusc	Actinobacteria	*Rhodococcus globerulus*	Schuppler et al., 1995
Rhodococcus ruberc	Actinobacteria	*Rhodococcus ruber*	Schuppler et al., 1998
Skermania piniformisc	Actinobacteria	*Skermania piniformis*	Eales et al., 2006
Sphaerotilus natans	Proteobacteria	*Sphaerotilus*	Eikelboom, 1975
Thiothrix form I	Proteobacteria	*Thiothrix*	Howarth et al., 1999
Tsukamurella pseudospumaec	Actinobacteria	*T. pseudospumae*	Nam et al., 2004
Type 0041/0675	TM7-likeBetaproteobacteria	Unknown*Aquaspirillum*	Hugenholtz et al., 2001Thomsen et al., 2002; Thomsen et al., 2006
Type 0092	Chloroflexi CFB	Unknown	Speirs et al., 2009Bradford et al., 1996
Type 0211	Unknown	Unknown	N.A.
Type 021N	Proteobacteria	*Thiothrix eikelboomii*	Howarth et al., 1999
Type 0411	CFB group	Unknown	Bradford et al., 1996
Type 0581	Unknown	Unknown	N.A.
Type 0803	Chloroflexi	*Caldilinea*	Kragelund et al., 2011
Type 0914	Chloroflexi	Unknown	Speirs et al., 2011
Type 0961	Unknown	Unknown	N.A.
Type 1701b	Betaproteobacteria	Unknown	Howarth et al., 1998
Type 1851	Kouleothrix aurantiaca	*Chloroflexi* (Phylum)	Beer et al., 2002
Type 1863	ProteobacteriaCFB group	*AcinetobacterMoraxella osloensisChryseobacterium*	Seviour et al., 1997

It is apparent that low dose ozonation has a differential effect on filamentous bacteria (Caravelli et al, 2006), hence its ability to reduce the organisms responsible for filamentous bulking without affecting biological treatment (van Leeuwen and Pretorius, 1988; Vergine et al, 2007). It is likely that filaments protruding from flocs come into immediate and direct contact with ozone, whereas those

within the floc are protected from the immediate effects, therefore ozone-damage occurs more substantially in the filamentous organisms (Seviour and Neilsen, 2010). Chu et al. (2009a) observed that there was no immediate decrease in ATP upon exposure to ozone, but immediate decrease in enzyme activities. This indicates that ozone first affects the filaments, destroying the floc, then disperses compact aggregates (potentially affecting enzymes embedded in EPS or on cell surfaces) and then affects bacterial cells leading to the decrease in ATP (Chu et al, 2009a). Foladori et al. (2010) noted that at high dose ozonation tended to reduce the number of small flocs (< 3 µm) and increase the number of medium flocs (7.5-30 µm) but that particle size generally remained stable at lower doses. ESEM images have shown a deformation of bacterial cells subjected to <0.17 g O_3/g TSS (Chu et al., 2008).

Yan et al. (2009) reported that there was little evidence of any impact on microbial communities, based on molecular analyses, for ozone dosages up to 20 mg O_3/g. Chu et al. (2009) noted that a systematic study of the changes in characteristics and activities of sludge exposed to low-dose ozone would be useful for optimization of a cost-effective sludge reduction process. In earlier studies, van Leeuwen (1987), using microscopic methods, noted differences in the types of filamentous organisms present, with apparently greater diversity in the ozonated sludge. The number of filaments appeared to be an order of magnitude lower in the ozonated treatment. The authors also indicted that ozonation promoted nitrification and biological removal of organic material without affecting phosphate removal.

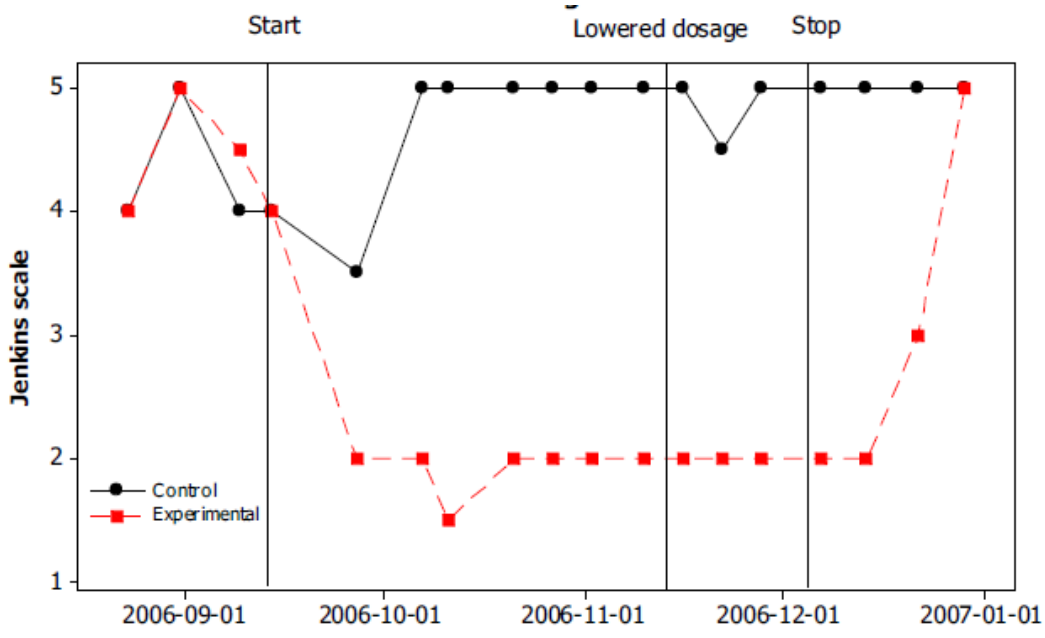


Figure 4. Floc density with and without treatment (from Wijnbladh, 2007).

