Vacuum ultraviolet irradiation for natural organic matter removal

James Thomson, Felicity A. Roddick and Mary Drikas

ABSTRACT

Low pressure mercury vapour lamps were used alone and in combination with hydrogen peroxide (H_2O_2) to investigate the removal of natural organic matter (NOM) from highly coloured surface water, high in total organic carbon (TOC). A potential benefit of vacuum ultraviolet (VUV) irradiation is additive-free degradation of NOM by hydroxyl radicals rather than concentration and subsequent disposal problems associated with many conventional techniques. For mineralization and chromophore removal the UV/VUV/H_2O_2 combination was most effective, followed by UV/VUV. Photooxidation alone was inappropriate because small (but much greater than normal UV disinfection doses) and intermediate doses increased chlorine demand, trihalomethane formation potential, nitrite, hydrogen peroxide and low molecular weight carbonyl compound concentrations. Subsequent biological treatment reduced the chlorine reactivity significantly, by removal of oxidized NOM intermediates. Low molecular weight carbonyl compound concentrations in the water increased significantly on irradiation, and differences in their speciation indicated that different reaction mechanisms were dominant in different treatments. Trihalomethane (THM) distribution shifted to more highly brominated compounds as the NOM concentration decreased with treatment. Results from this preliminary study indicate that NOM can be removed from water by VUV irradiation combined with biological treatment leading to improved drinking water quality.

Key words | chlorine, hydrogen peroxide (H_2O_2), low molecular weight carbonyl compounds, natural organic matter (NOM), nitrite (NO_2^-), vacuum ultraviolet (VUV) irradiation

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INTRODUCTION

Natural organic matter (NOM) is a problem in drinking water because it results in colour and odour. In drinking water treatment it is a problem because it competes with micropollutants for adsorption on activated carbon, consumes oxidants intended for micropollutant removal or microorganism inactivation, is a precursor to potentially harmful disinfection by-products, contributes to biofilm growth in distribution systems, interferes with particle separation processes (Gottschalk *et al.* 2000), fouls membranes and attenuates UV disinfection light intensity.

Novel treatment processes for the removal of NOM from drinking water are being sought to complement and enhance the performance of conventional techniques. Ultraviolet radiation generated by low-pressure mercury vapour lamps, whilst commonly used for wastewater disinfection and to a lesser extent for drinking water disinfection, has found only limited application without additives for removal of organics. Low-pressure mercury vapour lamps produce most of their radiant emittance at 254 nm (~83%), some visible light (~10%) and a small component at 185 nm (~7%) (Bolton 1999); the output at 185 nm may be greater depending on lamp construction. For most applications the use of ultraviolet (254 nm) for direct photolysis is generally too slow to be energy efficient (Legrini *et al.* 1993). The rate of oxidation can be increased significantly by the addition of hydrogen peroxide which photolyses to form hydroxyl radicals:

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \quad (1)$$

Hydroxyl radicals are both highly reactive and non-specific (von Sonntag *et al.* 1993); however some process disadvantages are: H_2O_2 scavenges hydroxyl radicals (Lopez *et al.* 2000), the molar absorptivity of H_2O_2 at 254 nm is low (19 M^{-1} cm^{-1}) and screening by other chromophores (particularly NOM) may make this process ineffective (Bolton 1999). For health reasons, hydrogen peroxide use may be limited because it is cytotoxic and a bacterial mutagen (Richardson 1998).

If the envelope encasing the mercury vapour arc is made of high purity quartz, the vacuum ultraviolet (VUV) radiation emitted at 185 nm can be used (von Sonntag *et al.* 1993) to generate radicals *in situ* from water photolysis (Gonzalez & Braun 1995):

$$H_2O + h\nu \rightarrow {}^{\bullet}OH + {}^{\bullet}H,\ \Phi_{184.9} = 0.3\ (\Phi = \text{quantum yield}) \quad (2)$$

$$H_2O + h\nu \rightarrow {}^{\bullet}OH + H^+ + e^-(aq),\ \Phi_{184.9} = 0.04 \quad (3)$$

Three different rapidly reacting species are formed. In aerated systems the hydrated electrons and hydrogen atoms react rapidly with oxygen to form superoxide (Gonzalez & Braun 1995). Hydroxyl is a more powerful radical than superoxide and generally dominates in aerated systems (Gonzalez & Braun 1995). These lamps are commonly used for preparation of ultrapure water in laboratories, and for the oxidation of organic matter in dissolved organic carbon (DOC) detectors (Huber & Frimmel 1991). Recently VUV radiation was found to be advantageous for the removal of nitroaromatics, because no additives, which attenuate the radiation and scavenge hydroxyl radicals, were required (Lopez *et al.* 2000).

The objectives of this work were to compare the effects of radiation from low pressure mercury vapour lamps producing UV plus VUV or UV only, alone and in combination with hydrogen peroxide, as a treatment for NOM removal.

MATERIAL AND METHODS

Water sample

Water collected in winter (August 2001) from Myponga Reservoir, South Australia, was used after filtration through hydrophilic 0.45 μm membranes (Durapore). The water was highly coloured, high in dissolved organic carbon and low in alkalinity (Table 1).

Table 1 | Myponga water characteristics

Description	Unit	Value
Alkalinity	$mgCaCO_3\ l^{-1}$	54
pH		7.8
Absorbance at 254 nm	Dimensionless (1 cm cell)	0.55
Non-purgeable dissolved organic carbon	$mgC\ l^{-1}$	14
Kjeldahl nitrogen as N	$mg\ l^{-1}$	0.77
Nitrate nitrogen as N	$mg\ l^{-1}$	0.25
Total nitrogen as N	$mg\ l^{-1}$	1.0
Bromine	$mg\ l^{-1}$	0.5

