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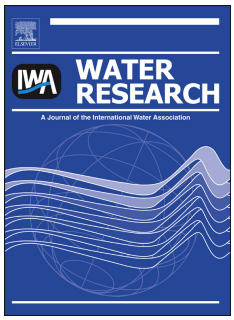

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Chemical and Biological Oxidation of NOM surrogates and effect on HAA Formation

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Abstract

Formation of disinfection by-products (DBPs) can be controlled by removal of disinfection by-product precursors before disinfection. Variable success has been reported, depending on the treatment used and water tested. Chemical and biological oxidation are candidate technologies to control DBP formation. Given the uncertainty over the identity of DBP precursors, the use of surrogates of natural organic matter (NOM) allows fundamental probing of the links between compound character, removal and DBP formation. Nine compounds were chosen to represent NOM and their removal by two advanced oxidation processes (AOPs), UV-C irradiation and biological treatment compared while haloacetic acid (HAA) formation before and after treatment was measured. Although AOPs were able to fully remove all compounds, incomplete mineralisation led to increased HAA levels, dramatically in the case of two amino

acids. Biological treatment was effective in removing amino acids but also moderately increased the HAA formation potential (HAAFP) of hydrophilic compounds. These findings indicate waters with high amino acid concentrations will be susceptible to raised HAA levels following AOP treatment and careful process selection for HAA control is required in such cases.

Key Words HAAs, AOPs, biotreatment, NOM, treatability

Introduction

The link between organic matter in drinking water and formation of disinfection by-products (DBPs) after chlorination was first made by Rook in 1974. Since then there has been a steady accumulation of literature on the health risks and formation of DBPs and how to minimise their presence in drinking water. Two classes of DBPs, the trihalomethanes (THMs) and haloacetic acids (HAAs), are considered to be the dominant DBPs on a weight basis in potable water (Krasner et al., 2006). It is established that many DBPs are mutagens, carcinogens or toxicants (Muellner et al., 2007). Some species are regulated to limit their exposure to humans, for example limits set by the US Environmental Protection Agency are 80 μg/L for THMs and 60 μg/L for HAA_5; while the UK limit for THM_4 is 100 μg/L. It is anticipated that future regulations in the UK may become more stringent and include a wider range of DBPs, including the HAAs.

Natural organic matter (NOM) acts as a precursor to DBPs. NOM is a complex and variable mix of organic compounds of biological and terrestrial origin, with a catchment-specific composition. It is often split into hydrophobic and hydrophilic fractions. There is conflicting literature regarding which NOM

types are predominant as precursors of THMs and HAAs. Some researchers report that hydrophilic/polar NOM is more prevalent in the formation of HAAs than THMs (Hwang et al., 2001), whereas others implicate hydrophobic/non-polar NOM (Liang and Singer, 2003). Knowledge of the identity of DBP precursors would allow the selection of appropriate process/es for their removal. As large, hydrophobic NOM is more amenable to removal by conventional treatments than small, hydrophilic NOM (Lee et al., 2003), where the latter has a higher HAA formation potential (HAAFP) than the former minimising HAA concentrations will be more difficult.

The advent of DBP regulations has motivated some water utilities to reduce chlorine doses or use alternative disinfectants in an attempt to reduce DBP levels (Singer, 1999). Of the other routes for controlling DBPs, removal of precursors before disinfection has received most attention (Singer, 1999). For example, the following reductions in HAAFP following treatment have been reported. Coagulation: 15-78% (Singer and Bilyk, 2002); biofiltration: -11-28% (Toor and Mohseni, 2007); nanofiltration: 67-97% (Allgeier and Summers, 1995) and advanced oxidation processes (AOPs): -74-74% (Chin and Bérubé, 2005; Toor and Mohseni, 2007). Levels of removal vary widely, while biofiltration and AOPs can actually increase HAA formation. It follows that removal of DBP precursors depends on their susceptibility to different types of treatment.

While most treatments are selective for certain NOM groups, AOPs are comparatively non-discriminatory (Crittenden et al., 2005). NOM is oxidised through a complex series of reactions initiated by the hydroxyl radical (·OH). Since ·OH is a very powerful oxidant it reacts with a wide spectrum of NOM of both hydrophobic and hydrophilic character. Rate constants for reactions between

76 ·OH and NOM have recently been directly measured at 1-5 x 10^8 M^{-1} s^{-1} (Westerhoff et al., 2007), some three to four orders of magnitude higher than for
78 other oxidants (Crittenden et al., 2005).

Since the precise identity of precursors in natural waters is largely
80 unknown, the use of analogues is attractive as it enables the linking of explicit chemical and physical properties to treatability and formation of DBPs. The aim
82 of this study was to compare HAA formation from nine NOM surrogates (Table 1) before and after treatment. The NOM surrogates were chosen from the NOM
84 groups listed by Croué et al. (2000), especially low molecular weight (MW) and hydrophilic NOM, which it was anticipated would be representative of a post-
86 coagulation organic residual. Specifically, amino acids are important components of algae-rich waters (Scully et al., 1985). The surrogates have been classified as
88 neutral or anionic at ambient pH based on their pK_a values and hydrophobic (log $K_{OW}>0$) or hydrophilic (log $K_{OW}<0$).

