

4 Ozone and UV irradiation

Ozone (O₃) and UV have both been used in the water treatment industry for over 100 years, though their use is not as widespread as chlorine for several reasons:

- a) they are relatively expensive with respect to both capital and operating costs,
- b) they are less simple to operate and maintain, and
- c) they leave no safe residual in the water: ozone has a half-life of less than an hour in pure water at pH 8 (Coleman *et al*, 1992) and this decreases significantly in water of lower purity.

For these reasons they are not often used in small treatment plants, such as those treating private swimming pools, and are always used in conjunction with a chlorine or bromine-based disinfectant to provide a residual disinfectant capability.

4.1 Ozone

4.1.1 Introduction

Ozonation has become prominent in drinking water treatment due partly to its capability of removing pesticides. It is produced by the electrical discharge of dry air or oxygen. Ozone is a strong oxidant, and is an effective bactericide and viricide (Section 2.2.7). It can be used in conjunction with H₂O₂ or UV for the oxidation of refractory species or for more powerful disinfection. As it is toxic, it must be removed from the water after treatment. De-ozonation is usually achieved through filtration through a carbon filter such as an anthracite or GAC filter. When used as a pre-chlorination process it can reduce the concentration of DBPs subsequently produced.

4.1.2 Ozone as a bactericide

Studies indicate that disinfection by ozone is a direct result of bacterial cell wall disintegration or the 'lysis phenomenon'. It is particularly effective against recalcitrant micro-organisms such as Giardia cysts (Glaze, 1987). In experiments by Muttamara, *et al* (1995), for a 99.9% coliform inactivation, a minimum dose of chlorine of 3mg/l was needed, but when ozone was used in conjunction, only 0.6 mg/l was needed and achieved a total kill in 15 minutes.

4.1.3 Ozone decomposition /consumption

One factor limiting the effectiveness of disinfection of water by ozone is its solubility. At 20°C the solubility of ozone is only 570 mg/l, about 12 times less than that of chlorine. The required contact time for ozone for deactivating most organisms, however, is much shorter than chlorine-based disinfectants due to their lower Ct values (Section 2.2.7).

Ozone naturally decomposes in water to form hydroxyl radicals ($\cdot\text{OH}$). These can then oxidise pollutants in the water, but are relatively unstable and so disappear quickly. This ozone consumption/degradation in water is a function of several water quality parameters, such as pH, alkalinity and TOC level (Yurteri and Gurol, 1988), and takes place via a complicated chain of oxidation reactions (Table 4.1).

Table 4.1 Rate constants of ozone consumption. Adapted from mechanistic model by Staehelin and Hoigne (1982 and 1985) at a pKa of 4.8

Reaction no.	Reaction	Note	Rate constant
1a	$\text{OIM} + \text{O}_3 \rightarrow \text{products}$	Direct oxidation of I and O solutes	$1-10^3 \text{ M}^{-1}\text{s}^{-1}$
1b	$\text{OIM} + \text{O}_3 \rightarrow \cdot\text{OH} + \text{products}$		
2 ¹	$\text{O}_3 + \text{OH}^- \rightarrow \cdot\text{O}_2^- + \cdot\text{HO}_2$	Self decomposition initiated by hydroxide ions	$70 \pm 7 \text{ M}^{-1}\text{s}^{-1}$
3	$\cdot\text{HO}_2 \leftrightarrow \text{H}^+ + \cdot\text{O}_2^-$	As in pure water with no OIM	
4	$\text{O}_3 + \cdot\text{O}_2^- + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{OH}^- + 2\text{O}_2$	Self decomposition of O_3 by attack of free radicals	
5	$\text{O}_3 + \cdot\text{OH} \rightarrow \cdot\text{HO}_2 + \text{O}_2$		
6a	$\text{OIM} + \cdot\text{OH} \rightarrow \cdot\text{HO}_2 + \text{products}$		
6b	$\text{OIM} + \cdot\text{OH} \rightarrow \text{products}$		

OIM= organic and inorganic matter and 'products' are those which will no longer react with ozone

