UV photooxidation facilitating biological treatment for the removal of NOM from drinking water

J. Thomson, F. A. Roddick and M. Drikas

ABSTRACT

The effects of UV-C (254 nm) radiation on the biodegradability and chlorine demand of natural organic matter (NOM) were investigated. Biodegradability was assessed using the biological regrowth potential and biodegradable dissolved organic carbon (BDOC) methods and remained unchanged for doses of 40 to 1,000 mJ cm^{-2}, but increased when the water was exposed to higher doses. The DOC concentration and UV absorbance values were reduced in UV-treated waters, but the chlorine demand remained the same as for raw water. Exposure of the UV-treated water to microbial treatment (via the BDOC test) gave a reduced DOC concentration and chlorine demand, indicating that the chlorine-consuming compounds resulting from irradiation were biodegradable. High performance size exclusion chromatography showed that both biodegradability assessment methods preferentially removed smaller molecules. Formaldehyde, acetaldehyde, glyoxal and glyoxylic acid were detected in UV-treated waters and were removed by the BDOC test. Chlorine demand correlated well with the concentration of low molecular weight (LMW) carbonyl compounds, which can be considered to be a surrogate for a large number of unidentified organics contributing to the chlorine demand and biodegradability.

Key words | biodegradable dissolved organic carbon (BDOC), chlorine demand, drinking water, low molecular weight carbonyls, natural organic matter (NOM), ultra-violet (UV-C) photooxidation

J. Thomson
F. A. Roddick (corresponding author)
Cooperative Research Centre for Water Quality and Treatment,
Private Mail Bag 3,
Salisbury, S.A. 5108,
Australia
and
Department of Chemical & Metallurgical Engineering,
RMIT,
GPO Box 2476V,
Melbourne, Victoria 3001,
Australia
Tel.: +61-3-9925-2080
Fax: +61-3-9925-3746
E-mail: *felicity.roddick@rmit.edu.au*

M. Drikas
Cooperative Research Centre for Water Quality and Treatment,
Private Mail Bag 3,
Salisbury, S.A. 5108,
Australia
and
Australian Water Quality Centre,
Private Mail Bag 3,
Salisbury, South Australia 5108,
Australia

INTRODUCTION

Australia is an arid country, which when combined with a number of other factors, such as vegetation and soil type, causes high dissolved natural organic matter (NOM) concentrations and colour in much of its surface water. NOM in drinking water is a direct problem due to colour and taste. Indirectly, NOM is a problem because it reacts with the most commonly used disinfectant, chlorine, to form disinfection by-products (DBPs). In addition, NOM acts as a food source for bacterial regrowth in potable water distribution systems, and reduces the efficiency of many water treatment operations, such as particle removal, and trace organics removal by oxidation or adsorption (Gottschalk *et al*. 2000).

A number of conventional unit operations are available for the removal of NOM from raw water; all have advantages and disadvantages. Coagulation/flocculation followed by sedimentation/dissolved air flotation creates large volumes of chemical-containing sludge and associated disposal problems. Membrane processes may be limited by capital cost, fouling and high energy costs. Ion exchange resins need to be chemically regenerated and often disposal of associated waste is problematic. Application of ozone is often limited by high capital costs or concerns over bromate formation. New drinking water treatment processes need to be investigated, especially as population growth places an increasing pollution load on natural water bodies. Any novel process will have its strengths and weaknesses and researchers will need to identify these to allow drinking water producers to make optimal process selections.

Advanced oxidation processes, involving the generation of hydroxyl radicals, have been proposed for the production of drinking water. Ultraviolet light (UV) combined with ozone (O_3) has been shown to be very effective for the removal of trihalomethane (THM) precursors, but may be limited by high cost (Glaze *et al*. 1982). UV combined with hydrogen peroxide (H_2O_2) has been investigated for the removal of taste and odour compounds, THM and colour (Andrews *et al*. 1996) but as H_2O_2 has a low extinction coefficient ($\epsilon_{254} = 19\ M^{-1}\ cm^{-1}$), high UV doses or concentrations of H_2O_2 are required, leading to higher costs and concerns with peroxide residuals in water (Gottschalk *et al*. 2000). In Germany, for example, H_2O_2 is regulated at <0.1 mg l^{-1} in drinking water (Gottschalk *et al*. 2000).

The use of UV (254 nm) produced by low pressure mercury vapour lamps alone, is generally not considered to be an effective process for the removal of organics from water (Legrini *et al*. 1993). However, for highly coloured waters, such as those often encountered in Australia, there may be sufficient chromophoric material to remove NOM by photooxidation, particularly if irradiation is followed by biological treatment. If the high energy consumption of the irradiation step can be reduced, the simplicity and lack of process chemicals may make this process combination very attractive. Furthermore, in the envisaged process, NOM would be mineralised and not merely concentrated or transferred from one medium to another, as is the case in many conventional processes.

