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Sources, Toxicological Effects and Removal Techniques of Nitrates in Groundwater: An Overview

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Nitrate is a major pollutant in groundwater in many parts of the world. Concentration of nitrate above 45 mg/L as nitrate and 10 mg/L as nitrate-nitrogen is unsuitable for domestic use. Usually nitrate as such is not potentially harmful for human health but metabolic reactions in the human body convert nitrate to toxic compounds, like nitrite and nitrosoamines. Nitrate levels above the maximum permissible limit in the human body cause methemoglobinemia or blue baby syndrome, increased infant mortality, abortions, birth defects, cancer, histopathological changes, deterioration of immune system of the body, hypertension, etc. Infants are more prone to diseases due to high nitrate consumption through drinking water compared to adults. This also affects animal health and causes eutrophication of water bodies due to nutrient abundance. Sources of nitrate in groundwater and surface water includes agrochemicals, surface runoff from irrigated lands, septic tanks, leakage from drainage networks, livestock wastes, manure storage, landfills, urban fertilizer use, industrial wastewater, sludge disposal, etc. Over fertilisation leaves traces of nutrients in the soil even after harvesting and causes accumulation of nitrate in vegetables thus reaching the food chain. Though treatment options, like electrodialysis, ion exchange, reverse osmosis, chemical and catalytic denitrification and biological denitrification are available, they are not cost effective, time consuming and have their own disadvantages. Of these, ion exchange method is the least expensive and most widely opted removal method following which is the biological denitrification method for nitrate reduction from water. Non-treatment methods recommended are mixing or blending the water having high and low concentration of nitrate to arrive at permissible levels, use the required amount of fertilizers for crops considering the already available nitrate in soil and water used for irrigation, alternate use of animal waste as organic manure and storing the manure on lined surfaces to prevent seepage and avoid leakage from septic tanks by proper construction, operation and maintenance measures. Pollution prevention by adopting strong policy measures for fertilizer use and educating the farmers may extend great support in the process.

KEYWORD

Nitrate, Groundwater, Fertilizers, Septic tanks, Methemoglobinemia, Eutrophication, Denitrification, Non-treatment options.

INTRODUCTION

Water is the elixir of life. Groundwater accounts for 97% of the fresh water and is widely preferred over surface water as it is comparatively less polluted than surface water. This reduces the cost on water treatment for drinking water supply. The main issues related to water is the quantity and quality. Even if sufficient quantity of water is available, it may not be useful if it is of inferior quality. As the quality of water is important many national and international organizations have recommended guidelines. Quality of groundwater depends on several factors including the geology of the aquifer, environment from where it has originated, flow mechanism, landuse, etc. Many ions, such as arsenic, fluoride, manganese, nitrate, sulphate, heavy metals, radioactive materials, etc., when found in excess than the prescribed limits affect the water quality due to their toxic nature. Both natural and anthropogenic sources may contribute to these ions in the aquatic environment. Human induced pollution is normally controllable by the use of alternate technology, substituting with less toxic substance, reducing the use of polluting substance or by treating the environment from the pollutant. Nitrate is a good example as it is contributed from agricultural fertilizers containing nitrogenous compounds apart from other origin, like septic tanks, landfills, industry, animal waste, etc., (Sacchi *et al.,* 2013; Pastén-Zapata *et al.,* 2014; Kim *et al.,* 2015; Ma *et al.,* 2016; Jakóbczyk-Karpierz *et al.,* 2017). It is an essential nutrient for crops but in excess can lead to water quality problems locally as well as regionally.

Nitrate, the main form of nitrogen is a colourless, odourless and tasteless polyatomic ion. All living systems need nitrogen for the production of complex organic molecules, such as proteins, nucleic acids, vitamins, hormones and enzymes (Mensinga *et al.,* 2003). But excess nitrates in drinking water causes serious health effects in humans. Natural processes, such as nitrification can contribute upto 20 mg/L of nitrates in the water (Frisch, 1987; Sanchis, 1991; Pulido-Bosch *et al.,* 2000). Normal level of ammonia or nitrate in surface water is typically low (less than 1 mg/L) and ranges up to 30 mg/L in the effluent from wastewater treatment plants (USEPA, 2012).

Threshold limit for nitrate in drinking water is 50 mg/L (WHO, 2007). Widely known health effects of excess nitrate consumption in humans are methemoglobinemia, cancer, stomach and gastrointestinal problems, birth defects, thyroid hypertrophy (Rao and Puttanna, 2000; Teton and Sorenson, 2002) to list a few. Moreover, groundwater discharge and surface runoff with elevated nitrate levels to coastal surface waters and/or streams can result in harmful effects on the ecological health of coastal wetlands, estuaries and riparian zones (Murgulet and Tick, 2009). Abundant growth of aquatic plants by utilizing the excess nitrate and oxygen causes depletion of dissolved oxygen in the water bodies leading to the death of animals in water. This commonly referred to as eutrophication, can change the odour, colour and taste of water.

Considering the importance of nitrate as a potential and common contaminant in groundwater, many researchers have reviewed the work carried in the past. However, these review articles are restricted to the agricultural (Singh and Sekhon, 1979) and non-agricultural sources (Wakida and Lerner, 2005) for nitrate pollution, the occurrence of nitrate in groundwater of USA (Spalding and Exner, 1993), biogeochemical processes controlling nitrate attenuation (Rivett *et al.,* 2008), nitrate removal methods (Kapoor and Viraraghavan, 1997; Shrimali and Singh, 2001; Bhatnagar and Sillanpää, 2011; Archna *et al.,* 2012; Zhang and Angelidaki, 2013; Su *et al.,* 2014; Ashok and Hait, 2015; Hakeem *et al.,* 2016; Xie *et al.,* 2017; Emamjomeh *et al.,* 2017). Nitrate removal methods include removal of nirate by microbial desalination- denitrification cell, use of slowly released carbon source from composite materials, Batch monopolar electrocoagulation, solid phase denitrification process and nanoscale zerovalent iron (nZVI) and Au doped nZVI particles, etc., biological denitrification (Matejù *et al.,* 1992; Bandpi *et al.,* 2013), natural and artificial denitrification (Hiscock *et al.,* 1991) and health issues due to nitrate in drinking water (Fan and Steinberg, 1996; Manassaram *et al.,* 2006; Fan, 2011; Bryan *et al.,* 2012; Su *et al.,* 2013; Fabro *et al.,* 2015; Zhai et al. 2016). The major associated health issue with nitrate is change of hemoglobin in red blood cells into methemoglobin especially in infants. Canter (1997) presented aspects related to nitrate in groundwater including methods of preve-

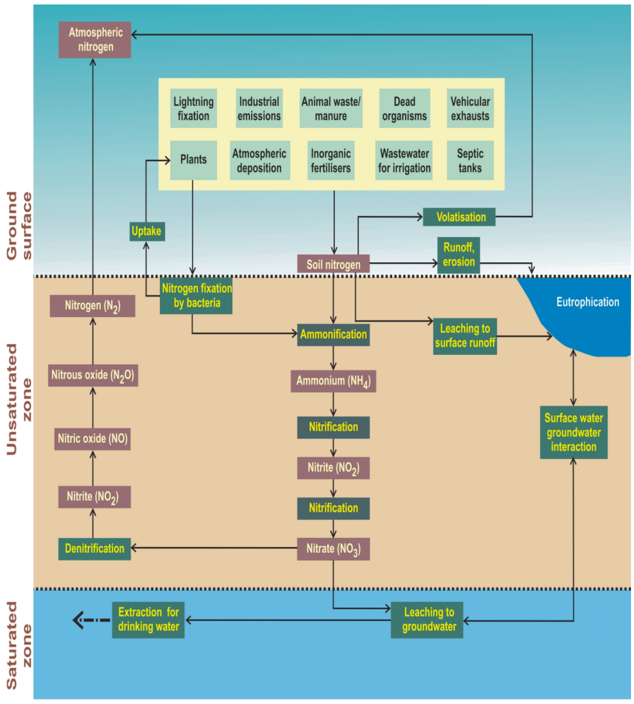

Figure 1. *Transformation of nitrogen into different forms in the environment*

ntion, assessment of the problem and remediation strategies. After this there is no review of research work on nitrate in groundwater. However, there has been several new findings and advancement in knowledge especially in the areas of natural, artificial denitrification processes (Hiscock *et al.*, 1991; Jensen *et al.*, 2012), biogeochemical processes (Rivett *et al.*, 2008) and health issues (Manassaram *et al.*, 2006; Fan, 2011; Bryan *et al.*, 2012). Hence, we present a comprehensive overview on nitrate which aims to address all the essential aspects of its occurrence, such as its properties and processes leading to its occurrence in groundwater, quantification techniques, sources, health effects in humans due to ingestion and remedial measures.

PROPERTIES

Nitrogen is an abundant element and essential to all life. Daniel Rutherford discovered nitrogen in the year 1772 (Lavoisier, 1965). Nitrogen may exist in organic and inorganic forms. Organic nitrogen is found in the cells of living organisms (nucleotides) and is an essential component that makes up proteins (amino acids). Inorganic nitrogen in water and soil include ammonia (NH_3^+), nitrate (NO_3^-) and nitrite (NO_2^-). Nitrogen has an atomic weight of 14.0067 and nitrate has a molecular mass of 62.0048 g/mole. Nitrate is measured as nitrate (NO_3^-) or nitrate-N (NO_3-N) which is very different from one another. Usually nitrate is quantified as mg/L in water and is the most soluble form of nitrogen. To convert nitrate to nitrate-N (mg/L): nitrate-N (mg/L) = 0.2259 x Nitrate (mg/L) and to convert nitrate-N (mg/L) to nitrate (mg/L): Nitrate (mg/L) = 4.4268 x Nitrate-N (mg/L).

