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EC90-2502 Perspectives on Nitrates

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Perspectives on Nitrates

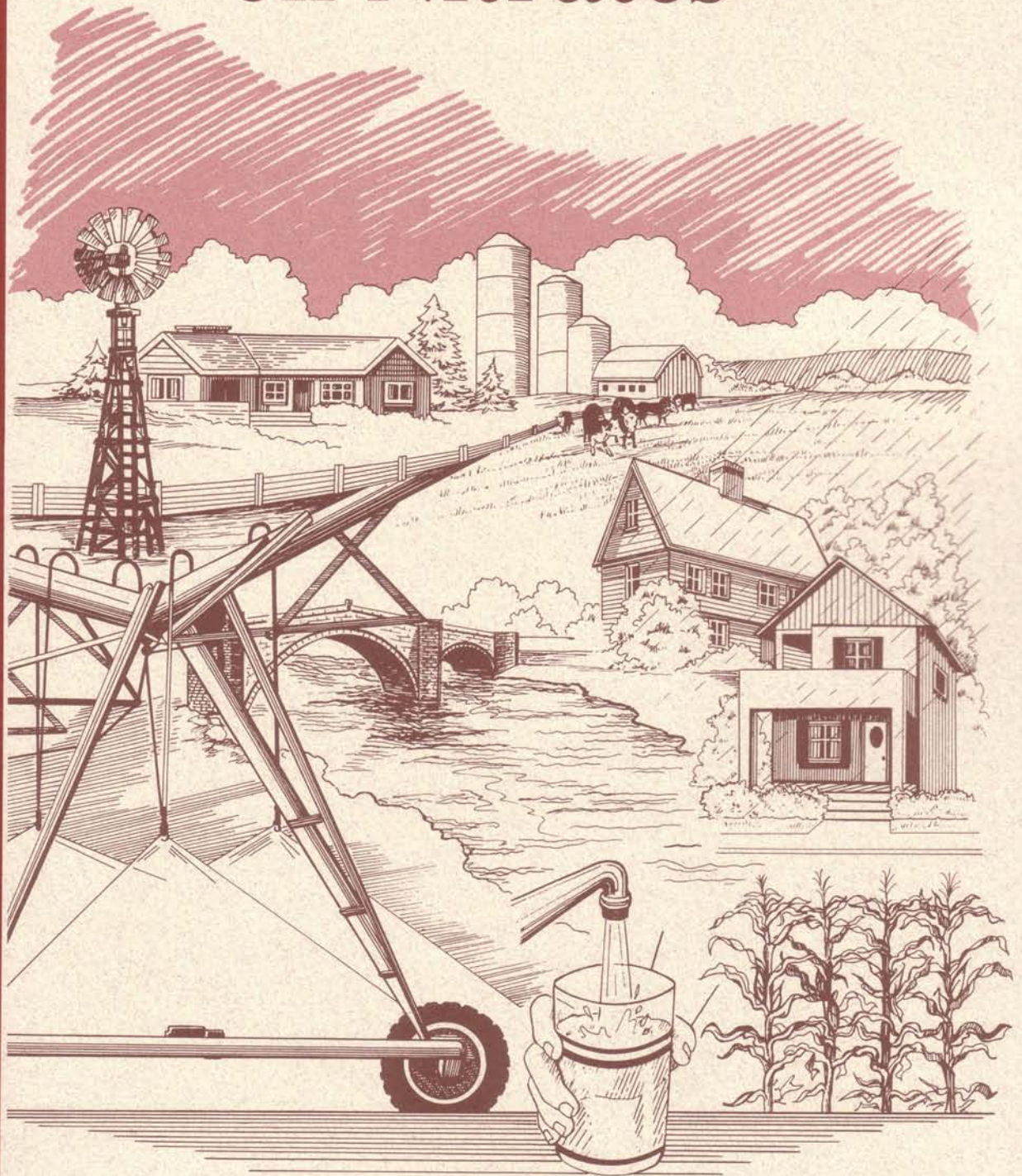
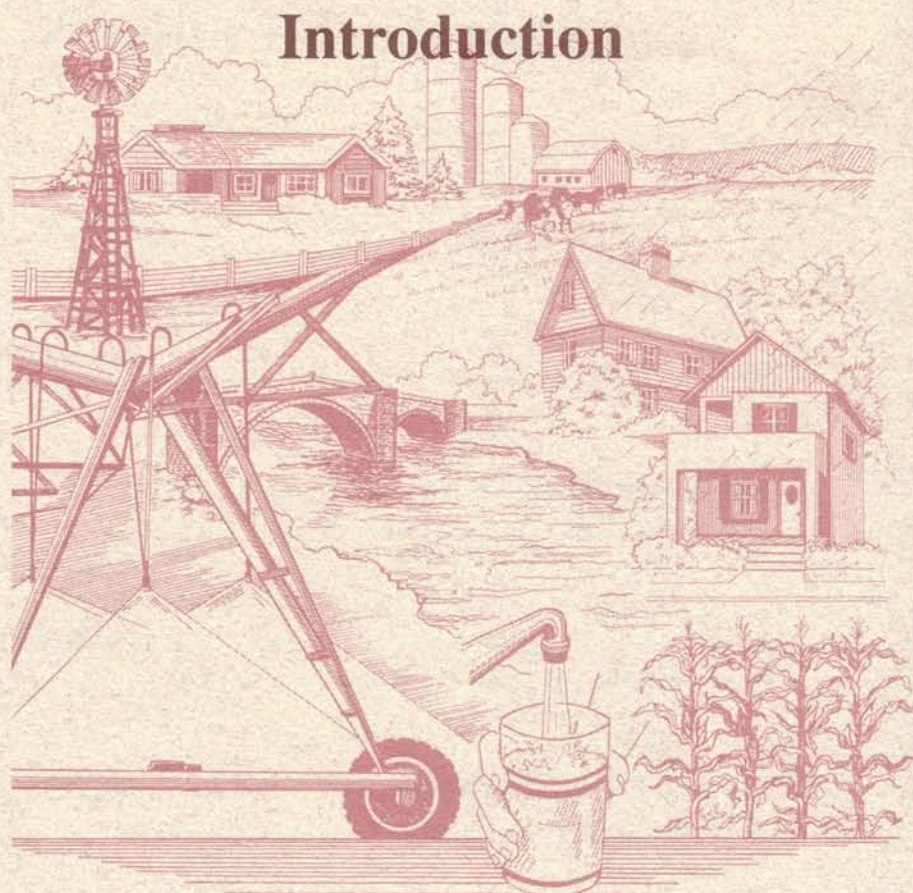


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Introduction



Approximately 10 years ago an Extension "Nitrate Task Force Committee" was organized to address concerns relating to nitrate-nitrogen accumulations both in ground water and plants. Members of that committee produced an Extension Circular entitled "Living with Nitrates." It was comprised of six papers that provided readers with insights on nitrogen in the environment and the potential effects of nitrate and its metabolites on both human and animal health.

Most of the authors who contributed to that earlier publication are represented in the present circular. In addition, there is a new section that addresses public policy and legislative-regulatory aspects of the nitrate problem.

The potential adverse consequences of nitrate on both human and animal health has long been recognized. A "References" section in the earlier circular included many research reports dating from the 1940s and 1950s, as well as two from 1895. A similar section has not been included in the present circular; even a selected bibliography would be prohibitively long and the extensive amount of current research would quickly date such a listing. Persons desiring additional information should request assistance from the nearest University of Nebraska Cooperative Extension office, the University of Nebraska Water Center, or the University of Nebraska Medical Center.

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Nitrogen in Our Environment

Gary W. Hergert and Richard A. Wiese

The use of nitrogen fertilizer was a breakthrough for agriculture—allowing for continuously high crop yields from the same soils. However, Nebraskans increasingly are concerned that nitrogen leached from the soil may be reaching drinking water supplies. The use of “best management practices” for nitrogen fertilizers and irrigation water can help ensure continued high yields while reducing nitrogen and water applications, and possible leaching of nitrogen from the soil.

Nitrogen has a unique place in our environment. Worldwide, it is the plant nutrient most limiting for production of food and fiber. Throughout recorded history, man has added nitrogen to crops by using animal manures, legume crops, or fertilizers. By world standards, the inexpensive food Americans enjoy can be attributed largely to the availability and use of nitrogen fertilizer.

Basic to Life

Nitrogen is a basic part of our environment. It is the building block of the protein that all living things need for growth and survival. Nitrogen accumulates in soils during the process of soil formation. During the thousands of years of soil development, nitrogen accumulated in soil from additions in rainfall, and from plant and microbial fixation of nitrogen gas from the atmosphere. It also accumulated in the organic matter produced from decaying plants and animal residues.

Many of our virgin prairie soils contained four to six thousand pounds of organically bound nitrogen when they were first plowed. However, once a soil is tilled and crops are grown, the organic matter and nitrogen content start to decrease.

Organic nitrogen in soils changes slowly to inorganic nitrogen during the growing season at a rate of about 1 to 2 percent per year. Soils that once contained 4 to 5 percent organic matter now contain 2 to 3 percent organic matter

after 50 years of continuous cropping with no additions of nitrogen. Agriculture systems that rely heavily on nitrogen reserves in the soil to meet plant requirements cannot efficiently produce high crop yields over long periods.

Adding Nitrogen for Food Production

The primitive slash and burn system, or the practice of shifting cultivation used in many tropical areas, can be productive without nitrogen fertilizer for a few years. However, new soil must be brought into production as repeated cropping depletes reserves of soil nitrogen. Old fields are allowed to return to native vegetation for several years to build up soil nitrogen reserves. In years before commercial fertilizer was available, farmers used crop rotations that included legumes to restore depleted nitrogen.

The use of nitrogen fertilizer was a breakthrough for agriculture because it meant the same field could be farmed continuously for grain production and the soil organic matter level could be maintained or increased in many soils while crop yields remained high.

Although most nitrogen in soils exists in organic forms, plants take up nitrogen in the mineral form as either nitrate (NO_3^-) or ammonium (NH_4^+) ions. Most nitrogen used by plants is absorbed as the nitrate ion. Plants do not take up organic forms of nitrogen. This means that organic sources of nitrogen must be converted to the nitrate form before they can be used by plants.

Several steps are needed to convert organic nitrogen to nitrate-nitrogen; these are shown in what is called the nitrogen cycle. General features of the nitrogen cycle are shown in Figure 1.

Nitrogen that has potential for plant use can enter this cycle at several points. Animal manures, compost, sewage sludge and legume crops are organic nitrogen sources. Some nitrogen fertilizers already contain nitrogen in the readily available nitrate form. In other types of fertilizers the nitrogen must be converted to the nitrate form.