The aim of this work was to investigate whether UV (254 nm) irradiation of a highly coloured water can facilitate biological treatment and significantly improve water quality. In this experimental programme water quality improvement was determined by measuring the two main problems caused by NOM in drinking water, bacterial regrowth and disinfection by-products. Bacterial regrowth was assessed using the bacterial regrowth potential (BRP) method. The biodegradable dissolved organic carbon (BDOC) method was used both to determine biodegradable organics and to act as the biological treatment step. Although the contact time in this test is much longer than used industrially, it is useful for simulating the removals attainable by biological treatments such as slow sand filtration, biological activated carbon (Graham 1999) or bank infiltration. Chlorine demand was chosen as an indirect measure of disinfection by-product formation potential. It is a bulk property that may be more comprehensive than measuring one of the many available disinfection by-product groups (trihalomethanes, haloacetic acids, total organic halide, chlorinated furanones, etc.). The disadvantage of using chlorine demand is that chlorine is both an oxidant and a halogenating agent, the latter action resulting in chlorinated DBPs, and the proportion of the total chlorine demand contributing to each reaction is unknown. From an operational point of view, chlorine demand is a useful tool to determine the required dose to ensure a chlorine residual is maintained at the end of the distribution system. High performance size exclusion chromatography and aldehyde/keto-acid analyses were also performed to gain further insights on the mechanisms of the processes.

MATERIALS AND METHODS

Water

The water used in this study was collected from the East Moorabool System, Victoria, on two occasions: March and November 2000. The sampling location (Anakie Basin) was fed by several reservoirs (Korweinguboora, Bostok, Upper and Lower Stony Creek). The water characteristics are listed in Table 1.

UV irradiation

All water was filtered through a pre-washed 0.45 μm hydrophilic membrane (Durapore PVDF) before irradiation. The UV reactor consisted of two quartz tubes (500 ml, i.d. 44 mm, height 415 mm, working liquid level 330 mm) mounted between two low pressure mercury vapour lamps (primary output at 254 nm quoted by the vendor as 38 μW cm^{-2} at 1 m). Mirrors were placed around the lamps and sample tubes and the whole enclosure was maintained at 25°C (±2°C) by a water-cooled peltier. The measured intensity was 1.73×10^{-6} einstein s^{-1} or 0.81 W at 254 nm per 500 ml tube (Parkinson *et al*.

Table 1 | East Moorabool water characteristics

DOC (mg C l^{-1})	March 2000	9.7	*Standard Methods* 1998 Method 5310 C heated persulphate oxidation method
	November 2000	9.5	
pH	November 2000	7.7	
Alkalinity to pH 3.7 (mg $CaCO_3$ l^{-1})	November 2000	31	*Standard Methods* 1998 Method 2320B potentiometric titration
SUVA ($l.mgC^{-1}.m^{-1}$)	March 2000	1.70	A_{254}/(DOC. pathlength)
	November 2000	3.80	
Total nitrogen (mg N l^{-1})	March 2000	0.54	*Standard Methods* 1998 Method 4500-N_{org} B Macro Kjeldahl and 4500-NH_3 F Phenate
Total phosphorus (mg P l^{-1})	March 2000	0.01	*Standard Methods* 1998 Method 4500-P B 5 persulphate digestion and 4500-E ascorbic acid

2000). The irradiated area used for all dose calculations was 454 cm^2 based on the assumption that radiation entered the cylinder from all angles. Typical doses applied ranged from 40 to 26,000 mJ cm^{-2}, corresponding to irradiation times of 20 seconds to 4 hours. The samples, open to atmosphere, were gently mixed by humidified air during irradiation. The progress of the reaction was monitored by dissolved nonpurgeable organic carbon (DOC) concentration (I O Analytical Model 1010 Wet Oxidation TOC Analyser) and absorbance at 254 nm (A_{254}) (Unicam UV/Vis Spectrophotometer Model UV2).

Biodegradability

The NOM biodegradability in the treated waters was measured using two techniques: biodegradable organic carbon (BDOC) and biological regrowth potential (BRP). For BDOC the method of Joret & Levi (1986) was used. The water sample was exposed to thoroughly washed, biologically active sand for 7 days under aerobic conditions. The DOC was measured daily and the BDOC was calculated as the initial DOC minus the lowest DOC recorded over the 7-day period. BRP determinations were undertaken as described by Withers and Drikas (1998). The growth of a natural inoculum of bacteria was monitored by turbidity increase over a 3-day period. The turbidity increase can be correlated to the growth of bacteria on pure water spiked with acetate, and a growth factor can be assigned in acetate carbon equivalents.

HPSEC

Molecular size distribution was determined using high performance size exclusion chromatography (HPSEC). The operating system consisted of a Waters 501 high-pressure pump, Waters 717 autosampler, a temperature controlled oven (30°C) and a Waters 484 UV/visible detector. A Shodex KW 802-5 glycol functionalised silica gel column, an isocratic flowrate of 1.0 ml min^{-1}, and an injected volume of 100 μl were used. The carrier solvent consisted of 0.02 M phosphate buffer (pH 6.8) adjusted to an ionic strength of 0.1 M with sodium chloride. Detection was by absorbance at 260 nm.

Chlorine demand

The chlorine demand was determined over an 8-day period. Equal volumes of sample and chlorine solution (prepared from $NaOCl_{(aq)}$) were thoroughly mixed before

being incubated in darkness at 20°C (±1°C). Chlorine concentration in the stock chlorine solution was determined iodometrically (*Standard Methods* 1998). Chlorine concentration was monitored periodically over the 8-day reaction period using the DPD colorimetric method (*Standard Methods* 1998). Losses were assumed to be pH independent. High purity water (Milli-Q) 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.

