CHAPTER 6

NITRATES IN THE GEOCHEMICAL ENVIRONMENT

Nitrates in the geochemical environment, particularly in the aquatic environment, are of special importance in view of health implications. With great emphasis being placed on increased food production and the concomitant use of nitrogenous fertilizers, nitrates figure prominently in the medical geochemistry of cancer and some other diseases notably in developing countries. Among the major threats to groundwater from which drinking water supplies are obtained are leachates from human and animal waste matter. Additionally industrial and agriculture leachates mostly from large farmlands contribute quite significantly to groundwater pollution.

The source of nitrates, their pathways in the geochemical cycle across the soil-water-plant and human/animal systems and their impact on the latter constitute an interesting study within the field of medical geology.

THE NITROGEN CYCLE

In the terrestrial ecosystem, the nitrogen cycle represents one of the most important nutrient cycles (Chapin et al., 2002; Smil, 2000; Townsend, 2007; Sprent, 1987). As an essential component of proteins, nucleic acids and other cell constituents, nitrogen plays a major role in plant physiology and is required in substantial quantities. Even though there is an abundant source of nitrogen in the earth's atmosphere, much of it, ~79% is in the form of a nearly inert gas and is hence not available to most organisms. For plants to use this nitrogen for their growth, it should be in the form of NH_4^+ and NO_3^- ions. The former is used less by plants for uptake as it could in large concentrations be toxic. Nitrates therefore are the most important form of nitrogen carriers in the growth cycle of plants. Figures 6.1 and 6.2 illustrate the nitrogen cycle in nature and the nitrogen transformations in soil.

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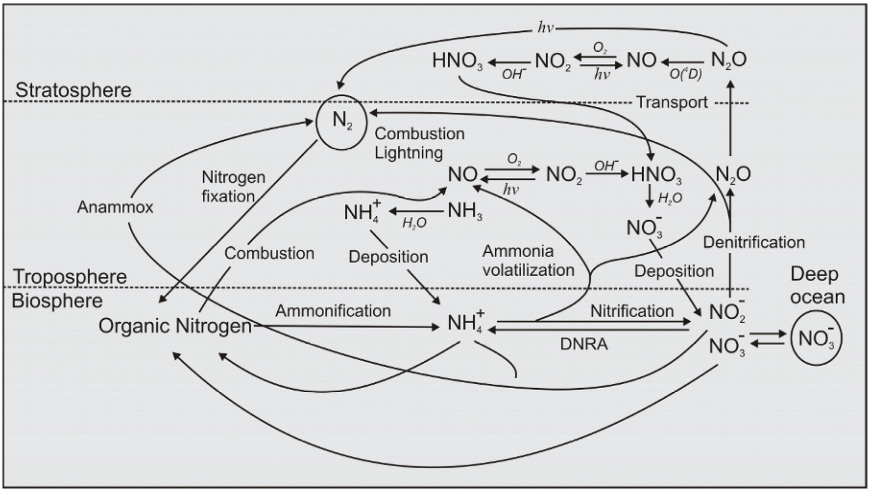

Fig. 6.1. The nitrogen cycle [Chemical species over arrows indicate reaction with that species to effect the transformation. Fixation, ammonification, assimilation, anammox, dissimilatory nitrate reduction to ammonia (DNRA), nitrification, and denitrification are enzyme-catalyzed processes-(graphics by Darrouzet-Nardi, 2005)]

While most plants obtain their nitrogen as inorganic nitrate from soil solutions in most ecosystems, nitrogen is stored primarily in living and dead organic matter. The transformation of organic nitrogen into inorganic nitrogen in the upper soil layers, is brought about by decomposition caused by the action of microorganisms. These are carried out by some types of bacteria, actinomycetes and fungi. Some bacteria convert N_2 into ammonia by the process of nitrogen fixation and these may be free-living or living in symbiotic associations with plants or other organisms. Ammonium is sorbed on surfaces of clay particles in soils due to the positive charge and they are held by soil colloids. When the ammonium ion is released from the colloid surface by cation exchange, bacteria belonging to the genus Nitrosomonas convert the ammonium ion into nitrite (NO_2^-) and another bacterium belonging to the genus Nitrobacter converts the nitrite to the nitrate (NO_3^-). These two processes, termed nitrification, involves oxidation.

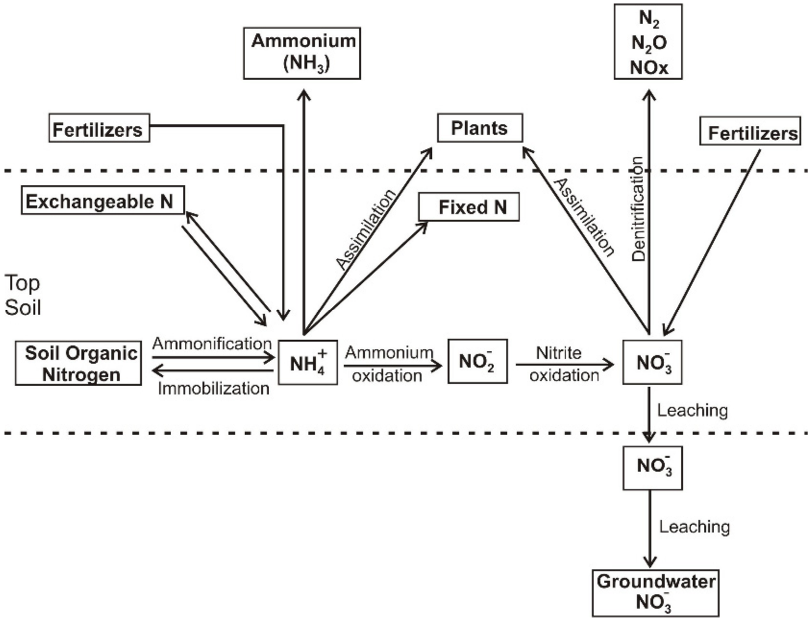

Fig. 6.2. Nitrogen transformations in soil (Rao and Puttanna, 2000)