Once nitrogen is added to the soil through fertilizers, crop residues, legumes or manures, it becomes part of the soil N system and some is eventually converted to nitrate-nitrogen as depicted by the N cycle. It's also important to note that a plant cannot distinguish between the original source of the nitrate-nitrogen it uses. The nitrate that results from the decomposition of manure, for example, is not different from the nitrate that comes from commercial fertilizer.

The total amount of nitrate-nitrogen generated through the nitrogen cycle is not necessarily used by plants. When the nitrate-nitrogen supply exceeds the amount used by plants, there is an increased potential for both nitrate-nitrogen accumulation and nitrogen loss from the system.

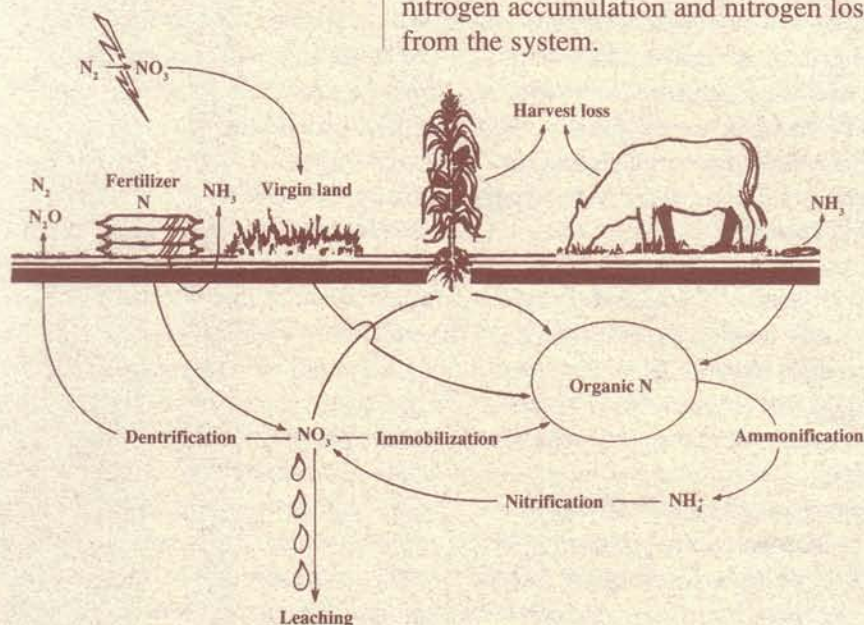


Figure 1. The nitrogen cycle.

How Nitrate-Nitrogen Gets Into Ground Water

Nitrate-nitrogen can be lost from soils by: a) leaching, b) denitrification, c) volatilization of nitrogen gases and tie-up by soil bacteria. Nebraskans are most concerned about losses due to leaching. Leaching is the downward movement of nitrate-nitrogen through the soil with water. Leaching cannot occur if there is no downward movement of water.

The potential for nitrogen leaching is not the same for all parts of Nebraska. Sandy soils are very permeable and will not hold much water. Other soils in the state will hold larger amounts of water. Therefore, the potential for nitrate-nitrogen leaching is greater in our sandy soils, but can occur on our fine textured soils. Leaching potential increases from west to east in Nebraska because average annual precipitation increases from 15 inches in western Nebraska to over 30 inches in eastern Nebraska.

The nitrate-nitrogen which moves downward through soils comes from many sources, not just nitrogen fertilizers. The breakdown of organic nitrogen sources (compost, manure, legume crops) through the nitrogen cycle process also produces nitrate-nitrogen. This nitrate-nitrogen can move through soils in the same manner as nitrate-nitrogen supplied as nitrogen fertilizers. Research in Nebraska has shown that large accumulations of nitrate-nitrogen occur several feet below the surface of some soils that have never been farmed or fertilized. This nitrate-nitrogen accumulated during the geologic past and has remained in the soil because of our relatively dry climate.

Since downward movement of nitrate-nitrogen through soils was taking place before human presence in Nebraska and will continue, it's unreasonable to expect that it can be stopped or eliminated. Alteration of the environment to produce food can increase the rate of this movement and the amount lost. There are, however, management practices farmers can use to minimize

the leaching of large amounts of nitrate-nitrogen from irrigated and dryland soils, especially sandy soils. Leaching can occur in eastern Nebraska under dryland because rainfall is high in many years.

Nitrogen Best Management Practices

The phrase “Best Management Practices” is a popular term that relates to the ability to manage the environment to improve environmental quality. Best management practices (BMPs) are defined as a part of federal laws for preventing pollution. There are five components to a BMP. The practice must be agronomically feasible, environmentally effective, implementable, economically achievable, and socially acceptable. These criteria can fit nitrogen management as it relates to ground water quality.

Management of two factors will reduce excessive nitrate-nitrogen leaching in all soils, but especially irrigated sandy soils. Leaching of nitrate can be reduced substantially if adequate, but not excessive, amounts of nitrogen fertilizer and organic nitrogen sources are used.

BMPs for nitrogen use, whether applied as commercial fertilizer or organic sources, should be every farmer’s goal. Crop growers have several priority steps that must be taken to improve nitrogen fertilizer use and to reduce leaching. These include:

- 1) determine a realistic yield goal;
- 2) determine residual soil nitrate;
- 3) determine the nitrogen contributions from irrigation water, legumes, and manures; 4) use the above three steps to calculate a fertilizer-nitrogen rate for their crop and decide on the best application method; and 5) practice good irrigation water management. A more

detailed explanation of these BMPs is given in NebGuide G87-829, “Fertilizer Nitrogen Best Management Practices.” Implementing these simple steps is both economically advantageous to the farmer and environmentally sound.

Choosing the rate of nitrogen application need not be left to chance. By taking soil samples to a depth of at least three feet, and selecting a realistic yield goal, a fertilizer-nitrogen application rate can be selected which will provide maximum economic yield without supplying excess nitrogen that could be subject to leaching.

Remember, leaching cannot occur if there is no downward movement of water. We cannot control the amount of rainfall. We can, however, control the amount of water supplied through irrigation systems. Research has shown that irrigation scheduling will substantially reduce the amount of water that moves through soils. These two factors—proper nitrogen rate, based on a realistic yield goal and soil samples to at least three feet, plus improved irrigation water management based on irrigation scheduling—are the keys to slowing down and reducing the amount of nitrate that moves to ground water.

It might appear that these management practices are too complex to use routinely. However, many Nebraska farmers have shown that using them is not difficult. In addition, yields have not been reduced when these practices are used. Farmers can use realistic yield goals for their soil and climate, soil testing for residual nitrate, irrigation scheduling, split application of nitrogen fertilizer, and nitrification inhibitors to obtain maximum use of fertilizer nitrogen without a reduction in yield while reducing the amount of nitrate that moves downward in the soil.

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Alternatives When Excessive Nitrate is Present in Drinking Water

DeLynn R. Hay and Ann Ziebarth

If there is excessive nitrate in your water supply, bottled water may be a short-term solution. In the long-term the answer may be alternative water supplies, a new water well or home treatment of drinking water by distillation, reverse osmosis, or ion exchange.

If excessive nitrate-nitrogen is present in your water supply, you have two basic choices — obtain an alternative water supply or use some type of treatment to remove the nitrate-nitrogen.

For livestock use, another supply is probably the only realistic alternative. The need for an alternative supply or nitrate-nitrogen removal should be definitely established before making an investment in equipment or an alternative supply. The decision to take action should not be made on the basis of a field test for nitrate in the water supply, but upon an analysis by a reputable laboratory. Samples may be submitted to the State Health Department Laboratory, some city-county health departments, some Natural Resources Districts, or to one of several commercial laboratories.

You may want to consult your physician and/or veterinarian for recommendations on the need to take action.

Alternative Water Supplies

A satisfactory alternative water supply possibly may be obtained by drilling a deeper well into a different aquifer material or a new well in a different location. If the source of the nitrate is a point source, such as livestock wastes, a new well location may provide water of satisfactory quality. If the water supply with high nitrate is coming from a shallow aquifer, there may be a deeper aquifer that is separated from the contaminated water by a clay layer that

prevents downward movement of water and contaminants. A new well should be constructed so that surface contamination cannot enter the well, and should be located away from any source of possible contamination. In some cases it may be possible to hook onto a community water supply or rural water district.

The State Department of Health, Division of Drinking Water and Environmental Sanitation, may be able to assist you in determining the cause of water contamination and make recommendations to correct the problem. The Division has field staff in Lincoln, Norfolk, North Platte, Scottsbluff and Grand Island. In addition, the Conservation and Survey Division of the University of Nebraska-Lincoln can provide general information on the possible location of a water supply with satisfactory quality. The Conservation and Survey Division has staff in Lincoln, Norfolk, North Platte and Scottsbluff.

Another alternative source of water is bottled water that can be purchased in stores or direct from bottling companies. This option might be considered when the primary concern is water for consumption by infants. Bottled water is regulated by the Food and Drug Administration as a food and, in most cases, must meet public water supply standards. The Nebraska Department of Agriculture licenses and inspects bottling companies, but does not routinely sample bottled water. You

should assure yourself of the nitrate content, general quality and bacterial quality of any water purchased. This may mean contacting the bottling company or having the water tested. In all cases, purchased water must be handled and stored in a manner to prevent contamination. Refrigeration will help to prevent bacterial growth after opening the container.

There are four basic types of bottled water:

- Distilled water or demineralized water has been treated to remove nearly all of the minerals that occur naturally in water. This water is produced by distillation, sometimes in combination with filtering, reverse osmosis or deionization. Nearly all the total dissolved solids (minerals) are removed. Distilled water may be considered flat and tasteless for drinking because of the lack of minerals.
- Drinking water may come from municipal water systems, wells or springs. It may be treated to remove some contaminants and may be disinfected. Treatment can include reverse osmosis and filtering.
- Natural water comes from a protected well or spring and is bottled without extensive treatment. Natural water will contain minerals commonly picked up by water as it moves through air, soil and rock materials. Disinfection and filtration are typically the only treatment used for natural water.
- Mineral water is obtained from a natural spring or other ground water source and usually contains large amounts of dissolved mineral salts, such as calcium, sodium, magnesium and iron. If mineral water contains carbon dioxide (carbonation), either naturally or added during bottling, it is called sparkling water.

Some retail stores may provide treated water for customers to bottle using their own bottles. This water normally will be treated using distillation or reverse osmosis. Clean bottles should be used

when obtaining water from this type of source. Storage under refrigeration will help control any potential bacterial growth.

Bottled water may have the advantage of being a source of low-nitrate water, but it is a relative expensive alternative water supply and generally should be considered a short-term alternative supply.

