



Review Article

**Nitrates in Groundwater: Health Hazards and Remedial Measures**

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**ABSTRACT**

The occurrence of high nitrate levels in groundwater has to be recognized as a threat to humans and animals. Infant methaemoglobinaemia and nitrate poisoning of livestock occur at unexpected times and places. An important reason is that nitrate concentrations are variable, particularly under extreme climatic conditions. All instances of nitrate pollution related to anthropogenic sources can be managed to reduce or eliminate nitrogen inputs and for protecting groundwater resources. Hence the purpose of this paper is to present the facts related to the health hazard, describe processes leading to nitrate pollution of groundwater, and to present strategies to eliminate nitrate pollution.

**Keywords:** Groundwater, Nitrates, Health, Hazards

**1. INTRODUCTION**

In recent years it has been recognized that the quality of groundwater is of nearly equal importance to the quantity [1]. The present realization is clear about the limited resources and competing demands. This indeed has placed urgency on the observation and the protection of quality of groundwater. Nitrate ( $\text{NO}_3^-$ ) is one of the integral part in the growth of life. It is essential for the growth of many plants species, including most of those which are edible, but it becomes a problem if it gets into water in which it is not required. This leads to major environmental problem and also as a health hazard [2]. Groundwater contamination by nitrate is a global problem and Nitrate is a widespread contaminant of ground and surface water worldwide. Numerous sources in the environment contribute to the total nitrate content of natural waters mainly by, agriculture, human and animal wastes etc.

Nitrogen (N) is an essential input for the sustainability of agriculture [3-5]. However, nitrate contamination of groundwater is a worldwide problem [6-7]. Nitrate is soluble and negatively charged and thus has a high mobility and potential for loss from the unsaturated zone by leaching [8]. Elevated nitrate concentrations in drinking water can cause methemoglobinemia in infants and stomach cancer in adults [9]. As such, the US Environmental Protection Agency (US EPA) has established a maximum contaminant level (MCL) of 10 mg/l  $\text{NO}_3\text{-N}$  (50 mg/l  $\text{NO}_3$ ) [10]. Groundwater pollution due to point and nonpoint sources is caused mainly by agricultural practices (noticeable is the use of inorganic fertilizers,

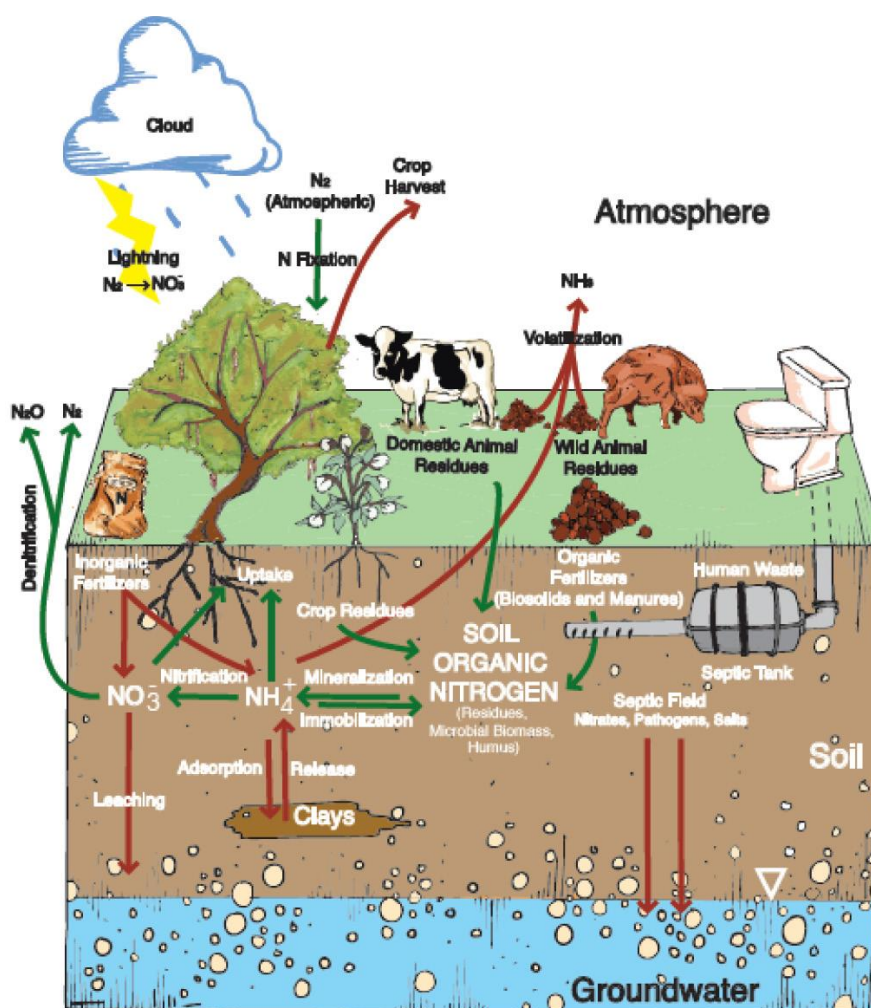
pesticides, and herbicides), localized industrial activities (organic pollutants and heavy metals), and inadequate or improper disposal of wastewater and solid waste (including hazardous materials) [11-12]. Nitrate is the most common pollutant found in shallow aquifers due to both point and nonpoint sources [13]. With nonpoint sources, groundwater quality may be depleted over time due to the cumulative effects of several years of practice [14-15]. Nonpoint sources of nitrogen from agricultural activities include fertilizers, manure application, and leguminous crops. The extensive use of fertilizers is considered a main nonpoint source of the nitrate that leaches to groundwater. In addition to agricultural practices, nonpoint sources of nitrogen involve precipitation, irrigation with groundwater containing nitrogen, and dry deposition. Point sources of nitrogen are shown to contribute to nitrate pollution of groundwater [16]. The major point sources include septic tanks and dairy lagoons. Many studies have shown high concentrations of nitrate in areas with septic tanks [17].

