Rolling Revision of the
WHO Guidelines for Drinking-Water Quality

Draft for review and comments

Nitrates and nitrites in drinking-water

World Health Organization
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Chapter 1
Origin of nitrate in drinking water

1.1 Introduction

Nitrate and nitrite are naturally occurring ions that are part of the nitrogen cycle. The nitrate ion ($\text{NO}_3^-$) is the stable form of combined nitrogen for oxygenated systems. Although chemically inert, it can be reduced by microbial action. The nitrite ion ($\text{NO}_2^-$) contains nitrogen in a relatively unstable oxidation state. Chemical and biological processes can further reduce nitrite to various compounds or oxidise it to nitrate. The physicochemical properties are given in Chapter 3. Nitrate concentrations have been expressed in different units depending on the source of information. For example, the European Water Quality Regulations express nitrate concentrations using mg $\text{NO}_3^-\text{ l}^{-1}$ whereas WHO use mg $\text{NO}_3^-\text{N l}^{-1}$. The WHO recommended maximum limit for nitrate concentration in drinking waters is 50 mg l$^{-1}$ $\text{NO}_3^-$, equivalent to 11.3 mg l$^{-1}$ as $\text{NO}_3^-\text{N}$ (Chilton, 1996). The latter unit of expression shall be used throughout this report unless stated otherwise.

Nitrate is mainly used in inorganic fertilisers. It is also used as an oxidising agent, in the production of explosives, and as purified potassium nitrate for glass making. Sodium nitrite is used as a food preservative, especially in cured meats. Nitrate is sometimes also added to serve as a reservoir for nitrite. In the last three to four decades a gradual decline in the quality of raw water for drinking water supplies has been observed in many industrialised countries as a result of increasing nitrate concentrations. Since the mid 1950s the concentration of nitrate in groundwater and surface waters have increased in many countries. In the Federal Republic of Germany for example, water supply companies were, and still are, predominantly using groundwater for public water supply. Denmark also relies on groundwater as a source for drinking water. Danish waterworks (for consumers and industry) abstract 98-100% from groundwater and 0-2% from surface water. In fact, groundwater is of great importance as a water source throughout Europe, with more than 65% of Europe’s drinking water needs being met this way (Holt, 2000). Table 1.1 shows the increase in nitrate concentrations in drinking water in the Federal Republic of Germany since 1926 and Figure 1.1. Shows increasing groundwater nitrate concentrations in France and Denmark.

Comparable problems are also known from many developing countries. Water quality assessments studies carried out by NEERI (National Environmental Engineering Research Institute, 1991) identified the States with high nitrate concentration in groundwaters in India (see Table 1.2).
Table 1.1  Trend in nitrate concentrations in drinking water in the Federal Republic of Germany

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of analyses</td>
<td>909</td>
<td>1830</td>
<td>984</td>
<td>5043</td>
<td>4462</td>
<td>7360</td>
</tr>
<tr>
<td>Nitrate concentrations (mg/l) in %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>up to 10</td>
<td>78.1</td>
<td>76.3</td>
<td>63.6</td>
<td>51.6</td>
<td>48.9</td>
<td>46.1</td>
</tr>
<tr>
<td>&gt;10-20</td>
<td>10.8</td>
<td>11.1</td>
<td>17.8</td>
<td>23.3</td>
<td>21.8</td>
<td>21.2</td>
</tr>
<tr>
<td>&gt;20-30</td>
<td>5.6</td>
<td>6.7</td>
<td>8.9</td>
<td>14.1</td>
<td>12.8</td>
<td>14.0</td>
</tr>
<tr>
<td>&gt;30-40</td>
<td>2.4</td>
<td>2.0</td>
<td>4.3</td>
<td>6.0</td>
<td>8.0</td>
<td>9.2</td>
</tr>
<tr>
<td>&gt;40-50</td>
<td>1.4</td>
<td>1.6</td>
<td>2.6</td>
<td>2.2</td>
<td>4.3</td>
<td>5.5</td>
</tr>
<tr>
<td>&gt;50</td>
<td>1.4</td>
<td>2.3</td>
<td>3.1</td>
<td>2.7</td>
<td>4.0</td>
<td>4.1</td>
</tr>
</tbody>
</table>

(Source: German Federal Environmental Agency, unpublished)

The widespread increases in nitrate concentrations in groundwater have been caused by an increase in the input of nitrogen into environment as a result of human activities. These nitrogen inputs have gone beyond the assimilation and elimination capabilities of the biosphere. Surface waters are predominantly polluted by nitrate from surface run-off, sub-surface flow or groundwater exchange. Intensive agricultural production, domestic and industrial wastes, sewage and atmospheric nitrogen pollution are considered to be the main sources of nitrate contamination in water.

Table 1.2: Information on the occurrence of excessive nitrate in groundwaters in India (NEERI, 1991)

<table>
<thead>
<tr>
<th>name of state/union territory</th>
<th>name of district</th>
<th>number of samples</th>
<th>number of samples with NO\textsubscript{3}\textsuperscript{-} &gt; 45 mg/l</th>
<th>number of samples with NO\textsubscript{3}\textsuperscript{-} &gt; 45 mg/l (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andhra Pradesh</td>
<td>Kurnool</td>
<td>143</td>
<td>26</td>
<td>18.2</td>
</tr>
<tr>
<td>Bihar</td>
<td>Rohtas</td>
<td>209</td>
<td>55</td>
<td>26.3</td>
</tr>
<tr>
<td>Bihar</td>
<td>Palamu</td>
<td>191</td>
<td>40</td>
<td>20.9</td>
</tr>
<tr>
<td>Gujarat</td>
<td>Mehsana</td>
<td>200</td>
<td>37</td>
<td>18.5</td>
</tr>
<tr>
<td>Gujarat</td>
<td>Amreli</td>
<td>49</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Haryana</td>
<td>Faridabad</td>
<td>200</td>
<td>45</td>
<td>22.5</td>
</tr>
<tr>
<td>Haryana</td>
<td>Gurgaon</td>
<td>415</td>
<td>104</td>
<td>25.1</td>
</tr>
<tr>
<td>Karnataka</td>
<td>Gulbarga</td>
<td>529</td>
<td>261</td>
<td>49.3</td>
</tr>
<tr>
<td>Lakshadweep</td>
<td></td>
<td>135</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Madhya Pradesh</td>
<td>Jhabua</td>
<td>55</td>
<td>11</td>
<td>20.0</td>
</tr>
<tr>
<td>Maharashtra</td>
<td>Nagpur (villages)</td>
<td>114</td>
<td>47</td>
<td>41.2</td>
</tr>
<tr>
<td>Maharashtra</td>
<td>Nagpur (city)</td>
<td>100</td>
<td>82</td>
<td>82.0</td>
</tr>
<tr>
<td>Maharashtra</td>
<td>Satara</td>
<td>1001</td>
<td>163</td>
<td>16.3</td>
</tr>
<tr>
<td>Maharashtra</td>
<td>Latur</td>
<td>220</td>
<td>92</td>
<td>41.8</td>
</tr>
<tr>
<td>Orissa</td>
<td>Phulbani</td>
<td>225</td>
<td>29</td>
<td>12.9</td>
</tr>
<tr>
<td>Orissa</td>
<td>Koraput</td>
<td>503</td>
<td>71</td>
<td>14.1</td>
</tr>
<tr>
<td>Rajasthan</td>
<td>Barmer</td>
<td>351</td>
<td>220</td>
<td>62.7</td>
</tr>
<tr>
<td>Tamil Nadu</td>
<td>Ramanathapuram</td>
<td>66</td>
<td>7</td>
<td>10.6</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>4696</td>
<td>1290</td>
<td>27.5</td>
</tr>
</tbody>
</table>
Table 1.3 illustrates a range of indirect and direct causes of groundwater nitrate pollution.

Table 1.3 Causes of nitrate pollution of groundwater

<table>
<thead>
<tr>
<th>Causes of nitrate pollution of groundwater</th>
<th>Agriculture</th>
<th>Municipal</th>
<th>Industrial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffuse sources</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Use of synthetic nitrogen fertilisers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Use of organic fertilisers (manure and slurry)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The amount depends on agricultural driving forces (e.g. crop types, crop management techniques, changes of land use etc.)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Combustion engines in vehicles</td>
<td>+</td>
<td></td>
<td>+ Atmospheric emissions (nitric oxide and nitrite) from energy production</td>
</tr>
<tr>
<td>+ Disposal of municipal effluents by sludge spreading on fields</td>
<td>+</td>
<td></td>
<td>+ Combustion engines in vehicles</td>
</tr>
<tr>
<td>+ Disposal of effluents by sludge spreading on fields</td>
<td>+</td>
<td></td>
<td>+ Disposal of effluents by sludge spreading on fields</td>
</tr>
<tr>
<td>+ Nitrogen-rich effluent discharge to rivers with important groundwater connections</td>
<td>+</td>
<td></td>
<td>+ Disposal of nitrogen-rich wastes using well injection techniques</td>
</tr>
<tr>
<td>+ Poorly constructed wells which allow an exchange between polluted and non-polluted aquifer layers</td>
<td>+</td>
<td></td>
<td>+ Old and badly designed landfills</td>
</tr>
<tr>
<td>+ Old and badly designed landfills</td>
<td>+</td>
<td></td>
<td>+ Old and badly designed landfills</td>
</tr>
<tr>
<td>+ Septic tanks</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Leaking sewerage systems</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Nitrogen-rich effluent discharge to rivers with important groundwater connections</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Poorly constructed wells which allow an exchange between polluted and non-polluted aquifer layers</td>
<td>+</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.2 Natural sources

Nitrate reserves of 2000 to > 25,000 kg N ha\(^{-1}\) are stored in soils of the temperate zone depending on the thickness of soils, climate, clay content and the stabilisation of organic material (Stahr et al., 1994). Of these reserves, 95-98 % are bound in the humus fraction and in dead biomass and are neither mobile nor directly available to plants. The remaining percentage is distributed over the living biomass, in ammonium bound to clay minerals and in the form of ammonium and nitrate, which are directly available to plants. Transformation processes take place constantly between these individual nitrogen pools. The organic fraction of the soil is degraded by microbial activity resulting in the conversion of molecular nitrogen to ammonia. This is accomplished by different sets of micro-organisms, one example being the symbiotic bacterium *Rhizobia*, associated with the roots of legumes. Once converted to ammonia, nitrogen becomes available to plants and is incorporated into the biomass.

As a rule, ammonium is quickly absorbed by the rock matrix of the soil, whereas nitrate is not bound and can move with soil water and therefore has the potential to be lost, through leaching from the soil. Microbial nitrification, oxidation of ammonium through nitrite to nitrate by means of micro-organisms under aerobic conditions, is the only process where nitrate is formed in natural systems (Anderson, 1990):
\[
\text{NH}_4^+ + 1.5 \text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + 2 \text{H}^+ \quad \text{by bacteria of the nitrosomonas genus}
\]
\[
\text{NO}_2^- + 0.5 \text{O}_2 \rightarrow \text{NO}_3^- \quad \text{by bacteria of the nitrobacter genus}
\]

In natural ecosystems a balance of nitrogen reserves prevails in soil (Figure.1.2); net losses of soil nitrogen are compensated by net gains. Net losses are due to denitrifying bacteria within the soil reducing nitrate to nitrogen gas, which is subsequently released into the atmosphere, and also through the leaching of nitrate into groundwater. Net gains are due to nitrogen fixation by symbiotic bacteria such as *Rhizobia* and asymbiotic bacteria such as *Azobacter* and *Clostridium*. Deposition of atmospheric nitrogen compounds on soil occurs to a lesser extent, providing an input of 1-5 kg N ha\(^{-1}\) compared 90-130 kg N a\(^{-1}\) by biological fixation (Toepfer, 1997) in the absence of human activities. Asymbiotic nitrogen fixation ceases if alternative sources of nitrogen are available and is insignificant fertilised, cultivated soils. Human activities have resulted in the additional fixation of approximately 150 kg N a\(^{-1}\) by energy production, fertiliser production and cultivation of crops such as legumes or rice (Galloway, 1998).

![Diagram of the natural nitrogen cycle](image)

**Figure 1.2** The natural nitrogen cycle (After Mohr and Schopfer, 1992, in Mohr 1994)

Background nitrate concentrations unaffected by human activities are between 0-10 mg NO\(_3^-\) l\(^{-1}\) in groundwater (ECETOC, 1988) and up to 5 mg NO\(_3^-\) l\(^{-1}\) in surface water, although less than 1 mg NO\(_3^-\) l\(^{-1}\) is common (Meybeck and Helmer, 1996). Nitrate levels above 5 mg NO\(_3^-\) l\(^{-1}\) in surface water suggests input from a pollution
1.3 Sewage and waste waters

Nitrate is formed where wastes and sewage rich in nitrogen are biologically decomposed under aerobic conditions. This process predominantly takes place in aerated soil zones, on the surface of the soil, as well as in sufficiently aerated waters.

Large quantities of organic and inorganic wastes and sewage rich in nitrogen (organically bound nitrogen or in the form of inorganic nitrogen compounds) arise from private households, livestock units, specific branches of industry and many lines of trade such as the food or fertiliser industry.

Figure 1.3 Waste volume (t a⁻¹) in the EU (estimate) (Lindner, 1995)

Figure 1.3 shows the estimated annual waste volume generated in the European Union (Lindner, 1995). Sewage (specifically sewage sludge), industrial and household wastes are potential nitrate pollution sources and potential stores of re-usable organic wastes. Organic wastes from agriculture (farm manure) are discussed in Chapter 5.

Industrialised countries have invested enormous sums of money and resources in the traditional technology of wastewater collection, treatment and disposal and they continue to do so by construction of additional facilities (Niemczynowicz 1996). Urban wastewater contains human excreta (blackwater), diluted with large amounts of domestic greywater (such as bathwater) and polluted industrial wastewater. Sewerage networks transport wastewater to centralised treatment plants where certain amounts of organic matter, harmful and toxic substances and nutrients are removed before the effluent is discharged to a recipient body of water, for example the sea, as the final destination.
In developed countries, urban groundwater can be affected by sewage discharges, resulting largely from damaged or leaking municipal sewerage systems. The degree of contamination by nitrate and/or ammonium, sulphate, chloride, volatile organic compounds and heavy metals, depends on the position of the sewer pipes in relation to the water table and the permeability of the subsurface materials. In rural areas, inhabitants of secluded dwelling-houses and small communities not served by centralised sewerage systems rely on sanitation systems as cesspits and septic tanks and, or to decentralised treatment facilities for disposal of excreta. Groundwater pollution is often the result of poorly sited soakage systems, of discharges of poorly treated sewage by decentralised and on-site facilities, and of poorly managed sanitation systems (Weiskel and Howes, 1992., Just, 1994., Moser, 1998).

Barrett et al. (1999) in Nottingham, UK, demonstrated that nitrogen isotopes may be used to distinguish between different pollution sources by comparing \( \delta^{15}N \) values of the groundwater potential discharge sources. In Nottingham, the shallow groundwaters in residential areas showed nitrogen isotope signatures indicative of a sewage source.

Studies by Barrett et al. (1999) and Yang et al. (1999) have identified sewage as the source of nitrate pollution in urban groundwaters by means of the nitrate and chloride ratio. The amounts of nitrogen and chloride generated in human excreta are about 4 kg N per capita per annum and 2 kg Cl per capita per annum respectively. The actual concentration of nitrate in groundwater depends upon the percentage leached, the population density, dilution by groundwater through flow, and other discharge sources. On condition that all chloride is leached and 20-60 % of the nitrogen will be oxidised and leached to groundwater, the \( \text{NO}_3^- : \text{Cl}^- \) ratio would range from 1.8 to 5.3. A high ratio between \( \text{NO}_3^- \) and \( \text{Cl}^- \) is indicative of a sewage source and a close agreement between the two values would suggest a single pollution source.

UNICEF (1989) estimates that 60% of families living in rural areas and 23% living in urban areas of developing countries are without safe water. A more recent estimate by Pure Water for the World states that 1200 million people in developing countries do not have access to safe water and that 25 million people die each year through disease contracted by contaminated water (Pure Water for the World, 2000). Table 1.4 illustrates the percentage of those living in urban and rural areas with access to safe drinking water in developing and developed countries.

Table 1.4 Percentage of populations in urban and rural areas with access to safe drinking water (to be provided)

In developing countries, existing methods of collection, treatment and disposal of sewage and wastes actually impair the water quality of the water supply resources. Because sewerage systems may be absent or limited in extent, large areas of high population density and mostly low income depend on poor on-site sanitation systems such as pit latrines, cesspits, cesspools, septic tanks or community latrines. On-site sanitation is the preferred form, but is also the main pollution source, in many urban
or urbanising areas of the developing world. Domestic wastewater is collected through natural drains, open canals or ditches and subsequently discharged into water courses or on land. More than 95% of urban sewage is discharged untreated (WRI, 1992). Furthermore because adequate waste disposal is absent improper disposal of night soil and indiscriminate dumping of household refuse (often mixed with industrial hazardous wastes) is known to occur.

Inadequate access to safe drinking water and sanitation facilities is a significant environmental health problem in developing countries. ESCAP (1992) reported that of the 3,119 towns and cities in India only 8 have full wastewater collection and treatment facilities and 209 have partial facilities. According to reports by the WRI (1995) by early 1993, 42.9% of the population of urban India and only 3.5% of the population of rural India had sanitation facilities available to them. Clean drinking water was available to 84.9% of the urban population in 1993, an increase from 69% in 1985. However, for the rural population, a decrease from 82% in 1985 to 78.4% in 1993 was observed.

![Figure 1.4](image)

**Figure 1.4** Levels of nitrate contamination in local village wells in Yeumbeul area, Senegal (Tandia and Diop, 1997)

Kanza and Ndesamburo (1996) report that over 82% of the residents of Dar-es-Salaam, Tanzania, are served by on-site sanitation systems (pit latrines or septic tanks), with the most prevalent form of sanitation being pit latrines. In urban areas of Thailand (Ankara, 1998) central wastewater treatment is practically non-existent, for example, in Bangkok only 2% of the inhabitants are connected to sewage treatment plants. In rural areas wastewater disposal occurs by pit latrines, cesspits or septic tanks or by direct discharge of the untreated wastewaters in surface waters.

The Yeumbeul area in Senegal, Africa is a densely populated, severely polluted area, which is subject to rapid growth. In the unconfined groundwater the nitrate concentration has risen from 100 mg l\(^{-1}\) in 1987 to more than 250 mg l\(^{-1}\) in 1996 (see Figure 1.4) (Tandia and Diop, 1997). The main nitrate sources are human excreta, wastewaters and other wastes without adequate disposal.

*Barrett et al, (1998) and Barrett and Taylor (1998) demonstrated that the degree of nitrate contamination in groundwater beneath urban or urbanising areas of sub-*
Saharan Africa correlate with population density, as illustrated in Figure 1.5. Even on a regional scale, the close NO$_3$/Cl$^-$ correlation showed that discharge from pit-latrines was the one single, major source of pollution. This leads to the conclusion that nitrate levels will continue to rise beneath such regions, unless an integrated approach to sanitation and groundwater resource management is implemented. Similar problems are known in many developing countries, although cases also exist in developed countries. For example, the Scottish population of 5 million produces approximately $1.1 \times 10^{-6}$ m$^3$ of liquid domestic sewage effluent per day, containing about 110,000 tonnes of solid matter. Inadequate treatment at sewage works and overflows from sewers carrying foul drainage are the cause of poor water quality in 33% of the rivers designated as polluted (SEPA, 2000). Not everyone in Europe has access to adequate sanitation. The percentage of the total population in Europe that is connected to sewage systems ranges from 73% in the Czech Republic to over 95% in Sweden, UK and The Netherlands. Rural regions tend to have less access to proper sanitation than urban areas (Baltic Environmental Forum, 2000).

Throughout the whole world improper recovery and disposal of wastes and sewage (both domestic and industrial) in the past has resulted in considerable environmental pollution. For decades in Germany large quantities of sewage have been disposed on irrigation fields (a type of sewage land treatment) over a total of more than 30,000 ha. This has resulted in the pollution of soil and groundwater over large areas (Sowa et al., 1993). In China an agricultural area of more than $1.4 \times 10^{-6}$ ha is irrigated by sewage treated to varying degrees (Wang, 1984, Ou and Sun, 1996). Irrigation with untreated, non-controlled sewage in the past resulted regionally in contamination of soil by heavy metals and organic pollutants; of groundwater by organic and inorganic pollutants; and of cultivated plants and plant products by heavy metals and organic pollutants. Nitrate pollution was only one of numerous problems.

![Figure 1.5 Data from published studies of sub-Saharan Africa (median values from each study are plotted (Barrett and Taylor, 1998))](image)

of soil by heavy metals and organic pollutants; of groundwater by organic and inorganic pollutants; and of cultivated plants and plant products by heavy metals and organic pollutants. Nitrate pollution was only one of numerous problems.
encountered. Comparable problems are known from Mexico where in the Mezquital Valley 85,000 ha of agricultural land is irrigated by sewage effluents from Mexico City (Siebe and Fischer, 1996). In the Gaza Strip the main aquifer is recharged from several sources, including rainwater, sewage, irrigation, and sea water intrusion. Between 90 and 95% of the population use cesspools or surface drainage to discharge all types of wastewater (Al-Agha, 1995). When these cesspools are filled with used water, they are pumped and sprayed onto agricultural or unused land. Such blackwater and greywater is one of the largest contributors to nitrate groundwater contamination in the Gaza Strip.

1.4 Agricultural activities

In the industrialised Western European and North American countries intensive agriculture is considered to be the main source of water pollution by nitrate. The present pollution of waters is the result of more than 40 years of intensive agricultural production. The degree of water pollution depends on the type of land use (increasing in the order forestry, agriculture, livestock industry) and on the intensity of use. Furthermore local pedological, hydrological and hydrogeological factors control the pollution. The impact of two different types of land use on the nitrate concentrations of the wells used for the waterworks at Grosskneten, Germany is illustrated in Figure 1.6.

![Figure 1.6](Image)

**Figure 1.6** Nitrate concentrations in the raw water of intake wells of the waterworks Grosskneten (Oldenburg-East Frisian Water Association, Federal Republic of Germany), sited in catchments with different types of land use (German Country Working Party Relating to Water, 1996a)

The difference between the sum of nitrogen supplied to agricultural land and nitrogen withdrawn by harvested crops and animal production is the surplus nitrogen per hectare of agricultural area. This can give an estimation of nitrogen losses in relation to the area. Nitrogen is either stored in the organic soil fraction until a new balance is reached between nitrogen mineralisation and organic nitrogen input, eliminated
through microbial denitrification and degassing of ammonia, or washed out into groundwater in the form of nitrate. In the longer term, it is released to the environment from agricultural land in the form of non-productive nitrogen compounds, affecting resources and polluting the environment. Table 1.5 compares the nitrogen balances of agriculture of some Western European countries (Isermann, 1990b, 1994b) and gives an estimate of the fate of the excess nitrogen in the environment (Isermann, 1990b). These nitrogen surpluses per agricultural area are country-wide averages and do not give an accurate representation of the pollution situation because fertiliser use and animal production vary strongly from region to region. In Germany for example, the nitrogen surplus in areas with intensive animal husbandry or intensive market crop cultivation exceeds 200 kg N ha⁻¹ a⁻¹ (Wendland et al., 1993).

Scheierling (1995) reported that the highest nitrogen application per hectare by Dutch farmers (in Jansen et al., 1999). The nitrogen input in 1990 averaged 460 kg ha⁻¹ (Oenema et al., 1997), more than half of this originating from animal manure. The resulting nitrogen surplus was 320 kg ha⁻¹ a⁻¹. Matcic (1999) reported an average net-balance nitrogen surplus for Slovenia to be about 56 kg ha⁻¹. The average input from fertiliser was relatively low compared with high input levels of about 90 kg ha⁻¹ from organic manure.

Table 1.5
Nitrogen balances of agriculture of some Western European countries (Isermann, 1990b, 1994b) and the nitrogen excess remaining in the environment (Isermann, 1990b)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>ISERMANN</td>
<td>STADELMANN</td>
<td>ISERMANN</td>
<td>BOCKMANN et al.</td>
<td>JANSSO N</td>
</tr>
<tr>
<td>N input (kg N/ha*a)</td>
<td></td>
<td></td>
<td>465</td>
<td>218</td>
<td>218</td>
<td>152</td>
<td>124</td>
</tr>
<tr>
<td>1.mineral fertiliser</td>
<td></td>
<td></td>
<td>244</td>
<td>70</td>
<td>126</td>
<td>115</td>
<td>78</td>
</tr>
<tr>
<td>2.imported fodder</td>
<td></td>
<td></td>
<td>173</td>
<td>25</td>
<td>47</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>3.atmosph. deposition</td>
<td></td>
<td></td>
<td>41</td>
<td>53</td>
<td>30</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>4.fixing of N</td>
<td></td>
<td></td>
<td>5</td>
<td>65</td>
<td>12</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>5.sewage sludge</td>
<td></td>
<td></td>
<td>2</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>output of N (kg N/ha*a)</td>
<td></td>
<td></td>
<td>465</td>
<td>218</td>
<td>218</td>
<td>152</td>
<td>124</td>
</tr>
<tr>
<td>1.animal products</td>
<td></td>
<td></td>
<td>84</td>
<td>35</td>
<td>28</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>2.plant products</td>
<td></td>
<td></td>
<td>14</td>
<td>10</td>
<td>23</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>excess of N (kg N/ha*a)</td>
<td></td>
<td></td>
<td>367</td>
<td>173</td>
<td>167</td>
<td>126</td>
<td>103</td>
</tr>
<tr>
<td>thereof:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.in soil</td>
<td></td>
<td></td>
<td>(n.d.) not determined</td>
<td>n. d.</td>
<td>47</td>
<td>n. d.</td>
<td>16</td>
</tr>
<tr>
<td>2.in environment</td>
<td></td>
<td></td>
<td>&gt;319</td>
<td>151</td>
<td>120</td>
<td>126</td>
<td>87</td>
</tr>
<tr>
<td>thereof</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1.atmosphere</td>
<td></td>
<td></td>
<td>193</td>
<td>135</td>
<td>69</td>
<td>65</td>
<td>n. d.</td>
</tr>
<tr>
<td>2.1.1.NH₃ emission</td>
<td></td>
<td></td>
<td>99</td>
<td>44</td>
<td>44</td>
<td>&lt;50</td>
<td>n. d.</td>
</tr>
<tr>
<td>2.1.2.denitrification</td>
<td></td>
<td></td>
<td>94</td>
<td>91</td>
<td>25</td>
<td>15</td>
<td>n. d.</td>
</tr>
<tr>
<td>2.2.hydrosphere</td>
<td></td>
<td></td>
<td>n. d.</td>
<td>n. d.</td>
<td>51</td>
<td>61</td>
<td>n. d.</td>
</tr>
<tr>
<td>2.2.1.washing out</td>
<td></td>
<td></td>
<td>126</td>
<td>16</td>
<td>50</td>
<td>n. d.</td>
<td>n. d.</td>
</tr>
<tr>
<td>2.2.2.direct input</td>
<td></td>
<td></td>
<td>n. d.</td>
<td>n. d.</td>
<td>1</td>
<td>n. d.</td>
<td>n. d.</td>
</tr>
</tbody>
</table>
The nitrogen surplus in agricultural areas of EU member states is illustrated in Table 1.6.