Treatment

Nitrate can be removed from drinking water by three primary methods: distillation, reverse osmosis and ion exchange. Home treatment equipment using these processes is available from several manufacturers.

All of the methods for removing nitrates described here are relatively expensive. Consider both initial cost and operating costs. Operating costs include the energy costs of operating the system along with repair and maintenance costs. Regardless of the quality of the equipment purchased, it will not perform satisfactorily unless it is maintained in accordance with the manufacturer's recommendations. Equipment maintenance may include periodic cleaning and replacement of some components. Also consider any special installation requirements that may increase the cost of the equipment. Be sure the equipment has adequate capacity to meet your daily water needs.

Purchase water conditioning equipment only from reputable dealers and manufacturers. A reputable dealer can assist you in evaluating available equipment. This helps to assure that the equipment will perform the necessary task and that maintenance and repair parts will be available when needed. Check to see if the equipment has been tested or evaluated by an independent agency. The Water Quality Association (WQA) and the National Sanitation Foundation (NSF) both operate voluntary programs to test water treatment equipment for manufacturers. Equipment that is listed by WQA and NSF has been evaluated and meets test

Bottled water may have the advantage of being a source of low-nitrate water, but it is a relative expensive alternative water supply and generally should be considered a short-term alternative supply.

Filters, disinfection (chlorination), or boiling the water will not remove or reduce the nitrate-nitrogen concentration in drinking water.

standards. Equipment that has been listed by WQA and NSF normally will have a label on the equipment. This label indicates that the manufacturer's claims have been verified by independent testing.

Distillation

The distillation process involves heating water to boiling causing it to evaporate. The resulting steam is collected and condensed using a cooled metal coil. Up to 99 percent of the nitrate-nitrogen can be removed by this process. Merely boiling water will increase rather than decrease the nitrate concentration. Pure water is obtained by collecting and condensing the steam generated as water is boiled. The mineral impurities from the water collect in the distiller boiling tank. These impurities must be removed from the distillation units. Cleaning should follow the schedule recommended by the manufacturer. Water can contain volatile organic contaminants. When the boiling point of these volatile contaminants is near that of water, it is difficult to separate those materials from water using distillation. Some distillers use activated carbon filters to assist in removing the organic contaminants. Other distillers preheat the water in a vented portion of the still before it enters the boiling chamber in order to help remove volatile contaminants.

The type of container used to store distilled water is important. First, the container must be sanitary, otherwise the water will become contaminated. Second, water which has been treated by an efficient, properly operated distillation unit is essentially mineral free. It is, therefore, highly corrosive. The container in which the water is stored must be resistant to corrosion. Stainless steel is commonly used but glass containers also may be used.

In addition to the buying considerations discussed above, you should also consider the following:

- What is the capacity of the boiling tank?

- How much treated water is stored in the unit?
- What is the energy requirement for the unit and what will the electrical costs be?
- Does the system use a batch or continuous system of processing?
- What automatic features are available?

Reverse Osmosis

Reverse osmosis, as the name implies, is the opposite to the natural process of osmosis. In osmosis, if water containing a high concentration of mineral impurities is separated from water containing a lower concentration of impurities by a semipermeable membrane, the water from the solution of lower concentration will pass through the membrane to the solution of higher concentration of impurities. In reverse osmosis, pressure is applied to the impure water forcing the higher concentration water in a reverse direction through the membrane. As the water passes through, the membrane filters out most of the impurities. According to manufacturers' literature, from 85 to 95 percent of the nitrate can be removed by this process. Actual removal rates may vary somewhat, depending on the initial quality of the water, the system pressure, and water temperature.

A disadvantage of this method is that only about 30 percent of the water entering the reverse osmosis unit is recovered as treated water. The remaining 70 percent is discharged as waste along with the impurities which have been removed from the product water. Disposal of the waste water must be considered when a reverse osmosis unit is to be installed. Efficiency of reverse osmosis units can usually be increased by softening the water before treatment.

Pressure is required to force the water in the reverse direction through the semipermeable membrane. Most home units now available operate using normal system pressure. If system pressure is too low, a pump will be

necessary to develop the required pressure. Units operating at low pressure will have a lower nitrate removal efficiency.

Many household units are designed to fit under the kitchen sink and include a small storage tank. The treated water is delivered to the sink with a separate faucet.

The appropriate type of membrane depends on the source of water. Some membranes cannot be used with chlorinated water. The membranes must be replaced periodically. The total dissolved solids in the water, the water pressure and water temperature will affect the life of the membrane. Manufacturer recommendations for replacing membranes are based on average water use, contamination level, pressure and temperature. Monitoring the total dissolved solids of the treated water is one way to monitor the effectiveness of reverse osmosis units and the need to replace the membrane.

Many reverse osmosis units will include a particulate filter ahead of the membrane and a carbon filter on the output side. The particulate filter helps to remove small solid contaminants that accelerate plugging of the membrane. The carbon filter removes organic contaminants, and tastes and odors from the water. Reverse osmosis is sometimes called ultrafiltration, but should not be confused with particulate filters and activated carbon filters. Carbon adsorption filters and particulate (mechanical) filters of various types do not remove nitrate-nitrogen.

Ion Exchange

The ion exchange process uses the principle that impurities in water consist of chemical ions each containing a small electrical charge. The water is passed through a treatment tank filled with a bead-like resin. The resin contains the opposite charge to the impurity to be removed. Ions of opposite charge are attracted to the resin and will remain with the resin as the water passes through the unit.

Household water softeners operate using ion exchange. In a water softener, calcium and magnesium ions are exchanged for sodium ions. However, a water softener does not remove nitrate-nitrogen.

For nitrate removal, special anion exchange resins are used that will exchange chloride ions for the nitrate and sulfate ions in the water as it passes through the resin. Most anion exchange resins have a higher selectivity for removing sulfate than nitrate. Thus, the level of sulfate in the water is an important factor in the efficiency of an ion exchange system. Another concern with nitrate ion exchange systems occurs when the resin becomes saturated with nitrate. When the resin is saturated with nitrate ions, the treated water may have a higher nitrate content than the untreated water.

Ion exchange is not commonly used for household water treatment. It is more applicable for large commercial or community water system installations. In these larger installations, the output water can be more easily monitored and the exchange resin recharged on a timely basis.

Summary

Two methods are currently available to address excessive nitrate-nitrogen in drinking water. These methods are:

1) using an alternative supply of water, and 2) using water treatment equipment to reduce the nitrate-nitrogen concentration.

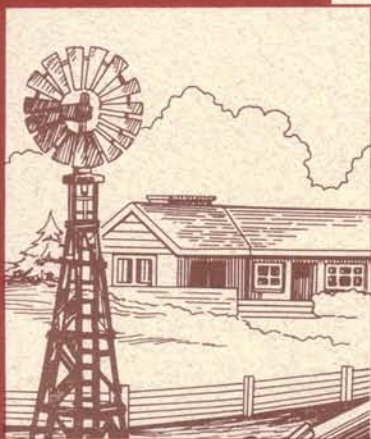
Possible alternative sources of supply include:

- a) drilling a deeper well,
- b) drilling a well in a different location,
- c) purchasing bottled water, or
- d) a public water supply.

Water treatment equipment that will reduce nitrate-nitrogen concentrations uses one of the following processes:

- a) distillation,
- b) reverse osmosis, or
- c) anion exchange.

DeLynn R. Hay is a water resources and irrigation specialist at UNL and Ann Ziebarth is a housing specialist at UNL.



Nitrates, Nitrites and Methemoglobinemia

Richard B. Davis

Methemoglobinemia is a blood disorder caused when nitrites interact with the hemoglobin in red blood cells to form methemoglobin. Unlike hemoglobin, methemoglobin cannot carry sufficient oxygen to the body's cells and tissues. While methemoglobinemia is rare among adults, some cases have been reported among infants. A chief cause has been well water contaminated with nitrates and used to mix formula and other baby foods.

Fatal methemoglobinemia is much less common than carbon monoxide poisoning, yet both disorders cause asphyxia of body tissue by preventing normal transport of oxygen in the blood to body cells. The hemoglobin of red blood cells serves as the oxygen carrier. To function in this capacity, iron in the hemoglobin molecule must be in the reduced or ferrous state (Fe^{++}). Oxidation of iron to the ferric state (Fe^{+++}) results in the formation of methemoglobin. Methemoglobin is continually produced in normal individuals, but formation is counterbalanced by a rapid reduction process (Figure 1). As a result, less than 1 percent of the total circulating hemoglobin in a healthy adult is present in the form of methemoglobin. The normal methemoglobin concentration in healthy infants is about 2 percent.

Methemoglobin is unable to bind oxygen, and in methemoglobinemia the hemoglobin-methemoglobin equilibrium is disturbed. Methemoglobin

accumulates as a brown pigment in red cells causing anoxemia and cyanosis. (Anoxemia is lack of oxygen supplied to tissues; cyanosis is blueness that may result.) Methemoglobinemia may arise as the result of 1) an inherited enzyme deficiency; 2) a structural defect in the hemoglobin molecule; or 3) a toxic substance which either oxidizes hemoglobin directly or facilitates its oxidation by oxygen (1). The primary health hazard from nitrates relates to their potential for reduction to nitrites (Table 1).

Nitrate in Drinking Water

Methemoglobinemia resulting from high nitrate concentrations in drinking water was first recognized by Hunter Comly in 1945 at the University of Iowa (2). Dr. Comly was a pediatric trainee who sought to understand the cause of cyanosis in two infants referred from rural Iowa. The father of one of the children suggested that cyanosis was due to well water, leading to the analy-

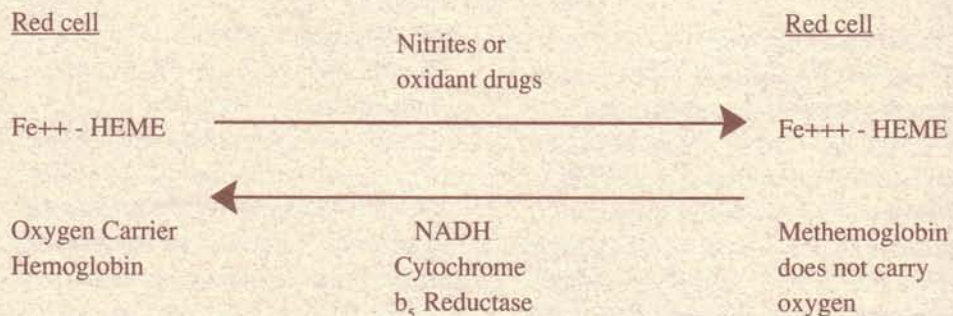


Figure 1. Methemoglobin reduction process.