Due to the very easy solubility of nitrates in water, leaching of nitrates from soils takes place rapidly, and these enter the hydrosphere through rivers and oceans. The process of denitrification, which is common in anaerobic soils, is carried out by heterotrophic bacteria and involves reduction of nitrates into the atmosphere. The oxygen needed for respiration by the bacteria is supplied by this process.

The nitrogen cycle as depicted in the Figures 6.1 and 6.2 is quite often interrupted or altered due to anthropogenic activities. Nitrate leaching and rates of denitrification increase when nitrogen fertilizers are applied to vast tracts of land. Nitrate pollution and eutrophication of aqueous systems then occur with the enhanced growth of algae. Human and animal wastes add a considerable load to the nitrogen and ammonia budget in the geochemical cycle and these bring about an increased nitrate concentration in the ground and surface waters.

The fact that amino acids which produce proteins are nitrogen-rich makes nitrogen an essential element. One of the most interesting features of nitrogen on earth therefore is the effect of its availability on living organisms and the ecosystems in which they live. Remote sensing of the earth's nitrogen cycle is assuming greater importance in quantifying biogeochemical cycles (Darrouzet-Nardi, 2005). As shown by Galloway et al. (2003, 2004) and Vitousek et al. (1997), the anthropogenic impact and alteration of the cycle is of much greater significance than ever before. The fixing of nitrogen by humans for use as fertilizer in agriculture and as a by product of fossil fuel combustion, though of great benefit in agriculture and transportation also has some negative influences (Darrouzet-Nardi, 2005). These may appear in the form of changes in the ecosystems manifesting further as changes in the physiological characteristics of organisms (Bowmann, 2000; Aber et al., 1989). Apart from the biological effects of fertilizer, reference has also been made to:

- (i) public health concerns
    - (a) as unbalanced diets
    - (b) respiratory ailments
    - (c) cardiac diseases
    - (d) cancer
    - (e) allergic pollen production
    - (f) dynamics of some vector-borne diseases (Townsend et al., 2007);

- (ii) ecosystem acidification as nitric acid in precipitation (Schindler et al., 1985; Aber et al., 1989; van Breeman et al., 1982)

- (iii) global warming as nitrous oxide (Houghton, 2001).

NITRATES, FERTILIZERS AND ENVIRONMENT

In order to feed the expanding world population, science-based agriculture has relied heavily on fertilizers, to increase crop production. In the tropics, where intense leaching of soils takes place, nutrients are rapidly lost and fertilizers are used extensively to replenish the essential nutrients N, P, and K.

Developing countries have around 76% of the global population and N-fertilizers are applied in quantities greater than that in developed countries. Figure 6.3 illustrates the world fertilizer consumption and Figure 6.4 shows the fertilizer consumption in South Asia, where India accounts for nearly 80% of fertilizer consumption. Pakistan and Bangladesh also have large fertilizer requirements.

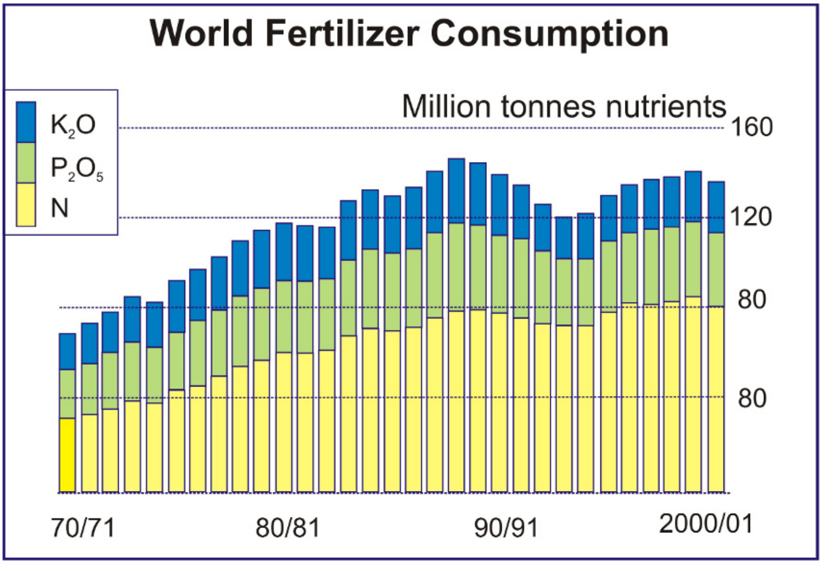

Fig. 6.3. Fertilizer nutrient consumption (IFA, 2004)

