Supporting Information

for

Quantifying Drought-Driven Temperature Impacts on Ozone Disinfection Credit and Bromate Control

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Fig. S1 Pilot plant Wattco heaters.

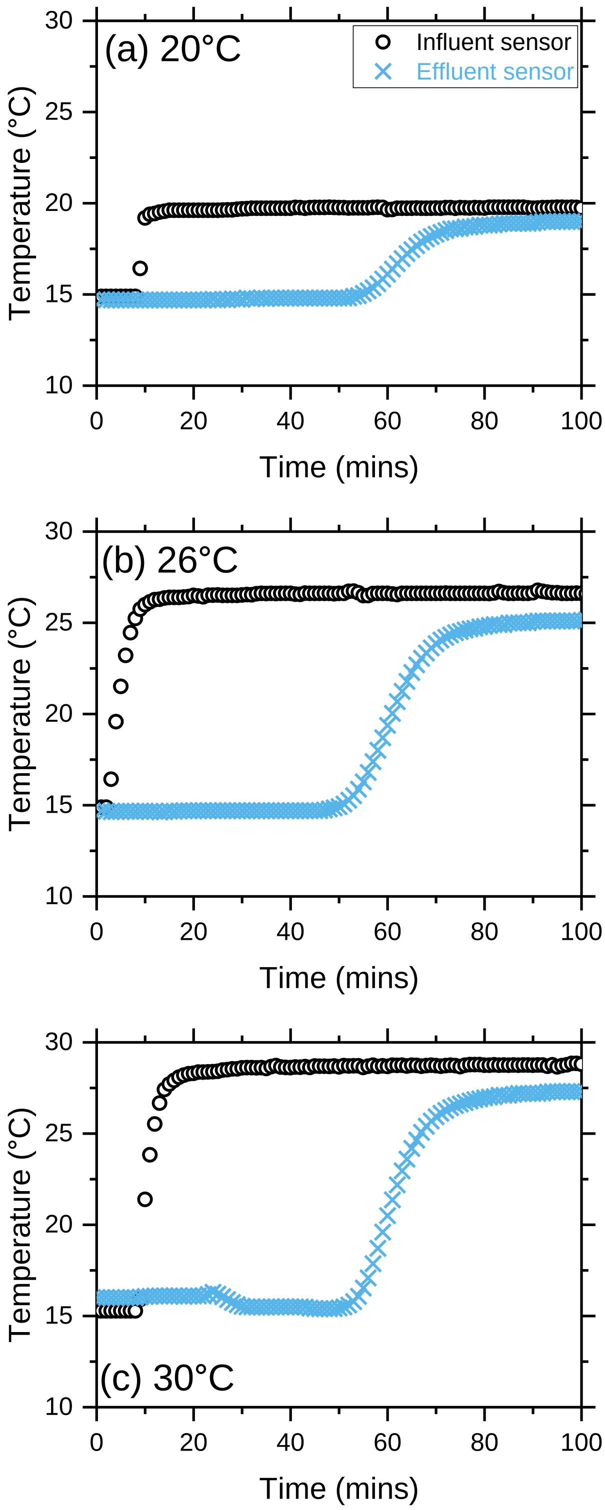

Fig. S2 Recorded temperature readings of selected tests representatives of different temperature conditions tested showing response of temperature when increased from 15ºC to (a) 20ºC¸(b) 26ºC, and (c) 30ºC. Results show quick response to the changes in temperature settings at the ozone effluent skid (4-5 min), while achieving steady state for the entire skid took around 60 min.

Text S1. Fluoride tracer tests to validate the ozone skid T_{10}/T assumptions

The pilot plant ozone skid was fed with raw Lake Mead water, and fluoride (as hexafluorosilicic acid, H_2SiF_6, commonly used for fluoridation in drinking water and it is expected to dissociate completely to fluoride[1]) was injected into each train at the last injection point of the raw water skid before the temperature control units. There was an additional ~73 seconds (for 4.4-4.6 gpm flow rate) or ~37 seconds (for 8.8-9.3 gpm flow rate) of contact time before the solution then entered the first ozone chamber (based on estimated pipe lengths/diameters and heater volumes). Experiment time was corrected considering this travel time from the injection point to the first ozone contactor.

All tracer tests followed the step input response method, i.e., fluoride injection was continuously and consistently maintained throughout each testing duration.[2] The measured original stock acid fluoride concentration was around 228,000 mg/L (as F), which was 100x diluted with raw water and dosed at a rate of 17 mL/min into the test train to obtain a final fluoride concentration near 2 mg/L. During each test, several samples were collected at the start of fluoride dosing to determine the background fluoride concentrations in the raw water (measured to be within 0.27-0.34 mg/L).

Fluoride concentrations were measured on site using a Hach HQ4300 meter equipped with a fluoride ion selective probe (ISEF121). Samples were taken directly from the last (8th) port of the ozone skid (end of column #6). The fluoride probe assembly was placed near the sample collection to allow instantaneous measurements. The frequency of sample collection and measurements varied, but samples were measured every 30-60 seconds around the time when 10% of the estimated concentration was expected (CT_{10}) to obtain a more accurate estimation.

