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EARTH SCIENCES

OVERVIEW OF NITRATE IN NEBRASKA'S GROUND WATER

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The primary concern over nitrate in ground water is the occurrence of a disease called *methemoglobinemia* in human infants who drink water containing the nitrate ion. Nitrate contaminated water leads to lack of oxygen in the blood, causing oxygen starvation of the brain and, in some severe cases, death. Infant farm animals, particularly piglets, are similarly affected by nitrate.

Two areas exist in Nebraska where nitrate contamination of ground water is becoming a serious problem. These problem areas are in Holt County and the Central Platte region. Most nitrate contamination is related to excessive application of commercial fertilizer on irrigated cropland with sandy topsoil and a shallow ground water table. Excess irrigation water dissolves the highly soluble nitrate ion, which results from the fertilizer, and the solution moves down to the ground water table.

Although several treatment processes to remove nitrate, including reverse osmosis, electrodialysis, and ion exchange, have been studied, none has proven economically feasible to use on a large scale. Instead, some communities with nitrate contaminated wells are replacing contaminated wells with new wells pumping non-contaminated water. On a smaller scale, some rural people with contaminated wells are using small home distillation units to provide nitrate-free water.

† † †

INTRODUCTION

Nitrogen is one of the most common elements in our environment. It is one of the elements essential to plant growth, so it is essential to food and fiber production. The nitrate ion is only one of many forms of nitrogen, but it is one of only two forms that crops can take up from the soil. Thus, nitrates are vital to Nebraska's agricultural industry.

Current levels of crop production are achieved because commercial fertilizers make continuous cropping of grain possible. In some cases, however, this has come at the expense of ground water quality. Nitrate levels in ground water under

widespread areas increased noticeably only after the use of commercial fertilizers in continuous, irrigated grain production became commonplace.

The terminology used in discussing nitrates can be a source of confusion. The term "nitrates" is commonly used in different ways, sometimes incorrectly. In this report, "nitrate" refers to the ion (NO_3^-), and "nitrates" to the entire group of compounds found in such sources as fertilizers, septic tanks, and ancient soil profiles. Nitrate concentrations can also be expressed in different ways. Concentrations in this report are expressed in terms of nitrate-nitrogen.

PROBLEMS RELATED TO HEALTH

Nitrate contamination of ground water is primarily a concern because it can cause a disease called *methemoglobinemia*. Another name for this disease is the blue baby syndrome. It affects only infants from birth to 6 months of age who consume water with nitrate concentrations in excess of 10 mg/l. Once the infant consumes this water, methemoglobinemia occurs as follows (Hammer, 1980): (1) Infants have gastric juice with a relatively high pH, allowing nitrate-reducing bacteria to grow in the intestine. These bacteria convert nitrate to nitrite. (2) The nitrite is rapidly absorbed into the blood, readily oxidizing the iron of hemoglobin to the ferric state to form methemoglobin. Because hemoglobin is necessary to transport oxygen to the brain, a considerable portion of the oxygen-carrying capacity of the blood is lost when hemoglobin is converted to methemoglobin. (3) The excess methemoglobin causes blood to become blue rather than red. This blue blood causes the skin to appear blue also (cyanosis). Methemoglobinemia can result in brain damage and, in severe cases, death.

Because it causes skin to change color, it is easily diagnosed and can be rapidly reversed by an injection of a dye called methylene blue.

The maximum allowable level of nitrates in drinking water is expressed in terms of a concentration of mass per unit volume of water. This concentration is 45 mg of nitrate (NO_3) per liter of water. If nitrate is measured as nitrogen (N) in water, the maximum level of nitrate in drinking water allowed by health standards is 10 mg/l nitrate-nitrogen ($\text{NO}_3\text{-N}$). This is the convention that is used more commonly to express the nitrate concentration of a water supply.

