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5 Formation of disinfection byproducts during the preparation of tea and coffee

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18 **Abstract**

19 This study examined the formation of selected disinfection byproducts (DBPs) during the
 20 chlorination of breakfast, Earl Grey and green tea, and from instant and filter coffee. Eight
 21 model compounds representing the organics in tea and coffee were also tested. Initially,
 22 experiments using water pre-spiked with chlorine demonstrated chlorine concentrations of
 23 1-19 mg·L⁻¹ were reduced by 5-19% through boiling in a kettle. The chloroform
 24 (trichloromethane) yield of 47.6±0.3% from chlorination of catechin hydrate is high
 25 compared with surrogates of drinking water natural organic matter (NOM). Chloroform
 26 yields from tea chlorinated under formation potential conditions were similar to reactive
 27 drinking water NOM isolates and higher than from coffee. Chloroform generated during the
 28 preparation of tea reached 30-43 µg·L⁻¹ at the highest chlorine dose of 14.2 mg·L⁻¹. Under
 29 the same conditions no chloroform was detected in instant coffee, whereas up to 3 µg·L⁻¹
 30 chloroform was generated from filter coffee. Overall, this study demonstrates the potential
 31 for DBP formation when tea is prepared in water containing elevated chlorine
 32 concentrations, such as following point-of-use treatment. Conversely, chloroform
 33 concentrations in tea prepared with water containing 1 mg·L⁻¹ chlorine were ≤4 µg·L⁻¹ and
 34 therefore trichloromethane (THM) concentrations in tea made using municipal tap water
 35 are likely to be insignificant.

36 **Keywords:** chlorination, tap water, trihalomethanes, chloroform, flavanols

37

38 **Introduction**

39 Chlorine is commonly applied for disinfecting drinking water, but also reacts strongly with
40 many organic and inorganic constituents in water. An unwanted result of these reactions
41 are disinfection byproducts (DBPs). The trihalomethanes (THMs) were the first DBPs to be
42 reported in chlorinated drinking water, in the 1970s.^{1, 2} Current regulations for the four
43 chlorinated/brominated THMs in the USA and EU are set at 80 and 100 $\mu\text{g}\cdot\text{L}^{-1}$, respectively.
44 Over the last four decades the number of identified DBPs has grown and now exceeds 600³,
45 which reflects the diversity of both organic precursors and disinfectants, as well as the
46 increasing sophistication of analytical methods. Previous research on the formation of THMs
47 has established humic substances as a key precursor pool. These incorporate both humic
48 and fulvic acids, which are mainly derived from terrestrial vegetation and have high lignin,
49 and consequently, aromatic content.⁴

50 Since their discovery the issue of whether exposure to DBPs is linked to cancer and
51 reproductive/developmental effects has also been investigated. Epidemiological studies
52 have shown that a lifetime exposure to chlorinated water is associated with an increased
53 risk of developing bladder cancer.⁵ Nonetheless, causal agent/s for the adverse human
54 health outcomes potentially associated with chlorination DBPs have yet to be identified,
55 although the halobenzoquinones, recently reported as DBPs, have been proposed as
56 putative bladder carcinogens.⁶

57 Human exposure to THMs and other DBPs can occur through multiple exposure routes,
58 including inhalation and dermal contact, although it has been estimated that 50-70% of
59 exposure to THMs comes from ingestion of tap water and beverages made using tap water.⁷
60 This context partly explains why a number of studies have investigated the impact of boiling
61 tap water on concentrations of DBPs, and consequently how this affects exposure to

humans.⁸⁻¹² Among these studies it has been reported that the concentration of chloroform (trichloromethane) was reduced by 34% in chlorinated water after 1 min boiling⁹ and the cytotoxicity of simulated tap water was reduced by 77% after boiling for 5 min.⁸

However, one topic that has received little attention is whether THMs and other DBPs might be generated when boiled water is used to prepare tea and coffee, through reactions between residual chlorine present in tap water and organic precursors present in these beverages. It is evident that tea and coffee are both rich in organic matter of similar character to humic substances found in drinking water, while the volatility and concentration of aqueous chlorine will also affect DBP formation. Tea and coffee are the most consumed beverages in the world, and over 80% of tap water consumption is estimated to be associated with the preparation of tea, coffee and other hot beverages.¹³ Global consumption of both tea and coffee are projected to increase in the future.^{14, 15}

The authors are aware of only one other relevant study on this topic, which reported that instant tea generated similar amounts of THMs as aquatic humic substances when chlorinated under formation potential conditions.¹⁶ Furthermore, these authors showed that 164-196 $\mu\text{g}\cdot\text{L}^{-1}$ as chloride of total organic halogen (TOX) was formed when instant tea was contacted with 4 $\text{mg}\cdot\text{L}^{-1}$ chlorine for 24 h.¹⁶ However, specific DBPs were not quantified under the latter conditions and only instant tea was considered. In this context, the first objective of this study was to evaluate the proportion of aqueous chlorine which remains in solution after boiling in a typical household kettle. The chlorine demand and DBP formation of organic surrogates and authentic tea and coffee samples chlorinated under both formation potential conditions and a contact time and temperature representative of real-life tea and coffee preparation were also examined.

