

## Agricultural Contamination of Subterranean Water with Nitrates and Nitrites: An Environmental and Public Health Problem

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### Abstract

Water contamination is a consequence of human settlement, agricultural, silvicultural, and industrial activity in a region. The nitrates and nitrites dissolved in groundwater are indirectly consumed by humans, where they cause negative health effects. Among the most commonly observed problems are the dysfunction of the thyroid gland, production of nitrosamines (which commonly cause cancer), and a decrease in the capacity of the blood to transport oxygen, also known as methemoglobinemia or, "blue baby syndrome". As part of the agreements signed by Mexico during the Conference of the United Nations on the Environment and Development in June, 1992, in Rio de Janeiro, Brazil, Agenda 21 was adopted as a normative document focused on achieving "sustainable development" in all fields. Modern concepts of production attempt to guarantee that human

consumer goods are innocuous, and are produced in a manner that promotes environmental sustainability, thus contributing to protection of consumer and ecosystem health.

**Keywords:** Nitrogen contamination, Leaching, Human water consumption, Methemoglobinemia, Cancer

## 1. Introduction

Freshwater is a scarce, unique natural resource, essential for life on Earth and the productive activities of human society. Agricultural systems continually increase their intensity of exploitation of soil and aquatic resources; affecting their quality and productive capacity. Thus, water contamination is a consequence of rural, agricultural, silvicultural, and industrial activities, as well as of human use. The negative impact from this contamination results in a series of environmental problems related to nutrient content, especially that of nitrogen ( $N_2$ ) produced by the application of large quantities of nitrogenous fertilizers. Coupled with irrigation, such applications have resulted in soil salinization and contamination of subterranean and surficial waters (Pacheco & Cabrera, 2003; Stigter, Ribeiro, & Carvalho, 2005). This phenomenon is increased in some types of soils because mobile contaminants such as nitrates ( $NO_3^-$ ) are more easily leached from them (Devito *et al.*, 2000).

World production of nitrogenous fertilizers is growing constantly. In developed countries, the average amount of  $N_2$  application is between 120 and 550 kg ha<sup>-1</sup>. In Mexico, applied quantities of  $N_2$  range from 120 to more than 600 kg of ha<sup>-1</sup>, without taking into account nutrient requirements of the crops or natural soil fertility (Garcia *et al.*, 1994; Cárdenas *et al.*, 2004). The contribution of  $NO_3^-$  in agriculture is not only from the application of nitrogenous fertilizers, but also from the mineralization of the organic  $N_2$  present in the ecosystem (Studdert, Carabaca, & Echeverria, 2000). Contamination from nitrogenous fertilizers in agroecosystems has been revealed by many studies, and that with intensified agricultural activity, and the increased supply of nitrogen, there is increased contaminant impact in water (Lucey & Goolsby, 1993; Richards *et al.*, 1996; Studdert, Carabaca, & Echeverria, 2000). Intensive ranching is another activity that produces abundant residues that can be used as fertilizers, but if not managed well, they can become contaminants because of their high content of  $N_2$  and organic matter (Gil, 2004).

Nitrates in aquatic systems increase the amount of algae and other green plants that cover the water surface, resulting in an increased consumption and reduction of dissolved oxygen in the aquatic environment. This reduction further results in a decrease in the amount of incident solar radiation penetrating to greater water depths. These two phenomena result in a reduction of depuration and photosynthetic capacity of aquatic organisms (Herrera *et al.*, 2004), leading to eutrophication (Toner, 1986).

It is known that nitrates and nitrites ( $NO_2^-$ ) dissolved in groundwater used for human consumption can cause harmful health effects (Freitas, Brilhante, & Almeida, 2001). Among the most common effects encountered are a decrease in thyroid gland function, low storage of vitamin A, production of nitrosamines (which are known as common causes of cancer), and a decrease in the oxygen transport capacity the blood (methemoglobinemia, or "blue baby syndrome") (Ageitos *et al.*, 1980; Gupta *et al.*, 2000; WHO, 2007).

Contamination of groundwater by nitrates is becoming more prominent because of growing world interest in consuming "innocuous" water and food. Thus, it is urgent that we intensify actions to preserve water quality such that agriculture and fisheries are less affected (FAO/CEPAL, 2007). Therefore the objective of this review was to describe the main causes of subterranean water contamination with nitrates and nitrites and their effects on human health found in different parts of the World.

