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Contamination Of Water By Nitrate: A General Discussion Problems Associated, Causes, Prevention And Effects

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Abstract:

This paper illustrates the source and significance of nitrogen for groundwater and presents a general study and discussion of nitrogen contamination with reference to its causes and prevention Nitrogen is a major constituent of the earth's atmosphere and occurs in many different gaseous forms such as elemental nitrogen, nitrate and ammonia. Natural reactions of atmospheric forms of nitrogen with rainwater result in the formation of nitrate and ammonium ions. While nitrate is a common nitrogenous compound due to natural processes of the nitrogen cycle, anthropogenic sources have greatly increased the nitrate concentration, particularly in groundwater. The largest anthropogenic sources are septic tanks, application of nitrogen-rich fertilizers to turfgrass, and agricultural processes. Levels of nitrates in groundwater in some instances are above the safe levels proposed by the EPA and thus pose a threat to human health. Particularly in rural, private wells, incidence of methemoglobinemia appears to be the result of high nitrate levels. Methemoglobinemia, or blue baby syndrome, robs the blood cells of their ability to carry oxygen. Due to the detrimental biological effects, treatment and prevention methods must be considered to protect groundwater aquifers from nitrate leaching and high concentrations. Treatment through ion-exchange and other processes can rehabilitate already contaminated water, while prevention, such as reduced dependence on nitrogen-rich fertilizers can lower the influx of nitrates.Major sources of nitrogen in rural aquifers are related to wastewater disposal (onsite systems and leaky sewers), solid waste disposal (landfills and waste tips). The most significant health effect associated with nitrate ingestion is Methemoglobinaemia (Blue baby Syndrome) in infants under six months of age. Another concern about nitrate ingestion is the possibility that nitrites in the stomach and intestines may contribute to the development of some cancers. The major source of nitrogen in the many districts of India are due to unplanned septic tanks.

Key words: Nitrogen Contamination, Groundwater Contamination,Diseases associated,Problems due to nitrate contamination

1.Introduction

Nitrate is a problem as a contaminant in drinking water (primarily from groundwater and wells) due to its harmful biological effects. High concentrations can cause methemoglobinemia, and have been cited as a risk factor in developing gastric an intestinal cancer. Due to these heath risks, a great deal of emphasis has been placed on finding effective treatment processes to reduce nitrate concentrations to safe levels. An even more important facet to reduce the problem are prevention measures to stop the leaching of nitrate from the soil. Some suggest that reducing the amount of fertilizers used in agriculture will help alleviate the problem, and may not hurt crop yields. Other new developments in leach pits and slurrystores help to control the nitrate that comes from stored manure. By installing these prevention methods and reducing the amount of fertilizer used, the concentration of nitrate in the groundwater can be reduced over time. Treatment processes, such as ion exchange can have an immediate effect on reducing levels in drinking water. These processes do not remove all the nitrate, but can help to bring the concentration down to the suggested level of 10mg/L.Water is literally, the source as well as sustainer of life on earth. About 70% of the earth is water but most part of it, is ocean i.e. practically only 3 percent of total water available on the earth is fresh where as rest 2 percent is located away in the form of ice caps and glaciers in the polar regions, far distant from the human habitation. Less than 1% of the earth's water is available for human consumption and more than 1.2 billion people still have no access to safe drinking water. Because of our indifferent attitude towards its utilization and conservation the large section of human population is not only deprived of their basic minimum requirement of water but the very natural life cycle on the planet is also endangered. Freshwater resources all over the world are threatened not only by over exploitation and poor management but also by ecological degradation. The main source of freshwater pollution can be attributed to anthropogenic activities such as discharge of untreated waste, dumping of industrial effluent, and run-off from agricultural fields etc. It is a generally accepted fact that the developed countries suffer from problems of chemical discharge into the water sources mainly groundwater, while developing countries face problems of agricultural runoff in water sources. Ground water can be contaminated through various sources like pesticides, sewage, nutrients, synthetic organics and acidification.

Polluted water with chemicals like lead, fluoride, nitrate, petrochemicals, chlorinated solvents, heavy metals and salts cause problem to health and lead to water borne diseases.

More than 50 per cent of India, Pakistan, China, Bangladesh, Indonesia, Thailand and Vietnam are dependent on groundwater. Groundwater accounts for over 80 per cent of the domestic water supply in rural India. The present paper presents an existential analysis of the condition of ground water contamination in rural India.

2.Major sources of nitrate pollution

Although there are many sources of nitrogen (both natural and anthropogenic) that could potentially lead to the pollution of the groundwater with nitrates, the anthropogenic sources are really the ones that most often cause the amount of nitrate to rise to a dangerous level. Waste materials are one of the anthropogenic sources of nitrate contamination of groundwater. Many local sources of potential nitrate contamination of groundwater exist such as, "sites used for disposal of human and animal sewage; industrial wastes related to food processing, munitions, and some polyresin facilities (Vomocil, 1987); and sites where handling and accidental spills of nitrogenous materials may accumulate" (Hallberg and Keeney, 1993, p. 303). Septic tanks are another example of anthropogenic source nitrogen contamination of the groundwater. Many areas of the United States and other countries have reported significant contamination of groundwater from septic tanks. Ground water contamination is usually related to the density of septic systems (Hallberg and Keeney, 1993). In densely populated areas, septic systems can represent a major local source of nitrate to the groundwater. However in less populated areas septic systems don't really pose much of a threat to groundwater contamination.

