EVALUATION OF SYSTEM PERFORMANCE OF A FULL-SCALE BIOLOGICAL DENITRIFICATION SYSTEM FOR THE TREATMENT OF DRINKING WATER IN COYLE, OKLAHOMA

By

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1.0 INTRODUCTION

Nitrate contamination of drinking water sources has become an increasingly urgent problem, particularly in rural areas. Primary contributors to these elevated nitrate levels are excessive use of nitrogen fertilizers and improper handling of human and animal wastes. Since 1945, nitrate has been known to cause methemoglobinemia or "blue baby" syndrome, an acute and sometimes fatal respiratory distress in infants (Shuval and Gruener, 1977). For this reason, a maximum contaminant level (MCL) of 10 mg/L nitrate (as nitrogen) has been established in the United States, regulating nitrate as a primary drinking water contaminant.

Conventional means of removing nitrate from drinking water include ion exchange and a variety of membrane technologies, such as reverse osmosis (Dahab, 1987). These processes have been proven effective in nitrate removal. However, disadvantages, including poor selectivity for nitrate, concentrated waste disposal issues, cost, and susceptibility to fouling (in the case of reverse osmosis), have fed the search for alternative nitrate removal technologies. One such technology is biological denitrification, a process used routinely in wastewater treatment.

It has been known for quite some time that many common bacteria, mostly heterotrophic, have the ability to reduce nitrate to nitrogen gas in the absence of oxygen, through a process called dissimilatory denitrification. Heterotrophic bacteria require an organic carbon energy substrate for growth. In municipal waste, organic carbon is present in abundance, but in the case of a drinking water source, particularly ground water, organic

carbon is in short supply. Thus, a carbon source such as acetic acid (commercial food-grade vinegar) or a glucose/fructose feed (commercial high-fructose corn syrup) must be provided for denitrification of drinking water.

Biological treatment of drinking water has been demonstrated in research projects. However, questions over the biological and chemical stability of a biologically-denitrified water have, until recently, kept biological treatment, as a stand-alone process, out of drinking water facilities in the United States. In addition, the proposal to add microorganisms to a drinking water source goes against all traditional approaches in which the goal has been to remove bacteria from the water supply. Public health officials and researchers have raised several concerns with the use of a biological process (Bouwer and Crowe, 1988; Dahab, 1987). First, is the water in the distribution system biologically stable? Since a carbon source must be supplied to the heterotrophic bacteria employed, there is a need to be certain that an optimum feed rate is maintained, so that there is no unused substrate present in the finished water. Also, adequate filtration must be provided to remove the constantly sloughing bacteria produced in the reactor. Second, is the finished water chemically safe? Trihalomethanes and haloacetic acids are often formed in utilities using chlorine as a disinfectant, due to the chlorination of the natural organic matter in the water. It is conceivable that metabolic by-products of the denitrification process may more readily combine with the chlorine present in the distribution system, resulting in an increased THM formation potential over conventional treatment methods. Also, there is concern over the possibility of toxic metabolic products and endotoxins being imparted to the treatment water (Dahab, 1991).

In the summer of 1998, the small town of Coyle, Oklahoma, installed the first full-scale stand-alone biological denitrification system in the United States. The purpose of this study is to:

- Evaluate the performance of the full-scale system at Coyle, as it is subjected to: (1) changing raw water quality, (2) normal plant operation and maintenance constraints, and (3) operation by a traditional licensed operator, as opposed to research staff. Anion levels (including nitrate and nitrite) as well as nonpurgeable organic carbon (NPOC) are to be monitored in the raw water and throughout the plant in order to evaluate the performance of each step of the treatment process.

- Estimate the presence of THM precursors throughout the water treatment facility by measurement of ultraviolet absorbance at 254 nm (UV_{254}) as a surrogate parameter.

- Identify areas which merit further investigation if biological denitrification is to become a viable technology for the treatment of drinking water.

2.0 REVIEW OF THE LITERATURE

The United States is often considered a world leader in providing safe and efficient drinking water to its citizens. The need to provide safe water has, however encouraged skepticism in adopting new treatment technologies such as biological drinking water treatment. Despite the lack of experience with biological drinking water treatment in the United States, there is a rather large body of research literature on the subject. Researchers have applied knowledge of wastewater denitrification to develop reactors for the study of drinking water. From this, different treatment configurations and processes have been proposed. Full-scale and demonstration plants have long been operated in Europe for the removal of organic carbon and nutrients. Recently, researchers from the University of Colorado at Boulder have operated two field demonstration reactors in Brighton, Colorado (Cook et al., 1990) and in Wiggins, Colorado (Lamarre, 1998).

Biological denitrification may have a number of significant advantages over physical/chemical nitrate removal systems that make it an attractive alternative. According to Dahab (1991):

- The process appears to be cheaper to install with comparable operation and maintenance costs to other treatment alternatives.

- The excess biological growth produced as waste is much easier and less expensive to dispose of than waste salts and brines from other methods.

- The process is extremely effective in reducing nitrates to near zero concentration in the treated water, regardless of nitrate concentration in the raw influent water.

- Process stability is excellent particularly when using static media reactor systems (i.e., biofilm systems).

- The process does not impart excess undesirable chemicals such as chlorides to the treated water.

- Biological treatment, in general, is probably better suited to the removal of various toxic and hazardous micro-pollutants than most physical-chemical systems.

On the other hand, several concerns have been identified, which have slowed the transfer of biological denitrification technology to water treatment. First, heterotrophic denitrification requires that an organic carbon source be added to the water to promote the presence and activity of microorganisms. Encouraging bacterial growth in a drinking water goes against all traditional philosophies and provides for many potential problems, including the possibility of high concentrations of residual carbon in the treated water. This may make it necessary to further treat the water and increase the disinfectant dosage, typically chlorine. The combination of high residual organics and a high chlorine dose may increase the potential to form carcinogenic disinfection by-products (DBPs) such as trihalomethanes (THM) and haloacetic acids (HAA). By nature, a biological treatment system will create additional volatile suspended solids which must be removed prior to distribution. In addition, products of microbial activity, such as endotoxins and soluble microbial products, often associated with taste and odor problems, may be introduced to the treated water. Furthermore, operational concerns

arise, in that few drinking water treatment system operators are familiar with the operation or even the fundamental theories of biological processes.

The following review of the literature will first explore the health effects associated with nitrate consumption, including methemoglobinemia in infants, as well as suspected links to cancer. Sources and distribution of nitrate contamination in the United States will be examined as well as some of the factors which put a ground water source at risk for nitrate contamination. A basic understanding of the nitrogen cycle will demonstrate the role that biological denitrification can to play in the treatment of drinking water. Understanding of these possibilities will be expanded by examining the research and applications that have already occurred in the United States and abroad, utilizing heterotrophic bacteria and a variety of biofilter configurations and filter media.

2.1 Health Effects of Nitrate Consumption

"Every year as spring approaches, parents of infants in the central Illinois city of Decatur line up to get free bottled water from their community. The practice isn't a goodwill gesture. It's required by the state's Environmental Protection Agency." (Lamarre, 1998) Not unlike many other small communities and larger cities nestled among agricultural lands, Decatur's ground waters are contaminated with nitrates. Ingestion of nitrate in drinking water has caused the potentially fatal disease methemoglobinemia in infants under six months of age (Lamarre, 1998). Recognizing the noncancerous acute toxicity associated with the ingestion of nitrate and nitrite, the U.S. Environmental Protection Agency (EPA) has established maximum contaminant levels (MCLs) of 10 mg/L NO_3-N,

1 mg/L NO_2-N, and 10 mg/L (NO_3-N + NO_2-N). This authority to set drinking water standards has been delegated to the USEPA by Congress through the Safe Drinking Water Act (SDWA) of 1974, amended in 1986 and 1996. National Primary Drinking Water Regulations (NPDWRs or primary standards) are legally-enforceable standards instituted to protect drinking water quality by limiting the levels of specific contaminants that can adversely affect public health and are known or are anticipated to occur in drinking water. These standards apply to public water systems (PWSs), which provide water for human consumption through at least 15 service connections, or regularly serve at least 25 individuals (USEPA, 1998). Montgomery (1985) reported that 23% of primary drinking water standard violations were due to excessive nitrate concentrations, according to a 1985 survey by the American Water Works Association (AWWA). "In 1995, Oklahoma had 25 public water supplies that exceeded the nitrate maximum allowable limit of 10 mg/l. . . . Although public water supplies in the State have a history of nitrate exceedances, there have been no reported cases of illness due to nitrates associated with a public water supply in Oklahoma." (Oklahoma DEQ, 1999) Regulation of nitrate/nitrite in drinking water based upon the threat to human health is not unique to the United States. Table 1 presents a summary of similar nitrate/nitrite limits that have been established by international regulatory agencies.

Date	Organization	Maximum Allowable NO_3^- (mg/L) as NO_3^-	Maximum Allowable NO_3^- (mg/L) as NO_3^--N	Maximum Allowable NO_2^- (mg/L) as NO_2^-	Maximum Allowable NO_2^- (mg/L) as NO_2^--N	Recommended Maximum NO_3^- (mg/L) as NO_3^-	Recommended Maximum NO_3^- (mg/L) as NO_3^--N	Reference
1962	United States Public Health Service (USPHS)					45	10	St. Amant and McCarty, 1969
1974	United States Environmental Protection Agency (USEPA)		10		1			USEPA, 1999
1977	World Health Organization (WHO)					50	11.3	Kurt et al., 1987
1980	European Economical Community (EEC)	50	11.3		0.03	25	5.65	Dries et al., 1988
1993	Health and Welfare Canada		10		3.2			Kapoor and Viraraghavan, 1997

Table 1: Limits on nitrate and nitrite in drinking water.

2.1.1 Methemoglobinemia

Ingestion of nitrate in drinking water has been known to cause methemoglobinemia or "blue baby" syndrome in infants and certain susceptible portions of the adult population (i.e., Navajos, Eskimos, pregnant women, and people with genetic deficiency of glucose-6-phosphate dehydrogenase or methemoglobin reductase) (Bitton, 1994). Although nitrate is relatively non-toxic, being readily absorbed and readily excreted, it is regulated because under certain circumstances, nitrate can be reduced to nitrite by bacteria in the gastrointestinal tract (National Academy of Sciences, 1972). Methemoglobinemia is caused when hemoglobin (Hb) in the blood is converted to a brown pigment, methemoglobin (MetHb), following oxidation, by nitrite, of Fe^{2+} in hemoglobin to Fe^{3+}. Since methemoglobin is incapable of binding molecular oxygen, the ultimate result is suffocation (Bitton, 1994).

The conversion of Hb to MetHb occurs all the time in the body, but the quantity of the latter is maintained at a low, steady-state level by reactions facilitated by methemoglobin reductase and diaphorase enzymes in the red blood cells (Jaffe, 1964; National Academy of Sciences, 1972). The National Academy of Sciences (1972) reported that

methemoglobin is normally present in the human body at levels of 1-2% of the total hemoglobin. Clinical symptoms of methemoglobinemia are not normally detectable until the MetHb level reaches about 10%. Concentrations of 30-40% are compatible with life but will normally lead to anoxic symptoms with death following at a level of 50-75%.

If detected early, methemoglobinemia is a condition that is easily treated. In mild cases, a change in drinking water sources is normally the only treatment required. The USEPA believes that water containing NO_3-N at or below 10 mg/L is acceptable for daily drinking over a lifetime and does not pose a methemoglobinemia health risk for infants or adults (Skipton and Hay, 1998). In severe cases, methemoglobinemia may require treatment by a solution of methylene blue administered intravenously. According to the National Academy of Sciences (1972), the onset of the disease occurs promptly after the nitrate or nitrite is ingested and at concentrations high enough to cause the characteristic symptoms.

> "Infants suffering from methemoglobinemia may seem healthy but show intermittent signs of blueness around the mouth, hands, and feet. They may have episodes of breathing trouble, some diarrhea and vomiting. In some cases, an infant with methemoglobinemia has a peculiar lavender color but shows little distress. Blood samples appear chocolate brown and don't turn pink when exposed to air. When the methemoglobin level is high, infants express a marked lethargy, excessive salivation, and loss of consciousness. Convulsions and death can occur at extreme methemoglobin levels." (Skipton and Hay, 1998)

While high nitrate levels in drinking water have been found to cause methemoglobinemia, other factors have been identified which increase the risk for infants and other susceptible portions of the adult population. Infants have a low concentration (about 60% of the adult concentration) of the enzymes responsible for converting MetHb back to Hb, as do some older individuals with an enzyme deficiency (Skipton and Hay, 1998). As a result, the conversion back to Hb may proceed slower than in a healthy adult, allowing for the accumulation of MetHb. In addition, fetal hemoglobin may be more readily oxidized to methemoglobin than adult hemoglobin. Stomach pH and gastrointestinal disturbances seems to be key factors as well. Normal infant stomach pH is less acidic than in healthy adults, allowing bacterial growth to establish itself in the stomach and upper intestine when gastrointestinal disturbances give enteric bacteria the opportunity to move higher in the gastrointestinal tract. Shuval and Gruener (1977) reported that when nitrate-reducing bacteria are not present in the stomach or upper intestine, most of the nitrate is probably absorbed in its original nitrate form before being converted to nitrite in the colon where most of the nitrate-reducing bacteria are found. Furthermore, fluid intake and individual nutrition may contribute to one's risk. Infants with average fluid intakes ingest more nitrate per gram of Hb than their adult counterparts. Foods such as spinach and rhubarb have been found to accumulate large amounts of nitrates; however, some nutrients like vitamin C can cure or prevent methemoglobinemia (Shuval and Gruener, 1977). The National Academy of Sciences (1972) has reported that infant poisonings associated with water have arisen from water used in the preparation of milk formulas. In some cases, the nitrate was presumably further concentrated by boiling.

2.1.2 Nitrosamines

Nitrates and nitrites in food and water, together with secondary and tertiary amines, are considered possible precursors of nitrosamines which have potential carcinogenic, teratogenic, and mutagenic properties (Dahab and Kalagiri, 1996; National Academy of Sciences, 1972; Shuval and Gruener, 1977). Mirvish (1991) reported that, in tests conducted upon rodents, nitrosamines induced tumors of the liver, kidney, esophagus, oral and nasal cavities, lungs, trachea, urinary bladder, pancreas, and thyroid. In addition, nitrosamides induced tumors of the stomach, intestine, brain, nervous system, bone and skin, acute leukemia, and T and B cell lymphoma. There is no other group of carcinogens that can produce such a wide variety of tumors (Mirvish, 1991). Greenblatt et al. (1971) reported just as many tumors resulting from the simultaneous feeding of nitrite and secondary amines as from the feeding of preformed nitrosamine. Shuval and Gruener (1977) note the possibility that similar simultaneous ingestions in the human diet, through food or water, may present a human hazard. Although n-nitrosamine compounds have been shown to cause cancer in test animals, the USEPA has not classified the carcinogenicity of nitrate and nitrite, because of insufficient long-term (e.g., 20 to 30 years) case studies (Dahab and Kalagiri, 1996; Dahab and Sirigina, 1994; Self and Waskom, 1992).

2.1.3 Additional Health Concerns

Less conclusive evidence exists relating nitrate and nitrite in drinking water to other health complications. Spalding and Exner (1993) report that a number of correlation studies have been conducted that provide only weak evidence of an association between

ingesting nitrate in drinking water and hypertension, increased infant mortality, central nervous system birth defects, certain cancers, and non-Hodgkin's lymphoma. A lifetime exposure to nitrates and nitrites above the MCL has the potential to cause diuresis, increased starch deposits, and hemorrhaging of the spleen according to the USEPA (1998). Skipton and Hay (1998) and Lamarre (1998) indicate that nitrate may be linked to miscarriages, and Shuval and Gruener (1977) report changes in heart blood vessels and behavioral effects in laboratory animals.

2.2 Nitrate Contamination of Ground Water

In 1990, the USEPA found, in the National Pesticide Survey (NPS), that approximately 11% of the 566 community drinking water supply wells tested in agricultural areas of the United States contained between 3 and 10 mg/L NO_3-N; 1.2% of the wells tested exceeded the 10 mg/L NO_3-N maximum contaminant level (MCL). Approximately 57% of the private wells tested contained detectable levels of nitrates, with 2.4% exceeding the MCL. This, according to the USEPA, indicates that up to 1,130 public and approximately 250,000 private domestic water supply wells may have been exceeding the MCL for nitrate in 1990 (Briskin, 1991). Significant evidence has been presented to indicate that nitrate ground water concentrations have been and are continuing to increase in agricultural portions of the world (Spalding and Exner, 1993). In 1992, the EPA estimated that 4.5 million people in the U.S., including 66,000 at-risk infants, used drinking water from either community supplies or domestic wells that exceeded the federal nitrate limit.

2.2.1 Sources of Contamination

A low background concentration of nitrate exists in most natural waters. Though nitrogen is the most abundant element in the Earth's atmosphere, the nitrate concentrations in natural surface waters are typically below 5 mg/L NO_3-N. Higher concentrations are often observed in ground water, because of a lack of dilution from surface runoff and because plant uptake and organic carbon for denitrification are minimal (Gregory and Sheiham, 1981; Fraser et al., 1980). Increases above the natural background nitrate concentration are most often attributed to agricultural practices and improper disposal of human and animal waste.

The application of nitrogen fertilizers, including manure, in excess of plant requirements to crops and fields is a significant source of nitrate contamination of ground water. Bacteria in the soil oxidize ammonium to nitrate, and because nitrate is both very soluble and negatively charged, it is quite mobile, moving at approximately the same rate as water. Once it reaches ground water, the nitrate ion is very stable and, since it does not volatilize, nitrate is likely to remain in water until it is consumed by plants or other organisms. As a result, steadily increasing nitrate concentrations are being experienced in many rural ground water sources (Cook et al., 1997; USEPA, 1998).

After the application of fertilizers, the most prevalent source of nitrate contamination is probably organic nitrogen from animal feed lots, septic systems, and municipal waste treatment discharge. Wild (1997) indicated that urban sewage effluents can contribute up to 40% of the nitrates present in surface water. There is an increasing trend toward the

reuse of sewage effluents. In semiarid areas with limited ground and surface water, such as Israel, this is an important source of water. In Israel, shallow ground water contamination by nitrates was attributed to applications of fertilizer and sewage effluent (Ronen and Magaritz, 1985; Spalding and Exner, 1993).

2.2.2 National Distribution of Nitrate Contamination

The first comprehensive, nation-wide evaluation of the areal distribution of nitrate in ground water was completed by Madison and Brunett (1985). Their study drew from data in the U.S. Geological Survey's Water Storage and Retrieval System (WATSTORE), representing a 25 year record of nitrate analyses in more than 87,000 wells. The map (Figure 1) resulting from this study indicates that the distribution of ground water nitrate is nonuniform, with greatest concentrations found in the central and western regions of the United States.

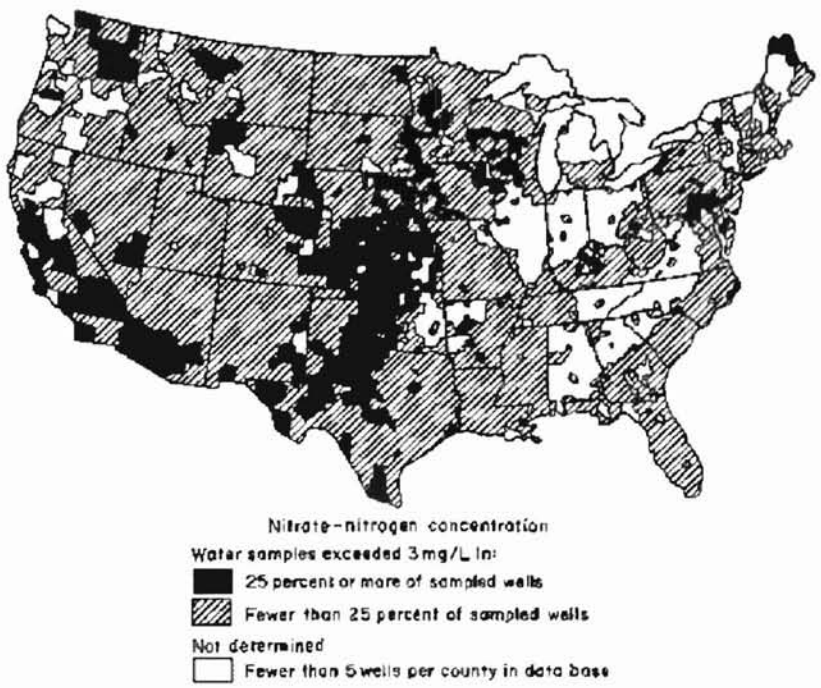

Figure 1: Areal distribution of NO_3-N concentrations in ground water in the continguous USA (Madison and Brunett, 1985)

Nolan et al. (1997; 1998) later confirmed this skewed distribution in their assessment of nitrate risk patterns in shallow ground water (less than 100 feet deep). Their study identified four levels of nitrate contamination risk, based upon nitrogen-input factors and aquifer-vulnerability factors (Table 2) but did not consider factors such as land use, aquifer type, and rainfall and irrigation amounts (Nolan et al., 1998). The resulting map of nitrate contamination potential is presented in Figure 2. This map has been verified by both historical nitrate data (Nolan et al., 1997), and by data from more than 1,400 wells sampled through the National Water-Quality Assessment (NAWQA) Program during 1993-1995 (Nolan et al., 1998).

Magnitude of Risk	Nitrogen-Input Factors	Aquifer-Vulnerability Factors
High (red areas on map)	High nitrogen loading (a) or high population density (b)	Well-drained soil and low woodland-to-cropland ratio
Moderately High (orange areas)	High nitrogen loading (a) or high population density (b)	Poorly drained soil or high woodland-to-cropland ratio
Moderately Low (yellow areas)	Low nitrogen loading (a) and low population density (b)	Well-drained soil and low woodland-to-cropland ratio
Low (green areas)	Low nitrogen loading (a) and low population density (b)	Poorly drained soil or high woodland-to-cropland ratio

(a) Nitrogen loading refers to nitrogen inputs from inorganic fertilizer, animal manure, and atmospheric deposition.
(b) Population density is used to indicate additional nonagricultural sources of nitrogen such as residential fertilizers, septic systems, and domestic animals.

Table 2: Four levels of nitrate contamination risk (Nolan et al., 1998; USGS)

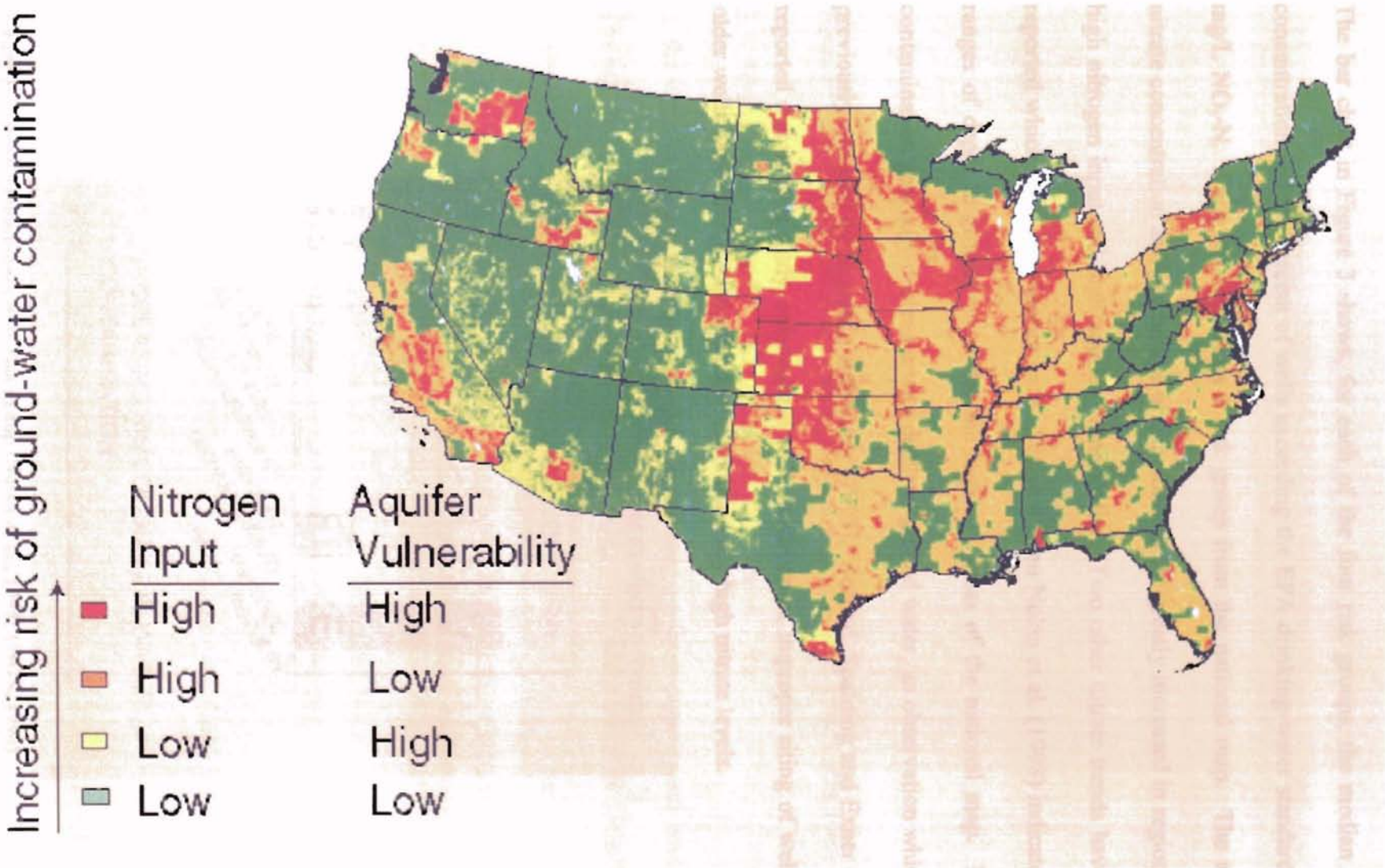

Figure 2: National map of ground water nitrate contamination potential (Nolan et al., 1998; USGS, 1998)

The bar chart in Figure 3 shows, for each of the four risk groups, the median nitrate concentration and the percent of wells exceeding the EPA drinking-water standard of 10 mg/L NO_3-N. Each bar represents a risk group from the national map. The median nitrate concentration and percentage of exceedances are greatly increased in regions with high nitrogen input and high aquifer vulnerability. Two other nitrate trends have been reported which merit mentioning here. Figure 4 from Nolan et al. (1998) indicates four ranges of depth to ground water for the high-risk areas of the national map. Nitrate contamination generally decreases with depth to ground water, an observation which was previously reported by Spalding and Exner (1993). Second, Spalding and Exner (1993) reported that in their study, substandard well construction, improper siting of wells, and older wells were strongly associated with anomalously high nitrate levels.

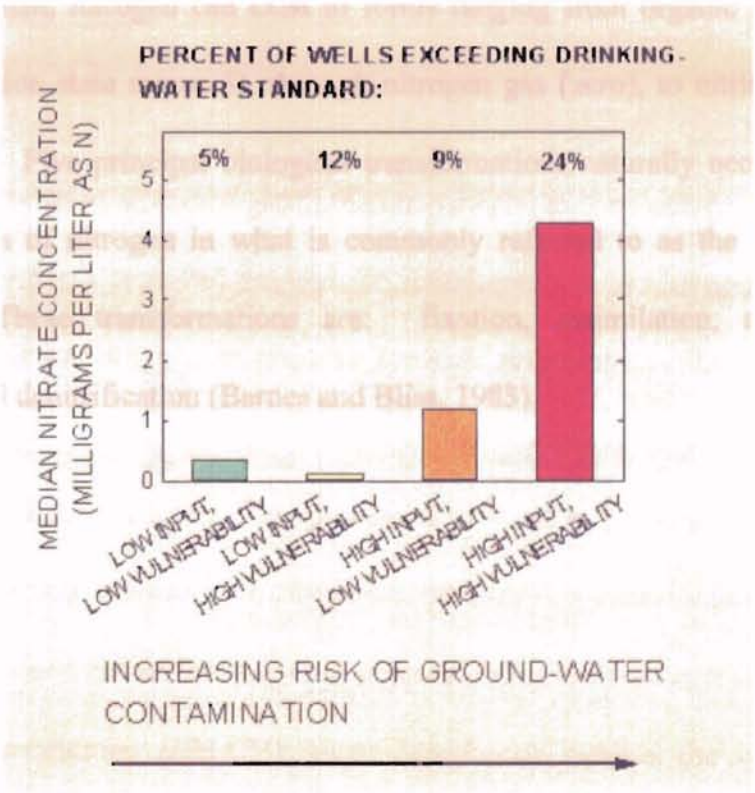

Figure 3: Nitrate contamination by risk group (Nolan et al., 1998; USGS, 1998)

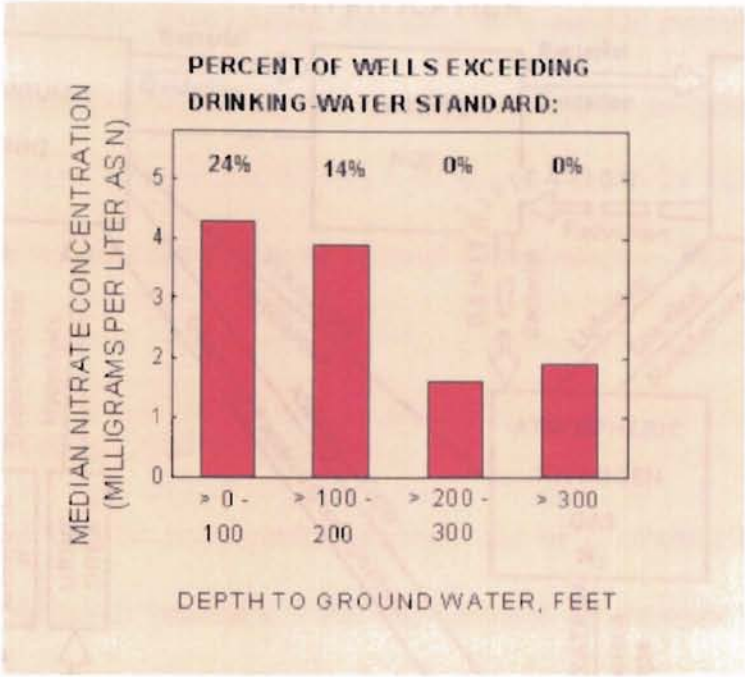

Figure 4: Nitrate contamination by depth to ground water (Nolan et al., 1998; USGS, 1998)

2.3 NITROGEN CYCLE

In the environment, nitrogen can exist in forms ranging from organic and ammonium nitrogen (oxidation state minus 3), through nitrogen gas (zero), to nitrite (plus 3), and nitrate (plus 5). Five principal biological transformations naturally occur between and link these forms of nitrogen in what is commonly referred to as the Nitrogen Cycle (Figure 5). These transformations are: fixation, assimilation, ammonification, nitrification, and denitrification (Barnes and Bliss, 1983).

