UV photooxidation of NOM: issues related to drinking water treatment

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ABSTRACT

The effect of UVA (300–400 nm), UVB (260–340 nm) and UVC (254 nm) wavelengths on absorbance spectra, dissolved organic carbon (DOC) levels, molecular size distributions, bacterial regrowth potentials (BRP) and trihalomethane formation potentials (THMFP) of aquatic natural organic matter (NOM) from a number of sources was examined to ascertain the use of photooxidation for the removal of NOM from drinking water. Differences were observed in the normalised UV spectra of the NOM samples, and UVC-irradiation resulted in the largest reduction in absorbance at 254 nm and DOC levels. The various UV wavelengths appeared to reduce the molecular size in a similar fashion with sequential degradation from high molecular weight to low molecular weight by-products. Treatment by UVA-, UVB- and UVC-radiation also resulted in increased BRP for all NOM samples. The THMFP of the UV-treated NOM samples HV MIEX and HV Raw appeared to be dependent on the characteristics of the NOM sample and the UV dose. The THMFP of UVA- and UVB-irradiated HV MIEX increased and an initial increase was observed for UVC-irradiated HV MIEX before decreasing with further treatment, while UVC-irradiated HV Raw showed decreased THMFP for all treatment times.

Key words | NOM, photooxidation, UVA, UVB, UVC, water treatment

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INTRODUCTION

The presence of natural organic matter (NOM) in water has been found to interfere with most processes used for treating drinking water and contributes to the formation of disinfection by-products, some of which are possible carcinogens (Suffet & MacCarthy 1989). Research into the removal of aquatic NOM has mainly involved improving current water treatment technologies, such as coagulation, membrane filtration and adsorption by granular activated carbon (Jacangelo *et al.* 1995). However, UV photooxidation can also be used to remove NOM, as it has been shown to remove organic carbon by mineralisation to CO_2 (Salonen & Vahatalo 1994; Corin *et al.* 1996; Dahlen *et al.* 1996; Kulovaara *et al.* 1996; Kulovaara 1996; Schmitt-Kopplin *et al.* 1998; Win *et al.* 2000). The advantages of NOM photooxidation compared with other removal processes are: there is no requirement for recycling of the substrate; no chemical addition is required; and sludge by-products are not formed. UV photooxidation is similar

to solar photochemical processes in that photons are absorbed by chromophores or UV-absorbing functional groups in NOM (Schwarzenbach *et al.* 1993). This absorption process can result in direct phototransformation, where the chromophores are degraded to non-UV absorbing components, and/or indirect photooxidation, where energy is transferred from the excited chromophore to other components such as oxygen. The active species formed are then able to react with NOM, forming transient organic radical species and resulting in the degradation of both UV- and non-absorbing components, with eventual mineralisation to CO_2 (Faust & Hoigne 1987).

Although there have been other studies on the photooxidation of NOM, these have applied UV wavelengths of varying intensity (Amador *et al.* 1989; Allard *et al.* 1994; Backlund 1994; Corin *et al.* 1996; Dahlen *et al.* 1996; Li *et al.* 1996; Kulovaara *et al.* 1996; Kulovaara 1996; Frimmel

Table 1 | Characteristics of the NOM samples and the isolate, HV MIEX

NOM	Colour (HU)	A_{254} (cm^{-1})	DOC (mg l^{-1})	SUVA (m^{-1} mg^{-1} · l)	Alkalinity (mgCaCO$_3$ l^{-1})	Iron (mg l^{-1})	pH	Av. MW (Da)	Cond. (µS cm^{-1})
HV Raw	12.7	0.118	8.2	1.4	90	0.015	7.90	1,010	513
EastMoor	28.1	0.181	8.1	2.2	33	1.2	7.6	1,030	194
HV MIEX	70.9	0.322	8.5	3.7	2.5	0.183	7.08	1,800	29

1998; Schmitt-Kopplin *et al.* 1998; Win *et al.* 2000; Del Vecchio & Blough 2002). In this paper the effect of irradiation on the physicochemical properties of aquatic NOM by a range of UV wavelengths (UVA (300–400 nm), UVB (260–340 nm) and UVC (254 nm)), at the same average dose, was investigated. The treated NOM was characterised by A_{254}, dissolved organic carbon (DOC) and high performance size exclusion chromatography (HPSEC), and the effect of photooxidation on the bacterial regrowth potential (BRP) and the formation of trihalomethanes (THMFP) was determined. The results are discussed in relation to the effect of UVA, UVB and UVC photooxidation of NOM when applied to the treatment of drinking water.

