Report for 2002ND11B: A Comparative Analysis of Fargo and Moorhead Ozonation Systems

There are no reported publications resulting from this project.

Report Follows:

A Comparative Analysis of Fargo and Moorhead Ozonation Systems

ND WRRI Graduate Research Fellowship Project
Rahul Bajpai, Fellow
Wei Lin, Advisor and Principal Investigator
Civil Engineering and Construction Department
North Dakota State University
Fargo, ND 58105

Abstract
Ozone has been increasingly used as a disinfectant in water treatment processes in the United Sates. Ozone is a strong oxidant that also can be used for taste and odor control and organic matter removal. The use of ozone for disinfection is thought to reduce the potential formation of trihalomethanes (THMs) and other harmful disinfection by products (DBPs) associated with chlorine disinfection. Also, ozone is able to achieve disinfection with less contact time and concentration than other disinfectants. However, ozone demand and reactions are highly dependent upon pH, temperature, organic concentration and other factors. Therefore, it is more difficult to control ozonation systems. Incomplete oxidation of organics under certain conditions may also produce toxic by-products. Two water treatment plants using the same source of water are investigated in this study to compare and contrast the performance their ozonation systems.The impact of operation conditions on ozone demand, odor removal efficiency, and ozonation by-product formations are investigated in the study.The information gained will be valuable for other possible ozonation applications in the aquatic environment. The type of organics and the oxidation by-products produced during the ozonation process will be identified.

STATEMENT OF THE WATER PROBLEM
Ozone has been increasingly used as a disinfectant in water treatment processes in the United Sates. Ozone is a strong oxidant that also can be used for taste and odor control and organic matter removal. The use of ozone for disinfection is thought to reduce the potential formation of trihalomethanes (THMs) and other harmful disinfection by products (DBPs) associated with chlorine disinfection. Also, ozone is able to achieve disinfection with less contact time and concentration than other disinfectants. However, ozone demand and reactions are highly dependent upon pH, temperature, organic concentration and other factors. Therefore, it is more difficult to control ozonation systems. Incomplete oxidation of organics under certain conditions may also produce toxic by-products.

Both the Fargo Water Treatment Plant, (FWTP) North Dakota and Moorhead Water Treatment Plant (MWTP), Minnesota use Red River water as their primary water source. The MWTP employs ozone for taste and odor control at a higher pH of 11 and as well as for disinfection at a lowered pH of 9.5. The FWTP uses ozone only for the purpose for disinfection at a lowered pH of 9.5. Both the plants are able to achieve its goals of disinfection and to produce high quality water with minimal THMs. One of the challenges that both FWTP and MWTP face is the high ozone demand in summer. As a

result, the plants have to use its full ozone generation capacity to maintain proper ozone concentration in the ozonation chambers. This leads to the formation of ozonation by-products (OBPs) due to incomplete oxidation under different ozonation systems. These by-products have been reported to be mainly aldehydes and carboxylic acids. Although no potential health effects have been observed for the concentrations of aldehydes and carboxylic acids formed in the drinking water during ozonation, these compounds are easily biodegradable. This increase in biodegradable dissolved organic carbon (BDOC) can lead to accelerated bacterial growth and re-growth in the distribution system if it is not removed in the treatment plant. The presence of BDOC that causes these adverse effects is commonly termed as biological instability.

OBJECTIVES
This proposal is to investigate the impact of operation conditions on ozone demand, odor removal efficiency, and ozonation by-product formations. The objectives include:

- To study the factors affecting the increased ozone demand in the Fargo & Moorhead WTPs during summer season leading to increased treatment costs.
- To understand and study the different operational procedures involved in the Fargo & Moorhead WTP to optimize the results so as to suggest the better of the ozonation systems employed at the FWTP & MWTP respectively.
- Identifying OBPs formed under various operational conditions.
- Investigating operational alternatives to improve ozonation efficiency and to reduce summer ozone demand.

During the course of this project, ozonation systems performance under different conditions and the parameters affecting them will be analyzed which will lead to an improved facility operation technique derived as a corollary of the experimental studies conducted and the conclusions reached, henceforth. Also, a detailed cost analysis approach will be obtained to help justify the recommendations in the ozonation systems operations. The water chemistry involved with the ozonation process will also be studied. The information gained will be valuable for other possible ozonation applications in the aquatic environment. The type of organics and the oxidation by-products produced during the ozonation process will be identified.

METHODOLOGY
This project will include analysis of existing data and information of existing data and information, experimental studies, plant sampling, and engineering alternative evaluation and design. The project will be broken down into three tasks.

Task 1. Literature Review.
The purpose of this task is to evaluate the design and operation of the existing ozonation Systems at the Fargo Water Treatment Plant (FWTP), North Dakota and Moorhead Water treatment Plant (MWTP), Minnesota. Literature review includes Fargo and Moorhead WTPs design documents, operational data, previous study reports and environmental engineering journal articles. The literature review will focus on (1) design and operation of ozonation systems (2) mechanisms of ozone disinfection (3) sampling

and sample analysis method (4) Factors affecting the ozone consumption rate variations with season (5) operational and control of ozonation systems in other water treatment plants. The theoretical and operational information obtained from literature is important for developing sampling methods, data analysis, and experimental study plans.

Task 2. Performance measurements and assessments of the ozonation systems in Fargo WTP.
The FWTP, & MWTP, use Red River water as primary water source and ozone as primary disinfectant. The raw water contains natural organic matter (NOM), which is characterized by aromaticity and biological stability. This NOM is not found to have any significant health impacts. However, ozonation of raw waters decreases the NOM by breaking the aromaticity and increased biodegradability. The ozone treatment process resembles a lightning storm. Lightning during a thunderstorm creates an electrical charge, which makes ozone that reacts with air. The operational success of the ozonation system is dependent upon the plant influent water quality as well as ozone dose, along with other factors like pH, temperature, alkalinity, etc. The ozone dose generally increases in the summer months, as the temperature of water is high, leading to higher reaction rates. This increases the ozone consumption rate, as the NOM is not completely degraded at small ozone dose. This causes increased ozone demands in summer, thus increasing the water treatment costs. Also in addition to this it leads to the formation of OBPs which a serious concern today with respect to their health impacts. In order to study the performance of the ozonation systems and the parameters affecting it, the samples will be collected in the ozonation chambers of the FWTP & MWTP locations specified below: -

- Samples of the influent water in the FWTP, ozone contact chamber and the distribution systems will be taken.
- Various Parameters like temperature, pH, alkalinity; etc. will be studied to analyze their affect on the ozonation system operation.

Task 3. Comparative Analysis of the two ozonation systems.
The data collected from the study conducted on the FWTP will be analyzed and compared with the data available through previous studies conducted on the MWTP. After the analysis it will be ascertained that which of the two WTPs possesses better ozonation systems in terms of minimal OBPs formation in the finished water. The final study report will be presented to both the FWTP & the MWTP.

EXPECTED RESULTS AND BENEFITS
During the course of this project, ozonation systems performance under different conditions and the parameters affecting them will be analyzed which will lead to an improved facility operation technique derived as a corollary of the experimental studies conducted and the conclusions reached, henceforth. Also, a detailed cost analysis approach will be obtained to help justify the recommendations in the ozonation systems operations. The water chemistry involved with the ozonation process will also be studied. The information gained will be valuable for other possible ozonation applications in the

aquatic environment. The type of organics and the oxidation by-products produced during the ozonation process will be identified.

FACILITIES

This project will be completed with the additional support from both Fargo & Moorhead Water Treatment Plants and The North Dakota State University.

The Water Treatment Plants (WTPs) will provide the necessary supplies including sampling equipment, etc. North Dakota State University will provide the necessary equipment and supplies for the sample testing. The North Dakota State University will also provide lab space, sample containers, chemicals, a pH meter and GC/MS instrument.

PROPOSED RESEARCH TIMELINE

A duration of 8 months is proposed starting May 2002. During this period, an interim report will be submitted. The report will summarize the analysis of performance studies of the ozonation systems employed in the cities of Fargo &Moorhead WTPs. A final report will be submitted by December 2002.

REFERENCES

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Moll, D. M. Summers, R. S. Fonseca, A. C. and Matheis W.,(1999) "impact of Temperature on Drinking Water Biofilter Performance and Microbial Community Structure", Environ. Sci. Technol., 33, 2377-2382.

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United States Environmental Protection Agency (EPA), (1999a) "Alternative Disinfectants and Oxidant Guidance Manual" , EPA 815-R-99-014, April 1999.

United States Environmental Protection Agency (EPA), (1999b) "Disinfection Profiling and Benchmarking Guidance Manual", EPA 815-R-99-013, August 1999.

PRELIMNARY APPROACH

A detailed analysis of the operational data for the FWTP ozonation system and other water characteristics, as well as sampling and sample analysis from the ozonation facility are provided. Sampling locations, parameters tested and the procedures and methods used for sample analysis are also provided.

Operational Data Analysis
The FWTP provided the operational data from 01/01/01 through 06/30/02. The operational data from 08/01/02 to 01/31/03 will be collected during the plant sampling being undertaken as part of the research. The operational data consist of plant inflow rates, temperature, pH, ozone dose, ozone flow rates, off-gas concentrations, total organic carbon (TOC), and alkalinity. The data provided by the FWTP is given as daily average. The data recorded during the sampling will not be presented as average.

The water flow rates, temperature, pH in the ozone contact basin, ozone residual, off-gas conc., ozone gas flows, were recorded by the online monitoring system.

Total organic carbon (TOC) will be used as a measure of organics present in the water. The TOC analysis at the FWTP is done thrice a week, on the raw water, presedimentation effluent, and secondary softening effluent; filter influent, transfer section, and tap water. The TOC values for the period of the operational data collection were averaged, but the samples collected during the slated sampling period will not be analyzed as averages.

The ozone gas-flows into the ozone contact chamber are measured by online flow meters and are used to find the ozone dose applied to the ozone contact chamber. The total ozone dose is calculated by the following equation:

Ozone Dose (ppm) = (gaseous ozone concentration * total gas flows) / (total water flow)

FWTP Sampling and Sample Analysis
The plant sampling and sample analysis will be conducted from 08/05/02 through 01/31/03. The sampling mainly concentrates on the detailed analysis of ozone contact chamber and the factors affecting the formation and amounts of the DBPs.

Analysis of ozone contact chambers
The major goal for the detailed analysis of the ozone contact chamber was to analyze the water quality changes across the ozone contact chambers. In order to study and compare the factors and the parameters affecting the overall DBP formation at the FWTP, to those with the parameters and the operational conditions, and the altogether different ozonation system at the MWTP; a detailed analysis for the ozonation chamber was conducted.

Parameters
The operational data recorded during the sampling phase of the project was in addition to the following parameters:

- UV 254 Absorbance
- Carbonyl compound analysis

There exists a strong correlation between the UV absorbance and the total organic content present in the water (Standard Methods 5910, 1998). As the oxidation of the carbon bonds takes place during the ozonation of the water in the contact chambers, the UV 254 absorbance decreases. This is because of the fact that number of carbon double bonds decrease after the ozonation and therefore resulting in the lower UV absorbance.

The ratio of the UV absorbance to the TOC gives a parameter called the specific UV absorbance (SUVA), and is used as a measure of the partial oxidation occurring in the ozone contact chambers.

The carbonyl compound analysis was done to analyze the DBPs formed in the ozone contact chamber. The majority of the ozone DBPs formed consists mainly of low molecular weight compounds like aldehydes, carboxylic acid, and ketones.

Sample Locations

The sample location details are shown in figure 1.

- **Influent to ozone contact chamber.** The samples are taken at this location in order to determine the amounts of organic content entering the ozone contact. This sample serves as the platform for the other sample locations and the sample analysis.
- **Stage 3.** The sample is picked up at this location as this being the first point of ozone application and thus, serves as the baseline for the disinfection by-products (DBPs) formation quantification and analysis. This is where the ozone first attacks the organic content present in the water and thus the results in formation of DBPs. Therefore the sample at this point is very important as it will provide a profile of the DBP formation and the magnitudes and amounts, in which they are carried through the rest of the system.
- **Stage 4.** Samples are taken at this location as the ozone application is continued and thus makes it important to be accounted for.
- **Filter Influent.** This sampling point is very important, as here the water is free of ozone, after falling over a three feet free fall over a concrete effluent weir, and resulting in the ozone stripping. This is the immediate step after the stage 6, where the water is allowed to stand for 30 minutes, so as to allow for the ozone to decompose completely and thus it will give an estimate of the organic content still left in the water going to the filters.

Sample Analysis

Total Organic Carbon

The TOC was measured at the FWTP using a Shimadzu model 5000 instrument; a total combustion TOC analyzer equipped with an ASI 5000 A autosampler. Three successive samples were recorded and averaged giving the TOC values. The TOC unit was calibrated daily using a potassium biphthalate solution.

Alkalinity
Alkalinity was determined at the FWTP using an Auto Titrator; Mettler 5000 was used for the measurement of total alkalinity.

UV 254 Absorbance
The UV 254 absorbance was analyzed at the FWTP using a Hach 4000 spectrophotometer with quartz cells 1 cm in thickness (Standard Methods 5910 B, 1998). The lab reagent water was used as a blank for analyzing the samples.

Carbonyl Compound Analysis
Carbonyl compounds were assessed using aqueous-phase derivatization with O-(2,3,4,5, 6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) and capillary gas chromatograph (GC) with mass spectrometry detection (EPA method 556, 1996 and Standard Methods, 6252 B, 1998).

Sample collection for carbonyl compound analysis
The samples will be collected in 40-mL vials with PTFE-faced silicon septa screw caps. Before adding the samples to the vials, 15 mg of copper sulfate pentahydrate is added to each of the sample vial. KI acts as biocide to inhibit bacteriological decay of the method analytes (EPA method 556, 1998). Adding 5 drops of 3-mg/L KI solution to the vials containing samples quenches residual ozone (Standard Methods 6252 B, 1998).