When natural sources contribute a high concentration of nitrate to the groundwater it is usually as a result of anthropogenic disturbance. One example of this is the effect of forested areas on the leaching of nitrate to the groundwater. Natural, mature forests conserve nitrogen but human disturbances can lead to nitrate pollution of the groundwater. However, while this is a potential problem for groundwater, forests represent a very small source of nitrogen compared to agriculture (Hallberg and Keeney, 1993).

2.1.Non-Agricultural

One potentially large source of nitrogen pollution of groundwater is the application of nitrogen-rich fertilizers to turfgrass. This occurs on golf courses and in residential areas. There are five fates for this nitrogen once it is applied to turfgrass. It may be:

2.1.1.<u>takenupbyplants</u>
2.1.2.<u>storedinsoil</u>
2.1.3.<u>losttoatmosphere</u>
2.1.4.<u>losttogroundwater</u>
2.1.5. <u>lost to runoff (Bocher, 1995)</u>

Many studies have shown that most of the nitrogen, about 30 to 50 percent is taken up by the plant. According to an United States Golfing Association study only one to two percent of the nitrogen is leached beyond the root zone (Bocher, 1995). This finding may be slightly biased because this is the result that the USGA desires. Also, this result may occur only when the nitrogen fertilizer is applied carefully and properly. Certain circumstances could lead to more of the nitrogen leaching to the groundwater. Six main factors affect nitrogen leaching:

1)nitrogen rate – One study showed that at one pound of nitrogen per 1,000 square feet, no leaching occurred.
2)nitrogen source - Slow-release fertilizers are a nitrogen source that can reduce the chance of leaching.
3)application timing - In late fall, plants take up less nitrogen and there is a greater chance for leaching to occur.
4)irrigation practices - The more irrigation that takes place the greater the chances for nitrate leaching.
5)soil texture - The sandier the soil the more chance for nitrate leaching.
6) age of site - Younger sites usually have less organic matter and need to be fertilized more therefore increasing the chance of leaching. (Bocher, 1995)

2.2.Agricultural: Fertilizers And Animal Wastes

The main source of nitrate pollution in the groundwater results from the actions of farmers. "Farming alone pollutes more of our groundwater resources than anything else. Because too many farmers are caught up in an escalating cycle of pollution" (Behm,1989, p. 2). The farmers first deplete the soil by "excessive, repeat planting" and then try to replenish the resulting less-productive soil by putting more and more nitrogen-based fertilizer on the land in an attempt to keep crop yields constant.

One example of proof that farming is a major cause of groundwater pollution is that nitrate problems are most common in the spring, which is the time that farmers apply nitrogen fertilizer to their fields. Also, in a study done by Burkart and Kolpin (1993) it is found that samples of water from wells surrounded by more than 25% land in corn and soybean have a dramatically larger frequency of excess nitrate (30%) than wells with approximately 25% of the surrounding land in corn or soybean (11%) . Also many of the same factors that effect nitrogen leaching in turfgrass affect it in crop fields. For example, the use of irrigation increases the chance of nitrate pollution. "The frequency of excess nitrate was also larger where irrigation was used within 3.2 km of a well (41%) than where no irrigation was used (24%)" (Burkart and Kolpin, 1993, p. 654). In areas where "the soils over the aquifer are predominantly sand, sorption of herbicides is limited and the rate of recharge is rapid, resulting in a relatively large potential for contamination of aquifers with ... nitrates" (Burkart and Kolpin, 1993, p. 654).

One problem caused by farms results from the grazed grasslands and feedlots. In grazing pastures animal wastes are concentrated in small pastures, this leads to inefficient use of nitrogen and causes the potential for groundwater contamination by nitrate. This problem is even worse in Europe where grazing pastures are usually more intensively fertilized than in the U.S., therefore there is more nitrate available to be leached to the groundwater (Hallberg and Keeney, 1993). Even small farms can contribute to the

problem of excess nitrates because of the high concentrations of manure that they may have in the barnyard or feedlot areas (Hallberg and Keeney, 1993).

One of the better ways to get rid of manure is to use it to fertilize cropland. "Such organic material is often considered a desirable nitrogen source because the nitrogen is in the mineralization-immobilization cycle longer and thus is more slowly available" (Hallberg and Keeney, 1993, p. 303). For this reason, it is a safer fertilizer than chemical fertilizer. However manure use does have many drawbacks such as variable composition and quality and the extra time for nitrogen to be mineralized may not coincide with the high rate of nitrogen needed by the crop. The main problem is the fact that an accurate estimation of net nitrogen availability is very difficult to determine (Hallberg and Keeney, 1993). Therefore farmers usually apply an excess of manure to the crop to insure that enough nitrogen will be available for the growing process.