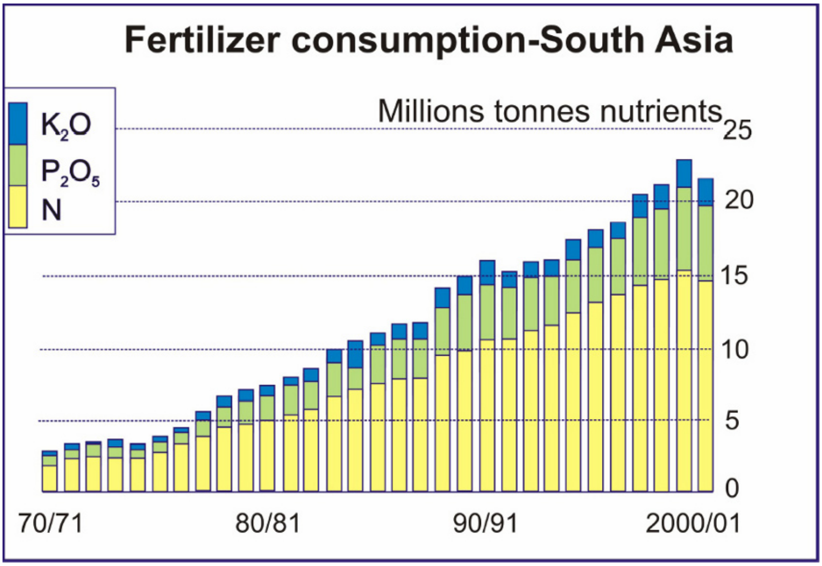

Fig. 6.4. Fertilizer nutrient consumption in South Asia (IFA, 2004)

Global fertilizer use increased at an annual rate of 5.5% from 27.4 million nutrient ions in 1959/60 to 143.6 million tons in 2001. In all developing regions, fertilizer use increased significantly (Table 6.1). The use of N-fertilizers by far outweighed that of phosphate and potash. In 1994/95, N-fertilizers accounted for 64% of the fertilizers consumed by developing countries, as compared to 25% for phosphate and 11% for potash.

Table 6.1. World Fertilizer Use (IFA, 2004) Notes: East Asia excludes Japan. West Asia/North Africa excludes Israel

Region/Nutrient	Fertilizer Use			Annual Growth	
	1959/60	1980/90	2020	1960-90	1990-2020
	(million nutrient tons)			(percent)	
Developed countries	24.7	81.3	86.4	4.0	0.2
Developing countries	2.7	62.3	121.6	10.5	2.2
East Asia	1.2	31.4	55.7	10.9	1.9
South Asia	0.4	14.8	33.8	12.0	2.8
West Asia/North Africa	0.3	6.7	11.7	10.4	1.9
Latin America	0.7	8.2	16.2	8.2	2.3
Sub-Saharan Africa	0.1	1.2	4.2	8.3	3.3
World total	27.4	143.6	208.0	5.5	1.2
Nitrogen	9.5	79.2	115.3	7.1	1.3
Phosphate	9.7	37.5	56.0	4.5	1.3
Potash	8.1	26.9	36.7	4.0	1.0

With the increasing use of N-fertilizers, mostly in developing countries, the possibility of nitrate pollution of groundwater will be strongly associated with fertilizer-N use efficiency (Singh et al., 1995). These authors have pointed out that due to the poor fertilizer-N use in many developing countries, notably in the irrigated soils of Asia and humid tropics of Africa, the potential for nitrate pollution of groundwater is quite large. Intense irrigation, apart from high rainfall, is now available to farmers of Asia and the increase of N-fertilizer use can be viewed as a future environmental hazard affecting the groundwater systems. It should be bear in mind that three quarters of the world population live in developing countries and a majority (60%) are engaged in farming. Farmers in developing countries possess ~54% of the arable land available in the world (FAO, 1991).

The proper fertilizer use is an important pre-requisite for retarding nitrate pollution of groundwater. The percent recovery of fertilizer-N by a crop often termed "fertilizer use efficiency" varies with the N source and the rate at which fertilizer is applied, the nature of the chemical and biochemical reactions between soil and fertilizer, the timing and placement of the fertilizer, the nature of crop and its N-requirement, the adequacy of other nutrients and a host of soil, climatic and management factors (Singh et al., 1995). When conditions are very favourable, ≥80% of the fertilizer-N may be recovered by the crop, but under most situations, efficiencies of ≤50% are common (Allison, 1966).

The excess accumulation of nitrogen in soil in relation to crop yield and N-fertilizer application is shown in Figure 6.5. In such cases where there is a large amount of residual nitrogen in soil, the potential for nitrate pollution is significantly high. In the highly permeable Ultisols and Oxisols in the humid regions where precipitation greatly exceeds evapotranspiration during the growing season, there can be extensive N-leaching. Even ≥50% of mineral-N initially in the soil may be lost through leaching between the onset of the rain and plant establishment (Osiname et al., 1983).

Leutenegger (1956) reports that in Tanzania only 7% of the fertilizer-N was recovered within the 120 cm depth of the uncropped bare plot one year after application. In Nigeria, in the humid tropics, both heavy rainfall and irrigation is present. It has been estimated (Adetunji, 1993) that ~30% of the N-applied to maize was lost below the root zone and over a 3 year period, the nitrate pollution of groundwater exceeded the maximum level accepted for potable water by a significant margin. In the city of Sokoto, Nigeria, Uma (1993) observed that in waters of over 40 wells in a shallow lateritic aquifer nitrate enrichment ranged from 20 to 100 mg/L.