The vials were filled to overflowing as to not allow any air bubbles in the sample vial. The vials were manually shaken for 1 minute and were kept refrigerated at 4 C till the analysis.

Procedure for carbonyl compound analysis
After collecting the samples at the FWTP, the samples were taken to the NDSU environmental engineering laboratory and allowed to equilibrate at room temperature. Twenty milliliters of the sample volume was pippeted out and discarded. The pH was adjusted to 4 by adding 200 mg KHP to each bottle containing 20 ml of sample. The surrogate standard (2,4,5 – Trifluoroacetophenone) was added in amount equal to 20 µL along with 1mL of PFBHA reagent at a concentration of 15 mg/mL. The samples were then kept into water bath at 35 C for 2 hours. After the incubation, the sample bottles were taken out and allowed to cool to room temperature for about 10 minutes. Four drops of concentrated sulfuric acid was added to each sample vial to quench the derivatization. Four milliliters of hexane containing the internal standard (1,2-dibromopropane) at a concentration of 400ug/L was added and then the samples were manually shaken for 3 minutes. The samples were then let stand for 5 minutes to allow for phase separation. The hexane layer was withdrawn from the sample bottles using a Pasteur pipette and placed into an 8-ml vial containing 3 ml of 0.02 N sulfuric acid. This is done to remove excess derivative. The samples were then shaken for 30 seconds and then allowed to stand for 5 minutes for phase separation. The hexane layer was drawn off and placed in 2 separate 2-mL vials. One µL was injected for the GC/MS analysis from one of the vials and the other was kept at 4C in the dark to serve as a backup extract.

Calibration for carbonyl compound analysis
A calibration standard was purchased from Accustandard at a concentration of 1000 ug/L in acetonitrile. The analytes included in the standard were formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, cyclohexanone, heptanal, octanal, benzaldehyde, nononal, decanal, glyoxal and methyl glyoxal.

Instrumentation for carbonyl compound analysis
The apparatus used for this analysis is a HP 6890 plus GC and a HP 5973 mass selective (MS) detector. The GC was equipped with a HP-5 MS column 30m long, with an inner diameter of 0.25 mm and a film thickness of 0.25 um. High-purity helium was used as carrier gas.

The data system used was a HP Kayak computer with chemstation software. This was use to control, execute and analyze all information required for the analysis.

The instrument settings are given as follows:

Injection parameters
- Inlet temperature: 250°C

Gas Chromatograph Settings
- Gas flow rate: constant 1.5 mL/minute
- Temperature program: 50°C for 1 minute, then rise at 4°C /minute to 220°C, then rise at 20°C /minute to 250°C , and then hold for 10 minutes.

Mass Spectrometer Settings
- Temperature: 280°C

Quality Control

Carbonyl compound analysis
The internal standard and the surrogate responses for any chromatographic run should line within ±30% from the average response of the calibration curve to pass the quality control. If a run did not comply with these limits, the sample was reanalyzed. If the run still doesn't comply, new standards were prepared and checked.

As suggested in the Method 556 (EPA 1999), a midpoint calibration standard was injected, before the run and the instrument was checked for the calibration. If the calibration was not met, the instrument was re-calibrated.

FWTP OPERATIONAL DATA ANALYSIS

Fargo Water Treatment Plant data are analyzed in this chapter. The FWTP staff provided the data for the period 01/01/01 through 06/30/02. Operational data from 08/05/02 through 01/31/03 will be collected during the project progress as part of the research task.

The operational data are analyzed in order to understand the normal plant operations and to seek information and understanding about determining additional sampling necessities and parameters for a complete understanding of the ozonation process.

Ozone Contact Chamber Influent Characteristics
The characteristics of the ozone contact chamber influent were analyzed to identify the parameters influencing the ozone demand and henceforth the DBPs formation in the contact chambers. The water quality parameters monitored at the FWTP include plant inflow rates, pH, temperature, alkalinity, and TOC.

Daily plant intake from periods of 01/01/01 to 06/30/02 is shown in figure 4-1 and 4-1(a). The total flow rate coming in to the FWTP remained less than 20 MGD at all the times and was always more than 7 MGD. A peak flow of 19.24 MGD was observed in the summer of 2001. The Red River water is used as the primary source of water.

The variation of the incoming water temperature from the periods 01/01/01 through 06/30/02 is shown in figure 4-2 and 4-2(a). The temperature increased to 84 F in summer at certain times and was never below 37 F. The water temperatures stabilized in winter months (December to February), ranging from 37 to 39F.

Total Organic Carbon (TOC) variations in the ozone contact chamber influent are shown in figure 4-3. The TOC generally ranged from 4 to 6 ppm in the influent and ranged from 3.5 to 5.5 ppm in the effluent. The TOC removal trend showed large variations with the change in the season and is shown in figure 4-4. The removal was lower in winter months as compared to summer months.

Operations performed by the ozone system
Variation of ozone dose with time followed the expected trend, as gained by the understanding from the previous research (Hurley, Stuart 2000). The ozone dose is more in summer months than when compared with the winter months, which is mainly due to increased ozone demand as the water temperature is high and thus it requires more ozone to achieve same disinfection goals. The ozone dose variation is shown in figure 4-5 and 4-5(a).

The ozone dose showed variations with the temperature of the incoming water supplies. The ozone dose increased significantly in summer, with the temperatures increasing sharply and then dropped down in the winter months. The trend is shown in figure 4-6.
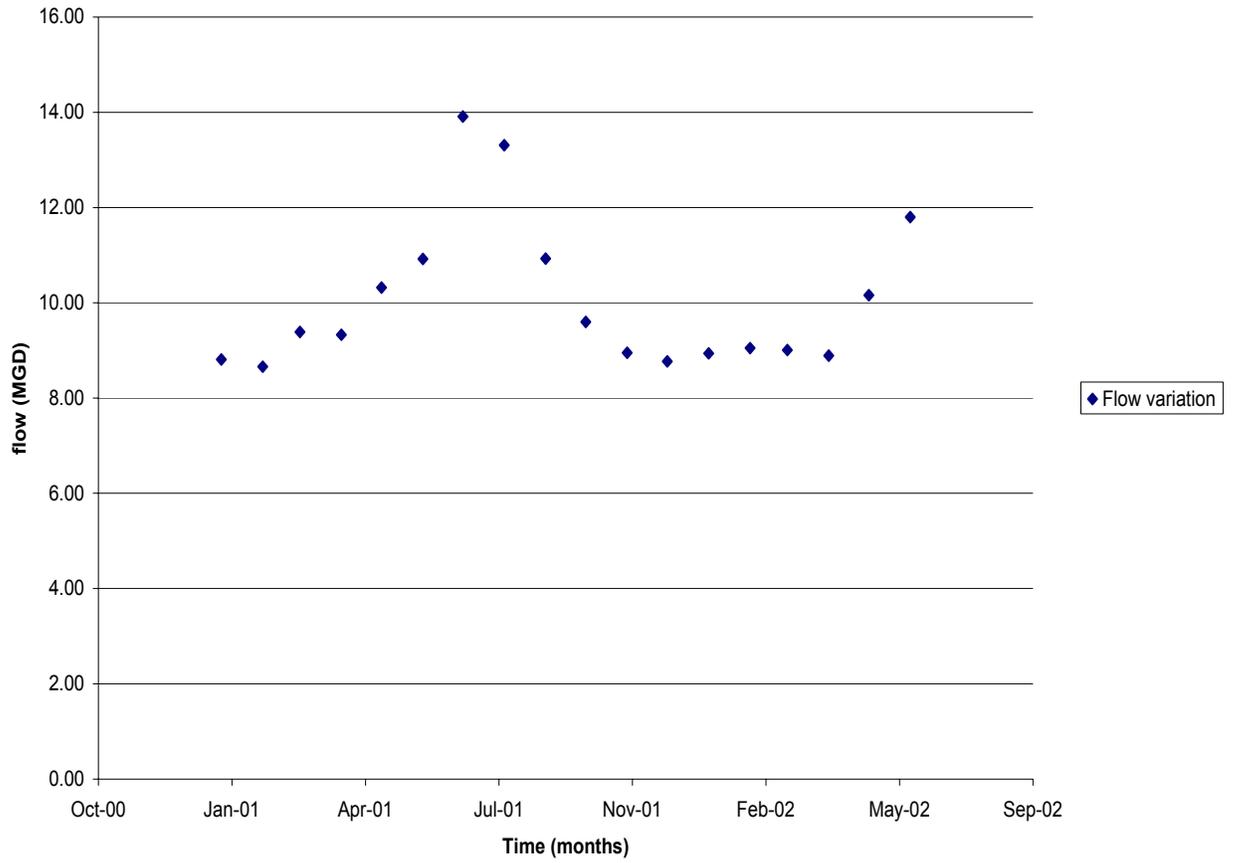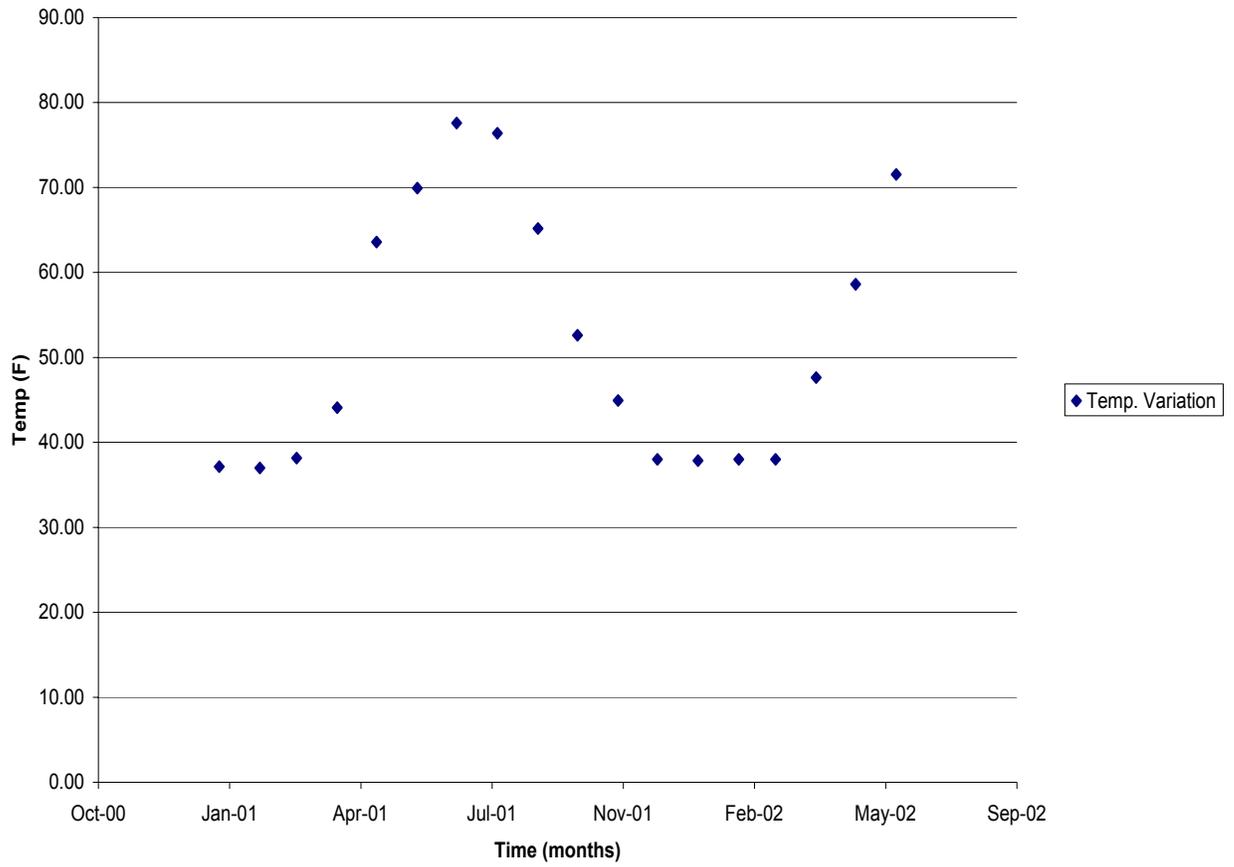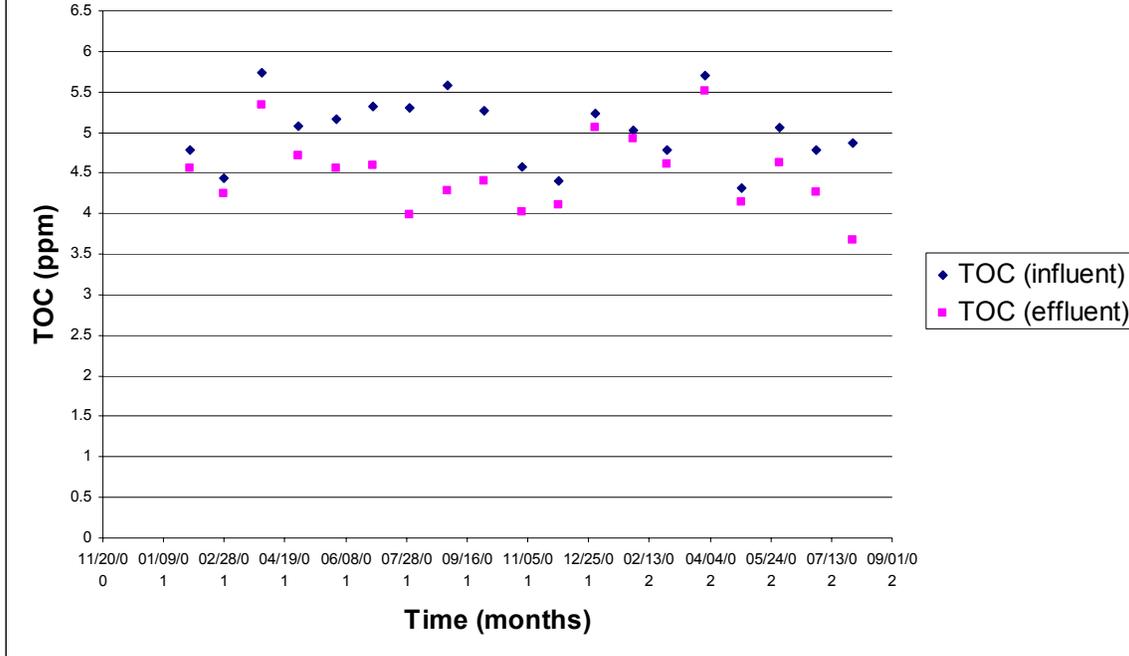
Average Flow Variation from Jan-2001 to June-2002