Table 1. Causes of Toxic Methemoglobinemia

1. Nitrates in well water
2. Nitrates in food
3. Drugs (sulfa drugs, pyridium, quinones)
4. Nitrobenzene (furniture, shoe polish)
5. Aniline dyes (marking ink, colored crayons)
6. Silver nitrate, amyl nitrate, bismuth subnitrate
7. Naphthalene (moth balls)

sis of the water and the discovery of a high concentration of nitrate (3). Drinking water may contain high concentrations of nitrogen salts as the result of pollution by organic materials or inorganic chemical fertilizers. The majority of reported cases have been in infants under the age of four months (4,5) and who are fed milk formulas made with contaminated well water. Since 1945, the testing of water quality has included measurement of the nitrate content, and toxic or fatal methemoglobinemia is uncommon, but still poses a threat to health (6). As Dr. Johnson (6) noted, a recent survey in South Dakota showed that 1/4 of 100 samples of well water which were tested had a nitrate concentration in excess of the permissible limit set by the EPA. Boiling well water is not effective since it merely concentrates the nitrate. Nitrates are usually absorbed before reaching the nitrate-reducing bacteria which reside in the intestinal tract. When nitrates are introduced directly into the colon, methemoglobinemia is readily produced (7). It appears that nitrate is converted to nitrite by intestinal bacteria, and nitrite in fact acts as the oxidizing agent to form methemoglobin in the red cell. Infants are especially susceptible to the action of nitrites because they have a low concentration (about 60 percent of the adult concentration) of the enzyme (Figure 1) which reduces methemoglobin to hemoglobin.

Most cases of methemoglobinemia due to contaminated well water have been associated with nitrate concentrations (as NO_3^-) in excess of 40 ppm. As a result, the U.S. Public Health Service and the World Health Organization have recommended drinking water standards of not greater than 45 ppm (8). Remember, 45 ppm NO_3^- equals 10 ppm $\text{NO}_3\text{-N}$.

One case of *adult* methemoglobinemia due to contaminated water has been reported. The water contained 94 ppm (as $\text{NO}_3\text{-N}$) and was used by the patient in home dialysis. Methemoglobin was identified spectro-photometrically, but was not determined quantitatively.

Sausages and other processed meats have been reported to cause methemoglobinemia (9), as has contaminated fish (10). Preservative used in the preparation of sausage contains nitrites or nitrate salts, and the nitrates may be reduced to nitrites by bacteria or enzymes present in the meat. The U.S. Food and Drug Administration has set maximum allowable nitrate and nitrite concentrations in food at 500 ppm and 200 ppm, respectively as $\text{NO}_3\text{-NO}_2$.

Nitrates in Leafy Vegetables

Leafy vegetables such as spinach, cauliflower, cabbage and beets have relatively high nitrate concentrations, which may be even higher because of fertilization practices. There have been several reports of methemoglobinemia following the consumption of spinach, but the conversion of nitrates to nitrites during storage, rather than the nitrates themselves was responsible for methemoglobinemia (11). Animal studies have suggested that high nitrate-containing vegetables do not induce methemoglobinemia. Furthermore, it has been suggested that other compounds, possibly ascorbic acid, present in leafy vegetables, may provide protection against *in vivo* reduction of nitrates to nitrites (12).

Cases of methemoglobinemia have also been reported as a complication of

Although adults are more resistant to the toxic effects of nitrites than infants, combinations of nitrites and drugs that produce methemoglobin might be more toxic than either agent alone.

silver nitrate therapy for burns (13) and the use of bismuth subnitrate in radiologic procedures (14). More recently, reports of fatal methemoglobinemia have implicated the ingestion or inhalation of "room odorizers" containing isobutyl nitrites (15), and food contaminated with cooling fluid (16). Although adults are more resistant to the toxic effects of nitrites than infants, combinations of nitrites and drugs that produce methemoglobin might be more toxic than either agent alone. Furthermore,

sodium nitrite given to pregnant rats causes methemoglobinemia in the mother, and will cross the placenta to cause methemoglobinemia in the fetus (17). Nevertheless, a computer-based literature search from the National Library of Medicine failed to reveal any papers in the past 10 years in which pregnancy was associated with methemoglobinemia, thus the potential problem of methemoglobinemia in pregnancy does not appear to be of significance in humans.

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Nitrates, Nitrites, N-Nitroso Compounds and Nutrition

Constance Kies and Carolyn Bednar

While nitrates are widespread in many foods and are relatively harmless, they can be potentially harmful when reduced to nitrites and N-nitroso compounds. For those concerned about nitrate levels in the diet, selection of foods low in nitrates, and proper treatment and storage of food can help reduce the risks. Increased nitrate levels in the water supply can have the greatest impact on the total amount of dietary nitrate.

While nitrates, nitrites and N-nitroso compounds are known to be related, that nutrition may also have some involvement is less well recognized. Nitrates are widespread in food products and sometimes in water but are relatively harmless as such to the human (WHO, 1978).

However, nitrates can be reduced under certain conditions to nitrites either in food before being consumed or within the human body. High levels of nitrites, regardless of source, can cause the blood abnormality, methemoglobinemia, and possibly other abnormalities. Nitrites also can react with various nitrogen compounds to form potentially cancer-causing N-nitroso compounds at almost any site within the gastro-intestinal tract (WHO, 1978).

Human Nutrition Involved

Human nutrition becomes involved in the nitrate/nitrite/ N-nitroso compound situation in several ways. These include: a) selection of foods and food patterns with low nitrate contents for those with concerns about high nitrate intake; b) treatment and care of food within the home to reduce the transformation of nitrates to nitrites; and c) delineation of involvement of nutrients in the conversion of nitrates to nitrites to N-nitroso compounds.

Plant products vary in their nitrate content depending upon the plant species, the part of the plant used, amount of nitrate in the soil (either residue or fertilization added), water nitrate levels,

other environmental factors, and agricultural practices (Wolff and Wasserman, 1972; WHO, 1978; Viets and Hageman, 1971; NRC, 1972). Some plant species naturally have a very high nitrate content. However, within the same species, nitrate content varies because of genetic makeup and the aforementioned environmental and agricultural practices.

Weekly intake of nitrate from vegetables for an average person might vary from 30 to 120 mg of nitrate depending on the amount of nitrogen fertilizer used in the field (Greenwood and Hunt, 1986). "Organic" vegetables have not been found to have differing nitrate levels from those grown by conventional methods (Schuster and Lee, 1987).

Nitrate in Food Products

The estimated amounts of nitrate and nitrite contributed by various food groups to the diet of adults in the United States are shown in Table 1. Vegetables contribute by far the greatest amount of gastric nitrite load (72 percent) followed by cured meats (9 percent), baked goods and cereals (7 percent), and fruits and juices (5 percent) (NRC, 1981).

In general, even food products which naturally contain high levels of nitrates contain proportionally much, much lower amounts of nitrites. Nitrates ordinarily found in food products may be changed to nitrites through microbiological action. This can occur in fresh

Table 1. Average Daily Gastric Nitrite Exposure in Adults in the United States Today with Normal Gastric Acidity (mg/person/day)

Source	Dietary Nitrite	Dietary Nitrate	Salivary Nitrite*	Gastric Nitrite	Percent Contribution
Cured meats	0.30	1.2	0.06	0.36	9%
Fresh meat	0.06	0.6	0.03	0.09	2%
Vegetables	0.12	65.0	3.00	3.10	72%
Fruits, juices	0.01	4.3	0.20	0.21	5%
Baked goods and cereals	0.26	1.2	0.06	0.32	7%
Milk and milk products	0.01	0.2	0.01	0.02	1%
Water	0.01	2.0	0.09	0.1	2%
TOTAL	0.77	75.0	3.50	4.2	

Table reprinted, with permission, from National Research Council (1981).

*Calculated by multiplying intake of nitrate by 6.3 mol % (0.05), according to Spiegelhalder et al. (1976) and Stephany and Schuller (1980).

or cooked vegetables which are allowed to stand at room temperature for extended periods of time or during storage of improperly processed food products (Hall and Hicks, 1977; Phillips, 1968). Several incidences of methemoglobinemia have occurred in young infants fed unrefrigerated spinach (WHO, 1978; Keating et al., 1973).

Nitrates and nitrites sometimes are added to cured meat products but in the United States there has been a substantial and continuing decrease both in nitrate-nitrite content of cured meats and per capita cured meat consumption (Hartman, 1982). Nitrites in cured meat products do offer benefits in preventing growth of *Clostridium botulinum*, the toxin which causes the extremely seri-

ous type of food poisoning, botulism (WHO, 1978; Wolff, 1972).

The amounts of nitrates or nitrites actually consumed are in part determined by the level of these substances in the specific foods consumed and in part by the amount and frequency of consumption of these foods (White, 1975). For example, spinach is one food that naturally contains high amounts of nitrates. However, typically, spinach isn't eaten very often by most people or in very large amounts. Hence, for most people foods such as spinach and turnip greens, which naturally have high nitrate contents, do not contribute much nitrate to the diet simply because most people don't eat them very often or in large amounts. However, fresh cabbage

or iceberg lettuce, which contain lower amounts of nitrates than do fresh spinach or turnip greens, probably contribute a fairly large amount of nitrates to the diet of the typical Nebraskan because they are generally well-liked and are eaten frequently by many people.

Water Contains Nitrate

Water is a form of food which is consumed more frequently and in larger amounts than any other food. For this reason, an elevation in the nitrate content of the water supply has a great impact on the total amount of nitrates consumed.

Obviously, when a drinking water supply is found to have a high nitrate content, the most effective approach is to find out why and to eliminate the problem. This isn't always possible. Other approaches include using bottled water or water purification systems. A third approach is to cut down on eating other nitrate foods so as to minimize the total, overall nitrate consumption. In Table 2, nitrate contents of some food products are listed. In Table 3, are some examples of high and low nitrate menus. These figures should be viewed only as estimates, not absolutes, since ranges in nitrate/nitrite content exist for all. Another problem in this approach is that it discourages consumption of many food products which have positive nutritional attributes as well as adding color, taste, and variety to meals.

Food Preparation

Food preparation procedures also have an impact upon the nitrate/nitrite problem (WHO, 1978; Mirvish, 1983; Weisburger, 1986). Obviously, addition of high nitrate or nitrite-containing water to a food product during preparation will increase the nitrate/nitrite content of the final product. Heating of the water either before its addition or as part of the preparation procedure will not reduce the nitrate/nitrite content. Use of minimal level nitrate/nitrite water in the preparation of infant

formulas or foods, as well as low-nitrate food in general, is important since infants are prone to the sometimes fatal blood disorder, methemoglobinemia, caused by a high intake of nitrates/nitrites. Rural families using private well water should take precautions if the nitrate/nitrite level is unknown. Well water may have elevated nitrate levels due to fertilizer run-off or contamination from a nearby feedlot or barnyard.