EXPERIMENTAL PROCEDURES

Design

NOM samples were obtained from the Hope Valley reservoir, South Australia, as both raw water (HV Raw, 8 mgC l^{-1}) and as a concentrate (HV MIEX) obtained by the use of a magnetic anion exchange resin, MIEX® (Bourke *et al.* 1999). Samples of raw water were also obtained from the Moorabool River, Geelong, Victoria (East Moor). All samples were mixed water column samples, obtained after a high rainfall period. The concentrate, HV MIEX, was diluted to 8 mgC l^{-1} DOC in distilled water. The samples were filtered (Whatman WCN, 0.45 µm) and stored at 4°C before use. Further characteristics of the raw water and HV MIEX samples are listed in Table 1.

Irradiation experiments

The UV batch reactor was developed for use with 15 W UVA (NEC Blacklight, Japan), UVB (Vilber-Loumart T-15M) and UVC (Sylvania G15 W, Japan) lamps. The UVA and UVB lamps had a polychromatic Gaussian-type spectral output with maxima at 340 and 310 nm, respectively, while the UVC lamp had a monochromatic spectral output at 253.4 nm. The NOM samples were irradiated in two quartz tubes (4.6 cm OD × 46 cm length), placed centrally at a distance of 7 cm from the two UV lamps. The photon flow through each irradiated tube was 1.73E-06 einstein · s^{-1} (ferrioxalate actinometry; volume 500 ml; surface area 482.5 cm^2) with an average fluence rate of 2.34, 1.92 and 1.75 mW · cm^{-2} for UVC, UVB and UVA, respectively.

Analytical methods

DOC was measured using a total carbon analyser (OI Analytical) equipped with an automatic sample injector. A double beam spectrophotometer (Unicam, UV2) was used for spectrophotometric analysis. Sample colour was determined at 446 nm using a 4 cm cell and the data was reported in Hazen units (HU) where 1 HU = 1 mg l^{-1} platinum units (Bennett & Drikas 1991). UV absorbance at 254 nm (A_{254}) was measured using a 1 cm pathlength cell. The specific UV absorbance (SUVA$_{254}$), the ratio of A_{254} divided by DOC and multiplied by 100, was used as an indication of the conjugation and aromaticity of NOM.

The effect of UVA-, UVB- and UVC-irradiation on the UV absorbance capacity and structure of NOM was monitored by measuring the change in A_{254} and DOC with

average dose. The average dose received by NOM in the reactor was calculated by multiplying the fluence rate (corrected for screening effects by use of the Morowitz correction factor (Harm 1980)) by the treatment time.

Size exclusion chromatography (HPSEC) was conducted at the Australian Water Quality Centre (AWQC), South Australia, as described by Parkinson *et al.* (2001). The HPSEC data was peakfitted using the computer program Peakfit v.4 (AISN Software); the chromatograms were manually fitted with Gaussian-type curves.

The bacterial regrowth potential (BRP) analysis, also conducted at the AWQC, is described elsewhere (Withers & Drikas 1996) and is based on the method developed by Werner & Hambsch (1986). Replicate analyses were obtained for all samples. Withers & Drikas (1998) correlated the increase in bacterial growth to acetate carbon equivalents to provide a better parameter for the assessment of treatment conditions; the results are reported in terms of acetate carbon and specific acetate equivalents (acetate equivalents/DOC).

The trihalomethane formation potential (THMFP) was determined by the AWQC using headspace gas chromatography based on the AS/NZS standard method (6232D:1999) (Standard Methods 1998).

RESULTS AND DISCUSSION

Irradiation and photooxidation of NOM

The absorbance spectra of the treated samples in the wavelength range of 190 to 500 nm were normalised against the untreated sample (A/A_o) to highlight any changes. The loss of absorbance for UVA-, UVB- and UVC-treated HV MIEX samples with the same average dose of $130 \pm 10 \times 10^4$ J m^{-2} was similar to that reported by Del Vecchio & Blough (2002) with absorbance loss over the entire spectrum and regions of higher loss at the spectral output of the lamps (Figure 1).

The greatest loss of absorbance for the UVA-irradiated samples was in the spectral region 270–410 nm, for the UVB-irradiated sample, 260–370 nm and for the UVC-irradiated sample, 230–300 nm. Del Vecchio & Blough (2002) attributed the regions of highest loss to direct
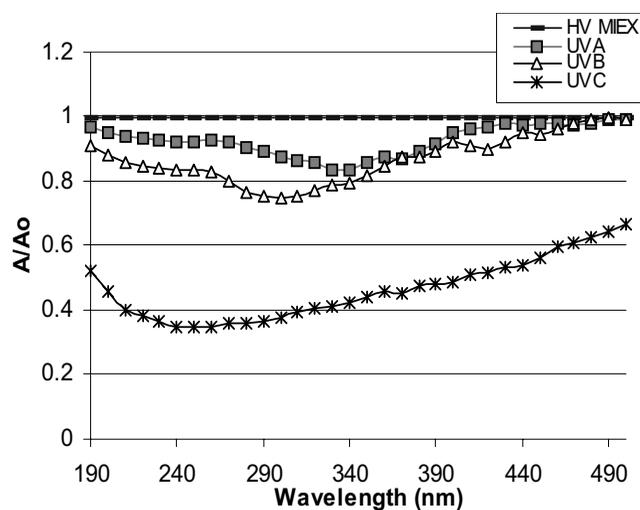