Table 1.6 Nitrogen surplus in agricultural areas of EU Member States, 1990–1995

<table>
<thead>
<tr>
<th>Country</th>
<th>1990</th>
<th>1993</th>
<th>1995</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>106</td>
<td>109</td>
<td>103</td>
</tr>
<tr>
<td>Belgium</td>
<td>93</td>
<td>92</td>
<td>72</td>
</tr>
<tr>
<td>Denmark</td>
<td>51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Finland</td>
<td>47</td>
<td>54</td>
<td>57</td>
</tr>
<tr>
<td>France</td>
<td>105</td>
<td>101</td>
<td>102</td>
</tr>
<tr>
<td>Greece</td>
<td>84</td>
<td>61</td>
<td>58</td>
</tr>
<tr>
<td>Ireland</td>
<td>47</td>
<td>60</td>
<td>62</td>
</tr>
<tr>
<td>Italy</td>
<td>62</td>
<td>83</td>
<td>76</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>124</td>
<td>124</td>
<td>121</td>
</tr>
<tr>
<td>Netherlands</td>
<td>229</td>
<td>212</td>
<td>213</td>
</tr>
<tr>
<td>Portugal</td>
<td>27</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>Spain</td>
<td>40</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>Sweden</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UK</td>
<td>40</td>
<td>39</td>
<td>40</td>
</tr>
<tr>
<td>EU 12/15</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

Source: Eurostat

A factor contributing considerably to the nitrogen surplus is the decoupling of nutrient cycles as a result of splitting agricultural production into animal and plant production. When not subject to a limitation of livestock units per hectare, large amounts of manure are produced in animal production and which may be no longer used appropriately on the available land areas. Their use is seen more as a form of waste disposal than a fertilisation measure. In general, farmers' valuation of farm manure is poor because the availability of nitrogen is difficult to calculate and manure has only an insignificant economic benefit owing to its low nutrient content. This results in incorrect usage such as inadequate application techniques and excessive quantities that are inappropriate to crop production and ecology (Döhler, 1996). An example of this is over-application of nitrogen fertiliser in Beijing as described by Steinbuch et al. (1993) (in Zhang et al., 1996). The amount of fertiliser applied for vegetable production reached 3,719 kg N ha\(^{-1}\) and the nitrogen surplus was 3,206 kg N ha\(^{-1}\). The problem of over-application is further enhanced by preferentially applying farm manure to types of crops that are not adversely affected by an oversupply of nitrogen, such as maize, rape and root crops (Bach et al., 1992).

Figure 1.7 shows the relation between agricultural yield, the quantities of nitrogen fertiliser used for producing these yields, the associated nitrogen emissions and the foodstuff supply situation in industrialised countries (Isermann, 1994a).
Figure 1.7 From overproduction to requirement-orientated agricultural production (Isermann, 1994a)

In plant production, market crop farms exhaust almost completely the yield potentials of cultivated plants by using cheap commercial mineral nitrogen fertiliser. These fertilisers may be composed of a variety of chemicals including ammonium compounds, calcium, potassium and sodium nitrates, and urea. The use of mineral fertiliser enables a close matching of the application rates to the requirements of the plants but, as a result of increasing use, nitrogen levels have grown in excess of requirements. Figure 1.8 shows the trend in the consumption of nitrogen mineral fertiliser in some industrialised western countries.
1.5 Atmospheric sources

Anthropogenic or anthropogenically-induced emissions of nitrogen compounds into the atmosphere contribute to increasing pollution of drinking water resources by nitrate. This is because all nitrogen compounds that are emitted to the atmosphere in the form of gas (this applies to N$_2$O to some extent only) reach terrestrial ecosystems sometimes after complex chemical and photochemical transformation processes in the atmosphere. The various nitrogen compounds emitted may be assigned quantitatively to their main pollutant source as follows:

- NO$_x$ emissions (sum of NO + NO$_2$) are produced during all combustion processes and are predominantly caused by transport and energy production. Although 90% of emissions from combustion processes are in the form of NO, potentially all of the NO can be converted very quickly to NO$_2$ in the atmosphere. Thus NO$_x$ emissions are often quoted as total quantities of NO$_2$. Lammel (1993) estimated the annual world-wide total NO$_x$ emissions to be $53 \times 10^6$ t of NO$_2$, of which 60% originated from anthropogenic sources.

- NH$_3$ comes mostly from agriculture, especially from animal husbandry.

- N$_2$O emissions are released predominantly from industrial processes and the microbial reduction of nitrate on agricultural land. Nitrate is degraded mainly into molecular nitrogen during denitrification and also into N$_2$O. The share of N$_2$O in the
total emissions is between 0.2 and > 30 % and is controlled by a whole range of factors (Hoffmann, 1991). Table 1.7 provides an overview of total atmospheric emissions in the Federal Republic of Germany in 1994.

The total deposition of atmospheric N consists of dry, moist and wet deposition. Dry deposition occurs mainly on the surface of plants as a result of their surface properties (combing-out effect of vegetation), moist deposition occurs through aerosols such as fog droplets which precipitate onto surfaces, and wet deposition occurs by washing out from the atmosphere by precipitation. Dry deposition is important near the sources, whereas wet deposition is important for locations further away from the sources. Deposition rate is affected by meteorological factors (wind conditions, rate, frequency and intensity of precipitation) and the local weather conditions (frequency of inversion, fog and clouds), the geographical location relative to the emitter, and the altitude and the exposure situation (leeward or windward).

Meixner (1994) estimated for Europe and eastern North America an atmospheric nitrogen input of 10 – 40 kg of N ha\(^{-1}\) a\(^{-1}\), and Wendland et al., (1993) assume an average pollution of fields of 30 kg N ha\(^{-1}\) a\(^{-1}\) for Germany. In areas with intensive animal husbandry which is connected with high ammonia emissions, such as in the Netherlands, deposition rates of more than 100 kg N ha\(^{-1}\) a\(^{-1}\) are not unusual. In exposed places, such as at the edges of woodlands downwind from emission sources (conurbations, animal husbandry farms), values of up to 200 kg N ha\(^{-1}\) a\(^{-1}\) may be reached.

Due to the larger leaf area and aerodynamic roughness in forests of trees compared with short crops, the rate of adsorption and absorption of nitrogen is 2-3 times greater (Brechtle, 1992). High nitrogen deposition rates combined with the low uptake of nitrogen by trees, and other environmental factors such as insignificant rates of groundwater recharge, degradation of soils and inhibition of denitrification by progressive acidification of forest soils, results in increased nitrate concentrations in groundwater in forest areas.

1.6. Other sources

Chloramination may give rise to the formation of nitrite within the drinking-water distribution system, and the concentration of nitrite may increase as the water moves towards the extremities of the distribution network. All water systems that practise chloramination should closely and regularly monitor their systems to verify disinfectant levels, microbiological quality, and nitrite levels. If nitrification is detected (e.g. reduced disinfectant residuals and increased nitrite levels), steps should be taken to modify the treatment train or water chemistry in order to maintain a safe water quality. Efficient disinfection must never be compromised.
Table 1.7 Overview of total atmospheric emissions of nitrogen compounds in the Federal Republic of Germany in 1994 (German Federal Environmental Agency 1997, preliminary data)

<table>
<thead>
<tr>
<th>Source of Emissions</th>
<th>NOx emission</th>
<th>NH3 emission</th>
<th>N2O emission</th>
<th>NOx emission</th>
<th>NH3 emission</th>
<th>N2O emission</th>
<th>N total in Gg N</th>
<th>N total in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>animal husbandry</td>
<td>533 Gg</td>
<td>439 Gg</td>
<td>439 Gg</td>
<td>439 Gg</td>
<td>33.8%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>application of fertiliser</td>
<td>58 Gg</td>
<td>86 Gg</td>
<td>48 Gg</td>
<td>45 Gg</td>
<td>7.1%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>waste management</td>
<td>4 Gg</td>
<td>2 Gg</td>
<td>2 Gg</td>
<td>2 Gg</td>
<td>0.2%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>use of solvents and products</td>
<td>6 Gg</td>
<td>3 Gg</td>
<td>3 Gg</td>
<td>3 Gg</td>
<td>0.2%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>industrial processes</td>
<td>23 Gg</td>
<td>8 Gg</td>
<td>81.3 Gg</td>
<td>7 Gg</td>
<td>42 Gg</td>
<td>56 Gg</td>
<td>4.3%</td>
<td></td>
</tr>
<tr>
<td>transport</td>
<td>1283 Gg</td>
<td>17 Gg</td>
<td>19.3 Gg</td>
<td>390 Gg</td>
<td>14 Gg</td>
<td>10 Gg</td>
<td>414 Gg</td>
<td>31.9%</td>
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<td>households</td>
<td>103 Gg</td>
<td>1 Gg</td>
<td>3 Gg</td>
<td>31 Gg</td>
<td>1 Gg</td>
<td>2 Gg</td>
<td>34 Gg</td>
<td>2.6%</td>
</tr>
<tr>
<td>small consumers</td>
<td>59 Gg</td>
<td>1 Gg</td>
<td>18 Gg</td>
<td>1 Gg</td>
<td>1 Gg</td>
<td>19 Gg</td>
<td>1 Gg</td>
<td>1.5%</td>
</tr>
<tr>
<td>industrial furnaces</td>
<td>254 Gg</td>
<td>1 Gg</td>
<td>5 Gg</td>
<td>77 Gg</td>
<td>1 Gg</td>
<td>3 Gg</td>
<td>81 Gg</td>
<td>6.2%</td>
</tr>
<tr>
<td>power stations and central heating stations</td>
<td>488 Gg</td>
<td>3 Gg</td>
<td>13 Gg</td>
<td>148 Gg</td>
<td>2 Gg</td>
<td>7 Gg</td>
<td>158 Gg</td>
<td>12.1%</td>
</tr>
<tr>
<td>total</td>
<td>2210 Gg</td>
<td>622 Gg</td>
<td>218.6 Gg</td>
<td>672 Gg</td>
<td>513 Gg</td>
<td>113 Gg</td>
<td>1298 Gg</td>
<td>100%</td>
</tr>
<tr>
<td>total, in %</td>
<td>51.8%</td>
<td>39.5%</td>
<td>8.7%</td>
<td>100%</td>
<td></td>
<td></td>
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2.1 Environmental levels and human exposure

2.1.1 Air

Atmospheric nitrate concentrations ranging from 0.1 - 0.4 µg m\(^{-3}\) have been reported, the lowest concentrations being found in the South Pacific (Prospero and Savoie, 1989). Mean monthly nitrate concentrations in air in the Netherlands range from 1 - 14 µg m\(^{-3}\) (Janssen et al., 1989). Indoor nitrate aerosol concentrations of 1.1 - 5.6 µg m\(^{-3}\) were found to be related to outdoor concentrations (Yocom, 1982).

Hoek et al. (1996) measured concentrations of atmospheric pollutants in three urban and five rural sites within the Netherlands. High ammonia concentrations (above 10 µg m\(^{-3}\)) were recorded at a site with intensive livestock farms. Daily average nitrous acid concentrations up to 20 µg m\(^{-3}\) were observed at sites with high traffic density.

The New York State Department of Environmental Conservation (NYSDEC) Air Quality Report 1996, reports stable concentrations of nitrogen dioxide since 1995 at all sites statewide. These levels remain below the air quality standard of 0.05 ppm, the highest mean concentration (0.042 ppm in both 1995 and 1996) occurring in upper Manhattan. Nitrate concentrations were found to fluctuate year to year with no distinct trend.

2.1.2 Water

Concentrations of nitrate in rainwater of up to 5 mg l\(^{-1}\) have been observed in industrial areas (van Duijvenboden and Matthijsen, 1989). In rural areas, concentrations are somewhat lower. The nitrate concentration in surface water is normally low (0 - 18 mg l\(^{-1}\)), but can reach high levels as a result of agricultural runoff, runoff from refuse dumps, or contamination with human or animal wastes. The concentration often fluctuates with the season and may increase when the river or stream is fed by nitrate-rich aquifers. Nitrate concentrations have gradually increased in many European countries in the last few decades and have sometimes doubled over the past 20 years. In the United Kingdom, for example, an average annual increase of 0.7 mg l\(^{-1}\) has been observed in some rivers (Young and Morgan-Jones, 1980).

Strebel et al. (1989) and Fried (1991) both observed a rising trend in groundwater nitrate concentrations in Europe including Belgium, Denmark, France, Germany, The Netherlands and England. The highest concentrations (above 50 mg nitrate l\(^{-1}\)) were found in sandy soils beneath intensely managed crops. Fertilisation and livestock manure are believed to be the principal sources of groundwater nitrates (Hudak, 2000).

The natural nitrate concentration in groundwater under aerobic conditions is a few milligrams per litre and depends strongly on soil type and on the geological situation. In the USA, naturally occurring levels do not exceed 4-9 mg l\(^{-1}\) for nitrate and 0.3 mg l\(^{-1}\) for nitrite (US EPA, 1987). As a result of agricultural activities, the nitrate
concentration can easily reach several hundred milligrams per litre (WHO, 1985b). For example, concentrations of up to 1,500 mg \(1^{-1}\) were found in groundwater in an agricultural area of India (Jacks and Sharma, 1983).

In the USA, nitrates are present in most surface water and groundwater supplies at concentrations below 4 mg \(1^{-1}\), concentrations exceeding 20 mg \(1^{-1}\) in about 3% of surface waters and 6% of groundwaters. In 1986, the Maximum Contaminant Level (MCL) for nitrate contamination (44 mg \(1^{-1}\) or 10 mg \(1^{-1}\) NO\(_3\)-N) was exceeded in 40 surface water and 568 groundwater supplies. Nitrite levels were not surveyed but are expected to be much lower than 3.3 mg \(1^{-1}\) (US EPA, 1987). Kolpin et al. (1994) measured nitrates in near-surface aquifers (less than 15m deep) in soya and corn producing areas in the midwestern US and recorded concentrations above 45 mg \(1^{-1}\) were recorded in 6% of 303 wells. Nitrite levels in drinking-water in the Netherlands are usually below 0.1 mg \(1^{-1}\). In 1993, a maximum value of 0.21 mg \(1^{-1}\) was detected (RIVM, 1993). In a survey of groundwater nitrate levels in north-central and west-central Texas, over 50% of observations exceeded the MCL (Hudak, 2000).

Pollution of groundwater by nitrates, nitrites and ammonium in Slovenia was evaluated between 1991 and 1994 (Maticic, 1999). The average annual nitrate concentrations in regions Pomursko and Celjsko were over 50 mg \(1^{-1}\) during 1993-1994. Extreme values over 100 mg NO\(_3\) \(1^{-1}\) were reached in these areas. Nitrate and ammonium values were also highest in these same regions, which are areas of intensive agriculture and livestock production.

The increasing use of artificial fertilisers, the disposal of wastes (particularly from animal farming), and changes in land use are the main factors responsible for the progressive increase in nitrate levels in groundwater supplies over the last 20 years. In Denmark and the Netherlands, for example, nitrate concentrations were increasing by 0.2-1.3 mg \(1^{-1}\) year\(^{-1}\) in some areas (WHO, 1985b). Pacheco and Cabrera (1997) reported nitrate contamination in a karstic limestone aquifer beneath the Yucatan Peninsula of Mexico and attributed this to human and agricultural wastewater. Conversion of land use from grasslands to intensive cultivation of grain corn caused nitrate pollution beneath the Asatian Plain in France (Bernhard et al., 1992). Use of fertilisers and livestock manure have been attributed to nitrate contamination in a sandstone aquifer beneath Nottingham, England (Rivers et al., 1996) and of groundwater in The Netherlands (Oenema et al., 1998). These are also the principal sources of nitrate contamination in groundwaters of southern Australia (Dillon, 1991) and New Zealand (Burden et al., 1982).

In Northern China the increase in nitrogen fertiliser since 1980 has resulted in over 50% of the 69 locations investigated having nitrate concentrations above 50 mg \(1^{-1}\) (Zhang et al., 1996). Concentrations up to 300 mg \(1^{-1}\) were found in groundwater below vegetable producing areas, farmers yards, small cities and towns (Zhang et al., 1996). Nitrate contamination of groundwater in Eastern Botswana, Africa, exceeded health limits following increasing concentrations over the past three decades (Lagerstedt et al., 1994). Nitrate pollution of the alluvial aquifer beneath the urban complex of Eskiehir, Turkey, was found to be greatest below densely populated and unsewered areas (Kacarogl and Gunay, 1997).

Because of the delay in the response of groundwater to changes in soil, some endangered aquifers have not yet shown the increase expected from the increased use
of nitrogen fertiliser or manure. Once the nitrate reaches these aquifers, they will remain contaminated for decades, even if there is a substantial reduction in the nitrate loading at the surface.

In most countries, nitrate levels in drinking-water derived from surface water do not exceed 10 mg l⁻¹. In some areas, however, concentrations are higher as a result of runoff and the discharge of sewage effluent and certain industrial wastes. In 15 European countries, the percentage of the population exposed to nitrate levels in drinking-water above 50 mg l⁻¹ ranges from 0.5%-10% (WHO, 1985b; ECETOC, 1988); this corresponds to nearly 10 million people. Individual wells in agricultural areas throughout the world are contributing to widespread nitrate-related toxicity problems, nitrate levels in well-water often exceed 50 mg l⁻¹.

Chloramination may give rise to the formation of nitrite within the drinking water distribution system, and the concentration of nitrite may increase as the water moves towards the extremities of the system. Nitrification in distribution systems can increase nitrite levels, usually by 0.2-1.5 mg of nitrite per litre, but potentially by more than 3 mg of nitrite per litre (AWWARF, 1995).

### 2.1.3 Food

Vegetables constitute the major source of nitrate, providing 80% of the average daily human dietary intake (Ximenes et al., 2000). Nitrate and nitrite are intentionally added to certain meat products to inhibit growth of *Clostridium botulinum* spores, and also to impart a characteristic flavour and colour to such products. Small amounts of nitrate and nitrite may be present in fish and dairy products. Levels of nitrate in the diet of dairy cows appears to have little effect on the nitrate concentrations in milk produced. Levels in liquid milk tend to remain between 1-5 mg NO₃ kg⁻¹ (NAS, 1981). Some countries may add nitrate to cheese (for example Belgium, Denmark, Norway) although Danish studies have shown nitrate and nitrite to be present in cheese made without these additions (Denmark SFI, 1981., in NAS, 1981).

Meat products may contain <2.7-9.45 mg NO₃ kg⁻¹ and <0.2-1.7 mg NO₂ kg⁻¹ (ECETOC, 1998). Cassens (1997) sampled bacon, bologna and sliced ham and found an average residual nitrite content of 10ppm. Residual nitrate was non-detectable. The average levels of nitrite (as NaNO₂) in cured meat products are in the range 10-40 mg kg⁻¹ (Sen and Baddoo, 1997) with values in the USA being in the lower part of this range. Dairy products may contain <3-27 mg NO₃ kg⁻¹ and <0.2-1.7 mg NO₂ kg⁻¹ (ECETOC, 1988).

The nitrate content of vegetables can be affected by the processing of the food, the use of fertilisers, and growing conditions, especially the soil temperature and (day)light intensity (Gangolli et al., 1994; WHO, 1995). Vegetables such as beetroot, lettuce, radish, and spinach often contain nitrate concentrations above 2,500 mg kg⁻¹, especially when they are cultivated in greenhouses. Nitrite levels in food are very low (generally well below 10 mg kg⁻¹) and rarely exceed 100 mg kg⁻¹. Exceptions to this are vegetables that have been damaged, poorly stored, or stored for extended periods, as well as pickled of fermented vegetables. In such circumstances, nitrite levels of up to 400 mg kg⁻¹ have been found (WHO, 1995).
2.1.4 Estimated total exposure and relative contribution of drinking-water

Air pollution appears to be a minor source of nitrate exposure. In general, vegetables will be the main source of nitrate intake when nitrate levels in drinking-water are below 10 mg l⁻¹ NO₃-N (Chilvers et al., 1984, US EPA, 1987, ECETOC, 1988).

When nitrate levels in drinking-water exceed 10 mg l⁻¹ NO₃-N, drinking-water will be the major source of total nitrate intake, especially for bottle-fed infants. In the Netherlands, the average population exposure is approximately 140 mg of nitrate per day (including the nitrate in drinking-water). The contribution of drinking-water to nitrate intake is usually less than 14%. For bottle-fed infants, daily intake from milk formula made with water containing 50 mg NO₃ would average about 8.3-8.5 mg NO₃ kg⁻¹ of body weight per day.

The mean dietary intakes determined by the duplicate portion technique (WHO, 1985a) range from 43 to 131 mg of nitrate per day and from 1.2 to 3 mg of nitrite per day. Estimates of the total nitrate intake based on the proportion of nitrate excreted in the urine (Bartholomew et al., 1979) range from 39 to 268 mg per day, the higher values applying to vegetarian and nitrate-rich diets (ECETOC, 1988). The estimated total daily intake of nitrate in the United Kingdom ranged from 50 to 81 mg per person (Bonnell, 1995, Schuddeboom, 1995), in Denmark from 70 to 172 mg per person (Bonnell, 1995), and in Germany from 70 to 110 mg per person (Bonnell, 1995). According to the US EPA, the average nitrate intake from food is approximately 40-100 mg per day for males. The daily nitrite intake ranges from 0.3 to 2.6 mg per day, primarily from cured meat (NAS, 1981).

Saleh et al. (1998) studied nutrients and chemical residues in an Egyptian total mixed diet. Dietary ingested nitrate and nitrites amounted to 296 mg per day which is approximately 140% of the acceptable daily intake with respect to females and 116% with regard to males. Hotchkiss (1988) estimated that the average western diet contained 62-124 mg nitrate per person per day and commented that this could be substantially increased by consuming vegetables and/or high nitrate water.

Nitrite present in cured meat has been reported to account for up to 70% of total dietary intake of this nitrite, depending on the quantity of such meat consumed and the origin and type of cured meat consumed. Mean dietary nitrite intake from all food sources has been reported to range from < 0.1 to 8.7 mg of nitrite per person per day for European diets (WHO, 1995).

2.2 Kinetics and metabolism in laboratory animals and humans

Ingested nitrate has a half-life of about 5 hours (CAST, 2000) and is readily and completely absorbed from the upper small intestine. Nitrite may be absorbed directly from both the stomach and the upper small intestine. Part of the ingested nitrite reacts with gastric contents prior to absorption.

Nitrate is rapidly distributed throughout body tissues. Approximately 25% of ingested nitrate is actively secreted and concentrated by a factor of 10 into saliva (Duncan et al., 1995) where it is partly (20%) reduced to nitrite by the oral microflora; nitrate and nitrite are then swallowed and re-enter the stomach. Salivary
nitrate and nitrite concentrations are roughly proportional to the amount of nitrate ingested (Bartholomew and Hill, 1984). Bacterial reduction of nitrate may also take place in other parts of the human gastrointestinal tract, but not normally in the stomach, which is virtually sterile. Exceptions are reported in humans with low gastric acidity, such as artificially fed infants and certain patients in whom hydrochloric acid secretion is slower than normal, or patients using antacids (Colbers et al., 1995). In rats, active secretion and reduction of nitrate in saliva are virtually absent (Walker, 1995). Total nitrate reduction in rats is probably less than in humans.

Nitrate is relatively non-toxic, but when reduced to nitrite by bacteria in the upper gastrointestinal tract toxicity greatly increases. Nitrite is absorbed into the bloodstream where it reacts with haemoglobin (Hb) to form methaemoglobin (MetHb) (Bruningfann and Kaneene, 1993), a form of haemoglobin in which the iron has been oxidised to its ferric state (McKnight et al., 1999). Methaemoglobin does not act as an oxygen carrier (Jaffe, 1981., US National Research Council, 1995).

\[
\text{NO}_2^- + \text{oxyHb (Fe}^{2+}) \rightarrow \text{metHb (Fe}^{3+}) + \text{NO}_3^-
\]

Cyanosis and anoxemia can result if the level of methaemoglobin becomes too high (Bruningfann and Kaneene, 1993).

Nitrite has been shown to cross the placenta and cause the formation of foetal methaemoglobinemia in rats. It may react in the stomach with nitrosatable compounds (e.g. secondary and tertiary amines or amides in food) to form N-nitroso compounds. Such endogenous nitrosation has been shown to occur in human as well as animal gastric juice, both \textit{in vivo} and \textit{in vitro}. It occurs mostly at higher pH values, when both nitrite and nitrosatable compounds were present simultaneously (Shephard, 1995: WHO, 1996).

The major part of ingested nitrate is eventually excreted in urine as nitrate, ammonia or urea. Faecal excretion is negligible. Little nitrite is excreted (WHO, 1985b: ICAIR Life System. Inc., 1987; Speijers et al., 1989).

### 2.2.1 Endogenous synthesis of nitrate and nitrite

Some individuals are more susceptible to nitrate exposure from drinking water or food because of endogenous synthesis. The excess nitrate excretion that has often been observed after low nitrate and nitrite intake originates from endogenous synthesis. In normal healthy humans, endogenous synthesis results in 1 mmol per day on average, corresponding to 62 mg nitrate per day or 14 mg nitrate-nitrogen per day. Gastrointestinal infections greatly increase nitrate excretion, as a result, (at least in part) of increased endogenous (non-bacterial) nitrate synthesis, probably induced by activation of the mammalian reticuloendothelial system (WHO, 1985b., 1996; Speijers et al., 1989; Wishnok et al., 1995). This endogenous synthesis of nitrate complicates the risk assessment of nitrate.

Increased endogenous synthesis of nitrate, as reported in animals with induced infections and inflammatory reactions, has also been observed in humans. Infections and non-specific diarrhoea played a role in the increased endogenous synthesis of nitrate observed by Tannenbaum et al. (1978), Green et al. (1981), Hegesh and...
Shiloah, (1982) Bartholomew and Hill, (1984), Lee et al. (1986) and Gangolli et al. (1994). These observations are all consistent with the induction of one or more nitric oxide synthases by inflammatory agents, analogous to the experiments described in animals and macrophages. This induction in humans has been difficult to demonstrate directly, but administration of [15N] arginine to two volunteers resulted in the incorporation of 15N into urinary nitrate in both individuals, confirming the arginine-nitric oxide pathway in humans (Leaf et al., 1989).