Aldehydes and keto-acids

Aldehydes were determined by the PFBHA, liquid–liquid extraction, GC/ECD method 6252 B (*Standard Methods* 1998). Keto-acids were determined using the same technique but with an additional diazomethane methylation step (Xie and Reckhow 1992).

RESULTS AND DISCUSSION

The effect of UV-photooxidation on A_{254} and DOC concentration

DOC concentration was only slightly reduced (by 16%) by the largest UV dose of 26,000 mJ cm^{-2} (Figure 1). In the non-irradiated, aerated control the DOC concentration remained unchanged, indicating that no process (e.g. biological, adsorption, evaporation) other than UV-irradiation caused the DOC concentration change (data not shown). This DOC loss is attributed to mineralisation by a complex sequence of photochemical reactions between NOM, reactive species and rapidly reacting species (including radicals) (Frimmel 1994). The UV absorbance at 254 nm (A_{254}) was halved by this dose (Figure 1) indicating that significant chemical changes had been made to the NOM. Conjugated double bonds (including unsaturated aldehydes and aromatics) absorb in this region, the reduction in A_{254} is indicative of a loss of these types of compounds. The maximum dose applied (26,000 mJ cm^{-2}) decreased the specific UV absorbance ($SUVA_{254}$) from 1.8 to 0.96 $l \cdot mgC^{-1} \cdot m^{-1}$ indicating that conjugated compounds were oxidised to smaller compounds. The responses of the more intensely coloured water collected in November to the maximum dose (26,000 mJ cm^{-2}) were smaller: 20% DOC and 26% A_{254} reduction, and $SUVA_{254}$ decreased from 3.8 to 3.1 $l \cdot mgC^{-1} \cdot m^{-1}$. Humic matter with a high aliphatic content appears to be most available as a bacterial growth substrate (Tranvik 1998), so the apparent loss of conjugated compounds may indicate enhanced biodegradability.

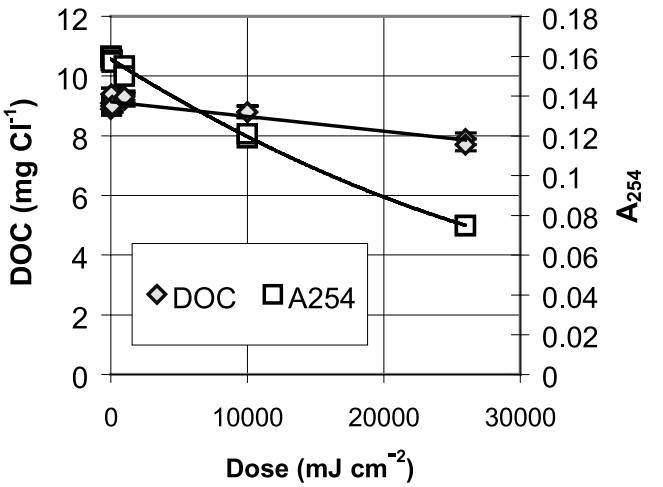

Figure 1 | The effect of UV dose on A_{254} and DOC concentration of East Moorabool water collected in March 2000.

UV enhanced biodegradability

Although no enhancement of biodegradability was detected using either the BRP or BDOC methods for doses of 40 (typical UV disinfection practice) up to 1,000 mJ cm^{-2}, both methods showed an increase at doses of 10,000 mJ cm^{-2} or more (Figures 2 and 3). Similar increases in the biodegradability (BRP method) of NOM have been reported for UV-A and B (Frimmel 1998), and UV-A, B and C irradiated water (Parkinson *et al*. 2000). In waters exposed to sunlight, a similar stimulation of microbial growth and activity has been observed. Mechanisms leading to this enhanced biodegradability behaviour may be similar to those occurring in sunlit systems, where sunlight degrades NOM into biologically labile photoproducts that can be classified into four groups: low

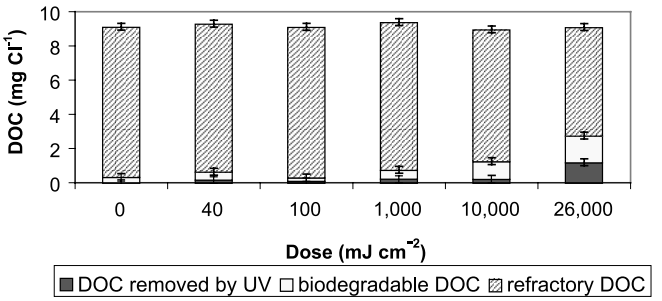

Figure 2 | The effect of UV dose on the biodegradability of NOM measured by the BDOC method. Source water, East Moorabool, collected in March 2000. Averages from two replicates shown. Error bars represent precision of DOC measurement.