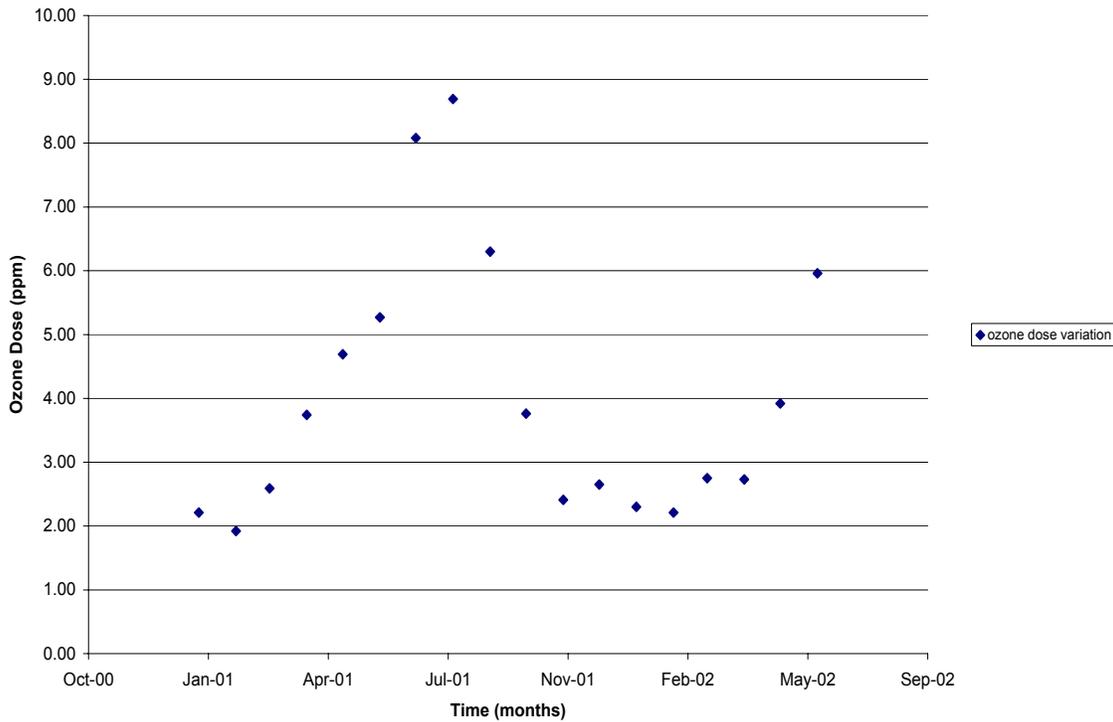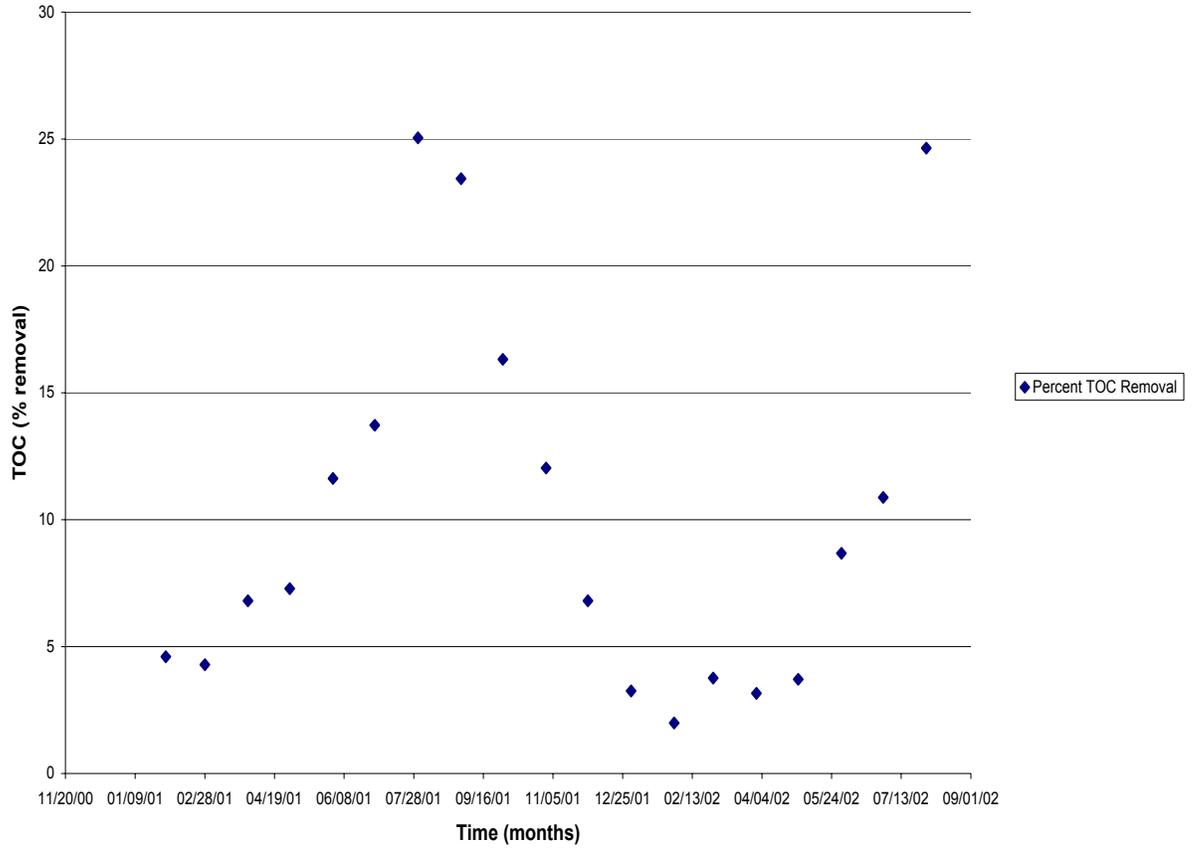**Figure 4-2. Temperature Variation from Jan-2001 to Jun-2002**

Figure 4-3. TOC variations in ozonation chamber influent and effluent
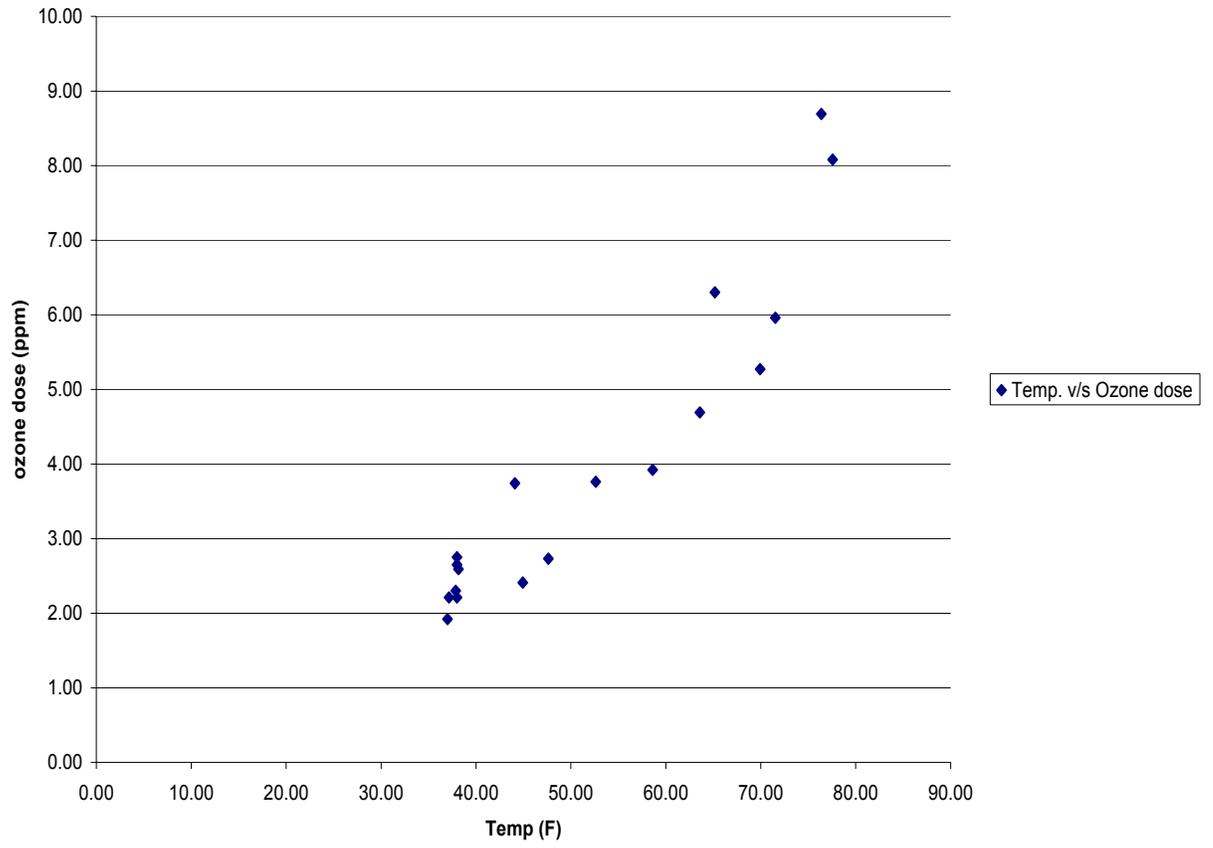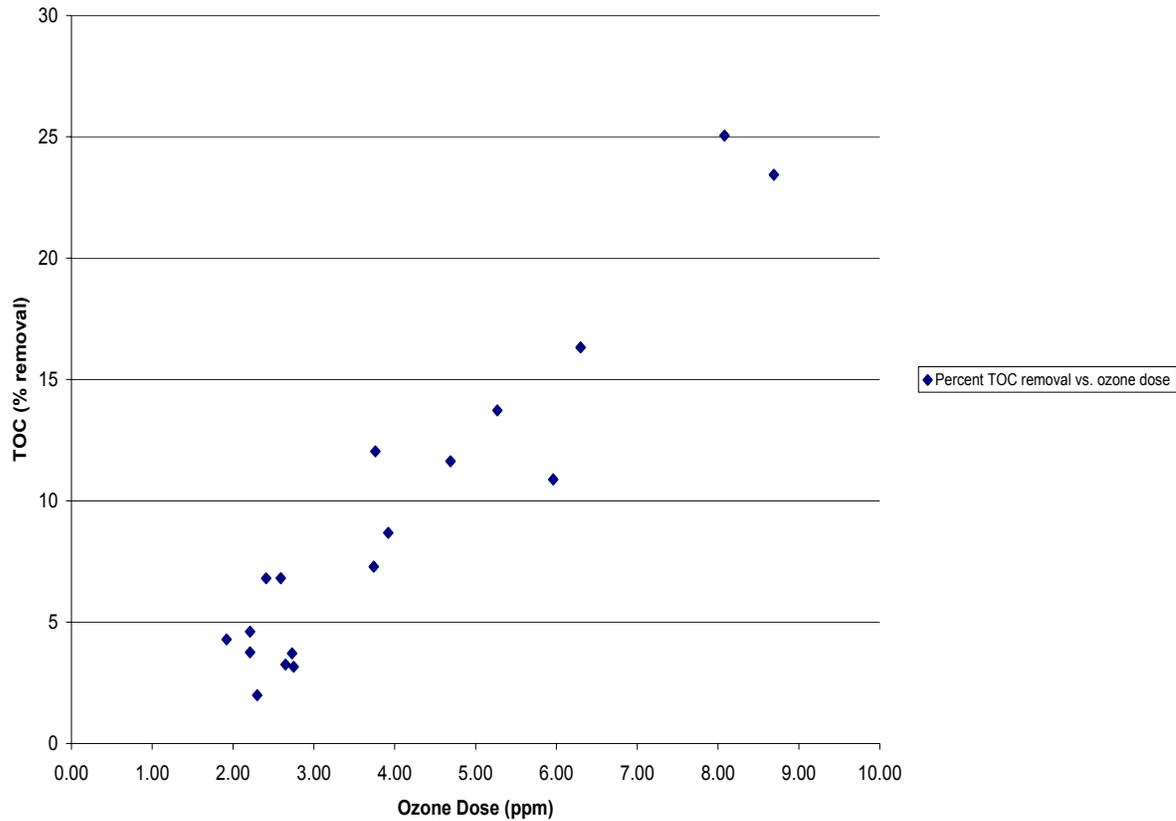

Variation of Ozone dose from Jan-2001 to Jun-2002

Percent TOC removal in the ozonation chamber influent and effluent

Temp. v/s Ozone dose variation from Jan-2001 to June-2002

Average monthly variation of percent TOC removal vs. ozone dose

Factors affecting the Ozone System Operations
The main purpose of the operational data analysis is to understand as to the parameters studied so far affects the operational efficiency of the ozonation system. The control parameter taken here is the ozone dose. This is because the increased demand in summer and henceforth the formation of DBPs be directly proportional to the ozone dose fed into the ozone contact chambers. This will serve as the basic tool in evaluating the impact of water conditions on the ozone system.

