

Formation of Haloacetonitriles, Haloacetamides, and Nitrogenous Heterocyclic Byproducts by Chloramination of Phenolic Compounds

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1 **Formation of haloacetonitriles, haloacetamides and nitrogenous**
2 **heterocyclic by-products by chloramination of phenolic**
3 **compounds**

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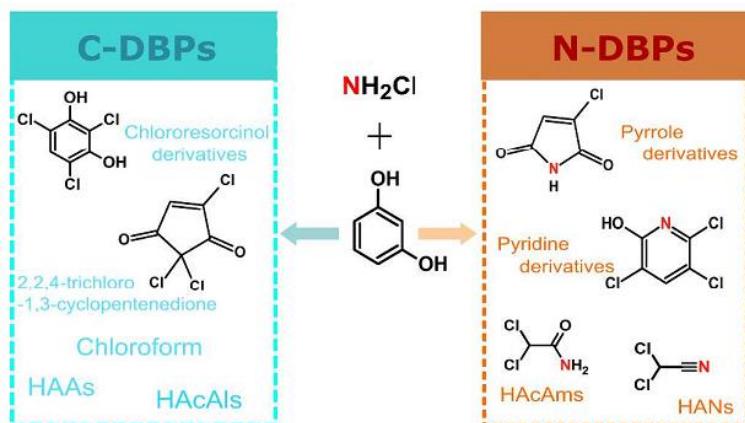
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17
18 **Abstract**

19 The potential formation of nitrogenous disinfection by-products (N-DBPs) was investigated from the
20 chloramination of nitrogenous and non-nitrogenous aromatic compounds. All molecules led to the
21 formation of known N-DBPs (e.g., dichloroacetonitrile, dichloroacetamide) with various production
22 yields. Resorcinol, a major precursor of chloroform, also formed di-/tri-chloroacetonitrile, di-/tri-
23 chloroacetamide, and haloacetic acids, indicating that it is a precursor of both N-DBPs and
24 carbonaceous DBPs (C-DBPs) upon chloramination. More detailed experiments were conducted on
25 resorcinol to understand N-DBPs formation mechanisms and to identify reaction intermediates. Based
26 on the accurate mass from high resolution Quadrupole Time-of-Flight GC-MS (GC-QTOF) and
27 fragmentation patterns from electronic impact and positive chemical ionization modes, several
28 products were tentatively identified as nitrogenous heterocyclic compounds (e.g., 3-chloro-5-hydroxy-
29 1H-pyrrole-2-one with dichloromethyl group, 3-chloro-2,5-pyrroledione). These products were
30 structurally similar to the heterocyclic compounds formed during chlorination, such as the highly

31 mutagenic MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone) or halogenated pyrroles. To
32 our knowledge, this is the first time that the formation of halogenated nitrogenous heterocyclic
33 compounds is reported from chloramination process. The formation of these nitrogenous by-products
34 during chloramination might be of concern considering their potential toxicity.

35 ABSTRACT ART



36

37

38 INTRODUCTION

39 As an alternative to chlorine, monochloramine (NH_2Cl) is often used as a secondary disinfectant to
40 obtain a more stable residual in distribution systems (Seidel et al., 2005). Chloramines generally form
41 less trihalomethanes (THMs), haloacetic acids (HAAs) and total organic halogen (TOX) than free
42 chlorine. However, the percentage of unknown TOX produced from chloramines is higher than that
43 from free chlorine (Hua et al., 2007).

44 During chloramination, NH_2Cl can be an additional source of nitrogen and produce halogenated
45 nitrogenous disinfection by-products (N-DBPs). N-DBPs, including haloacetonitriles (HANs) and
46 haloacetamides (HAcAms), generally form in lower amounts than regulated DBPs (i.e., THMs and
47 HAAs). It has been proposed that the mass of HANs represents around 10% of the THMs (Krasner
48 Stuart et al., 1989; Oliver, 1983) whereas HAcAms formation was reported to be approximately 10
49 times lower than HAAs (Krasner et al., 2006). Regardless of their relatively low occurrence, HANs
50 and HAcAms have been a growing health risk concern over the past decades because of their high
51 toxicity (Muellner et al., 2007; Plewa et al., 2004).

52 Nitrogen-containing organic compounds (e.g., amino acids, pyrroles and pyrimidines) are ubiquitous
53 in surface water (Westerhoff et al., 2002) and have been associated with the formation of N-DBPs
54 (Bond et al., 2011). Wastewater effluents and algal organic matter, which are enriched in organic
55 nitrogen, enhance N-DBPs formation during drinking water treatment process (Dotson et al., 2009). It

56 was recently reported that antibiotic chloramphenicols may contribute to the formation of HAcAms in
57 heavily wastewater-impacted waters (Chu et al., 2016).

58 Most of the previous studies exploring the sources of nitrogen in N-DBPs focused on chloramination
59 of nitrogenous model compounds (e.g., amino acids) or matrices enriched in nitrogen moieties (e.g.,
60 algal organic matter) by the application of isotopically labeled monochloramine (i.e., $^{15}\text{NH}_2\text{Cl}$).
61 Inorganic nitrogen incorporation into dichloroacetonitrile (DCAN) and dichloroacetamide (DCAcAm)
62 has been reported during chloramination of wastewater effluents, algal extracellular organic matter,
63 humic substances and free amino acids (i.e., aspartic acid and asparagine) (Huang et al., 2012).
64 ^{15}N -DCAN percentages in total DCAN were found to be 78% and 92% by chloramination of
65 tryptophan and Suwannee River NOM, respectively (Yang et al., 2010). More than 70% of DCAN
66 originated from monochloramine during chloramination of NOM isolates (Huang et al., 2012),
67 indicating that high amounts of inorganic nitrogen (i.e., Monochloramine) can be incorporated into
68 organic structure.

69 Only few studies are available on N-DBPs formation from non-nitrogenous precursors. Formaldehyde
70 reacts with NH_2Cl to form cyanogen chloride (Pedersen et al., 1999). Chloroacetonitrile and
71 N,2-dichloroacetamide formation was found from chloramination of chloroacetaldehyde (Kimura et
72 al., 2013). Recent studies on chloramination of lignin phenols and low-molecular weight organic acids
73 have reported the formation of DCAN, DCAcAm and trichloroacetamide (TCAcAm) through
74 chloramine-nitrogen incorporation (Chu et al., 2016; Chuang et al., 2015; Hua et al., 2014).