90 Two AOPs were used as treatments in comparison with UV-C oxidation and biological oxidation. The first AOP was UV/H_2O_2, where hydroxyl radicals
92 are formed from the photolysis of H_2O_2 by UV light. The second was vacuum UV (VUV), where radiation at 185 nm is able to produce ·OH directly from water
94 (Thomson et al., 2004). UV-C photo-oxidation is initiated when photons are absorbed by NOM, leading to direct and/or indirect photo-transformation (Corin
96 et al., 1996). The final treatment was biologically-active sand, where microbial degradation and adsorption are the principal removal mechanisms.

98 -Insert Table 1-

Materials and Methods

Representative molecules (Table 1) were obtained from Fisher Scientific and Univar/Ajax Firechem at analytical purity or above.

UV-C, UV/H_2O_2 and VUV experiments were undertaken in the annular reactor detailed by Thomson et al. (2004) and Buchanan et al. (2006). The N-lamp used for UV-C and UV/H_2O_2 experiments emitted at 254 nm, while the H-lamp used for VUV experiments emitted at both 254 nm and 185 nm and produced ·OH from direct photolysis of water, without the need for chemical addition. Average fluence values of 12.95 mJ s^{-1} cm^{-2} for the N-lamp and 17.8 mJ s^{-1} cm^{-2} for the H-lamp were obtained by hydrogen peroxide and methanol actinometry (Béltran et al., 1995; Heit et al., 1998).

Dissolved organic carbon (DOC) was determined with a Sievers 820 TOC analyser. Initial concentration of representative molecules was 7.5 mg L^{-1} as compound. Mass extinction coefficients of 10 mg C L^{-1} solutions were measured with a Jenway 6505 spectrophotometer and Shimadzu TOC-5000 A analyser.

For the UV/H_2O_2 experiments H_2O_2 was added at 68 mg L^{-1} (2 mM). The concentration of hydrogen peroxide solution was determined by potassium permanganate titration, with potassium oxalate used to standardise the permanganate solution, as described by Harris (1998).

The method of Joret and Levi (1986) for biodegradable dissolved organic carbon (BDOC) was used to assess the susceptibility of samples to biological treatment. Duplicate samples were contacted with biologically-active sand for 7-10 days, with sodium acetate as a positive control to verify biological activity. The sand sample came from the Yarra River, Victoria, Australia.

HAAFP of untreated and treated representative molecules was determined at the Australian Water Quality Centre, Adelaide, Australia, using gas chromatography with electron capture detection (GC-ECD). Treated samples were prepared so their DOC was approximately half the initial value, based on existing data. For the UV/H_2O_2 samples residual hydrogen peroxide was quenched with the enzyme catalase obtained from *Aspergillus niger*, at a dose of 60 μL L^{-1} (317 units L^{-1}) sample. The samples were shaken at 75 oscillations min^{-1} until visible gas generation ceased (5-6 hours). The chlorination period was 4 hours at 35°C and 7 HAAs were quantified: monobromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, monochloroacetic acid, dibromoacetic acid, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). Samples were quenched with ammonium chloride and quantified with USEPA method 552. For DCAA and TCAA, the major HAAs recorded, the limit of detection was 0.054 μg L^{-1}, the limit of reporting 1 μg L^{-1} and the precision of the method 3.4% and 3.5% relative standard deviations respectively.

The HAAFP of oxalic acid and L-aspartic acid were measured as a follow-up study at Cranfield University, UK by GC-ECD and an adapted version of USEPA Method 552.3. The chlorination period was 24 hours at 20°C±2°C with a chlorine dose 35 M/M of compound, duplicate samples were tested and all 9 HAAs were quantified: as above plus dibromochloroacetic acid and tribromoacetic acid

Results

Degradation of model compounds by the two AOPs occurred far more rapidly than by UV-C, with nearly complete removal possible for the majority of

compounds after 50 J cm^{-2} irradiation (Figure 1). To illustrate mean DOC removal for the nine compounds after the application of 47-48 J cm^{-2} was 97%, 91% and 13%, for VUV, UV/H_2O_2 and UV-C respectively (Table 2). Corresponding levels at a lower dose of 21 J cm^{-2} were 58%, 78% and 6% respectively, indicating that UV-C has limited treatment capacity and differences exist between VUV and UV/H_2O_2. The removal by UV/H_2O_2 compares well with Goslan et al. (2006), who reported DOC reduction of 78% for a reservoir water at a similar UV-C dose and identical H_2O_2 dose (UV-C 22 J cm^{-2}, H_2O_2 2 mM). The UV-C data are consistent with Thomson et al. (2002), who reported a DOC reduction of 16% for a raw water at UV-C fluence of 26 J cm^{-2}, thus underlining the similar treatability of the surrogates compared with a natural water. Overall these results illustrate the two AOPs were approximately 8 times more effective than UV-C at removing these compounds at a fluence of 47-48 J cm^{-2}. Buchanan et al. (2004) previously found VUV to be approximately 6 times more effective than UV-C in treating a raw water.

-Insert Figure 1-

-Insert Table 2-

Removal by UV-C was linked to hydrophobicity. Tannic acid and resorcinol were the most treatable compounds, with DOC removals of 95±5% and 98±5% respectively after a dose of 186 J cm^{-2} (0.52 $kWhm^{-2}$), compared with removals of 24-59±5% for the other molecules (Table 2). This can be explained by the higher mass extinction coefficients of resorcinol and tannic acid: 0.006 and 0.045 cm^{-1} L mg C^{-1} respectively, compared with the other molecules, all 0.000 cm^{-1} L mg C^{-1}. It is interesting that those compounds with very limited capacity

for UV-C absorption were still removed to a moderate,extent, albeit at high UV-C doses. UV photo-oxidation can proceed from direct photo-transformation or indirect photo-transformation, where activated NOM can transfer energy to form excited photo-reactants such as oxygen, which in turn can react with NOM (Corin et al., 1996). This indicates even the hydrophilic compounds were able to absorb enough energy to initiate these types of reactions.