Nitrate excretion in excess of nitrate intake by humans was reported as early as 1916, but this result remained unconfirmed until the end of the 1970s, when it was re-examined because of the potential involvement of nitrate in endogenous nitrosation. A relatively constant daily production of about 1 mmole nitrate was confirmed. A major pathway for endogenous nitrate production is conversion of the amino acid L-arginine by the enzyme nitric oxide synthase to nitric oxide and 1-citrulline (Culotta and Koshland, 1992) followed by oxidation of the nitric oxide to anhydride and then reaction of nitrous anhydride with water to yield nitrite. Nitrate is rapidly oxidised to nitrate through reaction with Hb. In addition to macrophages, many cell types can form nitric oxide, generally from arginine. Under some conditions, bacteria can form nitric oxide by reduction of nitrite. These processes can lead to nitrosation of amines at neutral pH, presumably by reaction with nitrous anhydride. The question of whether the arginine-nitrate pathway can be associated with increased cancer risk via exposure to N-nitroso compounds remains open. Nitric oxide is mutagenic towards bacteria and human cells in culture; it causes DNA strand-breaks, deamination (probably via nitrous anhydride), and oxidative damage. It can also activate cellular defence mechanisms. In virtually all of these cases, the biological response is paralleled by the final nitrate levels. Thus, while endogenously formed nitrate may itself be of relatively minor toxicological significance, the observed concentrations may serve as indicators for the potentially important nitric oxide-related processes that gave rise to it (Wishnok et al., 1995).

2.2.2 Reduction of nitrate to nitrite

As mentioned above, both in vitro and in vivo studies have shown that nitrate can be reduced to nitrite by bacterial and mammalian metabolic pathways, through widespread nitrate reductase (Gangolli et al., 1994). In humans, saliva is the major site for the formation of nitrite. About 5% of dietary nitrate is converted to nitrite (Spiegelhalder et al., 1976; Eisenbrand et al., 1980; Walters and Smith, 1981; Gangolli et al., 1994). A direct correlation between gastric pH, bacterial colonization, and gastric nitrite concentration has been observed in healthy people (Mueller et al., 1983, 1986). In individuals with gastrointestinal disorders and achlorhydria, high levels of nitrite can be reached (6 mg l⁻¹) (Rudell et al., 1976, 1978; Dolby et al., 1984). The situation in neonates is not clear. It is commonly accepted that infants younger than three months may be highly susceptible to gastric bacterial nitrate reduction, because the pH is generally higher than in adults (Speijers et al., 1989). However, the presence of acid-producing lactobacilli in the stomach may be important, because these organisms do not reduce nitrate and may maintain a pH low enough to inhibit colonisation by nitrate-reducing bacteria (Bartholomew et al., 1980). As mentioned above, nitrite may also be produced via the arginine-nitric oxide pathway, but would be undetectable because of the rapid oxidation to nitrate. One possible example of nitrite production by this route, however, is the
methaemoglobinaemia observed in infants suffering from diarrhoea (Gangolli et al., 1994).

2.3 Effects on laboratory animals and in vitro test systems

2.3.1 Acute exposure

Clinical signs of acute nitrate toxicity vary according to species. Whilst monogastric animals tend to exhibit severe gastritis, ruminants develop methaemoglobinaemia (Bruningfann and Kaneene, 1993). The acute oral toxicity of nitrate to laboratory animals is low to moderate. LD$_{50}$ values of 1,600-9,000 mg of sodium nitrate per kg of body weight have been reported in mice, rats and rabbits (Table 2.1).

Table 2.1 Acute oral toxicity of nitrate to laboratory animals

<table>
<thead>
<tr>
<th>Species</th>
<th>Nitrate salt</th>
<th>LD$_{50}$ oral values Mg kg$^{-1}$ body weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>rabbit</td>
<td>NaNO$_3$</td>
<td>2680</td>
</tr>
<tr>
<td>rat</td>
<td>KNO$_3$</td>
<td>3750</td>
</tr>
<tr>
<td>rabbit</td>
<td>KNO$_3$</td>
<td>1900</td>
</tr>
<tr>
<td>rat</td>
<td>NH$_4$NO$_3$</td>
<td>4820</td>
</tr>
<tr>
<td>rat</td>
<td>NH$_4$NO$_3$</td>
<td>2450</td>
</tr>
</tbody>
</table>


Ruminants are more sensitive to the effects of nitrate as a result of high nitrate reduction in the rumen; the LD$_{50}$ for cows was 450 mg of sodium nitrate per kg of body weight. Nitrite is more toxic than nitrate LD$_{50}$ values of 85-220 mg of sodium nitrite per kg of body weight have been reported for mice and rats (Speijers et al., 1989, WHO, 1996). Unlike nitrate, nitrite is capable of inducing methaemoglobinaemia in a wide range of species, for example cattle, sheep, dogs, rats and chickens (Table 2.2).

Table 2.2 The oral LD$_{50}$ of sodium nitrite

<table>
<thead>
<tr>
<th>Species</th>
<th>LD$_{50}$ oral values mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>mouse</td>
<td>214</td>
</tr>
<tr>
<td>rabbit</td>
<td>186</td>
</tr>
<tr>
<td>rat</td>
<td>180</td>
</tr>
</tbody>
</table>

Source: NIOSH (1987)

2.3.2 Short-term exposure

In a 13-week study in which nitrite was given to rats in drinking-water, a dose-related hypertrophy of the adrenal zona glomerulosa was observed at all dose levels (100, 300, 1000 or 3000 mg potassium nitrite per litre). Increased metHb levels were seen only in the highest dose group (Til et al., 1988). It was concluded by WHO (1995) that the no-observed-effect-level (NOEL) in this study was 100 mg of potassium nitrite per litre (equivalent to 5.4 mg kg$^{-1}$ of body weight per day expressed as nitrite ion), because the hypertrophy seen at this dose was not significantly
different from the controls.

An additional 13-week study in which nitrite was also given in drinking-water, including lower doses of potassium nitrite and two doses of sodium nitrite (equimolar to the low and high doses of potassium nitrite), confirmed the finding of the adrenal hypertrophy of the zona glomerulosa for potassium nitrite and also revealed hypertrophy in the animals given sodium nitrite. The NOEL for the adrenal hypertrophy of the zona glomerulosa was 50 mg of potassium nitrite per litre (equivalent to 5 mg of potassium nitrite per kg of body weight per day) (Til et al., 1997). Since then, studies designed to clarify the etiology of this hypertrophy and to establish its significance for human health have been conducted and are currently in progress. The studies already performed confirmed the adrenal hypertrophy in another rat strain. However, the effects only occurred at higher dose levels. It was also observed that the hypertrophy was still present after a 30-day recovery period but had disappeared after a 60-day recovery period. At present, the mechanism of hypertrophy induced by nitrite is not clear (Boink et al., 1995).

A variety of experimental and field studies in different mammals identified inorganic nitrate as a goitrogenic agent. It could be shown in rats by oral and parenteral application of potassium nitrate (Wyngaarden et al., 1953; Bloomfield et al., 1961; Alexander and Wolff, 1966; Wolff, 1994), of nitrate in hay (Lee et al., 1970), and of sodium nitrate (Höring et al., 1985; Seffner and Höring, 1987a,b). Antithyroid effects of nitrate were also found in sheep (Bloomfield et al., 1961) and in pigs by application of potassium nitrate (Jahreis et al., 1986, 1987). Furthermore, nitrate was goitrogenic to livestock, namely pigs (Körber et al., 1983), cattle (Körber et al., 1983, 1985), sheep (Körber et al., 1983) and goats (Prassad, 1983).

### 2.3.3 Long-term exposure

The only observed effect of nitrate in rats after two years of oral administration was growth inhibition, which occurred at dietary concentrations of 5% sodium nitrate and higher. The NOEL in this study was 1%, which corresponds to 370 mg of nitrate per kg of body weight per day (Speijers et al., 1989; WHO, 1996). A carcinogenicity study did not show carcinogenic effects at the highest dose levels of 1820 mg of nitrate per kg of body weight per day. However, this level could not be considered as a NOEL, because complete histopathological examinations were not performed (WHO, 1996).

One of the long-term effects of nitrite reported in a variety of animal species is vitamin A deficiency. This is probably caused by the direct reaction of nitrite with the vitamin. The most important effects reported in long-term animal studies were an increase in metHb level and histopathological changes in the lungs and heart in rats receiving nitrite in drinking-water for two years. The lowest-observed-adverse-effect-level (LOAEL) which gave a metHb level of 5%, was 1000 mg of sodium nitrite per litre. The NOEL was 100 mg of sodium nitrite per litre, equivalent to 10 mg of sodium nitrite per kg of body weight per day (or 6.7 mg kg⁻¹ of body weight per day expressed as nitrite ion) (Speijers et al., 1989).
2.3.4 Reproductive and development toxicity

The reproductive behaviour of guinea-pigs was found to be impaired only at very high nitrate concentrations (30 000 mg of potassium nitrate per litre); the NOEL was 10,000 mg l⁻¹ (Speijers et al., 1989; WHO, 1996). In rabbits, dose levels of 250 or 500 mg of nitrate per litre, administered during 22 weeks, revealed no detrimental effects on reproductive performance after successive gestations. In sheep and cattle, no abortions were observed at dose levels causing severe methaemoglobinemia (Speijers et al., 1989; Fan and Steinberg, 1996; WHO, 1996).

Nitrite appeared to cause fetotoxicity in rats at drinking-water concentrations equivalent to 200 and 300 mg of sodium nitrite per kg of body weight per day. These concentrations increased maternal metHb levels. However, after similar doses in feed in other studies, no embryotoxic effects were observed in rats. In a reproductive toxicity study in guinea-pigs at dose levels of 0, 50 or 60 mg of sodium nitrite per kg of body weight per day given by subcutaneous injection, foetal death followed by abortion occurred at the highest dose level. Teratogenic effects were not observed in reported studies in mice and rats (Speijers et al., 1989; WHO, 1996).

2.3.5 Mutagenicity and related end-points

Nitrate is not mutagenic in bacteria and mammalian cells in vitro. Chromosomal aberrations were observed in the bone marrow of rats after oral nitrite uptake, but this could have been due to exogenous N-nitroso compound formation (Nahas et al., 1984; Luca et al., 1987). Nitrite is mutagenic; it causes morphological transformations in in vitro systems. Mutagenic activity was also found in a combined in vivo-in vitro experiment with Syrian hamsters. The results of in vivo experiments were controversial (Speijers et al., 1989; WHO, 1996).

2.3.6 Carcinogenicity

Nitrate is not carcinogenic in laboratory animals. Some studies in which nitrite was given to mice or rats in the diet showed slightly increased tumour incidence. However, the possibility of exogenous N-nitroso compound formation in these studies could not be excluded. Increased tumour incidence was seen in studies in which high levels of nitrite and simultaneously high levels of nitrosatable precursors were administered (Speijers et al., 1989; WHO, 1996). These types of tumours could be characteristic of the presumed corresponding N-nitroso compound formed endogenously. However, this increase in tumour incidence was seen only at extremely high nitrite levels, of the order of 1000 mg l⁻¹ of drinking-water. At lower nitrite levels, tumour incidence resembled those of control groups treated with the nitrosatable compound only. On the basis of adequately performed and reported studies, it may be concluded that nitrite itself is not carcinogenic to animals (Speijers et al., 1989; WHO, 1996).

2.4 Effects on humans

2.4.1 Methaemoglobinemia
Methaemoglobinaemia is a rare condition which can have several causes. Certain chemicals such as perchlorates, sulphonamides, aniline dyes (Adam, 1980., in Terblanche, 1991) can convert Hb to metHb. Inherited metabolic deficiencies of, for example, NADH diaphorase (Kumar et al., 1989) can also induce formation of metHb.

The toxicity of nitrate to humans is mainly attributable to its reduction to nitrite. The major biological effect of nitrite in humans is its involvement in the oxidation of normal Hb to metHb, which is unable to transport oxygen to the tissues. The normal metHb level in humans is less than 2%, and less than 3% in infants under three months of age. At a metHb concentration of 5% of normal Hb no external signs or symptoms are generally noted. The reduced oxygen transport becomes clinically manifest when the metHb concentration is between 5 and 10% (Knotek and Schmidt, 1964). Hypoxic signs and symptoms may develop at about 20%, while death results at 50% metHb or higher (Shuval and Gruener, 1977).

The Hb of young infants is more susceptible to metHb formation than that of older children and adults. This higher susceptibility is believed to be the result of the large proportion of foetal Hb still present in the blood of infants. Foetal Hb is more easily oxidised to metHb. In addition, there is a deficiency in the metHb reductase responsible for the reduction of metHb back to Hb. The net result is that a dose of nitrite causes a higher metHb formation in young infants than in adults. Young infants are also more at risk from exposure to nitrate because of a relatively high intake of nitrate and, under certain conditions, a higher reduction of nitrate to nitrite by gastric bacteria due to the low production of gastric acid (Speijers et al., 1989; WHO, 1996). The higher reduction of nitrate to nitrite in young infants is not well understood, but it appears that gastrointestinal infections increase the risk of higher yield of nitrite and thus a higher metHb formation (ECETOC, 1988; Speijers et al., 1989; Möller, 1995; Schuddeboom, 1955; WHO, 1996).

Other groups particularly susceptible to metHb formation include pregnant women and people deficient in glucose-6-phosphate dehydrogenase or metHb reductase (Speijers et al., 1989).

**Adults and children above the age of three months**

Clinical cases of adult methaemoglobinaemia due to consumption of nitrate contaminated water have never been reported (Bruningfann and Kaneene, 1993). This is attributed to lower gastric acidity which inhibits nitrate-reducing bacteria and greater enzyme activity resulting in faster transformation of metHb to Hb. However, cases of methaemoglobinemia have been reported in adults consuming high doses of nitrate by accident or as a medical treatment. Fatalities have been reported after single intakes of 4-50 g of nitrate (equivalent to 67-833 mg of nitrate per kg of body weight) (Speijers et al., 1989; WHO, 1996). Many of these occurred among special risk groups in whose members gastric acidity was reduced. Toxic doses (with metHb formation as a criterion for toxicity) ranged from 2-9 g (equivalent to 33-150 mg of nitrate per kg of body weight) (WHO, 1996). In a controlled study, an oral dose of 7-10.5 g of ammonium nitrate and an intravenous dose of 9.5 g of sodium nitrate did not cause increased metHb levels in adults, although vomiting and diarrhoea occurred (Speijers et al., 1989; WHO, 1996).
Accidental human intoxications have been reported as a result of the presence of nitrite in food. The oral lethal dose for humans was estimated to range from 33-250 mg of nitrite per kg of body weight, the lower doses applying to children and elderly people. Toxic doses giving rise to methaemoglobinaemia ranged from 0.4-200 mg kg\(^{-1}\) of body weight (WHO, 1996).

Another source of information with respect to nitrite toxicity in humans is the use of sodium nitrite as a medication for vasodilation or as an antidote in cyanide poisoning. Doses of 30 - 300 mg per person (equivalent to 0.5-5 mg kg\(^{-1}\) of body weight) were reported not to cause toxic effects (WHO, 1996).

Few cases of methaemoglobinaemia have been reported in older children. A correlation study among children aged one to eight years in the USA showed that there was no difference in metHb levels between 64 children consuming high-nitrate well water (22-111 mg of nitrate-nitrogen per litre) and 38 children consuming low-nitrate water (<10 mg of nitrate-nitrogen per litre). These concentrations correspond to 100-500 and <44 mg of nitrate per litre, respectively. All the metHb levels were within the normal range, suggesting that older children are relatively insensitive to the effects of nitrate (Craun et al., 1981).

Infants under three months of age

Cases of methaemoglobinemia related to low nitrate appear to be restricted to infants. In infants under the age of three months, the conversion of nitrate to nitrite and metHb formation is high as discussed previously. Gastrointestinal disturbances play a crucial role, the reduction of nitrate to nitrite in the stomach being enhanced by bacterial growth at the high pH in the stomach of these infants. Toxic effects can therefore be induced at a much lower dose of nitrate than in adults. According to Corré and Breimer (1979), assuming an 80% reduction of nitrate to nitrite in young infants, the toxic dose ranged from 1.5-2.7 mg of nitrate per kg of body weight, using 10% formation of metHb as a toxicity criterion. However, in reported cases of methaemoglobinemia, the amounts of nitrate ingested were higher: 37.1-108.6 mg kg\(^{-1}\) of body weight, with an average of 56.7 mg nitrate per kg of body weight (WHO, 1996). In studies in which a possible association between clinical cases of infantile methaemoglobinemia or subclinically increased metHb levels and nitrate concentrations in drinking-water was investigated, a significant relationship was usually found, most clinical cases (97.7%) occurred at nitrate levels of 44.3-88.6 mg l\(^{-1}\) or higher (Walton, 1951, WHO, 1996), and almost exclusively in infants under three months of age (Walton, 1951). Some cases of infant methaemoglobinemia have indeed been described in which increased endogenous nitrate (nitrite) synthesis, as a result of gastrointestinal infection, appeared to be the only causative factor (WHO, 1996). As most cases of infantile methaemoglobinemia reported in the literature have been associated with the consumption of private and often bacterially contaminated well-water, the involvement of infections is highly probable. Consequently, most of these studies may be unsuitable for the quantitative assessment of the risk of nitrate intake for healthy infants. On the other hand, bottle-fed infants under three months of age have a high probability of developing gastrointestinal infections because of their low gastric acidity, which is another important reason to consider these infants as a risk group.
2.4.2 Carcinogenicity

Nitrite was shown to react with nitrosatable compounds in the human stomach to form $N$-nitroso compounds. Many of these $N$-nitroso compounds have been found to be carcinogenic in all the animal species tested, although some of the most readily formed compounds, such as $N$-nitrosoprophline, are not carcinogenic in humans. The $N$-nitroso compounds carcinogenic in animal species are probably also carcinogenic to humans. At least 75% of the 120 $N$-nitroso compounds have been found to be carcinogenic to animals (Gilli et al., 1984., in Terblanche, 1991). However, the data from a number of epidemiological studies are at most, only suggestive. The endogenous formation of $N$-nitroso compounds can also be observed in several animal species, if relatively high doses of both nitrite and nitrosatable compounds are administered simultaneously. Thus, a link between cancer risk and endogenous nitrosation as a result of high intake of nitrate and, or nitrite and nitrosatable compounds is possible (Speijers et al., 1989; WHO, 1996).

Several reviews of epidemiological studies have been published. Most of these studies are geographical correlation studies relating estimated nitrate intake to gastric cancer risk. The US National Research Council found some suggestion of an association between high nitrate intake and gastric and, or oesophageal cancer (NAS, 1981). However, individual exposure data were lacking and several other plausible causes of gastric cancer were present. Studies undertaken by Fraser and Chivers (1981) suggested evidence of a link between gastric cancer and high nitrate ingestion in parts of Colombia. Wells with nitrate concentrations (as NO$_3^-$) up to 300 mg l$^{-1}$ were associated with several of the high cancer risk areas.

A WHO review (WHO, 1985b), showed some of the earlier associations appeared to be weakened following the introduction of individual exposure data or after adjustment for socioeconomic factors. No convincing evidence was found of an association between gastric cancer and the consumption of drinking-water in which nitrate concentrations of up to 45 mg $l^{-1}$ were present. In addition, no firm evidence was found at higher levels either, but an association could not be excluded because of the inadequacy of the data available. More recent geographical correlation and occupational exposure studies have also failed to demonstrate a clear relationship between nitrate intake and gastric cancer risk, although these studies were well designed.

A case-control study in Canada, in which dietary exposure to nitrate and nitrite was estimated in detail, showed that exogenous nitrite intake, largely from preserved meat, was significantly associated with the risk of developing gastric cancer (ECETOC, 1988). In Taiwan, gastric cancer is the third leading cause of cancer mortality in males and the sixth leading cause in females (Yang et al., 1998). A study was conducted to evaluate the risk of gastric cancer associated with nitrate exposure from water in municipal supplies. A significantly positive association was demonstrated between drinking water nitrate exposure and gastric cancer mortality. Furthermore, results also suggested a significant protective effect of calcium and magnesium from drinking water against the risk of gastric cancer (Yang et al., 1998). A later study in Finland (Knekt et al., 1999) examined the relationship between intake
of nitrates, nitrites and N-nitrosodimethylamine (NDMA) and the risk of cancers of
the gastro-intestinal tract. An increased risk of colorectal cancer was found among
individuals with a high intake of NDMA, but no association was noted between intake
of NDMA and stomach cancer. Case-control studies based on food frequency
questionnaires tend to show a protective effect of the estimated nitrate intake on
gastric cancer risk. This is probably due to the known strong protective effect of
vegetables and fruits on the risk of gastric cancer (Möller, 1995; WHO, 1996). Boeing
(1991) observed no decrease in the development of gastric cancer with increasing
consumption of cooked vegetables, where protective antioxidants would have been
lost. Reducing agents found in fresh fruits and vegetables, such as ascorbic acid, have
been found to inhibit nitrosamine formation (Hansson et al., 1994., in Duncan et al.,
1997). Studies that have assessed the effect of nitrate from sources other than
vegetables, such as the concentration in drinking-water or occupational exposure to
nitrate dusts, have not shown a protective effect against gastric cancer risk. For other
types of cancer, there are no adequate data with which to establish any association
with nitrite or nitrate intake (Gangolli et al., 1994; Möller, 1995; WHO, 1996).

It has been established that the intake of certain dietary components present in
vegetables, such as vitamins C and E, decreases the risk of gastric cancer. Evidence
that a high-nitrate diet is not causally associated with gastric cancer has come from
repeated observations of vegetarians who have three times the nitrate intake of
omnivores (MAFF, 1992), and from those who consume large quantities of fresh fruit
and vegetables (and thus nitrate). These groups have shown lower standardised
mortality ratios for gastric cancer (Gonzalez et al., 1991; Key et al., 1996., in
McKnight et al., 1999). This is generally assumed to be at least partly due to the
resulting decrease in the conversion of nitrate to nitrite and the formation of N-nitroso
compounds. It is possible that any effect of a high nitrate intake _per se_ is masked in
correlation studies by the antagonizing effects of simultaneously consumed dietary
protective components. However, the absence of any link with cancer in occupational
exposure studies is not in agreement with this theory.

The known increased risk of gastric cancer under conditions of low gastric acidity
could be associated with the endogenous formation of N-nitroso compounds. High
mean levels of _N_-nitroso compounds, as well as high nitrate levels, were found in the
gastric juice of achlorhydric patients, who must therefore be considered as a special
risk group for gastric cancer from the point of view of nitrate and nitrite (NAS, 1981;

2.4.3 Other effects
Congenital malformations have been related to high nitrate levels in drinking-water in
Australia, although these observations were not confirmed. Other studies also failed
to demonstrate a relationship between congenital malformations and nitrate intake
(WHO, 1985b; ECETOC, 1988).

The possible relationship between nitrate intake and effects on the thyroid has also
been studied, because it is known that nitrate competitively inhibits iodine uptake. In
addition to effects of nitrate on the thyroid observed in animal studies and in
livestock, epidemiological studies have revealed indications for an anti-thyroid effect
of nitrate in humans. If dietary iodine is available at an adequate range (corresponding
to a daily iodine excretion of 150-300 µg per day), the effect of nitrate is weak with a
tendency to zero. The nitrate effect on thyroid function is strong if a nutritional iodine deficiency exists simultaneously (Höring et al., 1991; Höring, 1992). Groten et al. (2000) investigated the possibility that structurally unrelated food additives could show joint actions or interactions on target organs. A joint action/interaction on the thyroid by nitrate, erythosine and thiabendazole was noted, although not deemed to represent a significant health concern.

Hettche (1956a,b) described an association between high nitrate concentrations in drinking-water and goitre incidence in 1955. In addition, Höring and Schiller (1987), Sauerbrey and Andree (1988), Höring et al., (1991), Höring (1992), and van Maanen et al., (1994) found that inorganic nitrate in drinking water is a manifested factor of endemic goitre. A dose-response relationship could be demonstrated by Höring et al., (1991) (nitrate in drinking-water vs incidence of goitre) as well as by van Maanen et al., (1994) (nitrate in drinking-water vs thyroid volume). Both the experimental and epidemiological studies give the impression that nitrate in drinking-water has a stronger effect on thyroid function than nitrate in food. The differences in nitrate kinetics after ingestion with drinking-water and with food could be the cause of the difference in thyroid effects. However, no adequate studies investigating this aspect exist at present. Furthermore, some of the above mentioned studies demonstrate that dietary iodine deficiency is much more effective than nitrate exposure in causing goitre.

In addition to the effect of nitrite on the adrenal zona glomerulosa in rats, a study in humans indicated that sodium nitrite (0.5 mg of sodium nitrite per kg of body weight per day, during nine days) caused a decreased production of adrenal steroids, as indicated by the decreased concentration of 17-hydroxysteroid and 17-ketosteroids in urine (Til et al., 1988; Kuper and Til, 1995). Similar results were also found in rabbits (Violante et al., 1973). Although the mechanism is not clear, the effects of nitrite on rats seem relevant for the hazard assessment for humans, unless mechanistic studies prove otherwise.

2.4.4 Potential beneficial effects of nitrate

Studies relating cardiovascular effects to nitrate levels in drinking-water have given inconsistent results (WHO, 1985b). However, recent studies have indicated a potential role of nitrate in protection of the cardiovascular system. Platelet aggregation and adhesion are important in the pathogenesis of vascular occlusive disease (Davies and Thomas, 1981., in McKnight et al., 1999). When systemically administered, NO and the S-nitrosothiol, S-nitrosoglutathione are known to inhibit platelet aggregation (Radomski et al., 1990, 1992; de Belder et al., 1994., in McKnight et al., 1999). McKnight et al. (1997), however, observed large quantities of easily diffusible NO gas generated in the confined lumen of the stomach. In addition a normal diet already contains thiols which would be readily S-nitrosated in an acidic environment. McKnight et al. (1999) hypothesised that, locally, NO gas maintains the gastric microvasculature, and by nitrosating thiol groups, which due to the acidic environment will be mainly in the reduced form, it will be absorbed and exert an inhibitory effect on platelet aggregation. They proposed that oral nitrate has the potential to prevent thrombotic episodes.
McKnight et al. (1999) suggest that, in evolutionary terms, it is be unlikely that nitrate would be purposefully concentrated and secreted into the mouth, to be recycled, if this process was actually harmful, for example by causing carcinoma. It was further suggested that gastric acid alone was not a sufficient mechanism for killing pathogenic bacteria in the upper intestinal tract, but that the addition of nitrite following a meal synergistically enhances antibacterial activity (Dykhuizen et al., 1996., in McKnight et al., 1999). This antibacterial activity is stable at any given pH, and increases with nitrite concentration and length of exposure. It was proposed that dietary nitrate may have an important physiological role in augmenting salivary and gastric nitrite to concentrations that reduce the time required to kill ingested pathogens within the normal residence time of food in the stomach (McKnight et al., 1999). In this way, the recirculation of dietary nitrate may provide a non-immune mechanism of host defence against ingested, gastrointestinal pathogens.

2.5 Risk evaluation and guideline values

A health-based guideline value for nitrate of 50 mg l⁻¹ (expressed as nitrate ion) was recommended in the second edition of the WHO Guidelines for drinking-water quality to prevent methaemoglobinaemia, a condition that occurs when nitrate is reduced to nitrite, in infants (see section 2.3.1). Most clinical cases of methaemoglobinaemia occur at nitrate levels of 50 mg l⁻¹ and above, and almost exclusively in infants under three months of age. Accepting a relative potency for nitrite and nitrate with respect to methaemoglobin formation of 10:1 (on a molar basis), a provisional guideline value for nitrite of 3 mg l⁻¹ (expressed as nitrite ion) was proposed. Because of the possibility of simultaneous occurrence of nitrite and nitrate in drinking water, the sum of the ratios of the concentrations of each to its guideline value was not to exceed one.