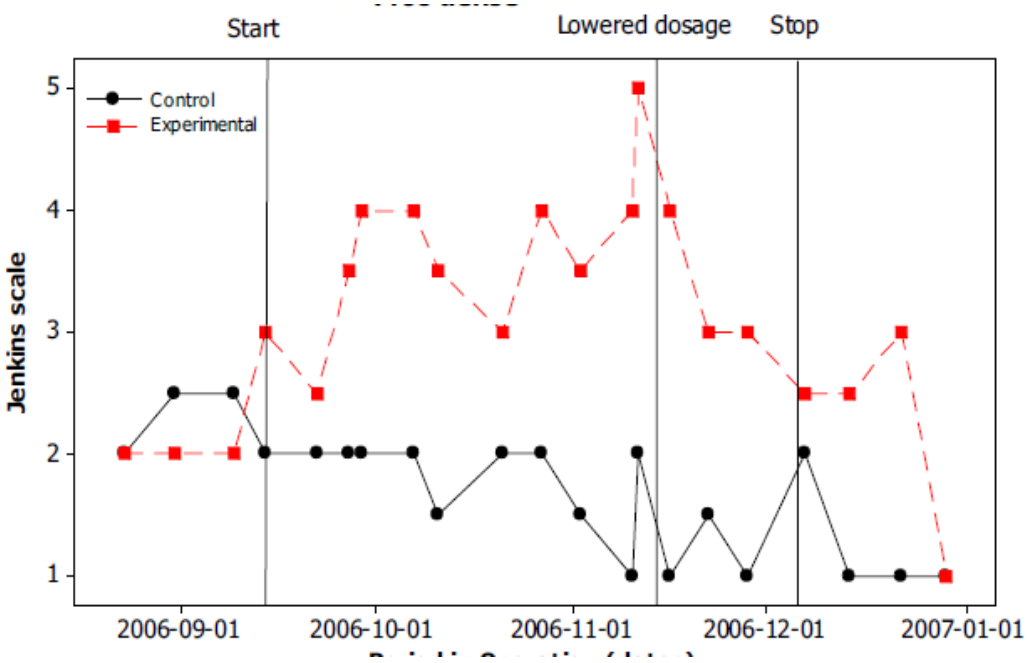


Figure 5. Filament presence with and without treatment (from Wijnbladh, 2007).

Wijnbladh (2007) observed that ozonation of activated sludge led to changes in the microscopic appearance of the filamentous bacterium *M. parvicella* in the reactor. Initially, the organism stained Gram positive and exhibited substantial storage of phosphate granules. However, after three weeks of ozonation of the return activated sludge, the bacteria appeared either Gram positive with many empty cells or even completely Gram negative. No changes were noted in a parallel control treatment train. The authors reported improved floc structure (Figure 4) directly after start up, with few *M. parvicella* remaining inside the sludge flocs (Figure 5). Similar observations were made two months from start-up of treatment. No effects on nitrification were observed in the study. Likewise, Paul and Debellefontaine (2007) reported that ozone caused filamentous bacteria to disappear, leading to the reduction of bulking and foaming in activated sludge and generating more compact flocs.

The influence of ozone on other wastewater treatment parameters is critical to the success of its use to reduce filaments or excess sludge. Some reported impacts on other microorganisms or biologically driven processes are given in Appendix 3b. Paul and Debellefontaine (2007) noted that there was a linear relationship between the log of biomass activity (reported as maximal oxygen uptake rate) and log ozone dose between 0.001 and 0.2 g O_3 transferred per g COD in the sludge). They concluded that ozonation does not affect any of the capabilities of an AS biological process; however other studies have reported contrary indications.

A decrease in nitrification rate has been shown to be proportional to increasing ozone dose (Dytczak et al. (2007); Appendix 3b). The literature is contradictory in the degree to which nitrification is affected. For example, van Leeuwen (1988) and Vergine (2007) did not experience any reductions in nitrification or total nitrogen removal at ozone doses of 1-4 mg/g MLSS/d and 6 mg/L applied to settled sewage or activated sludge respectively. In contrast, Böhler and Siegrist (2004) observed a reduction in the rate of nitrification capacity similar to the reduction in sludge production across

doses between 0.02 and 0.08 g O_3/g TSS and Kobayashi reported an 80 % reduction in nitrification rate at a rate of 0.05 g O_3/g TSS. It has been suggested that the decrease in nitrification, due in part to direct effects of ozone on nitrifiers and in part to competitive interactions with heterotrophs, may be offset by the increased sludge retention time occurring as a result of the decrease in excess sludge production (Paul and Debellefontaine, 2007; Foladori et al., 2010). Indeed, Déléris et al (2002) observed similar ammonia removal in both ozonated (0.062 g O_3/g TSS) and control activated sludge treatments.

The viability of phosphorus accumulating organisms (PAOs) and heterotrophic bacteria has been reported to decrease exponentially with the degree of sludge solubilization during ozonation in the range of 0.03–0.04 g O_3/g TSS (Saktaywin et al., 2005). This was corroborated by Lee et al (2005) who reported that an ozone dose of 0.05 g O_3/g TSS, inactivated 97 % of heterotrophic organisms and Yasui and Shibata (1994) who observed a 90 % decrease in colony forming units at less than 0.05 g O_3/g TSS. Some novel approaches to biological nutrient removal also have the potential to combine ozonation with other technologies to provide effective wastewater treatment while minimising excess sludge production. For example, Suzuki et al. (2006) proposed an anaerobic-oxic-anoxic system equipped with an ozonation tank and a P adsorption column. Trials demonstrated that despite a slight decrease in nutrient removal efficiencies, 34-127 % sludge reduction was obtained and 80% of P was recovered.

Reid et al (2007) suggested that a more cost effective ozone process for excess sludge reduction would follow the principle “partial oxidation as low as possible and biological oxidation as high as possible”. This minimises the use of ozone but maximises conversion of solids into biodegradable materials which can then be removed in cheaper biological reactors.

Cao et al. (2009) set out to investigate the effect of ozone on the formation of typical disinfection by-products during application of chlorine residual to tertiary treated wastewater for reclamation. This is also pertinent where treated effluent significantly influences raw water for abstraction. Ozonation was carried out in batch reactors prior to application of a chlorine dose of 5 mg/L. Ozonation led to an increase in the formation of all the DBPs measured, including THMs and HAAs, except $CHCl_3$, which decreased from 51.2 to 37.1 µg/L at consumed ozone doses of 0-10 mg/L. Total brominated THMs increased from 10.3 to 58.2, primarily through increases in $CHCl_2Br$ and $CHClBr_2$. This was thought to be due to the relatively high concentration of organic compounds in the tertiary wastewater. In contrast, Wert et al. (2007) found that ozonation reduced the formation of THMs and HAAs during chlorination by 20%. The same authors also reported that when applying an advanced oxidation processes with H_2O_2 and ozone, the lack of O_3 residual coupled with the presence of excess H_2O_2 inhibited bromate formation. Furthermore, it has been reported that an advanced oxidation process such as combined O_3-UV has the potential to remove DBP precursors from raw surface waters. Chin et al (2005) concluded that this combined AOP was more effective than either technology alone and reduced THM formation by around 80 % and HAA formation by around 70 % at 0.62 mg O_3/ML and 1.61 Ws/cm^2 UV dosage. Ozonation has also been reported to reduce the genotoxicity (based on the umu assay which relates to DNA damage) of the treated wastewater, both with and without chlorination. Genotoxicity decreased from 7 µg 4-NQO/L with neither chlorine nor ozonation, to just over1 µg 4-NQO/L with 10 mg/L ozone and 10 mg/L chlorine

(Cao et al, 2009). Takanashi et al. (2002) also noted that ozone treatment was effective in removing mutagen precursors from wastewater.

