Water Quality Fact Sheet:

Nitrate

WHO guideline value for nitrate (recommended limit): 50 mg/l (short term exposure)

WHO guideline value for nitrite (recommended limit): 3 mg/l (short term exposure)

WHO guideline value for nitrite (recommended limit): 0.2 mg/l (long-term exposure)

WHO guideline value for combined nitrate plus nitrite (recommended limit): the sum of the ratios of the concentration of each to its guideline value should not exceed 1

Typical range in groundwater: 0 – 100 mg/l

This is one of a series of information sheets prepared for a limited number of inorganic constituents of significant health concern that are commonly found in groundwater. The sheets aim to explain the nature of the health risk for each constituent, the origin and occurrence in groundwater, the means of testing and available methods of mitigation. The purpose of the sheets is to provide guidance to WaterAid Country Office staff on targeting efforts for water-quality testing and to encourage further thinking in the organisation on water-quality issues.

Health effects

The primary health concern regarding nitrate and nitrite is the formation of methaemoglobinaemia, so-called 'blue-baby syndrome'. Nitrate is reduced to nitrite in the stomach of infants, and nitrite is able to oxidize haemoglobin (Hb) to methaemoglobin (metHb), which is unable to transport oxygen around the body. This reduced oxygen transport becomes clinically manifest when metHb concentrations reach 10% or more of normal Hb concentrations; the condition, called methaemo-globinaemia, causes cyanosis and, at higher concentrations, asphyxia.

The Hb of young infants is more susceptible to metHb formation than that of older children and adults; this is believed to be the result of the large proportion of foetal Hb, which is more easily oxidized to metHb, still present in the blood of infants. In addition, there is a deficiency in infants of metHb reductase, the enzyme responsible for the reduction of metHb to Hb. The reduction of nitrate to nitrite by gastric bacteria is also higher in infants because of low gastric acidity. The level of nitrate in breast milk is relatively low; when bottle-fed, however, these young infants are at risk because of the potential for exposure to nitrate/nitrite in drinking-water and the relatively high intake of water in relation to body weight. The higher reduction of nitrate to nitrite in young infants is not very well quantified, but it appears that gastrointestinal infections exacerbate the conversion from nitrate to nitrite.

The weight of evidence is strongly against there being an association between nitrite and nitrate exposure in humans and the risk of cancer (WHO, 1998).

Occurrence in groundwater

Nitrate is one of the most commonly identified groundwater contaminants. Nitrate (NO_3^-) is the main form in which nitrogen occurs in groundwater, although dissolved nitrogen may also be present as nitrite (NO_2^-), ammonium (NH_4^+), nitrous oxide (N_2O) and organic nitrogen. The concentration, form and behaviour of nitrogen in water are governed by the chemical and biological processes forming the nitrogen cycle. In this cycle, atmospheric nitrogen gas is converted to organic nitrogen compounds by nitrogen fixers such as blue-green algae and some bacteria, such as those in the root nodules of leguminous plants. Nitrogen in organic form and ammonium can be converted by bacteria in aerobic conditions into nitrite and nitrate, a process termed 'nitrification'. Nitrate in anaerobic systems can be reduced by other strains of bacteria to nitrous oxide or nitrogen gas, by 'denitrification'.

Nitrate speciation in the aqueous environment is therefore redox controlled. In aerobic water nitrogen occurs as nitrate or nitrite ions. Nitrate is stable over a considerable range of conditions and is very mobile in water. Ammonium and organic forms are unstable and are generally considered to be indicators of pollution. In confined aquifers, where conditions are anaerobic, nitrate is converted to nitrogen gas by denitrification but nitrite or ammonium may persist.

The nitrate concentration in groundwater is normally low but can reach very high levels as a result of leaching or runoff from agricultural land together with contamination from human or animal wastes, (Laftouhi et al. 2003).