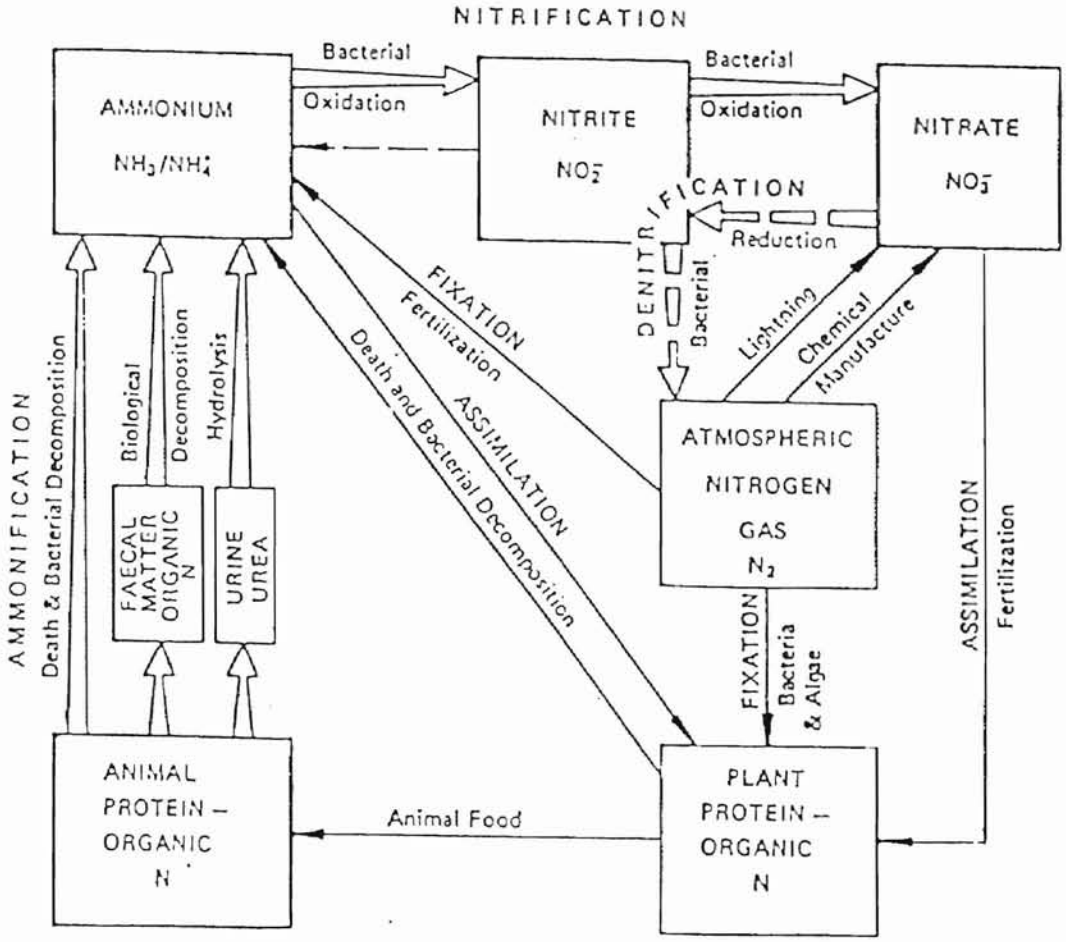

Figure 5: The nitrogen cycle with references to nitrogen control in wastewater treatment (Barnes and Bliss, 1983)

Nitrogen gas is the most abundant gas in the atmosphere, and as such provides a reservoir from which nitrogen is removed through the transformation of nitrogen fixation. Cells convert nitrate or ammonium to proteins through assimilation. Organic nitrogen is transformed to ammonia during the biological decomposition of dead plant or animal tissues and animal fecal matter. This process is referred to as ammonification. In the presence of molecular oxygen, two categories of nitrifying-bacteria are responsible for oxidizing ammonia to nitrate in a two-step process. *Nitrosomonas* oxidize ammonium to nitrite via hydroxylamine (NH_2OH); then, *Nitrobacter* oxidize the nitrite to nitrate (Bitton, 1994). Energy released during this nitrification transformation is used in

synthesizing cell material from carbon dioxide. In a similar manner, in an anoxic environment, many heterotrophic as well as some autotrophic bacteria are capable of transforming nitrate to nitrogen gas through a multi-step process by using nitrate as the terminal electron acceptor along with an external carbon source. This is referred to as denitrification.

2.4 Heterotrophic Denitrification

Nitrogen removal may be accomplished through one or a combination of physical, chemical, and biological processes. For the removal of nitrogen from municipal wastewater, by far the most common approach to treatment has been biological. In recent years, efforts have been made in the United States and abroad to take the biological denitrification processes used in the treatment of wastewater and adapt them to the treatment of drinking water as suitable alternatives to the expensive chemical/physical processes currently employed. The majority of this research has been conducted at the bench and pilot plant scales. Through these studies, a selection of reactor types and configurations have been proposed.

Biological denitrification processes are divided into two categories, heterotrophic and autotrophic, based upon the type of bacteria facilitating the reduction of nitrate to nitrogen gas. A suitable carbon and energy source must be available for biological denitrification to take place. Heterotrophic bacteria require an organic carbon source, which may also serve as the source of energy to fuel the reaction. Since drinking water sources, and ground waters in particular, are inherently low in organic carbon content, an

external carbon source may need to be provided. Autotrophic bacteria, on the other hand, are capable of assimilating inorganic carbon such as carbon dioxide and bicarbonate, while satisfying their energy requirement through the oxidation of molecular hydrogen or reduced sulfur species (Kruithof et al., 1988; Rutten and Schnoor, 1992). Biological denitrification occurs in a two step process. The organisms first reduce nitrates to nitrites, and then produce nitric oxide, nitrous oxide, and nitrogen gas (Dahab and Srinivas, 1993; Kurt et al., 1987). The pathway for nitrate reduction is:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

The last three compounds are gaseous products that can be released to the atmosphere. The microorganisms responsible for biological denitrification are facultative aerobes, meaning that they are capable of using nitrate and nitrite as terminal electron acceptors in the absence of molecular oxygen. Facultative bacteria will use available electron acceptors preferentially, based upon the which one will release the greater amount of free energy. In the case of facultative aerobe populations, preference will first be given to oxygen, followed by nitrate, iron III or manganese IV, sulfate, and finally carbon dioxide. Because the reduction of molecular oxygen releases a greater amount of free energy than the reduction of nitrates, the denitrification process must be carried out in an anoxic environment. According to Bitton (1994), denitrification may occur between 5 and 50°C with reactions slowing at the lower temperatures. Denitrification is most effective at a pH between 7.0 and 8.5, with the optimum being around 7.0. To avoid the performance variability associated with extreme variations in raw water characteristics,

biological denitrification in drinking water studies has been limited to treatment of ground waters.

Many genera of heterotrophic bacteria are known to denitrify, including: *Pseudomonas*, *Achromobacter*, *Alcaligenes*, *Bacillus*, *Hyphomicrobium*, *Chromobacterium*, *Halobacterium*, *Moraxella*, *Micrococcus*, *Neisseria*, *Paracoccus*, *Azospirillum*, *Rhodopseudomonas*, *Proteus*, *Thiobacillus*, *Vibrio*, *Xanthomonas*, and *Klebsiella* (Rittmann and Langeland, 1985). These bacteria use an organic carbon source to fulfill their requirements for both energy and carbon for cell synthesis. In traditional wastewater applications, it has been possible to take advantage of the organic material already existing in the water as a readily available carbon and energy source. Adaptation to the treatment of drinking water requires that an external carbon source be added to the water, since organic carbon concentrations in drinking water sources are typically too low to support significant denitrification. Sugar, corn syrup, acetic acid, propionic acid, ethanol, acetone, and methanol have all been studied as potential low-cost carbon and energy substrates for denitrification (Boehler and Haldenwang, 1992; Lamarre, 1998; St. Amant and McCarty, 1969). Of these, methanol has been the most commonly-used substrate for economical and operational (low solids production) reasons (Dahab and Lee, 1988). Although methanol is a known human poison, it is felt safe for use at the low concentrations required (St. Amant and McCarty, 1969).

When methanol is used as the carbon source, the energy and synthesis reactions can be represented as follows (Metcalf and Eddy, 1991):

Energy Reaction, Step 1: Nitrate to Nitrite

$$6NO_3^- + 2CH_3OH \rightarrow 6NO_2^- + 2CO_2 + 4H_2O$$

Energy Reaction, Step 2: Nitrite to Nitrogen Gas

$$6NO_2^- 3CH_3OH \rightarrow 3N_2 + 3CO_2 + 3H_2O + 6OH^-$$

Overall Energy Reaction:

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-$$

As represented by the production of hydroxide in the overall energy reaction above, one overall effect of denitrification is an increase in alkalinity and pH.

Metcalf and Eddy (1991) also reported the following equations developed by McCarty et al. (1969). In practice, 25-30% of the methanol utilized is required for bacterial cell synthesis (Metcalf and Eddy, 1991). Therefore, laboratory studies were used to develop an overall equation to describe the removal of nitrate.

Typical Bacterial Synthesis Reaction:

$$3NO_3^- + 14CH_3OH + CO_2 + 3H^+ \rightarrow 3C_5H_7O_2N + H_2O$$

Overall Nitrate-Removal Reaction (Empirical Equation):

$$NO_3^- + 1.08CH_3OH + H^+ \rightarrow$$

$$0.065C_5H_7O_2N + 0.47N_2 + 0.76CO_2 + 2.44H_2O$$

If all nitrogen to be removed is in the form of nitrate, and there is an absence of dissolved oxygen (as is frequently the case for ground water) the above empirical equation may be used to determine the overall methanol requirement. In some cases, non-negligible amounts of nitrite or dissolved oxygen may be present in the reactor influent, and the

carbon/energy source requirement will be correspondingly increased. Nitrite will elevate the methanol requirement according to the step two reaction above. The substrate demands for oxygen, which must be removed before denitrification will occur, can be estimated stoichiometrically from the following equation (St. Amant and McCarty, 1969):

Oxygen Demand Reaction:

$$3O_2 + 2CH_3OH \rightarrow 2CO_2 + 4H_2O$$

Combining these reactions, St. Amant and McCarty (1969) have proposed the following empirically derived equation for calculation of the total methanol requirement where nitrate, nitrite, and dissolved oxygen are present.

Overall Methanol Requirement:

$$C_m = 2.47N_0 + 1.53N_1 + 0.87D_0$$

where: C_m = required methanol concentration, mg/L

N_0 = initial nitrate-nitrogen concentration, mg/L

N_1 = initial nitrite-nitrogen concentration, mg/L

D_0 = initial dissolved-oxygen concentration, mg/L

Similar energy and empirical equations can be developed for each of the many carbon sources proposed for use in biological denitrification. When a simple carbon source such as methanol or acetic acid is chosen, the biological solids production by the system is small, a useful characteristic in that the overall sludge production is minimized (USEPA, 1975). "While different types of organic compounds may affect biomass yield

differently, the choice of a compound is generally based on economic comparison." (Dahab and Lee, 1988)

In addition to whether a biological denitrification reactor utilizes heterotrophic or autotrophic bacteria to accomplish nitrate removal, biofilters may also be classified by the way they retain biomass within the filter and bring it into contact with the water to be treated. Reactors may be of either the attached growth or suspended growth type. In 1994, Green et al. reported on ground water denitrification using an upflow sludge blanket (USB) reactor. Suspended growth systems retain biomass by sludge aggregation. Once flocs form, they then remain suspended in a sludge blanket where contact with the upward flowing treatment water occurs. Green et al. (1994) found that this type of reactor was strongly affected by the hardness of the water as a result of the mineral content of the flocculated sludge granules. In their study, water containing between 150 and 380 mg/L (average of 244 mg/L) of hardness (as $CaCO_3$) resulted in the formation of large granules with low mineral content (10-15% of TSS) and poor settling characteristics. Consequently, floating sludge and biomass washout occurred. High sludge blanket biomass concentrations of 30-40 g/(L sludge blanket) were maintained when a water with a hardness of 380-450 mg/L as $CaCO_3$ was used. This sludge had a mineral content of about 25% with very low sludge volume index (SVI) values of 15-30. Under these latter conditions the USB reactor exhibited stable operation at volumetric loading rates up to 4 kg N/m^3*day, corresponding to a retention time of 8 min (Green et al., 1994).

In an attached growth reactor, a support medium is supplied for the biomass to accumulate upon, forming a biofilm which the water then passes over. Attached growth biofilter systems are generally used to minimize the potential washout problems associated with continuous solids separation. Instead of continuous solids separation, a periodic air scour is used to breakup solids during a backwashing and solids wasting cycle (Cook et al., 1997). Anoxic biofilters tend to be operated in an upflow mode to aid in the release of nitrogen gas produced. In the published studies, the use of heterotrophic denitrification processes far exceeds the use of autotrophic processes. These processes generally employ a fixed film reactor followed by a filtration step to remove the biomass that has sloughed from the reactor.

In 1988, Dahab and Lee operated a static-bed upflow reactor for 10 months with a feed concentration of 100 mg/L NO_3-N. Their two-fold objective was to examine nitrate removal characteristics exhibited by static-bed reactors packed with two different types of commercially available media, one made of 25 mm spherical modules and the other of 16 mm cylindrical Pall rings. Second, the team sought to determine basic kinetic coefficients and develop a simplified kinetic model to describe the fundamentals of biological denitrification of drinking water. Laboratory reactors were constructed of Plexiglas tubes, 125 mm inner diameter by 1.20 m tall, packed with the different synthetic medium. The carbon to nitrogen ratio (C:N expressed as grams of carbon to grams of nitrogen) and hydraulic retention time were used as the principal variables throughout the study. Using acetic acid as the supplied carbon source, it was determined that an optimum C:N ratio was between 1.45-1.5:1. A C:N ratio of 1.45:1 resulted in

low soluble and suspended solids in the effluent, but such attempts to reduce the C:N ratio below 1.5:1 resulted in breakthroughs of nitrate into the reactor effluent. The background turbidity (turbidity of filtered samples) was used as a measure of colloidal matter in the reactor effluent. Turbidity levels were fairly high, indicating that additional treatment would be required to remove the colloidal material. It was noted however, that background turbidity continued to improve as the reactors aged (Dahab and Lee, 1988).

In a similar study, which lead to the development of the process installed in Coyle, Oklahoma, Cook, Silverstein, and Hogrewe (1997) operated and determined the kinetics of an upflow packed tower reactor developed at the University of Colorado, Boulder. This biofilm process featured the introduction of "intermittent fluidization of the buoyant high-porosity column packing media with air flow to minimize reactor clogging and associated deterioration in denitrification performance and to minimize discharge of suspended biofilm matter into the denitrified product water." (Cook et al., 1997) This "air scour" procedure, implemented every 21 days, was thought to be more easily achieved than operation of a continuously fluidized bed. In this study, two Plexiglas reactors (15.2 cm in diameter by 2.6 m tall) were operated in series. Each reactor was packed to a depth of 2.1 m with a buoyant polypropylene media (Jaeger Tri-Pak, #1, Polymer Piping and Materials, Houston, TX). The reactor influent was City of Boulder tap water augmented with nitrate, phosphate, sodium bicarbonate, and acetic acid. Flow rates averaged 1.14 liters per minute, resulting in an empty-bed detention time of 83 minutes. To facilitate the denitrification reaction, dissolved oxygen was stripped from the influent water before chemical addition by contact with nitrogen gas flowing at a rate

of 200 ml/min through a 5.1 cm diameter by 2.6 m tall Plexiglas tube. During two two-month periods of operation, the influent nitrate nitrogen was reduced from an average of 20 mg/L NO_3-N to an average of 2.9 mg/L NO_x-N by supplying acetic acid at a C:N ratio of 1.5:1. "First-order, zero-order, and half-order kinetic models of packed tower denitrification were evaluated, and it was found that the half-order model best fit the steady-state nitrate profiles, with a reaction constant of 0.0331 $(mg\text{-}NO_3\text{-}N/L)^{0.5}/min$." (Cook et al., 1997) In response to an influent pulse of 40 mg/l NO_3-N lasting 5 hours, nitrate reduction did not deviate from the 18 mg/L NO_3-N experienced under normal operation. This inability of the biofilm to respond to an instantaneous increase in influent nitrate is better explained by a zero-order model (Cook et al., 1997).

This process was later up-scaled to a yearlong demonstration project, conducted in Wiggins, Colorado, a small farming town (population 650) located 75 miles northeast of Denver (Lamarre, 1998). The process was scaled to two 3-ft diameter reactor columns each standing 10 ft tall and packed with highly porous polypropylene media. Researchers opted to provide food-grade corn syrup as the required carbon source because it is 40% carbon by weight, already approved for human consumption, has a low water content (minimizing the possibility of contamination by other bacteria), and is typically less expensive than vinegars with high levels of acetic acid (Lamarre, 1998). Researchers suggested that although corn syrup possesses the property of crystallization at low temperatures, it should not pose a problem as this can be overcome by the use of inexpensive heaters during cold periods. This demonstration plant which used sand filtration to remove residual bacteria and fine particles showed that it was capable of

consistently removing more than 85% of the incoming nitrate which had been augmented to 20 mg/L for testing purposes. "Data from the Wiggins demonstration enabled the town of Coyle, Oklahoma, to win state approval for the first commercial application of the technology." (Lamarre, 1998)

Although the full-scale installation at Coyle, Oklahoma is the first in the United States, similar processes have long been operated in Europe. Richard and Thébault (1992) reported on seven years of operation and progress with biological denitrification in full-scale municipal water treatment plants using the Nitrazur process in Europe. "The biological removal of nitrates first became operational in 1981, at the Château-Landon plant in France. From the setting up and operation of this first-generation plant, a number of design improvements emerged, resulting in second-generation plants such as those operating at Issoudun, in France, and at Hanau, in Germany. Considerable cost reductions, mainly in manpower expenditure, have been obtained by optimization of operating procedures." (Richard and Thébault, 1992) Figure 6 shows the general layout of the Nitrazur process at the first-generation Château-Landon plant in France which includes as its major stages:

- Nitazur D reactor – an up-flow bed reactor filled with Biolite L (grain size originally 1.7 mm but increased to 2.7 mm for improved biomass distribution) to a depth of 3 m. The reactor surface is 6.5 m^2 giving a nominal operating rate of 8 m/hr. Raw water, ethanol (carbon substrate), and phosphoric acid are introduced into the reactor through a manifold located near the reactor bottom. The reactor is reported to be capable of

denitrifying raw water with nitrate contents up to 150 mg/L (34 mg/L as nitrogen).

- Cascade aeration – used to oxygenate the water before filtration. Coagulants such as ferric chloride may be added at this point to improve filter operation.

- Filtration through granular activated carbon (GAC) – 6.5 m^2 by 1.2 m deep (empty bed contact time 9 minutes) used to trap residual floc from reactor, breakdown biodegradable organics (excess ethanol in particular), and return any nitrites present to their nitrate form as well as nitrify any ammonia which might be present.

- Filtered water tank – includes both 30 m^3 of unchlorinated storage for reactor wash water and 100 m^3 of chlorinated water storage providing sufficient disinfectant contact time.

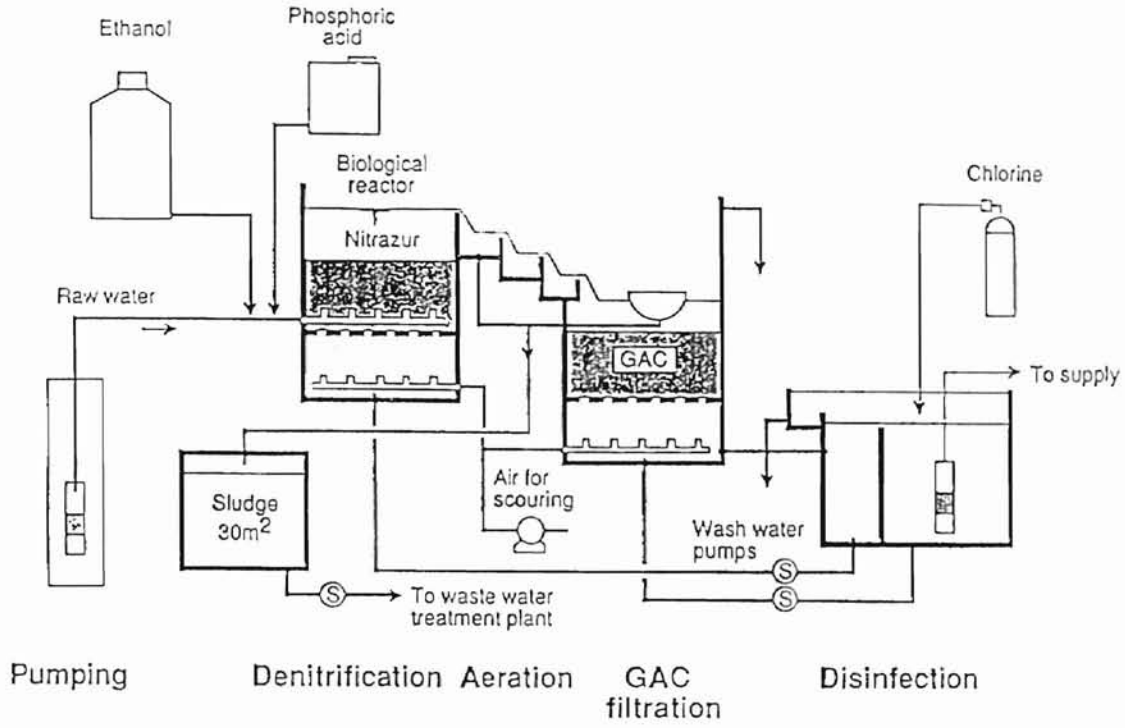

Figure 6: General lay-out of the Nitrazur process (Richard and Thébault, 1992)

Operation and maintenance of the system requires a reactor wash consisting of an air scour, followed by draining of the waste wash water to municipal waste, and then a rinse with treated but not chlorinated water. The system produces about 18 grams of sludge per 100 grams of nitrate removed. Problems encountered at the Château-Landon plant included nitrite formation and water loss.

Richard and Thébault (1992) reported that nitrite output, rather than nitrate content, became the more important operational parameter at the Chateau-Landon plant for the following reasons:

- The raw water nitrate content was relatively stable over time.

- The reduction in nitrate content was roughly proportional to the amount of carbon substrate (ethanol) applied.

- The plant was geared to produce water with a nitrate content less than half of the 50 mg/L (11.3 mg/L as nitrogen) allowable, providing a large margin of safety.

It was reported that residual nitrites were generally removed in the subsequent cascade aeration, activated carbon filtering, and chlorination stages, provided that nitrifying bacteria such as *Nitrobacter* , which colonize the activated carbon filter, are given time to adapt to the variation in nitrite content. Experience has shown that the appearance of nitrite is preceded by a decrease in the level of nitrate reduction for a given amount of injected alcohol as illustrated in Figure 7 by the region marked by arrows.

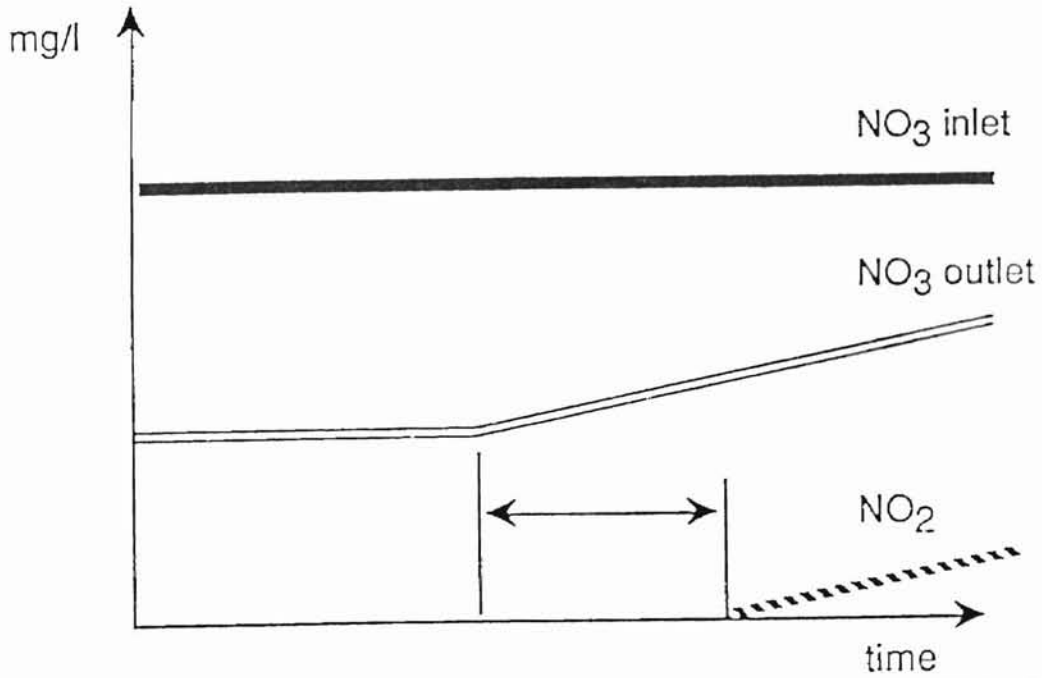

Figure 7: Reduction in nitrate removal prior to the release of intermediate nitrite (Richard and Thébault, 1992)

At the Chateau-Landon plant, the following changes were implemented to counter the nitrite problem:

- In April 1985, the use of acetic acid as carbon substrate was replaced by ethanol. In addition to less frequent and lower concentration nitrite occurrences in the reactor effluent (see Figure 8), the plant also experienced the benefit of a reduced operating cost and fewer problems with corrosion of substrate handling lines.

- In May 1985, the plant was equipped with an in-line nitrite meter which measures nitrite levels following the filtration and chlorination steps. Pumping is automatically halted, and duty staff alerted if nitrites ever exceed 1 mg/L (0.3 mg/L as nitrogen).

- The effective size of the Biolite filter media was increased from 1.7 mm to 2.7 mm to provide a more even distribution of biomass over the entire reactor depth. This change remained consistent with the need for efficient washing to remove old biomass and thus avoid the appearance of nitrites.

- A system was established to improve circulation throughout the reactor to prevent the accumulation of reagents at the bottom of the reactor during the operating cycle.

Richard and Thébault (1992) report that during their experiences with biological denitrification facilities, water loss occurred in two primary ways: as a result of reactor and filter washes, and by poor matching of water production to demand. They report that up to 20% of the total volume treated at the Chateau-Landon plant was lost through the overflow outlet due to insufficient tank capacity, especially in winter. In contrast, the plant at Issoudun was reported to have sufficient holding capacity. With efficient

management of water reserves, overflow losses were eliminated, and so losses of only 5% (yearly average) of the total volume pumped could be wholly attributed to washing operations.

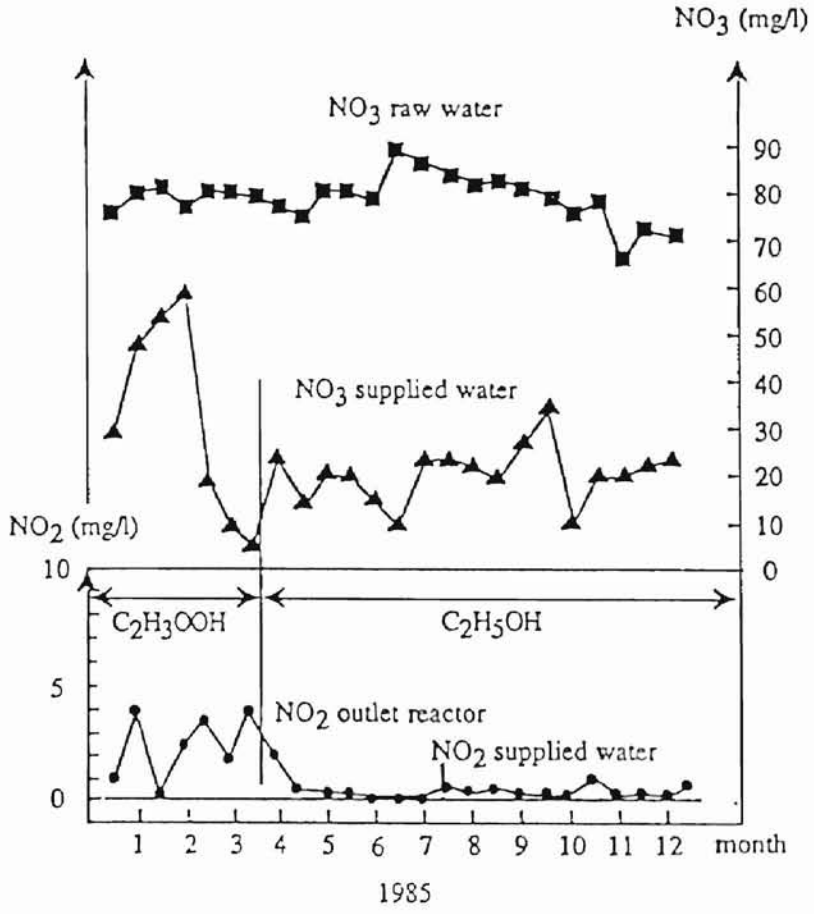

Figure 8: Replacement of acetic acid by ethanol (Richard and Thébault, 1992)

Investigation of start-up and operation of a fixed-bed denitrification reactor using ethanol as carbon substrate for biomass attached to various light to heavy carrier materials was conducted by Kappelhof et al. (1992). Start-up of the up-flow reactors was conducted with and without inoculation. The start-up procedure consisted of recirculation of a nutrient enriched medium (1000 mg/L NO_3^-, 400 mg/L ethanol, and 4 mg/L PO_4^{3-}) with renewal of the medium upon nitrate depletion. This initial recirculation phase was

followed by a step-wise increase in the superficial velocity each time the nitrate in the reactor effluent was reduced to less than 10 mg/L. This step-wise increase continued until the desired nitrate removal capacity was reached after 75 days, giving a total start-up time of 94 days. Start-up with inoculation was carried out in much the same way except that the reactor was inoculated with a biological denitrification reactor effluent that was augmented by the same nutrient enrichment used in the previous start-up. This medium was recirculated only until the nitrate concentration fell below 50 mg/L (achieved within two days) and then the step-wise increase of the superficial velocity began. With inoculation, the total start-up period was shortened to about 20 days. To avoid short-circuiting and maintain reactor performance, a reactor rinse was necessary. During the superficial velocity increase phase of start-up a rinse cycle, consisting of air flow at 50 m/h for 5 min followed by a water rinse until the effluent turbidity dropped below 4 NTU, was implemented each time nitrate concentrations increased due to nitrogen gas accumulation.

Kappelhof et al. (1992) presented their experiences with the necessity, effectivity, and control of rinsing procedures to maintain reactor biomass constant during normal operation. Sufficient rinsing is necessary to prevent biomass and nitrogen gas accumulation which may cause short-circuiting and poor effluent quality; however, overly-intensive rinsing must be avoided so that biomass concentrations remain high enough to provide the desired nitrogen removal capacity. The effectivity of the rinse depends upon the rinsing procedure used (separate air/water rinsing or combined

air/water rinsing followed by rinsing with water), velocities of air and water, duration of rinse, and the rinsing frequency.

Kappelhof et al. (1992) present the following five parameters which may be used to determine when the reactor rinses should occur:

- Increasing nitrate concentrations in the reactor effluent as a result of channeling;

- Increasing biomass concentration on the carrier material as indicated by the bed height (not a useful parameter at short-term as it may take weeks for the effects of biomass accumulation to be seen);

- Increasing headloss in the reactor due to production and accumulation of biomass and entrapment of nitrogen gas within the filter (only a reliable parameter for starting a rinsing procedure when headloss has not reached its maximum for the specific weight, grain size, and bed height of the carrier material, and when it continues to rise continuously between rinses);

- Increasing turbidity in the reactor effluent as a result of biomass wash-out; or

- Decreasing ratio of active biomass concentration (although the active biomass concentration may be estimated by ATP (Adenosine-Tri-Phosphate) measurement, the application of this parameter is still under development).

Three carrier materials were investigated by Kappelhof et al. (1992). A brief summary of their experiences with expanded schist (Filtraperl), anthracite, and sand is presented as

Table 3. In spite of a relatively high rinse water demand, sand was chosen as the preferred carrier material. All three carrier materials were capable of achieving good biomass attachment and nitrogen removal capacity; however, sand proved to be the least abrasive at the high rinse velocities required for effective biomass removal. At lower rinse velocities, the lighter expanded schist and anthracite experienced problems with the carrier material floating due to nitrogen gas accumulation in the excessive flocculent biomass which was not sufficiently removed. An additional benefit to the use of the heavier sand as carrier material is that it is more likely to lend itself to reactor control by headloss as described above.

