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CHEMICAL AND BIOLOGICAL EVALUATION OF DRINKING WATER DISINFECTANTS AT PILOT SCALE

by

CATHERINE ELIZABETH RODGER

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE
IN
ENVIRONMENTAL SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

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April 21, 1987

Faculty of Graduate Studies and Research
University of Alberta
Edmonton, Alberta

Re: Huck, P.M. (1986). Combined Chemical and Biological Evaluation of Drinking Water Treatment Alternatives on a Pilot Scale. (UP-A-391). Final report submitted to Health and Welfare Canada, Ottawa, Ontario, Department of Supply and Services Contract Number 1ST84-00176.

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Yours truly,

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Supervisor

D. T. Williams

DATE 22 April, 1987

To Richard and Krista Rodger

whose capabilities and understanding made it all possible

ABSTRACT

A pilot scale water treatment plant was constructed at Edmonton, Alberta to test biological and chemical parameters of process samples of treated surface waters. The plant was constructed of inert materials - glass, stainless steel, and fluorocarbons, to avoid organic contamination.

A common process prevailed up to the point of disinfection, where water was split into four parallel streams. Chloramines, chlorine, chlorine dioxide, and ozone were the four oxidants applied, and the streams were maintained entirely separate after this point.

Analysis for conventional drinking water treatment parameters was carried out, along with concentration of sample waters on XAD-2 macroreticular resins. Concentrated samples were then subject to mutagenicity testing and gas chromatography as methods to study the presence and effects of trace organics.

The objectives of this work are threefold: (1) to describe the physical facilities of a pilot scale water treatment plant having four disinfectant streams, (2) to outline the operating functions of the plant and describe some problems encountered, and (3) to apply the chi-square statistic to the numbers of peak counts appearing in process water gas chromatograms; to relate the chi-square

values to biological and chemical tests applied concurrently to the water samples.

Operational difficulties resulted from a changing raw water source as well as the unique aspects of the pilot plant system. Some operating and physical alterations were made as needed when difficulties were encountered.

Eluates of XAD-2 concentrated process samples were subjected to GC and, occasionally mass spectrometry. The resultant chromatograms were then divided into four divisions for a broad-spectrum analysis of the plethora of information given by the peak numbers.

The four divisions represented consistent retention times and corresponded to generally different types of compounds. Water samples were divided into three categories, each related to basic water types occurring with distinct weather periods: (1) winter water, (2) spring thaw water, and (3) spring-summer water.

It was found that the chlorine stream showed the least statistical variation and that the spring-summer water displayed the most changeable organic matrix. Large anomalies observed in the chi-square test for significance usually could be related to mutagenic episodes and/or major fluctuations in the raw water quality.

The consistency of the chlorine stream could be interpreted in a misleading way. Since significance in the chi-square results from both high and low counts, only examination of the peak counts (contingency tables) reveals consistent elevation of peak numbers.

Chlorine, therefore, as a primary oxidant yielded the most trace organics on a consistent basis in effluent waters and increased mutational effects. However, this finding was not the same for the post-chlorination tests, and it appears that chlorine used for distribution residual following activated carbon is an acceptable practice, at least insofar as state-of-the-art examination allows.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

The issue of toxic organic substances in drinking water has evolved with technological advances in detection and identification of organic compounds. Trihalomethanes (THMs) presented the first clearly identifiable halo-organic chemicals of presumed hazard to human health which were found in significant quantities in drinking water (AWWA, 1982). The fact that these could be formed in treatment processes became further cause for investigation.

Although THMs were the first compounds identified, many more organic compounds have since been found in drinking water. Because only about ten percent of these are identifiable, it is evident that current knowledge is not sufficient to adequately characterize chemicals present in drinking water supplies (Monarca, 1983).

While disinfection practices are essential to the microbiological safety of water supplies, it is imperative that treatment processes be evaluated to ensure that while producing safe water supplies, harmful by-products are not created in health-threatening quantities. Disinfection of typical North American surface waters has classically been achieved by the use of chlorine, in contrast to the European practice, particularly in more recent years, of ozonation.

This thesis arose from a study which examined the biological and chemical characteristics of process waters resulting from four parallel treatment trains in which the oxidants chlorine, chloramines, chlorine dioxide, and ozone were applied, and granular activated carbon (GAC) was examined. The study was performed at pilot scale using North Saskatchewan River water at Edmonton, Alberta. The biological quality of the treated water was assessed using the Ames Salmonella mutagenicity assay, while chemical identification was performed using gas chromatography/mass spectrometry (GC/MS).

Results of the complete investigation have been reported elsewhere (Huck, 1986). The writer was involved in the study as a pilot plant operator. Her contributions to the final report consisted of documentation of pilot plant operating history and problems, and tabulation of operating data. She also conducted her own statistical evaluation of the GC data using a chi-squared procedure. This provided a semi-quantitative means of comparing chromatograms among the four streams and over time. This thesis therefore concentrates on operation of the pilot plant and on comparison of the gas chromatograms using the chi-squared procedure.

CHAPTER 2

LITERATURE REVIEW

2.1 Mutagenicity Assessment of Drinking Water

Mutagenicity in bacteria is strongly correlated with carcinogenicity in animals, and presumably in man (Forster and Wilson, 1981). Mutagenicity is apparent by the induction of reverse mutations of histidine-requiring bacteria to histidine independence. This mutation is considered to be an indicator of genetic damage. (Direct-acting mutagens are those capable of causing mutations. Promutagens are mutagenic only after some degree or form of animal metabolism.) Certainly, some compounds mutagenic to bacteria are detoxified by mammalian metabolic pathways, but it is widely accepted that approximately 90% of carcinogenic compounds respond positively in the Ames Salmonella bioassay, a common initial screening test for mutagenicity.

Because of limitations in identification of chemical species in drinking water supplies, mutagenicity testing has been used as a screening technique. Mutagenic assessment provides a broad spectrum tool by which to define the need for more in-depth studies, and to show the existence of potential health effects where chemical testing fails.

Mutagenic activity was assessed in this study using the Ames test (Ames et al., 1975) as revised by Maron and Ames (1983). The method is described in Section 3.3.

This study concentrated on mutagenic effects as influenced by disinfection, but it is apparent that other treatment processes are influential. Monarca et al. (1983) cited sand filtration, granular activated carbon (GAC) filtration, and post chlorination as capable of substantially altering mutagenic activity in drinking water.

Raw water characteristics are highly variable and of great importance to drinking water mutagenicity results, as evidenced by the tremendous variability in relating raw water quality parameters to mutagenicity. Humic substance concentrations are certainly implicated. Huck (1986) reported increased mutagenicity during a spring-time peak of humic substance concentrations.

Prior to recent mutagenicity studies, chemical analyses such as total organic carbon (TOC), total organic halide (TOX), total trihalomethanes (TTHMs), and specific chemical tests were used to evaluate GAC performance as applied to drinking water (Monarca et al., 1983).

Mutagenically active compounds were known to exist among the large body of unidentifiable organic chemicals present. Monarca and co-workers carried out biological testing procedures on a drinking water plant in Cincinnati, Ohio, since this plant treated what was perceived to be a vulnerable surface water, potentially in need of full scale GAC filtration. From mutagenicity tests it was concluded that full scale GAC treatment removed direct-acting mutagens.

The same water facility provided the location for a study by Loper and co-workers (1985) in which water from on-line sampling was extracted onto XAD-2 resin and subjected to the Ames test. Sampling points included settled river water, chlorinated sand filtered water, and GAC-treated water. No mutagenicity was detected from settled water. It was therefore apparent that mutagenicity entering the GAC step was the product of chlorine disinfection. These workers found no mutagenicity after GAC, and also that this water, upon rechlorination, showed a greatly reduced potential for forming mutagenic compounds. Even when the GAC was exhausted in terms of TOC removal, it still maintained mutagen removal capability. Others have also found long-term effective mutagen removal with GAC (Van Hoof, 1983; Kruithof et al., 1985). Loper and co-workers demonstrated mutagenicity in all chlorinated water samples which had received only sand filtration. All of these waters became non-mutagenic after GAC treatment. They were then rechlorinated and stored for three days before distribution and still developed no detectable mutagenicity.

Kool and Van Kreijl (1984) of the Netherlands studied mutagenic effects of raw river waters compared to those of the same waters after processing for drinking supplies. They reported that mutagenicity of raw water usually required metabolic activation. That is, the causative compounds were promutagenic, requiring the presence of rat liver enzymes (S9 preparation). In contrast, they and others (Zoeteman et al., 1982) found the predominance of mutagenicity in treated water to be the result of direct-acting mutagens, those capable of causing reversions by themselves.

These workers found both chlorination and post chlorination to cause a strong increase in mutagenic activity, and even occasionally to convert a non-mutagenic water to a mutagenic one. Ozonation was proven by them to reduce mutagenicity except in one case where direct activity was slightly increased with Salmonella strain TA98. This strain appeared to be the most sensitive monitor for drinking water applications. It is possible that this strain exhibited mutational effects as a result of the more polar compounds formed in ozonation.

Also investigated by Kool and Van Kreijl (1984) were the effects of other processes in the water treatment train on the appearance of mutagenicity. Dune filtration and dune recharge greatly reduced mutagenic effects, but mutagenicity again increased after three week anaerobic storage. Longer storage caused a loss of this activity, which paralleled low TOC values. THM levels did not follow the same pattern, complicating the use of these chemical parameters as potential predictors of mutagenicity. Slow sand filtration could not be assessed accurately for mutagenicity since the XAD concentrates were toxic to the Ames Salmonella tester strains. Carbon filtration removed or reduced mutagenic activity except in one case of increased activity after passage through spent carbon (1.5 years use).

Seasonal fluctuations, such as those experienced by the pilot plant used in this study, cause water sources to vary broadly over a qualitative and quantitative range of organic background. Since the raw water provides the precursor pool from which mutagenic compounds can be formed, it is appropriate to consider a varying raw water organic matrix and seasonal effects on it. Grimm-Kibalo and co-workers (1981) studied river water in Des Moines, Iowa over a period of one year. Treatment at this site consisted of sand-gravel filtration and chemical treatment, including chlorination. The raw water source experienced urban input. Using predominantly TA98 and TA100, which they found to be the most sensitive, and in the absence of enzyme activation, mutagenic samples were found only in spring and summer and a lone incident in November. Mutagenic raw water was always accompanied by subsequent mutagenicity in the finished product. In contrast, mutagenic finished water was found where raw supplies were negative.

Quantitation of mutagenic activity was assessed by use of TA98 and TA100 after screening over several strains. Both the Grimm-Kibalo et al (1981) and the Kool (1984) studies found TA98 and TA100 to be most sensitive, as did Williams et al. (1982). Grimm-Kibalo et al attributed increases to agricultural runoff coincident with pesticide application and erosion, both exacerbated by heavy rains occurring during spring, summer, and early fall. The combination of this increased organic loading along with higher water temperatures enhanced formation of halogenated compounds with chlorination. Unexpected mutagenic episodes such as those in fall or winter water were thought to result from carryover of organics within the filter beds or from sporadic contamination of river water (Grimm-Kibalo et al., 1981). These theories could be applied to the North Saskatchewan River at Edmonton, or as well , many North American river systems.

2.2. Gas Chromatography

Gas chromatography (GC) involves the vaporization of a liquid sample followed by the separation of the gaseous components whereby they may be identified and quantitated (Sawyer and McCarty, 1978). The constant flow of carrier gas moves the volatilized components through a column. The gases travel at different rates because of chromatographic effects explained below. They emerge from the column at different times, and various detection methods are then employed. Detection occurs by chemical or physical means, and detector response is fed to a strip recorder, registering as peaks. Each peak is representative of a specific compound or mixture of compounds having the same rate of movement in the column. Specific to each compound, under constant conditions, is its retention time, the time for each to emerge from the column. Emergence is seen as a peak on the strip chart and area under the peak represents the quantity of that compound or mixture. Only those compounds which can be volatilized or can be converted to volatile compounds can be detected this way.

Chromatographic columns are glass or metal tubes packed with an inert solid impregnated with a nonvolatile liquid. As a gaseous sample passes through the column, its contents are partitioned between this stationary phase and the gas phase which carries it. Factors including the solubility of the compound in the liquid influence the partitioning of the compounds between the moving and stationary phase, resulting in different compound retention times. Suitable choices of stationary phases and column lengths provide separation of most gaseous materials in this manner.

Column temperature must be held appropriately high in order to maintain samples in the gaseous state throughout the time of movement along the column and subsequent detection. Types of commonly used detectors are: 1. thermal conductivity, 2. flame ionization, and 3. electron capture.

Mass spectrometry (MS) as an adjunct to GC provides identification and quantitation of compounds. The mass spectrometer separates charged gas ions and molecules according to their masses. A detector records the ions of different mass. Organic molecules can be "fingerprinted", each having a characteristic pattern of fragmentation. Comparison to known standards allows positive identification.

Gas chromatography provides a useful method for detection of trace organics in drinking water. Individual compound analysis over a wide range of raw water composition is a formidable task. A consistently reproducible method is required, and is provided by GC and GC/MS (Kool et al., 1982; Suffet, 1985).

Compound identification is facilitated by the especially effective combination of GC and MS (Harris and Kratochvil, 1981), and is virtually certain when mass spectra and retention characteristics agree with a known standard. Mass spectra libraries are expanding with respect to trace organics of drinking water. Other aids to identification are: 1. homologous series plots (net retention volumes vs number of—carbon atoms in the molecule) and 2. Kovats retention index (normal alkanes are assigned index values of 100 times the carbon number e.g. n-hexane is 600).

It is important with any identification procedures that the GC column and the experimental conditions remain constant.

Stevens et al. (1981) have studied GC/MS as an identifying procedure where raw water contains synthetic organic carbon (SOC), but also suggested that GC/FID profiles, the prominent analysis of this study, are useful to make comparative evaluations of water quality over a sequence of treatment processes or over time.

Since water samples generally contain low concentrations of organics, it is necessary to concentrate the samples prior to GC/MS. Recovery and elution techniques for this study have been reported in Section 3.1.

2.3. Interpretation of Complex Chromatograms

Gas chromatography, used in the chemical examination of drinking water, results in many cases in a large unmanageable amount of information. There may be great numbers of peaks present. When a large number of chromatograms must be compared, some procedure is required to quantitatively test for significant differences. Analysis of variance (ANOVA) is not an appropriate tool. Chromatograms are preferably divided into several retention time windows before analysis to provide more detailed information. There is no reason to expect that the number of peaks in each window would be the same and this would be a requirement for application of ANOVA. The chi-square (χ^2) statistic provides such a tool. A large amount of information is reduced to:

1. peak counts
2. calculation for difference
3. an objective statistical decision for similarity

(Gibs, 1983).

Fur identification efforts can then be focused on individual sample dates or locations which show the greatest deviation from usual conditions.

Chi-Square Analysis of Gas Chromatograms

The χ^2 distribution is used to test the deviation of a sample from an expected value. Under the null hypothesis, all chromatograms are the same, and so the number and size of peaks in each is identical. In applying the χ^2 procedure, the number of peaks in an individual chromatogram is compared to the overall average for all chromatograms. To facilitate analysis and provide more information, the chromatograms may be divided into several retention time "windows". The differences are tested for significance using χ^2. It is usual to reject the null hypothesis at the one or five percent level of significance (Kennedy and Neville, 1986).

Chi-square analysis has been used by others (Gibs, 1983) as a technique for comparing results of broad spectrum organic screening of drinking water samples. In samples for which the null hypothesis is rejected, that is, the χ^2 value exceeds the tabulated distribution value, then further organic analyses are indicated to identify the compounds which are different in that sample. One could then employ gas chromatography/mass spectrometry or other identification procedures. Compound testing, such as mutagenicity assays for a specific chemical, could be performed.

A restriction of the χ^2 statistic results from its high variability when the number of counts is low. An expected value of five per category is usually taken as the minimum (Gibs, 1983). Consequently, in this study χ^2 was not applied to post GAC water samples since the incidence of peaks was very small. Chi-square also loses applicability or validity if the calculated value is smaller than the number of degrees of freedom (Gibs, 1983). The application of χ^2 to samples of this study resulted in values shown in Chapter 5.

Prior to applying the χ^2 test, chromatograms were divided into four sections, the divisions based upon general compound classifications in respect to retention times (Daignault, 1986) as shown in Table 2.1.

Table 2.1. Compound Classification for χ^2 Analysis.*

Classification	Retention Time (minutes)	Compound Type
I	7.0 - 14.0	Primarily alkylated benzenes.
II	14.0 - 25.8	Resin artifacts, chlorobenzenes, phenols.
III	25.8 - 35.5	Primarily alkylated naphthalenes.
IV	35.5 - end	High molecular weight compounds, fatty acids, phthalates.

*The above classifications are general categories and are not to be construed as exact. However, given that caveat, they do provide markers by which to divide the chromatograms logically into several regions.

CHAPTER 3

METHODS

3.1 Sample Concentration, Elution and Workup

The following excerpt from the pilot plant final report (Huck, 1986) describes sampling and extract preparation:

"**Chemical Preparation**

Unless otherwise specified, all solvents used in this study were of ACS grade and were doubly distilled in glass in the laboratory using Vigreaux columns filled with Raschig rings. All water used for cleaning and preparations was distilled and then deionized using a Millipore Milli-Q® system. Glass wool used to hold the resin in the XAD-2 cartridges was cleaned by successively soaking it in acetone, hexane and then acetone again. It was found that after these three rinses a 15% (v/v) acetone in hexane extract of the wool produced a clean GC/FID profile. Sodium sulphate was heated to 500°C overnight. Nitrogen gas was pre-purified grade (Linde).

Resin Cartridge Preparation

XAD-2 resin was obtained from BDH Chemicals Canada Ltd. It was cleaned prior to use by first removing preservatives and fine particles with water and methanol (Rohm and Haas, 1978) and then by rinsing with acetone, methylene chloride and hexane according to the method proposed by Health and Welfare Canada (Williams, 1985). This resin was stored in acetone until use. Prior to packing the sampling cartridges, a final rinse with hexane followed by acetone was performed to remove any artifacts which may have been leached out of the resin during storage.

The stainless steel cartridge assembly design was based on a design provided by Health and Welfare Canada (Williams, 1985) and consisted of a pipe 3.5 cm in diameter and 40 cm long, with flanges welded at each end. The entire cartridge assembly was washed with Fisher "Sparkleen" detergent and water and then rinsed with acetone prior to packing. Each cartridge was packed with 350 mL of settled resin held in place by a glass wool plug, stainless steel screen (100 mesh) and teflon gasket on each end. About 0.5 L of acetone was passed through each cartridge, followed by 2-3 L of water to expel the acetone. About one hour later, another 0.5 L of water was passed through each cartridge and each was then sealed with stainless steel caps until use.

Sampling and Elution

The cartridges were taken to the pilot plant and inserted into the sampling ports. Routinely, water was sampled at 1 L/min for 24 hours, although initial runs and those during high turbidity conditions were only 12 hours long. Total flow through the cartridges was estimated using the run time and the average of the initial and final flow rate measurements. Flows at post-GAC positions remained constant throughout the run. Flows at the post filter position, however, decreased to about 0.8 - 0.9 L/min at the end of the 24 hour runs, because of the filtering effect of the resin and the higher turbidity of the water toward the end of these runs.

It had been originally planned to use the post-clarifier sampling point as a reference or control for all the disinfected samples. However once XAD-2 sampling began it was discovered that the post-clarifier turbidity was too high for this purpose. The resin became clogged and discoloured and flow was significantly restricted by the end of a sampling run. The fouling also raised doubts about the resin adsorption effectiveness under such conditions. It was therefore decided that the reference sample would be filtered before sampling. Initially, the reference sample was obtained by utilizing the idle ozone stream. A fifth stream containing only a dual media filter was installed and was used to obtain a non-disinfected reference or control sample for runs performed after March 6. The decision to sample only after filtration also meant that the sample points immediately following oxidant addition were not used during the study.

Cartridges were returned to the laboratory immediately after sampling and water remaining within the cartridge was drained with the aid of a slow flow of nitrogen. The cartridge was then filled with the eluant, 15% (v/v) acetone in hexane, and a small amount allowed to pass until the organic phase began to elute. Flow was then stopped and the solvent allowed to equilibrate with the resin for about 15 minutes. Elution was then resumed at a flow of about 10 mL/min and the entire 750 mL volume of eluant was collected in a separatory funnel. The aqueous layer was discarded and the organic layer dried with sodium sulphate and concentrated to approximately 20 mL by Kuderna Danish concentration. The sample was then made up to 25 mL with acetone and hexane by rinsing the Kuderna Danish glassware with elution solvent. It was necessary that the rinse solution contain acetone to dissolve precipitate which appeared in the Kuderna Danish apparatus as the acetone is quickly removed from the solvent mixture as an acetone/hexane azeotrope during the concentration procedure. 3.0 mL of this sample was retained for GC analysis. 10.0 mL of the sample was exchanged into dimethyl sulfoxide (DMSO) taking care that the sample never went dry. This portion was used for mutagenicity testing. The remaining 12 mL was further concentrated by gentle nitrogen flow to about 0.25 mL for GC/MS analysis.

Initially, the resin cartridges were regenerated by replacing the glass wool plugs, passing 750 mL of acetone through the cartridge and then expelling the acetone with water as discussed previously to ready the cartridge for another sampling. This method of regeneration was found to be inadequate for removing yellow-colored substances which generally loosely adhered to the resin used to sample post-filter positions. This discoloration appeared to be caused by the association of the alum floc with the resin, since sampling of higher turbidity water containing more floc produced more intensely colored resin. Most of the colored material could be removed from between the resin beads by stirring the resin in water, allowing it to settle, decanting the cloudy supernatant and repeating until the supernatant was clear. The alternate regeneration method used was as follows:

Immediately after elution, 200 mL of acetone was passed through the resin cartridge to rewet the resin.

This volume ensured contact of all the resin with acetone, as the void volume of the cartridge was about 150 mL. The cartridge was then stored while others were eluted until regeneration was possible (usually 1-2 days). The resin from all cartridges used for sampling post-filtration positions was then pooled and rinsed with water as described in the preceding paragraph. Next, resin from all the cartridges used in the sampling run was combined and mixed, resulting in a homogenized resin which was repacked into the cartridges. Fresh glass wool plugs were used, except for the cartridges used for sampling post-GAC positions. 0.5 L of acetone was then passed through the cartridges, followed by water to expel the acetone.

Elution Solvent Blank Preparation

While all solvents used in this study were doubly distilled, trace impurities could not be completely eliminated. Because the levels of impurities varied from batch to batch, and because several impurities were also found to be present as sample components, an eluant solvent blank was prepared for each sampling run. 750 mL of a solution of 15% acetone in hexane would be measured into a Kuderna-Danish flask and the solvent evaporated to a final volume of 25 mL. By comparing the solvent blank and sample chromatograms, substances present solely in the solvent and in both the solvent and sample were identified by their retention times and peak areas. GC/MS was then used to determine the chemical identities of these compounds."

3.2. GC and GC/MS Operating Conditions

Detailed GC and GC/MS methods have been reported elsewhere (Huck, 1986). The following excerpt briefly describes the procedures:

"All samples were analyzed by gas chromatography using an HP5890 gas chromatograph equipped with a 30 m × 0.25 mm DB-1 capillary column and flame ionization detector. The injector and detector temperatures were 225 and 300°C respectively and helium was used as the carrier gas at a flow rate of 1.5 mL/min measured at an oven temperature of 150°C. The oven was routinely temperature programmed as follows: initial temperature 35°C, hold 2 min, 3°C/min to 75°C, hold 3 min, 3°C/min to 90°C, hold 0 min, 5°C/min to 250°C and hold 5 min. One μL of sample was injected in splitless mode (purge-on after 30 sec) using the solvent wash technique with 1 μL dichloromethane as the solvent.