¹above pH 4, gives $2 \cdot\text{O}_2$

Organic and inorganic matter (OIM) reacts with both molecular ozone (O_3) directly and with $\cdot\text{OH}$ according to Reactions 1-6 in Table 4.1. This reaction of $\text{HO}\cdot$ with OIM affects the rate of ozone consumption since the highly reactive hydroxyl free radicals are non-selective. Since Reaction 4 is considerably faster than the reactions of $\cdot\text{O}_2^-$ with other solutes, it is proposed that O_3 is the only 'sink' for $\cdot\text{O}_2^-$. On the other hand, $\cdot\text{OH}$ can react with O_3 and all available impurities, and this reaction with certain

OIM species propagates the reaction cycle by way of intermediate radicals leading to $\cdot\text{O}_2^-$. For example, in Reaction 6a the $\cdot\text{HO}_2$ from this reaction generates $\cdot\text{O}_2^-$ in Reaction 3. This is not always the case, however, since OIM can ‘scavenge’ $\cdot\text{OH}$ without producing chain propagating radicals (Reaction 6b). The highly reactive $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ species are immediately consumed and do not accumulate. When Reaction 2 is allowed to proceed above pH 4, it accelerates Reaction 4 (by producing more $\cdot\text{O}_2^-$), and therefore initiates other reactions that accelerate the decomposition of ozone. Ozone is only stable in pure solutes at low pH, where the production of radical species is relatively low (Yurteri and Gurol, 1988).

Ozone will also react with halogens used for disinfection, affecting the DBPs that form. Table 4.2 shows measured rate constants for ozone consumption by various halogens. Table 4.3 shows the rate constants of other solutes present in natural waters and swimming pool water that may also consume ozone.

Table 4.2 Reaction rate constants of O_3 consumption by halogen compounds (Hoigné *et al*, 1985)

Halogen	Rate constants $\text{M}^{-1} \text{s}^{-1}$	pH
HOCl/OCl^-	95 ± 12	4.6-9.5
NH_2Cl	26 ± 4	6.2-8
$^1\text{HOBr}/\text{OBr}^-$	84 ± 10	5-10.4

$^1\text{Haruta}$ and Takayama (1981) measured $170 \text{ M}^{-1} \text{s}^{-1}$ and Garland *et al* (1980) measured $301 \text{ M}^{-1} \text{s}^{-1}$.

Table 4.3 Rate constants of ozone consumption from Hoigné *et al* (1985)

Solute	Rate constants $\text{M}^{-1} \text{s}^{-1}$	pH
$\text{NH}_4^+/\text{NH}_3$	~ 1	2.7-8
$\text{HNO}_2/\text{NO}_2^-$	$3.7 (\pm 0.5) * 10^5$	1.8-5
$\text{HCO}_3^-/\text{CO}_3^{2-}$	$<< 1$	8-10

Chloride may also be oxidised by molecular ozone, as evident from experiments by Hoigné *et al* (1985) where a chlorinous odour was evident following ozonation. The apparent rate constant for chloride consumption of ozone (at 23°C) in these experiments was only $0.003 \text{ M}^{-1} \text{s}^{-1}$ when measured at pH 2. The chlorinous odour was still evident after an extended reaction time even at pH 4. $\cdot\text{OH}$ radicals however, cannot oxidise Cl^- at this pH, suggesting therefore that it must be oxidised by O_3

itself. Yeatts and Taube (1949) measured a rate constant of $2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 0°C for consumption of O_3 by chloride ions, based on the reaction:



The authors also calculated a bromide consumption rate of $160 \text{ M}^{-1} \text{ s}^{-1}$ based on:



Chlorine will react at an appreciable rate with ozone when as OCl^- , but not at low pH when it is as HOCl . Reaction products are generally Cl^- and ClO_3^- . The rate constant of $120 \pm 15 \text{ M}^{-1} \text{ s}^{-1}$ for OCl^- indicates that O_3 and chlorine cannot co-exist for more than a few minutes where they are present in quantities of mg/l at pH 7; conditions such as those found in water treatment plants. Ammonia will only react with ozone in the un-protonated form (NH_3), producing nitrate. The low rate constant of $20 \text{ M}^{-1} \text{ s}^{-1}$ reported for free ammonia and apparent rate constant of $1 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{NH}_4^+/\text{NH}_3$ at pH 8 (Hoigne *et al*, 1985) shows that this reaction is not significant under conventional water treatment conditions where the ozone concentration is limited and secondary oxidants ($\cdot\text{OH}$ radicals) are consumed by competing reactions.