The following data were recorded/calculated:

1. Initial (background) fluoride concentration (C_i in mg/L) was measured before and during the first 5-15 minutes of each test. The background concentration is expected to be ~0.3-0.4 mg/L based on previous Lake Mead raw water quality analyses. The measured background concentrations were within this range, as shown by the C_i values of 0.28 ± 0.04 mg/L in **Table S1**.
2. Samples were collected at specific intervals (C_t) until fluoride concentrations were stabilized at a final concentration (C_f)
3. $C_{T10} = (C_f – C_i) \times 0.1 + C_i$
4. T_{10}/T was calculated as the ratio of the time to reach C_{T10} to the time to reach C_f

In all tests, T_{10} was determined based on linearly interpolating the two time points that C_{T10} was within. In contrast, T was determined based on the earliest recorded time when fluoride concentration was stabilized (within 2-3% of the highest measured concentration). Fluoride sampling and measurements were continued in all cases until at least 3-4 consecutive measurements were within 1% of each other. Note that despite the consistent and rigorous efforts in defining T_{10} and T, the calculations are sensitive and prone to high variations, especially considering that the final concentration (C_f) did not stabilize consistently in all tests (i.e., fluoride concentration continued to increase by 0.01-0.02 mg/L for 5-10 minutes in some tests, whereas in others the concentration was stabilized and did not fluctuate once it reached a specific value). Therefore, the following discussion and comparisons are based on apparent findings, and further tests and statistical analyses may be appropriate, depending on the level of analysis desired. An example of an individual tracer study results and calculations is depicted in **Fig. S3**.

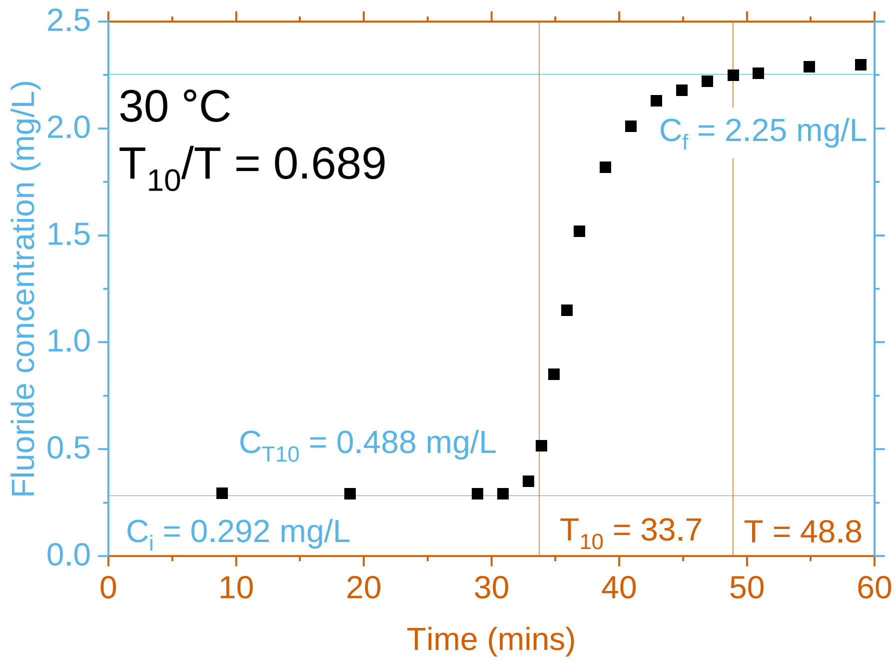

Fig. S3 A visual example of an individual tracer study showing the recorded fluoride concentrations over time and highlighting the calculated parameters to determine T_{10}/T.

Almost all tracer testing events yielded T_{10}/T close to or higher than the initially assumed 0.65 value based on previous tracer study of a pilot-scale plant with similar configurations. Out of 13 tests, 11 tests (84.6%) had $T_{10}/T > 0.650$ (that was assumed and implemented for the CT calculations of this study), and 3 tests (23.1%) had $T_{10}/T >$ 0.70 (which is the recommended USEPA proposed value for superior baffling conditions)[3]. When the pilot was operated in a parallel train configuration (theoretical HDT= 35-40 minutes, 5-7 minutes/column), there were no apparent differences in the calculated T_{10}/T between Train 1 and Train 2. For each consecutive set of tests (i.e., Tests 1&2, Tests 3&4, etc., as each set was done on the same day/time and under similar flow and temperature conditions), the differences between trains were within 2-6%. The in-series configuration (i.e., HDT of 3-3.5 minutes per cell) had T_{10}/T (at 13.6-13.7ºC) between 0.66-0.72. Regardless of the differences in experimental conditions, T_{10} and T were observed at 0.922 HDT (± 0.065 HDT) and 1.351 HDT (± 0.095 HDT), respectively.

The average T_{10}/T, including all tests, is 0.685 ± 0.033. The results in **Table S1** suggest that temperature could affect T_{10}/T, as it marginally increased from an average of 0.671 ± 0.033 (for 13-14 ºC) to 0.712 ± 0.024 (for 28-30ºC). Linear fitting of the T_{10}/T results vs. temperature was attempted, but the T_{10}/T was not linearly correlated (with an R^2 of 0.32 only), and further studies are needed to evaluate and understand the effect of temperature on T_{10}/T fully. These observations imply that future full-scale tracer tests at elevated temperatures may be beneficial as improved T_{10}/T may increase the calculated CT and disinfection credits.