Material	Exp. Schist	Anthracite	Sand
Grain Size	2.5-4.5	2.5-4.0	2.0-3.0
Max. Biomass Conc. (g/L)[a]	95	80	160
Removal Cap. (g/(m^3·h))	550	430	600
Removal of Biomass	hard	hard	hard
Complexity of Rinsing	complex	complex	simple
Process Stability	-	--	+
Quality of Material	not constant	good	good
Abbrasive	yes[c]	yes[c]	no
Rinsing-Water Demand (%)[b]	3	3	6

[a] maximum biomass concentration observed (in g biomass per liter carrier material)
[b] related to the treated water
[c] at high rinsing velocities

Table 3: Experiences with three types of carrier material in a fixed bed upflow denitrification reactor (Kappelhof et al., 1992)

In a more recent study (Dahab and Kalagriri, 1996), research was conducted on two-stage cyclically operated, fixed film bio-denitrification reactors in an effort to overcome the problem of residual carbon release. "In two-stage cyclic operation, two equally sized

reactors are operated in series. After a certain period of operation to maintain stability in the first (lead) reactor, the flow regime is reversed and the influent feed solution is transferred from the lead to the follow reactor. In the case of nitrate removal, the length of period between flow reversals is to be chosen on the basis of optimizing overall nitrate and residual organics removal in the combined system and once such removal begins to decline in the follow unit, then the flow reversal is effected. In this manner, the follow reactor is maintained in or near an endogenous respiration mode thus ensuring effective residual substrate removal in this unit. Thus, the two-stage cyclic operation would be capable of producing much lower organic concentrations than single-stage systems operating at the same organic loading." (Dahab and Kalagiri, 1996)

In the experiment conducted by Dahab and Kalagiri (1996), reactors were constructed of Plexiglas tubes standing 460 mm high with a 70 mm inner diameter. Dispersion rings were placed periodically throughout the length of the reactors to minimize the effects of short circuiting. Biomass was supported on 16 mm cylindrical Pall rings having a specific surface area of 0.44 mm^2/mm^3. Flow through the reactors was controlled by peristaltic tubing pumps delivering a solution intended to simulate a natural ground water with a nitrate concentration of 50 mg NO_3-N/L. Ethanol was added as the external carbon source. Throughout the experiment the reactors were monitored for nitrate, nitrite, COD, total suspended solids, pH, and turbidity. This experiment was operated in six phases with the hydraulic residence time (HRT) being set as the variable between phases. The two-phase cyclic reactor systems studied in phases one through six were operated at HRT values of 24 hr, 12 hr, 6 hr, 3 hr, 1 hr, and 30 min, respectively. Flow

through the two-stage reactor was such that the two units were operated in series with the lead unit receiving the full nitrate load and the follow unit receiving the effluent of the lead. Flow reversal occurred by changing the flow scheme so that the follow reactor took the lead position and vice versa, thus completing one full cycle (see Figure 9). During each phase of the experiment a single stage reactor was operated under identical flow rate and nitrogen loading conditions as the two-stage reactor and served as the experimental control.

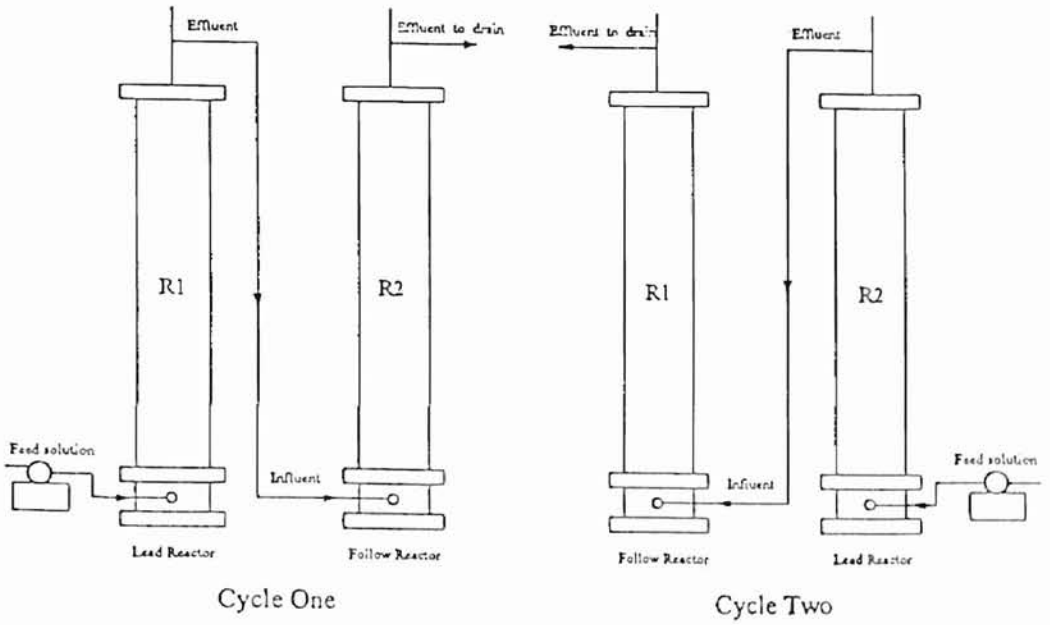

Figure 9: Schematic diagram of the two-stage cyclic reactor system (Dahab and Kalagiri, 1996)

Results of this study showed little variation in the nitrate removal efficiencies experienced by the one and two-stage denitrification reactors. Both configurations demonstrated the ability to sustain greater than 98% nitrate removal efficiencies at HRT values as low as 30 min. At HRT values of 3 hrs or less, intermediate nitrite began to appear as a result of the shortened contact times. The advantage of the two-stage reactor was demonstrated in its improved ability over the single stage reactor operating at the

same HRT and nitrate and COD loading rates to eliminate residual carbon and intermediate nitrite release in the final effluent, particularly at lower HRT values. This increased NO_2^- and COD removal efficiency comes from the exposure of the lead unit effluent to the high concentrations of biomass acquired in the follow unit as a result of its previous operation as the lead unit.

The two-stage reactor exhibited the ability to effectively deal with the shock loads experienced as a result of flow reversal. Dahab and Kalagiri (1996) noted that the lead reactor initially lost a portion of its nitrate removal capacity following flow reversal. Nitrate removal capacity nearly recovered after one week of operation with steady-state performance of the lead reactor typically regained after two to three weeks. Despite the reduction of lead reactor performance, overall two-stage performance remained nearly constant throughout the stage reversal process. The authors highlight the potential advantages of the two-stage process.

- The follow unit acts as a polishing unit to provide additional removal of nitrate, nitrite, and organic carbon breaking through the lead reactor.

- The follow unit serves as a "safety net" should the lead unit fail.

- The follow unit, having a high concentration of biomass capable of receiving extreme shock loads, serves as a stand-by unit which could easily be switched to the lead position at any time without any major anticipated loss of performance.

2.5 COMPETING TECHNOLOGIES

Although biological denitrification has been proven effective in the removal of nitrate and nitrite from drinking waters, as mentioned previously, concerns over the chemical and biological stability of the treated water have been raised. Until biological denitrification is able to address these issues and prove itself to be an economically viable alternative through operation of full-scale facilities such as the one installed in Coyle, Oklahoma, treatment of high nitrate drinking waters will continue to be dominated by the various physical and chemical processes currently in use. These processes include ion-exchange, reverse osmosis, and blending. Other methods are available to partially reduce nitrate concentrations such as distillation, electrodialysis (Kapoor and Viraraghavan, 1997), and to a very limited degree, chemical precipitation (Huang et al., 1998; Kapoor and Viraraghavan, 1997; Princz et al., 1987), but these methods have not yet been proven economical for use at full-scale (Dahab, 1987; Self and Waskom, 1992).

2.5.1 Ion Exchange

The process of ion exchange is frequently used for the removal of nitrates from water. In the ion exchange process, the contaminated water supply is passed through an ion exchange resin bed of porous granules or beads. During contact, nitrate ions in the water are exchanged for a similarly charged ion, such as chloride, according to the following reaction (Dahab, 1987).

$$R\text{-}Cl + NaNO_3 \rightarrow R\text{-}NO_3 + NaCl$$

"In the above reaction, 'R' represents the resin immobile (i.e., solid) phase. When the resin's exchange capacity is used up, the resin bed must be taken out of service and regenerated. Regeneration restores the bed's exchange capacity to its original state by reversing the reaction and thus forcing the nitrates out of the resin under the action of a concentrated (brine) solution." (Dahab, 1987) The regeneration reaction can be depicted as follows:

$$R\text{-}NO_3 + NaCl \rightarrow R\text{-}Cl + NaNO_3$$

After the bed has been regenerated and washed, it is ready to be returned to regular operation.

To date, nitrate removal by ion exchange has been limited by two basic problems, which have driven continued research into improving the ion-exchange process, as well as alternative treatment methods such as biological denitrification. The first problem is the need for an ion-exchange resin bed that shows a high selectivity for nitrate. Typically anion-exchange resins display the highest selectivity for sulfate, followed by nitrate, chloride, then bicarbonate (Kapoor and Viraraghavan, 1997). Sulfates are commonly found in ground waters at concentrations that are several times that of nitrate. In these cases, the nitrate removal capacity of the ion-exchange resin is reduced considerably by the sulfate ions which are preferentially exchanged. Some researchers, such as Jackson and Bolto (1990), have reported the development of nitrate selective resins. They report that the preference of an anion-exchange resin for nitrate over sulfate increases as the resin becomes more hydrophobic (less polar) and that nitrate-selective resins are more

difficult to regenerate with sodium chloride solutions than their sulfate-selective counterparts.

The second problem is disposal of the used regenerant. The regeneration process produces a waste that is very high in nitrate and chloride (in the case of chloride regeneration) and "although not considered hazardous, this waste stream typically represents about 3% of the original water input and can be costly to dispose of." (Lamarre, 1998) Regenerant waste disposal options currently available to ion-exchange facilities include discharge to local municipal waste treatment facilities, land application, and transport to other treatment works (Dahab, 1987, 1991).

2.5.2 Reverse Osmosis

Reverse osmosis is a process by which the water to be treated is forced across a semipermeable membrane by subjecting it to pressures exceeding its corresponding osmotic pressure. These pressures, which range from 300 psig (2,070 kPa) when treating brackish water to 1,500 psig (10,350 kPa) for desalinating seawater, have the effect of reversing the normal osmotic flow of water, leaving nitrates and other ionic species behind (Kapoor and Viraraghavan, 1997; Dahab, 1987, 1991).

"Membranes commonly used are made of cellulose acetate, while membranes made of polyamides and composite membranes are also available. These membranes do not show preference for any ion, but the degree of salt rejection is found to be proportional to the valence of ions present in the water supply." (Kapoor and Viraraghavan, 1997) As a result, reverse osmosis generally results in better removals of multivalent ions than

monovalent ions; therefore, it has been suggested by Montgomery (1985) that reverse osmosis might be used to remove sulfates from a water supply prior to ion-exchange for nitrate removal.

Fouling, compaction, hydrolytic deterioration, and concentration polarization are common problems associated with reverse osmosis membranes. The problems are caused by deposition of particles and soluble materials, excessive temperature, pH variations outside tolerance levels, and biological and chemical attacks (Dahab, 1991). Therefore, pretreatment is generally required in order to minimize these problems and associated maintenance. In addition, one-half to two thirds of the water remains behind the membrane as rejected water (Self and Waskom, 1992). This rejected water contains an elevated concentration of contaminants providing a disposal dilemma similar to that experienced with ion exchange.

2.5.3 Blending

Reduction of nitrate concentrations in drinking water may also be accomplished by blending the water with a lower nitrate water from a different source (i.e. water from a deeper well), such that the overall concentration of nitrate in the finished water is reduced to acceptable levels. It is important to note that this approach to solving the problem of high nitrates does nothing in the way of removing the contaminant from the water, but only dilutes it to a concentration considered safe for consumption. This alternative may be used where the cost of nitrate removal or total conversion to the new water source is considered excessive. This approach is often used in conjunction with

other denitrification processes in the form of a split train treatment when the process of choice is capable of treating water to levels well below the legal limit for nitrate. In this way, only a portion of the water is required to be denitrified, with a second portion bypassing the denitrification reactor and being remixed at an appropriate blend ratio.

3.0 MATERIALS AND METHODS

During this study of the effectiveness of the biological denitrification process at Coyle, Oklahoma, the water treatment facility was routinely monitored for anion concentrations ($C_2H_3OO^-$, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) and non-purgeable organic carbon (NPOC). During the latter part of the study, the water was also monitored for UV absorbance at 254 nm, "a measure of humic-like constituents with an aromatic character (both humic and fulvic acids)" which serves as an excellent surrogate parameter for estimating THM precursors in water (Quanrud et al., 1996; Edzwald et al., 1985).

3.1 SAMPLE COLLECTION

Sampling events during the study occurred between 7:00 and 7:45 AM on Mondays, Wednesdays, and Fridays at the Coyle, Oklahoma, water treatment facility. Coyle is a small town located approximately 20 miles southwest of Stillwater on state highway 33. "Construction of the Coyle, Oklahoma system was approved by the Oklahoma Department of Environmental Quality (DEQ) in the Spring of 1997. The system was installed during the summer of 1998 and has been operational since August of 1998. The system was put into service on December 3, 1998 after completion of the testing required by DEQ. The current system provides water to the 290 residents of Coyle and 400 school children." (NRT, 1999).

Seven taps throughout the facility, as indicated by Figure 10 (also included as Appendix A) were routinely sampled during the study. Table 4 identifies each tap for purposes of this study and indicates the tests that were routinely conducted on samples taken from

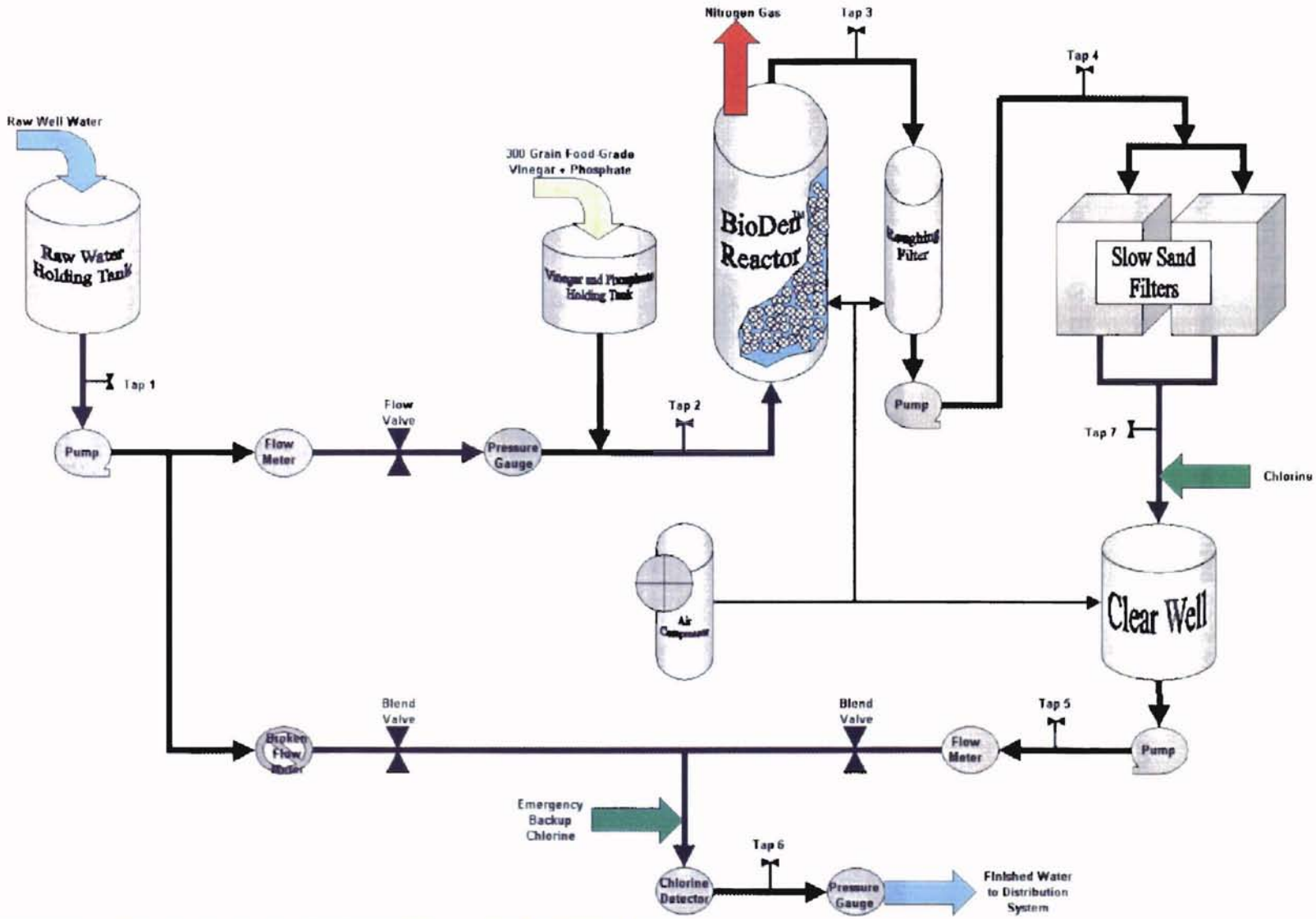

Figure 10: Schematic drawing of the Coyle, Oklahoma drinking water facility

each tap. Samples were collected in one-liter amber glass bottles with Teflon® cap liners. Before filling the sample bottles, the tap was opened and allowed to flush with several volumes of sample, and the sample bottle was rinsed once with water from the sample tap. A sample was obtained, then the samples were insulated and brought to the Oklahoma State University Environmental Engineering laboratories where they were analyzed the same day. If testing was unable to occur during the morning hours, sample bottles were kept refrigerated at 4°C until time of testing.

Tap #	Tap Name	Analysis
1	Raw	Anions, NPOC, UV_{254}, Temp.
2	Post Vinegar	Anions, NPOC, UV_{254}
3	Post Reactor	Anions, NPOC, UV_{254}
4	Post Roughing Filter	Anions, NPOC, UV_{254}
5	Post Clear Well Chlorinated	Anions, NPOC, UV_{254}
6	Mixed Chlorinated	Anions, NPOC, UV_{254}, Temp.
7	Post Sand Filter*	Anions, NPOC, UV_{254}

* This tap is numbered out of sequence with the rest of the taps because it was not made available until 8/27/99, nearly 3 months after testing began.

Table 4: Taps utilized at the Coyle, Oklahoma water treatment facility

3.2 Ion Chromatography

Monitoring of common anions in the Coyle water was conducted by ion chromatography (IC) on a Dionex (Sunnyvale, California), DX-120 Ion Chromatograph controlled by PeakNet 5.1 software. The chromatograph was equipped with an AS40 Automated Sampler accepting 5 ml disposable PolyVials with filter caps. Anion separation of the 25 µl sample injection volume occurred in an IonPac AS14 (4 x 250 mm) analytical column. The eluent used was 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$ at a flow rate of 1.2 mL/min.

Detection occurred by suppressed conductivity using an ASRS-ULTRA Anion Self-Regenerating Suppressor connected in the AutoSuppression Recycle Mode.

As a rule, 1000 mg/L (as compound) stock standards for each anion were made, and a four-point standard calibration curve was created for the IC shortly after the first of each month during the duration of this study. Stock standards were made in accordance with Standard Methods (APHA, 1992) and stored in one liter Nalgene plastic bottles refrigerated at 5°C. Table 5 indicates the chemical (type, brand, and purity) used in making each of the stock standards and the anion concentration found in each of the calibration and check standards routinely used. Before a freshly made stock standard was used in the development of a new calibration curve, it was first run as a check standard against the current calibration curve to verify consistency with previous standards. A check standard and duplicate were incorporated into each analysis schedule in order to monitor the consistency of performance of the ion chromatograph. Originally all samples were run in duplicate, but repeated analysis showed little variability between duplicates so the use of duplicates was reduced to one per sample schedule in order to conserve disposable vials.

Anion	Chemical	Brand	Purity	Stock Standard (mg/L)*	Calibration Standards (mg/L)*				Check Standard (mg/L)*
					Level 1	Level 2	Level 3	Level 4	
$C_2H_3OO^-$	$C_2H_4O_2$	Spectrum	Glacial, Reagent, A.C.S.	1000	1	30	60	100	40
Cl^-	NaCl	Spectrum	Crystal, Reagent, A.C.L.	1000	1	50	100	150	100
NO_2^-	$NaNO_2$	Fisher	Certified A.C.S.	1000	1	2	4	8	0.8
NO_3^-	$NaNO_3$	Spectrum	Crystal, Reagent, A.C.L.	1000	1	10	30	60	40
PO_4^{3-}	KH_2PO_4	EM Science	GR Crystals	1000	1	2	4	8	4
SO_4^{2-}	K_2SO_4	Fisher	Powder, Certified A.C.S.	1000	1	30	60	100	60

* Expressed as compound.

Table 5: Ion chromatography calibration standard data

3.3 TOTAL ORGANIC CARBON

The analysis of non-purgeable organic carbon (NPOC) was conducted on a Shimadzu (Columbia, Maryland), TOC-5000A Total Organic Carbon Analyzer with an ASI-5000A autosampler. The glass sample vials accepted by the autosampler contained approximately 3 ml of sample, or 32 ml of standard, and were sealed with Parafilm prior to being loaded into the autosampler tray to help prevent contamination during the analytical run time. Regular sensitivity analysis of the NPOC was performed using the acidification and sparge technique. The samples were acidified to a pH < 2 by the automatic addition of 50 µl of 2 N HCl. Just prior to injection, each sample was sparged with zero grade compressed air for 10 minutes. This air was used as the carrier gas and was supplied at a flow rate of 100 and 150 ml/min for sparging and carrier purposes respectively.

Stock standards and calibration curves for the determination of NPOC were also created near the first of the month and at other times deemed necessary by changes in the instrument operation or response or more commonly, a change in dilution water. The stock standard was a 1000 ppm TOC solution made in a 250 ml volumetric flask by dissolving potassium bipthalate ($C_8H_5KO_4$) in deionized water and acidifying to pH < 2 by the addition of sulfuric or phosphoric acid. The stock standard was kept refrigerated at 4°C. Before a freshly made stock standard was used in the development of a new calibration curve, it was first run as a check standard against the current calibration curve to verify consistency with previous standards. The stock standard was then used to create a low range (1, 2, 3 ppm) and a high range (4, 16, 24 ppm) calibration curve used in

analysis of the samples. For each NPOC determination, the sample was injected a maximum of 5 times with the best 3 or the first 3 to produce a standard deviation of less than 200 area counts or a coefficient of variance of less than 2% being used to determine the mean NPOC. These criteria were established by accepting the default limits built into the software. NPOC determinations for all samples were run in duplicate and two check standards (2 and 16 ppm) were incorporated into each analysis schedule in order to monitor the consistency of performance of the TOC analyzer.

3.4 Ultraviolet Absorbance at 254 nm

Ultraviolet absorbance at 254 nm (UV_{254}) was measured on a Shimadzu (Columbia, Maryland), UV-1601PC UV-Visible Spectrophotometer in the Oklahoma State University Microbiology and Molecular Genetics laboratory. The dual beam instrument was first zeroed by placing two matched 1-cm quartz cells filled with deionized water into the reagent and sample paths, respectively. Both unfiltered and filtered measurements were taken for water samples from each of the seven taps in Coyle. Filtering occurred via a 0.45 μm nylon syringe filter (FisherBrand). The filters for each sampling point were reused and were rinsed with approximately 35 ml of deionized water and 10 ml of sample before each use. The 5 ml plastic syringe used for transferring samples was triple rinsed with deionized water and then triple rinsed with sample before each use. The sample cell was well rinsed with a jet of deionized water between each use. To compensate for baseline drift, the instrument was rezeroed between measurements on each of the seven sample bottles.

Possible interferences to the determination of UV_{254} include pH and particulates (Edzwald et al., 1985) as well as NO_3^- and NO_2^- (Rittmann and Huck, 1989). Comparison of values measured from filtered and unfiltered portions of sample confirmed a positive interference in unfiltered samples, most apparent in reactor and roughing filter effluent samples where particulate matter was often visible. As a result, only UV_{254} measurements collected from filtered samples have been used in estimating changes in the presence of THM precursors throughout the facility. Measurements from unfiltered samples have been included in Appendix C for comparison purposes only, and in conjunction with the filtered values (also in Appendix C), may provide a rough indication of the relative presence of particulates at various pre-sand filter locations at the facility. Possible interference by NO_3^- and NO_2^- was investigated by preparing dilutions of each from IC stock standard solutions (see Table 5 above) and analyzing them for UV_{254}. Results of this procedure indicated that interferences by NO_3^- and NO_2^- were negligible over the range expected for samples in this study.

4.0 RESULTS AND DISCUSSION

This study has provided the first look at system operation and performance of a full-scale biological denitrification system in the United States under the control of a part-time operator as opposed to research personnel. Anion concentrations, including acetate, chloride, nitrite, nitrate, phosphate, and sulfate were monitored, along with non-purgeable organic carbon (NPOC). The system was monitored for 5 1/2 months with samples taken from the raw well water and following every major unit or operation in the facility. In addition, ultraviolet absorbance at 254 nm (UV_{254}) was measured during the final two months of testing as a surrogate parameter for estimating trihalomethane (THM) precursors. The data have been compiled and are presented here, along with discussions of trends as they relate to the data and operational events occurring at the facility.

To facilitate discussion, the operations and sampling taps at the drinking water facility have been divided into four functional groups: raw water, biological denitrification, filtration, and finished water. This section will first examine each of these groups individually, looking at system operation and performance with respect to time. Then, discussion will shift to examination of trends that occurred with respect to location in the facility, with the focus being placed on THM precursors.

4.1 RAW WATER

The ground water supply for the city of Coyle is quite shallow (approximately 20 feet). Since Coyle is located within a mile of the Cimarron River, it was suspected that the raw

well water quality is influenced by seasonal variations in precipitation and river conditions, and that any such changes would be made manifest within days of such an event. For this reason, measurement and monitoring of chloride in the raw water was carried out as a simple means of detecting changes in the raw water quality. The ground water is relatively high in chloride, reaching as high as 114.44 mg/L during this study. Figure 11 graphically presents the results of chloride monitoring in the raw well water. Note the large dip in chloride concentration beginning after June 23; this corresponds to a large rainfall event that occurred over a period of several days. During this dip, the chloride concentration reached a low value of 75.47 mg/L, the lowest recorded in the raw water during this study. One can see that after the dilution effects of the spring and early summer rains had passed, the chloride concentration began to steadily climb during the relatively dry summer and fall seasons. During the final weeks of testing, the chloride concentration began to stabilize until one final small rainfall event was experienced in late October, resulting in the small dip occurring at the end of the collected data.

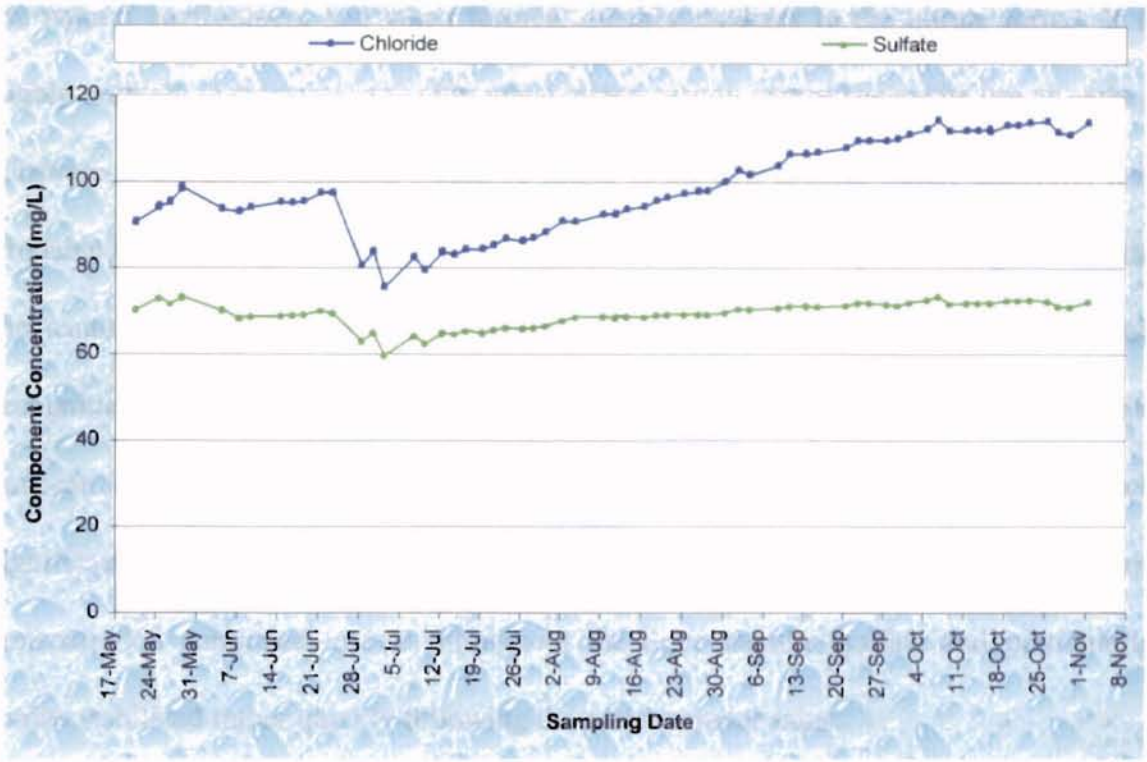

Figure 11: High Range IC Results from the Raw Water Tap

Coyle's water supply is also relatively high in sulfate (ranging from 59.66 to 73.41 mg/L during this study) and typically moderate in nitrate (4.07 to 7.35 mg/L as nitrogen). Sulfate is of interest because a number of organisms commonly found in natural waters, including some denitrifying bacteria, are capable of reducing sulfur in an anoxic environment, when organic carbon is supplied in quantities greater than that required for complete nitrate removal. This is a phenomenon observed by Cook et al. (1990) in research that eventually led to the development of the BioDen™ system installed at Coyle. In addition to the chloride data mentioned above, Figure 11 also presents the results of sulfate monitoring. Figure 12 indicates that of all the anions analyzed, only nitrate (as nitrogen) was detected in the range up to 10 mg/L in the raw water. As expected, no nitrite was detected in the raw water, since nitrite is relatively unstable in

the natural environment and when formed, quickly oxidizes to the nitrate form. It is highly unlikely that acetate, a readily metabolized carbon source (hence its use as carbon substrate at the Coyle facility), would be found in the raw ground water; therefore, it is probable that the single detection of acetate in the raw water sample on August 13, was the result of some form of cross contamination between samples or inaccurate peak recognition by the PeakNet software. The general trends in changing sulfate and nitrate concentrations appear to roughly parallel that of chloride, with dilution occurring at each significant rainfall event. One may note, however, that whereas the chloride concentration continued to rise throughout the drier months, sulfate and particularly nitrate stabilized rather quickly following the early summer rains.

