Supporting Information

Trihalomethane, haloacetic acid, haloacetonitrile behavior in electric storage water heaters

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Tracer studies

A tracer solution consisting of a mix of building feed water, previously flushed for 15 minutes and at around 22 ºC, and spiked sodium chloride was continuously pumped into the 50-gallon electric water heater for five theoretical tank residence times. The conductivity of the tracer solution was approximately 1.7 mS/cm. Three flow rates (1.5, 2.0 and 2.5 gpm) and two temperature settings (45 ºC and 60 ºC) were tested. Flow, temperature, and conductivity data were monitored every 2 seconds. Normalized operation time, or throughput, θ, is

$$\theta = t/\tau \qquad [S.1]$$

where t is time from the start of tracer injection in minutes,

Normalized conductivity during the fill portion of the experiment was calculated as:

$$C^{*} = \frac{C - C_0}{C_S - C_0} \qquad [S.2]$$

where C is conductivity, C_0 is conductivity in the water heater at the initiation of the tracer study, C_S is the conductivity of the tracer solution in the water heater influent water and C is the conductivity in the water heater effluent with time.

At time zero of the tracer experiment, water temperature within the tank was about 44.5 ºC and normalized conductivity was close to zero. As cold water with sodium chloride (initial temperature of 22 ºC and conductivity of 1.7 mS/cm) was pumped into the tank, conductivity and temperature gradually changed, and after two theoretical residence times conductivity was equal to the influent value and temperature of the tank effluent dropped to about 37 ºC. Temperatures within the tank were not measured. As cold water with tracer is introduced near the bottom of the

tank, it likely displaces hot tank water upwards and the tank behaves as a PFR. After 20 minutes of tank use, which corresponds to the simulated low use pattern in this study, approximately 60% of the tank volume had been displaced with fresh feed water, and the remaining 40% corresponds to hot tank water. As the tank behaved as a PFR at that point in time, it is expected that water quality in tank effluent samples would significantly differ from the feed water quality. After about one tank residence time, temperature difference between feed and tank water decreased, thus allowing mixing to occur, and possibly short-circuiting. At 40 minutes of tank use, which is the duration chosen for the simulated high use pattern in this study, the tank volume had been completely displaced, the temperature difference between influent water and water remaining in the tank decreased and the tank hydraulics approached a mixed reactor, thus causing tank water quality to be similar to the feed water quality (Figure 1). That is, after long periods of use, water in the tank effluent was a mixture of feed water and tank water. For the tanks under high use, the difference in water quality between an early use in the morning and a later use in the afternoon was also assessed. At the beginning of the first use, the hot water within the tank was partially displaced, whereas at the end of the third use, the tank had already been displaced three times throughout the day. Tank hydraulics are likely complex and require additional experimentation or computational fluid dynamic model to understand.

Samples were collected at three locations along the hot water system (Figure 1). The influent sample, or the cold-water supply of the tank, was taken from the feed sample port after the influent line had been flushed for 30 minutes. Flushing the feed line prior to use was intended to reduce the impact of water quality changes between the building entry point and the water heater supply installation on water heater operation and processes. Tank effluent samples were taken towards the end of the daily tank flushing cycle to evaluate initial water quality that remained stagnant in the tank before the actual use. Finally, POU samples were taken directly from the sample port before the showerhead. Samples were collected shortly after the beginning of a use period after water temperature had increased in the pipe connected to the POU sample port. POU samples helped to evaluate water quality consumers would likely be exposed to when using hot water for multiple uses in a house such as taking a shower, handwashing, etc.

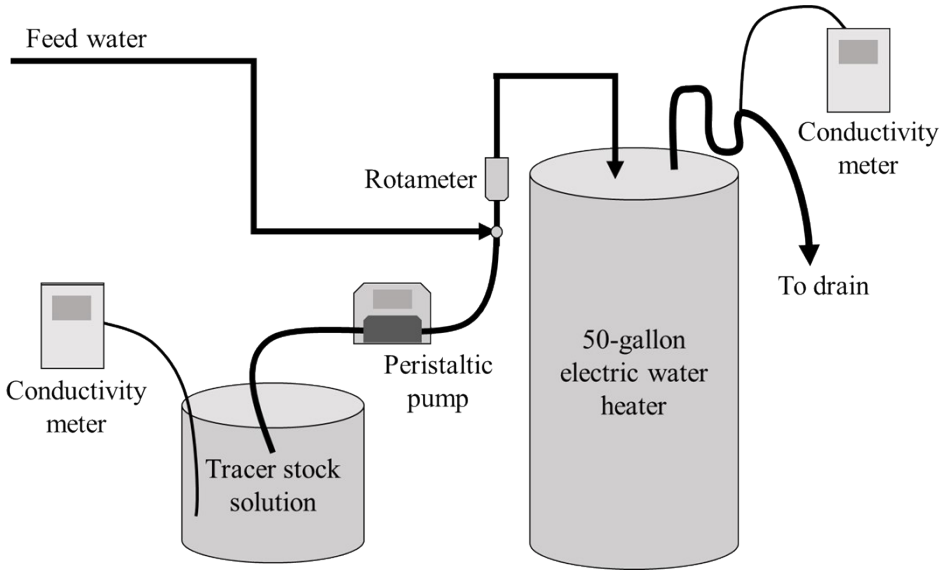

Figure S1. Schematic of the tracer study experimental setup.

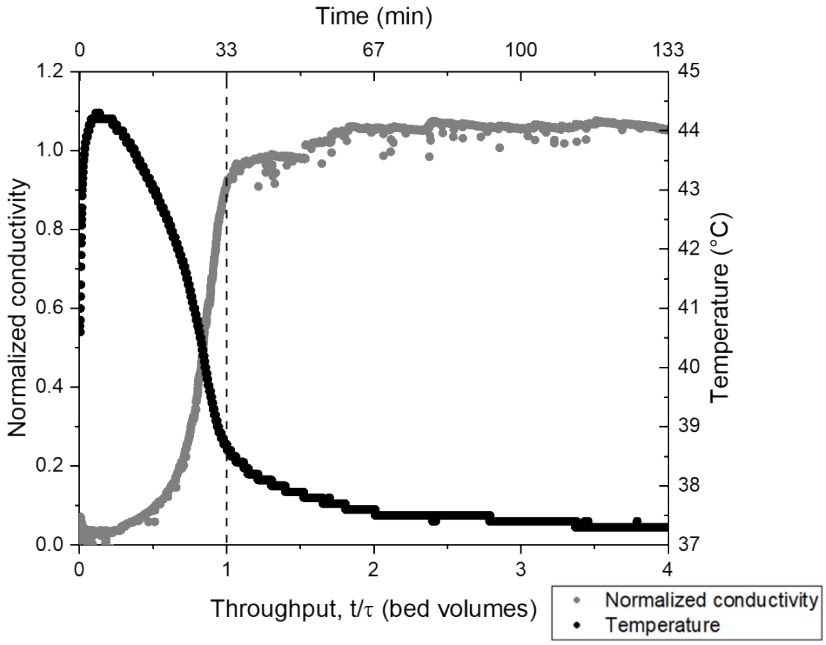

Figure S2. Normalized conductivity and temperature as a function of throughput in bed volumes.