In 1995, the Joint Expert Committee for Food Additives (JECFA) established Acceptable Daily Intake levels (ADI) for nitrate and nitrite and the US National Research Council published an evaluation of nitrate and nitrite in drinking-water. In light of this new information, the Coordinating Committee for the Updating of WHO Guidelines for drinking-water quality determined that there was a need to reassess the existing guideline values for nitrate and nitrite.

With respect to chronic effects, JECFA recently re-evaluated the health effects of nitrate and nitrite, confirming the previous acceptable daily intake (ADI) of 0-3.7 mg kg⁻¹ of body weight per day for nitrate ion and establishing an ADI of 0-0.06 mg kg⁻¹ of body weight per day for nitrite ion (WHO, 1995). The allocated ADI for nitrite was based on a NOAEL of 5.4mg kg⁻¹ body weight (90 day feeding study) and 6.7mg kg⁻¹ body weight per day (two year feeding study) in the rat, to which a 100-fold safety factor was applied (WHO, 1996., in Walton et al., 1999). However, it was noted that these ADIs do not apply to infants below the age of three months. Bottle-fed infants below three months of age are most susceptible to methaemoglobinaemia following exposure to nitrate and nitrite in drinking water.

For methaemoglobinaemia in infants (an acute effect), it was confirmed that the existing guideline value for nitrate ion of 50 mg l⁻¹ is protective. For nitrite, human data reviewed by JECFA support the current provisional guideline value of 3 mg l⁻¹. Data suggested that methaemoglobinaemia could be induced by nitrate values
ranging from 0.4 to more than 200 mg kg\(^{-1}\) of body weight. Following a conservative approach by applying the lowest level of the range (0.4 mg kg\(^{-1}\) of body weight), a body weight of 5 kg for an infant, and a drinking-water consumption of 0.75 litres per day, a guideline value for the nitrite ion of 3 mg l\(^{-1}\) (rounded figure) can be derived. The guideline value is no longer provisional.

It seems prudent to propose a guideline value for nitrite associated with chronic exposure based on JECFA's analysis of animal data showing nitrite-induced morphological changes in the adrenals, heart, and lungs. Using JECFA's ADI of 0.06 mg kg\(^{-1}\) of body weight per day, assuming a 60-kg adult ingesting 2 litres of drinking-water per day, and allocating 10% of the ADI to drinking-water, a guideline value of 0.2 mg of nitrite ion per litre (rounded figure) can be calculated. However, owing to the uncertainty surrounding the relevance of the observed adverse health effects for humans and the susceptibility of humans compared with animals, this guideline value should be considered provisional. Because of known interspecies variation in the conversion of nitrate to nitrite, the animal model was not considered appropriate for use in human risk assessment for nitrate.

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Chapter 3

Environmental transport, distribution and transformation

Nitrate is transported in both surface and ground waters, and therefore it is important to understand how nitrate reaches these essential water supply sources, and to understand the influence that human activities have on levels of nitrate contamination.

3.1 Soil and sub-soil

Subsoil is hydrologically subdivided into the water-unsaturated and the water-saturated zones, as illustrated in Figure 3.1 (Matthes, 1997). Soil can take up water, store and transport it. The intensity of water binding in soil is primarily a function of pore size and thus of the distribution of grain sizes. In the finest pores (equipotential diameter < 0.2x10^-6 m) water is bound adsorptively and is unable to percolate and unavailable to plants. The fine to medium-sized pores (equipotential diameter 0.2-50*10^-6 m) bind water adsorptively and in capillaries. This water is mostly able to infiltrate the soil and is available for uptake by plants. The size and distribution of pores within a soil type determines the quantity of water available to plants. Coarse pores are too permeable to store water, resulting in a downward movement under gravity. The quantity of water which a soil is capable of retaining after saturation and against gravity, for a period of time, is called the field capacity (FK). Percolation only occurs if the water content of the soil exceeds the field capacity.

When rain falls, some infiltrates into soil, displacing the water and dissolved substances that were previously retained to deeper soil layers. This results in a stratification of water in the percolating zone, and in the groundwater zone, by age and substance concentration, as newly infiltrating water displaces older water layers to deeper soil areas.

In water-unsaturated sub-soil, the water content only slightly exceeds the field capacity, therefore the volume of transport is also low. The rate of water percolation through fine and medium-sized pores is low. Long-lasting, heavy precipitation results in soil water content that greatly exceeds the field capacity. This surplus water can pass freely through an increasing number of coarse pores until reaching groundwater in the water-saturated zone. Water transport down to deeper regions occurs at a greater rate in solid rock areas, because percolating water is able to pass through joints and gaps in the rock.

In the water-saturated groundwater zone, water predominantly moves horizontally in the direction of the hydraulic gradient. This allows the stratification of the water by age and concentration to be maintained. In pore aquifers the rate of flow is between less than 1 m per day and a few metres per day. In karst and jointed aquifers flow rates are much higher, up to a few kilometres per day. With increasing depth groundwater becomes ever older and originates from percolation areas progressively farther upstream. Fig. 3.2 shows, in a simplified way by means of flow lines, the transport of nitrate in a pore aquifer.
The depth to which soil water may evaporate is marked by the hydraulic water divide. Water losses due to evaporation decrease with increasing depth. Particularly in arid and semiarid climatic zones, shallow groundwater (down to a depth of about 3-4 m) can be affected by evaporation, resulting in higher concentrations of dissolved substances.

In the water-unsaturated zone and in groundwater, microbially-mediated redox processes occur. The oxidising agents free oxygen and NO₃⁻, Mn⁴⁺, Fe³⁺, SO₄²⁻ and CO₂ are successively reduced by microbial oxidation of organic carbon, sulphides and
Denitrification is the process of microbial degradation of nitrate to nitrogen gas. In anoxic conditions, facultative anaerobes obtain oxygen for respiration from that bound within nitrate. In heterotrophic denitrification organic carbon serves as the oxidisable substance or reducing agent. The stoichiometric reaction equation is (Hoffmann, 1991):

$$5 \text{CH}_2\text{O} + 4 \text{NO}_3^- + 4 \text{H}^+ \rightarrow 2 \text{N}_2 + 5 \text{CO}_2 + 7 \text{H}_2\text{O}$$

The complete denitrification of nitrate to molecular nitrogen in this process occurs over several reaction stages, with different bacterial species carrying out different stages of nitrogen oxide reduction:

$$\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow (\text{NO} \rightarrow) \text{N}_2\text{O} \rightarrow \text{N}_2$$

In the soil zone (approximately the upper 2 – 3 m below arable land) the denitrification potential of the location is governed by the organic component of the soil, including the separation of the roots in the rhizosphere. Whilst the denitrification potential decreases with the consumption of organic matter by bacteria, it recovers due to excretion of new organic matter into the soil by plant roots. In the deeper subsoil the denitrification potential is restricted by the fossil particles present in the subsoil (Leuchs, 1985; Leuchs, 1988; Hoffmann, 1991), i.e. the microbially available share of peat, lignite and wood pieces. Percolating waters from the upper soil zone carry dissolved organic substances with them but the amounts are insufficient to allow degradation of nitrate on a large scale. Constant pollution of the deeper subsoil with high amounts of nitrate results in an irreversible degradation and consumption of the fossil material present and, consequently, in an increase in the nitrates present in groundwater.

Denitrification is affected by many factors which are of importance to microbial activity (Ottow and Benekiser, 1994). Essential factors for the reduction of nitrate are the availability of microbially oxidisable substances, the availability of nitrate and the presence of active, denitrifying micro-organisms. Regulating factors are temperature, pH and notably all factors which affect the diffusion of oxygen such as soil density, grain structure, porosity, and soil moisture. When soil moisture is high the supplementary supply of oxygen in soil pores is obstructed, and locations affected by groundwater and stagnant water show a significantly higher loss of nitrate due to denitrification than locations far away from the groundwater.

Activities that increase microbial activity in the top soil increase the consumption of oxygen. These include organic and mineral fertilisation, turning of soil, turning of grassland, irrigation and precipitation. Thus the microbial formation of nitrate through nitrification may increase at the same time as the anaerobic conditions favouring denitrification are enhanced. Nevertheless, intensive denitrification may take place in soil (and also in aquifers) even under aerobic conditions, occurring in dense soil aggregates, for example, anaerobic micro-zones, where the diffusion of oxygen is impeded.

As a rule, in well-aerated soils such as sand and loess soils, the degradation of
nitrate is not of significance. Denitrification occurs preferentially in microzones and in the rhizosphere during irrigation and precipitation. Because of the higher water content and the higher number of dense soil aggregates in argillaceous soils, the conditions for the degradation of nitrate are, in principle, better than in cohesionless soils.

In a humid, seasonally warm climatic zone, with fertilisation levels of 100-200 kg N ha\(^{-1}\) a\(^{-1}\), Germon (1985a) estimated losses due to denitrification of 10-15 kg N ha\(^{-1}\) a\(^{-1}\). Benckiser and Syring (1992) estimated an average nitrogen loss in rural locations of 15-20 kg N ha\(^{-1}\) a\(^{-1}\), assuming an average loss by denitrification of about 15% of the applied fertiliser. According to Li and Zhang (1999) 33.3-73.6% of applied nitrogen fertiliser is lost each year, the average loss rate from arable land being 60%, with 15% being attributed to denitrification. Favourable conditions for respiration may result in a loss of 30-50% of the fertiliser nitrogen. After events of heavy rain or intensive irrigation denitrification rates in summer may be as high as up to 0.4 kg N ha\(^{-1}\) per day. Compared with arable land, grassland shows a greater rate of nitrate decomposition. This is because the dense root systems contain a larger amount of microbially available organic matter, and the roots themselves create a strong oxygen demand. This results in a greater amount of biological activity.

During autrophic denitrification reduced inorganic compounds, predominantly sulphides, serve as reduction agents. The microbial oxidation of sulphides into sulphate, catalysed by bacteria, for example, of the *Thiobacillus denitrificans* genus, proceeds only under anaerobic conditions and thus predominantly in the aquifer. The stoichiometric reaction equation is (Kölle et al., 1983):

\[
5 \text{FeS}_2 + 14 \text{NO}_3^- + 4 \text{H}^+ \rightarrow 7 \text{N}_2 + 10 \text{SO}_4^{2-} + 5 \text{Fe}^{2+} + 2 \text{H}_2\text{O}
\]

The decomposition of nitrate results in an increase of the pH and a reduction of the redox potential. Iron and sulphate concentrations in groundwater increase, as do the concentrations of elements such as Ni, Co, Cu, As, Zn which occur with, and in, iron sulphides. These compounds are undesirable in drinking water supply (WHO, 1993). Thus the decomposition of nitrate may potentially result in other water quality problems in groundwater.

A large part of the anthropogenic and anthropogenically-induced nitrogen excess leaches out of the soil in the form of nitrate and is eliminated by microbial denitrification in the deeper subsoil. Under reducing conditions particulate iron sulphides are frequently found in porous rock aquifers as a component of lignite, as independent aggregates or as a coating of mineral grains. The quantity of sulphides in the fossil component of the aquifer is finite and the constant pollution of groundwater by nitrate results in the gradual exhaustion of the sulphide. Thus, in the long term, it results in an increase in the nitrate concentration in groundwater and in the percolating water zone and ultimately in surface water. Thus, the natural decomposition of nitrate is not a viable method of removing nitrates from drinking water supplies in the long term (German Country Working Party Relating to Water, 1996 a) and it should not be misused as an argument for delaying the implementation of water pollution control measures. Once drinking water resources have reached a
certain level of nitrate pollution the damage may only be repaired over a long period of time, if at all. For these reasons preventative water pollution control measures, which should start address the sources of nitrogen excess, should be given precedence over remedial measures of repair.

Figure 3.3 Measuring value profiles at the multi-level measuring point N10, Fuhrberg Field, Federal Republic of Germany (Duynsvelt et al., 1993)

In groundwater, microbial reduction consumes free oxygen, NO$_3^-$, Mn$^{4+}$, Fe$^{3+}$ and SO$_4^{2-}$ successively. Each of these respective microbial processes occur when a particular redox potential is reached. The result of microbial decomposition is a further reduction in the redox potential (Hoffmann, 1991). In the ideal case of a materially and physically homogeneous subsoil and a uniform land use, vertical zones are formed in the presence of organic carbon and sulphides. In each of the vertical zones redox reactions occur and the redox potential decreases with increasing depth. The formation of vertical reduction zones reflects the stratification of groundwater by age.

After consumption of the free oxygen in the upper zones, autotrophic degradation of nitrate in the denitrification zone results in an increase in the sulphate concentration (Figure 3.3). In the underlying desulphurisation zone this sulphate is heterotrophically reduced as the pH and alkalinity increase with depth. Denitrification and desulphurisation zones are clearly separated from each other, at a depth at which there is a significant change in redox potential (Figure 3.3).

The average distribution of the nitrogen compounds in surface waters in Germany is about 60% nitrate-N, 20% ammonium-N plus dissolved organic N and 20% particulate organic N. The most important sources of pollution of surface waters by nitrate are feeding with groundwater and the subsurface flow. In Figure 3.4 nitrate concentrations in the Elbe-river near Neu Darchau, Federal Republic of Germany, are represented as a function of the rate of flow (Röske et al., 1995). High nitrate concentrations occur when flow rates are high, as a result of precipitation. The formation of nitrate, or nitrate input from waste water discharges (from point sources) do not play an important role because the nitrate is diluted, as shown Figure 3.4. streams fed partly by low-nitrate pools (eg. located in mountains) have low nitrate concentrations, higher concentrations occur in lower-flow streams. Here seasonal nitrate peaks (correlating with the flow rate) are important, particularly if the stream is fed by a catchment area used for agricultural purposes.
During transport in surface water, microbial processes of decomposition by heterotrophic denitrification predominate, taking place in the river bed sediment and in the anaerobic micro-zones (Mohaupt et al., 1996; Mohaupt, 1988). The long retention times of water reservoirs and lakes provide favourable conditions for denitrification processes. Therefore, these water bodies are often less polluted with nitrate than the waters that feed them.

3.2 Factors that influence nitrate concentrations in water

3.2.1 Seasonal variations and trends

Since the 1950s, a constant increase in nitrate concentrations has been observed in raw waters abstracted for drinking water supply in industrialised countries. For example, in many places throughout Germany, an annual increase of 0.5-1 mg NO$_3^-$ l$^{-1}$ in groundwater has been found. Surface water nitrate concentrations are also increasing. Figure 3.5 illustrates the increase in nitrate concentrations since 1975 in well water at the waterworks Foehr-West, Germany.

**Figure 3.4:** Nitrate concentration in the Elbe river near Neu Darchau, Federal Republic of Germany, as a function of the rate of flow (Röske et al., 1995)
Figure 3.5: Trend in nitrate concentrations at the waterworks Foehr-West, Federal Republic of Germany (annual averages in well IV) (German Country Working Party Relating to Water 1996 a)

Figure 3.6: Long-term measurements of the nitrate-N concentration in the Rhine-river at the measuring station Bimmen/Lobith, Federal Republic of Germany (German Federal Ministry For The Environment, Nature Conservation And Nuclear Safety 1996 a)

Figure 3.6 shows the increasing trend in nitrate concentrations in the River Rhine, at the measuring station Bimmen/Lobith, Germany.

Data collected from major EU rivers indicate that overall nitrate concentrations have remained relatively constant, as illustrated in Figure 3.7. In groundwater, increasing concentrations of nitrate have been demonstrated in Denmark, as shown in Figure 3.8. Large variations in nitrate concentrations in ground and surface waters have been
observed in various parts of the world. For example, Table 3.1 illustrates results of studies across regions in China.

**Figure 3.7** Trends in nitrate concentrations in major rivers within Europe

![Figure 3.7](image)

Table 3.1. Regional differences in groundwater nitrate concentrations in China. (After Li and Zhang, 1999).

<table>
<thead>
<tr>
<th>Region</th>
<th>Province</th>
<th>Max NO\textsubscript{3}\textsuperscript{–} concentration in groundwater (mg l(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yuanmingyuan</td>
<td>Beijing</td>
<td>28.00</td>
<td>Jiang and Tang, 1984</td>
</tr>
<tr>
<td>Tai-hu lake</td>
<td>Jiangsu</td>
<td>79.35</td>
<td>Ma, 1987</td>
</tr>
<tr>
<td>Matan</td>
<td>Ganshu</td>
<td>290.6</td>
<td>Zhang <em>et al.</em>, 1990</td>
</tr>
<tr>
<td>West suburb</td>
<td>Beijing</td>
<td>16.67</td>
<td>Eryang <em>et al.</em>, 1996</td>
</tr>
<tr>
<td>Zhangzhou</td>
<td>Fujian</td>
<td>16.80</td>
<td>Unpublished</td>
</tr>
<tr>
<td>Doudian</td>
<td>Beijing</td>
<td>30.14</td>
<td>Wen, 1990</td>
</tr>
<tr>
<td>Hangzhou</td>
<td>Zhejiang</td>
<td>175.00</td>
<td>Wu, 1988</td>
</tr>
</tbody>
</table>

The WHO guideline value for drinking water is 50 mg l\(^{-1}\) NO\textsubscript{3}.

Groundwater abstracted for public drinking water supplies is, as a rule, a blend of waters. Its nitrate concentration represents the average nitrate concentration of the waters abstracted from the various aquifer horizons. The trend in nitrate concentration in abstracted raw water may be influenced by several factors:
• Constant intensive agricultural land use in the catchment area of the wells, over many years, may have resulted in older groundwater horizons being polluted by nitrate. The average nitrate concentration of the whole aquifer may be rising.

• As a result of intensification of agricultural land use in the catchment area of the wells, individual groundwater horizons may be becoming increasingly polluted by nitrate that has been infiltrating deeper soil layers over time. Increasing population density may be reflected in increasing nitrate concentrations in groundwater.

• The denitrification capacity of the deeper subsoil may be becoming exhausted. This results in a decline in the rate of decomposition of nitrate in the percolating water zone, and in groundwater. Consequently, the individual aquifer horizons become more and more saturated with nitrate infiltrating deeper layers.

General trends in nitrate concentrations are usually subject to seasonal fluctuations. In the humid climatic zone natural groundwater recharge takes place predominantly in the vegetation-free period of the winter. During this time, nitrate concentrations rise in shallow groundwaters as percolating water polluted by nitrate becomes groundwater. The nitrate concentration falls between the two phases of natural
groundwater recharge as a result of microbial nitrate degradation. Deep groundwater does not show such pronounced fluctuations.

The intensification of agricultural production and increasing pollution of groundwater also result in an increase in the nitrate concentration in surface water fed by groundwater and subsurface flow. The general trend of nitrate concentrations is subject to seasonal fluctuations depending on the rate of flow and temperature. In general, floodwaters are richer in nitrate because precipitation leads to leaching of nitrate from the land surface into the receiving waters by the subsurface flow. Furthermore, as the flow rate increases there is less time for the degradation of nitrate (Figure 3.4). Higher water temperatures reduce the oxygen concentration in the water and increase the rate of biological activity. Thus they support denitrification and the biological uptake of nitrate. This results in seasonal, temperature-related fluctuations in nitrate concentrations in surface waters in the temperate climatic zone, while in warmer climatic zones degradation of nitrate is generally promoted (Tisseau, 1998). New formation of nitrate from the nitrogen components of sewage, or direct discharge of nitrate (eg. in biologically treated sewage), have little effect on fluctuations in nitrate concentrations in surface waters.

3.2.2 Variations caused by depth of groundwater extraction
Deep groundwater is, as a rule, less polluted by nitrate than shallow groundwater because longer time periods are needed for nitrate loads to be transported, with percolating water, to these depths. During transport, they are exposed to nitrate degradation processes in the percolating water.

The retention time of nitrate in the water-unsaturated zone may be estimated by the depth of the groundwater table, the annual amount of percolating water and the field capacity (Bach, 1987):

\[
\text{annual depth of percolating water displacement (dm)} \sim \frac{\text{annual amount of percolating water (mm)}}{\text{water content at field capacity (mm/dm)}}
\]

\[
\text{retention time of percolating water in the water-unsaturated zone (a)} \sim \frac{\text{distance to the groundwater table (dm)}}{\text{annual depth of percolating water displacement (dm/a)}}
\]

In the groundwater profile the age of the water generally increases with increasing depth, with the water coming from percolation zones situated further and further upstream. A number of causes may influence the distribution of nitrate concentrations in the aquifer profile (eg. in a well):

• The spatial variability of land use in the catchment area of a well is connected with differences in nitrate leaching rates. This is reflected by the distribution of nitrate concentrations with depth, as shown in Figure. 3.9 (Rohmann and Sontheimer,
• The change in the intensity of land use in the catchment area of the wells over time, and the associated changes and delays in nitrate leaching with depth, are reflected in the distribution of the nitrate concentration.

• If substances are available in the aquifer for microbial oxidisation, nitrate concentrations are progressively degraded with increasing groundwater retention time. The older the groundwater the longer it has been subjected to nitrate degradation. In addition, in a homogeneous aquifer the denitrification capacity increases with increasing depth. Both result in a reduction of the nitrate concentration with depth.

• If the denitrification capacity of the subsoil is nearing exhaustion, nitrate pollution increases with increasingly deep aquifer zones. As with intensification of agricultural use, this effluent is reflected by the distribution of nitrate concentrations with depth.

3.2.3 Solid and porous rock aquifers and surface-water catchment areas

Assuming comparable land use, groundwater in solid rock areas is more polluted by nitrate than groundwater in porous rock areas. Solid rock is frequently covered by a thin layer soil which is susceptible to leaching processes. Infiltrating waters, rich in
oxygen, are quickly displaced to greater depths along joints and cracks. Because transport along joints and cracks in the groundwater zone is rapid, exchange of material with the aquifer is very restricted. Furthermore, solid rocks often only have insignificant fossil denitrification capacity. Thus, in solid rock areas conditions for degradation of are, in principle, less favourable than in porous rock areas.

Assuming comparable land use, significantly smaller nitrogen loads per area of farmland flow into surface waters in porous rock areas. This is because the degradation of nitrate in subsoil is greater than in solid rock areas, and also the retention in subsoil and groundwater delays the movement of nitrogen into surface waters (Mohaupt et al., 1995).

3.3 References


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Ministry of Environment and Energy, Denmark. Internet source http://mstex03.mst.dk/books/moe/pic082.htm


Wu, D.N. 1988 Types of groundwater contamination and causes in the city of Hangzou. Environmental Pollution and Control (Chinese), 10, 36-38.

Human settlements affect the surrounding environment. Ground and surface waters are vulnerable to nutrient inputs from on-site sanitation and sewerage systems, decentralised and on-site treatment and disposal systems, and other sources connected with human activities. Different approaches to the management of sewage and other wastewaters can have a significant impact on the potential for nitrate pollution of water bodies used for public water supplies. Where the availability of drinking water is scarce, appropriate methods of wastewater treatment and disposal may have to be found to ensure further contamination by nitrates does not occur.

Sewage and treated sludge are rich in nitrogen and may be considered a valuable resource, particularly for agricultural purposes. Certain uses of these wastes may increase the risk of contamination of water bodies with nitrate under particular conditions, or reduce the risk of contamination and resource depletion in other situations. Some of the different approaches to treating and disposing of sewage in developed and developing countries are reviewed with respect to their potential for nitrate pollution of water bodies.

4.1 Wastewater treatment plants
In order to minimise environmental pollution it is necessary to treat wastewater before it is discharged. Hence, developed countries have invested enormous sums of money and resources in technologies for wastewater treatment and disposal. Sewerage networks transport wastewaters to treatment plants where some of the organic matter, nutrients and harmful substances are removed from the sewage before the effluent is discharged to a receiving water body. Human excreta (blackwater) flushed from toilets is usually diluted with other domestic wastewater (greywater) and may also be mixed with industrial and commercial sewage in the sewerage network.

Table 4.1 shows the three different components of domestic wastewater from one person living in Sweden. About 12–16 g of nitrogen are excreted per capita per day. Of these blackwater components, urine contributes the greatest amount of nutrients. Untreated sewage from municipal sewerage systems contains only 20–80 mg N l\(^{-1}\), with an average of about 40 mg N l\(^{-1}\) (Metcalf and Eddy INC. 1991, WHO 1995) due to the high level of dilution with greywater. Nitrogen concentrations can vary significantly depending on the volume of other wastewater (e.g. industrial wastewaters, storm-water) present.

In industrialised countries sewage is mainly discharged into surface waters, usually after treatment in a sewage treatment plant. In principle, sewage treatment aims to purify the effluent by removal of harmful and hazardous substances and plant nutrients contained in sewage as solids and as dissolved or collooidally dissolved matter. Mechanical, biological and chemical treatment processes may be used. Biological treatment generally takes place under oxidising conditions because
puriﬁcation reactions occur faster and more completely under aerobic conditions than under anaerobic conditions. Hazardous and toxic substances are absorbed by microbial biomass. Puriﬁcation of wastewater aims at the removal of (Schoenborn and Hirth 1997):

• Pathogens.
• Oxygen consuming organic matter (due to potential oxidation).
• Nutrients.
• Harmful, hazardous and toxic substances.

<table>
<thead>
<tr>
<th>per person</th>
<th>urine</th>
<th>faeces</th>
<th>greywater</th>
</tr>
</thead>
<tbody>
<tr>
<td>volume (l/yr)</td>
<td>405</td>
<td>53</td>
<td>65,386</td>
</tr>
<tr>
<td>nutrient (kg/yr)</td>
<td>N : 4.11</td>
<td>N : 0.74</td>
<td>N : 0.44</td>
</tr>
<tr>
<td></td>
<td>P : 0.59</td>
<td>P : 0.11</td>
<td>P : 0.14</td>
</tr>
<tr>
<td>N-conc. (mg/l)</td>
<td>10,138</td>
<td>14,039</td>
<td>6.7</td>
</tr>
<tr>
<td>P-conc. (mg/l)</td>
<td>1,444</td>
<td>2,149</td>
<td>2.1</td>
</tr>
<tr>
<td>N/P rate</td>
<td>7</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>notes</td>
<td>primary sterile</td>
<td>high risk for pathogens</td>
<td>low concentration of pollutants</td>
</tr>
<tr>
<td></td>
<td>high dry mass</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nitrogen is eliminated only by biological treatment under aerobic conditions (nitrification step) and a subsequent biological treatment step under anaerobic conditions (denitrification step) releasing nitrogen predominantly in the form of molecular N₂. The effluent (treated sewage) is predominantly discharged into surface waters, but may also be used for irrigation and fertilisation in agriculture, for artiﬁcial groundwater recharge in natural areas, or for irrigation on unused areas. The EU Sewage Directive concerning urban wastewater treatment stipulates a maximum concentration of 10 – 15 mg N l⁻¹ for sensitive areas or a reduction of the nitrogen load by 70 - 80 % (Council of European Communities, 1991a). In the USA, treated sewage contains between 10 and 20 mg N l⁻¹ (Metcalf and Eddy INC., 1991). Depending on starting material and type and scope of treatment, the nitrogen present is distributed among varying portions of organically bound N, ammonium-N, nitrate-N and nitrite-N. Sewage subjected to biological treatment (with or without N elimination) contains large proportions of nitrate.