Figure 1 | Normalised absorbance spectra for UVA-, UVB- and UVC-irradiated HV MIEX samples at average dose, $130 \pm 10 \times 10^4$ J m^{-2}.

degradation of chromophores absorbing in this region and loss of absorbance outside this region either to the degraded chromophores having absorption bands outside the direct irradiation wavelength or to indirect degradation mechanisms. In all regions, the loss of absorbance was significantly higher for the UVC-irradiated sample, than UVB- and UVA-irradiated samples. The loss of absorbance for UVB-irradiated samples was only significantly greater than the UVA-irradiated samples for wavelengths less than 340 nm. The greater efficiency of UVC radiation for decreasing the absorbance of HV MIEX over a broad spectral range indicates that treatment at this wavelength is more efficient in both direct and indirect degradation mechanisms.

The greater efficiency of UVC radiation was also reflected in the loss of absorbance and DOC with increasing average dose (Figure 2). The loss of absorbance at 254 nm and loss of DOC for UVC-treated samples decreased in a non-linear fashion. This phenomenon was not observed for the UVA- and UVB-irradiated samples; however Andrews *et al.* (2000) reported that the change in the absorption coefficient with increasing average dose, for samples irradiated at 310 nm, was non-linear. They found that this non-linear decrease was best represented by a multipool model, where independent pools of chromophores with different quantum yields
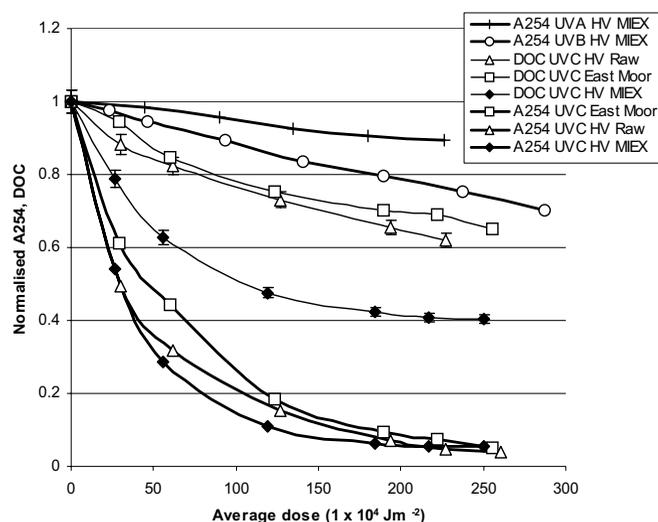
Figure 2 | The change in A_{254} for UVA- and UVB- irradiated HV MIEX and A_{254} and DOC for UVC-irradiated HV MIEX, East Moor and HV Raw with increasing average dose.

and extinction coefficients are photooxidised to form uncoloured organic material.

The non-linear change in absorbance and DOC for UVC-irradiated samples with increasing average dose (H_0) was approximated by using a parallel exponential function shown in Equation 1, where A_1 and A_2 are the weighting factors and k_1 and k_2, the efficiency coefficients. This model was developed by Thomson (2002) and is based on the premise that the chromophores can be divided into fast and slow reacting organics. The change in absorbance and DOC for UVA- and UVB-irradiated samples was best approximated by a single exponential function, most likely an outcome of insufficient variation in A_{254} and DOC to fit the parallel exponential function. The weighting factors and efficiency coefficients for the treated waters, as determined from non-linear least-square fitting to Equation 1, are given in Table 2.

$$y(H_0) = A_{1(0)}\exp(-k_1 H_0) + A_{2(0)}\exp(-k_2 H_0) \qquad (1)$$

The significantly higher efficiency coefficient (k_1) for the UVC-irradiated samples than for UVA- and UVB-irradiated HV MIEX indicates that photons of lower wavelength are more efficiently used by NOM for photoreactions. The increased efficiency is most likely due to the

higher absorption coefficient of NOM at lower wavelengths and more efficient transfer of photons of higher energy from the triplet excited state to intermediate reactive species such as singlet oxygen (Haag *et al.* 1984) resulting in elevated levels of direct and indirect photooxidation, respectively.