OCCURRENCE AND TRANSFORMATION

As nitrogen exists in many forms in the environment, it is quintessential to understand its transformation from one form to another and the processes by which nitrate reaches the groundwater. Nitrogen constitutes to 78.09% of the earth's atmosphere. Exceptionally high concentration of 1800 mg/L and 1620 mg/L nitrate was found in groundwater of Haryana (Handa, 1986; Majumdar and Gupta, 2000) due to different sources. The occurrence of nitrogen in different forms, chemical and biological reactions in the atmosphere, unsaturated and saturated zones are shown in figure 1.

Nitrogen fixation

Biological processes mediated by microorganisms especially bacteria play a significant role in the nitrogen cycle. Nitrogen from the atmosphere is fixed by bacteria in the soil as ammonium by the enzyme nitrogenase. Cyanobacteria and Archaea contribute a larger part in this process. Nitrogen fixation also occurs naturally by means of lightning where under very high temperature nitrogen gas is oxidised to nitrate (Figure 1). Industrial nitrogen fixation in the form of fertilizers and chemicals containing nitrogen also contribute to various forms of nitrogen in soil. Of these 3 processes, biological nitrogen fixation is the major source of nitrogen input in soils.

Ammonification or mineralization

Organic nitrogen which results from decomposition of faecal waste, dead plants and animals cannot be utilized by plants directly, yet, it accounts for 95% of the nitrogen in soil (Barbarick, 2013). Microbes help in the process to convert this organic nitrogen into ammonia which is utilizable to plants.

Plant uptake and immobilization

Ammonia or ammonium ion and nitrate in soil is used by the plants in developing amino acids which are building blocks of proteins. Only plants have the capability to convert the inorganic nitrogen compounds to organic nitrogen. Animals and humans receive these proteins by consuming the plants. Microbes also take up nitrogen during mineralization and convert to organic nitrogen which is called immobilization.

Nitrification

Ammonium ions in soil get oxidized to nitrite and then to nitrate in the presence of nitrifying bacteria. Nitrosomonas bacteria mediate the conversion of ammonium ions to nitrite. Nitrite is oxidized to nitrate in the presence of nitrobacter species. This is the principle step for the formation of nitrate in soil which is the most soluble and utilized form of nitrogen used by plants.

Denitrification

Biological reduction of nitrate to nitrogen gas through a series of intermediate steps (Figure 1) is termed as denitrification. This anaerobic process involves conversion of nitrate to nitrite initially which is then converted to nitric oxide. Nitrous oxide results from the nitric oxide which finally gives nitrogen gas.

Volatilization

Ammonium ion converts to ammonia gas and reaches the atmosphere. This loss of gaseous ammonia to the atmosphere occurs in soil having pH greater than 7.5. Volatilization depends on the type and method of fertilizer use; soil temperature and moisture; buffering capacity of the soil and crop residues. Other nitrogen transformations in the soil, though not very important, include dissimilatory nitrogen reduction to ammonium under anaerobic conditions, non-respiratory denitrification by reduction of nitrate to nitrogen gas (mainly nitrous oxide) without enhancing the growth of the microbe and can occur in aerobic environments, anaerobic ammonium oxidation (anammox) in which ammonium and nitrite are converted to nitrogen gas (Mulder *et al.,* 1995) and chemodenitrification when nitrite in soil reacts to form nitrogen gas or NOx (nitric oxide, nitrogen dioxide) (Robertson and Groffman, 2007).

QUANTIFICATION

Presence of nitrate in groundwater cannot be determined by physical examination, such as colour, taste or odour. Several methods are available for determination of nitrate in water either as nitrate or nitrate-N by chemical analysis. Nitrate ion selective electrode, ion chromatography, cadmium reduction, titanium chloride reduction, hydrazine reduction and brucine method are some of the procedures of determination of nitrate as suggested by American Public Health Association (APHA) and United States Environmental Protection Agency (USEPA).

Ion selective electrodes equipped with a selective sensor for nitrate give results rapidly and can be used both in the laboratory and in the field. Accuracy can be affected by the presence of high concentration of nitrite, chloride, bicarbonate or by varying pH (APHA, 1995). However, this technique offers to measure a wide range of nitrate concentration from 0.14 to 1400 mg/L.

In cadmium reduction method, nitrate is reduced to nitrite in the presence of cadmium and is diazotised to form a coloured azo dye which is measured by a colorimeter at 543 nm. Though this method may be hindered by the presence of suspended solids, high concentration of iron, copper and other metals, oil and grease that coats cadmium surface, residual chlorine and sample colour, it is highly sensitive method recommended for nitrate-N analysis for levels ranging from 0.01 mg/L to 1 mg/L (APHA, 1995). Turbidity and colour of the sample may interfere while using an automated cadmium reduction method. The use of environmentally hazardous heavy metal, such as cadmium to determine nitrate is now being replaced by non-toxic substance, such as nitrate reductase purified from corn leaf which reduces the risk of pollution. This method referred as 'nitrate reductase nitrate analysis method' (Campbell *et al.,* 2006; Campbell *et al.,* 2004) has proven to have a precision equal to the cadmium reduction method (Patton *et al.,* 2002).

Similar to the cadmium reduction method, hydrazine reduction technique uses hydrazine sulphate to reduce nitrate to nitrate which is diazotised to be determined by a colorimeter (Kamphake *et al.,* 1967; Downes 1978; APHA, 1998; USEPA, 1978). Applicable range of this method is 0.01-10 mg/L and the accuracy may be affected by the presence of sulphide ion or colour of the sample.

Another technique for the determination of nitrate by reduction is by the use of titanous chloride (Kolthoff and Robinson, 1926). The nitrate in the sample is converted to ammonia and this method employs a gas sensing electrode to detect the ammonia. As the nitrite and ammonia in the sample is also quantified, the effectiveness of this method is reduced. This is not a widely-recommended method while quantifying only nitrate.

Ion chromatograph is one of the advanced techniques used for the simultaneous determination of various anions rapidly. Nitrate and nitrite levels close to 0.1 mg/L can be measured (APHA, 1995). Substances having a retention time closer to nitrate may interfere with the results which can be overcome by sample dilution. This method requires specific training and routine maintenance.

Brucine method (Jenkins and Medsken, 1964) is based on the reaction of nitrate in the sample with brucine sulphate at a temperature of 100°C. A spectrophotometer is used to measure the colour of the resulting complex at 410 nm (USEPA, 1999). Temperature is a major controlling factor in this method. Also interference may be caused by a number of other factors like presence of dissolved organic matter, colour, presence of oxidizing or reducing agents, residual chlorine, presence of ferrous iron, ferric iron and quadrivalent manganese in concentrations above than 1 mg/L (USEPA, 1999).

Ultraviolet spectrophotometer is used as a rapid assessment method for screening nitrate in water. Nitrate and organic matter is absorbed at 220 nm and only organic matter is absorbed at 275 nm. This can be applicable to unpolluted natural waters and it is necessary that the samples are filtrated (0.45 micron) before analysis. Dissolved organic matter and nitrite significantly interfere with the analysis apart from surfactants, chlorite and chlorate.

SOURCE

Nitrate in the environment is contributed by natural and anthropogenic sources (Figure 1). Pollution resulting from human activities may be further classified as point and non-point sources.

Natural source

Background nitrate concentration upto 10 mg/L in groundwater could be natural (ECETOC, 1988). According to Madison and Burnett (1985), nitrogen concentration which included nitrite plus nitrate greater than 3 mg/L may be due to human activity. Naturally occurring nitrate levels do not exceed 4 to 9 mg/L of nitrate and 0.3 mg/L of nitrite in United States (USEPA, 1987). Surface water with nitrate concentration less than 1 mg/L is very common, but upto 5 mg/L is considered to be not interfered by human activity (Meybeck and Helmer, 1996) and above 5 mg/L may be due to contamination by external sources (WHO, 2004).

Researchers have reported various level of nitrate in rainwater. This depends on the atmospheric nitrogen composition. Less than 1% of the rainwater contains nitrate from 0.012 to 0.181 mg/L (Radojevic, 1967). Nitrate upto 5 mg/L have been observed in rainwater collected from industrial areas (van Duijvenboden and Matthijsen, 1989) and van Maanen (2001) recorded nitrate upto 4.5 mg/L in rainwater collected in the Netherlands.

Average nitrate concentration of 0.04 epm was measured in Israel (Yaalon, 1964). Morel and Hering (1993) observed an average nitrate concentration of 23.1 mg/L in rainfall at New Hampshire, USA. Nitrite in seawater varies between 0.001 to 0.01 mg/L (Orr *et al.,* 1926) and the concentration of nitrate and nitrite together ranged from 4.42 to 22.4 µM in Japan (Watanabe *et al.,* 2000). Along the Malaysian coast, nitrate concentration upto 0.08 mg/L was observed by Yap *et al.* (2005).