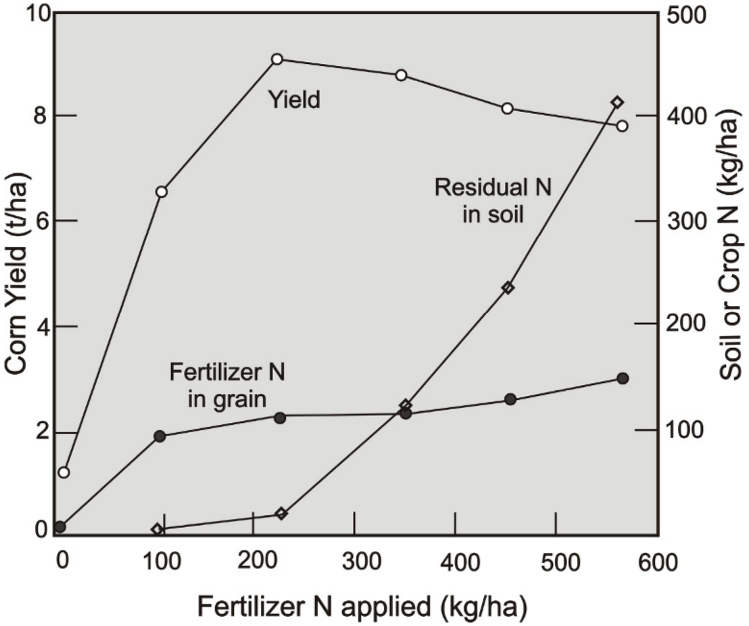

Fig. 6.5. Fertilizer application and crop yield (Broadbent and Rauschkolb, 1977)

Figure 6.6 illustrates a case study in Sri Lanka where the nitrate levels are exceptionally high due to excessive application of nitrogenous fertilizer. In view of the fact that the vast majority of the people living in developing countries of the tropics obtain their water supplies directly from the ground, the levels of nitrate fertilizers in groundwater are of vital importance.

There are several N-fertilizers that are available. Among these are: (a) anhydrous ammonia (82% N)- a liquid under high pressure (b) mixture of urea and ammonium nitrate (28 - 32% N) (c) aqua ammonia (21% N)- liquid under low pressure (d) urea (46% N) (e) ammonium nitrate (33% N) (f) ammonium sulphate (21% N) (g) calcium nitrate (16% N) (h) potassium nitrate (13% N) (i) sodium nitrate (16% N). From among these, urea [$CO(NH_2)_2$] is a widely used dry N-fertilizer. Upon application to the soil, urea is converted to ammonia which reacts with water to form ammonium within two to three days. The NH_4^+ ion then gets converted to nitrate (NO_3) through nitrification.

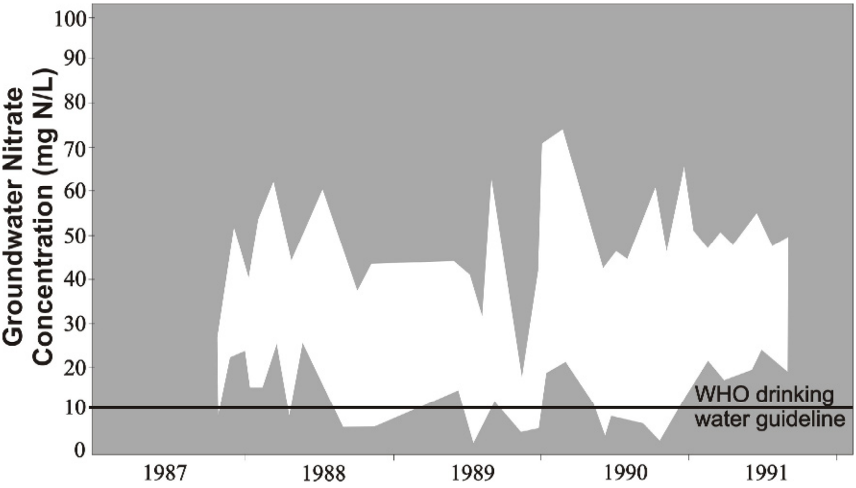

Fig. 6.6. Envelope of nitrate concentration in irrigation dug wells in the Kalpitiya Peninsula, Sri Lanka (source British Geological Survey, Technical Report WD/0S/86/21; reproduced with kind permission from the British Geological Survey)

NITROGEN LOADING IN RICE FIELDS

In South and Southeast Asia, rice (*Oryza sativa*) is the most important food, and is the only crop grown under flooded soils. The global rice area is 150.7 million ha; more than 90% of which lies in Asia (FAI, 1997). India is known to have the worlds largest rice cultivation area (47.2 million ha), followed by China (31.3 million ha) (Ghosh and Bhat, 1998). Rice cultivation uses a large share of fertilizer; urea being the most commonly used nitrogen-fertilizer. Since for most of the growing season rice fields are submerged, nitrate losses from rice fields can be high. Prediction of nitrate losses is complicated by the variable nature of soils and the complex set of N-transformation processes taking place under flooded soil conditions (Chowdary et al., 2004).