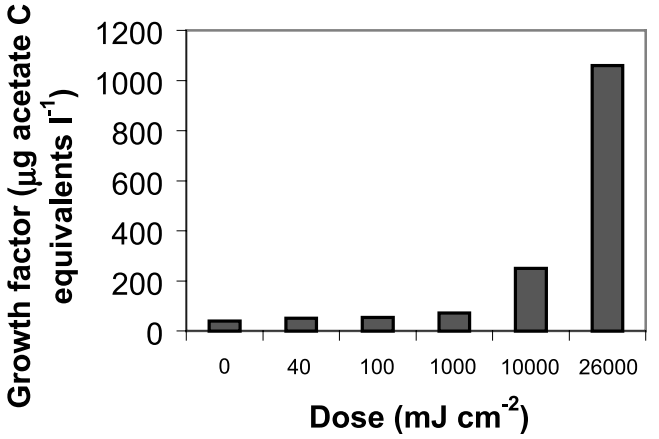

Figure 3 | The effect of UV dose on the biodegradability of NOM measured by the BRP method. Source water, East Moorabool, collected in March 2000. The averages of duplicate samples are shown.

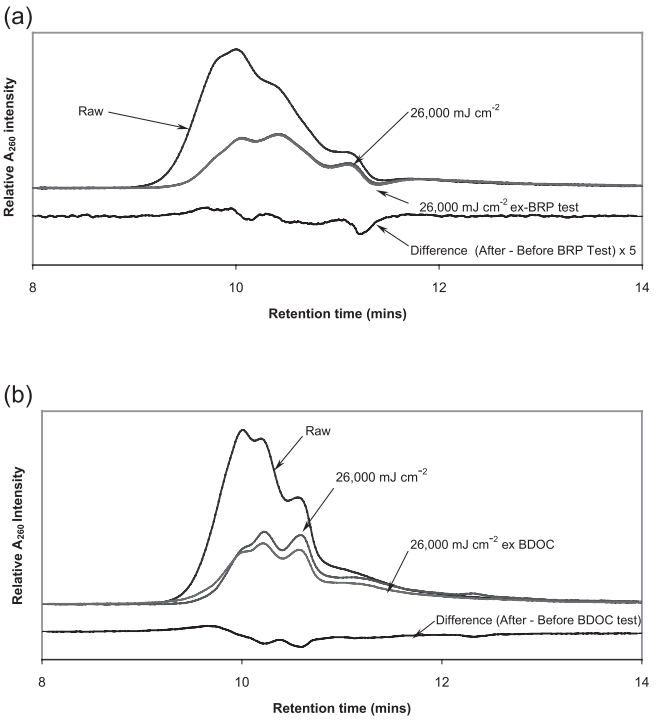

Figure 4 | HPSEC chromatograms for raw, UV-treated and UV-treated NOM after biodegradability determination. The charts are presented with retention time as the abscissa; in size exclusion chromatography larger molecules are unable to penetrate the smaller pores and elute earlier than smaller molecules. (a) After BRP test (chromatogram for water ex-BRP test has been corrected for dilution by the 1:11 nutrient solution addition); (b) after BDOC test.

molecular weight organic compounds; carbon gases (primarily carbon monoxide); unidentified bleached organic matter; and nitrogen- and phosphorus-rich compounds (including NH_4^+ and PO_4^{3-}) (Moran and Zepp 1997). Also, the formation of a mixed substrate by the addition of biologically labile photoproducts may trigger the removal of more refractory material (Tranvik 1998). It would seem from the results presented here that similar mechanisms are occurring in the systems examined in this study.

The effect of irradiation and biotreatment on the apparent molecular size distribution of the NOM

At doses of 26,000 mJ cm^{-2}, UV irradiation appeared to preferentially remove the larger molecules, leaving smaller molecules (Figure 4). The area under the curves was greatly reduced by UV-treatment and corresponds to the conversion of UV-absorbing structures (unsaturated compounds) to non-UV absorbing (saturated) ones by photo-reactions.

The apparent molecular size distributions before and after the BRP test are almost the same (Figure 4a). The difference chromatogram (note the five-fold magnification) shows that the amount of short retention time (i.e. larger molecular weight) material increased very slightly and that the amount of smaller molecular weight material decreased slightly. The increase in bacterial numbers was equivalent to 1.05 mg acetate C equivalents l^{-1}, a significant quantity of carbon/energy. This raises the question of the identity of the bacterial energy source, as the chromatograms indicate only a very slight change in the size

distribution of the NOM. Using size exclusion chromatography with DOC detection, Frimmel (1998) showed that suspended bacteria in the BRP test preferentially utilised small molecular weight, non-UV absorbing material. The bacteria in the present study may have preferentially utilised small, saturated compounds, which would explain the high growth rates with little loss of UV-absorbing material.

Exposure of irradiated water to a sand-attached biofilm for 7 days in the BDOC test had a more pronounced but similar effect to that of the suspended bacteria on the apparent molecular size distribution (Figure 4b). Although the exposure time was longer (cf. 3 days in the BRP test), it is unlikely that the suspended bacteria in the BRP test would have altered the size distribution further as they would have reached the stationary/death stages towards the end of the exposure period (Withers and Drikas 1998). In the BDOC test, compounds of lower molecular mass (retention time greater than 10 minutes) were removed; a possible removal mechanism is adsorption onto the biofilm/sand followed by bacterial utilisation. The chromatogram also indicated that a small quantity of apparently large molecular mass compounds were released into the solution. These may have been bacterial metabolites or compounds that desorbed from the biofilm/sand matrix. The removal by the biofilm of less biodegradable, unsaturated compounds suggests an enhanced microbial biodiversity when compared with the suspended bacteria. It is likely that the non-UV absorbing material would also have been utilised, either by the biofilm or by bacteria that left the biofilm to colonise the solution.