Most evidence supporting the maximum nitrate contaminant level of 10 mg/l is based on data collected in the 1940s (Hammer, 1980). A physician in Iowa City, Iowa, correlated incidents of cyanosis in infants to high nitrate concentrations in well water used to prepare formulas for babies. In one documented case, the concentration in the unboiled sample of water was 140 mg/l, and in another it was 90 mg/l. The typical well producing this high nitrate water was an old, dug well, rather than a new, drilled well. There were numerous openings into these wells through which nitrate contamination could occur. The physician recommended that well water used in infant feeding possess a nitrate content no higher than 10 mg or, at the most, 20 mg/l.

The U.S. Public Health Service reported in 1951 the results of a survey in the United States on the incidence of methemoglobinemia caused by nitrate contaminated drinking water (Hammer, 1980). In the 49 questionnaires returned, 17 of the states reported 214 verified cases of infant methemoglobinemia resulting from various nitrate concentrations in the water used in preparing formulas for feeding. No case was attributed to raw water with less than 10 mg/l. Five incidents (2.3% of the total) were associated with 11 mg/l to 20 mg/l, 36 cases (16.8%) corresponded to 21 mg/l to 50 mg/l, and the remaining 80.9% involved water containing more than 50 mg/l. The American Public Health Association committee conducting the survey pointed out that most of the cases studied were associated with a concentration in excess of 40 mg/l.

Farm animals, chiefly hogs and cattle, are affected by high nitrate concentrations in their diet. Piglets have about the same tolerance for nitrates as human infants and have been known to die from methemoglobinemia caused by high nitrate levels in their mothers' milk (Engberg, 1967). Because of their larger size and different kind of digestive tract, nursing calves are relatively less affected. Although many cattle have died from grazing on plants in which nitrates have accumulated, few cattle and swine have been known to die from drinking water high in nitrates. However, non-lethal amounts of nitrates in water can cause gastroenteritis or diarrhea (Engberg, 1967).

There is some evidence to indicate that abortion, lameness, stiffness, infertility, and several other maladies are associated with or caused by high nitrate or nitrite concentrations in the water supply (Engberg, 1967). It has also been suggested that the arbitrary range of 50 mg/l to 100 mg/l is a safe upper limit for nitrate concentrations in water consumed by livestock.

Nitrates hypothetically could be precursors for nitrosamines that are suspected carcinogens, because they have induced tumors in laboratory animals, although no human cancer has been positively attributed to them (Hammer, 1980). The main origin of nitrosamines appears to be foods and tobacco smoke. They are ingested as nitrosamines or produced by the conversion of nitrate to nitrite followed by the conversion of the nitrite to nitrosamines. The conversion of nitrate to nitrite occurs in the mouth by bacterial reduction of nitrate in ductal saliva. This produces about three-quarters of the ingested nitrite. Vegetables are the principal source of nitrate in the average adult diet, amounting to about 130 mg ingested per day. This amount is significantly greater than the intake in drinking water. For example, 2l/day at 10 mg/l would equal 20 mg/day.

NITRATE PROBLEM AREAS

Nitrate contamination of ground water occurs in Nebraska either as a widespread areal problem or as a localized problem at the site of a well. There currently are two areas in the state where widespread contamination occurs: the Central Platte region and the O'Neill-Atkinson area in northern Holt County. Localized contamination can occur anywhere in the state, although it generally is found in the eastern third of the state. The following sections review localized contamination problems and discuss widespread contamination in the Central Platte region and Holt County.

Localized Contamination

In cases of localized contamination, the nitrates in wells generally come from activity around the well. The more activity, the more potential for nitrate contamination of the well to occur. Contamination is usually due to poor well construction and local pollution from sources such as septic tanks and feedlots.

