

**DEMONSTRATION OF BIOLOGICAL  
DENITRIFICATION OF DRINKING  
WATER FOR RURAL COMMUNITIES**

**JoAnn Silverstein  
Department of Civil Environmental and  
Architectural Engineering  
University of Colorado, Boulder**

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**FINAL REPORT - PHASE 1**

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(NWRI)**

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**(January 1, 1996 - December 31, 1996)**

Cover photographs: top) building housing the drinking water denitrification demonstration located by the municipal wells supplying drinking water to the Town of Wiggins, Colorado; bottom) biological denitrification process reactors described by Dr. Gary Carlson, research associated at the University of Colorado supervising on-site operations and process monitoring.

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## EXECUTIVE SUMMARY

This is a report of results to-date of the project supported by the National Water Research Institute (NWRI) "Demonstration of the Biological Denitrification of Drinking Water for rural Communities," from January 1, 1996 to December 31, 1996. The purpose of the grant from NWRI for the amount of \$51,032 was to investigate performance of scaled-up process equipment and to demonstrate the drinking water denitrification in a rural community. We have designated this report as "Phase 1," which includes the background of the denitrification demonstration project, especially development of a novel packed-tower biofilm denitrification reactor for removal of nitrate from rural drinking water supplies at the University of Colorado, construction and start-up of the demonstration facility in Wiggins, Colorado, and technical performance of the demonstration to July 1, 1997. Given the extensive experience with the biofilm denitrification process both in the Environmental Engineering laboratory at the University of Colorado and in a field pilot operation in a nearby town, Brighton, Colorado, we were optimistic that both a large scale-up of process equipment and remote operation could be accomplished within one year. Unfortunately, there were a series of start-up problems which delayed the project by as much as eight months even after facility construction was completed. However, the demonstration has been operating extremely well since March 1997. We have received additional funding to produce a full data set demonstrating the water quality aspects of the drinking water denitrification process performance to November 1997. A detailed technical summary of the denitrification demonstration performance, through November 1997, will be included in the Phase 2 Final Report to be sent to NWRI at the end of 1997.

We anticipated that the drinking water denitrification demonstration in the Wiggins, Colorado facility would accomplish three things. First was to demonstrate the biological denitrification process developed at the University of Colorado as carried in equipment with a capacity typical for small drinking water utilities, 38 - 76 liters per minute (10 to 20 gallons per minute), in a rural community with actual source water (ground water), and during relatively unattended operation. A demonstration facility was designed and constructed in the Town of Wiggins, Colorado, a rural town with population of approximately 650 located 120 kilometers (75 miles) northwest of Denver on Colorado's eastern plains. The second objective of the demonstration was to involve the Colorado Department of Public Health and Environment (CDPHE) in the development of a monitoring plan so that by the end of the demonstration, sufficient water quality data would be collected to satisfy the drinking water regulatory agency that the denitrification process was effective, reliable and safe for use as a drinking water treatment process for small utilities. The third objective was to encourage commercialization of the denitrification process so that it would be available to rural utilities as an attractive alternative for treatment of nitrate-contaminated drinking water supplies.

As is discussed in this report, results of the denitrification demonstration in Wiggins, Colorado to-date indicate that all three of these objectives will be achieved by the end of 1997. In addition, there has been interest in using the biological denitrification technology to clean-up hazardous waste sites contaminated with mixtures of nitrate, other toxic oxy-anions, and toxic organic compounds. Investigations of the potential of the denitrification system to destroy other drinking water contaminants will add both to the fundamental knowledge of denitrifying biofilms and to the applications of the technology.

## **PROJECT OVERVIEW**

The drinking water denitrification process used in the demonstration has been designed for treatment of nitrate-contaminated drinking water supplies by small utilities whose economic resources are limited yet whose need for a reliable and easy-to-operate process for nitrate removal is great. The Wiggins facility was constructed to accommodate process equipment designed by Dr. JoAnn Silverstein of the Environmental Engineering program at the University of Colorado which was a scale-up of a system which had been operated in Brighton Colorado by the University of Colorado from 1989 to 1991. After a successful demonstration of the denitrification and filter polishing process under field conditions at Brighton, Colorado, we decided to carry out a demonstration at approximately full-scale with significant process monitoring in order to fully develop the novel drinking water denitrification system for timely application in the many rural communities whose drinking water supplies are contaminated with nitrate.

## **PROBLEM**

Nitrate contamination of groundwater in many areas of the United States is a growing problem. Nitrate in water is known to be the cause of infant methemoglobinemia, also known as “blue baby” disease. The link between nitrate in drinking water ingested by new-born infants and infant methemoglobinemia has been well documented both in epidemiological and controlled clinical studies (Fan et al., 1987; Comly, 1945). In 1986, the USEPA surveyed the scientific health findings in a “Criteria” document which was the basis for the EPA regulation for nitrate in drinking water (USEPA, 1987). Nitrate is

regulated as a primary drinking water contaminant with a maximum contaminant level (MCL) set at 10 mg/L nitrate as nitrogen ( $\text{NO}_3\text{-N}$ ) (USEPA, 1988).

Nitrate is an ubiquitous contaminant particularly of ground water in agricultural regions of the United States, and throughout the world. Furthermore, because of intensive application of nitrogen fertilizer and animal feedlot waste to agricultural land, and because there are few natural mechanisms for destruction of the nitrate ion in the ground water environment, nitrate pollution of much of rural drinking water seems to be increasing steadily. Spalding and Exner (1993) have summarized the nitrate pollution problem throughout the United States, noting the following. Ground water from 25% of municipal and special monitoring wells samples in agricultural areas of Delaware, Pennsylvania, central Minnesota, Wisconsin, western and northeastern Iowa, Texas, Oklahoma, Kansas, Nebraska, South Dakota, eastern Colorado, southeastern Washington, Arizona and central and southern California was contaminated with over 3 mg/L  $\text{NO}_3\text{-N}$ . In a National Pesticide Survey made in 1990, it was found that 1.2% of 566 community drinking water supply wells tested in agricultural areas of the US exceed the 10 mg/L  $\text{NO}_3\text{-N}$  MCL, and 11% of these wells had between 3 and 10 mg/L  $\text{NO}_3\text{-N}$ . In 1992 the USEPA estimated that 4.5 million people in the US, including 66,000 especially at-risk infants less than one year old used drinking water from either community supplies or individual domestic wells which exceeded the 10 mg/L  $\text{NO}_3\text{-N}$  MCL. In one area, six counties in southern California, it was estimated that 12% of the municipal drinking water wells exceeded the nitrate MCL. This situation had particular consequences for maximization of water supplies in arid southern California, with an estimated 4% of the domestic water supply in this region lost every year due to nitrate contamination. (Spalding and Exner compared the

consequences of nitrate pollution with the much more publicized problem of hazardous organic compounds, noting that less than 0.5% of the groundwater could not be used for drinking because of organic chemical contamination.) Recently, there have been reports of nitrate contamination of water used by larger drinking water utilities (Goodrich, 1997; Yeager, 1997), indicating that the impacts of nitrate pollution and the market for feasible treatment options may be significantly larger than that represented by small rural communities.

Nitrate contamination often has been a problem for small utilities in rural regions or in domestic well water. Because the nitrate ion is not removed or destroyed in conventional drinking water treatment processes like coagulation, oxidation, filtration or disinfection, nitrate removal from drinking water is an especially difficult problem for small utilities. In a report published by the USEPA in 1983: "Nitrate Removal for Small Public Water Systems," two processes were cited as effective for nitrate removal from drinking water: anion exchange and membrane processes such as reverse osmosis. However, implementation of either of these technologies is problematic for many rural utilities.

Common groundwater constituents interfere with anion exchange. In general, sulfate replaces nitrate absorbed on anion exchange media, especially when the molar sulfate concentration exceeds nitrate molar concentration by a factor of 2 to 4, as is the case in many groundwaters. As a result, a significant fraction of the anion exchange media capacity can be spent removing sulfate instead of nitrate, necessitating either larger ion exchange reactors or more frequent regeneration of the media, usually with concentrated sodium chloride (NaCl) brine. Efforts have been made to either reverse the exchange media selectivity or to recover and recycle, but these have met with limited success. Also



brine recovery efforts require more complex treatment process operation, a burden on small utilities. In the presence of high amounts of sulfate ion, ion exchange reactors can fail by as sulfate replaces nitrate from the exchange media surface and it is resolubilized in the product water. In that case, the product nitrate can actually exceed the influent nitrate concentration. (USEPA, 1983)

Dissolved iron, a common constituent in groundwater, has been found to foul ion exchange media. (USEPA, 1983). Finally, ion exchange media must be regenerated regularly with very high salinity NaCl brines (5 to 12%). Spent regenerant brine is a waste product which contains both high amounts of salts and nitrates. In general spent brine cannot be disposed of easily in inland communities by discharge to surface water or to most groundwater aquifers.

Reverse osmosis (RO) also can be difficult to operate in a rural utility. There are significant operations associated with RO including pretreatment of influent water, addition of anti-fouling chemicals, and membrane cleaning which are burdensome for a small utility which may have only one full-time (or even part time) operator. Although many improvements in RO membranes have been made in recent years, allowing operation at lower system pressure 690 to 1,724 kPa (100 to 250 psi) the energy requirement for operation of a pressurized RO system still is significant. Also, RO membranes have been reported to be fouled by bacterial slime, which is produced even with a “clean” groundwater source. This biofouling appears to resist cleaning in-place, necessitating more drastic procedures. Finally, like anion exchange, RO produces a concentrate wastewater by-product which must be disposed of. In one full-scale application in Brighton, Colorado, the concentrate volume produced is 25% of the influent water. RO concentrate also

contained high amounts of nitrate, removed from the water, and cannot be discharged into the environment easily.

## BACKGROUND

Research was conducted by faculty and students in the Department of Civil, Environmental and Architectural Engineering at the University of Colorado from 1987 to 1992 to develop process for drinking water treatment which used bacteria which reduced nitrate to  $N_2$ , called denitrification. The denitrification process has been used for decades for removing nitrate from treated wastewater, however the denitrification process had never been optimized for drinking water treatment, especially in small communities with limited operations resources. The results of research by the University of Colorado personnel were first observed in experiments using a nitrate-augmented surface water conducted in the environmental engineering laboratory at the University and confirmed in a field test using natural groundwater in Brighton, Colorado.

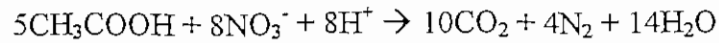
*Packed Tower Biofilm Denitrification.* Both the laboratory and field research denitrification reactors were 4.6 meters (14 feet) long and 15-cm (6-in.) diameter acrylic plastic tubes packed with high-porosity plastic media (Jaeger Tri-Pak) which supported an attached biofilm of denitrifying bacteria. Media porosity of 0.93 to 0.96 and specific surface area of 40 to 50  $m^2/m^3$ , allowed for a dispersed plug-flow regime in the reactor over the flow range investigated of 0.5 to 2.2 liters/minute (Hogrewe, 1990). The bacterial denitrification process is carried out by facultative bacteria which reduce nitrate in respiration, in the absence of oxygen. Therefore the denitrification biofilm packed towers were flooded to minimize dissolved oxygen and maximize nitrate reduction. The tower

was operated in a up-flow mode to enhance removal of the  $N_2$  gas produced in denitrification. It was found that the packed tower biofilm denitrified water completely in both laboratory and field operation in Brighton, Colorado over a hydraulic loading rate range of 1.8 to 7.2  $m^3/m^2/hr$  (0.75 to 3.0 gallons per minute/ $ft^2$ ). (Hogrewe, 1990; deMendonça and Silverstein, 1992)

Many species of non-pathogenic bacteria found commonly in soil and natural water will denitrify, so that inoculation of the plastic support media with a non-pathogenic seed from, for example, creek sediment resulted in rapid growth of a denitrifying biofilm.

Denitrifying bacteria in general are heterotrophic, which means that they require organic carbon for growth and energy. In wastewater, the carbon source is sewage, however, a new source had to be identified for drinking water application. Acetic acid ( $CH_3COOH$ ) was used during process development for several reasons. Acetic acid is an efficient substrate for many bacteria. Because it is not easily fermented, we thought that very little of the acetic acid would be used in futile side-reactions by non-denitrifying bacteria. Acetic acid is available in food-grade quality, so that addition to a drinking water supply would not add health risk. However, there were some drawbacks to use of acetic acid. The food-grade chemical is expensive, compared with other organic compounds such as methanol. Although acetic acid is a weak acid, some care must be exercised in storage and handling of the corrosive chemical. Also, glacial (pure) acetic acid freezes at approximately 17 °C (62 °F), requiring storage under warm enough conditions to allow pumping of the liquid.

The energy generating portion of the denitrification reaction, neglecting cell synthesis is:



Note that nitrate is completely destroyed, the acetic acid is oxidized by bacteria to mineral end-products:  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$ . During energy generation by denitrification in the cell, protons are used, meaning that the water acidity decreases. In an unbuffered system the water pH tends to increase during denitrification; however, most groundwater is very well buffered with high alkalinity, so that the pH did not change significantly during the field study in Brighton. (Cook et al., 1992)

Early in the University of Colorado research, the acetic acid requirement including cell synthesis was determined to be 1.5 grams of acetic acid carbon for denitrification of 1 gram of  $\text{NO}_3\text{-N}$  destroyed. (Ketellapper, 1988; Cook et al., 1989; Cook et al., 1990; Cook et al., 1991) The presence of dissolved oxygen in the water was found not to interfere with denitrification. Bacteria will grow more rapidly using oxygen in respiration than nitrate. However, if sufficient carbon substrate is added then the dissolved oxygen is consumed rapidly in the bio-tower and denitrification proceeds efficiently. We found that the requirement for acetic acid was increased by dissolved oxygen by the amount of 1 gram acetic acid carbon per gram dissolved oxygen.

Previous investigators (Harremöes, 1976) have reported that denitrification in a thick attached biofilm follows a half-order rate model:

$$(\text{NO}_3\text{-N})^{0.5} = (\text{Initial NO}_3\text{-N})^{0.5} - k \cdot \tau$$

where  $(\text{NO}_3\text{-N})$  = the effluent nitrate-nitrogen concentration, mg-N/L;  $(\text{Initial NO}_3\text{-N})$  = influent nitrate-nitrogen concentration, mg-N/L;  $k$  = half-order reaction constant ((mg-N/L)<sup>0.5</sup>/hr);  $\tau$  = reactor hydraulic detention time, hr. The half-order model was confirmed by us during laboratory experiments on the denitrification packed tower system, and the

half-order reaction constant was found to vary between 0.013 and 0.044 (mg-N/L)<sup>0.5</sup>/hr, depending on the hydraulic loading rate and biofilm thickness during both lab and field operation. (Hogrewe, 1990; deMendonça and Silverstein, 1992).

An important result of early research by the University of Colorado investigators is that the supply of organic carbon substrate (e.g., acetic acid) determines the performance of the denitrification reactor. Whenever there was failure in the carbon dosing to the reactors, denitrification slowed dramatically. However when the carbon dosing was restored, even after a down-time of over 24 hours, denitrification resumed almost immediately.

The packed tower reactor with attached biofilm was very efficient at minimizing sloughed biofilm and bacteria in the denitrified product water. However, the denitrifying biofilm attached to the media in the reactor grew denser after during continuous operation. Uniform flow through the denitrification reactor was maintained by regular air scour of the reactor media by a procedure developed at the University of Colorado. Every 21 days, flow to the tower reactors was stopped and approximately 10% of the reactor fluid drained. Then air flow was initiated at the bottom of the tower at the rate of 0.04 cubic meters per minute (1.5 cubic feet per minute) for 5 to 10 minutes. The plastic media is slightly buoyant with a specific gravity of 0.96 and during the air flow the packed bed expanded by approximately 15%, allowing much of the attached biofilm to detach. As the air flow stopped, the detached biomass solids settled to the liquid below the media and was drained from the bio-towers as a waste suspension of biomass particles. The wastewater was a suspension of approximately 2 grams/liter total suspended solids. At the 21-day frequency used, the waste biosolids volume was from 0.2 to 0.4% of product

water volume, depending on flow rate (Cook, et al., 1991) and can be easily disposed of in a sewer. Both on the basis of volume and disposability, the scoured by-product from the denitrification reactors is much easier to manage than wastewater from either ion exchange or reverse osmosis processes. The relatively gentle air scouring procedure only removed a fraction of the denitrifying biomass, and resumption of complete denitrification consistently occurred immediately when normal flow was restored.

Once the ranges of hydraulic loading rate and denitrification reaction rate for the biofilm reactor had been determined along with the requirement for acetic acid addition per amount of nitrate to be reduced, the packed tower denitrification reactor could be scaled for application to a wide range of process capacity and nitrate removal requirements.

*Filtration Polishing.* To meet potable standards, the denitrified water is treated in a slow sand filtration process. In our laboratory research we found that using conventional filter sand with an effective diameter ranging from 0.1 - 0.5 mm in a slow sand filter resulted in rapid clogging when treating denitrified water which contained organic colloids and cells sloughed from the biofilm. (Barrett and Silverstein, 1988) Instead, sand with an effective size of 0.85 to 1.0 mm and a low uniformity coefficient of 1.5 produced effective turbidity and bacteria removal. In the Brighton pilot tests during 1990 and 1991, the average effluent turbidity was 0.5 NTU and effluent total coliform bacteria concentration was from 1 to 10 cells/100 ml. No *E. coli* bacteria were ever detected in either the denitrified effluent or finished water. (Cook, et al., 1991)

In order to decrease the frequency of scraping the slow sand filter, a roughing filter was added to the polishing sequence, upstream of the slow sand filter. The roughing filter

was a column packed with the same high-porosity media as the denitrification bio-towers, but operated as a thin-film reactor with an aerobic biofilm. As the denitrified water was trickled over the roughing filter, more than 50% of the soluble organic carbon and one log of coliform bacteria were removed. Also the deoxygenated water from the anaerobic denitrification reactors was reaerated by passage across the roughing filter. Most important, with the roughing filter upstream of the slow sand filter, the period between scraping to restore filter flow increased from 30 to 120 days. (Cook et al., 1991)

A schematic of the denitrification packed tower, roughing filter and slow sand filter sequence operated during the field test in Brighton, Colorado for a flow range of 0.5 to 2.2 liters/min. (0.13 to 0.5 gallons/min.) is shown in Figure 1. Results of the field test indicated that biofilm denitrification followed by filter polishing reliably reduced nitrate from an average influent of 16 mg-NO<sub>3</sub>-N/L to detection levels, if sufficient carbon substrate was added. In general, acetic acid only was added to reduce the nitrate to approximately 4 mg-NO<sub>3</sub>-N/L to save on the cost of the substrate chemical, and to insure that sulfides would not be formed if substrate carbon remained after all the nitrate was destroyed. Other important results from the Brighton, Colorado field research were that neither high influent dissolved oxygen (4 to 6 mg/L), high hardness (> 250 mg/L CaCO<sub>3</sub>), nor high sulfate concentration (370 mg/L SO<sub>4</sub><sup>2-</sup>) interfered with the denitrification process. Furthermore filtered effluent turbidity, coliform bacteria and chlorine demand all exceeded standards for drinking water. (deMendonça and Silverstein, 1992; Cook et al., 1991)

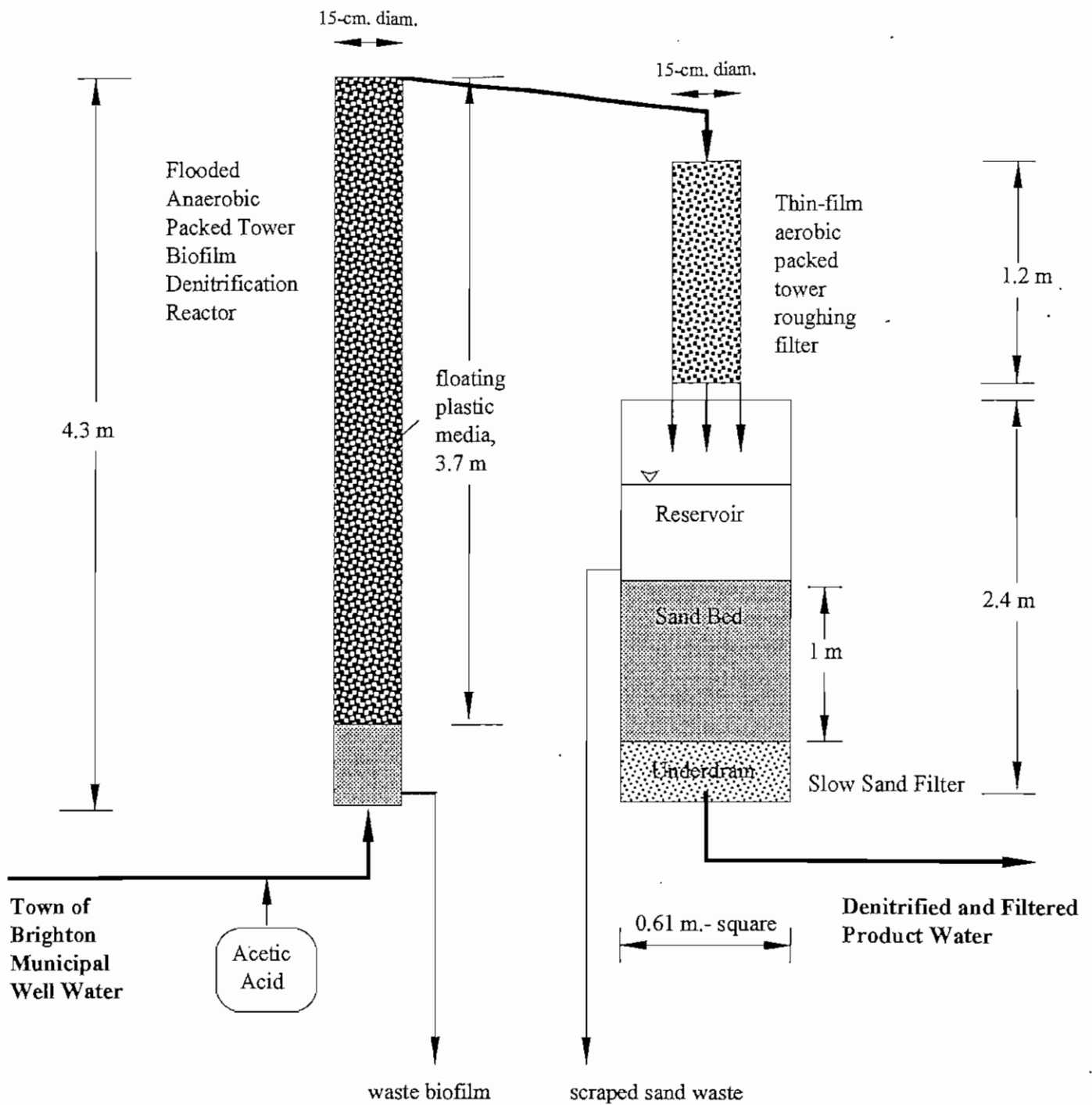


Figure 1: Schematic of 0.55 to 2 lpm drinking water treatment pilot plant consisting of packed tower biofilm denitrification reactor followed by roughing filter and slow sand filter polishing processes which was operated during field research at the Brighton, Colorado drinking water facility, 1990 - 1991.



## **FIELD DEMONSTRATION OF THE DRINKING WATER DENITRIFICATION PROCESS**

After the success of the process development research conducted between 1987 and 1992, we decided that a larger-scale field test of the drinking water denitrification process was necessary in order to demonstrate to both small utilities and government drinking water quality regulatory agencies that this novel process would in fact work reliably in a small community without intensive operator attention. A demonstration project was proposed with the objectives:

- operate a full-scale demonstration facility with a capacity of 38 to 76 liters per minute (10 to 20 gallons per minute) in a rural community
- intensive monitoring of the demonstration facility for chemical and bacteriological water quality parameters over several seasons of continuous operation using a monitoring schedule approved by the Colorado Department of Public Health and Environment as well as an external project advisory committee
- evaluation of process response to typical environmental stresses and process equipment failures

## **SPONSORSHIP OF THE DENITRIFICATION DEMONSTRATION. AT WIGGINS, COLORADO**

The Electric Power Research Institute (EPRI) and the National Rural Electric Cooperative Association (NRECA) along with co-sponsors Morgan County Rural Electric Association and Tri-State Generating and Transmission Association were the first to support in our efforts to implement the drinking water denitrification demonstration. In 1994, EPRI and NRECA approved a grant of \$100,000 to the project through the Small

Community Systems Committee of the Community Environmental Center of EPRI. This grant was critical to the project. First, the grant gave significant credibility to the University of Colorado efforts to find a host community in rural Colorado for the demonstration. Second, the grant made it easier for us to seek matching funds necessary for the complete project.