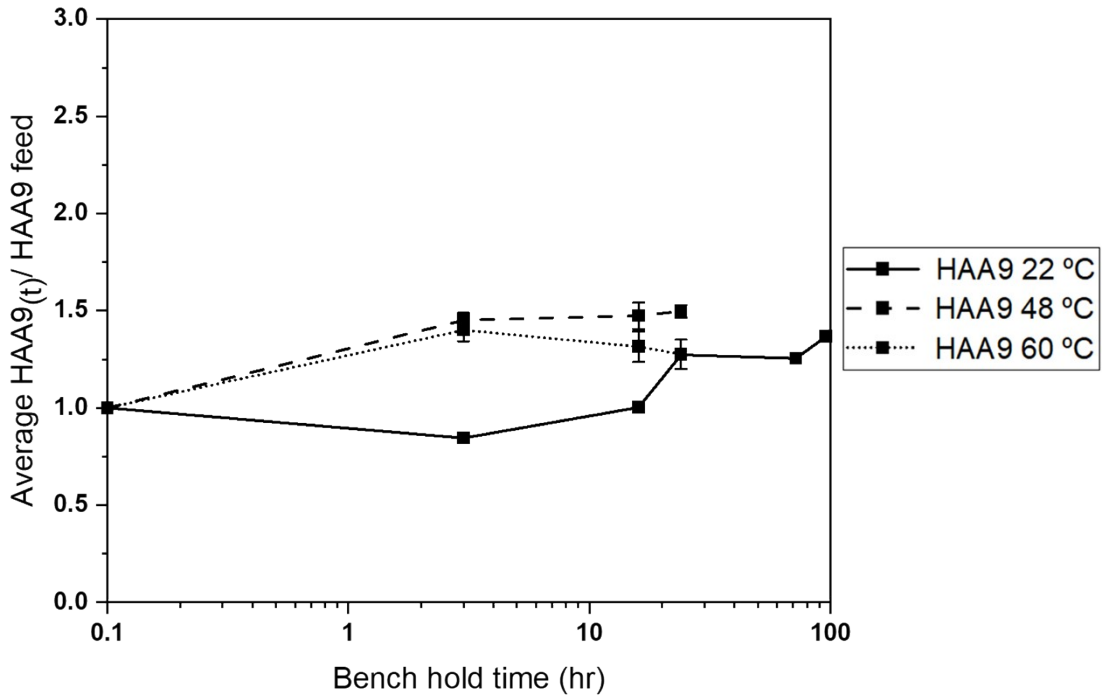

Figure S3. HAA9 kinetic behavior normalized to the initial HAA9 concentration (n = 36) as a function of bench hold time at free chlorine study site. Estimated travel time within the water distribution system is 24 hours to the lab feed. Average initial DBP concentration was: HAA9 = 28.8 ± 5.1 µg/L.

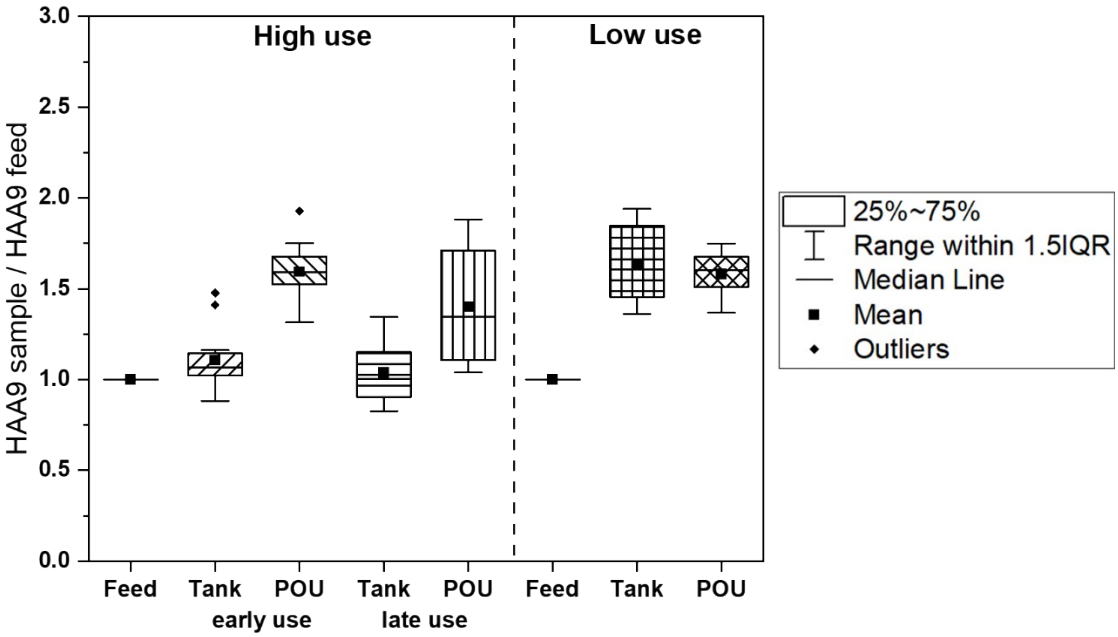

Figure S4. Average normalized HAA9 for all sample locations under the different use patterns in Phase 1 (48 ºC) in free chlorine system Boulder, CO (n = 83). Average feed concentration was 25.3 ± 9.8 µg/L.