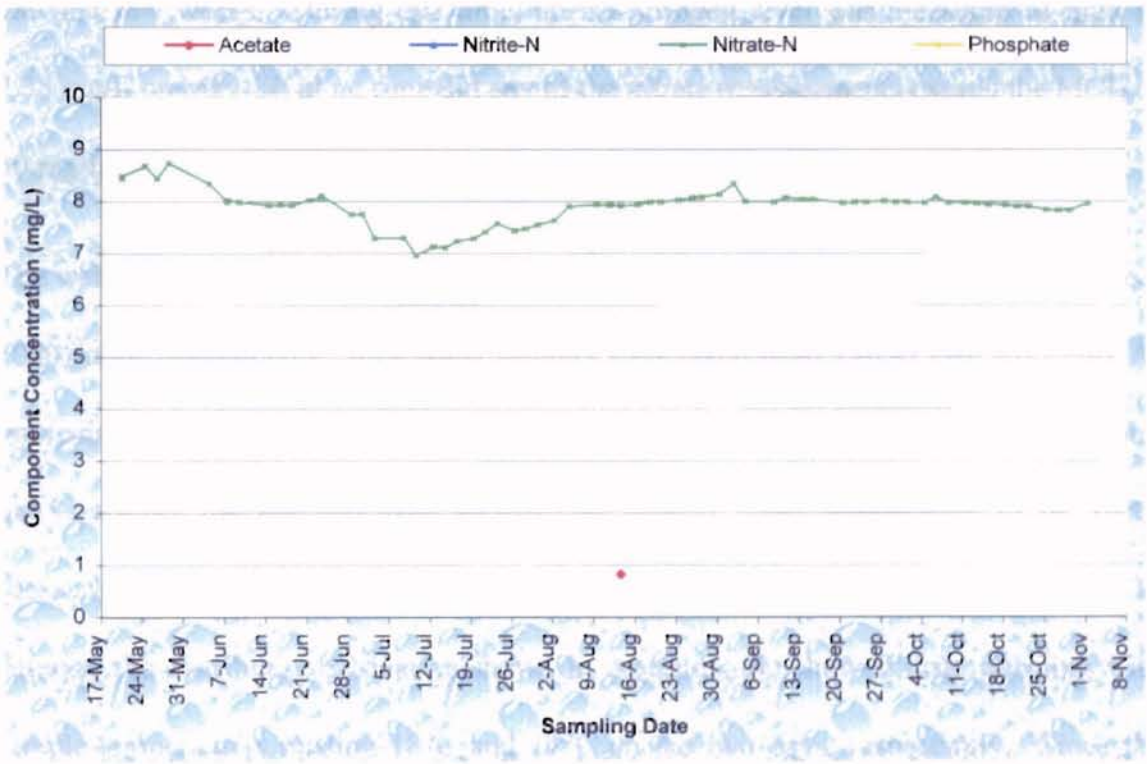

Figure 12: Low Range IC Results from the Raw Water Tap

Before sampling began, the expectation was that an increase in nitrate concentration in the raw water would be observed in response to rainfall events, as nitrate from fertilizer applications was carried into the shallow ground water. This expected response did not occur during the study period. Since sampling did not begin until the 20th of May, the sampling period could have been too late in the spring to detect any major seasonal variations or spikes in the nitrate concentration due to the timing of fertilizer application. Another possible scenario is that the rainfall occurring during this study may have been carrying with it a large amount of nitrate from the fields, but the amount of rainfall was proportionately higher such that the net effect of the rainfall event was a dilution of nitrate in the water supply. Nitrate levels during the study were at their highest during the first few weeks. During this time, nitrate-nitrogen level was measured as high as 7.35 mg/L on May 17; at no time did any of the nitrate measurements exceed the MCL of 10 mg/L NO_3-N.

The well pump at the Coyle facility is cyclically operated and pumps the raw water into a 1000 gallon holding tank. Raw water samples were taken from Tap #1 (see Appendix A) immediately following the holding tank. A spot check of water temperature at this point on September the 8th and 10th showed the ground water temperature to be 16°C. Measurement of the water temperature from Tap #6 (after blending and just prior to entering the distribution system as shown in Appendix A) showed little warming with sample temperatures reading 18°C and 17°C on the two days, respectively. Since the facility treats a ground water source, the water the temperature is expected to remain fairly consistent throughout the year. Organic carbon concentration in natural ground

waters is typically low, and the water at Coyle follows this trend. Throughout the study the raw water NPOC remained quite constant, ranging from 0.42 to 1.11 ppm, with an average concentration of 0.69 ppm, as illustrated in Figure 13.

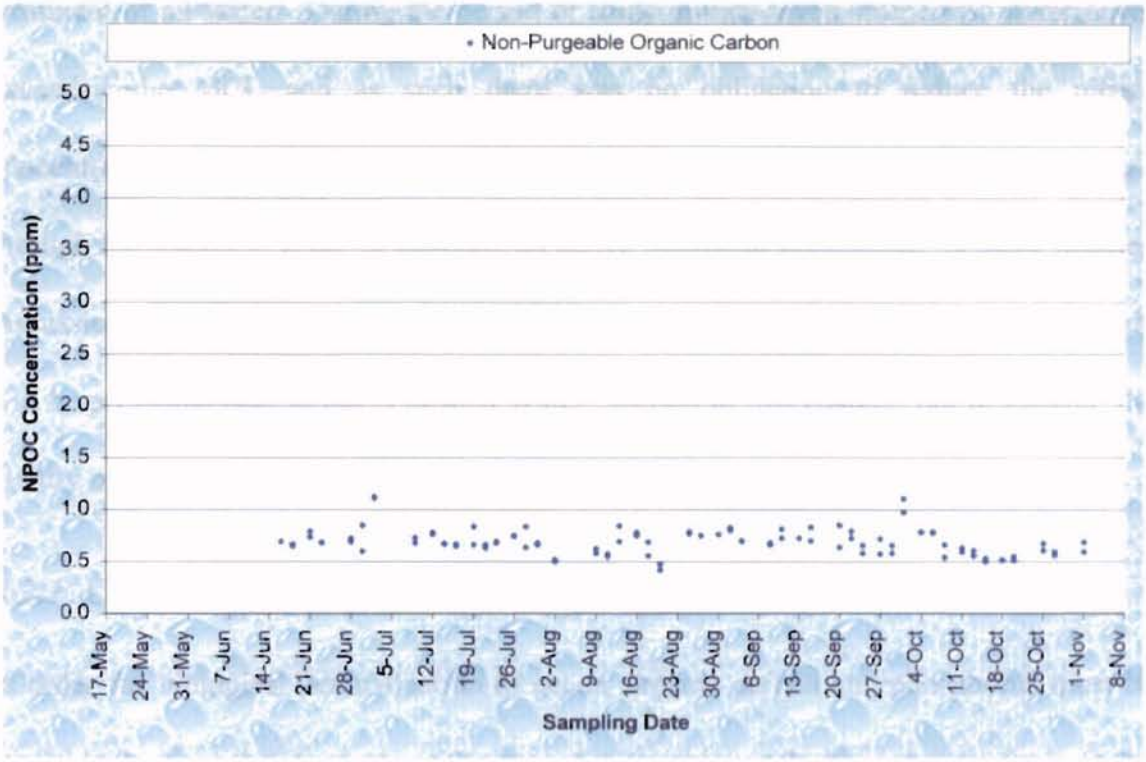

Figure 13: NPOC Results from the Raw Water Tap

4.2 Biological Denitrification

From the raw water holding tank, water enters the denitrification portion of the facility. The drinking water requirement is that nitrate-nitrogen in the finished water not exceed 10 mg/L. The use of biological denitrification to provide this treatment carries with it some operational costs (the cost of providing a carbon and phosphate source in particular) that increase with the amount of nitrogen removed. For this reason, it is important to provide a means of balancing effective nitrogen removal with the economics of doing so. This is accomplished by allowing for the treatment of a portion of the raw

water which will be reblended with a second portion of untreated raw water. In this manner, the nitrogen concentration in the finished water can be reduced to acceptable levels while avoiding the excessive cost of providing carbon and nutrients for the direct treatment of all water. During the period of study, nitrate levels in the raw water never exceeded the MCL and as such there was no obligation to reduce the nitrate concentration. With a biological system however, some flow must continue to be treated through the reactor in order to maintain an active microbial population. A more detailed discussion of blend ratios utilized at the Coyle water treatment facility during this study will be presented later in the "Finished Water" section of this chapter; but in general, the facility operated a 50:50 split stream (Appendix B).

4.2.1 Carbon and Phosphorous Dosing

In order for biological denitrification to occur, organic carbon and phosphorus must be available in quantities great enough to meet the stoichiometric requirements for both the removal of any dissolved oxygen and nitrate present. Since the 0.42 to 1.11 ppm range of NPOC present in the raw water is insufficient to meet these requirements, the portion of water to be biologically treated is augmented with an external carbon and phosphorous source. The BioDen™ technology uses commercially-available food-grade acetic acid as the carbon source. "Acetic acid was chosen because of its low price, availability, non-toxicity, and easy storage. It is not flammable, and no special handling, operator training, or storage permits are required" (NRT, 1999). During this study, Coyle was using a 300 grain (30%) food grade vinegar purchased from Burns Philp Food, San Ramon, California. The vinegar was supplemented on site with mono sodium phosphate

purchased from Van Waters & Rogers, Oklahoma City, Oklahoma. Dilution and analysis in the OSU Environmental Engineering laboratories estimated the vinegar to have an acetate concentration of 268,000 mg/L and an NPOC of 128,000 ppm. IC analysis also showed the phosphate concentration in the feed solution to be 47,000 mg/L with traces of sulfate present.

As the process water approached the inlet of the denitrification reactor, a pump injected the flow with a metered pulse of the carbon and phosphate feed. The feed pump was equipped with an in-line graduated cylinder that could be filled with the vinegar feed so that the feed rate could be determined by averaging the vinegar use per given amount of time. This calculation of vinegar feed rate was a standard entry in the voluntary record keeping (Appendix B) maintained by Joe Galloway, the system operator, and is a critical parameter in the successful operation of the system. If too much vinegar is added, the reactor may enter sulfate reducing conditions, producing hydrogen sulfide and releasing excess organics into the finished water; too little vinegar results in incomplete nitrate removal with possible accumulation of intermediate nitrite. This is to be avoided, as it is the potential for nitrates to convert to nitrite within the human body that has driven the regulation of nitrates in drinking water. As discussed previously, nitrite converts hemoglobin in the blood to methemoglobin causing the illness methemoglobinemia in infants and certain susceptible adults.

The electronic controls for the BioDen™ system include a digital flow meter and flow totalizer, both of which have experienced some technical difficulties since installation. Data from these meters have also been included in Appendix B. As part of the operating

information given to the system operator, NRT included the information in Table 6 as guidelines for carbon dosing rates. It is important to note that the table is derived for the elimination of 8.0 mg/l of nitrate-nitrogen where 7.5 mg/L of dissolved oxygen is present in the reactor influent. Neither of these parameters are frequently monitored within the system. According to the operator (Galloway, 1999), the table is only used as an occasional rough check to see that the actual feed rate is in a comparable range. Adjustments were made to the vinegar feed rate and/or the process water flow rate from time to time, after recording the daily reading, in order to keep them within historical operating ranges (see Appendix B).

Nitrate Removed = 8.0 mg/L **Dissolved Oxygen Concentration = 7.5 mg/L**	
Flow Rate (gpm)	**Metering Pump Flow Rate (ml/min)**
10	5.9
11	6.5
12	7.1
13	7.6
14	8.2
15	8.8
16	9.4
17	10.0
18	10.6
19	11.2
20	11.8
Equation: 0.59 x Flow Rate (gpm) = Vinegar Dosing Rate (ml/min)	

Table 6: NRT recommended carbon dosing rates

Figure 14 and Figure 15 show the amounts of acetate and phosphate detected in samples taken from the tap immediately following the point of addition. The other anions present in the water are displayed as well, but at this point in the process, the concentrations have

not altered significantly from that of the raw water. One will note the sudden drop in acetate and phosphorus addition that occurred during the week of June 28. Mr. Galloway, the system operator, was on vacation from June 28 through July 9. In his absence, daily checks on the system were left to another operator. During this time, the vinegar feed rate was not monitored regularly. The irregular pattern of carbon dosing beginning in August and continuing throughout the second half of the study does not appear to follow any strong correlation with operational changes or events taking place at the Coyle facility and may be the result of day-to-day drift of flow and feed rate settings. Throughout the project, the operation appeared to be lacking a logical and useable means by which the system operator could determine and then accurately administer a suitable carbon dose.

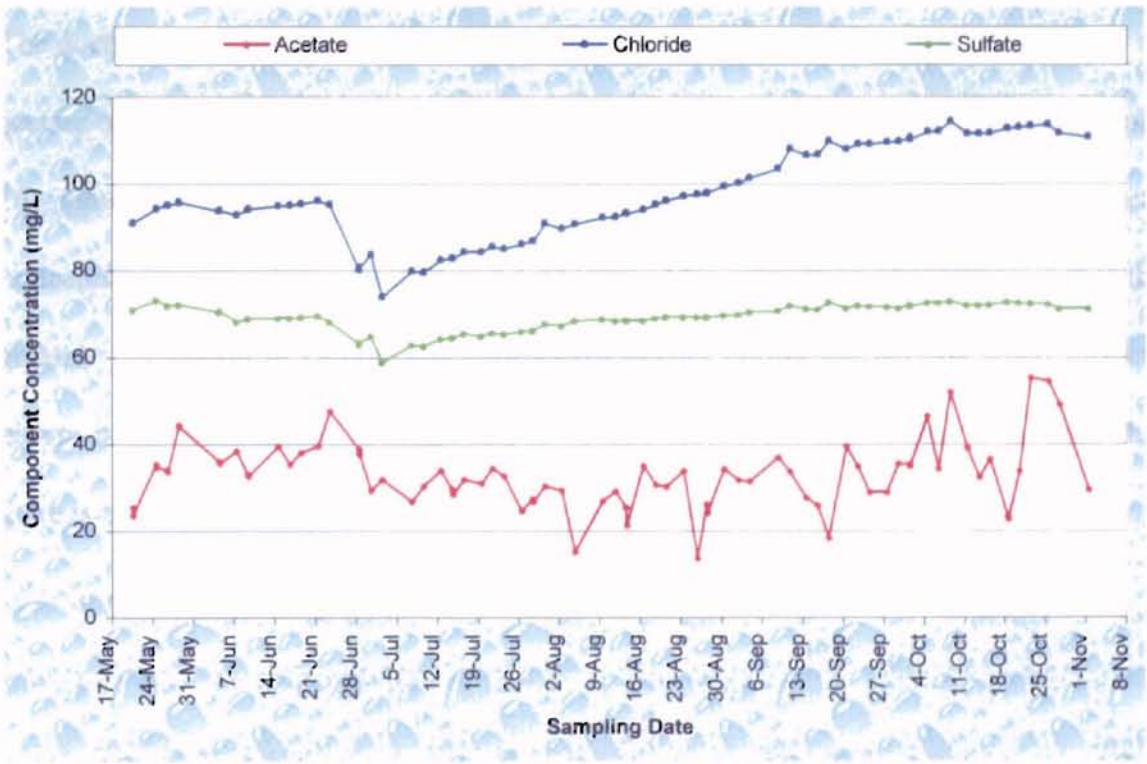

Figure 14: High Range IC Results from the Post Vinegar Tap

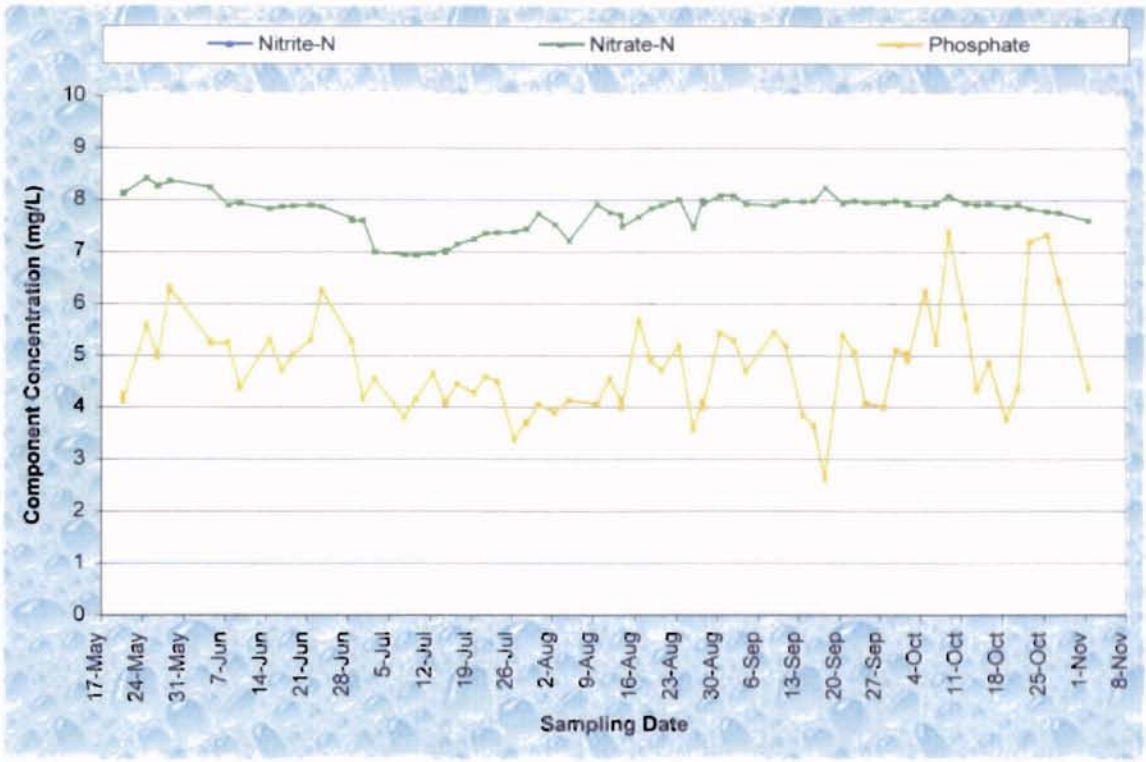

Figure 15: Low Range IC Results from the Post Vinegar Tap

The acetate concentration entering the reactor varied between 13.61 and 55.32 mg/L as acetate or 5.54 and 22.51 mg/L as carbon. The plot of data from NPOC analysis (Figure 16) shows the same basic trend as that of the acetate plot, as one would expect, and indicates a variation between 0.42 and 1.11 ppm. One interesting observation is that the greatest fluctuation in carbon and phosphorus occurs during the periods when influent nitrate is the most stable. Though this is by coincidence, it is a further indication that there is a need for improvements in carbon dosing control.

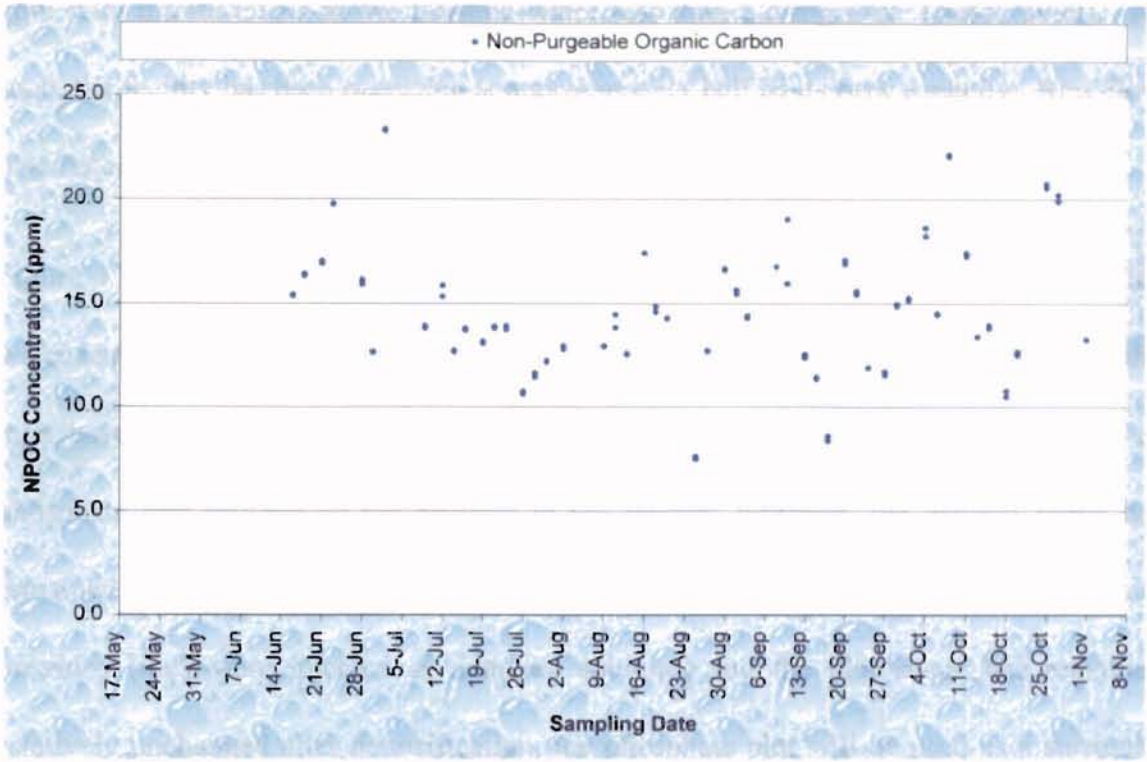

Figure 16: NPOC Results from the Post Vinegar Tap

4.2.2 Biological Reactor

After the raw water has been dosed with carbon and phosphorous, it enters into the reaction vessel. The reactor is packed with low density, high porosity, mesh spheres which provide a large surface area for microbial growth, while minimizing clogging or channeling within the reactor (NRT, 1999). Operation occurs in an upflow mode to facilitate the removal of the nitrogen gas created during denitrification. The feed rate through the reactor averaged 13.0 gpm during the study (this estimate may be low, as there were 8 days during the 5 1/2 month study where the flow totalizer jammed for a short period). The reactor was designed to treat up to 27.5 gpm of water with a maximum influent nitrate of 16 mg/L-N. This allows for the treated water to be blended with an additional 27.5 gpm of untreated water to provide a total design capacity of 55

gpm with nitrate levels in the finished water less than 8.0 mg/L-N (NRT, 1999). As such, the facility has been operating at approximately half of its flow capacity. Raw flow data recorded by the system operator are included as Appendix B.

Figure 17 shows the nitrate, nitrite, and phosphate data collected from the denitrified water leaving the reactor. For reference, nitrate and phosphate concentrations from the inlet have been superimposed on the chart. One will notice that a small amount of phosphate was utilized by the bacteria in the reactor; however, the general shape has remained the same. Since the addition of phosphate was proportional to the acetate provided (they were injected as a mixed solution) and the plot shape has remained relatively unchanged after denitrification, the phosphate plot will be used as a surrogate for the reactor influent acetate plot when discussing trends and occurrences in the data as they relate to high or low inputs of acetate.

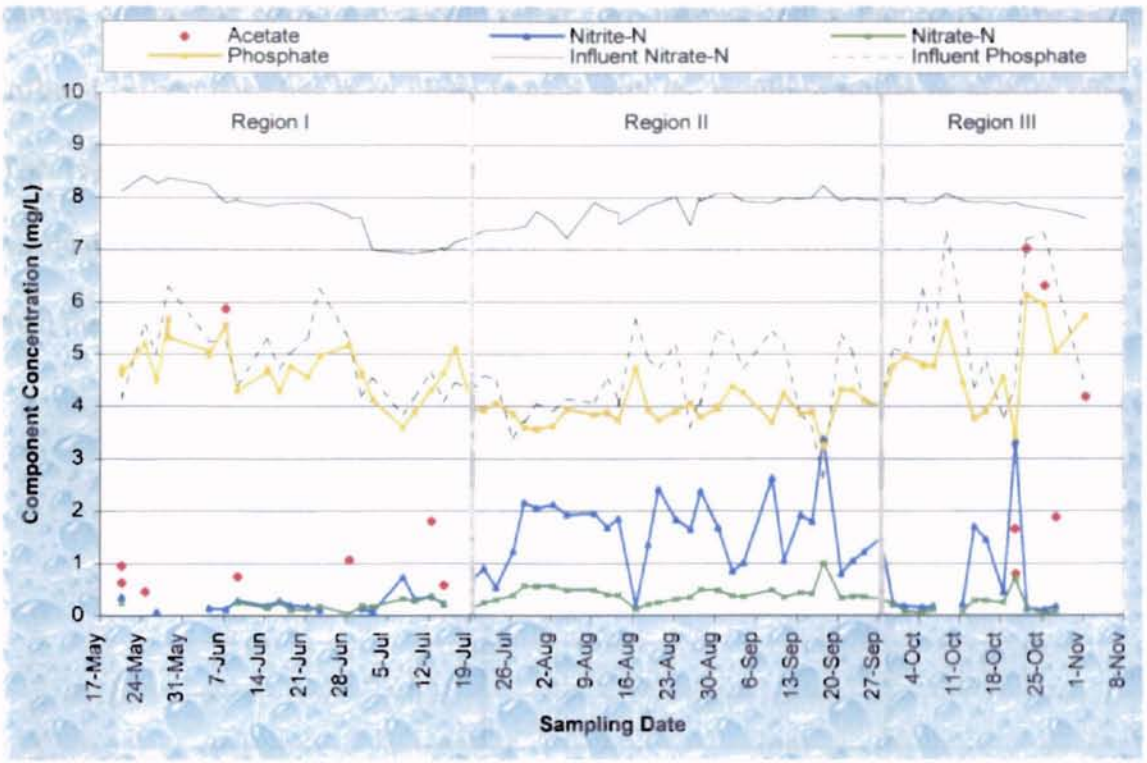

Figure 17: Low Range IC Results from the Post Reactor Tap

The chart may be broken into three regions relating to carbon addition and reactor response. The first and third regions, occurring roughly before July 19 and after September 27 respectively, are associated with higher carbon dosings (average C:N ratios of 1.81:1 and 1.98:1 respectively) resulting in near-complete removal of nitrate, but occasional occurrences of residual carbon are noticed in the reactor effluent (see also NPOC data in Figure 18). In contrast, lower doses of carbon (C:N ratio of 1.50:1) were supplied in the middle region, resulting in complete acetate removal with reduced nitrate elimination and a potentially serious accumulation of intermediate nitrite reaching as high as 3.38 mg/L NO_2-N on September 17. Although no acetate was detected in region two, one will notice that the NPOC has increased slightly from the average background concentration of 0.69 ppm found in the raw well water. These relationships between

carbon dosing and nitrite and acetate release are summarized in Figure 19. The reactor influent carbon dose has been plotted along with the resulting nitrite or acetate release. The reader will note that the carbon dose breakpoint between nitrite formation and residual organics release appears to occur at a C:N ratio of around 1.7:1, slightly higher than the theoretical dose of 1.5:1.

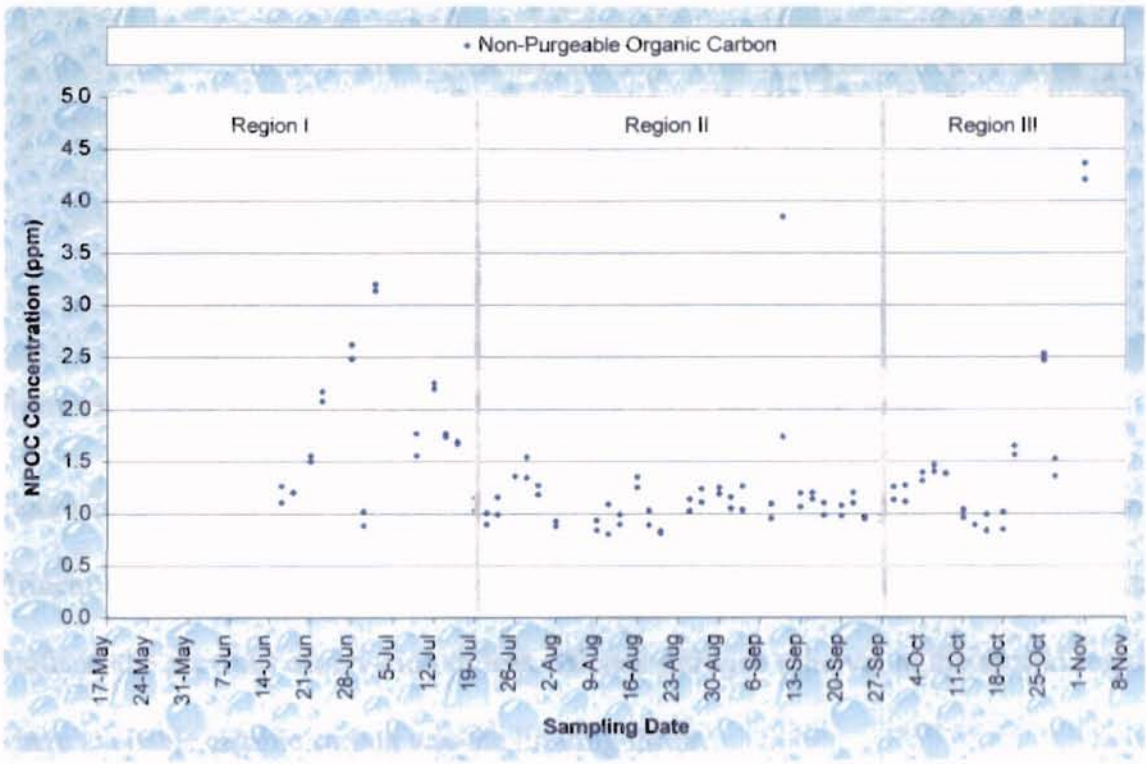

Figure 18: NPOC Results from the Post Reactor Tap

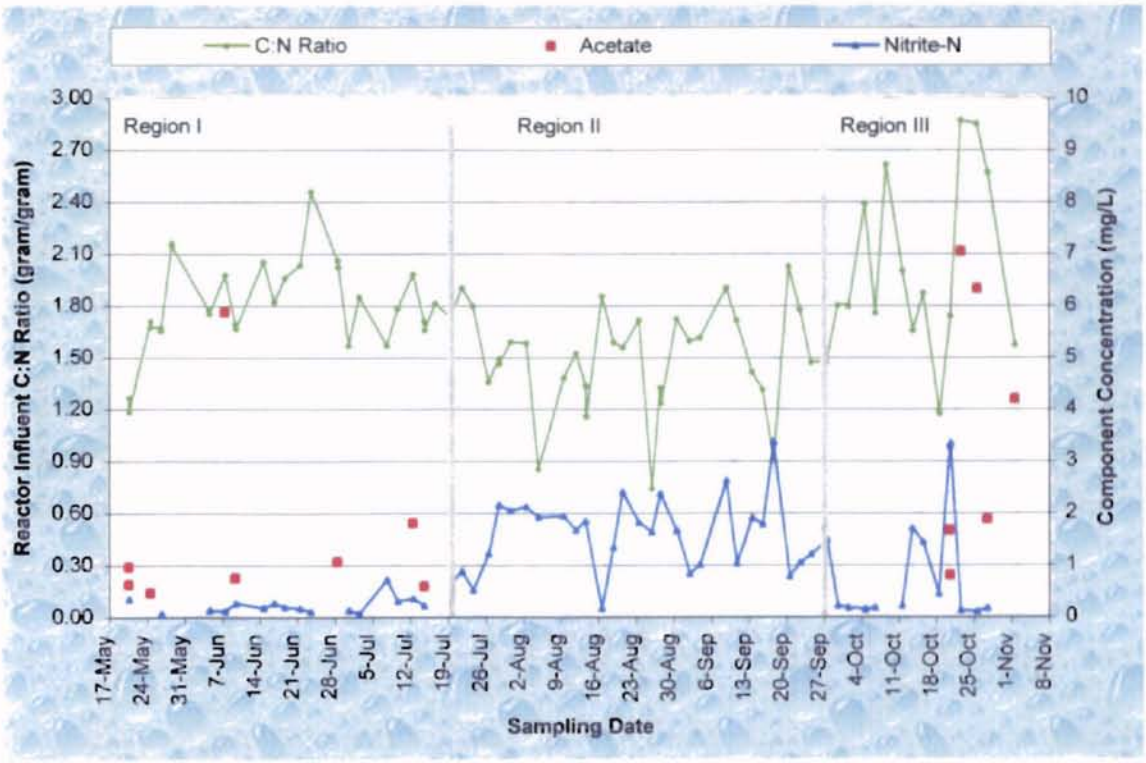

Figure 19: Reactor Influent C:N Ratio with Resulting Nitrite and Acetate Release

Figure 20 shows the total nitrogen (nitrate-N plus nitrite-N) concentration in influent and effluent to the reactor as well as the associated removal efficiency achieved. This chart confirms the previous observation of less efficient nitrogen removal in the second region where available organic carbon was the limiting factor.