The Town of Wiggins, Colorado agreed to host the demonstration in 1995. Wiggins, Colorado is a town of approximately 650 residents located on the eastern plains of Colorado 120 kilometers (75 miles) northwest of Denver. The economic activity of town residents centers around farming, including several small livestock operations. The University of Colorado was extremely fortunate that Wiggins cooperated to allow the demonstration facility to be built and operated at the location of their drinking water wells and well water disinfection and storage tank. The Town contributed use of the facility location, water, a pipeline to a groundwater recharge site for effluent disposal, and unlimited access to the Town-owned secured property where the demonstration facility is located. John Holdren, the Town Manager, has contributed many valuable insights about rural utility concerns which enabled us to assess and improve the denitrification process operations. Finally, the Town of Wiggins contributed significant funds for construction of the demonstration facility - \$2,500 from the Town and \$35,000 from a grant from the Colorado Department of Local Affairs which was made under the sponsorship of the Town.

A group of entrepreneurs, Nitrate Removal Technologies, LLC. (NRT) became interested in commercialization of the drinking water treatment process invented by Dr. JoAnn Silverstein at the University of Colorado. As part of a license agreement with the

University of Colorado in 1995, NRT was allowed to use all of its payment for an unrestricted license to the University of Colorado's intellectual property for the demonstration, \$22,500. A matching grant of \$51,000 was made by the National Water Research Institute (NWRI) in 1995 to complete funding for design, construction and operation of the drinking water denitrification demonstration in Wiggins, Colorado. In summary, after almost two years, \$211,000 had been raised from NWRI, EPRI, NRECA, the Town of Wiggins, the Colorado Department of Local Affairs and Nitrate Removal Technologies, LLC. to sponsor the demonstration project. An additional \$30,000 was contributed by the University of Colorado to bring the total funds spent for the project during 1995 and 1996, including the capital cost of the demonstration facility at Wiggins, to \$241,000. Recently, NRT has awarded the University of Colorado an additional \$55,000 to complete operation of the demonstration until November 1, 1997.

#### **FEATURES OF THE WIGGINS DENITRIFICATION DEMONSTRATION FACILITY**

The Wiggins demonstration facility was built adjacent to the Town of Wiggins well pump house, using water from a 3,000-gallon pressurized tank located in the same building with the two well heads and pumps. The pressure tank also functioned as a chlorine dosing and contact tank for the Town water supply. Three significant water supply and water quality problems resulted from the Wiggins water system. The existence of the potential problems had been anticipated, but not the severity. These will be discussed in more detail below. Figures 2 - 7 are the Wiggins facility site plan, process flow diagram, building floor plan of the denitrification demonstration system, and details of the denitrification bio-tower reactor, the roughing filter and slow sand filter,

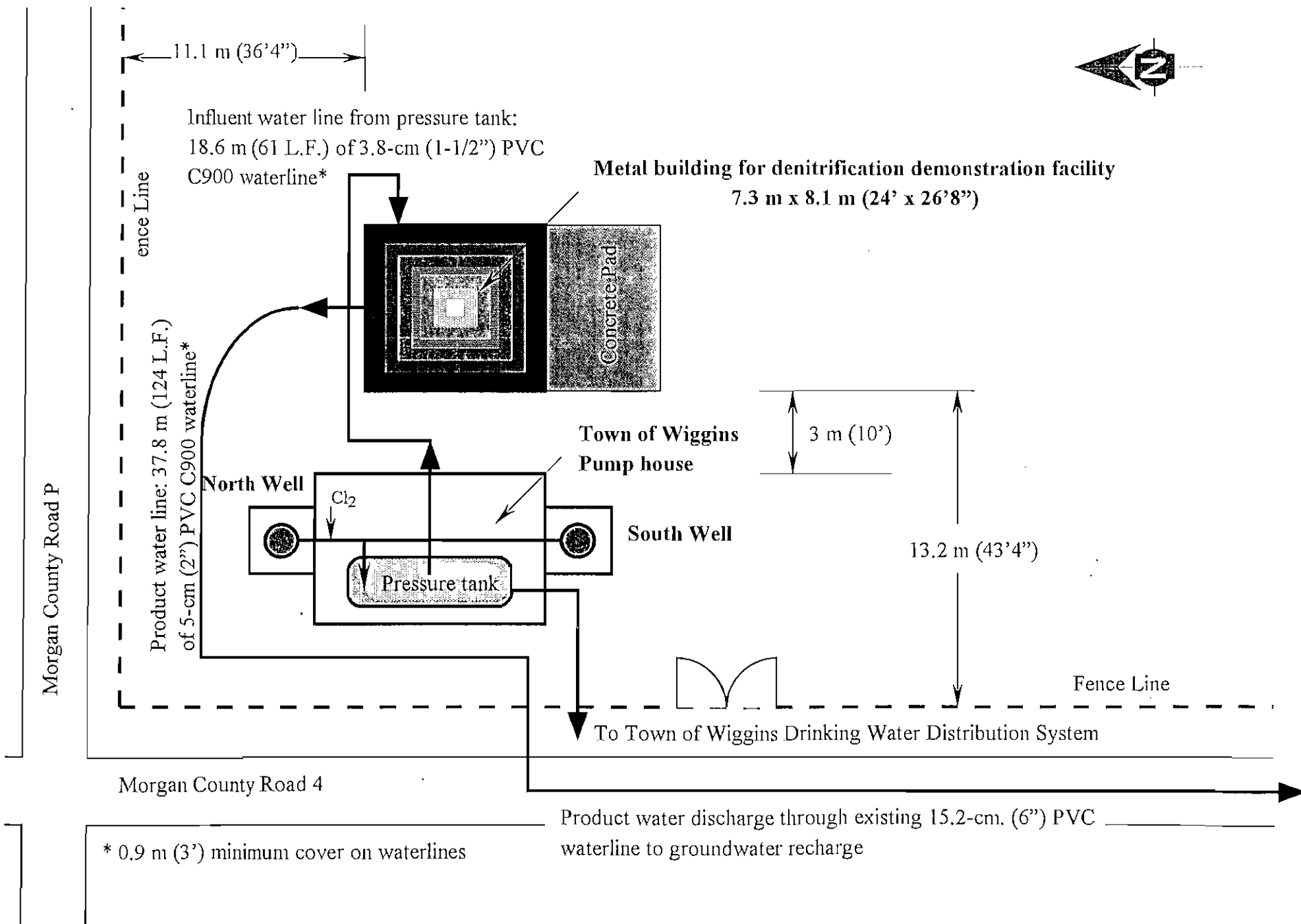


Figure 2: Site plan of drinking water denitrification demonstration facility adjacent to the Town of Wiggins pump house for the municipal drinking water system

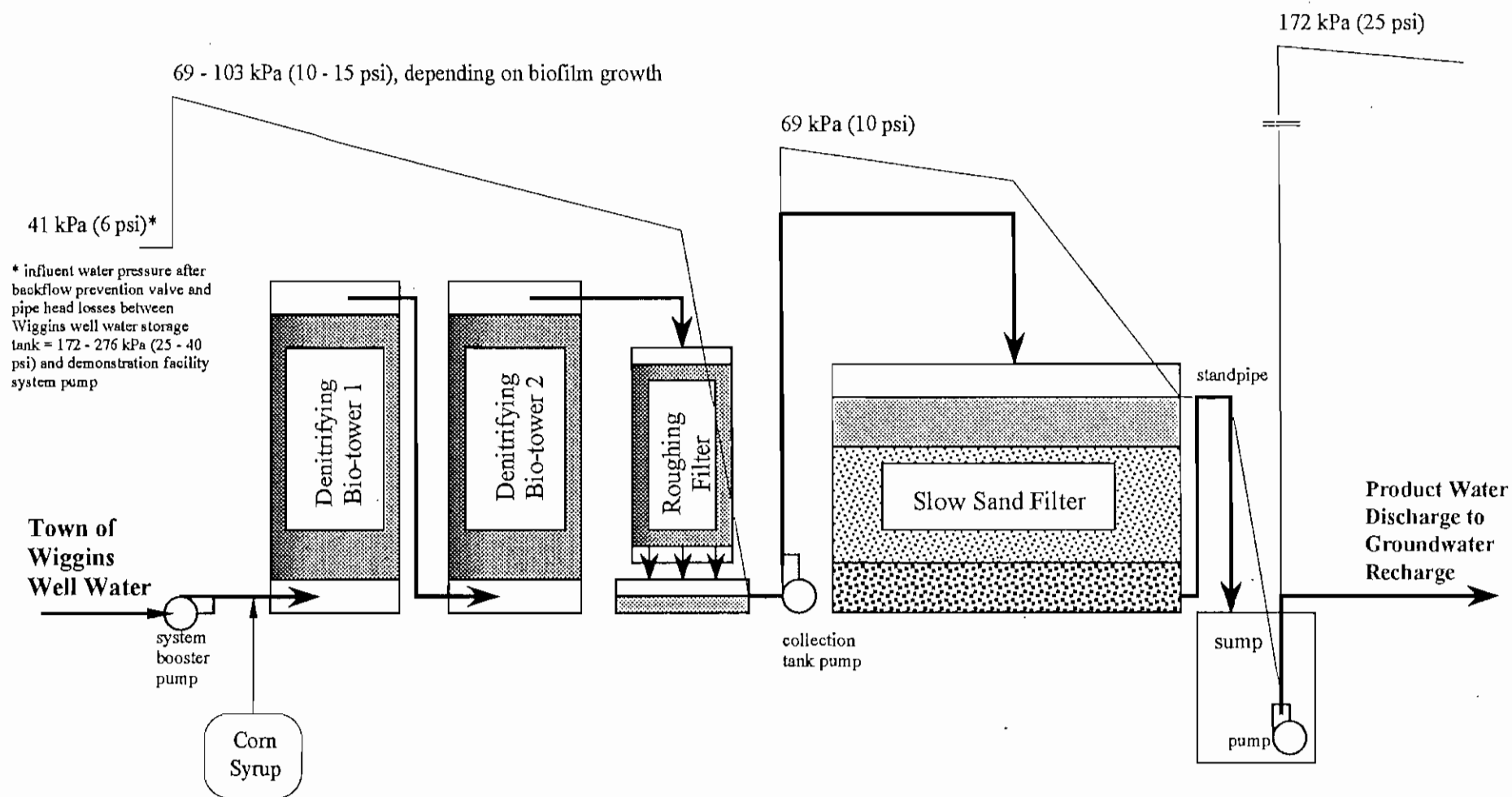


Figure 3. Denitrification demonstration plant at Wiggins, Colorado, process flow sequence and system pressure profile

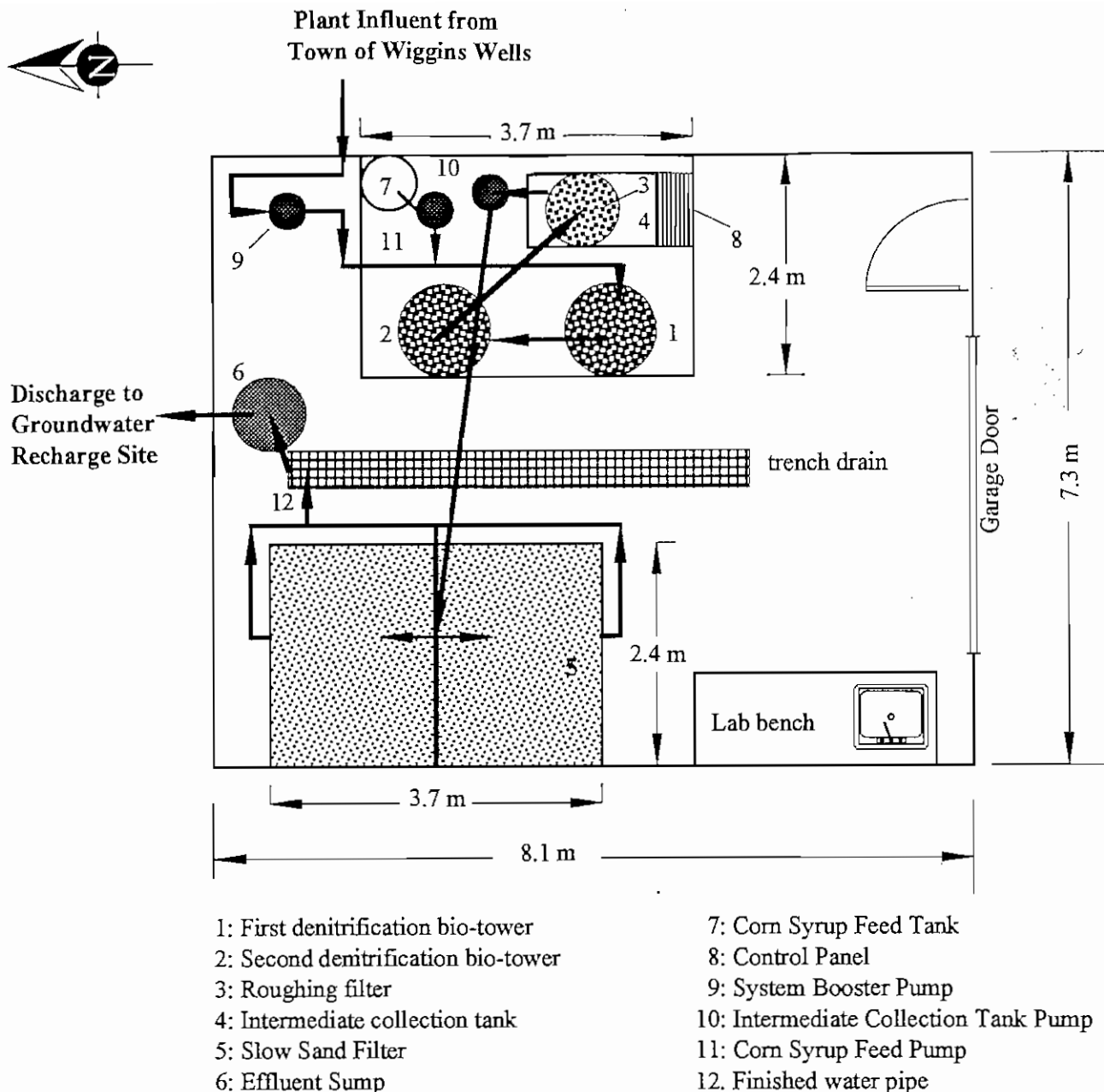


Figure 4: Floor plan and flow scheme of Denitrification Demonstration Plant at Wiggins, Colorado. Water (38 to 76 lpm) enters plant from Town of Wiggins well water storage tank by 18.6 LM 3.8-cm. diameter pipeline to the system booster pump (9). Concentrated corn syrup (7) is metered (11) into 3.8-cm. diameter influent water pipe before water flows through the series of two upflow denitrification bio-towers, (1) to (2), exits at the top of bio-tower 2 through downflow roughing filter (3) into intermediate collection tank (4). Water is pumped (10) from collection tank to slow sand filter (5) where it is split equally between halves. Process pumps (9, 10, and 11) are operated from control panel (8). Filtrate from both halves of the slow sand filter is combined in finished water pipe (12) and discharged to the sump (6) via the trench drain. Finished water is discharged by sump pumps via 20.3-cm. diameter pipeline to the groundwater recharge site 2.4 km from denitrification facility.

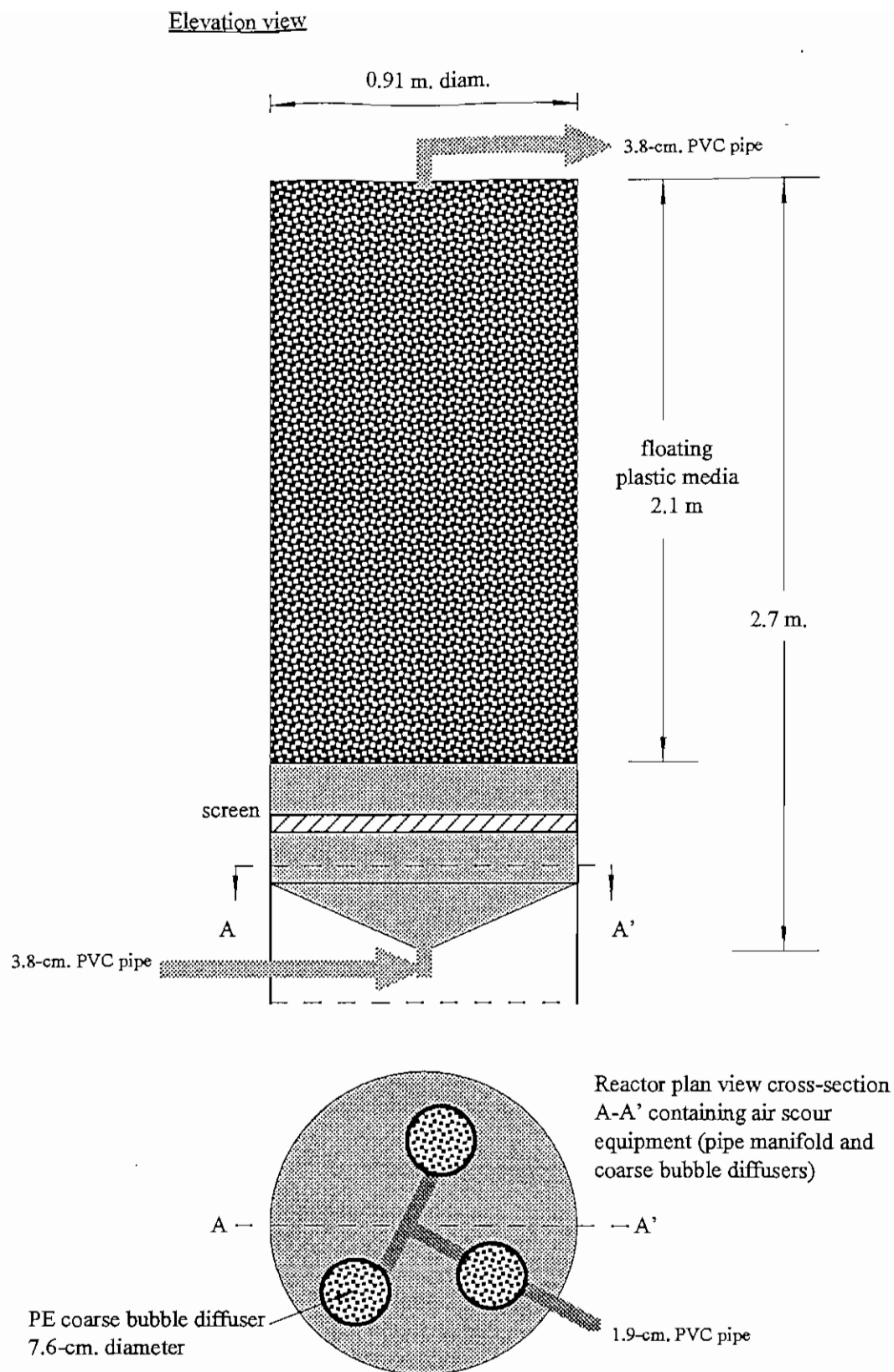


Figure 5: Detail of upflow anaerobic packed-tower denitrification reactor at the Wiggins, Colorado demonstration facility with media floating as during normal operation. Reactor cross-section shows air scour system diffusers.

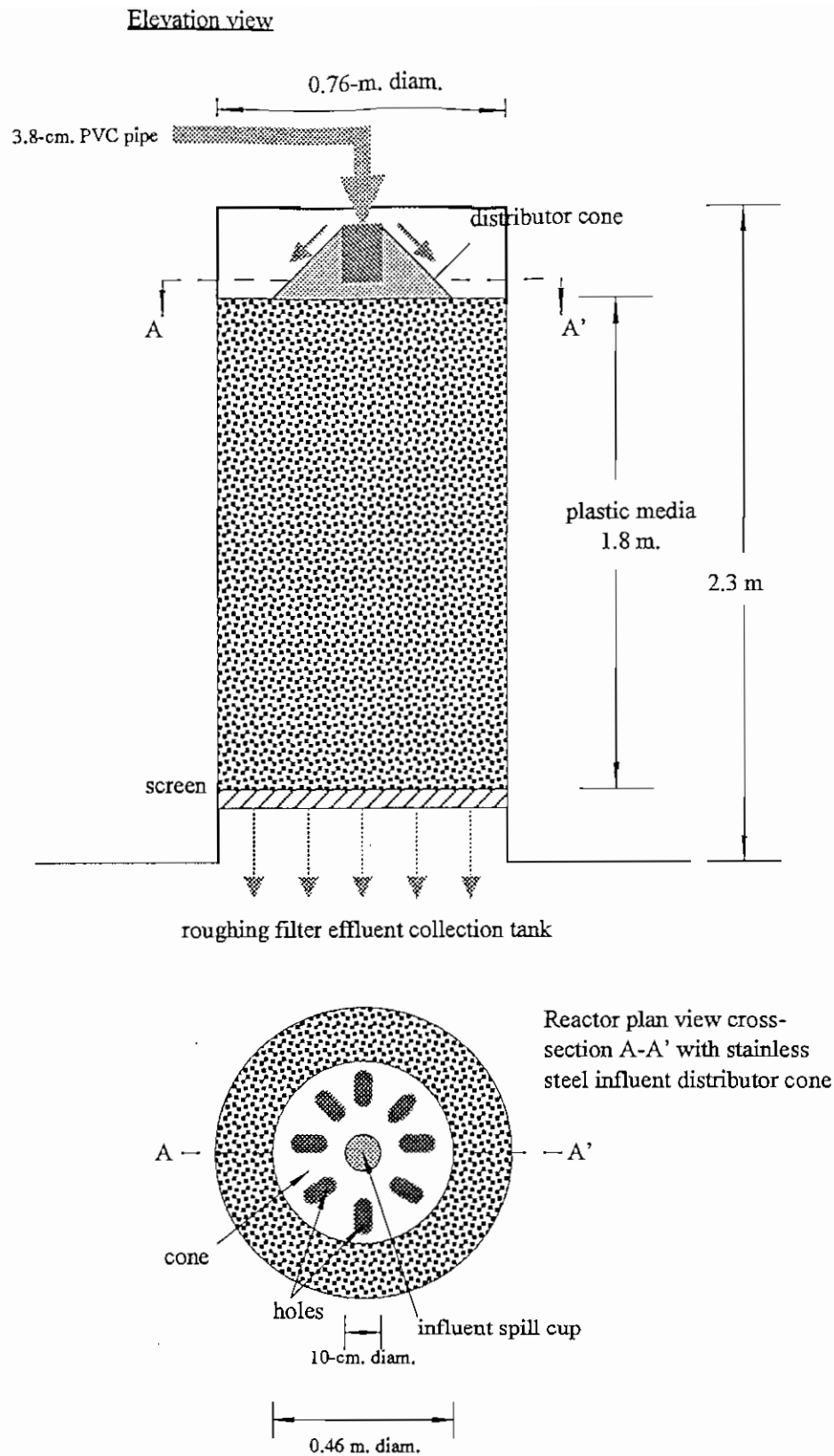


Figure 6: Detail of downflow aerobic biofilm roughing filter with trickling-filter-type flow at the Wiggins, Colorado demonstration facility. Reactor cross-section shows influent distributor cone resting on media surface.