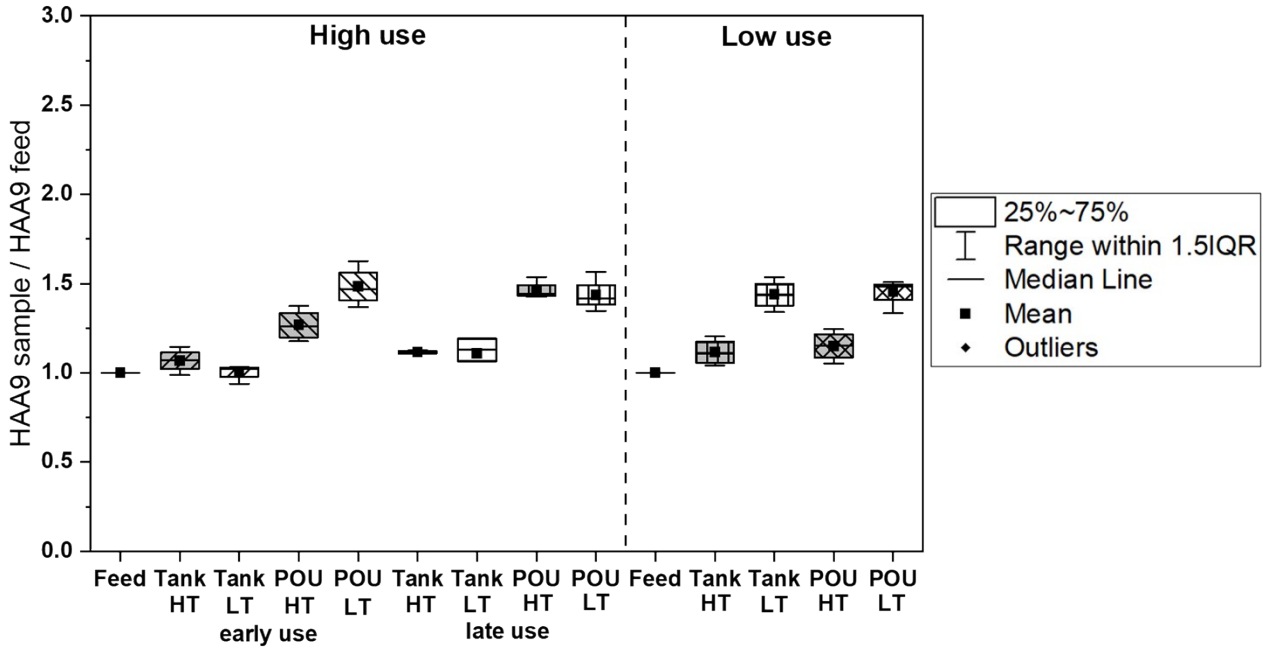

Figure S5. Average normalized HAA9 concentrations for all sample locations under the different use patterns in Phase 2 in free chlorine system Boulder, CO (n = 55). Average feed concentration was 23.1 ± 2.9 µg/L. HT = high temperature of 60 ºC; LT = low temperature of 45 ºC

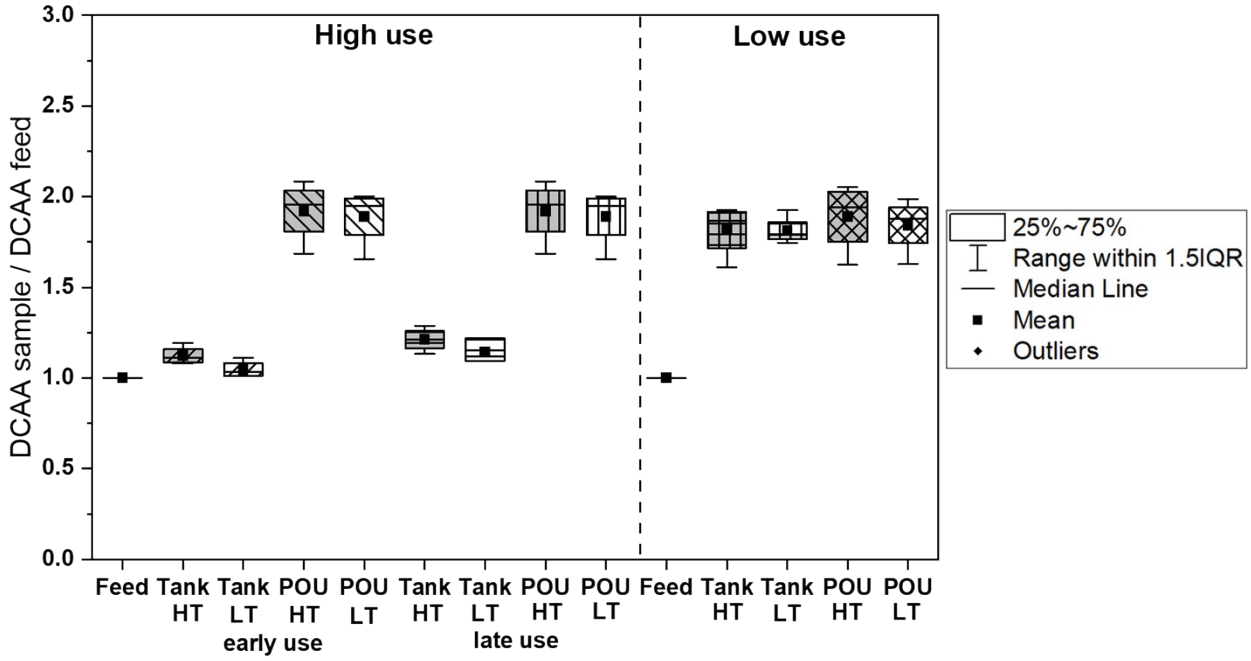

Figure S6. Average normalized DCAA concentrations for all sample locations under the different use patterns in Phase 2 in free chlorine system Boulder, CO (n = 55). Average feed concentration was 10.5 ± 1.1 µg/L. HT = high temperature of 60 ºC; LT = low temperature of 45 ºC

