Supporting Information

# Effects of Heating Temperature and Water Age on the Formation of Disinfection By-Products in Drinking Water

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## Text S1. Gas Chromatography (GC) Analysis Parameters

### 1. GC analysis of THMs and unregulated DBPs (US EPA, 1995)

Analytes were separated by DB-1 (J&W, 30 m × 0.25 mm × 1.0 μm) capillary column and detected with an electron capture detector (ECD) equipped on GC (Agilent 7890A, Santa Clara, USA). The column oven was temperature programmed as follows: the injection temperature was 15°C and hold for 0 min, then increased to 50°C at 2°C/min and hold for 10 min, increased to 225°C at 10°C/min and hold for 5 min until all expected compounds have eluted. The injector temperature was set at 200°C, and detector temperature at 290°C. The injection volume was set at 1 μL.

### 2. GC analysis of HAAs (US EPA, 2003)

Analytes were separated using DB-1701 (i.e., 30 m × 0.25 mm × 0.25 μm) capillary column and detected with an ECD equipped on GC (Agilent 7890A, Santa Clara, USA). The column oven was temperature programmed as follows: the injection temperature was 40°C and hold for 10 min, then increased to 65°C at 2.5 °C/min, increased to 85 ºC at 10 ºC/min, increased to 205 ºC at 20 ºC/min and hold for 7 min until all expected compounds have eluted. The injector temperature was set at 210°C, and detector temperature at 290°C. The injection volume was set at 1 μL.

## Text S2. Method Qualification

Blank controls (i.e., pure water) and qualification samples (i.e., pure water spiked with known concentrations of DBPs) were extracted and analyzed on GC in parallel with extracts from chlorinated drinking water samples. For every ten to twenty injections on GC, a qualification sample was analyzed, and deviations between measured and spiked DBP concentrations should be within ±10% for data qualification.

The detection limits (DLs) of DBPs were determined with a consecutive analysis of seven samples in pure water (Millipore Super-Q system, Millipore, USA) spiked with 0.1-μg/L DBPs and calculated based on Eq. S1. The minimum reporting levels (MRLs) of DBPs were established to be 3 times of DLs. Recoveries (R) of DBPs were calculated based on Eq. S2. The measured mean concentrations, DLs, MRLs and calculated recoveries of DBPs are shown in Table S1.

$$\mathrm{DL} = \mathrm{STD} \times t_{(n\text{-}1,\ 1\text{-}\alpha)} \qquad \text{(S1)}$$

where STD represents standard deviation of seven replicated analysis, $t\ (_{n\text{-}1,\ 1\text{-}\alpha})$ is the student-*t* value for a 1-α confidence with n-1 degrees of freedom (i.e., $t_{(6,\ 0.99)} = 3.143$ for 7 replicates at a 99% confidence level), $n$ is the number of replicated samples (i.e., 7), and $1\text{-}\alpha$ is the confidence level (0.99, $\alpha = 0.01$).

$$\mathrm{R}\ (\%) = (\mathrm{A}\text{-}\mathrm{B}) / \mathrm{C} \qquad \text{(S2)}$$

where A is the measured DBP concentration (μg/L) in spiked samples, B is the measured DBP concentration (μg/L) in blank controls, and C is the DBP concentration spiked (i.e., 0.1 μg/L).

Table S1. Measured mean concentrations, detection limits (DLs), minimum reporting levels (MRLs) and calculated recoveries of DBPs.[a]

| DBPs | Measured mean concentrations (μg/L) | RSD[b] (%) | Recoveries (%) | DLs (μg/L) | MRLs (μg/L) |
|---|---|---|---|---|---|
| Chloroform | 0.10 | 2 | 104 | 0.01 | 0.03 |
| BDCM | 0.10 | 8 | 99 | 0.02 | 0.07 |
| CDBM | 0.10 | 8 | 102 | 0.03 | 0.08 |
| Bromoform | 0.11 | 6 | 105 | 0.02 | 0.05 |
| MCAA | 0.10 | 19 | 102 | 0.06 | 0.18 |
| MBAA | 0.10 | 6 | 99 | 0.02 | 0.06 |
| DCAA | 0.10 | 5 | 100 | 0.02 | 0.05 |
| TCAA | 0.11 | 16 | 108 | 0.05 | 0.15 |
| BCAA | 0.12 | 13 | 124 | 0.04 | 0.12 |
| DBAA | 0.12 | 3 | 118 | 0.01 | 0.03 |
| BDCAA | 0.13 | 7 | 126 | 0.02 | 0.07 |
| CDBAA | 0.10 | 7 | 103 | 0.02 | 0.07 |
| TBAA | 0.10 | 16 | 101 | 0.05 | 0.15 |
| DCAN | 0.11 | 7 | 106 | 0.02 | 0.07 |
| TCAN | 0.10 | 3 | 101 | 0.01 | 0.03 |
| BCAN | 0.11 | 6 | 111 | 0.02 | 0.06 |
| DBAN | 0.11 | 9 | 110 | 0.03 | 0.08 |
| CH | 0.10 | 5 | 98 | 0.02 | 0.05 |
| Chloropicrin | 0.10 | 6 | 99 | 0.02 | 0.05 |
| 1,1-DCP | 0.11 | 3 | 106 | 0.01 | 0.03 |
| 1,1,1-TCP | 0.11 | 4 | 107 | 0.01 | 0.04 |

[a]: Determined at a target concentration of 0.1 μg/L in pure water. [b]: Relative standard deviation of measured concentrations.

## Text S3. Integration Procedures for Equation 2

$$\frac{dC}{dt} = k_1 M[HClO] - k_2 C \qquad (1)$$

where $C$ represents DBP concentration (μg/L) in heated drinking water, $t$ represents heating duration (i.e., 1 h in this study, or other preset values as required), $k_1$ represents the second-order DBP formation rate constant (L/(mol·h)), $k_2$ represents the first-order DBP decay rate constant ($h^{-1}$), $M$ and $[HClO]$ represent concentrations of organic precursors (μg/L) and free chlorine (mol/L), respectively.