The biodegradability of samples as measured by removal by biologically-active sand in the BDOC test was grouped according to organic type, with the amino acids demonstrating high DOC reductions of 80-91% contrasting with 23-56% for the other samples (Figure 2, Table 2). Similarly high removal of amino acids by biological activated carbon (BAC) has previously been reported by Jadas-Hécart (1989), with an average removal of 70%. Supporting this view Hwang et al. (2001) stated biodegradation is effective for removing non UV-absorbing low molecular weight acids. Given this information the aromatic character of tannic acid and resorcinol may explain their lower biodegradability; however the explanation for the two carbohydrates is less obvious. Charge does not seem to be a factor, since of the amino acids L-glutamic and L-aspartic acids were charged under ambient pH conditions (Table 2), instead differing chemical functionality is a more likely reason. Nor does size correlate with biodegradability. It has been stated that small compounds are expected to be more biodegradable as they are more easily transported across the cell membrane (Leisinger, 1981), however in this study there was no such relationship, even for compounds of the same chemical type (Table 2).

For the two AOPs there was no direct link between hydrophobicity and removal, which accords with Crittenden et al. (2005) who reported AOPs were

198 non-selective processes for removing a range of organic compounds. To illustrate, although the hydrophilic compound glycine was the slowest compound to
200 degrade, as quantified by pseudo first-order rate constants, the hydrophobic tannic acid was also initially slow to be mineralised (0-11 J cm^{-2}), as evidenced by the
202 convex shapes of its VUV degradation plot (Figure 1b and Table 2). It is possible the initially slow degradation of tannic acid by UV-C and VUV can be explained
204 by its larger size, which means multiple reactions were necessary before mineralisation was attained.

206 After 48 J cm^{-2} of VUV irradiation, all compounds except for glycine and L-leucine, which both recorded DOC reduction of 88±5%, were degraded by over
208 90%. For the UV/H_2O_2 system three compounds had a DOC reduction of under 90% after 47 J cm^{-2} irradiation: L-aspartic acid in addition to L-leucine and
210 glycine, the latter with the lowest removal of 55±5%. Kinetic analysis of the removal data revealed similar trends. Glycine was the slowest compound to
212 degrade by VUV, with an initial pseudo first-order rate constant 0.043 J^{-1} cm^{-2}; compared with 0.044-0.116 J^{-1} cm^{-2} for the other compounds, and also by
214 UV/H_2O_2: rate constants of 0.016 J^{-1} cm^{-2}, compared with 0.045-0.14 J^{-1} cm^{-2} respectively. The degradation of amino acids by AOPs has previously been
216 studied in some detail by Le Lacheur and Glaze (1996) who reported glycine to be less reactive than the other amino acids, as shown by its lower rate constant for
218 the reaction with the hydroxyl radical of ~ 10^7 M^{-1} s^{-1} compared with serine at 3.2 x 10^8 M^{-1} s^{-1}. The first step in these reactions is H-abstraction alpha to the amino
220 group, while reactivity is explained in terms of the stability of the radical intermediate thus formed. With the exception of glycine which forms a less stable
222 secondary radical, the other amino acids studied all form tertiary radicals. After

186 J cm^{-2} of UV-C exposure it was again glycine and L-leucine which were the most recalcitrant, with removals of 24±5% and 31±5% respectively. The similar ranking for the amino acid kinetic constants across the three UV-based systems, with glycine always the slowest to degrade, implies there may be common mechanistic pathways between UV-C and the AOPs, i.e., that the same or similar intermediates were formed. Since degradation by UV-C relies upon absorption of photons rather than reaction with •OH, as is the case for AOPs, this is an interesting observation. Alternatively it may be that the slower degradation of glycine by UV-C was a result of its smaller size (Table 1).

Tannic acid was the only compound to have significantly high HAAFP at 155 µg $mgDOC^{-1}$, with aspartic acid and resorcinol the next highest at 21 and 14 µg $mgDOC^{-1}$ respectively (Figure 3). In contrast, HAAFP of all other compounds was 0-1 µg $mgDOC^{-1}$. Resorcinol and tannic acid contain activated aromatic functionalities which react strongly with chlorine and can produce THM and HAAs (Singer, 1999).

-Insert Figure 3-

Reckhow and Kim (2008) found L-aspartic acid to be one of a small number of amino acids to produce high DBP levels, with DCAA formation of 387 µg $mgDOC^{-1}$. To investigate whether differences in chlorination time, between 4 h in this study and 48 h (Reckhow and Kim, 2008), could account for this discrepancy in HAA formation we measured the HAAs formed from L-aspartic acid after 1, 4 and 24 h chlorination. The respective values were 100±68, 82±2 and 671±30 µg $mgDOC^{-1}$, thus appearing to confirm that longer chlorination

248 periods are necessary for L-aspartic acid to achieve maximum HAA formation. The high DCAA formation of L-aspartic acid was explained by Hureiki et al. 250 (1994), who proposed a mechanism where 3-oxopropanoic acid is the main intermediate resulting from chlorination. In turn 3-oxopropanoic acid is a β-keto 252 acid structure similar to those reported as being high DBP formers by Dickenson et al. (2008). The latter study proposes β-keto acid structures as possible slow- 254 reacting DCAA precursors, where DCAA formation after 5 minutes is low relative to that after 24 h. Since it is likely DCAA formation from L-aspartic acid 256 will be slower still due to the extra steps required to form the β-keto acid intermediate, this supports the idea that higher DCAA yields require longer 258 chlorination times.