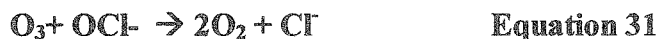
4.1.4 Ozone interaction with bromine

Ozone can oxidise bromide (Br^-) to HOBr and OBr^- , the rate of which is dependant on pH; the lower the pH, the faster the reaction. In the presence of NOM, water containing Br^- ion will form brominated THMs and other halogenated species upon subsequent chlorination (Miltner *et al*, 1992). In waters with a low bromine concentration ($< 35 \mu\text{g/l}$), a low ozone dose has little effect on CHBrCl_2 formation whereas a high dose results in a significant decrease in formation. Brominated THM formation has been attributed to the conversion of bromide to HOBr by HOCl (during subsequent chlorination) rather than ozone, since no brominated THMs or HAAs were measured in the effluent of the ozone contactor directly (Wang and Davidson, 1977; Miltner *et al*, 1992). Research by Siddiqui and Amy (1993) has indicated that ozone can lead to the formation of CHBr_3 by oxidising Br^- to HOBr/OBr^- in the presence of THM precursors. It is believed that in this reaction OBr^- serves as an intermediate to the eventual formation of bromate ion. There is also an increase in CHBr_3 formation at a lower pH, probably due to the higher concentration of HOBr which suggests that the reaction proceeds via the associated (protonated) species.

On the whole, ozone would be expected to lower the concentration of available precursors through their oxidation and reduce the concentration of available bromide by its conversion to bromate. However, Miltner *et al* (1992) noted the THM speciation changes during ozonation to depend heavily on the relative ozone dose. For example, below 1.5 O₃ mg/mg TOC the concentration of CHBr₂Cl increased by at least 60% (with a maximum at 0.5 mg O₃/mgTOC). Above this ratio, there is an active decrease in both CHBrCl₂ and CHBr₂Cl by 60% with CHCl₃ concentration remaining primarily unchanged.

4.1.5 Ozonation of chlorine and chloramines

Ozone may react with chlorine (as OCl⁻) as indicated in Equations 31 and 32 to give a ratio of around Cl⁻ to ClO₃⁻ of 3.4 : 1 at a pH of ~8 (Haag *et al*, 1983).



The second order rate constant of ozone with chlorine at pH 8 has been measured as 120 M⁻¹ s⁻¹ (Haag *et al*, 1983).

Oxidation reactions involving O₃ and chlorine primarily occur with the OCl⁻ species, and are therefore more prominent at a high pH. Since OCl⁻ predominates only above pH 7.5 then decreasing the pH below 7 limits the amount of reactant, which then reduces the reaction rate. Therefore below pH 7, combined chlorine reacts faster than free chlorine, (as only HOCl exists) favouring the formation of chloride ions and nitrate according to Equation 33 (Haag 1983):



At pH 7, the stoichiometry of products formed per mol of NH₂Cl consumed is: 0.99 (±0.05) mol NO₃⁻ and 0.95 (±0.1) mol Cl⁻, with 4 (±1) mol O₃ lost.

4.1.6 Ozonation of NOM

Ozone may transform dissolved organic substances into products that are more reactive towards chlorine, increasing the chlorine demand as previously noted (Section 4.1.3). Ozone can react with NOM as molecular ozone (the predominant reaction) or via an indirect pathway in which free radicals such as [•]OH and HO₂[•] are involved (Hoigné and Bader, 1979). Certain organic contaminants such as organic

acids, aldehydes, ketones and less highly activated aromatics are slow to react with ozone, and are thus more likely to react via the non-selective free radical pathway. For example, in natural waters, it appears that the free radical pathway dominates in reactions involving NOM (Glaze, 1986). Carbonate or bicarbonate are free radical scavengers which can shift the reaction towards the direct O₃ pathway (Stahelin and Hoigne, 1982).