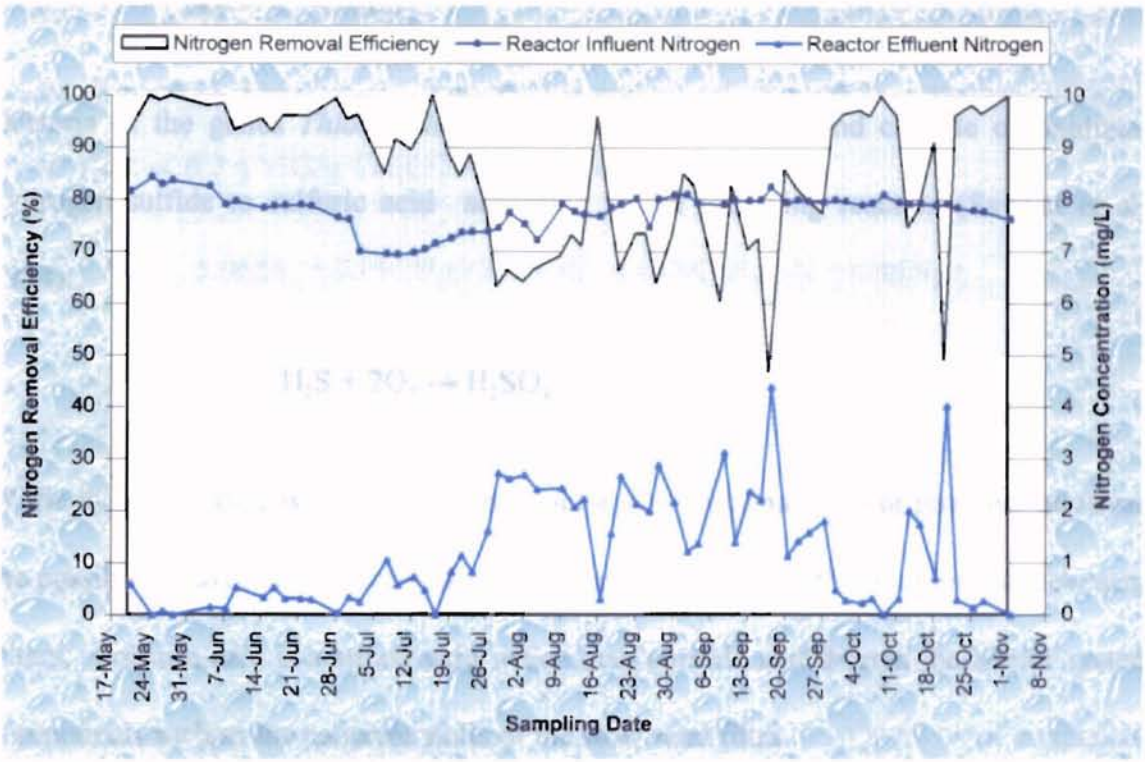

Figure 20: Reactor Nitrogen Removal Efficiency

Figure 21 is a plot of chloride and sulfate data collected from the post reactor tap. Plots of the sulfate data from the post vinegar tap has been superimposed for reference purposes. Note the distinct reduction in sulfate concentration that occurred on July 16, October 8, and from October 20 through the end of testing. These dates were also characterized by near, if not complete, nitrogen removal and frequent appearance of residual acetate in the reactor effluent. On these days, bacteria capable of sulfate reduction were able to begin utilizing the sulfate as an electron acceptor in the absence of dissolved oxygen and nitrate. The reduction of sulfate is an undesirable occurrence as it produces hydrogen sulfide, a noxious byproduct.

$$SO_4^{2-} + \text{organic matter} \rightarrow S^{2-} + H_2O + CO_2$$

$$S^{2-} + H^+ \Leftrightarrow HS^-$$

$$HS^- + H^+ \Leftrightarrow H_2S$$

Bacteria of the genus *Thiobacillus* are ubiquitous in nature and capable of oxidizing hydrogen sulfide to sulfuric acid according to the following reaction (Sawyer et al., 1994):

$$H_2S + 2O_2 \rightarrow H_2SO_4$$

While in the anoxic environment of the reactor, this reaction will not proceed; however, the possibility exists for the formation of sulfuric acid latter in the roughing or slow sand filters. Sulfuric acid is a strong acid which may corrode and shorten the life of system components such as the concrete walls of the slow sand filter.

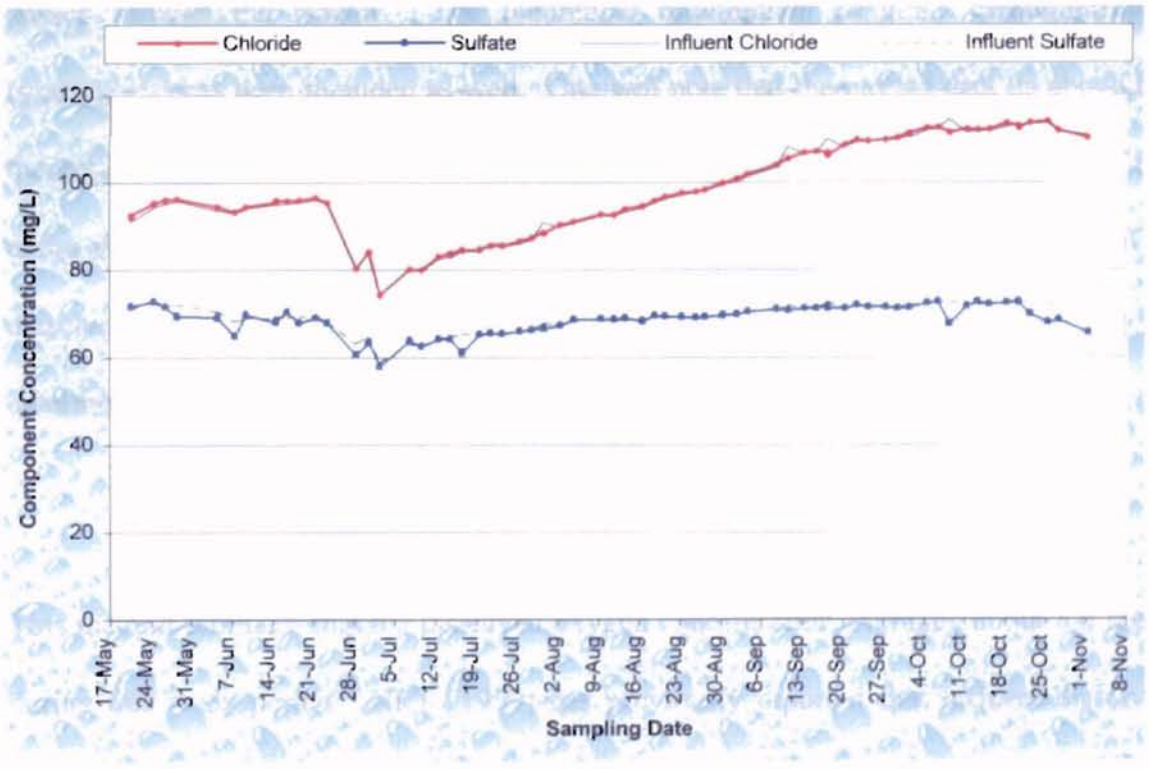

Figure 21: High Range IC Results from the Post Reactor Tap

Theoretical acetate consumption for denitrification is 1.5:1 grams carbon:gram nitrate-nitrogen reduced, based upon the following stoichiometric equation, assuming a biofilm mass yield of 0.2 g VSS/g CH_3COO^- (Cook et al., 1997):

$$1.0NO_3^- + 0.88CH_3COO^- + H^+ \rightarrow 0.09C_5H_7O_2N + 0.46N_2 +$$

$$0.42CO_2 + 0.88HCO_3^- + 1.07H_2O$$

where $C_5H_7O_2N$ is the empirical chemical formula for VSS. This theoretical requirement is valid in the absence of dissolved oxygen. Where oxygen is present, the actual requirement will be correspondingly higher. Figure 22 is a plot of the acetate-carbon consumed vs. total nitrogen (nitrate + nitrite) removed from the Coyle water supply as it passed through the reactor. The theoretical requirement of 1.5:1 carbon:nitrogen (gram/gram) has been included as well. One will note that the plotted data lie above the theoretical line, a result of acetate consumed to remove influent dissolved oxygen. If the entire amount of acetate-C consumed above the theoretical amount can be attributed to dissolved oxygen in the reactor influent, then this dissolved oxygen concentration may be determined using the following stoichiometric relationship:

$$2O_2 + C_2H_3OO^- + H^+ \Rightarrow 2CO_2 + 2H_2O$$

This method estimates that the dissolved oxygen concentration averaged about 8.6 mg/L during this study period. NRT (1999) has previously reported that influent dissolved oxygen at the Coyle facility remained steady at 7.3 mg/L with a standard deviation of ±0.1 mg/L during their testing between October 1998 and January 1999. The reader will

recall that carbon dosing guidance available to the operator (Table 6) is based on an influent dissolved oxygen concentration of only 7.5 mg/L.

By rearranging the acetate consumption data presented in Figure 22 and plotting the specific acetate consumption (acetate/nitrogen ratio), Figure 23 has been derived. A similar plot for phosphate consumption (Figure 24) has been created. A linear regression of the data points indicates that the system has gradually increased its consumption of both acetate and phosphate. A number of possibilities may account for this trend. First, the increase may be due to a gradual increase in influent DO. If the dissolved oxygen were to increase, the total acetate consumed would increase as well. Second, the trend may be a function of biofilm maturity. This appears unlikely, as the system has been in operation for nearly a year. This trend merits attention as a possible area for future study, since any increase in chemical consumption will eventually appear as an increase in operating cost.

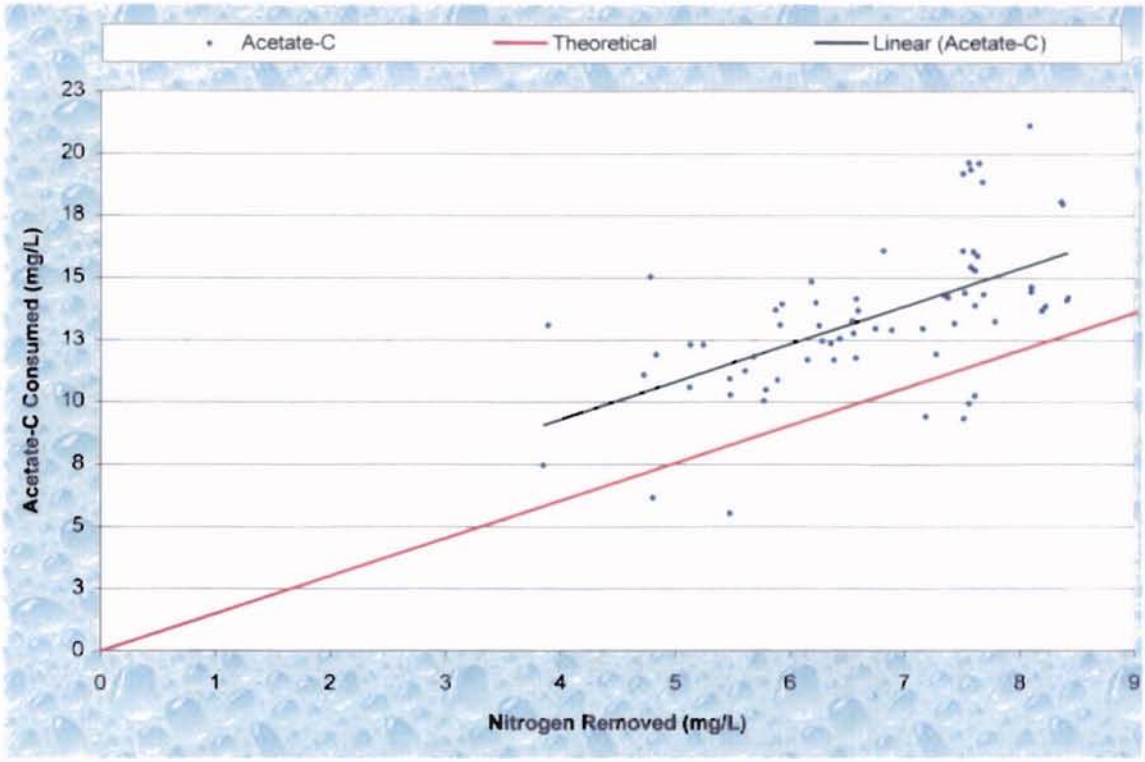

Figure 22: Reactor Acetate-C Consumption

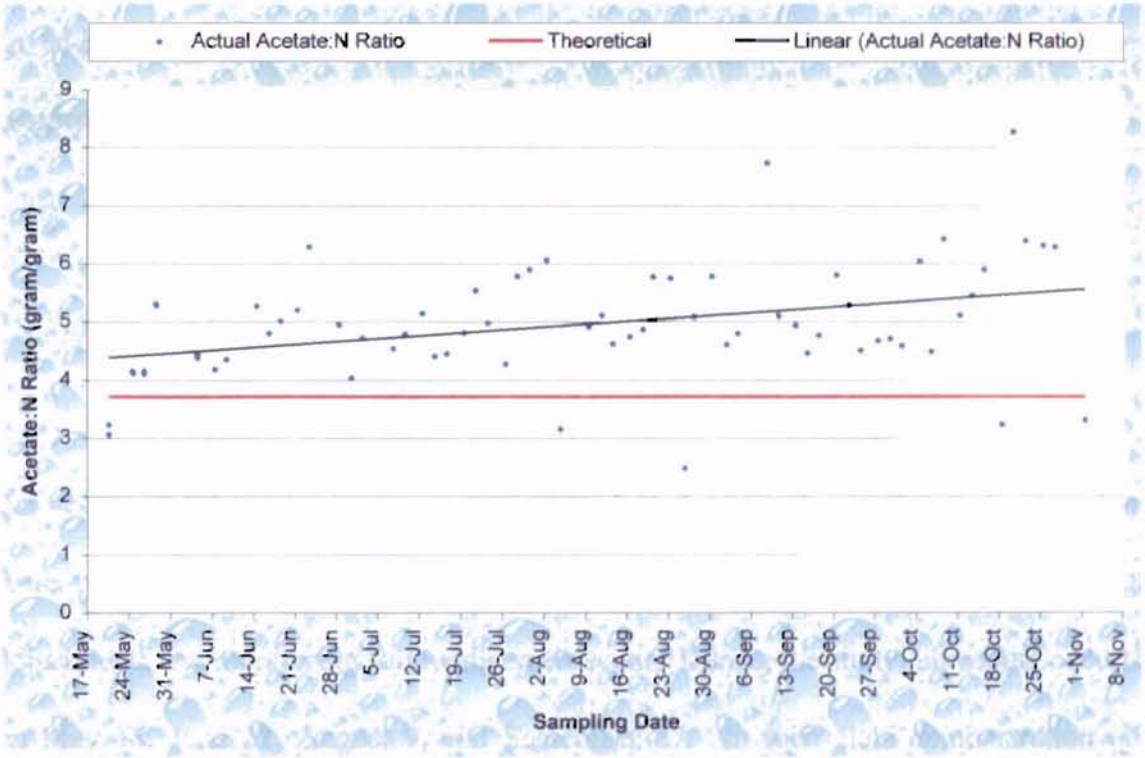

Figure 23: Reactor Specific Acetate Consumption

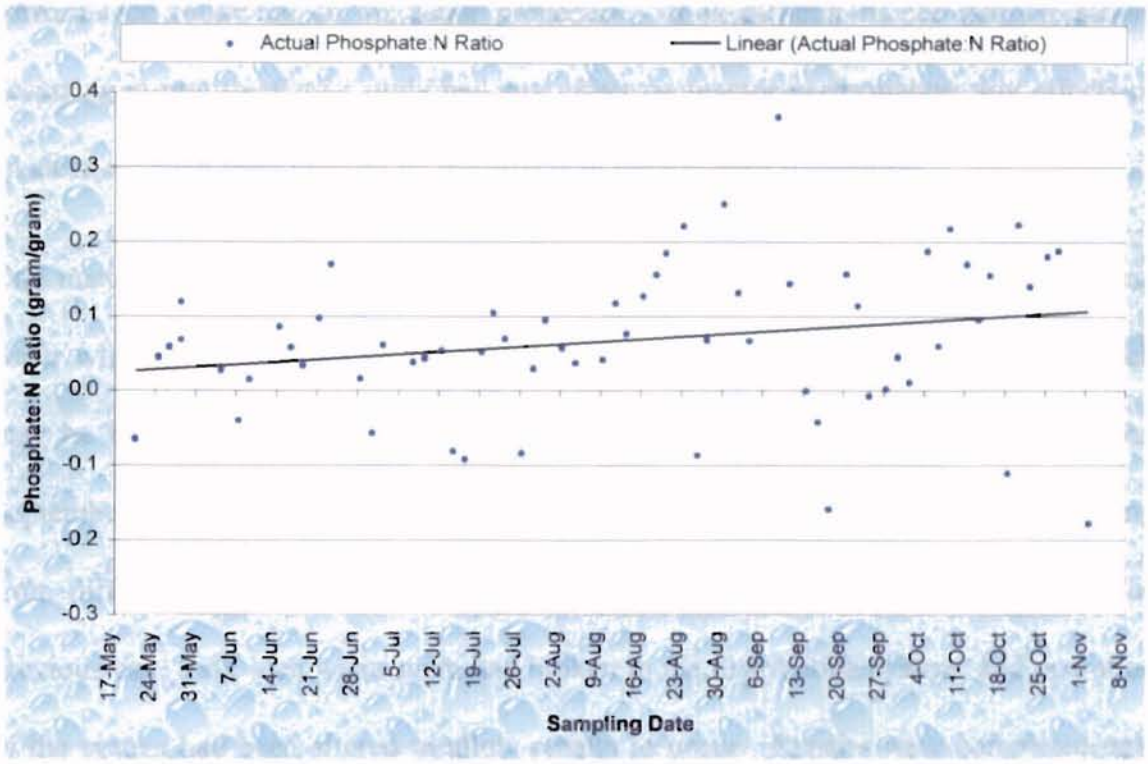

Figure 24: Reactor Specific Phosphate Consumption

In addition to daily inspection of equipment and operations, the BioDen™ system requires two other acts of scheduled maintenance. They are:

- An air-scour procedure to remove excess biomass from the reactor media in both the main reactor and the roughing filter.

- Scraping of the slow sand filter when excessive head loss develops.

Air scours of the reactor were required every 5 to 7 weeks during the study period and were typically scheduled to occur on a Monday, as the system often required slight adjustments and monitoring following an air scour. During the study, air scours occurred on May 18, June 21, August 9, and September 27. In their field demonstration of a similar denitrification reactor, Cook et al. (1990) reported a slight reduction in reactor

performance following an air scour procedure. It is difficult to see that air scours occurring during the Coyle study had any effect on reactor performance; any effects of an air scour have been masked by the effects of carbon dose fluctuation.

One matter of great concern is how a biological system for the treatment of drinking water will react to isolated incidents such as power outages or system shutdown which may be beyond the control of the system operator. One such incident occurred on September 17. When the samples were collected for that day, the system was recovering from difficulties that occurred the day before and extended through the night. The previous day, a six-inch water main had broken in the distribution system, and operation of the system had been altered to allow repairs to occur. Repairs were completed, and the system was brought back into service before the end of the day. During that night, a condition in the electrical distribution system had caused the electricity in the facility to blink on and off for an extended period of time. By early morning, power had been restored, and the facility was put back into operation just before samples were taken. As a result of this operational upset, nitrogen removal at the time of sampling was the least efficient recorded during the study (46.78 %). The facility recovered from the upset and by the next sampling date, three days later, system performance had returned to its previous level.

On October 20, the system was upset once again. When flow and feed rate data were collected that morning by the system operator, the water feed rate through the BioDen™ split was at 17.9 gpm (well above the 13.0 gpm average). This is the only day where high nitrite (more than 1.0 mg/L-N) and residual acetate appear together in the reactor

effluent. One probable explanation for the occurrence on October 20 is that the shift in feed rate had shortened the detention time in the reactor enough that the detention time had become the limiting factor. The established bacterial population was unable to achieve total denitrification before the process water was displaced. The flow rate was then reduced to 11.7 gpm. Post reactor results for the days following the readjustment of the feed rate indicate that perhaps the flow rate was readjusted too low for the established vinegar feed rate. By adjusting only the water flow rate and not simultaneously reducing the vinegar feed rate, the C:N ratio was increased, allowing for large amounts of residual acetate (as high as 1.66 mg/L) to leave the reactor.

It is extremely important to realize that these observations are based upon analytical system performance data that the system operator does not have at his disposal on a day-to-day basis, when decisions have to be made. This once again underscores the need to develop a logical and usable means by which the system operator can determine and then accurately administer an optimum carbon dose.

4.3 FILTRATION

Effluent from the denitrification reactor is void of dissolved oxygen, and as illustrated above, contains elevated amounts of NPOC which periodically includes residual acetate. The effluent also contains biomass (VSS) which has sloughed off the filter media through the natural course of aging. This was often evident in the water flushed from the post reactor tap before collecting samples. Removal of VSS and dissolved organics is essential to providing a biologically stable finished water. Reaeration, which occurs in

the roughing filter, both promotes the removal of residual dissolved organics and increases the palatability of the water. The water treatment facility in Coyle accomplishes these goals by treating the reactor effluent through an aerobic roughing filter to remove both particulate and soluble organics and then through a slow sand filter which serves as a "polishing" by removing additional organics by a combination of physical straining and biological activity.

4.3.1 Roughing Filter

The BioDen™ roughing filter is operated as an aerobic thin-film reactor. The biofilm is retained in the filter by the same media used in the denitrification reactor, but operation occurs in a downflow mode. The filter serves the purpose of re-oxygenating the treated water while biological activity consumes both dissolved and particulate organics and readjusts the pH, which has increased as a result of anaerobic denitrification.

Figure 25 shows anion concentrations experienced in the roughing filter effluent. The NO_3-N and NO_2-N concentrations from the post reactor tap have been superimposed on the figure for reference. Chloride and sulfate levels in the roughing and sand filter effluents did not significantly change from levels in the reactor effluent and so will not be discussed here. Chloride and sulfate data may be found in Appendix C and Appendix D. There are two occurrences worth discussing from Figure 25. First, one will notice that, with the exception of one occurrence on May 24, all residual acetate that was present in the reactor effluent has been removed post-reactor to non-detection levels. The second occurrence is that the nitrite that was found in the reactor effluent has begun

to oxidize to nitrate. Nitrite is an unstable oxidation state of nitrogen, and in the presence of dissolved oxygen, readily converts to nitrate. In a system operated under ideal, theoretical conditions, there would be no need for nitrite conversion to nitrate since all nitrogen would have been converted to nitrogen gas in the reactor. When intermediate nitrite does break through into the reactor effluent, it is important for nitrite to rapidly be oxidized to nitrate. First, it is the nitrite ion, whether by direct ingestion or by conversion of nitrate in the human body, that is responsible for methemoglobinemia in infants. Second, if nitrite is present at the time of chlorination, it will exhibit a chlorine demand as nitrite is oxidized to nitrate by the following reaction (Snoeyink and Jenkins, 1980):

$$H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-$$

$$2e^- + H^+ + HOCl \rightarrow Cl^- + H_2O$$

$$HOCl + NO_2^- \rightarrow NO_3^- + Cl^- + H^+$$

An increase in chlorine demand means that more chorine will be consumed and operating costs will similarly increase.

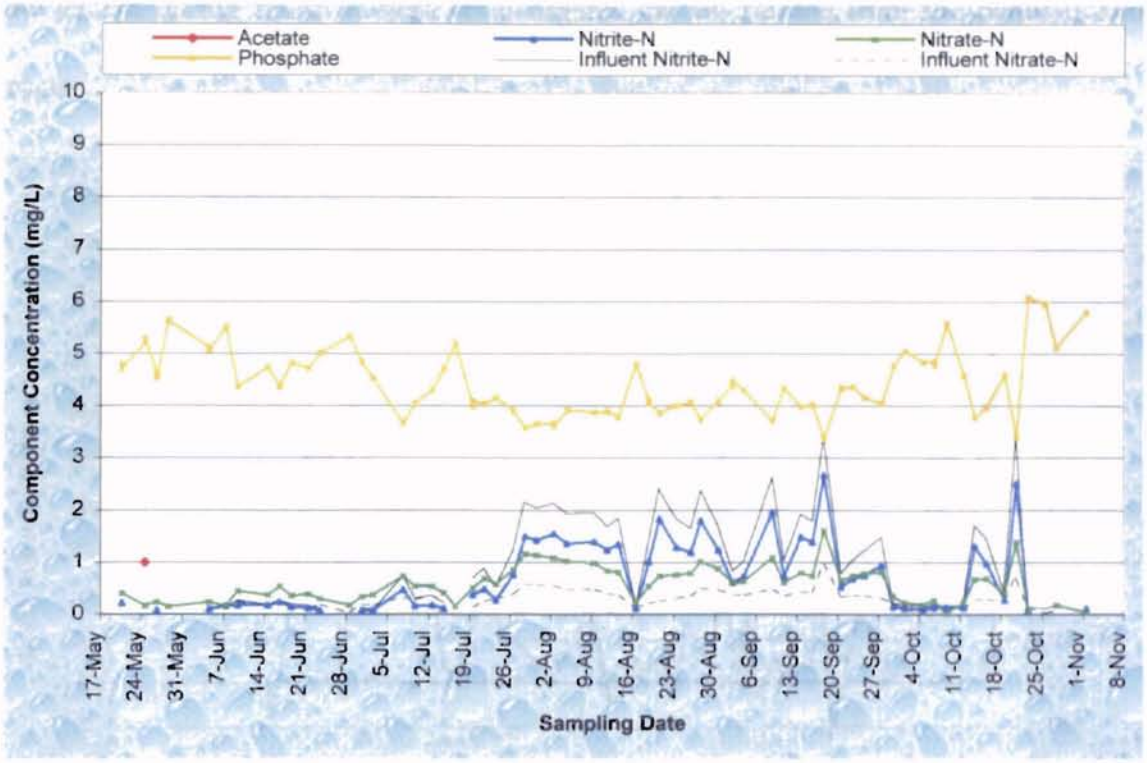

Figure 25: Low Range IC Results from the Post Roughing Filter Tap

An observation of NPOC data presented in Figure 26 shows that the roughing filter was successful in removing peak amounts of residual carbon leaving the denitrification reactor. With the exception of isolated occurrences on July 2 and September 10, NPOC in the roughing filter effluent remained fairly constant at an average concentration of 1.070 ppm. This is very close to the NPOC leaving the denitrification filter during times of compete acetate removal; little additional NPOC removal appears to have taken place in the roughing filter. In their "BioDen™ Technology Review," NRT (1999) indicate that the aerobic bacteria in the roughing filter should remove more than 50% of the particulate and soluble organic materials present in the denitrification reactor effluent. Figure 26 displays actual NPOC removal efficiencies achieved by the roughing filter during the study period. Notice that the actual removal efficiencies are typically quite

low except during times of high level organic carbon release from the denitrification reactor.

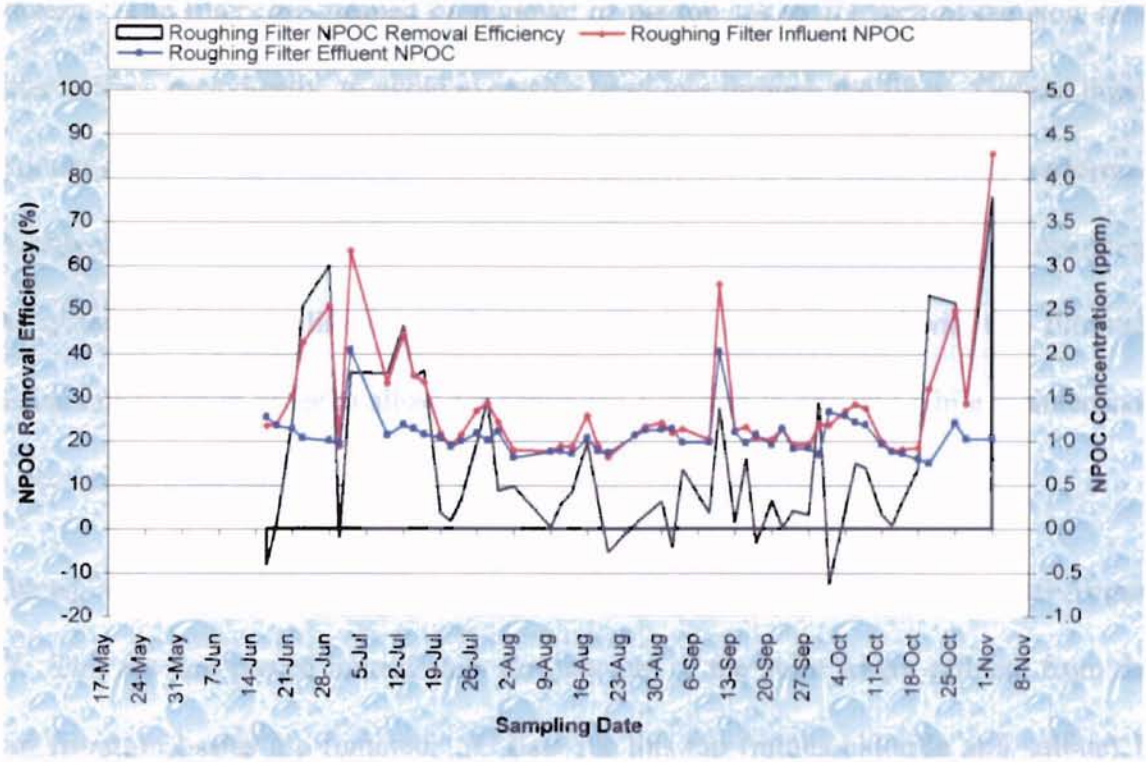

Figure 26: Roughing Filter NPOC Removal Efficiency

As mentioned in the previous section, a periodic air scour is required of the roughing filter to remove any excess biofilm that has accumulated. One air scour of the roughing filter occurred during the study, on September 15. No change in filter performance was apparent, with respect to residual nitrite conversion or NPOC removal efficiency.

4.3.2 Slow Sand Filter

The slow sand filtration process in Coyle consists of two concrete filtration basins operated in parallel. The basins are filled by a filter bed of sand (d_{10} = 0.8 - 1.2 mm; UC < 1.5) supported by gravel (NRT, 1999). The filters remove particulate materials by both physical filtration and by biological mechanisms. Operation of the slow sand filter leads

to the formation of a biological layer, called a "schmuzdecke," in the top few millimeters of sand. This layer is very effective in the removal of *Giardia*, *Cryptosporidium*, and bacteria. The filters are cleaned by removal of the top 1/4 to 1/2 inch of the slow sand filter surface periodically, to avoid excessive head-loss through the filter. Despite initial estimates of cleaning every four to six months (NRT, 1999), the Coyle facility performed its only cleaning, on one filter, during the sampling period. At the time of the operation the system had been on-line for nearly a year. The system is operated with two filtration basins in parallel in order to allow for continued filtration in one unit while maintenance is occurring in the other.

The tap at the outlet of the slow sand filters was not installed at the facility until August 27. This tap was placed immediately downstream of the point where effluent from the two filtration basins are remixed. IC data for this tap (minus chloride and sulfate) is presented in Figure 27. Note that nearly all nitrite has been removed by the sand filter. Of concern, however, is that nitrite was able to break through the sand filter on September 17 and October 20. The reader will recall that September 17 was the day following persistent electrical outages, and October 20 was the day on which the flow rate through the BioDen™ split stream had drifted to 17.9 gpm. In this figure (Figure 27), one can see that with the oxidation of intermediate nitrite occurring in the slow sand filter, nitrate levels increased over those recorded in the post roughing filter effluent.

