



Department of Civil and Environmental Engineering
University of Missouri

Missouri Water Resources Research Center (MoWRRC)
University of Missouri

Final Report

July 2008 through June 2009

**City of Columbia, MO:
Analysis of Water Quality for
Disinfection By-Products (DBPs)
and Evaluation of the DBP
Formation Potential**

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Executive Summary

Samples collected during this study show that current DBP formation potential did not notably change from the source waters in the wells through water treatment plant and into the distribution system. Samples also reveal that current DBP concentrations and future DBP formation potential near the compliance locations in the City of Columbia system will remain close (~74 to 85 µg/L) to the maximum contaminant limit (MCL) for Total Trihalomethanes (TTHM) of 80 µg/L. This tendency puts the City of Columbia at risk of being out of compliance with the MCL again in the future.

The most prominent treatment strategy for reducing DBP concentrations being considered by the City of Columbia is a switch from free chlorine to chloramines. Testing of finished water samples from the water treatment plant suggests that chloramines will stall DBP formation at approximately one-half of the current compliance sample concentrations.

Although the City is going forward with the switch to chloramines as the residual disinfectant in their distribution system, the recommendation of the MoWRRC is that the City also consider other modifications to the operation of the water treatment plant that would also effectively reduce DBP concentrations in the distribution system while allowing for the switch back to free chlorine as the residual disinfectant. Among these modifications under consideration should be enhanced softening, MIEX (magnetic ion exchange), and preoxidation.

1. Introduction

In order to meet new EPA standards for Disinfection By-Products (DBPs), the Columbia Water & Light Department needed more detailed data concerning the current and future DBP formation potential in their system. Hence the University of Missouri-Columbia and the City of Columbia are worked together to collect this information by sampling and analyzing water from several key points in the water treatment system. This research data includes Total Trihalomethanes (THM), Total Haloacetic Acid (HAA₅), and Total Organic Carbon (TOC), Ultra Violet light absorbance at 254 nanometers (UV₂₅₄), temperature and chlorine residual. The goal of this project was to develop a database of water quality parameters that influence the formation of THMs in the city's water. This enables the City to better develop an effective and sustainable Internal Compliance Plan in order to meet the new standards that will likely involve new operational and maintenance practices in the system. Listed in this report are various parameters that have been measured during the past year. The data is displayed on graphs and trends of the data throughout the wells and water plant are discussed.

1.1 Method

All the data obtained in this report were through sampling. Hence three types of samples were collected for the whole year, well samples, in-plant samples and distribution system samples. In order to understand the formation potential of Columbia water system, the formation potential tests were carried out for samples from both wells and plant. Meanwhile, it also designed a laboratorial experiment to demonstrate the possible results if switching chlorine to chloramines as a disinfectant residual.

1.2 Sample sites

In this study, samples were taken from three types of system: ground wells, water treatment plant and distribution system. The specific descriptions for sample sites are list below in Table 1.2.

Table 1 Sample Sites Descriptions

Site #	Wells	In-plant	Distribution System
1	Well #1	Raw water	Plant WET lab
2	Well #2	Aerator#1	Pipe Gallery
3	Well #3	Aerator#2	ASR well #10
4	Well #4	Aerator#3	PIT South pump
5	Well #5	Aerator#4	Worley FS
6	Well #6	Primary Clarifier #1	Rockbridge apts
7	Well #7	Primary Clarifier #2	ASR well#8
8	Well #8	Primary Clarifier #3	Mary Ann Circle
9	Well #9	Primary Clarifier #4	Clearview
10	Well #10	Secondary Clarifier #1	Prathersville FS
11	Well #11	Secondary Clarifier #2	Thrn-Leatherbrook
12	Well #12	Secondary Clarifier #3	Railroad
13	Well #13	Secondary Clarifier #4	Cliff Dr.
14	Well #14	Filter #1	Becky's
15	Well #15	Filter #2	Clenn Wesley
16		Filter #3	Stephens tower
17		Filter #4	
18		Filter #5	
19		Filter #6	
20		Filter #7	
21		Filter #8	
22		Finished Water #1	
23		Finished Water #2	

2. Analyses performed

Samples collected from all of the locations will be analyzed for the regulated DBP (TTHMs and HAA5) concentrations, total organic carbon (TOC), UV 254, free and total chlorine, and temperature. In order to get further understanding of City's water system. Wells samples and plant samples were both incubated respectively, for Formation Potential Analysis.

2.1 Disinfection Byproducts

Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two largest classes of DBPs on a weight basis formed during the chlorination of waters. The current maximum contaminant levels (MCLs), as determined for a locational running annual average in distribution system, is 80µg/L THMs and 60µg/L HAA₅ (US EPA, 2006). Hence our analysis was focusing on both of these major disinfection by-products.

2.1.1 TTHM

The samples collected for TTHM analysis were analyzed with a Varian 3800 gas chromatography (GC) system equipped with a mass spectrometer (MS) for detection. An analysis method similar to that described by EPA method 524.2 and Standard Method 6232 C was used. 5mL of sample was injected into a purge-and-trap system connected to the GC, and the concentrated volatile compounds were directly sent to the column for separation and later measurement.

2.1.2 HAA₅

The samples to be analyzed for HAA₅ concentrations were run with a Varian 3800 GC system equipped with an electron-capture detector (ECD). Procedures outlined for sample preparation and analysis in EPA method 552.2 and 6251 B were followed for HAA₅. A 40-mL water sample was analyzed for these tests.

2.2 Other Water Analyses

A few non-DBP analyses were also performed in parallel with DBP analysis to yield more information on which to base any conclusions resulting from the DBP concentration data.

2.2.1 UV₂₅₄

Samples from all sites were collected for determination of their absorbance of light at 254 nm (UV₂₅₄). Samples were transferred to the cuvette using a syringe and filtered prior to measurement using a 0.45-µm syringe filter. Absorbance values were obtained using the Varian CARY50Conc spectrophotometer in the University of Missouri's laboratory.

2.2.2 TOC

Samples from all sites were analyzed for non-purgeable organic carbon (NPOC) in the University of Missouri Environmental Engineering laboratory using a Shimadzu TOC analyzer. No additional sample preparations were required.

2.2.3 Free and Total Chlorine

Free and total chlorine concentrations at sample sites were measured on-site at the time other samples were collected and tested by using a Titration station.

2.2.4 Temperature and pH

Temperature and pH were obtained at sample sites by using a thermometer and pH meter, respectively.

3. Formation Potential

Formation Potential experiment of determine the potential for forming THMs and HAAs are useful in evaluating water treatment processes or water sources or predicting those two DBPs concentration in a distribution system. Hence we carried out formation potential test for both well samples and plant sample in the whole year sampling period.

All samples collected from wells and plant had been chlorinated for formation potential test. The dose amount of chlorine was 10mg/L for each sample. The chlorination was taken under the condition of $\text{pH } 8.5 \pm 0.2$ at 15 ± 1.0 °C in the winter and at 20 ± 1.0 °C during the summer time. The incubation time was three days and seven days, respectively. After incubation, ammonia chloride had been dosed as a quench agent to stop the formation reaction for THMs and HAA.

All the results of formation potential tests are displaying in the following passages.

3.1 Well Sample Results

Samples from wells were taken in the period from July, 2008 to May, 2009. Three-day and seven-day formation potential were carried out during this period. In this report, TTHMs, HAA5 and other additional analyses results are displaying by graphs.

3.1.1 TTHMs (Total Trihalomethanes)

The measured values for total trihalomethanes (TTHM) are the sum of the concentrations of chloroform, bromodichloromethane, dibromochloromethane, and bromoform. The MCL for TTHM is 80µg/L; for easy comparison of the analytical results with this requirement across the duration of the study, this concentration is indicated by dashed lines on the appropriate graphs.

Figure 7.1.1a is the graph for samples taken directly from wells. Meanwhile, we incubated those samples for three days and seven days respectively to investigate the formation potential of DBPs inhered in those samples. Except the sample for April 24th and May 22nd which incubated at 21°C, others were incubated at 15°C.

Figure 7.1.1a shows that the concentration of TTHMs is generally near or below the detection in the grabbed samples. But they were having formation potential of TTHMs when incubated them under chlorination condition, which are displaying in the figure 7.1.1b and 7.1.1c. After three days' incubation, the TTHMs concentration in most of well samples had exceeded 80µg/L. After seven days' incubation, the TTHMs concentration in wells generally exceeded the MCL, especially for the Well #2 and Well #6 collected on July, 2008, which almost reached 160µg/L. Those two formation potential graphs display that the well water had notable abilities for TTHMs formation in the source water system. As increasing the temperature, the formation concentration for TTHMs was also getting increase.