Some samples were also analyzed by gas chromatography/mass spectrometry (GC/MS). For this, a Varian 6000 gas chromatograph containing a 30 m × 0.25 mm

DB-1 capillary column was coupled to a VG Analytical 7070E mass spectrometer equipped with a VG system 11/250 data processing unit. The mass spectrometer was routinely operated in the electron ionization (EI) mode using a 70 eV source and was mass calibrated with perfluorokerosene before each use. The temperature of the GC injection port was 225°C and the helium carrier gas flow rate was nominally 1.5 mL/min. Oven temperature programming was adjusted as required to obtain the best component resolution and identification possible. The components of interest were tentatively identified by analysis of their mass spectra and by comparing these spectra to those of standard compounds stored in the library of the data system. Where possible, these identifications were substantiated by chromatographing commercially available standard compounds under routine GC conditions and by comparing the resulting chromatograms to those of the samples for retention time and peak shape. This gave identifications rated as 'confident'. If the sample was then rerun with the spectrometer in chemical ionization (CI) or accurate mass (AM) mode and the data were consistent with what was obtained previously, the identifications were rated as 'confirmed'. This rating system conforms to Environmental Science and Technology's suggested guidelines."

3.3. Mutagen Testing

The Ames Salmonella mutagenicity assay (Ames, 1975) was selected, using the procedure described by Maron and Ames (1983).

Four strains of *Salmonella typhimurium* were used: TA97, TA98, TA100 and TA102. Each strain contains a different type of mutation in the histidine operon (Maron and Ames, 1983; Hennig, 1984), thereby conferring a wider base of mutagenic susceptibility over the test series. The composition of strain TA102 is such that it is particularly sensitive to oxidative mutation, a characteristic beneficial to this study (Levin et al., 1982).

The negative control samples used were dimethyl sulfoxide (DMSO) and pH 7.0 sterile water. For positive controls, 2-aminoanthracene and benzo[a]pyrene were used, except for strain TA102, for which the positive control was mitomycin C. Supplementary positive controls used occasionally were 2-acetylaminofluorene and 2-nitrofluorene. Cell toxicity of a particular test compound in DMSO formed the basis by which to establish an appropriate dose range.

Huck et al. (1986) reported the following procedure:

"Cultures of the test strains used were incubated overnight in L-broth medium at 37°C in a waterbath shaker. For mutation induction, an aliquot of a particular test sample plus 0.5 mL of either the S9 mix, if required, or 0.1 M phosphate buffer (pH 7.4) were delivered into plastic tubes. In addition, 2.0 mL of soft agar which includes L-histidine and 0. 1 mL of a cell suspension of a test strain were added to each tube, the soft agar being held at 57°C and added just before the total contents were poured onto plates. The negative control tubes contained an appropriate volume of water or DMSO, instead of a test sample. The total volume of the contents and solvent concentration in each tube was maintained at a constant level for each experiment. The contents of each tube were then mixed on a vortex mixer and poured onto the surface of a plate containing Vogel-Bonner medium E. Plates were incubated at 37°C for about 48 hours.

For all experiments, unless otherwise noted, 100 μL of each sample was placed in the overlay [with or without the rat liver microsomal (S9) fraction], and immediately poured onto each plate. Four plates were used for each test. A positive mutagenic response was defined as a doubling or more of the number of revertants observed on the average of four plate counts when compared with the negative controls.

The preparation of S9 fraction was obtained from the Carcinogen Testing Laboratory, British Columbia Cancer Foundation. The mutagens used as positive controls were acquired from Sigma Chemicals, except for the 2-acetylaminofluorene which was obtained from Lancaster Synthesis Ltd."

CHAPTER 4

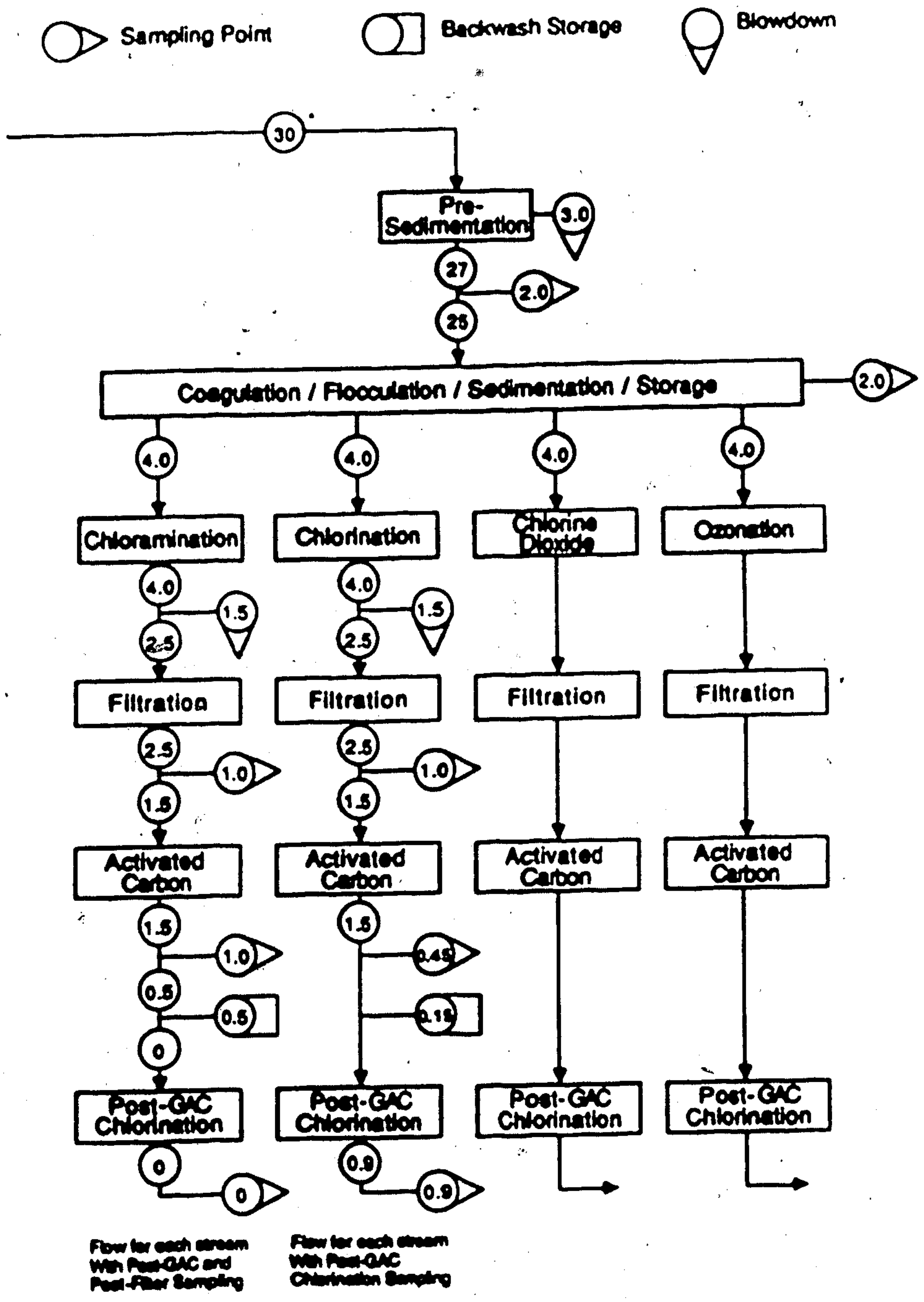
DESCRIPTION OF PILOT PLANT

4.1. Design

The pilot plant was designed to simulate typical North American surface water treatment practice with the addition of GAC. The pilot plant was housed on the fourth floor of the Recalcination Building, a facility located on the property of the Rossdale plant, one of two water treatment facilities in the City of Edmonton, Alberta. The plant is located in the center of the [illegible]ty such that the raw water may periodically contain runoff from some 85 storm sewer outlets (Hrudey, 1986).

Raw water for the city is provided by the North Saskatchewan River. Its headwaters arise on the Eastern slopes of the Rocky Mountains, passing through forested and parkland areas before reaching Edmonton 535 km easterly (Province of Alberta, 1986). This geographical area is covered in post-glacial till, and gives rise to surface waters containing relatively high sediment loadings. There are large annual temperature fluctuations which influence the raw water quality.

A block diagram (Figure 4.1) describes the pilot plant units and a process flowsheet for the pilot plant is



- Figures Indicate Flow in L/min.

Figure 4.1. Block diagram. Source: Huck, 1986.

shown in Figures 4.2 and 4.3. Design criteria were based generally on simulation of the Rossdale treatment process with the elimination of the softening step.

Process unit sizing was based on sampling requirements, with a progressively decreasing flow, such that almost no final effluent was produced. The XAD-2 resin cartridges, for which the design was provided by Health and Welfare Canada, required a flow rate of 1.0 - 1.1 L/min, approximately 1,500 L/day. For sizing purposes a flow rate of 2,000 L/day was chosen, and process units upstream of these were upscaled in accordance.

All materials that were exposed to process water were stainless steel, glass, or inert fluorocarbons. This conservative approach created some design challenges and added to expense, but was deemed necessary in order to avoid compromising test results by auto-contamination within the plant itself (Harris *et al.*, 1985). To protect each process from overloading, each was hydraulically limited at inlet. To accomplish this, overflow ports to waste were located along the system.

By progressively downsizing the subsequent units, cost was reduced while maintaining sufficient operational size to achieve reasonable simulation of full scale units.

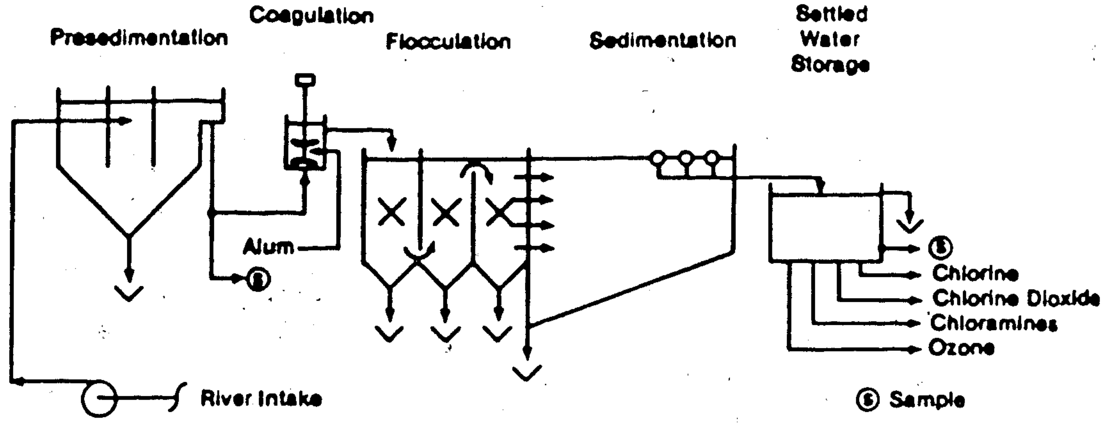


Figure 4.2. Simplified process flowsheet of pretreatment.
Source: Harris et al. (1985).

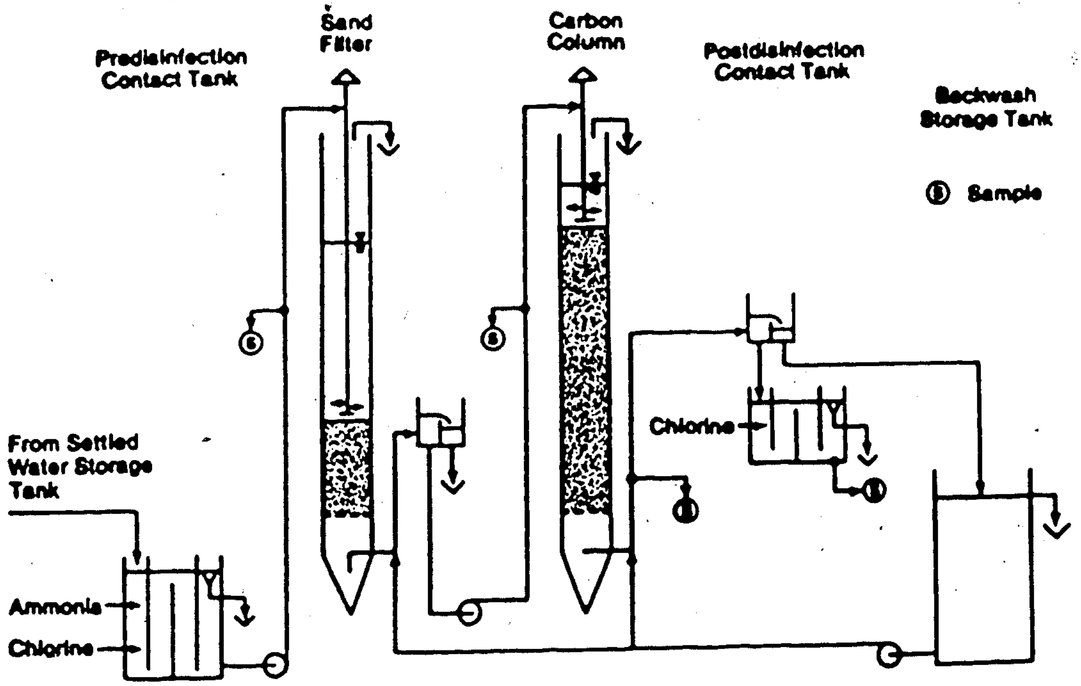


Figure 4.3. Simplified process flowsheet of chloramine disinfection/filtration (other streams are similar). Source: Harris et al. (1985).

4.1.1 Unit Descriptions (compiled from information contained in: Harris et al., 1985; Kellendonk, 1986; Huck et al., 1986)

Hydraulic parameters are given in Table 4.1.

Raw water supply

Pilot plant influent was pumped to the fourth floor by way of a 25 mm line drawing from the raw water supply of Rossdale #3 plant. The centrifugal raw water pump was preceeded by a filtering screen and followed by a pressure regulating valve.

Presedimentation tank

In consideration of the high silt loadings accompanying spring runoff, an inverted cone presettling tank was installed to protect subsequent units. This gravity settler was designed to remove silica particles greater than 0.5 mm diameter. A 10% continuous blowdown removed settled sludge.

Coagulant mixer

Liquid aluminum sulphate was pumped to a flash mixer immediately prior to mixing with gravity-fed raw water in a cylindrical chamber. A detention time of 18 seconds was achieved, accompanied by velocity gradients (GT) of 0 to greater than 300 sec^{-1}. A variable speed turbine turned impeller blades of opposite pitch on a center shaft;

Table 4.1. Pilot Plant Design Parameters.

Treatment Step	Parameter	Design Value
Presedimentation	Rise rate	5 cm/min
Coagulation	Detention time	18 s
	velocity gradient	variable
Flocculation	Detention time	45 min
rate	Velocity gradient	variable
Settled water storage	Detention time	15 min
Predisinfection contact tanks	Detention time	30 min
Dosage	variable*	
Filtration	Hydraulic loading rate	137 L/min/m^2
	Bed depth	
	- anthracite (d_{10}=1.0-1.1 mm)	450 mm
	- sand (d_{10}=0.35-0.45 mm)	300 mm
Granular activated carbon	Bed depth	1800 mm
(Filtrasorb 400)	Empty bed contact time	15 min
Postdisinfection contact tanks (chlorine in all streams)	Detention time	60 min (variable down to 20 min)
	Dosage	variable*

* To achieve the following residuals (after 30 min contact time, except 45 min for ozone): chloramine, 2.0 mg/L; chlorine 0.5 mg/L; chlorine dioxide, 0.5 mg/L; ozone, 0.5 mg/L. Source: Huck (1986).

mixing was enhanced by fixed baffles.

Flocculator

The alum-water mixture passed by gravity flow to a three-stage tapered flocculation system in a common tank; the sections were separated by baffles and each had a 60° sloped floor. Each compartment was equipped with four, four-bladed oppositely pitched propellers, a vari-speed turbine drive, and a manual blowdown valve. A factorial design was applied yielding GT values of $10^{4.5}$, $10^{4.1}$, and $10^{3.8}$ for water conditions at the outset of the analytical stage (cold, low turbidity winter water).

Hydraulic efficiency was indicated by rhodamine dye tracer tests which showed:

1. 81% dye recovery
2. a dispersion number of 0.158 by the method of Weber (1972).

Sedimentation

A perforated baffle allowed flocculated water to pass through to the cross-flow settling compartment. Ports were designed to enhance a smooth flow pattern and minimize floc-destroying shear.

Effluent withdrawal occurred via perforations in three pipe launders across the end of the clarifier.

Blowdown was automatically timed, and was initiated by adjustment of an electrically operated ball valve.

Sludge was collected by a perforated underdrain pipe lying along the bottom of the tank. Surface skimming was performed manually as necessary.

Settled water storage tank

Influent flow variations or blowdown effects of the flocculator/clarifier were hydraulically buffered by this open, rectangular unit. An overflow port carried excess water to waste in order to maintain consistent head. Severe flow reductions could be easily noticed, and downstream precautions were taken in such instances. Water from this point flowed by gravity in four equal streams (4 L/min) to the disinfection chambers, the point at which common treatment ceased.

Predisinfection contact tanks

Oxidant addition occurred along the influent pipe to disinfection tanks. Conditions approximating plug flow were achieved by around-the-end vertical baffles. Contact times of five to forty-five minutes were possible.

Ozone was generated by a Linde model SG4060 generator and fed to a 200 mm diameter by 2000 mm high stainless steel column through porous glass diffusers. Counter-current flow process water entered the column from the top where it was pumped from the settled water storage tank. Treated effluent flowed to a baffled chamber the same as the other three disinfection streams.

Filter feed pumps

Disinfected water was pumped to the top of the dual media filters by constant-speed centrifugal pumps with water contacting surfaces of Kynar® and ceramic. Throttling valves were adjusted manually to maintain flows of 2.5 L/min. Operator inspection of flow was facilitated by in-line orifice meters which registered approximate flow values on mercury filled glass U tubes fastened to the adjacent wall.

Dual media rapid sand filters

Glass tubing (150 mm ID) formed the walls of the 4.2 m glass filter columns. The three sections were joined by iron clamps, and cushioned by Teflon® gaskets. The base was tapered to a cone and was fitted with a backwash feed pipe. The base and central sections were connected by a flange clamp fastened to a steel support table. The column tops extended one meter through the cement ceiling slab and were housed in stainless steel enclosure boxes. The enclosures, as well as providing support and protection to the glass columns, permitted collection and drainage of spent backwash water.

Filter media consisted of 450 mm of anthracite coal on top of 300 mm of silica sand. This bed was supported by No. 100 stainless steel mesh held between perforated plates. Optimization of dual filter media included the selection of an intermediate size sand, having a uniformity coefficient of 1.5, and d_{10} and d_{60} respectively, of 0.45 and 0.64 mm.

To minimize turbulence at influent, the feed water was piped down inside the columns and emitted below the water line, close to the top of the filter bed. Effluent was pumped to collection tanks located in front of the columns and higher than the bed media to prevent air binding and negative h[illegible] the media. The effluent tanks were in equilibrium with overflow weirs to waste, providing smoothing of flow to the subsequent granular activated carbon (GAC) columns.

The hydraulic loading rate (winter) was 137 L/min/m^2 and the backwash flow rate (100% expansion) was 16,000 L/min/m^2.

Carbon column feed pumps

Water was pumped from the filter effluent weir boxes to the GAC filters by the same type of pumping system used for the filter feed pumps.

GAC columns

Design and operation was similar to the dual media filters. Carbon bed depth was 1.8 m of Filtrasorb 400 (Calgon Canada Ltd.). Empty bed contact time (EBCT) was 15 minutes at a loading rate of 88 L/min/m^2. Backwash bed expansion was 30%. Effluent was pumped to a weir box from which process water was divided between post disinfection contact chambers and backwash holding tanks.

Post disinfection contact tanks

These units were similar in configuration to, though smaller than, the predisinfection chambers. All four lines were disinfected with chlorine as NaOCl, simulating typical North American practice of providing oxidant residuals in the distribution system.

An adjustable overflow standpipe provided the means by which to control contact time.

Backwash water storage

Each stream terminated at a 400 L storage compartment, more than a sufficient quantity to enable 10 minute daily backwash of each dual media filter with effluent from its own stream. Two serial pumps provided power for backwash, the lines were flushed to avoid contamination between streams.

Sampling station

Gravity flow from the fourth floor pilot plant fed XAD-2 resin cartridges on the main floor of the Recalcination Building by way of eighteen stainless steel sampling lines. Flow through these lines during sampling runs was adjusted to 1.0 L/min by ball valves immediately above the cartridges.

Settled water filter

After plant operation commenced, it was found that alum carryover from the clarifier tended to blind the XAD resin, and did not provide a valid control sample without oxidant addition. In order to obtain a non-disinfected sample, a reference stream containing a filter of specifications similar to the dual media filters was installed and fed from the settled water storage tank.

Chemical feeds

Oxidants and alum were applied from 20 L glass carboys by valveless piston-type pumps constructed of Kynar®, Teflon®, and ceramic. Pump heads were fitted with 6 or 20 rpm drives, depending on the relative flow requirements. Pump calibrations permitted a graphical representation of pump setting vs feed rate, facilitating operator adjustment.

Chemicals used were:

1.chlorine, for prechlorination, chloramination, and postchlorination as aqueous sodium hypochlorite

2.ammonia for chloramination as aqueous ammonium sulphate

3.chlorine dioxide >98% pure, aqueous

4.ozone, generated from pure oxygen.

5. liquid alum as 48% by weight aluminum sulphate.

4.2. Operating History

4.2.1. General

Operations commenced along the treatment train as process units were completed. In June 1985, the raw water intake to the pilot plant was in working order, and water was fed to the presedimentation, coagulation, flocculation, and sedimentation chambers. Temporary water charges of newly-constructed units allowed for repair of leaks, and testing of flow requirements.

Construction and operation were severely hampered by dual media and GAC glass column fractures. Joint fittings were generally thought to be the source, but a contributing factor to glass damage could also have been the reverberations occurring within the Recalcination building itself. This facility housed large centrifuges for sludge concentration, and periodically the action of these caused the building to shake noticeably. Most breakages, fortunately, were repaired at the University glass shop, but the most severe required expensive replacements. Glass breakage plagued the project until January 1986, after which no further incidents occurred.

4.2.2. Hydraulics

Raw water was piped from a line just ahead of the intake for the Rossdale #3 plant. Consequently, flow changes or upsets at that location were reflected at the pilot plant. Rossdale #3 plant provides flexibility of reservoir levels for Rossdale, and consequently underwent flow decreases in winter months. Pilot plant intake could be severely reduced under these circumstances, in rare cases necessitating complete shutdown. Communications were established with main facility operators so that if dramatic flow reductions were anticipated, operators of the pilot plant could take precautionary measures. Dual media and GAC columns could be isolated by valve adjustments in order to keep the contents submerged during times of shutdown or insufficient flow.

Maintenance procedures at the Rossdale #3 plant were performed and also resulted in temporary inoperation at the pilot plant. Any of these upsets resulted in a few hours to 1-day operational interruptions.

A PAC spill into the pilot plant raw water supply occurred on April 10, 1986 as a result of maintenance procedures at #3 plant. Some carbon passed through the entire treatment process, but the major portion was diverted by stopping flow prior to the dual media filters and drawing off overflow from the settled water tanks. This was possible because design of the pilot plant provided operational flexibility in the by-passing, isolation, or stopping of flow at several process locations.