Obviously the more nitrogen fertilizer a farmer uses the greater the chance of nitrate pollution of groundwater. "Farmers still consider nitrogen fertilizer 'cheap insurance' against crop failure" (Looker, 1991). Approximately one dollar's worth of fertilizer could bring in ten dollars of corn if the soil has a lack of nitrogen. So the farmer would, financially speaking, much rather add too much nitrogen than too little. To add to this problem, it is very difficult to determine exactly how much nitrogen a crop will need before harvest time due to yearly change in yields and weather conditions. Even if farmers cut down on nitrogen fertilizer, there will still be some nitrate leaching. As Dennis Keeney, the director of the Leopold Center for Sustainable Agriculture at Iowa State University, states, "Even if farmers add no fertilizer to fields, tilling the earth with machinery makes land more susceptible to leaking nitrogen" (Looker, 1991). Although sustainable practices may not eliminate nitrates, it might lower them to a safe level. Obviously, if there is a chance of nitrogen pollution when no fertilizer is applied, the chance of pollution is greatly increased when a large amount of fertilizer is applied.

2.3. Manure Storage

Another potential source of nitrate leaching to the groundwater that deals with farming is the storage of the manure. Farmers commonly store manure in large holes in the ground. While this is convenient and relatively inexpensive for the farmer in the short term , it results in excessive leaching of nitrates. In an attempt to prevent leaching some of these manure lagoons have been built with liners. However, as a study at the University of Wisconsin at Madison showed, there is a gradual but continuous breakdown of the liner and after some years the liner no longer retains the ability to prevent leaching of contaminants from the manure to the soil below (Lagoon Reclamation, 1993). Problems also arise when these manure lagoons are left idle for a long period of time without being properly broken down. It has been found that an empty manure storage facility can be more hazardous to groundwater than a full one. The sides of an empty lagoon are directly exposed to the sun and air. This results in the drying and cracking of the soil material. Precipitation containing large amounts of dissolved oxygen will then convert the ammonium in the contaminated soil and leftover manure to nitrates which can easily be leached out (Lagoon Reclamation, 1993).

3. Environmental Protection Agency Regulations

The United States Environmental Protection Agency is currently establishing National Primary Drinking Water Regulations for over 80 contaminants under the Safe Drinking Water Act (Vogt and Cotruvo, 1987). The goal is to reduce the contaminant concentrations of all drinking water to levels near those prescribed in the Maximum Contaminant Level Goals (MCLGs) previously established by the EPA (Vogt and Cotruvo, 1987). MCLGs are "non enforceable health goals" at which "no known or anticipated adverse effects on health of persons occur and which allow an adequate margin of safety" (Vogt and Cotruvo, 1987, p. 213-215). The Maximum Contaminant Levels (MCLs) are to be set as close to the MCLGs as possible (Vogt and Cotruvo, 1987). In the case of nitrate concentrations, the MCL has been set at 10 mg/L (ppm) as nitrogen which is also the proposed MCLG (Vogt and Cotruvo, 1987). For many contaminants, carcinogenicity is the primary characteristic which determines the MCL; however, because there are no conclusive epidemiological studies which link nitrate to cancer in humans, carcinogenicity was not taken into account in the establishment of the MCL for nitrate (Kamrin, 1987). The determining factor in the EPA's decision to set the MCL at 10 mg/L was the occurrence of methemoglobinemia in infants under of six months. The MCL reflects the levels at which this condition may occur (Kamrin, 1987). Although the MCL for nitrogen was set at 10 ppm nitrate - nitrogen, in 1976 the EPA suggested that water having concentrations above 1 ppm should not be used for infant feeding (Rail, 1989). This guideline is very conservative and nitrate concentrations below 10 ppm are probably harmless as well. However, because concentrations this low are common, the EPA hopes this guideline will induce people in rural areas to have their wells tested so that severe nitrate contamination is detected and serious health problems are avoided in the future.

4. Problems Associated With High Nitrate Levels

When nitrate - nitrogen concentrations reach excessive levels there can be harmful biological consequences for the organisms which depend on groundwater. Of course, human interest is of primary concern when setting guidelines for acceptable nitrate levels and proper agricultural practices. The United States Environmental Protection Agency established the current drinking water standard and health advisory level of 10 mg/L nitrate-nitrogen (equivalent to 10 ppm nitrate-nitrogen or 45 ppm nitrate) based on the human health risks due to nitrate consumption (Kross, 1993). Although there have been studies performed attempting to link nitrate consumption to various illnesses, only methemoglobinemia, (also infant cyanosis or blue-baby syndrome) has been proven to result from ingestion of water containing high nitrate concentrations, above 10 ppm (Kross, 1993).

4.1. Blue-Baby Syndrome

Cases of blue-baby syndrome usually occur in rural areas which rely on wells as their primary source of drinking water. Often these wells become contaminated when they are dug or bored and are located close to cultivated fields, feedlots, manure lagoons or septic tanks (Comly, 1987; Johnson et al., 1987). The most contaminated wells are usually those that were dug rather than drilled and have poor or damaged casings (Comly, 1987; Johnson et al., 1987). Until recent awareness of the dangers of nitrate contaminated

groundwater prompted testing for nitrate concentrations, along with other contaminants, wells with dangerously high nitrate concentrations usually went unnoticed until health problems were brought to attention. A few isolated cases of methemoglobinemia, primarily in the rural United States, have served as the catalyst for what has grown into a broad awareness and concern for nitrate contamination.