Treatments

An annular UV reactor with a working volume of 0.9 l and pathlength 1.94 cm was employed. The small air space (0.4 l) under the air diffuser was irradiated by the end of the hairpin style lamp. Radiation from two lamps with identical physical dimensions was applied: one lamp with output primarily at 254 nm referred to hereafter as the 'N-lamp' (Australian Ultra Violet Services G36T15NU), and the 'H-lamp' with output at 254 and 185 nm (Australian Ultra Violet Services G36T15HU). The total absorbed light intensity, as determined by H_2O_2 actinometry (Beltrán *et al.* 1995), for the N-lamp was 1.2×10^{-5} einstein l^{-1} s^{-1} or 5.6 W l^{-1} for an input electrical power of 39 W. The irradiated area corresponding to 0.9 l was 322 cm^2, and the doses applied ranged up to 450 J cm^{-2} (or 8 h), significantly more than typical UV disinfection doses (40 mJ cm^{-2}). The intensity of 185 nm radiation emitted by the H-Lamp was measured using methanol actinometry (Heit *et al.* 1998) as 2.0×10^{-6} einsteins l^{-1}

s^{-1} or 1.3 W l^{-1}. The power draw of the H-lamp was quoted by the vendor as 46 W. During all experiments the air or nitrogen circulating past the lamp was maintained at 28 ± 1°C and the water sample at 23 ± 1°C by a peltier cooled water stream. The samples were mixed and aerated by humidified air during irradiation. For enhanced photooxidation processes a single hydrogen peroxide (Riedel-deHaën 30% extra pure) dose of 12.5 (± 1.5) mg l^{-1} was used, which is below the dose (17 mg l^{-1}) allowed in Germany for production of drinking water (Kleiser & Frimmel 2000). To compare the four different treatments, three doses were applied in each: an extended dose and doses resulting in samples with absorbances (A_{254}) of 0.45 and 0.3.

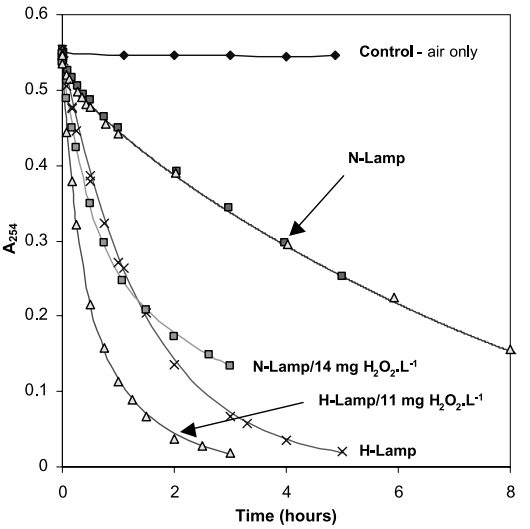

Figure 1 | Kinetics of NOM bleaching. Symbols represent experimental data and lines show kinetic models. The control experiment was a water sample aerated without irradiation in the reactor for the periods shown.

Analytical methods

Non-purgeable dissolved organic carbon was determined by photocatalytic oxidation in an AnaTOC Series 2 Analyser (SGE). Hydrogen peroxide concentration was determined colorimetrically (Bader *et al.* 1988). Aldehydes were determined by MGT Environmental Consulting, Oakleigh, using the PFBHA derivatization, liquid–liquid extraction, GC/ECD method 6252 B (*Standard Methods* 1998). Keto-acids were determined using the same technique but with an additional methylation step using diazomethane (Xie & Reckhow 1992).

The NOM biodegradability in the treated waters was measured using the biological dissolved organic carbon (BDOC) method (Joret & Levi 1986). Prior to the BDOC test residual hydrogen peroxide in samples treated by enhanced photooxidation was quenched by the addition of 10 ml l^{-1} catalase ($\sim$40 units) in pH 7 buffer, prepared from bovine liver (Sigma 2390 units per mg solid).

The chlorine demand was determined over an 8-day period. Equal volumes of sample and chlorine solution (prepared from Mallinckrodt AR $NaOCl_{(aq)}$ 10% available chlorine) were thoroughly mixed before being incubated in darkness at 20°C (± 1°C). Prior to dosing (14 mgCl_2 l^{-1} in flask), the concentration of the stock chlorine solution was determined iodometrically and was monitored periodically over the 8-day reaction period using the DPD colorimetric method 4500-Cl G (*Standard Methods* 1998). High purity water was used as a control to estimate losses of chlorine to atmosphere and wall reactions. Chlorine demand values were corrected for these losses and represent reaction with components in the natural water only. High purity water was produced by reverse osmosis and electrodeionization treatments (Millipore Elix10) followed by UV (254 & 185 nm) oxidation, adsorption and ultrafiltration (Millipore Milli-Q Gr A10).

Trihalomethane formation potential (THMFP) was determined using procedure 5710 B (*Standard Methods* 1998), but at 20°C to match the Cl_2 demand determinations. Liquid–liquid extraction was used to concentrate the trihalomethanes (*Standard Methods* 1998 procedure 6232 B) prior to analysis using a Shimadzu GC-17A gas chromatograph equipped with an electron capture detector. A cyanopropylphenol polysiloxane lined capillary column (SGE BP624, 30 m × 0.32 mm ID × 1.8 μm) was used with helium carrier gas (35 cm s^{-1} at 40°C), a split ratio of 30 and an oven temperature programme of 40°C held for 3 min after 0.4 μl injection, before ramping at 10°C min^{-1} to 150°C, which was held for 2 min prior to cool down.

Nitrite ion (NO_2^-) in the range 1 to 21 μM was determined colorimetrically after diazotization (Hach 1999) using NitriVer 3 Nitrite Reagent powder pillows. The concentration of stock nitrite solution for standard preparation was determined by the heated permanganate titration method (*Standard Methods* 1998; 4500-NO_2^- B).

Table 2 | Kinetic model parameters for NOM bleaching

Treatment	Model	R^2	$S_{y/x}$	$A_1(0)$	k_1 (h^{-1})	$A_2(0)$	k_2 (h^{-1})
N-lamp	Parallel 1st order	0.998	0.005	0.034	11.4	0.519	0.145
H-lamp	1st order	0.998	0.009	0.548	0.675		
N-lamp/H_2O_2 14 mg l^{-1}	Parallel 1st order	0.999	0.006	0.237	2.23	0.307	0.280
H-lamp/H_2O_2 11 mg l^{-1}	Parallel 1st order	0.999	0.006	0.264	4.05	0.284	0.931

Note: $S_{y/x}$ is the standard error of the estimate, and represents the predicted error in model prediction of absorbance at a certain time.

A Unicam Spectrophotometer Model UV2 was used for all absorbance measurements.

