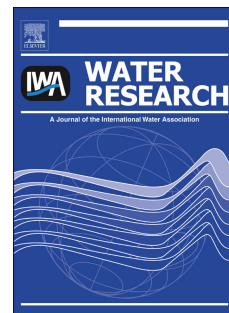


Accepted Manuscript

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

Authors: T. Bond, E.H Goslan, B. Jefferson, F. Roddick, L. Fan, S.A Parsons



PII: S0043-1354(09)00159-6

DOI: [10.1016/j.watres.2009.03.036](https://doi.org/10.1016/j.watres.2009.03.036)

Reference: WR 7330

To appear in: *Water Research*

Received Date: 7 January 2009

Revised Date: 6 March 2009

Accepted Date: 9 March 2009

Please cite this article as: Bond T., Goslan E.H, Jefferson B., Roddick F., Fan L., Parsons S.A. Chemical and Biological Oxidation of NOM surrogates and effect on HAA Formation, Water Research (2009), doi: 10.1016/j.watres.2009.03.036

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Chemical and Biological Oxidation of NOM surrogates and effect on HAA

Formation

2

4 T. Bond^a, t.bond@cranfield.ac.uk E.H Goslan^a, E.H.Goslan@cranfield.ac.uk B.
 Jefferson^{a,*}, B.Jefferson@cranfield.ac.uk F. Roddick^b,
 6 felicity.roddick@rmit.edu.au L. Fan^b, linhua.fan@rmit.edu.au and S.A Parsons^a,
S.A.Parsons@cranfield.ac.uk

8 ^aCentre for Water Science, Cranfield University, Bedfordshire, MK43 0AL, UK

^b School of Civil, Environmental and Chemical Engineering, RMIT University

10 GPO Box 2476V, Melbourne, VIC 3001, Australia

*Corresponding author. Tel.: +44 (0)1234 754813. Fax: +44 (0) 1234 751671

12

Abstract

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

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

32 **Key Words** HAAs, AOPs, biotreatment, NOM, treatability

34 **Introduction**

The link between organic matter in drinking water and formation of
36 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
38 risks and formation of DBPs and how to minimise their presence in drinking
water. Two classes of DBPs, the trihalomethanes (THMs) and haloacetic acids
40 (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,
42 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
44 Protection Agency are 80 µg/L for THMs and 60 µg/L for HAA₅; while the UK
limit for THM₄ is 100 µg/L. It is anticipated that future regulations in the UK may
46 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
48 complex and variable mix of organic compounds of biological and terrestrial
origin, with a catchment-specific composition. It is often split into hydrophobic
50 and hydrophilic fractions. There is conflicting literature regarding which NOM

types are predominant as precursors of THMs and HAAs. Some researchers report
52 that hydrophilic/polar NOM is more prevalent in the formation of HAAs than
THMs (Hwang et al., 2001), whereas others implicate hydrophobic/non-polar
54 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,
56 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
58 formation potential (HAAFP) than the former minimising HAA concentrations
will be more difficult.

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

While most treatments are selective for certain NOM groups, AOPs are
72 comparatively non-discriminatory (Crittenden et al., 2005). NOM is oxidised
through a complex series of reactions initiated by the hydroxyl radical ($\cdot\text{OH}$).
74 Since $\cdot\text{OH}$ 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 $\cdot\text{OH}$ and NOM have recently been directly measured at $1\text{--}5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
(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 ($\log K_{\text{OW}} > 0$) or hydrophilic ($\log K_{\text{OW}} < 0$).

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 $\cdot\text{OH}$ 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

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

102 UV-C, UV/H₂O₂ and VUV experiments were undertaken in the annular
reactor detailed by Thomson et al. (2004) and Buchanan et al. (2006). The N-lamp
104 used for UV-C and UV/H₂O₂ experiments emitted at 254 nm, while the H-lamp
used for VUV experiments emitted at both 254 nm and 185 nm and produced •OH
106 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-
108 lamp were obtained by hydrogen peroxide and methanol actinometry (Béltran et
al., 1995; Heit et al., 1998).