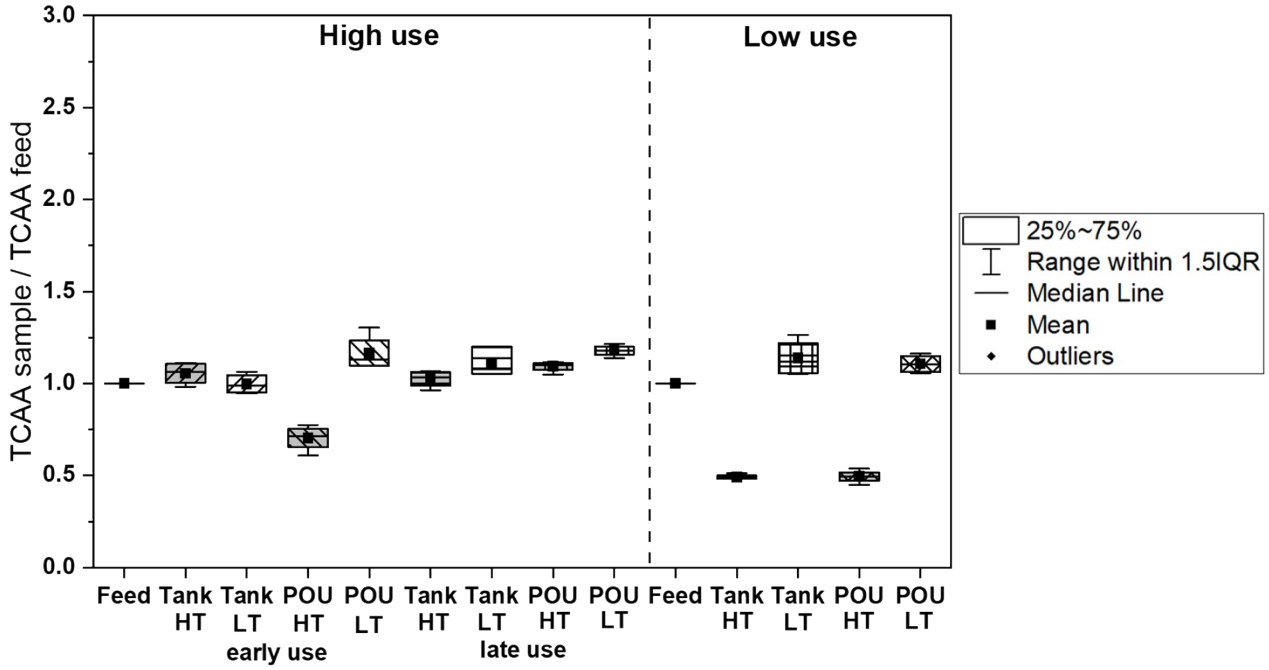

Figure S7. Average normalized TCAA concentrations for all sample locations under the different use patterns in Phase 2 in Boulder, CO (n = 55). Average feed concentration was 10.7 ± 1.1 µg/L. HT = high temperature of 60 ºC; LT = low temperature of 45 ºC

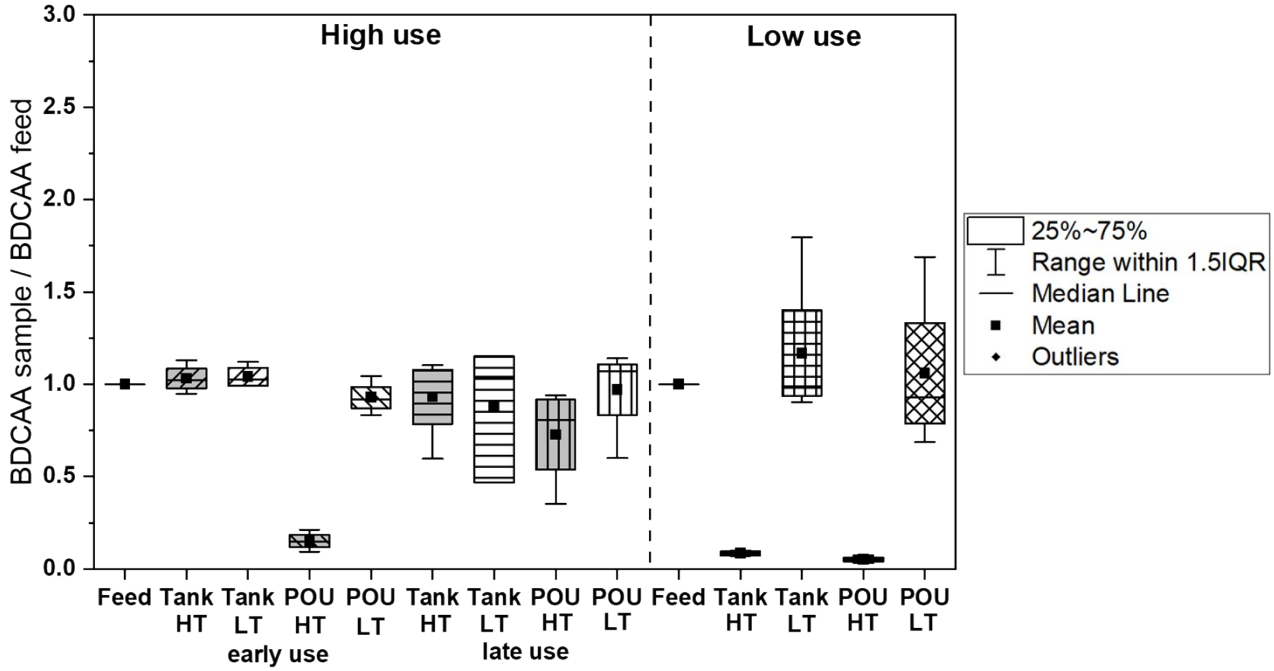

Figure S8. Average normalized BDCAA concentrations for all sample locations under the different use patterns in Phase 2 in free chlorine system Boulder, CO (n = 55). Average feed concentration was 0.6 ± 0.2 µg/L. HT = high temperature of 60 ºC; LT = low temperature of 45 ºC.