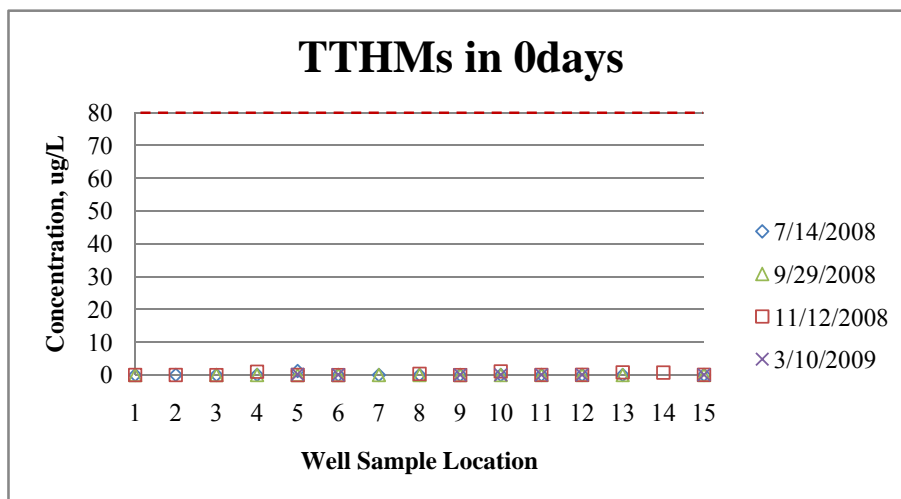


Figure 7.1.1a – TTHMs of well samples in 0day

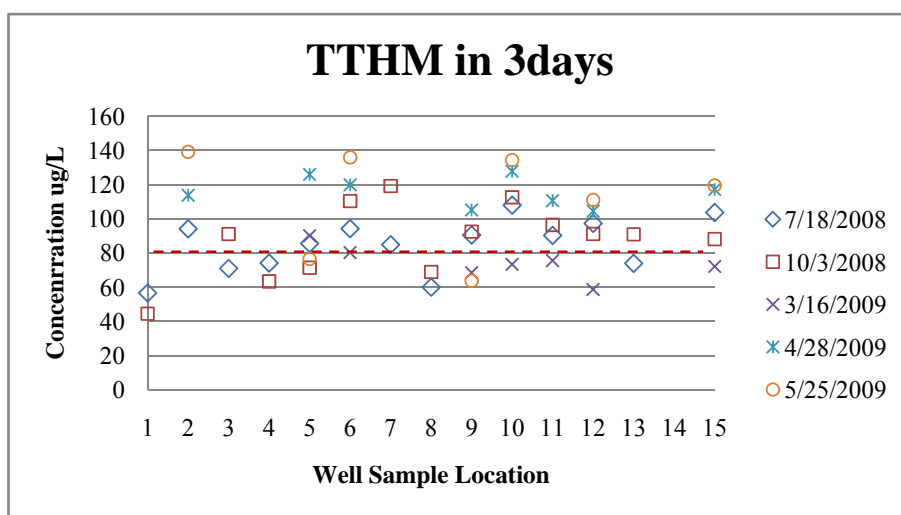


Figure 7.1.1b – TTHMs of well samples in 3days

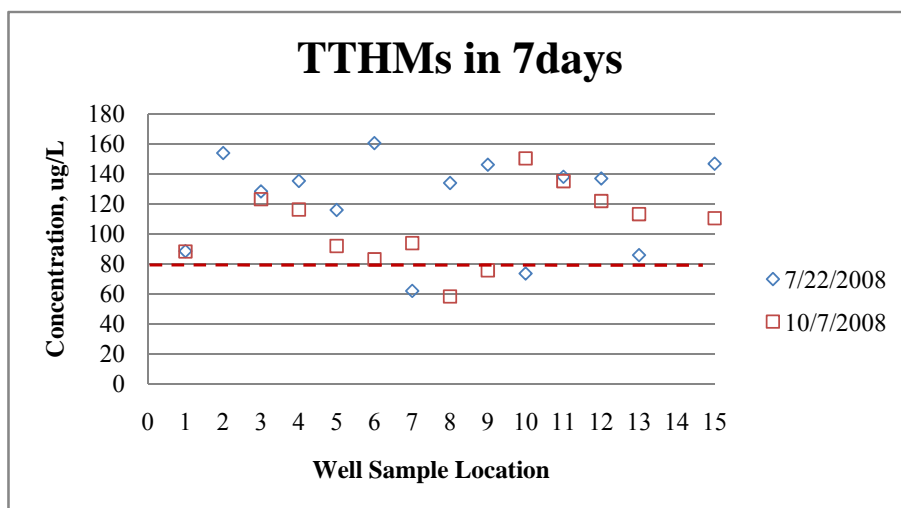


Figure 7.1.1c TTHMs of well samples in 7days

3.1.2 HAA₅

For the HAAs species, we just recorded the HAA₅ which includes five species of the total haloacetic acid, they are dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), dibromoacetic acid (DBAA), monochloroacetic acid (MCAA), and monobromoacetic acid (MBAA).

Figure 7.1.2a is the HAA₅ concentration for samples taken directly from wells. Figure 7.1.2b and figure 7.1.2c are the figures for 3days and 7days, respectively. It shows well samples have the potential for HAA₅ formation.

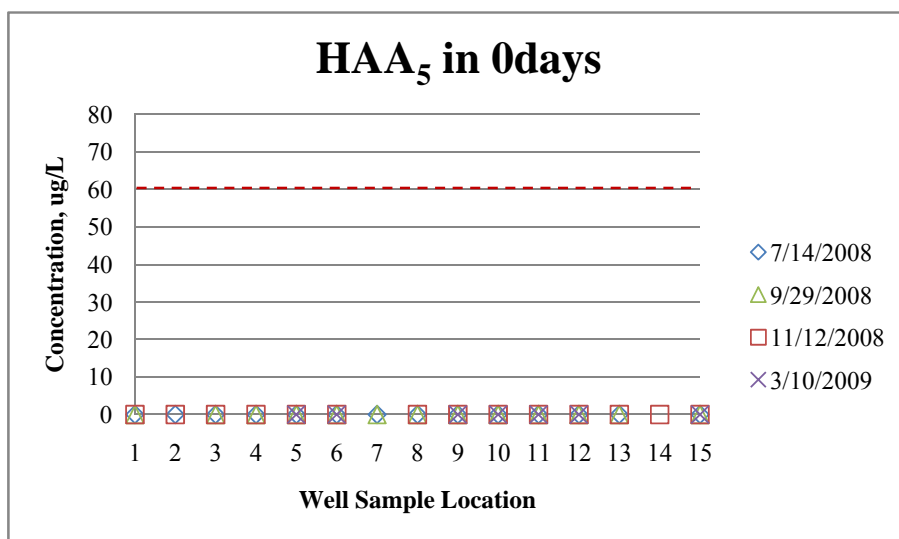


Figure 7.1.2a – HAA₅ of well samples in 0day

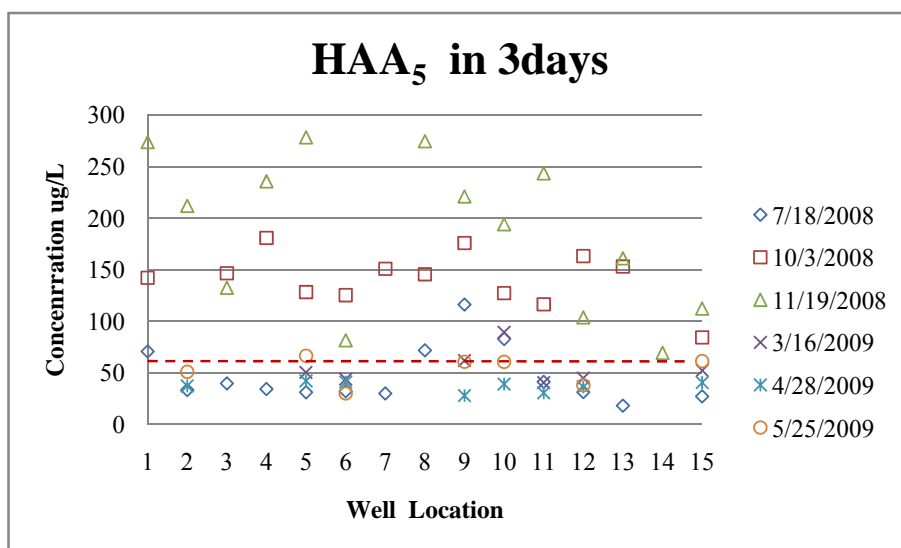


Figure 7.1.2b – HAA₅ of well samples in 3days

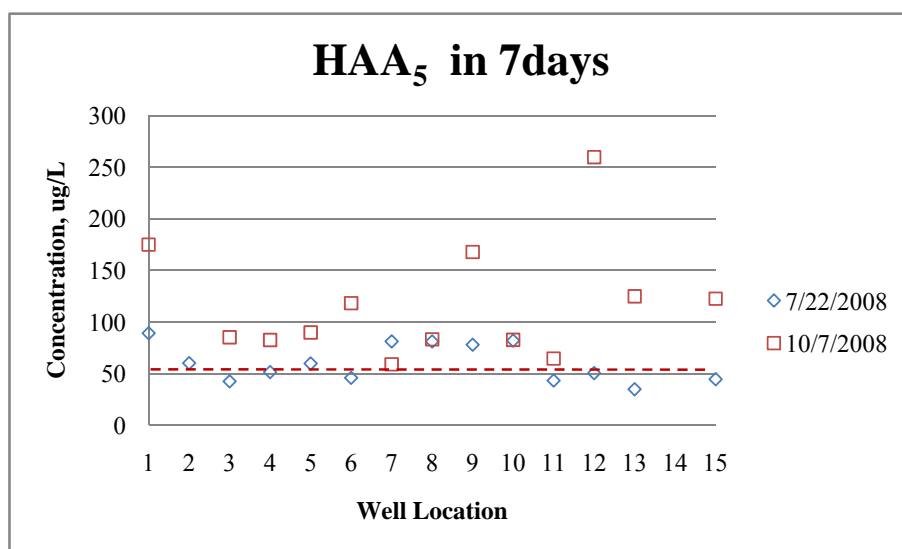


Figure 7.1.2c – HAA₅ of well samples in 7days

3.1.3 Results from additional analyses

Following discussion are the results from additional analyses. DBP formation is highly dependent on seasonal variations and spatial variations. It was expected that these results might still be able to illuminate other factors, an adjustment of which might help control DBP levels for Columbia drinking water system.