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

114 For the UV/H₂O₂ experiments H₂O₂ was added at 68 mg L⁻¹ (2 mM). The
concentration of hydrogen peroxide solution was determined by potassium
116 permanganate titration, with potassium oxalate used to standardise the
permanganate solution, as described by Harris (1998).

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

122 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/H₂O₂ 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

148 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
 150 13%, for VUV, UV/H₂O₂ 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
 152 UV-C has limited treatment capacity and differences exist between VUV and
 UV/H₂O₂. The removal by UV/H₂O₂ compares well with Goslan et al. (2006),
 154 who reported DOC reduction of 78% for a reservoir water at a similar UV-C dose
 and identical H₂O₂ dose (UV-C 22 J cm⁻², H₂O₂ 2 mM). The UV-C data are
 156 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
 158 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
 160 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
 162 raw water.

-Insert Figure 1-

-Insert Table 2-

166 Removal by UV-C was linked to hydrophobicity. Tannic acid and
 resorcinol were the most treatable compounds, with DOC removals of 95±5% and
 168 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
 170 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
 172 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
174 doses. UV photo-oxidation can proceed from direct photo-transformation or
indirect photo-transformation, where activated NOM can transfer energy to form
176 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
178 enough energy to initiate these types of reactions.

The biodegradability of samples as measured by removal by biologically-
180 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-
182 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
184 Jadas-Hécart (1989), with an average removal of 70%. Supporting this view
Hwang et al. (2001) stated biodegradation is effective for removing non UV-
186 absorbing low molecular weight acids. Given this information the aromatic
character of tannic acid and resorcinol may explain their lower biodegradability;
188 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
190 were charged under ambient pH conditions (Table 2), instead differing chemical
functionality is a more likely reason. Nor does size correlate with
192 biodegradability. It has been stated that small compounds are expected to be more
biodegradable as they are more easily transported across the cell membrane
194 (Leisinger, 1981), however in this study there was no such relationship, even for
compounds of the same chemical type (Table 2).

196 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 $88 \pm 5\%$, 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 $55 \pm 5\%$. 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 $0.043 \text{ J}^{-1} \text{ cm}^{-2}$;
 compared with $0.044\text{--}0.116 \text{ J}^{-1} \text{ cm}^{-2}$ for the other compounds, and also by
 214 UV/ H_2O_2 : rate constants of $0.016 \text{ J}^{-1} \text{ cm}^{-2}$, compared with $0.045\text{--}0.14 \text{ J}^{-1} \text{ cm}^{-2}$
 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 $\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ compared with serine at 3.2
 $\times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. 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
 224 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,
 226 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
 228 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
 230 interesting observation. Alternatively it may be that the slower degradation of
 glycine by UV-C was a result of its smaller size (Table 1).

232 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
 234 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
 236 functionalities which react strongly with chlorine and can produce THM and
 HAAs (Singer, 1999).

238

-Insert Figure 3-

240

Reckhow and Kim (2008) found L-aspartic acid to be one of a small
 242 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
 244 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
 246 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 $1 \mu\text{g mgDOC}^{-1}$ (Figure 3) the HAAFP rises by 5, 50, 52 and $36 \mu\text{g}$
 264 mgDOC^{-1} after biotreatment, UV-C VUV and UV/H₂O₂ 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-H₂O₂ 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/H₂O₂ treatment at UV fluence of 3000 mJ cm^{-2} and
 270 H₂O₂ concentration of $10\text{-}20 \text{ mg L}^{-1}$ gave reductions in TCAA formation potential
 (TCAAFP) of 69% and THMFP of 73%, but DCAAFP increased by 74%. Note

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

274 -Insert Figure 4-

276 For the two hydrophobic compounds the pattern was somewhat different
compared with the hydrophilic compounds (Figures 3 and 4). Treatment of tannic
278 acid caused its HAAFP to decrease from an untreated value of $155 \mu\text{g mgDOC}^{-1}$
(Figure 3) by 7, 69, 101 and $110 \mu\text{g mgDOC}^{-1}$ after biotreatment, UV-C VUV and
280 UV/H₂O₂, respectively (Figure 4). Thus for tannic acid AOPs caused the greatest
fall in HAAFP. Resorcinol has an untreated HAAFP of $14 \mu\text{g mgDOC}^{-1}$ (Figure
282 3) which changes by 28, 81, 20 and $-1 \mu\text{g mgDOC}^{-1}$ following biotreatment, UV-
C VUV and UV/H₂O₂ respectively (Figure 4). Thus for resorcinol UV-C effected
284 the greatest increase in HAAFP.