85

86 **Experimental**87 **Selection of tea and coffee surrogates**

88 Tea is produced from the leaves of *Camellia sinensis* and is classified into three types, based
89 on the extent of fermentation: unfermented green tea, partially fermented oolong, and fully
90 fermented black teas.¹⁷ Its composition is dominated by polyphenolic compounds, mostly
91 flavan-3-ols, which comprise up to 30% of the dry weight of tea leaves, approximately a
92 third in the form of epigallocatechin gallate (EGCG; Table 1).¹⁸ Other components include
93 amino acids and carbohydrates. During the fermentation of green tea, the proportion of
94 polyphenolic compounds changes, whereas other components largely remain unchanged.¹⁹
95 Coffee beans are the fruit of coffee plants, with *Coffea Arabica* and *Coffea Robusta* being
96 the most common species.²⁰ Polysaccharides (polymeric carbohydrates) form more than
97 50% of green coffee beans, with a large percentage as cellulose. The brown colour of coffee
98 is attributed to melanoidins, which are brown nitrogenous polymers of uncertain
99 structure.²¹ Based on the above, eight tea and coffee surrogates were selected (Table 1).
100 Epigallocatechin gallate and catechin hydrate (CH) were selected to represent the flavanols
101 commonly found in tea. Chlorogenic acid (CGA), quinic acid (QA) and gallic acid (GA) are
102 representative of organics found in coffee. Catechol (CAT) is a simple structure found as a
103 component of polyphenols in tea and coffee. As cellulose is insoluble in water, galactose
104 (GLA) was selected instead to represent the saccharides prevalent in coffee. Finally, caffeine
105 (CF) is a well-known constituent of both beverages.

106 **Chlorination conditions**

107

108 Four different types of chlorination tests were undertaken: kettle boiling, chlorine demand,
109 disinfection byproduct formation potential (DBPFP, which use excess chlorine) and those
110 using a representative contact time and temperature (see Table 2 for experimental
111 conditions, including concentrations of chlorine and precursors). Three types of tea -
112 Twinings English Breakfast tea, Twinings Pure Green tea, and Twinings Earl Grey tea (all of
113 which are tea bags) - and two types of coffee - Carte Noire Instinct whole bean instant
114 coffee (100% Arabica coffee) and Lavazza Qualita Rossa filter coffee – were used during the
115 chlorine demand, DBPFP and representative contact time tests (Table 2). For comparison
116 the chlorine demand and DBPFP of the eight model compounds was measured. In all types
117 of chlorination tests a sodium hypochlorite solution (Sigma Aldrich, UK) was used as the
118 chlorine source, with chlorine concentrations monitored using the *N,N*-Diethyl-*p*-
119 phenylenediamine - ferrous ammonium sulphate (DPD-FAS) titration method.²² All samples
120 were prepared in duplicate in reverse osmosis (RO) treated ultrapure water at pH 7±0.2 (10
121 mmol, phosphate buffer) containing chlorine at pre-determined doses. For the kettle boiling
122 experiments 1 L of RO water was spiked with chlorine; 200 mL was set aside to measure the
123 initial chlorine concentration, whilst the remaining 800 mL was boiled in a kettle (Breville,
124 UK), and left to cool for 10 minutes, before measuring the final chlorine concentration.
125 When boiling 800 mL of RO water it took ~2:09 min to reach boiling, plus another ~12 sec
126 boiling, before the kettle turned itself off. Chlorine demand of the eight model compounds
127 and five types of beverage was determined from chlorine concentrations taken before and
128 after the contact time of 24 h. The chlorine dose of 35 mol Cl₂/mol surrogate used to
129 measure the chlorine demand of the model compounds (Table 2) is based on a study which
130 investigated aquatic natural organic matter surrogates.²³

All tea and coffee samples were prepared in 250 mL water. When preparing tea samples one tea bag was brewed for 3 min before being removed. The contents of the breakfast, green and Earl Grey tea bags weighed 2.6, 2.4 and 2.6 g, respectively. Both coffee types were made using 4 g of coffee, with filter coffee samples prepared in a cafetière, with the filter plunged after 3 min. For the experiments to measure THMs in tea and coffee prepared at a representative contact time and temperature samples were made in disposable cups. The selected chlorine doses were 1, 4 and 14.2 mg·L⁻¹. In the UK water companies generally maintain residual chlorine at <0.5 mg·L⁻¹ (DWI, 2010); in the USA up to 4 mg·L⁻¹ is permitted in distribution²⁴, while point-of-use (POU) treatment may leave higher chlorine residuals and the highest dose of 14.2 mg·L⁻¹ has been previously used to simulate POU conditions.²⁵ After 20 min contact between the tea/coffee and chlorine-spiked water the residual chlorine was quenched with ascorbic acid (3:1 mol/mol of ascorbic acid: chlorine) and samples acidified prior to DBP analysis.

