

UNDERSTANDING NITRATE POLLUTION IN SMALL AND NATIVE AMERICAN COMMUNITIES

FINAL TECHNICAL REPORT

Utah Water Research Laboratory
Utah State University
Logan, UT 84322-8200

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Mission Statement**

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The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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CHAPTER 1

INTRODUCTION

1.1 PROBLEM STATEMENT

Small drinking water systems face continuing challenges in meeting the requirements of the Safe Drinking Water Act (SDWA). In general, water quality issues associated with small systems are directly related to the quality of the water source. Recent surveys by the National Research Council (NRC) (National Research Council, 1997) and the American Water Works Association (Anonymous, 1997) have highlighted several key drinking water quality issues facing small water systems. Based on 1993 data, there are approximately 35,600 water systems in the U.S. that serve fewer than 500 residents and 18,600 systems that serve populations of 500 to 10,000. Ninety four percent of the total number of operating drinking water systems serve small communities that collectively represent about 21 percent of the U.S. population. Groundwater is the dominant water source for about 80 percent of small water systems with minimal water treatment provided between the point of extraction of groundwater and water consumption (MacDonald, Zander, and Snoeyink, 1997; National Research Council, 1997).

Due to limited financial and technical resources for infrastructure maintenance and water system management, the existing water quality database for small water systems is limited. However, over 90 percent of reported SDWA compliance issues are associated with small water systems (MacDonald et al., 1997). Key water quality compliance issues relate to coliform contamination, nitrate in groundwater, and failure to meet water quality monitoring schedules consistently. Limited data are available on other parameters such as nonbacterial pathogens (enteric viruses, *Cryptosporidium*, *Giardia*), organic contaminants, metals, and radionuclides.

The problems associated with consistent and reliable production of safe drinking water are even more critical in Native American communities. Health risks may be associated with microbial contamination as shown on figure 1; the presence of nitrates, metals, radioactivity; and hydrocarbon contamination. There is a need to evaluate the current status of tribal water systems and develop realistic approaches to improve the effectiveness of water treatment practices. This project was a laboratory and field-testing effort to demonstrate that low cost, appropriate technologies can reduce nitrate in drinking water to safe levels.

Nitrate contamination of drinking water wells is a serious problem in many areas of the U.S. Health effects associated with nitrate nitrogen levels in excess of 10 mg NO_3^- -N/L as nitrogen include methemoglobinemia (blue-baby syndrome), a serious and potentially fatal condition in which nitrate interferes with oxygen transport in the bloodstream (Lichtenberg and Shapiro, 1997). The population at risk for methemoglobinemia includes infants under the age of 6 months, pregnant women, or individuals with enzyme disorders. A recent review (Avery, 1999) suggests that nitrate consumption by infants only enhances the severity of methemoglobinemia and is not the cause of the condition. Methemoglobinemia may be the result of bacterial or viral gastroenteritis in many cases. Avery (1999) calls for a review of the current 10 mg NO_3^- -N/L drinking water standard with a view toward relaxing it. Nitrate has also been implicated as a cause of miscarriages (Morbidity and Mortality Weekly Report, 1996).

Nitrate contamination has been reported in drinking water wells in many locations. Sources of nitrate and other contaminants in groundwater include septic systems, fertilizers, irrigation runoff, livestock management practices, underground fuel and chemical storage, proximity of sumps, landfills, hazardous waste sites, or chemical spills. Site-specific land use and management practices, local groundwater geochemistry, aquifer depth, well construction, and wellhead protection practices are major factors influencing groundwater quality. In rural communities that have on-site wastewater treatment using septic tank systems and absorption fields, water supply protection can be improved by strategic siting of water supply wells, well-head protection programs, and systematic maintenance of wastewater treatment systems.

Water treatment technologies can be used to reduce health risks associated with poor water quality by removing specific contaminants from a water supply. In conjunction with treatment, wellhead and watershed protection programs can facilitate long-term improvements of source water quality. The optimum treatment systems and best management practices (BMPs) for a drinking water source depend on the degree and form of contamination present and the availability of financial, energy, and institutional resources.

1.2 RESEARCH OBJECTIVES

This research project was designed to develop practicable short and long-term drinking water protection measures to control nitrate levels in drinking water supplies derived from groundwater. The project focused on tribal water systems that have documented nitrate contamination with varying geochemical conditions. The specific project objectives were:

1. Compile drinking water quality and public health information for groundwater systems at risk from nitrate contamination.
2. Conduct bench-scale testing of a denitrification system.
3. Develop recommendations for short-term and long-term improvement of drinking water quality including best management practices and wellhead protection measures.

1.3 BACKGROUND

A survey conducted by the U.S. Environmental Protection Agency (U.S. EPA) on Pesticides in Drinking Water Wells concluded that nitrate was the contaminant most detected U.S. Environmental Protection Agency, (1990a). Nitrate in drinking water is a nationwide problem and threatens the health of people in areas susceptible to nitrate contamination. Among these people are Native American people, whose major economic livelihood is agriculture. Nitrate can be harmful to human and animal health. While nitrate itself is not highly toxic, it may be microbially reduced in the gastrointestinal tract to highly toxic nitrite (Atlas and Bartha, 1993). It is important to understand the different forms and chemistry of nitrogen and how it can enter the environment and be transformed to nitrate and nitrite. This can be illustrated by the nitrogen cycle depicted in figure 2.

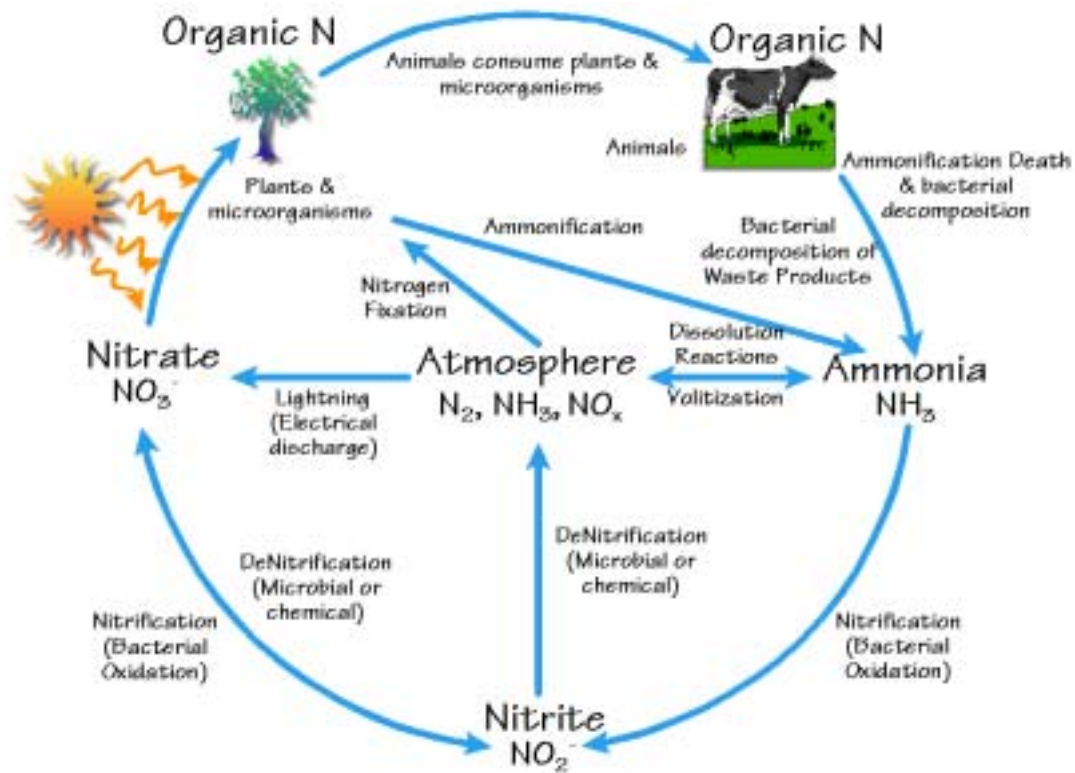


Figure 2.— Nitrogen Cycle (Tchobanoglous and Schroeder, 1985; U.S. Environmental Protection Agency, 1994).

The atmosphere contains 79 percent nitrogen gas and serves as the reservoir for nitrogen. Nitrogen exists in many forms in the environment. The movement and transformation of the nitrogen compounds through the biosphere is described in the following sections.

Nitrogen can form a variety of compounds due to its different oxidation states. Where nitrogen is bonded to hydrogen or carbon it has a negative oxidation state. When nitrogen is bonded to oxygen it has a positive oxidation state. Table 1 lists the nitrogen compounds found in the environment.

Table 1.—Nitrogen Species Found in the Nitrogen Cycle. Adapted from EPA (1993) and Brown et al. (1991)

Nitrogen Compound	Formula	Nitrogen Oxidation State
Ammonia	NH ₃	-3
Ammonium ion	NH ₄ ⁺	-3
Nitrogen Gas	N ₂	0
Nitrous oxide	N ₂ O	+1
Nitric oxide	NO	+2
Nitrite ion	NO ₂ ⁻	+3
Nitrogen dioxide	NO ₂	+4
Nitrate ion	NO ₃ ⁻	+5

1.3.1 Nitrogen Fixation

Biological processes are the primary processes by which nitrogen is transformed in the environment. With the exception of some bacteria, organisms cannot directly use nitrogen gas from the atmosphere. They can only take up nitrogen when it has been fixed or converted to another form that is usable. This process is called nitrogen fixation. Table 2 lists major nitrogen fixing processes and their end products.

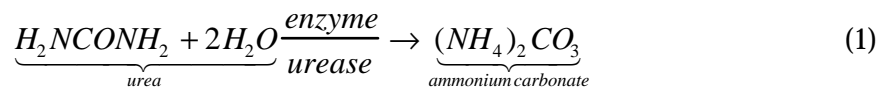
Table 2.—Nitrogen Fixation Processes. Adapted from EPA (1993)

	Fixation Process	End Product
N ₂ Gas	→ Biological	→ Organic nitrogen compounds
	→ Lightning	→ Nitrate
	→ Industrial	→ Ammonium and nitrate

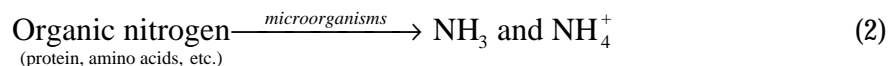
Nitrogen fixation is accomplished biologically by certain bacteria including some cyanobacteria (blue-green algae). These organisms convert nitrogen gas into amino acids and other organic nitrogen compounds through a complex series of biochemical reactions using an enzyme complex referred to as nitrogenase. These enzymes act as catalysts that overcome the strength of the nitrogen triple bond (Atlas and Bartha, 1993). Lightning drives a natural conversion in which, under extremely high temperature, nitrogen gas is oxidized to nitrate. Industrial fixation includes the production of fertilizers and other chemicals containing nitrogen. Atmospheric fixation by lightning and industry processes plays small, but significant roles in fixing nitrogen on a global scale (U.S. Environmental Protection Agency, 1993).

1.3.2 Ammonification

This process converts organic nitrogen into the ammonia or ammonium form. It is sometimes called deamination. An example of ammonification would be the hydrolysis reaction involving urea, a nitrogen compound found in urine (equation 1; (U.S. Environmental Protection Agency, 1993):

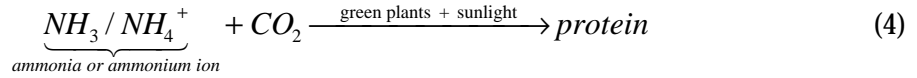
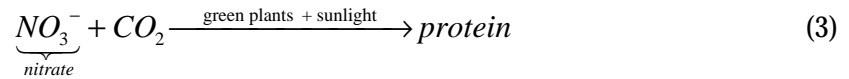


In general, ammonification occurs during decomposition of animal and plant tissue and animal fecal matter (equation 2; (Atlas and Bartha, 1993; U.S. Environmental Protection Agency, 1993):



1.3.3 Synthesis

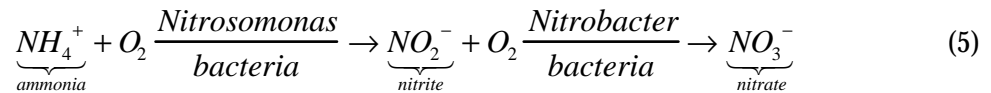
Synthesis involves biochemical mechanisms that utilize ammonium or nitrate compounds to produce plant protein and other nitrogen-containing compounds. Equations 3 and 4 describe the two processes (U.S. Environmental Protection Agency, 1993):



Animals acquire nitrogen by obtaining it in organic compounds from plants and other animals. They are not generally capable of transforming inorganic nitrogen into organic nitrogen forms (U.S. Environmental Protection Agency, 1993).

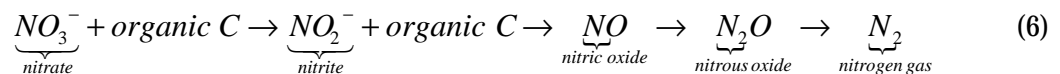
1.3.4 Nitrification

This process involves oxidation of ammonium ions to nitrate by bacteria in the presence of oxygen. This process is conducted in two steps: First, conversion to the nitrite form, then to the nitrate form. This process is catalyzed primarily by a group of aerobic chemoautotrophs called nitrifiers (Atlas and Bartha, 1993). Equation 5 depicts the nitrification process (U.S. Environmental Protection Agency, 1993).



1.3.5 Denitrification

Denitrification is the biological reduction of nitrate to nitrogen gas or to organic nitrogen compounds by bacteria under anoxic conditions (Atlas and Bartha, 1993). This process can proceed through several steps, with the ultimate production of nitrogen gas. The denitrification sequence is as follows (equation 6; U.S. Environmental Protection Agency, 1993):



A wide range of heterotrophic bacteria are involved in the denitrification process. They require an organic compound energy source (Atlas and Bartha, 1993) (U.S. Environmental Protection Agency, 1993).

1.4 SOURCES OF NITROGEN CONTAMINATION

There are many sources of nitrogen, both natural and anthropogenic, (man caused) which could possibly lead to nitrate contamination of groundwater. When natural sources contribute a high concentration of nitrate to groundwater it is usually as a result of anthropogenic disturbance. In

reality, anthropogenic sources seem to be the most problematic and often cause the amount of nitrate to rise above dangerous levels.

1.4.1 Natural Sources

Natural sources of nitrogen contamination include permeable natural geological formations. Williams et al., reported an incident in Sierra Pelona basin in Los Angeles County, California, where 10 percent of nitrate contamination was supplied from rocks and natural soils and the remaining contamination from sewage and indeterminate sources. In addition, Edmunds and Gaye (1997) conclude that in semiarid and arid regions, nitrate contamination of groundwater was difficult to explain by anthropogenic pollution. For example, in the Kalahari, groundwaters were found with levels of nitrate in the range of 4.8 to 37 mg NO₃⁻-N/L. These concentrations were produced from nitrogen naturally present in the soil. In Sudan, concentrations of nitrate were at levels as high as 2,800 mg NO₃⁻-N/L. The levels were attributed to very low recharge rates and accumulation of vegetation over many centuries. High concentrations of nitrate were also found in desert soils of the Mojave Desert in California and Arizona. These high concentrations were attributed to geological sources and litter decomposition, respectively. It has also been found that in arid regions of Australia, high concentrations of nitrate were attributed to nitrogen fixation by cyanobacteria in soil crusts and bacteria in termite mounds.

1.4.2 Anthropogenic Sources

Sources of nitrogen related to human activity include inorganic fertilizer application, management of livestock waste, atmospheric deposition, industrial discharge, and domestic sewage. Anthropogenic sources can be characterized in two main groups: point sources and non-point sources. Commercial fertilizer and animal manure are two of the major non-point sources of nitrogen (Puckett, 1994). Another non-point source not given much recognition is atmospheric deposition. Point source pollution includes industrial sources and municipal sewage treatment plants. A diagram illustrating the major sources of nitrogen is shown in figure 3. These general areas are discussed in the following paragraphs.

From figure 3, it can be seen that the majority of nitrogen is coming from non-point source pollution and 93.5 percent of non-point source pollution can be attributed to agriculture (Puckett, 1994). A numerical breakdown of nitrogen releases annually can be seen in table 3.