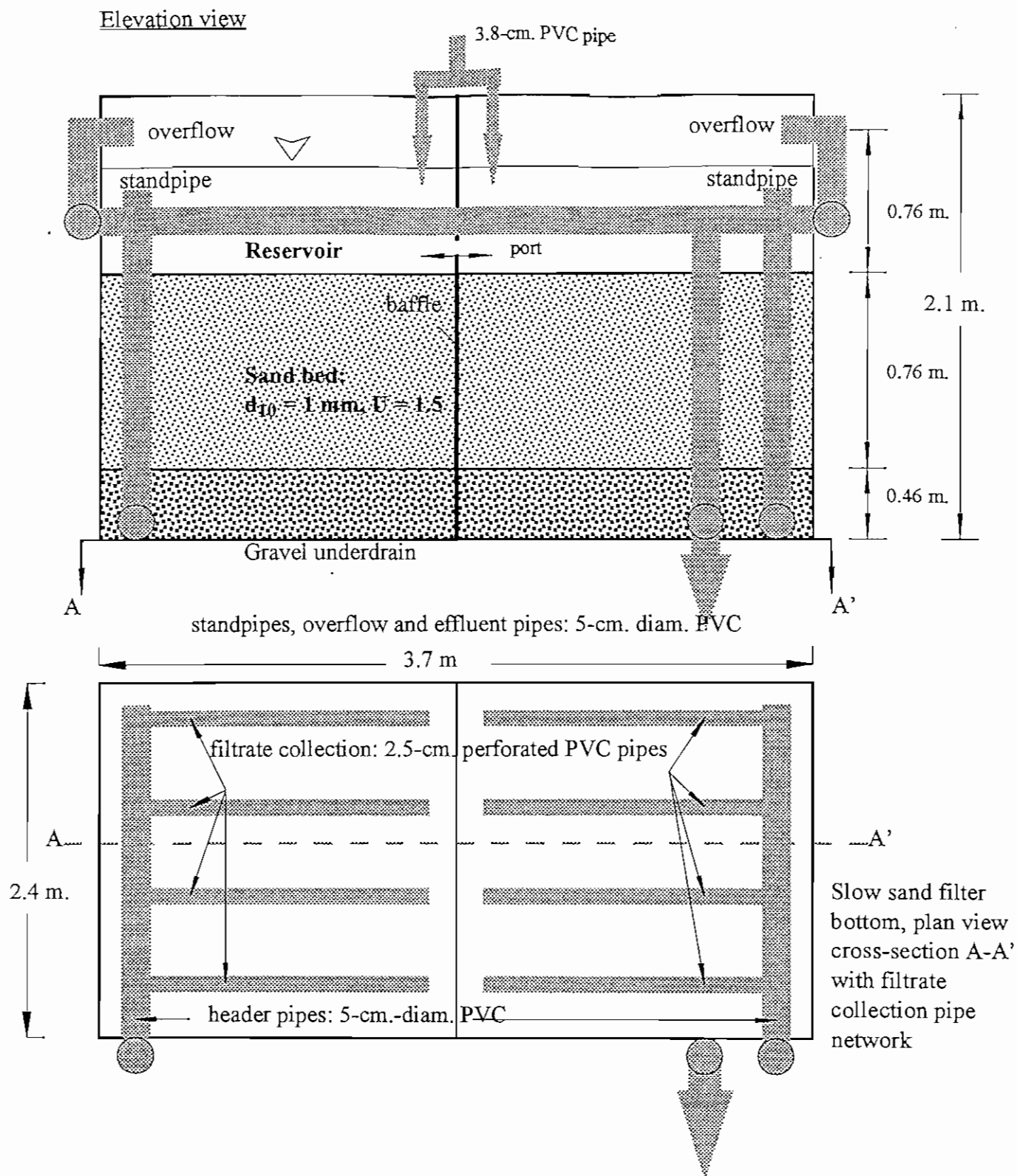


Figure 7: Detail of slow sand filter at Wiggins, Colorado demonstration facility.  
Filter plan-view cross-section at bottom of tank shows filtered water collection pipes

respectively. The denitrification process equipment, including the two bio-towers and the roughing filter were sized for a capacity of 76 liters per minute (lpm), or 20 gallons per minute (gpm), governed by the hydraulic loading rate for the denitrifying bio-towers of  $7.2 \text{ m}^3/\text{m}^2/\text{hr}$  ( $3 \text{ gpm}/\text{ft}^2$ ). However due to size constraints, flow to the slow sand filter, which had a design hydraulic of  $0.25 \text{ m}^3/\text{m}^2/\text{hr}$  ( $0.1 \text{ gpm}/\text{ft}^2$ ), was limited to 38 lpm (10 gpm).

The features of the Wiggins denitrification demonstration system are summarized in Table

1. The Town of Wiggins has two wells located approximately 8 meters (25 feet) apart

| FEATURE   | VALUE   |
|---|---|
| DEMONSTRATION FACILITY LOCATION   | <ul style="list-style-type: none"> <li>adjacent to Town of Wiggins' drinking water supply pump house (2 wells)</li> </ul>   |
| WATER SOURCE  | <ul style="list-style-type: none"> <li>Town of Wiggins drinking water supply (wells <math>\approx</math> 100 ft. deep)</li> </ul>   |
| NOMINAL DESIGN CAPACITY: denitrification bio-towers and roughing filter | <ul style="list-style-type: none"> <li>20 GPM (76 l/min)</li> </ul>   |
| NOMINAL DESIGN CAPACITY: slow sand filter                               | <ul style="list-style-type: none"> <li>10 GPM (38 l/min)</li> </ul>   |
| BUILDING  | <ul style="list-style-type: none"> <li>prefabricated, insulated, 22' x 25', area = 550 ft<sup>2</sup> (58 m<sup>2</sup>); height = 12' (3.7 m); built on concrete slab/foundation wall</li> </ul>   |
| SKID-MOUNTED PROCESS EQUIPMENT  | <ul style="list-style-type: none"> <li>2 @ 8' x 12' (2.4 x 3.7 m) steel skids</li> </ul>  |
| DENITRIFYING BIOTOWERS (2 in series)                                    | <ul style="list-style-type: none"> <li>epoxy-coated steel tanks (cyl.), 3' (0.9 m) diam. x 9' (2.7 m) height</li> </ul>   |
| BIOFILM ROUGHING FILTER (1)   | <ul style="list-style-type: none"> <li>epoxy-coated steel tank (cyl.), 2.5' (0.8 m) diam. x 6' (1.8 m) height</li> </ul>  |
| BIOTOWER AND ROUGHING FILTER MEDIA                                      | <ul style="list-style-type: none"> <li>1.5 in. (3.8 cm) diam. Norpac, polypropylene rings; specific surface area = 150 ft<sup>2</sup>/ft<sup>3</sup> (45 m<sup>2</sup>/m<sup>3</sup>), spec. grav. = 0.96; porosity = 0.94</li> </ul>   |
| SLOW SAND FILTER (1 tank divided in two sections)                       | <ul style="list-style-type: none"> <li>epoxy-coated rectangular steel tank, surf. area = 100 ft<sup>2</sup> (9.3 m<sup>2</sup>)</li> </ul>  |
| FILTER SAND   | <ul style="list-style-type: none"> <li>washed quartz silica sand, d<sub>10</sub> = 1 mm, U = 1.5, sphericity &gt; 0.85</li> </ul>   |
| PUMPS   | <ul style="list-style-type: none"> <li>1 system pump, cap. = 45 gpm (170 lpm)</li> <li>1 roughing filter effl., cap. = 20 gpm (76 lpm)</li> <li>1 carbon feed dosing, cap. = 50 mlpm</li> <li>2 effluent sump, cap. = 25 gpm ea. (95 lpm)</li> </ul>  |
| PIPING  | <ul style="list-style-type: none"> <li>PVC, 2" (5 cm) OD</li> </ul>   |
| SYSTEM & PROCESS CONTROLS   | <ul style="list-style-type: none"> <li>flow meters (influent)</li> <li>pressure monitors (influent and bio-towers);</li> <li>control panel for by-pass valves and pumps, with shut-down and visible/audible alarms</li> <li>process tank overflows to sump</li> <li>water level controls (roughing filter effl., slow sand filter reservoir and effluent sump)</li> </ul> |
| OPERATOR PRESENCE   | <ul style="list-style-type: none"> <li>intermittent</li> </ul>  |
| DISCHARGE   | <ul style="list-style-type: none"> <li>sump to 1.5-mi. 8" pipeline to groundwater recharge or crop irrigation</li> </ul>  |

Table 1. Features of the Drinking Water Denitrification Facility at Wiggins, Colorado

used alternately for drinking water supplies, depending on the season. The water quality from the wells, which both draw water from a depth of 30 to 45 meters (100 to 150 feet), is similar and has been summarized below in Table 2.

| Chemical                                 | Value         |
|--|---------------|
| Nitrate-nitrogen (NO <sub>3</sub> -N)    | 5 - 10 mg/L   |
| Sulfate (SO <sub>4</sub> <sup>2-</sup> ) | 450 mg/L      |
| Alkalinity (CaCO <sub>3</sub> )          | 230 mg/L      |
| Hardness (CaCO <sub>3</sub> )            | 200 mg/L      |
| dissolved organic carbon (DOC)           | 1.5 - 3 mg/L  |
| turbidity                                | 0.1 NTU       |
| pH                                       | 7.2 - 7.3     |
| temperature                              | 13 - 18 °C    |
| total coliform                           | 0 (Absent)    |
| <i>E. coli</i>                           | 0 (Absent)    |
| dissolved oxygen*                        | 1 - 8 mg/L    |
| chlorine residual*                       | 0.5 - 15 mg/L |

\* after air-pressurized chlorine contact tank

Table 2. Water quality in Town of Wiggins wells used for drinking water supply and for the denitrification demonstration. The variation in nitrate reflects seasonal variations and differences between the two wells used alternately for drinking water supply. Dissolved oxygen in the well water varies between 1 and 2 mg/L, however, depending on detention time in the pressurized tank, influent dissolved oxygen to the denitrification process had transient dissolved oxygen concentrations as high as 8 mg/L. In general the chlorine residual was less than 2 mg/L - which we had found to be not to inhibit the dense denitrifying biofilm in the bio-towers. However, due to an anomaly in the chlorine gas dosing control system, there were frequent transients as high as 15 mg/L, requiring addition of sodium thiosulfate to destroy the residual chlorine before the water entered the bio-towers.

#### START-UP OF WIGGINS DRINKING WATER DENITRIFICATION FACILITY

A denitrifying biofilm was inoculated into the packed tower reactors using a suspended growth bacterial seed inoculated with sediment from Boulder Creek in Boulder, Colorado. The sediments were chosen after testing several soil and sediment samples from

the vicinity of Boulder, Colorado for *E. coli* bacteria. None were detected in the Boulder Creek sediment, so laboratory enrichment in anoxic conditions suitable for denitrification began. After several weeks of acclimation in the University of Colorado Environmental Engineering labs, approximately 200 liters of suspension was brought to the Wiggins facility and dosed into the two denitrifying packed tower reactors (bio-towers). The two bio-towers had a volume of 1,550 liters (410 gallons) each, so that the inoculum was diluted approximately 8-to-1 and recirculated for 5 days. During recirculation stock solutions of nitrate, the carbon substrate which was acetic acid, and phosphate buffer were added three times. There were equipment problems, including failure of the recirculation pump, and the towers were re-inoculated with fresh seed to insure that the denitrifying biofilm would grow in the bio-towers.

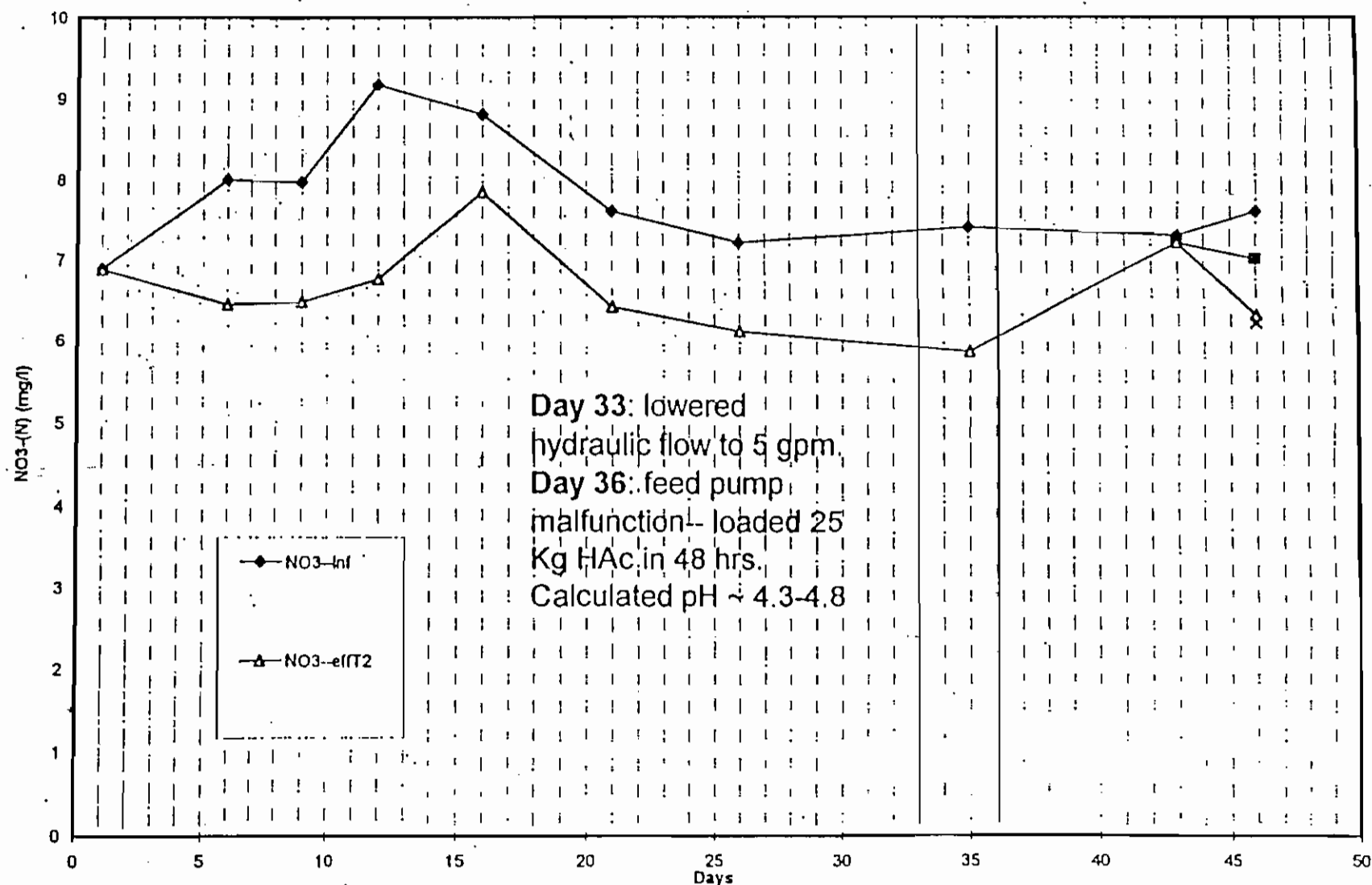
#### **START-UP PROBLEMS, JULY - OCTOBER 1996**

Figure 8 is the nitrate nitrogen influent and bio-tower effluent at the Wiggins plant during July through mid-August 1996. Nitrate removal was very disappointing, averaging less than 25%. On the 43rd day of the initial operation, the acetic acid dosing pump failed by over-dosing concentrated acetic acid at approximately 10 times the intended rate, and the pH of the bio-tower dropped to the range of 4.3 to 4.8. The pump was removed for repairs, and during that time, experiments were done in the Environmental Engineering laboratories to pinpoint the reason for the poor denitrification performance. Factors considered included: water pH, dissolved oxygen, lack of trace nutrients and chlorine.

Low pH. As can be seen in Figure 8, denitrification completely stopped when the water pH dropped on day 43, and so experiments were done to assess the effects of low

Figure 8.

Influent and effluent nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ): biotower influent ("NO3-inf") and effluent ("NO3-effT2") data from July 10 to August 25, 1996 (days 1 - 46 on x-scale). On day 46, intermediate samples from between the two denitrifying biotowers ("NO3-effT1") and from the slow sand filter effluent ("NO3-effSSF") were added. (In "malfunction" note, "HAc" stands for acetic acid. Note refers to pump failure when acetic acid was dosed in at approximately 12 time the design rate, resulting in a pH drop to 4.3-4.8.)



pH on the denitrifying biofilm using bench-scale biofilm reactors built to simulate the Wiggins denitrification process. For the test, a 5-liter packed-tower reactor with an acclimated denitrifying biofilm was exposed to water at a pH of 4.5 - 4.8 by buffering with acetic acid, simulating the pump failure event at Wiggins. After 24 hours, the reactor was drained and refilled with water with nitrate and acetate at a normal pH of 7.1. Figure 9 is the recovery profile. Even with an acclimated biofilm, there was a lag of over 2 days before denitrification began. Complete denitrification occurred only after 3 days, when before the low-pH incident, denitrification of the same influent had taken less than 4 hours.

Because failure of the dosing pump would always be a possibility in the future, it was decided to investigate alternate carbon substrate sources. Corn syrup was an attractive candidate. Other investigators have shown that sugars can be used by denitrifying bacteria for growth and energy. Corn syrup is readily available in food grade and is significantly less expensive than food-grade acetic acid. Like acetic acid, corn syrup can be pumped in the concentrated form. Furthermore, in the concentrated form, the water activity in corn syrup is too low for bacterial contamination so that storage is simple. Although corn syrup will crystallize at low temperatures, this can be easily prevented by an inexpensive drum or tank heater which keeps the corn syrup temperature above 20 °C. Experiments were done in the lab using the bench-scale denitrification reactor to determine the denitrifying biofilm requirement for corn syrup. The final result is shown in Figure 10, where a dose of 2.2 grams corn syrup carbon per gram nitrate-nitrogen was found to produce complete denitrification. Currently at the Wiggins process, 1.8 g-carbon:g-nitrogen is being added to the influent water.

Figure 9: Results of laboratory simulation of low-pH condition which occurred at the Wiggins facility caused by overdosing of acetic acid. pH was reduced to 4.8 for 24 hours and then normal nitrate feed with approximately 100 mg/L  $\text{NO}_3\text{-N}$ , acetate substrate and buffer to maintain  $7.1 < \text{pH} < 7.4$  was added. Before low-pH event, nitrate was completely reduced in less than 4 hours in the lab biofilm reactor. After 24 hours at pH 4.8, denitrification was completely inhibited for 48 hours and then resumed slowly, with complete reduction taking 4 - 5 days.

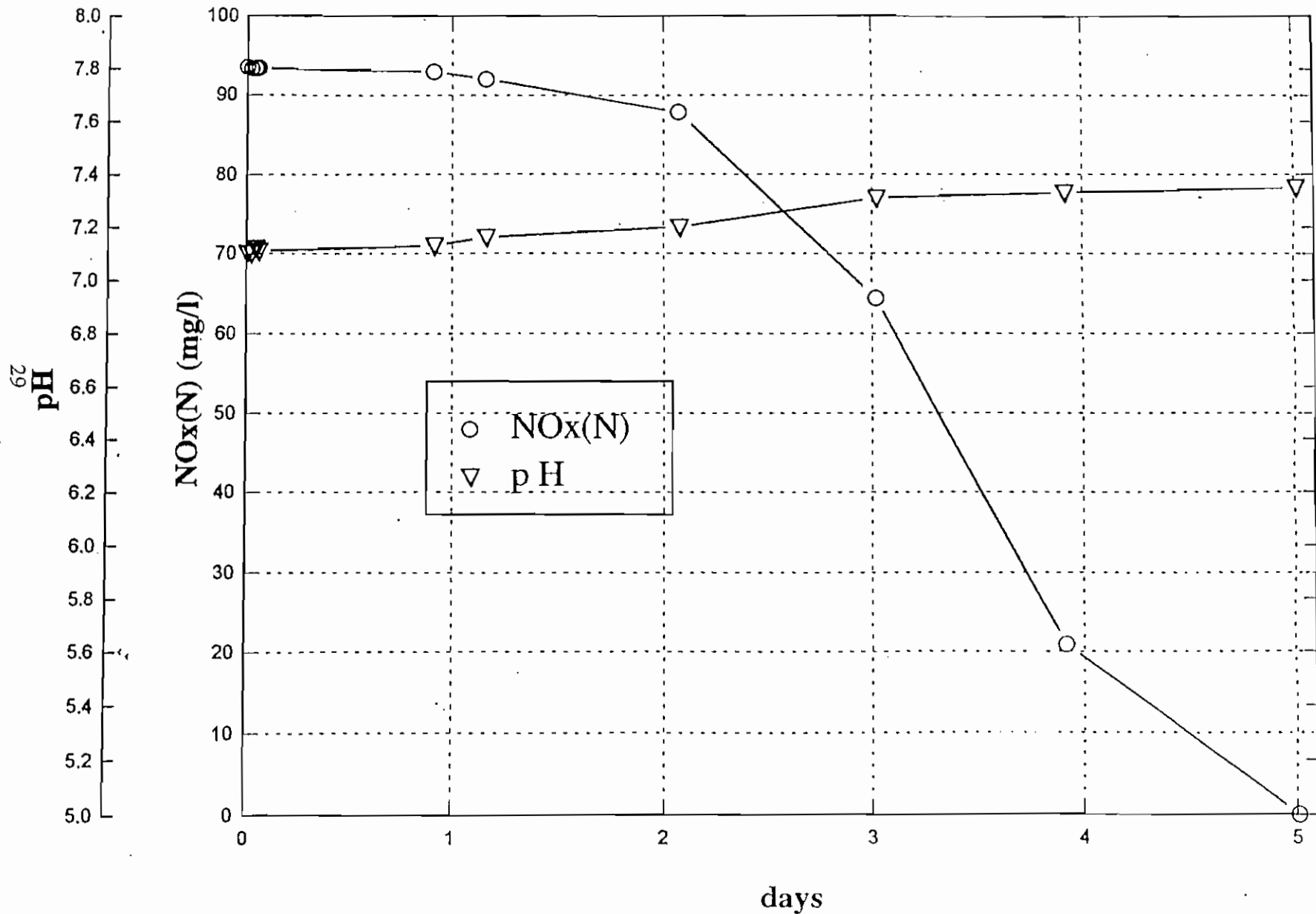
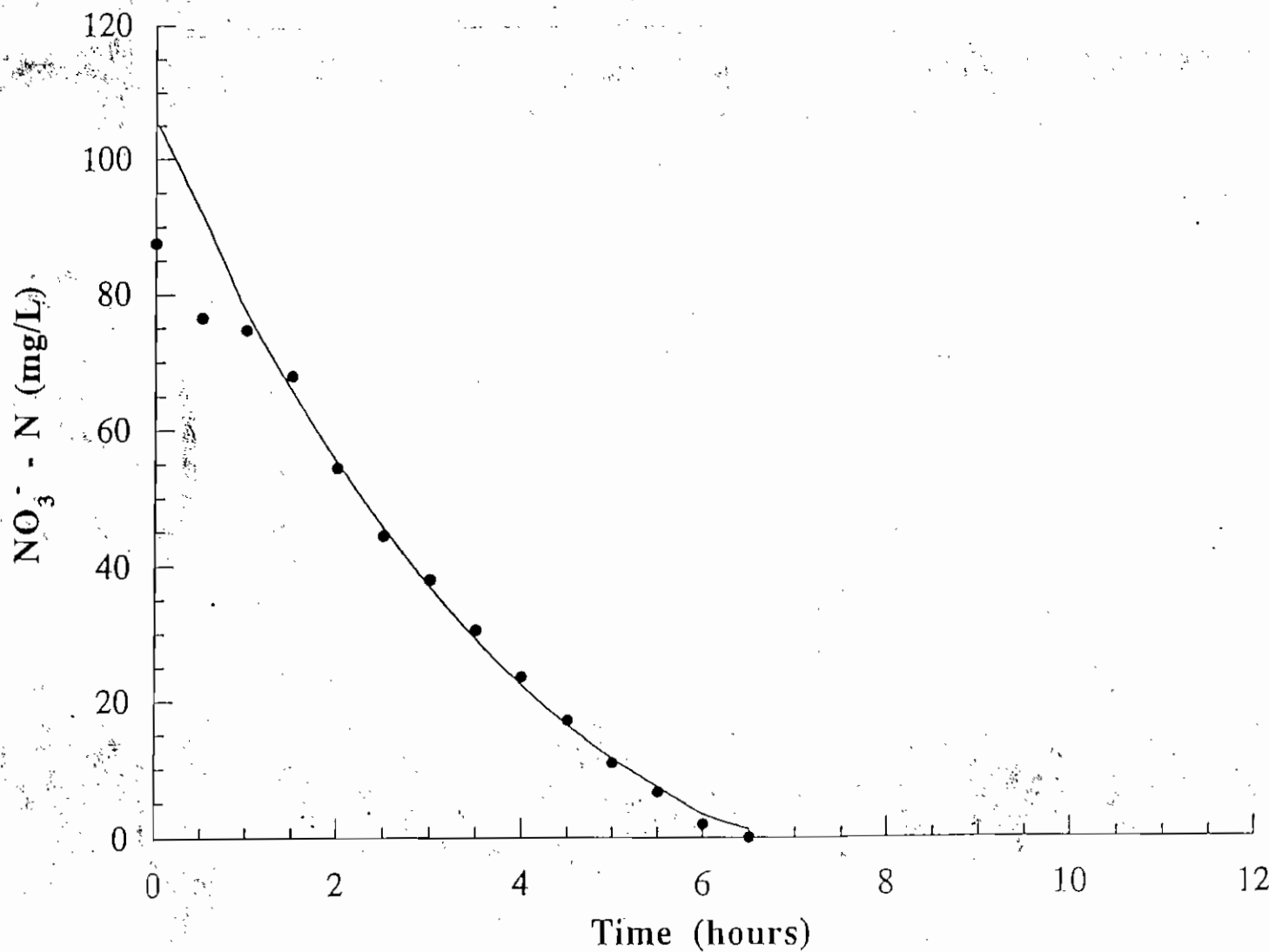