Since methemoglobinemia is caused by nitrites, rather than nitrates, conversion of nitrates to nitrites in food preparation procedures should be avoided. Do not allow fresh vegetables to stand at room temperature for extended periods of time after being harvested. For this reason "fresh" vegetables purchased in grocery stores are usually higher in nitrite content than are their frozen or canned counterparts. The latter are usually quickly processed following harvest allowing less time for conversion of nitrates to nitrites.

Cooking or canning tends to lower nitrate levels in vegetables, since the nitrate leaches into the cooking liquid (Schuster and Lee, 1987; Abo Bakr, 1985; Phillips, 1968). Cooking losses of nitrates were 79 percent for spinach, 34 percent for beans, 16 percent for peas and 51 percent for carrots (Abo Bakr, 1985). Research comparing nitrate levels in commercially and some home processed vegetables suggests that the amount of water used in processing affects the nitrate content of the end vegetable product (Bednar and Kies, 1989). Discarding the cooking liquid of high-nitrate vegetables would lower nitrate content of the diet, but some other water-soluble nutrients including vitamin C also would be lost. Conventional home canning and freezing practices will minimize nitrate/nitrite conversion by eliminating or limiting the microbial action responsible for the change.

Lack of Oxygen

Methemoglobinemia is caused by the reaction of nitrites with the hemoglobin

Table 2. Nitrate Contents of Selected Vegetables*

Food	Nitrate Content mg/100 g food	Food	Nitrate Content mg/100 g food
Artichoke (frozen)	1.2	Mustard greens (canned)	136.0
Asparagus (canned)	0.3	Mustard greens (frozen)	239.0
Asparagus (fresh)	2.1	Okra (frozen)	7.4
Asparagus (frozen)	1.6	Okra (canned)	0.2
Beans (dry)	1.3	Onions (fresh)	13.4
Beans, green (canned)	10.0	Onions (chopped frozen)	3.3
Beans, green (frozen)	27.0	Onions (whole frozen)	12.8
Beans, lima (fresh)	5.4	Peas (fresh)	2.8
Beans, lima (frozen)	2.7	Peas, green (frozen)	2.0
Beans, snap (fresh)	25.3	Peas, green (canned)	0.6
Beets (canned)	145.0	Pea pods, Chinese (frozen)	1.3
Beets (fresh)	301.0	Peas, blackeyed (frozen)	0.9
Broccoli (fresh)	78.3	Peppers, sweet green (canned)	6.2
Broccoli, spears (frozen)	46.4	Peppers, sweet (frozen)	5.0
Broccoli, chopped (frozen)	57.3	Pickles	5.9
Brussel sprouts (frozen)	8.4	Potatoes (fresh)	11.9
Cabbage (fresh)	78.4	Potatoes, hash browns (frozen)	3.7
Carrots (canned)	20.5	Potatoes, small whole (frozen)	15.0
Carrots (fresh)	7.2	Potatoes, whole (canned)	6.3
Carrots (frozen)	9.7	Potatoes, sliced (canned)	6.9
Cauliflower (fresh)	54.7	Radishes (fresh)	240.0
Cauliflower (frozen)	25.4	Pumpkin (fresh)	41.3
Celery (fresh)	234.0	Salad, mixed (fresh)	81.9
Collard greens (canned)	264.0	Sauerkraut (fresh)	19.1
Collard greens (frozen)	245.0	Sauerkraut (canned)	6.8
Corn (frozen)	4.5	Spinach (canned)	57.3
Corn (fresh)	4.5	Spinach (canned)	222.0
Cucumbers (fresh)	2.4	Spinach (frozen)	214.0
Eggplant (fresh)	30.2	Squash, acorn (fresh)	3.4
Endive (fresh)	66.3	Squash, butternut (fresh)	67.8
Kale (canned)	277.0	Squash, zucchini (fresh)	66.5
Kale (frozen)	160.0	Squash, zucchini (frozen)	53.3
Lettuce, iceberg (fresh)	110.0	Squash (frozen)	16.0
Lettuce, romaine (fresh)	140.0	Sweet peppers (fresh)	12.5
Melons (fresh)	43.3	Sweet potatoes (fresh)	5.3
Mushrooms (fresh)	6.3	Tomatoes (fresh)	6.2
Mushrooms (whole canned)	1.7	Turnip greens (frozen)	346.0
Mushrooms (sliced canned)	0.6	Turnip greens (canned)	223.0

*Values given were converted from values reported by McNamara et al. (1971), White (1975) and Siciliano (1975). All values are mean values, which in some cases, represent considerable ranges. Since analyses were done by different laboratories at different times on different samples, values should be considered more relative than absolute.

Table 3. Examples of High and Low Nitrate Meals*

High Nitrate Meals	Low Nitrate Meals
Example 1	Example 1
Spinach salad	Cucumber salad
Sliced cold ham	Sliced pork
Whole wheat bread & butter	Whole wheat bread & butter
Ice cream	Ice cream
Milk	Milk
Example 2	Example 2
French fried potatoes	French fried potatoes
Frankfurter on bun	Ground beef patty on bun
Celery and radishes	Pickles
Melon slice	Peaches
Lettuce salad	Tomato salad
Milk	Milk
Example 3	Example 3
Beet salad	Pea salad
Knotwurst and turnip greens	Pork chops
Boiled potatoes	Boiled potatoes
Apple Pie	Apple Pie
Milk	Milk

*Some high nitrate containing foods may contain appreciable amounts of protective factors such as vitamin C and fiber.

in red blood cells to form methemoglobin, which lacks the oxygen-carrying ability of normal hemoglobin (WHO, 1978; Lukens, 1987; Grant, 1981). This means that in methemoglobinemia, the blood lacks the ability to carry sufficient oxygen to individual cells of the body. Most *adult* humans have the ability to rapidly convert methemoglobin back to oxyhemoglobin; hence, the total amount of methemoglobin within red blood cells remains low in spite of relatively high levels of nitrate/nitrite intake. In *young infants*, enzyme systems for reducing methemoglobin to oxyhemoglobin are incompletely developed; hence, methemoglobin within blood cells can build up with excessive nitrite

intake and methemoglobinemia can occur. In a 1978 survey of Nebraska physicians, doctors reported having seen 15 infants with suspected nitrate-induced methemoglobinemia (Grant, 1981). Most cases of infant methemoglobinemia occur when infant formula and other infant foods are prepared with nitrate-contaminated water (Johnson et al., 1987). This also may happen in *older* individuals who have genetically impaired enzyme systems for the reduction of methemoglobin.

Nitrates in the diet may be converted to nitrites in the mouth, and in the small and the large intestines. This also may occur in the stomach if the contents are insufficiently acidic (Tannenbaum et al.,

Most cases of infant methemoglobinemia occur when infant formula and other infant foods are prepared with nitrate-contaminated water.

1976; Reddy and Cohen, 1986; WHO, 1978). Typically, the stomach contents of the infant are less acidic than are those of the adult, which suggests another reason for greater susceptibility of the infant to the dangers of high nitrate content. Both nitrates and nitrites may be absorbed into the body. Nitrates and nitrites which are absorbed may be excreted in the urine. About 25 percent of ingested nitrates are recycled through the saliva where microbial action in the mouth changes a portion to nitrites, and it passes into the gastrointestinal system (Mirvish, 1983). Thus, saliva is the major source of nitrites to the human, but this nitrite is simply dietary nitrate that is being recycled. According to several researchers, endogenous synthesis of nitrate also occurs in the human body (Green et al., 1981; Wagner et al., 1983; Lee et al., 1986; Hotchkiss, 1988). Nitrite consumed in foods such as cured meat may be metabolized and excreted from the human body as nitrate (Lee et al., 1986).

The effect of absorbed nitrate/nitrite content is unresolved (WHO, 1978). Animal studies suggest that this transfer is relatively low; however, there is considerable variability among animal species. Thus, the question of degree of risk of pregnant women or nursing mothers consuming high nitrate water/diets is unknown. Since most parents or future parents do not favor assuming unknown risks for their children, nursing mothers and pregnant women are generally included on lists of individuals who should avoid high nitrate water.

Carcinogenic Compounds

Nitrates and nitrites which are not absorbed or which are recycled back into the gastrointestinal tract may undergo further transformation with amines or amides to form nitrosamines or nitrosamides (N-nitroso compounds). N-nitroso compounds are also found in small amounts in food and water; hence, may be directly consumed. The Food and Drug Administration has been

active in reducing nitrosamine levels in bacon, malt and beer, and has monitored other foods for nitrosamine content (Havery and Fazio, 1985). Most cured meats when fried contain only minute amounts of nitrosamines in the edible portion (Sen et al., 1979). However, higher amounts of both volatile and nonvolatile nitrosamines have been detected in fried bacon and fried out bacon fat (Sen and Seaman, 1985; Hotchkiss et al., 1985). Since the fried out bacon fat may contain several times more nitrosamines than the edible portion of bacon, the use of bacon fat for frying or seasoning other foods is not advisable. Alpha-tocopherol has proved to be the most effective inhibitor of nitrosamine formation in bacon since it is fat-soluble, stable upon storage and reacts with nitrite only during the frying of bacon (Sen, 1986). These N-nitroso compounds may be absorbed into the body. The breakdown products of N-nitroso compounds or the N-nitroso compounds themselves are, for the most part, quickly removed from the body either in the urine or expired into the air (WHO, 1978). However, a high proportion of N-nitroso compounds have been shown to be carcinogens. The organ affected seems to be related to species, specific N-nitroso compound tested, level of dosage, and length of time of exposure.

Implications of the importance of N-nitroso compounds in the incidence of human cancer have not been fully defined. In animal studies designed to determine whether or not a substance can cause cancer, proportionally much higher levels of the test substance are fed than are realistically found in human diets. This is done in part because certain individuals within a human population may be far more susceptible to cancer triggering agents than are others. While this technique is very useful and is scientifically sound, it sometimes causes another problem, that of over-concern.

Epidemiological studies have shown a correlation between gastric cancer death

Since the fried out bacon fat may contain several times more nitrosamines than the edible portion of bacon, the use of bacon fat for frying or seasoning other foods is not advisable.

rates and estimated nitrate consumption from food and water in some countries (Lu et al., 1986; Dutt et al., 1987; Tannenbaum et al., 1979; Cuello et al., 1976; Mirvish, 1983). The diet of populations at high risk for this type of cancer is also usually deficient in fresh fruits and vegetables (Mirvish, 1983). In the United States, however, gastric cancer rates are low and have declined over the last 50 years. A recent statistical analysis comparing levels of contaminants in drinking water of Nebraska communities with death rates from various diseases showed no relationship between nitrate levels and cancer (Bednar and Kies, 1988).