By far, agriculture has been the major nitrogen polluter in the United States. Farming results in excessive use of nitrogen fertilizers and/or organic fertilizer (animal manure) to produce constant crop yields. Ammoniacal nitrogen not used by the plants or returned to the atmosphere is converted to nitrate in the soil, which is soluble in water and can easily infiltrate to the underlying groundwater (Guimera, 1998). Although fertilizer is associated with agriculture, inorganic fertilizers are also applied to lawns and golf courses in urban areas where they can potentially contaminate groundwater if applied in excess.

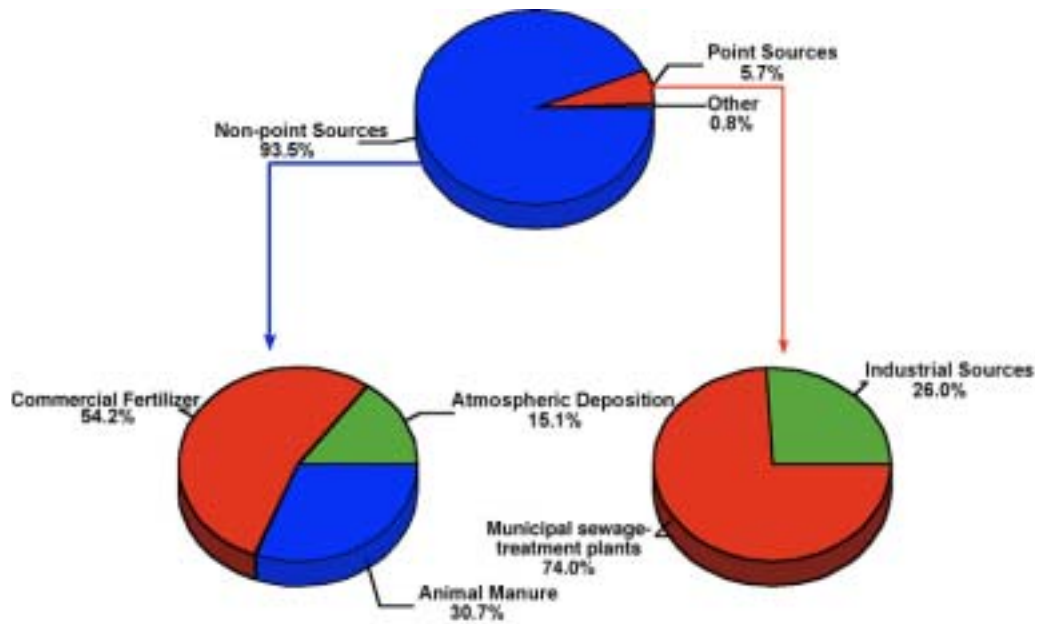


Figure 3.—Major Sources of Nitrogen (Puckett, 1994).

Table 3.—Inventory of Nitrogen Sources. Adapted from Puckett (1994)

Source		Nitrogen Released Annually	
		Individual	Total
Point Sources	Industrial Sources	0.33 million tons	1.3 million tons
	Municipal Sewage-Treatment Plants	0.96 million tons	
Non-point Sources	Commercial Fertilizer	11.5 million tons	21.4 million tons
	Animal Manure	6.5 million tons	
	Atmospheric Deposition	3.2 million tons	

Animal wastes can comprise a large source of nitrogen in groundwater if not managed properly. Animal manures are concentrated in large livestock operations for poultry, dairy, pork, and beef production. Manure can contribute to the nitrogen load in the runoff and via associated water into groundwater. One preferred method of disposal of animal wastes is to re-use the manure on the soil to provide nutrients. This method is often more desirable, due to the nitrogen being in the mineralization-immobilization cycle longer and thus more slowly available (Follett, 1989). However, there is often an abundance of manure and farmers apply it to croplands at rates the crop cannot assimilate, therefore providing an additional potential for nitrate contamination.

Another source of nitrogen is atmospheric deposition. Airborne nitrogen compounds are emitted by point sources such as fossil fuel facilities (figure 4), automobiles, and other forms of transportation. Atmospheric deposition can be in a wet form as rain, snow, hail, fog, and freezing rain or in a dry form as particulates, gases, and droplets (Puckett, 1994). Once dispersed

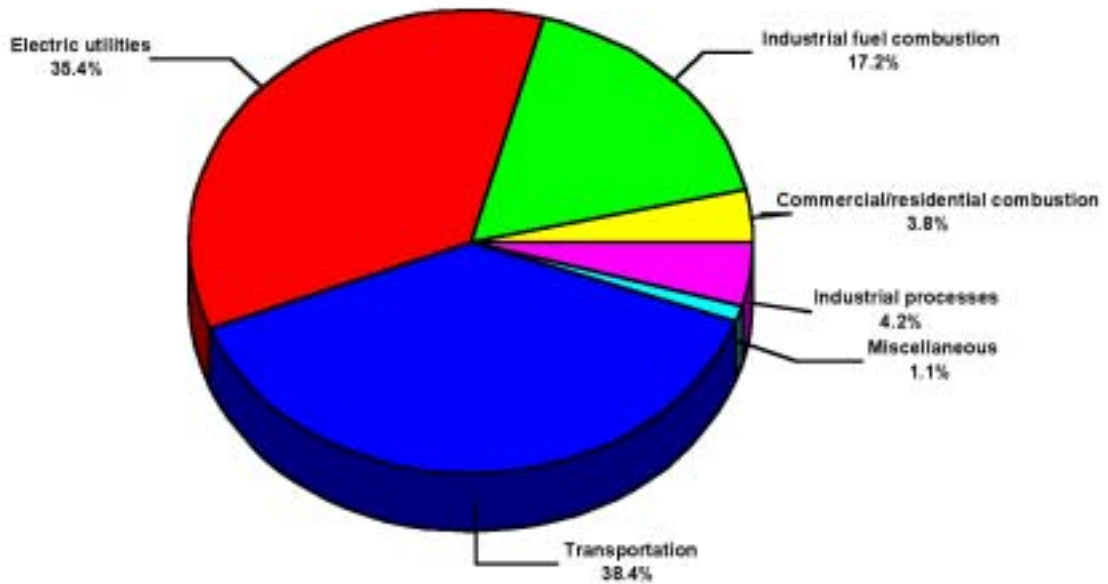


Figure 4.—Nitrogen Oxide Emission Sources in the U.S. in 1998 (Puckett, 1994).

into the atmosphere, the airborne nitrogen compounds are considered non-point sources (Nolan, Ruddy, Hitt, and Helsel, 1997). Atmospheric nitrogen then can enter the aquatic environment through two paths: “inorganic nitrogen that is solubilized in rainwater or particulate organic and mineralized nitrogen that either settles by gravity or is scrubbed by rain onto the receiving water surface” (U.S. Environmental Protection Agency, 1993). The nitrogen contribution from the atmosphere varies regionally, depending on industrial fossil fuel combustion facilities and population density. Table 4 summarizes the mean composition of rain at Hubbard Brook in New Hampshire (Morel and Hering, 1993). Figure 4 quantifies the 1988 nitrogen oxide emission sources in the U.S. in 1988.

Table 4.—Mean Composition of Rain at Hubbard Brook in New Hampshire. Adapted from Morel et al. (1993)

Parameter	Concentration (mg/L)
H ⁺	73.9
Ca ²⁺	4.3
Na ⁺	5.2
Mg ²⁺	2.1
NH ₄ ⁺	12.9
SO ₄ ²⁻	29.9
NO ₃ ⁻	23.1
PH	4.13

Industrial and municipal wastewater treatment facilities contribute to the nitrogen loading in surface waters. These nitrogen sources are considered point sources in that they directly discharge into streams and rivers at a discrete point. Puckett (1994) reported that point sources contributed 1.3 million tons of nitrogen per year, but only represented 5.7 percent of the total nitrogen added to the environment, as shown in figure 3 and table 3.

Septic systems, which are not mentioned in the graphs above, can also pose a potential risk to nitrate contamination of groundwater. Approximately 25 percent of the U.S. population is served by individual septic systems (U.S. Environmental Protection Agency, 1993). Approximately 22 million septic systems discharge about one trillion gallons of wastewater annually (National Drinking Water Clearinghouse, 1998). Studies found that effluent from a typical septic system had a total nitrogen concentration of 25-60 mg/L and less than 1 mg NO_3^- -N/L. Furthermore, septic system effluent can be characterized as containing approximately 7 mg/L organic nitrogen, 25 mg/L ammonia-nitrogen, and 0.3 mg NO_3^- -N/L (U.S. Environmental Protection Agency, 1993). If not properly maintained or sited, the untreated wastewater can enter the underlying groundwater, bypassing natural soil treatment and contributing to nitrate and bacterial contamination. Most cases of septic tank contamination have been seen in densely populated areas because the soil could not provide proper treatment due to overloading or because the soil properties (e.g., texture and structure) were inadequate to treat wastewater.

1.5 HEALTH EFFECTS

Although nitrate is relatively non-toxic, nitrite can be extremely harmful to certain individuals. (Bruning-Fann and Kaneene, 1993) reviewed the human health effects of nitrate, nitrite and N-nitroso compounds. Nitrate can be converted readily by bacteria into nitrite. This can occur in the environment, in foods, and in the mouth and gastrointestinal tract of humans and animals. This conversion can cause harmful and in some cases fatal health effects. One of the better documented and proven health effects associated with nitrate include infantile methemoglobinemia (Lichtenberg and Shapiro, 1997). The cause and effect relationship between nitrate ingestion and methemoglobinemia has been recently called into question (Avery, 1999). Other health effect claims associated with intake of nitrate contaminated groundwater involve birth defects (Spalding and Exner, 1993), spontaneous abortions (Morbidity and Mortality Weekly Report, 1996), hypertension, thyroid hypertrophy, and certain types of cancer (Nitrate Elimination Co., Inc., 1999, <http://www.nitrate.com/nitrate1.htm>). Brief descriptions of each of these health effects are described below.

1.5.1 Methemoglobinemia

Methemoglobinemia, or blue baby syndrome, occurs when NO_3^- is reduced to NO_2^- facilitated by bacteria within the saliva or digestive tract of humans or animals. NO_2^- enters the bloodstream, causing the oxidation of hemoglobin to methemoglobin. The ferrous iron (Fe_2^+) present in the hemoglobin group is oxidized to ferric iron (Fe_3^+) (Kross, Ayebo, and Fuortes, 1992; U.S. Environmental Protection Agency, 1987). This reaction inhibits transport of oxygen by the blood and may cause suffocation of the individual.

Individuals most vulnerable to methemoglobinemia are infants under the age of 6 months. However, there have been cases of school-aged children and adults experiencing this condition.

In addition, some minority groups lack a hereditary enzyme that reduces the methemoglobin levels in the body. These groups include Native Americans, Alaskan Eskimos, and African Americans, making them even more susceptible to methemoglobinemia (Balsamo, Hardy, and Scott, 1964; Scott and Hoskins, 1958).

Methemoglobinemia was first reported in 1945 by Dr. Hunter Comly of Iowa (Comly, 1945). The cases he treated were associated with NO_3^- contamination of shallow drinking water wells located near barnyards and outhouses (Kross et al., 1992; U.S. Environmental Protection Agency, 1987). Since then there have been other studies linking NO_3^- consumption to infantile methemoglobinemia. The review by Avery (1999) emphasizes that more recent research has established that the causes of infantile methemoglobinemia can be varied and complex. Infantile methemoglobinemia is often accompanied by gastrointestinal infection. The infection leads to the production of nitric oxide (NO) in gastrointestinal tissue. NO metabolism produces NO_2^- , which leads to methemoglobinemia. Consumption of NO_3^- may aggravate this condition by leading to the production of additional NO_2^- .

1.5.2 Birth Defects and Spontaneous Abortion

Central nervous system birth defects may be related to the consumption of water containing nitrate concentrations above the maximum contaminant level (MCL), but further study of this relationship is needed (Arbuckle, Sherman, Walters, and Lo, 1988). Spontaneous abortions have also been linked to consumption of water from nitrate contaminated wells. Multiple spontaneous abortions have also been reported from women drinking well water located 0.5 to 1 mile of a nitrate source (Morbidity and Mortality Weekly Report, 1996).

1.5.3 Hypertension and Thyroid Hypertrophy

Hypertension developed in individuals around 50 to 59 years of age exposed to nitrate contamination (Malberg, Savage, and Osteryoung, 1978). Comparably, non-exposed individuals developed hypertension around 70 to 79 years of age.

Thyroid hypertrophy was observed in individuals consuming water with concentrations of nitrate greater than 11 mg NO_3^- -N/L, resulting in 26 percent increase in thyroid volume as compared with a group exposed to less than 11 mg NO_3^- -N/L (Van Maanen et al., 1994).

1.5.4 Cancer

The U.S. EPA (U.S. Environmental Protection Agency, 1998a) has not found adequate evidence to state whether nitrates or nitrites have the potential to cause cancer from a lifetime of exposure from drinking water. However, researchers have expressed concern about the possible connection between nitrate and cancer. Nitrate, converted to nitrite, may react with amines (proteins found in some foods, medications, and water) to produce nitrosamines, which have been found to be carcinogenic in animals (Bonner, 1996). Some of the types of cancer linked to this reaction include, non-Hodgkin's Lymphoma (NHL) (Nolan et al., 1997) and gastric, stomach, and esophageal cancer (Katers and Zanoni, 1998).

Additional nitrate exposure health effects include nervous system disorders, heart damage, mutagenic and teratogenic effects, behavioral and developmental abnormalities, and cardiovascular disease (Mitchell and Harding, 1996). However, there is inadequate evidence to relate these illnesses to consumption of high levels of nitrate in drinking water.

1.6 ENVIRONMENTAL EFFECTS

Besides being harmful to humans and animals, nitrate can also affect the environment. The following paragraphs describe problems associated with nitrate pollution in the environment and its effects on wildlife.

1.6.1 Eutrophication

Eutrophication has been defined as the over stimulation of the growth of aquatic plants and algae due to an overload of nutrients, primarily phosphorus and nitrogen (Saul, 1990). Nutrients include nitrates that enter surface waters through the sources previously described. Excessive growth of aquatic plants and algal blooms can decrease the oxygen concentration in the water at night. The depletion of oxygen affects the respiration of fish and aquatic invertebrates, leading to a decrease in animal and plant diversity (U.S. Environmental Protection Agency, 1992). Algal blooms and overgrowth of aquatic plants also cause discoloration, taste, and odor in the water. If the water is used as a source for a drinking water supply, clogging of water treatment filters can also become a problem. In some cases, eutrophication may cause the release of toxins produced by algae into water supplies (Sykora et al., 1980).

1.6.2 Health Effects in Animals

Nitrate in excessive levels can also be potentially harmful to animals. It was reported by Self and Waskom (1992) that levels above 100 mg NO_3^- -N/L can affect animals in the same way as humans. Baby animals are most susceptible for the same reasons that human infants are susceptible. Pregnant animals are also affected in the same manner as pregnant women.

Ruminant animals, like cattle and sheep, are also susceptible to nitrate toxicity. This happens when bacteria, present in the rumen, convert nitrate to nitrite. Horses, although monogastric, are also sensitive to nitrate poisoning because their cecum acts like a rumen. Non-ruminant animals like swine and poultry do not have these bacteria and are not as susceptible to nitrate toxicity (Jennings and Sneed, 1996; Self and Waskom, 1992; Tyson, Dixon, and Segars, 1992).

Some of the symptoms observed from nitrate poisoned animals include abdominal pain, diarrhea, muscular weakness, or poor coordination, and brown or chocolate colored blood. Self and Waskom, (1992) conclude that it is difficult to determine the toxicity of nitrate in animals due to the rate at which the animal consumes the nitrate-contaminated substance. A few hundred milligrams of nitrate can cause poisoning if consumed within a few hours. However, if consumed over an entire day, 1,000 milligrams may not cause any toxic effects.

