

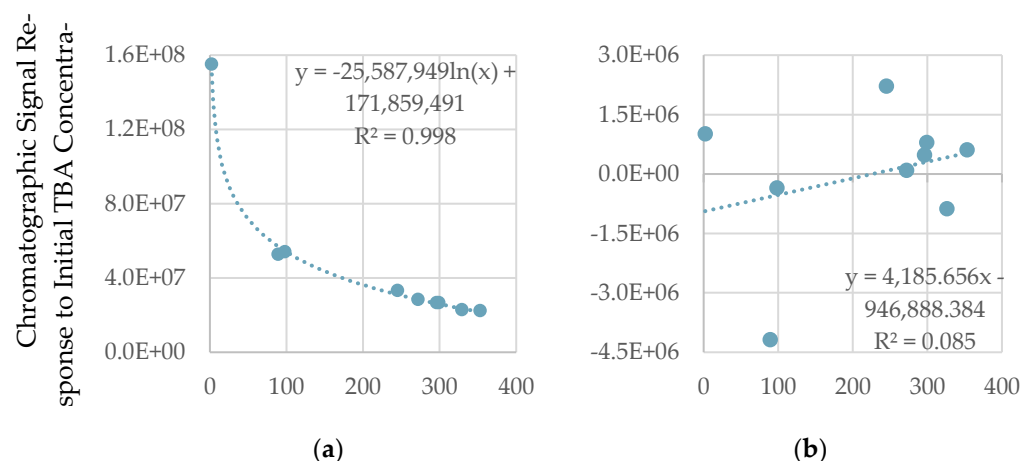
Supplementary Materials

S1. Chromatography Data Correction Process

S1.1. Chromatographic Analysis Parameters

The analysis method was similar to existing HS-GC-MS and HS-SPME methods for TBA [97–100]. Analyses were performed using a Bruker Scion 436 gas chromatograph coupled to a Bruker Scion TQ mass spectrometer, equipped with a PAL autosampler. Samples were 5 ml and combined with 1.405g (within 0.04 g) sodium chloride in deactivated, amber glass, screw cap headspace vials. Samples were introduced into the agitator and heated to 40 °C for 20 minutes. A Hamilton 1-ml gastight headspace syringe was heated to 70 °C and used to withdraw 1000 µl. The syringe was inserted into the 220 °C injection port, injected in splitless mode, then switching to 10:1 split flow after 1 minute. The compounds were separated using a DB-Wax capillary column (Bruker, 30 m × 0.25 mm i.d., film thickness 0.25 µm) operating at 7 psi column head pressure, resulting in a helium (grade 5.0) carrier gas flow of 1.2 mL/min. The temperature program was isothermal, starting at 35 °C for 5 min, then increased to 105 °C at 10 °C per min and held for 1 min, and then increased to 250 °C at 100 °C per min and held for 2.55 min. The transfer line to the mass spectrometer was maintained at 250 °C, the ionization source was 220 °C, and the MS quadrupole was 150 °C. Electron impact ionization energy was 70 eV. Scans were taken at 1 per 500 ms, operating in SIM quantifying ion 59.2 with 0.7 resolution. The GC column was equilibrated for 5 min prior to each analysis. The data were analyzed on Bruker DataAnalysis software (version 8.2.1) and all peaks were integrated using a 45 s peak width. MS spectra were compared to the NIST 2014 compound library. Stock and reaction sample peaks appeared consistent with TBA, showing the most significant ion as 59.2 m/z at a consistent retention time of 9.00 ± 0.1 min. The average peak time for this set of 369 samples was 8.981 mins, with a median of 8.985. The average signal to noise ratio was 388 with a median of 392. Section S1.2. Chromatographic Data Processing Data processing required accounting and adjusting for a significant, declining trend present across the data set. This was most likely a function of TBA and its breakdown products fouling the GCMS over time, speculated to be the ion source. The injection liner and ion source were cleaned at the beginning of sampling, with no other maintenance performed during the three-week main testing period. Prolonged periods of disuse restored a fraction of response magnitude. These phenomena were also observed and corrected for in the previous trials' data set.

The data collected are presented as percentages of TBA removed. To reduce the amount of unnecessary samples required, the initial concentration sample for TBA concentration was only taken once per batch of reaction water. Concentration curves were also generated with subsequent 10% and 1% dilutions of these samples. The 100% dilution values for batches 1 through 7 were found to have a strong correlation with a logarithmic trend. A trend of initial values was generated for batches 1-7 as described below in Figure S1(a).