The HAAFP of the hydrophilic compounds increases after treatment, 260 especially by the UV based systems. Partial biodegradation increased the HAAFP of most of the representative molecules, although the increases were generally 262 more modest. L-glutamic acid illustrates this most strikingly, from an untreated value of 1 μg $mgDOC^{-1}$ (Figure 3) the HAAFP rises by 5, 50, 52 and 36 μg 264 $mgDOC^{-1}$ after biotreatment, UV-C VUV and UV/H_2O_2 respectively (Figure 4). Thus the UV-based systems all caused a sharp increase in HAAFP. This shift to 266 enhanced HAA levels post-treatment has literature precedent . In their study using UV-H_2O_2 and/or biological activated carbon (BAC) to treat a raw surface 268 water, Toor and Mohseni (2007) found the AOP could increase DCAA formation potential (DCAAFP). UV/H_2O_2 treatment at UV fluence of 3000 mJ cm^{-2} and 270 H_2O_2 concentration of 10-20 mg L^{-1} gave reductions in TCAA formation potential (TCAAFP) of 69% and THMFP of 73%, but DCAAFP increased by 74%. Note

that all values were reported in μg L^{-1} rather than μg $mgDOC^{-1}$. BAC alone did not provide significant reduction in DCAAFP, TCAAFP or THMFP.

-Insert Figure 4-

For the two hydrophobic compounds the pattern was somewhat different compared with the hydrophilic compounds (Figures 3 and 4). Treatment of tannic acid caused its HAAFP to decrease from an untreated value of 155 μg $mgDOC^{-1}$ (Figure 3) by 7, 69, 101 and 110 μg $mgDOC^{-1}$ after biotreatment, UV-C VUV and UV/H_2O_2, respectively (Figure 4). Thus for tannic acid AOPs caused the greatest fall in HAAFP. Resorcinol has an untreated HAAFP of 14 μg $mgDOC^{-1}$ (Figure 3) which changes by 28, 81, 20 and -1 μg $mgDOC^{-1}$ following biotreatment, UV-C VUV and UV/H_2O_2 respectively (Figure 4). Thus for resorcinol UV-C effected the greatest increase in HAAFP.

It has been established that DCAA and TCAA,, which were the dominant HAAs in this study, have disjunct formation mechanisms (Reckhow and Singer, 1986). Therefore it is interesting to observe the differing effects that treatment had on formation of the two species. For the hydrophilic species DCAA was largely responsible for the increase in HAAs after treatment. This was exemplified by L-glutamic acid (Figure 5). From an initial value of 1 μg $mgDOC^{-1}$ DCAA rose to 3, 37, 20 and 29 μg $mgDOC^{-1}$ following treatment by biodegradation, VUV, UV/H_2O_2 and UV-C, respectively. Again the behaviour of the hydrophobic molecules differs from that of the hydrophilics. For resorcinol TCAA was most common before treatment: total HAAs 14 μg $mgDOC^{-1}$, TCAA 10 μg $mgDOC^{-1}$ and this dominance was maintained in the biotreated sample: total HAAs 42 μg $mgDOC^{-1}$, TCAA 33 μg $mgDOC^{-1}$ and UV-C treated sample: total HAAs 95 μg

mgDOC^{-1}, TCAA 56 µg mgDOC^{-1}, while in the VUV and UV/H_2O_2 treated
298 samples DCAA was dominant: total HAAs 39 µg mgDOC^{-1}, DCAA 16 µg
mgDOC^{-1} and total HAAs 13 µg mgDOC^{-1}, DCAA 7 µg mgDOC^{-1} respectively.
300 For tannic acid DCAA was the commonest species in the untreated sample with
significant amounts of DCAA and TCAA in all treated samples.

302

-Insert Figure 5-

304 **Discussion**

A notable aspect of the results was the increase in HAAFP of the
306 representative molecules following partial biological and chemical oxidation. In
particular the untreated hydrophilic representative molecules did not form
308 significant amounts of any HAAs, however AOP treatment increased their
DCAAFP. This trend was most marked for two amino acids: L-glutamic acid and
310 L-leucine. Since DCAA was the most problematic HAA species, effort is required
to further elucidate the identity of DCAA precursors and confirm them as AOP
312 products or intermediates. Meanwhile resorcinol, a known reactive THM
precursor (Singer, 1999), behaved differently from the hydrophilic compounds by
314 forming predominantly TCAA, both when untreated and after UV-C irradiation
(Figure 5). There is a support for such a distinction in natural water studies: Liang
316 and Singer (2003) also found DCAA precursors to be less hydrophobic than
TCAA precursors. Mechanistic studies have linked a rise in levels of DCAA to
318 diketone and then aldehyde formation after oxidation (Reckhow and Singer,
1986). Conversely, and in agreement with the resorcinol data, TCAA formation
320 has been likened to THM formation and may proceed through common
intermediates (Reckhow et al., 1990). This information all points towards the idea

322 that post-coagulation/hydrophilic waters can have the potential to form high levels of DCAA.