The United Nations Environment Programme (UNEP, 1997) has proposed national policies and measures to ensure that all waste disposal conforms with national and international quality guidelines by the year 2025:

1. Identification of major sewage sources and areas where sewage poses major environmental and health-related hazards.
3. Provision of sufﬁcient training and education for local administrations to plan, build and run adequate sewage treatment facilities.
4. Formulation and implementation of awareness campaigns for the general public to gain general recognition for the need for the installation of appropriate and environmentally sound sewage facilities.

An example of action measures being implemented can be found in the Baltic States. Estonia, Latvia and Lithuania aim to increase nutrient removal from wastewater. The “polluter pays” principle has been introduced in all three countries to provide an incentive to industry and municipalities to reduce pollutants in wastewater. Taxes are charged on the pollutant load discharged into surface waters and the money is allocated to the Environment Fund, which funds protection measures including investment in wastewater treatment facilities. In Europe, the EC Urban Waste Water Treatment Directive (91/271/EEC) (UWWT) specifies a series of minimum standards for differing sizes of conurbations according to the type of waters they discharge. A single population equivalent (pe) is the organic, biodegradable load with a five day BOD of 60 g day\(^{-1}\), which is nominally equivalent to the load from a single person’s domestic waste (Environmental Agency, 2000). These standards are to come into force before 2005. Scottish Water Authorities estimate that £1,300 million will be required to upgrade sewers and sewage treatment works by 2005 (SEPA, 2000).

4.2 Sewage sludge

The more intensive the biological sewage treatment process the larger the amount of sewage sludge generated (sludge consists predominantly of biomass). As a result of the requirements of the Sewage Directive (Council of European Communities 1991a) the volume of sewage sludge in the EU is expected to grow by 50–60 % within a period of few years (Lindner, 1995). Sewage sludge contains the pollutants and foreign matter not eliminated during the course of the treatment process (Wilderer, et al., 1996). The sewage sludge is partly aerobically or anaerobically stabilised, dewatered by pressing, drying or thickening, and subsequently disposed of as solid waste or used as shown in Table 4.2 (Lindner, 1995).
Table 4.2  Municipal sewage sludge generated and disposed of in Europe in 1992

<table>
<thead>
<tr>
<th>country</th>
<th>amount (1000 t dw/y)</th>
<th>disposal method (%)</th>
<th>agriculture</th>
<th>landfilling</th>
<th>incineration</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>170</td>
<td>18</td>
<td>35</td>
<td>34</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Belgium</td>
<td>59.2</td>
<td>29</td>
<td>55</td>
<td>15</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Denmark</td>
<td>170.3</td>
<td>54</td>
<td>20</td>
<td>24</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Finland</td>
<td>150</td>
<td>25</td>
<td>75</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>France</td>
<td>865.4</td>
<td>58</td>
<td>27</td>
<td>15</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Germany</td>
<td>2681.2</td>
<td>27</td>
<td>54</td>
<td>14</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Greece</td>
<td>48.2 1)</td>
<td>10</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ireland</td>
<td>36.7</td>
<td>12</td>
<td>45</td>
<td>0</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Italy</td>
<td>816</td>
<td>33</td>
<td>55</td>
<td>2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Luxembourg</td>
<td>8</td>
<td>12</td>
<td>88</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Netherlands</td>
<td>335</td>
<td>26</td>
<td>51</td>
<td>3</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Norway</td>
<td>95</td>
<td>56</td>
<td>44</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Portugal</td>
<td>25</td>
<td>11</td>
<td>29</td>
<td>0</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td>350</td>
<td>50</td>
<td>35</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>200</td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Switzerland</td>
<td>270</td>
<td>45</td>
<td>30</td>
<td>25</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>UK</td>
<td>1107</td>
<td>44</td>
<td>8</td>
<td>7</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>TOTAL/AVG.</td>
<td>7387</td>
<td>36.4</td>
<td>41.6</td>
<td>10.9</td>
<td>11.1</td>
<td></td>
</tr>
</tbody>
</table>

1) other authors give 200 000 t dw/y

Source: Lindner, 1995

Pathogenic organisms and pollutants in wastes and sewage represent a significant risk to the environment and human health (Siebe and Fischer, 1996). To protect the environment and human health, national laws have been put in place to regulate the re-use of sewage sludge. Certain criteria must be met before sewage sludge can safely be re-used in, for example, land application for agricultural or landscaping purposes. Governing bodies and environmental organisations (e.g. The Council of European Communities, 1981, 1991; US EPA, 1993; Wilderer et al., 1996) mandate the following measures:

- Limit values for heavy metals in soil, and in sewage sludge. Placement-related assessments according to the pH or cation exchange capacity of the soils to determine whether sewage sludge can be used without detrimental effects.

- The consideration of persistent organic pollutants.

- Limitation of the quantities of sewage sludge applied to farmland which, in conjunction with limits for pollutants in sewage, would regulate the loading of persistent organic pollutants and nutrients, such as nitrogen and phosphorus. Table 4.3 illustrates permissible amounts of sewage applied to agricultural land for different countries.

- Prohibition of the application of sewage sludge to specific crops (for example, grassland and vegetable crops) to prevent ingestion of pathogenic organisms and pollutants through contaminated plants (Diez, 1994).

The origin of the sewage sludge is reflected in the proportion of pollutants to nutrients. Sewage sludge originating from towns and cities may contain a greater proportion of pollutants from industrial sewage than that originating from rural areas. Nitrogen and phosphorus concentrations are less likely to be affected by the origin of
the sludge.

**Table 4.3**  Permissible amounts of sewage sludge used on agricultural land in selected countries

<table>
<thead>
<tr>
<th>country</th>
<th>average quantity placed a year (t dm/ha/y)</th>
<th>period of annual/single placements (years)</th>
<th>maximum/single quantity placed (t dm/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgium</td>
<td>1 - 4</td>
<td>3</td>
<td>3 - 12</td>
</tr>
<tr>
<td>Denmark</td>
<td>10</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Germany</td>
<td>1.66</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Finland</td>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>France</td>
<td>3</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Ireland</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Italy</td>
<td>2.5 - 5</td>
<td>3</td>
<td>7.5 - 15</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Netherlands</td>
<td>1 - 10</td>
<td>1</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Norway</td>
<td>2</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Austria</td>
<td>2.5</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Sweden</td>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Switzerland</td>
<td>1.66</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>USA</td>
<td>10</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

1. Grassland 3 - 6, farmland 6 - 12 t dm/ha*3 a
2. In the case of low-pollutant sewage sludge up to 75 t dm/ha*10 a
3. Depending on the cation exchange capacity and the pH
4. Depending on the degree of dewatering and the pollutant load
5. 50 % of the quantities permitted for farmland are applicable to grassland

Source: Lindner, 1995

If pollutants in sewage sludge could be reduced, farmers would be more willing to use the sludge as a source of nitrogen fertiliser. To improve the quality of sewage sludge, more stringent requirements have to be placed on sewage discharged into the municipal sewerage system by industry and business. To ensure this, monitoring of dischargers must be improved (Sauerbeck, 1994) and sufficient information made available for educating the public. In addition, sufficient storage capacity must be available for sewage, the demand for which is not as constant as the rate of generation.

Sewage sludge is, primarily, a source of nutrients. It is a product extremely heterogeneous in composition, as illustrated in Table 4.4 (Poletschny, 1994). The nutrient content may vary widely depending on the sewage, the type and scope of treatment, and particularly the degree of moisture removal (Gutser, 1994). During dehydration, sewage sludge loses Nitrogen (more NH$_4^+$-N than organically bound N), because a large part of NH$_4^+$-N will separate with the effluent or escape as NH$_3$ during thickening and drying. Nevertheless, this process results in a relative enrichment of organic nitrogen in the sewage sludge.

**Table 4.4**  Variation range of N contents (kg N/t dry mass) in sewage sludge (n = 6,000)

<table>
<thead>
<tr>
<th>N content (kg N/t dry mass)</th>
<th>minimum value</th>
<th>maximum value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>246</td>
</tr>
<tr>
<td>average value</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>
4.3 Land disposal and treatment of wastewaters

In addition to technical (engineering) methods of sewage treatment, some countries try to use natural treatment methods to achieve purification of wastewaters. Such methods are similar in principle to purification by technical methods, because both rely on microbiological processes. Nitrogen removal generally takes place by nitrification and subsequent denitrification.

Land treatment of untreated (or pretreated) sewage by irrigation is a natural type of treatment and sewage disposal, making use of the periodic flooding of wetlands (Meissner and Klapper, 1992). Using the natural biological, chemical and physical purification capacity of the soil (by microbial degradation, absorption and filtering) sewage is subjected to comprehensive treatment. According to Meissner and Klapper (1992) efforts have to be made to achieve an optimum combination of engineering and natural methods of sewage treatment. For example in Wisconsin, USA, a number of different types of land disposal systems (land treatment and disposal using wetlands) are used for industrial wastewaters (Witt and Sauer, 1985). As these industries are food related, the wastewaters have high organic loadings but generally low levels of toxic substances. Bachand and Horne (1999) compared nitrogen removal and transformation between six prototype macrocosms and the larger, constructed wetlands. The location was within the Prado Basin, southern California’s largest wetland. This is fed by the Santa Ana River, which during the dry season (May to December) was polluted by municipal effluent (2-18 mg NO$_3$-N day$^{-1}$). Very high removal rates were reached in the free-surface macrocosms (2,800 mg N m$^{-2}$ day$^{-1}$) and were within the range occurring on adjacent wetland. The results established the macrocosms as a model for studying wetland management practices, with an aim to enhance nitrogen removal within the Prado Basin.

The major criteria, which are used to assess the likelihood that the system will operate properly, are the wastewater characteristics, the loading rate of the wastewater and the site conditions. Type of soil, climate and depth to groundwater are of major importance in the design or acceptability of a land disposal system. To provide proper land treatment of wastewaters, the soil must be capable of holding the wastewater in the aerobic unsaturated zone long enough to allow soil micro-organisms to break down the waste and oxidise it. Soils that are very permeable may not provide adequate retention time for treatment, while soils which are too dense will not aerate well or allow the waste to seep properly. The groundwater table must be deep enough or wastewater will not be treated adequately before it reaches the groundwater. Loading rates to land disposal systems are generally controlled by the limitation of either the hydraulic loading rate, or the organic rate. Nitrogen removal occurs in the aerated upper soil by nitrification of nitrogen to nitrate and subsequent denitrification in anaerobic deeper soil zones.

The use of organic wastes and sewage in agriculture for irrigation, fertilisation, and artificial groundwater recharge has a long tradition in many countries of the world (WHO, 1989). In many industrialised countries, the recovery of recyclable organic wastes and sewage for use as secondary raw materials (Kummer, 1997; Lindner, 1995) is given priority over disposal. In developed countries, strict controls on
sewage quality, higher requirements for industrial and commercial dischargers to the municipal sewerage system, the control of these dischargers, and the provision of relevant information to private households, are the basic prerequisites for obtaining sewage that satisfies re-use criteria (possibly after a mechanical, chemical and biological pretreatment). Groundwater recharge with comprehensively treated sewage may be preferable to disposal by discharge into surface waters (Kunowski et al., 1994; Melsheimer, 1997). In this way, quantity deficits in groundwater that is predominantly used for drinking water supply and as fertiliser (combined with sewage) could be compensated. Furthermore, the quality of surface waters may improve.

If wastewater is used for crop irrigation on dry farmland, a balance between N uptake by the crop and the available nitrogen in the wastewater must be provided to avoid nitrate pollution of groundwater. In this case nitrogen is often the limiting factor in the determination of an acceptable rate of application (Wolff and Wacker, 1985; Min et al., 1992). Problems arise due to the sheer volume and constant generation of sewage that requires disposal by some means (disposal pressure) and because the use of biochemically unsuitable sewage. Below wetlands (e.g. paddy fields) and pools, the percolating water is mostly insignificantly polluted by nitrate because pronounced zones of nitrification and denitrification are formed. The upper soil zone shows an extremely high nitrification capacity and high rates of degradation of organic pollutants, while the deeper soil zones have a high denitrification capacity (Min et al., 1992; Sowa et al., 1993).

In Israel, the complete re-use of sewage in agriculture (for example by storing sewage in the vegetation-free period in deep reservoirs) is a declared aim of the national water resources policy to help minimise environmental pollution (WHO 1989 Shelef, 1982; Juanico, 1993). The use of deeper ponds (deep storage ponds) was investigated, because of the need to reduce the land area required for pond systems. Deep reservoirs are now used widely in Israel for untreated and partly treated effluents (Hosetti and Frost, 1998).

4.4 Disposal of composted waste
Composts are produced during aerobic or anaerobic treatment (stabilisation) of green wastes and biowastes. In all stabilised composts, the rates of mineralisation of the organically bound nitrogen are lower in the year of application than those of farm manure, because a proportion of readily mineralised matter degrades during the composting process.

Biowaste and green composts have a lower content of nitrogen and organic matter than sewage sludge (see Table 4.5). They are used more efficiently to enrich humus and improve soil quality than to fertilise it. An increased humus content stabilises soil structure, improves the water balance and increases the exchange capacity of the soil, and thus its fertility.
Table 4.5  Annual generation of some organic wastes in the Federal Republic of Germany and their content of N and organic matter

<table>
<thead>
<tr>
<th></th>
<th>sewage sludge (t/a)</th>
<th>composites (green and bio waste composts) (t/a)</th>
<th>altogether (t/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>total amount</td>
<td>60 * 10^6</td>
<td>8 * 10^6</td>
<td>68 * 10^6</td>
</tr>
<tr>
<td>dry mass</td>
<td>3 * 10^6</td>
<td>5 * 10^6</td>
<td>8 * 10^6</td>
</tr>
<tr>
<td>organ. mass</td>
<td>1.5 * 10^6</td>
<td>2 * 10^6</td>
<td>3.5 * 10^6</td>
</tr>
<tr>
<td>N content</td>
<td>150 000</td>
<td>50 000</td>
<td>200 000</td>
</tr>
</tbody>
</table>

Source: Poletschny, 1994

The slow mineralisation rate of compost led Mays et al. (1973) to suggest the addition of nitrogen and phosphorus using municipal wastewater sludge. However, the high metal content of sewage sludge made it unsuitable. Recent work by Makaly Biey et al. (2000) demonstrated Multiple Integrated Re-use of Refuse (MIROR), which avoided this contamination. The MIROR method digests grey municipal wastewater to recover the NH₃ in the biogas produced. The re-use of wastewater may improve the agricultural value of compost in areas where industrial fertiliser application is inadvisable.

The nutrient properties of municipal wastes are very similar to those of farm manure (Döhler, 1996). Depending on the starting material, treatment and storage, very large differences in the nitrogen content and the distribution of nitrogen fractions may occur. Thus batch analysis forms the basis of proper use of organic wastes and of farm manure in agriculture. Organic wastes with a high NH₄⁺ content are more suited to the selective fertilisation of plants with N, because it takes several years or decades for organically bound N to mineralise and to become available to plants.

Figure 4.1  Characteristic content of nitrogen (kg N t⁻¹ of wastes) in various domestic wastes (After Döhler, 1996)
In all types of organic fertilisers (wastes, farm manure) the fertilisation efficiency of nitrogen increases significantly in the year of application with the rising share of NH$_4^+$ in the total nitrogen, and the falling C/N ratio in the organic fraction. This is because the share of NH$_4^+$ potentially directly available to plants rises, the organically bound N is released faster (Gutser, 1994) and the immobilisation of NH$_4^+$ as a result of organic matter rich in carbon is reduced. However, farm manure and organic wastes with a high C/N ratio (for example, fresh composts and liquid manure) may have rates of NH$_4^+$-N immobilisation of 20 % and over (Döhler, 1996). Annual rates of N mineralisation from any previous applications of organic wastes in the past must be considered during fertilisation planning for the future. Figure 4.1 shows the characteristic proportions of nitrogen compounds (kg N t$^{-1}$ of wastes) in various domestic wastes.

Use of organic wastes in agriculture should in principle be based on the nutrient requirements of the crop. In the Federal Republic of Germany, the Fertiliser Act and the Fertilisation Ordinance (German Federal Ministry for Food, Agriculture and Forestry 1977, 1996) regulate the use of organic wastes in agriculture. The nutrient that meets the demand of the plant first should always be the limiting nutrient. In the case of organic wastes this is, as a rule, the content of phosphate (Gutser, 1994).

4.5 Recirculation and re-use systems

Unsolved water and sanitation problems in cities of developing countries are one of the greatest obstacles to the progress of sustainable development in urban areas. Present technology used in the water and sanitation sector is serving developed countries well, but is at present unachievable for many developing countries, mainly due to economic reasons. Present technology uses large amounts of clean water to flush away a small amount of human excreta, usually contributing to the pollution of streams, lakes and groundwater, and the sea (Winblad, 1996).

This technology is expensive in the long term due to its excessive use of natural resources. In addition it does not solve the problem of open material flow between urban and rural areas. Developing countries, in particular, cannot afford large losses of a natural resource, such as potable water, during the process of sewage treatment and disposal.

It is estimated that in more than 90% of developing countries, sewage is directly discharged into rivers, lakes and coastal waters without treatment of any kind (WRI, 1996-97). Leaching of sewage effluent has caused deterioration of groundwater quality through nitrate contamination. Nkotagu (1996) studied nitrate contaminated groundwater in Tanzania to deduce the source of contamination. It was concluded that high nitrate contamination in the aquifer originated from dispersal of sewage effluent through macrophores to reach the water table below. Similarly, Girard and Hillaire-Marcel (1997) used $^{15}$N/$^{14}$N ratios to determine the source of nitrate contamination of the aquifer in the semi-arid Niamey region (Niger). Unregulated urbanisation (homemade pit latrines) was deemed to be the source of nitrate contamination. Such systems are widespread in Africa (Table 4.7). In India also, improper sewage disposal in Mysore City was identified, using H$_2$S-strip tests, as the cause of high nitrate concentrations in well waters (Nagaraju and Sastri, 1999). Many rural areas in particular in Africa, south America and Asia suffer from inadequate sanitation.
facilities (Table 4.6).

New low-cost, novel technical solutions for water management and treatment in cities can close material cycles between agricultural land and a city and focus on the recycling of nutrients. Such methods are based on local traditions and are decentralised and ecologically sound. In large parts of the world sewage has been, and still is, used for irrigation and groundwater recharge. Notably in arid and semiarid areas, sewage is used instead of clean water for dry farmland and wetland irrigation and for groundwater recharge. The main reasons for the re-use of sewage are:

- Shortage of fresh water for irrigation.
- Limited funds for the purchase of mineral fertilisers.
- Recycling existing nutrients and the water for plant and food production and/or to compensate deficits in groundwater (by groundwater recharge).
- Protection of surface waters against pollution by sewage discharge.
- A low level of technical sewage treatment can be compensated by (further) natural treatment of wastewater combined with its re-use.

![Figure 4.2 Wastewater treatment systems according to energy use and degree of recycling (After Jenssen, 1996)](image)

Recycling is more easily facilitated by decentralised treatment, well-managed on-site treatment and on-site sanitation systems (e.g., systems with source separation). Decentralised treatment offers better source control and sometimes shorter transport distances and can also be applied to large cities. Jenssen (1996) grouped wastewater treatment systems according to their degree of recycling and energy use (see Figure 4.2). Extensive systems with a high recirculation are the best ecological alternative. Advantages of using natural treatment methods include:

- High purification efficiency (University of Hannover, 1998).
- Low investment costs and operating costs.
• Use of maintenance-free engineering.
• Dependability.

Some examples of different wastewater treatment systems with recirculation or re-use are sanitation systems with source separation, pond systems, wetlands and irrigation systems (Guenther, 1996; Jenssen, 1996; Winblad, 1996; University of Hannover, 1998).

4.5.1 Sanitation systems with source separation

Urine is the black water component that contributes the greatest amount of nutrients. Systems with source separation require toilets that use little or no water and are best suited for the harmless use of the resources in human excreta for agriculture. Well-constructed collection tanks and well-managed collection, transport and re-use systems are essential prerequisites. Source separation requires a change of sewage system infrastructure in developed countries and is similar to the practice of nightsoil management in China. Domestic greywater can usually be treated using simple methods, such as source separating toilets, because the nutrient load tends to be insignificant. In China the nightsoil management systems, used by most of China's urban population, recycle the valuable nutrients phosphorus and nitrogen contained in human excreta through agriculture and pisciculture (Schertenleib, 1995). Types of source separating toilets are:

• Cheap well-constructed and managed home and community latrines for proper collection of excreta.
• Water-saving toilets.
• Composting toilets and latrines.
• Urine separating toilets.
• Desiccating latrines.

4.5.2 Pond systems

Various types of pond systems for wastewater treatment and use have been pioneered in China and India (Jenssen, 1996). Stabilisation ponds for liquid waste treatment are variously referred to as oxidation ponds, sewage lagoons, redox ponds, naturation ponds and facultative ponds (Hosetti and Frost, 1998). They have been classified according to the availability of oxygen for the stabilisation process as aerobic, anaerobic or facultative. Additionally, they have been designated according to the type of organisms supported by the ponds, such as algae, macrophytes and fish. A stabilisation pond fulfils what is necessary for the primary and secondary treatment of sewage and other organic wastes. Treatment occurs mainly through aerobic and anaerobic biological processes. The effluent may be used for irrigation and fertilisation in agriculture. The pond designer has to ensure the optimum nutritional and environmental conditions to maximise biological purification. Ponds represent the only mechanism in many different communities whereby people can be protected from the hazards of local effluents. The diversity of interest in the complex biological and chemical system associated with the simple technology of the oxidation pond, shows that these ponds are of enormous international significance. The mechanisms
contributing to nitrogen retention in ponds are: nitrification and subsequent denitrification as the main process; sedimentation of organic matter; and up-take of nitrogen by micro-organisms and higher plants.

Different types of pond systems are:

- **Aerobic ponds.**
- **Anaerobic ponds.**
- **Facultative ponds.** The upper layers are usually aerobic and the bottom layers anaerobic, which promotes nitrogen removal.
- **Night soil ponds** used, for example, in Israel, India and China. The effluents are frequently used for irrigation and pisciculture.
- **High rate algal facultative ponds.** Nitrogen removal occurs through up-take by bacteria and algae. The algae are then harvested for protein extraction.
- **Polishing ponds.** Protozoans reduce algal biomass, bacterial numbers and total suspended solids from secondary treatment effluents.
- **Macrophyte ponds.** These maturation ponds have floating or rooted aquatic plants, which take up nitrogen and phosphate. They have a similar structure to natural wetlands. Different types of macrophytes and microbes purify wastewater.
- **Maturation ponds.** The size and number of ponds varies according to the quality of the effluent from the preceding treatment unit. Final effluent is used for irrigation and fisheries. The maturation process removes organic matter, viruses and invertebrate eggs. Up to 95% NH₄-N is removed by a four-stage pond system, with water hyacinth and duckweed filters in Stage 1, zooplankton in Stage 2, glass shrimp in Stage 3, and fish in the final pond.
- **Fish ponds.** Fish are fed with diluted sewage or nightsoil. These ponds may also be used for rearing ducks and for cultivating floating macrophytes for use as poultry or cattle feed. The use of an active culture of micro-organisms (as in sewage) as a highly digestible diet for young fish, is a long established practice.
- **Deep storage ponds.** The use of deeper ponds has been investigated because of the need to reduce the land area required for pond systems. Deep reservoirs are used widely in Israel for untreated and partly treated effluents.

### 4.5.3 Wetlands

Calcutta wetlands are an example of low-cost wastewater treatment and highly productive, multilevel aquaculture. This system is used for the recycling of the solid waste portion of wastewater, and also for food production, with vegetables, fruit trees and fish as the end products. China has a long tradition of ecologically sound wastewater recycling in multilevel biological systems based on aquaculture. The Stensund Wastewater Aquaculture integrates sewage treatment, biomass cultivation (algae, higher plants and fish) and waste heat reclamation. The sewage is treated by a constructed food chain of bacteria, phytoplankton, invertebrates, fish and higher plants. They all work together to detoxify the wastewater and reuse the nutrients.
Constructed and natural wetlands are a type of land treatment and disposal of sewage and effluents by periodic flooding. Wetlands work in a similar fashion to facultative (aerated) ponds, forming pronounced zones of nitrification and denitrification (Sonnenburg, 1991). They are efficient denitrifying units and can also be used for plant production (e.g. in paddy fields). An ecological, land treatment system for sewage has been developed in China. This soil infiltration system is a technique that uses the natural environment and conditions, requires low level technology, and does not exacerbate the water shortage problem. It involves carefully controlled spreading of sewage on the land-surface, to achieve a desired degree of sewage treatment. The natural physical, chemical and biological processes that take place in the plant-soil-water system are responsible for the sewage treatment. This method minimises the release of pollutants into the environment, thereby reducing pollution (Ou and Sun, 1996).

Clarification basins planted with water plants for biological treatment of pretreated wastewater have also been developed. These aim to purify settled or pretreated effluent from on-site sanitation systems even further by degradation of organic matter under oxidising conditions and subsequent nitrogen removal under anaerobic conditions.

In Sweden wetlands and pond systems have been constructed (restored) on a large scale to reduce the loading of nitrogen from agriculture to southern Swedish coastal water (Jansson et al., 1994, Fleischer et al., 1994).

### 4.5.4 Irrigation systems

Constructed sub-surface infiltration or irrigation systems are low-level, natural systems that generally lead to a loss of nutrients. The pretreated effluent (mainly settled effluent), or soakage from on-site sanitation systems (e.g. cesspits, septic tanks) is treated further in the subsoil (Jenssen, 1996). Provided that they are well designed and constructed, these systems can show a high purification capacity and high nitrogen removal rates by the formation of pronounced nitrification and denitrification zones (Ankara, 1998).

### 4.6 References


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Chapter 5

Agricultural practice and risk avoidance

The basic minimum requirement of agriculture, in the interests of water pollution control, is to reduce the nutrient surplus added to agricultural land to the lowest possible level (Lammel, 1994). Recommendations relating to the implementation of these requirements in agricultural production, are given in this chapter.

A nitrogen excess of between 50 and 100 kg N/ha* a has been proposed as the limit beyond which the environment will be degraded, particularly by agricultural activities (Paris-Convention for the Prevention of Marine Pollution, 1993; Krayl, 1993; Head Organization for Agricultural Research et al., 1995). Total surplus nitrogen from EU member states for 1990, 1993 and 1995 were 7.0, 7.1 and 7.2 million tonnes respectively (EEA, 2000). In 1990, 320 kg ha$^{-1}$ per year of the total nitrogen surplus in Europe was attributed to Holland (Jansen et al., 1999). An assessment of the Lower Fraser Valley in Canada, found the nitrogen surplus for the study area as a whole, to be 68 kg N ha$^{-1}$. In individual districts, nitrogen surplus values up to 238 kg N ha$^{-1}$ were discovered (Zebarth et al., 1999).

This chapter suggests some approaches for reducing excess nitrogen application to agricultural land and makes some recommendations for agricultural practices aimed at protecting water resources from nitrate pollution.