Minute quantities of nitrate may occur naturally in the environment depending on the geology of a region. Rocks and minerals containing nitrate may weather or undergo changes and contribute to their occurrence. Nitrogen exists as relict organic matter in sedimentary rock or as ammonium substituting for potassium in sedimentary, igneous and metamorphic rocks (Stevenson, 1962). Ammonium bearing aluminosilicate minerals have been identified in a number of geologic settings worldwide (Lowe and Wallace, 2001). Ammonium bearing illite is associated with low grade metamorphic rocks associated with a coal seam in Pennsylvania (Juster *et al.,* 1987). Thus, ammonium bearing minerals are present in several rocks which may contribute to nitrate in groundwater. These geological media has contributed to nitrate content between 4 mg/L and 207 mg/L in desert areas of Najran region, Saudi Arabia (Alabdula'aly *et al.,* 2010). Schwiede *et al.* (2005) reported natural nitrate enrichment in the soils under termite mounds of Kalahari deserts of Botswana having extremely high concentrations of up to 750 mg/kg as nitrate-N.

Anthropogenic source

More reasonably, anthropogenic nitrate sources can be differentiated as agricultural and non-agricultural. The non-agricultural sources in urban areas include leakage from water supply and disposal networks, on-site sewage disposal, animal waste, contaminated land, industry, river and aquifer interaction, atmospheric deposition, urban fertilizer use, storm water and house building (Wakida and Lerner, 2005). Impact of climate change on nitrate content in groundwater is also of concern. Risk of nitrate contamination in groundwater varies across many countries. Some reported cases of nitrate contamination in Australia, Bangladesh, Canada, China, Czechoslovakia, Egypt, France, India, Iran, Israel, Japan, Morocco, Saudi Arabia, Scotland, South Korea, Spain, Sri Lanka, Thailand, Turkey, USA and other countries are given in table 1.

Agricultural source : First and foremost sources contributing to nitrate in the environment are predominantly the inorganic fertilizers. Expanding population has increased our agricultural needs also exponentially. With scientific and technological advancements, farmers have now gone from one time cropping in a year to intensive modern agriculture practises where the land is irrigated many times in a year and is subjected to tremendous change often. Fertility of the soil also is reduced. Furthermore, the economy of many developing countries is depended on agriculture. The world potential nitrogen balance as a percentage of global total demand is expected to remain between 3% to 5% between 2011 and 2013 and is likely to increase to 7% in 2014 and 10% in 2015 (FAO, 2011). FAO (2011) predicts the world demand of nitrogen fertilizer in the year 2015 to be 112.9 million tonne from the 155.3 million tonne in 2011 with 68% demand in Asia, 18% in America, 10% in Europe, 3% in Africa and 1% in Oceania. Asian countries especially India and China are the largest consumer as well as producer of fertilizer in the world and the total fertilizer nutrient consumption in Asia is 60 % of the world total mostly in South and East Asia (FAO, 2011). It is a general tendency that farmers apply more fertilizers expecting better yield from the crop. Though it is true that fertilizer increase crop yield, application in excess may retain small quantities in soil. This should be accounted after deducting the nitrogen losses to the atmosphere from soil when applying fertilizer for the next cropping. Mismanagement of this nature not only pollutes the soil but decreases its fertility and leads to high nitrate content in vegetables. Severity of pollution depends on the permeability of soil and climatic factors,

Table 1. *Selected case studies of nitrate concentration in groundwater and source*

Country, place	Source	Year of analysis	Nitrate concentration (nitrate-N wherever specified)	Reference
Bangladesh, central-west region	Fertilizer	2005	<0.10 to 75.12 mg/L	Majumder *et al.* (2008)
Cameroon	Livestock breeding, untreated wastewater flows	No info	1 to 300 mg/L	Ngatcha and Daira (2010)
Chad	Septic tanks, fertilizers, agriculture return flow	No info	8.80 to 167.20 mg/L	Ngatcha and Daira (2010)
China, Beijing	Fertilizer	2004 to December 2005	Upto 76.3 mg/L	Du *et al.* (2011)
China, Hangzhou	Domestic wastewater, septic tank, fertilizer	2001 and February 2002,	0.07 to 34.41 mg N/l	Jin *et al.* (2004)
China, Huantai county	Fertilizer	1998 to 1999; 2002 and 2003	36.6 mg/L (maximum mean) as nitrate-N	Liu *et al.* (2005)
China, Jiutai	Fertilizer	2008	42.04 mg/L as nitrate-N	Li *et al.* (2010)
Czechoslovakia	Fertilizer	1980's	up to 43 mg/L	Bene *et al.* (1989)
Egypt, Greater Cairo	Fertilizer, reuse of sewage wastewater for irrigation	1996-1997 ??	>90 mg/L	El Arabi (1999)
Egypt, Helwan	Industrial activities, wastewater drains and leakage from sewage system, fertilizer	2009	0.4 and 85 mg/L	Abdalla and Scheytt (2012)
France, Brittany	Hog manure, sewage effluents	1999 to 2000	3.2± 0.2 to 245 ± 12 mg/L	Widory *et al.* (2004)
Gaza strip	Animal manure, fertilizers, and wastewater/sludge	2006 and 2007	31 to 452 mg/L	Shomar *et al.* (2008)
Gaza strip	Municipal solid waste landfills leachate	1995, 1999, 2001 and 2008	40 to 119 mg/L	Alslaibi *et al.* (2011)
India, Andhra Pradesh	Fertilizers, animal waste	2008-2009	Upto 879.65 mg/L	Brindha *et al.* (2010, 2013)
India, Madhya Pradesh	Fertilizer	2008	8 to 192 mg/L	Avtar *et al.* (2013)
India, Pune	Landfill leachate	2006, 2007	1 to 90 mg/L	Kale *et al.* (2010)
India, Rajasthan	Fertilizer, poor soil profile, irrigation mechanisms	2009	7.1 to 162 mg/L	Suthar (2011)
India, Uttar Pradesh	Animal wastes, fertilizer	2003-2004	1 to 166 mg/L as nitrate–N	Sankararamakrishnan *et al.* (2008)
Iran, Hamadan	Fertilizer	2000	3 to 252 mg/L	Jalali (2005)
Iran, Khozestan	Nitrogen fertilizer	2004	4 to 43.4 mg/L	Mahvi *et al.* (2005)
Japan, Shiroishi Plain	Fertilizer	2000	0.1 to 60 mg/L as nitrate-N	Gunatilake and Iwao (2010)
Lebanon, Terbol	Fertilizer	2007 and 2009	>200 mg/L	Darwish *et al.* (2011)
Morocco	Fertilizer, human wastewater, livestock faeces and organic debris	1996–2000	0.6 and 435 m/L	Laftouhi *et al.* (2003)

Continued...

Nepal	Sewage, to lesser extent by fertilizer	1993	>100 mg/L	Chettri and Smith (1995)
Northeastern Australia	Fertilizer and organic sources, such as sewage, septic or feedlot overflows	1993-2000	upto 113 mg/L	Thorburn *et al.* (2003)
Northern China	Fertilizer	1993 and 1994	0 to 300 mg/L	Zhang *et al.* (1996)
Palestine, West Bank	Manure, fertilizers, atmospheric deposition, cesspits and legumes	1981 to 2004	up to 285 mg/L	Anayah and Almasri (2009)
Saudi Arabia	Agriculture practices and human activities, geological factors in desert areas	between 2000 and 2004	1.1 to 880 mg/L	Alabdula'aly *et al.* (2010)
Scotland	Fertilizer	1980s to 1999	0 to 30 mg/L as nitrate-N	Robins (2002)
Senegal, Niayes region	Fertilizers, inadequate sanitation of waste and sewage water	2007	5 to 900 mg/L	Sall and Vanclooster (2009)
Siberia and Kosova	Pit latrines	1996-2000	up to 330 mg/L	Banks *et al.* (2002)
South Korea, Kwangju province	Fertilizer	2006	0.01 to 0.71 mg/L	Das *et al.* (2009)
Spain, Campo de Dalías	Diffuse pollution from agricultural practices	1996	0.08 to 310 mg/L	Pulido-Bosch *et al.* (2000)
Spain, Plana de Vic	Intensive pig farming and use of pig manure	2005 to May 2006	10 to 529 mg/L	Otero *et al.* (2009)
Spain, Vitoria-Gasteiz	Fertilizer	1986-2000	>200 mg/L in 1995,	Pérez *et al.* (2003)
Sri Lanka, Udunuwara	Fertilizer	1998	1 to 62 mg/L as nitrate-N	Gunatilake and Iwao (2010)
Turkey, Antalya basin	Fertilizer	2009	0.01 to 102.5 mg/L as nitrate-N	Kurunc *et al.* (2011)
Turkey, Eskiºehir	Fertilizer and septic tanks	1986 to 1988.	2.2 to 257 mg/L	Kacaroglu and Gunay (1997)
Turkey, Konya	Fertilizer, municipal and industrial wastewater, septic tanks, urban drainage and many more	1998 and 2001	0.4 to 32 mg/L	Nas and Berktay (2006)
UK, South Dorset	Fertilizer and livestock	2000-2001	6.78 to 8.86 mg/L as nitrate-N	Limbrick (2003)
USA, Alabama	Fertilizers, sewage breakthrough, animal waste	2006 and 2007	up to 121 mg/L	Murgulet and Tick (2009)
USA, Oregon	Septic tank effluent	2000	>1 to >10 mg/L nitrate-N	Hinkle *et al.* (2007)
USA, Texas	Fertilizer	2000-2008	0.05 to 473.7 mg/L	Enwright and Hudak (2009)
USA, Texas	Fertilizer, animal waste and mineralization of soil organic nitrogen	1990–98	0 to 1483.7 mg/L as nitrate-N	Hudak (2000)

such as rainfall. Understanding the crop needs and the current level of nitrate availability in soil and water used for irrigation will reduce the amount of fertilizer application.