75 Previous studies indicated that non-nitrogenous precursors can produce N-DBPs via inorganic
76 nitrogen incorporation. However limited information is available on the nature of these N-DBPs
77 precursors as well as the chloramine-nitrogen incorporation mechanism. Recent results showed that
78 organic matter isolates enriched in aromatic moieties (i.e., high SUVA value) produced more N-DBPs
79 by chloramine-nitrogen incorporation as compared to low-aromatic-content organic matter (Le Roux
80 et al., 2016). In addition, chloramination of aromatic model compounds (i.e., phenol and resorcinol)
81 formed more DCAN and DCAcAm than amino acids (e.g., tyrosine, aspartic acid), which were
82 previously considered as important precursors of N-DBPs.

83 Meta-dihydroxybenzene structures were proposed as main reactive sites of NOM for the formation of
84 THMs upon chlorination (Norwood et al., 1980; Rook, 1977). 1,3-hydroxybenzene (resorcinol) has
85 been extensively studied as a model compound and is a major precursor of chloroform (TCM) during
86 chlorination (Boyce et al., 1983; Norwood et al., 1980; Rook, 1980). The reaction of resorcinol with
87 monochloramine follows a similar mechanism to chlorination, involving aromatic ring-substitution,
88 oxidation, hydrolysis and decarboxylation reactions (Heasley et al., 1999). However, the reactions
89 involving the formation of N-DBPs from resorcinol by incorporation of nitrogen from
90 monochloramine have not been investigated yet.

91 The objective of this study was to investigate the formation of HANs and HAcAms from
92 chloramination of resorcinol in comparison with TCM and HAAs formation and to elucidate their

93 formation mechanisms through the identification of intermediate products. Effects of monochloramine
94 dose, reaction time, and pH on by-products formation were examined. GC-MS/MS and high
95 resolution GC-QTOF full scan analysis were conducted for the identification of unknown products.

96

97 **EXPERIMENTAL SECTION**

98 **Materials.** All chemicals were of analytical grade or higher and were used as received without further
99 purification. Milli-Q water (18.2 MΩ.cm, Millipore) was used for all experiments. Resorcinol
100 (≥ 99.0%) and other model compounds were purchased from Sigma-Aldrich (Table S1). Sodium
101 hypochlorite (5.65-6%, Fisher Scientific) and ammonium chloride (99.6%, Acros Organics) were used
102 for monochloramine preparation. ¹⁵N- labeled ammonium chloride was obtained from Sigma-Aldrich
103 (98%). Sodium thiosulfate (Fisher Scientific) was applied to quench residual oxidant. A
104 trihalomethanes (THM) calibration mix, a mixed standard (EPA 551B Halogenated Volatiles Mix)
105 containing haloacetonitriles (HANs), and a mixed standard (EPA 552.2 Methyl Ester Calibration Mix)
106 containing 9 haloacetic acids (HAAs) were supplied from Supelco (Sigma-Aldrich). Chloro-,
107 dichloro- and trichloroacetamide were obtained from Sigma-Aldrich. Decafluorobiphenyl (99%,
108 Sigma-Aldrich, Supelco) was used as a surrogate standard. 2-bromopropionic acid (Fluka Analytical)
109 was used as a surrogate for HAAs extraction and analysis. Fisher Scientific Methyl tert-butyl ether
110 (MTBE) and ethyl acetate (> 99%) were used for DBP extractions.

111 **Experimental procedures.** Experiments were conducted at room temperature (22 ± 1°C) in
112 headspace-free amber glass bottles (individual bottle per contact time). Preformed monochloramine
113 and ¹⁵N-labeled monochloramine stock solutions were daily prepared by dissolving ammonium
114 chloride or ¹⁵N-labeled ammonium chloride, respectively, in Milli-Q water adjusted to pH 8.5 with
115 sodium hydroxide. Sodium hypochlorite was then slowly added to the rapidly stirred solution (N:Cl
116 molar ratio of 1.2:1). Initial NH₂Cl and NHCl₂ concentrations were spectrophotometrically measured
117 at 245 and 295 nm (Schreiber et al., 2005). Predetermined volumes of monochloramine and each
118 model compound stock solution were injected into 65 mL of 10 mM acetate (pH = 4.0-5.5), phosphate
119 (pH = 7.0-8.0) or carbonate (pH = 10) buffer to get the desired initial concentrations
120 (monochloramine:model compound molar ratio of 5.6 or 11.2). The concentration of residual oxidant
121 was iodometrically determined (Eaton et al., 1995). Residual monochloramine was quenched with a
122 slight excess of sodium thiosulfate. Samples were extracted immediately after quenching to avoid any
123 loss of by-products.

124 **GC-MS and GC-QTOF-MS/MS Analysis.** TCM and two HANs (dichloroacetonitrile,
125 trichloroacetonitrile) were analysed after liquid-liquid extraction following EPA Method 551. Three
126 HAcAms (chloroacetamide, dichloroacetamide, trichloroacetamide) were analysed following the

127 same protocol that was applied for HANs; however, the extraction solvent MTBE was replaced by
128 ethyl acetate since it was shown to improve the recovery of HAcAms (Chu and Gao, 2009). HAAs
129 were extracted and analysed following the EPA Method 552.2, which is based on a liquid-liquid
130 extraction with MTBE in acidic condition followed by derivatization to methyl esters using acidic
131 methanol. All DBPs were quantified using a gas chromatograph (Agilent 7890A) coupled with a mass
132 spectrometer (Agilent 5975C, GC-MSD). Since ¹⁵N-labeled DBPs are not commercially available,
133 their concentrations were determined using ¹⁴N-DBPs standards, based on the assumption that ¹⁵N-
134 DBPs and ¹⁴N-DBPs have a similar MS response (Huang et al., 2012). DBPs were separated on a DB-
135 1701 (30m × 250 μm × 0.25 μm) capillary column.