## 2. General description of nitrogen compounds

The forms of  $N_2$  of more important interest based on their oxidation state are, in decreasing order, nitrate, nitrite, ammonia, and organic nitrogen. All are biologically interconvertible and form part of the nitrogen cycle (Hill, 1996). The nitrates ( $NO_3^-$ ) and nitrites ( $NO_2^-$ ) contain nitrogen ( $N_2$ ) and oxygen ( $O_2$ ). The nitrate is the stable form under aerobic conditions, but can be reduced under anaerobic conditions. Due to the low potential of  $N-NO_3^-$  for co-precipitation or adsorption, conventional filtration processes, or water softening, are not adequate for their elimination. Nitrites contain nitrogen in a relatively unstable state of oxidation and are produced by the reduction of nitrate through microbial action under anaerobic conditions, and by the biological oxidation of amines and ammonia ( $NH_3$ ) (Hunter, Wang, & Van Cappellen, 1998).

## 3. Source and use of nitrates in agriculture

Nitrate is chiefly used as a source of inorganic nitrogen in the production of fertilizers and is the most important and assimilated form of nitrogen in agricultural production. Nitrogen can be based on urea ( $CO(NH_2)_2$ ), ammonia ( $NH_4^+$ ), or nitrate ( $NO_3^-$ ), which have the same models of reaction where nitrogen is-liberated through biochemical processes (Pacheco, Pat, & Cabrera, 2002). Nitrates can be found in superficial and subterranean

water sources as a result of rainwater runoff from agricultural areas and the excessive application of inorganic nitrogen and fertilizers, the inadequate disposal of industrial and domestic sewage, and the oxidation of human and animal excreta (WHO, 2007).

#### 4. Forms and mobilization of nitrates and nitrites in the environment

In subtropical and tropical regions with high temperatures and abundant rain, aquifers are exposed to rapid contamination by organic N<sub>2</sub> from the decomposition of organic matter found in soils such as animal or human fecal residues that are directly or indirectly deposited on the soil surface (De Miguel & Vasquez, 2006).

Nitrogen becomes an aquatic contaminant when its concentration surpasses the permissible limits for its use in each of the activities regulated by national and international norms, whether as part of the organic matter in suspension or from the influence of commercial nitrogenous fertilizers. Nitrogen is mobilized as soluble salts that are difficult to precipitate, and its decomposition is carried out, basically, by means of its long-term biological assimilation in limited quantities. Inorganic nitrate is formed naturally by the decomposition of nitrogenous compounds such as proteins and urea to produce ammonia and ammonium (Hunter, Wang, & Van Cappellen, 1998). The concentration of inorganic nitrogen in uncontaminated groundwater seldom exceeds 10 mg L<sup>-1</sup>.

Nitrites can be found naturally in soils with pH over 7.7. Nitrogenous fertilizers can be transformed to nitrites directly when they are applied to soils with pH between 7.0 and 7.3 (Figure 1). In this case, the concentration of nitrites can reach 100 mg L<sup>-1</sup> (De Miguel & Vasquez, 2006).

An excess of nitrites in water is particularly harmful for humans and animals. It is suspected that one of the causes of nitrites in water is recent fecal contamination (Standard Methods, 2005). Nitrites may also be found in environments with low oxygen levels, or due to the overflow or leaching by water on contaminated lands. Part of the mixture lost by leaching contaminates aquifers and reduces the efficiency of removal of nitrogenous fertilizers (Feigenbaum *et al.*, 1987; Arauzo, Díez, & Hernáiz, 2003).

#### 5. Process of nitrate leaching in agricultural soils

N<sub>2</sub> is found in organic form in the soil and constitutes between 95 and 98% of the total nitrogen. This organic form is transformed into ammonium by bacterial action, which at the same time oxidizes to nitrate (NO<sub>3</sub><sup>-</sup>). Both compounds (ammonium and nitrate) can be absorbed by plants or assimilated by microbes in the soil (García, 1996).

The content of nitrogen in soils is highly variable, with values for the arable and tilled layer fluctuating between 0.2 and 0.7% and tending to decrease with depth. Such percentages increase with low soil temperature and higher precipitation (Navarro & Navarro, 2003). Plants can only use nitrogen as nitrates, while other forms eventually leach toward the aquifers, where concentrations will depend on the frequency, quantity, form of application, as well as the type of fertilizer (De Miguel & Vasquez, 2006).