1.7 WATER QUALITY STANDARDS FOR NITRATE AND NITRITE

The U.S. EPA has established the National Primary Drinking Water Regulation in which certain contaminants are assigned a concentration limit called a Maximum Contaminant Level (MCL). The regulatory goal is to reduce the concentrations of all drinking water contaminants to levels close to the Maximum Contaminant Level Goals (MCLGs) established by EPA. MCLGs are non-enforceable water quality goals for which “no known or anticipated adverse effects on health of persons occur and which allow an adequate margin of safety” (American Water Works Association, 1990). The MCLs are set as close to the MCLGs as feasible. For nitrate, the MCL has been set at 10 mg NO₃⁻-N/L, which is also the proposed MCLG. Table 5 summarizes different nitrate and nitrite standards developed in Canada and by the World Health Organization (WHO).

Table 5.—Comparison of Water Quality Standards for Nitrate and Nitrite (Droste, 1997)

Constituent	WHO (mg N/L)	Canada (mg N/L)	U.S. SDWA	
			MCLG (mg N/L)	MCL (mg N/L)
Nitrate	11.3	10	10	10
Nitrite	0.91	1	1	1

The health effect EPA used to determine the MCL for nitrate was the occurrence of methemoglobinemia in infants less than 6 months of age. Methemoglobinemia occurrence was studied by a number of people during the period of the late 1940's to the early 1970's. The MCL for nitrate was set at 10 mg NO₃⁻-N/L in 1976 (American Water Works Association, 1990).

A survey conducted by (Walton, 1951) found that more than 278 cases of cyanosis in infants were associated with nitrate contaminated water. There were no cases of cyanosis in infants associated with water containing 10 mg NO₃⁻-N/L or less (U.S. Environmental Protection Agency, 1987).

Bosch, Rosefield, Huston, Shipman, and Woodard, (1950) evaluated 139 cases of cyanosis due to methemoglobinemia reported by physicians in Minnesota. All cases involved infants 8 days to 5 months old, and 90 percent of the cyanosis was occurring in infants less than 2 months of age (U.S. Environmental Protection Agency, 1998b). A study was conducted to determine the nitrate content of the wells that supplied the infants with water. None of the wells contained less than 10 mg NO₃⁻-N/L nitrate.

The studies conducted by Walton and Bosch are considered convincing evidence that infant methemoglobinemia does not occur at drinking water levels of 10 mg NO₃⁻-N/L or less (U.S. Environmental Protection Agency, 1998b). Additional studies support these findings and can be found in the “Criteria Document for Nitrate/Nitrite” provided by the U.S. EPA (U.S. Environmental Protection Agency, 1986).

1.8 ANALYTICAL METHODS FOR MEASURING NITRATE

Because nitrate is colorless, odorless, and tasteless, it has to be chemically detected. Nitrate can be measured by a variety of methods, depending on the situation, availability of equipment, and the budget of the project. The methods differ in sensitivity, simplicity, interferences, and expense. Tables 6 and 7 summarize all methods accepted by the American Public Health Association (American Public Health Association, 1995) for measurement of nitrate and nitrite, respectively.

1.9 TREATMENT OF NITRATE CONTAMINATION

After nitrate has been detected in water, various treatment techniques can be implemented to remove it. Although there are a number of treatment methods to remove nitrate, there are only three that are accepted and recommended by U.S. EPA (U.S. Environmental Protection Agency, 1994). These methods of removal, plus some alternative techniques, are presented in the following paragraphs. Table 8 summarizes the methods for removing nitrate from water.

1.9.1 Ion Exchange

Ion exchange has been demonstrated and proven on a large scale and is the most commonly used method in the United States for removing nitrate from water (Brown, 1995). This process involves passing the nitrate-contaminated water through a resin bed containing a strong base anion exchange resin. The resin is in a chloride or bicarbonate form, and nitrate exchanges with the chloride or bicarbonate site on the resin. The resin will become exhausted when virtually all available sites have been exchanged for nitrate, and the resin will require regeneration. The regenerate is a concentrated sodium chloride or sodium bicarbonate solution which is backwashed through the resin bed (Kapoor and Viraraghavan, 1997). After regeneration has occurred, a brine consisting of high levels of nitrate, sodium, and chloride is produced. The byproduct can be difficult and expensive to dispose of (Van Der Hoek and Klapwijk, 1987).

To date, ion exchange has been the least expensive removal technology for nitrate contamination (table 8). However, there are some disadvantages to the process, which are outlined in table 9.

1.9.2 Reverse Osmosis

Osmosis is the process by which “water spontaneously passes through a semipermeable membrane from a dilute solution to a concentrated solution in order to equilibrate concentrations” (National Research Council, 1997). RO is implemented by applying enough pressure on a concentrated solution to reverse the flow and force the water across the membrane from a concentrated solution to the less concentrated solution, hence leaving contaminants behind (Kapoor and Viraraghavan, 1997). This process is highly efficient in removing inorganic ions (nitrate and nitrite), salts, some organic compounds, and in some cases microbiological contaminants (National Research Council, 1997). This process also has its advantages and disadvantages, which are outlined in table 9.

Table 6.—Summary of Methods for Measuring Nitrate (NO₃⁻) Concentration (American Public Health Association, 1995)

Method	Sensitivity (mg NO ₃ ⁻ -N/L)	Field or Lab Use	Interferences
Ultraviolet Spectrophotometer Screening Method	0.01-11	Field or Lab	Dissolved organic matter, surfactants, NO ₂ ⁻ , Cr ₆ ⁺ , chlorite and chlorate.
Ion Chromatography Method	0.1-55	Lab	Substances with retention times that are similar to and overlap NO ₃ ⁻ . Solutions with particles that are < 0.45 microns.
Nitrate Electrode Method	0.14-1400	Field or Lab	Chloride and bicarbonate ions, NO ₂ ⁻ , CN ⁻ , S ₂ ⁻ , Br ⁻ , I ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , pH, and ionic strength,
Cadmium Reduction Method	0.01-1.0	Field or Lab	Suspended matter, high concentrations of iron, copper and other metals, oil and grease, residual chlorine, and sample color
Automated Cadmium Reduction Method	0.01-1.0	Lab	Sample turbidity and color
Titanous Chloride Reduction Method	0.1-20	Lab	NH ₃ , and NO ₂ ⁻
Automated Hydrazine Reduction Method	0.01-10	Lab	Sample color and sulfide ion

Table 7.—Summary of Methods for Nitrite (NO₂) Detection (American Public Health Association, 1995;
Orion Research Inc., 1996)

Method	Sensitivity (mg NO ₂ -N)	Field or Lab Use	Interferences
Colorimetric Method	0.005-1	Field or Lab	Free chlorine, nitrogen trichloride (NCl ₃), Sb ³⁺ , Au ³⁺ , Bi ³⁺ , Fe ³⁺ , Pb ²⁺ , Hg ²⁺ , Ag ⁺ chloroplatinate (PtCl ₆ ²⁻), metavanadate (VO ₃ ²⁻), cupric ion, colored ions, and suspended solids.
Ion Chromatography Method	0.1-20	Lab	Substances with retention times that are similar to and overlap NO ₂ . Solutions with particles that are < 0.45 microns.
Nitrite Electrode Method	0.02-100	Field or Lab	Salicylate, iodide, bromide, chlorate, acetate, bicarbonate, nitrate, sulfate, chloride, perchlorate, and fluoride
Cadmium Reduction Method	0.01-1.0	Field or Lab	Suspended matter, high concentrations of iron, copper and other metals, oil and grease, residual chlorine, and color

Table 8.—Summary of Nitrate Removal Technology

U.S. EPA Best Available Technologies		
Removal Technique	Removal Efficiency	Cost/1000 gallons
Ion Exchange	> 80% ¹	\$0.30 ¹
Reverse Osmosis	85-99% ²	\$1.00 ¹
Electrodialysis	20-80% ¹	\$0.85 ¹
Alternative Removal Techniques		
Biological Denitrification	85-95% ⁴	\$0.53 ³
Chemical Reduction	60-95% ³	*
Catalytic Reduction	98% ³	*

¹(U.S. Environmental Protection Agency, 1994).

²(National Research Council, 1997).

³(Kapoor and Viraraghavan, 1997).

⁴(Lee, Dahab, and Bogardi, 1992).

*No data available for this technique.

1.9.3 Electrodialysis

Electrodialysis involves passing nitrate and other ions through a semipermeable membrane using an electrical current (Kapoor and Viraraghavan, 1997). The ions are transferred through the membrane from a less concentrated solution to a concentrated solution (brine).

A positive electrode (cathode) and a negative electrode (anode) are used to attract oppositely charged ions through the membranes into the concentrated solutions. Like RO, this process also produces brine which requires proper disposal. Table 9 outlines some advantages and disadvantage to this process.

1.9.4 Biological Denitrification

This process is widely used throughout Europe and is being tested as an alternative method in the United States (Kapoor and Viraraghavan, 1997; Solt, 1987). This process involves the reduction of nitrate to nitrogen gas by anoxic biological activity. Specific bacterial species are concentrated into a biological reactor where they use nitrate as a respiratory electron. There are serious concerns for bacterial contamination when implementing this process for drinking water treatment, which is one of the main reasons the United States has not accepted this method. These considerations are outlined in table 9.

1.9.5 Chemical and Catalytic Denitrification

Kapoor and Viraraghavan (1997) state that nitrate removal can also be achieved by a chemical process in which ferrous iron or aluminum powders are used to reduce nitrate concentrations. Catalytic denitrification can also be implemented in which Palladium-alumina catalysts reduce

Table 9.—Advantages and Disadvantages to Nitrate Removal Techniques

Removal Technology	Advantages	Disadvantages
Ion Exchange (IX)	<p>Relatively insensitive to flow and temperature variations^{1,3}</p> <p>Low-capital cost⁵</p> <p>Operates on demand¹</p> <p>Relatively simple to operate^{3,5}</p>	<p>Disposal of spent regenerate brine solution¹</p> <p>Sensitive to high levels of TDS, sulfates and carbonates pose problems for effectiveness of the process¹</p> <p>Large volumes of salt required for regeneration²</p> <p>Water may require pre-treatment due to suspended solids, organic matter, iron and other oxidizing agents, to prevent anion resin fouling^{3,4}</p> <p>Requires post-treatment due to corrosivity of product water³</p> <p>Does not completely remove nitrate from water⁵</p>
Reverse Osmosis (RO)	<p>Insensitive to temperature variations³</p> <p>No post-treatment required³</p> <p>Relatively easy to operate³</p> <p>Removes virtually all contaminants, producing the highest quality of water^{1,5}</p> <p>Bacteria and particles are removed¹</p>	<p>High capital and operation and maintenance costs due to power consumption</p> <p>Requires pretreatment of water to remove organic matter, suspended and colloidal particles and other contaminants³</p> <p>Sensitive to pH and pressure⁵ variation and chlorine content³</p>
Electrodialysis (ED)	<p>Does not require extensive pretreatment compared to RO³</p> <p>Insensitive to scaling or fouling compared to RO^{3,5}</p> <p>Removal of nitrate accomplished without the use of additional chemicals³</p> <p>Can operate at higher TDS levels⁵</p> <p>Relatively insensitive to pH and temperature variations⁶</p>	<p>High capital and operation and maintenance costs due to power consumption</p> <p>Sensitive to iron, manganese, hydrogen sulfide (H₂S), chlorine, and hardness^{5,6}</p>
Biological Denitrification	<p>Produces a small amount of biological waste for disposal⁴</p> <p>Completely eliminates nitrate</p> <p>Low land area requirements</p>	<p>Possible risk of bacterial contamination of treated water, post-treatment would be required²</p> <p>Production of nitrite²</p> <p>Sensitive to pH and temperature variations³</p> <p>Requires close monitoring of complex operation³</p> <p>Sensitive to presence of dissolved oxygen³</p> <p>Start up time may be up to 3 weeks</p>

¹(U.S. Environmental Protection Agency, 1990b).

²(Van Der Hoek and Klapwijk, 1987).

³(Kapoor and Viraraghavan, 1997).

⁴(Clifford and Liu, 1993).

⁵(Bureau of Reclamation, 1997).

⁶(National Research Council, 1997).

nitrate to nitrogen gas. These processes, however have been discouraged for water treatment at this time due to high costs and post-treatment requirements associated with the process. The above techniques are still in the development stages and require further research.

1.10 BEST MANAGEMENT PRACTICES TO MINIMIZE NITRATE CONTAMINATION

If possible, prevention practices should be implemented to avoid expensive treatment costs as outlined in the previous section. This can be done with best management practices (BMPs). BMPs are a series of management options that can minimize or eliminate nitrate contamination (Keeney, 1986). The following are potential BMPs for sources of nitrate contamination.

1.10.1 Agricultural

As noted earlier, agriculture is one of the major sources of nitrate contamination. Many management practices can be implemented to minimize contamination. These BMPs include:

- Modifying or reducing fertilizer use by considering all potential available nitrogen sources for a crop. These sources include nitrogen already present in manure, soil, water, legumes, and organic matter. This amount can then be subtracted from calculated fertilizer needs. This can reduce fertilizer costs and still provide sufficient nitrogen for crops and minimize potential for nitrate contamination (Keeney, 1986; Self and Waskom, 1992; Tyson et al., 1992).
- Proper management of livestock operations such as implementing manure storage sites. Storing manure in concrete pits or bunkers prevents nitrate that is leached from manure from entering groundwater or surface water (L. Haller, P. McCarthy, T. O'Brien, J. Riehle, and T. Stuhldreher, 1998; <http://www.nd.edu/~jriehle1/>). Storing animal wastes during the winter and eliminating manure application to poorly drained areas is recommended by EPA (Maas, Smolen, Jamieson, and Weinberg, 1987). Restrict access of animals to streams. Divert runoff to bypass barnyard areas.
- Timing and rate of application of fertilizer is an important consideration. Maas et al., (1987) recommended the elimination of fall and winter fertilizer applications. Tyson et al., (1992) state, "On coarse-textured, highly permeable soils, split or sidedress applications of nitrogen generally result in increased nitrogen efficiency and decreased potential for nitrogen loss because of the shorter time between fertilizer application and crop uptake." When calculating fertilizer rates, consideration of the specific crop, productivity capacity of the soil, and moisture content should be considered.
- Farmers need to set realistic yield goals. Yield goals are the basis of fertilizers rate recommendations. Setting unrealistically high yield goals can result in over-fertilization and potential for nitrate contamination (Self and Waskom, 1992; Tyson et al., 1992).

- Proper water management methods, such as irrigation scheduling for applying the proper amount of water at the right time, can reduce nitrate loss from agricultural land. Ferguson, Eisenhauer, Bockstadter, and Buttermore, (1990) recommend scheduling irrigation according to available soil-water depletion to reduce deep percolation and minimize the potential for contaminating groundwater.

Implementing these practices can reduce nitrate leaching to groundwater from agricultural operations.

1.10.2 Septic Systems

Improperly locating, installing, and operating individual septic systems can cause nitrate contamination of groundwater. There are a number of general rules that can be used to lower the risk of groundwater contamination when using a septic system. These rules include the following:

- Location of the septic system is extremely important. It is recommended by EPA, (U.S. Environmental Protection Agency, 1990b), that a septic system be downgradient 100 feet from nearby wells.
- Limit the number of septic systems in an area. It was recommended by Tyson et al. (1992) that in Georgia, there should be one septic system per 1.5 acres when drinking water is supplied by individual wells. This area may be more or less depending on site and soil conditions. Implementing housing density zones can reduce the potential for nitrate contamination from septic systems (Keeney, 1986).
- Consider the type of soil in which the wastewater will drain; conduct a percolation test and ensure that percolation rates are neither too fast nor too slow. Appropriate percolation rates for on-site wastewater treatment and disposal are often set by state or local regulations.
- Ensure adequate distance between the bottom of the drain field and water table. Minimal distances are usually specified by state or local regulations.
- Proper design of the septic system is important. Design the system to sustain the household, ensuring that the volume and type of discharges are compatible with system design.
- Maintenance of the septic system is important to ensure that the system is working properly. It is recommended by the National Drinking Water Clearinghouse (1998) that septage should be pumped from the tank every three to five years, depending on tank size.
- Prohibit any discharge of solvents into the septic system. Solvents can disrupt or inhibit the biological activity of the septic system, making it dysfunctional.

When installing a septic system, it is very important that the location of the drinking water well is known so prevention of potential nitrate contamination can be implemented.