136 In order to identify unknown by-products, full scan analysis in electronic impact (EI) and positive
137 chemical ionization (PCI, using methane as reagent gas) modes were performed on MTBE extracts at
138 various reaction times. Two different GC-MS systems were used for full scan analysis: an Agilent
139 5975C GC-MSD and an Agilent 7200 Accurate-Mass Quadrupole Time-of-Flight (GC-QTOF).
140 MS/MS analysis at three different collision energies (i.e., 20 eV, 40 eV and 60 eV) were performed on
141 GC-QTOF for all main peaks detected. Agilent MassHunter Qualitative analysis B.07.00 was used for
142 deconvolution of data from GC-QTOF. The column used for GC-MSD was a DB-1701 (30 m × 250
143 μm × 0.25 μm) or a ZB-5MS (30 m × 250 μm × 1 μm). GC separation on GC-QTOF was performed
144 with a DB-5MS UI column (30 m × 0.25 mm × 0.25 μm).

145 Details on quantification of DBPs and full scan analysis of unknown by-products are provided in Text
146 S1.

147

148 **RESULTS AND DISCUSSION**

149 **N-DBPs Formation from Model Aromatic Compounds.** Preliminary experiments were conducted
150 at pH 7 (10 mM phosphate buffer) for 72 h to investigate the formation potential of DCAN and
151 DCACAm from several aromatic compounds (250 μM) during chloramination (1.4 mM). ¹⁵NH₂Cl was
152 applied to nitrogenous model compounds and ¹⁴NH₂Cl to others. N-DBPs formation was observed
153 from both nitrogenous and non-nitrogenous compounds (Table 1). In the case of nitrogenous
154 compounds (aniline and amino acids), more than 50% of DCAN and DCACAm incorporated ¹⁵N
155 originating from ¹⁵NH₂Cl. Model compounds (i.e., resorcinol, phenol, aniline, and 3-hydroxybenzoic
156 acid), including an aromatic ring activated by electron donating groups (i.e., –OH and –NH₂) in their
157 structure, were the most important precursors of DCAN and DCACAm. Despite their similar
158 structures, tyrosine formed more DCAN and DCACAm (i.e., 0.50% and 0.10% molar yield,
159 respectively) than phenylalanine (i.e., 0.12% and 0.05%, respectively). The activation of the aromatic
160 ring by a hydroxyl group in the case of tyrosine favours chlorine electrophilic substitution leading to
161 N-DBPs formation via ring-cleavage reaction (Hureiki et al., 1994). Phenol produced the highest

162 proportion of DCAN (4.44%) and resorcinol produced the highest proportion of DCACAm (0.83%).
 163 Resorcinol is more reactive than phenol because of its additional hydroxyl group in meta position,
 164 resulting in chlorine substitutions in ortho and para positions of hydroxyl groups. Interestingly, TCM
 165 was the highest DBP produced from resorcinol, while DCAN was the dominant species from phenol
 166 (molar yield of TCM: 4.8% for resorcinol; 0.4% for phenol), suggesting different DBPs formation
 167 pathways from these two precursors. In this study, resorcinol was selected to explore N-DBPs
 168 formation mechanisms, since it produced DCAN and DCACAm in relatively high concentrations.

169 Table 1. N-DBP yields from model aromatic compounds during chloramination^a

	Molar yield (%) (SD) ^b		¹⁵ N-DBP proportion (%)	
	DCAN	DCACAm	¹⁵ N-DCAN	¹⁵ N-DCACAm
Non-nitrogenous compounds				
Resorcinol	1.14(0.08) ^c	0.83(0.04) ^c	NA	NA
Phenol	4.44(0.29) ^c	0.22(0.01) ^c	NA	NA
3-Hydroxybenzoic acid	1.00(0.07)	0.22(0.01)	NA	NA
Benzoic acid	0.17(0.01)	0.09(0.01)	NA	NA
3-Phenylpropionic acid	0.10(0.01)	0.04(0.01)	NA	NA
Nitrogenous compounds				
Aniline	1.73(0.11)	0.12(0.01)	85	74
Tyrosine	0.50(0.03) ^c	0.10(0.01) ^c	83	70
Phenylalanine	0.12(0.01)	0.05(0.01)	83	56

^aChloramination conditions: [model compound] = 250 μM; [NH₂Cl] = 1.4 mM; pH = 7.0 in 10 mM phosphate buffer; contact time 72h; NA: not applicable. ^bSD=Standard Deviation on 3 replicates. ^cPreviously published data (Le Roux et al., 2016)

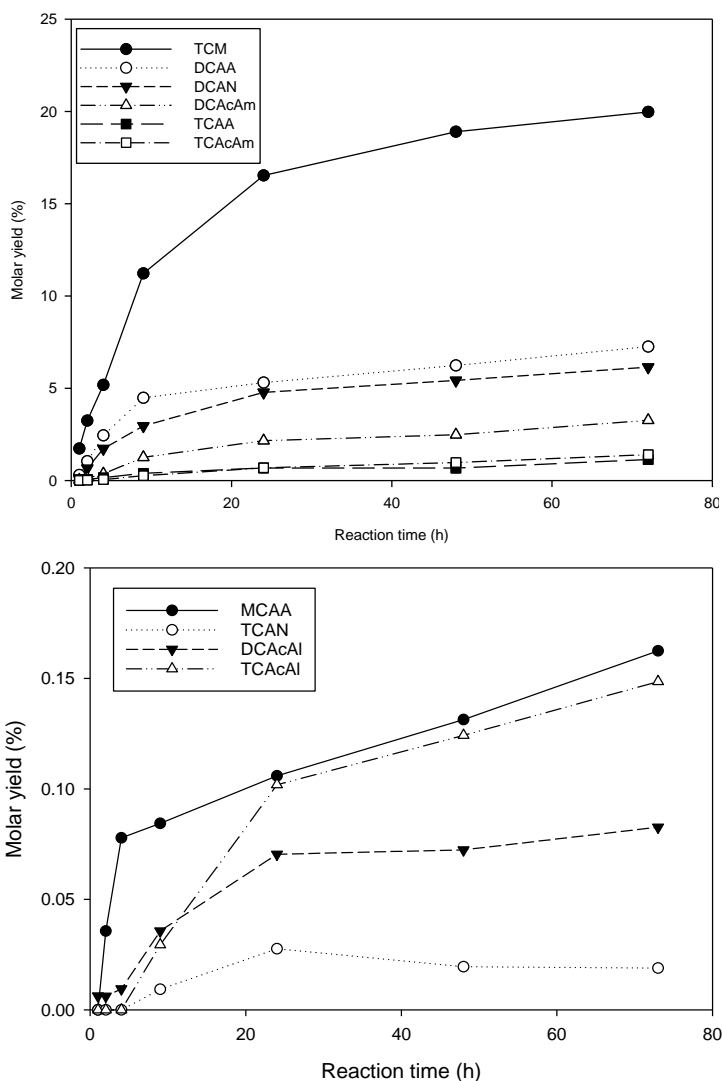
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171 **Effect of monochloramine dose.** Experiments were performed with resorcinol (500 μM) for 72 h
 172 using different NH₂Cl: resorcinol ratios (i.e., 1:1, 5:1 and 11.2:1) at pH 7 (10 mM phosphate buffer).
 173 TCM was the dominant DBP identified for all ratios (i.e., 0.3%, 11% and 20% yield), followed by
 174 DCAA (i.e., 0.1%, 3% and 7%) (Figure S1). As hypothesized, the concentration of DBPs increased
 175 with increasing monochloramine dose since the application of higher oxidant doses facilitates the
 176 production of smaller and more halogenated by-products (Boyce and Hornig, 1983). The increase in
 177 DCAN and DCACAm concentrations were proportionally higher than those in TCM and DCAA. The
 178 highest dose (i.e., 11.2:1 ratio) was selected in the following experiments since it maximized DBP
 179 formation.