3.1.3.1 Temperature

Figure 7.1.3.1 shows the temperature records for the whole year sample period. It generally remains around from 14 to 16°C.

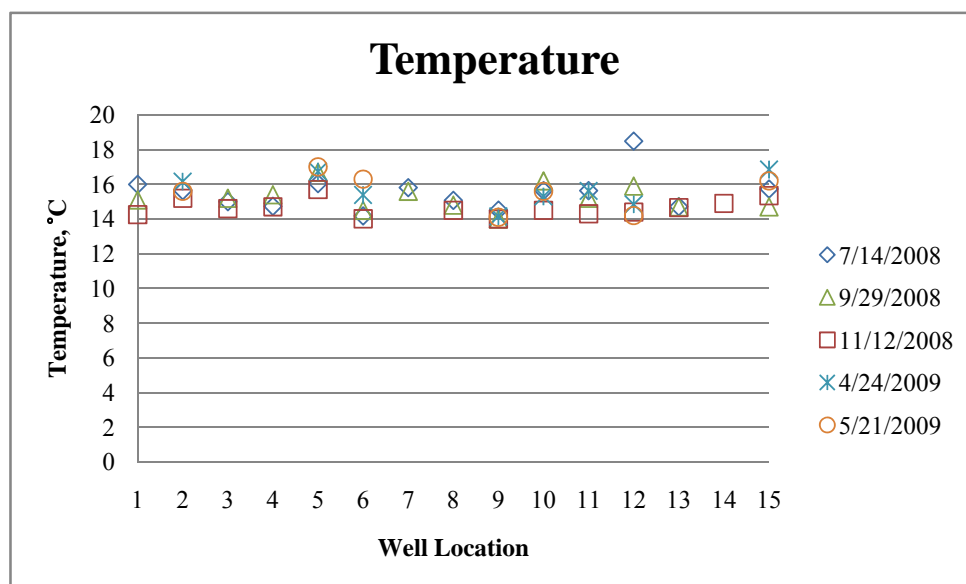


Figure 7.1.3.1 Temperature of well samples collected

3.1.3.2 pH

As measured by the handy instrument, the pH value for the whole sample year is constantly around 7.

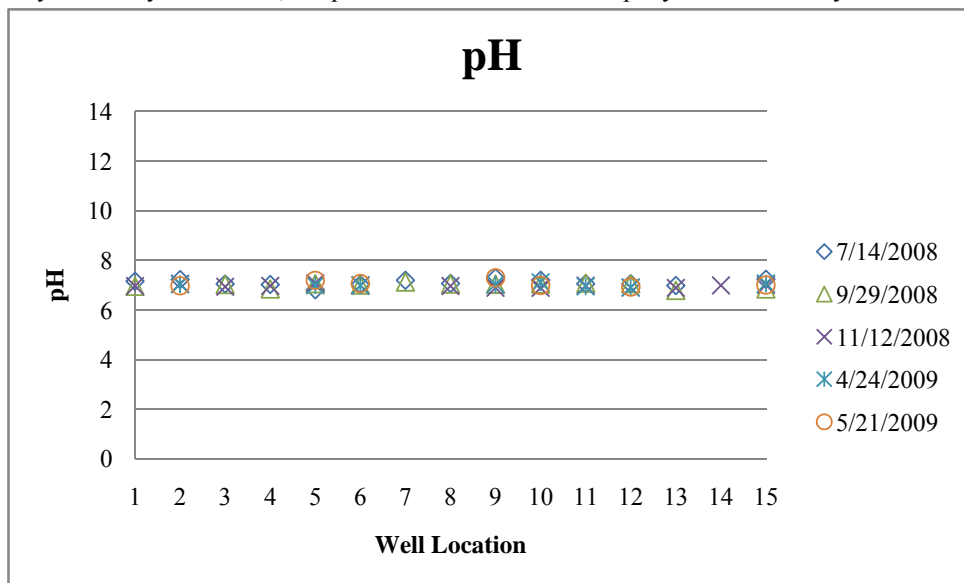


Figure 7.1.3.2 pH of well samples

3.1.3.3 UV₂₅₄

Figure 7.1.3.3 displays that UV₂₅₄ values are from 0 to 0.15 for the whole year sample period. But as circled showing, Well #5, Well #6 and Well #12 had comparable higher value for each sample round.

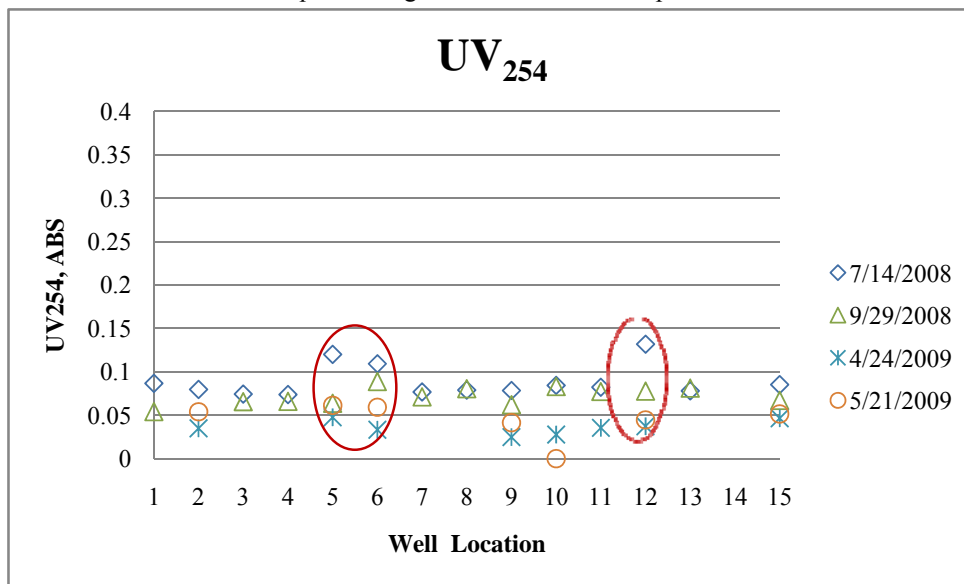


Figure 7.1.3.3 UV₂₅₄ of well samples in 0day

3.1.3.4 TOC

Figure 7.1.3.4 displays the TOC data for grabbed samples. The data of May 21st is the most trustful results. The average of TOC concentration in those samples is 2.1mg/L.

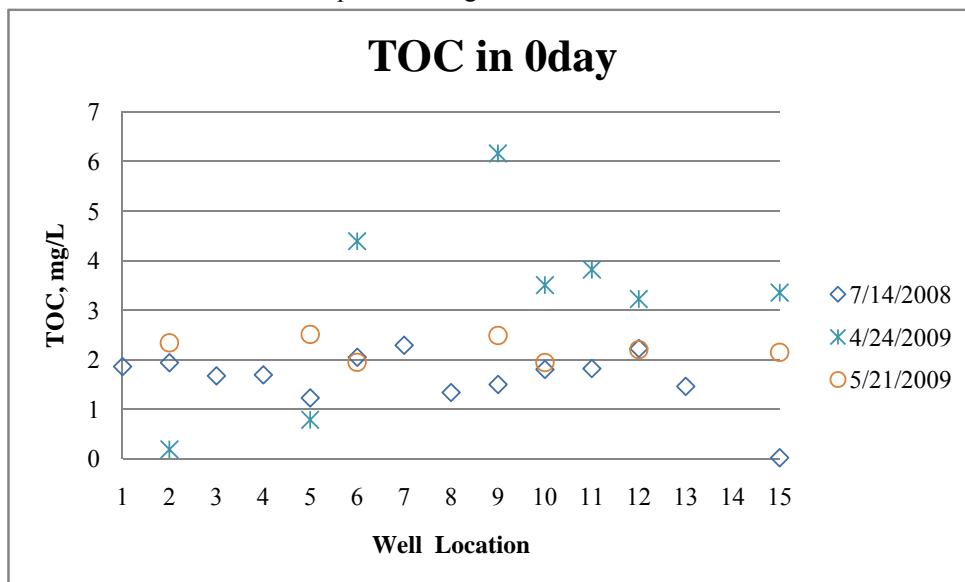


Figure 7.1.3.4 TOC of well samples in 0day

3.1.3.5 ORP

Figure 7.1.3.5 is the ORP data for grabbed well samples in the sampling period. The values of ORP are in the range from -120mV to 38mV.