Methemoglobinemia is the condition in the blood which causes infant cyanosis, or blue-baby syndrome. Methemoglobin is probably formed in the intestinal tract of an infant when bacteria converts the nitrate ion to nitrite ion (Comly, 1987). One nitrite molecule then reacts with two molecules of hemoglobin to form methemoglobin. In acid mediums, such as the stomach, the reaction occurs quite rapidly (Comly, 1987). This altered form of blood protein prevents the blood cells from absorbing oxygen which leads to slow suffocation of the infant which may lead to death (Gustafson, 1993; Finley, 1990). Because of the oxygen deprivation, the infant will often take on a blue or purple tinge in the lips and extremities, hence the name, blue baby syndrome (Comly, 1987). Other signs of infant methemoglobinemia are gastrointestinal disturbances, such as vomiting and diarrhea, relative absence of distress when severely cyanotic but irritable when mildly cyanotic, and chocolate-brown colored blood (Johnson et al., 1987; Comly, 1987).

Treatment of infant cyanosis is simple once the condition has been recognized. If the patient is mildly affected, then he/she must simply refrain from drinking from the contaminated well for a few days and the body will replenish the hemoglobin by itself in a few days (Johnson et al., 1987). However, if the patient is severely cyanotic, methylene blue must be administered intravenously in a dosage of 1-2 mg/kg of body weight for a ten-minute period and improvement should be prompt (Johnson et al., 1987).

Methemoglobinemia most often affects infants of less than six months in age. Comly cites several factors that make infants more susceptible to nitrate compounds that adults. The primary reason is that infants possess much less oxidizable hemoglobin than adults, so a greater percentage of their hemoglobin is converted to methemoglobin which greatly decreases the blood's ability to carry oxygen. Other possible reasons are that nitrite ions may be more strongly bound by infantile hemoglobin due to immaturity of certain enzymes, and that the kidneys of infants have inferior excretory power which may favor retention of nitrite for longer periods of time (1987).

Steps can be taken to prevent the child from becoming a victim of methemoglobinemia. Residents of rural areas should have their wells tested, especially if pregnant women or infants are consumers of the well water. If the well is contaminated, other water source alternatives are other safe wells, bottled water, a new, deeper well, or a water purification system which is capable of removing the nitrates (Johnson et al., 1987). Comly suggests that because cyanotic babies usually contract methemoglobinemia from the water used to prepare their formulas, formulas which use diluted whole milk are less risky than those prepared from powdered or evaporated milk which require large amounts of water in preparation (Lukens, 1987). Breast feeding or the use of bottled water in formula preparation offer the safest solution, especially if the groundwater quality is unknown (Johnson et al., 1987).

Since 1945, there have been over 2000 cases of infant methemoglobinemia reported in Europe and North America with 7 to 8 percent of the afflicted infants dying (Rail, 1989). However, problems can be severe as shown in a specific 1950 report, there were 144 cases of infant methemoglobinemia with 14 deaths in a 30 day period in Minnesota (Johnson et al., 1987). This of course was an isolated case. However, it shows that nitrate concentrations in well water can increase to deadly levels rapidly and the issue of nitrate contamination should not be ignored.

4.2.Stomach And Gastrointestinal Cancer

Although many studies have been performed attempting to link stomach and gastrointestinal cancer to nitrate intake, there is no conclusive evidence that there is a correlation. In fact, two particular studies in the United Kingdom have shown an inverse relationship where instances of stomach cancer are highest in areas where the groundwater concentration of nitrate is lowest and vice versa (Payne, 1993; Forman et al., 1985). Scientists claim that nitrate represents a potential risk because of nitrosation reactions which, with appropriate substrates present, form N-nitroso compounds which are strongly carcinogenic in animals (Forman, 1985). In other areas of the world such as Columbia, Chile, Japan, Denmark, Hungary, and Italy, similar studies have suggested a correlation, although there still exists no concrete evidence to support this theory (Forman, 1985). At present, no other toxic effects have been observed under conditions of high nitrate levels. Even at exposure to levels of 111mg/L there were no adverse conditions in infants except for methemoglobinemia (Gustafson, 1993). Other claims that intake of nitrate contaminated groundwater is linked to birth defects, and hypertension and high blood pressure in adults are also unsubstantiated. This inconsistency suggests that nitrate alone cannot be the only cause of elevated regional gastric cancer mortality rates, but these could result from a number of other factors, such as high pesticide levels, presence of coliform bacteria, and/or other groundwater contaminants.

4.3.Clean-Up Of Nitrate From Water

Nitrate causes problems as a contaminant in drinking waters taken primarily from aquifers. In dealing with the nitrate problem in subsurface waters, there are two options for achieving safe nitrate levels. First of all there are non-treatment techniques that consist of blending drinking waters, or changing water sources. The second alternative is the use of treatment processes, such as ion exchange, reverse osmosis, biological denitrification and chemical reduction to actually remove portions of the pollutant. However, the most important thing to note about these clean-up procedures is that neither of these methods are completely effective in removing all the nitrogen from the water. Treatment can remove some of the nitrate, but with varying efficiencies, much of which can depend on other substances found in the water. The non-treatment processes attempt to bring the nitrate concentration down to a safer level, through blending with cleaner waters.