It is clear that the nature of the water to be treated is critical in determining the degrees of DPB formation.

4.3 Oxidation of inorganic compounds

One of the aims of ozone application in wastewater treatment is to remove toxic inorganic substances and this mainly involves the removal of cyanide (CN-) mostly associated with metal processing and electronics industry wastewaters. It can be present in its free form which reacts quickly with ozone but more often it is complexed with iron or copper (Gottschalk et al., 2000). The complexed forms of cyanide are more stable to ozone attack and therefore advanced oxidation processes are more appropriate for its removal.

Nitrite (NO_2^-) and sulphide (H_2S/S^{2-}) react quickly with ozone and therefore their removal is sometimes carried out using ozonation, however more cost-efficient biological treatment alternatives are more often employed for these contaminants.

4.4 Oxidation of organic compounds

Most often in industrial wastewater treatment, ozone is applied to remove target organic compounds that can be present at a wide range of concentrations. These wastewaters include landfill leachate, textile, pharmaceutical and chemical industry wastewaters that can contain many refractory organics including humic compounds, aromatic compounds containing metals, pesticides and surfactants. The main aims of ozonation in this case are (Gottschalk et al., 2000):

- The transformation of toxic organics that are often present in low concentrations and as complex mixtures
- The improvement of biodegradability of refractory organics by partial oxidation
- The removal of colour

Usually complete mineralisation by ozone is not economical and combination with other processes is preferable. The most frequent problems associated with wastewater ozonation include foaming and precipitation of inorganic salts such as calcium oxalate, calcium carbonate and ferrous hydroxide which can lead to reactor clogging. A number of full-scale ozonation systems has been used in Germany to treat landfill leachate prior to effluent discharge to water bodies and due to the complex nature of the organics the ozonation stage is commonly operated between two biological systems (Bio-O_3-bio) (Gottschalk et al., 2000). The main aim of ozone application in the treatment of textile wastewaters is removing non-biodegradable colour but additionally the removal of surfactants and partial oxidation of DOC can be achieved but again a multistage treatment system is usually necessary. Low ozone doses are sufficient for the removal of colour but if a high degree of DOC removal is required the treatment costs increase dramatically.

A number of studies have focused on the coupling of ozone and aluminosilicates to remove volatile organic carbon compounds (VOCs) (Brodu et al., 2012). In this case methyl ethyl keton was used in the treatment studies and showed that ozonation regeneration is a promising step in VOC removal (Brodu et al., 2012).

The use of ozone in water reuse applications is becoming increasingly popular due to its efficacy in removing trace organics with limited to no chemical addition and the potential for reduced energy requirements (Gerrity and Snyder, 2011). Ozone and OH• radicals are extremely effective in oxidizing most trace organic compounds, particularly the steroid hormones linked to feminisation of aquatic species, but the required level of treatment in each application is relatively subjective (Gerrity and Snyder, 2011). The potential of ozonation as a tertiary treatment prior to industrial water re-use (paper mill effluent, textile wastewater, food and chemical industry effluents) was recently investigated at lab scale with promising results (Mauchauffee et al., 2012). Several issues are associated with the use of ozone in wastewater including the formation of bromate, N-nitrosodimethylamine (NDMA), and other potentially toxic oxidation by-products (Gerrity and Snyder, 2011). Some utilities are mitigating the potential effects of ozone by-products through subsequent biological filtration with acclimated sand or activated carbon (Gerrity and Snyder, 2011). Reliability and maintenance issues has hampered the application of ozone in wastewater treatment plants and the limited experience makes it difficult to extrapolate existing design knowledge, which is primarily based on drinking water applications, to wastewater matrices with their higher oxidant demand, turbidity, organic content, UV absorbance, and radical-scavenging capacity (Gerrity and Snyder, 2011).

Due to low ozone reactivity with a number of compounds, advanced oxidation processes that promote the formation of OH• has been studied in recent years. One such process is photocatalytic ozonation ($TiO_2/UV/O_3$) which has been studied to treat inorganic anions, such as cyanide ions, simple organic molecules, such as monochloroacetic acid, oxalate anions and formic acid, and environmentally problematic organic compounds, such as pesticides, additives, and textile dyes (Sun et al., 2013). Bobu et al. (2013) employed ozone based AOPs (O_3/UV, $O_3/UV/H_2O_2$ and $O_3/UV/H_2O_2/Fe(II)$) for the degradation of two antibiotics (enrofloxacin and ciprofloxacin)achieving the highest degradation with the $O_3/UV/H_2O_2/Fe(II)$ treatment (93 and 99% TOC removal respectively).

Table 19. Ozone applications in wastewater treatment.