Analytical methods

The ultraviolet (UV) absorbance and non-purgeable organic carbon (NPOC, equivalent to dissolved organic carbon (DOC)) of 1:100 (vol/vol) diluted tea and coffee samples were measured using a Shimadzu UV-2401PC spectrophotometer and a Shimadzu TOC-5000 analyser, respectively. UV and DOC values reported in the remainder of the paper are for undiluted samples, taking into account the dilution factor.

Following (DBPFP) tests samples were extracted into 3 mL of methyl tertiary-butyl ether (MTBE) following acidification to pH ~ 3.5 with H₂SO₄ and addition of 1 g copper sulphate and 10 g pre-baked sodium sulphate, following USEPA method 551.1.²⁶ Since the degradation of chloropicrin (trichloronitromethane) and trichloroacetonitrile (TCAN) is

154 accelerated in the presence of sulphite²⁷, no quenching agent was used.²³ DBPs were
155 subsequently quantified by gas chromatography with electron capture detection (GC-ECD,
156 Perkin Elmer Clarus 500 GC) using a modified version of USEPA method 551.1 and a Restek
157 Rxi-5 Sil MS column (of dimensions 30 m × 0.25 mm × 0.25 µM). Procedural blanks (which
158 had the same composition as samples, except chlorine was absent) were included in each
159 set of samples and the internal standard was 1-bromo-4-fluorobenzene (1 µg·mL⁻¹). The
160 quantified DBPs were chloroform (trichloromethane), chloropicrin (trichloronitromethane),
161 dichloroacetonitrile (DCAN), TCAN, 1,1-dichloropropanone (1,1-DCP) and 1,1,1-
162 trichloropropanone (1,1,1-TCP). These DBPs are available in a standard mix (Sigma Aldrich,
163 UK). Method detection limits for these species were 0.1, 0.5, 0.1, 0.5, 0.1 and 0.2 µg·L⁻¹,
164 respectively. Method recoveries ranged from 89-113%. As noted previously by Wu et al¹⁶,
165 severe foaming occurs when extracting undiluted tea/coffee samples into MTBE, so after
166 the representative contact time and temperature tests THMs were instead quantified using
167 a headspace solid-phase microextraction (SPME) GC-ECD (Varian 450) method at CELW Ltd
168 (Bangor University, UK). Note that the additional, less volatile, DBPs monitored by USEPA
169 method 551.1 are not captured by headspace methods and were therefore not recorded
170 after these experiments. A carboxen/Polydimethylsiloxane SPME fibre assembly (Sigma
171 Aldrich, UK) and a Restek MX1 30 m x 0.53 mm x 0.7 µm column were used, based on the
172 method of Sarrión et al.²⁸ Detection limits for four THMs were 0.5, 0.1, 0.1 and 0.5 µg·L⁻¹ for
173 chloroform, dichlorobromomethane, dibromochloromethane and bromoform, respectively,
174 and procedural blanks for the five types of tea and coffee were also analysed. No bromide
175 was added to samples and the small amounts (typically under 1 µg·L⁻¹) of brominated THMs
176 observed in both blanks and samples therefore resulted from contamination and are not
177 reported.

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179 **Results**180 **Kettle boiling experiment**

181 Before investigating any DBPs generated during preparation of tea and coffee a preliminary
182 question needed to be addressed: how much aqueous chlorine actually remains available
183 for reaction after the water has been boiled in a typical household kettle? The answer to
184 this is that, at initial chlorine concentrations of up to $19 \text{ mg}\cdot\text{L}^{-1}$ as Cl_2 , only 5.1-19.0% of
185 chlorine was removed by boiling in a kettle (Figure 1). At the lowest initial chlorine dose of
186 $1.1 \text{ mg}\cdot\text{L}^{-1}$ the reduction in chlorine concentration was greatest at $19\pm 10\%$, but at higher
187 initial chlorine doses the reduction was consistently $\leq 10\%$. In other words only $< 20\%$ of
188 chlorine was removed by boiling in a kettle under representative conditions. A recent study
189 by Zhang²⁹ looked at the efficacy of boiling for removing residual chlorine found in tap
190 water, with disproportionation of hypochlorite (OCl^-) to chloride (Cl^-) and chlorate (ClO_3^-)
191 believed to be an important degradation route. At an initial chlorine concentration of 2
192 $\text{mg}\cdot\text{L}^{-1}$ as Cl_2 it required 33 min of boiling to completely remove the aqueous chlorine.²⁹ This
193 data is consistent with that in the current study, given that the kettle used in the latter only
194 boils water for ~ 12 sec before turning itself off.