Temperature
The temperature variation experienced by the FWTP is very large over the seasons and thus the ozone demand too, fluctuates. The ozone decomposition increases with the increase in temperature and henceforth, the ozone dose. The temperature affects the influent and effluent water quality through the ozone contact basin, as the formations of the DBPs are proportional to the ozone applied and this increases with the increased temperatures, affecting ozone system operations.

pH

The pH in ozone contact basin is very important tool in assessing the overall efficiency of the ozone operations. The ozone decomposition starts with the formation of hydroxide ions and the more the temperature, the rapid the reaction is. The FWTP keeps a constant pH in the ozone contact basin, as the purpose of the ozone usage is to provide disinfection and that is best served at a low pH.

Organic Content

The organic content present in water impacts the overall oxidation under the ozone application. The ozone required to meet the disinfection standards will increase with amount of increased organic content in the water. The parameter used to study is TOC. The influent TOC to the ozone chamber varied from 4 to 6 ppm and the effluent TOC varied from 3.5 to 5.5 ppm, over the period from 01/01/01 to 06/30/02. As the TOC concentrations increased, more ozone was applied to the water and vice versa.

Summary

The FWTP operational data analysis was important in selecting the sampling locations to undertake and meet the research goals. The analysis helped in limiting the sampling locations in and around the ozone contact chamber.

RESULTS AND DISCUSSIONS

The sampling at the FWTP was undertaken on August 5, 2002. The results are being shown and described in this chapter till September 2, 2002. The sampling parameters studied were pH, temperature, total organic carbon (TOC), UV 254 absorbance, specific UV 245 absorbance (SUVA), total alkalinity, ozone residual and off-gas concentrations, ozone dose, and total aldehydes.

The variations in the pH in the secondary softening effluent, stage 3 effluent of the ozone contact chamber, stage 4 effluent of the ozone contact chamber, and the filter influent are shown in table 5-1. The pH for the secondary softening effluent was consistent around 9.1-9.3. The average pH values for the stage 3 and 4 effluents of the ozone contact chambers were around 8.2 and 8.05 respectively, indicating that there was no considerable difference in the two stages of the ozone application. The highest pH recorded in the stage 3 and the stage 4 effluents was 8.84 and 8.63 respectively. The pH values for the filter influent were averaged around 8.21. The graphical representation of pH trends of the water entering and leaving the ozone contact basin is shown in the figure 5-1.

Table 5-1. pH values of the samples collected at the sampling locations

Date	pH - SS	pH - S3	pH - S4	pH - FI	pH - FE
8/5/2002	8.18	7.67	8.15	8.38	
8/7/2002	9.31	8.03	7.95	8.13	
8/9/2002	9.31	8.03	7.95	8.13	
8/12/2002	9.93	8.84	8.63	8.62	
8/14/2002	9.26	8.18	8.18	8.38	
8/16/2002	8.76	8.14	8.12	8.41	
8/19/2002	9.2	8.24	7.98	8.75	8.35
8/21/2002	9.1	7.98	7.78	8.53	8.32
8/23/2002	8.78	8.25	8.18	8.38	8.34
8/26/2002	8.09	8.24	7.35	7.23	8.34
8/28/2002	9.52	8.48	8.38	8.29	7.84
8/30/2002	9.09	8.31	8.24	8.17	8.39
9/2/2002	9.1	7.95	7.86	7.38	8.36

Figure 5-1. pH variations in the Secon. Soft, Stage 3, Stage 4, Filter Influent
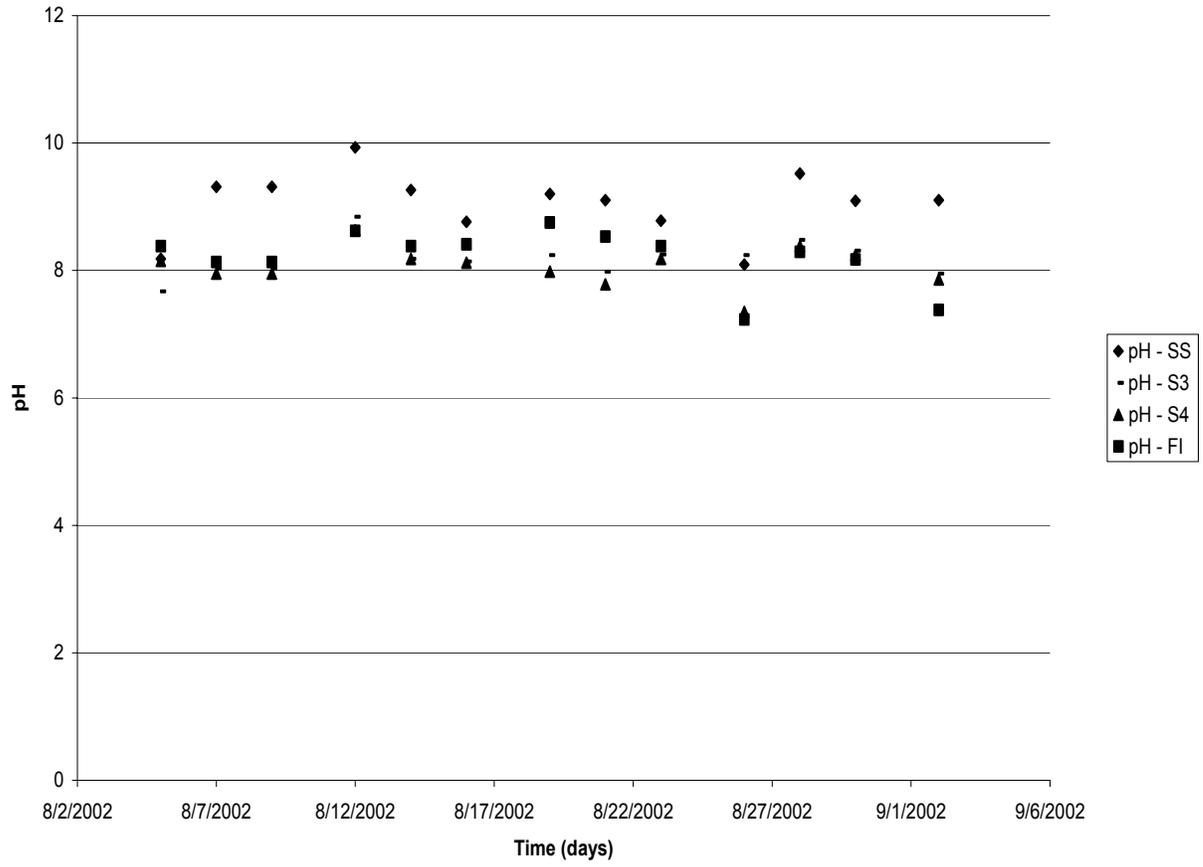
Table 5-2. Temp. values of the samples collected at the sampling locations
(All values indicated in degree celsius)

Date	T - SS	T - S3	T - S4	T - FI	T - FE
8/5/2002	23.5	22.4	22.2	21.9	
8/7/2002	21.3	20.7	21.1	21.1	
8/9/2002	21.3	20.7	21.1	21.1	
8/12/2002	24.7	24.7	24.6	24.7	
8/14/2002	21.7	22.6	22.1	22	
8/16/2002	21.7	21.4	19.9	20.7	
8/19/2002	22	21.6	21.7	21.6	21.7
8/21/2002	19.9	20.3	20.1	19.9	20.1
8/23/2002	20.3	20.4	19.9	20.3	20.1
8/26/2002	22	22.4	22.4	22.2	22.4
8/28/2002	23.7	24.1	24.1	22.6	23.8
8/30/2002	23.1	23	23.8	23.4	23.6
9/2/2002	23	21.7	22.7	22.9	21.7

Figure 5-2. Temp. varitions in Secondary Softening, Stage 3, Stage 4, Filter Influent
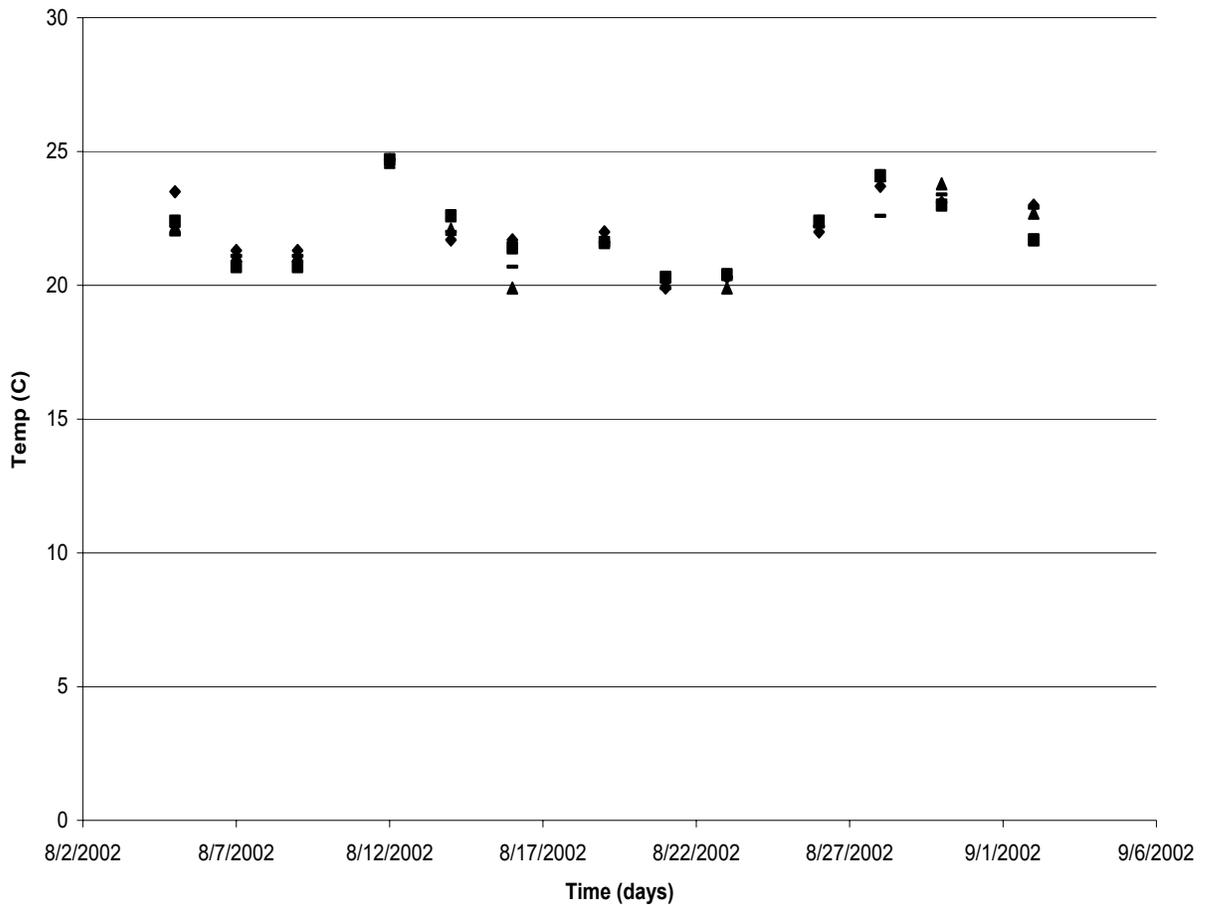
The temperature is a very important factor in ozone disinfection, as this decides the amounts of the ozone to be applied to the water in order to achieve the disinfection requirements. The temperature variations of the secondary softening effluent and thus the ozone contact influent and the ozone application stages, and the ozone contact effluent shown in table 5-2. The average temperature for the stage 3 and 4 of the ozone application was 22°C and 21.97°C respectively. The temperature for the filter influent was observed to be averaged around 21.87°C. The results thus state that there was minimal or negligible change in the water temperature during the water treatment operations. With the winters approaching, the temperature values are expected to drop considerably. The graph depicting the temperature trends in the different sampling locations is shown in figure 5-2.

The total organic carbon (TOC) content signifies the amount of the natural organic matter present in the water. This is again a very important parameter in determining the disinfection efficiency. Higher the TOC content, more will the formation of the DBPs in the treated water. This is because of the reason that higher organic content will require more ozone application and this could result in an incomplete oxidation of the organic matter, thus resulting in the formation of DBPs. The TOC values are presented in the

table 5-3. The TOC showed a declining trend with the lower water temperatures entering the plant, indicating that the ozone disinfection will be more effective in the winter season, as the water temperature, and the organic content and the pH in the ozone contact basin will be lowered. This is because lower organic content and water temperature will result in lowered ozone requirements, which will be sufficed by the lower pH at the point of application, making ozone more stable, thus allowing better disinfection. The average ozone contact influent and the effluent TOC ranged from 5.05 mg/L to 4.33 mg/L. The TOC variations for the samples taken at the different sampling locations are graphed in the figure 5-3.