Septic tank : One of the major sources for groundwater pollution is the on-site disposal of sewage through septic tanks and cesspits. With nitrates, pathogenic microbes occur as the other major co-contaminant. Usually the septic tanks contain nitrate concentration as less as 1 mg/L, but the concentration of ammonium varies from 20 to 55 mg/L (Canter, 1997). Oxidation of these ammonium ions may contribute to nitrate in groundwater through seepage.

Domestic wells located at shallow depths are more susceptible to contamination due to seepage from septic tanks. These tanks are designed to treat the solids, reduce their volume and prevent them from entering the wastewater disposal network, but do not treat the wastewater for nitrogen compounds (Mooers, 1996; MPCA, 1999). This type of waste disposal without pre-treatment requires continuous maintenance. These structures may fail due to clogging, improper design, construction, uneven distribution of effluent and frequency of sludge removal (Canter and Knox, 1985). Geological formation plays a significant role as the permeability of soil may reflect on the time taken for the liquid waste to reach the groundwater.

Due to high population density in cities, large number of sewage disposal systems is present. In rural areas, though the number of disposal systems is less, use of low cost material for construction may pose trouble. Both urban and rural areas are at risk of pollution by this source. Other factors that induce pollution are the presence of more oxygen for ammonium to convert to nitrate and the depth of wells from which groundwater is extracted for domestic use. Rosen *et al.* (2006) conducted a nitrogen mass balance study to calculate the total dissolved nitrogen potentially reaching the groundwater table in Nevada, USA which ranged from 25 to 29 mg/L. Recently efforts are on to recover the nutrients including nitrogen from wastewater and sewage sludge to use them as a resource (Bridle and Pritchard, 2004; Wang *et al.,* 2009; Zhang and Chen, 2009; Cai *et al.,* 2013; Guadie *et al.,* 2013).

Leakage from sewer lines : This is a common source of nitrate especially in urban groundwater. Wastewater disposal networks transport untreated raw sewage to the centralized treatment units. Industrial wastes connected to the common sewer lines may also contain nitrate alongwith other harmful chemicals. Cesspit waste disposal replaced with central sewage network helped substantially to decrease nitrate pollution in Israel (Avisar *et al.,* 2009). But, unexpected failure of these wastewater networks maybe due to improper installation, tree root invasion, worsening because of long time, seismic activity, land subsidence and flooding among other reasons. Significant outbreak from sewer lines and seepage to groundwater can be easily detected by change in colour, foul smell and unacceptable taste not only due to nitrate but by the presence of microbes, organics and other chemicals. Sewage from broken and leaking pipes pose a great risk for groundwater quality in Egypt increasing the nitrate concentration upto 85 mg/L (Abdalla and Scheytt, 2012).

Livestock wastes and manure storage : Animal excreta are rich source for nitrogen. Excreta, dung and urine from animals are a potential source for nitrate pollution alongwith potassium and pathogenic contamination of soil and water (Wakida and Lerner, 2005). Rearing of pets in urban areas and livestock activities for dairy, meat, fibre and labour will result in large amount of animal waste. Improper management of this manure can result in significant loading of nitrogen compounds into streams by runoff and groundwater though seepage. Usually in rural areas, agriculture and cattle farming are adopted as major activities. A total livestock population of 1.62 million in rural areas of Rajasthan, India can produce 42,055.07 tonne of nitrogen per year which are usually stored in heaps on unlined ground surface (Suthar *et al.,* 2009). In Wisconsin, USA, animal manure contributes to 300,000 tonne of nitrogen (Bundy *et al.,* 1994). When animal wastes are available in abundance and cost effective, the farmers may have a tendency to use large quantity of the manure as a substitute for synthetic fertilizers. Adopting such habits without knowing the existing soil conditions in an uncontrolled manner may increase pollution. Dead and decaying organic matter from the animals is another way for nitrogen to reach the soil and water. In rural areas of Southern India, nitrate level upto 1500 mg/L was reported due to leaching of excreta into groundwater (Jacks and Sharma, 1983).

Impact of climate change : Climate change occurring due to human induced stress may probably affect the nitrate content in groundwater globally. It is expected to affect the hydrological cycle with changes to recharge, groundwater levels and resources and flow processes (Stuart *et al.,* 2011). Also, the average surface temperature of the earth and the precipitation patterns has changed with raising levels of carbon dioxide and other greenhouse gases. All these processes may affect the agricultural nitrate source term through changes in both soil processes and agricultural productivity (Stuart *et al.,* 2011). Nutrient loads are expected to increase under climate change (Bouraoui *et al.,* 2002) that may lead to eutrophication. Somers and Savard (2008) stated that with current land-use practices in Prince Edward Island, Canada, the nitrate content in groundwater will increase by over 10% by the year 2050 and considering the potential adaptations to climate change by the agricultural sector this increase could triple. Whitehead *et al.* (2006) simulated the effects of nutrients released from agriculture and from sewage treatment on the river Kennet in terms of projected nitrate and ammonia concentrations which increased over time as higher temperatures enhance nitrogen release from the soil and lower river flows reduce the dilution capacity of the river. Many researchers have modeled the potential impact of climate change on nitrate load (Ye and Grimm, 2013; Martínková *et al.,* 2011; Whitehead *et al.,* 2006; Ferrier *et al.,* 1995).

Soil pollution : Mining and sanitary landfill, improper solid waste disposal in heaps, sludge spreading, applying treated wastewater to agricultural lands, etc., can contaminate the soil. Application of treated sewage effluent for pasture irrigation threatened the long term sustainability of the practice due to high content of nutrients (Gwenzi and Munondo, 2008). Application of wastewater rich in nutrients in peri-urban Pakistan lead to high concentration of heavy metals in soil, crops and groundwater (Ullah *et al.,* 2012). Though the authors did not study the nitrate content in groundwater, it is expected to be high.

Content of nitrate in landfill leachate varies from country to country. Landfill leachate has nitrate content upto 440 mg/L (Ministry of Health, Palestine, 2001) and had raised the nitrate level in groundwater around 2 landfill sites upto 119 mg/L in Gaza (Alslaibi *et al.,* 2011). In India, leachate had nitrate level of 115 mg/L after rainfall and 55 mg/L during pre-monsoon (Kale *et al.,* 2010) indicating the increase in concentration due to rainfall percolation. Nitrate in groundwater of this area varied from 1 to 90 mg/L. Another site in India (Gazipur, Delhi) recorded nitrate in leachate as 380 mg/L and surrounding groundwater till 56 mg/L (Mor *et al.,* 2006). Apart from these, the dead and decaying animals and plants add to soil organic nitrogen. Other cause of soil contamination is excess fertilizer application more than the assimilation level of crops.

Industries : Industries, mining, military and agriculture sectors require nitrogen based compounds for various purposes. Nitrogen as liquid or gas is widely used in aerospace, aircraft, transportation equipment, chemicals, energy sector, food and beverage, healthcare, metal production, oil and gas, pharmaceutical, biotechnology, refining, welding, metal fabrication (Praxair, 2013) to name a few apart from other applications. Commonly used industrial forms of nitrogen are ammonia, organic nitrates, nitric acid, urea and cyanides. Gaseous emission and chemical spillage if any during the industrial processes may contribute nitrate to the environment. Wastewater from fertilizer manufacturing and other industries reach the sewer network. Emission of nitrogen gas from industrial operations is another source.

Atmospheric deposition : Gaseous emission of nitrogen compounds in the atmosphere is through vehicular exhausts, combustion of fossil fuels, industrial emissions, etc. Many disasters involving burst of ammonium nitrate storing units due to inadequate handling or unexpected accidents, like fire have been reported. This potentially hazardous chemical is also largely used in making explosives. Ammonia emissions from animal farming also account for the atmospheric deposition. The nitrogenous compounds reach soil and subsequently aquatic resources by rain, snow and particulate matter, such as dust and droplets (Puckett, 1994).

Urban fertilizer use : Fertilizers are not just used in agricultural areas but also in urban areas, like house lawns, gardens and golf courses. Amador *et al.* (2007) studied the leaching losses of nitrate-N ranged from 0.17 kg N/ha in the woodlands to 34.97 kg N/ha under ground covers. More than 150,000 km^2 of urban grasslands add to potential residential and commercial landscaping fertilizer applications in Maryland, USA (Groffman *et al.,* 2009). Golf courses, operational and as well as under construction displayed high nitrate concentrations in streams on courses indicating input from fertilizer applications in excess of turf requirements in Toronto, Canada (Winter and Dillon, 2005). Surface water bodies, like creeks, ponds and coastal areas passing through or adjacent to golf courses had high nitrate due to fertilizers (Mallin and Wheeler, 2000; Lewis *et al.,* 2002) which may eventually lead to groundwater pollution. Urban runoff from the mentioned sources as well as from roads and highways having fine deposits of vehicular exhausts may also be a source of nitrate pollution.