During submergence of the soils of the rice fields, changes in physico-chemical and biological properties of the soils take place. The root zone of the rice plant gets converted from an aerobic to an anaerobic environment, the process being governed mostly by microorganisms. As shown in Figure 6.7, the rice plant obtains its nitrogen fixation by algae and bacteria of inherent NH_4^+ and NO_3^- nitrogen in the soil and addition of nitrogen through chemical fertilizers (Ghosh and Bhat, 1998).

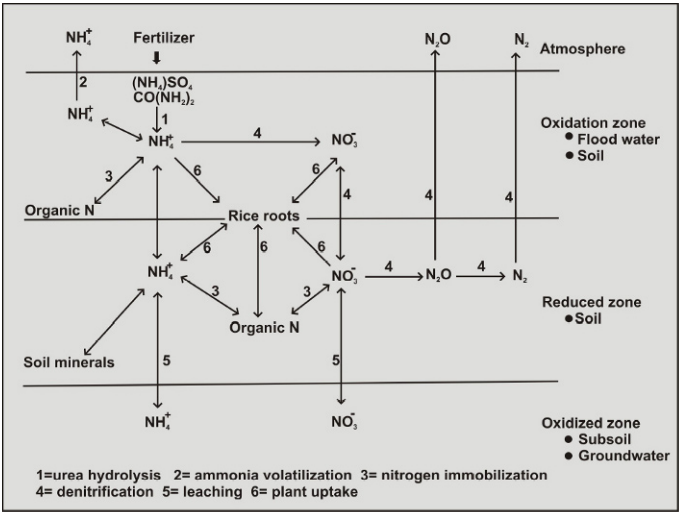

Fig. 6.7. Fate of fertilizer in wetland soils (Ghosh and Bhat, 1998)

Part of the nitrogen fertilizer applied to the rice field undergoes leaching and percolates down the soil profiles and mixes with the groundwater, which then gets contaminated with NO_3-N. In India, high nitrate concentrations have been reported in some states such as Maharashtra, Tamilnadu, Haryana, Rajastan, and Andra Pradesh (Ozha et al., 1993; Vijay Kumar et al., 1993) as well as in areas in Punjab and Delhi (Rao and Puttanna, 2000). It was observed that 70% of the wells surveyed contained nitrate exceeding the permissible limit of 45 mg/L (=10 mgN/L). A level as high as 7400 mg/L indicating extreme contamination had also been recorded.

NITRATES FROM HUMAN AND ANIMAL WASTES

The risks to health caused by groundwater contamination from on-site sanitation are a concern in many overpopulated developing countries notably in the tropics. On-site sanitation systems dispose of human excreta into the ground, mostly from pit latrines and septic tanks. Sanitation has been defined as "*the means of collecting and disposing of excreta and community liquid wastes in a hygienic way so as not to endanger the health of individuals and the community as a whole*" (WHO, 1987).

The two main health risks associated with the degradation of water quality due to on-site waste disposal systems are (a) faecal-oral disease transmission and (b) nitrate poisoning. Pollution from on-site waste disposal is influenced by a variety of complex factors (Fourie and van Ryneveld, 1995):

i) Varying sub-surface conditions: in addition to the variety of subsurface soils present, within any soil the most critical distinction is between the saturated and the unsaturated zone.

ii) Varying contaminants: different contaminants show different characteristics, such as mobility and persistence, and these are affected in different ways in the sub-surface.

iii) Varying polluting mechanism and movement of pollutants.

Pathogens are defined as disease-causing organisms. Human excreta are known to contain worm eggs, protozoa, bacteria, and viruses and from among these, eggs and protozoa are effectively screened by soil during groundwater flow. The smaller bacteria and viruses are therefore of the greatest health concerns, bearing in mind that in most developing countries, water-borne diseases affect millions of people. Pathogens cannot travel farther and faster than the water in which they are suspended and groundwater hydrology therefore has a marked influence on aquifer pollution. As noted by Cave and Kolsky (1999) the key factor that affects the removal and elimination of bacteria and viruses from groundwater is the maximisation of the effluent residence time between the source of contamination and the point of water abstraction. Because of the very low velocities of unsaturated flow, the unsaturated zone is the most important line of defence against faecal pollution of aquifers.

From a geochemical standpoint, nitrates and their pathways in the aqueous systems closely associated with on-site waste disposal, have aroused great interest. Nitrates are considered as significant health indicators:

(a) Excessive concentrations of nitrates are directly associated with methaemoglobinaemia or “blue baby syndrome”

(b) Nitrates and nitrites are precursors of carcinogenic nitroso-compounds

(c) Nitrates are useful as rough indicators of faecal pollution when microbiological data are lacking.

In the developing countries of the humid tropics, pit latrine soakaways (Fig. 6.8) often pose a threat to potable groundwater supplies in view of the large number of inhabitants confined to a smaller area and using water from wells located close to pit latrines.

Lawrence (1986) outlined the conditions under which water-supply tube wells in basement aquifers are most vulnerable to this type of pollution:

(i) the water-table is shallow and the unsaturated zone is thin.

(ii) the overburden is thin and pit latrines penetrate to, or close to, the top of the bedrock.

(iii) groundwater movement is completely restricted to joints and fissures.

(iv) population density is high (particularly urban fringe developments) where there is pressure to reduce the separation between latrines and water-supply wells.