Chromatographic sampling order of initial TBA concentration samples

Figure S1. (a) Declining GC-MS response to initial TBA concentration including concentration curve generated from batches 1- 7; (b) Subtracting the initial concentration curve from the initial concentration data removes almost all correlation.

To generate final values for each trial, the individual triplicate samples were first combined into their trial respective average TBA peak area signals (mass spectrometry peak areas shortened to “signal” in this section). The resulting average signal represents the concentration of TBA in the processed reactor water. The average sample signal is subtracted from, then divided by, the initial TBA concentration trend, which was generated from the initial concentration strength samples used in creating Figure S1. The calculation of removal rate data in this way therefore inherently accounts for the decay rate of the mass spectrometer response to subsequent samples. The initial concentration curve was generated with the sample order (shown as the X-axis in Figure S1) and decays at the same rate as the processed samples, since the effect of reduced response to TBA is the same for both calibration and processed samples. Comparison can then be made between any sample and any point on the initial concentration curve, accounting for decay by finding the approximate initial concentration with respect to sample order using the initial concentration trend line from Figure S1. This process relies on the assumption that sufficient calibration points are generated, to minimize the potential for uncertainty. Due to unforeseen issues with the GCMS and autosampler used, lower density of calibration points was obtained than desired. The calibration points showed little variation from the predicted trend, having a correlation coefficient (R^2) of 0.998, which supports the necessary assumption that the TBA response declined in a consistent logarithm. It is shown in Figure S1(b) that subtracting the generated initial concentration signal values from the recorded data removes nearly all correlation from the initial concentration points, with a negligible trend remaining.

Batches 8 and 9 were collected separately in time, such that they had incompatible initial TBA concentration signals with the batch 1 – 7 initial trend described above. There was a 9 day pause between the final sample of batch 7 and the first samples of batch 8, which caused a spike in TBA response at the same (initial) TBA concentration, shown in Figure S2, below. The difference between the batch 1-7 initial concentration trend and the batch 8 initial concentration response was added to the equation describing the initial concentrations, allowing for the batch 8 samples to be compared to their initial concentration values while accounting for the declining response to TBA in the same manner as the rest of the data. Batch 9 was collected further apart from batch 8, and was only used self-referentially, to determine whether there was any change observed between initial and aged

samples of reaction water, and did not need comparison to the initial concentration trend to conclude that age did not affect signal response.

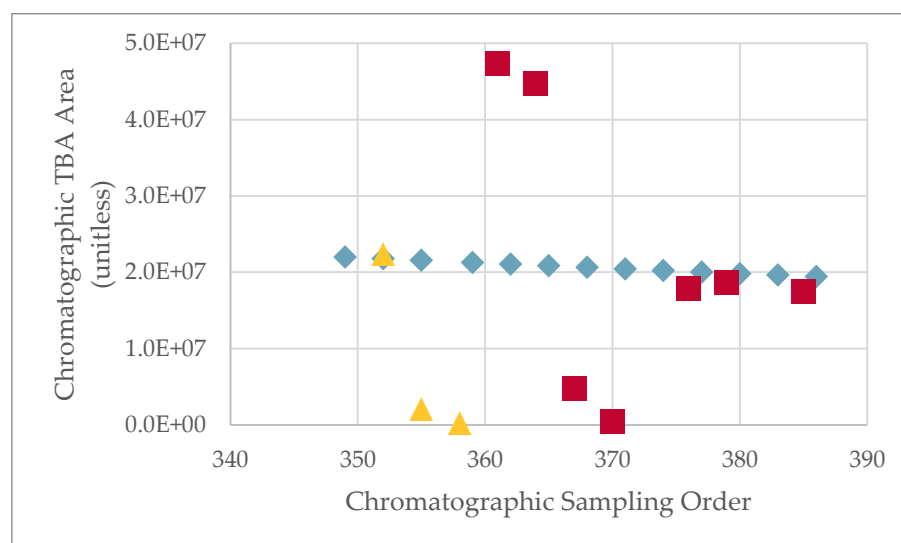


Figure S2. Chart showing the GCMS response to the initial concentration of TBA changing after a 9 day pause in sampling. Batch 7 initial concentration, 10% and 1% dilutions shown in yellow, batch 8 initial concentrations, 10% and 1% dilutions shown as first four red markers, batch 8 processed samples shown as last three red markers, and the initial concentration trend established for processing batches 1 through 7, extended through to batch 8, shown in blue, (blue).