5.1 Determining the nitrogen balance

Different agricultural practices have the potential to pollute water bodies and therefore water pollution control has to be considered for each individual process. This requires the determination of any nitrogen surpluses by means of a nitrogen balance (i.e. the difference between nitrogen input and nitrogen loss in a system limited in space and time) (Bach, 1987). There are three possible approaches to balancing the application of nitrogen:

1. The farm as a whole, i.e. farmyard gate balance (Paris-Convention for the Prevention of Marine Pollution 1993; German Federal Environmental Agency, 1994b).
2. Plant production balance, i.e. area, plot or crop balances.
3. Animal production balance, i.e. stable or livestock pen balance.

Figure 5.1 illustrates potential sources of nitrogen loss from livestock and crop production.
Figure 5.1 Calculation of the nitrogen losses from livestock rearing and crop production

Fig. 2. Conceptual model of the calculation method.
Determination of the nitrogen balance for a given area, or the plot balance, through assessment of present plant cultivation and animal production methods, gives an indication of the potential risk of nitrate contamination. It is also a starting point for deciding measures to reduce any nitrogen surplus (Frede and Bach, 1993; German Association for Water Management and Land Cultivation 1995).

The nitrogen surplus of an area is calculated as the difference between quantifiable nitrogen inputs to the area and the nitrogen loss with the crop yield. It is possible to calculate average nitrogen surpluses for an average cultivated area (area balance) as well as nitrogen surpluses for an individually cultivated area (plot balance) or for areas cultivated by a specific crop (crop balance). The nitrogen balance reflects the nitrogen surplus per cultivated area (as a rule, per hectare). Inputs include the nitrogen concentration in crop residues, the nitrogen concentration in organic manure (farm manure and wastes) that is available to plants, leaching and atmospheric deposition (Table 5.1). Outputs include the unquantifiable loss by release of nitrogen into the atmosphere as a result of denitrification and leaching, and microbial immobilisation of mineral nitrogen.

**Table 5.1 Calculation of nitrogen surplus for a given area**

<table>
<thead>
<tr>
<th>input of N per ha</th>
<th>loss of N per ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>N in mineral N fertiliser</td>
<td>N in harvested substance</td>
</tr>
<tr>
<td>+ N in farm manure (reduced by loss of</td>
<td></td>
</tr>
<tr>
<td>N in the stable and during storage and</td>
<td></td>
</tr>
<tr>
<td>placement)</td>
<td></td>
</tr>
<tr>
<td>+ N in organic wastes such as sewage sludge,</td>
<td></td>
</tr>
<tr>
<td>composts</td>
<td></td>
</tr>
<tr>
<td>+ legume fixation of N</td>
<td></td>
</tr>
<tr>
<td>+ atmospheric deposition of N</td>
<td></td>
</tr>
<tr>
<td>+ input of N by irrigation</td>
<td></td>
</tr>
</tbody>
</table>

**total input of N**  |  **total loss of N**

Agricultural management practice determines the nitrogen balance. However, when the nitrogen surplus can be calculated it only gives an approximate indication of the quantity of nitrogen that may be leached to water bodies; a high nitrogen surplus does not necessarily indicate a definite risk of water pollution. When organic manure is applied to the land much of the organically-bound nitrogen is stored in the soil and is mineralised slowly over years or decades. Only the proportion of nitrogen that is present in mineral form is at risk of leaching from the area balance surplus. Cultivating crops with a high share of crop residues rich in nitrogen may also result in a high nitrogen surplus although this may not result in a high input to water bodies. Nitrogen inputs to water bodies are best determined from the mean nitrogen surplus, for example over a crop rotation.

Management practices in the past are responsible for the pollution of waters over long periods (Hanus et al., 1994). The long-term application of organic manure results
in an accumulation of organic nitrogen compounds in the soil, and a high nitrogen mineralisation potential which releases large quantities of mineralised nitrogen each year. If this is not taken into account during fertilisation planning, it may result in pollution of water bodies over many years because it is not reflected in the current nitrogen balances.

5.2 Natural groundwater recharge and nitrate concentrations

The displacement of nitrate with percolating waters below the effective root zone is called nitrate leaching. The annual quantity of percolating water can be derived from the water balance equation or the basic hydrological equation (Matthes and Ubell, 1983; Wendland et al., 1993; Baumgartner and Liebscher, 1996). Natural groundwater recharge is the influx of infiltrating water into groundwater, indicated as natural groundwater recharge rate (mm a⁻¹).

\[ GR + A_i = PW = P - E - A_o \]

Where

- \( GR \) = level of natural groundwater recharge (mm a⁻¹)
- \( A_i \) = level of subsurface flow (mm a⁻¹)
- \( PW \) = amount of percolating water (mm a⁻¹)
- \( P \) = amount of precipitation (mm a⁻¹)
- \( E \) = amount of evaporation (mm a⁻¹)
- \( A_o \) = level of surface runoff (mm a⁻¹)

In a subsoil with a heterogeneous structure, part of the percolating water is quickly removed to receiving waters by subsurface flow and only the remaining proportion of percolating water becomes proper groundwater. The term ‘groundwater’ refers to the saturated zone beneath the water table (Chilton, 1996).

sand: 2 - 0.05 mm
silt: 0.05 - 0.002 mm
clay: below 0.002 mm
Figure 5.2 Classification of types of fine soil according to the US-Taxonomy (Russell 1973; Scheffer and Schachtschabel, 1992)

Figure 5.2 shows the classification of types of fine soil according to the USA soil taxonomy. Figure 5.3 illustrates the characteristic soil water curve, which is the relationship between the intensity of water binding, the water gauge and water content for three different types of soil.

Figure 5.3 Characteristic soil water curve for three different types of soil (Rohmann and Sontheimer, 1985)

The field capacity (FK) is the quantity of water which a soil may retain for a few days against gravity, after saturation with water. The usable field capacity (nFK) is the soil water quantity which can be taken up by plants. The remaining water, the ‘dead water fraction’ is adsorptively bound to the rock matrix and neither available to plants nor able to percolate. The permanent wilting point forms the limit between usable field capacity and the dead water fraction. In addition to the pore size distribution, the soil density and the content of organic substance affect the water storage capacity of the soil.

Theoretically, in the plant soil zone (the effective root zone, FK_RZ) plants are able to use all soil water in the usable field capacity. The maximum quantity of water available to plants (nFK_RZ) (mm or l⁻¹m²) depends upon the quantity of water in the field capacity and the depth of the effective root zone.

The annual exchange frequency of soil water gives some indication of the risk of nitrate leaching from the root zone (German Pedological Society, 1992., Frede and Dabbert, 1997). Table 3.7 illustrates the soil water exchange frequencies for soils with different field capacities in the root zone. If the frequency of exchange is greater or equal to 100% the nitrate present in the soil zone before percolation of water is considered to have been displaced from the effective root zone:
EF = (PW/FK_{RZ}) * 100

Where EF = exchange frequency of soil water (% a⁻¹)
PW = amount of percolating water
FK_{RZ} = field capacity in the effective root zone (mm)

Table 5.2  Frequency of soil water exchange in the effective root zone (Frede and Dabbert, 1997)

<table>
<thead>
<tr>
<th>FK_{RZ} (mm)</th>
<th>average quantity of percolating water (mm/a)</th>
<th>frequency of exchange EF (%/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>100 100 200 300 400 600 800</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>50 100 150 200 300 400</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>33 67 100 133 200 267</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>25 50 75 100 150 200</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>20 40 60 80 120 160</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>17 33 50 67 100 133</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>13 25 38 50 75 100</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>10 20 30 40 60 80</td>
<td></td>
</tr>
</tbody>
</table>

wash-out factor WF
at wash-out frequencies < 100 % WF = EF/100
at wash-out frequencies ≥ 100 % WF = 1

Nitrate pollution of percolating water is influenced by the N-balance_{min.} surplus and the annual nitrogen net mineralisation rate \( M \) (\( N_{min} \) is the quantity of mobile nitrate-N and exchangeable ammonium-N that is available to plants). The medium N-balance_{min.} is derived from the actual nitrogen surplus (e.g. the average over a crop sequence). The annual nitrogen net mineralisation includes the nitrogen returned through mineralisation in organic manure, residues remaining in the soil from past crops and further nitrogen supply from the soil. Therefore to minimise a nitrogen surplus, farmers should take into account past farming practices and nitrogen fertiliser application.

The potential hazard to water can be represented by the long-term average nitrate concentration in percolating water under optimised nitrate fertilisation. This can be calculated as follows:

\[
\text{NO}_3^-_{PW} = ((\text{N-balance}_{min.} + M - I - D) \times WF / PW) \times 4.43 \times 100
\]

\[
= ((\text{N-balance}_{min.} + M - I - D) / FK_{RZ}) \times 4.43 \times 100 \quad \text{for } EF < 1
\]

\[
= ((\text{N-balance}_{min.} + M - I - D) / PW) \times 4.43 \times 100 \quad \text{for } EF \geq 1
\]

Where \( \text{NO}_3^-_{PW} \) = potential nitrate concentration in percolating water (mg/l)
\( \text{N-balance}_{min.} \) = mineral N share in the N-balance: N area balance (kg N/ha*a) (average over a few years, respectively the mean over a crop rotation), reduced by N from organic manuring (farm manure, wastes) not available in the respective year of application and N content in crop residues
\( M \) = N net mineralisation (kg N/ha*a) (N return supply from application of organic manure and from crop residues in the past and subsequent N supply from soil)
I = N immobilisation (kg N/ha*a) (as far as not yet included in N-balance_{min. } )
D = N loss by denitrification (kg N/ha*a)
PW = annual amount of percolating water (mm)
FK_{RZ} = field capacity in the root zone (mm)
4.43 = conversion factor from nitrogen into nitrate

Agricultural systems in industrialised countries produce large nitrogen surpluses each year. \( N_{min} \) which is not washed out accumulates in the root zone until every year the whole N-balance_{min} surplus plus the N net mineralisation (reduced by the loss due to denitrification and N immobilisation) leaches from the root zone irrespective of the amount of percolating water.

The long-term average nitrate concentration in percolating water can then be calculated as follows:

\[
\text{NO}_3^{-}\_\text{PW} = \left( \frac{(\text{N-balance}_{\text{min.}} + M - I - D)}{\text{PW}} \right) \times 4.43 \times 100
\]

The following factors affect the risk of nitrogen leaching (Duynisveld and Strebel, 1986.; Duynisveld et al., 1993):

- The differing water quantities at FK_{RZ} or nFK_{RZ} in the root zone influence nitrate leaching in different types of soil.
- The larger the FK_{RZ} in the effective root zone of a soil, the smaller the risk of leaching.
- The nFK_{RZ} is depleted during crop growth. After the crop is harvested, precipitation first replaces the nFK_{RZ} before percolation occurs. The larger the usable field capacity, the smaller the amount of percolating water.
- In the event of strong rain and intensive irrigation, soils with a small nFK_{RZ} tend to form percolating water before harvest.
- The higher the nFK of a soil the higher its water conductivity in an unsaturated state and the more likely it will be that plants will use the nFK_{RZ} in the effective root zone during the vegetation period.
- Different climates influence the risk of leaching through different amounts and distribution of precipitation. During fallow periods, the amount of nitrate displacement from the soil will increase with the amount of precipitation.
- The depth to the groundwater table affects the transport of nitrate. In locations close to groundwater, with the fringe capillary in the effective root zone, nitrate that has already been washed out may be transported back to the root zone. When evaporation rates are high, water from the groundwater zone can be made available to plants again due to capillary action through plant roots. The quantities of nitrate which are transported back to the root zone have to be considered in fertilisation planning for the cultivation of crops. Crops can contribute to the reduction of the N-balance surplus. The maximum depth from which the water balance in the root zone may be affected by water rising from the
groundwater zone, due to capillary action, is approximately 1 m in the case of gravely sands and up to 4 m if overlying strata contain a high proportion of fine and medium-grained material.

- Different crops affect the rate of nitrate leaching due to differing root depths and cultivation periods.
- The earlier the main vegetation period, the earlier the formation of percolating water will be stopped.
- The later the main vegetation period, the later the formation of percolating water will set in.
- The crop-specific rooting depth determines the depth down to which the nFK may be used. The rooting density affects the degree to which the nFKRZ is exhausted.
- Apart from crop rotation, which determines the length of the vegetation-free period, planting of intercrops and catch crops are important measures to reduce the pollution of percolating water by nitrate. These crops biologically fix residual nitrate and nitrogen which mineralises in the vegetation-free period.

Studies have been undertaken on the effects of nitrogen fixation with intercropping of different crops. Danso et al. (1987) observed that, when intercropped with barley, nitrogen fixation in faba bean crops increased (in Kessel and Hartley, 2000). Similarly, at final harvest, the percentage of nitrogen derived from nitrogen fixation was significantly higher when pea was intercropped with barley, than for monocropped pea (Jensen, 1996, in Kessel and Hartley, 2000). Peterson and Russelle (1991) calculated that nitrogen fertiliser inputs in the mid-western USA could be substantially reduced, without a loss in production, by proper management of alfalfa in rotation with corn (in Graham and Vance, 2000). It has been estimated that, worldwide, legumes are grown on approximately 250 Mha and they fix about 90 Tg of nitrogen per year (Kinzig and Socolow, 1994, in Graham and Vance, 2000). Intercropping is practised throughout the world but it is more common in the tropics (Kessel and Hartley, 2000).

5.3 Measures to reduce nitrogen surpluses in plant cultivation

5.3.1 Planning of fertilisation

The demand of plants for nitrogen nutrients is determined by the extraction of nitrogen from the total mass of plants (German Association of Gas and Water Specialists, 1993) or the extraction of nitrogen by main and accessory crops and by the residual plant which may not be harvested (Frede and Dabbert, 1997; Timmermann, 1993):

Demand of plants for N = plant-specific N content (kg N/dt) * location-related plant mass (dt/ha)

= N extraction by harvested crops (kg N/dt) * location-related crop yield (dt/ha) + additional N for residual plants which
The demand for fertilisation, i.e. the amount of fertiliser which is required to cover the demand for nutrients (Council of European Communities 1991b; German Federal Ministry for Food, Agriculture and Forestry 1996; Frede and Dabbert, 1997) can be obtained from:

\[
\text{demand for N from fertilisation} = \text{demand of plants for N} \\
\quad \text{less } N_{\text{min}} \text{ reserves before the cultivation of crops} \\
\quad \text{less } \text{return of N from crop residues, intercropping and organic manure} \\
\quad \text{from applications in the past} \\
\quad \text{less } \text{subsequent supply of N by soil during the vegetation period (if a soil rich in humus is available with a high subsequent N supply)}
\]

Note: The demand for N from fertilisation is equal to the N from mineral fertiliser + N from organic manure (farm manure and wastes) available in the year of application.

The type, quantity and time of fertilisation have to be adapted to the plants' requirements. The total quantity of nitrogen supplied during the period of growth must be sufficient to achieve a qualitatively optimum and site-specific yield of plants, whilst avoiding the leaching of nitrate.

Fertilisation regimes that aim to protect water resources should take the following into account (Hanus et al., 1994; Lammel, 1994; Frede and Dabbert, 1997):

- Realistic, site-adapted yield expectations.
- Fertilisation should take place only at times when plants grow and require nutrients. The adaptation of fertilisation to the plants’ requirements, in terms of quantity and time, will result in higher yields, and reduce the surplus of nitrogen, provided the change in demand for plant nitrogen is taken into account.
- The plant-available $N_{\text{min}}$ content of soil in the root zone is taken into consideration before crops are cultivated;
- Because it is assumed that plants may use only a part of the nitrogen that is applied by fertilisation, nitrogen requirements are often overestimated to avoid a loss in yield as a result of insufficient fertilisation. However, fertilisation that exceeds the demand of the crops is mostly superfluous. The subsequent nitrogen supply of the soil and the atmospheric nitrogen deposition in the vegetation period is, as a rule, sufficient to ensure that subject to realistic yield expectations, the demand of the plants for nitrogen will be met.
- Nitrogen mineralisation from the previous years’ application of organic nitrogen fertilisers, such as farm manure, sewage sludge, compost and harvest residues, should be included in fertilisation planning.
- Determination of $N_{\text{min}}$ after harvest provides information about the location-related return, and subsequent supply, of nitrogen during the cultivation period.
This information may help to optimise fertilisation.

- Leaching of nitrogen may be minimised by intercropping, catch cropping and organisation of crop rotation.

It has been suggested that ‘precision’ farming strategies, such as site-specific management (SSM), could potentially reduce nitrogen surplus run-off, because nitrogen applications are more precisely matched to specific requirements (Rejesus and Hornbaker, 1999). Instead of uniform fertilisation application rates across a field, different amounts are applied depending on the productive characteristics of the soil. Greater amounts of nitrogen fertiliser would only be applied to the soil types that required it, reducing the amount of nitrogen surplus.

5.3.2 The use of farm manure in livestock farming areas

Nitrogen is contained in farm manure in a mineral form, as ammonia, and in an organically bound form. The share of NH$_4^+$-N in the total nitrogen varies between 10 and 90% depending on the type of manure and type of livestock (Figure 5.4) (Fürchtenicht et al., 1993; German Federal Environmental Agency, 1994a; Döhler, 1996). However, the components and distribution of nitrogen may vary widely depending on treatment and storage, the species and feed (see Figure 5.5) Frede and Dabbert, 1997). Table 5.2 indicates the emissions of manure, nitrogen and NH$_3$ due to pig farming in France, Denmark and The Netherlands. In areas of intensive livestock production, the concentration of nitrogen in manure may exceed the nutrient uptake capacity of crops.

![Figure 5.4](image_url) Characteristic nitrogen concentration in various types of farm manure (Döhler, 1996)
From a fertilisation aspect, farm manure with a high content of NH$_4^+$ is best for the supply of nitrogen (Döhler and Schultheiss, 1994). Organically bound nitrogen is only mineralised and made available to plants over the course of years to decades. The total concentration of NH$_4^+$ is not necessarily available in the year of application. Depending on the C/N ratio, a substantial nitrogen immobilisation may occur (20% or more) (also see Chapter x.x). Figure 5.6 shows the potential cumulative use of nitrogen as a percentage of the total nitrogen applied, from a single application of different types of farm manure.
Figure 5.7 Potential rate of mineralisation as percentage of the organically bound nitrogen quantity placed annually, depending on the period of application (Frede and Dabbert, 1997, according to Döhler, 1996)

Figure 5.7 shows the annual rates of mineralisation as a percentage of the amount of organically bound nitrogen applied annually. The annual mineralisation is strongly controlled by site-related mineralisation conditions (e.g. soil, climate, intensity of soil tillage). Long-term application of farm manure results in an enrichment of organically bound nitrogen in the soil, building up a high mineralisation potential. Fertilisers with a high concentration of organically bound nitrogen and a large input of organic manure are deemed as critical, and illustrate the need for optimum fertilisation and operational management.

In order to protect water resources when applying farm manure in agriculture the following conditions should be applied (Döhler and Schultheiss, 1994; Döhler, 1996):

- Adaptation of livestock numbers to the available agricultural area. This allows appropriate use of farm manure for plant production in a rotation system of farming. It must also be noted that the concentration of phosphate may be a limiting factor in the growth of crops.
- No application should be made in the fallow period, but only at times of actual nutrient demand. Sufficient storage capacity for the manure must be available.
- Farm manure should be analysed for its nutrient content.
- Liquid or semi-liquid manure should be homogenised prior to application.
- The mineralisation of nitrogen from applications of organic manure in the past has to be considered in any planning of fertilisation in the future.
- Minimisation of loss of nitrogen from livestock buildings, and during storage and application.
• Calculation of nutrient application rates can be improved by supplementary mineral fertilisation. The recommended amount is approximately one quarter to one third of the total nitrogen requirement.

5.3.3 Management practices to minimise emissions of nitrogen by farm manure

Nitrogen losses from farms can be reduced by modifications to management practices. The following practices, described by Mandersloot et al. (1995) and Kuipers and Mandersloot (1999) are based on the influence on nitrogen losses on a dairy farm in The Netherlands, but many of the principles can be applied to other livestock production units:
• Injection of slurry into soil reduces ammonia emissions by 80-100% compared with surface spreading.
• Covering slurry storage facilities with a roof or straw crust reduces ammonia emissions by 60-80% (Verboon, 1995).
• Generating higher milk yields per cow, to reduce the number of cows per hectare, reduces nitrogen losses.
• Reducing application of nitrogen fertiliser by taking into account differences in soil productivity due to water supply, rate of mineralisation and amount of mineral nitrogen in the soil prior to application.
• Restricted grazing, for example keeping cows indoors at night, results in less urine excretion on land and lower nitrate losses through leaching.
• Combining grass products with low nitrogen feeds, such as maize silage, reduces nitrogen losses for the farm as a whole.
• Rinsing slatted floors and construction of soli. Sloping floors reduce ammonia volatilisation by 20-50% in livestock buildings.

To avoid an increased loss of nitrogen during high air temperatures, increased wind speeds and solar radiation (Figure 5.8), all farm manure should be applied in the evening hours, ideally before or during light precipitation.
The low nitrogen efficiency of animal production can be increased by improving nutrient use through various feeding-related measures. Optimised feeding allows the excretion of nitrogen to be reduced by 10 - 25 % (Federation Europeenne des Fabricants d’Adjuvants pour la Nutrition Animale (FEFANA), 1992). Isermann (1993) calculated the potential reduction in the nitrogen concentration in excreta at 20 % for Germany. Farms with small livestock density are under less pressure to optimise feeding than farms with a high livestock density. Apart from livestock reduction, optimisation of feeding is often the only way to reduce nitrogen surpluses in farms.

FEFANA (1992) calculated that the following reductions of nitrogen in excreta could be achieved through optimised feeding:

**Figure 5.8** Cumulative NH$_3$ emissions as percentage of the NH$_4^+$ amounts applied, depending on air temperature and type of liquid manure (Frede and Dabbert, 1997)
Factors  estimated reduction of N in farm manure in % (accumulation is possible to some extent only)

**Feed additives**
- increased use of amino acids and related compounds in combination with a lowered protein level: 20 - 25
- enzymes: carbohydrates: 5
- efficiency promoters: 5

**Feeding measures**
- rations adapted to the demand: 10 - 15
- phased feeding (feeding adapted to the development and efficiency level): 10
- increased use of highly digestible raw materials: 5

### 5.3.4 Crop rotation, catch cropping, tillage and nitrogen leaching

The choice and sequence of individual crops in a crop rotation, catch cropping and intercropping have a decisive influence on the type and quantity of nitrogen leaching into the hydrosphere. The design of the crop rotation system and of the coverage of soil by catch crops in the fallow period should aim at maximising the period of closed plant stands on arable land, and thus at maximising the use of nitrogen. In this way the amount of water percolation, and thus nitrate leaching, can be reduced, conserving N_{min} residues in the soil from preceding crops, from formation during the fallow period, from organic manure and from atmospheric deposition. Crops that have a high nitrogen demand but low content in the harvested material (e.g. vegetables), those with large quantities of degradable nitrogen in crop residues (e.g. rape, beet) and those that require intensive tillage upon harvest (e.g. potatoes) can be included in crop rotation by subsequent planting of a catch crop with a high nitrogen uptake (Wildenhayn, 1994; Claupein, 1994).

Catch crops are, as a rule, planted for use as forage or for green manuring for the following crop using, for example, the mulch seed technique. Fertilisation of catch crops depends on the crop and the aim of cultivation. To ensure a dense plant stock and maximum uptake of nitrogen fertiliser, leguminous plants should not be cultivated. Catch cropping is used to reduce the nitrogen balance surplus in the following crop and therefore the subsequent nitrogen supply by green manuring has to be taken into account when planning fertilisation for the following crop. For the maximum effect it should be ploughed into the soil as late as possible (Auersbach, 1993).

Reduced soil tillage has the advantage of reducing erosion. The risk of nitrate leaching decreases with decreasing frequency, intensity and depth of soil tillage. Furthermore, soil tillage should not take place before periods in which there is a risk of leaching.
5.3.5 Grassland farming

Compared with arable land, grassland has more humus and nitrogen because the grassland soil is covered with plants all year round and is not tilled. Grassland farming aims to maintain a dense plant stock which can use the maximum amount of nutrients.

The type of grassland and the intensity of its use effects the risk of leaching (Elsässer, 1994). Depending on the yield potential only limited numbers of animals per hectare can be considered to be ecologically compatible. The EU's Nitrate Directive (Council of European Communities, 1991b), for example, limits the application of nitrogen from farm manure on grassland to a maximum of 210 kg N/ha* a in nitrate rehabilitation areas. Yet, in the interests of water pollution control it is absolutely necessary to adapt livestock density to the location.

Grassland that is used exclusively for cutting uses nitrogen well and is one of the forms of land use with the lowest nitrate leaching risk, provided fertilisation is appropriate for the site and the frequency of cutting (Frede and Dabbert 1997). The nitrogen fertilisation requirement on meadows is equal to the nitrogen removed, less any symbiotic fixation of nitrogen.

Fertiliser application measures with the intention of protecting water supplies should assume (Frede and Dabbert, 1997):

- Uniform fertilisation of areas near and areas distant from the farm.
- Less fertilisation during dry periods. Less fertilisation of soils with a low usable field capacity in the root zone.
- No fertiliser application before heavy precipitation because grassland soil has many biogenic macro-pores.
- Reduction of fertilisation in late summer.
- Application of the total quantity of nitrogen over several individual applications.
- Liquid manure cannot be worked into grassland and shows a high loss of ammonia. If applied over many years only about 75 % of the total nitrogen applied annually is used in the year of application. Dilution of liquid manure reduces the loss of ammonia.

Grazing contributes to a large increase in nitrate leaching (Strebel et al., 1984). Depending on the fertilisation regime and the properties of the location, Ryden et al. (1984) found that below pastures nitrate leaching is about five times higher than below meadows. The non-uniform distribution of excrements, sward destruction, overgrazing and selective grazing result in extremely high nitrogen loads (point sources) in soil and excessive nitrogen leaching within a pasture. This results in a reduced overall efficiency of the nitrogen in excreta. Of the nitrogen taken up through feed by grazing animals, 75-95% returns to the area through animal faeces and therefore this has to be included in fertilisation planning. Owing to the high loss of nitrogen, the fertilisation effect amounts only to about 65 % of the effect of mineral
fertilisers (Frede and Dabert, 1997) and therefore the nitrogen fertilisation requirement on pastures is equal to the nitrogen fertilisation requirement on meadows minus the quantity of effective nitrogen fertiliser in the excreta.

Nitrate leaching on grassland can be reduced by:

- Adaptation of livestock density to the capacity of the site. Under- or overgrazing must be avoided.
- Avoidance of selective grazing behaviour by mixed grazing with different animals.
- Grazing periods should be shortened. Transition from all-day to half-day pastures.
- Distribution of individual piles of excrement by means of, for example, pasture levelling.
- Regular, subsequent mowing.
- Second sowing if the sward is patchy.
- Frequent change of watering, resting and feeding places.