A review of communities with nitrate concentrations approaching or exceeding the 10 mg/l health standard showed scattered Nebraska communities had problems due to poor well construction and local sources of contamination. Some factors causing nitrate contamination for these towns include: (1) ground cracks in clayey soils in eastern Nebraska due to expansion and contraction as moisture content changes; (2) old wells designed and constructed to old, inadequate standards;

(3) nitrate-contaminated water from a perched water table reaching a well; (4) local sources of contamination including abandoned wells, septic tanks, feedlots, old cesspools, and irrigation wells back-siphoning liquid nitrogen stored at the surface for applying fertilizer; and (5) a thin, generally alluvial aquifer with little volume that can be contaminated rapidly. All communities that had nitrate concentrations that exceeded the health standard due to these causes have taken action to correct their problems. Some have provided a new supply, others have mixed existing supplies to reduce the concentration, and many have provided bottled water.

Widespread Contamination

A gradual increase in nitrate concentrations has occurred in the Central Platte region (Spalding et al., 1978). For Merrick County the average concentration was 2.8 mg/l for the period 1947 to 1951, 7.5 mg/l for 1961, 11.0 mg/l for 1972, and 12.1 mg/l for 1974. From 1976 through 1977 nitrate concentrations exceeded 10 mg/l in 183 of the 256 ground water samples collected from parts of Buffalo, Hall, and Merrick counties (Gormly and Spalding, 1979). Several samples exceeded 30 mg/l. Sources of nitrates which have caused the problem to grow include: (1) soil organic nitrogen, which can become a nitrate source when cropland is farmed; (2) commercial fertilizer containing nitrogen applied to cropland; (3) precipitation; (4) barnyard and feedlot wastes; and (5) effluent discharge and sludge from septic tanks (Exner and Spalding, 1974).

A major research project on ground water nitrate contamination has been conducted in the Central Platte area. The purpose of this project was to determine the source(s) of nitrates in the ground water. The concentrations of different nitrogen isotopes were measured to make the determination (Gormly and Spalding, 1979). The project report concluded that the major source of contamination of the ground water in this area was inorganic fertilizer. Many researchers, however, question this conclusion. Only a small percentage of the ground water contained significant concentrations of nitrates derived from animal wastes.

Two research activities concerning the ground water nitrate-contamination problem in the O'Neill area have been conducted in the past 20 years. One sampled 71 wells in a 29 km by 58 km area in northern Holt County (Engberg, 1967), and the second sampled wells throughout Holt County (Exner and Spalding, 1979).

The ground water sampling for a portion of Holt County was done from 1963 through 1966. Nitrate concentrations were found to range from 0.02 to 90.90 mg/l (Engberg, 1967). The water from 22 wells contained more than 10 mg/l. A local source of contamination could be identified for

nearly all the stock and domestic wells yielding high nitrate water.

The countywide sampling and data analysis project conducted in 1976 established that there were areas north of the Elkhorn River where ground water nitrate levels exceeded 10 mg/l. These areas were located north of Atkinson and northwest and northeast of O'Neill. Nitrate concentrations north of the Elkhorn River averaged 11.3 mg/l while concentrations in the area south of the river averaged 1.5 mg/l. The rate of increase in ground water nitrate concentrations beneath fertilized and irrigated land in the O'Neill-Atkinson area averaged 1.1 mg/l/yr from the time of well construction to 1976 (Exner and Spalding, 1979). This was calculated by dividing the nitrate concentration of the wells sampled by the age of the wells.

One nitrate source that has received little attention, but which is contributing to nitrate contamination of ground water, is naturally occurring ancient nitrates. These nitrates were deposited during prehistoric times. They are not in the soil profile due to human activity. Contamination of water supplies by ancient nitrates was documented in a recharge investigation in Hamilton County (Lichtler et al., 1980). It has been shown that ancient nitrates also exist in several other locations, so it is possible that ground water could be contaminated in other areas (Olson et al., 1973).

MECHANISMS OF NITRATE CONTAMINATION OF GROUND WATER

Generally, the largest contributor of nitrates to ground water is fertilizer applied to irrigated cropland. The problem becomes more serious when (1) the cropland is over irrigated and fertilized, (2) the cropland has relatively highly permeable sandy topsoil, and (3) the water table is shallow, as in alluvial river valleys and in portions of the Sand Hills.