180 Previous studies on chloramination of resorcinol and its chlorinated derivatives have been conducted
 181 in ether solution (~0.3M) with NH₂Cl:model compound ratio of 3:1 (Heasley et al., 1999). In these
 182 conditions, chloroketones were the major by-products identified (compound II and III in Scheme 1),
 183 and the formation of nitrogenous compounds was not reported, which could be due to the lower
 184 chloramine dose employed as compared to this study.

185

186 **Effect of reaction time.** Kinetic experiments were performed with 500 μM resorcinol at pH 7
 187 (10 mM phosphate buffer). Initial NH_2Cl was 5.6 mM (NH_2Cl : resorcinol ratio of 11.2:1) and the total
 188 oxidant concentration remained in excess during all the reaction time (Figure S2). Figure 1 illustrates
 189 the kinetic profiles of DBPs formation. TCM was the major DBP found (20% yield after 72 h),
 190 followed by DCAA (7.2%). MCAA and DCAA were rapidly formed during the first 9 h, suggesting
 191 that they might form directly from ring-cleavage. DCAN followed the same profile as TCM and
 192 reached 6.1% yield after 72 h. DCACAm and TCACAm formation was slow within the first 4 h and
 193 then gradually increased, reaching 3.3% and 1.4% yield after 72 h, respectively. Unlike DCAA and
 194 MCAA, TCAA increased slowly with time and its profile was very similar to that of TCACAm. Low
 195 amounts of trichloroacetaldehyde (TCACAl) (0.14% at 72 h), dichloroacetaldehyde (DCACAl)
 196 (0.08%) and TCAN (0.02%) were detected.



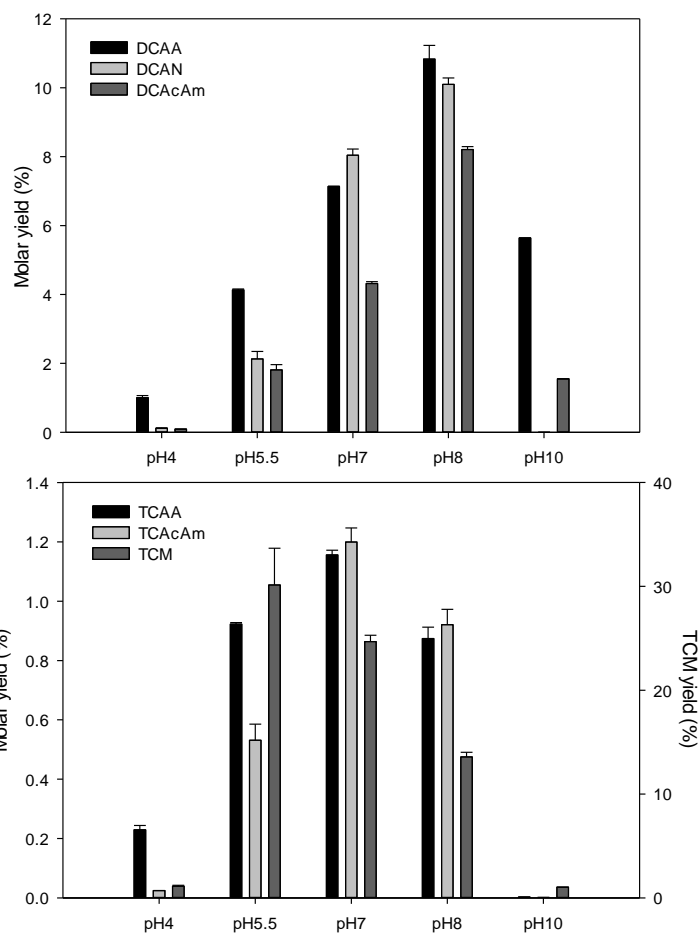
198 Figure 1. Kinetics of DBPs formation from chloramination of resorcinol.
 199 Resorcinol= 500 μM ; NH_2Cl = 5.6 mM; pH=7.0 (10 mM phosphate buffer)
 200