1.10.3 Well Siting and Construction

Installation of a drinking water well must be carefully thought out in order to prevent any potential contamination. There are guidelines and rules that a well driller must comply with. These general guidelines are listed below:

- It is recommended that the well be a minimum of 100 feet up-gradient and up-hill of the absorption field and at least 100 feet from feedlots, barnyards, lagoons, and chemical storage facilities (Self and Waskom, 1992; Tyson et al., 1992).
- Ensure that the well is properly constructed. Properly seal or cap the well to prevent entrance of any contaminants. Earth berms or a concrete slab should be built to divert surface water runoff away from the wellhead. The well casing should extend above ground. Wells should be grouted in at least the top 10 feet below the ground surface (Tyson et al., 1992). Ensure that the well casing is not cracked. Cracks can lead to potential contamination (National Drinking Water Clearinghouse, 1998).
- Do not conduct any chemical mixing activities near the well and use check valves to prevent back siphonage if the well water is used to mix fertilizers or pesticides. Siphoning could lead to direct contamination of a well (U.S. Environmental Protection Agency, 1990b).
- Properly seal or cap abandoned wells. The same precautions outlined above apply to abandoned wells so that contamination does not reach the groundwater.

To protect public health, we must reduce the nitrate loading into the groundwater through BMPs or alternative measures or avoid drinking contaminated groundwater by obtaining alternative water supplies or by treating the water.

CHAPTER 2

METHODS AND MATERIALS

2.1 FIELD STUDY

2.1.1 New Mexico Community

Well water was sampled in a northern New Mexico community. The community's economy has been agriculturally based, but the importance of agriculture has diminished in recent years. Farming on the reservation is limited to 40 acres due to water availability, but 144 acres are available for additional farming (Tiller, 1996). The crops farmed are primarily vegetables and hay for individual use. The community has now focused on developing a long-term land use plan. The plan involves commercial development and leasing lands that are commercially desirable.

The community is supplied with drinking water through well systems. The water is disinfected with chlorine. Wastewater is disposed of through a lagoon system.

2.1.2 Arizona Community

Well water from a south-central Arizona community was also sampled. The community covers 52,600 acres with a population of 4,856. The reservation is composed mostly of agricultural lands. These lands are capable of producing a variety of crops including cotton, watermelon, honeydew, casaba, cantaloupe, potato, brown onions, and carrots. The economy is based on commercial, industrial, and agricultural enterprises. There are approximately 10,686 acres in cultivation; about 23 percent of the reservation (Tiller, 1996).

The community is supplied with drinking water through well systems. One well supplies a number of households.

2.2 LABORATORY STUDY

2.2.1 Apparatus Description and Background

The laboratory study consisted of a UV denitrification system developed and patented by a team from the Bureau of Reclamation (Murphy, Moody, and Henthorne, 1999). The denitrification system included three individual processes: UV conversion, acidification, and air stripping. Figure 5 illustrates the denitrification process.

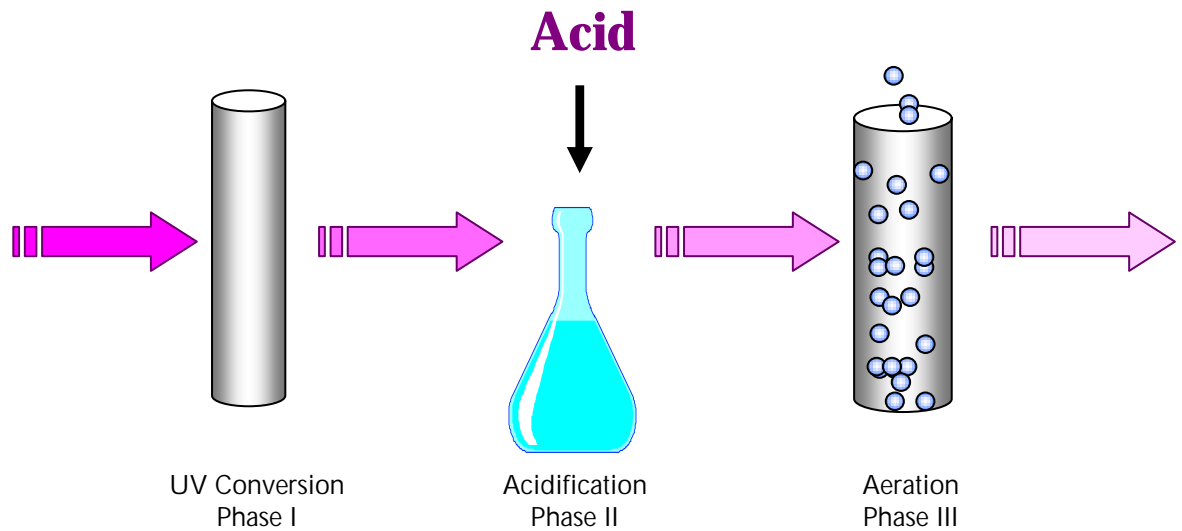
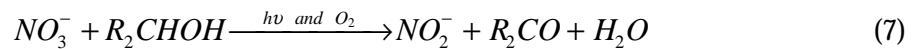


Figure 5.—UV Denitrification System (Murphy, Moody, and Henthorne, 1996).

2.2.2 Phase I - UV Conversion

The UV conversion process consists of an ultraviolet water disinfection unit that photochemically reduces NO_3^- in the water to NO_2^- . Under natural water conditions, this reaction can be described by the following equations (Sonntag and Schuchmann, 1992):



R represents an organic compound moiety. In the absence of oxidizable substances, the net reaction is (Sonntag and Schuchmann, 1992):



The reactions described above are desired to accomplish the first step of the denitrification system. Jelight Company, Inc. (Irvine, California) manufactured the ultraviolet lamp unit used in this study. Jelight Model UVJ1000 emits light with maximum intensity at a wavelength of 253.7 nanometer (nm). During batch reactor tests, the lamp was immersed in a 250 milliliter (mL) graduated cylinder. The Jelight's stainless steel chamber was used as the reactor for flow-through tests. Water was pumped through the chamber at a rate of 1.9 liters per minute (L/min) (0.5 gallons per minute [gal/min]).

2.2.3 Phase II - pH Reduction

Phase II of the UV denitrification system study evaluated the effect of reducing the pH of the water following ultraviolet exposure. Nitrate is the anion of a strong acid, and nitrite is the

anion of a weak acid. The purpose of the acid addition was to produce a weak acid (HNO_2), which can ultimately be removed by air stripping. The following equations describe the reactions.



$$\log \frac{\text{NO}_3^-}{[\text{HNO}_3]} = 0.00 + \text{pH} \quad (10)$$



$$\log \frac{\text{NO}_2^-}{[\text{HNO}_2]} = -3.35 + \text{pH} \quad (12)$$

Equations 9 and 10 show that nitrate is in the ionized form and cannot be partitioned from water to the air. Equations 11 and 12 show that at a pH of 3.35, half of the nitrite is un-ionized and can be partitioned out of the water into air (Murphy et al., 1999).

Following ultraviolet exposure in the batch reactor, the water was transferred into a 500 mL flask with a magnetic stirring bar for mixing purposes. Sulfuric acid (H_2SO_4) was used to reduce the pH of the water to 2 to 3. H_2SO_4 was used to avoid analysis interference from Cl^- or NO_3^- that would occur if HCl or HNO_3 were added.

2.2.4 Phase III - Air Stripping

Phase III of the process involved the use of air to strip out un-ionized forms of nitrogen compounds in the final test water. The air-stripping unit consisted of a 500 mL glass graduated cylinder packed with aeration media. The aeration media filled the cylinder to the level of the water. Tygon® tubing with a Teflon air diffuser was used to provide air to the cylinder.

2.2.5 Experimental Parameters and Sampling

Samples were taken throughout the process to monitor nitrate and nitrite concentrations. A minimum of three, 5 mL, replicate samples were taken when sampling. Samples were taken before phase I (UV irradiation) to determine initial nitrate and nitrite concentrations. After Phase I, samples were taken to determine changes in concentration. Nitrate and nitrite were also analyzed after Phase III (air stripping) to determine end concentrations. For one test, a total of nine samples were analyzed.

The nitrate source was sodium nitrate (NaNO_3) from which a stock solution of 1,000 mg NO_3^- -N/L was made. Sodium nitrate (6.0679 g) was dissolved in reagent grade deionized water and diluted to 1 L. This stock solution was then used to prepare a solution of various nitrate concentrations by dilution. Nitrate concentrations varied from 5 to 50 mg NO_3^- -N/L, depending on the goal of the test.

Waters of various qualities were tested to determine their effect on nitrate removal in the UV denitrification system. Reagent grade ($> 18 \text{ M}\Omega$) water; Logan, Utah, tap water; and Native American community site water were used in the tests.

pH was varied in phase I (UV irradiation) to determine if there was a difference in nitrate reduction. The pH conditions included an acidic run (pH 2.0 – 3.0) and neutral run (6.0 – 7.0). To reduce the pH of the water, $\sim 6 \text{ N H}_2\text{SO}_4$ was used to titrate to a pH of 2.0 to 3.0. A magnetic stirrer and stirring rod was used to assure complete mixing. The pH was monitored with a pH electrode. Temperature was monitored throughout the process using a thermocouple sensor on the pH electrode. Conductivity was measured with a conductivity cell and meter.

The flow-through testing consisted of pumping test water through the ultraviolet device for a desired amount of time at the desired flow rate. Only Phase I was conducted in flow-through mode. All other phases were conducted in batch reactors.

2.2.6 Analytical Procedures

In the field, screening analyses were conducted to determine if nitrate and other substances of interest were present. A number of analyses were conducted at the New Mexico and Arizona community sites. Table 10 summarizes the analyses performed and the methods used.

Table 10.—Summary of Screening Tests Conducted on Drinking Water Samples

Parameter	Field or Lab	Type of test	Community	
			NM	AZ
General water quality analyses				
Alkalinity (as CaCO ₃)	F	Titration ¹	X	X
Conductivity	F	Probe	X	X
Hardness (as CaCO ₃)	F	Titration ¹	X	X
pH	F	Probe	X	X
Silica (SiO ₂)	F	Colorimetric test kit ¹	X	
Temperature	F	Probe		
TDS	F	Probe	X	X
UV absorption	L	UV Spectrophotometer	X	
Inorganic cations				
Calcium (Ca)	F	Titration ¹	X	X
Magnesium (Mg)	F	Calculated (from Total Hardness and Calcium)	X	X
Total Iron	F	Colorimetric test kit ¹	X	
Ferrous Iron (Fe II)	F	Colorimetric test kit ¹	X	
Inorganic Anions				
Chloride (Cl)	F	Colorimetric test kit ¹	X	
Fluoride (F)	F	Colorimetric test kit ¹	X	
Phosphate (PO ₄)	F	Colorimetric test kit ¹	X	
Sulfate (SO ₄)	F	Colorimetric test kit ¹	X	
Sulfide (S ²⁻)	F	Colorimetric test kit ¹	X	
Nitrogen				
Ammonia (NH ₃)	F	Colorimetric test kit ¹ / Probe	X	
Nitrate (NO ₃)	F	Colorimetric test kit ¹ / Probe	X	X
Nitrite (NO ₂)	F	Colorimetric test kit ¹	X	
Microbial Pathogens				
Total Coliform	F/L	Presence/absence incubation ²	X	X
Enterococci	F/L	Presence/absence incubation ³	X	

¹Test kits from the LaMotte SMART™ Water Analysis Field Laboratory.

²Positive Presence/absence tests are from CPI Colitag™ field kits. All positive (presence) samples were resampled and tested for Most Probable Number (MPN).

³Enterolert test is from IDEXX field test system.

CHAPTER 3 RESULTS AND DISCUSSION

3.1 FIELD WATER QUALITY TESTING

3.1.1 New Mexico Community

A total of 6 wells were tested during a one-week period in the New Mexico community. The results of the testing are presented in table 11.

None of the samples contained nitrate concentrations that exceeded the federal drinking water MCL of 10 mg/L as nitrogen. However, there were other potential water quality problems.

Well F had an excessive level of fluoride and exceeded the MCL for fluoride of 4 mg/L. The water also tested positive for coliform bacteria. It had been taken offline and was not being used as a drinking water source due to the high fluoride concentration. All other water quality parameters fell within the MCLs. The UV absorbance was also measured to indicate the presence of organic matter. It can be concluded from the results that there was minimal evidence of background organic matter. McQuillan et al. (1998) conducted a study on public water supply wells in this community and reported similar results. Private wells typically contained higher levels of chloride and TDS than public wells. Uranium was detected in 50 percent of the wells they examined. Cations in the well water were dominated by sodium. The water has low levels of calcium. The lack of calcium provides no geochemical removal mechanism for fluoride or uranium (Levine, 1998).

Because levels of calcium and magnesium are extremely low, an analysis of corrosivity was conducted. A total of five corrosivity indices were computed and included in table 11. The precipitation potential and Langelier Index are commonly used to evaluate the potential for solubilizing copper and lead from distribution pipes. The indices should have values slightly greater than zero for optimum water quality in distribution pipes. The Ryznar index, the aggressiveness index, and the alkalinity ratio confirmed that the waters have a potential to be corrosive, with wells A and E slightly more corrosive than wells B, C, D, and F (Levine, 1998).

3.1.2 Arizona Community

The Arizona community's wells were sampled in July 1998 and November 1998 to screen the groundwater for potential nitrate contamination (tables 12 and 13). Excessive nitrate levels were identified in Well 1 and water from this well was analyzed in more detail. Water samples from Well 1 were tested in February 1999 (table 14) for nitrate removal potential.

From table 12, it can be seen that wells 1 and 12 exceed the MCL for nitrate. These wells are currently not used for drinking water sources, but are used for irrigation. Well 1 was, at one time, a drinking water source and the community would like to utilize it again if feasible.

Table 11.—New Mexico Community Water Quality Results

Parameter	Well Number					
	A	B	C	D	E	F
Electrode Analyses						
Temperature (°C)	16.90	19.80	18.40	17.60	18.50	19.60
PH	8.25	8.86	8.60	8.93	7.78	9.17
Conductivity (µS/cm)	*	*	437.00	*	370.00	*
TDS (mg/L)	*	*	*	*	243.00	*
Colorimetric Analyses						
Ammonia - NH ₃ (mg/L as N)	0.08	0.31	0.07	0.66	0.24	0.43
Fluoride – F ⁻ (mg/L)	0.94	0.00	0.62	0.50	0.00	15.40
Total Iron – Fe (mg/L)	0.06	0.04	0.12	0.04	0.09	0.47
Nitrate – NO ₃ ⁻ (mg/L as N)	0.82	0.04	0.03	0.04	0.01	0.07
Nitrite – NO ₂ ⁻ (mg/Las N)	0.03	0.01	0.02	0.01	0.01	0.01
Phosphate – PO ₄ (mg/L)	0.12	0.14	0.11	1.33	0.02	1.28
Silica – SiO ₂ (mg/L)	0.26	46.00	0.00	0.09	0.00	0.00
Sulfate – SO ₄ (mg/L)	92.00	54.00	38.00	31.00	28.00	39.00
Sulfide – S ₂ ⁻ (mg/L)	0.02	0.02	0.02	0.00	0.01	0.00
Ferrous Iron – Fe II (mg/L)	0.027	0.030	0.025	0.024	0.028	0.080
Titration Analyses						
Alkalinity (mg/L as CaCO ₃)	128.95	102.45	136.85	122.15	129.45	112.55
Hardness (mg/L as CaCO ₃)	35.90	10.75	14.90	11.70	50.65	6.75
Calcium – Ca (mg/L)	23.65	11.35	11.15	7.10	32.50	5.55
Magnesium – Mg (mg/L)	12.25	0.00	3.75	4.60	18.15	1.20
Chloride – Cl (mg/L)	25.00	26.00	12.00	18.00	17.00	20.00
Microbial Analyses						
Total Coliform Bacteria (P/A) [§]	A	A	A	A	A	P
<i>E. coli</i> (P/A)	A	A	A	A	A	P
Enterococci (P/A)	A	A	A	A	A	P
USU Laboratory Analyses						
UV abs. @ 203 nm (cm ⁻¹)	0.564	0.064	0.052	0.055	0.033	0.129
UV abs. @ 254 nm (cm ⁻¹)	0.005	0.005	0.002	0.003	0.001	0.022
Corrosivity Analyses						
Precipitation Potential	1.58	0.76	0.67	-0.14	6.02	0.62
Langelier Index	-0.14	0.10	-0.05	0.02	-0.43	0.13
Ryznar Index	8.54	8.65	8.69	8.88	8.66	8.90
Aggressiveness Index	11.73	11.92	11.78	11.87	11.42	11.96
AIK/(Cl + SO ₄)	1.10	1.30	2.70	2.50	2.90	4.90

Shaded regions represent values that are not in compliance or excessively high in concentration.