Other factors that promote the leaching of nitrates toward the subsoil are rain, irrigation, and the type of soil (Cepuder & Kumar, 2002). The majority of soils possess abundant colloidal organic and inorganic particulates, being negatively charged, causing the nitrate anions to be repelled and, thus, leached with greater ease. However, many tropical soils are positively charged and, therefore more strongly retain their composition. For example, a sandy soil (negatively charged) can strongly reduce the chemical fertility of the soil, thus requiring fertilization. High doses of fertilizers and the use of large amounts of irrigation water to permeable soils lead to the leaching of high quantities of nitrates that ultimately contaminate the groundwater (Medina & Cano, 2001; Civeira *et al.*, 2003). Karstic subsoils (e.g. carbonated rocks), in turn, permit rainwater to infiltrate the aquifers more easily, bringing with it the nitrogenous compounds that contaminate the aquifers (Granel & Gález, 2002).

In a clay soil, the particles are expanded and the soil surface is waterproofed, and the water containing high levels of nitrates drains superficially, contaminating the surface water (Perdomo, Casanova, & Ciganda, 2001; Estrada-Botello *et al.*, 2007). Hence, leaching also occurs in clay soils, although the process is slower than for the soil types mentioned previously. Consequently, for removal of nitrate contaminants it will be necessary to install subterranean drainage for individual plots.

In essence, leaching is a process where the unabsorbed nitrates by the crops emigrate in solution through the soil profile where they are eventually incorporated into the groundwater. Even if the nitrates are transported to water deeper in the soil strata, it is possible that they can rise by capillary action during periods of drought. Nitrates also are transported from lower soil layers to higher layers when aquifer levels rise. Such transportation includes a great deal of nitrogen originating from inorganic fertilizers, and that formed by mineralization in deep strata.

Hence, nitrates can be located within reach of crop roots, or they can descend as a result of rain and irrigation (Navarro & Navarro, 2003).

## 6. Evaluation of Agricultural Practice: Aquifer Contamination

Numerous investigations around the world have been working on evaluating abiotic and biotic indicators of nitrogen contamination in waters and the impact of agricultural practices on the deterioration of natural resource quality. In addition, social and cultural indicators also are used in the assessment of the degree of aquatic contamination and its effect on human health (Table 1).

The presence of nitrates and nitrites in groundwater in some countries (Tables 2, 3) imposes serious threats to the provision of water for human domestic use (Muñoz *et al.*, 2004). In Mexico, diverse contaminants (especially arsenic and nitrate) have been detected in the aquifers of the states of Coahuila, Chihuahua, Durango, Hidalgo, Guanajuato, Zacatecas, Morelos, Veracruz, and Yucatan. Concentrations of nitrates ( $\text{N-NO}_3^-$ ) have been found ranging from 0 to 224  $\text{mg L}^{-1}$  (Pacheco, Cabrera, & Pérez, 2004; Pérez & Pacheco, 2004; Palomo, Martínez, & Figueroa, 2007). The municipal councils of Water Quality have the responsibility to prohibit the use of aquifers for human consumption when contaminant levels exceed the PML of 10  $\text{mg L}^{-1}$  (SSA, 1994). Higher concentrations of nitrates and nitrites relative to these standards means higher potential hazards (Shafiu, Alan, & Richard, 2003), since the presence of nitrates in water for human consumption often is related to the prevalence of other elements such as chromium, barium, or arsenic, resulting in public health risks (Bednar & Kies, 1991).

This problem is a consequence of the lack of regulation in the application and use of inorganic (mineral) and organic fertilizers (manure and other organic solids). Organic solids are unique compounds supervised for use, although legislation establishes only the permissible maximum limits (PML) for heavy metals and not the dose of nitrogen that should be applied to the soil (Figueroa, Flores, & Palomo, 2003). Thus, it is necessary to regulate the application of fertilizers in agriculture to reduce the risks of aquifer contamination (Figueroa *et al.*, 2006).