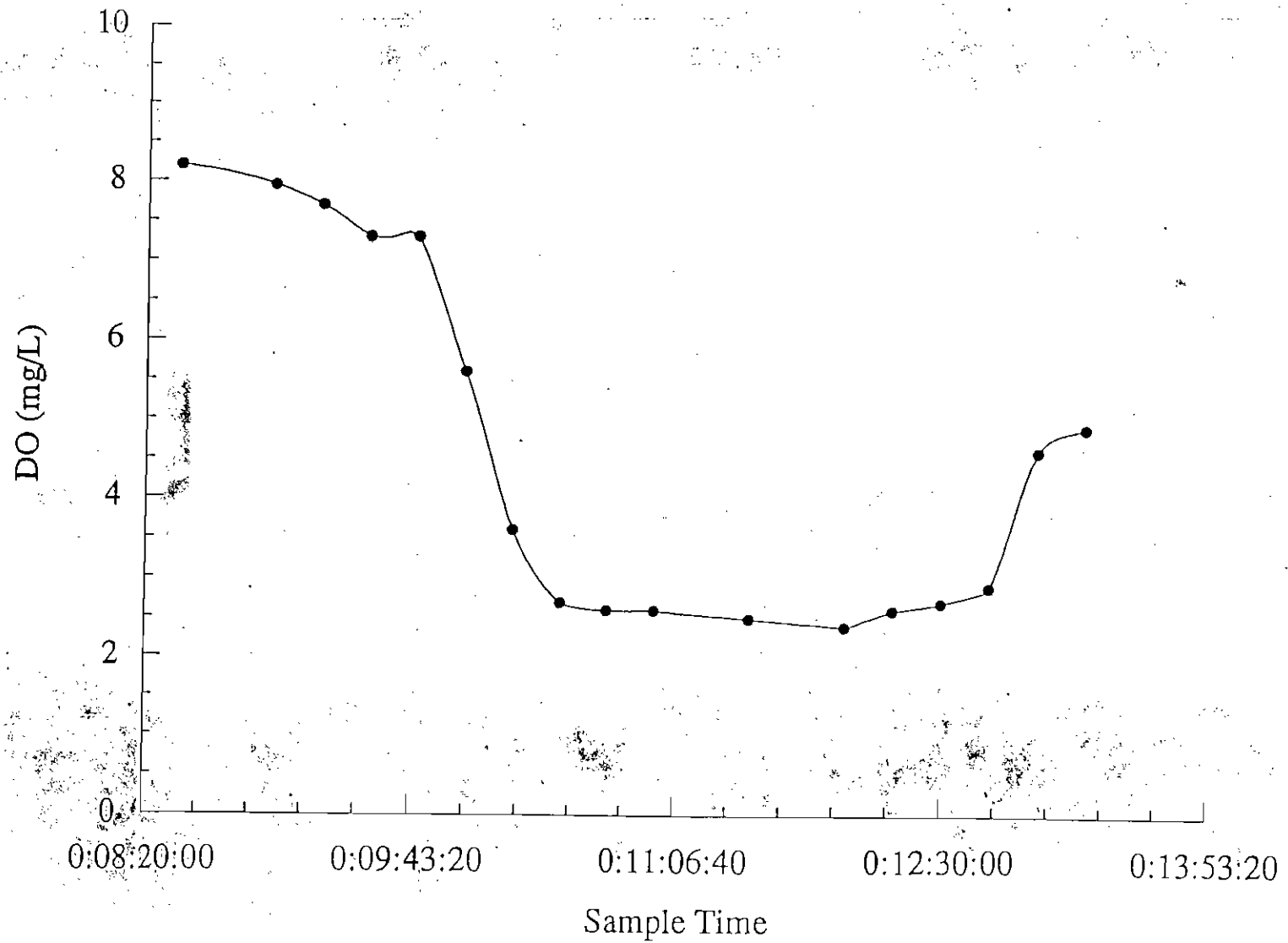
Figure 10. Nitrate profile showing complete reduction of nitrate in bench-scale biofilm reactor with corn syrup used for carbon and energy substrate. Corn syrup was added to achieve a ratio of 2.2 grams dissolved organic carbon-to-1 gram nitrate-nitrogen.



The carbon content of acetic acid and corn syrup which is composed primarily of glucose and fructose is the same: 40% by weight. However, on a weight basis, corn syrup is significantly less expensive than food-grade glacial (pure) acetic acid. Acetic acid costs vary depending on quantity and proximity of the supplier. For the Wiggins facility, the food-grade acetic acid cost was approximately \$2.00 per kilogram (\$0.91 per pound). Currently we are paying \$0.51 per kilogram (\$0.23 per pound) for corn syrup, a savings of 75%. The cost of removing 20 mg/L  $\text{NO}_3\text{-N}$  from water with acetic acid as the substrate at the carbon dosing rate used at Wiggins would be approximately \$0.18/m<sup>3</sup> (\$0.33/1,000 gallons) treated. In comparison, the estimated unit cost of using corn syrup under the same dosing conditions is \$0.045/m<sup>3</sup> (\$0.08/1,000 gallons) treated.

Dissolved oxygen. Figure 11 is a profile of dissolved oxygen in water influent to the Wiggins denitrification plant, with samples measured from 8:20 AM to 1:53 PM. The dissolved oxygen level fluctuated over a surprisingly wide range: from a high of 8 mg/L to approximately 2.5 mg/L. During earlier research at the pilot plant in Brighton, Colorado operated by the University of Colorado (Cook et al., 1991), dissolved oxygen averaged over 5 mg/L without inhibiting the denitrification process. However, in the presence of dissolved oxygen bacteria in the bio-tower biofilm will use carbon substrate to reduce oxygen instead of nitrate. That means that extra carbon must be added to account for influent dissolved oxygen. A difficulty at Wiggins was that the fluctuation in dissolved oxygen made it difficult to determine the extra carbon requirement. It was decided to add carbon for an average dissolved oxygen concentration of 4 mg/L, and to expect some minor fluctuation in denitrification performance. (This problem would not occur in a system designed to be a municipal water supply where the well pump design could be

Figure 11. Profile of influent well water dissolved oxygen at Wiggins demonstration, October 1996.



adjusted to accommodate the need for a constant and relatively low level of influent dissolved oxygen.)

Trace Nutrient Deficiency and Toxicity. Although it seemed unlikely in a groundwater with high dissolved solids, one concern was that deficiency in trace nutrients was responsible for the poor initial denitrification. Table 3 shows the results of analysis for five metals using ICP-AES (inductively coupled plasma-atomic emission spectrometry). Two, molybdenum (Mo) and vanadium (V), have been reported to be essential co-factors for denitrification enzymes. Copper (Cu) has been reported to be toxic to denitrifying bacteria. Both molybdenum and vanadium were found in sufficient quantity and no copper was detected. Phosphate was measured using an ion chromatograph at 1 to 1.5 mg/L, sufficient for bacterial growth. Unfortunately the phosphorus measurement was erroneous. Phosphate was reanalyzed later and found to be very deficient. Phosphate now is added to the influent water at Wiggins.

| Inorganic chemical                      | Well Water<br>(mg/L) | Denitrified<br>Water<br>(mg/L) | Slow Sand Filter<br>Effluent<br>(mg/L) |
|---|----------------------|--------------------------------|--|
| Iron, Fe (total)                        | 0.003                | 0.000                          | 0.006                                  |
| Manganese, Mn (total)                   | 0.271                | 0.304                          | 0.155                                  |
| Molybdenum, Mo                          | 0.018                | 0.079                          | 0.018                                  |
| Vanadium, V                             | 0.005                | 0.005                          | 0.007                                  |
| Copper, Cu                              | 0                    | 0                              | 0                                      |
| Phosphate, PO <sub>4</sub> <sup>-</sup> | ~1*                  | --                             | --                                     |

\*erroneous measurement; phosphate re-analyzed to be below detection limit

Table 3: Dissolved inorganic compounds in the Town of Wiggins municipal well water, after denitrification and slow sand filtration

Chlorine. The influent chlorine residual was measured frequently during the weekdays when we usually sampled the system at Wiggins, and was always less than 2 mg/L. However, we detected a very high chlorine residual of over 15 mg/L one Sunday,

and decided to investigate further. We found that during the summer months, the well pump could be shut off due to low system demand in town, but chlorine gas was continuously dosed because the pump motor remained on. This resulted in frequent transients (1 - 2 per day) lasting an hour or more when super-chlorinated water with a residual of 10 - 15 mg/L chlorine was pumped into the Wiggins system. We thought that these transients were seriously harming the denitrifying biofilm and decided to add sodium thiosulfate to quench the residual. Figure 12 is a chlorine profile after thiosulfate addition was begun, controlling the influent chlorine residual to less than 0.4 mg/L chlorine.

Restart. After the Wiggins denitrification system had been shut down for over one month, the bio-towers were re-inoculated and the system started up again on October 1, 1996, using corn syrup as carbon feed and with sodium thiosulfate added to destroy influent chlorine. This time, the system flow rate was initially low, 5 gpm, compared with the bio-tower design capacity of 20 gpm. The flow rate was increased gradually through December to 10 gpm. Figure 13 is a profile of influent and effluent nitrate during that period. Denitrification performance was greatly improved with removals averaging 75%. Figure 14 shows the fluctuation in influent dissolved oxygen during this time.

#### **OPERATION CHANGES AT WIGGINS, JANUARY AND FEBRUARY 1997**

In a visit to the Wiggins plant at the end of December 1996, Jerry Biberstine, Director of the Drinking Water Section of the Colorado Department of Public Health and Environment suggested that we increase the influent nitrate over the relatively low levels at Wiggins (5 to 10 mg/L  $\text{NO}_3\text{-N}$ ) to over 20 mg/L  $\text{NO}_3\text{-N}$ . At the same time we reanalyzed the phosphate and found it to be insufficient for sustaining growth of the

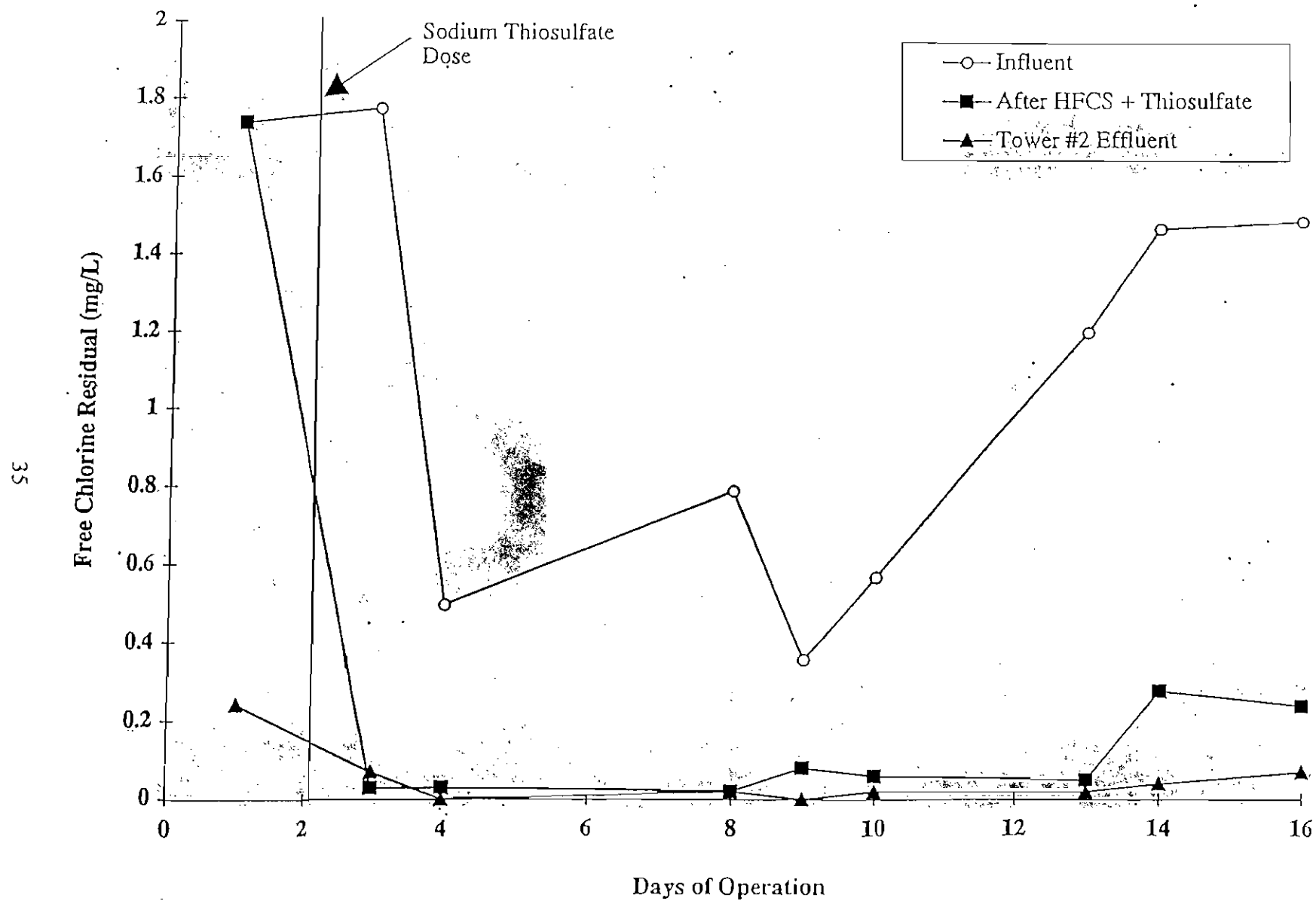


Figure 12. System Free Chlorine Residual Profiles, October 1 - 16, 1996

Figure 13. Denitrification at Wiggins after second start-up.

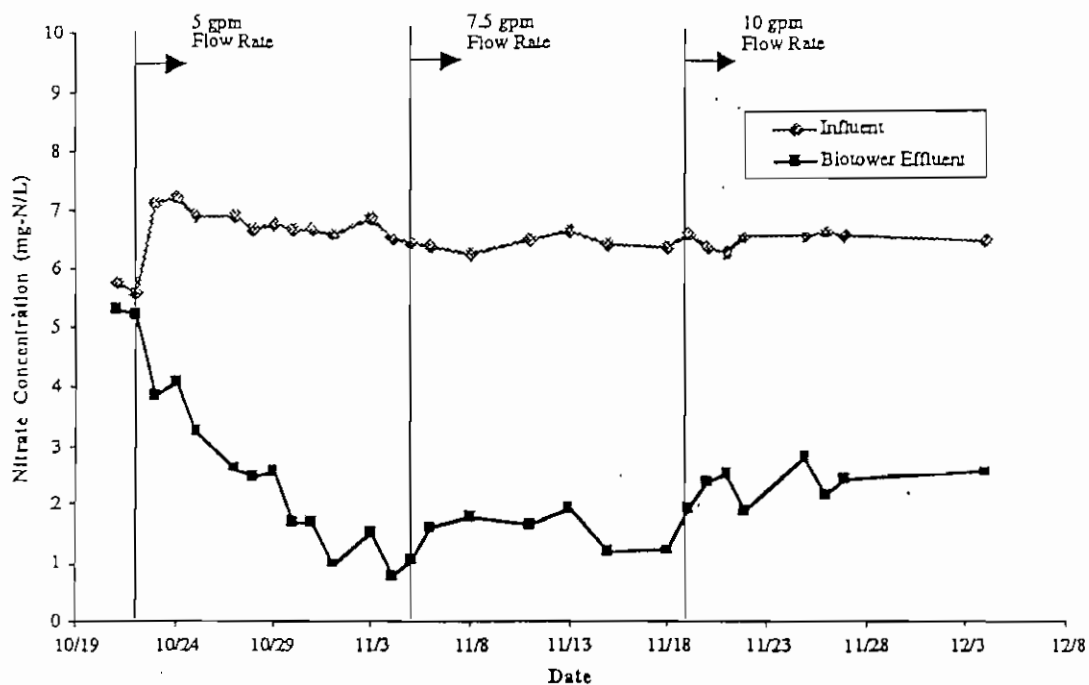
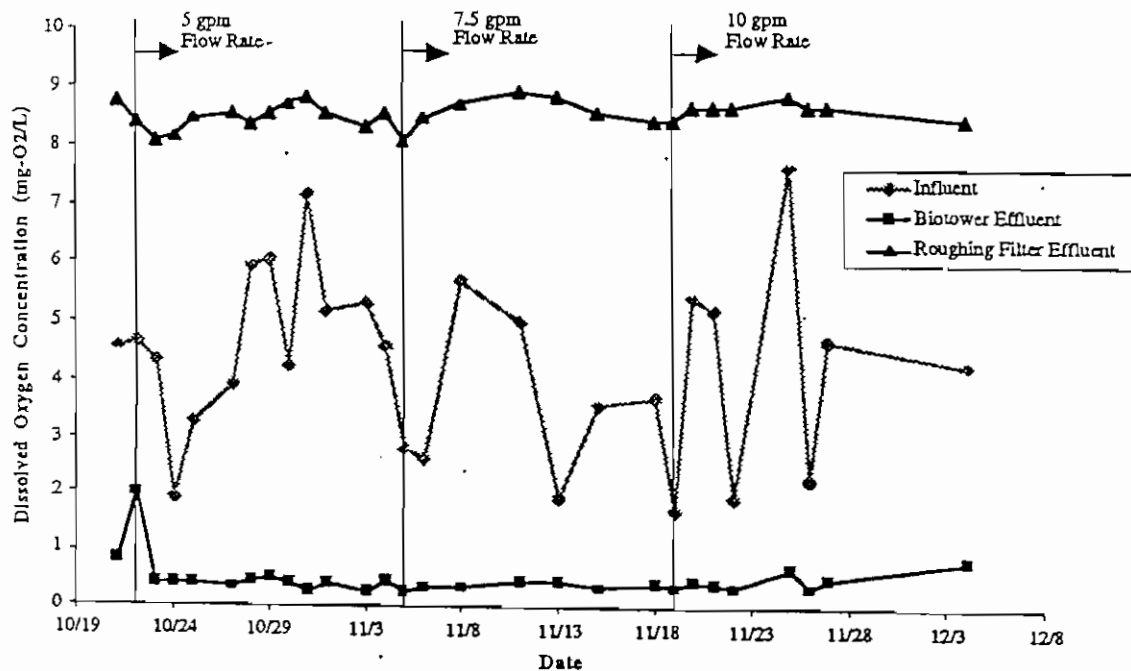


Figure 14. Dissolved oxygen profiles during second period of operation



denitrifying bacteria. Accordingly, both nitrate and phosphate addition was begun in March 1997.

#### **CURRENT OPERATION OF WIGGINS PLANT, MARCH 1997 TO THE PRESENT**

Influent nitrate now varies between 20 and 25 mg/L, with the variation the result of the fluctuation in the well water nitrates. Flow through the system is being maintained at 38 lpm (10 gpm), in order to insure steady hydraulic loading of the slow sand filter, which was only designed for a capacity of 38 lpm. (It was found that loading at 76 lpm (20 gpm) resulted in rapid clogging necessitating frequent scraping.) With the exception of one failure in the carbon dose pump which shut down the carbon feed, denitrification in the bio-towers has been complete, as a function of the carbon fed to the system. In general, some nitrate residual in the effluent is desirable to prevent the unwanted bacterial side-reaction of sulfide production. The nitrate profile showing the well water influent, augmented denitrification system effluent and bio-tower effluent nitrate is shown in Figure 15. Consistent denitrification even during well water influent nitrate fluctuation in early April, as shown in Figure 15 is evidence of the adaptability of the biofilm denitrification process. The two spikes of effluent  $\text{NO}_3\text{-N}$  on May 8 and May 21 coincided with failure of the corn syrup dosing pump, underscoring the importance of the carbon substrate to the denitrification process. Figure 16 shows that over 75% of the denitrification is occurring in the first bio-tower, indicating that reactor capacity is higher than the current demand.



Figure 15. System nitrate profile showing overall denitrification of the two packed tower biofilm reactors ("Biotower") in series denitrification during the period of April through June 1997 after nitrate was added to achieve an average influent  $\text{NO}_3\text{-N}$  level of approximately 20 mg/L. Nitrate concentration of the well ("raw") water fluctuates between 6 and 8 mg/L  $\text{NO}_3\text{-N}$ . Effluent nitrate spikes on May 8 and May 21 are due to failure of the corn syrup dosing pump.

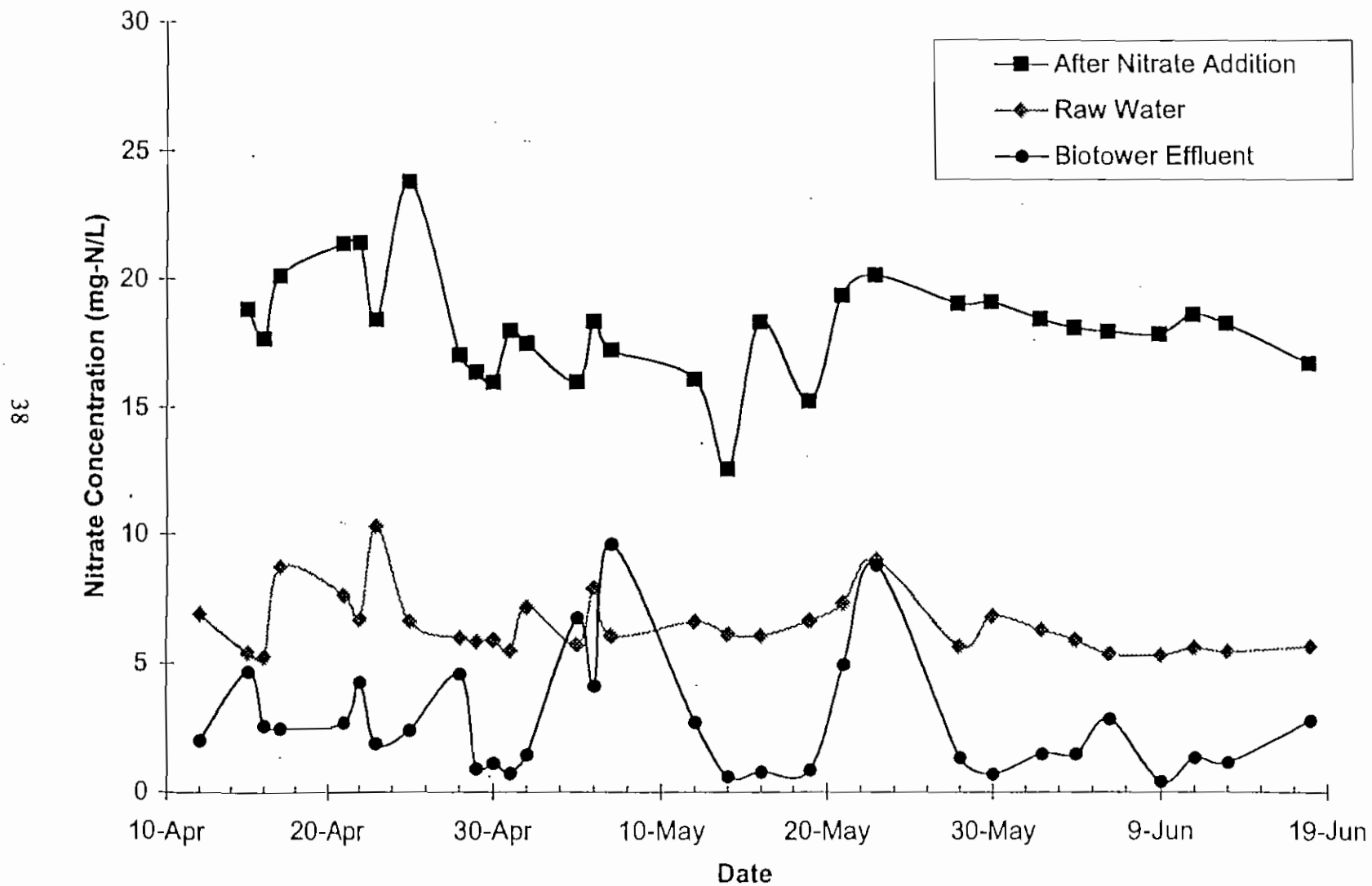
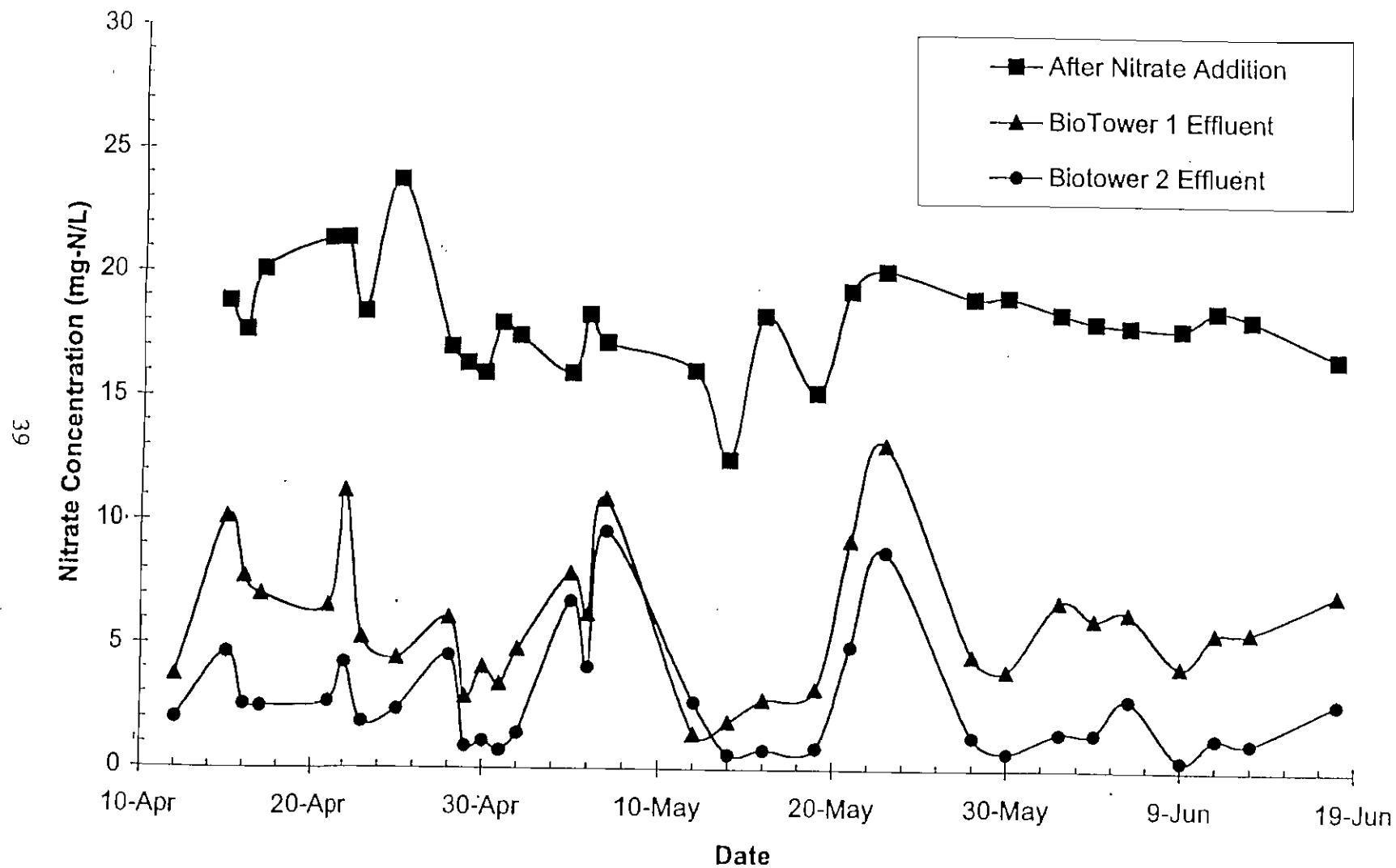