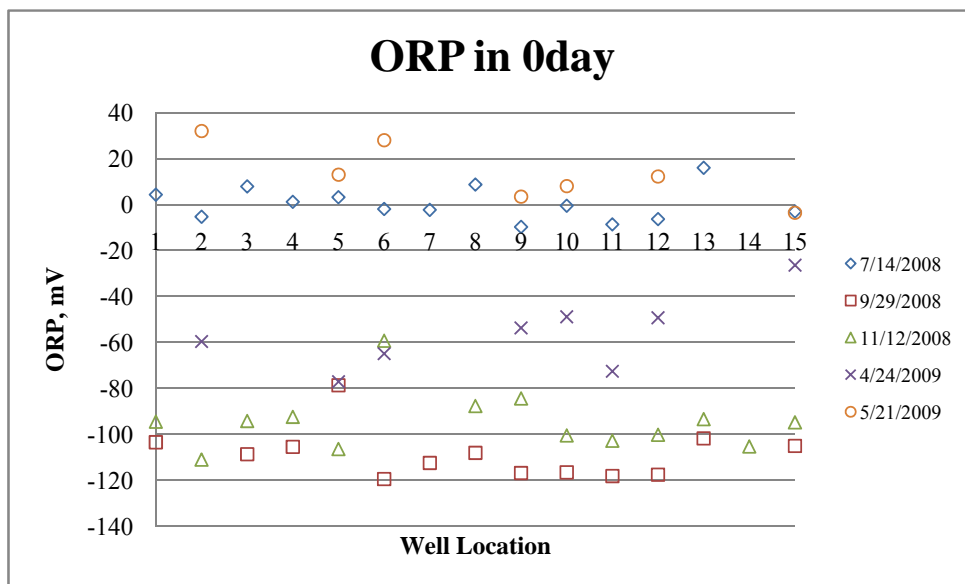


Figure 7.1.3.5 ORP of well samples in 0day

3.2 In-plant Sample Results

Three-day and seven-day formation potential test also were carried out during this period for the formation investigation. TTHMs, HAA5 and other additional analyses results are displaying by graphs as well.

3.2.1 TTHMs

Figure 7.2.1a, figure 7.2.1b and 7.2.1c are the graphs for the TTHMs concentration in 0day, 3days and 7days, respectively. In the 0day as seen in figure 7.2.1a, the concentration of TTHM rose up once the water went through the secondary clarifier where chlorine had been added. It generally had higher TTHMs concentration during the warmer season in a year, as showing on July and August. But at sites such as Filter #2 and Filter #5 exceeded the limitation level of 80µg/L. In the figure 7.2.1b, it displays the TTHMs concentration in 3days' incubation except the data on Oct. 22nd which just had been incubated for two days. As displaying in this figure, most of sites in plant can reach or exceed the TTHMs limitation after three days' incubation. But it generally exceeded limitation of the 80µg/L in the sample for seven days as seen in the figure 7.2.1c.

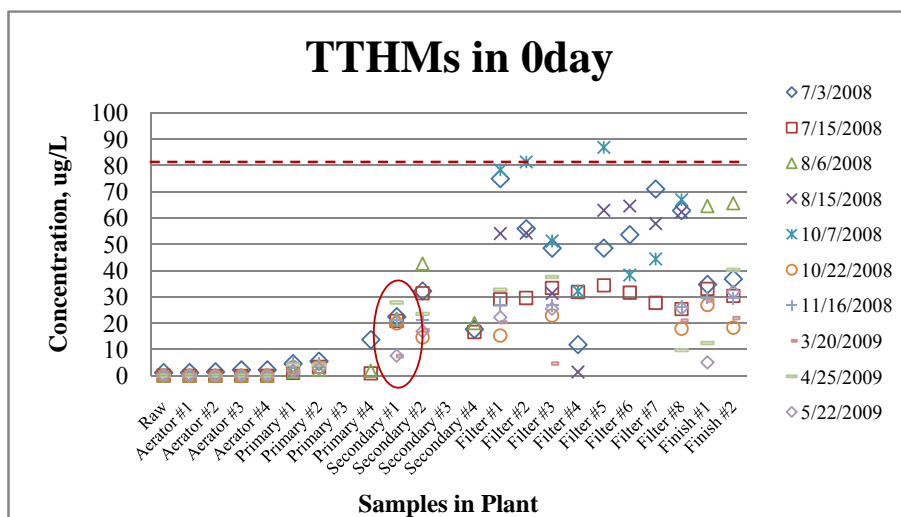


Figure 7.2.1a – TTHMs in 0day for in-plant sample

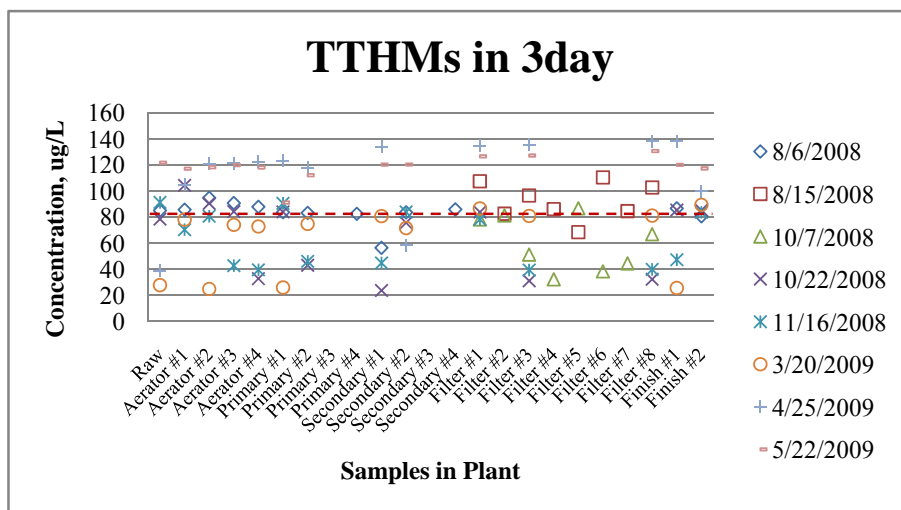


Figure 7.2.1b – TTHM formation potential for 3day incubation for in-plant samples

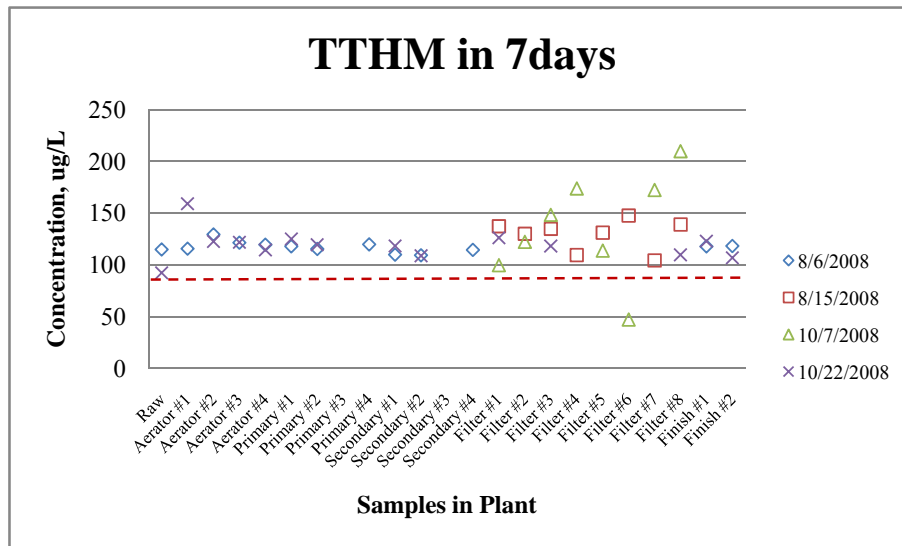


Figure 7.2.1c – TTHM formation potential for 7day incubation for in-plant samples

3.2.2 HAA₅

Figure 7.2.2a, figure 7.2.2b and figure 7.2.2c are the HAA₅ concentration of plant samples in 0days, 3days and 7days. It presents the HAAs level in treatment plant is not a problem. It is as lower as about 20µg/L even in the highest point. However, when incubate them for three days and seven days, the concentration in plant samples till can break through the limitation and stand in the higher level of the concentration as showing in figure 7.2.2b and 7.2.2c. The red dash lines indicate the MCL of 60µg/L.