It has been established that DCAA and TCAA, which were the dominant
286 HAAs in this study, have disjunct formation mechanisms (Reckhow and Singer,
1986). Therefore it is interesting to observe the differing effects that treatment had
288 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-
290 glutamic acid (Figure 5). From an initial value of $1 \mu\text{g mgDOC}^{-1}$ DCAA rose to 3,
37, 20 and $29 \mu\text{g mgDOC}^{-1}$ following treatment by biodegradation, VUV,
292 UV/H₂O₂ and UV-C, respectively. Again the behaviour of the hydrophobic
molecules differs from that of the hydrophilics. For resorcinol TCAA was most
294 common before treatment: total HAAs $14 \mu\text{g mgDOC}^{-1}$, TCAA $10 \mu\text{g mgDOC}^{-1}$
and this dominance was maintained in the biotreated sample: total HAAs $42 \mu\text{g}$
296 mgDOC^{-1} , TCAA $33 \mu\text{g mgDOC}^{-1}$ and UV-C treated sample: total HAAs $95 \mu\text{g}$

mgDOC⁻¹, TCAA 56 µg mgDOC⁻¹, while in the VUV and UV/H₂O₂ 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
 $0 \mu\text{g mg DOC}^{-1}$. 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/H₂O₂ and BAC treatment, contrasting with an increase of 74% for
380 UV/H₂O₂ 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
 398 microbial disinfection. Interestingly, these results indicate that exposure of natural
 water to sunlight (and UV-C), which can involve high energy levels, has the
 400 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
 402 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
 404 to 1 and 4 days of clear summer weather respectively. Under these conditions
 HAAFP decreased by up to 50%.

Conclusions

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

Acknowledgements

418 Anglian Water, Northumbrian Water, Severn Trent Water, United Utilities and
 Yorkshire Water are all gratefully acknowledged for their financial support of this
 420 project.

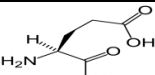
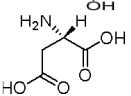
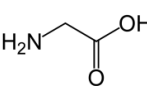
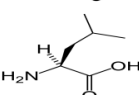
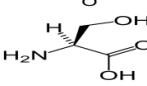
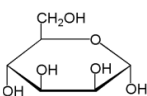
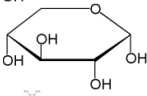
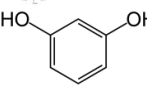
422 **References**