Table 5-3. TOC values of the samples collected at the sampling locations
(All values indicated in mg/L)

Date	TOC - SS	TOC - S3	TOC - S4	TOC - FI	TOC - FE
8/5/2002	5.129	4.51	4.484	4.129	
8/7/2002	5.125	4.65	4.7	4.523	
8/9/2002	5.023	4.78	4.986	4.652	
8/12/2002	4.63	4.28	4.19	3.59	
8/14/2002	5.125	4.85	4.63	4.12	
8/16/2002	4.44	4.12	4.13	3.87	
8/19/2002	4.24	4.11	4.03	3.68	4.02
8/21/2002	5.61	5.25	5.18	5.13	5.13
8/23/2002	5.35	4.79	4.73	4.72	4.72
8/26/2002	5.78	4.94	4.88	5.01	5.01
8/28/2002	5.42	4.46	4.37	4.41	4.41
8/30/2002	4.78	4.21	4.19	4.19	4.19
9/2/2002					

Figure 5-3. TOC variations in Secondary Softening, Stage 3, Stage 4, Filter Influent
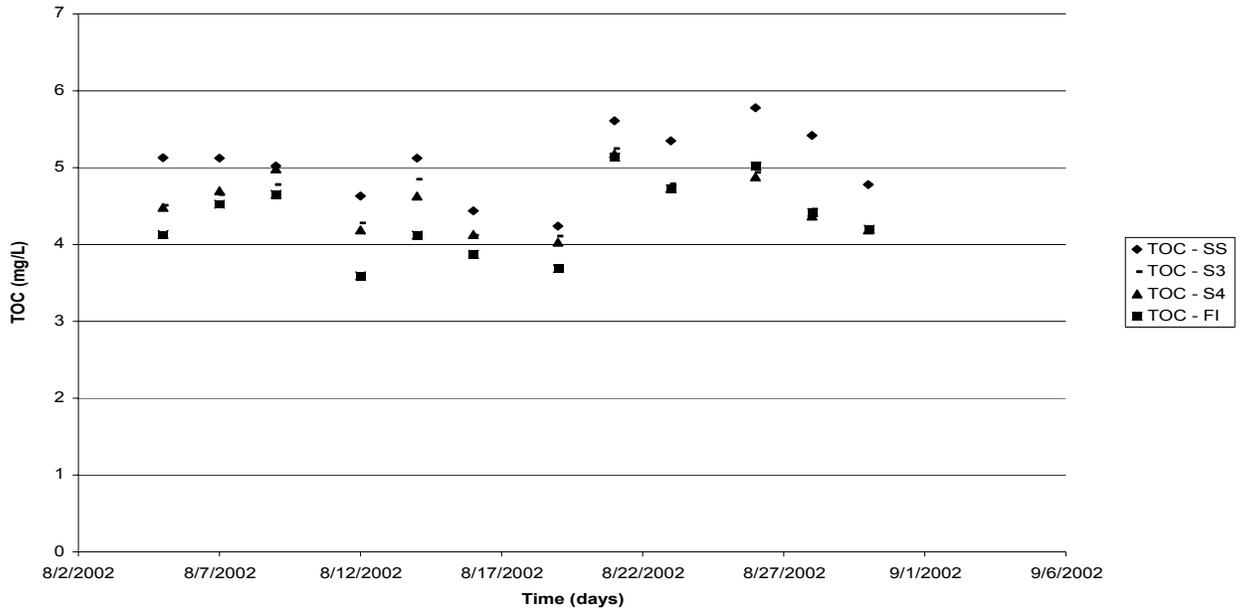

Total alkalinity was measured for the different samples and is tabulated in table 5-4. The total alkalinity showed inconsistent trend over the time period and thus it is difficult to predict the future behavioral trends. The plot showing the total alkalinity variations is graphed in figure 5-4.

Table 5-4. Total Alkalinity values of the samples collected at the sampling locations

(All values indicated in mg/L (ppm))

Date	Alk - SS	Alk - S3	Alk - S4	Alk - FI	Alk - FE
8/5/2002	67	64	63	61	
8/7/2002	67	64	64	64	
8/9/2002	55	60	60	60	
8/12/2002	48	56	56	60	
8/14/2002	56	60	60	60	
8/16/2002	63	64	63	64	
8/19/2002	63	61	61	61	61
8/21/2002	48	55	56	55	55
8/23/2002	52	56	60	56	56
8/26/2002	69	68	69	69	68
8/28/2002	76	72	73	75	73
8/30/2002	66	65	66	65	65
9/2/2002	72	68	68	68	68

Figure 5-4. Total Alkalinity variations in Secondary Softening, Stage 3, Stage 4, Filter Influent
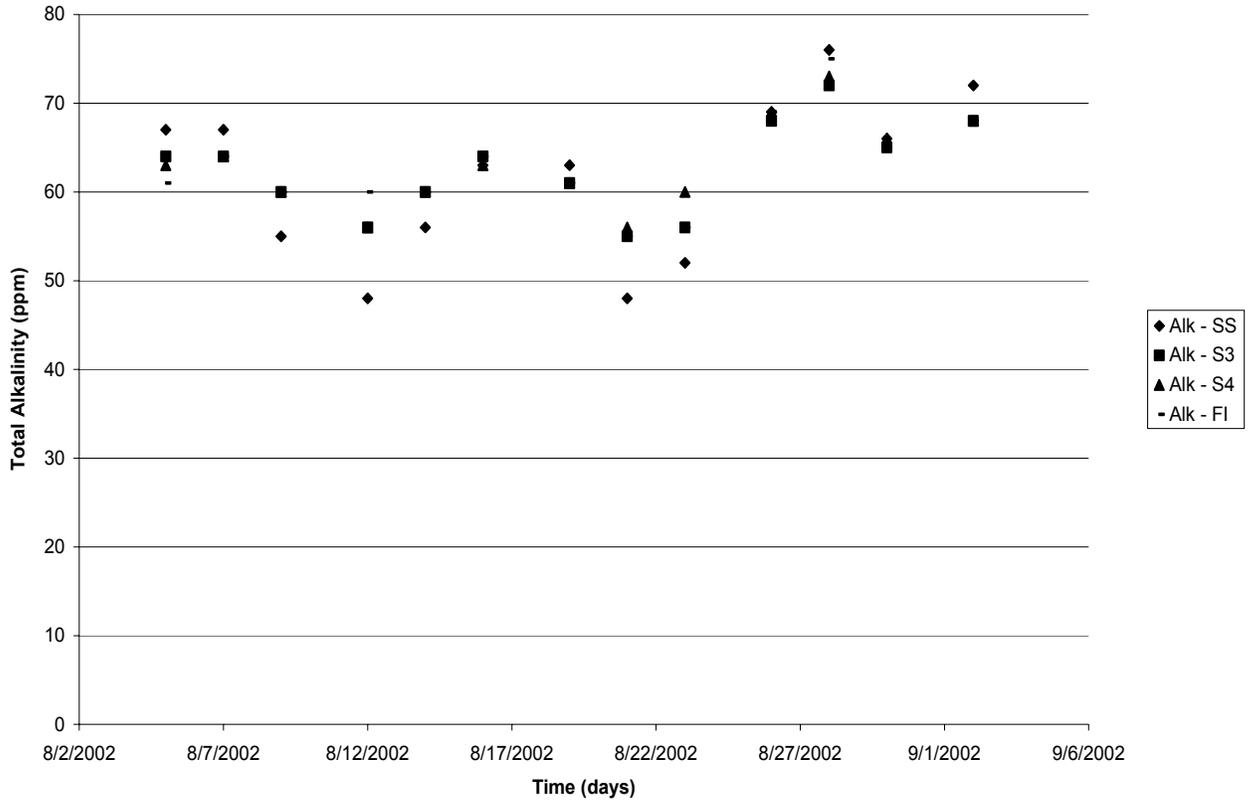

UV 254 absorbance is a measure of the incomplete oxidation of the organic content present in the water and the UV 254 values showed a declining trend across the ozonation chamber. Though the UV 254 values for the first three sampling days were unexpectedly higher, the rest of the data followed the expected trend. The values usually were smaller than 0.1 cm^{-1}. The results are shown in the table 5-5 and the values are plotted in the figure 5-5. This parameter was measured specifically to understand the incomplete oxidation trends and thus the further removal of the organic contaminants from the treated water.

Table 5-5. UV values of the samples collected at the sampling locations

(All values indicated in cm-1)

Date	UV - SS	UV - S3	UV - S4	UV - FI	UV - FE
8/5/2002	0.099	0.73	0.52	0.734	
8/7/2002	0.062	0.691	0.574	0.537	
8/9/2002	0.062	0.691	0.574	0.537	
8/12/2002	0.082	0.04	0.036	0.038	
8/14/2002	0.082	0.062	0.028	0.102	
8/16/2002	0.081	0.037	0.032	0.042	
8/19/2002	0.08	0.034	0.032	0.057	0.035
8/21/2002	0.094	0.044	0.043	0.046	0.048
8/23/2002	0.087	0.036	0.039	0.039	0.048
8/26/2002	0.092	0.042	0.041	0.043	0.045
8/28/2002	0.086	0.051	0.039	0.054	0.051
8/30/2002	0.087	0.034	0.033	0.034	0.045
9/2/2002	0.104	0.043	0.041	0.041	0.049

Figure 5-5. UV variations in Secondary Softening, Stage 3, Stage 4, Filter Influent
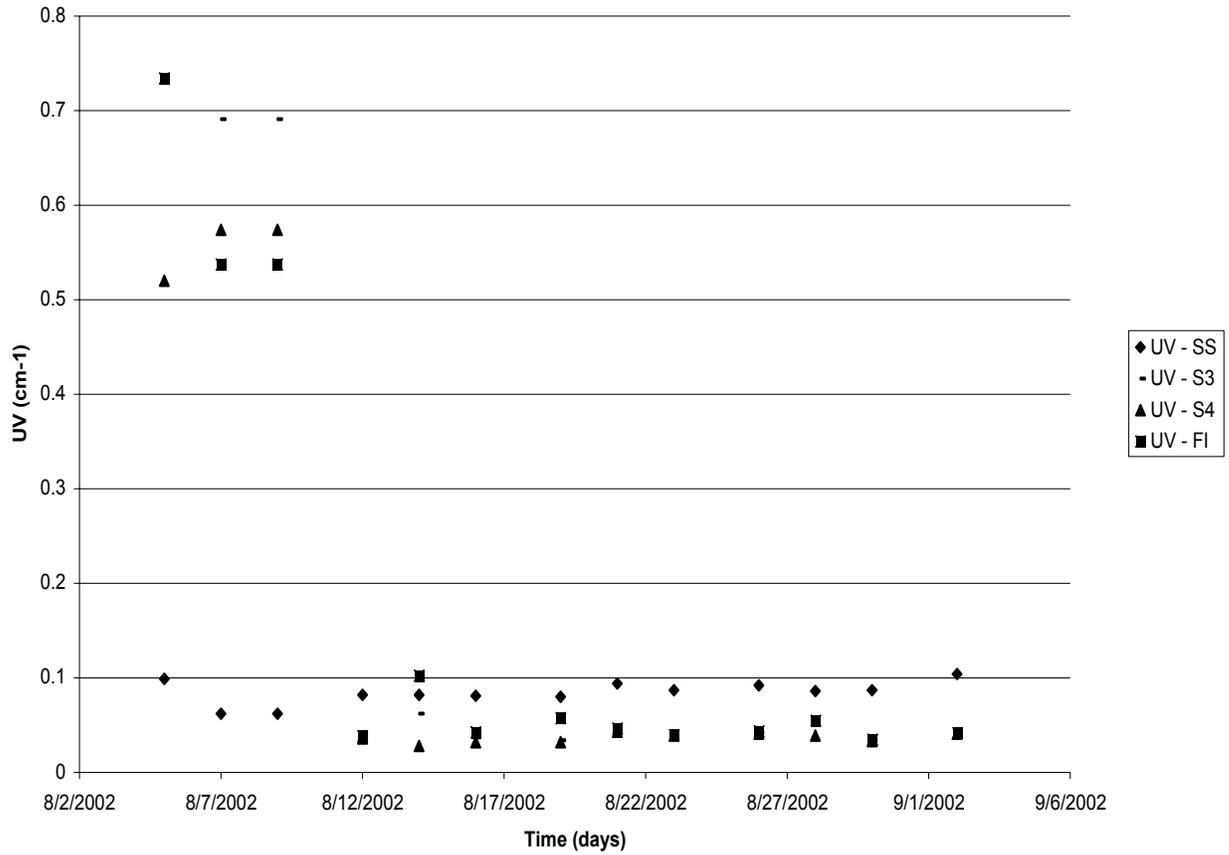

Specific UV 254 absorbance is defined as the ration of the UV 254 absorbance to the total organic carbon (TOC). This parameter is expressed in L/mg-m. The SUVA is measured in order to understand the overall oxidation process, which is being performed by the ozone, when made to react with the organic content in the water. The SUVA values decreased in magnitude across the ozone contact basin indicating complete oxidation. The SUVA values ranged from a minimum of 0.78 L/mg-m to 1.88 L/mg-m. The values are shown in table 5-6 and the variations are plotted in figure 5-6.