Other source

Due to hydraulic connectivity between groundwater and surface water, nitrate levels in one resource can pollute the other. Mixing of soil during house building provides aeration for soil microbes to accumulate nitrate. Wakida (2002) estimated potential nitrate loss from construction sites as 59 kg N/ha/year. Direction of groundwater flow and regional geological formation also affects nitrate concentration dynamically. Seasonal variations in nitrate concentration are due to local recharge and discharge, source of pollution, changes in precipitation and evaporation, groundwater level fluctuation (Kaçaroglu and Günay, 1997; Nas and Berktay, 2006). In several cases, multiple sources attribute to nitrate pollution. Handa (1975), (from Majumdar and Gupta, 2000) observed nitrate in shallow aquifers upto 100 mg/L in humid areas and 1000 mg/L in arid and semi arid regions of India due to animal or human sources or irrigation return flows. Isotopic studies now made it possible to differentiate the contribution of nitrate from natural, agricultural, animal waste and other sources. Shomar *et al.,* (2008) differentiated the main sources of nitrate pollution in groundwater to be primarily from manure and septic effluents followed by sludge and synthetic fertilizers in Gaza. Some published cases around the world on various concentrations of nitrate and their sources are tabulated in table 1.

TOXICOLOGICAL EFFECT

Human exposure to nitrogen may be by means of plants and animals as food, soil, atmosphere and groundwater. Of these modes, vulnerability in the form of nitrate is through dietary intake, that is groundwater used for drinking and domestic purpose as well as plants and animals as vegetables and meat, respectively. Ingestion of nitrate higher than the permissible limit for consumption may lead to deleterious effects on the human body. However, nitrate as such is not of direct health concern, but they undergo metabolic reactions in the human body to form nitrite and nitrosoamines which pose the threat (Tirado, 2007).

Many studies have compiled the health effects

Table 2. *Water quality standard for nitrate and nitrite, in mg/L*

Nitrogen compound	USEPA (1997)	WHO (1984)	European Union (EC, 1998)	Canada (Health Canada, 2012)	China (Ministry of Envir-onmental Protection China, 2002)	India (BIS, 2003)	Australia (NHMRC, NRMMC, 2011)	New Zealand (Ministry of Health, New Zealand, 2008)
Nitrate	45	50	50	45	-	45	50	50
Nitrite	-	-	0.50	3.2	-	-	3	0.2 (long term) 3 (short term)
Nitrate-N	10	-	-	10	10	-	-	-
Nitrite-N	1	-	-	1	-	-	-	-
Nitrate-N + Nitrite-N	10	-	-	-	-	-	-	-

due to nitrogen compounds (Anjana *et al.,* 2007; Bryan and van Grinsven, 2013; Gupta *et al.,* 2008; Ward *et al.,* 2005; Fan and Steinberg, 1996). Methemoglobinemia is the widely known health issue due to consumption of high nitrate food and water. Other health impacts include cancer, increased infant mortality, abortions, birth defects, recurrent diarrhoea, recurrent stomatitis, histopathological changes in cardiac muscles, alveoli of lungs and adrenal glands, deterioration of immune system of the body, hypertension, thyroid hypertrophy (Gupta *et al.,* 2008; Teton and Sorenson, 2002; Fan, 2011).

Negative effects of high concentration of nitrate not only affect humans but also livestock, marine biota and agricultural crop growth. The maximum contaminant level (MCL) for nitrate in drinking water is 45 mg/L as nitrate and 10 mg/L as nitrate-N. Several countries and international organisations have set forth standards for the maximum permissible limit for nitrate and nitrite in drinking water (Table 2).

In the United States, the average intake of nitrate per person is about 40 to100 mg/day (California Environmental Protection Agency, 1997) and 0.3 to 2.6 mg/day/person for nitrite which is primarily from cured meat (National Academy of Sciences, 1981). The mean dietary intake of nitrate in Europe is about 50 to 140 mg/day/person and nitrite intake is from < 0.1 to 8.7 mg/day/person (FAO/WHO, 1995). Similarly the average dietary intake of nitrate has been studied in various countries by many researchers. Results of various studies cited here are compiled from WHO (2011) and European Commission (EC, 1997) which show a wide variation in the mean nitrate uptake level in of many countries. In Belgium, the mean intake was 154 mg/day (Dejonckheere *et al.,* 1994); in Finland it was 54 mg/day (Laitinen *et al.,* 1993); France was 121 mg/day according to Cornee *et al.* (1992) and 141 mg/day/person according to EFSA (2008); in Germany calculated daily intakes for males and females was maximum 422 mg/day and 310 mg/day, respectively (Anonymous, 1994) while Bonnell (1995) reported the total daily intake of nitrate to range from 70 to 110 mg/day/person; in the Netherlands it was reported to be about 143 mg/day (van Duijvenbooden and Matthijsen, 1989); in Denmark from 70 to 172 mg/day as per Bonnell (1995) and 54 mg/day was estimated by Mortensen and Larsen (1989) and National Food Agency of Denmark (1990). WHO (2011) reported the estimated total daily intake of nitrate in the United Kingdom ranged from 50 to 81 mg/person (Bonnell, 1995; Schuddeboom, 1995; EFSA, 2008) indicated average nitrate consumption was 91 mg/day/person. Mean chronic daily intake of nitrate was 0.051 mg/kg/person in Malaysia (Jamaludin *et al.,* 2013).

Methemoglobinemia

Of the several toxicological effects of high nitrate intake, methemoglobinemia or widely called as 'blue-baby' syndrome is known from long ago to have adverse effects (Comly, 1945). This disease caused by high nitrate consumption happens due to the conversion of nitrate to nitrite mediated by bacteria in the mouth and the gastrointestinal track of humans (Comly, 1987). Of the ingested nitrate, 20% is reduced by bacteria in the saliva to nitrite while most of the nitrate is reduced in the digestive track and stomach under suitable conditions. Nitrite which enters the bloodstream causes oxidation of hemoglobin to methemoglobinemia which reduces the ability of red blood cells to carry oxygen.

The 'heme' group in the hemoglobin comprises of ferrous ion which facilitate to carry oxygen to the tissues. Nitrite oxidises this ferrous ion to ferric ion and disrupts the hemoglobin from carrying oxygen as it is converted to methemoglobinemia (Fan *et al.,* 1987). This results in cyanosis and asphyxia (WHO, 2007). Mainly infants less than 6 months old are adversely affected by the consumption of water containing high concentration of nitrate. This is because of the fact that they possess less oxidisable hemoglobin than the adults and hence there is quick conversion of all the hemoglobin to methemoglobinemia resulting in hypoxia (Comly, 1987). Comly (1945, 1987) also relates this possibility to the stronger bonding of nitrite ions with the hemoglobin of infants due to immaturity of certain enzymes. The excretory power of the kidneys in infants will also be less and may retain the nitrite for a long time. Due to hypoxia, the children develop blueness of the skin and hence the disease is also called 'blue baby syndrome'. This may lead to serious illness and even death. Vitamin C has been shown to have a protective effect (Fan, 2011) and methylene blue is an effective antidote (Orgeron *et al.,* 1957). Walton (1951) reviewed various cases of infant methemoglobinemia in USA. Drinking water having nitrate nitrogen levels between 22.9 and 27.4 mg/L from wells caused methemoglobinemia in 2 infants in Wisconsin, USA (Knobeloch *et al.,* 2000). Recurrent acute respiratory tract infections in infants most likely caused by methemoglobinemia were noted by Gupta *et al.,* (2000a). Gupta *et al.* (2000b) also observed high methaemoglobin levels in the age group of less than 1 and above 18 years while people between 1 to 18 years had less methaemoglobin level probably due to better cytochrome b_5 reductase activity and its adaptation to increasing nitrate concentration in water thus reducing the rick of the disease.

Cancer and genotoxic effect

Of the ingested nitrate, 25% is actively secreted into saliva of which 20% is reduced to nitrite (Spiegelhalter *et al.,* 1976; WHO, 2007). Similar reaction can also occur in the intestine and colon (Ward *et al.,* 2005). Like the reduction of nitrate to nitrite leading to methemoglobinemia, the nitrites also react with amines to form nitrosamines or N-nitro compounds which are potentially carcinogenic. This process of conversion of nitrites to nitrosamines or N-nitro compounds is called nitrosation. The carcinogenicity of N-nitro compounds was realised in 1967 and about 300 different *N*-nitrosamines are known to cause cancer in nearly 30 animal species (Gilli *et al.,* 1984; Hill, 1999; Hecht, 1997).

A clear association between ingested nitrate and cancer rick is considered to be not clearly known. Adequate evidence to prove the cause of cancer by ingestion of nitrates or nitrites is lacking (van Grinsven *et al.,* 2006; Gangolli *et al*., 1994; WHO, 1998. Speijers and Van Den Brandt, 2003; USEPA, 1998a). Possibility of ingested nitrate or nitrite resulting in endogenous nitrosation may be considered to be carcinogenic to humans (Speijers *et al.,* 1989; FAO/WHO, 1996, 2003a,b; IARC, 2010). Several cases of stomach and oesophageal cancer reported worldwide due to nitrates and nitrites have been compiled by IARC (2010).