## 7. Nitrates and Health

Food is the main source of exposure to nitrates and nitrites, especially vegetables which accumulate nitrates in their green parts (e.g. spinach and lettuce), and water provides between 10 and 15% of the total nitrates consumed. Nitrates and nitrites are soluble in water. Nitrates are not reactive compounds, as opposed to nitrites which oxidize compounds having iron, such as hemoglobin, and some amines and amides (WHO, 2007). Medical-toxicological studies have shown that from 5 to 10% of the total consumption of nitrates is transformed into nitrites by bacteria in the saliva, stomach, and the small intestine of humans. Nitrates by themselves are not toxic; the harmful effects from nitrates are due to its conversion (reduction) to nitrites, a reaction that is present, in part, during human metabolism. The nitrites can react with amines, substances obtained from protein metabolism (e.g. from meat, fish, eggs, milk), to produce nitrosamines, which are potentially carcinogenic agents (Tulupov, Prikhod'ko, & Fimochenko, 2001; Del Puerto, Sardiñas, & Romero, 2008).

From an organismal health perspective, records of nitrates in humans and animals are not available because no country operates a permanent monitoring program for this compound for which observed effects occur only after the onset of health problems (WHO, 2007).

The presence of nitrates in public water supplies is a risk to human health, above all in infants less than 4 months of age who consume water having more than 50  $\text{mg L}^{-1}$  of nitrate ion (equivalent to 10  $\text{mg L}^{-1}$  of  $\text{N-NO}_3^-$ ). As consequence, rapid intoxication occurs, called methemoglobinemia, or blue baby syndrome (Vitoria *et al.*, 1991; Larios *et al.*, 2004; WHO, 2007). Methemoglobinemia has its origin in the reduction of nitrates to nitrites, or as a consequence of the direct consumption of nitrites. Nitrites transform the hemoglobin of the blood to methemoglobin. This phenomenon reduces the capacity of the blood to transport oxygen, resulting in afflictions known as cyanosis (blue color), hypoxia (lack of oxygen), tachycardia, nausea, vomiting, convulsions, coma, and occasionally death (Martínez & Velásquez, 1998; Gupta *et al.*, 2000).

Between 1945 and 1965, 300 cases of methemoglobinemia were reported in industrialized countries, with most cases being a consequence of the consumption of water originating from wells located near cattle farms where high nitrate concentrations were registered (Pacheco, 1997). In a study carried out in Indiana (USA), the consumption of water with concentrations of  $\text{N-NO}_3^-$  between 19 and 29  $\text{mg L}^{-1}$  increased the frequency of miscarriages (Nolan, 1999). Investigations in India showed that nursing for less than a year increased infant susceptibility to excessive nitrate exposure, and productions of rapid intoxication in children of later ages (Gupta *et al.*, 2000). Further risks exist for pregnant women and for patients with gastric medical conditions such as hereditary deficits in methemoglobin-reductase NADH and G6PD, and in patients with hemoglobinopathy (Freitas, Brilhante, & Almeida, 2001). Cattle, such as dairy cows, can also present symptoms of

metahemoglobinemia including problems with coordination, respiration, blue coloring in mucous membranes, vomiting, and abortions (Davison *et al.*, 1964).

In Chile, Zaldívar and Robinson (1973) carried out an epidemiological investigation on the association between stomach cancer and nitrogenous fertilizers, and found that 49.4% of the people exposed to sodium nitrate died. Studies in England showed that nitrates cannot be excluded as etiological factors in the development of gastric cancer and resultant mortality (Peter & Clough, 1983), and there is a statistically significant relation ( $r^2=0.46$ ) between this type of cancer and the consumption of water contaminated with nitrates (Sandor *et al.*, 2001). In an investigation carried out in 258 municipalities of the province of Valencia, Spain, increased consumption of drinking water contaminated with nitrates elevated mortality rate in both sexes via stomach and prostate cancer (Morales, Llopis, & Tejerizo, 1995).

To prevent metahemoglobinemia, the World Health Organization (WHO) established  $50 \text{ mg L}^{-1}$  as a permissible maximum limit for nitrates. The maximum quantity of nitrates that can be consumed daily by an individual, throughout life, without producing adverse effects on health, is defined as admissible daily consumption (ADC). This value was established by the joint committee of FAO/WHO (JEFCA) (Table 4).

Given the extensive epidemiological information for support, WHO proposed guideline values to prevent overingestion of water containing nitrates and nitrites that can be present simultaneously. The sum of the relations between the concentration and the guideline value for both parameters ( $50 \text{ mg L}^{-1}$  for nitrates and  $3 \text{ mg L}^{-1}$  for nitrites) should not surpass a value of 1 according to the expression:  $[\text{nitrate}] / 50 + [\text{nitrite}] / 3 \leq 1$  (WHO, 2007).