324 Model compounds with a known high DCAA formation are β-dicarbonyl acid species (Dickenson et al., 2008) and a small number of amino acids, notably 326 aspartic acid and asparagine (Reckhow and Kim, 2008), both of which are probably oxidised to a β-dicarbonyl acid species (Hureiki et al., 1994, Dickenson 328 et al., 2008). Since both mechanistic studies and model compound work suggest β-dicarbonyl acid structures are important in DCAA formation, it is tempting to 330 implicate their formation through oxidation in the raised DCAA levels recorded.

Small acidic compounds are those most commonly identified as oxidation 332 products of NOM. A range of products including mono and dibasic acids and keto acids were semi-quantitatively identified by Corin et al. (1996) following UV 334 irradiation of reference humic and fulvic acids and a surface water. Amongst these were β-dicarbonyl acids, including 3-hydroxypropanoic and 3-oxobutanoic acids, 336 as well as other dicarbonyl acids of unspecified isomer. The reactions of the hydroxyl radical with glycine (Berger et al., 1999) and serine (Le Lacheur and 338 Glaze, 1996) have been previously studied. Both propose a reaction scheme where the initial step is hydrogen abstraction alpha to the amine group. For serine this 340 yields mixed functional keto acids retaining the amino acid backbone, such as ketomalonic acid, 3-hydroxyoxopropanoic acid and dioxopropanoic acid. 342 However, while these three-carbon species contain the β-keto acid moiety they also have a carbonyl group in the alpha position, and thus no hydrogen available 344 for chlorine substitution as necessary in the mechanism of Reckhow and Singer (1986). For glycine, which has a backbone of only two carbons, formation of β-346 keto acid species is not possible by this scheme. The observation that glycine only

experienced minimal HAAFP increases after AOP treatment (Figure 3) supports the idea that β-keto acids are important. For serine the non-specific nature of radical reactions means three-carbon intermediates are unlikely to accumulate, while smaller and more inert products such as oxalic acid may do so (Le Lacheur and Glaze, 1996). Oxalic acid was also tentatively identified as the major product of the glycine reaction scheme. To determine whether oxalic acid might be responsible for the enhanced HAAFP we measured its HAAFP and found it to be 0 μg mg DOC^{-1}. Thus oxalic acid was not responsible for the enhanced HAAFP reported here. More generally simple monobasic acids cited as oxidation products of NOM do not contain functionalities thought to be reactive DBP precursors (Singer, 1999), which also indicates the involvement of other compounds. To summarise, while β-dicarbonyl acid species have been identified as UV products in natural waters, their occurrence as AOP products has still to be confirmed. Thus further work is needed to establish which compounds are key for enhanced DCAA formation and whether β-dicarbonyl acid species are involved.

In water where hydrophilic species contain a significant HAA generating capacity additional treatment may be key to controlling final HAA formation. The successful implementation of any treatment would depend on the specific composition of NOM present, and not solely on the reactive DBP precursors. Since AOPs were found to be capable of degrading both hydrophilic and hydrophobic surrogates, this makes them an attractive option for treatment of the post-coagulation residual, which is largely hydrophilic (Sharp et al., 2006). However, based on these results AOPs carry the risk of increased HAAs, which would need to be investigated in the relevant water under varying AOP doses. It can be inferred this risk will be greater in waters with high concentration of

372 hydrophilic species and especially amino acids. Such waters may well have a high proportion of algal organic matter (AOM) and/or a wastewater influence. Algae
374 are known as an important source of amino acids, and it has been recorded that the protein concentration of different lake waters rose from an average of 0.1-1 mg L^{-1}
376 during an algal bloom (Scully et al., 1985). Caution is advised in such cases. Using AOPs in combination with biotreatment may reduce the risk of increased
378 DCAA. Toor and Mohseni (2007), reported a DCAAFP reduction of 63% from combined UV/H_2O_2 and BAC treatment, contrasting with an increase of 74% for
380 UV/H_2O_2 alone. Such a combination is analogous to the combination of ozone-biological activated carbon, where ozone is used to generate a higher proportion
382 of biodegradable material for removal by the BAC.

In hydrophilic-rich waters biotreatment alone is also a viable process
384 option and has been found to be effective for amino acid removal. Since increases in HAAFP of biologically treated samples were generally less than those caused
386 by UV based oxidation, the risk of raised HAA levels in natural waters is less. However the biologically available DOC content of untreated natural waters is
388 typically only around 15% (Tranvik, 1998: Buchanan et al., 2004), while amino acids only comprise up to 5% of the DOC of raw surface waters (Thurman, 1985).
390 Therefore biotreatment is only likely to reduce DBP formation in cases where highly reactive precursors belong to a readily biodegradable group such as the
392 amino acids and/or pre-treatment has increased the bioavailable content.

The necessity of a high energy input makes UV-C treatment inefficient
394 and expensive for DOC removal at a larger scale. This is especially true where NOM has a low UV-absorbing capacity, as the hydrophilic compounds studied
396 here. Typical UV disinfection practice is 40 mJ cm^{-2} (Thomson et al., 2002) so the

maximum mineralisation observed here (at 186 J cm^{-2}) would not occur during microbial disinfection. Interestingly, these results indicate that exposure of natural water to sunlight (and UV-C), which can involve high energy levels, has the potential to alter the composition of DBP precursors. For example UV-C irradiation of resorcinol can increase levels of TCAA. This idea is given credence by Chow et al., (2008), who studied the impact of simulated sunlight on DBPs. Irradiation of raw waters for 1403 and 5612 J cm^{-2} at 300-800 nm were equivalent to 1 and 4 days of clear summer weather respectively. Under these conditions HAAFP decreased by up to 50%.