Integration of Eq. 1 obtains Eq. S3. If $t = 0$ h, $C = C_0$, Eq. S3 can thus transform to Eq. S4.

$$C = a + \int_0^t (k_1 M[HClO] - k_2 C)dt \qquad \text{(S3)}$$

where $a$ is an integrating constant.

$$C = C_0 + \int_0^t \left(k_1 M[HClO] - k_2 C\right)dt \qquad \text{(S4)}$$

where $C_0$ represents DBP concentration (μg/L) prior to heating

The concentration of organic precursors ($M$) can be illustrated with the following equation (Eq. S5).

$$M = M_0 - M_r \qquad \text{(S5)}$$

where $M_0$ represents total concentration of organic precursors (μg/L) present in drinking water, and $M_r$ represents concentration of organic precursors (μg/L) that has been reduced due to reactions with free chlorine.

A stoichiometric relationship exists between the total amount of organic precursors ($M_0$, μg/L) and the theoretical maximum DBP formation ($C_m$, μg/L; Eq. S6), or between consumed organic precursors ($M_r$, μg/L) and DBPs formed (i.e., $C + C'$, where $C'$ is DBP concentration reduced due to decays, μg/L; Eq. S7). Assuming $k_1' = k_1 \cdot [HClO] \cdot q$., Eq. S4 can transform to Eq. S8.

$$M_0 = qC_m \tag{S6}$$

$$M_r = q(C + C') = q\left(C + \int_0^t k_2 C dt\right) \tag{S7}$$

where $q$ is a stoichiometric constant, $C_m$ represents the theoretical maximum DBP formation (μg/L) in heated drinking water with DBP decays excluded, and $C'$ represents decreased DBP concentration (μg/L) due to decays.

$$C = C_0 + \int_0^t (k'_1\left(C_m - \left(C + \int_0^t k_2 C dt\right)\right) - k_2 C) dt \tag{S8}$$

Derivation of Eq. S8 achieved Eq. S9, and integration of Eq. S9 obtained Eq. S10, with detailed integration process described elsewhere (Zhang et al., 2013).

$$\frac{dC}{dt} = k'_1\left(C_m - \left(C + \int_0^t k_2 C dt\right)\right) dt - k_2 C \tag{S9}$$

$$C_{(T)} = me^{-k_2 t} + ne^{-k_1' t} \tag{S10}$$

where $m$ and $n$ are integrating constants.

If $t = 0$ h, $C = C_0$; if $t \longrightarrow \infty$ and $k_2$ is negligible (i.e., ~0 $h^{-1}$), $C = C_m$. Therefore, $m$ and $n$ can be illustrated with Eq. S11 and Eq. S12, respectively.

$$m = C_m \tag{S11}$$

$$n = C_0 - C_m \tag{S12}$$

Substituting Eq. S11 and Eq. S12 into Eq. S10 obtained Eq. 2.

$$C = C_0 e^{-k'_1 t} + C_m \left( e^{-k_2 t} - e^{-k'_1 t} \right) \qquad (2)$$

Table S2. Reported decay rate constants ($k_2$) of monohaloacetic acids (MHAAs) and dihaloactic acids (DHAAs) in drinking water.

| Category | DBPs | $k_2$ ($h^{-1}$) [a] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 15ºC | 65ºC | 70ºC | 81ºC | 82ºC | 83ºC | 102ºC |
| MHAAs | MCAA | $5.44×10^{-6}$ | N.A. [b] | N.A. | N.A. | 0.00536 | N.A. | 0.0288 |
| | MBAA | $5.08×10^{-5}$ | 0.0101 | 0.00760 | 0.09 | 0.0508 | 0.0835 | N.A. |
| DHAAs | DCAA | $1.16×10^{-6}$ | N.A. | $5.51×10^{-4}$ | N.A. | 0.00161 | N.A. | N.A. |
| | BCAA | $1.41×10^{-5}$ | N.A. | N.A. | N.A. | 0.00141 | N.A. | N.A. |
| | DBAA | $6.70×10^{-6}$ | N.A. | 0.00115 | N.A. | 0.00670 | 0.0107 | N.A. |

[a]: $k_2$ values measured only at pH 7.5-8.5 (i.e., near to pH 8.0 in the current study) were summarized in the table (Senter, 1907 and 1909; Lifongo et al., 2010).

[b]: Not available.

Table S3. Reported decay rate constants ($k_2$) of trihaloacetic acids (THAAs) in drinking water.*

| THAAs | $k_2$ (h$^{-1}$) [a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4ºC | 20ºC | 23-25ºC | 35-36ºC | 44-45ºC | 50ºC | 55-56ºC | 60-61ºC | 65ºC | 70ºC | 75-77ºC | 80-100ºC |
| TCAA | N.A.[b] | $1.12\times10^{-5}$[c] | $1.33\times10^{-5}$ | $1.38\times10^{-4}$ | $6.62\times10^{-4}$, $7.88\times10^{-4}$ | 0.00222, 0.00144, 0.00217 | 0.00316, 0.00511 | 0.0125, 0.0116, 0.0149 | 0.0279, 0.0276 | 0.0616, 0.0587 | 0.128, 0.151, 0.138 | 0.277, 0.259 (80°C), 0.529, 0.745 (85-86°C), 1.12, 1.06 (90°C), 2.15 (95°C), 3.96, 4.75 (100°C) |
| BDCAA | $1.17\times10^{-6}$ | $5.75\times10^{-5}$[c] | $5.00\times10^{-5}$ | $6.88\times10^{-4}$ | | 0.00975 | | N.A. | N.A. | N.A. | | N.A. |
| DBCAA | $5.63\times10^{-6}$ | $2.95\times10^{-4}$[c] | $2.83\times10^{-4}$ | 0.00326 | | 0.0425 | | N.A. | N.A. | N.A. | | N.A. |
| TBAA | $6.58\times10^{-5}$ | 0.00148[c] | 0.00172, 0.00176 | 0.00461 (30°C), 0.0117, 0.0143, 0.0799 | 0.0275 (40°C), 0.0637 | 0.126, 0.146, 0.167 (47°C) | 0.304 | 0.677, 0.824 | 1.48, 1.70 | 2.94 | 4.18 | N.A. |

*: $k_2$ values measured at pH 6-9 were summarized in the table. $k_2$ values of THAAs were less impacted by pH (i.e., 6-9) in drinking water (Zhang and Minear, 2002).