Under the same WHO criteria, the European legislation established  $50 \text{ mg L}^{-1}$  as a maximum concentration of nitrates permitted in water for human consumption (Directiva 91/676/CEE, 1991). It is possible that some confusion exists on the matter, since the U.S. Environmental Protection Agency (EPA) establishes  $10 \text{ mg L}^{-1}$  of nitrogen as the maximum concentration in human drinking water, which is approximately  $50 \text{ mg L}^{-1}$  of nitrates; two different means of expressing the same concentration. The Mexican legislation in an Official Norm established  $10 \text{ mg L}^{-1}$  of nitrogen ( $\text{N-NO}_3^-$ ) and  $0.05 \text{ mg L}^{-1}$  of nitrogen ( $\text{N-NO}_2^-$ ) as PMLs for water intended for human consumption (SSA, 1994).

In order to protect human health, it is necessary to monitor for nitrates and nitrites in agricultural production and subterranean water, as well as to inform farmers and authorities about the impacts of using excessive amounts of nitrogen-based fertilizers for crops and pastures, and the excessive production of nitrogen-laden industrial waste. In Mexico, the sanitary control of nitrogen content in food exists only at the borders by screening the quality of foods destined for import and export; however, such quality control is not carried out inside the country due to lack of an adequately maintained or enforced public health infrastructure. Therefore, it is necessary to widely inform and educate people about the dangers of water and food contaminated with nitrogen, and to promote the manufacturing, distribution, and sale, at a large scale, of individual portable nitrate and nitrite meters for improved individual recognizance.

#### **8. Alternatives for the long- and short-term reduction and control of subterranean water contaminated with nitrates and nitrites**

Nitrates already exist in groundwater and will be present there for many years because of their 25-year half-life (Follett *et al.*, 1991; Rubin *et al.*, 1998). Given the nonpoint/diffuse nature of such contamination, there are no known means of extracting and treating all water from aquifers prior to human and animal use, and the use and production of nitrogenous compounds in agriculture and society is unavoidable. In Mexico, for example, distribution and installation of water treatment apparatus for each and every home (e.g. reverse osmosis, ion exchange, electrodialysis; Aguado, 2009; Arellano, 2009) requires that all such homes have proper connections and repair capacities. Since most of Mexico is impoverished (approximately 65%), and a large proportion of the citizens utilize untreated well-water because city-supplied water is costly, or not available, such programs would be extremely costly to initiate and maintain. Therefore, the most practical and realistic alternatives revolve around the long-term reduction of subterranean nitrate and nitrite contaminated water by limiting the use of nitrogen-based fertilizers; use of multiseasonal/ multiperiod applications instead of applying all needed fertilizer in one application; use of fertilizers in liquid form together with irrigation water on irrigated lands; application of solid fertilizers using less irrigation water to reduce deep water percolation and nitrate leaching; use of ammonia-based fertilizers rather than nitrate-based (where and when possible); use of organic fertilizers rather than mineral forms; application of time-release nitrogen fertilizers to extend the time of availability of an application similar to that for organic compost; and reducing the levels of nitrates and nitrites in industrial (including livestock production) and community (e.g. household, gardens) discharges. While these are long-term

management goals, they do not address more immediate health concerns regarding consumption. In the short-term, extension and outreach programs/workshops can be implemented not only to teach people about the dangers of such contaminated waters, but to inform them of the different reduction/treatment options available, and to train them to use probes or other devices to monitor the nitrates and nitrites in their groundwater supplies. Such devices could be cost-effectively distributed to individual homes to allow residents to ascertain for themselves whether or not the water is safe for consumption. If the water is not safe for consumption, residents must be provided with alternative sources of drinking water. With the aid of government-funded programs, such communities could be provided with a treatment facility where residents could go to acquire treated water that is safe for consumption. Such facilities are expensive to operate, and would not be able to continue into the distant future. Hence, these community-based water monitoring programs would actually operate as parts of a larger interconnected monitoring system. The ultimate goal of such long-term programs is to reduce the need and continuance of the treatment plants.