Ozonation of extracted fulvic acid by Legube *et al* (1989) showed that the rate of ozone consumption was fast during the first few minutes and led to a slight increase of the lower apparent molecular weight material and an increase of carboxyl content, with some aldehyde formation. According to this study, ozonation leads to a decrease in organic halide formation potential. Killops (1986) reported ozonation not to increase the *amount* of volatile compounds in humic acid, suggesting that the volatile matter in the humic material was retained within the macromolecular structure of the HA. The *type* of volatiles did change, however, as an increase in n-alkanes and disappearance of alkyl-naphthalene was noted. Legube *et al* (1980), suggested that polysubstituted methyl benzenes in the humic materials could account for an increase in methyl ketone content following ozonation.

Ozonated humic material has been reported as being more hydroxylated, more polar, and of lower molecular weight than the NOM precursor material (Maier, 1974; van Breeman *et al*, 1979; Mallevialle *et al*, 1978), and in general ozonation produces low molecular weight oxygenated by-products (Table 4.4). Research by Chang and Singer (1991) has shown that ozonation has an almost negligible effect on the overall TOC concentration, but that its nature is clearly altered, as evidenced by the reduction in UV absorbance at 254nm (Reckhow, 1984) and in true colour of the ozonated water. Reduction in UV absorbance and true colour has been shown to be indicative of a change in organic material structure, namely a reduction in aromaticity and degree of unsaturation. Both Miltner *et al* (1992) and Jacangelo *et al* (1989) have shown that ozonation breaks carbon double bonds. Ozonation at low doses (<1mg O₃/ mg TOC) thus appears not to mineralise NOM to any significant degree, but reduces its aromaticity and its degree of unsaturation.

Table 4.4 Summary of products of ozonation of NOM

Reference	NOM used	Products formed
Lawrence <i>et al</i> , 1980; van Hoof, 1985; Killops, 1986.	HA	Alkanes, aliphatic diacids, aldehydes, aliphatic keto compounds, benzoic acids, phthalates, furans.
Sayato <i>et al</i> , 1989	naphthoresorcinol ¹	Aldehydes, aldehydic acids, ketoacids, and dicarboxylic acid.
Lawrence <i>et al</i> , 1980	FA	Numerous alkyl phthalates, mono and di- carboxylic and aliphatic acids, and a few cyclic keto compounds.

¹ A compound which is thought to be a constituent of humic acid

4.1.7 Effect of pre-ozonation on DBP formation

The effect of pre-ozonation (ozonation followed by chlorination) on DBP formation and TOC concentration has been found to be highly dependent on the ozone dose used (Table 4.5), ozone contact time, the nature of the DBP precursors and the length of time between ozonation and chlorination. Depending on the dose and time, pre-ozonation can reduce or increase the amount of NOM that will readily form DBPs upon subsequent chlorination. In general at higher O₃ doses and longer reaction times subsequent DBP production is decreased. Subsequent chlorination at high pH appears to be more desirable for reducing mutagenic organohalides specifically (Meier *et al* 1983). A summary of ozonation experiments carried out on HA, NOM and raw drinking water can be seen in Table 4.5.

In experiments by Coleman (1992) pre-ozonation of HA produced monocarboxylic acids up to C₂₄, dicarboxylic acids (C₃ to C₁₀) keto acids, furan carboxylic and benzene mono di and tri carboxylic acids. Contrary to other studies (Glaze *et al*, 1989), aldehydes and ketones were not formed in abundance. Other products that were formed included chloroform, di- and tri-chloroacetic acid. Table 4.6 shows the results of experiments conducted where varying ozone doses were used to oxidise a solution of 1g/l of DOC (sourced from HA). In general chloroform concentration, following post-chlorination decreased at higher ozone doses.