Reduced flow problems were also associated with malfunction of the pressure regulating valve. However, the problem peaked on February 28, 1986, and since this marked the beginning of a large runoff episode, it was attributed to sedimentation plugging of the valve. Subsequent installation of a raw water screen ahead of the pressure regulating valve, and frequent backflushing of this device served to smooth out future flow reductions.

Minor flow adjustments to the clarifier could be made by regulation of the underflow valve from the presedimentation unit.

Flow adjustments along the treatment train occurred at the following locations, and any change at one location resulted in the necessity to re-adjust all downstream locations:

1. influent PRV
2. presedimentation feed and underflow
3. flash-mixer feed
4. clarifier blowdown
5. pumps to dual media filters and effluents of these, including valve to waste
6. pumps to GAC columns and effluent valves
7. pumps to post-chlorination and backwash reservoirs
8. lines to the 18 sampling sites

4.2.3. Coagulation

Once optimization of the clarifier was achieved, the function of this unit remained quite stable. The tanks were emptied and cleaned approximately once a month to remove sludge buildup.

Rossdale feed rates of alum were closely followed, and adjusted to pilot plant specifications with regard to clarifier effluent turbidity.

Maintenance of the alum feed pump was a constant operational requirement. The liquid alum used was 650 mg/mL in concentration and precipitated rapidly, resulting in clogging of the pump and feed lines.

Coagulation optimization was required after the initial shakedown period, when actual hydraulic behavior was established. Excess alum carryover out of the clarifier resulted in blinding of the XAD resins. A 2^3 factorial design was employed for optimization. The variables were:

1. flocculator speeds
2. rapid mixing speed
3. alum dose

Efforts were concentrated on 1. and 2. above, since alum doses were established by following those of the full scale plant.

Clarifier effluent turbidity was reduced from about

10 NTU to 4-5 NTU, achieved by a rapid mixer speed of 180 rpm and flocculator speeds of 50, 25, and 15 rpm in the three consecutive chambers.

Coagulation performance during runoff episodes demanded constant adjustment of alum doses, and response time delays occasionally resulted in higher than optimal turbidities. This resulted in rapid filter head loss and necessitated more frequent backwashing.

4.2.4. Oxidants

Chlorine dioxide solution was generated on site in order to feed at the desired concentration, and because transport of this chemical can be hazardous (Masschelein, 1979). The Standard Methods (APHA, 1985) procedure was scaled up by a factor of 10 and this protocol provided many experimental challenges. The resulting procedure yielded ClO_2 consistently in the 2,000 mg/L concentration range. Pump settings were adjusted for different batch concentrations and progressive loss of ClO_2 from the disinfectant feed container. Both ClO_2 and NaOCl feed jars were kept dark to minimize oxidant losses due to light exposure.

Chemical feed pumps frequently broke down as a result of oxidant corrosion, and required maintenance, repair, or replacement on a regular basis.

The chloramine stream presented the least problems from an operational viewpoint, and adjustments for demand/residual fluctuations were the easiest to control.

Ozone disinfection presented many operational difficulties, and the ozone generator required almost exclusive attention from one operator during many periods of pilot plant operation, particularly around the times of sampling, when careful control of dose and residual was critical. The unit employed was on loan from the Department of Civil Engineering, and its capability exceeded the needs of the project. Consequently, a major problem existed in maintaining a feed low enough. Piping leaks, both interior and exterior, were frequently under repair in the early weeks of ozone treatment, and caused occasional shutdown of the generator. An oxidant monitor of the plant ambient air assured operator knowledge of leakage problems. The ozone line eventually functioned well after the initial trouble shooting activities. Valve and venting changes were made to the ozone contact system (a steel column), when gas transfer appeared to be a problem. Dr. R.G. Rice (Rice, 1985) suggested a glass contactor column for easy viewing of bubble activity, and this change may be a recommendation for future studies. In full scale ozonation many of the problems encountered would not exist, given the use of fully enclosed systems, and automatic feedback monitoring (LePage, 1985).

4.2.5. Dual media filters

The sand-anthracite filters were backwashed on the basis of three parameters:

1. 24 hours use
2. excessive head loss
3. effluent turbidity of >1.0 NTU if sampling run in progress.

Generally, backwashing was carried out once per day, but if one of the other conditions arose, a column was backwashed as required. Backwashing was performed serially on each filter for 10 minutes at 90-100% bed expansion, using finished water specific to each column. Airlocks were frequently encountered, and corrected by first running backwash and column water in turn to the waste stream.

Optimization of the dual media filter efficiency was performed to achieve filter runs of 24 hours and effluent turbidities of less than 1.0 NTU throughout the run. The results were as follows:

1. alum dose reduction did not lead to a sufficient decrease in turbidity and therefore was not employed
2. filter sand of a smaller size (20/40) meeting AWWA specification B-50 was substituted
3. the design flow rate of 3.2 $L/m^2/s$ was reduced to 2.3

$L/m^2/s$.

Filter life with respect to head loss became approximately 30 hours and effluent turbidities at 24 hours were normally maintained below 0.8 NTU.

4.2.6. Granular activated carbon filters

These columns were quite sensitive to flow reductions and occasionally had to be slightly backflushed to remove air entrained at the top. They were fully backwashed about once a week, at a relatively slow rate to achieve clearing of effluent without carbon loss. Maintenance of head over the filters required frequent adjustment of effluent valves.

4.2.7. Laboratory analyses

A significant portion of operator time, usually greater than 50%, was given to routine lab tests. Those analyses and measurements performed at the plant on a regular basis were:

Clarifier

1. Temperature
   - raw (measured at presedimentation tank)
   - post-clarifier (measured at settled water storage tank)

2. pH
    - raw
    - post-clarifier
3. Turbidity
    - raw
    - post-clarifier
4. Alum dose
5. Flow rate out of clarifier

Dual media filters

1. Turbidity
2. Head loss
3. Flow rate

Chlorine and chloramine streams

1. Free and total chlorine at three locations
2. Flow rates
3. Dosages of ammonia and chlorine

Chlorine dioxide stream

1. Chlorine dioxide speciation of the feed container
2. Chlorine dioxide speciation at three locations
3. Feed rate

Ozone

1. O_3 concentration at three locations
2. Dosage

Detailed operating data are to be found in the appendix.

Other operator functions included general plant maintenance, care of instrumentation, proper disposal of ClO_2 generation wastes, and preparation of reagents.

The pilot plant received some media attention, and was of interest to individuals associated with water treatment. Consequently, visitors appeared on a regular basis, and were shown the plant as time permitted.

4.3. Daily Operating Routine of Pilot Plant

Backflush PRV.

Check water levels in tanks and filter columns.

Call charge operator at Rossdale. Ask about: (a) that day's alum feed rate; (b) any flow changes to #3 plant.

Record the following, and the times performed:

Clarifier - these performed at least twice daily.

Raw and post-clarifier temperature, pH, and turbidity.

Measure flow rate out of clarifier - make adjustments

Calculate alum dose rate - adjust if necessary.

Check alum pump for clogging.

Comment on unusual circumstances.

Dual Media Filters - at least twice daily (before and after backwash)

Take samples for turbidity.

Measure headloss.

Check flowrates.

Backwash each column for ten minutes.

Chlorine and Chloramine lines - twice daily

(Sampling locations are described in Figure 4.4.)

Analyze 1-1, 1-2, 1-3, 2-1, 2-2, and 2-3 locations for free and total combined chlorine residuals.

Analyze 1-4, 2-4, 3-4, and 4-4 locations for above when post-disinfection is in operation.

Analyze NaOCl feed jar for free chlorine.

Calculate NH_3N and chlorine feed rates.

Adjust feed pumps as necessary to maintain appropriate residuals. Record pump settings.

Chlorine Dioxide line - at least twice daily

Perform ClO_2 speciation technique on following samples: ClO_2 collector bottle (feed jar), 3-1, 3-2, 3-3.

Ozone - once or twice daily

Analyze ozone residuals at 4-1, 4-2, 4-3, and direct generator collector flask.

Sample data sheets are given in Tables 4.2, 4.3, 4.4, 4.5, and 4.6

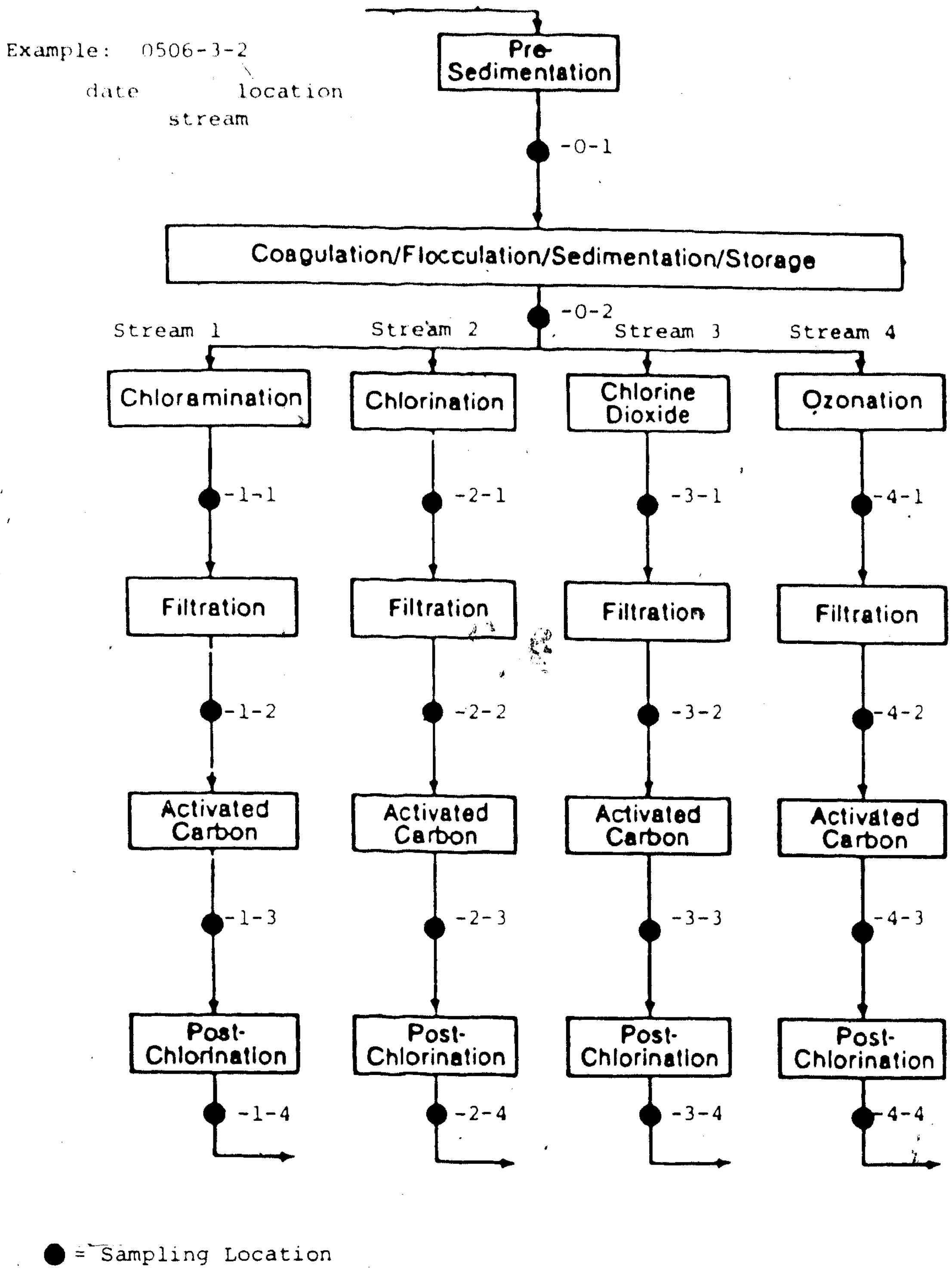


Figure 4.4. Sample numbering scheme. Source: Huck, 1986.

Table 4.2. Typical Clarifier Daily Log.

Date	Time	Temperature (°C)		pH		Flow (L/min)	Alum Dose (mg/L)	Turbidity (NTU)		Comments
		Raw	Post. Clar.	Raw	Post. Clar.			Raw	Post. Clar.	
Jan 20	0900	5.0	6.0	8.07	7.54	17.3	25	1.9	4.0	
	1600	5.0	6.0	8.07	7.54	17.6	24	1.9	3.8	
	1630	-*	-	-	-	-	-	-	-	drain & wash tank
Jan 21	-	-	-	-	-	-	-	-	-	clarifier run ran dry overnight
	1200	5.0	6.0	8.10	7.62	17.3	23	1.9	3.9	
	1600	5.0	6.0	8.09	7.63	17.3	-	1.9	3.5	
Jan 22	1020	5.0	6.2	8.08	7.71	17.3	-	4.5	4.7	
	1400	5.0	6.2	8.08	7.71	17.3	35	4.0	5.5	
	2030	5.0	6.2	8.10	7.62	17.8	39	4.2	4.9	adjust alum down to 170
Jan 23	0230	5.0	6.2	8.03	7.56	18.6	37	2.3	5.2	
Jan 24	0900	5.0	6.2	8.17	7.44	17.3		-	-	try repair today Tb meter down
	1150	5.0	6.2	8.17	7.44	17.3	36	4.0	4.2	adjust alum down to 150
Jan 25	0930	5.0	6.3	8.08	7.57	17.9	31	2.0	4.6	
	1500	5.5	6.5	8.14	7.69	18.5	30	1.8	3.9	increase underflow
	1615					23.6				increase underflow, adjust PRV down
	1645					17.0				

* - indicates no data.

Table 4.3. Typical Dual Media Filter Daily Log.

Date	Time	Filter #1			Filter #2			Filter #3			Filter #4		
		Tb (NTU)	FH* (cm)	Flow (L/min)	Tb (NTU)	FH (cm)	Flow (L/min)	Tb (NTU)	FH (cm)	Flow (L/min)	Tb (NTU)	FH (cm)	Flow (L/min)
Jan 27	0900	0.64	238		0.67	224		0.48	204		0.43	226	
	1130			bw**									
	1155						bw						
	1210									bw			
	1225												bw
	1345	0.37	120		0.46	120		0.43	115		0.52	120	
Jan 28	0900			bw									
	0920						bw						
	0940									bw			
	1000												bw
	1045	0.40	123	2.5	0.40	119	2.5	0.43	119	2.5	0.35	120	2.5
	2119	9.54	169	2.5	9.45	169	2.5	9.63	161	2.5	9.44	165	2.5
Jan 29	0900	0.90	260	2.5	0.85	250	2.5	0.79	242	2.5	0.82	250	2.5
Jan 30	0930	0.81	250		0.62	252		0.83	198		0.51	229	
	1015			bw									
	1030						bw						
	1045									bw			
	1105												bw
	1500	0.41	133		0.34	129		0.30	120		0.26	128	

* FH = filter head (cm).

** bw denotes backwash.

Table 4.4. Typical Chlorine and Chloramine Daily Log.

Date	Time	Line #	Ammonia[1] (mL/min)	Ammonia[1] (mg/L) as NH_3-N	Chlorine[2] (mL/min)	Chlorine[2] (mg/L)	Flow (L/min)	Residuals: Free Cl (mg/L)	Residuals: Combined Cl (mg/L)	Comments
Jan 28	2146	2 pf	0	0	0.127	1.54	4.0	0.50	0.20	decrease Cl pump to 119
		2 pf						0.59	0.13	
		2 pf						0.60	0.10	
		2 pd						0.68	0.25	
		2 pd						0.68	0.27	
	2310	1 pd	0.32	0.97	0.16	2.00	4.0	0.11	2.05	
		1 pd						0.12	2.08	
Jan 29	0940	1 pf						0.15	1.98	
		1 pf						0.13	2.01	
	1230	2 pf			0.124	1.56	4.0	0.54	0.21	
		2 pf						0.57	0.13	
Jan 30	0945	1 pg	0.32	0.97	0.16	2.00	4.0			
		1 pf						0.06	2.51	Should be ok when flow increases
		1 pd						0.03	2.63	
		2 pg			0.124	1.55	4.0	0	0	
		2 pf						0.62	0.78	
		2 pd						0.82	0.19	
Jan 31	0930	1 pg	0.32	0.97	0.16	2.00	4.0	0	0	
		1 pf						0.07	2.12	
		1 pd						0.05	2.25	
		2 pg			0.124	1.55	4.0	0	0	
		2 pf						0.76	0.03	decrease Cl pump to 118
		2 pd						0.87	0.12	

[1] $$[NH_3] = \frac{\text{pump flow rate } \left(\frac{\text{mL/min}}{1000}\right) \times \text{feed conc. } (NH_4)_2SO_4 \times 0.26}{q} = \text{mg/L}$$

[2] $$[Cl] = \frac{\text{pump flow rate } \left(\frac{\text{mL/min}}{1000}\right) \times \text{feed conc. Cl}}{(\text{L/min})} = \text{mg/L}$$

pH at all locations was done on test days

pd = -1 location, pf = -2 location, pg = -3 location

Table 4.5. Typical Chlorine Dioxide Daily Log.

Date	Time	Source **	Sample Vol (mL)	Titrant N	Vol* A (mL)	Vol B (mL)	Vol C (mL)	Vol D (mL)	ClO_2^- (mg/L)	ClO_2 (mg/L)	Cl_2 (mg/L)	Comments
Jan 28	1445	3 pg	200	.00564	0	0	0	0	0	0	0	O.K. (one only)
	1500	3 pd	200		0.53	2.42	0.02	0.80	0.38	0.77	0.12	
	1520	3 pd	200		0.50	2.30	0.04	0.57	6.27	0.82	0.07	redo old sample
	1550	3 pd	200	.00564	0.52	2.35	0.05	0.58	0.28	0.84	0.08	O.K.
	2110	3 pf	200	.00564	0.35	2.24	0.02	1.11	0.53	0.54	0.07	
					0.34	2.92	0.02	1.11	0.53	0.86	0.11	
	2145	3 pf	200		0.35	2.28	0.02	1.13	0.54	0.54	0.06	O.K.
	2230	3 pd	200									
	2320	3 pd	200		0.52	2.45	0.05	0.63	0.30	0.87	0.06	
Jan 29	1430	3 pf	200		0.40	2.39	0.02	0.90	0.43	0.71	0.03	Cl down 1 unit
Jan 30	1445	3 pf	200	.00564	0.38	2.41	0.06	1.16	0.55	0.6	0.07	
		3 pd	200	.00564	0.56	2.55	0.11	0.74	0.35	0.86	0.11	
NEW FEED BOTTLE at 1630												
Jan 31	1300	C.B.	2.0	0.1	0.46	1.75	0.01	0.04	33.7	1442	58	
	1330	3 pf	200	.00564	0.33	2.15	0.04	1.01	0.48	0.54	0.04	
	1400	3 pd	200		0.51	2.19	0.17	0.83	0.39	0.65	0.17	
	1430	3 pg	200	.00564	0	0	0	0				
February 1, 2, & 3 - pilot plant shut down due to problems within plant #3.												

* As per method of Aieta et al (1984).

** C.B. denotes collector bottle (i.e. feed solution). pd = -1 location, pf = -2 location, pg = -3 location

Table 4.6. Typical Ozone Daily Log.

Date	Time	Locat	Sample Vol	Absorbance @ 600 Δcm			O_3 (mg/L)	Titration (10 min)				Dose rate (mg/L)	pH	Flow Calib	Pres psi	Comments	
				Samp	Blank	Net		Vol A (mL)	Vol B (mL)	net (mL)	O_3[1] (mg/L)						
A 17	1020	4-1	50	.595	.854	.079	.332							7.08	72	8	flow up 74
		4-2	90	.774	.854	.079	.052							7.07	72	8	
		4-3	90	.802	.854	.052	.034							7.12	72	8	
		G	50					15.0	0	15.0	73.4		1.62		72	8	
	1045	4-1	50	.188	.833	.695	.768							6.80	72	8	
		4-2	90	.730	.833	.105	.060							6.82	72	8	
		4-3	90	.813	.833	.020	.020							6.97	72	8	
		G	50					12.9	0	12.9	63.1		1.45		72	8	
A 18	1715	4-1	90	.411	.839	.428	0.280										
		G/B	50					9.80	0	9.8	17.9		1.10		71	8	up 72
A 19 - O_2 line empty - no ozonation																	
A 21	0900	new bottle attached to system, set at 72													72	8	
	1300	4-1	90	.567	.834	.177	.119								72	8	requires set of flow up 75
A 22	1300	4-1	90	.795	.834	.039	.02								75		
		4-2	90	.834	.834	0	0										
		4-3	90	.840	.834	0	0										
	G							7.02			33.6		0.58		78		up to 78 overnight
	1330	shut down ozonator and look for leaks.															

[1] $O_3\ (\text{mg/L}) = \dfrac{59.52 \times \Delta A}{V}$; Dose rate $= \dfrac{O_3\ (\text{mg/L}) \times .90}{(10)(4)}$

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Typical Chromatograms

Data were generally classified by the three raw water types experienced throughout the study period:

1. Winter Water (December 5, 1985 to February 21, 1986)
2. Spring Thaw (February 28 to March 6, 1986)
3. Spring-Summer Water (March 19 to June 17, 1986)

Water conditions and some operating parameters are given in Table 5.1. It was expected that the spring thaw water would present the most difficult treatment challenges, as well as the "busiest" chromatograms. In contrast to winter water, it had consistently high turbidity and TOC levels.

Spring-summer water, while closer in nature to winter supplies, was subject to fluctuations brought about by mountain runoff and progressive snowmelt in the watershed.

The vulnerability of the Rossdale plant to urban runoff is noted by Figure 5.1, and has been documented by Hrudey (1986). This is particularly severe during spring runoff and results in an elevated concentration of extractable organics. Rural runoff co[illegible] high

Table 5.1. Characterization of Raw Water Types.

	Winter Water	Spring Thaw	Spring-Summer
Turbidity, NTU	< 3.0	7.5-25	<3.0*
TOC, mg/L	≈ 4	up to 16**	3-10*
Extractable organics, μg/L***	no results	up to 2,000	no results
Alum dose, mg/L	≈ 35	35-98	40-120
Chloramine dose, mg/L	1-2	1.6-3	2-5
Chlorine dose, mg/L	1-2	1.6-5	1-2.6
ClO_2 dose, mg/L	1-2	2.7-4.5	1-2
Ozone dose, mg/L	not operational	not operational	1.3-3.4

* These experienced surges with mountain snow melt at the end of May.

** Values up to 23 mg/L (DOC) were reported by Hrudey (1986) at the peak of spring runoff in March.

***Reported by Hrudey (1986).

Source: Pilot plant records (Huck, 1986), except as noted.

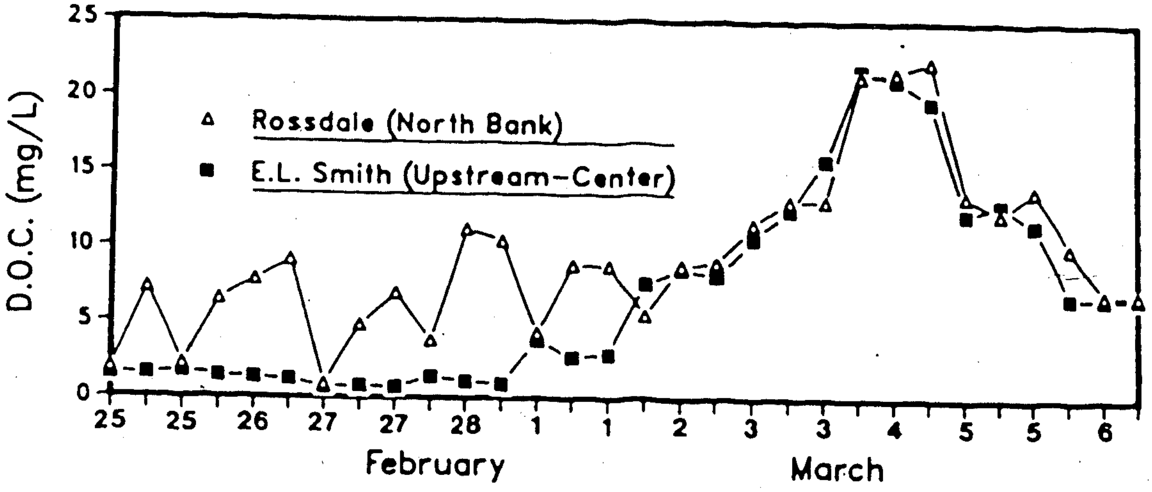


Figure 5.1. Dissolved organic carbon at water treatment plant intakes.