Table S1. Details of testing conditions, measured concentrations, and performed calculations for all pursued tracer tests. HDT refers to the theoretical detention time calculated based on measured flow rate and volume. Series refer to ozone skid configuration by which trains 1 and 2 were connected sequentially.

Test ID	Train/ Series	Temp (ºC)	Flow rate (gpm)	HDT (min)	C_i (mg/L)	C_f (mg/L)	C_{T10} (mg/L)	T (min)	T_{10} (min)	T_{10}/T
1	1	13	4.1	39.5	0.295	2	0.466	48.8	32.3	0.662
2	2	14	4.6	35.2	0.291	1.97	0.459	45.9	31.6	0.689
3	1	14	4.5	36	0.281	2.01	0.454	50.9	32.7	0.642
4	2	14	4.5	36	0.279	2.02	0.401	48.9	30.7	0.628
5	1	21	4.6	35.2	0.279	2.3	0.481	50.9	33.9	0.685
6	2	21	4.5	36	0.279	2.3	0.481	46.9	31.5	0.673
7	1	28	4.5	35.2	0.294	2.4	0.505	44.9	33.1	0.738
8	2	29	4.4	36.8	0.292	2.25	0.488	48.8	33.7	0.689
9	1	30	4.1	39.5	0.203	1.56	0.339	48.8	35.4	0.726
10	2	30	4.2	38.6	0.201	1.51	0.332	48.9	33.9	0.694
11	Series	14	8.3	39.1	0.285	2.54	0.511	59.4	39.1	0.658
12	Series	14	8.9	36.4	0.335	2.45	0.547	54.4	37.9	0.698
13	Series	14	7.6	42.7	0.330	3.11	0.608	59.3	42.9	0.723

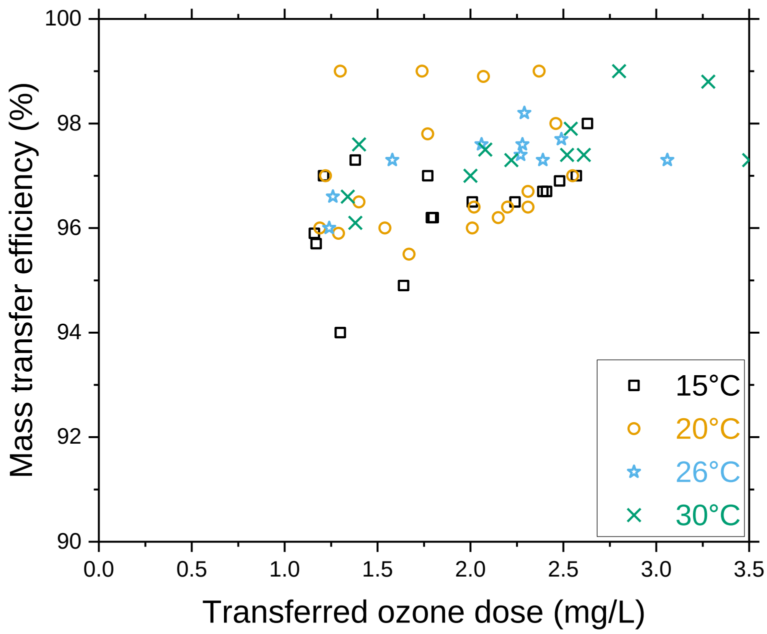

Fig. S4 Effect of transferred ozone doses on mass transfer efficiencies for the different temperatures tested. The figure shows that the transfer efficiency was always maintained within 94-99%.

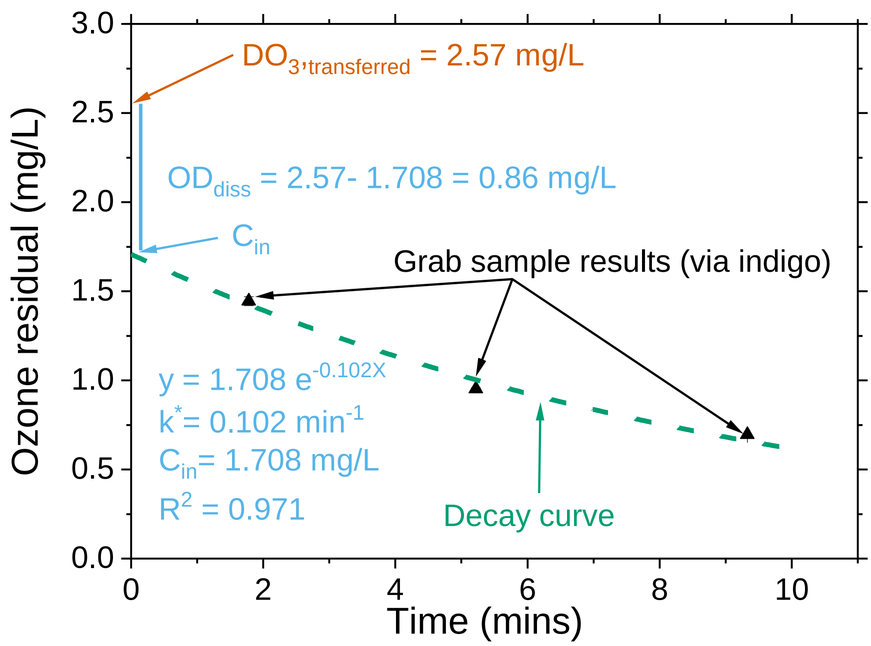

Fig. S5 Visual depiction of ozone decay from a single example experiment, with measured and calculated values indicated. The symbols/text in black refer to dissolved ozone concentrations measured in grab samples with the indigo method,[4] whereas colored text indicates calculated values with transferred ozone dose marked in orange.