The efficiency coefficients, k_1 and k_2, were similar for both loss of absorbance and DOC for UVC-irradiated HV MIEX and HV Raw; the only difference was that HV MIEX had a higher weighting factor for the fast reacting organics. This corresponds with HV MIEX being an isolate of HV Raw; the difference in the sample characteristics were due to preferential isolation of charged, high molecular weight and coloured organics by the MIEX® resin. Therefore, it is possible that similar chromophores are present in both HV Raw and HV MIEX, however at proportionally higher concentrations in HV MIEX as also shown by the difference in the SUVA ratio. The East Moor sample had significantly lower k_1 values for both A_{254} and DOC loss than HV Raw and HV MIEX, indicating that the significantly higher concentration of dissolved iron in East Moor did not lead to more efficient loss of absorbance and DOC. This is in contrast to findings by some authors that the presence of dissolved iron and iron complexes increased the mineralisation of NOM (Gao & Zepp 1998; Bertilsson & Tranvik 2000). This discrepancy may be because the effect of dissolved iron on the loss of absorbance and DOC is significantly less than other contributing factors; however, further work is required to ascertain the possibility of this scenario.

Despite extensive phototransformation of the UV-absorbing compounds by UVC radiation, complete mineralisation was not achieved for all samples. Mineralisation was greatly retarded after extensive treatment (average dose $>120 \times 10^4$ J m^{-2}), with DOC removals of 36%, 40% and 72%, for East Moor, HV Raw and HV MIEX, respectively. Kulovaara *et al.* (1996) and Opsahl & Benner (1998) also observed a reduction in the mineralisation rate after extensive UVC-irradiation of NOM in natural water and for photooxidation of lignin in river water by sunlight, respectively. Opsahl & Benner suggested that the retarded mineralisation rate might either be because a fraction of the dissolved lignin is resistant to photooxidation, or because of the loss of

Table 2 | The weighting factors and efficiency coefficients for the change in normalised A_{254} and DOC with average dose for UVA-, UVB- and UVC-irradiated NOM samples

A_{254}	$A_{1(0)}$ (cm^{-1})	k_1 (J m^{-2})	$A_{2(0)}$ (cm^{-1})	k_2 (J m^{-2})	R^2
UVA HV MIEX	1	4.842×10^{-8}			0.992
UVB HV MIEX	1	1.28×10^{-7}			0.997
UVC HV MIEX	0.63	3.79×10^{-6}	0.37	9.38×10^{-7}	0.999
UVC HV Raw	0.55	3.79×10^{-6}	0.45	9.60×10^{-7}	0.999
UVC East Moor	0.65	2.00×10^{-6}	0.35	7.763×10^{-7}	0.997
DOC	$A_{1(0)}$ (mg l^{-1})	k_1 (J m^{-2})	$A_{2(0)}$ (mg l^{-1})	k_2 (J m^{-2})	R^2
UVA HV MIEX	1	2.04×10^{-8}			0.988
UVB HV MIEX	1	4.68×10^{-8}			0.964
UVC HV MIEX	0.49	2.05×10^{-6}	0.51	9.68×10^{-8}	0.999
UVC HV Raw	0.15	2.35×10^{-6}	0.85	1.36×10^{-7}	0.998
UVC East Moor	0.2	1.43×10^{-6}	0.8	7.68×10^{-8}	0.982

photochemical chromophores. The latter proposal is more likely to explain the observations in this study, as the retarded mineralisation rate of UVC-irradiated HV MIEX, HV Raw, Horsham and East Moor corresponded with the loss of the UV-absorbing organics ($A_{254} < 0.005$). This confirms that degradation of NOM by UV radiation follows photochemical processes, with the degradation dependent on the rate of absorption of radiation and the efficiency with which photons are utilised by the reacting system.

Previous studies have shown that photooxidation of NOM resulted in the formation of low molecular weight by-products (Mopper & Stahovec 1986; Amador *et al.* 1989; Allard *et al.* 1994; Pettersson & Rahm 1996; Frimmel 1998; Opsahl & Benner 1998; Schmitt-Kopplin *et al.* 1998; Win *et al.* 2000). However, these studies did not establish the relative sizes of the products of UVA-, UVB- and UVC-irradiated NOM.

The untreated HV MIEX sample was peakfitted with six apparent molecular weight fractions with peaks at 264,

374, 682, 967, 1,310 and 1,893 Da (Figure 3). Regardless of the irradiation wavelength, photooxidation resulted in the fragmentation of the NOM samples into lower molecular weight fractions of similar size as shown by the peaks fitted to the chromatograms of UVA-, UVB- and UVC-irradiated HV MIEX samples (Figure 3). Frimmel (1998) also reported that HPSEC analysis of UVA- and UVB-irradiated samples indicated that similar size fractions formed after both treatments.