Reference	WW/substrate treated	System scale	Treatment mode	Ozone dose applied	Contact time	Removal	Comments
Gago-Ferrero et al., 2013	Benzophenone-3 (BP3)-personal care product in DI water	Lab-scale	Batch		60 min	>99%	Initial conc. (BP3)= 5.1 mg/L; BP3 shows higher reactivity through radical pathways compared to direct ozonation
Li et al., 2007	Benzophenone-3 (BP3) in tertiary effluent	Full-scale	Continuous	5-6 mg/L	180 min	20%	Initial conc. (BP3)= 311 ng/L
Jagadevan et al., 2013	Spent metalworking fluids (model wastewater)	Lab-scale	Batch	2500 mg/L		27% after ozonation; 72% overall	Initial COD 3100 mg/L; ozonation followed by biological stage
Bertanza et al., 2011	Bisphenol A in WW	Pilot-scale		8 mg/L	80 min	90%	Initial conc. BPA = 2 - 4.3 x 10^{-4} mg/L
Mohapatra et al., 2012	Bisphenol A in WW sludge	Lab-scale	Batch	24.14 mg/g SS	16.47 min	100%	24 g/L SS, pH 6.23
Muz et al., 2013	EDCs (diltiazem, carbamazepine, butyl benzyl phthalate, acetaminophen, estrone and progesterone) in activated sludge	Lab-scale	Batch	1.1 mg O_3/L	4 x 6 min	>99%	Ozone pulsing of waste sludge on 4 successive days reduced aerobic digestion from 30 to 4 days with MLSS reduction over 80% in the same period
Qiang at al., 2012	EDCs (estrone (E1), estriol (E3), 17a-ethynylestradiol (EE2), bisphenol A (BPA), and 4-nonylphenol (NP)) in activated sludge	Lab-scale	Semi-batch	100 mg O_3/g SS		majority of estrogens removed; BPA 83%; NP 64%	E1, EE2, E3 and BPA spiked at 2 μg L^{-1}; NP conc. in activated sludge adequately high (ca. 76 μg/L)
Turhan and Ozturkcan, 2013	anionic sulphonated azo dye (Reactive orange 16) in synthetic WW	Lab-scale	Semi-batch	24 mg/L	8 min	Complete	best treatment efficiency achieved at basic conditions (pH 12)
Qian et al., 2013	Bio-treated textile wastewater	Lab-scale	Batch	3.1 mg O_3/mg COD	5 min	Turbidity 95.8%, colour 97.5%, COD 88.1%, DOC 68.7% UV254 90.5%	Combined treatment process (coagulation + O_3/GAC) studied here

Table-continued……Ozone applications in wastewater treatment

Reference	WW/substrate treated	System scale	Treatment mode	Ozone dose applied	Contact time	Removal	Comments
Gagnon et al., 2008	Primary effluent containing trace organics (salicylic acid, clofibric acid, ibuprofen, 2-hydroxy-ibuprofen, naproxen, triclosan, carbamazepine, and diclofenac)	Pilot-scale		20 mg/L	18 min	> 70% apart for ibuprofen and 2-hydroxyl ibuprofen	The primary effluent: pH 8.1 - 8.2, TSS 5 mg/L, DOC 90 - 110 mg/L, and residual Al (0.6 - 0.9 mg/L) and Fe (0.3 - 0.4 mg/L)
Wert et al., 2009	Tertiary treated WW containing range of trace organics	Pilot-scale	Continuous	O_3/TOC = 1	24 min	> 80%	
Sundaram et al., 2009	Secondary effluent with 30 monitored trace organics	Pilot scale	continuous	7 mg/L		All > 90%	High bromate formation reported
Hollender et al., 2009	WW effluent containing 220 monitored trace organics	Full-scale	continuous	O_3/DOC = 0.6	4-10 min	Only 11 compounds detected > 100 ng/L^{-1}	

4.5 Enhancement of sludge degradation

Ozonation is a widely used chemical method to improve anaerobic degradability of sludge. However, sludge ozonation was first used in combination with the activated sludge process for wastewater treatment and a treatment system based on these processes has been commercialised by the Japanese Kurita company (ca. 30 installations have been implemented) and another industrial process has been proposed by Ondeo-Degremont (Suez): the Biolysis® O process (Carrère et al., 2010). Ozonation has also been combined with anaerobic digestion as a pre-treatment or post-treatment with a recycle back to the anaerobic digester. Better performance and lower ozone consumption has been observed in the case of post-treatment and recycling in the digester (Carrère et al., 2010). Disintegration of sludge by ozonation as a pre-treatment process to accelerate the digestion processes has been of recent interest (Erden et al., 2010). An ozone dose of 0.1 g O_3/kg total solids increased the aerobic degradability of the sludge with the volatile suspended solids (VSS) reduction achieved in the digester increasing to 34% in comparison to 22% reduction without the ozonation pre-treatment. Ozonation pre-treatment did not have any major effect on the dewaterability of the sludge. The advantages of ozonation pre-treatment of secondary sludge is that it can improve the sludge solubilisation and it can also simultaneously degrade organic pollutants such as bisphenol A (Mohapatra et al., 2012).

5.0 Environmental Implications

It is thought that the changes brought about through ozonation of wastewater may modulate or possibly increase the toxicity of effluents toward aquatic organisms. The availability and mobilisation of heavy metals and other chemicals could be affected by ozonation, notably where dissolved organic matter contains substantial amounts of protein or humic acids. Direct effects of ozonation on shrimp hatching rates have been observed (Sellars et al., 2005). However, it is the indirect effects of altered wastewater chemistry that are most likely to pose a risk to aquatic biota. For example, T lymphocyte proliferation in Rainbow Trout decreased dramatically in fish exposed to ozonated effluent compared to fish exposed to either the primary-treated effluent or to aquarium water (Hebert et al., 2008).

However, at the appropriate dosage, beneficial effects of ozonation have been highlighted. For example, Wei et al (2012) took samples from a wastewater treatment plant and a connected reclamation treatment plant in Beijing to evaluate some of the treatment processes from a toxicological view point. Ozonation was applied to secondary effluent at 0, 5, 10 and 15 mg/L with contact times of 0, 5, 10, 15 and 20 minutes, after which residual ozone was removed. Further to this, ozonated effluent (contact times up to 45 minutes) was passed through an activated carbon filter. Effluent from both ozone only and ozone plus activated carbon were pre-treated and biotoxicity tests applied. For 15 mg/L of ozone dose and 5 min contact time, acute toxicity and genotoxicity decreased the former to a greater extent. Combining ozone application with activated carbon treatment provided more effective reduction in toxicity.

More in-depth research is required to better understand interactions between ozone and wastewaters and their impacts on the ecology of receiving waters.