[a]: Verhoek, 1934; Fairclough, 1938; Johnson and Moelwyn-Hughes, 1940; Diefallah and El-Nadi, 1978; Zhang and Minear, 2002, Chen, 2011.

[b]: Not available.

[c]: Predicted with a quantitative structure－property relationship (QSPR) model proposed by Chen (2011).

Table S4. Reported decay rate constants ($k_2$) of selected unregulated DBPs in drinking water.*

| Category | DBPs | $k_2$ ($h^{-1}$) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 4ºC | 15ºC | 20ºC | 21ºC | 22ºC | 25ºC | 30ºC | 35ºC | 40ºC | 50ºC |
| HAL[a] | CH | 0 | 0 | 0.000525[i], 0.00165 | 0.00180 | 0.00895[i] | 0.002 | N.A. | 0.0144, 0.013 | 0.043 | 0.050 |
| HANs[b] | DCAN | 0 | 0 | 0.0027, 0.0054, 0.0130[e], 0.0195[f], 0.0143[g], 0.0152[h], 0.00407[i] | 0.014[j] | N.A. | 0.006, 0.0231 | N.A. | 0.002[l], 0.031 | N.A. | 0.206 |
| | BCAN | N.A.[m] | N.A. | 0.00613[e], 0.00295[i] | 0.007[k] | N.A. | 0.0126 | N.A. | 0.002[l], 0.068[k] | N.A. | N.A. |
| | DBAN | N.A. | N.A. | ~0, 0.00286[e], 0.00209[i] | 0.004[k] | N.A. | 0.00815 | N.A. | 0.002[l], 0.032[k] | N.A. | N.A. |
| | TCAN | N.A. | N.A. | 0.123[e], 0.626[h], 0.0617[i] | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| HNM[c] | Chloropicrin | 0 | 0 | 0.0342[h] | N.A. | N.A. | 0.006 | N.A. | 0.013 | N.A. | 0.039 |
| HKs[d] | 1,1-DCP | 0 | 0 | 0.00360, 0.00396, 0.0219[i] | 0.022[k] | N.A. | 0.002 | 0.010[l], 0.071[k] | 0.016 | N.A. | 0.212 |
| | 1,1,1-TCP | 0 | 0.005 | 0.263[h], 0.0112[i] | 0.182[k] | N.A. | 0.034 | 0.062[l], 1.393[k] | 0.344 | N.A. | 2.02 |

HAL: haloacetaldehyde, HANs: haloacetonitriles, HNM: halonitromethane, HKs: haloketones.

*: $k_2$ values measured at pH 7.5-8.5 (i.e., near to pH 8.0 in the current study) were summarized in the table.

[a]: Luknitskii, 1975, Koudjonou et al., 2008, Chen, 2011, Zhang et al., 2013, Ma et al., 2016.

[b]: Trehy and Bieber, 1981, Croue and Reckhow, 1989, Nikolaou et al., 2000, Reckhow et al. 2001, Yang et al., 2007, Chen, 2011, Zhang et al., 2013, Yu and Reckhow, 2015, Vu et al., 2019.

[c]: Croue and Reckhow, 1989, Zhang et al., 2013.

[d]: Croue and Reckhow, 1989, Nikolaou et al., 2001, Chen, 2011, Zhang et al., 2013.

[e]: Calculated using a Bayesian model proposed by Yu and Reckhow (2015) in the presence of 1 mg $Cl_2$/L chlorine at pH 8.

[f]: Calculated using a model proposed by Reckhow et al. (2001) in the presence of 1 mg $Cl_2$/L chlorine at pH 8.

[g]: Calculated using a model proposed by Vu et al. (2019) at pH 8. The model did not consider the effects of free chlorine.

[h]: Measured in aqueous solution with 5-100 μg/L initial DBP concentrations at pH 8.5 (Croue and Reckhow, 1989). The $k_2$ value of chloropicrin (i.e., 0.0342 $h^{-1}$) was not included for calculating its $E_a$ value.

[i]: Predicted with a QSPR model proposed by Chen (2011).

[j]: Measured with a relatively low initial CH concentration (i.e., 20 μg/L) at pH 8.5 (Ma et al., 2016).

[k]: Measured in fortified drinking water with unknown pH (Nikolaou et al., 2001), thus not included for calculating $E_a$ values.

[l]: Measured in pure water with unknown pH (Nikolaou et al., 2001), thus not included for calculating $E_a$ values.

[m]: Not available.