- 424 Allgeier, S.C. and Summers, R.S. (1995) Evaluating NF for DBP control with the
RBSMT. *J. Am. Water Works Assoc.* 87 (3), 87-99.
- 426 B  ltran, F.J., Overjero, G., Garcia-Araya, J.F. and Rivans, J. (1995) Oxidation of
polynuclear aromatic hydrocarbons in water 2: UV radiation and ozonation in
the presence of UV radiation. *Ind. End. Chem. Res.* 34, 1607-1615.
- 428 Berger, P., Karpel Vel Leitner, N., Dor  , M. and Legube, B. (1999) Ozone and
hydroxyl radicals induced oxidation of glycine. *Water Res.* 33 (2), 433-441.
- 430 Buchanan, W., Roddick, F.A. and Porter, N. (2004) Enhanced biodegradability of
UV and VUV pre-treated natural organic matter. *Water Sci. Technol.: Water*
432 *Supply.* 4 (4), 103-111.
- Buchanan, W., Roddick, F. and Porter, N. (2006) Formation of hazardous by-
434 products resulting from the irradiation of natural organic matter: comparison
between UV and VUV irradiation. *Chemosphere.* 63 (7), 1130-1141.
- 436 Chin, A. and B  rub  , P.R. (2005) Removal of disinfection by-product precursors
with ozone-UV advanced oxidation process. *Water Res.* 39 (10), 2136-2144.
- 438 Chow, A.T., Leech, D.M., Boyer, T.H. and Singer, P.C. (2008) Impact of
simulated solar irradiation on disinfection byproduct precursors. *Environ. Sci.*
440 *Tech.* 42 (15), 5586–5593
- Corin, N., Backlund, P. and Kulovaara. (1996) Degradation products formed
442 during UV-C irradiation of humic Waters. *Chemosphere*, 33 (2), 245-255
- Crittenden, J.C., Trussell, R. R., Hand, D.W., Howe, K. J. and Tchobanoglous, G.;
444 MWH (2005) *Water treatment: principles and design*, 2nd Edn. John Wiley &
Sons, Inc., Hoboken, New Jersey
- 446 Crou  , J. -P., Korshin, G. V. and Benjamin, M. (2000) Characterization of natural
organic matter in drinking water, report 90780, AWWA Research
448 Foundation, USA.
- Dickenson, E.R., Summers, R.S., Crou  , J.-P. and Gallard. H. (2008) Haloacetic
450 acid and trihalomethane formation from the chlorination and bromination of
aliphatic β -dicarbonyl acid model compounds. *Environ. Sci. Tech.*, 42 (9),
452 3226–3233
- Goslan, E. H.; Gurses, F.; Banks, J. and Parsons, S. A. (2006) An investigation
454 into reservoir NOM reduction by UV photolysis and advanced oxidation
processes. *Chemosphere*, 65 (7), 1113-1119.
- 456 Harris, D.C, 1998. *Quantitative chemical analysis*, 5th Edn. W.H Freeman and Co.
New York.
- 458 Heit, G., Annette, N., Saugy, P.Y. and Braun, A.M. (1998) Vacuum-UV (172nm)
actinometry: The quantum yield of the photolysis of water. *Phys. Chem. A.*
460 102, 5551-5561.
- Hureiki, L., Crou  , J.-P. and Legube, B. (1994) Chlorination studies of free and
462 combined amino acids, *Water Res.*, 28(12), 2521-2531.

- Hwang, C.J., Krasner, S.W., Schlimenti, M.J., Amy, G.L., Dickenson, E.,
 464 Bruchet, A., Prompsy, C., Filippi, G. Croué, J.P. and Violleau, D. (2001)
 Polar NOM: characterization, DBPs, treatment, report 90877, AWWA
 466 Research Foundation, USA.
- Jadas-Hécart, A. (1989) Contribution à l'étude de la demande en chlore à long
 468 terme d'une eau potable: modélisation et identification des précurseurs
 organiques. Ph.D thesis. Université de Potiers, France.
- Joret, J.C., Levi, Y. (1986) Methode rapide d'evaluation du carbone eliminable
 470 des eaux par voiebiologique. La Tribune du Cebedeau. 510 (39), 3-9.
- Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R.,
 472 Scilimenti, M. J., Onstad, G.D. and Thruston Jr., A.D. (2006) Occurrence of a
 474 new generation of disinfection byproducts. Environ. Sci. Technol. 40 (23),
 7175-7185.
- Le Lacheur, R.M. and Glaze, W.H., (1996) Reactions of ozone and hydroxyl
 476 radicals with serine. Environ. Sci. Technol. 30 (4), 1072-1080.
- Lee, S., Cho, J., Shin, H., Son, B. and Chae, S. (2003) Investigation of NOM size,
 478 structure and functionality (SSF): impact on water treatment process with
 480 respect to disinfection by-products formation. J. Water Supply Res. Technol.
 – AQUA. 52 (8), 555-564.
- Leisinger (ed.) (1981) Microbial degradation of xenobiotics and recalcitrant
 482 compounds. Academic Press, London, UK.
- Liang, L. and Singer, P.C. (2003) Factors influencing the formation and relative
 484 distribution of haloacetic acids and trihalomethanes in drinking water.
 486 Environ. Sci. Technol. 37 (13), 2920-2928.
- Muellner, M.G., Wagner, E.D., Mccalla, K., Richardson, S.D., Woo, Y.T. and
 488 Plewa, M. J. (2007) Haloacetonitriles vs. regulated haloacetic acids: Are
 nitrogen-containing DBFs more toxic? Environ. Sci. Technol. 41 (2), 645-
 490 651.
- Reckhow, D.A. and Kim, J. (2008) Role of proteins and amino Acids in DBP
 492 Formation, IWA NOM: from Source to Tap conference, September 2nd-4th,
 Bath, UK
- Reckhow, D.A. and Singer, P.C. (1986) Mechanisms of organic halide formation
 494 during fulvic acid chlorination and implications with respect to preozonation.
 496 In Water Chlorination: Environmental Impact and Health Effects, Lewis
 Publishers, Chelsea, MI.
- Reckhow, D.A., Singer, P.C. and Malcolm, R.L. (1990) Chlorination of humic
 498 materials: byproduct formation and chemical interpretations. Environ. Sci.
 500 Technol. 24 (11), 1655-1664.
- Rook, J.J. (1974) Formation of halogens during the chlorination of natural water.
 502 Water Treatment and Examination. 23, 234-243.
- Scully, F. E., Howell, G. D., Kravitz, R., Jewell, J. T., Hahn, V. and Arber, R. P.
 504 (1985) Contribution of proteins to the formation of trihalomethanes on