To accomplish such a task, an achievable and realistic goal (e.g. a 10% reduction) must be set over a reasonable time-frame (measured in years, or decades given the half-life of nitrates) for a defined region (e.g. a watershed). Then, each and every source of contaminant contribution (e.g. industry, farm, home, etc.) is assessed for their input relative to the total amount measured from previously established monitoring wells, with the larger contributors asked to reduce more than the smaller contributors. The process of reduction within the unit of interest (the watershed in this example) can be monitored for societal effects (e.g. income reduction) to see how well the unit and its component parts (the homes, farms, and industries) are managing during the time period for reduction. All of this data may then be compiled to help form a predictive model for the unit of interest (the watershed), and to address the question "How difficult will it be to achieve a reduction of X% in Y amount of time?" If the cost is low, the process can be continued until a point of resistance is attained beyond which no further reduction is possible without severe societal costs. Or, a predetermined level can be put forward to be gradually approached over the long-term. Points of resistance can be matched by government subsidies to help offset the costs of achieving the desired long-range goal. Ideally, watersheds can be linked to form larger-scale models for large-scale management and enforcement of legislation programs. Ultimately, this multiscaled (i.e. individual property, community, watershed, region, etc.) integrated effort combining communities, universities, and government will link back upon itself to provide up-to-date real-time data for use in community and regional planning. It must also be kept in mind that aquifers supply water to rivers, streams, and lakes, and are, in turn, fed by these water bodies as well. Thus, the monitoring of aquifers must also include the monitoring of surface waters.

The suggested approach provided here has the capacity to be applied in many developing or underdeveloped regions of the world, and is sufficiently flexible to accommodate different political, economic, cultural, and ecological conditions. More developed regions are expected to have higher economic capacities to employ more home-based filtration systems, or community-level programs. As well, such regions would also have the capacity to better control application and discharge of nitrates and nitrites, leading to more rapid response, control, and management of these contaminants.

## 9. Conclusions

Humans and other animals are exposed to nitrates and nitrites through water. Over the last decade of the 20th century, there has been a constant worry about the health and protection of the environment, and about chemical contamination of water and food because of its accumulation in living organisms and other natural resources (FAO, 2000). The existence of high nitrate levels in groundwater constitutes one of the most serious problems of contamination in various places of the world, and has been attributed to the misuse/abuse and poor management of agrochemicals for crops. Nevertheless, insufficient evidence exists to indicate that the presence of nitrates in drinking water is a direct cause of certain types of cancer in humans.

As a consequence of the growing amount of agricultural and industrial waste (liquid and solid) in surface waters, a significant increase in the concentration of contaminants has been observed that affects ecosystems. Hence, there is a reduction in the potential use of water, because it is a health risk for humans in areas of influence.

Given this knowledge, and as a part of the commitments signed by Mexico during the Conference of the United Nations on the Environment and Development, in Rio de Janeiro, Brazil, Agenda 21 was adopted (ONU, 1992) as a normative document having the objective to achieve "sustainable development" in all environments. This agenda recognizes that the intensive use of fertilizers is related to the eutrophication of water bodies, soil acidification, and contamination of water with nitrates (Gallardo & Vallejos, 1999). Achieving this objective is complex, and requires a combination of ecosystem (biological, physical and chemical) as well as social

(socioeconomic and productive) components to find an equilibrium that permits better natural self regulation, thus improving the health and sustainability of nature, man, and agroecosystems (Bertollo, 1998; Altieri & Nicholls, 2000). Indeed, given the modern concepts of production ("Good Agricultural Practices"), it is imperative that human consumer goods comply with the requirements of innocuousness, providing security for workers, traceability of food of agricultural origin, and environmental sustainability; thus contributing to the protection and health of consumers and ecosystems (Siller *et al.*, 2002).

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Table 1. Advances and considerations relating the presence of nitrates in the environment in countries of the Americas