Figure 1 is a diagram showing a portion of the nitrogen cycle as it occurs on fertilized cropland (Watts, 1982, personal communication). It will help explain how nitrate contamination of ground water occurs. The cycle starts when fertilizer, such as urea, anhydrous ammonia (NH_3), or ammonium nitrate (NH_4NO_3) is applied to the cropland. In the case of urea, hydrolysis occurs and urea is converted from $\text{CO}(\text{NH}_2)_2$ to ions that include ammonium (NH_4^+). If the fertilizer is applied as anhydrous ammonia, a portion of it can be lost to the atmosphere as a gas. The balance is converted to ammonium by hydrolysis. Under some conditions ammonium can be converted to ammonia and lost as a gas by the process of volatilization. The remaining ammonium is converted to other forms of nitrogen depending on time, soil moisture, and soil temperature.

If the ammonium is transformed into organic nitrogen by soil bacteria, it is said to be immobilized. Nitrogen tied up in soil organic matter is not very likely to leach through the soil. As the organic matter decays, soil bacteria convert the organic nitrogen back to ammonium by the process of mineralization. Finally, the ammonium can be nitrified (converted to nitrate) by other soil bacteria.

The nitrate can also be immobilized (converted to organic nitrogen) in the soil, or it can be converted to gaseous nitrogen (N_2) and/or nitrous oxide (N_2O) through the process of denitrification by soil bacteria. Finally, it can remain in the soil as residual nitrate which can be taken up by the crop or become lost to the plant by leaching through the soil, and ultimately contaminate the ground water.

The preceding discussion concentrated on the soil root zone. This is only part of the vadose zone (the entire soil volume above the water table). Nitrates leached past the root zone normally move through the rest of the vadose zone

in slugs. This happens because nitrates tend to accumulate in the root zone until heavy rainfall occurs or excessive irrigation water is applied to cropland. The nitrates are mobilized in the wetting front and move with it toward the ground water. These slugs of nitrates generally cannot be stopped, particularly on very permeable sandy soils. This process of leaching and movement of nitrates, which is largely responsible for their buildup in ground water, could only be halted by modifying current farming practices. Even then, the slugs of nitrates already in the vadose zone would continue moving downward until the last slug finally reached the water table.

An investigation (Hergert, 1982) of the amount of nitrates leached out of the root zone and their movement through the vadose zone found that nitrates from mineralized soil organic nitrogen and fertilizer moved through the vadose zone at the rate of about 2.1 m/yr. The amount of nitrates leached from corn on irrigated sandy soils at the University of Nebraska Sandhills Agricultural Laboratory (UNSAL) near Tryon ranged from a low of about 40 kg to 50 kg N/ha/yr from unfertilized plots to more than 100 kg N/ha/yr for plots that received nitrogen fertilizer in excess of what is required for producing maximum yield (Hergert, 1982). The fertilizer rate on plots receiving excess fertilizer was 210 kg N/ha, which led to a buildup of residual nitrates in the soil. As both the unfertilized and over-fertilized plots received water based on the evapotranspiration of the latter, the unfertilized plots were in effect over-irrigated. Normal precipitation at UNSAL moved residual nitrates deeper into the soil over the winter and early spring (Hergert, 1982). This moisture leached nitrates deep enough to stay ahead of root growth, so they were essentially lost for crop production. They ultimately will contaminate the ground water.

Whether or not nitrates were subject to denitrifying bacteria and converted to nitrous oxide and molecular nitrogen gas was not determined. Two conditions must exist for microbial denitrification to occur: oxygen must be absent, and a source of carbon (organic material) must be present. The presence of organic material would depend on the site's pre-historic conditions or movement of soluble carbon to the nitrate-rich zone. The presence of oxygen would depend on the thickness of the unsaturated zone and the porosity of the material in it. If the thickness of the unsaturated zone below the root zone is relatively large and the soil has a fine texture with relatively poor structure or aggregation, oxygen may not diffuse throughout the entire unsaturated zone. The conditions under which porosity, unsaturated zone depth, and level of organic material become factors in denitrification are not known.