Conclusions

1. AOP treatment of L-glutamic acid and L-leucine leads to dramatically increased amounts of HAAs, specifically DCAA
2. Biological treatment is particularly effective at removing amino acids but can also increase HAA formation of hydrophilic compounds
3. UV-C irradiation also has the potential to increase the HAAFP of NOM surrogates
4. Investigation is recommended before AOPs are implemented for HAA control in waters with relatively high amino acid concentrations

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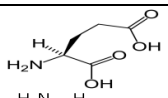
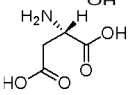
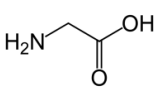
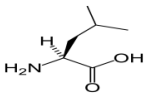
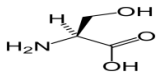
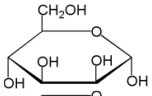
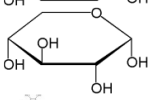
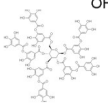
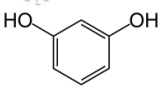
Table 1: Model compound properties

Compound	Structure	log K_{OW}	MW g/mol	pK_a, pK_b, pK_c	Classification	Chemical group	E (254 nm) cm^{-1} L mg C^{-1}
L-Glutamic acid		-3.69	147	2.16, 9.58, 4.15	Hydrophilic anionic	Amino acid	0.000
L-Aspartic acid		-3.89	133	1.95 9.66 3.71	Hydrophilic anionic	Amino acid	0.000
Glycine		-3.21	75	2.34, 9.58, NA	Hydrophilic neutral	Amino acid	0.000
L-Leucine		-1.52	131	2.32, 9.58, NA	Hydrophilic neutral	Amino acid	0.000
L-Serine		-3.07	105	2.13, 9.05 NA	Hydrophilic neutral	Amino acid	0.000
D-Mannose		-3.24	180	12.08, NA, NA	Hydrophilic neutral	Carbohydrate	0.000
D-Xylose		-1.98	150	12.14, NA, NA	Hydrophilic neutral	Carbohydrate	0.000
Tannic acid		13.3	1701	3.2, NA, 8.7	Hydrophobic anionic	Phenolic	0.045
Resorcinol		0.80	110	9.32, NA, 11.1	Hydrophobic neutral	Phenolic	0.006

Note. E = mass extinction coefficient. pK_a, pK_b and log k_{ow} values from USEPA EPI Suite™ for Microsoft® Windows, v 3.2. Washington, DC and Chemspider chemical data base search. Available at: http://www.chemspider.com/Search.aspx (Accessed December, 2008).

Table 2: Results Summary

Compound	UV-C			VUV			UV/H_2O_2			Biodegradation
	% DOC loss		k^1	% DOC loss		k^2	% DOC loss		k^3	Max % DOC loss
	23 J cm^{-2}	186 J cm^{-2}		21 J cm^{-2}	48 J cm^{-2}		23 J cm^{-2}	47 J cm^{-2}		
L-Glutamic acid	10±5	59	0.0103	72 ± 5	102	0.0739	79±5	93	0.0576	80±3
L-Aspartic acid	11±5	61	0.0106	63 ± 5	96	0.0665	76±5	83	0.0352	N/A
Glycine	6±5	24	0.0032	47 ± 5	88	0.0425	28±5	55	0.0156	86±1
L-Leucine	4±5	31	0.0072	35 ± 5	88	0.0436	78±5	89	0.0446	87±1
L-Serine	5±5	51	0.0078	75 ± 5	99	0.1108	88±5	98	0.0871	91±0
D-Mannose	4±5	47		71 ± 5	99	0.1155	90±5	99	0.1092	56±10
D-Xylose	2±5	48		65 ± 5	98	0.094	92±5	100	0.1359	23±31
Tannic acid	-1±5	95		55 ± 5	99	0.1021	83±5	98	0.0884	5±6
Resorcinol	14±5	98		36 ± 5	99	0.0914	87±5	99	0.0941	38±2
Mean	6	57	0.0078	58	97	0.0802	78	91	0.0644	62

k^1: Zero-order rate constant, (0-186 J cm^{-2}), mg C L^{-1} min^{-1} or mg C L^{-1} J cm^{-2}. Only amino acids followed zero-order degradation behaviour
k^2: Initial first-order rate constant (0-48 J cm^{-2}), J^{-1} cm^2
k^3: Initial first-order rate constant (0-47 J cm^{-2}), J^{-1} cm^2