Source: Hrudey, 1986.

levels of humic substances (up to 23 mg/L DOC in 1986). Upon implementation of the primary recommendation of the Hrudey report (Hrudey, 1986), that is, relocation of the Rossdale intake, the elevated urban input to the downstream plant would not occur. Graphically Figure 5.1 illustrates the urban runoff DOC contribution to the Rossdale water supply, occurring immediately prior to the spring thaw peak beginning on March 1.

A typical reference stream sample chromatogram is shown in Figure 5.2. These "blank", or reference stream samples denoted by the (0-2) designation, had been processed by presedimentation, coagulation-clarification, and passage through the steel dual media filter.

Sample chromatograms at the (-2) location for each of the three water periods are shown in Figure 5.3. These had been exposed to oxidant treatment as well as the foregoing processes.

Figure 5.4 illustrates a typical post-GAC chromatogram, and as mentioned in Section 2.3, it is clear that there are insufficient peaks on which to perform chi-square analysis.

Chi-square calculations were based on peak numbers in four chromatographic regions. A sample chromatogram showing these divisions and their respective peak counts is shown in Figure 5.5.

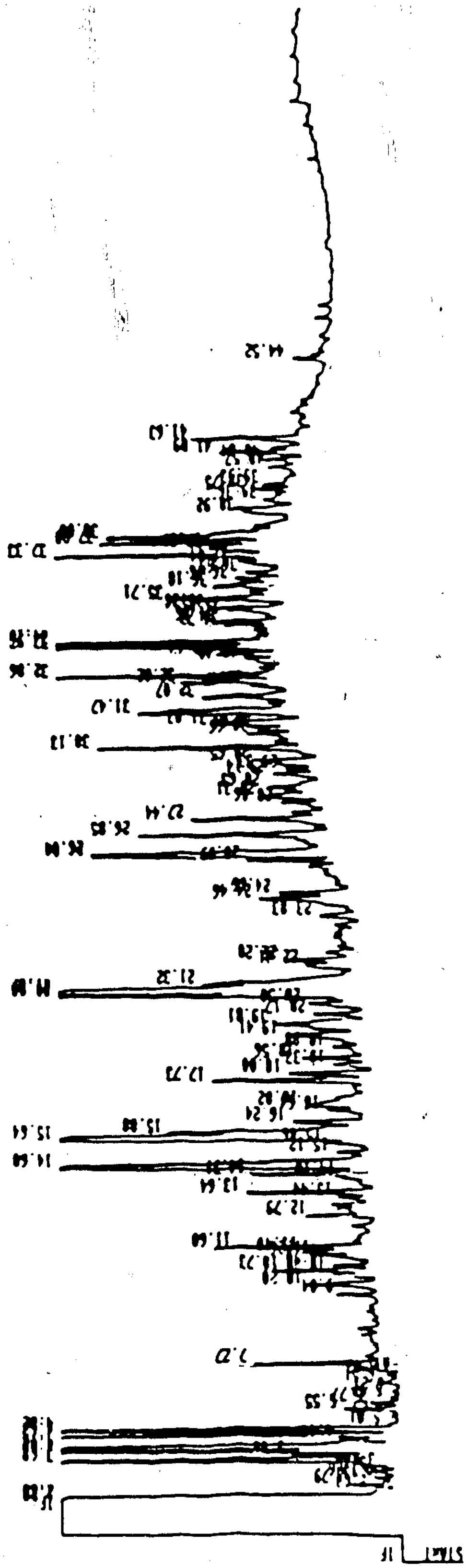
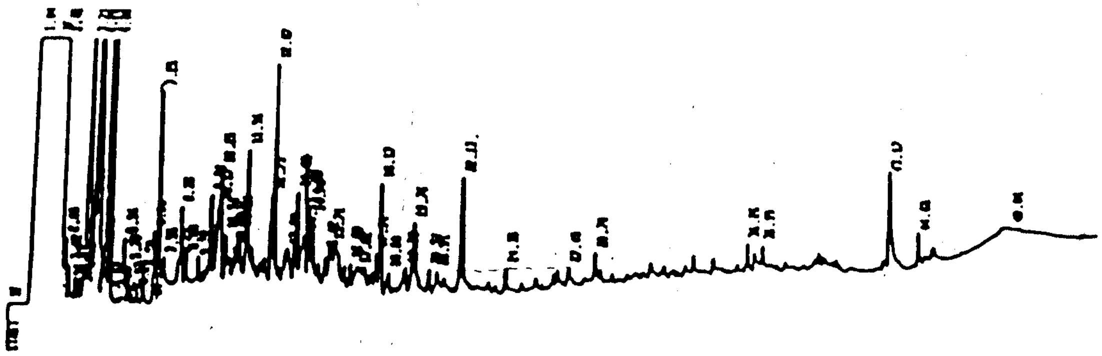
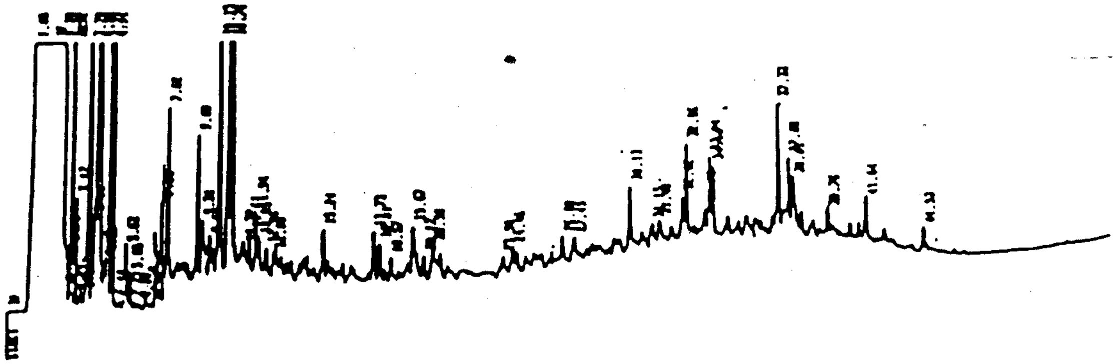


Figure 5.2. Sample chromatogram at (0-2) location, reference stream.



a. Winter



b. Spring Thaw

c. Spring-summer

Figure 5.3. Sample chromatograms at (-2) location

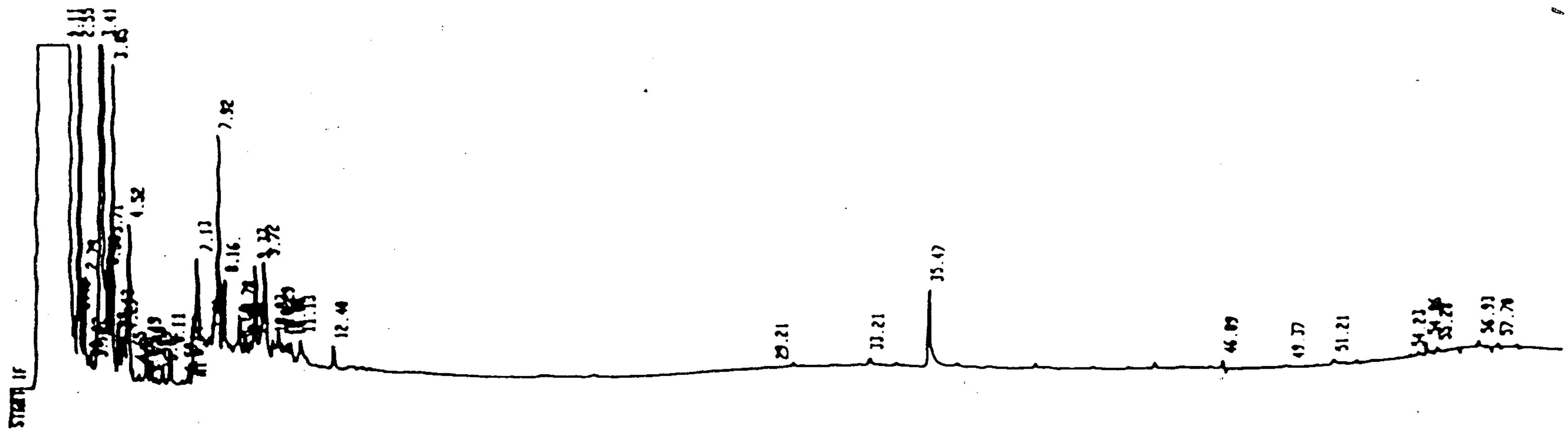


Figure 5.4. Sample chromatogram at (-3) location (post GAC).

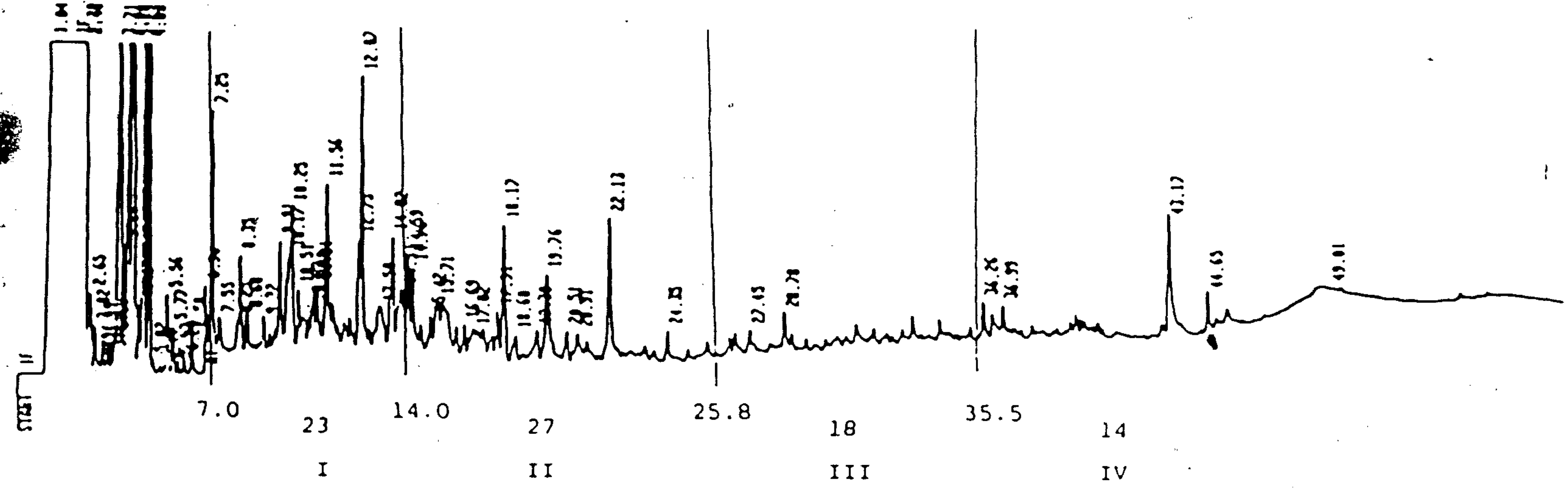


Figure 5.5. Sample chromatogram showing divisions I-IV and peak counts.

5.2. Chi-Square Analysis

Peak numbers in the divisions I to IV were counted, taking 1.5 mm as the minimum size for a peak to qualify. This peak height corresponds to approximately 0.06 mg/L of fluorene, the internal standard employed. This amount represents a concentrated sample. Raw water had been concentrated by a factor of 60,000 for a 24 hour sample. Some error exists as a result of blurred multiple peak areas, inconsistencies of internal standard peak height, and in the earlier chromatograms, the absence of an internal standard. Solvent impurities and resin artifacts are also present. It is to be stressed, therefore, that this method does not represent a quantitative assessment procedure but serves its purpose as a screening tool.

Tabulation of peak numbers follow in Tables 5.2-5.5. Average peak counts are given in Table 5.6.

5.2.1. Sample χ^2 Calculation

Chi-square was calculated from the peak counts in the following manner:

$$\chi^2 = \Sigma \frac{(O - E)^2}{E}$$

where O = the observed number of peaks in a division, i.e. the peak count.

E = The expected number of peaks in the same division in the reference sample. This was

Table 5.2. Chromatogram Peak Counts - Winter Water.

Date	Division			
	I	II	III	IV
0122-0-2	30	41	48	43
0128-0-2	28	24	18	3
0211-0-2	33	43	40	30
0220-0-2	26	29	20	20
x̄	29.2	34.2	31.5	24.0
0122-1-2	29	41	40	35
2-2	31	41	37	31
3-2	33	39	39	31
0128-1-2	21	26	17	14
2-2	31	33	24	17
3-2	29	24	24	22
0211-1-2	28	32	29	20
2-2	38	36	26	24
3-2	30	37	26	11
0220-1-2	23	27	18	14
2-2	33	27	18	16
3-2	26	24	16	9
x̄	29.3	32.2	26.2	20.3

Table 5.3. Chromatogram Peak Counts - Spring Thaw Water.

Date	Division			
	I	II	III	IV
0301-0-2	26	38	39	40
0304-0-2	27	42	36	38
0305-0-2	16	28	32	22
0306-0-2	23	31	33	34
x̄	23.0	34.8	35.0	33.5
0301-2-2	31	31	33	24
0304-2-2	31	32	32	30
0305-1-2	19	26	21	15
2-2	30	31	33	25
3-2	14	15	13	4
0306-1-2	20	33	19	18
2-2	29	41	37	39
3-2	26	30	21	17
x̄	25.0	29.9	26.1	21.5

Table 5.4. Chromatogram Peak Counts - Spring-Summer Water.

Date	Division			
	I	II	III	IV
0506-0-0	14	0	0	0
0521-0-0	9	1	7	3
x̄	11.5	0.5	3.5	1.5
0319-0-2	16	21	20	16
0402-0-2	19	24	3	10
0410-0-2	31	40	39	37
0416-0-2*	35	40	43	43
0429-0-2*	34	37	31	30
0506-0-2	34	25	25	22
0521-0-2*	9	1	5	6
0527-0-2	16	7	8	14
0617-0-2*	20	8	4	5
x̄	23.8	22.6	19.8	20.3
x̄ excluding *	23.2	23.4	19.0	19.8
0319-1-2	13	24	19	18
2-2	27	33	32	22
3-2	20	19	21	16
4-2	12	10	2	3
0402-1-2	22	31	18	27
2-2	28	29	18	13
3-2	27	31	15	17
4-2	17	21	7	4
0410-1-2	37	30	41	59
2-2	31	35	34	27
3-2	34	42	38	50
4-2	29	33	22	33
0506-1-2	36	29	30	17
2-2	32	29	25	20
3-2	31	31	31	26
4-2	29	26	24	19
0527-1-2	24	17	17	27
2-2	27	14	20	29
3-2	21	14	13	25
4-2	18	12	14	15
x̄	25.8	25.5	22.0	23.4

Values denoted by asterisk excluded since there were no corresponding post-filter samples on that day.

Table 5.5. Chromatogram Peak Counts - Spring-Summer Water (Post-chlorination Position).

Date	Division			
	I	II	III	IV
0416-1-4	16	8	1	3
2-4	30	15	7	6
3-4	29	14	7	6
4-4	[illegible]	18	7	8
0429-1-4	22	2	1	3
2-4	25	4	2	1
3-4	23	6	2	6
4-4	33	12	10	15
0506-1-4	27	8	7	3
0521-1-4	24	10	4	5
2-4	24	7	3	3
3-4	24	10	3	3
4-4	25	10	6	3
0617-1-4	26	7	5	14
2-4	19	10	6	5
3-4	21	6	6	6
4-4	19	7	4	3
$\bar{x}$	24.8	9.0	4.8	5.5

Table 5.6. Contingency Table for Reference Samples.

Water Type	Observed Value (0) by Division*				
	I	II	III	IV	$\bar{X}$
Winter	29.2	34.2	31.5	24.0	29.7
Spring Thaw	23.0	34.8	35.0	33.5	31.6
Spring-Summer	23.2	23.4	19.0	19.8	21.4
Average (E)	25.1	30.8	28.5	25.8	27.6

[*] Average of 0-2 samples in that time period.

derived from an average of all the blanks of each water type for that division, or another average as noted in subsequent statistical tests.

For example, if E = 26.1 and O = 29, (O [illegible] E [illegible]0.322, and this was summed with all the other values in that division and for the particular water type to yield χ^2.

5.3 Consistency of Raw Water with Respect to Time

Table 5.7 shows no significant variability at the 5% level in the reference (i.e. non-disinfected) samples when the average for each time period was compared to the appropriate divisional average over all time periods. However, the calculated χ^2 value is very close to being significant. Also, despite similar peak counts, other characteristics of the water (e.g. TOC, turbidity) were different in the three time periods as noted previously.

Chi-square values were then calculated for reference samples within each time period, comparing individual peak counts of the four divisions on each run date to the averages for a particular time period, in each division. Table 5.8 reveals significant variability within each period, the greatest occurring during winter and spring-summer. Larger variabilities that occurred within each

Table 5.7. $(O-E)^2/E$ for all Reference Samples. (Comparison of Average Values in Each Period to Overall Average)

Water Type	Division			
	I	II	III	IV
Winter	0.6697*	0.3753	0.3158	0.1256
Spring Thaw	0.1757	0.5195	1.4824	2.2981
Spring-Summer	0.1438	1.7779	3.1667	1.3953
E =	25.1	30.8	28.5	25.8

$\chi^2 = 12.446$: compare to 12.592**

---

*Values are $(O-E)^2/E$ for average peak count of each division in each time period.

**Tabulated value for χ^2 at six degrees of freedom, 95% confidence level (Kennedy and Neville, 1986).

Table 5.8. $(O-E)^2/E$ for Reference Samples in Each Time Period.

Date	Division			
	I	II	III	IV
Winter				
0122-0-2	0.0219	1.3520	8.6428	15.0417
0128-0-2	0.0493	3.0421	5.7857	18.3750
0211-0-2	0.4945	2.2643	2.2936	1.5000
0220-0-2	0.3507	0.7906	4.1984	0.6667
E =	29.2	34.2	31.5	24.0
χ^2 = 64.869: compare to 16.919*				
Spring thaw				
0301-0-2	0.3913	0.2942	0.4571	1.2612
0304-0-2	0.6956	1.4896	0.0286	0.6045
0305-0-2	2.1304	1.3287	4.8286	3.9478
0306-0-2	0	0.4149	0.1143	0.0075
E =	23.0	34.8	35.0	33.5
χ^2 = 17.994: compare to 16.919*				
Spring-summer				
0319-0-2	2.2345	0.2461	0.0526	0.7293
0402-0-2	0.7603	0.0154	13.4737	4.8505
0410-0-2	2.6224	11.7761	21.0526	14.9414
0506-0-2	5.0276	0.1094	1.8947	0.2444
0527-0-2	2.2345	11.4940	6.3684	1.6990
E =	23.2	23.4	19.0	19.8
χ^2 = 101.827: compare to 36.415*				

*Tabulated values for χ^2 at appropriate degrees of freedom, 95% confidence level.

time period were expected. The reasons for this were the same factors as those relating to disinfected samples, and are discussed in a subsequent section.

It may be expected then, in the ensuing χ^2 analyses, that statistics calculated within a time period will display greater variability than those calculated over all time periods.

5.4 Examination of χ^2 for Disinfected Streams

Various additions of the individual elements of the χ^2 summation permit different evaluations of the data. From the peak counts (contingency tables) individual $(O-E)^2/E$ values were calculated. Tables 5.9 - 5.12 show the individual elements ($(O-E)^2/E$) of the χ^2 summation. To test for significant changes over time and among the four streams, χ^2 was derived from individual summations of all the data for each time period. E values were divisional averages of non-disinfected (reference) samples. All comparisons were made at the 5% level of significance, corresponding to 95% probability of drawing the correct conclusion. Degrees of freedom were (R-1)(C-1)(S-1), where R, C and S represent rows, columns, and streams respectively and χ^2 was compared to values in Kennedy and Neville (1986).

Table 5.9. $(O-E)^2/E$ of Chromatogram Counts - Winter Water.

Date	Division			
	I	II	III	IV
E = $\bar{x}$ of blanks (non-disinfected samples)	29.2	34.2	31.5	24.0
	Individual χ^2 Values			
0122-1-2	0.0014	1.3520	2.2936	5.0417
2-2	0.1109	1.3520	0.9603	2.0417
3-2	0.4945	0.6737	1.7857	2.0417
0128-1-2	2.3027	1.9661	6.6746	4.1667
2-2	0.1109	0.0421	1.7857	2.0417
3-2	0.0014	3.0421	1.7857	0.1667
0211-1-2	0.0493	0.1415	0.1984	0.6667
2-2	2.6520	0.0947	0.9603	0
3-2	0.0219	0.2292	0.9603	7.0417
0220-1-2	1.3164	1.5158	5.7857	4.1667
2-2	0.4945	1.5158	5.7857	2.6667
3-2	0.3507	3.0421	7.6270	9.3750
Σ	7.9066	14.9671	36.6030	39.4170

Chi square = 98.894.

Compare to tabulated value of 28.869.

Degrees of freedom = (4-1)(4-1)(3-1) = 18.

Table 5.10. $(O-E)^2/E$ of Chromatogram Peak Counts - Spring Thaw Water

Date	Division			
	I	II	III	IV
E = $\bar{x}$ of blanks (non-disinfected samples)	23.0	34.8	35.0	33.5
	Individual χ^2 Values			
0301-2-2	2.7826	0.4149	0.1143	2.6940
0304-2-2	2.7826	0.22[illegible]	[illegible]2571	0.3657
0305-1-2	0.6956	2.2253	5.6000	10.2164
2-2	2.1304	0.4149	0.1143	2.1567
3-2	3.5217	11.2655	13.8286	25.9776
0306-1-2	0.3913	0.0931	7.3143	7.1716
2-2	1.5652	1.1046	0.1143	0.9030
3-2	0.3913	0.6620	5.6000	8.1269
Σ	14.2607	16.4056	32.9429	57.6119

Chi square for 0305 and 0306 = 111.585.

Compare to tabulated value of 12.592.

Degrees of freedom = 6.

Table 5.11. $(O-E)^2/E$ of Chromatogram Peak Counts - Spring-Summer Water.