Sources of nitrate pollution in groundwater

Agriculture

Large increases in food production in developing countries have resulted from the highest rates of increase in nitrogen fertiliser use during recent years and rates have tripled since 1975. In Asia a quarter of the growth in rice production has been attributed to increased fertiliser use (BGS et al. 1996).

A wide variation in nitrate leaching losses from agriculture occurs, resulting from differences in soil and crop types, fertiliser application rates and irrigation practices. High rates of nitrogen leaching from the soil can be anticipated in areas where soils are permeable and aerobic, and nitrogen applications are made to relatively short duration crops, e.g. vegetables or wheat. The nitrogen loading will be greatest where cultivation is intensive and double or triple cropping is practised. Especially high nitrogen leaching can occur from soils where irrigation is excessive and not carefully controlled (BGS et al. 1996).

The amount of annual recharge from precipitation will influence the amounts of nitrate in groundwater through dilution effects so that in arid or semi-arid regions concentrations will be proportionately greater than for an equivalent environment in a humid region.

Continuous crop cover e.g. sugar cane, citrus groves or coffee plantations, tends to reduce nitrogen leaching loss. Losses beneath paddy cultivation are likely to be low as a result of volatile losses and denitrification in the waterlogged, anaerobic soil.

Figure 1 shows the nitrate concentrations in groundwater that could be anticipated from a range of typical crops, illustrating the results from case studies:

1. Intensive cultivation of two crops per year of onions and chillies on a shallow coastal sand aquifer in Sri Lanka produced concentrations of up to 220 mg/l of nitrate in groundwater, equivalent to 70% of the applied nitrogen, after taking into account recycling in irrigation water pumped from shallow on-the-plot irrigation wells (Mubarak et al, 1992; Morris et al. 2003).

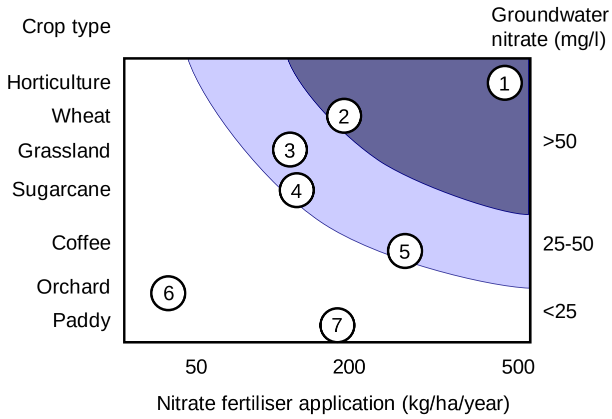

Figure 1. Anticipated groundwater nitrate concentrations for a range of crop types (circled numbers correspond to text examples).

2. Increasingly intensive cultivation of cereals in temperate European regions has produced average nitrogen leaching in the range 40-70 kg/ha from annual applications of 150-200 kg/ha, as determined from unsaturated zone nitrate concentrations of 50-80 mg/l in infiltrating recharge (Foster et al. 1982).

3. Similar unsaturated zone profiling techniques have confirmed that unfertilised and ungrazed grassland produces negligible nitrate leaching. However, applications to intensive grassland of 150 kg N/ha/yr produce leaching losses in the same range as drinking water standards, and the considerably higher applications sometimes encountered produce correspondingly greater losses (Chilton and Foster, 1991).

4. The continuous crop cover and strong root development of sugar cane plantations combined with limited irrigation contributes to moderate nitrate leaching to groundwater from yearly nitrogen applications of some 130 kg/ha (Chilton et al. 1995).