A small subset of samples had one or more triplicates measured separately from the other triplicates, resulting from an ongoing issue with autosampler calibration drift, which caused multiple samples in batches 1 and 2 to fail to be pierced and injected. Out of 125 trials, only 12 had fewer than three triplicate samples measured together. Diagnosis this required interrupting the flow of sampling with multiple runs of sampling performed in between sample triplicate series'. Where this occurred, the repeated triplicates measured after multiple other samples had lower TBA signals than samples measured earlier (as described above). The result is that the latter triplicate tends to exhibit an artificially higher removal rate than the former samples. When this occurred, the resolution was to correct both data points separately, using their respective initial concentrations given by their average sample order, then taking the average of those results. This minimized the impact of different removal rates with respect to the initial value trend line for the same trial. Other times, samples would be lost, or appear to deviate more than 2 standard deviations from two of three triplicates, and only one group, or one triplicate could be used to describe a trial.

S1.2. Data Quality

The results of the data collection were analyzed in Microsoft Excel 365 (version 2410). The data collection process yielded approximately 372 individual chromatographs. This pool represents a collection of data points supported by triplicate, duplicate, and single data points. Approximately 125 trials were conducted, after removing duplicate entries for points re-ran, troubleshooting or otherwise ignored entries, 112 data points remained to represent individual trials included in the study. Of the remaining 112, 4 had only one sample, and thus had a variance of zero, while 5 had excessive variance, and were not used. The remaining 107 data points were included in the study. The average coefficient of variance (CoV) for all remaining data points included was 0.037, while the average CoV for the remaining three center point runs was 0.032, shown in Figure S2 below. The low CoV associated with each data point is a result of the quality of the chromatographic

method used to measure each sample, implying that the data points used should be accurate to the TBA concentrations therein.

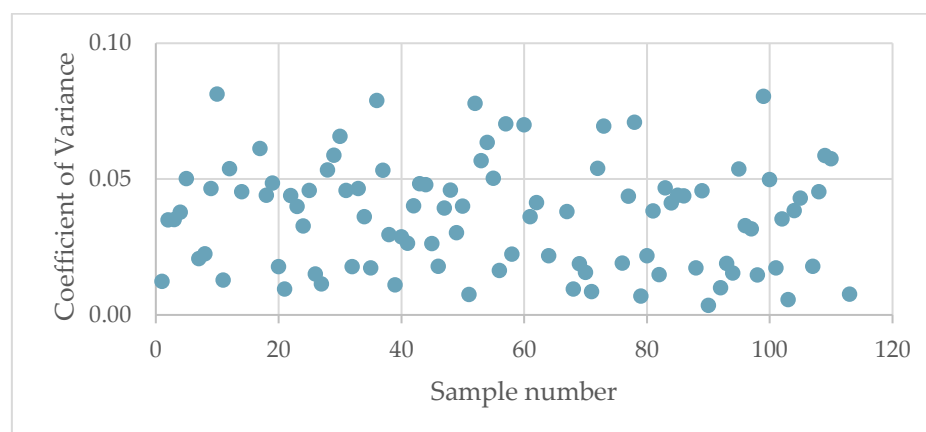


Figure S2. Coefficient of Variation (CoV) of each data point used in this study.

S2. ANOVA Test Result Summaries

All group comparisons were made against a level of significance (α) of 0.05 and equal variances were not assumed.

S2.1. Summary of ANOVA testing on TBA Stability

Table S1. Summary of ANOVA results for the effect of age on batch TBA Concentration.

Comparison groups	Group names	Number of values tested	Welch's Test (F and P Value)	Games-Howell Method
All fresh samples in age group 0 (disregarding sampling order) versus samples aged 1–5 days.	0, 1, 2, 3, 4, 5 (w.r.t. age)	15, 3, 2, 3, 3, 3	F = 2.27, p = 0.203. No significant difference between means.	No means or differences of means significantly different.
Comparing all fresh samples (taken immediately) against all samples aged > 0 days.	0, 1	15, 14	F = 0.26, p = 0.616. No significant difference between means.	No means or differences of means significantly different.
Fresh samples measured at the start, in the middle, and at the end of the chromatographic sampling (for this batch)	0, 1, 2	6, 3, 6	F = 0.34, p = 0.724. No significant difference between means.	No means or differences of means significantly different.

S2.2. Summary of ANOVA testing on Ozonation of TBA

Table S2. Summary of ANOVA results for the effect of Initial pH on Ozonation TBA Removal.