Table S2. For various testing conditions, free and total chlorine were measured at different sample locations. Background measurements were also collected when no chlorine-ammonium was added, and chlorine was always below detection in these cases. Post-chlorine and post-ammonium measurements were taken before heating the raw water, so measurements were representative of different temperature conditions.

<table>
<tr><th>Tap Location</th><th colspan="4">Total Chlorine (mg/L)</th><th colspan="4">Free Chlorine (mg/L)</th></tr>
<tr><th colspan="9">Conditions Tested: 0.5 mg/L Cl_2 + 0.1 mg/L NH_4^+-N;</th></tr>
<tr><th></th><th>15°C</th><th>20°C</th><th>26°C</th><th>30°C</th><th>15°C</th><th>20°C</th><th>26°C</th><th>30°C</th></tr>
<tr><td>Post Chlorine</td><td colspan="4">0.45</td><td colspan="4">0.31</td></tr>
<tr><td>Post Ammonium</td><td colspan="4">0.47</td><td colspan="4">0.36</td></tr>
<tr><td>Ozone Influent</td><td>0.45</td><td>0.46</td><td>0.47</td><td>0.48</td><td>0.07</td><td>0.03</td><td>0.14</td><td>0.14</td></tr>
<tr><td>Final Sample Tap</td><td>0.18</td><td>0.17</td><td>0.07</td><td>0.09</td><td>0.07</td><td>0.01</td><td>0.03</td><td>0.06</td></tr>
<tr><th colspan="9">Conditions Tested: 0.5 mg/L Cl_2 + 0.3 mg/L NH_4^+-N;</th></tr>
<tr><th></th><th>15°C</th><th>20°C</th><th>26°C</th><th>30°C</th><th>15°C</th><th>20°C</th><th>26°C</th><th>30°C</th></tr>
<tr><td>Post Chlorine</td><td colspan="4">0.52</td><td colspan="4">0.34</td></tr>
<tr><td>Post Ammonium</td><td colspan="4">0.65</td><td colspan="4">0.04</td></tr>
<tr><td>Ozone Influent</td><td>0.46</td><td>0.46</td><td>0.48</td><td>0.46</td><td>0.18</td><td>0.08</td><td>0.1</td><td>0.03</td></tr>
<tr><td>Final Sample Tap</td><td>0.13</td><td>0.11</td><td>0.24</td><td>0.23</td><td>0.1</td><td>0.09</td><td>0.08</td><td>BDL</td></tr>
<tr><th colspan="9">Conditions Tested: 0.5 mg/L Cl_2 + 0.5 mg/L NH_4^+-N;</th></tr>
<tr><th></th><th>15°C</th><th>20°C</th><th>26°C</th><th>30°C</th><th>15°C</th><th>20°C</th><th>26°C</th><th>30°C</th></tr>
<tr><td>Post Chlorine</td><td colspan="4">0.58</td><td colspan="4">0.59</td></tr>
<tr><td>Post Ammonium</td><td colspan="4">0.52</td><td colspan="4">0.31</td></tr>
<tr><td>Ozone Influent</td><td>0.56</td><td>0.56</td><td>0.52</td><td>0.55</td><td>0.04</td><td>0.08</td><td>0.05</td><td>0.13</td></tr>
<tr><td>Final Sample Tap</td><td>0.19</td><td>0.17</td><td>0.22</td><td>0.24</td><td>0.07</td><td>0.07</td><td>BDL</td><td>0.03</td></tr>
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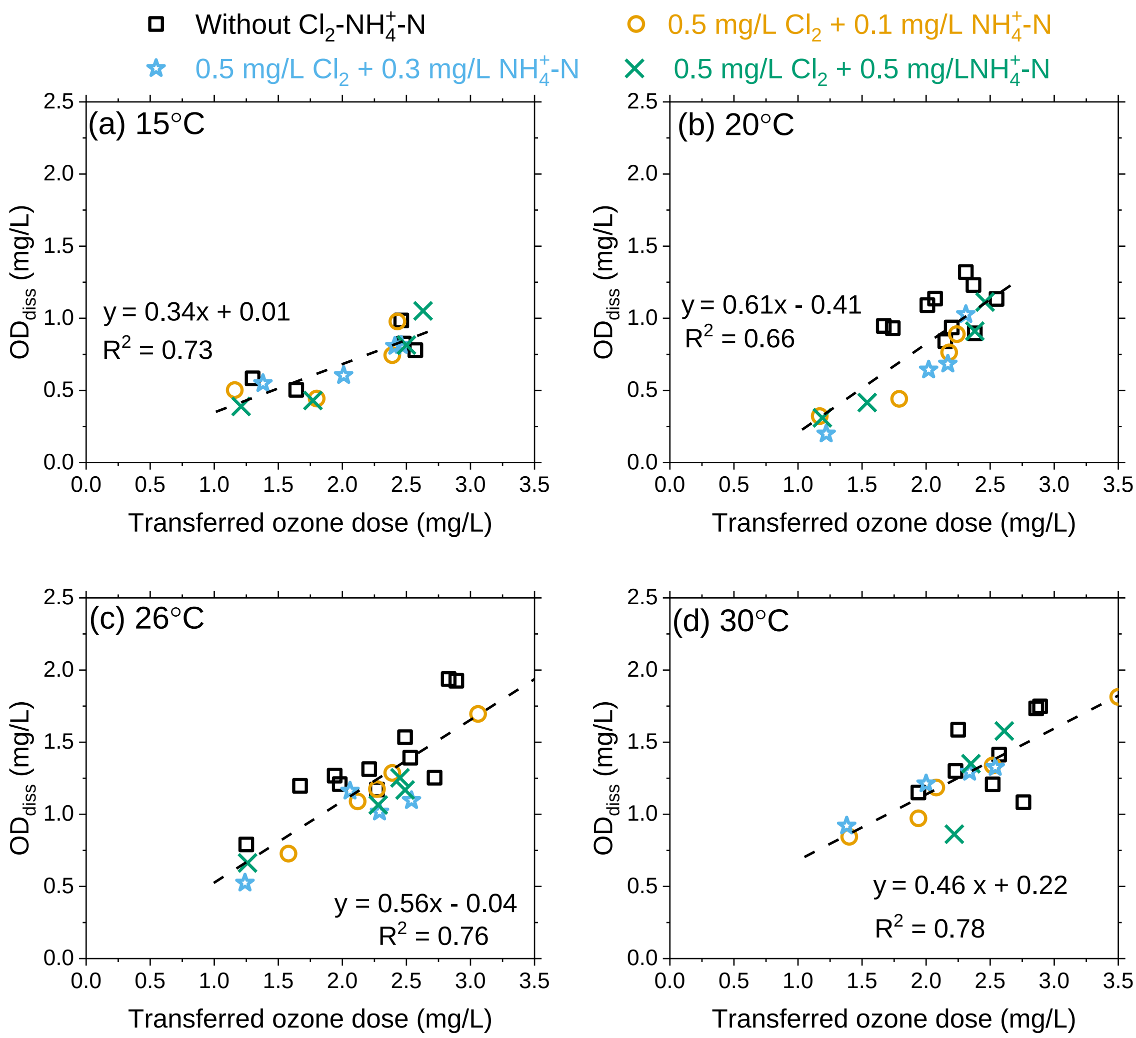