4.4.Non-Treatment

The non-treatment sources are quite easy to understand in their logic; combine water with lower levels of nitrate with waters of higher levels until a safe quantity is reached, or if possible just avoid the problem by utilizing another source. These methods

attempt to reach the suggested nitrate level of 10mg/L or less in potable water (Moore, 1991). In order to use any of these options the nitrate problem must be localized to a very precise area. According to Guter (1981) four common alternatives are:

1) Raw water source substitution: In this case an entirely new sources of drinking water is used to replace the heavily polluted water.

2) Blending with low nitrate waters: As a simple example, if the current well water supply contains 15 mg/L of nitrates, then this could be combined with an equal amount of water with a concentration of 5 mg/L to achieve a safe concentration of 10 mg/L.

3) Connection to an existing regional system: This involves using a system that is already set up to service the area, instead of drawing water from the contaminated well.

4) Organizing a regional system: This is similar to the use of an existing regional system. One can "...form a new regional utility by joining with other nearby systems which may be having similar water quality problems..." (Guter, 1981, p. 19).

The advantages of these methods, especially combining existing resources, is the spread of the costs of monitoring water quality amongst many different areas. This greatly reduces expenses and helps to provide safer drinking water to larger numbers of people. However, these applications can only be utilized if the contamination of nitrate is confined to a specific area, otherwise tapping into other local or regional sources to dilute the water would only result in perpetuating the problem.

Besides these methods of providing safer waters with lower nitrate concentrations, there are treatment methods. The most important idea to note about these processes, however, is that none of them are completely effective in removing all nitrate from well water, or any other subsurface water. Each one of these method's success rates depends on the conditions of plant operation and the other contaminants found in the water. The main sources of research for nitrate removal consist of ion exchange, bio-chemical denitrification, and reverse osmosis. Today the primary system in use is ion exchange.

4.5. Ion Exchange

In the ion exchange process special resins are used to substitute chloride ions (C1-) for the nitrate radical. This method of removal requires several steps for successful decontamination. Essentially, the process relies on the fact that water solutions must be electronically neutral, and therefore by inserting a negative ion, another negative ion can be removed from the water. Besides the negative nitrate radical (NO_3-), common anions include sulfate radical, chloride ion, bisulfate ion, bicarbonate ion and carbonate ion. Some of the common cations or positive ions are calcium, magnesium and sodium (Guter, 1981).

The first part of the process is the selection of an appropriate resin for the removal of the specific problematic ion, which in this case is nitrate. However, current resins are not completely nitrate selective, and often remove other anions before removing the nitrogenous compound. "Resin beds are made up of millions of tiny spherical beads, which usually are about the size of medium sand grains" (Guter,1981, p. 21). As the solution passes through these beds, the chloride anions are released into the water, removing first the sulfate ion, then the nitrate radical. The entire process is composed of four major steps to remove the selected ions from solution:

1) Resin recharge
2) Anion exchange
3) Resin becomes "exhausted"
4) Resin regeneration

In the first step of the process, the bed is recharged, reaching its maximum exchange capacity. The resin at this time has enough chloride ions to carry out the exchange as the solution passes through the complex. The ion exchange is the next part of the process. The resin bed begins to remove the sulfate radicals first, then when the majority of $S04_2-$ has been removed from the water the exchange of nitrate and chloride begins. The completion of this phase is the third step as the resin becomes "exhausted" of the ion used for exchange. At this point no more anions leave the solution. Finally, in the fourth component of the process, the bed is regenerated by passing a strong solution over the resin displacing the removed ions with the chloride (Cl-) ion (Guter, 1981).

This method of nitrate removal does not completely eliminate the contaminant from solution. However, "one such facility [of ion exchange] in the San Joaquin Valley resulted in a nitrate reduction from 16 to 2.6mg/L" (Moore, 1991,p. 238). The cost of the removal amounted to 24.2 cents/1000 gal (Moore, 1991). So far this has proven to be the most effective and efficient treatment process.

4.6. Bio-Chemical Denitrification

By using denitrifying bacteria and microbes, the nitrate ion can be reduced into its elemental state of N2. These organism are able to carry out this process through a reaction such as:

$$6H+ + 6NO_3- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 13H_2O \text{ (Zajic, 328)}.$$
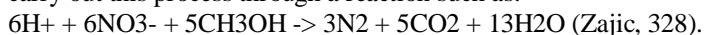
By using a chemical such as ethanol, the removal of nitrate is possible. Sometimes it is necessary to convert the nitrogen from the ammonium ion into nitrite with the use of nitrosomas (specialized bacteria) to facilitate the removal of all nitrogen from the solution (Shuval, 1977). The nitrite compound is then oxidized to nitrate, which can then be eliminated by the reaction shown above.