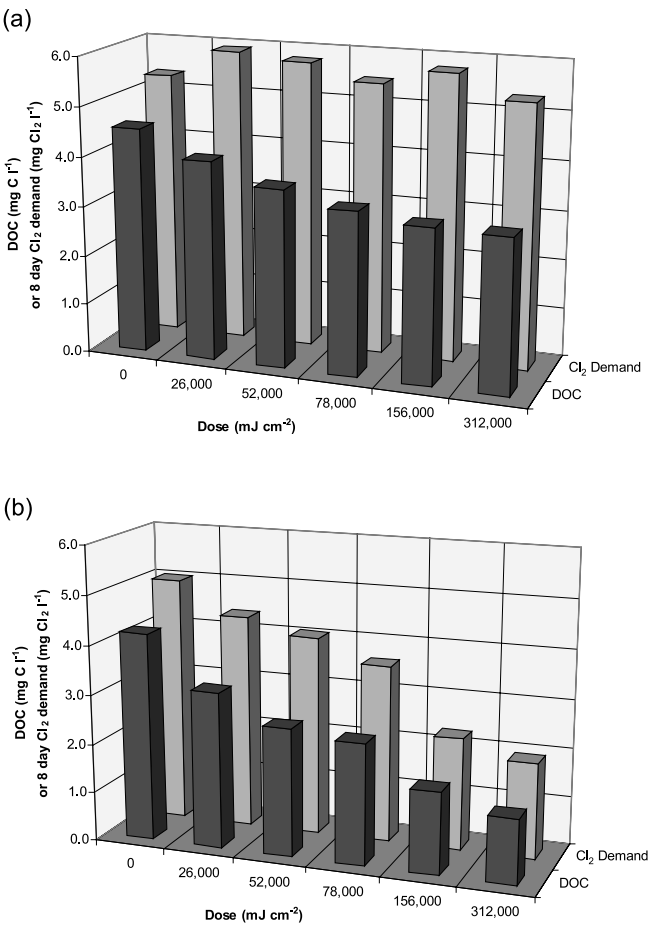

Figure 5 | The effect of treatment on the chlorine demand and DOC concentration. 'Bio' treatment was exposure to biologically active sand for 7 days (i.e. the BDOC test). Water, East Moorabool, collected in March 2000. Trends for sample collected in November were similar (data not shown). (a) Effect of UV irradiation alone on DOC and 8 day chlorine demand; (b) effect of UV irradiation combined with biological treatment on DOC and 8 day chlorine demand.

The effect of treatment on chlorine demand

The chlorine demand of irradiated water samples was slightly higher than that of the raw water (Figure 5a), despite a decrease in the DOC concentration, indicating significant changes to the NOM chemistry and size distribution. Reckhow *et al.* (1990) suggested that phenolic structures and aromatic amines account for much of the chlorine demand of aqueous humic and fulvic acid solutions. As these chemical species absorb strongly at 254 nm and the A_{254} of the samples subjected to the highest UV dose was reduced by approximately 85%, it is unlikely that large quantities of these compounds were present in the highly irradiated samples. It is possible that this small amount of remaining UV-absorbing matter was humic/fulvic acid building block material, but it would need to have been extremely chlorine reactive to account for the observed chlorine demand. Other insights into the nature of the compounds that could have been formed can be found in ^{13}C NMR studies such as those of Schmitt-Kopplin *et al.* (1998), who found that humic acids exposed to UV radiation (>290 nm) lost their phenolic groups and

gained carboxylic derivatives and ketones. Hanna *et al.* (1991) found that ketones and methoxyl groups (as well as oxygenated aromatics) reacted strongly with chlorine. Similarly, in the present study, UV irradiation appeared to destroy one group of chlorine reactive compounds (e.g. phenolics) in the original NOM and replace them with another group or other groups (e.g. carbonyls).

The chlorine demand responded with UV dose in a manner similar to the THM formation potentials (THMFP) reported by others for UV (254 nm) irradiated water. Li *et al.* (1996) irradiated humic acid solutions with doses up to 48,000 mJ cm^{-2} and found that the THMFPs exceeded those of raw water. Using higher doses (288,000 mJ cm^{-2}), Kleiser and Frimmel (2000) reported that THMFP and adsorbable organic halide levels were 93% and 81%, respectively, of those of the untreated river water.

Biological treatment decreased the DOC concentration and chlorine demand of raw water only very slightly showing that biological treatment alone is ineffective (Figure 5a and b). In contrast, biological treatment of the irradiated samples via the BDOC test reduced the chlorine demand and DOC concentration (Figure 5b); the chlorine demand was approximately linearly related to DOC concentration (Cl_2 demand $= 1.1 \times [DOC] + 0.70$, $R^2 = 0.89$, $N = 9$). This suggests that some of the chlorine reactive compounds created by irradiating the water were removed by biodegradation. Thus, by following UV photooxidation with a biological treatment step, the quality of the water is enhanced in terms of reduced DOC, reduced chlorine demand, reduced colour and reduced biological regrowth potential.