Studies in Taiwan (Yang *et al.,* 1997) and the Netherlands (van Loon *et al.,* 1998) to understand the possible link between the risk of gastric cancer and nitrate intake have shown negative association. Exposure level and the relative risk of stomach, bladder, prostrate and colon cancer due to consumption of water with high nitrate concentration showed a positive correlation in the population of Spain (Morales-Suarez-Varela *et al.,* 1995). Few other reported cases include thyroid cancer (Kilfoy *et al.,* 2011), gastric cancer (González *et al.,* 2006; Katers and Zanoni, 1998), brain, oesophageal and nasopharyngeal cancers (Eichholzer and Gutzwiller, 1998), colon cancer (De Roos *et al.,* 2003), non-Hodgkin's Lymphoma (Nolan *et al.,* 1997; Ward *et al.,* 1996; Freedman 2000; Weyer *et al.,* 2001) and bladder cancer (Ward *et al.,* 2003).

Genotoxic effects were observed on humans consuming high nitrate in a part of Argentina (Poli *et al.,* 2012). These effects can cause damages to the genetic information in human calls resulting in mutations in future. Kleinjans *et al.* (1991) studied chromosomal damage in the peripheral lymphocytes of human populations exposed to different levels of nitrate which showed dose-dependent increases in nitrate body load, but does not appear to be associated with peripheral lymphocyte sister chromatid exchange frequencies. However, these issues are still debated upon due to lack of evidence and it not yet confirmative that ingestion of high nitrate is the only reason for these health issues.

Spontaneous abortion and developmental effect

Spontaneous abortions, stillbirths, premature birth, or intrauterine growth retardation have been related to high nitrate in drinking water (Ward *et al.,* 2005; Manassaram *et al.,* 2006). Fewtrell (2004); Morbidity and Mortality Weekly Report (1996); Speijers *et al.* (1989) and FAO/WHO (1996) also linked possibility of high nitrate ingestion with spontaneous abortions. Adverse reproductive effects in animals were observed when exposed to extremely high levels of nitrate and nitrite (Fan *et al.,* 1987, 1996). Associations between nitrate in drinking water and congenital malformations have also been researched (Ward *et al.,* 2005). High nitrate in drinking water supplied to pregnant mothers and congenital malformation was investigated in Australia (Scragg *et al.,* 1982; Dorsch *et al.,* 1984). Nevertheless all these conclusions are still in experimental stages and needs further studies.

Cardiovascular effect and hypertension

Hypertension was reported by Malberg *et al.,* (1978) in humans exposed to nitrate in the age group of 50-59 years. Studies associating cardiovascular effects with nitrate levels in drinking water have given inconsistent results (WHO, 1985b).

Thyroid hypertrophy

Nitrate can suppress thyroid activity by inhibiting iodine metabolism and induce hypertrophic changes (Bloomfield *et al.,* 1961). Effects on thyroid due to nitrate depend on the availability of iodine in the human system (WHO, 2007). No effects on thyroid function or thyroid hormones plasma concentrations were observed at exposure to 15 mg/kg of sodium nitrate among humans (Hunault *et al.,* 2007). But, van Maanen *et al.,* (1994) observed difference in the volume of thyroid in different exposure groups and development of hypertrophy at nitrate concentrations above 50 mg/L.

Health benefit

Health benefits of nitrate in humans also exist. Nitric oxide formed within the human body from the ingested nitrate nitric oxide has beneficial effects, like blood pressure reduction, inhibition of platelet aggregation, vasoprotective activity, prevent cardiovascular disease and type 2 diabetes (Lundberg *et al.,* 2011; Webb *et al.,* 2008; McKnight *et al.,* 1999). Formation of nitric oxide endogenously due to nitrate ingestion is considered beneficial to the human body as nitric oxide is the most important molecule in regulating blood pressure and maintaining vascular homeostasis (Bryan and van Grinsven, 2013). Other significance of nitrate and its endogenous products are given in Lundberg *et al.* (2011) and Bryan and van Grinsven (2013).

To date, of the several health effects on humans, only methemoglobinemia is profoundly confirmed to be caused by consuming water with high nitrate. Cancer, cardiovascular issues and many other health problems due to consumption of nitrate need of in depth investigation for conformation and for now, people consuming high nitrate are considered to be at the risk of acquiring these diseases (Ward *et al.,* 2011; Bryan and van Grinsven, 2013). With the emergence of evidence for the beneficial effects due to nitrate in the human system, Lundberg *et al.* (2011) predicts that nitrate might be recognized as an essential nutrient in future.

Environmental issue

Eutrophication : Excess nitrate leads to a serious environmental issue that degrades the water quality of surface water bodies, like ponds, lakes, reservoirs, etc. In 1968, Vollenweider (1968) first reported the combined effect of nitrogen and phosphorous leading to eutrophication, a problem due to excessive growth of aquatic plants resulting due to abundance availability of nutrients. Nitrates reach the surface water bodies through natural processes, like surface runoff, erosion and groundwater-surface water interaction (Figure 1). Of these processes, runoff and erosion contribute to most of the nitrates in surface water bodies. Due the over availability of nutrients, the phytoplankton and algae in the water bodies grow excessively leading to a shortage of dissolved oxygen available for growth of various aquatic species. This population increase of algae causing the change of colour of water is also called as 'algal bloom'. Oxygen shortage affects the growth of fish and other species in the aquatic ecosystem including the plants. Due to overcrowding, the aquatic death rate of plants and fish increase and make the water unsuitable for any intended use due to the bad odour and taste. The problem worsens if the algae produce biotoxins that can affect both marine organisms and humans if the water is used for urban supply (Anderson *et al.,* 2002, 2008; Viviani, 1992; Shumway, 1990). Anderson *et al.* (2002) reviewed some cases of eutrophication in Chesapeake Bay and the Albemarle-Pamlico estuaries in USA, Inland Sea of Japan, the Black Sea and Chinese coastal waters. High phytoplankton biomass and productivity due to excess nutrients resulted in red tide problems in Bohai Bay, China (Jingzhong, 1985) and Dokai Bay, Japan (Tada *et al.,* 2001).

Animal health issue : Negative impact on animal health is possible due to high nitrate ingestion through water or by the accumulated nitrate in plants that they consume. Nitrate levels above 100 mg/L can affect animals similar to humans (Self and Waskom, 1992). Methemoglobinemia is also observed in animals especially ruminants (National Academy of Sciences, 1972) as they have the capability to convert nitrate to nitrite and then to ammonia and bacterial protein by the microorganisms. Non-ruminants are unable to do this but monogastric animals exposed to high nitrate exhibit severe gastritis. Nitrite is capable of inducing methem-oglobinemia in a wide range of species, that is cattle, sheep, swine, dogs, guinea pigs, rats, chickens and turkeys (Bruning-Fann and Kaneene, 1993). The level of toxicity will differ from species to species and also the rate of consumption of nitrate contaminated water and food. Clinical signs of acute nitrate poisoning in cattle include depression, respiratory distress, tremors, ataxia, rapid heartbeat and terminal convulsions (Puschner, 2008). Other symptoms include abdominal pain, diarrhea, muscular weakness or poor coordination, change of blood colour from red to brown or chocolate colour, decreased feed consumption and interference with vitamin A and E metabolism (Teton and Sorenson, 2002; Bruning-Fann and Kaneene, 1993). Effect on animals in their younger age is more than in adult animals due to the same reason as in humans. Safe levels of $\%NO_3$ and $\%NO_3$-N for various livestock is <0.5 and <0.12, respectively on a dry (moisture free) basis (Yaremcio, 1991). Concentration above 1 as $\%NO_3$ and 0.23 as % NO_3-N are harmful and can cause death and abortions in beef cattle and sheep (Johns and Yaremcio, 2004, revised 2008). Long term exposure to 10 mg/L of

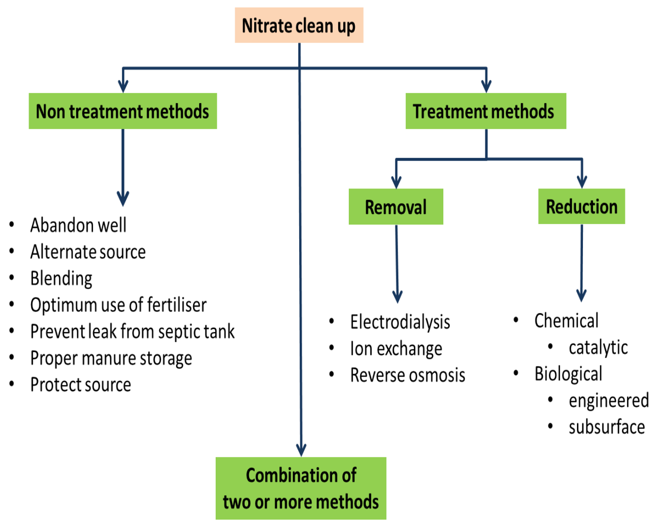

Figure 2. *Methods of nitrate removal from groundwater*

nitrate-N can adversely affect freshwater invertebrates, fishes and amphibians (Camargo *et al.,* 2005).