5. High coffee yields in Costa Rica are coupled to large additions of nitrogen from chemical fertilisers. High rates of nitrogen uptake by both coffee and shade trees, if present, coupled with soil denitrification reduce overall leaching to groundwater to 3-8% of the applied nitrogen (Babbar and Zak, 1995)

6. Coconut plantations with low nutrient inputs and leaching to groundwater were the traditional crop in areas of Sri Lanka. (Morris et al, 2003)

7. Little leaching of nitrate from paddy soils in India and China was found despite high application rates and 2 – 3 crops per year (BGS el al. 1996; Ghosh and Bhat, 1998: Zhu et al, 2003). Plant uptake, volatile losses of ammonia

Table 1. Groundwater nitrate concentrations beneath selected urban areas

City/ suburb	Population during study (millions)	Disposal systems	Aquifer type	Groundwater nitrate concentration range (mg/L)	Reference
Lucknow, India	1.1	Septic tanks, latrines and soakaways	Alluvium (0 – 100 m)	10 – 600	BGS et al. (1996)
Hat Yai, Thailand	0.14	On-site sanitation and canal	Semi-confined coastal alluvium	<5 (N present as NH_4^+)	Lawrence et al. (2000)
Yogyakarta, Indonesia		Septic tanks	Volcanic deposits (0 – 45 m)	30 - 180	Smith et al. (1999)
Taejon, Korea	1.3	Piped sewerage, septic tanks and latrines	Alluvium and weathered granitic rocks (0 – 50 m)	0 - 170	Jeong (2001)
Yeumbeul, Dakar, Senegal	0.007	Latrines	Shallow coastal sand Semi-confined infrabasalt	40 - 370	Tandia et al. (1999)
Cotonou, Benin	0.7		Coastal sands and alluvium Confined sands and clays	5 - 130 10 - 120	Boukari et al. (1996)
Merida, Mexico	0.5	Septic tanks, soakaways and cesspits	Shallow karst limestone	20 - 130	Morris et al. (1994)
Santa Cruz, Bolivia	0.7	On-site sanitation	Shallow alluvial outwash plain deposits (0 – 50 m) Deep semiconfined (>50 m)	50 – 180	Morris et al. (1994)

and denitrification are the predominant processes.

Livestock

Nitrogen leaching from ungrazed grassland is normally low since grass provides continuous ground cover. However leaching from intensively grazed land can be a problem since 80% of the nitrogen consumed by grazing animals is returned to the soil as urine or dung. Ryden et al (1984) demonstrated that, for the same chalk soils, leaching losses were five times greater for grazed grassland than for an equivalent cut grassland.

Discharge of effluent from areas of livestock concentration can also be a common source of groundwater pollution (Cho et al. 2000). Leachate from manure heaps, leaking slurry storage pits and slurry or manure spreading can also be a major source of nitrogen in groundwater.

Urban unsewered sanitation

Nitrogen is present in sewage in a range of reduced and organic forms, such as ammonia and urea. These can be oxidised in aerobic groundwater systems to nitrate, although there is uncertainty about the proportion of nitrogen which is leached and oxidised. There is major concern with the subsurface contaminant load associated with unsewered sanitation units such as septic tanks, cesspits and latrines. Troublesome nitrate concentrations are likely to develop from the infiltration of effluent to underlying aquifers except where water use is high and population density is low. In vulnerable karstic environments, such as the Yucatan, Mexico, all nitrogen deposited in sanitation systems may be leached and oxidised. Especially high concentrations are also likely to occur in those arid regions with low per capita water usage (Morris et al. 1994).

Surveys of groundwater quality in a range of cities with incomplete or no piped drainage out of the city have shown that nitrate concentrations can reach very high levels, such as those found under Lucknow (Table 1). The work at Hat Yai, however, has demonstrated that nitrate may not give problems where the aquifer is confined and the nitrogen is not oxidised.

In many cities, especially those on low-lying coastal alluvial plains which are underlain by a shallow water table, disposal of excreta to the ground is not possible, particularly in areas affected by the monsoon because of surfacing of the water table during periods of heavy rainfall. Thus wastes are discharged directly or indirectly into surface water courses which can themselves become major line sources of groundwater pollution.

Urban wastewater disposal and reuse

The expanding demands on groundwater and greater problems of wastewater disposal have led to the greater recognition of the value of wastewater as an important resource. There are now many examples of schemes which use wastewater, with varying degrees of treatment, for agricultural irrigation.