Effect of treatment on the low molecular weight carbonyl compound concentrations

The chemical species responsible for the increased chlorine demand of UV-treated waters may be aldehydes, ketoaldehydes and keto-acids. Varying concentrations of these compounds have been identified in ozonated waters (Weinberg *et al.* 1993; Melin & Ødegaard 1999), in natural waters exposed to sunlight (Kieber *et al.* 1990), in natural waters exposed to medium pressure UV (Andrews *et al.* 1996) and in UV-disinfected tertiary treated wastewater effluent (Oppenheimer *et al.* 1997). Furthermore, some of these compounds have been shown to be biodegradable (Moran & Zepp 1997) and highly reactive with chlorine (McKnight & Reckhow 1992).

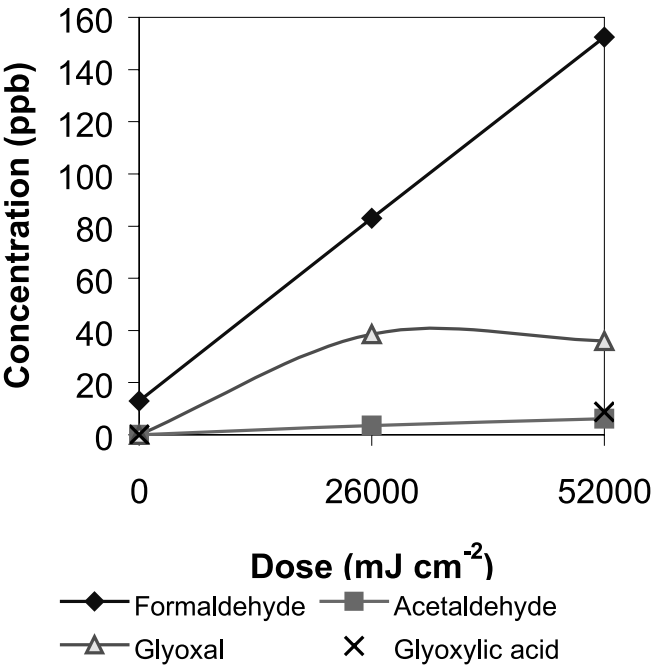

Figure 6 | Concentration of LMW carbonyl compounds in irradiated East Moorabool water collected in November 2000.

Formaldehyde, acetaldehyde, glyoxal and glyoxylic acid were all detected at greater concentrations in irradiated water than in raw water (Figure 6). Propanal, butanal, pentanal, hexanal, benzaldehyde, methyl glyoxal and pyruvic acid were not found in concentrations greater than their detection limits. For the two UV doses used the glyoxal concentrations were similar, possibly because this compound is photolabile and therefore did not accumulate in the system. Formaldehyde and acetaldehyde are not photolabile and their concentrations increased with irradiation dose. The formaldehyde formation rate was 32 nM m^2 W^{-1} h^{-1} which is similar to the sunlight formation rate of 25 nM m^2 W^{-1} h^{-1} reported by Kieber *et al.* (1990) for coastal water with a similar absorbance (A_{300}) to the water used in this study.

There are some health concerns with formaldehyde, and its concentration in drinking water is often regulated;

Table 2 | Low molecular weight carbonyl concentrations in East Moorabool water after various treatments. (Average of duplicate measurements shown; if one of the duplicates was below the detection limit it was assumed to be zero.)

Sample ID	Formaldehyde (ppb) HCHO	Acetaldehyde (ppb) $CH_3.CHO$	Glyoxal (ppb) CHO.CHO	Glyoxylic acid (ppb) CHO.COOH
Raw	13	<5	<10	<5
26,000 mJ cm^{-2} UV only	83	4	39	Not done
52,000 mJ cm^{-2} UV only	152	6	36	9
26,000 mJ cm^{-2} UV + bio	8	<5	8	<5
52,000 mJ cm^{-2} UV + bio	9	<5	12	3

for example in Australia the guideline value is 500 μg l^{-1} (NHMRC 1996). At the highest radiation doses this limit was not exceeded and biological treatment reduced this concentration to the levels found in raw water.

Biological treatment (exposure to gently aerated, sand-attached biofilm for 7 days (i.e. the BDOC test)) removed a significant proportion of LMW carbonyl compounds (Table 2) as well as reducing the chlorine demand. The relative importance of biological, adsorption and air stripping mechanisms will be the subject of future work. If these compounds were non-purgeable, they would account for up to 4% of the BDOC. For the limited number of datapoints ($N=5$), there appears to be a linear relationship between the LMW carbonyl compound concentration and specific chlorine demand (Figure 7). This was surprising since formaldehyde was the dominant product identified and has been reported to be unreactive with chlorine by McKnight and Reckhow (1992) (this result has been confirmed by chlorine demand determinations in our laboratory). The concentrations of the remaining three by-products are hardly sufficient to explain the difference in chlorine demand of the irradiated plus biologically treated and irradiated only samples. Weinberg *et al.* (1993) suggest that these LMW aldehydes can be considered as a surrogate measure for a large number of other polar organics. These include low molecular weight carboxylic acids, for example malonic and citric acid, which are cited as NOM photoproducts by Moran and Zepp (1997) and as