Protective Effect of Vegetables and Fruits

The apparent protective effect of fruits and vegetables in the diet may be related to their content of vitamin C and vitamin E. In both animal and human experiments, ascorbate and alpha-tocopherol have been shown to inhibit the in vivo formation of N-nitroso compounds from nitrite (Mirvish, 1983; Lu et al., 1986; Wagner et al., 1985; Kamm, 1977). Polyphenols which are found in tea, coffee, vegetables and fruits also have been shown to inhibit formation of N-nitroso compounds (Mirvish, 1983). An epidemiological study in China found that the mortality rate from gastric cancer was considerably lower among people who habitually consumed garlic in comparison to those who seldom ate garlic (Liu, 1988). Beta-carotene or vitamin A is another component of fruits and vegetables that may possibly contribute to this protective effect.

These results imply that individuals consuming marginal or inadequate amounts of fruits and vegetables might be particularly susceptible to nitrate/nitrite hazards. Nitrate/nitrite toxic-prone individuals, including those with low stomach acidity such as young infants or individuals receiving selected medications, might also receive some protection by addition of vitamins C and E to the diet.

Other reports suggest that increases in dietary fiber offer a protection against possible carcinogenic effects of nitrosamines by acting as a dilution agent since fecal bulk is increased, decreasing time exposure of intestinal surface to carcinogens by decreasing fecal transit time, or by surface absorption of carcinogen on fiber materials (Burkitt et al., 1971; Kies et al., 1978).

Nutrition Can Help

In conclusion, for individuals living with a high nitrate water problem, nutrition cannot be expected to completely overcome the difficult situation. Young infants, pregnant and nursing women are groups of particular concern.

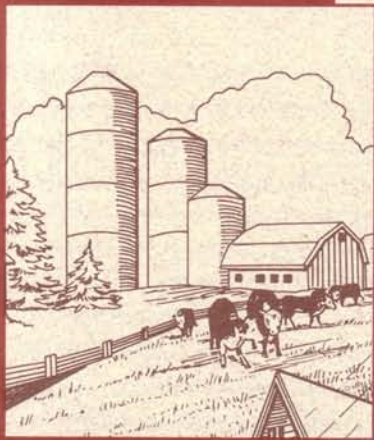
Of more practical concern to the consumer relative to the nitrate/nitrite problem are food selection and preparation procedures within the home. Hazards associated with high nitrogen fertilization or use of high nitrate water for home gardens, consumption of high nitrate/nitrite foods or possible conversion of nitrates to nitrites in high nitrate-containing vegetables due to improper food handling are situations with which the consumer should be aware.

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Excessive Nitrate/Nitrite Exposure: Nitrate Poisoning and Related Animal Health Effects

Norman R. Schneider, Alex Hogg and Robert A. Britton

Many domestic animals, especially ruminants, are susceptible to nitrate/nitrite poisoning. The most common cause is consumption of nitrate-accumulating plants by animals not accustomed to high dietary amounts of nitrate. Contaminated well water is rarely the sole cause of excessive nitrate exposure in livestock. The risk of nitrate/nitrite poisoning can be reduced by mixing high nitrate feed with low nitrate feed to reduce overall dietary nitrate intake, and by slowly adapting livestock to higher nitrate concentrations while providing additional energy in the diet.

Nitrate (NO_3^-) and nitrite (NO_2^-) are potential poisons which have become increasingly important environmental chemicals, and are appropriately discussed together because of their similarity. Nitrite is 10 times more toxic than nitrate. Many species of animals are susceptible to nitrate/nitrite poisoning, but cattle are most frequently affected. Ruminants in general are especially vulnerable to poisoning by nitrate/nitrite because of the ability of rumen bacteria to change nitrate to nitrite. Rumen bacteria convert nitrate to ammonia, with nitrite as an intermediate product. Some experts suggest cattle may be more susceptible to nitrate poisoning than are sheep; this may be due either to cattle's ability to convert nitrate to nitrite in the rumen or to the greater ability of sheep to convert nitrite to ammonia. Goats (especially Angora goats) may be more susceptible to nitrate poisoning than either sheep or cattle.

The large intestine of horses, mules and donkeys may serve as a site for bacterial nitrate reduction and nitrite production, but not to the same extent as ruminants. Young pigs and human infants also have gastrointestinal bacteria capable of reducing nitrate to nitrite, but mature single-stomach animals (except horses) are more resistant to nitrate toxicosis because this ability is age limited.

Acute poisoning due to nitrite in animals is primarily by methemoglobin (MHb) formation in blood with resultant

lack of oxygen. Possible secondary effects are due to blood vessels becoming dilated by nitrite; these effects are reportedly more important in producing poisoning in sheep than are the effects from MHb formation. Nitrite is involved in other processes in the body besides MHb formation, and may result in the alteration of certain protein enzymes. Another acute effect involved in exposure is that nitrates may have a direct irritant action on the lining of the digestive tract, causing abdominal pain and diarrhea.

Subacute or chronic effects and related problems from nitrates and nitrites have been reported. Results of some studies have been interpreted as evidence that nitrate/nitrite poisoning may result in poor growth rates, reduced milk production, vitamin A deficiency, minor transitory effects on the thyroid gland and increased susceptibility to infections. Excessive nitrate in the diet often has been associated with abortions late in pregnancy and other health problems in cattle and other livestock. Many published observations resulted from field investigations that lacked proper controls, but contradictory results have been reported by other researchers on the basis of experimental studies.

A current theory in nitrate-induced abortions in cattle is that nitrite produced may cause a rapid decrease in oxygen transfer across the placenta to the fetus. Any nitrite that does not immediately react with maternal hemoglobin readily passes through the

Nitrate/nitrite poisoning occurs most commonly in domestic animals not accustomed to eating nitrate/nitrite-containing plants, but accidental exposure to or consumption of fertilizer or other chemicals may serve as an occasional source of excessive nitrate exposure in animals.

placenta and can produce fetal MHb, but decreased oxygen supply to the fetus is due primarily to MHb in maternal blood rather than excess fetal MHb. Fetal death and spontaneous abortion or still births can result if maternal oxygen transfer to fetal blood decreases too rapidly or for a prolonged period of time, especially during the last third of pregnancy. Excessive nitrate/nitrite thus may be at least a contributing factor in cattle abortions or stillborn calves. Excessive nitrate in the diet also may reduce effective copper use in cattle and contribute to the development of a disorder sometimes called the "alert downer cow syndrome." Beef breeds are most commonly involved. Affected cattle often are additionally stressed by cold weather, prolonged inadequate nutritional diet and late pregnancy, and also show evidence of low blood calcium, low blood magnesium and selenium/vitamin E deficiency. Sudden collapse and death can result.

Causes of Nitrate/Nitrite Poisoning

Animals may be exposed to nitrite and nitrate from both man-made and natural sources. Nitrites and/or nitrates, for example, often are added to pickling and curing brines for preserving meats, contained in certain machine oils and antirust tablets, used in the preparation of gunpowder and explosives, and used in medicines for various disease conditions (such as cyanide poisoning).

Nitrate/nitrite poisoning occurs most commonly in domestic animals not accustomed to eating nitrate-containing plants, but accidental exposure to or consumption of fertilizer or other chemicals may serve as an occasional source of excessive nitrate exposure in animals. Although nitrate concentrations are steadily increasing in ground water on a national basis, nitrate-containing well water is rarely the sole cause of excessive nitrate exposure in livestock.

All plants contain some nitrate, but excessively high amounts are likely to occur in forages grown under stress conditions such as shading or low light

intensity, hot and dry weather, herbicide applications and plant diseases. Anything that stunts growth will increase nitrate accumulation in the lower part of the plant. Nitrate amount in plants also will depend on soil type, specific plant part, stage of maturity, extent of nitrogen fertilization and plant species.

Crops which readily concentrate nitrate include cereal grasses (especially oats, millet and rye), corn and sorghum. Weeds commonly found to have high nitrate concentrations are pigweed, lamb's quarter, thistles, Jimson weed, sunflower, fireweed (kochia), smartweed, dock, and Johnson grass. Anhydrous ammonia and nitrate fertilizers tend to increase nitrate content in forage because the supply of nitrate is more readily available. Of course, soils naturally high in nitrogen will enhance the potential for growing plants to also contain high amounts of nitrate. Any plant type, even pasture grasses, can contain excessive nitrate if grown on heavily fertilized soil.

Excessive nitrate uptake in plants is generally associated with damp weather conditions and cooler temperatures (55° F), although high concentrations are likely to develop when growth is rapid during hot, humid weather. Drought conditions, however, particularly when plants are immature, may leave the vegetation with high nitrate content; plants are unable to utilize crude nitrogenous material present as food because root uptake systems are not affected while absorption pathways are, and this material accumulates as nitrate. Soils with a low pH favor nitrate absorption. Low amounts of molybdenum, sulfur or phosphorus in soil tend to increase nitrate uptake, whereas soils deficient in copper, cobalt or manganese tend to have the opposite effect. Decreased light, cloudy weather and shading associated with crowding conditions also can cause increased concentrations of nitrates within plants.

Some systemic herbicides, such as 2,4-D and 2,4,5-T, cause elevated nitrate concentrations in early stages of

stimulated abnormal plant growth and result in a high nitrate residual (10-30 percent) in surviving plants, which are lush and eaten with apparent relish (such as Jimson weed) even though previously avoided.

Nitrates do not selectively accumulate in the fruits or grain of plants, but are found instead in the vegetative parts, especially the lower stalk. Nitrate in plants can be converted to nitrite under the proper conditions of moisture, heat and microbial activity after forage is harvested.

Water from both surface and underground sources in most areas of the United States may contain potentially hazardous concentrations of nitrate, and some of the highest incidences of nitrate contamination in ground water relate to the Great Plains and Midwest, where intense agricultural activity and heavy nitrogen fertilizer application are commonplace. Deep wells are not as likely to contain high nitrate concentrations as are shallow wells or surface waters. High nitrate waters with high coliform bacteria contamination have greater potential to cause adverse health effects and lowered productivity in animals than do either nitrate or bacteria alone. Livestock losses have occurred during very cold weather due to the concentrating effect of freezing that increased nitrate content of remaining water in stock tanks. Nitrate concentrations considered safe in total diets of livestock reflect both forage and water contributions.