Table 5-6. SUVA values of the samples collected at the sampling locations
(All values indicated in L/mg-m)

Date	SUVA - SS	SUVA - S3	SUVA - S4	SUVA - FI	SUVA - FE
8/5/2002	1.9302008	16.1862528	11.596789	17.776701	
8/7/2002	1.2097561	14.8602151	12.212766	11.872651	
8/9/2002	1.2343221	14.4560669	11.512234	11.543422	
8/12/2002	1.7710583	0.93457944	0.8591885	1.0584958	
8/14/2002	1.6	1.27835052	0.6047516	2.4757282	
8/16/2002	1.8243243	0.89805825	0.7748184	1.0852713	
8/19/2002	1.8867925	0.82725061	0.7940447	1.548913	0.8706468
8/21/2002	1.6755793	0.83809524	0.8301158	0.8966862	0.9356725
8/23/2002	1.6261682	0.75156576	0.8245243	0.8262712	1.0169492
8/26/2002	1.5916955	0.85020243	0.8401639	0.8582834	0.8982036
8/28/2002	1.5867159	1.14349776	0.8924485	1.2244898	1.1564626
8/30/2002	1.8200837	0.80760095	0.7875895	0.8114558	1.0739857
9/2/2002					

Figure 5-6. SUVA variations in Secondary Softening, Stage 3, Stage 4, Filter Influent
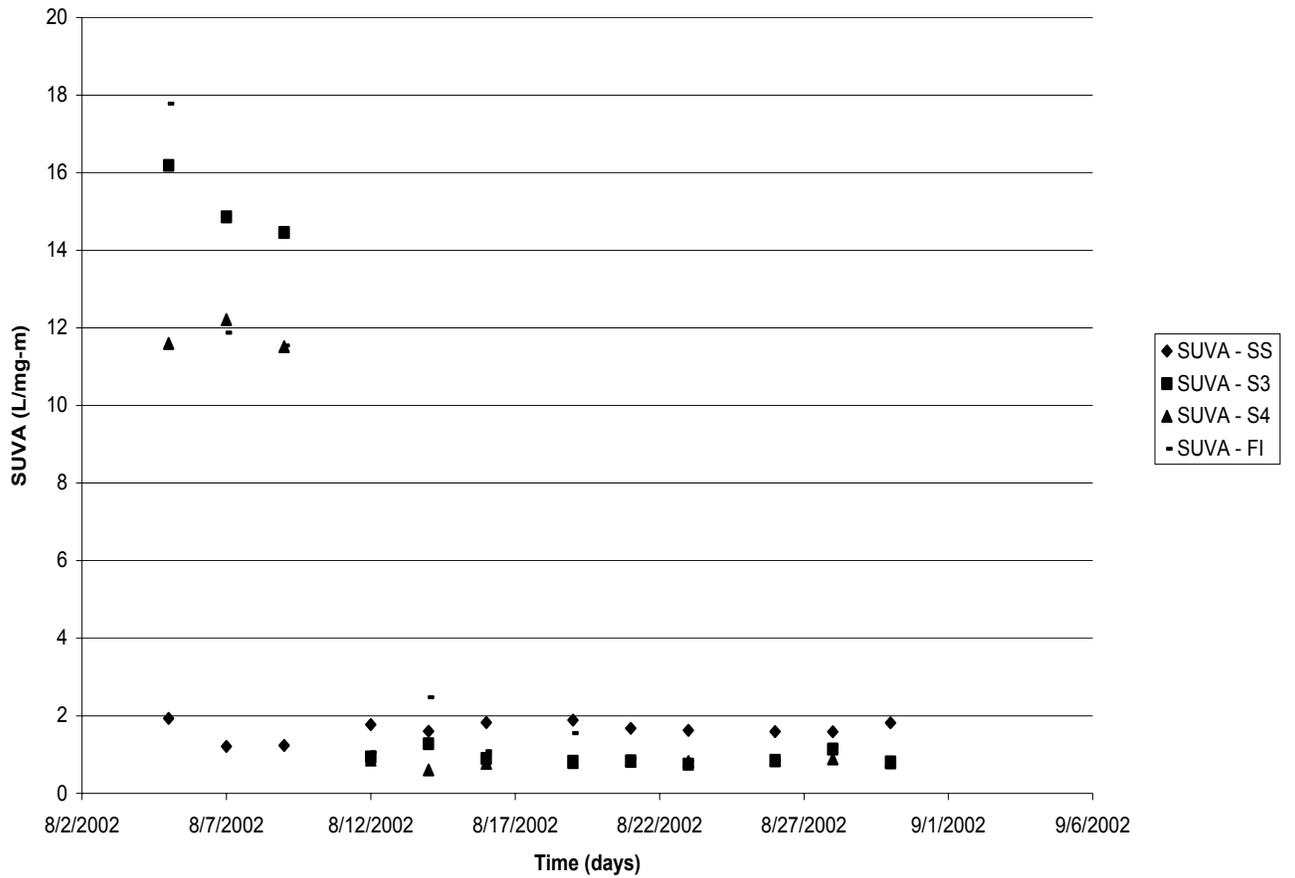
The overall results for each sampling location, with all the parameters measured at that particular location, indicated with proper units are shown in table 5-7 through 5-10. The total aldehydes quantified in the ozone contact influent and the effluent is shown in table 5-11 through 5-14.

Figure 5-6. SUVA variations in Secondary Softening, Stage 3, Stage 4, Filter Influent
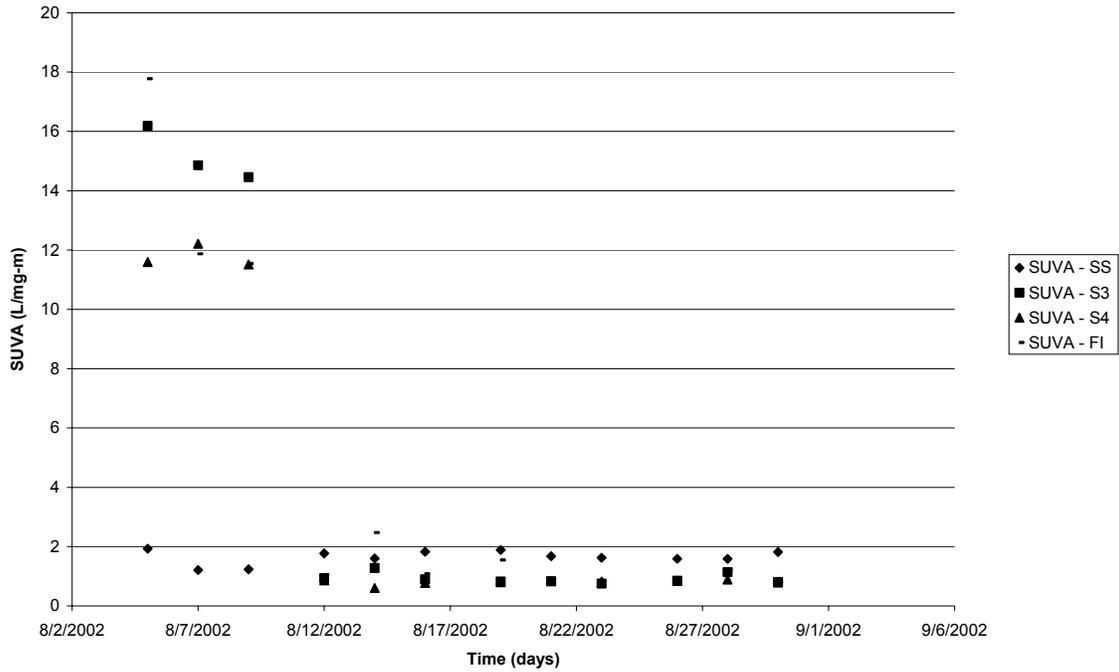

Table 5-7.   Parametric Details of Secondary Softening Effluent

Date	pH	Total Alk.	Temp.	TOC	UV	SUVA	Oz.residual	Oz. gas flow	SUVA
		ppm	C	mg/L	cm-1	L/mg-cm	ppm	cfm	L/mg-m
8/5/2002	8.18	67	23.5	5.129	0.099	0.019302	0	0	1.930201
8/7/2002	9.31	67	21.3	5.125	0.062	0.012098	0	0	1.209756
8/9/2002	9.31	55	21.3	5.023	0.062	0.012343	0	0	1.234322
8/12/2002	9.93	48	24.7	4.63	0.082	0.017711	0	0	1.771058
8/14/2002	9.26	56	21.7	5.125	0.082	0.016	0	0	1.6
8/16/2002	8.76	63	21.7	4.44	0.081	0.018243	0	0	1.824324
8/19/2002	9.2	63	22	4.24	0.08	0.018868	0	0	1.886792
8/21/2002	9.1	48	19.9	5.61	0.094	0.016756	0	0	1.675579
8/23/2002	8.78	52	20.3	5.35	0.087	0.016262	0	0	1.626168
8/26/2002	8.09	69	22	5.78	0.092	0.015917	0	0	1.591696
8/28/2002	9.52	76	23.7	5.42	0.086	0.015867	0	0	1.586716
8/30/2002	9.09	66	23.1	4.78	0.087	0.018201	0	0	1.820084
9/2/2002	9.1	72	23		0.104	0	0	0	0

Table 5-8. Parametric details of Stage 3 Effluent

Date	pH	Total Alk.	Temp.	TOC	UV	SUVA	Oz.residual	Oz. gas flow	SUVA
		ppm	C	mg/L	cm-1	L/mg-cm	ppm	cfm	L/mg-m
8/5/2002	7.67	64	22.4	4.51	0.73	0.161863	0.108	23.5	16.18625
8/7/2002	8.03	64	20.7	4.65	0.691	0.148602	0.193	25.5	14.86022
8/9/2002	8.03	60	20.7	4.78	0.691	0.144561	0.193	23.7	14.45607
8/12/2002	8.84	56	24.7	4.28	0.04	0.009346	0.116	24.4	0.934579
8/14/2002	8.18	60	22.6	4.85	0.062	0.012784	0.15	21.6	1.278351
8/16/2002	8.14	64	21.4	4.12	0.037	0.008981	0.165	19.3	0.898058
8/19/2002	8.24	61	21.6	4.11	0.034	0.008273	0.133	19.8	0.827251
8/21/2002	7.98	55	20.3	5.25	0.044	0.008381	0.2	23.3	0.838095
8/23/2002	8.25	56	20.4	4.79	0.036	0.007516	0.125	22.5	0.751566
8/26/2002	8.24	68	22.4	4.94	0.042	0.008502	0.124	28.6	0.850202
8/28/2002	8.48	72	24.1	4.46	0.051	0.011435	0.16	31.7	1.143498
8/30/2002	8.31	65	23	4.21	0.034	0.008076	0.177	32.9	0.807601
9/2/2002	7.95	68	21.7		0.043	0	0.193	18.1	0

Table 5-9. Parametric variations of Stage 4 Effluent

Date	pH	Total Alk.	Temp.	TOC	UV	SUVA	Oz.residual	Oz. gas flow	SUVA
		ppm	C	mg/L	cm-1	L/mg-cm	ppm	cfm	L/mg-m
8/7/2002	7.95	64	21.1	4.7	0.574	0.122128	0.108	2.72	12.21277
8/9/2002	7.95	60	21.1	4.986	0.574	0.115122	0.108	2.78	11.51223
8/12/2002	8.63	56	24.6	4.19	0.036	0.008592	0.067	2.81	0.859189
8/14/2002	8.18	60	22.1	4.63	0.028	0.006048	0.072	2.54	0.604752
8/16/2002	8.12	63	19.9	4.13	0.032	0.007748	0.09	0.58	0.774818
8/19/2002	7.98	61	21.7	4.03	0.032	0.00794	0.073	0.293	0.794045
8/21/2002	7.78	56	20.1	5.18	0.043	0.008301	0.103	2.4	0.830116
8/23/2002	8.18	60	19.9	4.73	0.039	0.008245	0.035	2.25	0.824524
8/26/2002	7.35	69	22.4	4.88	0.041	0.008402	0.05	2.6	0.840164
8/28/2002	8.38	73	24.1	4.37	0.039	0.008924	0.05	2.96	0.892449
8/30/2002	8.24	66	23.8	4.19	0.033	0.007876	0.013	2.87	0.787589
9/2/2002	7.86	68	22.7		0.041	0	0.023	0.322	0

From the tables 5-7 through 5-10, the ozone residual variations in the stage 3 and the stage 4 of the ozone contact basin are plotted in figure 5-7 and figure 5-9 respectively. The ozone gas flows in the stage 3 and stage 4 are plotted in figure 5-8 and figure 5-10 respectively. The ozone residual and was higher in stage 3 as compared to the stage 4, mainly because of the fact that more ozone is applied in the stage 3 then in the stage 4. The amount of ozone application is directly proportional to the incoming water temperature and the organic content. The higher these values are the more ozone is required for the disinfection. The ozone residual in stage 3 was found to range between a maximum of 0.193mg/L to a minimum of 0.108 mg/L. The ozone gas flow was varying between 32.9 cubic feet per minute (cfm) to 19.3 cfm for stage 3. The ozone residual for

stage 4 was varying between 0.108mg/L to 0.072 mg/L. The ozone gas flow was found to range between 2.87 cfm to 0.293 cfm.

Table 5-10.   Parametric Variations of Filter Influent

Date	pH	Total Alk.	Temp.	TOC	UV	SUVA	Oz.residual	Oz. gas flow	SUVA
		ppm	C	mg/L	cm-1	L/mg-cm	ppm	cfm	L/mg-m
8/5/2002	8.38	61	21.9	4.129	0.734	0.177767	0.001	0	17.7767
8/7/2002	8.13	64	21.1	4.523	0.537	0.118727	0.001	0	11.87265
8/9/2002	8.13	60	21.1	4.652	0.537	0.115434	0.001	0	11.54342
8/12/2002	8.62	60	24.7	3.59	0.038	0.010585	0.001	0	1.058496
8/14/2002	8.38	60	22	4.12	0.102	0.024757	0.001	0	2.475728
8/16/2002	8.41	64	20.7	3.87	0.042	0.010853	0.001	0	1.085271
8/19/2002	8.75	61	21.6	3.68	0.057	0.015489	0.001	0	1.548913
8/21/2002	8.53	55	19.9	5.13	0.046	0.008967	0.001	0	0.896686
8/23/2002	8.38	56	20.3	4.72	0.039	0.008263	0.001	0	0.826271
8/26/2002	7.23	69	22.2	5.01	0.043	0.008583	0.001	0	0.858283
8/28/2002	8.29	75	22.6	4.41	0.054	0.012245	0.001	0	1.22449
8/30/2002	8.17	65	23.4	4.19	0.034	0.008115	0.001	0	0.811456
9/2/2002	7.38	68	22.9		0.041	0	0.001	0	0