201

202 **Effect of pH.** Formation potential of DBPs from resorcinol upon 72 h of chloramination was
203 evaluated at different pH values (Figure 2). Dichlorinated DBPs (i.e., DCAA, DCAN and DCAcAm)
204 exhibited a maximum formation at pH 8, while the highest formation of trichlorinated DBPs (i.e.,
205 TCAA and TCAcAm) was found at pH 7. Taking into account the analytical error recorded at pH 5.5
206 (standard deviation: 3.5% of molar yield), the TCM yields obtained at pH 5.5 and pH 7 should be
207 considered as relatively similar. Generally, the concentration of TCM increases with increasing pH
208 during chlorination of natural water due to base-catalyzed reaction (Hua and Reckhow, 2008). In
209 contrast to this, the TCM yields from chloramination of resorcinol gradually decreased as pH
210 increased from pH 7. Our result is consistent with previous observations, where the formation of TCM
211 from chloramination of resorcinol also decreased with increasing pH (pH 6.5-12) under similar
212 experimental conditions (Cimetiere et al., 2010). It was proposed that the free chlorine released from
213 NH_2Cl hydrolysis plays a significant role on TCM formation during chloramination of resorcinol
214 (Cimetiere et al., 2010). In the organic-free solution of monochloramine, the concentration of free
215 chlorine is the lowest around pH 8.4 and increases with increasing pH (Cimetiere et al., 2010).
216 However, the free chlorine species shift from HOCl to OCl^- as pH increases. TCM was also
217 demonstrated to form in significantly lower amounts during chlorination of resorcinol in alkaline
218 conditions (pH > 10) (Boyce et al., 1983), most likely due to the less reactivity of OCl^- with
219 intermediate precursors of chloroform. Therefore, the pH-dependency of TCM yield might be related
220 to the free chlorine from the hydrolysis of monochloramine, as well as the distribution of free chlorine
221 species with pH. Most DBPs exhibited a substantially lower formation at pH 10, suggesting that an
222 alternative degradation pathway of resorcinol may exist. Reduction of N-DBPs from pH 8 to pH 10
223 was possibly related to their base catalysed hydrolysis as well (Reckhow et al., 2001; Yu et al., 2015).
224 No resorcinol or chlorinated analogues were detected in samples at pH 7, 8 and 10, indicating that
225 they completely decomposed to intermediates or final by-products after 72 h, but large peaks of
226 mono-, di- and tri-chlororesorcinol were still detected from GC-MS full scan after 72 h at pH 4
227 (Figure S3). This might explain the low non-aromatic DBP formation at pH 4, as the reaction did not
228 lead to significant ring-opening of resorcinol.

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Figure 2. Effect of pH on DBPs formation from chloramination of resorcinol. Resorcinol= 500 μ M; NH_2Cl = 5.6 mM; 72h; Error bars represent standard deviation (n=2)

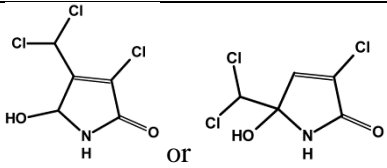
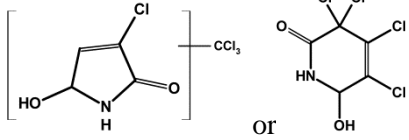
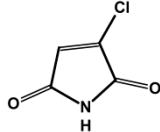
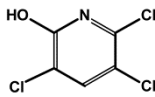
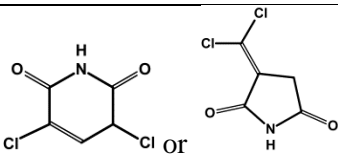
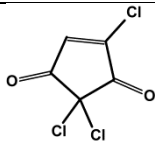
235 **Identification of nitrogenous heterocyclic compounds.** Resorcinol (500 μ M) was chloraminated
236 (5.6 mM NH_2Cl) at pH 7 to investigate its decomposition mechanism and to identify the intermediate
237 products that could lead to the formation of N-DBPs (e.g., DCACAm). Several peaks were observed in
238 the PCI chromatogram recorded on the GC-QTOF such as DCAN (retention time (RT) =3.7 min),
239 DCACAm (RT = 7.5 min), TCACAm (RT = 8.6 min), and other unknown compounds (P131 at RT =
240 8.5 min, P197 at RT= 10.6 min, P215 at RT = 11.0 min and P249 at RT = 11.5 min) (Figure S4). P215
241 and P249 were two major compounds exhibiting larger peak areas than known DBPs (i.e., DCAN,
242 DCACAm and TCACAm). Molecular formulas and structures of these compounds were proposed
243 based on their accurate mass obtained from GC-QTOF and fragmentation patterns observed in EI and
244 PCI modes (Table 2).

245

246

247

248 Table 2. Chloramination by-products of resorcinol detected by GC-QTOF

Compound	Exact Mass	Accurate Mass	Error (ppm)	Molecular Formula	Proposed Structures
P215	215.9380 [M+H] ⁺	215.9379 [M+H] ⁺	0.64	C ₅ H ₄ NO ₂ Cl ₃	
P249	249.8990 [M+H] ⁺	249.8988 [M+H] ⁺	1.06	C ₅ H ₃ NO ₂ Cl ₄	
P131	131.9845 [M+H] ⁺	131.9847 [M+H] ⁺	-0.13	C ₄ H ₂ NO ₂ Cl	
P197 ^a	197.9270 [M+H] ⁺	197.9262 [M+H] ⁺	6.43	C ₅ H ₂ NOCl ₃	
P179 ^b	178.9540	N.D	N.D	C ₅ H ₃ NO ₂ Cl ₂	
P198 ^c	197.9042	197.9252	-106.05	C ₅ HO ₂ Cl ₃	

^aConfirmed by NIST database (94% similarity)

^bDetected by GC-MSD; also reported in a previous study (Haddon et al., 1996); N.D: not detected by GC-QTOF.

^cConfirmed by NIST database (95% similarity); also reported in previous studies (Norwood et al., 1980; Boyce and Hornig, 1983).