Date	Division I	Division II	Division III	Division IV
E = $\bar{x}$ of blanks (non-disinfected samples)	23.8	22.6	19.8	20.3
	Individual χ^2 Values			
0319-1-2	4.9008	0.0867	0.0323	0.2606
2-2	0.4302	4.7858	7.5172	0.1424
3-2	0.6067	0.5734	0.0727	0.9108
4-2	5.8504	7.0248	16.0020	14.7434
0402-1-2	0.1361	3.1221	0.1636	2.2113
2-2	0.7411	1.8124	0.1636	2.2651
3-2	0.4302	3.1221	1.1636	0.5364
4-2	1.9428	0.1133	8.2747	13.0882
0410-1-2	7.3210	2.4230	22.6990	73.7778
2-2	2.1781	6.8035	10.1838	2.2113
3-2	4.3714	16.6531	16.7293	43.4527
4-2	1.1361	4.7858	0.2444	7.9453
0506-1-2	6.2538	1.8124	5.2545	0.5364
2-2	2.8252	1.8124	1.3656	0.0044
3-2	2.1782	3.1221	6.3354	1.6005
4-2	1.1361	0.5115	0.8909	0.0832
0527-1-2	0.0017	1.3876	0.3960	2.2113
2-2	0.4302	3.2726	0.0020	3.7286
3-2	0.3294	3.2726	2.3354	1.[illegible]
4-2	1.4134	4.9717	1.6990	1.3837
Σ	44.6129	71.4689	101.5250	172.18[illegible]6

Chi square = 389.788.

Compare to tabulated value of 59.703.

Degrees of freedom = 36.

Table 5.12. $(O-E)^2/E$ of Chromatogram Peak Counts - Spring-Summer Water (Post-chlorination).

Date	Division			
	I	II	III	IV
E = $\bar{x}$ of post-treatment peak averages	24.8	9.0	4.8	5.5
	Individual χ^2 Values			
0416-1-4	3.1226	0.1111	3.0083	1.1364
2-4	1.0903	4.0000	1.0083	0.0454
3-4	0.7113	2.7778	1.0083	0.0454
4-4	3.4129	9.0000	1.0083	1.1364
0429-1-4	0.3161	5.4444	3.0083	1.1364
2-4	0.0016	2.7778	1.6333	3.6818
3-4	0.1306	1.0000	1.6333	0.0454
4-4	2.7113	1.0000	5.6333	16.4091
0521-1-4	0.0258	0.1111	0.1333	0.0454
2-4	0.0258	0.4444	0.6750	1.1364
3-4	0.0258	0.1111	0.6750	1.1364
4-4	0.0016	0.1111	0.3000	1.1364
0617-1-4	0.0581	0.4444	0.0083	13.1364
2-4	1.3564	0.1111	0.3000	0.0454
3-4	0.5822	1.0000	0.3000	0.0454
4-4	1.3564	0.4444	0.1333	1.1364
Σ	14.9288	28.8887	20.4663	41.4545

Chi square = 105.738.

Compare to 40.113.

Degrees of freedom = 27.

Data for 0506 omitted since only one stream sampled.

1. *Winter water*. Differences were very significant. Although significant differences were not expected in this relatively stable water season, the deviations that occurred could be attributed to urban input or to brief runoff episodes.

2. *Spring thaw water*. For the [illegible] dates having a sufficient number of values to qualify for analysis, there was a significant difference.

3. *Spring-summer water*. A significant difference occurred.

4. *Spring-summer water (post chlorination)*. The values used for E were post-treatment peak averages and χ^2 was significantly greater than the tabulated value. However these must be interpreted with caution because of low E values in divisions III and IV.

The extremely large variability seen in the spring-summer water arises mainly from divisions III and IV, and confirms the tremendously changeable raw water matrix of this time period. Examination of Table 5.4 reveals markedly high and low peak counts, both of which correspond equally to relative degrees of variation from expected values.

Changes with respect to time and among the four streams are discussed separately in the next section.

5.5. Consistency of χ^2 Within Each Time Period

Tables 5.13 through 5.16 show how partial χ^2 values for each date are derived by the addition of the individual $(O-E)^2/E$ from Tables 5.9 through 5.12. Table 5.17 summarizes the findings of this type of data manipulation. Rather than comparison to critical values of χ^2 distribution, the partial chi squares are used qualitatively for purposes of comparison to each other, as done previously by others (Gibs, 1983; Suffet, 1985). E values were divisional averages for each time period.

Winter water exhibited the least amount of variability, as expected with its more stable raw water supply. An elevated variability on Feb. 20 was reflected by mutagenicity data of the same date where the reference stream and all three process streams prior to GAC were toxic to strain TA97 (without S9).

Spring thaw water showed partial χ^2 values more than twice as variable as winter water. For the complete test dates, March 5 and 6, there was reference stream toxicity, as was the case in most raw waters of the heavy runoff week. However, March 5 chlorinated water was mutagenic to strains TA97, TA98, and TA100 and was toxic to strain TA100 in the chloramine and chlorine dioxide lines.

Examination of Table 5.3 reveals that a major portion

Table 5.13. Grouping of Partial χ^2 Values by Date - Winter Water

	Division				
Date	I	II	III	IV	Total
0122	0.6068	3.3777	5.0396	9.1251	18.1492
0128	2.4150	5.0503	10.2460	6.3751	24.0864
0211	2.7232	0.4654	2.1190	7.7084	13.0160
0220	2.1616	6.0737	19.1984	16.2084	43.6421

Table 5.14. Grouping of Partial χ^2 Values by Date - Spring Thaw Water

	Division				
Date	I	II	III	IV	Total
0305	6.3477	13.9057	19.5429	38.35507	78.1470
0306	2.3478	1.8597	13.0286	16.2015	33.4376

Table 5.15. Grouping of Partial χ^2 Values by Date - Spring-Summer Water

	Division				
Date	I	II	III	IV	Total
0319	11.7881	12.4707	23.6242	16.0572	63.9402
0402	3.2502	8.1699	9.7655	18.1010	39.2866
0410	15.0066	30.6654	49.8565	127.3871	222.9156
0506	12.393	7.2584	13.8464	2.2245	35.7226
0527	2.1747	12.9045	4.4324	8.4118	27.9234

Table 5.16. Grouping of Partial χ^2 Values by Date - Spring-Summer Water (Post chlorination).

Date	Division				Total
	I	II	III	IV	
0416	8.3371	15.8889	6.0332	2.3636	32.6228
0429	3.1596	10.2222	11.9082	21.2727	46.5627
0521	0.0790	0.7777	1.7833	3.4546	6.0946
0617	3.3531	1.9999	0.7416	14.3636	20.4582

Table 5.17. Partial Chi-square for Sampling Dates.

Date	Partial χ^2	$\bar{x}$
Winter (-2 location)		
0122	18.1492	24.7
0128	24.0864	
0211	13.0160	
0220	43.6421	
Spring Thaw (-2 location)		
0305	78.1470	55.8
0306	33.4376	
Spring-Summer (-2 location)		
0319	63.9402	78.0 41.7*
0402	39.2866	
0410	222.9156	
0506	35.7226	
0527	27.9234	
Spring-Summer (-4 location)		
0416	32.6228	26.4
0429	46.5627	
0521	6.0946	
0617	20.4582	

*Excluding 0410.

of the March 5 variability resulted from low peak counts in the chlorine dioxide line. As a check, the chromatogram was repeated. Maintenance of an appropriate oxidant residual during the week of spring thaw required large increases in dosages. The chlorine dioxide dosage requirements peaked on March 4-5 (Table 5.18), more than quadrupling the usual amount. The large ClO_2 applications were probably responsible for the very substantial reduction in the number of chromatographable organic species, as organic substrates were removed. Reference water toxicity was usually removed by chlorine dioxide treatment, and could have been recreated in this case by large chlorite (ClO_2^-) residuals resulting from high oxidant dosages (Bull, 1982; Condie, 1986).

Spring-summer water variabilities are highest if the April 10 sample is included. Since this water was subjected to a rather unusual event, averages for partial χ^2 were calculated both with and without its inclusion. Tables 5.4 and 5.11 show very large variabilities occurring on April 10, particularly in the chloramine and chlorine dioxide lines. High peak counts were registered, but neither toxicity nor mutagenicity appeared. Raw water turbidity was high, 69 NTU; resulting from a spring melt episode. The pilot plant also experienced the presence of PAC in the raw water, caused by an accidental spill of PAC

Table 5.18. Oxidant Dosages for Pilot Plant During Spring Thaw.

Date	Line 1		Line 2	Line 3
	mg/L as chlorine	mg/L of NH_3-N	mg/L as chlorine	mg/L as ClO_2
Feb. 28/86	1.6*	1.0	1.5	1.0
Mar. 1/86	1.6	1.0	1.8	under repair
Mar. 2/86	2.3	1.0	2.2	re-start
Mar. 3/86	2.3	1.0	3.1	2.0
Mar. 4/86	2.9	1.0	5.0	4.5
Mar. 5/86	2.9	1.0	7.1	4.3
Mar. 6/86	2.9	1.0	4.9	2.7

*All dosages are average for the day.

at Rossdale Plant #3, which backed up into the raw water line. While it may be expected that the carbon could have "cleared" the chromatograms, the ensuing operational difficulties may have overridden such an effect.

In general, the rather erratic peak counts of spring-summer water result in greater statistical variabilities, and clearly reflect treatment challenges on the fluctuating raw water matrix.

Final chlorination of treated waters was operational during the spring-summer sampling period. Peak count variabilities were particularly prevalent on April 16 and 29, and accrued from both elevated and reduced peak counts, as well as a lone large contributor on June 17 at division IV in the chloramine line. A feasible explanation for these aberrations is difficult, unless they are again a function of the raw water organic matrix, possibly as a result of upstream contamination.

Post-chlorination peak counts, as seen by their averages in Table 5.5 are characterized by the largest number occurring in division I, with a sharp drop thereafter, levelling off to counts of about 5 for divisions III and IV.

5.6. Differences Among Oxidants

Individual elements of χ^2 summation, grouped according to oxidant stream, yield partial χ^2 values for comparison. E values were divisional averages of the reference streams. Table 5.19 relates to winter water, and shows clearly that divisions III and IV are much more strongly subject to variability. The chlorine stream shows the least variability. Looking at the peak counts in Table 5.2, it can be seen that chlorine counts are more consistent than the other two process lines, and also that variability usually arises from count elevations. Chloramine and chlorine dioxide streams show wider extremes of peak numbers and hence, greater variabilities. The largest variability of all the divisions occurred in division IV of the chlorine dioxide stream and the major contributors were two very low counts on Feb. 11 and 20. Chlorine dioxide dosages were not remarkable on these dates, but raw water and all three disinfected waters were toxic to Salmonella strain TA97 (without S9) on Feb. 20.

Table 5.20, describing spring thaw water samples, corroborates winter findings but the extremes are much wider. The chlorine stream, again, showed the least variability with very consistently elevated peak counts

Table 5.19. Grouping of Partial χ^2 Values by Oxidant Type - Winter Water.*

	Division				
Oxidant	I	II	III	IV	Total
Chloramine	3.6698	4.9754	14.9523	14.0418	37.6
Chlorine	3.3683	3.0046	9.4920	6.7501	22.6
Chlorine Dioxide	0.8685	6.9871	12.1587	18.6251	38.6

*Individual values taken from Table 5.9.

Table 5.20. Grouping of Partial χ^2 Values by Oxidant Type - Spring Thaw Water.*

	Division				
Oxidant	I	II	III	IV	Total
Chloramine	1.0869	2.3184	12.9143	17.3880	33.7
Chlorine	3.6956	1.5195	0.2286	3.0597	8.5
Chlorine Dioxide	3.9130	11.9275	19.4286	34.1045	69.4

*Individual values taken from Table 5.10.

the cause of all variability. The chlorine stream on March 5 was mutagenic to strains TA97 and TA100 (without S9) and on March 6 was toxic to both strains as well as mutagenic to TA97.

Both the chloramine and chlorine dioxide lines expressed toxicity on these dates. Their considerably higher variabilities resulted predominantly from low peak counts.

The reference stream toxicity and the high levels of oxidant application during this time period make interpretation of data rather difficult, but it can be seen from Table 5.3 that chlorination consistently produced higher numbers of chromatographable species. Toxic and mutagenic events in the chlorine stream were numerous throughout the spring thaw period (see Appendix 3).

Spring-summer waters were subjected to a fourth operating stream, that of ozonation. Table 5.21 shows the derivation of partial χ^2 values. Chromatograms of chlorinated samples continued to display the same relatively consistently elevated peak counts (Table 5.4) and again the lowest total variability along with the preponderance of mutagenicity.

The stream processed by chloramination showed the greatest variability in this time period in relation to

Table 5.21. Grouping of Partial χ^2 Values by Oxidant Type - Spring-Summer Water.*

	Division				
Oxidant	I	II	III	IV	Total
Chloramine	18.6134	8.8318	28.5454	78.9974	135.0
Chlorine	6.6084	18.4867	19.2322	8.3517	52.7
Chlorine Dioxide	7.9159	26.7433	26.6364	47.5886	108.9
Ozone	11.4788	17.4071	27.1110	37.2438	93.2

*Individual values taken from Table 5.11.

other disinfectants. This was the only line other than chlorine to exhibit mutagenicity, which occurred on May 27. Peak counts were quite unremarkable on this date, but plant records show there had been fluctuating raw water turbidities (up to 80 NTU) and noticeable color (probably humic substances) over several days. Both of these characteristics are common with snowmelt and agricultural runoff and followed an unseasonal snowfall the previous week.

5.7. Effects of Post-chlorination

Statistical analysis of chromatograms at the -4 location is shown in Table 5.22. Variabilities were not remarkably disparate, although ozone is the highest at 44.9. More than half of this value was contributed by the chromatogram of April 29 where peaks were greatly elevated over all divisions, most notably in division IV. The only apparent aberration accompanying this anomalous event was reference stream toxicity to TA97. Perhaps the offending species were not amenable to ozonation and remained in the water to provide precursors for the post-chlorination step.

Table 5.22. Grouping of Partial χ^2 Values by Oxidant Type - Spring-Summer Water (Post-chlorination Site).*

	Division				
Oxidant	I	II	III	IV	Total
Chloramine	3.5226	6.1110	6.1582	15.4546	31.2
Chlorine	2.4741	7.3333	3.6166	4.9090	18.3
Chlorine Dioxide	1.4499	4.8889	3.6166	1.2723	11.2
Ozone	7.4822	10.5555	7.0749	19.8183	44.9

*Individual values taken from Table 5.12.

5.8. Summary Comment

While χ^2 has allowed summarization and initial interpretation of large amounts of GC data, it represents only a semiquantitative analysis and is also based only on peak counts. The size of the peaks or their identity is not a factor in the analysis. While in many cases, anomalous peak counts correlated in this investigation to toxic or mutagenic events, the χ^2 analysis should be used as a means of focussing further analytical or identification efforts rather than as an end in itself.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

1. Average reference stream peak counts do not differ significantly from one time period to another, however, significant variability does occur within each sampling period.
2. Values of χ^2 were significant where date and stream data were summed. Part of this significance arose from inter-stream differences and part from aberrations on specific dates. The χ^2 statistic does not distinguish between these two sources.
3. Significant differences in χ^2 values occurred within each time period for each oxidant stream. This variability was due to both high and low peak counts.
4. Chromatograms of the chlorine disinfection stream prove this oxidant to be the most consistent in terms of peak counts. Closer evaluation shows this consistency to result largely from the sustaining of larger numbers of organic components.

5. Variations in peak counts were highest in the chromatogram divisions III and IV (the high molecular weight compounds).
6. The post-chlorination χ^2 values were most consistent in the chlorine dioxide stream where several very low peak counts were observed.
7. Mutagenic activity frequently accompanied episodes of high χ^2 variability.
8. The χ^2 statistical evaluation of gas chromatograms permits a broad spectrum analysis of temporal and unit process effects in drinking water treatment. It provides a simple but useful tool for the assessment of large quantities of data.

6.2. Recommendations

1. It would be useful to study the effects of ozonation over greater time periods, particularly to characterize chromatograms of the ozone stream during spring thaw.
2. Further studies are necessary to complete the annual cycle of all four oxidant streams.

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APPENDIX 1

TABULATION OF OPERATING HISTORY

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June 85	- equipment collection and ordering - plant was under construction (hydraulic, electrical) - raw water flow began to front-end units - ClO_2 generation system was being developed at University labs - problems arose with glass column fittings - study completed on safety procedures in use and generation of ClO_2 and O_3
July 85	- glass column fittings continued to leak and various sealing methods were sought - plant was operational through clarifier to settled water storage tank - design completed for resin cartridge sampling station - several changes made to optimize ClO_2 generation - on-site trial run of O_3 generator - plant construction continued

Aug. 85 - glass columns were caulked over Teflon tape, and caulking material was tested for organic leaching
- construction of sampling station continued
- ClO_2 generation produced desired concentration
- completion of electrical installations
- flow extended through all process units
- extensive testing of XAD-2 resin concentration and extraction techniques were performed

Sept. 85 - ClO_2 generation system was completed and speciation analyses begun
- a fume hood was installed adjacent to the pilot plant to provide a suitable on-site ClO_2 generating station
- tracer dye tests were conducted on the clarifier and predisinfection tanks to establish hydraulic characteristics
- chemical feed systems were installed

Oct. 85 - construction of ClO_2 generating station was completed
- continuous operation of processes up to the dual media filters was initiated
- dual media filter backwash procedures were

established

- a raw water screen was designed to prevent future damage to the raw water impeller after an incident in which a small rock was drawn into the raw water line
- meetings were conducted with Rossdale plant operators to enable them to perform certain off-hour inspections in the absence of University personnel. Pilot plant operators were scheduled to be on call if problems arose.
- excessively high turbidities complicated operations, and a 2^3 factorial design was applied to optimize flocculator, clarifier, and dual media filter effluents
- studies continued off-site on ClO_2 generation
- sample location identification was established

Nov. 85 - flocculator speeds were optimized to improve clarification to turbidities of 4.0 to 5.0 NTU in the clarifier effluent

- dual media filter performance was improved after experimentation, by flow reduction and the selection of a coarser sand size
- a post-filtration 12-hour XAD sample run was conducted

- a steel mesh stair-case was adjoined to the "porch", the elevated area outside the pilot plant room, and the location of the ClO_2 generation system
- a turbidimeter was borrowed from the City, and completed the pilot plant laboratory instrumentation requirements
- slight modifications were made to the Aieta (Aieta et al, 1984) ClO_2 speciation method
- chemical and physical tests were performed on the XAD resin to determine artifact effects with respect to leaching and bead breakage
- chromatograms done to date on sample runs were studied to distinguish sample and artifact peaks in future analyses

Dec. 85

- continuous operation of the chloramine and chlorine streams began, but was interrupted by a crack in one of the glass filter columns
- repair of the above was followed by XAD sample runs at the 1-2, 1-3, 2-2, and 2-3 locations
- ClO_2 generation began on-site
- oxidant residual values were tentatively established in consultation with City staff and Dr. Ben Lykins of the USEPA

- the carbon used to date was removed from the GAC columns
- the system was shut down and cleaned on December 23
- chemical tests continued on resin artifacts and solvent behavior

Jan. 86 - major plant clean-up
- continuous operation of the ClO_2 stream was initiated
- full start-up was delayed by another crack in a glass filter column. A design change was made to the support flange, and operations commenced January 13
- the GAC columns were charged with fresh carbon
- a stainless steel settled water filter column was installed to provide a blank sample free of alum carry-over
- the sampling frequency was increased to the maximum capacity of equipment and staff, in order to obtain a wider range of results
- sporadic flow decreases were attributed to maintenance procedures and operational changes at Rossdale #3 plant, which supplied raw water
- oxidant residuals were confirmed by the

principal investigator after discussions with Alberta Environment and the Scientific Authority. A primary operator function became the control of these levels throughout the effective six-month testing duration

- sampling times of 24 hours were established, except where poor raw water quality caused excessive turbidity and resultant fouling of XAD resins, when 12-hour runs were necessitated

Feb. 86 - several problems became apparent with the ozone generator, causing delay in start-up of the fourth treatment stream
- stainless steel settled water filter was tested and prepared for use
- plant operation was streamlined by the following:
- 1. change in dual media filter backwashing technique
- 2. change in pre-disinfection sampling technique
- 3. the acquisition and use of a Gilmont flowmeter for quick and accurate setting of cartridge flow rates
- four test runs were conducted; of these, two

were partial and supplementary to the schedule program in order to catch a heavy run-off condition

Mar. 86 - the ozone line was initiated and analyses begun for residual concentrations and generator output

- a vent, suspended over the length of the pre-disinfection chambers, was installed
- five XAD runs were performed
- sampling for TOC, TOX, coliforms, and standard plate counts was adopted as regular procedure
- ozone generation was problematical with respect to leaks, production levels, gas flow rates, and contactor performance. One operator spent a large portion of time managing these difficulties in order to maintain the sampling schedule.
- operator time requirements were considerably heavier with increased test runs, so weekend duties were reduced to essentials. Rossdale operating staff were very helpful during several weeks when they back-flushed the pilot plant raw water screen, sometimes as often as 4-hourly

- freeze-thaw weather patterns created a wide diversity of raw water quality, and consequently some very challenging operational manoeuvers

Apr. 86
- post-disinfection units were brought into operation and sampling began at this location
- ozone dosing was optimized and changes were made in production practices
- project members attended the Second National Conference on Drinking Water
- Conference participants were given tours of the pilot plant
- two members of the project team presented papers to the Conference, describing the plant and such results available to date
- four XAD sampling runs were conducted

May 86
- the ozone residual analysis method was changed
- mountain snow melt and rural run-off created excessively high raw water turbidities and required large alum doses
- three XAD sampling runs were conducted

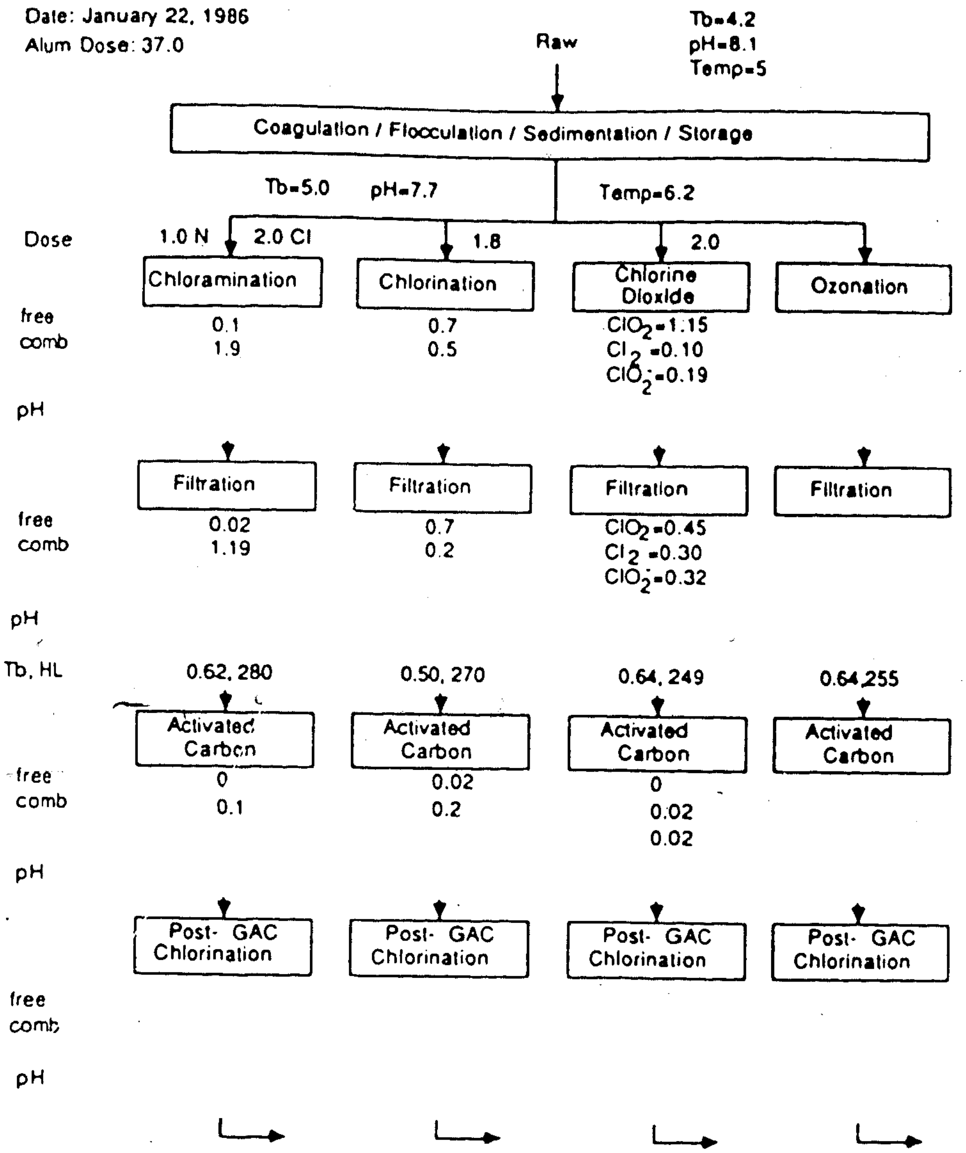
June 86 - one XAD sampling run was conducted
- hydraulic characteristics were re-examined by the performance of tracer dye studies
- chemical analyses were conducted as soon as possible considering the relocation of the Environmental Engineering laboratories
- extensive cleaning and shutdown procedures were carried out
- project members prepared final reports
- the principal investigator was awarded funding from the AWWA Research Foundation to conduct a phase II study utilizing the existing plant facilities