- chlorination of natural water. In *Water Chlorination: Environmental Impact and Health Effects*, vol. 5, Ann Arbor Science, Ann Arbor Michigan.
- Sharp, E.L., Jarvis, P., Parsons, S.A. and Jefferson, B. (2006) Impact of fractional character on the coagulation of NOM. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 286 (1-3), 104-111.
- Singer, P. C., ed. (1999). *Formation and control of disinfection by-products in drinking water*, AWWA, USA
- Singer, P. C., Bilyk, K. (2002) Enhanced coagulation using a magnetic ion exchange resin. *Water Res.* 36 (16), 4009-4022.
- Thomson, J., Parkinson, A. and Roddick, F.A. (2004) Depolymerization of chromophoric natural organic matter. *Environ. Sci. Technol.* 38 (12), 3360-3369.
- Thomson, J., Roddick, F.A. and Drikas, M. (2002) UV photooxidation facilitating biological treatment for the removal of NOM from drinking water. *J. Water Supply Res. Technol. – AQUA*. 51 (6), 297-306.
- Thurman, E. M. (1985), *Organic geochemistry of natural waters*, Nijhoff/Junk Publishers, Dordrecht, The Netherlands.
- Toor, R. and Mohseni, M. (2007) UV-H₂O₂ based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water. *Chemosphere*. 66 (11), 2087-2095.
- Tranvik, L.J., 1998. Degradation of dissolved organic matter in humic waters by bacteria. In Hennsen, D. O. and Tranvik, L. J. (Eds.) *Aquatic Humic Substances: Ecology and Biogeochemistry*, Springer, Berlin.
- Westerhoff, P., Mezyk, S. P., Cooper, W. J and Minakata, D. (2007). Electron pulse radiolysis determination of hydroxyl radical rate constants with Suwannee river fulvic acid and other dissolved organic matter isolates. *Environ. Sci. Technol.* 41 (13), 4640-4646.

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, 8.7, NA	Hydrophobic, anionic	Phenolic	0.045
Resorcinol		0.80	110	9.32, 11.1, NA	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		k ¹	VUV		k ²	UV/H ₂ O ₂		k ³	Biodegradation
	% DOC loss			% DOC loss			% DOC loss			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 cm²