**1.1. The Nitrogen Cycle**

Nitrogen (N) exists in many forms in the environment and has a very dynamic cycle. For example, the atmosphere is 78% nitrogen gas and it also contains trace amounts of other nitrogen gases produced naturally and from pollution such as from burning fossil fuel. The soil environment contains many forms of N, including organic (carbon-based) forms produced from decaying plant and animal residues. During the decay process inorganic forms of N are also produced, including ammonia gas, which reacts with water to form ammonium, and

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**Figure 1:** The nitrogen cycle. revised from pollution science (18)

nitrate. Nitrate is very mobile in soil and groundwater because, unlike ammonium, nitrate does not adsorb onto soil or aquifer geologic materials, and only precipitates as a mineral under dry conditions. However, in the soil environment nitrate can be taken up by plants and microorganisms and recycled back into plant and animal tissue or transformed into nitrous oxide or transformed back into harmless nitrogen gas, as shown in Figure 1. Nitrous oxide, produced in water-logged soils and by animals, is a 'greenhouse' gas, partly responsible for global warming.

Nitrate ( $NO_3^-$ ) is one of the chemical forms of nitrogen. It coexists with other forms of nitrogen in a complex cycle. Nitrogen in soil and water originates from atmospheric deposition, application of fertilizer, manure, waste material and dead plant and animal tissue. Under aerobic (occurring in the presence of oxygen) conditions, nitrate is a fairly stable form of nitrogen. Ammonium ( $NH_4^+$ ) and organic nitrogen are other nitrogen forms that frequently convert quickly to nitrate. Most of the nitrogen on earth is in the atmosphere, which consists of 78%  $N_2$  gas. Other forms of nitrogen, originating mainly from power plant emissions,

internal combustion engines, fertilizer and manure, also occur in the atmosphere. These include nitrogen oxides ( $NO_x$  and  $N_2O$ ), nitric acid ( $HNO_3$ ) and ammonia ( $NH_3$ ). Atmospheric nitrogen interacts with the earth's surface when  $N_2$  is "fixed" (changed chemically) by legumes or lightning, or when pollutants are dispersed in precipitation.