APPENDIX 2

DETAILED OPERATING DATA FROM PILOT PLANT

Source: Huck, 1986

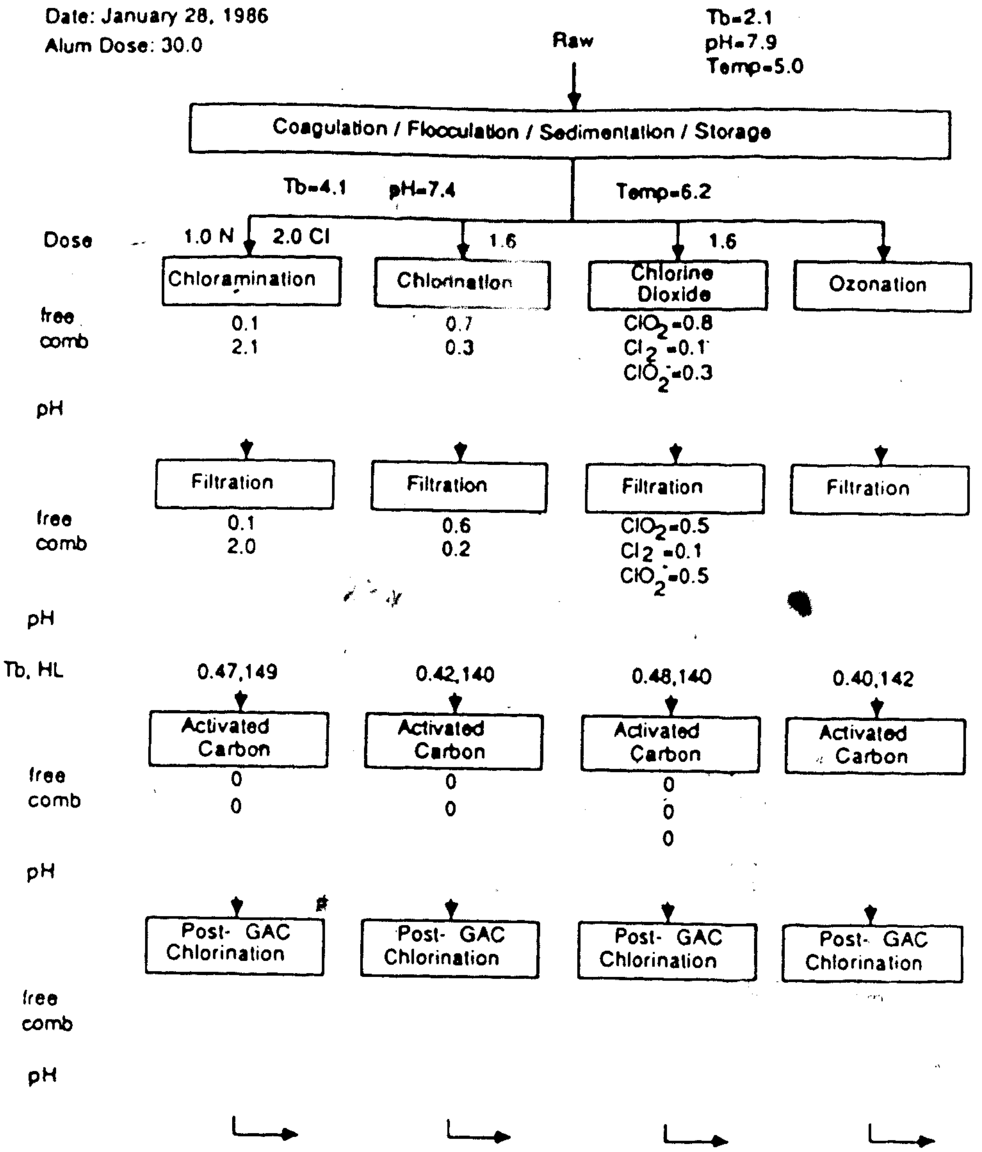
(tabulated by the author of this thesis)



Notes: pH 7.6 throughout after disinfectant addition

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

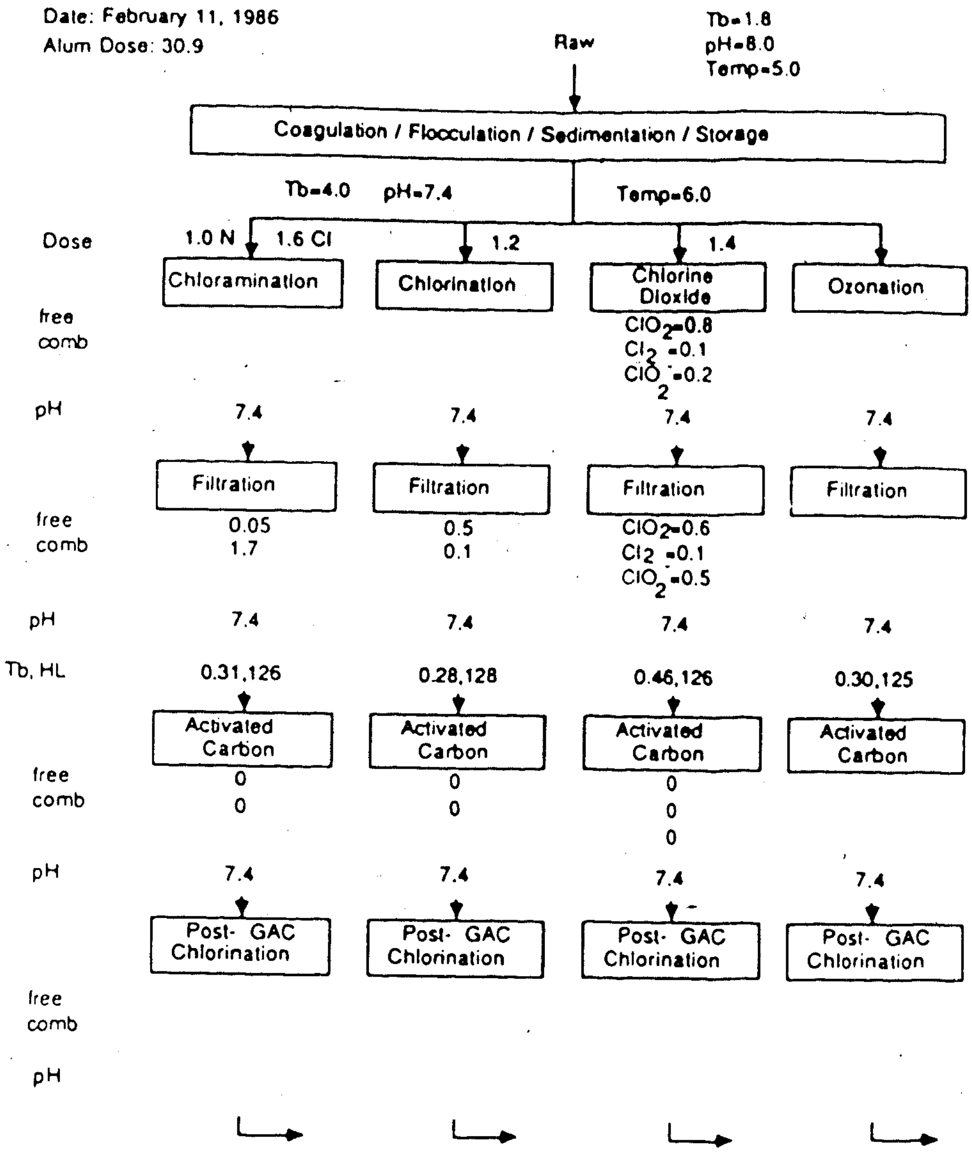
Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss



Notes:

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss

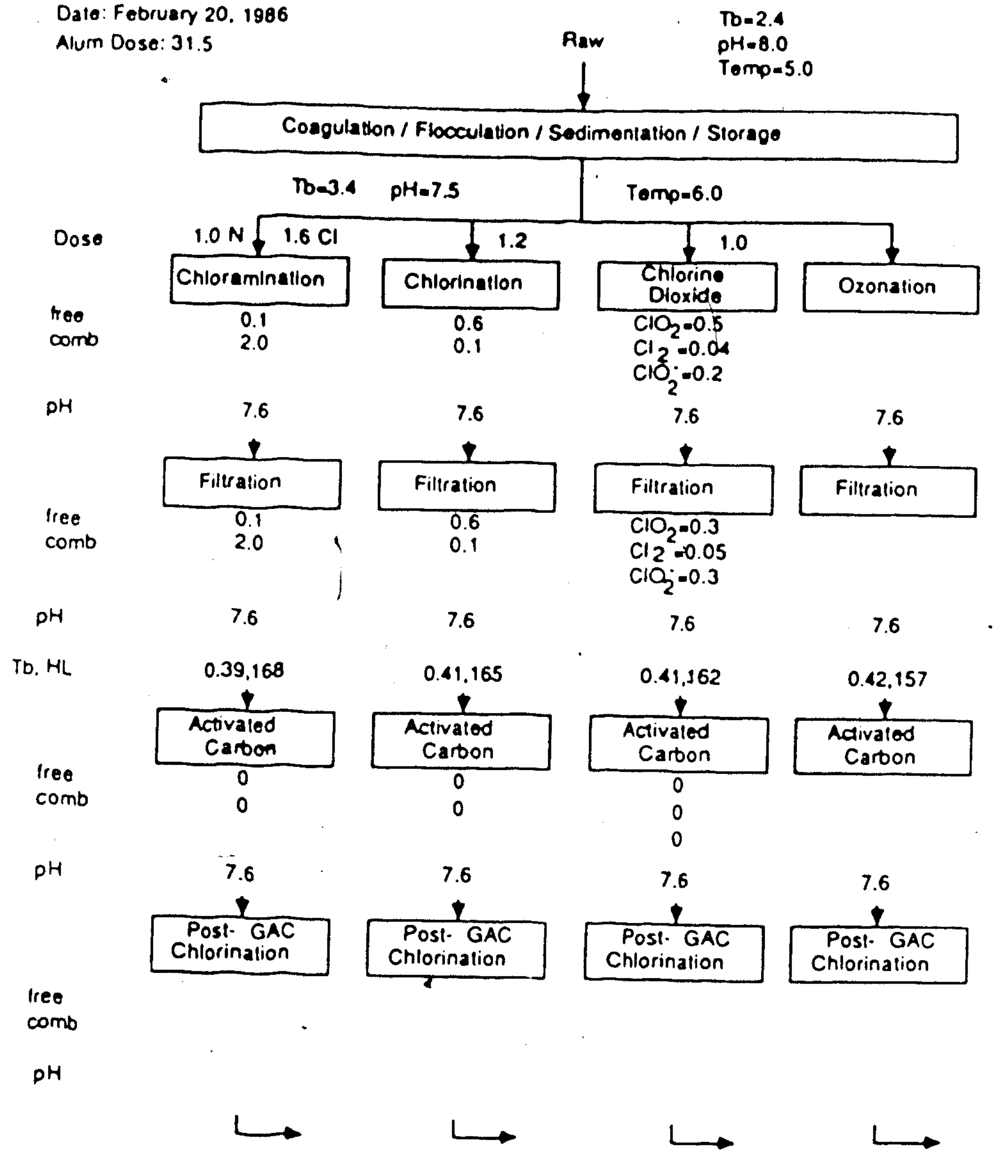


Notes:

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss

Date: February 20, 1986
Alum Dose: 31.5

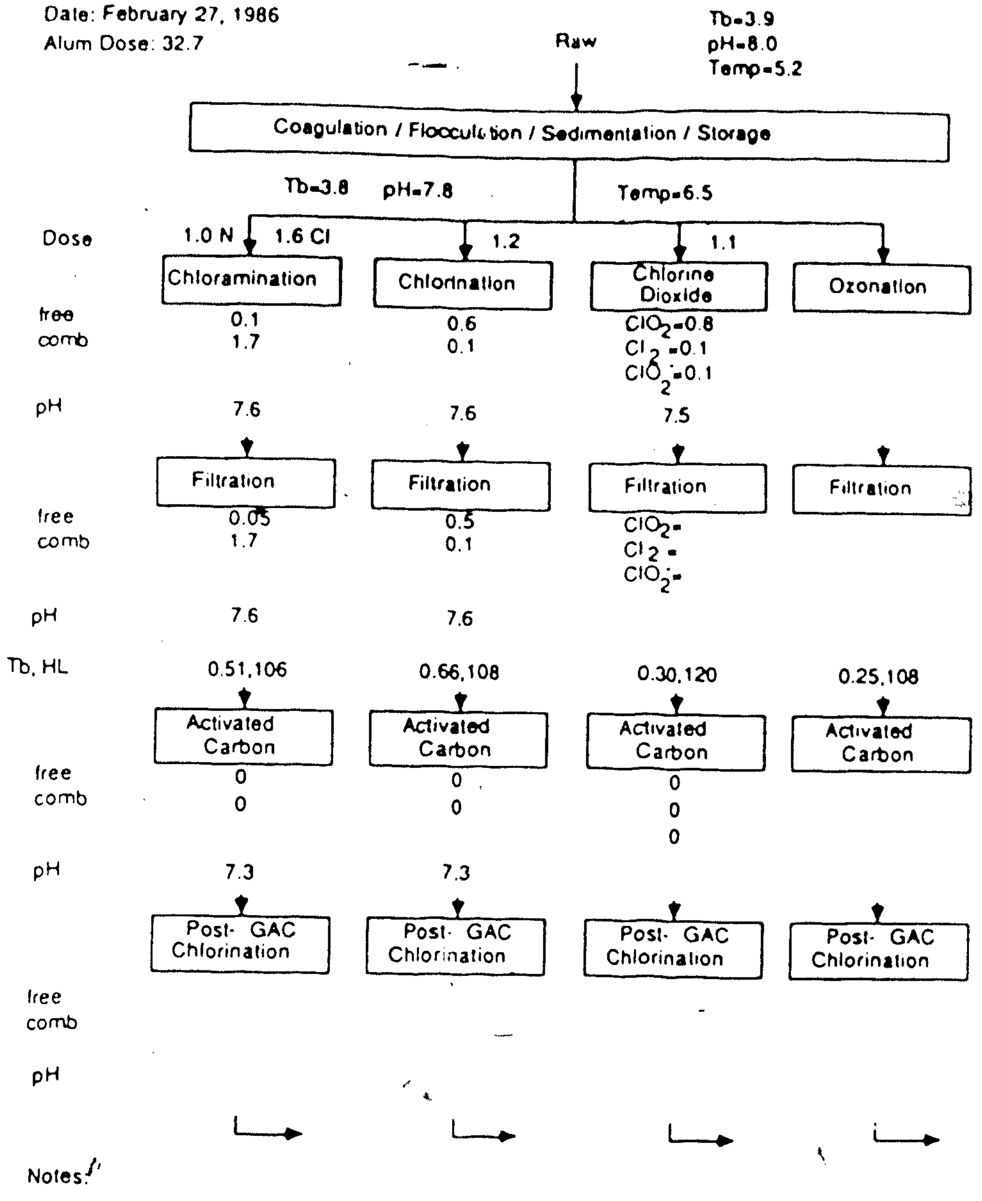


Notes: serious decrease in raw water flow occurred during run

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss

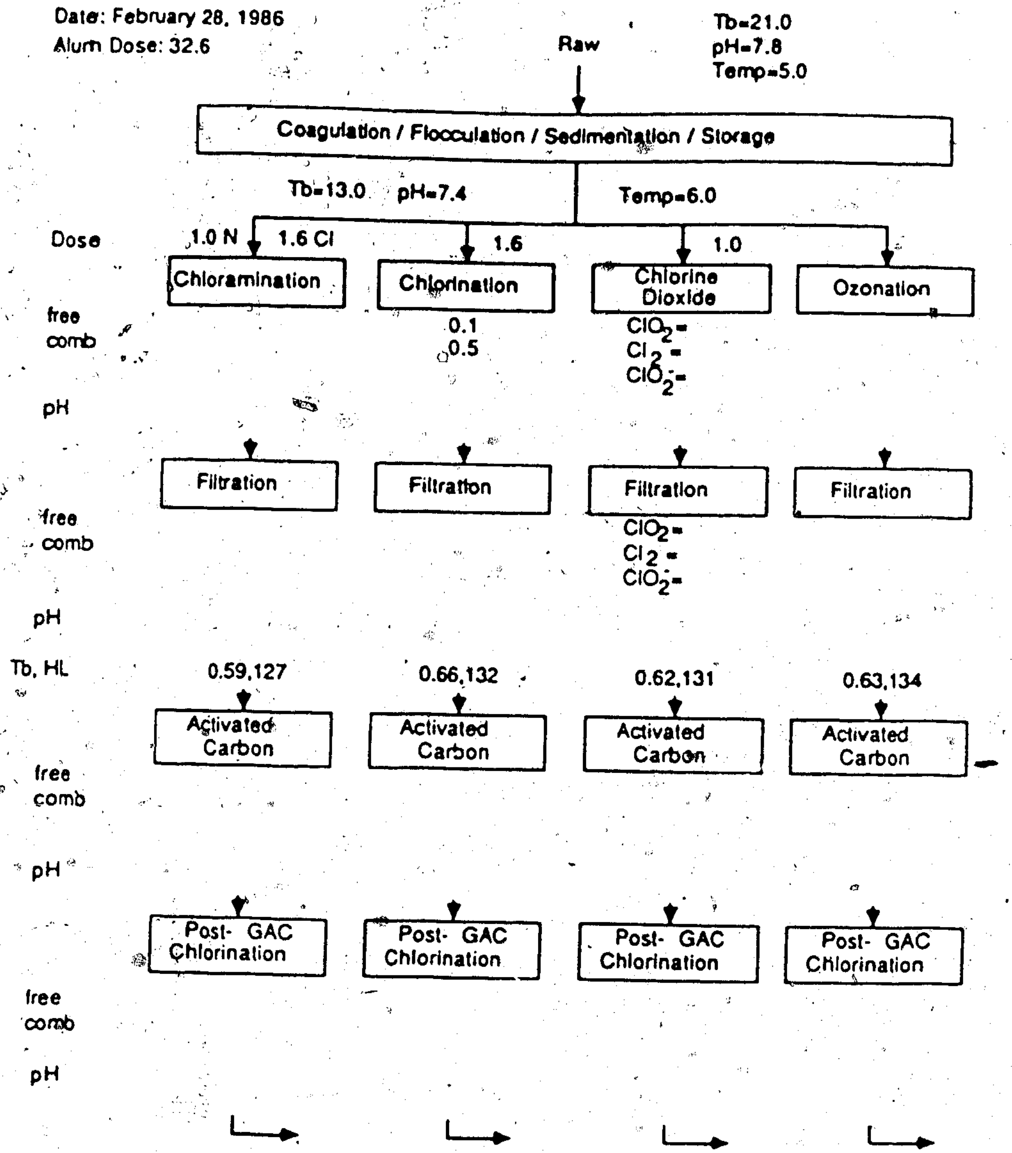
Date: February 27, 1986
Alum Dose: 32.7



Notes:

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss

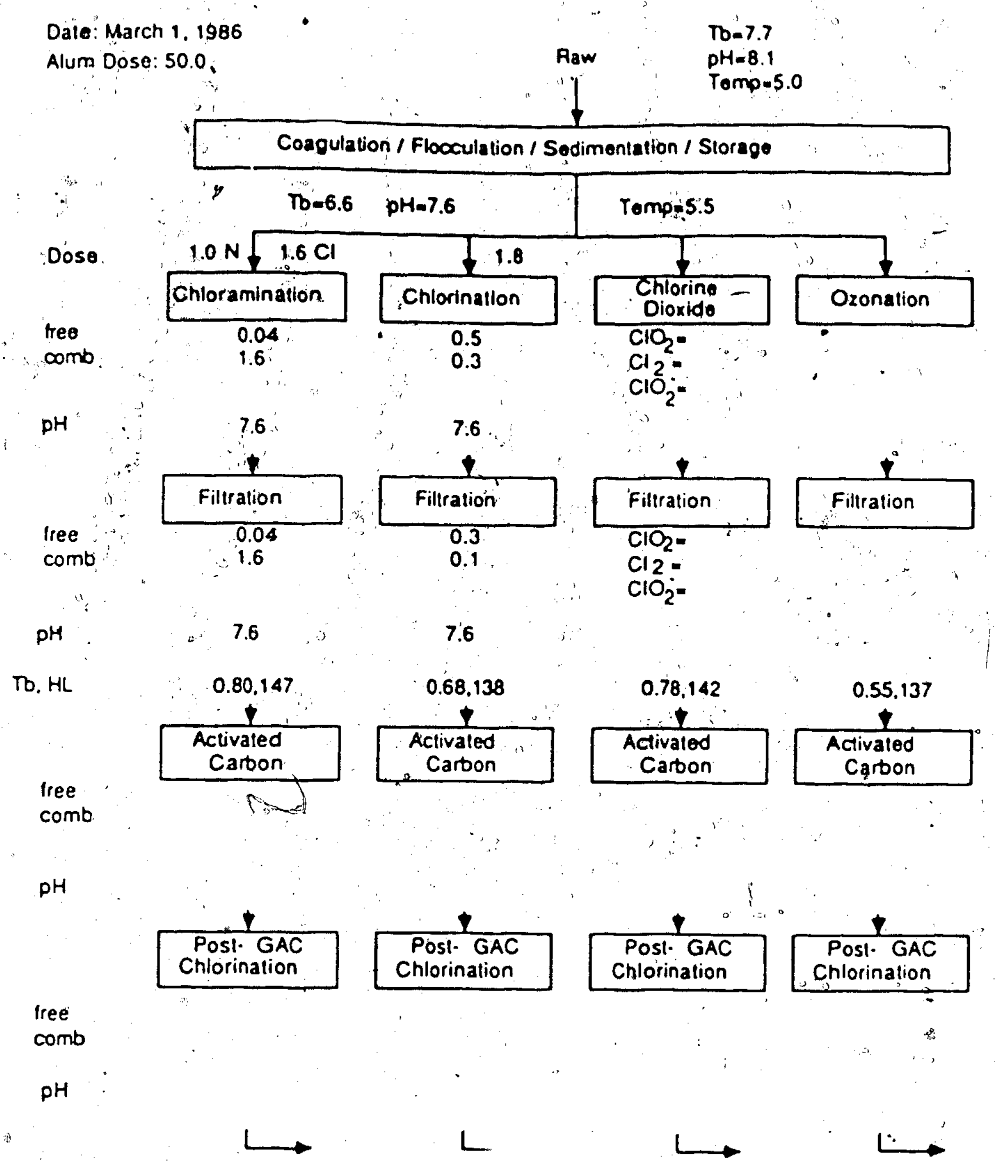


Notes: power failure early in the day, only chlorine line tested for evening run
flow reduction problem, run-off situation occurred