At the bottom of the vadose zone is the water table, the beginning of the saturated zone. The location of nitrates in the saturated zone depends on the amount of mixing that

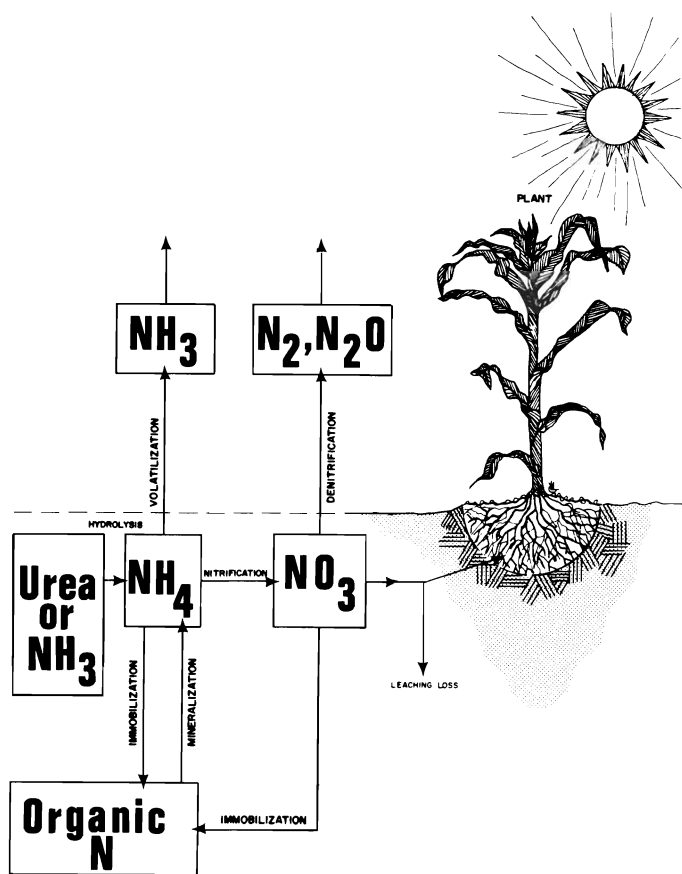


FIGURE 1. A portion of the nitrogen cycle as it occurs on fertilized cropland according to D. G. Watts (1982, personal communication).

takes place. Once nitrates leach down to the water table they tend to stratify at the top of the saturated zone and not mix with deeper ground water. This is why sampling wells to determine contamination can be misleading. If a shallow well is sampled in an area with nitrate-contaminated ground water, it would indicate considerable contamination even though deeper ground water may not contain nitrates.

The amount of nitrates in the saturated zone is affected by denitrification in the ground water. As in the vadose zone, oxygen must be absent and organic material must be present for this to occur. Neither of these factors has been studied in detail.

POSSIBLE REMEDIES

Solutions to the nitrate-contamination problem in Nebraska can be divided into two types. One concentrates on treatment of the problem at its source. In Nebraska, this involves controlling the amount of nitrogen leached from cropland. The second involves treating the water to remove nitrates after contamination has occurred.

Correction at the Source

The Hall County Water Quality Special Project (HCWQSP), a demonstration project in the Grand Island area, attempted to show how to reduce nitrate leaching from cropland and curb nitrate contamination of ground water. The purposes of the project were to persuade farmers to utilize the best management practices on their land to reduce leaching of nitrates from fertilized, irrigated cropland, to monitor the ground water nitrate concentration in the project area, and to predict the amount of nitrates leaching through the root zone in the project area using a computer model.