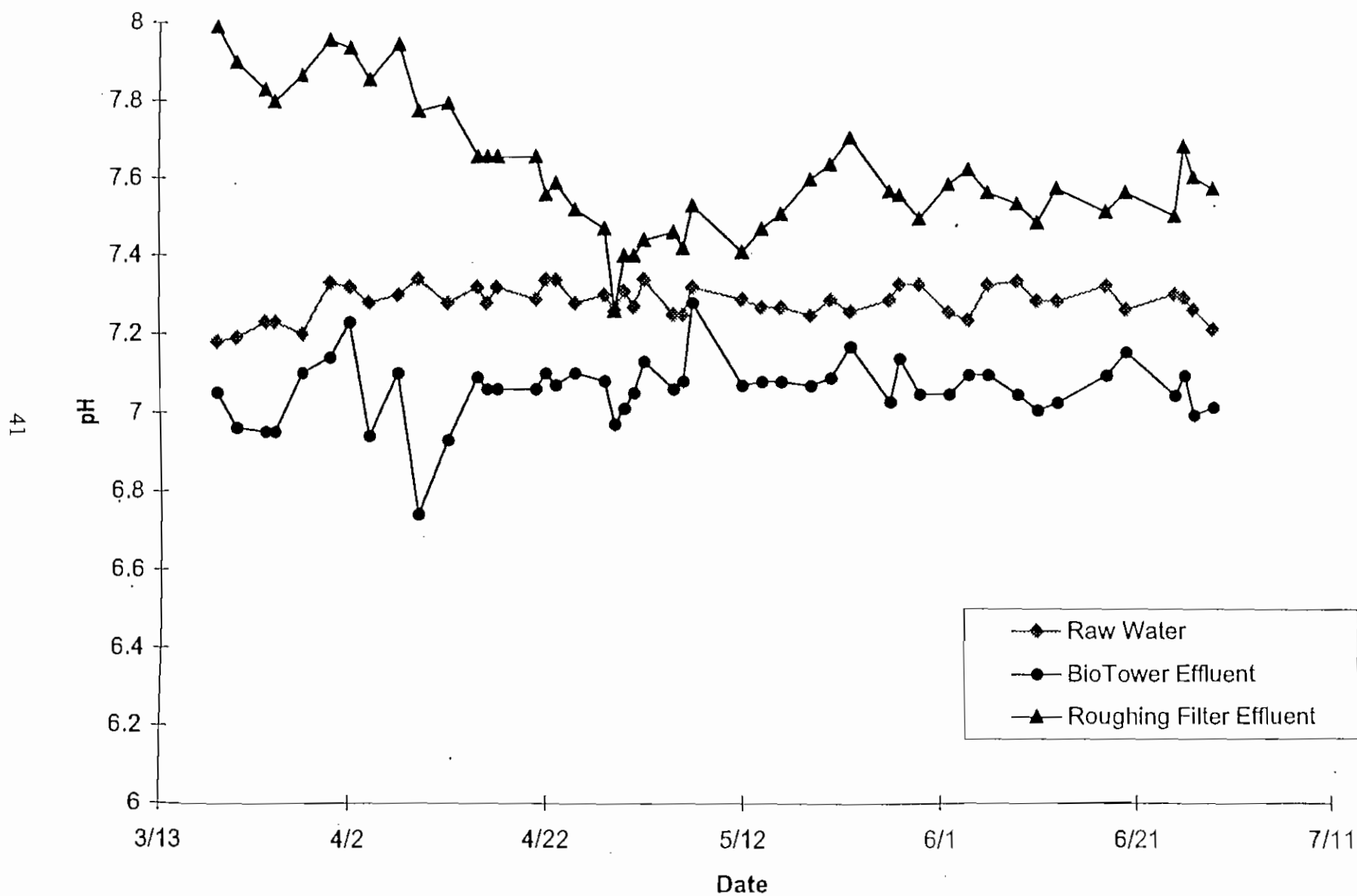
Figure 16. Nitrate profiles showing separate performance of each packed tower biofilm reactor ("Biotower 1 and 2") separately during the period of April through June 1997 after nitrate was added to achieve an average influent  $\text{NO}_3\text{-N}$  level of approximately 20 mg/L. Effluent nitrate spikes on May 8 and May 21 are due to failure of the corn syrup dosing pump.



Excess biofilm removal. An air scour process is used to remove excess biomass from the bio-tower media every 21-25 days. Normal pressure head at the bio-tower inlet is approximately 48 kPa (7 psi). When the influent pressure rises to 83 - 90 kPa (12 - 13 psi), air scour is done. The flow to both bio-towers stops and the two towers are isolated from each other by valves. For each tower, a drain valve is opened to removed approximately 15% of the bio-tower liquid and then closed. A flow of compressed air, 0.3 cubic meters per minute at 172 kPa (25 psi) is added through three coarse bubble diffusers at the bottom of the tower for 5 minutes, fluidizing the buoyant media in the tank and gently scouring excess biofilm. The drain is reopened without interrupting air flow until the tank is completely drained. After air scouring, the bio-tower system valves are returned to normal condition and water flow is restarted. Denitrification occurs immediately at a level of approximately 50%, and complete denitrification takes approximately two tank detention times. The scoured biomass suspension varies between 2 and 3 g/L total suspended solids.

Roughing Filter and Slow Sand Filter. The roughing filter is designed to strip excess carbon dioxide, reoxygenate the water, and most important, to remove excess dissolved organic carbon and small biofilm and cell fragments. The latter has been found to prolong the run-time for the slow sand filter. Figure 17 is a pH profile through the denitrification system to the roughing filter effluent. As indicated by the pH increase after the roughing filter, the filter is performing successfully for gas transfer. recent measurements of dissolved organic carbon (DOC) through the system verify that DOC is reduced from 5-7 mg/L in the water leaving the bio-towers to 3-4 mg/L after the roughing filter. Figure 18 contains dissolved oxygen profiles for the system. There are two points of

Figure 17. pH profile through the denitrification biotowers and roughing filter during the period of March through June 1997. pH drop after denitrification is due to supersaturation of denitrified water with  $\text{CO}_2$  created during the biological reaction. pH increase after the roughing filter rises due to stripping of  $\text{CO}_2$  in the aerobic packed tower pre-filter.



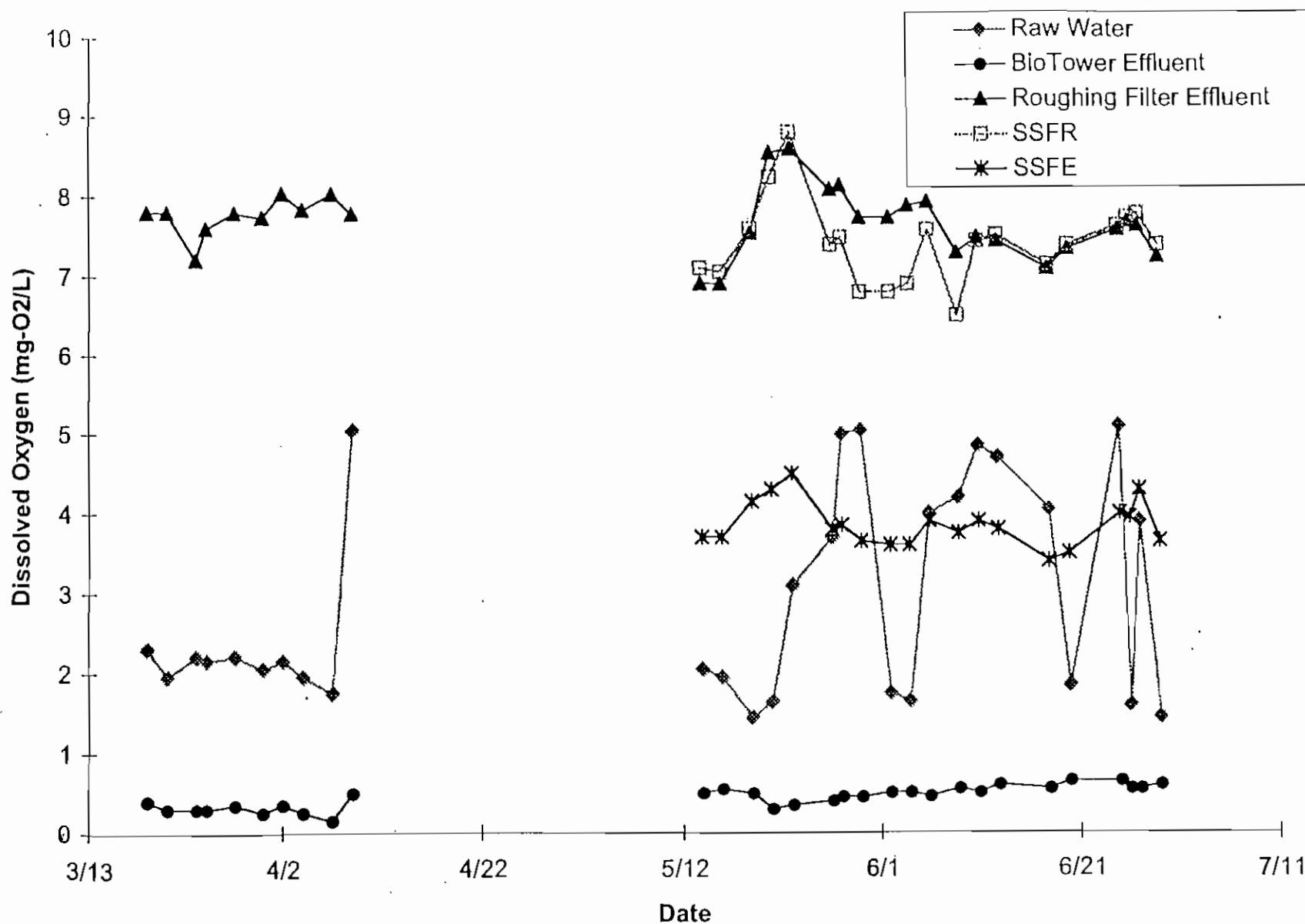


Figure 18. Dissolved oxygen (DO) profile through the denitrification biotowers, roughing filter, slow sand filter reservoir ("SSFR") and at the final effluent ("SSFE") during the period of March through June 1997. Of particular interest is the large fluctuation in the influent dissolved oxygen (gray line) between 2 and 5 mg/L, which does not interfere with consistent denitrification, as shown in Figure 16. At the end of the anoxic denitrification biotowers, dissolved oxygen is less than 0.5 mg/L as expected. The DO rises after the aerobic roughing filter to saturation, indicating the effectiveness of gas transfer in the pre-filter.

special interest in Figure 18. First, the influent dissolved oxygen fluctuates significantly, between 2 and 5.5 mg/L, probably due to changes in the detention of the well water influent in a pressurized equalization tank which is part of the Wiggins water system. This variance represents a changing carbon substrate demand because many of the bacteria in the denitrifying biotowers will use oxygen instead of nitrate in metabolism. Additional carbon is added to anticipate this demand, but the carbon addition is based on an estimated average dissolved oxygen concentration, yet consistent denitrification seems to be maintained in spite of dissolved oxygen fluctuations. (In an actual design, it would not be recommended to use an air-pressurized equalization tank preceding the denitrification biotower(s), although apparently even this could be accommodated.) Secondly, the dissolved oxygen data support the pH profiles in Figure 17, demonstrating that the roughing filter is performing as a gas stripping process very effectively. Figure 19 shows the system turbidity profile from April through June 1997. Turbidity is one of the key parameters which indicate that the polishing processes - the roughing filter and the slow sand filter - are successful in removing particles sloughed from the denitrifying biotowers. The well water turbidity varies between 0.1 and 0.3 NTU. The denitrified biotower effluent turbidity has significantly more variance, between 1 and 6 NTU, resulting from the biofilm inputs. However, it is gratifying to see that this turbidity is consistently removed to produce a filtered product water always less than 0.5 NTU, responding immediately as can be seen in Figure 19, even when the biotower effluent turbidity doubles from 3 to 6 NTU in two days as it did on June 12. This performance easily meets not only the standard for slow sand filtration of 1 NTU, but also meets the standard for rapid sand filtration of 0.5 NTU. Presence/absence tests for coliform bacteria have been carried out in March and

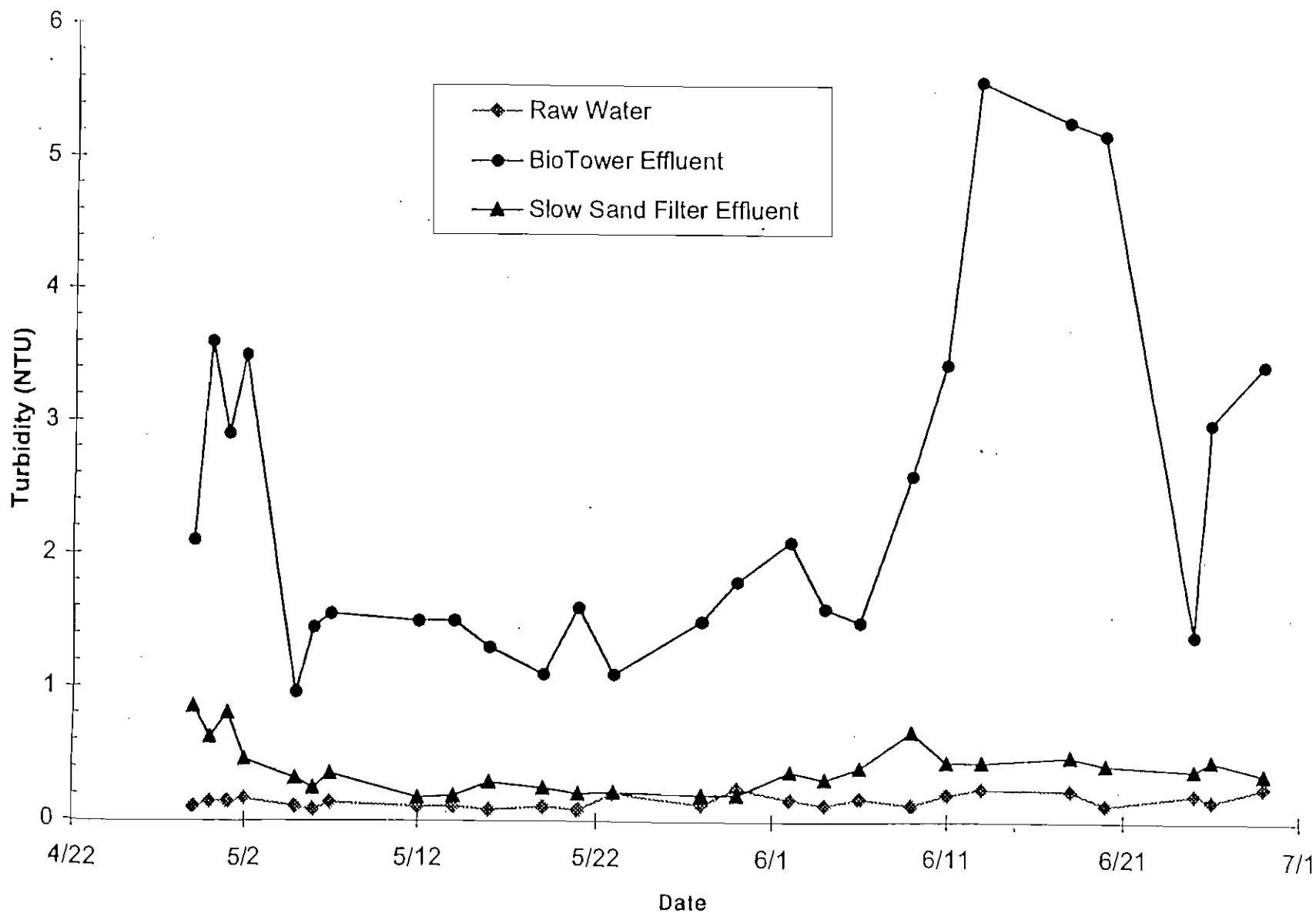


Figure 19. System water turbidity including profiles for the influent ("raw") water, denitrified effluent from the anoxic packed tower biofilm reactors ("BioTower Effluent") and the final effluent ("Slow Sand Filter Effluent") for the period from April through June 1997.

April. No *E. coli* have ever been detected, but coliform bacteria, while not present in the well water, are always present throughout the system.

#### **WIGGINS PROJECT COMPLETION - MONITORING, MAY - NOVEMBER 1997**

Because of the multiple start-up problems, we have found ourselves at the end of the project funding with approximately six more months monitoring data to collect, including very important analyses for bacteria, and chemicals like trihalomethanes. Fortunately we have raised funds to complete the monitoring of the Wiggins Denitrification Demonstration from May through October 1997. Table 4 is a schedule of the parameters to be monitored, the analytical method used, the locations in the process train and the frequency. All samples will be analyzed at the University of Colorado Environmental Engineering laboratories according to EPA-approved standard methods and QA/QC procedures, with the exception of MPN tests for total and fecal coliform bacteria and standard heterotrophic plate count bacteria assays, which will be done at certified commercial laboratories. A final report of the Wiggins Denitrification Demonstration will be made by December 1997. The analytical data for nitrate ( $\text{NO}_3\text{-N}$ ), nitrite ( $\text{NO}_2\text{-N}$ ), pH, dissolved oxygen, and turbidity samples collected at the Wiggins demonstration facility are in the Appendix A.

#### **COMMERCIALIZATION**

The University of Colorado has been granted a patent for the process: "Biological Denitrification of Water," for the process invested during lab and pilot-plant testing from 1987 through 1991. A start-up company, Nitrate Removal Technologies, LLC. (NRT) of Golden, Colorado has licensed the technology from the University in order to



Table 4. Wiggins Denitrification Demonstration Sampling Schedule  
May 1 - October 31, 1997

| Water Quality Parameter   | Analytical Method   | Sampling Frequency                                  |
|---|---|---|
| <i>Chemical</i>   |   |   |
| Nitrate ( $\text{NO}_3^-$ )   | Ion Chromatography, AS-10 column, Specific Conductance Detector (Dionex Model DX-300) | 3 time/week @ 6 points                              |
| Nitrite ( $\text{NO}_2^-$ )   | Ion Chromatography, AS-10 column, Specific Conductance Detector (Dionex Model DX-300) | 3 time/week @ 6 points                              |
| Sulfate ( $\text{SO}_4^{2-}$ )  | Ion Chromatography, AS-10 column, Specific Conductance Detector (Dionex Model DX-300) | 3 time/week @ 6 points                              |
| Phosphate ( $\text{PO}_4^{3-}$ )  | Ion Chromatography, AS-10 column, Specific Conductance Detector (Dionex Model DX-300) | 3 time/week @ 6 points                              |
| Turbidity   | Nephelometer (Hach On-Line Model)   | Continuous @ process effluent                       |
| Dissolved Organic Carbon (DOC)  | High-Temperature Autoanalyzer (Shimadzu Model 5000)                                   | 2 times/week @ 6 points                             |
| Trihalomethane Formation Potential (THMFP)                              | EPA method, Gas Chromatograph Electron Capture Detector (Hewlett Packard Model 5890)  | 2 times/month @ 4 points for 4 months               |
| Chlorine Demand   | Titration   | 2 times/month @ well and process effluent, 4 months |
| <i>Bacteria</i>   |   |   |
| Total Coliform and <i>E. coli</i> (fecal coliform) (indicator bacteria) | Presence/Absence (P/A) (Colilert method)  | 3 times/week, @ well and effluent, triplicate       |
| Total Coliform and <i>E. coli</i> (fecal coliform) (indicator bacteria) | Most Probable Number (MPN), multiple tube fermentation (Boulder County Health Dept.)  | 2 times/month @ 4 points                            |
| Heterotrophic Bacteria (approx. total bacteria)                         | Heterotrophic Plate Count (HPC) on R2-A agar plates (AccuLabs, Denver)                | 1 time/month @ 4 points                             |

commercialize the denitrification technology. NRT has begun marketing the process to small communities, with significant interest from utilities in the Midwest and California. In addition to their long-term interest in commercialization of the drinking water denitrification process invented by Dr. Silverstein at the University of Colorado, NRT has been involved significantly in the demonstration at Wiggins. They constructed the process equipment at Wiggins using the process design specifications developed by Dr. Silverstein in 1995-1996. More recently, NRT has agreed to finance the remaining six months operation and monitoring data analyses for the facility in order to fulfill the requirements suggested by the Colorado Department of Public Health and Environment. The data demonstrating process reliability for nitrate removal and for production of high-quality drinking water is essential both for approval of the denitrification process for treatment of potable water supplies and for credibility with utilities.

#### SUMMARY

After a very difficult start, we are pleased to report that the denitrification demonstration at Wiggins is working smoothly now, and that we anticipate continued success in the monitoring results through October 1997. The initial \$100,000 grant from EPRI and NRECA through the EPRI-CEC was essential to the implementation of this demonstration, as was the support of the Morgan County Rural Electric Association and Tri-State Generating and Transmission Association. When the project is complete at the end of this year, approximately \$300,000 will have been spent on the denitrification demonstration at Wiggins, Colorado. Over half of that, \$152,000, for design and construction of the building and process equipment. The remaining funds have been spent

on supplies (chemicals, sample collection and analyses) and stipends to student research assistants and the post-doctoral research associate, Dr. Gary Carlson, who is the on-site project manager. The grant from EPRI and NRECA not only provided a significant fraction of the project's resources, but also enabled us to successfully obtain matching funding from several institutions: the National Water Research Institute, the Town of Wiggins, Colorado and the Colorado Department of Local Affairs, and Nitrate Removal Technologies, LLC.