6.0 Conclusions & Recommendations

- Ozone disinfection of drinking water is fairly well established across arrange of countries in Europe and within the US. It has been demonstrated to be highly effective against a wide range of pathogens, including the particularly resistant organism, Cryptosporidium. There is potential for the use of ozone in combination with a chlorine residual to protect against regrowth within the distribution network and for regulatory monitoring where detection of a residual is required.
- A key consideration of ozone treatment for any of the above processes is the ability to deliver the appropriate dosage efficiently. This is one of the major challenges with ozonation due to its low solubility. Improved ozone transfer technologies will enhance the cost effectiveness of this process. Deriving the appropriate dosage for drinking waters disinfection is likely to be straightforward through the utilisation of a range of available models and provided attention is given to influent water quality data. In contrast, it is likely to be more difficult to define dosing for wastewater applications, where the standard CT approaches do not hold.
- A further key consideration is the relationship between ozone and water quality. Because ozone is such a powerful oxidant, it is important to evaluate the outcome of its application to waters at a given point in the treatment train and to determine whether this placement a) makes the most of the effect of ozone in terms of both disinfection and degradation of pollutants, and b) will not result in the formation and subsequent discharge of unacceptable levels of disinfection by-products. Or, if this is likely to occur, whether it is possible and /or cost-effective to add on a further treatment step to deal with those additional pollutants.
- Implementation of ozone treatments is likely to be most effective if evaluated on a site by site basis as this not only promotes a thorough evaluation of how to implement the technology for effective disinfection, but would also allow the operators to determine whether ozone interventions at multiple points would be more cost effective for overall treatment and/or whether the inclusion of additional treatment stages before or after ozonation would be required.
- Cyst and sporular forms of protozoans and bacteria present the most difficult treatment challenge for ozone disinfection. High CT values can control these pathogens, but it is recommended that a physical barrier is also provided for water sources containing these micro-organisms.
- The main limitation of applying ozone in drinking water systems is the production of bromate as a DBP. Methods of controlling bromate formation have been developed, principally through controlling pH and understanding prevailing water quality conditions. Empirical models are one way by which bromate formation can be predicted and controlled, but these models are only accurate when developed for a specific water source.
- POU/POE systems are widely available, mainly from North American suppliers, that can generate and deliver ozone from mains electricity. A filtration system needs to be supplied after the ozone when these are used in order to prevent precipitated solids from being present in treated water – it is not always evident that the proprietary systems have these as supplied. Who manages and replaces spent filtration systems and adequate off-gas control must therefore be also considered for POU systems.
- Ozonation of final effluent can also be effective, however higher ozone doses tend to be required which not only increases cost but also increases the likelihood of formation of disinfection by products. Careful integration with other treatment processes such as

biological filtration can allow this approach to work, however and Potential to couple biological and filtration based treatments with ozone treatment and disinfection towards a more cost-effective approach to use of ozone at WWTPs.

- Ozone has been shown to be an effective non-specific inhibitor of filamentous organisms in activated sludge systems and has provided effective long term management of bulking and foaming sludge. While there is a limited amount of literature relating to this application, most reports are positive in terms of effectiveness in restoring floc structure and minimising filaments. There is on-going debate of the effect on other microbiota within the system and therefore of effects upon nitrification and phosphate accumulation. Further research would help to elucidate the parameters controlling the range of process effects.
- A wide range of organic and inorganic contaminants can be degraded by ozone. High concentrations of ozone are needed for effective degradation of bulk natural organic matter and is therefore not recommended for this application. The most effective use of ozone is for oxidation of metals and organic micropollutants in combination with a physical/adsorptive process.
- The higher contaminant and scavenging load in wastewater means that much higher doses must be applied for these waters in order to achieve satisfactory levels of removal/disinfection. There are many examples of ozone having been used in wastewater for small scale and pilot treatment systems, but few cases of large WWTWs using ozone due to the high cost of having to add such high concentrations of ozone.
- Ozone is a widely used chemical in water and wastewater treatment as well as numerous industrial applications. The ability of ozone to effectively oxidise a wide range of contaminants and disinfect a broad sweep of micro-organisms have made it an essential component of many treatment flowsheets across the world.

7.0 Future Research and Direction

Understanding water quality interactions with ozone is critical to its effective use for inactivation of any unwanted microorganisms across the spectrum of drinking, wastewater and reclamation treatment systems. Existing water quality data for influent waters and effluents from each treatment stage should provide valuable information within which to evaluate where within a given system to implement ozonation to best and most efficient effect. The development of a simple decision tree based on predominant water quality trends could be utilised to fulfil this purpose. Further trials on realistic pilot scale systems to develop process based rules to relate water parameters to all round treatment efficacy provide a useful and realistic research direction, alongside continuing development of ozone contactor systems to provide the highest efficiency transfer.

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Appendix 1: A synthesis of Ozone inactivation of *Cryptosporidium* in Water and Wastewater

Process	Ozone (mg/L)	contact time (min)	*CT* value (mg.min/L)	Inactivation Rate (%)	Conditions	Additional notes	Reference
Primary disinfection	-	-	40 25-35 <25	99.9 >90<99 <90	Laboratory batch reactor Buffer soln. pH7; 1 ºC	Bovine source Oocysts pH effects. Old Oocysts may have been more susceptible to Ozone	Driedger. (2001)
	-	-	22 15-18 <15	99.9 >90<99 <90	Laboratory batch reactor Buffer soln. pH7; 5 ºC		
	-	-	12 8-10 <8	99.9 >90<99 <90	Laboratory batch reactor Buffer soln. pH7; 10 ºC		
	-	-	1.5 1 <1	99.9 >90<99 <90	Laboratory batch reactor Buffer soln. pH7; 20 ºC		
Sequential disinfection with ozone and free chlorine	-	-	1.4	90	Laboratory batch reactor Buffer soln. Greater synergy was observed at pH 6 than at pH 7.5, and no synergy was observed at pH 8.5.	Bovine source Oocysts pH effects. Old Oocysts may have been more susceptible to Ozone	
Inactivation in demand free water	1[T]	3 5 10	3[c] 5-10 10[c]	90 90-99 99-99.9	Laboratory experiments. Ozone demand-free water at pH7; 25ºC.	Oocysts from calves.Based on mouse infectivity assays and excystation assays	Korich et al. (1990).
Inactivation in DI water	4[T] 2[T]	7 < 10	21[c] <20[c]	~99 ~99	Laboratory study in DI water; 20ºC; pH 7.	Oocysts from calf. Based on fluorescent staining and SEM.	Ran et al. (2010)
Inactivation in DI water of differing turbidity (Kaolinite added)	3[T]	7	21[c]	99.2	Laboratory study in DI water Turbidity 0.1 NTU; 22ºC; pH 7		
Inactivation in DI water of differing turbidity (Kaolinite added)	3[T]	7	21[c]	86.2	Laboratory study in DI water Turbidity 20 NTU; 22ºC; pH 7		
Inactivation in DI water, differing pH	3[T]	5	15[c]	~ 99	Laboratory study in DI water; 20ºC;pH 6		
Inactivation in DI water, differing pH	3[T]	5	15[c]	~ 39	Laboratory study in DI water; 20ºC; pH 9		