k^3 : Initial first-order rate constant (0-47 J cm⁻²), J⁻¹ cm²

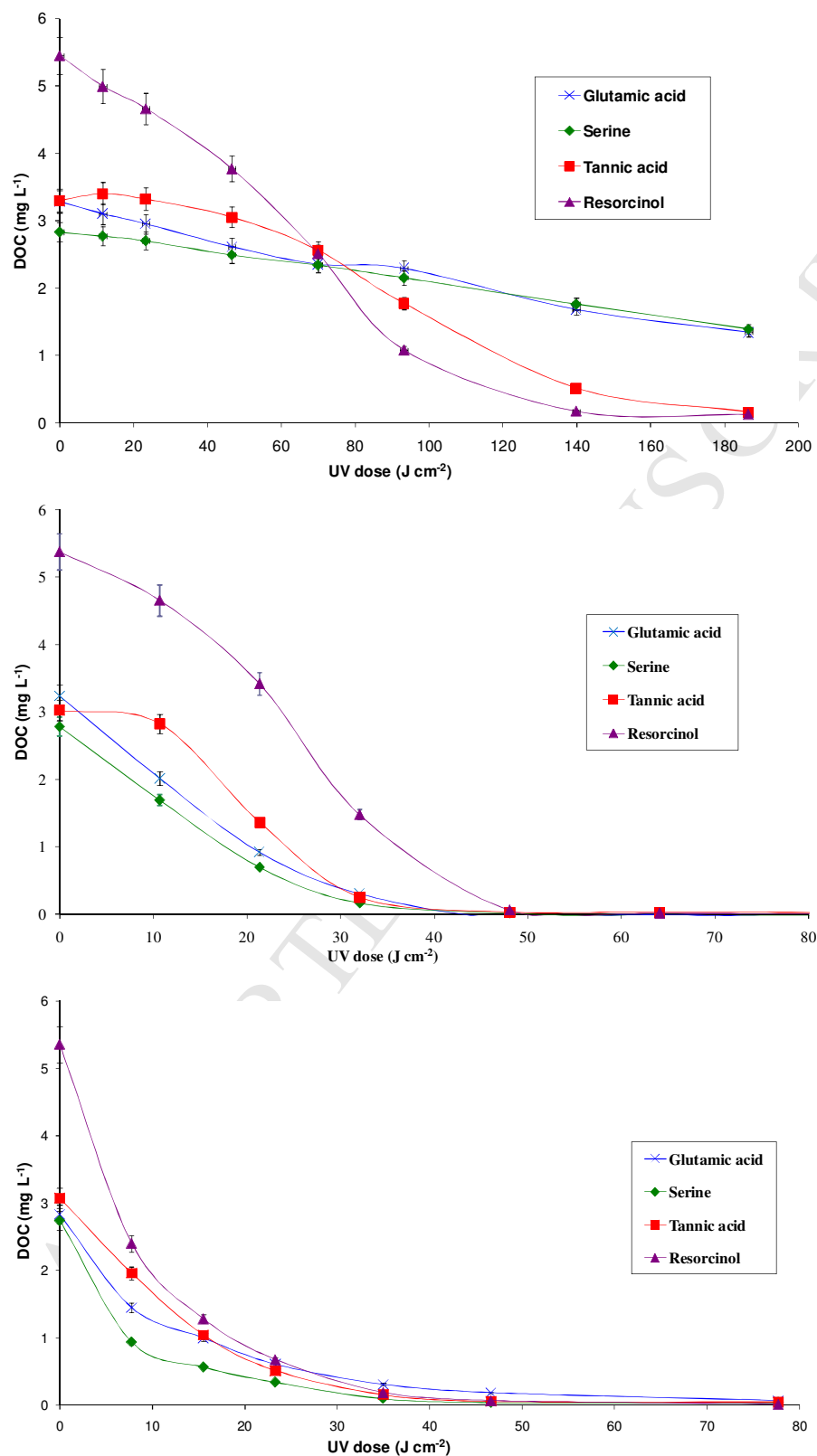


Figure 1 a, b, c: Degradation of selected model compounds by UV-C, VUV and UV/H₂O₂ (from top to bottom respectively).