195 **Chlorine demand of tea and coffee**

196 Chlorine demand of the eight tea and coffee surrogates ranged from 0.6 to 11.3 mol of
197 Cl_2 /mol of surrogate (abbreviated to mol/mol hereafter) (Figure 2), comparable to many low
198 molecular-weight compounds which have been used to represent components of aquatic
199 NOM.³⁰ The chlorine demand of galactose³¹ and catechol³² were previously reported as 0.8

mol/mol (pH 8, 72 h, galactose $2 \text{ mg}\cdot\text{L}^{-1}$ as DOC, chlorine dose 5.1 mol/mol) and 4.1 mol/mol (pH 7, 15 h, chlorine dose 20 mol/mol), respectively. Equivalent values in the current study were 1.3 ± 0.03 and $3.6\pm0.13 \text{ mol/mol}$, respectively (at pH 7, 24 h and a chlorine dose 35 mol/mol), which agree well with the literature data, especially given the differences in experimental conditions. From Figure 1 it can be seen that the two surrogates with the highest chlorine demand were catechin hydrate and caffeine, which consumed 11.3 ± 0.11 and $9.3\pm0.13 \text{ mol/mol}$, respectively, while epigallocatechin gallate had the lowest chlorine demand of $0.6\pm0.05 \text{ mol/mol}$. Aromatic compounds with electron-donating substituents, such as catechin hydrate, are known to have relatively high chlorine demand, since the amount of ring activation promotes electrophilic substitution reactions.³³ Ortho or para substituted compounds with two electron-donating groups, for example, catechol, typically have lower chlorine demand than meta substituted isomers, since interactions between ortho/para substituents are antagonistic with respect to chlorine demand.³³ Meanwhile, the relatively high chlorine demand of caffeine is most likely related to the presence of multiple amine and nitrile groups.

DOC concentrations of the three types of tea tested were from $892\text{--}1017 \text{ mg}\cdot\text{L}^{-1}$, while concentrations in filter coffee and instant coffee were higher still at respectively 2018 ± 9 and $5318\pm22 \text{ mg}\cdot\text{L}^{-1}$ (Figure 3). Total organic carbon (TOC) concentrations of (untreated) surface waters are typically from $1\text{--}20 \text{ mg}\cdot\text{L}^{-1}$ ³⁴ and significantly lower in (treated) drinking water. Hence, DOC concentrations found in tea are well in excess of 45x those typically found in treated water, with concentrations in coffee over 100x higher. The chlorine demand of tea and coffee, when expressed in $\text{g}\cdot\text{Cl}_2/\text{g}\cdot\text{DOC}$, presented the opposite trend to DOC results, reflecting that tea contained a greater proportion of high chlorine demand material (Figure 3). The chlorine demand of tea samples were between 6.9 ± 0.56 and $9.6\pm0.69 \text{ g}\cdot\text{Cl}_2/\text{g}\cdot\text{DOC}$

224 for green tea, Earl Grey tea and breakfast tea, respectively, which were higher than the
225 respective values for instant and filter coffee of 2.9 ± 0.2 and 5.0 ± 0.41 g-Cl₂/g·DOC (Table SI
226 1).

227 For comparison, the chlorine demand of 10 Suwannee River NOM isolates, which have been
228 studied extensively in drinking water research, varied between 0.8 and 2.8 g-Cl₂/g·DOC, with
229 the highest value for the ultrahydrophilic humic acid (uHA) fraction (chlorination conditions:
230 Cl₂/DOC 4 mg/mg; pH 8, 72 h, 20 °C).⁴ Thus, the chlorine demand of tea in particular is
231 higher than typically found in drinking water sources. Solutions of tea and coffee are acidic,
232 as evidenced by pH values of (undiluted and non-buffered) samples ranging from 4.7 for
233 instant coffee to 5.3 for green tea. The specific UV absorbance at 254 nm (SUVA₂₅₄,
234 calculated by dividing the UV absorbance of a sample by its DOC concentration) of the five
235 beverages ranged from 1.6 to 2.7 L/mg·m⁻¹, respectively (Table SI 1). SUVA₂₅₄ is used to
236 indicate the aromatic content (and consequently hydrophobic/hydrophilic character) of
237 drinking water sources, with SUVA₂₅₄ values from 2-4 L/mg·m⁻¹ previously categorised as
238 having medium SUVA₂₅₄.³⁵ This applies to filter coffee, breakfast tea and Earl Grey tea,
239 whereas instant coffee and green tea can be classified as having low-SUVA₂₅₄ using drinking
240 water terminology (Table SI 2).³⁵ Equivalent SUVA values at 272 nm (i.e. SUVA₂₇₂) ranged
241 from 2.1 to 3.7 L/mg·m⁻¹, respectively, and interestingly SUVA₂₇₂ correlated more strongly
242 with chlorine demand (in g-Cl₂/g·DOC) than SUVA₂₅₄: the respective Pearson product-
243 moment correlation coefficients (r) were 0.64 and 0.89, respectively (Table SI2). The
244 underlying basis for this observation is that activated aromatic species (i.e. those with
245 electron-donating substituents), which are known to react strongly with chlorine, tend to
246 have absorbance maxima around 272 nm³⁶.