RESULTS AND DISCUSSION

The effect of treatment on A_{254}, DOC and H_2O_2 concentrations

The H-lamp (UV/VUV producing) plus H_2O_2 was clearly the most effective for removal of chromophores, and the N-lamp (UV producing) was the least effective (Figure 1). H-lamp alone and N-lamp/H_2O_2 had intermediate chromophore removal rates; when H_2O_2 was present chromophore removal by the N-lamp/H_2O_2 process was faster than by the H-lamp alone (Figure 1). Removal of chromophores by the H-lamp followed first order kinetics (Table 2), possibly indicating reaction with an oxidant in steady state concentration. This is likely to have been hydroxyl radical created by water photolysis. For the other cases the behaviour was slightly more complex and parallel first order kinetics were applied:

$$CDOM_1 \xrightarrow{k_1} uncolouredDOM \tag{4}$$

$$CDOM_2 \xrightarrow{k_2} uncolouredDOM \tag{5}$$

$$-\frac{dA_1(t)}{dt} = k_1 A_1(t) \tag{6}$$

$$-\frac{dA_2(t)}{dt} = k_2 A_2(t) \tag{7}$$

$$A_T(\mathrm{t}) = A_1(0) \cdot \exp(-k_1 \cdot t) + A_2(0) \cdot \exp(-k_2 \cdot t) \tag{8}$$

where $A_n(t)$ = absorbance at 254 nm of chromophores in group n or total T at time t (h), k_n = reaction rate constant of chromophores in group n (h^{-1}). These equations were solved using Solver in Microsoft Excel to manipulate k_1 and $A_1(0)$, which fixed k_2 and $A_2(0)$, to minimize the sum of squares of the difference between model and experimental data. This simple model implies that there are two categories of chromophores reacting at different rates. For the N-lamp plus H_2O_2 case, the two distinct groups may be related to those which reacted with $^{\bullet}OH$ while H_2O_2 was present, and those which were photochemically removed. For the H-lamp plus H_2O_2 case the rate constants were much higher. For the N-lamp irradiated system a small quantity of chromophores reacted extremely quickly, with the remainder reacting at a much slower rate (Table 2).

Mineralization rates decreased in the order H-lamp plus H_2O_2, H-lamp, N-lamp plus H_2O_2 and N-lamp, whilst aeration only in the reactor did not affect the non-purgeable dissolved organic carbon concentration (Figure 2). Calculated electrical energies (E_{EO}; Bolton *et al.* 2001) required to reduce DOC concentration by one order of magnitude increased in the order N-lamp plus H_2O_2 (87 kWh kl^{-1}), H-lamp plus H_2O_2 (220 kWh kl^{-1}), H-lamp (290 kWh kl^{-1}) and N-lamp (1,200 kWh kl^{-1}). Mineralization was best approximated using zero-order kinetics for the N-lamp case ($k = 0.439$ mgC l^{-1} h^{-1}, $R^2 = 0.599$), indicating DOC concentration was not limiting mineralization. The H-lamp and H-lamp plus H_2O_2 cases both followed first order kinetics ($k = 0.40$ h^{-1}, $R^2 = 0.994$ and $k = 0.53$ h^{-1}, $R^2 = 0.999$, respectively),

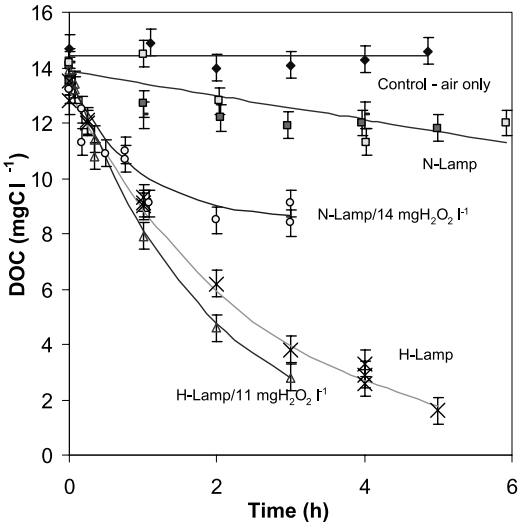

Figure 2 | Mineralization rates. Symbols show experimental data and lines represent kinetic models. The control experiment was a water sample aerated without irradiation in the reactor for the periods shown.

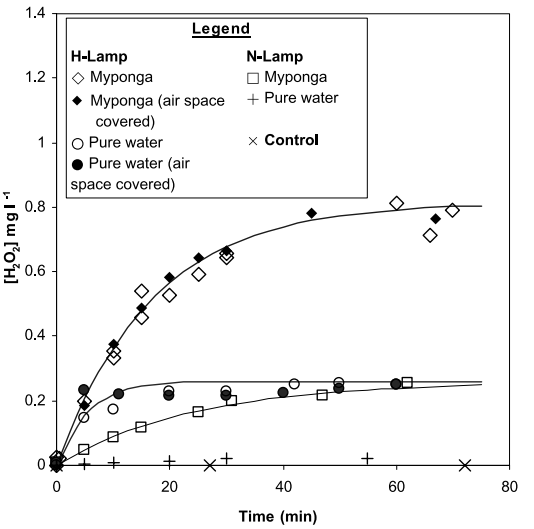

Figure 3 | Formation of H_2O_2 by irradiation. The control was Myponga water aerated in the reactor without irradiation. Symbols show data and lines are trendlines.

indicating reaction with an oxidant in constant concentration. For the N-lamp/H_2O_2 treatment, mineralization followed first order kinetics while there was H_2O_2 in the reactor ($k = 1.15\ h^{-1}$, $R^2 = 0.859$), leaving 8.5 mgC l^{-1} remaining. For the pure batch process treatment used, the E_{EO} values indicate that the H-lamp/H_2O_2 process was the most economic; the low E_{EO} determined for the N-lamp/H_2O_2 process is misleading because the kinetics that applied only to the initial fast reaction period were used to determine it and a one order of magnitude reduction was not obtained. This low E_{EO} result is interesting and suggests that a semi-batch process should be investigated in future work.