### 1.2. Nitrates as a Health Hazard

In India, high concentration of groundwater nitrate (more than 45 ppm) have been found in many districts of Andhra Pradesh, Bihar, Delhi, Haryana, Himachal Pradesh, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Tamilnadu, Rajasthan, West Bengal and Uttar Pradesh[19]. The highest groundwater nitrate concentration of 3080 ppm was found in Bikaner in Rajasthan[20]. The study carried out by [21] in Anantapur district revealed that 65% of samples have shown nitrate levels above the desirable limit (45 ppm) [22].

### 1.3. Mechanism of Nitrate Pollution in the Groundwater

Occurrence of nitrate in groundwater is normally of anthropogenic nature due to the contact of soil cover with contaminants like nitrate fertilizers.

Factors which contribute to the aquifer contamination comprise the secondary porosity of aquifer and the porous and permeable soil cover. Aquifer could contaminate by leaching source, Point source and Biochemical source [23].

#### 1.4. Leaching Mechanism

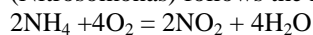
The use of nitrogen (N)-fertilizer in agriculture has significantly increased over the past 30 years to meet the food and living requirements of the speedily growing population. Therefore, the use of nitrate in fertilizers causes a foremost predicament in groundwater contamination. Some of the fertilizers infiltrate with the irrigation and/or rainwater to recharge the aquifer. The increased uses of nitrate fertilizers in the villages enhance the contamination of groundwater. The local farmers of the study area admitted the use of excessive nitrate fertilizers and believe that it is necessary to have better agricultural productivity.

### 2. POINT SOURCE MECHANISM

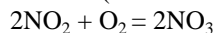
Wastewater in the upper soil layer either from the cesspools or the disposal ponds could infiltrate to the groundwater aquifer. The absence of a sewage system encourages such types of contamination by nitrate. Thus, the level of nitrate in groundwater will continue to increase as the sources of contamination. These sources are more dangerous than the leaching ones, because of the daily use of water, which then recharges the aquifer.

### 3. BIOCHEMICAL MECHANISM

The interaction of nitrogen compounds with the surrounding media leads to oxidation of nitrogen compounds, which finally contaminate the aquifer. Generally, organic matter -nitrate bearing- is distributed on the surface or near surface of the ground (sewage water, cesspools and drainage) produces nitrate. Oxidation of ammonia (from waste water, e.g. cesspools, sewage water and disposal ponds) into nitrite by bacteria (Nitrosomonas) follows the reaction below:



Nitrite is then oxidized to nitrate by another type of bacteria (Nitrobacteria)



This conversion of ammonia into nitrates is called nitrification. The nitrification rate increases in the presence of oxidation conditions and in the case of a high population of nitrifying bacteria.

### 4. IMPACT OF AGRICULTURE ON GROUNDWATER

#### 4.1. Major Sources of Nitrate Pollution:

There are number of sources of nitrate contamination of groundwater such as, human and animal waste, industrial wastes from food processing, fertilizer processing industries and septic tanks; the major source of nitrate pollution in

the densely populated areas is the septic systems of that area. Another major reason for the nitrate pollution may be taken as the disturbances in the natural systems due to the changes made by the mankind for its facilities; one example of this is the effect of forested areas on the leaching of nitrate to the groundwater. Natural, dense forests conserve nitrogen but cutting of such forests by the human causes lesser conservation of nitrogen, which in turn leads to nitrate pollution of the groundwater [24-25]. Another major source of nitrogen pollution of groundwater is the application of nitrogen-rich fertilizers to the agricultural land areas. The nitrogen provided to such areas in the form of fertilizers can be consumed in number of ways such as; it may be: taken up by plants; stored in soil; lost to atmosphere and it may be lost to groundwater [26].

There are number of reasons or factors that could lead to more of the nitrogen leaching to the groundwater. Some of them are summarized here under:

1. Nitrogen content
2. Nitrogen source
3. Irrigation practices
4. Soil texture

#### 4.2. Problems Associated With High Nitrate Levels

Nitrate incorporation in humans takes place via drinking water and food. The water used for drinking and cooking in the rural areas is high in nitrate content [27]. Although there have been studies performed attempting to link nitrate consumption to various illnesses, a few are stated here under:

##### 4.2.1. Methemoglobinemia

Cases of *Blue-Baby Syndrome* usually occur in rural areas which rely on wells as their primary source of drinking water. Often these wells become contaminated when they are located close to cultivated fields, feedlots and septic tanks. *Methemoglobinemia* is the condition in the blood which causes *Infant Cyanosis* or *Blue-Baby Syndrome*. In the GIT of an infant certain bacteria converts the nitrate ion to nitrite ion, which then reacts with two molecules of hemoglobin to form methemoglobin; In acid mediums, such as the stomach, the reaction occurs quite rapidly. This altered form of blood protein (hemoglobin) prevents the blood cells from transporting oxygen, which leads to the oxygen deprivation in the infant; due to which infant often take on a blue or purple tinge in the lips and extremities, hence named as, *Blue Baby Syndrome*. Other signs of Methemoglobinemia are gastrointestinal disturbances, vomiting, diarrhea and relative absence of distress when severely cyanotic but

irritable when mildly cyanotic. Methemoglobinemia most often affects infants of less than six months in age; the primary reason is that infants possess much less oxidizable hemoglobin than adults, so a greater percentage of their hemoglobin is converted to methemoglobin which greatly decreases the blood's ability to carry oxygen [28-30].

#### 4.2.2. Stomach and Gastrointestinal Cancer

Scientists claim that nitrate represents a potential risk because of nitrosation reactions which, with appropriate substrates present in the body Nitrates form N-nitroso compounds which are strongly carcinogenic in animals. There is still no concrete evidence to support this theory of carcinogenicity of nitrates. This inconsistency suggests that nitrate alone cannot be the only cause of elevated regional gastric cancer mortality rates, but these could result from a number of other factors, such as high pesticide levels, presence of coli form bacteria and/or other groundwater contaminants [31].

#### 4.2.3. Thyroid Problems

Histo-morphological changes in thyroid are observed due to 250 and 500 mg/l of Nitrates. Number of experimental studies or data suggests that Nitrates impairs thyroid function involving the hypothalamo-hypophysis-thyroid axis [32-33].

#### 4.2.4. Reproductive Problems:

Few studies have been published regarding water nitrate and the outcomes of spontaneous abortions, stillbirths, premature birth, or intrauterine growth retardation. Results of these studies have been inconsistent, possibly indicating no true effect of water nitrate on reproductive outcomes at the levels evaluated in these studies.

Alternatively, the inconsistencies may be due to the differing periods over which exposure was assessed, differing levels of water nitrate across studies, or differences in exposure to other cofactors[34].

#### 4.2.5. Livestock Health

Nitrate intake by dairy cattle is related to the levels found in forage and drinking water. According to research conducted on dairy cattle [35], nitrate-nitrogen in drinking water at levels under 10 mg/l is safe for animals. Between 10-20 mg/l nitrate-nitrogen, water is safe for livestock unless their feed has high nitrate levels. Problems for livestock can occur between 20 – 40 mg/l nitrate-nitrogen if feed contains more than 1,000 ppm. If well water is between 40-100 mg/l nitrate-nitrogen, feed should be low in nitrate, well balanced and fortified with vitamin A. At levels between 100 - 200 mg/l nitrate-nitrogen in water, studies report decreased appetite[36-37].

#### 4.2.6. Aquatic Life

Nitrate does not appear to be acutely toxic to adult fish except at extremely high concentrations. where mortality is due to salinity effects[38]. However, available research indicates that nitrate concentrations lower than the drinking water standard cause substantial egg and fry mortality in some salmonid fish species [39].

### 5. TREATMENT TECHNIQUES

Nitrate is a stable and highly soluble ion with low potential for co precipitation or adsorption. Thus conventional treatment technologies cannot be used.

#### 5.1. Reverse osmosis for denitrification

Nitrates could be removed by reverse osmosis cells under pressures ranging from 300 to 1,500 psi to reverse the normal osmotic flow of water. Membranes used were made of cellulose acetate, polyamides and composite materials. Problems associated with reverse osmosis membranes included fouling, compaction and deterioration with time. These problems resulted from deposition of soluble materials, organic matter, suspended and colloidal particles, and other contaminants, pH variations and chlorine exposure; thus the reverse osmosis process required pretreatment. A 15-gpm spiral wound cellulose acetate reverse osmosis system was tested for 1,000 h and up to 65% nitrate separation was observed for influent  $\text{NO}_3$  concentrations ranging from 18 to 25 mg/L15 [40].