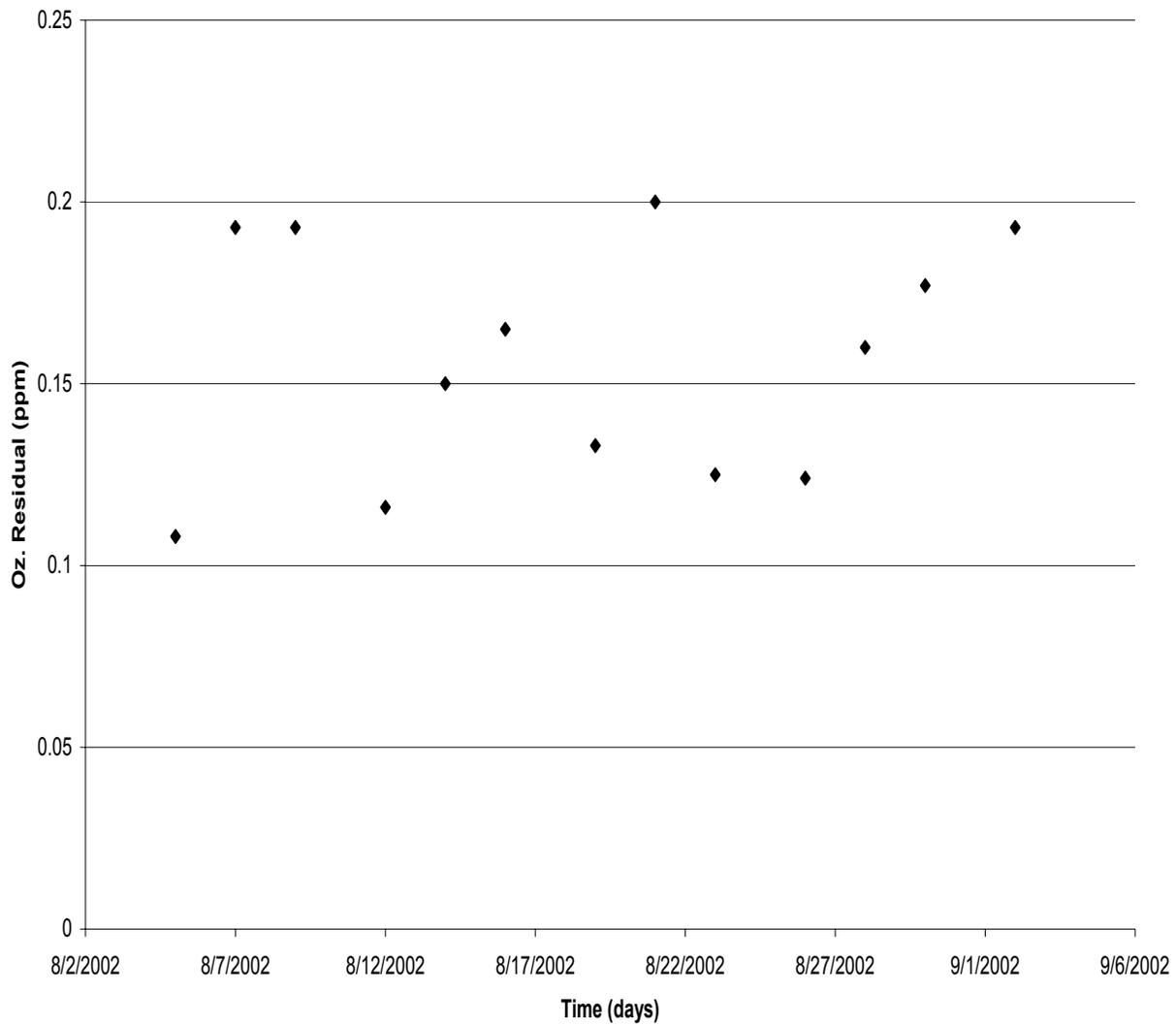**Figure 5-7. Ozone residual variations in Stage 3 effluent of ozone cntact basin**

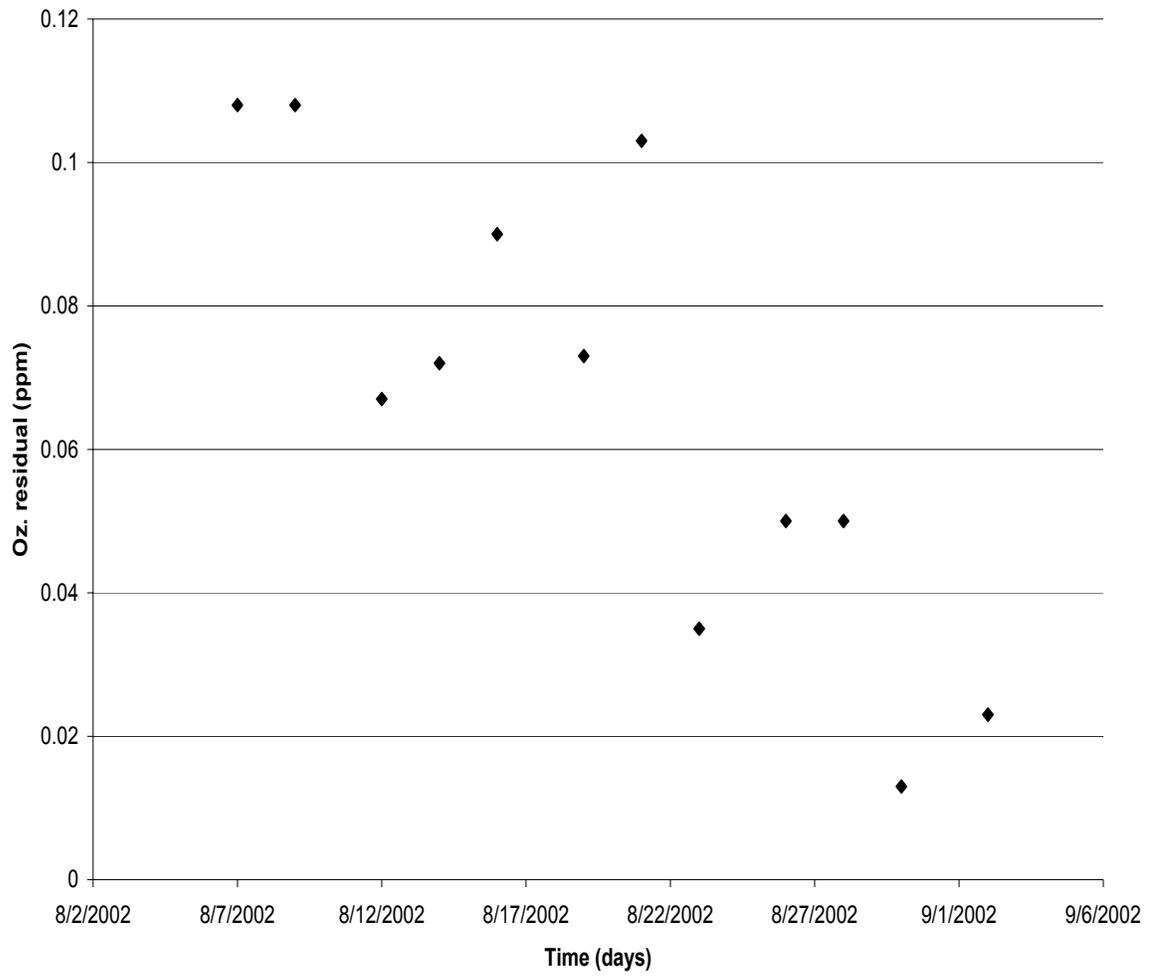**Figure 5-9. Ozone residual variation in Stage 4 effluent of the ozone contact basin**

Figure 5-8. Ozone gas flow variation in Stage 3 effluent of ozone contact basin
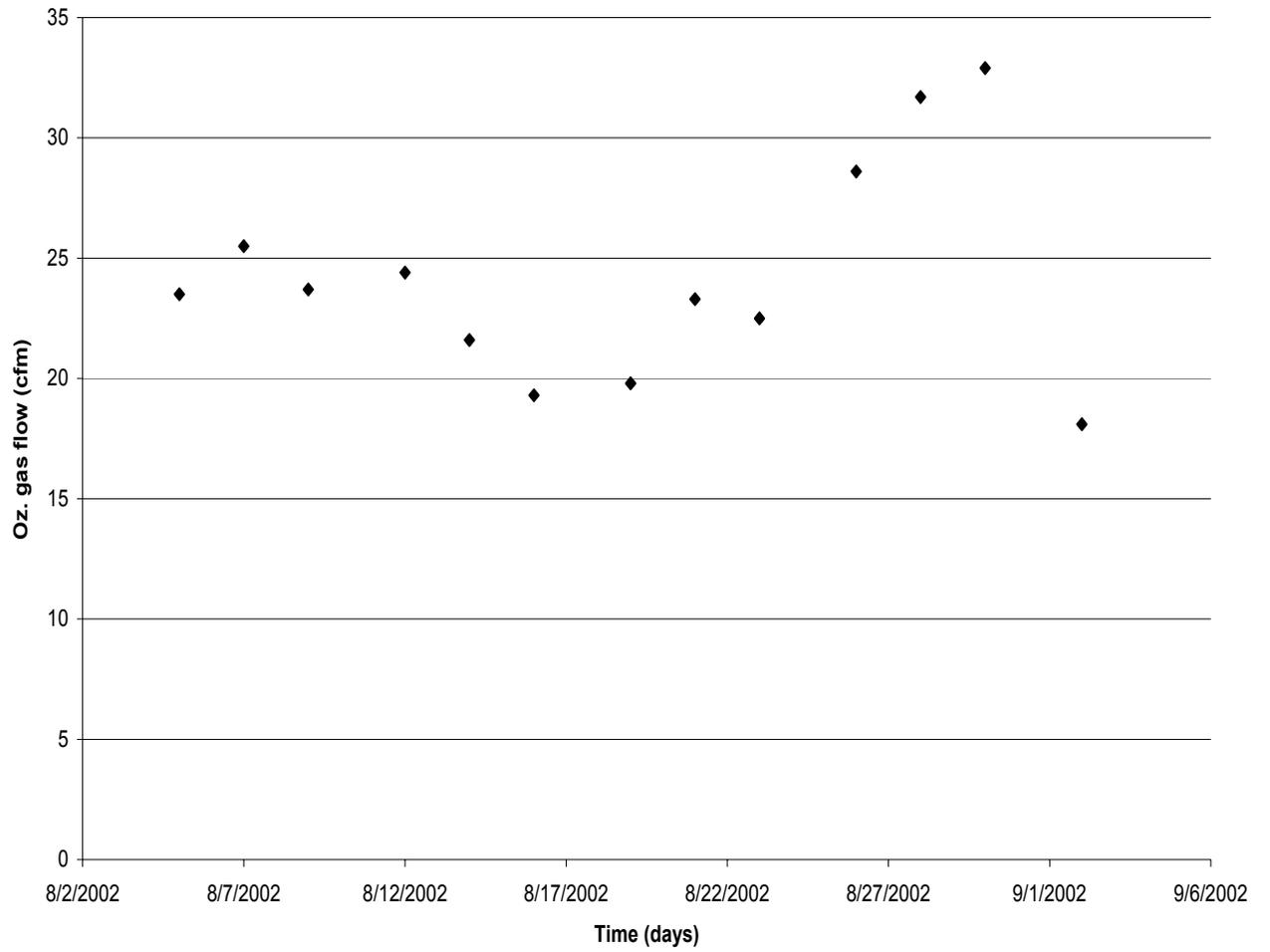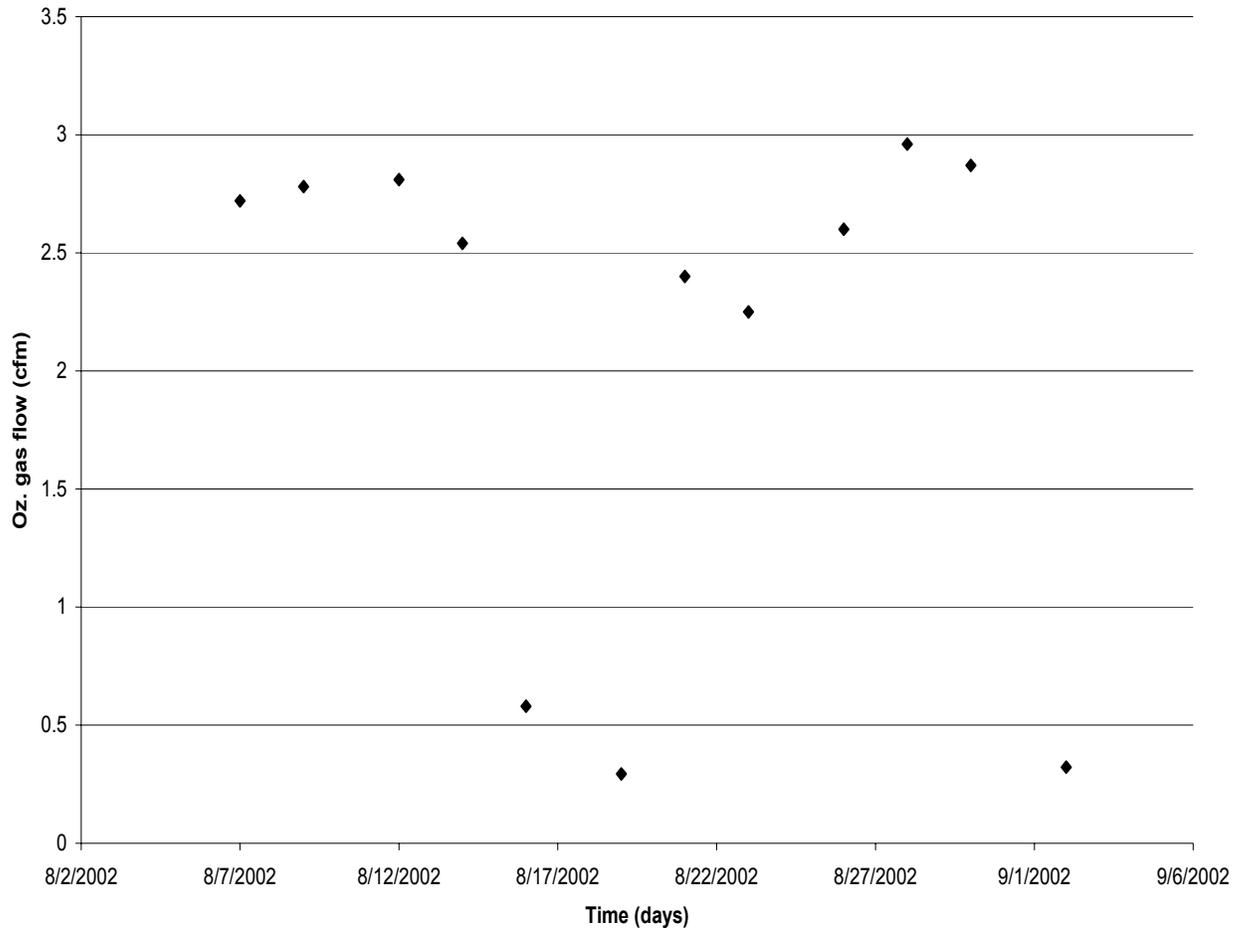
Figure 5-10. Ozone gas flow variation in Stage 4 of the ozone contact basin

The graphical representation of the aldehydes formation at the different sampled water treatment processes is shown in figure 5-11 through 5-14. The aldehydes considered for the comparative study, were formaldehyde, acetaldehyde, butanal, glyoxal, and methyl glyoxal. This is because of the fact that the other aldehydes formation is usually very low in amounts (Hurley, Stuart 2001) and the moreover the formaldehyde is the major cause of concern, as this being a carcinogen.