Hydrogen peroxide removal in the enhanced photooxidation experiments followed kinetics based on the photochemical rate equation (Leifer 1988) with attenuation by NOM chromophores (data not shown). Hydrogen peroxide was formed in high purity and Myponga waters by H-lamp irradiation and in Myponga water by N-lamp irradiation (Figure 3). The hydrogen peroxide ($\sim$0.2 mg l^{-1}) detected in H-Lamp irradiated high purity water was probably formed mainly from hydrogen atoms (see Equation 2) combining with oxygen to produce superoxide (Gonzalez & Braun 1995):

$$O_2 + H^{\bullet} \rightarrow HO_2^{\bullet} \quad (9)$$

$$HO_2^{\bullet} \Leftrightarrow O_2^{\bullet -} + H^+ \quad (10)$$

$$O_2^{\bullet -} + HO_2^{\bullet} \rightarrow HO_2^- + O_2 \quad (11)$$

$$HO_2^- + H^+ \Leftrightarrow H_2O_2 \quad (12)$$

Other, lesser, superoxide precursors are hydrated electrons formed from water homolysis via Equation (3) (Gonzalez & Braun 1995):

$$O_2 + e_{aq}^- \rightarrow O_2^{\bullet -} \quad (13)$$

Also hydroxyl radical recombination results in hydrogen peroxide (Gonzalez & Braun 1995):

$$2^{\bullet}OH \rightarrow H_2O_2 \quad (14)$$

All three mechanisms are likely to have contributed to the observed H_2O_2 formation.

Hydrogen peroxide was not detected in N-lamp irradiated high purity water, so its formation ($\sim$0.25 mg l^{-1}) in Myponga water was probably due to NOM (Figure 3). Photochemical formation of H_2O_2 in natural waters is

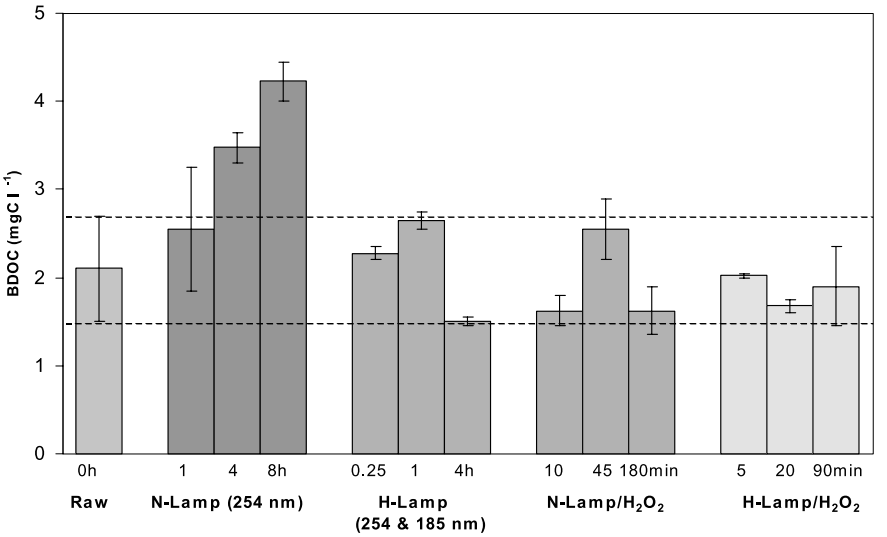

Figure 4 | Effect of irradiation on biodegradability. Averages of duplicates shown here with difference between duplicates indicated by uncertainty bars.

thought to result from superoxide which can form from NOM via a number of reaction pathways, for example (Cooper *et al.* 1989):

$$^1HS + h\nu \rightarrow {}^1HS^* \xrightarrow{ISC} {}^3HS^* \quad (15)$$

$$HS^* \text{ or } {}^3HS^* \rightarrow [HS^{+\bullet} + e^-] \rightarrow HS^{+\bullet} + e^-_{(aq)} \quad (16)$$

with the hydrated electrons forming superoxide as shown in Equation (13).

Hydrogen peroxide formed (~ 0.8 mg l^{-1}) in H-lamp irradiated Myponga water as a consequence of water photolysis and indirectly from NOM photoreactions. If ozone production in the irradiated air space below the air diffusers were significant, then ozone photolysis could also contribute:

$$O_{2(g)}(\Sigma g^-) + h\nu(185\text{ nm}) \rightarrow O_{2(g)}(\Sigma u^-) \quad (17)$$

(Dohan & Masschelein 1987)

$$O_{2(g)}(\Sigma u^-) + O_{2(g)}(\Sigma g^-) \rightarrow O_{3(g)} + ({}^3P)O \quad (18)$$

(Dohan & Masschelein 1987)

$$O_{3(aq)} + h\nu + H_2O \rightarrow H_2O_2 + O_2 \quad (19)$$

(von Sonntag *et al.* 1993).

When the air space was covered the same amount of hydrogen peroxide formed as when the air space was uncovered (Figure 3), indicating that ozone production in the irradiated humidified sparge air was insignificant. This was expected since neither long pathlengths ($\varepsilon_{O_2,184.9\text{ nm}} = 0.1$ atm^{-1} cm^{-1}, i.e. low) nor dry air, which are required if ozone is to be effectively formed from irradiated air (Dohan & Masschelein 1987), were present.

Hydrogen peroxide is cytotoxic, a bacterial mutagen, and the suggested drinking water tolerance limit is 0.1 mg l^{-1} in Europe (Richardson 1998). The concentrations found were above this. Biological filtration has been shown to remove hydrogen peroxide (Urfer & Huck 1997) and could be expected to remove this and also improve the biological stability of the water.

The effect of irradiation on the biodegradable dissolved organic carbon content of the water

Approximately 14% of the raw water DOC was removed in the BDOC test (Figure 4), which is identical to the fraction of biologically labile DOC reported in lakes (Tranvik 1998). The BDOC for N-lamp (254 nm) treated samples increased with increasing dose, in stark contrast to the processes involving hydroxyl radicals which either