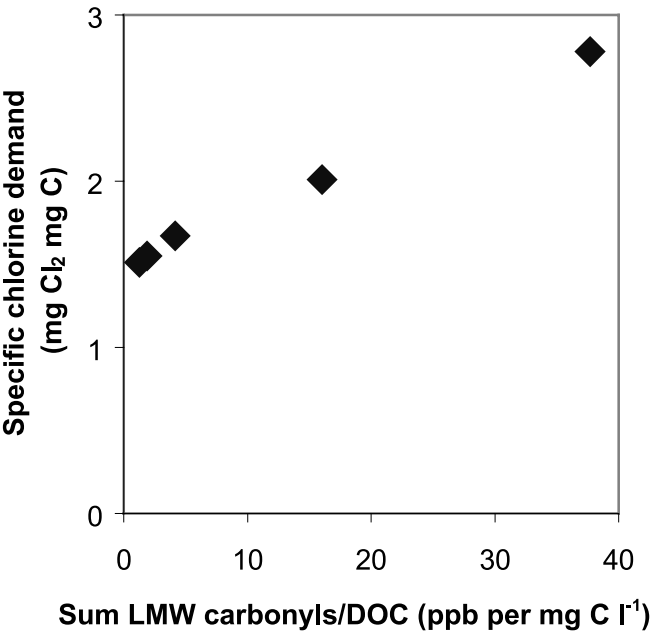

Figure 7 | The relationship between specific chlorine demand (7 day) and sum of LMW carbonyl compound concentration (DOC normalised). Water, East Moorabool, collected in November 2000. The data points are (left to right): Raw; 26,000 mJ cm^{-2} UV+bio; 52,000 mJ cm^{-2} UV+bio; 26,000 mJ cm^{-2} UV; 52,000 mJ cm^{-2} UV. 'Bio' treatment was exposure to biofilm in the BDOC test for 7 days.

THM precursors by Rice (1980). These polar organics may be the compounds responsible for part of the enhanced chlorine demand of irradiated waters found in the present work.

The cause and effect relationship between the identified LMW carbonyl compounds, chlorine demand and biological treatment may be more subtle. There is evidence (Figure 4b) that the sand-attached biota removed some low molecular weight compounds containing conjugated double bonds. These compounds are likely to be humic/fulvic acid building block molecules liberated from the NOM core by UV-induced depolymerisation/photooxidation reactions. They have been shown to be THM precursors (Rice 1980) and their removal may also have contributed to a reduced chlorine demand. It is possible that UV irradiation photo-chemically conditioned the NOM, providing the microbes with a mixed substrate, which allowed them to remove low molecular weight compounds containing conjugated double bonds. This would explain the strong linear relationship between chlorine demand and LMW carbonyl concentration even though their concentrations are insufficient to account for the chlorine demand. Regardless of mechanism, or combination thereof, biological treatment following UV photooxidation led to an improvement in water quality.

CONCLUSIONS

For the NOM samples used in this study:

1. The UV-C radiation doses applied reduced the concentration of conjugated double bond compounds (as inferred from the reduced A_{254}) and slightly reduced the DOC concentration.
2. UV photooxidation applied in doses ≥10,000 mJ cm^{-2} increased the biodegradability of the NOM as measured by the BDOC and BRP methods.
3. Although there was considerable microbial growth, the suspended bacteria in the BRP test only slightly altered the apparent molecular weight distribution of the irradiated NOM as detected by UV absorbance. This bacterial growth must have been supported by saturated compounds. The more diverse microflora in the biofilm in the BDOC test removed some of the smaller, unsaturated compounds.
4. UV photooxidation decreased the DOC concentration, but not the chlorine demand. UV-irradiation followed by biological treatment reduced the DOC concentration and chlorine demand, indicating that some of the compounds causing the enhanced chlorine demand in the photooxidised sample were biodegradable.
5. UV photooxidation produced measurable quantities of LMW carbonyl compounds (formaldehyde, acetaldehyde, glyoxal and glyoxylic acid) and significant quantities of these compounds were removed by biotreatment.
6. UV photooxidation followed by biological treatment improved the water quality as measured by decreased chlorine demand, decreased DOC and decreased A_{254}. Water from this process can be expected to be biologically stable.

ACKNOWLEDGEMENTS

The authors wish to acknowledge: Malcolm Hobday, Department of Applied Chemistry, RMIT University, for helpful discussions; Greg Simes and Naomi Withers, Australian Water Quality Centre, Bolivar, South Australia, for BRP and HPSEC analyses; Thames Water for nitrogen and phosphorus analyses; Barwon Water for permission to collect water; and MGT Environmental Consulting for low molecular weight carbonyl determination.

REFERENCES

Andrews, S. A., Huck, P. M., Chute, A. J., Bolton, J. R. & Anderson, W. A. 1996 UV oxidation for drinking water: feasibility studies for addressing specific water quality issues. *Proceedings of the Water Quality Technology Conference*, New Orleans, LA, November 12–16 1995, American Water Works Association, pp. 571–577.