Inactivation in DI water, differing DOM	3 [T]	7	21 [c]	99.1	Laboratory study in DI water; 20ºC; pH7; Turbidity 1 NTU; DOM 0 mg L^{-1}.		
Inactivation in DI water, differing DOM	3 [T]	7	21 [c]	98.3	Laboratory study in DI water; 20ºC; pH7; Turbidity 1 NTU; DOM 1 mg L^{-1}.		
Inactivation in DI water, differing DOM	3 [T]	7	21 [c]	84.9	Laboratory study in DI water; 20ºC; pH7; Turbidity 1 NTU; DOM 2 mg L^{-1}.		
Inactivation in DI water, differing DOM	3 [T]	7	21 [c]	62.1	Laboratory study in DI water; 20ºC; pH7; Turbidity 1 NTU; DOM 10 mg L^{-1}.		
Natural river water	-	7.4*	6	99	24.5 ±1.6 ºC; pH 8.24 ±0.20		Owens et al. (2000)
	-	-	3.5	99	22ºC; pH 6.9		Finch et al., (1993)
	-	-	4.02-4.62	99	22ºC; pH 7		Peeters et al., (1989)
Batch liquid, modified batch ozone	0.6	4	2.4-3.2	99	25 ºC		Langlais et al., (1990)
Semi Batch system	-	-	5.39	99	20.8 ºC, pH=7, Phosphate buffer		Rennecker et al., 1999 (cited by Facile et al. ,2000)
Advanced water treatment plant.	2.5 (~0.3 [R])	5	7.5 [c]	66	24 ºC; pH 7.1	No information on whether filtration was before or after ozonation. No water quality data.	Wohlsen et al., 2007
Continuous ozone generation in contact tank. Water extracted and added to seeded containers.	2.5 (~0.05 [R])	10	25 [c]	92	24 ºC; pH 7.1		
	2.5 (~0.7 [R])	5	7.5 [c]	82	18.9 ºC; pH 6.9		
	2.5 (~0.15 [R])	10	25 [c]	93	18.9 ºC; pH 6.9		
Laboratory experiment; 80 ml stirred beakers.	0.3	2	0.6 [c]	1-85	22 9 ºC; pH; 6.3-6.7	Ozonated DI water; 10^7 oocysts per beaker.	Bukhari et al (2000).
	0.4	2	0.8 [c]	0-99	22 9 ºC; pH; 6.3-6.7	Comparison of methods for detecting inactivation of oocysts. Up to 99% differences in outcome dependent on method used.	
Clarified and clarified filtered secondary municipal effluent	15	10	150 [c]	< 15	17-27 (mean 20 and 22) ºC; pH 6.7-8.6.	Primary screening, sedimentation,pre ppt. with $pAlCl_3$; secondary – AS and sedimentation; clarification (experimental samples removed here), flocculation with 30-40mg L-1 $pAlCl_3$; 6 h sedimentation, chlorine.	Liberti et al. (2000)
Natural waters	-	-	52	99	3 ºC; pH 6.2-8.2; turbidity 0.2-2.5.	Experimental and modelled data. Range of conditions.	Oppenheimer et al (2000)
	-	-	29	99	7 ºC; pH 6.2-8.2; turbidity 0.2-2.5.		
	-	-	18	99	10ºC; pH 6.2-8.2; turbidity 0.2-2.5.		
	-	-	3.9	99	20ºC; pH 6.2-8.2; turbidity 0.2-2.5.		
	-	-	2.9	99	22ºC; pH 6.2-8.2; turbidity 0.2-2.5.		
	-	-	1.8	99	25ºC; pH 6.2-8.2; turbidity 0.2-2.5.		

*Theoretical contact time [T] = transferred ozone concentration; [R] = residual ozone concentration [C]= calculated by Avery as product of prior two columns. Ozone dose is given as applied dose unless otherwise stated.

Appendix 2: A synthesis of Ozone disinfection of final effluent

Process	Ozone (mg/L)	contact time (min)	*CT* value (mg.min/ L)	Organism	Inactivation Rate	Conditions / noted	Reference
Wastewater	5 [T]	1.5	7.5 [c]	MS2 Coliphage	6.5 log removal	HiPOX™ Reactor	Ishida et al (2008)
Disinfection (WWTP)	-	-	1	Total coliforms	Not detected	Microfiltred water	
Natural Water subject to inputs of sewage and agricultural drainage	Sat	5-10	-	Aerobic mesophiles	>2-log	At higher starting densities ~ 10^8 CFU ml^{-1} Aerobic mesophiles; 10^3-10^5 CFU ml^{-1} Total Coliforms Spore forms appeared to disappear after 15 minutes but re-emerged after 30 minutes indicating germinationhad occurredgerminate	Voidaru et al (2007)
	Sat	30	-	Aerobic mesophiles	7-8-log (not detected)		
	Sat	5-10	-	Total coliforms	>2-log		
	Sat	15-20	-	Total coliforms	3.5-4-log (not detected)		
	Sat	10-15	-	Faecal coliforms	>2-log		
	Sat	15	-	Faecal coliforms	2.5 log (not detected)		
	Sat	10-15	-	Enterococcus	>2-log		
	Sat	15	-	Enterococcus	2.5 log (not detected)		
	Sat	15	-	C. perfringens (cells)	1 log (not detected)		
Secondary sewage	0.3 [R]	~2	0.6 [c]	Faecal coliforms	1.4	Single pulse	Tyrrell et al (1995)
Effluent (after activated sludge)	0.3 [R]	~2	0.6 [c]	Enterococci	1.1		
	0.3 [R]	~2	0.6 [c]	C perfringens	0.1		
	0.3 [R]	~2	0.6 [c]	F+ coliphage	>2.4		
	0.3 [R]	~2	0.6 [c]	Somatic coliphage	>1.9		
	0.3 [R]	~2	0.6 [c]	Faecal coliforms	1.1		
	0.3 [R]	~2	0.6 [c]	Enterococci	1.0		
	0.3 [R]	~2	0.6 [c]	C perfringens	0.2		
	0.3 [R]	~2	0.6 [c]	F+ coliphage	>2.8		
	0.3 [R]	~2	0.6 [c]	Somatic coliphage	2.2		
Secondary sewage	0.3 [R]	~2	0.6 [c]	Faecal coliforms	1.5		
Effluent (after rotating biological contactor)	0.3 [R]	~2	0.6 [c]	Enterococci	1.2		
	0.3 [R]	~2	0.6 [c]	C perfringens	0.1		
	0.3 [R]	~2	0.6 [c]	F+ coliphage	>2.8		
	0.3 [R]	~2	0.6 [c]	Somatic coliphage	>2.8		
Secondary sewage	0.3 [R]	~2	0.6 [c]	Faecal coliforms	1.5		
Effluent (after activated sludge)	0.3 [R]	~2	0.6 [c]	Enterococci	1.2		
	0.3 [R]	~2	0.6 [c]	C perfringens	0.1		
	0.3 [R]	~2	0.6 [c]	F+ coliphage	>2.2		
	0.3 [R]	~2	0.6 [c]	Somatic coliphage	>2.1		
Secondary effluent after activated sludge	5	5-10	25-50 [c]	Total coliforms, Faecal coliforms, *E. coli*	1.1-1.4	COD 78 mg L^{-1} 40 NTU, pH 7.1 "high" organic content. Ambient temperature (India).	Tripathi et al (2011)
	10	5-10	50-100 [c]	Total coliforms, Faecal coliforms, *E. coli*	2.5-2.6		
	15	5-10	75-150 [c]	Total coliforms, Faecal coliforms, *E. coli*	2.8-3		
Anaerobic effluent from an Upflow	5 (3.8 [T])	5	25 [c]	Total coliforms	2.2		Silva et al (2010)
				E.coli	2.6		
Anaerobic Sludge	5 (4.0 [T])	10	50 [c]	Total coliforms	2.2		