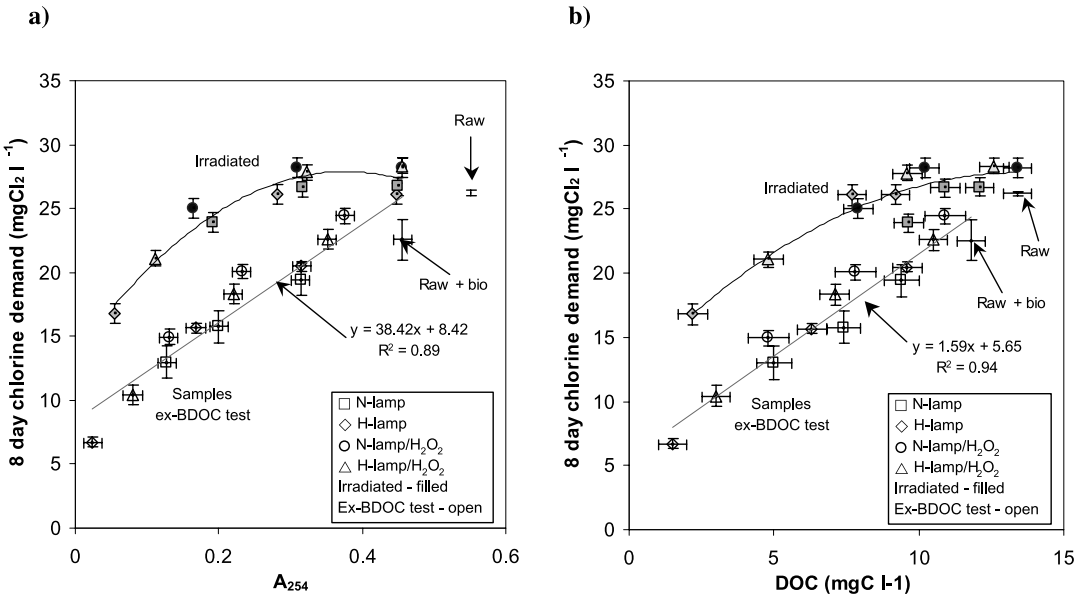

Figure 5 | Effect of treatment on chlorine demand. Degree of treatment indicated by (a) absorbance (A_{254}) and (b) DOC. Average of duplicates shown.

remained the same or decreased with increasing dose (Figure 4). Both quantity and quality of the carbon source, and presence/absence of toxicity are factors which may influence BDOC concentration. Glyoxylic acid is reported to be a bacterial mutagen (Richardson 1998), but is also an important intermediate in the anaplerotic glyoxylate cycle (Brock 1979), so concentration is likely to be important in determining toxicity. This compound was detected in the samples dosed with peroxide and may have contributed to the lower BDOC in these samples. Alternatively, the concentration of biodegradable material is likely to be greater in water treated by irradiation at 254 nm, than in water from the hydroxyl radical processes.

Hydroxyl radical oxidizes organics in a powerful and non-selective manner in contrast to NOM photooxidation by irradiation at 254 nm, which, if a direct photochemical process, proceeds at a rate proportional to the rate of light absorption (Leifer 1988). If chromophoric NOM can be likened to a regular chromophoric polymer, then longer chains could be expected to have a higher probability of being struck by a photon, and hence have a higher molar absorptivity and rate of light absorption, than shorter chains. The longer chains could be expected to react fastest, fragmenting rapidly into smaller and hence slower reacting chromophores or non-reacting non-absorbing molecules, leading to an accumulation of smaller molecules. Smaller molecules are more biodegradable because they can be transported across cell membranes and be metabolized without the use of extracellular enzymes (Tranvik 1998). In this way, and possibly others, the fundamental chemistry of the processes appears to have influenced the quantity of biodegradable material.

Theory aside, from a water treatment perspective, all of the treated waters can be considered to have potential to cause biological regrowth in the distribution system and a biological treatment post-irradiation seems necessary.

The effects of UV-irradiation and the BDOC test on chlorine demand and THMFP

Small doses (~6,000 to 230,000 mJ cm^{-2}) increased the chlorine demand and only high doses caused decreases (Figure 5). For irradiated samples there were no clear differences between treatments; samples with similar

absorbances had similar chlorine demands irrespective of how the reduction of absorbance (A_{254}) was brought about (Figure 5). The chlorine demand of irradiated samples did not vary with DOC as strongly because the DOC was not significantly reduced in the majority of samples (Figure 5). In all cases the chlorine demand of irradiated samples after the BDOC test was lower than that of raw water, and correlated well with A_{254} (Cl_2 demand ex-BDOC($mgCl_2\ l^{-1}$) $= 38 \times [A_{254}] + 8.4$, $R^2 = 0.89$) and DOC concentration (Cl_2 demand ex-BDOC($mgCl_2\ l^{-1}$) $= 1.6 \times [DOC] + 5.7$, $R^2 = 0.94$) (Figure 5). Correlation between THMFP and chlorine demand was weaker (THMFP(μM) $= 0.29 \times Cl_2$ demand ($mgCl_2\ l^{-1}$), $R^2 = 0.75$). To obtain water with low chlorine reactivity both the absorbance and DOC concentration need to be reduced by a combination of photooxidation followed by biological treatment.

Benzene and substituted aromatics (e.g. phenol, aniline, anisole, benzoic acid) have peaks in their absorption spectra at 254 and 269–280 nm, respectively (Lambert *et al.* 1998); absorbance at 254 nm of NOM-containing solutions may be due to similar aromatic structures in NOM. A strong correlation between chlorine consumption and activated aromatic structures (hydroxyl and nitrogen substituted) was found (Reckhow *et al.* 1990). Hypochlorous acid reacts with bromide ion to form hypobromite/hypobromous acid, which reacts at higher rates (Oliver 1979) and with a greater variety of activated aromatics (i.e. combinations of hydroxy-, carboxyl- and methoxy-substituted) than hypochlorous acid (Rook 1979). Figure 5 indicates that, for samples with similar absorbance, the chlorine demand was considerably greater in irradiated-only samples than those that had been subsequently biodegraded. Chlorine also reacts with carbon activated by adjacent carbonyl groups (McKnight & Reckhow 1992); low molecular weight carbonyl compounds have been reported to be abundant in irradiated natural water (Thomson *et al.* 2002) and are biodegradable (Weinberg *et al.* 1993). Compounds such as these may be contributing to the difference in chlorine demand and THMFP found in the present study.