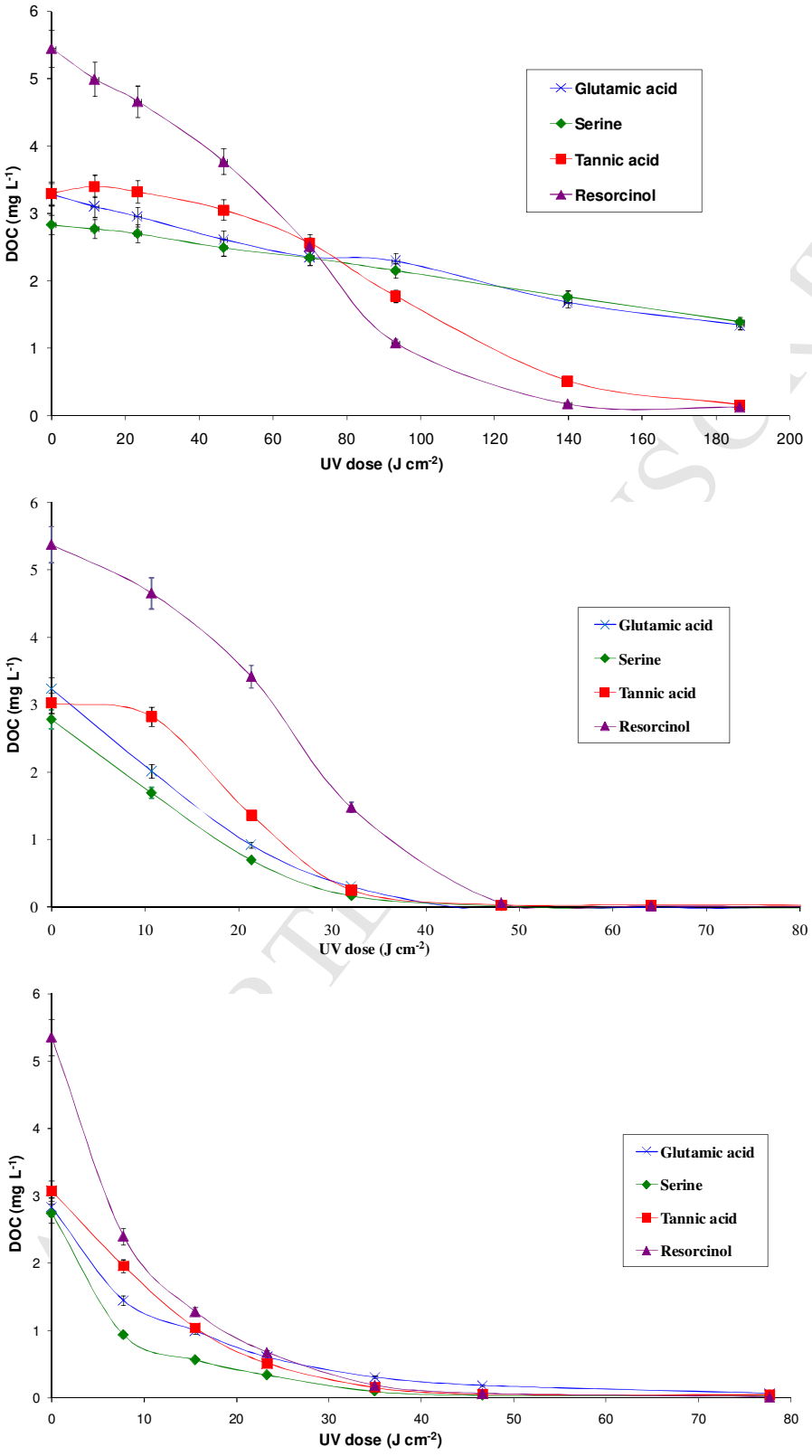


Figure 1 a, b, c: Degradation of selected model compounds by UV-C, VUV and UV/H_2O_2 (from top to bottom respectively).