Blanket (UASB) reactor				E.coli	2.7	
	5 (4.0 [T])	15	75 [c]	Total coliforms	2.4	
				E.coli	2.9	
	8 (5.4 [T])	5	40 [c]	Total coliforms	3.0	
				E.coli	3.2	
	8 (5.2 [T])	10	80 [c]	Total coliforms	3.0	
				E.coli	3.2	
	8 (5.7 [T])	15	120 [c]	Total coliforms	3.0	
				E.coli	3.5	
	10 (7.1 [T])	5	50 [c]	Total coliforms	3.2	
				E.coli	4.0	
	10 (7.1 [T])	10	100 [c]	Total coliforms	3.6	
				E.coli	4.2	
	10 (7.7 [T])	15	150 [c]	Total coliforms	3.7	
				E.coli	4.3	
Tertiary wastewater effluent	4.9 [T]	18	88	Total coliforms	>3	Wert et al. (2007)
				Faecal coliforms	>3	
	7.3 [T]	18	131	Total coliforms	>3	
				Faecal coliforms	>3	
	8.7 [T]	18	157	Total coliforms	>3	
				Faecal coliforms	>3	
	2.1 [T]	6	13	Total coliforms	>1	
				Faecal coliforms	>2	
	3.6 [T]	18	65	Total coliforms	> 3	
				Faecal coliforms	> 3	
	7.1 [T]	10	71	Total coliforms	>2	
				Faecal coliforms	> 3	

Ozone dose is assumed to be applied dose unless denoted [T] to indicate transferred or consumed ozone. Sat = saturation. [C] denotes contact time calculated using dose x time.

Appendix 3a: Ozone impacts on filamentous bacteria

Process	Ozone Dose	contact time (min)	Organism	Inactivation Rate or other effect	Conditions	Additional notes	Reference
AS	18 µg g^{-1} VSS	5-30	Whole floc respiration reduction	54-60 %			Caravelli et al. (2006)
AS	18 µg g^{-1} VSS	5-30	Filamentous bacteria respiration reduction	87 %		Filamentous bulking was controlled under these conditions.	
AS	1-4 g^{-} kg-MLSS^{-1} d^{-1}	-	Sludge volume index decrease	50 mL g^{-1}	Continuous dosing	No effect on nitrification-denitrification even at30 mg g^{-1} MLSS d^{-1}	Van Leeuwen (1987)
AS for biological N removal	0.05-0.1 kg kg TS^{-1} (T)	-	Excess sludge reduction Microthrix parvicella reduction Nocardioforms reduction	39% 3-5 to <2 (Jenkins scale) 1-3 to 0-1(Jenkins scale)	Wastwater dominated by textile waste Anoxic pre-denitrification basin; aerobic nitrification. Praxair system applied to part of RAS stream. Ozonated sludge returned to nitrification basin.	No effect on COD and TN removal Disappearance of biological foaming	Vergine et al (2007)
Sudge from municipal WWTP in Beijing	20 mg L^{-1}	15	Oxygen uptake rate Decrease	59%	Bubble column, batch operation, lab scale. TSS 4400-4800 mg L^{-1}; 63-72 % VSS.	Continuous ozonation	Chu et al (2009a)
Settled sewage, pilot plant, Municipal WWTP, Pretoria	3 mg L^{-1} (T)	-	Filamentous organisms reduced SS Reduction	Little effect Little effect	Continuous dosing		Van Leeuwen and Pretorius, (1988)
Settled sewage, pilot plant, Municipal WWTP, Pretoria	6 mg L^{-1} (T)	-	Filamentous organisms reduced SS Reduction	1 order of magnitude 33 %	Continuous dosing	Increased settleability of sludge;no effects on N or P removal, increased organics removal	Van Leeuwen and Pretorius, (1988)
Excess sludge production	0.01 g O_3 g TSS^{-1}	-	Excess Sludge production reduced.	50%	Intermittent ozonation of AS	Required only 30% of the ozone dose required for continuous ozonation.	Kamiya and Hirotsuji (1998)
	0.02 g O_3 g TSS^{-1}	-	Excess Sludge Reduction	100%			

Ozone dose is assumed to be applied dose unless denoted (T) to indicate transferred or consumed ozone.

Appendix 3b: Ozone impacts on other microbiota or microbial processes

Process	**Ozone** (g ozone/g TSS unless otherwise stated)	**Inactivation Rate**	**Reference**
Phosphate accumulating organisms	0.03-0.04$^{(T)}$	Exponential decrease	Saktaywin et al., 2005
Heterotrophic bacteria	0.03-0.04$^{(T)}$	Exponential decrease	
Heterotrophic bacteria	0.05	97 %	Lee et al (2005)
Heterotrophic bacteria	<0.05	90 %	Yasui and Shibata (1994)
Nitrifying bacteria	0.05	80 %	Kobayashi et al., 2001 (cited by Chu et al 2009b)
Pathogens - coliforms	>0.1	Significant effectiveness	Foladori et al (2010)
Streptococcus and *Salmonella*	0.2-0.4	100%	Park et al (2008)
Electron transport activity	0.04	Increased slightly and reduced quickly	Zhao et al. (2007)
Dehydrogenase activity	>0.04	May be affected	Nishimura et al., 1999
Maximum O_2 uptake rate	0.9-13.6 mg $O3^{g\ COD_{(T)}}$	Decreased	Dziurla et al. (2005)
Alteration in bacterial community DNA	0.02$^{(T)}$	No effect	Yan et al. (2009)
	0.03-0.06$^{(T)}$	Some species lost	
	>0.06$^{(T)}$	Only two strains survived	
	0.08$^{(T)}$	DNA failed to amplify (inactivated)	

Ozone dose is assumed to be applied dose unless denoted $^{(T)}$ to indicate transferred or consumed ozone.