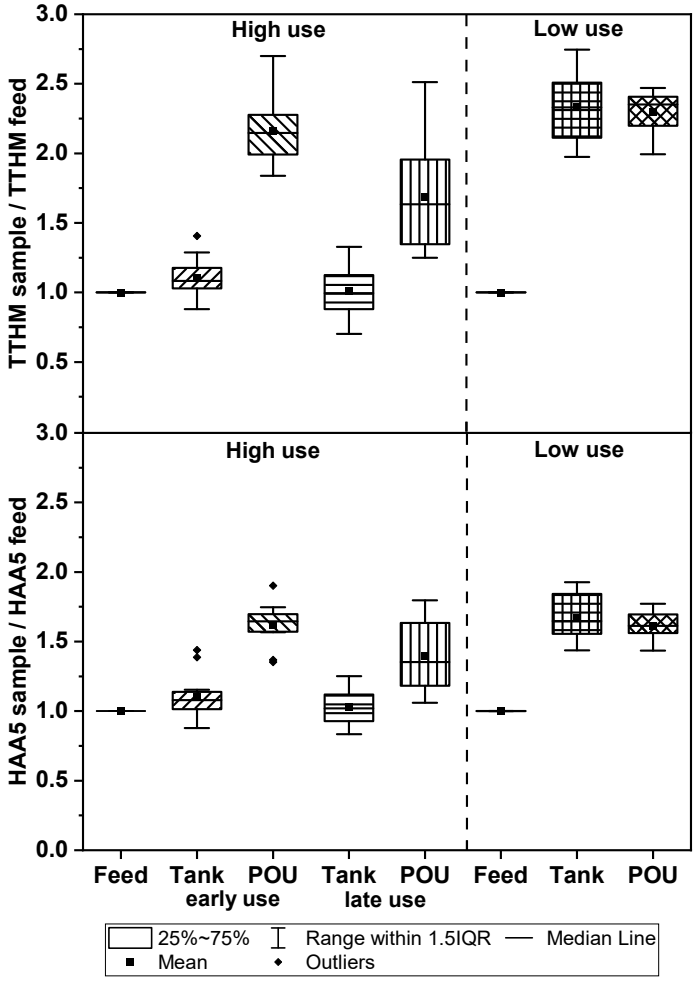

Figure S9. Average normalized TTHM and HAA5 for all sample locations under the different use patterns in Phase 1 (45ºC) - free chlorine system (n = 83). Average feed TTHM concentration was 26.1 ± 7.4 µg/L. Average HAA5 feed concentration was 22.9 ± 9.0 µg/L.

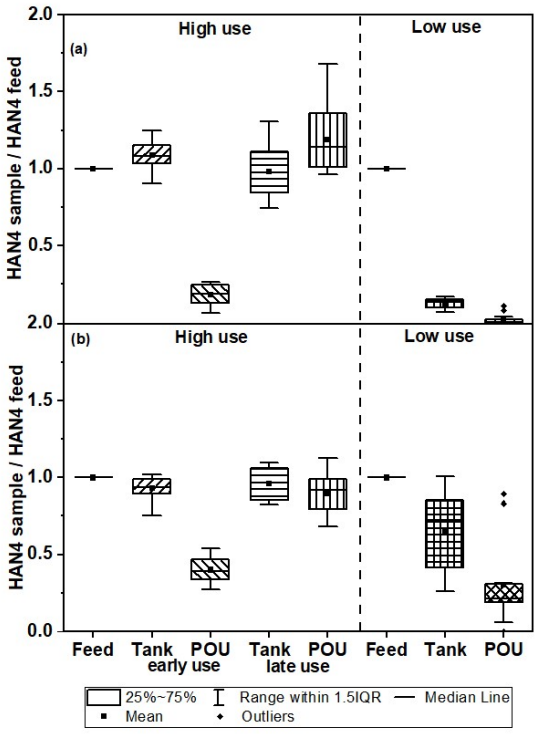

Figure S10. Average normalized HAN4 concentrations for all sample locations under the different use patterns in Phase 1 (45ºC) in the (a) chlorine system (n = 83) and (b) chloramine system (n=82). Average HAN4 feed concentration in the chlorine system was 1.49 ± 0.24 µg/L. Average HAN4 feed concentration in the chloramine system was 2.38 ± 0.63 µg/L.

TABLES

Table S1. Sampling schedule and collection. Note: Tanks 3 and 4 = high use; Tanks 1 and 2 = low use.

		Sample collection	
Time	**Activity**	**Day prior to use**	**Day of use**
7:00 AM - 7:30 AM	Feed flush tank = 30 min	Feed sample taken during last 5 min of flush	Feed sample taken during last 5 min of flush
7:30 AM - 8:10 AM	Tank #3 (1st use) = 40 min		POU high early sample taken at beginning of use (when stable temperature)
8:10 AM - 8:15 AM	Feed flush = 5 min		
8:15 AM - 8:55 AM	Tank #4 (1st use) = 40 min		POU high early sample taken at beginning of use (when stable temperature)
8:55 AM - 9:00 AM	Feed flush = 5 min		
9:00 AM - 9:20 AM	Tank #1 = 20 min	Tank low use sample taken during last 5 min of use	POU low use sample taken at beginning of use (when stable temperature)
9:20 AM - 9:25 AM	Feed flush = 5 min		
9:25 AM - 9:45 AM	Tank #2 = 20 min	Tank low use sample taken during last 5 min of use	POU low use sample taken at beginning of use (when stable temperature)
11:10 AM - 11:50 AM	Tank #3 (2nd use) = 40 min		Tank high late sample taken at 5 min before end of use
11:55 AM - 12:35 PM	Tank #4 (2nd use) = 40 min		Tank high late sample taken at 5 min before end of use
2:50 PM - 3:30 PM	Tank #3 (3rd use) = 40 min	Tank high early sample taken during last 5 min before end of use	POU high late sample taken at beginning of use (when stable temperature)
3:35 PM - 4:15 PM	Tank #4 (3rd use) = 40 min	Tank high early sample taken during last 5 min before end of use	POU high late sample taken at beginning of use (when stable temperature)

Table S2. ANOVA for the free chlorine control study DBP formation between the experimental temperatures 48 ºC and 60 ºC for the reaction times of 3, 16, and 24 hours (n = 93).