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss

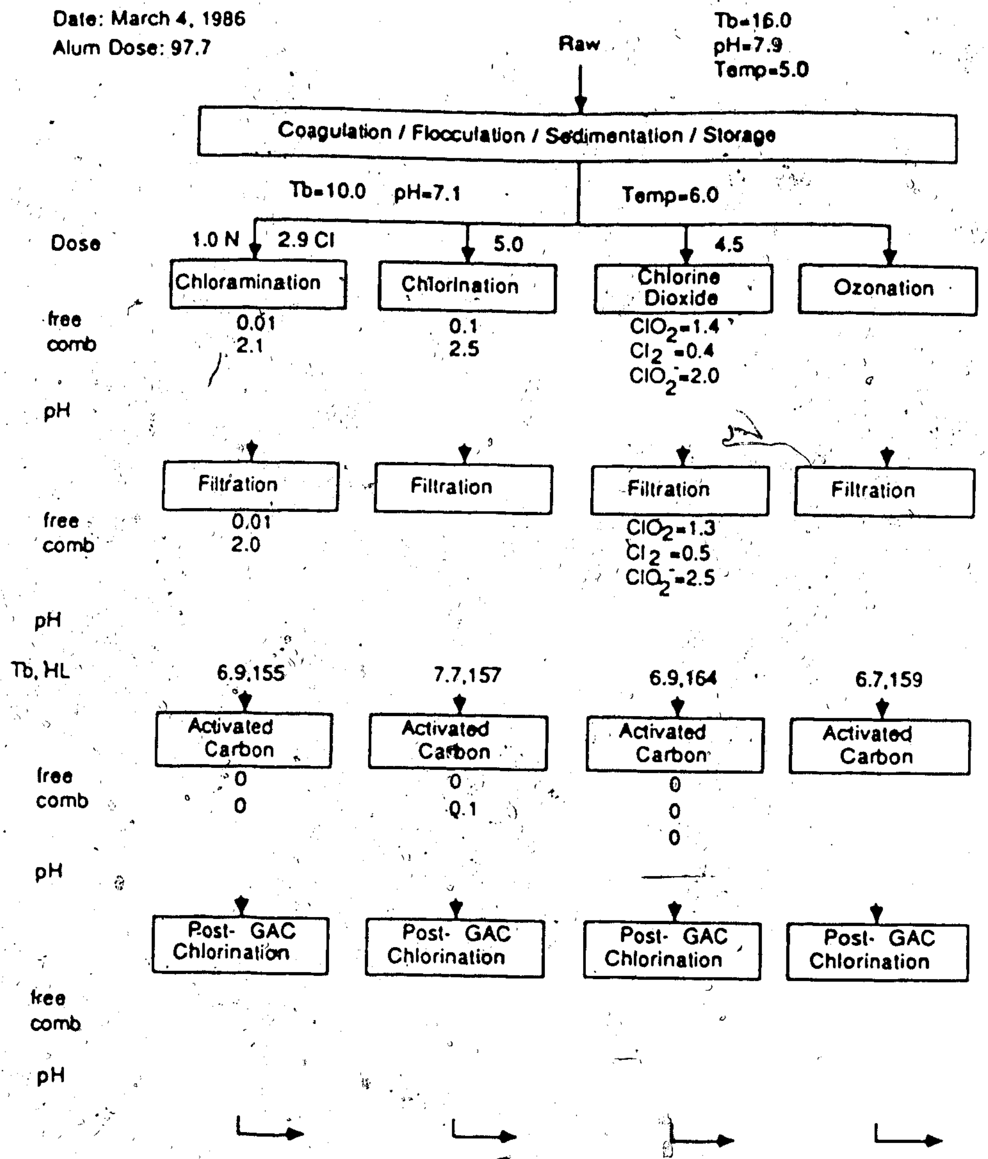
Date: March 1, 1986
Alum Dose: 50.0



Notes: alum dose increased twice during run

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

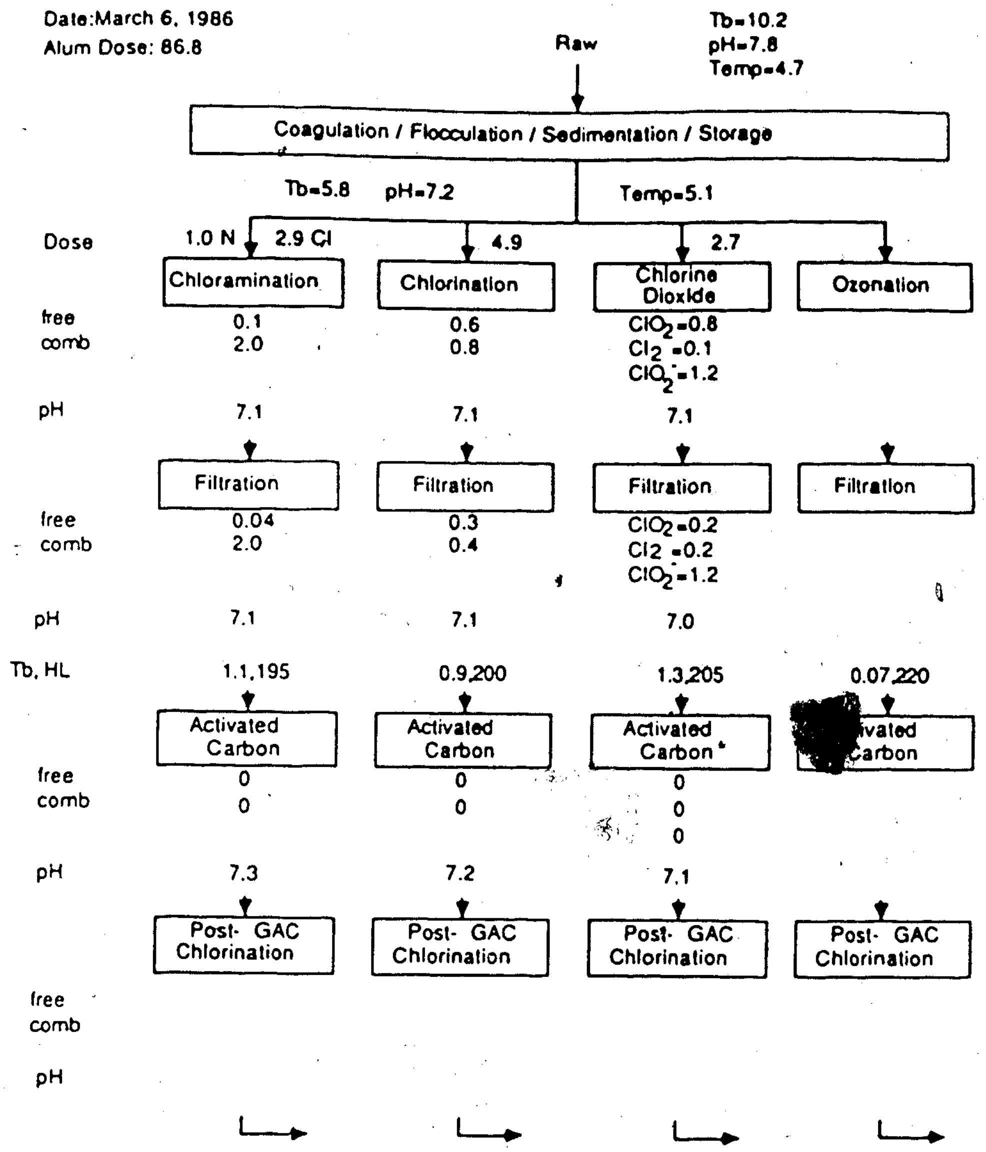
Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss



Notes: run-off continues accompanied by high [illegible]

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss



Notes:

All disinfectant doses in mg/L

Cl_2 = chlorine, ClO_2 = chlorine dioxide

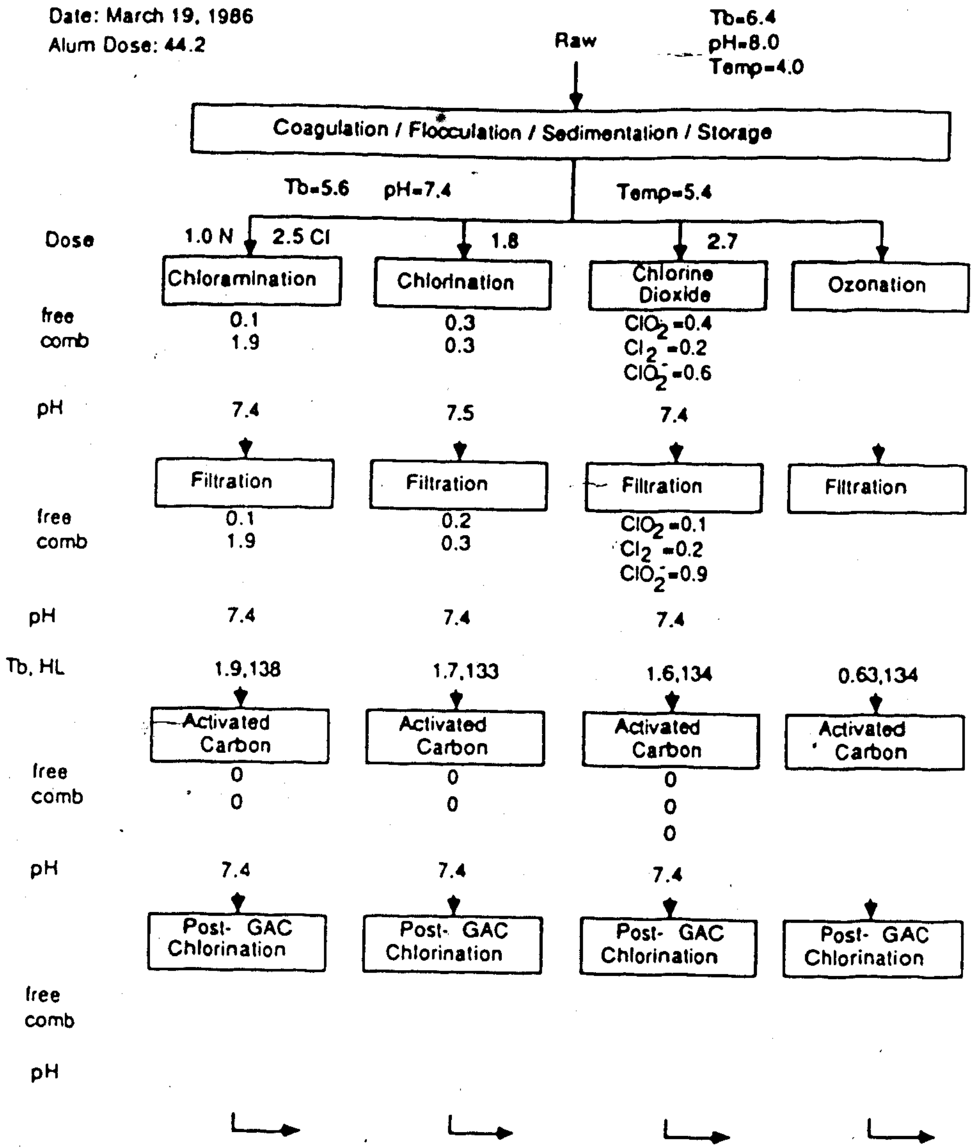
ClO_2^- = chlorite

free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)

Temp denotes temperature (°C)

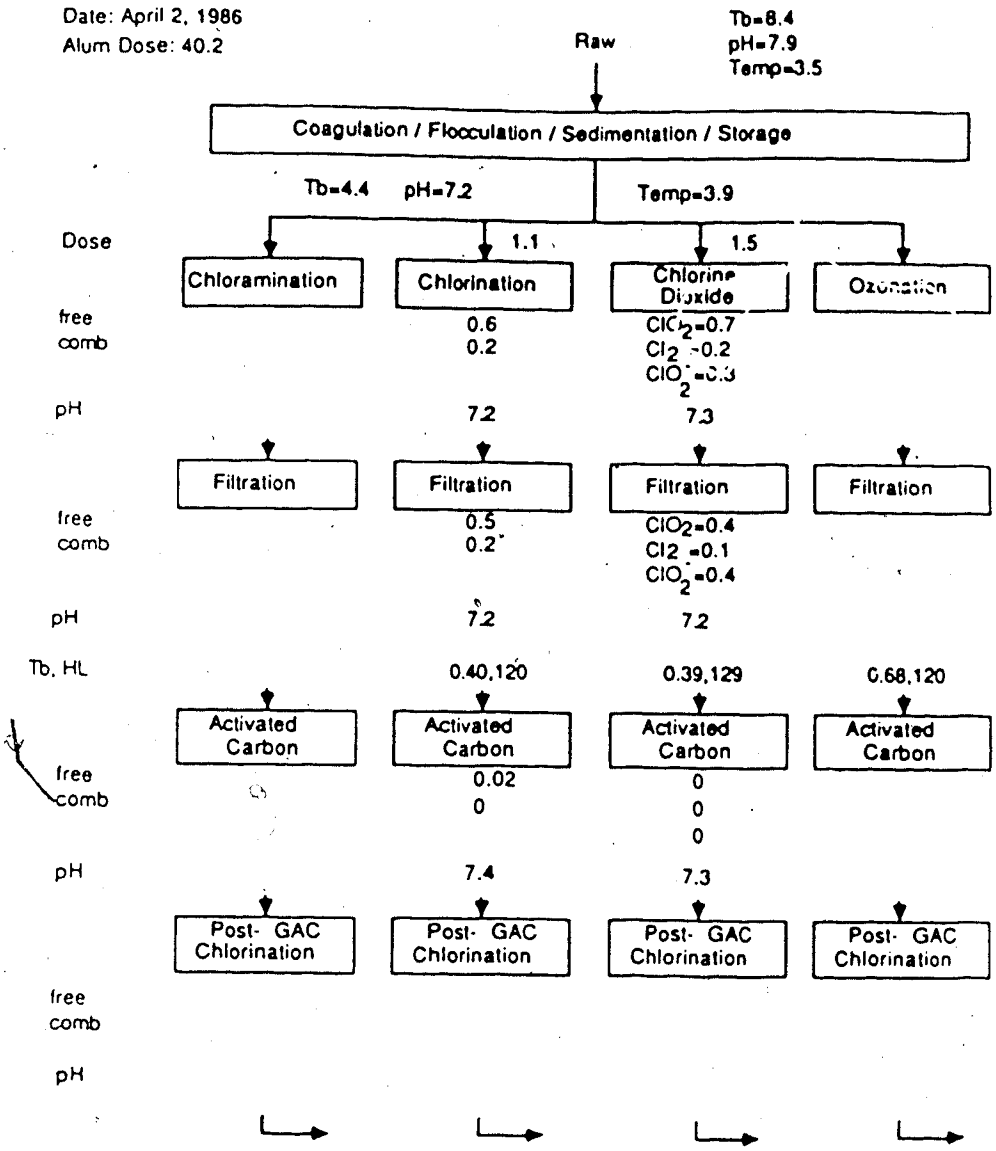
HL denotes head loss



Notes:

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

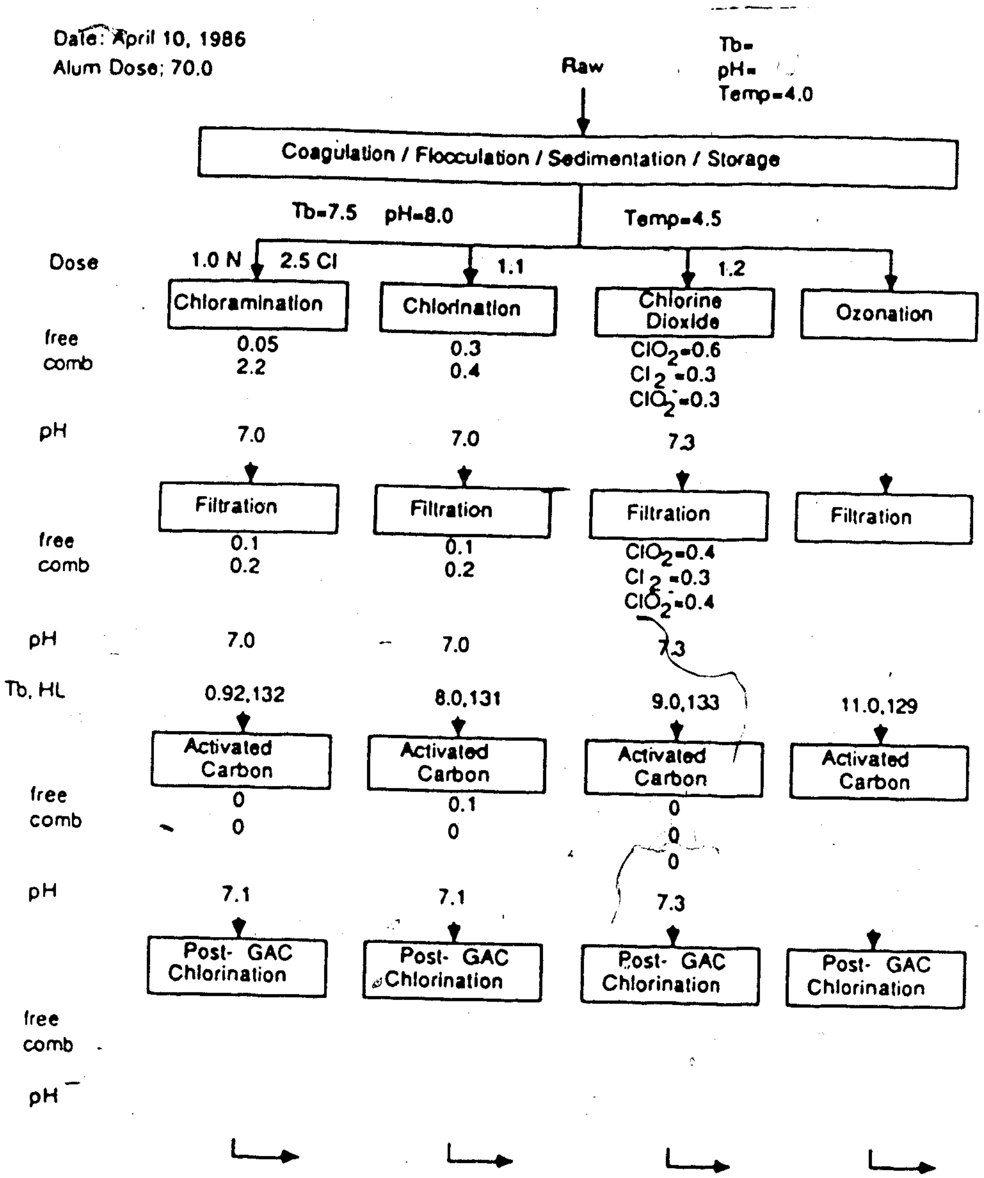
Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss



Notes: pump failure on chloramine stream

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

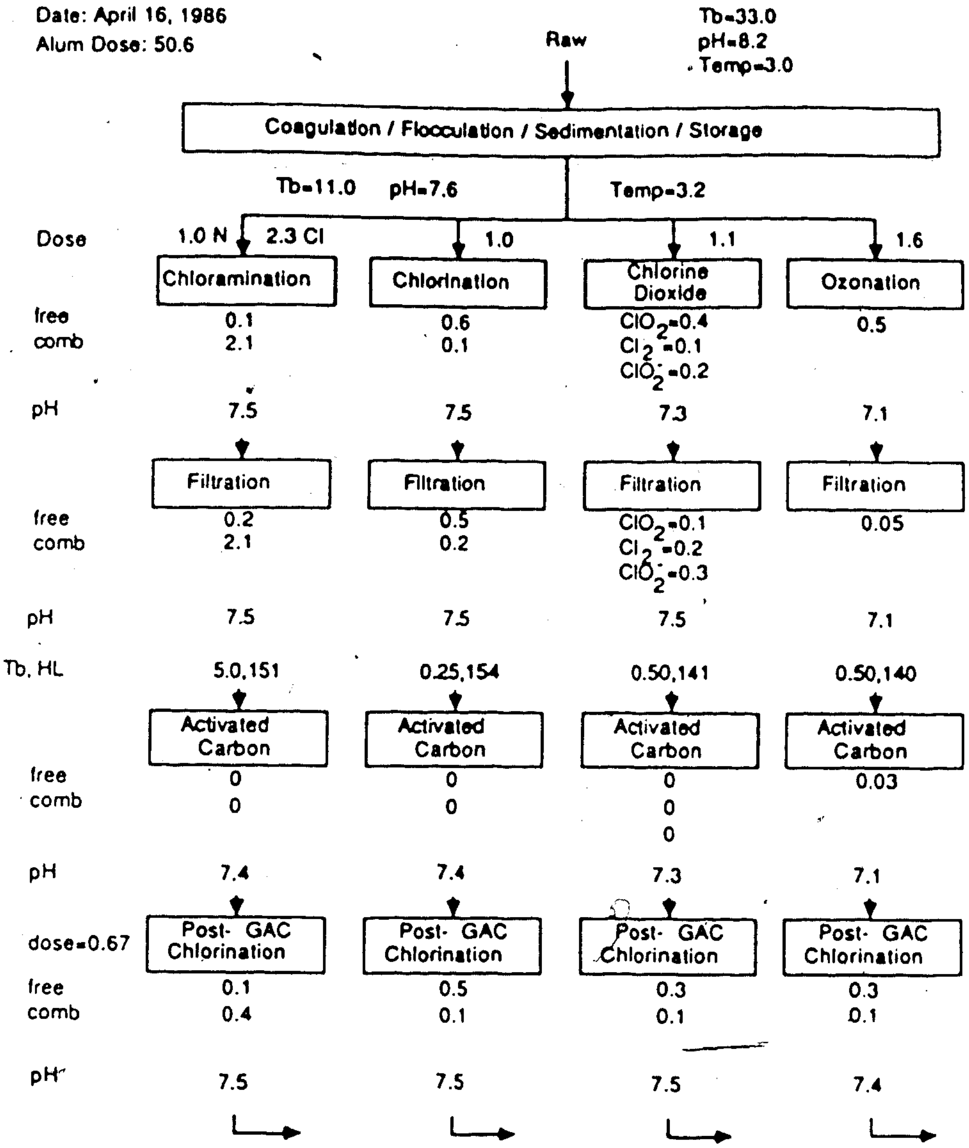
Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss