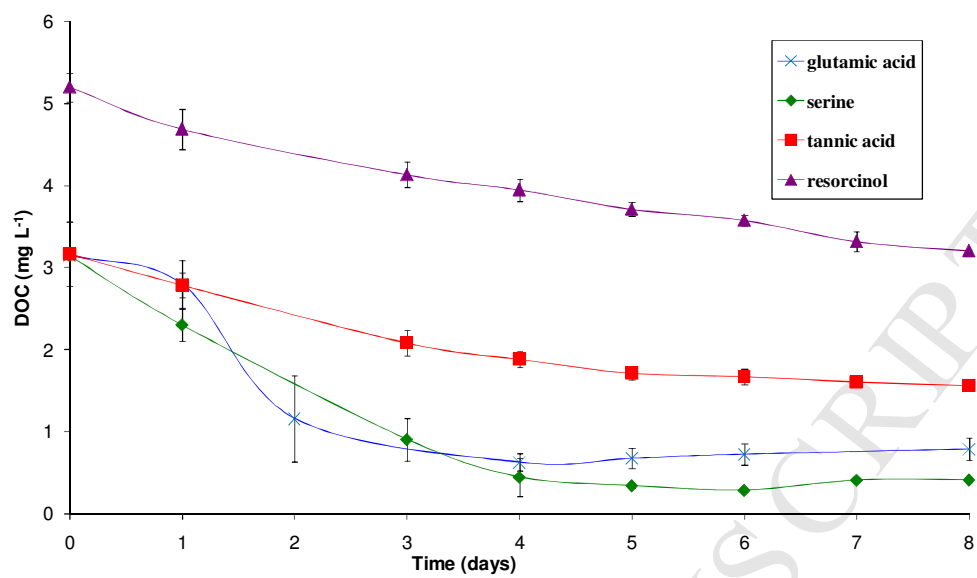


Figure 2: Biodegradation of selected model compounds

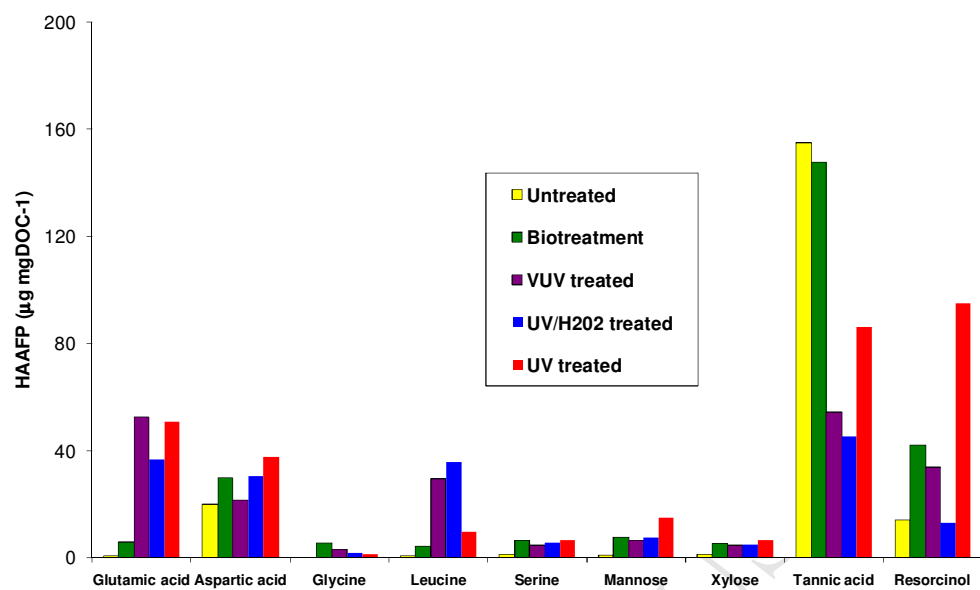


Figure 3: HAAFP (µg mg C⁻¹) of untreated and treated model compounds

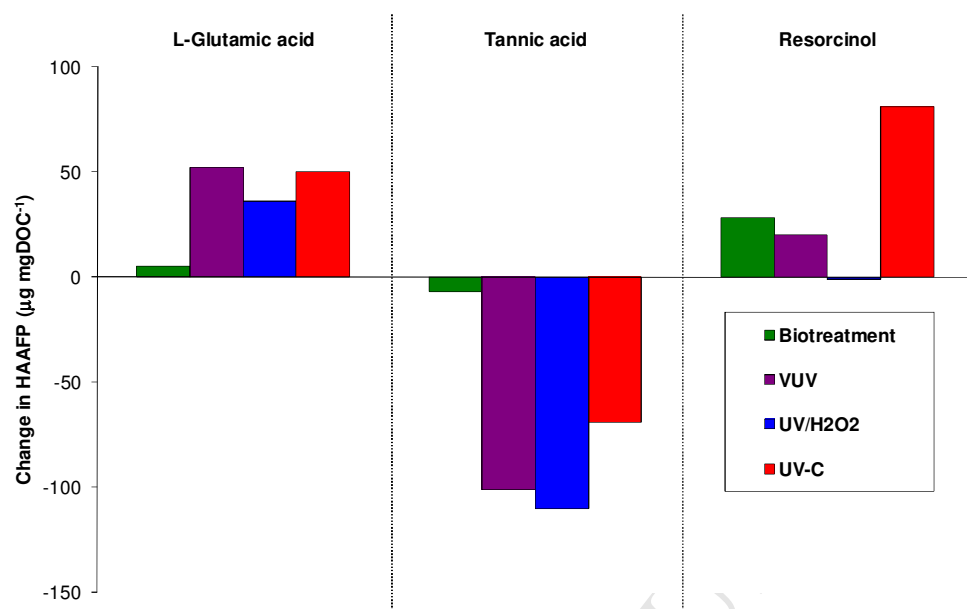
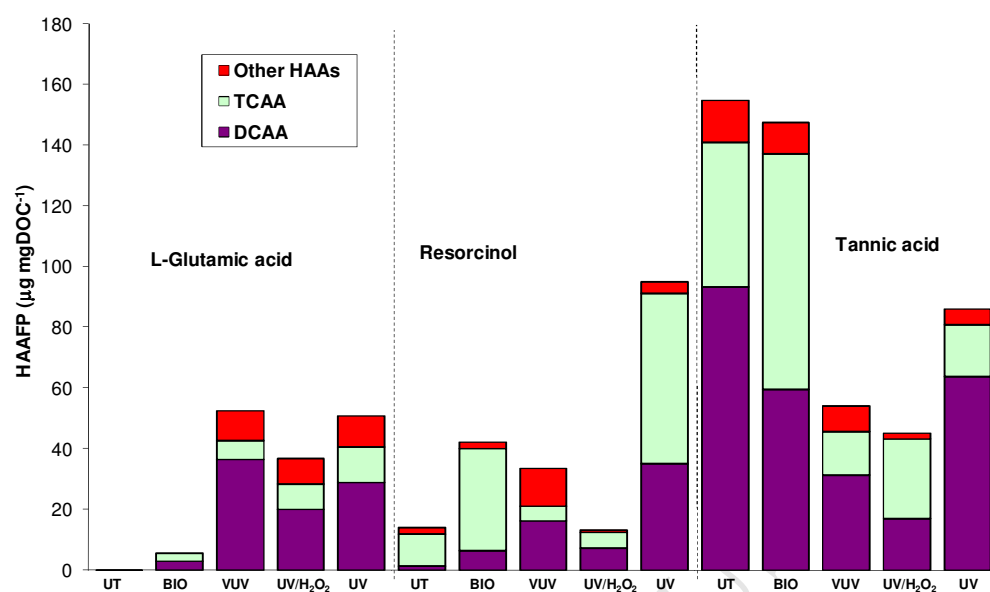


Figure 4: Effect of treatment on HAA formation of L-glutamic acid, resorcinol and tannic acid



Note: UT = untreated; BIO = biodegradation

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



DSPACE

<https://dspace.org/>

Chemical and biological oxidation of NOM surrogates and effect on HAA formation

Bond, Tom; Goslan, Emma H.; Jefferson, Bruce; Roddick, Felicity A.; Fan, Linhua ...

2009-06

Elsevier

<http://dx.doi.org/10.1016/j.watres.2009.03.036>

T. Bond, E.H. Goslan, B. Jefferson, F. Roddick, L. Fan, S.A. Parsons, Chemical and biological oxidation of NOM surrogates and effect on HAA formation, Water Research, Volume 43, Issue 10, June 2009, Pages 2615-2622