	Temp (ºC)	**Time 1 (hr)**	**Time 2 (hr)**	**p < 0.005**
TTHM				
	48	3	16	no
		16	24	no
		3	24	no
	60	3	16	no
		16	24	no
		3	24	no
	48 - 60	3	3	no

	Temp (°C)	Time 1 (hr)	Time 2 (hr)	p < 0.005
	48 - 60	16	16	no
	48 - 60	24	24	no
HAA5				
	48	3	16	no
		16	24	no
		3	24	no
	60	3	16	no
		16	24	no
		3	24	yes
	48 - 60	3	3	no
	48 - 60	16	16	yes
	48 - 60	24	24	yes
HAA9				
	48	3	16	no
		16	24	no
		3	24	no
	60	3	16	no
		16	24	no
		3	24	yes
	48 - 60	3	3	no
	48 - 60	16	16	yes
	48 - 60	24	24	yes
DCAA				
	48	3	16	no
		16	24	no
		3	24	no
	60	3	16	no
		16	24	no
		3	24	no
	48 - 60	3	3	no
	48 - 60	16	16	no
	48 - 60	24	24	no
TCAA				
	48	3	16	no
		16	24	no
		3	24	no
	60	3	16	yes
		16	24	no
		3	24	yes
	48 - 60	3	3	no
	48 - 60	16	16	yes
	48 - 60	24	24	yes
DBCAA				

	Temp (ºC)	Time 1 (hr)	Time 2 (hr)	p < 0.005
	48	3	16	no
		16	24	no
		3	24	no
	60	3	16	yes
		16	24	no
		3	24	yes
	48 - 60	3	3	no
	48 - 60	16	16	yes
	48 - 60	24	24	yes
HAN4				
	48	3	16	yes
		16	24	no
		3	24	yes
	60	3	16	yes
		16	24	no
		3	24	yes
	48 - 60	3	3	yes
	48 - 60	16	16	no
	48 - 60	24	24	no

Table S3. DBP yields – DBP/TOC (µg DBP/mg TOC) in free chlorine system

	Sample	Avg TTHM/ TOC	Std dev	Avg HAA5/ TOC	Std dev	Avg HAA9/ TOC	Std dev
UFC (Summers et al. 1996)	10 treated surface waters 24 hr, 20 ºC	29.4	7.2	18.9*	2.8	-	-
Control Lab temp study - 22 ºC (n = 18)	Feed	15.8	-	13.2	-	14.0	-
	3-day and 4-day hold at 22 ºC	36.3	3.5	22.7	0.1	23.9	0.1
Control High temperature study - 48 ºC and 60 ºC (n=93)	Feed	14.7	1.4	12.1	0.8	13.6	1.0
	High temperature samples (3 hr-, 16 hr- and 24 hr-hold at 48 ºC and 60 ºC)	34.6	6.2	18.5	3.3	20.1	3.4
Combined BLOQ control samples (n = 84)	High temp samples (3 hr-, 16 hr- and 24 hr-hold at 48 ºC and 60 ºC) and 3-day and 4-day hold at 22 ºC	34.8	6.1	18.8	3.4	20.4	3.4
Tank study - Boulder Phase 1 – 45 ºC (n=81)	Feed	17.8	5.3	15.7	5.9	17.1	6.0
	All POU samples and tank low use samples	36.7	10.1	23.8	8.0	25.7	8.2
Tank study -	Feed	20.9	6.6	15.1	4.3	16.2	4.6

Boulder Phase 2 – 45 ºC and 60 ºC (n=55-70)	All POU samples and tank low use samples at 45 ºC and 60 ºC	42.7	14.0	22.7	6.2	23.8	6.5

Note:
Uniform formation conditions (UFC) tests: (hold time 24 ± 1 h, pH 8.0 ± 0.2, 24 hour free chlorine residual 1.0 ± 0.4 mg/L and temperature 20 ± 1 °C [41]) *Data was based on HAA6/TOC.

Table S4. Average water quality parameters in Phase 1 (45 ºC) – free chlorine system Boulder, CO (n = 290).

		Free chlorine (mg/L)		pH		TOC (mg/L)	
Use pattern	**Sample**	**Average**	**Standard deviation**	**Average**	**Standard deviation**	**Average**	**Standard deviation**
High	**Feed**	0.8	0.1	7.9	0.1	1.7	0.6
High early	**Tank**	0.6	0.1	7.9	0.1	1.7	0.5
	POU	BLOQ	-	8.0	0.1	1.7	0.6
High late	**Tank**	0.7	0.1	7.9	0.1	1.6	0.5
	POU	BLOQ	-	7.9	0.1	1.6	0.5
Low	**Feed**	0.8	0.1	7.9	0.1	1.7	0.6
	Tank	BLOQ	-	8.4	0.3	1.7	0.5
	POU	BLOQ	-	8.4	0.2	1.4	0.7

Table S5. Average water parameters in Phase 2 - free chlorine system Boulder, CO (n = 200).

			Free chlorine (mg/L)		pH		TOC (mg/L)	
Use pattern	**Temp (ºC)**	**Sample**	**Average**	**Standard deviation**	**Average**	**Standard deviation**	**Average**	**Standard deviation**
High		**Feed**	0.7	0.1	7.9	0.1	1.5	0.3
High early	**60**	**Tank**	0.5	0.04	7.9	0.1	1.5	0.3
	45	**Tank**	0.6	0.1	7.9	0.1	1.5	0.3
	60	**POU**	BLOQ	-	8.1	0.2	1.4	0.3
	45	**POU**	BLOQ	-	8.0	0.2	1.4	0.3
High late	**60**	**Tank**	0.5	0.04	8.0	0.3	1.5	0.4
	45	**Tank**	0.6	0.04	8.0	0.1	1.5	0.4
	60	**POU**	BLOQ	-	8.0	0.2	1.5	0.4
	45	**POU**	BLOQ	-	7.9	0.1	1.5	0.4
Low		**Feed**	0.7	0.03	7.9	0.2	1.5	0.3
	60	**Tank**	BLOQ	-	8.3	0.3	1.4	0.3
	45	**Tank**	BLOQ	-	8.2	0.1	1.5	0.3
	60	**POU**	BLOQ	-	8.3	0.2	1.4	0.3
	45	**POU**	BLOQ	-	8.1	0.2	1.4	0.3

Table S6. Average water quality parameters in Phase 1 (48 ºC) - chloramination system Philadelphia, PA (n = 273).

		Total chlorine (mg/L)		pH		TOC (mg/L)	
Use pattern	**Sample**	**Average**	**Standard deviation**	**Average**	**Standard deviation**	**Average**	**Standard deviation**
High	**Feed**	1.6	0.5	7.5	0.5	1.3	0.3
High early	**Tank**	1.3	0.5	7.4	0.5	1.3	0.2
	POU	0.8	0.3	7.6	0.4	1.4	0.2
High late	**Tank**	1.5	0.4	7.5	0.4	1.3	0.2
	POU	1.1	0.3	7.4	0.3	1.3	0.1
Low	**Feed**	1.7	0.2	7.6	0.6	1.3	0.3
	Tank	1.4	0.4	7.5	0.4	1.2	0.4
	POU	0.9	0.5	7.6	0.4	1.3	0.2

Table S7. Average water quality parameters in Phase 2 - chloramination system Philadelphia, PA (n = 194).