DBP formation from tea and coffee surrogates

Among the DBPs analysed in this study, chloroform was the dominant DBP observed from all tea and coffee surrogates, although limited formation of 1,1-DCP and 1,1,1-TCP was also recorded: ≤ 0.34 and ≤ 0.17 % mol DBP/mol precursor (% mol/mol) (Figure 4). It is noted that only chlorinated DBPs were observed, due to the absence of bromide in samples. The highest chloroform yield recorded was 47.6 ± 0.3 % mol/mol from catechin hydrate, followed by 4.6 ± 0.3 % mol/mol from epigallocatechin gallate, and all other surrogates had yields ≤ 1.32 % mol/mol (Figure 4). Chloroform yields from catechol and galactose were 1.20 ± 0.00 % and 0.53 ± 0.01 % mol/mol, respectively (Figure 4). A slightly lower chloroform yield for catechol was previously reported: 0.4% mol/mol after 15 h reaction (pH 7, chlorine dose 20 mol/mol; ³²). The discrepancy can be explained by the shorter chlorine contact time used in the earlier study. THM formation from carbohydrates is pH dependent³¹, with the chloroform yield from galactose rising from ~ 0.04 % mol/mol at pH 5 to ~ 3.17 % mol/mol at pH 8 (72 h, chlorine dose 5 mg/mg precursor).³¹ Again these data compare well with the pH 7 chloroform formation recorded in the current study. The chloroform yield from catechin hydrate is notably high when compared to NOM surrogates studied during drinking water treatment research. The recorded value of 47.6 ± 0.3 % is equivalent to 309 ± 2 $\mu\text{g}(\text{mg}\cdot\text{DOC})^{-1}$ and only 28 out of 184 (or 15%) compounds listed as THM precursors³⁰ had higher chloroform formation yields. The potency of catechin hydrate and epigallocatechin gallate, relative to the other surrogates, can be explained by these precursors containing a resorcinol (1,3-dihydroxybenzene) functionality, which is a well-known reactive THM precursor structure. Upon chlorination resorcinol is converted to chloroform in yields over 90% mol/mol.^{32, 37} Moreover, the behaviour of fast-reacting THM precursors in drinking water sources is consistent with that of resorcinol, since chloroform forms from the latter

within 30 min.³⁸ This is relevant given the limited time available for DBP formation during the preparation of tea and coffee.

DBP formation from authentic tea and coffee samples

Samples of tea and coffee chlorinated under formation potential conditions all formed significant levels of DBPs, predominantly chloroform (Figure 5). Yields of chloroform from the two types of coffee were lower than from the three types of tea. Respective amounts of chloroform produced from chlorination of filter coffee, instant coffee, breakfast tea, Earl Grey tea and green tea were 25.9 ± 5.4 , 14.7 ± 1.2 , 47.8 ± 1.6 , 62.4 ± 4.7 and 55.3 ± 0.0 $\mu\text{g} \cdot \text{mg} \cdot \text{DOC}^{-1}$ (Table SI2). For comparison, 10 Suwannee River NOM isolates generated from 23 – 63 $\mu\text{g} \cdot \text{mg} \cdot \text{DOC}^{-1}$ of chloroform (Cl_2/DOC 4 mg/mg; pH 8, 72 h, 20 °C).⁴ The lowest and highest chloroform yields were from the ultrahydrophilic neutral (uHPIN) and uHA fractions, respectively.⁴ These data illustrate that the two types of coffee had chloroform yields towards the lower end, or lower than, what is typically recorded in drinking water NOM, whereas yields from tea are comparable to the more reactive drinking water NOM isolates. Wu and co-workers¹⁶ also reported that two types of instant tea formed similar amounts of THMs as aquatic humic substances chlorinated under the same conditions (pH 7 or pH 8.5, 24 h, Cl_2/DOC 2.5). Similar to the relationships calculated with chlorine demand, SUVA_{272} showed a stronger correlation with chloroform formation than SUVA_{254} , with respective correlation coefficients being 0.74 and 0.36 (Table SI2). This implicates activated aromatic compounds as an important group of chloroform precursors in tea and coffee. In addition to chloroform, smaller amounts of the other quantified DBPs were also detected from the chlorination of tea and coffee samples (Figure 5). All five types of tea and coffee generated DCAN ($\leq 1.04 \mu\text{g} \cdot \text{mg} \cdot \text{DOC}^{-1}$), chloropicrin ($\leq 0.26 \mu\text{g} \cdot \text{mg} \cdot \text{DOC}^{-1}$), 1,1-DCP ($\leq 0.49 \mu\text{g} \cdot \text{mg} \cdot \text{DOC}^{-1}$)

and 1,1-TCP ($\leq 1.32 \mu\text{g}\cdot\text{mg}\cdot\text{DOC}^{-1}$). The highest formation of DCAN, 1,1-DCP and 1,1-TCP came from Breakfast tea, filter coffee and instant coffee, respectively, while Earl Grey and green tea both formed $0.26 \mu\text{g}\cdot\text{mg}\cdot\text{DOC}^{-1}$ of chloropicrin.