Besides the use of special bacteria, photosynthetic algae can remove nitrates from water. Using the stoichiometric relationship of (Zajic, 329):

$$aCO_2 + cNO_3- + ePO_4 3- + (c+3e)H+ + 1/2(b-c-3e)H_2O \rightarrow$$
$$C_aH_bN_cO_dP_e + (a+b/4+c/5-d/2-5e/4)O_2$$
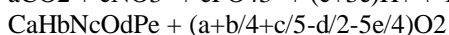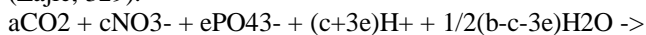
Both of these processes can be somewhat effective in removing nitrate, however, biological organism are influenced by other toxic chemicals or compounds that may be found in the water. These toxins can reduce greatly the effectiveness and efficiency with which the organisms eliminate the nitrate solution (Organization for Economic Co-Operation and Development, 1974). Another important note about these processes is that "... the practice of prechlorination greatly reduces the effectiveness of such techniques. Nitrates are, in most cases, rapidly oxidized by chlorine..." (Moore, 1991, p. 238). However, the greatest benefit of the bio-chemical

denitrification is the fact that the nitrogen is completely removed in its gaseous elemental form (Organization for Economic Co-Operation and Development, 1974). There is no residue or problems with disposal.

5.Prevention

5.1.Non-Agricultural
Based on the six factors affecting nitrate leaching in turfgrass, seven practices can be adopted by turfgrass managers to help prevent the leaching of nitrates. One of the most important steps is to limit the amount of nitrogen applied; "Use slow-release nitrogen sources, or low rates of soluble nitrogen applied more often, where possible"(Bocher, 1995, p. 66). Also the turfgrass manager should be very cautious about adding nitrogen during periods in which the ground is not yet frozen but the grass is not growing. The manager should avoid over-irrigation, which increases the chance of nitrate leaching while doing nothing for the plant. Effort should be made to reduce the amount of nitrogen applied to older sites and collect drainage water instead of allowing it to drain into a river or stream. Finally, the turfgrass manager should use zeolite amendments. Zeolite is, "a mineral with a high cation exchange capacity that can hold on to things like potassium, calcium, phosphorous, magnesium or ammonium" (Bocher, 1995, p. 66). Most of these steps of prevention are even more important in areas of sandy soil. By following these steps the turfgrass manager will greatly reduce the chances of nitrate leaching into groundwater. If proper measures are taken, the fertilizing of golf courses, and athletic fields will not result in nitrogen pollution of groundwater (Neal, 1995).

5.2.Agricultural
Many of these same steps can be implemented by farmers as well to prevent nitrate leaching. The most important step for farmers is to reduce the amount of nitrogen applied to the crops. This is easier said than done because most farmers consider nitrogen fertilizer to be "cheap insurance" against a crop failure (Looker, 1991). As previously mentioned, nitrogen is a definite limiting factor in crop yields. "If soil lacks nitrogen, a dollar spent on the fertilizer can bring $10 in extra corn" (Looker, 1991). Therefore, from a financial standpoint, a farmer would obviously rather add too much nitrogen to his crop than too little.
In 1990, according to the U.S. Department of Agriculture, the rate of nitrogen fertilizer use in Iowa (a state whose farmers lead the nation in cutting back on nitrogen) was 127 pounds per acre (Looker, 1991). However, the director of the Leopold Center for Sustainable Agriculture at Iowa State University, Dennis Keeney, believes that farmers could eventually use only 75 pounds per acre and still have no drop off in yields. Mr. Dan Stadtmueller is an example of an Iowan farmer who greatly reduced his fertilization practices. According to an article in the Des Moines Register, Mr. Stadtmueller "is a miser with nitrogen fertilizer". Some of Stadtmueller's fields get as little as 60 pounds of fertilizer per acre, without displaying a decreasing yield (Looker, 1991).
There have been some steps taken to try and lessen the amount of nitrogen fertilizer used by farmers. One such measure is a law written by then member of the Iowa House of Representatives, Paul Johnson. This law taxed fertilizer and pesticides and used the money raised from this tax to research and show farmers how to use fewer chemicals without losing money (Looker, 1991). Also, Alfred Blackmer, an Iowa State University agronomist devised a test that enables farmers to measure nitrogen already in the soil more accurately. Dan Stadtmueller, the "miser" of nitrogen fertilizer, switched to a method of farming called ridge tillage in 1975. This method enables him to put small amounts of fertilizer in permanent seedbeds instead of covering the entire field. Stadtmueller switched to this method in 1975 and insists that it is more profitable. However in 1991 only about two percent of farmers in Iowa used the method (Looker, 1993). Stadtmueller figures that this is because the majority of the farmers are afraid of change (Looker, 1993). This also represents the problem with the tests and laws that have recently been formed, it might take some time to convince farmers that they can switch to new techniques without losing money in the process.

5.3.Manure Storage Sites
Another method of prevention in the area of farming deals with manure lagoons. This is an easier problem to solve because there are proven solutions which are also better for the farmer in the long run. One technique of manure storage that is better than the aforementioned manure lagoons is storing the manure in concrete pits. Another possible solution is the installation of a storage facility termed a Slurrystore. These facilities are proven to store manure without leaking and are actually more convenient for the farmer once they are installed.