249

250 The EI mass spectrum of P215 exhibited two dominant ion clusters (*m/z* 132/134 and 114/116)
 251 comprising one chlorine atom, with a difference of 18 Da corresponding to the loss of one water
 252 molecule (i.e., dehydroxylation) (Figure S5a). The corresponding PCI mas spectrum contained a
 253 major ion cluster *m/z* 216/218/220/222 (i.e., [M+H]⁺) with relative abundance, suggesting that this
 254 compound had three chlorine atoms (Figure S5b). The odd-numbered nominal mass (i.e., 215 Da)
 255 indicated an odd-number of nitrogen atoms. Loss of 83 along with two chlorine was observed from
 256 *m/z* 215 to *m/z* 132, indicating the loss of a (-CHCl₂) group. The PCI mass spectrum obtained from
 257 GC-QTOF showed an accurate mass of 215.9379 for [M+H]⁺. Accordingly, C₅H₄NO₂Cl₃ was
 258 confirmed to be the molecular formula of this compound (0.64 ppm). Based on the fragmentation
 259 pattern and accurate mass of fragments obtained from EI and PCI modes (Table S2), the proposed
 260 molecular structure of this compound is 3-chloro-5-hydroxy-1H-pyrrole-2-one with dichloromethyl
 261 group. It is structurally very similar to MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone),
 262 the strong mutagen found from chlorinated drinking water and humic water (Hemming et al., 1986;

263 Kronberg et al., 1988). Additionally, the corresponding methyl ester form of P215 was also detected
264 after derivatization of the MTBE extract using acidic methanol, with a molecular formula of
265 $C_6H_6NO_2Cl_3$ (9.52ppm). The corresponding EI and PCI mass spectra presented a loss of 31 Da (–
266 OCH_3 group) from m/z 229 to m/z 198 (Text S2).

267 A similar method was used for the identification of other compounds. P249 exhibited a similar EI
268 mass spectrum to P215, with dominant ion clusters m/z 132/134 and 114/116. However, its PCI mass
269 spectrum showed a main molecular ion (i.e., $[M+H]^+$) at m/z 250 including four chlorine atoms.
270 Therefore, we proposed P249 as an analogue of P215 with an additional chlorine atom or as 6-
271 hydroxy-2-pyridone with four chlorine atoms (Text S3).

272 The EI mass spectrum of P131 contained ion clusters m/z 131/133, 103/105 and 88/90, which was
273 similar to the mass spectrum of 3-chloro-2,5-furandione present in the NIST database (Figure S6).
274 However the molecular ion m/z 132 (i.e., a nominal mass of 131 Da) obtained from PCI mass
275 spectrum suggested the presence of a nitrogen atom. The accurate mass of ion m/z 131.9847 (i.e.,
276 $[M+H]^+$ adduct) supported a molecular formula of $C_4H_2NO_2Cl$ (-0.13 ppm). Accordingly, P131 was
277 tentatively identified as 3-chloro-2,5-pyrroledione (chloromaleimide) (Text S4).

278 Product P197 was confirmed as 2-hydroxy-3,5,6-trichloropyridine because a library match of its
279 spectrum was obtained from NIST database (94% similarity) and the corresponding formula
280 ($C_5H_2NOCl_3$) was derived from its accurate mass (Figure S7).

281 Product P179 was proposed as another pyridine-based compound (i.e., dichloro-pyridine-dione) or its
282 isomer, chloro-pyrrole-dione with dichloromethylene group. The formation of the latter was reported
283 during chlorination of poultry chiller water (Haddon et al., 1996). P179 was only detected from GC-
284 MSD (DB-1701 column) (Figure S8), but was not found by high resolution analysis on GC-QTOF.
285 2,2,4-trichloro-1,3-cyclopentenedione (P198) and its isomer were detected (95% similarity with NIST
286 database) from the MTBE extract after derivatization using acidic methanol (RT= 9.7min) (Figure
287 S9). The formation of 2,2,4-trichloro-1,3-cyclopentenedione has been reported as a chlorination by-
288 product of resorcinol (Boyce et al., 1983; Norwood et al., 1980).

289 Because of the lack of analytical standards, the proposed structures of P215, P249, P131 and P179
290 could not be confirmed. However, the formation of halogenated heterocyclic compounds (e.g.,
291 halogenated furanones and pyrroles), which are structurally similar to the compounds found from this
292 study, has been reported in several chlorination studies (Table S3). The most known halogenated
293 furanone formed by chlorination of drinking water is the highly mutagenic MX and its analogues
294 (Hemming et al., 1986; Kronberg and Vartiaine, 1988; Meier et al., 1986). In a previous study on
295 chlorination of phenolic compounds, resorcinol was found to produce MX, but in low concentration at
296 acidic pH (i.e., 0.01 mmol/mol, pH 2) (Långvik et al., 1991). Several compounds similar to MX were
297 identified from chlorination of orcinol (Tretyakova et al., 1994). Moreover, it was found that MX can
298 be produced during chloramination of humic water (Backlund et al., 1988) and fulvic acid solution

299 (Kanniganti et al., 1992). Dichloromaleic anhydride (3,4-dichloro-2,5-furandione) and
300 monochloromaleic anhydride (3-chloro-2,5-furandione), which are structurally similar to the
301 chlorinated pyrroledione found from this study (i.e., P131), are major chlorination by-products of
302 resorcinol (Rook, 1980) or swimming pool waters (Richardson et al., 2010). Similarly, 3-bromo-2,5-
303 furandione was reported from bromination of resorcinol (Boyce et al., 1983). Dichlorinated analogue
304 of P131, 3,4-dichloro-2,5-pyrroledione, was detected with three other chlorinated cyclic imides in
305 chlorinated poultry chiller water (Haddon et al., 1996). These five-carbon chlorinated cyclic imides
306 were structurally similar to P215 and found to be direct acting Ames mutagens (Freeman et al., 2001;
307 Haddon et al., 1996). Moreover, the presence of brominated pyrroles was reported from chlorinated
308 saline wastewater effluents (M. Yang et al., 2014). Tribromopyrrole is a major chlorination by-
309 product of bromide-containing waters and has been demonstrated to be strongly cytotoxic and
310 genotoxic to mammalian cells (Richardson et al., 2003).

311 Based on the potential toxicity of halogenated furanone, cyclic imide and pyrrole compounds
312 (Freeman et al., 2001; Haddon et al., 1996; Hemming et al., 1986; Kronberg et al., 1988; Richardson
313 et al., 2003), the halogenated nitrogenous heterocyclic compounds identified from this study could be
314 also strong mutagenic products and would require toxicity assays.