As treatment decreased the DOC concentration, the THM speciation shifted to more brominated compounds (Figure 6). Bromine incorporation into THMs was

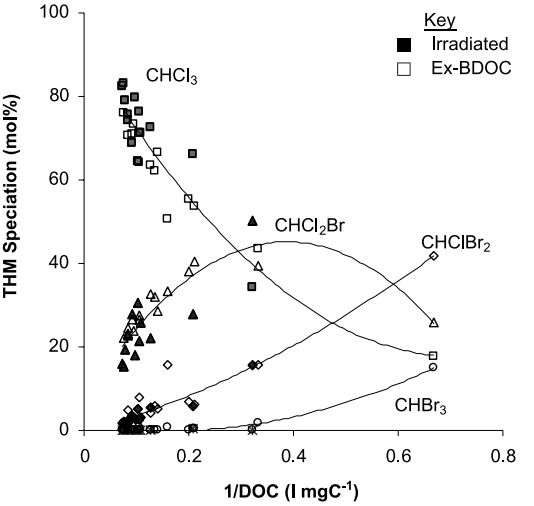

Figure 6 | THM speciation of Myponga water after various treatments. Symbols show experimental data. Trendlines also shown. There was little variation in THM speciation between the irradiation treatments and in the interests of clarity N-lamp, H-lamp, N-lamp/H_2O_2 and H-lamp/H_2O_2 data points are not distinguished and are shown as filled symbols.

constant at about 2.1 μM, approximately one-third of that in the raw water, whereas chlorine incorporation decreased with increasing DOC removal, consistent with the higher reactivity of hypobromite/hypobromous acid. For similar DOC concentrations the distributions of THM species were similar, irrespective of treatment type; however, biological treatment following UV treatment appeared to be the most effective way to reduce the DOC and hence influence the speciation. Similar results have been reported for ozonation plus biofiltration (Koechling *et al.* 1996). The transition through the THM species for diluted humic acid solutions with constant bromide concentration (Figure 7) was similar to the behaviour of the natural water for which the DOC (but presumably not bromide) concentrations were reduced by combinations of irradiation and biodegradation (Figure 6). Oliver (1979) reported similar results when the concentration of bromide ion was varied and the humic acid concentration was kept constant.

In the present work more bromine-substituted compounds formed as the number of sites for halogen substitution decreased. THM speciation is very important from a health point of view, because the different species have different health risks associated with them. The US EPA

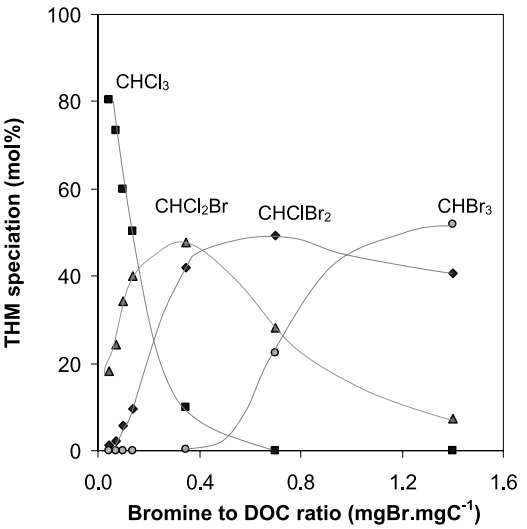

Figure 7 | Effect of bromine:DOC ratio on THM speciation in chlorinated Aldrich humic acid solutions. Bromide concentration constant at 0.7 mg l^{-1}, DOC varied from 0.5 to 15 mgC l^{-1}. Hypochlorite added in excess at 5 $mgCl_2 \cdot mgC^{-1}$.

has assigned drinking water concentrations associated with a one in a million (10^{-6}) excess cancer risk as 0.6, 4 and 6 μg l^{-1} for bromodichloromethane, bromoform and chloroform, respectively (Zavaleta *et al.* 1999). The relative cancer risks for different treatments can be compared by summing the individual THM concentrations divided by the one in a million risk concentration, and despite the apparent shift to higher risk by-products, in absolute terms the risk appears to reduce with increasing NOM removal for our data.

Low molecular weight carbonyl compounds

As seen graphically in Figure 8, and in detail in Table 3, the low molecular weight carbonyl compound concentration and speciation varied considerably between the different treatments. Formaldehyde was the dominant species present in the H-lamp irradiated systems on a molar basis, whereas in the N-lamp irradiated systems formaldehyde accounted for approximately half of the moles present. High concentrations of propanal and butanal seemed to be unique to the N-lamp samples irradiated in the absence of H_2O_2 (Table 3). Butanal reacts very rapidly with hydroxyl radicals ($k = 3.9 \times 10^9$ M^{-1} s^{-1}; Buxton *et al.* 1988) and would not accumulate in the processes where the hydroxyl radical concentrations were high (i.e. H-lamp, H-lamp/H_2O_2 and N-lamp/H_2O_2). Glyoxylic acid was found in hydroxyl radical containing systems

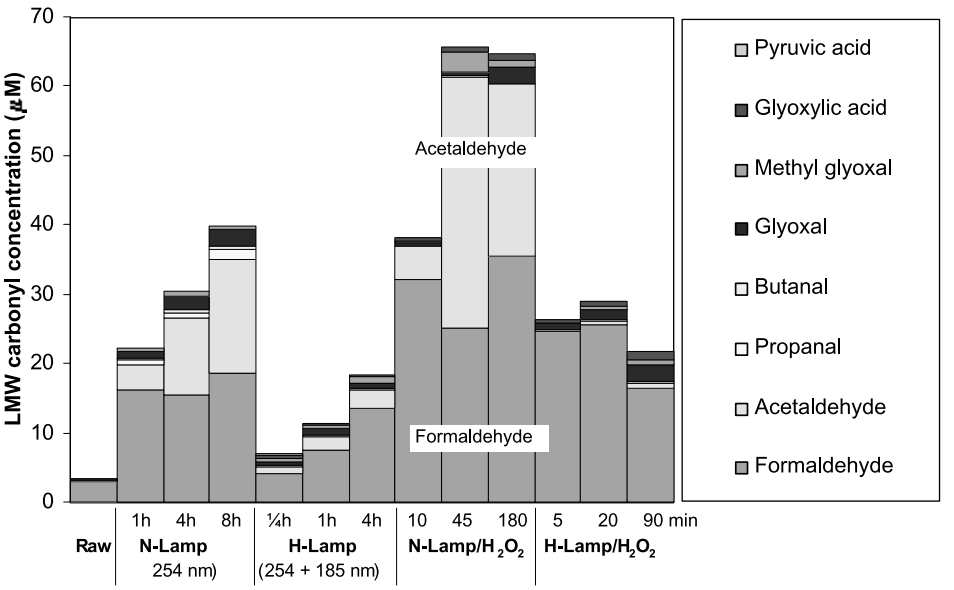

Figure 8 | Formation of low molecular weight carbonyl compounds.