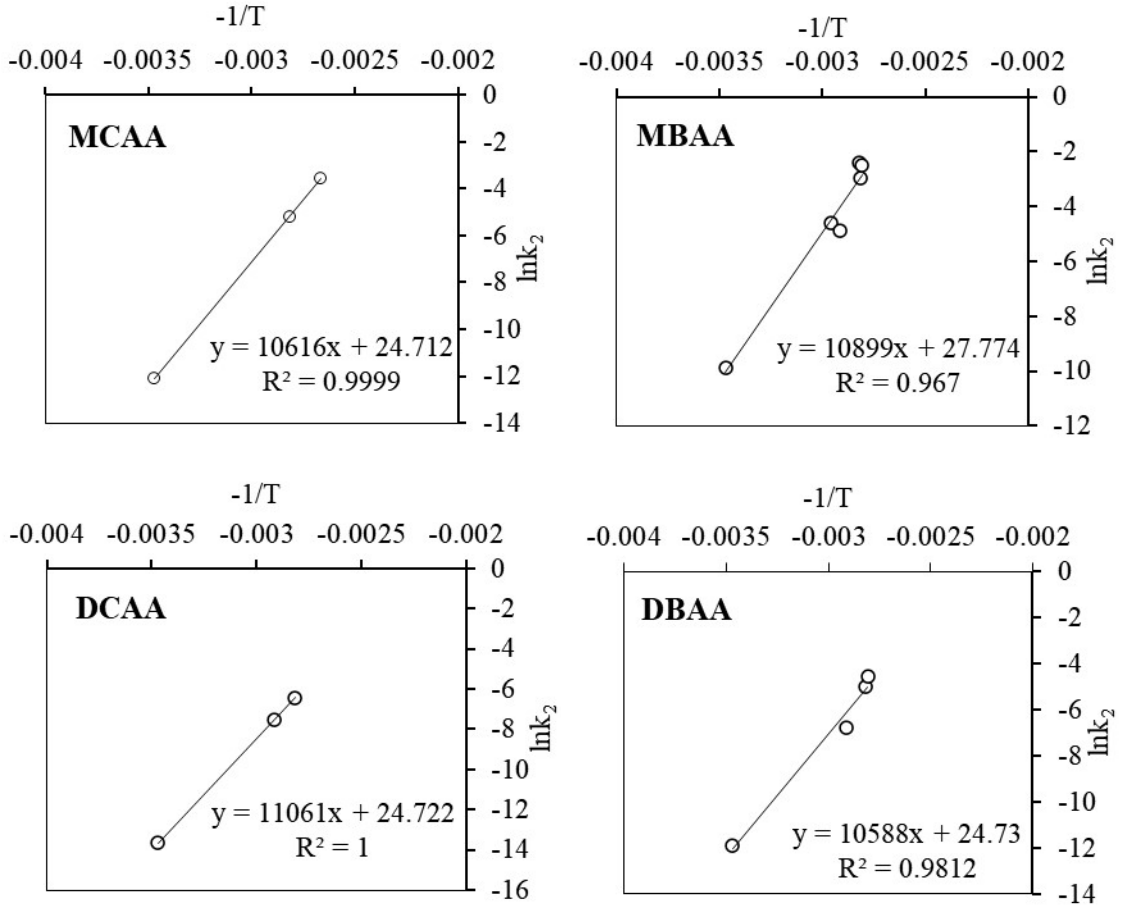

Figure S1. Plots of $\ln k_2$ against -1/T for calculating $E_a$ values of MHAAs and DHAAs in drinking water. $E_a$ = Interception × 8.314 J/mol.

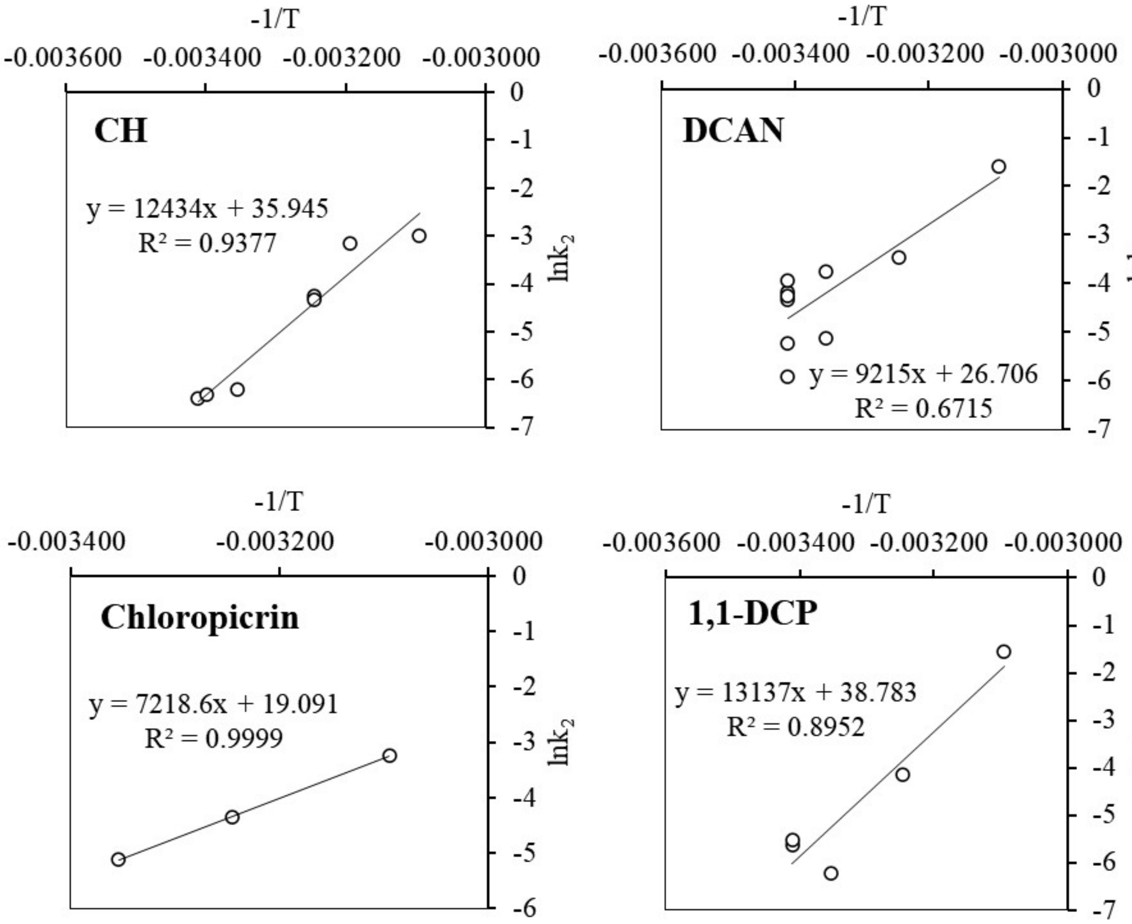

Figure S2. Plots of ln$k_2$ against -1/T for calculating $E_a$ values of selected unregulated DBPs in drinking water. $E_a$ = Interception × 8.314 J/mol.

## Text S4. Derivation Procedures for Equation 4-6

$$C = C_0 e^{-k'_1 t} + C_m \left( e^{-k_2 t} - e^{-k'_1 t} \right) \tag{2}$$

where $C_0$ represents DBP concentration (μg/L) in unheated drinking water, $k'_1$ represents the pseudo-first-order DBP formation rate constant ($h^{-1}$) at target heating temperature $T$ (ºC), $t$ represents heating duration (i.e., 1 h in this study, or other preset values as required), and $C_m$ represents the maximum DBP formation (μg/L) in heated drinking water with decays excluded.