Subsequently chloroform formation was quantified from tea and coffee samples prepared with freshly-boiled ultrapure water pre-spiked with chlorine and left for 20 min before being quenched with ascorbic acid (Figure 5). At the three chlorine doses tested chloroform formation from instant coffee, which also had the lowest chloroform formation potential (Figure 5), was always under the detection limit, whereas the formation from filter coffee increased from under detection limits at a chlorine dose of $1 \text{ mg}\cdot\text{L}^{-1}$ to 2.2 ± 0.1 and $3.2\pm0.2 \mu\text{g}\cdot\text{L}^{-1}$ at applied doses of 4 and $14.2 \text{ mg}\cdot\text{L}^{-1}$, respectively. The three types of tea all formed greater amounts of chloroform, especially at the highest chlorine dose of $14.2 \text{ mg}\cdot\text{L}^{-1}$ (Figure 5), chosen to represent a point-of-use disinfection method. Overdosing with chlorine, as typified by this dose, may be fairly common during POU treatment in developing countries in particular.²⁵ The highest chloroform formation came from Earl Grey tea: $42.6\pm4.4 \mu\text{g}\cdot\text{L}^{-1}$ at a chlorine dose of $14.2 \text{ mg}\cdot\text{L}^{-1}$, while breakfast tea and green tea generated 30.4 ± 0.2 and $36.8\pm5.2 \mu\text{g}\cdot\text{L}^{-1}$, respectively, under these conditions. At the chlorine dose of $4 \text{ mg}\cdot\text{L}^{-1}$, the maximum chlorine level permissible in US distribution systems, chloroform formation was respectively 4.9 ± 0.5 , 5.2 ± 0.4 and $12.5\pm0.2 \mu\text{g}\cdot\text{L}^{-1}$ from breakfast, Earl Grey and green tea (Figure 5). Equivalent values at a chlorine dose of $1 \text{ mg}\cdot\text{L}^{-1}$ were 3.9 ± 0.5 , 2.9 ± 1.2 and $4.1\pm0.3 \mu\text{g}\cdot\text{L}^{-1}$. The higher chloroform formation (Figure 5) of tea compared with coffee can be linked with higher concentrations of reactive THM precursors. Although their exact identity is uncertain these are most plausibly the flavanols which are widespread in tea, for example, catechin hydrate and epigallocatechin gallate (Table 1). Conversely, the higher concentration of polysaccharides, known for their relatively low THM yields (at neutral or

acidic pH) and slow chlorination kinetics,^{30, 31} in coffee likely manifests itself in lower chlorine demand (Figure 3) and chloroform formation (Figure 5) than tea.

Discussion: implications for exposure to DBPs

This study has demonstrated that concentrations of chloroform produced during the preparation of three types of tea at a representative contact time and temperature increased from 3-4 $\mu\text{g}\cdot\text{L}^{-1}$ at a chlorine dose of 1 $\text{mg}\cdot\text{L}^{-1}$ to 5-12 $\mu\text{g}\cdot\text{L}^{-1}$ at a chlorine dose of 4 $\text{mg}\cdot\text{L}^{-1}$, and 30-43 $\mu\text{g}\cdot\text{L}^{-1}$ at a chlorine dose of 14.2 $\text{mg}\cdot\text{L}^{-1}$. Based on the results of the experiments chlorinating tea and coffee under formation potential conditions, dihaloacetonitriles (DHANs), halonitromethanes (HNMs) and haloketones can also be expected, albeit at concentrations much lower than observed for chloroform. Given the large quantities of tea which many people consume, above 1 kg per capita per annum in many countries,^{39, 40} this has the potential to account for a significant proportion of exposure to DBPs where drinking water supplies contain relatively high levels of chlorine, e.g. following point-of-use treatment. The kettles used to prepare tea and coffee in this study only boiled water for ~12 sec, which is insufficient to depress chlorine concentrations by more than 5-19% at initial concentrations up to 19 $\text{mg}\cdot\text{L}^{-1}$ as Cl_2 (Figure 1).