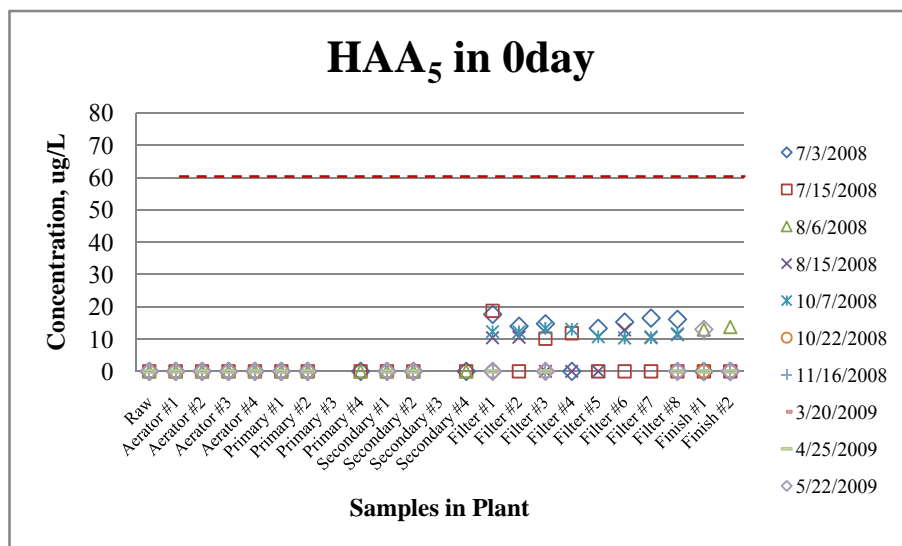


Figure 7.2.2a – HAA₅ in 0day for samples in plant

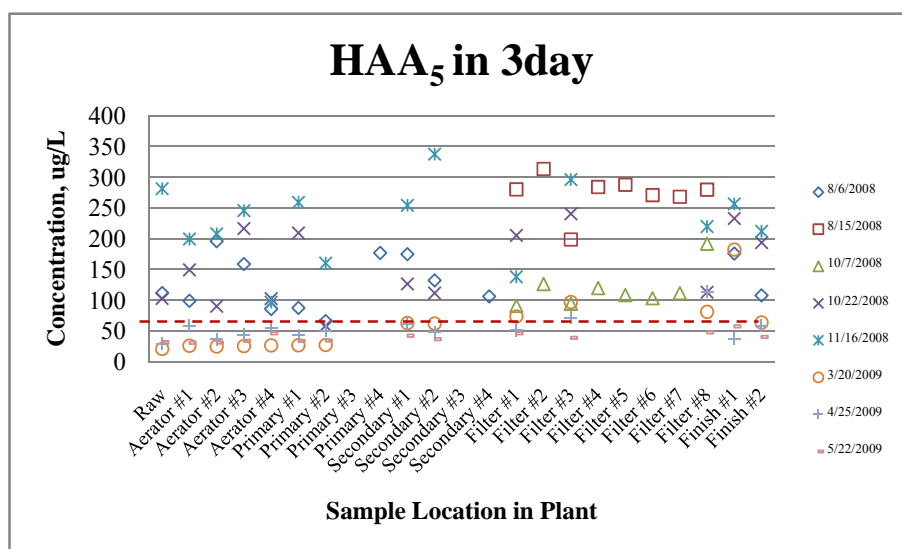


Figure 7.2.2b - HAA₅ formation potential for 3day incubation for samples in plant

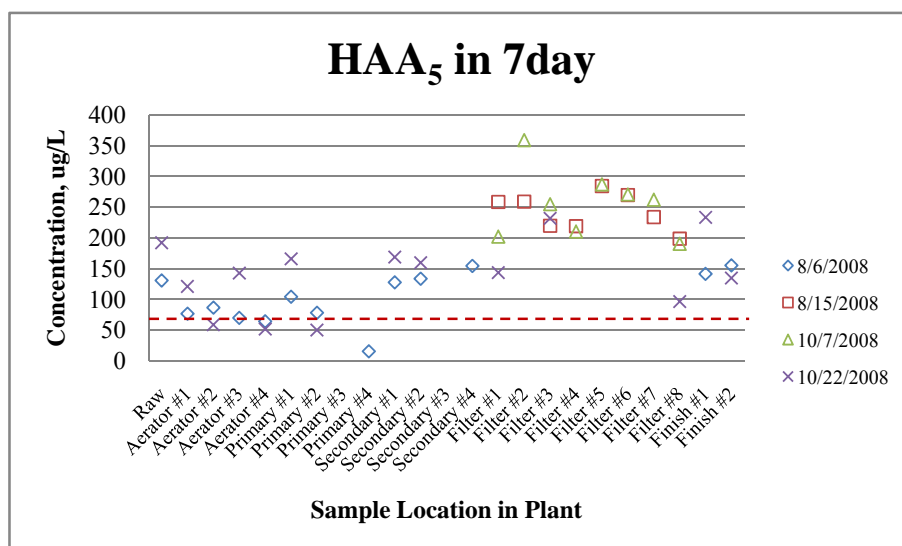
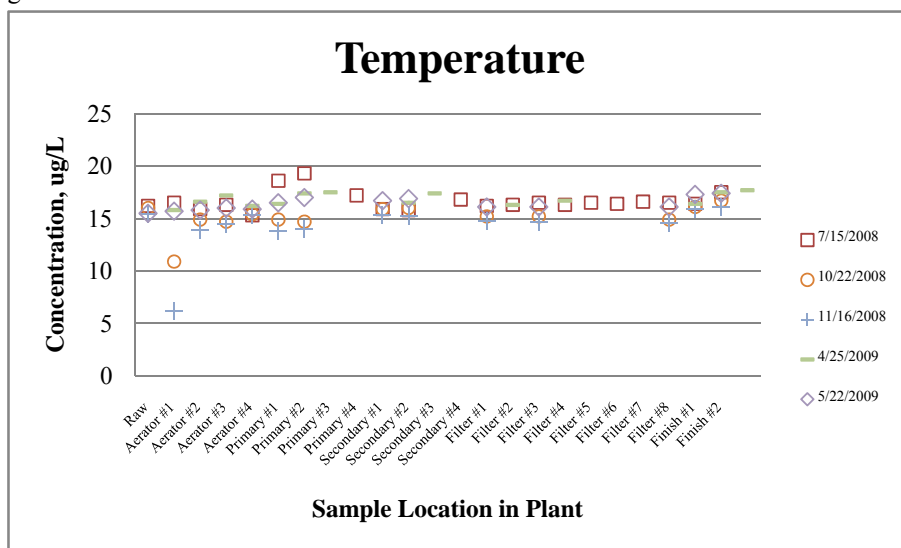


Figure 7.2.2c - HAA₅ formation potential for 3day incubation for samples in plant

3.2.3 Results from additional analyses

3.2.3.1 Temperature

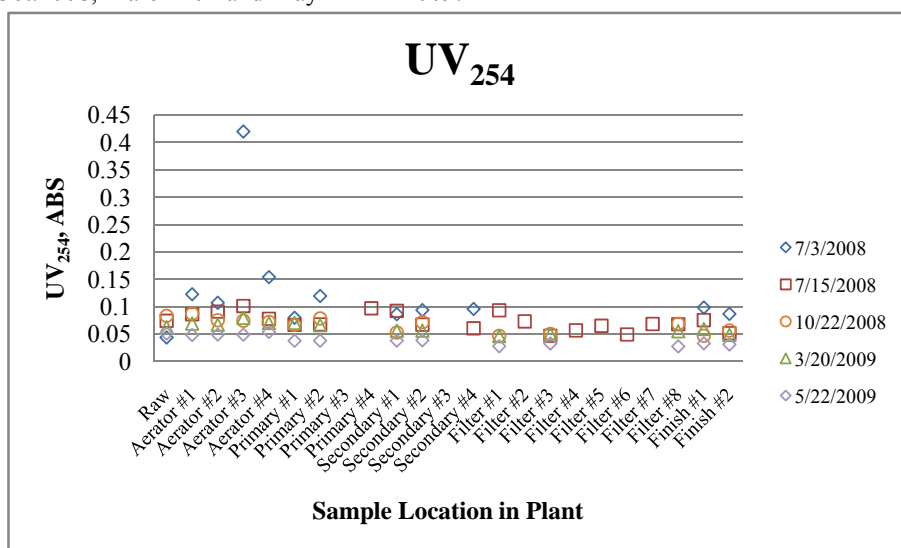
Figure 7.2.3.1 is the graph for the temperature of the plant samples during the last whole year. We collected those data when we were grabbing samples. As giving in this figure, the temperature for the whole treatment process generally didn't fluctuate too much for the sampling period except some site such as Aerator #1, Primary #1 and #2. It generally stays in the range from ~15 to 20 °C.



7.2.3.1 - Temperature of samples in plant

3.2.3.2 UV₂₅₄

Figure 7.2.3.2 is the figure for the UV data during the sampling period. They are generally in the range of ~ 0.15. However, it has been observed that 3rd of July, 2008 displayed the highest absorbance; the followings are 15th of July, 2008, 22nd of Oct.2008, March 20th and May 22nd in 2009.



7.2.3.2 – UV254 of samples in plant

3.2.3.3 TOC

Figure 7.2.3.3 is the TOC data for the sampling period. It indicates the TOC concentrations for each sample site. But when looking into the trustful data on 22nd of May, 2009, it shows that there is no extremely decrease when water went through the treatment processes.

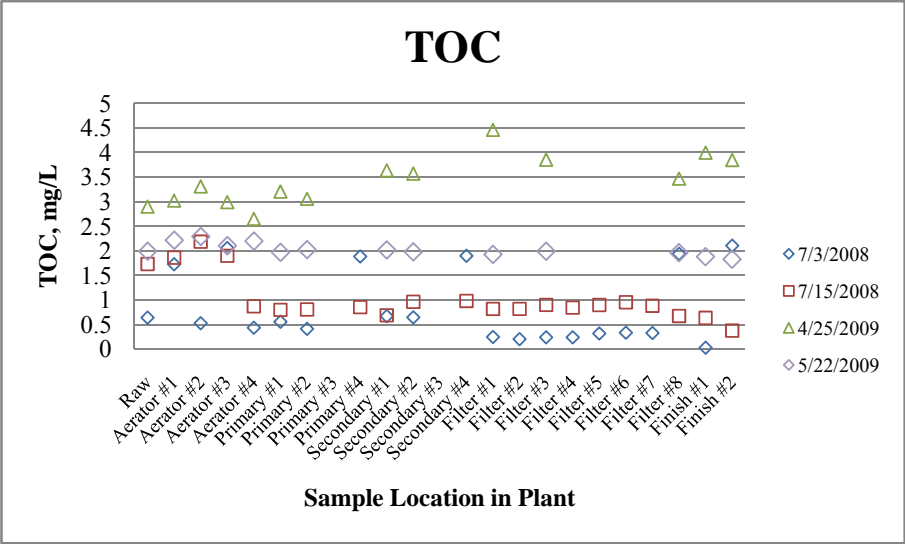


Figure 7.2.3.3 – TOC of samples in plant

3.3 Distribution system

In order to monitor the DBPs' level in the distribution system, we collected samples from distribution system once a month since Oct. of 2008 until now except the vacations.