Many farmers apply excessive amounts of nitrogen fertilizer (Hoover and Oscar, 1982), which eventually is leached to the ground water as nitrates. Not only is the ground water quality adversely affected, but the nitrates lost from the plant root zone represent an economic loss to the farmer. Data from the HCWQSP included information on the economics of using nitrates already in ground water and residual nitrates in topsoil to help meet plant nitrogen requirements while maintaining yield goals (Anonymous, 1984). Table I shows the fertilizer savings realized by the farm cooperators in the HCWQSP for the 1980-1983 growing seasons. It also shows the cost savings for anhydrous ammonia, urea, ammonium nitrate, and urea ammonium nitrate for each of the four growing seasons. A discussion of the calculation of the nitrogen balance is required to explain how these savings were calculated.

TABLE I. Hall County Water Quality Special Project: reported savings*.

| Year | Fertilizer Savings (kg/ha) | Average Fertilizer Cost (\$/kg) | | | |
|---------|----------------------------|---------------------------------|-------|------------------|-----------------------|
| | | Anhydrous Ammonia | Urea | Ammonium Nitrate | Urea Ammonium Nitrate |
| 1980 | 92 | 23.92 | 42.32 | 41.40 | 45.08 |
| 1981 | 101 | 26.26 | 46.46 | 45.45 | 49.49 |
| 1982 | 88 | 22.88 | 40.48 | 39.60 | 43.12 |
| 1983 | 73 | 18.98 | 33.58 | 32.85 | 35.77 |
| Average | 89 | 23.14 | 40.94 | 40.05 | 43.61 |

*Source: Anonymous (1984).

The following is the nitrogen balance equation:

$$\text{Required N} = 0.50 (\text{N Fertilizer} + \text{N Residual} + \text{N Ground water} + \text{N Mineralized} + \text{N Precipitation})$$

where:

Required N = the amount of nitrogen that must be available to the plant,

N Fertilizer = nitrogen in the soil due to fertilizer,

N Residual = nitrogen in the soil from the previous growing season,

N Precipitation = nitrogen in the root zone due to rainfall,

N Ground water = nitrogen in the root zone due to nitrate-contaminated ground water used for irrigation, and

N Mineralized = nitrogen in the soil converted from organic nitrogen to ammonium during the growing season.

The term Required N in the equation is the nitrogen required by the plant to meet a specified yield goal. The amount of fertilizer the farmer needs to apply to provide the required nitrogen, assuming plant use efficiency is 50%, can be calculated by rearranging the terms in the equation to solve for N Fertilizer .

In the HCWQSP, technicians sampled the nitrate-contaminated ground water used for irrigation and determined its

nitrogen content. They also sampled the soil to determine the amount of residual nitrogen (Anonymous, 1984). Both the nitrogen in the ground water and the residual nitrogen were included in the calculations when making fertilizer recommendations to the cooperators, which reduced the amount of fertilizer needed. This reduction is shown as the fertilizer savings in Table I. It should be emphasized that the preceding equation is not the equation used to calculate the fertilizer savings noted in Table I. The actual equation used was based on a nitrogen balance similar to the preceding equation, but it had coefficients specifically for the HCWQSP area and it did not include the ^{15}N Mineralized" and ^{15}N Precipitation" terms noted in the preceding equation.

The plant nitrogen requirements met by utilization of nitrates in the ground water pumped for irrigation can also be calculated. For instance, a 30-cm depth of irrigation water containing 30 mg/l nitrate applied over 1 ha represents 90 kg/ha of nitrogen. If it is assumed the plant recovers 50% of the nitrogen available, 45 kg/ha of nitrogen would be recovered by the plant, while the remainder would be lost, probably to the ground water.

The Hall County project was authorized to determine if nitrates in ground water could be utilized effectively under field conditions. The effect on the resulting nitrate concentrations in the aquifer has not been determined. Another research project based on computer simulation of cropping systems using ground water nitrates was conducted to estimate the potential for reducing nitrate concentrations. A computer model was used to simulate the movement of nitrates through the root zone of field corn at sites in the Central Platte Valley where the soils are sandy, the nitrate concentration in the ground water can be high, and ground water is close to the surface. Field testing at the sites was primarily for calibration and verification of the simulation model. The verification results indicated that the model accurately simulated leaching losses of nitrogen for preplant applications of fertilizer (Martin and Watts, 1982).