More research is needed to comprehensively evaluate the net effect of tea and coffee preparation on DBP concentrations, i.e. whether formation due to chlorination of organic matter is outweighed by removal of existing volatile species, such as the THMs, during boiling. This should also consider a wider range of water quality parameters (e.g. pH and bromide) than monitored in this study. It is notable though that many studies on the reduction in DBPs through boiling have considered boiling times of 1 min and upwards, for

341 example 1, 2 and 5 min⁹ and 5 or 10 min⁸, rather than the ~12 sec boiling time, plus ~2:09
342 min to reach boiling, that the kettle used here took to boil 800 mL water. Therefore, the
343 reductions in DBP concentrations reported in studies such as these are likely to be more
344 than resulting from kettle usage.

345 THMs are terminal DBPs, the presence of which also signifies the formation of additional,
346 intermediate, DBPs. It is established that THM formation tends to increase at alkaline pH,
347 due the importance of base-catalysed reaction steps.⁴¹ Solutions of non-buffered tea and
348 coffee are acidic, which is therefore not optimal for THM formation. Moreover, other
349 conditions applying to tea and coffee preparation, where contact times are much shorter
350 than in municipal drinking water supply systems and organic matter present in excess,
351 relative to chlorine concentrations, will also favour the formation of intermediate DBPs over
352 THMs. Wu et al¹⁶ proposed that the significant levels of TOX they recorded (164-196 $\mu\text{g}\cdot\text{L}^{-1}$
353 as chloride; chlorine dose 4 $\text{mg}\cdot\text{L}^{-1}$, 24 h exposure) were likely to be predominantly
354 composed of macromolecular species. However, the current study has also shown that low
355 molecular weight DBPs, specifically the THMs, can also be generated under representative
356 beverage-making contact times and temperatures. Given the high phenolic content of tea in
357 particular additional products are predicted to include the halobenzoquinones, highlighted
358 as DBPs of concern due to their status as putative bladder carcinogens and known to be
359 produced from the chlorination of phenol.⁶ The halobenzoquinones are more stable at
360 acidic pH, as found in tea and coffee samples. More specifically, at pH levels at under 6.8,
361 2,6-dichloro-1,4-benzoquinone was stable, whereas it was easily hydrolyzed at pH 7.6.⁶ In
362 addition, there are also a variety of other halogenated phenols, including the dihalo-4-
363 hydroxybenzaldehydes, dihalo-4-hydroxybenzoic acids, dihalo-salicylic acids, and trihalo-
364 phenols, which have been detected in water chlorinated in the presence of bromide⁴² and

are also thought to be of toxicological significance. Furthermore, bromophenols which can be responsible for taste-and-odour issues in drinking water, are generated during the chlorination of phenol- and bromide-containing waters⁴³ are also potentially formed during the preparation of tea and coffee in waters with high ambient bromide concentrations.

Finally, as a counterpoint to the above, the health benefits of drinking tea should not be forgotten when discussing this issue. The same features that make phenolic compounds such as flavanols effective THM precursors also translates into antioxidant properties which have been associated with public health benefits. In particular, consumption of tea has been reported to have positive effects with respect to weight management, type 2 diabetes and cardiovascular disease.⁴⁴

Conclusions

This study has examined the generation of selected DBPs following chlorination of tea and coffee samples, as well as their chlorine demand. Eight surrogates chosen to represent organics in tea and coffee were also tested in parallel. The following are the key findings of this study:

- Aqueous chlorine at initial concentrations of 1-19 mg·L⁻¹ was reduced by between 5-19% upon boiling in a kettle, indicating the majority of chlorine remained available for reaction with organic matter in tea and coffee.
- The chlorine demand of eight tea and coffee surrogates ranged from 0.6 to 11.3 mol/mol, comparable to many low molecular-weight compounds which have been used to represent components of drinking water NOM. The chloroform yield of

387 47.6±0.3% from catechin hydrate is notably high compared with surrogates studied
388 during drinking water treatment research.

- 389 • Specific yields of chloroform ($\mu\text{g}\cdot\text{mg}\cdot\text{DOC}^{-1}$) from two types of coffee chlorinated
390 under formation potential conditions were towards the lower end, or lower than,
391 typically recorded from fractions of drinking water NOM, whereas the specific yields
392 from tea were comparable to the more reactive drinking water NOM isolates.
393 Chloroform concentrations generated during preparation of tea at a representative
394 contact time and temperature reached 5-12 $\mu\text{g}\cdot\text{L}^{-1}$ at a chlorine dose of 4 $\text{mg}\cdot\text{L}^{-1}$ and
395 30-43 $\mu\text{g}\cdot\text{L}^{-1}$ at a chlorine dose of 14.2 $\text{mg}\cdot\text{L}^{-1}$. Under the same conditions no
396 chloroform was detected in instant coffee samples, whereas formation from filter
397 coffee reached 3 $\mu\text{g}\cdot\text{L}^{-1}$ at the highest chlorine dose of 14.2 $\text{mg}\cdot\text{L}^{-1}$.
- 398 • Overall, this study demonstrates the potential for significant DBP formation when
399 tea is prepared in water containing elevated chlorine concentrations, such as
400 following point-of-use treatment. Conversely, chloroform concentrations in tea
401 prepared with water containing 1 $\text{mg}\cdot\text{L}^{-1}$ chlorine did not exceed 4 $\mu\text{g}\cdot\text{L}^{-1}$ and
402 therefore THM concentrations in tea made using municipal tap water are likely to be
403 insignificant.