Comparison of the change in relative area of the fitted fractions indicated that there was a sequential decrease in the large molecular weight fractions with a concomitant increase in the small molecular weight fractions for the UVA-, UVB- and UVC-irradiated HV MIEX samples (Figure 4). For UVA-irradiated HV MIEX, after absorption of 134×10^4 J m^{-2} of energy, there was a significant decrease in the 1880 fraction from 67 to 13% with an associated increase in the 1320 fraction from 18 to 42%. With further treatment (average dose, 271×10^4 J m^{-2}), a decrease in the relative area of this fraction from 42 to
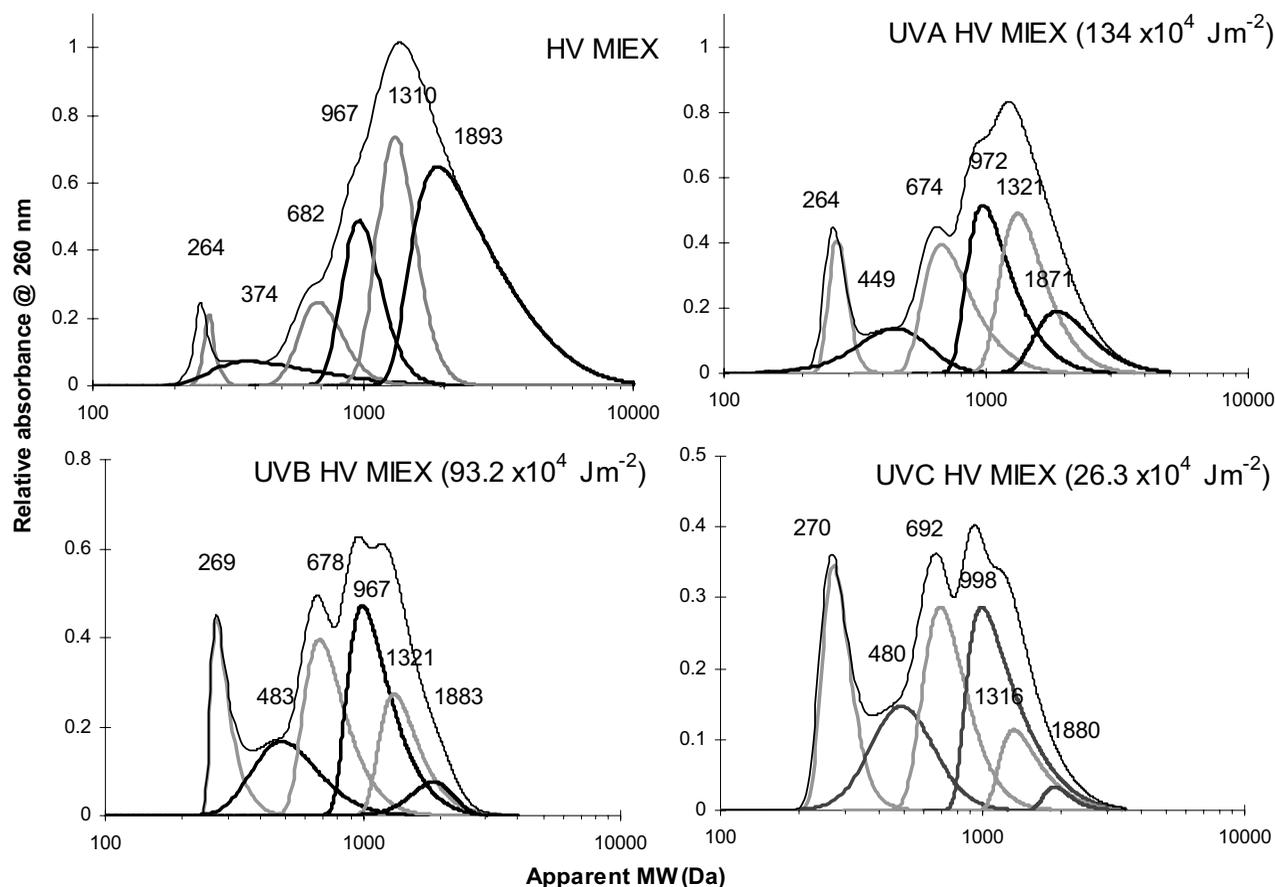
Figure 3 | The peak-fitted HPSEC chromatograms for untreated, UVA-, UVB- and UVC-irradiated HV MIEX.