Fig. S6. The effect of transferred ozone doses on ozone demand in the dissolution zone at different temperatures of (a) 15ºC, (b) 20ºC, (c) 26ºC, and (b) 30ºC. The figure differentiates different Cl_2-NH_4^+-N dosing conditions.

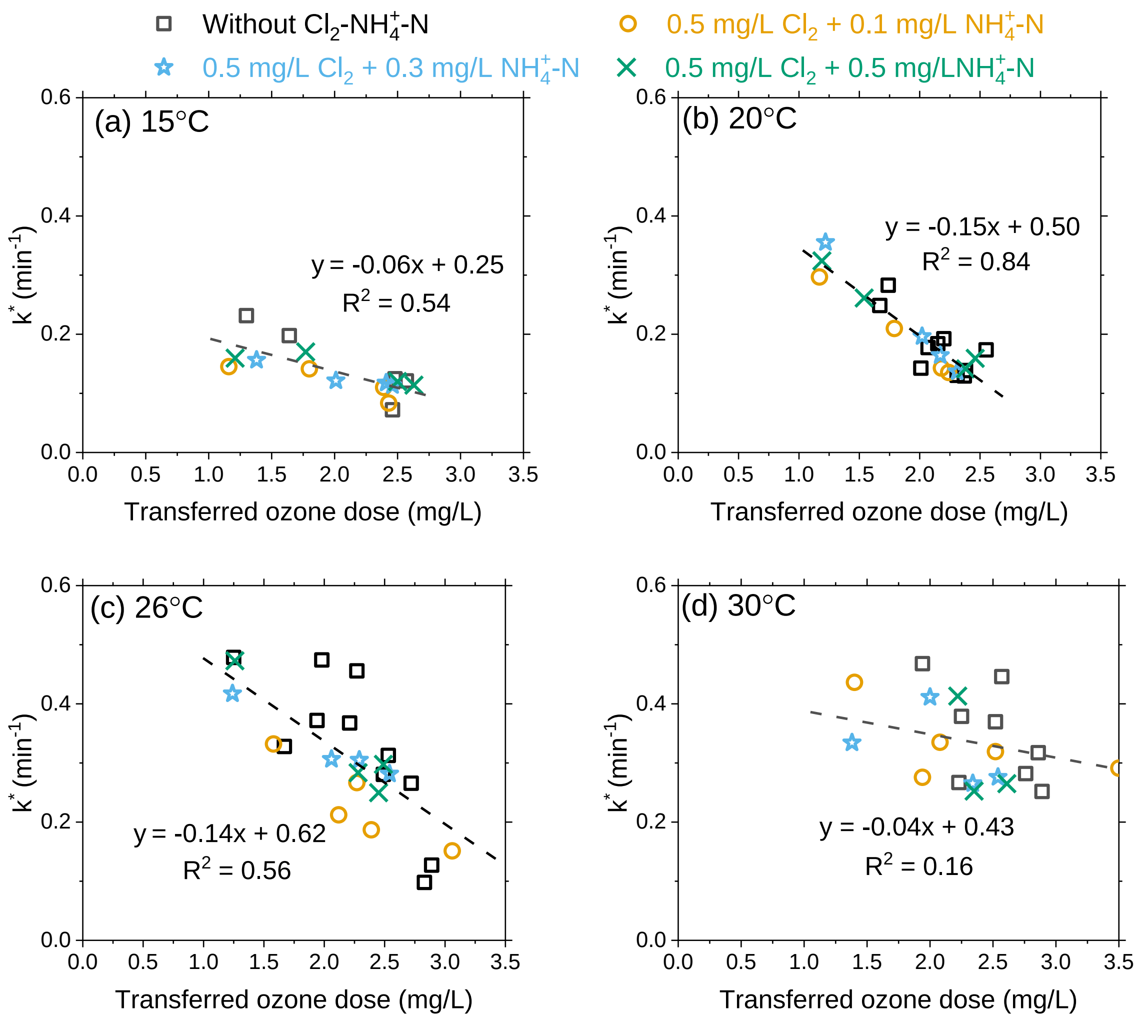

Fig. S7 The effect of transferred doses on decay rates at different temperatures of (a) 15ºC, (b) 20ºC, (c) 26ºC, and (b) 30ºC. The figure differentiates different Cl_2-NH_4^+-N dosing conditions.

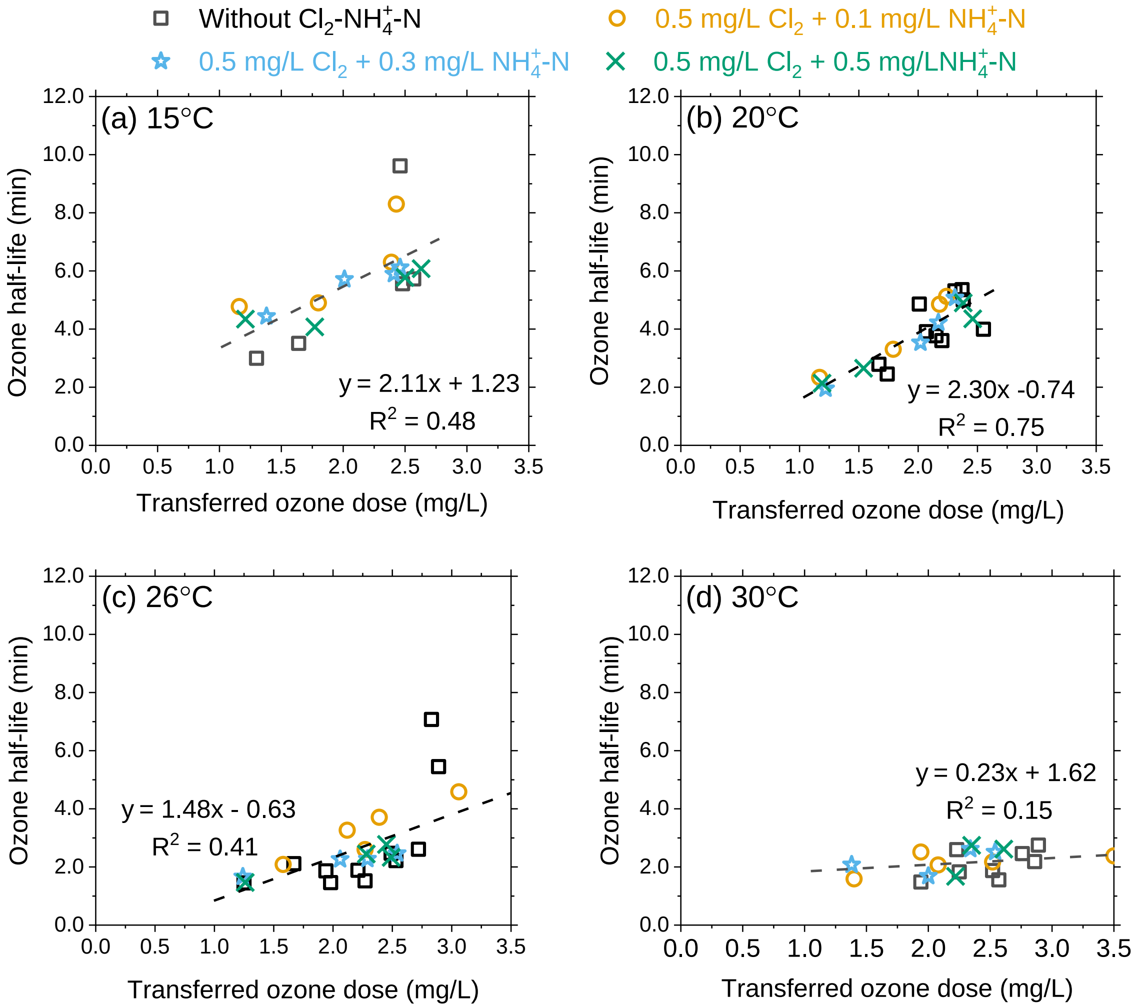

Fig. S8 The effect of transferred doses on ozone half-life at different temperatures of (a) 15ºC, (b) 20ºC, (c) 26ºC, and (b) 30ºC. The figure differentiates different Cl_2-NH_4^+-N dosing conditions.