5.3.6 Special crops

Even if fertilisation is optimal problematic crops, such as many types of vegetable, leave high quantities of mineral $N_{\text{min}}$ and mineralisable plant residues in the soil after their harvest. This may result in serious groundwater pollution by nitrate because (Frede and Dabbert, 1997, German Association of the Gas and Water Branch reg. association 1993):

- They are predominantly cultivated on well-structured and light sandy-loamy soils.
- They are harvested predominantly in the vegetative state and need a minimum amount of nitrogen prior to their harvest.
- Many vegetable varieties have comparatively shallow roots.
- Intensive crop rotation, with several harvests a year, is carried out.
- Many crop residues that are easily mineralised remain on the field after harvest.
- Intensive soil tillage, a high organic content and high soil moisture as a result of irrigation result in high nitrogen mineralisation rates.
- Intensive irrigation results in leaching of nitrate in the vegetation period if it is not adapted to the field capacity of the rooting zone of the soil.
In order to calculate the optimum application of nitrogen fertiliser that will not have an impact on water resources, the nitrogen uptake by the type of vegetable and the minimum nitrogen reserves up until the harvest, have to be determined. Determination of $N_{\text{min}}$ during each stage of cultivation provides a measure of the actual nitrogen reserves in the soil. The demand for nitrogen fertiliser can then be obtained by estimating the mineralisation of nitrogen from crop residues and the soil up to the time of harvest (Lorenz et al., 1989).

Nitrogen leaching may be eased by organising crop rotation (cultivation of vegetables with various rooting depths and a differing demand for nitrogen), by cultivation of deep-rooting catch crops with a high uptake of nitrogen and by late ploughing under of mulch and of crop residues or composting of crop residues.

5.4 Further measures to reduce nitrate pollution of water bodies

In some circumstances, minimising nitrogen surpluses by optimising agricultural production may not be an adequate method of protecting drinking water resources against nitrate contamination. Many countries, for example Germany (German Federal Ministry for the Environment, Nature Conservation and Reactor Security, 1996b) and the UK, have established water protection areas. Nitrate Vulnerable Zones (NVZs) have been designated in 68 areas throughout England and Wales (Environment Agency, 1999). Farmers within NVZs are required to comply with The Action Programme for Nitrate Vulnerable Zones (England and Wales) Regulations, 1998. These include keeping accurate field records of details of cropping, livestock numbers and the use of manufactured nitrogen fertilisers and organic manures, for at least five years. Crop requirements must not be exceeded when applying nitrogen fertilisers, closed periods must be adhered to and nitrogen fertiliser spreading and storage conditions must be followed.

In many water protection areas of the Federal Republic of Germany (Ministry for the Environment Baden-Württemberg, 1991; Timmermann, 1993; Grigoleit, 1997) the mineral nitrogen reserves in soil $N_{\text{min}}$ in the rootable soil zone (mostly only the displaceable nitrate nitrogen reserves) are determined before the main leaching period. A maximum, location-specific nitrogen soil limit must be adhered to in order to prevent high concentrations of nitrate pollution in drinking water sources.

Other measures taken to protect drinking water supplies are:

- Limitation of the quantity of nitrogen fertiliser applied and on the time of application, if required.
- Reduced tillage, grassing, cultivation of catch crops and spray irrigation adapted to demand.
- Change of use and set-aside of land. The most efficient method of reducing the risk of nitrogen leaching below fallow areas is to sow productive grasses and to eliminate biologically fixed amounts of nitrogen from the area by cutting (Schultheiss and Isselstein, 1994). Changing the use of areas from farmland to grassland, which is cut regularly, is the most efficient method of rehabilitating land with a very high nitrogen content. As a rule, afforestation is not recommended because the high annual rates of mineralisation of the organic
matter contained in forest soil may release high quantities of nitrogen which may not be taken up by the forest stand.


- Prohibition of the ploughing of grassland. Ploughing of grassland results in a release of substantial quantities of nitrogen by mineralisation of the organic matter contained in soil (Figure 5.9).

- Promotion of an inter-farm use of farm manure.

- Restriction or prohibition of pasture farming.

- Limitation or prohibition of application of farm manure and organic wastes.

**Figure 5.9** Degradation of N stocks of soil after turning grassland (Strebel et al., 1984)
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Chapter 6

Water treatment processes for reducing nitrate concentrations

This chapter provides a summary of water treatment processes for reducing nitrate concentrations in raw waters. Because the nitrate ion is stable and highly soluble it is not amenable to removal by conventional water treatment processes such as coagulation and precipitation or adsorption and filtration. Specialised processes have to be used involving catalysts, high temperature and pressure. A wide variety of chemical reducing agents have been used to reduce nitrates but not all are suitable for the treatment of drinking water. Examples of those that have been tested are; active metals (such as aluminium), ammonia and hydrogen. Three reduction processes using an energy source to overcome the high chemical stability of the nitrate ion have been studied; electrochemical, photochemical and thermal. Although a range of reduction processes are discussed below, the most detail is provided for ion-exchange and heterotrophic biological denitrification, because these are the most widely applied and preferred options. A comprehensive review of nitrate removal techniques has been published by Kapoor and Viraghaven (1997).

6.1 Ion exchange denitrification

6.1.1 Basic principles

In ion-exchange denitrification water is passed through a bed of synthetic resin beads which remove anions including nitrate from the water, exchanging them for equivalent amounts of chloride. Once the exchange capacity of the resin is reached, the resin bed is taken out of service and the resin is regenerated using sodium chloride solution (brine), which returns the resin to the chloride form. After rinsing with clean water the bed is returned to service. The spent regenerant contains a high concentration of sodium chloride together with the anions (nitrate and sulphate) removed from the resin bed.

6.1.2 Plant and equipment

The main features of an ion-exchange nitrate removal plant are shown in Figure 6.1. At least two pressure shells containing strong base anion exchange resin beds are used: one bed is “in service” treating water while the other is being regenerated or is on standby. Pipework and valves allow service flow, regeneration, rinsing and backwashing of the beds. The pressure shells are typically up to 3 m high and 4 m in diameter, containing beds up to 2 m deep. A salt saturator is used to produce concentrated brine for regeneration. Storage tanks are used to hold the regenerant, rinse water and the spent regenerant prior to disposal.
Figure 6.1  Schematic representation of an ion exchange plant

The maximum flow rates achievable are 30 m$^3$ per m$^2$ bed area per hour and 25 m$^3$ per m$^3$ bed volume per hour. At these flow rates the headloss across the bed will be 5 to 10 m water. Plant operation is normally fully automatic.

6.1.3 Operation and performance

The type of resin and the regeneration conditions have an impact on the overall performance of the process

Resin type

Conventional anion exchange resins have a higher affinity for sulphate than for nitrate. This means that they preferentially remove sulphate and reduce the capacity for nitrate, leading in turn to higher running costs (for regenerant) and greater volumes of waste for disposal. As a result, nitrate-selective resins which give better uptake of nitrate in the presence of sulphate and reduce process costs are preferred. In addition, nitrate-selective resins overcome the problems of high concentrations of nitrate in the treated water as a result of displacement by sulphate.
Nitrate-selective resins also add less chloride to the treated water because of the lower sulfate removal. This is desirable because high chloride concentrations and chloride:bicarbonate ratios are associated with increased corrosion of certain metals.

*Regeneration conditions*

Longer run times can be achieved by increasing either, or both, the brine concentration or volume up to a point where salt usage (and hence costs) increases disproportionately to the improvement in performance. The impact on wastes must also be considered. Typically, regeneration is performed using two to three bed volumes of 6-10% (m/m) NaCl with a similar volume of rinse water. Under these conditions run times of 24 hours can be achieved. The run is stopped and regeneration is initiated shortly before the treated water nitrate concentration approaches that of the feed, or at a pre-determined nitrate level. Provided that the influent nitrate concentration is approximately constant, initiation of regeneration can be based on volume treated (or time for a constant flow rate plant); otherwise monitoring of the product water, based on ion-selective electrode or ultraviolet absorbance monitors, will be necessary.

Regeneration is normally carried out counterflow; i.e. with the regenerant passing through the bed in the opposite direction to the treated water flow (usually upflow regeneration with treated water downflow). This mode of operation maintains a low nitrate concentration in the treated water when the bed is first brought back into operation.

Even when using nitrate-selective resins, the concentrations of nitrate, sulphate, bicarbonate and chloride vary during a run as shown in Figure 6.2. These variations can be balanced out by operating two or more beds out of phase and blending the products or by installing large mixing tanks prior to distribution (Andrews and Harward, 1994).

Sodium bicarbonate can be used to alleviate potential corrosive problems due to elevated chloride and reduced bicarbonate. Although sodium bicarbonate alone is inefficient as a regenerant, it can be used after regeneration with sodium chloride. This converts the resin in the lower part of the bed to the bicarbonate form and reduces the chloride to bicarbonate ratio during the early part of the run (Fletcher et al., 1991).

The total volume of spent brine and used wash water can be up to 2% of the volume of water treated. It is possible to use electrodialysis to concentrate the waste and to reduce the volume for disposal, but this may not be economic. An alternative is to use combined ion-exchange with biological denitrification to remove nitrate from the brine (see Section 6.x) which allows re-use of the brine, or easier and more environmentally acceptable disposal.

An alternative approach is the carbon dioxide regenerated ion exchange process (CARIX) (Hagen et al., 1986) which uses a mixed bed of weak-acid resin in free acid form and an anion exchanger (not nitrate selective) in bicarbonate form. The exchangers remove neutral salts from solution and liberate an equivalent amount of carbon dioxide. When used for nitrate removal the regenerant is a strong solution of
carbon dioxide in water, together with calcium carbonate to increase the bicarbonate concentration. The waste from the process contains only the neutral salts removed from the water and is therefore environmentally compatible.

Figure 6.2  Typical changes in treated water quality from a nitrate-selective resin

6.2 Biological denitrification

6.2.1 Basic principles

Biological denitrification exploits the ability of certain naturally-occurring bacteria to use nitrate for respiration under anoxic conditions (absence of oxygen). The overall process is the reduction of nitrate to nitrogen gas and proceeds as follows:

$$\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$$

Denitrification can be achieved using both heterotrophic and autotrophic bacteria. In heterotrophic denitrification an organic carbon substrate, such as methanol, ethanol or acetic acid, is required as a food source for the bacteria. In autotrophic denitrification an inorganic energy source such as sulphur, reduced sulphur species (e.g. thiosulphate) or hydrogen is required; the carbon needed for bacterial growth is obtained from bicarbonate in the water.

Various unit processes have been developed for biological denitrification, using different substrates and different reactor configurations to support bacterial growth. Heterotrophic denitrification systems are applied more widely than autotrophic processes.
6.2.2 Heterotrophic denitrification

Several different types of heterotrophic denitrification plants have been operated at full-scale. Designs include fluidized bed upflow reactors and both upflow and downflow reactors. Support media include sand, anthracite, expanded aluminosilicate and plastics media. Some of the designs are outlined below. Figure 6.3 is a generalised illustration of the process.

![Generalized heterotrophic denitrification process](image)

It is necessary to dose a carbon source into the raw water; usually ethanol, methanol or acetic acid. Sufficient substrate has to be dosed to achieve complete removal of dissolved oxygen (DO) as well as the desired nitrate reduction. Table 6.1 illustrates approximate quantities required for each of these carbon sources.
Table 6.1 Substrate dose requirements (Hall, 1997)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>mg required per mg DO</th>
<th>mg required per mg NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1.0</td>
<td>0.56</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.5</td>
<td>0.45</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1.2</td>
<td>0.79</td>
</tr>
</tbody>
</table>

For some waters it is also necessary to dose phosphate as a trace nutrient to support microbiological growth; the phosphate requirement (as P) is 2.26 µg l⁻¹ per mg l⁻¹ NO₃ removed (Rogalla et al., 1990).

The dosed water passes to the denitrification reactor where reduction of nitrate occurs. This reactor has to incorporate a means of cleaning the filter or support medium to remove excess biomass. Because organic carbon is added to the water and the growth of heterotrophic bacteria is enhanced, an efficient polishing stage is required. Typically this involves re-aeration followed by filtration on alternatively aerated filters can be used. If the substrate is under-dosed it is possible to obtain very low residual concentrations; however, this can lead to the presence of nitrite in the treated water. Whilst the nitrite can easily be oxidised to nitrate by chlorination, its presence reduces efficiency and increases operating costs. The alternative is to overdose slightly to obtain complete denitrification; the excess carbon source is then removed by biological activity in the polishing filter.

6.2.3 Plant and equipment

Many different designs can be used for heterotrophic denitrification, including fixed-bed and fluidised bed reactors. Fluidised bed reactors enable higher nitrate removal rates and avoid problems due to clogging and gas entrapment with filters.

A downflow fixed-bed process described by Richard (1989) uses thermally expanded aluminosilicate as the support medium and ethanol as the carbon source. The denitrification reactor is followed by a dual media Granular Activated Carbon (GAC) and sand filter for polishing. The process is operated under pressure to avoid breaking head and to prevent the formation of gas bubbles within the filter. An upflow fixed bed process, using acetic acid or ethanol as the substrate, was also described by Richard (1989). This process uses GAC as the support; the upflow operation prevents the accumulation of released nitrogen gas. Fixed bed reactors typically have an empty bed contact time of 10-15 minutes. The backwashing regime for fixed-bed reactors is similar to that for conventional filters.

Biological fluidised bed (BFB) upflow reactors employ fine sand (0.3-0.5 mm) to support the biological growth. Water dosed with ethanol, methanol or acetic acid flows upwards at a velocity sufficient to give 40-50% bed expansion (typical upflow velocities are 20-30 m per hour) and a detention time of 5-10 minutes. The combination of high biomass concentration and high upflow rate permits relatively
small reactor volumes and areas. The reactor area is determined by the upflow velocity and the height by the concentrations of DO and nitrate to be removed (DO removal occurs preferentially, in the lower part of the fluidised bed). To remove the biomass which builds-up on the sand, a cleaning system, such as a centrifugal pump, hydrocyclone and screen, is used to remove excess biomass and return the cleaned sand to the reactor. Post-filtration is used to remove any biomass carried over from the fluidised bed.

6.2.4 Biological fluidized bed operation and performance

A start-up period of 4-6 weeks is required, during which high upflow rates are achieved using recycle, in order to develop the necessary biomass concentration in the reactor. The carbon source dose is progressively increased, and the amount of recycle is decreased to lower the upflow rate. As biomass develops on the sand grains, the reduced particle density enables fluidisation to be maintained at lower upflow rates.

Once adequate biomass concentrations have developed, the carbon source dose is adjusted to that necessary for removal of all DO and the required removal of nitrate. If the carbon source is under-dosed it is possible to limit its concentration in the treated water, but this can lead to the presence of nitrite. The alternative approach is to over-dose slightly to completely denitrify the water and to rely on biological activity in the post-denitrification clarification or filtration stage to remove excess carbon source. Control of the carbon source dose is critical to the operation of the process and on line analysers are available for monitoring the residual concentration in the treated water.

Hirata and Meutia (1996) describe denitrification in an anoxic two-phase fluidized bed bioreactor. Methanol provided the carbon source and nitrate degrading bacteria were immobilised on CB particles. A high efficiency of removal was demonstrated by the maximum volumetric denitrification rate of 18.7kg-N m⁻³ per day.

6.2.5 Autotrophic denitrification

The sulphur-limestone process was developed for treatment of groundwater (e.g. van der Hoek et al., 1992) and it is illustrated in Figure 6.4. The process is based on autotrophic denitrification by *Thiobacillus denitrificans* in a mixed bed (1:1 by volume) of sulphur and limestone (CaCO₃) granules (2-6 mm). A vacuum de-aerator is used to remove oxygen from the water. The deoxygenated water then flows upwards through the filter at a filtration rate of 0.5 m per hour, similar to that in a slow sand filter. Under the anoxic conditions within the filter, nitrate is converted into nitrogen gas whilst elemental sulphur acts as an electron donor and is converted into sulphate. Denitrification is accompanied by the formation of hydrogen ions. The purpose of the limestone is to maintain the optimal pH range (pH 6.4-6.8) and to provide a source of inorganic carbon for the bacteria. Excess biomass is removed by backwashing. After re-aeration, the water can be further treated (e.g. by artificial recharge).
Sulphur-based autotrophic denitrification is being used by the Orange County Water District, California, to remove nitrates from well water (US Water News Online, 1998). *Thiobacillus denitrificans* has reportedly been used to reduce nitrate levels to 0.3 mg per litre, well below the federal and state maximum contaminant level of 45 mg per litre. Furthermore, initial tests have reported operational costs to be substantially less than other treatment methods; a 60% reduction compared to reverse osmosis and 50% less than ion exchange processes.

An alternative process involves dosing hydrogen for use as an electron donor by naturally occurring autotrophic bacteria. In the absence of oxygen, nitrate ions provide the source of nitrogen and are reduced to nitrogen. Full scale application of this method using fixed-bed reactors has been described by Gros and Treutler, 1986, and other studies are summarised in Kapoor and Viraraghavan (1997).

### 6.3 Combination processes

It is possible to combine ion-exchange with heterotrophic denitrification in order to reduce the quantity of waste regenerant for disposal. Upflow fluidised bed denitrification is able to denitrify highly saline solutions, and a combined ion-exchange and biological denitrification process can result in a 90% or more reduction in waste brine (e.g. van der Hoek and Klapwijk, 1987).

### 6.4 Other methods

Membrane separation techniques, such as reverse osmosis and electrodialysis, can be used for nitrate removal but are up to eight times more expensive to operate than ion exchange processes and are not selective for nitrate ion removal (Reddy and Lin, 2000). The relatively high capital and operating costs of these processes tends to make them uneconomic. However, a number of treatment technologies have been tested.

For example, Murphy (1991) describes a chemical process in which aluminium powder reduces small amounts of nitrates in water to ammonia, nitrogen gas and nitrite;

\[
3\text{NO}_3^- + 2\text{AL} + 3\text{H}_2\text{O} \rightarrow 3\text{NO}_2^- + 2\text{AL(OH)}_3
\]
2. \( \text{NO}_2^- + 2\text{AL} + 3\text{H}_2\text{O} \rightarrow \text{NH}_3 + 2\text{AL(OH)}_3 + \text{OH}^- \)

3. \( 2\text{NO}_2^- + 2\text{AL} + 4\text{H}_2\text{O} \rightarrow \text{N}_2 + 2\text{AL(OH)}_3 + 2\text{OH}^- \)

Nitrate reduction was found to be pH dependant. At pH values less than eight no nitrate reduction took place. Above pH 10.5 nitrate was reduced upon addition of the aluminium powder. Aluminium powder has been suggested for the denitrification of sodium-based nuclear wastes, employing the nitrate to ammonia and ceramic (NAC) process (Mattus et al., 1993, 1994., In Fanning, 2000). However, processes involving the use of active metals such as aluminium to purify drinking water supplies have not been fully developed.

Reddy and Lin (2000) describe a catalytic reduction process to remove \( \text{NO}_3^- \) selectively from groundwater using three catalysts: palladium, platinum and rhodium on carbon (5-10%). Of these, rhodium was the most efficient. It was proposed that this catalytic reduction process could potentially be suitable to serve the water purification needs of small communities at a relatively low cost. The rhodium catalyst can be coated onto a fibreglass mesh and the desired redox potential can be achieved with a photovoltaic cell. Using sunlight as the energy source to activate the catalyst would reduce operating costs.

Liquid-phase hydrogenation using a Pd-Cu bimetallic catalyst has been found to promote the reduction of nitrate in drinking water. A theoretical study undertaken by Lecloux (1999) indicated that Pd alone is not an efficient decomposer of nitrate and Cu is not suited to decompose nitrite. As Pd alone will dissociate nitrite, a Cu/Pd surface atom ratio of 5/1 was deemed optimum for selective reduction of nitrate to nitrite. At each step of the reduction process, through \( \text{NO}_2^- \), NO and atomic nitrogen formation, atomic oxygen produced absorbs strongly onto the catalytic surface, blocking active sites and reducing efficiency. An increase in the partial pressure of hydrogen was found to promote cleaning of the catalytic surface and formation of \( \text{N}_2 \). During hydrogenation hydroxide ions are formed which maintain electroneutrality in the solution. However, hydroxide ions are an undesirable by-product of the reaction and can be dealt with using \( \text{CO}_2 \) if needed (Fanning, 2000).

Gasparovicova et al. (1999) also studied nitrate removal following catalytic hydrogenation over polymer supported Pd-Cu catalysts. The nitrate content in water was reduced from 100mg l\(^{-1}\) to less than 50mg l\(^{-1}\) after 4 hours of batch treatment with a hydrogen-nitrogen mixture of 43% volume \( \text{H}_2 \). Catalysts containing acid sites demonstrated a higher selectivity (about 60% molecular volume) than catalysts without acid sites (about 20% molecular volume) demonstrating the importance of acid sites on selectivity of removal.

Other methods of nitrate removal are being developed;

Pintar and Batista (1999) investigated catalytic liquid-phase nitrate reduction in isothermal bubble-column fixed-bed (BCFR) and trickle-bed reactors. In the BCFR with distilled water as the reaction medium, nitrates were efficiently removed and none were detected in the reactor effluent. A lower rate of nitrate conversion was detected in the trickle-bed reactor and was attributed to shorter mean residence times and reduced contact with the catalytic particles within the reactor. However, when
drinking water was used as the reaction medium instead of distilled, the presence of dissolved ionic species resulted in a decrease in the rate of nitrate removal, and nitrates were detected in the reactor effluent. It was concluded that in this study the use of supported Pd-Cu bimetallics for direct purification of contaminated drinking water did not selectively remove nitrates.

Electrochemical techniques are being developed to remove nitrates from water on a commercial basis. Li et al. (1988) obtained intermediate formation of nitrite using Ni, Pb, Zn and Fe cathodes, with ammonia as the final product. After an electrolysis time of 60 minutes, 90% nitrate reduction occurred with the Zn and Pb cathodes. Chew and Zhang (1998) used electrokinetics coupled with a zero-valent iron (Fe-O) treatment wall to treat nitrate contaminated soil. When the Fe-O wall was placed near the anode and a constant current switched on, nitrate-nitrogen transformation was 84-88%. This research demonstrated the potential use of electrokinetics/iron wall in remediation of nitrate contaminated groundwater.

Photochemical methods have demonstrated that light can activate the nitrate ion directly or indirectly via a catalyst for reaction with a reducing agent. However, reducing nitrate with water photochemically is an uphill energy process (Fanning, 2000) and not suitable for large scale water treatment.

6.5 Advantages and limitations of treatment methods

This discussion is limited to ion-exchange and heterotrophic biological denitrification as the most commonly used processes for nitrate removal. Ion-exchange is generally suitable for treatment of groundwaters but not surface waters in which the content of organics and suspended solids could compromise the performance of the resin. Ion-exchange plants are relatively simple to automate and are suitable for installation at groundwater abstraction sites, which tend to have few existing treatment plants, other than for disinfection. The capital costs for ion-exchange plants are about two and a half to three times lower than for heterotrophic denitrification plants, with approximately equivalent operating costs.

The main disadvantage of ion-exchange is the requirement for regeneration and disposal of the spent regenerant (Murphy, 1991; Reddy and Lin, 2000). The costs of regeneration over a 20 year plant life can be more than twice the initial capital costs. The treatment and disposal of spent regenerant, and consequent costs, vary according to local circumstances and where the costs of ion-exchange are quoted it is not always clear if this factor has been included. Green and Shelef (1994) compared biological denitrification and ion-exchange methods and concluded that although ion-exchange would be less expensive, the large amounts of waste generated would limit ion-exchange processes to areas close to large receiving waters. Ion-exchange increases the chloride content of the water, which will tend to make it more corrosive, especially towards brass.

Heterotrophic denitrification is a process suitable for treatment of surface waters. The process can cope with organics and suspended solids in the feed water and with variable water quality such as changes in suspended solids, dissolved solids nitrate and sulfate. However, it is temperature-sensitive, with lower denitrification rates being obtained in colder water. This may limit the application of biological
denitrification in cooler climates (Rantanen, 2000). The operating costs are broadly the same as for ion-exchange, although capital costs are at least twice as high. The biological processes actually reduce nitrate to nitrogen gas, in contrast to ion-exchange which displaces the nitrate from the feed water to the spent regenerant (which may itself require treatment to remove nitrate).

Heterotrophic denitrification is more widely applied than the autotrophic processes. The rate of heterotrophic denitrification is substantially higher, permitting the use of smaller reactors and capital costs, which are up to six times lower. Biological treatment using fluidised beds gives faster nitrate removal than fixed bed systems, and avoids problems due to blockage and channelling in filters. However, fluidised beds require more complex plant and monitoring for recycling of biomass, and cleaning and recycling of support sand.

The main concerns with biological denitrification are the potential for contamination of the treated water with bacteria, residual carbon source in the treated water and the possibility of nitrite formation. Post-treatment with clarification and/or filtration is necessary to remove any bacteria carried-over from the bio-reactor, and to enable microbiologically mediated removal of any excess carbon source. The presence of residual carbon source is undesirable because it could encourage microbiological proliferation within the denitrification system. The presence of carbon sources, such as methanol, may also be considered undesirable on health grounds. Whilst under-dosing can avoid such problems, it can also lead to nitrite formation. Overall, a high degree of monitoring and control is required to ensure proper operation of the process.

Heterotrophic biological denitrification processes require a long start up period of up to six weeks. Consequently, they are unsuitable for short-term intermittent operation. Waste sludge is produced, but this amounts to less than 0.1% by volume of the water treated, assuming on-site sludge thickening.

Overall, therefore, ion-exchange is generally preferred for treatment of groundwater and biological denitrification for treatment of surface waters.

6.6 References


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Chapter 7

Problem evaluation and management

7.1 Monitoring and assessment

The objectives of the water quality monitoring and assessment programme determine the structure of the monitoring network, the type and frequency of the variables to be analysed and the extent of spatial and temporal sampling (Meybeck et al. 1996). All of these aspects may be modified by financial constraints. A comprehensive and meaningful monitoring system should include ground and surface waters and should take into account the users of these water bodies. In addition to assessing the quality of the source water intended for public supply, potable water should be monitored continuously to check that no variables exceed the health limits prior to distribution through a water distribution network. Whereas this may be feasible for large water supply schemes provided by local authorities or water companies, it is usually not feasible for small group or private schemes. Such small schemes should carry out a thorough analysis of the water on a regular basis, such as monthly for areas at risk of contamination or annually for relatively pristine waters.

In most water quality measurement programmes, nitrate is an important variable because the concentrations can give an indication of pollution resulting from human activities. In combination with other variables, nitrate is also a measure of the nutrient balance and of potential productivity within a waterbody. Because of the potential health risks associated with high nitrate concentrations, their presence may limit the use of water as a drinking water source.

7.1.1 Groundwaters

Groundwater usually has a good natural quality and is often suitable for use as a drinking water source with little or no treatment. The quality of groundwater is comparatively stable unless subject to pollution. The residence time of water in most aquifers ranges from years to decades because of the very slow movement of the water through the ground. As a consequence, once groundwater becomes polluted it can take years or decades for remedial measures to restore the water quality to its original condition (Chilton, 1996). Efforts to speed up this process can involve very expensive engineering measures.