27% was observed along with an increase in the relative area of the 990 fraction from 22 to 41%. A similar trend was observed for the UVB-treated HV MIEX, however at lower energy doses. The 1320 fraction made the highest contribution of 38% after treatment with an average dose of 46.1×10^4 J m^{-2}, while the 990 fraction made the highest contribution of 45% after treatment with an average dose of 140×10^4 J m^{-2}. UVC-irradiated HV MIEX gave the greatest fragmentation for the least dose; the highest fraction was the 990 fraction (40%) after 26.3×10^4 J m^{-2}, followed by the 670 fraction (42%) after 120×10^4 J m^{-2}. With extended treatment, all other fractions except the 990 and 270 Da fractions decreased to a minimum. Amador *et al.* (1989) also observed a similar trend of sequential degradation for the photooxidation of [^{14}C]-labelled humic acid, where with increasing UVA-

irradiation the radioactivity of [^{14}C] glycine-humic acid shifted to progressively lower molecular weight fractions.

Decreased average molecular weight has been correlated with increased bacterial growth for UV-irradiated NOM by a number of researchers; low molecular weight carboxylic acids, aldehydes and ketones were named as potential bacterial substrates (Herndl *et al.* 1997; Moran & Zepp 1997; Bertilsson & Tranvik 1998). Schmitt-Kopplin *et al.* (1998) determined that the proportion of phenol subunits and low molecular weight carboxylic acids increased in UVB-photooxidised humic and fulvic acids. Biologically active low molecular weight keto acids and aldehydes have been identified in UVC-irradiated humic and fulvic acids (Corin *et al.* 1996), and low molecular weight organic acids identified in sunlight-treated and UVA-, UVB- and UVC-irradiated NOM samples (Allard
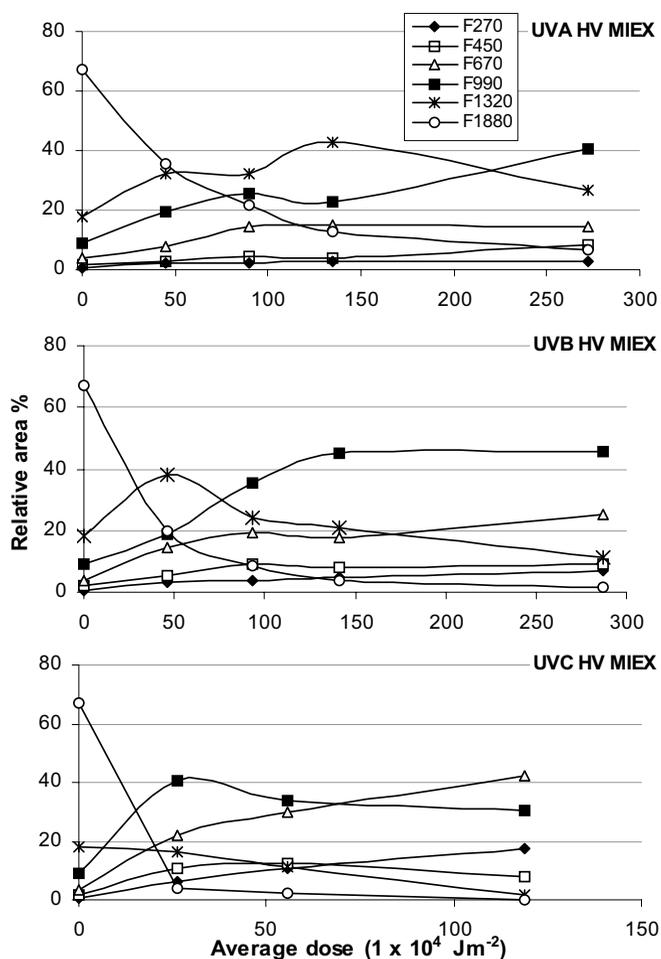
Figure 4 | The change in the relative areas with average dose of the peakfitted molecular weight fractions for UVA-, UVB- and UVC-treated HV MIEX.
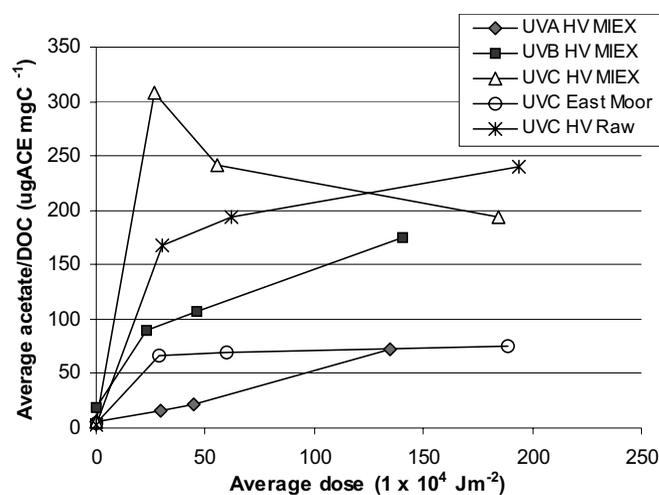

Figure 5 | Variation of the average acetate/DOC values with average dose for UVA-, UVB- and UVC-irradiated HV MIEX and UVC-irradiated HV Raw and East Moor.

et al. 1994; Dahlen *et al.* 1996; Bertilsson & Tranvik 1998; Thomson *et al.* 2002).