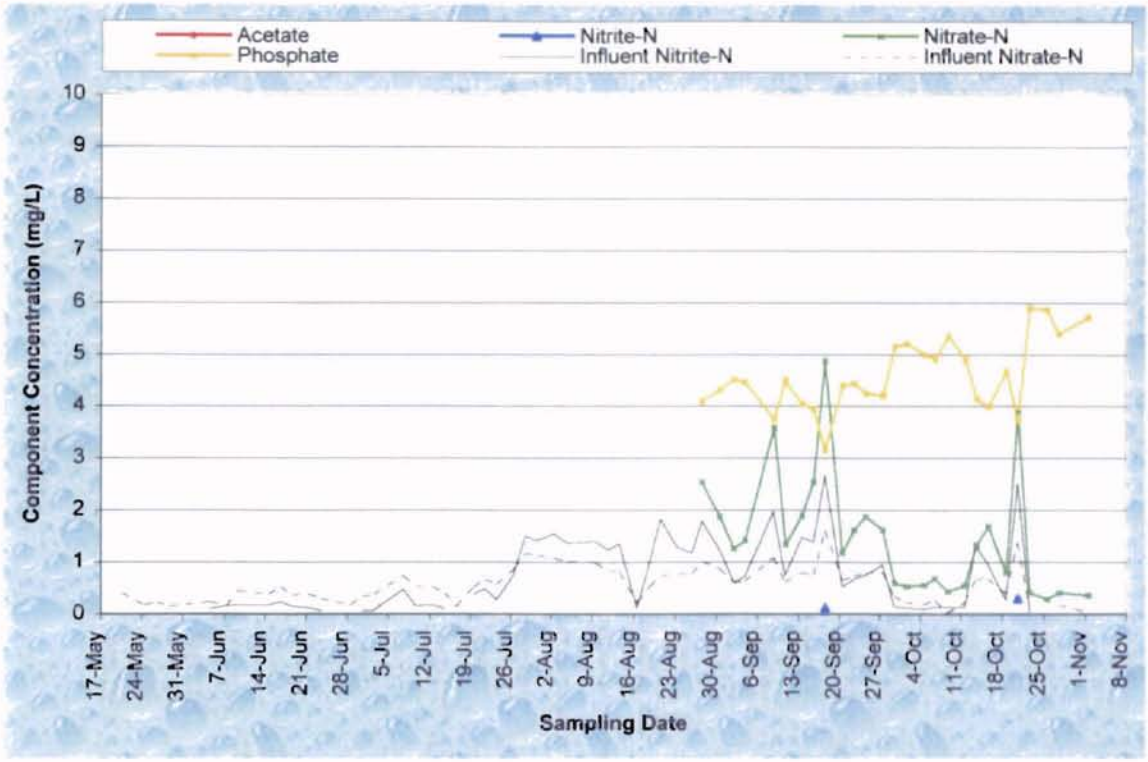

Figure 27: Low Range IC Results from the Post Sand Filter Tap

Figure 28 includes the NPOC data collected at the post sand filter tap. Figure 29 and Figure 30 illustrate the NPOC removal efficiencies experienced across both the slow sand filter and total filtration. In Figure 30 the dark line represents the NPOC removal efficiency experienced across the entire filtration process (NPOC removal from reactor effluent to slow sand filter effluent). The upper and lower shaded areas beneath the dark line represent the portion of the total NPOC removal contributed by the slow sand filter and roughing filter respectively. The reader will note that despite major fluctuations in post-reactor NPOC concentrations, the sand filter consistently removed an average 24.42% of the post-reactor NPOC. In contrast, the roughing filters NPOC removal efficiency was much more dependent upon influent NPOC concentration. As a result, the roughing filter served only to guard against peak releases of residual organics.

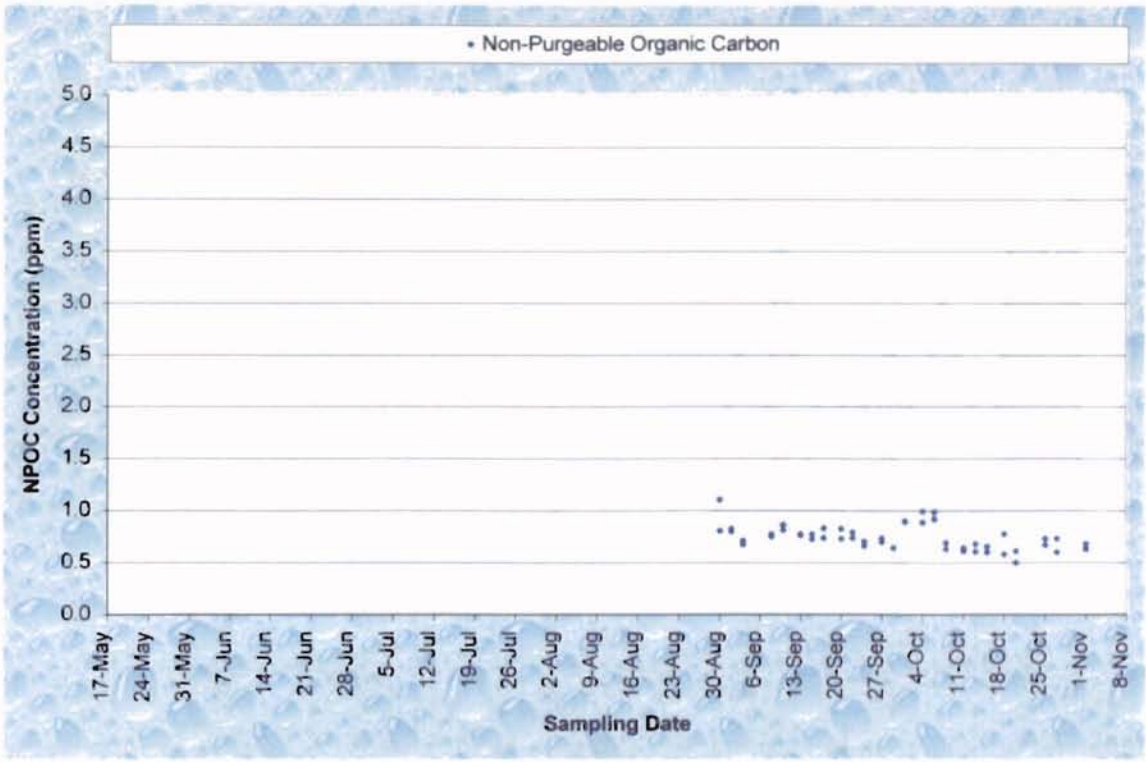

Figure 28: NPOC Results from the Post Sand Filter Tap

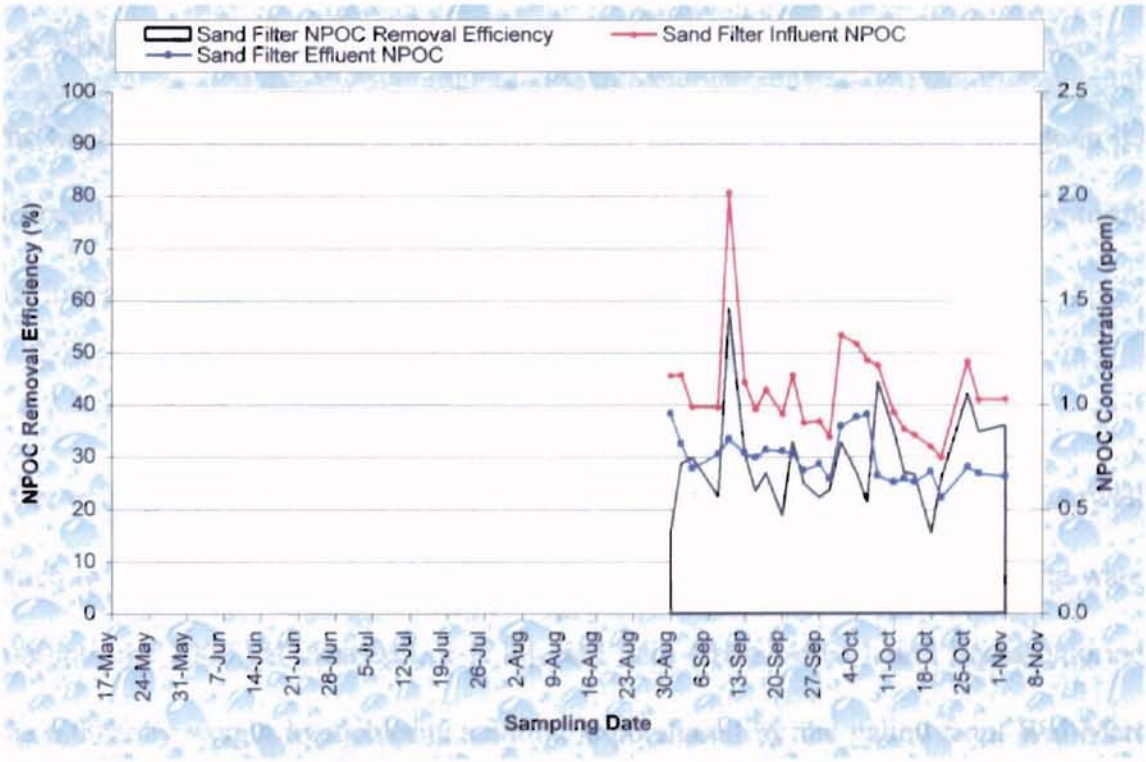

Figure 29: Sand Filter NPOC Removal Efficiency

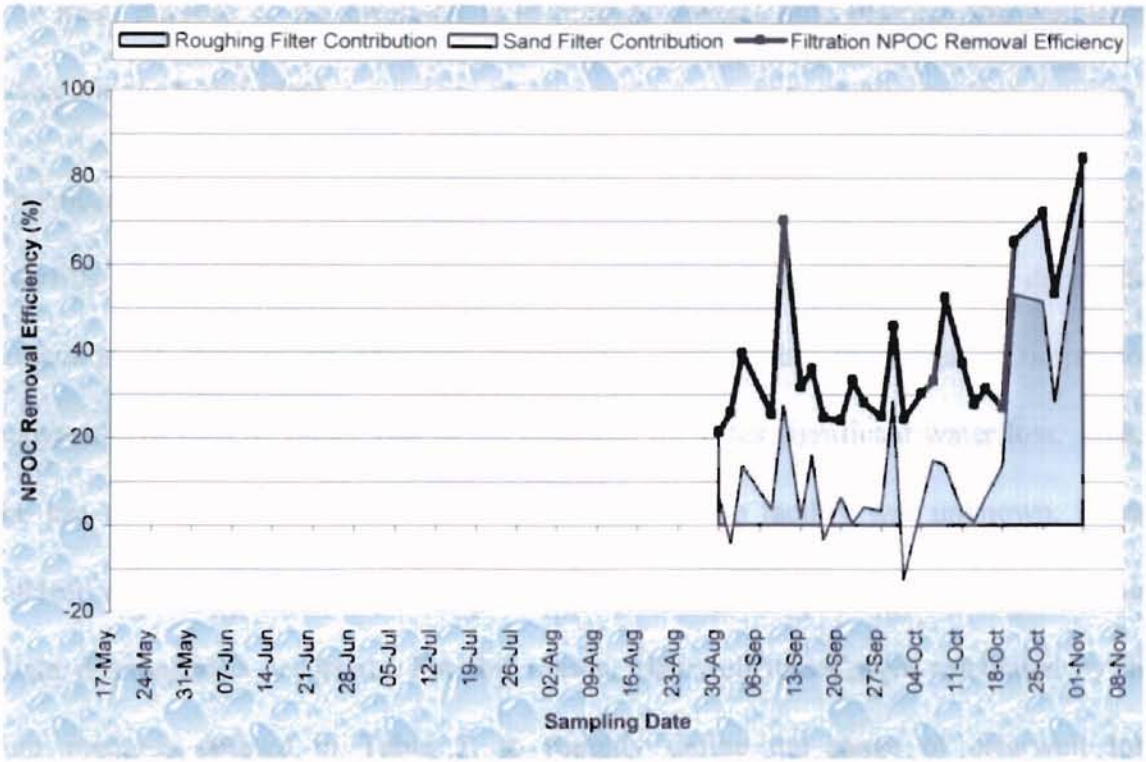

Figure 30: Overall Filtration NPOC Removal Efficiency

4.4 FINISHED WATER

The final group of processes at the Coyle facility consists of chlorination, storage in the clearwell, and reblending with a raw water split stream in preparation for release to the distribution system.

4.4.1 Clearwell

After exiting the sand filters, the denitrified water flows by gravity to the clearwell, which is located below ground level in a recessed corner of the building. As the water falls into the 1000 gal clearwell, it is injected with Great Value brand liquid chlorine. The 6.00% by weight hypochlorite solution is purchased by the gallon from Wal-Mart.

The main purpose of the clearwell is to provide contact time between the denitrified water and the disinfectant.

The clearwell is plumbed with an overflow outlet that dumps to waste if the clearwell overfills. On many occasions, water was observed coming out of the overflow during the collection of samples on Monday, Wednesday, and Friday mornings. Comparison between flow data on either side of the clearwell indicates significant water loss. Since the last calibration date of the flow meters used at the facility was unknown, it was unclear which flow rates recorded throughout the facility were the most reliable when slight discrepancies occurred. For this reason, clearwell losses were calculated by the four methods defined in Table 7, to roughly define the range of clearwell loss experienced (Figure 31). Flow data for this comparison came from the digital flow meter and totalizer installed to measure flow to the BioDen™ system, and an older flow totalizer located just downstream of the clearwell but prior to the blend station. Waste flow has been determined by the simple difference between daily usage at the points. Flow data have not been included for days affected by the malfunction of the digital flowmeter as noted in Appendix B. Water is required to be consumed for the occasional scouring of reactors, but continuous wasting of water, particularly post-treatment water, can become a sizable portion of the operating costs due to the additional acetate, phosphate, chlorine, and electricity consumed in the pumping and treatment of the wasted water.

Blend Corrected Flow Rate Estimate (gpd) Derived From:		Prior to Clearwell*	
		A BioDen™ Flow Totalizer[a]	B BioDen™ Flow Meter[b]
Following Clearwell	C Blend Flow Totalizer[c]	Water Loss = Rate A - Rate C	Water Loss = Rate B - Rate C
	D Timed Calculation from Blend Flow Meter[d]	Water Loss = Rate A - Rate D	Water Loss = Rate B - Rate D

* Total flows based upon raw flow data from the pre-clearwell meters were determined with consideration given to the blend ratio recorded. These flows will be a bit high as no water loss adjustments were able to be made to measured flows prior to applying the blend ratio.

[a] Corresponds to Appendix B, "Total Flow" column.

[b] Corresponds to Appendix B, "Feed Rate" column.

[c] Corresponds to Appendix B, "Total Flow to Blending Station" column.

[d] Corresponds to Appendix B, "Water Pumped" column.

Table 7: Definition of four methods used to estimate water loss from the clearwell overflow

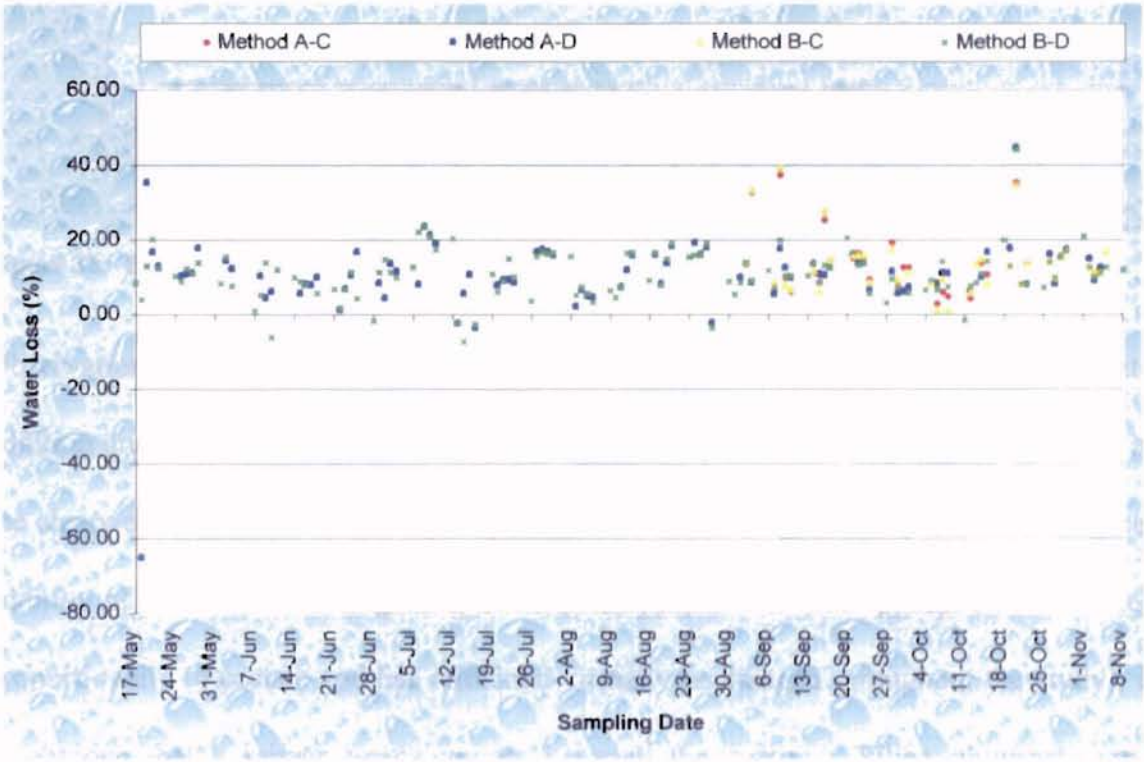

Figure 31: Estimated Clearwell Water Loss

As would be expected, there is little change to the anion profile in the clearwell. The chloride concentration is increased slightly as a result of chlorination (see Figure 32) and nitrite has completely returned to the nitrate form.

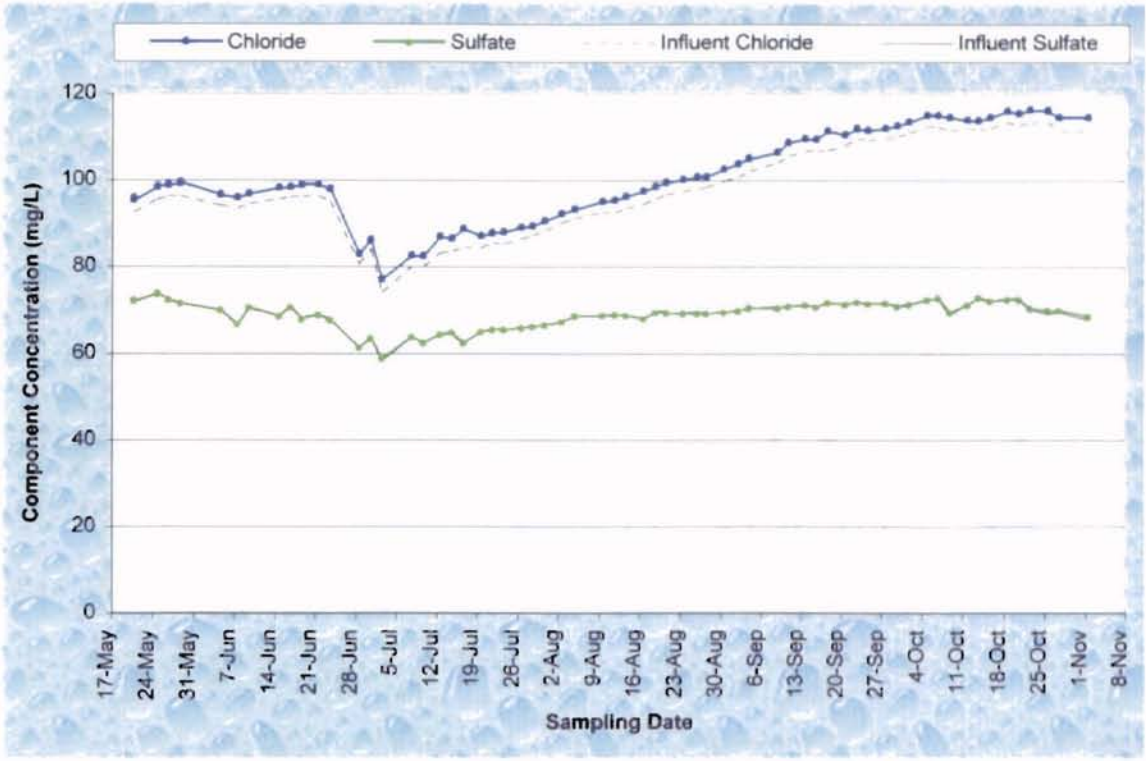

Figure 32: High Range IC Results from the Post Clearwell Tap

Observation of the post clearwell effluent demonstrates the relationship between acetate addition and nitrate removal. Figure 33 is a plot of the nitrate and phosphate present in the clearwell effluent. Using the phosphate curve as a surrogate to represent the original addition of acetate (valid for general comparison purposes because phosphate was added proportionally to acetate and has remained virtually unchanged throughout the study), it is obvious that a mirror image occurs between the curves. When phosphate, and therefore acetate, doses were high, nitrate was reduced to low levels. When acetate addition was insignificant, nitrate removal was low. NPOC levels remained steady in the clearwell effluent at an average concentration of 0.787 ppm. This is approximately the NPOC level originally experienced in the raw water.

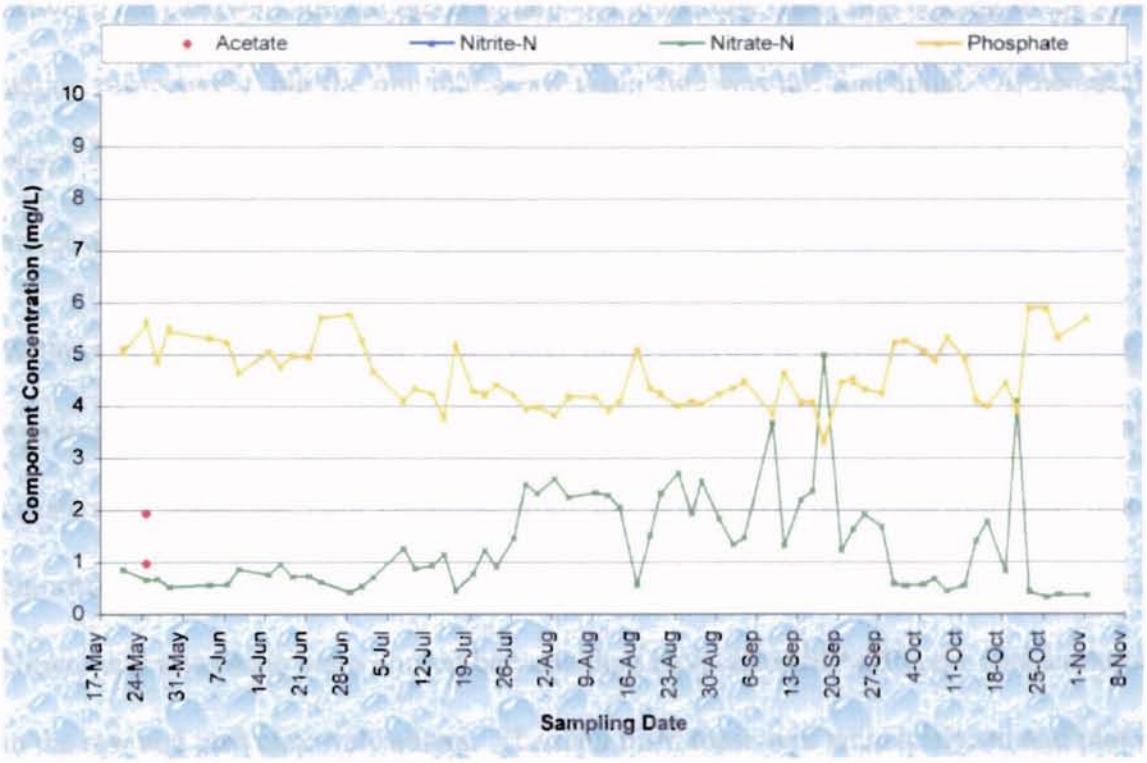

Figure 33: Low Range IC Results from the Post Clearwell Tap

4.4.2 Blended Water

Since it is unnecessary to treat drinking water to extremely low nitrate levels, the BioDen™ system treats only a portion of the raw water to low levels and then reblends with a portion of raw water such that the blended water contains an acceptable nitrate concentration with an adequate margin of safety (i.e., blended NO_3-N < 8.0 mg/L). At Coyle, water from the clearwell is brought up to line pressure by pump and then mixed with raw water via two identical blend valves. The blend ratio for the system was reported as a ratio of the two readings on the incremented flow valves. Throughout most of the study period, the blend ratio was 50:50. On three occasions, July 12 - 14, August 27 - September 1, and September 7, the flow rate was adjusted by increasing the percentage of raw water in the blend. Two identical flow totalizers were in place

between the clearwell and the blend station and in the raw water line leading to the blend station respectively, but the one in the raw water line was not functional. Although the blend valves were identical, they were old and the pressure behind each valve was unknown.

Without the flow data from two of the three pipes entering or leaving the blend station, it was impossible to directly confirm the recorded blend ratio. In the absence of flow data, nitrate and phosphate data collected from the raw water, post clearwell, and mixed chlorinated taps were used to complete a mass balance and confirm the blend ratio. Nitrate and phosphate were chosen because they have distinctly different concentrations in the raw and post clearwell waters. The data from these taps were analyzed and plotted in Figure 34 as a percent recovery of the measured concentration in the blended water by the theoretical blend concentration calculated from raw and post clearwell data according to the following equation:

$$\% \text{ Recovery} = [(R*r + C*c)/(r + c)]/M*100$$

where:

	R	=	Measured raw water concentration, mg/L
	r	=	Reading from raw water blend valve, % open
	C	=	Measured post clearwell concentration, mg/L
	C	=	Reading from the treated water blend valve, % open
	M	=	Measured mixed water concentration, mg/L

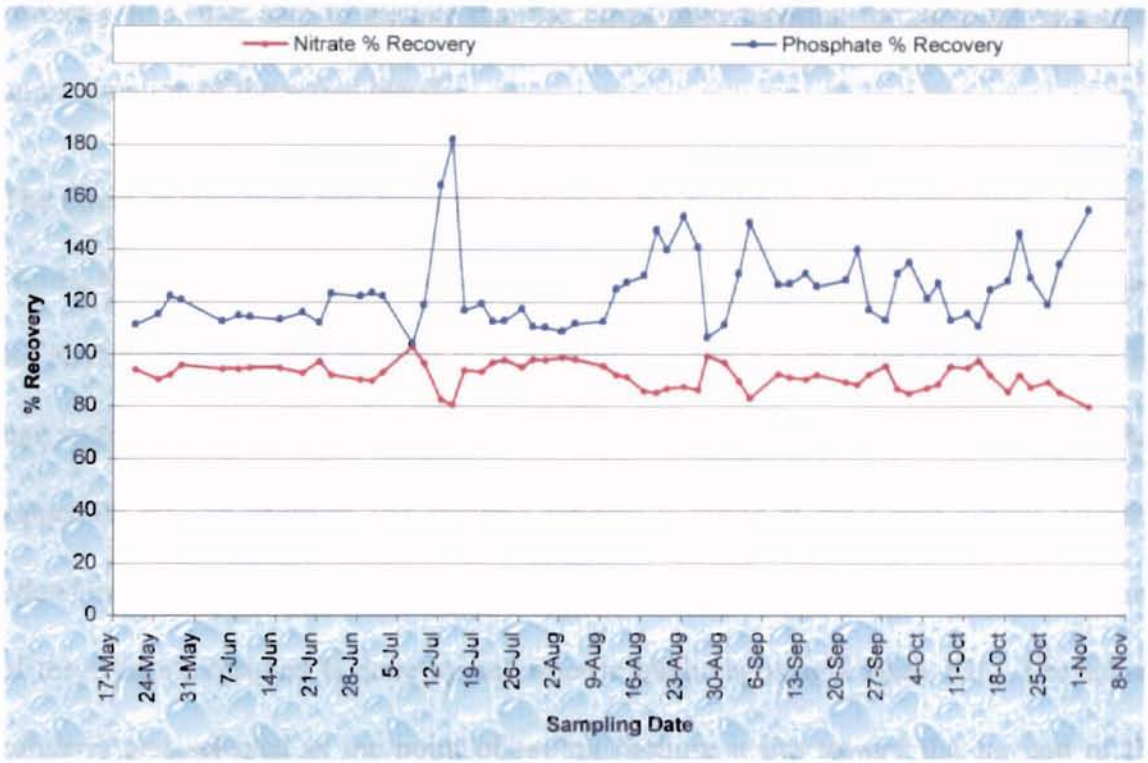

Figure 34: Blend Ratio Confirmation at the Post Clearwell Tap

One will notice that the percent recovery curves bear resemble each other in shape and are mirror images of their corresponding concentration curves throughout the treatment facility. Taken separately, neither curve would indicate 100% recovery; but, taken together, the two curves appear to be centered well about the 100% (or only slightly higher) recovery mark. It is the belief of the author that the apparent mirror image deviation from the 100% recovery line by the two plotted lines is a result of nitrate and phosphate being adjacent peaks in ion chromatography elution. Interferences may occur in the integration of peak areas of the adjacent peaks when one is much larger than the other, causing some portion of the peak area to be inaccurately accounted to the wrong peak. It is believed that based upon the data's reflective position about the 100%

recovery line, it is safe to assume that the blend ratio reported for each day is a close approximation of the actual blend.

The direct chlorination that regularly occurs in the facility is in the clearwell. In other words, the raw water that is used for blending relies on chlorine in the clearwell stream for its disinfection. Free chlorine is constantly monitored in the blended water by an in-line digital chlorine meter and recorded every morning by the system operator (see Appendix B). In addition, the chlorine residual is tested at the Coyle school cafeteria upon competition of daily monitoring and maintenance at the treatment facility. Testing of the chlorine residual is done by colormetric methods using a Hach Kit. The school cafeteria was selected as the point of testing because it lies toward the far end of the distribution system. From the residual chlorine concentration, it is suspected that the average residence time of water in the system is very short. Free chlorine leaving the plant averaged 1.14 mg/L and chlorine residual in distribution averaged 0.86 mg/L during the time encompassed by this study. The chlorine monitor at the Coyle facility is wired to start an emergency back-up chlorine pump if the detected chlorine residual drops too low. This back-up pump injects directly into the blended water.

Figure 35 and Figure 36 present the anion concentrations found in the blended water. This represents the final water that is released to the distribution system. Figure 37 shows the nitrate-nitrogen concentrations present in the raw and blended water along with a graphical depiction of the overall nitrate removal efficiency experienced by the facility during this study. The average NPOC in the blended water was 0.689 ppm.

Blending had little effect on the NPOC since the NPOC concentration in the clearwell and raw water were nearly identical.