Table 4.5 Effect of pre-ozonation on DBP formation and TOC concentration

Reference	Experimental procedure	Effect
Trussel & Umphres (1978); Rice (1989); Scrivner (1980)	Pre-ozonation of 'raw water'	THMFP decreases
Reckhow <i>et al</i> (1986)	Pre-ozonation of 'raw drinking water'	CHCl ₃ decreases by 59% as O ₃ :Cl ratio increased from 1:1 to 3:1
Doré & Legube (1983); Bailey (1972)	Pre-ozonation at O ₃ :TOC ratio of 0.7 mg/mg	DBP reduction maximum of 20-30% of THMs, HAAs and TOX. Reduction not improved at higher dose
Jacangelo <i>et al</i> (1989); Rosen (1979)	Pre-ozonation of raw drinking water in WTP	Increased THM formation
Chang & Singer (1991)	Pre-ozonation of raw drinking water in WTP	Lowered THMFP by ~10% to 54.7 µg/l per mg/l TOC. TOC also lowered by 12-57%.
Singer <i>et al</i> (1999)	Pre-ozonation of 'raw water'	Lower higher and unchanged levels of halogenated DBPs., depending on nature of pollutants: hydrophobic OC and OM with high phenolic C conc. more likely to result in reduced DBPs
Reckhow & Singer (1984)	Pre-ozonation of NOM	Only trace CHBrCl ₂ formed with NO CHBr ₂ Cl or CHBr ₃ . depends on contact time.
Rook (1976)	Pre-ozonation of raw water	Immediate chlorination resulted on 50% reduction in tTHMs When chlorinated up to 24 hrs after O ₃ , THM formation increased up to levels without O ₃
Doré <i>et al</i> (1978)	Pre-ozonation of HA	CHCl ₃ production almost doubled when ozonated up to 25 mins. Even after 50 mins. of ozonation CHCl ₃ conc. still higher than with no ozonation

Table 4.6 DOC reduction and chloroform formation due to pre-ozonation (from Coleman 1992)

O ₃ : DOC: chlorine ratio	DOC reduction upon ozonation (%)	Chloroform formed upon chlorination (mg/l)
1:1:2	11	46
2:1:2	20	31
3:1:2	39	19

Mallevalle (1979) observed ozonation to generate an increase in acidity of up to six-fold, which might then reduce the rate of THM formation attained over chlorination alone. Riley *et al* (1978) reported the effect of pre-ozonation of HA on chloroform

formation to be extremely pH dependent, concluding that ozonation of HA at neutral pH destroyed sites on the HA molecule that otherwise would have produced chloroform upon chlorinated.

As noted in Section 3.7.3, concern has been expressed recently by the USEPA (2003) over the possible level of brominated DBPs that form due to pre-ozonation of drinking waters. Ozonation has been noted by many authors (Table 4.5) to *reduce* the overall concentration of DBPs such as THMs formed. However, this reduction appears to be mainly due to the decrease in non-brominated DBPs such as CHCl_3 . In many water treatment works, and especially those where the influent is high in Br^- , the concentration of brominated DBPs rises, and may exceed maximum contaminant levels set by the USEPA (Richardson *et al*, 2003).

4.1.8 Ozonation and bio-treatment

Since ozone is toxic it must be removed from water before being circulated back to the pool. GAC not only removes ozone but can also remove organic pollutants as well. As GAC is more effective at adsorbing DBP precursors than DBPs it is often used before chlorination in water treatment plants (Montgomery, 1985). McGuire *et al* (1991) investigated the benefit of using GAC for THM control and found it to significantly reduce THMs in water that is subsequently chlorinated. The efficacy of removal of NOM from influent waters by GAC depends on the level of pre-ozonation, the type of NOM, the empty bed contact time (EBCT) of the filtration process and the age of the GAC filter material. GAC will also remove a higher percentage of CHCl_3 than those of brominated THMs (Zabel, 1980).

GAC can also provide a level of biotreatment through the formation of biofilms. Bacterial growth in GAC filters is enhanced by preozonation, and therefore the process is often used in association with ozonation for the removal of organic contaminants. This is sometimes referred to as the biologically activated carbon (BAC) process. Miltner *et al* (1992) and Huck *et al* (1990) noted that ozonation effectively increases the assimilability of carbon by converting large organic molecules into smaller aldehydes and ketones. The use of 'biotreatment' alongside ozonation helps to remove the precursors of THMs and haloacetic acids (HAAs). Furthermore, where biodegradation and absorption are taking place in GAC filters,

degradation of biodegradable compounds may increase the GAC adsorption capacities for the non biodegradable solutes. This biotreatment in the GAC affects the nature of the NOM as the dissolved organic carbon decreases and the reactivity of the NOM to subsequent chlorination can be significantly reduced. Chlorine demand is also reduced by 25-50% after biofiltration, again yielding a lower concentration of halogenated DBPs (Bailey, 1972).