*Parameter was not measured.

[§]P/A = Presence or absence

Table 12.—Arizona Community Well Water Quality, July 1, 1998

Parameter	Units	Well			
		0	10	1	12
Electrode analyses					
pH		7.58	7.51	7.3	7.12
Conductivity	μS/cm	1462	1469	3040	3050
Total Dissolved Solids (TDS)	mg/L	958	947	2270	1980
Colorimetric analyses					
Ammonia (NH ₃)	mg/L	0.48	0.79	1.8	0.27
Nitrate (NO ₃ ⁻ -N)	mg/L	0.78	3.38	46.4	27.4
Nitrite (NO ₂ ⁻ -N)	mg/L	0.01	0.02	0.02	0.01
Titration Analyses					
Alkalinity (as CaCO ₃)	mg/L	144	170	244	288
Hardness (as CaCO ₃)	mg/L	250	384	*	*
Calcium (Ca)	mg/L	172	248	*	*
Magnesium (Mg)	mg/L	78	136	*	*
Microbial Analyses					
Total Coliform Bacteria	P/A	I	I	I	I
<i>E. coli</i> Bacteria	P/A	A	A	A	A
Enterococci	P/A	A	A	A	A
USU Laboratory Analyses					
UV absorbance @ 203 nm	cm ⁻¹	> 3.2	> 3.2	> 3.2	> 3.3
UV absorbance @ 254 nm	cm ⁻¹	0.298	0.201	0.231	0.233

Shaded regions represent values that are not in compliance or excessively high in concentration.

I - Inconclusive, could not determine result.

P/A - Present/Absent.

It is suspected that a defunct cattle feedlot operation, approximately 100 ft. from the well, is the source of nitrate contamination. The cattle feedlot covered about 160 acres and was in operation for about 27 years (1963 to 1990). The operation started with 1,500 to 3,000 head of cattle and by the time of closure there were 60,000 to 65,000 head of cattle in the feedlot daily. The manure generated from the cattle operation was piled in mounds at the site and sold to farmers when possible. For a period of 3-5 years, manure and woods chips were used to generate mulch at the feedlot.

Results of a detailed analysis on Well 1 are summarized in table 14. Included in table 14 is each parameter tested; the resulting concentration; the standard deviation, if replicates were analyzed; the respective MCL from the National Drinking Water Regulation; the method used to determine the parameter; and the detection limit for the method used.

Table 13.—Arizona Community Well Water Quality, November 4-6, 1998

Parameter	Units	Well								
		1	2	3	4	5	6	7	8	9
Electrode Analyses										
pH		6.96	7.86	8.15	7.82	*	8.05	7.95	7.17	6.89
Conductivity	µS/cm	2860	1233	1243	621	*	1225	1224	985	999
Total Dissolved Solids (TDS)	mg/L	1941	818	821	409	*	809	808	652	658
Ion Chromatography Analyses										
Fluoride (F ⁻)	mg/L	2.54	0.31	0.82	0.98	0.95	0.93	0.96	0.32	0.38
Chloride (Cl ⁻)	mg/L	850	343	357	77.9	77.7	334	330	174	94.5
Nitrite (NO ₂ ⁻ -N)	mg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromide (Br ⁻)	mg/L	1.3	ND	ND	ND	ND	ND	ND	ND	ND
Nitrate (NO ₃ ⁻ -N)	mg/L	51.6	3.1	0.8	1.2	1.0	2.3	2.5	1.2	0.4
Phosphate (PO ₄ ³⁻)	mg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sulfate (SO ₄ ²⁻)	mg/L	467	53.9	45.4	26.9	26.8	45.8	45.5	58.6	322
Colorimetric Analysis										
Nitrate (NO ₃ ⁻ -N)	mg/L	0.02	0.05	0	0.13	*	0.05	0.06	0.05	0.17
Titration Analyses										
Alkalinity (as CaCO ₃)	mg/L	230	158	104	200	*	132	136	208	154
Hardness (as CaCO ₃)	mg/L	> 600	208	68	90	*	164	152	144	284
Calcium (Ca as CaCO ₃)	mg/L	*	154	44	66	*	94	80	90	189
Magnesium (Mg as CaCO ₃)	mg/L	*	54	24	24	*	70	72	54	95
Microbial Analyses										
Total Coliform Bacteria	P/A	*	A	I	A	*	A	A	I	*
<i>E. coli</i>	P/A	*	A	I	A	*	A	A	I	*

Shaded regions represent values that are not in compliance or excessively high in concentration.

*Not measured.

I = Inconclusive, could not determine result.

P/A = Present/Absent.

Table 14.—Detailed Analysis of Well 1 in the Arizona Community

Parameter	Concentration	Standard Deviation	Maximum Contaminant Level (MCL)	Analytical Method	Method Detection Limit (MDL)
General Water Quality					
Alkalinity (mg/L as CaCO ₃)	230		No MCL	2320 ¹	20
Conductivity (µS/cm)	2910		No MCL	2510 ¹	No MDL
Hardness (mg/L as CaCO ₃)	869		No MCL	2340 ¹	No MDL
pH	6.96		No MCL		No MDL
Total Dissolved Solids (TDS) (mg/L)	1880		No MCL ³	2510 ¹	No MDL
Inorganics					
Aluminum (mg/L)	< MDL		No MCL	6010B ²	0.05
Arsenic (mg/L)	< MDL		0.05	6010B ²	0.2
Barium (mg/L)	0.08		1.0	6010B ²	0.04
Boron (mg/L)	1.30		No MCL	6010B ²	0.1
Bromide (mg/L)	1.2	±0.005	No MCL	4110 ¹	0.1
Calcium (mg/L)	216		No MCL	6010B ²	0.4
Cadmium (mg/L)	< MDL		0.005	6010B ²	0.02
Chloride (mg/L)	850	±0.5	No MCL	4110 ¹	0.1
Chromium (mg/L)	< MDL		0.1	6010B ²	0.02
Cobalt (mg/L)	< MDL		No MCL	6010B ²	0.02
Copper (mg/L)	< MDL		1.3	6010B ²	0.05
Fluoride (mg/L)	0.53	±0.2	4.0	4110 ¹	
Iron (mg/L)	< MDL		No MCL	6010B ²	0.05
Lead (mg/L)	< MDL		0.0	6010B ²	0.05
Magnesium (mg/L)	79.8		No MCL	6010B ²	0.4
Manganese (mg/L)	< MDL		No MCL	6010B ²	0.02
Molybdenum (mg/L)	< MDL		No MCL	6010B ²	0.05
Nickel (mg/L)	< MDL		No MCL	6010B ²	0.1
Nitrate (mg/L-N)	44.0	±0.02	10.0	4110 ¹	0.02
Nitrite (mg/L-N)	ND	±0.0	1.0	4110 ¹	0.03
Phosphate (mg/L)	ND	±0.0	No MCL	4110 ¹	0.1
Phosphorus (mg/L)	< MDL		No MCL	6010B ²	2.0
Potassium (mg/L)	8.33		No MCL	6010B ²	2.0
Selenium (mg/L)	< MDL		0.01	6010B ²	0.5
Silica (mg/L)	15.0		No MCL	6010B ²	0.05
Sodium (mg/L)	333		No MCL	6010B ²	0.2
Strontium (mg/L)	2.35		No MCL	6010B ²	0.03
Sulfate (mg/L)	422	±0.5	No MCL	4110 ¹	0.1
Sulfur (mg/L)	107				0.2
Zinc (mg/L)	< MDL		No MCL	6010B ²	0.05

Table 14.—Detailed Analysis of Well 1 in the Arizona Community (continued)

Parameter	Concentration	Standard Deviation	Maximum Contaminant Level (MCL)	Analytical Method	Method Detection Limit (MDL)
Microbial Analysis					
Total Coliform Bacteria (P/A)	Interference		Absent	9221D ¹	No MDL
<i>E. coli</i> (P/A)	Interference		Absent	9221D ¹	No MDL
Corrosivity Analysis					
Langelier Index	-0.24		No MCL		
Ryznar Index	7.44		No MCL		
Agressiveness	12.26		No MCL		

Shaded regions represent values that are not in compliance or excessively high in concentration.

¹APHA, 1995.

²Test Methods for Evaluating Solid Waste (U.S. Environmental Protection Agency, 1986).

³The National Secondary Maximum Contaminant Level (SMCL) for TDS is 500 mg/L. SMCLs for Cl⁻ and SO₄²⁻ are 250 mg/L, respectively.

ND – Not detected.

The water in Well 1 was “extremely hard” (Tchobanoglous and Schroeder, 1985). The hardness was calculated from the individual concentrations of calcium, magnesium, and strontium—the divalent cations. The well water would also require treatment to remove some of the more than 2,000 mg of total dissolved solids (TDS)/L to provide suitable drinking water. The water contains excessive levels of sodium, chloride, and sulfate.

Corrosivity indices were calculated for Well 1 to determine if the water has the potential to corrode distribution pipes or form scale. The value calculated for the Langelier index (LSI), -0.24 characterize this water as being corrosive, i.e., CaCO₃ would dissolve, and that scale formation should not be expected. The Ryzner index (RI) of 7.44 also indicates that the water is corrosive. The aggressiveness index indicates that this water is non-aggressive, suggesting that asbestos fibers would not be released from asbestos-cement pipe (Tchobanoglous and Schroeder, 1985; Viessman and Hammer, 1985).

3.2 BENCH SCALE MODEL TESTING

3.2.1 Batch Testing

3.2.1.1 Reaction Kinetics

The rate of reaction is the term used to describe the loss or formation of a particular substance. In this study, nitrate in groundwater was the substance of focus. The goal was to determine the order and rate of reaction of nitrate conversion to nitrite by UV light. These variables can be determined by a variety of methods including the *method of integration* and the *method of initial rates*. Both methods were used on the data obtained from the experimental data for nitrate conversion under UV (phase I).

The experiments were conducted on deionized water and Logan, Utah, tap water spiked with nitrate. The results are graphically depicted in figures 6 and 7. The rate of conversion of nitrate levels off after about 30 minutes for the deionized water (DDW) and 50 minutes for the tap water. It is possible that the accumulation of nitrite in the batch reactor could have interfered with further conversion of nitrate. Further testing would be required to optimize the ratio of nitrate to nitrite in the UV irradiation step of the process.

3.2.1.1.1 Method of Integration

This method is the simplest method to determine the reaction rate and order. The order of a reaction can be determined graphically by evaluating the linearity of the experimental data or the transformed data. In the method of integration the rate of nitrate removal is evaluated by $dC/dt = -kC^n$. If n is zero, then a plot of concentration as a function of time will yield a straight line. If n is one, then the logarithm of the concentration is evaluated as a function of time. If n is two, the inverse of the concentration is used in the graphical analysis. If a straight-line plot is obtained, then it is assumed that the order of the reaction corresponds to the reaction model plotted (Tchobanoglous and Schroeder, 1985). The reaction rate can then be determined by the slope of the line. This method was used on the data obtained from the experiments on nitrate conversion under UV irradiation. The experiments were conducted using reagent-grade ($> 18 \text{ M}\Omega$), deionized water and Logan, Utah, tap water spiked with nitrate. The results are graphically depicted in figures 8 and 9.

It can be seen in the deionized water analysis shown in figure 8 that a line fits the second-order plot (c) best (i.e., the regression line has the highest R^2 value). Thus, we conclude that this reaction is, apparently, second-order. However, the improvement in fit over the first-order plot is small and may not be of practical significance. It can be seen in figure 9, which presents results for the tap water analysis, that a line fits the first-order reaction (b) the best. These determinations were based on the correlation constant R^2 , the constant nearest one indicating the best correlation. The reaction rates can then be determined from the slope of the lines. The apparent reaction orders and reaction rates are **boldly highlighted** in table 15 for each analysis. The reaction rates in deionized water and tap water were $0.0005 \text{ L/mg NO}_3^- \text{-N min}$ and 0.0137 min^{-1} , respectively.

3.2.1.1.2 Method of Initial Rates

The data obtained from the batch testing were also analyzed with the method of initial rates to compare with the method of integration results. In this method, a sequence of experiments was carried out at differing initial concentrations ($\sim 5, 9, 25, \text{ and } 50 \text{ mg NO}_3^- \text{-N/L}$) and the water was exposed to UV for ~ 50 minutes. The data were then plotted. The slope of the line provides an estimate of the order and the intercept an estimate of the logarithm of the rate. Specifically, the \log of $(-\Delta\text{NO}_3^-/\Delta t)$ was plotted versus the \log of initial NO_3^- concentration. The linearity of the data was assessed and an equation was derived for each line to determine the slope and intercept. The logarithm of the change in nitrate concentration ($\text{mg NO}_3^- \text{-N/L}$) per minute [$\log(-\Delta\text{NO}_3^-/\Delta t)$] was plotted versus the logarithm of initial NO_3^- concentration. A linear regression analysis was then performed to determine the slope and intercept. The results of the analysis can be seen in figure 10 and table 16. The deionized water and tap water data analyses resulted in slopes, or estimates of reaction order, of 1.6 and 1.3, respectively. The intercepts of -3.078 for deionized water and -2.5099 for tap water give rates of 0.0008 and $0.003 \text{ mg NO}_3^- \text{-N/L min}$, respectively.

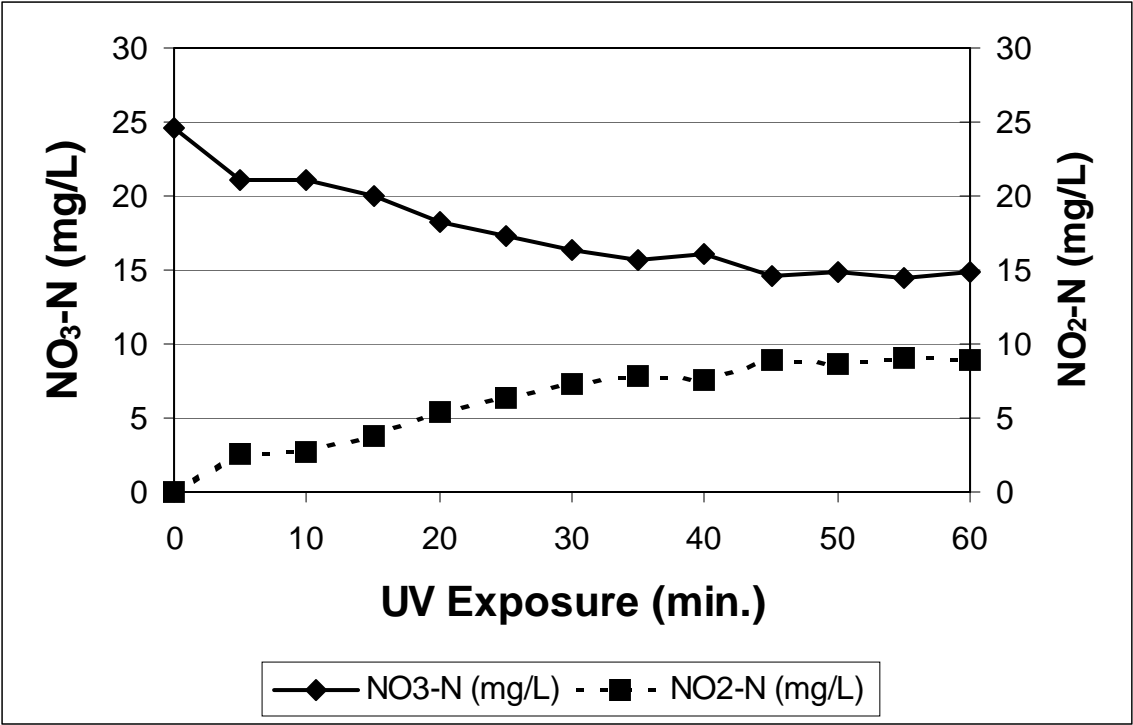


Figure 6.—Nitrate Reduction to Nitrite by UV Irradiation in Deionized Water Under Batch Conditions.