Clinical Findings

In acute nitrate/nitrite poisoning, nitrite in contact with red blood cells reacts with hemoglobin to form MHb. Methemoglobin is not capable of transporting oxygen, causing lack of oxygen in vital tissues. Nitrite also dilates blood vessels. Signs of nitrite poisoning appear suddenly due to decreased supply of oxygen to tissues and low blood pressure resulting from dilated blood vessels. Nitrate/nitrite poisoning becomes apparent when MHb

concentrations reach 20-30 percent of total hemoglobin, and death from lack of oxygen may occur when methemoglobinemia exceeds 75 percent. Any normal animal not severely anemic can usually tolerate a 50 percent methemoglobinemia.

Rapid, weak heartbeat, subnormal body temperature, muscular tremors, weakness and staggering are early signs of poisoning. Brown mucous membranes develop rapidly; this change may be easily seen in the unpigmented lining of female reproductive organs. Rapid, difficult breathing, anxiety and frequent urination are commonly observed. Exercised animals are more likely to show problems with breathing. In some single-stomach animals, the direct irritant action of nitrate may cause salivation, vomiting, diarrhea, abdominal pain and hemorrhage; however, these signs are usually associated with excessive nitrate exposure from non-plant sources.

Affected animals may die suddenly without appearing ill, after convulsions within an hour after ingestion of a lethal amount of nitrate, or after a course of 12 to 24 hours or longer. Under certain conditions, adverse effects of excessive nitrate exposure may not be apparent until animals have eaten nitrate-containing forages for days to weeks. Some affected animals develop temporary lung damage as the result of prolonged gasping for air, but most of these recovering animals have normal lung function with no residual effects within 10-14 days. Pregnant animals surviving an acute episode may abort in 24-72 hours.

Lesions

Blood containing MHb usually has a chocolate-brown color, although dark red hues of other forms of hemoglobin also may be observed. Congestion or hemorrhage on surfaces of internal organs may be observed. Dark brown discoloration in terminal or recently dead animals is not absolute evidence of nitrate poisoning, however, and must

Rapid, weak heartbeat, subnormal body temperature, muscular tremors, weakness and staggering are early signs of poisoning.

be differentiated from other MHB producing chemicals, such as chlorate.

Diagnosis

Excessive nitrate exposure in domestic animals, especially livestock, may be evaluated through laboratory analysis for nitrite and nitrate in specimens from either live or dead animals. Plasma from unclotted blood is the preferred specimen from live animals, but serum from a clotted blood sample is acceptable. Additional recommended specimens from dead animals where poisoning or abortion is being investigated include fluids from the eye, fetal pleural or thoracic cavities, fetal stomach content, maternal uterine fluid and urine. All specimens are best kept refrigerated or frozen in clean plastic or glass containers prior to submitting to a laboratory for analysis. The amount of nitrate found in rumen content *is not* representative of concentrations of nitrate in the diet; therefore, collection and evaluation of rumen contents is not recommended. Also, blood MHB determination alone is not a reliable indicator of excessive nitrate/nitrite exposure because MHB is unstable and must be analyzed soon after blood is collected; immediate access to a laboratory is often unavailable.

Field tests for nitrate include diphenylamine blue (1 percent DPB in concentrated sulfuric acid) and nitrate dipsticks (nitrate test strips, EM Science, Gibbstown, NJ). The DPB test is more suitable to determine presence or absence of nitrate in suspected forages; apply a drop or two on a cross-section of plant stalk material, then note any dark blue color change as an indicator of excessive nitrate content in the sample checked. Actual nitrate concentrations are difficult to predict with DPB test results. Nitrate dipsticks are used primarily for testing water supplies. The dipstick method is rapid and gives indications of both nitrite and nitrate concentrations over a relatively wide range. Field tests are presumptive and should be confirmed by standard

analytical methods at a recognized laboratory.

Treatment

Contact your veterinarian immediately. The specific antidote for nitrate/nitrite poisoning is methylene blue, given intravenously. The decision to use this antidote, the proper dosage selected and the actual administration should be accomplished by a qualified veterinarian. Pumping cold water and antibiotics into the rumen may serve as an aid to stop the continuing bacterial production of nitrite. Trace mineral supplements and a balanced diet may help prevent nutritional/ metabolic disorders associated with long term excessive dietary nitrate consumption. Always consult a veterinarian with regard to the best treatment for livestock health effects associated with nitrate poisoning or excessive nitrate/nitrite exposure.

Control

Feed/forage with nitrate concentrations in excess of 2250 ppm $\text{NO}_3\text{-N}$ (10,000 ppm $\text{NO}_3\text{-}$) have a high risk of causing acute nitrate poisoning in ruminants and possibly horses. Diets of pregnant beef cows should not exceed 1125 ppm $\text{NO}_3\text{-N}$ (5,000 ppm $\text{NO}_3\text{-}$). High nitrate feed may be appropriately mixed with low nitrate feed to achieve a safe diet.

Grazing animals may adapt to higher nitrate content in feeds to reduce risk, especially in pasturing summer annuals such as sorghum-sudan hybrids. Feeding grain with high nitrate forages may provide additional energy to convert nitrate protein in the rumen and reduce nitrite production that would more likely occur with roughage alone. Most producers could supplement grain while adapting cattle to high nitrate forages. Multiple small feedings rather than one large feeding increases the total amount of nitrate that can be consumed daily by livestock without adverse effects and helps animals adapt.

High nitrate forages may also be harvested and stored as ensilage rather

than dried hay or greenchop. Up to half the nitrate content in forages may be lost during the ensiling process. Since higher nitrate concentrations in plants are found in the lower stalk, raising cutter heads of machinery during harvesting operations will selectively leave the more hazardous stalk bases in the field.

Hay with high nitrate appears to be more hazardous than fresh greenchop or pasture with similar nitrate content. High nitrate forages that have been greenchopped should not be stockpiled long enough to heat by composting prior to feeding, since heating could assist bacterial conversion of nitrate present to nitrite and make an even more hazardous feed source. Avoid feeding high nitrate hay, straw or fodder that has been damp or wet for several days for the same reason. Large round bales with excessive nitrate are especially potentially dangerous if stored outside; rain or snow can leach and concentrate most of the total nitrate present into the lower third of the bales.

Avoid livestock water supplies containing over 35 ppm $\text{NO}_3\text{-N}$ (~ 150 ppm NO_3^-), even though health effects in animals are usually associated with concentrations greater than 100 ppm

$\text{NO}_3\text{-N}$ (450 ppm NO_3^-). Acute poisoning may be expected when water sources contain nitrate in excess of 225 ppm $\text{NO}_3\text{-N}$ (~ 1,000 ppm NO_3^-). Livestock water transported in improperly cleaned liquid fertilizer tanks can be extremely high in nitrate, and this practice should be carefully monitored. Young unweaned livestock can be more sensitive to nitrate in water, but do derive much of their fluid intake from nursing. Nitrate is not secreted significantly in milk, but is excreted extensively in the urine. Water sources for young livestock should contain less than 35 ppm $\text{NO}_3\text{-N}$ (~ 150 ppm NO_3^-).

Several units of concentration for nitrite and nitrate are used in scientific literature and laboratory reports. This practice has caused confusion at times. Certain scientific disciplines prefer reporting nitrate concentrations as percent KNO_3 , others as ppm $\text{NO}_3\text{-N}$ or ppm NO_3^- . A table of conversion factors is provided to expedite conversion between various units of concentration. To use, multiply the current unit of concentration by the appropriate factor to find the desired unit of concentration, i.e. ppm $\text{NO}_3\text{-N}$ x 4.426 = ppm NO_3^- .

Conversion Factors For Units of Nitrate/Nitrite
(1% = 10,000 ppm)

FROM to	$\text{NO}_3\text{-N}$	NO_3	KNO_3	$\text{NO}_2\text{-N}$	NO_2
$\text{NO}_3\text{-N}$	1.000	0.226	0.139	1.000	0.305
NO_3	4.426	1.000	0.613	4.426	1.348
KNO_3	7.217	1.631	1.000	7.217	2.198
$\text{NO}_2\text{-N}$	1.000	0.226	0.139	1.000	0.305
NO_2	3.284	0.742	0.455	3.284	1.000

Find current unit of concentration on top row. Find desired unit of concentration at left column. Obtain conversion factor at intersection of row and column. Desired concentration = current concentration x conversion factor.

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Nitrates and Ground Water Quality Protection Policies

J. David Aiken

While federal law requires communities to provide safe drinking water to their residents, federal law does not regulate a major cause of rural ground water contamination—the over-application of fertilizer and irrigation water. Pesticide and fertilizer applications may be regulated in special ground water quality protection areas and in ground water management areas to protect ground water quality. Regulation of fertilizer use in Nebraska is likely to increase significantly in the next five years.

Author's note: Public policies related to fertilizer and pesticide use and ground water quality protection are developing rapidly. Some of the programs described in this report are likely to change in coming years. To obtain the latest information regarding agricultural chemical use regulations, contact your Extension office or officials of any of the agencies discussed in this report.

One of the most important policy issues facing Nebraska is reducing and preventing ground water contamination from agrichemical use. When soluble agricultural chemicals, such as commercial fertilizer, are applied to farmland and/or crops, some of the chemical may leach into ground water supplies as the result of rainfall or irrigation. It may take decades before agrichemical use results in significant ground water contamination.

Similarly, it will take decades to slow or stop nitrate contamination from commercial fertilizer use.

While federal law requires public water suppliers to deliver safe drinking water to customers, it does not regulate the sources of drinking water contamination. There are, however, a variety of existing and proposed state and federal ground water quality protection programs relating to nitrate contamination of ground water. Two state programs

already attempt, through chemical use best management practices, to slow or prevent fertilizers from reaching ground water supplies. The federal Environmental Protection Agency will likely restrict the use of pesticides contaminating drinking water, although this program will not initially apply to fertilizers. The 1990 Farm Bill establishes financial incentives to implement agrichemical best management practices. Long-term prospects for agrichemical pollution control include reducing agrichemical use and improved water treatment to remove chemicals from drinking water. Increased state spending is needed to deal with the ground water quality issue, and a potential source of funding is a tax on agrichemicals.

Safe Drinking Water Act

In 1974 Congress enacted the Safe Drinking Water Act (SDWA) to ensure that water delivered by public water suppliers (such as municipalities or rural water districts) is safe to drink.¹ In Nebraska the SDWA is administered by the Department of Health (DOH). The SDWA specifies minimum quality standards for drinking water but does not regulate the sources of pollution—such as fertilizer use—although the new wellhead protection program has this as its objective. The SDWA also does not

¹A public water supplier subject to SDWA regulation must have at least 15 service connections or regularly serve at least 25 people. Public water suppliers include community and noncommunity systems. Noncommunity systems include self-supplied school districts, restaurants, motels, and rural districts.

apply to private drinking water wells, such as wells on farmsteads and rural acreages.