Table 3 | Formation of low molecular weight carbonyl compounds

		LMW carbonyl concentration (μM)								LMW carbonyls as	
.		Formaldehyde (CH_2O)	Acetaldehyde (C_2H_4O)	Propanal (C_3H_6O)	Butanal (C_4H_8O)	Glyoxal ($C_2H_2O_2$)	Methyl glyoxal ($C_3H_4O_2$)	Glyoxylic acid ($C_2H_2O_3$)	Pyruvic acid ($C_3H_4O_3$)	%BDOC	%Cl_2 demand drop in BDOC test*
Raw water		2.8	0.2	0	0.1	0.3	0	0	0	2	1
N-Lamp	1 h	16.2	3.5	0.7	0.3	1.1	0.3	0	0	13	10
	4 h	15.5	11.0	0.8	0.5	1.9	0.5	0	0	16	20
	8 h	18.5	16.4	1.5	0.6	2.2	0.5	0	0	18	30
H-Lamp	0.25 h	4.2	0.8	0.2	0.1	0.4	0.6	0.4	0.2	5	4
	1 h	7.5	1.9	0.3	0	0.9	0.5	0.2	0	7	4
	4 h	13.5	2.6	0.1	0.1	0.9	0.8	0.2	0	19	6
N-Lamp/H_2O_2	10 min	32.2	4.6	0.1	0	0.5	0.2	0.4	0	31	24
	45 min	25.2	36.2	0.1	0	0.6	2.8	0.9	0	51	86
	180 min	35.5	24.8	0	0	2.4	0.9	1.1	0	70	47
H-Lamp/H_2O_2	5 min	24.5	0.3	0.1	0	0.9	0.1	0.3	0	16	2
	20 min	25.5	0.4	0.2	0.1	1.5	0.4	0.8	0	24	2
	90 min	16.5	0.6	0.2	0.1	2.2	0.7	1.3	0.1	18	2

*Low molecular weight carbonyl compounds as a percentage of chlorine demand reduction in the BDOC test, calculated assuming complete reaction and the following stoichiometric coefficients (McKnight and Reckhow 1992): acetaldehyde n=2.6 (pH=7), propanal n=1.2 (pH=9), butanal n=1.2 (pH=9), methyl glyoxal n=1.4 (pH=7), pyruvic acid n=1.3 (pH=7), formaldehyde n=0 (own determination), glyoxylic acid n=0, glyoxal n=0.

(Table 3) but not in the N-lamp irradiated samples. Acetaldehyde concentrations were lower in H-lamp irradiated systems. Glyoxal accumulated in all processes possibly because of its lower reactivity (e.g. with hydroxyl radical $k = 6.1 \times 10^7$ M^{-1} s^{-1}; Buxton *et al.* 1988). The differences in low molecular weight carbonyl compound speciation indicate that different formation and removal mechanisms were dominant in the different systems.

Low molecular weight carbonyl compounds were effectively removed by the BDOC test, with only traces of formaldehyde, acetaldehyde, methyl glyoxal and glyoxal remaining (data not shown). Others have reported that the glyoxal and methyl glyoxal are less biodegradable (Weinberg *et al.* 1993; Kostakis 2001). Whilst biological uptake is likely to be the dominant removal mechanism, mass transfer to the air and abiotic reactions may also occur. Low molecular weight carbonyl compounds are effective linking and cross-linking agents, and may react with functional groups on NOM; however, the rates of biological uptake are likely to be much greater (Mopper & Stahovec 1986). In the BDOC test the samples were aerated (100 ml min^{-1}) for 7 days, and low molecular weight carbonyl compounds may have been partially stripped. In the non-aerated biological regrowth potential (BRP) test, the formaldehyde, acetaldehyde, pyruvic and glyoxylic acid concentrations were significantly reduced in ozonated Myponga water samples (Kostakis 2001), suggesting that biological uptake is the dominant removal mechanism. Data from water treatment plants show that formaldehyde and acetaldehyde, created by reaction between ozone and NOM, are removed by biological activated carbon treatment (Weinberg *et al.* 1993), indicating that they can be removed from drinking water by treatment plants including biological treatment.

Low molecular weight carbonyl compounds represent an appreciable percentage of the BDOC of the irradiated samples (Table 3). Non-purgeable DOC concentrations were used to calculate the BDOC. Given the short sparge times (~3 min) used to remove dissolved inorganic carbon in the DOC analysis technique, and the relatively high apparent partition coefficients (K_H) of 5,087 and 23 M atm^{-1} for formaldehyde and acetaldehyde, respectively (Zhou & Mopper 1990) (compared with 0.039 M atm^{-1} for carbon dioxide/carbonic acid (Hem 1992)), these compounds could be expected to be included in the non-purgeable DOC concentration (where $C_{aq} = K_H \times p$, where C_{aq} = aqueous phase concentration (M), K_H = apparent partition coefficient at 20°C (M atm^{-1}), p = partial pressure of compound (atm)).

The chlorine demand equivalent to the quantity of these compounds removed by the BDOC test can be estimated and compared with the difference in the chlorine demand of irradiated water before and after biodegradation. Low molecular weight carbonyl compounds accounted for a large proportion of the chlorine demand drop of N-lamp irradiated samples, mainly attributable to the large amounts of acetaldehyde in these samples (Table 3). Only a small proportion of the chlorine demand reduction caused by the BDOC test could be attributed to the LMW carbonyl compounds that had been formed in samples irradiated using the H-lamp (Table 3).

Formation of nitrite

Nitrite, a substance particularly toxic to infants, forms from photolysis (at 254 nm) of nitrate and subsequent radical–radical recombination reactions (von Sonntag *et al.* 1993):

$$NO_3^- + h\nu \rightarrow NO_2^{\bullet} + O^{\bullet -} \quad (20)$$

$$2NO_2^{\bullet} + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \quad (21)$$

Fortunately, although the quantum yield of nitrite is quite high ($\Phi = 0.1$), the molar absorptivity of nitrate at 254 nm is low ($\varepsilon = 4$ M^{-1} cm^{-1}) and UV doses used for disinfection do not cause problematic nitrite levels (von Sonntag *et al.* 1993; Sharpless & Linden 2001). In the present work much higher UV doses and shorter wavelengths were employed and investigation of nitrite formation was warranted. Nitrite formed in irradiated Myponga water from precursor nitrate and total Kjeldahl nitrogen (18 and 55 μM, respectively) (Figure 9). As predicted by Equations 20–21, irradiation of the natural water at 254 nm led to a steady increase in the concentration of nitrite.