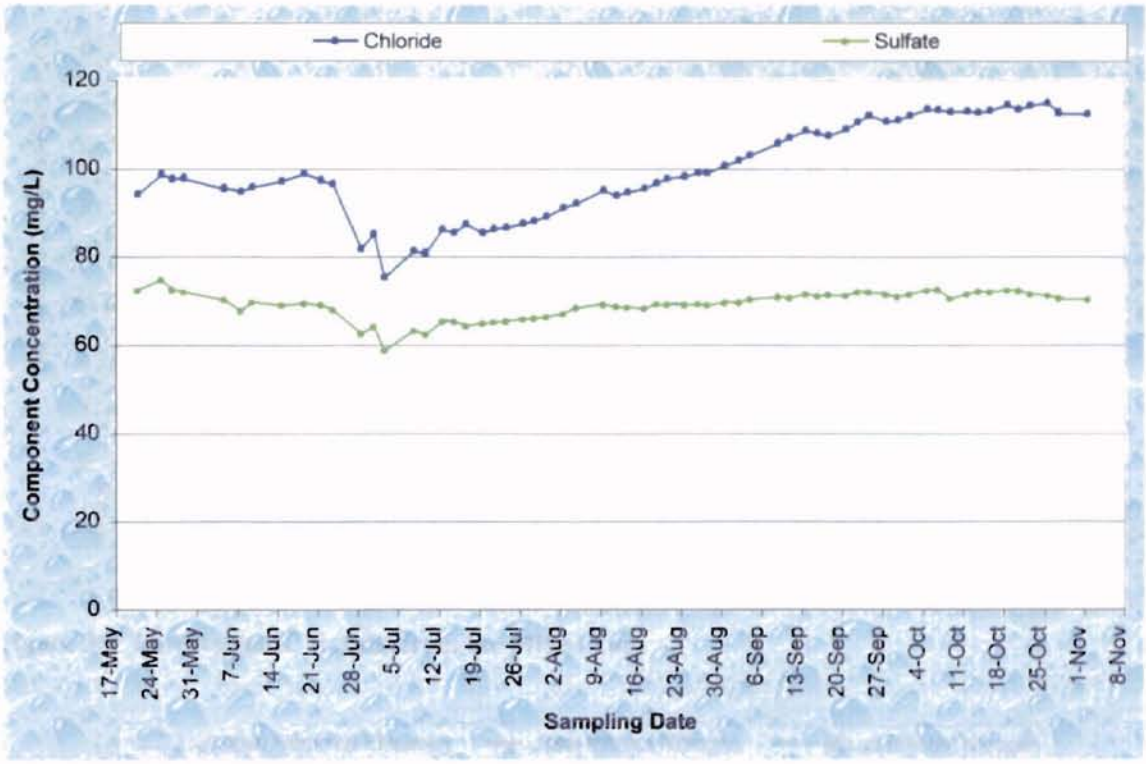

Figure 35: High Range IC Results from the Mixed Tap

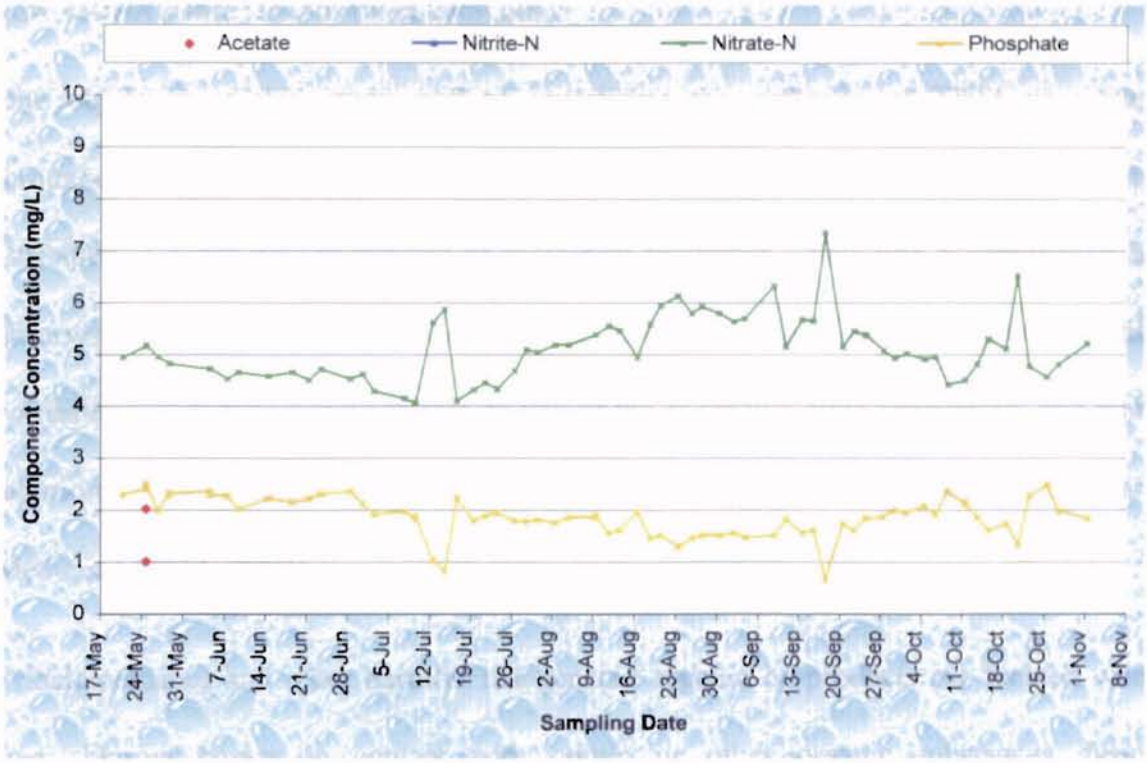

Figure 36: Low Range IC Results from the Mixed Tap

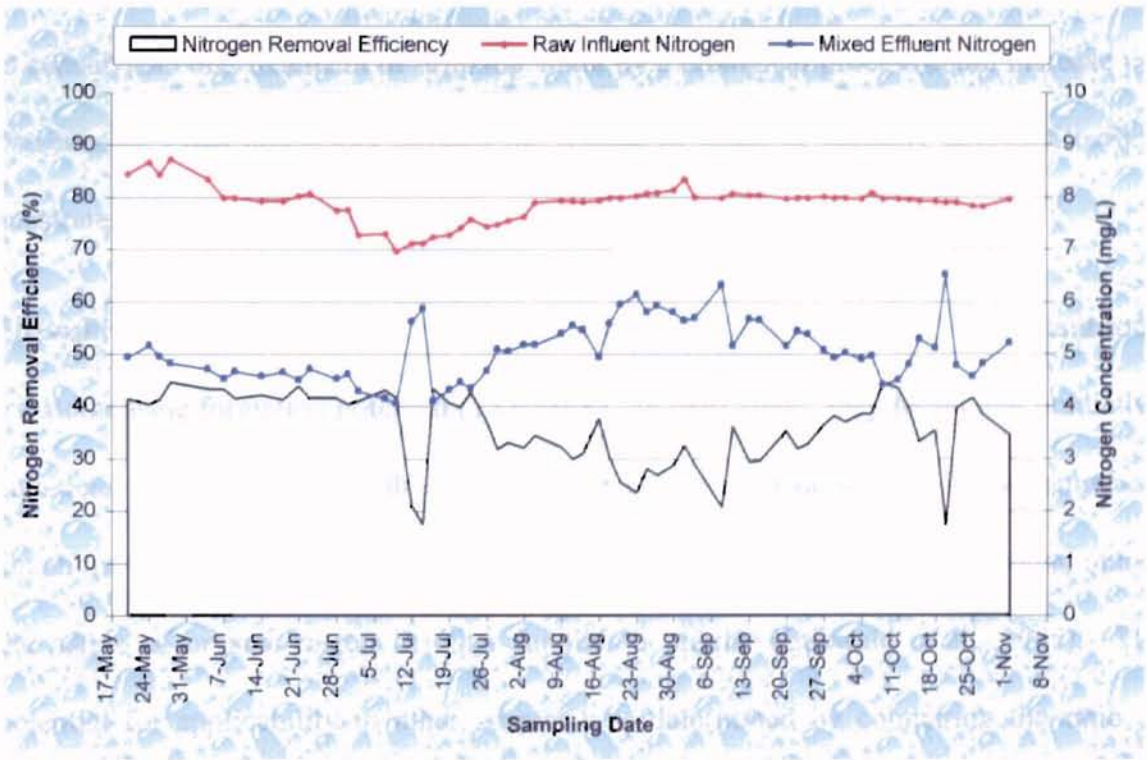

Figure 37: Total Plant Nitrogen Removal Efficiency

4.5 TRIHALOMETHANE PRECURSORS

One objective of this study was to investigate the presence of THM precursors throughout the facility, and note any fluctuations across unit processes that may be attributed in some way to the use of biological treatment. This was accomplished by observance of the ultraviolet absorbance at 254 nm of samples in conjunction with corresponding NPOC measurements, in lieu of the expensive, time-consuming, and more laborious trihalomethane formation potential (TFP) analysis described in Standard Methods (APHA, 1992).

Trihalomethanes and other harmful halogenated organic by-products are formed when free chlorine comes in contact with humic or other organic substances during chlorination or subsequent contact time with in the distribution system. Consequently, it is conceivable that treatment of drinking water by a biological process could increase the presence of THM precursors through the release of intact or partially degraded carbon substrate or decaying biomass.

Edzwald et al. (1985) reported good linear correlation between NPOC, UV_{254}, and total trihalomethane formation potential (TTHMFP). In their study, they found that predictive equations could be derived that could relate the three parameters. These empirical equations however, were found to be site-specific when applied to natural waters, unless the nature of organic matter in other supplies is similar (Edzwald et al., 1985). The potential for applicability to other sources was determined by comparing the ratio of UV_{254} to TOC of the two waters.

Figure 38 and Figure 39 show the range of NPOC and UV_{254} values respectively, measured at each point throughout the Coyle facility during the UV_{254} analysis period. In the case of the UV_{254} chart, it appears at first that there may be a slight increase occurring throughout the facility, but further observance of individual dates indicates that this trend is only obvious on a few select days such as September 10 and 13. The NPOC chart, however, displays great fluctuation throughout the facility. The drastic difference in the general appearance of the two charts (UV_{254} is relatively stable, NPOC increases drastically with vinegar addition and then declines) calls into question the similarity of water at the different taps throughout the facility and, thus, the ability to estimate THM precursors throughout the facility by use of UV_{254} and NPOC data alone.

Figure 40 shows the range of specific absorbances (UV_{254}/NPOC ratio) determined throughout the facility. The specific absorbance gives an indication of the similarity of the nature of organic material in the water at each location. Those taps exhibiting a similar range of specific absorbances, such as the raw, post clearwell, and mixed water taps, have a similar organic nature and are better suited to comparison with each other with respect to THM precursors via the UV_{254} and NPOC surrogate parameters than those taps such as the post vinegar tap where the specific absorbance is drastically different. Fortunately, the specific absorbance for taps at the head and tail ends of this system are roughly the same. The reader will notice that in both figures (Figure 38 and Figure 39), little fluctuation is detectable between the values measured in the raw water and those measured at locations following filtration, seeming to indicate that the biological

treatment process did not drastically change the relative concentration of THM precursors.

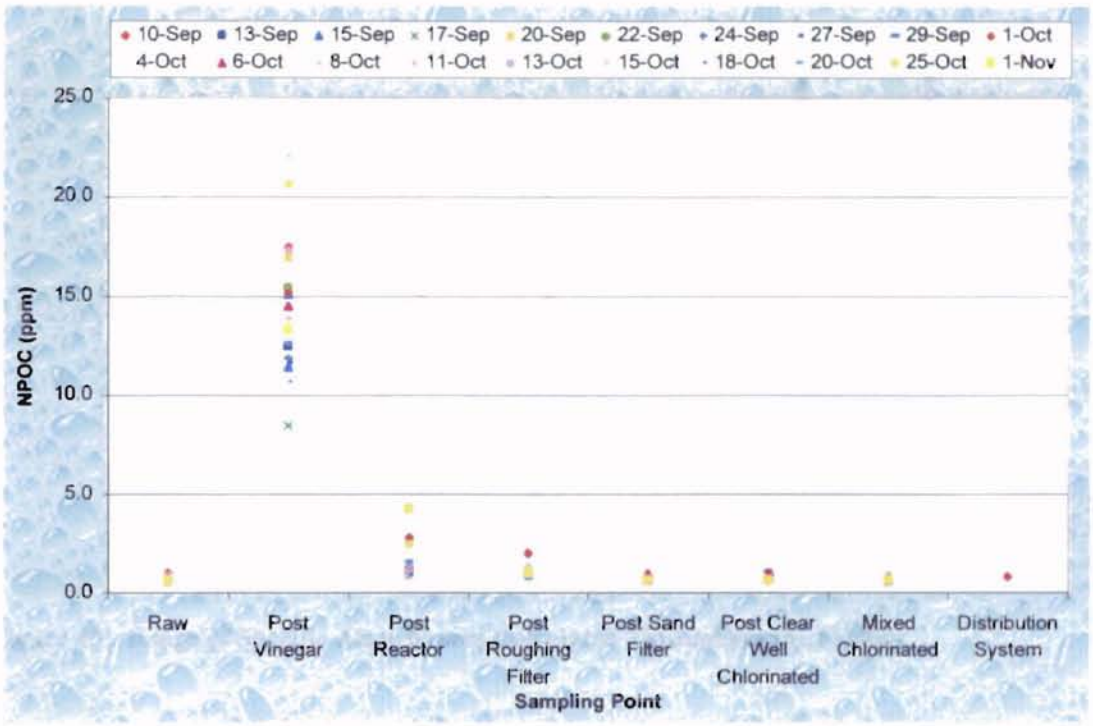

Figure 38: Range of NPOC Measured Throughout the Facility During UV_{254} Testing

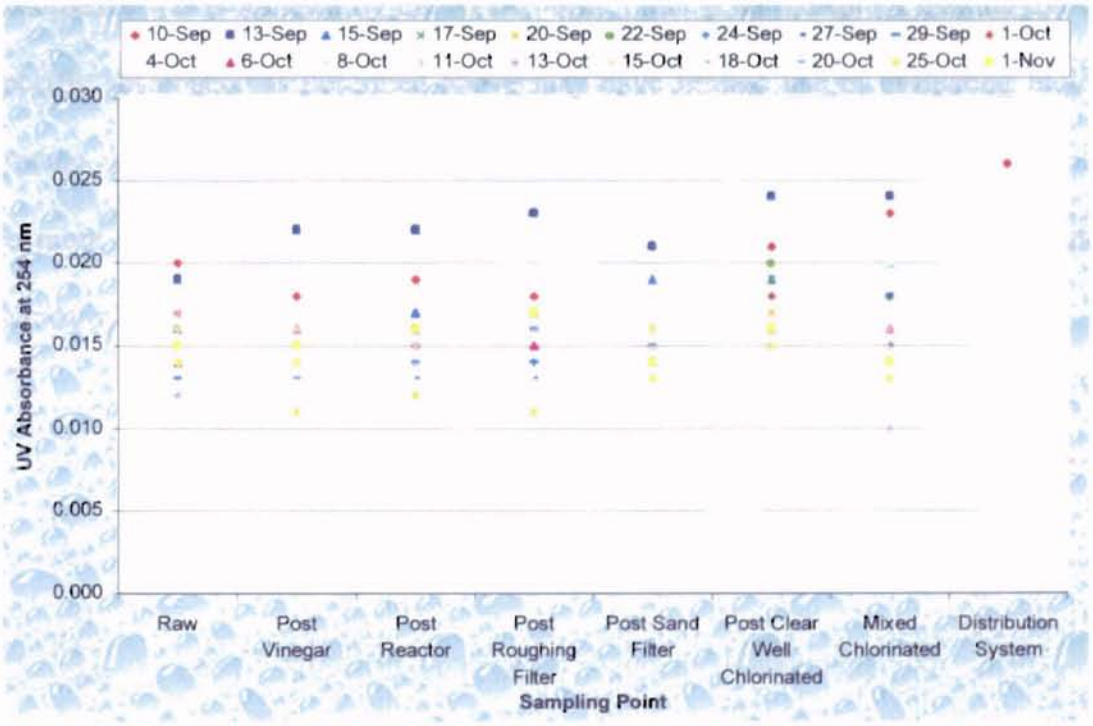

Figure 39: Range of Ultraviolet Absorbance at 254 nm Measured Throughout the Facility

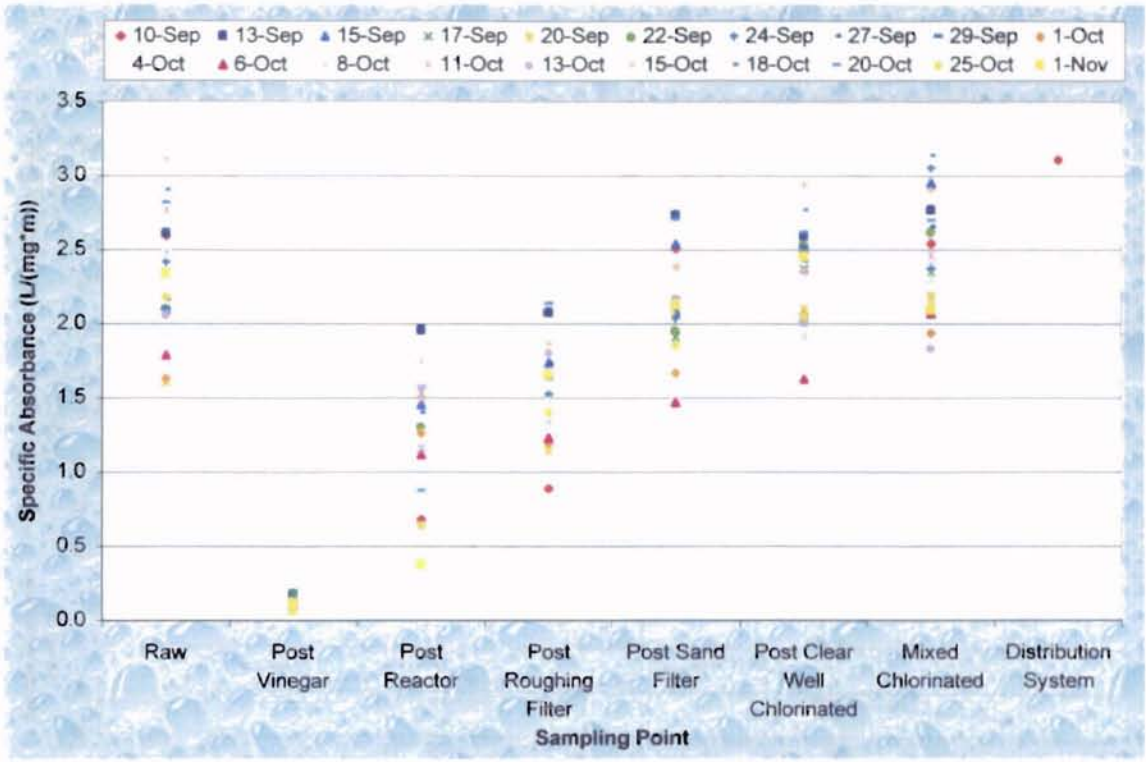

Figure 40: Range of Specific Absorbances Calculated Throughout the Facility

It is obvious that throughout the majority of the facility, the determination of the specific absorbance was dominated by the NPOC term. This is an indication that the use of the specific absorbance as described above may have limited use in evaluating biological systems where large amounts of organic substrate are added. In these instances, it may be more appropriate to apply one of the THM formation potential tests outlined in Standard Methods (APHA, 1992).

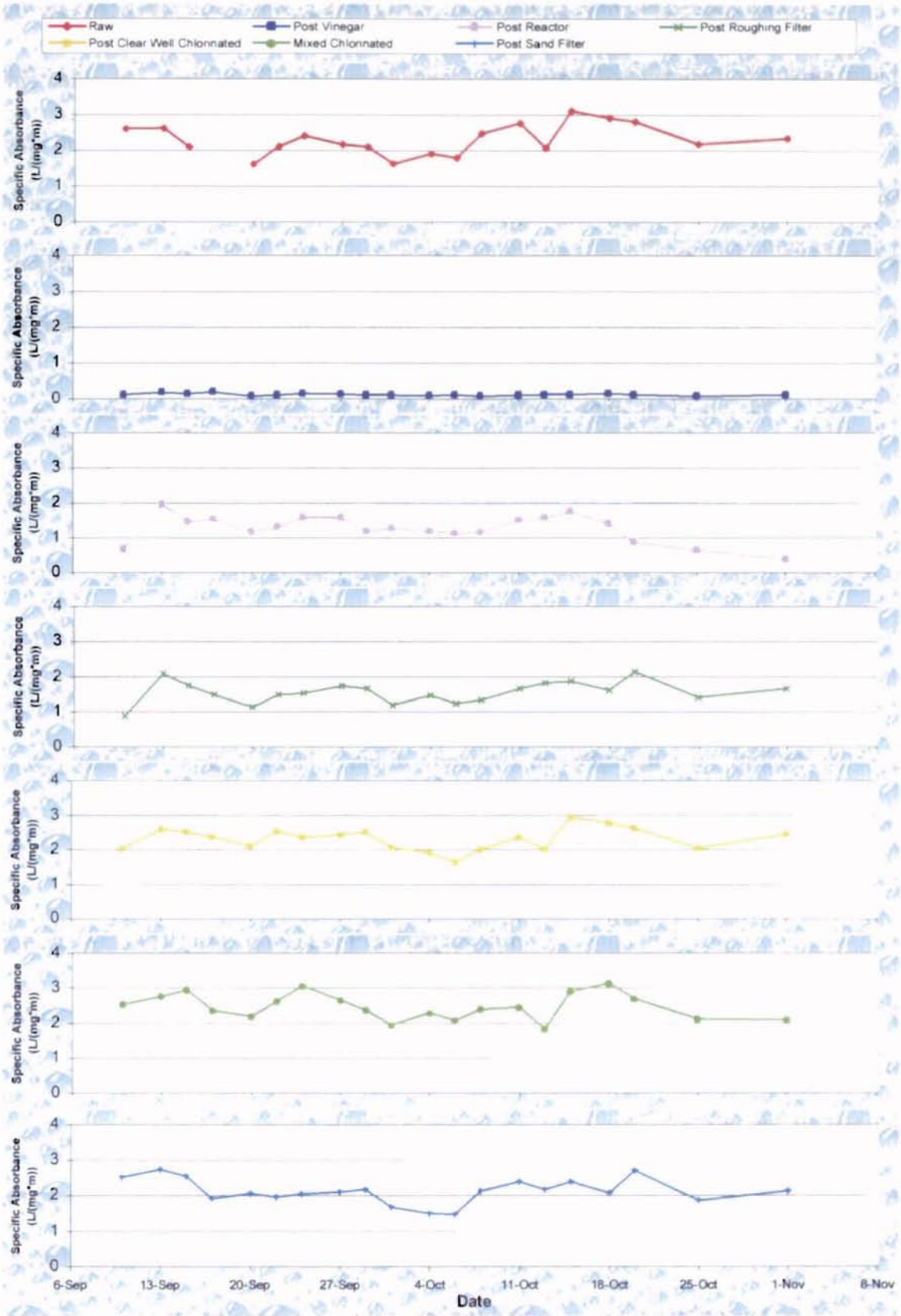

Figure 41: Specific Absorbance Fluctuation with Time Throughout the Facility

5.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

This study has been the first to investigate a commercially installed, full-scale stand-alone biological denitrification process for the treatment of drinking water in the United States. During the 5 1/2 month study of system performance at the Coyle, Oklahoma drinking water treatment facility valuable data and experiences were gathered in order to fulfill the three-fold purpose of this study. The purpose of this study was to:

- Evaluate the performance of the full-scale system at Coyle, as it is subjected to: (1) changing raw water quality, (2) normal plant operation and maintenance problems, and (3) operation by a traditional licensed operator, as opposed to research staff.

- Estimate the presence of THM precursors throughout the water treatment facility.

- Identify areas which merit further investigation if biological denitrification is to become a viable technology for the treatment of drinking water.

5.1 Evaluation of System Performance

Throughout the study it became clear that biological denitrification was not a treatment method best suited to the needs of the facility at Coyle, Oklahoma. The raw water quality experienced by the Coyle facility was much more stable than originally anticipated. At no time during the study did nitrate concentrations in the raw water ever exceed the established MCL of 10 mg/L NO_3-N, thereby requiring nitrate removal. The biological reactor and roughing filters employ living microorganisms and as such must

be operated continuously in order to maintain an active microbial population. As a result, the biological system consumed carbon and phosphate substrate, energy required for pumping, and operator man-hours during the full 5 1/2 month study with minimal improvement to the quality of the finished water (NO_3-N between the raw and distributed water was reduced from an already acceptable concentration of about 8 mg/L NO_3-N by an average of approximately 3 mg/L NO_3-N). Despite the poor suitability of biological denitrification to the needs of the Coyle facility, additional information was gathered on system performance, operation, and maintenance that should be of value in determining the suitability and operation of future applications.

As discussed in the previous chapter, the studied system was capable of achieving good nitrate removal (> 90% of nitrate-N + nitrite-N removed from water flowing through the reactor) when carbon substrate in the form of acetate was supplied in sufficient quantities. The facility was lacking, however, in the ability to consistently provide an appropriate carbon dose for the biological activity occurring in the reactor. Periods of insufficient carbon addition resulted in potentially serious accumulations of intermediate nitrite (as high as 3.36 mg/L NO_2-N). Excessive carbon dosing resulted in both residual organics up to 4.36 ppm NPOC being released in the reactor effluent as well as the occasional onset of sulfate reducing activity. This lack of consistency was due less to the effects of changing raw water quality as originally anticipated and more to the lack of a means by which the system operator could accurately determine and administer the carbon dose, a problem complicated by the attempt to denitrify a raw water with an already acceptable nitrate concentration.

Filtration processes at the facility were effective in providing opportunity, within an oxygen rich environment, for the intermediate nitrite to oxidize to nitrate and residual organic carbon to be removed via physical straining and biological consumption. This essential step insured that neither nitrite nor organic carbon was released to the distribution system at levels significantly higher than in the raw water. As a result, filtration served more as a safety net than a final polishing step in the treatment of reactor effluent. The roughing filter was found to be most effective in the elimination of large concentration breakthroughs of NPOC (> 1.5 ppm) and did little to reduce lower levels of residual NPOC (< 1.5 ppm) or intermediate nitrite. The slow sand filters consistently removed approximately 30% of the residual NPOC reaching them as well as the remaining intermediate nitrite (with the exception of two instances on September 17 and October 20 when nitrite broke through the sand filter but was not detected in the clearwell effluent).

Reactor performance during the study indicated the need for a better method of determining and applying a carbon dose appropriate to the water to be treated. A number of factors continue to hinder the accurate determination of this dose. The current method in use by the system operator relies heavily upon maintaining flow rates and substrate feed rates within historical operating ranges and is supplemented by a chart of theoretical matchings of flowrate to feed rate (presented previously as Table 6) developed by NRT. This approach makes use of two assumptions that may be inappropriate for use. First, it assumes that historical operating ranges have produced desired results. The current practice of tweaking the flow or feed rates because they appear to have increased or

decreased significantly from the previous day or over a period of several days provides opportunity for the operating ranges to drift from the optimal range if actual performance is not frequently checked. This introduces the second hindrance to determining the carbon dose to be applied. The current tables available to the system operator for determination of carbon feed rates are based upon an estimated 8.0 mg/L NO_3-N removal from a water containing 7.5 mg/L of dissolved oxygen. There is a problem in that frequent analysis for these parameters, along with TOC, is not currently required. As a result, the system operator has no way of verifying the NO_3^- or DO concentration of the reactor influent (allowing for the determination of dose by mathematically tabulated values), or of knowing the concentrations of NO_3^-, NO_2^-, and TOC in the final product water (adding credibility to the use of historical operating ranges and facilitating the development of valuable operator experience).

Normal operation of the facility calls for a routine air scour of both the main reactor and the roughing filter in order to remove excess accumulations of biomass. In addition, the slow sand filter must be serviced by removing the top layer of sand when headloss through the filter becomes excessive. These routine operations posed few problems for the operator who was able to conduct them without the assistance of a second operator. Non-routine operating and maintenance incidents did however cause temporary problems with system performance. Electrical outages on the night of September 16 and high water flow rates on October 20, resulted in only 50% nitrogen removal from reactor influent accompanied by high residual carbon being released on the second date. The

system recovered quickly from the upsets and regained typical nitrogen removals by the following sampling dates.

One finding of great concern, from an operational and economic perspective, was the amount of water loss that occurred throughout the facility. Water loss from the system was found to occur in one of two primary ways: through routine air scours required for reactor maintenance or as waste through the clearwell overflow. Water required to maintain the system in normal operating condition can hardly be considered wasted and should be viewed as part of normal operating costs. Overflow losses on the other hand, resulting from poor matching of flow rate to the demand and storage capacity of the system, can be avoided by optimization of water management. These losses resulted in an average of 4559 gpd of treated, unblended water, or approximately 12.5% of the water flowing through the reactor being released to waste throughout the study. This is water that would ideally have been mixed with an equal portion of untreated water (assuming the 50:50 blend ratio used during the study period) to create 9118 gpd of additional finished water for release to distribution. Water loss reduces the maximum treatment capacity of the reactor and in this quantity, can account for a large portion of the operating cost of the system since 12.5% of the acetate and phosphate supplied, as well as a portion of the electrical power required for pumping are allocated to the treatment of the wasted water.

5.2 Estimation of the Presence of Trihalomethane Precursors

This study found no indication that the concentration of trihalomethane precursors increased throughout the facility as a result of biological denitrification or successive filtration. Calculated values of the specific absorbance at 254 nm followed an increasing trend throughout the treatment process indicating that a proportionately larger amount of the organics present later in the treatment process belonged to potential THM precursors, but further investigation revealed that this increase in the UV_{254}/NPOC ratio was due primarily to the reduction of NPOC throughout the treatment process and not to an increase in the presence of THM precursors. Specific absorbance values throughout the facility were heavily dominated by the NPOC term, thus indicating that the use of this parameter may have limited use when applied to the evaluation of biological systems where proportionately large amounts of carbon substrate are added.

5.3 Recommendations for System Improvement and Future Study

Biological denitrification merits further research and consideration as an emerging treatment method for the removal of nitrates from drinking water because it has shown the ability, under controlled conditions, to achieve good nitrate reduction with minimal maintenance demands. This study has however, revealed a number of concerns, some quite serious, that deal with various operational aspects of the system that should be addressed in system operation and maintenance.

First, a simple and standardized method must be developed that will provide a traditionally licensed operator the ability to consistently determine and administer a

carbon dose appropriate to the influent raw water quality. There appears to be two general approaches that would work in the determination of the carbon dose: theoretically (based upon stoichiometric values derived for a known influent raw water quality) and empirically (based upon measured reactor performance). In either case, it appears that it will be necessary to provide scheduled analytical determination of water quality (NO_3^-, NO_2^-, and organics) in the raw and/or finished water for the determination of the carbon dose or verification of reactor performance. Drinking water facilities considering the use of biological treatment would do well to prepare themselves for this increased volume of water quality analysis since inconsistent reactor performance in this study indicates that the system should be closely monitored for nitrites and organic carbon released in the finished water.

Though not the only solution, similar installations in France have had success with full automation including an in-line nitrite meter (Richard and Thebault, 1992). Automation of both normal operation and reactor washes allowed for the reduction of manpower expenditure from every morning to two mornings a week to check and maintain sensors and automatic systems as well as actual plant control operations. The fully automated plant automatically ceases water production and alerts operating staff when there is low chlorine, high nitrites, high nitrates, or reactor clogging. Where automation is not practical, other options exist. The operator may be provided with equations or mathematically derived tables and/or charts that are applicable over the whole range of anticipated influent conditions and reactor performance needs. This approach should

account for the possibility of changing raw water quality and its application should be based upon periodic checks of actual influent NO_3^- and DO.

Second, water management practices between the plant and distribution system must be optimized in order to avoid water loss through holding tank overflows. Waste through overflow appears to be a common problem for biological facilities which typically require uninterrupted use and has been documented previously by Richard and Thebault (1992). Since biological denitrification, and the BioDen™ system in particular, is a technology that may be retro-fitted into an existing treatment works that may not have been operated continuously in the past, capacity issues should become key parameters in the design of future installations. It must be understood that the installation of biological denitrification technologies into a relatively simple groundwater facility has the effect of changing the facility from batch process operation into continuous operation. This change in operation validates the need to take a broad look at the size and sufficiency of the whole treatment and distribution system. Not only should the system be sized to accommodate peak demands, but the system should also provide adequate storage to meet continuous off-peak production. The operator should be provided with the knowledge or guidance required to adjust system production without disturbing system performance, as seasonal water usage changes.

Third, since nitrate levels in natural ground waters can exhibit seasonal fluctuation, it appears that it would be beneficial for researchers to investigate the development of an economical "stand-by" mode that the reactor could be put into during times of low influent nitrate. Unlike ion-exchange and reverse osmosis, biological denitrification

reactors cannot be temporarily shutdown when seasonal variation provides an influent raw water quality meeting the MCL for nitrates; they require continuous operation to maintain an active microbial population. This "stand-by" operation may take the form of a recirculation mode requiring the addition of small amounts of nitrate and carbon substrate in order to maintain an active microbial population. Key parameters to be investigated would be the ability and speed with which the system could be revived and brought back into service and the cost of feeding the recirculating system vs. the cost of regular operation during times of low nitrate contamination.