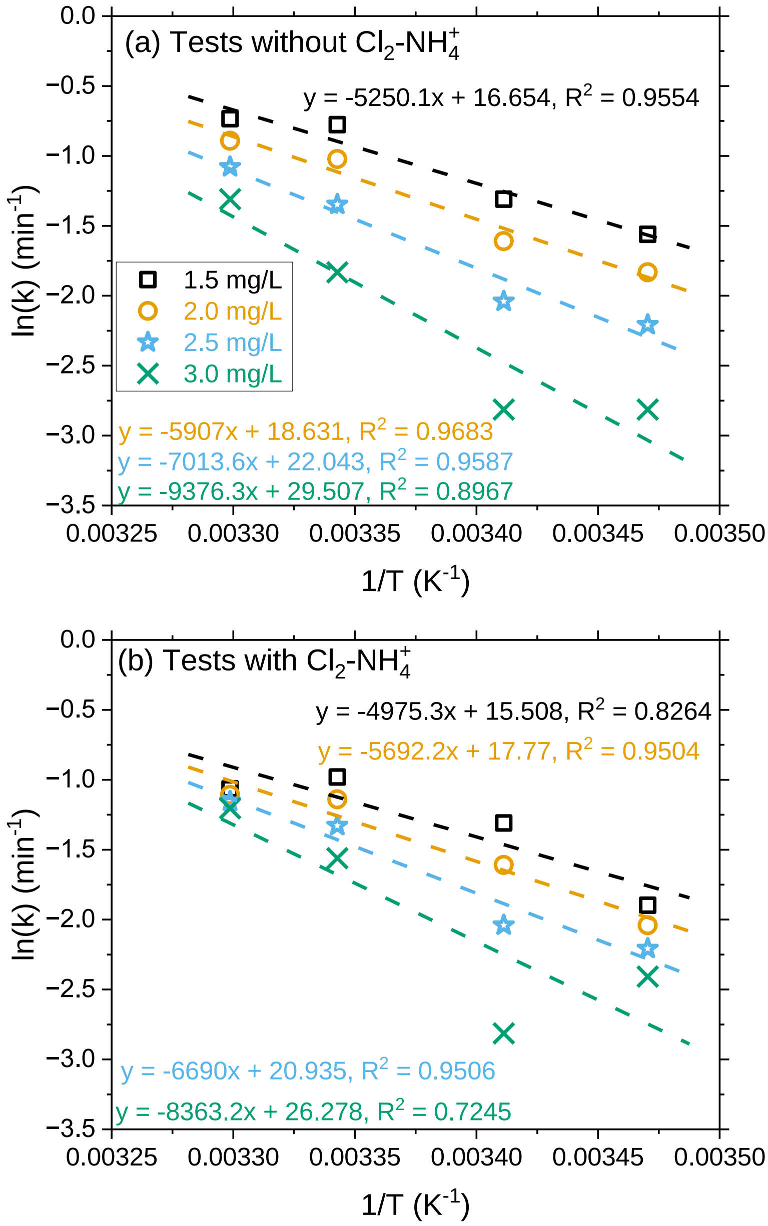

Fig. S9 Arrhenius plots for the ozone decay rate as the overall reaction with the tested water matrix at different temperatures for tests conducted (a) without and (b) with Cl_2-NH_4^+-N pretreatment.