Comparison groups	Group names	Number of values tested	Welch's Test (F and P Value)	Games-Howell Method
Initial pH groups of each Ozonation trial	5, 7, 9	2, 3, 2	F = 90.17, p = 0.011. Reject null hypothesis; at least one group mean is different	Initial pH groups 5 and 7 not significantly different (p = 0.103), Initial pH 9 significantly different from both pH 5 and pH 7 groups.
Initial pH groups of each Ozonation trial (using Ozone normalized TBA Removal)	5, 7, 9	2, 3, 2	F = 89.39, p = 0.011. Reject null hypothesis; at least one group mean is different	All initial pH groups differ (using Tukey-corrected confidence intervals). Groups 5 and 7 differ by a mean of 2.99%, 7 and 9 by 10.23%, and 5 and 9 by 13.22%, with corrected p = 0.03, 0.001 and 0.001.

S2.3. Summary of ANOVA testing on Electrolysis of TBA

Table S3. Summary of ANOVA results for the effects of Initial pH and Applied Current on Electrolysis TBA Removal.

Comparison groups	Group names	Number of values tested	Welch's Test (F and P Value)	Games-Howell Method
All groups separately, from low pH and low current to high pH and high current	1, 2, 3, 4	2, 3, 3, 3	1.10, 0.462. No significant difference between means.	No significant difference between means.
Initial pH groups for low and high current tests	5, 9	5, 6	4.49, 0.064. No significant difference between means at $\alpha = 0.05$.	95% confidence interval difference of means between 5 and 9 of 1.24% with p-value 0.064. No significant difference between pH groups
Applied current groups for low and high pH tests	0.080, 0.400	6, 5	0.04, 0.851. No significant difference between means.	No significant difference between means.

S2.4. Summary of ANOVA testing on ECO Factors

Table S4. Summary of ANOVA results for the effects of individual factors on ECO.

Comparison Groups	Group names	Number of Values Tested	Welch's Test (F and P Value)	Games-Howell Method
Initial pH groups	5, 7, 9	18, 18, 16	F = 2.61, p = 0.089. No significant difference between means at $\alpha = 0.05$.	95% confidence interval difference of means between pH 9 and 5 of 11.59% with p-value 0.091. No significant difference between pH groups
Initial pH on Ozone Normalized Removal	5, 7, 9	18, 18, 16	F = 6.84, p = 0.003. Significant difference between at least one mean.	Significant difference between 95% confidence interval means of levels 5 and 9, of 3.35% at p = 0.002, insignificant difference elsewhere.
Ozone Generator Level ¹	4, 5, 6	18, 20, 16	F = 7.95, p = 0.002. Significant difference between at least one mean.	Significant difference between 95% confidence interval means of levels 6 and 4, of 19.62% at p = 0.001, levels 5 and 4, of 12.26% and p = 0.040, but insignificant difference between 6 and 5 of 7.36% and p = 0.086.
Ozone Generator Level on Ozone Normalized Removal	4, 5, 6	18, 17, 17	F = 0.082, p = 0.922. No significant differences.	No significant differences between any groups.
EOS Category groups, grouping all categories of ECO test from 6 to 1 based on their planned EOS ratio ²	1, 2, 3, 4, 5, 6	9, 12, 7, 9, 9, 9	F = 6.47, p = 0.001. Significant difference between at least one mean.	Group means 1 and 6 are significantly different from others, group means 2 and 5 and different from some others, and group means 3 and 4 are not significantly different from any other groups. Significant difference between 95% confidence interval means of 5 and 1, 6 and 1, 6 and 2, with 5 and 2 and 6 and 3 insignificant with p values between 0.05 and 0.01.

¹: Ozone generation rate (g/h) used to generate plots & modelling results, but ozone generator level was used to have categories of values for ANOVA. ²: As above in footnote 1, EOS groups (as intended, described in Section 2.2) had to be used instead of applied current groups, to perform ANOVA.