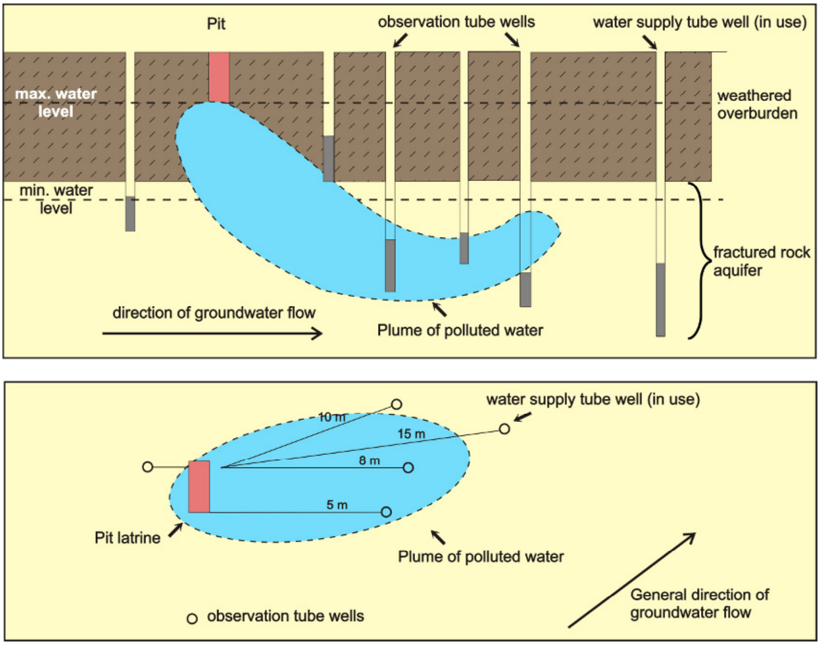

Fig. 6.8. Nitrate pollution by pit latrine soakaways in Sri Lanka. The bottom diagram illustrates the sketch plan of the site (Lawrence, 1986; reproduced with kind permission from the British Geological Survey)

(v) water-flush pit latrines are commonly used and this type of latrine increases the fluid loading and hence the likelihood of microbiological contamination of groundwater.

(vi) water-table gradients are steep, thus increasing the rate of groundwater movement

Figure 6.9 illustrates a case study in Sri Lanka showing the plume of polluted water from pit latrines in limestone terrain. Such cases are very common in the tropics and as outlined above, the general soil and climatic conditions aid in the mobility of the pollution species.

In Francistown located in Botswana, in mid 2000 nitrate pollution had reached alarming levels (Fig. 6.10). Areas with pit latrines, sewage ponds and/or cemeteries posed a groundwater hazard in terms of organic substances, bacteria and nitrates. In fact, because of the extreme nitrate pollution, nitrates served as the key indicator of overall groundwater quality in all environmental hydrogeology studies carried out by the Environmental Geology Division of BGR, Germany (Vogel, 2002).

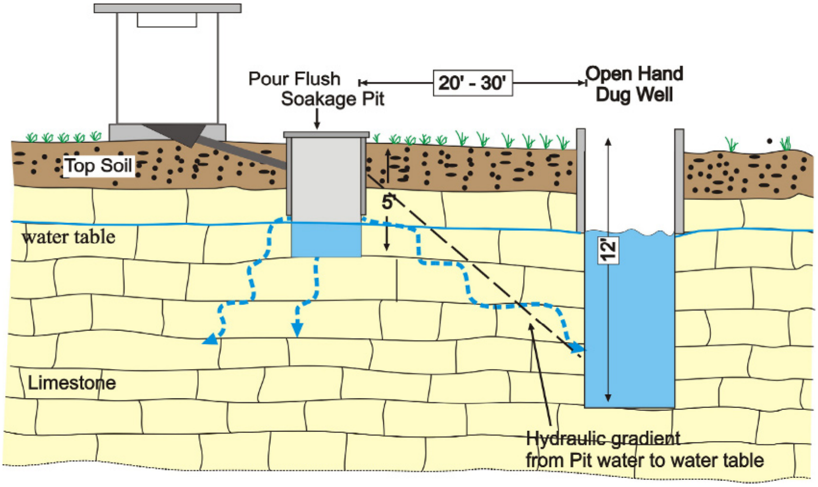

Fig. 6.9. Pit latrine in a limestone in Jaffna, Sri Lanka

Among the three main pollution sources namely (a) pit latrines (b) mine waste dumps (c) landfills, pit latrines were found to have had the worst impact on groundwater quality. The chemical analysis of water from a total of 48 public and private wells sampled within and around Francistown showed that nitrate concentrations were frequently well above the WHO maximum levels. In some cases, they had even reached levels between 100 to 300 mg/L (Mafa, 2003). By mid 2000, the major groundwater pollutant was nitrate where there was a clear correlation of elevated nitrate levels with pit latrines.

In Senegal in the Yeumbeul area close to Dakar, the capital city, high nitrate levels above the WHO limits have been observed (Tandia et al., 1999). In this area, shallow groundwater provided nearly all of the water supply for 7000 families from traditional wells. Close to every well is a family latrine and the distance separating the wells from the latrines varied between 2 and 36 m. The population had virtually no sanitation system and human waste was disposed directly into the environment causing a water quality hazard.