<b>Countries</b>	<b>Nitrates in the Environment: Advances and Considerations</b>
Canada	The quality of water reserves is affected by insecticides, by nutrients in agricultural soils, and by levels of irrigation. The $N_2$ originating in the drainage effluents from processing systems of domestic sewage is causing nitrate contamination of the drinking water supplies and the eutrophication of coastal waters. Nitrate levels in effluents from Canadian agricultural areas surpass the limit of $10 \text{ mg L}^{-1}$ of $N\text{-NO}_3^-$ for drinking water (Patni, Masse, & Jui, 1996).
United States	The Department of Agriculture has investigated, since 1990, the effectiveness of existing systems at controlling the concentration of nitrates in aquifers and developing friendly agricultural technologies for the environment. Higher concentrations of nitrates in agricultural lands have been found than in those lands dedicated to other uses. The results suggest that much of the production of petroleum, similar to agriculture, has impacted water quality. The concentration of nitrates in groundwater of the north coastal plain of Carolina surpasses the limit of $10 \text{ mg L}^{-1}$ of $N\text{-NO}_3^-$ established by the U.S. Environmental Protection Agency (EPA) for the drinking water. This level of contamination is attributed to fertilizers applied to grasses and crops in this region (Dukes & Evans, 2006).
Argentina	In a study carried out in the pampas aquifer, 70% of the samples analyzed showed nitrate levels of $160 \text{ mg L}^{-1}$ , surpassing the limit established in the Argentina Food Code (SEMA-EMS, 1999). The contamination of the surface waters by nitrates in this country results from the high production of domestic and industrial residues and direct runoff from agricultural areas of rain water carrying nitrogenous fertilizers. Consequently, the concentration of nitrates in surface and groundwater has increased, and the quality of the drinking water has deteriorated (Larios, 2008).

Table 2. Advances and considerations relating the presence of nitrates in the environment to international levels

Countries	Nitrates in the environment: Advances and Considerations
Spain	<p>In more than 18 communities of Valencia, the levels of nitrates in human drinking water surpass the 150 mg L<sup>-1</sup>, indicating a risk for the health of children and adults. The groundwater of north Maresme (NE of Barcelona) has concentrations 10 times the permissible limit for drinking water (50 mg L<sup>-1</sup>), with a maximum concentration of 567 mg L<sup>-1</sup>, representing an increase of 29% compared to 2002. The most prominent increases in the concentration of nitrates in groundwater occurred in the Unites States, Hungary, Sweden, Finland, and Germany (AEMA, 2004).</p>
France	<p>The north half of France, on the Burgundy-Strasbourg border, has water with nitrate concentrations over 50 mg L<sup>-1</sup>, whose origin is from surface and groundwater, from areas with intensive stockbreeding and farming. Institutions of scientific investigation consider that the deterioration of aquifer water quality throughout Europe is due, in part, to the intensification of agricultural practices in recent decades. This increased activity represents a potential threat to the quality of drinking water in rural areas (Larios, 2008).</p>
Lebanon	<p>The Arabian-German cooperation project (BGR, ACSAD, NCRS 1997-2000) on the protection and sustainable use of soils and groundwater has revealed that concentrations of nitrates in relatively deep irrigation wells of Bekaa Central are over 200 mg L<sup>-1</sup>. This confirms the vulnerability of relatively deep groundwater to contamination by nitrates (Darwish <i>et al.</i>, 2008). The groundwater of the Akkar plain in the northern part of the country, which supports a population of nearly 75 000 inhabitants, is seriously contaminated with nitrates from the intensive fertilization of agricultural fields. Such high levels of nitrates can have adverse effects on the health of the inhabitants, especially children (Larios, 2008).</p>
India	<p>The concentration of nitrates in groundwater from Gujarat, Rajasthan, Bengal and the north and south of the Krishna delta was found to be between 0.1 and 870 mg L<sup>-1</sup> primarily as a result of the fertilization of agricultural lands. These nitrate levels in human drinking water are frequent causes of methemoglobinemia and recurrent strong respiratory tract infections, not only in children less than 1 year of age, but in all inhabitants of the state of Rajasthan (Subramaniam, 2004; Mondal, Saxena, &amp; Singh, 2008).</p>
Thailand	<p>Nearly 30% of the drinking water from deep wells in Thailand and the Philippines showed levels of nitrates over the permissible maximum limit of 50 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup> established by WHO. The highest concentrations of nitrate (&gt;150 mg L<sup>-1</sup>) were found in fields of intensive cultivation in Kanchanaburi, Thailand (Tirado, 2007). Nitrate concentrations over the established limits can cause anoxia during nursing (Garcia-Luna, Parejo, &amp; Pereira, 2006; Larios, 2008).</p>
Senegal	<p>Studies confirm that the water from 133 deep wells in the region of Niayes is affected by high nitrate concentrations exceeding 50 mg L<sup>-1</sup>. These levels occur with greater frequency in residential areas than in cultivated fields due to the leaching of residential waste that extensively contaminates the aquifers (Sall &amp; Vanclooster, 2009).</p>