S3. Experimental Data Compilation

Batch	O3 Gen. Level	Initial pH	Applied Current (A)	% TBA Removal	Avg DO3 (ppm)	Initial pH	Final pH	Avg. Tot. Iron (mg/L)	O2 Press. (psi)	O2 Flow (SLPM)	O3 Gen. (g/h)	% TBA Removal per g O3	EOS (unitless)
1	4	5	0.065	5.88	3.31	4.97	5.18	12.2	6.5	2.69	3.94	2.98	67.8
1	4	5	0.108	18.29	2.91	5.27	5.14	14.9	12.5	3.45	4.10	8.92	42.4
1	4	5	0.151	24.93	2.69	5.12	5.14	18.6	13.25	3.55	4.12	12.11	30.5
1	4	5	0.194	37.15	2.31	5.16	5.06	37.2	13	3.52	4.11	18.07	23.7
1	4	5	0.237	46.72	2.47	5.05	5.18	37.6	9	3.01	4.02	23.22	19.0
1	4	5	0.323	46.91	1.59	5.06	5.38	50.4	24	4.92	4.64	20.22	16.0
1	5	5	0.08	30.46	3.48	5.04	5.16	10.4	24	4.92	5.96	10.22	83.2
1	5	5	0.13	40.32	2.96	4.97	4.88	21.8	22.5	4.72	5.78	13.94	49.7
1	5	5	0.19	51.37	3.54	4.98	5.27	29.4	22	4.66	5.73	17.92	33.7
1	5	5	0.24	52.72	3.28	5.01	4.89	40	21.5	4.60	5.68	18.55	26.4
1	5	5	0.3	61.22	2.62	4.93	5.28	56.8	21	4.53	5.64	21.71	21.0
1	5	5	0.4	63.69	2.8	4.93	5.27	61.6	21	4.53	5.64	22.59	15.7
1	6	5	0.1	45.28	7.46	4.81	4.61	17.8	13.75	3.62	6.25	14.49	69.8
1	6	5	0.16	57.83	6.74	4.65	4.55	26.6	13	3.52	6.21	18.63	43.3
1	6	5	0.22	59.83	6.02	5.06	4.6	36.6	14	3.65	6.26	19.11	31.8
1	6	5	0.28	71.35	3.04	4.88	5.03	44.6	15.5	3.84	6.35	22.48	25.3
1	6	5	0.35	75.59	3.61	4.87	4.73	41.6	15.5	3.84	6.35	23.82	20.3
1	6	5	0.47	76.53	3.37	4.82	5.17	76.4	15.5	3.84	6.35	24.11	15.1
2	4	7	0.065	11.99	5.74	6.95	5.83	13.3	8	2.89	4.00	6.00	68.7
2	4	7	0.108	43.14	4.67	7.6	5.25	19.4	9	3.02	4.03	21.43	41.6
2	4	7	0.151	48.27	3.59	7.5	5.25	32.4	8.8	2.99	4.02	24.01	29.7
2	4	7	0.194	52.55	3.66	7.75	5.25	31.8	9	3.01	4.03	26.11	23.2
2	4	7	0.237	55.02	3.78	7.45	5.1	37.8	10.5	3.20	4.06	27.10	19.1
2	4	7	0.323	61.91	2.93	7.3	5.1	54.8	18	4.16	4.25	29.12	14.7
2	5	7	0.08	43.1	3.74	7.3	5.1	14.3	19.5	4.35	5.52	15.61	77.1
2	5	7	0.13	50.39	3.54	7.05	5.18	21.7	19	4.28	5.49	18.37	47.1
2	5	7	0.19	56.54	3	7.15	5.4	30.8	18	4.15	5.43	20.84	31.9
2	5	7	0.24	56.82	3.9	7.45	5.3	36.6	16	3.90	5.32	21.35	24.8
2	5	7	0.3	63.31	2.55	7.3	5.35	53.2	16	3.90	5.32	23.78	19.8
2	5	7	0.4	64.41	3.63	7.05	5.35	60	16.5	3.96	5.35	24.09	14.9
2	6	7	0.1	46.06	3.59	7.15	5.6	17.3	16	3.90	6.38	14.44	71.2
2	6	7	0.16	56.51	5.75	7.15	5.38	26.6	17	4.03	6.44	17.54	45.0
2	6	7	0.22	59.75	3.88	7.15	5.48	41.4	16.1	3.91	6.38	18.72	32.4
2	6	7	0.28	63.89	2.56	7.2	5.6	48	15.5	3.84	6.35	20.13	25.3
2	6	7	0.35	69.07	2.79	7.3	5.65	50.8	13.5	3.58	6.23	22.17	19.9
2	6	7	0.47	72.32	2.38	7.25	5.6	84.8	13	3.51	6.21	23.31	14.7
3	4	9	0.065	41.61	4.05	9.2	5.8	11.4	11.5	3.33	4.08	20.38	70.1
3	4	9	0.108	46.31	2.94	9.16	5.6	17.4	10.25	3.17	4.06	22.84	41.9
3	4	9	0.151	52.04	3.19	9	5.3	25.6	12	3.39	4.09	25.43	30.3
3	4	9	0.194	59.61	2.24	9	5.7	32.8	14	3.65	4.14	28.83	23.8
3	4	9	0.237	65.25	2.17	9	5.75	47.6	11	3.27	4.07	32.05	19.2
3	4	9	0.323	65.8	1.72	9	5.85	62.4	11.5	3.33	4.08	32.23	14.1
3	5	9	0.08	47.63	4.05	9.2	5.6	15.9	11.5	3.33	5.16	18.48	72.0
3	5	9	0.13	59.2	4.61	8.95	5.75	24.6	12.5	3.46	5.19	22.81	44.6
3	5	9	0.19	60.92	3.2	9	5.75	34	13	3.52	5.21	23.39	30.6
3	5	9	0.3	67.48	3.11	8.95	5.8	57.6	10.5	3.20	5.12	26.36	19.1
3	5	9	0.4	68.85	3.73	9.04	5.8	71.2	9.6	3.09	5.09	27.07	14.2
3	6	9	0.1	48.15	6.76	9.19	5.7	25.5	9.5	3.07	6.02	15.99	67.3
3	6	9	0.16	57.5	8.45	9.05	5.75	27	10.6	3.21	6.08	18.90	42.5
3	6	9	0.22	64.48	7.47	9.01	5.8	35.4	10.4	3.19	6.07	21.23	30.8
3	6	9	0.35	71.51	2.99	9.08	5.86	63.6	10.5	3.18	6.07	23.57	19.4
3	6	9	0.47	78.96	1.91	8.98	5.85	90	10.5	3.18	6.07	26.02	14.4
4	0	7	0	-2.94	0	7.05	6.99	0	10.5	3.20	0.00	7.85	0.0
4	0	7	0	2.25	0	7.08	6.95	0	9.75	3.10	0.00	6.56	0.0
4	0	7	0	-1.28	0	7.29	5.25	0	9.8	3.11	0.00	7.37	0.0
4	5	7	0	19.94	6.71	7.24	5.35	0	9.5	3.07	5.08	3.69	NA
4	5	7	0	16.66	8.71	7.39	5.15	0	9.4	3.06	5.08	1.01	NA
4	5	7	0	18.71	10.14	7.4	5.38	0	9.4	3.06	5.08	4.85	NA