5.4.Flood Plain Management
One method of prevention of nitrate pollution of groundwater that is unrelated to farming is actually a method not of new technology but of going back to old ideas. "Traditionally, flood plains in Britain were not vigorously farmed, but land drainage now allows these zones to be plowed up or managed more intensively as grassland" (Haycock, 1990, p. 291). They point out that this action results in the rapid conduction of nitrate contaminated groundwater across the flood plain whereas this water was once allowed to drain slowly across the flood plain. After work in the upper Thames Basin in England, Haycock and Burt discovered that a grass-covered flood plain can greatly reduce the nitrate concentration of groundwater throughout the winter. One example they use to prove this point is that as a result of a major runoff incident in 1990, the nitrate concentration of groundwater increased by about 400% while the grass covered flood plain maintained a nitrate-buffering capacity near its mean level (Haycock,1990). Haycock and Burt conclude that, "flood plains need to be preserved in (or returned to) their undrained state as these areas sustain a potential to reduce nitrate concentrations in ground water throughout the year" (Haycock, 1990, p. 291).

6.Sources Of Nitrate In Groundwater
The wide range of pollutant sources and the complexity of recharge make the estimation of pollutant load a difficult task. This is also true for the various forms of nitrogen (oxidized and reduced forms) that are present in many possible recharge sources of aquifers. They include sewage and mains leakage, septic tanks, industrial spillages, and contaminated land, landfills, river or

channel infiltration, fertilizers used in gardens, house building, storm water and direct recharge. Weather, soil types, and the depth of the aquifer also affect contamination of groundwater. If it is less than 100 feet to the water table, the vulnerability of contamination is increased. Once nitrate is formed, its movement in soil and potential for contamination of groundwater depend on several factors including the soil characteristics, location and characteristics of the underground water formations (aquifers), and climatic conditions. Potential for nitrate contamination of drinking water also depends on the depth and construction of wells. Identifying the source of nitrates for an individual well is often very difficult. Because nitrates move with the flow of groundwater, the source may be located a considerable distance from the well. In many cases, the time needed for nitrate to pass through the soil into groundwater is difficult to predict due to many variables including application rate, the soil type, and the depth to the water table.

6.1. Natural Sources
Nitrate is a naturally occurring compound that is formed in the soil when nitrogen and oxygen combine.

6.2. Anthropogenic Sources

6.2.1. Agricultural Sources
Negligent agricultural practices are easily recognized as the leading cause for nitrate contamination of water. Farmers apply different rates of fertilizers into the soils where they want to grow higher yielding crops. When the producer applies too high of a rate of nitrogen or other fertilizer, it exceeds the soil's need for it, and the soil allows some of the nitrogen to permeate its structure. When this happens repeatedly, a buildup can occur in the underground water source. Agricultural practices contribute greatly toward the percentage of nitrates found in our rural groundwater. Although farmers are the biggest supplier of nitrates into groundwater, everyone is responsible for additional contamination in one way or another. Those who over-fertilize their lawns or gardens contribute to the effects of nitrate pollution. Domestic animals in residential areas have also led to an increase of nitrates in the water supply. We know that the results of these practices as well as many others accumulate underground rather quickly and damage the quality of the water supply.

6.2.2. Non-Agricultural Sources Of Nitrogen
The sources of nitrogen in the rural environment are a mixture of point sources (e.g. landfills and coal gasification works), multipoint sources (e.g. soakaways and leaky sewers) and diffuse sources (atmospheric deposition, house building and recreation areas). The most common sources of nitrate are municipal and industrial wastewaters, refuse dumps; animal feed lots, and septic systems. Nitrogen compounds given off from automobiles are introduced into the ground when it rains. Leaky septic systems can cause a significant increase in the concentration of nitrates in the groundwater.

Leakage from sewerage and water supply networks provides the highest percentage of water recharge to aquifers underlying many cities through out the world. Water mains and sewers leak because of improper installation or deterioration through age, subsidence or earthquakes. Sewage leakage occurs when sewers are situated above the water table. Few studies have attempted to quantify the recharge and pollutant load from leaky sewers. Leaky sewers contribute with a wide range of pollutants such as bacteria or organic and inorganic compounds. On-site sewage disposal encompasses cesspools, septic tanks and pit latrines. Septic tanks are common in developing countries. The concentration of total nitrogen in effluents from a typical septic tank system ranges from 25 to 60 mgl_1,with ammonia making up the vast majority of this total. Ammonium ions in the effluents may be oxidized to nitrate, which can be transported in the subsoil beneath the septic tank absorption, and subsequently to groundwater. The density of systems is the most important factor in groundwater contamination by septic tanks. A minimum lot size of 0.4 to 0.6 ha is needed to insure against groundwater contamination. Other factors that can contribute to the hazard of groundwater pollution by septic tanks are improper design, poor maintenance and depth of the water table (Yates, 1985 and Abdulla *et al.* 2003). A greater threat to groundwater quality is the use of pit latrines because of the discharge of waste without pre-treatment. Animals are, or have been a common feature in many rural areas Somasudaran *et al.* (1993) suggested the substantial number of oxen, cows and buffaloes in Madras, India, is one of the sources of the high nitrate concentration in shallow groundwater. Excreta, dung and urine produced by animals constitute a potential source of contaminants such as nitrate, potassium and bacteria. They can enter groundwater by the way of storm water channels, river, and recharge basin or through direct recharge.