For this study, treatment by all wavelengths was also found to increase the biodegradability of NOM as shown by significant increases in the specific acetate ratios with increasing dose for all treated samples (Figure 5). Even samples with only minor decreases in A_{254} and DOC, such as the HV MIEX samples irradiated with UVA or UVB, had specific acetate values greater than 70 μgACE mgC^{-1} and average acetate values significantly greater than the biostable classification of 80 μg l^{-1} (Withers & Drikas 1998). These samples were found to have greater than 30% decrease in the average molecular weight, indicating that

fragmentation had occurred with the production of lower molecular weight compounds. Of all the treated samples, only UVC-irradiated HV MIEX demonstrated significant decreases in acetate values and specific acetate ratios where an initial peak in the ratio at 300 μgACE mgC^{-1} decreased to 200 μgACE mgC^{-1} with further treatment. This result correlates with the low residual DOC for this sample and indicates that oxidation of bacterially assimilable compounds to CO_2 or biostable organics can occur. It should also be noted that even UVC-irradiated HV MIEX, HV Raw and East Moor samples with minimal A_{254} and up to 60% removal of DOC (average dose $>200 \times 10^4$ J m^{-2}) could not be classified as biologically stable indicating that compounds resistant to UVC-radiation are highly biodegradable.

The THMFP for UVA- and UVB-irradiated HV MIEX samples increased by 28% (262–337 μg l^{-1}) and 18% (262–311 μg l^{-1}), respectively, during the treatment time; a linear increase in the specific THMFP (THMFP/DOC) was observed with increasing average dose (Figure 6). The UVC-irradiated HV MIEX differed from UVA- and UVB-irradiated HV MIEX in that the initial small increase in THMFP (262–271 μg l^{-1}) was followed by a significant reduction to 179 μg l^{-1} for extended treatment. This decrease was found to correlate with a significant decrease in DOC as shown by the lack of change in specific
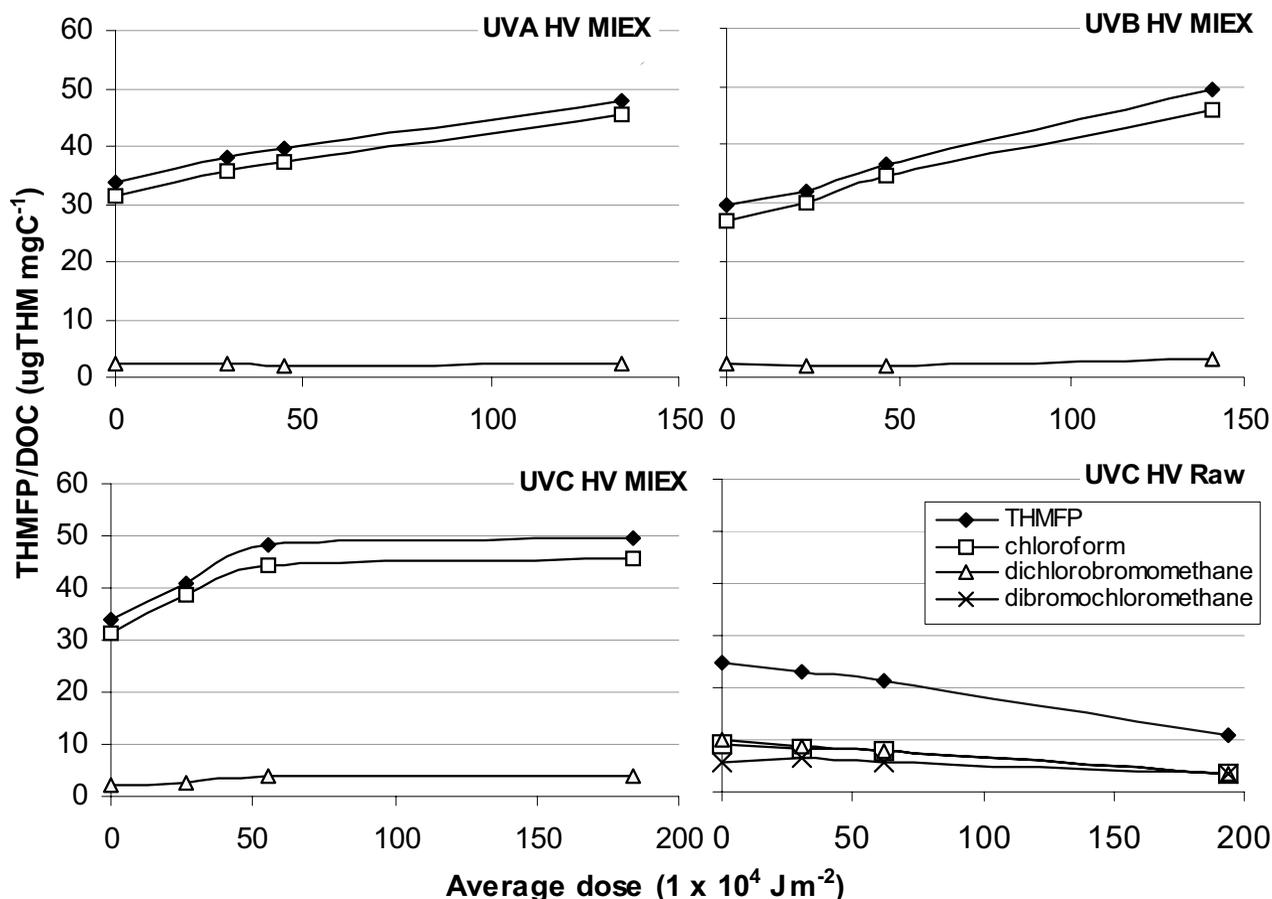
Figure 6 │ Variation of the THM/DOC species with average dose for HV MIEX treated with UVA, UVB and UVC radiation and HV Raw treated with UVC radiation.