In conclusion, the demonstration of drinking water denitrification at Wiggins, Colorado is fulfilling the project objectives stated at the beginning of this report:

1. The denitrification and filter polishing system constructed in Wiggins, Colorado is consistently destroying nitrate, reducing 20 - 25 mg/l  $\text{NO}_3\text{-N}$  in the influent to 2 to 4 mg/L  $\text{NO}_3\text{-N}$  in the effluent. The finished water has always exceeded the most stringent turbidity standards for drinking water. Currently, the process equipment at the Wiggins facility is visited three days per week for approximately 4 hours each day during which time all activities, including sample collection, operations such as air scouring the biotowers, changing feed tanks and calibrating pumps; and even maintenance procedures, are completed.
2. The monitoring of the denitrification system is continuing to November 1997. As shown in Table 4, the sample analyses are anticipated to provide assurance of the potability of the denitrified product, within guidelines suggested by the Colorado Department of Public Health and Environment. (The original monitoring plan document and notification by CDPHE are in Appendix B.)

3. Although all the start-up problems were frustrating, most resulted in improvements to system operation. Probably the most significant was the change from using glacial acetic acid to corn syrup for a carbon substrate for denitrification. Food-grade corn syrup is significantly less expensive than acetic acid, is safer and easier to handle and overdosing will not result in a deterioration of system performance. Like acetic acid, corn syrup comes in liquid form and can be easily pumped into the influent water stream. Overall, we are now confident that the denitrification process is not vulnerable to catastrophic failure and/or abrupt loss of performance. The only mechanical parts of the system are pumps, and simple visible and audible alarms can be used to summon an operator if one does fail.

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#### ACKNOWLEDGMENT

Many individuals and institutions have contributed to the success of the demonstration at Wiggins, Colorado of biological denitrification of drinking water for a rural community. The National Water Research Institute (NWRI) of Fountain Valley, California has been an important supporter of this demonstration of biological denitrification of drinking water for rural communities. NWRI provided critical financial support to the demonstration during 1996 which

allowed us to actually begin construction of the demonstration facility at Wiggins and operate the plant. In addition, the Director, Dr. Ron Linsky and several members of NWRI's Research Advisory Board, Dr. Anita Highsmith, director of the Drinking Water section of the US Center for Disease Control and Prevention, Dr. Herman Bouwer, director of the USDA Water Research Lab, Dr. Roy Spalding, director of the Water Research Center at the University of Nebraska and Dr. David White of the University of Tennessee Center for Environmental Biotechnology have made special efforts to contribute their significant scientific and technical expertise to the project, especially helping to analyze start-up problems and encouraging development of the technology for application in small utilities..

Two sponsors, the Electric Power Research Institute Community Environmental Center (EPRI-CEC) and the National Rural Electric Cooperative Association (NRECA), made the initial grant which has been key to successful technology transfer of the novel treatment process for application in rural communities, often neglected by technology development for infrastructure. We would like particularly to thank Mr. Tom Yeager, Chair of EPRI-CEC's Small Community Systems group and Chair of the EPRI Project Advisory Committee for the drinking water denitrification demonstration. Mr. Yeager provided extraordinary support for this project, especially by his insights and encouragement during the significant and often disappointing delays and start-up problems.

We appreciate the contributions of Mr. John Neal, Director of Energy Research for the National Rural Electric Cooperative Association in Arlington, Virginia, co-sponsor of this demonstration, who has been especially supportive of our efforts to commercialize the drinking water denitrification process. Also, Mr. Vernon Tryon of the Morgan County Rural Electric Cooperative Association in Fort Morgan, Colorado, and Mr. Warren White of the Tri-State

Generating and Transmission Association of Denver, Colorado, the utility co-sponsors of the drinking water denitrification demonstration at Wiggins, have helped us understand the concerns of rural electric power suppliers in developing the infrastructure of rural communities.

The purpose of this project was demonstration of a novel drinking water treatment process especially developed for small utilities, operating in a rural community. For the success of the demonstration, it was essential to have the close involvement of a rural drinking water utility. Although the demonstration represented an opportunity to assess a potentially beneficial technology for its own future use, hosting the demonstration also presented significant technical and operational challenges for a rural utility. From the inception of the demonstration project activities, Mr. John Holdren, the Town Manager for the Town of Wiggins, Colorado, has had the foresight to anticipate that the University of Colorado's denitrification process might provide a feasible drinking water treatment alternative not only for his community, but for many other rural utilities similarly at risk for nitrate pollution of their water supplies. Moreover, Mr. Holdren provided the leadership to implement the agreement between the Town of Wiggins and the University of Colorado which allowed us to build and operate the denitrification demonstration facility adjacent to the Town's drinking water wells. Finally, Mr. Holdren has provided significant technical support for this project, including making available the denitrified water product disposal pipeline and recharge site, accommodating operation of the Town drinking water wells to water usage of the demonstration facility and frequent consultation on the important constraints of rural utilities, with respect to both equipment and managerial issues.

The State of Colorado has made significant contributions to this project. Mr. Kent Gumina, the Regional Director of the Colorado Department of Local Affairs, helped us to obtain financial support for the demonstration at Wiggins. More important however, was his role as a

very effective liaison between the University, the Town of Wiggins and other Colorado State agencies, solving bureaucratic problems and always maintaining optimism about the project. The advice and suggestions of Colorado Department of Public Health and Environment have been essential to fulfilling the denitrification demonstration project objectives. Mr.'s. Jerry Biberstine, Greg Akins and Glenn Bodnar all have responded generously to requests for meetings, technical information about drinking water regulations and even site visits. Primarily as a result of the insights of CDPHE staff, commercialization efforts seem to be easily meeting the concerns of regulatory agencies in states other than Colorado.

The other significant non-profit sponsor of the denitrification demonstration is the National Water Research Institute (NWRI) of Fountain Valley, California. NWRI provided essential financial support to the demonstration during 1996. In addition, the director, Dr. Ron Linsky and several members of NWRI's Research Advisory Board, Dr. Anita Highsmith, director of the Drinking Water section of the US Center for Disease Control and Prevention, Dr. Herman Bouwer, director of the USDA Water Research Lab, and Dr. Roy Spalding, director of the Water Research Center at the University of Nebraska have contributed their significant expertise and encouragement to the project, especially as start-up problems occurred.

The success of the demonstration of drinking water denitrification in Wiggins depended on the efforts of students and a research assistant in the Environmental Engineering program of the Department of Civil, Environmental and Architectural Engineering at the University of Colorado, Boulder. Dr. Gary Carlson is a post-doctoral research associate who has managed on-site operations at the Wiggins facility, contributed critical technical insights in biofilm process behavior which ensured the success of the demonstration, and has supervised process monitoring and data collection. Dan Thompson received his MS degree in Civil Engineering at the University



of Colorado developing the monitoring plan, including data quality control/quality assurance. He helped solve many problems during plant start-up and carried out important fundamental research which led to the change from acetic acid to corn syrup substrate addition. Students Jude Grounds and Juan Paez assisted with microbiological analyses and lab enrichment of the denitrifying biofilm inoculum.

Finally, Dr. Nevis Cook, Jr. of the Department of Environmental Science and Engineering at the Colorado School of Mines has consistently contributed his technical expertise to this demonstration. Dr. Cook helped to develop the biological denitrification process while he was on the faculty at the University of Colorado, and his extensive understanding of the biofilm denitrification process was invaluable during process start-up.

## **Appendix A**

**Laboratory data from analyses of samples from  
denitrification demonstration plant at Wiggins,  
Colorado**

| <u>Sample</u> | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|---------------|----------------|-------------------------|
| 1-2 Raw       | 78990800       | 5.66364036              |
| 1-2 HFCS      | 80712420       | 5.787080514             |
| 1-2 TT1       | 48321584       | 3.464657573             |
| 1-2 TT2       | 30832258       | 2.210672899             |
| 1-2 RF        | 30217928       | 2.166625438             |
| 1-2 SSF       | 24119400       | 1.72936098              |
| 1-3 Raw       | 79518578       | 5.701482043             |
| 1-3 HFCS      | 78135854       | 5.602340732             |
| 1-3 TT1       | 52260288       | 3.74706265              |
| 1-3 TT2       | 32588556       | 2.336599465             |
| 1-3 RF        | 31405544       | 2.251777505             |
| 1-3 SSF       | 20093318       | 1.440690901             |
| 1-7 Raw       | 77351134       | 5.546076308             |
| 1-7 HFCS      | 77861922       | 5.582699807             |
| 1-7 TT1       | 53049244       | 3.803630795             |
| 1-7 TT2       | 37130346       | 2.662245808             |
| 1-7 RF        | 37178250       | 2.665680525             |
| 1-7 SSF       | 21538286       | 1.544295106             |
| 1-8 Raw       | 81070242       | 5.812736351             |
| 1-8 HFCS      | 80166830       | 5.747961711             |
| 1-8 TT1       | 53629236       | 3.845216221             |
| 1-8 TT2       | 41501718       | 2.975673181             |
| 1-8 RF        | 40989566       | 2.938951882             |
| 1-8 SSF       | 14697770       | 1.053830109             |
| 1-9 Raw       | 79944024       | 5.731986521             |
| 1-9 HFCS      | 80697464       | 5.786008169             |
| 1-9 TT1       | 44423072       | 3.185134262             |
| 1-9 TT2       | 28573714       | 2.048735294             |
| 1-9 RF        | 26271178       | 1.883643463             |
| 1-9 SSF       | 2601736        | 0.186544471             |
| 1-13 Raw      | 78789700       | 5.64922149              |
| 1-13 HFCS     | 84969962       | 6.092346275             |
| 1-13 TT1      | 49643918       | 3.559468921             |
| 1-13 TT2      | 29683940       | 2.128338498             |
| 1-13 RF       | 28110236       | 2.015503921             |
| 1-13 SSF      | 2279284        | 0.163424663             |
| 1-16 Raw      | 96449753       | 6.91544729              |
| 1-16 HFCS     | 101093333      | 7.248391976             |
| 1-16 TT1      | 64629452       | 4.633931708             |
| 1-16 TT2      | 50257638       | 3.603472645             |
| 1-16 RF       | 48334373       | 3.465574544             |
| 1-19 Raw      | 135423200      | 9.70984344              |
| 1-19 HFCS     | 105385035      | 7.55610701              |
| 1-19 TT1      | 71673932       | 5.139020924             |
| 1-19 TT2      | 75403220       | 5.406410874             |
| 1-19 RF       | 84884087       | 6.086189038             |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 1-20 Raw          | 106641658      | 7.646206879             |
| 1-20 HFCS         | 117960986      | 8.457802696             |
| 1-20 TT1          | 74882664       | 5.369087009             |
| 1-20 TT2          | 46402000       | 3.3270234               |
| 1-20 RF           | 51981303       | 3.727059425             |
| 1-22 Raw          | 109899883      | 6.247170929             |
| 1-22 HFCS+Nitrate | 556986680      | 31.66146224             |
| 1-22 TT1          | 326330800      | 18.55001326             |
| 1-22 TT2          | 239444400      | 13.61102536             |
| 1-22 RF           | 480752800      | 27.32800831             |
| 1-23 Raw          | 128127200      | 7.283288182             |
| 1-23 HFCS+Nitrate | 385091400      | 21.89021256             |
| 1-23 TT1          | 319999800      | 18.19013263             |
| 1-23 TT2          | 287912400      | 16.36615005             |
| 1-23 RF           | 299768200      | 17.04008351             |
| 1-28 Raw          | 132432200      | 7.528002463             |
| 1-28 HFCS+Nitrate | 317926400      | 18.07227187             |
| 1-28 TT1          | 280916438      | 15.96847018             |
| 1-28 TT2          | 299487200      | 17.02411029             |
| 1-28 RF           | 260473759      | 14.80642245             |
| 1-29 Raw          | 104599642      | 5.94588297              |
| 1-29 HFCS+Nitrate | 287994649      | 16.37082543             |
| 1-29 TT1          | 274695498      | 15.61484583             |
| 1-29 TT2          | 275349249      | 15.65200778             |
| 1-29 RF           | 254102291      | 14.44424145             |
| 1-31 Raw          | 127052000      | 7.222169298             |
| 1-31 HFCS+Nitrate | 433323800      | 24.63194475             |
| 1-31 TT1          | 291934761      | 16.59479794             |
| 1-31 TT2          | 254004800      | 14.43869965             |
| 1-31 RF           | 387667582      | 22.03665356             |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 2-3 Raw           | 129667658      | 7.370854285             |
| 2-3 HFCS+Nitrate  | 577044200      | 32.80161591             |
| 2-3 TT1           | 291501993      | 16.57019759             |
| 2-3 TT2           | 213604468      | 12.1421751              |
| 2-3 RF            | 203676632      | 11.5778352              |
| 2-6 Raw           | 147657200      | 8.393455408             |
| 2-6 HFCS+Nitrate  | 396275000      | 22.52593536             |
| 2-6 TT1           | 295004000      | 16.76926638             |
| 2-6 TT2           | 305393661      | 17.35985834             |
| 2-6 RF            | 250325969      | 14.22957945             |
| 2-7 Raw           | 127261132      | 7.23405724              |
| 2-7 HFCS+Nitrate  | 457451597      | 26.00347007             |
| 2-7 TT1           | 198304151      | 11.27244082             |
| 2-7 TT2           | 2642141000     | 150.1903914             |
| 2-7 RF            | 164655972      | 9.359737004             |
| 2-10 Raw          | 116742829      | 6.63615272              |
| 2-10 HFCS+Nitrate | 249866400      | 14.20345561             |
| 2-10 TT1          | 216096457      | 12.28383022             |
| 2-10 TT2          | 131433655      | 7.471240972             |
| 2-10 RF           | 137350516      | 7.807580202             |
| 2-11 Raw          | 91894740       | 5.22368298              |
| 2-11 HFCS+Nitrate | 382381919      | 21.73619428             |
| 2-11 TT1          | 163408658      | 9.288834437             |
| 2-11 TT2          | 133038058      | 7.562441977             |
| 2-11 RF           | 128895923      | 7.326985626             |
| 2-16 Raw          | 170347393      | 9.683261277             |
| 2-16 HFCS+Nitrate | 552163598      | 31.387298               |
| 2-16 TT1          | 305338364      | 17.35671503             |
| 2-16 TT2          | 252596203      | 14.35862908             |
| 2-16 RF           | 247763558      | 14.08392124             |
| 2-17 Raw          | 142361219      | 8.092409605             |
| 2-17 HFCS+Nitrate | 316612537      | 17.99758638             |
| 2-17 TT1          | 211501060      | 12.02260855             |
| 2-17 TT2          | 163484545      | 9.293148173             |
| 2-17 RF           | 136036408      | 7.732880784             |
| 2-18 Raw          | 102622876      | 5.833515288             |
| 2-18 HFCS+Nitrate | 287756806      | 16.35730543             |
| 2-18 TT1          | 173934500      | 9.887167505             |
| 2-18 TT2          | 140199804      | 7.969545699             |
| 2-18 RF           | 183066303      | 10.40625754             |
| 2-19 Raw          | 86030872       | 4.625879987             |
| 2-19 HFCS+Nitrate | 475417097      | 25.56317731             |
| 2-19 TT1          | 307782442      | 16.54946191             |
| 2-19 TT2          | 159999093      | 8.603151231             |
| 2-19 RF           | 159021285      | 8.550574494             |
| 3 ppm N Std.      | 116190674      | 6.247572541             |

## February Data

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 2-24 Raw          | 120343872      | 6.470889997             |
| 2-24 HFCS+Nitrate | 252352043      | 13.56896935             |
| 2-24 TT1          | 215434965      | 11.58393807             |
| 2-24 TT2          | 169602211      | 9.119510885             |
| 2-24 RF           | 136510616      | 7.340175822             |
| 10 ppm N Std.     | 1085743660     | 58.3804366              |
| 2-27 Raw          | 103868294      | 5.584998168             |
| 2-27 HFCS+Nitrate | 271829880      | 14.61629265             |
| 2-27 TT1          | 195120894      | 10.49165047             |
| 2-27 TT2          | 152891996      | 8.221002625             |
| 2-27 RF           | 166724836      | 8.964794432             |
| 1 ppm N Std.      | 17274685       | 0.928859812             |

| <u>Sample</u>       | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|---------------------|----------------|-------------------------|
| 3-4 Raw             | 109163564      | 5.969936988             |
| 3-4 HFCS+Nitrate    | 284931661      | 15.58234268             |
| 3-4 TT1             | 241873207      | 13.22756194             |
| 3-4 TT2             | 205893089      | 11.25988125             |
| 3-4 RF              | 208333770      | 11.39335721             |
| 3-6 Raw             | 102654516      | 5.613970171             |
| 3-6 HFCS+Nitrate    | 268644893      | 14.69165191             |
| 3-6 TT1             | 223663024      | 12.23168346             |
| 3-6 TT2             | 176137517      | 9.63260853              |
| 3-6 RF              | 156203366      | 8.54244968              |
| 3-10 Raw            | 110815072      | 6.060254658             |
| 3-10 HFCS+Nitrate   | 234666878      | 12.83346222             |
| 3-10 TT1            | 183101344      | 10.0134463              |
| 3-10 TT2            | 121268852      | 6.631950978             |
| 3-10 RF             | 124963100      | 6.833982013             |
| 2.5 ppm Std.        | 457256487      | 2.500644276             |
| 3-11 Raw            | 103636050      | 5.667648302             |
| 3-11 HFCS+Nitrate   | 253434454      | 13.85982342             |
| 3-11 TT1            | 194744234      | 10.65017267             |
| 3-11 TT2            | 149389052      | 8.169788476             |
| 3-11 RF             | 155214424      | 8.48836642              |
| 3-17 Raw            | 94853408       | 4.975820077             |
| 3-17 HFCS+Nitrate   | 365594031      | 19.17833168             |
| 3-17 TT1            | 338356842      | 17.74952322             |
| 3-17 TT2            | 281002739      | 14.74084168             |
| 3-17 RF             | 278876466      | 14.62930165             |
| 0.75 ppm N Old Std. | 127747661      | 0.67013868              |
| 3-19 Raw            | 151068878      | 7.924771202             |
| 3-19 HFCS+Nitrate   | 454993972      | 23.86807378             |
| 3-19 TT1            | 315169561      | 16.53316483             |
| 3-19 TT2            | 221595045      | 11.62443287             |
| 3-19 RF             | 186838906      | 9.801195331             |
| 2.50 ppm N Old Std. | 468373310      | 2.45699271              |
| 3-21 Raw            | 131925833      | 6.913269849             |
| 3-21 HFCS+Nitrate   | 391589259      | 20.52033446             |
| 3-21 TT1            | 272545080      | 14.28209806             |
| 3-21 TT2            | 125812249      | 6.592901541             |
| 3-21 RF             | 144527665      | 7.573639871             |
| 0.25 ppm N Std.     | 39637826       | 0.20771291              |
| 3-24 Raw            | 114707208      | 6.010967409             |
| 3-24 HFCS+Nitrate   | 366489777      | 19.20505384             |
| 3-24 TT1            | 245710030      | 12.87586899             |
| 3-24 TT2            | 61664699       | 3.231396722             |
| 3-24 RF             | 50083301       | 2.624500197             |
| 0.50 ppm N Std.     | 84300527       | 0.441757523             |

March Data

| Sample            | IC Area   | Nitrate-N (mg/L) |
|-------------------|-----------|------------------|
| 3-25 Raw          | 109973823 | 5.762925255      |
| 3-25 HFCS+Nitrate | 358222526 | 18.77182756      |
| 3-25 TT1          | 247243515 | 12.95622774      |
| 3-25 TT2          | 65345891  | 3.424301122      |
| 3-25 RF           | 62348712  | 3.26724085       |
| 3-28 Raw          | 96074424  | 5.039872134      |
| 3-28 HFCS+Nitrate | 347116958 | 18.20906138      |
| 3-28 TT1          | 217121682 | 11.38976919      |
| 3-28 TT2          | 148506208 | 7.790338659      |
| 3-28 RF           | 155873626 | 8.176818673      |
| 0.50 ppm N Std.   | 81832032  | 0.429274473      |
| 3-31 Raw          | 87193365  | 4.573989541      |
| 3-31 HFCS+Nitrate | 340950530 | 17.8855829       |
| 3-31 TT1          | 177121360 | 9.291432303      |
| 3-31 TT2          | 78234757  | 4.104038883      |
| 3-31 RF           | 79648916  | 4.178222836      |
| 0.75 ppm N Std.   | 127232764 | 0.667437633      |



| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 4-2 Raw           | 85113029       | 4.464859275             |
| 4-2 HFCS+Nitrate  | 364661688      | 19.12942283             |
| 4-2 TT1           | 269760841      | 14.1511142              |
| 4-2 TT2           | 215568346      | 11.30828429             |
| 4-2 RF            | 220276775      | 11.55527906             |
| 2.75 ppm N Std.   | 500649847      | 2.626308967             |
| 4-4 RAW           | 94821610       | 4.974152017             |
| 4-4 HFCS+NITRATE  | 321991767      | 16.89104411             |
| 4-4 TT1           | 81031232       | 4.250736368             |
| 4-4 TT2           | 9923536        | 0.520568851             |
| 4-4 RF            | 12092194       | 0.634332313             |
| 1.25 ppm N Std.   | 214386460      | 1.124628492             |
| 4-7 Raw           | 98369618       | 5.379637669             |
| 4-7 HFCS+Nitrate  | 348159778      | 19.04016194             |
| 4-7 TT1           | 59137465       | 3.234109686             |
| 4-7 TT2           | 8980998        | 0.491152819             |
| 4-7 RF            | 15083670       | 0.824895745             |
| 1.0 ppm N Std.    | 177686970      | 0.971734502             |
| 4-9 Raw           | 100447605      | 5.493278622             |
| 4-9 HFCS+Nitrate  | 324066972      | 17.72257456             |
| 4-9 TT1           | 69402925       | 3.795507162             |
| 4-9 TT2           | 10655705       | 0.582739195             |
| 4-9 RF            | 9958182        | 0.544593057             |
| 0.25 ppm Std.     | 45945452       | 0.251266488             |
| 4-12 Raw          | 124648549      | 6.892154825             |
| 4-12 HFCS+Nitrate | 532112382      | 29.4219303              |
| 4-12 TT1          | 66905321       | 3.699375842             |
| 4-12 TT2          | 35961876       | 1.988429221             |
| 4-12 RF           | 23880444       | 1.320414226             |
| 0.80 ppm Std.     | 143333127      | 0.792527559             |
| 4-15 raw          | 97258330       | 5.377675663             |
| 4-15 HFCS+Nitrate | 339677074      | 18.78166255             |
| 4-15 TT1          | 182976743      | 10.11727816             |
| 4-15 TT2          | 84027368       | 4.646100051             |
| 4-15 RF           | 56688581       | 3.134464703             |
| 1.45 ppm Std.     | 259167719      | 1.433008294             |
| 4-16 Raw          | 94242868       | 5.210942627             |
| 4-16 HFCS+Nitrate | 319296550      | 17.65476835             |
| 4-16 TT1          | 139315054      | 7.703105486             |
| 4-16 TT2          | 46069222       | 2.547291671             |
| 4-16 RF           | 30029672       | 1.660421645             |
| 0.15 ppm Std.     | 34613720       | 0.191388604             |
| 2.30 ppm Std.     | 417455930      | 2.30822655              |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 4-17 Raw          | 164556389      | 8.707172211             |
| 4-17 HFCS+Nitrate | 379684200      | 20.09023007             |
| 4-17 TT1          | 131708409      | 6.969087045             |
| 4-17 TT2          | 995915841      | 52.69689489             |
| 4-17 RF           | 61317200       | 3.244477004             |
| 0.45 ppm Std.     | 80814800       | 0.427615351             |
| 4-21 Raw          | 144002400      | 7.619598991             |
| 4-21 HFCS+Nitrate | 404151005      | 21.38484213             |
| 4-21 TT1          | 123239200      | 6.52095579              |
| 4-21 TT2          | 50170400       | 2.654666375             |
| 4-21 RF           | 122396000      | 6.476339548             |
| 1.35 ppm Std.     | 245910400      | 1.3011857               |
| 4-22 Raw          | 126532400      | 6.695208881             |
| 4-22 HFCS+Nitrate | 404813200      | 21.41988085             |
| 4-22 TT1          | 211194200      | 11.1749187              |
| 4-22 TT2          | 80370200       | 4.252628393             |
| 4-22 RF           | 81670200       | 4.321415293             |
| 0.10 ppm Std.     | 45820400       | 0.242449483             |
| 4-23 Raw          | 191547087      | 10.29527283             |
| 4-23 HFCS+Nitrate | 342808008      | 18.42524481             |
| 4-23 TT1          | 97665853       | 5.249344267             |
| 4-23 TT2          | 34333405       | 1.845351852             |
| 4-23 RF           | 407140722      | 21.88299953             |
| 0.85 ppm Std.     | 170694282      | 0.917447627             |
| 4-25 Raw          | 123611132      | 6.643851123             |
| 4-25 HFCS+Nitrate | 442765856      | 23.79777923             |
| 4-25 TT1          | 82492694       | 4.433817317             |
| 4-25 TT2          | 43928965       | 2.361094011             |
| 4-25 RF           | 29674962       | 1.594969858             |
| 1.60 ppm Std.     | 298853603      | 1.606278345             |
| 4-28 Raw          | 111568085      | 5.996561433             |
| 4-28 HFCS+Nitrate | 317078352      | 17.04232726             |
| 4-28 TT1          | 113350811      | 6.09237939              |
| 4-28 TT2          | 85118305       | 4.574938657             |
| 4-28 RF           | 21014967       | 1.129512446             |
| 0.20 ppm Std.     | 57520990       | 0.309163817             |
| 4-29 Raw          | 110498594      | 5.835541248             |
| 4-29 HFCS+Nitrate | 310096994      | 16.37653235             |
| 4-29 TT1          | 54426224       | 2.874303316             |
| 4-29 TT2          | 16613815       | 0.877392184             |
| 4-29 RF           | 13487122       | 0.7122684               |
| 4-29 SSFR         | 14308674       | 0.755655383             |
| 4-29 SSFE         | 12974016       | 0.685170759             |
| 1.00 ppm Std.     | 184515976      | 0.974447321             |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 4-30 Raw          | 111843009      | 5.906541148             |
| 4-30 HFCS+Nitrate | 302694478      | 15.98559808             |
| 4-30 TT1          | 77244213       | 4.079344133             |
| 4-30 TT2          | 20909736       | 1.104264068             |
| 4-30 RF           | 42345152       | 2.236289822             |
| 4-30 SSFR         | 23010711       | 1.215218659             |
| 4-30 SSFE         | 25395858       | 1.341180657             |
| 2.65 ppm Std.     | 502599627      | 2.65427889              |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 5-1 Raw           | 103991945      | 5.491918607             |
| 5-1 HFCS+Nitrate  | 340707425      | 17.99309982             |
| 5-1 TT1           | 64024353       | 3.381190106             |
| 5-1 TT2           | 13448533       | 0.710230476             |
| 5-1 SSFE          | 13181942       | 0.696151539             |
| 0.60 ppm Std.     | 117404055      | 0.620022555             |
| 5-2 Raw           | 139421541      | 7.189494836             |
| 5-2 HFCS+Nitrate  | 339227329      | 17.49279998             |
| 5-2 TT1           | 93202116       | 4.806116235             |
| 5-2 TT2           | 27487939       | 1.417459555             |
| 5-2 SSFE          | 10550060       | 0.544030724             |
| 0.15 ppm Std.     | 28390914       | 0.146402291             |
| 5-5 Raw           | 111125437      | 5.73036096              |
| 5-5 HFCS+Nitrate  | 309867991      | 15.97883874             |
| 5-5 TT1           | 152808212      | 7.879799945             |
| 5-5 TT2           | 131587475      | 6.785518688             |
| 5-5 SSFE          | 184543150      | 9.516262799             |
| 1.22 ppm Std.     | 232783327      | 1.200384471             |
| 5-6 Raw           | 153473351      | 7.914098902             |
| 5-6 HFCS+Nitrate  | 355713220      | 18.34292133             |
| 5-6 TT1           | 120895514      | 6.234170612             |
| 5-6 TT2           | 79587407       | 4.104051982             |
| 5-6 SSFE          | 85043866       | 4.38542302              |
| 0.87 ppm Std.     | 157736470      | 0.813393345             |
| 5-7 Raw           | 117933964      | 6.081453548             |
| 5-7 HFCS+Nitrate  | 334155324      | 17.23125393             |
| 5-7 TT1           | 211473378      | 10.90496309             |
| 5-7 TT2           | 186611274      | 9.622908922             |
| 5-7 SSFE          | 125344532      | 6.463591344             |
| 0.34 ppm Std.     | 67220632       | 0.346633944             |
| 5-12 Raw          | 128850188      | 6.644366105             |
| 5-12 HFCS+Nitrate | 312499206      | 16.11452156             |
| 5-12 TT1          | 26783425       | 1.381130164             |
| 5-12 TT2          | 52062962       | 2.684709936             |
| 5-12 SSFE         | 23816254       | 1.228123244             |
| 5-14 Raw          | 108736962      | 6.134634933             |
| 5-14 HFCS+Nitrate | 222418654      | 12.54823769             |
| 5-14 TT1          | 33187200       | 1.8723289               |
| 5-14 TT2          | 10156640       | 0.57300919              |
| 5-14 RF           | 12009847       | 0.67756194              |
| 5-14 SSFE         | 15656800       | 0.883312817             |
| 2.30 ppm Std.     | 423740281      | 2.390624018             |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 5-16 Raw          | 107594400      | 6.070174784             |
| 5-16 HFCS+Nitrate | 324736000      | 18.32069586             |
| 5-16 TT1          | 48941600       | 2.761148036             |
| 5-16 TT2          | 13503846       | 0.761849181             |
| 5-16 RF           | 16628800       | 0.938150335             |
| 5-16 SSFE         | 16778000       | 0.946567782             |
| 0.70 ppm Std.     | 131828118      | 0.74373733              |
| 5-19 Raw          | 118167000      | 6.66651272              |
| 5-19 HFCS+Nitrate | 270432000      | 15.25701623             |
| 5-19 TT1          | 57213200       | 3.227808547             |
| 5-19 TT2          | 14864800       | 0.838630395             |
| 5-19 RF           | 33828800       | 1.908526175             |
| 5-19 SSFE         | 14301200       | 0.806833661             |
| 1.00 ppm Std.     | 183732000      | 1.036564499             |
| 5-21 Raw          | 130439400      | 7.359025718             |
| 5-21 HFCS+Nitrate | 343263493      | 19.36596514             |
| 5-21 TT1          | 164663000      | 9.289825404             |
| 5-21 TT2          | 88131000       | 4.972104253             |
| 5-21 RF           | 89698000       | 5.060510006             |
| 5-21 SSFE         | 85238600       | 4.808923144             |
| 1.35 ppm Std.     | 248324600      | 1.400977862             |
| 5-23 Raw          | 160127516      | 9.033946096             |
| 5-23 HFCS+Nitrate | 357487762      | 20.16845857             |
| 5-23 TT1          | 233274502      | 13.16069423             |
| 5-23 TT2          | 156718686      | 8.841629452             |
| 5-23 RF           | 208070614      | 11.73876144             |
| 5-23 SSFE         | 188516338      | 10.63556394             |
| 0.20 ppm Std.     | 41818228       | 0.235926733             |
| 5-28 Raw          | 100926778      | 5.69400622              |
| 5-28 HFCS+Nitrate | 338294650      | 19.08563693             |
| 5-28 TT1          | 81279864       | 4.585582343             |
| 5-28 TT2          | 23481110       | 1.324738479             |
| 5-28 RF           | 21638360       | 1.220775684             |
| 5-28 SSFE         | 19301764       | 1.08895148              |
| 5-30 Raw          | 115174266      | 6.860009631             |
| 5-30 HFCS+Nitrate | 321534409      | 19.15123247             |
| 5-30 TT1          | 67029748       | 3.99242585              |
| 5-30 TT2          | 89415204       | 5.325748381             |
| 5-30 RF           | 11326694       | 0.674640548             |
| 5-30 SSFE         | 13359992       | 0.795747844             |
| 1.45 ppm Std.     | 238245355      | 1.419036983             |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 6-2 Raw           | 106217080      | 6.326501719             |
| 6-2 HFCS+Nitrate  | 310565790      | 18.49791958             |
| 6-2 TT1           | 114119762      | 6.797201264             |
| 6-2 TT2           | 24496372       | 1.459052909             |
| 6-2 RF            | 22990900       | 1.369383986             |
| 6-2 SSFE          | 7802600        | 0.464738461             |
| 1.95 ppm Std.     | 300298450      | 1.788637628             |
| 6-4 Raw           | 99648519       | 5.935265089             |
| 6-4 HFCS+Nitrate  | 304587923      | 18.14186587             |
| 6-4 TT1           | 102383516      | 6.09816698              |
| 6-4 TT2           | 24565584       | 1.463175314             |
| 6-4 RF            | 24524000       | 1.460698488             |
| 6-4 SSFE          | 23429300       | 1.395495967             |
| 2.20 ppm Std.     | 385994400      | 2.299059845             |
| 6-6 Raw           | 90471300       | 5.388651571             |
| 6-6 HFCS+Nitrate  | 301960898      | 17.98539501             |
| 6-6 TT1           | 106594320      | 6.348970888             |
| 6-6 TT2           | 47456600       | 2.826610009             |
| 6-6 RF            | 75631600       | 4.504769359             |
| 6-6 SSFE          | 20554800       | 1.224284998             |
| 0.30 ppm Std.     | 53764600       | 0.320232711             |
| 6-9 Raw           | 89485158       | 5.329914981             |
| 6-9 HFCS+Nitrate  | 300566826      | 17.90236129             |
| 6-9 TT1           | 70295400       | 4.186934615             |
| 6-9 TT2           | 6676800        | 0.397683562             |
| 6-9 RF            | 12210400       | 0.727275845             |
| 6-9 SSFE          | 25563619       | 1.522620275             |
| 1.45 ppm Std.     | 242958553      | 1.447109733             |
| 6-11 Raw          | 108788610      | 5.621401208             |
| 6-11 HFCS+Nitrate | 360921438      | 18.64978519             |
| 6-11 TT1          | 107843140      | 5.57254622              |
| 6-11 TT2          | 25480488       | 1.316645612             |
| 6-11 RF           | 19442264       | 1.004634275             |
| 6-11 SSFE         | 31401740       | 1.62261269              |
| 2.14 ppm Std.     | 427258174      | 2.207758345             |
| 6-13 Raw          | 105767630      | 5.465299015             |
| 6-13 HFCS+Nitrate | 354415924      | 18.31362772             |
| 6-13 TT1          | 109185590      | 5.641914236             |
| 6-13 TT2          | 21878488       | 1.130520547             |
| 6-13 RF           | 73097714       | 3.777156246             |
| 6-13 SSFE         | 9398478        | 0.485644734             |
| 0.95 ppm Std.     | 189055760      | 0.976902157             |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrate-N (mg/l)</u> |
|-------------------|----------------|-------------------------|
| 6-18 Raw          | 109577416      | 5.662160944             |
| 6-18 HFCS+Nitrate | 323901982      | 16.73688995             |
| 6-18 TT1          | 138575320      | 7.160560938             |
| 6-18 TT2          | 52966458       | 2.736919894             |
| 6-18 RF           | 39420560       | 2.036966771             |
| 6-18 SSFE         | 20046484       | 1.035855954             |
| 0.24 ppm Std.     | 87187828       | 0.450523048             |

| <u>Sample</u>     | <u>IC Area</u> | <u>Nitrite-N (mg/L)</u> |
|-------------------|----------------|-------------------------|
| 6-2 Raw           | 0              | 0                       |
| 6-2 HFCS+Nitrate  | 0              | 0                       |
| 6-2 TT1           | 28794602       | 1.741822908             |
| 6-2 TT2           | 25285152       | 1.529531715             |
| 6-2 RF            | 24435716       | 1.478148227             |
| 6-2 SSFE          | 16465652       | 0.996028695             |
| 1.95 ppm Std.     | 306848411      | 1.856165928             |
| 6-4 Raw           | 0              | 0                       |
| 6-4 HFCS+Nitrate  | 0              | 0                       |
| 6-4 TT1           | 19514991       | 1.180487175             |
| 6-4 TT2           | 15874830       | 0.960289104             |
| 6-4 RF            | 15342190       | 0.928069018             |
| 6-4 SSFE          | 10136830       | 0.613190025             |
| 2.20 ppm Std.     | 368584308      | 2.229614395             |
| 6-6 Raw           | 0              | 0                       |
| 6-6 HFCS+Nitrate  | 0              | 0                       |
| 6-6 TT1           | 12120612       | 0.733191577             |
| 6-6 TT2           | 9216368        | 0.557510082             |
| 6-6 RF            | 9697944        | 0.58664124              |
| 6-6 SSFE          | 12074756       | 0.730417688             |
| 0.30 ppm Std.     | 49309316       | 0.298278463             |
| 6-9 Raw           | 0              | 0                       |
| 6-9 HFCS+Nitrate  | 0              | 0                       |
| 6-9 TT1           | 3739340        | 0.226197538             |
| 6-9 TT2           | 1238174        | 0.074898755             |
| 6-9 RF            | 2141122        | 0.129519253             |
| 6-9 SSFE          | - 0            | 0                       |
| 1.45 ppm Std.     | 242958553      | 1.469687872             |
| 6-11 Raw          | 0              | 0                       |
| 6-11 HFCS+Nitrate | 0              | 0                       |
| 6-11 TT1          | 12677784       | 0.740377514             |
| 6-11 TT2          | 15824305       | 0.924133082             |
| 6-11 RF           | 18447898       | 1.077349864             |
| 6-11 SSFE         | 22394142       | 1.307808935             |
| 0.214 ppm Std.    | 37707236       | 0.22020875              |
| 6-13 Raw          | 0              | 0                       |
| 6-13 HFCS+Nitrate | 0              | 0                       |
| 6-13 TT1          | 4093182        | 0.239040192             |
| 6-13 TT2          | 1945798        | 0.113633825             |
| 6-13 RF           | 5234408        | 0.305687333             |
| 6-13 SSFE         | 9374826        | 0.547486088             |
| 0.095 ppm Std.    | 17073362       | 0.099707751             |



| Sample            | IC Area | Nitrite-N (mg/L) |
|-------------------|---------|------------------|
| 6-18 Raw          | 0       | 0                |
| 6-18 HFCs+Nitrate | 0       | 0                |
| 6-18 TT1          | 1678158 | 0.098003756      |
| 6-18 TT2          | 2218852 | 0.129580069      |
| 6-18 RF           | 4296040 | 0.250887018      |
| 6-18 SSFE         | 9359736 | 0.546604839      |
| 0.024 ppm Std     | 3738670 | 0.021833683      |

pH

| <u>Date</u> | <u>Raw</u> | <u>T1 Effluent</u> | <u>T2 Effluent</u> | <u>RF Effluent</u> | <u>SSF Reservoir</u> | <u>SSF Effluent</u> |
|-------------|------------|--------------------|--------------------|--------------------|----------------------|---------------------|
| 2/27        | 7.3        | 7.15               | 7.11               | 7.7                |                      |                     |
| 2/28        | 7.3        | 7.16               | 7.12               | 7.72               |                      |                     |
| 3/4         | 7.3        | 7.21               | 7.18               | 7.74               |                      |                     |
| 3/6         | 7.3        | 7.2                | 7.15               | 7.73               |                      |                     |
| 3/7         | 7.3        | 7.2                | 7.15               | 7.65               |                      |                     |
| 3/10        | 7.3        | 7.18               | 7.13               | 7.67               |                      |                     |
| 3/11        | 7.3        | 7.21               | 7.17               | 7.71               |                      |                     |
| 3/17        | 7.3        | 7.2                | 7.26               | 7.71               |                      |                     |
| 3/19        | 7.2        | 7.14               | 7.05               | 7.99               |                      |                     |
| 3/21        | 7.2        | 7.03               | 6.96               | 7.9                |                      |                     |
| 3/24        | 7.2        | 7.03               | 6.95               | 7.83               |                      |                     |
| 3/25        | 7.2        | 7.03               | 6.95               | 7.8                |                      |                     |
| 3/28        | 7.2        | 7.08               | 7.1                | 7.87               |                      |                     |
| 3/31        | 7.3        | 7.16               | 7.14               | 7.96               |                      |                     |
| 4/2         | 7.3        | 7.25               | 7.23               | 7.94               |                      |                     |
| 4/4         | 7.3        | 7.02               | 6.94               | 7.86               |                      |                     |
| 4/7         | 7.3        | 7.05               | 7.1                | 7.95               |                      |                     |
| 4/9         | 7.3        | 6.85               | 6.74               | 7.78               |                      |                     |
| 4/12        | 7.3        | 6.97               | 6.93               | 7.8                |                      |                     |
| 4/15        | 7.3        | 7.12               | 7.09               | 7.66               |                      |                     |
| 4/16        | 7.3        | 7.08               | 7.06               | 7.66               |                      |                     |
| 4/17        | 7.3        | 7.1                | 7.06               | 7.66               |                      |                     |
| 4/21        | 7.3        | 7.09               | 7.06               | 7.66               |                      |                     |
| 4/22        | 7.3        | 7.12               | 7.1                | 7.56               |                      |                     |
| 4/23        | 7.3        | 7.11               | 7.07               | 7.59               |                      |                     |
| 4/25        | 7.3        | 7.11               | 7.1                | 7.52               |                      |                     |
| 4/28        | 7.3        | 7.1                | 7.08               | 7.47               |                      |                     |
| 4/29        | 7.3        | 7.01               | 6.97               | 7.26               | 7.44                 | 7.42                |
| 4/30        | 7.3        | 7.06               | 7.01               | 7.4                | 7.44                 | 7.42                |
| 5/1         | 7.3        | 7.06               | 7.05               | 7.4                | 7.41                 | 7.46                |
| 5/2         | 7.3        | 7.15               | 7.13               | 7.44               | 7.53                 | 7.46                |
| 5/5         | 7.3        | 7.07               | 7.06               | 7.46               | 7.54                 | 7.48                |
| 5/6         | 7.3        | 7.08               | 7.08               | 7.42               | 7.5                  | 7.46                |
| 5/7         | 7.3        | 7.27               | 7.28               | 7.53               | 7.61                 | 7.54                |
| 5/12        | 7.3        | 7.05               | 7.07               | 7.41               | 7.5                  | 7.44                |
| 5/14        | 7.3        | 7.08               | 7.08               | 7.47               | 7.52                 | 7.44                |
| 5/16        | 7.3        | 7.08               | 7.08               | 7.51               | 7.53                 | 7.44                |
| 5/19        | 7.3        | 7.07               | 7.07               | 7.6                | 7.56                 | 7.45                |
| 5/21        | 7.3        | 7.12               | 7.09               | 7.64               | 7.54                 | 7.41                |
| 5/23        | 7.3        | 7.16               | 7.17               | 7.71               | 7.64                 | 7.46                |
| 5/27        | 7.3        | 7.03               | 7.03               | 7.57               | 7.42                 | 7.34                |

pH

| <u>Date</u> | <u>Raw</u> | <u>T1 Effluent</u> | <u>T2 Effluent</u> | <u>RF Effluent</u> | <u>SSF Reservoir</u> | <u>SSF Effluent</u> |
|-------------|------------|--------------------|--------------------|--------------------|----------------------|---------------------|
| 5/28        | 7.3        | 7.08               | 7.14               | 7.56               | 7.61                 | 7.53                |
| 5/30        | 7.3        | 7.03               | 7.05               | 7.5                | 7.48                 | 7.4                 |
| 6/2         | 7.3        | 7.06               | 7.05               | 7.59               | 7.5                  | 7.44                |
| 6/4         | 7.2        | 7.1                | 7.1                | 7.63               | 7.46                 | 7.41                |
| 6/6         | 7.3        | 7.11               | 7.1                | 7.57               | 7.52                 | 7.43                |
| 6/9         | 7.3        | 7.06               | 7.05               | 7.54               | 7.47                 | 7.4                 |
| 6/11        | 7.3        | 7.07               | 7.01               | 7.49               | 7.49                 | 7.39                |
| 6/13        | 7.3        | 7.04               | 7.03               | 7.58               | 7.35                 | 7.4                 |
| 6/18        | 7.3        | 7.12               | 7.1                | 7.52               | 7.53                 | 7.43                |
| 6/20        | 7.3        | 7.19               | 7.16               | 7.57               | 7.6                  | 7.4                 |
| 6/25        | 7.3        | 7.09               | 7.05               | 7.51               | 7.55                 | 7.39                |
| 6/26        | 7.3        | 7.11               | 7.1                | 7.69               | 7.7                  | 7.52                |
| 6/27        | 7.3        | 7.02               | 7                  | 7.61               | 7.58                 | 7.45                |
| 6/29        | 7.2        | 7.03               | 7.02               | 7.58               | 7.61                 | 7.42                |

Turbidity

| Date | Raw | T1 Effluent | T2 Effluent | R1 Effluent | SSF Reservoir                | SSF Effluent |
|------|-----|-------------|-------------|-------------|------------------------------|--------------|
| 2/27 | 0.1 | 0.18        | 0.21        | 0.25        |                              |              |
| 2/28 | 0.1 | 0.18        | 0.23        | 0.23        |                              |              |
| 3/10 | 0.1 | 0.22        | 0.24        | 0.24        |                              |              |
| 3/11 | 0   | 0.22        | 0.22        | 0.25        |                              |              |
| 3/17 | 0.1 | 0.13        | 0.18        | 0.21        |                              |              |
| 3/19 | 0.1 | 0.21        | 0.32        | 0.55        |                              |              |
| 3/21 | 0   | 0.29        | 0.47        | 0.62        |                              |              |
| 3/24 | 0.1 | 2           | 4.3         | 4.5         |                              |              |
| 3/25 | 0.1 | 2           | 4.45        | 0.2         |                              |              |
| 3/28 | 0.1 | 1.2         | 1.2         | 0.8         |                              |              |
| 3/31 | 0.1 | 0.76        | 0.96        | 0.85        |                              |              |
| 4/2  | 0.1 | 0.52        | 0.89        |             |                              |              |
| 4/4  | 0.1 | 1.45        | 1.85        | 1.5         |                              |              |
| 4/7  | 0.1 | 0.89        | 1.2         | 1.5         |                              |              |
| 4/9  | 0.4 | 2.35        | 5.5         | 2.9         |                              |              |
| 4/12 | 0.1 | 6.3         | 6.65        | 5.9         |                              |              |
| 4/15 | 0.1 | 1.5         | 3.3         | 3.45        |                              |              |
| 4/17 | 0.2 | 2.7         | 4.05        | 3.5         |                              |              |
| 4/21 | 0.1 | 1.1         | 1.5         | 1           | ----- Samples run 1 day late |              |
| 4/22 | 0.1 | 2.4         | 3           | 1.6         |                              |              |
| 4/23 | 0.2 | 2.2         | 2.4         | 1.4         |                              |              |
| 4/25 | 0.1 | 1.8         | 2.25        | 1.45        |                              |              |
| 4/28 | 0.1 | 2.15        | 2.05        | 1.55        |                              |              |
| 4/29 | 0.1 | 1.85        | 2.1         | 1.9         | 1.9                          | 0.85         |
| 4/30 | 0.1 | 2           | 3.6         | 1.7         | 1.8                          | 0.62         |
| 5/1  | 0.1 | 2.5         | 2.9         | 2.3         | 2.2                          | 0.8          |
| 5/2  | 0.2 | 2.8         | 3.5         | 2.4         | 2                            | 0.46         |
| 5/5  | 0.1 | 0.79        | 0.96        | 0.66        | 0.77                         | 0.31         |
| 5/6  | 0.1 | 1.4         | 1.45        | 0.92        | 0.77                         | 0.24         |
| 5/7  | 0.1 | 1.25        | 1.55        | 1.2         | 1.2                          | 0.35         |
| 5/12 | 0.1 | 1.6         | 1.5         | 1.1         | 0.9                          | 0.17         |
| 5/14 | 0.1 | 1.5         | 1.5         | 1.1         | 1.1                          | 0.18         |
| 5/16 | 0.1 | 1.45        | 1.3         | 1           | 0.95                         | 0.28         |
| 5/19 | 0.1 | 1.2         | 1.1         | 0.9         | 0.83                         | 0.24         |
| 5/21 | 0.1 | 1.1         | 1.6         | 1.25        | 1.3                          | 0.2          |
| 5/23 | 0.2 | 0.88        | 1.1         | 1.2         | 1.1                          | 0.21         |
| 5/28 | 0.1 | 1.45        | 1.5         | 1.2         | 1.05                         | 0.19         |
| 5/30 | 0.2 | 2.2         | 1.8         | 1.45        | 1.05                         | 0.19         |
| 6/2  | 0.2 | 1.8         | 2.1         | 1.75        | 1.6                          | 0.37         |
| 6/4  | 0.1 | 1.8         | 1.6         | 1.2         | 1.1                          | 0.31         |
| 6/6  | 0.2 | 1.95        | 1.5         | 1.2         | 1.05                         | 0.4          |