Frimmel, F. H. 1994 Photochemical aspects related to humic substances. *Environ. Int.* **20**(3), 373–385.

Frimmel, F. H. 1998 Impact of light on the properties of aquatic natural organic matter. *Environ. Int.* **24**(5/6), 559–571.

Glaze, W. H., Peyton, G. R., Lin, S., Huang, R. Y. & Burleson, J. L. 1982 Destruction of pollutants in water with O_3 in combination with UV radiation 2. Natural trihalomethane precursors. *Environ. Sci. Technol.* **16**(8), 454–458.

Gottschalk, C., Libra, J. A. & Saupe, A. 2000 *Ozonation of Water and Wastewater: A Practical Guide to Understanding Ozone and its Application*. Wiley-VCH, Weinheim.

Graham, N. J. D. 1999 Removal of humic substances by oxidation/biofiltration processes—a review. *Wat. Sci. Technol.* **40**(9), 141–148.

Hanna, J. V., Johnson, W. D., Quezada, R. A., Wilson, M. A. & Lu, Xiao-Qiao 1991 Characterization of aqueous humic substances before and after chlorination. *Environ. Sci. Technol.* **25**(6), 1160–1164.

Joret, J. C. & Levi, Y. 1986 Méthode rapide d'évaluation du carbone éliminable des eaux par voie biologique. *Trib. Cebedeau* **510**(39), 3–9.

Kieber, D. J., Zhou, X. & Mopper, K. 1990 Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea. *Limnol. Oceanogr.* **35**(7), 1503–1515.

Kleiser, G. & Frimmel, F. H. 2000 Removal of precursors for disinfection by-products (DBPs)—differences between ozone- and OH-radical-induced oxidation. *Sci. Total Environ.* **256**, 1–9.

Legrini, O., Oliveros, E. & Braun, A. M. 1993 Photochemical processes for water treatment. *Chem. Rev.* **93**, 671–698.

Li, J. W., Yu, Z., Gao, M. & Zhang, L. 1996 Effect of ultraviolet irradiation on the characteristics and trihalomethanes formation potential of humic acid. *Wat. Res.* **30**(2), 347–350.

McKnight, A. & Reckhow, D.A. 1992 Reactions of ozonation by-products with chlorine and chloramines. *Proceedings of the 1992 AWWA Annual Conference, Vancouver, British Columbia*, pp. 399–409.

Melin, E. S. & Ødegaard, H. 1999 Biofiltration of ozonated humic water in expanded clay aggregate filters. *Wat. Sci. Technol.* **40**(9), 165–172.

Moran, M. A. & Zepp, R. G. 1997 Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* **42**(6), 1307–1316.

NHMRC 1996 *Australian Drinking Water Guidelines—Summary* [online] www.nhmrc.health.gov.au/publicat/pdf/eh20.html

Oppenheimer, J. A., Jacangelo, J. G., Laîné, J-M. & Hoagland, J. E. 1997 Testing the equivalency of ultraviolet light and chlorine for disinfection of wastewater to reclamation standards. *Wat. Environ. Res.* **69**(1), 14–24.

Parkinson, A., Barry, M., Hobday, M. & Roddick, F. A. 2000 The effect of a range of UV wavelengths on aquatic natural organic matter. *IHHS10—10th International Meeting of the International Humic Substances Society, Toulouse, France*, 24–28 July 2000, PROGEP, Toulouse, pp. 57–60.

Reckhow, D. A., Singer, P. C. & Malcolm, R. L. 1990 Chlorination of humic materials: byproduct formation and chemical interpretation. *Environ. Sci. Technol.* **24**(11), 1655–1664.

Rice, R. G. 1980 The use of ozone to control trihalomethanes in drinking water treatment. *Ozone Sci. Engng* **2**, 75–99.

Schmitt-Kopplin, P., Hertkorn, N., Schulten, H-R. & Kettrup, A. 1998 Structural changes in a dissolved soil humic acid during photochemical degradation process under O_2 and N_2 atmosphere. *Environ. Sci. Technol.* **32**, 2531–2541.

Standard Methods for the Examination of Water and Wastewater 1998 20th edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.

Tranvik, L. J. 1998 Degradation of dissolved organic matter in humic waters by bacteria. In *Aquatic Humic Substances—Ecology and Biogeochemistry* (ed. D. O. Hessen & L. J. Tranvik), Ecological Studies Series, Vol. 133, Chapter 10. Springer-Verlag, Berlin.

Weinberg, H. S., Glaze, W. H., Krasner, S. W. & Sclimenti, M. J. 1993 Formation and removal of aldehydes in plants that use ozonation. *J. Am. Wat. Wks Assoc.* **85**(5), 72–82.

Withers, N. & Drikas, M. 1998 Bacterial regrowth potential—quanititative measure by acetate carbon equivalents. *Water (J. Aust. Water & Waste Water Assoc.)* **25**(5), 59–62.

Xie, Y. & Reckhow, D. A. 1992 A new class of ozonation by-products: the ketoacids. *Proceedings of the 1992 AWWA Annual Conference, Vancouver, British Columbia*, pp. 251–265.

First received 20 August 2001; accepted in revised form 8 January 2002