In the Dodoma area, located in a terrain of crystalline basement rock in Tanzania, in a semi-arid climate, nitrate levels in the groundwater had reached an average of 150 mg/L (Nkotagu, 1996). These high nitrate concentrations were found in both deep and shallow groundwaters and originated from sewage effluents.

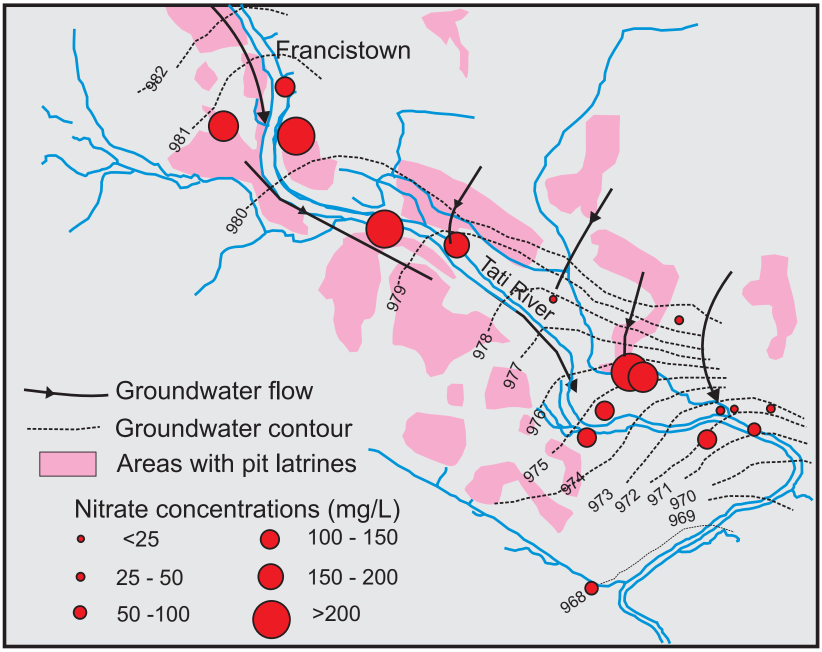

Fig. 6.10. Nitrate pollution in Francistown, Botswana (after Mafa, 2003)

In a different geological setting in the Essaouira Basin of Morocco, where fractured karstic materials were dominant, nitrate levels in groundwater had reached as much as 400 mg/L. The aquifer systems are interconnected through a network of fractures and stratification joints facilitating the transport of nitrogen loaded water (Laftouhi et al., 2003). Livestock excreta, agricultural fertilizers and human wastes were considered to be the sources of the excess nitrates.

A well water survey carried out in two districts of the Republic of Guinea (Gelinas et al., 1996) showed that there was widespread well water contamination from nitrate and faecal bacteria in both districts. In these areas, the water distribution network was primitive, domestic sewage untreated and sanitation only by poorly managed pit latrines and septic tanks. There was no storm water drainage system. As no fertilizers were used in the area, the very high nitrate levels were attributed to human excreta, domestic sewage aided by the high permeability of the soil. The high nitrate levels were correlated with high contents of organic matter probably due to incomplete degradation of organic nitrogen due to naturally low dissolved oxygen levels.

NITRATES AND HEALTH

Nitrates are natural components of all fruits and vegetables and as discussed earlier drinking water may also contain nitrates. They are also added to some meat and fish products as preservatives. Over the last few decades, dietary nitrate has been implicated in the formation of infantile methaemoglobinaemia and gastric/intestinal cancer through the production of carcinogenic N-nitrosamines. Comly (1945) first noted that consumption of drinking water environmentally contaminated with nitrate was associated with methaemoglobinaemia. The National Academy of Science of USA (1977) set a limit of 10 mgN/L as nitrogen (45 mg/L nitrate) as the maximum permissible level.

Nitrates and Methaemoglobinaemia

Nitrate itself is considered to be relatively non-toxic and it is the reduced species, nitrite that greatly increases the toxicity. Nitrate is reduced to nitrite by bacteria in the upper gastro-intestinal tract. Nitrite is then absorbed into the bloodstream, where it reacts with haemoglobin to form methaemoglobin (Bruning-Fann and Kaneene, 1993a). Methaemoglobin does not have the capacity to carry oxygen and this results in cyanosis and anoxemia if the level of methaemoglobin (met-Hb) reaches high levels. Cyanosis becomes evident when the concentration of met-Hb reaches about 10 g/L (5-10% of the total haemoglobin (Hb) is in the met-Hb form), becomes severe at 30 g/L and may result in death when levels exceed 60 g/L (Robertson and Riddell, 1949). It is the reduced oxygen delivery to the tissues that causes the death of the individual. Met-Hb however, is known to be converted back to Hb by the enzyme methaemoglobin reductace present in the erythrocytes. This enzyme normally keeps the met-Hb level between 1-2% but it is much less active in children under 3 months and hence the common occurrence of methaemoglobinaemia in such children.

In the case of animals, clinical signs of acute nitrate toxicity vary according to species. Nitrate is capable of inducing methaemoglobinaemia in a wide range of species e.g. cattle, sheep, swine, dogs, guinea pigs, rats, chicken and turkey. In general, ruminant animals develop methaemoglobinaemia while monogastric animals exhibit severe gastritis (Bruning-Fann and Kaneene, 1993b).