Assuming $C = C_1'$, $C_0 = C_1$, or $C = C_2'$, $C_0 = C_2$, Eq. 2 can transform to Eq. 4.

$$C_m = \frac{C_1' - C_1 e^{-k_1' t}}{e^{-k_2 t} - e^{-k'_1 t}} \text{ or } C_m = \frac{C_2' - C_2 e^{-k_1' t}}{e^{-k_2 t} - e^{-k'_1 t}} \tag{4}$$

where $C_1'$ and $C_2'$ represent DBP concentrations (μg/L) in heated drinking water with water ages $t_1$ and $t_2$ (h), respectively, $C_1$ and $C_2$ represent DBP concentrations (μg/L) in unheated drinking water with water ages $t_1$ and $t_2$ (h), respectively.

Assuming $C_0 = C_1$, $C = C_0$, or $C = C_2$, Eq. 2 can transform to Eq. 5.

$$C_0 = C_1 + (C_m' - C_1) \left( 1 - e^{-k_1'(t_0 - t_1)} \right) \text{ or } C_0 = C_2 e^{k_1'(t_2 - t_0)} + C_m' \left( 1 - e^{k_1'(t_2 - t_0)} \right) \tag{5}$$

Eq. 5 can transform to Eq. S13-17.

$$C_1 + (C_m' - C_1) \left( 1 - e^{-k_1'(t_0 - t_1)} \right) = C_2 e^{k_1'(t_2 - t_0)} + C_m' \left( 1 - e^{k_1'(t_2 - t_0)} \right) \tag{S13}$$

$$C_m' \left( 1 - e^{-k_1'(t_0 - t_1)} \right) + C_1 e^{-k_1'(t_0 - t_1)} = C_2 e^{k_1'(t_2 - t_0)} + C_m' \left( 1 - e^{k_1'(t_2 - t_0)} \right) \tag{S14}$$

$$C_m' \left( e^{k_1'(t_2 - t_0)} - e^{-k_1'(t_0 - t_1)} \right) = C_2 e^{k_1'(t_2 - t_0)} - C_1 e^{-k_1'(t_0 - t_1)} \tag{S15}$$

$$C_m' \left( e^{k_1' t_2} - e^{k_1' t_1} \right) = C_2 e^{k_1' t_2} - C_1 e^{k_1' t_1} \tag{S16}$$

$$C_m' = \frac{C_2 e^{k_1' t_2} - C_1 e^{k_1' t_1}}{e^{k_1' t_2} - e^{k_1' t_1}} = \frac{C_2 - C_1 e^{-k_1'(t_2 - t_1)}}{1 - e^{-k_1'(t_2 - t_1)}} \tag{S17}$$

Eq. S17 can transform to Eq. 6.

$$C_m' = \frac{C_2 - C_1 e^{-k_1'(t_2-t_1)} + C_1 - C_1}{1-e^{-k_1'(t_2-t_1)}} = C_1 + \frac{C_2 - C_1}{1-e^{-k_1'(t_2-t_1)}} \tag{6}$$

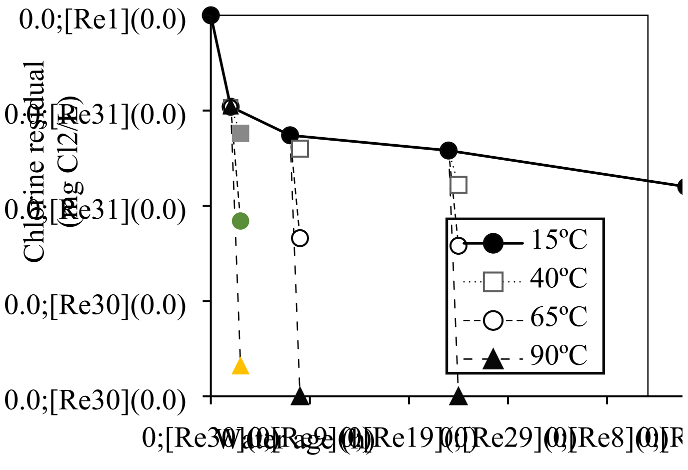

Figure S3. Free chlorine residuals in unheated (i.e., at 15°C) and heated (i.e., at 40, 65 or 90°C, heating duration 1 h) drinking water with 2, 8, 24 and 48-h water ages (i.e., contact time in the simulated distribution system [SDS] at 15°C).

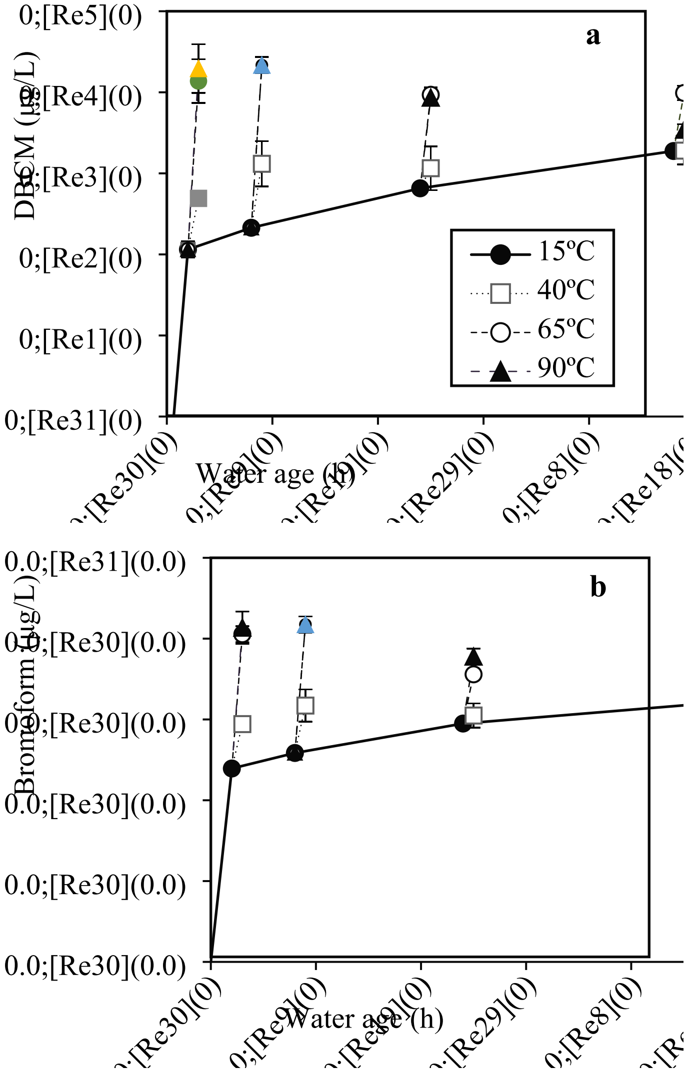

Figure S4. Concentrations of (a) dibromochloromethane (DBCM) and (b) bromoform in unheated and heated drinking water with different water ages.