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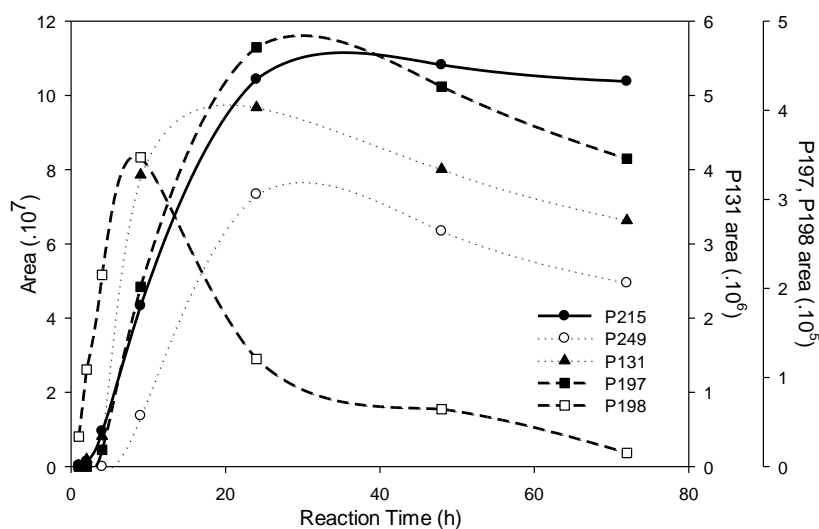
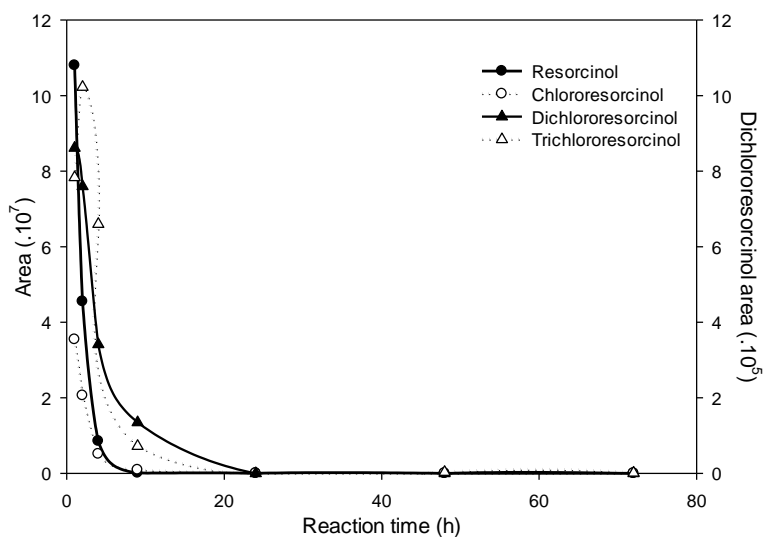


Figure 3. (a) Degradation of resorcinol and its chlorinated derivatives and (b) formation of by-products during chloramination (5.6 mM) of resorcinol (500 μ M) at pH=7.0 (10 mM phosphate buffer)

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331 **Effect of reaction time and pH on heterocyclic compounds formation.** Figure 3 shows the

332 evolution of peak areas of chlorinated derivatives of resorcinol and identified by-products with

333 reaction time. Mono-, di- and tri-chlorinated derivatives of resorcinol were detected after 1 h of

334 reaction time, indicating a fast electrophilic substitution of the aromatic ring by chlorine. The majority

335 of resorcinol and its chlorinated derivatives (>90%) decomposed within the first 9 h of reaction

336 (Figure 3a). It has been proposed that chlorination and chloramination of aqueous solutions of

337 resorcinol lead to the formation of a pentachlororesorcinol intermediate (compound I in Scheme 1),

338 which then undergoes hydrolysis and decarboxylation to produce chloroform and other chlorinated

339 compounds (Boyce et al., 1983; De Leer et al., 1985; Heasley et al., 1999; Rook, 1980). The

340 nitrogenous heterocyclic compounds found in this study exhibited the largest peak areas on GC-MS

341 chromatograms, suggesting that inorganic nitrogen incorporation is a major reaction pathway during

342 chloramination of resorcinol. A chloramination mechanism of resorcinol is proposed on Scheme 1,

343 where the carbonyl group of the pentachlororesorcinol intermediate is attacked by electron pairs of

344 nitrogen atom from NH_2Cl or oxygen atom from H_2O . The ring-cleavage by-product from nitrogen
345 attack then undergoes intramolecular nucleophilic substitution to form a nitrogenous heterocyclic
346 compound and finally P249 (Scheme 1a). A similar ring contraction mechanism is proposed for the
347 formation of 2,2,4-trichloro-1,3-cyclopentenedione (i.e., P198), based on its formation pathway
348 previously proposed during chlorination of resorcinol (Rook, 1980; Tretyakova et al., 1994) (Scheme
349 1b). P198 was formed rapidly from 1 h to 9 h and gradually degraded (Figure 3b). We propose that in
350 excess of NH_2Cl , P198 will be an intermediate product of nitrogenous heterocyclic compounds (i.e.,
351 P131, P215 and P249) through nitrogen attack and intramolecular nucleophilic substitution. As
352 shown in Figure 3b, P131 and P249 started to degrade after 24 h of reaction time. These compounds
353 comprise a Cl-C-CO-NH- moiety, which could be responsible for HAcAms and haloacetaldehydes
354 (HAcAls) formation with an excess of oxidant (Scheme 1).

355 Figure S10 presents the peak area of P131, P197, P198 and P215 after 72 h of reaction time at
356 different pHs. The highest formation was found in neutral (pH 7 for P197 and P215) or weak acidic
357 (pH 5.5 for P131 and P198) condition. Low formation of these compounds at pH 4 is in accordance
358 with the higher formation of chlorinated derivatives of resorcinol (Figure S3), supporting the
359 hypothesis that the reaction at pH 4 did not lead to significant ring-opening of resorcinol. Little or no
360 nitrogenous heterocyclic compounds were detected in alkaline conditions (pH 8.5 and 10), suggesting
361 that they might decompose at higher pH to form other by-products. To support our hypothesis, MX
362 mainly undergoes hydrolytic degradation at pH higher than 8 (Kronberg et al., 1989).