404

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408

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Figure 1: Impact of boiling in a kettle on concentration of aqueous chlorine spiked into ultrapure water ($n=2$).

Figure 2: Chlorine demand of tea and coffee surrogates (n=2)

Figure 3: Dissolved organic carbon (DOC) concentrations (above) and chlorine demand (below) of tea and coffee (n=2).

Figure 4: DBP concentrations from chlorination of tea and coffee surrogates under formation potential conditions

Figure 5: DBP concentrations from chlorination of tea and coffee under formation potential conditions (top) and chloroform formation from preparation of tea and coffee under representative conditions (made with freshly-boiled water spiked with chlorine and quenched after 20 min contact time) (below) ($n=2$)

Table 1: Coffee and tea surrogates

Surrogate (abbreviation)	Classification	Structure
Caffeine (CF)	Alkaloid
D (-) quinic acid (QA)	Carboxylic acid
D (+) galactose (GLA)	Monosaccharide
catechol (CAT)	Phenolic
chlorogenic acid (CGA)	Phenolic
(+) catechin hydrate (CH)	Phenolic
epigallocatechin gallate (EGCG)	Phenolic
gallic acid (GA)	Phenolic

Table 2: Summary of experimental conditions

Name	Conditions
Kettle boiling	800 mL water, chlorine concentration measured before and after boiling.
Chlorine demand of surrogates	Surrogate 40 μM ; chlorine 35 mol of Cl_2 /mol of surrogate (mol/mol). 24 h, pH 7 ± 0.2 , 20 ± 2 °C.
Chlorine demand of tea and coffee	1:100 (vol/vol) diluted tea and coffee, chlorine 200 $\text{mg}\cdot\text{L}^{-1}$ (2.82 mM), 24 h, pH 7 ± 0.2 , 20 ± 2 °C
DBPFP tests on surrogates	Surrogate 5 μM ; chlorine 35 mol Cl_2 /mol surrogate (mol/mol). 24 h, pH 7 ± 0.2
DBPFP tests on tea and coffee	1:100 (vol/vol) diluted tea and coffee; chlorine 100 $\text{mg}\cdot\text{L}^{-1}$ (1.41 mM), 24 h, pH 7 ± 0.2 , 20 ± 2 °C
THM formation from tea and coffee at a representative contact time and temperature	Chlorine dose 0, 1, 4 and 14.2 $\text{mg}\cdot\text{L}^{-1}$. Freshly boiled water used to prepare tea and coffee. pH 7 ± 0.2 . Quenched after 20 min with ascorbic acid (3:1 mol/mol).

Supporting information for:

Formation of disinfection byproducts during the preparation of tea and coffee

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This supporting information (SI) contains two tables (S1-S2).

Table SI 1: summary of water quality parameters for tea and coffee samples

Samples	Chlorine demand g-Cl ₂ /g-DOC	DOC mg·L ⁻¹	UV ₂₅₄ cm ⁻¹	UV ₂₇₂ cm ⁻¹	SUVA ₂₅₄ L/mg·m ⁻¹	SUVA ₂₇₂ L/mg·m ⁻¹	pH	Chloroform FP μg·mg-DOC ⁻¹
Filter coffee	5.0	2018	0.4	0.5	2.1	2.6	5.2	25.9
Instant coffee	2.9	5381	1.0	1.1	1.9	2.1	4.7	14.7
Breakfast tea	9.6	976	0.3	0.3	2.7	3.6	5.0	47.8
Earl Grey tea	8.4	892	0.2	0.3	2.7	3.7	5.0	62.4
Green tea	6.9	1017	0.2	0.3	1.6	2.5	5.3	55.3

Table SI 2: Pearson product-moment correlation coefficients (r) for water quality of tea and coffee

	Chlorine demand	DOC	UV ₂₅₄	UV ₂₇₂	SUVA ₂₅₄	SUVA ₂₇₂	pH
DOC	-0.88						
UV ₂₅₄	-0.84	0.99					
UV ₂₇₂	-0.84	0.99	1.00				
SUVA ₂₅₄	0.64	-0.38	-0.27	-0.28			
SUVA ₂₇₂	0.89	-0.71	-0.63	-0.64	0.89		
pH	0.37	-0.75	-0.80	-0.80	-0.25	0.08	
Chloroform FP	0.86	-0.87	-0.87	-0.87	0.36	0.74	0.49