			Total chlorine (mg/L)		pH		TOC (mg/L)	
Use pattern	**Temp**	**Sample**	**Avg**	**Std dev**	**Avg**	**Std dev**	**Avg**	**Std dev**
High		**Feed**	0.3	0.3	6.7	0.4	1.4	0.2
High early	**60 ºC**	**Tank**	0.4	0.4	6.8	0.3	1.6	0.2
	45 ºC	**Tank**	0.4	0.4	7.0	0.2	1.5	0.2
	60 ºC	**POU**	BLOQ	0.2	7.0	0.2	1.5	0.2
	45 ºC	**POU**	BLOQ	0.2	6.9	0.3	1.4	0.2
High late	**60 ºC**	**Tank**	0.7	0.6	7.0	0.4	1.4	0.2
	45 ºC	**Tank**	0.7	0.7	7.0	0.3	1.5	0.2
	60 ºC	**POU**	BLOQ	0.2	7.1	0.3	1.4	0.1
	45 ºC	**POU**	0.3	0.3	6.9	0.3	1.5	0.2
Low		**Feed**	0.3	0.4	6.7	0.3	1.4	0.2
	60 ºC	**Tank**	BLOQ	0.1	6.8	0.2	1.4	0.1
	45 ºC	**Tank**	0.2	0.3	7.1	0.3	1.5	0.1
	60 ºC	**POU**	BLOQ	0.0	7.1	0.3	1.4	0.1
	45 ºC	**POU**	BLOQ	0.1	7.2	0.4	1.4	0.2

Note: Avg – average; Std dev – standard deviation

Table S8. p-values obtained from paired t-tests to evaluate the impact of tank replication on water quality in the free chlorine system (Boulder, CO) and in the chloramination system (Philadelphia, PA) during experimental phase 1 (48 ºC).

Boulder - Phase 1 p-values								
Samples		**Chlorine Residual**	**pH**	**TOC**	**Norm THM**	**Norm HAA5**	**Norm HAA9**	**Norm HAN4**
Tank high early – replicate 1	Tank high early – replicate 2	1.80×10^{-5}	0.584	0.164	0.763	0.185	0.267	0.585
Tank low – replicate 1	Tank low – replicate 2	0.066	0.600	0.797	0.226	0.046	0.057	0.152
POU high early – replicate 1	POU high early – replicate 2	BLOQ	0.054	0.959	0.223	0.495	0.508	0.209
POU low – replicate 1	POU low – replicate 2	BLOQ	0.962	0.880	0.399	0.114	0.213	0.178
Tank high late – replicate 1	Tank high late – replicate 2	0.007	0.338	0.689	0.939	0.571	0.603	0.676
POU high late – replicate 1	POU high late – replicate 2	BLOQ	0.419	0.651	0.272	0.934	0.781	0.484
Samples		**Chlorine Residual**	**pH**	**TOC**	**THM**	**HAA5**	**HAA9**	**HAN4**
Day 0 feed	Day 1 feed	0.830	0.903	0.833	0.409	0.431	0.493	0.959

Philadelphia - Phase 1 p-values								
Samples		**Total Chlorine Residual**	**pH**	**TOC**	**Norm THM**	**Norm HAA5**	**Norm HAA9**	**Norm HAN4**
Tank high early – replicate 1	Tank high early – replicate 2	0.116	0.353	0.337	0.085	0.160	0.141	0.056
Tank low – replicate 1	Tank low – replicate 2	0.804	0.809	0.223	0.899	0.175	0.095	0.791
POU high early – replicate 1	POU high early – replicate 2	0.917	0.315	0.475	0.385	0.364	0.064	0.309
POU low – replicate 1	POU low – replicate 2	0.247	0.514	0.374	0.067	0.547	0.762	0.377
Tank high late – replicate 1	Tank high late – replicate 2	0.172	0.603	0.491	0.841	0.882	0.323	0.867
POU high late – replicate 1	POU high late – replicate 2	0.502	0.618	0.761	0.815	0.110	0.217	0.638
Samples		**Total Chlorine Residual**	**pH**	**TOC**	**THM**	**HAA5**	**HAA9**	**HAN4**
Day 0 feed	Day 1 feed	0.367	0.618	0.467	0.409	0.415	0.350	0.335

Note: Norm - normalized

Table S9. Normalized DBP concentrations, DBP concentration/ DBP concentration of feed (or initial for control), at the POU sample locations and at the point that the chlorine was below the DL in the control studies

Sample point temperature	Time or location	TTHM		HAA5		HAA9		HAN4	
		mean	**stdev**	**mean**	**stdev**	**mean**	**stdev**	**mean**	**stdev**
control									
22 ºC *	72 hr	2.16	-	1.36	-	1.25	-	1.03	
48 ºC	3 hr	2.22	0.16	1.48	0.04	1.45	0.04	1.28	0.12
60 ºC	3 hr	2.26	0.31	1.43	0.04	1.40	0.06	0.31	0.06
P1 - 45 ºC									
High Early	POU	2.16	0.23	1.62	0.15	1.59	0.17	0.18	0.07
High Late	POU	1.69	0.38	1.40	0.25	1.40	0.31	1.19	0.22
Low	POU	2.30	0.16	1.61	0.11	1.58	0.13	0.02	0.04
P2 - 45 ºC									
High Early	POU	1.87	0.26	1.53	0.11	1.48	0.11	0.18	0.10
High Late	POU	1.84	0.09	1.47	0.09	1.44	0.09	1.31	0.12
Low	POU	1.98	0.29	1.48	0.10	1.45	0.08	0.06	0.04
P2 - 60 ºC									
High Early	POU	1.75	0.30	1.31	0.10	1.27	0.09	0.01	0.01
High Late	POU	1.83	0.09	1.50	0.05	1.46	0.05	0.48	0.14
Low	POU	1.86	0.38	1.19	0.10	1.15	0.08	0.01	0.01

*n=1

Table S10. p-values obtained from **paired t-tests** to evaluate the impact of water use pattern on DBP concentrations during experimental Phase 1 (45 ºC)- free chlorine system Boulder, CO.