# Turbidity

| Date | Raw | T1 Effluent | T2 Effluent | Rf Effluent | SSF Reservoir | SSF Effluent |
|------|-----|-------------|-------------|-------------|---------------|--------------|
| 6/9  | 0.1 | 1.8         | 2.6         | 2.2         | 1.9           | 0.67         |
| 6/11 | 0.2 | 2.9         | 3.45        | 2.05        | 1.6           | 0.44         |
| 6/13 | 0.2 | 5.4         | 5.6         | 2.1         | 2.3           | 0.44         |
| 6/18 | 0.2 | 3.5         | 5.3         | 2.3         | 1.8           | 0.48         |
| 6/20 | 0.1 | 4           | 5.2         | 1.7         | 1.1           | 0.42         |
| 6/25 | 0.2 | 1.7         | 1.4         | 0.8         | 0.5           | 0.38         |
| 6/26 | 0.2 | 3.1         | 3           | 1           | 0.85          | 0.45         |
| 6/29 | 0.3 | 5.3         | 3.45        | 1.65        | 1.35          | 0.35         |

Dissolved Oxygen

| <u>Date</u> | <u>Raw</u> | <u>T1 Effluent</u> | <u>T2 Effluent</u> | <u>RF Effluent</u> | <u>SSF Reservoir</u> | <u>SSF Effluent</u> |
|-------------|------------|--------------------|--------------------|--------------------|----------------------|---------------------|
| 5/14        | 2.1        | 0.5                | 0.5                | 6.9                | 7.1                  | 3.7                 |
| 5/16        | 2          | 0.55               | 0.55               | 6.9                | 7.05                 | 3.7                 |
| 5/19        | 1.5        | 0.5                | 0.5                | 7.55               | 7.6                  | 4.15                |
| 5/21        | 1.7        | 0.5                | 0.3                | 8.55               | 8.25                 | 4.3                 |
| 5/23        | 3.1        | 0.4                | 0.35               | 8.6                | 8.8                  | 4.5                 |
| 5/27        | 3.7        | 0.2                | 0.4                | 8.1                | 7.4                  | 3.8                 |
| 5/28        | 5          | 0.25               | 0.45               | 8.15               | 7.5                  | 3.85                |
| 5/30        | 5.1        | 0.35               | 0.45               | 7.75               | 6.8                  | 3.65                |
| 6/2         | 1.8        | 0.35               | 0.5                | 7.75               | 6.8                  | 3.6                 |
| 6/4         | 1.7        | 0.35               | 0.5                | 7.9                | 6.9                  | 3.6                 |
| 6/6         | 4          | 0.35               | 0.45               | 7.95               | 7.6                  | 3.9                 |
| 6/9         | 4.2        | 0.4                | 0.55               | 7.3                | 6.5                  | 3.75                |
| 6/11        | 4.9        | 0.4                | 0.5                | 7.5                | 7.45                 | 3.9                 |
| 6/13        | 4.7        | 0.45               | 0.6                | 7.45               | 7.53                 | 3.8                 |
| 6/18        | 4.1        | 0.55               | 0.55               | 7.1                | 7.15                 | 3.4                 |
| 6/20        | 1.9        | 0.4                | 0.65               | 7.35               | 7.4                  | 3.5                 |
| 6/25        | 5.1        | 0.35               | 0.65               | 7.6                | 7.65                 | 4                   |
| 6/26        | 1.6        | 0.35               | 0.55               | 7.7                | 7.75                 | 3.95                |
| 6/27        | 3.9        | 0.4                | 0.55               | 7.65               | 7.8                  | 4.3                 |
| 6/29        | 1.5        | 0.35               | 0.6                | 7.25               | 7.4                  | 3.65                |

## **Appendix B**

**Denitrification demonstration monitoring plan  
prepared for the staff of the drinking water section  
of the Colorado Department of Public Health and  
Environment**

# STATE OF COLORADO

Ken Komer, Governor  
Pat Schwader, Acting Executive Director

is dedicated to protecting and improving the health and environment of the people of Colorado.

1400 Cherry Creek Dr. S. Laboratory Building  
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Phone (303) 692-2000 Denver, Colorado 80220-3710  
(303) 691-4700



Colorado Department  
of Public Health  
and Environment

November 15, 1995

JoAnn Silverstein, P.E.  
University of Colorado  
Room OT 5-34, Engineering Center  
Campus Box 428  
Boulder, CO 80309-0428

RE: Town of Wiggins, Demonstration Project  
PWSID 144035, Morgan County

Dear JoAnn:

I apologize for the delay in responding to your request for a letter outlining the required tests associated with the denitrification demonstration plant for the Town of Wiggins. Our goal is to define the necessary tests such that, after the testing is complete, the system will be an approved technology for use in Colorado.

We concur with the proposed testing as outlined on page 4 of the monitoring plan. However, to verify the accuracy of the tests, we would like finished water bacteriological and nitrate samples split once per month with a certified laboratory. The THM and TOC samples should be split at the middle and end of the test period. The THM test must simulate the addition of chlorine and maximum detention time in the distribution system.

The acetate additive must be a food grade product having either an FDA or NSF approval. The equipment must also have NSF approval.

During the demonstration project, the Division would like to set-up a series of meetings, held at the site, to discuss the plant's performance. This would provide a perfect opportunity to discuss any potential problems or concerns that may have arisen during the test period.

We look forward to working with you on this project and if you have any questions please call me at (303) 692-3545

Sincerely,

Greg Akins  
Drinking Water Program  
Water Quality Control Division

cc: File Sec. 2  
Victor Sainz, CDH-Field Support  
County Health Dept.



# **Wiggins Denitrification Demonstration**

## **Performance Monitoring**

### **1.0 Objectives**

The proposed denitrification plant at Wiggins is a biological process designed to remove nitrate from ground water and treat the water to potable standards. Previous demonstrations (on a smaller scale) of this process have shown this design to be capable of this. However, if this design is to be implemented on a practical scale, verification of the previous results must be demonstrated by the Wiggins plant. In addition, the effluent water quality must satisfy the potable drinking water standards promulgated by the Colorado Department of Health and the Environment (CDPHE) and the Environmental Protection Agency (EPA). Therefore the sampling program must be designed to provide sample data which is not only comparable to previous data but is also obtained within an acceptable level of precision and accuracy to satisfy the relevant regulatory agencies.

### **2.0 Variability**

Although the variability of the current system is not known, an estimation of the variability of a few select parameters (Nitrate, TOC, pH, turbidity) can be inferred from the data previously obtained during a pilot demonstration of the same process in Brighton, Co. (Mendonca, M. et. al. 1991). Analysis of these data yielded statistical results (Table 1). For the current system it is assumed that the data will exhibit similar variation. The rationale for establishing the sampling frequencies at the Wiggins plant is based on this assumption.

| Previously Sampled Parameter | Number of Samples | Arithmetic Mean (mg/l) | Standard Deviation of the Mean |
|------------------------------|-------------------|------------------------|--------------------------------|
| Nitrate                      | 75                | 5.7                    | 2.5                            |
| pH                           | 11                | 7.4                    | 0.2                            |
| TOC                          | 29                | 2.2                    | 0.6                            |
| Turbidity                    | 20                | 4.2                    | 0.21                           |

Table 1: Summary Statistics for Brighton Demonstration

### 3.0 Sampling Frequency

The sampling frequencies for the Wiggins plant is based on three factors:

1. availability of plant analysts,
2. State and EPA regulations,
3. precision of the data based on estimated system variability.

The primary analysts for the system will be Professor JoAnn Silverstein and Research Assistant, Dan Thompson, both of whom reside in Boulder County. To avoid unnecessary expenditure of time and research funds, the analysts will be visiting the plant site three times per week. This will enable a maximum of 3 manual samples to be taken at each sampling point. A sampling frequency of 3/week will be more than adequate to satisfy all State and EPA regulatory requirements for most of the water quality parameters of concern, except turbidity. State regulations require that turbidity be monitored at least once per day for a municipality the size of Wiggins. This requirement will be met by the use of an automated sampler installed at the site.

The sampling frequencies for each water quality parameter and the corresponding sampling points are shown in Table 2 and Table 3 respectively. The estimated precision of the mean is given for those parameters for which previous data was obtained during the Brighton demonstration. These precision

values were obtained with the assumption that the previously obtained summary statistics (i.e. mean, standard deviation) were of independent, randomly sampled, normally distributed data. The basic equation for the calculation of the precision (p) can then be stated as:

$$p = \frac{t_{95} \cdot \sigma}{\sqrt{N}} \quad (\text{Montgomery, H.A.C. et. al. 1974})$$

where:

$t_{95}$  = student-t at the 95% confidence level

$\sigma$  = estimated standard deviation of the mean

N = number of samples.

N is determined by the product of the sampling frequency and the period of sampling;  $\sigma$  is calculated from the previous sample values; and  $t_{95}$  is taken from standard statistical tables.

For the parameters on which no previous data is available it is assumed that their variability will not exceed the values which would result in an unacceptable precision in the calculation of their mean. In other words, the chosen frequencies for these parameters will yield results which will be an acceptable representation of the true population in the system at a 95% confidence level.

| Parameter/<br>Sample Points               | Sampling Method                   | Analytical Method | Sampling<br>Frequency | Estimated Precision<br>of the mean          |
|---|-----------------------------------|-------------------|-----------------------|---|
| Nitrate<br>(pt. #5)<br>(pt. #1,2,3)       | automatic (grab)<br>manual (grab) | IC                | 3/week<br>3/week      | +/- 0.82 mg/l<br>or<br>14.30%               |
| Nitrite<br>(pt. #5)<br>(pt. #1,2,3)       | automatic (grab)<br>manual (grab) | IC                | 3/week<br>3/week      | NA  |
| Acetate<br>(pt. #5)<br>(pt. #1,2,3)       | automatic (grab)<br>manual (grab) | IC                | 3/week<br>3/week      | NA  |
| turbidity<br>(pt. #5)<br>(pt. #1,3,4)     | automatic (grab)<br>manual (grab) | Nephelometer      | 1/day<br>3/week       | +/-0.04 NTU or 9.5%<br>+/-0.07 NTU or 16.0% |
| pH<br>(pt. #1, 5)                         | manual (grab)                     | ion meter         | 3/week                | +/-0.06 or 0.80%                            |
| coliform: total & fecal<br>(pt. #1,3,4,5) | manual (grab)                     | Coilert           | 1/week                | N/A   |

Table 2: Sampling Schedule for Principle parameters

| Parameter/<br>Sample Points            | Sampling Method | Analytical Method | Sampling<br>Frequency      | Estimated Precision<br>of the Mean |
|--|-----------------|-------------------|----------------------------|------------------------------------|
| alkalinity<br>(pt. #1,5)               | manual (grab)   | titration         | 1/month                    | N/A                                |
| hardness (Ca & Mg)<br>(pt. #1,5)       | manual (grab)   | titration or IC   | 1/month                    | N/A                                |
| sulfate<br>(pt. #1,5)                  | manual (grab)   | IC                | 1/month                    | N/A                                |
| Fe(II), Fe(III) & Mn<br>(pt. #1,3,4,5) | manual (grab)   | Hach kit          | special<br>study           | N/A                                |
| TOC<br>(pt. #1,3,4,5)                  | manual (grab)   | autoanalyzer      | 1/month                    | +/-0.19 mg/l or 8.6%               |
| THMFP<br>(pt. #1,3,4,5)                | manual (grab)   | GC                | bimonthly &<br>spec. study | N/A                                |

Table 3: Sampling Schedule for Additional Parameters

#### 4.0 Sampling Points

For the purposes of research and development sampling points #1 - 4 were carefully chosen to represent water quality at the respective influents and effluents of the unit processes in the system. Analysis of the samples from these points will

aid further understanding the individual mechanisms and their respective effects on water quality. Sample point #5 was chosen to represent the effect the whole system has on water quality. The data collected at this point will represent the effluent quality of the system and will be reported monthly to the CDPHE for regular quality standards assessment.

## **5.0 Sampling Methods**

For sample points #1 - 4 a manual "grab" (discrete) sampling method will be employed to obtain representative samples. This method, although not as consistent or precise as automatic sampling, will be adequate enough to satisfy the objectives of this sampling program. The use of a discrete, as opposed to a composite sampling method at these points was chosen due to the relatively infrequent sampling regime and for its tendency to more accurately represent the variability of the system.

For sample point #5 an automatic "grab" sampling method using an ISCO automatic sampler will be implemented. The use of an automated sampling device at this point is apparent due to the frequency for which turbidity must be monitored under State and EPA regulations. The ability to obtain more frequent samples at point #5 precludes the need to have someone present at the site on a daily basis.

Samples for the analysis of coliform bacteria at sample point #5 will be taken manually to reduce the time between sampling and culturing. The examination then will indicate more accurately the true microbial content of the water at the time of sampling.

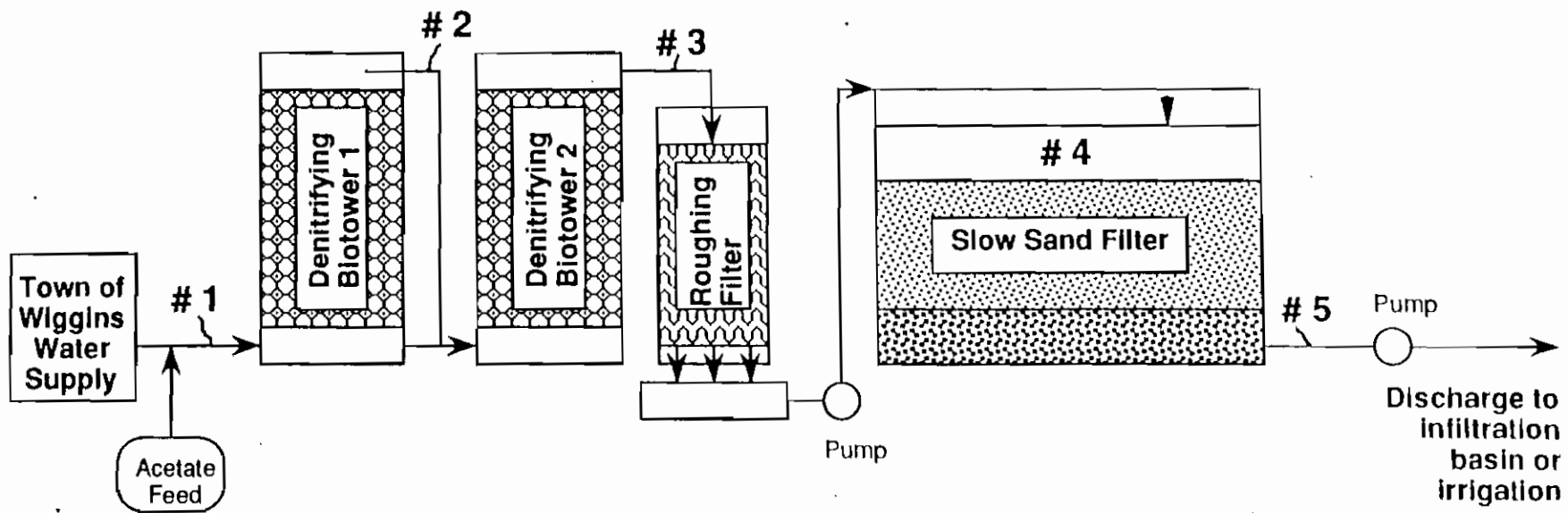


Figure 1. Demonstration Plant Process Flow Diagram and Sample Points (# 1)

## **6.0 Quality Assurance / Quality Control**

**6.1 Sampling and Analysis Responsibility:** Bench- and pilot-scale research on the biological denitrification system will be performed at the University of Colorado and the plant site in Wiggins, Colorado respectively. Dr. JoAnn Silverstein and a CU graduate student (research assistant) will be the principle investigators for the project. Dr. Silverstein will be accountable for the laboratory activities, including examination of all data and maintenance of the quality assurance program. She will also be involved with periodic sample collection. The graduate student will be primarily responsible for sample collection, preservation, analysis and data compilation. This person will implement the quality assurance procedures described here, particularly the quality control performance evaluation samples. The quality control data will be collated and reported to the CDPHE.

## **7.0 Quality Assurance Objectives**

The quality assurance objectives for data obtained in this project will be defined in terms of determination (accuracy and precision) and control of data quality. Precision and accuracy will be used as described below.

**7.1 Precision:** Analytical precision will be assessed by comparing the results of analyses of duplicate samples. The objective of precision will be a relative deviation of less than 15% between duplicate samples. Precision will be expressed in terms of a coefficient of variation (c.v.), defined as the percent difference of one standard deviation from the sample mean. All reported parameter values will be expressed as the average (mean), plus/minus the c.v. (%).

**7.2 Accuracy:** Accuracy of the analytic procedures used will be determined by analysis of spiked samples using quality control standards. Internal standards for all chemical measurements will be obtained from the EPA. For those

parameters for which there are no external quality control standards available, we will do one of two things: 1) make up an internal standard or 2) designate a second method of measurement, and the results of the two methods compared. When the external or internal standards and when two methods of analysis are employed, the objective for accuracy will be agreement to within 20% of either the external/internal standard value or of the second method of measurement. Analysis of the chick standards and by the second method of measurement will be performed monthly during the demonstration run.

## **8.0 Sampling Procedures**

**8.1 Sample containers:** In general sample containers will be glass bottles which have been acid washed and rinsed with deionized or distilled (Milli-Q) water. Containers will be closed with teflon-lined screw caps. Samples for trihalomethane analysis will be collected in brown glass bottles which have been washed with detergent, rinsed with deionized and distilled water, and oven dried at 250° C for 2 hours. The brown glass bottles will be filled (no gas head space) and capped with teflon-lined screw caps.

**8.2 Sample Collection:** All manual samples will be collected through installed sample lines. The sample lines will be flushed for two minutes before sample collection is made. The samples will be filtered on site using a 0.22 µm filter in a vacuum filtration apparatus.

**8.3 Sample preservation:** Samples containers used for automatic collection at point #5 will have been previously inoculated with an appropriate bactericide. Samples collected for total coliform analysis at this point will be collected manually. All other samples will not be preserved, but analyzed within 24 hours of collection. The samples will be stored in the dark at 4° C.



## **9.0 Sample Custody**

Samples collected by Dr. Silverstein will be transferred to the graduate student for laboratory analysis. A chain-of-custody record will accompany each sample or group of samples. The record will contain the following information: sample number; signature of collector; date, time, and address of collection; sample type; signatures of persons involved in chain of possession; and inclusive dates of possession. Sample custody procedures will not be required for samples collected by the graduate student. This person will be responsible for sample collection, preservation, storage, analysis, data recording and interpretation.

## **10.0 Calibration Procedure and Frequency**

A number of instruments will be used which require blanks and standards for calibration: e.g., an ion chromatograph, a nephelometer, a gas chromatograph, and a pH ion meter. For all instruments, stock standard solutions will be prepared and preserved by methods described in Standard Methods (17th Edition, 1989) and /or the instrument manufacturer's specifications. Aqueous calibration standards, dilutions of stock solutions, will be made each day of analysis.

**10.1 Blanks:** A reagent water blank will be analyzed daily to rule out the possibility of analytical system interferences.

**10.2 Calibration Curves:** For all analyses a calibration curve for each analyte will be prepared weekly by analyzing a set of at least four calibrations standards which bracket the concentration of the analyte of interest. Lower and upper limits for the analyses will fall within the manufacturer-specified precision limits for each instrument, or the analytical limits suggested in Standard Methods (1989).

**10.2.1** The calibration curve will be verified each day by measurement of one or more calibration standards.

**10.2.2** If the linear or areal value for any calibration standard differs by more than 20% from the value determined by the standard calibration curve, a new calibration curve will be prepared.

## **11.0 Analytical Procedures**

Individual analytical methods for the principle parameters are described below. When available, EPA external check standards have been noted; otherwise internal standards have been added. All analytical procedures will be carried out in the CU. Environmental laboratories except heterotrophic plate counts which will be handled by an approved laboratory.

**11.1 Nitrate:** Nitrate will be analyzed routinely by the ion chromatography (IC) method #4500-NO<sub>3</sub> - C. in Standard Methods (1989). (EPA External Check Standards NFL and NUT).

**11.2 Nitrite:** Nitrite will be analyzed by the IC method # 4500-NO<sub>2</sub> - C. (Standard Methods, 1989). An internal check standard for nitrite will be prepared.

**11.3 Acetate:** Acetate will be analyzed by the IC method #4110-B. (Standard Methods, 1989). Acetate analysis will be checked using an internal standard.

**11.4 Turbidity:** Turbidity will be measured as Nephelometric turbidity using method # 2130-B (Standard Methods, 1989) on a Hach 2100A turbidimeter. (EPA External Check Standard - TUR.)

**11.5 pH:** pH will be measured using the electrometric method # 4500-H<sup>+</sup> - B. (Standard Methods, 1989). An internal standard will be prepared as one of the primary standards for pH in Standard Methods (1989).

**11.6 Coliform bacteria:** Total and Fecal coliform will be detected by Colilert as described in Edberg et. al. 1988. (EPA External Check Standard - ESC).

## **12.0 Data Analysis, Validation and Reporting**

The data analyses to be applied to the raw data are cited in the analytical procedures for each method. As stated in section 4.0, data calculations will be performed by the graduate student performing the analysis. This individual will examine finished data as it is generated to check if they follow existing trends set in previous analyses. If the data do not conform to this trend, a duplicate sample, if available, will be analyzed. If results are still suspect, the experiment will be repeated. Decisions to disregard any results will be made only after consultation with Dr. Silverstein. All finished data, whether deemed "erroneous" or not, will be incorporated in the laboratory notebooks and electronic data storage files. Validated data will be included in reports to the CDPHE.

## **13.0 Internal Quality Control**

**13.1 Spikes:** Spiked samples will be prepared for 5% of the field samples. If the percent recovery is unsatisfactory, the data from these samples will be discarded and the procedure will be repeated with new samples. Laboratory spikes will also be prepared and analyzed for interferences.

**13.2 Duplicates:** Analytical precision will be assessed by analysis of 5% of the samples in duplicate. Precision will be calculated as the percent deviation of duplicate results from the original sample measurement.

**11.3 Standards:** Instrument accuracy will be evaluated regularly for each method of analysis by using either external standards or a second method of analysis. As a minimum, analysis of internal and external standards will be applied whenever analysis of known additions does not result in acceptable recovery. For instrument calibration, three different dilutions of the standards will be measured when an analysis is initiated. Subsequently, verification of the standard curves will

be analyzed within the linear range, as specified in the individual method (Standard Methods, 1989).

**11.4 Control Charts:** All quality control data for each instrument will be recorded using three types of charts:

- 1) Means chart - constructed from the average and standard deviation of a standard with upper and lower warning levels
- 2) Means chart - for reagent blank results
- 3) Range chart - for replicate analysis

Actions taken will be based on the statistical parameters outlined in Standard Methods (1989).

## **12.0 Preventative Maintenance**

Daily maintenance of all instruments and laboratory equipment is carried out by researchers and the supervising laboratory technician at the CU environmental engineering laboratories. In addition, the CU Department of Civil Engineering and College of Engineering both have electronics technicians on staff to correct instrument problems.

## **13.0 Corrective Action**

Should the precision evaluation indicate a relative deviation of greater than 15% between duplicates, or greater than 20% against QA external check standards and/or second methods, the standard and duplicate or check sample will be reanalyzed. A new standard will be analyzed if the precision or accuracy are still outside these deviation limits. If the new standard value is outside the limit, the instrument will be recalibrated and the analysis repeated. If the measurements still do not meet criteria for precision and accuracy, instrument will be recalibrated and the analysis repeated. If the measurements still do not meet criteria for precision

and accuracy, instrument maintenance will be performed and the analytical process repeated. If, finally, the relative deviation still is greater than 20% for precision or 25% for accuracy, the experiment will be repeated.

#### **14.0 Quality Assurance Reports**

Quality assurance reports will be made monthly for the CDPHE, including a detailed report of data precision and accuracy for each analysis. Any significant QA problems will be reported along with recommendations for correction. Any changes in QA procedures or analytical procedures will be submitted in writing to the CDPHE for approval.