THMFP. The increase in THMFP for UVA-, UVB- and UVC-irradiated HV MIEX samples demonstrates that photooxidation and fragmentation of NOM results not only in increased biodegradability, but also increased chlorine reactivity. Further treatment was also shown to decrease this reactivity as shown by the decrease in THMFP for UVC-irradiated HV MIEX samples (average dose $>56 \times 10^4$ J m^{-2}). Li *et al.* (1996) reported a similar trend in the THMFP for UVC-treated humic acid.

Potential chlorine active compounds in NOM include aromatic structures activated with -OH groups (Rook 1976) that can be degraded to unsaturated carboxylic acids with oxidation. Evidence for these aromatic oxygenated compounds being formed in UVC-irradiated aquatic NOM was reported by Corin *et al.* (1996) who found that aromatic hydroxycarboxylic acids and aromatic car-

boxylic acids increased with low UV doses, but declined with further irradiation. The THMFP and specific THMFP were lower for all UVC-irradiated HV Raw samples, decreasing from 180 to 41 μg l^{-1}. The decrease indicates that there was no formation of reactive precursor compounds; however, this may be due to the formation and subsequent degradation of such compounds before the initial sample was analysed. The difference in specific THMFP ratios for HV MIEX and HV Raw can be attributed to the fact that HV MIEX has a higher proportion of aromatic and conjugated type compounds than HV Raw, as indicated by the respective colour (70.9 cf. 12.7 HU) and SUVA values of these samples (3.7 cf. 1.9 m^{-1} mg^{-1}·l). Aromatic and conjugated compounds have been implicated as potential THM precursor compounds (Reckhow *et al.* 1990) and a good correlation

between the colour of the NOM samples and the formation of THM compounds has been observed (Oliver & Thurman 1983).

For the untreated and UVA-, UVB- and UVC-irradiated HV MIEX samples, chloroform was the largest contributor to the THMFP, with a minor contribution from the dichlorobromomethane and no contribution measured from the dibromochloromethane (Figure 6). In contrast, the THMFP speciation for the untreated HV Raw sample showed similar contributions from chloroform, dichlorobromomethane and dibromochloromethane. The difference in the speciation between HV Raw and the isolate HV MIEX is likely to be due to lower levels of the bromide anion in HV MIEX, as indicated by the significantly lower conductivity of the isolate.

CONCLUSIONS

The normalised UV spectra for UVA-, UVB- and UVC-irradiated NOM samples showed loss of absorbance over the entire spectra with the highest regions of loss corresponding to the output wavelength of the lamps. The UVC-irradiated sample had the highest loss across the entire spectrum for the same average dose, indicating better efficiency for both direct and indirect photooxidation mechanisms.

Similar molecular weight fractions were peakfitted to the HPSEC chromatograms of UVA-, UVB- and UVC-irradiated HV MIEX samples. It was proposed that irrespective of the irradiation wavelength, similar size molecular products were formed. Photooxidation of the NOM samples appeared to occur in a sequential fashion, with the decrease in high molecular weight fractions associated with an increase in the lowest molecular weight fraction.

UV-treatment by all wavelengths resulted in increased BRP, with average acetate values greater than the bio-stable classification of 80 μg l^{-1}. The different THMFP results obtained for the UV-irradiated HV MIEX and UVC-irradiated HV Raw, showing both the formation and degradation of THM precursor compounds, indicated that formation of disinfection precursor compounds with

UV treatment is dependent on the UV dose and the characteristics of the NOM sample.

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