#### 5.2. Ion exchange process

The ion exchange process involved passage of nitrate water through a resin bed containing strong base anion (SBA) exchange resins on which nitrate ions were exchanged for chloride or bicarbonate ions until the resin exhausted. The exhausted resin was regenerated using a concentrated solution of sodium chloride or sodium bicarbonate [41].

A pilot-scale study was conducted to evaluate nitrate removal from drinking water by ion exchange, reverse osmosis (RO) and electro dialysis (ED)[42]. The raw water contained 18-25 mg/L, 43 mg/L sulfate and 530 mg/L total dissolved solids (TDS). All processes were able to reduce nitrate concentration below 10 mg/L.

#### 5.3. Denitrification using a membrane bioreactor

Immersed heterotrophic membrane bioreactor (MBR) produced high quality product water<sup>34</sup> when  $\text{NO}_3$  contaminated water was made to flow through the lumen of tubular microporous membranes.  $\text{NO}_3$  diffused through the membrane pores. Denitrification took place on the shell side of the membranes[43]. The MBR achieved over 99%

NO<sub>3</sub> removal at an influent concentration of 200 mg NO<sub>3</sub>/L.

#### 5.4. Biological denitrification

Many bacteria belonging to different genera can grow anaerobically by reducing ionic nitrogenous oxides to gaseous products. Nitrates or nitrites served as the terminal electron acceptors instead of oxygen and resulted in generation of ATP [44]. Such denitrification was dissimilatory nitrate reduction [45]. When electrons are transferred from the donor to the acceptor, the organism gains energy which was applied for the synthesis of a new cell mass and the maintenance of the existing cell mass. The enzymes associated with denitrification are synthesized under anaerobic or partially aerobic conditions [46].

#### 5.5. Mitigation measures

The deleterious health and socio-economic effects of nitrate in drinking water sources are generating a serious concern in urban and rural communities. It is therefore imperative to develop groundwater nitrate management strategy, particularly for understanding the pollution processes and the role of the unsaturated zone in groundwater protection. A groundwater protection strategy should comprise a two-fold approach: legislation and enforcement for pollution control and for minimizing nitrogenous inputs to the environment which can be complimented by public mobilization and enlightenment programme. Groundwater has often been slighted in water supply planning and management. For a long time, it was believed that ground water could not be as easily evaluated as surface water, in terms of its availability, development, chemical quality and the economics of recovery. On the contrary, new hydrogeologic information and understanding, along with substantial progress in analytical capability, have improved the ability to plan, develop and manage ground water. Scientific analysis of ground water systems has opened the door to more effective use and protection of ground water. Inadequate communication between the ground water expert and the planning expert is partly responsible for the lack of integration of ground water into water resources planning. Closer affiliation of these experts is fostering increased mutual understanding of ground water and its important role in the nation's water supply. Ground water is now recognized to be a fundamental component in the comprehensive joint management of land, water and waste throughout the nation.

#### 5.6. Public awareness

A public awareness and education programme forms an essential part of the groundwater

protection strategy. This is a key component that will ensure the success of the legislative and pollution control approach for reducing nitrogenous inputs to the environment. The fact is that not all polluting activities in remote areas can be controlled by the authorities. For this reason, the public, including the farming community and other rural communities have to be convinced to own groundwater resources.

#### 6. CONCLUSION

The occurrence of nitrate in groundwater is a serious problem. Nitrate in groundwater can be derived from various sources which can be grouped into two main categories: anthropogenic nitrogenous pollution, and natural nitrate accumulation, primarily present in arid and semiarid regions. Pollution point sources are generally associated with specific activities, e.g. sewage sludge drying beds, land application of sludge, and irrigation of (partly) treated wastewater. At the large cities, high levels of sewage sludge application to land have caused serious groundwater pollution. The above confirms that the main source of nitrate in groundwater is anthropogenic pollution but such nitrate inputs are manageable. In the rural setting voluntary action regarding nitrate management is essential, but overall legislation and control are also needed. The three treatment processes that have been applied full-scale for nitrate removal include ion exchange, biological de-nitrification and reverse osmosis.

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