3.3.1 TTHMs

Figure 7.3.1 is the TTHMs concentration graph for distribution system. They generally increase as the chlorine residual decreasing in the distribution system. It exceeded 80µg/L at some sites in distribution system as the red circle showing. It consists with results from the formation potential tests in 3days.

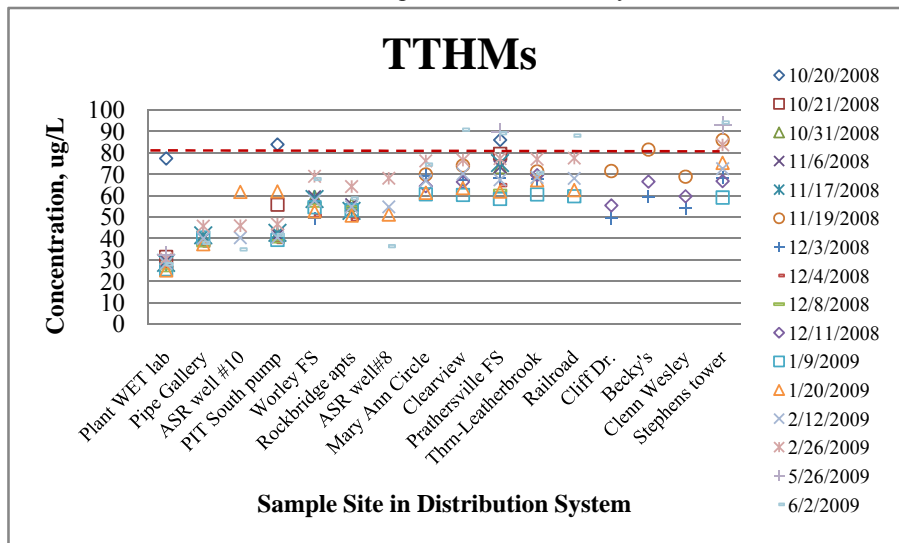


Figure 7.3.1TTHMs in the samples from distribution system

3.3.2 HAA₅

Figure 7.3.2 shows the concentration level of HAA₅ in distribution system. It is good to see the HAA₅ staying in such a lower level. It is far away from the requirement of the MCL limitation.

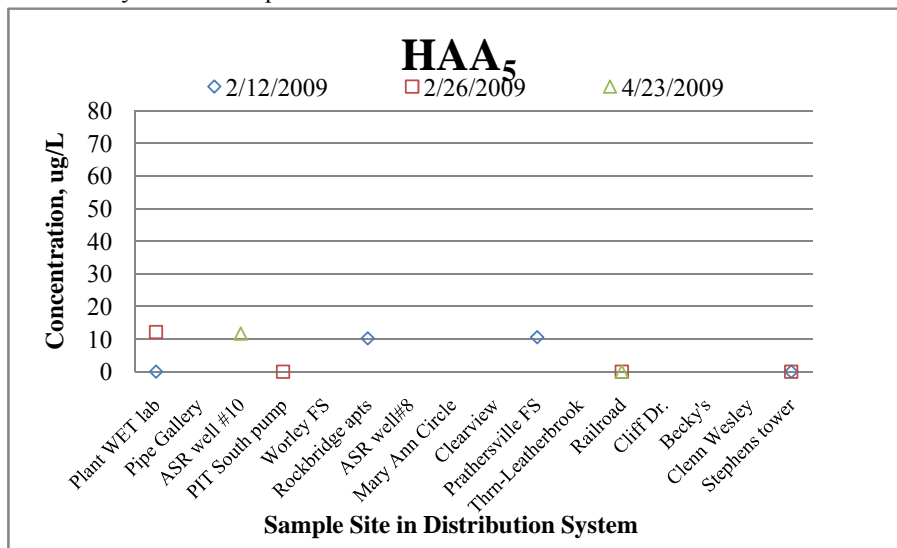


Figure 7.3.2 HAA5 in the samples from distribution system

3.3.3 Results from additional analyses

3.3.3.1 Temperature

The temperature data showing in the figure 7.3.3.1 displays the fluctuated changes during the sampling year. The temperature in distribution system is kind affected by the seasonal changing. The highest temperature appeared in the summer and the lowest appeared in the winter.

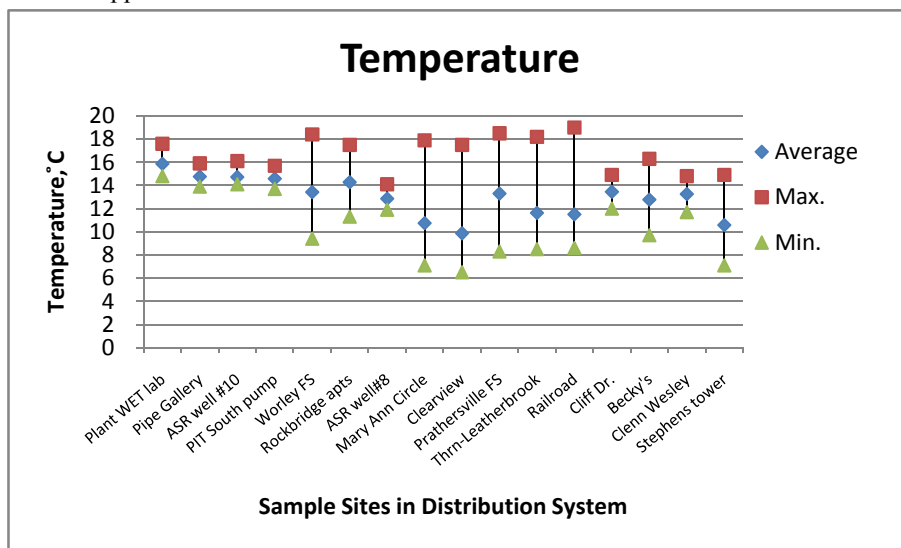


Figure 7.3.3.1 Temperature in the samples from distribution system

3.3.3.2 Free chlorine residual

Figure 7.3.3.2 is the graph for free chlorine existed in distribution system. It shows a decrease trend as the sample sites. At some sites, the chlorine seems had been consumed all.

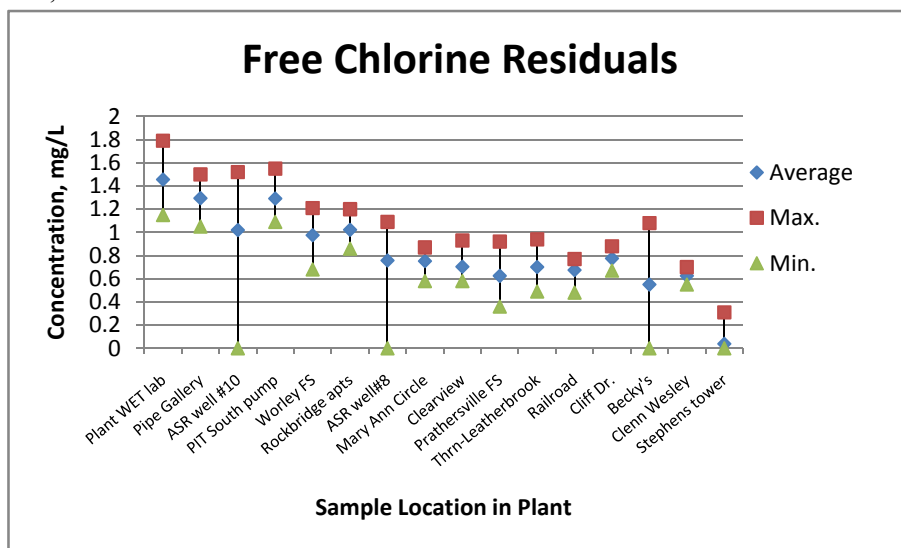


Figure 7.3.2 - Free chlorine residual in samples from distribution system

4. Data from DNR

Figure 8.1 is TTHMs data collected by DNR from Columbia drinking water system. It consists with our results for the drinking system. This graph indicates the affect on TTHMs formation by seasonal change. It displays that the TTHMs concentration is easily to exceed the limitation during the summer time.

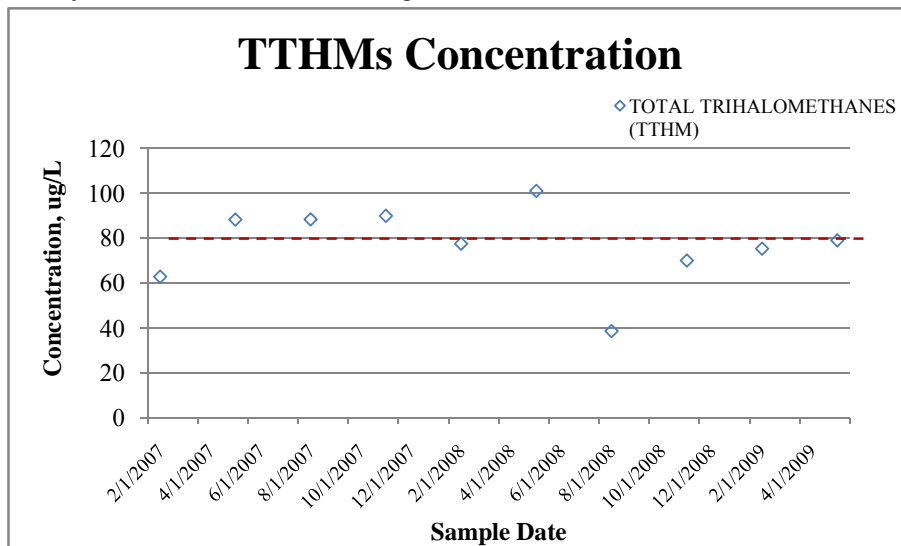


Figure 8.1 – TTHMs in distribution system collected by DNR

Figure 8.2 is still the data collect by DNR but for HAA₅ concentration of the Columbia drinking water system. Still consisted with the results from our laboratory analyses, the HAA₅ remains in the lower level, less than 30µg/l which is far away from the limitation.