The biological process may also impact on nitrate. Wang *et al* (1989) reported that the application of post-ozonation treatment comprising sand filtration followed by BAC produced 90% removal of ammoniacal nitrogen. Ozonation also converted organic N to ammonia, NO_2^- and NO_3^- , and BAC completed the nitrification process when sufficient O_2 was present. When no oxygen was present, denitrification occurred, resulting in a loss of nitrate and an increase in nitrite and N_2 production. The nitrate formation seen in the presence of oxygen was attributed to nitrifying bacteria in both the BAC and sand filter. DOC may also be removed during this process (Legube *et al*, 1989). However, when the DOC concentration is reduced by biofiltration, the bromine to DOC ratio is increased such that subsequent chlorination leads to a higher % of brominated DBPs.

4.1.9 Ozone and UV for oxidation of refractory compounds

It is well known that the combination of ozonation and UV irradiation enhances the oxidation rate of refractory compounds and destroys more THM precursors than ozonation alone (Prengle *et al*, 1975; Glaze, 1982), the enhancement being attributable to the promotion of hydroxyl radical formation. Ikemizu (1987a) found the oxidation rate of pollutants could be increased up to 10^4 times with varied degrees of TOC reduction depending on the THM precursors present. Kusakabe (1990) reported that HA can successfully be decomposed by ozone and UV irradiation at pH 6.9. Major final products of ozonation were acetic acid, formic acid and oxalic acid, which are refractory to ozone and not significant THM precursors. Subsequent chlorination resulted in a decrease in CHCl_3 and total organic halides. Backlund (1994) found that combining UV with ozonation resulted in a substantial decrease in chlorine consumption rate which was dependent on the doses used. The UV 254nm wavelength absorbance of the final solution decreased by 80% following a 12 minute contact time, indicating a substantial decrease in conjugated double bonds in general

and aromaticity specifically. It follows that chlorine demand is also decreased (Section 3.5.1).

An optimum UV intensity of 3Wm^{-2} at a wavelength of 253.7 nm has been reported for TOC reduction when using a recirculating system. A trace level of TOC was detected even after a O_3/UV contact time of 5 hrs, implying that the destruction of humic substances produced refractory compounds (Ikemizu, 1987b). These compounds included saturated alcohols and carboxylic acids and in particular, acetic and oxalic acids. These are major end products of ozonation of organic compounds, and are very resistant to further ozonation.

4.2 UV

4.2.1 Introduction

UV radiation refers to electromagnetic energy transmitted at wavelengths of $\sim 380 - 150$ nm. The UV wavelengths that are most effective at inactivating micro-organisms are in the abiotic range of 200-380 nm (Diamant, 1996), with the 253.7 nm line emitted by low pressure mercury lamps achieving the optimum microbial inactivation for both bacteria and viruses. Since UV radiation leaves no disinfecting residual it must be used in conjunction with chemical disinfection, usually chlorine or bromine, to provide local disinfection for point source pollution in pools.

4.2.2 Disinfection properties of UV

UV light is strongly absorbed by nucleic acid, it is generally accepted that the absorbed energy leads to disruption of molecules preventing their reproduction. As such, UV light does not immediately inactivate micro-organisms in the way that chemical disinfectants do (Meuleman, 1987).

The efficiency of disinfection depends on several parameters:

- the emission spectra of the UV source (measured in nm),
- the intensity of irradiation,
- the exposure time,
- sensitivity of the particular organism, and

- turbidity (or specifically UV transmittivity) of the water: the recommended maximum level of suspended solids is 15 mg/l (PWTAG, 1999).

The required UV dose for inactivation depends on the morphology of the individual micro-organism. In general, a gram positive bacterium with a thick protective layer of mureine is more difficult to destroy than a gram negative bacterium with a thin capsule. Viruses have the same sensitivity as most bacterium, whilst algae need a hundred times more energy for inactivation to occur.