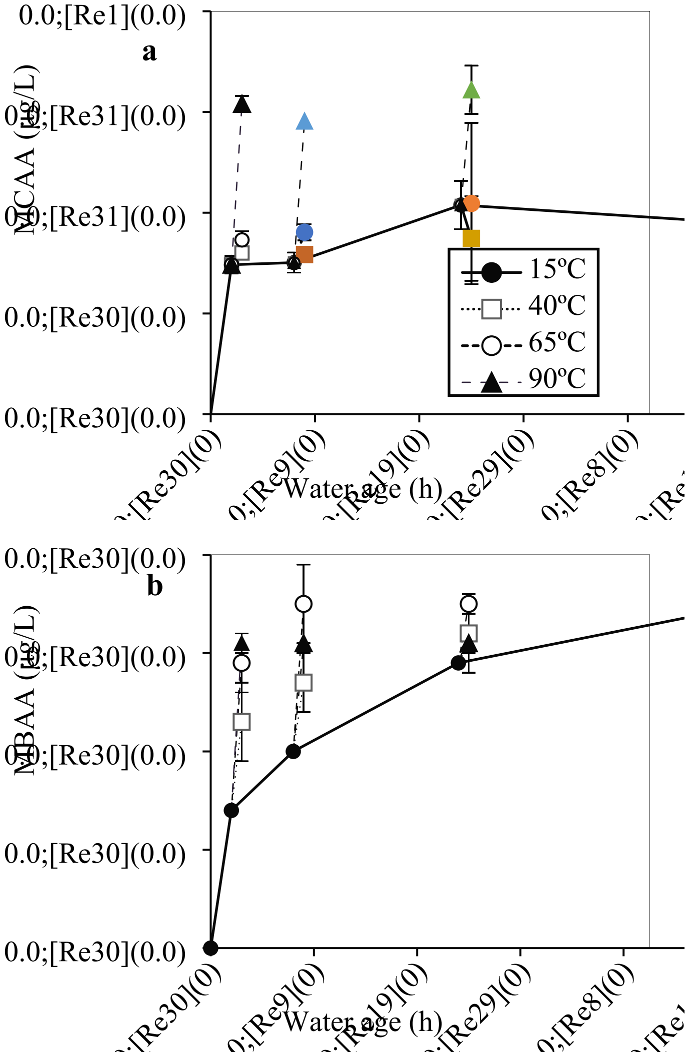

Figure S5. Concentrations of (a) monochloroacetic acid (MCAA) and (b) monobromoacetic acid (MBAA) in unheated and heated drinking water with different water ages.

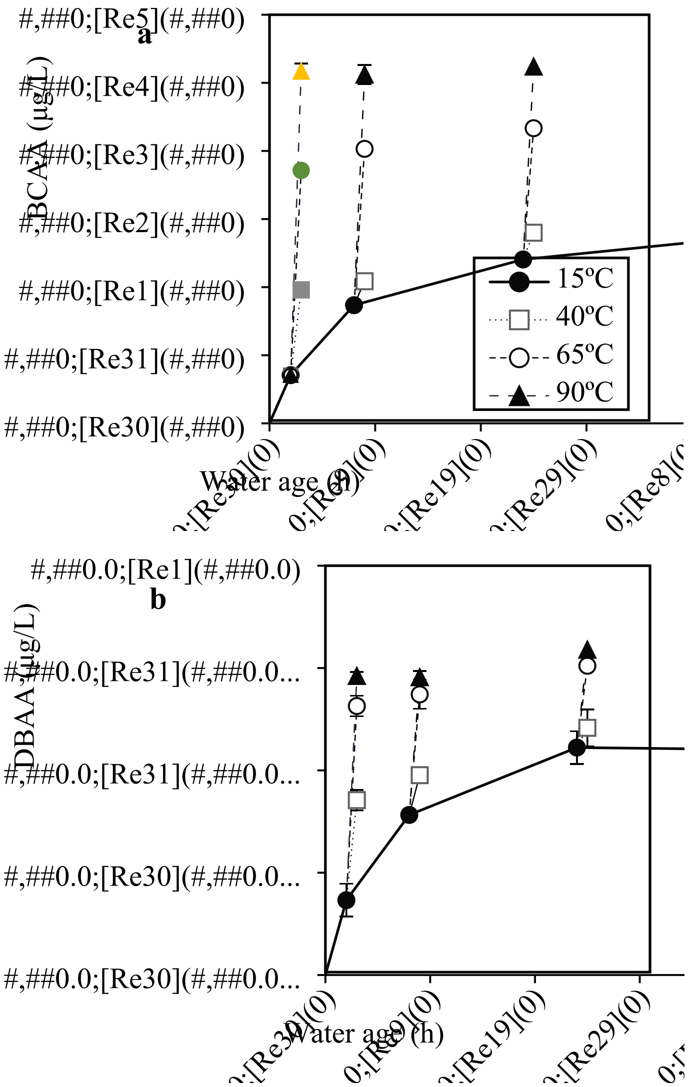

Figure S6. Concentrations of (a) bromochloroacetic acid (BCAA) and (b) dibromoacetic acid (DBAA) in unheated and heated drinking water with different water ages.