Methods for reuse of water range from localised, peri-urban, often informal irrigation of small gardens by collected but untreated wastewater, through large canal commanded irrigation schemes still using untreated water to highly sophisticated, heavily controlled and managed soil aquifer treatment in which the reabstracted, fully treated effluent can be used to grow unrestricted types of crop.

The largest and longest established of these schemes pipes the wastewater produced by Mexico City into the adjacent valley where it is used to produce a large area of crops without any pre-treatment (CNA et al. 1998). This has resulted in some 30% of local public supply boreholes containing nitrate at >50 mg/l with maximum concentrations of 70 – 80 mg/l. This only represents a fraction of the total nitrogen loading in the incoming water since a large fraction is utilised by the crops.

Nitrogen concentration in the irrigation water can also be reduced by impounding the wastewater in a series of basins using flooding and drying cycles. These promote oxidation to nitrate and subsequent denitrification to nitrogen gas (Bouwer, 1985). Problems can also arise from infiltration directly from such stabilisation ponds, for example from the Es-Samra ponds, serving Amman, Jordan (Al-Kharabsheh, 1999).

Solid waste disposal

Leachate arising from solid waste disposal is a highly mineralised mixture of inorganic and organic compounds. In humid tropical conditions leachate can be generated in relatively large volumes potentially leading to extensive groundwater plumes. Leachate is generally anaerobic and may contain a high concentration of ammoniacal nitrogen. Such nitrogen is readily absorbed to clay minerals in the aquifer and may not migrate for large distances, but it can also be oxidised in the aquifer giving rise to high concentrations of nitrate.

Groundwater in drinking water wells in two suburbs of Ibadan and Lagos were found to have very poor water quality, including unacceptable concentrations of nitrate and ammonia, ascribed to local waste disposal sites (Ikem et al., 2002). Down gradient wells were particularly heavily affected.

A study at Chiang Mai, Thailand found that even ten years after an open waste dump had been closed and covered with soil, there was still evidence for pulses of contaminants, included nitrate, moving away from the site in the rainy season. During the dry season the aquifer became anaerobic and nitrate was only detected at a few points (Morris et al. 2003).

Natural sources

It is important to recognise that other sources of groundwater nitrate exist (Edmunds and Gaye, 1997). These include:

- geological sources, such as the saltpetre deposits of Northern Chile;
- naturally high baseline concentrations in semi-arid areas, thought to be derived from nitrogen fixing indigenous plants, such as the acacia species found in areas of the Sahara/Sahel region of North Africa;
- atmospheric deposition.

Distinguishing sources of nitrate

Due to the large number of nitrogen sources it can be difficult to determine the origin of nitrate in groundwater. The simplest indication can come from looking at the ratio of concentrations with other waste components, such as chloride. The ratio of chloride to nitrogen in groundwater beneath unsewered sanitation is often about 2:1. If the waste has been subject to a process which removes nitrogen for example application to agricultural land the ratio is increased (Figure 2).

The use of other species present appears an attractive method for distinguishing between sources of nitrate. This requires the indicator to be present in only one recharge source and detectable in groundwater. Such indicators are rare and have included:

- boron or optical brighteners from laundry detergents in domestic sources;

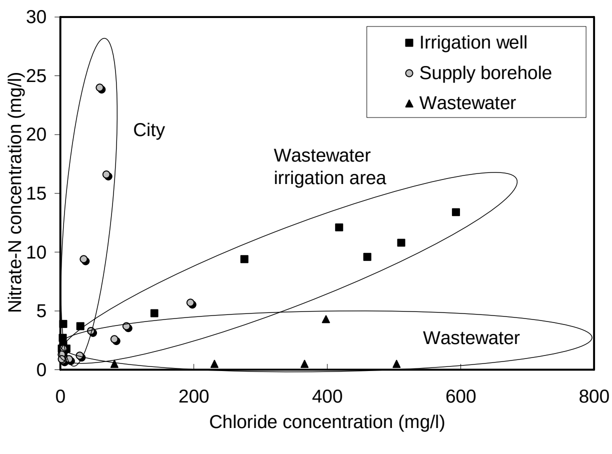

Figure 2 Groundwater nitrogen and chloride from Leon, Mexico

- coliform bacteria from sewage;
- specific compounds, such as silver from photographic industry or zinc from metal working.