Appendix 4: Disinfection Byproduct Formation during Ozonation of water and wastewater

Process	Water Characteristics (mean or approximate)											Ozone treatment		DBPs formed		Reference
	pH	Alkal-ilnity	COD	TOC	TSS	TS	NH_4^+	BrO_3^-	Br^-	Nitrate	temperature	Dose (mg/L)	Time	DBP	(ug/L)	
USAB Effluent	6.5		183		82	388						5-10	5-15	Aldehydes	upto 187	Silva et al. (2010)
	6.5		183		82	388						5-10	5-15	Glyoxal	Upto 46	
Tertiary Wastewater	7.0	120	-	7	-	-	< 0.08	<0.001	0.25	14	20	<3.6	Upto 24	Bromate	<2	Wert et al. (2007)
	7.0	120	-	7	-	-	< 0.08	<0.001	0.25	14	20	3.6 -<5	Upto 24	Bromate	<10	
	7.0	120	-	7	-	-	< 0.08	<0.001	0.25	14	20	5-7.1	Upto 24	Bromate	>20<40	
	7.0	120	-	7	-	-	< 0.08	<0.001	0.25	14	20	>8.5<11.5	Upto 24	Bromate	50-65	
	7.0	120	-	7	-	-	< 0.08	<0.001	0.25	14	20	2.1	6	Aldehydes	0	
														Carboxylic acids	396	
	7.0	120	-	7	-	-	< 0.08	<0.001	0.25	14	20	3.6	18	Aldehydes	114	
														Carboxylic acids	623	
	7.0	120	-	7	-	-	< 0.08	<0.001	0.25	14	20	7.0	18	Aldehydes	211	
														Carboxylic acids	397	
Tertiary Wastewater – ozonated then chlorinated (5 mg L^{-1})	7.2	-	9.1	6.7 (DOC)	5	-	0.6		0.7	-	-	0 (T)	-	$CHCl_3$	51	Cao et al (2009)
														$CHCl_2Br$	5	
														$CHClBr_2$	3	
														CHBr	1	
														MCAA	2	
														MBAA	1	
														DCAA	14	
														DBAA	2	
														TCAA	9	
Tertiary Wastewater – ozonated then chlorinated (5 mg L^{-1})	7.2	-	9.1	6.7 (DOC)	5	-	0.6		0.7	-	-	1 (T)	-	ChCl3	47	
														ChCl2Br	18	
														ChClBr2	14	
														ChBr	1	
														MCAA	2	
														MBAA	1	
														DCAA	22	
														DBAA	2.5	
														TCAA	13	
Tertiary Wastewater – ozonated then	7.2	-	9.1	6.7 (DOC)	5	-	0.6		0.7	-	-	3 (T)	-	ChCl3	38	
														ChCl2Br	16	
														ChClBr2	15	

chlorinated (5 mg L^{-1})													ChBr	2
													MCAA	3
													MBAA	1
													DCAA	21
													DBAA	3
													TCAA	8
Tertiary Wastewater – ozonated then chlorinated (5 mg L^{-1})	7.2	-	9.1	6.7 (DOC)	5	-	0.6	0.7	-	-	5 (T)	-	ChCl3	29
													ChCl2Br	15
													ChClBr2	20
													ChBr	3
													MCAA	3
													MBAA	2
													DCAA	26
													DBAA	4
													TCAA	12
Tertiary Wastewater – ozonated then chlorinated (5 mg L^{-1})	7.2	-	9.1	6.7 (DOC)	5	-	0.6	0.7	-	-	10 (T)	-	ChCl3	28
													ChCl2Br	22
													ChClBr2	34
													ChBr	4
													MCAA	4
													MBAA	2
													DCAA	32
													DBAA	5
													TCAA	14
Tertiary Wastewater – ozonated then chlorinated (10 mg L^{-1})	7.2	-	9.1	6.7 (DOC)	5	-	0.6	0.7	-	-	0 (T)	-	$CHCl_3$	84
													$CHCl_2Br$	19
													$CHClBr_2$	18
													CHBr	2
													MCAA	4
													MBAA	1
													DCAA	42
													DBAA	1
													TCAA	28
Tertiary Wastewater – ozonated then chlorinated (10 mg L^{-1})	7.2	-	9.1	6.7 (DOC)	5	-	0.6	0.7	-	-	1 (T)	-	ChCl3	80
													ChCl2Br	38
													ChClBr2	20
													ChBr	1
													MCAA	5
													MBAA	2
													DCAA	49
													DBAA	2
													TCAA	34
Tertiary Wastewater – ozonated then	7.2	-	9.1	6.7 (DOC)	5	-	0.6	0.7	-	-	3 (T)	-	ChCl3	80
													ChCl2Br	41
													ChClBr2	30

chlorinated (10 mg L^{-1})													ChBr 2 MCAA 5 MBAA 2 DCAA 57 DBAA 3 TCAA 35
Tertiary Wastewater – ozonated then chlorinated (10 mg L^{-1})	7.2	-	9.1	6.7 (DOC)	5	-	0.6	0.7	-	-	5 (T)	-	ChCl3 78 ChCl2Br 40 ChClBr2 32 ChBr 2 MCAA 5 MBAA 2 DCAA 55 DBAA 4 TCAA 36
Tertiary Wastewater – ozonated then chlorinated (10 mg L^{-1})	7.2	-	9.1	6.7 (DOC)	5	-	0.6	0.7	-	-	10(T)	-	ChCl3 50 ChCl2Br 39 ChClBr2 31 ChBr 2 MCAA 6 MBAA 2 DCAA 53 DBAA 5 TCAA 27

Ozone dose is assumed to be applied dose unless denoted (T) to indicate transferred or consumed ozone.

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