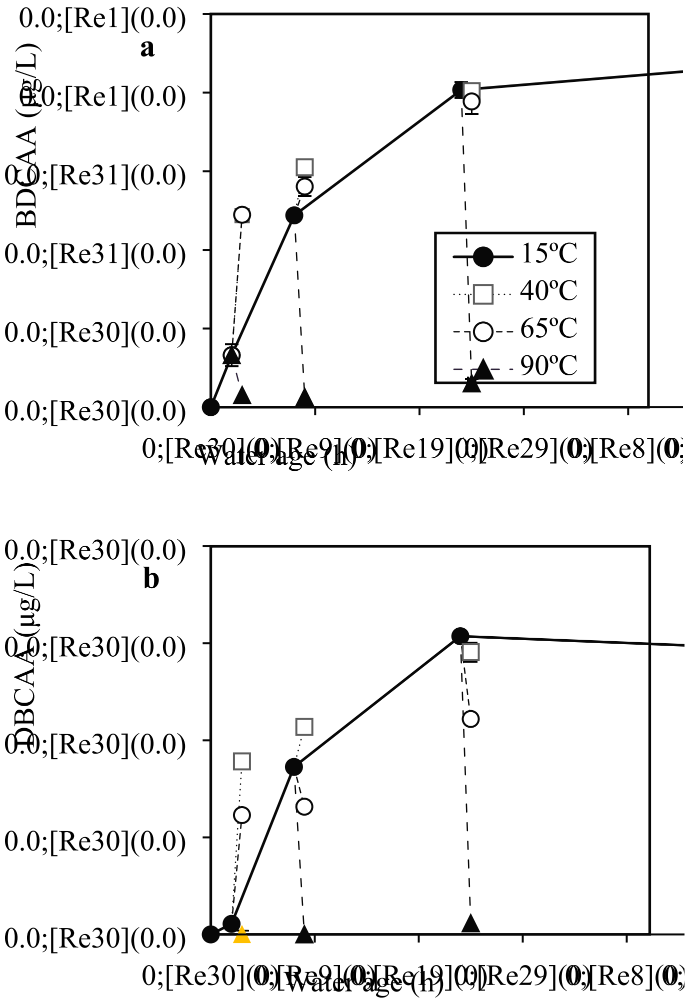

Figure S7. Concentrations of (a) bromodichloroacetic acid (BDCAA) and (b) dibromochloroacetic acid (DBCAA) in unheated and heated drinking water with different water ages.

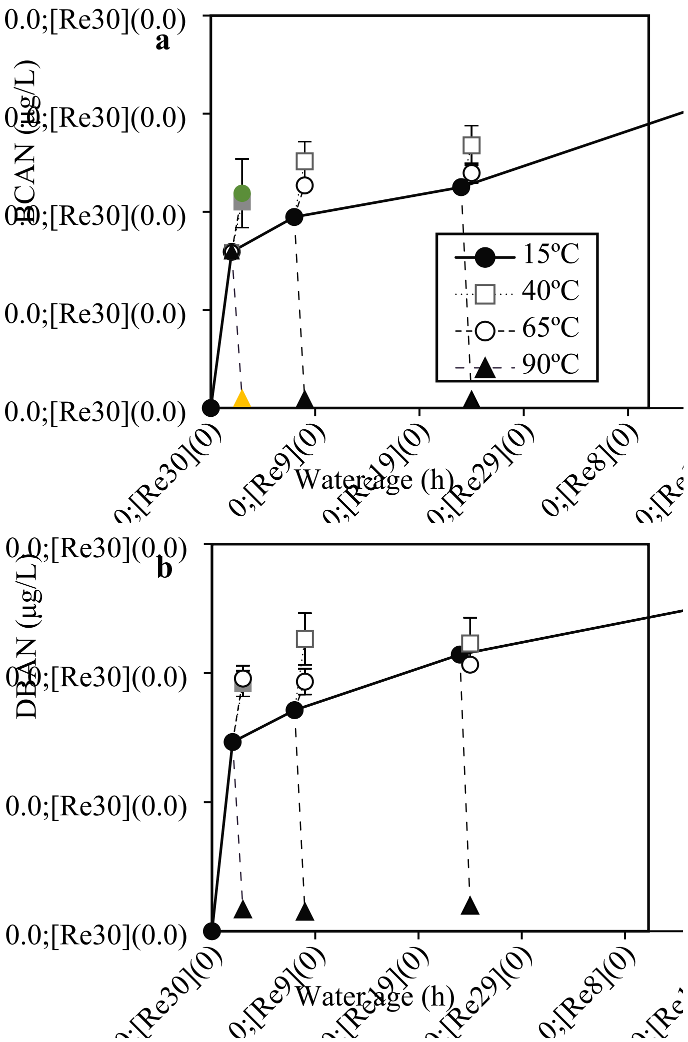

Figure S8. Concentrations of (a) bromochloroacetonitrile (BCAN) and (b) dibromoacetonitrile (DBAN) in unheated and heated drinking water with different water ages.

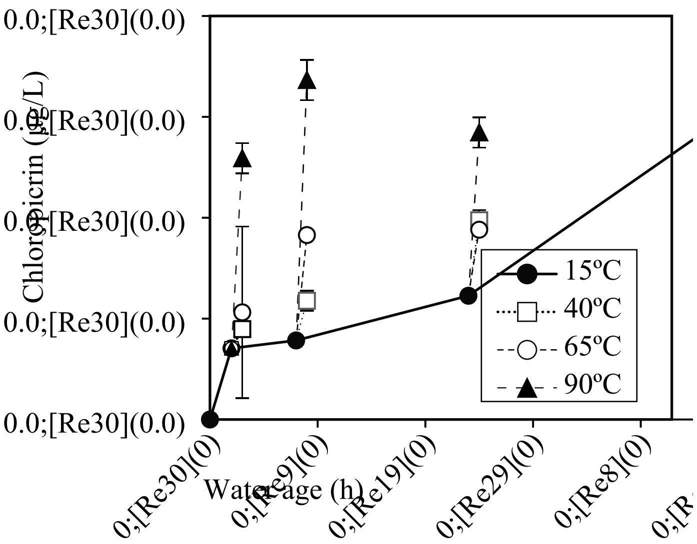

Figure S9. Concentrations of chloropicrin in unheated and heated drinking water with different water ages.