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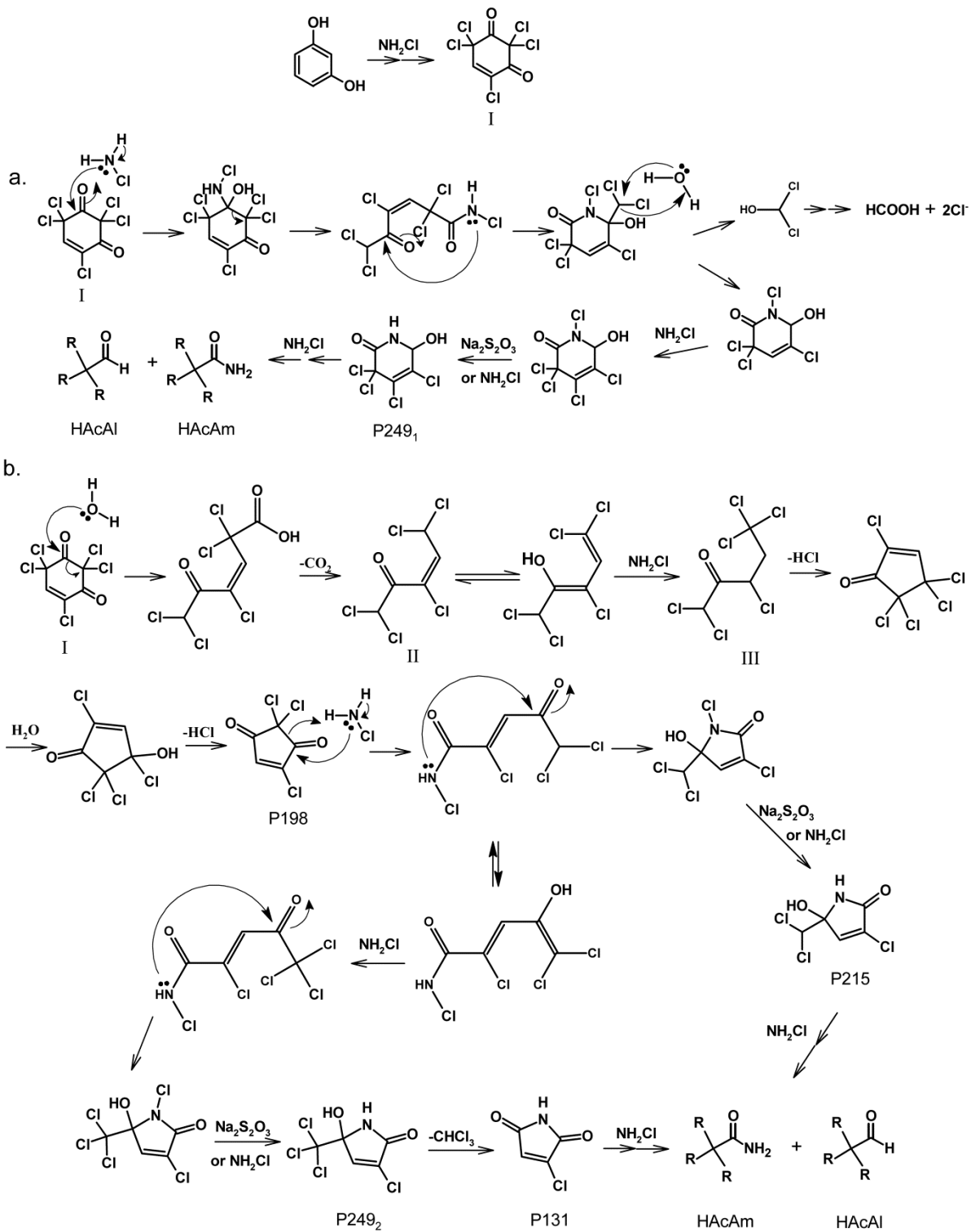
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374 Scheme 1. Proposed formation pathway of by-products from chloramination of resorcinol (I:
 375 pentachlororesorcinol; II, III: compounds identified in a previous study (Heasley et al., 1999). b:
 376 adapted from previous studies (Rook, 1980; Heasley et al., 1999; Tretyakova et al., 1994). P215,
 377 P249_{1,2}: possible structures for P215, P249).



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381 **ENVIRONMENTAL SIGNIFICANCE**

382 High concentrations of model compounds and high monochloramine doses were used in this study to
383 maximize the formation of by-products and thus facilitate their detection and identification by GC-MS
384 in full scan mode. The possible reasons why the products identified in this study (i.e., chlorinated
385 nitrogenous heterocyclic compounds) have not yet been observed during the chloramination of real
386 water samples, include: (1) many studies about the identification of unknown DBPs were mainly
387 focused on chlorination process, and less on chloramination; (2) the amounts of by-products formed in
388 real case disinfection scenarios (i.e., low precursors concentration and low monochloramine doses)
389 were not sufficient to be detected during analytical screenings. From another study we detected a
390 compound likely to be dibromo-pyrrole-dione (molecular ion m/z 253), similar base structure to P131,
391 during chloramination (14.9 mg/L Cl_2) of a treated wastewater effluent (5 mg/L DOC) containing 2.5
392 mg/L of bromide ion. It exhibited a similar mass spectrum to dibromo-furan-dione (m/z 254). The
393 accurate mass obtained from GC-QTOF (m/z 252.8408) supports the molecular formula of
394 $C_4HNO_2Br_2$ (11 ppm) (Figure S11). The occurrence of brominated pyrroledione indicated that this
395 class of compounds can be formed during real chloramination scenarios. Similar screening of
396 chlorinated or brominated pyrroledione compounds should be performed during chloramination of
397 natural waters or NOM in order to confirm their formation from other organic matrices.

398 Aromatic compounds that do not contain nitrogen can react with monochloramine to produce N-DBPs
399 through inorganic nitrogen incorporation. The potential formation of nitrogenous heterocyclic
400 compounds is of importance for water treatment facilities using chloramine as disinfectant since they
401 could be substantially toxic due to their similarity to known mutagenic compounds (e.g., MX). The
402 removal of aromatic NOM must be optimized to avoid the production of these potentially toxic
403 N-DBPs.

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405 **SUPPORTING INFORMATION**

406 Detailed information on analytical methods, total ion chromatogram from GC-MS and mass spectrum
407 of each compound in EI and PCI mode are available in supporting information.

408 **SUPPORTING INFORMATION**

409 We acknowledge the financial support from Water Research Australia and Water Corporation of
410 Western Australia (WaterRA Postgraduate Scholarship).

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