Notes: spill of PAC into raw water at Rossdale plant #3 entered pilot plant

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss

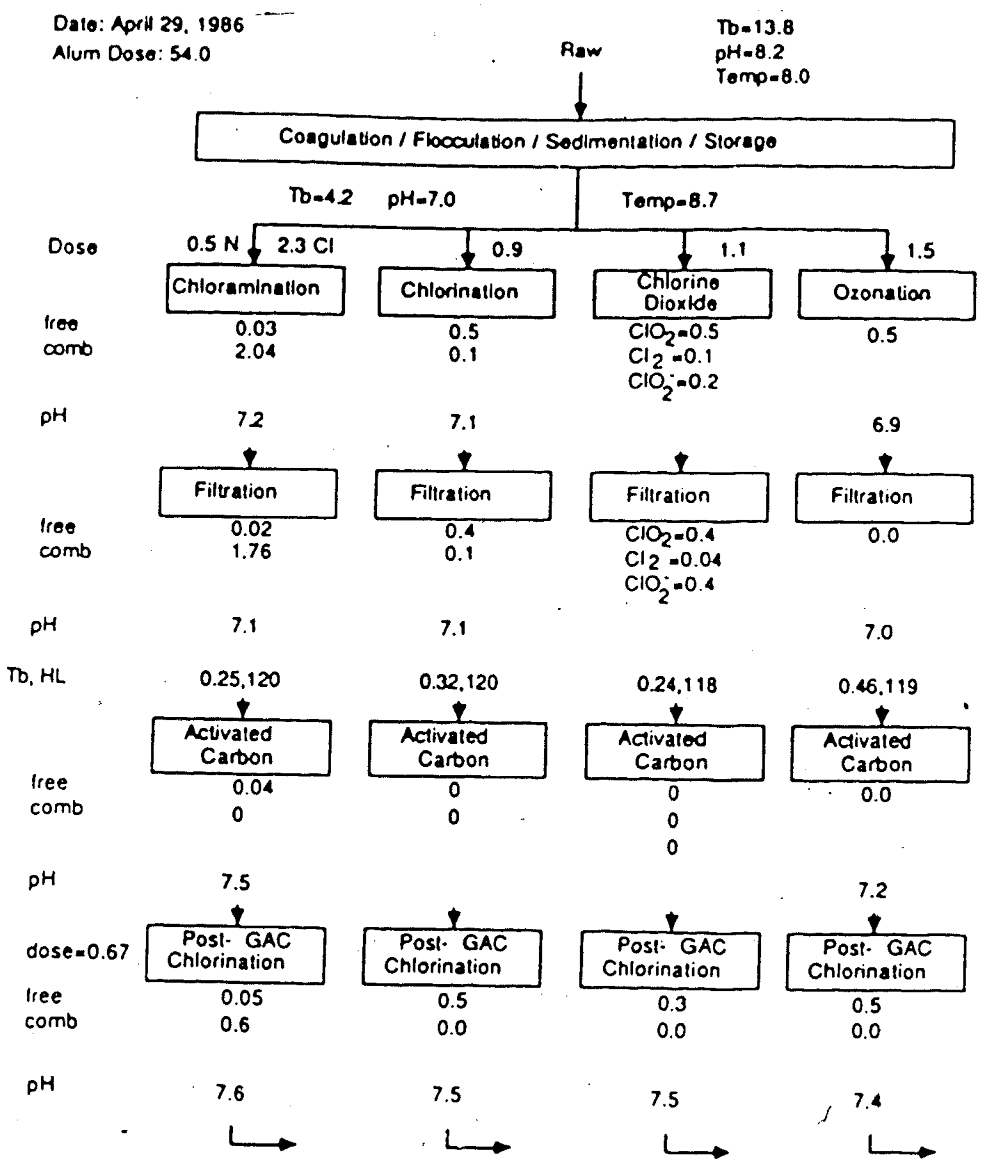


Date: April 16, 1986
Alum Dose: 50.6

Notes: alum dose increased twice during the run, heavy evening rainfall

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

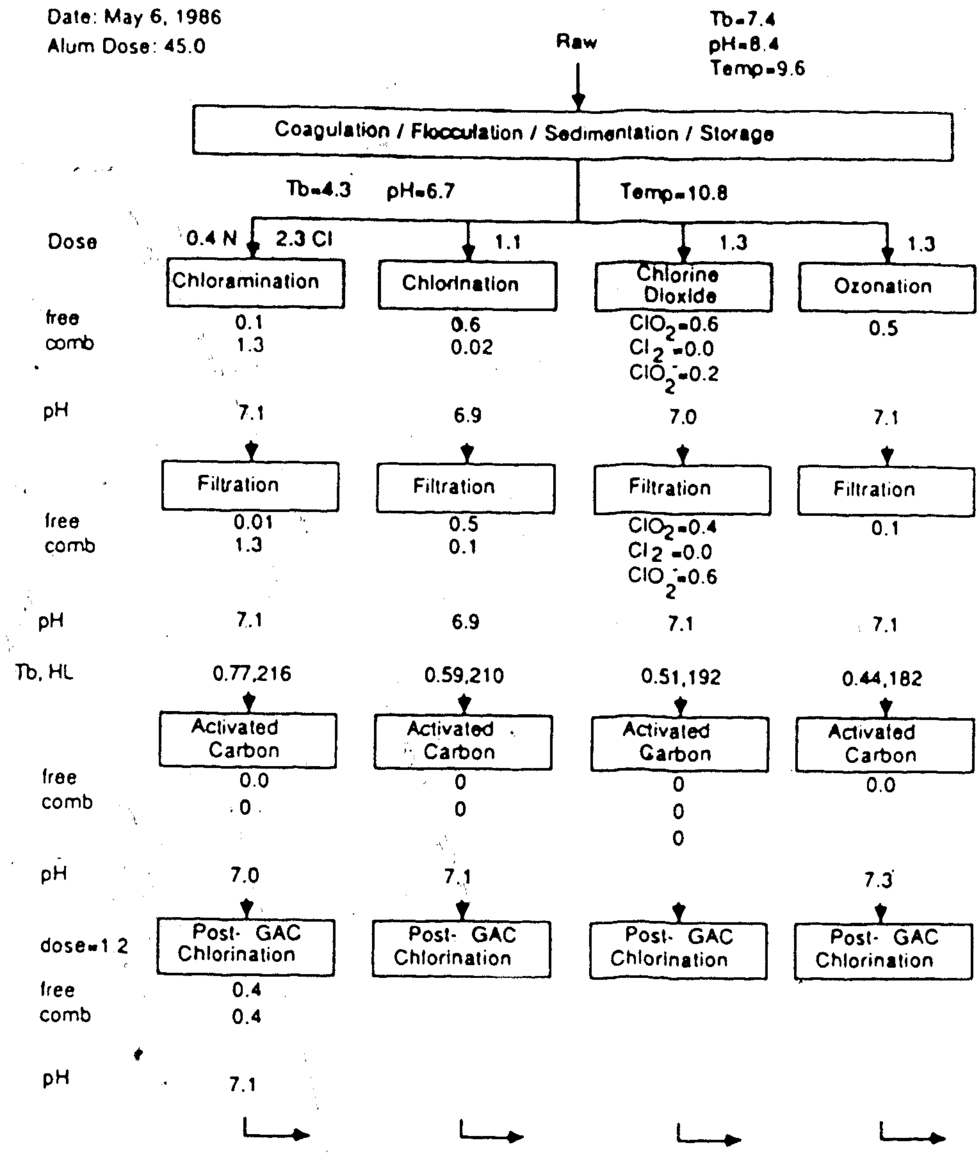
Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss



Notes: experienced some low flow problems

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss

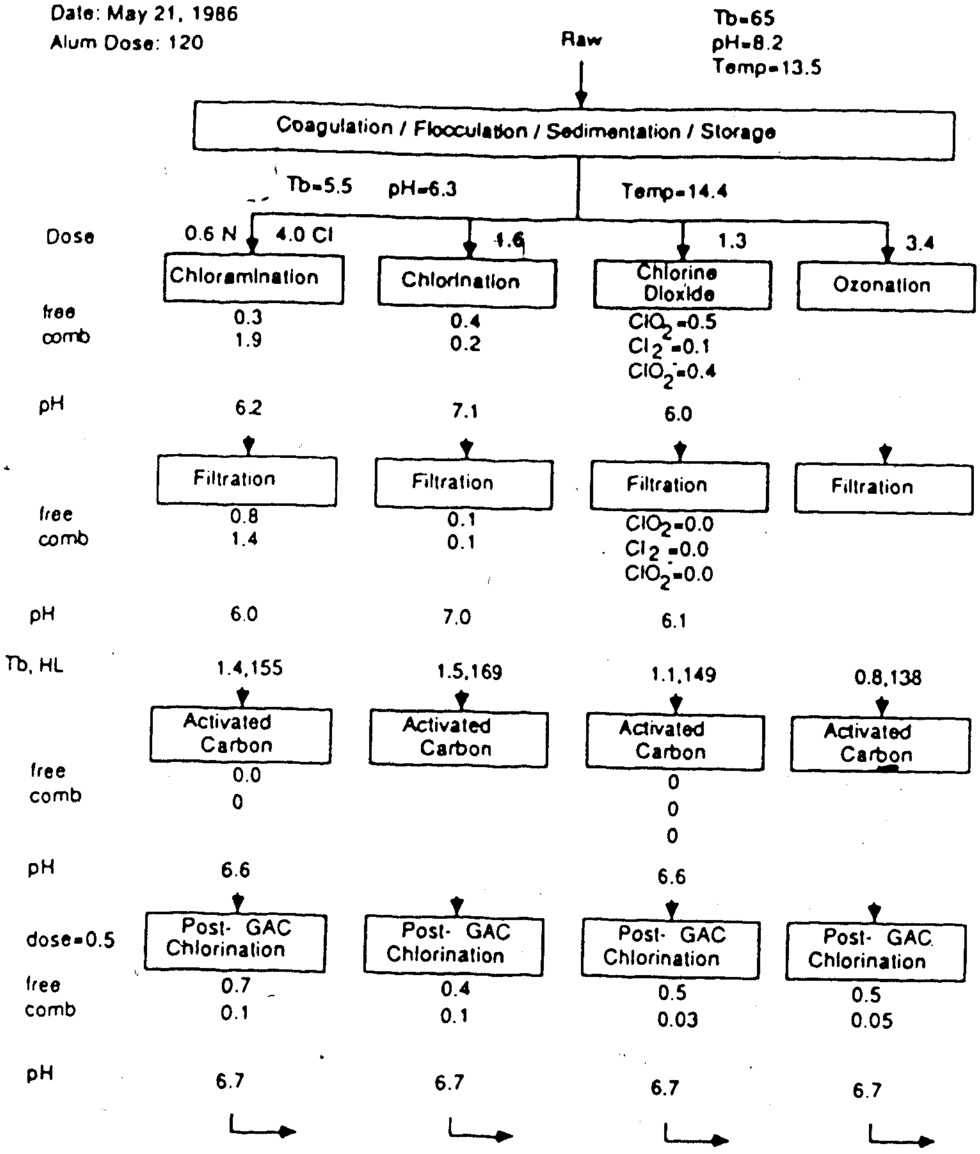


Notes:

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss

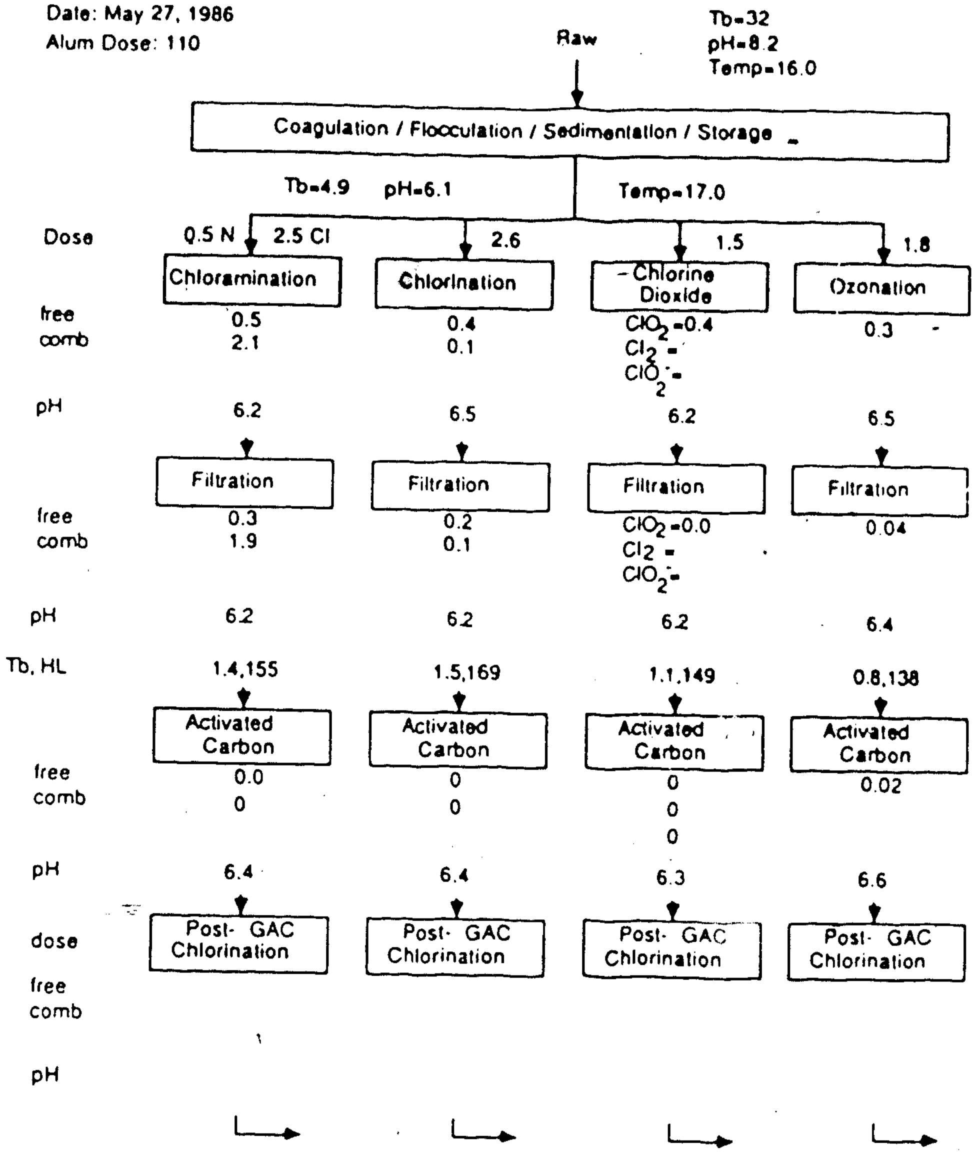
Date: May 21, 1986
Alum Dose: 120



Notes: alum pump operated at maximum capacity

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

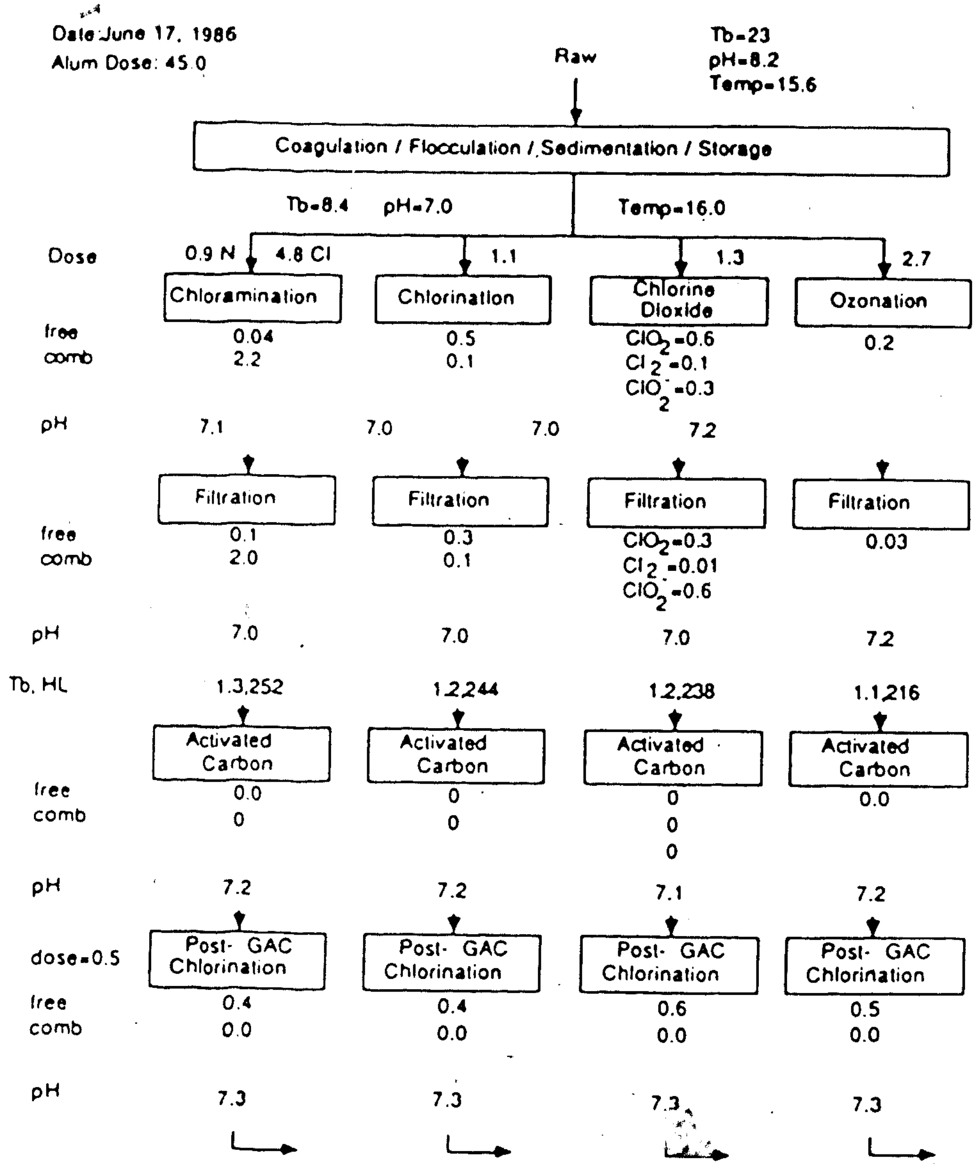
Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss



Notes:

All disinfectant doses in mg/L
Cl_2 = chlorine, ClO_2 = chlorine dioxide
ClO_2^- = chlorite
free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)
Temp denotes temperature (°C)
HL denotes head loss



Notes:

All disinfectant doses in mg/L

Cl_2 = chlorine, ClO_2 = chlorine dioxide

ClO_2^- = chlorite

free and comb (combined) refer to residual chlorine or ozone concentrations

Tb denotes turbidity (NTU)

Temp denotes temperature (°C)

HL denotes head loss

APPENDIX 3

MUTAGENICITY RESULTS

(Summary Figures for Strains TA97, TA98 and TA100)

Source: Huck, 1986

Summary of Mutagenicity Results for Strain TA97 (without S9)

☐ non-mutagenic ■ mutagenic ▨ toxic

Sample Date	Liter Equivalent *	Reference stream	After Disinfectant and Filtration				After GAC				After Post-Chlorination			
			NH_2Cl	Cl_2	ClO_2	O_3	NH_2Cl	Cl_2	ClO_2	O_3	NH_2Cl	Cl_2	ClO_2	O_3
Winter														
Dec 5	3	☐	☐											
Dec 17		☐	☐	☐			☐	☐						
Jan 22	6	☐	☐	☐	☐		☐	☐	☐					
Jan 28	6	☐	☐	☐	☐		☐	☐	☐					
Feb 11	6	☐	☐	☐	☐		☐	☐	☐					
Feb 20	6	▨	▨	▨	▨			☐	☐					
Spring Thaw														
Feb 28	5	☐		▨										
Mar 1	6	☐		▨										
Mar 4	3	▨		■										
Mar 5	3	☐	☐	■	☐									
Mar 6	3	☐	☐	■**	☐									
Spring Summer														
Mar 19	6	▨		☐	▨	▨								
Apr 2	6	☐	▨	▨	☐	▨		▨						
Apr 10	6	☐	☐	☐	☐	☐								
Apr 16	6	☐					☐	☐	☐	☐	☐	☐	☐	☐
Apr 29	6	▨					☐	▨	☐	▨	▨	▨	▨	▨
May 6	6	☐	☐	■	☐	☐					☐			
May 21	6	☐					☐	☐	▨	☐	☐	☐	☐	☐
May 27	6	☐	■	■	☐	☐								
Jun 17	6	☐					☐	☐	☐	☐	☐	☐	☐	☐

* Liter Equivalent = sample time(12 or 24 hrs) X flow rate(1 L/min) X volume plated(0.1 mL) / final volume of sample(25 mL)

** Mutagenic with discontinuities in background lawn indicating toxicity.

Summary of Mutagenicity Results for Strain TA98 (with S9)

☐ non-mutagenic ■ mutagenic ▨ toxic

Sample Date	Liter Equivalent *	Reference stream	After Disinfectant and Filtration				After GAC				After Post-Chlorination			
			NH_2Cl	Cl_2	ClO_2	O_3	NH_2Cl	Cl_2	ClO_2	O_3	NH_2Cl	Cl_2	ClO_2	O_3
Winter														
Dec 5	3	☐	☐											
Dec 17	3	☐	☐	☐			☐	☐						
Jan 22	6	☐	☐	☐	☐		☐	☐	☐					
Jan 28	6	■	☐	☐	☐		☐	☐	☐					
Feb 11	6	☐	☐	☐	☐		☐	☐	☐					
Feb 20	6	☐	☐	☐	☐			☐	☐					
Spring Thaw														
Feb 28	5	☐		☐										
Mar 1	6	☐		☐										
Mar 4	3	☐		☐										
Mar 5	3	☐	☐	☐	☐									
Mar 6	3	☐	☐	☐	☐									
Spring Summer														
Mar 19	6	☐	☐	■	☐	☐								
Apr 2	6	☐	☐	☐	☐	☐		☐						
Apr 10	6	☐	☐	☐	☐	☐								
Apr 16	6	☐					☐	☐	☐	☐	☐	☐	☐	☐
Apr 29	6	☐					☐	☐	☐	☐	☐	☐	☐	☐
May 6	6	☐	☐	☐	☐	☐					☐			
May 21	6	☐					☐	☐	☐	☐	☐	☐	☐	☐
May 27	6	☐	☐	■	☐	☐								
Jun 17	6	☐					☐	☐	☐	☐	☐	☐	☐	☐

* Liter Equivalent = sample time(12 or 24 hrs) X flow rate(1 L/min) X volume plated(0.1 mL) / final volume of sample(25 mL)

Summary of Mutagenicity Results for Strain TA100 (without S9)

☐ non-mutagenic ■ mutagenic ▨ toxic

Sample Date	Liter Equivalent *	Reference stream	After Disinfectant and Filtration				After GAC				After Post-Chlorination			
			NH_2Cl	Cl_2	ClO_2	O_3	NH_2Cl	Cl_2	ClO_2	O_3	NH_2Cl	Cl_2	ClO_2	O_3
Winter														
Dec 5	3	☐	☐											
Dec 17	3	☐	☐	■			☐	☐						
Jan 22	6	☐	☐	☐	☐		☐	☐	☐					
Jan 28	6	☐	☐	☐	☐		☐	☐	☐					
Feb 11	6	☐	☐	☐	☐		☐	☐	☐					
Feb 20	6	☐	☐	☐	☐			☐	☐					
Spring Thaw														
Feb 28	5	☐		▨										
Mar 1	6	▨		▨										
Mar 4	3	☐		■										
Mar 5	3	▨	▨	■	▨									
Mar 6	3	▨	▨	▨	▨									
Spring Summer														
Mar 19	6	▨	▨	■	▨	▨								
Apr 2	6	☐	▨	☐	▨	☐		☐						
Apr 10	6	☐	☐	☐	☐	☐								
Apr 16	6	☐					☐	☐	☐	☐	☐	☐	☐	☐
Apr 29	6	☐					☐	☐	☐	☐	☐	☐	☐	☐
May 6	6	☐	▨	■	☐	☐					☐			
May 21	6	☐					☐	☐	☐	☐	☐	☐	☐	☐
May 27	6	☐	■	■	☐	☐								
Jun 17		☐					☐	☐	☐	☐	☐	☐	☐	☐

* Liter Equivalent = sample time(12 or 24 hrs) X flow rate(1 L/min) X volume plated(0.1 mL) / final volume of sample(25 mL)