Accumulation in food : Most of the nitrate reaches the human body through the food as in vegetables and meat depending on the diet rather than from drinking water. Nitrate concentration in plants may increase due to wide possibility of reasons, like excess fertilizers, drought, cloudy weather and low temperature (Puschner, 2008). Vegetables can be broadly classified into 3 groups based on their nitrate content as : (i) High (> 1000 mg/kg)–beetroot, lettuce, spinach, other green leafy vegetables and herbs; (ii) average (50 to 1000 mg/kg) – potatoes and other vegetables; (iii) low (0.5 to 50 mg/kg)–berries, fruits, cereals, pod vegetables (Tamme *et al.,* 2006). Nitrate ranged between 54 and 2440 mg/kg, while nitrite levels ranged between 1.1 and 57 mg/kg in different varieties of cabbage, lettuce, spinaches, parsley and turnips in Portugal (Correia *et al.,* 2010). Nitrate content of cereals ranged from 20 to 76 ppm; pulses, 39 to 114 ppm; leafy vegetables, 30 to 270 ppm; nuts and oil seeds, 8 to 113 ppm; other vegetables 180 to 4000 ppm; roots and tubers 31 to 2043 ppm and in condiments and spices, 145 to 4680 ppm in Andhra Pradesh (Gundimeda *et al.,* 1993). Nitrate in cured meat, that is preserved with sodium nitrate may also result in negative health effects. In general, 80 to 95% of nitrate is contributed by vegetables while the prime source of nitrite is cured meat (Pennington, 1998; Ximenes *et al.* 2000; Wogan *et al.,* 1995; Walker, 1990). Average nitrite in fish was recorded 1.2 mg/kg in United Kingdom (U.K., Ministry of Agriculture, Fisheries and Food, 1992). Meat, and meat products contributed 69% of nitrite intakes in Finland (Laitinen *et al.,* 1993) and 28% from cured meat in France (Cornee *et al.,* 1992). All these studies emphasis the need to follow the guidelines as per European Commission (EC, 2002, 2004, 2005) to ensure safe level of ingestion of nitrate from vegetables.

REMOVAL TECHNIQUE

Sophisticated techniques as well as remediation of nitrate pollution without treatment, that is not using chemicals or microbes, by best management practices is also available (Figure 2). Some of the existing and emerging options for nitrate removal are discussed.

Treatment method

Largely targeted to treat potable drinking water these involve either removal or reduction of nitrate. Due to the high soluble nature of nitrate, its removal by chemical coagulation and lime softening are not feasible. Other best available methods are briefly explained and their pros and cons based on Jensen *et al.,* (2012), Kapoor and Viraraghavan (1997), Teton and Sorensen (2002), Shrimali and Singh (2001) and others are tabulated in table 3.

Electrodialysis : Groundwater containing nitrate ions is passed through semipermeable membranes using direct electric current. Membranes allow the ions to pass through them by diffusion, that is from highly concentrated place to less concentrated place. These membranes are either cation or anion selective and so allow only ions of interest to pass through them. Usually in the treatment process, multiple membranes are placed in a row with alternative cation selective membrane and anion selective membrane so that the cation selective membranes with negative charge will reject

Table 3. *Nitrate removal method : Advantage and disadvantage* (Jensen et al., 2012; Kapoor and Viraraghavan, 1997; Teton and Sorensen, 2002 and others)

Treatment method	Advantage	Disadvantage
Electrodialysis	No harmful chemicals Less pre-treatment Long lasting membranes Selective removal of target species Relatively insensitive to pH and temperature Can operate at high TDS Flexibility in removal rate through voltage control Better water recovery (lower waste volume) Feasible automation Multiple contaminant removal	Disposal of brine Sensitive to hardness, iron, manganese, suspended solids, hydrogen sulphide and chloride High operation and maintenance demands High capital cost Need to vent gaseous byproducts Potential for precipitation with high recovery High system complexity
Ion exchange	Best understood and widely used Multiple contaminant removal Selective nitrate removal Low capital cost Relatively simple to operate Use in small and large systems Ability to automate	Disposal of waste brine Potential for nitrate dumping specifically for non-selective resin use for high sulphate waters Pre-treatment to remove hardness, iron, manganese, suspended solids, organic matter and chlorine to prevent anion resin fouling Requires post-treatment due to corrosivity of product water Large volume of salt required for regeneration
Reverse osmosis	High quality product water Multiple contaminant removal Feasible automation Relatively easy to operate	Disposal of waste concentrate Typically high capital, operational and maintenance costs due to power consumption Need to address membrane susceptibility to hardness, iron, manganese, suspended solids, silica, organic matter, and chlorine Sensitive to pH and pressure variation High energy demands Lack of control over target constituents
Chemical denitrification	Conversion of nitrate to other Nitrogen species No brine or concentrate waste stream Potential for more sustainable treatment High water recovery Multiple contaminant removal	Potential reduction of nitrate beyond nitrogen gas to ammonia Possibility of partial denitrification Possible dependence of performance on pH, temperature and iron Lack of full-scale chemical denitrification systems resulting in unknown reliability, costs and operational complications

Continued...

Biological denitrification	High water recovery No brine or waste concentrate Low sludge waste Less expensive operation Limited chemical input Low land area required Increased sustainability Complete nitrate removal	Need for substrate and nutrient addition High monitoring needs Significant post-treatment requirements due to risk of bacterial contamination High capital costs Sensitivity to environmental conditions Possibility of partial denitrification

the negative charged ions and allow positive charge ions to flow through it. Anion selective membrane which is positively charged and is placed next to the cation selective membrane will allow the negatively charged ions to flow through. Most ions are removed from the groundwater by this method and the concentrated brine solution containing excess amount of most ions remains. Not only that this method involves huge initial investment and high cost of operation and maintenance, also the proper disposal of the resulting concentrated brine is an impediment.

Ion exchange : One of the most successful and commonly used methods to date involves passing the contaminated water through a resin bed containing a strong base anion wherein the nitrates are removed. These resins are in the form of beads and provide high surface area for ion exchange. Groundwater with high nitrate is passed through an anion exchange resin where the negatively charged nitrate ions are exchanged for negatively charged chloride or bicarbonate ions on the resin. When all the negatively charged sites on the resin are exchanged for nitrate, that is the resin is exhausted, it is regenerated by back washing with sodium chloride or sodium bicarbonate and can be reused. However, the challenge is to dispose the brine which is rich in nitrate, sodium, chloride and bicarbonate ions by environmentally safe techniques. Other considerations include pretreatment to avoid resin fouling, cost of nitrate selective resins and frequency of replacing these resins. It may be an ineffective if the water contains high concentration of total dissolved solids and sulphate as it may compete with the nitrate to exchange with other negative ions on the resin. Though ion exchange in comparison with other methods has lower capital costs, the costs involved with regeneration of the resin and treatment and disposal of the brine are high.

Reverse osmosis : Reverse osmosis is a general water purification method wherein nitrate as well as other ions is removed by forcing water across a semipermeable membrane. In normal osmosis, water with ions spontaneously moves from the side where the concentration is low to the side where the concentration of ions is high through a membrane. This is reversed by applying pressure (exceeding the corresponding osmotic pressure) ranging from 300 to 1,500 psi (Kapoor and Viraraghavan, 1997) on the high concentration side to reverse the process and allow water to flow from concentrated solution side to the less concentrated solution across the semipermeable membrane and hence the term reverse osmosis. Cellulose acetate, polyamides and composite materials are used as semipermeable membranes. Common problems associated with reverse osmosis membranes include fouling, scaling, compaction and deterioration with time. Hindrance to this technique result from the deposition of soluble materials, organic matter, suspended and colloidal particles and other contaminants, variation in pH and chlorine exposure (Kapoor and Viraraghavan, 1997). This technique may be used as a pre-treatment for ion exchange because it removes a large percentage of sulphate.

Chemical denitrification : Reduction of nitrate to nitrogen gas with the help of chemicals can help to bring down the nitrate content in groundwater. Chemical denitrification is accomplished by use of metals, such as iron and aluminium (Kapoor and Viraraghavan, 1997). Due to high costs, large quantities if iron sludge produced during the process and the requirement of removal of ammonia by air striping, the denitrification using ferrous iron (equation 1) in the presence of a copper catalyst was not preferred (Sorg, 1978).

$$NO_3^- + 8Fe(OH)_2 + 6H_2O \rightarrow NH_3 + 8Fe(OH)_3 + OH^- \quad ...(1)$$

Powdered aluminum reduces nitrate to nitrite (equation 2) and then to either ammonia (equation 3) or nitrogen gas (equation 4) at optimum pH of 10.25 as per following reactions :

$$3NO_3^- + 2Al + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_3 \quad ...(2)$$

$$NO_2^- + 2Al + 5H_2O \rightarrow NH_3 + 2Al(OH)_3 + OH^- \quad ...(3)$$

$$2NO_2^- + 2Al + 4H_2O \rightarrow N_2 + 2Al(OH)_3 + 2OH^- \quad ...(4)$$

Loss of aluminum due to its reaction with water (equation 5) was less than 2% at pH between 9.1 and 9.3 (Murphy, 1991). This method, should be complemented with other methods, such as air stripping to remove ammonia which is the principle reaction product (60-95%).