5	5	5	0	9.37	9.13	5.29	4.3	0	9.5	3.07	5.08	16.81	NA
5	5	5	0	12.35	7.27	5.08	4.86	0	9.6	3.10	5.09	18.17	NA
5	5	9	0	43.02	5.06	9.15	5.55	0	10.4	3.20	5.12	7.85	NA
5	5	9	0	46.49	4.91	8.95	5.6	0	10.3	3.19	5.12	6.56	NA
6	0	5	0.08	1.74	0	5	5.1	13	10	3.08	0.00	NA	0.0
6	0	5	0.08	0.18	0	5.11	5.35	12.7	10	3.08	0.00	NA	0.0
6	0	5	0.08	1.09	0	5.15	5.5	13	10	3.08	0.00	NA	0.0
6	0	5	0.4	1.1	0	5.05	8.9	39.6	10	3.08	0.00	NA	0.0
6	0	5	0.4	2.77	0	5.08	8.87	38	10	3.08	0.00	NA	0.0
7	0	9	0.08	1.39	0	9.05	9.22	13.3	10	3.09	0.00	NA	0.0
7	0	9	0.08	-1.02	0	8.98	9.35	12.1	10	3.09	0.00	NA	0.0
7	0	9	0.08	0.42	0	9.05	9.27	12.4	10	3.09	0.00	NA	0.0
7	0	9	0.4	-1.08	0	9.15	9.25	41.2	10	3.09	0.00	NA	0.0
7	0	9	0.4	0.54	0	9.11	9.31	55.2	10	3.09	0.00	NA	0.0
7	0	9	0.4	0.555	0	9.18	9.35	50.4	10	3.09	0.00	NA	0.0
8	5	7	0.24	59.25	6.45	7.12	4.81	41.8	10	3.13	5.10	23.23	23.7
8	5	7	0.24	57.2	7.32	7.04	4.83	38.8	10	3.13	5.10	22.43	23.7
8	5	7	0.24	59.41	7.23	7.42	4.89	38.8	10	3.13	5.10	23.30	23.7