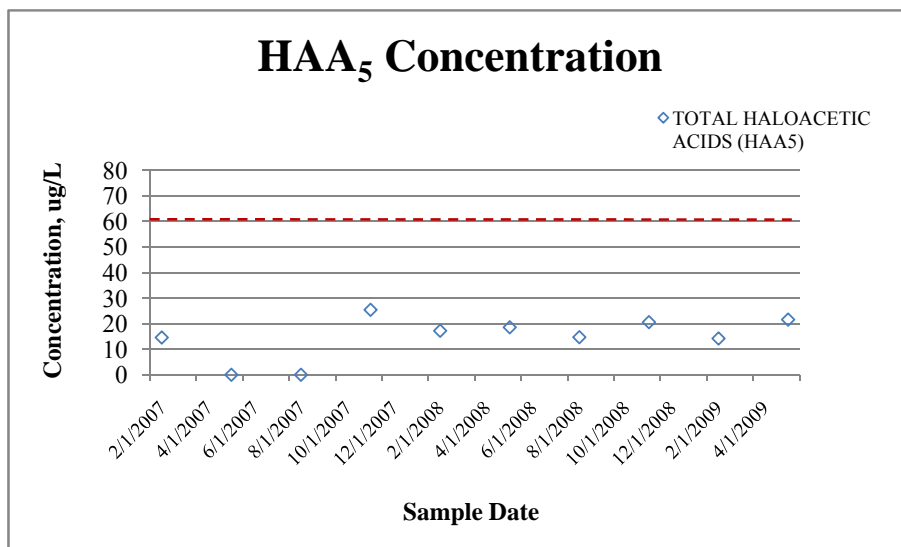


Figure 8.2 – HAA₅ in distribution system collected by DNR

5. Treatment Options for Control of DBPs

There are some approaches for controlling of DBPs: enhanced softening, MIEX (magnetic ion exchange), potassium permanganate, and chloramines.

Enhanced softening can obtain improved removal of DBP precursors by precipitative softening. But increasing the chemical doses directly increases sludge production, the chemical storage and feed facilities in an existing water treatment plant may not be adequate, and the overall cost of chemicals for precipitation and for final pH adjustment will increase. MIEX process is also used for removal of disinfection by-product (DBP) precursors such as dissolved organic carbon and bromide. Anion exchange was shown to be a useful process for removing natural organic material (NOM) from raw drinking water. Potassium permanganate (KMnO₄) as a less powerful disinfectant is used primarily to control taste and odors, remove color, control biological growth in treatment plants, and remove iron and manganese. But in a secondary role, potassium permanganate also can be used in controlling the formation of THMs and other DBPs by oxidizing precursors and reducing the demand for other disinfectants. The mechanism of reduced DBPs is to oxidize organic precursors at the head of the treatment plant minimizing the formation of byproducts at the downstream disinfection stage of the plant. Chloramines can be used as a disinfectant as effective as chlorine for the deactivation of bacteria and other microorganisms, however the reaction mechanism is slower and it react with organic matter less often than chlorine which lead to little trihalomethanes (THM) and other disinfection byproducts are formed during chlormaine disinfection. Hence it helps control the TTHMs level in drinking water system. Monochloramine is the most effective disinfectant. In order to predicting the DBPs' formation level in Columbia drinking water system when switching chloramines as a residual. We had carried out the chloramines test. All of these experiments are through sampling. The results are displaying below.

5.1 Chloramines Test

Samples are collected from finish water in the lab of water treatment plant. Then the test uses the bench-scale techniques to compare an estimate of concentration of TTHMs in the chloramines and non-chloramines samples that has been incubated under the stimulated condition and time as in city's distribution system. Hence two parallel incubation systems are set up, one is added chloramines, and another is non-chloramination. For non-chloramination system, samples collected from finish water are incubated directly at 15 or 21±1 °C in the dark for 5hours, 24hours and 72hours before analysis. For chloramination system, based on the chlorine residual level exited in the finish water, ammonia are added at a certain weight ratio of chlorine to ammonia at 4:1 to 3:1. Then incubate them as the same way as the chlorination.

5.1.1 TTHM results

Figure 9.1.1a and figure 9.1.1b are the TTHMs concentration as incubation time increasing for both under chloramination and chlorination (non-chloramintation).

For both these two graphs, they indicate the TTHMs concentration double increased when we changed the incubation temperature from 15 °C to 21 °C no matter under chloramination or chlorination situation. However, when comparing chloramination and chlorination results for the formation of TTHMs from these two figures, we can notice that the average TTHMs concentration under chloramination at 15 °C is half less than the average TTHMs under chlorination at 15 °C. It suggests that the TTHMs concentration could be controlled by switching chloramines as a residual according to the laboratory experiment.

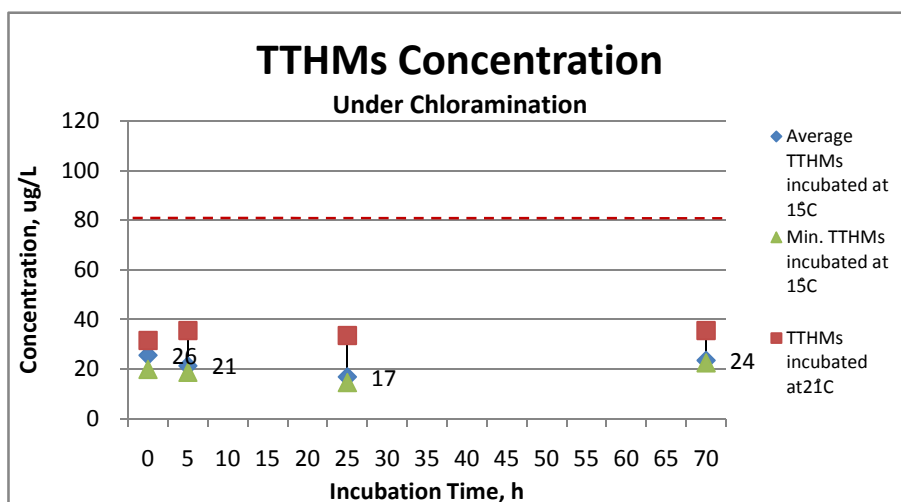


Figure 9.1.1a – TTHMs concentration of the finished water after chloramination

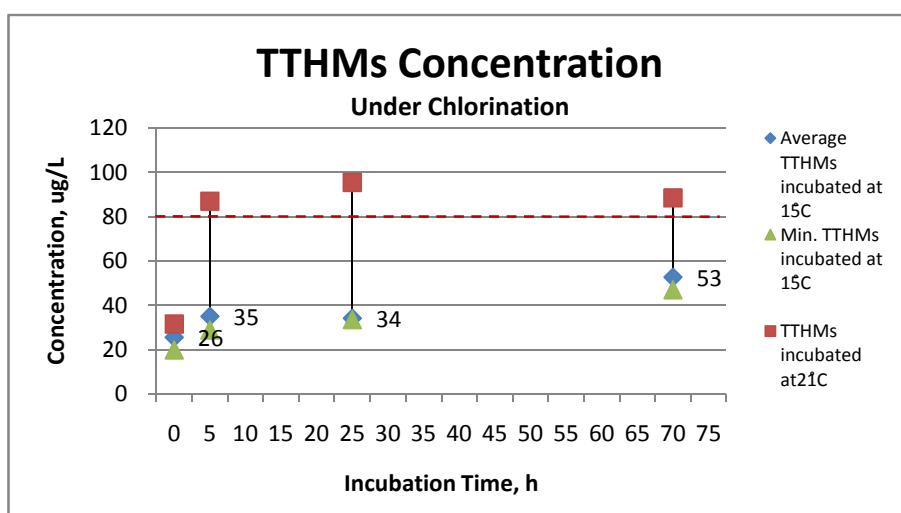
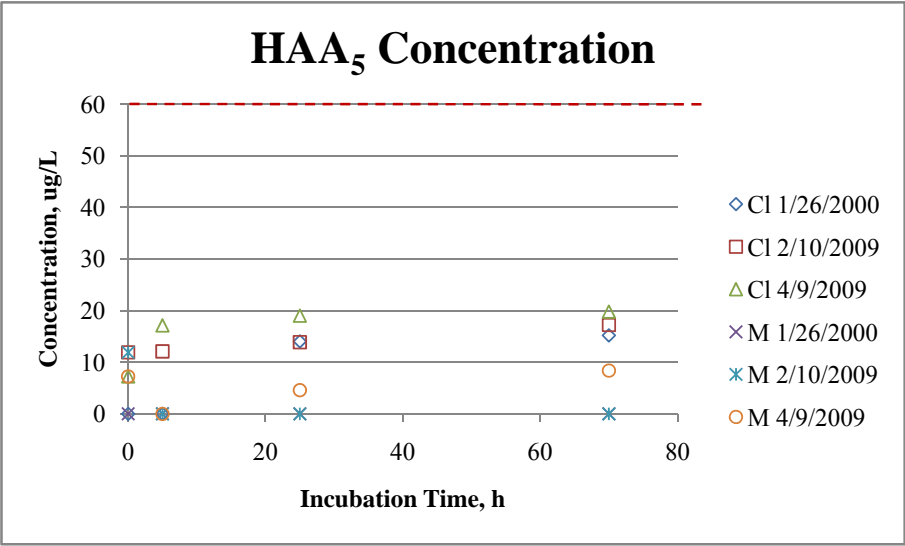