When combined 254/185 nm irradiation was used, nitrite formation rates were higher. Hydrogen atoms and

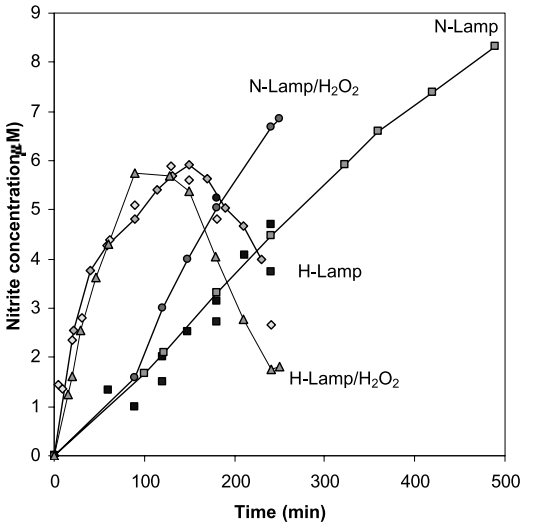

Figure 9 | Nitrite formation in irradiated Myponga water. Symbols show experimental data points; lines added to guide the eye.

hydrated electrons, formed by water homolysis at 185 nm, can reduce nitrate to nitrite (Gonzalez & Braun 1995):

$$NO_3^- + H^\bullet \rightarrow NO_3H^{\bullet -} \quad (22)$$

$$NO_3^- + e^- \rightarrow (NO_3^\bullet)^{2-} \quad (23)$$

$$(NO_3^\bullet)^{2-} + H^+ \Leftrightarrow NO_3H^{\bullet -} \quad (24)$$

$$NO_3H^{\bullet -} + H_2O \rightarrow NO_2^\bullet + HO^- \quad (25)$$

$$2NO_2^\bullet \rightarrow N_2O_4 \quad (26)$$

$$N_2O_4 \rightarrow NO_3^- + NO_2^- + 2H^+ \quad (27)$$

and may account, in part for this. Nitrite can be oxidized back to nitrate by hydroxyl radical (Gonzalez & Braun 1995):

$$NO_2^- + {}^\bullet OH \rightarrow NO_3H^{\bullet -} \quad (28)$$

$$NO_3H^{\bullet -} \Leftrightarrow (NO_3^\bullet)^{2-} + H^+ \quad (29)$$

$$(NO_3^\bullet)^{2-} + O_2 \rightarrow NO_3^- + O_2^{\bullet -} \quad (30)$$

and this may explain why the nitrite concentrations decreased after prolonged irradiation.

The reason nitrite concentrations did not decrease after longer irradiation times in the hydroxyl radical-containing N-lamp/H_2O_2 system may be that, whilst hydrogen peroxide and hence hydroxyl radical were present, the DOC concentration was also high and consumed hydroxyl radicals at a much faster rate ($k = 2.3 \times 10^4$ l mgC^{-1} s^{-1} (Brezonik & Fulkerson-Brekken 1998)) than nitrite ($k = 2.5 \times 10^9$ M^{-1} s^{-1} (Gonzalez & Braun 1995)). In the later stages hydrogen peroxide was depleted, so no hydroxyl radical could form to oxidize nitrite back to nitrate and hence nitrite steadily increased. The increased rate of formation of nitrite when hydrogen peroxide was dosed may have been because of faster removal of chromophoric NOM and hence reduced attenuation.

The nitrite levels detected were below the US EPA maximum contaminant level of 71 μM (Sharpless & Linden 2001), but exceeded the European limit of 2 μM (von Sonntag *et al.* 1993). Suitable methods for removing the nitrite may need to be investigated.

CONCLUSIONS

For the natural water treated the most effective process for DOC concentration and chromophore reduction was irradiation at 254 plus 185 nm (H-lamp) in the presence of H_2O_2. Irradiation at these wavelengths in the absence of H_2O_2 was almost as effective, providing an additive-free treatment process, owing to *in situ* generation of hydroxyl radicals. Irradiation at 254 nm (N-lamp) produced the highest amounts of biodegradable DOC (up to twice that of the raw water), in contrast to the other processes for which the BDOC remained the same as for the raw water.

Formaldehyde was the dominant low molecular weight carbonyl compound detected in all treatments. Acetaldehyde was the second most abundant carbonyl compound detected, with higher concentrations detected in N-lamp irradiated water. Higher concentrations of propanal and butanal were found in N-lamp irradiated water without H_2O_2 addition. The different speciation suggests that different formation and removal mechanisms were

dominant in the different treatments. These compounds were removed by the BDOC test and accounted for an appreciable percentage of the BDOC and the chlorine reduction in samples subjected to this test.

Chlorine demand and THMFP increased for small and intermediate radiation doses, even though the absorbance at 254 nm was reduced, and only decreased for larger doses. The chlorine demand decreased with absorbance at 254 nm only after the BDOC test suggesting significant biological reduction of the number of chlorine reactive sites formed by irradiation. THM speciation was found to depend on DOC concentration, with more highly brominated compounds detected in samples with lower DOC. The higher cancer risk associated with brominated THMs was considered to be outweighed by reduced overall THM concentrations; as a result, the samples with low DOC had the least risk.

Nitrite and hydrogen peroxide concentrations in irradiated samples exceeded the European guideline values, suggesting that UV-treatment should be followed by further (possibly biological) treatment. Irradiation at 254 nm alone increased nitrite concentrations. Irradiation at 254 and 185 nm initially increased and then decreased nitrite concentrations suggesting that when the DOC levels are low, hydroxyl radical oxidation of nitrite exceeded photo-reduction of nitrate.

Results from this preliminary study indicate that NOM can be removed from water by vacuum ultraviolet irradiation combined with biological treatment, leading to improved drinking water quality. Doses used were thousands of times greater than those used for UV disinfection and the results do not imply that disinfection of drinking water would result in the effects shown in this research.

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