Table 3. Concentrations of nitrates and nitrites in groundwater from different regions of the world (De Miguel & Vasquez, 2006)

Regions of the World	Average Concentration mg L <sup>-1</sup>	
	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>
Southern Siberia	---	0.03
Depresión Kansko-Tasévkaya	1.2	0.08
Barakínskay Plain	5.52	0.07
Salairski Krysh	1.33	0.19
Sayano Altay	0.74	0.10
Southern states of the U.S.	2.10	---
California	3.40	---
Southwest Appalachians	4.30	---
Sierra Nevada	0.20	---
Western Nigerian Zone	1.63	0.09
African Occidental Valley	1.63	0.09
Hawaiian Islands	0.90	---
Finland (Plandia territory)	0.93	0.01
Switzerland	1.20	0.01
Other tropical and subtropical countries	1.87	0.07
Southern zone of the Cauto Valley (Cuba)	11.70	0.176
Holguín Province (Cuba)	22.25	0.274

Table 4. Daily permissible human intake (DPHI) of nitrates and nitrites

Ion	DPHI
Nitrate (NO <sub>3</sub> <sup>-</sup> )	0 – 3.7 mg/kg of body weight
Nitrite (NO <sub>2</sub> <sup>-</sup> )	0 – 0.06 mg/kg of body weight

Source: FAO/WHO (2002)

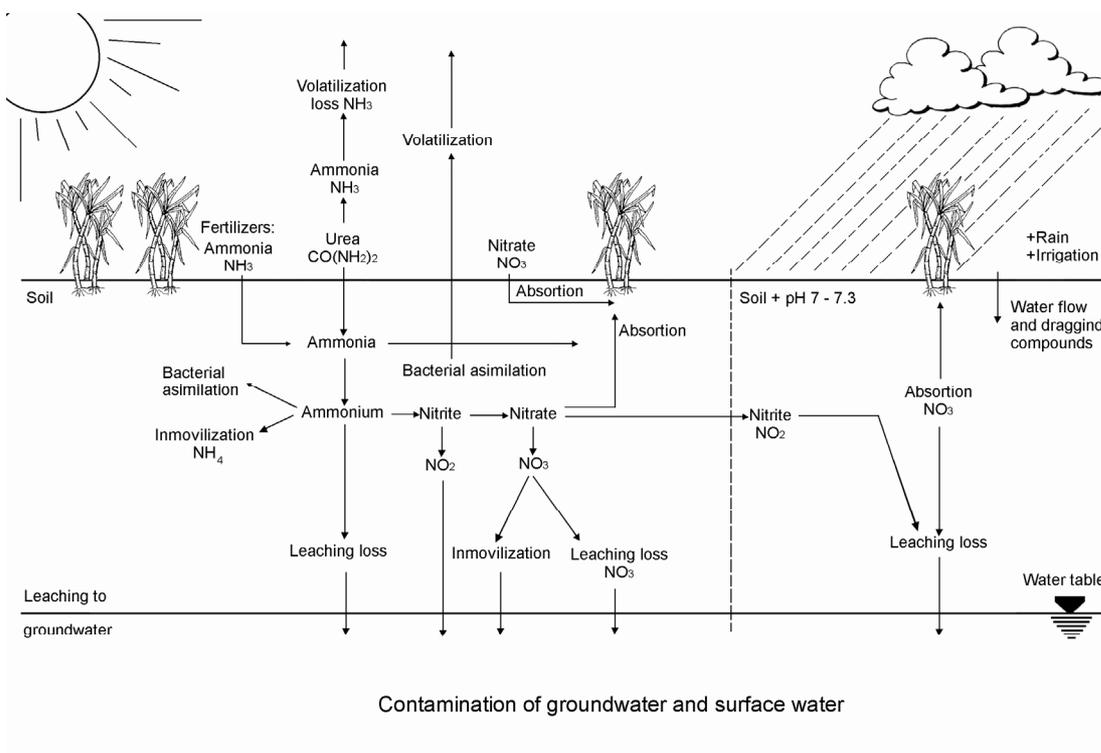


Figure 1. Forms and mobilization of nitrogenous compounds in the environment (Based on the schematic representation of the nitrogen cycle reported by Eldor (2007))