Figure 5-11. Aldehyde formation in secondary softening effluent from 08/05/02 to 09/02/02
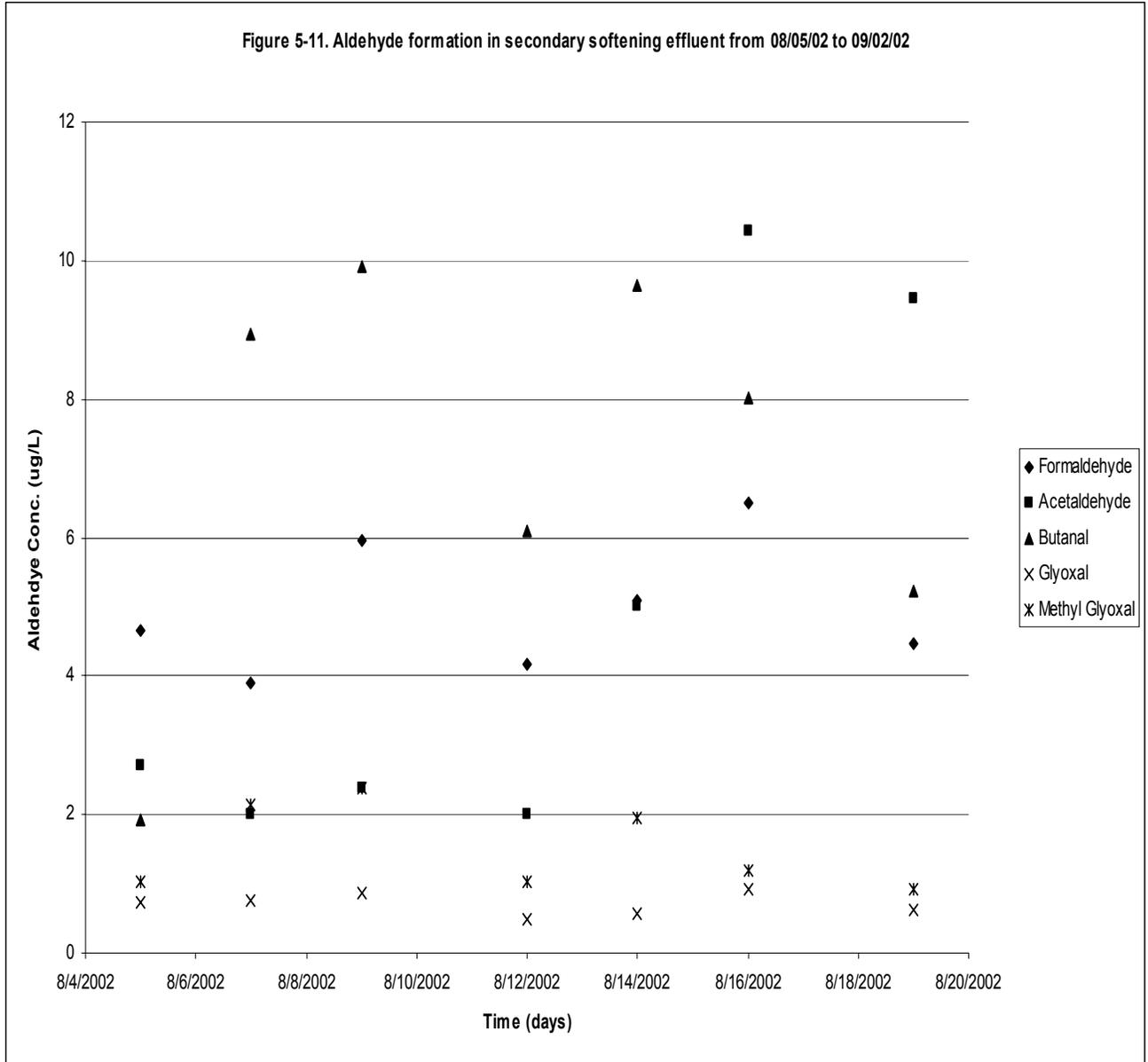
The aldehydes were usually low in amounts in the water entering the ozone contact basin, and then after the ozone application, the amounts soared significantly. This was primarily due to the reason that the incomplete oxidation of the organic matter took place and thus resulted in the DBPs formation. Aldehydes were considerably reduced in amounts after the ozone was stripped out, before the treated entered the filters. The amount of aldehydes entering and leaving the ozone contact basin were low in amounts in the secondary softening effluent and the filter influent, because of the reason that in the first case, there was no ozone application and in the latter case, the ozone was stripped out, so as to make the water suitable for the biological filtration, as ozone is toxic in nature to the microorganisms. The aldehydes were largely formed in stage 3 and 4 of the ozone contact

chamber, as because of the incomplete oxidation of the organic matter present in the river water, occurred on ozone application.

Fiure 5-12. Aldehyde formation variations in Stage 3 Effluent of the ozone contact basin from 08/05/02 through 09/02/02
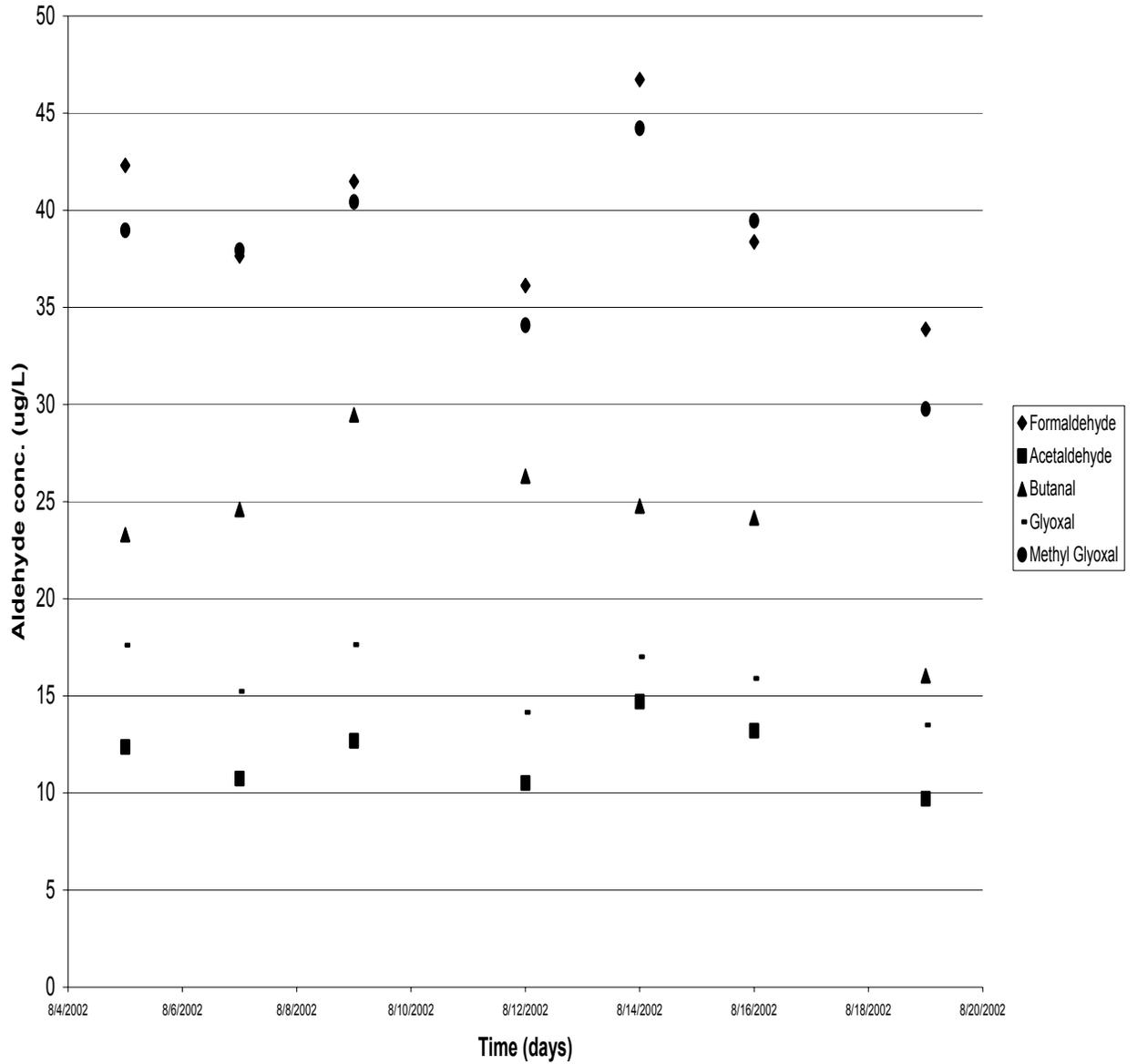
Figure 5-13. Aldehyde formation variation in stage 4 effluent of the ozone contact basin from 08/05/02 to 09/02/02
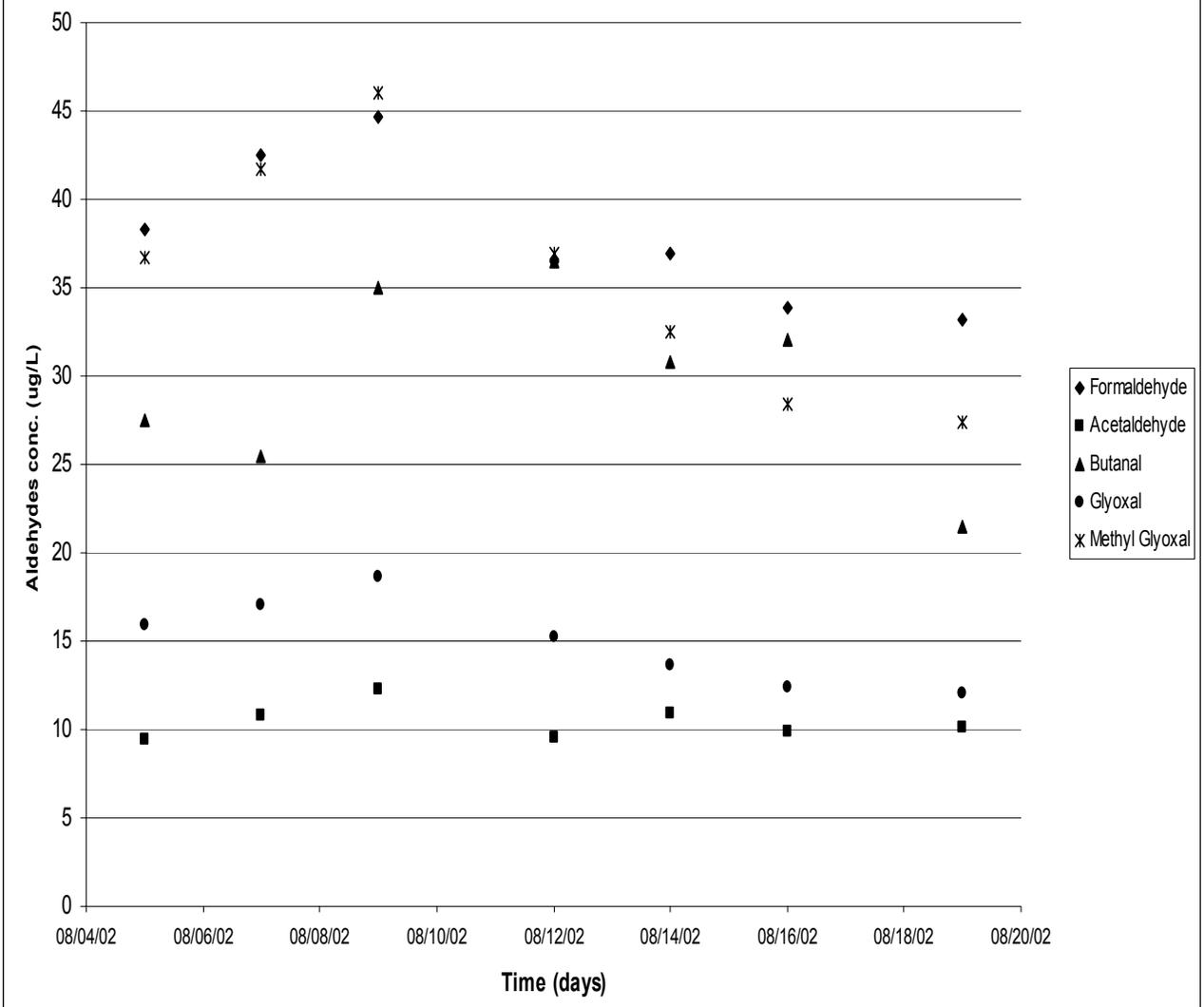
Figure 5-14. Aldehyde formation variation in the filter influent from 08/05/02 to 09/02/02