Under the SDWA, the U.S. Environmental Protection Agency (EPA) establishes drinking water quality standards that public water suppliers must meet. The standards, referred to as maximum contaminant levels (MCLs), are established after lengthy tests estimating the short- and long-term human health effects of ingesting the contaminant. MCLs have been established for only a relatively few contaminants because of the complexity of testing involved.

A major difficulty with establishing MCLs is the high degree of uncertainty involved in estimating the long-term human health effects of ingesting chemicals where there is little or no direct evidence of those health effects. The 10 parts-per-million (ppm) nitrate-nitrogen MCL is somewhat controversial because it is based on protecting infants from methemoglobinemia, a disease that prevents an infant's blood from carrying oxygen. The long-term health risks to older children or adults of drinking high-nitrate water are not known, and may not be known for decades. Some agricultural groups have sought to have EPA increase the nitrate-nitrogen MCL, but EPA has recently reaffirmed the 10 ppm MCL. Thus the 10 ppm nitrate-nitrogen MCL will be a major factor in Nebraska water quality policies in the foreseeable future.

MCLs are enforced through regular monitoring of public water supplies. If a sample indicates that an MCL has been exceeded, and a violation of the MCL is confirmed, DOH will put the public water supplier on a compliance schedule to deliver to customers water meeting drinking water standards. Dozens of rural Nebraska communities have violated the nitrate-nitrogen MCL. Alternatives to begin supplying water meeting drinking water standards include:

- installing a new water well yielding low-nitrate water, if low-nitrate water can be found;

- blending low-nitrate water from a new well with nitrate-contaminated water from existing wells to ensure that water meeting drinking water standards is delivered to customers;

- installing advanced water treatment to remove nitrates (or pesticides) from drinking water; or

- connecting the water system violating the nitrate standard to another public water system with low-nitrate water.

Each alternative is expensive, typically costing hundreds of thousands of dollars. Meeting these requirements will test the financial resources of rural communities already feeling financial stress. If water delivered through a public water supply system is in violation of the nitrate-nitrogen MCL, the situation must be remedied before the nitrate level reaches 20 ppm. The public water supplier must notify its customers of the MCL violation, and must supply bottled water to families with infants or pregnant women until it can supply water meeting the 10 ppm nitrate-nitrogen drinking water standard.

Point Sources of Water Pollution

Most "point" sources of pollution (such as factory discharges, feedlots, leaky chemical storage tanks, landfills, and chemigation) are already regulated by the Nebraska Department of Environmental Control (DEC).

Chemigation. The chemigation program is a new program specifically designed to prevent fertilizers and other agrichemicals from polluting ground water supplies. Chemigation refers to applying fertilizers and pesticides through an irrigation system by adding the chemicals directly to the irrigation water. Chemigation poses the risk that agrichemicals may be siphoned down the irrigation well if the well pump stops. In order to chemigate in Nebraska, two major requirements must be met:

- the chemigator must be certified by DEC by completing a training program and passing a written exam, and

A major difficulty with establishing MCLs is the high degree of uncertainty involved in estimating the long-term human health effects of ingesting chemicals where there is little or no direct evidence of those health effects.

- the chemigation system must be inspected by the local Natural Resources District to ensure that proper safety equipment has been installed to prevent fertilizers and pesticides from siphoning into ground water supplies.

Nonpoint Sources of Water Pollution

While most "point" sources of ground water contamination have been regulated by DEC, most "nonpoint" sources, such as agrichemical use, traditionally have not been. However, agrichemical use may now be regulated in special ground water quality protection areas and ground water management areas. Dozens of Nebraska communities have violated the nitrate MCL, largely because of agrichemical use in farming, and more will do so in the future. Reducing pollution from agrichemical use may slow this trend. Regulating agrichemical use will not stop ground water contamination, however, because fertilizers applied years ago are still gradually being leached into ground water supplies. Even if fertilizer use were prohibited, it might be decades before nitrate levels in ground water stopped increasing.

Special Ground Water Quality Protection Areas

Fertilizer use is likely to be regulated in coming years to prevent or limit ground water contamination. Agrichemical use regulations may be established by Natural Resources Districts (NRDs) if DEC designates a special ground water quality protection area (SPA). Possible SPA agrichemical-use regulations include:

- training programs in proper agrichemical use;
- voluntary irrigation and agrichemical scheduling programs, to insure that irrigation water and chemicals are applied only when needed and only in the amounts needed;
- requiring that nitrate already available in soil and irrigation water be recognized in making fertilizer application decisions;

- prohibiting fall fertilization for spring-planted crops;
- requiring the use of nitrogen inhibitors;
- establishing mandatory agrichemical best management practices (BMPs), such as irrigation and agrichemical application scheduling; and
- limiting the amount of specific fertilizers (and pesticides) applied.

An NRD cannot prohibit fertilizer (or pesticide) use in an SPA. However, despite widespread nitrate contamination in Nebraska, only one SPA has been designated by DEC in the first four years of the SPA program. This primarily reflects the low level of state funding for SPA program implementation.

Ground Water Management Areas

Regulations similar to SPA regulations may be established by NRDs in ground water management areas (GWMAs) where the NRD first prepares a ground water management plan describing the effect of the proposed regulations on ground water quality. The Central Platte NRD (CPNRD) has already restricted fall fertilizer application and established voluntary fertilizer BMPs in Nebraska's first regulatory GWMA. The CPNRD fertilizer-use restrictions are an important regulatory precedent in Nebraska.

The CPNRD is located in the intensively-irrigated central reach of the Platte River valley. Soil and water tests from NRD test plots indicate that an average of 128 pounds of nitrate-nitrogen per acre are already available from soil and irrigation water within the NRD, approximately 55 percent of the commercial fertilizer needed to grow corn.

Phase I. The CPNRD agrichemical regulations vary depending on the severity of nitrate contamination. In Phase I areas (average nitrate-nitrogen levels 0-12.5 ppm), application of commercial fertilizers is prohibited on sandy soils before March 1. Farmers are also encouraged to test soil and irrigation water for nitrogen levels

Long-term prospects for agrichemical pollution control include reducing agrichemical use and improved water treatment to remove chemicals from drinking water.

to make better fertilizer use decisions.

Phase II. In Phase II areas (average nitrate-nitrogen levels 12.6-20 ppm), application of commercial fertilizers is prohibited on sandy soils before March 1. Application on heavier soils is allowed after November 1, but only if an approved nitrogen inhibitor is also used. In addition, farmers must attend irrigation and fertilizer management training courses and receive nitrogen management certification.

Finally, in Phase II areas, soil and irrigation water must be tested annually for nitrate-nitrogen content. The farmer must report annually to the CPNRD on:

- the water nitrate testing results for each irrigation well;
- the soil nitrate testing results for each 40-acre tract;
- the crop to be grown and the farmer's yield goal;
- the commercial fertilizer use recommendation to accomplish the farmer's yield goal;
- the actual commercial fertilizer applied; and
- the actual yield achieved.

Presumably if farmers set unrealistic yield goals and over-fertilize as a result, or fail to take credit for the nitrogen already available in the soil and irrigation water, the reporting requirements will make this clear to the farmer and the CPNRD. The 1988 reports indicate that farmers overestimated their corn yield by approximately 8 percent, but overfertilized by nearly 30 percent. Thus there would appear to be opportunities for improved nitrogen management.

Phase III In Phase III areas (average nitrate-nitrogen levels exceed 20.1 ppm), commercial fertilizer application on all soils before March 1 will be banned. Spring applications of commercial fertilizer will be:

- split (preplant and sidedress) application, or
- applied with an approved inhibitor if more than 50 percent is applied pre-plant.

All other Phase II regulations will apply.

Phase I and II areas have been established in the Central Platte GWMA, but no Phase III areas have. This may change, however. The 1988 average nitrate-nitrogen reading from irrigation wells in the CPNRD Phase II area was approximately 18.8 ppm. If these nitrate levels increase further, significant portions of the Phase II area could move into Phase III regulation.

The Central Platte GWMA program is an important innovation for which the NRD deserves commendation. More stringent regulations, however, including direct regulation of the amount of nitrogen applied, may ultimately be required to control ground water contamination from commercial fertilizer use.

Editorial comment: In the author's opinion, fertilizer and pesticide BMPs should be required *statewide*, not just in high-nitrate areas:

- to protect uncontaminated water from pollution, and
- to slow the further pollution of water already contaminated, even if the MCL has not been contaminated.

Future Issues

Further NRD regulation of fertilizer use within the next five years is very likely. EPA is likely to restrict the use of pesticides contaminating drinking water, although this program will not initially apply to fertilizers. In addition, the 1990 Farm Bill includes provisions to reduce ground water pollution from fertilizer and pesticide use by providing financial incentives to farmers to reduce agrichemical use.

The 1990 Farm Bill also includes funding for low input-sustainable agriculture (LISA) research and allows farmers to adopt LISA farming practices without losing farm program benefits.

Regulating fertilizer use will not remove nitrates from already contaminated ground water. Even prohibiting fertilizer use will not remove nitrates

In the author's opinion, fertilizer and pesticide BMPs should be required statewide, not just in high-nitrate areas:

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-

An agrichemical tax could help fund SPA and GWMA programs, fund BMPs and LISA research, and provide loans and grants to communities with contaminated water supplies.

already found in ground water supplies, because fertilizer applied years ago is still gradually leaching into ground water supplies. Nitrate contamination of ground water supplies took decades to develop, just as it will take decades to slow or stop. The ultimate solution is likely to be a combination of:

- reduced fertilizer use to slow agrichemical contamination of ground water through BMPs, and
- more wide-spread water treatment (public and private) to remove nitrates (and pesticides) from drinking water. Many rural households have already turned to home water treatment systems to improve drinking water quality. Community water treatment costs, now very high, may decrease as treatment technologies improve.

Financing state ground water quality protection programs poses a major

policy challenge. Implementation of existing SPA and GWMA programs have been hampered through limited state funding. Replacing contaminated public water supplies typically costs hundreds of thousands of dollars. One possible source of funding for these programs is an excise tax on agrichemicals, similar to the 1988 Iowa agrichemical checkoff. Funds could be used to support the SPA and GWMA programs, to conduct research on water quality BMPs and LISA, and to provide grants and loans to communities required to develop new drinking water supplies for their citizens.

Everyone wants a clean, safe supply of drinking water. Protecting the quality of Nebraska's drinking water supplies to provide that safe drinking water is a policy challenge we have no choice but to meet.

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