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \quad ...(5)$$

When metals catalysts, for example palladium alumina are used to facilitate the reduction, it is referred as catalytic denitrification. In recent times, many metals and nanoparticles have been used for the removal of nitrate, such as sulphamic acid and zinc metal (Sabzali *et al.,* 2006), zero-valent magnesium (Kumar and Chakraborty, 2006) and zero-valent iron (Choe *et al.,* 2000). Chen *et al.* (2003) used powder catalysts and catalytic membranes for denitrification which had an efficiency of 80%. Palladium, platinum and rhodium were tested as catalysts by Reddy and Lin (2000). This method highly depends on pH, temperature, total reaction time, initial concentration of nitrate and the presence of other ions in water.

Biological denitrification : Reduction of nitrate to nitrogen gas occurs by bacterial activity under anoxic conditions. This can either be engineered or occur naturally in the subsurface environment both of which have been tested. Heterotrophic as well as autotrophic bacteria facilitate denitrification and the overall process in the reduction of nitrate to nitrogen gas proceeds in 4 steps as follows:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad ...(6)$$

Ethanol, methanol, acetate and other organic carbon substrate are supplied as the food source to facilitate the heterotrophic denitrification (Washington State Department of Health, 2005) which is widely preferred than autotrophic denitrification. Inorganic energy source, for example sulphur, reduced sulphur species or hydrogen is essential for autotrophic denitrification. In this case, the carbon source is from the bicarbonate in water. A detailed review of the microbiology and stoichiometry of biological denitrification is available from Matejù *et al.* (1992). *In situ* biological denitrification by means of subsurface permeable barriers of sand or gravel rich in organic carbon source derived from woodchips, straw, or sawdust can be constructed perpendicular to the groundwater flow direction (Washington State Department of Health, 2005) or various carbon sources can be injected through injection wells into aquifers at a distance from the supply wells to enhance the process. However, it is very expensive and requires proper maintenance. Bioremediation using *Pseudomonas* and *Bacillus*, aquatic plants, like *Lemma, Wolffia*, urticularia and pteridophites, etc., have also been studied (Rao and Puttanna, 2006).

Some of these methods have been combined to remove nitrate, such as ion exchange and biological denitrification (Matejù *et al.,* 1992; Kapoor and Viraraghavan, 1997). These treatment methods are usually adopted for treatment of potable water in urban cities that include considerable investment in the form of capital costs and operations and maintenance costs which vary based on the system design and capacity. Full scale implementation of these methods for potable water treatment has been adopted around the world except for chemical denitrification which requires further research. Biological denitrification is the most common potable water treatment method adopted in Europe and is being tested in the Unites States (Kapoor and Viraraghavan, 1997; Jensen *et al.,* 2012). Heterotrophic denitrification is widely preferred than autotrophic denitrification when it comes to drinking water treatment (Matejù *et al.,* 1992). Comparatively, ion exchange has been the least expensive removal technology for nitrate following which biological denitrification is widely used. Due to the challenges associated with brine disposal in ion exchange, reverse osmosis and electrodialysis, destruction of nitrate by both biological and chemical denitrification has greater prospects in future if full scale application of these methods provides consistent success. It should be understood that no single treatment option can be considered best for nitrate removal (Jensen *et al.,* 2012) as these methods are site specific, that is depends on the concentration of nitrate ions in groundwater, its sources, presence of co-contaminants, volume that need to be treated, output required and investment possible.

Non treatment option

These are methods that do not involve treatment and are best management options that are sustainable, less expensive and should be given first priority (Jensen *et al.,* 2012). Non treatment methods are a common choice to treat groundwater locally or regionally when remediation by pump and treat is extremely expensive and technically not feasible. These options include a wide choice, such as abandoning contaminated wells and look for an alternate source of water for intake, protecting the source, developing an alternate source, optimum use of fertilizers, preventing animal waste and septic tanks from contamination, proper construction of wells, etc. Artificial recharge of rainwater to reduce the overall ionic content in groundwater can also be useful. To overcome the problem of groundwater pollution due to nitrate, it is better to prevent, such as situation.

Blending : A very simple non-treatment method is to mix water from multiple wells or sites having high and low concentration of nitrates to arrive at a desired nitrate concentration in water for supply and use. No chemicals are required for this process and no harmful waste are created during the process making it safe unless the nitrate concentration is monitored continuously. Initial cost may be significant if the high and low nitrate areas are located far apart. Installation of new wells may be required for the blending purpose.

Optimum use of fertilizer : Agriculture fertilizers have known to contribute to nitrate pollution in groundwater significantly. To reduce the impact, quantity of fertilizer applied could be cut down if nitrogen already present in soil and water of an area are computed. This brings down the amount of fertilizer, that is essential for the crops. Soil fertility is also maintained for a longer time. Water with relatively high nitrate can be used for irrigation for supplying the necessary nitrogen for the plants. This reduces not only the amount of fertilizer but also the cost spent on them. Organic farming is an alternate option to preserve the soil and water environment. To promote environmentally friendly growth in fertilizer use and supply in 2020, Bumb and Baanante (1996) suggested a complex management option of a conducive and stable policy environment, including macroeconomic stability, price incentives, credit availability, efficient organizational arrangements, research and extension support, regulatory frameworks and environmental monitoring will be essential.

Animal manure : Storing the animal wastes on properly lined surfaces and pits is essential. Concrete surfaces prevent the leaching of the animal waste rich in nitrate and from reaching the water table. Installing a common community manure storage sites in rural areas is useful and convenient. The stored animal waste can be used as an alternate source of nitrogen for plants and could be beneficial helping to reduce the fertilizer use. Placing of wells at appropriate distance from septic tanks and manure storage sites is essential.

Seepage from septic tank : Pollution from septic tank can be prevented by adopting proper construction and sewer leakage control. Regulating and placing the groundwater extraction wells at proper distance from the septic tanks considering the topography and groundwater flow conditions is important as pollution from septic tanks result not only in nitrate contamination but also pathogens. Standards differ from country to country for placement of septic tanks. Normally, septic tanks are located at a distance of 50 feet from well and manure stacks at a distance of 250 feet (Water well setback distances, 1998). It's also essential to clean and maintain the septic tanks every 3 to 5 years.

Prevention : All 'clean up' processes require investment of money and time. It is better to prevent a problem from occurring rather than remediate the environment to its original state after the unexpected has occurred. This includes appropriate protection of the origin and management of the groundwater resource as well as the sources of nitrate. One possible option is the optimum use of fertilizers and the alternate profitable use of animal manure which were discussed before.

These non-treatment options are not mainly targeted to treat groundwater for drinking purpose but to reduce the overall nitrate pollution in groundwater. Except for blending, other non-treatment options does not involve any cost. Regions with nitrate levels beyond few mg/L of the prescribed limits can be managed by these methods. But if nitrate levels significantly exceed the limits in areas where groundwater is used for drinking, these techniques can be used as a pre-treatment measure to reduce the costs on nitrate removal or reduction methods mentioned earlier. Following these methods in regions with high nitrate groundwater around the world will avoid degradation of groundwater and help to protect the resource.

SUMMARY AND CONCLUSION

Nitrogen is an abundant element forming about 78% of the earth's atmosphere and is essential for all life forms as organic nitrogen is present in nucleotides of cells and aminoacids which are the building blocks of nucleic acids (DNA, RNA) and proteins, respectively. Though a good understanding of the important processes of the nitrogen cycle, that is nitrogen fixation, ammonification or mineralization, plant uptake and immobilization, nitrification, denitrification and volatilization is developed, the environmental significance of other nitrogen transformations, such as the dissimilatory nitrate reduction to ammonium and the recently discovered anammox are not fully known. Maximum contaminant level for nitrate in drinking water is 45 mg/L as nitrate and 10 mg/L as nitrate-N. These standards also vary in different countries. Ingesting nitrate above these limits through drinking water or food and vegetables can cause gastrointestinal track illness in humans. Another widely known toxicological effect of high nitrate intake is methemoglobinemia. Though incidences of cancer, genotoxic effects, spontaneous abortions and birth defects, etc., have been reported, a clear association between these effects and ingested nitrate is not established.

Natural origin of nitrate is very less and is mostly in groundwater as a result of human activity. This review show that the major sources of nitrate pollution is the fertilizers applied for agriculture and mostly Asian countries are widely affected as they are the major producers and consumers of fertilizers. Urban groundwater is affected by municipal and industrial wastewater networks, leakage from septic tanks, landfills and fertilizer use for lawns, gardens and golf courses. Protection of shallow aquifers that are more prone to anthropogenic pollution is essential. Ion exchange is considered as a cost-effective method for nitrate removal but disposal of brine from this treatment is a major challenge. Biological denitrification has emerged as a common method for nitrate reduction in many developed countries. With further research in biological and chemical denitrification, the scope for their improvement and full-scale implementation of these methods, respectively are promising. While these nitrate removal and reduction methods are preferred for treating groundwater supplied for drinking purpose, for large scale remediation of the groundwater environment, non-treatment methods, such as blending, optimum fertilizer use, proper operation and maintenance of manure storage pits, septic tanks, wastewater disposal networks, etc., should be adopted. Preventing nitrate pollution is a much easier way to save time and money provided a good understanding of the sources and precautionary measures are achieved. The analysis of incidence and effects of nitrate on human as well as animal health establishes the fact that even with several scientific and technical advances in the recent decades, this problem still persists in developed, developing as well as under developed countries. Need to improve groundwater quality is emphasized as it is the only available source of fresh water for the 7+ billion people (in 2013) living in the world and for the future generations.

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