The potential sources of nitrate contamination are characterised by unique ranges of the $\delta^{15}N$ isotopic signature. This can be used to distinguish between nitrogen derived from inorganic fertilisers and animal or sewage wastes (Girard and Hillaire-Marcel, 1997). Determination of nitrogen stable isotopes is very expensive and this limits its potential application.

Testing for nitrate

Test strips are available for use in field-testing which give semi-quantitative results. These cover the sensitivity range 0-50 mg/l for NO_3 and 0-3 mg/l for NO_2.

Nitrate can be determined in the field using an ion-selective electrode. This has a limit of detection of about 0.2 mg/l. Chloride and bicarbonate interfere when present in ratios of > 10 and may be removed by precipitation with silver sulphate or acidification to pH4 by addition of a suitable buffer solution.

Nitrate and nitrite are normally measured by formation of the red-purple azo dye produced by diazotised sulphanilic acid and N- (1-naphthyl)-ethylene diamine dihydrochloride. Nitrite reacts with the reagent directly. Total oxidised nitrogen is determined separately after a reduction step in which nitrate is reduced to nitrite and nitrate is determined by difference. In the field the colour is measured using a commercial colour comparator kit. In the laboratory a spectrophometer is used. This method can be automated and is usually carried out in modern laboratories by flow injection analysis.

Nitrate and nitrite can also be determined together with other anions by ion chromatography.

Control measures

The options for control can be divided into those implemented at the point of abstraction and those designed to control the amount of nitrogen entering the aquifer. The former include:

- blending low and high nitrate water from different supplies;
- closure of supplies and development of alternatives;
- treatment to remove nitrate;
- drilling deeper to draw on low-nitrate water.

These options will achieve the desired results for limited number of major abstraction sites, although at often great expense, but it is difficult to envisage their implementation for large number of relatively small abstractions in rural areas.

In these circumstances effective control of rising nitrate concentrations means reducing the inputs by cutting losses from the surface. For agricultural nitrate this means restrictions on the timing and amounts of fertiliser application, and using improved crop strains, cultivation practices and irrigation methods to promote more effective use of nutrients (Bijay-Singh et al, 1995; Cuttle and Scholefield, 1995; Schepers et al, 1995; Shrestha and Ladha, 2002). If such improvements are insufficient then the only approach is to consider radical changes in land use in designated vulnerable zones around abstraction points, introducing land uses from which nitrate losses are small. Any such agricultural control measures may have serious economic consequences for the farmers involved, and may be difficult to monitor and enforce.

For some urban areas abandoning a shallow aquifer due to progressive contamination is not an option in social or economic terms, because low income and socially deprived districts may be dependent on the underlying shallow aquifer for handpumps and public standpipes. In such situations the demands of supply and waste disposal have to be balanced and there is no easy prescriptive solution. One possible measure could be to use urban housing density controls to limit contaminant loading.

Water treatment

Nitrate can be removed from drinking water by ion-exchange. Units for point of supply operation comprise a pressure vessel containing anion-exchange resin, distribution and collection systems, and effluent storage tanks. In the exchange process, nitrate ions are retained on the resin and replaced in the water by chloride. When the capacity of the resin is exhausted and nitrate starts to break through into the processed water, the resin can be regenerated, normally using salt. The disadvantage of this technique is the need for disposal of saline effluent from regeneration.

Other treatment techniques include chemical reduction, biological denitrification, reverse osmosis and electrodialysis. Of these, reverse osmosis has proved to be effective but is relatively expensive.

Data sources

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British Geological Survey 2004