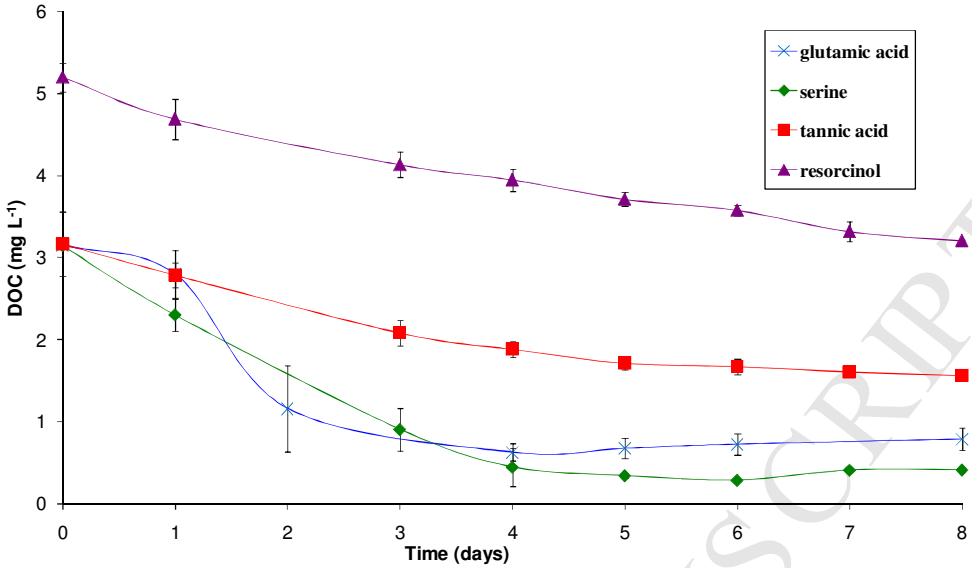


Figure 2: Biodegradation of selected model compounds

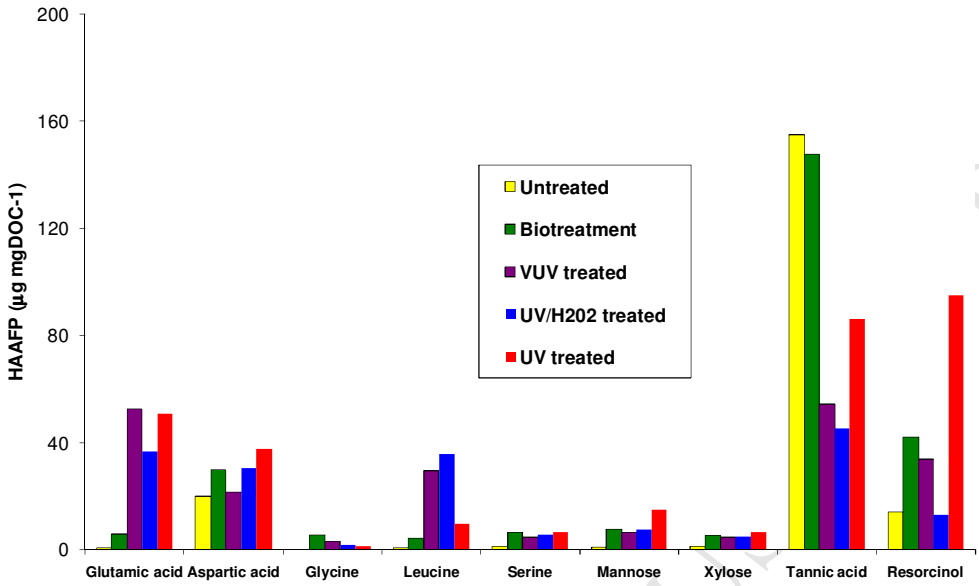


Figure 3: HAAFP (µg mg C^{-1}) of untreated and treated model compounds

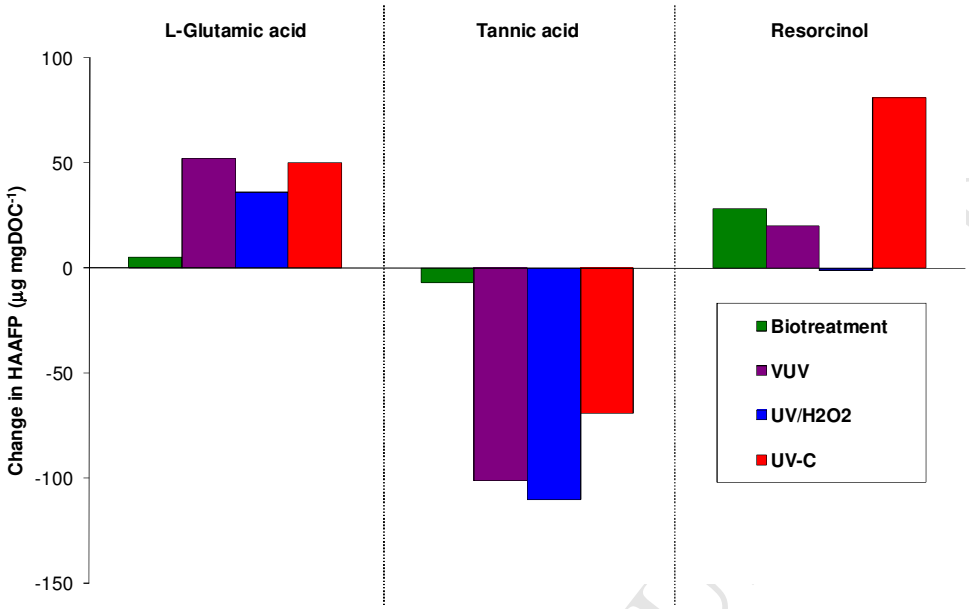
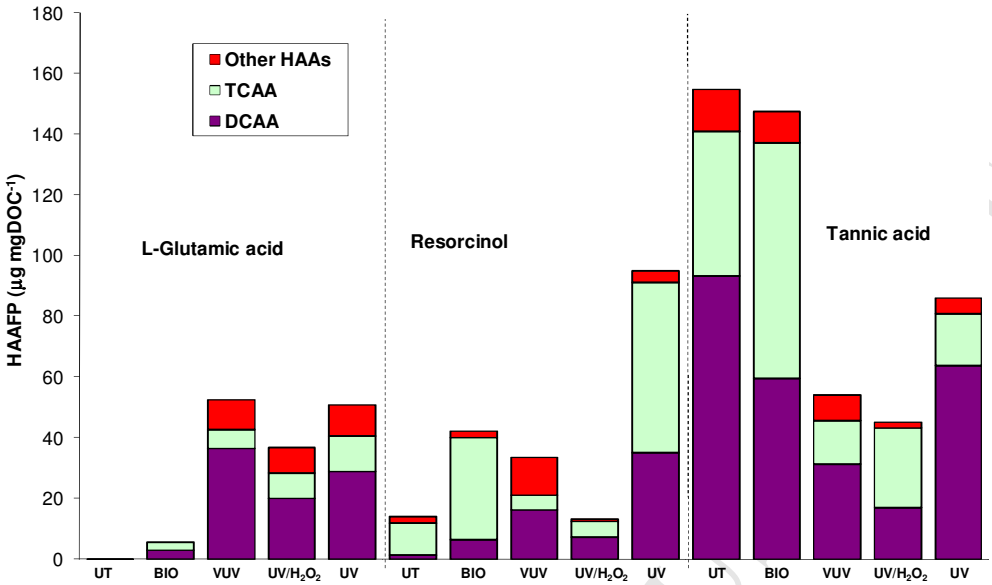


Figure 4: Effect of treatment on HAA formation of L-glutamic acid, resorcinol and tannic acid



Note: UT = untreated; BIO = biodegradation

Figure 5: HAA speciation of untreated and treated L-glutamic acid, resorcinol and tannic acid