The bactericidal power of UV can be calculated using the Beer-Lambert Law

$$\text{Log } (N/N_0) = k D$$

Equation 34

where:

N_0 = original number of organisms

N = number of surviving organisms

D = UV dose in mWs/cm² (or mJ/cm²) (i.e power*exposure time/exposure area)

k = a constant

Typical doses resulting in 10% survival are 2.9 mWs/cm² for *E. coli* and 3.2 mWs/cm² for the polio virus.

Gilpin *et al* (1985) experimented with UV in re-circulating recreational water systems, such as spas and hot tubs. The authors found that the process of maintaining adequate chlorine residuals during the day and employing superchlorination at night did not always lead to the removal of *Pseudomonas* from hot tubs water if organic levels were elevated. Experiments using *Legionella* at an applied UV intensity of 1 $\mu\text{W}/\text{cm}^2$ revealed that the time required for 50% kill ranged from 5 to 30 minutes, and the time for 99% and 100% kill from 33-63 and 45-93 minutes respectively.

4.2.3 Effect of UV on NOM and THMFP.

Photo-oxidation by UV irradiation usually relies on higher energy, and thus shorter UV wavelengths, than those used for disinfection. The rate of photo-oxidation of NOM (fulvic acid) is dependent on pH, increasing with increasing pH (Chen 1978). However, in experiments by Chen (1978) at a wavelength of 253.7 nm in acid solution the majority (up to 91%) of fulvic acid was oxidised to CO₂ and H₂O. Under neutral conditions, about 90% of the organic carbon was oxidised to inorganic

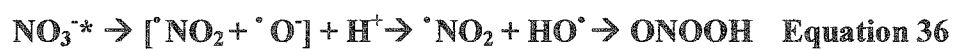
carbonate (i.e. mineralised). Only the most stable components, such as aliphatic n-fatty acids, were found to be resistant to oxidation. Li *et al* (1996), reported that UV irradiation of HA at a wavelength of 253.7, a dose of 10mW/cm² and a pH of 6.5-7, resulted in a considerable reduction of TOC in batch treatment: 50% after 100 hours and 66% after 350 hours. The slowing of the reaction after 150 hours indicated that the destruction of humic acid produced refractory compounds that were then oxidised relatively slowly. Infrared Spectroscopy (I.R) analysis of the irradiated solution of HA at pH 7 revealed that UV irradiation caused the COOH and COO⁻ groups to change, suggesting that decarboxylation reactions to be of major importance. Aromatic and aliphatic C=C bonds and C-C carbohydrate bonds were also partly destroyed. Changes in Hydrogen Nuclear Magnetic Resonance (HNMR) spectra implied that the structures of H-C-O or OCH₃ and OCH₂ groups had also been changed, and the intensity of bands associated with some aromatic or phenolic compounds, such as benzene and trimethyl(1-methylethyl)-benzene, was decreased. Chlorination of pre-irradiated HA resulted in a higher yield of chloroform, increasing with time up to a maximum of 30 minutes, and decreasing thereafter. This was possibly a result of the severing of some chemical bonds in the humic acid molecule by the UV irradiation, degrading the organic matter to simpler compounds which are expected to be ketonic, carbonyl and/or phenolic in nature. Such compounds are known THM precursors (Section 3.5.1). The decrease in THMFP noted after 30 minutes could be attributed to continued decomposition to non-THM precursors.

4.2.4 Effect of UV irradiation on nitrate

UV has been reported to react with nitrate to form nitrite, a reaction which is highly dependent on pH and UV wavelength (Sharpless and Linden, 2001). The production of nitrite in UV irradiation experiments conducted by Sharpless and Linden at a wavelength of 228nm was approximately double that produced at a wavelength of 254nm.

The pH dependence of nitrite formation from nitrate is thought to be due to the influence of the acid-base pair ONOOH/ONOO⁻ for which the pK_a is around 6.6 (Goldstein *et al*, 1997). The formation of these pairs is not fully understood. However two mechanisms have been suggested which involve the isomerisation of an excited

state NO_3^- (Equation 35) and $^{\bullet}\text{OH}$ and $^{\bullet}\text{NO}_2$ radicals produced from an excited state NO_3^- (Equation 36) (Sharpless and Linden 2001):



where * indicates species in an excited state.