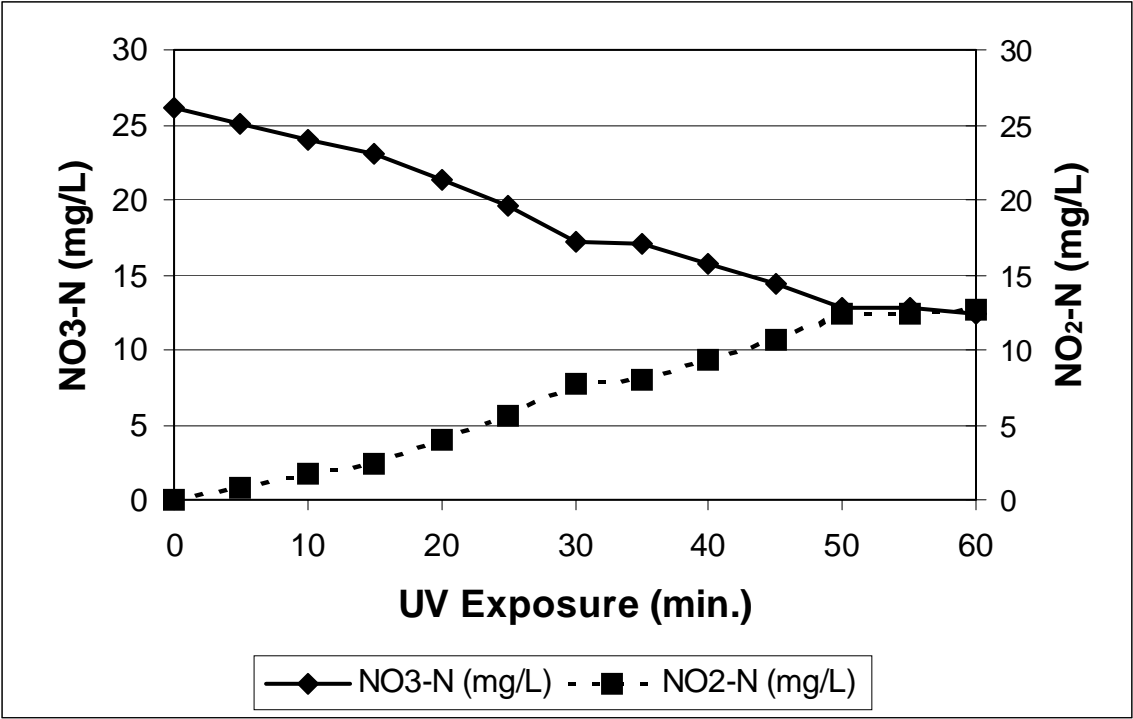


Figure 7.—Nitrate Reduction to Nitrite by UV Irradiation in Tap Water Under Batch Conditions.

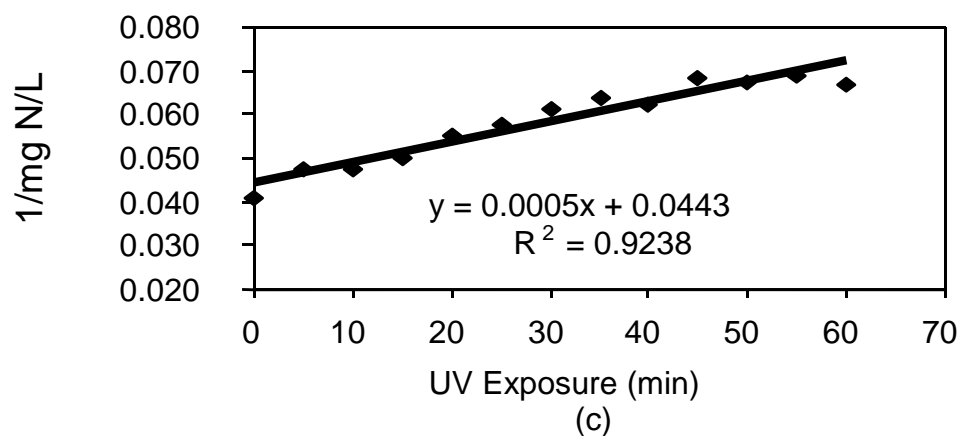
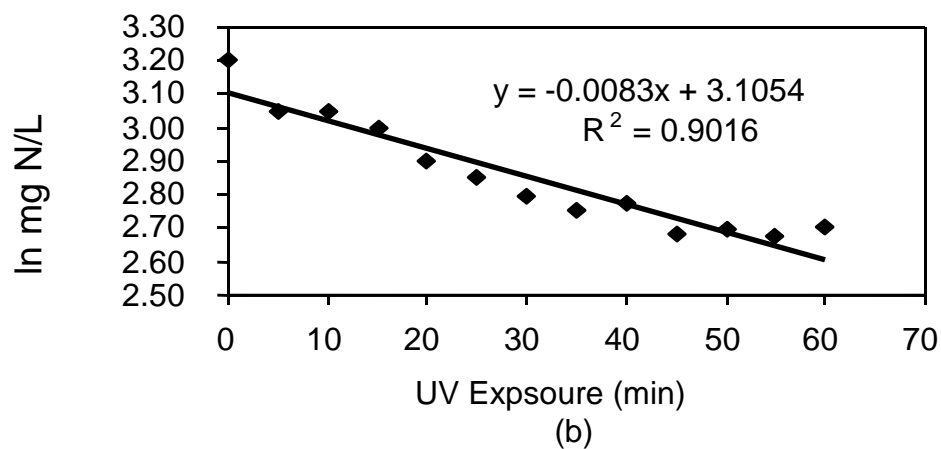
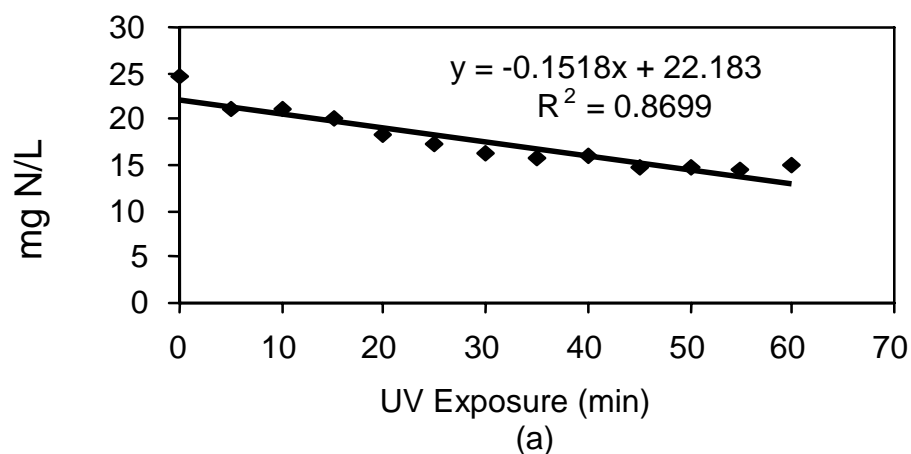


Figure 8.—Regression Analysis for the Determination of Reaction Order and Rate Constants for UV Treatment of NO_3^- in Deionized Water: (a) Zero Order Reaction; (b) First-Order Reaction; and (c) Second-Order Reaction.

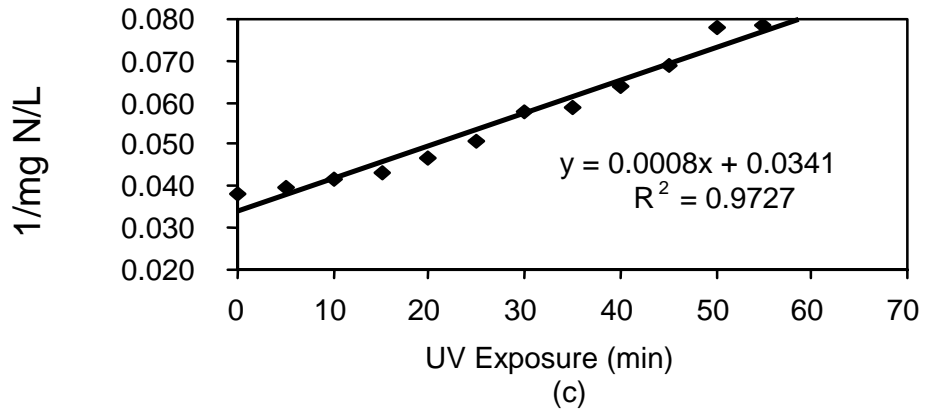
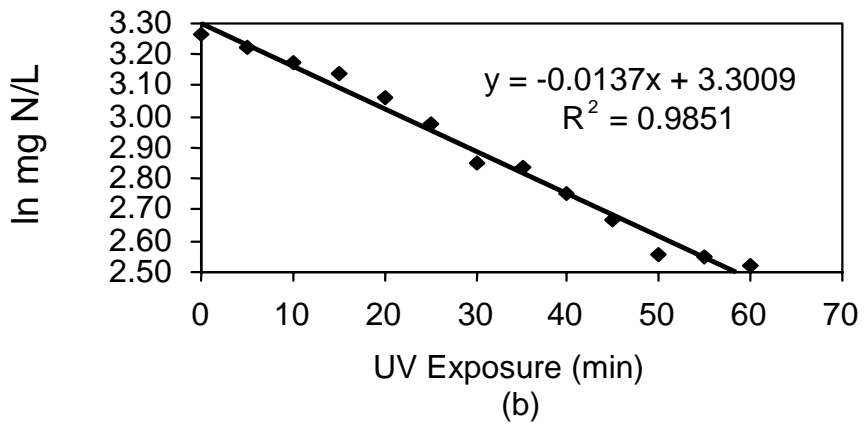
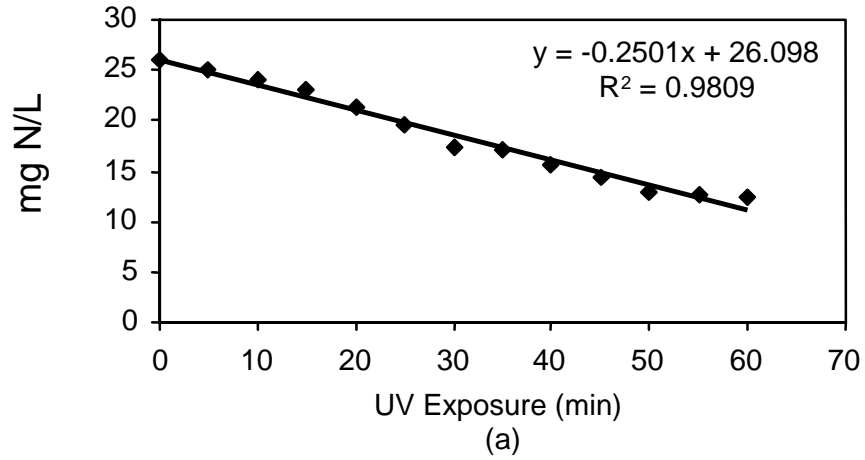


Figure 9.—Regression Analysis for the Determination of Reaction Order and Rate Constants for UV Treatment of NO_3^- in Tap Water: (a) Zero Order Reaction; (b) First-Order Reaction; and (c) Second-Order Reaction.

Table 15.—Summary of Integral Graphical Method Order and Reaction Rate Estimates for Reagent and Tap Water

Order	Units	Deionized Water		Tap Water	
		K	R ²	k	R ²
Zero	$\frac{\text{mg NO}_3^- - \text{N}}{\text{L min}}$	0.1518	0.8699	0.2501	0.9809
First	$\frac{1}{\text{min}}$	0.0083	0.9016	0.0137	0.9851
Second	$\frac{\text{L}}{\text{mg NO}_3^- - \text{N min}}$	0.0005	0.9238	0.0008	0.9727

3.2.1.2 Batch Temperature Changes

The rates of most reactions in natural waters increase with temperature (Chapra, 1997). Also, it can be assumed, as a first approximation, that the rate will approximately double for each 10° C rise in temperature. Throughout the series of batch tests conducted, it was evident that there was a rise in temperature due to heat transferred from the ultraviolet lamp to the water. The rates of temperature increase ranged from 2 to 0.6 °C/min and averaged 0.9 °C/min in deionized water and tap water. The increasing temperature throughout the experiment may affect the reaction rates presented in the previous section. Bayliss and Bucat (1975) concluded that increases in temperature increase nitrite production.

3.2.1.3 Effects of pH on Nitrate Conversion

The pH of the testing solution was adjusted at the beginning of some experiments to see if there was any change in pH during the process. The pH of the testing solution was then monitored through the entire denitrification process. These tests were conducted on deionized water and tap water spiked with nitrate. Figures 11 and 12 illustrate the effects of pH on the denitrification process.

It can be seen in Figures 11 and 12 that the pH effects the conversion of nitrate throughout the process. An acidic pH of 3.0 inhibits reduction of nitrate during phase I (UV irradiation) of the process in both the deionized water and tap water tests. Phase I is most important in this process, since this is the phase that initiates the denitrification process. The test solutions that are at neutral pH (6.0-7.0) have better nitrate reduction results. Nitrate concentration decreased from ~ 25 mg NO₃⁻-N/L to ~ 15 mg NO₃⁻-N/L at neutral pH.

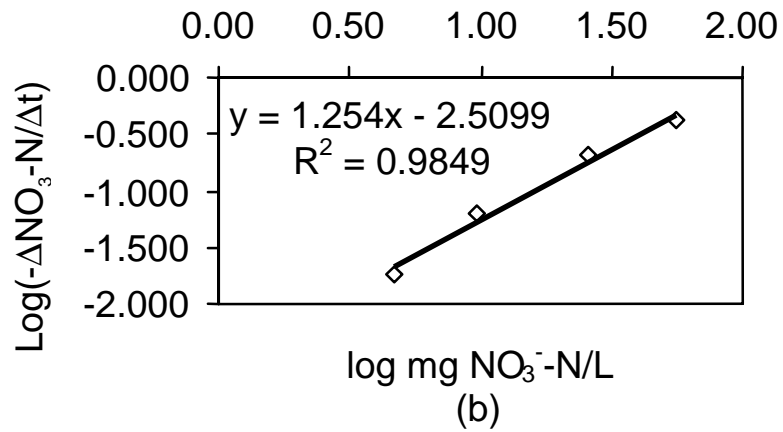
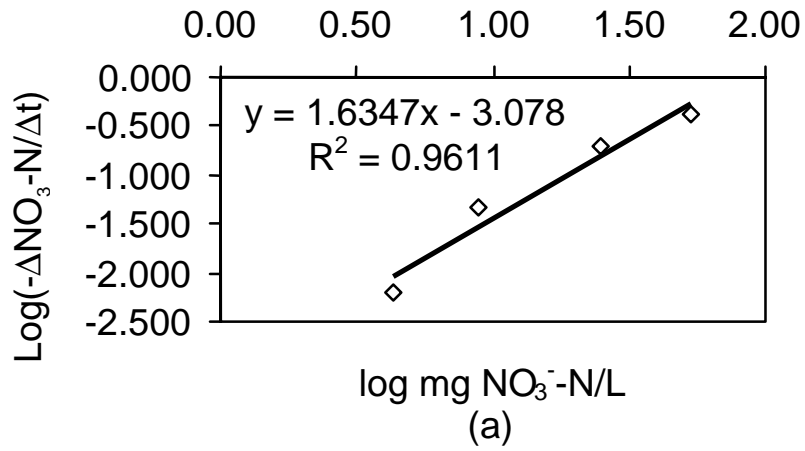


Figure 10.—Method of Initial Rates Plots for Deionized Water (a) and Tap Water (b).