Further computer modeling predicted that nitrates could be removed from ground water pumped for irrigation, thereby reducing the nitrate concentration in the ground water supply, if the rate of fertilizer N application was 45 kg/ha, and the initial water nitrate concentrations were greater than 22 mg/l. For a fertilizer application rate of 135 kg/ha, it was shown that nitrates could essentially not be removed from ground water pumped for irrigation (Martin and Watts, 1982).

Improvement of Contaminated Water Supplies

Communities providing public water supplies are required by the Nebraska Department of Health (NDOH) to take corrective action when the nitrate concentration in their water

supply reaches 10 mg/l. Several processes for removal of nitrate are available, but they are difficult to design and operate, and they are expensive. Substituting a new supply is generally easier and cheaper.

Three treatment processes have been recognized for nitrate removal from drinking water supplies for communities: reverse osmosis, electro dialysis, and ion exchange. These processes require a high degree of technical capability in design, construction, and operation and are extremely costly to purchase and operate. The NDOH has hesitated to recommend or accept nitrate removal by any of these processes for these reasons. The breakdown of costs, in 1977-dollar values, for the three treatment processes is shown in Table II. It is based on actual review of treatment plant costs adjusted to the 1977-dollar value.

All water needing treatment differs in chemical composition, which influences the efficiency of the treatment technique selected. For example, if the source for raw water contains calcium or magnesium salts in solution, the efficiency of nitrate removal by ion exchange will suffer. In many instances, it may be necessary to process the water through two resin contact beds, one to remove calcium and magnesium and one to remove nitrates. This process would increase the cost by as much as 70% over the cost of removing nitrates without

TABLE II. The cost of nitrate reduction by treatment*.

| Costs | Treatment Process (Percentage Removal) | | |
|--|---|--------------------------|--------------------------|
| | Reverse Osmosis (90%) | Ion Exchange (98%) | Electrodialysis (80%) |
| Capital Cost in 1977-dollars | | | |
| Population 200 | 283,700 | 69,600 | 290,000 |
| Population 1,000 | 545,000 | 85,200 | 539,000 |
| Annual Capital Cost | | | |
| Population 200 | 35,219 | 8,640 | 36,000 |
| Population 1,000 | 67,656 | 10,577 | 66,911 |
| Annual Operation and Maintenance Cost | | | |
| Population 200 | 64,280 | 1,400 | 50,230 |
| Population 1,000 | 114,600 | 2,310 | 93,990 |
| Total Annual Cost | | | |
| Population 200 | 99,500 | 10,040 | 86,230 |
| Population 1,000 | 182,256 | 12,887 | 160,901 |

*Source: Anonymous (1983).

the presence of calcium and magnesium ions. Because the ground water that serves as the water supply for most communities is known to contain calcium and magnesium, the estimated costs for ion exchange presented in Table II are low in most instances. Further, the figures presented do not include the expense associated with pilot studies of plants, which would be necessary in varying degrees, for determining the most economic treatment design.

A fourth process for removing nitrates, distillation, is satisfactory for home use but not for the larger demands of communities. The distillation process involves heating the water to boiling and collecting and condensing the steam. Most impurities remain in the heating tank. Nitrate reduction of up to 99% can be attained through this process (Lee and Axthelm, 1981).

As an alternative to treatment for nitrate removal, NDOH has encouraged communities to mix their existing contaminated supply with water from an uncontaminated source, or in cases where mixing is not feasible, to find a substitute supply. Mixing or substitution can be accomplished by consolidating water systems or drilling new water supply wells. Johnson and Palmyra, Nebraska, have consolidated with larger water systems to solve their nitrate problem. Communities that have opted to drill new wells include Elmwood, Gibbon, Hardy, Pickerell, Roca, Tobias, Verdon, and Wood River (Lee, 1983, personal communication).

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