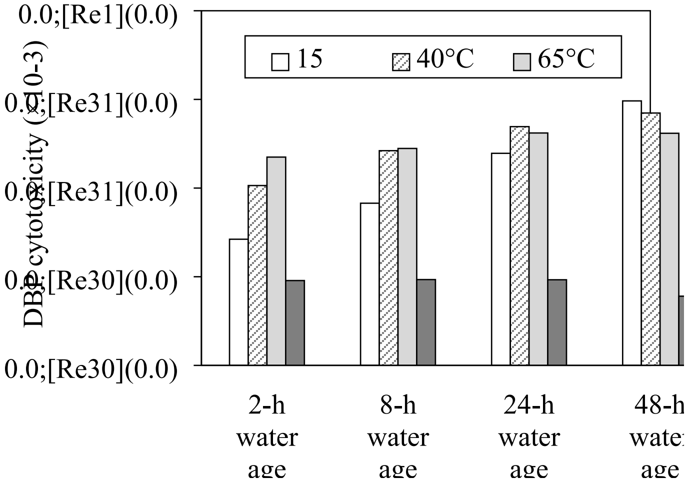

Figure S10. Calculated total DBP cytotoxicity in unheated (i.e., at 15°C) and heated (i.e., at 40, 65 or 90°C) drinking water with different water ages. Heating duration was set at 1 h.

Table S5. Relative contributions of different DBPs to the calculated total cytotoxicity in drinking water.

| Category | DBPs | Relative contributions to total cytotoxicity (%) | | | |
|---|---|---|---|---|---|
| | | 15°C | 40°C | 65°C | 90°C |
| THMs | Chloroform | 1 | 1 | 2-3 | 11-14 |
| | BDCM | 0 | 0 | 1 | 1-2 |
| | DBCM | 0 | 0 | 0 | 1 |
| | Bromoform | 0 | 0 | 0 | 0 |
| | **Total** | **2** | **2** | **3-4** | **14-16** |
| HAAs | MCAA | 1-2 | 1-2 | 2-3 | 9-12 |
| | MBAA | 14-18 | 16-18 | 19-22 | 48-52 |
| | DCAA | 0-1 | 0-1 | 0-1 | 2-4 |
| | BCAA | 1 | 1-2 | 2-3 | 8-9 |
| | DBAA | 0-1 | 1 | 1 | 2-3 |
| | TCAA | 0-1 | 0-1 | 0-1 | 1-3 |
| | BDCAA | 0-2 | 1 | 1 | 0 |
| | DBCAA | 0-2 | 1 | 0-1 | 0 |
| | TBAA | 0 | 0 | 0 | 0 |
| | **Total** | **19-27** | **23-26** | **27-31** | **73-81** |
| HANs | DCAN | 8-12 | 9-12 | 10-12 | 1 |
| | BCAN | 29-34 | 30-32 | 27-29 | 0-3 |
| | DBAN | 30-36 | 29-33 | 28-29 | 0-7 |
| | **Total** | **70-78** | **71-74** | **64-68** | **1-11** |
| Other DBPs tested | CH | 1 | 1 | 1 | 0 |
| | Chloropicrin | 0 | 0 | 0 | 1-2 |
| | 1,1-DCP | N.A.[a] | N.A. | N.A. | N.A. |
| | 1,1,1-TCP | N.A. | N.A. | N.A. | N.A. |

[a]: Not available. Toxicological data of 1,1-DCP and 1,1,1-TCP are unavailable and thus they were not evaluated for cytotoxicity.

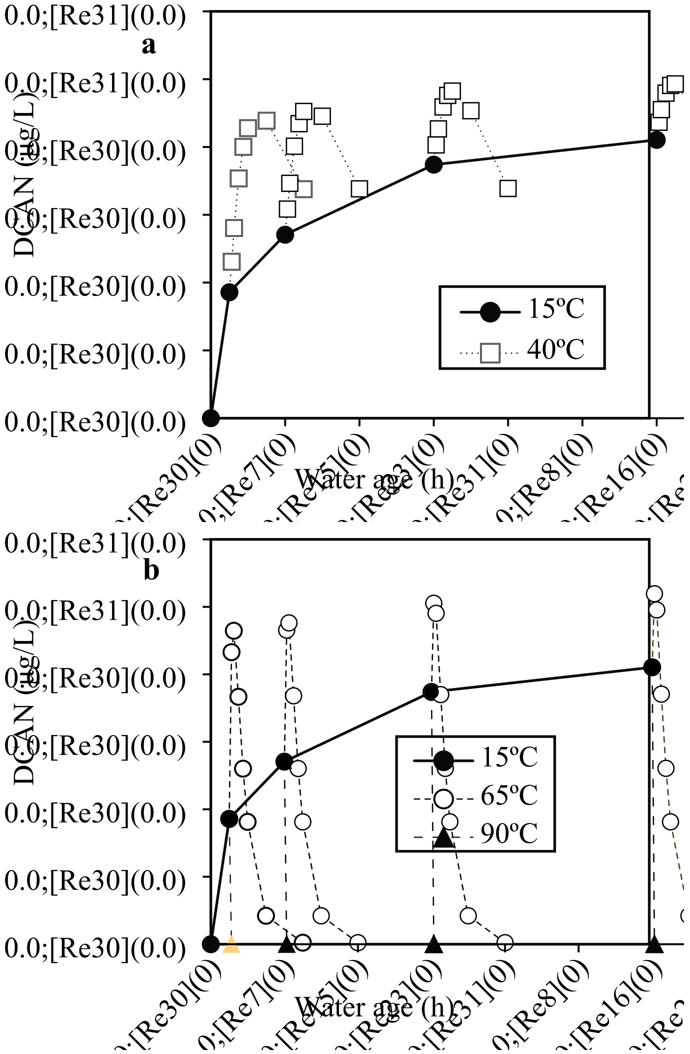

Figure S11. Modeled DCAN concentrations in drinking water heated at (a) 40°C, (b) 65 and 90°C with different heating duration (i.e., 0.25, 0.5, 1.0, 1.5, 2, 4 and 8 h).

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