Table 16.—Summary of Method of Initial Rates Order and Reaction Rates

	Deionized Water	Tap Water
Order	1.6	1.3
Rate (<i>k</i>) (mg NO ₃ ⁻ -N/L min)	.0008	.003

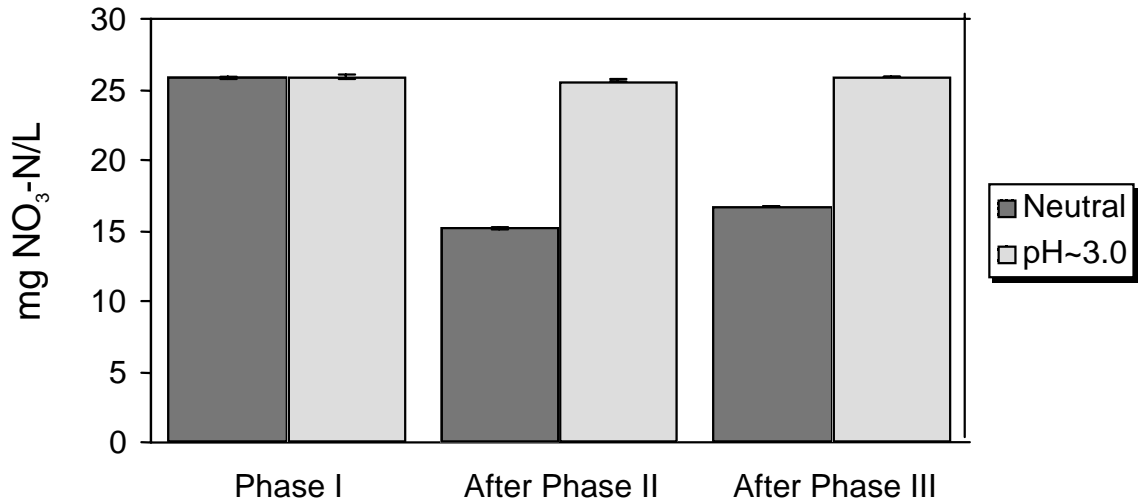


Figure 11.—pH Effects on Nitrate Conversion in Deionized Water. Error Bars Are \pm Standard Deviation.

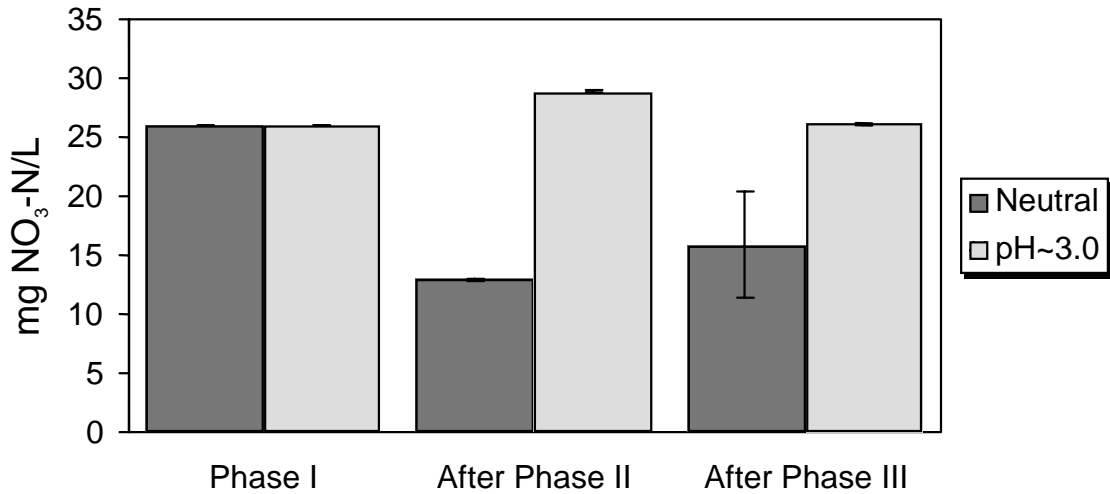


Figure 12.—pH Effects on Nitrate Conversion in Logan, Utah, Tap Water. Error Bars Are \pm Standard Deviation.

The results of the effects of pH on nitrate conversion exposed to UV are further supported by studies conducted by Bayliss and Bucat (1975). They found that the photoreduction of nitrate to nitrite was pH dependent. The nitrite quantum yield (nitrite production) was greater in alkaline solutions.

3.2.1.4 Comparison of Laboratory Contaminated Water to Arizona Community Water

The two main objectives of this study were to confirm that the UV denitrification process actually could reduce elevated nitrate concentrations below the drinking water MCL in a laboratory setting, and to see how the system would perform on actual nitrate-contaminated water. The nitrate-contaminated water came from the Arizona Native American community described previously.

Figure 13 shows the nitrate reduction and nitrite production for the nitrate spiked Logan tap water. The spiked tap water was run through the entire denitrification process (phase I-III). Phase I consisted of a 50-minute exposure time; Phase II, a reduction in pH with sulfuric acid to approximately 3.0; and Phase III, a 20-minute air sparge. The initial nitrate concentration was approximately 26 mg NO_3^- -N/L, and the process reduced the level to a final concentration of approximately 16 mg NO_3^- -N/L. Nitrite was also monitored throughout the process. In Phase I there was no nitrite present. However, after Phase III there was 1.8 mg NO_2^- -N/L.

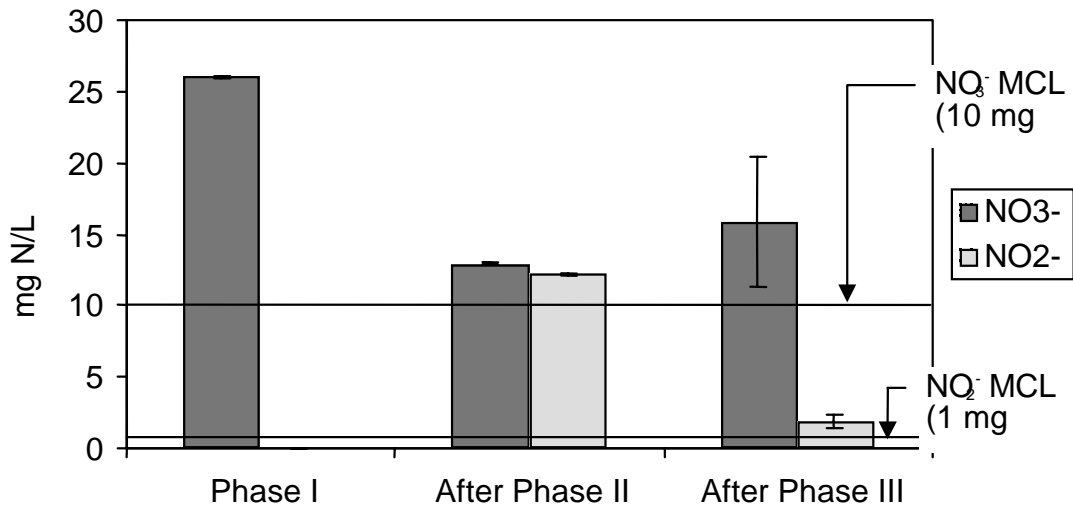


Figure 13.—Nitrate Reduction and Nitrite Production in Logan, Utah, Tap Water Spiked with Nitrate. Error Bars Are \pm Standard Deviation.

Nitrate contaminated water from the Arizona community was then tested in the UV denitrification process (figure 14). Phase I consisted of a 60 minute UV exposure; phase II, a pH reduction to ~ 3.0 with sulfuric acid; and phase III, a 20-minute air sparge. The water contained ~ 45 mg NO_3^- -N/L and no detectable levels of nitrite initially. After phase III, the nitrate concentration was ~ 41 mg NO_3^- -N/L and the nitrite concentration was ~ 1.29 mg NO_2^- -N/L.

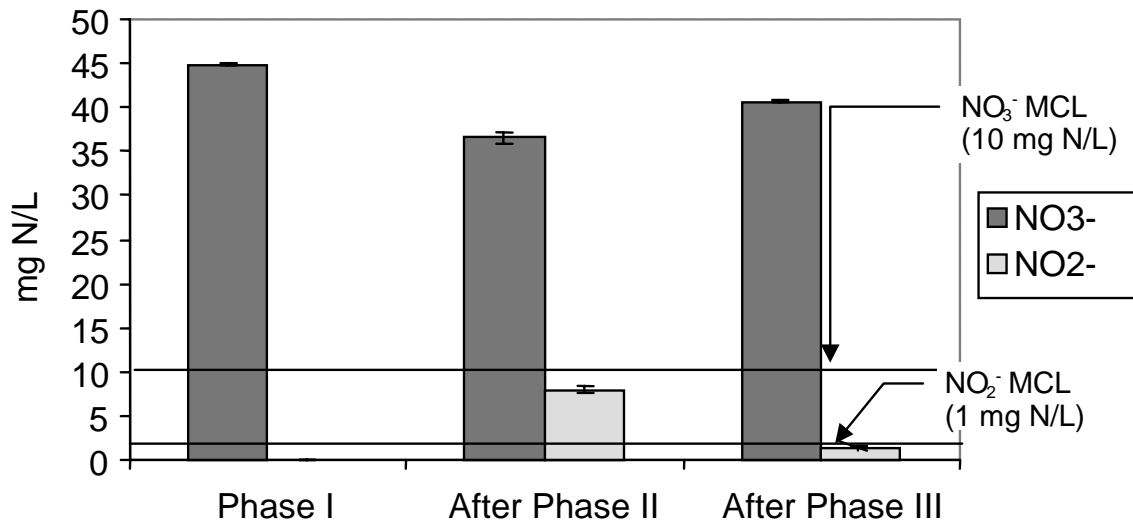


Figure 14.—Nitrate Reduction and Nitrite Production in Contaminated Arizona Reservation Groundwater. Error Bars Are ± Standard Deviation

The initial pH of these waters was approximately neutral. In neither of the tests were nitrate levels reduced below the MCL of 10 mg NO₃⁻-N/L. Furthermore, the detection of residual nitrite after phase III is cause for concern. It may be possible to eliminate the residual nitrite problem by extending the air sparge time. Treatment of the tap water resulted in a 38 percent reduction in nitrate concentration, while the treatment of the Arizona water achieved only a 9 percent reduction. The reason for this relatively low performance in the Arizona water is unknown. It is noteworthy that a precipitate film formed on the UV lamp during treatment of the Arizona water. It is conceivable that this film absorbed UV radiation and reduced the dose to the water. The composition of the film is unknown, but it is conceivable that it included carbonate minerals that precipitated on the warm surface of the UV lamp. It is also conceivable that the high dissolved solids content of the water interfered in some other way with the efficiency of UV energy transfer.

3.2.2 Flow-Through Testing

The flow-through testing consisted of controlling the flow rate and residence time in the ultraviolet unit. Only Phase I (UV irradiation) was operated in flow-through mode. Phases II and III (acidification and sparging, respectively) were conducted in batch mode as described previously. This series of experiments consisted of testing tap water spiked with nitrate. UV exposure was varied in 1-hour intervals from 1 to 4 hours duration. Figures 15 and 16 show the results of the nitrate and nitrite monitoring during the test.

All test solutions had a ~ 26 mg NO₃⁻-N/L initial concentration. Longer UV exposure times resulted in more conversion to nitrite and reduction in nitrate. The overall reduction in nitrate for the 60-minute UV exposure resulted in a final nitrate concentration of 19.3 mg NO₃⁻-N/L. The 120-, 180-, and 240-minute UV exposures resulted in a final concentration of 16.7, 14.8, and 12.7 mg NO₃⁻-N/L. However, the production of nitrite resulted in a residual nitrite

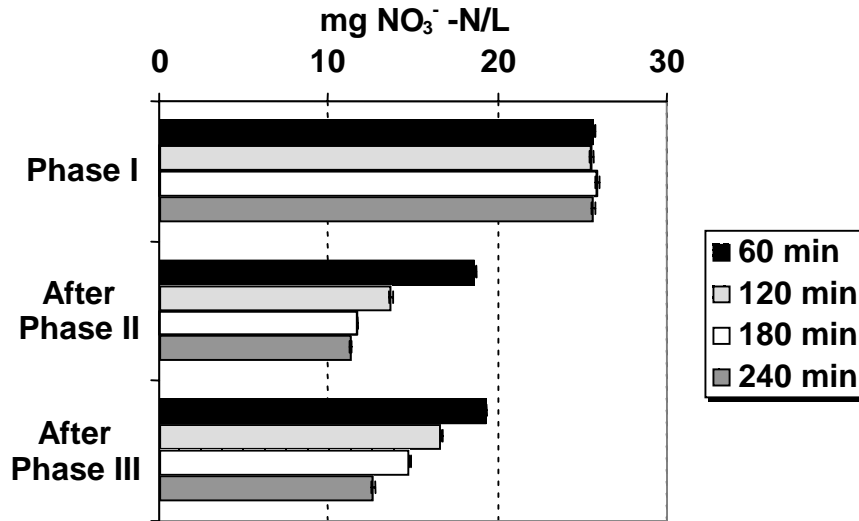


Figure 15.—Flow-Through Nitrate Removal Results. Error Bars Are \pm Standard Deviation.

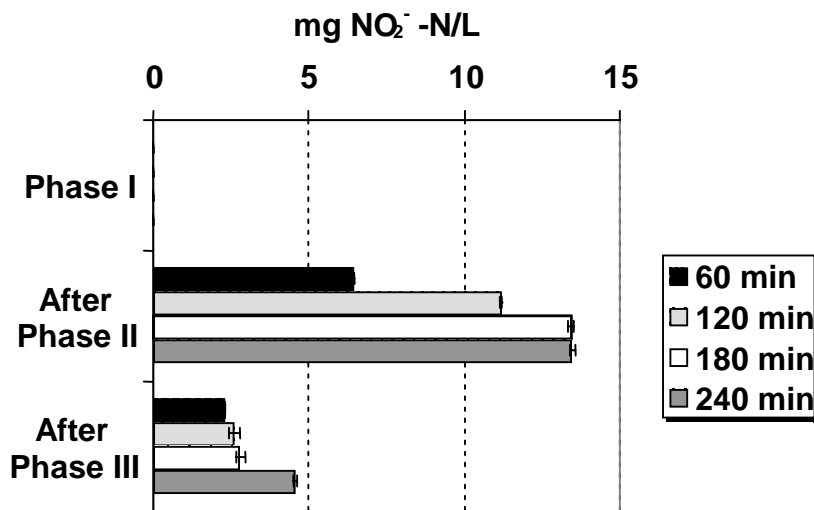


Figure 16.—Flow-Through Nitrite Production Results. Error Bars Are \pm Standard Deviation.

concentration after phase III. The final nitrite concentrations for the 60, 120, 180, and 240-minute UV exposures were 2.3, 2.6, 2.8, and 4.6 mg NO₂⁻-N/L, respectively. The air sparge was kept constant (20 minute) for all exposure times. It should be noted that the sparge time could be extended to compensate for the increase in nitrite production in phase II.

3.2.2.1 Flow-Through Temperature Changes

Water temperature was monitored throughout the flow-through testing for exposure periods of 10, 20, 40, and 60 minutes. The temperature increase rate ranged from 0.3 to 0.5° C/min in deionized water and from 0.3 to 0.6° C/min in tap water and averaged 0.4° C/min in both waters. This is less than half the average rate observed in the batch tests.

CHAPTER 4

SUMMARY

4.1 HEALTH EFFECTS

Nitrate may enter drinking water from both natural sources and the residuals of mankind's activities. Agricultural fertilizers and wastes have been the principal source of nitrate pollution in the United States.

Nitrate has relatively low toxicity for the majority of adult humans but may have serious health effects for some people when consumed at low doses. Nitrate consumption by infants less than 6 months old has been associated with methemoglobinemia (blue baby syndrome). The U.S. Environmental Protection Agency has set an MCL for NO_3^- -N at 10 mg/L to protect against this disease. Avery (1999) has reviewed the complexity of the causes of infantile methemoglobinemia and suggested that the MCL should be reconsidered and possibly adjusted to a higher concentration.

Other health effects that have been ascribed to nitrate exposure include birth defects, spontaneous abortions, hypertension, thyroid hypertrophy, and certain types of cancer. Cancer links may exist because of the potential for the formation of carcinogenic nitrosamines when nitrate is reduced to nitrite in the digestive tract.

Ruminant animals may be poisoned by nitrate due to the reduction of nitrate to toxic nitrite by bacteria in the rumen. Nitrate exposure may be the cause of spontaneous abortion in animals.

Nitrate is an anion radical that is very soluble in water. It does not react effectively with the cation exchange complex of soils and aquifer materials and is, therefore, highly mobile in soil, aquifers, and sediments. Because it is mobile, it may move relatively quickly from its source to wells or surface water from which people or animals may be exposed.