In view of the importance of groundwater as a drinking water source, and as part of the hydrological cycle, preservation of its natural condition or its return to a non-polluted state has been embodied in law in many countries. Comprehensive and continuous monitoring of groundwaters for quality and quantity are required to meet the requirements of these laws. Ensuring that a high standard is maintained in the supply of drinking water, going beyond mere compliance with limit values, is sometimes combined with active measures to preserve the aquatic environment. In Austria, for example, the groundwater pollution threshold value is 60% of the Austrian drinking water limit for nitrate (Vogel, 1995). If this threshold value is
exceeded at more than 25% of the measuring stations in a specific groundwater region of the monitoring network, the area is designated as a rehabilitation area and measures have to be taken to reinstate the water to its unpolluted condition.

Examples in many countries show that protection of wells is always less costly than treatment of raw water with poor quality. High quality groundwater intended for human consumption may be ensured by establishing drinking water retention and drinking water protection areas. Comprehensive protection of groundwater in the catchment area of public water supplies should be an obligatory part of any groundwater management policy. To safeguard drinking water supplies it is essential to analyse raw waters continuously and to establish monitoring wells that can give advance warning of groundwater pollution. These wells should encompass all of the potentially endangered groundwater flows into the drinking water supply wells. For this purpose they should be arranged such that they can detect horizontal and vertical differences in water quality in flows towards the supply well (for information on the siting of observation wells see Chilton, 1996). Ideally, the distance between supply wells and observation wells should be sufficiently large to ensure that a one-year warning period would be available to enable the introduction of preventative and precautionary measures if a pollution event occurs (Toussaint, 1990). Further details on the design of monitoring and assessment programmes for groundwater are available in Chilton (1996).

Groundwater sampling methods

Groundwater wells used as drinking water sources are usually equipped with a pump and therefore samples can be taken directly from the point of discharge. Due to the risk of contamination from piping material, water should be allowed to flow for several minutes before sampling to avoid inclusion of water resident in the systems piping (Bartram et al., 1996).

When sampling from springs without an overflow, or from shallow wells without a pump, special care must be taken to prevent the sample container touching the bottom of the well or surface area surrounding the spring or well. This would cause resuspension of sediment resulting in contamination of the sample. Occasionally, when a spring catchment is higher than the surrounding ground, water may be siphoned into the sample bottle. In such instances, the hose should be rinsed thoroughly by allowing water to pass through for 2 to 3 minutes before collection of the sample.

The depth within an aquifer from which a sample of water is collected from the well is determined by the location of the well screen. This depth cannot be varied by the collector because water enters a well at the level of the screen. Consequently, a groundwater sample can only be obtained as a grab sample (Figure 7.1) from a selected depth, and at a specified location and time.

7.1.2 Surface waters

Surface waters are highly sensitive to pollution from the atmosphere, land run-off and direct discharges. Nitrate concentrations in surface waters can fluctuate within quite short time scales (e.g. hours to days) depending on flow rate and discharge, direct
inputs from point sources, land run-off within the catchment and with biological activity. Therefore monitoring of surface waters to record the full variability in nitrate concentrations requires relatively frequent sampling and possibly even event-controlled sampling, especially when surface waters are used as a drinking water source. Nitrate measurements are incorporated into most water quality monitoring programmes for surface waters because nitrate is one of the main nutrients for aquatic productivity and because of the possible health risks associated with high nitrate concentrations in drinking water (see Chapter 2).

Surface waters serving as raw waters for drinking water supplies are monitored to check compliance with source water or drinking water quality guidelines or with water quality targets. A water quality target for a substance is considered to be complied with if the percentile (e.g. the 90 or 95 percentile) concentration does not exceed the value of the quality target. As a rule, guideline values and maximum allowable concentrations (MACs) for nitrate are based on the WHO guideline value for drinking water of 50 mg l⁻¹ NO₃⁻ (WHO, 1993). However, as a precaution, limits for raw surface waters may be set that are more stringent than the health-based guideline value. In Germany, for example, the target for nitrate in surface waters is that 90% of surface water samples must not have a concentration higher than 25 mg l⁻¹ NO₃⁻, which is half the drinking water limit (Mohaupt et al., 1996).

In addition to monitoring to check whether surface waters are meeting quality targets, it may be necessary to carry out special monitoring programmes to establish sources and patterns of elevated nitrate concentrations or the effects of remedial or management actions to reduce nitrate concentrations in freshwaters. The design of the monitoring programme, including the distribution of the sample locations, frequency, depth and types of water samples are all determined by the objectives of the monitoring programme. Further information on monitoring programme design is available in Bartram and Balance (1996) and Chapman (1996).

Surface water sampling methods

Samples from lakes and reservoirs can be taken using a grab sampler such as that illustrated in Figure 7.1. A typical grab sampler consists of a tube approximately 30 cm in length and 10 cm in diameter, fastened to a frame upon which it can slide. Projections at each end of the frame prevent the tube from sliding off. Spring-loaded flaps cover the ends of the tube and can be held fully open by latches. The latches can be released and the tube closed by applying a small amount of pressure with a small weight, or “messenger”, that is dropped down the lowering rope. When the sampler is in use, the end flaps are latched into the open position and the sampler is lowered to the required depth with the lowering rope. Water passes through the open ends so that, at any depth, the water in the sampler is the water from that depth. Upon reaching the desired depth, the messenger is dropped down the rope, the latch is tripped and the ends close. Once brought to the surface, the contents are transferred to a sample bottle and transported to the laboratory for analysis.

Figure 7.1 Depth or grab sampler (After Bartram et al., 1996) To be provided.

A typical sampler frequently used in flowing streams or rivers, is a multi-purpose sampler (see Figure 7.2). The multi-purpose sampler consists of a weighted platform
equipped to hold a sample bottle, a rudder to maintain position in flowing water and rings at the top and bottom to which lowering ropes can be attached. For sampling near the surface, it is simply immersed in the water and allowed to fill up. For samples from greater depths, it must be lowered in the inverted position and righted using the configuration of the lowering ropes once the desired depth has been reached. Care must be taken to avoid contamination of the sample by fine floating particles on the surface. If the water is flowing, the open mouth of the bottle should point upstream.

Figure 7.2 Multi-purpose sampler (After Bartram et al., 1996) To be provided.

Usually, the quantity of water obtained by grab samples is sufficient for all the chemical and physical analyses required. However, if the sampler is too small and many analyses are required, two grab samples can be taken at the same monitoring station and subsequently mixed in the same sample bottle or transport container.

Certain monitoring objectives may require that results represent the value for a given area or depth of water body. To meet these objectives, composite or integrated samples may be taken. There are several different types of composite samples:

- **Depth-integrated.** These most commonly comprise two or more equal parts collected at predetermined depth intervals between the surface and the bottom.

- **Area-integrated.** These are made by combining a series of samples taken at various sampling points spacially distributed in the water body (usually all at one depth or predetermined depth intervals).

- **Time-integrated.** These are made by mixing equal volumes of water collected at regular time intervals.

- **Discharge-integrated.** These are particularly important for rivers subject to fluctuations in flow with rainfall. Samples are collected at regular intervals and the rate of discharge is measured at each sampling event over the period of interest. A common arrangement is to sample every two hours over a 24 hour period. The composite sample is then made by mixing portions of the individual samples in proportion to the rate of discharge at the time the sample was taken.

### 7.2 Analytical methods

There are many methods available for measuring nitrogen in freshwaters, soils and sediments. The choice of method depends on access to equipment and reagents, the availability of technical staff and their expertise, the anticipated range of concentrations and the level of accuracy required. Detailed descriptions of methods are published by a number of recognised agencies and organisations. Whenever possible, internationally recognised and standardised methods should be used, such as those published by the International Organization for Standardization (ISO) which is based in Geneva, Switzerland (see reference list). Brief descriptions of some of the
most commonly used methods for analysis of nitrogen, ammonia, nitrate and nitrite are outlined here. It is recommended that quality control and assurance procedures should be followed whenever any programme of sampling and analysis is undertaken (Briggs, 1996).

7.2.1 Water samples

Samples taken for the determination of nitrate and/or nitrite should be collected in polyethylene or glass bottles and then filtered and analysed immediately. If this is not possible, the addition of 2-4 ml of chloroform per litre will retard bacterial decomposition and the sample can be cooled and then stored at 3-4 °C. Due to interference from other substances present in the water, determination of nitrate can be difficult. The precise choice of method for determination may vary according to the expected concentration of nitrate as N. Alternatively, one portion of the sample can be chemically analysed for total inorganic nitrogen and the other for nitrite, and the nitrate concentration obtained from the difference between the two values. Nitrite concentrations can be determined using spectrophotometric methods. Some simple field determinations, of limited accuracy, can be made using colormetric comparator methods available as kits (Ballance, 1996b; Chapman and Kimstach, 1996).

7.2.2 Nitrogen, ammonia

Ammonia is produced during microbiological degradation of nitrogenous organic matter, and is present in many surface and groundwaters. Water polluted by sewage, agricultural wastes, fertilisers or industrial wastes containing organic nitrogen will contain higher concentrations of ammonia. Ammonia may be converted to nitrites and then nitrites by certain forms of aerobic bacteria. These nitrogenous compounds provide nutrition for aquatic micro-organisms and can be a contributing factor to eutrophication in lakes and rivers. Subsequent anaerobic conditions can result in formation of ammonia via natural reduction processes (Ballance, 1996a).

Sample handling

Determination of ammonia content should be undertaken very soon after sampling. If this is not possible the sample should be stored at 4°C. Chemical preservation may be achieved by adding either 1ml H₂SO₄ or 20-40mg HgCl₂ to 1 litre of sample. Distillation of ammonia under alkaline conditions into a solution of boric acid may be followed by titration with standard acid. Determination of ammonia nitrogen is given by:

\[ \text{Ammonia nitrogen (as N)} = \frac{100V_2}{V_1} \text{ mg l}^{-1} \]

where \( V_1 \) = volume of sample taken (ml)
\( V_2 \) = volume of 0.00714 mol l⁻¹ acid used (ml)

Spectrophotometric methods

Distillation is the preferred method of removal of ammonia from the sample. The concentration of ammonia may then be determined colorimetrically using Nessler's reagent. Direct nesslerisation of the sample is quick but subject to considerable interference. The Berthelot reaction is commonly used for spectrophotometric
determination of ammonia. Here, the ammonia in the sample is made to react with a phenolic compound and a chlorine-donating reagent at a high pH in the presence of a catalyst. This method is reported to be highly specific for ammonia over other nitrogen-containing compounds, and to be more sensitive than methods based on Nessler's reagent (Crompton, 1992).

Direct titration
The ammonia must be distilled under alkaline conditions into boric acid, where it is titrated against standard hydrochloric acid to a purple end-point using bromothymol blue as an indicator. This method is particularly suitable for the analysis of polluted surface and ground waters that contain sufficient ammonia to neutralise at least 1ml of 0.00714 mol l\(^{-1}\) HCl.

7.2.3 Nitrogen, Kjeldahl

Kjeldahl nitrogen is defined as the sum of ammonia nitrogen and those organic nitrogen compounds converted to ammonium sulphate under the conditions of the Kjeldahl digestion procedure (Ballance, 1996a). The organic Kjeldahl nitrogen is obtained by subtracting the value of ammonia nitrogen from the Kjeldahl nitrogen value. Macro- or semi-macro-Kjeldahl methods are chosen on the basis of organic nitrogen concentration. Macro-Kjeldahl analysis is applicable for samples containing either low or high concentrations of organic nitrogen, but where low concentrations are present, relatively large sample volumes are required. In the semi-macro-Kjeldahl method, applicable to samples containing high concentrations of organic nitrogen, the sample should be chosen to contain organic plus ammonia nitrogen in the range of 0.2 to 2mg.

Sample handling
Fresh samples should ideally be used to obtain reliable results; conversion of organic nitrogen to ammonia may occur in samples during the time between collection and analysis. If immediate analysis is not possible, samples can be preserved by the addition of 2 ml sulphuric acid per litre of sample, with storage at 4 °C. Preservation with HgCl\(_2\) is not recommended because mercuric salts interfere with ammonia removal.

The Kjeldahl method requires that the sample is heated in the presence of sulphuric acid and a catalyst. To ensure removal of oxidised nitrogen, alcohol is also added. Following digestion, the solution is diluted and the ammonia determined by photometry or distilled from solution and titrated if sufficiently large volumes are present.

Titrimetric distillation following mineralisation and distillation

Whilst the Kjeldahl procedure or any other method cannot guarantee the complete breakdown of every organic nitrogen compound to ammonia, nitrate and nitrite are removed during mineralisation and distillation.

As with other methods, analysis should be carried out immediately on samples taken. If it is not possible to do this within 24 hours, addition of 2 ml concentrated
sulphuric acid to 1 litre of sample will aid preservation. It must be noted that sulphuric acid is capable of entrapping ammonia vapour.

The organic content of the sample is mineralised in an acid medium and in the presence of a catalyst. Addition of ethyl-alcohol will eliminate interference due to oxidised forms of mineral nitrogen. The ammonia obtained is steam distilled in an alkaline medium and then determined by either direct or back titration.

The Kjeldahl nitrogen content is given by:

\[ N = \frac{(V_1 - V_0)c \times 1.000 \times 28}{V} \]  

where:  
- \( V_1 \) = the volume of 0.05 or 0.01mol l\(^{-1} \) sulphuric acid (ml) used for the determination  
- \( V_0 \) = the volume of 0.05 or 0.01mol l\(^{-1} \) sulphuric acid (ml) used for the blank test  
- \( c \) = the molarity (0.05 or 0.01mol l\(^{-1} \)) of the standard solution of sulphuric acid used for the determination  
- \( V \) = the volume of the sample taken for analysis

Spectrophotometric method after mineralisation

Samples should be analysed as soon as possible after collection. Acidification (for preservation) should be avoided for the determination of low concentrations, because sulphuric acid is capable of entrapping ammonia.

Organic matter within the sample is mineralised in an acid medium and in the presence of a catalyst. Indophenol blue spectrophotometry at a wavelength of approximately 630nm is used to determine the Kjeldahl nitrogen content.

7.2.4 Nitrogen, nitrate

Nitrate is the end product of the aerobic decomposition of organic nitrogenous matter. It is common in surface and groundwaters, particularly those receiving input of chemical fertilisers, drainage from animal feedlots and domestic and some industrial wastes. Determination of nitrate concentrations in waters provides some degree of assessment of the state of pollution. Unpolluted waters usually contain only minute amounts of nitrate. However, determination of nitrate in water, particularly in wastewaters, can be difficult due to the higher concentrations of numerous interfering substances.

The various techniques employed for the determination of nitrate are limited by concentration ranges, therefore a method should be selected to suite both the range of nitrate concentration and probable interferences. Ion chromatography has successfully been applied to waters containing nitrate plus nitrite at the 5µg l\(^{-1} \) level. As this method is free from interference and has a high specificity and sensitivity of the
electrochemical detection mode, it is suitable for the determination of trace levels of both nitrate and nitrite in surface and groundwaters (Crompton, 1992). Applicable ranges for other methods are (Clesceri, et al., 1989):

- Nitrate electrode method, 0.14-1400 mg NO$_3^-$ N l$^{-1}$
- Cadmium reduction method, 0.01-1 mg NO$_3^-$ N l$^{-1}$
- Titanous chloride method, 0.01-10 mg NO$_3^-$ N l$^{-1}$
- Hydrazine reduction method, 0.01-10 mg NO$_3^-$ N l$^{-1}$
- Automated cadmium reduction method, 0.5-10 mg NO$_3^-$ N l$^{-1}$
- Devardas alloy method, >1 mg NO$_3^-$ N l$^{-1}$

Two methods of nitrate determination are outlined here: Devardas alloy method and the cadmium reduction method.

**Devardas alloy method (reduction to ammonia)**

This method is applicable to nitrate concentrations exceeding 1mg l$^{-1}$ (Ballance, 1996a). The procedure can be performed on the original sample or on the residue remaining in the flask after the distillation process required in the determination of ammonia nitrogen. This distillation step also serves to eliminate interference and thus is applicable to analysis of wastewater and polluted surface water.

If a delay between sampling and analysis cannot be avoided, changes in the nitrogen balance due to biological activity can be delayed through storage at a temperature just above freezing point, with or without preservatives. Examples of preservatives are 0.8 ml concentrated sulphuric acid or 40 mg of mercury (as mercuric chloride) per litre of sample. If sulphuric acid is used for preservation, the sample should be neutralised to pH7 before analysis is begun.

Devardas alloy is composed of 59% aluminium, 39% copper and 2% zinc. Use of this alloy reduces nitrate to ammonia by nascent hydrogen. The ammonia is subsequently distilled and its concentration determined by titration. Nitrites are also reduced by Devardas alloy and their concentration can be determined rapidly and readily. Subtraction of the nitrite fraction from the total oxidised nitrogen will give the nitrate concentration.

\[
\text{Nitrate nitrogen (as N)} = \frac{(a-b) * 100 - n}{V} - n \text{ mg l}^{-1}
\]

where: 
- $a$ = volume of 0.00714mol l$^{-1}$ acid used for titration of the distillate of the sample
- $b$ = volume of 0.00714mol l$^{-1}$ acid used for titration of distillate of the blank (ml)
- $V$ = volume of the undiluted sample (ml)
- $n$ = concentration of nitrite nitrogen in mg l$^{-1}$ N, determined separately.

**Cadmium reduction method**

Nitrate is reduced to nitrite in the presence of cadmium. This method involves the use of commercially available cadmium granules treated with copper sulphate and packed in a glass column. The cadmium reduction column is illustrated in Figure 7.3.
The nitrite produced is determined colorimetrically following reaction with a diazotizing reagent (sulphanilamide) and a coupling reagent N-(1-naphthyl)-ethylenediamine dihydrochloride. This produces a pinkish-purple coloured azo dye that is measured between wavelengths of 510 and 550 nm. Particulate matter can be removed from the sample by filtration and pre-extraction of the sample with an organic solvent will eliminate interference by oil or grease. Addition of EDTA to samples containing high concentrations of iron, copper or other metals will eliminate this source of interference. Because the cadmium reduction method is very sensitive, it is recommended for use where nitrate levels are below 0.1 mg NO$_3^-$ N l$^{-1}$.

**Figure 7.3** Cadmium reduction column (After Ballance, 1996a)

### 7.2.5 Nitrogen, nitrite

Nitrite is formed in water by the oxidation of ammonia or reduction of nitrate. It is an unstable stage in the nitrogen cycle and concentrations within a sample can change rapidly due to biochemical processes (Ballance, 1996a). Naturally, nitrite is present in waters at very low concentrations (a few tenths of a milligram per litre) but can occur at much higher concentrations in sewage and industrial wastes, in treated sewage effluents and in polluted waters.

Determination of nitrite should be undertaken immediately due to its instability in water. Acid preservation of samples to be analysed for nitrite should not be used. Instead, short-term preservation of 1 to 2 days may be achieved through the addition of 40 mg mercuric ion, as HgCl$_2$, per litre of sample, with storage at 4 °C.

In a strongly acidic medium nitrite reacts with sulphanilamide to produce a diazo compound which couples with N-(1-naphthyl)-ethylenediamine dihydrochloride. An intensely red azo dye is formed, the absorbance of which is proportional to the concentration of nitrite present. The absorbance of standards and samples is measured at 540 nm. A calibration curve is prepared by plotting the absorbance of the standards against the concentration of nitrite. From this, the concentration of nitrite in the samples can be read directly. For samples less than 50 ml, nitrite concentrations can be calculated from the following:

\[
\text{Nitrite nitrogen (as N)} = \frac{mg \text{ l}^{-1} \text{ from standard curve} \times 50 \text{ mg l}^{-1}}{ml \text{ sample}}
\]

Flow injection analysis and gas chromatography methods can also be used with detection limits as low as 0.2 µg l$^{-1}$ and 0.5 µg l$^{-1}$ respectively (Crompton, 1992).

### 7.3 Soil and organic matter

Agricultural soils need to be tested for their nitrate (NO$_3^-$-N) content to enable recommendations to be made to farmers concerning the appropriate rate of nitrogen fertiliser application. As is the case with water samples, microbial activity within soil can influence the balance of NO$_3^-$-N during the period between sampling and nitrate
analysis. Mineralisation of organic N will increase the proportion of NO$_3^-$-N whilst denitrification will decrease soil NO$_3^-$-N. Ideally, samples should be analysed as soon as possible after being taken. Samples should be kept refrigerated until they can be dried. They should be air-dried in thin layers (<1 cm) on paper, or oven-dried at approximately 60 °C (Griffin et al., 2000).

Water or dilute salt solutions can be used to extract NO$_3^-$-N from most soils, because essentially all the NO$_3^-$-N in soils that have a low anion exchange capacity is water soluble. However, the low ionic strength of water can cause dispersion and results in cloudy filtrates. Salt solutions can cause problems with the subsequent analysis depending on which method of nitrate determination is used. If nitrate is measured by ion chromatography or ion selective electrodes, chloride (Cl$^-$) can interfere with the analysis. However, if the soils to be analysed have appreciable anion exchange capacity, or if exchangeable and water-soluble ammonium-N are to be measured, 2M KCl is ideal as an extractant.

Another extractant which could be used is 0.01M CaSO$_4$. This provides a clear filtrate and the sulphate in the extract does not interfere with most methods of determination, including ion chromatography. If the nitrate selective electrode is to be used, the preferred extractant is 0.04M (NH$_4$)$_2$SO$_4$.

Examples of methods to determine NO$_3^-$-N in soil extracts include the nitrate specific ion electrode, the cadmium reduction method, ion chromatography, steam distillation and colormetric procedures, where NO$_3^-$-N is measured directly or following reduction to nitrite (NO$_2^-$-N).

**Nitrate electrode method**

Whilst this method has advantages of speed, apparent simplicity and relatively low cost of required equipment, nitrate electrodes are subject to numerous interferences and to subtle variations in sample handling. Electrode calibration, the reference electrodes, electrode preparation and even differences between NO$_3^-$-N electrodes supplied by the same manufacturer can all affect results. In addition, some of the main extractants cause interference, such as 2M KCl and acetone. Furthermore, relatively small soil:extractant ratios (eg. 1:2.5) are required to measure NO$_3^-$-N in some soils due to the low sensitivity of the electrode. However, successful procedures have been developed that use the extractant 0.04M (NH$_4$)$_2$SO$_4$ with H$_3$BO$_3$ as a preservative.

**Ion chromatography method**

High-pressure liquid chromatography involves injecting sample extracts into columns containing a solid phase exchange surface which can differentially retard the movement of inorganic ions depending on their size and charge. The relative retention times of different ions in the column can be measured by chromatographic instruments, allowing identification and quantification of individual ions in the sample.

Columns and instruments should be selected according to sensitivity, linear range, susceptibility to contamination by soil organics and potential interference from the anion used in the extracting solution. Although the linear range for NO$_3^-$-N determination can be adjusted, if the soil extract contains extremely high
concentrations of NO$_3$-N, dilution of the sample may be necessary to avoid exceeding the separation capacity of the column. Interference from anions in the extraction solution (e.g. sulphate) is minimal as long as sufficient separation exists between the NO$_3$-N peak and that part of the anion. If cations interfere with nitrate determination, pre-treatment cartridges can be used which remove the cations via ion-exchange. Soluble organic matter may be absorbed onto the column, decreasing its capacity to retain anions. Addition of charcoal in the extraction procedure aids removal of such soluble organics. Whilst ion chromatography can be automated, it tends to be slower than continuous flow instruments, for example the cadmium reduction method.

**Cadmium reduction method**

Cadmium reduction procedures are both very sensitive and free from potential interference by soil cations and organic matter. The minimum reproducible concentration of NO$_3$-N that could be detected in soil extracts by a manual cadmium reduction procedure was 0.014 mg NO$_3$ N l$^{-1}$ (Dorich and Nelson, 1984). The maximum concentration measured without dilution was 20 mg NO$_3$ N l$^{-1}$. Compared to manual cadmium reduction, the automated method has the advantage of speed, allowing 20 to 120 sample extracts to be analysed per hour, depending on manufacturer and quality of equipment. Further advantages are good precision and uniformity of flow rate through the reduction column from sample to sample. However, equipment is expensive and the working concentration range for some systems is only 0 to 2 mg NO$_3$-N l$^{-1}$. For soil extracts containing NO$_3$-N concentrations above 2 mg l$^{-1}$, extracts must be manually diluted, the size of the sample and diluent lines on the manifold must be adjusted or a predilution loop must be added to the manifold. The working concentration range of newer automated systems has been increased to 0 to 20 mg NO$_3$-N l$^{-1}$.

### 7.4 Situation assessment and management action

Data generated by routine and frequent analysis of drinking water supplies for nitrate concentrations should be assessed immediately for compliance with the recommended health guideline or maximum allowable concentration. Whenever concentrations in excess of the limit are detected, the sampling and analytical records should be checked first to determine whether the results are due to analytical or reporting error or sample contamination. If no other cause can be found, a genuine change in water quality can be verified by repeat sampling and analysis. If the concentrations are unacceptably high appropriate action should be taken.

The action taken depends on the magnitude of the problem, i.e. whether a few or very many people may be affected (see Figure 7.4). If only a few people are affected, the simplest action may be to change their water supply, at least until the source of the increased nitrate can be identified and remedial measures taken that restore the nitrate concentration to an acceptable level for drinking water. People at high risk, such as the elderly or young infants, should also be identified and an alternative source of water provided to them, such as bottled water, until the problem is solved. In the meantime, high risk groups may need to be kept well-informed about the risks and medical surveillance may even need to be put in place (Figure 7.5). Where an alternative water supply cannot be provided to populations at risk, options such as blending the high nitrate supply with purer water (in order to reduce nitrate
concentrations), or provisional treatment of the supply for nitrate reduction (see Chapter 6) may be required.

Once the immediate health risk has been reduced by appropriate action, efforts can be made to identify the origin of the increased nitrate concentrations. This may involve detailed monitoring surveys in the catchment and waterbody, especially if the likely source of contamination is agricultural activities in the catchment. Wastewater discharges may also need to be monitored. Depending on the source(s) of increased nitrate concentrations, appropriate remedial measures may be possible such as upgrading wastewater treatment facilities with nitrate removal stages (see Chapter 4). Diffuse sources may require regulation of poor agricultural practices or the definition of water protection areas (see Chapter 5). When such measures are not appropriate or applicable, it may be necessary to blend a high quality source water with the contaminated source water to produce a raw water in which the nitrate concentrations are acceptable for the subsequent water treatment process or that meet national regulations concerning raw water quality.

Once remedial measures are in place, and regardless of the action taken to ensure that the population is not at risk from high nitrate concentrations in the potable water supply, follow-up monitoring on the water source is needed to ensure that remedial measures are working and that the source water is returning to an acceptable quality for future use.
Figure 7.4 Actions required in the event of detecting high nitrate concentrations in a drinking water supply
Figure 7.5 Actions required in the event of detecting high nitrate concentrations in the drinking water supply of populations likely to suffer from associated health problems
7.5 References


Vogel, W.R. 1995 The Austrian Water Quality Monitoring System and its intergration into the Water Management Concept. In, Richardson (Ed.): Environmental Toxicology Assessment. Taylor and Francis, S. 229-245


**Internationally Standardised Methods**


ISO 1992 *Water Quality - Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulphate using liquid chromatography of...*