7. Article In Press
Contaminated land, such as abandoned landfills, abandoned industrial sites; contribute a significant quantity of nitrogen to groundwater. Current industry is another potential source of nitrogen to groundwater. Nitrogen compounds are used extensively in industrial processes. Some examples of industrial uses are plastic and metal treatments, raw materials for the textile industry, particleboard and plywood, household cleaning and the pharmaceutical industry. Nitrate contamination may result from inadequate handling, disposal or use of these compounds.

Aquifer contamination by river or unlined canal carrying highly polluted water has been reported in many places. There are two factors that lead to aquifer contamination by a river; firstly, the river has received a high proportion of raw or treated wastewater, and secondly the river is infiltrating water to an aquifer. Usually, the second factor occurs when pumping stations are near the river.

The emission of nitrogen to the atmosphere can be in its oxidized or reduced forms. The oxidized forms are mostly generated by the car engines and industries (NOx); the reduced species (ammonia) are mainly from agriculture and intensive feedstock rearing. These forms can later be deposited and be carried in roof and storm water runoff.

Nitrate leaching from fertilizers applied to lawns, gardens and plots for cultivation of vegetables is likely to be a significant source of nitrogen to groundwater. Urban food production is increasing around the

Nitrate leaching due to house building is potentially equivalent to that due to ploughing of pasture, which has been identified as a major source of nitrate in groundwater beneath agricultural land. Soil disturbance during house building increases the soil aeration and the mixing of nitrogen and carbon sources with soil organisms. Soil microbial activity in favorable conditions leads to an accumulation of nitrate due to mineralization and nitrification processes. Nitrate will be leached by drainage of excess water if plants do not take it up earlier.

Effluent from septic tanks is a frequently cited source of high nitrate concentrations in urban groundwater. The issue of wastewater disposal is a more serious problem in developing countries. There are areas, which are unplanned, pit latrines or septic tanks are common. In some places in India, septic tanks and pit latrines are the only way to dispose of sewage, while groundwater is the main water-drinking source.

Non-agricultural sources of Nitrates are linked to other pollutants that threaten groundwater quality more seriously, such as bacteria and organic compounds in sewage, leachate from landfills, or phenol, BTEX and heavy metals from coal gasification plants. Therefore the groundwater can be seriously polluted. However, the pollution extent and nature will depend on natural attributes such as geology, climate, industry types present, population density, and conditions and location of sewerage and mains network.

8. Effect Of Nitrates On Human Health

Nitrates contamination of the world's underground water supply poses as a potentially serious health hazard to the human inhabitants on earth. Small amounts of nitrate are normal, but excess amounts can pollute supplies of groundwater. High levels can build up over time as nitrate accumulates in the water, but even at elevated levels, they are not likely to be a health hazard for most adults. However, the ingestion of excessive amounts of nitrate can cause adverse health effects in very young infants and susceptible adults. Consequently, the government has established a maximum acceptable level, known as the Maximum Contaminant Level (MCL), for nitrate in public drinking water supplies. This level is 10 milligrams per liter (mg/l), often expressed as 10 parts per million (PPM), measured on the basis of the nitrogen content of nitrate.

High nitrate levels found in well water have been proven to be the cause for numerous health conditions across the globe. High levels can build up over time as nitrate accumulates in the water, but even at elevated levels, they are not likely to be a health hazard for most adults. However, the ingestion of excessive amounts of nitrate can cause adverse health effects in very young infants and susceptible adults. Consequently, the federal government has established a maximum acceptable level, known as the Maximum Contaminant Level (MCL), for nitrate in public drinking water supplies. This level is 10 milligrams per liter (mg/l), often expressed as 10 parts per million (PPM), measured on the basis of the nitrogen content of nitrate.

The most significant health effect associated with nitrate ingestion is methemoglobinemia in infants under six months of age. This condition results from the presence of high nitrite levels in the blood. Symptoms of Methemoglobinemia include anoxic appearance, shortness of breath, nausea, vomiting, diarrhea, lethargy, and in more extreme cases, loss of consciousness and even death. When nitrate is ingested it is converted into another chemical form, nitrite. Nitrate then

reacts with hemoglobin, the proteins responsible for transporting oxygen in the body, converting them to methemoglobin, a form that is incapable of carrying oxygen. As a result, the victim suffers from oxygen deprivation, or more commonly stated, the individual slowly suffocates. Infants in the first six months of life are particularly susceptible to nitrite-induced methemoglobinemia. Finally, infants have a higher intake of water for their weight than adults; so consequently, they ingest a relatively higher amount of nitrate. In addition to small infants, some adults may be susceptible to the development of nitrite, induced methemoglobinemia. These include pregnant women with a particular enzyme deficiency, adults with reduced stomach acidity, and those with a deficiency in the enzyme needed to change methemoglobin back to normal hemoglobin, a condition that can be hereditary.

 Although, Methemoglobinemia is the most immediate life-threatening effect of nitrate exposure, there are a number of equally serious longer-term, chronic impacts. In numerous studies, exposure to high levels of nitrate in drinking water has been linked to a variety of effects ranging from hypertrophy (enlargement of the thyroid) to 15 types of cancer, two kinds of birth defects, and even hypertension

Nitrate in groundwater is of concern not only because of its toxic potential, but also because it may indicate contamination of the groundwater. If the source of contamination is animal waste or effluent from septic tanks, bacteria, viruses, and protozoa may also be present.

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