4.2 NITRATE MANAGEMENT AND TREATMENT

Prevention of nitrate contamination of groundwater and surface water is, of course, preferable to relying on treatment technology to remove nitrate contamination. Special attention should be paid to preventing contamination of ground water resources used for drinking water supplies. In small communities, this often means carefully managing the placement of septic tanks and other systems for sewage treatment and disposal. Septic tank drain field placement relative to drinking water supply wells should be closely regulated. Concentrating too many septic tank drain fields in too small of an area can prevent the dilution of nitrate by ground water that is needed to prevent nitrate concentrations from becoming too high. In addition, careful management of chemical fertilizer and manure application rates to land is needed to prevent too much nitrate from leaching into ground water. Well construction to prevent contamination of the well water from surface runoff and from contaminated shallow ground water is also very important.

Water may be treated to remove nitrate using ion exchange, reverse osmosis, electrodialysis, or biological denitrification technologies. Installation and operation of any of these technologies is

expensive relative to conventional water treatment costs. Developing technologies for nitrate removal include chemical reduction and catalytic reduction. These technologies are also anticipated to be relatively expensive. A proposed technology that uses UV irradiation to reduce nitrate to nitrite followed by acidification and air sparging to remove the nitrite from the treated water was evaluated as part of the study reported here.

CHAPTER 5

CONCLUSIONS

The laboratory study of a UV denitrification system (Murphy, Moody, and Henthorne, 1999) evaluated nitrate removal in batch and flow-through simulations using laboratory reagent grade water, tap water, and a nitrate contaminated, high dissolved solids well water from Arizona. The results have led to the following conclusions:

1. The UV denitrification process was capable of reducing nitrate levels but removal was incomplete. When initial NO_3^- -N concentrations were about 25 mg/L, the 10 mg/L MCL was not achieved in either a batch or a flow-through experimental system. In the flow-through system, the water was recirculated past the UV lamp for up to 240 minutes followed by air sparging for 20 minutes. Forty-nine percent of the initial nitrate in tap water was removed in the flow-through system after 240 minutes of UV treatment and 20 minutes of air sparging.
2. A nitrite residual accumulated in the treatment process. In the 240-minute recirculating flow-through system, an average of 4.6 mg NO_2^- -N/L was produced.
3. Both first and second order reaction models fit the nitrate removal data well. The first-order rate of NO_3^- -N removal in batch experiments was 0.008/min. in reagent grade deionized water and 0.01/min. in tap water. Second-order reaction rates were 0.0005 L/mg NO_3^- -N/min. and 0.0008 L/mg NO_3^- -N/min. in deionized water and tap water, respectively.
4. Heat from the UV lamp increased the temperature of the treated water. In flow-through experimental systems, water temperature increased at an average rate of 0.4° C/min.
5. pH affected the removal efficiency of nitrate in the UV process. The initial pH needed to be near neutral for the system to reduce nitrate effectively.
6. The experiments conducted to determine if the UV denitrification process would effectively remove nitrate from contaminated groundwater from Arizona did not remove nitrate to drinking water standards. This water had a TDS concentration of approximately 1900 mg/L, a concentration that may not be acceptable for a drinking water source. The efficiency of treatment may have been adversely affected by the high dissolved solids content of the water. A film developed on the UV lamp that may have reduced the UV dose.
7. The major advantage of the UV denitrification process is that it does not produce a residual product that requires disposal. Costs of treatment are limited to equipment purchase and installation, maintenance, power consumption, and chemical (acid and base) costs. Cost estimates were not performed for this study.

8. Further investigations for improvement of the UV denitrification process are needed. It is plausible that this system can become a viable alternative for small scale and point-of-use treatment of nitrate contaminated drinking source water.

CHAPTER 6

RECOMMENDATIONS

Nitrate contamination of a Native American community or individual drinking water source can present many challenges to those responsible for protecting public health. Under no conditions should the problem be ignored or the implementation of the solution to the problem be delayed longer than is absolutely necessary. The known and suspected health effects of nitrate exposure above the MCL of 10 mg NO₃⁻-N/L are serious.

Options for management of nitrate contamination in drinking water include:

1. Seeking a noncontaminated source. This may include drilling a new well away from known or suspected sources of nitrate contamination or diverting and treating surface water that has suitable quality.
2. Blending contaminated water with noncontaminated water. Dilution may be used to reduce nitrate concentrations to acceptable levels.
3. Implementing nitrate removal treatment. Treatment is costly but costs can be minimized if the water that must be treated can be reliably limited to water for which there is a reasonable risk of human consumption.

Subsequent phases of process development for the UV denitrification system should focus on:

1. Optimizing the mechanism for removing nitrite produced in the reduction process. This may include the development of a high efficiency air sparging system, for example.
2. Optimizing the UV dose rate. This might include finding an optimal water thickness flowing past the UV lamp, improving turbulent mixing in the UV exposure process, and/or optimizing the time that the water is exposed to UV irradiation.
3. Determining the water quality limitations for efficient use of the UV system. The role of hardness and TDS concentrations in process efficiency needs to be well described, for example.
4. Minimizing pH adjusting chemical use.
5. Minimizing heat transfer from the UV lamp.

LITERATURE CITED

- American Public Health Association. (1995). *Standard methods for the examination of water and wastewater*. (19th ed.). American Public Health Association, Washington, DC.
- American Water Works Association. (1990). *Water quality and treatment*. (4th ed.). McGraw Hill, New York, NY.
- Anonymous. (1997). Research needs for small water systems: a survey. *J. AWWA*, 89:101-113.
- Arbuckle, T.E., G.J. Sherman, D. Walters, and B. Lo. (1988). Water nitrates and CNS birth defects: a population-based case-control study. *Arch. Environ. Health*, 43(2):162-167.
- Atlas, R.M., and R. Bartha. (1993). *Microbial ecology fundamentals and applications*. (3rd ed.). Benjamin Cummings, San Francisco, CA.
- Avery, A.A. (1999). Infantile methemoglobinemia: reexamining the role of drinking water nitrates. *Environ. Health Perspect.*, 107(7):583-586.
- Balsamo, P., W.R. Hardy, and E.M. Scott. (1964). Hereditary methemoglobinemia due to diaphorase deficiency in Navajo Indians. *J. Pediat.*, 68(6):928-930.
- Bayliss, N.S., and R.B. Bucat. (1975). The photolysis of aqueous nitrate solutions. *Austral. J. Chem.*, 28:1865-1878.
- Bosch, H.M., A.B. Rosefield, R. Huston, H.R. Shipman, and F.L. Woodard. (1950). Methemoglobinemia and Minnesota well supplies. *J. AWWA*, 42:161-170.
- Brown, T. (1995). Solving nitrate contamination. *Am. City Cty.*, 110(October):46.
- Bruning-Fann, C.S., and J.B. Kaneene. (1993). The effects of nitrate, nitrite, and N-nitroso compounds on human health: a review. *Vet. Human Toxicol.*, 35(6):521-538.
- Bureau of Reclamation. (1997). *Nitrate fact sheet*. : Bureau of Reclamation. Denver, CO.
- Chapra, S.C. (1997). *Surface water-quality modeling*. WCB/McGraw-Hill, New York, NY.
- Clifford, D., and X. Liu. (1993). Ion exchange for nitrate removal. *J. Am. Water Works Assoc.*, 85:135-143.
- Comly, H.H. (1945). Cyanosis in infants caused by nitrates in well water. *J. Am. Med. Assoc.*, 129:112-116.
- Droste, R.L. (1997). *Theory and practice of water and wastewater treatment*. John Wiley and Sons, New York, NY.
- Edmunds, W.M., and C.B. Gaye. (1997). Naturally high nitrate concentrations in groundwaters from the Sahel. *J. Envir. Qual.*, 26:1231-1239.

- Ferguson, R.B., D.E. Eisenhauer, D.H. Bockstadter, and G. Buttermore. (1990). Water and nitrogen management in Central Plate Valley in Nebraska. *J. Irrig. Drain. Eng.*, 116(Jul/Aug):557-565.
- Follett, R.F. (1989). *Nitrogen management and groundwater protection*. Elsevier, New York, NY.
- Guimera, J. (1998). Anomalously high nitrate concentrations in ground water. *Ground Water*, 36(2):275-282.
- Jennings, G.D., and R.E. Sneed. (1996). *Nitrate in drinking water*. Number: AG-473-4. North Carolina Cooperative Extension Service, North Carolina State University. Raleigh, NC.
- Kapoor, A., and T. Viraraghavan. (1997). Nitrate removal from drinking water review. *J. Env. Eng.*, 123(4):371-380.
- Katers, J.F., and A.E. Zaroni. (1998). Nitrogen removal. *Wat. Envir. Technol.*, 10(3):32-36.
- Keeney, D. (1986). Sources of nitrate to groundwater. *Crit. Rev. Environ. Control*, 16(3):257-304.
- Kross, B.C., A.D. Ayebo, and L.J. Fuortes. (1992). Methemoglobinemia: nitrate toxicity in rural America. *Am. Fam. Phys.*, 46:183-188.
- Lee, Y.W., M.F. Dahab, and I. Bogardi. (1992). Nitrate risk management under uncertainty. *J. Water Resour. Plann. Manage. Div. ASCE*, 118(2, March/April):151-161.
- Levine, A.D. (1998). *Results of groundwater field screening tests at the Pueblo of Pojoaque*. Utah Water Research Laboratory, Utah State University. Logan, UT.
- Lichtenberg, E., and L.K. Shapiro. (1997). Agriculture and nitrate concentrations in Maryland community water system wells. *J. Envir. Qual.*, 26:145-153.
- Maas, R.P., M.D. Smolen, C.A. Jamieson, and A.C. Weinberg. (1987). *Setting priorities: the key to nonpoint source control*. Number: EPA/841-B-87-110. U.S. Environmental Protection Agency. Washington, D.C.
- MacDonald, J.A., A.K. Zander, and V.L. Snoeyink. (1997). Improving service to small communities. *J. AWWA*, 89(1):58-64.
- Malberg, J.W., E.P. Savage, and J. Osteryoung. (1978). Nitrates in drinking water and the early onset of hypertension. *Envir. Pollution*, 15(3):155-160.
- McQuillan, D., C. Whitman, R. Montes, and R. Pine. (1998). *Groundwater geochemistry: Pojoaque Pueblo, New Mexico*. New Mexico Environment Department. Santa Fe, NM.

- Mitchell, T.J., and A.K. Harding. (1996). Who is drinking nitrate in their well water? A study conducted in rural northeastern Oregon. *J. Environ. Health*, 59:14-19.
- Morbidity and Mortality Weekly Report. (1996). Spontaneous abortions possibly related to ingestion of nitrate-contaminated well water--La Grange County, Indiana, 1991-1994. *MMWR*, 45(26):569-572.
- Morel, F.M.M., and J. Hering. (1993). *Principles and applications of aquatic chemistry*. John Wiley and Sons, New York, NY.
- Murphy, A.P., C.D. Moody, and L.R. Henthorne. (1999). Water denitrification process using air stripping (REC-3603), *U.S. Patent and Trademark Office, Washington, DC*. USA: United States of America, Secretary of the Interior, Washington, DC.
- National Drinking Water Clearinghouse. (1998). Septic systems. How can leaching into wells be prevented? *On Tap*, 7(2):18-19.
- National Research Council. (1997). *Safe water from every tap: improving water service to small communities*. National Academy Press, Washington, DC.
- Nolan, B.T., B.C. Ruddy, K.J. Hitt, and D.R. Helsel. (1997). Risk of nitrate in groundwaters of the United States—a national perspective. *Environ. Sci. Technol.*, 31:2229-2236.
- Orion Research Inc. (1996). Nitrite Electrode Instruction Manual, Model 97-46-ionplus . Beverly, MA: Orion Research, Inc.
- Puckett, L.J. (1994). *Nonpoint and point sources of nitrogen in major watersheds of the United States*. Number: 94-4001. U.S. Geological Survey. Reston, VA.
- Saull, M. (1990). Nitrates in soil and water. *New Scient.*, 127(37):1-4.
- Scott, E.M., and D.D. Hoskins. (1958). Hereditary methemoglobinemia in Alaskan Eskimos and Indians. *Blood*, 13(8):795-802.
- Self, J.R., and R.M. Waskom. (1992). *Nitrate in drinking water*. Number: 0.517. Colorado State University. Fort Collins, CO.
- Solt, G. (1987). Removing nitrate from potable water. *Chem. Eng.* (436 (May)):33-36.
- Sonntag, C.V., and H.P. Schuchmann. (1992). UV disinfection of drinking water and by-product formation: some basic considerations. *Aqua (Oxford)*, 41(2):67-74.
- Spalding, R.F., and M.E. Exner. (1993). Occurrence of nitrate in groundwater--a review. *J. Envir. Qual.*, 22:392-402.
- Sykora, J.L., G. Keleti, R. Roche, D.R. Volk, G.P. Kay, R.A. Burgess, M.A. Shapiro, and E.C. Lippy. (1980). Endotoxins, algae and *Limulus* amoebocyte lysate test in drinking water. *Water Res.*, 14:829-839.

- Tchobanoglous, G., and E.D. Schroeder. (1985). *Water quality characteristics modeling and modification*. Addison-Wesley, Reading, MA.
- Tiller, V.E.V. (1996). *Tillers guide to Indian country: economic profiles of American Indian reservations*. , BowArrow Publishing, Albuquerque, NM.
- Tyson, A., M.L. Dixon, and W. Segars. (1992). *Your drinking water: nitrates*. Circular 819-5. Cooperative Extension Service, University of Georgia. Athens, GA.
- U.S. Environmental Protection Agency. (1986). *Quality criteria for water 1986*. Number: EPA 440/5-86-001. U.S. Environmental Protection Agency. Washington, DC.
- U.S. Environmental Protection Agency. (1986). *Test methods for evaluating solid waste*. Number: SW-846. U.S. Environmental Protection Agency. Washington, D.C.
- U.S. Environmental Protection Agency. (1987). *Nitrate-nitrite health advisory*. U.S. Environmental Protection Agency. Washington, D.C.
- U.S. Environmental Protection Agency. (1990a). *National pesticide survey--nitrate*. U.S. Government Printing Office. Washington, D.C.
- U.S. Environmental Protection Agency. (1990b). *Technologies for upgrading existing or designing new drinking water treatment facilities*. Number: EPA/625/4-89/023. U.S. Environmental Protection Agency. Cincinnati, OH.
- U.S. Environmental Protection Agency. (1992). *The quality of our nation's water*. Number: EPA/841-k-92-001. U.S. Environmental Protection Agency. Washington, D.C.
- U.S. Environmental Protection Agency. (1993). *Nitrogen control*. Number: EPA/625/R-93/010. U.S. Environmental Protection Agency. Washington, D.C.
- U.S. Environmental Protection Agency. (1994). *Drinking water treatment for small communities: focus on EPA's research*. Number: EPA/640/K-94/003. U.S. Environmental Protection Agency. Washington, D.C.
- U.S. Environmental Protection Agency. (1998a). *IRIS--Integrated Risk Information System—nitrate and nitrite*. Available: <http://www.epa.gov/ngispgm3/iris/subst/0076.htm> [January 31].
- U.S. Environmental Protection Agency. (1998b). *Technical drinking water and health contaminant specific fact sheet—nitrate and nitrite*. Office of Groundwater and Drinking Water, U.S. Environmental Protection Agency. Washington, DC.
- Van Der Hoek, J.P., and A. Klapwijk. (1987). Nitrate removal from ground water. *Water Resources*, 21(8):989-997.
- Van Maanen, J.M.S., A. Van Dijk, K. Mulder, M.H. De Baets, P.C.A. Menheere, D. Van Der Heider, P.L.J.M. Mertens, and J.C.S. Kleinjans. (1994). Consumption of drinking water high in nitrate levels causes hypertrophy of the thyroid. *Toxicol. Lett.*, 72:365-374.

Viessman, W., Jr., and M.J. Hammer. (1985). *Water supply and pollution control*. (4th ed.). Harper and Row, New York, NY.

Walton, G. (1951). Survey of literature relating to infant methemoglobinemia due to nitrate contaminated water. *Am. J. Pub. Health*, 41:986-996.