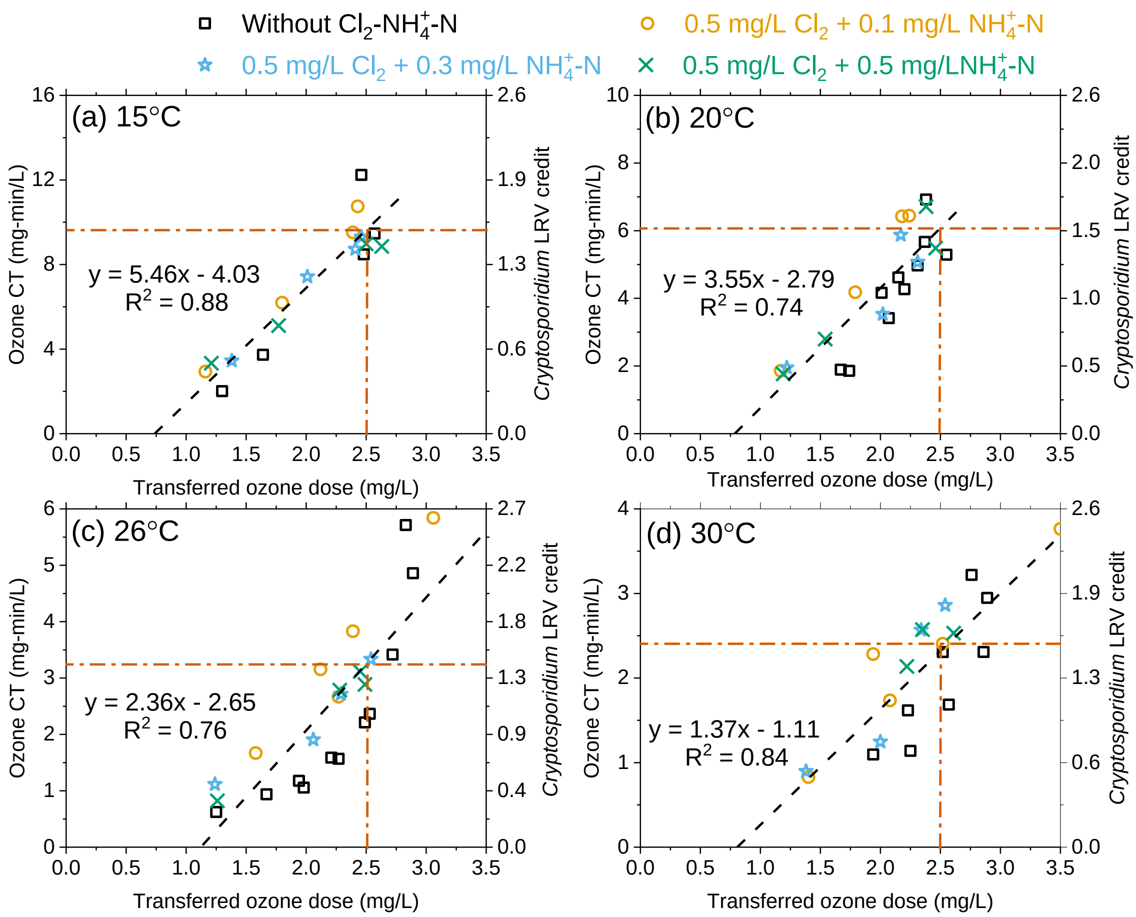

Fig. S10 The effect of the transferred ozone dose on CTs (and their corresponding *cryptosporidium* LRV at the right y-axis) at different temperatures of (a)15ºC, (b) 20ºC, (c) 26ºC, and (d) 30ºC. *Cryptosporidium* LRV and ozone CT were calculated following the LT2ESWTR guidance manual[5] and using the extended integrated T_{10} method,[6] respectively. The fitting equations correspond to the CT as a function of transferred ozone dose (left y-axis).

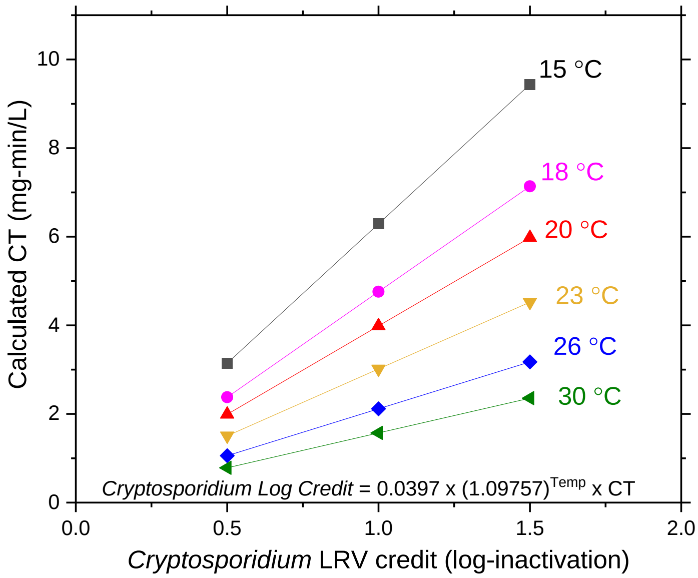

Figure S11. The effect of temperature (15-30 ºC) on calculated CT for 0.5-1.5 *cryptosporidium* LRV credits, based on the LT2ESWTR Toolbox Guidance Manual equation as shown. [5]

REFERENCES

1. Urbansky ET. Fate of Fluorosilicate Drinking Water Additives. *Chem Rev*. 2002;102(8):2837-2854. doi:10.1021/cr020403c
2. Benjamin MM, Lawler DF. *Water Quality Engineering: Physical / Chemical Treatment Processes*. John Wiley & Sons; 2013.
3. USEPA. Guidance manual for compliance with the filtration and disinfection requirements for public water systems using surface water sources. Published online 1991.
4. Rakness KerwinL, Wert EricC, Elovitz M, Mahoney S. Operator-Friendly Technique and Quality Control Considerations for Indigo Colorimetric Measurement of Ozone Residual. *Ozone Sci Eng*. 2010;32(1):33-42. http://10.0.4.56/01919510903467864
5. USEPA. Long Term 2 Enhanced Surface Water Treatment Rule: Toolbox Guidance Manual. Published online 2010:EPA 815-R-09-016.

6. Rakness KL, Najm I, Elovitz M, Rexing D, Via S. Cryptosporidium log-inactivation with ozone using effluent CT10, geometric mean CT10, extended integrated CT10 and extended CSTR calculations. *Ozone Sci Eng*. 2005;27(5):335-350. doi:10.1080/01919510500250267