Figure 9.1.1b – TTHMs concentration of the finished water after chlorination

5.1.2 HAA₅ results

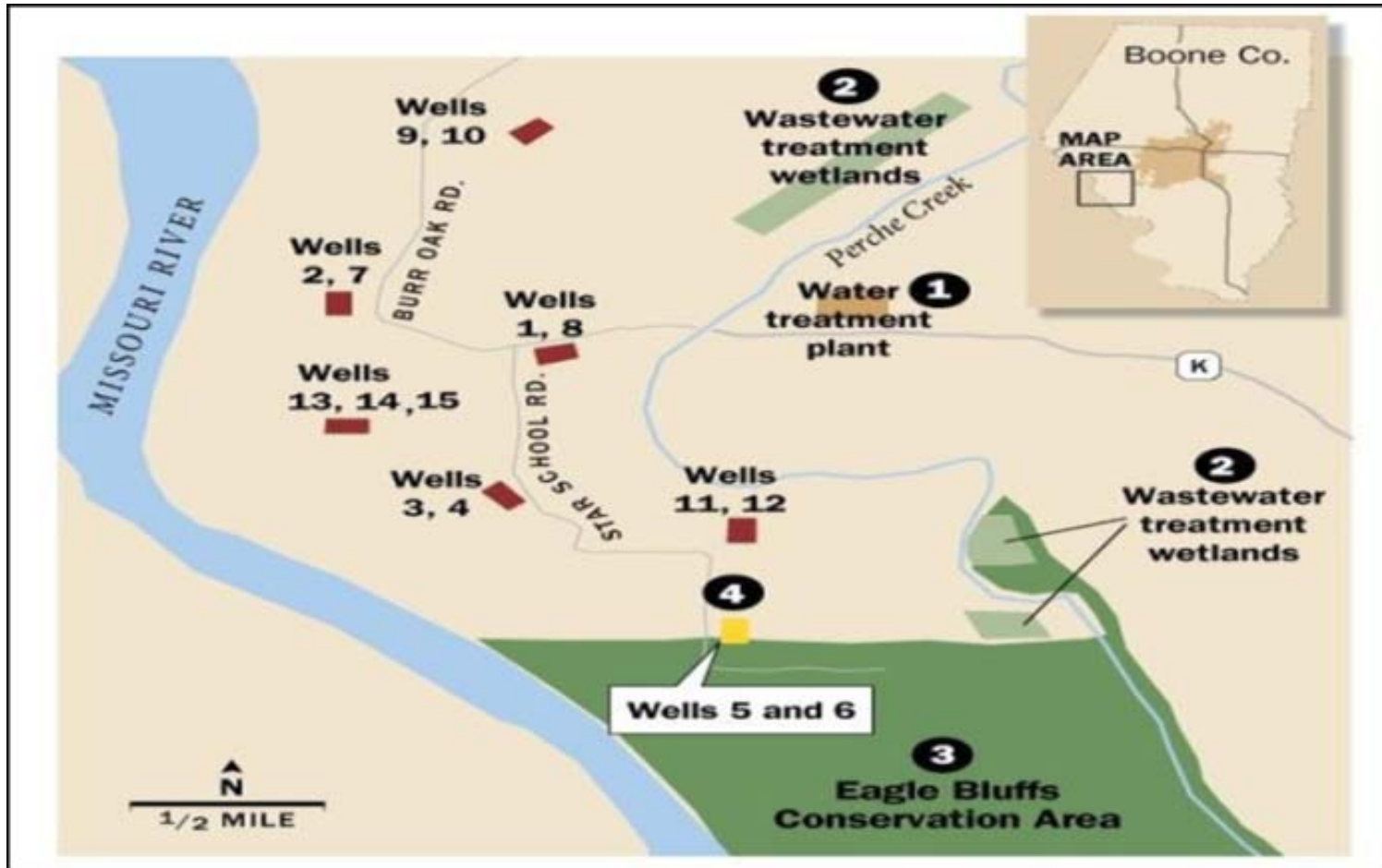
Figure 9.1.2 is the results of HAA₅ for both under chloramination and chlorination. It displays a lower concentration of HAA₅ no matter under chloramination or chlorination. However, the chloramination still seemed be able to control the formation of HAA₅ in comparison with chlorination situation.



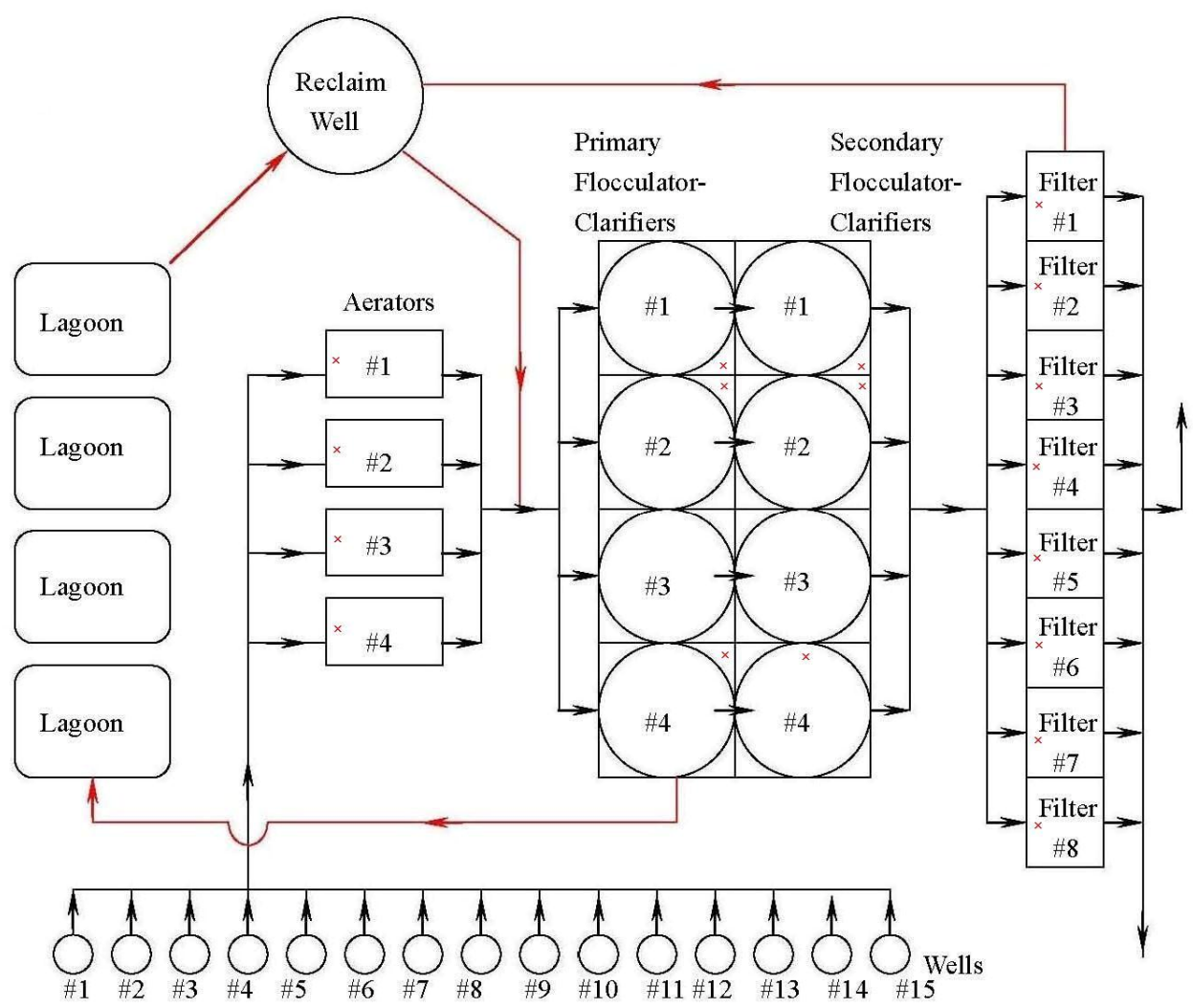
APPENDIX I: DATA FOR WELL SAMPLES, PLANT SAMPLES, AND DISTRIBUTION SYSTEM

(in attached Excel [file](#) titled Columbia_Combined_Data_0708_to_0609.x

APPENDIX II: WELL LOCATIONS ON THE MAP OF MCBAIN, MO



APPENDIX III: ILLUSTRATION OF SAMPLING LOCATIONS WITHIN THE WATER TREATMENT PROCESS



APPENDIX IV: DISTRIBUTION SYSTEM SAMPLE LOCATIONS ON THE MAP OF COLUMBIA