Boulder - Phase 1 p-values					
Samples		**THM**	**HAA5**	**HAA9**	**HAN4**
Tank high early	Tank low	1.11×10^{-9}	1.31×10^{-7}	8.51×10^{-7}	5.15×10^{-12}
POU high early	POU low	0.038	0.806	0.714	6.04×10^{-5}
Tank high early	Tank high late	0.256	0.323	0.404	0.163
POU high early	POU high late	0.006	0.026	0.086	5.85×10^{-9}

Table S11. p-values obtained from paired t-tests to evaluate the impact of water use pattern on water quality during Phase 2 - free chlorine system Boulder, CO.

Boulder - Phase 2 p-values					
Samples		**THM**	**HAA5**	**HAA9**	**HAN4**
Tank high early HT	Tank low HT	0.006	0.245	0.324	5.10×10^{-5}
Tank high early LT	Tank low LT	0.003	0.004	0.004	2.09×10^{-4}
POU high early HT	POU low HT	0.089	0.084	0.106	0.374
POU high early LT	POU low LT	0.016	0.219	0.412	0.016
Tank high early HT	Tank high late HT	0.212	0.325	0.235	0.455
Tank high early LT	Tank high late LT	0.465	0.214	0.261	0.531
POU high early HT	POU high late HT	0.605	0.016	0.022	0.002
POU high early LT	POU high late LT	0.846	0.078	0.041	1.34×10^{-4}

Note: HT = high temperature of 60 ºC; LT = low temperature of 45 ºC

Table S12. p-values obtained from **paired t-tests** to evaluate the impact of **temperature** on water quality during experimental Phase 2 in free chlorine system Boulder, CO.

Boulder - Phase 2 p-values					
Samples		**THM**	**HAA5**	**HAA9**	**HAN4**
Tank high early HT	Tank high early LT	0.088	0.035	0.040	0.003
Tank low HT	Tank low LT	0.055	0.013	0.014	0.018
POU high early HT	POU high early LT	0.044	0.012	0.015	0.022
POU low HT	POU low LT	0.061	3.21×10^{-4}	0.001	0.057
Tank high late HT	Tank high late LT	0.164	0.797	0.924	0.203
POU high late HT	POU high late LT	0.909	0.257	0.333	4.62×10^{-5}

Note: HT = high temperature of 60 ºC; LT = low temperature of 48 ºC

Table S13. Average normalized DBP values (DBP samples/DBP feed) in Phase 1- Philadelphia, PA chloramination system (n = 328). Average feed concentration was TTHM = 22.9 ± 4.6 µg/L, HAA5 = 21.8 ± 6.7 µg/L and HAA9 = 28.8 ± 6.7 µg/L, HAN4 = 2.4 ± 0.6 µg/L.

		Normalized TTHM		**Normalized HAA5**		**Normalized HAA9**		**Normalized HAN4**	
Use pattern	**Sample**	**Avg**	**Std dev**	**Avg**	**Std dev**	**Avg**	**Std dev**	**Avg**	**Std dev**
	Feed	1.00	-	1	-	1	-	1	-
High early	Tank	0.96	0.07	1.00	0.04	0.99	0.03	0.93	0.08
	POU	1.14	0.10	1.12	0.07	1.07	0.07	0.40	0.08
High late	Tank	0.99	0.06	1.02	0.02	1.01	0.03	0.96	0.10
	POU	1.12	0.11	1.07	0.03	1.05	0.04	0.90	0.13
Low	Tank	1.05	0.09	1.06	0.09	1.04	0.08	0.65	0.26
	POU	1.12	0.11	1.12	0.07	1.07	0.07	0.33	0.27

Table S14. p-values obtained from paired t-tests to evaluate the impact of water use pattern on water quality in Philadelphia, PA - chloramination system during Phase 1 (48 ºC).

Philadelphia - Phase 1 p-values					
Samples		**THM**	**HAA5**	**HAA9**	**HAN4**
Tank high early	Tank low	0.010	0.096	0.138	1.11×10^{-3}
POU high early	POU low	0.947	0.563	0.556	0.616
Tank high early	Tank high late	0.180	0.157	0.127	0.495
POU high early	POU high late	0.697	0.040	0.524	1.48×10^{-6}

Table S15. Average normalized TTHM, HAA5, HAA9 and HAN4 for all sample locations under the different use patterns during Phase 2 - chloramination system Philadelphia, PA. Average feed concentration were TTHM = 46.7 ± 10.4 µg/L, HAA5 = 20.6 ± 6.6 µg/L, HAA9 = 27.6 ± 8.5 µg/L, and HAN4 = 3.3 ± 0.8 µg/L.

Use pattern	**Use time**	**Sample point**	**TTHM (µg/L)**				**HAA5 (µg/L)**				**HAN4 (µg/L)**			
			Low temp 45°C		**High temp 60°C**		**Low temp 45°C**		**High temp 60°C**		**Low temp 45°C**		**High temp 60°C**	
			Avg	**Std dev**	**Avg**	**Std dev**	**Avg**	**Std dev**	**Avg**	**Std dev**	**Avg**	**Std dev**	**Avg**	**Std dev**
		Feed	1	-	1	-	1	-	1	-	1	-	1	-
High	early	Tank	0.95	0.13	0.96	0.14	1.11	0.21	1.15	0.11	1.15	0.30	1.17	0.31
		POU	1.06	0.14	1.15	0.09	1.22	0.09	1.17	0.16	0.64	0.31	0.31	0.20
	late	Tank	0.95	0.09	0.92	0.18	1.10	0.11	1.01	0.05	0.85	0.24	0.84	0.29
		POU	1.02	0.06	1.02	0.17	1.07	0.08	1.02	0.08	0.80	0.12	0.33	0.13
Low		Tank	1.01	0.05	1.00	0.10	0.89	0.14	0.99	0.12	0.46	0.32	0.34	0.09
		POU	1.13	0.09	1.13	0.11	1.06	0.02	1.03	0.09	0.22	0.16	0.08	0.07

Use pattern	**Use time**	**Sample point**	**HAA9 (µg/L)**			
			Low temp 45°C		**High temp 60°C**	
			Avg	**Std dev**	**Avg**	**Std dev**
		Feed	1	-	1	-
High	early	Tank	1.06	0.16	1.10	0.03
		POU	1.13	0.02	1.03	0.08
	late	Tank	1.08	0.15	0.99	0.08
		POU	1.04	0.08	0.95	0.06
Low		Tank	0.84	0.12	0.92	0.07
		POU	0.97	0.03	1.01	0.24