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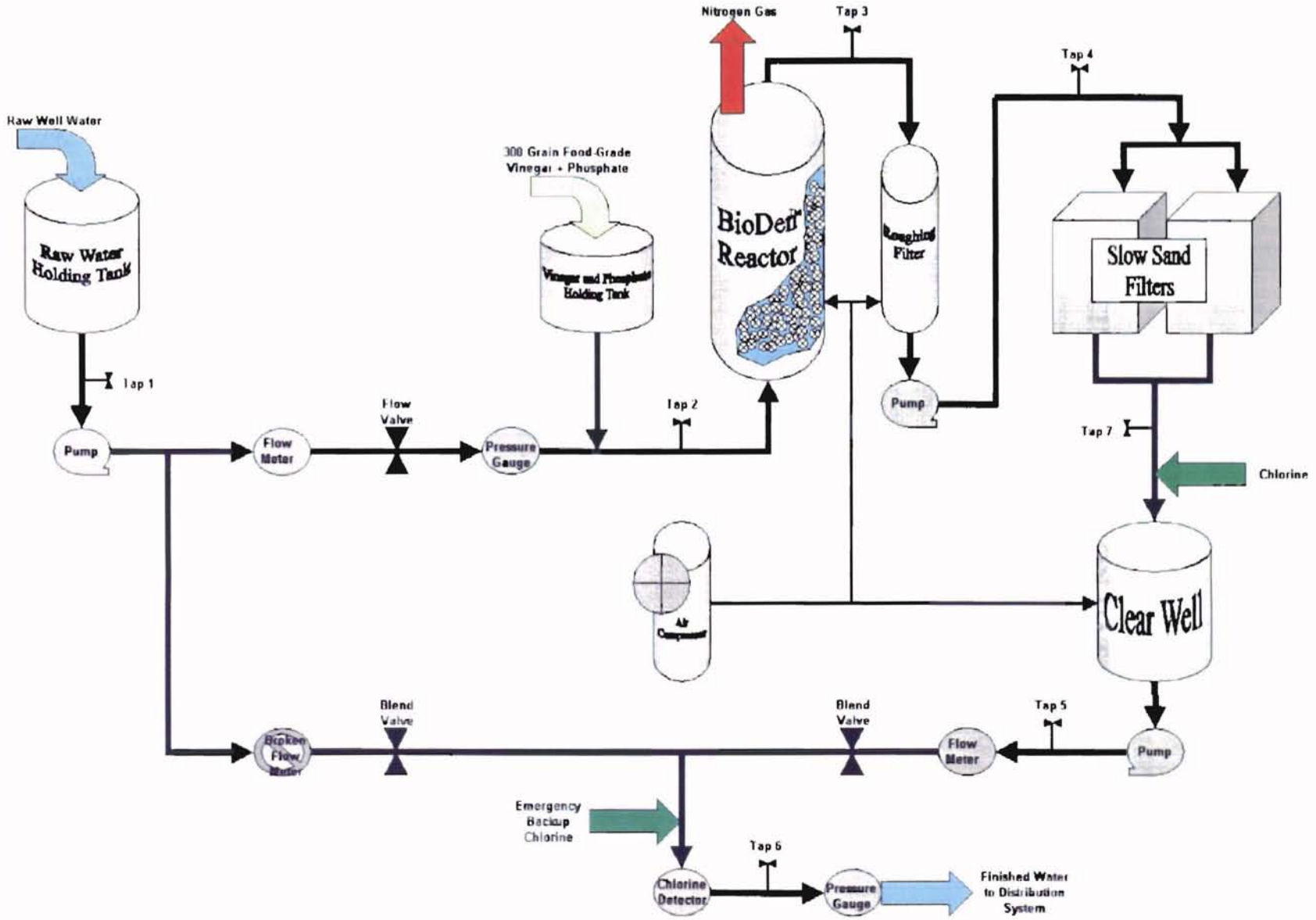
APPENDICES

APPENDIX A

FACILITY SCHEMATIC


Nitrogen Gas
Tap 3
Tap 4
Raw Well Water
300 Grain Food-Grade
Vinegar + Phosphate
BioDen™
Reactor
Roughing
Filter
Slow Sand
Filters
Raw Water
Holding Tank
Vinegar and Phosphate
Holding Tank
Tap 1
Pump
Flow
Meter
Flow
Valve
Pressure
Gauge
Tap 2
Pump
Tap 7
Chlorine
Air
Compressor
Clear Well
Blend
Valve
Blend
Valve
Tap 5
Broken
Flow
Meter
Flow
Meter
Pump
Emergency
Backup
Chlorine
Tap 6
Chlorine
Detector
Pressure
Gauge
Finished Water
to Distribution
System

APPENDIX B

FACILITY OPERATION DATA

May	Time	Blend Ratio			Feed Rate (gpm)	Total Flow (gal)		Vinegar Feed (ml/min)	Total Flow To Blending Station (gal)	Water Pumped (gpd)	Chlorine (plant)	Chlorine (residual)	Alkalinity	pH	Stability	Room Temp (C)	Comments
1										37440	1.11	0.96	360	7.2	-10		
2										37440	1.25	0.98	360	7.2	-10		
3										37440	1.29	0.79	360	7.2	-10		
4										36420	1.29	0.79	360	7.2	-10		
5										35210	1.25	0.73	360	7.2	-10		
6										34620	1.15	0.63	360	7.2	-10		
7	7:35	50:	50	*	13.5	2961853		6.50		31680	1.03	0.60	360	7.2	-10		
8										31680	1.11	0.61	360	7.2	-10		
9										31680	1.14	0.71	360	7.2	-10		
10	7:10	50:	50		13.2	3020578		6.50		31680	1.22	0.81	362	7.2	—		
11	7:05	50:	50		12.9	3039065		6.50		34560	1.34	0.91	359	7.2	-3		
12	7:15	50:	50		13.2	3057939		6.30		34560	1.17	1.20	359	7.2	-3		
13	7:10	50:	50		12.0	3075661				31680	1.29	1.10	359	7.2	-3		
14	7:10	50:	50		14.2	3094724		6.60		31680	1.08	0.95	359	7.2	-3		
15										30240	1.20	0.91	359	7.2	-3		
16										30240	1.21	0.78	359	7.2	-3		
17	8:15	50:	50		13.1	3150890		6.20		34560	1.16	0.77	359	7.2	-3		
18	7:15	50:	50		13.0	3161789				36000	1.23	0.82	359	7.2	-3		Air Scour
19	7:15	50:	50		13.8	3188494		6.75		34560	1.69	1.00	359	7.2	-3		
20	7:05	50:	50		14.4	3208341		6.50		33120	1.20	0.97	359	7.2	-3	22	
21	7:05	50:	50		13.1	3227327		6.50		33120	1.27	0.96	359	7.2	-3		
22										33120	1.21	0.92	359	7.2	-3		
23										33120	1.31	0.98	359	7.2	-3		
24	7:10	50:	50		12.8	3284165		6.50		33120	1.17	0.46	359	7.2	-3	20	
25	7:05	50:	50		12.6	3302594				33120	1.21	1.00	359	7.2	-3		
26	7:03	50:	50		13.1	3321150	^	6.25		33120	1.17	0.82	359	7.2	-3	20	
27	7:08	50:	50		12.9	3339718		7.00		33120	1.14	0.79	359	7.2	-3		
28	7:10	50:	50		12.2	3358075		7.25		30240	1.29	0.82	359	7.2	-3	19	
29										30240	1.11	0.61	359	7.2	-3		
30										28800	1.20	0.80	359	7.2	-3		
31										20800	1.16	0.79	359	7.2	-3		

^ Indicates that feed rate was increased by operator after recording flow for the day.
v Indicates that feed rate was decreased by operator after recording flow for the day.
* Indicates that flow meter was not working when flow data was taken.

June	Time	Blend Ratio			Feed Rate (gpm)	Total Flow (gal)		Vinegar Feed (ml/min)	Total Flow To Blending Station (gal)	Water Pumped (gpd)	Chlorine (plant)	Chlorine (residual)	Alkalinity	pH	Stability	Room Temp (C)	Comments
1	7:07	50:	50		12	3427803		7.00		31680	1.45	1.01	359	7.2	-3		
2	7:05	50:	50		13	3446299		7.00		31680	1.15	0.96	359	7.2	-3		
3	7:08	50:	50		11.9	3464313				31680	1.20	0.95	359	7.2	-3		
4										31680	1.14	0.92	359	7.2	-3		
5										31680	1.18	0.90	359	7.2	-3		
6										31680	1.19	0.90	359	7.2	-3		
7	7:10	50:	50	^	11.1	3535392		6.90		31680	1.20	0.91	370	7.1	-----	24	
8	7:10	50:	50		11.6	3553036				31680	1.23	0.91	360	7.2	-10		
9	7:02	50:	50	v	14.5	3571849		7.00		36000	1.06	0.74	360	7.2	-10	25	
10	7:05	50:	50	^	11.2	3590077				34272	1.16	0.91	360	7.2	-10		
11	7:10	50:	50	*	12.5	3601882		6.90		31680	1.25	0.94	360	7.2	-10	—	
12										31680	1.19	0.91	360	7.2	-10		
13										31680	1.15	0.90	360	7.2	-10		
14	6:58	50:	50		12.2	3648932				31680	1.22	0.92	360	7.2	-10	22	
15	7:05	50:	50		13.7	3667991		6.50		36000	1.10	0.84	360	7.2	-10		
16	7:06	50:	50		13.0	3686771		6.80		34560	1.06	0.80	360	7.2	-10	22	
17	7:05	50:	50	^	11.0	3703947				31680	1.30	0.92	360	7.2	-10		
18	7:10	50:	50		12.2	3722325		6.50		33120	1.17	0.90	360	7.2	-10	21	
19										31680	1.30	0.91	360	7.2	-10		
20										31680	1.40	0.97	360	7.2	-10		
21	7:03	50:	50	*	11.8	3772038		6.50		31680	1.25	0.91	360	7.2	-10	24	Air Scour
22	7:10	50:	50	^	11.2	3788057	v	7.75		31680	1.07	0.81	360	7.2	-10		
23	6:57	50:	50		11.8	3805030		7.50		31680	1.38	0.97	360	7.2	-10	23	
24	7:05	50:	50		12.4	3822692				31680	1.18	0.89	360	7.2	-10		
25	9:40	50:	50		11.5	3841712		7.50		31680	1.17	0.89	360	7.2	-10		
26										31680	1.18	0.90	360	7.2	-10		
27										31680	1.27	0.91	360	7.2	-10		
28	7:20	50:	50		10.8	3889390		7.50		31680	1.27	0.91	360	7.2	-10		
29	7:00	50:	50		12.4	3906653				31680	1.10	0.84	360	7.2	-10		
30	6:55	50:	50		12.9	3923196				31680	1.01	0.80	360	7.2	-10		

^ Indicates that feed rate was increased by operator after recording flow for the day.
v Indicates that feed rate was decreased by operator after recording flow for the day.
* Indicates that flow meter was not working when flow data was taken.

July	Time	Blend Ratio			Feed Rate (gpm)	Total Flow (gal)	Vinegar Feed (ml/min)	Total Flow To Blending Station (gal)	Water Pumped (gpd)	Chlorine (plant)	Chlorine (residual)	Alkalinity	pH	Stability	Room Temp (C)	Comments
1	7:10	50:	50		12.4	3941526			31680	1.34	0.99	360	7.2	-10		
2	7:05	50:	50		12.2	3959421			31680	1.30	0.93	360	7.2	-10	26	
3									31680	1.21	0.90	360	7.2	-10		
4									31680	1.13	0.87	360	7.2	-10		
5	7:30	50:	50		12.6	4016342			31680	1.16	0.80	360	7.2	-10		
6	7:00	50:	50		14.1	4033539			31680	1.12	0.79	360	7.2	-10		
7	6:50	50:	50		14.4	4054217			31680	1.27	0.81	360	7.2	-10	28	
8	7:00	50:	50		13.9	4074306			31680	1.41	1.00	360	7.2	-10		
9	7:05	50:	50		13.3	4093844			31680	1.19	0.80	360	7.2	-10		
10									31680	1.22	0.81	360	7.2	-10		
11									31680	1.30	0.90	360	7.2	-10		
12	7:00	40:	60		13.8	4148846	6.14		31680	1.24	1.13	360	7.2	-10		
13	7:10	40:	40	^	12.7	4167100			37440	1.23	1.12	360	7.2	-10		
14	7:00	30:	60	^	12.1	4186896	6.40		37440	1.22	1.12	360	7.2	-10		
15	7:00	50:	50		11.5	4205414			33120	1.27	1.13	360	7.2	-10		
16	7:05	50:	50		11.2	4221365	6.50		33120	1.27	1.13	360	7.2	-10		
17									33120	1.18	1.00	360	7.2	-10		
18									33120	1.25	0.97	360	7.2	-10		
19	7:10	50:	50		14.0	4269673	6.00		36000	1.27	0.98	360	7.2	-10		
20	7:10	50:	50		13.3	4289190			36000	1.25	0.97	370	7.3	----		
21	7:03	50:	50		13.7	4309004	6.25		36000	1.20	0.82	364	7.1	-6		
22	7:05	50:	50		14.7	4328819			36000	1.23	0.91	364	7.1	-6		
23	7:00	50:	50		13.9	4348475	6.60		36000	1.22	0.91	364	7.1	-6		
24									36000	1.22	0.91	364	7.1	-6		
25									36000	1.15	0.87	364	7.1	-6		
26	7:05	50:	50	^	14.0	4410396	6.00		38880	1.19	0.90	364	7.1	-6	28	
27	7:10	50:	50		16.0	4433735			38880	1.13	0.86	364	7.1	-6		
28	7:10	50:	50		16.2	4457247	6.00		38880	1.11	0.85	364	7.1	-6	28	
29	7:07	50:	50		16.1	4480551			38880	1.12	0.86	364	7.1	-6		
30	7:07	50:	50		16.2	4503651	6.30		38880	1.11	0.85	364	7.1	-6	28	
31									38880	1.08	0.83	364	7.1	-6		

^ Indicates that feed rate was increased by operator after recording flow for the day.
v Indicates that feed rate was decreased by operator after recording flow for the day.
* Indicates that flow meter was not working when flow data was taken.

August	Time	Blend Ratio			Feed Rate (gpm)	Total Flow (gal)		Vinegar Feed (ml/min)	Total Flow To Blending Station (gal)	Water Pumped (gpd)	Chlorine (plant)	Chlorine (residual)	Alkalinity	pH	Stability	Room Temp (C)	Comments
1		50:	50							38880	1.05	0.81	364	7.1	-6		
2	7:05	50:	50		16	4573232		6.75		38880	1.08	0.83	364	7.1	-6	28	
3	7:00	50:	50		15.8	4595286				43200	1.15	0.92	364	7.1	-6		
4	7:10	50:	50		16.2	4618405		6.50		43200	1.05	0.81	364	7.1	-6		
5	7:10	50:	50		15.9	4641097				43200	1.01	0.80	364	7.1	-6		
6	7:00	50:	50		15.5	4663684		6.50		43200	1.19	0.93	364	7.1	-6		
7		50:	50							43200	1.13	0.90	364	7.1	-6		
8		50:	50							43200	1.16	0.91	364	7.1	-6		
9	7:05	50:	50		15.5	4731390	v	7.25		41760	1.12	0.89	363	7.2	—	26	Air Scour
10	7:05	50:	50	*	15.7	4749587		6.25		43200	1.38	0.98	360	7.1	-3		
11	7:07	50:	50		15.6	4772103		6.40		41760	1.11	0.79	360	7.1	-3	28	
12	7:15	50:	50		15.8	4793655				38016	1.11	0.79	360	7.1	-3		Nitrate-N = 5.5 mg/l.
13	7:00	50:	50		15.6	4815865		6.25		37440	1.10	0.86	360	7.1	-3	27	
14		50:	50							37440	1.22	0.90	360	7.1	-3		
15		50:	50							31680	1.19	0.99	360	7.1	-3		
16	7:10	50:	50		14.3	4877844	v	7.90		37440	1.19	0.99	360	7.1	-3	26	
17	7:05	50:	50		14.4	4898408		6.40		34560	1.15	0.81	360	7.1	-3		
18	7:10	50:	50		14.1	4918771		6.40		37440	1.05	1.07	360	7.1	-3	25	
19	7:10	50:	50		14.1	4938800		6.10		34560	1.14	0.78	360	7.1	-3		
20	7:05	50:	50		14.2	4959054		6.08		33120	1.03	0.79	360	7.1	-3	23	
21		50:	50							33120	1.11	0.82	360	7.1	-3		
22		50:	50							33120	1.05	0.80	360	7.1	-3		
23	7:03	50:	50		13.6	5019651		6.25		33120	1.10	0.74	360	7.1	-3	—	
24	7:10	50:	50		13.1	5039205		6.25		31680	1.05	0.87	360	7.1	-3		
25	7:10	50:	50		13.1	5058057		6.00		31680	1.06	0.80	360	7.1	-3	24	
26	7:05	50:	50		13.6	5077360		6.00		31680	1.03	0.77	360	7.1	-3		
27	7:05	40:	60	^	13.5	5097064		5.60		40320	1.03	0.69	360	7.1	-3	26	
28										33120	0.89	0.58	360	7.1	-3		
29										33120	1.14	0.78	360	7.1	-3		
30	7:05	40:	60		13.7	5157326		5.80		36000	1.04	0.61	360	7.1	-3	26	
31	7:05	40:	60	*	13.2	5169112		5.80		36000	1.23	0.85	360	7.1	-3		

^ Indicates that feed rate was increased by operator after recording flow for the day.
v Indicates that feed rate was decreased by operator after recording flow for the day.
* Indicates that flow meter was not working when flow data was taken.

September	Time	Blend Ratio			Feed Rate (gpm)	Total Flow (gal)		Vinegar Feed (ml/min)	Total Flow To Blending Station (gal)	Water Pumped (gpd)	Chlorine (plant)	Chlorine (residual)	Alkalinity	pH	Stability	Room Temp (C)	Comments
1	7:05	41:	46		13.1	5188264		6.50	5194300	34560	1.18	0.96	361	7.2	-----	25	
2	7:10	50:	50		13.4	5207460		6.50	5210900	33200	1.09	0.87	360	7.2	-1		
3	7:05	50:	50		13.2	5226324		6.30	5223600	34560	1.18	0.95	360	7.2	-1	25	System Off.
4										34560	1.32	1.02	360	7.2	-1		
5										40320	0.95	0.90	360	7.2	-1		
6	7:50	50:	50		13.6	5289609		6.50	5282600	34560	1.23	0.97	360	7.2	-1		
7	7:05	30:	40		13.5	5308606			5300400	36000	1.25	1.01	360	7.2	-1		
8	6:55	50:	50	v	15	5329536		6.50	5313500	34560	1.11	0.84	360	7.2	-1	24	NRT system off. Temp @ 1-16C, 6-18C.
9	7:00	50:	50		13.4	5349286			5331300	34560	1.28	1.06	360	7.2	-1		
10	7:00	50:	50		13.4	5368430		6.00	5349300	34560	1.09	1.00	360	7.2	-1	24	Temp @ 1-16C, 6-17C, School-26C, Ballpark-25C.
11										37440	1.07	0.97	360	7.2	-1		
12										33120	1.06	0.97	360	7.2	-1		
13	7:05	50:	50		13.4	5430193		6.00	5401100	34560	1.25	0.97	360	7.2	-1	22	
14	7:15	50:	50		13.9	5450154		6.00	5418800	34560	1.20	1.01	360	7.2	-1		
15	7:05	50:	50		13.1	5469514	^	5.30	5436500	34560	1.18	0.92	360	7.2	-1	22	Air scour roughing filter.
16	7:05	50:	50		14.4	5489584			5451500	36000	1.02	1.02	360	7.2	-1		
17	7:10	50:	50		16.0	5512620		5.90	5471200	40320	1.14	1.03	360	7.2	-1		
18										40320	1.04	1.02	360	7.2	-1		
19										38000	1.10	1.05	360	7.2	-1		
20	7:10	50:	50		13.2	5570228		6.40	5520300	30240	0.99	0.69	360	7.2	-1		
21	7:10	50:	50		13.2	5589080			5536300	31680	1.19	0.89	360	7.2	-1		
22	7:10	50:	50		12.9	5607740		6.00	5551900	32256	0.97	0.68	360	7.2	-1		
23	7:05	50:	50		12.8	5626089			5567400	31680	1.12	0.85	360	7.2	-1		
24	7:05	50:	50		12.7	5644555		5.50	5584100	34560	1.13	0.83	360	7.2	-1	20	
25										34560	1.19	0.86	360	7.2	-1		
26										34560	1.25	0.91	360	7.2	-1		
27	7:00	50:	50		13.4	5699978		6.00	5637000	37440	1.20	0.89	360	7.2	-1	23	Air Scour
28	7:05	50:	50		12.7	5718688	v	6.90	5652100	33120	1.29	0.96	360	7.2	-1		
29	7:00	50:	50		12.4	5736218		6.00	5668300	33120	1.08	0.80	360	7.2	-1	17	
30	7:00	50:	50			5753838			5683700	33120	1.09	0.81	360	7.2	-1		

^ Indicates that feed rate was increased by operator after recording flow for the day.
v Indicates that feed rate was decreased by operator after recording flow for the day.
* Indicates that flow meter was not working when flow data was taken.

October	Time	Blend Ratio			Feed Rate (gpm)	Total Flow (gal)		Vinegar Feed (ml/min)	Total Flow To Blending Station (gal)	Water Pumped (gpd)	Chlorine (plant)	Chlorine (residual)	Alkalinity	pH	Stability	Room Temp (C)	Comments
1	8:15	50:	50		12.2	5771699	^	6.00	5699300	33120	1.13	0.86	360	7.2	-1	18	
2		50:	50							33120	1.12	0.86	360	7.2	-1		
3										33120	1.12	0.85	360	7.2	-1		
4	7:10	50:	50		12.3	5824242		6.75	5746300	33120	1.13	0.86	360	7.2	-1	16	
5	7:10	50:	50	*	13.2	5837150		6.70	5763700	34560	1.04	0.87	360	7.2	-1		
6	7:05	50:	50		12.3	5855174		6.40	5781200	33120	1.12	0.80	391	7.2	-----	18	
7	7:15	50:	50	v	12.8	5872948			5797900	31620	1.10	0.80	380	7.3	11		
8	7:05	50:	50		10.8	5889112			5813300	28800	1.18	0.78	380	7.3	11		
9										33120	0.97	0.79	380	7.3	11		
10										31680	1.02	0.74	380	7.3	11		
11	7:00	50:	50		12.3	5932512		6.60	5863300	36000	0.95	0.96	380	7.3	11	20	
12	7:10	50:	50		13.2	5951227			5881200	35136	1.02	0.61	380	7.3	11		
13	7:05	50:	50	*	14.2	5963533		7.00	5898900	37440	0.87	0.66	380	7.3	11		
14	7:00	50:	50		14.6	5984332			5916800	37440	0.87	0.74	380	7.3	11		
15	7:10	50:	50		14.0	6005053		6.30	5935300	34560	1.09	0.70	380	7.3	11	22	
16										37440	0.98	0.79	380	7.3	11		
17										33120	0.23	0.90	380	7.3	11		
18	7:05	50:	50	*	15.0	6051754			5990600	34560	1.14	0.85	380	7.3	11	16	
19	7:05	50:	50		13.8	6072733			6007900	34560	0.95	0.71	380	7.3	11		Air Scour
20	7:15	50:	50	v	17.9	6098732		8.00	6024700	28800	0.53	0.78	380	7.3	11	18	
21	7:05	50:	50	*	11.1	6113178		7.30	6039400	29400	1.33	0.79	380	7.3	11		
22	7:05	50:	50		11.1	6129158		7.30	6053200	29400	1.04	0.77	380	7.3	11	18	
23										29400	1.03	0.81	380	7.3	11		
24										29400	0.93	0.80	380	7.3	11		
25	7:05	50:	50		11.0	6176678		7.00	6096500	29400	0.89	0.63	380	7.3	11	18	
26	7:10	50:	50		11.3	6193377			6110500	28000	1.12	0.85	380	7.3	11		
27	7:10	50:	50		11.7	6209914		7.00	6125700	30400	1.00	0.77	380	7.3	11	18	
28	7:05	50:	50		11.8	6226920			6140100	28800	0.98	0.76	380	7.3	11		
29	7:10	50:	50		11.8	6243995		6.80	6154200	28200	1.04	0.77	380	7.3	11	21	
30										28200	1.19	0.90	380	7.3	11		
31										28200	1.07		380	7.3	11		

^ Indicates that feed rate was increased by operator after recording flow for the day.
v Indicates that feed rate was decreased by operator after recording flow for the day.
* Indicates that flow meter was not working when flow data was taken.

November	Time	Blend Ratio			Feed Rate (gpm)	Total Flow (gal)	Vinegar Feed (ml/min)	Total Flow To Blending Station (gal)	Water Pumped (gpd)	Chlorine (plant)	Chlorine (residual)	Alkalinity	pH	Stability	Room Temp (C)	Comments
1	7:10	50:	50		12.4	6290339	6.50	6191800	28200	1.04	0.74	380	7.3	11	18	
2	7:05	50:	50		10.5	6305850		6205000	26400	1.24	0.80	380	7.3	11		
3	7:05	50:	50	^	10.2	6320362	6.50	6218000	26400	1.00	0.74	380	7.3	11		
4	6:57	50:	50		10.3	6335447		6231200	26400	1.20	0.71	380	7.3	11		
5	7:05	50:	50		10.5	6330536	6.50	6243800	26400	1.09	0.69	380	7.3	11		
6									26400	0.98	0.73	380	7.3	11		
7									26400	1.18	0.74	380	7.3	11		
8	7:00	50:	50		10.4	6394941		6280100	26400	1.07		380	7.3	11		
9																
10																
11																
12																
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^ Indicates that feed rate was increased by operator after recording flow for the day.
v Indicates that feed rate was decreased by operator after recording flow for the day.
* Indicates that flow meter was not working when flow data was taken.

APPENDIX C

THM PRECURSOR ESTIMATION DATA

NPOC (ppm)	10-Sep	13-Sep	15-Sep	17-Sep	20-Sep	22-Sep	24-Sep	27-Sep	29-Sep	1-Oct
Raw	0.770	0.728	0.765		0.745	0.761	0.621	0.648	0.619	1.043
Post Vinegar	17.495	12.470	11.405	8.491	16.960	15.500	11.890	11.630	14.910	15.210
Post Reactor	2.795	1.126	1.167	1.042	1.025	1.149	0.957	0.955	1.191	1.188
Post Roughing Filter	2.021	1.109	0.979	1.076	0.959	1.144	0.917	0.924	0.847	1.338
Post Sand Filter	0.837	0.769	0.749	0.785	0.779	0.766	0.687	0.717	0.646	0.898
Post Clear Well Chlorinated	1.033	0.926	0.759	0.800	0.811	0.789	0.638	0.661	0.636	0.872
Mixed Chlorinated	0.904	0.867	0.678	0.765	0.731	0.687	0.590	0.679	0.591	0.774
Distribution System	0.837									

UV_{254}	10-Sep	13-Sep	15-Sep	17-Sep	20-Sep	22-Sep	24-Sep	27-Sep	29-Sep	1-Oct
Raw	0.020	0.019	0.016		0.012	0.016	0.015	0.014	0.013	0.017
Post Vinegar	0.018	0.022	0.016	0.016	0.011	0.015	0.016	0.015	0.014	0.015
Post Reactor	0.019	0.022	0.017	0.016	0.012	0.015	0.015	0.015	0.014	0.015
Post Roughing Filter	0.018	0.023	0.017	0.016	0.011	0.017	0.014	0.016	0.014	0.016
Post Sand Filter	0.021	0.021	0.019	0.015	0.016	0.015	0.014	0.015	0.014	0.015
Post Clear Well Chlorinated	0.021	0.024	0.019	0.019	0.017	0.020	0.015	0.016	0.016	0.018
Mixed Chlorinated	0.023	0.024	0.020	0.018	0.016	0.018	0.018	0.018	0.014	0.015
Distribution System	0.026									

UV_{254}/NPOC [L/(mg*m)]	10-Sep	13-Sep	15-Sep	17-Sep	20-Sep	22-Sep	24-Sep	27-Sep	29-Sep	1-Oct
Raw	2.60	2.61	2.09		1.61	2.10	2.42	2.16	2.10	1.63
Post Vinegar	0.10	0.18	0.14	0.19	0.06	0.10	0.13	0.13	0.09	0.10
Post Reactor	0.68	1.95	1.46	1.54	1.17	1.31	1.57	1.57	1.18	1.26
Post Roughing Filter	0.89	2.07	1.74	1.49	1.15	1.49	1.53	1.73	1.65	1.20
Post Sand Filter	2.51	2.73	2.54	1.91	2.06	1.96	2.04	2.09	2.17	1.67
Post Clear Well Chlorinated	2.03	2.59	2.50	2.38	2.10	2.53	2.35	2.42	2.52	2.07
Mixed Chlorinated	2.54	2.77	2.95	2.35	2.19	2.62	3.05	2.65	2.37	1.94
Distribution System	3.11									

NPOC (ppm)	4-Oct	6-Oct	8-Oct	11-Oct	13-Oct	15-Oct	18-Oct	20-Oct	25-Oct	1-Nov
Raw	0.787	0.783	0.604	0.614	0.581	0.515	0.517	0.533	0.642	0.642
Post Vinegar	18.420	14.480	22.100	17.320	13.395	13.885	10.665	12.595	20.655	13.275
Post Reactor	1.350	1.429	1.384	1.001	0.893	0.917	0.930	1.603	2.502	4.286
Post Roughing Filter	1.293	1.215	1.192	0.968	0.885	0.858	0.802	0.749	1.211	1.029
Post Sand Filter	0.941	0.954	0.661	0.629	0.645	0.629	0.679	0.556	0.700	0.658
Post Clear Well Chlorinated	0.842	0.985	0.699	0.681	0.745	0.579	0.579	0.573	0.732	0.653
Mixed Chlorinated	0.873	0.773	0.624	0.650	0.546	0.517	0.478	0.519	0.613	0.669
Distribution System										

UV_{254}	4-Oct	6-Oct	8-Oct	11-Oct	13-Oct	15-Oct	18-Oct	20-Oct	25-Oct	1-Nov
Raw	0.015	0.014	0.015	0.017	0.012	0.016	0.015	0.015	0.014	0.015
Post Vinegar	0.014	0.016	0.016	0.016	0.015	0.016	0.015	0.013	0.014	0.015
Post Reactor	0.016	0.016	0.016	0.015	0.014	0.016	0.013	0.014	0.016	0.016
Post Roughing Filter	0.019	0.015	0.016	0.016	0.016	0.016	0.013	0.016	0.017	0.017
Post Sand Filter	0.014	0.014	0.014	0.015	0.014	0.015	0.014	0.015	0.013	0.014
Post Clear Well Chlorinated	0.016	0.016	0.014	0.016	0.015	0.017	0.016	0.015	0.015	0.016
Mixed Chlorinated	0.020	0.016	0.015	0.016	0.010	0.015	0.015	0.014	0.013	0.014
Distribution System										

UV_{254}/NPOC [L/(mg*m)]	4-Oct	6-Oct	8-Oct	11-Oct	13-Oct	15-Oct	18-Oct	20-Oct	25-Oct	1-Nov
Raw	1.91	1.79	2.48	2.77	2.07	3.11	2.90	2.81	2.18	2.34
Post Vinegar	0.08	0.11	0.07	0.09	0.11	0.12	0.14	0.10	0.07	0.11
Post Reactor	1.19	1.12	1.16	1.50	1.57	1.75	1.40	0.87	0.64	0.37
Post Roughing Filter	1.47	1.23	1.34	1.65	1.81	1.86	1.62	2.14	1.40	1.65
Post Sand Filter	1.49	1.47	2.12	2.39	2.17	2.38	2.06	2.70	1.86	2.13
Post Clear Well Chlorinated	1.90	1.63	2.00	2.35	2.01	2.94	2.77	2.62	2.05	2.45
Mixed Chlorinated	2.29	2.07	2.41	2.46	1.83	2.90	3.14	2.70	2.12	2.09
Distribution System										

VITA

Cody Don Blair

Candidate for the Degree of

Master of Science

Thesis: EVALUATION OF SYSTEM PERFORMANCE OF A FULL-SCALE BIOLOGICAL DENITRIFICATION SYSTEM FOR THE TREATMENT OF DRINKING WATER IN COYLE, OKLAHOMA

Major Field: Environmental Engineering

Biographical:

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Experience: Previously employed as a lab assistant by School of Civil and Environmental Engineering at Oklahoma State University; previously employed as a research assistant by the School of Civil and Environmental Engineering at Oklahoma State University; previously employed as a research associate by the School of Civil and Environmental Engineering at Oklahoma State University; currently employed by **USI**nfrastructure, Inc. as a civil engineer intern since, January, 2000.

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