Nitrates and Cancer

Cancer, after heart disease is recognized as a leading killer disease. A large number of causative factors which have been isolated are in one way or another environmental. The relationship between cancer and the environment has been known since 1775, when a correlation between scrotal skin cancer and heavy exposure to soot among chimney sweepers was observed (Miller and Miller, 1972). Since then, many environmental pollutants have been shown to produce cancer in various parts of the body. Whereas the carcinogenicity of many laboratory synthesized chemical components have been the subject of intensive study, the effect of the natural environment on cancer is much less known. Epidemiological studies have indicated the importance of, for e.g. the quality of potable waters, the chemistry of the soils and the plants growing on them in geographically separated areas, quality of the air we breathe on human cancer. Since correlations by themselves rarely justify mechanistic interferences and only are recognised as weak suggestions of causality (Tannenbaum and Correa, 1985), evidence from epidemiology cannot often be used to draw conclusions on biological mechanisms.

However, epidemiology has its own virtues and if used intelligently, useful preliminary information may be obtained. There are certain parts of the world where some specific diseases, including cancer, show anomalous incidences clearly pointing to some features unique to that environment. Oesophageal cancer, for example, was highly prevalent in parts of Transkei (Laker et al., 1980), Iran, Central Asia and northern China (Kibblewhite, 1982). In these regions cancer was a more important cause of death than coronary heart diseases in Europe and USA. During the last 50 years, substantial evidence has been accumulated which show a relationship between geology, soils and climate and the widespread occurrence of oesophageal cancer. As pointed out by Laker (1979), such an integration of environmental factors leads to distinct soil properties and it has been proved possible to identify certain soil types as being common to areas of high cancer incidence. Figure 6.11 illustrates the relationship between environmental factors and incidence of cancer.

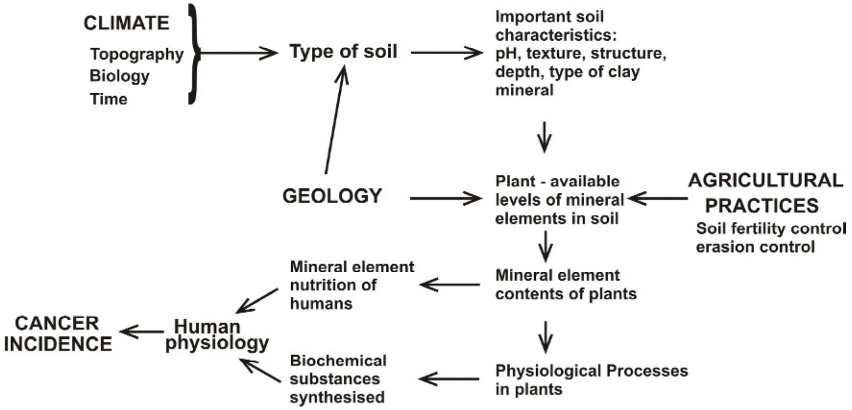

Fig. 6.11. Relationship between environmental factors and cancer incidence.

Nitrates can react with amines in the stomach or lungs to form N-nitrosamines, which have induced tumours in laboratory animals. Although the causation of human tumours is not directly linked to these compounds, exposure to them is considered as being potentially capable of initiating human cancer (National Research Council, 1978). Figure 6.12 illustrates the geochemical environment and the cancer forming nitrogen-bearing compounds.

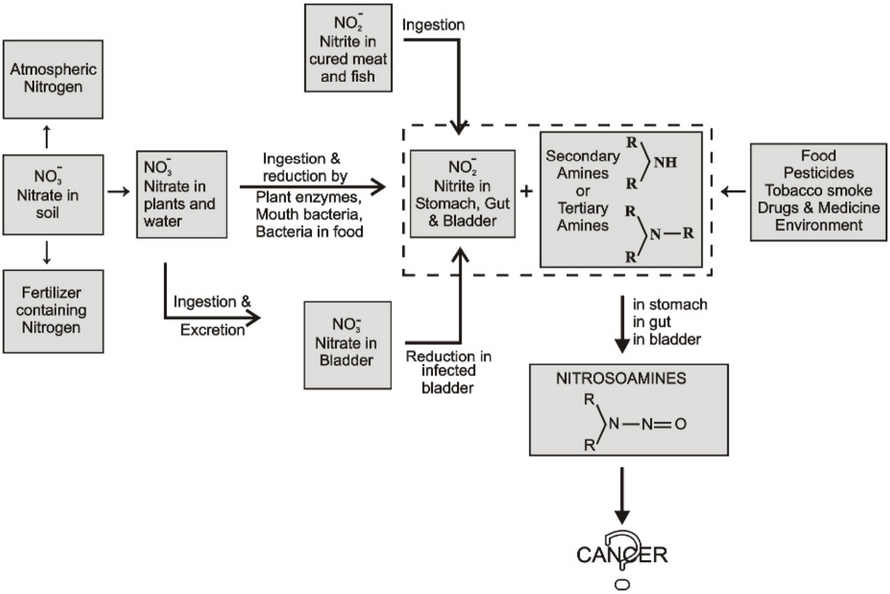

Fig. 6.12. Sources of nitrate and nitrosamines and some sites of formation of carcinogenic nitrosamines (Fishbein, 1979)